Bond Orbitals and Intramolecular Interactions. 1. Barriers to Rotation and Nonbonded Interactions

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Abstract: Hypotheses of Brunck and Weinhold (BW) concerning the origin of barriers to internal rotation are examined in the light of BW's bond-orbital approach. Predictions by BW, based on an INDO study with an implicitly orthogonal AO set, are tested using nonorthogonal AOs in the framework of extended Hückel theory. In accordance with these predictions, we find that the stability of staggered relative to eclipsed conformations of ethane and other simple compounds is lost when σ/σ^* mixing is prevented by deletion of antibond basis orbitals, provided that basis orbitals are Löwdin orthogonalized. As forecast by BW, however, the barrier is little affected when σ^* orbitals are deleted if nonorthogonalized basis σ and σ^* orbitals are adopted. Our results are, then, substantially in accord with the BW interpretation of the σ/σ^* interaction origin of the barrier except as follows. Their original suggestion that the effect reduces to an intrinsic difference, mediated by σ/σ^* interactions, between cis and trans stabilities is not, by itself, a complete rationale for threefold barriers. The BW scheme of employing orthogonalized bond orbitals as basis orbitals is shown to have several interpretational advantages. It is found, among other things, that intramolecular nonbonded atom-atom interactions reduce to the form popularly associated with nonbonded repulsions only when through-bond effects are shut off by deleting σ^* basis orbitals.

I. Introduction

In recent papers[2] Brunck and Weinhold (BW) proposed an appealingly simple model, based on a linear combination of bond orbital-molecular orbital (LCBO-MO) approach, to explain the origin of the forces acting during rotation about single bonds. They state that this approach makes it possible to identify the essential interactions among bond orbitals that are ultimately responsible for the existence of the barrier to internal rotation. Moreover, they claim that the effect is so elemental that it should survive progressively drastic semiempirical modifications of the SCF-MO theory and, hence, be well represented in any reasonably realistic version of the LCAO-MO theory.

One such simple theory that has enjoyed wide success in studies of molecular geometry and conformation is extended Hückel theory (EHT).[3] It is therefore a natural model to examine in the light of the BW analysis. Since it was parameterized from the beginning to reproduce the experimental barrier for ethane there is little to be learned about magnitudes of barriers from such a study. Instead we seek to test whether the diagnosis of Brunck and Weinhold applies to such a simple LCAO-MO model. An additional incentive is to test the BW analysis with an AO basis that is explicitly nonorthogonal; the basis was implicitly orthogonal in the INDO SCF-MO approximation studied by BW.

II. Theory

Basis Transformations. The following paragraphs give a brief account of the transformations from a Slater atomic orbital (STO) basis to hybrid atomic orbitals (HAO) to bond orbitals (BO). Orbital orthogonality, a problem which is crucial to BW's argument, is also discussed. The treatment is restricted to valence s and p orbitals, and follows essentially the lines of ref 2.

Combinations of STOs to yield hybrids of various composition and directions can be performed on the basis of geometrical considerations, given the appropriate mixing ratios of s and p, and using orthonormality conditions. Examples of such procedure can be found in ref 4. Bond orbitals can then be generated, together with their antibond partners, by forming normalized linear combinations

$$(\phi_{\mathrm{BO}})_{ij} = N_{ij}[(\phi_{\mathrm{HAO}})_i + (\phi_{\mathrm{HAO}})_j]$$

$$(\phi_{\mathrm{BO}}^*)_{ij} = N_{ij}^*[(\phi_{\mathrm{HAO}})_i - (\phi_{\mathrm{HAO}})_j]$$

of couples of hybrids centered on different atoms and appropriately directed along the bond directions. Orbitals not implied in such couplings remain as nonbond orbitals (such as the lone pairs on oxygen or nitrogen). Let **A** be a block-diagonal matrix transforming from STOs to HAOs, and **T** a matrix transforming from HAOs to BOs. Then

$$\phi_{\mathrm{HAO}} = \mathbf{A}\phi_{\mathrm{STO}}$$

$$\phi_{\mathrm{BO}} = \mathbf{T}\phi_{\mathrm{HAO}} = \mathbf{TA}\phi_{\mathrm{STO}} \equiv \mathbf{F}\phi_{\mathrm{STO}}$$

