It is interesting to note that each α-CH_3 substitution on the cyclobutanone ring increases $\sim$2 times the $\sigma_Q{}^2$ value for the $^3(\pi^* \leftsquigarrow n)$ transition, caused by energy transfer from $C_6H_6(^3B_{1u})$, relative to that for CB (triplet energy transfer probability of 0.01/collision), whereas no such increase on the $\sigma_Q{}^2$ values for the $^1(\pi^* \leftsquigarrow n)$ transition, caused by energy transfer from $C_6H_6(^1B_{2u})$, is observed.[20]

The σ^2 values for $^1(\pi^* \leftsquigarrow n)$ by energy transfer from $C_6H_6(^1B_{2u})$ to CH_3-substituted acetones show instead substantial reduction with increased CH_3 substitution,[10,21] and this observation has been explained on the basis of steric hindrance.[10] The true origin of this steric hindrance can be easily rationalized on the basis of the model for the gas-phase singlet energy transfer mechanism involving the combination of the Dexter type ("short range" exchange) and the Förster type ("long range" dipole–dipole) interactions between the singlet aromatic excitation donor ($^1D^*$) and the carbonyl acceptor (A).[22] With the $C_6H_6(^1B_{2u})$ as $^1D^*$, the exchange mechanism contributes more than the dipole–dipole mechanism to the electronic quenching,[22] and hence the steric hindrance for the short-range interaction between $^1D^*$ and A plays an important role.

The origin of the CH_3-group enhanced and *particularly* Cl-atom (α-substitution) enhanced triplet energy transfer rates, $^3(\pi^* \leftsquigarrow n)$, may lie with the operation of the exchange mechanism (Dexter type),[9,23] since these substituent groups could *enhance* the spectral overlap of the donor deexcitation ($T_1 \rightarrow S_0$) with the acceptor excitation ($T_1 \leftarrow S_0$) by lowering the triplet energies of the acceptor upon α-substitution.[9] The degree of the overlap can greatly be enhanced here, particularly, because the triplet energies (E_T) of $^3D^*$ and $^3A^*$ are very close to each other, *e.g.*, 84.4 and 80–84 kcal/mol, respectively.[24]

In the $C_6H_6(^1B_{2u})$/CB system, the spectral overlap is nearly complete and hence the singlet energy transfers efficiency is insensitive to the E_S values of ketones as expected.[22]

The extent of energy lowering of E_S (and probably E_T) in 2-chlorocyclobutanone (**2**) as compared with CB (**1**) by the chlorine atom substitution is quite substantial ($\leqslant 1500$ cm^{-1}) and it is surprising. Chloro CB (**2**) quenches $C_6H_6(^3B_{1u})$ with a collision efficiency of 0.3–0.4, comparable to 1,3-butadiene (E_T = 59.6 kcal/mol)[25] whose collision efficiency is $\sim$0.7.[8,9] It would be of interest to extend the present study to more highly substituted chlorocyclobutanones, and to compare the triplet energy transfer mechanism with the singlet energy transfer mechanism.

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(20) G. M. Breuer, Ph.D. Thesis, University of California, Irvine, 1972. In singlet benzene ($^1B_{2u}$) quenching in the gas phase, $\sigma_Q{}^2$ for CB, *cis*-2,4-DMCB, *trans*-2,4-DMCB, cyclopentanone (CP), and *trans*-2,5-DMCP are insensitive to the α-methyl substitutions and are 25, 27, 24, 24, and 25 Å^2, respectively.

(21) $\sigma_Q{}^2$ for acetone, 3-pentanone, 2,4-dimethyl-3-pentanone, and 2,2,4,4-tetramethyl-3-pentanone are 10.4, 13.1, 8.9, and 3.0 Å^2, respectively.[10]

(22) G. M. Breuer and E. K. C. Lee, *Chem. Phys. Lett.*, **14**, 407 (1972).

(23) See for a review, A. A. Lamola in "Techniques of Organic Chemistry. XIV. Energy Transfer and Organic Photochemistry," P. A. Leermakers and A. Weissberger, Ed., Interscience, New York, N. Y., 1969, p 17.

(24) E_T of $C_6H_6(^3B_{1u})$ is 29,510 cm^{-1}. The first excited singlet energy (E_S) of cyclobutanone is 30,291.2 cm^{-1} (D. C. Moule, *Can. J. Phys.*, **47**, 1235 (1969)) and E_S of cyclopentanone is 30,514.0 cm^{-1} (H. E. Howard-Lock and G. W. King, *J. Mol. Spectrosc.*, **36**, 53 (1970)). Assuming an E_S–E_T splitting of 1000–1500 cm^{-1}, E_T for these unsubstituted cyclic ketones could be at 28,900–29,400 cm^{-1}.

(25) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

Localized Charge Distributions. V. Internal Rotation Barriers in Methylamine, Methyl Alcohol, Propene, and Acetaldehyde

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Abstract: The internal rotation barriers of methylamine, methyl alcohol, propene, and acetaldehyde are investigated within the context of localized charge distributions defined in earlier papers. It is shown that, as for ethane, hydrogen peroxide, and borazane, the barriers can be understood in terms of changes in vicinal interference interactions within those orbitals adjacent to the axial bond. These vicinal interactions are compared with those in molecules studied previously. Such a comparison leads to a straightforward explanation of the observed trends in the barriers.

It has been demonstrated in earlier papers[2-4] that localized molecular orbitals (LMO's) are not generally completely localized on one or two atoms as in idealized valence-bond or lone-pair orbitals but rather have physically significant "tails" on atoms dihedrally displaced from the bond or lone pair. We have re-

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(1) (a) North Dakota State University. (b) Iowa State University.

(2) (a) Paper I: W. England and M. S. Gordon, *J. Amer. Chem. Soc.*, **93**, 4649 (1971); (b) Paper II: *ibid.*, **94**, 4818 (1972).

(3) Paper III: M. S. Gordon and W. England, *ibid.*, **94**, 5168 (1972).

(4) Paper IV: M. S. Gordon and W. England, *Chem. Phys. Lett.*, **15**, 59 (1972).

