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A Theoretical View on the Conformer Stabilization of Butane

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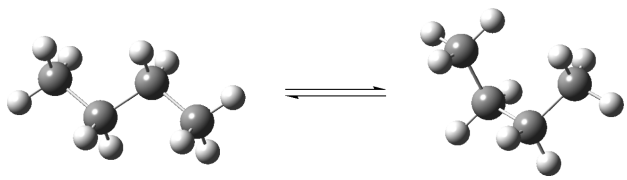

The rotational barrier and conformer energies of butane are well-known, but the contributing effects to its conformational isomerism are still unclear. Calculated potential energy surfaces for the relaxed and vertical (bond distances and angles frozen) structures, together with NBO analysis, suggest that approaching or distancing methyl groups involve substantial energy costs between the *gauche* and *anti* isomers, while hyperconjugative interactions play an important, but not prevalent, role for the conformational isomerism of butane.

Butane is a classical system that undergoes rotational isomerization around C−C chemical bonds. The rotational barriers, as well as the energies of the stable rotamers *gauche* and *anti*, have been extensively studied in both the gas and liquid phases.[1−5] However, the governing effects ruling the rotamer stabilization have been shown to be difficult to measure and estimate. For ethane, a basic model for modern chemical reaction kinetic theory and molecular dynamics, some controversy and no general consensus remain about the origins of the internal rotation barrier between the eclipsed and staggered conformers.[6−9] For butane, discussion on this issue is more scarce, and the amount of contributions from classical (steric and electrostatic) and quantum (hyperconjugation) effects has been complicated to understand and dissected into energy components.[9] Butane is a textbook example when introducing the concept of steric hindrance in organic chemistry. Therefore, it is a suitable model to study the real interactions governing rotational isomerisms.

The effect of stretching bonds and bending bond angles in methylcyclohexane and methylheterocyclohexanes, making bulky groups closer to each other or not, has demonstrated that steric hindrance does not play an important role in the *equatorial−axial* isomerization; hyperconjugative interactions have been invoked instead.[10] This approach may provide important insights on the nature of dynamics for butane, and is not limited to natural bond orbital (NBO) predictions, which is supposed to overestimate interactions in ethane and other systems.[8,11] Preliminary NBO analyses for butane suggest that the energy differences between the stable conformers are similar in magnitude to the *anti* stabilization due to hyperconjugation.[12] 1,2-Disubstituted ethanes experience the *gauche* effect, a hyperconjugative effect understood as the tendency to keep electronegative groups close (*gauche*) in an ethane fragment.[13,14] This effect does not take place in butane, since there are no polar groups in this molecule.

Therefore, torsional curves were computed for butane at the B3LYP/aug-cc-pVTZ level, considering both the fully relaxed structure and those with a central C−C bond and/or C−C−C bond angles frozen, in order to find the energetic costs of approaching or distancing methyl groups from each other. This approach may be compared to NBO analysis (or supported by its trends), in order to enable us to give a robust explanation of the relevant effects governing the rotational isomerism of butane. Each point of the torsional curves with all hyperconjugative interactions removed was computed by using the NBODEL/NOSTAR keyword.[15]

The equilibrium C_2-C_3 distance in butane was calculated to be 1.53 Å. The effect of lengthening and shortening this distance by 0.1 Å was investigated (Figure 1a); in all cases, the *anti* conformer remains the main form, while the *gauche* conformer is disfavored by 0.2 kcal mol^{-1} when the C_2-C_3 distance is diminished to 1.44 Å, as a result of approaching the methyl groups. On the other hand, the *gauche* conformer is stabilized by 0.2 kcal mol^{-1} when the C_2-C_3 distance is elongated to 1.64 Å, as a result of alleviating the steric repulsion between the methyl groups. The effect of varying the C_2-C_3 bond distance was more significant on the torsional barrier than over the energy minima, since the eclipsed structures are more susceptible to steric

