

# A Molecular Orbital Study of Internal Rotation

Mark S. Gordon<sup>1</sup>

Contribution from the Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213. Received October 11, 1968

**Abstract:** The CNDO/2 molecular orbital method is used to predict and explain the barriers to internal rotation in a number of molecules. The observed 3:2:1 ratio of the barriers in ethane, methylamine, and methyl alcohol is approximately reproduced as are most trends in the barriers of fluoro-substituted propenes; however, the calculated trends for fluoro-substituted ethanes are incorrect. The barriers in H<sub>2</sub>O<sub>2</sub>, F<sub>2</sub>O<sub>2</sub>, N<sub>2</sub>H<sub>4</sub>, N<sub>2</sub>F<sub>4</sub>, and NH<sub>2</sub>OH and the effect of geometry optimization on these barriers are also discussed. The major source of the barriers in the first group of molecules is predicted to be due primarily to nonbonded interactions across the axial bonds, while interactions between the lone pairs on the axial bonds are found to be important in the latter group. It is concluded that CNDO will be applicable to further barrier studies only if nonbonded interactions involving highly electronegative atoms (e.g., F) are unimportant.

The nature of the forces which give rise to barriers to internal rotation has been an important and intriguing problem for quite some time. In recent years accurate SCF molecular orbital calculations have been used with increasing frequency in an attempt to reproduce and explain the origin of these barriers.<sup>2-10</sup> However, owing to the complexity of the calculation of accurate molecular wave functions, *ab initio* results for internal rotation barriers have been limited to rather small molecules. The method of complete neglect of differential overlap (CNDO) developed by Pople, Santry, and Segal<sup>11-13</sup> is much reduced in complexity with respect to *ab initio* calculations and is therefore applicable to a much wider range of molecules. Since CNDO has proved to be quite successful in predicting and explaining many molecular properties,<sup>13-20</sup> the present work was undertaken to determine the applicability of the method to the problem of internal rotation.

## Method of Calculation

The coordinates of all molecules investigated were obtained using the "Model-Builder" program (MBLD) described elsewhere.<sup>21</sup> The approximations involved in CNDO have been described in detail<sup>11-13</sup> and will not be repeated here; however, the energy expressions derived in ref 11 are pertinent to the discussion of bar-

riers and will be described briefly. If one writes a molecular orbital  $\phi_i$  as a linear combination of atomic orbitals  $\chi_\mu$

$$\phi_i = \sum_{\mu} \chi_{\mu} C_{\mu i} \quad (1)$$

where the  $C_{\mu i}$ 's are the LCAO coefficients, then the total energy of a molecule may be written in terms of matrix elements over atomic orbitals

$$E = \frac{1}{2} \sum_{\mu} \sum_{\nu} P_{\mu\nu} (H_{\mu\nu} + F_{\mu\nu}) + \sum_{A < B} Z_A Z_B / R_{AB} \quad (2)$$

The first term in eq 2 is the electronic energy, and the second is the nuclear repulsion.  $Z_A$  is the core charge on atom A and  $R_{AB}$  is the internuclear distance.  $H_{\mu\nu}$  is the one-electron matrix element between atomic orbitals  $\chi_\mu$  and  $\chi_\nu$  and contains the kinetic energy and electron-nuclear attraction.  $F_{\mu\nu}$  is a matrix element of the two-electron operator, containing contributions from the Coulomb and exchange interactions.  $P_{\mu\nu}$  is an element of the bond order-electron density matrix which, within the CNDO framework,<sup>11</sup> may be written

$$P_{\mu\nu} = 2 \sum_{i}^{\text{occ}} C_{\mu i} C_{\nu i} \quad (3)$$

the summation being over all occupied molecular orbitals. The diagonal element  $P_{\mu\mu}$  is then the total electron density on orbital  $\chi_\mu$ . Using the CNDO approximations, one may derive a convenient expression in which the total energy is separated into a sum of one- and two-center terms<sup>11</sup>

