Synthesis and Spectroscopy of Highly-Unsaturated Carbon Chain Molecules: Species of Relevance to the Interstellar Medium and to Titan

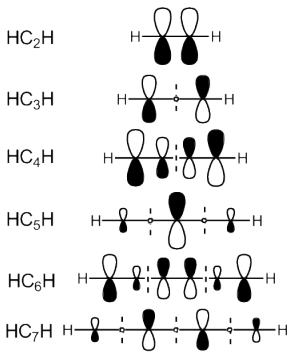
Christopher J. Shaffer and Robert J. McMahon*

Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, WI 53706

cshaffer@chem.wisc.edu

Despite lying at the extremity of high energy organic species, highly unsaturated carbon chains comprise many of the over 140 identified chemical species in the interstellar medium. Direct detection of the HC_nH ($n > 1$) series by radioastronomy is precluded due to a lack of a permanent dipole moment. Within this series, carbon chains with an odd carbon count ($HC_{2n+1}H$) are open shell species with electronic absorptions in the visible spectrum. Previous studies in our lab have investigated the diradical 1,3-cumulene nature of HC_3H[1] and the localized carbon-centered carbene of HC_5H.[2] Our systematic experimental investigation into the electronic structure of the $HC_{2n+1}H$ series continues with HC_7H (Scheme 1). Anticipated to be a 3,5-cumulene diradical, experimental results on HC_7H could make a significant contribution to understanding the $HC_{2n+1}H$ series and the respective patterns in electronic structure.

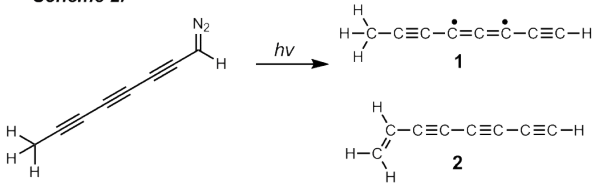
Scheme 1.



While sizable experimental effort allowed these species to be studied in the gas phase, a number of critical experiments have been excluded. Alternatively, we have completed the synthesis and matrix isolation of 1-diazo-octa-2,4,6-triyne, the photochemical precursor to MeC_7H (**1**) (Scheme 2). These studies have allowed characterization of **1** by IR, UV/vis, and EPR spectroscopy. Gratifyingly, our results for the electronic spectra of MeC_7H are consistent with those previously measured for HC_7H.[3]

Additionally, in the IR characterization of matrix-isolated MeC_7H (**1**), we observed the formation of a second product. Photoexcitation of **1** initiates a 1,2-hydrogen shift, producing enetriyne **2**. An independent synthesis of **2** confirms the identity of this product.

Scheme 2.



Similar highly unsaturated species play a significant role in planetary chemistry. Known to form through photochemical processes in the upper atmosphere of Titan, diacetylene, cyanoacetylene and cyanogen may undergo further chemical processes if present on a planetary surface. Measuring infrared reflectance, the Visual Infrared Mapping Spectrometer onboard the Cassini-Huygens probe offers a unique opportunity to remotely detect these compounds on the surface of Titan. When compared to transmittance spectroscopy, infrared reflectance is subtle yet significant in its differences, warranting our renewed study on cyanoacetylene and cyanogen such that accurate interpretations of VIMS data can be made.

1. Seburg, R.A.; DePinto, J.T.; et al. *J. Am. Chem. Soc.* **1995,** 117, (2), 835-836.
2. Bowling, N.P.; Halter, R.J.; et al.. *J. Am. Chem. Soc.* **2006,** 128, (10), 3291-3302.
3. Fulara, J.; Freivogel, P.; et al. *J. Chem. Phys.* **1995,** 103, (20), 8805-8810.