MATRIX-ISOLATION, PHOTOCHEMISTRY, AND SPECTROSCOPY OF BENZOTHIENYL DIAZO COMPOUNDS

by

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Dedicated to my wife, my family, and all my friends along the way.

Without each of you none of this would be possible.

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MATRIX-ISOLATION PHOTOCHEMISTRY AND SPECTROSCOPY OF BENZOTHIOPHENE DIAZO COMPOUNDS

Laura Anne Kopff

Under the supervision of Professor Robert J. McMahon
at the University of Wisconsin—Madison

Photolysis of matrix-isolated 3-thienyl diazomethane generates triplet s-*Z* and s-*E*-3-thienyl carbene, which is characterized by IR, UV-vis, and EPR spectroscopy. The EPR spectrum of the triplet carbene proved unusual, and so a variety of NBO and spin density calculations, as well as simulations of the spectra were carried out to better understand the experimental findings. (Chapter 4)

To build on previous work, the remainder of this work focused on the photochemistry and spectroscopy of the unsubstituted and methyl substituted 2- and 3-benzothienyl diazo compounds. While the methyl substituted 2-benzothienyl diazoethene was successful in generating the corresponding carbene, irradiation of 2-benzothienyl diazomethane under any conditions was unsuccessful in generating 2-benzothienyl carbene. Instead, 2-benzothienyl diazomethane opens up to a cyclic allene (irradiation at $\lambda > 534$ nm) and a bicyclic cyclopropene (irradiation at $\lambda > 363$ nm). Narrow band irradiation was carried out in an attempt to convert the cyclic allene to either 2- or 3-benzothienyl carbene, however these attempts were unsuccessful. (Chapter 1)

3-Benzothienyl diazomethane was matrix isolated and its photochemistry explored. The photochemistry of the benzannulated compound mirrored that of the parent 3-thienyl diazomethane, except that no triplet carbene was detected. Upon irradiation ($\lambda > 472$ nm) the diazo compound is converted to a bicyclic cyclopropene, which, at $\lambda = 340$ nm opens to give a mixture of E- and Z-vinyl acetylene thiones as well as a cyclopropene thione. This cyclopropene thione is a deep purple color, due to its aromatic charge-transfer character. Further irradiation at $\lambda = 300$ converts some of the acetylenic species to the same cyclic allene observed upon irradiation of 2-benzothienyl diazomethane. (Chapter 2)

The last member of this family, 1-(3-benzothienyl) diazoethane, was successful in generating triplet 1-(3-benzothienyl) ethylidene upon irradiation at $\lambda > 571$ nm as characterized by UV-vis and EPR spectroscopy. The EPR spectrum shows the same unusual characteristics as 3-thienyl carbene, with a large difference in D values between the s-*E* and s-*Z* rotamers of the carbene. Shorter wavelength irradiation ($\lambda > 472$ nm) converts the carbenes to *E*- and *Z*-vinyl benzothiophene. (Chapter 3)

Approved: ______________________________ Date: _________________

Robert J. McMahon
Professor of Chemistry

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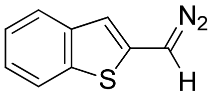
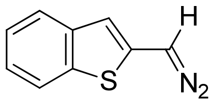
Chapter 1 – Photochemistry and Spectroscopy of 2-Benzothienyl Diazomethane

Abstract

The photochemistry of matrix-isolated 2-benzothienyl diazomethane (**1**) was studied by IR, UV-vis, and EPR spectroscopy in an attempt to generate and characterize the 2-benzothienyl carbene. Calculations were done to characterize the C_9H_6S potential energy surface as well as to predict the vibrational frequencies and infrared intensities of the isomers.



1 *s-E*



1 *s-Z*

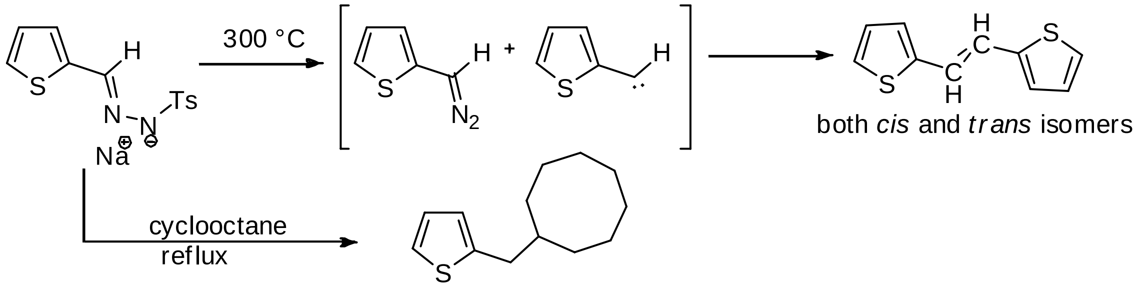
Introduction

The chemistry of aryl and hetero-aryl carbenes is of interest to the field of reactive organic intermediates, particularly in relation to combustion, atmospheric chemistry, and astrochemistry.[1,2,3,4] The structure and reactivity of these species has been studied by a variety of techniques such as matrix-isolation spectroscopy, time-resolved spectroscopy, and computational methods. The spectroscopy of singlet arylchlorocarbenes[5,6], including heteroaryl systems [7,8,9,10,11,12,13,14,15] has been thoroughly investigated. However, less is known about the non-halogenated heteroaryl carbene systems which are currently under investigation. These are of interest due to their predicted triplet ground states, and the fact that they are likely to be present in the harsh reaction environments of combustion or the interstellar medium.[16] Additionally, these heteroaryl carbenes represent the formal addition of atomic carbon to a closed-shell aryl substrate, a process which is of great interest to astrochemists.

Background

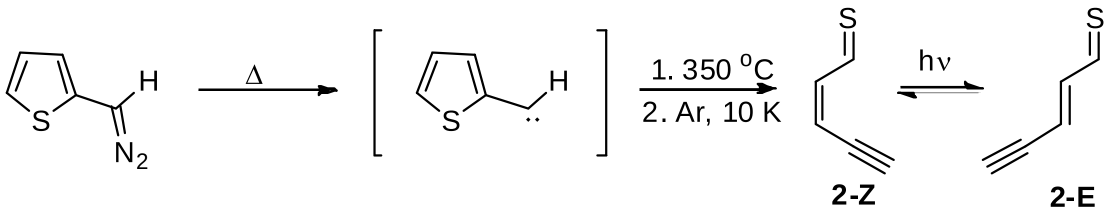
The chemistry of 2-thienyl diazomethane has been investigated previously. Shechter pyrolyzed the sodium salt of the 2-thienylcarboxaldehyde tosylhydrazone and saw both *cis*- and *trans*-1,2-di(2-thienyl)ethene being formed, presumably by the reaction of the diazomethane with a transient 2-thienyl carbene (**Scheme 1.1**).[17] Trapping experiments utilizing cyclooctane as a trapping agent under the same reaction conditions yielded 2-(cyclooctyl-methyl)thiophene, thus lending credence to the intermediacy of a carbene in the dimerization. (**Scheme 1.1)**

Scheme 1.1



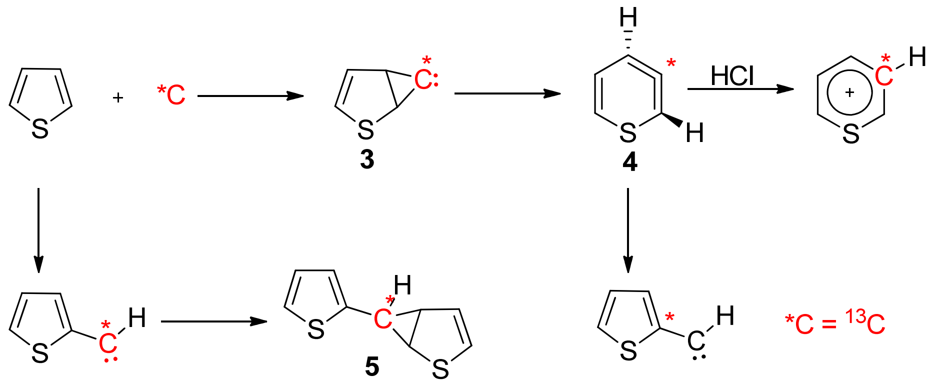
Sander was the first to matrix-isolate the products of the thermolysis of 2-thienyl diazomethane and saw only formation of the *Z*-thialmethylenecyclopropene (**2**).[18] Subsequent photolysis of this matrix led to isomerization to give a mixture of *E*- and *Z*-thialmethylenecyclopropene. Matrix isolation of 2-thienyl diazomethane and photolysis at $\lambda >$ 435 nm lead directly to a mixture of *E*- and *Z*-thialmethylenecyclopropene.[18] (**Scheme 1.2**) Again, a thienyl carbene was proposed – but not observed – as an intermediate in this process.

Scheme 1.2



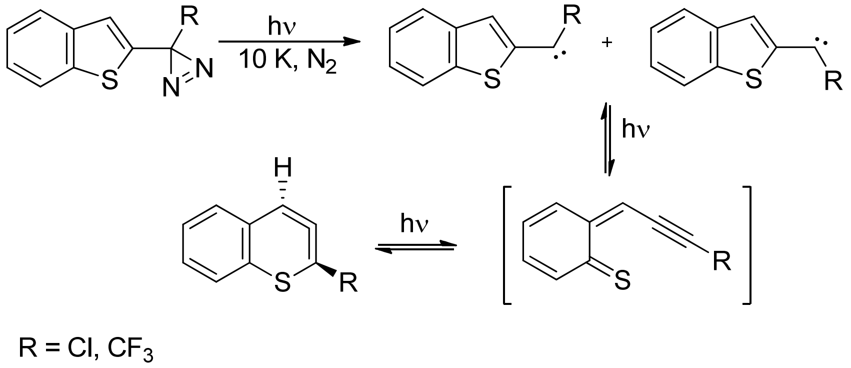
In order to probe the possibility of thiophene carbenes being formed by atomic carbon reactions, Shevlin reacted ^{13}C atoms with thiophene at 77 K and trapped the products with HCl/DCl.[19] Analysis of the acid-trapped products reveals that atomic carbon most likely adds to one of the double bonds in thiophene to give **3** (**Scheme 1.3**), which undergoes a ring-expansion to the allenic thiacyclohexa-2,3,5-triene, **4**. A similar experiment in the absence of acid yielded product **5**, most likely the result of a reaction between thiophene and 2- thienyl carbene. Product distribution lends credence to the rearrangement of **4** to 2-thienyl carbene. However, with these experiments no direct study on the formation or spectroscopy of the thienyl carbenes was carried out. Theoretical studies on this system reveal several possible pathways to interconvert between thiacyclohexa-2,3,5-triene (**4**) and 2-thienyl carbene.[20]

Scheme 1.3



Recently the matrix-isolation photochemistry of both 2-benzothienylchlorocarbene and 2-benzothienyl(trifluoromethyl)carbene has been investigated by Sheridan.[21,22] When 2-benzothienylchlorodiazirine was photolyzed, both rotamers of the singlet carbene, as well as 5,6-benzo-1-thiacyclohexa-2,3-diene, were observed.[21] (**Scheme 1.4**) Additionally, the carbenes and 5,6-benzo-1-thiacyclohexa-2,3-diene could be repeatedly interconverted photochemically. The proposed pathway from the carbenes to the allene involves a ring-opening to a thioquinomethide, however this species was not observed. Matrix isolation and subsequent photolysis of 2-benzothienyl(trifluoromethyl)diazirine led first to generation of the singlet 2-benzothienyl(trifluoromethyl)carbenes. Further irradiation showed conversion of the carbenes to a thioquinomethide species, which, upon prolonged irradiation isomerized to the analogous allene.[22] (**Scheme 1.4**)

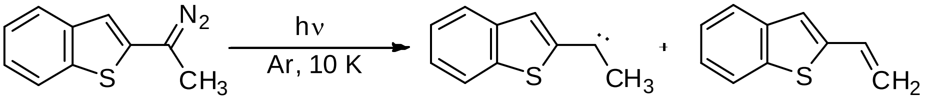
Scheme 1.4



Attempts at the direct isolation of the unsubstituted 2-thienyl carbene species have proven unsuccessful.[18,23,24] However, when 2-benzothienyl diazoethane was matrix isolated and photolyzed, the expected hydrogen shift product was dominant but a detectable amount of 2-

benzothienyl ethylidene was also generated.[24] (**Scheme 1.5**) In this work, the unsubstituted, 2-benzothienyl diazomethane was matrix isolated and the resulting photochemistry and spectroscopy was studied.

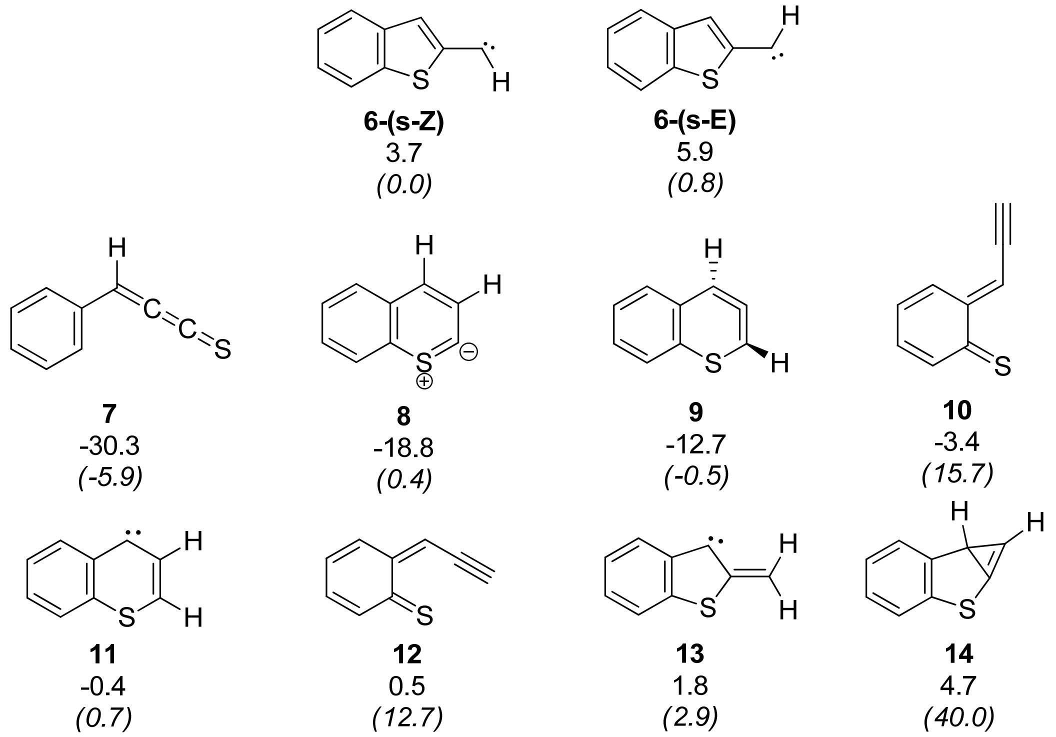
Scheme 1.5



Results and Discussion

Computational Study

In anticipation of matrix isolation studies, computational studies were carried out at the B3LYP/6-31G* level to determine the energies, geometries, symmetries, vibrational frequencies and infrared intensities of a variety of C_9H_6S isomers. This information is presented in Figure 1.1. The two rotamers of 2-benzothienyl carbene are close in energy (ΔE = 0.8 kcal/mol) thus both are expected to be seen in any experimental work, with little preference for one conformation over the other. Additionally, both rotamers are triplet ground states, as to be expected since the carbene center lacks strong electron-donating groups. However, the calculated singlet-triplet gaps are small (3.7 kcal/mol for **6 (s-*Z*)** and 5.1 kcal/mol for **6 (s-*E*)**).



6-(s-Z)
3.7
(0.0)

6-(s-E)
5.9
(0.8)

7
-30.3
(-5.9)

8
-18.8
(0.4)

9
-12.7
(-0.5)

10
-3.4
(15.7)

11
-0.4
(0.7)

12
0.5
(12.7)

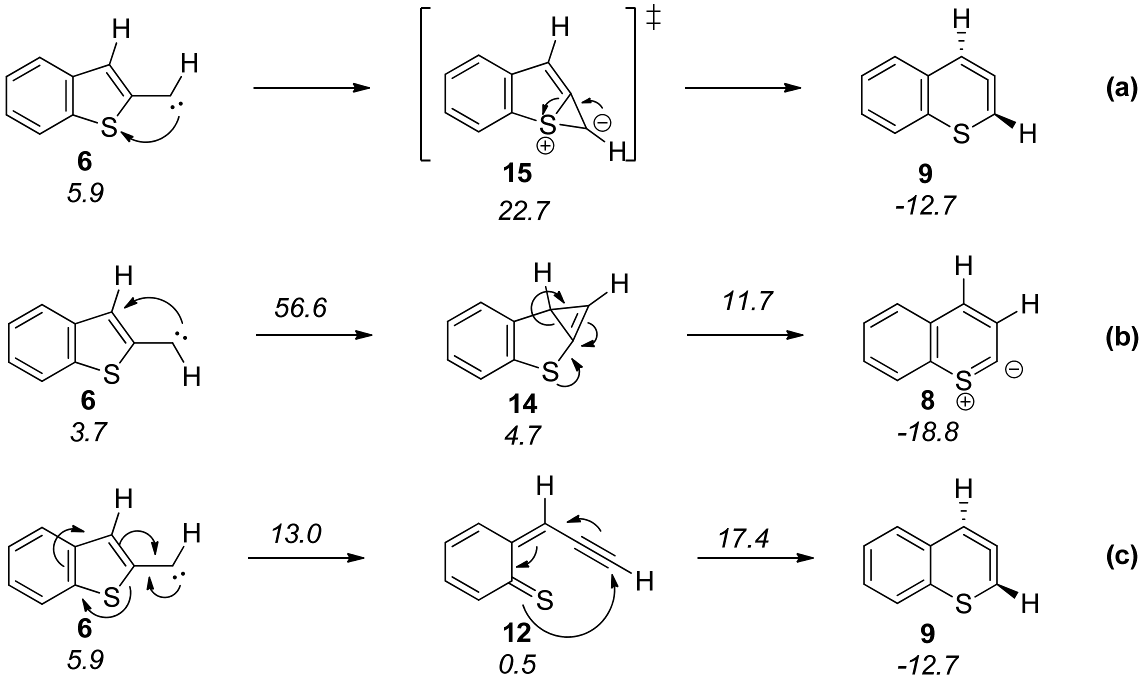
13
1.8
(2.9)

14
4.7
(40.0)

Figure 1.1. B3LYP/6-31G* calculated energies for selected C_9H_6S isomers. Energies are in kcal/mol and include ZPVE. Energies are for singlet and (triplet) species.

Both rotamers of the carbene lie about 15-20 kcal/mol above the ring-expansion product, **9**. It is thought that the carbene could proceed to these bicyclic products via a tricyclic intermediate (**15**) followed by ring opening of the three-membered ring (**Scheme 1.6 (a-b)**). Another possible route to the ring-expanded products is through a ring opening reaction followed by ring closure to the larger ring system. (**Scheme 1.6 (c)**) Transition states linking the carbene, bicyclic intermediates, acetylenic intermediates, and ring-expansion products have been located. Intrinsic Reaction Coordinate (IRC) calculations have verified that these stationary points are first-order transition states. This information is available in the supplemental information.

Scheme 1.6. Calculated reaction pathways. Energy barriers (B3LYP/6-31G*) are for singlet species, include ZPVE, and are reported in kcal/mol.

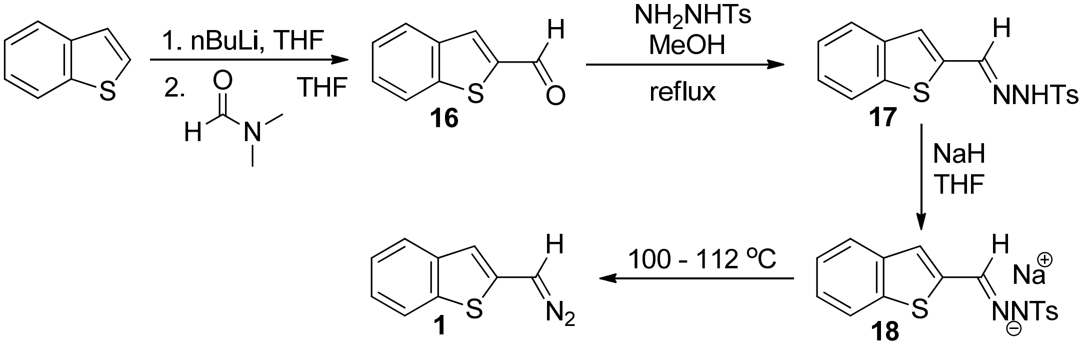


Some calculated structures for C_9H_6S isomers are not included in Figure 1.1 due to their high energy. It is reasoned that these isomers, most of which would require opening both rings, are not relevant to our current experiments. Atom-centered density matrix propagation (ADMP) calculations were run on both rotamers of the singlet and triplet carbene to elucidate alternative pathways to products. ADMP calculations are a variety of *ab initio* molecular dynamic (AIMD) calculations, where quantum descriptions of the potential energy are combined with the propagation of nuclear degrees of freedom.[25,26] ADMP calculations vary from other AIMD calculations in that nuclei are not treated as classical particles, so that systems where tunneling or electronic excitation are important can more accurately be investigated. For ADMP calculations, an optimized structure of a starting material is given a fixed amount of energy and a random trajectory. The molecule propagates through the initial trajectory and, if enough energy exists, will overcome any barriers to reaction. By simulating the isomerization with differing random starting trajectories, it is possible to predict the likely rearrangement pathways. All pathways depicted in Scheme 1.6 were observed; however, no additional pathways were seen.

Synthesis of Tosylhydrazone Precursors and Generation of 2-Benzothienyl Diazomethane

The synthesis of benzo[b]thiophene-2-carbaldehyde (**16**) was adapted from Stille, and is shown in **Scheme 1.7**.[27] Benzothiophene is selectively lithiated at the 2-position, generating a nucleophile that readily undergoes formylation in the presence of dimethyl formamide (DMF). Once aldehyde **16** is obtained, the tosylhydrazone (**17**) is formed by reaction with *p*-toluenesulfonyl hydrazide.

Scheme 1.7



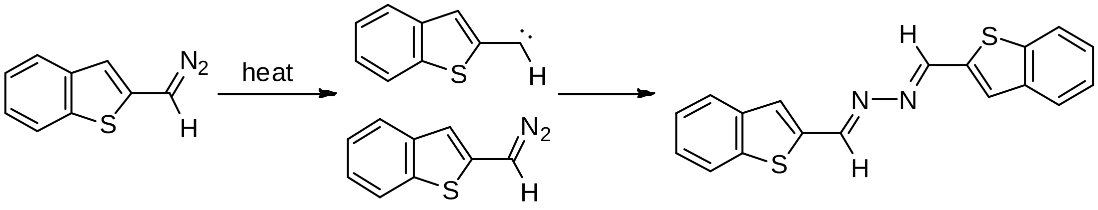
To generate the diazo compound, benzo[b]thiophene-2-carbaldehyde tosylhydrazone (**17**) is deprotonated by NaH, yielding the sodium salt of the tosylhydrazone (**18**). When the sodium salt is heated to between 100 – 112 °C under vacuum, the salt decomposes to give purple-pink 2-benzothienyl diazomethane (**1**) in a modified Bamford-Stevens reaction.[28] The tosylhydrazone sodium salt (**18**) is stable for a couple of days when stored in a desiccator or under vacuum, while the diazo compound (**1**) decomposes at room temperature over the course of several minutes (as evidenced by a color change from pink to yellow). The diazo compound can be stored in solution in the freezer (0 °C) for a longer period of time. The monodeuterated diazo compound is easily prepared by reacting the lithiated benzothiophene with perdeuterated DMF, then following the procedure as for the fully protio species.

Photochemistry of Matrix Isolated 2-Benzothienyl Diazomethane (1)

The photochemistry of matrix-isolated 2-benzothienyl diazomethane (**1**) was to be followed by comparison of experimentally obtained IR spectra to computationally calculated vibrational frequencies of the most likely photochemical products. Infrared spectroscopy is a valuable tool in matrix isolation because experimental IR spectra can be compared with calculated spectra to confirm molecular structure, and thus identify photoproducts which may not be stable enough for other types of characterization, such as NMR.

The apparatus and experimental details for low-temperature matrix isolation spectroscopy have been described elsewhere.[29] When diazo compound **1** was first generated, and then deposited onto the spectroscopic window, insufficient absorbance in the matrix was seen. Several different low-temperature slush baths were used to slowly warm the diazo compound in order to deposit it onto the CsI window. Once the temperature of the diazo compound got above 0 °C, the color changed from pink to yellow, an indication of decomposition.

Scheme 1.8



The diazo compound was not volatile enough to give a sufficient absorbance, thus deposition of the diazo compound directly from the tosylhydrazone sodium salt was chosen as a better method for matrix isolation. For matrix isolation experiments, a small amount of **18** was placed in a curved short-path deposition tube attached to the cold head on the matrix isolation cart. The deposition tube was quickly heated to between 100-112 °C and held for 45-60 minutes, during which time 2-benzothienyl diazomethane (**1**) was generated and co-deposited with N_2 on a CsI window held at 25 K, then cooled to 10 K. This technique gave a good amount of diazo compound on the window, however the spectra also contained contaminants from the solvent used to make the sodium salt (THF).

The solution UV-vis spectrum of diazo compound (**1**) showed a broad visible absorption from 410-590 nm, so initial irradiation of matrix isolated 2-benzothienyl diazomethane (**1**) was carried out at $\lambda > 571$ nm. After 22 hours of irradiation at $\lambda > 571$ nm, a small decrease in the absorption of the intense $\nu_{C=N=N}$ peak was seen in the IR, but a significant amount of diazo compound remained, so irradiation was continued at a shorter wavelength, $\lambda > 534$ nm. After 47 hours irradiation at $\lambda > 534$ nm, a good amount (~ 2 abs units) of diazo compound was still visible in the IR, however small peaks at 1346, 1228, 731, 705, 626, 535, and 427 cm^{-1} are visible in the subtraction spectrum. Comparison with calculated spectra of possible photoproducts led to the assignment of the new species in the matrix as the bicyclic allene **9**. (**Figure 1.2, Figure S1.1**)

Irradiation was continued at $\lambda > 497$ nm for 26 hours, followed by $\lambda > 472$ nm for 16 hours. It was not until irradiation at $\lambda > 472$ nm that most of the diazo absorption was gone. Continued irradiation at $\lambda > 472$ nm led to a small increase in the absorption of the peaks associated with allene, **9**, as well as weak new absorptions at 1739, 1446, 1027 cm^{-1}, which are tentatively assigned to 4-thia-2,3-benzobicyclo[3.1.0]hexa-2,5-diene (**14**). (**Figure 1.3**) Upon shorter wavelength irradiation, $\lambda > 363$ nm, the peaks associated with allene **9** decrease, however, the absorptions associated with cyclopropene **14** remain. (**Figure 1.4**) In both spectra strong peaks at 1070 and 895 cm^{-1} are present due to the presence of THF (impurity from direct deposition of the sodium salt) on the matrix.

The assignment of allene **9** was confirmed by generating the analogous compound, deuterated at the aldehyde position, and comparing the computed isotopic shifts with those observed in a separate matrix isolation experiment, as shown in **Figure 1.5**. The presence of deuterium causes a slight red-shift in the allenic $\nu_{C=C=C}$ stretch, from 1820 cm^{-1} in the protio species, to 1809 cm^{-1} in the mono-deuterated compound. As expected, a C-D stretch is apparent in both the diazo compound and allene **9** at around 2300 cm^{-1}. No peaks for the deuterated carbene were seen. (Figure S1.2) The subtraction IR spectrum after irradiation at $\lambda > 472$ nm does not show any peaks for the analogous mono-deuterated cyclopropene, **14-d_1**. (Figure S1.3)

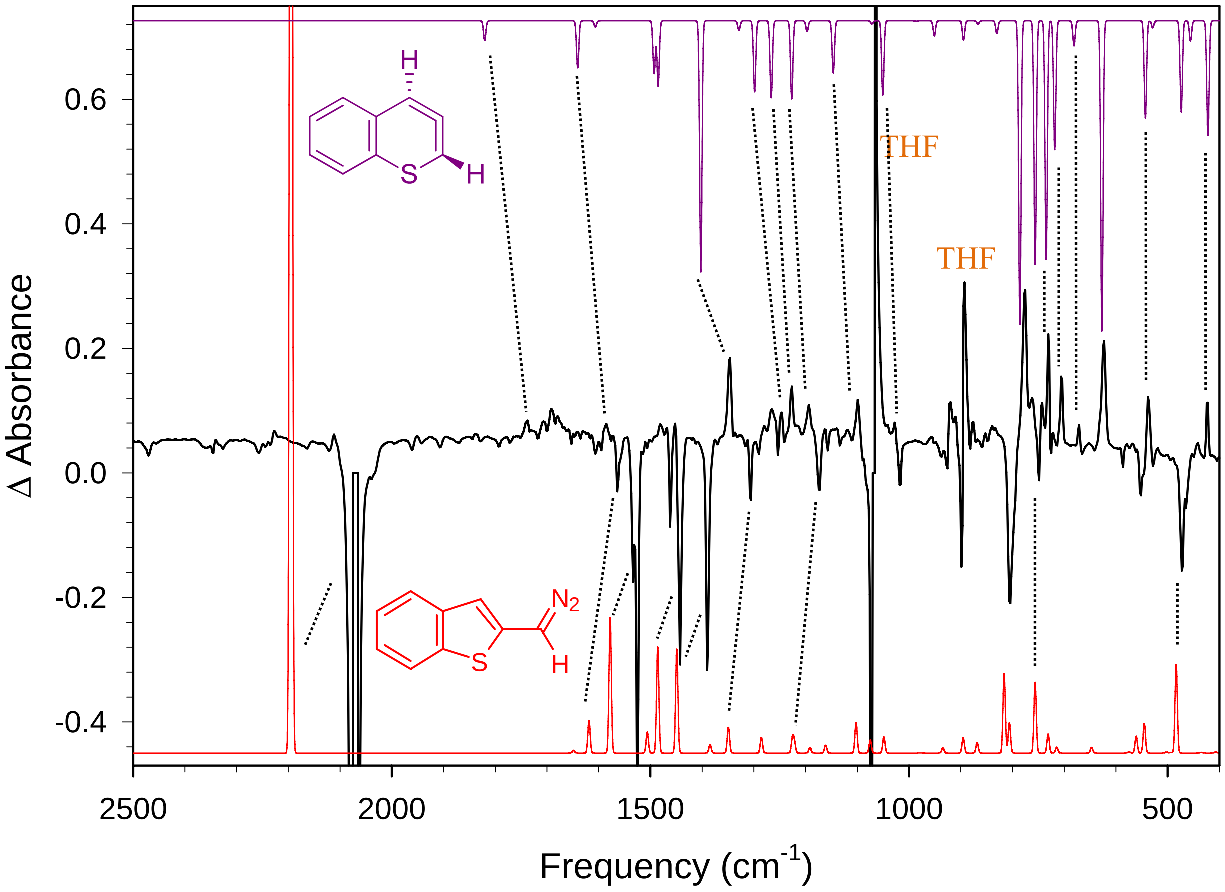


Figure 1.2. IR subtraction spectrum (N_2, 10 K) (black trace, middle) showing the disappearance of 2-benzothienyl diazomethane (**1)** and the growth of peaks corresponding to allene **9**, after irradiation at λ > 534 nm, 25 h. The top and bottom spectra are calculated (B3LYP/6-31G*) spectra of s-*E*-2-benzothienyl diazomethane (red, bottom) and allene, **9** (purple, top). Only one rotamer of the diazo compound is shown for clarity, but both are present in the matrix. Calculated spectra are unscaled. The large peaks at 1070 and 895 cm^{-1} are due to THF in the matrix.

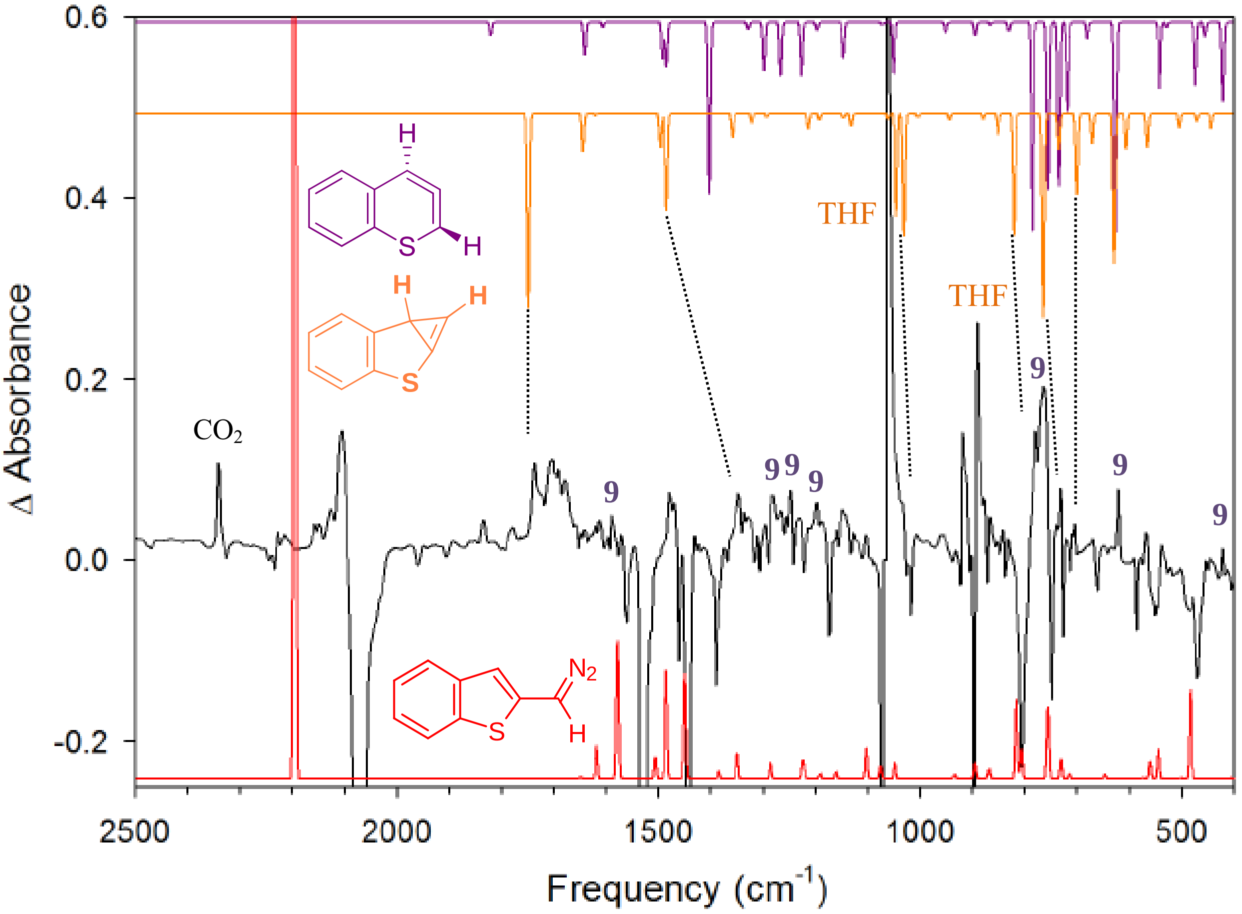


Figure 1.3. IR subtraction spectrum (N_2, 10 K) (black trace, middle) showing the disappearance of 2-benzothienyl diazomethane (**1**) and the growth of peaks corresponding to allene **9**, and 4-thia-2,3-benzobicyclo[3.1.0]hexa-2,5-diene, **14**, after irradiation at λ > 472 nm, 25 h. The top and bottom spectra are calculated (B3LYP/6-31G*) spectra of s-*E*-2-benzothienyl diazomethane (red, bottom), allene, **9** (purple, top), and cyclopropene, **14** (orange, top). Only one rotamer of the diazo compound is shown for clarity, but both are present in the matrix. Calculated spectra are unscaled. The large peaks at 1070 and 895 cm^{-1} are due to THF in the matrix.

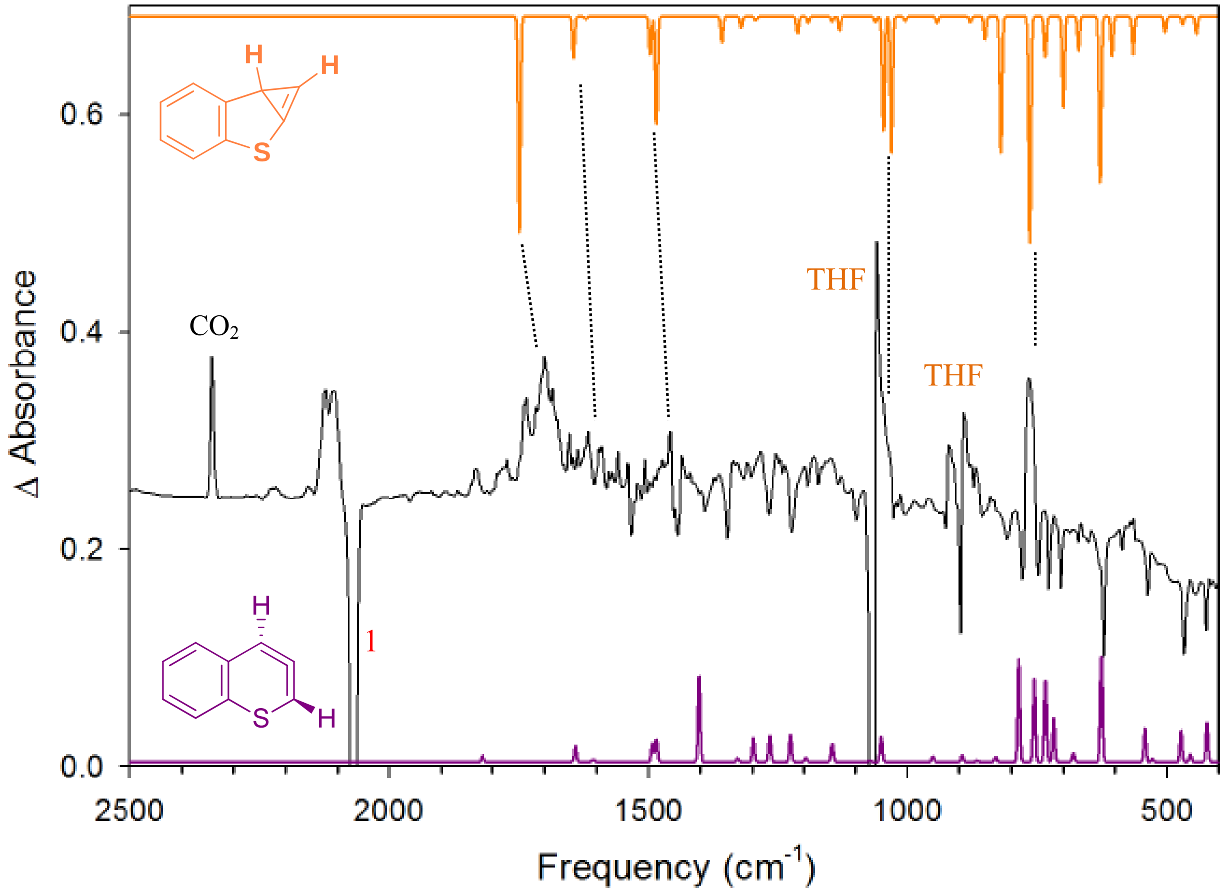


Figure 1.4. IR subtraction spectrum (N_2, 10 K) (black trace, middle) after irradiation at $\lambda > 363$ nm, 53 h, showing the growth of small peaks corresponding to 4-thia-2,3-benzobicyclo[3.1.0]hexa-2,5-diene (**14**) and the disappearance of peaks corresponding to allene **9**. The top and bottom spectra are calculated (B3LYP/6-31G*) spectra of cyclopropene, **14** (top, orange), and allene **9** (bottom, purple) and are unscaled.

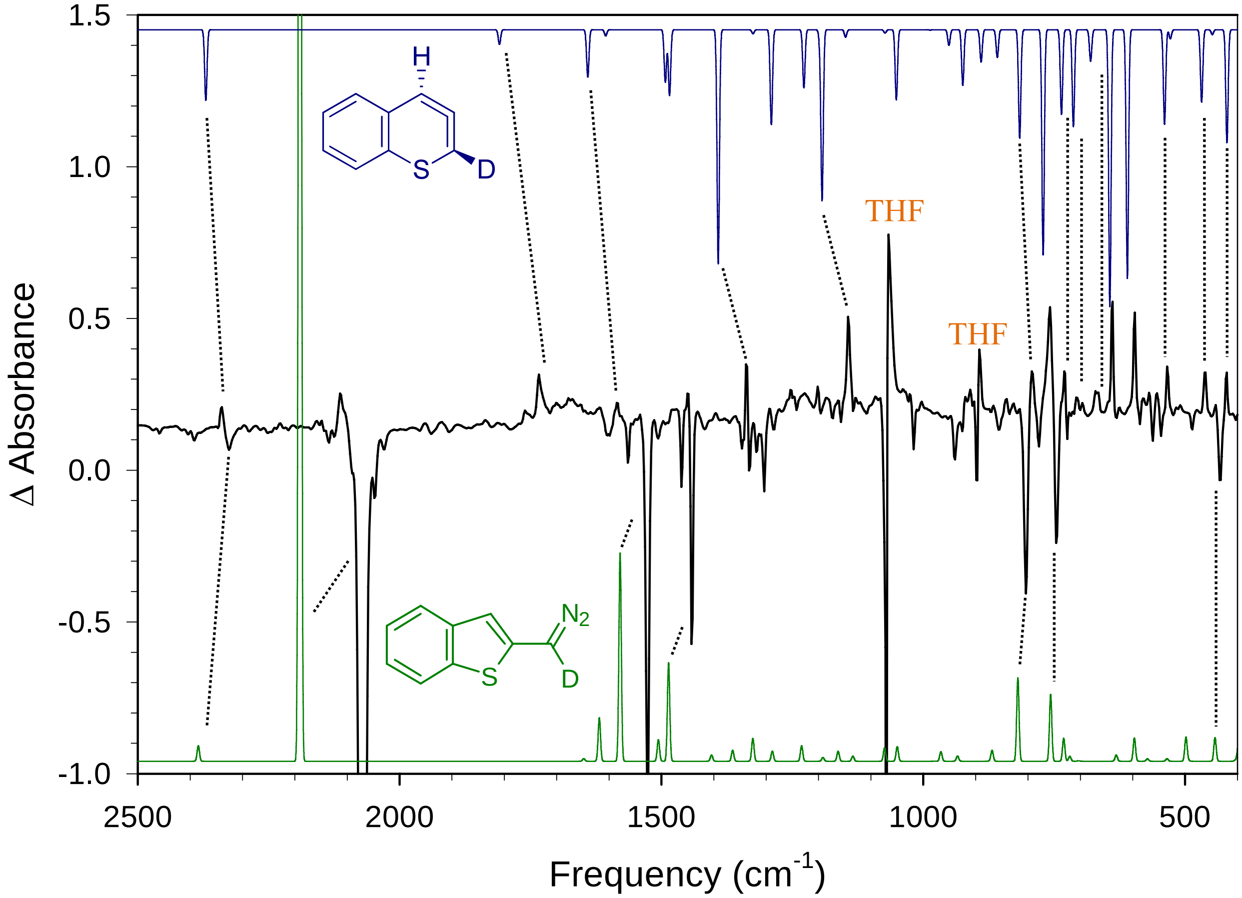


Figure 1.5. IR subtraction spectrum (N_2, 10 K) (black trace, middle) showing the disappearance of 2-benzothienyl diazomethane (**1-*d*$_1$**) and the growth of peaks corresponding to allene (**9-*d***), after irradiation at λ > 472 nm, 24 h. The top and bottom spectra are calculated (B3LYP/6-31G*) spectra of s-*E*-2-benzothienyl diazomethane-d_1 (green, bottom) and allene, (**9-*d***) (blue, top). Only one rotamer of the diazo compound is shown for clarity, but both are present in the matrix. Calculated spectra are unscaled. The large peaks at 1070 and 895 cm^{-1} are due to THF in the matrix.

Electronic absorption spectroscopy was carried out to further characterize the species being formed upon photolysis of 2-benzothienyl diazomethane (**1**). Since UV-vis is a more sensitive technique than IR, the small amount of photoproduct being formed upon photolysis of the **9**, may be detectable. For matrix isolation UV-vis experiments, a small amount of **18** was placed in a curved short-path deposition tube attached to the cold head on the matrix isolation cart. The deposition tube was quickly heated to 100-112 °C for four to six minutes, during which time the 2-benzothienyl diazomethane (**1**) was generated and co-deposited with argon on a sapphire window held at 25 K, then cooled to 10 K.

As shown in **Figure 1.6**, the UV-vis spectrum of the matrix-isolated diazo compound, **1**, shows a very weak absorption between 400-600 nm, as well as strong absorptions between 297-328 nm and below 250 nm. Upon irradiation of the matrix at $\lambda > 613$ nm for 48 hours, the strong absorptions between 297-328 nm lessened, and the color of the matrix changed from pink-purple to yellow-gold. These absorptions, as well as the absorption below 250 nm, continue to disappear as the wavelength of irradiation is lowered to $\lambda > 571$ nm, and then $\lambda > 534$ nm, while a new peak appears at 390 nm.

Irradiation of (**1**) at $\lambda > 472$ nm, 4 h, shows the growth of a broad visible absorption with a λ_{max} at 395 nm. (**Figure 1.6**). Time-dependent density function theory (TD-DFT) calculations on allene, **9**, predict a moderately intense absorption at 415 nm (intensity = 0.548), consistent with the observed spectrum. Narrow-band irradiation of this matrix at $\lambda = 420$ nm (± 10 nm) leads to a slight decrease in this peak. Continued narrow-band irradiation at $\lambda = 375$ nm , and $\lambda = 315$ nm shows a growth of new weak absorptions at $\lambda = 373$ and $\lambda = 353$ nm, potentially due to the formation of cyclopropene **14**. (**Figure 1.7**) The lowest energy calculated transitions for cyclopropene **14** are at 311 nm (intensity = 0.0284) and 258 nm (intensity = 0.0026).

9			**14**		
Wavelength (nm)	Oscillator Strength (*f*)	Experimental (nm)	Wavelength (nm)	Oscillator Strength (*f*)	Experimental (nm)
415.6	0.055	395	311.3	0.0284	373
328.7	0.044		258.4	0.0026	353

Table 1.1. TD-DFT (B3LYP/6-31G*) calculations of allene **9** and cyclopropene **14** showing the lowest energy calculated electronic transitions and their respective intensities as well as experimentally assigned absorptions. λ_{max} in nm

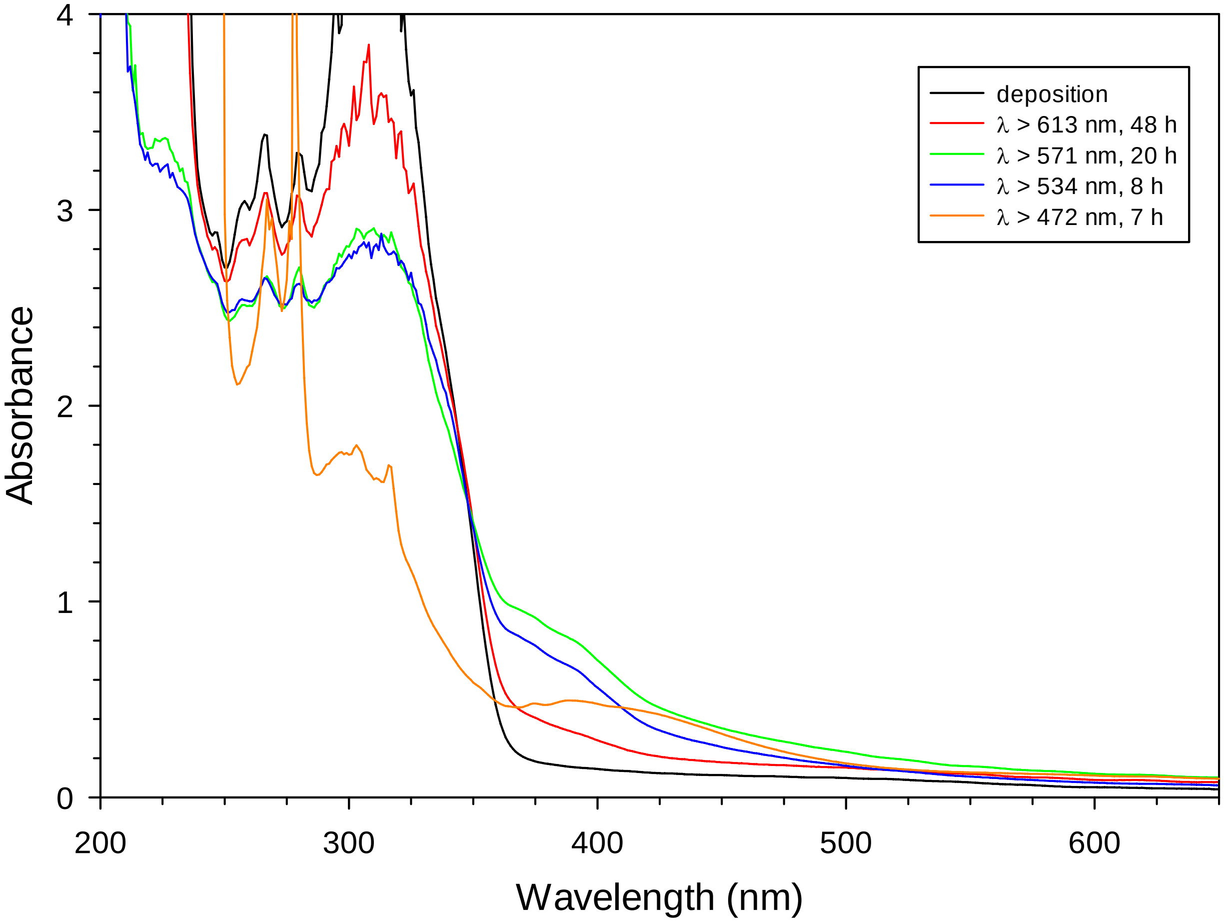


Figure 1.6. UV-vis spectra (Ar, 10 K) showing a matrix containing 2-benzothienyl diazomethane (**1**) (initial deposition, black trace). Irradiation at λ > 571 nm 20 h (green trace), and λ > 534 nm 8 h (blue trace) shows partial conversion of the diazo compound to allene **9**. Irradiation at λ > 472 (orange trace) completes this conversion to allene **9**, which is characterized by a broad visible absorption from 370 – 490 nm.

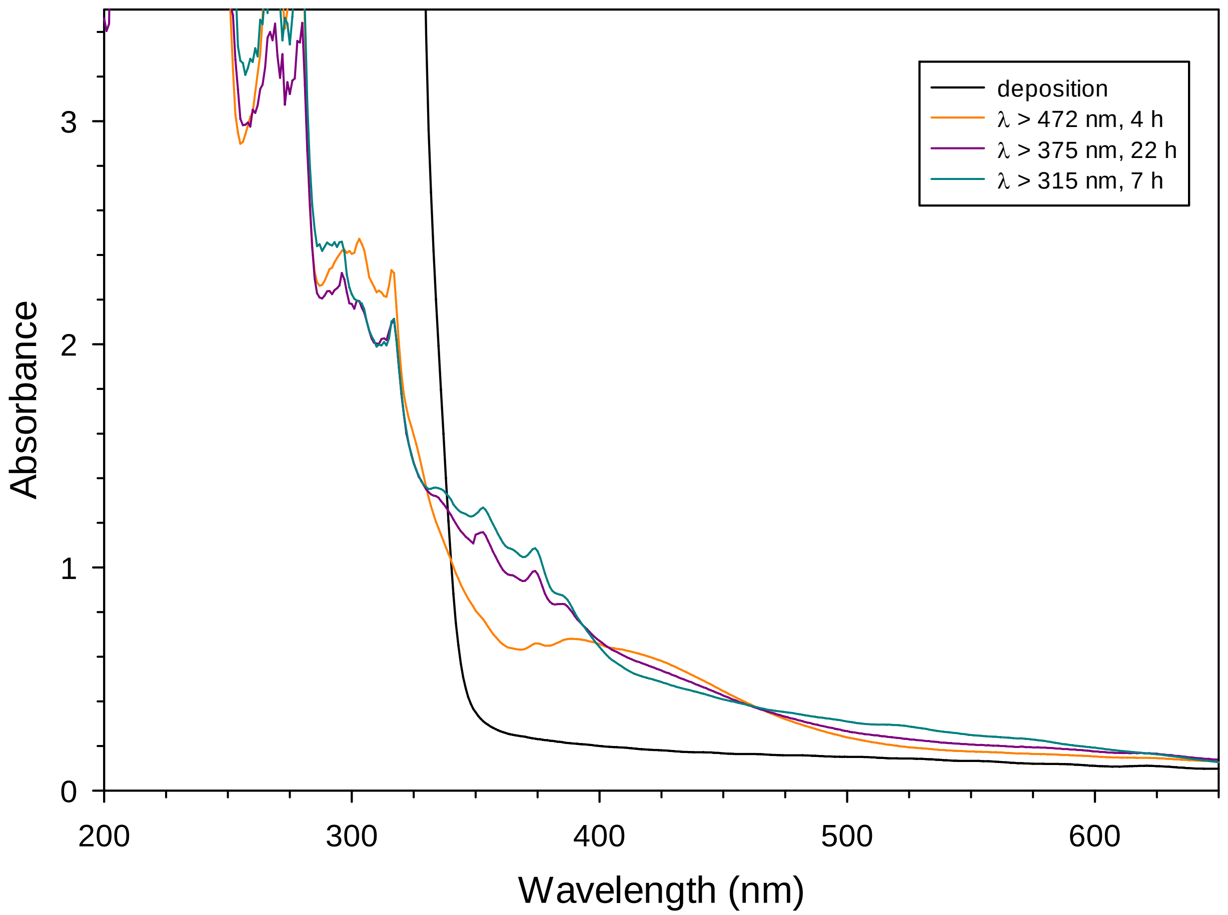


Figure 1.7. UV-vis spectra (Ar, 10 K) showing a matrix containing 2-benzothienyl diazomethane (**1**) (initial deposition, black trace). Irradiation at λ > 472 nm 7 h (orange trace) shows conversion of the diazo compound to allene **9**. Narrowband irradiation at λ = 375 nm (purple trace) shows a slight decrease in the amount of allene **9**, and growth of new peaks at λ = 373 nm and λ = 353 nm, tentatively assigned to cyclopropene **14**. Shorter wavelength irradiation shows no change in the spectrum.

At this point it is beneficial to make a comparison between the current investigation and previous studies on related aryl and heteroaryl carbene systems where direct formation of the carbene from the analogous diazo compounds was observed. Both the phenyl and 1- and 2-naphthyl carbene systems have been thoroughly investigated. Generation of phenyl carbene from phenyl diazomethane occurred with irradiation at λ > 478 nm. Phenyl carbene was characterized by IR, EPR, and UV-vis spectroscopy (ref), with the longest wavelength absorptions in the UV-vis at 430 and 423 nm. When phenyl carbene is benzannulated the resulting naphthyl carbenes can exist as either the 1- or 2- naphthyl carbene isomers. Both of these naphthyl carbenes are easily generated from their respective diazo precursors at λ > 300 nm, and have been fully characterized.[30,3] Both naphthyl carbenes have their lowest energy visible absorptions at 558 (1-naphthyl carbene) and 562 (2-naphthyl carbene). The addition of the second benzene ring causes a significant red shift in the absorptions of the carbenes, however the two isomeric naphthyl carbenes have very similar electronic absorption spectra. The effect of substituting a methyl group for the hydrogen on the carbene carbon of phenyl carbene causes a slight red shift (19 nm) of the lowest energy UV absorption (from 430 nm in phenyl carbene to 449 nm for the methyl substitution). For the analogous 1-(2-naphthyl) ethylidene, the UV spectrum was dominated by the H-shift product, so no visible absorptions for the carbene could be assigned.

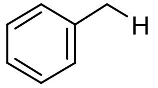
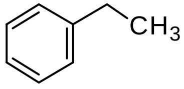
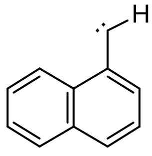
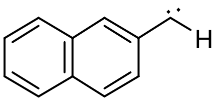
			
19	**20**	**21**	**22**
430 nm 423 nm	449 nm	558 nm	562 nm

Table 1.2. Experimental UV-vis absorptions for different aryl carbenes.

While no triplet carbene was detected upon photolysis of 2-thienyl diazomethane, photolysis of isomeric 3-thienyl diazomethane (λ > 571 nm) was successful in generating 3-thienyl carbene. The UV-vis spectrum of 3-thienyl carbene shows absorptions at 467 and 457 nm.[24] The methyl-substituted derivative, 1-(3-thienyl)ethylidene, has visible absorptions at 473, 471, and 444 nm, which is in agreement with studies on phenyl carbene, that methyl substitution causes a slight red shift in the absorption spectrum.[23] Additionally, the absorptions for both 1-(2-benzothienyl) ethylidene[23] and 1-(3-benzothienyl) ethylidene (Chapter 3) follow the same trend as the two naphthyl carbene isomers, they show very similar absorptions (515 and 479 nm for 2-substitution, and 520 and 497 nm for 3-substitution). Thus, based on the absorption spectrum of 1-(2-benzothienyl)ethylidene (main absorptions are 515 and 479 nm) we would expect that 2-benzothienyl carbene would have absorption features shifted just slightly to the blue of these. In the present study, however, no absorptions appear in this region (see Figure S1.X).

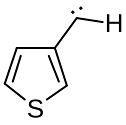
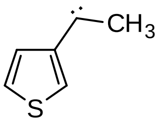
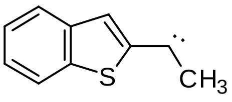
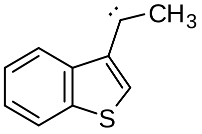
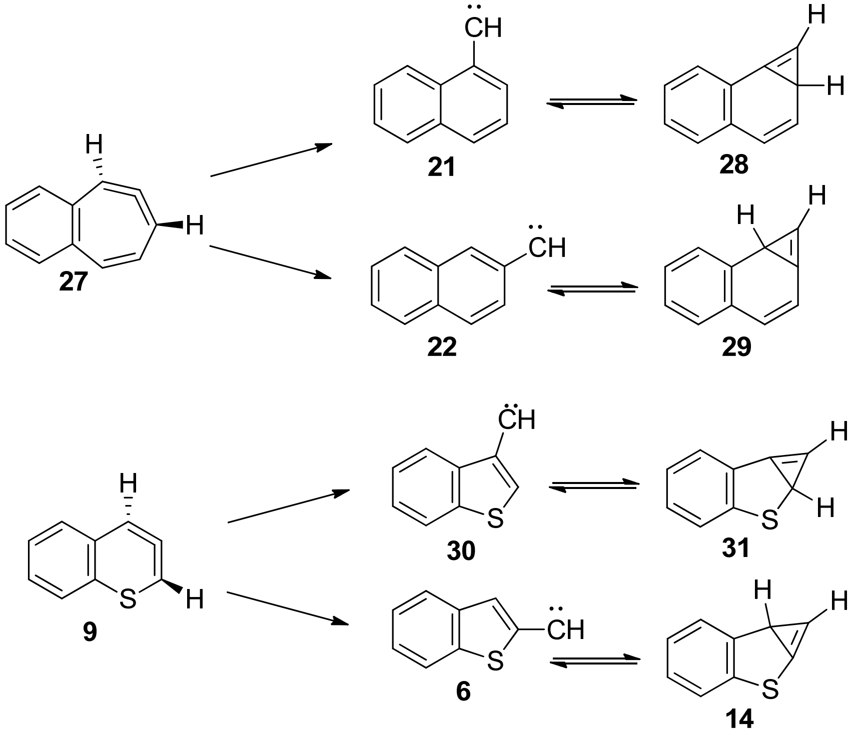
 **23**	 **24**	 **25**	 **26**
467 nm	473 nm	515 nm	520 nm
457 nm	444 nm	479 nm	497 nm

Table 1.3. Experimental UV-vis absorptions for a family of heteroaryl carbenes.

The formation of 5,6-benzo-1-thiacyclohexa-2,3-diene, **9**, is of particular note. Studies by Sheridan on 2-benzothienylchlorocarbene and 2-benzothienyl(trifluoromethyl)carbene both show the photochemical conversion of the carbenes to the corresponding 5,6-benzo-1-thiacyclohexa-2,3-diene.[22,21] Additionally, studies on the related naphthylcarbene system showed that the analogous cycloheptatetraene would photochemically ring-contract to give either 1-

naphthylcarbene (**21**) or 2-naphthylcarbene (**22**). Either of these two carbenes could then insert into one of the naphthyl C-H bonds resulting in the cyclopropene derivatives, **28**, and **29**.[30,31,32] (**Scheme 1.9**) A photoequilibrium was set up between the cyclopropenes and their respective carbenes. Thus, we explored if the benzothienyl carbene system displayed similar photoreactivity by selectively irradiating the allene at shorter wavelengths through use of a monochromator.

Scheme 1.9



Narrowband irradiation was carried out in an attempt to promote a ring contraction of allene **9** to either the 2- or 3-benzothienyl carbene (**6** or **30**) and followed by both UV-vis and IR spectroscopy. Initial broadband irradiation was carried out at $\lambda > 472$ nm to generate a large amount of allene **9**, characterized by a broad, weak visible absorption with a λ_{max} around 395 nm. A monochromator was used to selectively irradiate at $\lambda = 420$ (± 10 nm, 17 h) as it is near the

λ_{max} of the broad absorption. After photolysis, the strong absorption at 275 nm has gone away and the broad absorption with a λ_{max} of 310 nm has increased slightly. Also a new, weak, absorption centered at 620 nm is observed. Irradiation was then carried out at λ = 620 nm (± 10 nm) for 24 h, leading to a new visible absorption at λ = 520 nm. Irradiation was continued at λ = 520 nm, 375 nm, and 315 nm, into the lowest energy absorption until the spectra were unchanged with further photolysis. The spectra and irradiation scheme are provided in the supporting information (Scheme S1.1, Figures S1.4-7). Attempts were made to carry out the same irradiation scheme in an IR experiment to identify the photochemical transformations seen, however the low concentration of photoproducts in the matrix made this impossible.

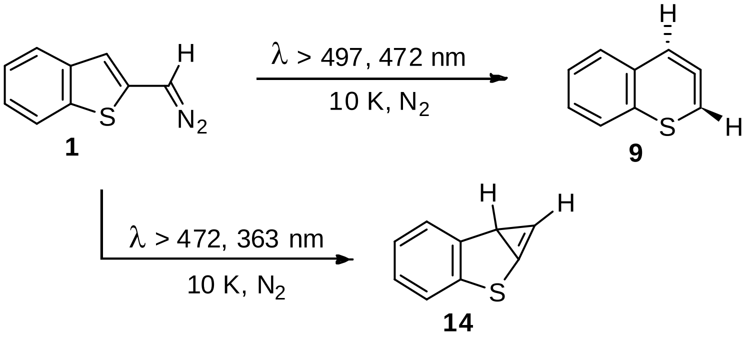
Possible detection of the triplet 2- or 3- benzothienyl carbene was of great interest, so electron paramagnetic resonance (EPR) spectroscopy was performed. EPR spectroscopy was used to detect the presence of any unpaired spins in the matrix during irradiation. In this case, unpaired spins should only be due to the presence of triplet carbene species. The limit of detection for EPR is very small, much more sensitive than IR, so any carbene generation, even in minute quantities, should be detectable.

2-Benzothienyl diazomethane (**1**) was co-deposited with Ar on a copper rod which was placed in the EPR cavity. Before irradiation, no signals were seen in the EPR. After irradiation at λ > 571 nm, 42 h, a strong g = 2 peak at 3445 Gauss was observed (Figure S1.8), but no other peaks were visible. Broadband irradiation was continued with successively shorter wavelengths and no other signals were observed. Additionally, narrowband irradiation using the same sequence as with the previous UV-vis and IR experiment was carried out, but no signals (other than g = 2) were seen after irradiation at any wavelength. Thus it was concluded that no triplet species were being formed.

Summary

Irradiation of a matrix-isolated sample of 2-benzothienyl diazomethane (**1**) at λ ≥ 472 nm results in conversion of the diazo compound to allene **9**. Further photolysis at shorter wavelengths shows the disappearance of the allene and growth of peaks tentatively assigned to 4-thia-2,3-benzobicyclo[3.1.0]hexa-2,5-diene (**14**). Narrowband irradiation was carried out in an attempt to promote a ring contraction of the bicyclic allene to either the 2- or 3-benzothienyl carbene, however no evidence for the ring contraction was seen. The initial conversion does not progress through a triplet carbene species, as evidenced by both the lack of infrared peaks associated with the carbene species, as well as the absence of a signal with EPR spectroscopy. Photochemical formation of the bicyclic allene was confirmed using the monodeuterio isomer.

Scheme 1.10



Experimental Details

***Note:** All diazo compounds are potentially explosive and should be generated with the necessary precautions. While there were no problems during the experimental work presented in this thesis, it is not advisable to attempt to scale-up the amount of diazo compound generated, as the possibility of detonation increases.

Benzo[b]thiophene-2-carboxaldehyde (16). Procedure adapted from Stille.[27] A solution of benzo[b]thiophene (1.39 g, 10 mmol) in 10 mL freshly distilled THF was added to a 50 mL round-bottom flask equipped with a magnetic stirbar and cooled to -78 °C under a nitrogen atmosphere. A solution of *n*-butyl lithium in hexanes (9.09 mL, 10 mmol) was added, and the solution was stirred for 45 min at -78 °C. A solution of dimethyl formamide (0.774 mL, 10 mmol, dried over 3Å molecular sieves) in 10 mL freshly distilled THF was cooled to -78 °C. The milky, pink solution of 2-benzo[b]thienyl lithium was transferred to the DMF solution via cannula and the resulting clear solution was stirred for an additional 10 min at -78 °C before slowly being warmed to room temperature. Once at room temperature, the reaction mixture was quenched with 50 mL saturated NH_4Cl and extracted 3 x 25 mL with diethyl ether. The combined organic layers were washed with 25 mL of brine, and then dried over anhydrous magnesium sulfate. Following filtration, solvent was removed *in vacuo* to afford a dark gold oil (1.32 g, 82% yield). ^{1}H NMR (acetone-d_6) δ 10.15 (s, 1H), 8.23 (s, 1H), 8.01 (t, 2H), 7.54 (m, 1H), 7.46 (m, 1H) ppm. ^{13}C NMR (acetone-d_6) δ 186.19, 144.68, 143.35, 140.11, 136.28, 129.38, 127.64, 126.51, 124.43 ppm.

Benzo[b]thiophene 2-carboxaldehyde tosylhydrazone (17). Benzo[b]thiophene 2-carboxaldehyde (1.5549g, 9.54 mmol) was dissolved in 10 mL methanol (dried over 3Å molecular sieves). One equivalent of *p*-toluenesulfonyl hydrazide (1.7771g, 9.54 mmol) and 30 mL dry methanol were added and the round-bottom flask was equipped with a reflux condenser. The clear yellow reaction mixture was refluxed overnight then allowed to cool to room temperature. Deionized water (50 mL) was added to the yellow solution, and the resulting solid hydrazone was isolated and recrystallized from methanol to afford yellow crystals (0.9777 g, 31 % yield). NMR shows only peaks for desired product, so no further purification was done. ^{1}H NMR (acetone-*d*$_6$) δ 8.29 (s, 1H), 7.85 (m, 4H), 7.58 (s, 1H), 7.38 (m, 4H), 2.38 (s, 3H) ppm. ^{13}C NMR (acetone- *d*$_6$) δ 20.7, 122.5, 124.4, 124.9, 126.2, 127.4, 127.8, 129.6, 136.6, 139.5, 139.6, 139.9, 142.2, 144.0 ppm. ESI-EMM *m/z*: $[M+H]^+$ 331.0570. ESI-MS *m/z*: 330.9 (17), 301.1 (100), 296.0 (22), 255.0 (12), 245.0 (5), 139.0 (4).

Benzo[b]thiophene 2-carboxaldehyde tosylhydrazone sodium salt. For a typical IR experiment, 20 mL THF was added to a 50 mL round bottom flask containing 2-benzothiophene carboxaldehyde tosylhydrazone (0.2500g, 0.758 mmol) and NaH (0.0303g, 0.758 mmol) under a nitrogen atmosphere. The reaction mixture was stirred for one hour. Hexane was added to the milky white solution; the resulting tosylhydrazone salt was collected by vacuum filtration, covered, and stored in a desiccator overnight. Yield (0.2603 g, 97%)

2-Benzo[b]thienyl diazomethane (1). 2-Benzothiophene carboxaldehyde tosylhydrazone sodium salt is placed in a sublimator equipped with a cold finger under vacuum. The cold finger is kept at -78 °C and the sublimator is placed in an oil bath and heated to 110-115 °C. During this time, purple-pink diazo compound is collected on the cold finger. ^{1}H NMR ($CDCl_3$) δ 7.70 (d, 1H), 7.56 (d, 1H), 7.31 (m, 1H), 7.19 (t, 1H), 6.82 (s, 1H), 5.29 (s, 1H) ppm. UV-vis (acetonitrile) broad absorption 410-590 nm, λ_{max}: 495 nm. IR (N_2, 10 K): 2956, 2075, 1533, 1527, 1462, 1441, 1369, 1341, 1291, 1242, 807, 748, 727, 664, 475 cm^{-1}.

Benzo[b]thiophene-2-carboxaldehyde-d$_1$ (16-*d*$_1$). The monodeuterated aldehyde was synthesized as above, except dimethyl formamide-*d*$_7$ was used to incorporate the deuterium label.

Benzo[b]thiophene 2-carboxaldehyde-*d*$_1$ tosylhydrazone (17-*d*$_1$). The monodeuterated tosylhydrazone was synthesized as above, starting with the deuterated aldehyde. ^{1}H NMR (acetone-*d*$_6$) δ 7.85 (m, 4H), 7.59 (s, 1H), 7.42 (m, 4H), 2.38 (s, 3H) ppm. ^{13}C NMR (acetone-*d*$_6$) δ 21.7, 123.5, 125.5, 125.9, 127.2, 128.5, 128.9, 130.7, 137.5, 140.7, 141.1, 145.1 ppm. ESI-EMM *m/z*: $[M+H]^+$ 332.0633. ESI-MS *m/z*: 331.9 (56), 322.0 (4), 267.9 (22), 171.1 (19), 170.1 (14).

Benzo[b]thiophene 2-carboxaldehyde-*d*$_1$ tosylhydrazone sodium salt. The monodeuterated sodium salt was prepared as above, starting with the deuterated tosylhydrazone.

2-Benzo[b]thienyl-*d*$_1$ diazomethane (1-*d*$_1$). The monodeuterated diazo compound was prepared as above, starting with the deuterated sodium salt. IR (N_2, 10 K): 2859 (m), 2331 (w), 2069 (s), 1567 (w), 1528 (m), 1436 (m), 804 (m), 741 (m), 433 (w) (cm^{-1})

Matrix Isolation Experiments

In a typical IR matrix isolation experiment, the matrix isolation cart is fitted with 2 outer KBr windows and an inner window of CsI. Deposition of the diazo compound was carried out directly from the sodium salt onto the inner CsI window. For these experiments, the sodium salt was loaded into a short-path curved deposition tube which was attached to the matrix-isolation cart and held under vacuum (pressure = 10^{-8} torr). The cold head was cooled to 25 K and a thin layer of Ar or N_2 was deposited onto the CsI window. Then the salt was heated with an oil bath to ~110 °C, at which point the pink diazo compound was released and co-deposited with either Ar or N_2 onto the CsI window.

Deposition for a UV-vis experiment is nearly the same, however the outer windows are quartz and the inner window is sapphire. Additionally, due to the higher sensitivity of electronic absorption spectroscopy, a much thinner film is used. Deposition at the same rate as for IR experiments is carried out, but for only 6-9 minutes (4-8 torr of gas).

General

All chemicals and solvents were purchased from commercial sources and used without further purification, unless otherwise noted. Tetrahydrofuran (THF) was dried over KOH, predistilled from CaH_2, then distilled from Na/benzophenone immediately prior to use. NMR spectra (^{1}H-NMR, ^{13}C-NMR) were taken on a Bruker AC+ 300 (^{1}H-NMR) and a Varian MercuryPlus 300 (^{13}C-NMR). Chemical shifts are reported as ppm downfield of a $SiMe_4$ internal standard. Infrared spectra were taken on a Thermo-Nicolet Nexus 870 FT-IR spectrometer with a MCT-B detector. EPR spectra were taken using a Bruker ESP 300 E spectrometer. Electronic absorption spectra were taken on a Varian Cary 5000 UV-Vis-NIR spectrometer.

Computational

All calculations were run utilizing the Gaussian03[33] and Gaussian09[34] software packages. The three-parameter hybrid functional of Becke[35], along with the correlation functional of Lee, Yang, and Parr[36] (B3LYP)[37] was employed for all calculations, with the 6-31G(d) (6-31G*) basis set. Harmonic vibrational frequency calculations at the B3LYP level were used to confirm the nature of each stationary point (zero imaginary modes for minima, one imaginary mode for transition states), as well as to provide zero-point vibrational energy (ZPVE) corrections. Intrinsic Reaction Coordinate calculations were used to confirm reaction pathways between minima and transition states. Computed frequencies and infrared intensities were used to compare with experimental work, and were not scaled. Time-dependent density functional theory calculations were carried out at the B3LYP/6-31G* level with a 50/50 mix of singlet and triplet states.

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(37) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

Supporting Information for Chapter 1 – Photochemistry and Spectroscopy of 2-Benzothienyl Diazomethane

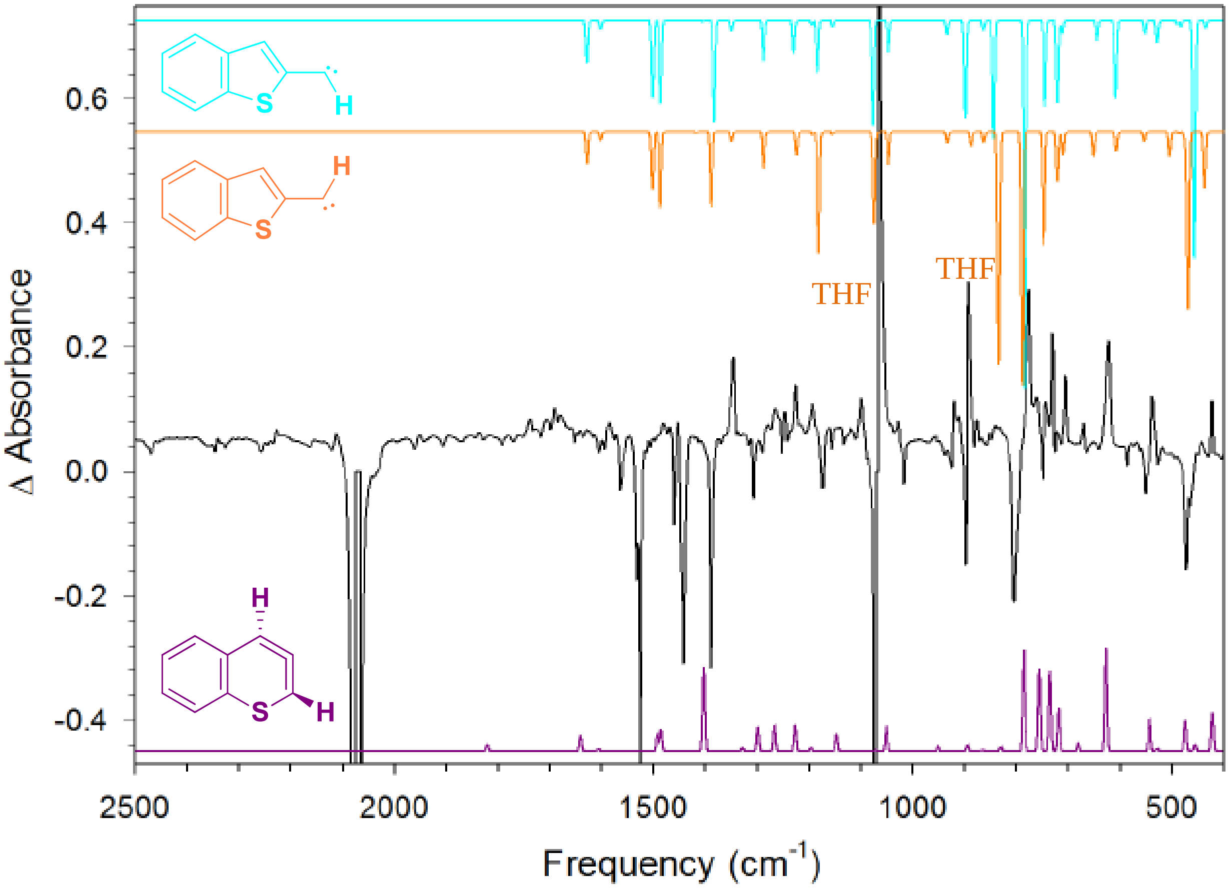


Figure S1.1. IR subtraction spectra (N_2, 10 K) of a matrix containing 2-benzothienyl diazomethane (**1**) after irradiation at λ > 534 nm, 24 h (black trace, middle) showing the growth of peaks corresponding to 4,5-benzo-1-thiacyclohexa-2,3-diene (**9**). The top and bottom spectra are calculated (B3LYP/6-31G*) spectra of **9** (bottom spectra, purple) and the two rotamers of 2-benzothienyl carbene (**6-s-*E***, orange and 6-**s-*Z***, aqua). The calculated spectra for the carbenes do not match the observed data.

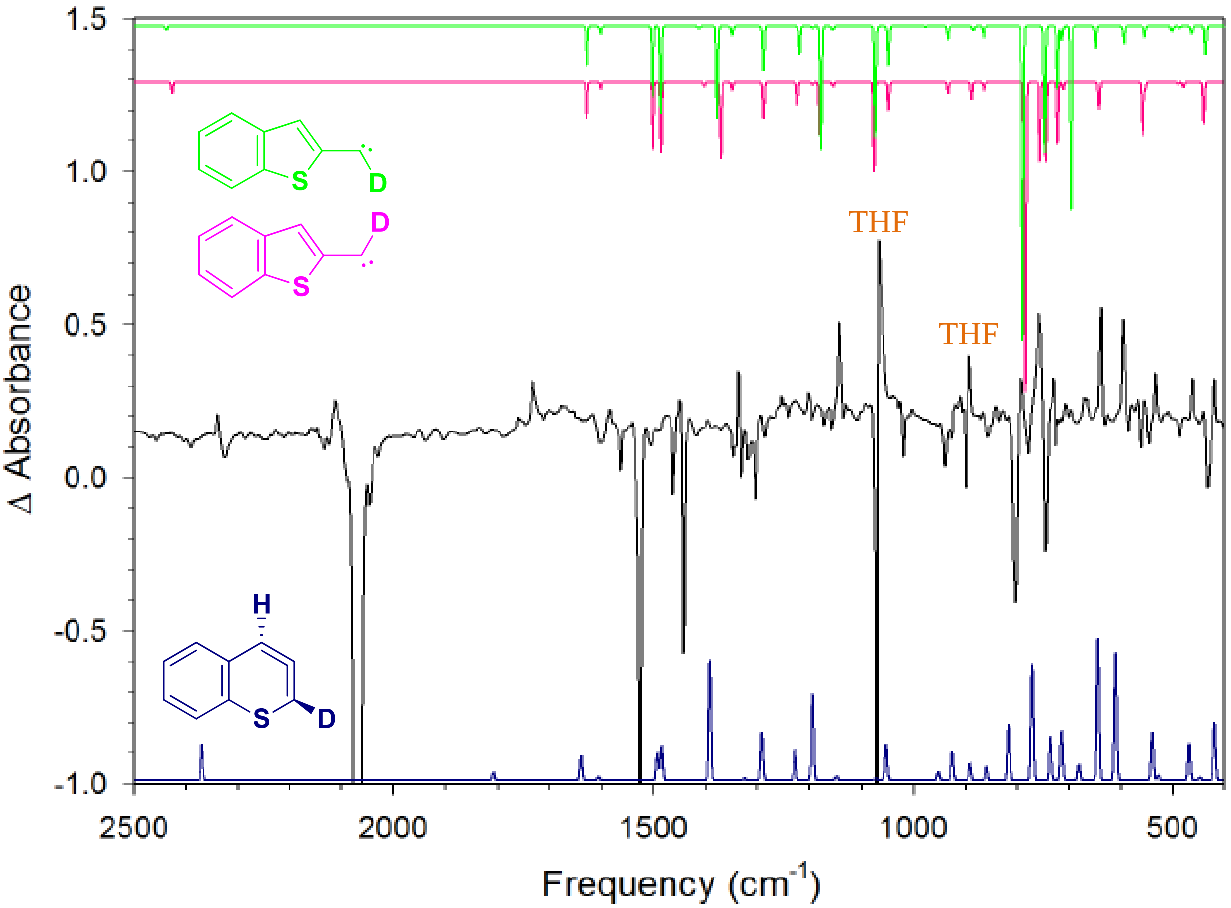


Figure S1.2. IR subtraction spectra (N_2, 10 K) of a matrix containing mono-deuterated 2-benzothienyl diazomethane (**1-*d*$_1$**) after irradiation at λ > 472 nm, 24 h (black trace, middle) showing the growth of peaks corresponding to 4,5-benzo-1-thiacyclohexa-2,3-diene (**9-*d*$_1$**). The top and bottom spectra are calculated (B3LYP/6-31G*) spectra of **9-*d*$_1$** (bottom spectra, blue) and the two rotamers of 2-benzothienyl carbene (**6-s-*E*-*d*$_1$**, pink and 6**-s-*Z*-*d*$_1$**, green). The calculated spectra for the carbenes do not match the observed data.

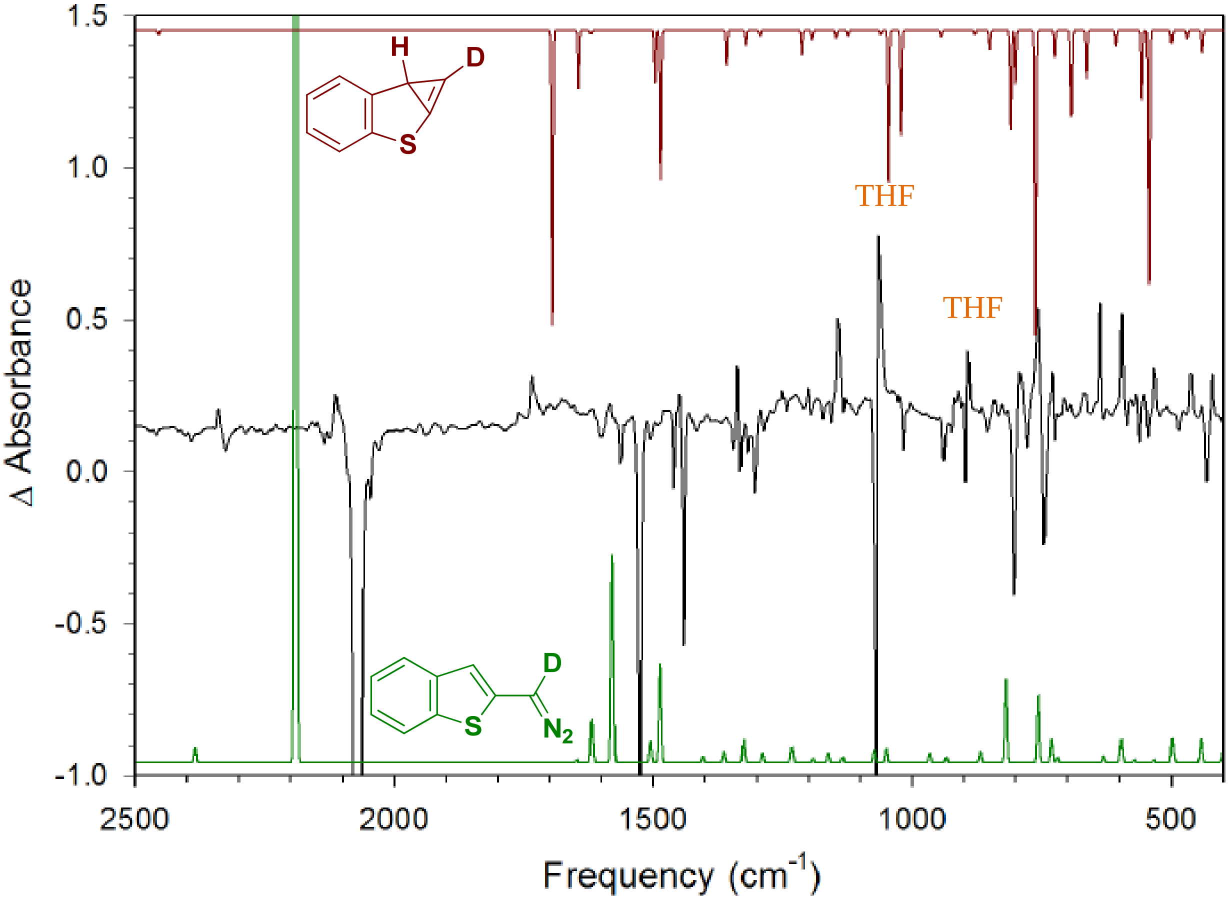
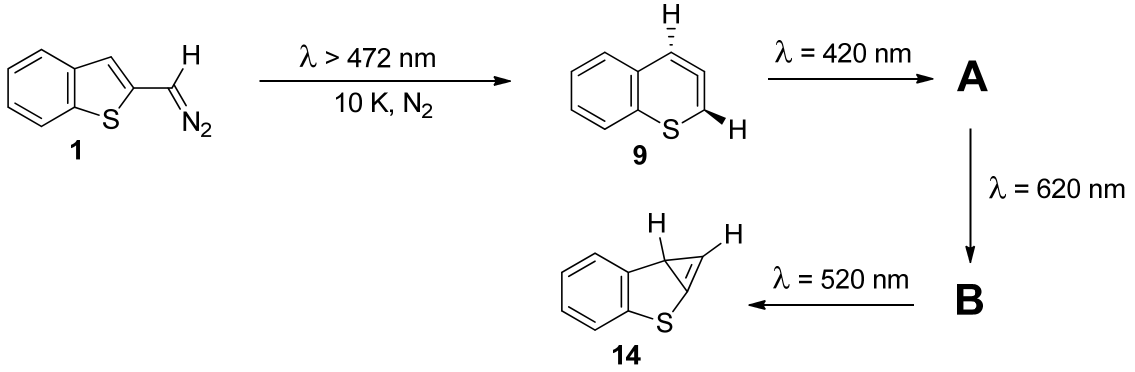


Figure S1.3. IR subtraction spectra (N_2, 10 K) of a matrix containing mono-deuterated 2-benzothienyl diazomethane (**1-*d*$_1$**) after irradiation at λ > 472 nm, 24 h (black trace, middle). The top and bottom spectra are calculated (B3LYP/6-31G*) spectra of 2-benzothienyl diazomethane (**1-*d*$_1$**, green spectrum, bottom) and 4-thia-2,3-benzobicyclo[3.1.0]hexa-2,5-diene, (**14-*d*$_1$**, red spectrum, top). No peaks for **14-*d*$_1$** are visible.