Table I. Comparison of INDO and Experimental Barriers[a]

Molecule	$\Delta E_{\mathrm{Exptl}}$	ΔE_{MBLD}	ΔE_{OPT}	ΔI_{MBLD}	ΔI_{OPT}	Δg_{MBLD}	Δg_{OPT}	ΔG_{MBLD}	ΔG_{OPT}
CH_3NH_2	1.97[b]	1.56	1.91	1.40	1.85	3.32	−13.09	2.75	−11.74
CH_3OH	1.07[c]	0.78	1.21	0.64	1.07	1.72	−11.46	1.90	−6.70
CH_3CHCH_2	1.978[d]	1.22	1.55	1.01	1.98	−9.41	−7.97	−10.63	−9.10
CH_3CHO	1.17[e]	0.60	0.77	1.12	1.38	−5.10	54.71	−6.42	51.64

[a] Energies in kcal/mol; $\Delta E = E$(least stable) − E(most stable rotamer). [b] T. Nishikawa, T. Itoh, and K. Shimada, *J. Chem. Phys.*, **23**, 1735 (1955). [c] E. V. Ivash and D. M. Dennison, *ibid.*, **21**, 1804 (1953). [d] D R. Lide and D. Christensen, *ibid.*, **35**, 1374 (1961). [e] D. R. Herschbach, *ibid.*, **31**, 91 (1959).

Table II. Geometries for Methylamine and Methyl Alcohol[a]

	Methyl Amine								
	Bond lengths				Angles				
	CN	NH	CH_3	CH_4	H_3CN	H_4CN	H_3CH_4	CNH	HNH
Eclipsed	1.403	1.070	1.126	1.123	110.76	112.77	106.46	113.69	106.34
Staggered	1.402	1.072	1.126	1.123	114.58	110.34	106.78	111.48	106.22
Exptl	1.474	1.011	(1.093)	(1.093)	(109.5)	(109.5)	(109.5)	112.3	105.8
	Methyl Alcohol								
	CO	OH	CH_3	CH_4	H_4CO	H_3CO	H_3CH_4	COH	
Eclipsed	1.369	1.037	1.122	1.124	109.84	112.91	107.87	109.00	
Staggered	1.368	1.036	1.122	1.124	111.92	108.20	108.34	107.69	
Exptl[c]	1.434	0.937	(1.093)	(1.093)	109.5	109.5	109.5	105.93	

[a] Bond lengths in ångströms; angles in degrees. Parentheses indicate experimentally assumed values. [b] T. Nishikawa, T. Itoh, and K. Shimada, *J. Chem. Phys.*, **23**, 1735 (1955). [c] E. V. Ivash and D. M. Dennison, *ibid.*, **21**, 1804 (1953).

cently shown that, within the context of INDO[5] localized charge distributions,[2a,6] the barriers to internal rotation in ethane,[2a] hydrogen peroxide,[2b] and borazane[4] may be explained in terms of changes in one-electron, two-center interference interactions[2a,7] in the LMO's adjacent to the axial bond. These interactions occur between the large bonding lobes and the small contributions on the vicinal bonds and may be viewed as interaction energies due to the wave nature of electrons.[2,7] For all three molecules the resulting net *vicinal interference barrier* (ΔI) reproduces the calculated INDO barrier (ΔE) with reasonable accuracy, and, in contrast to other recently proposed barrier analyses,[8] ΔI is relatively insensitive to optimization of molecular geometry. Similar results were obtained for ethane using *ab initio* LMO's.[2a]

Clearly, the nature and magnitudes of the interference interactions contributing to a particular barrier will depend on the types of LMO's adjacent to the axial bond. We denote the sum of all vicinal interference changes within a particular LMO λ_i as ΔI_i such that

$$\Delta I = \sum_i \Delta I_i \qquad (1)$$

For example, the ethane barrier is due to $6\Delta I_{\mathrm{CH}}$, the sum of H–H interference changes across the axial bond[2a] in the CH orbitals. Similar changes within the NH and BH bonds explain the barrier in borazane[4] and the small value of ΔI_{NH} in this molecule explains the relatively smaller barrier. The cis barrier in hydrogen peroxide can be explained in a similar way, while the trans barrier is due to lone-pair interferences which strengthen the OO bond in the skewed configuration.[2b]

In order to gain a general understanding of the nature of internal rotation, as well as to investigate the generality of the interference analysis, it is important to extend the method to as wide a range of rotors as possible. In the present paper, the internal rotation barriers in methylamine, methyl alcohol, propene, and acetaldehyde are analyzed. In addition to lending added credence to the interference interpretation of internal rotation, these calculations provide interesting insight into the effect of chemical environment on the vicinal interactions which contribute to the barrier.

Results and Discussion

A. Preliminary. The calculated barriers are compared with experiment in Table I where it is seen that the ΔE and ΔI are consistent with those obtained for ethane[2b] and borazane,[4] and in reasonable agreement with experiment. The subscripts OPT and MBLD stand for geometry-optimized and standard[9] frozen-frame calculations, respectively. Geometry optimization was carried out by varying all bond lengths and bond angles to an accuracy of 0.001 Å and 0.05°, respectively. The only assumption made in both rotamers of all four molecules was that of C_s symmetry. For all four molecules, optimization of geometry improves the agreement between the calculated and experimental barriers. It is also noteworthy that the interference barriers ΔI are in good agreement with the calculated barriers. Upon geometry optimization, the increase in ΔI is similar in magnitude to that for ΔE, and, in fact, of all the calculated energy differences (including ΔE_{OPT}), ΔI_{OPT} best reproduces the experimental values. *From these results we conclude that, as before, it is reasonable to describe the barriers in these molecules in terms of changes in vicinal interference interactions within the LMO's adjacent to the axial bond.*

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(5) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

(6) W. England and M. S. Gordon, *J. Amer. Chem. Soc.*, **91**, 6864 (1969).

(7) K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962).

(8) L. C. Allen, *Chem. Phys. Lett.*, **2**, 597 (1968).

