

# Theoretical Analysis of the Rotational Barrier of Ethane

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Received March 6, 2006

## ABSTRACT

The understanding of the ethane rotation barrier is fundamental for structural theory and the conformational analysis of organic molecules and requires a consistent theoretical model to differentiate the steric and hyperconjugation effects. Due to recently renewed controversies over the barrier's origin, we developed a computational approach to probe the rotation barriers of ethane and its congeners in terms of steric repulsion, hyperconjugative interaction, and electronic and geometric relaxations. Our study reinstated that the conventional steric repulsion overwhelmingly dominates the barriers.

## 1. Perspectives of Current Views on the Origin of the Rotational Barrier in Ethane

The existence of hindered rotation about the carbon–carbon single bond is one of the most fundamental concepts in conformational analysis, and an understanding of its origin is of great interest. Modern quantum mechanical calculations can yield accurate results on relative conformational energies of organic compounds, and quantum chemical theory has provided fundamental insight into the nature of the torsional barrier.<sup>1,2</sup> However, surprisingly, there is still controversy in a seemingly simple problem that is presented in the very beginning of organic chemistry textbooks. A prototypical example is the hindered internal rotation about the C–C bond in ethane, first discovered by K. S. Pitzer in 1936,<sup>3</sup> who showed that only when an internal rotation barrier of about 3 kcal/mol is taken into account could one obtain thermodynamic quantities in agreement with experiment.<sup>4</sup> The controversy is concerned with the origin of the rotational barrier in ethane, whether it is the result of stronger hyperconjugation stabilization of the staggered conformation than the eclipsed form or the torsional barrier originates from greater steric repulsion in the eclipsed

configuration due to electrostatic and Pauli exchange interactions. In this Account, we summarize recent studies that led to a consistent conclusion and present results from our laboratories and others, demonstrating that the internal rotational barrier in ethane is largely due to steric effects with modest contributions from hyperconjugation stabilization.

The intuitive, steric repulsion theory was proposed in the early stages of theoretical chemistry, which remains a popular explanation in organic textbooks.<sup>5</sup> This theory suggests that the preference of the staggered structure of ethane over the eclipsed structure comes from reduced Pauli exchange interactions between the two methyl groups. On the other hand, hyperconjugation stabilization of the staggered conformation in ethane, owing to greater orbital overlap, provides another mechanism.<sup>6–9</sup> Here, the hyperconjugation effect refers to the vicinal interactions between occupied  $\sigma_{\text{CH}}$  bond orbitals of one methyl group and virtual antibonding  $\sigma_{\text{CH}}^*$  orbitals of the other methyl group in ethane. Notably, Mulliken laid out a theoretical strategy to analyze hyperconjugative interactions, but he also cautiously predicted that “hyperconjugation in ethane should have little or no direct effect in restricting free rotation” because it is “only of second order”.<sup>6</sup> Brunck and Weinhold first showed that hyperconjugative interactions could be a dominant force responsible for the rotational barrier in ethane. In that work, they expressed molecular orbitals (MOs) as a linear combination of bond orbitals at the semiempirical level.<sup>10</sup> Subsequently, Bader et al. offered an alternative explanation, in terms of the polarization of charge density in the central carbon–carbon bond as a result of variations in symmetry.<sup>11</sup> On the basis of the natural bond orbital (NBO) method,<sup>12</sup> Goodman et al.<sup>13–15</sup> recently renewed the hyperconjugation idea<sup>10,16</sup> in a series of publications using a “flexing” analysis in terms of energies associated with structural, steric, exchange, and hyperconjugative interactions during methyl rotation. Surprisingly, it was found that steric repulsion favors the eclipsed conformation, when  $\sigma_{\text{CH}} - \sigma_{\text{CH}}^*$  hyperconjugative interactions were removed in the calculation.<sup>17</sup>

