Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, the director of the Wisconsin Initiative for Science Literacy (WISL) encouraged all Ph.D. chemistry candidates to include a chapter in their Ph.D. thesis communicating their research to non-specialists. The goal is to explain the candidate's scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, state legislators, and members of the U.S. Congress.

Ten Ph.D. degree recipients have successfully completed their theses and included such a chapter, less than a year after the program was first announced; each was awarded $500.

WISL will continue to encourage Ph.D. chemistry students to share the joy of their discoveries with non-specialists and also will assist in the public dissemination of these scholarly contributions. WISL is now seeking funding for additional awards.

Wisconsin Initiative for
Science Literacy

The dual mission of the Wisconsin Initiative for Science Literacy is to promote literacy in science, mathematics and technology among the general public and to attract future generations to careers in research, teaching and public service.

UW-Madison Department of Chemistry
1101 University Avenue
Madison, WI 53706-1396
Contact: Prof. Bassam Z. Shakhashiri
bassam@chem.wisc.edu
www.scifun.org

January 2011

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

by

Laura Anne Kopff

A dissertation submitted in partial fulfillment of the

requirements for the degree of

Doctor of Philosophy

(Chemistry)

at the

UNIVERSITY OF WISCONSIN – MADISON

2012

Date of final oral examination: 08/08/2012

The dissertation is approved by the following members of the Final Oral Committee:

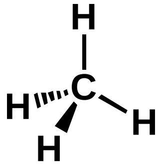
Robert J. McMahon, Professor, Chemistry
Judith Burstyn, Professor, Chemistry
Mark D. Ediger, Professor, Chemistry
Clark Landis, Professor, Chemistry
Steven Nelsen, Professor, Chemistry

Appendix B: Doing the Impossible – Matrix Isolation as a Way to Study Highly Reactive Molecules

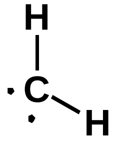
Many of us, at some point in our lives, have looked up at the night sky and wondered what was out there. Scientists give us a lot of different answers – planets, stars, asteroids, lots of empty space. And some scientists ask how these things came to be – how did planets form, how did we form?

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.

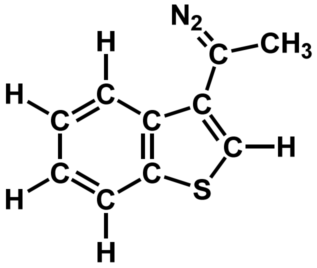


Carbon is most stable when it has four bonds (8 electrons) around it

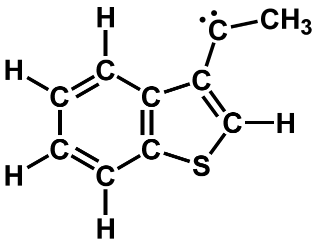


In a carbene, there are two bonds and two other electrons around carbon, making it very reactive