Scheme S1.1. Irradiation of matrix-isolated 2-benzothienyl diazomethane (**1**). Broadband irradiation generates allene, **9**, and a series of narrowband irradiations generate two unidentified species before the final photoproduct, **14**, is generated.



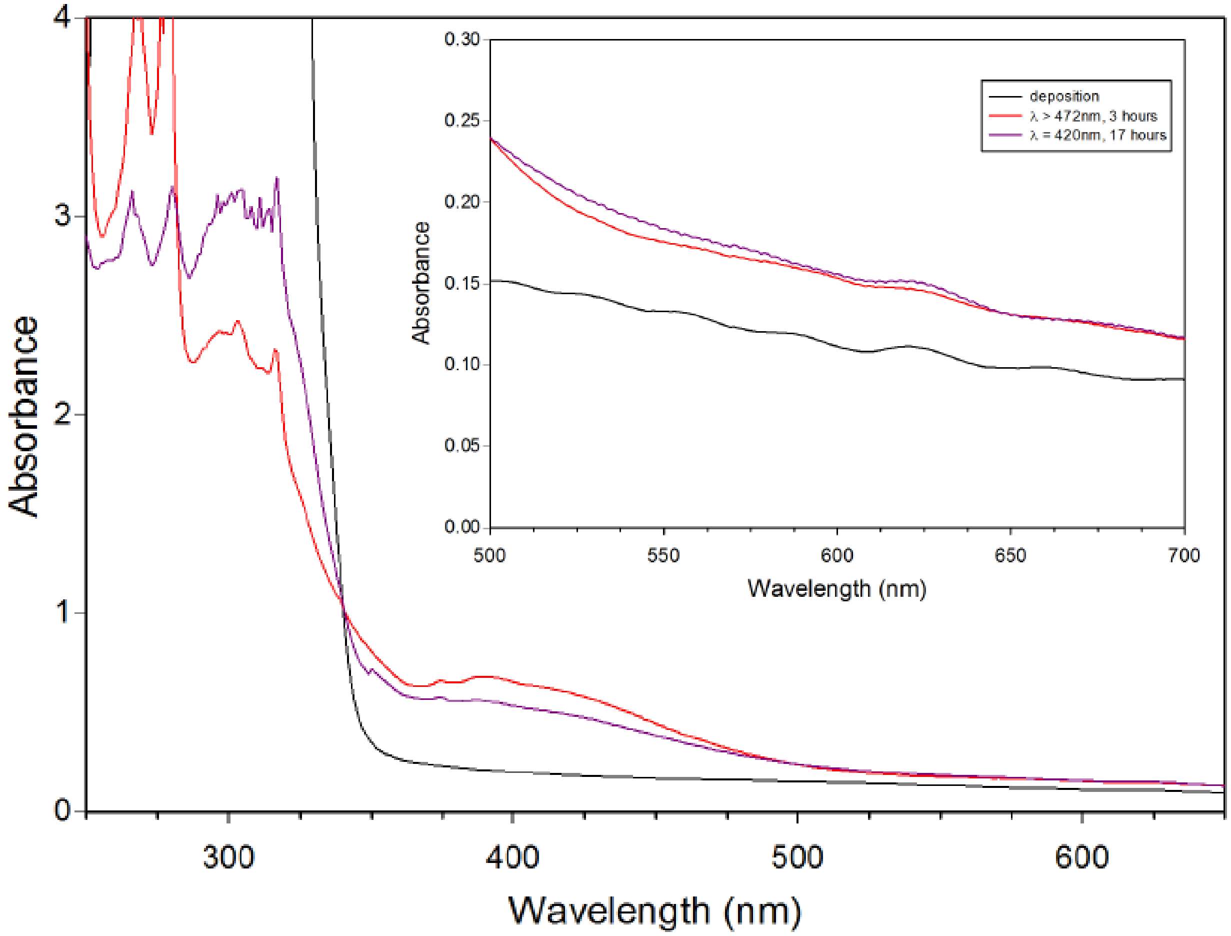


Figure S1.4. Electronic absorption spectra (Ar, 10 K) of a matrix containing 2-benzothienyl diazomethane (**1,** black trace). Irradiation at λ > 472 nm, 3 h generates allene, **9** (red trace) with a visible absorption at λ_{max} = 395 nm. Irradiation into this absorption at λ = 420 nm, 17 h (purple trace) shows a decrease in the 395 nm absorption, and the appearance of a new weak absorption at λ = 620 nm (see Figure S1.5), assigned to the product, **A**.

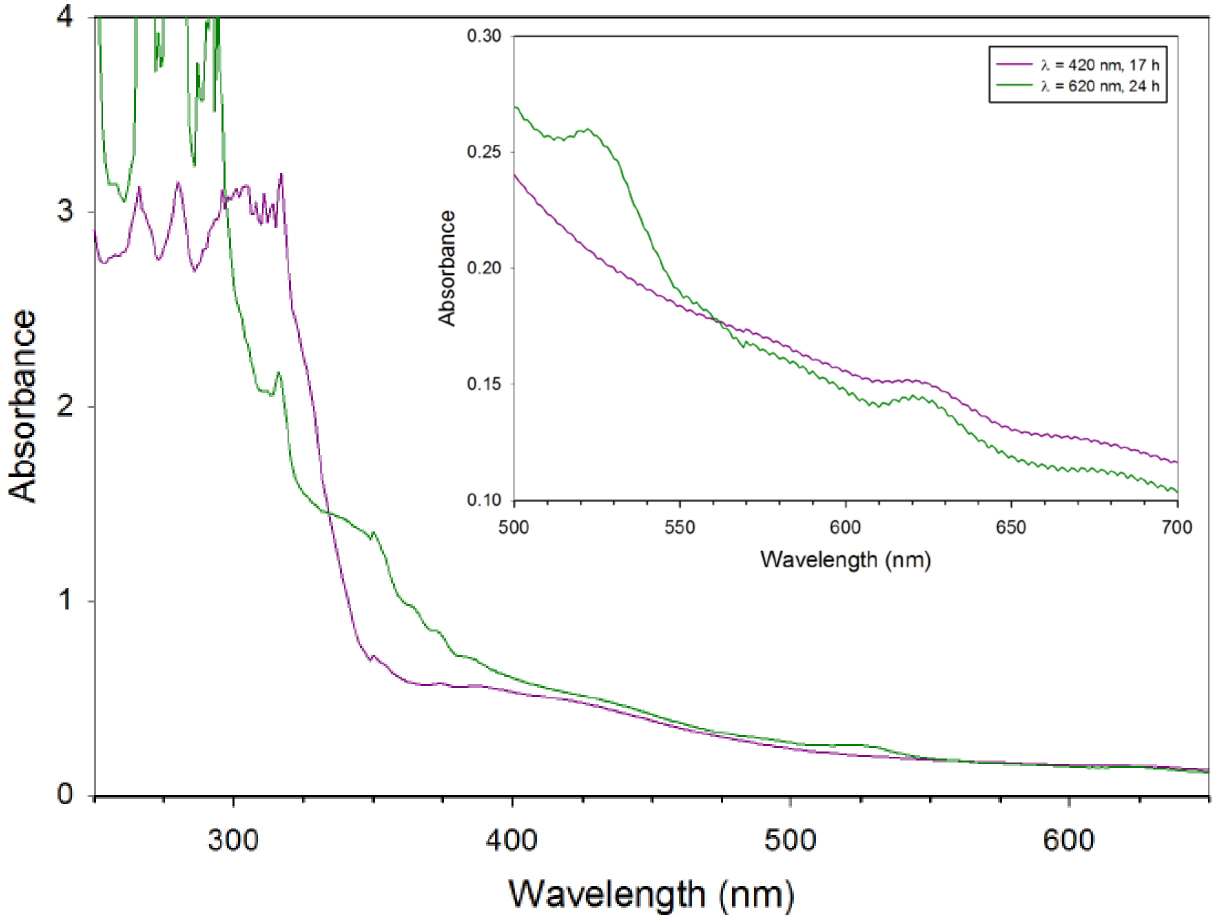


Figure S1.5. Electronic absorption spectra (Ar, 10 K) of the previous matrix after irradiation at λ = 420 nm (17 h) (purple trace). The 620 nm absorption is shown in the expansion. Irradiation into this absorption (green trace) generates a new absorption, assigned to compound, **B**.

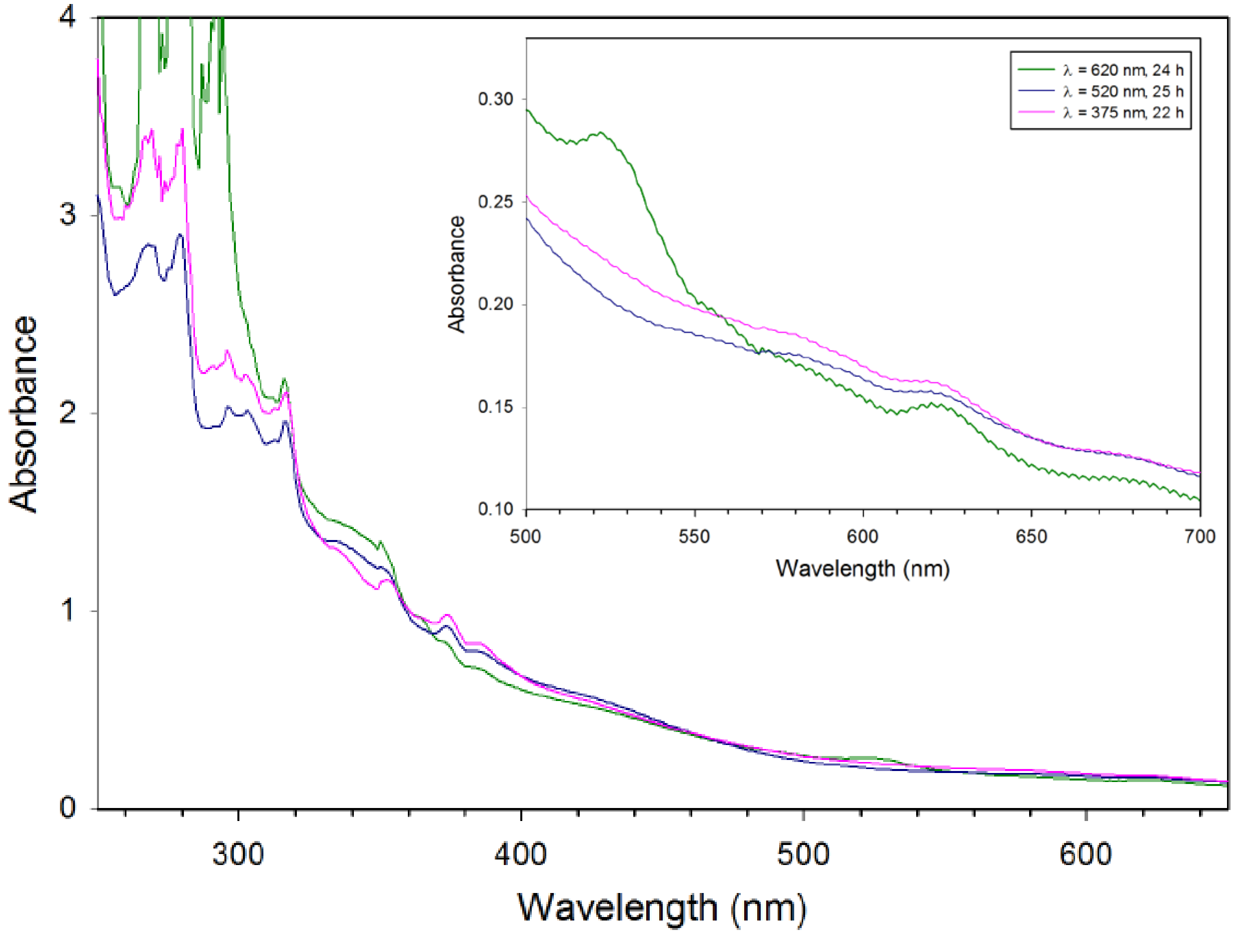


Figure S1.6. Electronic absorption spectra (Ar, 10 K) of the previous matrix after irradiation at λ = 620 nm (24 h) (green trace). The 520 nm absorption is shown in the expansion. Irradiation into this absorption (blue trace) causes its disappearance, and the appearance of new absorptions at 373 and 353 nm, assigned to cyclopropene **14**.

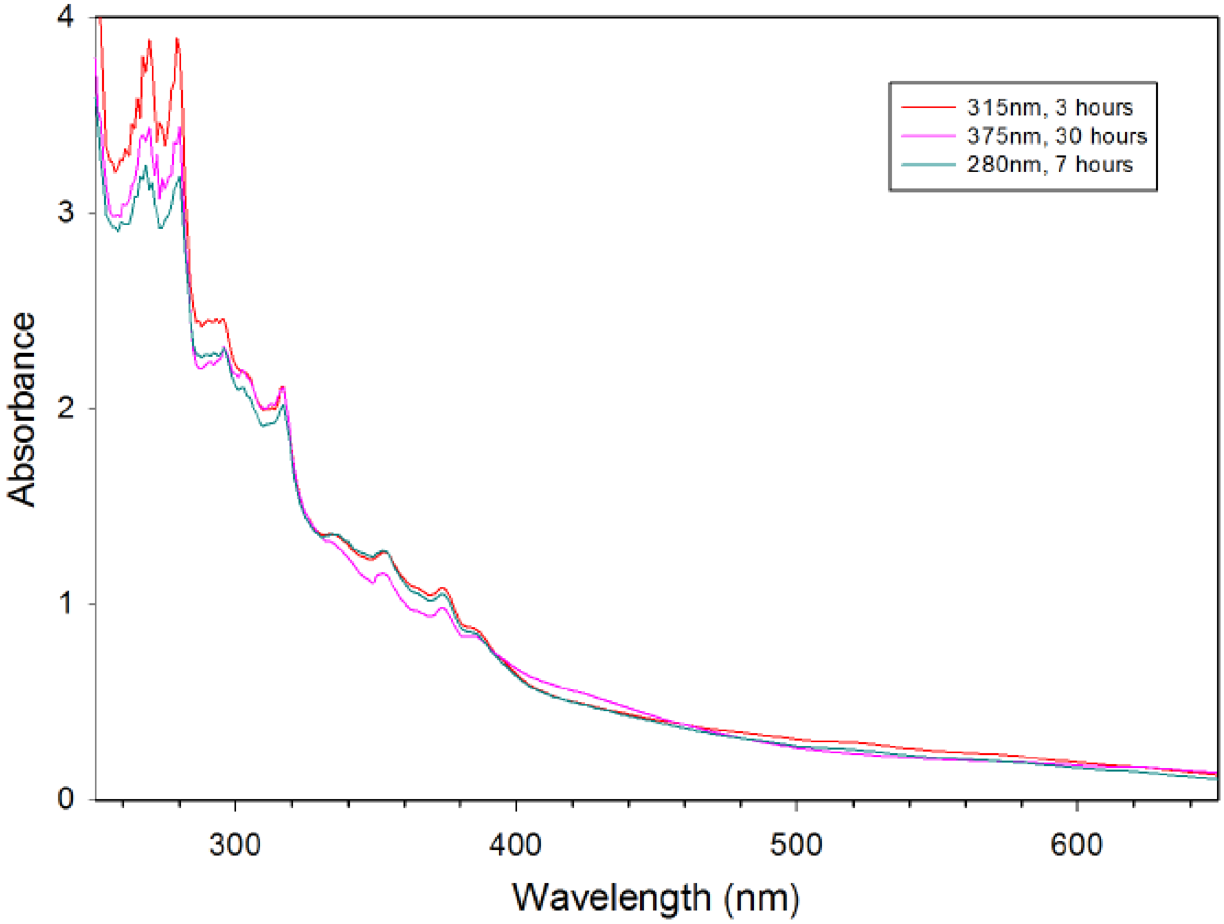


Figure S1.7. Electronic absorption spectra (Ar, 10 K) of the previous matrix after irradiation at λ = 375 nm (aqua trace), 315 nm (red trace), and 280 nm (pink trace). No change in the electron absorption spectrum is seen with varying short wavelength irradiation.

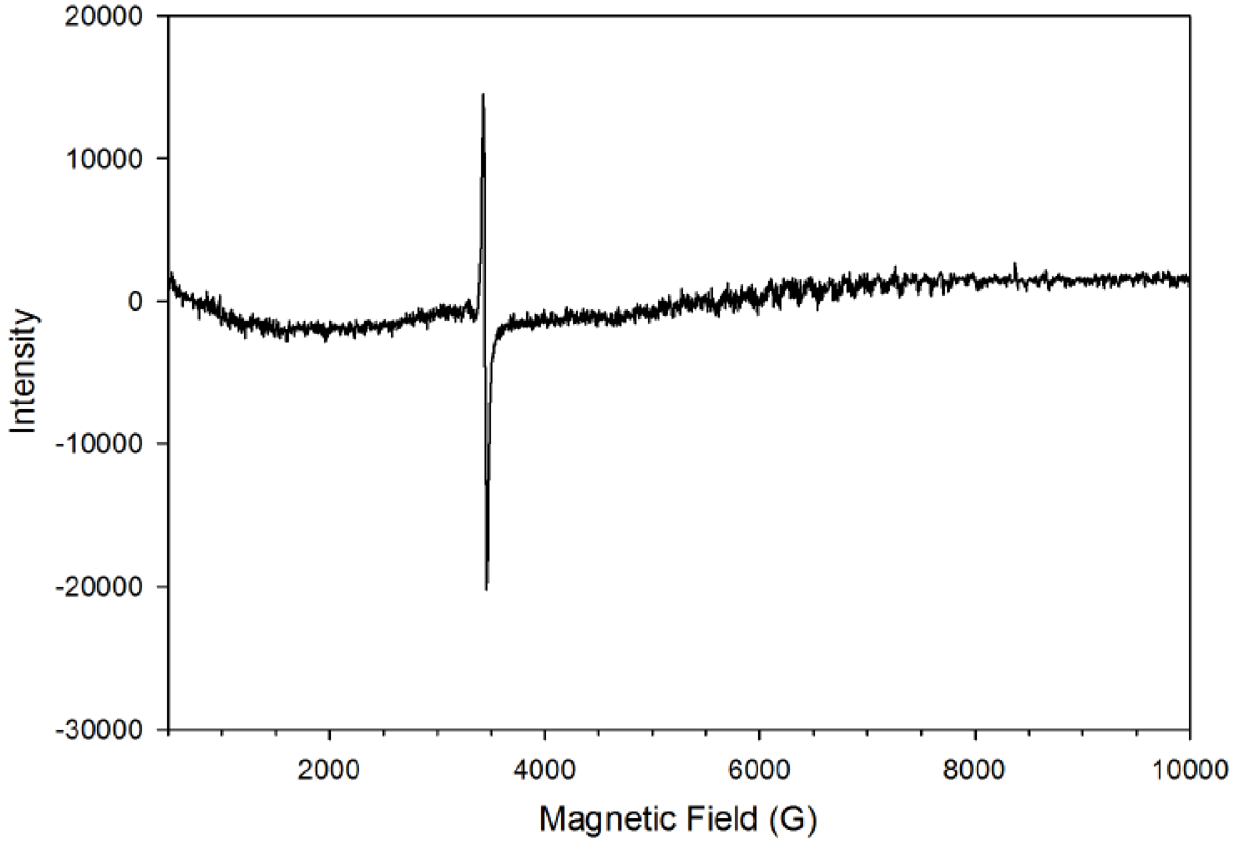
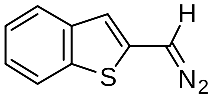


Figure S1.8. EPR spectrum of a matrix containing 2-benzothienyl diazomethane (**1**) (Ar, 15 K) after irradiation at λ > 571 nm, 42 h. The g = 2 peak is present at 3500 G, but no other peaks are visible.

2-Benzothienyl diazomethane (^{1}1-s-*Z*)



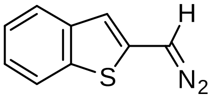
Charge	**Multiplicity**	**Theory/Basis Set**	**Full Point Group**
0	1	RB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.128298	-854.205800	-854.077502	1.8966
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-854.066868	-854.113274		

Symmetry	**Vibrational Frequency (cm^{-1})**	**Intensity**
A"	50.1397	0.1306
A'	98.3411	1.6454
A"	135.7085	4.1372
A"	193.4976	0.1892
A'	257.2002	1.7741
A"	292.2171	0.5841
A'	385.1857	0.4976
A'	405.2868	0.5417
A"	430.0505	0.0033
A"	472.9640	19.4320
A'	494.0058	0.3002
A"	498.7074	11.6458
A"	559.4287	11.4148
A"	582.1618	3.4695
A'	599.1658	8.3344
A'	657.6034	4.7561
A'	708.7796	0.3107
A'	723.9170	2.4372
A"	732.1108	10.6336
A"	757.0074	25.1501
A"	819.7801	36.1726
A"	868.2762	4.7061
A'	876.0022	0.2193
A"	934.2696	2.0418
A"	977.2290	0.0082
A'	1049.6384	5.7565

Atom	**Coordinates (Angstroms)**		
	X	**Y**	**Z**
C	0.000000	1.158655	0.000000
C	1.274454	0.537924	0.000000
C	2.419569	1.356845	0.000000
C	2.277661	2.738468	0.000000
C	1.003880	3.332244	0.000000
C	-0.146161	2.546271	0.000000
C	-0.108232	-1.359093	0.000000
C	1.180435	-0.894222	0.000000
H	3.407375	0.903283	0.000000
H	3.162214	3.369419	0.000000
H	0.912252	4.414654	0.000000
H	-1.131145	3.004184	0.000000
H	2.044166	-1.551094	0.000000
S	-1.290656	-0.040750	0.000000
C	-0.511197	-2.743386	0.000000
H	0.217965	-3.544418	0.000000
N	-1.758699	-3.118788	0.000000
N	-2.856271	-3.450680	0.000000

A'	1074.2116	5.5767
A'	1145.5368	1.1068
A'	1164.7775	3.6985
A'	1191.5647	1.2326
A'	1214.0748	2.4293
A'	1261.0677	10.0200
A'	1290.5681	4.2975
A'	1330.6438	6.7078
A'	1369.5407	6.0866
A'	1428.8095	0.0024
A'	1489.7469	38.2085
A'	1507.0125	7.8539
A'	1582.7554	87.5350
A'	1618.7901	19.6879
A'	1648.6566	0.7483
A'	2191.9325	981.5361
A'	3184.5206	1.9996
A'	3193.8157	3.8287
A'	3202.9149	25.8370
A'	3213.3679	29.8475
A'	3217.1798	7.8745
A'	3236.0245	3.7271

2-Benzothienyl diazomethane (^{3}**1**-s-*Z*)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.126523	-854.176703	-854.050180	4.8352

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-854.039583	-854.086683

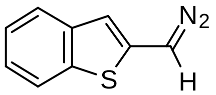
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	65.2043	0.3992
A'	105.5458	3.0668
A"	164.6804	3.3137
A"	197.4076	0.3609
A"	245.4882	1.8412
A'	304.9289	1.4861
A"	324.9811	0.3729
A'	358.4381	6.6979
A'	428.0215	4.2620
A"	441.8920	3.2694
A'	490.1969	0.2791
A"	515.6805	3.2462
A"	562.3562	4.6874
A'	584.5656	15.5279
A'	664.8116	11.4680
A'	705.0750	1.4197
A'	717.4628	3.5949
A"	726.3294	6.4306
A"	755.7823	30.3801
A"	785.4143	1.1063
A"	831.9873	38.0336
A"	870.2849	3.0489
A'	877.1248	1.3324
A"	943.0842	1.7676
A"	983.9465	0.0279
A'	1046.0947	0.0891

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.000000	1.198131	0.000000
C	1.262429	0.539572	0.000000
C	2.440737	1.318370	0.000000
C	2.345447	2.700489	0.000000
C	1.087226	3.333537	0.000000
C	-0.091266	2.590460	0.000000
C	-0.201054	-1.309021	0.000000
C	1.125388	-0.875319	0.000000
H	3.410635	0.828350	0.000000
H	3.248106	3.304475	0.000000
H	1.032954	4.418451	0.000000
H	-1.057703	3.085735	0.000000
H	1.962870	-1.565231	0.000000
S	-1.338287	0.055479	0.000000
C	-0.642159	-2.635137	0.000000
H	0.070134	-3.459254	0.000000
N	-1.995744	-2.918053	0.000000
N	-2.463528	-4.034330	0.000000

A'	1056.1756	28.9522
A'	1082.0265	24.3328
A'	1159.4545	1.1685
A'	1181.7081	13.3913
A'	1195.4733	1.4583
A'	1276.5935	14.7816
A'	1298.2802	0.3016
A'	1304.8058	2.7370
A'	1360.5115	1.3145
A'	1405.3265	2.9042
A'	1430.1382	21.7887
A'	1488.6323	3.1031
A'	1509.9180	9.6631
A'	1603.6117	2.9969
A'	1636.4177	35.1414
A'	1647.8558	69.6872
A'	3165.2401	10.1234
A'	3190.6324	0.4750
A'	3198.4613	3.2773
A'	3208.3693	18.8015
A'	3217.2835	26.9434
A'	3223.4922	4.1502

2-Benzothienyl diazomethane (^{1}**1-s-*E***)



Charge	**Multiplicity**	**Theory/Basis Set**	**Full Point Group**
0	1	RB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.128338	-854.205465	-854.077127	0.6080
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-854.066466	-854.113139		

Symmetry	**Vibrational Frequency (cm^{-1})**	**Intensity**
A"	46.3604	0.8688
A'	96.0631	1.2296
A"	124.9915	5.0687
A"	192.6326	0.2542
A'	253.2493	3.6833
A"	296.3786	0.8415
A'	387.4571	0.7719
A'	406.8815	0.4278
A"	435.5692	0.2232
A"	482.8208	35.6855
A'	493.8303	0.2649
A"	501.8422	0.4988
A"	544.8952	11.6691
A'	560.7288	6.7852
A"	574.9238	0.4453
A'	647.0045	2.2343
A'	714.3965	2.3574
A"	731.6591	7.6261
A"	756.4058	28.7612
A'	806.3326	12.1748
A"	817.3817	31.3635
A"	868.4835	4.2817
A'	895.4442	6.2362
A"	934.8829	2.0442
A"	977.6434	0.0154
A'	1048.7698	6.4091

Atom	**Coordinates (Angstroms)**		
	X	**Y**	**Z**
C	0.609016	-1.211837	0.000000
C	1.074798	0.127462	0.000000
C	2.464448	0.353992	0.000000
C	3.338109	-0.725452	0.000000
C	2.853847	-2.045054	0.000000
C	1.484568	-2.298767	0.000000
C	-1.240965	0.500036	0.000000
C	0.000000	1.079207	0.000000
H	2.844731	1.372225	0.000000
H	4.410167	-0.548806	0.000000
H	3.552356	-2.876984	0.000000
H	1.109230	-3.318113	0.000000
H	0.156112	2.153101	0.000000
S	-1.150303	-1.267319	0.000000
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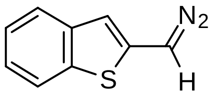
H	-3.471386	0.536939	0.000000
N	-2.692756	2.403062	0.000000
N	-2.791254	3.544707	0.000000

A'	1075.2706	5.2676
A'	1102.6640	12.3172
A'	1161.1046	3.1253
A'	1191.9649	2.1544
A'	1222.4104	5.3675
A'	1225.4143	4.5709
A'	1285.6115	6.3143
A'	1349.4036	10.4161
A'	1384.7876	3.2972
A'	1448.7607	42.0094
A'	1485.8679	41.8729
A'	1505.7049	8.9737
A'	1577.9371	54.1813
A'	1618.5459	13.3501
A'	1648.9336	1.1158
A'	2194.9478	950.9655
A'	3185.1416	1.6519
A'	3193.8547	2.4113
A'	3203.1253	25.5295
A'	3213.4338	30.5012
A'	3217.2896	4.6688
A'	3244.7256	6.4792

2-Benzothienyl diazomethane (^{3}1-s-*E*)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.126832	-854.172905	-854.046073	3.7931

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-854.0355	-854.08255

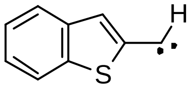
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	78.3184	0.9904
A"	117.4725	3.3148
A'	133.8361	1.6514
A"	194.9133	0.0136
A"	249.4428	1.3419
A'	263.2757	2.3280
A"	348.7975	0.2934
A'	378.8462	2.9168
A'	440.1556	10.2170
A"	442.3457	3.5104
A'	491.7727	0.7308
A"	519.8671	2.9580
A"	566.4039	5.7662
A'	577.9161	6.3396
A'	643.9562	7.8309
A'	713.3521	2.3111
A"	729.2982	8.3833
A"	760.2349	41.2578
A"	766.1150	0.0669
A'	808.7838	1.4497
A"	847.1313	15.7427
A"	877.0883	8.1596
A'	898.9705	0.0897
A"	945.6762	2.0151
A"	986.1082	0.0106
A'	994.8436	8.9035

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-1.268561	0.371884	0.000000
C	0.000000	1.018083	0.000000
C	0.045586	2.430091	0.000000
C	-1.136407	3.152026	0.000000
C	-2.381286	2.492315	0.000000
C	-2.458238	1.101891	0.000000
C	0.677168	-1.239793	0.000000
C	1.081422	0.094546	0.000000
H	1.006981	2.936131	0.000000
H	-1.106735	4.237668	0.000000
H	-3.297371	3.076110	0.000000
H	-3.421483	0.600566	0.000000
H	2.127823	0.375627	0.000000
S	-1.101278	-1.375459	0.000000
C	1.457694	-2.408175	0.000000
H	0.986769	-3.384576	0.000000
N	2.846532	-2.461469	0.000000
N	3.613496	-1.525873	0.000000

A'	1046.3195	1.6397
A'	1077.4297	7.7174
A'	1159.4061	1.2634
A'	1187.5789	21.3056
A'	1191.9539	13.0558
A'	1207.8089	10.0169
A'	1287.0888	7.6926
A'	1352.0696	3.7792
A'	1365.6613	25.4703
A'	1392.6711	10.5107
A'	1437.5611	35.6780
A'	1490.8203	8.0258
A'	1509.7562	16.9329
A'	1602.1298	1.5733
A'	1638.1590	20.0226
A'	1656.9310	143.6394
A'	3192.1500	0.0768
A'	3200.0264	2.5661
A'	3209.6967	17.5010
A'	3217.9729	24.2215
A'	3230.4155	3.4347
A'	3244.4791	0.8583

s-*E*-2-Benzothienyl carbene (^{1}6-s-*E*)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.116542	-744.631073	-744.514532	3.6250

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.505906	-744.547045

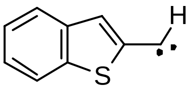
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	131.5604	0.4573
A"	197.9972	0.0605
A"	203.0143	2.7026
A'	264.9964	2.8555
A'	395.2187	6.8398
A"	425.8034	0.1993
A"	489.3929	14.3293
A'	504.3116	1.6895
A'	534.3243	1.6162
A"	578.7032	30.3612
A'	583.4032	10.1124
A"	618.4339	6.8239
A'	711.3031	4.8844
A"	754.2784	32.3147
A'	772.3475	0.9252
A"	781.5517	19.7519
A"	861.1713	21.5013
A'	877.9316	65.3382
A"	878.4848	0.1864
A"	949.0918	0.9017
A"	991.8899	0.0001
A'	1047.9420	10.3299
A'	1052.6032	0.3167
A'	1084.4515	0.9192
A'	1145.9264	0.1851
A'	1172.0024	3.2256
A'	1198.2629	3.4438

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.000000	0.649463	0.000000
C	0.332053	-0.719627	0.000000
C	1.652059	-1.174298	0.000000
C	2.666299	-0.220725	0.000000
C	2.360895	1.150602	0.000000
C	1.041001	1.587731	0.000000
C	-1.454330	0.884326	0.000000
C	-2.133652	-0.335716	0.000000
H	1.883151	-2.235628	0.000000
H	3.703741	-0.542659	0.000000
H	3.168177	1.877597	0.000000
H	0.805037	2.648766	0.000000
H	-3.212903	-0.421841	0.000000
S	-1.132086	-1.724670	0.000000
C	-2.244303	2.066255	0.000000
H	-1.553957	2.940417	0.000000

A'	1215.0119	19.9262
A'	1293.1917	13.3341
A'	1365.2722	7.5017
A'	1371.6460	2.5404
A'	1444.3081	160.0107
A'	1492.5885	37.5064
A'	1506.9335	5.4948
A'	1617.9249	1.3115
A'	1650.5393	0.9417
A'	2918.5817	120.7569
A'	3187.4068	0.1601
A'	3195.3399	0.8659
A'	3204.1838	17.5179
A'	3214.5431	23.0624
A'	3272.0389	6.6256

s-*E*-2-Benzothienyl carbene (^{3}6-s-*E*)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.115766	-744.636464	-744.520697	1.0941

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.511881	-744.554236

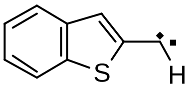
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	143.1128	0.1697
A"	200.2282	0.8021
A"	242.7862	0.3316
A'	257.6445	0.0452
A'	392.6866	2.6662
A"	403.4526	19.9931
A"	429.4079	12.2153
A"	490.7331	1.5196
A'	497.5940	0.8501
A'	533.0749	0.5101
A'	565.0181	2.2884
A"	604.6315	0.2099
A"	684.5673	37.5199
A'	712.2023	6.6438
A"	741.9010	14.0153
A"	770.8882	30.1355
A'	778.4909	0.6123
A'	827.9411	43.7527
A"	869.3473	0.0866
A'	891.4375	4.1923
A"	940.6807	0.8510
A"	981.5633	0.0353
A'	1054.6859	5.7714
A'	1063.6675	8.0686
A'	1147.5902	6.9012
A'	1164.3191	0.3151
A'	1197.5868	1.1861

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.000000	0.642210	0.000000
C	0.298069	-0.736125	0.000000
C	1.615285	-1.201944	0.000000
C	2.648347	-0.268952	0.000000
C	2.369862	1.106859	0.000000
C	1.056247	1.563619	0.000000
C	-1.452462	0.907051	0.000000
C	-2.165963	-0.299789	0.000000
H	1.828519	-2.267001	0.000000
H	3.679320	-0.611534	0.000000
H	3.188142	1.821362	0.000000
H	0.846331	2.629702	0.000000
H	-3.242652	-0.400219	0.000000
S	-1.165596	-1.723690	0.000000
C	-2.031191	2.158124	0.000000
H	-1.679289	3.180407	0.000000

A'	1230.7470	0.7568
A'	1289.4597	8.3626
A'	1341.7935	5.1290
A'	1361.1267	0.2425
A'	1405.1227	5.8977
A'	1492.1710	24.7714
A'	1501.2789	3.5278
A'	1617.5604	0.2659
A'	1647.8600	2.2555
A'	3186.6586	0.0729
A'	3194.8709	3.3283
A'	3204.2532	21.8277
A'	3213.5953	22.3488
A'	3268.2389	1.6499
A'	3273.6146	3.1279

s-*Z*-2-Benzothienyl carbene (^{1}6-s-*Z*)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.116609	-744.631363	-744.514754	3.2010

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.50608	-744.547379

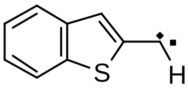
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	121.6737	15.2523
A"	182.0720	6.5063
A"	199.7935	8.4455
A'	259.3536	12.0852
A'	397.8017	3.7157
A"	428.2286	5.4646
A"	485.8998	1.9677
A'	506.6206	1.6406
A'	535.5352	4.9052
A"	581.2637	28.1958
A'	585.0963	2.3515
A"	619.9713	1.0986
A'	711.8916	2.1436
A"	757.2544	24.8510
A'	778.7696	3.3551
A"	785.9740	31.3757
A"	823.2375	17.7901
A'	870.9253	51.7710
A"	884.5125	1.9087
A"	958.8781	1.7717
A"	1003.5041	0.2538
A'	1045.0545	8.1821
A'	1050.9647	0.5592
A'	1111.9003	49.1709
A'	1135.2487	0.5975
A'	1174.3389	17.4343
A'	1198.6487	5.3093

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.000000	0.642653	0.000000
C	0.344628	-0.721596	0.000000
C	1.671683	-1.158259	0.000000
C	2.669523	-0.187819	0.000000
C	2.345622	1.181108	0.000000
C	1.021364	1.601646	0.000000
C	-1.448424	0.873979	0.000000
C	-2.127287	-0.346718	0.000000
H	1.919430	-2.215683	0.000000
H	3.711725	-0.494578	0.000000
H	3.144751	1.917209	0.000000
H	0.744710	2.651704	0.000000
H	-3.203809	-0.471826	0.000000
S	-1.113251	-1.733366	0.000000
C	-2.037888	2.168693	0.000000
H	-3.140103	2.024904	0.000000

A'	1226.1768	16.6365
A'	1284.7369	11.6918
A'	1372.3662	1.1989
A'	1394.1023	1.1221
A'	1429.5627	178.2240
A'	1491.1391	30.6313
A'	1508.7565	1.8674
A'	1616.8170	1.3210
A'	1651.9472	0.7875
A'	2939.1446	161.5482
A'	3189.4779	1.7973
A'	3200.7091	11.0734
A'	3211.3997	16.8467
A'	3219.6750	10.0214
A'	3255.0379	2.1626

s-*Z*-2-Benzothienyl carbene (^{3}6-s-*Z*)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.115932	-744.637339	-744.521407	0.1423

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.512642	-744.554906

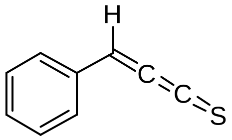
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	146.4336	0.3892
A"	199.8835	3.2268
A"	245.4864	1.6620
A'	250.5871	3.0415
A'	389.5103	1.4727
A"	417.2347	10.2452
A"	471.8613	6.3979
A"	495.7134	6.3040
A'	498.5924	0.1609
A'	526.0989	3.8383
A'	574.6841	0.7311
A"	605.9668	1.4385
A"	673.2033	43.6414
A'	710.2475	4.9816
A"	744.6337	14.7132
A'	773.5719	2.4657
A"	775.1788	29.7276
A'	821.1949	4.5858
A"	873.6065	0.2368
A'	915.1439	42.5399
A"	946.3490	1.2033
A"	984.3148	0.0025
A'	1052.4492	6.4628
A'	1063.9959	8.2416
A'	1142.7588	4.1792
A'	1161.3763	1.8079
A'	1196.7169	0.8138

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.000000	0.646208	0.000000
C	0.332473	-0.723239	0.000000
C	1.661230	-1.154917	0.000000
C	2.668555	-0.193844	0.000000
C	2.354468	1.174738	0.000000
C	1.029658	1.597184	0.000000
C	-1.451658	0.879566	0.000000
C	-2.143332	-0.342970	0.000000
H	1.903368	-2.213730	0.000000
H	3.708293	-0.509067	0.000000
H	3.154490	1.909676	0.000000
H	0.782504	2.655114	0.000000
H	-3.217203	-0.472015	0.000000
S	-1.108842	-1.745278	0.000000
C	-2.040733	2.125663	0.000000
H	-3.053938	2.504143	0.000000

A'	1232.3697	0.6415
A'	1284.0241	7.0358
A'	1352.4176	2.3460
A'	1359.4492	0.5436
A'	1401.6920	3.7375
A'	1492.8116	24.0493
A'	1503.5189	4.9321
A'	1618.1831	0.3011
A'	1649.4690	2.8187
A'	3187.2308	0.3364
A'	3196.5954	4.4626
A'	3205.5615	19.2089
A'	3213.6759	21.4544
A'	3264.6305	0.3560
A'	3269.6499	2.6437

Benzothioketene (^{1}7)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.118187	-744.693782	-744.575595	4.8100

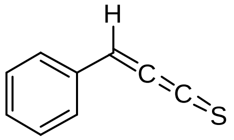
$\Delta H_{(298)}$	$\Delta G_{(298)}$	
-744.566111	-744.610619	(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A'	51.9237	0.1721
A"	54.2104	0.0891
A"	183.0656	0.1487
A'	246.1002	1.8025
A"	265.6289	2.5933
A'	336.1970	0.0143
A'	399.5850	0.6217
A"	414.6690	0.0008
A"	476.4559	5.7825
A"	542.2822	0.7535
A'	602.2193	51.1591
A'	629.4588	0.3483
A"	696.5287	19.9626
A'	761.1809	29.3623
A"	762.9821	29.8363
A'	843.9044	20.3508
A"	858.0789	0.8219
A"	890.5288	6.6230
A"	951.8077	6.0114
A"	979.5686	0.0129
A"	1007.0112	0.0851
A'	1015.8014	5.5297
A'	1053.5074	0.4801
A'	1115.6619	2.8292
A'	1195.0039	1.1108
A'	1207.0534	53.5021

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	1.040404	3.300135	0.000000
C	-0.102463	2.506084	0.000000
C	0.000000	1.100956	0.000000
C	1.280986	0.511013	0.000000
C	2.419231	1.306427	0.000000
C	2.303165	2.702198	0.000000
H	0.949226	4.382572	0.000000
H	-1.087636	2.966367	0.000000
H	1.359387	-0.572151	0.000000
H	3.402085	0.843689	0.000000
H	3.196451	3.320738	0.000000
C	-1.214826	0.299028	0.000000
H	-2.147798	0.871109	0.000000
C	-1.283439	-1.037106	0.000000
C	-1.383439	-2.298406	0.000000
S	-1.501839	-3.884644	0.000000

A'	1242.0246	87.3147
A'	1286.1709	56.3625
A'	1360.0642	6.6339
A'	1372.8819	2.5018
A'	1483.3197	15.6317
A'	1531.1717	0.1968
A'	1551.0710	7.9595
A'	1632.7467	0.0058
A'	1653.4402	55.1508
A'	2118.7193	1306.1236
A'	3099.0527	19.2873
A'	3184.4030	4.0546
A'	3192.3167	0.8242
A'	3202.0382	14.5636
A'	3211.0535	20.9335
A'	3217.3004	19.8353

Benzothioketene (^{3}7)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.116009	-744.652597	-744.536587	1.6860

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.526868	-744.572694

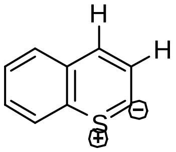
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	56.1198	0.0038
A'	59.4345	0.0856
A"	180.1471	0.0352
A'	228.8015	0.2020
A"	251.6176	2.5381
A'	320.7382	0.3610
A"	398.1776	0.1640
A"	416.3111	0.0002
A'	435.6680	0.1855
A"	479.0199	10.8298
A'	606.5720	20.4522
A'	630.3857	0.4655
A"	654.2447	9.4151
A"	698.9680	16.4474
A'	735.1095	13.3582
A"	774.2303	45.6324
A'	842.6100	1.3454
A"	842.8094	0.2912
A"	906.5653	4.2013
A"	961.7967	0.0422
A"	989.0498	0.0475
A'	1006.7099	0.1721
A'	1051.7348	1.1308
A'	1113.5885	3.2432
A'	1190.2745	0.1579
A'	1199.7298	0.9507

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	1.088864	3.291589	0.000000
C	-0.068110	2.522396	0.000000
C	0.000000	1.108698	0.000000
C	1.280224	0.503105	0.000000
C	2.431009	1.280007	0.000000
C	2.346083	2.677618	0.000000
H	1.012980	4.375726	0.000000
H	-1.042600	3.004741	0.000000
H	1.355535	-0.580968	0.000000
H	3.404013	0.795781	0.000000
H	3.249549	3.280612	0.000000
C	-1.216329	0.337686	0.000000
H	-2.161636	0.880250	0.000000
C	-1.303878	-1.028307	0.000000
C	-1.409891	-2.285084	0.000000
S	-1.544105	-3.887649	0.000000

A'	1206.4757	9.6671
A'	1230.7069	0.7908
A'	1339.7009	3.2202
A'	1368.0705	0.2188
A'	1419.2818	1.3679
A'	1503.1893	6.0860
A'	1528.8420	11.4263
A'	1613.8276	1.0132
A'	1633.4963	0.5776
A'	1923.5683	36.3317
A'	3151.7182	0.8172
A'	3179.7295	6.9794
A'	3184.8275	1.1699
A'	3194.8268	8.5506
A'	3201.0167	33.9228
A'	3212.5112	26.9962

1-benzothiopyran-2-ylidene (^{1}8)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.119200	-744.676438	-744.557238	4.7108

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.548925	-744.589547

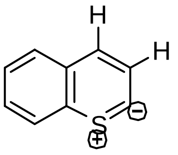
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	118.9682	0.6262
A"	161.4257	1.8783
A'	310.2045	0.0336
A"	321.1372	3.2868
A"	417.1744	7.5425
A'	438.7238	0.3038
A'	452.9083	4.0780
A"	459.2595	4.0974
A'	544.5808	10.8072
A"	584.9022	0.2835
A'	688.3044	1.2868
A'	741.4176	13.2129
A"	751.7998	8.9186
A'	762.6743	0.4260
A"	764.5630	27.4312
A"	857.7663	17.8098
A'	877.1757	0.5086
A"	886.5639	4.4496
A"	963.2879	1.9510
A"	1000.5052	0.0432
A"	1023.7680	0.0053
A'	1050.5570	0.9098
A'	1073.8299	5.9565
A'	1120.3638	12.4098
A'	1171.2083	0.7390
A'	1199.9804	0.5219

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	2.267976	1.440952	0.000000
C	0.904350	1.682727	0.000000
C	0.000000	0.605691	0.000000
C	0.475584	-0.731100	0.000000
C	1.877802	-0.945377	0.000000
C	2.757295	0.118879	0.000000
H	2.965568	2.274111	0.000000
H	0.524532	2.701349	0.000000
C	-0.433928	-1.839239	0.000000
H	2.249358	-1.967334	0.000000
H	3.828574	-0.060151	0.000000
C	-1.806030	-1.748654	0.000000
C	-2.588796	-0.549262	0.000000
H	0.022356	-2.829339	0.000000
H	-2.362082	-2.687117	0.000000
S	-1.747114	0.897548	0.000000

A'	1259.7945	13.1770
A'	1270.1787	11.8378
A'	1295.1812	5.9025
A'	1389.3768	11.2053
A'	1459.5019	17.5491
A'	1462.5311	7.7319
A'	1523.5936	6.8159
A'	1555.2437	25.6715
A'	1623.4878	10.0498
A'	1655.9366	6.6376
A'	3137.7624	14.7275
A'	3159.8791	39.6054
A'	3183.9904	3.6742
A'	3188.7707	1.3396
A'	3200.7584	18.6428
A'	3213.5014	23.4244

1-benzothiopyran-2-ylidene (^{3}8)



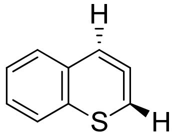
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.117412	-744.644048	-744.526637	1.4525
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-744.518024	-744.560363		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	88.2060	0.1201
A"	167.7113	0.0186
A"	248.7858	2.6519
A'	322.9870	1.1397
A'	405.1353	1.5567
A"	430.9674	7.8284
A'	441.5635	0.4000
A"	464.9030	0.0060
A'	544.4377	0.2862
A"	546.8698	0.2037
A'	672.4895	2.3230
A"	683.5352	15.5159
A'	714.7285	5.6813
A"	733.5870	4.6097
A'	762.7236	10.3636
A"	768.1674	60.2001
A"	866.2791	3.2118
A'	867.2307	1.1879
A"	872.7971	0.4819
A"	933.1042	2.4755
A"	976.7479	0.0052
A'	1045.1365	24.6695
A'	1070.7639	0.9917
A'	1122.1325	0.6212
A'	1154.4966	3.6934
A'	1193.7098	0.0177

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	2.275614	1.406628	0.000000
C	0.901098	1.647080	0.000000
C	0.000000	0.582383	0.000000
C	0.448296	-0.768273	0.000000
C	1.850541	-0.969829	0.000000
C	2.746645	0.089725	0.000000
H	2.969418	2.242115	0.000000
H	0.528104	2.668138	0.000000
C	-0.439681	-1.898177	0.000000
H	2.219433	-1.992582	0.000000
H	3.815039	-0.107510	0.000000
C	-1.842098	-1.776856	0.000000
C	-2.441283	-0.557277	0.000000
H	0.002648	-2.889747	0.000000
H	-2.455382	-2.676223	0.000000
S	-1.754628	1.013961	0.000000

A'	1235.5927	0.3831
A'	1292.3230	7.9723
A'	1297.3234	9.2294
A'	1335.0980	7.9405
A'	1385.4565	10.9533
A'	1467.9455	9.5358
A'	1506.1669	13.7484
A'	1534.4045	6.6467
A'	1601.3534	0.1447
A'	1626.9701	0.0258
A'	3172.0980	4.2906
A'	3181.6431	3.7105
A'	3187.0239	0.3952
A'	3198.9816	13.2645
A'	3202.7156	20.7495
A'	3213.5087	21.3725

2*H*-1-benzo-2,3-dehydrothiopyran (^{1}9)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_1

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.118338	-744.665859	-744.547522	1.6521

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.539052	-744.579786

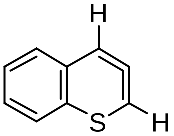
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	138.8815	1.6275
A	165.6426	0.4077
A	300.7732	7.7303
A	333.9137	3.9306
A	388.4438	4.7540
A	422.1504	15.4294
A	455.9794	2.6917
A	473.7032	12.2394
A	528.9603	0.9310
A	543.0259	13.0594
A	627.1598	41.6601
A	681.0536	3.3491
A	718.3581	17.3188
A	734.8485	32.0397
A	756.1937	32.7415
A	785.7849	40.7739
A	830.2144	1.6972
A	866.6097	0.4455
A	894.7876	2.5730
A	951.0825	2.0170
A	986.7783	0.0446
A	1050.7599	9.9615
A	1071.9288	0.4113
A	1146.4144	6.9455
A	1149.1475	0.1058
A	1197.1166	1.4466
A	1226.8426	10.4743

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-2.469380	-0.945423	0.072350
C	-1.162578	-1.417039	-0.032031
C	-0.088046	-0.519653	-0.060704
C	-0.335255	0.880996	-0.036563
C	-1.662442	1.327057	0.079153
C	-2.722036	0.428630	0.136690
H	-3.291709	-1.654451	0.111931
H	-0.974957	-2.486636	-0.065527
H	-1.850425	2.397473	0.103013
H	-3.741820	0.794084	0.217016
C	0.801176	1.772778	-0.321929
C	1.986621	1.329115	0.094669
C	2.477596	0.147183	0.458101
S	1.564583	-1.228744	-0.185382
H	0.658800	2.633537	-0.972034
H	3.212849	-0.045981	1.233283

A	1266.4086	10.3315
A	1298.5697	9.5311
A	1328.9157	1.2596
A	1402.5284	33.7181
A	1485.0352	8.7621
A	1492.8225	7.0855
A	1606.6827	0.8228
A	1640.6755	6.2998
A	1820.3175	2.6322
A	3176.8732	13.7951
A	3186.2148	1.5691
A	3192.7013	3.5203
A	3202.7200	15.5044
A	3203.0768	17.9120
A	3214.0626	24.0721

2*H*-1-benzo-2,3-dehydrothiopyran (^{3}9)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.116952	-744.645047	-744.528095	0.9190

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.51946	-744.561698

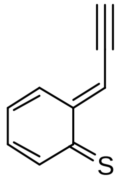
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	102.0909	0.5146
A"	164.3099	0.6095
A"	271.3417	0.4676
A'	327.6331	1.3289
A'	405.9820	0.0450
A'	436.9669	0.3918
A"	447.7693	1.3229
A"	459.7697	6.1832
A"	541.4397	4.4652
A'	544.0134	0.1156
A"	614.6054	31.9329
A'	678.6060	3.8550
A'	691.2388	0.3338
A"	716.5456	0.6239
A"	740.7435	9.3827
A'	761.1073	12.0284
A"	774.8751	53.1240
A'	867.9014	1.2499
A"	868.4735	1.3511
A"	937.4076	2.4020
A"	978.1645	0.0059
A'	1055.8359	12.4036
A'	1074.0590	2.6928
A'	1101.4975	4.3683
A'	1156.1813	3.0880
A'	1195.3410	0.0507
A'	1217.0245	0.0499

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	2.268435	1.400595	0.000000
C	0.892328	1.616394	0.000000
C	0.000000	0.538682	0.000000
C	0.487356	-0.800598	0.000000
C	1.890501	-0.982741	0.000000
C	2.766420	0.092358	0.000000
H	2.947024	2.248490	0.000000
H	0.504174	2.631786	0.000000
H	2.274298	-1.999919	0.000000
H	3.838561	-0.083807	0.000000
C	-0.398941	-1.939525	0.000000
C	-1.759170	-1.741450	0.000000
C	-2.521748	-0.629714	0.000000
S	-1.733931	0.963019	0.000000
H	0.032630	-2.936007	0.000000
H	-3.604868	-0.592850	0.000000

A'	1253.7920	7.8929
A'	1291.0233	10.0576
A'	1337.1283	4.7439
A'	1407.6974	15.4723
A'	1445.3514	19.3108
A'	1485.7453	6.5439
A'	1527.1115	3.4584
A'	1602.6387	2.9546
A'	1635.0178	0.0361
A'	3183.2232	3.3972
A'	3188.3222	0.6445
A'	3198.9485	1.1304
A'	3200.6684	25.3518
A'	3214.2891	21.9867
A'	3233.9141	1.5566

2-(*E*-vinylacetylene)-3,5-cyclohexadien-1-thione (^{1}10)



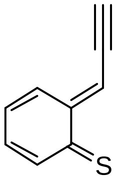
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.116401	-744.649069	-744.532668	4.2845
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-744.522924	-744.567228		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	62.0455	1.2327
A"	114.1716	0.0105
A'	124.9319	0.3199
A"	233.5435	0.0552
A'	260.0486	1.5728
A'	359.6683	4.6682
A'	434.4770	14.8600
A"	435.7781	0.6177
A"	448.8829	1.2037
A'	490.8725	2.2807
A"	516.3952	11.1703
A'	608.2083	11.2769
A"	615.2121	44.2329
A'	620.6421	46.3609
A"	735.5802	7.1768
A'	740.4182	4.5900
A"	780.1453	34.4094
A'	837.5976	5.1890
A"	871.7299	0.6856
A"	940.9798	6.3568
A"	986.0144	0.1441
A"	1012.5930	0.3603
A'	1022.3855	6.8659
A'	1054.9189	7.6335
A'	1101.3325	48.5839

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.929387	-1.955032	0.000000
C	-0.245589	-1.116672	0.000000
C	0.000000	0.350119	0.000000
C	1.365111	0.836514	0.000000
C	2.419015	-0.018159	0.000000
C	2.191263	-1.438199	0.000000
H	0.767534	-3.027594	0.000000
H	1.516695	1.911442	0.000000
H	3.437181	0.359629	0.000000
H	3.047110	-2.108549	0.000000
S	-1.768996	-1.816865	0.000000
C	-1.056735	1.231554	0.000000
C	-0.951055	2.632688	0.000000
C	-0.907337	3.846341	0.000000
H	-0.868409	4.912456	0.000000
H	-2.060531	0.807523	0.000000

A'	1163.9283	76.0315
A'	1190.9462	12.0470
A'	1233.9820	16.5558
A'	1295.8396	13.5362
A'	1355.3898	3.0060
A'	1444.2322	26.4676
A'	1487.0488	24.3658
A'	1566.6756	100.8366
A'	1579.9056	15.8557
A'	1682.6551	34.6536
A'	2190.1881	18.5953
A'	3163.8924	0.8471
A'	3190.4896	10.9011
A'	3203.8363	6.0341
A'	3218.9219	12.5936
A'	3226.9806	9.5820
A'	3490.4312	97.7941

2-(*E*-vinylacetylene)-3,5-cyclohexadien-1-thione (^{3}10)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.114295	-744.616558	-744.502263	1.3151

ΔH$_{(298)}$	ΔG$_{(298)}$
-744.492305	-744.537715

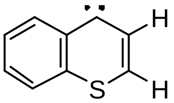
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	89.9392	0.3272
A'	114.3671	0.0167
A"	132.6197	0.0222
A'	211.8117	0.4999
A"	259.1307	0.7606
A'	343.6235	0.6097
A'	421.1941	2.0204
A"	429.2703	18.2139
A"	445.6733	7.5919
A"	460.8775	38.1671
A'	468.5142	2.5334
A"	508.7330	0.2551
A'	622.9954	21.3170
A'	634.3861	27.1582
A"	675.9701	10.4051
A'	713.6612	3.4395
A"	751.3589	4.9155
A"	769.2899	41.3198
A'	838.2646	3.7842
A"	864.8970	0.2316
A"	940.0767	1.9726
A"	977.1779	0.0260
A'	1052.2781	25.5264
A'	1064.6228	2.9319
A'	1087.1193	6.4603
A'	1151.3462	1.2149

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	1.094416	-1.860882	0.000000
C	-0.076593	-1.092808	0.000000
C	0.000000	0.334860	0.000000
C	1.291200	0.924326	0.000000
C	2.441283	0.154716	0.000000
C	2.344859	-1.243834	0.000000
H	1.028878	-2.945196	0.000000
H	1.353975	2.008255	0.000000
H	3.415444	0.634928	0.000000
H	3.241484	-1.857106	0.000000
S	-1.632554	-1.931134	0.000000
C	-1.187482	1.130680	0.000000
C	-1.218471	2.519093	0.000000
C	-1.265815	3.739662	0.000000
H	-1.309655	4.804920	0.000000
H	-2.149656	0.617472	0.000000

A'	1192.9686	3.3261
A'	1243.9373	1.5012
A'	1291.8082	4.5365
A'	1315.9917	12.8622
A'	1421.4273	6.7012
A'	1461.6322	0.2515
A'	1489.0264	52.2739
A'	1581.6230	7.6284
A'	1615.8186	9.6950
A'	2091.0818	15.1373
A'	3132.3578	25.7535
A'	3188.8065	0.2813
A'	3198.5170	5.7927
A'	3208.8555	15.6062
A'	3217.8844	16.4650
A'	3488.9471	75.5437

1-Benzothiopyran-4-ylidene (^{1}11)



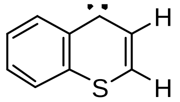
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.118009	-744.645869	-744.527860	3.3426
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-744.519283	-744.560744		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	73.4350	3.6318
A"	137.0039	8.1057
A"	268.0351	5.1591
A'	334.0543	4.5654
A"	375.8531	0.6656
A'	425.0007	1.3302
A'	454.3921	3.0919
A"	455.5194	1.0150
A"	545.9418	4.8031
A'	552.2090	0.7373
A'	687.0722	3.4717
A"	733.2296	3.5769
A'	738.2301	9.4186
A"	770.4067	15.6330
A"	793.8727	47.7026
A'	819.7287	10.5485
A'	863.2173	0.4599
A"	881.9875	0.5409
A"	978.9633	1.7464
A"	983.2947	0.1826
A"	1014.3031	0.0925
A'	1052.8624	3.9020
A'	1071.9422	2.6241
A'	1097.5957	4.2602
A'	1152.4802	2.2605
A'	1197.9459	0.9798
A'	1216.1475	16.7740

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	2.223904	1.494386	0.000000
C	0.851382	1.682418	0.000000
C	0.000000	0.562419	0.000000
C	0.507729	-0.772566	0.000000
C	1.926894	-0.898368	0.000000
C	2.769081	0.196416	0.000000
H	2.881268	2.359935	0.000000
H	0.435524	2.687350	0.000000
C	-0.245909	-2.009818	0.000000
H	2.307772	-1.914917	0.000000
H	3.847234	0.063450	0.000000
C	-1.669271	-1.862449	0.000000
C	-2.394189	-0.696177	0.000000
H	-2.274249	-2.772886	0.000000
H	-3.483064	-0.682482	0.000000
S	-1.720763	0.880124	0.000000

A'	1271.6037	5.9063
A'	1328.2959	1.9273
A'	1348.3416	50.4337
A'	1422.2961	5.2710
A'	1470.6375	16.3679
A'	1472.3136	5.4659
A'	1493.5626	53.5358
A'	1584.7753	10.5421
A'	1645.9074	18.8793
A'	3110.4288	42.7787
A'	3176.8408	13.3173
A'	3178.2713	2.2619
A'	3193.5143	11.0758
A'	3206.7791	18.6830
A'	3221.8468	12.2186

1-Benzothiopyran-4-ylidene (^{3}11)



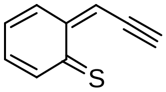
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.117186	-744.643347	-744.526160	0.2435
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-744.517517	-744.559914		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	87.9813	2.4279
A"	158.5065	1.3056
A"	259.5851	0.0406
A'	318.1658	2.2068
A'	416.5163	1.0264
A"	428.1007	6.1205
A'	432.2970	0.2210
A"	460.2460	0.2301
A'	542.6489	0.1849
A"	545.9354	3.9055
A"	641.4249	34.8504
A'	680.5634	2.8958
A'	708.2238	3.6116
A"	726.1169	5.1315
A"	761.7481	48.3032
A'	789.5262	6.6331
A'	857.3819	0.6345
A"	865.9431	0.0046
A"	882.0403	3.4789
A"	933.3672	2.1678
A"	977.9605	0.0005
A'	1054.1969	16.6349
A'	1070.9156	4.3174
A'	1131.9982	6.1131
A'	1149.5380	0.1031
A'	1174.5536	5.3800
A'	1193.7441	0.0288

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	2.197467	1.576937	0.000000
C	0.806266	1.695398	0.000000
C	0.000000	0.556847	0.000000
C	0.587538	-0.745348	0.000000
C	1.999243	-0.831375	0.000000
C	2.790266	0.310191	0.000000
H	2.812791	2.471814	0.000000
H	0.345368	2.680074	0.000000
C	-0.253166	-1.884247	0.000000
H	2.452755	-1.818086	0.000000
H	3.872541	0.215598	0.000000
C	-1.632223	-1.962621	0.000000
C	-2.417275	-0.826248	0.000000
H	-2.128905	-2.931421	0.000000
H	-3.501166	-0.861342	0.000000
S	-1.770130	0.806635	0.000000

A'	1286.1836	4.4789
A'	1317.4673	12.1315
A'	1342.7308	20.0715
A'	1407.1867	12.2603
A'	1442.3609	4.3143
A'	1475.7006	4.4108
A'	1498.7064	13.4615
A'	1596.5283	4.5729
A'	1623.9729	0.1094
A'	3171.6585	6.8715
A'	3184.9411	1.1703
A'	3193.3766	5.1698
A'	3206.1362	17.8965
A'	3215.7947	21.1249
A'	3226.9383	1.5666

2-(*Z*-vinylacetylene)-3,5-cyclohexadien-1-thione (^{1}12)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.116277	-744.642727	-744.526451	3.3318

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.516718	-744.560979

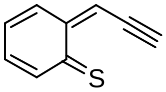
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	40.0482	1.4297
A'	145.5147	1.8125
A"	147.6295	0.1514
A'	245.9069	1.0271
A"	250.7839	0.0066
A'	358.6095	7.3816
A'	390.2046	1.8196
A"	432.3614	5.2198
A"	451.4324	2.1853
A'	506.6131	3.2589
A"	519.1778	0.1241
A'	582.4689	49.8397
A'	633.4217	12.3960
A"	652.1420	36.6955
A'	684.1074	4.2891
A"	746.4492	0.6793
A"	758.0657	36.8445
A"	860.6247	6.4274
A'	860.6864	0.3453
A"	903.2782	13.6369
A"	977.4781	0.8875
A"	1010.0235	0.4446
A'	1020.4621	9.2396
A'	1086.0922	5.0684
A'	1103.9364	36.0784
A'	1171.7510	23.5967
A'	1191.7891	2.5346

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-1.868831	-0.872157	0.000000
C	-0.441357	-0.651015	0.000000
C	0.000000	0.762779	0.000000
C	-1.011992	1.803974	0.000000
C	-2.338991	1.518732	0.000000
C	-2.771304	0.150017	0.000000
H	-2.198988	-1.905495	0.000000
H	-0.671599	2.836403	0.000000
H	-3.076068	2.316181	0.000000
H	-3.836051	-0.068904	0.000000
S	0.593743	-1.967997	0.000000
C	1.311724	1.194755	0.000000
C	2.512970	0.473572	0.000000
C	3.647282	0.034732	0.000000
H	4.593029	-0.458712	0.000000
H	1.452781	2.276144	0.000000

A'	1242.7449	18.3261
A'	1274.0263	5.4517
A'	1413.3198	26.9431
A'	1426.1682	8.7951
A'	1489.7340	17.2613
A'	1560.1981	72.0064
A'	1591.7443	33.3355
A'	1682.5892	37.8340
A'	2177.6064	51.3954
A'	3146.5633	2.2929
A'	3183.8444	1.8319
A'	3192.1880	15.5019
A'	3212.3749	21.3995
A'	3224.6573	9.9385
A'	3490.6737	66.6903

2-(*Z*-vinylacetylene)-3,5-cyclohexadien-1-thione (^{3}12)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.113858	-744.620978	-744.507120	1.1453

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.497001	-744.54282

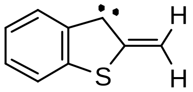
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	42.9981	0.7055
A'	154.4396	1.0544
A"	159.8980	0.2258
A'	195.7950	4.8527
A"	238.9078	1.8442
A"	337.0197	49.7256
A'	339.9821	0.9091
A'	383.0244	6.3227
A"	437.8274	10.8217
A"	452.5628	2.5152
A'	486.7015	0.6375
A"	524.0198	0.4662
A'	618.4827	20.8503
A'	645.8266	31.7665
A"	683.7628	3.5619
A'	687.5546	3.4357
A"	726.4202	10.8971
A"	772.9589	47.1394
A'	854.3796	2.0064
A"	860.9686	1.0457
A"	937.4565	1.8964
A"	972.9747	0.0917
A'	1050.7407	8.1640
A'	1071.4304	14.4420
A'	1091.8467	1.3134
A'	1156.8677	0.3453
A'	1194.1459	2.9517

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.866739	1.804652	0.000000
C	0.000000	0.699173	0.000000
C	0.550555	-0.623508	0.000000
C	1.964953	-0.759597	0.000000
C	2.800835	0.340825	0.000000
C	2.247532	1.631328	0.000000
H	0.449650	2.807436	0.000000
H	2.382495	-1.763403	0.000000
H	3.878613	0.207232	0.000000
H	2.894824	2.503844	0.000000
S	-1.732557	0.982037	0.000000
C	-0.266025	-1.789424	0.000000
C	-1.653026	-1.800574	0.000000
C	-2.874343	-1.952434	0.000000
H	-3.939076	-2.013290	0.000000
H	0.231076	-2.757052	0.000000

A'	1230.4322	8.3718
A'	1275.4645	12.9997
A'	1342.4958	0.4734
A'	1420.2628	4.1715
A'	1466.0099	0.6595
A'	1487.5126	28.4805
A'	1579.7449	6.0934
A'	1619.9462	15.5132
A'	2019.8960	29.6195
A'	3177.5160	0.5593
A'	3184.9617	4.7007
A'	3191.9716	3.5878
A'	3204.1745	18.6738
A'	3215.0261	25.3637
A'	3483.3221	87.7139

^{1}**13**



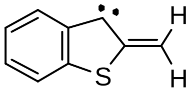
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.117327	-744.641695	-744.524368	1.4657
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-744.515582	-744.55719		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	87.8805	7.5857
A"	173.4098	2.1846
A"	237.1727	1.8780
A'	267.3758	6.3595
A'	400.8566	0.1415
A"	439.7708	0.7364
A'	476.6822	1.3852
A"	489.7319	0.3754
A'	490.1483	8.4633
A'	517.7242	24.0669
A"	542.7210	4.8717
A'	646.7933	3.2701
A"	702.4104	0.1981
A'	705.6921	5.2885
A"	737.8939	7.1843
A"	785.6521	46.3940
A'	867.8988	13.1984
A"	879.4360	0.1064
A'	970.5438	17.5461
A"	978.7508	1.6758
A"	1002.3574	28.9589
A"	1004.4724	0.1898
A'	1044.9391	2.7998
A'	1063.7334	10.7002
A'	1136.1782	3.5905
A'	1171.6510	26.2529
A'	1199.8719	6.6774

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	2.074803	-0.621187	0.000000
C	0.657249	-0.590955	0.000000
C	0.000000	0.691805	0.000000
C	0.740576	1.877948	0.000000
C	2.130801	1.792524	0.000000
C	2.804094	0.554075	0.000000
H	2.559994	-1.592568	0.000000
H	0.251819	2.847252	0.000000
H	2.712027	2.711546	0.000000
H	3.889705	0.532662	0.000000
C	-0.169740	-1.750041	0.000000
C	-1.536447	-1.284008	0.000000
C	-2.614351	-2.092702	0.000000
H	-2.454096	-3.166107	0.000000
S	-1.740228	0.557996	0.000000
H	-3.637712	-1.725464	0.000000

A'	1266.9904	11.6634
A'	1330.5347	104.5285
A'	1338.0366	38.7732
A'	1437.2567	53.7938
A'	1455.5938	31.4456
A'	1492.1509	53.0252
A'	1583.9808	7.0492
A'	1640.3627	112.8732
A'	1665.2468	67.6588
A'	3172.8767	4.5033
A'	3187.8826	4.3611
A'	3205.1640	6.4365
A'	3212.9428	14.2761
A'	3222.2497	17.8436
A'	3270.1972	1.5038

^{3}13



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.116379	-744.639110	-744.522731	0.7348

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.513943	-744.556352

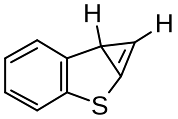
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	111.3301	1.4853
A"	188.1357	0.4415
A'	252.6918	1.5230
A"	284.0751	0.0249
A'	386.6190	0.5789
A"	430.5963	2.4755
A'	472.4252	0.7508
A'	481.7471	1.0323
A"	495.8139	1.7894
A"	531.8898	0.0107
A"	578.5346	1.1452
A'	610.1385	5.2228
A'	641.6297	2.2256
A'	708.5891	2.7019
A"	720.9886	4.8344
A"	747.6930	26.7579
A"	759.5236	65.1775
A"	860.7300	0.1792
A'	872.8829	1.9137
A"	932.8821	1.2480
A"	976.4408	0.0400
A'	1022.0126	1.1476
A'	1046.7179	7.9425
A'	1072.3220	9.9853
A'	1149.0358	0.9395
A'	1191.2020	0.3702
A'	1201.9448	8.6428

Atom	Coordinates (Angstroms) X	Y	Z
C	2.149661	-0.491326	0.000000
C	0.739929	-0.540988	0.000000
C	0.000000	0.682241	0.000000
C	0.649678	1.913785	0.000000
C	2.045752	1.935523	0.000000
C	2.787431	0.741194	0.000000
H	2.719132	-1.415810	0.000000
H	0.082926	2.840644	0.000000
H	2.563461	2.890469	0.000000
H	3.872792	0.784885	0.000000
C	-0.148833	-1.634735	0.000000
C	-1.520111	-1.396924	0.000000
C	-2.583395	-2.268009	0.000000
H	-2.405026	-3.337460	0.000000
S	-1.746506	0.407076	0.000000
H	-3.609867	-1.920524	0.000000

A'	1271.2201	5.1059
A'	1325.3328	0.4908
A'	1369.1579	8.4512
A'	1406.1505	2.5055
A'	1462.3543	9.0201
A'	1491.6606	6.3378
A'	1525.2434	4.3602
A'	1598.2513	2.0738
A'	1624.0964	5.7415
A'	3189.1334	1.3342
A'	3190.1221	0.1433
A'	3198.6929	4.7787
A'	3208.6432	20.1164
A'	3217.1474	22.3933
A'	3282.5652	2.1568

4-Thia-2,3-benzobicyclo[3.1.0]hexa-2,5-diene (^{1}14)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_1

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.118005	-744.637742	-744.519737	1.2817

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.51133	-744.551944

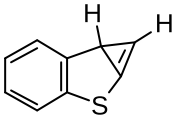
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	143.1146	1.0853
A	174.7272	0.3809
A	279.8328	4.6522
A	308.4131	2.8819
A	368.5169	1.0691
A	444.1439	3.2403
A	470.7255	1.5210
A	504.5921	2.9068
A	565.8043	6.9579
A	606.5683	7.4254
A	629.4813	31.0304
A	671.1287	6.2566
A	700.2506	16.9420
A	735.1729	7.4594
A	764.6670	42.2639
A	820.2640	25.3600
A	850.8804	4.3255
A	878.9980	1.0475
A	943.3079	1.1331
A	982.3611	0.0079
A	1004.3861	0.7379
A	1030.6039	25.4942
A	1046.1196	21.2938
A	1061.5039	0.9653
A	1131.9488	2.5890
A	1146.5945	0.9024

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	1.391340	-1.346859	0.120209
C	0.203628	-0.633792	-0.030700
C	0.192847	0.777358	-0.135335
C	1.412273	1.456522	-0.105803
C	2.608564	0.752469	0.050211
C	2.595839	-0.640130	0.164000
H	1.385858	-2.429799	0.204961
H	1.423287	2.539618	-0.200342
H	3.552118	1.290029	0.083518
H	3.528680	-1.183880	0.286151
C	-1.179673	1.327244	-0.412692
H	-1.297384	1.930442	-1.316790
C	-2.284806	1.270913	0.628193
H	-2.691888	1.716249	1.525362
C	-2.102972	0.186896	-0.075746
S	-1.432682	-1.422900	-0.112305

A	1192.8282	1.2042
A	1213.0999	3.1139
A	1293.5378	0.6877
A	1321.5325	1.9587
A	1358.6695	4.8334
A	1485.0685	20.1247
A	1496.8163	7.0247
A	1620.8792	0.4021
A	1644.0008	7.7415
A	1748.5521	40.3459
A	3094.9745	45.9038
A	3183.9493	1.3713
A	3191.9977	5.9699
A	3202.7606	22.4213
A	3212.4259	24.2813
A	3273.1026	1.0868

4-Thia-2,3-benzobicyclo[3.1.0]hexa-2,5-diene (^{3}14)



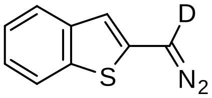
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_1
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.116235	-744.578524	-744.462289	2.5635
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-744.453858	-744.495509		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	144.5995	0.1283
A	170.6628	0.4510
A	286.1028	3.0284
A	333.9534	0.9721
A	346.1786	7.2036
A	440.3838	4.1711
A	469.8349	2.5787
A	487.6406	9.3579
A	540.8328	14.9872
A	611.0393	3.0169
A	672.7008	14.3277
A	708.1418	4.9858
A	723.9861	2.7850
A	750.8528	10.1549
A	759.8591	38.9312
A	802.6255	27.2476
A	846.1597	1.7227
A	878.0801	0.8245
A	933.4600	18.5126
A	943.0204	4.4705
A	963.1721	5.0759
A	984.0183	0.0990
A	1015.4015	9.0366
A	1052.1848	6.2580
A	1070.3812	2.4878
A	1147.9669	2.6717

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	1.392161	-1.365953	0.113893
C	0.205804	-0.647270	-0.028422
C	0.199239	0.760269	-0.124870
C	1.416001	1.444794	-0.113687
C	2.609794	0.732793	0.024135
C	2.597739	-0.661253	0.139636
H	1.381990	-2.449432	0.187582
H	1.429795	2.528159	-0.200186
H	3.555272	1.267384	0.045053
H	3.533051	-1.204391	0.241824
C	-1.164645	1.319119	-0.294699
H	-1.272564	2.218965	-0.907778
C	-2.275549	1.163920	0.736429
H	-2.184886	1.005308	1.808421
C	-2.209854	0.239338	-0.399451
S	-1.441675	-1.330033	-0.093293

A	1192.2210	1.6751
A	1201.5226	4.5240
A	1220.2216	5.2419
A	1285.0270	3.8512
A	1334.1599	1.0318
A	1365.6648	1.0181
A	1487.9686	9.0359
A	1499.8753	5.4446
A	1621.4716	3.4200
A	1639.6413	0.8455
A	3094.0612	1.9750
A	3187.7073	0.3351
A	3190.6544	20.1016
A	3196.0219	6.6647
A	3206.3704	19.6597
A	3215.4389	20.6504

2-Benzothienyl diazomethane –d_1 (1-s-*Z*-d_1)



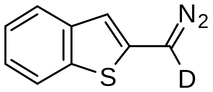
Charge	**Multiplicity**	**Theory/Basis Set**	**Full Point Group**
0	1	RB3LYP/6-31G(d)	C_1
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.125204	-854.205795	-854.080591	1.8965
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-854.069786	-854.116554		

Symmetry	**Vibrational Frequency (cm^{-1})**	**Intensity**
A	48.9779	0.1405
A	97.8083	1.6395
A	127.5198	3.9420
A	192.6083	0.1639
A	254.6616	1.7281
A	278.3508	0.9732
A	382.7090	0.5655
A	397.9643	7.8390
A	403.7765	0.5110
A	442.8189	9.5008
A	493.6449	0.3115
A	498.3876	9.6973
A	534.6321	1.0254
A	571.9589	0.9963
A	596.8114	9.3443
A	631.6511	2.5247
A	703.1270	0.1576
A	720.2563	1.9690
A	731.8874	9.1917
A	756.7565	26.8603
A	819.3985	33.5343
A	868.6686	4.3787
A	873.5157	0.0883
A	934.6553	2.1063
A	966.3949	3.8217
A	977.1299	0.0094
A	1049.7684	5.7896

Atom	**Coordinates (Angstroms)**		
	X	**Y**	**Z**
C	-0.993490	-0.596203	0.000003
C	-1.117033	0.815985	0.000001
C	-2.408454	1.376478	0.000055
C	-3.520108	0.543864	0.000067
C	-3.373799	-0.853878	0.000008
C	-2.108094	-1.435548	-0.000001
C	1.221049	0.606538	-0.000053
C	0.159341	1.472301	-0.000105
H	-2.527837	2.456861	0.000082
H	-4.516278	0.977660	0.000126
H	-4.254764	-1.489414	-0.000054
H	-1.993894	-2.515750	-0.000044
H	0.278132	2.550912	-0.000077
S	0.699067	-1.085706	-0.000038
C	2.615364	0.973324	-0.000117
H	2.927009	2.010728	0.000396
N	3.579174	0.096820	0.000015
N	4.428527	-0.673515	0.000132

A	1073.9740	5.3454
A	1134.5273	2.0577
A	1162.6484	3.9792
A	1191.6956	1.5153
A	1232.3504	6.1571
A	1288.2264	4.0854
A	1325.4087	9.1468
A	1364.0971	4.3885
A	1404.4809	2.5024
A	1486.3773	39.5583
A	1505.8928	8.6778
A	1578.9490	83.7052
A	1618.6005	17.4359
A	1648.4011	1.0563
A	2190.3905	980.8836
A	2384.4547	6.2402
A	3184.7129	1.7723
A	3193.5596	3.9306
A	3203.0158	25.5759
A	3213.2167	30.1011
A	3217.4223	7.7609

2-Benzothienyl diazomethane (1-s-*E*-d_1)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_1
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.125240	-854.205475	-854.080234	0.6079

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-854.069411	-854.116407

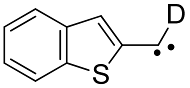
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	46.2182	0.9135
A	96.1040	1.2239
A	117.8415	4.5732
A	192.7933	0.2205
A	250.8322	3.5765
A	283.3503	1.3638
A	385.1961	0.7717
A	399.4962	11.2873
A	404.9148	0.4779
A	439.0239	6.0993
A	493.6054	0.2807
A	498.8639	7.8923
A	538.8382	3.4728
A	554.2805	6.7457
A	569.8262	0.8457
A	641.2209	2.2270
A	714.1515	2.5794
A	731.0772	7.8990
A	756.2037	27.6777
A	786.9569	11.0950
A	816.1252	32.1955
A	868.3696	4.1878
A	884.8932	1.8727
A	934.6319	2.0075
A	963.1159	7.3860
A	977.9323	0.0144
A	1049.1439	5.6147
A	1075.2078	4.8898

Atom	Coordinates (Angstroms) X	Y	Z
C	1.197286	-0.637147	0.000000
C	0.803556	0.725076	0.000000
C	1.806837	1.712937	0.000000
C	3.143615	1.336763	0.000000
C	3.510881	-0.020062	0.000000
C	2.539933	-1.018338	0.000000
C	-1.301759	-0.308953	0.000000
C	-0.623594	0.880805	-0.000001
H	1.528847	2.763716	-0.000001
H	3.916515	2.100398	0.000000
H	4.561687	-0.295433	0.000001
H	2.822602	-2.067168	0.000001
H	-1.116706	1.847480	-0.000001
S	-0.206541	-1.699010	0.000000
C	-2.722853	-0.570391	-0.000001
H	-3.143463	-1.567630	0.000000
N	-3.586271	0.405337	-0.000001
N	-4.326334	1.280187	0.000002

A	1097.1459	10.2037
A	1161.1938	3.0722
A	1191.8428	1.9226
A	1222.1810	1.4671
A	1285.0431	6.7669
A	1346.8363	18.1612
A	1376.1656	7.8180
A	1392.6687	39.8319
A	1483.7468	35.1314
A	1505.9109	7.5583
A	1576.7477	56.6017
A	1618.5623	13.3942
A	1648.8172	1.0664
A	2193.5680	951.7788
A	2392.6635	7.8171
A	3184.7478	1.6469
A	3193.1492	2.3351
A	3202.6172	25.3900
A	3212.9533	30.5027
A	3217.3841	5.0807

s-*E*-2-Benzothienyl carbene-*d*$_1$ (^{3}6-s-*E*-*d*$_1$)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.112886	-744.641565	-744.528679	1.5347

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.519634	-744.562482

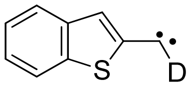
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	116.0602	1.0290
A"	189.2488	0.0710
A'	238.0891	3.0184
A"	278.4771	0.4695
A"	355.7324	14.9167
A'	369.7339	1.5662
A"	440.3529	6.5603
A'	478.6596	0.9046
A'	488.9604	0.3091
A"	520.6070	0.0006
A"	552.3527	1.3802
A'	557.4315	8.3228
A'	641.3615	4.2279
A'	710.2640	1.1949
A"	720.7027	9.7058
A"	744.9516	12.3910
A'	756.3305	12.3259
A"	783.3716	48.6314
A"	862.8792	1.3400
A'	886.1079	2.6102
A"	932.9801	1.7692
A"	975.6265	0.0244
A'	1046.9177	4.3680
A'	1075.5194	14.0076
A'	1154.2143	0.7792
A'	1179.9310	8.2277
A'	1193.5325	0.4369

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.000000	0.692273	0.000000
C	0.634565	-0.582708	0.000000
C	2.046383	-0.636369	0.000000
C	2.779266	0.541034	0.000000
C	2.132179	1.790064	0.000000
C	0.739738	1.873676	0.000000
C	-1.647818	-1.247813	0.000000
C	-0.295575	-1.656134	0.000000
H	2.547265	-1.600848	0.000000
H	3.864880	0.500112	0.000000
H	2.721841	2.702397	0.000000
H	0.244465	2.840323	0.000000
H	-0.013602	-2.703208	0.000000
S	-1.754395	0.547989	0.000000
C	-2.771576	-2.013393	0.000000
H	-2.997508	-3.070386	0.000000

A'	1222.7538	3.5397
A'	1286.9939	5.6306
A'	1348.1512	1.2770
A'	1369.5430	11.8789
A'	1402.7896	0.7910
A'	1485.7247	10.9831
A'	1501.2972	10.5079
A'	1601.5690	1.1820
A'	1628.4266	5.7249
A'	2426.1648	1.7214
A'	3186.6832	0.9362
A'	3195.0272	3.7292
A'	3204.6389	24.0477
A'	3214.3136	25.2065
A'	3226.9654	5.2810

s-*Z*-2-Benzothienyl carbene-d_1 (^{3}6-s-Z-d_1)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.112844	-744.642862	-744.530018	0.6775

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.520949	-744.563846

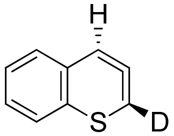
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	113.2159	1.3269
A"	187.5374	0.1855
A'	238.3836	2.0608
A"	275.8257	0.0401
A"	362.8018	19.8024
A'	371.7051	4.4080
A"	437.3449	3.7944
A'	463.7245	1.1168
A'	486.8779	0.2046
A"	502.2497	0.7261
A"	553.6736	1.5515
A'	594.4956	2.3000
A'	648.0998	2.8641
A'	695.6062	24.1666
A'	712.8840	1.9299
A"	721.0094	8.2993
A"	746.8343	16.6052
A"	788.4953	41.5102
A"	863.2298	1.6186
A'	882.9679	0.5547
A"	932.8661	1.7620
A"	975.7146	0.0260
A'	1046.8999	5.1084
A'	1073.6808	14.6575
A'	1154.7966	0.4536
A'	1177.6405	16.2097
A'	1192.9784	0.1574

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.000000	0.680015	0.000000
C	0.652582	-0.585909	0.000000
C	2.064997	-0.618301	0.000000
C	2.780922	0.569541	0.000000
C	2.115833	1.808878	0.000000
C	0.722072	1.872162	0.000000
C	-1.617703	-1.297562	0.000000
C	-0.259364	-1.674197	0.000000
H	2.579693	-1.575453	0.000000
H	3.866999	0.544334	0.000000
H	2.691921	2.729856	0.000000
H	0.212752	2.831439	0.000000
H	0.039026	-2.716388	0.000000
S	-1.753090	0.511957	0.000000
C	-2.717631	-2.092787	0.000000
H	-3.791196	-1.976139	0.000000

A'	1218.1159	3.7494
A'	1287.1262	5.8348
A'	1348.2441	1.2619
A'	1376.8604	12.2406
A'	1412.8540	0.2006
A'	1486.1934	11.4577
A'	1501.8685	9.3097
A'	1601.6814	1.2242
A'	1627.9094	5.0788
A'	2436.8467	0.4546
A'	3187.0163	0.8296
A'	3195.3535	3.9362
A'	3205.0085	23.9309
A'	3214.5145	24.9305
A'	3231.6045	3.6987

2*H*-1-benzo-2,3-dehydrothiopyran-2-d_1 (^{1}9-d_1)



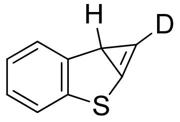
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_1
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.115171	-744.665859	-744.550688	1.6521
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-744.542061	-744.583085		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	135.6968	1.8464
A	162.5761	0.3496
A	295.0649	8.9516
A	330.2358	3.7703
A	370.4628	3.9263
A	420.0840	15.1635
A	448.0660	0.6385
A	468.4800	9.7200
A	528.2356	1.2127
A	539.2849	12.6996
A	610.2903	33.4192
A	643.6048	37.2066
A	680.4954	4.2087
A	713.3183	13.0021
A	736.0261	11.3830
A	771.1983	30.2686
A	815.8620	14.5675
A	858.6112	3.7282
A	889.5676	4.3284
A	924.5863	7.4728
A	951.0769	2.0855
A	986.7831	0.0424
A	1051.4346	9.4126
A	1073.0630	0.4320
A	1148.4970	0.9883
A	1193.1858	22.5776
A	1197.0819	1.7403

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-2.469380	-0.945423	0.072350
C	-1.162578	-1.417039	-0.032031
C	-0.088046	-0.519653	-0.060704
C	-0.335255	0.880996	-0.036563
C	-1.662442	1.327057	0.079153
C	-2.722036	0.428630	0.136690
H	-3.291709	-1.654451	0.111931
H	-0.974957	-2.486636	-0.065527
H	-1.850425	2.397473	0.103013
H	-3.741820	0.794084	0.217016
C	0.801176	1.772778	-0.321929
C	1.986621	1.329116	0.094669
C	2.477596	0.147184	0.458101
S	1.564583	-1.228744	-0.185382
H	0.658800	2.633537	-0.972034
D	3.212849	-0.045980	1.233283

A	1227.9638	7.7803
A	1290.1084	12.7538
A	1325.1713	0.5246
A	1391.5941	31.4533
A	1484.5143	8.8319
A	1492.5863	7.0449
A	1606.5616	0.8205
A	1640.6422	6.3501
A	1809.3488	1.9471
A	2370.0811	9.4818
A	3176.8763	13.7392
A	3186.2137	1.5725
A	3192.7037	3.4127
A	3202.9605	20.1386
A	3214.0633	24.1394

4-Thia-2,3-benzobicyclo[3.1.0]hexa-2,5-diene-6-d_1 (^{1}14-d_1)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_1
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.115073	-744.637742	-744.522670	1.2816

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.514074	-744.555065

(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	137.8946	1.1703
A	172.3223	0.3498
A	250.0592	4.3530
A	302.6624	2.7171
A	362.1547	1.0242
A	441.0091	2.9905
A	469.5448	1.1281
A	499.6140	1.7017
A	543.4523	34.1205
A	556.7022	9.3214
A	606.5336	2.0706
A	663.3007	6.4523
A	693.1370	11.4643
A	725.4483	3.6439
A	762.1397	40.8879
A	800.0588	7.1212
A	809.9296	13.2236
A	849.8478	2.4684
A	879.6091	0.5258
A	943.7461	0.8311
A	982.4252	0.0334
A	1021.7298	14.0791
A	1045.1214	20.4022
A	1060.8867	0.4974
A	1124.3343	0.7101
A	1146.4086	1.0631
A	1192.8140	1.2818

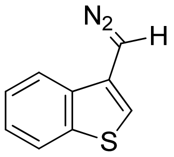
Atom	Coordinates (Angstroms)		
	X	Y	Z
C	1.391340	-1.346859	0.120209
C	0.203628	-0.633792	-0.030700
C	0.192847	0.777358	-0.135335
C	1.412273	1.456522	-0.105803
C	2.608564	0.752469	0.050211
C	2.595839	-0.640130	0.164000
H	1.385858	-2.429799	0.204961
H	1.423287	2.539618	-0.200342
H	3.552118	1.290029	0.083518
H	3.528680	-1.183880	0.286151
C	-1.179673	1.327244	-0.412692
H	-1.297384	1.930442	-1.316790
C	-2.284806	1.270913	0.628193
H	-2.691888	1.716249	1.525362
C	-2.102972	0.186896	-0.075746
S	-1.432682	-1.422900	-0.112305

A	1213.0812	3.1888
A	1293.3581	0.6873
A	1321.4135	1.9531
A	1358.2814	4.7376
A	1485.0474	19.9816
A	1496.8122	7.0366
A	1620.5631	0.4368
A	1643.9830	7.8402
A	1694.6706	39.5663
A	2454.9668	0.5222
A	3094.9768	45.8283
A	3183.9467	1.3702
A	3191.9944	5.9693
A	3202.7582	22.4192
A	3212.4228	24.2673

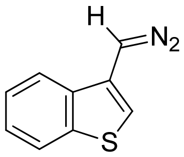
Chapter 2 – Photochemistry and Spectroscopy of 3-Benzothienyl Diazomethane

Abstract

The photochemistry of matrix-isolated 3-benzothienyl diazomethane (**1**) was studied by IR, EPR, and UV-vis spectroscopy in an attempt to generate 3-benzothienyl carbene. Calculations were done to characterize the C_9H_6S potential energy surface as well as to predict the harmonic vibrational frequencies and infrared intensities of the isomers.



