



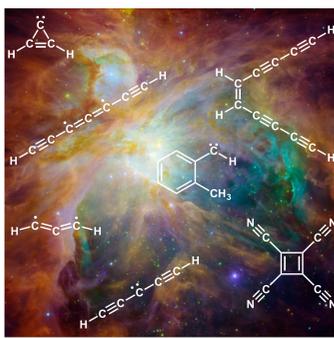
# McMahon Research Group

## Synthesis, Matrix Isolation, Spectroscopy, Mechanistic Studies, and Computational Chemistry



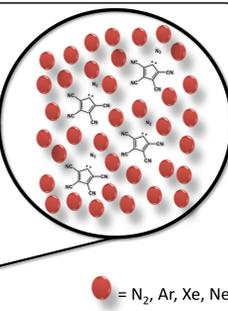
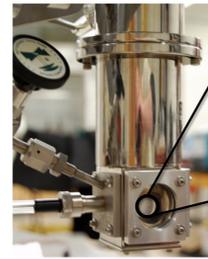
### Introduction

The McMahon group has an interest in the areas of astrochemistry, reactive intermediates, and combustion chemistry. The inherent complexity of these chemical environments demands an integrated approach involving organic synthesis, matrix isolation spectroscopy, mechanistic studies, rotational spectroscopy, and computational chemistry. Through these combined efforts, it is possible to generate and characterize the prototypical reactive intermediates in organic chemistry and to probe their structure in unprecedented detail. These fundamental structural, spectroscopic, and mechanistic data provide a foundation for understanding the chemistry of organic matter in harsh environments.



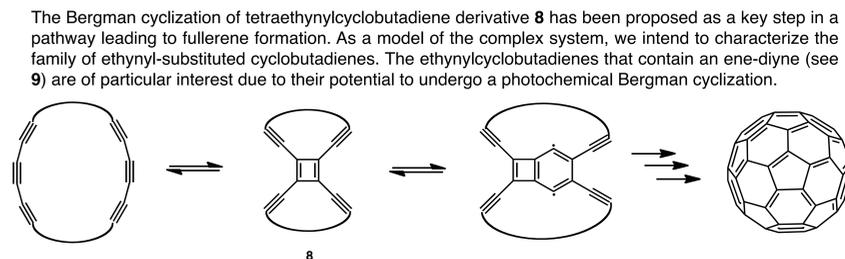
Orion Nebula viewed from the Hubble Telescope

### Matrix Isolation

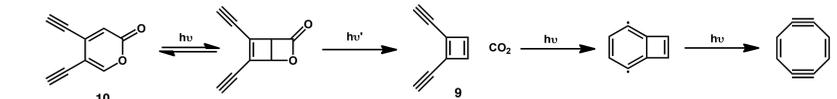


A precursor, or a reactive intermediate, is generated in the gas phase and then frozen in an inert gas (N<sub>2</sub>, Ar, Xe, Ne) at 10 to 25 K on a spectroscopic window. The matrix-isolated compounds can then be studied using IR, UV-vis, or EPR spectroscopy. Often, irradiation of the precursor using either a Hg or Xe lamp yields the reactive species, whose identity is confirmed by comparison to calculated spectra. The matrix can then be further irradiated with varying wavelengths of light to study the photochemical properties and reactivity of these species.

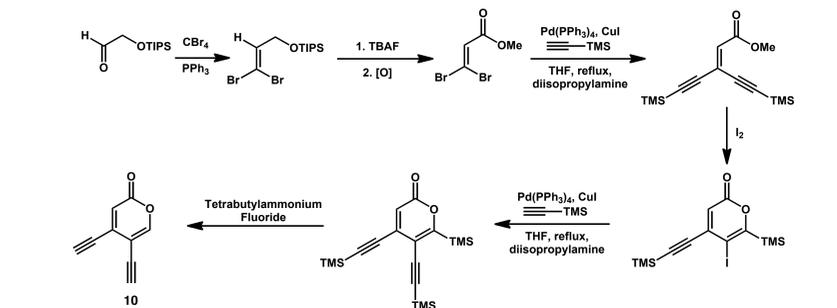
### Ethynyl-Cyclobutadienes



The Bergman cyclization of tetraethynylcyclobutadiene derivative **8** has been proposed as a key step in a pathway leading to fullerene formation. As a model of the complex system, we intend to characterize the family of ethynyl-substituted cyclobutadienes. The ethynylcyclobutadienes that contain an ene-diyne (see **9**) are of particular interest due to their potential to undergo a photochemical Bergman cyclization.

