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ON THE CONTRIBUTIONS OF RESONANCE, HYBRIDIZATION AND NONBONDED INTERACTIONS TO THE STRUCTURE OF BUTADIENE

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Abstract—A recent *ab initio* molecular orbital calculation on butadiene has been interpreted by Skaarup, Boggs and Skancke as indicating that the shortness of the central C–C bond is due primarily to hybridization. Resonance was considered to make a minor contribution and nonbonded interactions were judged to be unimportant. Unfortunately, this analysis failed to take into account the crucial rôle of geminal nonbonded interactions, and the calculations were, accordingly, not designed to discriminate between the hybridization and nonbonded models. A more direct investigation of intramolecular nonbonded interactions based on *ab initio* computations has been carried out on other systems, however, providing evidence that the effects of nonbonded contributions are substantial.

Butadiene has long been a popular subject for analysis by theorists seeking to understand the connection between electronic structure and molecular properties. In particular, quantum chemists attempted in their earliest treatments to relate the central C–C bond length in butadiene to π-electron delocalization.[1] While the C–C bond length[2] at 1.463(3)Å is conspicuously shorter than the 1.534Å length found in saturated hydrocarbons,[3] the fact that the bond environment differs markedly from that in alkanes in respects other than π-delocalization led some workers [4–8] to challenge the resonance interpretation. In a recent paper[9] based on one of the most definitive quantum-theoretical studies of butadiene yet to appear, Skaarup, Boggs and Skancke attempted to analyze the relative importance of the proposed contributions to the C–C bond shortening. They interpreted their results as supporting the hybridization argument advanced by Dewar and Schmeising[4] and suggested that conjugation is responsible for only about 0.02Å of the observed shortening. In reviewing Bartell's[7,8] explanation invoking "lesser nonbonded repulsion" in the unsaturated than in the saturated molecules, they concluded[9] that such "nonbonded repulsions are not responsible for sp^2–sp^2 bonds being shorter than sp^3–sp^3 bonds."

The purpose of this short paper is to point out that Skaarup *et al.*[9] took into account only nonbonded interactions more remote than geminal as a consequence of their misconception of the nonbonded model. They neither made calculations nor advanced arguments capable of discriminating between the Dewar and Schmeising "hybridization" point of view[4] and the "nonbonded interaction" account.[7] Indeed, as pointed out both by Bartell[7] and by Dewar,[5] the situations in which the one picture might be expected to be significant are just those in which the other arises naturally. Therefore, no simple observables such as those examined by Skaarup *et al.*, whether determined experimentally or theoretically, can resolve the argument.

Crucial to the argument are the following considerations. If two tetrahedrally coordinated ("sp^3") atoms are bonded together, they suffer *six* geminal nonbonded interactions across the bond. By contrast, for two trigonally coordinated ("sp^2") atoms, there are only *four*. The relief of two geminal interactions in the "sp^2–sp^2" case is quite enough to account for the observed shortening if geminal interactions are assumed to follow the repulsive force laws indicated by Urey–Bradley spectroscopic analyses.[8,10] Support for force laws implying repulsions comparable to those inferred from Urey–Bradley analyses has recently come from quantum calculations of the intramolecular interactions in methane[11,12] and ethane.[13] Moreover, when such force laws are built into "molecular mechanics" force fields for hydrocarbons,[14] it is possible to account very naturally for subtle trends in structures and isomerization energies with a smaller number of disposable parameters than when non-Urey–Bradley fields[15] are used.

Therefore, in the two decades since the nonbonded model was first formulated, additional supportive evidence, both empirical and theoretical, has accumulated. To be sure, virtues and limitations of the model of geminal nonbonded interactions are now much better understood.[11,13] More definitive information is needed before the problem can be laid to rest. The recent treatment of Skaarup, Boggs, and Skancke, important though it be in other respects, adds no new insight to help decide between the hybridization and nonbonded contributions the authors originally proposed to assess.

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