1 (s-*E*)



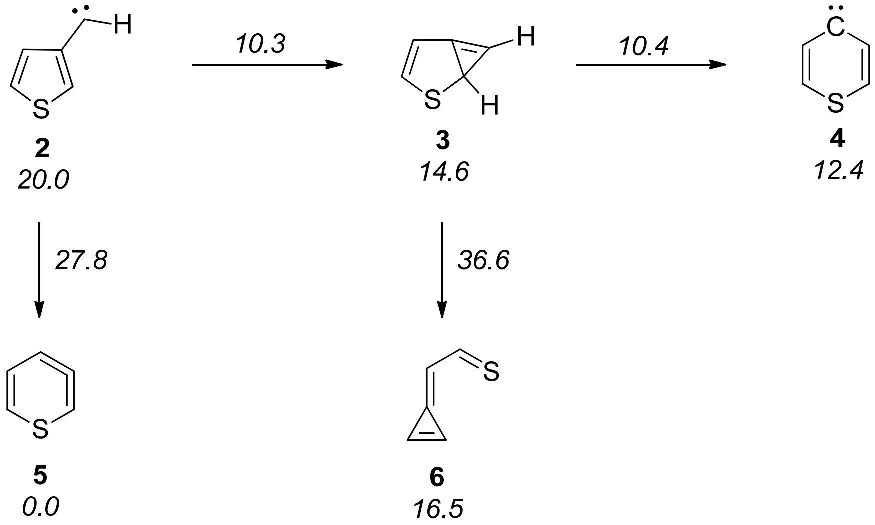
1 (s-*Z*)

Background

Initial studies on 3-thienyl diazomethane were carried out by Shechter in the 1970s.[1] His study on both the 2- and 3-thienyl diazomethanes suggested the intermediacy of the corresponding carbenes in both cases due to the isolation of products of insertion into the C-H bond of cyclooctane and products resulting from the formal dimerization of the thienyl carbenes.

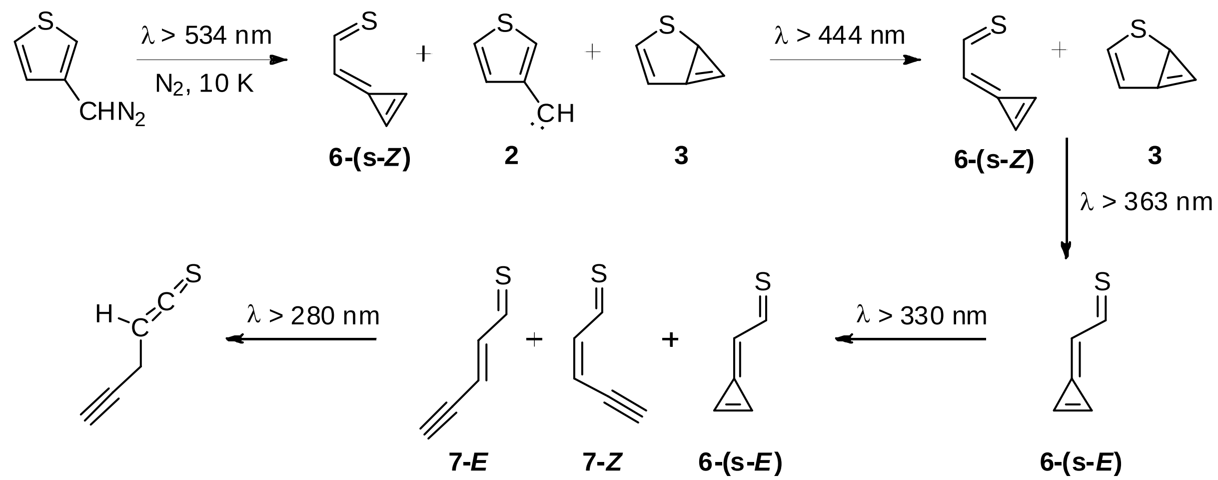
The reaction of thiophene with atomic carbon was studied both experimentally and computationally by Shevlin, as a way to probe the formation of both 2- and 3-thienyl carbene.[2,3] Computationally, the lowest energy pathway starting from triplet 3-thienyl carbene (**2**) is a ring expansion to give **4**, proceeding via 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**3**). Overall this pathway was calculated to be exothermic by 7.6 kcal/mol with a barrier of 10.4 kcal/mol. An additional pathway was explored in which 3-thienyl carbene is converted to thiacyclohexa-2,3,5-triene (**5**) directly; however this process has a large barrier of 27.8 kcal/mol.

Scheme 2.1. Calculated (B3LYP/6-31G*) potential reaction pathways of 3-thienyl carbene. Energies are in kcal/mol and include ZPVE. All species are singlets, except **2**, which is a triplet. Numbers over the arrows are computed transition state energies.



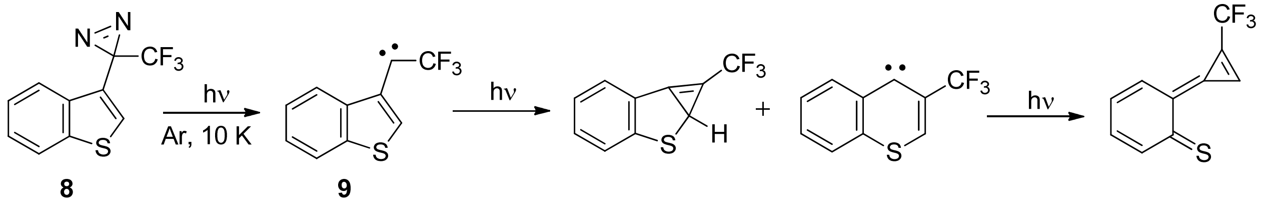
Sander matrix isolated 3-thienyl diazomethane and studied its photochemical rearrangements.[4] Upon irradiation of an Ar matrix containing 3-thienyl diazomethane, the α-thial methylenecyclopropene (**6**) was generated. Sander proposed the formation of methylenecyclopropene, **6**, occurred via 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**3**), which was not observed. While the carbene was not directly detected, its intermediacy was concluded by doping a matrix containing 3-thienyl diazomethane with O_2, and, upon irradiation, generating the carbonyl-*O*-oxide as well as thiophene-3-carboxaldehyde. In her work in the McMahon group, Pharr generated, matrix isolated, and studied the photochemistry of 3-thienyl diazomethane.[5,6] The observed photochemistry is depicted in Scheme 2.2.

Scheme 2.2



The only report of a 3-benzothienyl carbene derivative to date, is by Sheridan.[7] Matrix-isolation and subsequent photolysis of 3-benzothienyl(trifluoromethyl)diazirine (**8**) yields the singlet carbene (**9**), which undergoes further photochemical transformations, as shown below.

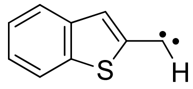
Scheme 2.3



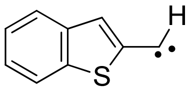
Results and Discussion

Computational Study

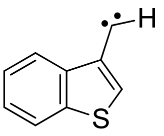
In order to identify photoproducts present in the experimental infrared spectra, several C_9H_6S isomers were studied computationally. Optimized geometries, energies, harmonic vibrational frequencies, and infrared intensities were calculated at the B3LYP/6-31G(d) level. A selection of low-lying isomers and their energies are shown in Figure 2.1, a complete list of isomers with Cartesian coordinates, energies, vibrational frequencies, and infrared intensities can be found in the supporting information. The two rotamers of triplet 3-benzothienyl carbene (**11-(s-*Z*)** and **11-(s-*E*)**) are close in energy ($\Delta E = 0.45$ kcal/mol) thus both are expected to be seen in any experimental work, with little preference for one conformation over the other. Both rotamers are predicted to be triplet ground states, however, the singlet-triplet gaps are predicted to be small (3.9 kcal/mol for **11-(s-*Z*)** and 4.2 kcal/mol for **11-(s-*E*)**. The expected 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (**16**) lies almost 10 kcal/mol below either rotamer of 3-thienyl carbene (**11-s-*Z*** and **11- s-*E***).



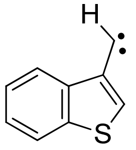
10-(s-*Z*)
34.0
(30.3)



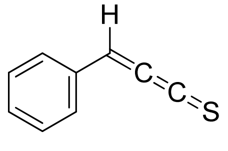
10-(s-*E*)
36.3
(31.1)



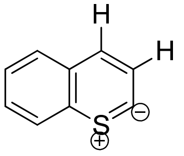
11-(s-*Z*)
38.2
(34.0)



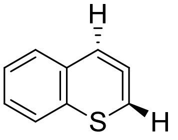
11-(s-*E*)
37.6
(34.5)



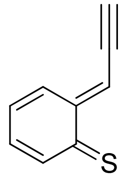
12
0.0
(24.5)



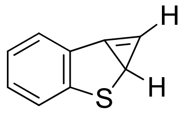
13
11.6
(30.7)



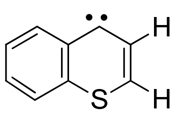
14
17.6
(29.8)



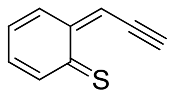
15
27.0
(46.0)



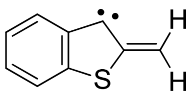
16
28.9
(73.4)



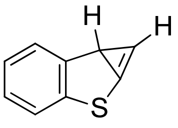
17
30.0
(31.1)



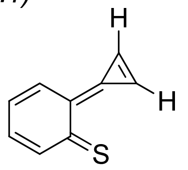
18
30.9
(42.9)



19
32.1
(33.2)



20
35.1
(70.3)



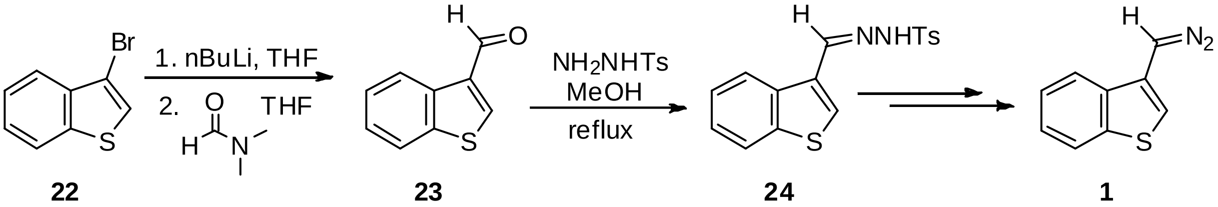
21
36.6

Figure 2.1. Calculated energy values for selected C_9H_6S isomers at the B3LYP/6-31G* level. All energies are in kcal/mol and corrected for ZPVE. Energies are reported for both *singlets* and *(triplets)*.

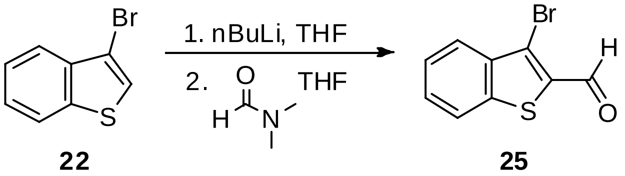
Synthesis of 3-Benzothiophene Diazomethane

Initially, synthesis of 3-benzothiophene carbaldehyde (**23**) was attempted via the procedure of Houssain.[8] (**Scheme 2.4**) Careful analysis of the reaction mixture revealed that instead of initial lithium-halogen exchange, 3-bromobenzothiophene (**22**) was deprotonated by *n*-butyl lithium at the 2-position and subsequently formylated, giving 3-bromo-benzothiophene-2-carbaldehyde (**25**), as seen in Scheme 2.5. Commercial sources were then found for **23**.

Scheme 2.4

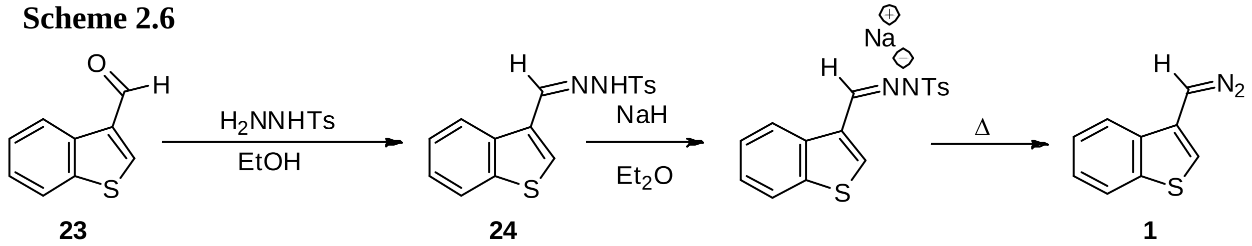


Scheme 2.5



3-Benzothiophene carbaldehyde (**23**) was converted into the corresponding tosylhydrazone (**24**) by combining the aldehyde and *p*-toluene sulfonylhydrazide in absolute ethanol and heating at reflux overnight. The tosylhydrazone was deprotonated to give the sodium salt which, upon heating under vacuum, produced a bright pink/red diazo compound (**1**). (**Scheme 2.6**)

Scheme 2.6



Photochemistry of Matrix Isolated 3-Benzothienyl Diazomethane

Matrix isolation spectroscopic experiments were initially carried out in the same manner as with 2-benzothienyl diazo methane, with direct deposition of the diazo compound from the sodium salt onto the sample window. However, with this method matrix-isolation was hard to control. The salt would release the diazo as soon as the temperature reached 110 °C, thus it was very difficult to ensure an adequate degree of matrix isolation.

3-Benzothienyl diazomethane (**1**) is less sensitive to temperature changes than 2-benzothienyl diazomethane. Unlike 2-benzothienyl diazomethane, 3-benzothienyl diazomethane can be generated and manipulated without significant decomposition. At room temperature, the diazo compound slowly deposits onto the spectroscopic window. To overcome problems with the relatively low volatility of 3-benzothienyl diazomethane, a short-path deposition tube with no stopcock was used to deposit the diazo compound. By keeping the diazo compound at -78 °C, volatility was suppressed, and no diazo compound would deposit, but once the slush bath was removed, the deposition tube slowly warmed up to room temperature and a clean deposition of diazo compound was seen onto the matrix window. With this technique there were no solvent peaks visible in the IR spectrum, and CO_2 and water were also excluded.

For a typical IR experiment, the diazo compound was allowed to slowly warm up to room temperature while a constant flow of Ar or N_2 gas was co-deposited onto a CsI window held at 25 K. Deposition was continued for approximately 60 – 90 minutes, or until the diazo compound in the deposition tube was all gone or decomposed (as evidenced by a change to a yellow color, indicative of azine formation). The CsI window was then cooled to 10 K and IR spectra showed a large amount of diazo compound present in the matrix (absorbance of ν C=N=N > 6 absorbance units).

Initial irradiation of a matrix containing 3-benzothienyl diazomethane (**1**) at λ > 472 nm (Ar, 10 K) shows complete disappearance of the diazo compound after 38 hours. New peaks can clearly be seen growing in at 1624, 974, 743, 700, and 647 cm^{-1}. Upon comparison with calculated infrared absorptions, the new species is determined to be 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene. (**16**) (**Figure 2.2**)

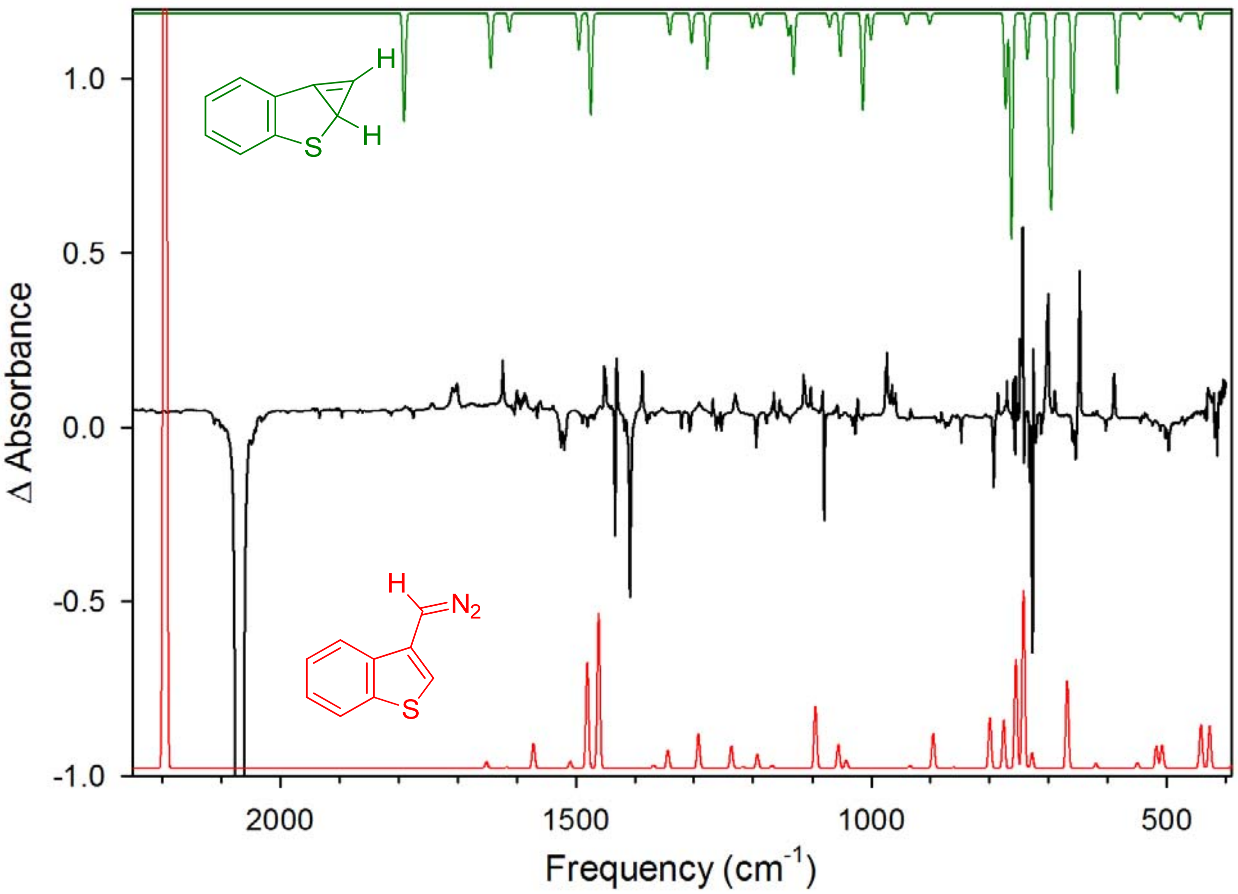


Figure 2.2. IR subtraction spectrum (Ar, 10 K) (black trace, middle) showing the disappearance of 3-benzothienyl diazomethane (**1**) and the appearance of 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (**16**) after irradiation at λ > 472 nm 38 h. The top and bottom spectra are calculated (B3LYP/6-31G*) spectra of s-*E*-3-benzothienyl diazomethane (red, bottom) and 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (green, top). Only one rotamer of the diazo compound is shown for clarity, but both are present in the matrix. Calculated spectra are unscaled.

As with the 2-benzothienyl diazomethane system, narrow-band irradiation was carried out to determine if photoproducts were being formed but also reacting at the given wavelength of irradiation. After broadband irradiation at $\lambda > 472$ nm of a matrix containing 3-benzothienyl diazomethane (**1**) to give the 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (**16**), further irradiation was performed at $\lambda = 340$ nm $\pm$ 10 nm. After 16 hours irradiation, visual inspection of the matrix revealed a dark purple colored matrix, unlike any previously seen. The infrared spectrum of this purple matrix showed intense absorptions at 1702, 1439, 1396, and 1079 cm^{-1}, and the disappearance of all peaks associated with 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (**16**). (**Figure 2.3**) The new species was confirmed as 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (**21**). The new peaks at 2078, 1611, 1445, 1099, 760, and 656 cm^{-1} are assigned to a mixture of *E* and *Z* cyclohexadiene thione acetylenes, **15** and **18**. (**Figure 2.4**) The acetylenic C-H stretches in these compounds are not observed in the spectra; the presence of water contamination in the matrix obscures details in this region. (**Figure S2.3**) The analogous acetylenic species (**25** and **26**) were generated in studies on the parent 3-thienyl diazomethane.[6] Comparison of the subtraction spectrum obtained after irradiation with other possible photoproducts are presented in the supporting information, **Figures S2.1 – S2.3**.

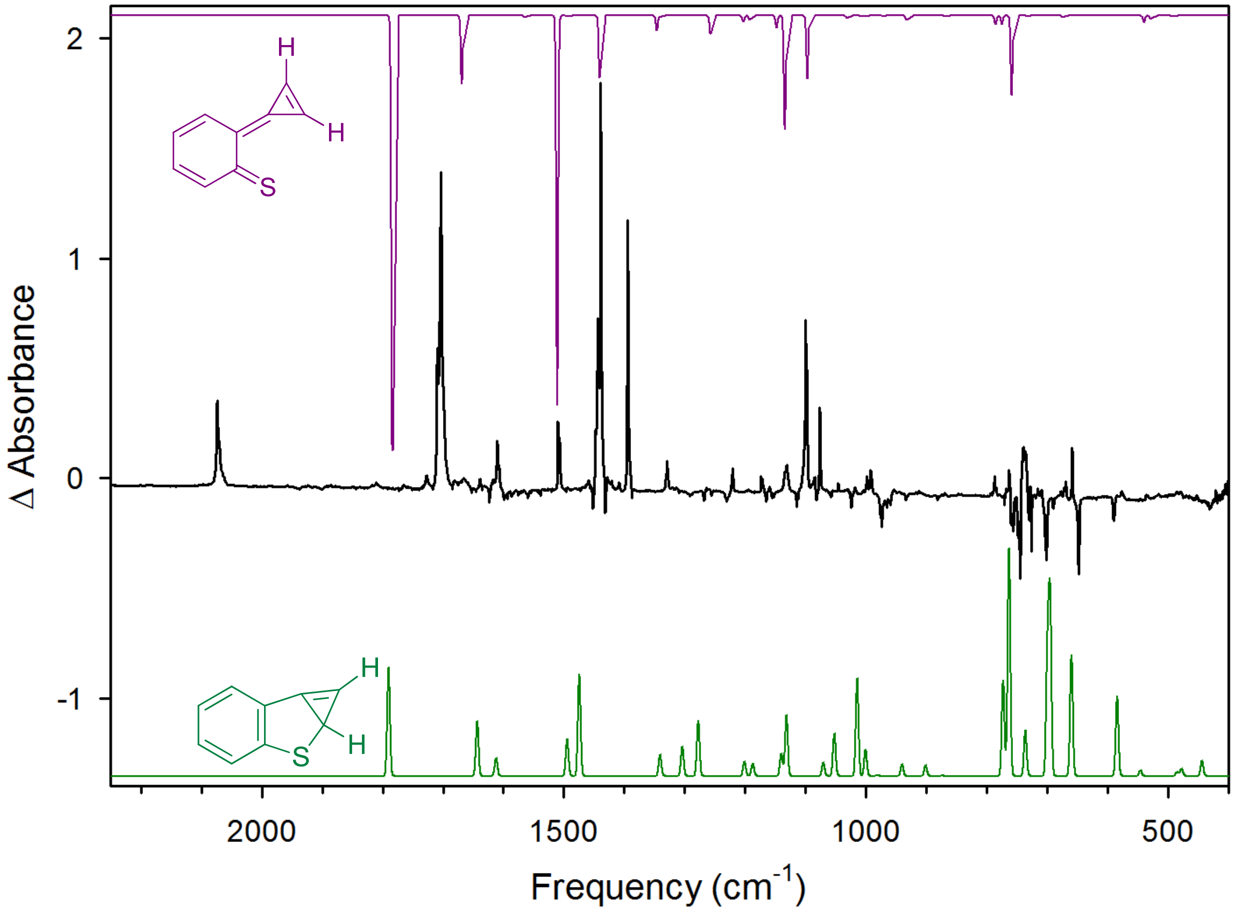


Figure 2.3. IR subtraction spectrum (Ar, 10 K) (black trace, middle) showing the disappearance of 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (**16**) and growth of 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (**21**) after irradiation at λ = 340 nm 16 h. The top and bottom spectra are calculated (B3LYP/6-31G*) spectra of 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (green, bottom) and 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (purple, top). Calculated spectra are unscaled.

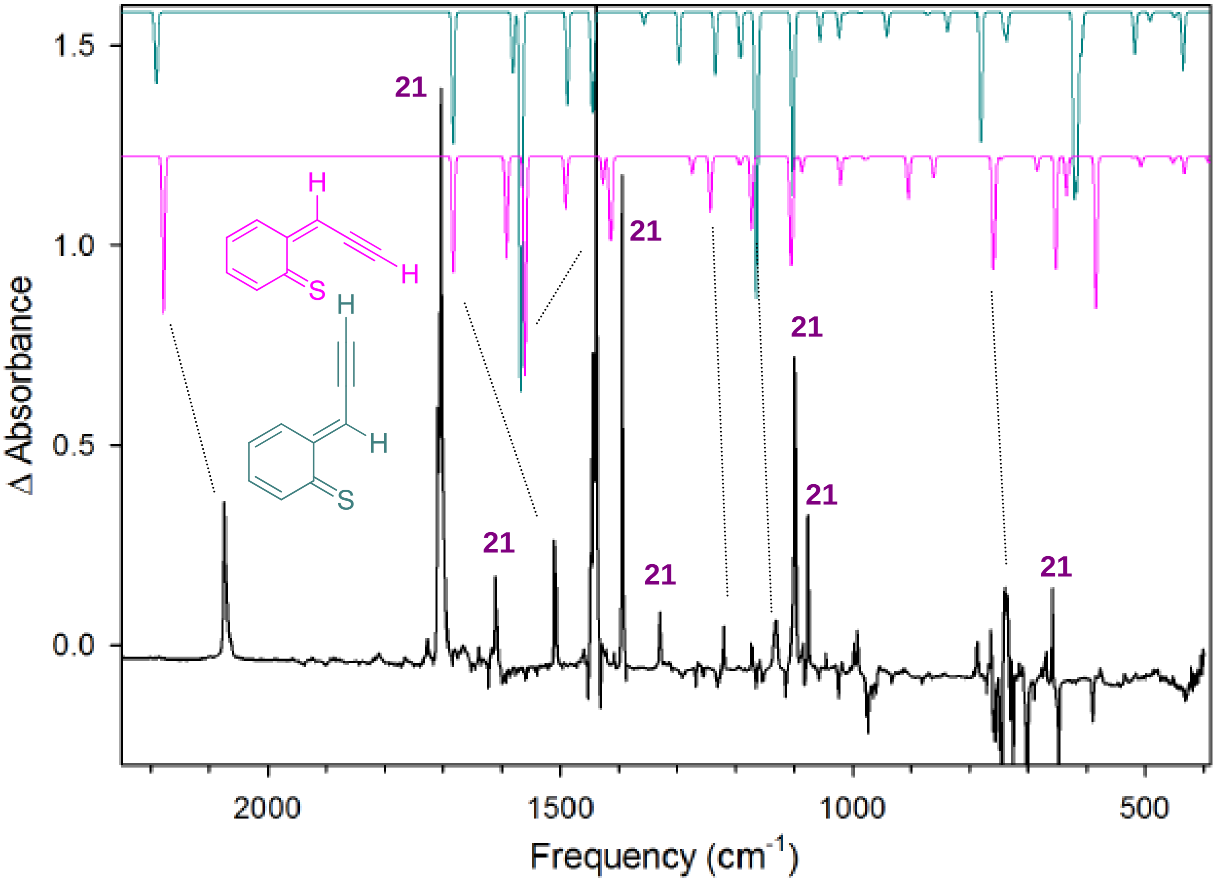
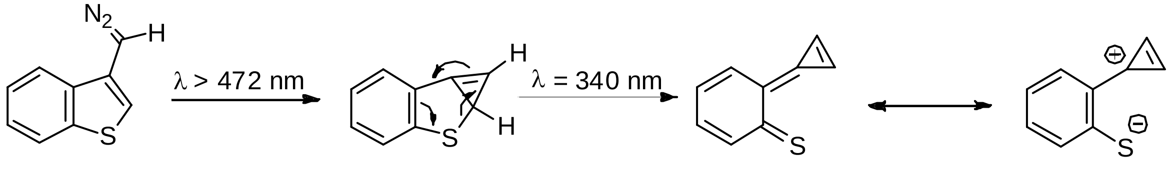


Figure 2.4. IR subtraction spectrum (Ar, 10 K) (black trace, middle) after irradiation at λ = 340 nm 16 h showing the disappearance of 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (**16**) and growth of 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (**21**) and *E*- and *Z*-vinylacetylenes **15** and **18**. This subtraction spectrum is the same as in Figure 2.3. The top spectra are calculated (B3LYP/6-31G*) spectra of *E*- and *Z*- 2-(vinylacetylene)-3,5-cyclohexadien-1-thione isomers (**15**, aqua and **18**, pink). Calculated spectra are unscaled.

2-(2-Cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (**21**) is not unexpected under these reaction conditions. (**Scheme 2.7**) With the non-benzannulated 3-thiophene diazomethane, ring opening to the analogous cyclopropene-thione was seen with initial irradiation at λ > 534 nm; however, a highly colored matrix was not observed. For this species, **21**, the benzene ring adds stabilization by allowing for an aromatic charge-transfer complex.

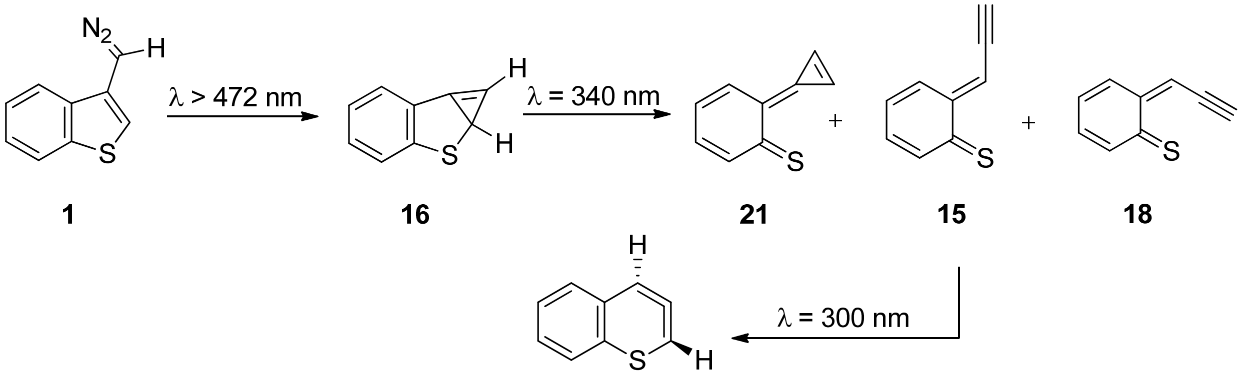
Scheme 2.7



1 **16** **21**

Irradiation of a matrix containing 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (**21**) at λ = 620 nm results in the decrease of some of the 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione. Further irradiation at a variety of longer or shorter wavelengths does not drive away all of the 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione. At shorter wavelength irradiation (λ = 300 nm, 19 h) peaks associated with the **21**, **15**, and **18** decrease and new peaks grow in at 1183, 1021, 976, 700, and 647 cm^{-1}. These new absorptions are very weak and are tentatively assigned to allene **14**. (**Figure S2.4**)

Scheme 2.8. Observed photochemistry of 3-benzothienyl diazomethane



1 **16** **21** **15** **18**

14

Electronic absorption spectroscopy was carried out to characterize, and possibly identify, the species being formed after irradiation of 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (**21**). The electronic absorption spectra of the 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (**16**) and 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (**21**) were also recorded.

Broadband irradiation of a matrix containing 3-benzothienyl diazomethane (**1**) converts the diazo compound to 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (**16**) which shows an ultraviolet absorption with a λ_{max} at 325 nm. (**Figure 2.5**) Irradiation into this band converts 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (**16**) to 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (**21**), as characterized by a disappearance of the absorption at 325 nm and the appearance of a strong, very broad visible absorption centered at 540 nm. (**Figure 2.5**)

Irradiation at λ = 540 nm leads to a moderate decrease in this absorption, and a new peak at λ = 400 nm. (**Figure 2.5**) Irradiation at a variety of wavelengths never led to the disappearance of the visible absorption associated with 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (**21**). This could be due to the 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione having a large molar absorptivity, which would limit the amount of light getting to the inner parts of the matrix, thus limiting the overall conversion of 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione.

The acetylic species, **15** and **18**, which were formed upon λ = 340 nm irradiation are also expected to have visible absorptions. TD-DFT calculations predict both isomers to have absorptions above 500 nm. These are other contributing members to the broad visible peak at λ = 540 nm. With λ = 540 nm irradiation, a slight shift in the λ_{max} of the visible absorption in seen, most likely due to **21** isomerizing while the acetylenes **15** and **18** remain.

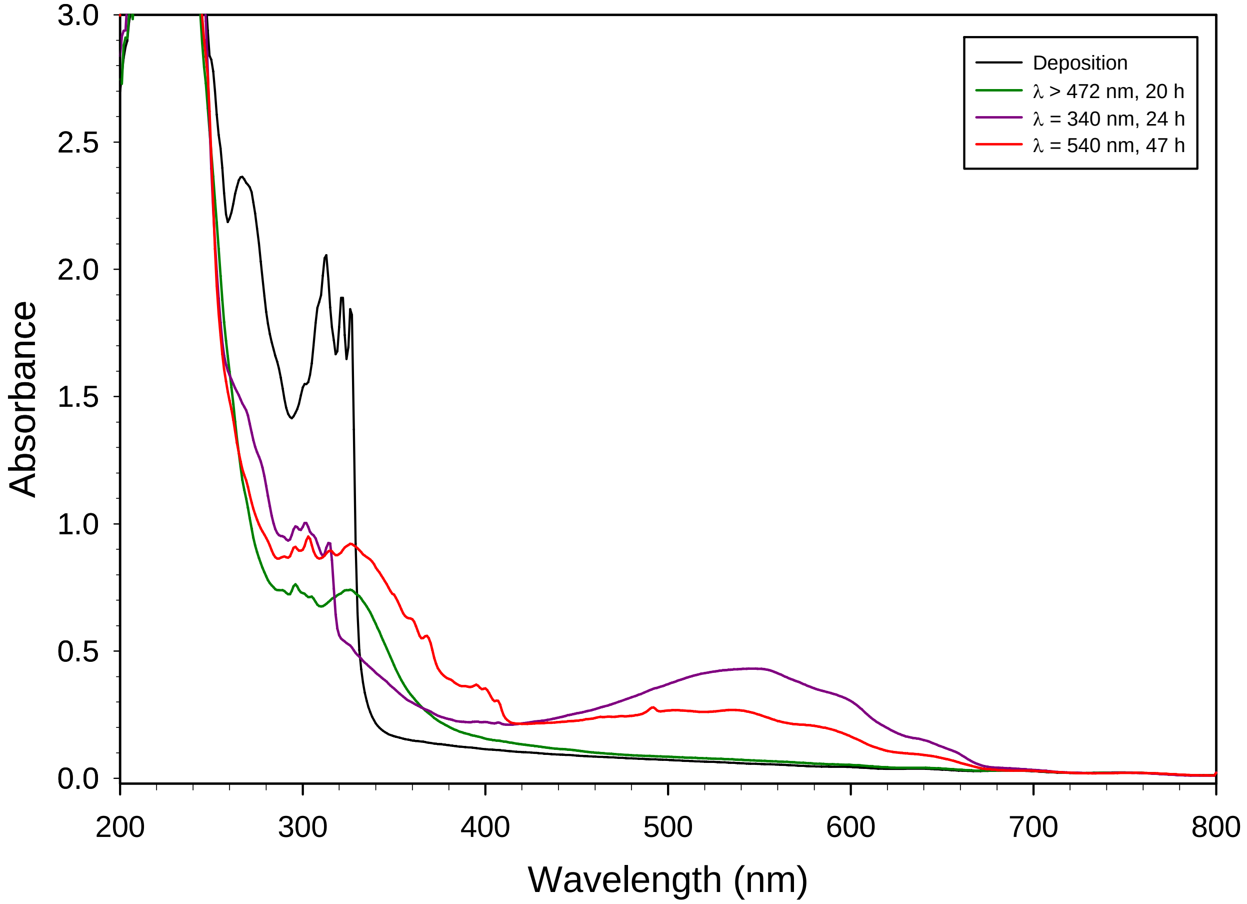


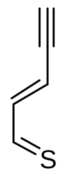
Figure 2.5. UV-vis spectra (Ar, 10 K) showing a matrix containing 3-benzothienyl diazomethane (**1**) (initial deposition, black trace). Irradiation at λ > 472 nm 20 h converts the diazo compound into 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (**16**) (green trace) with a λ_{max} = 325 nm. Irradiation into this band gives a mixture of 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (**21**) and acetylenes **15** and **18**. (purple trace) characterized by a broad visible absorption centered at 540 nm. Further irradiation at λ = 540 nm drives away some **21**, and generates new absorptions at 330 nm and 400 nm.

Time-dependent density functional theory (TD-DFT) calculations were carried out to help explain the observed electronic absorption spectra.[6] The calculated absorptions and intensities for 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (**16**) and 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (**21**) are given in Table 2.1. The tricyclic **16** is calculated to have moderately intense peaks at λ = 323 and 261 nm, while the cyclopropene-thiophene is calculated to have two visible absorptions at λ = 496 and 431 nm. This correlates with the observed spectra (experimental **16** λ_{max} = 325 nm, **21** λ_{max} = 540 nm).

16			**21**		
Wavelength (nm)	Oscillator Strength (*f*)	Experimental (nm)	Wavelength (nm)	Oscillator Strength (*f*)	Experimental (nm)
323.0	0.0346	325	496.0	0.0368	540
260.7	0.0122		431.1	0.0814	
244.6	0.0062		297.5	0.0423	
235.5	0.2941		279.8	0.0684	
234.4	0.0083				

Table 2.1. TD-DFT (B3LYP/6-31G*) calculations of 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (**16**) and 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (**21**) showing the lowest energy calculated electronic transitions and their respective intensities as well as experimentally assigned absorptions. λ_{max} in nm

The electronic absorption spectra of the two isomeric acetylenes were also calculated, since they were observed in the IR experiments. Additionally, the analogous acetylenic species (**25** and **26**) were generated in studies on the non-benzannulated 3-thienyl diazomethane,[5] and so the benzothienyl-acetylene isomers warrant special attention. Based on the TD-DFT calculations, the acetylenic species are calculated to have absorptions at λ = 513 nm and 323 nm for the *Z* isomer (**18**) and λ = 525 nm and 331 nm for the *E* isomer (**15**). This is in agreement with observed absorptions at 519 nm and 329 nm, however it is not possible to determine which isomer is responsible for which absorptions. The IR experiments show a mixture of both *E* and *Z* isomers present, and so both isomers are expected to be in the matrix for the UV-vis experiments.



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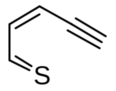

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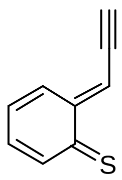

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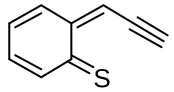


18

15

Wavelength (nm)	Oscillator Strength (*f*)	Experimental (nm)
525	0.143	519
331	0.170	329
294	0.019	

18

Wavelength (nm)	Oscillator Strength (*f*)	Experimental (nm)
513	0.088	519
323	0.143	329
233	0.184	
223	0.458	

Table 2.2. TD-DFT (B3LYP/6-31G*) calculations of *E*- and *Z*- 2-(vinylacetylene)-3,5-cyclohexadien-1-thione (**15** and **18**, respectively) showing the lowest energy calculated electronic transitions and their respective intensities as well as experimentally assigned absorptions. λ_{max} in nm

EPR spectroscopy was employed to determine if the initial conversion from 3-benzothienyl diazomethane (**1**) to 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (**16**) proceeds through triplet 3-benzothienyl carbene (**11**), but perhaps at concentrations too low to detect with IR spectroscopy. Irradiation was carried out at λ > 497 nm and λ > 472 nm of a matrix containing 3-benzothienyl diazomethane (**1**). Neither of these irradiation conditions yielded an EPR spectrum with peaks other than the g = 2 peak at 3500 G. (**Figure 2.6**) Further shorter wavelength irradiation shows no change in the spectra.

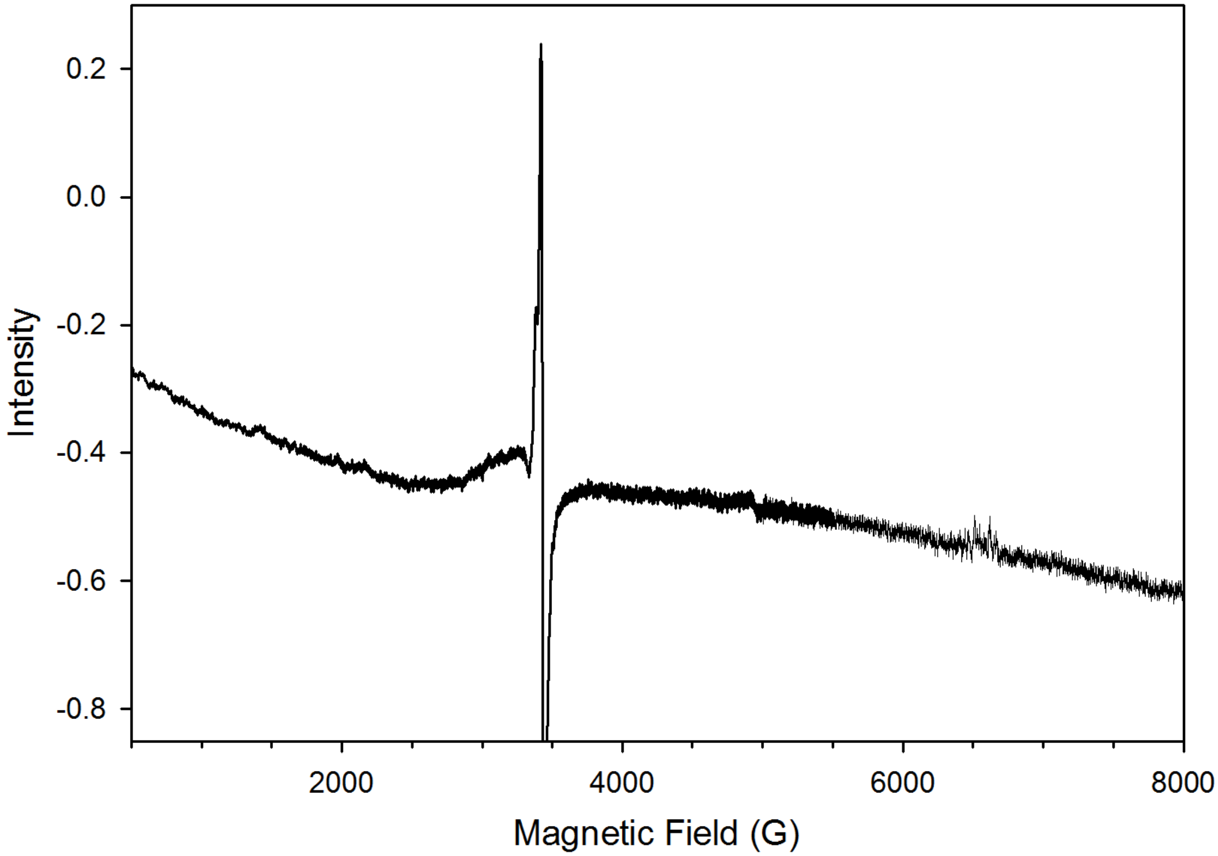
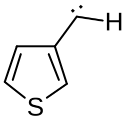
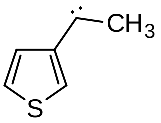


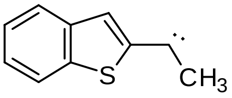
Figure 2.6. EPR spectrum of a matrix containing 3-benzothienyl diazomethane (**1**) after irradiation at λ > 497 nm 20 h. The g = 2 peak is present at 3500 G, but no other peaks are visible.

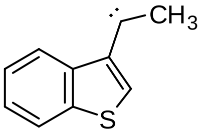
The photochemistry displayed by this system parallels that seen in the 3-thienyl diazomethane system, but without the detection of a triplet carbene intermediate. With the benzannulated system, 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (**21**) is resonance stabilized and thus displays a large visible transition, giving it a deep purple color.

Based on previous studies[5] of other members of the thienyl carbene family, we would expect UV-vis absorptions for 3-benzothienyl carbene to appear around 515 nm, since a red shift of about 50 nm occurs upon benzannulation, and a red shift of approximately 10 nm occurs when a methyl is substituted for a hydrogen on the carbene carbon (see chapter one for more data). While the broad absorptions of both the acetylenes (**15** and **18**) and the cyclopropene-thione (**21**) obscure this region of the spectrum, any triplet carbene formed should have been detected by EPR spectroscopy.







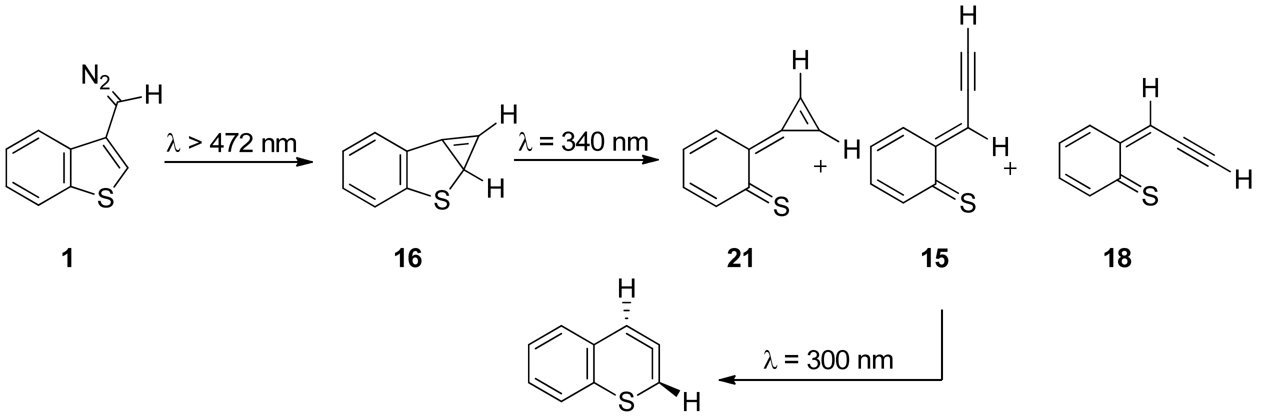


27	**28**	**29**	**30**
467 nm	473 nm	515 nm	520 nm
457 nm	444 nm	479 nm	497 nm

Table 2.3. Experimental UV-vis absorptions for a family of heteroaryl carbenes.

Summary

Irradiation of a matrix-isolated sample of 3-benzothienyl diazomethane (**1**) at λ > 472 nm leads to the conversion of the diazo compound into 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (**16**) with concomitant loss of N_2. Narrow-band irradiation of the matrix containing **16** at λ = 340 nm leads to a ring opening of the **16** to give 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (**21**) which gives the matrix a deep purple color. In addition to **21**, both isomers of 2-(vinylacetylene)-3,5-cyclohexadien-1-thione (**15** and **18**) are observed with λ = 340 nm irradiation. Further irradiation of the matrix containing **21** results in a slight decrease of this compound, as seen in both the IR and UV-vis spectra. EPR experiments were carried out to determine if the initial conversion of the diazo compound (**1**) to 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (**16**) occurred via a triplet carbene, however no evidence for a triplet species was seen in the EPR spectra.



1 **16** **21** **15** **18**

14

Experimental Details

Benzothiophene 3-carbaldehyde tosylhydrazone (24). Commerically available benzothiophene-3-carbaldehyde (Sigma-Aldrich, 1.088 g, 6.7 mmol) was added to a round-bottom flask with a stirbar along with *p*-toluene sulfonylhydrazide (1.488 g, 8.0 mmol, 1.2 eq) and absolute ethanol (40 mL). The clear yellow solution was heated at reflux under nitrogen for 3 h. The reaction mixture is cooled to room temperature and water (100 mL) is added to cause the tosylhydrazone to precipitate. The precipitate is collection by filtration to give a gummy pale yellow solid, which is dried on a vacuum line overnight. NMR shows only peaks for desired product, so no further purification done. Yield (1.635 g, 73 %). ^{1}H-NMR ($CDCl_3$) δ 8.54 (d, 1H), 8.05 (s, 2H), 7.92 (d, 2H), 7.83 (d, 1H), 7.61 (s, 1H), 7.45 (m, 2H), 7.28 (d, 2H), 2.39 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$) δ 21.8, 122.7, 125.4, 125.5, 125.7, 128.2, 129.9, 130.5, 132.2, 135.4, 135.8, 140.7, 144.1, 144.6 ppm. ^{13}C-NMR ($CDCl_3$) δ 144.6, 144.2, 140.7, 135.8, 135.4, 132.2, 130.5, 130.0, 128.2, 125.7, 125.5, 125.4, 122.7, 21.8 ppm. ESI-EMM m/z: $[M+H]^+$ 331.0570. ESI-MS *m/z*: 331.0 (4), 324.1 (10), 320.1 (12), 317.0 (11), 187.0 (12)

Benzothiophene 3-carbaldehyde tosylhydrazone sodium salt. For a typical IR experiment tosylhydrazone (0.200 g, 0.60 mmol), sodium hydride (60% in mineral oil, 0.0256 g, 0.64 mmol, 1.1 eq), and anhydrous diethyl ether (15 mL, dried over CaH) are added to a round-bottom flask and stirred under nitrogen at room temperature for 2 h. After stirring a couple minutes the solution turns milky. After 2 h, ~20 mL hexanes are added to precipitate the sodium salt. The solid is filtered through a medium or dense frit funnel and washed with a couple milliliters of hexanes. The sodium salt is then transferred to a small flask and kept under vacuum until used (overnight). Yield (0.200 g, 100 %)

3-Benzothienyl diazomethane (1). The sodium salt is transferred to the bottom of a sublimator and held under vacuum. The salt is heated to ~110 °C, at which time the pink diazo compound is released from the salt and collected on a cold finger held at -78 °C. After collection of the diazo compound is complete, the sublimator is flushed with N_2, and the diazo compound is washed into a deposition tube with a small amount of dry diethyl ether. IR: 2066 (s), 1434 (m), 1410 (m), 1323 (w), 1310 (w), 1080 (m), 793 (m), 758 (m), 725 (m), 655 (w), 498 (w) cm^{-1}. UV-vis (MeOH) λ_{max} = 499 nm.

3-Bromo-benzothiophene-2-carbaldehyde (22). To an oven-dried 50 mL round-bottom flask charged with a stirbar under N_2 at -78 °C is added 1.0 mL (1.629 g, 7.62 mmol) 3-bromobenzothiophene and 12.0 mL dry THF. 4.8 mL *n*-butyl lithium (1.6 M, 7.62 mmol) are added and the solution is stirred at -78 °C. After 45 min, 0.89 mL (1.5 eq, 11.43 mmol) *N*,*N*-dimethylformamide is added via syringe. The reaction mixture is stirred and allowed to warm to room temperature over 90 min. The reaction is then quenched with 10 mL H_2O and the organic layer is extracted 2 x 15 mL with Et_2O. The combined organic layers are washed with 25 mL of brine then dried over $MgSO_4$, filtered, and solvent is removed in vacuo to yield an orange solid. ^{1}H-NMR ($CDCl_3$) δ10.30 (s, 1H), 8.03 (m, 1H), 7.89 (m, 1H), 7.56 (m, 2H) ppm. EI-MS *m/z*: $[M]^+$ 241.6 (98), 240.6 (90), 239.6 (100), 238.6 (89), 213.6 (69), 212.6 (45), 211.6 (69), 210.6 (45), 160.8 (10).

Matrix Isolation Experiments

In a typical IR matrix isolation experiment, the matrix isolation cart is fitted with 2 outer KBr windows and an inner window of CsI. Early experiments involved direct deposition of 3-benzothiophene diazomethane from the sodium salt onto the inner CsI window. For these experiments, the sodium salt was loaded into a short-path curved deposition tube which was attached to the matrix-isolation cart and held under vacuum (pressure = 10^{-8} torr). The cold head was cooled to 25 K and a thin layer of Ar or N_2 was deposited onto the CsI window. Then the salt was heated with an oil bath to ~110 °C, at which point the pink diazo compound was released and co-deposited with either Ar or N_2 onto the CsI window. Deposition was carried out until 40-80 torr of gas was deposited, about 60-90 minutes.

Later experiments were carried out in a more traditional method. First, the sodium salt was heated under vacuum in a sublimator and the diazo compound collected on a cold finger held at -78 °C. Next, a couple of milliliters of dry diethyl ether were used to rinse the diazo compound into a short path deposition tube with a bulb on the end. The diazo in the deposition tube was transferred onto the matrix-isolation cart and cooled to -78 °C before the solvent was removed by vacuum. The cold head was then cooled to 25 K and a thin layer of Ar or N_2 was deposited onto the CsI window. The slush bath was removed from the tube with the diazo compound, and allowed to warm to room temperature. During warming, the pink diazo compound was co-deposited with either Ar or N_2 onto the CsI window. Deposition was carried out until 40-80 torr of gas was deposited, about 60-90 minutes. This method produced a much cleaner IR spectrum.

Deposition for a UV-vis experiment is nearly the same, however the outer windows are quartz and the inner window is sapphire. Additionally, due to the higher sensitivity of electronic absorption spectroscopy, a much thinner film is used. Deposition at the same rate as for IR experiments is carried out, but for only 6-9 minutes (4-8 torr of gas).

General

All chemicals and solvents were purchased from commercial sources and used without further purification, unless otherwise noted. Tetrahydrofuran (THF) was dried over KOH, pre-distilled from CaH_2, then distilled from Na/benzophenone immediately prior to use. NMR spectra (^{1}H-NMR, ^{13}C-NMR) were taken on a Bruker AC+ 300 (^{1}H-NMR) and a Varian MercuryPlus 300 (^{13}C-NMR). Chemical shifts are reported as ppm downfield of a $SiMe_4$ internal standard. Infrared spectra were taken on a Thermo-Nicolet Nexus 870 FT-IR spectrometer with a MCT-B detector. EPR spectra were collected using a Bruker ESP 300 E spectrometer. Electronic absorption spectra were obtained on a Varian Cary 5000 UV-Vis-NIR spectrometer.

Computational

All calculations were run utilizing the Gaussian03[9] and Gaussian09[10] software packages. The three-parameter gradient-corrected exchange functional of Becke[11], along with the correlation functional of Lee, Yang, and Parr[12] (B3LYP) was employed for all calculations, with the 6-31G(d) (6-31G*) basis set. Harmonic vibrational frequency calculations at the B3LYP level were used to confirm the nature of each stationary point (zero imaginary modes for minima, one imaginary mode for transition states), as well as to provide zero-point vibrational energy (ZPVE) corrections. Computed harmonic vibrational frequencies and infrared intensities were used to compare with experimental work, and were not scaled. Time-dependent density functional theory calculations were carried out at the B3LYP/6-31G* level with a 50/50 mix of singlet and triplet states.

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Supporting Information for Chapter 2 – Photochemistry and Spectroscopy of 3-Benzothienyl Diazomethane

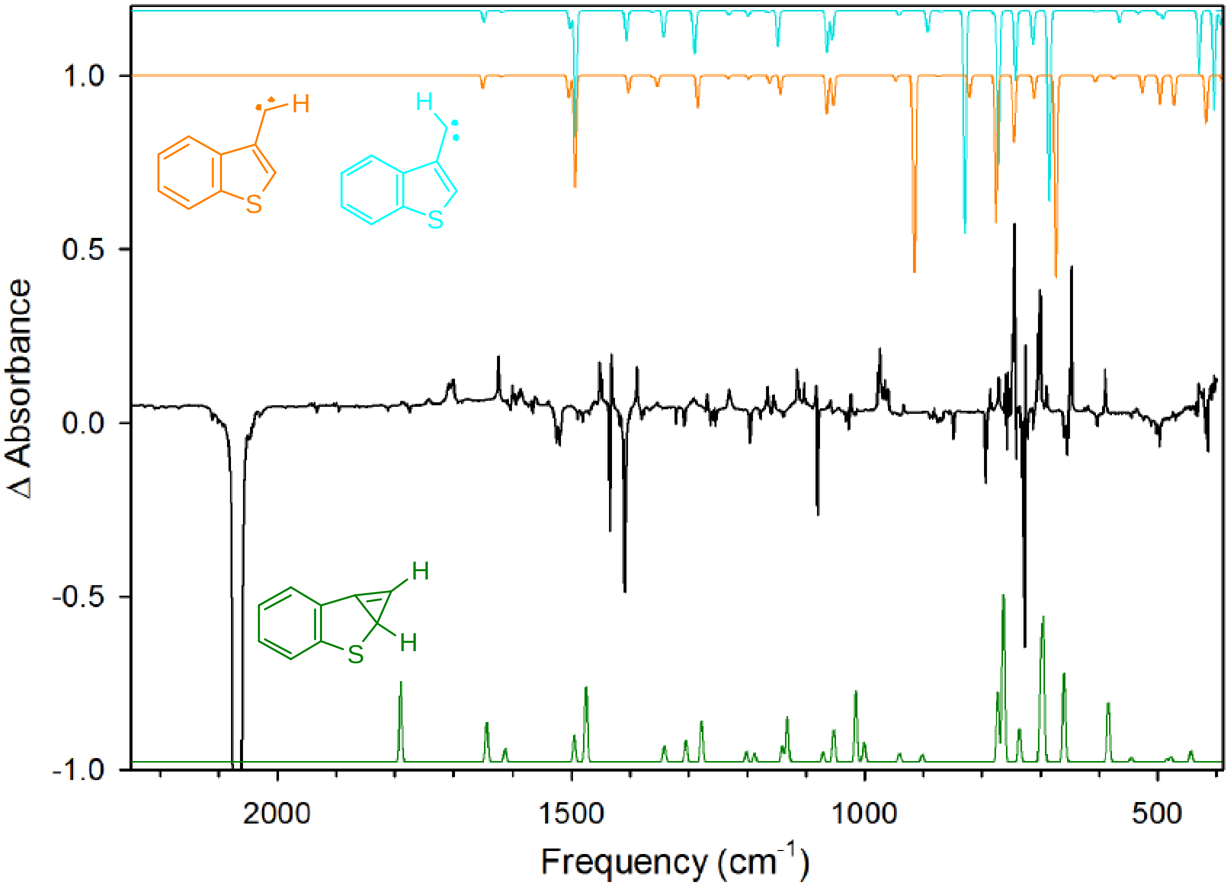


Figure S2.1. IR subtraction spectrum (Ar, 10 K) of a matrix containing 3-benzothienyl diazomethane (**1**) after irradiation at λ > 472 nm, 38 h (black trace, middle) showing the growth of peaks corresponding to 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (**16**). The top and bottom spectra are calculated (B3LYP/6-31G*) spectra of **16** (bottom spectra, green) and the two rotamers of 3-benzothienyl carbene (**11-s-*E***, aqua and **11-s-*Z***, orange). The calculated spectra for the carbenes do not match the observed data.

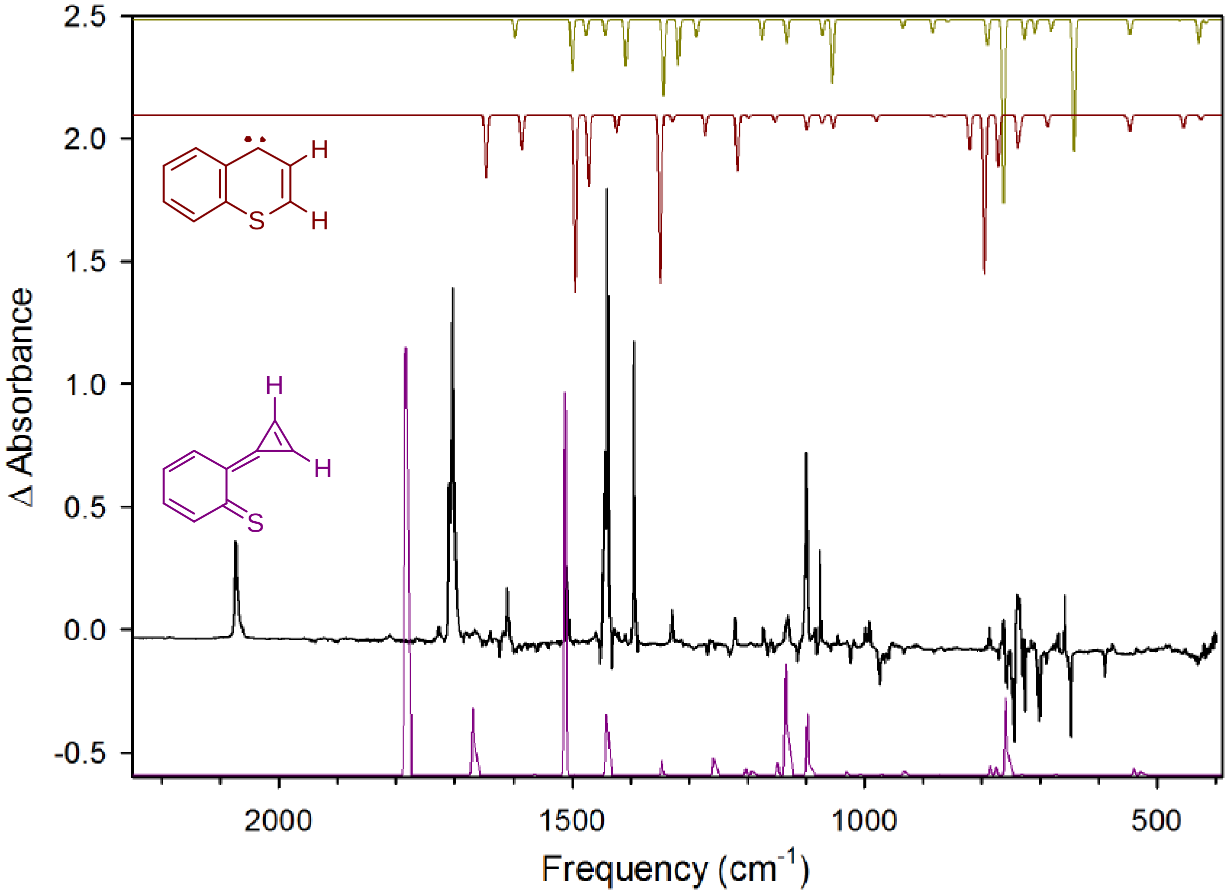


Figure S2.2. IR subtraction spectrum (Ar, 10 K) of a matrix containing to 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (**16**) after irradiation at λ = 340 nm, 16 h (black trace, middle) showing the growth of peaks corresponding to 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (**21**). The top and bottom spectra are calculated (B3LYP/6-31G*) spectra of **21** (bottom spectra, purple) and the singlet and triplet 1-benzothiopyran-4-ylidene (^{3}**17**, gold and ^{1}**17**, red). The calculated spectra for carbene **17** do not match the observed data.

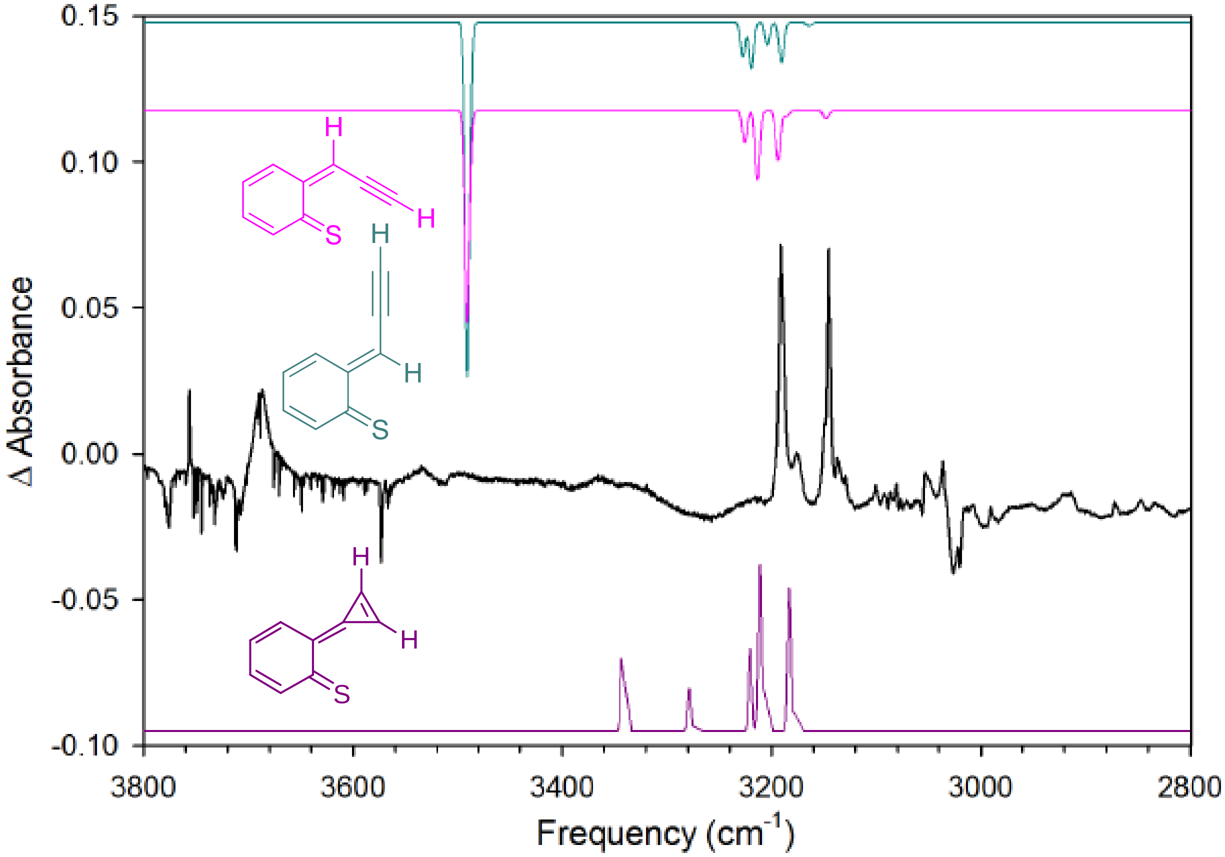


Figure S2.3. IR subtraction spectrum (Ar, 10 K) of a matrix containing to 2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (**16**) after irradiation at λ = 340 nm, 16 h (black trace, middle), with a blow up of the C-H stretching region, showing the growth of peaks corresponding to 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (**21**), and *E*- and *Z*-vinylacetylenes **15** and **18**. This is the same spectrum as **Figure 2.4**. The top and bottom spectra are calculated (B3LYP/6-31G*) spectra of **21** (bottom spectrum, purple) and the *E*- and *Z*- 2-(vinylacetylene)-3,5-cyclohexadien-1-thione isomers (**15**, aqua and **18**, pink, top spectra).

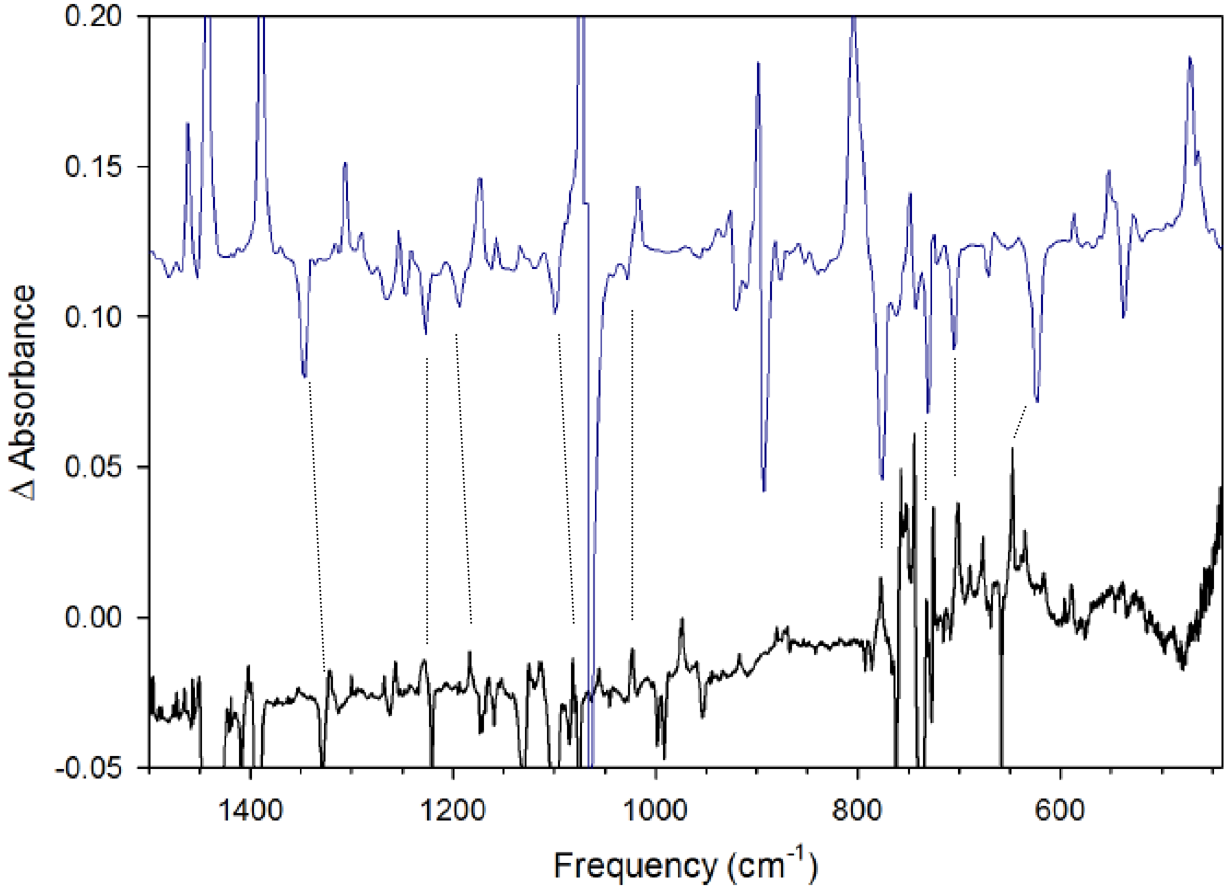


Figure S2.4. IR subtraction spectrum (Ar, 10 K) of a matrix containing to2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (**21**) after irradiation at λ = 300 nm, 19 h (black trace, middle) showing the disappearance of peaks corresponding to 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (**21**) and both *E*- and *Z*- 2-(vinylacetylene)-3,5-cyclohexadien-1-thione isomers (**15** and **18**) and the growth of small peaks at 1183, 1021, 976, 700, and 647 cm^{-1}. These peaks are tentatively assigned to allene **14** based on comparison with previous experimental data (blue spectrum, top). The top spectrum is a subtraction spectrum (N_2, 10K) showing the growth of allene 14 (negative peaks) after irradiation (λ > 534 nm) of a matrix containing 2-benzothienyl diazomethane (positive peaks, see chapter one).