The intriguing results of ref 17 triggered additional investigations.<sup>18–20</sup> Bickelhaupt and Baerends evaluated the Pauli and electrostatic interactions explicitly using a zeroth-order wave function constructed from fragment MOs of methyl group. It was concluded that although hyperconjugation favors the staggered ethane conformer, Pauli exchange repulsions are the dominant force responsible for the rotational barrier in ethane.<sup>18</sup> This and subsequent calculations<sup>18–20</sup> suggest that hyperconjugative stabilization was overestimated in ref 17 due to the choice of localized orbitals that were not optimal.<sup>17</sup> However, Weinhold<sup>21</sup> analyzed the overlap contamination effect in these calculations,<sup>18</sup> using a four-electron destabilizing-interaction diagram. In this picture, the molecular orbitals

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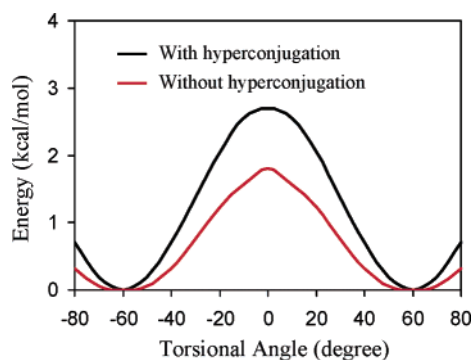
must be the eigenfunctions of a Hermitian Hamiltonian operator and thus should be orthogonal, suggesting that the results of ref 18 may be affected by the use of nonorthogonal fragment MOs. Note that this is a result based on perturbation theory using two unperturbed interacting orbitals (one filled and one unfilled) when the stabilization energy is evaluated. If energies are evaluated on the basis of the overall molecular wave functions, there is no such overlap contamination effect. For example, if a Slater determinant is used to represent the molecular wave function, reorthogonalization of orbitals may change the energies of the individual molecular orbitals as Weinhold pointed out, but it will not alter the expectation energy of the wave function.

Recall that nonorthogonal orbitals have been widely used in ab initio valence bond (VB) theory,<sup>22</sup> which provides a direct approach to examining hyperconjugation and steric effects. We have computed the hyperconjugation energy using ab initio VB method, and our results are in good accord with the findings of Bickelhaupt and Baerends. In particular, although the hyperconjugation effect favors the staggered conformation, its contribution to the rotational barrier is only secondary.<sup>19,20</sup> Recent experimental observations also support the steric repulsion theory for the origin of the torsional barrier in ethane.<sup>23</sup>

Understanding the origin of the rotation barrier in ethane requires the use of a variational method that can provide an adequate definition of the charge-localized, diabatic state to compute hyperconjugation energies. The delocalized nature of molecular orbitals within the current molecular orbital theory makes it difficult to accomplish this goal, whereas post-SCF (self-consistent field) analyses often generate an intermediate wave function that is not variationally optimized for the diabatic state. In this Account, we summarize the results from ab initio VB studies of the internal rotation in ethane. Then, we describe an alternative approach to quantify hyperconjugation and steric effects within molecular orbital theory. In particular, we follow Mulliken's original strategy<sup>6</sup> by assigning the eight electrons involved in hyperconjugative interactions to two sets of methyl group functions *in the absence of hyperconjugation delocalization*. In addition, we design an energy decomposition scheme to obtain various energy terms, including steric repulsion and electronic and geometric relaxations. The computations are based on our recently developed block-localized wave function (BLW) method, which combines the advantages of valence bond and molecular orbital theories.<sup>24–27</sup> Our analyses show that both hyperconjugation stabilization and steric repulsion contribute to the internal rotation in ethane, but the conventional steric effect is the dominant factor.

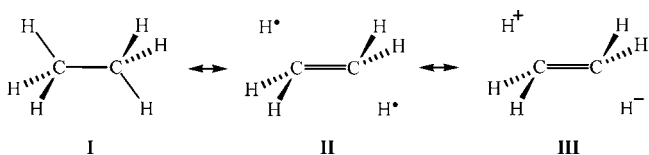
## 2. Methods

**2.1. Hyperconjugative Stabilization in Ethane. 2.1.1. Interpretation from Valence Bond Theory.** In VB theory, a molecular system is described by a set of localized



**FIGURE 1.** Ab initio VB computations of the ethane rotation barriers with the hyperconjugation effect included (black curve) and excluded (red curve).