Therefore, any matrix in an MO calculation can be transformed from the ϕ_{STO} to the ϕ_{BO} basis by

$$\mathbf{S}_{\mathrm{BO}} = \mathbf{F}\mathbf{S}_{\mathrm{STO}}\mathbf{F}^{\dagger}$$

$$\mathbf{H}_{\mathrm{BO}} = \mathbf{F}\mathbf{H}_{\mathrm{STO}}\mathbf{F}^{\dagger} \qquad (1)$$

Overlap and Orthogonality. Both the ϕ_{STO} and the ϕ_{BO} overlap considerably. EHT uses the overlap matrix elements over STOs to estimate the **H** matrix elements, by one of several recipes. In the present study the common formula

$$(H_{ij})_{\mathrm{STO}} = \frac{1}{2}K(H_{ii} + H_{jj})(S_{ij})_{\mathrm{STO}} \qquad (2)$$

for off-diagonal elements is adopted, the diagonal elements of the **H** matrix being approximated by the valence orbital ionization potentials (VOIPs) of the orbital under consideration. However, if the transformation

$$\mathbf{H}_{\mathrm{BO}} = \mathbf{F}\mathbf{H}_{\mathrm{STO}}\mathbf{F}^{\dagger} \qquad (3)$$

is carried out, then

$$(H_{ij})_{\mathrm{BO}} \neq \frac{1}{2}K(H_{ii} + H_{jj})_{\mathrm{BO}}(S_{ij})_{\mathrm{BO}}$$

In testing the BW hypothesis it is necessary that the basis functions be orthogonal in order to make their contributions independent. Therefore, a Löwdin orthogonalization of the basis functions is performed. This can be done[5] by a transformation represented by matrix $\mathbf{S}_{\mathrm{BO}}^{-1/2}$ such that

$$\mathrm{I} = \mathbf{S}_{\mathrm{BO}}^{-1/2}\mathbf{S}_{\mathrm{BO}}\mathbf{S}_{\mathrm{BO}}^{-1/2} \qquad (4)$$

MO Calculations in Various Basis Sets. Truncation. Our procedure starts by calculating the overlap matrix $\mathbf{S}_{\mathrm{STO}}$, and from this the $\mathbf{H}_{\mathrm{STO}}$ matrix according to eq 2. Then the transformations (1) are performed, and, if desired, the orthogonalization. All the transformations being such that the eigen-

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Table I. Slater Exponents, VOIPs, and Bond Distances Used in the Calculations

	Slater Exponents and VOIPs	s	p
C	1.625	−21.4	−11.4
H	1.25	−13.6	
N	1.95	−27.5	−14.49
O	2.275	−35.5	−17.76
F	2.6	−34.5	−12.96
	Bond Distances (Å)		
C-H	1.10	C-N	1.48
C-C	1.54	O-H	0.96
C-F	1.20	N-H	1.014
C-O	1.427		

values of the secular matrix are unchanged, they do not affect the total electronic energy.

An interesting feature of the basis sets ϕ_{HAO} and ϕ_{BO} is that some of the basis functions can be excluded from the basis set, the resulting truncation being chemically meaningful. That is, it is feasible to suppress certain bonds or antibonds, or unneeded hybrids in cases in which not all the ordinary valences of an atom are saturated. This would of course be impossible to accomplish in an ordinary STO basis set. Accompanying a truncation is a modification of the total energy. This change is useful in diagnosing the source of various electronic interactions according to BW. Once it is decided which basis functions are to be excluded, the secular equation

$$(\mathbf{H}_{\mathrm{BO}} - E_i\mathbf{S}_{\mathrm{BO}})\mathbf{C}_{i\mathrm{BO}} = 0$$

is solved, in which the size of each matrix has been reduced by whatever truncation is involved. The $\mathbf{C}_{i\mathrm{BO}}$ can be back-transformed to wave functions over STOs by

$$\mathbf{C}_{i\mathrm{STO}} = \mathbf{F}^{\dagger}\mathbf{C}_{i\mathrm{BO}} \tag{5}$$

In case of truncation, only the appropriate rectangular block of $\mathbf{F}^{\dagger}$ will be needed.