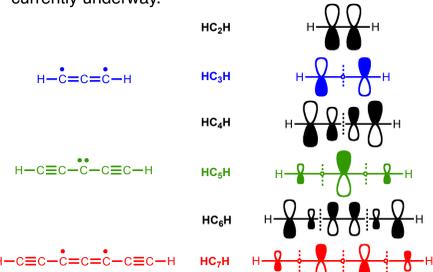


We will synthesize and matrix isolate the desired  $\alpha$ -pyrone precursors (see **10**) and photochemically produce the cyclobutenes. Upon characterization utilizing predicted IR frequencies, we will then investigate the photochemical and/or thermal transformations.

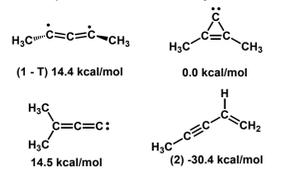


### Unsaturated Carbon Chains

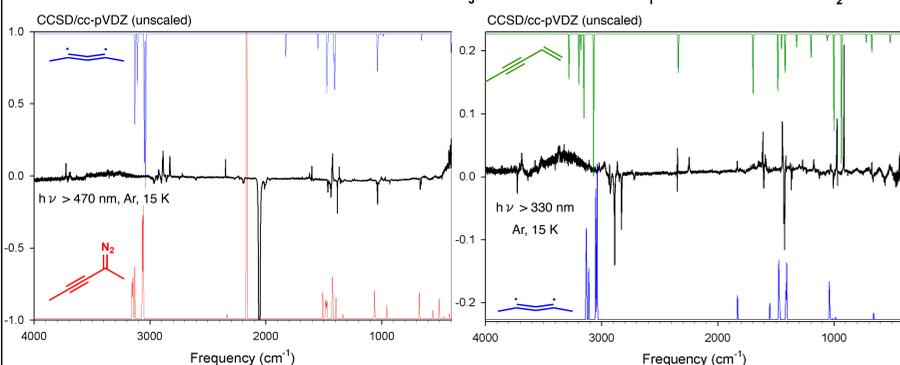
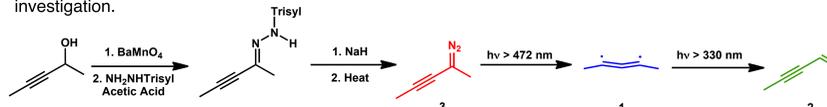
The exploration of unsaturated carbon chains of varying lengths has been a primary focus of the group. The HC<sub>3</sub>H, HC<sub>5</sub>H, and HC<sub>7</sub>H systems have been synthesized and characterized. They are believed to be important molecules in the Interstellar Medium (ISM). Further studies of the substituted RC<sub>3</sub>R are currently underway.



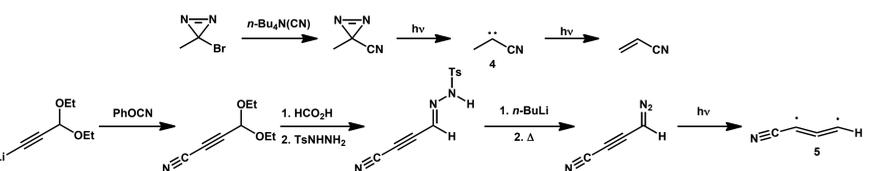
Shown below are isomers of CH<sub>3</sub>C<sub>3</sub>CH<sub>3</sub> and their relative energies predicted at the CCSD/cc-pVDZ level of theory.



A diazo precursor for dimethylpropynylidene (**1**) has been synthesized and matrix isolated. Irradiation of diazo **3** under matrix-isolation conditions leads to triplet dimethylpropynylidene (**1**) which can undergo a hydrogen shift to methylvinylacetylene (**2**). The photochemistry of the CH<sub>3</sub>C<sub>3</sub>CH<sub>3</sub> system is still under investigation.