$$E = \sum_A E_A + \sum_{A < B} E_{AB} \quad (4)$$

where

$$E_A = \sum_{\mu}^A P_{\mu\mu} U_{\mu\mu} + \frac{1}{2} \sum_{\mu}^A \sum_{\nu}^A (P_{\mu\mu} P_{\nu\nu} - \frac{1}{2} P_{\mu\nu}^2) \gamma_{AA} \quad (5)$$

is the energy due to atom A. The superscript A on the summation means that only orbitals on atom A are included.  $U_{\mu\mu}$  is the one-electron energy of atomic orbital  $\chi_\mu$  in the isolated atom.  $\gamma_{AB}$  is a two-electron integral between an electron on atom A and one on B; that is

$$\gamma_{AB} = \int \chi_A^*(1) \chi_A(1) 1/r_{12} \chi_B^*(2) \chi_B(2) d\tau_1 d\tau_2 \quad (6)$$

- (1) Department of Chemistry, Iowa State University, Ames, Iowa.
- (2) R. M. Pitzer and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 1995 (1963).
- (3) R. M. Pitzer, *ibid.*, **47**, 965 (1967).
- (4) E. Clementi and D. R. Davis, *ibid.*, **45**, 2593 (1966).
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- (9) A. Veillard, *Theoret. Chim. Acta*, **5**, 413 (1966).
- (10) W. H. Fink, D. C. Pan, and L. C. Allen, *J. Chem. Phys.*, **47**, 895 (1967).
- (11) J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, S129 (1965).
- (12) J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965).
- (13) J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).
- (14) D. P. Santry and G. A. Segal, *ibid.*, **47**, 158 (1967).
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- (16) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).
- (17) G. A. Segal, *J. Chem. Phys.*, **47**, 1876 (1967).
- (18) G. A. Segal and M. L. Klein, *ibid.*, **47**, 4236 (1967).
- (19) K. B. Wiberg, *J. Am. Chem. Soc.*, **90**, 59 (1968).
- (20) C. Giessner-Pretre and A. Pullman, *Theoret. Chim. Acta*, **9**, 279 (1968).
- (21) M. S. Gordon and J. A. Pople, Quantum Chemistry Program Exchange, Program No. 135.

The two-atom energy,  $E_{AB}$ , is given by

$$E_{AB} = E_{AB}^{(1)} + E_{AB}^{(2)} + E_{AB}^{(3)} \quad (7)$$

$$E_{AB}^{(1)} = 2 \sum_{\mu}^A \sum_{\nu}^B P_{\mu\nu} S_{\mu\nu} \beta_{AB}^0 \quad (8)$$

$S_{\mu\nu}$  is an atomic overlap integral and  $\beta_{AB}^0$  is an empirical bonding parameter; thus each term in  $E_{AB}^{(1)}$  measures the contribution of the bonding (or antibonding) between  $\chi_{\mu}$  on atom A and  $\chi_{\nu}$  on atom B to the two-atom energy. Since  $\beta_{AB}^0$  is negative, a negative  $E_{AB}^{(1)}$  means that the net interaction between atoms A and B is bonding.

$$E_{AB}^{(2)} = -\frac{1}{2} \sum_{\mu}^A \sum_{\nu}^B P_{\mu\nu}^2 \gamma_{AB} \quad (9)$$

represents a stabilization due to exchange interactions. The final contribution to the two-atom energy,  $E_{AB}^{(3)}$ , is given by

$$E_{AB}^{(3)} = P_{AA}P_{BB}\gamma_{AB} - P_{AA}Z_B\gamma_{AB} - P_{BB}Z_A\gamma_{AB} + Z_A Z_B / R_{AB} \quad (10)$$

