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Natural Bond Orbital Analysis of Internal Rotation Barriers and Related Phenomena

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Abstract. The origin of barriers to internal rotation in ethane-like molecules has been investigated with ab initio molecular orbital theory and natural bond orbital (NBO) analysis. The "hyperconjugative" (vicinal $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$) nature of these interactions, as previously suggested on the basis of semiempirical INDO studies, is confirmed at higher 4-31G, 6-31G* levels of theory. Wave functions lacking such hyperconjugative interactions, but satisfying the Pauli principle, are shown to generally exhibit unphysical barrier behavior (i.e., wrong sign), contrary to the implication of the "Pauli-repulsions" model of Sovers et al. Each *trans* vicinal $\sigma \rightarrow \sigma^*$ interaction is found to contribute about 0.7 kcal/mol to stabilization of the staggered conformer. Geminal interactions and Rydberg orbital contributions are found to be relatively unimportant. The consistency of NBO analysis is exhibited for the methyl series $\text{CH}_3\text{-X}$ ($\text{X} = \text{CH}_3, \text{NH}_2, \text{OH}, \text{F}$) and the family of fluoromethanes, to demonstrate the essential continuity that relates internal rotation barrier forces to static and kinetic anomeric effects, *gauche* effects, anionic hyperconjugation, bond strengthening in polyhalogenated methanes, (e, 2e) spectroscopic evidence of lone pair delocalization, and other stereoelectronic phenomena.

1. INTRODUCTION

Whereas the elementary Lewis picture of localized electron pair bonds might lead one to expect relatively free rotation of the two methyl groups of ethane about the C-C single bond, Kemp and Pitzer's 1936 calorimetric measurement¹ indicated that residual noncovalent interactions favor the staggered conformation by about 3 kcal/mol. The small conformational energy differences, though dwarfed by typical covalent bond energies, exert a profound influence on molecular shape and reactivity. Possible explanations of the electronic origin of torsional interactions have been formulated in terms of steric repulsions, electrostatic models, valence bond theory, f-orbital contributions to hybrids, hyperconjugation, and other concepts, but the nature of these forces has remained controversial after more than a half-century of experimental and theoretical study.²⁻⁵

In 1976, Brunck and Weinhold^{6,7} traced the origin of barriers to internal rotation in ethane-like molecules to the preferential stabilizing effect of vicinal bond-antibond interactions in antiperiplanar (*trans*) arrangements.

These interactions lead to slight delocalization of covalent bonding electrons into vicinal unfilled orbitals, favoring staggered conformations. Their work was based on a bond orbital (BO) transformation of semiempirical self-consistent field (SCF)-molecular orbital (MO) wave functions,⁸ using "nominal" sp^3 hybrids of standard Slater-Pauling type. Such a transformation allows the wave function to be examined in a formally exact way in terms of orbitals associated with the localized bonds of a formal Lewis structure, both bonding and antibonding types. While the primary purpose of the BO basis set is to describe covalent bonding, it was recognized that such a basis set might also simplify the description of *noncovalent* effects. Particularly important in this respect are the *antibond* BOs (out-of-phase combinations of bonding hybrids), which represent residual portions of the atomic valence spaces not saturated in covalent bond

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formation. These residual functions, unoccupied in the formal Lewis structure description, play an important role in "noncovalent interactions," the set of phenomena lying outside the framework of an idealized Lewis structure picture.

More quantitative application of the bond-antibond delocalization concept, however, required a significant generalization of bond-orbital methodology to allow more flexible description of BOs and permit application to general *ab initio* wave functions. This generalization was carried out in the Natural Bond Orbital (NBO) procedure,⁹⁻¹² which permits the form of the BOs to be fully optimized with respect to a maximum-occupancy criterion based solely on the first-order reduced density matrix, and which could therefore be applied to any wave function (or perturbative Møller-Plesset treatment, etc.) leading to a density matrix. Applications of the NBO method to a variety of intra- and intermolecular interaction phenomena have been recently reviewed.¹³

Since the earlier conclusions of the Brunck-Weinhold semiempirical study of torsional interactions have not gained universal acceptance,¹⁴⁻¹⁷ it seems useful to reexamine a number of questions related to barriers in ethane-like molecules from the perspective of modern NBO treatment of *ab initio* MO wave functions. This will also permit some objections to the bond-antibond interpretation to be addressed and allow this picture to be examined in the context of a unified NBO description of noncovalent interactions, including phenomena not considered in the earlier analysis.

2. THE INTERNAL ROTATION BARRIER OF ETHANE

The electronic structure of ethane appears to be well described by a Lewis structure involving one C-C bond and six C-H bonds. At the RHF/6-31G* level of theory,¹⁸ the percentages of electrons that are described by Lewis structure NBOs of ethane in its staggered and eclipsed conformations are 99.742 and 99.798%, respectively. The natural hybrid orbitals (NHOs) for the two conformers are nearly identical: the carbon hybrids for the C-H bonds and the C-C bond are $sp^{3.09}d^{0.01}$ and $sp^{2.72}d^{0.00}$, respectively, in both conformers. The C-H bond NBOs are 0.1% more polarized toward carbon in the eclipsed conformer, the polarization coefficients on carbon being 0.7788 and 0.7794 for staggered and eclipsed conformer, respectively. The occupancies of the carbon core NBOs are identical in the two conformers, being 1.99953. The bonds (particularly, σ_{CH}) have somewhat higher occupancies in the eclipsed conformation: the σ_{CC} and σ_{CH} NBOs have occupancies of 1.99760 and 1.99281 in the staggered conformer, and 1.99781 and 1.99445 in the eclipsed conformer.

At the SCF level, one has the opportunity to separate "Lewis" and "non-Lewis" contributions to the total energy E . This is done by evaluating the energy E_{Lewis} of a determinant composed of the doubly occupied "Lewis NBOs," comprising the core, lone pair, and bond NBOs of the natural Lewis structure. Since the $N/2$ Lewis NBOs are fully occupied, there is no variational freedom in this wave function, and the energy E_{Lewis} can be simply evaluated by the single-pass Fock matrix deletion method,^{10,19} deleting all antibond and Rydberg NBOs from the NBO Fock matrix. Adding the remaining antibond and Rydberg (non-Lewis) NBOs to the variational space, a stabilizing interaction E_{deloc} will occur, lowering the total energy to its full SCF value E :

$$E = E_{Lewis} + E_{deloc} \quad (1)$$

In practice, E_{deloc} is evaluated as the difference between E and E_{Lewis} and it represents the interaction energy between the Lewis and non-Lewis sets. Table 1 presents E and E_{deloc} for the two conformers of ethane (and also, methylamine and methanol; see Section 3) with the 4-31G and 6-31G* basis sets. In staggered and eclipsed ethane at the HF/6-31G* level, E_{Lewis} is found to represent 99.9275 and 99.9371%, respectively, of the total energy.

