Origin and Nature of Bond Rotation Barriers: A Unified View

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ABSTRACT: Bond rotations are common and important in molecular studies such as drug design and enzymatic reactions. Steric hindrance and hyperconjugation are often borrowed to justify the origin of bond rotation barriers. However, there exists no consensus, even for as simple molecules as ethane, on which the effect is more significant. Here, we show that a unified view is possible. To that end, we employ two energy partition schemes from density functional theory to investigate the flexible rotation barrier of six molecules with one rotatable dihedral angle: ethane, methylamine, methanol, hydrazine, hydroxylamine, and hydrogen peroxide. Our results suggest that, even though steric and quantum effects play indispensable roles, it is the electrostatic interaction that governs the barrier height of all these different types of systems. This work not only consolidates earlier views about the role of steric and quantum effects, it also provides new insights about the origin and nature of the bond rotation barrier, which should be applicable to many different types of chemical bonds.
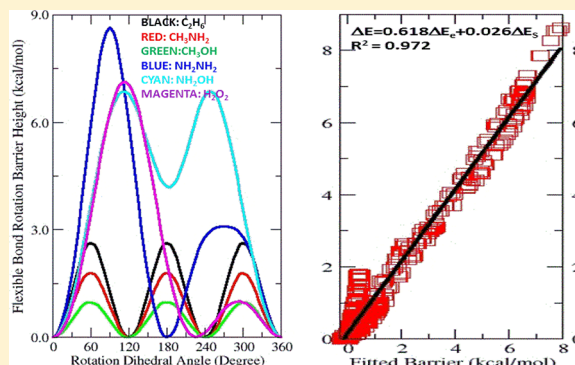
I. INTRODUCTION

Steric and quantum (via orbital interactions such as hyperconjugation) effects have long been known to play imperative roles in determining the barrier of bond rotations,[1−6] yet no consensus is available on which one is more important.[7−12] Several reasons might have contributed to the controversy. At first, these effects cannot be explicitly expressed in a formula as energetic components of the rotation barrier height. Because of this, it is difficult to make the comparison for them and impossible to distinguish causes from consequences. Second, there is no unique way to quantify these effects from theory. To many, this is the root of the dispute. In addition, contributions from these effects are often different for different molecules, making it unlikely to draw a conclusion that is general and applies to other systems. In this work, we employ two different energy partition schemes from density functional theory (DFT),[13−15] to discern the key factors dictating the rotation barrier height.

II. THEORETICAL AND COMPUTATIONAL DETAILS

In DFT, the conventional energy decomposition scheme is as follows:[13,14]

$$\Delta E[\rho] = \Delta T_s[\rho] + \Delta E_e[\rho] + \Delta E_{xc}[\rho] \tag{1}$$

where the energy difference is taken between a conformer generated from bond rotation and the global minimum, ρ signifies the total electron density of the system, T_s stands for the noninteracting kinetic energy, E_e denotes the electrostatic energy, and E_{xc} represents the exchange-correlation energy component. The electrostatic term consists of the nuclear-electron attraction, V_{ne}, classical electron−electron Coulombic repulsion, J, and nuclear−nuclear repulsion, V_{nn}, $E_e[\rho] = V_{ne}[\rho]$

$+ J[\rho] + V_{nn}$. Recently, we proposed an alternative scheme of energy partition in DFT:[15,16]

$$\Delta E[\rho] = \Delta E_s[\rho] + \Delta E_e[\rho] + \Delta E_q[\rho] \tag{2}$$

where the total energy difference comes from the contribution from three independent effects, steric ΔE_s,[17] electrostatic ΔE_e, and fermionic quantum due to exchange and correlation effects ΔE_q. The common term in these two schemes is the electrostatic contribution ΔE_e. Key benefits of employing these formulas to examine rotation barriers are that (i) energy components are directly related to the rotation barrier height, i.e., the total energy difference ΔE, so one will have clear ideas of which components contribute positively or negatively and dominantly or negligibly to ΔE, and (ii) we can identify whether or not there is any strong correlation between the barrier height and any of these energy components. These two schemes have been applied to study a few chemical processes earlier by us.[18−24]