Population Analysis. By performing a Mulliken population analysis[6] over the $\mathbf{C}_{i\mathrm{BO}}$, the charges in each bond orbital can be calculated. These quantities should be approximately 2 for occupied nonbonds and bond orbitals, and approximately zero for antibonds, in ordinary molecules. Larger deviations from these values occur as molecules are distorted from equilibrium, if the bond orbitals are not orthogonalized, or if the electronegativity difference between bound atoms increases (in the present work no polarization parameter was allowed in forming the bond combinations between hybrids involving different atoms). An energy-weighted population analysis (EWPA)

$$\epsilon_{\mu\nu} = \sum_{\mathrm{occ}} N(i)C_{i\mu\mathrm{BO}}C_{i\nu\mathrm{BO}}H_{\mu\nu\mathrm{BO}} \tag{6}$$

where the sum over the $\epsilon_{\mu\nu}$ elements adds up to the total energy, can quantify the interaction between atomic orbitals or bond orbitals in a given molecule. Of course, after the back-transformation (5) has been performed the ordinary Mulliken population analysis can be carried out over wave functions in terms of STOs, to give bond overlap populations. By an analogous energy-partitioning procedure, an EWPA can be carried out on atomic orbitals via

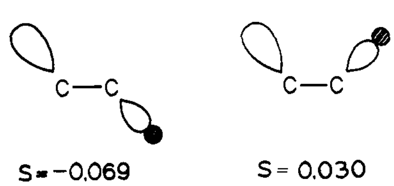


Figure 1. Trans and cis σ/σ^* interactions with values of the $\sigma_{\mathrm{CH}}/\sigma_{\mathrm{CH}}^*$ overlap integral.

$$\epsilon_{\mathrm{mn}} = \sum_{\mathrm{occ}} N(i)C_{im\mathrm{STO}}C_{in\mathrm{STO}}H_{mn\mathrm{STO}}(K-1)/K \tag{7}$$

and atom-atom interaction energies can be obtained (see footnote 8 of ref 7). As a consequence of orthogonalization and basis set truncation, however, the meaning of the above-defined quantities can change, and in some cases be somewhat obscure.

It should not be overlooked that the EWPA sketched above is one of an infinite number of alternative formulations. It is perhaps the simplest but its significance is complicated by its apportionment of substantial energies to diagonal elements which are not invariant with respect to shifts in geometry. The present EWPA should be regarded only as a preliminary but helpful scheme.

All the manipulations described in the above paragraphs have been incorporated into a FORTRAN program of considerable generality. Given the Cartesian coordinates of the atoms in a molecule, the hybridization geometry is automatically found, and the bond and antibond combinations, as well as the remaining nonbonds, are also automatically detected. The program proceeds then to truncate the basis set as desired, to solve the secular equation, and to perform the population analyses.

III. Results

Test of Brunck-Weinhold Hypothesis. Table I shows some calculational details. Molecular geometries have been chosen as a reasonable compromise between experimental values and the general need for simplicity and uniformity. Bond angles were taken to be 109.47°.

Table II shows the results for the values of the barriers to rotation about single bonds. The agreement with experimental barriers is fair. The calculated barrier is somewhat sensitive to the Slater exponent for the H atoms, ranging for ethane from 4.169 kcal/mol for $\alpha_{\mathrm{H}} = 1.0$ to 2.421 for $\alpha_{\mathrm{H}} = 1.30$.

The essential point of BW's analysis is that a stabilizing trans σ/σ^* bond-antibond interaction is ultimately responsible for the greater stability of the staggered conformations. More effective σ-σ^* mixing in the case of trans interactions than cis is supposed to be reflected in the larger magnitude of the trans overlap as depicted in Figure 1. Therefore, if the antibonds are excluded from the basis set, this crucial difference no longer exists, and the stabilization of the staggered form (and hence

Table II. Barriers to Rotation about Single Bonds ($E_{\mathrm{ecl}} - E_{\mathrm{stag}}$, kcal/mol)[g]

	FBS	OTBS	NOTBS	BW-FBS[a]	BW-OTBS[a]	exptl	ab initio[b]
ethane	2.701	−0.892	1.995	2.26	0.25	2.93[c]	3.26
fluoroethane	2.481	−0.793	1.847	2.00	0.23	3.30[d]	3.63
methylamine	1.432	−0.270	1.398	1.51	0.19	1.98[e]	2.13
methyl alcohol	0.406	−0.009	0.703	0.75	0.12	1.07[f]	1.12

[a] Reference 2. [b] Reference 9. [c] S. Weiss and G. E. Leroi, *J. Chem. Phys.*, **48,** 962 (1968). [d] D. R. Herschbach, *ibid.*, **25,** 358 (1956). [e] D. R. Lide, *ibid.*, **27,** 343 (1957). [f] E. V. Ivash and D. M. Dennison, *ibid.*, **21,** 1804 (1953). [g] FBS, full basis set; OTBS, orthogonalized truncated basis set (no antibonds); NOTBS, nonorthogonalized truncated basis set; BW, Brunck and Weinhold's INDO results.