(Lewis) resonance structures.<sup>28,29</sup> Whereas each resonance structure is expressed by a Heitler–London–Slater–Pauling (HLSP) function, the molecular wave function is a superposition of all possible resonance structures. Consequently, the electron delocalization effect can be uniquely determined “by subtracting the actual energy of the molecule in question from that of the most stable contributing structure”.<sup>30</sup> The remarkable difference between VB and MO theories is that in VB theory all orbitals are nonorthogonal, whereas molecular orbitals are orthogonal in MO theory. Of course, in the extreme of full CI, these two theories are equivalent. For the case of ethane, 1 neutral Lewis structure **I** plus 9 biradical structures **II** and 18 monoionic structures **III** (actually more ionic structures can be written out, but they are either irrelevant to the hyperconjugation effect or insignificant due to very high energies) are sufficient to describe the ground state of ethane.



We constructed the HLSP function ( $\Psi^{\text{Loc}}$ ) for the Lewis structure **I** and the overall molecular wave function ( $\Psi^{\text{Del}}$ ) and quantified the hyperconjugation effect as the energy difference between  $\Psi^{\text{Del}}$  and  $\Psi^{\text{Loc}}$ . We stress here that both the diabatic Lewis structure and the delocalized wave functions are self-consistently optimized in our ab initio VB calculations. Figure 1 shows the torsional energy profiles of both the electron-localized diabatic and electron-delocalized adiabatic states. On the basis of ab initio VB computations (Table 1), we found that the hyperconjugation effect favors the staggered structure but accounts for only about one-third of the total rotation barrier, most of which comes from the steric hindrance (see below).

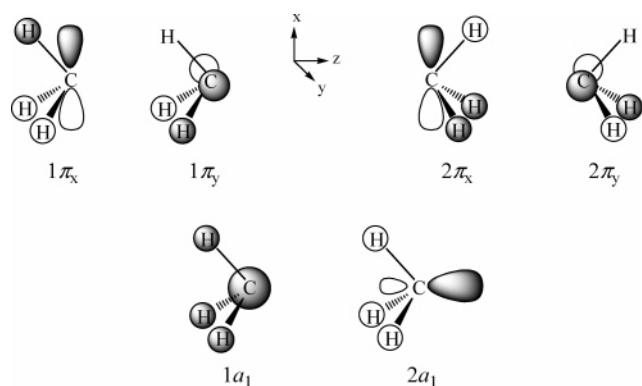
### 2.1.2. Interpretation from Molecular Orbital Theory.

An alternative consideration of hyperconjugation interactions is based on molecular orbital theory, which is the stabilization energy due to charge delocalization from an occupied bonding orbital to a vicinal unoccupied antibonding orbital.<sup>31</sup> In contrast, the steric effect reflects the interactions between neighboring occupied bond orbitals,

**Table 1. Computed Hyperconjugation Energies  $E_{\text{hc}}$  and Contributions ( $\Delta E_{\text{hc}}$ ) to the Ethane Rotation Barrier (kcal/mol) Using ab initio VB Method**

basis set	conformation	$E(\Psi^{\text{Loc}})$ (au)	$E(\Psi^{\text{Del}})$ (au)	$E_{\text{hc}}$	$\Delta E_{\text{hc}}$
6-31G(d) <sup>a</sup>	staggered	-79.32024	-79.33811	-11.21	0.91
	eclipsed	-79.31737	-79.33379	-10.30	
6-311G(d,p) <sup>b</sup>	staggered	-79.33900	-79.35988	-13.10	0.98
	eclipsed	-79.33611	-79.35543	-12.12	

<sup>a</sup> Hartree–Fock energies for the staggered and eclipsed conformations are -79.22876 and -79.22400 au, respectively. <sup>b</sup> Hartree–Fock energies for the staggered and eclipsed conformations are -79.25179 and -79.24690 au, respectively.



**FIGURE 2.** e- and a-symmetric group orbitals of methyl groups in ethane.  $1\pi_x$  and  $1\pi_y$  orbitals are degenerate and occupied, whereas the degenerate  $2\pi_x$  and  $2\pi_y$  orbitals are unoccupied. For a orbitals,  $1a_1$  is doubly occupied and  $2a_1$  is singly occupied and responsible for the formation of the C–C  $\sigma$  bond.

which generally consist of classical electrostatic and quantum mechanical Pauli exchange repulsion. Since hyperconjugation and steric effects coexist in ethane, a plausible approach to differentiate these two conflicting effects is to deactivate the stabilizing hyperconjugative interaction and probe the subsequent rotational barrier that is solely associated with the steric interaction. We make this separation because the contribution from hyperconjugation interactions to the torsional barrier is of second order<sup>6</sup> and thus the coupling between the hyperconjugative and steric interactions is expected to be small.

