The effect of steric repulsion on the torsional potential of *n*-butane: a theoretical study

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ABSTRACT

The origin of the rotational barriers in *n*-butane and *gauche* conformational energy, the prototypes of steric repulsion, has been re-examined by using energy decomposition analysis. The Pauli repulsion was found to be an important factor, but not the source of the barriers and *gauche/anti* energy difference. Rather, it should be considered as a driving force for structural changes accompanying the rotation. The repulsion (steric) energy partly transfers into the deformation energy of ethyl fragments and also affects a decrease in electrostatic, orbital and dispersion interactions by inducing the structural changes, particularly the central CC bond lengthening, while it becomes less destabilizing during the *anti*-butane rotation.

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1. Introduction

The rotational energy profile of *n*-butane is a textbook example of steric repulsion. Thus, the rotation of *anti* conformer by 360° encounters three nonequivalent barriers: *anti→gauche*, *gauche→gauche* and *gauche→anti*, which have been estimated experimentally[1] as 3.62±0.06 kcal/mol, 3.27±0.06 kcal/mol and 2.95±0.03 kcal/mol, respectively, and theoretically[2] as 3.3−3.7 kcal/mol and 4.9−5.4 kcal/mol. The third one corresponds to the *anti→gauche* barrier minus the energy difference between the *gauche* and the *anti* form. The latter was estimated to be by 0.6−0.9 kcal/mol higher than the energy of the *anti* conformer.[1,2a−c] The barriers are traditionally attributed to steric repulsion arising from the eclipsing of H/CH$_3$ and CH$_3$/CH$_3$ groups in *anticlinal* (*ac*) and *syn* transition structures, in addition to torsional strain also present in ethane rotation. The steric repulsion between the two CH$_3$ groups accounts for the difference in energy between *gauche* and *anti* forms.[3]

While the origin of the rotational barrier in ethane has been extensively studied and debated,[4] much less attention has been given to butane. The classical steric repulsion model has been confirmed as a major contribution to the rotational barriers, with hyperconjugative interactions playing a minor role.[2d,5]

Quantification of the steric effect within the density functional theory also proved that *syn* conformation contains larger steric energy, whereas contributions from other energy components were found to be more complicated to explain.[6] Although, a hint on an insignificance of steric interactions as a factor responsible for the *gauche/anti* energy difference has been given before.[7] An overview of studies aimed at understanding the origin of rotational barriers in alkanes has been given, recently.[8]

Usually, the steric repulsion is considered to involve both the classical electrostatic interactions and the quantum-mechanical Pauli repulsion, the latter arising from the fact that two electrons with same spin cannot occupy the same region in space. With an aim to differentiate between them and also to obtain information on contributions from other energy terms, we performed an energy decomposition analysis of the rotational energy profile of butane. The results showed that some improvements of the traditional model should be included in a more detailed analysis of torsional potential of butane and possibly of other organic molecules based on the butane fragment, such as substituted alkanes. A particular attention should be paid to the sensitivity of various energy components on geometry changes occurring during the rotation.

2. Computational details

Geometries of butane at various diedral angles (differing by 10°) were optimized at the MP2/6-31G(d) level[9,10] by using the Gaussian 09 program package.[11] In the energy decomposition analysis (EDA),

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done at the same theory level, butane molecule has been built from two ethyl radicals, taken with opposite spin (α and β superscripts in Scheme 1) so that they can form a bond.

$$CH_3CH_2^{\alpha} + {}^{\beta}CH_2CH_3 \rightarrow CH_3CH_2-CH_2CH_3$$
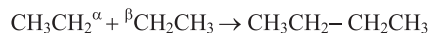
Scheme 1. Formation of *n*-butane from two ethyl radicals.

Total binding energy ΔE between them can be decomposed into two major parts (Eq. 1).

$$\Delta E = \Delta E_{prep} + \Delta E_{int} \qquad (1)$$

The preparation energy ΔE_{prep} corresponds to the energy required to deform two isolated ethyl radicals from their equilibrium geometry to the geometry they adopt in the molecule. The interaction energy ΔE_{int} represents the energy change occurring when prepared (deformed) fragments combine to form the molecule. The latter energy term can be further decomposed into five components (Eq. 2) by using the localized molecular orbital energy decomposition analysis (LMOEDA),[12] implemented in the Gamess program package.[13]

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{ex} + \Delta E_{rep} + \Delta E_{pol} + \Delta E_{disp} \qquad (2)$$

The electrostatic energy ΔE_{elstat} corresponds to nucleus-nucleus and electron-electron repulsion, and nucleus-electron attraction between the two prepared radical fragments that adopt their positions in the final molecule, and is usually stabilizing (negative energy contribution). The exchange energy ΔE_{ex} refers to the quantum mechanical exchange between the same-spin electrons and is simultaneously counteracted by the repulsion energy ΔE_{rep}. Taken together, they form the exchange repulsion[14] or Pauli repulsion[15] of other EDA schemes, which is a destabilizing interaction (positive energy contribution). Herein, we use the sum of ΔE_{ex} and ΔE_{rep} to represent the Pauli repulsion. The polarization energy ΔE_{pol} is an orbital relaxation energy accounting for the bond formation, charge transfer (donor-acceptor interactions between occupied orbitals on one fragment with empty orbitals on the other) and polarization (empty-occupied orbital mixing within one fragment due to the presence of another fragment). The dispersion energy component ΔE_{disp} comes from electron correlation. The latter two energy terms are stabilizing interactions. The energy change that follows butane rotation is calculated as a difference between the total binding energy ΔE of a given conformation (having diedral angle from 0° to 170°) and the most stable *anti* conformer (with diedral angle of 180°). The change in the ΔE_{prep} reflects gain or loss in energy due to structural changes within ethyl fragments that accompany the rotation, while the change in the ΔE_{int} is associated with the change in the nature of chemical bonding.