Similarly, the rotation barrier ΔE of ethane, the difference between the energies of the eclipsed and staggered conformers, can be decomposed as

$$\Delta E = \Delta E_{Lewis} + \Delta E_{deloc} \quad (2)$$

It is tempting to think that ΔE_{deloc} might be of negligible importance, since E_{deloc} is such a small fraction of the total energy. However, the absolute magnitude of E_{deloc} , 30-40 kcal/mol (see Table 1), is appreciable on the chemical energy scale and an order of magnitude larger than the internal rotation barrier of ethane. Table 2 presents values of ΔE , ΔE_{Lewis} , and ΔE_{deloc} for ethane, methylamine, and methanol at the 4-31G and 6-31G* basis-set levels. In qualitative agreement with the previous results of Brunck and Weinhold obtained with semiempirical INDO wave functions,^{6,7} ΔE_{deloc} is the dominant contribution to ΔE and strongly favors the staggered conformer. It is also seen that E_{Lewis} and E_{deloc} are not very basis-set sensitive, in accord with the finding that the rotation barrier of ethane (experimental value: 2.9 kcal/mol) is rather insensitive to the level of theory.²⁰

Not all the terms contributing to E_{deloc} for the two conformers are associated with interactions between the two methyl groups in ethane. These energies also include *geminal* bond-antibond interactions within each methyl group and between each methyl group and the C-C bond

Table 1. Total Energies (E , in a.u.) and Contributions to Total Energies due to Antibond/Rydberg NBOs (E_{deloc} , in kcal/mol)^a

Compound	E	E_{deloc}	$E_{\text{deloc}}^{(\text{vic})}$	$E_{\text{deloc}}^{(\text{vv})}$
HF/6-31G*				
CH ₃ CH ₃ (st)	-79.227745	-36.06	-27.69	-19.86
CH ₃ CH ₃ (ec)	-79.222192	-31.25	-22.96	-14.46
CH ₃ NH ₂ (st)	-95.208195	-38.14	-34.00	-23.80
CH ₃ NH ₂ (ec)	-95.204684	-35.16	-31.12	-20.53
CH ₃ OH(st)	-115.033871	-36.97	-33.61	-22.96
CH ₃ OH(ec)	-115.032213	-35.53	-32.21	-21.43
HF/4-31G				
CH ₃ CH ₃ (st)	-79.114840	-40.13		
CH ₃ CH ₃ (ec)	-79.109649	-35.69		
CH ₃ NH ₂ (st)	-95.068036	-39.08		
CH ₃ NH ₂ (ec)	-95.064644	-36.34		
CH ₃ OH ₂ (st)	-114.870205	-36.47		
CH ₃ OH(ec)	-114.868420	-35.07		

^aValues are listed for the staggered (st) and eclipsed (ec) conformations of CH₃CH₃, CH₃NH₂, and CH₃OH (with ideal bond lengths and angles), HF/6-31G* and HF/4-31G levels of theory. Also given at the HF/6-31G* level (in kcal/mol) are the vicinal ($E_{\text{deloc}}^{(\text{vic})}$) and valence vicinal ($E_{\text{deloc}}^{(\text{vv})}$) contributions to E_{deloc} . (E_{deloc} , $E_{\text{deloc}}^{(\text{vic})}$, and $E_{\text{deloc}}^{(\text{vv})}$ are defined in the text.)

Table 2. NBO Energetic Decomposition of the Internal Rotation Barriers ΔE of CH₃CH₃, CH₃NH₂, and CH₃OH^a

Parameter	CH ₃ CH ₃	CH ₃ NH ₂	CH ₃ OH
HF/6-31G*			
ΔE	+3.48	+2.20	+1.04
ΔE_{oo}	-1.33	-0.78	-0.40
ΔE_{deloc}	+4.81	+2.98	+1.44
$\Delta E_{\text{deloc}}^{(\text{vic})}$	+4.73	+2.88	+1.40
$\Delta E_{\text{deloc}}^{(\text{vv})}$	+5.40	+3.27	+1.53
$\Delta E_{\text{deloc}}^{(2)}$	+4.44	+2.98	+1.35
$\Delta E_{\text{deloc}}^{(2)}(\sigma \rightarrow \sigma^*)$	+4.44	+2.84	+1.19
$\Delta E_{\text{deloc}}^{(2)}(n \rightarrow \sigma^*)$	0.00	+0.14	+0.16
HF/4-31G			
ΔE	+3.26	+2.13	+1.12
ΔE_{oo}	-1.18	-0.61	-0.28
ΔE_{deloc}	+4.44	+2.74	+1.40
Experiment ^b			
ΔE	+2.9	+2.0	+1.1

^aAll values are in kcal/mol (see text for definition of symbols).

^bExperimental barrier values from refs 20, 40, 41.

and antibond. The geminal interactions are expected to be rather insensitive to molecular conformation, since they involve no *direct* coupling between groups on opposite ends of the rotor axis. It is therefore useful to carry out a more selective Fock matrix deletion where only the NBO Fock matrix elements involving *vicinal* interac-

tions between the two methyl groups are set to zero. We denote the resulting energy as $E_{\text{deloc}}^{(\text{vic})}$, "vic" standing for vicinal, and the difference in $E_{\text{deloc}}^{(\text{vic})}$ between eclipsed and staggered conformers as $\Delta E_{\text{deloc}}^{(\text{vic})}$. The values (at the HF/6-31G* level) are given in Tables 1 and 2. It is seen that $E_{\text{deloc}}^{(\text{vic})}$ is about 10 kcal/mol smaller in magnitude than E_{deloc} , and that ΔE_{deloc} and $\Delta E_{\text{deloc}}^{(\text{vic})}$ are nearly identical, being +4.81 and +4.73 kcal/mol, respectively, and showing that the geminal (non-methyl-methyl) interactions included in E_{deloc} are essentially constant with respect to internal rotation. This result contradicts suggestions by other workers^{21,22} that geminal interactions are of significant importance in rotation barriers.

