Are Isomers of the Vinyl Cyanide Ion Missing Links for Interstellar Pyrimidine Formation?

Partha P. Bera[1,2],* Timothy J. Lee[2] and Henry F. Schaefer III[1]*
[1] Center for Computational Chemistry, University of Georgia, Athens, Georgia, 30602
[2] NASA Ames Research Center, Moffett Field, CA, 94035

Abstract: In the interstellar medium (ISM) there are many regions where the formation of molecules is kinetically driven rather than thermochemically, which can lead to the formation of many isomers even though some may be fairly higher in energy relative to the molecular global minimum. Recent laboratory experiments where noble gas cations are reacted with pyrimidine favored the formation of $C_3H_3N^+$, but the molecular structure(s) of this fragment was not determined. Microscopic reversibility means that pyrimidine could form under interstellar conditions should the required $C_3H_3N^+$ reactant be detected in the ISM. Hence $C_3H_3N^+$ could be a strong candidate for involvement in the formation of heterocyclic biomolecules like pyrimidine in the ISM. In this study, we have investigated the low energy isomers of the acrylonitrile ion ($C_3H_3N^+$) using density functional theory as well as high levels of *ab initio* theory, namely the singles and doubles coupled-cluster theory that includes a perturbational correction for connected triple excitations, denoted CCSD(T). An automated stochastic search procedure, Kick, has been employed to find isomers on the ground state doublet potential energy surface. Several new structures, along with all the previously reported minima, have been found. The global minimum H_2CCCNH^+ is energetically much lower than either $H_2CC(H)CN^+$ the acrylonitrile ion, or $HCC(H)NCH^+$, the most likely intermediate of the reaction between $HCCH^+$ and HCN. These isomers are connected to the global minimum via several transition states and intermediates. The results indicate that not only the global minimum, but also several higher energy isomers of the $C_3H_3N^+$ ion, could be important in interstellar pyrimidine formation. The isomeric molecules have the necessary CCNC backbone needed for the reaction with HCN to form the cyclic pyrimidine framework. The structural and rotational parameters of all the isomers studied in this work have been predicted at the CCSD(T) level of theory with the anticipation that it will expedite their laboratory as well as astronomical identification.