

Barriers to Rotation in 2-Butyne and Analogous Compounds

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The relative stability of specific molecular conformers of $R_3C-C\equiv C-CR_3$ and analogous compounds are investigated. Over the past two decades, there has been a live exchange in the chemical literature on explanations for the relative stability of the conformers of ethane, in particular, the roles of steric vs. hyperconjugative effects. We ask a similar question of the 2-butyne compounds, which are model fragments of alkyne precursors in cyclization reactions in organic chemistry. The interactions between the terminal fragments are much weaker here, but preliminary investigations suggest that the locations of the minima are dependent on the electron donating/withdrawing powers of the substituents. The systems we consider have the general formula $R_3C-C\equiv C-CR_3$, where $R = H, CN, F, Cl, Br, I$ and At . All of our conformational analyses have been carried out at both the B3PW91 and MP2 (full) levels using the cc-pVTZ quality basis sets, with pseudopotentials included for Br, I and At. It was observed that for $R = H, Cl, Br, I$ and At , the most stable conformer was the eclipsed form. For $-CN$, the staggered conformation was preferred. At the B3PW91 level, the preferred isomer for the fluorinated alkyne was unclear, but the MP2 calculations showed it to be of the staggered conformation as well.