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A Critical Analysis on the Rotation Barriers in Butane

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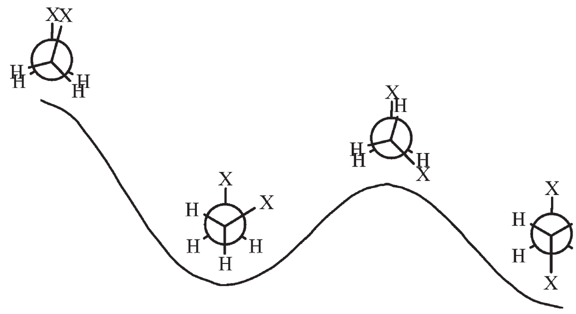

As a textbook prototype for the introduction of steric hindrance in organic chemistry, the elucidation of the butane rotation barriers is fundamental for structural theory, and requires a consistent theoretical model to differentiate the steric and electronic effects. Here we employed the BLW method to probe the electronic (hyperconjugative) interactions. Results show that although there are stronger hyperconjugative interactions in the staggered anti and gauche conformers than the eclipsed structures, the energy curve and barriers are dominated by the steric repulsion.

One key to the computer simulations of macromolecules such as polymers and proteins is the quality of force fields where the potential energy of a system is expressed as a sum of bonded and nonbonded energy terms. Among these terms the torsional potential functions are of particular significance as the energy variations in terms of torsional angles are usually small and can be easily overcome at ambient conditions. For instance, saturated alkanes exhibit low barriers (3−10 kcal/mol) to rotations about single C−C bonds with preference for trans−gauche conformers. As a consequence, minima corresponding to various torsional angles can transform to each other at extremely high rates.[1] As rotations around C−C bonds in alkanes have important consequences in molecular structure and dynamics, the understanding of rotational barriers is central to conformational chemistry and the proper mathematical description of torsional potentials is fundamental to the development of force fields to obtain an accurate representation of three-dimensional structures of macromolecules.[2,3] It has been shown that changes to the torsional potentials can severely affect the accuracy of force fields.[3,4] Of particular relevance to the torsional potential is the reproduction and prediction of phase behavior of chemicals such as alkanes.[5] At the molecular mechanical level, the torsional potential function is usually expanded in a Fourier series.[6]

Quantum mechanically, however, as rotations do not involve any bond making or breaking, the corresponding barriers can be derived fairly accurately even at quite low levels, largely due to the comparability of the electron correlation effect on isomers of the same molecule.[7] While both experiments and theories can produce comparable values for rotation barriers, fundamental insights into the nature of torsional barriers can only be gleaned with approximated computational approaches. But we note that the decomposed contributions to the overall barriers are not experimentally measurable and can only be scrutinized by indirect experimental proofs and theoretical rationales. As such, controversies linger over the origin of torsional barriers, which is a seemingly simple but enormously significant problem.[8−13]

Butane is a textbook prototype for the introduction of steric hindrance in organic chemistry. As rotational barriers are highly sensitive to the local chemical structure of focused C−C bonds, based on the relative positions of two terminal methyl groups, there are two different staggered conformers with respect to the central C−C bond, one is the anti conformer and the other is the gauche conformer, in addition to two different eclipsed conformers with either H/CH_3 or CH_3/CH_3 eclipsed, as shown in Scheme 1 ($X = CH_3$). Both staggered conformers are minima at the energy profile, thus the continuing rotation around the central C−C bond starting from the anti conformer experiences two successive barriers of 3.3 and 5.1−5.5 kcal/mol, respectively.[14,15] The

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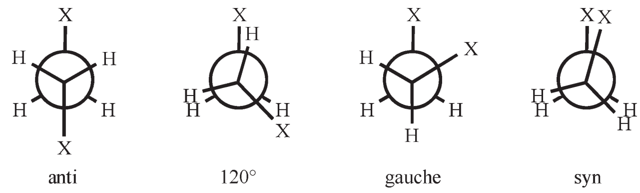
SCHEME 1



rotation about the central C−C bond of butane is of general interest as it is a prototype for studying longer alkane chains. Specifically, the differentiation of the electronic and steric contributions to conformational isomerism is essential for the development of force fields, as there is no rigid and generally accepted approach to measure the effects either experimentally or computationally.[10,16] Most recently, Cormanich and Freitas calculated the potential energy surfaces for the relaxed and rigid (with bond distances and angles frozen) rotations, and concluded that the steric repulsion between methyl groups is the important effect defining the relative conformational energies.[17]

