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On the Stability of Branched Hydrocarbons

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Abstract

Nearly a half-century ago I published a paper which successfully calculated the relative stabilities of a large number of hydrocarbons. Calculations were based on empirical atom-atom potential energies I had introduced in 1960, which had been deliberately biased to take into account the differences between branched and u n b r a n c h e d hydrocarbon molecules. Little controversy arose until quite recently when Gronert revived this old work and entered into what evolved into a bitter controversy with the Grimme, Wiberg, and Schleyer accounts of stabilities of branched vs. unbranched hydrocarbons. Gronert invoked 1-3 nonbonded interactions to reproduce successfully the relative stabilities of the various hydrocarbons. His opponents carried out careful quantum computations including electron correlation energies (not feasible to calculate in 1960 when the empirical interaction potentials were formulated). The purpose of this paper is to resolve the controversy by showing that while the two approaches differ in verbal explanations; they are equivalent in concrete results.

Introduction

To get to the heart of what is involved, consider the fact that the relative stabilities of isomers are built into the force-fields of the molecules concerned. Molecular-mechanics computations based on the force-fields yield both the structures and energies of the molecules. Note that the primary difference between normal and iso potential energies in hydrocarbons can be expressed as [1]:

$$V_{normal} - V_{iso} = 2\ V_{C-H} - (V_{C-C} + V_{H-H})\ (1)$$

Where V_{ij} 's are the potential energies of the i,j (1-3) interactions evaluated at their appropriate geminal nonbonded distances. First of all, the idea that that geminal distances (bond angles) around a central atom are based on a 1960 model [2] *invoking the close packing of repelling ligands*, rather than by presumed effects of hybridization or even by the interactions proposed by the popular VSEPR model. This account has since been confirmed in detail by the author of the VSEPR papers, and his colleagues [3-13]. What is it then that causes the geminal potential energies in Eq.1 to make branched hydrocarbons to be more stable than unbranched ones?

Empirical Approach

One answer is that it doesn't matter as long as computations correctly account for experimental results. To get quickly to the point of the present argument, the Gronert force field [14], based closely on Bartell's empirical field of 1960 [2], incorporated nonbonded interactions, which inserted into Eq. 1, deliberately biased them to make the C-H interactions more repulsive than the sum of the C-C and H-H interactions. This stratagem successfully accounted for observations of a large number of unbranched, singly, and multiplies branched hydrocarbons [1]. No explanation was advanced to account for this bias except that it was needed to account for the extra stability of branched molecules.

A More Fundamental Approach

Once it became feasible to include accurate electron correlation energies in quantum chemical computations, Wiberg [15,16], Grimme [17] and Schleyer [18-20] found electron correlation to be essential to account for experimental results. They showed that simple steric interactions between ligands (as yielded by Hartree-Fock computations) were incapable of reproducing experimental isomeric differences. As Grimme [16] showed by partitioning the electron correlation energies,

the stabilizing energies were greater for C-C and H-H interactions than for the C-H. Accordingly, this accounted for the imbalance of terms in Eq. 1. Therefore, the extra stability of branched hydrocarbons is explained by Wiberg, Grimme, and Schleyer at a more fundamental level than by Gronert's model.

Conclusion

Both the Gronert and the Wiberg-Grimme-Schleyer treatments account for what Schleyer calls protobranching stability. It cannot be denied that electron correlation energies are responsible for the extra stability of branched hydrocarbons. But that fact in no way implies that Gronert's approach is *wrong*. Except for explanations, the two approaches are equivalent in content if not in the words used to describe them.

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