Teaching the Right Reasons: Lessons from the Mistaken Origin of the Rotational Barrier in Ethane**

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…when will chemistry textbooks begin to serve as aids, rather than barriers, to this enriched quantum-mechanical perspective…
F. Weinhold (2001)

When I was first properly introduced to chemistry in the 9th grade, electrons ("chemical glue") were simply described as single dots around atoms. Magically, sharing the dots meant a "chemical bond" and one had only to count up to eight to figure out how many electrons were shared and how many bonds you would have. Easy. We counted ions, balanced redox reactions, and had fun with oxidation numbers for inorganic and simple organic species. Then things became more complicated. We were introduced to Bohr's model, in which you could only have two electrons in the innermost shell and eight in the next; beyond that, who knows what. That all had to do with some complicated quantum theory that we could not possibly understand in detail, so we were asked just to accept it. We did, until two years later when suddenly we were told that Bohr's model is really too much of an approximation and that chemical bonding is far more complicated. It should be expressed using the intricate laws of quantum mechanics, namely, in terms of molecular orbitals. All bond types (multiple, metallic, back-bonding, etc.) suddenly became unique and things were *really* complicated mathematically. I remember well the funny-looking dumbbell-shaped, colorful styrofoam models of the various *d* orbitals, and thought that nature could not possibly be that complicated; in any case, two years from then they would tell us otherwise anyway. So I decided not to accept anything that had to do with this awkward quantum theory, only to be quizzed in the next class session. Needless to say, I received the worst grade in my chemical life and was embarrassed in front of the entire class. Shortly thereafter I decided to become a chemist.

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The reason that I am telling this story is because there are, as always, two sides to it. Teachers, on the one hand, can confuse and frustrate their students by trying to depict chemistry in the most up-to-date, albeit complicated fashion. On the other hand, motivated students will despise simple models if more appropriate ones continually replace them. Frustration may be the final result. The simplification approach may be acceptable at the high school level because easily understandable explanations, although possibly inadequate, do get the message across. At higher scholastic levels, however, this is no longer acceptable because we owe it to the students to teach them our current knowledge and interpretation of science. The convenience of visually pleasing explanations for intricate chemical phenomena must not outweigh proper physical descriptions. These are available through modern quantum mechanics within the Born–Oppenheimer approximation that allows approximate solutions of the electronic Schrödinger equation in the form of potential energy hypersurfaces. Hence, quantum mechanics provides us with an accurate theoretical description. The subsequent interpretation is a model that may be useful but not absolutely necessary for our understanding.

A timely case in point is the rotational barrier of ethane, an old, yet much debated subject.[1] Understanding the origin of such a barrier is essential to just about any form of structural chemistry, from the conformational analysis of simple alkanes to protein folding.[2]

A recent paper by Pophristic and Goodman[3] on this topic, which emphasized the importance of hyperconjugative interactions[4] in the preferred staggered conformation of ethane, came as somewhat of a surprise to me, simply because I thought the conclusions had been reached in the work of others published long ago. As an admirer of the elegance and non-intuitive beauty of molecular orbital theory, I have been telling my students exactly what is detailed in the paper, and I had apparently falsely assumed that everybody else did just the same. Skimming through several undergraduate organic textbooks, however, quickly revealed that virtually all of them (with a few notable exceptions[5–7]) make steric repulsion of the hydrogen atoms ("bumping") or of the C–H bonds responsible for the barrier in ethane. I learnt that I was quite lucky to have had organic chemistry teachers who chose not to "fall" for, as Goodman and Pophristic put it, the seductively transparent steric repulsion explanation, and instead present-

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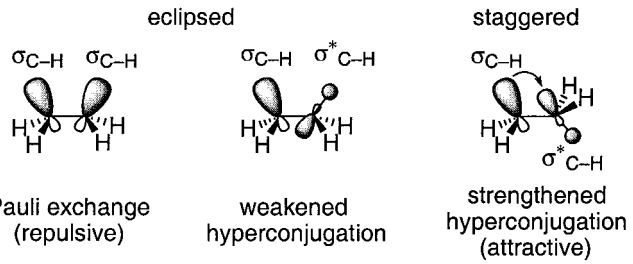
ed the subtle quantum superposition-based hyperconjugation model.[8]

While the notion of a hindered rotation in ethane is often credited to Pitzer and Kemp (1936),[9] Ebert (1929)[10] and then Wagner (1931)[11] may have been the first to propose this. Their physicochemical measurements based on the molar heat capacity of ethane were first left unconfirmed[12] but were supported soon thereafter by Eucken and Weigert in 1933.[13] Teller and Weigert established the presence of a hindered rotation by quantum theoretical computations on the temperature dependence of the molar heat capacity of ethane.[14] Needless to say, even then these propositions were discussed vehemently, and the Kemp and Pitzer paper, which does, however, not cite the earlier work of Ebert or Wagner, seems to settle the dispute between the various groups.[9] Independently, Wilson (incidentially, not citing the 1936 Kemp and Pitzer publication) emphasized the presence of an appreciable rotational barrier of about 3 kcal mol^{-1} and showed that this cannot be a consequence of nuclear spin and symmetry effects.