Rotation barriers are influenced by a few factors which can be generalized as stabilizing hyperconjugation (more broadly electron delocalization, which includes conjugation) and repulsive steric effects. Hyperconjugation is an electronic effect and concerns charge transfer from an occupied bond orbital to a vicinal unoccupied antibond orbital, while steric effect reflects the interaction between neighboring occupied bond orbitals, which generally comprises the classical electrostatic (or local dipole−dipole interaction) term and the quantum mechanical Pauli exchange repulsion. A plausible approach to distinguish the hyperconjugative effect and the steric effect is to deactivate the electron transfer among bond orbitals and the subsequent rotation barrier is presumed to be wholly ascribed to the steric interactions. This is due to the usually small magnitude of the hyperconjugative interactions, which is in accord with the conventional understanding that electrons in alkanes are relatively localized, and thus there is little coupling between the hyperconjugative and steric interactions. In other words, the rotation barrier is assumed to be composed of the hyperconjugative and steric contributions.

In VB theory,[18,19] an electron-localized (resonance) state can be defined by the Heitler−London−Slater−Pauling (HLSP) wave function where each bond is formed by two nonequivalent localized orbitals. The BLW method,[20,21] however, can be regarded as the simplest variant of the VB theory as it similarly adopts localized orbitals but allows them to be doubly occupied. In this way, the computational cost is greatly reduced but the characteristics (localization and nonorthogonality of orbitals) of the VB theory are retained. Using the BLW method, we can define a wave function for the electron-localized Lewis structure of butane as

$$\Phi_L = \hat{A}\left\{\prod_{i=1}^{4} K_C^2(i)\prod_{j=1}^{10}\sigma_{CH}^2(j)\prod_{k=1}^{3}\sigma_{CC}^2(k)\right\} \qquad (1)$$

where K refers to carbon core orbitals and σ_{CH} denotes a doubly occupied C−H bond orbital that is expanded with the basis functions of only the bonding C and H atoms. Similarly, σ_{CC} corresponds to a C−C single bond orbital expanded with the bases on two bonding carbon atoms. Apparently, due to the expansion constraints, all these bond orbitals are nonorthogonal. The removal of the restraint of limited expansion on these bond orbitals results in the familiar Hartree−Fock (HF) wave function Ψ corresponding to an electron-delocalized state. The energy difference between Φ_L and Ψ is generally defined as the electron delocalization energy (DE)

$$\mathrm{DE} = E(\Phi_L) - E(\Psi) \qquad (2)$$

which in the current case of butane involves not only the hyperconjugative interactions among C−H and C−C bonds, but also the geminal interactions among the C−H bonds sharing common apex carbon atoms.[22] The hyperconjugative and geminal interactions occur simultaneously, but generally the latter is a little stronger and conserved among different conformers, as proved in the case of ethane.[13] Similar procedures have been extensively applied to the studies of the dual property of the π electrons in benzene by Shaik et al.,[23] the π-electron conjugation in carboxylic acids and enols by Hiberty and co-worker,[24] conjugative and hyperconjugative stabilization in diynes, dienes, and related compounds by Frenking and co-workers,[25] and hyperconjugative interaction in ethane and the π aromatic energy in benzene and many other systems by us and others.[11−13,26] We also note that the NBO method defines the Lewis structure in the same way, but the bond orbitals are projected from the delocalized wave function and thus nonoptimal.