The starting point for a more detailed decomposition of ΔE_{deloc} is the examination of the major second-order energy estimates from the off-diagonal NBO Fock matrix elements. The most important of these, as found previously,^{6,7} are $\sigma_{\text{CH}} \rightarrow \sigma_{\text{CH}}^*$ in nature. The second-order estimates $E^{(2)}$ for $\sigma_{\text{CH}} \rightarrow \sigma_{\text{CH}}^*$ interactions in ethane, as a function of H-C-C-H dihedral angle, are -0.50 (0°, *cis*), -0.06 (60°, *gauche*), -1.04 (120°), and -3.32 kcal/mol (180°, *trans*). This dihedral angle dependence is consistent with the orbital plots given by Brunck and Weinhold^{6,7} which showed that the $\sigma_{\text{CH}}-\sigma_{\text{CH}}^*$ overlap²³ is strongest in the *trans* arrangement and that interference effects significantly reduce the overlap in the *cis* arrangement. Figure 1 illustrates these interactions for ethane at the RHF/6-31G* level. In the staggered con-

former, the only significant $\sigma_{\text{CH}} \rightarrow \sigma_{\text{CH}}^*$ interactions are of the stronger *trans* type, each σ_{CH} NBO contributing a σ_{CH}^* delocalization energy of -3.32 kcal/mol by the second-order estimate. In the eclipsed conformer, significant donation from each σ_{CH} NBO into each σ_{CH}^* NBO occurs, there being a single *cis* interaction and two 120° interactions for a total second-order estimate of -2.58 kcal/mol per C–H bond. The methyl–methyl stabilization energy per C–H bond is thus reduced by 0.74 kcal/mol in magnitude upon performing the 60° dihedral rotation that takes ethane from the staggered to the eclipsed conformation. The total second-order $\sigma_{\text{CH}} \rightarrow \sigma_{\text{CH}}^*$ estimate of ΔE_{deloc} is $+4.44$ kcal/mol, not far from the true value of ΔE_{deloc} of $+4.81$ kcal/mol.²⁴ Since this second-order estimate involves *vicinal* interactions within the *valence* atomic orbital (AO) space, we denote it as $\Delta E_{\text{w}}^{(2)}$ (see Table 2).

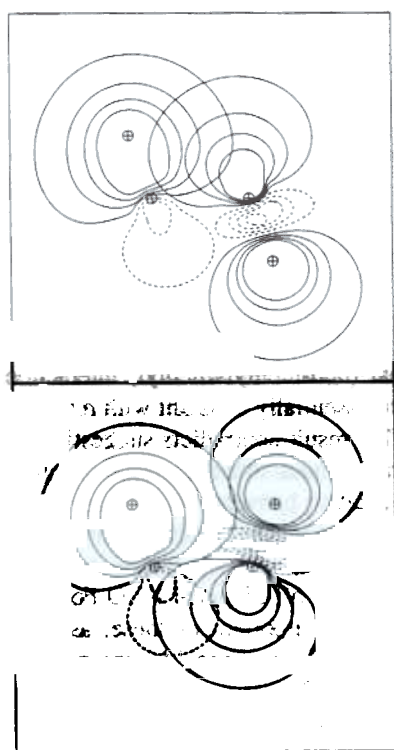


Fig. 1. Orbital contour diagrams of $\sigma_{\text{CH}} \rightarrow \sigma_{\text{CH}}^*$ NBO interaction for ethane (RHF/6-31G* level, idealized Pople–Gordon geometry), showing the more favorable interaction in *trans* (top) than in *cis* (bottom) arrangement. The plotted orbitals are “pre-NBOs” (cf. ref 23) whose overlaps reflect the strength of the associated NBO Fock matrix elements. Crosses mark the positions of in-plane H–C–C–H atomic nuclei.

The methyl–methyl interaction contribution to the barrier, $\Delta E_{\text{deloc}}^{(\text{vic})}$, can itself be decomposed by zeroing restricted sets of Fock matrix elements. The obvious starting point is to zero only the vicinal $\sigma_{\text{CH}}-\sigma_{\text{CH}}^*$ matrix elements, yielding a “valence vicinal” contribution $\Delta E_{\text{deloc}}^{(\text{v})}$ of $+5.40$ kcal/mol to the barrier. (The corresponding values $E_{\text{deloc}}^{(\text{v})}$ for the two conformations are given in Table 1.) Zeroing the major $\sigma_{\text{CH}} \rightarrow \text{C(Rydberg)}$ and $\text{C(core)} \rightarrow \text{C(Rydberg)}$ interactions changes this to $+4.40$ kcal/mol.²⁵ Thus, the contribution of interactions with Rydberg orbitals to the rotation barrier is not of great significance compared to the $\sigma_{\text{CH}} \rightarrow \sigma_{\text{CH}}^*$ contributions, even though the Rydberg interactions contribute around 10 kcal/mol to the value of $E_{\text{deloc}}^{(\text{vic})}$ (i.e., the Rydberg interactions have a much weaker orientational dependence). The conclusions that were drawn by Brunck and Weinhold concerning the origin of the ethane rotation barrier from semiempirical calculations are thus upheld at the *ab initio* SCF level using a reasonably large basis set (6-31G*).

There has been considerable controversy in the literature concerning bond orbital analysis of rotation barriers,^{26–32} particularly when nonorthogonal functions are employed. It was noted by Corcoran and Weinhold³³ that bond orbital formation does not commute with orthogonalization; that is, orthogonalizing a set of AOs and using these to form BOs is not the same as orthogonalizing the BOs formed from a set of nonorthogonal AOs (or, what is the same, simply using these nonorthogonal BOs in a single Slater determinant). The latter procedure, unfortunately, has often been preferred, but it corresponds (if the BOs are back-transformed to AOs) to using “atomic orbitals” that are grossly distorted with respect to the expected free-atom form, having “orthogonality tails” that are typically a factor of *two* greater than optimum (symmetric) orthogonalization would require.³⁴ Conclusions concerning the physical interpretation of such orbitals can therefore be grossly misleading, as discussed in ref 34.