(9) J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

Table III. Localized Orbitals in Methylamine[a]

	CH_3		CH_4		NH_7		Lp	
	S	E	S	E	S	E	S	E
C2 s	0.3631	0.3649	0.3634	0.3617	−0.0054	−0.0066	−0.0073	−0.0043
C2 p_x	0.5359	0.5514	−0.2801	−0.2659	0.0444	−0.0462	−0.1124	0.1118
C2 p_y	0.0	0.0	0.4777	0.4776	−0.0623	0.0621	0.0	0.0
C2 p_z	−0.2288	−0.1924	−0.1968	−0.2153	0.0039	0.0029	0.0224	0.0266
N2 s	0.0125	−0.0285	−0.0816	0.0016	0.3377	0.3408	0.5688	0.5576
N2 p_x	−0.0017	0.0139	−0.0120	0.0054	0.3394	−0.3350	−0.7504	0.7626
N2 p_y	0.0	0.0	0.0362	0.0347	−0.5039	0.5042	0.0	0.0
N2 p_z	0.0165	−0.0157	−0.0082	0.0077	0.2235	0.2274	0.3053	0.2955
H_3	0.7259	0.7222	−0.0173	−0.0181	−0.0224	0.0298	0.0740	−0.0610
H_4	−0.0186	−0.0189	0.7190	0.7212	0.0514	−0.0424	−0.0271	0.0404
H_5	−0.0186	−0.0189	−0.0135	−0.0117	−0.0167	0.0249	−0.0271	0.0404
H_6	−0.0172	0.0343	−0.0109	0.0293	−0.0164	−0.0168	0.0028	0.0083
H_7	−0.0172	0.0343	0.0556	−0.0356	0.6763	0.6756	0.0028	0.0083

[a] S = staggered; E = eclipsed.

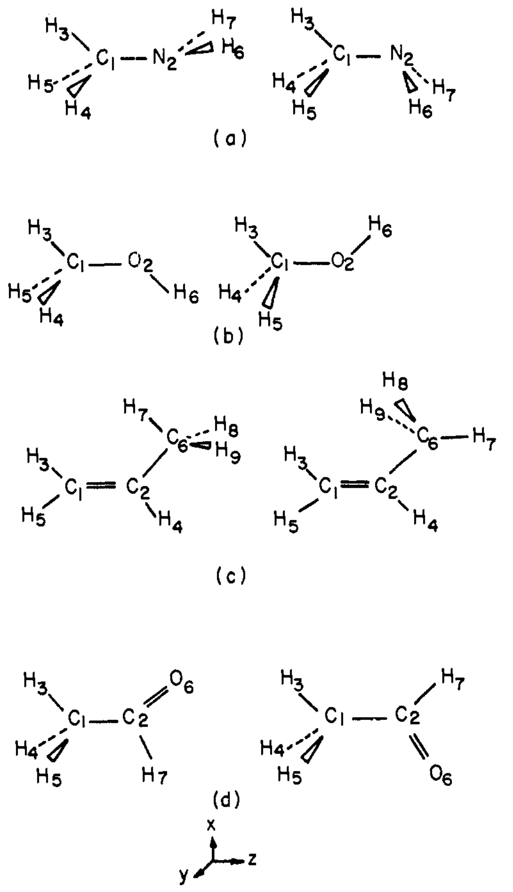

Figure 1. Coordinate axes and numbering system in (a) staggered and eclipsed methylamine, (b) staggered and eclipsed methanol, (c) *s-trans-* and *s-cis*-propene, (d) *s-trans-* and *s-cis*-acetaldehyde.

The behavior of the nuclear (Δg) and electron (ΔG) repulsions is rather different. With the exception of propene, where both sets of repulsion energies oppose the barrier, optimization of geometry results in a change in sign as well as magnitude. This illustrates once again the need for caution when describing internal rotation as a balance between attractive and repulsive energies.

Finally, it is interesting to point out that while the individual energy difference components (*e.g.*, electron repulsion) for a particular rotamer are generally orders of magnitude larger than the barrier itself, the individual vicinal interference interactions are similar to the barrier in magnitude.

With these general comments in mind, we proceed to discuss the four molecules in greater detail. From this point on we will consider only the geometry-optimized results.

B. Methylamine. The calculated and experimental geometries of CH_3NH_2 are compared in Table II. The calculated bond lengths and angles are in reasonable agreement with experiment and quite similar to the CNDO results reported earlier.[10] In analogy with ethane and borazane, the bond lengths are essentially unchanged by rotation, while there are significant changes in the angles. Because of the presence of the nitrogen lone pair in methylamine, these angle changes are somewhat larger than in ethane and borazane. Note also that, as found experimentally, the methyl axis is skewed from the CN bond by 2.87° such that it passes through the NH_2 triangle (see Figure 1a). The experimental tilt angle is 3.5°[11] in the same direction. The calculated tilt angle in eclipsed methylamine is 1.31° and again passes through the NH_2 triangle.

The localized orbitals in methylamine which contribute to the interference barrier are listed in Table III. The numbering system and coordinate axes are shown in Figure 1. Some brief comments on the changes in these orbitals due to internal rotation will enhance the discussion below. First note that the behavior of the CH bonds is similar to that observed in ethane.[2a] In the staggered rotamer, the principle overflow of electron density (tail) is on the trans vicinal atom. There is no such atom for CH_3 (see Figure 1a) and therefore only the characteristic small negative tail (destructive interference) on the gauche atoms is present. On rotation to eclipsed, the tail of CH_3 becomes larger on these atoms and changes sign, while that of CH_4 spreads over both amino hydrogens and also changes sign.

It is also of interest to compare the NH bonds with those in borazane[4] since they are somewhat different. Because of the polarity and large bond length of the BN bond, the tails in borazane are smaller and there is only a sign change which accompanies the rotation to the eclipsed configuration. In methylamine, the behavior of the NH bonds is similar to that of the CH

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(10) M. S. Gordon, *J. Amer. Chem. Soc.*, **90**, 3122 (1969).

(11) T. Nishikawa, T. Itoh, and K. Shimada, *J. Chem. Phys.*, **23**, 1735 (1955).