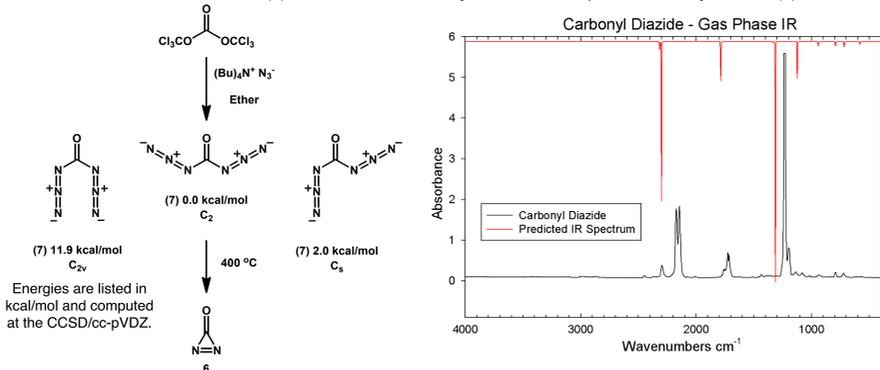


Cyano-containing molecules are a class of compounds that have been detected in the ISM, but a significant number of them have yet to be isolated and completely characterized. Proposed syntheses of cyanomethylcarbene (**4**) and *t*-HC<sub>4</sub>N (**5**) are shown below.

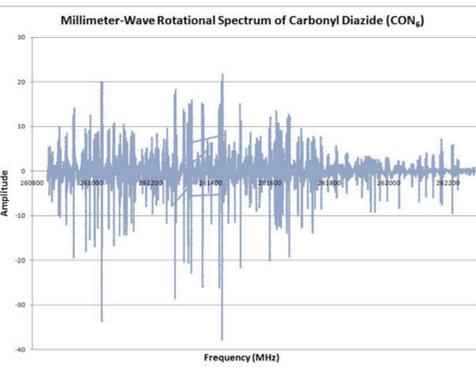
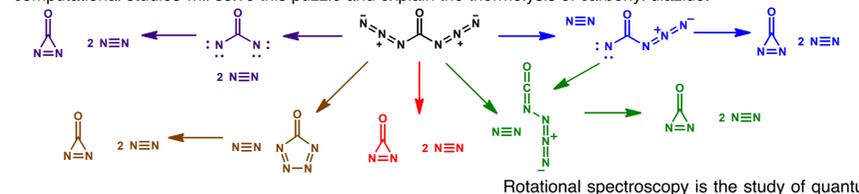


### Carbonyl Diazide & Diazirone

Our interest in prospective molecules to be found in the Interstellar Medium lead us to investigate the metastable molecule diazirinone (**6**), which can be thermolyzed from the explosive carbonyl diazide (**7**).

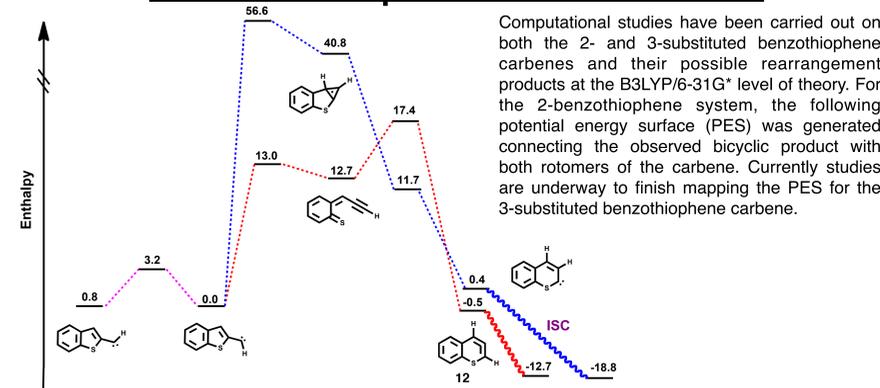


Under matrix-isolation conditions, carbonyl diazide (**7**) will photolyze to produce two isomers of CON<sub>4</sub> and N<sub>2</sub>, but diazirinone (**6**) was not observed (Beckers, H. and coworkers *Angew. Chem. Int. Ed.* **2010**). Under thermolysis conditions, diazirinone was made from carbonyl diazide by the loss of two molecules of dinitrogen (Beckers, H. and coworkers *Angew. Chem. Int. Ed.* **2011**). Thus far, computational studies of the pathways below have not identified any viable pathway to diazirinone from carbonyl diazide. We are hopeful that further computational studies will solve this puzzle and explain the thermolysis of carbonyl diazide.