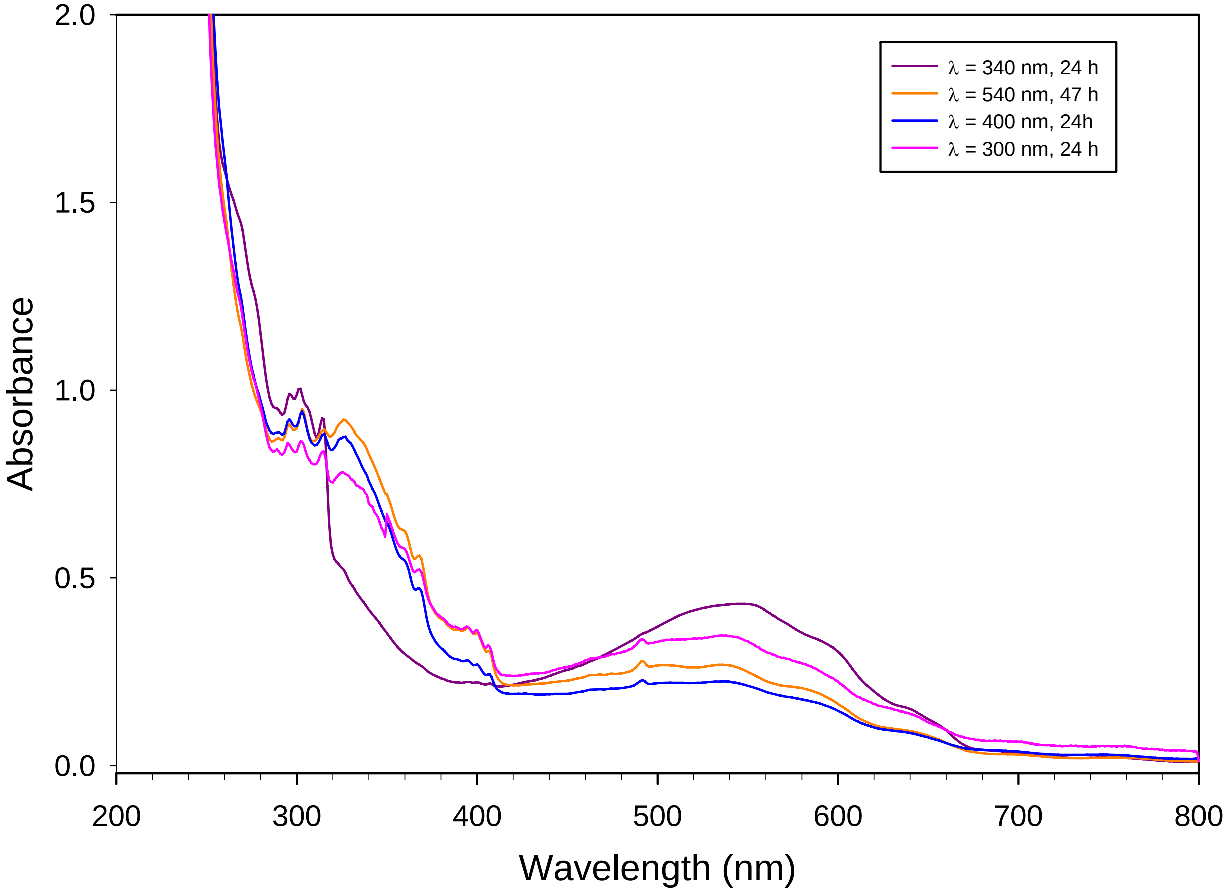
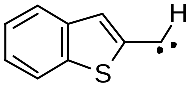


Figure S2.5. Electronic absorption spectra (Ar, 10 K) of a matrix containing 3-benzothienyl diazomethane (**1**) after irradiation at a variety of wavelengths. Initial irradiation was carried out at λ > 472 nm, followed by irradiation at λ = 340 nm, and at λ = 540 nm. (see text of chapter) Irradiation was then carried out at shorter wavelengths, in the order shown in the legend. Irradiation of 2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (**21**) (purple trace) at λ = 540 and 400 nm leads to a decrease in the absorption at 540 nm, but never its disappearance. However, when irradiation is carried out at λ = 300 nm, a significant growth in the peak at 540 nm is seen, with a concomitant decrease in absorption at 320 nm. This supports the theory that a small amount of tricycle **16** was reformed upon 540 nm irradiation, and, at shorter wavelength irradiation will regenerate **21**.

s-*E*-2-Benzothienyl carbene (^{1}10-s-*E*)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.116542	-744.631073	-744.514532	3.6250

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.505906	-744.547045

(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	131.5604	0.4573
A"	197.9972	0.0605
A"	203.0143	2.7026
A'	264.9964	2.8555
A'	395.2187	6.8398
A"	425.8034	0.1993
A"	489.3929	14.3293
A'	504.3116	1.6895
A'	534.3243	1.6162
A"	578.7032	30.3612
A'	583.4032	10.1124
A"	618.4339	6.8239
A'	711.3031	4.8844
A"	754.2784	32.3147
A'	772.3475	0.9252
A"	781.5517	19.7519
A"	861.1713	21.5013
A'	877.9316	65.3382
A"	878.4848	0.1864
A"	949.0918	0.9017
A"	991.8899	0.0001
A'	1047.9420	10.3299
A'	1052.6032	0.3167
A'	1084.4515	0.9192
A'	1145.9264	0.1851
A'	1172.0024	3.2256
A'	1198.2629	3.4438

Atom	Coordinates (Angstroms)		
	X	Y	Z
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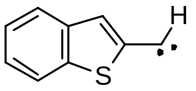
C	0.332053	-0.719627	0.000000
C	1.652059	-1.174298	0.000000
C	2.666299	-0.220725	0.000000
C	2.360895	1.150602	0.000000
C	1.041001	1.587731	0.000000
C	-1.454330	0.884326	0.000000
C	-2.133652	-0.335716	0.000000
H	1.883151	-2.235628	0.000000
H	3.703741	-0.542659	0.000000
H	3.168177	1.877597	0.000000
H	0.805037	2.648766	0.000000
H	-3.212903	-0.421841	0.000000
S	-1.132086	-1.724670	0.000000
C	-2.244303	2.066255	0.000000
H	-1.553957	2.940417	0.000000

A'	1215.0119	19.9262
A'	1293.1917	13.3341
A'	1365.2722	7.5017
A'	1371.6460	2.5404
A'	1444.3081	160.0107
A'	1492.5885	37.5064
A'	1506.9335	5.4948
A'	1617.9249	1.3115
A'	1650.5393	0.9417
A'	2918.5817	120.7569
A'	3187.4068	0.1601
A'	3195.3399	0.8659
A'	3204.1838	17.5179
A'	3214.5431	23.0624
A'	3272.0389	6.6256

s-*E*-2-Benzothienyl carbene (^{3}10-s-*E*)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.115766	-744.636464	-744.520697	1.0941

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.511881	-744.554236

(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
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A"	200.2282	0.8021
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A'	257.6445	0.0452
A'	392.6866	2.6662
A"	403.4526	19.9931
A"	429.4079	12.2153
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A'	533.0749	0.5101
A'	565.0181	2.2884
A"	604.6315	0.2099
A"	684.5673	37.5199
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A"	741.9010	14.0153
A"	770.8882	30.1355
A'	778.4909	0.6123
A'	827.9411	43.7527
A"	869.3473	0.0866
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A"	940.6807	0.8510
A"	981.5633	0.0353
A'	1054.6859	5.7714
A'	1063.6675	8.0686
A'	1147.5902	6.9012
A'	1164.3191	0.3151
A'	1197.5868	1.1861

Atom	Coordinates (Angstroms)		
	X	Y	Z
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C	2.648347	-0.268952	0.000000
C	2.369862	1.106859	0.000000
C	1.056247	1.563619	0.000000
C	-1.452462	0.907051	0.000000
C	-2.165963	-0.299789	0.000000
H	1.828519	-2.267001	0.000000
H	3.679320	-0.611534	0.000000
H	3.188142	1.821362	0.000000
H	0.846331	2.629702	0.000000
H	-3.242652	-0.400219	0.000000
S	-1.165596	-1.723690	0.000000
C	-2.031191	2.158124	0.000000
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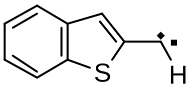
A'	1492.1710	24.7714
A'	1501.2789	3.5278
A'	1617.5604	0.2659
A'	1647.8600	2.2555
A'	3186.6586	0.0729
A'	3194.8709	3.3283
A'	3204.2532	21.8277
A'	3213.5953	22.3488
A'	3268.2389	1.6499
A'	3273.6146	3.1279

s-*Z*-2-Benzothienyl carbene (^{1}10-s-*Z*)



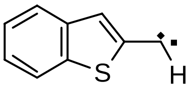
Charge	**Multiplicity**	**Theory/Basis Set**	**Full Point Group**
0	1	RB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.116609	-744.631363	-744.514754	3.2010
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-744.50608	-744.547379		

Symmetry	**Vibrational Frequency (cm^{-1})**	**Intensity**
A"	121.6737	15.2523
A"	182.0720	6.5063
A"	199.7935	8.4455
A'	259.3536	12.0852
A'	397.8017	3.7157
A"	428.2286	5.4646
A"	485.8998	1.9677
A'	506.6206	1.6406
A'	535.5352	4.9052
A"	581.2637	28.1958
A'	585.0963	2.3515
A"	619.9713	1.0986
A'	711.8916	2.1436
A"	757.2544	24.8510
A'	778.7696	3.3551
A"	785.9740	31.3757
A"	823.2375	17.7901
A'	870.9253	51.7710
A"	884.5125	1.9087
A"	958.8781	1.7717
A"	1003.5041	0.2538
A'	1045.0545	8.1821
A'	1050.9647	0.5592
A'	1111.9003	49.1709
A'	1135.2487	0.5975
A'	1174.3389	17.4343
A'	1198.6487	5.3093

Atom	**Coordinates (Angstroms)**		
	X	**Y**	**Z**
C	0.000000	0.642653	0.000000
C	0.344628	-0.721596	0.000000
C	1.671683	-1.158259	0.000000
C	2.669523	-0.187819	0.000000
C	2.345622	1.181108	0.000000
C	1.021364	1.601646	0.000000
C	-1.448424	0.873979	0.000000
C	-2.127287	-0.346718	0.000000
H	1.919430	-2.215683	0.000000
H	3.711725	-0.494578	0.000000
H	3.144751	1.917209	0.000000
H	0.744710	2.651704	0.000000
H	-3.203809	-0.471826	0.000000
S	-1.113251	-1.733366	0.000000
C	-2.037888	2.168693	0.000000
H	-3.140103	2.024904	0.000000

A'	1226.1768	16.6365
A'	1284.7369	11.6918
A'	1372.3662	1.1989
A'	1394.1023	1.1221
A'	1429.5627	178.2240
A'	1491.1391	30.6313
A'	1508.7565	1.8674
A'	1616.8170	1.3210
A'	1651.9472	0.7875
A'	2939.1446	161.5482
A'	3189.4779	1.7973
A'	3200.7091	11.0734
A'	3211.3997	16.8467
A'	3219.6750	10.0214
A'	3255.0379	2.1626

s-*Z*-2-Benzothienyl carbene (^{3}10-s-*Z*)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.115932	-744.637339	-744.521407	0.1423

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.512642	-744.554906

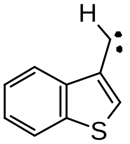
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	146.4336	0.3892
A"	199.8835	3.2268
A"	245.4864	1.6620
A'	250.5871	3.0415
A'	389.5103	1.4727
A"	417.2347	10.2452
A"	471.8613	6.3979
A"	495.7134	6.3040
A'	498.5924	0.1609
A'	526.0989	3.8383
A'	574.6841	0.7311
A"	605.9668	1.4385
A"	673.2033	43.6414
A'	710.2475	4.9816
A"	744.6337	14.7132
A'	773.5719	2.4657
A"	775.1788	29.7276
A'	821.1949	4.5858
A"	873.6065	0.2368
A'	915.1439	42.5399
A"	946.3490	1.2033
A"	984.3148	0.0025
A'	1052.4492	6.4628
A'	1063.9959	8.2416
A'	1142.7588	4.1792
A'	1161.3763	1.8079
A'	1196.7169	0.8138

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.000000	0.646208	0.000000
C	0.332473	-0.723239	0.000000
C	1.661230	-1.154917	0.000000
C	2.668555	-0.193844	0.000000
C	2.354468	1.174738	0.000000
C	1.029658	1.597184	0.000000
C	-1.451658	0.879566	0.000000
C	-2.143332	-0.342970	0.000000
H	1.903368	-2.213730	0.000000
H	3.708293	-0.509067	0.000000
H	3.154490	1.909676	0.000000
H	0.782504	2.655114	0.000000
H	-3.217203	-0.472015	0.000000
S	-1.108842	-1.745278	0.000000
C	-2.040733	2.125663	0.000000
H	-3.053938	2.504143	0.000000

A'	1232.3697	0.6415
A'	1284.0241	7.0358
A'	1352.4176	2.3460
A'	1359.4492	0.5436
A'	1401.6920	3.7375
A'	1492.8116	24.0493
A'	1503.5189	4.9321
A'	1618.1831	0.3011
A'	1649.4690	2.8187
A'	3187.2308	0.3364
A'	3196.5954	4.4626
A'	3205.5615	19.2089
A'	3213.6759	21.4544
A'	3264.6305	0.3560
A'	3269.6499	2.6437

(s-*E*)-3-benzothienyl carbene (^{1}11-s-*E*)



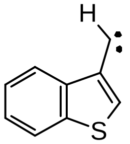
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.116542	-744.631073	-744.514532	3.6250
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-744.505906	-744.547045		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	131.5604	0.4573
A"	197.9972	0.0605
A"	203.0143	2.7026
A'	264.9964	2.8555
A'	395.2187	6.8398
A"	425.8034	0.1993
A"	489.3929	14.3293
A'	504.3116	1.6895
A'	534.3243	1.6162
A"	578.7032	30.3612
A'	583.4032	10.1124
A"	618.4339	6.8239
A'	711.3031	4.8844
A"	754.2784	32.3147
A'	772.3475	0.9252
A"	781.5517	19.7519
A"	861.1713	21.5013
A'	877.9316	65.3382
A"	878.4848	0.1864
A"	949.0918	0.9017
A"	991.8899	0.0001
A'	1047.9420	10.3299
A'	1052.6032	0.3167
A'	1084.4515	0.9192
A'	1145.9264	0.1851
A'	1172.0024	3.2256
A'	1198.2629	3.4438

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.000000	0.649463	0.000000
C	0.332053	-0.719627	0.000000
C	1.652059	-1.174298	0.000000
C	2.666299	-0.220725	0.000000
C	2.360895	1.150602	0.000000
C	1.041001	1.587731	0.000000
C	-1.454330	0.884326	0.000000
C	-2.133652	-0.335716	0.000000
H	1.883151	-2.235628	0.000000
H	3.703741	-0.542659	0.000000
H	3.168177	1.877597	0.000000
H	0.805037	2.648766	0.000000
H	-3.212903	-0.421841	0.000000
S	-1.132086	-1.724670	0.000000
C	-2.244303	2.066255	0.000000
H	-1.553957	2.940417	0.000000

A'	1215.0119	19.9262
A'	1293.1917	13.3341
A'	1365.2722	7.5017
A'	1371.6460	2.5404
A'	1444.3081	160.0107
A'	1492.5885	37.5064
A'	1506.9335	5.4948
A'	1617.9249	1.3115
A'	1650.5393	0.9417
A'	2918.5817	120.7569
A'	3187.4068	0.1601
A'	3195.3399	0.8659
A'	3204.1838	17.5179
A'	3214.5431	23.0624
A'	3272.0389	6.6256

(s-*E*)-3-benzothienyl carbene (^{3}11-s-*E*)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.115766	-744.636464	-744.520697	1.0941

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.511881	-744.554236

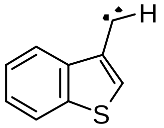
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	143.1128	0.1697
A"	200.2282	0.8021
A"	242.7862	0.3316
A'	257.6445	0.0452
A'	392.6866	2.6662
A"	403.4526	19.9931
A"	429.4079	12.2153
A"	490.7331	1.5196
A'	497.5940	0.8501
A'	533.0749	0.5101
A'	565.0181	2.2884
A"	604.6315	0.2099
A"	684.5673	37.5199
A'	712.2023	6.6438
A"	741.9010	14.0153
A"	770.8882	30.1355
A'	778.4909	0.6123
A'	827.9411	43.7527
A"	869.3473	0.0866
A'	891.4375	4.1923
A"	940.6807	0.8510
A"	981.5633	0.0353
A'	1054.6859	5.7714
A'	1063.6675	8.0686
A'	1147.5902	6.9012
A'	1164.3191	0.3151

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.000000	0.642210	0.000000
C	0.298069	-0.736125	0.000000
C	1.615285	-1.201944	0.000000
C	2.648347	-0.268952	0.000000
C	2.369862	1.106859	0.000000
C	1.056247	1.563619	0.000000
C	-1.452462	0.907051	0.000000
C	-2.165963	-0.299789	0.000000
H	1.828519	-2.267001	0.000000
H	3.679320	-0.611534	0.000000
H	3.188142	1.821362	0.000000
H	0.846331	2.629702	0.000000
H	-3.242652	-0.400219	0.000000
S	-1.165596	-1.723690	0.000000
C	-2.031191	2.158124	0.000000
H	-1.679289	3.180407	0.000000

A'	1197.5868	1.1861
A'	1230.7470	0.7568
A'	1289.4597	8.3626
A'	1341.7935	5.1290
A'	1361.1267	0.2425
A'	1405.1227	5.8977
A'	1492.1710	24.7714
A'	1501.2789	3.5278
A'	1617.5604	0.2659
A'	1647.8600	2.2555
A'	3186.6586	0.0729
A'	3194.8709	3.3283
A'	3204.2532	21.8277
A'	3213.5953	22.3488
A'	3268.2389	1.6499
A'	3273.6146	3.1279

(s-*Z*)-3-benzothienyl carbene (^{1}**11**-s-*Z*)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.116609	-744.631363	-744.514754	3.2010

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.50608	-744.547379

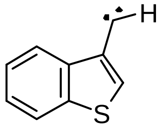
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	121.6737	15.2523
A"	182.0720	6.5063
A"	199.7935	8.4455
A'	259.3536	12.0852
A'	397.8017	3.7157
A"	428.2286	5.4646
A"	485.8998	1.9677
A'	506.6206	1.6406
A'	535.5352	4.9052
A"	581.2637	28.1958
A'	585.0963	2.3515
A"	619.9713	1.0986
A'	711.8916	2.1436
A"	757.2544	24.8510
A'	778.7696	3.3551
A"	785.9740	31.3757
A"	823.2375	17.7901
A'	870.9253	51.7710
A"	884.5125	1.9087
A"	958.8781	1.7717
A"	1003.5041	0.2538
A'	1045.0545	8.1821
A'	1050.9647	0.5592
A'	1111.9003	49.1709
A'	1135.2487	0.5975
A'	1174.3389	17.4343

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.000000	0.642653	0.000000
C	0.344628	-0.721596	0.000000
C	1.671683	-1.158259	0.000000
C	2.669523	-0.187819	0.000000
C	2.345622	1.181108	0.000000
C	1.021364	1.601646	0.000000
C	-1.448424	0.873979	0.000000
C	-2.127287	-0.346718	0.000000
H	1.919430	-2.215683	0.000000
H	3.711725	-0.494578	0.000000
H	3.144751	1.917209	0.000000
H	0.744710	2.651704	0.000000
H	-3.203809	-0.471826	0.000000
S	-1.113251	-1.733366	0.000000
C	-2.037888	2.168693	0.000000
H	-3.140103	2.024904	0.000000

A'	1198.6487	5.3093
A'	1226.1768	16.6365
A'	1284.7369	11.6918
A'	1372.3662	1.1989
A'	1394.1023	1.1221
A'	1429.5627	178.2240
A'	1491.1391	30.6313
A'	1508.7565	1.8674
A'	1616.8170	1.3210
A'	1651.9472	0.7875
A'	2939.1446	161.5482
A'	3189.4779	1.7973
A'	3200.7091	11.0734
A'	3211.3997	16.8467
A'	3219.6750	10.0214
A'	3255.0379	2.1626

(s-*Z*)-3-benzothienyl carbene (^{3}11-s-*Z*)



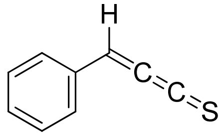
Charge	**Multiplicity**	**Theory/Basis Set**	**Full Point Group**
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.115932	-744.637339	-744.521407	0.1423
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-744.512642	-744.554906		

Symmetry	**Vibrational Frequency (cm^{-1})**	**Intensity**
A"	146.4336	0.3892
A"	199.8835	3.2268
A"	245.4864	1.6620
A'	250.5871	3.0415
A'	389.5103	1.4727
A"	417.2347	10.2452
A"	471.8613	6.3979
A"	495.7134	6.3040
A'	498.5924	0.1609
A'	526.0989	3.8383
A'	574.6841	0.7311
A"	605.9668	1.4385
A"	673.2033	43.6414
A'	710.2475	4.9816
A"	744.6337	14.7132
A'	773.5719	2.4657
A"	775.1788	29.7276
A'	821.1949	4.5858
A"	873.6065	0.2368
A'	915.1439	42.5399
A"	946.3490	1.2033
A"	984.3148	0.0025
A'	1052.4492	6.4628
A'	1063.9959	8.2416
A'	1142.7588	4.1792
A'	1161.3763	1.8079

Atom	**Coordinates (Angstroms)**		
	X	**Y**	**Z**
C	0.000000	0.646208	0.000000
C	0.332473	-0.723239	0.000000
C	1.661230	-1.154917	0.000000
C	2.668555	-0.193844	0.000000
C	2.354468	1.174738	0.000000
C	1.029658	1.597184	0.000000
C	-1.451658	0.879566	0.000000
C	-2.143332	-0.342970	0.000000
H	1.903368	-2.213730	0.000000
H	3.708293	-0.509067	0.000000
H	3.154490	1.909676	0.000000
H	0.782504	2.655114	0.000000
H	-3.217203	-0.472015	0.000000
S	-1.108842	-1.745278	0.000000
C	-2.040733	2.125663	0.000000
H	-3.053938	2.504143	0.000000

A'	1196.7169	0.8138
A'	1232.3697	0.6415
A'	1284.0241	7.0358
A'	1352.4176	2.3460
A'	1359.4492	0.5436
A'	1401.6920	3.7375
A'	1492.8116	24.0493
A'	1503.5189	4.9321
A'	1618.1831	0.3011
A'	1649.4690	2.8187
A'	3187.2308	0.3364
A'	3196.5954	4.4626
A'	3205.5615	19.2089
A'	3213.6759	21.4544
A'	3264.6305	0.3560
A'	3269.6499	2.6437

Benzothioketene (^{1}12)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.118187	-744.693782	-744.575595	4.8100

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.566111	-744.610619

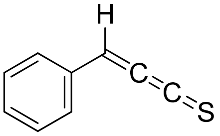
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A'	51.9237	0.1721
A"	54.2104	0.0891
A"	183.0656	0.1487
A'	246.1002	1.8025
A"	265.6289	2.5933
A'	336.1970	0.0143
A'	399.5850	0.6217
A"	414.6690	0.0008
A"	476.4559	5.7825
A"	542.2822	0.7535
A'	602.2193	51.1591
A'	629.4588	0.3483
A"	696.5287	19.9626
A'	761.1809	29.3623
A"	762.9821	29.8363
A'	843.9044	20.3508
A"	858.0789	0.8219
A"	890.5288	6.6230
A"	951.8077	6.0114
A"	979.5686	0.0129
A"	1007.0112	0.0851
A'	1015.8014	5.5297
A'	1053.5074	0.4801
A'	1115.6619	2.8292
A'	1195.0039	1.1108
A'	1207.0534	53.5021
A'	1242.0246	87.3147

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	1.040404	3.300135	0.000000
C	-0.102463	2.506084	0.000000
C	0.000000	1.100956	0.000000
C	1.280986	0.511013	0.000000
C	2.419231	1.306427	0.000000
C	2.303165	2.702198	0.000000
H	0.949226	4.382572	0.000000
H	-1.087636	2.966367	0.000000
H	1.359387	-0.572151	0.000000
H	3.402085	0.843689	0.000000
H	3.196451	3.320738	0.000000
C	-1.214826	0.299028	0.000000
H	-2.147798	0.871109	0.000000
C	-1.283439	-1.037106	0.000000
C	-1.383439	-2.298406	0.000000
S	-1.501839	-3.884644	0.000000

A'	1286.1709	56.3625
A'	1360.0642	6.6339
A'	1372.8819	2.5018
A'	1483.3197	15.6317
A'	1531.1717	0.1968
A'	1551.0710	7.9595
A'	1632.7467	0.0058
A'	1653.4402	55.1508
A'	2118.7193	1306.1236
A'	3099.0527	19.2873
A'	3184.4030	4.0546
A'	3192.3167	0.8242
A'	3202.0382	14.5636
A'	3211.0535	20.9335
A'	3217.3004	19.8353

Benzothioketene (^{3}12)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.116009	-744.652597	-744.536587	1.6860

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.526868	-744.572694

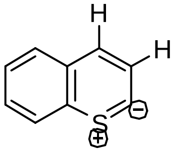
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	56.1198	0.0038
A'	59.4345	0.0856
A"	180.1471	0.0352
A'	228.8015	0.2020
A"	251.6176	2.5381
A'	320.7382	0.3610
A"	398.1776	0.1640
A"	416.3111	0.0002
A'	435.6680	0.1855
A"	479.0199	10.8298
A'	606.5720	20.4522
A'	630.3857	0.4655
A"	654.2447	9.4151
A"	698.9680	16.4474
A'	735.1095	13.3582
A"	774.2303	45.6324
A'	842.6100	1.3454
A"	842.8094	0.2912
A"	906.5653	4.2013
A"	961.7967	0.0422
A"	989.0498	0.0475
A'	1006.7099	0.1721
A'	1051.7348	1.1308
A'	1113.5885	3.2432
A'	1190.2745	0.1579
A'	1199.7298	0.9507
A'	1206.4757	9.6671

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	1.088864	3.291589	0.000000
C	-0.068110	2.522396	0.000000
C	0.000000	1.108698	0.000000
C	1.280224	0.503105	0.000000
C	2.431009	1.280007	0.000000
C	2.346083	2.677618	0.000000
H	1.012980	4.375726	0.000000
H	-1.042600	3.004741	0.000000
H	1.355535	-0.580968	0.000000
H	3.404013	0.795781	0.000000
H	3.249549	3.280612	0.000000
C	-1.216329	0.337686	0.000000
H	-2.161636	0.880250	0.000000
C	-1.303878	-1.028307	0.000000
C	-1.409891	-2.285084	0.000000
S	-1.544105	-3.887649	0.000000

A'	1230.7069	0.7908
A'	1339.7009	3.2202
A'	1368.0705	0.2188
A'	1419.2818	1.3679
A'	1503.1893	6.0860
A'	1528.8420	11.4263
A'	1613.8276	1.0132
A'	1633.4963	0.5776
A'	1923.5683	36.3317
A'	3151.7182	0.8172
A'	3179.7295	6.9794
A'	3184.8275	1.1699
A'	3194.8268	8.5506
A'	3201.0167	33.9228
A'	3212.5112	26.9962

1-benzothiopyran-2-ylidene (^{1}13)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.119200	-744.676438	-744.557238	4.7108

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.548925	-744.589547

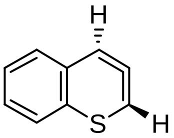
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	118.9682	0.6262
A"	161.4257	1.8783
A'	310.2045	0.0336
A"	321.1372	3.2868
A"	417.1744	7.5425
A'	438.7238	0.3038
A'	452.9083	4.0780
A"	459.2595	4.0974
A'	544.5808	10.8072
A"	584.9022	0.2835
A'	688.3044	1.2868
A'	741.4176	13.2129
A"	751.7998	8.9186
A'	762.6743	0.4260
A"	764.5630	27.4312
A"	857.7663	17.8098
A'	877.1757	0.5086
A"	886.5639	4.4496
A"	963.2879	1.9510
A"	1000.5052	0.0432
A"	1023.7680	0.0053
A'	1050.5570	0.9098
A'	1073.8299	5.9565
A'	1120.3638	12.4098
A'	1171.2083	0.7390
A'	1199.9804	0.5219

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	2.267976	1.440952	0.000000
C	0.904350	1.682727	0.000000
C	0.000000	0.605691	0.000000
C	0.475584	-0.731100	0.000000
C	1.877802	-0.945377	0.000000
C	2.757295	0.118879	0.000000
H	2.965568	2.274111	0.000000
H	0.524532	2.701349	0.000000
C	-0.433928	-1.839239	0.000000
H	2.249358	-1.967334	0.000000
H	3.828574	-0.060151	0.000000
C	-1.806030	-1.748654	0.000000
C	-2.588796	-0.549262	0.000000
H	0.022356	-2.829339	0.000000
H	-2.362082	-2.687117	0.000000
S	-1.747114	0.897548	0.000000

A'	1259.7945	13.1770
A'	1270.1787	11.8378
A'	1295.1812	5.9025
A'	1389.3768	11.2053
A'	1459.5019	17.5491
A'	1462.5311	7.7319
A'	1523.5936	6.8159
A'	1555.2437	25.6715
A'	1623.4878	10.0498
A'	1655.9366	6.6376
A'	3137.7624	14.7275
A'	3159.8791	39.6054
A'	3183.9904	3.6742
A'	3188.7707	1.3396
A'	3200.7584	18.6428
A'	3213.5014	23.4244

2*H*-1-benzo-2,3-dehydrothiopyran (^{1}14)



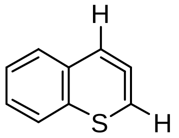
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_1
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.118338	-744.665859	-744.547522	1.6521
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-744.539052	-744.579786		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	138.8815	1.6275
A	165.6426	0.4077
A	300.7732	7.7303
A	333.9137	3.9306
A	388.4438	4.7540
A	422.1504	15.4294
A	455.9794	2.6917
A	473.7032	12.2394
A	528.9603	0.9310
A	543.0259	13.0594
A	627.1598	41.6601
A	681.0536	3.3491
A	718.3581	17.3188
A	734.8485	32.0397
A	756.1937	32.7415
A	785.7849	40.7739
A	830.2144	1.6972
A	866.6097	0.4455
A	894.7876	2.5730
A	951.0825	2.0170
A	986.7783	0.0446
A	1050.7599	9.9615
A	1071.9288	0.4113
A	1146.4144	6.9455
A	1149.1475	0.1058

Atom	Coordinates (Angstroms) X	Y	Z
C	-2.469380	-0.945423	0.072350
C	-1.162578	-1.417039	-0.032031
C	-0.088046	-0.519653	-0.060704
C	-0.335255	0.880996	-0.036563
C	-1.662442	1.327057	0.079153
C	-2.722036	0.428630	0.136690
H	-3.291709	-1.654451	0.111931
H	-0.974957	-2.486636	-0.065527
H	-1.850425	2.397473	0.103013
H	-3.741820	0.794084	0.217016
C	0.801176	1.772778	-0.321929
C	1.986621	1.329115	0.094669
C	2.477596	0.147183	0.458101
S	1.564583	-1.228744	-0.185382
H	0.658800	2.633537	-0.972034
H	3.212849	-0.045981	1.233283

A	1197.1166	1.4466
A	1226.8426	10.4743
A	1266.4086	10.3315
A	1298.5697	9.5311
A	1328.9157	1.2596
A	1402.5284	33.7181
A	1485.0352	8.7621
A	1492.8225	7.0855
A	1606.6827	0.8228
A	1640.6755	6.2998
A	1820.3175	2.6322
A	3176.8732	13.7951
A	3186.2148	1.5691
A	3192.7013	3.5203
A	3202.7200	15.5044
A	3203.0768	17.9120
A	3214.0626	24.0721

2*H*-1-benzo-2,3-dehydrothiopyran (^{3}14)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.116952	-744.645047	-744.528095	0.9190

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.51946	-744.561698

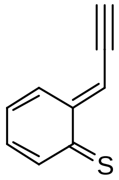
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	102.0909	0.5146
A"	164.3099	0.6095
A"	271.3417	0.4676
A'	327.6331	1.3289
A'	405.9820	0.0450
A'	436.9669	0.3918
A"	447.7693	1.3229
A"	459.7697	6.1832
A"	541.4397	4.4652
A'	544.0134	0.1156
A"	614.6054	31.9329
A'	678.6060	3.8550
A'	691.2388	0.3338
A"	716.5456	0.6239
A"	740.7435	9.3827
A'	761.1073	12.0284
A"	774.8751	53.1240
A'	867.9014	1.2499
A"	868.4735	1.3511
A"	937.4076	2.4020
A"	978.1645	0.0059
A'	1055.8359	12.4036
A'	1074.0590	2.6928
A'	1101.4975	4.3683
A'	1156.1813	3.0880
A'	1195.3410	0.0507

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	2.268435	1.400595	0.000000
C	0.892328	1.616394	0.000000
C	0.000000	0.538682	0.000000
C	0.487356	-0.800598	0.000000
C	1.890501	-0.982741	0.000000
C	2.766420	0.092358	0.000000
H	2.947024	2.248490	0.000000
H	0.504174	2.631786	0.000000
H	2.274298	-1.999919	0.000000
H	3.838561	-0.083807	0.000000
C	-0.398941	-1.939525	0.000000
C	-1.759170	-1.741450	0.000000
C	-2.521748	-0.629714	0.000000
S	-1.733931	0.963019	0.000000
H	0.032630	-2.936007	0.000000
H	-3.604868	-0.592850	0.000000

A'	1217.0245	0.0499
A'	1253.7920	7.8929
A'	1291.0233	10.0576
A'	1337.1283	4.7439
A'	1407.6974	15.4723
A'	1445.3514	19.3108
A'	1485.7453	6.5439
A'	1527.1115	3.4584
A'	1602.6387	2.9546
A'	1635.0178	0.0361
A'	3183.2232	3.3972
A'	3188.3222	0.6445
A'	3198.9485	1.1304
A'	3200.6684	25.3518
A'	3214.2891	21.9867
A'	3233.9141	1.5566

2-(*E*-vinylacetylene)-3,5-cyclohexadien-1-thione (^{1}15)



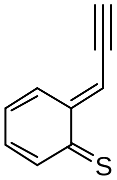
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.116401	-744.649069	-744.532668	4.2845
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-744.522924	-744.567228		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	62.0455	1.2327
A"	114.1716	0.0105
A'	124.9319	0.3199
A"	233.5435	0.0552
A'	260.0486	1.5728
A'	359.6683	4.6682
A'	434.4770	14.8600
A"	435.7781	0.6177
A"	448.8829	1.2037
A'	490.8725	2.2807
A"	516.3952	11.1703
A'	608.2083	11.2769
A"	615.2121	44.2329
A'	620.6421	46.3609
A"	735.5802	7.1768
A'	740.4182	4.5900
A"	780.1453	34.4094
A'	837.5976	5.1890
A"	871.7299	0.6856
A"	940.9798	6.3568
A"	986.0144	0.1441
A"	1012.5930	0.3603
A'	1022.3855	6.8659
A'	1054.9189	7.6335
A'	1101.3325	48.5839

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.929387	-1.955032	0.000000
C	-0.245589	-1.116672	0.000000
C	0.000000	0.350119	0.000000
C	1.365111	0.836514	0.000000
C	2.419015	-0.018159	0.000000
C	2.191263	-1.438199	0.000000
H	0.767534	-3.027594	0.000000
H	1.516695	1.911442	0.000000
H	3.437181	0.359629	0.000000
H	3.047110	-2.108549	0.000000
S	-1.768996	-1.816865	0.000000
C	-1.056735	1.231554	0.000000
C	-0.951055	2.632688	0.000000
C	-0.907337	3.846341	0.000000
H	-0.868409	4.912456	0.000000
H	-2.060531	0.807523	0.000000

A'	1163.9283	76.0315
A'	1190.9462	12.0470
A'	1233.9820	16.5558
A'	1295.8396	13.5362
A'	1355.3898	3.0060
A'	1444.2322	26.4676
A'	1487.0488	24.3658
A'	1566.6756	100.8366
A'	1579.9056	15.8557
A'	1682.6551	34.6536
A'	2190.1881	18.5953
A'	3163.8924	0.8471
A'	3190.4896	10.9011
A'	3203.8363	6.0341
A'	3218.9219	12.5936
A'	3226.9806	9.5820
A'	3490.4312	97.7941

2-(*E*-vinylacetylene)-3,5-cyclohexadien-1-thione (^{3}15)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.114295	-744.616558	-744.502263	1.3151

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.492305	-744.537715

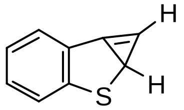
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	89.9392	0.3272
A'	114.3671	0.0167
A"	132.6197	0.0222
A'	211.8117	0.4999
A"	259.1307	0.7606
A'	343.6235	0.6097
A'	421.1941	2.0204
A"	429.2703	18.2139
A"	445.6733	7.5919
A"	460.8775	38.1671
A'	468.5142	2.5334
A"	508.7330	0.2551
A'	622.9954	21.3170
A'	634.3861	27.1582
A"	675.9701	10.4051
A'	713.6612	3.4395
A"	751.3589	4.9155
A"	769.2899	41.3198
A'	838.2646	3.7842
A"	864.8970	0.2316
A"	940.0767	1.9726
A"	977.1779	0.0260
A'	1052.2781	25.5264
A'	1064.6228	2.9319
A'	1087.1193	6.4603
A'	1151.3462	1.2149

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	1.094416	-1.860882	0.000000
C	-0.076593	-1.092808	0.000000
C	0.000000	0.334860	0.000000
C	1.291200	0.924326	0.000000
C	2.441283	0.154716	0.000000
C	2.344859	-1.243834	0.000000
H	1.028878	-2.945196	0.000000
H	1.353975	2.008255	0.000000
H	3.415444	0.634928	0.000000
H	3.241484	-1.857106	0.000000
S	-1.632554	-1.931134	0.000000
C	-1.187482	1.130680	0.000000
C	-1.218471	2.519093	0.000000
C	-1.265815	3.739662	0.000000
H	-1.309655	4.804920	0.000000
H	-2.149656	0.617472	0.000000

A'	1192.9686	3.3261
A'	1243.9373	1.5012
A'	1291.8082	4.5365
A'	1315.9917	12.8622
A'	1421.4273	6.7012
A'	1461.6322	0.2515
A'	1489.0264	52.2739
A'	1581.6230	7.6284
A'	1615.8186	9.6950
A'	2091.0818	15.1373
A'	3132.3578	25.7535
A'	3188.8065	0.2813
A'	3198.5170	5.7927
A'	3208.8555	15.6062
A'	3217.8844	16.4650
A'	3488.9471	75.5437

2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (^{1}16)



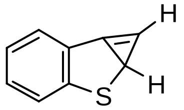
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_1
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.118048	-744.647602	-744.529554	1.6031
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-744.521165	-744.561733		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	137.8934	1.8737
A	178.9208	0.7389
A	304.2012	8.2513
A	336.6869	2.1898
A	350.1638	0.3901
A	443.2351	3.0036
A	477.1648	1.4837
A	484.5342	0.7927
A	545.0788	1.1410
A	583.2985	15.6740
A	659.0810	23.3181
A	694.6465	32.6795
A	698.9165	24.9200
A	735.4947	9.0789
A	762.7024	44.1927
A	772.4295	18.7624
A	874.0363	0.0284
A	900.5878	2.0917
A	940.0110	2.2723
A	981.3479	0.0686
A	1000.1608	5.3262
A	1013.7226	18.8421
A	1051.8285	8.3895
A	1070.1565	2.6342
A	1131.0356	11.8454
A	1139.4320	4.3096

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.242290	0.786027	-0.131649
C	0.213921	-0.634565	-0.014237
C	1.412465	-1.332231	0.142155
C	2.621681	-0.632582	0.111832
C	2.648286	0.757521	-0.034978
C	1.454874	1.473116	-0.145243
C	-1.128515	1.248661	-0.117428
C	-2.198146	0.253659	-0.422377
H	1.407892	-2.412293	0.255188
H	3.554580	-1.183190	0.198032
H	3.597769	1.284294	-0.053848
H	1.461935	2.554802	-0.240048
H	-2.757644	0.220482	-1.356372
S	-1.414127	-1.377446	0.008137
C	-2.251554	1.380378	0.550421
H	-2.730315	1.775126	1.435875

A	1187.0692	2.3818
A	1200.6369	2.8892
A	1277.6870	10.8607
A	1303.6112	5.7615
A	1340.3437	4.2136
A	1474.2310	19.9221
A	1494.2565	7.1352
A	1612.2166	3.5515
A	1643.2350	10.7109
A	1790.3683	21.1898
A	3139.7742	35.0737
A	3188.2830	1.4586
A	3200.1199	5.7733
A	3208.3994	18.9195
A	3216.4852	19.2524
A	3273.5111	0.4967

2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (^{3}16)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_1

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.115980	-744.574656	-744.458676	1.7003

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.450205	-744.492005

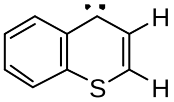
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	128.1861	0.5196
A	166.5848	1.6509
A	281.7718	0.7225
A	322.3068	9.5496
A	348.6583	4.3711
A	448.4288	5.1570
A	479.8798	2.0806
A	491.6252	1.0276
A	548.3486	1.3814
A	594.6984	0.1260
A	681.7702	27.8246
A	702.1305	9.8064
A	729.2879	16.3035
A	749.4889	17.4326
A	775.2968	53.6044
A	800.4374	12.4815
A	844.1341	19.7734
A	870.6071	0.0224
A	926.3414	8.6183
A	950.9459	2.6207
A	965.2895	22.8301
A	987.1949	0.0333
A	1007.6863	24.2053
A	1048.8072	3.6955
A	1069.3985	8.4811
A	1137.4546	1.4675

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.193958	0.760197	-0.208558
C	0.189491	-0.657986	-0.052689
C	1.380994	-1.367058	0.119172
C	2.582857	-0.661676	0.140932
C	2.605214	0.737790	0.008169
C	1.422848	1.446021	-0.156678
C	-1.116382	1.336195	-0.419621
C	-2.172777	0.299027	-0.264699
H	1.373077	-2.446251	0.240448
H	3.515677	-1.203837	0.269754
H	3.554470	1.264990	0.034865
H	1.428751	2.526709	-0.264349
H	-3.059603	0.283336	-0.901296
S	-1.435122	-1.356699	-0.029841
C	-2.077293	1.426874	0.718472
H	-1.903876	1.365933	1.791039

A	1158.3551	0.3054
A	1192.7247	4.7652
A	1218.4222	0.9895
A	1283.0098	8.3164
A	1334.7525	8.1167
A	1370.0871	6.7170
A	1469.5177	16.8295
A	1487.1401	8.3662
A	1593.5552	14.0821
A	1627.4073	31.0124
A	3124.4459	2.4512
A	3179.0672	25.6504
A	3189.4895	0.6680
A	3199.8149	3.6287
A	3208.5937	17.9816
A	3216.3825	21.7529

1-Benzothiopyran-4-ylidene (^{1}17)



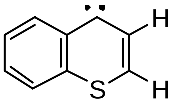
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.118009	-744.645869	-744.527860	3.3426
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-744.519283	-744.560744		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	73.4350	3.6318
A"	137.0039	8.1057
A"	268.0351	5.1591
A'	334.0543	4.5654
A"	375.8531	0.6656
A'	425.0007	1.3302
A'	454.3921	3.0919
A"	455.5194	1.0150
A"	545.9418	4.8031
A'	552.2090	0.7373
A'	687.0722	3.4717
A"	733.2296	3.5769
A'	738.2301	9.4186
A"	770.4067	15.6330
A"	793.8727	47.7026
A'	819.7287	10.5485
A'	863.2173	0.4599
A"	881.9875	0.5409
A"	978.9633	1.7464
A"	983.2947	0.1826
A"	1014.3031	0.0925
A'	1052.8624	3.9020
A'	1071.9422	2.6241
A'	1097.5957	4.2602
A'	1152.4802	2.2605
A'	1197.9459	0.9798
A'	1216.1475	16.7740

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	2.223904	1.494386	0.000000
C	0.851382	1.682418	0.000000
C	0.000000	0.562419	0.000000
C	0.507729	-0.772566	0.000000
C	1.926894	-0.898368	0.000000
C	2.769081	0.196416	0.000000
H	2.881268	2.359935	0.000000
H	0.435524	2.687350	0.000000
C	-0.245909	-2.009818	0.000000
H	2.307772	-1.914917	0.000000
H	3.847234	0.063450	0.000000
C	-1.669271	-1.862449	0.000000
C	-2.394189	-0.696177	0.000000
H	-2.274249	-2.772886	0.000000
H	-3.483064	-0.682482	0.000000
S	-1.720763	0.880124	0.000000

A'	1271.6037	5.9063
A'	1328.2959	1.9273
A'	1348.3416	50.4337
A'	1422.2961	5.2710
A'	1470.6375	16.3679
A'	1472.3136	5.4659
A'	1493.5626	53.5358
A'	1584.7753	10.5421
A'	1645.9074	18.8793
A'	3110.4288	42.7787
A'	3176.8408	13.3173
A'	3178.2713	2.2619
A'	3193.5143	11.0758
A'	3206.7791	18.6830
A'	3221.8468	12.2186

1-Benzothiopyran-4-ylidene (^{3}17)



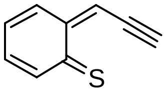
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.117186	-744.643347	-744.526160	0.2435
ΔH$_{(298)}$	**ΔG$_{(298)}$**	(Energies in Hartrees/particle)	
-744.517517	-744.559914		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	87.9813	2.4279
A"	158.5065	1.3056
A"	259.5851	0.0406
A'	318.1658	2.2068
A'	416.5163	1.0264
A"	428.1007	6.1205
A'	432.2970	0.2210
A"	460.2460	0.2301
A'	542.6489	0.1849
A"	545.9354	3.9055
A"	641.4249	34.8504
A'	680.5634	2.8958
A'	708.2238	3.6116
A"	726.1169	5.1315
A"	761.7481	48.3032
A'	789.5262	6.6331
A'	857.3819	0.6345
A"	865.9431	0.0046
A"	882.0403	3.4789
A"	933.3672	2.1678
A"	977.9605	0.0005
A'	1054.1969	16.6349
A'	1070.9156	4.3174
A'	1131.9982	6.1131
A'	1149.5380	0.1031
A'	1174.5536	5.3800

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	2.197467	1.576937	0.000000
C	0.806266	1.695398	0.000000
C	0.000000	0.556847	0.000000
C	0.587538	-0.745348	0.000000
C	1.999243	-0.831375	0.000000
C	2.790266	0.310191	0.000000
H	2.812791	2.471814	0.000000
H	0.345368	2.680074	0.000000
C	-0.253166	-1.884247	0.000000
H	2.452755	-1.818086	0.000000
H	3.872541	0.215598	0.000000
C	-1.632223	-1.962621	0.000000
C	-2.417275	-0.826248	0.000000
H	-2.128905	-2.931421	0.000000
H	-3.501166	-0.861342	0.000000
S	-1.770130	0.806635	0.000000

A'	1193.7441	0.0288
A'	1286.1836	4.4789
A'	1317.4673	12.1315
A'	1342.7308	20.0715
A'	1407.1867	12.2603
A'	1442.3609	4.3143
A'	1475.7006	4.4108
A'	1498.7064	13.4615
A'	1596.5283	4.5729
A'	1623.9729	0.1094
A'	3171.6585	6.8715
A'	3184.9411	1.1703
A'	3193.3766	5.1698
A'	3206.1362	17.8965
A'	3215.7947	21.1249
A'	3226.9383	1.5666

2-(*Z*-vinylacetylene)-3,5-cyclohexadien-1-thione (^{1}18)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.116277	-744.642727	-744.526451	3.3318

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.516718	-744.560979

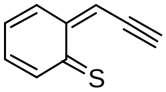
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	40.0482	1.4297
A'	145.5147	1.8125
A"	147.6295	0.1514
A'	245.9069	1.0271
A"	250.7839	0.0066
A'	358.6095	7.3816
A'	390.2046	1.8196
A"	432.3614	5.2198
A"	451.4324	2.1853
A'	506.6131	3.2589
A"	519.1778	0.1241
A'	582.4689	49.8397
A'	633.4217	12.3960
A"	652.1420	36.6955
A'	684.1074	4.2891
A"	746.4492	0.6793
A"	758.0657	36.8445
A"	860.6247	6.4274
A'	860.6864	0.3453
A"	903.2782	13.6369
A"	977.4781	0.8875
A"	1010.0235	0.4446
A'	1020.4621	9.2396
A'	1086.0922	5.0684
A'	1103.9364	36.0784
A'	1171.7510	23.5967
A'	1191.7891	2.5346

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-1.868831	-0.872157	0.000000
C	-0.441357	-0.651015	0.000000
C	0.000000	0.762779	0.000000
C	-1.011992	1.803974	0.000000
C	-2.338991	1.518732	0.000000
C	-2.771304	0.150017	0.000000
H	-2.198988	-1.905495	0.000000
H	-0.671599	2.836403	0.000000
H	-3.076068	2.316181	0.000000
H	-3.836051	-0.068904	0.000000
S	0.593743	-1.967997	0.000000
C	1.311724	1.194755	0.000000
C	2.512970	0.473572	0.000000
C	3.647282	0.034732	0.000000
H	4.593029	-0.458712	0.000000
H	1.452781	2.276144	0.000000

A'	1242.7449	18.3261
A'	1274.0263	5.4517
A'	1413.3198	26.9431
A'	1426.1682	8.7951
A'	1489.7340	17.2613
A'	1560.1981	72.0064
A'	1591.7443	33.3355
A'	1682.5892	37.8340
A'	2177.6064	51.3954
A'	3146.5633	2.2929
A'	3183.8444	1.8319
A'	3192.1880	15.5019
A'	3212.3749	21.3995
A'	3224.6573	9.9385
A'	3490.6737	66.6903

2-(*Z*-vinylacetylene)-3,5-cyclohexadien-1-thione (^{3}18)



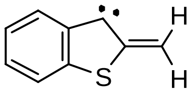
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.113858	-744.620978	-744.507120	1.1453
ΔH$_{(298)}$	**ΔG$_{(298)}$**	(Energies in Hartrees/particle)	
-744.497001	-744.54282		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	42.9981	0.7055
A'	154.4396	1.0544
A"	159.8980	0.2258
A'	195.7950	4.8527
A"	238.9078	1.8442
A"	337.0197	49.7256
A'	339.9821	0.9091
A'	383.0244	6.3227
A"	437.8274	10.8217
A"	452.5628	2.5152
A'	486.7015	0.6375
A"	524.0198	0.4662
A'	618.4827	20.8503
A'	645.8266	31.7665
A"	683.7628	3.5619
A'	687.5546	3.4357
A"	726.4202	10.8971
A"	772.9589	47.1394
A'	854.3796	2.0064
A"	860.9686	1.0457
A"	937.4565	1.8964
A"	972.9747	0.0917
A'	1050.7407	8.1640
A'	1071.4304	14.4420
A'	1091.8467	1.3134
A'	1156.8677	0.3453
A'	1194.1459	2.9517

Atom	Coordinates (Angstroms) X	Y	Z
C	0.866739	1.804652	0.000000
C	0.000000	0.699173	0.000000
C	0.550555	-0.623508	0.000000
C	1.964953	-0.759597	0.000000
C	2.800835	0.340825	0.000000
C	2.247532	1.631328	0.000000
H	0.449650	2.807436	0.000000
H	2.382495	-1.763403	0.000000
H	3.878613	0.207232	0.000000
H	2.894824	2.503844	0.000000
S	-1.732557	0.982037	0.000000
C	-0.266025	-1.789424	0.000000
C	-1.653026	-1.800574	0.000000
C	-2.874343	-1.952434	0.000000
H	-3.939076	-2.013290	0.000000
H	0.231076	-2.757052	0.000000

A'	1230.4322	8.3718
A'	1275.4645	12.9997
A'	1342.4958	0.4734
A'	1420.2628	4.1715
A'	1466.0099	0.6595
A'	1487.5126	28.4805
A'	1579.7449	6.0934
A'	1619.9462	15.5132
A'	2019.8960	29.6195
A'	3177.5160	0.5593
A'	3184.9617	4.7007
A'	3191.9716	3.5878
A'	3204.1745	18.6738
A'	3215.0261	25.3637
A'	3483.3221	87.7139

^{1}19



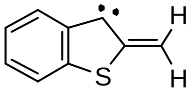
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.117327	-744.641695	-744.524368	1.4657
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-744.515582	-744.55719		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	87.8805	7.5857
A"	173.4098	2.1846
A"	237.1727	1.8780
A'	267.3758	6.3595
A'	400.8566	0.1415
A"	439.7708	0.7364
A'	476.6822	1.3852
A"	489.7319	0.3754
A'	490.1483	8.4633
A'	517.7242	24.0669
A"	542.7210	4.8717
A'	646.7933	3.2701
A"	702.4104	0.1981
A'	705.6921	5.2885
A"	737.8939	7.1843
A"	785.6521	46.3940
A'	867.8988	13.1984
A"	879.4360	0.1064
A'	970.5438	17.5461
A"	978.7508	1.6758
A"	1002.3574	28.9589
A"	1004.4724	0.1898
A'	1044.9391	2.7998
A'	1063.7334	10.7002
A'	1136.1782	3.5905
A'	1171.6510	26.2529
A'	1199.8719	6.6774

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	2.074803	-0.621187	0.000000
C	0.657249	-0.590955	0.000000
C	0.000000	0.691805	0.000000
C	0.740576	1.877948	0.000000
C	2.130801	1.792524	0.000000
C	2.804094	0.554075	0.000000
H	2.559994	-1.592568	0.000000
H	0.251819	2.847252	0.000000
H	2.712027	2.711546	0.000000
H	3.889705	0.532662	0.000000
C	-0.169740	-1.750041	0.000000
C	-1.536447	-1.284008	0.000000
C	-2.614351	-2.092702	0.000000
H	-2.454096	-3.166107	0.000000
S	-1.740228	0.557996	0.000000
H	-3.637712	-1.725464	0.000000

A'	1266.9904	11.6634
A'	1330.5347	104.5285
A'	1338.0366	38.7732
A'	1437.2567	53.7938
A'	1455.5938	31.4456
A'	1492.1509	53.0252
A'	1583.9808	7.0492
A'	1640.3627	112.8732
A'	1665.2468	67.6588
A'	3172.8767	4.5033
A'	3187.8826	4.3611
A'	3205.1640	6.4365
A'	3212.9428	14.2761
A'	3222.2497	17.8436
A'	3270.1972	1.5038

^{3}19



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.116379	-744.639110	-744.522731	0.7348

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.513943	-744.556352

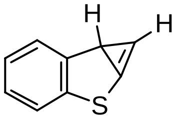
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	111.3301	1.4853
A"	188.1357	0.4415
A'	252.6918	1.5230
A"	284.0751	0.0249
A'	386.6190	0.5789
A"	430.5963	2.4755
A'	472.4252	0.7508
A'	481.7471	1.0323
A"	495.8139	1.7894
A"	531.8898	0.0107
A"	578.5346	1.1452
A'	610.1385	5.2228
A'	641.6297	2.2256
A'	708.5891	2.7019
A"	720.9886	4.8344
A"	747.6930	26.7579
A"	759.5236	65.1775
A"	860.7300	0.1792
A'	872.8829	1.9137
A"	932.8821	1.2480
A"	976.4408	0.0400
A'	1022.0126	1.1476
A'	1046.7179	7.9425
A'	1072.3220	9.9853
A'	1149.0358	0.9395
A'	1191.2020	0.3702
A'	1201.9448	8.6428

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	2.149661	-0.491326	0.000000
C	0.739929	-0.540988	0.000000
C	0.000000	0.682241	0.000000
C	0.649678	1.913785	0.000000
C	2.045752	1.935523	0.000000
C	2.787431	0.741194	0.000000
H	2.719132	-1.415810	0.000000
H	0.082926	2.840644	0.000000
H	2.563461	2.890469	0.000000
H	3.872792	0.784885	0.000000
C	-0.148833	-1.634735	0.000000
C	-1.520111	-1.396924	0.000000
C	-2.583395	-2.268009	0.000000
H	-2.405026	-3.337460	0.000000
S	-1.746506	0.407076	0.000000
H	-3.609867	-1.920524	0.000000

A'	1271.2201	5.1059
A'	1325.3328	0.4908
A'	1369.1579	8.4512
A'	1406.1505	2.5055
A'	1462.3543	9.0201
A'	1491.6606	6.3378
A'	1525.2434	4.3602
A'	1598.2513	2.0738
A'	1624.0964	5.7415
A'	3189.1334	1.3342
A'	3190.1221	0.1433
A'	3198.6929	4.7787
A'	3208.6432	20.1164
A'	3217.1474	22.3933
A'	3282.5652	2.1568

4-Thia-2,3-benzobicyclo[3.1.0]hexa-2,5-diene (^{1}20)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_1

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.118005	-744.637742	-744.519737	1.2817

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.51133	-744.551944

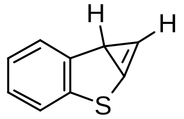
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	143.1146	1.0853
A	174.7272	0.3809
A	279.8328	4.6522
A	308.4131	2.8819
A	368.5169	1.0691
A	444.1439	3.2403
A	470.7255	1.5210
A	504.5921	2.9068
A	565.8043	6.9579
A	606.5683	7.4254
A	629.4813	31.0304
A	671.1287	6.2566
A	700.2506	16.9420
A	735.1729	7.4594
A	764.6670	42.2639
A	820.2640	25.3600
A	850.8804	4.3255
A	878.9980	1.0475
A	943.3079	1.1331
A	982.3611	0.0079
A	1004.3861	0.7379
A	1030.6039	25.4942
A	1046.1196	21.2938
A	1061.5039	0.9653
A	1131.9488	2.5890
A	1146.5945	0.9024

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	1.391340	-1.346859	0.120209
C	0.203628	-0.633792	-0.030700
C	0.192847	0.777358	-0.135335
C	1.412273	1.456522	-0.105803
C	2.608564	0.752469	0.050211
C	2.595839	-0.640130	0.164000
H	1.385858	-2.429799	0.204961
H	1.423287	2.539618	-0.200342
H	3.552118	1.290029	0.083518
H	3.528680	-1.183880	0.286151
C	-1.179673	1.327244	-0.412692
H	-1.297384	1.930442	-1.316790
C	-2.284806	1.270913	0.628193
H	-2.691888	1.716249	1.525362
C	-2.102972	0.186896	-0.075746
S	-1.432682	-1.422900	-0.112305

A	1192.8282	1.2042
A	1213.0999	3.1139
A	1293.5378	0.6877
A	1321.5325	1.9587
A	1358.6695	4.8334
A	1485.0685	20.1247
A	1496.8163	7.0247
A	1620.8792	0.4021
A	1644.0008	7.7415
A	1748.5521	40.3459
A	3094.9745	45.9038
A	3183.9493	1.3713
A	3191.9977	5.9699
A	3202.7606	22.4213
A	3212.4259	24.2813
A	3273.1026	1.0868

4-Thia-2,3-benzobicyclo[3.1.0]hexa-2,5-diene (^{3}20)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_1

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.116235	-744.578524	-744.462289	2.5635

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.453858	-744.495509

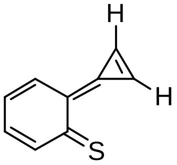
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	144.5995	0.1283
A	170.6628	0.4510
A	286.1028	3.0284
A	333.9534	0.9721
A	346.1786	7.2036
A	440.3838	4.1711
A	469.8349	2.5787
A	487.6406	9.3579
A	540.8328	14.9872
A	611.0393	3.0169
A	672.7008	14.3277
A	708.1418	4.9858
A	723.9861	2.7850
A	750.8528	10.1549
A	759.8591	38.9312
A	802.6255	27.2476
A	846.1597	1.7227
A	878.0801	0.8245
A	933.4600	18.5126
A	943.0204	4.4705
A	963.1721	5.0759
A	984.0183	0.0990
A	1015.4015	9.0366
A	1052.1848	6.2580
A	1070.3812	2.4878
A	1147.9669	2.6717

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	1.392161	-1.365953	0.113893
C	0.205804	-0.647270	-0.028422
C	0.199239	0.760269	-0.124870
C	1.416001	1.444794	-0.113687
C	2.609794	0.732793	0.024135
C	2.597739	-0.661253	0.139636
H	1.381990	-2.449432	0.187582
H	1.429795	2.528159	-0.200186
H	3.555272	1.267384	0.045053
H	3.533051	-1.204391	0.241824
C	-1.164645	1.319119	-0.294699
H	-1.272564	2.218965	-0.907778
C	-2.275549	1.163920	0.736429
H	-2.184886	1.005308	1.808421
C	-2.209854	0.239338	-0.399451
S	-1.441675	-1.330033	-0.093293

A	1192.2210	1.6751
A	1201.5226	4.5240
A	1220.2216	5.2419
A	1285.0270	3.8512
A	1334.1599	1.0318
A	1365.6648	1.0181
A	1487.9686	9.0359
A	1499.8753	5.4446
A	1621.4716	3.4200
A	1639.6413	0.8455
A	3094.0612	1.9750
A	3187.7073	0.3351
A	3190.6544	20.1016
A	3196.0219	6.6647
A	3206.3704	19.6597
A	3215.4389	20.6504

2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (^{1}21)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.116895	-744.634156	-744.517262	6.5030

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-744.50793	-744.55113

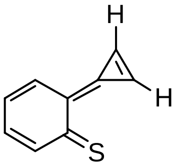
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	76.6517	4.8446
A'	142.9719	4.0162
A"	155.9928	0.4977
A"	185.6751	0.4964
A'	293.3620	3.1914
A'	374.4682	8.3949
A"	378.9986	3.4544
A"	489.6738	2.4263
A'	491.0651	1.4053
A"	527.8771	3.2709
A'	539.1002	6.0968
A'	670.6804	13.3023
A"	730.6395	0.7245
A"	758.3001	76.7615
A'	774.5277	7.6867
A"	784.8656	8.5099
A"	866.9821	1.9364
A'	932.1935	3.7158
A"	932.9250	0.0414
A"	956.2378	0.0000
A'	969.5314	0.6844
A"	1006.8614	0.4873
A'	1028.6199	20.5121
A'	1096.5387	60.8871
A'	1133.7772	109.9011

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	2.671660	-0.239674	0.000000
C	1.687532	-1.193539	0.000000
C	0.288734	-0.860051	0.000000
C	0.000000	0.574978	0.000000
C	1.060586	1.547230	0.000000
C	2.367197	1.156836	0.000000
H	3.714046	-0.550505	0.000000
H	1.941364	-2.248561	0.000000
H	0.793624	2.601640	0.000000
H	3.168944	1.888881	0.000000
C	-1.304383	1.014217	0.000000
C	-2.302797	2.012818	0.000000
H	-2.572324	3.060472	0.000000
C	-2.685681	0.733755	0.000000
H	-3.458041	-0.018910	0.000000
S	-0.892793	-2.075777	0.000000

A'	1147.5323	11.9136
A'	1191.4071	4.9213
A'	1202.4360	5.9938
A'	1256.6913	19.5775
A'	1345.5775	14.4529
A'	1440.4760	60.2940
A'	1491.2801	28.5246
A'	1510.7626	378.8082
A'	1561.6726	38.6365
A'	1668.7870	66.2870
A'	1783.9518	423.9975
A'	3177.3670	3.2948
A'	3183.1196	20.0031
A'	3210.8140	23.3368
A'	3220.1371	11.5801
A'	3278.4430	5.9825
A'	3341.8497	18.7219

2-(2-cyclopropen-1-ylidene)-3,5-cyclohexadien-1-thione (^{3}21)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.113670	-744.570950	-744.457281	2.8929
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-744.44738	-744.492562		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	93.1128	2.5876
A'	118.9782	1.0256
A"	159.4635	3.5746
A"	186.2878	2.2869
A'	241.8401	0.2661
A"	264.7422	1.2010
A'	356.6466	0.3417
A"	441.5033	1.0614
A'	458.6316	3.6500
A'	483.0283	14.8597
A"	508.3032	0.2412
A"	610.5533	43.4047
A'	665.2258	2.9954
A"	687.6675	3.5754
A"	724.3586	50.0386
A'	746.0330	20.7933
A'	759.7084	26.0056
A"	816.5353	1.3732
A"	875.9145	0.4699
A"	903.4646	2.3753
A'	945.9536	1.0244
A"	948.5625	0.2448
A'	1037.9834	41.1213
A'	1051.2313	2.4797
A'	1055.5804	13.1871

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	2.716409	-0.276823	0.000000
C	1.685262	-1.226847	0.000000
C	0.350816	-0.833590	0.000000
C	0.000000	0.568811	0.000000
C	1.085291	1.508581	0.000000
C	2.401645	1.093046	0.000000
H	3.750568	-0.607351	0.000000
H	1.932201	-2.285413	0.000000
H	0.841238	2.567659	0.000000
H	3.198157	1.832578	0.000000
C	-1.313422	1.000474	0.000000
C	-2.306850	2.053512	0.000000
H	-2.549180	3.105861	0.000000
C	-2.735671	0.802051	0.000000
H	-3.574927	0.121054	0.000000
S	-0.931184	-2.054355	0.000000

A'	1114.2898	36.8504
A'	1157.6286	2.8956
A'	1183.7406	1.4741
A'	1268.4865	7.5514
A'	1319.2475	12.2510
A'	1439.4274	24.7128
A'	1455.4772	5.4827
A'	1543.2896	12.6721
A'	1563.1057	19.5400
A'	1598.3750	13.4867
A'	1758.2364	48.8030
A'	3178.7056	6.3997
A'	3183.7749	3.4882
A'	3196.2649	25.6162
A'	3211.4656	24.3502
A'	3267.5252	12.2883
A'	3314.8730	4.0828

Chapter 3 – Photochemistry and Spectroscopy of 1-(3-benzothienyl) diazoethane

Introduction and Background

Previous work in the McMahon group reported the spectroscopic detection and characterization of triplet 3-thienyl carbene, 3-thienyl ethylidene, and 2-benzothienyl ethylidene.[2,1] Our attempts at generating 2-benzothienyl carbene and 3-benzothienyl carbene have been unsuccessful. (Chapters 1 and 2) Herein we report the spectroscopic detection and characterization of 1-(3-benzothienyl) ethylidene by UV-vis and EPR spectroscopy. Computational studies on the $C_{10}H_8S$ potential energy surface were carried out to help elucidate the photochemistry and reactivity of these compounds.

Results and Discussion

Computational Study

The optimized geometries, harmonic vibrational frequencies, and infrared intensities of several $C_{10}H_8S$ isomers were calculated at the B3LYP/6-31G* level in order to build a library of IR spectra to compare with experimental data. (**Figure 3.1**) As with previously studied thienyl and benzothienyl carbenes, 1-(3-benzothienyl) ethylidene is calculated to be triplet ground state with a small (< 5 kcal/mol) singlet-triplet gap. There is a small energy difference (1.4 kcal/mol) between the two rotamers of 1-(3-benzothienyl) ethylidene. Unsurprisingly, the lowest energy $C_{10}H_8S$ isomer is s-*Z*-3-vinyl benzothiophene (**2-s-*Z***), which lies < 1 kcal/mol below the s-*E*-3-vinyl benzothiophene (**2-s-*E***), both of which represents the product of a [1,2] hydrogen atom migration to the carbene center from the adjacent methyl group.

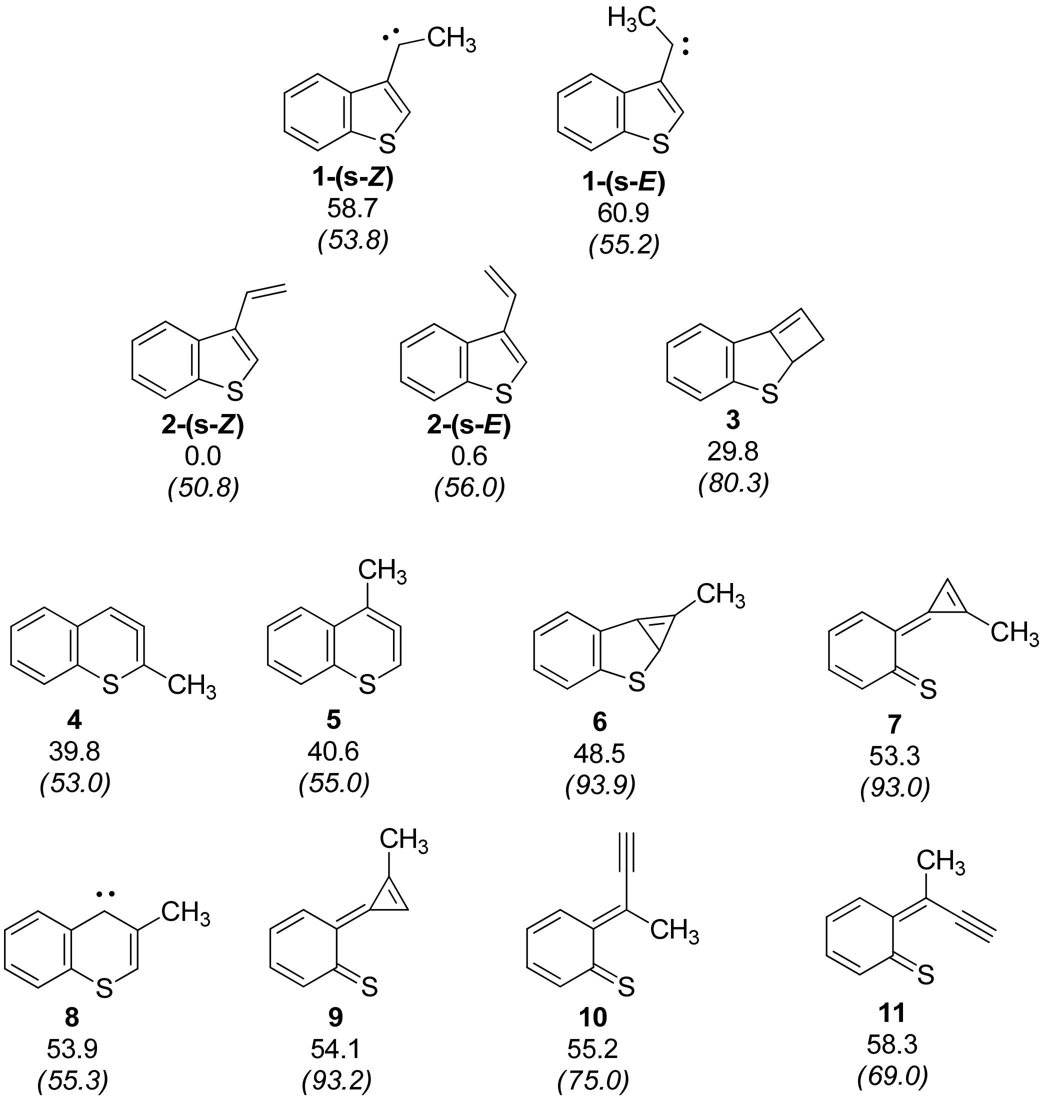
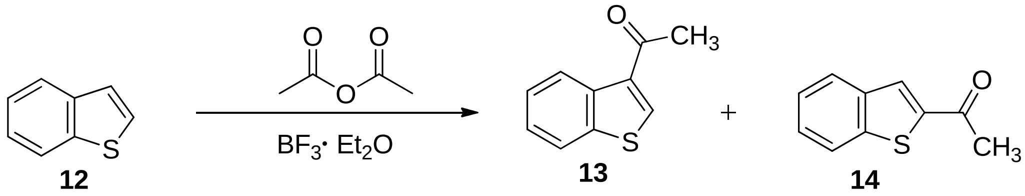


Figure 3.1. B3LYP/6-31G* calculated energies for selected $C_{10}H_8S$ isomers. Energies are in kcal/mol and include ZPVE. Energies are for singlet and (triplet) species.

Synthesis of 1-(3-Benzothienyl) Diazoethane

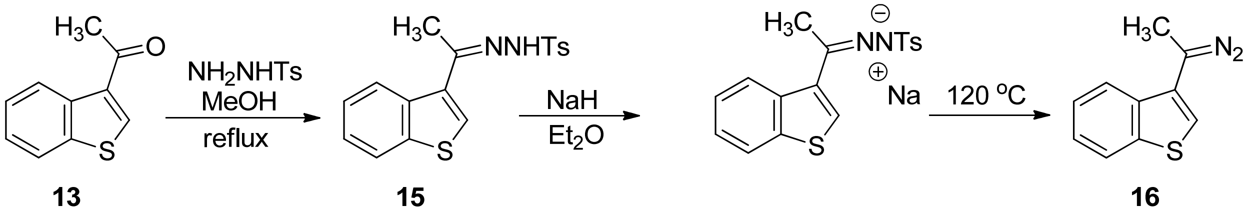
After a few attempts following different literature procedures,[3,4] the procedure put forth by Farrar and Levine[5] was successful in obtaining 3-acetylbenzothiophene, though in low yield (**Scheme 3.1**). For this reaction, a solution of benzothiophene in acetic anhydride was heated and boron trifluoride etherate was added. The mixture was stirred for one hour, after which it was quenched with water and extracted to give a mixture of 3- and 2-acetylbenzothiophene (3:1, 3-acetyl:2-acetyl), which were separated via column chromatography.

Scheme 3.1



With the ketone in hand, 3-acetylbenzothiophene tosylhydrazone was easily prepared, by combining ketone **13** and *p*-toluene sulfonylhydrazide in methanol and heating at reflux overnight. Following isolation, the tosylhydrazone (**15**) was then deprotonated with sodium hydride and the resulting sodium salt was heated under vacuum to generate 1-(3-benzothienyl) diazoethane (**16**).

Scheme 3.2



Photochemistry of Matrix Isolated 1-(3-benzothienyl) diazoethane

Due to the quick decomposition of 1-(3-benzothienyl) diazoethane (**16**) at temperatures above -78 °C, matrix isolation experiments were carried out by direct deposition of the diazo compound from the tosylhydrazone sodium salt onto the cold window. A small amount of the sodium salt was placed in a curved short-path deposition tube attached to the cold head on the matrix isolation cart. The deposition tube was quickly heated to 115 - 120 °C and held for 45-60 minutes, during which time 1-(3-benzothienyl) diazoethane (**1**) was generated and co-deposited with Ar on a CsI window held at 25 K, then cooled to 10 K. This technique gave a sufficient amount of diazo compound on the window.

Initial broadband irradiation was carried out at $\lambda > 571$ nm for 24 h. At this wavelength, however, little change in the infrared spectrum was seen, just a small decrease in the intensity of the diazo stretching vibration (νC=N=N). Decreasing the wavelength of irradiation to $\lambda > 534$ nm gave a very different spectrum after 25 hours of irradiation. (**Figure 3.2**) Diazo compound (**16**) clearly decreases, and a mixture of s-*E* and s-*Z*-3-vinylbenzothiophene (**2**) appears (new peaks at 1636, 1433, 1423, 1332, 1256, 1096, 1053, 905, 857, 788, 765, 734, 717, 536 cm^{-1}) and no peaks for the corresponding carbenes (**Figure S3.1**). Shorter wavelength broadband irradiation ($\lambda > 497$ nm, $\lambda > 472$ nm) of **16** led to a small increase in the peaks associated with 3-vinylbenzothiophene (**2**).

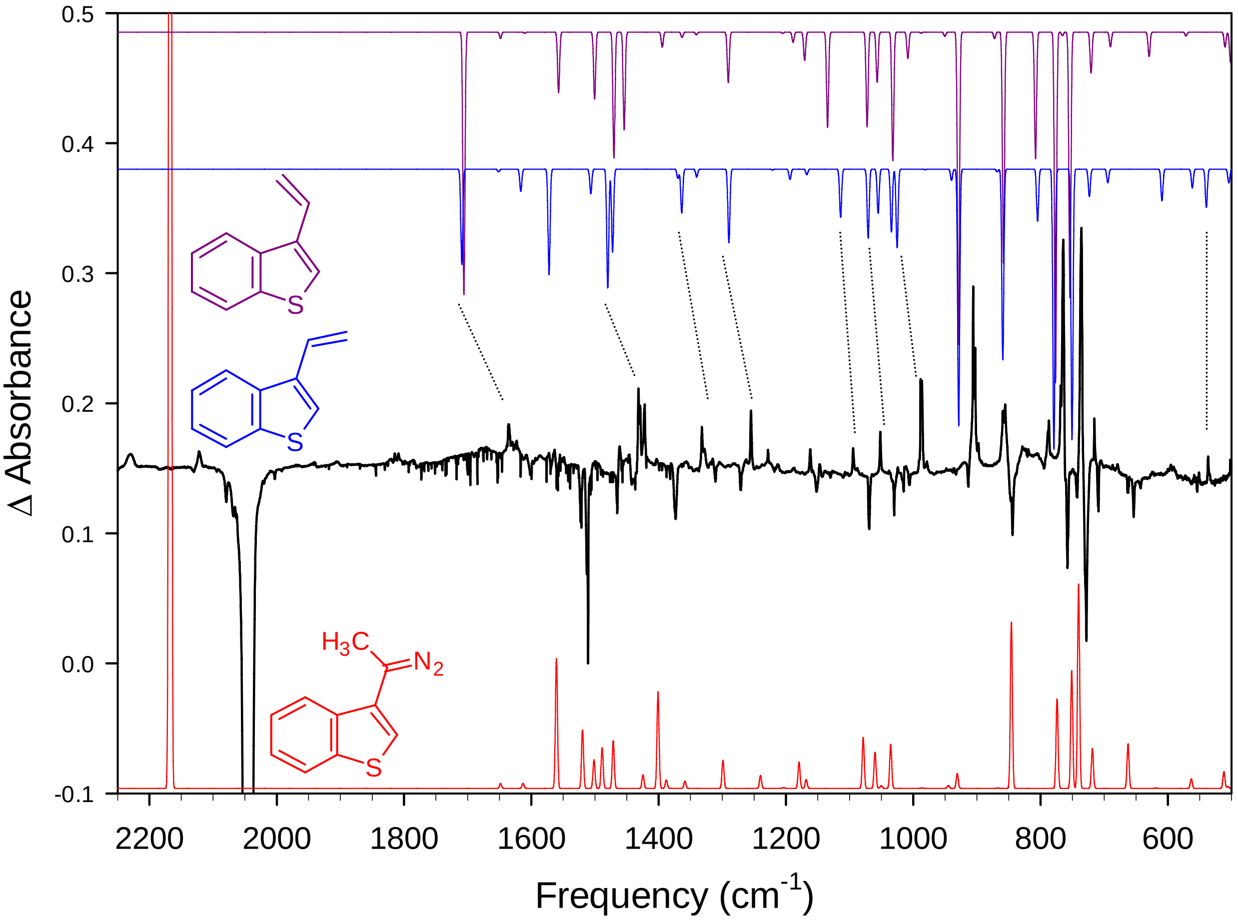
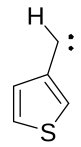
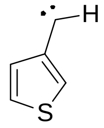


Figure 3.2. IR subtraction spectrum (Ar, 10 K) (black trace, middle) showing the disappearance of 1-(3-benzothienyl) diazoethane (**16**) and the appearance of 3-vinylbenzothiophene (**2**) after irradiation at λ > 534 nm 25 h. Calculated (B3LYP/6-31G*) spectra of s-*E*-3-vinylbenzothiophene (purple, *top*), s-*Z*-3-vinylbenzothiophene (blue, *top*) and 1-(3-benzothienyl) diazoethane (**16**) (red, *bottom*). Only one rotomer of the diazo compound is shown for clarity, but both are present in the matrix. Calculated spectra are unscaled.

EPR spectroscopy was carried out to determine if a triplet species was being formed in the process of going from 1-(3-benzothienyl) diazoethane (**16**) to 3-vinylbenzothiophene (**2**). Deposition of the diazo compound onto a copper rod was carried out via direct deposition from the sodium salt of the tosylhydrazone with a constant flow of Ar. Initially, irradiation was carried out at λ > 534 nm for16 h, and the EPR spectrum showed peaks for two different triplet species present in the matrix. Based on comparison to previous work in the McMahon group on both 1-(2-benzothienyl) ethylidene, 1-(3-thienyl) ethylidene, and 3-thienyl carbene, these two sets of signals are assigned to the s-*Z* and s-*E* rotamers of the carbene (**1-s-*Z*** and **1-s-*E***). (**Figure 3.4**)



17-s-*E*



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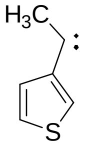

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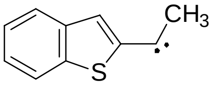
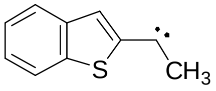
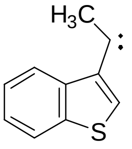


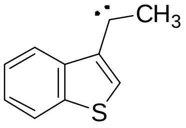
19-s-*E*



19-s-*Z*



1-s-*E*



1-s-*Z*

	17-s-*E*	**17-s-*Z***	**18-s-*E***	**19-s-*E***	**19-s-*Z***	**1-s-*E***	**1-s-*Z***
D/hc (cm^{-1})	0.579	0.5081	0.5028	0.4028	0.3943	0.4039	0.4679
E/hc (cm^{-1})	0.0315	0.0554	0.0541	0.0375	0.0266	0.0372	0.0501

Table 3.1. Experimental *D/hc* and *E/hc* values for the family of thiophene and benzothiophene carbenes.[1]

The s-*E* rotamer is the major species present after irradiation at λ > 534 nm. At λ > 497 nm, the s-*E* rotamer disappears and peaks for the s-*Z* rotamer intensify. The s-*E* rotamer has Z_1 = 782.9 G, X_2 = 4858.6 G, Y_2 = 5866.2 G, and Z_2 = 7752.2 G transitions, and calculated values of |*D/hc*| = 0.4039 $cm^{-1}$and |*E/hc*| = 0.0372 cm^{-1}. The s-*Z* rotamer has Z_1 = 1437.1 G, X_2 = 4417.7

G, Y_2 = 6468.0 G, and Z_2 = 8399.2 G transitions, and calculated values of |D/hc| = 0.4679 cm^{-1} and |*E/hc*| = 0.0501 cm^{-1}. (Microwave frequency of 9.618 GHz)

The large difference in *D* values (ΔD = 0.06 cm^{-1}) for the two rotamers of the carbene is not surprising, as this has been seen with all 3-thienyl carbenes previously studied.[2] Natural bond orbital (NBO) calculations were carried out on triplet 1-(3-benzothienyl) ethylidene (**1**) to determine the spin densities on all heavy atoms. (**Figure 3.3**) If the two carbon atoms beta to the carbene center have very different spin densities, the two rotamers of the carbene are expected to have a large difference in *D* values. As with 3-thienyl carbene, there is a much larger spin density on the β-carbon adjacent to the sulfur atom than the β-bridgehead carbon for both rotamers. The carbene rotamer in which the electron density in the carbene sp orbital is pointed towards the β-carbon with the higher spin density has been shown to have the smaller *D* value.[6] Thus the carbene with a calculated *D* value of 0.4271 is assigned to the s-*E* rotamer (**1-s-*E***).

1-s-*E*
D/hc: 0.4039 cm^{-1}
E/hc: 0.0372 cm^{-1}

1-s-*Z*
D/hc: 0.4679 cm^{-1}
E/hc: 0.0501 cm^{-1}

Figure 3.3. NBO calculated (B3LYP/6-31G*) spin densities for the β-carbons for both rotamers of triplet 1-(3-benzothienyl) ethylidene.

It was noted in both the 3-thienyl carbene and 1-(3-thienyl) ethylidene that NBO calculations revealed an interaction of the electron density in the sp orbital of the carbene carbon with the adjacent C-S antibonding orbital for the s-*Z* rotamer, that was significantly reduced in the s-*E* rotamer. [2,1] For s-*Z*-3-thienyl carbene, the energy of this interaction is 0.37 kcal/mol, and for s-*Z*-1(3-thienyl) ethylidene the energy of the interaction is 0.26 kcal/mol.[1] This trend holds true for the 1-(3-benzothienyl) ethylidene rotamers as well, although the energy of this interaction is weaker (s-*Z*, 0.29 kcal/mol, s-*E* below threshold for reporting (threshold = 0.25 kcal/mol)). [2]

Shorter wavelength broadband irradiation (λ > 497 nm, 25 h) resulted in the disappearance of EPR transitions associated with the s-*E* rotamer of carbene **1**. (**Figure 3.5**) Further irradiation at λ > 472 nm for 24 h led to the disappearance of all EPR transitions associated with the s-*Z* rotamer . (**Figure 3.6**)

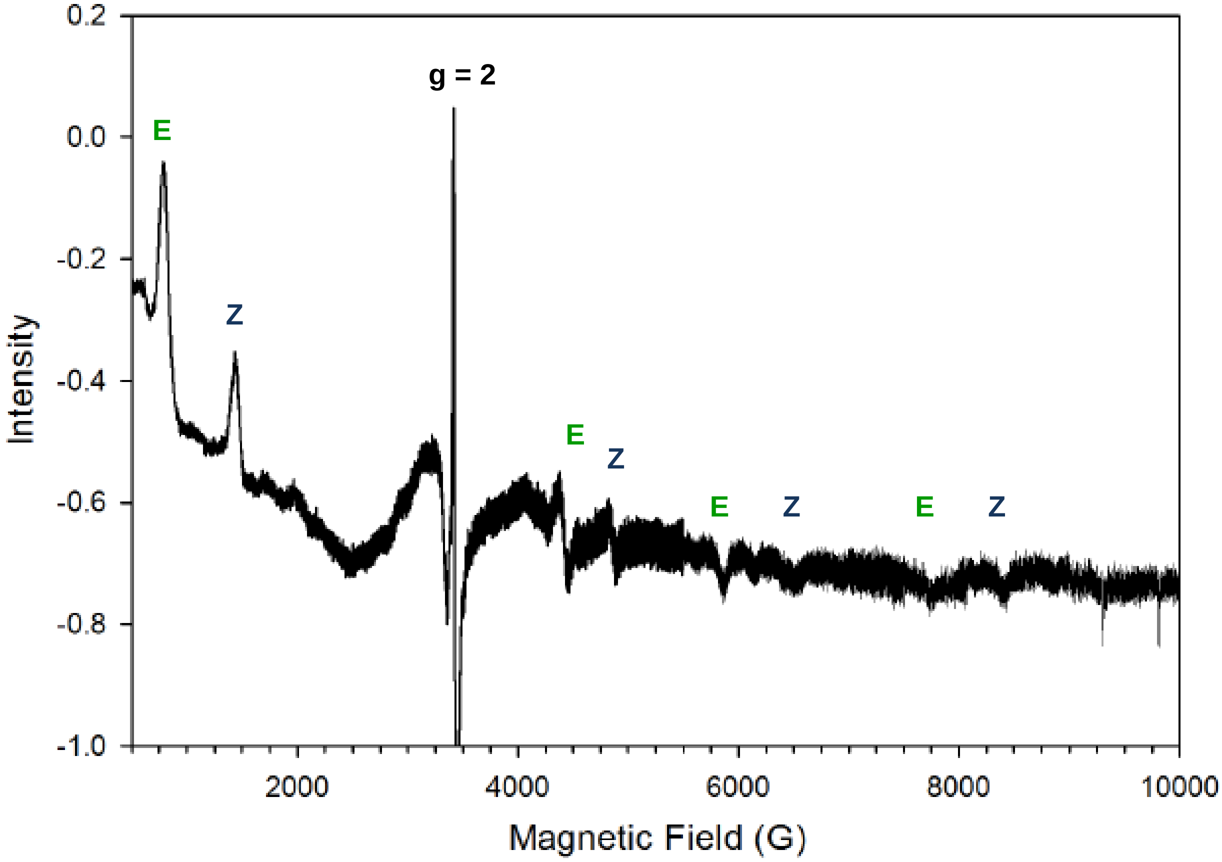


Figure 3.4. EPR spectrum (Ar, 15 K) after irradiation of a matrix containing 1-(3-benzothienyl) diazoethane (**16**) at λ > 534 nm, 16 h. Two sets of peaks are visible, and are assigned to triplet s-*E*-1-(3-benzothienyl) ethylidene (**1-s-*E***) and s-*Z*-1-(3-benzothienyl) ethylidene (**1-s-*Z***).

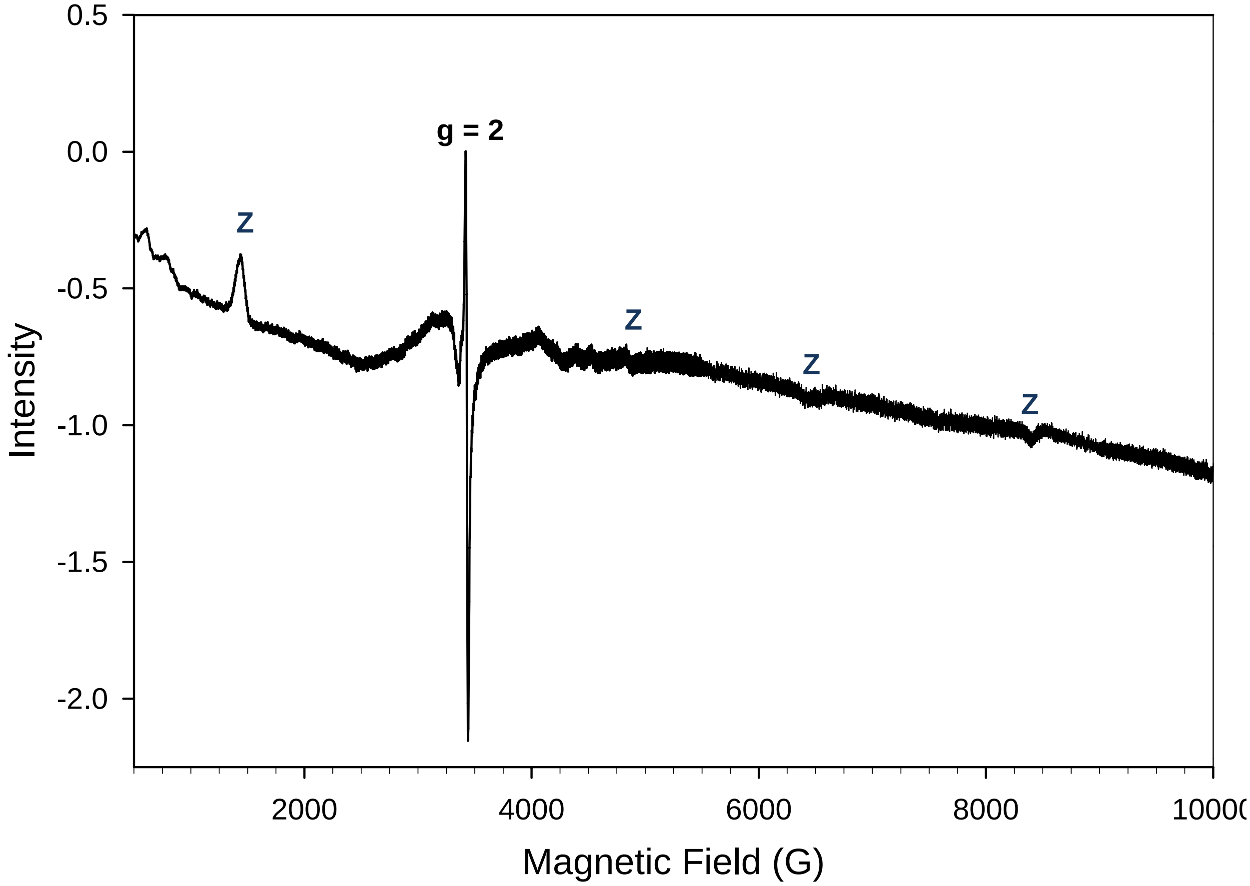


Figure 3.5. EPR spectrum (Ar, 15 K) after irradiation of the spectrum shown in Figure 3.4 at λ > 497 nm, 25 h. All transitions associated with triplet s-*E*-3-benzothienyl ethylidene (**1-s-*E***) have decreased, but peaks for s-*Z*-3-benzothienyl ethylidene (**1-s-*Z***) are still present.

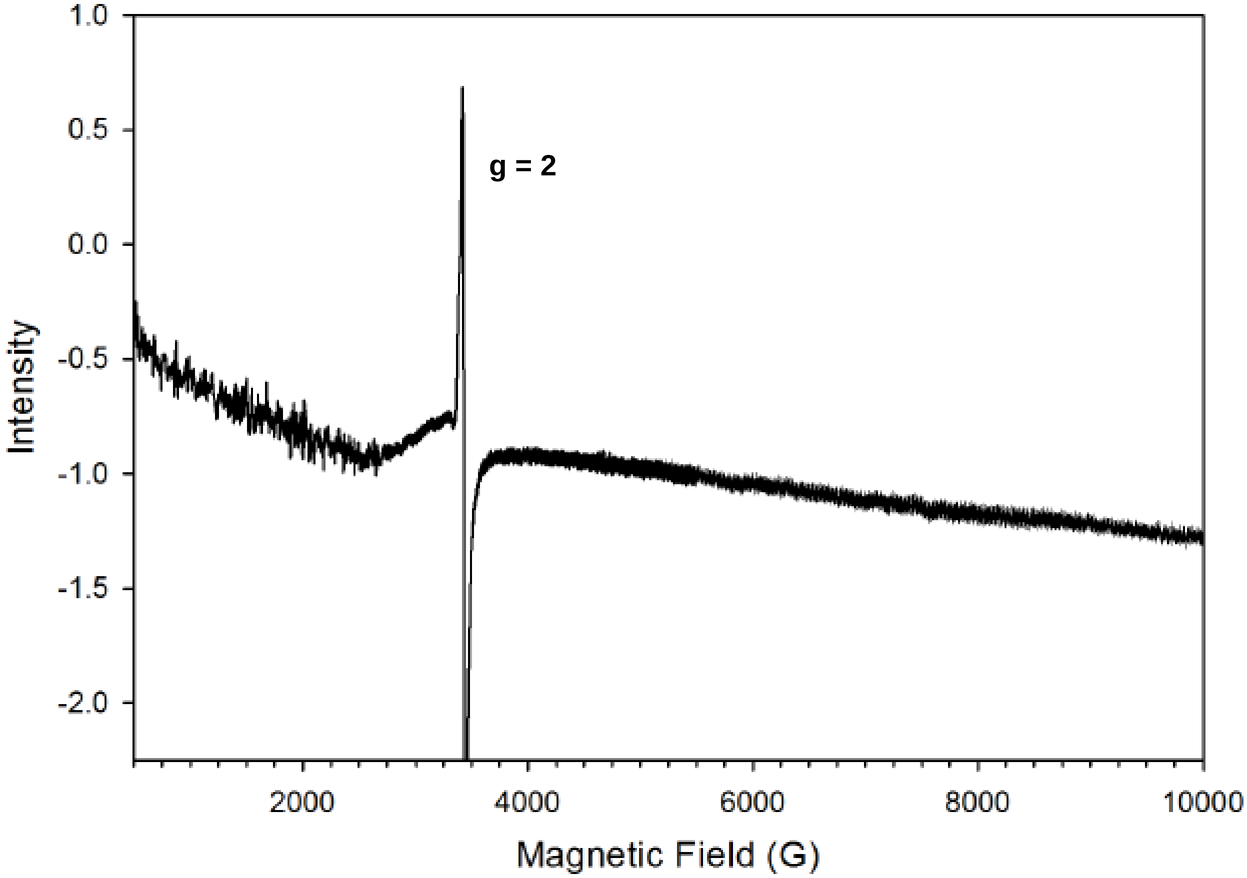


Figure 3.6. EPR spectrum (Ar, 15 K) of the matrix in Figure 3.5 after irradiation at λ > 472 nm. No triplet species are present in the matrix.

To support the assignment of triplet 1-(3-benzothienyl) ethylidene (**1**) electronic absorption spectroscopy was employed. Deposition of diazo compound **16** was carried out directly from the sodium salt onto the sapphire window until a thin film was obtained. After irradiation at $\lambda > 534$ nm for 4 h, small absorptions at $\lambda = 497$ nm and $\lambda = 514$ nm are seen. (**Figure 3.7**) When the irradiated matrix is left to sit in the dark for 40 hours, the absorption at $\lambda = 497$ nm decreases and the peak at $\lambda = 514$ nm grows, as shown in Figure 3.7. While there was no direct irradiation of the matrix during this time, the possibility of ambient light reaching the matrix cannot be fully ruled out. When irradiation is then continued at $\lambda > 534$ nm for an additional 22 h the absorption at $\lambda = 514$ nm disappears and the peak at $\lambda = 497$ nm grows. Irradiation into this absorption ($\lambda > 497$ nm, 25 h) results in the decrease, but not disappearance of this peak. Shorter wavelength irradiation at $\lambda > 472$ nm, 24 h, which was shown to drive away all triplet species (via EPR spectroscopy), results in the disappearance of the peak at $\lambda = 497$ nm.