In this Note, geometries of butane at various dihedral angles of $\varphi = \angle$C−C−C−C were optimized at the MP2/6-31G(d) level with Gaussian,[27] and the subsequent BLW computations were carried out with XMVB.[19] Compared with ethane, butane exhibits a remarkably different rotational energy profile about the central C−C bond due to the two substituted methyl groups. Figure 1 shows the consistent torsional energy profiles with the basis set of 6-31G(d) at the MP2 and HF levels. Starting from the anti conformer (φ = 180°), the approaching of the two methyl groups is accompanied by two nonequivalent barriers, which are 3.6 or 3.7 and 5.3 or 5.4 kcal/mol at the MP2 or HF level. These data

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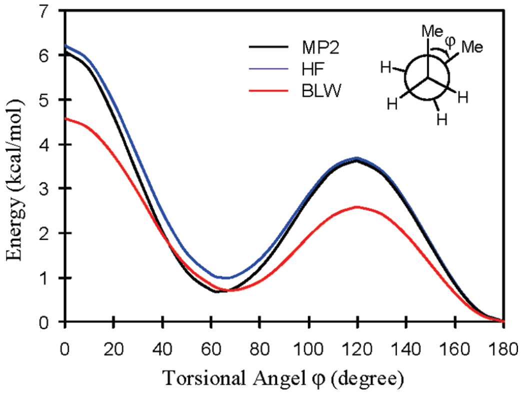

FIGURE 1. Rotational potential energy profiles for butane around the central C−C bond with the MP2, HF, and BLW and the 6-31G(d) basis set.

TABLE 1. Electron Delocalization Energies in the Key Rotamers of Butane

energy	anti	120°	gauche	syn
E(HF) (au)	−157.29789	−157.29202	−157.29630	−157.28799
E(BLW) (au)	−157.25092	−157.24682	−157.24974	−157.24364
DE (kcal/mol)	29.47	28.36	29.22	27.83

TABLE 2. Electron Delocalization Energies in Simple Linear Alkanes C_nH_{2n+2} Based on the BLW (kcal/mol)

system	DE	*n*
CH_4	2.52	1
C_2H_6	11.62	2
C_3H_8	20.55	3
C_4H_{10}	29.47	4

are only slightly different from the very accurate G2 results od 3.3 and 5.1 kcal/mol[14] or the Schrödinger limits in the Born−Oppenheimer approximation of 3.31 and 5.51 kcal/mol,[15] once again indicating the insensitivity of rotational barriers in alkanes to the theoretical level used in calculations. It should be noted that all theoretical studies have resulted in a much higher energy difference between the syn ($\varphi = 0°$) and anti conformers than the experimental estimate (3.78 kcal/mol[28]). Unlike other 1,2-disubstituted ethanes with polar groups, the gauche conformer ($\varphi \approx 60°$) of butane is slightly destabilized by less than 1 kcal/mol compared with the anti conformer. Intuitively, the much larger size of the methyl group than the hydrogen atom invokes the steric repulsion model, as the barrier gets high with the approaching of the two terminal methyl groups. This is verified by our BLW computations for the Lewis structure, which slightly lower the rotation barriers to 2.6 and 3.8 kcal/mol, but do not change the shape of the torsional energy curve (in red), as also shown in Figure 1. The comparison between the HF and BLW curves indicated that the anti structure is more stable than the gauche structure by a similar amount of energy, thus in both structures the hyperconjugative interactions are of comparable strengths. The reduced barriers, however, highlight the fact there are stronger hyperconjugative interactions in staggered structures than eclipsed structures, though the steric effect still plays a dominant role in the barriers. We note that recently Liu et al. quantified the steric effect within the DFT theory and showed that an eclipsed conformer has a larger steric energy than a staggered conformer,[29] and this is in accord with the present BLW analysis. In essence, our findings are identical with those in ethane,[9,11,13] i.e., the steric effect dominates the rotational barriers in butane, while the hyperconjugation effect plays a secondary role and contributes about 25% to the barriers. Table 1 listed the absolute energies for the electron-delocalized and electron-localized states as well as the corresponding delocalization energies defined in eq 2 for the four key rotational isomers of butane.