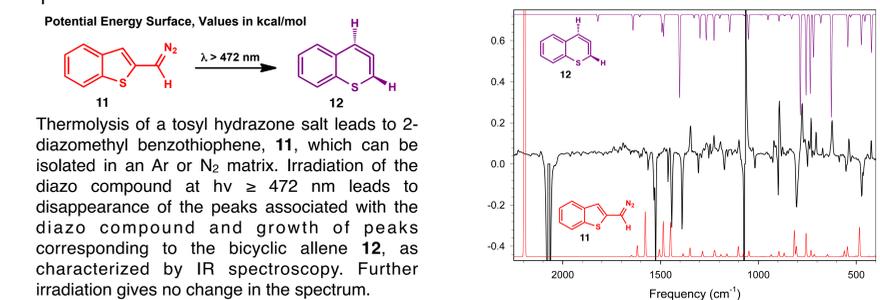


Rotational spectroscopy is the study of quantum energy levels associated with the rotational motion of molecules. Spectra, typically in the microwave or millimeter wave regions, can give incredibly precise information about the moments of inertia, and thus geometry, of gaseous molecules. Spectra can consist of hundreds or thousands of individual transitions; solving these spectra is difficult, but once solved, they can be used to unambiguously identify molecules, in the lab, or in space using radio telescopes. Hundreds of spectral lines of carbonyl diazide (**7**) in the C<sub>s</sub> and/or C<sub>2v</sub> conformations have been observed. Further spectroscopic work is still required in order to fully understand the complex rotational spectrum. After studying the parent isotopomer, <sup>13</sup>C and <sup>15</sup>N isotopomers will also be studied, helping to pin down a very precise molecular geometry for the observed conformations of carbonyl diazide.

### Benzothiophene Carbenes



Computational studies have been carried out on both the 2- and 3-substituted benzothiophene carbenes and their possible rearrangement products at the B3LYP/6-31G\* level of theory. For the 2-benzothiophene system, the following potential energy surface (PES) was generated connecting the observed bicyclic product with both rotomers of the carbene. Currently studies are underway to finish mapping the PES for the 3-substituted benzothiophene carbene.



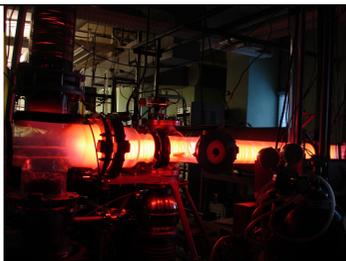
### Selected Recent Publications

Menke, J. L.; McMahon, R. J., Photochemistry of Matrix-isolated 5-cyano-2H-pyran-2-one ( $\delta$ -cyano- $\alpha$ -pyrone) and cyanocyclobuta-1,3-diene. *Can. J. Chem.* **2011**, *89* (2), 186-194.

Thomas, P. S.; Bowling, N. P.; Burmann, N. J.; McMahon, R. J., Dialkynyl Carbene Derivatives: Generation and Characterization of Triplet *tert*-Butylpentadiynylidene (*t*-Bu-C $\equiv$ C-C $\equiv$ C-C $\equiv$ C-H) and Dimethylpentadiynylidene (Me-C $\equiv$ C-C $\equiv$ C-C $\equiv$ C-Me). *J. Org. Chem.* **2010**, *75* (19), 6372-6381.

Menke, J. L.; Patterson, E. V.; McMahon, R. J., Effects of Cyano Substituents on Cyclobutadiene and Its Isomers. *J. Phys. Chem. A* **2010**, *114* (22), 6431-6437.

Shaffer, C. J.; Esselman, B. J.; McMahon, R. J.; Stanton, J. F.; Woods, R. C., Attempted Isolation and Characterization of Diazirinone (N<sub>2</sub>CO). *J. Org. Chem.* **2010**, *75* (6), 1815-1821.



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### Funding