Aufderheide²⁹ has criticized the Brunck–Weinhold picture on the basis that antibonds are an unfamiliar and unintuitive feature of valence theory. However, in the BO framework these functions are simply the unused parts of the atomic valence shells, unsaturated by covalent bond formation. As Dewar and Pettit³⁵ pointed out some years ago, neglect of antibonds in a BO formation is tantamount to partial neglect of AO valence space.

The vicinal $\sigma \rightarrow \sigma^*$ interactions leading to stabilization of staggered structures in ethane could be described as generalized donor–acceptor (“Lewis acid–base”) or “hyperconjugative”^{36,37} interactions, leading to departures from a strictly localized Lewis picture. It is inter-

sting that Mulliken himself was apparently the first to consider the possibility that the ethane rotation barrier might be due to sigma-type hyperconjugation (called "secondary hyperconjugation" in his terminology).³⁶ Unfortunately, he significantly underestimated the magnitude of this effect on the basis of a crude calculation (whereas "primary" hyperconjugation was often overestimated³⁸), and this apparently deterred consideration of the hyperconjugative hypothesis for some time.³⁹

3. OTHER ETHANE-LIKE MOLECULES

Analysis of the rotation barriers of methylamine and methanol yields results similar to that of the ethane case (see Tables 1 and 2): ΔE_{deloc} contributes much more strongly to the barrier ΔE than does ΔE_{Lewis} , these two contributions again being of opposite sign, and $\Delta E_{\text{deloc}}^{(\text{vic})}$ is close to ΔE_{deloc} , revealing again that the barrier is determined by *vicinal*, as opposed to *geminal*, interactions. In addition, ΔE_{deloc} is also roughly equal to $\Delta E_{\text{deloc}}^{(\text{vic})}$ and to $\Delta E_{\text{deloc}}^{(\text{w})}$, where the "valence vicinal" interactions now include $n \rightarrow \sigma^*$ as well as $\sigma \rightarrow \sigma^*$. The $\sigma_{\text{CH}} \rightarrow \sigma_{\text{NH}}^*$, $\sigma_{\text{NH}} \rightarrow \sigma_{\text{CH}}^*$, $\sigma_{\text{CH}} \rightarrow \sigma_{\text{OH}}^*$, and $\sigma_{\text{OH}} \rightarrow \sigma_{\text{CH}}^*$ interactions have magnitudes and dihedral angle dependences that are similar to those of the $\sigma_{\text{CH}} \rightarrow \sigma_{\text{CH}}^*$ interactions of ethane, as judged from the second-order estimates. For all these vicinal $\sigma \rightarrow \sigma^*$ interactions, $E^{(2)}(0^\circ)$ ranges from -0.1 to -0.8 kcal/mol, and $E^{(2)}(180^\circ)$ from -3.1 to -3.5 kcal/mol, going through a minimum in magnitude of around -0.05 kcal/mol in the region of 60 – 90° and sharply increasing in magnitude from 120 to 180° . The total $\sigma \rightarrow \sigma^*$ contributions to the barriers are therefore roughly proportional to the number of *trans* $\sigma \rightarrow \sigma^*$ interactions in the staggered conformer, these being $+4.44$ kcal/mol in CH_3CH_3 (six *trans* $\sigma \rightarrow \sigma^*$), $+2.84$ kcal/mol in CH_3NH_2 (four *trans* $\sigma \rightarrow \sigma^*$), and $+1.19$ kcal/mol in CH_3OH (two *trans* $\sigma \rightarrow \sigma^*$), according to the second-order estimates. Note that these $\sigma \rightarrow \sigma^*$ estimates are each nearly equal to the corresponding values of ΔE_{deloc} and that the barriers can thus be crudely estimated on the basis of these interactions alone.

Indeed, the roughly 3:2:1 ratio between the experimental barrier values (2.9, 2.0, 1.1 kcal/mol)^{20,40,41} (which is also reflected in the corresponding HF/6-31G* ΔE_{deloc} values: 4.8, 3.0, 1.4 kcal/mol), for the series CH_3CH_3 , CH_3NH_2 , and CH_3OH , appears to have its origin in the 6:4:2 ratio of the number of *trans* $\sigma \rightarrow \sigma^*$ interactions in the staggered conformations of these species. The reason that this occurs is that the $n \rightarrow \sigma^*$ interactions in these species give only slight contributions to the rotation barriers, the second-order estimates of the total vicinal $n \rightarrow \sigma^*$ contributions to ΔE_{deloc} being $+0.14$ and $+0.16$ kcal/mol in CH_3NH_2 and

CH_3OH , respectively. This behavior is somewhat surprising, given the fact that the *trans* $n \rightarrow \sigma^*$ interactions in these cases are around 2–3 times stronger than the *trans* $\sigma \rightarrow \sigma^*$ interactions, and arises from the fact that the *cis* $n \rightarrow \sigma^*$ interactions are quite significant, in contrast to *cis* $\sigma \rightarrow \sigma^*$ interactions. In CH_3NH_2 , for example, the second-order estimates of the $n \rightarrow \sigma_{\text{CH}}^*$ interaction, as a function of the n – σ^* dihedral angle, are -6.18 (0°), -4.39 (30°), -1.26 (60°), -0.03 (90°), -2.41 (120°), -6.6 (150°), and -8.62 kcal/mol (180°).⁴² The origin of the strong *cis* $n \rightarrow \sigma^*$ interaction is presumably related to the value of the n – σ^* overlap integral,²³ the nodal surface of the antibond causing less cancellation with the lone pair (compacted toward the rotor axis) than with a corresponding two-center bond orbital.

It would seem, however, that the possibility of a negligible influence of $n \rightarrow \sigma^*$ interactions on conformational preference is limited to cases involving methyl groups. Placement of electronegative substituents on the methyl group or replacement of carbon with nitrogen or oxygen (with consequent loss of one or two vicinal antibonds), leads to a strong influence of $n \rightarrow \sigma^*$ (particularly, $n \rightarrow \sigma_{\text{CX}}^*$, X being an electronegative element) interactions on the conformational preference, as was found by Brunck and Weinhold. They pointed out already in 1976 that the drive toward maximization of the number of *trans* $n \rightarrow \sigma_{\text{CX}}^*$ interactions is the simple origin of the *gauche* effect.