where

$$P_{AA} = \sum_{\mu}^A P_{\mu\mu} \quad (11)$$

is the total electron density on atom A.  $E_{AB}^{(3)}$  represents the electrostatic interaction between atoms A and B. This may be seen by recognizing that at large internuclear separation,  $\gamma_{AB}$  may be approximated as  $1/R_{AB}$  so that  $E_{AB}^{(3)}$  reduces to

$$E_{AB}^{(3)} = (P_{AA} - Z_A)(P_{BB} - Z_B) / R_{AB} = Q_A Q_B / R_{AB} \quad (12)$$

where  $Q_A$  and  $Q_B$  are the net charges on atoms A and B, respectively. The procedure to be followed will be to compare these various terms ( $E_A$  and  $E_{AB}$ ) in the energy breakup for different rotational configurations of a molecule in an attempt to gain an understanding of the origin of the barrier. All calculations were performed on the Bendix G-21 and CDC 1604 computers at Carnegie-Mellon University.

## Results and Discussion

**C<sub>2</sub>H<sub>6</sub>, CH<sub>3</sub>NH<sub>2</sub>, CH<sub>3</sub>OH.** In Table I the calculated barriers are compared with the experimental values<sup>22-24</sup> as well as with the results of *ab initio* calculations.<sup>2-6</sup> All three molecules are in the staggered configuration in their unperturbed ground states with the least stable configuration being the eclipsed form (see Figure 1). Thus the barrier height is simply the difference in energy between these two configurations. All calculations quoted in Table I predict the staggered configuration to be most stable. Although the CNDO barriers are too small, they are consistently so, and in fact the observed 3:2:1 ratio of the barriers is approximately reproduced.

For ethane, methylamine, and methyl alcohol  $\sum_A \Delta E_A$  is 0.08, 0.12, and 0.16 kcal/mole, respectively, the staggered configuration being preferred in all three cases. Since the corresponding barriers are 2.18, 1.57, and 0.78 kcal/mole, respectively, the major source of

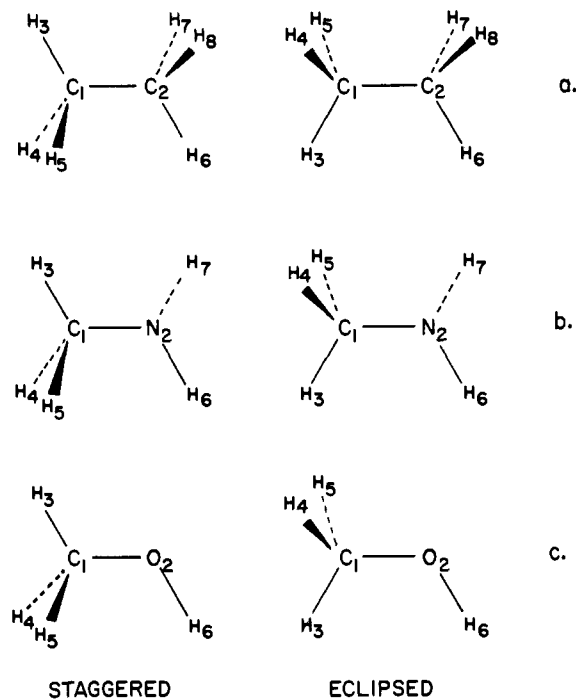


Figure 1. Staggered and eclipsed configurations: (a) ethane, (b) methylamine, (c) methyl alcohol.

these barriers must be the difference in the two-atom energies  $\Delta E_{AB}$ . The barriers in these simple molecules are often attributed to nonbonded interactions of some sort,<sup>25</sup> usually H...H interactions across the axial

Table I. Comparison of CNDO Barriers with Experimental and *Ab Initio* MO Results for C<sub>2</sub>H<sub>6</sub>, CH<sub>3</sub>NH<sub>2</sub>, and CH<sub>3</sub>OH