The employed theory level has been shown previously to give satisfactory results for studying rotations.[2d] In order to confirm that conclusions of the work are not affected by the basis set or theory level, additional calculations have been done at the MP2/6-311++G(d,p)//MP2/6-311++G(d,p),[9,10] B3LYP/6-31G(d)//B3LYP/6-31G(d)[10,16] and B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p)[10,16] levels. These results are presented in the Supplementary Data and are in accord with the MP2/6-31G(d)//MP2/6-31G(d) results. All interaction energy terms are corrected for the basis set superposition error.[17]

Such an analysis of the interaction energy between two or more fragments constituting a molecule has been applied to study the rotational barrier in ethane[4b,h,12] and in group 13-elements (E=B–Tl),[18] conformational preferences in 1,2-difluoroethane,[19] 1-chloro-2-fluoroethane,[20] (protonated) 2-haloethanol and 2-haloethylamine (X=F, Cl),[20] distortion to the *trans*-bent geometry in heavier ethylene homologues,[21] the isomerization energy of

heterocyclic[22] and polycyclic[23] compounds, the strength of conjugation and hyperconjugation,[24] and the nature of covalent bonds.[25]

3. Results and discussion

3.1. Molecular geometry

The MP2/6-31G(d) optimized structural parameters for *anti* and *gauche* conformers, *ac* and *syn* transition structures are given in Table S1 in the Supplementary Data. The values for the two conformers compare well with the experimental data obtained from electron diffraction,[26] which are also included in the table.

The most important structural changes occurring upon *anti→ac* rotation are the C2–C3 bond lengthening by 0.017 Å and the eclipsed ethyl groups bending away from each other, involving the H–C2–C3 bond angles widening by 0.4° (*syn* to the C–C bond on the other carbon) and by 1.2° (*syn* to the C–H bond on the other carbon), while the CCC bond angles do not change. Other bond length and bond angle changes are less than 0.002 Å and 0.2° (Table S1). The *anti→gauche* conformational isomerization is followed by the small C2–C3 bond elongation by only 0.003 Å, while larger changes are observed for bond angles: the CCC angle increases by 1° and the H–C1–C2 bond angle containing the hydrogen pointing to the CH₃ group on the other carbon widens by 0.9°. The H–C1–C2 and H–C2–C3 bond angles involving hydrogen, which is *anti* to the CC bond on the other carbon reduce by 0.5° and 0.3°, respectively. Obviously, these strucural changes tend to increase the distance between the *gauche* oriented CH₃ groups. Other bond lengths and bond angles change by less than 0.002 Å and 0.1° (Table S1). The *anti→syn* rotation increases the central C2–C3 bond length by 0.027 Å, the CCC bond angles by 3.5° and the H–C1–C2 bond angles containing the inner hydrogen atoms by 1°. The H–C1–C2 bond angles involving the outer hydrogen atoms close by 1.6°. The C1–C2 bonds slightly increase their lengths by 0.003 Å, while changes in other bond lengths are less than 0.002 Å (Table S1). Here, again, the molecule tends to increase the distance between the two eclipsed CH₃ groups. The observed structural changes are in accord with previous theoretical results.[2a]

3.2. Energy decomposition analysis

Energy decomposition results for *anti* and *gauche* conformers, *ac* and *syn* transition structures are listed in Table 1, along with the total energy (ΔE) and individual energy changes accompanying the rotations from *anti* form to *ac*, *gauche* and *syn* conformations. The calculated *anti→gauche* (3.44 kcal/mol), *gauche→gauche* (5.10 kcal/mol) and *anti→syn* (5.78 kcal/mol) barriers are in good agreement with previous theoretical results, which are 3.3–3.7 kcal/mol, 4.9–5.4 kcal/mol and 5.4–5.6 kcal/mol, respectively.[2a–c] The energy of *gauche* conformer was calculated to be by 0.68 kcal/mol higher than the energy of the *anti* conformer, which is also in accord with experimental (0.67 kcal/mol)[1] and theoretical (0.6–0.9 kcal/mol)[2a,b,5,7] data. Energy decomposition of the full rotational profile from 0° to 180° is shown in Fig. 1.

The full black line in Fig. 1 corresponds to the total energy change as a function of the CCCC diedral angle, relative to the most stable *anti* conformer. In the performed EDA, it is composed of two main parts: ΔE_{prep} (dotted black line) and ΔE_{int} (broken black line). The ΔE_{prep} line shows gain in energy due to the structural changes within the two ethyl fragments that occur during the rotation. It amounts 0.51 kcal/mol for the *anti→gauche* conformational isomerization (Table 1), corresponding to 75% of the total *gauche/anti* energy difference. Higher values were calculated for the *anti→ac* (1.32 kcal/mol) and *anti→syn* (2.98 kcal/mol) rotations, which constitute 38% and 52% of the total *ac/anti* and *syn/anti* energy difference, respectively. The ΔE_{int} line reflects changes in bonding