Origin of Staggered Conformational Preference in Methanol

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Building on recent work on ethane internal rotation, we present a Hartree−Fock analysis that determines the origin of the conformational preference in methanol. The conformational preference origin is not inferred from barrier studies but is analyzed directly, by determining conformations the molecule would assume when particular classes of interactions are missing. We find that it is the hyperconjugative, and not the steric, interactions that determine the equilibrium structure of methanol. Rehybridization effects and bond strength changes induced by skeletal relaxations accompanying internal rotation play a critical role in the torsional mechanism.

1. Introduction

A recent interaction removal study has established that the staggered conformational preference in ethane stems from hyperconjugative stabilization of the staggered conformer, rather than from the long and widely believed steric destabilization of the eclipsed form.[1] This direct analysis of the ethane staggered structural preference origin validates a number of hyperconjugative model proposals (e.g., refs 2 and 3). However, ethane has 3-fold symmetry, which has the portent for making ethane a special case. There is historical precedent for symmetry induced special behavior (the invariance of the ethane rotational barrier to skeletal relaxation may be such an example). Methanol, a still simple molecule, but with additional electronic features (lone pairs and polar bonds), provides a more general test for the increasingly held picture: hyperconjugative forces determine structure in simple methyl molecules.

An understanding of the methanol conformational preference origin requires consideration of internal rotation. In methanol, this occurs around the C−O bond, leading the molecule from its staggered (S) form to eclipsed (E) (Figure 1). The barrier to this motion is generally agreed to be slightly greater than 1 kcal/mol, only one-third that of ethane (1.1 kcal/mol, obtained from experimental thermodynamic data[4]).[5,6] This ratio suggested a seductive way of relating methanol to ethane, through comparison of the number of eclipsing bonds in the top-of-barrier conformer. There are three C−H bonds in each ethane rotor, but only one (O−H) in methanol (Figure 1). In this view, Pauli exchange (or overlap) repulsion between C−H and O−H bonds should decrease 3-fold from ethane.[7] Thus, methanol appeared at first sight to fit the traditional steric repulsion model for torsional barrier origins. This conclusion was derived from an analysis of methanol with idealized geometry, i.e., with no relaxation, using small basis sets, as well as from approximating total exchange repulsion by its pairwise counterpart.[8,9]

However, all of these assumptions have been shown, in the case of ethane,[10] to give an incorrect appreciation of Pauli repulsion. Moreover, three recent methanol studies provide an important modification of the earlier conclusions. The 1990 Bader et al.,[11] 1991 Reed and Weinhold[12] and, most recently, Badenhoop and Weinhold[13] ab initio studies conclude that the barrier stems from alterations of attractive potential energy rather than an increase in repulsive energy. In particular, the Weinhold studies conclude that it is the change in delocalization energy (i.e., hyperconjugative interactions) that is the barrier forming interaction.[12−14] In our earlier work,[6,15,16] we pointed out the importance of structural changes in the barrier mechanism. Internal rotation is *not* pure rotation; it involves simultaneous changes in other bond lengths, angles and distances, sometimes fairly remote from the "action". In ethane only C−C bond expansion is involved; in methanol, the internal rotation coordinate space includes angular openings as well as bond lengthenings. In particular, if COH angular opening relaxation is neglected, the role of oxygen σ lone pair rehybridization is necessarily missed.

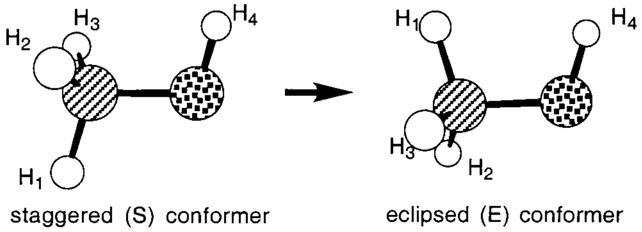

Figure 1. Methanol equilibrium (staggered, S) and top-of-barrier (eclipsed, E) conformers.