We consider the interaction between two methyl groups of  $C_{3v}$  symmetry. Occupied molecular orbitals in a tetrahedral group are categorized into two types of irreducible bases, fully symmetric  $a_1$  and degenerate  $e$  (denoted as  $\pi_x$  and  $\pi_y$  hereafter). Only e-symmetric orbitals are relevant to the barrier as orbitals of a symmetry are invariant with the rotation. Each methyl group has two occupied degenerate  $1\pi_x$  and  $1\pi_y$  orbitals and two unoccupied  $2\pi_x$  and  $2\pi_y$  orbitals as depicted in Figure 2. Whereas the interaction between the occupied e orbitals in one methyl group ( $1\pi'$  or  $1\pi''$ ) and unoccupied e orbitals in the other methyl group ( $2\pi''$  or  $2\pi'$ ) stabilize the system (Figure 3a), the interaction between the occupied e orbitals in the two groups leads to the destabilization of the system (Figure 3b). The attractive interaction is referred to as a  $\sigma_{\text{CH}}-\sigma_{\text{CH}}^*$  interaction, or the vicinal hyperconjugation, which is a focus of recent interest.<sup>17–19,21</sup> The latter destabilizing interaction is the

steric repulsion, which is a combination of the Pauli repulsion and electrostatic interaction. In the orbital interaction diagrams in Figure 3a,b, we maintain the nonorthogonality between the orbitals from different methyl groups such as  $1\pi'$  and  $1\pi''$ . Note that orthogonalization of these orbitals will split the two interacting degenerate orbitals, but it will not vary the molecular wave function and its energy.

For generality, we maintain the  $C_{3v}$  symmetry for ethane as  $C_{3v}$  is the common sub point group of  $D_{3d}$  for the staggered structure and  $D_{3h}$  for the eclipsed structure of ethane. The molecular wave function for ethane (adiabatic state) can be written as

$$\Psi = \hat{A}(1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 1e^4 2e^4) \quad (1)$$

where  $1a_1$  and  $2a_1$  are core orbitals of carbon atoms,  $3a_1$  and  $4a_1$  are MOs primarily composed of the two 2s atomic orbitals of carbons (see  $1a_1$  for methyl groups in Figure 2), and  $5a_1$  corresponds to the C–C  $\sigma$  bond (by  $2a_1$  in Figure 2). We emphasize here that the two pairs of degenerate molecular orbitals  $1e$  and  $2e$  in eq 1 include both the hyperconjugative and steric interactions as shown in Figure 3c. If we deactivate the hyperconjugation effect and consider the steric effect only, the subsequent diabatic state or the localized Lewis structure can be expressed by the following BLW:<sup>24–26</sup>

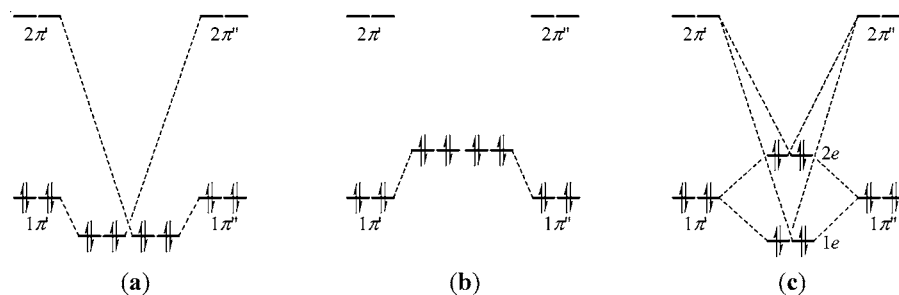
$$\Phi_L = \hat{A}(1a_1^2 2a_1^2 3a_1^2 4a_1^2 5a_1^2 1\pi'^4 1\pi''^4) \quad (2)$$

