

Origin and Nature of Bond Rotation Barriers: A Unified View

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Abstract

Bond rotations are common and important in molecular studies such as drug design and enzymatic reactions. Steric hindrance and hyperconjugation are often borrowed to justify the origin of bond rotation barriers. However, there exists no consensus, even for as simple molecules as ethane, on which effect is more significant. Here we show that a unified view is possible. To that end, we employ two energy partition schemes from density functional theory to investigate the flexible rotation barrier of six molecules with one rotatable dihedral angle, ethane C_2H_6 , methylamine CH_3NH_2 , methanol CH_3OH , hydrazine NH_2NH_2 , hydroxylamine NH_2OH , and hydrogen peroxide H_2O_2 . Our results suggest that even though steric and quantum effects play indispensable roles, it is the electrostatic interaction that governs the barrier height of all these different types of systems. This work not only consolidates earlier views about the role of steric and quantum effects, it also provides new insights about the origin and nature of the bond rotation barrier, which should be applicable to many different types of chemical bonds.