In this article, we directly analyze the methanol structural preference, rather than infer it from studies of the barrier origin. At the same time, we reexamine the barrier origin problem from the aspect of skeletal relaxation and all electron reorganization. There are two outcomes: the first is conclusive validation of Reed and Weinhold's inference obtained from Hartree−Fock (HF) barrier studies that hyperconjugative interactions lead to the staggered equilibrium structure. The second is establishment of the controlling role skeletal changes play in the barrier origin mechanism. All of the analysis is carried out within the HF model.

2. Energetic Analysis

The results of HF/6-311++G(3df,2p) level energy calculations, based on MP2/6-311G(3df,2p) geometries (Table 1), agree with previous studies: both equilibrium (S) and rotated (E) structures have C_s symmetries, and the barrier (1.03 kcal/mol) converges to ∼1 kcal/mol.[6] Major geometrical changes ac-

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TABLE 1: MP2/6-311G(3df,2p) Methanol Optimized Geometries (Bond Lengths in Å, Angles in Degrees)

conformation	R_{C-O}	$R_{C-Hip}{}^{a}$	$R_{C-Hop}{}^{a}$	R_{O-H}	$\angle H_{op}CO$	$\angle H_{ip}CO$	$\angle COH$
S	1.414	1.086	1.092	0.958	112.3	106.8	107.9
E	1.418	1.090	1.089	0.956	109.7	112.5	108.3

[a] $C-H_{ip}$ and $C-H_{op}$ refer to in-plane and out-of-plane methyl C−H bonds (H_1 and H_2, H_3 in Figure 1), respectively.

TABLE 2: Relaxation Effects on Potential Energy Partitioning (kcal/mol)[a,b]

	model[c]			
	RR	CO	RR + CO	FR
ΔE_B	1.99	0.06	2.03	1.02
ΔE_{ee}	9.30	−39.68	−30.44	−29.31
ΔE_{nn}	8.91	−37.95	−29.09	−32.97
ΔE_{ne}	−16.22	78.19	62.07	63.40

[a] HF/6-311++G(3df,2p) energy, MP2/6-311G(3df,2p) geometry. [b] Rounded off to the nearest 0.01 kcal/mol. [c] For designations, see Appendix.

companying the methyl torsion are C−O and $C-H_{ip}$ bond lengthenings and $H_{ip}CO$ angle opening (Table 1).

A useful starting point is energy partitioning into potential energy components: nuclear−nuclear, electron−electron repulsion and nuclear−electron attraction effects, discussed in section 2a. We then turn to developing a more complete picture of the methanol internal rotation mechanism in terms of localized orbitals, to gain a chemically intuitive view of the energetic changes accompanying methanol torsion. Within the natural bond orbital (NBO)[17] framework, energy changes due to bond and hybridization alterations (section 2b), as well as Pauli exchange repulsion (section 2c) and hyperconjugative (section 2d) alterations are considered. Details are described in the Appendix.

Direct analysis of the structural preference in methanol is achieved by constructing potential curves that arise from a description of the molecule with exchange repulsion absent. Comparison of these potentials to those with the exchange repulsion present reveals the geometry-exchange repulsion connection. We then optimize the methanol geometry with selected hyperconjugative interactions deleted, to elucidate the geometry-hyperconjugation connection. The effect of Coulomb repulsion is considered first, in section 2a.

(a) Coulomb Repulsion and Nuclear−Electron Attraction. As can be seen from Table 2, Coulomb repulsion strongly depends on the coordinate space used to describe methanol internal rotation (Appendix). These repulsions increase in the rigidly rotated eclipsed conformer, as opposed to the decrease on going to the fully relaxed E conformer. In particular, it is C−O bond lengthening that drastically changes the Coulombic repulsion behavior. Even C−O bond lengthening alone (without rotation) leads to the same trend. Thus, it is the nonrotational component of the torsional space that is relevant to the decrease in Coulomb repulsion in the E conformer.