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

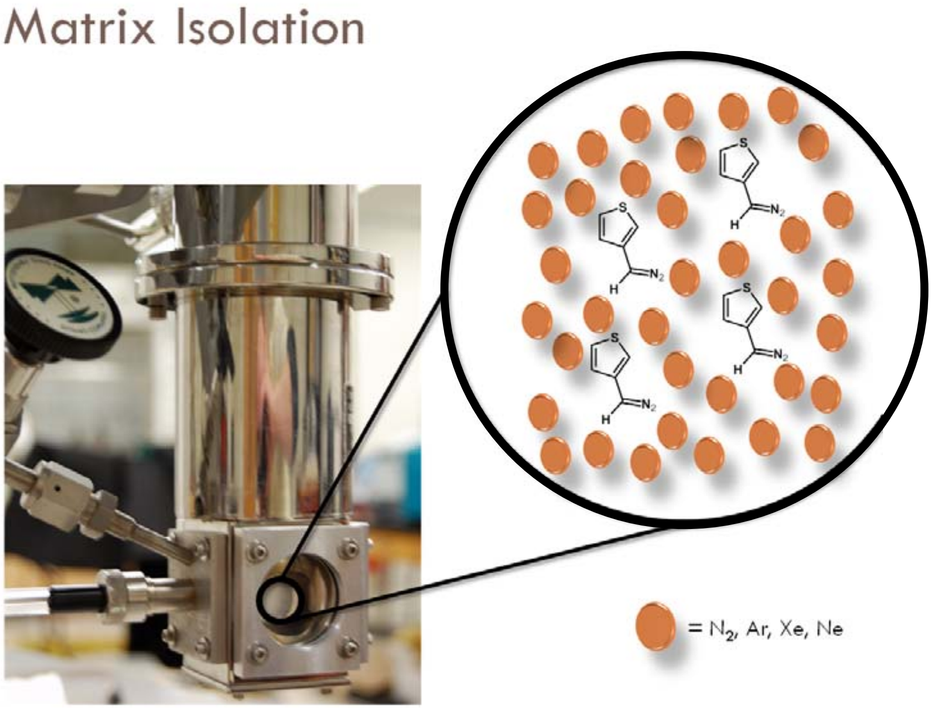


1-(3-benzothienyl) ethylidene
(triplet carbene)

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.

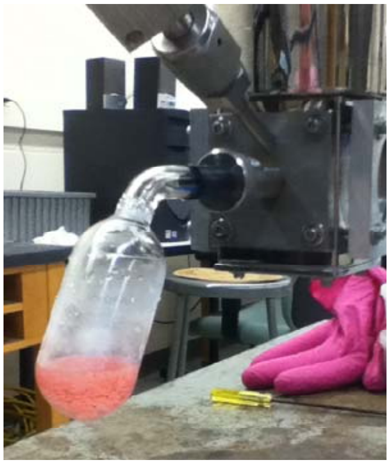


Once we have our diazo compound matrix isolated, we shine light on our matrix to knock off the N_2 molecule and give us a reactive intermediate (hopefully a carbene). We use three different methods to probe what new molecules are formed after irradiation – infrared spectroscopy, electronic absorption 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.

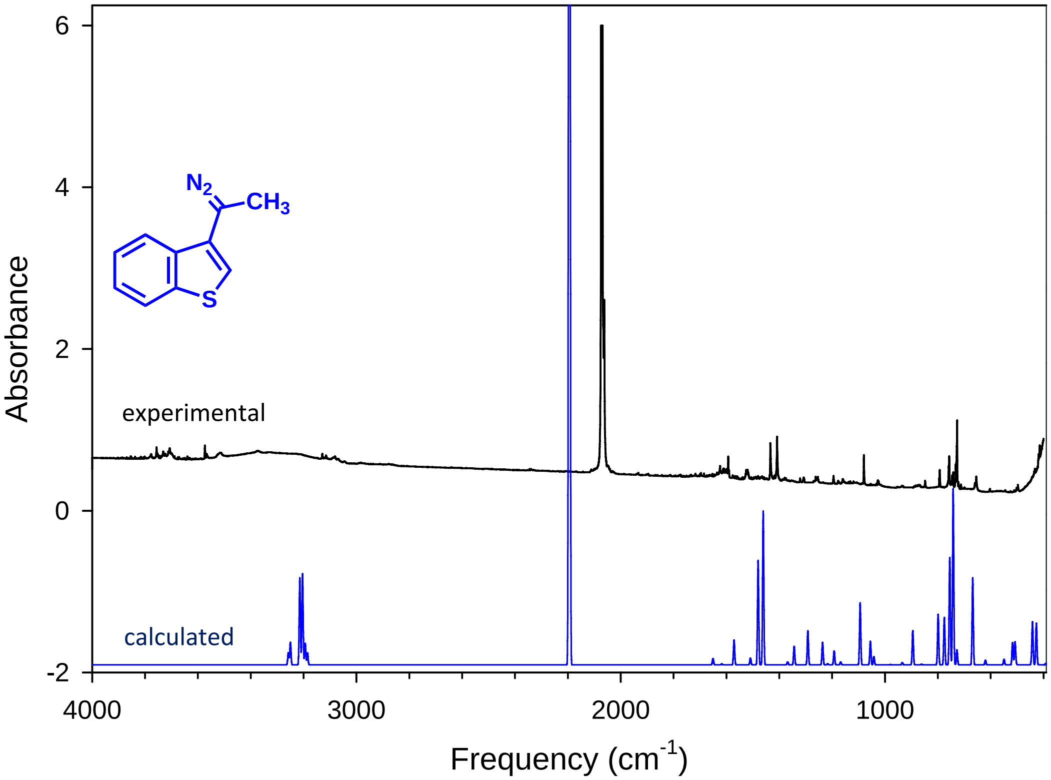
When I was studying 1-(3-benzothienyl) diazoethane (Chapter 3), the first step was to generate the diazo compound and transfer it to a deposition tube, so that I could matrix-isolate the diazo compound on our matrix-isolation carts.