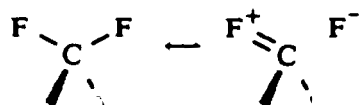
Tossell et al.⁴³ have presented evidence for the preferential delocalization of the nitrogen lone pair in methylamine onto the methyl hydrogen *trans* to the lone pair lobe, based on electronic momentum distributions inferred through (e, 2e) spectroscopy. This is the direct experimental manifestation of the $n \rightarrow \sigma^*$ hyperconjugation interactions discussed above. Other evidence for stereoelectronically specific influence of lone pairs on adjacent saturated groups is provided by NMR and IR spectroscopic structure studies⁴⁴ as well as by extensive solution kinetic and reactivity data.⁴⁵

4. BOND STRENGTHENING IN FLUOROMETHANES

Though CH_3F , the final molecule of the "methyl series," cannot have a rotation barrier, significant $n \rightarrow \sigma^*$ stabilization should nevertheless be present, just as in CH_3NH_2 and CH_3OH . This molecule, and its polyfluorinated analogs CH_2F_2 , CHF_3 , and CF_4 , are interesting to consider in the present context.

In 1937 Brockway⁴⁶ introduced the concept of "double bond–no bond" resonance to explain the fact that the carbon halogen bonds in polyhalogenated methanes are shorter than those in the parent methyl halides. This concept invoked resonance between the molecular Le-

wis structure and resonance structures in which one halogen is double bonded, having a formal positive charge, another halogen being unbonded and having a formal negative charge, viz.,



In the polyfluoromethanes, there are associated increases of C–F bond energies with increased fluorine substitution which also seem explainable on the basis of double bond–no bond resonance.⁴⁷ Lucken⁴⁸ presented an MO counterpart of this model, using it to interpret the anomalously low, nuclear-quadrupole resonance frequencies of ³⁵Cl found in chlorofluoromethanes and in a number of chlorine-containing ethers, sulfides, fluorides, alkenes, and alkynes. This MO treatment focused on the interaction of a p orbital of the *geminal* substituent (O, S, F, C=C, C≡C) with the carbon–chlorine antibonding σ^* orbital. To rationalize the trends of C–F bond-length and bond-energy in the polyfluoromethanes, Williams⁴⁹ applied Lucken's⁴⁸ $n \rightarrow \sigma^*$ MO (i.e., as opposed to valence-bond) description of double bond–no bond resonance, the lone pair n being a p_x lone pair on fluorine, and considered $n \rightarrow \sigma_{\text{CF}}^*$ interactions to be stronger than $n \rightarrow \sigma_{\text{CH}}^*$. Such a picture of the bonding in these species has been reinforced by a perturbational MO (PMO) treatment of Wolfe et al.⁵⁰ and has been widely discussed by other workers (e.g., refs 51–54).

With the NBO analysis methods, the importance of these interactions can be quantitatively examined, and we therefore computed HF/6-31G* wave functions for the series CH_4 , CH_3F , CH_2F_2 , CHF_3 , CF_4 at ideal geome-

tries¹⁸ (i.e., tetrahedral bond angles and bond lengths of 1.09 Å and 1.36 Å for C–H and C–F, respectively). Table 3 depicts the occupancy depletion of the fluorine p_x (or n_x) lone pairs and the consequent occupancy increase of the σ^* orbitals found in the NBO analyses, along with the trends in the occupancies of the other NBOs. In CH_3F , the second-order estimate of the $p_x \rightarrow 3\sigma_{\text{CH}}^*$ interaction energy of one fluorine p_x lone pair with the three vicinal σ_{CH}^* orbitals is –14 kcal/mol, compared to the corresponding estimate of –26 kcal/mol for each $p_x \rightarrow 3\sigma_{\text{CF}}^*$ interaction in CF_4 . Thus, $n_F \rightarrow \sigma_{\text{CF}}^*$ is about twice as strong as $n_F \rightarrow \sigma_{\text{CH}}^*$. This is consistent with the Brinck–Weinhold finding that the more polar σ_{CF}^* can interact more strongly with vicinal lone pairs than σ_{CH}^* due to stronger antibond amplitude on carbon and the consequent opportunity for increased lone-pair overlap.²³ In addition, the $p_x \rightarrow \sigma_{\text{CF}}^*$ energy difference is somewhat less than that of $p_x \rightarrow \sigma_{\text{CH}}^*$: 1.14 vs. 1.33 a.u., for example, in CH_2F_2 at the HF/6-31G* level.⁵⁵

From their PMO analysis of this series of compounds, Wolfe et al.⁵⁰ concluded that lone-pair antibond stabilization accounted for the progressive increase of C–F bond energy with increased fluorine substitution. The cause of the C–F bond shortening with increased substitution, however, has been somewhat more controversial.⁵⁰ The role played by $n \rightarrow \sigma^*$ interactions in this effect is somewhat ambiguous since not only are partial C–F π bonds being formed, but also the C–F σ antibonds are being strongly occupied. A more complete analysis⁵⁶ reveals a complex interplay of hyperconjugative and inductive effects, with the most important role being played by electron-withdrawing fluorines in reducing the effective covalent radius of carbon.

Table 3. Individual NBO Occupancies and Percent Occupancy of Lewis Structure for the Series CH_xF_y , HF/6-31G* Level, Ideal Geometries^a

Parameter	CH_4	CH_3F	CH_2F_2	CHF_3	CF_4
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^aSince there are 10 Rydberg (Ryd.) NBOs on each C and F atom, only the total Rydberg occupancies are given. Note the dramatic decrease in the % Lewis occupancy with increasing fluorination.