Table IV. Localized Orbitals in Methanol[a]

	CH_3		CH_4		OH		Lp	
	S	E	S	E	S	E	S	E
C2 s	0.3767	0.3731	0.3756	0.3770	0.0005	−0.0011	−0.0110	−0.0103
C2 p_x	0.5571	0.5416	−0.2677	−0.2811	−0.0822	0.0818	0.0412	−0.0428
C2 p_y	0.0	0.0	0.4726	0.4742	0.0	0.0	0.0845	0.0823
C2 p_z	−0.1695	−0.2058	−0.1983	−0.1802	0.0100	0.0079	0.0082	0.0096
O2 s	−0.0170	0.0059	0.0004	−0.0111	0.3026	0.3062	0.5590	0.5568
O2 p_x	0.0262	0.0062	0.0004	−0.0166	−0.6661	0.6638	0.3206	−0.3268
O2 p_y	0.0	0.0	−0.0101	0.0096	0.0	0.0	0.6992	0.6996
O2 p_z	−0.0030	0.0125	0.0087	0.0008	0.1928	0.1985	0.2857	0.2826
H_3	0.7172	0.7235	−0.0184	−0.0172	0.0483	−0.0441	−0.0200	0.0328
H_4	−0.0174	−0.0172	0.7236	0.7206	−0.0214	0.0250	−0.0251	0.0363
H_5	−0.0174	−0.0172	−0.0201	−0.0211	−0.0214	0.0250	0.0634	−0.0509
H_6	0.0543	−0.0278	−0.0090	0.0324	0.6462	0.6452	−0.0086	−0.0068

[a] S = staggered; E = eclipsed.

bonds. The nitrogen lone pair behaves much like the bond orbitals. In the staggered form, the tail resides principally on the trans (H_3) hydrogen, is positive (constructive interference), and spreads over all three methyl hydrogens in eclipsed. The biggest change occurs on H_3.

We calculate the net H–H interference energy between each methyl hydrogen and its vicinal amino hydrogen neighbors (ΔI_{Me}) to be

$$\Delta I_{Me} = \Delta I_{CH_3} + 2\Delta I_{CH_4} = -2.71 + 3.50 = 0.79 \text{ kcal/mol} \quad (2)$$

The positive value for the CH_4 orbital arises from the change from constructive to destructive interference between H_4 and the tail on H_7 (see Table III) as the molecule rotates from staggered to eclipsed. The concomitant negative ΔI_{CH_3} arises from the change to the positive tails on both amino hydrogens as discussed above. In ethane, ΔI_{Me} is 1.224 kcal/mol.[2a] This value comes from the interactions between a methyl hydrogen and each of the three vicinal hydrogens. In methylamine, there are only *two* vicinal hydrogens; thus, the appropriate comparison is of ΔI_{Me} (methylamine) and $^2/_3\Delta I_{Me}$ (ethane). The latter value is 0.816 kcal/mol, so the CH interference contributions to the barrier are only very slightly smaller in methylamine.

The net H–H interference energy between the amino hydrogen in each NH orbital and the vicinal methyl hydrogens ($2\Delta I_{NH}$) is defined similarly and found to be

$$\Delta I_{NH_2} = 0.84 \text{ kcal/mol} \quad (3)$$

which is again close to the $^2/_3\Delta I_{Me}$ (ethane) value, the positive value being due to the dominance of the trans in-plane vicinal interactions. Thus, we see that the average change in vicinal H–H interference interactions within each NH orbital is the same as the similar interactions in the methylamine and ethane CH orbitals.

If we ignore the contribution of the lone pair, we find for the INDO interference barriers

$$\Delta I(\text{methylamine}) = {}^2/_3\Delta I(\text{ethane}) = 1.63 \text{ kcal/mol} \quad (4)$$

by summing the ΔI_{Me}(methylamine) and ΔI_{NH_2} terms. As is well known, the experimental barriers also closely satisfy the relation

$$\Delta E(\text{methylamine}) \approx {}^2/_3\Delta E(\text{ethane}) = 1.92 \text{ kcal/mol} \quad (5)$$

but the magnitudes involved are slightly larger. Hence, if we ignore the contribution of the lone pair, we obtain an approximation to the methylamine barrier which satisfies eq 5. Although the *total* INDO barriers do not satisfy eq 5 as well, we feel that our interference results (eq 4) provide interesting insight.

Let us now include the lone-pair interferences, which involve the interaction of the main lobe of the lone pair on N with its tail on the vicinal hydrogens. We calculate

$$\Delta I_{lp} = 0.219 \text{ kcal/mol} \quad (6)$$

so the *net* interference barrier becomes

$$\Delta I = \Delta I_{Me} + \Delta I_{NH_2} + \Delta I_{lp} = 1.85 \text{ kcal/mol} \quad (7)$$

With this result we have an interference barrier for methylamine which is in good agreement with both the INDO OPT and experimental barriers.

Finally, we remark that ΔI_{NH} in methylamine is larger than in borazane.[4] From Table III it may be seen that this comes mostly from the larger NH tail in the former, which, as pointed out above, reflects the shorter bond length and smaller polarity of the (methylamine) CN bond.

C. Methyl Alcohol. The experimental and INDO geometries for CH_3OH are also listed in Table II. The OH bond length is somewhat overestimated, and, as for methylamine, we have distinguished the two different methyl hydrogens so that a direct comparison with experiment is difficult. The bond lengths are essentially constant with internal rotation, while there are again significant changes in the angles. As in methylamine, the methyl axis is tilted from the CO bond such that it passes through the OH bond in both rotamers: 2.51° in staggered (in good agreement with the experimental value[12] of 3.4°) and 2.02° in eclipsed.

The pertinent localized orbitals are listed in Table IV with the corresponding numbering system shown in Figure 1b. The behavior of these LMO's with internal rotation is similar to that observed for methylamine. Thus, the tail of orbital CH_3 is exclusively on H_6 (there being no other vicinal bonds) and rotation simply reduces this tail and changes its sign. Just the opposite behavior is observed for orbital CH_4, so we expect the vicinal interference interaction to favor staggered in CH_3 and eclipsed in the out-of-plane CH bonds. The net methyl contribution to the H–H part

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(12) L. E. Sutton, Ed., "Interatomic Distances," The Chemical Society, London, 1958.