Diazo compound (pink) collecting on a cold finger



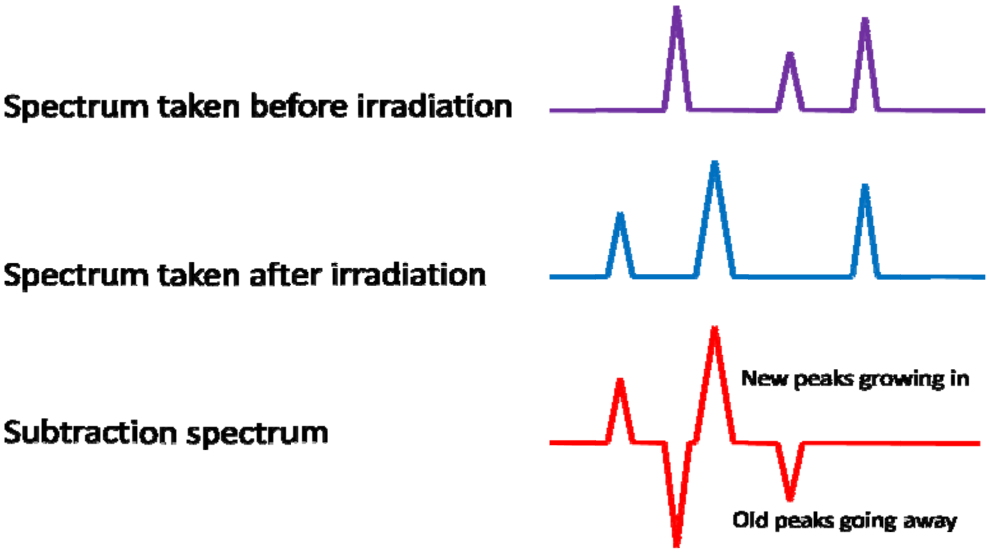
Diazo compound in a deposition tube ready to be matrix-isolated

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**).

