New Insight into Fundamental Issues of Structural Organic Chemistry

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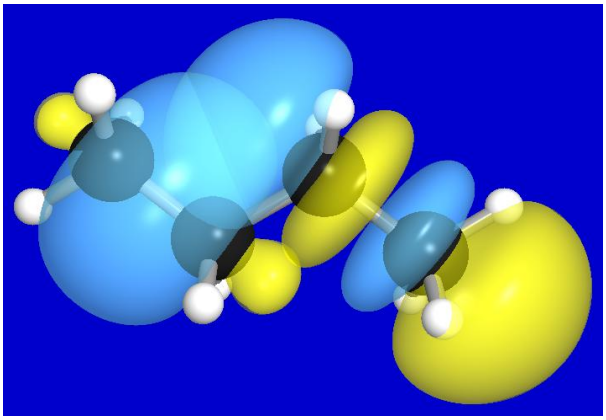

Understanding the relationship between the structure of a molecule and its stability is a central concern to many chemists. Most would agree that hydrocarbons, the simplest class of organic compounds, are well understood and that other classes of compounds present more interesting problems. But hydrocarbons may not be as simple as they seem. The past five years have witnessed a hotly contested controversy in the literature involving several leading physical organic chemists. Factors that are responsible for the varying stabilities of hydrocarbons are at issue, and competing empirical models have been proposed that appear to be largely at odds with each other. I will review the controversy and describe a new model, the *vicinal interactions* (VI) model, that is based on simple steric and delocalizing orbital interactions. Unlike the empirical models, the VI model is based on quantum chemistry calculations but is fit to reproduce experimental enthalpies of formation. The VI model is applied to gas-phase alkanes, alkenes, alkyl radicals, and amines. Application to the latter class of compounds suggests that several amines have experimental enthalpies of formation that are significantly in error.