Table V. Geometries in Propene and Acetaldehyde[a]

				Bond Lengths			
	C_1C_2	C_2C_6	CH_4	CH_7	CH_8	CH_3	CH_5
C_3H_6 s-Cis	1.323	1.453	1.124	1.123	1.123	1.116	1.115
s-Trans	1.323	1.452	1.124	1.122	1.123	1.115	1.116
Exptl[b]	1.336	1.501	1.09	1.085	1.098	1.091	1.081
	CO	CC	C_2H_7	C_1H_3	C_1H_4		
C_2H_4O s-Cis	1.264	1.446	1.127	1.120	1.122		
s-Trans	1.263	1.454	1.128	1.120	1.121		
Exptl[c]	1.216	1.501	1.114	1.086	(1.086)		
				Angles			
	$H_4C{=}C$	CCC	H_7CC	H_8CC	H_7CH_8	H_3CC	H_5CC
C_3H_6 s-Cis	116.87	129.11	113.05	112.33	106.72	124.71	124.22
s-Trans	117.65	129.28	113.96	111.36	106.22	124.59	124.33
Exptl[b]	119.0	124.3	111.2	110.65	109.0	120.5	121.5
	HCO	CCO	H_3CC	H_4CC	H_3CH_4		
C_2H_4O s-Cis	117.54	126.09	112.92	110.57	107.73		
s-Trans	116.21	127.03	133.98	109.62	108.10		
Exptl[c]	118.60	123.92	113	(113)	108.27		

[a] Bond lengths in ångströms; angles in degrees. [b] D. R. Lide and D. Christensen, *J. Chem. Phys.*, **35**, 1374 (1961). [c] R. W. Kilb, C. C. Lin, and E. B. Wilson, *ibid.*, **26**, 1695 (1957). Values in parentheses are assumed experimentally.

of the interference interaction is given by

$$\Delta I_{\mathrm{Me}} = \Delta I_{\mathrm{CH}_3} + 2\Delta I_{\mathrm{CH}_4} = 2.780 - 2.410 = 0.370 \text{ kcal/mol} \quad (8)$$

Following the previous section, this should be compared with $^1/_3\Delta I_{\mathrm{Me}}$ in ethane (0.408 kcal/mol) and $^1/_2\Delta I_{\mathrm{Me}}$ in methylamine (0.395 kcal/mol).

The behavior of the OH bond is also consistent with previous results. In the staggered form the tail is principally on the trans methyl hydrogen, H_3, while in the eclipsed it spreads more evenly over all three methyl hydrogens accompanied by the familiar sign change. We find

$$\Delta I_{\mathrm{OH}} = 0.442 \text{ kcal/mol} \quad (9)$$

about the same as ΔI_{NH} in methylamine (0.42) and ΔI_{CH} in ethane or methylamine.

Again, if we ignore the lone pairs we find the INDO interference barrier in methanol to be

$$\Delta I(\text{methanol}) = {}^1/_2\Delta I(\text{methylamine}) = {}^1/_3\Delta I(\text{ethane}) = 0.812 \text{ kcal/mol} \quad (10)$$

by adding ΔI_{Me}(methanol) and ΔI_{OH}. Again this reproduces the approximate empirical results

$$\Delta E(\text{methanol}) \approx {}^1/_2\Delta E(\text{methylamine}) \approx {}^1/_3\Delta E(\text{ethane}) = 1.07 \text{ kcal/mol} \quad (11)$$

rather well. It is our feeling that eq 10, in view of the smaller contributions from the lone pairs in both cases (methanol is discussed below), provides much of the rationale for eq 11.

The lone-pair interferences occur between the positive lobes on oxygen and the tails on the methyl hydrogens. As in methylamine, these tails behave very much like those of the bonding orbitals. Here we calculate

$$2\Delta I_{\mathrm{lp}} = 0.254 \text{ kcal/mol} \quad (12)$$

which is smaller than $2\Delta I_{\mathrm{lp}}$ (methylamine) = 0.438 kcal/mol. Thus, lone-pair interference effects are not, on the *average*, the same in methylamine and methanol and in fact it is the *total* contributions from the lone pairs which are about the same.

The *net* interference barrier is thus

$$\Delta I = \Delta I_{\mathrm{Me}} + \Delta I_{\mathrm{OH}} + 2\Delta I_{\mathrm{lp}} = 1.07 \text{ kcal/mol} \quad (13)$$

which is again close to both the experimental and OPT results. Finally, we mention that while both the *net* INDO ΔI and ΔE satisfy the first approximate equality (eq 11), the second relation is less well satisfied.

Finally, notice that within the CH orbitals no tail effects in the vacant sites were considered in either methylamine or methanol, whereas the methyl protons are represented within the lone pairs. This is because the former are very small; when the large positive lobes spread significantly beyond the heavy geminal atoms, they do so onto bonds. This situation also obtained in H_2O_2.[2b]

D. Propene. The propene geometries are compared with experiment in Table V. The values are in reasonable agreement and, as has been found consistently, the bond lengths are virtually unaffected by internal rotation. At first glance the methyl angle changes seem counter to those found in previous molecules since the H_7CC angle is actually *smaller* in s-cis than in s-trans Note, however, that the CC "double bond" is a pair of banana bonds which eclipse the out-of-plane methyl hydrogens in the s-cis rotamer. The methyl axis is again tilted from the C–C bond axis by 1.71° (0.46°) in s-trans (s-cis) such that it passes through the C=C (CH_4 bond). Experimentally[13] the two axes are believed to be within 1° of each other.