The significant difference between  $\Psi$  and  $\Phi_L$  lies in the e-symmetric orbitals. In  $\Psi$ , the two e orbitals are molecular orbitals delocalized to the entire molecule, whereas, in  $\Phi_L$ , the orbitals  $1\pi'$  and  $2\pi''$  are localized orbitals confined to only each of the two methyl groups as Mulliken initially suggested (Figure 3).<sup>6</sup> In our BLW calculations, both  $\Psi$  and  $\Phi_L$  are optimized variationally, and the energy difference between the two wave functions  $\Psi$  and  $\Phi_L$  yields the hyperconjugative stabilization depicted in Figure 3a:

$$E_{\text{hc}} = E(\Psi) - E(\Phi_L) \quad (3)$$

Note that by adopting the functional-group-localized orbitals, geminal hyperconjugation within a methyl group is completely retained in  $\Phi_L$  and the stabilizing hyperconjugation energy solely comes from the vicinal hyperconjugation between the two methyl groups. For comparison, in our ab initio VB calculations,<sup>19</sup> the hyperconjugation energies listed in Table 1 contain contributions both from the geminal bonding–antibonding interactions within each methyl group and from interactions between each methyl group and the CC orbitals.<sup>10,16</sup> Although these geminal interactions remain constant with respect to the internal rotation if the molecular geometry is kept the same, hyperconjugation energies in Table 1 are exaggerated compared with the values from the BLW calculations in this section (see below).

**2.2. Steric Repulsion in Ethane.** The rotational barrier in ethane has two main contributing factors, the attractive



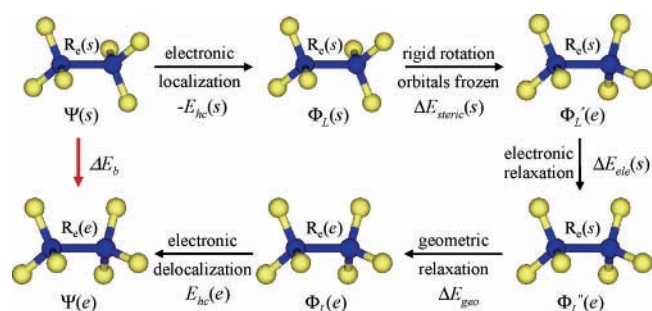
**FIGURE 3.** Orbital interactions in ethane: (a) hyperconjugative interaction; (b) steric interaction; (c) overall interactions.

electronic effect (hyperconjugation) and the repulsive steric effect. Consequently, it is possible to estimate the magnitude of the steric effects by subtracting the hyperconjugation energy from the overall rotation barrier. However, it is desirable to determine the steric energy directly without it being affected by the uncertainty in the computed hyperconjugation energies. It has been proposed that structural factors may affect the individual energy components in that the symmetry-induced polarization increases the carbon–carbon bond length, leading to a decrease in the attractive interactions in ethane.<sup>11</sup> Moreover, Goodman et al. showed that the interpretation of the barrier was influenced by the slight change of the central CC bond distance. In other words, although rigid rotations and relaxed rotations have very similar barriers, the contributions from hyperconjugation stabilization and steric repulsion could be different.<sup>17,32,33</sup> Thus, the ability to calculate the hyperconjugative and steric interaction energies separately is essential to further explore the effects of structural relaxation (flexing) and electronic relaxation (polarization) of the central CC bond.

We propose an algorithm to probe the “pure” steric effect by freezing the occupied group orbitals  $1\pi$  and  $1\pi'$  during the rotation when the hyperconjugation effect is deactivated.<sup>19,20</sup> The procedure is as follows. First, we use the optimized structure of the staggered configuration to generate the optimal localized function  $\Phi_L$ . Second, we freeze all orbitals in  $\Phi_L$  and all geometrical parameters except the torsional angle, which is rotated by  $60^\circ$  to the eclipsed conformation. Then, we compute the energy using these frozen orbitals without further optimization. In this step, a Jacobian  $2 \times 2$  matrix transformation is applied to the p and d orbitals of the rotated methyl group. Finally, we assign the energy difference due to the above rigid rotation as the steric effect since in this procedure all orbitals are frozen and there are no electronic or structural relaxations. The computed steric energy is thus purely due to the Pauli exchange repulsion and Coulombic electrostatic interaction. Similarly, we can compute the steric effect as ethane undergoes either rigid or relaxed changes from the eclipsed to the staggered structure.