What is it then that forms the barrier? Table 2 demonstrates that it is the change in nuclear−electron attraction that is barrier forming. And, more specifically, it is the changes in σ orbitals and interactions among them rather than the π orbitals that are the primary source of the barrier.[15]

Although the inference of the above conclusions is that the preference for the staggered equilibrium structure stems from attractive, rather than repulsive forces, we address this question directly, by examining the nuclear−electron attractive and nuclear−nuclear and electron−electron repulsive energy dependence on torsional angle. Figure 2a graphically demonstrates Coulomb repulsion increase that takes place as the molecule undergoes rigid rotation. However, fully relaxed rotation (Figure 2c) yields quite a different picture. It is the nuclear−electron attraction energy that minimizes for the staggered conformation, whereas repulsions have their maxima at this conformation (i.e., torsional angle = 0°). We emphasize that the internal motion responsible for this behavior is C−O bond lengthening (Figure 2b): by invoking this relaxation alone, one obtains a correct appreciation of the conformational preference origin. The clear conclusion is that the rotation-induced C−O bond lengthening

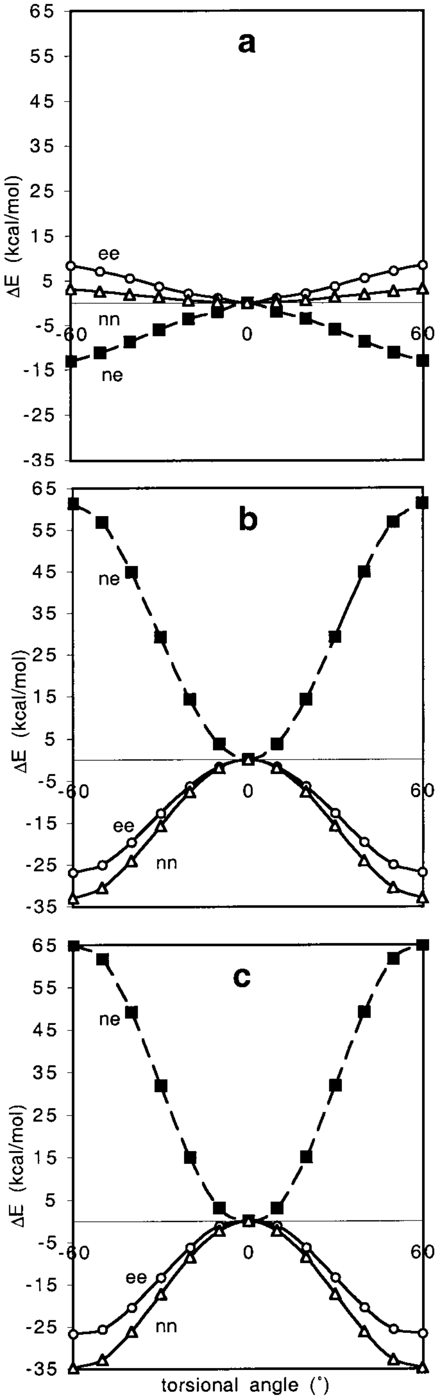

Figure 2. Torsional angle dependence of nuclear−nuclear (nn) and electron−electron (ee) repulsions and nuclear−electron (ne) attraction energy changes for rigid rotation (a), rigid rotation with C−O bond lengthening (b), and fully relaxed rotation (c). 0° denotes the staggered conformer; ±60°, the eclipsed one. MP2/6-311G(3df,2p) geometry, HF/6-311G(3df,2p) energy calculation.

TABLE 3: Exchange Repulsion Relaxation Dependence (kcal/mol)[a]

	$\Delta E_{\text{exchange}}$
RR	−3.21
RR + COH	−3.70
RR + CH_3	−2.72
RR + CO	−4.43
CO	−1.26
FR	−4.37

[a] See footnotes a, b and c, Table 2.

plays a controlling role in the nature of the forces behind the methanol internal rotation barrier.