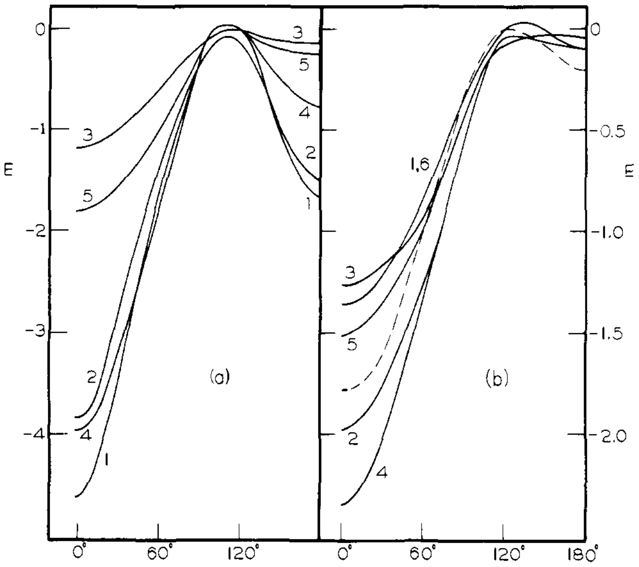


Figure 2. Bond/antibond and nonbond/antibond vicinal interaction energies (kcal/mol) by EWPA, eq 6. (a) Curve 1: n/σ_{CH}* in methylamine. Curve 2: n/σ*$_{CH}$ in methyl alcohol. Curves 3 and 4: σ_{CF}/σ_{CH}* and σ_{CH}/σ_{CF}* in fluoroethane. Curve 5: σ_{CH}/σ_{CH}* in ethane. (b) Curve 1: σ_{CC}/σ_{CC}* in IV. Curve 2: σ_{CH}/σ_{CH}* in I. Curves 3 and 4: σ_{CH}/σ_{CC}* and σ_{CC}/σ_{CH}* in II. Curve 5: σ_{CC}/σ_{CC}* in III. Curve 6: σ_{CC}/σ_{CC}* in V. Dashed line is σ_{CH}/σ_{CH}* in ethane (curve 5 of part a).

Table III. Energy Variations (kcal/mol) for the Occupied MOs of Ethane on Going from Staggered to Eclipsed[a]

	OTBS	FBS	NOTBS
a_g	−0.178	−0.119	−0.113
e_g	+1.200	+1.660	+1.390
e_u	−1.352	−0.960	−0.889
a_u	+0.028	+0.056	+0.077
a_g	+0.006	+0.014	+0.032

[a] Minus sign means stabilization.

the barrier to rotation) vanishes. As can be seen from Table II, this disappearance of the barrier is indeed the case with the BW INDO calculations where antibonds are excluded. Since, however, in INDO the basis set is implicitly orthogonal, a comparable test by EHT is best carried out by calculations of the barrier with truncations of both the nonorthogonalized and orthogonalized BO basis sets. Table II shows that, while a substantial part of the barrier survives truncation of the nonorthogonalized BOs (as predicted by BW), the barrier disappears (or, even more strikingly, changes sign) after truncation of the orthogonalized BO basis set. This result lends support to BW's contention that the origin of the barrier is to be found in interactions of "tails" of the localized molecular orbitals introduced via the antibonds by Löwdin orthogonalization.

Furthermore, the argument that upper and lower MOs of e symmetry make nearly canceling contributions to the rotational barrier when only the bonding σ basis set is considered is in accord with our results, shown in Table III. In the full basis set (FBS), and in the nonorthogonalized truncated basis set (NOTBS) calculations, the differential stabilization leading to the barrier is evident, while in the orthogonalized truncated basis set (OTBS) the magnitude of this differential stabilization is greatly reduced, and its sign is changed. This leads to a slight stabilization of the eclipsed form.

According to Brunck and Weinhold, the barrier is expected to survive deletion of the σ* orbitals in the case of the nonorthogonalized basis set. This is because the bond orbitals in the nonorthogonalized set necessarily include significant contributions attributable to the antibonding combinations in the orthogonalized set. Brunck and Weinhold's theoretical inference that this built-in antibonding mixing should be sufficient to recover a reasonable rotation barrier is well supported by our numerical computations.

