Rotational Barrier in Ethane

The Magnitude of Hyperconjugation in Ethane: A Perspective from Ab Initio Valence Bond Theory[**]

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An understanding of the origin of the torsional barriers in ethane-like molecules is essential to addressing many structural and conformational questions in chemistry and bio-

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chemistry. The barrier to rotation about the C–C bond in ethane has been traditionally attributed to Pauli exchange repulsions, or steric hindrance, between the vicinal C–H bonds.[1] At first glance, this appears to be a simple problem and indeed, this concept has been widely adopted as a standard explanation in organic chemistry textbooks.[2] However, the steric-repulsion mechanism has been challenged in a number of studies by using natural bond orbital (NBO) analyses.[3–6] It was suggested that the dominant factor bringing about the conformational preference in ethane is hyperconjugative interactions between the occupied σ_{C-H} orbitals of one methyl group and the antibonding σ^*_{C-H} orbitals of the other methyl group and that such delocalization interactions stabilize the staggered conformation more than the eclipsed form. In this theory, the emphasis is on the stabilizing effects owing to the delocalization of electron density in the molecule. A surprising and somewhat counter-intuitive finding in the study by Pophristic and Goodman is that the eclipsed conformer is even more stable than the staggered structure after the σ_{C-H}–σ^*_{C-H} hyperconjugative interactions are removed in the NBO analysis, which suggests that electrostatic and Pauli repulsions actually favor the eclipsed configuration.[5] This analysis has immediately led to the suggestion that organic textbooks need be revised to reflect the stabilizing features in conformational analysis.[7]

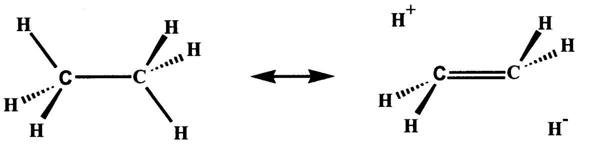
Although there have been numerous studies of the conformational preference in ethane, the issue is still controversial, differing mainly in the roles of steric hindrance (repulsion model) and hyperconjugation (stabilization model).[6,8,9] Early studies based on valence theory suggest that the torsional barrier in ethane is due to the repulsive exchange interactions between electrons in the two methyl groups.[1] More recently, Bickelhaupt and Baerends estimated the energies owing to steric effects by constructing a localized wavefunction with fragmental molecular orbitals of the two methyl groups, and concluded that Pauli exclusion repulsions are the driving force for the barrier in ethane.[9] Although consistent with the traditional picture, the calculation has been questioned because the localized wavefunction used in that work was neither optimized self-consistently nor an eigenfunction of the spin operator.[6] The possible role of hyperconjugative interactions on the rotation barrier in ethane was described by Mulliken as early as 1939[10] and later by Epiotis et al.,[11] but its effects on hindered rotation were considered to be small. Energetic estimates of the hyperconjugation effects by using the NBO theory showed that interactions between the σ_{C-H} occupied orbitals in one methyl group and the σ^*_{C-H} antibonding orbitals in the other methyl group significantly stabilize the staggered conformation more than the eclipsed form, while the computational results are very sensitive to the small difference in the C–C bond length between the two conformers.[3,4]

Hyperconjugation interactions arise from the delocalization of σ electrons, which leads to net stabilization of the system.[12] To quantitatively estimate the stabilization energy of hyperconjugation effects, it is necessary to know the energy of a hypothetical system that has no hyperconjugative interactions. Computationally, this requires the construction of a molecular wavefunction from localized bond orbitals. Conventional molecular orbital (MO) theory does not provide a unique procedure for strictly localizing the occupied orbitals.[13,14] As a result, post self-consistent-field (SCF) analyses, such as the NBO theory, have been developed to derive localized orbitals from a delocalized wavefunction. Although major insights can be obtained on electronic interactions, it is a serious drawback for the investigation of small energy effects, such as the rotational barriers about a single bond, because the NBO approach tends to yield a higher energy for the localized reference state than that generated by self-consistent field (SCF) calculations.[9,13,15] This situation leads to overestimations in the computed hyperconjugation energy, which can be greater than the small energy difference to be analyzed.[9]