### 3. Decomposition of the Ethane Rotation Barrier

Using the methods for computing hyperconjugative and steric interactions, we further propose a stepwise decom-



**FIGURE 4.** A decomposition scheme to explore the nature of rotation barriers in ethane and its congeners.

position scheme to analyze the origin of the rotation barrier in ethane (Figure 4). The decomposition procedure<sup>20</sup> starts from the optimal geometry of the staggered structure with an adiabatic wave function  $\Psi(s)$ . Here, we use “s” and “e” in parentheses to specify the geometry of ethane in the optimized staggered and eclipsed configuration, respectively. First, deactivation of the hyperconjugation effect leads to a diabatic state described by the wave function  $\Phi_L(s)$ . The energy change corresponds to the loss of hyperconjugative energy,  $-E_{hc}(s)$ , at the staggered geometry. Then, the methyl groups are brought to the eclipsed conformation by rigid rotation (i.e., without alteration of bond lengths and bond angles). In this step, all orbitals of the wave function  $\Phi_L(s)$  are kept unchanged, and the wave function at the eclipsed conformation is denoted by  $\Phi_L'(e)$ . The energy change,  $\Delta E_{steric}(s)$ , solely comes from the steric repulsion, in which the CC distance is fixed at the value of the staggered conformation. In the third step, we relax the electron density in the rigid eclipsed diabatic state by optimizing all orbitals, resulting in the molecular wave function  $\Phi_L''(e)$  along with the electronic relaxation energy  $\Delta E_{ele}(s)$  (Figure 4). Step four involves geometric relaxation to the optimal eclipsed structure, which results in the lengthening of the carbon–carbon bond, and reoptimization of the localized diabatic wave function at the eclipsed geometry,  $\Phi_L(e)$ . The accompanying energy change,  $\Delta E_{geo}$ , is related to the change of the molecular geometry from the staggered to the eclipsed configuration. Finally, we allow the electrons to delocalize in the entire molecule, which is the gain in hyperconjugation energy in the eclipsed structure,  $E_{hc}(e)$ . Overall, the rotation barrier ( $\Delta E_b$ ) is the sum of the contributions from hyperconjugation ( $\Delta E_{hc}$ ), steric repulsion ( $\Delta E_{steric}(s)$ ), electronic re-

**Table 2. Energy Analyses of the Rotation Barriers from Staggered Structures to Eclipsed Structures (kcal/mol)**

molecule	basis set	$\Delta E_{\text{hc}}$	$\Delta E_{\text{steric}(s)}$	$\Delta E_{\text{ele}(s)}$	$\Delta E_{\text{geo}}$	$\Delta E_{\text{b}}$
ethane	6-31G(d)	0.76	2.73	-0.01	-0.50	2.98
CH <sub>3</sub> CH <sub>3</sub>	6-311+G(d,p)	0.76	2.87	-0.03	-0.54	3.06
disilane	6-31G(d)	0.30	0.71	0.00	-0.06	0.95
SiH <sub>3</sub> SiH <sub>3</sub>	6-311+G(d,p)	0.26	0.77	-0.01	-0.04	0.98
digermane	6-31G(d)	0.09	0.78	-0.01	-0.05	0.81
GeH <sub>3</sub> GeH <sub>3</sub>	6-311+G(d,p)	0.14	0.67	0.00	-0.08	0.73
methylsilane	6-31G(d)	0.38	1.16	-0.01	-0.13	1.40
CH <sub>3</sub> SiH <sub>3</sub>	6-311+G(d,p)	0.37	1.27	-0.02	-0.16	1.46

