

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

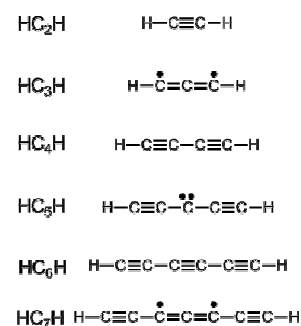
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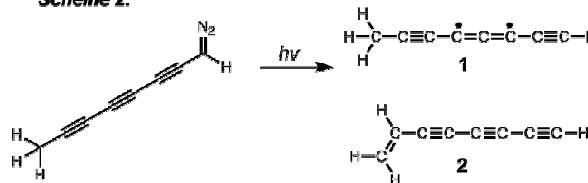
Despite lying at the extremity of high energy organic species, highly unsaturated carbon chains comprise many of the over 140 identified chemical species in the interstellar medium. Direct detection of the parent molecules of the HC_nH ($n > 1$) series by radioastronomy is precluded due to a lack of 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 cumulenic diradical nature of HC_3H^1 and the carbene character of HC_5H^2 . Our systematic experimental investigation into the electronic structure of the HC_{2n+1}H series continues with parent HC_7H , which is anticipated to be a cumulenic diradical (Scheme 1). Additionally, we continue to study new derivatives of the previously-studied parent HC_3H and HC_5H molecules, in order to better understand the effects that substituents have on the electronic nature and photo-rearrangements of these highly-reactive molecules.

Scheme 1.



We have completed the synthesis and matrix isolation of 1-diazo-octa-2,4,6-triyn-8-ene, the photochemical precursor to MeC_7H (**1**) (Scheme 2). These studies have allowed characterization of **1** by IR, UV/vis, and EPR spectroscopy. 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.



In order to further extend our knowledge of the HC_{2n+1}H series, tosylhydrazone precursors to new derivatives of HC_3H and HC_5H have been synthesized. In specific, the monomethyl and dimethyl substituted derivatives of the tosylhydrazone precursors to HC_3H have been prepared. Additionally, the monophenyl, diphenyl, and mono-(trimethylsilyl) tosylhydrazone precursors to HC_5H have been synthesized. Our future work will involve using these precursors, as well as ones synthesized previously, to generate substituted $\text{RC}_3\text{R}'$ and $\text{RC}_5\text{R}'$ species, in order to better understand the photochemical reactivity of molecules in the $(\text{RC}_{2n+1}\text{R}')$ series.

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