Table IV. Ethane Bond-Bond Interaction Energy Variations (EWPA, eq 6) on Going from Staggered to Eclipsed[a]

	OFBS	NOFBS	NOTBS
σ_{CH}/σ_{CH} diagonal	−3.666	−12.234	−6.042
σ_{CC}/σ_{CC}	−0.169		
σ_{CH}/σ_{CH} vicinal	0.006	6.942	6.834
σ_{CH}/σ_{CH} geminal	0.360	2.832	1.420
σ_{CH}/σ_{CH}* vicinal	7.200	6.132	
σ_{CH}/σ_{CH}* geminal	0.024	−0.032	
σ_{CH}*/σ_{CH}* geminal	−0.954	−0.162	
σ_{CH}*/σ_{CH}* vicinal	−0.072	−0.186	
total of above entries	2.729	3.292	2.212
total barrier	2.701	2.701	1.995

[a] Minus sign means stabilization. Each entry (kcal/mol) is the sum over the whole molecule for each type of interaction.

Further insight can be gained by means of EWPA (eq 6). It might be imagined, as argued by BW, that eclipsed bonds are destabilizing and staggered, more favorable. That this may not be correct is suggested by the evidence in Figure 2. In this figure it can be seen that σ/σ* and n/σ* interaction energies are most strongly stabilizing at cis (0°), neutral at 120°, and only slightly stabilizing at trans (180°). It is the sum of all the contributions in ethane, as given in Table IV, not just the cis or trans interactions, that determines the conformational stability. Of these interactions, the σ/σ* contributions account for the largest (and most essential) part of the stabilization of staggered relative to eclipsed ethane. It therefore appears that, although BW's argument is in qualitative agreement with ours in that the barrier is to be traced to σ/σ* interactions, our EWPA results indicate that BW overemphasized the special role of cis vs. trans interactions. In the last analysis, of course, it cannot simply be a matter of cis vs. trans because such a resolution implies only the onefold barrier component. Onefold components cannot contribute to the barrier of ethane.

Table IV deserves further comment. EWPA is not of interest in the OTBS calculations, since truncation and orthogonalization reduce the EWPA matrix to diagonal form. The most conspicuous differences between OFBS and NOFBS (Table IV) are as follows. The diagonal σ/σ element preference for the eclipsed conformation is enhanced in the NO basis set; the σ/σ* stabilization is still present, but other major stabilizations are due to geminal and vicinal. As a consequence, the picture is less clear, stabilizations and destabilizations being scattered among many different contributions.[8] It is interesting to notice how the σ/σ vicinal stabilization in the NO basis sets (which is absent in the orthogonalized basis set) survives truncation.

Low-Order Barrier Components of Four-Atom Fragments. One of the noteworthy results of our analysis is a demonstration (Figure 2a) that the EHT trend in σ/σ* interactions as a function of torsion angle is qualitatively the same, regardless of the types of bonds involved. This observation suggested the possible utility of surveying the systematics of low-order barrier components for rotation about single bonds, a point recently found to be of importance in molecular mechanics.[7] Such decompositions in one-, two-, and threefold barrier components have been done for molecules in which the low-order contributions do not cancel.[9-11] Even in symmetric molecules where these contributions cancel, in sum, there is evidence[7] that one- and twofold contributions are meaningfully associated with individual dihedral components. It seemed plausible to investigate individual components through the use of molecular

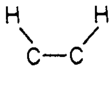
Table V. Low-Order Barrier Components (kcal/mol) for Internal Rotation about Single Bonds[a]

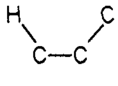
fragments	A_1	A_2	A_3	B_1	B_2	B_3	C_1	C_2	C_3
I	−2.916	−0.8888	0.044						
II				−2.460	−0.618	0.104			
III							−2.781	−0.852	−0.011
ethane			0.057						

fragments	P	Q	R	ΔE_g^{intr}
I-III	−0.777	−0.504	0.581	−0.410
IV	−0.252	−0.268	1.562	0.024
V	−0.379	0.473	0.881	0.141

[a] *A, B, C, P, Q, R:* see text. Intrinsic energies obtained by subtracting from the total EHT energies the nonbonded repulsions calculated according to Mulliken's formula.[12]

fragments, taking the advantage of the possibility offered by the bond orbital formalism of actually lifting out unwanted orbitals from the basis set. The fragments considered were I-IV