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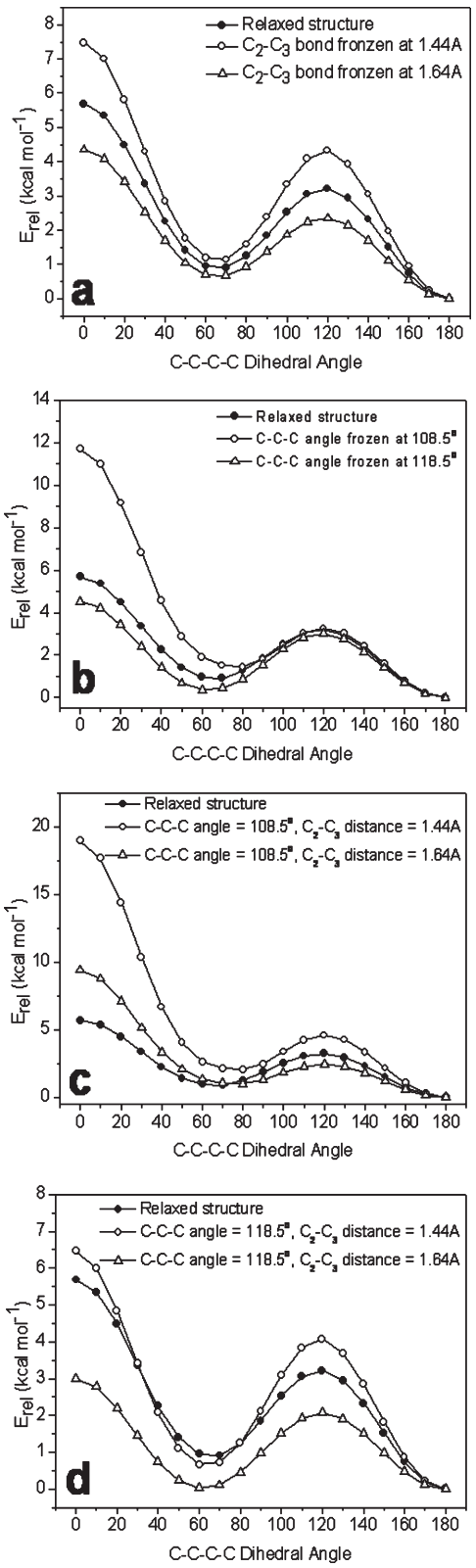


FIGURE 1. Torsional curves containing the fully relaxed structure, and (a) frozen C_2-C_3 bond distance, (b) frozen C−C−C bond angle, (c) frozen C_2-C_3 bond distance and C−C−C bond angle at 108.5°, and (d) frozen C_2-C_3 bond distance and C−C−C bond angle at 118.5°.

hindrance. To compensate for the perturbation caused by lengthening and shortening the C_2-C_3 distance,

TABLE 1. Geometrical (bond distances in Å and angles in deg) and Energetic (kcal mol^{-1}) Parameters Obtained from the DFT Calculations

	E_{rel}	C_1C_2	C_2C_3	$C_1C_2C_3$	$C_1C_2C_3C_4$
gauche (relaxed)	0.9	1.53	1.53	114.4	66.2
hypothetical *gauche* 1	3.7	1.54	1.44[a]	115.3	66.0
hypothetical *gauche* 2	3.5	1.52	1.64[a]	113.4	66.2
hypothetical *gauche* 3	2.7	1.53	1.55	108.5[a]	77.3
hypothetical *gauche* 4	1.7	1.53	1.53	118.5[a]	62.9
anti (relaxed)	0.0	1.53	1.53	113.4	180.0
hypothetical *anti* 1	2.6	1.53	1.44[a]	114.2	180.0
hypothetical *anti* 2	2.8	1.52	1.64[a]	112.5	180.0
hypothetical *anti* 3	1.3	1.53	1.54	108.5[a]	180.0
hypothetical *anti* 4	1.3	1.53	1.52	118.5[a]	180.0

[a]frozen parameters.

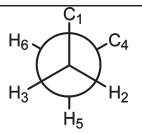
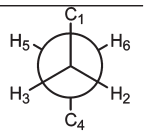
other geometrical parameters were naturally altered from the equilibrium geometry, particularly the C−C−C bond angles. For the *gauche* conformer, the C−C−C angle increased by 0.9° and decreased by 1.0° when the C_2-C_3 distances were 1.44 and 1.64 Å, respectively, in comparison to the equilibrium C−C−C bond angle of 114.4°. The corresponding effects for the *anti* conformer were smaller (Table 1).