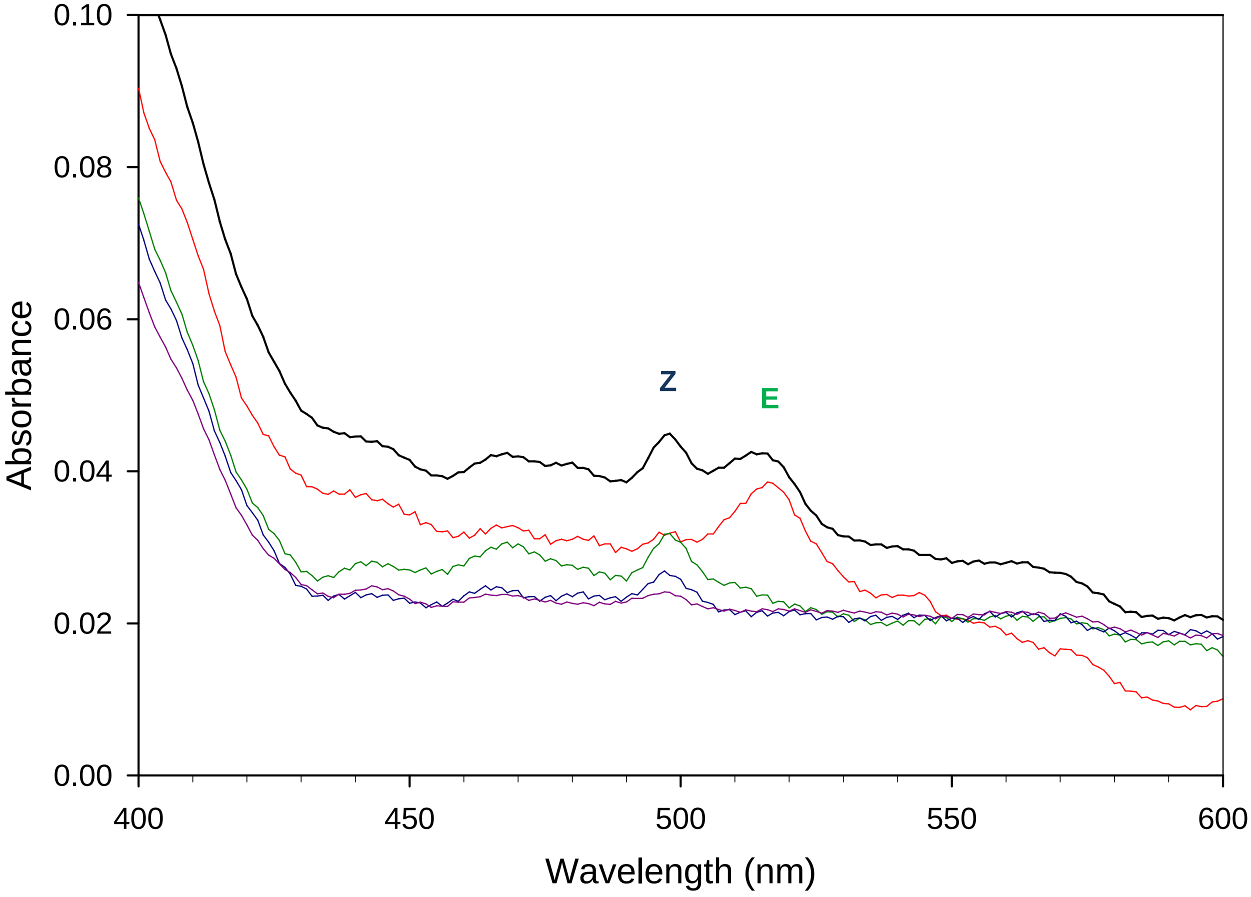
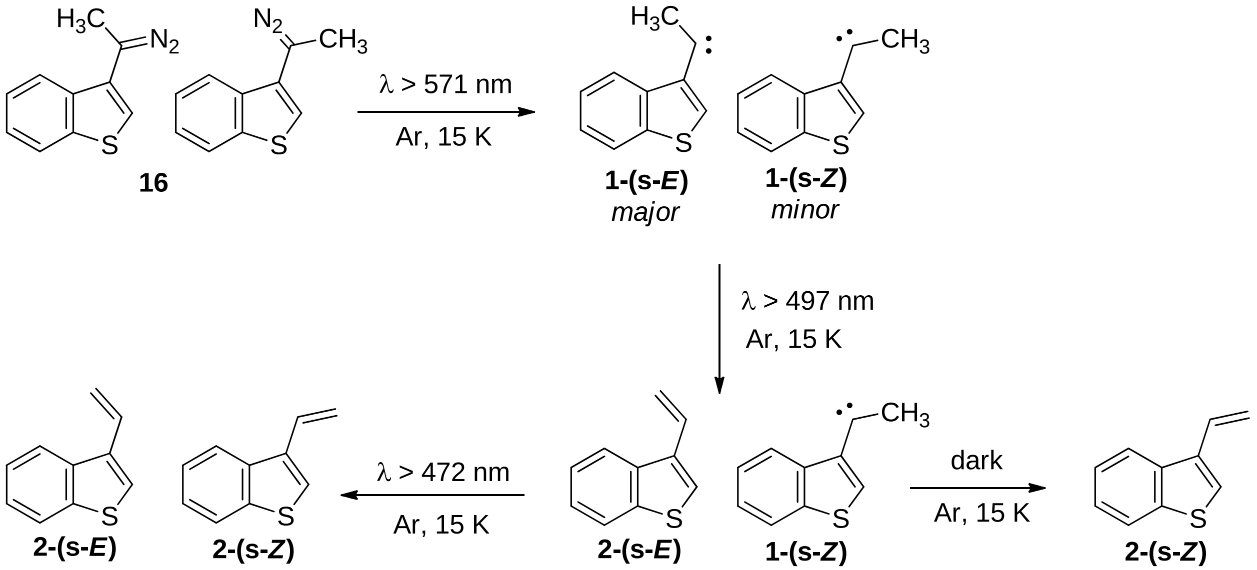


Figure 3.7. UV-vis spectra (Ar, 10 K) showing a matrix containing 1-(3-benzothienyl) diazoethane (**1**) after irradiation at λ > 534 nm, 4 h (black trace), showing absorptions for both s-*E*-1-(3-benzothienyl) ethylidene (**1-s-*E***, λ = 520 nm) and s-Z-1-(3-benzothienyl) ethylidene (**1-s-*Z***, λ = 497 nm). After sitting in the dark for 40 h (red trace) the concentration of **1-s-*Z*** has clearly decreased. Further irradiation at λ > 534 nm, 26 h (green trace) drives away all of **1-s-*E*** and generates more **1-s-*Z***. Shorter wavelength irradiation (λ > 497 nm , 24 h, blue trace) drives away some **1-s-*Z***, and irradiation at λ > 472 nm, 17 h, completely drives away this species.

To further explore the transformations observed in the UV-vis experiments, additional EPR experiments were carried out. Since the λ_{max} for the s-*E* carbene is at 520 nm, initial irradiation was carried out at $\lambda > 571$ nm, 19 h. This generated triplet s-*E*-1-(3-benzothienyl) ethylidene. Continued irradiation ($\lambda > 571$ nm, 41 h) shows a significant increase in the amount of the s-*E* rotamer, as well as a small amount of the s-*Z* rotamer. (**Figure 3.8**) Irradiation at $\lambda > 534$ nm for 23 h showed no change in the spectrum. (**Figure 3.9**)

The matrix containing the carbenes was kept in the dark for 51 h, to see if any thermal rearrangements were occurring; however, no change in the intensity of the signals for either rotamer was observed. It was thought that this could be due to a low concentration of the s-*Z* rotamer in the matrix, making a small change in the intensity of its Z_1 transition difficult to detect. (**Figure 3.10**) Irradiation was continued at $\lambda > 497$ nm (44 h) to drive away the s-*E* rotamer and generate a larger amount of the s-*Z* rotamer. (**Figure 3.11**) With a higher concentration of s-*Z*-1-(3-benzothienyl) ethylidene present, the matrix was again allowed to sit in the dark for 47 h (**Figure 3.12**). In the UV-vis experiment, it seems that the s-*Z* rotamer disappears upon sitting in the dark for 40 h, with an increase in the s-*E* rotamer. In the EPR, a small decrease in the intensities of the Z_1 transition of the s-*Z* rotamer was observed after sitting in the dark for 47 h, thus supporting the thermal rearrangement observed in the UV-vis. (**Figure 3.13**) Continued sitting in the dark (79 h total) does not lead to a further decrease in intensity of the Z_1 transition, possibly due to different matrix sites being governed by different rate constants.[7] Irradiation at $\lambda > 472$ nm, 17 h, led to the disappearance of all triplet species in the matrix, **Figure 3.14**.

Scheme 3.3 Observed photochemistry of **16**



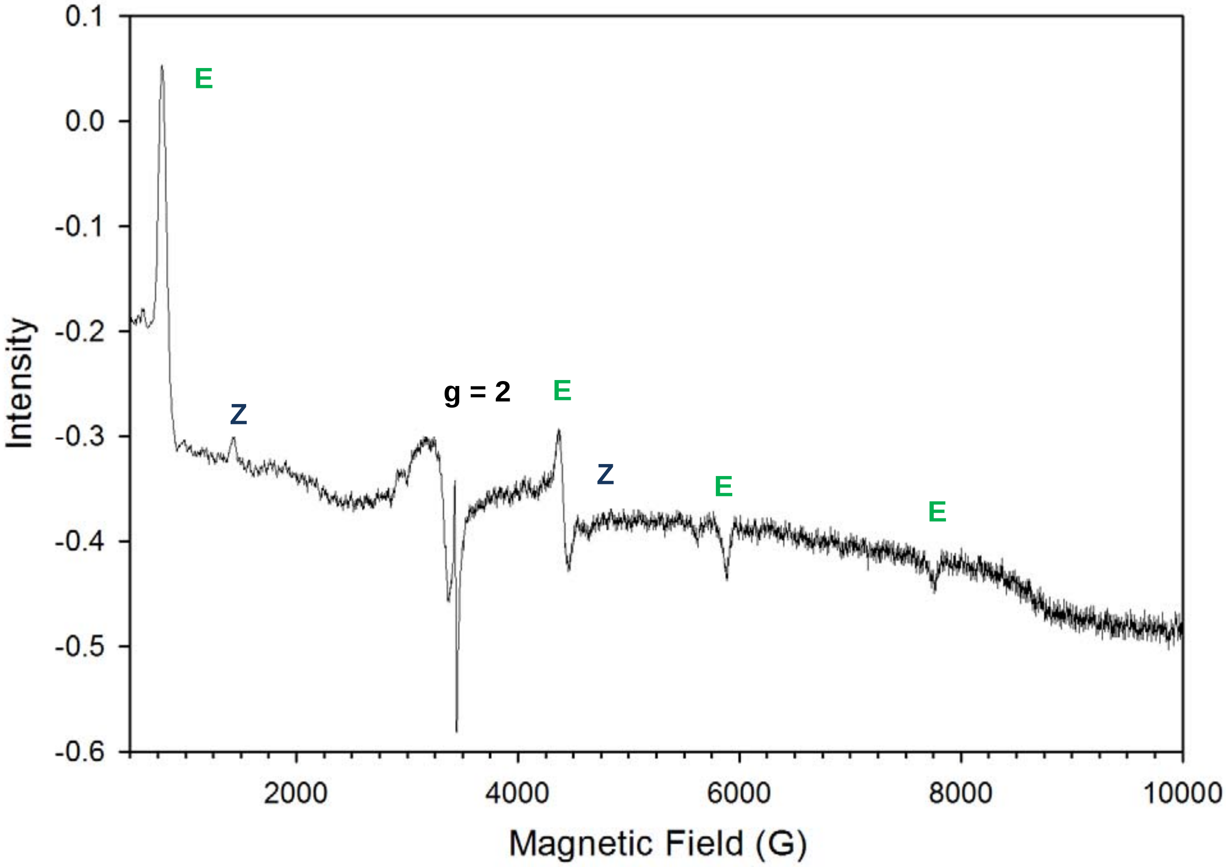


Figure 3.8. EPR spectrum (Ar, 15 K) after irradiation of a matrix containing 1-(3-benzothienyl) diazoethane (**16**) at λ > 571 nm, 41 h. Transitions for both triplet s-*E*-1-(3-benzothienyl) ethylidene (**1-s-*E***) and s-*Z*-1-(3-benzothienyl) ethylidene (**1-s-*Z***) are present.

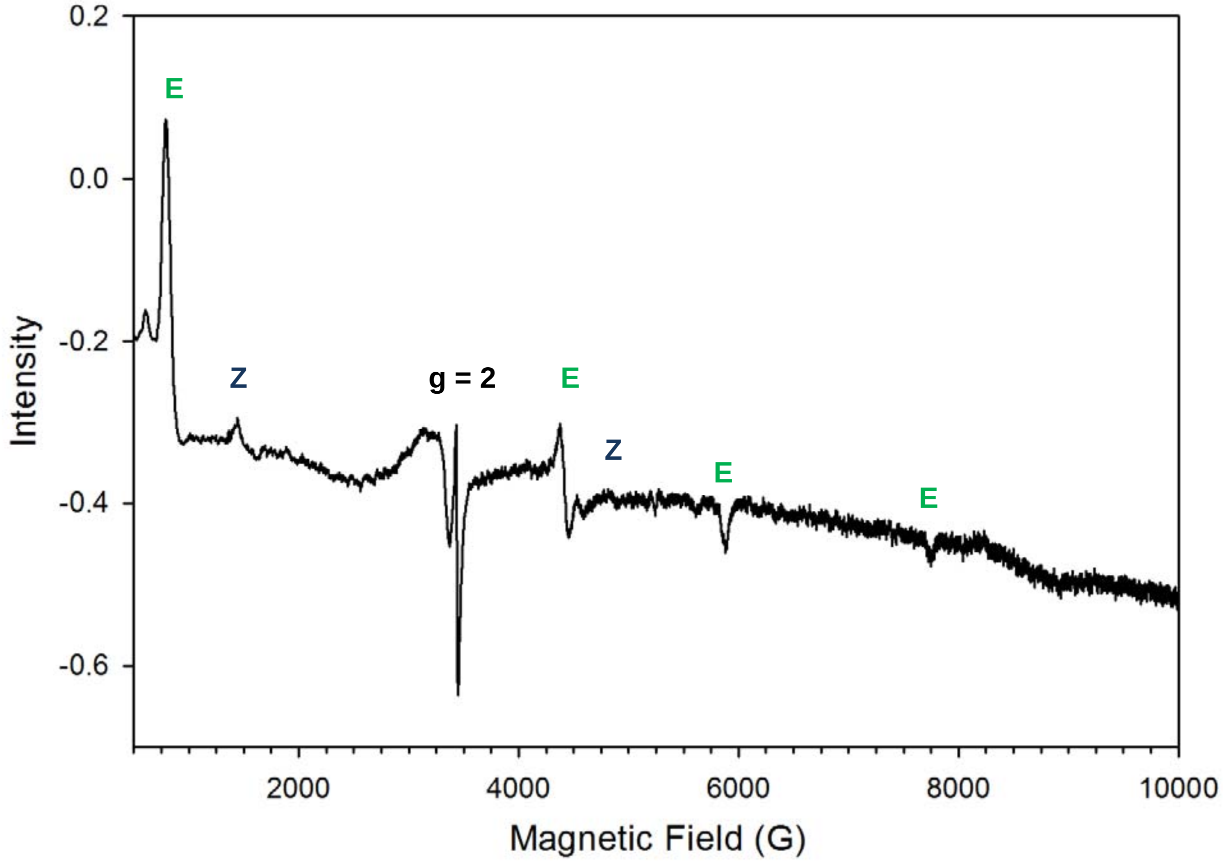


Figure 3.9. EPR spectrum (Ar, 15 K) after irradiation of a matrix containing 1-(3-benzothienyl) diazoethane (**16**) at λ > 534 nm, 44 h. Transitions for both triplet s-*E*-1-(3-benzothienyl) ethylidene (**1-s-*E***) and s-*Z*-1-(3-benzothienyl) ethylidene (**1-s-*Z***) are present. There is no change in the spectrum from λ > 571 nm irradiation.

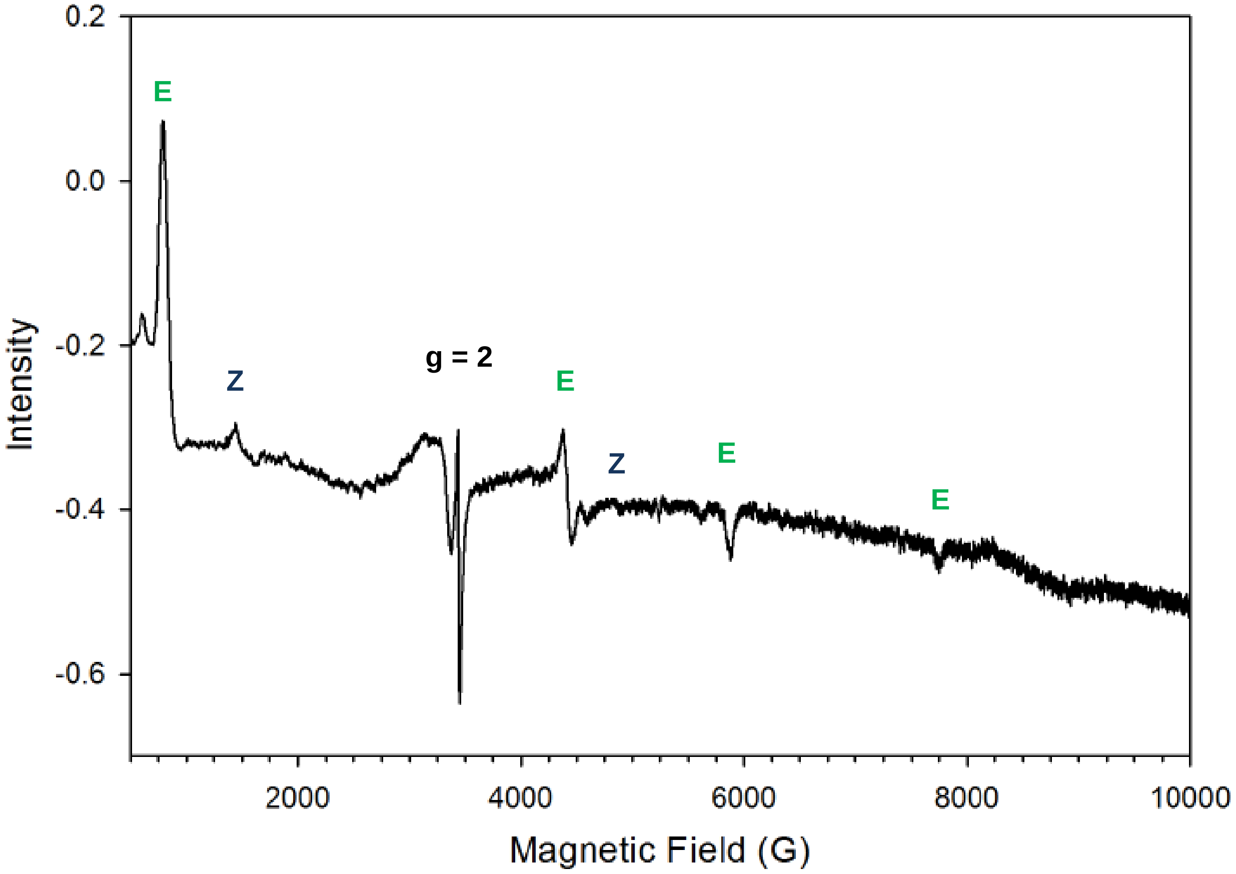


Figure 3.10. EPR spectrum (Ar, 15 K) after a matrix containing both s-*Z*-1-(3-benzothienyl) ethylidene and s-*E*-1-(3-benzothienyl) ethylidene is kept in the dark, 51 h (after λ > 534 nm irradiation); all peaks remain unchanged.

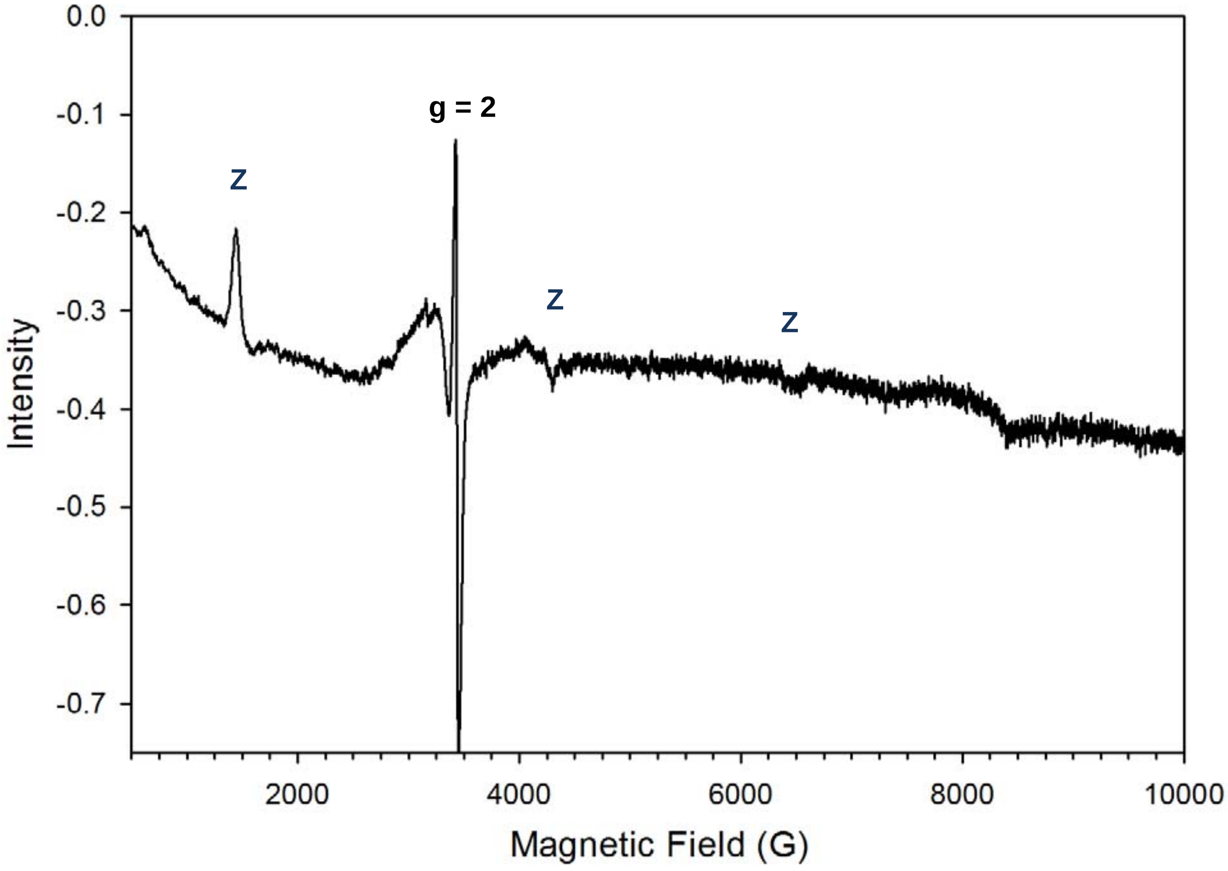


Figure 3.11. EPR spectrum (Ar, 15 K) of the previous matrix after irradiation at λ > 497 nm, 41 h. Transitions for triplet s-*E*-1-(3-benzothienyl) ethylidene (**1-s-*E***) have all disappeared but triplet s-*Z*-1-(3-benzothienyl) ethylidene (**1-s-*Z***) is still present.

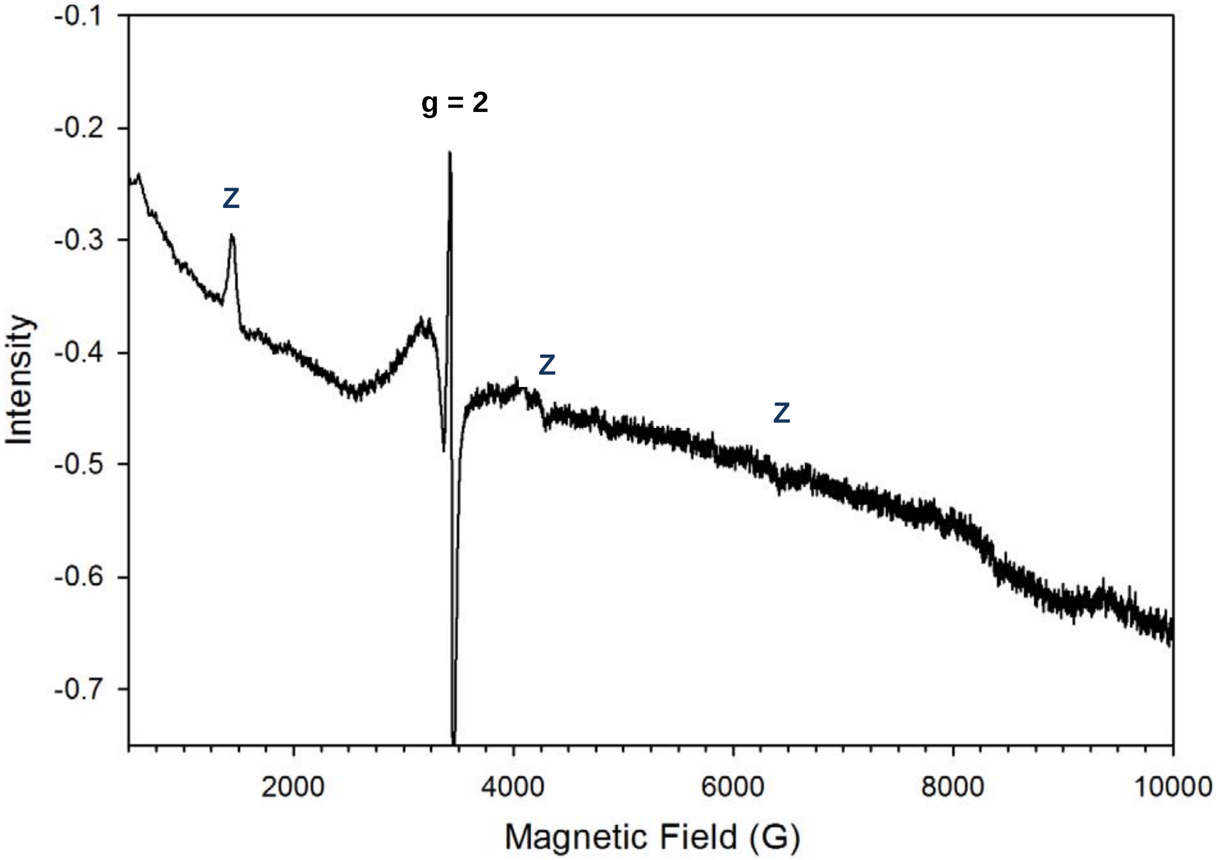


Figure 3.12. EPR spectrum (Ar, 15 K) after keeping the previous matrix in the dark for 79 h. A small change in the intensity of the Z_1 transition for **1-s-*Z*** is observed.

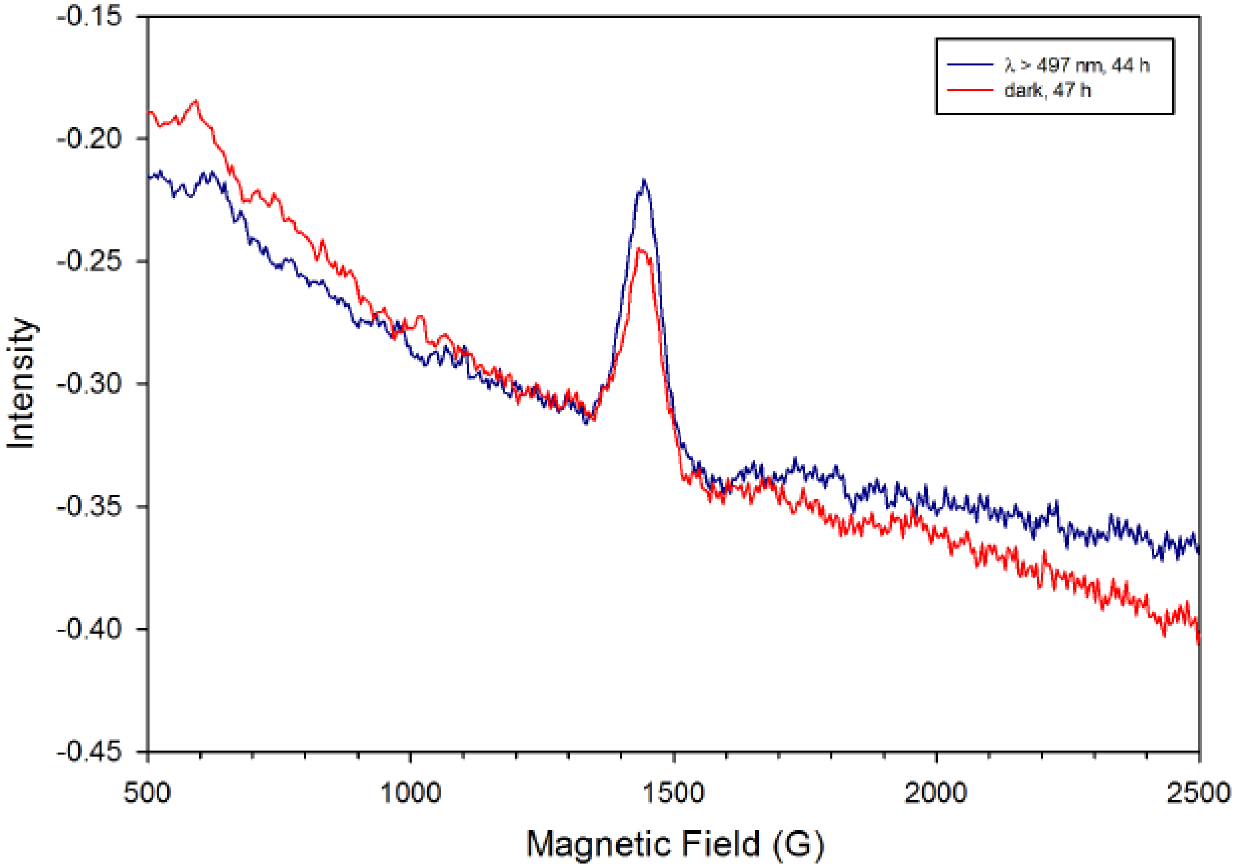


Figure 3.13. EPR spectrum (Ar, 15 K) containing s-*Z*-1-(3-benzothienyl) ethylidene (**1-s-*Z***) after irradiation at λ > 497 nm, 44 h (blue trace), and then after keeping the matrix in the dark for 79 h. (red trace). After sitting in the dark, a decrease in the Z_1 transition for the triplet carbene is observed.

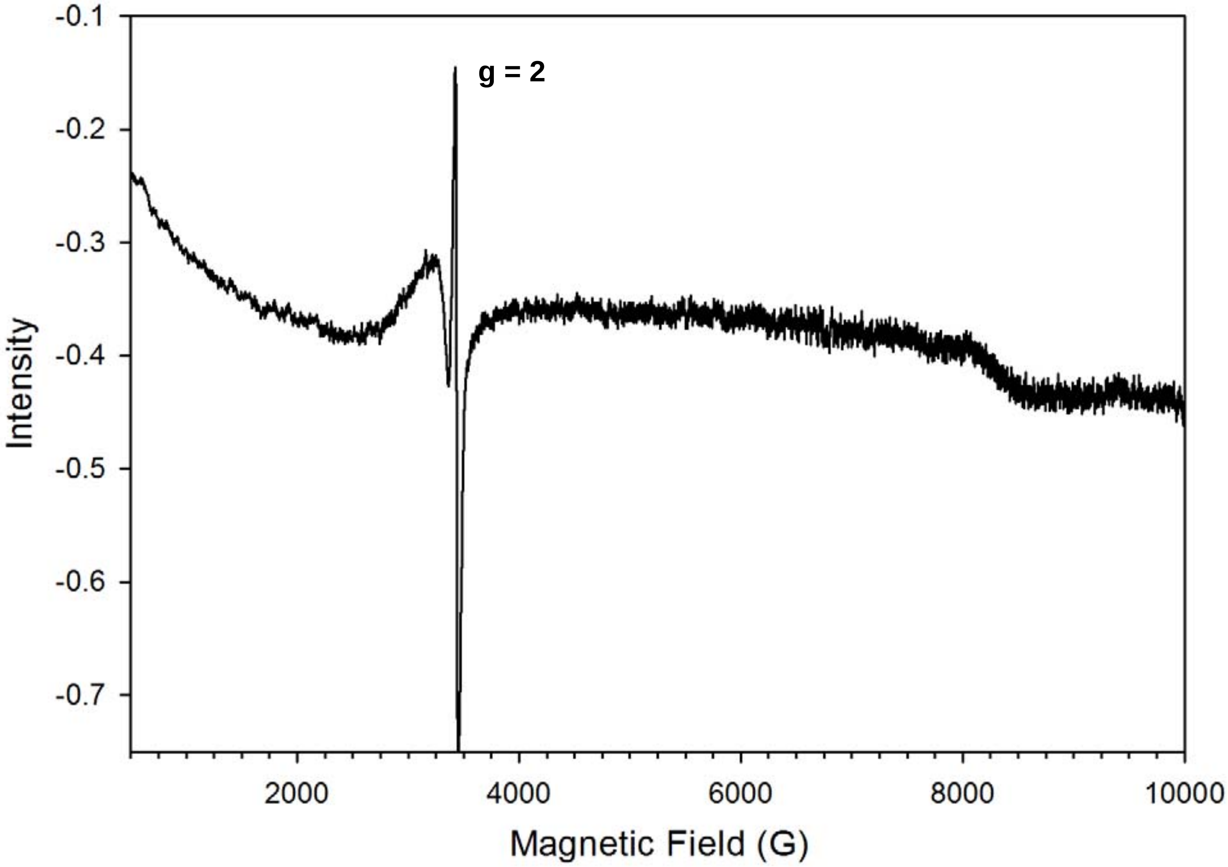


Figure 3.14. EPR spectrum (Ar, 15 K) after irradiation of the previous matrix at λ > 472 nm, 17 h. All triplet species are gone.

Time-dependent density functional theory (TD-DFT) calculations (B3LYP/6-31G*) were carried out to help explain the electronic absorption spectra. TD-DFT calculations are known to overestimate the energy of the transitions in a related series of triplet arylcarbenes; however the general trends have been shown to be accurate.[2] The calculated absorptions and intensities for both rotamers are given in Table 1. Triplet s-*E*-1-(3-benzothienyl) ethylidene is calculated to have a moderately intense peak at λ = 436 nm, while triplet s-*Z*-1-(3-benzothienyl) ethylidene is calculated to have a lower intensity peak at λ = 424 nm. This correlates with the observed spectra, where the higher λ peak is associated with the s-*E* rotamer, and the absorption for the s-*Z* rotamer is at a slightly shorter wavelength (experimental s-*E* λ_{max} = 516 nm, s-*Z* λ_{max} = 498 nm).

1-s-*E*			**1-s-*Z***		
Wavelength (nm)	Oscillator Strength (*f*)	Experimental (nm)	Wavelength (nm)	Oscillator Strength (*f*)	Experimental (nm)
435.9	0.0106	516	424.5	0.0046	498
360.0	0.0048	372	326.0	0.0388	332
325.6	0.0120		321.8	0.0169	
314.2	0.0106		313.9	0.0364	
310.9	0.0683	320			
235.2	0.0087				

Table 3.2. TD-DFT (B3LYP/6-31G*) calculations of triplet s-*E*-1-(3-benzothienyl) ethylidene (**1-s-*E***) and triplet s-*Z*-1-(3-benzothienyl) ethylidene (**1-s-*Z***) showing the lowest energy calculated electronic transitions and their respective intensities.

It is interesting that we were able to detect the formation of 1-(3-benzothienyl) ethylidene when the analogous unsubstituted carbene, 3-benzothienyl carbene, was not detected under similar conditions. This is especially puzzling since in every case studied with the non-benzannulated 3-thienyl carbenes, generation of the triplet carbene was facile.[2,1] However, these findings agree with our previous work on the 2-substituted benzothienyl carbenes. For the 2-substituted series, the triplet carbene was easily generated upon photolysis of 1-(2-benzothienyl) diazoethane[1] but no carbene was detected upon photolysis of 2-benzothienyl diazomethane. Furthermore, 1-(2-benzothienyl) ethylidene was the only triplet carbene ever detected for substitution at the 2-position on the thiophene ring.

Summary

Broadband irradiation at $\lambda > 571$ nm of matrix-isolated 1-(3-benzothienyl) diazoethane (**16**) leads to generation of the corresponding triplet 1-(3-benzothienyl) ethylidenes (**1-s-*E*** and **1-s-*Z***), as characterized by EPR and UV-vis spectroscopy. The concentration of carbene in the matrix was too small to be characterized via IR spectroscopy. Further irradiation of the matrix at $\lambda > 497$ nm sees the disappearance of the s-*E* isomer of the carbene, while irradiation at $\lambda > 472$ nm gives full conversion of both carbene rotamers to their respective 3-vinylbenzothiophenes, as characterized by appearance of peaks for 3-vinylbenzothiophene in the IR and disappearance of all signals for the triplet carbenes in the EPR and UV-vis spectra.

Experimental Details

3-Acetylbenzothiophene (12). The procedure of Farrar and Levine[5] proved most successful for the generation of 3-acetylbenzothiophene. Benzothiophene (1.35 g, 10.1 mmol) and 1.3 mL acetic anhydride were added to a three-neck 25 mL round-bottom flask and heated to 60 °C under N_2. BF_3•Et_2O (0.4 mL, 0.3 mmol) was added and the heating was discontinued. Addition of the boronfluoride etherate gave a dark orange-brown solution. The reaction was stirred for 2 h and quenched with 5 mL deionized H_2O then extracted several times with ether. The combined organic layers were washed with Na_2CO_3, dried over $MgSO_4$, filtered, and the solvent removed to yield a yellow-gold oil. 3-Acetylbenzothiophene was isolated via flash column chromatography with hexane:EtOAc (95:5). (yield 0.8909 g, 50 %). ^{1}H-NMR ($CDCl_3$) δ 8.75 (d, 1H), 8.15 (s, 1H), 7.79 (m, 1H), 7.39 (m, 2H), 2.55 (s, 3H) ppm. EI-EMM *m/z*: [M-Me$^+$] 161.0056. EI-MS *m/z*: 161.8 (10), 122.7 (29), 120.7 (88), 118.7 (100), 116.7 (17), 81.8 (80).

3-Acetylbenzothiophene tosylhydrazone (14). 3-Acetylbenzothiophene (0.8909g, 5.1 mmol) was added to a round-bottom flask with a stirbar along with *p*-toluene sulfonyl hydrazide (1.1794 g, 6.3 mmol, 1.2 eq) and absolute ethanol (45 mL). The clear yellow solution was heated at reflux under nitrogen for 3 h. The reaction mixture was cooled to room temperature and water (100 mL) is added to cause the tosyl hydrazone to precipitate. The solid is collected by filtration to give a gummy pale yellow solid, which is dried on a vacuum line overnight. NMR shows only peaks for desired product, so no further purification done. Yield (0.6309 g 35.9%). ^{1}H-NMR ($CDCl_3$) δ 8.59 (d, 1H), 7.96 (d, 2H),7.81 (m, 1H), 7.66 (m, 1H), 7.60 (s, 1H), 7.38 (m, 2H), 7.31 (m, 2H), 3.40 (s, 3H), 2.27 (s, 3H) ppm. EI-EMM *m/z*: [M$^+$] 344.0648 EI-MS *m/z*: [M]$^+$ 344.0 (17), 189.0 (43), 176.0 (61), 161.0 (100), 133.0 (22), 115.0 (12), 91.1 (24), 89.0 (18), 65.1 (7)

3-Acetylbenzothiophene tosylhydrazone sodium salt. For a typical IR experiment, tosyl hydrazone (0.1488 g,0.43 mmol), sodium hydride (60% in mineral oil, 0.0246 g, 0.59 mmol, 1.3 eq), and anhydrous diethyl ether (15 mL, dried again over CaH) were added to a round-bottom flask and stirred under nitrogen at room temperature for 2 h. After stirring a couple minutes the solution turned milky. After 2 h, ~20 mL hexanes were added to precipitate the sodium salt. The solid was filtered through a medium or dense frit funnel and washed with a couple milliliters of hexanes. The sodium salt was then transferred to a small flask and kept under vacuum until used (overnight). Yield (0.1125 g, 76.3 %)

1-(3-benzothienyl) diazoethane (16).Heating 3-acetylbenzothiophene tosylhydrazone sodium salt to 115-120 °C under vacuum leads to the formation of red diazo compound. IR (Ar, 10 K): 2046 (s), 1510 (m), 1466 (w), 1373 (m), 1271 (w), 1154 (w), 1067 (w), 1029 (w), 843 (m), 755 (m), 728 (m), 708 (w), 653 (w) cm^{-1}.

Matrix Isolation Experiments

In a typical IR matrix isolation experiment, the matrix isolation cart is fitted with 2 outer KBr windows and an inner window of CsI. Deposition of the diazo compound was carried out directly from the sodium salt onto the inner CsI window. For these experiments, the sodium salt was loaded into a short-path curved deposition tube which was attached to the matrix-isolation cart and held under vacuum (pressure = 10^{-8} torr). The cold head was cooled to 25 K and a thin layer of Ar or N_2 was deposited onto the CsI window. Then the tosylhydrazone sodium salt was heated with an oil bath to ~110 °C, at which point the pink diazo compound was released and co-deposited with either Ar or N_2 onto the CsI window. Deposition was carried out until 40-80 torr of gas was deposited, about 60-90 minutes.

Deposition for a UV-vis experiment is nearly the same, however the outer windows are quartz and the inner window is sapphire. Additionally, due to the higher sensitivity of electronic absorption spectroscopy, a much thinner film is used. Deposition at the same rate as for IR experiments is carried out, but for only 6-9 minutes (4-8 torr of gas).

General

All chemicals and solvents were purchased from commercial sources and used without further purification, unless otherwise noted. ^{1}H-NMR spectra were taken on a Bruker AC+ 300 spectrometer. Chemical shifts are reported as ppm downfield of a $SiMe_4$ internal standard. Infrared spectra were taken on a Thermo-Nicolet Nexus 870 FT-IR spectrometer with a MCT-B detector. EPR spectra were taken using a Bruker ESP 300 E spectrometer. Electronic absorption spectra were obtained on a Varian Cary 5000 UV-Vis-NIR spectrometer.

Computational

All calculations were run utilizing the Gaussian09[8] software package. The three-parameter gradient-corrected exchange functional of Becke[9], along with the correlation functional of Lee, Yang, and Parr (B3LYP)[10] was employed for all calculations, with the 6-31G(d) (6-31G*) basis set. Harmonic vibrational frequency calculations at the B3LYP level were used to confirm the nature of each stationary point (zero imaginary modes for minima, one imaginary mode for transition states), as well as to provide zero-point vibrational energy (ZPVE) corrections. Computed frequencies and infrared intensities were used to compare with experimental work, and were not scaled. Time-dependent density functional theory calculations were carried out at the B3LYP/6-31G* level with a 50/50 mix of singlet and triplet states.

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Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian, Inc.: Wallingford, CT, 2009.

(9) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(10) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

Supporting Information for Chapter 3 – Photochemistry and Spectroscopy of 1-(3-Benzothienyl) Diazoethane

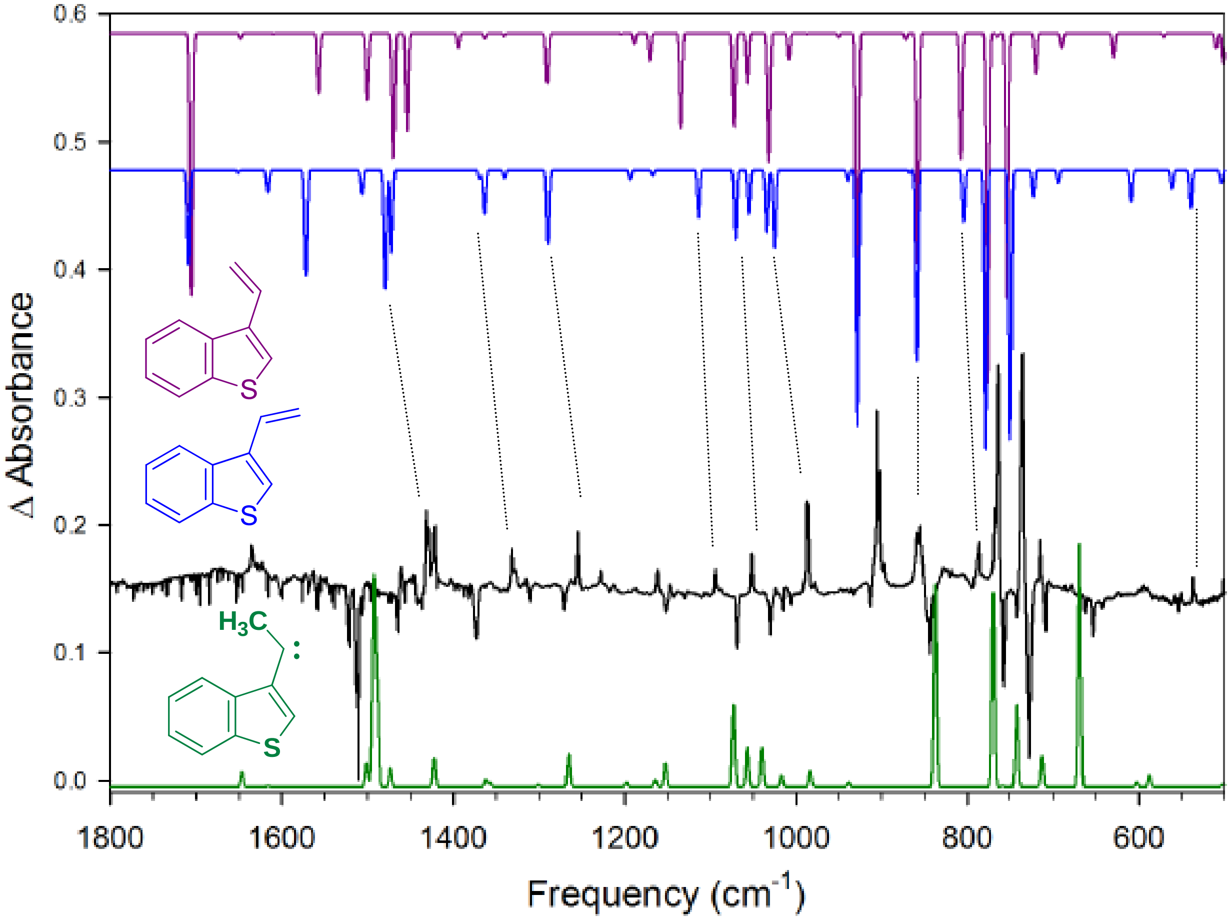
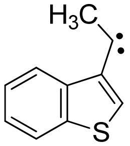


Figure S3.1. IR subtraction spectrum (Ar, 10 K) after irradiation of a matrix containing 1-(3-benzothienyl) diazoethane at λ > 534 nm, 25 h. Calculated spectra (B3LYP/6-31G*) are shown for comparison. The top spectra (purple and blue) are the two 3-vinyl benzothiophene isomers (**2**), and the bottom spectrum (green) is s-*E*-1-(3-benzothienyl) ethylidene (**1**). Peaks for **2** are clearly seen, while **1** cannot definitively be assigned.

s-*E*-1-(3-benzothienyl) ethylidene (^{1}1-s-*E*)



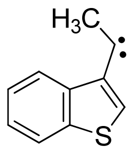
Charge	**Multiplicity**	**Theory/Basis Set**	**Full Point Group**
0	1	RB3LYP/6-31G(d)	C_1
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.144897	-783.952766	-783.807869	2.5432
ΔH$_{(298)}$	**ΔG$_{(298)}$**	(Energies in Hartrees/particle)	
-783.79766	-783.842548		

Symmetry	**Vibrational Frequency (cm^{-1})**	**Intensity**
A	72.0436	1.9282
A	150.7458	3.5176
A	158.6636	2.2985
A	202.3772	1.3591
A	233.0930	2.5802
A	310.9867	14.0003
A	348.1971	4.4845
A	411.5581	1.5606
A	431.1689	2.1379
A	497.8029	1.6006
A	503.6054	0.8779
A	506.4635	0.0754
A	605.5725	1.6593
A	633.7570	2.9109
A	710.4186	10.2069
A	749.0335	12.9218
A	756.4933	16.5671
A	776.2447	30.5647
A	794.9293	83.4370
A	842.6591	18.9555
A	869.9463	23.6049
A	876.3680	0.6138
A	947.4074	0.9890
A	988.8466	0.0058
A	1013.7716	2.9410
A	1056.8527	6.0877
A	1065.4977	7.8034

Atom	**Coordinates (Angstroms)**		
	X	**Y**	**Z**
C	0.050007	-0.366081	-0.100927
C	-0.985524	0.585017	0.040203
C	-2.332061	0.228374	0.128367
C	-2.657673	-1.123139	0.064078
C	-1.652546	-2.088909	-0.095483
C	-0.313239	-1.721825	-0.182372
C	1.379778	0.267467	-0.185002
C	1.253821	1.652977	-0.163388
H	-3.105125	0.984134	0.234639
H	-3.698062	-1.429004	0.127593
H	-1.923866	-3.139137	-0.156520
H	0.444986	-2.482645	-0.326447
H	2.092404	2.332446	-0.235965
S	-0.347866	2.237873	0.074431
C	2.729450	-0.190564	-0.136473
C	2.960066	-1.594136	0.310733
H	3.954135	-1.716184	0.757892
H	2.208817	-2.074000	0.959596
H	3.000099	-2.176672	-0.630108

A	1085.7590	2.4163
A	1149.1945	0.7376
A	1167.8719	1.6052
A	1199.8618	1.7535
A	1220.1763	36.8074
A	1301.7843	3.0289
A	1359.0241	6.3932
A	1367.1819	8.5129
A	1381.1601	21.5933
A	1435.2168	109.6141
A	1450.1474	21.9818
A	1494.4582	30.2563
A	1502.0088	1.3874
A	1538.6955	3.6466
A	1615.4437	0.9372
A	1648.1244	1.8137
A	2962.0736	12.8834
A	3015.0122	46.1995
A	3080.5008	34.7173
A	3189.4006	0.4715
A	3199.2060	10.5569
A	3211.7715	24.3400
A	3234.1552	8.4861
A	3279.5230	4.9249

s-*E*-1-(3-benzothienyl) ethylidene (^{3}1-s-*E*)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.144265	-783.961194	-783.816930	1.4639

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-783.806341	-783.853219

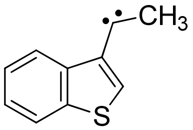
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	78.3861	0.9608
A"	116.2883	0.4330
A'	138.0947	0.5137
A"	172.7841	0.5122
A"	203.8658	2.2193
A"	250.9436	0.2805
A'	313.4909	3.1723
A'	404.1309	1.2892
A"	425.9663	1.8963
A"	489.0883	0.5382
A'	496.5463	0.6830
A'	501.8766	0.4342
A'	587.9318	1.7746
A"	602.5626	0.7462
A"	669.4942	37.7063
A'	713.1009	4.7689
A"	742.7626	12.6315
A'	759.6078	0.1516
A"	770.0868	30.1225
A'	837.8007	31.3843
A"	868.6111	0.0234
A"	938.8296	0.7101
A"	980.3978	0.0608
A'	983.9077	2.5097
A"	1017.0030	1.7854
A'	1039.9710	6.1793
A'	1056.8756	6.1725

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.000000	0.328674	0.000000
C	0.936204	-0.728399	0.000000
C	2.313142	-0.492639	0.000000
C	2.762107	0.824880	0.000000
C	1.848019	1.889246	0.000000
C	0.477699	1.647906	0.000000
C	-1.396421	-0.152729	0.000000
C	-1.423941	-1.555655	0.000000
H	3.017580	-1.319572	0.000000
H	3.829418	1.027910	0.000000
H	2.213284	2.912415	0.000000
H	-0.218604	2.480406	0.000000
H	-2.312580	-2.171699	0.000000
S	0.147488	-2.306525	0.000000
C	-2.531747	0.634592	0.000000
C	-2.937121	2.047615	0.000000
H	-4.031194	2.139055	0.000000
H	-2.572684	2.587475	0.889448
H	-2.572684	2.587475	-0.889448

A'	1073.0453	12.7016
A'	1152.7156	3.6495
A'	1164.4188	1.0755
A'	1198.1571	0.6887
A'	1265.4416	5.0990
A'	1301.0519	0.3483
A'	1357.3659	0.5872
A'	1362.0874	1.1800
A'	1422.4500	4.4111
A'	1473.5513	2.8676
A'	1489.0811	14.2577
A'	1492.6172	29.1696
A"	1494.7711	6.6594
A'	1501.7113	3.6119
A'	1616.3877	0.1898
A'	1646.7153	2.3153
A'	2977.6509	35.9373
A"	3022.9219	21.2833
A'	3072.1926	16.1726
A'	3187.0183	0.4119
A'	3197.6300	8.9017
A'	3208.7977	25.9783
A'	3218.3539	14.7342
A'	3268.4447	2.3719

s-*Z*-1-(3-benzothienyl) ethylidene (^{1}1-s-*Z*)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_1

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.144729	-783.956102	-783.811374	1.7446

ΔH$_{(298)}$	ΔG$_{(298)}$
-783.801043	-783.846213

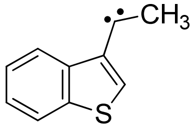
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	86.0866	6.8984
A	133.3182	15.0195
A	161.7179	5.6182
A	189.3098	6.5830
A	201.0111	3.0636
A	254.2133	4.1643
A	320.3419	0.4419
A	419.2025	3.5936
A	431.2131	4.0606
A	501.3142	2.2495
A	504.3219	0.9447
A	551.3559	3.7163
A	586.0186	4.0597
A	619.3885	2.5530
A	716.6724	3.7881
A	752.8510	22.2464
A	771.1829	1.6677
A	778.7693	36.2073
A	809.5248	14.3112
A	872.4745	49.4059
A	880.4663	1.0529
A	895.2774	11.8290
A	955.6671	1.3940
A	997.7565	2.4515
A	998.8336	4.6445
A	1046.5452	8.0680
A	1064.4070	7.8506

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-4.769928	-1.128911	0.052449
C	-3.366636	-1.021755	0.011219
C	-2.715867	0.212803	-0.057513
C	-3.502489	1.360812	-0.081413
C	-4.905233	1.274601	-0.026989
C	-5.541506	0.041286	0.039613
C	-5.241271	-2.516200	0.101608
C	-4.158367	-3.392165	0.103719
H	-1.632140	0.277650	-0.090240
H	-3.024080	2.334749	-0.136816
H	-5.496127	2.186423	-0.032990
H	-6.622201	-0.049771	0.093695
H	-4.203535	-4.471889	0.165618
C	-6.608110	-2.862082	0.311578
C	-7.019751	-4.244285	-0.041793
H	-7.667530	-4.117580	-0.927479
H	-6.253599	-4.995271	-0.314361
H	-7.690347	-4.660836	0.721506
S	-2.615847	-2.623129	0.107296

A	1095.7409	11.4893
A	1145.6002	0.2644
A	1172.1150	0.9917
A	1197.8375	0.9944
A	1243.0745	71.8572
A	1287.3543	3.3060
A	1362.1497	3.0916
A	1374.6988	1.7473
A	1383.6511	7.5191
A	1416.1921	171.9276
A	1469.5949	14.8606
A	1490.7167	34.6512
A	1505.0566	0.8799
A	1514.7282	6.4354
A	1616.4240	0.3439
A	1651.0876	0.5597
A	2935.4437	87.1126
A	3015.8829	16.8003
A	3075.0924	15.9646
A	3187.4692	1.6630
A	3198.8203	11.5468
A	3209.5915	19.4797
A	3217.4257	12.8918
A	3263.5063	1.3956

s-*Z*-1-(3-benzothienyl) ethylidene (^{3}1-s-*Z*)



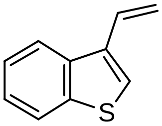
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.142137	-783.966386	-783.824249	1.0758
ΔH$_{(298)}$	**ΔG$_{(298)}$**	(Energies in Hartrees/particle)	
-783.814008	-783.859835		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	-74.9202	27.7918
A"	81.5234	0.1113
A"	156.8902	6.6327
A"	176.9082	2.0494
A'	181.4629	0.0943
A"	260.8386	1.7474
A'	318.0175	0.2713
A"	353.6851	0.0170
A'	426.2506	0.8394
A"	428.8642	0.6534
A'	477.1306	0.1816
A"	494.8328	2.6946
A'	523.4689	1.2705
A'	590.2624	4.1205
A"	596.9726	6.1931
A"	638.4914	41.2077
A'	701.1668	3.4026
A"	726.7037	6.3914
A"	763.3677	44.9998
A'	765.0145	0.4155
A'	861.2227	35.9168
A"	867.8592	0.0688
A"	876.7925	9.3314
A"	930.2005	1.3624
A'	952.4037	5.7825
A"	973.5138	0.0624
A'	1033.0287	2.9591

Atom	Coordinates (Angstroms) X	Y	Z
C	0.000000	0.538237	0.000000
C	-1.088228	-0.364437	0.000000
C	-2.406063	0.066545	0.000000
C	-2.661608	1.445648	0.000000
C	-1.604736	2.358475	0.000000
C	-0.281891	1.913010	0.000000
C	1.298780	-0.122862	0.000000
C	1.115780	-1.590737	0.000000
H	-3.225822	-0.646007	0.000000
H	-3.688396	1.800074	0.000000
H	-1.811029	3.424991	0.000000
H	0.530389	2.634399	0.000000
H	1.893522	-2.338048	0.000000
C	2.524749	0.503631	0.000000
C	3.775904	-0.159341	0.000000
H	3.855828	-1.240012	0.000000
H	4.701125	0.405423	0.000000
S	-0.551867	-2.072581	0.000000
H	2.538128	1.591470	0.000000

A'	1054.3219	9.5213
A'	1085.6617	9.1442
A'	1112.3938	7.3451
A'	1154.8095	3.4731
A'	1192.8644	0.2043
A'	1228.0104	3.5606
A'	1281.7534	3.9000
A'	1324.7432	5.4612
A'	1356.7564	2.4172
A'	1382.1047	3.5273
A'	1482.4347	19.3620
A'	1494.8173	20.8375
A'	1516.0089	2.0064
A'	1556.1777	2.8793
A'	1622.0548	1.3726
A'	1643.4892	15.7853
A'	3174.6300	6.5346
A'	3188.0035	0.4439
A'	3189.7204	7.7413
A'	3196.5964	2.7237
A'	3205.0539	20.3905
A'	3214.7781	25.4315
A'	3280.7832	12.5514
A'	3295.9050	2.3689

s-*Z*-3-vinylbenzothiophene (^{1}2-s-*Z*)



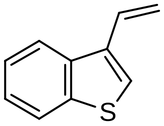
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_1
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.147405	-784.052295	-783.904890	0.6211
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-783.894986	-783.93934		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	73.8380	0.3238
A	136.8607	0.2677
A	178.6302	0.2327
A	206.9424	2.1145
A	244.1561	0.7791
A	324.7812	0.8951
A	417.1703	1.5222
A	433.2482	2.7846
A	482.9814	0.2723
A	504.1682	1.7600
A	539.4802	4.8831
A	561.5351	2.4012
A	609.2250	4.0486
A	694.3144	1.7456
A	723.2938	3.5063
A	750.5264	34.6933
A	777.2210	2.9167
A	779.0843	34.3812
A	804.6207	6.6661
A	859.2733	24.4651
A	868.1211	0.3278
A	928.5764	32.8836
A	939.8063	1.4427
A	980.9923	0.0679
A	1025.3462	10.0413
A	1034.3034	8.0719
A	1055.1332	5.6748

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-4.756457	-1.234895	-0.010575
C	-3.352127	-1.087359	-0.111310
C	-2.738682	0.169064	-0.109189
C	-3.544083	1.297680	-0.006447
C	-4.940814	1.174187	0.098999
C	-5.545793	-0.075458	0.101918
C	-5.170925	-2.628834	-0.024820
C	-4.098060	-3.467511	-0.142742
H	-1.659123	0.261415	-0.186278
H	-3.087970	2.283710	-0.005096
H	-5.552786	2.067879	0.183760
H	-6.624774	-0.158102	0.197779
H	-4.125300	-4.546653	-0.218419
C	-6.571816	-3.058262	0.057275
C	-7.009928	-4.228032	0.538933
H	-6.335161	-4.969481	0.959558
H	-8.066512	-4.478044	0.534039
S	-2.558639	-2.651501	-0.226627
H	-7.304990	-2.342972	-0.314430

A	1070.8123	8.8485
A	1114.1098	6.1527
A	1167.1890	0.7116
A	1193.6844	1.3151
A	1221.2576	0.1079
A	1289.6004	9.4130
A	1340.2170	1.0087
A	1363.6736	5.6264
A	1369.7414	1.1729
A	1472.3623	10.6436
A	1479.8855	15.2477
A	1506.5690	3.1236
A	1572.1455	13.5071
A	1616.5595	2.8229
A	1651.4730	0.3325
A	1709.2101	12.2273
A	3155.8596	12.1209
A	3168.2256	5.4882
A	3185.7000	0.4041
A	3194.7167	5.0480
A	3203.9415	27.0364
A	3212.7784	23.0171
A	3248.0400	15.0349
A	3261.9618	0.6179

s-*Z*-3-vinylbenzothiophene (^{3}2-s-*Z*)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_1

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.142411	-783.966390	-783.823979	1.1011

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-783.813031	-783.860429

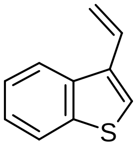
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	80.8829	0.0654
A	102.0513	19.3402
A	161.0689	12.6723
A	178.1725	5.1681
A	181.4707	0.5349
A	262.6182	3.1699
A	318.7823	0.3871
A	358.6499	0.1394
A	426.3687	0.9205
A	429.3635	0.6388
A	477.3861	0.1311
A	496.2275	2.7434
A	523.7376	1.1525
A	590.0872	3.9529
A	598.9281	6.0038
A	645.2289	41.2159
A	701.2370	3.1466
A	726.8137	6.8349
A	763.1175	41.8300
A	765.4014	3.0526
A	860.6920	34.1941
A	867.7491	0.1083
A	880.5278	9.3648
A	929.8903	1.3730
A	956.7310	5.5559
A	973.3272	0.0637
A	1032.8561	2.8048

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-4.790009	-1.197571	0.055871
C	-3.386867	-1.079743	-0.073655
C	-2.752549	0.150571	-0.150893
C	-3.534547	1.313980	-0.098565
C	-4.922281	1.225419	0.029575
C	-5.550136	-0.018853	0.107418
C	-5.249322	-2.578302	0.124994
C	-4.092392	-3.499827	0.057372
H	-1.672871	0.216135	-0.249536
H	-3.053147	2.285941	-0.157298
H	-5.520729	2.131078	0.070303
H	-6.630393	-0.072734	0.209105
H	-4.134980	-4.572929	-0.048027
C	-6.558081	-2.990592	0.243640
C	-6.980248	-4.338314	0.323314
H	-6.278897	-5.164133	0.302795
H	-8.031991	-4.584217	0.415076
S	-2.574966	-2.674823	-0.124628
H	-7.329536	-2.224257	0.279469

A	1054.0628	9.6770
A	1085.5138	8.6091
A	1114.1765	7.5191
A	1154.9747	3.3435
A	1192.7723	0.2070
A	1227.4084	3.5280
A	1281.5580	3.8490
A	1324.9371	5.2916
A	1357.0006	2.4736
A	1382.0265	3.5179
A	1481.8656	18.4873
A	1494.4828	21.3110
A	1516.4794	1.9017
A	1552.8719	3.1473
A	1621.7483	1.4242
A	1642.6514	15.6516
A	3174.1442	6.5688
A	3187.9962	0.4277
A	3189.5499	7.5470
A	3196.5820	2.7495
A	3205.0526	20.4322
A	3214.7849	25.4531
A	3279.7644	12.4165
A	3289.5047	2.4564

s-*E*-3-vinylbenzothiophene (^{1}2-s-*E*)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_1
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.147699	-784.051626	-783.903926	0.4509

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-783.89411	-783.93813

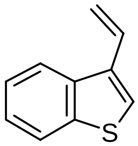
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	86.1707	0.8234
A	143.8193	1.0538
A	191.3534	0.7750
A	206.5759	2.0908
A	256.6399	1.1866
A	343.8065	0.4309
A	411.8973	0.6200
A	432.4478	3.4700
A	485.7979	0.2404
A	501.7574	3.1860
A	510.3023	1.5669
A	571.8042	0.4223
A	630.2152	2.5238
A	690.4396	1.5834
A	721.2452	4.3477
A	753.7311	29.7753
A	766.2324	0.3300
A	776.6236	38.3166
A	808.7920	13.6983
A	859.6558	24.0094
A	871.5148	0.7530
A	925.8216	34.2939
A	946.1769	0.4516
A	984.1373	0.0891
A	1011.4171	2.6356
A	1033.2953	13.9794
A	1059.0078	5.5673

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.043639	-0.367362	-0.050638
C	-0.989896	0.598365	0.042818
C	-2.340916	0.242630	0.091257
C	-2.673265	-1.105540	0.032330
C	-1.669319	-2.080619	-0.091415
C	-0.328086	-1.723173	-0.136022
C	1.365088	0.247750	-0.094288
C	1.277158	1.613512	-0.073976
H	-3.112515	1.003571	0.165930
H	-3.717066	-1.404443	0.069816
H	-1.945682	-3.129149	-0.159577
H	0.429117	-2.487999	-0.263178
H	2.106565	2.309340	-0.097574
S	-0.345079	2.233633	0.047581
C	2.670371	-0.418792	-0.140180
C	2.982097	-1.654576	0.274416
H	4.002288	-2.019304	0.200667
H	2.261086	-2.327729	0.724949
H	3.476232	0.204413	-0.528145

A	1074.4242	9.7260
A	1137.7801	10.0230
A	1174.4070	2.9216
A	1194.6863	1.0101
A	1210.6457	0.1695
A	1296.0733	5.5860
A	1348.4199	0.2293
A	1364.1602	0.4937
A	1398.9232	1.7391
A	1462.2523	12.6917
A	1476.4433	10.2262
A	1505.2936	6.9167
A	1560.3867	6.5425
A	1613.3008	0.1190
A	1651.1422	0.6164
A	1709.4706	26.9989
A	3149.0938	19.0440
A	3181.8333	5.3875
A	3187.4316	0.6535
A	3198.1932	11.8765
A	3210.3668	27.0378
A	3231.3235	10.7365
A	3252.8947	1.5914
A	3262.9311	14.7763

s-*E*-3-vinylbenzothiophene (^{3}2-s-*E*)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_1

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.142769	-783.958467	-783.815698	1.0669

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-783.805002	-783.851742

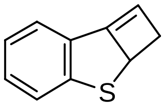
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	69.5399	0.1589
A	140.2730	0.5930
A	157.6848	0.4648
A	204.6351	2.0064
A	224.3777	5.6987
A	316.0575	18.1562
A	336.9645	3.3799
A	383.0872	11.6632
A	410.3608	2.9224
A	420.5899	5.2358
A	472.1566	1.5715
A	489.1415	1.2283
A	507.3672	1.7161
A	602.2317	2.4420
A	621.9040	2.3170
A	661.5039	49.1180
A	700.7245	2.7021
A	740.0770	14.0975
A	757.0902	3.5082
A	769.9090	31.3414
A	843.4706	40.1676
A	872.6053	0.7845
A	876.0217	9.6069
A	934.4369	1.1750
A	975.9000	0.7336
A	983.3152	2.6351
A	1019.2547	6.0338

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.056576	-0.379612	-0.066613
C	-0.975257	0.584780	0.045446
C	-2.314851	0.236429	0.113741
C	-2.661792	-1.121583	0.049772
C	-1.671411	-2.091158	-0.098015
C	-0.322664	-1.728663	-0.163399
C	1.390449	0.216568	-0.109390
C	1.269207	1.699936	-0.219658
H	-3.083435	0.998345	0.205874
H	-3.707641	-1.410893	0.100294
H	-1.945903	-3.139449	-0.173948
H	0.426129	-2.493987	-0.327342
H	2.097619	2.384261	-0.092007
S	-0.350240	2.260458	0.067224
C	2.629583	-0.387247	-0.024604
C	2.954232	-1.738716	0.241384
H	3.984835	-2.068918	0.174057
H	2.227698	-2.461617	0.589419
H	3.480107	0.280513	-0.163914

A	1057.1365	15.4306
A	1066.2137	3.6657
A	1141.0457	0.9691
A	1158.7035	2.4062
A	1193.3704	0.0115
A	1213.1881	0.9751
A	1256.2754	0.3314
A	1319.1599	7.7035
A	1348.8608	3.3766
A	1416.5748	9.2751
A	1473.0378	14.7974
A	1490.6095	12.6186
A	1520.1406	10.6173
A	1542.2842	5.2363
A	1623.8943	0.5787
A	1640.1041	22.7121
A	3144.1880	17.6246
A	3189.5846	0.7152
A	3192.3987	5.4329
A	3200.6693	10.6571
A	3212.3623	25.8583
A	3237.2902	8.4086
A	3252.3576	5.9610
A	3288.2716	9.3613

3,4-Benzo-2-thia-bicyclo[3.2.0]hepta-3,5-diene (^{1}3)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_1
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.148437	-784.005876	-783.857439	1.3956

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-783.848252	-783.890823

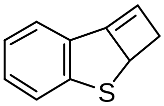
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	108.1341	1.7342
A	154.3067	0.2075
A	211.3294	0.5569
A	260.2232	1.4351
A	320.6223	0.2400
A	398.2927	3.1052
A	441.3446	1.1014
A	454.1811	3.1879
A	477.5868	0.2811
A	547.8501	0.3509
A	570.5454	4.3863
A	676.0192	2.6619
A	693.5422	3.5885
A	723.2750	4.8976
A	742.1644	2.4505
A	764.1938	60.3715
A	807.9236	23.0158
A	876.3134	0.7586
A	890.8070	2.7187
A	923.0130	3.7429
A	939.5142	1.4319
A	970.0168	3.6971
A	979.7179	0.0969
A	1008.8713	2.2052
A	1050.4152	10.7522
A	1061.1226	8.3229

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.416241	-0.691684	0.143864
C	0.639073	0.701718	-0.006301
C	1.932084	1.198489	-0.145557
C	3.007608	0.303391	-0.125173
C	2.796896	-1.069684	0.023587
C	1.498935	-1.571000	0.152843
H	2.106536	2.264217	-0.262299
H	4.019741	0.686863	-0.222975
H	3.643379	-1.750109	0.041270
H	1.328171	-2.637867	0.268184
S	-0.858675	1.702246	-0.061277
C	-1.019464	-0.930022	0.183978
C	-2.046049	-1.602910	-0.377927
C	-1.853583	0.265343	0.554779
C	-3.028700	-0.449194	-0.206973
H	-2.050822	0.410820	1.621745
H	-3.294035	0.041499	-1.149296
H	-3.941740	-0.614891	0.379499
H	-2.130675	-2.563141	-0.878422

A	1095.7163	2.9571
A	1113.9346	3.6561
A	1138.6593	3.7707
A	1179.4011	3.7325
A	1194.5122	1.0829
A	1204.8770	2.0522
A	1255.9829	22.0858
A	1262.2320	7.3538
A	1290.4692	2.7212
A	1316.3175	3.2612
A	1354.4402	11.2823
A	1481.6954	25.4481
A	1499.1759	5.0715
A	1504.3953	1.8079
A	1620.4475	0.9794
A	1643.4907	16.8343
A	1697.1085	6.9250
A	3049.9984	69.2949
A	3083.8979	18.9697
A	3108.1097	20.6092
A	3185.5990	0.3021
A	3194.4130	5.9860
A	3204.1679	20.4723
A	3212.5809	21.9509
A	3213.1453	19.2170

3,4-Benzo-2-thia-bicyclo[3.2.0]hepta-3,5-diene (^{3}3)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_1
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.144678	-783.921647	-783.776968	1.0320

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-783.767318	-783.811866

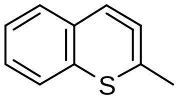
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	88.4839	2.2784
A	136.3763	2.5545
A	196.0703	4.0687
A	252.5293	0.7850
A	272.2547	8.3160
A	370.4630	9.3991
A	435.4121	7.0993
A	469.0516	0.6620
A	481.2574	5.3476
A	503.8114	12.7358
A	536.5872	2.0505
A	539.9559	2.5052
A	633.7507	18.8532
A	693.6224	6.9698
A	722.3146	6.0786
A	727.4146	9.6846
A	756.9097	42.0473
A	826.8381	4.2711
A	851.5996	0.1443
A	914.2836	0.7955
A	922.7131	6.5547
A	924.7822	2.5780
A	964.9699	10.7921
A	969.8789	0.5440
A	1022.3644	8.5913
A	1046.0628	3.9198
A	1055.3408	19.7891
A	1067.3650	5.7541

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.350705	0.672396	-0.387431
C	0.616047	-0.732653	-0.233839
C	1.890672	-1.197094	0.068362
C	2.925258	-0.270992	0.245021
C	2.679462	1.111698	0.143872
C	1.413189	1.586322	-0.154928
H	2.079710	-2.259809	0.190581
H	3.925416	-0.625280	0.477520
H	3.494848	1.812481	0.301026
H	1.223298	2.652671	-0.239277
S	-0.842862	-1.731489	-0.377686
C	-0.983029	0.955085	-0.744452
C	-2.012974	1.779139	-0.005556
C	-1.887934	-0.254599	-0.711338
C	-2.726237	0.497400	0.393014
H	-2.483551	-0.444949	-1.609702
H	-2.501507	0.156984	1.414356
H	-3.813442	0.458255	0.241615
H	-1.877368	2.691536	0.569897

A	1075.5870	1.3729
A	1156.1985	2.7132
A	1167.8866	2.6877
A	1187.9743	3.3270
A	1217.2211	1.4553
A	1246.1579	13.2368
A	1266.6761	3.1043
A	1285.9431	4.9122
A	1341.3855	6.6367
A	1416.8362	0.5893
A	1457.4203	10.9562
A	1477.9265	2.8474
A	1488.8228	11.9245
A	1578.6701	6.7041
A	1600.7813	10.9783
A	3019.2741	32.2100
A	3063.5130	6.3115
A	3086.3811	30.2586
A	3186.0210	0.8350
A	3191.8373	36.2027
A	3194.7352	4.4422
A	3203.6129	25.7007
A	3213.0765	24.9375

2*H*-1-benzo-2,3-dehydro-2-methylthiopyran (^{1}4)



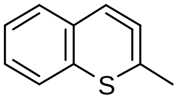
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_1
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.146278	-783.987790	-783.841511	1.2067
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-783.831303	-783.875984		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	86.9238	1.6600
A	133.3448	0.3611
A	145.9375	0.1459
A	216.2504	1.5322
A	278.1923	2.9092
A	316.3286	2.9020
A	351.9381	5.3454
A	403.4549	1.9069
A	434.5673	4.6240
A	460.8123	7.7150
A	509.0522	22.7686
A	530.2238	1.3032
A	555.0390	12.9305
A	624.9861	34.2264
A	641.2876	18.0321
A	682.3497	5.0907
A	727.3117	2.5348
A	763.3109	37.7831
A	810.1655	22.2848
A	853.4326	3.4268
A	886.4795	2.1389
A	944.0614	34.9985
A	949.8261	1.9072
A	985.3503	0.0307
A	1050.1860	12.7526
A	1058.8682	2.1888
A	1072.1196	0.6009
A	1126.8718	31.0042

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-2.792678	-0.978020	0.277693
C	-1.503152	-1.427242	0.000352
C	-0.457089	-0.511600	-0.165158
C	-0.718173	0.884522	-0.094456
C	-2.026395	1.307352	0.195313
C	-3.055683	0.391463	0.383420
H	-3.591792	-1.700522	0.418962
H	-1.304139	-2.493269	-0.065955
H	-2.226136	2.374380	0.253959
H	-4.061587	0.740032	0.599733
C	0.360324	1.795319	-0.508615
C	1.599803	1.364964	-0.271570
C	2.153376	0.192970	0.044505
S	1.175143	-1.186281	-0.524347
H	0.118917	2.666719	-1.114457
C	3.331057	-0.059299	0.938189
H	4.133202	-0.590021	0.408429
H	3.734158	0.895322	1.290784
H	3.046746	-0.674714	1.800061

A	1150.2533	5.4097
A	1196.4418	1.1800
A	1228.1274	8.6734
A	1251.1524	1.9578
A	1298.2060	8.4020
A	1330.2874	0.7549
A	1418.8216	23.7395
A	1433.8597	7.5928
A	1485.9475	2.2793
A	1493.1186	4.5245
A	1502.6041	13.5158
A	1517.0619	1.8914
A	1607.4467	0.6582
A	1640.9143	5.9851
A	1831.9478	15.0110
A	3039.1709	25.0638
A	3094.6815	12.7229
A	3132.3338	10.5169
A	3169.3977	18.1759
A	3184.0473	1.7228
A	3190.8930	3.6769
A	3201.1848	21.1473
A	3212.2553	26.8410

2*H*-1-benzo-2,3-dehydro-2-methylthiopyran (^{3}4)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.144972	-783.965339	-783.820367	0.2585

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-783.809967	-783.856244

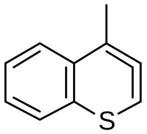
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	68.4722	1.4203
A"	121.4227	0.1879
A"	146.1158	0.1660
A'	237.4760	1.7852
A"	238.6107	0.1191
A"	295.4908	2.4291
A'	348.4223	0.1372
A'	369.3676	1.0426
A'	443.8571	0.1429
A"	449.2246	3.2095
A"	470.4108	0.8458
A'	542.6411	0.1504
A"	542.8011	1.6395
A'	612.5742	2.2779
A'	683.8770	3.2615
A"	708.8981	4.5561
A'	713.9458	2.9612
A"	737.3548	5.6860
A"	772.5627	56.3210
A'	846.3246	3.0787
A"	866.6596	1.4277
A"	935.2644	2.2911
A'	945.8055	11.9483
A"	975.7862	0.0018
A'	1055.6733	13.4825
A"	1056.2459	0.7053
A'	1078.3248	1.9696
A'	1111.6500	11.6316

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-1.380318	2.717067	0.000000
C	-0.123791	2.114869	0.000000
C	0.000000	0.721582	0.000000
C	-1.160071	-0.104855	0.000000
C	-2.420142	0.539318	0.000000
C	-2.532281	1.921472	0.000000
H	-1.458823	3.800243	0.000000
H	0.771547	2.731380	0.000000
H	-3.312786	-0.081371	0.000000
H	-3.515407	2.384121	0.000000
C	-1.067508	-1.542692	0.000000
C	0.166956	-2.149919	0.000000
C	1.437048	-1.695818	0.000000
S	1.667123	0.083113	0.000000
H	-1.984674	-2.124568	0.000000
C	2.702340	-2.503062	0.000000
H	3.316800	-2.289240	0.884765
H	2.459174	-3.568904	0.000000
H	3.316800	-2.289240	-0.884765

A'	1156.8040	1.1087
A'	1194.0387	0.1722
A'	1213.1488	0.7061
A'	1239.5247	1.9118
A'	1289.4362	11.5512
A'	1336.8024	10.7639
A'	1402.0757	16.2715
A'	1433.0859	2.6099
A'	1463.2466	16.6352
A'	1492.5271	6.3305
A"	1502.4792	8.5970
A'	1514.2029	3.9683
A'	1559.3451	3.0196
A'	1604.1524	1.5614
A'	1636.0823	0.0875
A'	3031.4200	46.3537
A"	3078.2823	17.9173
A'	3140.5810	8.5809
A'	3181.0816	3.6158
A'	3186.4004	0.4603
A'	3194.0874	2.2580
A'	3198.5443	26.7292
A'	3212.7425	24.8575

2*H*-1-benzo-2,3-dehydro-4-methylthiopyran (^{1}5)



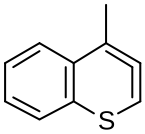
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_1
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.146326	-783.986521	-783.840195	1.7934
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-783.830034	-783.874499		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	116.6042	0.3470
A	130.0164	0.9572
A	165.9090	0.6881
A	187.0542	1.2096
A	250.9025	1.2272
A	332.7557	12.7605
A	354.8204	2.7299
A	418.7003	4.6042
A	431.1921	9.0465
A	478.6442	4.3998
A	493.4445	6.1951
A	526.2769	4.7164
A	576.9845	25.5590
A	598.6515	21.6243
A	679.3415	5.1469
A	728.9398	43.5794
A	740.4513	11.6524
A	761.9468	4.4028
A	772.3037	28.5599
A	793.5486	24.0398
A	878.0452	0.2693
A	950.1318	1.5895
A	953.1659	21.1649
A	985.9942	0.0615
A	1051.0451	8.3852
A	1057.8973	0.9872
A	1066.0370	3.3231

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-2.734308	-0.696299	-0.057053
C	-1.549450	-1.406462	-0.234312
C	-0.311756	-0.766942	-0.088366
C	-0.263787	0.629686	0.181464
C	-1.475957	1.315599	0.369134
C	-2.700237	0.665594	0.258071
H	-3.686067	-1.211725	-0.152277
H	-1.584239	-2.469161	-0.457529
H	-1.445928	2.379554	0.588355
H	-3.624615	1.217763	0.401865
C	1.048508	1.304211	0.056487
C	2.076982	0.548835	0.454805
C	2.294113	-0.754289	0.600246
S	1.159117	-1.782452	-0.298239
H	2.933221	-1.235100	1.334655
C	1.164304	2.638541	-0.629171
H	0.733845	3.443070	-0.016666
H	2.213958	2.885073	-0.810957
H	0.623484	2.638921	-1.583447

A	1101.4335	2.5651
A	1155.0797	2.1299
A	1197.8450	1.5533
A	1238.7240	2.1490
A	1277.6075	37.8897
A	1306.0857	4.3051
A	1325.4305	1.6839
A	1386.3795	38.2284
A	1432.6254	1.0823
A	1479.6417	15.5709
A	1491.7268	5.2981
A	1506.6895	5.7681
A	1518.8639	1.8417
A	1606.2310	0.7167
A	1641.0103	6.9235
A	1830.2601	15.1889
A	3034.1014	22.4919
A	3087.0633	16.4805
A	3139.6959	14.4638
A	3185.4704	0.3274
A	3192.5633	3.3515
A	3199.5449	15.4361
A	3202.1298	20.9539
A	3212.7363	24.3774

2*H*-1-benzo-2,3-dehydro-4-methylthiopyran (^{3}5)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.145087	-783.962269	-783.817181	0.9773

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-783.806946	-783.852622

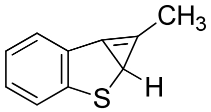
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	98.0414	0.1629
A"	122.4422	0.2571
A"	193.4706	2.5853
A"	205.2100	0.6587
A'	267.4777	0.4069
A"	307.6106	0.7838
A'	359.6627	0.1764
A'	389.6440	1.6985
A"	447.6959	1.1832
A'	450.9850	0.4234
A"	484.0158	0.6497
A'	521.2295	0.9157
A"	567.2491	0.3065
A"	616.9551	27.1740
A'	670.4414	1.8912
A'	684.5197	1.7568
A"	732.8133	6.4641
A'	737.5348	9.0015
A"	765.3206	46.6512
A'	766.9632	6.6790
A"	864.1869	0.1549
A"	935.2894	1.8762
A'	963.1643	8.8411
A"	977.4630	0.0011
A"	1052.9493	0.5787
A'	1057.4905	9.5651
A'	1064.2721	6.1864
A'	1105.9037	5.1140

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-2.822425	0.332301	0.000000
C	-1.984756	-0.780305	0.000000
C	-0.593496	-0.632536	0.000000
C	0.000000	0.665436	0.000000
C	-0.884216	1.771022	0.000000
C	-2.263832	1.613012	0.000000
H	-3.900080	0.197828	0.000000
H	-2.413432	-1.779332	0.000000
H	-0.466468	2.771955	0.000000
H	-2.905311	2.490023	0.000000
C	1.442184	0.865172	0.000000
C	2.239839	-0.258920	0.000000
C	2.005210	-1.584974	0.000000
S	0.327364	-2.161257	0.000000
H	2.753474	-2.368881	0.000000
C	2.042309	2.248021	0.000000
H	1.737774	2.826078	0.883541
H	3.133546	2.186989	0.000000
H	1.737774	2.826078	-0.883541

A'	1155.8308	0.3981
A'	1197.5327	0.6955
A'	1208.1454	0.3952
A'	1277.6623	6.8218
A'	1298.8828	12.1784
A'	1331.3320	5.6685
A'	1362.4070	0.0420
A'	1432.0625	3.5905
A'	1458.2243	32.1019
A'	1477.9885	7.9839
A"	1512.5489	6.5494
A'	1514.6752	8.9943
A'	1543.4368	8.2951
A'	1604.2918	5.8242
A'	1635.2085	0.1428
A'	3023.0931	38.2239
A"	3066.7706	23.5626
A'	3137.2958	14.1059
A'	3183.5799	0.8732
A'	3192.1320	10.3571
A'	3210.0042	22.6407
A'	3221.1184	13.3054
A'	3231.7700	1.2885

6-methyl-2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (^{1}6)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_1
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.146446	-783.974088	-783.827642	1.8711

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-783.817494	-783.86234

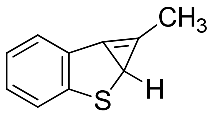
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	80.2104	1.1453
A	128.0929	0.5980
A	135.7400	1.3085
A	181.2385	0.7683
A	235.4629	1.1916
A	332.3413	2.0373
A	407.0220	5.1156
A	427.4433	1.8226
A	459.4156	9.1458
A	472.9422	0.8170
A	484.3676	0.7783
A	560.3749	0.8566
A	584.8300	39.6704
A	673.5520	13.1964
A	691.3293	4.3913
A	724.4889	3.9280
A	739.9038	5.8185
A	763.4017	21.4885
A	766.8736	36.6047
A	874.4269	0.0463
A	937.8043	2.6462
A	978.9896	0.0700
A	984.9531	3.0618
A	1022.9094	9.3462
A	1043.8727	12.4806
A	1052.0283	8.9388
A	1054.4774	4.5097

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-0.424589	-0.655257	-0.359483
C	-0.702706	0.689415	0.024153
C	-1.990255	1.033187	0.436678
C	-3.001469	0.068287	0.405071
C	-2.734538	-1.241680	-0.001242
C	-1.440122	-1.609092	-0.376133
C	1.002452	-0.762925	-0.591579
C	1.758224	0.504787	-0.811671
H	-2.212763	2.048187	0.752500
H	-4.010566	0.348185	0.695588
H	-3.531664	-1.979189	-0.018502
H	-1.218002	-2.628521	-0.677415
H	2.146731	0.827853	-1.777725
S	0.700249	1.801910	0.010260
C	2.207365	-0.704255	-0.064793
C	3.198835	-1.224459	0.901358
H	4.186114	-1.355118	0.440749
H	3.318077	-0.500038	1.717610
H	2.878918	-2.179974	1.328868

A	1076.7230	13.4286
A	1141.2232	1.1040
A	1166.9695	3.4362
A	1195.1505	0.9974
A	1242.2524	3.3011
A	1272.5849	18.7278
A	1305.8966	4.3971
A	1346.0277	6.5704
A	1427.4707	3.9408
A	1474.4649	18.1811
A	1494.9705	4.9231
A	1497.7056	9.1207
A	1514.2040	10.6033
A	1614.4817	2.0423
A	1644.5569	7.8928
A	1874.0650	15.5967
A	3039.7819	27.4035
A	3094.0346	14.3031
A	3126.6564	38.6257
A	3127.8805	15.0915
A	3186.6744	1.1712
A	3198.2377	6.7312
A	3206.8989	20.9338
A	3214.8453	21.5923

6-methyl-2-thia-3,4-benzobicyclo[3.1.0]hexa-3,5-diene (^{3}6)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_1
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.144200	-783.899497	-783.755297	1.4762

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-783.745099	-783.790987

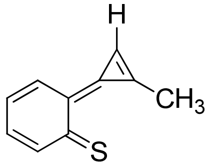
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	83.4216	0.8176
A	117.1585	1.4093
A	145.5006	0.3061
A	170.2938	2.2364
A	237.7593	1.4663
A	326.4646	0.6591
A	381.1627	6.3430
A	446.2137	1.8713
A	453.3766	2.7268
A	488.3293	0.2600
A	491.7205	1.3766
A	553.4502	0.5430
A	593.4419	2.5939
A	693.9450	6.9462
A	702.7157	6.0507
A	731.5264	6.0190
A	736.3343	9.2936
A	769.4280	32.3353
A	788.2844	22.0889
A	861.0749	9.8639
A	879.7621	4.8212
A	927.1618	23.1123
A	948.8709	2.2759
A	985.1347	0.0717
A	1014.9887	10.6912
A	1049.5118	1.9407
A	1053.1527	5.9559

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-0.352342	-0.570312	-0.518340
C	-0.554055	0.747783	-0.017057
C	-1.800723	1.154003	0.464566
C	-2.854880	0.241426	0.448546
C	-2.670810	-1.067796	-0.026062
C	-1.429595	-1.475546	-0.498548
C	0.983764	-0.817106	-1.023872
C	1.870118	0.352273	-0.762399
H	-1.947403	2.158952	0.849589
H	-3.830732	0.548725	0.814669
H	-3.505256	-1.763249	-0.023221
H	-1.278472	-2.484280	-0.872035
H	2.602196	0.701007	-1.494072
S	0.923475	1.723444	-0.003431
C	2.157461	-0.966856	-0.106536
C	2.326032	-1.339075	1.318865
H	3.340746	-1.092534	1.657700
H	1.628398	-0.785473	1.969618
H	2.165110	-2.411005	1.477670