(b) Structural Effects. We now turn to the structural relaxation effects, i.e., the effect of the structural relaxations (triggered by rotation) on bond strengths and lone pair hybridizations. The largest barrier forming term comes from the oxygen σ lone pair orbital.[15] This is due to its rehybridization ($sp^{1.07} \rightarrow sp^{1.11}$), driven by methyl group rotation and concomitant skeletal flexings. In the E conformer, the two out of plane hydrogens ($C-H_{op}$) have moved to the same side of the molecule as that of the σ lone pair, with a consequent destabilizing Coulomb field on both the lone pair and $C-H_{op}$ bonds. The increase in the p character of the σ lone pair orbital moves the orbital centroid away from the interaction region. The mutual destabilization rationalizes barrier forming characters of both the lone pair and $C-H_{op}$ bond orbital.

Another structural effect involves the $C-O(\sigma)$ bond. Its increase in energy is a direct result of the 0.004 Å bond lengthening, with consequent bond weakening. It is clear that this C−O bond relaxation induced barrier contribution is not encompassed by rigid rotation. Both the C−O bond weakening and σ lone pair orbital rehybridization rationalize (at least in part) the increase in the σ component of the nuclear−electron attraction energy change.[6,15]

In summary, when compared to ethane, for which the rotational coordinate is only contaminated by C−C bond expansion with associated C−C bond weakening,[18] in methanol both angular and bond length contamination lead to three structural relaxation energy changes: lone pair rehybridization, C−O and $C-H_{op}$ bond weakenings. The outcome is that structural relaxation energy changes in methanol assume a more enhanced role in the barrier energy mechanism than in ethane.

(c) Pauli Exchange Repulsion. The effect of total exchange repulsion in methanol is antibarrier, as noted in Badenhoop and Weinhold's recent HF/6-31G(d) rigid rotation study.[13] The fully relaxed model not only confirms this trend but significantly enhances the antibarrier character (Table 3).[19]

The flexing that brings rigid rotation exchange repulsion to the fully relaxed value is C−O bond lengthening. However, when compared to the controlling importance of C−C expansion on exchange repulsion in ethane, rotation gains importance in methanol. Rotation itself brings about 70% of the fully relaxed exchange repulsion and becomes instrumental not only as a trigger of skeletal relaxations that control exchange repulsion energetics but also as a direct origin of energy changes in this molecule.

The antibarrier character of exchange repulsion suggests, but by itself does not prove, that the equilibrium structure of methanol is determined by other forces. To make this definitive, the torsional dependence of the total energy and energy with exchange repulsion missing is shown in Figure 3 (Appendix). The result is that *even when exchange repulsion is not present, the preferred conformer is staggered*. This conclusion extends our finding for ethane. Together, they strongly oppose the conventional wisdom that exchange repulsion is primarily responsible for the conformational preference in molecules undergoing internal rotation around single bonds.

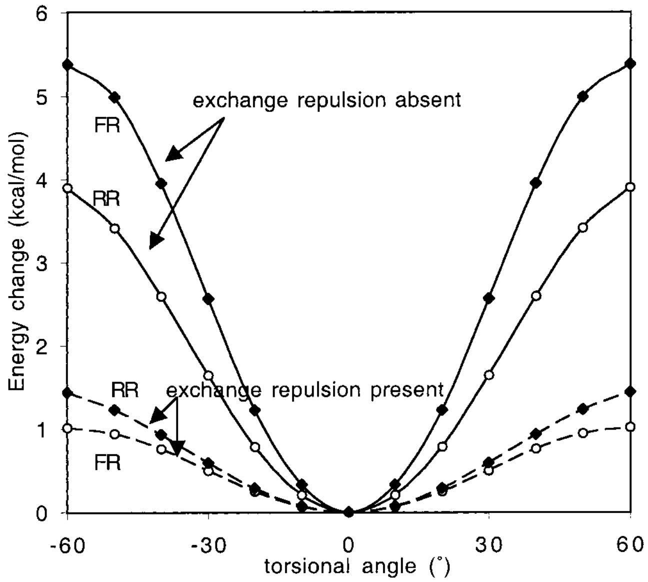

Figure 3. Torsional angle dependence of energy for the real methanol molecule, all interactions present (dashed) and a hypothetical methanol molecule with exchange repulsion absent (solid). FR denotes fully relaxed rotation; RR, rigid rotation. 0° denotes the staggered conformer; ±60°, the eclipsed one. MP2/6-311G(3df,2p) geometry, HF/6-311++G-(3df,2p) energy calculation.