5. ANOMERIC AND RELATED EFFECTS

Closely related is the set of problems in carbohydrate chemistry associated with the anomeric effect.⁵² This refers to the tendency of an electronegative substituent at the anomeric (C_1) center of a pyranoid ring to assume the axial rather than equatorial orientation, in contrast to what would be expected on the basis of steric considerations. Jeffrey and co-workers⁵⁷ suggested that there might be a connection between the anomeric effect and the observed shortening of the C_1-O_1 bonds of pyranose sugars. Crystallographic studies of halogenated 1,4-dioxanes, dithianes, and thioxanes at Leiden also showed "anomeric effects" on conformation and bond lengths, the C_1-O_1 bonds again being shortened and the axial anomeric-carbon-halogen bond being lengthened.⁵⁸ Altona⁵⁹ used the Lucken model to rationalize these anomeric effects. This orbital interaction model has since gained fairly wide (but not universal)^{22,60} acceptance.⁶¹ Within the orbital interaction model, the anomeric effect can be seen to be equivalent to negative hyperconjugation and to the *gauche* effect.⁶²

There is in addition abundant evidence of a kinetic anomeric effect.^{45,52} Indeed, Deslongchamps⁴⁵ has come to the conclusion that "the reactivity of most types of organic molecules depends upon relative *stereochemistry of particular electron pairs, bonded or nonbonded*.... It is also through the concept of *stereoelectronic effects* that it becomes possible to acquire the knowledge of the stereochemistry of the transition states of most chemical reactions." He also points out the relevance that this has in biological processes: "...a much deeper understanding of the events (in three dimensions) which take place during an enzyme-catalyzed process is gained through the application of stereoelectronic principles." Belleau and collaborators⁶³ have proposed that stereoelectronic effects about the basic nitrogen of morphinans play an important role in the interaction of these molecules with the analgesic receptors and the induction of analgesia. Kirby⁵² has pointed out the relationship between the anomeric effect and the Elcb reaction mechanism, illustrated by the example of the instability of the fluoroethyl anion,⁶⁴ a case of very strong negative hyperconjugation.⁶⁵

6. DISCUSSION

The Brunck-Weinhold picture of ethane-like barriers is closely related to the concept of "second-order hyperconjugation,"³⁶ as formulated in a bond-orbital framework. Unlike steric models of the barrier, such as the Pauli-repulsions model of Sovers et al.,^{16,20} it emphasizes the *stabilizing* effect of sigma delocalization in staggered conformations rather than the "repulsions" of eclipsed groups. Particular importance is attached to the role of

antibonds as acceptor orbitals for the intramolecular donor-acceptor delocalization. We have shown that this general hyperconjugative picture is upheld at the ab initio level and is supported by a wealth of other experimental and theoretical evidence pertaining to sigma-delocalization effects.

We have also provided additional examples to contradict the central premise of the Pauli-repulsions model,^{16,20} namely, that satisfaction of the Pauli principle is sufficient to give reasonable barrier values for any BO or MO wave function. On the contrary, as shown in Tables 1 and 2, properly antisymmetrized wave functions for ethane-like molecules typically lead to barriers of the wrong sign if $\sigma \rightarrow \sigma^*$ interactions are deleted, even if the calculated energies and densities are very close (>99.9%) to the full SCF values. Such examples may be multiplied at will.

We mention an additional failure of the steric-repulsions model and its variants, which stems from experimental investigation of torsion-vibration coupling effects in overtone states of hydrogen peroxide.⁶⁶ In a steric-repulsions picture of X-A-A-X torsions, one would suppose that the X-A-A-X barrier is reduced if the distance between the repelling groups X...X is increased, as by stretching an A-X bond. However, Döbal and Crim⁶⁶ found compelling experimental evidence for a dramatic *increase* in the *trans* rotation barrier of hydrogen peroxide upon vibrational overtone excitation (up to $v = 5$ in the OH stretch). This result, though paradoxical from a "repulsions" point of view, is readily understood from the hyperconjugative $\sigma \rightarrow \sigma^*$ picture (the σ^* energy being lowered by bond stretching, so that the stretched σ^* becomes a better acceptor) and is well reproduced by accurate ab initio calculations and NBO analysis.⁶⁷

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REFERENCES

- (1) Kemp, J.D.; Pitzer, K.S. *J. Chem. Phys.* 1936, 4: 749; *J. Am. Chem. Soc.* 1937, 59: 276.
- (2) Wilson, E.B., Jr. *Adv. Chem. Phys.* 1959, 2: 367 and references therein.
- (3) Radom, L.; Hehre, W.J.; Pople, J.A. *J. Am. Chem. Soc.* 1972, 94: 2371.
- (4) Lowe, J.P. *Science* 1973, 179: 527.
- (5) Orville-Thomas, W.J., Ed. *Internal Rotation in Molecules*; Wiley: New York, 1974.