The pertinent localized orbitals of propene are listed in Table VI, and behave in a predictable manner based on previous discussion. In order to compare the barrier with those of ethane[2a] and acetaldehyde, it is convenient to write ΔI as a sum of two terms

$$\Delta I = \Delta I_{\mathrm{Me}} + \Delta I'_{\mathrm{Me}} = 1.98 \text{ kcal/mol} \quad (14)$$

with

$$\Delta I_{\mathrm{Me}} = \Delta I_{\mathrm{Me,C_1}} + \Delta I_{\mathrm{Me,H_4}} = 1.117 \text{ kcal/mol} \quad (15)$$

and

$$\Delta I'_{\mathrm{Me}} = \Delta I_{\mathrm{C=C}} + \Delta I_{\mathrm{CH_4}} = 0.869 \text{ kcal/mol} \quad (16)$$

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(13) D. R. Lide and D. Christensen, *J. Chem. Phys.*, **35**, 1374 (1961).

Table VI. Localized Orbitals in Propene[a]

	C_1C_2		C_2H_4		C_6H_7		C_6H_8	
	T	C	T	C	T	C	T	C
C_12 s	0.3384	0.3385	−0.0178	−0.0175	−0.0169	0.0271	0.0162	−0.0063
C_12 p_x	0.0015	0.0030	−0.0774	−0.0784	0.0009	−0.0073	−0.0063	−0.0021
C_12 p_y	0.5029	0.5026	0.0	0.0	0.0	0.0	0.0688	−0.0674
C_12 p_z	0.3649	0.3650	0.0042	0.0045	−0.0077	0.0184	0.0112	−0.0023
C_22 s	0.3277	0.3272	0.3573	0.3569	−0.0129	0.0008	−0.0010	−0.0082
C_22 p_x	0.0034	0.0060	−0.5217	−0.5239	0.0400	−0.0298	−0.0116	0.0247
C_22 p_y	0.4907	0.4911	0.0	0.0	0.0	0.0	−0.0720	0.0701
C_22 p_z	−0.3782	−0.3782	0.2795	0.2763	−0.0326	0.0400	0.0235	−0.0143
H_3	−0.0038	−0.0038	0.0607	0.0613	0.0016	0.0008	0.0011	0.0014
H_4	−0.0021	−0.0017	0.7092	0.7093	0.0500	−0.0393	−0.0181	0.0278
H_5	−0.0029	−0.0028	−0.0384	−0.0391	0.0095	−0.0138	−0.0086	0.0032
C_62 s	−0.0035	−0.0033	−0.0084	−0.0088	0.3538	0.3499	0.3458	0.3471
C_62 p_x	0.0118	0.0112	−0.0450	−0.0416	0.5351	−0.1697	−0.0061	0.3545
C_62 p_y	0.0572	0.0567	0.0	0.0	0.0	0.0	−0.4821	0.4823
C_62 p_z	−0.0300	−0.0311	0.0446	0.0441	−0.2717	0.5770	0.3620	−0.0719
H_7	−0.0173	0.0280	0.0531	−0.0400	0.7131	0.7143	−0.0124	−0.0118
H_8	0.0559	−0.0453	−0.0184	0.0290	−0.0133	−0.0124	0.7109	0.7108
H_9	−0.0230	0.0323	−0.0184	0.0290	−0.0133	−0.0124	−0.0071	−0.0078

[a] T = s-trans; C = s-cis.

ΔI_{Me} is the interference energy within the methyl CH orbitals (C_6H_7 and C_6H_8 of Table VI) arising from the interactions between the methyl H's and the vicinal atoms C_1 and H_4. Because of the bent, out-of-plane character of the banana bonds (C_1C_2 in Table VI), the vicinal interference between the methyl hydrogens and C_1 is much stronger in the out-of-plane bonds (C_6H_8, C_6H_9). Thus, in C_6H_7 in the s-trans rotamer, the principal part of the tail is on the trans, coplanar atom (H_4) as usual, and C_1 takes the role of, *e.g.*, the hydrogens gauche to the CH bonds in ethane. Upon rotation to s-cis, the expected sign changes and spreading of the tail more evenly over these centers is observed. Just the opposite is found for C_6H_8, the major portion of the tail being on C_1 in s-trans and s-cis. As a result, we have

$$\Delta I_{Me,C_1} = \Delta I_{CH_7}(H_7,C_1) + 2\Delta I_{CH_8}(H_8,C_1) = -1.566 + 2.452 = 0.886 \text{ kcal/mol} \quad (17)$$

for the methyl hydrogen–"vicinal" banana bond interactions, and

$$\Delta I_{Me,H_4} = \Delta I_{CH_7}(H_7,H_4) + 2\Delta I_{CH_8}(H_8,H_4) = 2.339 - 2.168 = 0.231 \text{ kcal/mol} \quad (18)$$

for the corresponding methyl hydrogen–vinyl hydrogen interference energies. Note that the latter (eq 18) are less than their ethane analog ($\Delta I_{CH} = 0.408$ kcal/mol) by about 0.2 kcal/mol, while the former (eq 17) are greater than their analog, $2\Delta I_{CH}$ (ethane), by about 0.1 kcal/mol, and thus

$$\Delta I_{Me}(\text{propene}) \approx \Delta I_{Me}(\text{ethane}) = 1.224 \text{ kcal/mol} \quad (19)$$

to within about 0.1 kcal/mol.

The energy $\Delta I'_{Me}$ is analogous to ΔI_{Me} in that it involves interferences between the same atoms, but these now occur in the C_1C_2 ($\Delta I_{C=C}$) and C_2H_4 (ΔI_{CH_4}) orbitals. The banana bonds (C_1C_2) have a positive tail (constructive interference) on the "trans" out-of-plane methyl hydrogen (H_8 in Table VI) and much smaller negative values on the other methyl hydrogens in the s-trans rotamer, while the usual sign change and spreading of the tail is observed in s-cis. Accordingly

$$\Delta I_{C=C} = 0.64 \text{ kcal/mol} \quad (20)$$

the positive value arising from the aforementioned change from destructive to constructive interference on H_8. This is smaller than the ethane analog ($2\Delta I_{CH}$) by about 0.2 kcal/mol.

