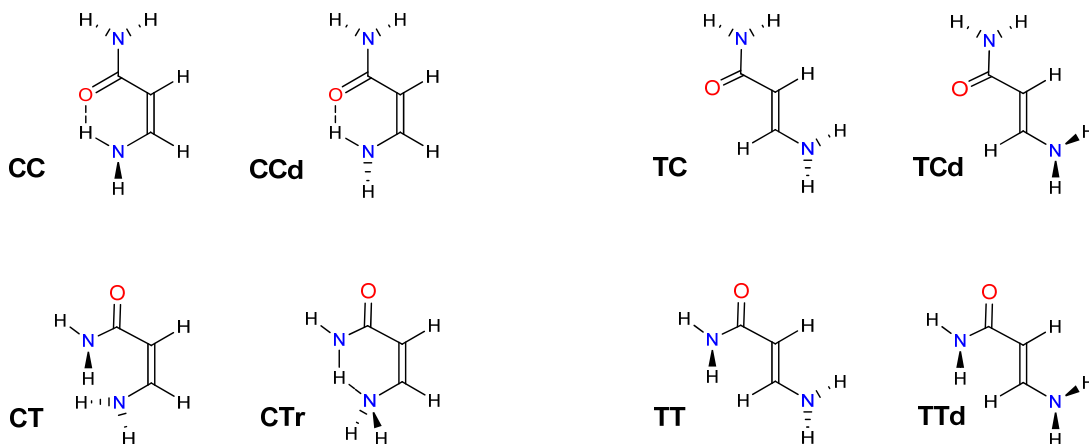


## $\beta$ -Aminoacrylamide. Ab Initio Study of a Fluxional Diamine with Nonlocal Anharmonicities and Extremely-Low-Barrier Double-Well

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$\beta$ -Aminoacrylonitrile (AAN) has been of astrochemical interest for several reasons. Hydration of AAN may lead to  $\beta$ -aminoacrylamide (AAA) and we present the results of an ab initio study of the structure of AAA.  $\beta$ -Aminoacrylamide can form geometrical isomers with regard to the alkene double bond (*Z*- or *cis*-isomer **C** vs. *E*- or *trans*-isomer **T**) and conformers depending on the orientation of the amide group (*s-cis* **C** vs. *s-trans* **T**). This occurrence of structures with pyramidal nitrogens adds complexity to the potential energy surface analysis, and isomers **CC**, **TC** and **TT** can result in diastereoisomeric structures depending on the relative orientation of the pyramidalization of the amino- and amide-NH<sub>2</sub> groups.



The potential energy surface contains seven unique pairs of chiral stationary structures. The thermal energies of the umbrella modes of the NH<sub>2</sub> groups in  $\beta$ -aminoacrylamide are close to or exceed the energy barrier(s) for the inversion(s) of the amino group(s) in the **CC**, **TC**, and **TT**-configured structures. The resulting structural flexibility causes significant nonlocal anharmonic effects and requires double-well potential (DWP) thermochemical analysis. To compute thermal energies and entropies, we have employed the complete classical partition function derived by Katzer and Sax to describe symmetric and unsymmetrical  $\cos^2$ -DWP and construct the quantum mechanical partition function with the Pitzer-Gwinn correction.