- (6) Brunck, T.K.; Weinhold, F. *J. Am. Chem. Soc.* 1979, 101: 1700.
- (7) Brunck, T.K. Ph.D. Thesis; Stanford University, 1976. For related treatments see also Gavezzotti, A.; Bartell, L.S. *J. Am. Chem. Soc.* 1979, 101: 5142; Tyrrell, J.; Weinstock, R.B.; Weinhold, F. *Int. J. Quantum Chem.* 1981, 19: 781; Wesenberg, G.; Weinhold, F. *Int. J. Quantum Chem.* 1982, 21: 487. Note that Klessinger (Klessinger, M. *Croat. Chem. Acta* 1983, 56: 397; cf. also Klessinger, M. *J. Chem. Phys.* 1970, 53: 225) concurs that the ethane barrier is mainly of $\sigma \rightarrow \sigma^*$ origin (though, using a fragment MO approach, he refers to the interaction as being of $\pi \rightarrow \pi^*$ type). For a discussion of Klessinger's result, cf. also Herigonte, P. *Struct. Bonding (Berlin)* 1972, 12: 1.
- (8) (a) Brunck, T.K.; Weinhold, F. *University of Wisconsin Theoretical Chemistry Institute Report WIS-TCI-560* 1976, unpublished. (b) Weinhold, F. *QCPE* 1980, 13: 408.
- (9) Foster, J.P.; Weinhold, F. *J. Am. Chem. Soc.* 1980, 102: 7211.
- (10) Reed, A.E.; Weinhold, F. *J. Chem. Phys.* 1983, 78: 4066.
- (11) Reed, A.E.; Weinstock, R.B.; Weinhold, F. *J. Chem. Phys.* 1985, 82: 2679.
- (12) Reed, A.E.; Weinhold, F. *QCPE Bull.* 1985, 5: 141.
- (13) (a) Reed, A.E.; Curtiss, L.A.; Weinhold, F. *Chem. Rev.* 1988, 88: 899. (b) Weinhold, F.; Carpenter, J.E. In *The Structure of Small Molecules and Ions*; Naaman, R.; Vager, Z., Eds.; Plenum Press: New York, 1988; p. 227.
- (14) The current situation is perhaps best summarized by Houk et al. (ref 15), who refer to "the forever controversial question of the source of the rotational barrier in ethane," stating that "The explanation of this fundamental effect has been narrowed down to two viewpoints: (1) the eclipsed conformation is destabilized by four-electron repulsions (closed-shell overlap repulsion arising from the Pauli exclusion principle) between vicinal bonds, which have greater overlap in the eclipsed conformation (ref 16 is cited), or (2) the staggered conformation is more stabilized by the antiperiplanar arrangement of six σ_{CH} orbitals with respect to six σ_{CH}^* orbitals. In the eclipsed conformations, these overlaps are of the smaller syn-periplanar variety (refs 6 and 17 are cited). As a third alternative, both of these effects may contribute to some extent (ref 17 is cited)."
- (15) (a) Houk, K.N.; Rondan, N.G.; Brown, F.K. *Isr. J. Chem.* 1983, 23: 3. (b) Houk, K.N.; Rondan, N.G.; Brown, F.K.; Jorgensen, W.L.; Madura, J.D.; Spellmayer, C.D. *J. Am. Chem. Soc.* 1983, 105: 5981.
- (16) Sovers, O.J.; Kern, C.W.; Pitzer, R.M.; Karplus, M. *J. Chem. Phys.* 1968, 49: 2592.
- (17) Lowe, J.P. *J. Am. Chem. Soc.* 1970, 92: 3799.
- (18) 6-31G* basis: Hehre, W.J.; Ditchfield, R.; Pople, J.A. *J. Chem. Phys.* 1972, 56: 2257; Hariharan, P.C.; Pople, J.A. *Theor. Chim. Acta* 1972, 28: 213. 4-31G basis: Ditchfield, R.; Hehre, W.J.; Pople, J.A. *J. Chem. Phys.* 1971, 54: 724. The calculations in this work were carried out with the GAUSSIAN 82 program system: Binkley, J.S.; Frisch, M.J.; DeFrees, D.J.; Raghavachari, K.; Whiteside, R.W.; Schlegel, H.B.; Pople, J.A. *GAUSSIAN 82 (release H version)*; Carnegie-Mellon University, 1984. For simplicity, all calculations were carried out with idealized Pople-Gordon geometries (Pople, J.A.; Gordon, M. *J. Am. Chem. Soc.* 1967, 89: 4253), since geometry optimization is generally found (see, e.g., ref 5) to have a relatively minor effect on calculated barriers.
- (19) Deletion of orbitals or Fock matrix elements is a standard program option of the general NBO program;¹² cf. ref 10. Deletion of all non-Lewis orbitals ("NOSTAR" option) by this method corresponds rigorously to the variational expectation value of the determinant of doubly occupied Lewis NBOs. When only some of the non-Lewis orbitals are deleted by the single-pass Fock matrix deletion method, the result is not strictly equivalent to the variational result of removing these basis functions from the SCF calculation. However, Weinstock has shown (Weinstock, R.B. Ph.D. Thesis; University of Wisconsin, 1981) for the case of the water dimer that a procedure of transforming the integrals into the NBO basis and doing an SCF calculation in the truncated basis set led to results within 0.1 kcal/mol of that obtained with the single-pass method.
- (20) Pitzer, R.M. *Acc. Chem. Res.* 1983, 16: 207.
- (21) Musso, G.F.; Magnasco, V. *J. Chem. Soc. Faraday Trans.* 1982, 78: 1609; *Chem. Phys. Lett.* 1984, 111: 468; *Mol. Phys.* 1984, 53: 615.
- (22) Dewar, M.J.S. *J. Am. Chem. Soc.* 1984, 106: 669.
- (23) Fock matrix interaction elements can be roughly estimated on the basis of overlap integrals between nonorthogonal "pre-NBOs" (omitting interatomic orthogonalizations), closely related to simple orbital diagrams. This is the bond-orbital equivalent of the Mulliken approximation. Thus, although the actual NBOs are strictly orthonormal, we may speak informally of the "overlap" between NBOs as a measure of their Fock matrix interaction elements.
- (24) In our experience, the second-order estimates $E^{(2)}$ display a typical accuracy of around 10–20% when the energies are in the range of 0.1 to 20 kcal/mol; due to third- and higher-order effects, they display a certain degree of nonadditivity.
- (25) Since the energies from the Fock matrix deletions are strictly variational only when all Fock matrix elements connecting Lewis and non-Lewis NBOs are set to zero (ref 19) and will become "less variational" as fewer elements are zeroed, small energy differences (on the order of a few tenths of a kcal/mol) from different deletions should be interpreted with caution. Thus, the difference between the -4.4 kcal/mol figure quoted here and the -4.8 kcal/mol value of ΔE_{deloc} is probably