Similarly, the effect of freezing the C−C−C bond angle at 5° smaller and larger than the optimum angle was evaluated, demonstrating that it was more significant than the effect of the C_2-C_3 bond distance (Figure 1b). For the hypothetical situation of a C−C−C bond angle of 108.5°, *anti* butane would be favored by 1.4 kcal mol^{-1} (0.5 kcal mol^{-1} more stable than the real system), but only 0.3 kcal mol^{-1} more stable than *gauche* if the C−C−C angle was 118.5°. If the difference in relation to the equilibrium C−C−C bond angle was ca. 10° larger, the *gauche* conformer would become more stable than the *anti* by 0.7 kcal mol^{-1}. Again, freezing the bond angle causes distortions in the geometry, particularly in the central C−C distance, and mainly in the C−C−C-C dihedral angle for the *gauche* conformer (from 66° of the real system to 77° of the hypothetical situation), to minimize repulsion.

Thus, in order to eliminate the dependency between the C_2-C_3 distance and the C−C−C bond angle, both parameters were frozen simultaneously. Energy minima of the fully relaxed structure are practically congruent with those of the structure in which the C_2-C_3 distance and the C−C−C bond angle are frozen at 1.64 Å and 108.5°, respectively (Figure 1c). Shortening the C_2-C_3 distance to 1.44 Å increases the *gauche* energy by 1.2 kcal mol^{-1}. In both cases, the energy of the transition state with methyl groups eclipsed is significantly higher than that of the relaxed structure. When increasing the C−C−C bond angle to 118.5° (Figure 1d), the shape of the torsional curves becomes closer to those of Figure 1a, demonstrating the dominant effect of varying C−C−C bond angles in comparison to changes in the C_2-C_3 bond distance. However, an important detail in Figure 1d is that the *gauche* conformer of the structure with larger C_2-C_3 distance and C−C−C bond angle is equivalent in energy to the *anti* conformer; this clearly demonstrates that, when methyl groups are far from one another in butane, the energies of the stable conformers tend to equalize, as well as the rotational barriers.

Natural bond orbital analysis was carried out to evaluate the hyperconjugative nature of the butane rotational isomerism, but also to give support to the findings above,

TABLE 2. Hyperconjugation Contribution (kcal mol^{-1}) of Selected Antibonding Orbitals

Orbitals removed		
σ^*_{C1-C2} and σ^*_{C3-C4}	23.3	18.3
σ^*_{C2-H2} and σ^*_{C3-H6}	22.7	19.8
σ^*_{C2-H3} and σ^*_{C3-H5}	21.7	19.8

i.e., that steric repulsion plays a significant role in defining the conformational preferences and rotational barrier of butane. According to the NBO results, removal of key acceptor orbitals, i.e., those antibonding orbitals involved in antiperiplanar interactions, causes a larger detriment for the *gauche* stabilization (Table 2). This indicates that, even less stabilized by vicinal antiperiplanar hyperconjugation, the *anti* conformer is ca. 0.9 kcal mol^{-1} more stable than the *gauche*, suggesting a dominant steric contribution for the rotational isomerism of butane. The torsional curves for the fully relaxed and for the structure relaxed with all hypeconjugative interactions deleted are shown in Figure 2a; the minima for the hypothetical structure are now corresponding to the eclipsed conformers, similar to ethane.[6] Mo and Gao[8] suggested for ethane, and probably for butane, that hyperconjugation stabilization is overestimated due to the choice of localized orbitals, which were not optimal. However, the hypothetical minimum with methyl groups eclipsed is higher in energy than the other eclipsed conformer, indicating the steric component of the groups' interaction. The picture remains the same when considering the torsional curves of the hypothetical structures with the central C−C bond frozen at 1.44 and 1.64 Å (Figure 2b).

