ORIGIN OF METHYL TORSIONAL BARRIERS

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We present a picture of the ethane torsional barrier mechanism that differs from intuitively satisfying repulsion (both exchange and Coulombic) between closely approached C-H bonds in the eclipsed conformer. We supplant this by a more subtle complex barrier mechanism involving changes in structural and delocalization energies, where the structural energy change is largely controlled by weakening of the C-C bond and to lesser extent by concomitant strengthening of the C-H bonds. Understanding the barriers in ethanelike molecules requires appreciation of how the balance of competing terms in the energy decomposition varies from one case to another. We apply lessons learned from analyzing the ethane structure and barrier to ethane related molecules, including methanol, dimethyl ether and disilane.