Hereby, we consider the flexible bond rotation in this work. For the flexible bond rotation, each time a dihedral angle is altered, a geometrical optimization with that dihedral angle fixed will be performed. The dihedral angle considered for ethane is ∠H−C−C−H, for methylamine ∠H−C−N−H, for methanol ∠H−C−O−H, for hydrazine ∠H−N−N−H, for hydroxylamine ∠H−N−O−H, and for hydrogen peroxide ∠H−O−O−H. The dihedral angle change range is from 0° to 360° with the interval of 5°. For each of CH_3CH_3, CH_3NH_2, and CH_3OH, there is only one difference, eclipsed−staggered ($\Delta E > 0$), but for NH_2NH_2, NH_2OH, and H_2O_2, three differences are possible for each system because these three

molecules each have three isomers, cis, tran, and skew. We define the energy difference in such a manner that ΔE is always greater than zero. To that end, we always choose the most stable state as the reference, whose rotating dihedral angle is set to be zero. Total energy difference profiles for all six molecules as a function of the dihedral angle from $0°$ to $360°$ will be plotted. We employed the NWCHEM[25] suite of packages, a publicly accessible computational chemistry package, for all the calculations. We used the DFT hybrid B3LYP functional[25,27] and Dunning's aug-cc-pVTZ basis set[28] for all the runs. The tight self-consistent field convergence criterion and ultrafine integration grids are employed throughout.

III. RESULTS AND DISCUSSION

Figure 1 shows a few strong linear relationships between ΔE and its components for ethane from $360°$ of flexible C–C
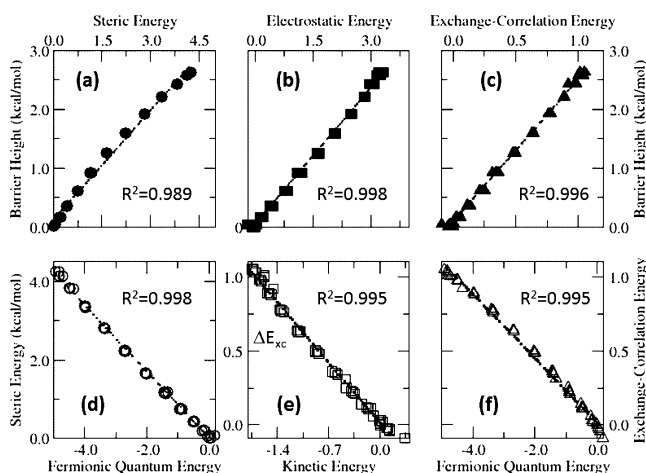

Figure 1. Strong linear relationships between the total energy difference and energy components, and among energy components for ethane: (a) ΔE_s vs ΔE; (b) ΔE_e vs ΔE; (c) ΔE_{xc} vs ΔE; (d) ΔE_q vs ΔE_s; (e) ΔT_s vs ΔE_{xc}; and (f) ΔE_q vs ΔE_{xc}.

single bond rotations. We find that, during the course of bond rotation, the barrier height ΔE is positively proportional to the following three energy components: steric ΔE_s (Figure 1a), electrostatic ΔE_e (Figure 1b), and exchange-correlation ΔE_{xc} (Figure 1c), with the correlation coefficient R^2 all equal to or larger than 0.99, suggesting that steric, electrostatic, and exchange-correlation interactions all positively contribute to the formation of the rotation barrier. Figure 1 also displays three strong converse correlations among the energy components, ΔE_s vs ΔE_q (Figure 1d), ΔE_{xc} vs ΔT_s (Figure 1e), and ΔE_{xc} vs ΔE_q (Figure 1f), with all R^2 also larger than 0.99. These strong correlations demonstrate that, during the flexible rotation of the C–C bond, all energy components participate in the ultimate formation and thus eventual determination of the barrier height. Some components contribute to it positively, whereas others do so negatively, canceling the contributions from other effects. It is the net sum of all these combined effects that work together and simultaneously generate the barrier of the bond rotation.