The overflow of electron density in the CH_4 bond is typical of a secondary vinyl CH bond;[3] however, the only part of the tail that changes with internal rotation is on the methyl hydrogens, the change being similar to those described above for the other vicinal H–H interactions. The contribution of CH_4 is

$$\Delta I_{CH_4} = \Delta I_{CH_4}(H_4,H_7) + 2\Delta I_{CH_4}(H_4,H_8) = 2.455 - 2.226 = 0.229 \text{ kcal/mol} \quad (21)$$

again being positive because of the change in the in-plane (H_7) part of the tail. As noted for $\Delta I_{C=C}$, ΔI_{CH_4} is also smaller than its ethane analog by about 0.2 kcal/mol. Hence, we have

$$\Delta I_{Me}(\text{ethane}) - \Delta I'_{Me}(\text{propene}) = 0.355 \text{ kcal/mol} \quad (22)$$

which accounts for most of the difference between their *net* interference barriers (0.468 kcal/mol).

E. Acetaldehyde. The experimental and INDO geometries for acetaldehyde are compared in Table V, the agreement being about the same as for propene. The calculated tilt angles of the methyl axis are calculated to be 2.87 and 1.53° in s-trans and s-cis, respectively; the direction of the tilt being the same as in propene. The corresponding experimental values are not available. It was pointed out above that geometry optimization changes the signs of Δg and ΔG in this molecule, but not in propene. This can be understood in the following way. In acetaldehyde, the opening of the CCO angle upon rotation from cis to trans increases the C_1O_6 distance by about 0.02 Å, while no such increase is observed for the CCC angle in propene. Furthermore, the C_1C_2 distance increases by about 0.01 Å in acetaldehyde and the C_2C_6 distance in propene is virtually unchanged. Thus, we are not surprised by the different behavior of the repulsion quantities in the two molecules relative to the frozen frame results.

A partial rationale is that the repulsive interaction between the strongly polar oxygen and the cis hydro-

Table VII. Localized Orbitals in Acetaldehyde[a]

	C_2O_6		C_2H_7		C_1H_3		C_1H_4	
	T	C	T	C	T	C	T	C
$C_1 2$ s	−0.0013	−0.0071	−0.0181	−0.0185	0.3615	0.3583	0.3485	0.3486
$C_1 2$ p_x	0.0199	−0.0216	−0.0510	0.0480	0.5541	0.5581	−0.2925	−0.2873
$C_1 2$ p_y	0.0294	0.0296	0.0	0.0	0.0	0.0	0.4890	0.4904
$C_1 2$ p_z	−0.0030	−0.0007	−0.0061	−0.0090	−0.2512	−0.2378	−0.2195	−0.2280
$C_2 2$ s	0.2806	0.2798	0.4000	0.3994	−0.0056	−0.0105	−0.0069	−0.0040
$C_2 2$ p_x	0.3020	−0.3065	−0.4938	0.4888	0.0653	0.0641	−0.0333	−0.0362
$C_2 2$ p_y	0.4325	0.4318	0.0	0.0	0.0	0.0	0.1136	0.1149
$C_2 2$ p_z	0.2247	0.2194	0.2594	0.2702	−0.0039	−0.0122	−0.0136	−0.0099
H_3	−0.0194	0.0301	0.0489	−0.0316	0.7013	0.7049	−0.0106	−0.0100
H_4	−0.0250	0.0345	−0.0138	0.0281	−0.0120	−0.0120	0.6979	0.6958
H_5	0.0595	−0.0513	−0.0138	0.0281	−0.0120	−0.0120	−0.0011	−0.0007
$O_6 2$ s	0.3087	0.3088	−0.0070	−0.0069	−0.0112	0.0167	0.0097	−0.0050
$O_6 2$ p_x	−0.3426	0.3461	0.0236	−0.0234	0.0126	0.0219	−0.0130	−0.0050
$O_6 2$ p_y	0.5554	0.5581	0.0	0.0	0.0	0.0	−0.0612	−0.0616
$O_6 2$ p_z	−0.2554	−0.2506	−0.0033	−0.0038	0.0155	−0.0204	−0.0113	0.0076
H_7	−0.0134	−0.0132	0.7228	0.7229	0.0468	−0.0314	−0.0134	0.0279

[a] T = s-trans; C = s-cis.

gen (H_3) in s-trans acetaldehyde is greater than the corresponding H_3,H_7 interaction in the cis isomer, while in propene the corresponding interactions (C_1,H_7 and H_4,H_7, respectively) are approximately balanced. Moreover, in propene the H_5,H_4 interaction would tend to inhibit the opening of the CCC angle.

The appropriate acetaldehyde-localized orbitals are listed in Table VII. Their behavior with internal rotation is about the same as described for propene. As a result, we define the interference behavior

$$\Delta I = \Delta I_{\mathrm{Me}} + \Delta I'_{\mathrm{Me}} = 1.380 \text{ kcal/mol} \qquad (23)$$

where

$$\Delta I_{\mathrm{Me}} = \Delta I_{\mathrm{Me,O}} + \Delta I_{\mathrm{Me,H_7}} = 0.654 \text{ kcal/mol} \quad (24)$$

and

$$\Delta I'_{\mathrm{Me}} = \Delta I_{\mathrm{C=O}} + \Delta I_{\mathrm{CH_7}} = 0.726 \text{ kcal/mol} \quad (25)$$

All quantities in eq 23–25 are direct analogs to the propene quantities (eq 14–16). We shall see that all terms but $\Delta I_{\mathrm{C=O}}$ are less than their propene counterparts.