Freezing angles was found to be more relevant in differentiating the relaxed structure without any interaction removed from those with frozen C−C−C bond angles and hyperconjugation absent; at a smaller angle (108.5°), only one minimum is observed for the hypothetical structure, while the *syn* conformer is the most stable form when considering an angle of 118.5° (Figure 2c). This means that not only hyperconjugation is operating and favoring both *gauche* and *anti* conformers in relation to the eclipsed structures, but also the energy of the *syn* hypothetical conformer experiencing only classical steric and electrostatic effects is largely affected by bending the C−C−C angle. When freezing both the C_2−C_3 distance and the C−C−C bond angle, the curve profiles for the systems with hyperconjugative interactions absent are similar to the corresponding curves with only the latter parameter fixed (Figure 2d).

Overall, very simple approaches based on constraining bond lengths and angles to account for the steric repulsion between methyl groups in butane were capable of defining this traditional interaction as an important effect of the conformational energies of this model compound. Also, we recognize the relevance of hypercojugative interactions as ruling forces for this isomerism, but the conventional interpretation based on steric repulsion may not be ignored, since slight approaching or distancing of methyl groups (±5° from the equilibrium geometry) causes significant changes in conformer stabilities and torsional barriers. The classical interactions become still

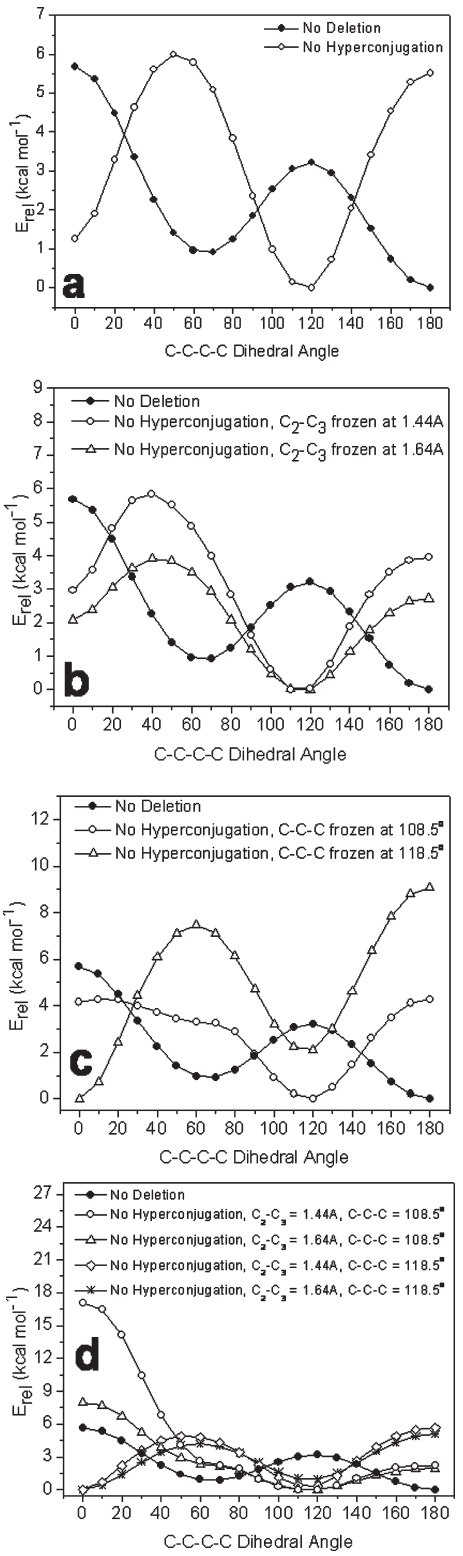


FIGURE 2. Torsional curves containing the relaxed structure with no hypeconjugation deleted, and (a) all hyperconjugative interactions removed, (b) all hyperconjugative interactions removed and frozen C_2−C_3 bond distance, (c) all hyperconjugative interactions removed and frozen C−C−C bond angle, and (d) all hyperconjugative interactions removed and frozen C_2−C_3 bond distance and C−C−C bond angle.

more evident when analyzing torsional curves with all hyperconjugative interactions removed. These findings may be transferred for other organic molecules based on the butane fragment, such as substituted alkanes, where hyperconjugation takes place more efficiently depending on the electron donor/acceptor ability of substituent groups.

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