We applied the same strategy to the five other systems. Figure 2a exhibits the profile of the total energy difference with respect to the $360°$ flexible rotation with the step size of $5°$ for each of the six different single bonds, C–C, C–N, C–O, N–N, N–O, and O–O. As can be seen from the Figure, these energy
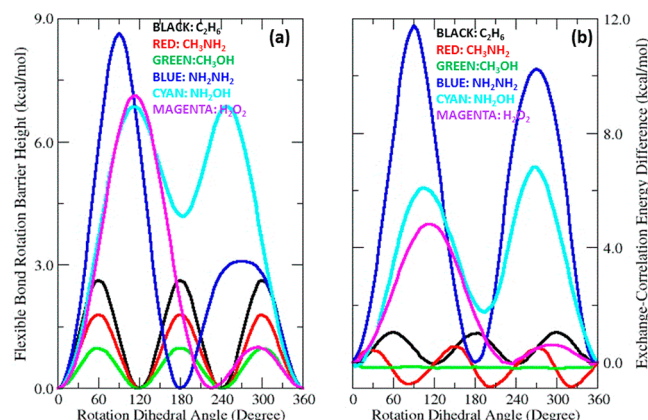

Figure 2. Profiles of (a) the total energy difference and (b) exchange-correlation energy difference with respect to the $360°$ dihedral angle rotation of six simple molecules studied in this work: C_2H_6, CH_3NH_2, CH_3OH, NH_2NH_2, NH_2OH, and H_2O_2.

profiles are vastly different from one another in both barrier heights and curve shapes. For ethane, methylamine, and methanol, two distinct conformers, staggered and eclipsed, were found, but for hydrazine, hydroxylamine, and hydrogen peroxide, there are three different conformations, cis, trans, and skew. The barrier heights obtained in this work are in good agreement with the experimental data.[19] Shown in Figure 2b as an example is the profile of the exchange-correlation energy difference, ΔE_{xc}, with respect to the bond rotation, from which we find that this energy component profile exhibits markedly different behaviors from one another as well. The same is observed for other energy components.[19]

One basic question that we are to answer in this work is whether or not there is a single energy component that is solely responsible for the existence and height of the rotation barrier. The best correlation obtained from the results of these six species is the relationship between ΔE_e and ΔE, as shown in Figure 3a, with the correlation coefficient $R^2 = 0.930$. This reasonably good correlation suggests that the electrostatic interaction is the main effect to determine the barrier height of single-bond rotations. Much less strong correlations of ΔE vs ΔE_{xc} and ΔE vs ΔE_s were obtained with $R^2 = 0.65$ and 0.49 (plots not shown), respectively, both with positive slopes, indicating that these latter components also positively
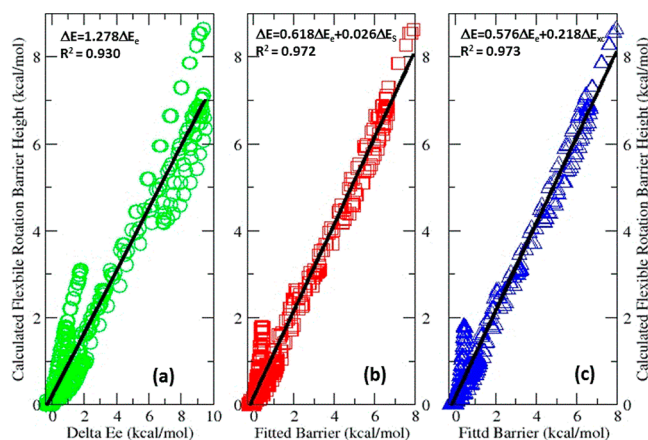

Figure 3. Least-square fittings with one and two energy components for the rotation barrier of all six molecules studied in this work.

Table 1. Computed and Fitted Total Energy Differences and Their Decompositions for Distinct Isomers of the Six Molecules Studied in This Work; Units in kcal/mol

	ΔE_q	ΔE_s	ΔE_e	ΔE_{xc}	ΔT_s	ΔE	model 1[a]	model 2[b]
C_2H_6 eclipsed−staggered	−4.92	4.25	3.31	1.05	−1.72	2.63	2.15	2.14
CH_3NH_2 eclipsed−staggered	5.77	−4.86	0.89	−0.30	1.20	1.79	0.43	0.45
CH_3OH eclipsed−staggered	2.51	−3.51	1.97	−0.17	−0.82	0.98	1.13	1.10
NH_2NH_2 trans−skew	−83.51	82.79	9.35	11.76	−12.47	8.63	7.90	7.95
NH_2NH_2 cis−trans	0.49	−2.50	7.55	1.52	−3.53	5.53	4.60	4.68
NH_2NH_2 cis−skew	−84.00	85.29	1.80	10.24	−8.94	3.10	3.29	3.27
NH_2OH cis−trans	−7.91	5.14	6.96	1.88	−4.65	4.19	4.43	4.42
NH_2OH skew−cis	−30.18	30.53	2.31	4.19	−3.84	2.67	2.21	2.24
NH_2OH shew−trans	−38.09	35.67	9.27	6.07	−8.49	6.86	6.64	6.66
H_2O_2 trans−skew	−3.27	2.36	1.90	0.61	−1.52	1.01	1.23	1.23
H_2O_2 cis−trans	−29.29	27.91	7.50	4.23	−5.62	6.11	5.35	5.24
H_2O_2 cis−skew	−32.56	30.27	9.40	4.84	−7.14	7.12	6.58	6.47

