

Rotational Barriers in Alkynes and Related Compounds – Steric Bonding and  
Hyperconjugative Effects

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The electronic basis for the relative stability of specific molecular conformers, even as small as ethane, remains a topic of interest. For ethane, it is now understood that steric and hyperconjugative effects contribute to the stability of staggered conformations to significant extents. However, little work has been done for even slightly larger molecules, which limits our understanding of the balance between these effects. In this poster, we carry out a stepwise study of the rotational barrier of  $R_3C-C\equiv C-CR_3$  systems (where  $R = H, CN, F, Cl, Br, I, At$ ) at the B3PW91 and MP2 (full) levels. The cc-pVTZ basis set was employed, with pseudopotentials, too, in the cases of Br, I, At. We find that for  $R = H, Cl, Br, I, At$ , the most stable conformer is a  $D_{3h}$  (eclipsed) form, while hexacyano-2-butyne preferred the  $D_{3d}$  (staggered) conformation. At the B3PW91 level, the isomeric preference for hexafluoro-2-butyne is unclear due to the flat potential energy surface, but the MP2 treatment support a preference for the  $D_{3d}$  symmetry. Additional investigations have been carried out to study the influence of weak through-space interactions on energy barriers, including intra-molecular hydrogen bonding. The latter structures show a  $D_{3h}$  preference with barrier heights as large as  $\sim 3.30$  kcal/mol.