A	1080.4963	5.2112
A	1082.8617	13.8346
A	1149.7008	0.2291
A	1173.3312	0.0949
A	1192.8294	4.6935
A	1244.4514	7.1652
A	1291.7651	7.6034
A	1336.7681	10.7443
A	1408.9062	7.5517
A	1434.1923	11.8921
A	1471.0984	14.0360
A	1487.9832	6.7890
A	1495.3894	4.1457
A	1499.4904	5.4715
A	1596.7437	10.3542
A	1627.2814	24.3478
A	2989.6246	13.3360
A	3068.1712	19.9752
A	3111.0651	16.0523
A	3117.2467	2.8210
A	3187.8079	0.4045
A	3197.7009	3.5802
A	3206.6122	19.7144
A	3214.6093	24.1472

2-(*Z*-2-methylcyclopropen-1-ylidene)-cyclohexa-3,5-dien-1-thione (^{1}7)



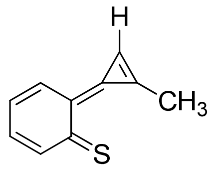
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.145104	-783.965042	-783.819939	6.5590
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-783.809653	-783.855312		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	-90.3936	2.3719
A"	52.6648	2.2068
A"	123.0308	0.7805
A'	125.3151	3.8311
A"	175.4485	1.0932
A'	243.1318	0.7136
A'	300.8669	6.1012
A"	314.8954	4.0639
A'	410.1754	6.6098
A"	420.3180	0.0005
A'	488.5868	2.2787
A"	494.6980	4.2635
A'	549.5640	3.9616
A"	586.0449	1.1912
A'	668.8976	15.3713
A"	735.7573	6.5923
A"	765.7738	36.8225
A'	773.6292	7.9139
A'	812.4827	4.4079
A"	832.0755	19.3701
A"	867.4821	2.3646
A"	954.0586	0.0032
A'	979.6088	0.5820
A"	1006.1192	0.4954
A'	1030.7972	22.6742
A'	1049.5966	1.6862

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-2.684610	1.459013	0.000000
C	-2.375435	0.122772	0.000000
C	-1.021422	-0.358693	0.000000
C	0.000000	0.684801	0.000000
C	-0.361918	2.075840	0.000000
C	-1.670874	2.463537	0.000000
H	-3.728933	1.763688	0.000000
H	-3.162181	-0.624553	0.000000
H	0.436090	2.815045	0.000000
H	-1.942871	3.514607	0.000000
C	1.346773	0.368663	0.000000
C	2.697207	0.757595	0.000000
C	2.417960	-0.555117	0.000000
S	-0.701711	-2.026240	0.000000
C	2.871912	-1.956811	0.000000
H	2.453786	-2.468968	0.871974
H	2.453786	-2.468968	-0.871974
H	3.962842	-2.027170	0.000000
H	3.437298	1.546551	0.000000

A"	1056.9866	5.6324
A'	1097.5845	80.9547
A'	1137.4435	98.2451
A'	1191.1014	6.7332
A'	1201.3840	5.2378
A'	1244.3705	21.1169
A'	1260.8457	7.0052
A'	1347.3898	29.4245
A'	1424.1168	28.4154
A'	1439.5627	51.4092
A'	1473.2898	57.1119
A"	1481.2354	10.0434
A'	1492.1820	33.3650
A'	1539.6949	471.0834
A'	1577.3340	190.5574
A'	1666.3851	80.2927
A'	1854.9547	214.1445
A'	3071.7872	8.3113
A"	3141.5803	0.2300
A'	3159.2215	22.9598
A'	3176.7989	3.6547
A'	3182.2679	20.9722
A'	3210.4501	25.2006
A'	3220.6868	12.3204
A'	3283.5110	6.4859

2-(*Z*-2-methylcyclopropen-1-ylidene)-cyclohexa-3,5-dien-1-thione (^{3}7)



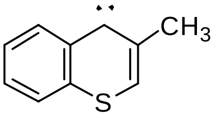
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.142373	-783.899098	-783.756725	3.2483
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-783.745229	-783.794248		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	59.8343	1.5394
A'	99.4491	0.7670
A"	123.8898	0.0105
A"	144.3245	0.0183
A"	175.4133	5.4532
A'	202.7125	0.3033
A"	269.7701	2.0911
A'	273.7335	0.4404
A"	374.6880	2.1832
A'	387.6904	0.8791
A"	443.1271	1.9308
A'	458.2347	0.8319
A"	509.8431	0.2923
A'	516.2626	4.5664
A'	661.9885	2.6263
A"	686.2183	1.6467
A"	708.8225	15.1251
A"	721.5956	55.4191
A'	735.5112	1.2557
A'	764.1157	22.9402
A"	815.5254	1.7105
A"	901.7755	2.3717
A"	947.2451	0.2183
A'	954.3018	0.2058
A'	978.5837	23.0162
A'	1038.4947	40.7563
A'	1054.1589	7.6218

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-2.736912	1.481562	0.000000
C	-2.396871	0.121266	0.000000
C	-1.065937	-0.283290	0.000000
C	0.000000	0.692489	0.000000
C	-0.392301	2.073838	0.000000
C	-1.719890	2.451866	0.000000
H	-3.782518	1.773925	0.000000
H	-3.184863	-0.627636	0.000000
H	0.394012	2.824243	0.000000
H	-1.977553	3.507875	0.000000
C	1.339977	0.341371	0.000000
C	2.732418	0.718333	0.000000
C	2.448061	-0.578087	0.000000
S	-0.671594	-2.009738	0.000000
C	2.916179	-1.980191	0.000000
H	2.527280	-2.506219	0.880356
H	2.527280	-2.506219	-0.880356
H	4.008214	-2.038201	0.000000
H	3.485304	1.493102	0.000000

A"	1059.4114	3.4595
A'	1095.8031	39.1443
A'	1145.6896	3.0569
A'	1161.9488	4.1558
A'	1183.2356	1.6595
A'	1268.1733	7.2013
A'	1320.1543	16.2752
A'	1428.2983	3.5146
A'	1438.6505	26.7496
A'	1455.2904	4.1114
A"	1498.4659	10.2958
A'	1498.7973	4.5089
A'	1547.0534	4.1625
A'	1594.0789	83.1707
A'	1599.2544	9.5838
A'	1844.7068	15.4523
A'	3048.2936	15.6238
A"	3105.1354	3.8268
A'	3141.2315	14.2247
A'	3177.2370	7.1718
A'	3182.1344	4.0483
A'	3195.0799	26.5456
A'	3210.6258	26.1564
A'	3288.4996	8.1857

3-Methyl-1-benzothiopyran-4-ylidene (^{1}8)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.145684	-783.964655	-783.818971	2.8399

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-783.808627	-783.854615

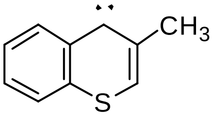
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	27.3634	4.3676
A"	112.9372	0.0044
A"	140.8476	7.0199
A"	243.8531	1.7115
A'	257.5001	3.3682
A"	274.1358	2.4961
A'	378.6964	3.7927
A'	406.8484	0.8913
A"	416.7078	0.0179
A'	453.3553	4.4069
A"	475.9989	0.3252
A'	514.7127	0.1866
A"	548.5290	4.0568
A'	637.9181	2.2542
A'	697.9939	3.2926
A"	738.8542	2.8930
A"	779.1720	47.7463
A"	849.6777	7.7360
A'	852.9573	9.5815
A'	859.3095	0.1013
A"	880.5010	0.3557
A'	969.6214	5.9855
A"	978.6083	1.6391
A"	1013.0673	0.0518
A'	1045.5176	16.9885
A'	1054.8628	5.5905
A"	1064.9576	5.2455

Atom	Coordinates (Angstroms) X	Y	Z
C	-2.825922	1.188261	0.000000
C	-2.286787	-0.087192	0.000000
C	-0.888377	-0.247371	0.000000
C	0.000000	0.871596	0.000000
C	-0.617990	2.157118	0.000000
C	-1.988561	2.321175	0.000000
H	-3.905858	1.311310	0.000000
H	-2.938184	-0.958010	0.000000
C	1.442733	0.856629	0.000000
H	0.060817	3.004221	0.000000
H	-2.425690	3.315679	0.000000
C	2.078802	-0.433191	0.000000
C	1.428650	-1.645030	0.000000
H	1.962821	-2.594266	0.000000
S	-0.272230	-1.878835	0.000000
C	3.596966	-0.441714	0.000000
H	3.971209	0.096621	0.877908
H	4.022265	-1.452496	0.000000
H	3.971209	0.096621	-0.877908

A'	1083.8385	4.3868
A'	1142.6135	9.9375
A'	1182.0533	17.2215
A'	1198.0942	0.4548
A'	1270.4826	7.4628
A'	1281.4182	5.4703
A'	1338.4760	21.2840
A'	1392.4868	40.6186
A'	1434.1283	0.2283
A'	1470.1216	10.9098
A'	1474.6913	10.1498
A'	1495.0761	7.9289
A"	1500.0334	5.3728
A'	1536.9841	45.0882
A'	1583.3515	7.9059
A'	1646.4256	20.5866
A'	3044.2551	38.4602
A"	3115.2773	13.7642
A'	3115.3056	19.5147
A'	3168.2529	11.4567
A'	3178.7293	2.0312
A'	3193.1327	11.6727
A'	3206.3120	20.5802
A'	3221.6664	13.2006

3-Methyl-1-benzothiopyran-4-ylidene (^{3}8)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.145047	-783.961770	-783.816723	0.4922

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-783.806269	-783.85295

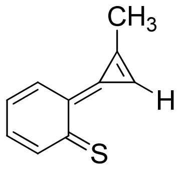
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	68.6094	2.0927
A"	82.9108	0.0448
A"	159.9483	1.3659
A"	206.4396	0.4860
A'	240.2121	1.9231
A"	272.1568	0.4247
A'	360.0737	0.9081
A'	400.1455	1.7680
A'	429.9999	0.3006
A"	443.5643	1.2819
A'	501.1661	0.0204
A"	507.7321	0.5881
A"	576.3297	0.2001
A'	633.6063	0.6376
A"	674.4000	23.1217
A'	692.1179	2.6714
A"	725.7222	6.6144
A"	760.3244	47.0189
A'	815.8629	7.4347
A'	854.9359	0.7973
A"	865.1913	0.3203
A"	931.4818	1.8408
A'	973.5941	5.6206
A"	975.9082	0.0003
A'	1035.0214	9.3347
A'	1055.6425	13.7069
A"	1064.6988	2.6244

Atom	Coordinates (Angstroms) X	Y	Z
C	-2.797387	1.318426	0.000000
C	-2.286100	0.019475	0.000000
C	-0.907718	-0.196783	0.000000
C	0.000000	0.906188	0.000000
C	-0.550690	2.210620	0.000000
C	-1.924241	2.411929	0.000000
H	-3.872307	1.473264	0.000000
H	-2.963344	-0.831063	0.000000
C	1.390815	0.660627	0.000000
H	0.131861	3.055279	0.000000
H	-2.319865	3.423817	0.000000
C	2.105755	-0.530549	0.000000
C	1.415905	-1.728294	0.000000
H	1.924577	-2.687097	0.000000
S	-0.333841	-1.885596	0.000000
C	3.620806	-0.524420	0.000000
H	4.008017	-0.002843	0.882703
H	4.021638	-1.542284	0.000000
H	4.008017	-0.002843	-0.882703

A'	1078.9984	4.5801
A'	1148.2389	5.2601
A'	1192.2397	0.1542
A'	1208.2221	0.7853
A'	1283.7173	4.6015
A'	1306.2527	5.7166
A'	1323.2661	1.8318
A'	1376.2098	25.2839
A'	1436.7831	0.1840
A'	1464.5142	3.5767
A'	1477.6886	3.5539
A'	1504.5357	15.1398
A"	1508.4163	6.0020
A'	1530.6119	13.3791
A'	1594.5208	3.1808
A'	1623.1497	0.0221
A'	3052.8997	31.9376
A"	3111.2500	15.7958
A'	3134.6614	16.4238
A'	3183.3314	1.4827
A'	3191.2552	5.4838
A'	3204.6557	18.2538
A'	3210.9950	2.8638
A'	3214.2808	22.8375

2-(*E*-2-methylcyclopropen-1-ylidene)-cyclohexa-3,5-dien-1-thione (^{1}9)



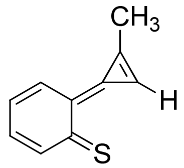
Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.145264	-783.963928	-783.818665	7.7766
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-783.807591	-783.855145		

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	72.6383	2.2733
A"	83.2794	1.4066
A'	100.4530	1.7563
A"	107.7904	1.9820
A"	185.1537	0.8318
A'	216.2733	2.0156
A"	333.8563	4.5905
A'	343.5302	3.7361
A'	378.8093	6.3373
A"	415.7773	0.0148
A'	495.4241	4.6961
A"	497.5067	6.2325
A'	550.9270	1.2414
A"	580.7920	1.4905
A'	670.4563	15.5591
A"	737.1845	6.0093
A'	761.1817	1.3229
A"	763.4716	36.8710
A'	815.0048	11.4207
A"	841.2569	16.3015
A"	866.1279	2.1783
A'	951.0857	1.2394
A"	951.6335	0.0194
A"	1005.3027	0.4620
A'	1030.3922	21.5893
A'	1041.6543	12.5166
A"	1058.6335	3.8687

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	2.378884	1.805686	0.000000
C	2.440684	0.435825	0.000000
C	1.264553	-0.390804	0.000000
C	0.000000	0.341760	0.000000
C	-0.025679	1.778465	0.000000
C	1.132093	2.501599	0.000000
H	3.302601	2.380267	0.000000
H	3.399199	-0.073012	0.000000
H	-0.992225	2.277924	0.000000
H	1.113167	3.587187	0.000000
C	-1.197527	-0.346522	0.000000
C	-2.610231	-0.428818	0.000000
C	-1.894955	-1.563515	0.000000
H	-1.831288	-2.640473	0.000000
S	1.393047	-2.083578	0.000000
C	-3.913578	0.268053	0.000000
H	-4.748383	-0.437107	0.000000
H	-3.988640	0.916041	0.881297
H	-3.988640	0.916041	-0.881297

A'	1098.6659	116.6440
A'	1141.7582	40.3580
A'	1190.0692	11.5768
A'	1196.6815	18.7125
A'	1242.1683	33.4338
A'	1265.1596	3.8134
A'	1346.0857	21.8465
A'	1426.9230	11.1250
A'	1441.1191	82.8747
A'	1490.2921	21.7503
A'	1494.7863	103.4681
A"	1500.9014	10.2027
A'	1538.1225	479.9199
A'	1578.4937	170.3241
A'	1666.6771	76.2381
A'	1855.4095	189.1634
A'	3056.3656	5.9331
A"	3115.1280	1.8740
A'	3152.9314	9.3286
A'	3173.0572	4.9171
A'	3180.7843	21.4751
A'	3208.9555	24.5721
A'	3218.9011	12.9142
A'	3328.3968	16.6768

2-(*E*-2-methylcyclopropen-1-ylidene)-cyclohexa-3,5-dien-1-thione (^{3}9)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.142342	-783.898769	-783.756427	3.7750

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-783.744884	-783.794148

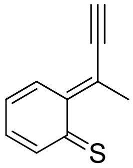
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	80.8451	0.7638
A'	88.6557	0.6099
A"	90.3909	1.6512
A"	138.3190	0.1747
A'	180.0837	0.1972
A"	193.3764	4.5523
A"	255.6209	1.9495
A'	311.1204	0.4419
A'	357.4898	0.1572
A"	371.2476	1.7282
A"	445.7814	3.3759
A'	469.5480	1.4103
A"	510.9009	0.0708
A'	515.0582	3.1924
A'	664.0277	3.3330
A"	687.3120	1.8436
A"	720.8156	40.4370
A'	721.8317	9.1629
A"	740.1454	25.7364
A'	763.0986	6.0620
A"	812.9805	1.2011
A"	901.5724	2.3176
A"	945.5222	0.3652
A'	968.6570	3.7711
A'	977.9639	14.7096
A'	1039.2493	33.5833
A'	1054.2865	12.4519

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	2.435002	1.812402	0.000000
C	2.462952	0.410349	0.000000
C	1.284599	-0.328899	0.000000
C	0.000000	0.335120	0.000000
C	0.016713	1.771473	0.000000
C	1.199339	2.482986	0.000000
H	3.367467	2.368500	0.000000
H	3.419559	-0.106055	0.000000
H	-0.937656	2.292067	0.000000
H	1.172094	3.569679	0.000000
C	-1.193052	-0.365802	0.000000
C	-2.633714	-0.424383	0.000000
C	-1.975250	-1.576164	0.000000
H	-2.010779	-2.656204	0.000000
S	1.352478	-2.098629	0.000000
C	-3.916514	0.309701	0.000000
H	-4.771713	-0.372032	0.000000
H	-3.979535	0.960706	0.880961
H	-3.979535	0.960706	-0.880961

A"	1056.6719	3.5863
A'	1094.4132	23.7965
A'	1137.5101	10.4323
A'	1168.2299	10.1541
A'	1184.5434	2.9259
A'	1268.8348	7.9513
A'	1319.5077	14.1222
A'	1428.4518	3.6198
A'	1438.7146	29.4062
A'	1455.0158	4.9267
A"	1500.6828	8.3072
A'	1501.2079	5.6121
A'	1546.3666	3.1330
A'	1598.2944	44.0534
A'	1601.6500	54.0907
A'	1845.5841	14.1624
A'	3044.3537	26.5267
A"	3098.5615	6.7435
A'	3138.8793	11.9986
A'	3175.3574	8.1695
A'	3181.6459	3.1187
A'	3193.3106	28.9041
A'	3210.4675	25.4678
A'	3286.6028	6.9489

2-(*E*-but-1-yn-3-ylidene)-cyclohexa-3,5-dien-1-thione (^{1}10)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.144410	-783.961353	-783.816943	4.1140

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-783.805812	-783.853314

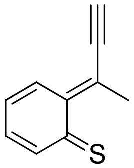
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	35.1761	1.3767
A"	75.2299	0.0074
A'	158.3125	0.2704
A"	186.1818	0.7469
A'	258.3016	2.7488
A"	264.3768	0.7831
A"	304.0455	1.9081
A'	310.9354	0.2172
A'	363.5755	10.0973
A"	440.4434	0.8022
A'	485.2155	1.5517
A"	492.8132	2.4770
A'	497.3361	6.4366
A"	597.5609	4.4705
A'	607.2257	1.1852
A'	616.5768	50.8345
A"	619.0196	39.1103
A'	675.9344	10.3899
A"	746.5533	12.2279
A'	772.3639	0.5371
A"	784.4736	29.9852
A"	872.0346	0.2607
A'	939.0413	7.3011
A"	981.9051	0.1582
A"	1010.0181	0.4142
A'	1032.2144	27.5580
A"	1033.5210	2.5878

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-2.104710	-1.017224	0.000000
C	-0.661060	-1.019069	0.000000
C	0.000000	0.305624	0.000000
C	-0.850498	1.482684	0.000000
C	-2.206893	1.406625	0.000000
C	-2.846195	0.127264	0.000000
H	-2.585546	-1.989374	0.000000
H	-0.365217	2.451823	0.000000
H	-2.806843	2.311890	0.000000
H	-3.931742	0.069946	0.000000
S	0.104644	-2.523495	0.000000
C	1.384317	0.513014	0.000000
C	1.899896	1.837490	0.000000
C	2.431873	2.928193	0.000000
H	2.882665	3.895150	0.000000
C	2.452470	-0.543127	0.000000
H	2.347535	-1.205808	0.867564
H	2.347535	-1.205808	-0.867564
H	3.442105	-0.080742	0.000000

A'	1082.1032	24.1934
A'	1090.4781	43.0382
A'	1146.2758	22.2107
A'	1185.0679	8.4575
A'	1235.1468	1.4291
A'	1265.3943	25.8658
A'	1339.7594	4.6027
A'	1417.2372	20.0608
A'	1429.6617	15.7046
A'	1480.5492	54.8141
A"	1483.6717	9.6698
A'	1495.2390	4.7147
A'	1516.4482	103.0908
A'	1573.9328	26.9333
A'	1682.1403	29.4946
A'	2186.2243	10.6007
A'	3044.6215	2.6666
A"	3087.1005	1.2985
A'	3148.2696	25.9694
A'	3189.3795	11.5202
A'	3205.3397	13.5566
A'	3225.1548	6.4035
A'	3229.8861	9.3679
A'	3489.2967	95.9145

2-(*E*-but-1-yn-3-ylidene)-cyclohexa-3,5-dien-1-thione (^{3}10)



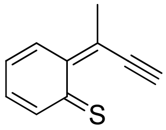
Charge	**Multiplicity**	**Theory/Basis Set**	**Full Point Group**
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.142724	-783.928055	-783.785331	0.7378
$\Delta H_{(298)}$	**$\Delta G_{(298)}$**	(Energies in Hartrees/particle)	
-783.773919	-783.822571		

Symmetry	**Vibrational Frequency (cm^{-1})**	**Intensity**
A"	48.7002	0.1992
A"	115.1376	1.1035
A'	145.4980	0.1152
A"	175.6891	0.6027
A"	210.9299	1.4934
A'	223.4689	0.2060
A'	279.8837	0.0457
A"	309.5762	0.1191
A'	346.7250	0.3327
A"	419.5211	50.2225
A"	462.1842	0.6045
A'	465.6744	1.5666
A'	475.6838	1.0538
A"	508.8701	3.2251
A"	595.3898	0.2077
A'	612.8245	3.0697
A'	621.3310	46.7843
A'	676.8690	0.4522
A"	726.5199	1.7138
A'	747.8040	7.1365
A"	778.7800	55.7147
A"	870.4783	0.5460
A'	933.9206	0.7350
A"	944.4329	3.7694
A"	978.5222	0.0226
A"	1031.4676	0.4849

Atom	**Coordinates (Angstroms)**		
	X	**Y**	**Z**
C	-2.158120	-0.848825	0.000000
C	-0.753048	-0.886456	0.000000
C	0.000000	0.331899	0.000000
C	-0.754161	1.539990	0.000000
C	-2.135795	1.562236	0.000000
C	-2.849471	0.357407	0.000000
H	-2.713864	-1.782693	0.000000
H	-0.201791	2.473559	0.000000
H	-2.661024	2.512974	0.000000
H	-3.935667	0.353640	0.000000
S	-0.061486	-2.518211	0.000000
C	1.443768	0.413262	0.000000
C	2.078029	1.660939	0.000000
C	2.681049	2.722170	0.000000
H	3.202052	3.652241	0.000000
C	2.358850	-0.788612	0.000000
H	2.211408	-1.416896	0.889744
H	2.211408	-1.416896	-0.889744
H	3.404645	-0.468622	0.000000

A'	1050.0334	21.7438
A'	1059.2513	14.2695
A'	1096.3480	3.5730
A'	1143.3331	1.0030
A'	1197.4999	2.6245
A'	1244.2435	1.3169
A'	1289.0941	9.3356
A'	1309.8958	7.1996
A'	1345.8091	6.6129
A'	1426.5246	2.1630
A'	1456.4524	5.6794
A'	1485.2221	39.0657
A'	1511.5031	29.0366
A"	1520.5445	16.8713
A'	1580.7975	5.5668
A'	1625.0562	4.9851
A'	2095.6449	1.1330
A'	3015.0218	8.5820
A"	3064.2937	6.2676
A'	3126.9227	7.1590
A'	3183.2662	1.9104
A'	3195.4564	8.4681
A'	3209.9566	18.5681
A'	3221.5242	9.4033
A'	3489.0764	82.6027

2-(*Z*-but-1-yn-3-ylidene)-cyclohexa-3,5-dien-1-thione (^{1}11)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	1	RB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.144288	-783.956215	-783.811926	3.8542

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-783.800553	-783.848751

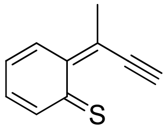
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A"	27.1391	1.4092
A"	82.7547	0.0719
A"	160.9506	1.0935
A'	172.5670	1.3944
A"	183.4090	0.1884
A'	207.5317	2.1226
A"	292.2368	1.3604
A'	320.2477	0.5647
A'	363.6106	7.9990
A"	444.7242	0.0945
A'	452.7441	0.2197
A"	489.8735	3.4695
A'	505.4823	5.5318
A'	573.9633	54.7129
A"	601.1731	0.0497
A'	605.6583	2.5882
A'	661.8403	16.5740
A"	666.0639	34.9801
A"	747.4164	19.9903
A"	773.6120	25.7851
A'	774.9149	0.0318
A"	865.6789	0.6935
A'	952.1231	4.0149
A"	973.5564	0.1083
A"	1008.9521	0.3847
A'	1032.3292	13.3271
A"	1046.9840	1.3343

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	2.251154	-0.511181	0.000000
C	0.816018	-0.683283	0.000000
C	0.000000	0.553728	0.000000
C	0.702320	1.823075	0.000000
C	2.059349	1.906782	0.000000
C	2.849616	0.713026	0.000000
H	2.843989	-1.419499	0.000000
H	0.123129	2.738254	0.000000
H	2.547737	2.876965	0.000000
H	3.933949	0.789003	0.000000
S	0.210330	-2.248730	0.000000
C	-1.393646	0.579202	0.000000
C	-2.238104	-0.550066	0.000000
C	-3.184868	-1.316754	0.000000
C	-2.166783	1.891189	0.000000
H	-1.929305	2.492983	0.885086
H	-1.929305	2.492983	-0.885086
H	-3.239357	1.695170	0.000000
H	-3.886453	-2.120484	0.000000

A'	1072.3038	3.8565
A'	1097.0464	58.2943
A'	1169.5950	12.3594
A'	1182.6584	6.8278
A'	1231.8564	8.4671
A'	1257.0906	15.6038
A'	1345.1757	8.2295
A'	1423.8230	23.6752
A'	1427.0276	2.0007
A'	1483.7077	49.2027
A'	1518.8195	29.8200
A"	1521.9250	7.7595
A'	1538.0816	66.0616
A'	1576.8285	8.8959
A'	1680.3144	25.5423
A'	2152.9932	40.9764
A'	3051.0553	12.1548
A"	3107.3233	9.7241
A'	3169.0586	8.7365
A'	3188.8585	10.6987
A'	3204.1637	15.0102
A'	3224.6928	9.2847
A'	3236.1129	14.2006
A'	3487.2214	62.1908

2-(*Z*-but-1-yn-3-ylidene)-cyclohexa-3,5-dien-1-thione (^{3}11)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_S

Zero-point Energy	Electronic Energy	Electronic and Zero-Point Energy	Dipole Moment (D)
0.141974	-783.936942	-783.794968	1.6760

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-783.78317	-783.83313

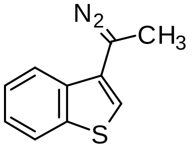
(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A''	24.8796	0.4089
A''	115.0119	0.6778
A'	133.6794	3.4504
A''	159.1324	1.1176
A'	180.7677	1.0159
A''	186.4113	1.4989
A'	287.4757	0.0102
A''	291.7553	7.3636
A''	319.4401	44.6294
A'	365.9683	4.3666
A'	422.3189	0.8407
A''	447.7192	0.1652
A''	491.9649	2.3728
A'	493.3203	0.5979
A''	566.5518	0.4525
A'	584.9226	1.7132
A'	620.5601	58.2166
A'	676.6276	3.6973
A''	722.9575	10.5907
A'	752.6735	1.4294
A''	761.1512	38.0206
A''	857.0890	0.0308
A''	934.8036	1.1935
A'	948.3166	1.0338
A''	972.1246	0.1534
A''	1036.6890	0.7159
A'	1058.0800	12.3434

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	2.232410	-0.400577	0.000000
C	0.835857	-0.548047	0.000000
C	0.000000	0.615090	0.000000
C	0.637207	1.884071	0.000000
C	2.015619	2.009541	0.000000
C	2.819140	0.860844	0.000000
H	2.859339	-1.287471	0.000000
H	0.023759	2.778718	0.000000
H	2.469943	2.996132	0.000000
H	3.902087	0.948068	0.000000
S	0.171054	-2.173407	0.000000
C	-1.431857	0.512065	0.000000
C	-2.082124	-0.720458	0.000000
C	-2.868365	-1.672245	0.000000
C	-2.311910	1.744028	0.000000
H	-2.126172	2.367561	0.884463
H	-2.126172	2.367561	-0.884463
H	-3.367738	1.465850	0.000000
H	-3.447752	-2.567779	0.000000

A'	1063.9823	8.4711
A'	1097.4676	14.9151
A'	1158.3776	0.7311
A'	1197.1011	2.7101
A'	1239.6231	10.4486
A'	1285.5151	11.8609
A'	1336.9842	2.3055
A'	1365.8584	7.2077
A'	1431.8458	0.0600
A'	1465.6149	5.0450
A'	1481.8549	25.0105
A"	1513.2704	6.9961
A'	1524.5735	12.6205
A'	1584.6759	7.7378
A'	1620.9340	11.0315
A'	1981.1994	23.6838
A'	3032.7405	23.2642
A"	3081.4820	17.0984
A'	3150.6635	10.4304
A'	3187.0662	0.1850
A'	3197.6105	7.6177
A'	3208.8164	24.7807
A'	3220.1702	17.2600
A'	3479.6056	91.3596

s-*E*-1-(3-benzothienyl) diazoethane (^{1}16-s-*E*)



Charge	**Multiplicity**	**Theory/Basis Set**	**Full Point Group**
0	1	RB3LYP/6-31G(d)	C_1
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.157014	-893.517216	-893.360202	2.1992

$\Delta H_{(298)}$	**$\Delta G_{(298)}$**
-893.348074	-893.398196

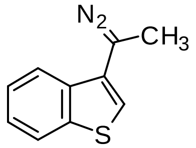
(Energies in Hartrees/particle)

Symmetry	**Vibrational Frequency (cm^{-1})**	**Intensity**
A	26.7385	1.2694
A	89.9226	0.5734
A	131.8409	0.8097
A	176.8491	0.9611
A	196.3645	0.9588
A	207.9327	1.1609
A	216.6081	1.0567
A	294.2670	1.4470
A	320.0213	0.5284
A	397.3665	1.8742
A	427.3347	1.9691
A	435.2720	2.7418
A	496.1409	0.7677
A	506.0478	0.6293
A	524.6437	6.9765
A	575.9276	0.7375
A	617.8005	1.2690
A	653.8744	11.3850
A	722.0534	5.7400
A	743.2866	28.1860
A	752.3344	1.3836
A	767.1664	43.0275
A	777.6575	3.5365
A	843.2519	20.8318
A	865.3200	0.2890
A	938.9943	0.6565
A	948.2923	4.1927
A	980.3178	0.1465

Atom	**Coordinates (Angstroms)**		
	X	**Y**	**Z**
C	-0.552216	-0.356482	-0.002598
C	-1.531219	0.669228	0.027681
C	-2.899595	0.394100	-0.058421
C	-3.305215	-0.928709	-0.182261
C	-2.354007	-1.961936	-0.229961
C	-0.995890	-1.686464	-0.145049
C	0.800397	0.180003	0.099787
C	0.791228	1.547164	0.187195
H	-3.627843	1.199677	-0.032193
H	-4.363807	-1.163411	-0.248668
H	-2.684559	-2.991026	-0.339671
H	-0.282958	-2.500766	-0.196998
H	1.652470	2.194672	0.289178
S	-0.799393	2.258784	0.148884
C	2.030831	-0.623040	0.098010
C	2.173079	-2.042211	0.606415
H	3.204470	-2.233065	0.919272
H	1.526732	-2.198737	1.475808
H	1.915842	-2.795878	-0.149443
N	3.124724	-0.032255	-0.292934
N	4.090358	0.489122	-0.636239

A	1030.6365	18.5790
A	1058.8874	8.0388
A	1062.0566	0.9987
A	1079.4673	19.0636
A	1165.3709	3.2674
A	1180.0611	4.0055
A	1203.1685	0.4434
A	1277.5937	2.9752
A	1297.4839	8.0448
A	1329.2010	6.9278
A	1365.8592	0.3911
A	1414.9912	23.7039
A	1443.1347	8.1590
A	1474.6289	17.9925
A	1503.3437	2.9752
A	1510.2136	11.9851
A	1536.5545	16.5012
A	1559.4677	4.5203
A	1614.0718	0.1203
A	1650.6579	1.3475
A	2169.5165	646.2105
A	3036.5168	32.1443
A	3099.9598	16.6402
A	3133.3348	13.0871
A	3188.1427	1.0651
A	3198.6529	11.4512
A	3211.1143	26.5605
A	3236.0444	11.9144
A	3257.4663	2.6751

s-*E*-1-(3-benzothienyl) diazoethane (^{3}16-s-*E*)



Charge	**Multiplicity**	**Theory/Basis Set**	**Full Point Group**
0	3	UB3LYP/6-31G(d)	C_S
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.155163	-893.490115	-893.334952	3.9710

$\Delta H_{(298)}$	**$\Delta G_{(298)}$**
-893.322902	-893.373452

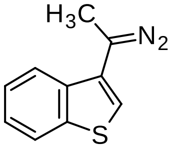
(Energies in Hartrees/particle)

Symmetry	**Vibrational Frequency (cm^{-1})**	**Intensity**
A"	39.7113	1.9440
A"	85.5378	0.1869
A'	159.0906	1.1948
A"	179.9005	0.0030
A"	208.9370	1.2204
A"	226.4540	2.4417
A"	260.8858	0.0960
A'	276.4343	2.6495
A'	324.9423	2.9129
A'	393.5198	1.7377
A"	413.2841	0.6301
A'	415.6554	1.0254
A"	446.7336	3.0553
A'	503.5009	0.2173
A"	514.6876	0.0051
A'	588.3719	1.2748
A"	631.1616	0.0429
A'	657.3476	41.1089
A'	720.2626	2.5799
A"	745.7221	19.6664
A'	753.8230	6.5190
A"	770.7342	53.1466
A"	784.6600	1.1258
A'	849.2280	14.2208
A"	870.0884	0.0372
A'	896.9329	38.9979
A"	944.0367	0.6853
A"	986.3575	0.0548

Atom	**Coordinates (Angstroms)**		
	X	**Y**	**Z**
C	0.000000	0.668700	0.000000
C	1.382674	0.980215	0.000000
C	1.859105	2.292576	0.000000
C	0.936536	3.332684	0.000000
C	-0.438259	3.055770	0.000000
C	-0.906503	1.746443	0.000000
C	-0.232175	-0.780950	0.000000
C	0.974718	-1.473223	0.000000
H	2.926361	2.494031	0.000000
H	1.283911	4.361816	0.000000
H	-1.151465	3.875083	0.000000
H	-1.974052	1.571615	0.000000
H	1.077253	-2.548785	0.000000
S	2.380271	-0.470424	0.000000
C	-1.486186	-1.469184	0.000000
C	-2.840615	-0.819969	0.000000
H	-3.613318	-1.592013	0.000000
H	-2.986695	-0.188121	0.885097
H	-2.986695	-0.188121	-0.885097
N	-1.402333	-2.861575	0.000000
N	-2.334153	-3.632294	0.000000

A'	1013.0756	5.4017
A"	1041.6072	0.8676
A'	1063.1657	6.4807
A'	1075.4852	15.5511
A'	1137.1214	2.4996
A'	1167.3391	0.8013
A'	1188.0276	0.2666
A'	1208.9919	2.2096
A'	1282.0891	30.5727
A'	1311.8455	2.4945
A'	1357.8587	0.1079
A'	1387.7447	1.0866
A'	1424.3542	2.5547
A'	1439.1895	66.5026
A'	1498.8094	45.6619
A'	1503.9553	1.6254
A"	1513.9200	9.1622
A'	1517.5114	19.0778
A'	1614.5442	4.8370
A'	1634.1981	60.6948
A'	1651.0208	0.4461
A'	3039.3566	9.7868
A"	3091.1726	10.8431
A'	3148.2377	4.4727
A'	3191.7141	0.9236
A'	3201.9830	10.5649
A'	3214.1556	23.2307
A'	3257.5907	6.2263
A'	3284.4841	6.6120

s-*Z*-1-(3-benzothienyl) diazoethane (^{1}16-s-*Z*)



Charge	**Multiplicity**	**Theory/Basis Set**	**Full Point Group**
0	1	RB3LYP/6-31G(d)	C_1
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.157110	-893.520203	-893.363092	1.1684
ΔH$_{(298)}$	**ΔG$_{(298)}$**	(Energies in Hartrees/particle)	
-893.350971	-893.401604		

Symmetry	**Vibrational Frequency (cm^{-1})**	**Intensity**
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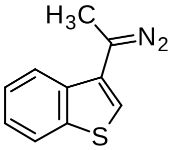
A	97.6578	0.4827
A	138.1566	2.4390
A	177.9607	0.3681
A	199.9739	0.3788
A	214.5696	0.8582
A	224.6698	1.0277
A	290.1588	0.4034
A	325.0293	0.0961
A	409.1090	1.0601
A	422.3295	0.9059
A	430.3468	3.1037
A	488.0865	0.9960
A	505.7212	0.3403
A	512.0130	3.1501
A	563.7443	1.8418
A	619.8713	0.0739
A	662.8862	8.7237
A	719.3711	7.7669
A	740.7874	40.3446
A	751.5131	4.5932
A	751.8083	21.6163
A	774.7494	16.6087
A	848.0811	31.9542
A	866.6147	0.0987
A	933.4497	2.8054
A	940.6856	0.5711
A	982.7366	0.0867

Atom	**Coordinates (Angstroms)**		
	X	**Y**	**Z**
C	0.416492	0.293085	0.016657
C	1.579509	-0.517634	-0.020050
C	2.867690	0.025639	-0.016265
C	3.006386	1.407052	0.028264
C	1.870813	2.231939	0.073483
C	0.591838	1.690458	0.069678
C	-0.804794	-0.510712	0.007002
C	-0.520287	-1.851994	-0.023723
H	3.739772	-0.621319	-0.045373
H	3.998628	1.849311	0.031281
H	1.991315	3.310784	0.113860
H	-0.259860	2.357850	0.111426
H	-1.229858	-2.667009	-0.039211
S	1.182565	-2.226033	-0.051438
C	-2.186528	-0.042440	0.035208
C	-3.351745	-0.999949	0.144443
H	-3.395838	-1.673288	-0.721948
H	-3.261776	-1.618115	1.046441
H	-4.299290	-0.457801	0.197289
N	-2.485618	1.219239	-0.079223
N	-2.803009	2.321253	-0.172055

A	1040.4271	8.2085
A	1060.8174	0.8403
A	1062.4184	7.1127
A	1081.3927	9.0564
A	1171.4147	1.8583
A	1184.8451	5.3446
A	1209.0164	0.1660
A	1245.2552	2.3245
A	1304.7164	5.6641
A	1360.0233	1.3449
A	1391.6115	1.3466
A	1402.9097	18.0637
A	1440.2003	3.0710
A	1476.5305	8.9790
A	1505.3583	8.1699
A	1506.3092	5.7833
A	1534.0508	10.4560
A	1563.8882	26.0018
A	1615.8888	0.8891
A	1651.3083	0.9697
A	2167.9110	630.7747
A	3034.3216	28.2382
A	3085.5929	18.7823
A	3143.1419	9.8093
A	3188.8110	0.7722
A	3199.7189	12.3164
A	3211.5217	24.6627
A	3245.5241	5.5980
A	3273.6428	4.3322

s-*Z*-1-(3-benzothienyl) diazoethane (^{3}16-s-*Z*)



Charge	Multiplicity	Theory/Basis Set	Full Point Group
0	3	UB3LYP/6-31G(d)	C_1
Zero-point Energy	**Electronic Energy**	**Electronic and Zero-Point Energy**	**Dipole Moment (D)**
0.154894	-893.482944	-893.328051	3.0124

$\Delta H_{(298)}$	$\Delta G_{(298)}$
-893.315897	-893.366713

(Energies in Hartrees/particle)

Symmetry	Vibrational Frequency (cm^{-1})	Intensity
A	35.1076	3.0633
A	93.7897	0.3268
A	155.2660	0.9734
A	178.6410	1.6034
A	201.3341	1.1936
A	214.9370	0.5023
A	225.2966	0.3197
A	248.6964	1.6452
A	311.9051	0.3839
A	394.9730	3.0199
A	419.4477	1.2243
A	446.3739	3.1887
A	483.9439	9.6335
A	506.5316	1.7368
A	515.1728	0.0643
A	547.9163	2.8265
A	616.1719	4.4614
A	643.9021	6.1887
A	719.5288	6.5633
A	742.2267	16.1657
A	749.5776	3.2322
A	763.3080	47.9467
A	780.9105	5.8866
A	862.7873	16.8964
A	869.8791	1.4800
A	913.5864	30.4516
A	949.1644	0.9263
A	988.9613	0.1412

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	0.405714	-0.301925	-0.050996
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C	2.822719	0.203473	0.036085
C	3.098849	-1.148689	-0.124011
C	2.050404	-2.070224	-0.265963
C	0.722536	-1.661903	-0.234315
C	-0.891674	0.389616	-0.028045
C	-0.711807	1.761198	0.067934
H	3.623833	0.930808	0.130017
H	4.130048	-1.489556	-0.146665
H	2.276335	-3.123912	-0.402018
H	-0.065063	-2.396397	-0.332839
H	-1.491961	2.507910	0.111795
S	0.933046	2.274237	0.185917
C	-2.235282	-0.134749	-0.114526
C	-3.381473	0.766218	-0.487293
H	-3.629154	1.466280	0.324163
H	-3.157132	1.364192	-1.377723
H	-4.269126	0.159045	-0.677260
N	-2.638474	-1.421917	0.193837
N	-2.010435	-2.331489	0.696070

A	1015.4667	2.2665
A	1043.4681	1.6679
A	1062.4086	6.8051
A	1080.0789	8.8616
A	1166.7545	0.4068
A	1180.5492	3.1442
A	1191.8463	25.8271
A	1211.2110	2.3271
A	1255.0210	15.9716
A	1306.7368	10.8825
A	1360.5457	1.0684
A	1386.2921	13.7606
A	1428.0062	16.1050
A	1436.1703	20.1860
A	1494.8382	20.8876
A	1503.9377	2.7779
A	1508.4200	10.7881
A	1516.7245	24.9145
A	1589.0495	136.8934
A	1612.7812	2.0986
A	1649.7596	1.0647
A	3027.1491	13.3020
A	3091.5751	14.3379
A	3154.9406	7.2774
A	3190.9016	0.9352
A	3202.0484	12.0975
A	3213.3481	23.3473
A	3255.3647	1.5625
A	3275.7384	1.7549

Chapter 4: Photochemistry of Furyl- and Thienyldiazomethanes: Spectroscopic Characterization of Triplet 3-Thienylcarbene

Chapter 4: Photochemistry of Furyl- and Thienyldiazomethanes: Spectroscopic Characterization of Triplet 3-Thienylcarbene

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Abstract: Photolysis ($\lambda > 543$ nm) of 3-thienyldiazomethane (**1**), matrix isolated in Ar or N_2 at 10 K, yields triplet 3-thienylcarbene (**13**) and α-thial-methylenecyclopropene (**9**). Carbene **13** was characterized by IR, UV/vis, and EPR spectroscopy. The conformational isomers of 3-thienylcarbene (*s-E* and *s-Z*) exhibit an unusually large difference in zero-field splitting parameters in the triplet EPR spectrum ($|D/hc| = 0.508$ cm^{-1}, $|E/hc| = 0.0554$ cm^{-1}; $|D/hc| = 0.579$ cm^{-1}, $|E/hc| = 0.0315$ cm^{-1}). Natural Bond Orbital (NBO) calculations reveal substantially differing spin densities in the 3-thienyl ring at the positions adjacent to the carbene center, which is one factor contributing to the large difference in *D* values. NBO calculations also reveal a stabilizing interaction between the *sp* orbital of the carbene carbon in the *s-Z* rotamer of **13** and

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the antibonding sigma orbital between sulfur and the neighboring carbon – an interaction that is not observed in the *s-E* rotamer of **13**. In contrast to the EPR spectra, the electronic absorption spectra of the rotamers of triplet 3-thienylcarbene (**13**) are indistinguishable under our experimental conditions. The carbene exhibits a weak electronic absorption in the visible spectrum (λ_{max} = 467 nm) that is characteristic of triplet arylcarbenes. Although studies of 2-thienyldiazomethane (**2**), 3-furyldiazomethane (**3**), or 2-furyldiazomethane (**4**) provided further insight into the photochemical interconversions among C_5H_4S or C_5H_4O isomers, these studies did not lead to the spectroscopic detection of the corresponding triplet carbenes (2-thienylcarbene (**11**), 3-furylcarbene (**23**), or 2-furylcarbene (**22**), respectively).

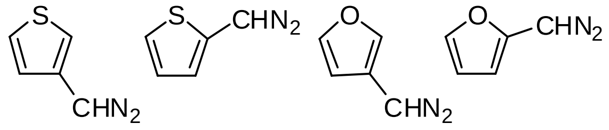
Introduction

The chemistry of aryl and hetero-aryl carbenes constitutes a subject of longstanding interest in the field of organic reactive intermediates.[1-3] Basic relationships concerning the structure, reactivity, and spectroscopy of these intermediates have been deduced through product analyses, matrix-isolation spectroscopy, time-resolved spectroscopy, and computational studies. Characteristic features of any particular system are often governed by the electronic ground state (singlet or triplet) of the carbene in question. In the singlet series, the chemistry and spectroscopy of arylchlorocarbenes (phenyl,[4,5] pyridyl,[6] furanyl,[7,8] thienyl,[9,10] and their benzo analogs[11-14]) have been extensively investigated. Our own interest in arylcarbenes focuses on the triplet series because these species – lacking the halogen substituent – are more directly relevant to the harsh reaction environments encountered in combustion or in astrochemistry.[15] That the chemistry of atomic carbon is important in astronomical environments invites attention to aryl- and hetero-aryl carbenes, as these intermediates may be formed upon addition of a carbon atom to a stable, closed-shell aryl substrate. In the current study, we focus on the isomeric furyl- and thienylcarbenes, which have eluded detection and characterization to the present time.[16,17] These fundamental studies of reactive thienyl intermediates are also germane to an understanding of the electronic structure of doped states of thiophene derivatives – materials that have achieved wide use in conducting polymers and other electronic applications.[18-20]

Background

Shechter and coworkers reported detailed product analyses associated with thermolysis of the isomeric thienyldiazomethanes (**1** and **2**) and furyldiazomethanes (**3** and **4**) (Scheme 4.1).[21,22] The intermediacy of the corresponding thienyl- and furylcarbenes was inferred from the isolation of the products of insertion into the C-H bond of cyclooctane and the formal products of dimerization. Fragmentation of the ring, to afford ring-opened products, was also observed. Shevlin and workers later postulated the intermediacy of 2- and 3-thienylcarbene in the reaction of atomic ^{13}C with thiophene.[23,24] Saito and coworkers devised intriguing systems in which the thermal furylcarbene fragmentation reaction is driven in the reverse direction under photochemical conditions. Thus, an acyclic enynal or enynone will undergo photocyclization to a 2-furylcarbene derivative, which can be trapped in either an inter- or intramolecular fashion.[25]

Scheme 4.1 (Thienyl) and (Furyl)diazomethanes (**1-4**).



1 **2** **3** **4**

Thermal cyclization reactions of azo-ene-ynes are analogous, proceeding via a heteroaryl carbene intermediate.[26-28] Albers and Sander elucidated key aspects of the photochemistry and spectroscopy of C_5H_4S and C_5H_4O isomers through their study of the photochemistry of 3-thienyldiazomethane (**1**), 3-furyldiazomethane (**3**), and 2-furyldiazomethane (**4**) under matrix isolation conditions.[16,17] None of the carbene intermediates, however, were detected. In terms of computational studies, McKee, Shevlin, and Zottola described an insightful, comprehensive study of the C_5H_4S potential energy surface.[24] The mechanism of ring-opening of 2-furylcarbene, 2-thienylcarbene, and related compounds has been the subject of several computational and theoretical investigations.[7,24,29-31] Herges[29] described the reaction as a coarctate transformation, while Birney[31] interpreted it as a pseudopericyclic process.

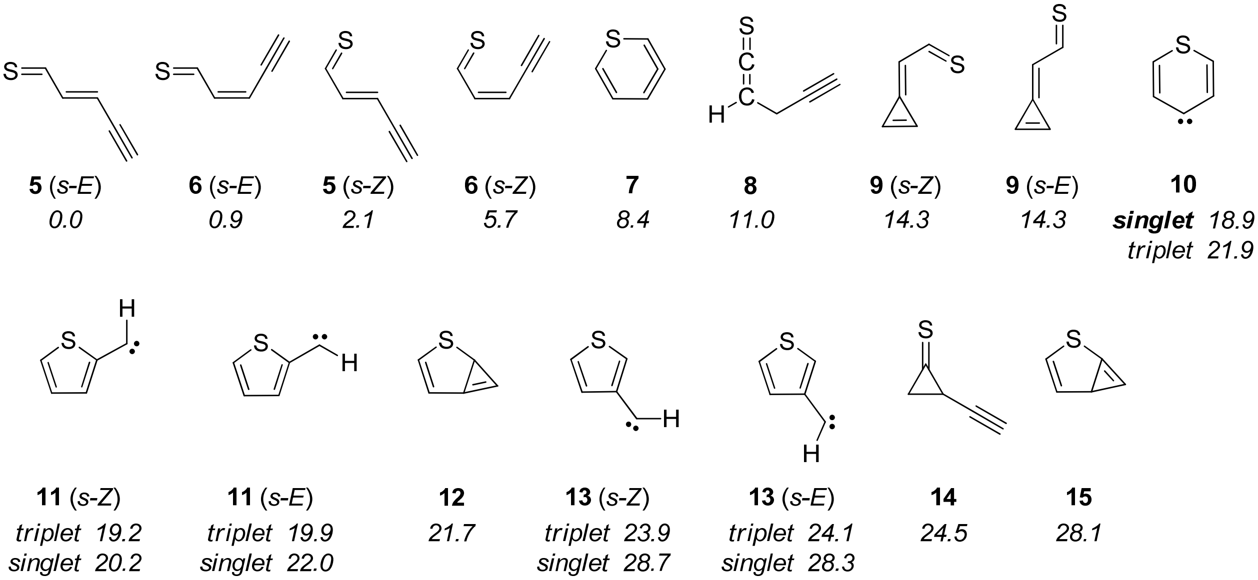
Results and Discussion

Computed Energies of C_5H_4S and C_5H_4O Isomers

In order to provide context for interpreting our experimental observations, we performed computational studies of the C_5H_4S and C_5H_4O potential energy surfaces at the B3LYP/6-31G* level of theory. Structures and relative energies are depicted in Schemes 2 and 3, and additional details are provided as Supporting Information. This methodology is adequate for providing qualitatively reliable predictions of infrared spectra and relative energies across a range of molecular structures. In terms of relative energies, Density Functional Theory (DFT) methods often over-emphasize delocalization in conjugated π-electron systems,[32-34] and the B3LYP functional biases the calculation of singlet-triplet energy gaps by ca. 1-3 kcal/mol by underestimating the stability of the singlet, relative to the triplet.[35,36] Because the singlet-triplet energy gaps of the thienylcarbenes are of particular interest to us, we sought to corroborate the

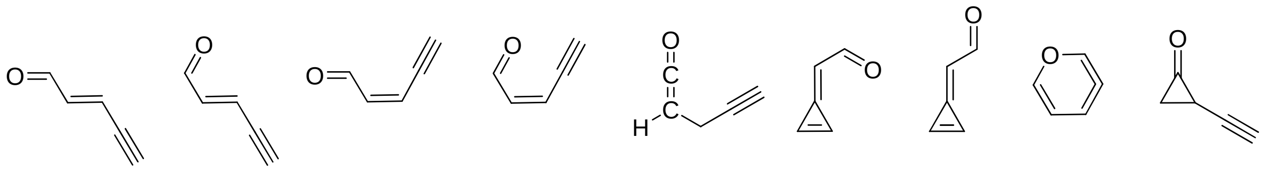
DFT predictions using ab initio methods. The results of coupled-cluster calculations, performed at a moderate level of theory (CCSD/cc-pVTZ), show good agreement with those obtained using density functional theory for 2- and 3-thienylcarbene (Scheme 4.4). Both computational methods predict a triplet electronic ground state for both carbenes.

Scheme 4.2. C_5H_4S Isomers and Their Computed Relative Energies.[a]

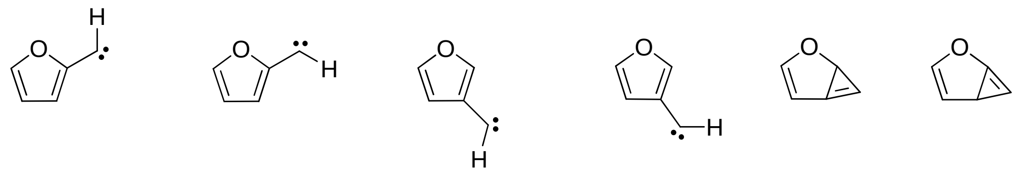


[a] Energy (kcal/mol; ZPVE included). B3LYP/6-31G* level of theory.

Scheme 4.3. C_5H_4O Isomers and Their Computed Relative Energies.[a]



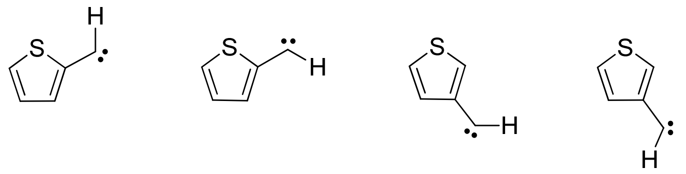
16 (*s-E*)	**16** (*s-Z*)	**17** (*s-E*)	**17** (*s-Z*)	**18**	**19** (*s-Z*)	**19** (*s-E*)	**20**	**21**
0.0	*0.9*	*1.3*	*3.9*	*7.4*	*14.5*	*14.7*	*21.6*	*24.5*



22 (*s-Z*)	**22** (*s-E*)	**23** (*s-E*)	**23** (*s-Z*)	**24**	**25**
singlet *28.6*	***singlet*** *30.5*	*triplet 36.5*	*triplet 36.6*	*39.2*	*50.3*
triplet 31.6	*triplet 31.8*	*singlet 38.9*	*singlet 40.2*		

[a] Energy (kcal/mol; ZPVE included). B3LYP/6-31G* level of theory.

Scheme 4.4. Thienylcarbenes and Their Computed Relative Energies.[a]



	11 (*s-Z*)	**11** (*s-E*)	**13** (*s-Z*)	**13** (*s-E*)
B3LYP/6-31G*				
	triplet 0.0	*triplet 0.8*	*triplet 4.8*	*triplet 4.9*
	singlet 1.0	*singlet 2.8*	*singlet 9.5*	*singlet 9.1*
CCSD/cc-pVTZ				
	triplet 0.0	*triplet 0.6*	*triplet 3.2*	*triplet 3.3*
	singlet 2.2	*singlet 3.0*	*singlet 7.5*	*singlet 7.0*

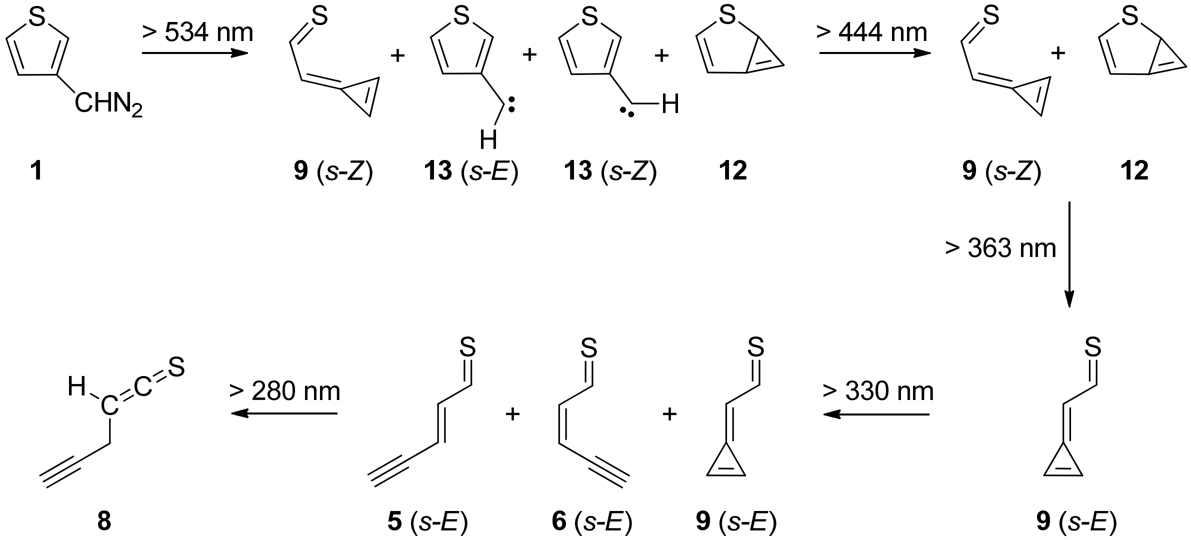
[a] Energy (kcal/mol; ZPVE included).

Of the isomers that we investigated, the structurally analogous thioaldehyde **5** (C_5H_4S) and aldehyde **16** (C_5H_4O) are the lowest-energy structures on their respective potential energy surfaces. Portions of these surfaces have been investigated, previously, although the issue of conformational isomerism (*s-E*, *s-Z*) in thioaldehydes (**5**, **6**) or aldehydes (**16**, **17**) has not been explored in detail.[16,17,24] The (*s-Z*) rotamer is commonly drawn in mechanistic schemes, but there is only one case throughout the photochemistry of diazo compounds **1**, **2**, **3**, and **4** where an (*s-Z*) rotamer of any pentenyne (*s-Z*-**6**) is actually observed in the matrix (see below). The computed IR spectra of the (*s-Z*) and (*s-E*) rotamers are quite different and allow clear analysis and differentiation of the peaks present in the experimental spectrum.

Primary Photochemistry of 3-Thienyldiazomethane (1)

Irradiation of 3-thienyldiazomethane (**1**) ($\lambda > 534$ nm; N_2, 10 K) gives a mixture of (s-*Z*)-α-thial-methylenecyclopropene (**9**), *s-E*-3-thienylcarbene (*s-E*-**13**), *s-Z*-3-thienylcarbene (*s-Z*-**13**), and a minor amount of a species tentatively assigned as 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**12**) (Scheme 4.5; Figure S4.1).[37] IR assignments are based upon comparison of experimental spectra with computed IR spectra (B3LYP/6-31G*), as well as comparison with previously-reported spectral data of **9** and **12**.[16,38] EPR and UV/vis experiments, performed under analogous conditions, provide strong support for the assignment of triplet 3-thienylcarbene (*s-E*- and *s-Z*-**13**). The EPR spectrum of **13** affords direct evidence for the triplet species, and the spectroscopic features are generally consistent with those expected for an arylcarbene (Figure 4.1).[39-41] A detailed analysis of the EPR spectrum will be provided as part of the Discussion section. The electronic absorption spectrum exhibits the weak visible absorption features that are characteristic of triplet aryl carbenes (and the benzyl radical) (Figure 4.2).[39] The spectroscopic assignment of triplet 3-thienylcarbene (**13**) is further supported by the wavelength-dependent photochemistry, in which the IR, UV/vis, and EPR signals attributed to **13** disappear upon photoexcitation into the visible absorption feature at λ_{max} ca. 467 nm (Figures 4.2 and 4.3).

Scheme 4.5. Photochemistry of 3-Thienyldiazomethane (**1**) (N_2, 10 K).



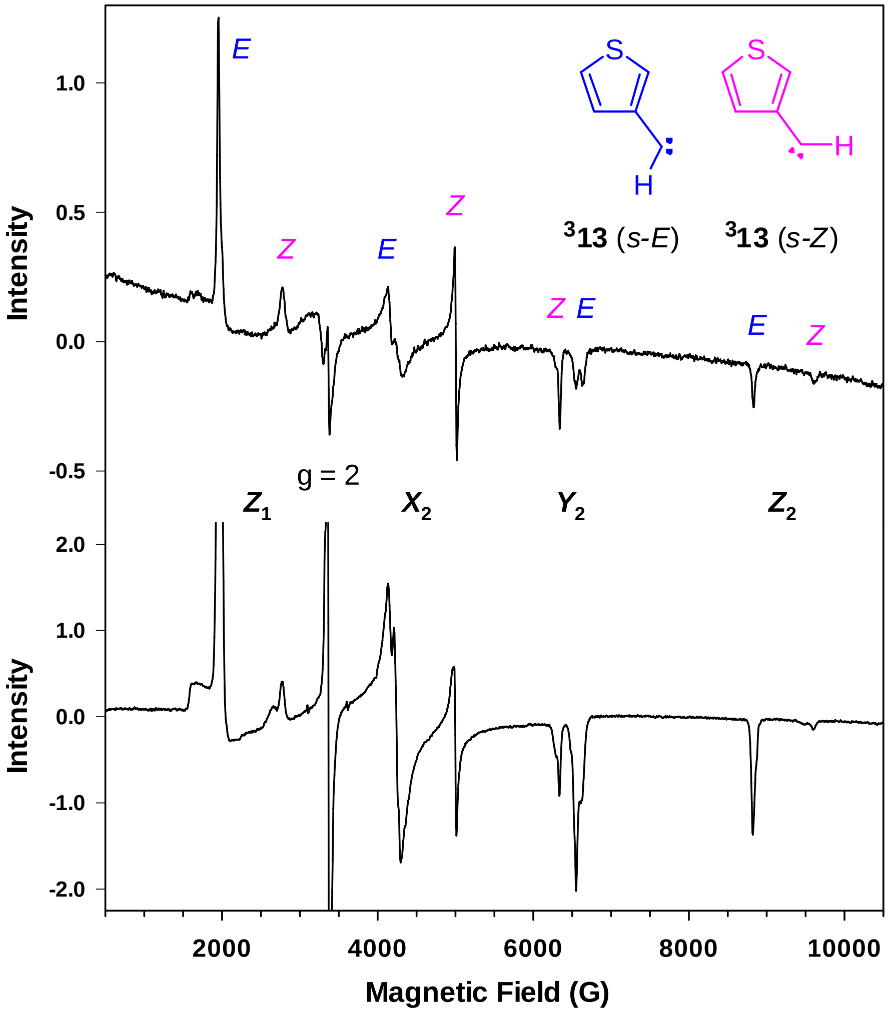


Figure 4.1. EPR spectra. Top: spectrum of triplet (*s*-*E*) and (*s*-*Z*) 3-thienylcarbene (**13**), obtained upon irradiation (λ > 571 nm, 22 h) of 3-thienyldiazomethane (**1**) (Ar, 15 K). Bottom: spectrum of triplet **13** obtained upon continued irradiation (λ > 571 nm, 22 h; > 534 nm, 4.5 h; > 497 nm, 17.5 h; > 472 nm, 22.5 h) of diazo compound **1**. (Note difference in y-axis scales.)

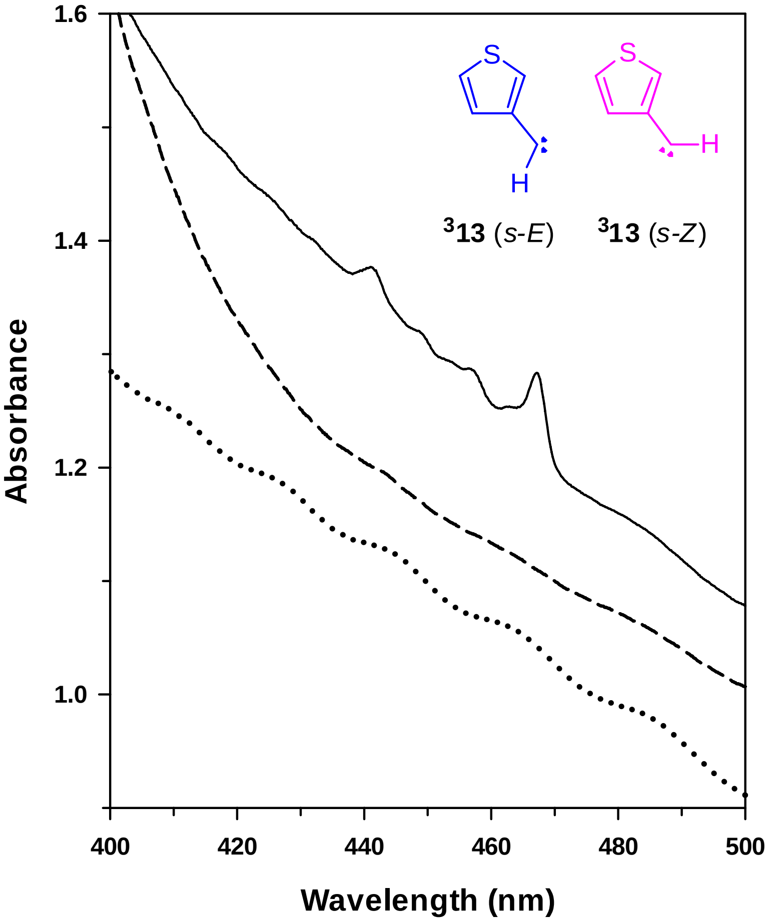


Figure 4.2. Electronic absorption spectra. Dotted line: matrix containing (3-thienyl)diazomethane (**1**) (Ar, 10 K) before irradiation. (The visible absorption of **1** is not observable because of the low concentration.) Solid line: spectrum of (*s*-*E*) and (*s*-*Z*) triplet 3-thienylcarbene (**13**) observed upon photolysis of diazo compound **1** (λ > 472 nm, 19 h). Dashed line: spectrum showing the disappearance of carbenes (*s*-*E*)-**13** and (*s*-*Z*)-**13** upon irradiation (λ > 444 nm, 22 h).

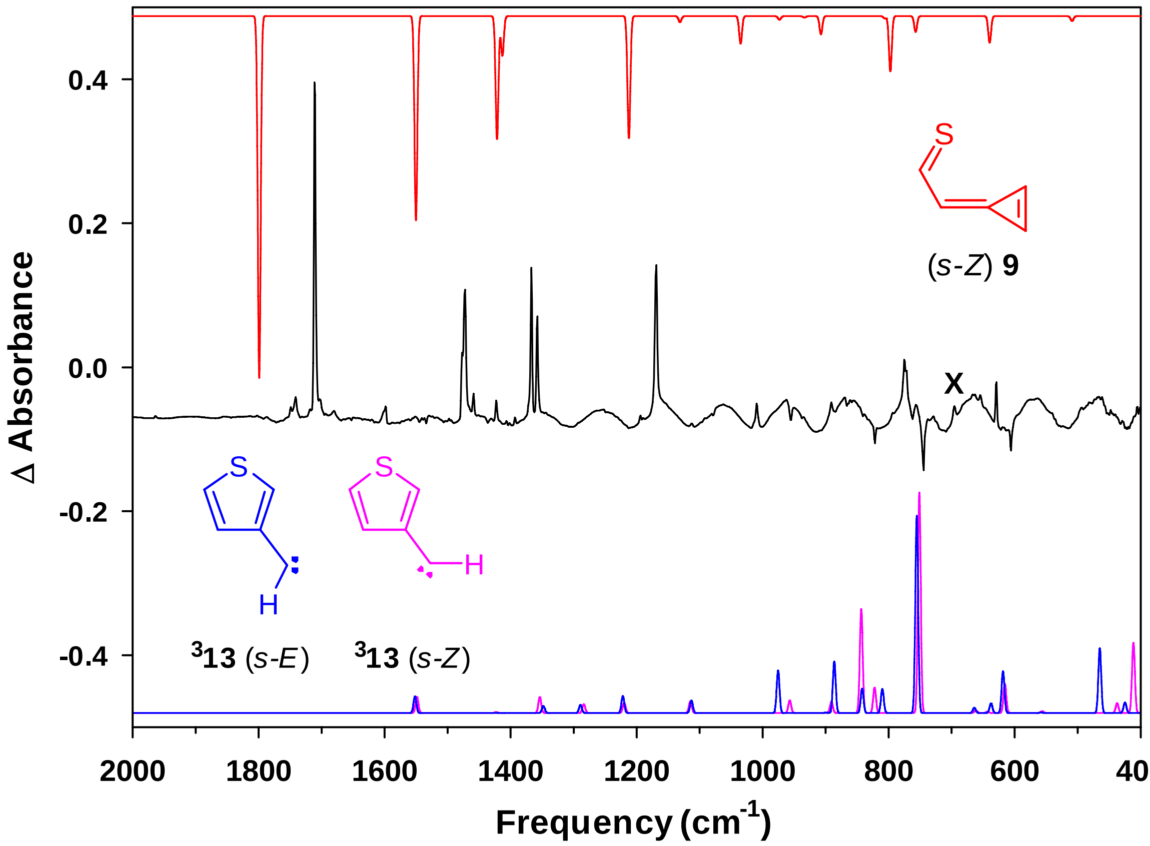


Figure 4.3. IR subtraction spectrum showing spectral changes observed upon selective irradiation (λ = 467 ± 10 nm, 4 h) of a matrix that contains a mixture of (3-thienyl)diazomethane (**1**), (*s*-*Z*)-α-thial-methylenecyclopropene (**9**), 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**12**), and triplet 3-thienylcarbene (**13**) (N_2, 10 K). The spectrum shows the disappearance of 3-thienylcarbene (**13**) and the growth of **9**. Under these irradiation conditions, diazo compound **1** exhibits virtually no change in concentration, while bicyclic compound **12** displays only a very small increase (**X** = the major peak associated with **12**). Computed IR spectra for both conformers of triplet 3-thienylcarbene (**13**) are superimposed at the bottom of the figure, while the computed IR spectrum for (*s*-*Z*)-**9** is shown at the top of the figure.

Comparison of the electronic absorption spectra of 3-thienyldiazomethane (**1**) and triplet 3-thienylcarbene (**13**) shows that diazo compound **1** absorbs at slightly longer wavelength (broad absorption with λ_{max} = 494 nm) than carbene **13** (λ_{max} = 467 nm). (The 494-nm absorption of diazo compound **1**, which was measured in acetonitrile solution, is not observable in the matrix spectrum depicted in Figure 2 because of the low concentration.) It is possible, therefore, to irradiate diazo compound **1** under long-wavelength, broadband conditions without inducing secondary photochemistry in the incipient 3-thienylcarbene (**13**). Long-wavelength irradiation of 3-thienyldiazomethane (**1**) exhibits a subtle wavelength dependence, which we tentatively ascribe to differential photoreactivity of *s-E-* and *s-Z-* conformers of the diazo compound. Irradiation of diazo compound **1** at λ > 571 nm results in a mixture of *s-E-* and *s-Z-* conformers of triplet 3-thienylcarbene (**13**), with the *s-Z* conformer growing more quickly, as measured by the greater intensity of the X_2 and Y_2 signals in the EPR spectrum (Figure 1 and Figure S8). Both conformers continue to grow upon irradiation at slightly shorter wavelength (λ > 534 nm, > 497 nm, > 472 nm), but the X_2 and Y_2 signals of the *s-E* conformer grow more quickly, such that the *s-E-* conformer of triplet 3-thienylcarbene (**13**) becomes the major conformer in the EPR spectrum (Figure 1). Since both conformers appear to be stable to the irradiation conditions, and each disappears rapidly upon irradiation at λ > 444 nm or λ = 467 ± 10 nm, we ascribe the differential rates of formation to the differential absorption and/or quantum yield for carbene formation from the conformational isomers of 3-thienyldiazomethane (**1**). (TD-DFT calculations predict the electronic absorption spectra for the conformational isomers of 3-thienyldiazomethane (**1**) to be similar – see Supporting Information.)

With the EPR and visible spectra of triplet 3-thienylcarbene (**13**) in hand, we expended considerable effort in an attempt to optimize the experimental conditions to enhance the production of carbene **13** and/or minimize the formation of methylenecyclopropene derivative **9**. (These efforts included extensive studies of the wavelength dependence of the photolysis of 3-thienyldiazomethane (**1**), as well as broad-band "flash" irradiation.[42]) Although our attempts were largely unsuccessful, they help us understand the photochemical reactivity of this system. An important observation is that the methylenecyclopropene derivative (**9**) is always formed, even under conditions where triplet 3-thienylcarbene (**13**) is stable to the irradiation conditions. Plausible mechanisms for the formation of **9**, under these conditions, involve a hot ground-state reaction of carbene **13** or a reaction in the excited state of diazo compound **1**. Both explanations have ample precedent in the field of carbene chemistry. The first mechanistic scenario posits that N_2 loss from the excited state of 3-thienyldiazomethane (**1**) yields carbene **13** with excess vibrational energy, and that **9** arises from a hot ground-state reaction of carbene **13**. To probe for the involvement of a hot ground-state carbene, we performed the photolysis of diazo compound **1** in Ar and N_2 matrices, as well as a 2-methyltetrahydrofuran (2-MeTHF) glass. These media are increasingly effective in vibrational cooling of guest molecules, owing to an increasing density of vibrational states.[43,44] We found, however, that the matrix medium does not influence the photochemistry, as judged by the fact that the intensity of the EPR signal of triplet 3-thienylcarbene (**13**) was not enhanced (relative to Ar) in either an N_2 matrix or a 2-MeTHF glass. Thus, we do not favor the mechanism involving hot ground-state 3-thienylcarbene (**13**). Such an explanation would also seem to be at odds with the relatively high thermal barrier (> 30 kcal/mol) separating singlet 3-thienylcarbene (**13**) and α-thial-methylenecyclopropene (**9**).[24] The more likely explanation, therefore, involves the excited state of the diazo compound. As observed in several other systems,[45,46] the excited state of diazo compound **1** may partition between two pathways: N_2 loss, to give 3-thienylcarbene (**13**), and N_2 loss with concomitant rearrangement, to give α-thial-methylenecyclopropene (**9**) without the intervention of the carbene.

Electronic Absorption Spectrum of Triplet 3-Thienylcarbene (13)

3-Thienylcarbene (**13**) exhibits a weak electronic absorption in the visible region of the spectrum (λ_{max} = 467 nm) that is characteristic of triplet arylcarbenes (and the benzyl radical) (Figure 4.2).[39] The vibronic structure associated with the corresponding electronic transition in triplet phenylcarbene (λ_{max} = 430 nm) has been analyzed in detail.[47] Time-dependent density functional theory calculations (TD-DFT) do a reasonably good job of reproducing the general features of the absorption spectrum of triplet phenylcarbene (Table 4.1), although the energy of the visible excitation is overestimated. Analogous calculations for triplet 3-thienylcarbene (**13**) predict the visible absorption to be red-shifted relative to phenylcarbene (Table 4.1), in accord with experimental observation. The absorption spectra of the rotamers of triplet 3-thienylcarbene (**13**) are indistinguishable under our experimental conditions – a result that is also borne out by the TD-DFT calculations. In this respect, triplet 3-thienylcarbene (**13**) is unlike the related singlet arylchlorocarbenes (furanyl,[7,8] thienyl,[9,10] and their benzo analogs[11-13]), in which the absorption spectra of the conformational isomers exhibit significant differences. In the lowest singlet state, however, the absorption spectra of the conformers of 3-thienylcarbene are predicted to be readily distinguishable (λ_{max} 995 nm vs. 1045 nm; Table 4.1).

Table 4.1. Computed Electronic Absorption Spectra of Carbenes.[a]

	(*s*-*E*)-3-thienyl carbene (**13**)		(*s*-*Z*)-3-thienyl carbene (**13**)		phenyl carbene		phenyl carbene (expt)[b]
	λ_{max}	*f*	λ_{max}	*f*	λ_{max}	*f*	λ_{max}
triplet (T_0)							
	388	0.0021	389	0.0020	373	0.0000	430
	355	0.0022	356	0.0016	354	0.0012	
	333	0.0006	337	0.0002	337	0.0015	
	328	0.0006	328	0.0005	313	0.0001	
	322	0.0196	322	0.0196	310	0.0324	300
	321	0.0001	314	0.0002	306	0.0002	
	295	0.0002	302	0.0010	274	0.0973	
	278	0.1056	278	0.1045	243	0.1607	246
singlet (S_1)							
	995	0.0013	1045	0.0018	1140	0.0012	
	316	0.0039	317	0.0001	320	0.0007	
	307	0.0037	314	0.0111	311	0.0214	
	303	0.0132	307	0.0098	308	0.0086	
	285	0.0130	291	0.0007	285	0.0036	
	278	0.0044	268	0.0279	272	0.0082	
	256	0.1976	263	0.0549	271	0.0315	
	252	0.0048	256	0.1549	260	0.2462	

[a] (TD)M06/aug-cc-pVTZ // B3LYP/6-31G*; λ_{max} (nm), *f* = oscillator strength. Eight lowest-energy excitations reported. [b] reference 47.

Photochemistry of 3-Thienylcarbene (13) and other C_5H_4S Isomers

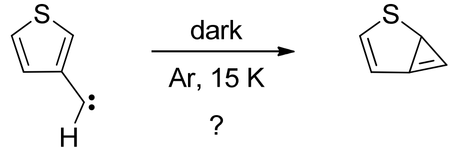
Photoexcitation into the visible absorption feature (λ_{max} ca. 467 nm) of triplet 3-thienylcarbene (**13**), using either broadband ($\lambda > 444$ nm) or narrow-band ($\lambda = 467 \pm 10$ nm) irradiation conditions, leads to the rapid disappearance of the IR, UV/vis, and EPR signals of carbene **13** and the growth of (*s*-*Z*)-α-thial methylenecyclopropene (**9**), as well as the growth of a small amount of 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**12**) (Figures 4.3, S4.3). This behavior explains the inability of Albers and Sander to observe carbene **13** in their study of the photochemistry of 3-thienyldiazomethane (**1**).[16] Our findings establish that carbene **13** is not stable to the photolysis conditions used in the earlier experiment ($\lambda > 435$ nm).

The UV/vis spectrum of **9** exhibits an absorption at ca. 300-400 nm (Figure S4.11). Irradiation into this absorption feature ($\lambda > 363$ nm) results in photoisomerization of the *s*-*Z* conformer to the *s*-*E* conformer (Figure S4.4). At slightly shorter wavelength ($\lambda > 330$ nm), the IR bands of the *s*-*E* conformer continue to grow, and the IR bands of the acyclic isomers, pent-2-en-4-ynethial (**5** and **6**), slowly appear (Figure S4.5). At $\lambda > 280$ nm, another acyclic isomer, propargyl thioketene (**8**), appears in the IR spectrum, accompanied by the decrease in the IR absorptions of **5**, **6**, and **9** (Figure S4.6). Our findings corroborate those described earlier by Sander and coworkers,[16] while adding some additional detail in terms of the conformational isomerism of pent-2-en-4-ynethial (**5** and **6**) and methylenecyclopropene derivatives (**9**), as well as the shorter-wavelength chemistry that affords thioketene **8**.

Possible Thermal Chemistry of Triplet 3-Thienylcarbene (13)

Allowing a matrix containing triplet 3-thienylcarbene (**13**) to stand in the dark at 15 K for an extended period of time (30-80 hours) affords a small, but reproducible, decrease in the EPR signal of (*s*-*E*)-**13** (Figure 4.4 and S4.10) and the visible absorption of **13** (Figure S4.12). These data suggest that the (*s*-*E*) conformer of triplet 3-thienylcarbene (**13**) undergoes a very slow thermal reaction at 15 K. IR experiments were performed under identical conditions to try to determine the product of this reaction, but the low concentration of triplet 3-thienylcarbene (**13**) in the matrix, and the presence of several other photoproducts, did not permit us to quantify carbene disappearance or product growth. In general, measurements of reaction kinetics – whether by EPR, UV/vis, or IR – were problematic because of a combination of low signal intensity and very slow reaction rates. Thermal reactions of reactive intermediates trapped in matrices at cryogenic temperatures are not uncommon, and these processes typically occur via a quantum mechanical tunneling mechanism[48-50] – even in cases where the reaction is formally forbidden by virtue of a change in spin multiplicity.[51,52] We consider the cyclization of (*s*-*E*) 3-thienylcarbene (**13**) to 2-thiabicyclo[3.1.0]hexa-3,5-diene (**12**) to be a likely candidate for such a process, although we cannot exclude other possibilities (Scheme 4.6). The rearrangement of triplet **13** to singlet **12**, which does not involve extensive motion of the heavy atoms, is computed to be slightly exothermic (ca. 2 kcal/mol).

Scheme 4.6. Possible Tunneling Reaction of 3-Thienylcarbene (**13**).



13 (*s*-*E*) **12**

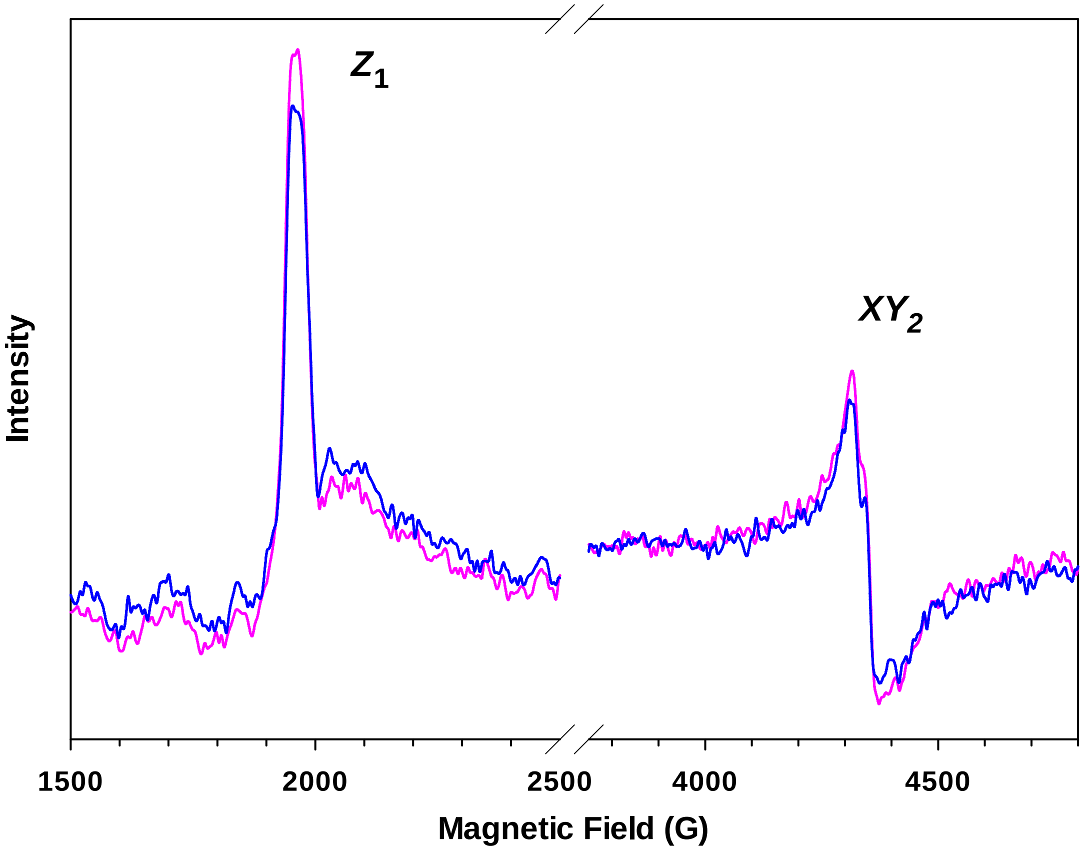
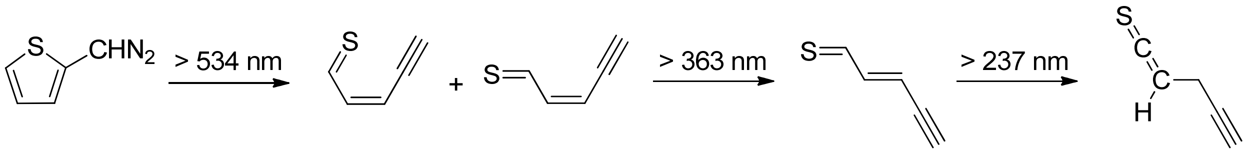


Figure 4.4. EPR transitions of triplet (*s*-*E*) 3-thienylcarbene (**13**) (Ar, 15 K). **Pink:** carbene **13** formed upon irradiation of (3-thienyl)diazomethane (**1**) (λ > 472 nm, 26 h). **Blue:** spectrum showing decrease in signal intensity after standing in the dark at 15 K (46 h).

Photochemistry of 2-Thienyldiazomethane (2)

Irradiation of 2-thienyldiazomethane (**2**), under the same conditions that led to the successful generation of triplet 3-thienylcarbene (**13**) (λ > 534 nm; Ar, 10 K), failed to afford IR or EPR features attributable to triplet 2-thienylcarbene (**11**) (Scheme 4.7). In accord with the results of earlier studies,[16] the ring-opened product, *Z*-pent-2-en-4-ynethial (**6**), is the only species observed by IR spectroscopy (Figure S4.13). Careful examination of the spectrum establishes that both *s-E*- and *s-Z*- rotamers of **6** are present. Further irradiation (λ > 363 nm) results in *cis-trans* photoisomerization of *Z*-pent-2-en-4-ynethial (**6**) and *E*-pent-2-en-4-ynethial (**5**) (present only as the *s-E*- conformer; Figure S4.14). Irradiation at λ > 237 nm affords propargyl thioketene (**8**) (Figure S4.15).

Scheme 4.7. Photochemistry of 2-Thienyldiazomethane (**2**) (Ar, 10 K).



2 **6** (*s-Z*) **6** (*s-E*) **5** (*s-E*) **8**

The nature of the electronic ground state of 2-thienylcarbene (**11**) – singlet or triplet – remains unclear at this time. Our DFT calculations predict a triplet ground state with a small singlet-triplet gap (1-2 kcal/mol) for both conformers of 2-thienylcarbene (**11**) (Scheme 4.2). We are not overly confident in the prediction of the ground state multiplicity, since the two states lie so close in energy and this computational methodology typically underestimates the energy of the singlet, relative to the triplet, by 1-3 kcal/mol.[35,36] McKee's calculations predict a singlet ground state for carbene **11** with a singlet-triplet gap of 4.1 kcal/mol,[24] but we are not overly confident in that prediction, either. Energies reported in the earlier study were estimated using an additivity scheme that utilized both QCISD(T) and MP2 energies. The application of MP2 methodology to carbenes, however, is problematic because of spin contamination. It is evident from the data in Table 1 of reference [24] that the QCISD(T) single-point calculation predicts a triplet ground state for **11**, while two different MP2 single-point calculations predict a singlet ground state.[53] We are inclined to discount the additivity scheme because of its reliance on MP2 data, and focus on the results afforded by CCSD (Scheme 4), QCISD(T),[24] or B3LYP (Scheme 4), which each predict a triplet ground state with small singlet-triplet gap.