[a]Predicted by the formula $\Delta E = 0.618\Delta E_e + 0.026\Delta E_s$. [b]Predicted by the formula $\Delta E = 0.576\Delta E_e + 0.218\Delta E_{xc}$.

contribute to the height of rotation barriers, but their correlations are less significant. The similar behavior of the ΔE_e dominance was observed in transition state barriers of SN_2 reactions.[21]

In an effort to establish better correlations with the rotation barrier, shown in Figure 3b,c are two least-squares fittings using two variables from eqs 1 and 2, respectively. Better fittings with $R^2 = 0.97$ have been obtained when two variables are used. Figure 3b uses ΔE_e and ΔE_s, whereas Figure 3c employs ΔE_e and ΔE_{xc}. As can be seen from the fitted formulas in the plots, in both cases, ΔE_e is the dominant contributor with a much larger coefficient, 0.618 vs 0.029 in Figure 3b and 0.576 vs 0.218 in Figure 3c, suggesting that a smaller electrostatic interaction is the main cause of the rotation barrier. Smaller but positive coefficients of ΔE_s and ΔE_{xc} in these two-variable models indicate that steric and quantum effects due to exchange-correlation interactions contribute positively to the barrier height as well, but their contributions are not predominant.

Applying these two relationships to distinct isomers of the six compounds, we have estimated their relative stability. The results are shown in Table 1. ΔE and ΔE_e always have the same sign, confirming that ΔE_e is the dominant factor contributing to $\Delta E > 0$. Also, in most cases in the Table, we have positive ΔE_s and ΔE_{xc}, suggesting that steric and exchange-correlation effects often, though not always, contribute to the rotation barrier as well. Quantitatively good agreement with the calculated energy difference was obtained, except for CH_3NH_2, for which because ΔE_s and ΔE_{xc} are less than zero the predicted stability deviation is larger than 1.0 kcal/mol. Yet, the predicted stabilty order for its staggered and eclipsed conformations is correct.

As the main results of this work, Figure 3a−c provides a novel explanation for the nature of bond rotation barriers. Our results unambiguously show that the electrostatic interaction is the dominant contributor to the rotation barrier height. The higher the barrier, the smaller the electrostatic interaction. However, our present work also confirms and consolidates the earlier explanations in the literature, where both steric repulsion and hyperconjugation effects were employed to validate the rotation barriers. As can be seen from Figure 3b,c, though with a smaller coefficient, both steric effect and exchange-correlation interactions positively contribute to the rotation barrier, suggesting that the higher the bond rotation barrier, the stronger the steric repulsion and the smaller the quantum effect due to exchange-correlation interactions.

IV. CONCLUSIONS

In summary, we report an account of bond rotation barriers in this contribution from a different perspective, providing new insights about how the barrier of flexible bond rotations is originated and what their nature should be. As has been illustrated for ethane, using two different energy partition schemes from density functional theory, we found that the rotation barrier originates from the net contribution from all effects involved. These effects, electrostatic, steric, kinetic, exchange-correlation, and Fermionic quantum, have different trends as a chemical bond rotates. Some effects contribute positively to the barrier height, while others do so negatively, canceling other contributions. For all six systems studied in this work, it has been unveiled that the rotation barrier strongly correlates with the electrostatic interaction, indicating that it is the dominant contributor to the barrier. This work also unifies earlier controversial viewpoints about the origin of the rotation barrier using either steric repulsion or hyperconjugation. We show that, by incorporating these effects into the fitting, substantially better correlations can be obtained. In our two-variable models, these latter effects are found indispensable, but not prevalent. These earlier explanations using steric and hyperconjugation effects are the two sides of the same coin, offering complementary yet insufficient justifications about the nature of the bond rotation barrier.

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Notes
The authors declare no competing financial interest.

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