Ab initio valence bond (VB) theory provides an ideal approach for deriving localized wavefunctions through SCF optimizations,[16–18] but it has not been used to study hyperconjugation effects in ethane previously, primarily because of its very long computational time. The recently developed computational algorithm in our laboratory is very efficient,[18] making such calculations feasible, and we apply this method to assess the hyperconjugation energy in ethane. Our approach differs from other methods, in particular, the energy decomposition approach[9] and the NBO analysis,[4,5] in that the localized wavefunctions are derived by SCF calculations in VB theory. In addition, we compare the VB results with those obtained from a block-localized wavefunction (BLW) method.[13,15,19]

With our definition of hyperconjugation we found that both steric hindrance and hyperconjugative interactions contribute significantly to the observed preference of the staggered conformation in ethane. However, the larger effect is the steric hindrance, whereas hyperconjugative interactions stabilize the gauche conformer by about 4 kJ mol^{-1} relative to the eclipsed form, or one third of the overall barrier height (12 kJ mol^{-1}). Thus, the traditional picture for the origin of torsional barrier in ethane (steric hindrance) is basically valid, but a more complete explanation should take account contributions from hyperconjugation stabilization.

VB Interpretation of the Rotational Barrier: Within the framework of resonance theory, the wavefunction for ethane can be described by the resonance of one covalent structure and a total of 18 singly ionic structures, each corresponding to that with one proton in one methyl group and one hydride in the other group [Eq. (1)].



(1)

Accordingly, the hyperconjugative stabilization energy E_{hc} is defined as the energy difference between the lowest energy state, which is a superposition of the covalent and ionic resonance structures, and the charge-localized covalent structure. The theoretical and computational details are given in the Computational Methods section.

We have carried out valence-bond calculations using the 6-31G(d) and 6-311G(d,p) basis sets for the localized and delocalized electronic structures at the HF/6-31G(d) optimal geometries for the staggered and eclipsed conformers. The computed barrier heights for ethane are 11.3 and 11.7 kJ mol^{-1} at the VB–SCF level using the 6-31G(d) and 6-311G(d,p) basis set, respectively. They are in accord with the experimental value of 12.0 kJ mol^{-1},[20] and consistent with all other theoretical results.[21] In the work of Bickelhaupt and Baerends,[9] a barrier height of 10.6 kJ mol^{-1} was obtained at the density-functional level using the Becke88–Perdew86 functional and a large STO basis set. Figure 1 depicts the adiabatic (fully relaxed ethane geometries) torsional energy profiles determined with and without the hyperconjugation effects in ethane using the VB-SCF/6-31G(d) model. The computed delocalization energies are listed in Table 1, and it is reassuring that the size of the basis set has a relatively small effect on the calculated hyperconjugation energies.[13,15] Importantly, the effect is even smaller when we examine the relative hyperconjugation energies between the staggered and eclipsed conformations. We note that the total hyperconjugation stabilization energies in Table 1 also include contributions from the geminal bonding and antibonding orbital interactions with the C–C bond.[4] These geminal interactions are constant with respect to internal rotation owing to symmetry.

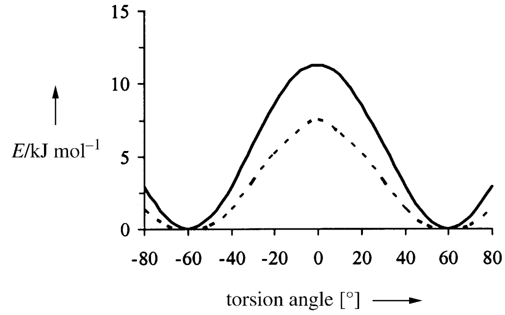


Figure 1. Comparison of energy profiles (energy E versus dihedral angle) for the ethane rotation where the hyperconjugation effect is considered (——) or screened out (– – –).

Table 1: Computed total hyperconjugation energies (E_{hc}) and contributions to the rotation barrier (ΔE_{hc}) using the ab initio valence bond method at the HF/6-31G(d) optimal geometries.[a]

Basis set	Ab initio VB[b]			NBO analysis[c]		
	E_{hc} (eclipsed)	E_{hc} (staggered)	ΔE_{hc}	E_{hc} (eclipsed)	E_{hc} (staggered)	ΔE_{hc}
6-31G(d)	−43.1	−46.9	3.8	−136.8	−160.2	23.4
6-31G(d,p)	−50.7	−54.8	4.1	−137.7	−158.6	20.9

[a] Energies are given in kJ mol^{-1}. [b] This work. [c] Ref. [4].