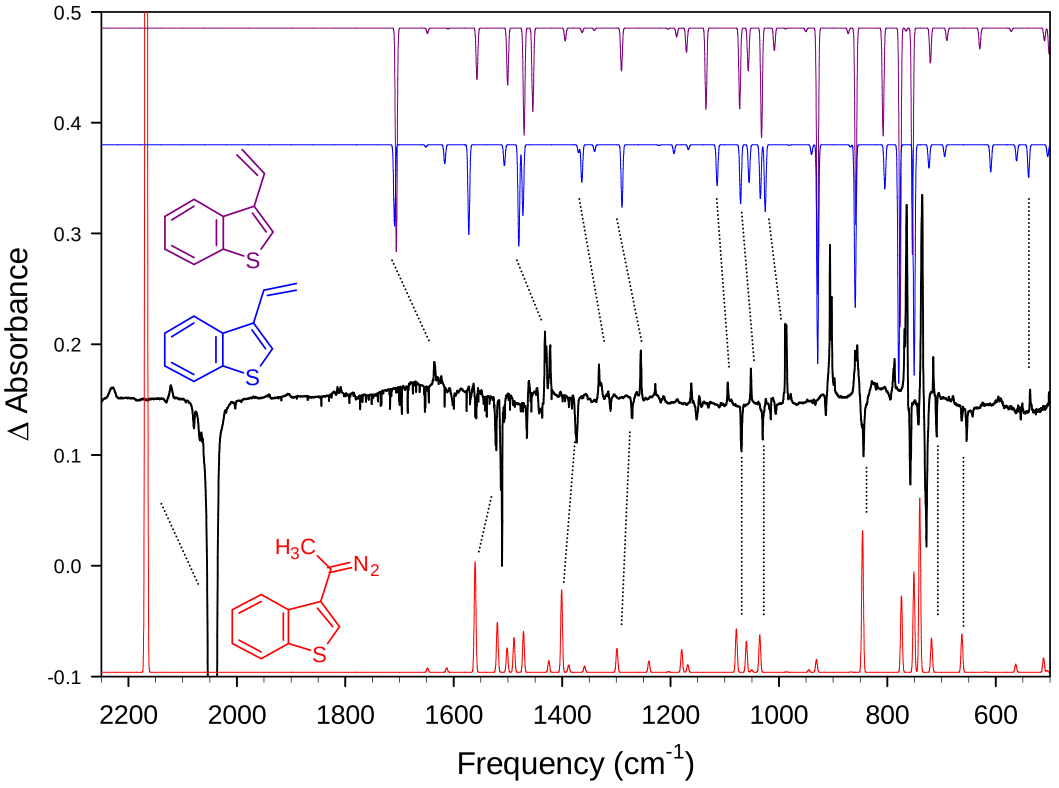


Figure 1. IR subtraction spectrum (Ar, 10 K) of a matrix containing 1-(3-benzothienyl) diazoethane (red) after irradiation at λ > 534 nm, showing peaks for 3-vinylbenzothiophene (blue and purple).

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.

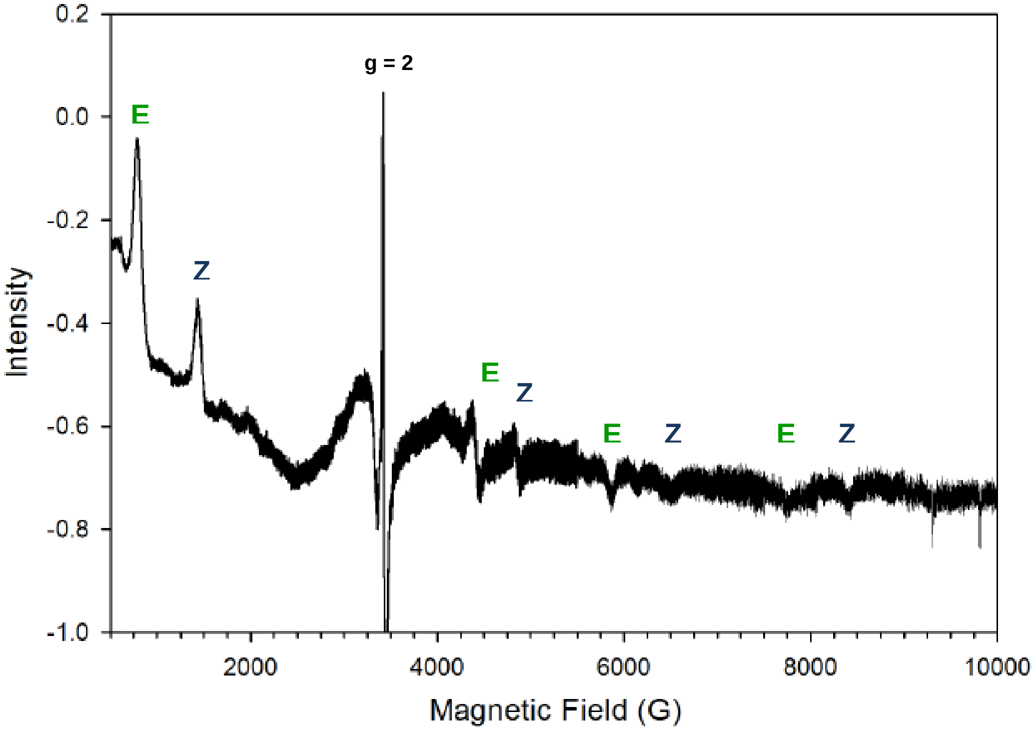


Figure 2. EPR spectrum (Ar, 10 K) after irradiation at λ > 534 nm, showing peaks for 1-(3-benzothienyl) ethylidene (***E*** and ***Z***).

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.