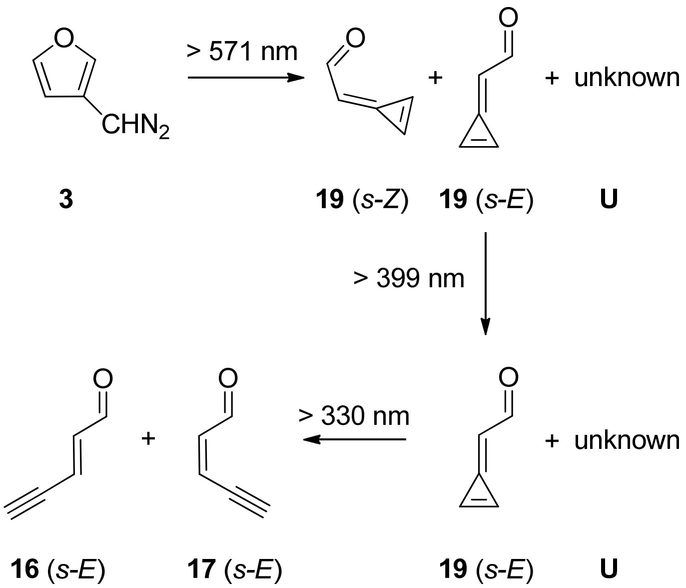
Spectroscopic data for C_5H_4S isomers. 3-Thienylcarbene (*s*-*E*-**13**): IR (N_2, 10 K) 744 s cm^{-1}; UV/vis (Ar, 10 K) λ_{max} 441, 449, 457, 467 nm; EPR (Ar, 15 K), $|D/hc|$ = 0.508 cm^{-1}, $|E/hc|$= 0.0554 cm^{-1}, Z_1 = 1954.7 G, X_2 = 4250.0 G, Y_2 = 6550.4 G, Z_2 = 8823.2 G, microwave frequency = 9.491GHz. 3-Thienylcarbene (*s*-*Z*-**13**): IR (N_2, 10 K) 744 s cm^{-1}; UV/vis (Ar, 10 K) λ_{max} 441, 449, 457, 467 nm; EPR (Ar, 15 K), $|D/hc|$= 0.579 cm^{-1}, $|E/hc|$= 0.0315 cm^{-1}, Z_1 = 2770.0 G, X_2 = 5000.0 G, Y_2 = 6337.0 G, Z_2 = 9600.0 G, microwave frequency = 9.491GHz. (*s*-*E*)-*E*-pent-2-en-4-ynethial (**5**): IR (Ar, 10 K) 3319 s, 1575 s, 1362 w, 1255 m, 1163 m, 1159 m, 976 w, 971 w, 962 m, 776 w, 694 w, 643 w, 640 w, 631 w cm^{-1}. (*s*-*E*)-*Z*-pent-2-en-4-ynethial (**6**): IR (Ar, 10 K) 3317 s, 2109 w, 1560 s, 1404 s, 1258 w, 1218 m, 1130 s, 1031 s, 862 w, 854 w, 777 s, 700 m, 643 s, 629 m, 465 w cm^{-1}. (*s*-*Z*)-*Z*-pent-2-en-4-ynethial (**6**): IR (Ar, 10 K) 3327 s, 2109 w, 1554 m, 1410 m, 1364 w, 1257 m, 1128 m, 1134 m, 944 w, 858 w, 638 s, 629 m, 465 w cm^{-1}. Propargyl thioketene (**8**): IR (N_2, 10 K) 3316 m, 1779 s, 1318 w, 1253 w, 645 w, 637 w, 613 w cm^{-1}. IR (Ar, 10 K) 3324 w, 1781 s, 1315 w, 1245 w cm^{-1}. (*s*-*Z*)-α-thial methylenecyclopropene (**9**): IR (N_2, 10 K) 3141 w, 1718 s, 1498 w, 1474 m, 1367 m, 1358 m, 1189 w, 1169 m, 1009 w, 775 m, 696 w, 646 w, 629 w cm^{-1}. (*s*-*E*)-α-thial methylenecyclopropene (**9**): IR (N_2, 10 K) 3143 w, 1719 s, 1714 m, 1496 s, 1480 m, 1412 w, 1362 w, 1353 w, 1190 m, 1164 m, 1104 w, 1007 w, 912 w, 908 w, 843 w, 834 w, 718 w cm^{-1}.

Photochemistry of 3-Furyldiazomethane (3)

Irradiation of 3-furyldiazomethane (**3**), under the same conditions that led to the successful generation of triplet 3-thienylcarbene (**13**) from 3-thienyldiazomethane (**1**) (λ > 571 nm or > 534 nm; Ar, 10 K), failed to afford IR or EPR features attributable to triplet 3-furylcarbene (**22**) (Scheme 4.8). Long-wavelength irradiation (λ > 571 nm) of **3** yields a mixture of (α-formyl)methylenecyclopropene (*s*-*Z*-and *s*-*E*-**19**) and an unidentified species (**U**) exhibiting an IR band in the acetylenic C-H stretching region (3429 m, 1636 m, 1476 m cm^{-1}, Figure S4.16). Irradiation at λ > 399 nm drives (*s*-*Z*)-**19** away, while (*s*-*E*)-**19** and **U** continue to grow (Figure S4.17). Subsequent irradiation (λ > 330 nm) causes **19** to decrease in intensity and a mixture of *E*-pent-2-en-4-ynal (**16**) and *Z*-pent-2-en-4-ynal (**17**) appear. As in the case of the sulfur analogs, the pent-2-en-4-ynals (**16** and **17**) are present in the *s*-*E* conformation (Figure S4.18). The IR assignments for **16**, **17**, and **19** are in good agreement with those reported previously.[17]

The photochemical appearance and disappearance of compound **U** is reproducible across multiple experiments, yet the identity of this species eludes us. We initially suspected propargyl ketene (**18**) – the oxygen analog of propargyl thioketene (**8**) that was observed in the photochemistry of the related sulfur-containing system. The observed IR absorptions of **U**, however, are inconsistent with the IR spectrum computed for ketene **18**. (The apparent absence of ketene or carbonyl stretching vibrations in the spectrum of **U** is telling.) We considered several other C_5H_4O isomers that contain a terminal alkyne moiety (Scheme S4.2), but none of the computed IR spectra shows a good correlation with the experimentally observed bands of **U**. We also considered the possibility of a photofragmentation reaction, but the observed IR absorption at 3429 cm^{-1} does not correspond to that of either acetylene[54] or diacetylene.

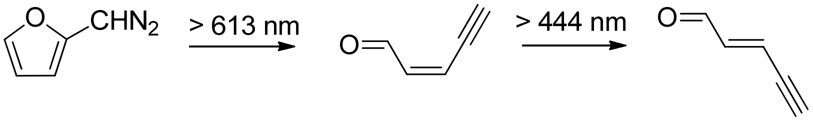
Scheme 4.8. Photochemistry of 3-Furyldiazomethane (**3**) (Ar, 10 K).



Photochemistry of 2-Furyldiazomethane (4)

Under gentler conditions than those that led to the successful generation of triplet 3-thienylcarbene (**13**) (λ > 571 nm; Ar, 10 K), irradiation of (2-furyl)diazomethane (**4**) (λ > 613 nm; Ar, 10 K) failed to afford IR or EPR features attributable to triplet 2-furylcarbene (**22**) (Scheme 4.9). In accord with the results of earlier studies,[17] irradiation of diazo compound **4** (λ > 613 nm; Ar, 10 K) causes fragmentation of the furan ring, yielding *Z*-furylpent-2-en-4-yne (**17**) (Figure S4.19). Subsequent irradiation at λ > 444 nm gives rise to *E*-furylpent-2-en-4-yne (**16**) (Scheme 4.9, Figure S4.20).

Scheme 4.9. Photochemistry of 2-Furyldiazomethane (**4**) (Ar, 10 K).



4 **17** (*s*-*E*) **16** (*s*-*E*)

Spectroscopic data for C_5H_4O isomers. (*s*-*E*)-*E*-pent-2-en-4-ynal (**16**): IR (Ar, 10 K) 3313 m, 1710 s, 1594 m, 1264 w, 1124 s, 963 m, 716 w, 641 m, 583 w cm^{-1}. (*s*-*E*)-*Z*-pent-2-en-4-ynal (**17**): IR (Ar, 10 K) 3324 m, 2845 w, 2826 w, 2743 w, 1699 s, 1582 m, 1266 w, 1096 w, 909 m, 643 w cm^{-1}. (*s*-*Z*)-(α-formyl)methylenecyclopropene (**19**): IR (Ar, 10 K) 1749 s, 1647 s, 1494 m, 1344 w, 1114 w, 1080 w, 729 w, 705 m, 602 m cm^{-1}. (*s*-*E*)-(α-formyl)methylenecyclopropene (**19**): IR (Ar, 10 K) 1743 w, 1690 s, 1665 w, 1511 m, 1146 w, 1016 w, 799 w cm^{-1}. Unknown (**U**): IR (Ar, 10 K) 3429 m, 1636 m, 1476 m cm^{-1}.

EPR Spectrum and Electronic Structure of Triplet 3-Thienylcarbene (13)

The triplet EPR spectrum obtained upon irradiation of 3-thienyldiazomethane (**1**) (Figure 4.1) exhibits several unusual features, with respect to the spectra of triplet arylcarbenes.[39,55-57] Conformational isomerism, a heavy atom effect of sulfur, and site effects in the matrix may all be manifest in the spectrum, and a proper interpretation is not readily apparent upon cursory inspection. The assignment of the individual EPR transitions to major and minor conformational isomers derives from the differential rate of appearance as a function of photolysis wavelength (λ > 571 vs. λ > 472 nm; Figure 4.1 and Figure S4.8), as well as comparison with EPR spectra of other 2- and 3-thienylcarbene derivatives obtained in subsequent investigations.[58,59] The zero-field splitting parameters of the major and minor isomers were calculated in the usual way, using the best fit of the EPR transitions with the spin Hamiltonian under the assumption that $g_x = g_y = g_z = g_e$.[60] The striking result is the large difference in magnitude of the D values between the major ($|D/hc| = 0.508$ cm^{-1}) and minor ($|D/hc| = 0.579$ cm^{-1}) isomers observed in the triplet EPR spectrum.

Simulation. Simulation of the triplet EPR spectrum, using the program XSophe (Bruker), was accomplished by manually varying values of D, E, and g to give an optimal fit. The experimental and simulated spectra exhibit excellent agreement (Figure 4.5). The best fit was obtained with $g = 2.0$ and the zero-field parameters D and E given in Table 4.2. In the experimental spectrum, the major isomer exhibits subtle features in the X_2 and Y_2 transitions, which we attribute to inequivalent sites in the argon matrix. These features are well-reproduced, in the simulated spectrum, by two species (A and A′) that differ only slightly in terms of E value (Table 4.2). Although the $g = 2$ signal in the experimental spectrum appears to be intense, its contribution in terms of percent of spins is negligible (0.3%), as established by the simulation. The quality of the simulated spectrum, and the excellent agreement of the zero-field parameters determined from the experimental spectrum and from the simulated spectra, give confidence in the correctness of the analysis.

That the EPR spectrum of triplet 3-thienylcarbene (**13**) could be interpreted and simulated using $g = 2.0$ was not obvious to us, at the outset, because of the possible influence of a heavy-atom effect by sulfur. Sulfur-containing radicals have been widely studied in biological systems.[61] In cases where an unpaired electron is localized on sulfur, g values range from 1.96 to 2.073.[62] In the case of carbene **13**, the fact that little spin density resides at sulfur (see below), and that the nature of the EPR spectrum is much more sensitive to the values of D and E than to the value of g, suggest that any manifestation of spin-orbit coupling on g, through the heavy-atom effect of sulfur, is minimal.

Table 4.2. Zero-Field Splitting Parameters (in cm^{-1}) of Triplet 3-Thienylcarbene (**13**).

	experimental		XSophe simulation		
conformer	$\lvert D/hc \rvert$	$\lvert E/hc \rvert$	$\lvert D/hc \rvert$	$\lvert E/hc \rvert$	% spins
A	0.508	0.0554	0.505	0.05454	56
A′			0.505	0.05707	28
B	0.579	0.0315	0.575	0.03128	16
$g = 2$					0.3

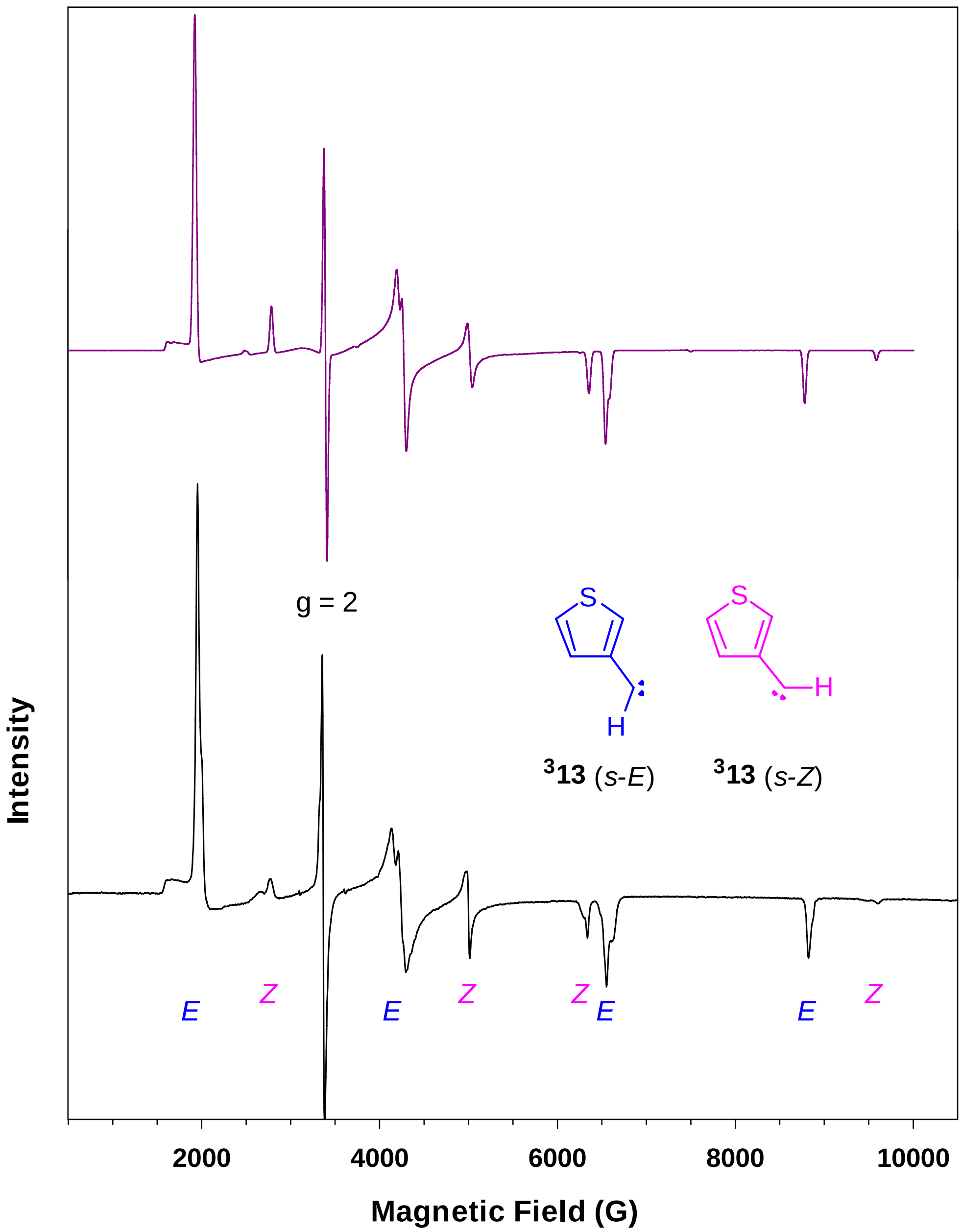
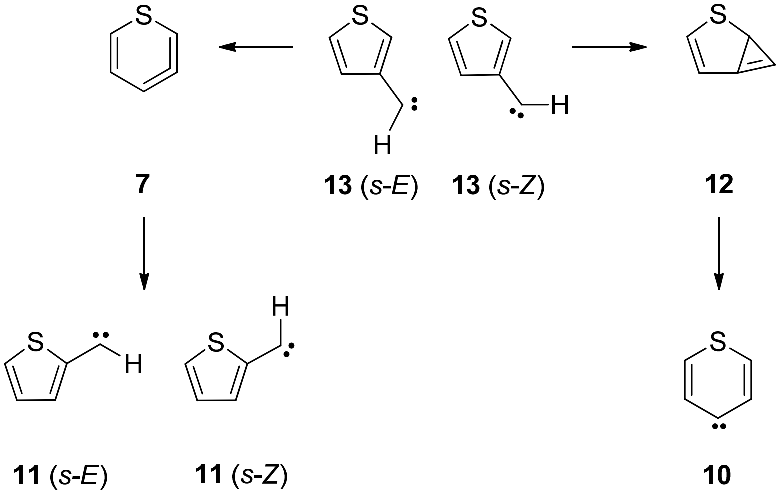


Figure 4.5. Bottom: EPR spectrum of triplet *s-E* and *s-Z* 3-thienylcarbene (**13**), obtained upon irradiation (λ > 472 nm, 22 h) of 3-thienyldiazomethane (**1**) (Ar, 15 K). Top: simulated spectrum of triplet 3-thienylcarbene (**13**) (see text).

Spectroscopic Assignments. The preceding analysis provides the zero-field splitting parameters for the major and minor species observed in the matrix, but it does not establish the spectroscopic assignments. In making the assignments, we consider several interpretations of the EPR spectrum (Figure 4.4). In the first, which is the assignment that we ultimately favor, we hypothesize that the transitions for the major and minor isomers arise from *s-E* / *s-Z* conformational isomerism of triplet 3-thienylcarbene (**13**). (In other words, the EPR spectra of the conformational isomers are quite different.) In this scenario, the spectral doubling of the X_2 and Y_2 transitions is attributed to matrix site splitting.

In the second interpretation of the EPR spectrum, we hypothesize that the transitions for the major isomer – for which the X_2 and Y_2 transitions exhibit features of spectral doubling – arise from conformation isomers of triplet 3-thienylcarbene (**13**). (In other words, the EPR spectra of the conformational isomers are quite similar.) We hypothesize that the transitions for the minor isomer – which are quite different – arise from a *different* triplet species. In our mind, a plausible candidate is 4-thia-2,5-cyclohexadienylidene (**10**) (Scheme 4.10), which could be readily envisioned to form upon photochemical or hot molecule rearrangement of 3-thienylcarbene (**13**) and bicyclic compound **12**. DFT calculations by McKee et al.[24] and by us (Scheme 2), however, predict a singlet ground state for 4-thia-2,5-cyclohexadienylidene (**10**). We therefore reject the assignment of **10** as a carrier of a triplet EPR signal.

Scheme 4.10. Plausible Carbene Rearrangements

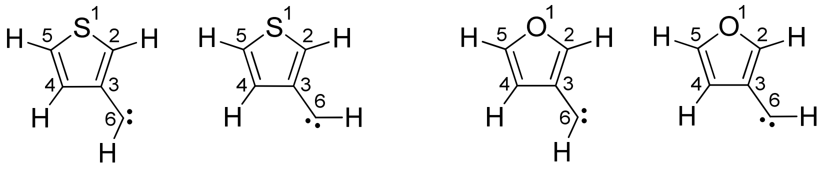


In the third interpretation of the EPR spectrum, we hypothesize that the transitions for the major and minor isomers arise from the presence of a mixture of triplet 2-thienylcarbene (**11**) and 3-thienylcarbene (**13**). (In this scenario, the doubling of spectral transitions might arise through either *s-E* / *s-Z* conformational isomerism or multiple matrix sites.) That triplet 2-thienylcarbene (**11**) cannot be generated by direct irradiation of (2-thienyl)diazomethane (**2**) does not exclude the possibility that triplet **11** might be formed and observable under different reaction conditions (e.g. photochemical or hot molecule rearrangement of 3-thienylcarbene (**13**) or 4-thiacyclohexa-1,2,5-triene (**7**); Scheme 4.10). Although this scenario seems improbable – given the very low barrier for ring opening of singlet 2-thienylcarbene (**11**) – we cannot rigorously exclude it.

Conformational Isomerism. Here, we follow the analysis of Roth and coworkers assigning geometric isomers for triplet arylcarbenes.[55-57] If the conformational isomers of a triplet carbene experience different dipolar coupling between the unpaired electrons, the conformers will exhibit different *D* values. Differences in dipolar coupling may arise as a consequence of differences in spin density at the β-positions of a triplet carbene in which one unpaired electron is delocalized across a π-electron system. Thus, we computed natural spin densities for both triplet 3-thienylcarbene (**13**) and 3-furylcarbene (**23**) (Table 4.3). The finding of a large difference in spin density at the β-positions of the carbene (C2 = +0.42, C4 = +0.13) is consistent with a large difference in the *D* values of the conformational isomers of 3-thienylcarbene (**13**) (0.508 cm^{-1} vs. 0.579 cm^{-1}). Empirical correlations establish that the larger *D* value arises when the sp orbital of a triplet carbene is oriented *anti* with respect to the β-position bearing the larger spin density.[55-57] Since C2 is the β-position bearing higher spin density in triplet 3-thienylcarbene (**13**), the *s-Z* conformer of **13** is assigned as the isomer with the larger *D* value (minor isomer in Figure 4.5), and the *s-E* conformer of **13** is assigned as the isomer with the smaller *D* value (major isomer in Figure 4.5). It is interesting to note that the difference in *D* values between the two conformers of 3-thienylcarbene (ΔD = 0.071 cm^{-1}) is substantially larger than the difference observed for conformers of most arylcarbenes ($\Delta D \approx$ 0.02-0.03 cm^{-1}), vinylcarbenes ($\Delta D \approx$ 0.05 cm^{-1}), and α-carbonylcarbenes ($\Delta D \approx$ 0.05 cm^{-1}).[55-57] The value rivals that reported for the conformers of benzoyl phenyl carbene (ΔD = 0.08 cm^{-1}).

In an effort to obtain independent evidence bearing on the assignment of the conformational isomers of triplet 3-thienylcarbene (**13**), we sought to utilize newly developing methods for the first-principles calculation of zero-field splitting parameters. Neese's ORCA program shows considerable promise for the analysis of a variety of high-spin organic reactive intermediates.[63-66] Unfortunately, we find that the ORCA calculations for the zero-field splitting parameters of triplet 3-thienylcarbene (**13**) are not robust. The computed values of *D* and *E* are

Table 4.3. Natural Spin Densities and Zero-Field Splitting Parameters for Triplet 3-Thienylcarbene (**13**) and Triplet 3-Furylcarbene (**23**).[a]



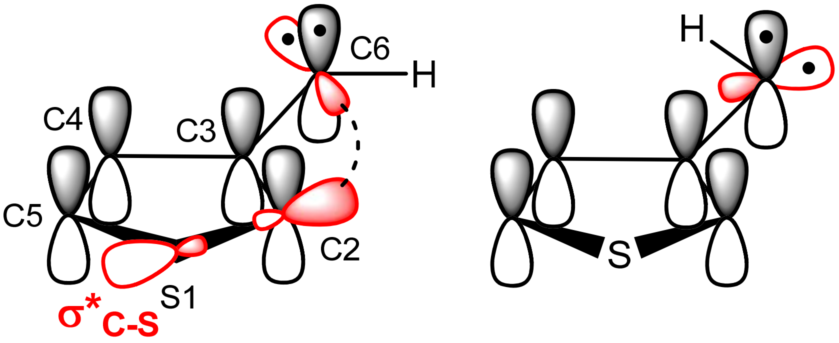
	3-thienylcarbene (**13**)		3-furylcarbene (**23**)	
Atom	(*s*-*E*)-**13**	(*s*-*Z*)-**13**	(*s*-*E*)-**23**	(*s*-*Z*)-**23**
1	+0.071	+0.087	+0.043	+0.052
2	+0.415	+0.431	+0.416	+0.435
3	−0.180	−0.182	−0.179	−0.180
4	+0.128	+0.105	+0.121	+0.097
5	−0.076	−0.078	−0.060	−0.063
6	+1.67	+1.67	+1.69	+1.68
	experimental		computed	
$\lvert D/hc \rvert$ cm^{-1}	0.508	0.579	0.506	0.531
$\lvert E/hc \rvert$ cm^{-1}	0.0554	0.0315	0.0323	0.0297

[a] NBO spin densities at B3LYP/6-31G*; zero-field splitting parameters at B3LYP/EPRIII.

much too sensitive to the basis set and level of theory. These problems are not manifest in calculations of the corresponding 3-furylcarbene (**23**) and therefore appear to be related to the presence of the second-row atom (sulfur). For species composed only of first-row elements, the spin-spin interaction term makes the dominant (sole) contribution to *D*. These systems appear to be well-handled by ORCA. For species that include heavier elements, Neese has shown that the spin-orbit interaction term makes the dominant contribution to *D*.[64]

Comparison of 3-thienylcarbene (**13**) and 3-furylcarbene (**23**) is instructive. The computed zero-field splitting parameters of 3-furylcarbene (**23**) exhibit the expected effects of conformational isomerism (Table 4.3), and the prediction that the (*s*-*Z*) conformer displays the larger *D* value is consistent with the qualitative expectations described in the preceding section. The difference in *D* values between the two conformers of 3-furylcarbene (**23**) (ΔD = 0.025 cm^{-1}), however, is significantly smaller than that of 3-thienylcarbene (**13**) (ΔD = 0.071 cm^{-1}). While the very good agreement between the *D* values for the (*s*-*E*) conformers of these carbenes is undoubtedly fortuitous (0.508 cm^{-1} observed for **13**; 0.506 cm^{-1} computed for **23**), it serves to focus attention on the fact the experimental and computed *D* values for the (*s*-*Z*) conformers differ substantially (0.579 cm^{-1} observed for **13**; 0.531 cm^{-1} computed for **23**). Although the computed spin densities in both systems are quite similar (Table 4.2), there appears to be an interaction in the (*s*-*Z*) conformer of triplet 3-thienylcarbene (**13**) that renders it uniquely different, in terms of its zero-field splitting parameter *D*.

We employed NBO calculations to investigate the possible electronic interactions between the sulfur heteroatom and the triplet carbene center in 3-thienylcarbene (**13**). Perhaps the most important conclusion from these studies is the absence of a readily identifiable, dominant interaction between these centers. The analysis does reveal a weak interaction between the filled sp orbital at the carbene carbon and the empty antibonding sigma orbital of the C2-S1 bond in the *s*-*Z* isomer (Figure 4.6). This interaction was absent in the *s*-*E* isomer. The energy of this interaction is not large (0.37 kcal/mol), but it does reveal a subtle distinction in the electronic structure of the conformational isomers.



13 (*s-Z*) **13** (*s-E*)

Figure 4.6. Natural bond orbital analysis of triplet 3-thienylcarbene (**13**).

In summary, our analysis of conformational isomerism in triplet 3-thienylcarbene (**13**) is commensurate with a conventional interpretation, in which differences in spin density at the non-equivalent *ortho* positions give rise to differences in dipolar spin-spin coupling. NBO analyses provide a tenuous hint concerning differential electronic interactions between sulfur and the carbene moiety in the *s-E* and *s-Z* conformers of triplet **13**. It should be noted, however, that nothing in the analysis rigorously requires the assignment of conformers to be correct. The structural assignment is based upon model systems that do not contain a heavy atom.[57] Literature precedent, although sparse, suggests that the spin-orbit contribution in a system that contains a heavy atom will be dominant.[64] It is conceivable that a significant spin-orbit contribution could reverse the predictions of which conformer has the larger or smaller *D* value, thereby reversing the assignments of *s-E* and *s-Z* conformers of triplet 3-thienylcarbene (**13**).

Absence of the Other Carbenes

The inability to generate and characterize triplet 3-furylcarbene (**23**) was the biggest disappointment for us in the current investigation. The electronic absorption spectrum of 3-furyldiazomethane (**3**) is quite similar to the corresponding sulfur analog (**1**), and we did not anticipate a significant difference in the photochemistry of these diazo compounds. For both oxygen- and sulfur-containing carbenes (**23** and **13**), DFT calculations predict triplet ground states for both *s-E* and *s-Z* conformers, with small singlet-triplet energy gaps (ca. 2-5 kcal/mol) (Schemes 4.2-4). The computed singlet-triplet gaps of the 3-furylcarbenes (**23**) are slightly smaller than those of the 3-thienylcarbenes (**13**) – the species that are spectroscopically observed. One conclusion to be gleaned from the computational data shown in Schemes 2 and 3 is that the methylenecyclopropene derivatives, which are formed as the major products during the initial photolysis, lie significantly lower in energy than the singlet carbenes for the oxygen series (ca. 24 kcal/mol lower), compared to the sulfur series (ca. 14 kcal/mol lower). This situation is consistent with a scenario in which a vibrationally hot 3-furylcarbene (**23**) would be more prone to suffer rearrangement to methylenecyclopropene (**19**) than the corresponding 3-thienylcarbene (**13**) – relative to undergoing vibrational cooling by the matrix.

The inability to generate and characterize 2-thienylcarbene (**11**) or 2-furylcarbene (**22**) is less surprising. DFT calculations, by us and by others,[30,31] predict a *singlet* ground state for both conformers of 2-furylcarbene (**22**). The recent analysis by Herges and Haley reveals a substantial thermodynamic stabilization of heteroaryl carbenes.[28] Ring opening of 2-thienylcarbene (**11**) or 2-furylcarbene (**22**) to the corresponding pentenynal is exothermic, relative to the singlet carbenes, by 20 kcal/mol in the sulfur case and 30 kcal/mol in the oxygen case. The computed barriers for ring-opening of *syn* and *anti*-2-furylcarbene (**22**) are very low

(2-4 kcal/mol).[30,31] Herges[29] described the reaction as a coarctate transformation, while Birney[31] interpreted it as a pseudopericyclic process. Independent of the classification, in terms of orbital symmetry, the reaction is one that may be envisioned to occur via a tunneling mechanism (at least at cryogenic temperature). Our experiments, of course, do not establish that either 2-thienylcarbene (**11**) or 2-furylcarbene (**22**) is directly involved in the photochemistry of the corresponding diazo compounds. The literature contains many examples in which reactions occur in an excited state of a diazo compound, circumventing a carbene intermediate altogether.[45,46]

Conclusions

Triplet 3-thienylcarbene (**13**) has been generated upon irradiation of 3-thienyldiazomethane (**1**) ($\lambda > 534$ nm) and characterized by IR, UV/vis, and EPR spectroscopy. The *s-E* and *s-Z* conformers of the triplet carbene exhibit substantially different zero-field splitting parameters ($D = 0.508$ cm^{-1} and 0.579 cm^{-1}, respectively), which arise as a consequence of a large difference in spin density at the two *ortho* positions in the thiophene ring. Despite finding experimental conditions for the successful generation of triplet 3-thienylcarbene, the conditions were not transferable for generating triplet 2-thienylcarbene (**11**) or the isomeric 2- or 3-furylcarbenes (**22**, **23**).

Methods Section

General. ^{1}H NMR spectra (300 MHz) were obtained in Me$_2$SO-d_6; chemical shifts (δ) are reported as ppm downfield from internal SiMe$_4$. Mass spectra and exact mass measurement (EMM) were obtained using electrospray ionization (ESI). Thiophene-3-carboxaldehyde, thiophene-2-carboxaldehyde, furan-3-carboxaldehyde, and furan-2-carboxaldehyde were purchased from commercial sources and purified by vacuum distillation. The matrix isolation apparatus and technique have been described previously,[67,68] and additional details are provided as Supporting Information.

Computational Methods. Optimized geometries, energies, and infrared intensities were obtained at the B3LYP/6-31G* level of theory using the Gaussian software package.[69] The nature of stationary points was confirmed by calculation of the harmonic vibrational frequencies, which also provided zero-point vibrational energy (ZPVE) corrections. Vibrational frequencies were not scaled. Geometries, harmonic vibrational frequencies, and singlet-triplet energy gaps for 2- and 3-thienylcarbene (**11** and **13**) were also computed using coupled-cluster methodology, CCSD,[70] which includes single and double excitations. The correlation-consistent cc-pVTZ basis set was used.[71-73] All CCSD calculations were done in the frozen-core approximation with the CFOUR program system.[74] Natural bond orbital (NBO) calculations were performed at the B3LYP/6-31G* level of theory using the NBO program.[75] Electronic absorption spectra were computed at the B3LYP/6-31G* geometries using time-dependent density functional theory methods (M06 and CAM-B3LYP) and the aug-cc-pVTZ basis set, as implemented in Gaussian09.[69] First-principles calculations of zero-field splitting parameters *D* and *E* were performed at the B3LYP/6-31G* geometries using the B3LYP functional and the EPRIII basis set, as implemented in the ORCA program.[76] Simulations of EPR spectra of randomly oriented triplets were performed using the XSophe program,[77] as supplied by Bruker Instruments. The matrix diagonalization method was utilized (with 1600 partitions and 8 segments).

General Procedure for Preparation of Tosylhydrazones. The tosylhydrazone precursors to compounds **1**, **2**, **3**, and **4** were synthesized using a modified method given by

Katritzky.[78] *p*-Toluenesulfonhydrazide (4.65 g, 25 mmol) was added to a solution of the corresponding aldehyde (25 mmol) in 30 mL of methanol and refluxed for 12 h. The solution was diluted with water (50 mL) and the precipitate was collected by suction filtration. The crude product was recrystallized from methanol and collected once the solution had cooled.

Thiophene-3-Carboxaldehyde Tosylhydrazone. White crystals, yield 70%; mp 155-157 ˚C (lit.[22] 157.5-159 ˚C); ^{1}H NMR (Me$_2$SO-d_6) δ 2.35 (s, 3H), 7.27 (d, *J* = 4.6 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.56 (dd, *J* = 4.9, 2.8 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 1.9 Hz, 1H), 7.93 (s, 1H), 11.28 (s, 1H); MS (ESI) (MH$^+$) 281.1; MS (EMM) (MH$^+$) calculated 281.0413, measured 281.0413.

Thiophene-2-Carboxaldehyde Tosylhydrazone. White crystals, yield 83%; mp 145-146 ˚C (lit.[22] 142-143.5 ˚C); ^{1}H NMR (Me$_2$SO-d_6) δ 2.29 (s, 3H), 7.06 (dd, *J* = 4.9, 3.6 Hz, 1H) 7.35 (dd, *J* = 3.5, 1.1 Hz, 1H) 7.40 (d, *J* = 8.3 Hz, 2H) 7.59 (d, *J* = 4.1 Hz, 1H) 7.71 (d, *J* = 8.2 Hz, 2H) 8.08 (s, 1H); MS (ESI) (MH$^+$) 281.1; MS (EMM) (MH$^+$) calculated 281.0413, measured 281.0410.

Furan-3-Carboxaldehyde Tosylhydrazone. Tan crystals, yield 36%; mp 118-120 ˚C (lit.[22] 116-119 ˚C); ^{1}H NMR (Me$_2$SO-d_6) δ 2.36 (s, 3H), 6.62 (s, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.68 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.85 (s, 1H), 8.02 (s, 1H), 11.26 (s, 1H); MS (ESI) (MH$^+$) 265.1 MS (EMM) (MH$^+$) calculated 265.0642, measured 265.0638.

Furan-2-Carboxaldehyde Tosylhydrazone. Light tan crystals, yield 44%; mp 113-115 ˚C (lit.[22] 125-126 ˚C); ^{1}H NMR (Me$_2$SO-d_6) δ 2.31 (s, 3H), 6.55 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.79 (d, *J* = 3.2 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 1.6 Hz, 1H), 7.77 (s, 1H), 11.43 (s, 1H); MS (ESI) (MH$^+$) 265.1; MS (EMM) (MH$^+$) calculated 265.0642, measured 265.0654.

Preparation of Tosylhydrazide Sodium Salts. Sodium hydride (1.1 eq, 60% suspension in mineral oil) was added to the corresponding tosylhydrazone (1 eq) in THF and allowed to stir at room temperature for 1 h. The resulting precipitate was filtered and dried on a vacuum line. This reaction was run on a 500 mg scale with respect to the tosylhydrazone.

Preparation of the Diazo Compounds 1-4. The diazo compounds were generated by heating the corresponding tosylhydrazone sodium salts to 110˚C under vacuum. The highly colored diazo compound was collected on a cold finger at -78 ˚C and rinsed into a deposition tube with CH_2Cl_2. After solvent removal under vacuum at -41 ˚C, the diazo compound was deposited onto a cold window (IR, UV/vis) or copper rod (EPR) with a constant flow of argon or nitrogen. This procedure yielded the matrix isolated samples of diazo compounds **1**, **2**, **3**, or **4**.

Procedure for Determining Extinction Coefficients for Diazo Compounds 1-4. Diazo compounds **1-4** were formed via the procedure given above, but were rinsed from the cold finger with CD_3CN instead of CH_2Cl_2 to permit the use of ^1H NMR spectroscopy. An NMR sample was made with one milliliter of the original sample and the remaining sample was used to make stock solutions at varying concentrations. The NMR solution was spiked with a known amount of benzene to serve as an internal standard. This allowed the molar quantity of diazo compound to be determined, based upon the integration of the peaks in the spectrum. Finally, dividing the moles of diazo compound in the original sample by the one milliliter sample size used for NMR spectroscopy, the molarity of the original solution could be determined. The different stock solutions were used to determine λ_{max} in the visible and ultraviolet regions of the UV/vis spectrum and the Beer-Lambert law was used to determine extinction coefficients. Samples and solutions were kept in dry ice when they were not being used, in order to minimize decomposition. Solutions slowly warmed to room temperature during the course of NMR or UV/vis spectroscopic measurements.

(3-Thienyl)diazomethane (1). Red liquid. UV/vis (CH_3CN) λ_{max} (nm) (ε) (L mol^{-1} cm^{-1}): 494 (5.98), 260 (2,820), 229 (2,950), 192 (2010); IR (N_2, 10 K) 2065 s, 1597 w, 1544 w, 1534 w, 1435 w, 1404 w, 859 w, 841 w, 763 m, 709 w, 622 w, 485 w, 445 w cm^{-1}; ^{1}H NMR (CD_3CN) δ 5.31 (s, 1H), 6.78 (dd, J = 1.3, 5.0 Hz, 1H), 6.83 (dd, J = 1.3, 3.0 Hz, 1H), 7.44 (dd, J = 3.0, 5.0 Hz, 1H).

(2-Thienyl)diazomethane (2). Red liquid. UV/vis (CH_3CN) λ_{max} (nm) (ε) (L mol^{-1} cm^{-1}): 502 (8.13), 297 (8,620), 204 (6,120); IR (Ar, 10 K) 2071 s, 1597 w, 1523 w, 1449 w, 1381 w, 1306 w, 1077 w, 803 w, 680 w cm^{-1}; ^{1}H NMR (CD_3CN) δ 5.54 (s, 1H), 6.86 (dd, J = 1.0, 3.5 Hz, 1H), 6.99 (dd, J = 3.5, 5.0 Hz, 1H), 7.15 (dd, J = 1.0, 5.0 Hz, 1H).

(3-Furyl)diazomethane (3). Orange-red liquid. UV/vis (CH_3CN) λ_{max} (nm) (ε) (L mol^{-1} cm^{-1}): 491 (8.51), 251 (8,050), 211 (5,260); IR (Ar, 10 K) 2066 s, 1594 w, 1509 w, 1416 w, 1368 w, 1170 w, 1065 w, 1028 w, 874 w, 763 w, 589 w cm^{-1}. ^{1}H NMR (CD_3CN) δ 5.03 (s, 1H), 6.29 (s, 1H), 7.34 (m, 1H), 7.49 (m, 1H – very small coupling). (The NMR sample was spiked with a known quantity of benzene to enable the determination of the solution concentration of diazo compound. The ^{1}H NMR resonance of benzene interferes with the 7.34-ppm resonance of diazo compound **3**, precluding an accurate determination of chemical shift / integration / coupling constant.)

(2-Furyl)diazomethane (4). Orange-red liquid. UV/vis (CH_3CN) λ_{max} (nm) (ε) (L mol^{-1} cm^{-1}): 496 (16.3), 278 (10,800); IR (Ar, 10 K) 2076 s, 1593 w, 1516 w, 1428 w, 1007 w, 927 w, 884 w, 767 w, 713 w, 657 w, 593 w cm^{-1}; ^{1}H NMR (CD_3CN) δ 5.36 (s, 1H), 6.03 (d, J = 3.3 Hz, 1H), 6.45 (dd, J = 2.0, 3.3 Hz, 1H), 7.42 (dd, J = 0.7, 2.0 Hz, 1H).

ASSOCIATED CONTENT

Supporting Information. Matrix-isolation spectra (IR, UV/vis, EPR) associated with the photolyses of diazo compounds **1-4**; details concerning XSophe simulation of triplet EPR spectra; computed energies, harmonic vibrational frequencies, infrared intensities, and Cartesian coordinates of all computed structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(37) Our ability to observe the IR absorption of triplet 3-thienylcarbene (**13**) relied on the use of a nitrogen matrix instead of an argon matrix. IR experiments carried out in argon failed to reveal any bands attributable to the carbene, due to the unfortunate overlap between a strong absorption of 3-thienyldiazomethane (**1**) (disappearing) and the strongest absorption of triplet 3-thienylcarbene (**13**) (appearing). The nitrogen matrix shifts the peaks just enough that the absorption of carbene **13** can be observed.

(38) The IR bands of the minor species in the matrix are weak (Figure S1), and hence the comparison with the computed spectrum of 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**12**) does not establish the structural assignment with a high degree of certainty. We therefore considered alternative structural assignments. 4-Thiacyclohexa-1,2,5-triene (**7**) is another low-energy isomer on the C_5H_4S potential energy surface, but the computed IR spectrum of **7** exhibits poor agreement with the experimental IR bands (Figure S2). Each of the other C_5H_4S isomers (Scheme 2) was also considered, but, in the end, the computed spectrum of **12** remained the most plausible assignment.

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Supporting Information

Photochemistry of Furyl- and Thienyldiazomethanes: Spectroscopic Characterization of Triplet 3-Thienylcarbene

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Tables of Carteisan corrdinates, absolute energies, computed harmoinic vibrational frequencies

and IR intensities can be found online at

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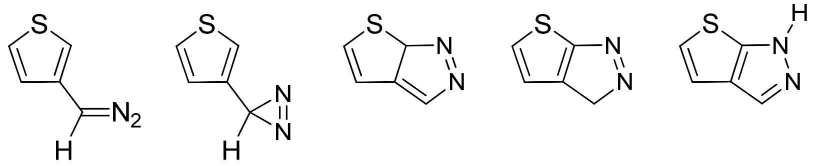
Matrix Isolation Spectroscopy. The matrix isolation apparatus and technique has been described previously.[1,2] Irradiation was carried out with an ILC Technology LX300UV 300 W high-pressure xenon arc lamp, and wavelength selection was achieved with cut-off filters (λ > 613 nm, Corning 2-58; λ > 497 nm, Corning 3-69; λ > 472 nm, Corning 3-71; λ > 444 nm, Corning 3-72; λ > 399 nm, Corning 3-74; λ > 363 nm, Corning 3-075; λ > 330 nm, Corning 3-28; λ > 300 nm, Schott WG 320; λ > 280 nm, Pyrex; λ > 261 nm; Corning 0-53; λ > 237 nm, Corning 0-56) or a Spectral Energy GM 252 monochromator (bandpass of 20 nm). IR spectra were recorded on a Nicolet Nexus™ 870 FT-IR spectrometer equipped with a DTGS detector at a resolution of 2 cm^{-1}. UV/vis spectra were recorded with a Varian Cary 5000 UV/vis/NIR spectrophotometer utilizing a spectral bandwidth of 1.0 nm. EPR spectra were obtained on a Bruker ESP 300 spectrometer with a Bruker ER 042 MRH E microwave bridge and an EIP Model 625A microwave frequency counter. Zero-field splitting parameters were determined by a best fit of the observed spectrum to the spin Hamiltonian (assuming $g_x = g_y = g_z = g_e$).[3]

EPR Experiments in Organic Glasses. The diazo compound was prepared by thermolysis of the tosylhydrazone sodium salt in the usual manner. The diazo compound was rinsed from the cold finger with 3-methylpentane. The UV/vis spectrum of the solution was measured in order to determine the concentration of diazo compound. Solutions for EPR measurement were prepared by diluting the stock solution to ca. 1-5 mM. The solution was introduced into a quartz EPR sample tube, purged with Ar, subjected to four freeze-pump-thaw cycles, and the tube was flame-sealed under vacuum. Under a wide variety of photolysis conditions, irradiation of 3-thienyldiazomethane (**1**) afforded an extremely weak EPR spectrum in which only the strongest Z_1 transition of triplet 3-thienylcarbene (**13**) was observable at 4.2 K.

Photochemistry derived from (3-thienyl)diazomethane (1).

Efforts at elucidating the photochemistry of 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**12**) were attempted by using a monochromator to irradiate at various wavelengths between 350 and 250 nm. Irradiation was carried out in incremental 20 nm steps from 350 to 250 nm. The experiment was begun with broad-band irradiation (λ > 534 nm) of 3-thienyldiazomethane (**1**) to give a mixture of triplet 3-thienylcarbene (**13**), 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**12**), and (*s*-*Z*)-α-thial methylenecyclopropene (**9**), and residual **1**. The matrix was then selectively irradiated at λ = 467 nm with a monochromator to drive away carbene **13**. After this photochemical transformation was complete, irradiation of a matrix containing **1**, **12**, and **9** at λ = 350 nm was begun. Interestingly, irradiation at this wavelength causes **1**, **13** and (*s*-*E*) **9** to grow into the matrix while **12** and (*s*-*Z*) **9** disappear (Figure S7). The growth of (*s*-*E*) **9** was to be expected, as a decrease in (*s*-*Z*) **9** and the corresponding growth of (*s*-*E*) **9** is observed upon broadband irradiation of the matrix at similar wavelengths. The growth of **1**, however, was surprising to us, and we considered the possibility that the minor product in the matrix was not **12**, but rather resulted from a rearrangement of diazo compound **1** to give an alternate structure such as (3-thienyl)diazirine (**34**), 6a*H*-thieno[2,3-c]pyrazole (**35**), or H shift products of 6a*H*-thieno[2,3-c]pyrazole (**36** and **37**) (Scheme S1).

Scheme S4.1. Suspected products from an intramolecular photochemical reaction of (3-thienyl)diazomethane (**1**) and their computed relative energies.[a]



1	**34**	**35**	**36**	**37**
17.1	*29.5*	*33.3*	*16.2*	*0.0*

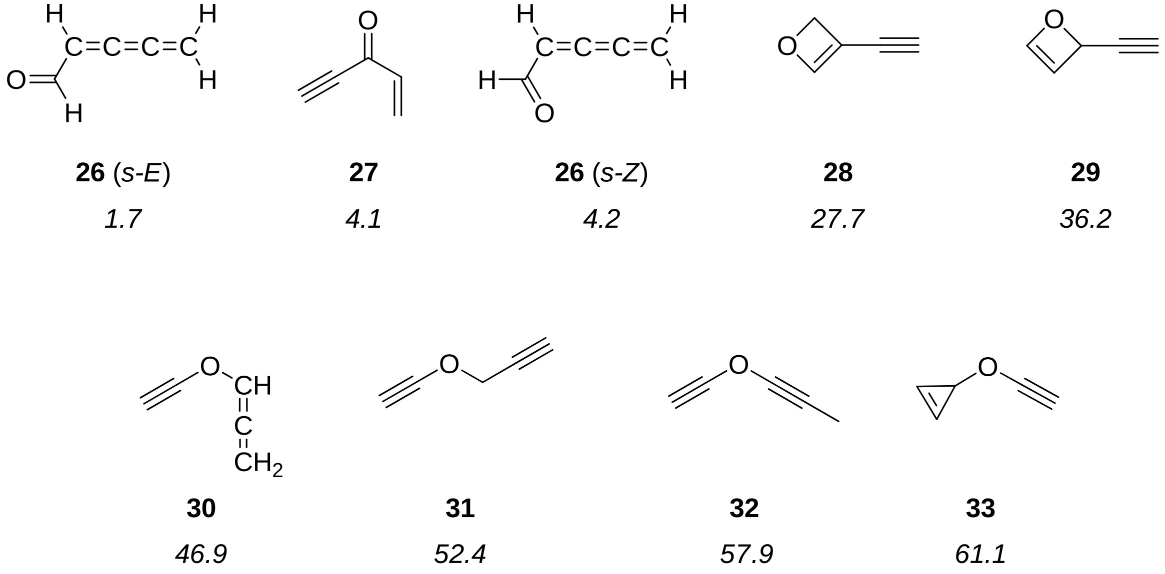
[a] Energy (kcal/mol; ZPVE included). B3LYP/6-31G* level of theory.

The computed spectra of these compounds display poor agreement with the experimentally observed bands. The irradiation conditions were repeated to verify these results and the spectra was reproduced. Further irradiation became markedly more complicated due to the number of species present in the matrix and was not helpful in providing evidence to support a positive identification of the compound of interest (currently assigned as **12**). We are left then, in agreement with Albers and Sander,[4] tentatively assigning **12** to 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene. It is conceivable that **12** photochemically reverts back to carbene **13**, which in an excited state could react with nitrogen in the matrix to regenerate the starting material **1**.

Photochemistry derived from (3-furyl)diazomethane (3).

An unidentified intermediate (**U**, 3429 m, 1636 m, 1476 m cm^{-1}, Figure S16), likely a C_5H_4O isomer, was observed during the photolysis of (3-furyl)diazomethane (**3**). In addition to the structures depicted in Scheme 3 of the manuscript, we also considered the structures depicted in Scheme S2, but none of the computed IR spectra shows a good correlation with the experimentally observed bands of intermediate **U**.

Scheme S4.2. Additional C_5H_4O isomers considered as possible photoproducts from (3-furyl)diazomethane (**3**).



Computed Electronic Absorption Spectrum of 3-Thienyldiazomethane (1).

EPR experiments on triplet 3-thienylcarbene (**13**) reveal a wavelength dependence in the photolysis of 3-thienyldiazomethane (**1**) (Figure 1 and S8). Knowing that the conformational isomers of singlet arylhalocarbenes exhibit distinct differences in their electronic absorption spectra,[5-9] we wondered if the same might be true for the conformers of 3-thienyldiazomethane (**1**). TD-DFT calculations suggest that this is not the case for the visible absorption (Table S.1), which is the region of the spectrum where the wavelength dependence was observed. The only notable difference between the computed absorption spectra of the conformers of **1** involves the oscillator strength of the UV absorption near 245 nm. The computed transitions exhibit modest agreement with the experimental spectrum of 3-thienyldiazomethane (**1**).

It is worth noting that, because of a change in the priority of the substituents involved in naming the compounds, the (*s*-*Z*) conformer of diazo compound **1** correlates with the (*s*-*E*) conformer of carbene **13**, and vice versa (Scheme S3).

Scheme S4.3. Conformational isomers of Diazo Compounds and Carbenes.

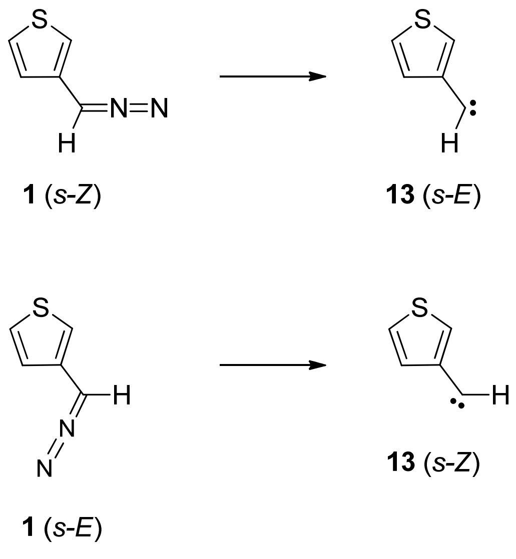
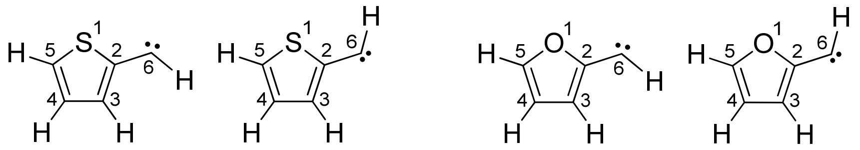


Table S4..1. Computed Electronic Absorption Spectra of Diazo Compounds.[a]

(*s*-*Z*)-3-thienyl diazomethane (**1**)		(*s*-*E*)-3-thienyl diazomethane (**1**)		3-thienyl diazomethane (**1**) (expt; N_2, 10 K)	phenyl diazomethane		phenyl diazomethane (expt)
λ_{max}	*f*	λ_{max}	*f*	λ_{max}	λ_{max}	*f*	λ_{max}
519.5	0.0001	520.0	0.0001	494 [b]	508.9	0.0000	490 [c,d]
312.0	0.0001	314.5	0.0000		305.3	0.0001	
289.1	0.1450	291.0	0.0004	302 sh	285.2	0.0440	
285.8	0.0032	283.9	0.1368	289	283.8	0.0001	
282.4	0.0008	279.5	0.0006		276.9	0.0018	
267.4	0.0001	266.8	0.0009		272.2	0.3992	275 [c,e]
261.0	0.0002	264.3	0.0703	256	256.8	0.0152	
258.9	0.0315	263.8	0.0052		254.4	0.0006	
248.0	0.0063	250.0	0.0002	232 sh	252.9	0.0044	
245.3	0.0533	246.0	0.2087	227	247.0	0.0013	
237.7	0.0011	238.7	0.0003		234.4	0.0008	
235.8	0.0008	233.8	0.0000		230.2	0.0004	
231.7	0.0003	231.3	0.0006		226.2	0.0001	
228.1	0.0000	227.8	0.0004		223.4	0.0894	229 [e]
227.8	0.0030	227.0	0.0065		218.6	0.0006	

[a] (TD)M06/aug-cc-pVTZ // B3LYP/6-31G*; λ_{max} (nm), *f* = oscillator strength. Fifteen lowest-energy singlet excitations reported. [b] in CH_3CN. [c] reference 10. [d] reference 11. [e] reference 12.

Table S4..2. Natural Spin Densities for Triplet 2-Thienylcarbene (**11**) and Triplet 2-Furylcarbene (**22**).[a]



Atom	2-thienylcarbene (**11**)		2-furylcarbene (**22**)	
	(*s*-*E*)-**11**	(*s*-*Z*)-**11**	(*s*-*E*)-**22**	(*s*-*Z*)-**22**
1	+0.098	+0.146	+0.056	+0.078
2	–0.203	–0.215	–0.174	–0.176
3	+0.393	+0.377	+0.390	+0.372
4	–0.119	–0.124	–0.097	–0.103
5	+0.314	+0.322	+0.283	+0.291
6	+1.55	+1.53	+1.58	+1.58

[a] NBO spin densities at B3LYP/6-31G*.

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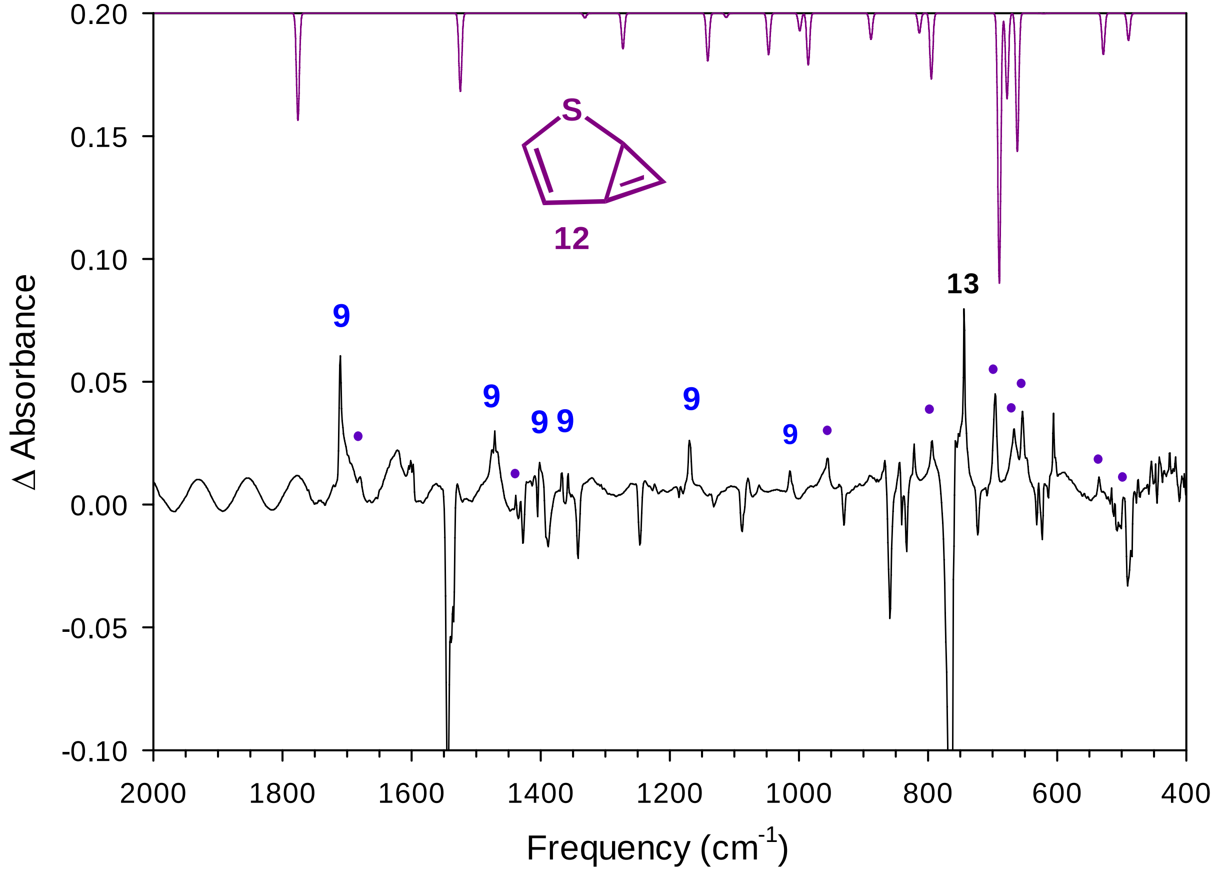


Figure S4.1. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 534 nm, 18 h) of 3-thienyldiazomethane (**1**) (N_2, 10 K). The spectrum shows the disappearance of **1** and the growth of bands attributed to 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**12**) (marked with purple •). The B3LYP/6-31G* calculated IR frequencies of **12** can be seen on top of spectrum. (*s*-*Z*)-α-thial methylenecyclopropene (**9**) and (*s*-*Z*) and (*s*-*E*) 3-thienylcarbene (**13**) are also present in the matrix and labeled accordingly.

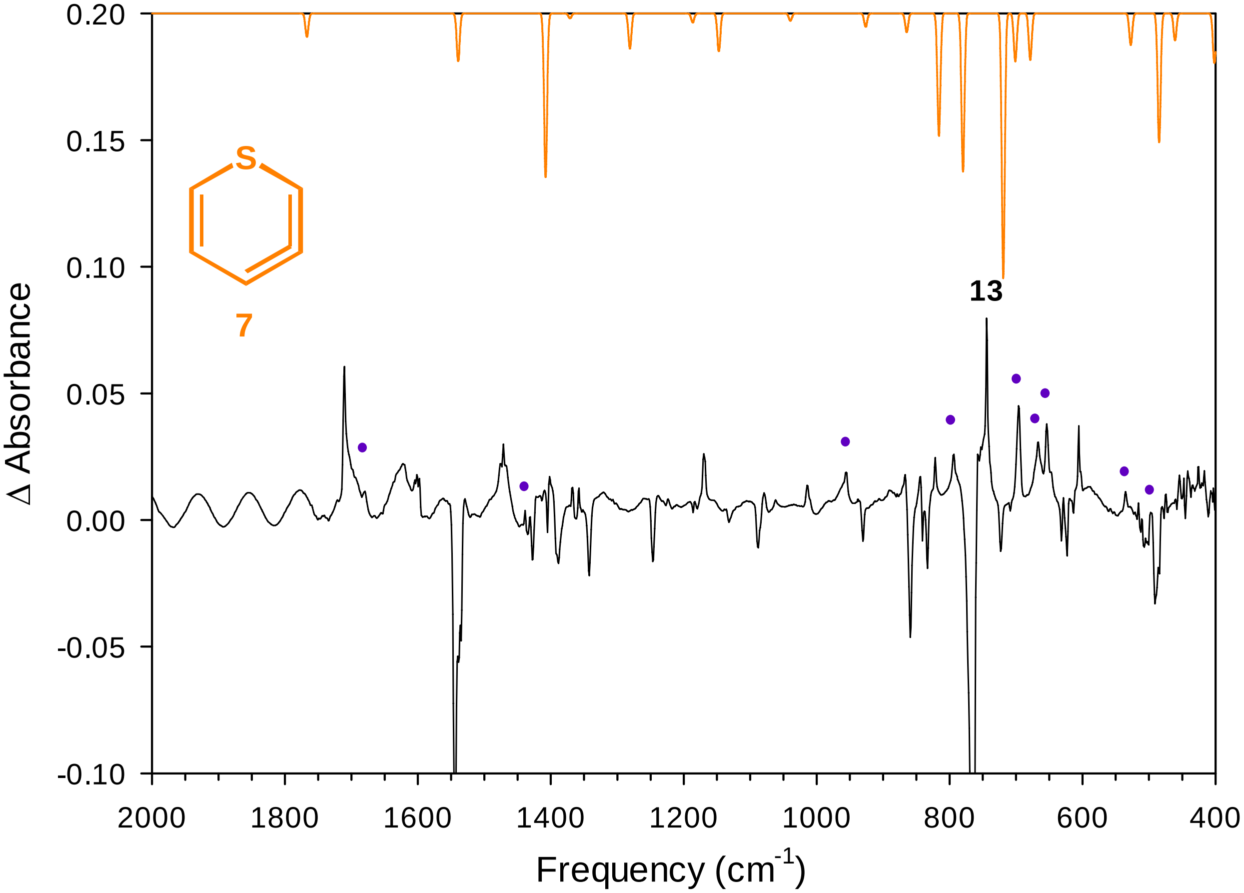


Figure S4.2. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 534 nm, 18 h) of 3-thienyldiazomethane (**1**) (N_2, 10 K). The spectrum shows the disappearance of **1** and the growth of bands attributed to 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**12**) (marked with purple •). The B3LYP/6-31G* calculated IR frequencies of thiabicyclohexa-2,3,5-triene (**7**), another low lying isomer on the C_5H_4S potential energy surface can be seen on top of spectrum. The purpose of this spectrum is to illustrate that the experimentally observed bands assigned to **12** do not match up with **7**.

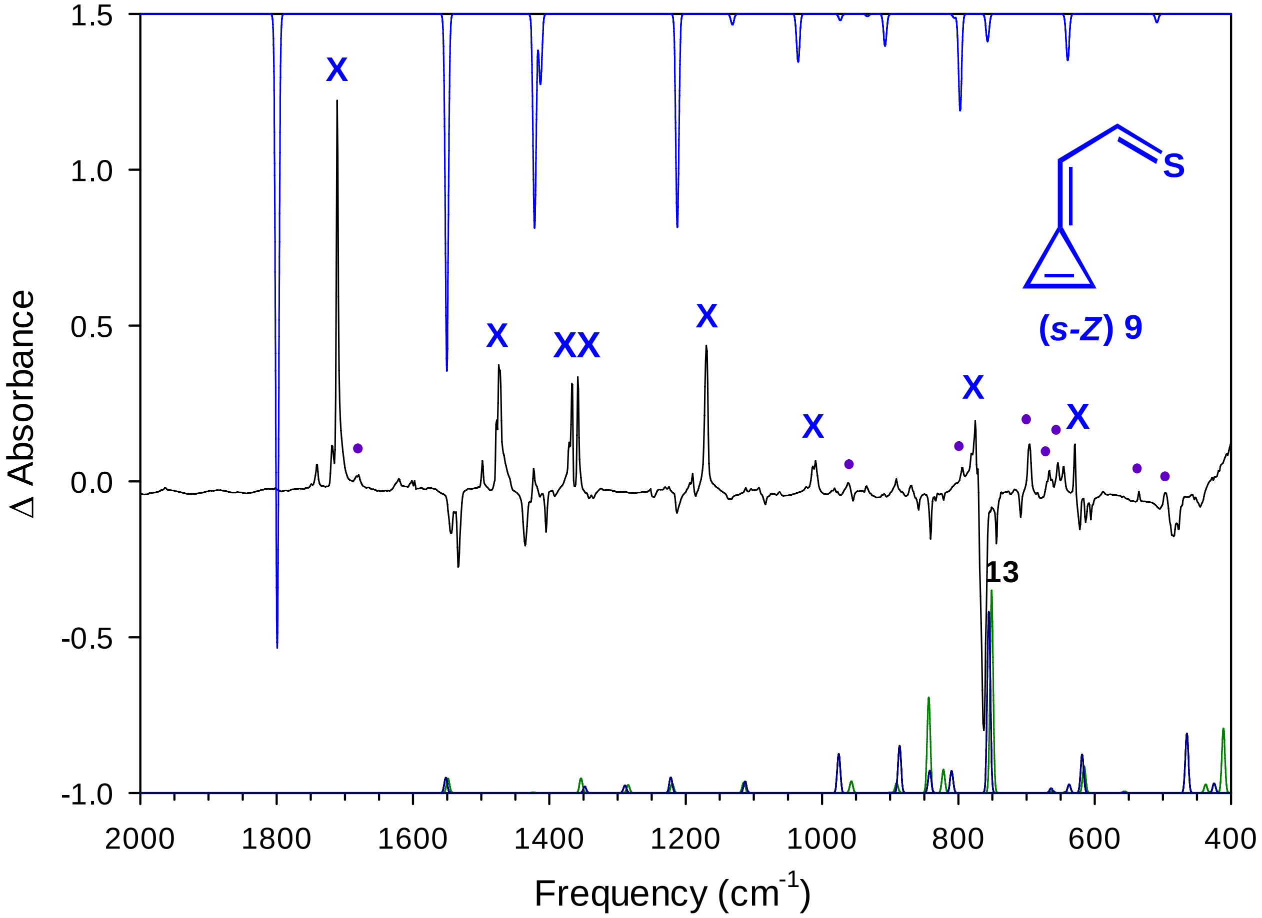


Figure S4.3. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 444 nm,15 h) of a mixture of 3-thienyldiazomethane (**1**), 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**12**), (*s*-*Z*)-α-thial methylenecyclopropene **9**), and 3-thienyl carbene rotamers (**13**) (N_2, 10 K). The spectrum shows the disappearance of **1** and **13** and the growth of **9** (marked with blue **X**) and **12** (marked with purple •). B3LYP/6-31G* calculated IR frequencies for **13** are seen on the bottom of the spectrum, and the major band for **13** is labeled. Calculated IR frequencies for **9** are seen along the top of the spectrum.

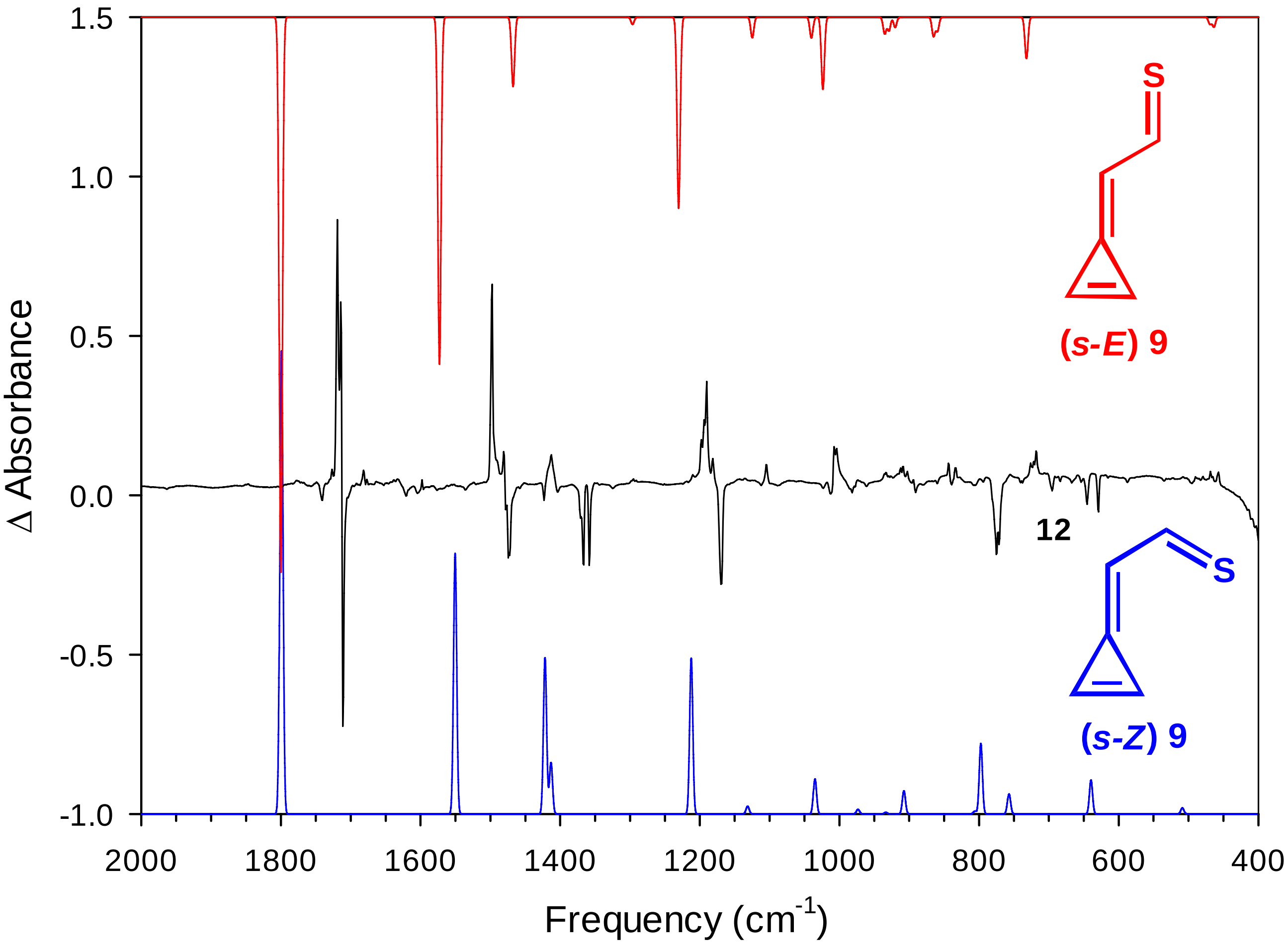


Figure S4.4. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 363 nm, 18 h) of a mixture of a minor amount of 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**12**) and (s-Z)-α-thial methylenecyclopropene (**9**) (N_2, 10 K). The spectrum shows the disappearance of **12**, a decrease in the amount of (*s*-*Z*) **9**, and the growth of (*s*-*E*)-α-thial methylenecyclopropene (**9**).

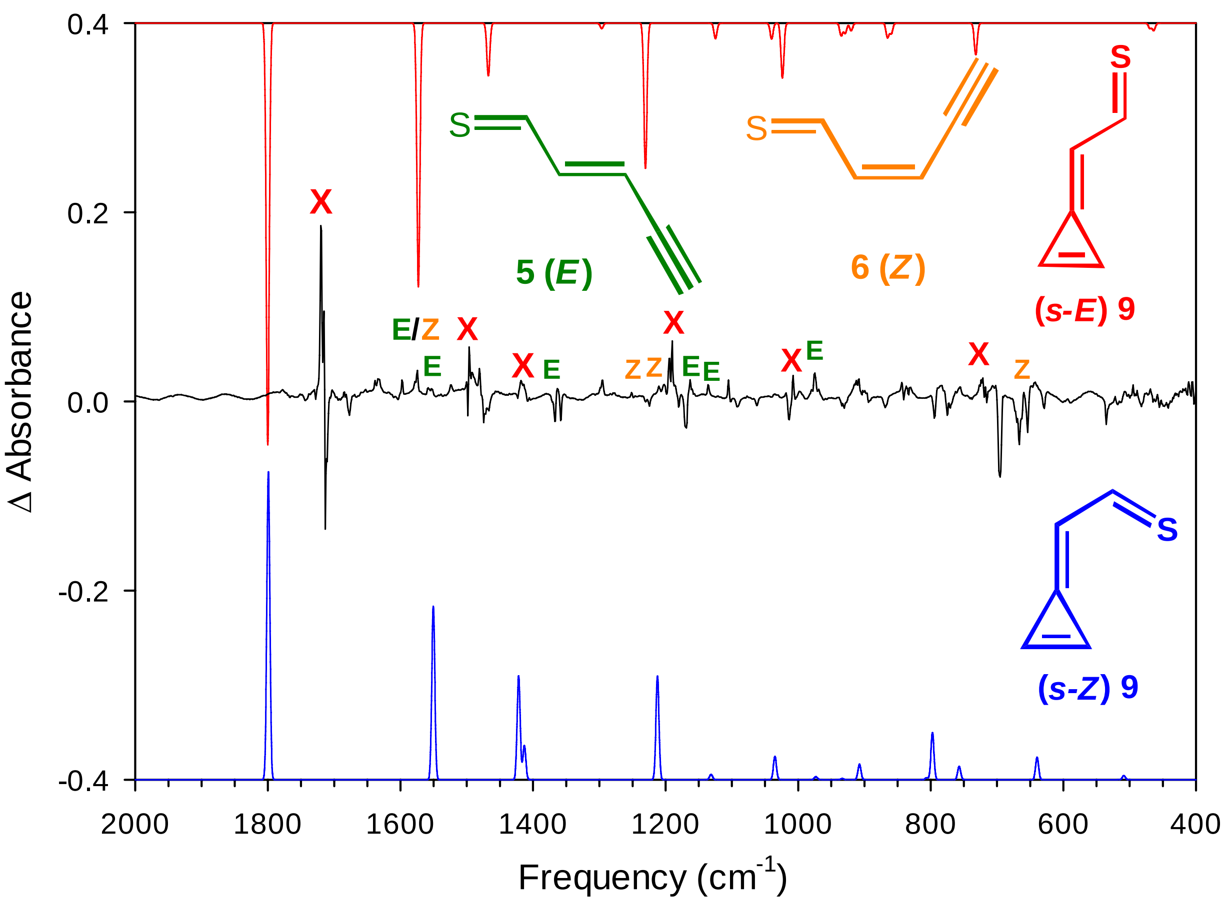


Figure S4.5. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 330 nm, 27 h) of a mixture of (*s*-*Z*)- and (*s*-*E*)-α-thial methylenecyclopropene (**9**) (N_2, 10 K). The spectrum shows further decrease in the amount of (*s*-*Z*)-**9** and the growth of (*s*-*E*)-**9** as the major product (marked with red X's). Minor products *E*-pent-2-en-4-ynethial (**5**) and *Z*-pent-2-en-4-ynethial (**6**) are also observed and are labeled accordingly with *E* or *Z*.

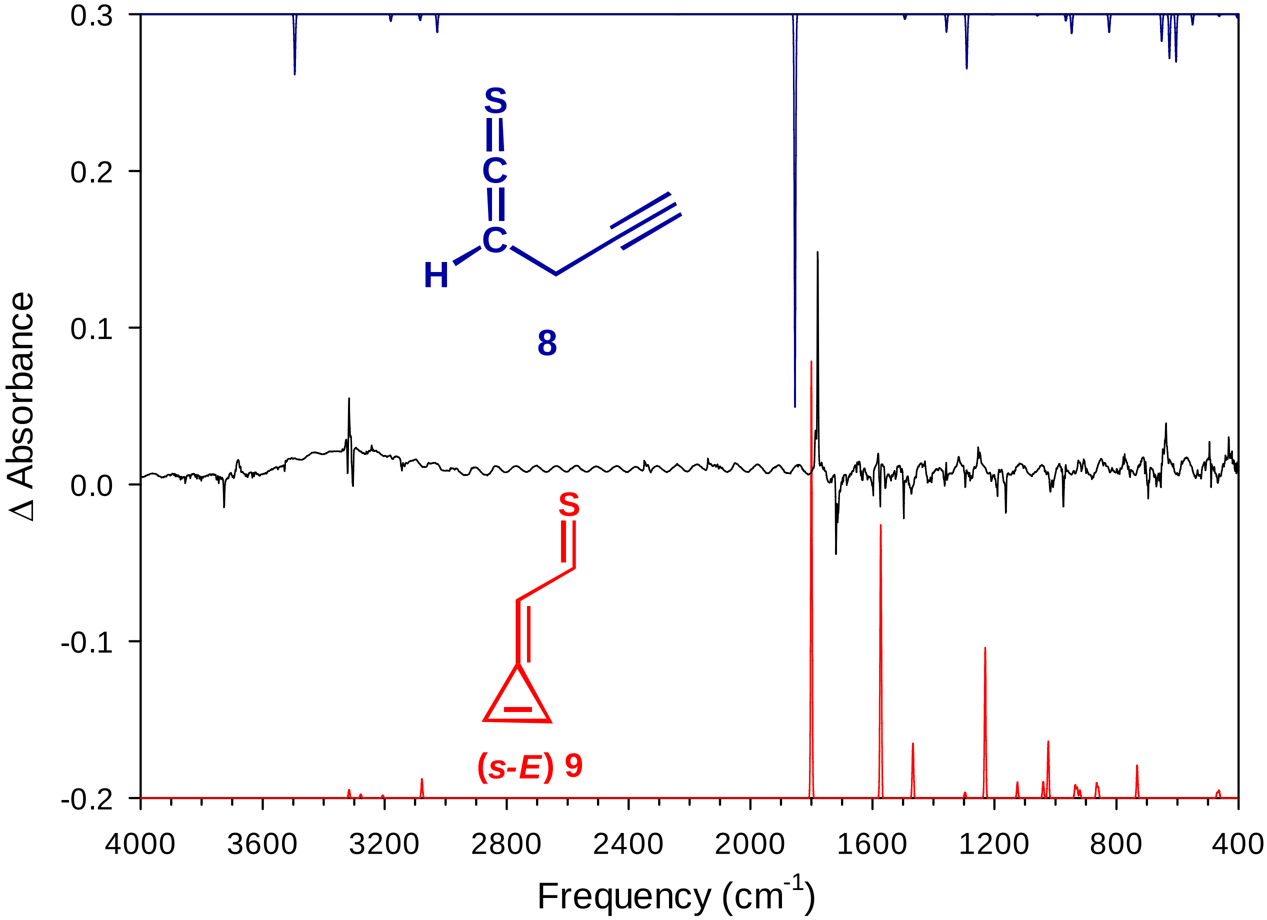


Figure S4.6. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 280 nm, 24 h) of a mixture of (*s*-*Z*)- and (*s*-*E*)-α-thial methylenecyclopropene (**9**), and minor amounts of *E*-pent-2-en-4-ynethial (**5**) and *Z*-pent-2-en-4-ynethial (**6**) (N_2, 10 K). The spectrum shows decreases in **5**, **6**, and **9** (major) and the growth of propargylthioketene (**8**).

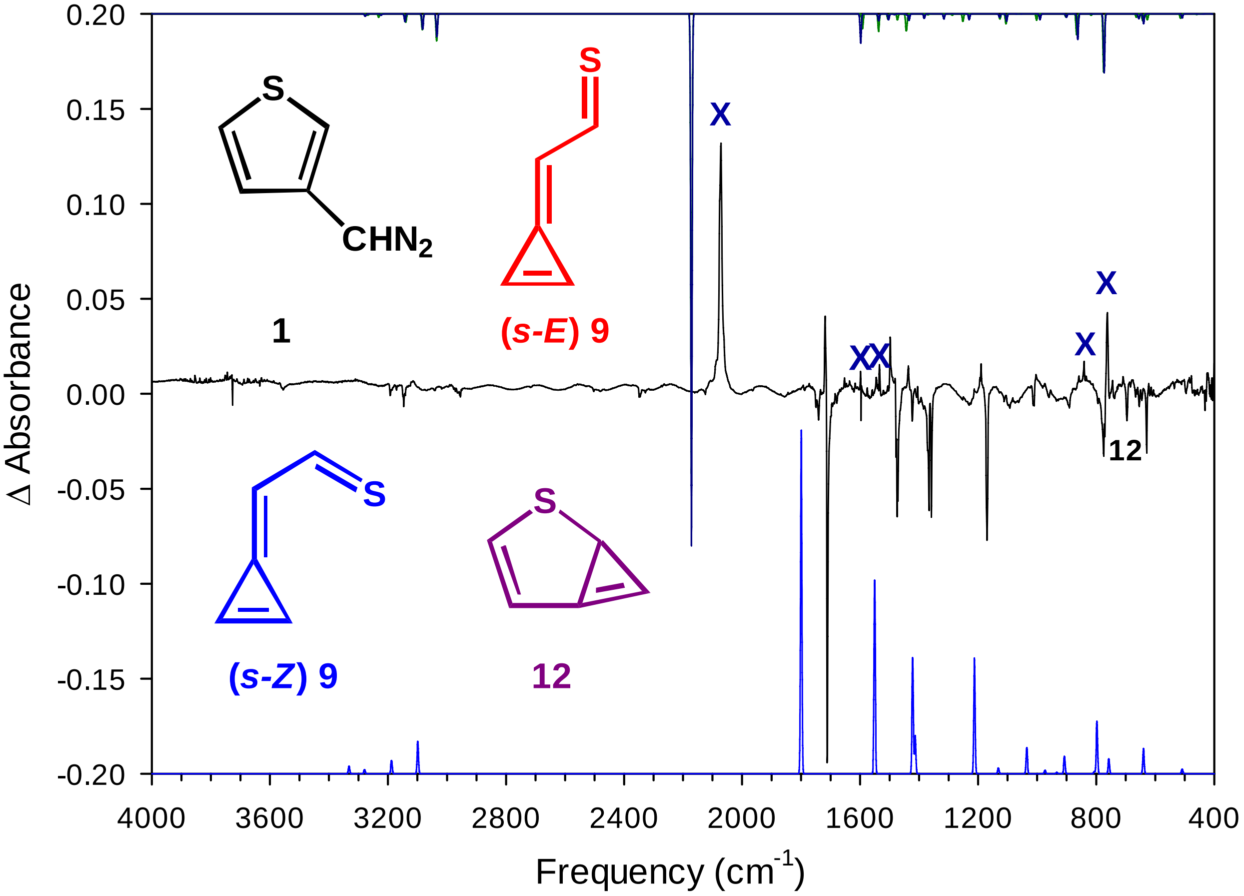


Figure S4.7. IR subtraction spectrum showing spectral changes observed upon irradiation with a monochromator (λ = 350 nm, 5.5 h) of a mixture of 3-thienyldiazomethane (**1**), 3-thienylcarbene (**13**), 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**12**), (*s*-*Z*)- and (*s*-*E*)-α-thial methylenecyclopropene (**9**) (N_2, 10 K). The spectrum shows the growth **1** (marked by blue **X**), a minor amount of **13** (unmarked because of small amount), and (*s*-*E*)-**9**. A decrease in the amount of **12** and (*s*-*Z*)-**9** is observed. The B3LYP/6-31G* calculated IR frequencies of **1** are seen at the top of spectrum. The calculated spectrum of (*s*-*Z*)-**9** is seen along the bottom of the spectrum.

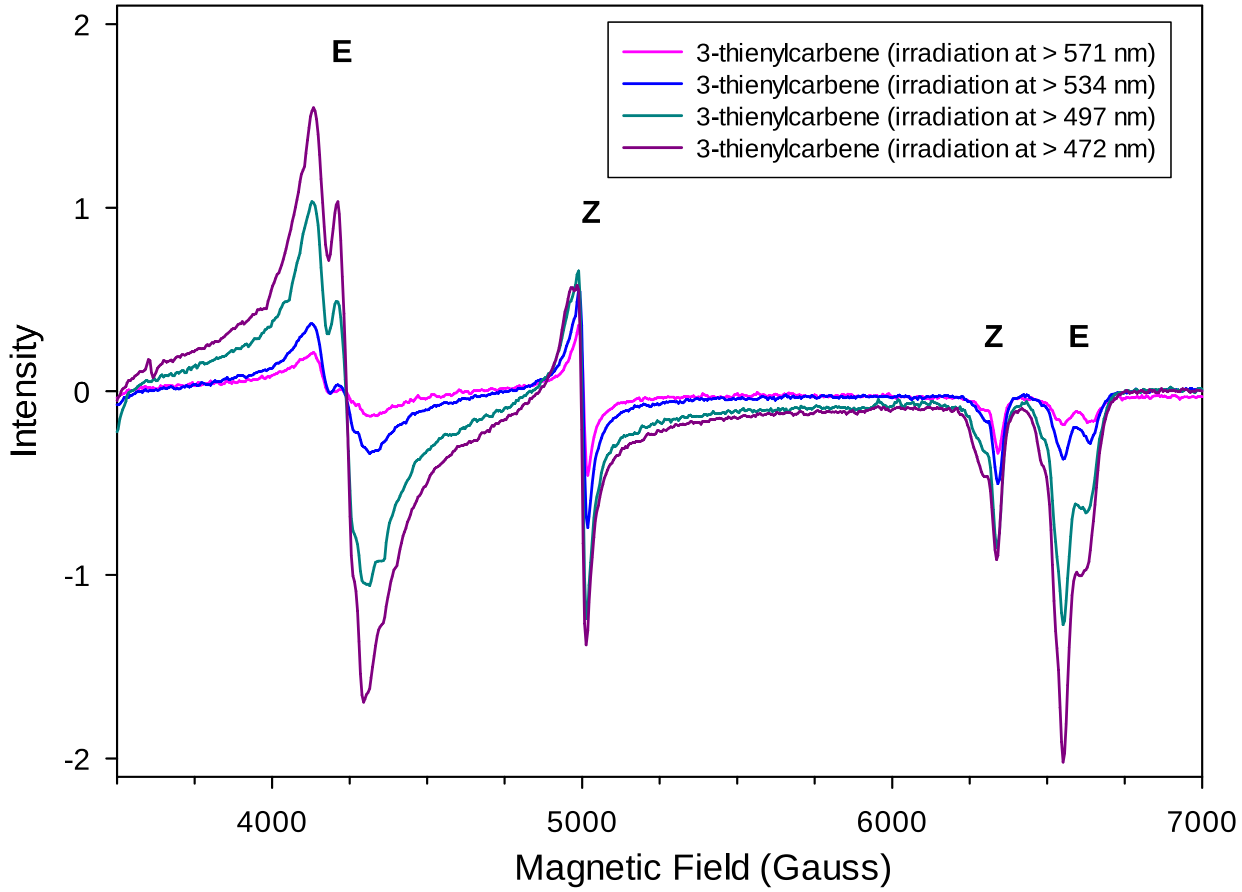


Figure S4.8. EPR spectra of *s*-*Z* and *s*-*E* 3-thienylcarbene (**13**) illustrating the wavelength dependence in the photolysis of 3-thienyldiazomethane (**1**) (Ar, 15 K). The *s*-*Z* conformer is formed in greater proportion upon irradiation at λ > 571 nm, while the *s*-*E* conformer becomes the major photoproduct upon shorter-wavelength irradiation (λ > 534, > 497, > 472 nm). Both rotamers decrease in intensity upon irradiation at > 444 nm (not shown).