As the delocalization energy in Table 1 is contributed by both the vicinal hyperconjugative and geminal interactions,[22] it would be ideal to differentiate these two types of interactions. The strict separation, however, seems only available for ethane based on the Mulliken strategy which we realized in 2007.[13] But if we assume that the overall delocalization energy in the all-trans structure of a linear alkane C_nH_{2n+2} is a sum of individual geminal and hyperconjugative interactions, we can express the DE as

$$\mathrm{DE} = na + (n-1)b \qquad (3)$$

where *a* refers to the geminal interaction energy for each apex carbon atom, and *b* is the hyperconjugative interaction energy between two methyl or methylene groups. Table 2 lists the delocalization energies in methane, ethane, propane and butane. A fitting to eq 2 shows an excellent correlation (R = 1.0) and $a = 2.6$ kcal/mol and $b = 6.4$ kcal/mol. Note that our explicit evaluation for the hyperconjugation energy in the staggered structure of ethane is just 6.4 kcal/mol.[13] This together with the perfect correlation coefficient prove the addictiveness of the individual energy terms. By removing the geminal energy term, we thus can derive the hyperconjugation energies in the four torsional isomers of butane as 19.5, 18.4, 19.2, and 17.8 kcal/mol, respectively.

Extensive research on the anti/gauche energetics of butane has been conducted both experimentally[28,30,31] and computationally.[14,15,32] The experimental value for the energy of the gauche form relative to the anti conformer is 0.69 ± 0.10 kcal/mol.[31] Again, the exploration of the nature of

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rotational barriers is important for the rational parametrization of force fields. In molecular mechanics,[6,33,34] a popular expression for the torsional potential energy is

$$V(\varphi) = \frac{V_1}{2}(1+\cos\varphi) + \frac{V_2}{2}(1-\cos 2\varphi) + \frac{V_3}{2}(1+\cos 3\varphi) \qquad (4)$$

where the first-order torsional constant V_1 is related to dipole−dipole interactions, the second one V_2 is associated with the planarity of unsaturated systems and hyperconjugation in alkanes, and V_3 can be considered as steric repulsion.[35] While it is clear that both the steric and electronic effects contribute to the torsional energy, the relative weights differ among different versions of force fields. For example, the values of V_1, V_2, and V_3 vary from 0.20, 0.27, and 0.093 in MM2[36] to 0.185, 0.170, and 0.520 in MM3[34] to 0.239, 0.024, and 0.637 in the most recent MM4.[33] The capability of the BLW method in dividing up the energetics of the torsional energy can be especially helpful for the justification of force fields. In our BLW analysis, however, the electrostatic interaction has been implied into the steric energy. Thus, both the first and third terms in eq 4 refer to the steric effect, while the second term corresponds to the hyperconjugative contribution in the butane torsional potential energy. As for the energy difference between the anti and gauche conformers, Table 1 shows that the steric and hyperconjugative interactions contribute approximately 75% and 25%. This is actually identical with our previous findings in the rotational barriers in ethane and its analogues derived with the same BLW procedure, where we also confirmed that the electron correlation plays a trivial role for the energy analysis among rotamers of the same system.[13] Peculiarly, if we scale the HF curve in Figure 1 by a factor of 75%, it will nearly overlap with the BLW curve. The implication is that the relative contributions from the steric and hyperconjugative interactions are almost unchanged along the whole torsional process. In other words, they are not linearly independent. This may explain the large variations of V_1, V_2, and V_3 parameters from MM2 to MM4.

In summary, to probe the exact role of hyperconjugation effect in butane, we employed the block-localized wave function (BLW) method,[13,20] which is the simplest variant of valence bond (VB) theory, to explicitly derive the optimal wave function for the Lewis structure of butane where all electrons are strictly localized on their respective bonds and any electron delocalization is turned off. By comparing the torsional potential energy profiles for the hypothetical electron-localized Lewis structure (corresponding to the most stable resonance structure in terms of resonance theory) and the real electron-delocalized butane, we are able to divide up the energetics of the system in terms of steric and electronic effects, and conclude that the hyperconjugative interactions play a secondary role and the conventional steric repulsion dominates the energy curve and barriers in butane.

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Supporting Information Available: Cartesian coordinates and absolute energies for all optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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