I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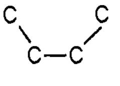
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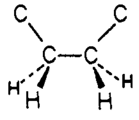

IV

including only the hybrids needed to form the bonds shown, with their antibond partners, and two electrons for each bond. As can be seen from Figure 2b, the σ/σ^* interaction trends are qualitatively the same as those inferred for the full molecules; the decomposition of the barriers gives

$$\text{I} \quad E^{\text{HH}} = A_1 \cos \tau + A_2 \cos 2\tau + A_3 \cos 3\tau$$

$$\text{II} \quad E^{\text{HC}} = B_1 \cos \tau + B_2 \cos 2\tau + B_3 \cos 3\tau$$

$$\text{III} \quad E^{\text{CC}} = C_1 \cos \tau + C_2 \cos 2\tau + C_3 \cos 3\tau$$

$$\text{IV} \quad E = P \cos \tau + Q \cos 2\tau + R \cos 3\tau$$

$$P = A_1 - 2B_1 + C_1$$

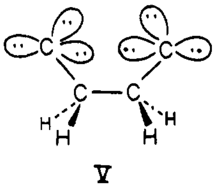
$$Q = A_2 - 2B_2 + C_2$$

$$R = 4A_3 + 4B_3 + C_3$$

while for ethane one gets

$$E = 9A_3 \cos 3\tau$$

In order to separate out for inspection "intrinsic" components to the barriers, as required by the molecular mechanics model (in which nonbonded interactions between atoms account for a small fraction of the total barrier), the nonbonded energies should be subtracted from the total electronic energy. Nonbonded repulsions were estimated by using a simple formula, suggested by Mulliken,[12] based on the extent of overlap between the orbitals occupied by the electrons present in the fragments. Another fragment, more realistic in some respects, was also considered (V), in which each carbon atom retained


V

all its four valence hybrids, and the total number of electrons equals the number of electrons in butane. Before nonbonded energies were subtracted trans was *less* stable than gauche by 0.52 kcal/mol for IV, but *more* stable by 1.0 kcal/mol for V. Of course, neither fragment IV nor fragment V possesses *methyl* hydrogens which must account for a substantial fraction of the observed 0.966 kcal/mol trans stabilization.[13] When Mulliken nonbonded corrections were made (which are larger for V than for IV), the remaining "intrinsic" conformer stabilities of IV and V agree to within 0.12 kcal/mol as shown in Table V. It is worth noting that the σ/σ^* trends are quite similar in IV and V (see Figure 2b) and are also qualitatively the same as in the full molecules (compare Figures 2a and 2b).

Results for the low-order barriers are shown in Table V. Numerical values for I-V show a certain consistency, and, although they do not reproduce exactly the "intrinsic" trans-gauche energy difference, 0.3 kcal/mol, proposed in ref 7, they provide at least a rationalization that intrinsic interactions (missing from most molecular mechanics force fields) may be significant. Quantitative results cannot be expected from the present treatment, considering the simplified fragments and the primitive theory adopted. The tabulated results provide support for the existence of the previously postulated low-order components of the "intrinsic" interaction (i.e., not "through-space" interactions, 1 · · · 4 and more remote) and illustrate a possible source of discrimination between isomer stabilities that has received scant attention to date.

Atom-Atom Energies and Nonbonded Interactions. One final result of significance emerged from energy-partitioning studies. When atom-atom energies based on eq 7 are calculated via EHT for pairs of rare-gas atoms, the correspondence with observed nonbonded interactions is pleasing.[14,15] On the other hand, when intramolecular atom-atom energies of nonbonded pairs in covalent molecules are calculated by this equation,[15] there are large excursions, some positive, some negative, from corresponding intermolecular interactions at the same distances and from nonbonded formulas[16] commonly invoked in "molecular mechanics". These excursions have been discussed previously in terms of through-bond coupling effects.[17] It is of interest, then, to find what happens to atom-atom energies when the σ/σ^* interactions are turned off. Equation 7 can be applied to wave functions over STOs after back-transforming (eq 5) whether full or truncated basis sets are adopted. A striking difference is observed between the two cases. Plotted as a function of internuclear distance in Figure 3 are H · · · H energies so calculated for the various geminal and vicinal (cis, gauche, trans, etc.) hydrogen atom pairs encountered in molecular examples adopted for Figure 2 and for the sequel to the present paper. Atom-atom energies computed from full basis set wave functions exhibit a considerable scatter. By contrast the curve obtained from the truncated basis set is much smoother and in better agreement with the semiempirical nonbonded interaction curve of the MUB-2 model force field[18] and of Mulliken's "magic formula".[12] This illustrates that through-bond coupling via σ/σ^* interactions appears to be a significant factor distorting nonbonded atom-atom interactions from the commonly proposed "classical nonbonded interaction laws".