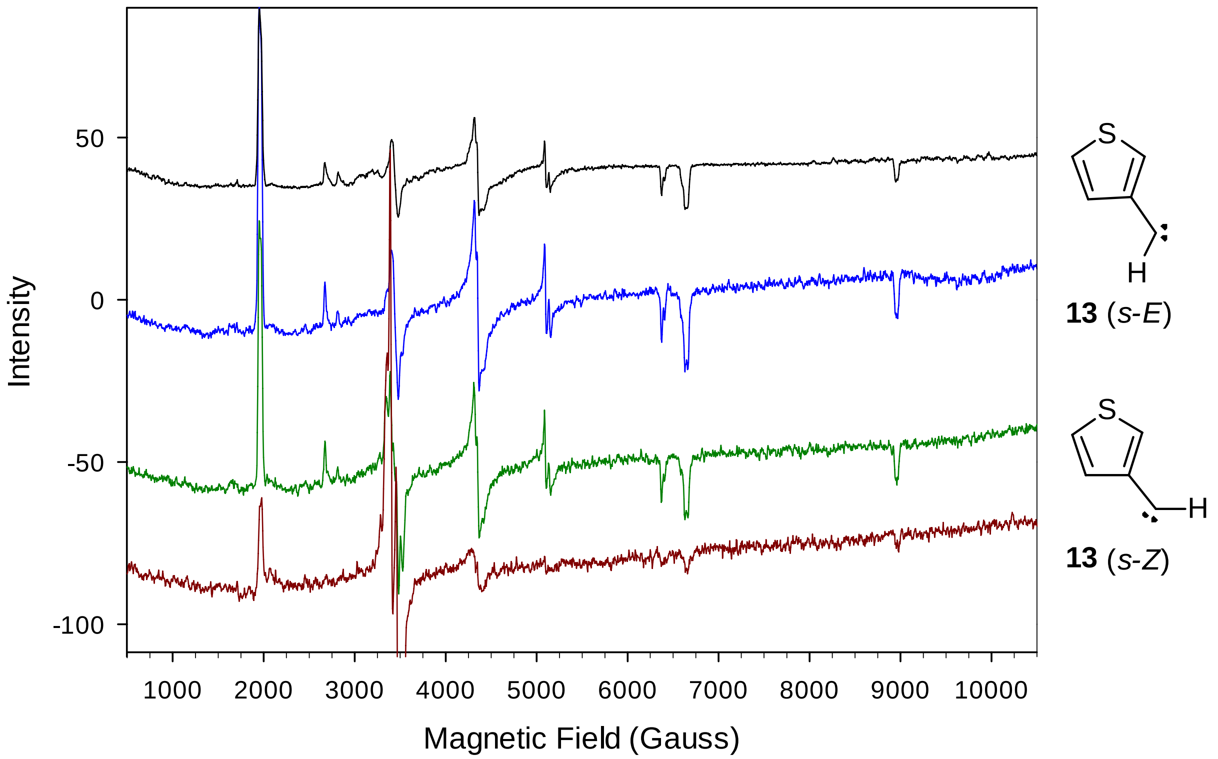


Figure S4.9. EPR spectra of 3-thienylcarbene rotamers (*s-Z* **13** and *s-E* **13**) upon formation and being annealed (N_2, 15 K). Top (black): 3-thienylcarbene (**13**) after irradiation ($\lambda > 472$ nm, 17 h) (Receiver Gain = 1.25×10^4). Second from top (blue): **13** after being annealed to 24 K (Receiver Gain = 1.00×10^5). Second from bottom (green): **13** after being annealed to 29 K (Receiver Gain = 1.00×10^5). Bottom (dark red): **13** after being annealed to 35 K (Receiver Gain = 1.00×10^5).

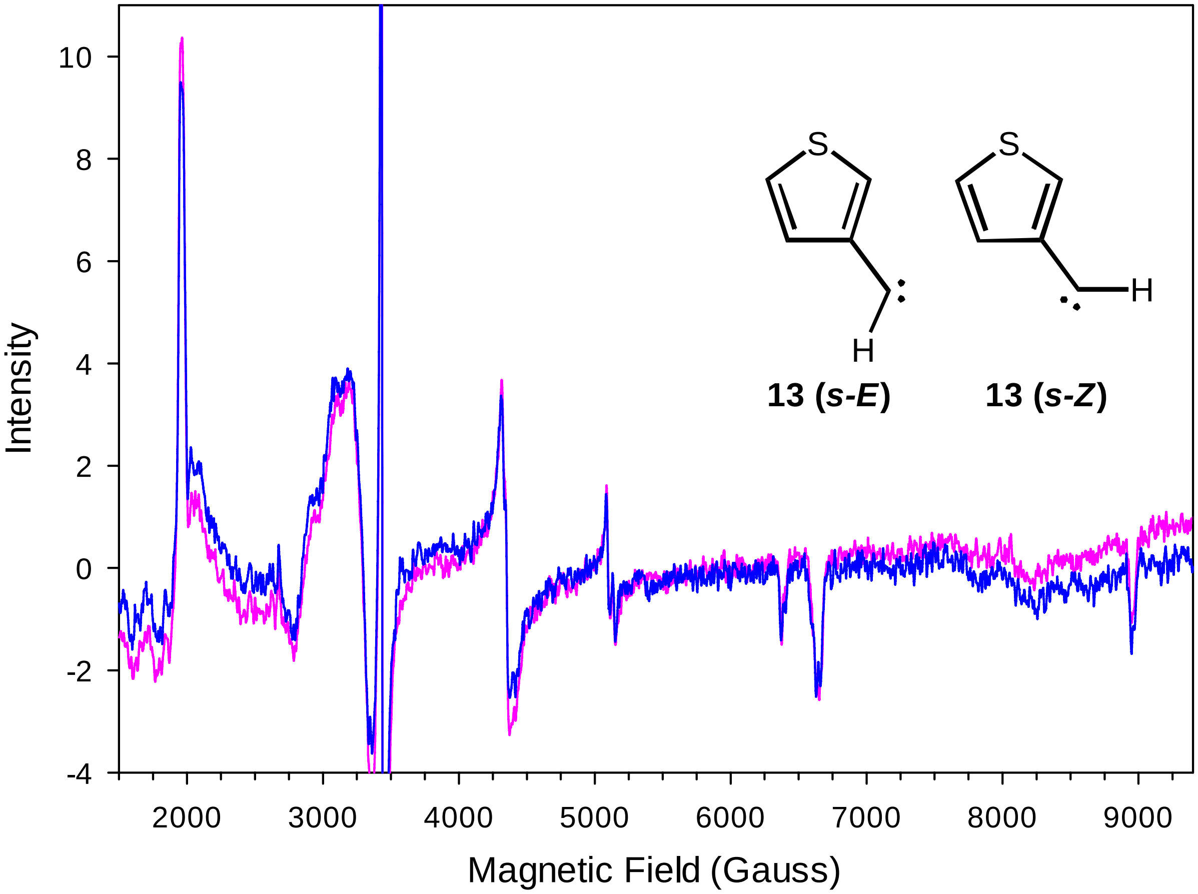


Figure S4.10. Pink: EPR spectrum of *s*-*Z* and *s*-*E* 3-thienylcarbene (**13**) formed upon irradiation of (3-thienyl)diazomethane (λ > 472 nm, 26 h; Ar, 15 K). Blue: EPR spectrum of *s*-*Z* and *s*-*E* 3-thienylcarbene (**13**) after standing in the dark for 46 h. Spectra are on the same scale.

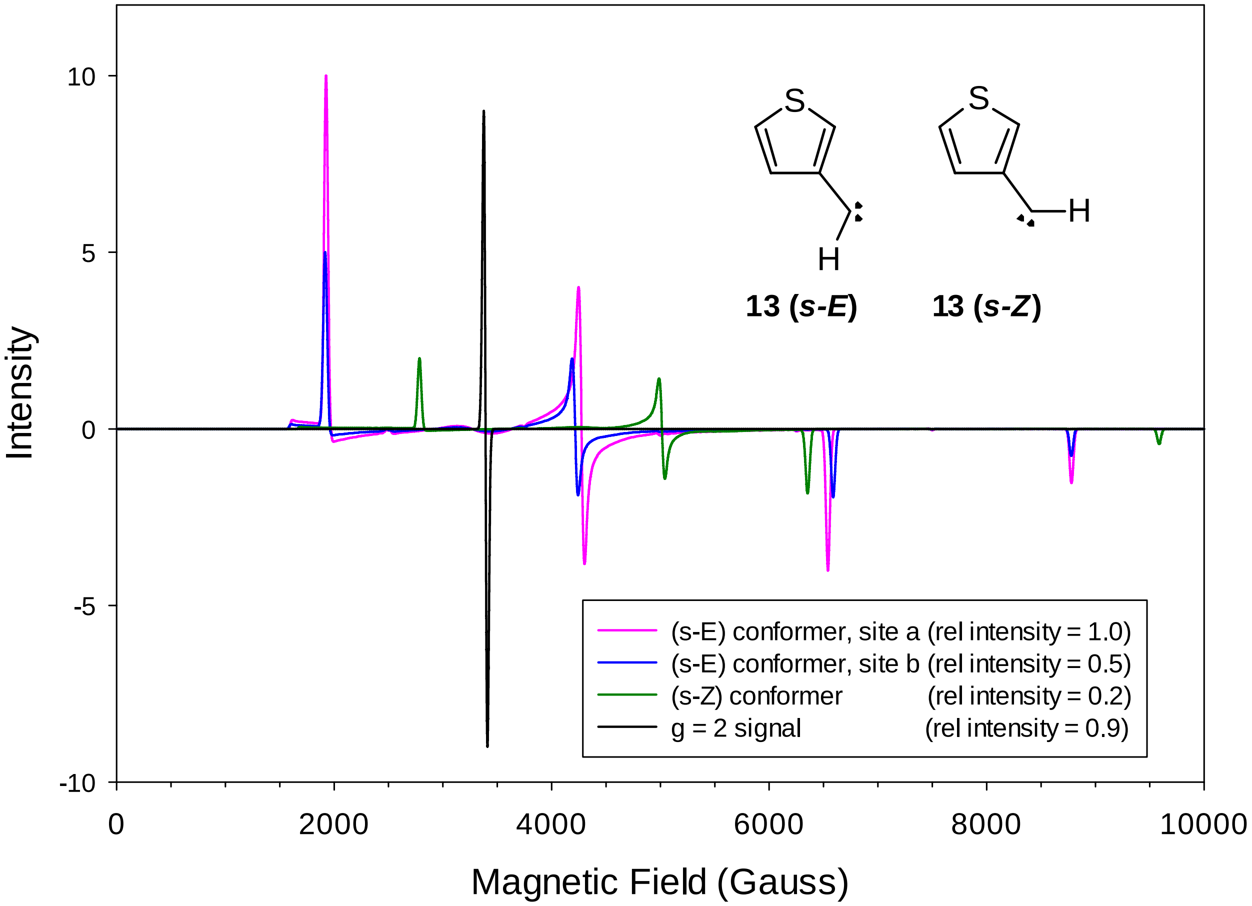


Figure S4.10a. Simulated EPR spectrum of triplet 3-thienylcarbene (**13**) using data from XSophe. Individual components and relative intensities are given in the figure legend.

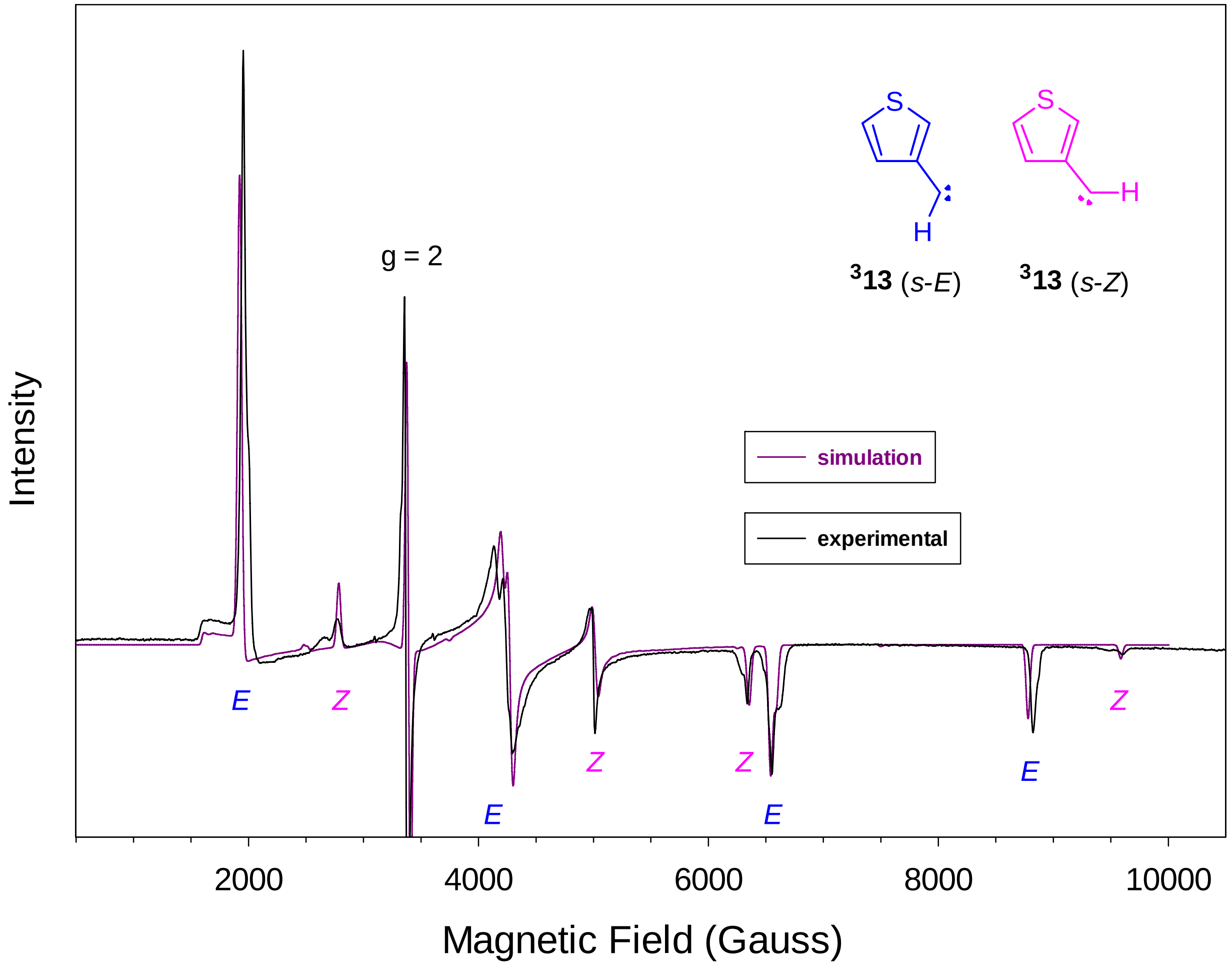


Figure S4.10b. Overlay of experimental and simulated EPR spectra of triplet 3-thienylcarbene (**13**). This figure represents a direct overlay of the spectral data depicted in Figure 5 of the manuscript.

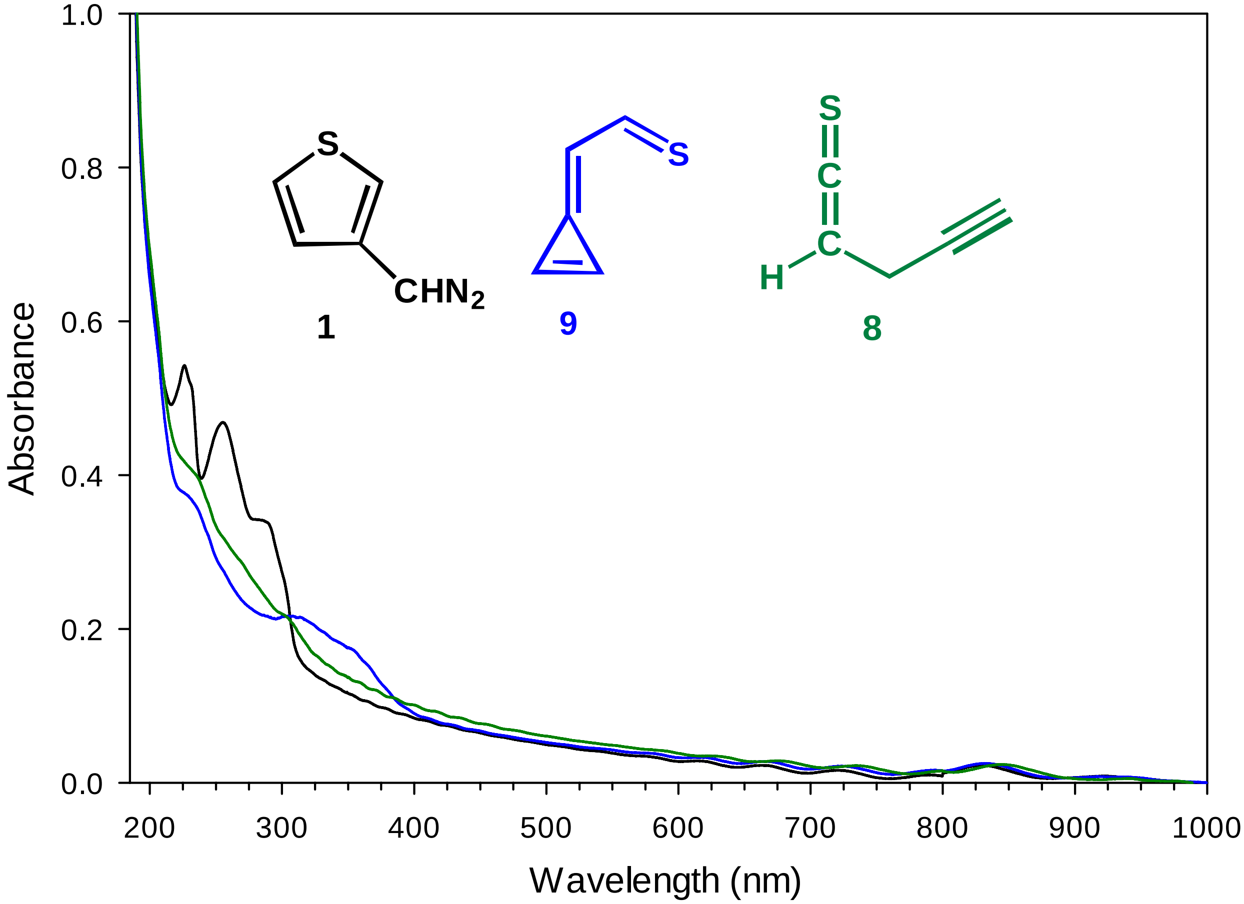


Figure S4.11. UV/vis spectra. **Black:** 3-thienyldiazomethane (**1**) (prior to irradiation; N_2, 10 K). **Blue:** (*s*-*Z*)-α-thial methylenecyclopropene (**9**) (λ > 497 nm, 15 h; N_2, 10 K). **Green:** propargyl thioketene (**8**) (λ > 280 nm, 24 h; N_2, 10 K).

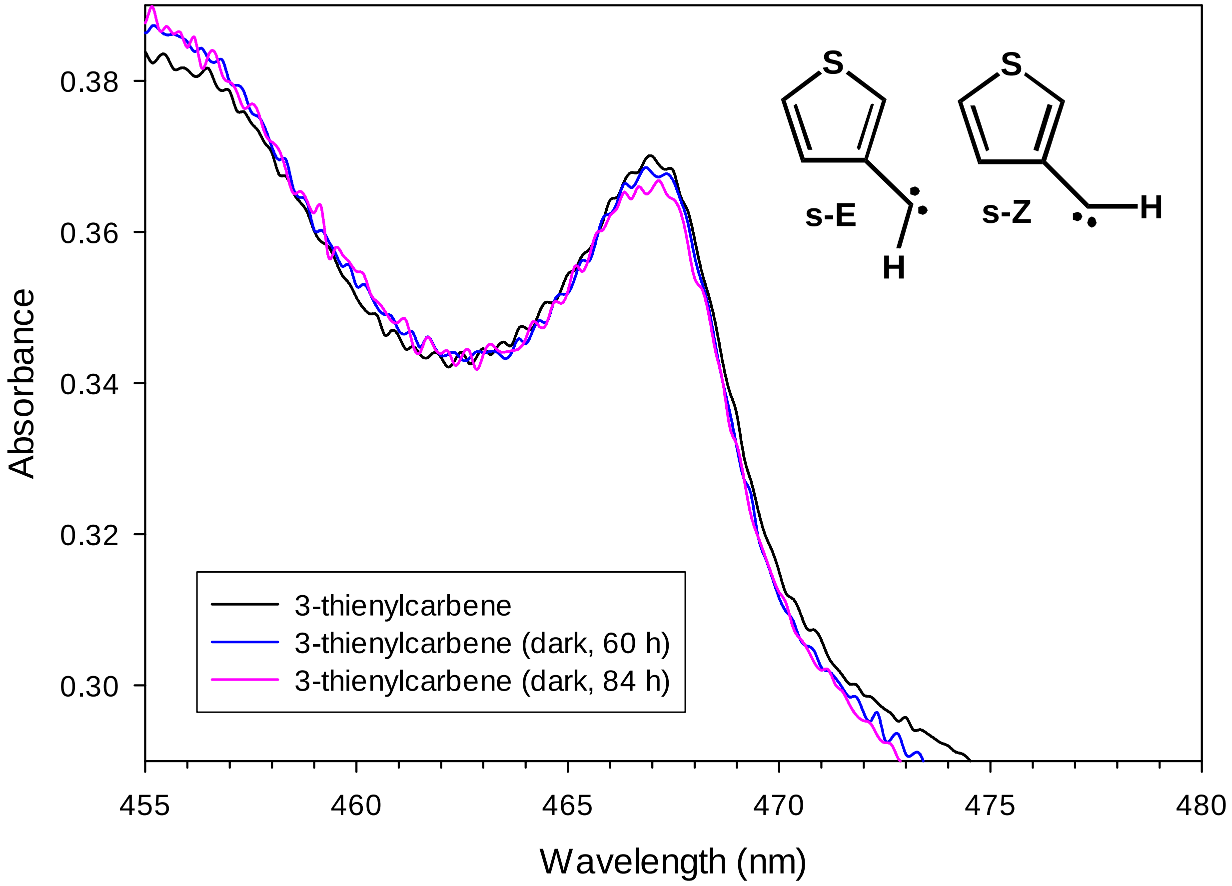


Figure S4.12. Visible spectra. **Black:** *s-Z* and *s-E* triplet 3-thienylcarbene (**13**) after irradiation of 3-thienyldiazomethane (**1**) (λ > 472 nm, 26 h; Ar, 15 K). **Blue:** spectrum obtained after standing in the dark for 60 h. **Pink:** spectrum obtained after standing in the dark for 84 h. Spectra are on the same scale.

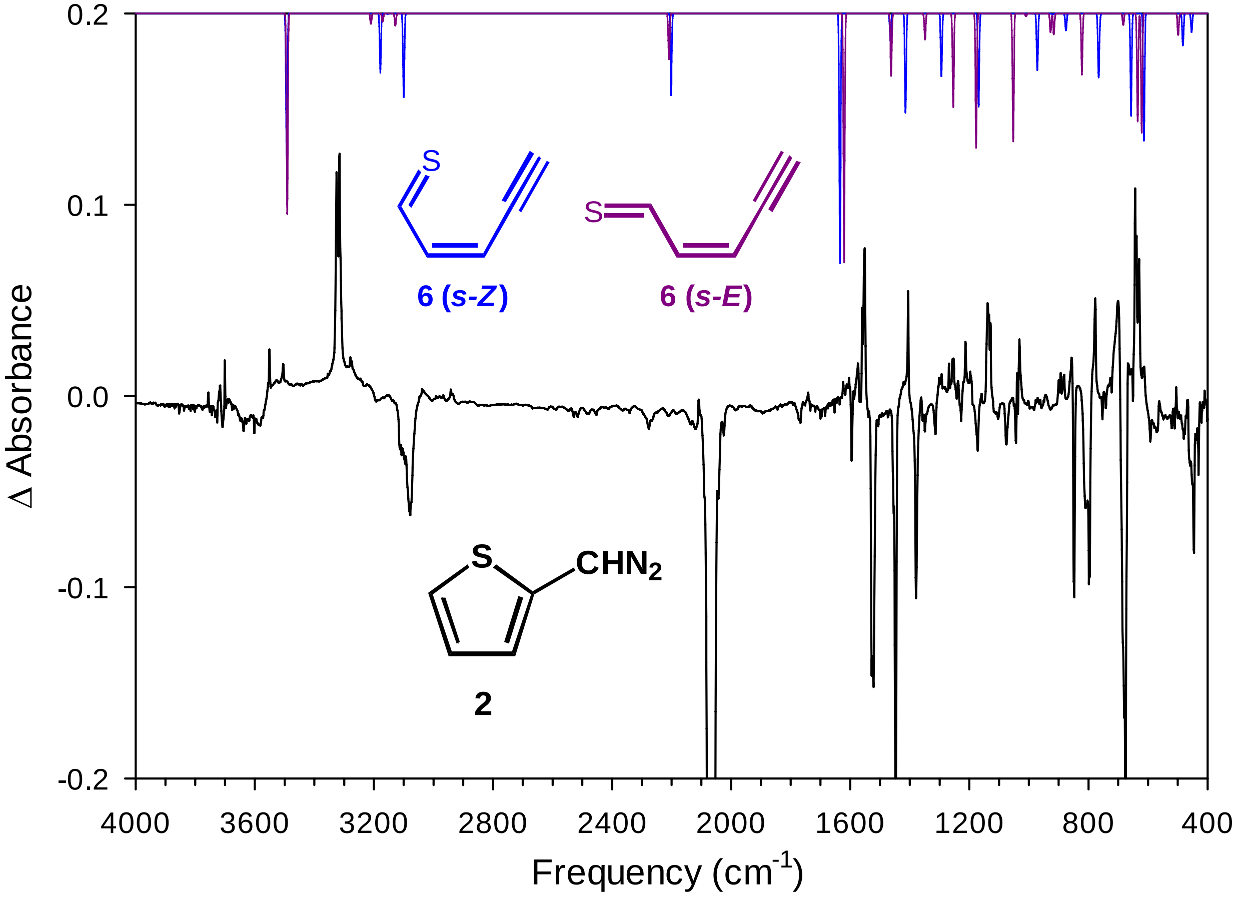


Figure S4.13. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 534 nm, 22 h) of (2-thienyl) diazomethane (**2**) (Ar, 10 K). The spectrum shows the disappearance of **2** and the growth of (*s*-*Z*) and (*s*-*E*)-Z-pent-2-en-4-ynethial (**6**).

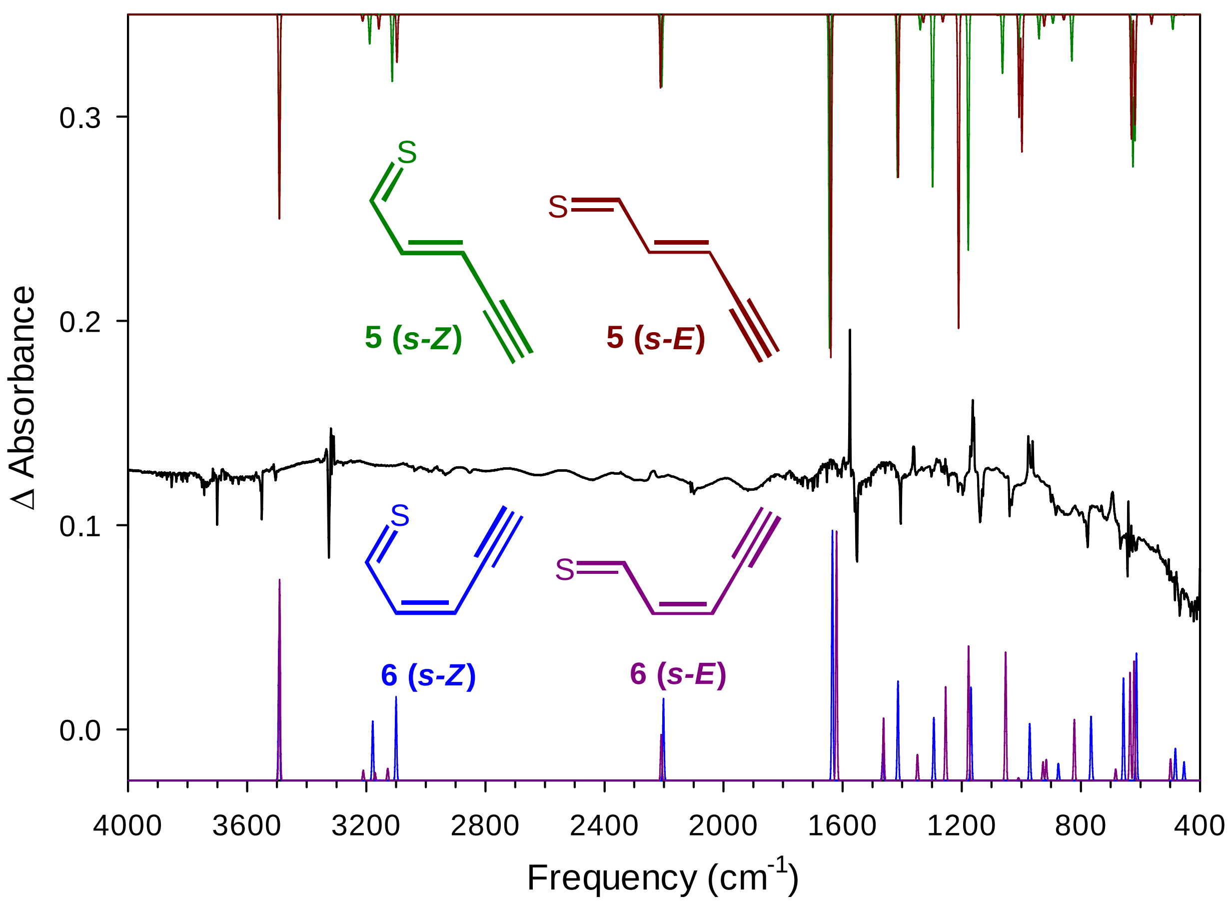


Figure S4.14. IR subtraction spectrum showing spectral changes observed upon irradiation of the matrix shown in Figure S13 (λ > 363 nm, 20 h) of (*s*-*Z*) and (*s*-*E*)-*Z*-pent-2-en-4-ynethial (**6**) (Ar, 10 K). The spectrum shows the disappearance of **6** and the growth of (*s*-*E*)-*E*-pent-2-en-4-ynethial (**5**). The calculated spectrum of (*s*-*Z*)-*E*-pent-2-en-4-ynethial is also shown (green) for comparison purposes.

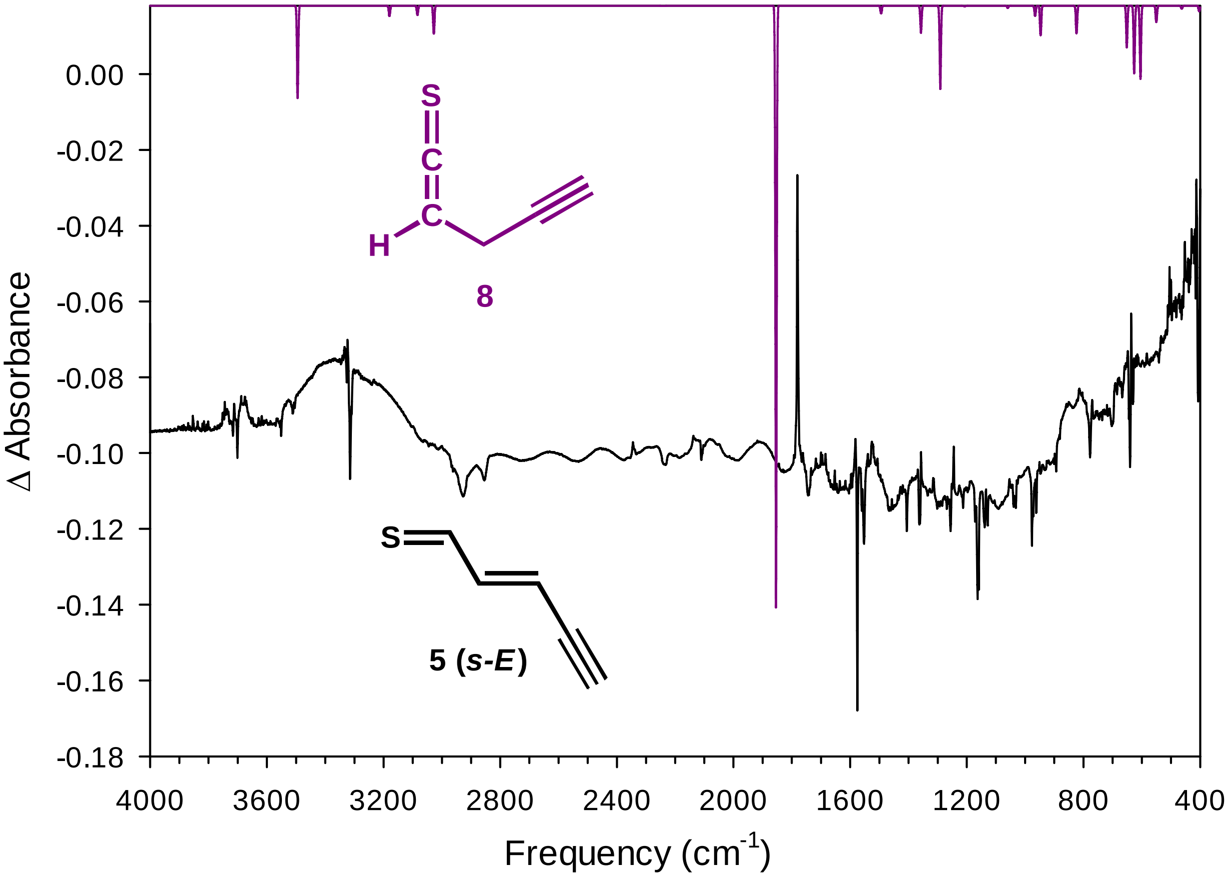


Figure S4.15. IR subtraction spectrum showing spectral changes observed upon irradiation of the matrix shown in Figure S14 (λ > 237 nm, 4 h) of *E*-pent-2-en-4-ynethial (**5**) (Ar, 10 K). The spectrum shows the disappearance of (*s*-*E*)-**5** and the growth of propargyl thioketene (**8**).

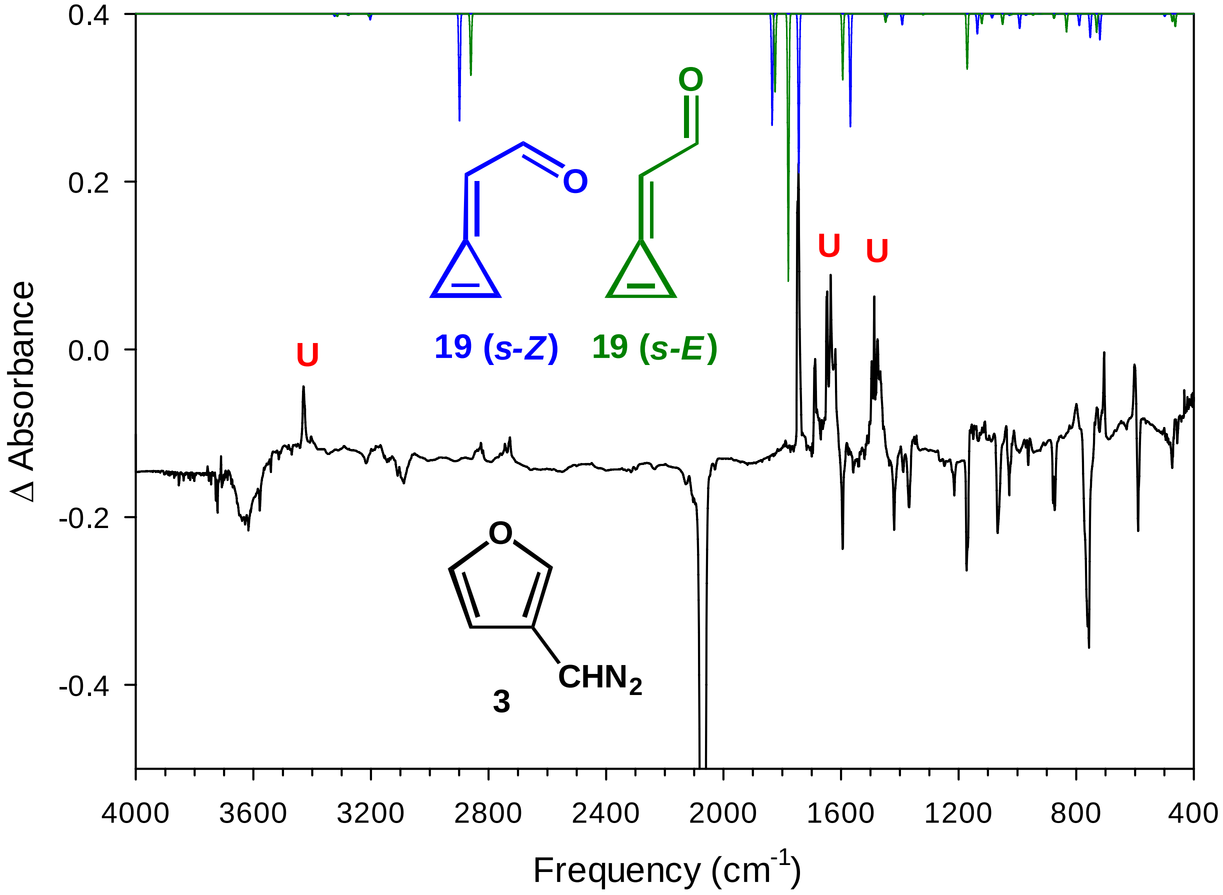


Figure S4.16. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 472 nm, 19 h) of (3-furyl) diazomethane (**3**) (Ar, 10 K). The spectrum shows the disappearance of **3** and the growth of the growth of (*s*-*Z*) and (*s*-*E*)-(α-formyl)methylenecyclopropene (**19**) and an unknown species (**U**).

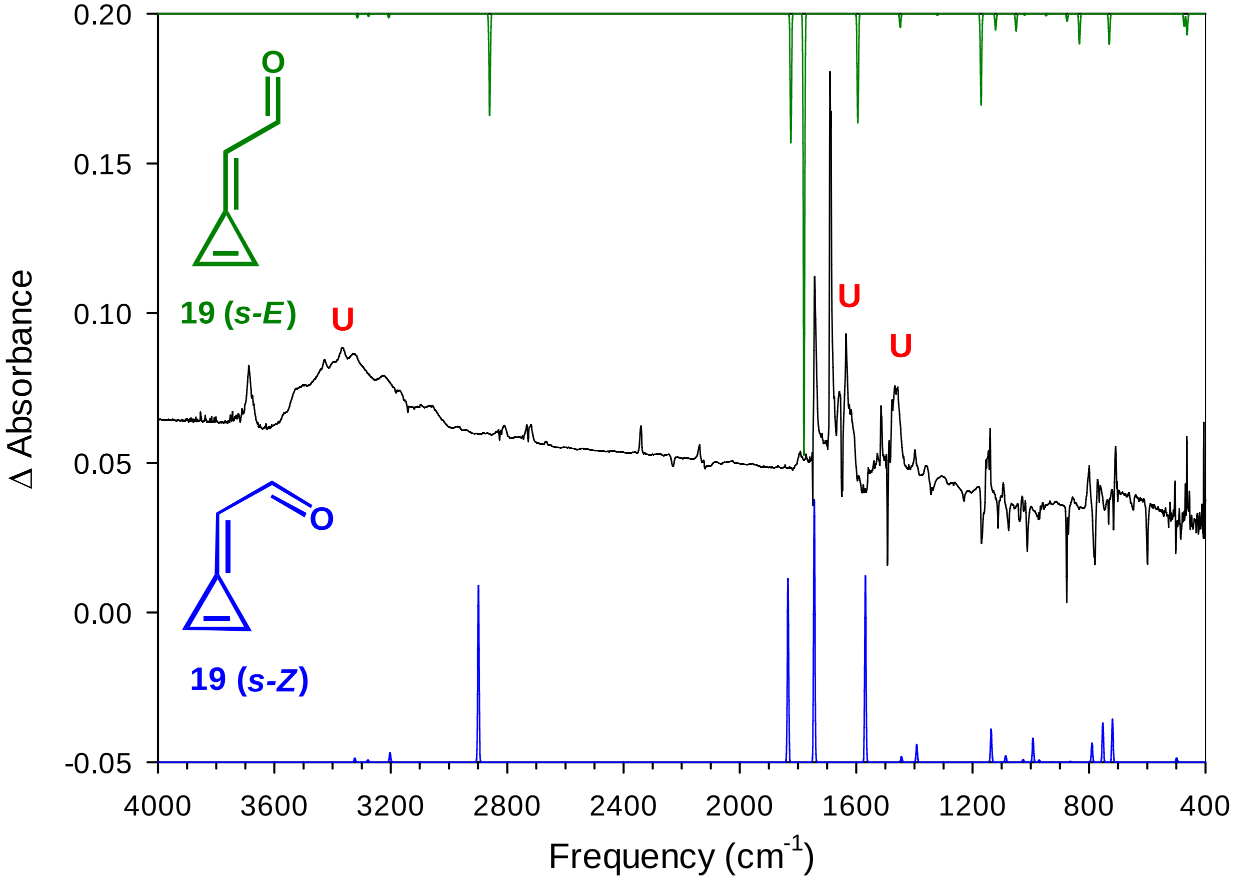


Figure S4.17. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 399 nm, 10 h) of mixture of (*s*-*Z*) and (*s*-*E*)-(α-formyl)methylenecyclopropene (**19**) and an unknown species (**U**) (Ar, 10 K). The spectrum shows the disappearance of (*s*-*Z*)-**19** and the growth of (*s*-*E*)-**19** and **U**.

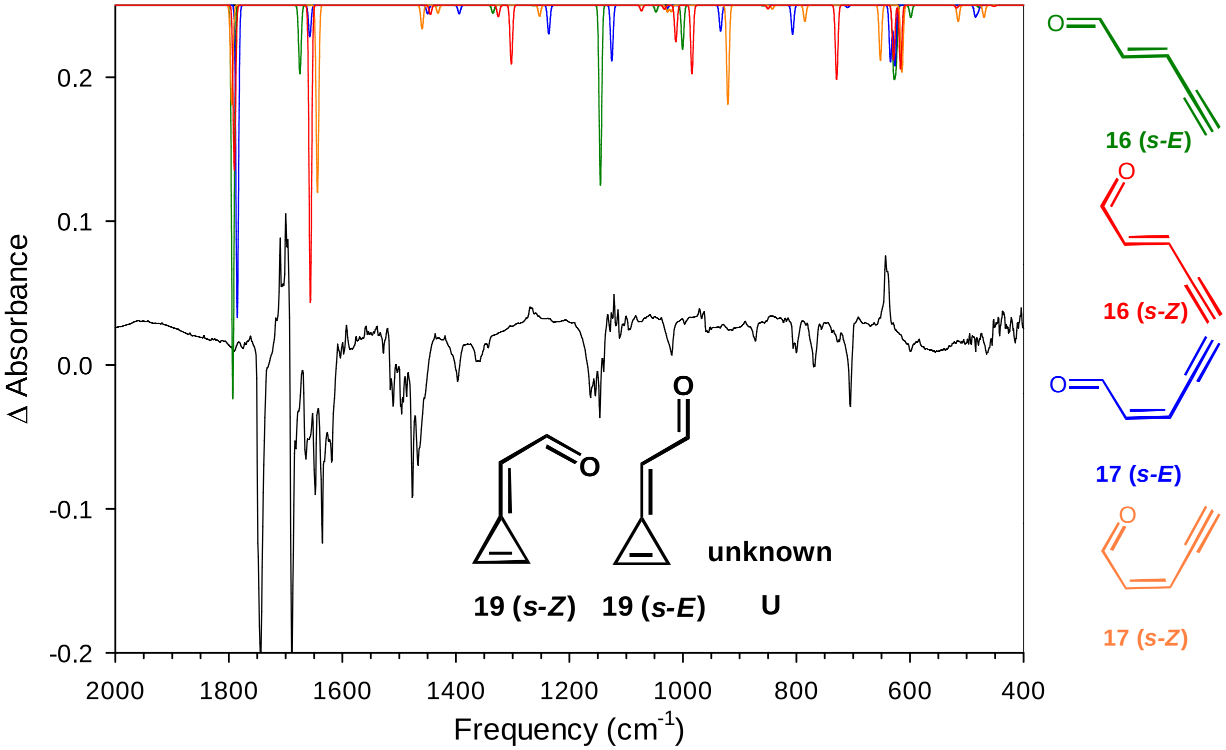


Figure S4.18. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 330 nm, 20 h) of mixture of (*s*-*Z*) and (*s*-*E*)-(α-formyl)methylenecyclopropene (**19**), and an unknown species (**U**) (Ar, 10 K). The spectrum shows the disappearance of **19** and the growth of *E*-pent-2-en-4-ynal (**16**) and *Z*-pent-2-en-4-ynal (**17**). Calculated spectra for (*s*-*Z*) and (*s*-*E*) rotamers of **16** and **17** are seen at the top of the spectrum. Experimental IR stretches are best matched with the (*s*-*E*) rotamers of **16** and **17**.

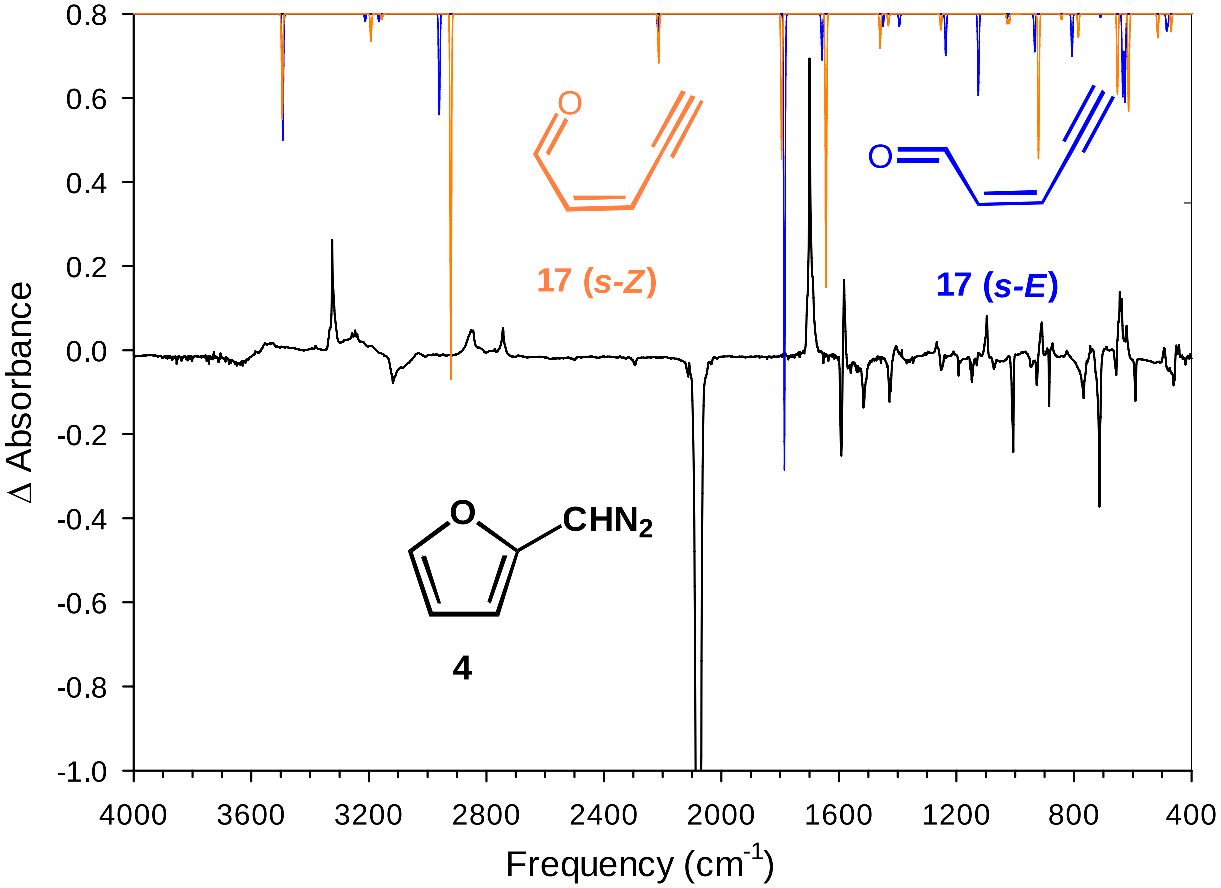


Figure S4.19. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 613 nm, 22 h) of (2-furyl) diazomethane (**4**) (Ar, 10 K). The spectrum shows the disappearance of **4** and the growth of (*s*-*E*)-Z-pent-2-en-4-ynal (**17**). B3LYP/6-31G* calculated IR frequencies of (*s*-*Z*) and (*s*-*E*)-**17** can be seen at the top of the spectrum.

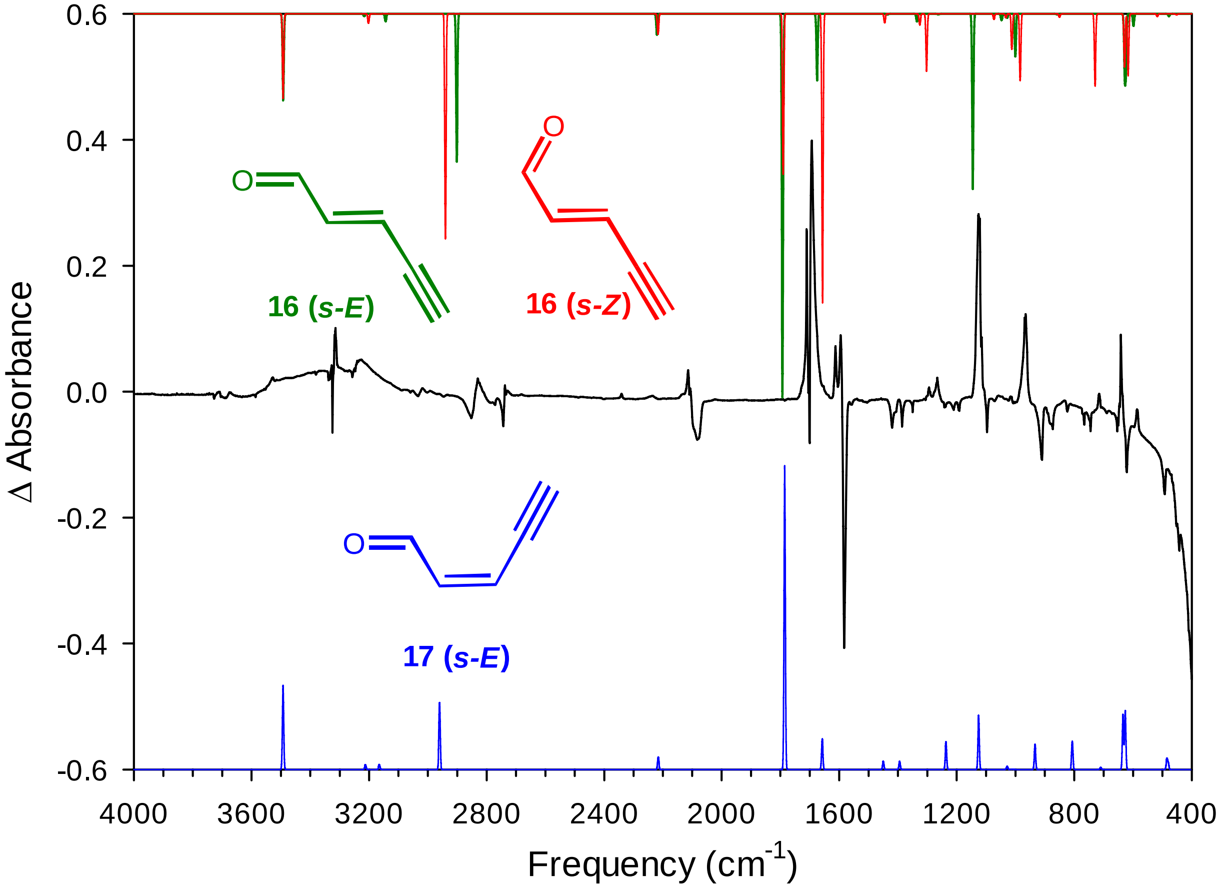
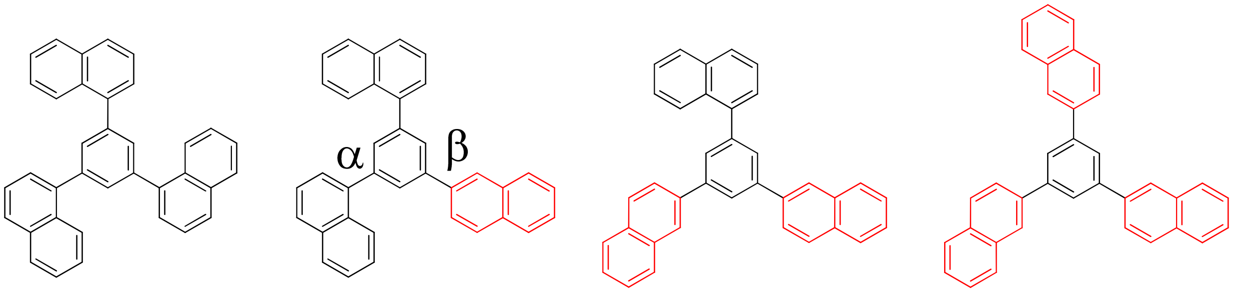


Figure S4.20. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 444 nm, 24 h) of *Z*-pent-2-en-4-ynal (**17**). The spectrum shows the disappearance of (*s*-*E*)-**17** and the growth of (*s*-*E*)-*E*-pent-2-en-4-ynal (**16**).

Appendix A: Updated Synthesis of Trisnaphthyl Benzenes

The initial synthesis of a family of trisnaphthyl benzenes (TNBs) (Figure A1) were published by Whitaker and McMahon in 1996. The most recent synthesis of these molecules is described below.



α,α,α-TNB
1

α,α,β-TNB
2

α,β,β-TNB
3

β,β,β-TNB
4

Figure A1. Structure of the four TNB isomers.

1,3,5-tris(1-naphthyl)benzene (**1**) (**α,α,α-TNB**)

Tribromobenzene (1.0153 g, 3.2 mmol), 1-naphthyl boronic acid (1.5603 g, 9.1 mmol), toluene (10 mL), and absolute ethanol (2.2 mL) were added to a 50 mL round-bottom flask with a stirbar and stirred under N_2 for 20 min at room temperature. $Pd(PPh_3)_4$ (0.301 g, 0.26 mmol) and 2 M aqueous Na_2CO_3 (6.4 mL) were added and the reaction was heated at reflux overnight (23 h at 85 °C). The reaction is cooled, quenched with 50 mL H_2O, then passed through a silica plug to remove the spent palladium. The reaction was transferred to a separatory funnel and extracted 2 x 50 mL benzene. The combined organic layers are washed with 50 mL saturated brine solution, then dried over $MgSO_4$, filtered, and concentrated to give a dark brown oil. To purify, the brown oil was dissolved in CH_2Cl_2 and silica gel was added (1:1 by weight). The mixture was dried to give a brown powder that was loaded onto a silica gel column and separated by column chromatography (9:1 hexane: CH_2Cl_2) to yield a white solid. The solid was dissolved in a minimal amount of CH_2Cl_2 and passed through a micropore filter (0.2 μm PFTE). Excess CH_2Cl_2 was removed and the product was recrystallized from methanol. (yield = 0.98 g, 2.1 mmol, 71.5 %)

1,3-dibromo-5-(2-naphthyl)benzene

Tribromobenzene (5.0021 g, 15.9 mmol), 2-naphthyl boronic acid (2.9991 g, 17.4 mmol), 2 M aqueous Na_2CO_3 (22 mL), toluene (30 mL), and absolute ethanol (7.5 mL) were added to a 100 mL round-bottom flask with a stirbar and stirred under N_2 for 20 min at room temperature. $Pd(PPh_3)_4$ (0.8015 g, 0.69 mmol) were added and the reaction was heated at reflux overnight (20 h at 85 °C). The reaction mixture was cooled and passed through a silica plug to remove the spent palladium. The reaction is transferred to a separatory funnel and extracted 2 x 50 mL CH_2Cl_2. The combined organic layers are washed with 50 mL NH_4Cl, 50 mL $NaHCO_3$, and 50 mL saturated brine solution, then dried over $MgSO_4$, filtered, and concentrated to give a dark semi-solid. To purify, the brown semi-solid was dissolved in CH_2Cl_2 and silica gel was added (1:1 by weight). The mixture was dried to give a brown powder that was loaded onto a silica gel column and separated by column chromatography (9:1 hexane: CH_2Cl_2) to yield a white solid. (yield = 1.8 g, 4.9 mmol, 30.8 %)

1,3-bis(1-naphthyl)-5-(2-naphthyl)benzene (**2**) (**α,α,β-TNB**)

1,3-dibromo-5-(2-naphthyl)benzene (1.8 g, 4.9 mmol), 1-naphthyl boronic acid (2.4996 g, 14.5 mmol), 2 M Na_2CO_3 (12 mL), toluene (45 mL), and absolute ethanol (7 mL) were added to a 100 mL round-bottom flask with a stirbar and stirred under N_2 for 20 min at room temperature. $Pd(PPh_3)_4$ (0.5003 g, 0.43 mmol) were added and the reaction was heated at reflux overnight (15 h at 85 °C). The reaction mixture was cooled and passed through a silica plug to remove the spent palladium. The reaction is transferred to a separatory funnel and extracted 2 x 50 mL CH_2Cl_2. The combined organic layers are washed with 50 mL NH_4Cl, 50 mL $NaHCO_3$, and 50 mL saturated brine solution, then dried over $MgSO_4$, filtered, and concentrated to give a dark brown oil. To purify, the brown oil was dissolved in CH_2Cl_2 and silica gel was added (1:1 by weight). The mixture was dried to give a brown powder that was loaded onto a silica gel column and separated by column chromatography (9:1 hexane: CH_2Cl_2) to yield a white solid. The solid was dissolved in a minimal amount of CH_2Cl_2 and passed through a micropore filter (0.2 µm PFTE). Excess CH_2Cl_2 was removed and the product was recrystallized from methanol. (yield = 0.8218 g, 36.7 %)

1,3-dibromo-5-(1-naphthyl)benzene

Tribromobenzene (2.2340 g, 7.1 mmol), 1-naphthyl boronic acid (1.1030 g, 6.4 mmol), 2 M aqueous Na_2CO_3 (6.5 mL), toluene (10 mL), and absolute ethanol (2 mL) were added to a 50 mL round-bottom flask with a stirbar and stirred under N_2 for one hour at room temperature. $Pd(PPh_3)_4$ (0.2544 g, 0.22 mmol) were added and the reaction was heated at reflux overnight (23 h at 85 °C) until complete by TLC. The reaction mixture was cooled and passed through a silica plug to remove the spent palladium. The reaction is transferred to a separatory funnel and extracted 2 x 50 mL benzene. The combined organic layers are washed with 50 mL saturated brine solution, then dried over $MgSO_4$, filtered, and concentrated to give a dark brown oil. To purify, the brown oil was dissolved in CH_2Cl_2 and silica gel was added (1:1 by weight). The mixture was dried to give a brown powder that was loaded onto a silica gel column and separated by column chromatography (9:1 hexane: CH_2Cl_2) to yield a white solid.Rf = 0.42 (yield = 1.1662 g, 3.22 mmol, 50.3 %)

1,3-bis(2-naphthyl)-5-(1-naphthyl)benzene (**3**) (**α,β,β-TNB**)

1,3-dibromo-5-(1-naphthyl)benzene (0.7033 g, 1.9 mmol), 2-naphthyl boronic acid (0.8043 g, 4.7 mmol), 2 M Na_2CO_3 (4 mL), toluene (20 mL), and absolute ethanol (4 mL) were added to a 50 mL round-bottom flask with a stirbar and stirred under N_2 for 20 min at room temperature. $Pd(PPh_3)_4$ (0.1813 g, 0.16 mmol) were added and the reaction was heated at reflux overnight (20 h at 85 °C). The reaction mixture was cooled and passed through a silica plug to remove the spent palladium. The reaction was transferred to a separatory funnel, 100 mL H2O was added, and the reaction mixture was extracted 2 x 50 mL CH_2Cl_2. The combined organic layers are washed with 50 mL saturated brine solution, then dried over $MgSO_4$, filtered, and concentrated to give a dark brown oil. To purify, the brown oil was dissolved in CH_2Cl_2 and silica gel was added (1:1 by weight). The mixture was dried to give a brown powder that was loaded onto a silica gel column and separated by column chromatography (9:1 hexane: CH_2Cl_2) to yield a white solid. The solid was dissolved in a minimal amount of CH_2Cl_2 and passed through a micropore filter (0.2 μm PFTE). Excess CH_2Cl_2 was removed and the product was recrystallized from methanol. (yield = 0.4814 g, 55.5 %)

1,3,5-tris(2-naphthyl)benzene (**4**) (**β,β,β-TNB**)

Tribromobenzene (0.5004g, 1.59 mmol), 2-naphthyl boronic acid (1.0006 g, 5.81 mmol), dimethoxyethane (20 mL), absolute ethanol (4 mL), and barium hydroxide (1.8522 g, 10.79

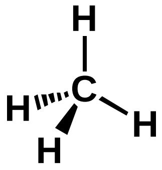
mmol) are added to a 50 mL round-bottom flask with a stirbar and stirred under N_2 for 25 min at room temperature. During this time the reaction changes from brown and cloudy to an opaque pale beige. $Pd(PPh_3)_4$ (0.2309 g, 0.199 mmol) was added and the reaction was heated at reflux overnight (18 h). 50 mL H_2O is added and the reaction mixture is passed through a silica plug to remove the palladium. The organic layer is extracted 2 x 50 mL CH_2Cl_2; the combined organic layers are washed with 50 mL H_2O followed by 50 mL saturated brine solution. The organic phase is dried over $MgSO_4$ and concentrated to give 1.0353 g of a dark brown solid. To purify, the brown solid was dissolved in CH_2Cl_2 and 1.06 g silica gel was added (1:1 by weight). The mixture was dried to give a brown powder that was loaded onto a silica gel column and separated by column chromatography (9:1 hexane: CH_2Cl_2) to yield a white solid (R_f = 0.10). The solid was dissolved in a minimal amount of CH_2Cl_2 and passed through a micropore filter (0.2 μm PFTE). Excess CH_2Cl_2 was removed and the product was recrystallized from methanol. (yield = 0.4949 g, 68.5 %)

Appendix B: Doing the Impossible – Matrix Isolation as a Way to Study Highly Reactive Molecules

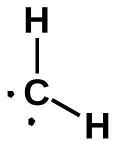
Many of us, at some point in our lives, have looked up at the night sky and wondered what was out there. Scientists give us a lot of different answers – planets, stars, asteroids, lots of empty space. And some scientists ask how these things came to be – how did planets form, how did we form?

What we try to do is look even smaller, studying small molecules that we think should be found in outer space. When we think about the interstellar medium (ISM), the space between stars and star systems, we think of an area that is cold (average temperature around 10 K, which is - 442 °F), and where there are very few molecules (only about 10^6 molecules per m^3, as opposed to 10^{25} molecules per m^3 on earth). There are also cosmic rays to deal with in space, waves of energy emanating from stars. All of this leads to a harsh environment where molecules exist that cannot (easily) exist on Earth. And these are the types of molecules that we like to study.

The types of molecules we are interested in are carbenes – a carbon atom that, instead of having four bonds to other atoms, has two bonds to other atoms, and two electrons that are not bonded to anything.

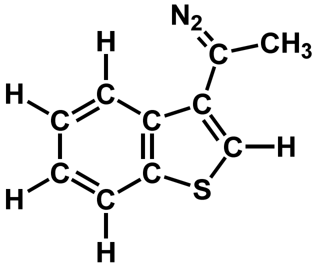


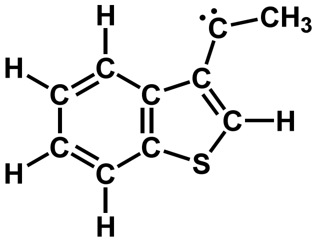
Carbon is most stable when it has four bonds (8 electrons) around it



In a carbene, there are two bonds and two other electrons around carbon, making it very reactive

This means that instead of having a total of eight electrons around this carbon atom, there are only six electrons around it, which makes the molecule very reactive. Depending on the nature of the two groups bonded to the carbene carbon, the carbene will exist as either a singlet (where the two electrons are paired up and in the same orbital) or a triplet (where the two electrons are not paired and so are in different orbitals). Singlet and triplet carbenes have different properties and will react differently. What I have been studying are triplet carbenes, specifically benzothienyl triplet carbenes.

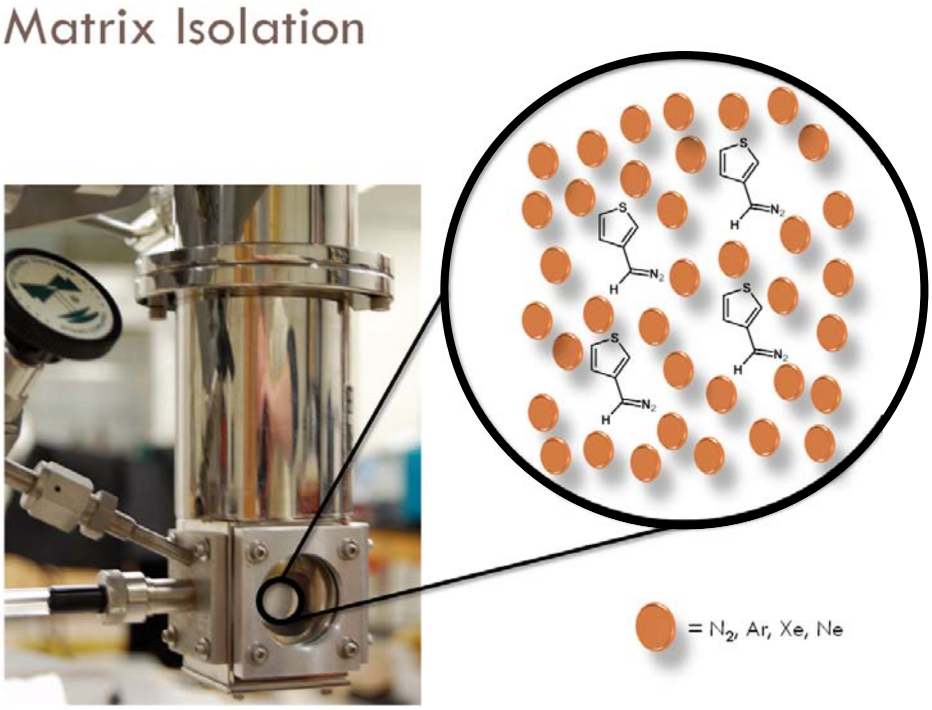

1-(3-benzothienyl) diazoethane


1-(3-benzothienyl) ethylidene
(triplet carbene)

The way we study these types of molecules is by using a combination of photochemistry and spectroscopy. Photochemistry is when you use light to do a chemical reaction or transformation. With our work, we first use light to make our carbenes from a precursor diazo compound, and then we use light to model cosmic rays so that we can observe what chemical rearrangements are taking place in these highly reactive molecules.

The first step in this process is to do a bit of organic synthesis to make a diazo compound (think of this diazo compound as a “pre-carbene”). These diazo compounds all have a carbon double bonded to a nitrogen which is also double bonded to another nitrogen (this is the “***di***azo” part, literally “two nitrogens”). Diazo compounds are pretty reactive and most will decompose when they are warmed to room temperature, so we have to be careful when we handle them. They are also potentially explosive, since it would be easy for them to lose a molecule of nitrogen (N_2, nitrogen gas). We use diazo compounds because we want them to lose an N_2 molecule (that's how we can form carbenes from diazo compounds), but under controlled conditions.

Since we can't hang out in outer space to do our experiments, we use a technique called matrix isolation to simulate the ISM in our lab here on Earth. We take our diazo compound and deposit it onto a small (about 1" diameter) window along with a lot of an inert gas (usually Ar or N_2). The goal here is to isolate single molecules of our diazo compound surrounded by the inert gas. This simulates the emptiness of space – the carbenes or other molecules we form won't react with the inert gas, so it's like the reactive molecules are completely isolated from one another. The window is kept at 10 K (- 442 °F) and under vacuum to further simulate outer space.

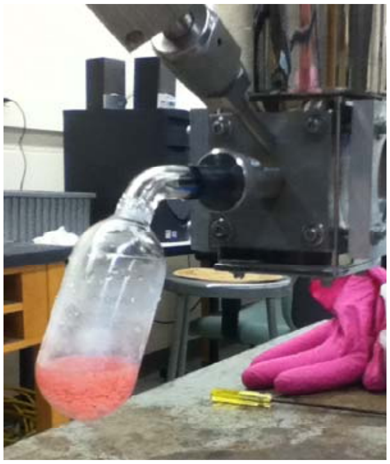


Once we have our diazo compound matrix isolated, we shine light on our matrix to knock off the N_2 molecule and give us a reactive intermediate (hopefully a carbene). We use three different methods to probe what new molecules are formed after irradiation – infrared spectroscopy, electronic absorption spectroscopy, and electron paramagnetic resonance spectroscopy. Infrared spectroscopy (IR) shows us how the bonds in the molecules are stretching, bending, and wagging. Just like every person has a unique fingerprint, every molecule has a unique IR spectrum. Using quantum calculations we can predict these molecular motions, and so we can predict what the IR spectrum of different molecules should be. Comparing our experimental IR spectra with calculated IR spectra is the main way we determine what molecules are forming in our matricies.

Electronic absorption spectroscopy (also called UV-vis spectroscopy) tells us what wavelengths of light molecules absorb. While every molecule has its own UV-vis spectrum, these spectra aren't as definitive as IR spectra. Additionally, it is much harder to predict the electronic absorption spectrum of a molecule without complication, high-level calculations. Electron paramagnetic resonance (EPR) spectroscopy is a very sensitive technique to detect unpaired electrons in a molecule. If a triplet carbene is present then you will see several peaks in the spectrum, but if there is not a triplet carbene, then you won't see any signals. Another benefit of EPR is its sensitivity – you only need a small amount of the carbene to see peaks, whereas with IR a much higher concentration of the molecule is needed in order to detect it.

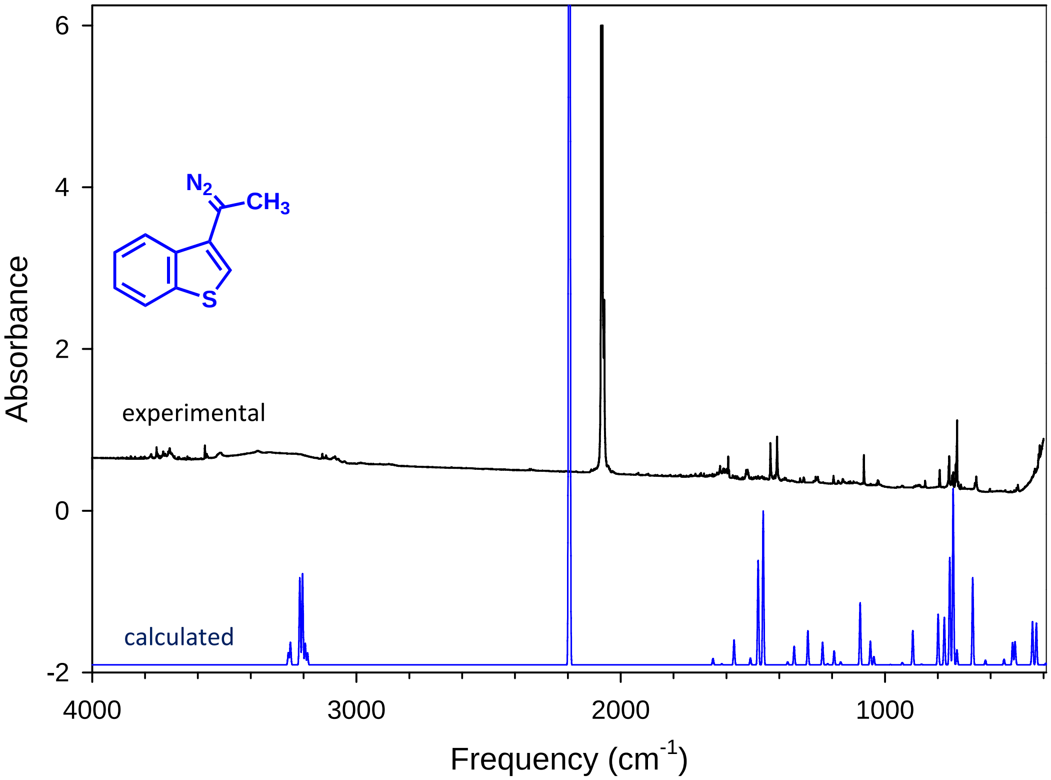
When I was studying 1-(3-benzothienyl) diazoethane (Chapter 3), the first step was to generate the diazo compound and transfer it to a deposition tube, so that I could matrix-isolate the diazo compound on our matrix-isolation carts.

Diazo compound (pink) collecting on a cold finger



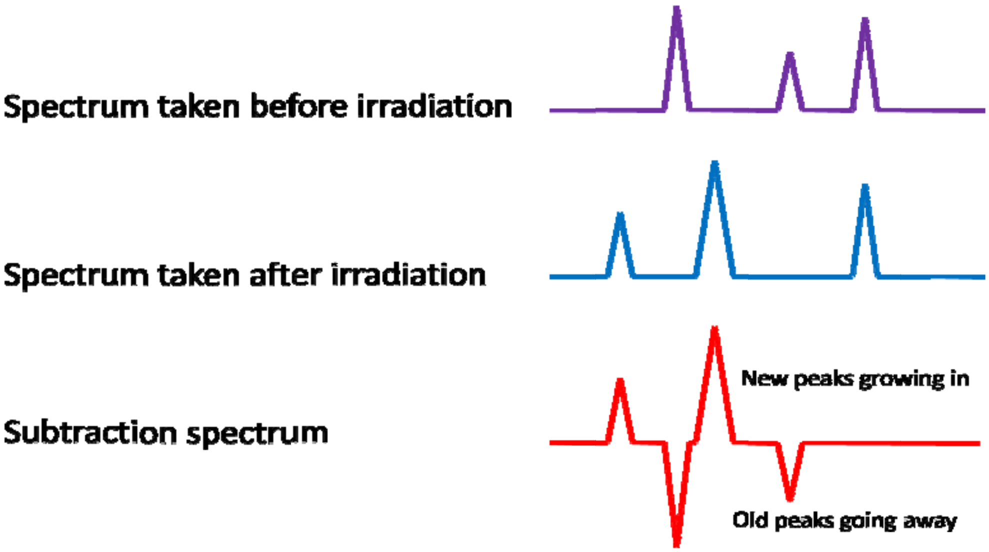
Diazo compound in a deposition tube ready to be matrix-isolated

Once the diazo compound is matrix-isolated, we start by taking an IR spectrum, to confirm that we have the diazo compound.



Next, we begin irradiating at some wavelength. We always start with longer wavelengths and move to shorter wavelengths because longer wavelength light has lower energy. The more energy you give a molecule, the more things it can potentially do, so we start off irradiating at low energy light and move to higher energy light.

The changes we expect to see in the IR are pretty subtle, so we look at subtraction spectra instead of “normal” IR spectra. In a subtraction spectrum you have both positive and negative peaks. The positive peaks are due to molecules that are in the matrix after irradiation that were not present before irradiation, and the negative peaks are from molecules that disappeared upon irradiation. If there are molecules in the matrix that do not react at that wavelength of light then you will not see them in the subtraction spectrum.



When I irradiated a matrix containing 1-(3-benzothienyl) diazoethane at λ > 534 nm I saw conversion of the diazo compound to a new molecule – 3-vinylbenzothiophene. This was confirmed by comparing the experimental data to the calculated IR spectra (**Figure 1**).

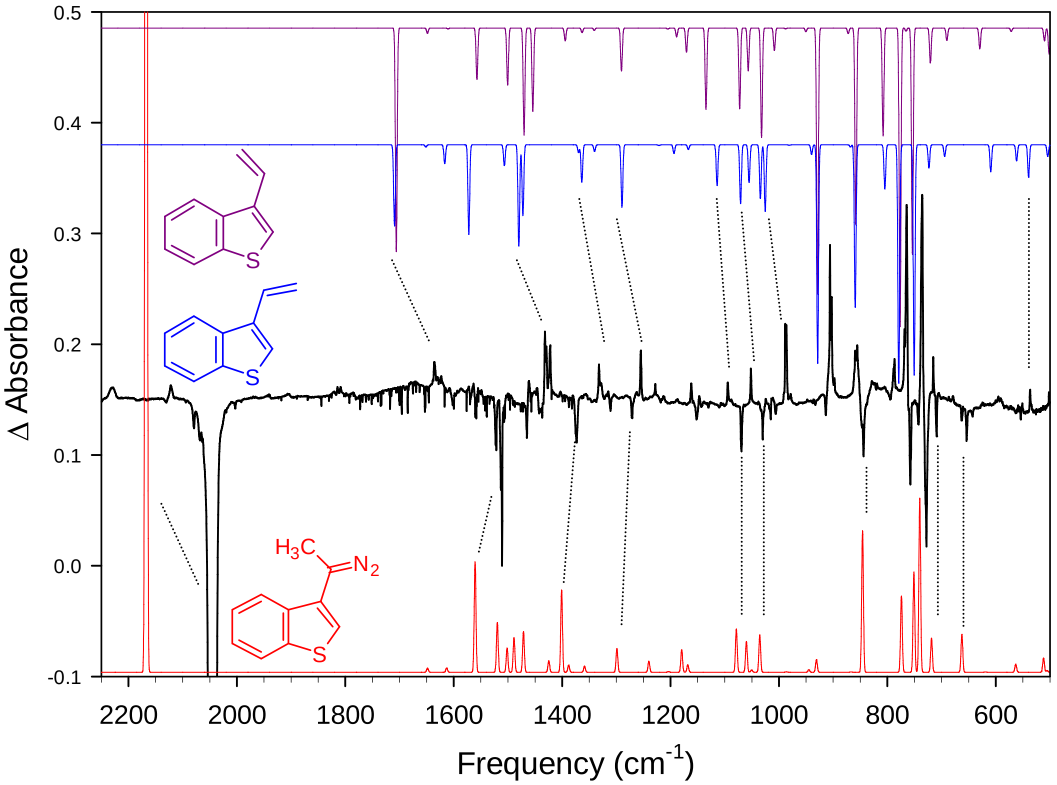


Figure 1. IR subtraction spectrum (Ar, 10 K) of a matrix containing 1-(3-benzothienyl) diazoethane (red) after irradiation at λ > 534 nm, showing peaks for 3-vinylbenzothiophene (blue and purple).

This type of rearrangement is very common when you have a $–CH_3$ group next to a carbene. In order to determine if a carbene is involved in this rearrangement, I did EPR spectroscopy. Any peaks seen in EPR are due to unpaired electrons; in this case, the only unpaired electrons would be due to a triplet carbene. The EPR spectrum of the matrix after irradiation shows peaks for the triplet carbene (**Figure 2**). The carbene peaks are labeled “E” and “Z” because there are actually two different triplet carbenes present in the matrix.

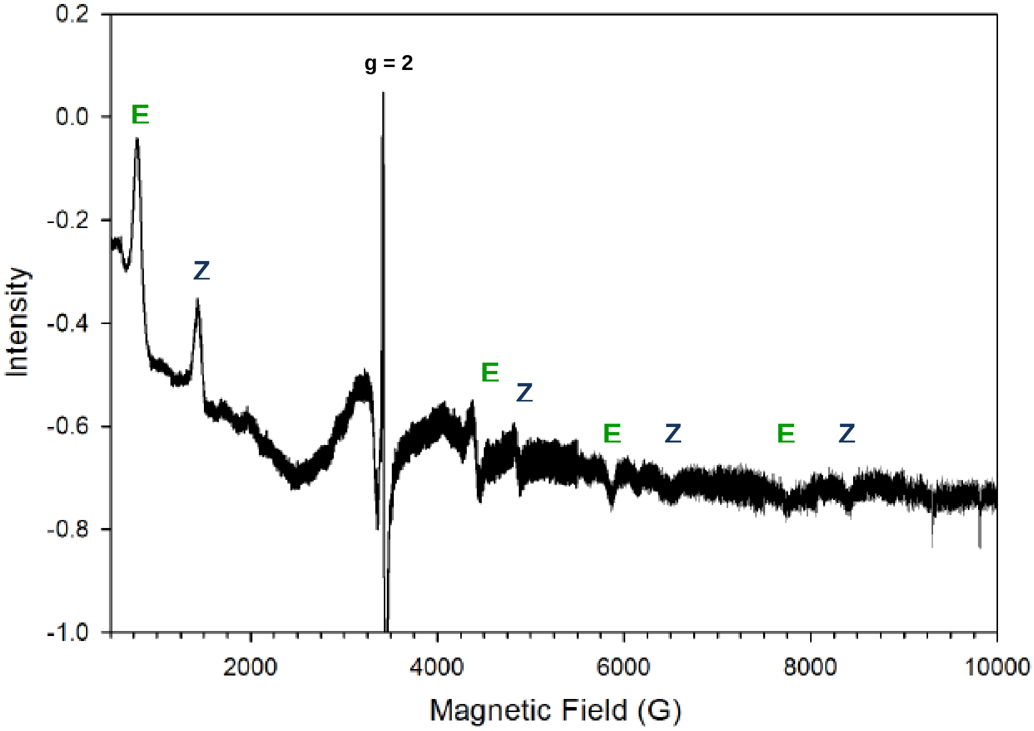


Figure 2. EPR spectrum (Ar, 10 K) after irradiation at λ > 534 nm, showing peaks for 1-(3-benzothienyl) ethylidene (***E*** and ***Z***).

The EPR spectrum proves that this transformation is occurring via a triplet carbene. When we irradiate this matrix with shorter wavelength light (higher energy) we can see the peaks for the carbenes decrease, and disappear altogether, as the carbene is transformed into 3-vinylbenzothiophene. If we look at the UV-vis spectrum (**Figure 3**), we also see peaks for the triplet carbene, which disappear when irradiate at shorter wavelengths.

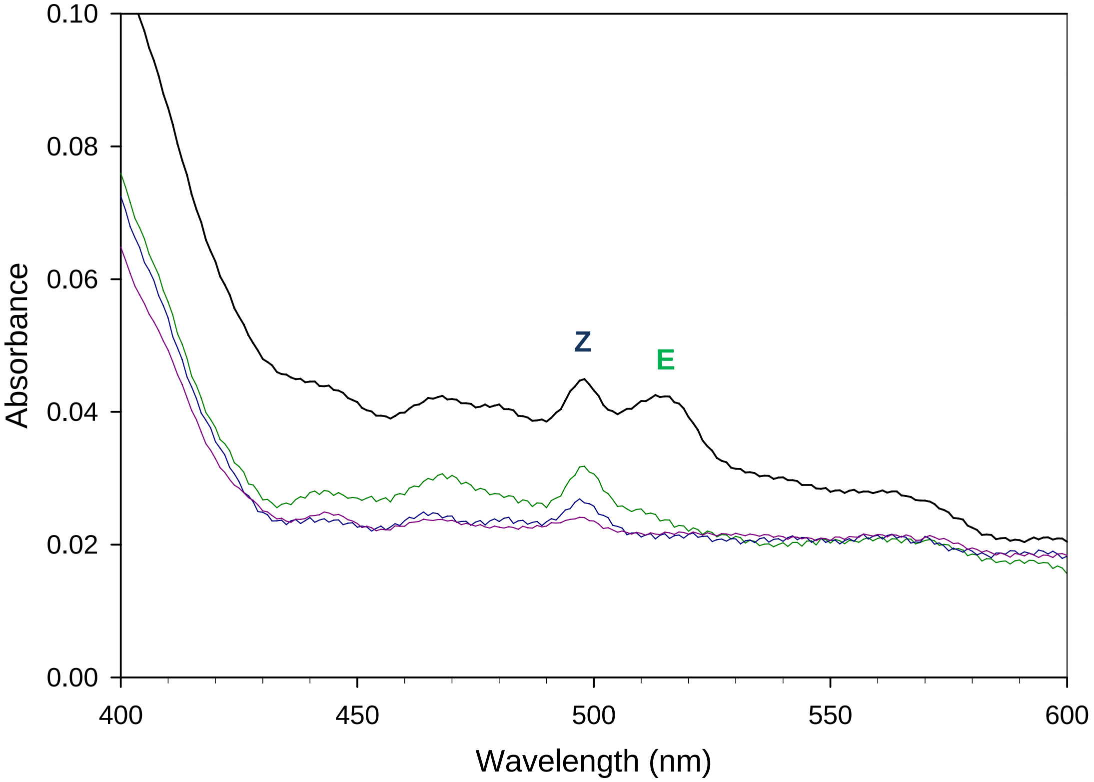
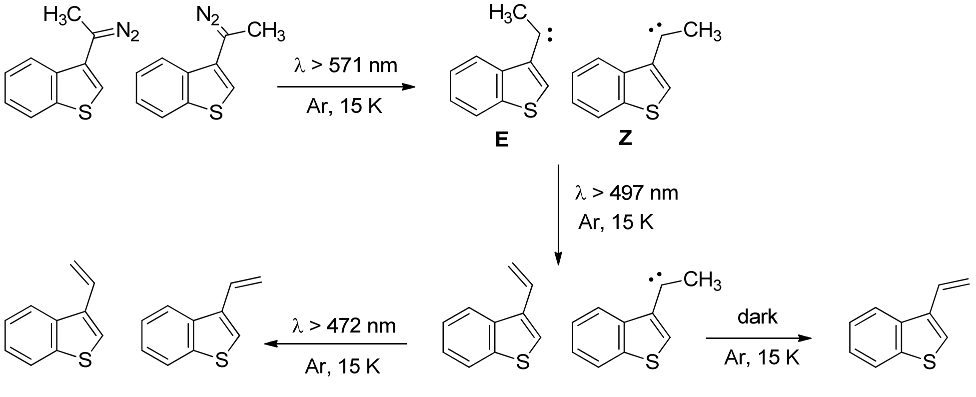


Figure 3. UV-vis spectra (Ar, 10 K) after irradiation at λ > 534 nm, 4 h (black trace), showing absorptions for both s-*E*-1-(3-benzothienyl) ethylidene (***E***) and s-Z-1-(3-benzothienyl) ethylidene (***Z***). Further irradiation at λ > 534 nm, 26 h (green trace) drives away all of ***E***. Shorter wavelength irradiation (λ > 497 nm , 24 h, blue trace) drives away some ***Z***, and irradiation at λ > 472 nm, 17 h, completely drives away this species.

If we look at these three types of spectroscopy together, we can get a good idea of the rearrangements that are taking place in this system. When we shine light on the diazo compound, it will lose a molecule of N_2 to generate a carbene. This carbene is unstable, even at low temperatures, and will rearrange to form a more stable compound, 3-vinylbenzothiophene. This rearrangement will happen in the dark, or, we can get it to happen much more quickly if we use photochemistry again.



By using matrix isolation we are able to generate and study the behavior of these highly reactive molecules. We can successfully simulate outer space by working at very low pressures, using matrix isolation to isolate single molecules from one another (mimicking the "emptiness" of space), and using photochemistry (instead of cosmic rays) to initiate transformations.