- not significant.
- (26) Whangbo, M.-W.; Schlegel, H.B.; Wolfe, S. *J. Am. Chem. Soc.* 1977, **99**: 1296.
 - (27) Morokuma, K.; Umeyama, H. *Chem. Phys. Lett.* 1977, **49**: 333.
 - (28) Musso, G.F.; Magnasco, V. *J. Chem. Soc. Faraday Trans.* 1982, **78**: 1609; *Chem. Phys. Lett.* 1984, **111**: 468; *Mol. Phys.* 1984, **53**: 615.
 - (29) Aufderheide, K.H. *Croat. Chem. Acta* 1984, **57**: 811.
 - (30) Allen, L.C.; Basch, H. *J. Am. Chem. Soc.* 1971, **93**: 6373.
 - (31) Surján, P.R. *Croat. Chem. Acta* 1983, **56**: 289.
 - (32) See also ref 16 and the discussion in refs 6 and 7. Surján (ref 31) has recognized the mathematical problem involved, but does not prefer one treatment over the other, stating that "there exists no unique explanation to the origin of barrier forces, because the same physical effect can be described by different 'reasons' in different mathematical frameworks." We believe there are substantive conceptual reasons for rejecting "mathematical frameworks" and "explanations" based intrinsically on the use of nonorthogonal orbitals (ref 34).
 - (33) Corcoran, C.T.; Weinhold, F. *J. Chem. Phys.* 1980, **72**: 2866.
 - (34) Weinhold, F.; Carpenter, J.E. *J. Mol. Struct. (Theor. Chem.)* 1988, **165**: 189.
 - (35) Dewar, M.J.S.; Pettit, R. *J. Chem. Soc.* 1954: 1625.
 - (36) (a) Mulliken, R.S. *J. Chem. Phys.* 1939, **7**: 339. (b) Mulliken, R.S.; Rieke, C.A.; Brown, W.G. *J. Am. Chem. Soc.* 1941, **63**: 41.
 - (37) (a) Hirsch, J.A. *Concepts in Theoretical Organic Chemistry*; Allyn and Bacon: Boston, 1974. (b) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976; pp. 80–85. (c) Gold, V. *Pure Appl. Chem.* 1979, **51**: 1760.
 - (38) Dewar, M.J.S. *Hyperconjugation*; Ronald Press Company: New York, 1962.
 - (39) cf. Coulson, C.A.; Crawford, V. *J. Chem. Soc.* 1953: 2052; Loftus, A. *J. Am. Chem. Soc.* 1957, **79**: 24.
 - (40) Methylamine: Lide, D.R., Jr. *J. Chem. Phys.* 1957, **27**: 343.
 - (41) Methanol: Ivash, V.; Dennison, D.M. *J. Chem. Phys.* 1953, **21**: 1804.
 - (42) The situation is more complicated in methanol since the two oxygen lone pair NBOs are not equivalent (one is of pure p character and the other is $sp^{1.1}$, with slightly different occupancies).
 - (43) Tossell, J.A.; Lederman, S.M.; Moore, J.H.; Coplan, M.A.; Chornay, D.J. *J. Am. Chem. Soc.* 1984, **106**: 976.
 - (44) See, e.g., Forsyth, D.A.; Yang, J.-R. *J. Am. Chem. Soc.* 1985, **108**: 2167.
 - (45) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon Press: New York, 1983.
 - (46) Brockway, L.O. *J. Phys. Chem.* 1937, **41**: 185.
 - (47) (a) Patrick, C.R. *Adv. Fluorine Chem.* 1961, **2**: 1.
 - (b) Hine, J. *J. Am. Chem. Soc.* 1963, **85**: 3239.
 - (48) Lucken, E.A.C. *J. Chem. Soc.* 1959: 2954.
 - (49) Williams, J.F.A. *Trans. Faraday Soc.* 1961, **57**: 2089.
 - (50) Wolfe, S.; Whangbo, M.-H.; Mitchell, D.J. *Carbohydr. Res.* 1979, **69**: 1.
 - (51) Epiotis, N.D.; Cherry, W.R.; Shaik, S.; Yates, R.L.; Bernardi, F. *Structural Theory of Organic Chemistry; Top. Curr. Chem.* 1977, **70**: 1.
 - (52) Kirby, A.J. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*; Springer-Verlag: Berlin, 1983.
 - (53) Schleyer, P.v.R. *Jeremy Musher Lecture on Hypervalent Molecules*; Jerusalem, 1985 (private communication).
 - (54) See, e.g., (a) David, S.; Eisenstein, O.; Hehre, W.J.; Salem, L.; Hoffmann, R. *J. Am. Chem. Soc.* 1973, **95**: 3806; Schleyer, P.v.R.; Kos, A.J. *Tetrahedron* 1983, **39**: 1141. (b) Eisenstein, O.; Anh, N.T.; Jean, Y.; Devaquet, A.; Cantacuzene, J.; Salem, L. *Tetrahedron* 1974, **30**: 1717; Lehn, J.-M.; Wipff, G. *J. Am. Chem. Soc.* 1976, **98**: 7498; Jeffrey, G.A.; Yates, J.H. *J. Am. Chem. Soc.* 1979, **101**: 820.
 - (55) With increasing fluorination, the various n , σ , and σ^* NBO orbital energies each decrease significantly (by on the order of 0.10 a.u. from CH_3F to CF_4), but the $p_n \rightarrow \sigma^*$ energy differences remain relatively constant.
 - (56) Reed, A.E.; Schleyer, P.v.R. *J. Am. Chem. Soc.* 1987, **109**: 7362.
 - (57) Berman, H.M.; Chu, S.S.C.; Jeffrey, G.A. *Science* 1967, **157**: 1576.
 - (58) (a) Altona, C.; Knobler, C.; Romers, C. *Acta Crystallogr.* 1963, **16**: 1217. (b) Altona, C.; Romers, C. *Acta Crystallogr.* 1963, **16**: 1225. (c) Altona, A.; Romers, C. *Rec. Trav. Chim.* 1963, **85**: 1080. (d) de Wolf, N.; Romers, C.; Altona, C. *Acta Crystallogr.* 1967, **22**: 715.
 - (59) (a) Altona, C. Ph.D. Thesis; University of Leiden, 1964. (b) Romers, C.; Altona, C.; Buys, H.R.; Havinga, E. *Top. Stereochem.* 1969, **4**: 39.
 - (60) Eliel, E.L.; Allinger, N.L.; Angyal, S.J.; Morrison, G.A. *Conformational Analysis*; Am. Chem. Soc.: Washington, 1981.
 - (61) See refs 45, 51, 52, 54; *The Anomeric Effect: Origin and Consequences*; *Am. Chem. Symp. Ser.*, Vol. 87; Szarek, W.A.; Horton, D., Eds.; Am. Chem. Soc.: Washington, 1979.
 - (62) See refs 45, 50, 52, 54a and references therein.
 - (63) Belleau, F. In *Chemical Regulation of Biological Mechanism*; Burlington House: Cambridge, 1982.
 - (64) Bach, R.D.; Badger, R.C.; Lang, T.J. *J. Am. Chem. Soc.* 1979, **101**: 2845.
 - (65) See, e.g., Schleyer and Kos, ref 54a.
 - (66) Dúbal, H.-R.; Crim, F.F. *J. Chem. Phys.* 1985, **83**: 3863.
 - (67) Carpenter, J.E.; Weinhold, F. *J. Phys. Chem.* 1988, **92**: 4295, 4307.