This early work demonstrated that the internal rotational potential energy of ethane has three degenerate minima corresponding to the only stable conformation: the staggered conformer.[15] These conformers are separated from each other by slightly higher-lying (about 3 kcal mol^{-1}),[16] degenerate eclipsed conformations. But what is the origin of the rotational barrier? Steric repulsion between bonds arising from the overlap of two filled C–H bond orbitals (and hence violating the Pauli exclusion principle)[17] in the eclipsed conformation indeed seems an attractive explanation. Pophristic and Goodman showed, however, by using a computational method that allowed them to "switch off" this interaction, that the two curves representing the torsional angle between the two methyl groups—one curve with all interactions present, the other with the exchange repulsion absent—coincide. That is, the staggered conformation is preferred regardless of the presence of exchange repulsion. It is therefore not valid to assume, as most textbooks do, that steric considerations play the leading role in deciding the minimum conformation of ethane, and possibly many other structures. This finding is also transferable to other simple systems such as the internal rotational barriers of methanol[18] and methylamine that are both much lower (1 – 2 kcal mol^{-1}) than for ethane, despite shorter central heavy-atom – carbon bond lengths (see below).[19] Steric interactions seem to dominate, however, for *n*-butane and higher alkanes that suffer from exchange repulsion between the two methyl group C–H bonds within van der Waals contact.

Clearly, there must be a second, less obvious, quantum-mechanical interaction responsible for the observed conformational preference: namely, hyperconjugation.[20] This interaction arises from partial electron transfer from filled $\sigma_{C\text{-}H}$ bonding and unfilled $\sigma^*_{C\text{-}H}$ orbitals. Despite the fact that a lower-lying occupied orbital interacts with a higher-lying empty orbital, quantum mechanics tells us that this interaction is stabilizing in nature.[21] If the hyperconjugative interactions between the methyl groups are turned off in Pophristic and Goodman's model calculations, the preference for the staggered conformation of ethane is lost. Hence, the preferred conformation does not relieve steric congestion, but achieves optimal "internal delocalization" (resonance) stabilization (Scheme 1).

It is noteworthy that Mulliken concluded as early as 1939 that "…hyperconjugation in ethane [is present but] should not



Scheme 1. Steric and quantum-mechanical models for explaining the preference for the staggered form of ethane.

appreciably hinder free rotation" and, somewhat inconsistently, "…that the observed hindering potentials are entirely consistent with the existence of appreciable energy effects due to hyperconjugation, which might manifest themselves in other ways than in conjunction with free rotation."[20]

Hyperconjugation is largely responsible for inducing the elongation of the carbon – carbon bond that accompanies the internal rotation.[22] That is, the torsional coordinate includes expansion of the C–C bond;[23, 24] if this elongation is not taken into consideration, the $\sigma_{C\text{-}H} \rightarrow \sigma^*_{C\text{-}H}$ rationalization may therefore not be valid. This finding is also supported by the large decrease in the barrier for disilane (ca. 1 kcal mol^{-1})[25] that is a result of the attenuation of the pairwise repulsions, which are more important in the more polarized Si–H bonds of disilane than in ethane and the diminished hyperconjugation between the Si–H bonds.[26]

The hyperconjugative model also explains related conformational preferences such as the anomeric effect (that is, the hydroxyl group in glucose at the anomeric carbon atom next to the oxygen atom in the ring is often in the sterically crowded axial position. This axial orientation results from the electronic preference of an OCOC unit for the synclinal rather than antiperiplanar orientation).[27, 28] The anomeric interaction is very often incorrectly described as a dipole – dipole repulsive interaction[29] ("rabbit ears" on oxygen atoms in sugars, for example), rather than an attractive interaction. A simple comparison of the heats of formation of, for example, 1,3- versus 1,4-dioxane, emphasizes the inherently stabilizing nature of this effect: 1,3-dioxane is 5.5 kcal mol^{-1} more stable.[30]

There are many examples of this kind where we attempt to take the easy way out, or worse, actually believe what we have heard over and over again, even if it is incorrect. Take Lewis structures, for example, which only describe geometries but not electronic structures:[31] ammonium cations do not have a positive partial charge on the nitrogen atom, despite the formal electron count. The charge resides on the electropositive elements, that is, the hydrogen atoms in NH_4^+.[32] Bases abstract protons from ammonium cations and do not attack the nitrogen atom! The same is true for many oxygen-containing cations (hydronium, oxonium, acyl cation, proto-

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nated enols, etc.) that virtually never contain a positively charged oxygen atom.[33]

Although the key paper under consideration is a convincing validation of the hypothesis that hyperconjugation controls the ethane barrier, this idea is by no means new. As already noted above, Mulliken appears to have been the first to propose this possibility in 1939,[20] and there was a continuous flow of publications that utilized increasingly sophisticated studies of this attractive idea, especially those of Lowe,[34–36] England and Gordon,[37] as well as Brunck, Weinhold, and Reed.[2, 19, 38] The Pophristic and Goodman paper re-emphasizes, by analyzing in detail a straightforward yet intricate problem, that chemistry often is not as easy as we hope it to be and as we would like to teach it. In this context, Weinhold cunningly states: "when will chemistry textbooks begin to serve as aids, rather than barriers, to this enriched quantum-mechanical perspective […]?"[39]

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