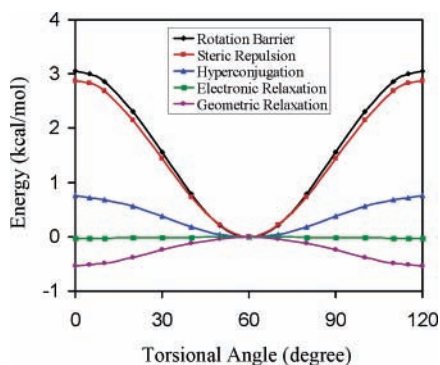
laxation ( $\Delta E_{\text{ele}(s)}$ ), and geometric relaxation ( $\Delta E_{\text{geo}}$ ) terms:

$$\Delta E_{\text{b}} = \Delta E_{\text{hc}} + \Delta E_{\text{steric}(s)} + \Delta E_{\text{ele}(s)} + \Delta E_{\text{geo}} \quad (4)$$

where  $\Delta E_{\text{hc}} = E_{\text{hc}(e)} - E_{\text{hc}(s)}$ .

Table 2 lists the computed energy contributions to the rotational barriers of ethane, disilane, digermane, and methylsilane (a complete survey of all group 14 ethane congeners using the NBO method can be found in ref 34). In all cases, we found that electronic relaxation causes minimal energy changes in the rotation, while geometric variation, which lengthens the central bonds from staggered to eclipsed structures, slightly stabilizes the systems, notably in ethane. This indicates that a small central bond perturbation in the rotation can make a modest energy variation to the rotation barrier; however, this does not affect the discussion of factors contributing to the torsional barrier. In Table 2, the dominant contribution to the overall rotational barrier is the steric term, and the rigid rotation and relaxed rotation have the same mechanism. The hyperconjugative interaction favors staggered structures, but its magnitude is no more than 30% of the total rotation barriers in all cases. Figure 5 illustrates the changes of various energy terms with respect to the torsional angle in ethane. Interestingly, the geometric relaxation and hyperconjugative interaction have opposite effects, and they mostly cancel out. Consequently, the steric repulsion curve is very close to that of the total rotation barrier.

It should be noted that the geometric relaxation is a combined structural response to both the steric repulsion and hyperconjugative attraction, although it is often regarded as part of the steric effect as the repulsive force is much stronger than the attractive force. If we analyze



**FIGURE 5.** Rotation barrier along with the steric repulsion, hyperconjugation, electronic relaxation, and geometric relaxation energy changes with respect to the torsional angle.

**Table 3. Computed Hyperconjugation Energies in Ethane and Propene Based on the NBO and BLW Methods (kcal/mol)**

method	basis set	ethane		propene	
		$E_{\text{hc}(e)}$	$E_{\text{hc}(s)}$	$\Delta E_{\text{hc}}$	$E_{\text{hc}}$
NBO1	6-31G(d)	-15.2	-20.9	6.1	-15.5
	6-311+G(d,p)	-17.3	-23.8	6.9	-15.4
NBO2	6-31G(d)	-15.9	-22.0	5.7	-18.3
	6-311+G(d,p)	-15.6	-22.5	6.5	-18.9
BLW	6-31G(d)	-5.6	-6.4	0.8	-5.0
	6-311+G(d,p)	-6.6	-7.3	0.7	-5.9

the energy components, starting from the eclipsed configuration to obtain the steric and geometrical energies,  $\Delta E_{\text{steric}(e)}$  and  $\Delta E_{\text{geo}}$ , we observe a slight reduction of both terms, with their sum unchanged. Thus, the conclusions are not affected by the sequence of the decomposition scheme in Figure 4.

Experimental support for the proposal that steric effects dominate the torsional barrier in ethane was provided by the elegant experiment designed by Bohn,<sup>23</sup> who determined the microwave spectra of 3-hexyne, in which the presence of the triple bond essentially eliminated steric effects. Hyperconjugation is dependent on the orbital symmetry, which would still stabilize the *trans* conformation if it were indeed the primary factor of conformational preference. Yet, the observed structure has a *cis* conformation between the two terminal methyl groups due to the long-range dispersion attraction interactions.