The data in Table 1 reveal that hyperconjugation stabilization is only 3.8 to 4.1 kJ mol^{-1} greater in the staggered conformation than in the eclipsed structure, which accounts for about 33 % of the total rotational barrier in ethane. Importantly, when hyperconjugative interactions are screened out from the calculation using the wavefunction defined by Equation (2) (Computational Methods) for the localized reference state, there is still a significant barrier of 7.5 kJ mol^{-1} using the 6-31G(d) basis set. In this case, the rotational barrier in the reference state can be entirely attributed to steric hindrance, which represents the collective contributions from the Pauli exchange repulsion and electrostatic interactions between the vicinal methyl groups. Thus, our ab initio VB–SCF study demonstrates that both steric hindrance and hyperconjugation effects are important to the understanding of the origin of the torsional barrier in ethane, however, the contribution of the steric effects is twice as large as that of the hyperconjugative, electron delocalization interaction.

We also compare in Table 1 the estimates of relative hyperconjugation energies derived from the NBO analyses,[4] which yield values of 20.9 and 23.4 kJ mol^{-1} in favor of the staggered conformer, far greater than our results (about 4 kJ mol^{-1}) and also far greater than the total barrier height (12 kJ mol^{-1}). This leads to the counter-intuitive result that the eclipsed conformation is more stable than the staggered conformation by 11.3 kJ mol^{-1}.[22] Bickelhaupt and Baerends rationalized the exceptionally large hyperconjugative delocalization energy as a result of the construction of the Lewis determinant wavefunction for the localized reference state from the occupied NBOs,[9] which is overly destabilized relative to the Hartree–Fock determinant.[13] Clearly, the concept and significance of steric hindrance and hyperconjugation in rationalizing the cause of the rotational barrier in ethane depend on the method used to derive the wavefunction of the localized reference state. The present ab initio VB theory allows us to fully optimize the localized valence bond orbitals in a self-consistent fashion, which results in a reference state that is more stable than that constructed using orbitals derived from localization methods.

The BLW Calculations: As a further exploration of the role of hyperconjugation in ethane, we designed a computational model to screen out the geminal interactions contained in the ab initio VB–SCF calculations.[13,15,19] If we reduce the point-group symmetry of ethane from D_{3d} (staggered form) or D_{3h} (eclipsed form) to C_s, and take the plane H1C1C2H4 as the principal plane (Figure 2), hyperconjugation in ethane can be thought of as the resonance or conjugation between the p_π group orbitals in the two methyl groups, which is analogous with the π delocalization in butadiene (Figure 2). Thus, an examination of the conjugation energy in butadiene provides an alternative way of verifying our computational approach in the calculation of hyperconjugation energy. The conjugation effects can be studied using the BLW method,[13,15,19] which combines the advantages of both MO and VB theories. In the BLW method, the wavefunction Ψ^{BLW} corresponds to a localized Lewis structure, whereas the delocalized structure is represented by the HF wavefunction Ψ^{HF}, and the

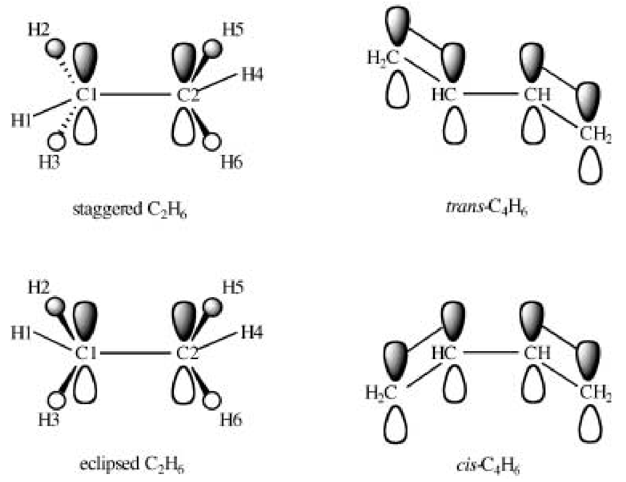


Figure 2. Schematic comparison of the similarity between hyperconjugation interactions in ethane and π-conjugation in 1,3-butadiene.

conjugation delocalization energy E_{del} can be determined by Equation (5) (Computational Methods).

In ethane, the relative hyperconjugation energies are 3.2 and 3.5 kJ mol^{-1} in favor of the staggered conformer using the 6-31G(d) and 6-311G(d,p) basis set, respectively (Table 2).