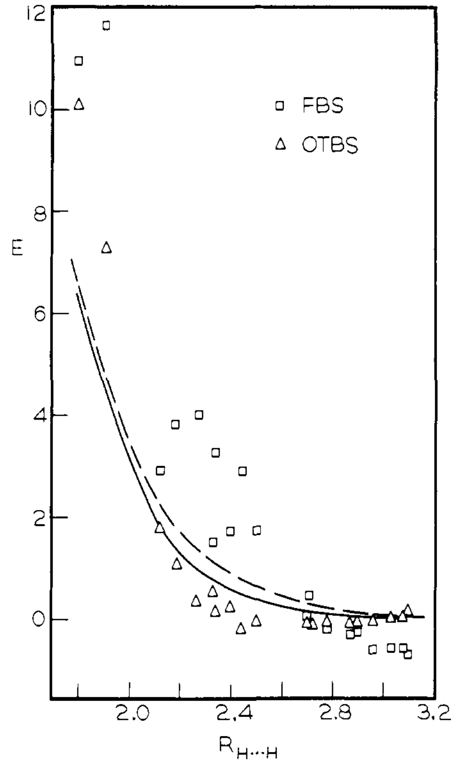


Figure 3. H···H nonbonded intramolecular energies (kcal/mol) calculated by EWPA (see text). Squares: full basis set. Triangles: orthogonalized truncated basis set. For comparison, the full line is the MUB2 H···H nonbonded energy curve,[18] and the broken line is the H···H nonbonded repulsion from Mulliken's formula.[12]

IV. Conclusions

Brunck and Weinhold have shown how the introduction of orthogonalized bond orbitals makes it possible to test hypotheses in chemically natural ways and to reduce certain problems to their most primitive elements. Particularly attractive is the way they account for various through-bond interactions via σ/σ^* orbital mixing. Extending their studies, we observe that intramolecular nonbonded interactions (in the cases so far examined) follow force laws popularly ascribed to them provided, and *only* provided, that through-bond σ/σ^* interactions are turned off by deletion of σ^* basis orbitals. We also verify through EWPA studies that BW's scheme offers the opportunity to calculate plausible magnitudes of components to rotational barriers attributable to such fragments as H_i-X-Y-H_j either by resolving the H_i-X-Y-H_j contributions in a calculation based on H_mXYH_n or by computing the energy of the six-electron fragment all by itself by simply deleting unwanted orbitals and associated electrons. Remarkably consistent behavior has been found in trends of individual bond-antibond interaction energies as a function of torsion in a wide variety of molecules and molecular fragments. This leads us to the original purpose of the study, investigating the hypotheses of Brunck and Weinhold. According to these authors, the barrier to rotation about single bonds depends essentially upon interactions between orthogonalized bond and antibond orbitals. BW predicted, further, that the effect should be reproduced satisfactorily by any reasonable approximation within the MO theory. Our results are, indeed, reasonably consistent with these ideas in that truncation of the basis set to exclude antibonds considerably reduces the value of the barrier (generally, in our work, even changing the sign) if and only if the basis set is orthogonalized before the exclusion. In one particular, however, we differ from BW's conclusions. We do not find the crucial contribution to restricted rotation to be attributable to the difference between energies of cis and trans fragments. In fact, in our work, eclipsed (cis) fragments were the most stable. It was the *sum* over all contributions that favored the staggered conformations when full σ/σ^* mixing was allowed; here anti-gauche (120°) contributed most heavily to destabilizing eclipsed ethane. Therefore, the analogy BW drew between the barriers to internal rotation in ethane and ethylene loses some of its force.

Finally, the opportunity afforded by the BW approach of substantially localizing the interactions responsible for intramolecular forces makes it worthwhile to apply their approach in investigations of force constants for molecular deformations. Results of such a study are the subject of a forthcoming paper.[19]

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References and Notes

(1) Istituto di Chimica Fisica, Universita degli Studi di Milano, Milan, Italy.

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