TABLE 4: Effect of Bond/Antibond Interaction Deletions on Torsional Angle of the Optimized Conformation[a]

deleted type of interactions	torsional angle (deg)	conformer
no deletion	0	S
no hyperconjugation	60	E
no vicinal hyperconjugation	60	E
no geminal hyperconjugation	0	S

[a] HF/6-31G(d,p) geometry optimization. These trends are found to be basis set independent (see ref 23).

(d) Hyperconjugation. Parallel to what was found in ethane, the delocalization energy change in methanol is found to be barrier forming. Vicinal bond−antibond hyperconjugation interactions remain responsible for the energy increase.[12,16] As pointed out by Weinhold,[2] in ethane each C−H bond allows 3 possible charge transfers between methyl groups, resulting in a total of 18 hyperconjugative interactions. In methanol, 2 C−H bonds and antibonds are replaced by 2 lone pairs (without associated antibonds), reducing the number of possible delocalization interactions. The large barrier reduction on going from ethane to methanol can then be rationalized primarily by the reduced number of delocalization interactions and secondarily by their reduced magnitude.[12,16]

Although the barrier forming character of hyperconjugation implies an important role in determining the methanol structure, a direct approach is to consider which conformation methanol adopts upon optimization if selected bond/antibond delocalization interactions are absent. Upon removal of all weakly occupied orbitals, methanol assumes the eclipsed structure (Table 4), conclusively demonstrating that *an idealized methanol Lewis structure would be eclipsed, the top-of-barrier conformation*.

As seen from Table 4, deletion of all of the hyperconjugative interactions between the methyl and hydroxyl groups (i.e., vicinal delocalization) changes the structure to eclipsed, whereas

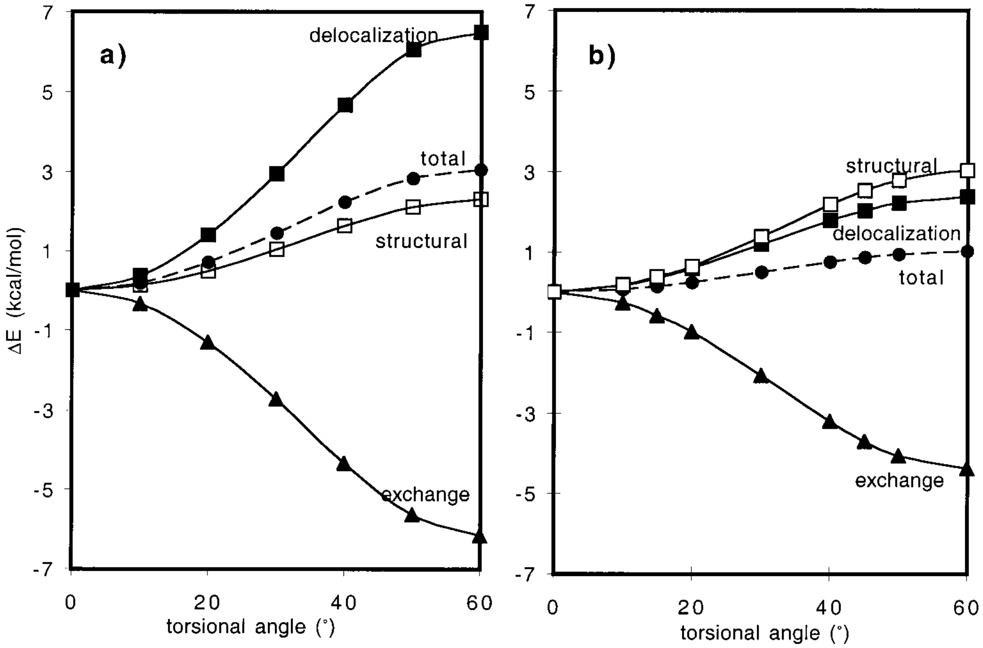

Figure 4. Rotational dependence of the energy components (solid curves) of the fully relaxed internal rotation energy (dashed curve) as defined in eq 1: ethane (a), taken from ref 16; methanol (b). Basis sets/levels as in Figure 3.