Table 2: Computed delocalization (E_{del}) and differential (ΔE_{hc}) hyperconjugation energies using the BLW method.[a]

Basis set	Ethane			Butadiene		
	E_{del} (eclipsed)	E_{del} (staggered)	ΔE_{hc}	E_{del} (*cis*)	E_{del} (*trans*)	ΔE_{del}
6-31G(d)	−11.7	−13.3	3.2	−36.9	−42.5	5.6
6-311G(d,p)	−14.3	−16.1	3.5	−40.2	−45.5	5.3

[a] Energies are given in kJ mol^{-1}.

This result is in agreement with the ab initio VB results discussed above. Since geminal interactions are not included in the BLW calculation, the agreement confirms that these interactions, which are involved in the VB energy decomposition analysis, do not change appreciably as a function of the internal rotation.

The rotational barrier is not necessarily the sum of hyperconjugative and steric effects since electronic relaxation, particularly in the central C–C bond, may be involved in the process of rotation. Therefore, it is desirable to evaluate the steric energy independently. A plausible strategy is to examine the energetic change as a function of the torsional angle by freezing the bond orbitals obtained either at the staggered or the eclipsed conformation for the localized reference state [Eq. (2); Computational Methods]. This can be conveniently achieved by using the ab initio VB method [localized wavefunction from bond orbitals of Equation (3) (Computational Methods). We first obtain the optimal VB function for the staggered conformation in SCF optimizations. Then, we vary the torsional angle and recompute the electronic energy by fixing all bond orbitals without further SCF optimization. Since all orbitals are frozen without further electronic relaxation in this step, the energy change is purely due to the difference in Pauli exchange and electrostatic interactions, which are collectively termed as steric effects.

Table 3: Estimated steric energies for the conversion of staggered→eclipsed conformations obtained by freezing the bond orbitals at the initial configuration during the torsional rotation using the ab initio VB method.[a]

Basis set	ΔE_{steric}	
	Ψ(staggered)[b]	Ψ(eclipsed)[c]
6-31G(d)	7.8	7.4
6-311G(d,p)	7.8	7.4

[a] Energies are given in kJ mol^{-1}. [b] Computed using the optimal VB function for the staggered conformation. [c] Computed using the optimal VB function for the eclipsed conformation.

Table 3 lists the change in total steric energy (ΔE_{steric}) by rigid rotation from the staggered conformation to the eclipsed conformation when all the orbitals are frozen at the optimized staggered reference state, and from the eclipsed state to the staggered state using fixed VB orbitals optimized at the eclipsed configuration. Both basis sets are used for comparison. In either direction, we obtain similar results, which are independent of the two basis sets used. The net steric effect is estimated to be 7.4 to 7.8 kJ mol^{-1}, which is similar to the adiabatic results (Figure 1) where the geometry of ethane is fully relaxed along the rotational coordinate. This conclusion is in contrast to the findings of Pophristic and Goodman,[5] who obtained a net stabilization of 11.3 kJ mol^{-1} at the *eclipsed* conformation. We note that Bickelhaupt and Baerends further analyzed the intricate balance of exchange and electrostatic interactions and their dependence on the C–C bond distance,[9] which ultimately leads to greater steric repulsion at the eclipsed form.

In conclusion, our results, which are obtained from ab initio self-consistent field VB calculations, indicate that both steric effects and hyperconjugative interactions play important roles in stabilizing the staggered conformation. While steric effects make the dominant contribution, hyperconjugation interactions contribute about one third of the total torsional barrier in ethane.

Computational Methods

Ab initio valence bond theory: Within the framework of the VB theory, the covalent resonance structure for ethane is constructed using a Heitler–London–Slater–Pauling function[16–18] [Eq. (2) the atomic labels are shown in Figure 2], where $K1$ and $K2$ represent the core (1s) orbitals of the two carbon atoms C1 and C2, respectively,

$$\Psi^{\text{Loc}} = \hat{\text{A}}(K1\,K2\,\sigma_{\text{C1C2}}\sigma_{\text{C1H1}}\sigma_{\text{C1H2}}\sigma_{\text{C1H3}}\sigma_{\text{C2H4}}\sigma_{\text{C2H5}}\sigma_{\text{C2H6}}) \tag{2}$$

which are doubly occupied in the form of MOs. Â is the antisymmetry operator, σ_{ij} is a localized bond orbital between atoms i and j, constructed from two group localized orbitals φ_i and φ_j that are expanded over the basis functions on each methyl group [Eq. (3)]

$$\sigma_{ij} = \hat{\text{A}}[\varphi_i\varphi_j(\alpha\beta - \beta\alpha)] \tag{3}$$

where α and β represent the spin states of electrons. The fully delocalized wavefunction for ethane can be constructed by linear combination of the covalent structure [Eq. (2)] and all ionic structures.