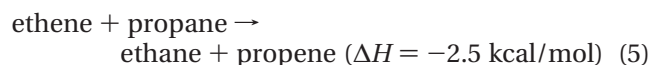
#### 4. Comparison Between BLW and NBO Results

We have compared the results obtained from analyses using the NBO and BLW methods as well as from relevant experimental data. In the NBO method, hyperconjugation energies can be computed by deleting either off-diagonal elements (NBO1) or antibonding orbitals (NBO2). Table 3 lists the computed hyperconjugation stabilization energies for ethane and propene.<sup>35</sup> Previously, Reed and Weinhold derived vicinal delocalization energies of -27.7 and -23.0 kcal/mol for the staggered and eclipsed ethane using the 6-31G(d) basis set, in reasonable agreement with the data listed in Table 3.<sup>16</sup>

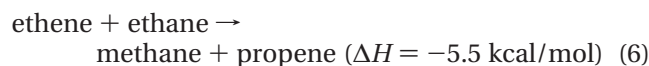
Both the NBO and BLW methods yield consistent results with different basis sets. The main difference between the two computational methods is that the BLW hyperconjugation energies are smaller than those obtained using the NBO analysis. If we equally divide the total hyperconjugation energy among the six principal pairs of  $\sigma_{\text{CH}}-\sigma_{\text{CH}}^*$  in ethane, each  $\sigma_{\text{CH}}-\sigma_{\text{CH}}^*$  hyperconjugative interaction stabilizes ethane by about 0.9–1.2 kcal/mol from the BLW calculation, whereas it is 2.5–4.0 kcal/mol from the NBO analysis. Since the charge-delocalized states of the staggered and eclipsed conformations are treated exactly the same in both the NBO and BLW calculations, the difference in the two results is from the calculation of the energies of the charge-localized states. In the NBO analysis, the computational procedure involves deletion of the relevant antibonding orbitals,<sup>12,35</sup> while the occupied orbitals remain the same as they are optimized in the presence of the deleted orbitals. In the BLW calculation,

the diabatic state is defined by construction of an effective localized wave function, which is further variationally optimized. This leads to the lowering of the energy of the diabatic (charge-localized) state and a smaller delocalization energy.

Although there are no direct experimental data for comparison, it is possible to consider the first-order hyperconjugation effect in propene, which can be measured at least indirectly. The first approach is to use the difference between the heats of hydrogenation for propene and ethene as an estimate of the hyperconjugation effect in the propene.<sup>36–38</sup>



However, recent studies reveal that propane can be stabilized by about the same amount due to the “proto-branching” effect, which does not exist in the other three molecules in eq 5.<sup>39</sup> Thus, an alternative approach is to evaluate the hyperconjugation energy in propene by the following reaction:<sup>40</sup>



On the basis of eq 6, the hyperconjugative interaction between the methyl group and the double bond in propene stabilizes the system by about 5.5 kcal/mol. This “experimental” evaluation is in agreement with the BLW results of 5.0–5.9 kcal/mol (Table 3).

## 5. Conclusions

Computational studies from different analysis schemes have identified two dominant contributing factors responsible for the internal rotational barrier in ethane. The first is the hyperconjugation interactions due to the charge delocalization from the occupied  $\sigma_{\text{CH}}$  orbitals of one methyl group into the antibonding  $\sigma_{\text{CH}}^*$  orbitals of the other methyl group. At the staggered conformation, the bonding and antibonding orbitals have the optimal overlap, and thus, hyperconjugation interactions stabilize the staggered conformation more than the eclipsed conformation. The second contributing factor is the steric repulsion due to both classical electrostatic and quantum mechanical Pauli exchange interactions between the vicinal CH bonds. Steric effects are strongest in the eclipsed conformer because of a greater orbital overlap between the occupied  $\sigma_{\text{CH}}$  orbitals, destabilizing it more than the staggered conformation. In some analyses, it was found that the hyperconjugation effects are dominant,<sup>13–17</sup> leading to the conclusion that stabilization of the staggered conformation is responsible for the rotational barrier in ethane. In other studies, it was proposed that the steric repulsion is the critical force that causes the hindered rotation.<sup>18,19</sup> Our study and those by Bickelhaupt and Baerends<sup>18</sup> showed that it is important to generate optimal diabatic state wave functions in energy decomposition analysis. Using ab initio valence bond and molecular orbital theory,<sup>20</sup> we found that although the hyperconju-

gation effect favors the staggered structure, the steric repulsion nevertheless dominates the rotation barriers of ethane and its analogs, consistent with conventional interpretations.

*This work has been supported by the Western Michigan University (Y.M.) and the National Institutes of Health (J.G., Y.M.).*

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AR068073W