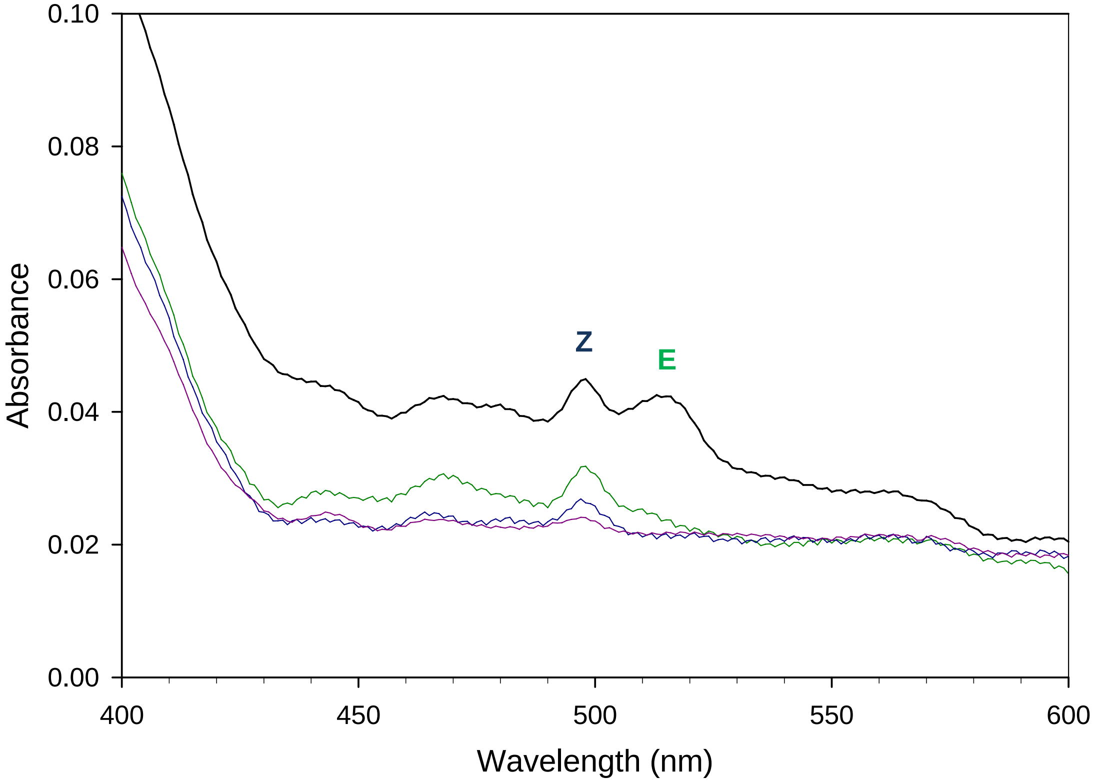
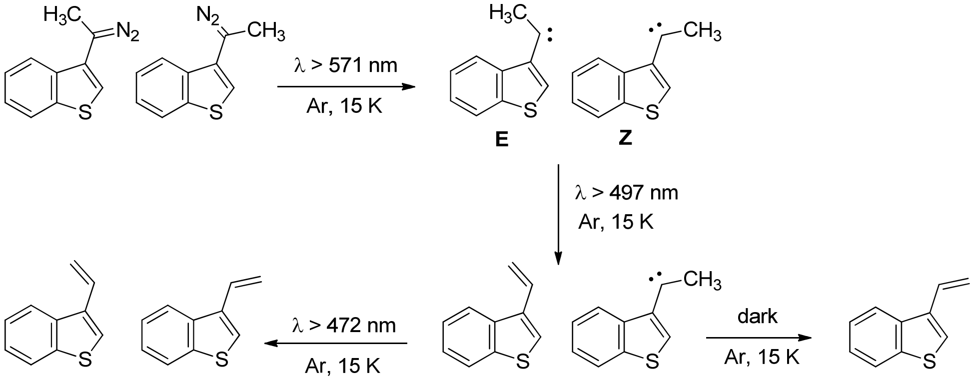


Figure 3. UV-vis spectra (Ar, 10 K) after irradiation at λ > 534 nm, 4 h (black trace), showing absorptions for both s-*E*-1-(3-benzothienyl) ethylidene (***E***) and s-Z-1-(3-benzothienyl) ethylidene (***Z***). Further irradiation at λ > 534 nm, 26 h (green trace) drives away all of ***E***. Shorter 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.