To begin with

$$\Delta I_{\mathrm{Me,O}} = \Delta I_{\mathrm{Me,O}}(\mathrm{O,H_3}) + 2\Delta I_{\mathrm{Me,O}}(\mathrm{O,H_4}) = \\ -1.127 + 1.716 = 0.589 \text{ kcal/mol} \quad (26)$$

and

$$\Delta I_{\mathrm{Me,H_7}} = \Delta I_{\mathrm{Me,H_7}}(\mathrm{H_7,H_3}) + 2\Delta I_{\mathrm{Me,H_7}}(\mathrm{H_7,H_4}) = \\ 1.827 - 1.762 = 0.065 \text{ kcal/mol} \quad (27)$$

both less than the propene energies by factors of about $^2/_3$ and $^1/_3$, respectively. Furthermore

$$\Delta I_{\mathrm{CH_7}} = \Delta I_{\mathrm{CH_7}}(\mathrm{H_7,H_3}) + 2\Delta I_{\mathrm{CH_7}}(\mathrm{H_7,H_4}) = \\ 1.913 - 1.862 = 0.051 \text{ kcal/mol} \quad (28)$$

has decreased by a factor of $^1/_5$, while the remaining term, $\Delta I_{\mathrm{C=O}}$, is relatively unchanged.

$$\Delta I_{\mathrm{C=O}} = 0.675 \text{ kcal/mol} \qquad (29)$$

Thus, the smaller interference barrier in acetaldehyde relative to propene arises from a decrease in all vicinal interferences except those within the banana bonds. It was noted in the previous section that this latter intra-banana bond interference change in propene is smaller than the corresponding contribution in ethane, so that the present interference analysis explains the relative barriers observed in these three molecules.

Conclusions

From the results of the preceding section and previous papers in this series,[2,4] one may draw the following conclusions.

(1) The interference interpretation of internal rotation within the localized orbital context appears to provide a viable, consistent understanding of this phenomenon, particularly for methyl rotations. It is likely that the method will be equally applicable to other rotors, and this latter assumption is presently being investigated.

(2) Barriers may be generally understood in terms of changes in vicinal interference interactions within bond orbitals adjacent to the axial bond, such changes being relatively insensitive to geometry optimizations.

(3) One may define the average change in vicinal interference energy within the CH bonds of a methyl group, ΔI_{Me}(av), as the net methyl contribution, ΔI_{Me}, divided by the number of vicinal bonds. These ΔI_{Me}(av) are listed in Table VIII, where it is seen that *in all of the molecules but acetaldehyde the average interference contribution from the CH orbitals to the net barrier is nearly the same, and ΔI_{Me}, which represents the net methyl contribution, depends only on the number of vicinal bonds.*

Table VIII. Interference Energies Involving Methyl Hydrogens[a]

Methyl CH orbitals		Other orbitals	
Molecule	ΔI_{Me} (av)	Orbital	ΔI
CH_3CH_3	0.408	OH	0.442
CH_3NH_2	0.395	NH	0.420
CH_3CHCH_2	0.372	CO (banana)	0.383
CH_3OH	0.370	CC (banana)	0.320
CH_3CHO	0.218	CH (vinyl, propene)	0.229
		N_{lp}	0.219
		O_{lp}	0.127
		CH (vinyl, acetaldehyde)	0.051

[a] Energy units are kcal/mol.

(4) The other interference terms also appear in Table VIII. The OH and NH orbital contributions are larger than ΔI_{Me}(av) in ethane by about the same amount that ΔI_{Me}(av) in methanol and methylamine are smaller. Thus, *the decrease in the barriers in the order ethane > methylamine > methanol is largely due to the loss of vicinal bonds* (three in ethane, two in methylamine, one in methanol). This is slightly distorted, however, by the smaller contributions from the lone pairs. *In propene, the lower barrier (relative to ethane) is mostly due to the smaller contribution from the vinyl CH orbital, while in acetaldehyde this contribution and the reduced contributions from the methyl CH orbitals are responsible for the lower barrier.*

Except for H_2O_2, the molecules studied within the localized charge distribution analysis contain at least one methyl rotor. Work is presently underway to investigate the two-rotor analogs of the molecules discussed in this paper. Of particular interest will be the so-called steric hindrance in the all-eclipsed rotamers. Also being investigated is the applicability of the method to geometric isomerization, keto–enol tautomerism, ring strain, pseudorotation, and hydrogen bonding. The results will appear in future publications.

Acknowledgments. The authors gratefully acknowledge the computer time made available to them by the North Dakota State University Computer Center and the support of Professor Klaus Ruedenberg. One of us (M. S. G.) was supported in part by a National Science Foundation Institutional Grant to North Dakota State University.

Localized Molecular Orbitals for 1,2- and 1,6-Dicarbahexaborane(6). The Open Three-Center Bond and Implications for Carborane Topology

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Received August 28, 1972

Abstract: Localized molecular orbitals (LMO's) have been calculated for the 1,2 and 1,6 isomers of $C_2B_4H_6$ by the Edmiston–Ruedenberg procedure. The 1,2 isomer is the first example found in LMO calculations of the existence of the open three-center bond, and it occurs here only for the BCB nuclear configuration. The LMO structure for the 1,6 isomer is best interpreted in terms of fractional three-center bonding. We discuss the implications of these results for the general application of topological methods to boranes and carboranes.

The carboranes constitute a fascinating series of molecules for experimental and theoretical chemists alike. The polyhedral geometries and the peculiar bonding properties of these compounds give rise to such recently discovered phenomena as carborane analogs of ferrocene,[2] commercially significant high-temperature carborane–siloxane polymers,[3] and the fractional three-center bond.[4,5]

Although self-consistent-field (SCF) and localized molecular orbital (LMO) studies have been of enormous utility in elucidating the nature of chemical bonding in the boron hydrides,[6] only two carboranes, 2,4-$C_2B_5H_7$[4b] and 4,5-$C_2B_4H_8$,[5] have been studied by SCF and LMO methods. In these studies, special attention was paid both to the applicability of the topological theory of the boron hydrides[7,8] to carboranes and also to the relationship between the topological theory and the LMO approach. Briefly, it was found that neither the LMO's of $C_2B_5H_7$ nor those of $C_2B_4H_8$ closely correspond to a valence structure which satisfies the set of rules proposed by Epstein and Lipscomb (E–L) in their simplified topological treatment of the boron hydrides.[8] However, with a modification suggested earlier[9] for the bonding rules in $C_2B_4H_8$, we have found simple linear combinations of E–L allowed structures which correctly describe the relative bond strengths and atomic charges obtained from the SCF calculations in both of these molecules. By recognizing that complex molecules may require a linear combination of a few or several valence structures for their description, one can thus preserve the important simplification that conservation of orbitals, electrons, and topology[8] may be achieved with only two-center and three-center bonds in the boron or boron–carbon framework. In view of the potential usefulness of the topo-

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