However, the covalent structure is much lower in energy than the ionic structures because of the long separation of charges and the distorted double-bond character in the ionic configurations. Thus, the wavefunction for ethane can be compactly constructed with Coulson–Fischer orbitals [Eq (4)],[17,25] where the orbital σ'_{ij} contains Coulson–Fischer basis orbitals φ'_i and φ'_j, which are expanded in the whole basis space of ethane, rather than a subspace of one methyl group as in φ_i and φ_j. The use of Coulson–Fischer orbitals includes effectively all the ionic structures in the calculation.

$$\Psi^{\mathrm{Del}} = \hat{\mathrm{A}}(K1\,K2\,\sigma'_{\mathrm{C1C2}}\sigma'_{\mathrm{C1H1}}\sigma'_{\mathrm{C1H2}}\sigma'_{\mathrm{C1H3}}\sigma'_{\mathrm{C2H4}}\sigma'_{\mathrm{C2H5}}\sigma'_{\mathrm{C2H6}}) \qquad (4)$$

With the definition of the localized and delocalized wavefunctions as in Equations (2) and (4), the hyperconjugative stabilization energy in ethane E_{hc} can be determined by Equation (5).

$$E_{\mathrm{hc}} = E(\Psi^{\mathrm{Del}}) - E(\Psi^{\mathrm{Loc}}) \qquad (5)$$

We note that both Ψ^{Loc} and Ψ^{Del} are expanded into $2^7 = 128$ Slater determinants for a total of 14 electrons in our VB calculations, and all the orbitals $\{\varphi_i\}$ and $\{\varphi'_i\}$ are optimized self-consistently, in contrast to post-SCF analysis schemes.

The block-localized wavefunction (BLW) model: To make the BLW computations feasible for ethane, we decompose the hyperconjugative interactions between the two methyl groups into two components; one lies in the principal (xz) plane H1C1C2H4, and the other is perpendicular to this plane (y direction). To form the BLW orbitals, we partition the orbitals (subsequently transformed from basis functions to become the basis of irreducible representations of the C_s point group) and electrons into three blocks. The first block consists of the p_y orbital of carbon and the anti-combination of 1s orbitals of H2 and H3 atoms of one methyl group (namely of a″ symmetry), while the second block includes the corresponding p_y and the anti-combination of 1s orbitals of the hydrogen atoms of the other methyl group. The third subgroup contains the remaining orbitals in the principal plane, which possess a′ symmetry. Because orbitals with a″ and a′ symmetry do not mix and the in-plane hyperconjugation interactions are already included in the third block of the BLW wavefunction, the energy difference, E_{del}, between this three-block BLW wavefunction and the HF wavefunction accounts for delocalization interactions purely resulting from the perpendicular components, which, due to symmetry, is one half of the total hyperconjugation effects ($E_{\mathrm{hc}} = 2E_{\mathrm{del}}$) in ethane.

As a validation of the BLW approach, we investigated the delocalization energies estimated using the BLW approach for butadiene, for which experimental data are available for comparison. The computed π-electron delocalization energies of *cis*- and *trans*-butadiene using the BLW method are compared with the resonance energy derived from experimental heats of hydrogenation.[23] The experimental resonance energy is estimated to be $-35.6\,\mathrm{kJ\,mol^{-1}}$,[15] which can be compared with the computed E_{del} values for *cis*- and *trans*- butadiene (Table 2). The agreement is excellent, which suggests that the BLW results can be used to provide further support to the ab initio VB calculation. Interestingly, the difference in conjugation energy between the *s-cis* and *s-trans* configurations of butadiene is only about $5.5\,\mathrm{kJ\,mol^{-1}}$ using both basis sets, which is about one third of the total energy difference ($16.7\,\mathrm{kJ\,mol^{-1}}$) between the two conformers (the experimental value is $16.7\,\mathrm{kJ\,mol^{-1}}$[24]).

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