the absence of geminal interactions leaves the molecule in the no-deletion staggered structure. There is a clear conclusion: it is the vicinal interactions that are dominant in controlling the staggered structure.

3. Discussion

A useful way to summarize the internal rotation energetics and compare them across molecules is to break down the barrier energy, ΔE_B in the following manner:[16]

$$\Delta E_B = \Delta E_{struct} + \Delta E_{deloc} + \Delta E_{exchange} \qquad (1)$$

The usefulness of eq 1 is that it focuses on ubiquitous chemical concepts: exchange repulsion (a.k.a. steric repulsion), hyperconjugation and bond strength. Its disadvantage is that the terms in eq 1 are not completely independent, and thus are difficult to calculate by ab initio procedures. Despite this obstacle, hyperconjugation, exchange repulsion and bond strengths are such widely used concepts that this kind of deconstruction can be a more meaningful tool in understanding barrier energetics than potential energy partitioning (eq A.1). The term ΔE_{struct} incorporates effects discussed in section 2b. A first-order estimate of the structural effect can be obtained from the NBO energy changes. A useful algorithm is to obtain ΔE_{struct} as the difference between the barrier energy and delocalization and exchange energy changes.

Following the deconstruction inherent in eq 1, methanol's internal rotation energetics is dominated by two classes of interactions: delocalization changes and structural alterations (Figure 4b). When compared to ethane (Figure 4a), the exchange energy is still antibarrier and has approximately the same magnitude, but the barrier forming delocalization effects are strongly reduced. A consequence of the hyperconjugation attenuation is emergence of the structural energy change as the main barrier determining factor. It can be rationalized by three energetically unfavorable processes accompanying internal rotation: oxygen lone pair σ rehybridization and C$-$H$_{op}$ and C$-$O bond weakenings.[15] This conclusion finds support by the energy decomposition given in Table 2, since the structural energy is related to the nuclear$-$electron attraction term. In this picture the σ part of ΔE_{ne} is dominated by the σ lone pair and C$-$O bond energy changes.[16]

This internal rotation energetic analysis reveals an important difference between ethane and methanol. In ethane, rotation triggers skeletal relaxations, which then play an important, but not controlling role in the individual barrier energetics. The outcome is a trade off between decreased exchange repulsion and increased hyperconjugation; the barrier itself is little affected by the presence (or absence) of relaxation. In methanol, on the other hand, exchange repulsion-hyperconjugation trade off is unbalanced by the increased importance of structural energy changes. Rigid rotation neglects skeletal changes which induce structural energy changes, and consequently subdues the role of the structural energy term. The order of importance of various interactions is different than in the course of a fully relaxed rotation. A consequence of this rebalancing is a large (almost 100%) difference in barrier height between rigid and fully relaxed rotation models in methanol, as opposed to the barrier height insensitivity in ethane.

Among the most important conclusions is that methanol's equilibrium structure is primarily determined by hyperconjugative interactions, and not, as widely believed, by exchange repulsion. This work conclusively shows that within the HF model it is hyperconjugation (more specifically, vicinal hyperconjugation) that is essential for the structural choice this molecule makes.

Appendix

Methods. Several relaxation models are used for analysis of the structural and barrier origins. Fully relaxed (FR) rotation is defined as a globally optimized rotation; i.e., S, E and intermediate conformers are fully optimized (with exception of the dihedral angle defining the methyl rotation). Separation of the effects of skeletal motion accompanying torsion from the torsion itself is accomplished by reference to rigid rotation (RR), defined as methyl rotation with no change in internal coordinates; i.e., all bond lengths and angles are restricted to their equilibrium values.

Partially relaxed rotations allow insight into the torsional coordinate space, by examining the roles that individual internal coordinates (Q_i) play in the torsional process. Here, only one bond length or angle is allowed to relax to its top-of-barrier value, keeping all of the other coordinates frozen, while rotating the methyl group. These rotations are named after the flexing coordinate (e.g., ∠COH partially relaxed rotation is denoted as RR + COH, to designate the skeletal motion occurring along with rigid rotation). To definitively separate the effect of relaxation from the torsion itself, an additional partial relaxation is used: an internal coordinate is allowed to assume its top of barrier value, *but no rotation is performed*. These relaxations are designated by the coordinate name (e.g., CO for C−O bond lengthening alone). Comparison of RR + Q_i and Q_i relaxation models reveals the extent to which the rotation itself, or the rotation induced skeletal motion, influences energetics.

Potential−kinetic energy partitioning is performed according to the following equation:

$$\Delta E_{\mathrm{B}} = \Delta E_{\mathrm{ne}} + \Delta E_{\mathrm{nm}} + \Delta E_{\mathrm{ee}} + \Delta E_{\mathrm{k}} \qquad \text{(A.1)}$$

where ΔE_{B} is the barrier energy, ΔE_{ne} is the change in nuclear−electron attraction energy, ΔE_{nn} and ΔE_{ee} are changes in nuclear−nuclear and electron−electron repulsion energies, and ΔE_{k} is the kinetic energy change. Although this partitioning is not unique, it allows insight into the roles of σ and π effects by partitioning ΔE_{ne} into $\mathrm{A}'(\sigma)$ and $\mathrm{A}''(\pi)$ subcategories characteristic of the methanol C_s symmetry group, comprising interactions among σ and π orbitals, respectively.

The barrier origin problem involves assessment of the relative importance of Pauli exchange repulsion and delocalization, as well as bond strength and hybridization changes. The natural bond orbital (NBO) formalism[17] allows chemically intuitive analysis of these interaction classes. NBO's are one and two centered orbital transforms of molecular orbitals. Thus an NBO representation of a molecule consists of bonds, lone pairs, antibonds and physically insignificant Rydberg orbitals. As discussed in many papers by Weinhold (referred to in ref 17), they correspond closely to the Lewis picture of a molecule, and thus can be considered a "chemist's basis set".

Bond strengthenings (or weakenings), as well as the energy consequence of lone pair rehybridizations are assessed through NBO energy changes between E and S conformers. Hybridization is determined from the atomic orbital composition of the corresponding lone pair NBO.

Pauli exchange (a.k.a. overlap) repulsion is a consequence of the Pauli exclusion principle, which prevents crowding of too many electrons into a same spatial region. Within the NBO framework the exchange energy (E_{exchange}) is calculated as the energy change resulting from interatomic orthogonalization, which converts preorthogonal NBO's (PNBO's) to corresponding orthogonal NBO's.[20] This procedure reflects the principal energetic consequence of antisymmetrization.

Delocalization or hyperconjugative stabilization is determined as the energy raising associated with deletion of low occupancy NBOs.[21,22] Thus, the delocalization energy of a conformer (E_{deloc}) is estimated by removing antibond (and Rydberg) orbitals from the orbital space and recalculating the SCF energy for a system with these orbitals absent. In the case where all of the low occupancy orbitals are removed, the remaining structure is exactly the Lewis structure, with all the bonds, lone pairs and core orbitals having occupancies 2.0.[22] This procedure is referred to as "no hyperconjugation". Removals of vicinal and geminal interaction blocks are termed "no vicinal hyperconjugation" and "no geminal hyperconjugation". Both exchange repulsion and delocalization effects in this article are represented relative to the values in the equilibrium conformer, and thus are denoted as $\Delta E_{\mathrm{exchange}}$ and $\Delta E_{\mathrm{deloc}}$.

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