Molecule	Barrier, kcal/mole	Molecule	Ref <sup>a</sup>
C <sub>2</sub> H <sub>6</sub>	2.18	CNDO	This work
	2.875	Experiment	22
	3.3-3.5	STO	2,3
	3.6	Gaussian	4
	2.88	Gaussian	5
	3.45	Gaussian (P orb. on H)	5
CH <sub>3</sub> NH <sub>2</sub>	2.52	Gaussian	6
	1.57	CNDO	This work
	1.97	Experiment	23
	2.02	Gaussian	5
	2.42	Gaussian	6
CH <sub>3</sub> OH	0.78	CNDO	This work
	1.07	Experiment	24
	1.59	Gaussian	5
	1.34	Gaussian	6
	1.10	Gaussian (P orb. on H)	6

<sup>a</sup> References quoted refer to text.

bonds. If this hypothesis is correct, then one should be able to sum all contributions  $\Delta E_{AB}$  for A bonded to B and obtain a negligible contribution to the barriers. That is, if a barrier arises primarily from nonbonded interactions, any given  $\Delta E_{AB}$  for A bonded to B should arise only as a manifestation of nonbonded interactions

(22) K. S. Pitzer, *Discussions Faraday Soc.*, **10**, 66 (1957).  
 (23) T. Nishikawa, T. Itoh, and K. Shimoda, *J. Chem. Phys.*, **23**, 1735 (1955).  
 (24) E. V. Ivash and D. M. Dennison, *ibid.*, **21**, 1804 (1953).

(25) See, for example, E. A. Mason and M. Kreevoy, *J. Am. Chem. Soc.*, **77**, 5808 (1955); E. N. Lassette and L. B. Dean, Jr., *J. Chem. Phys.*, **17**, 317 (1949); L. Pauling, *Proc. Natl. Acad. Sci. U. S.*, **44**, 211 (1958); R. A. Scott and H. A. Sheraga, *J. Chem. Phys.*, **42**, 2209 (1963).

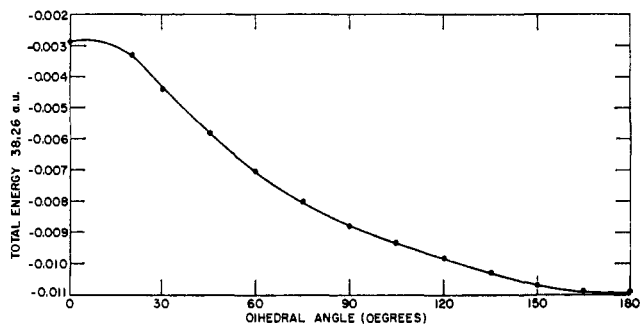


Figure 2. Total energy vs. dihedral angle for  $\text{H}_2\text{O}_2$  (experimental geometries).

being transmitted through the bonds, and the sum of all such contributions should be small.

$$\sum_{A<B} \sum \Delta E_{AB} = \left( \sum_{A<B} \sum \Delta E_{AB} \right) \text{bond} + \left( \sum_{A<B} \sum \Delta E_{AB} \right) \text{no bond} = \Delta E_{AB}^b + \Delta E_{AB}^n \approx \Delta E_{AB}^n \quad (13)$$

This is indeed found to be the case for ethane, methylamine, and methyl alcohol,  $\Delta E_{AB}^b$  for these molecules being 0.05, 0.07, and 0.11 kcal/mole, respectively. Furthermore, these contributions are all opposite in sign to the corresponding values of  $\sum_A \Delta E_A$ .

The only remaining terms which significantly contribute to the barriers in these molecules involve  $\Delta E_{AB}$ , where A and B are hydrogens on opposite ends of the axial bonds. The individual contributions as well as their sums are listed in Table II. The numbering system corresponds to Figure 1 so that, for example, in ethane hydrogens 3 and 6 are *trans* in the staggered and *cis* in the eclipsed form while atoms 3 and 7 are separated by a dihedral angle of  $60^\circ$  in the staggered and  $120^\circ$  in the eclipsed form. For ethane, the total contribution to the barrier from differences in  $\Delta E_{\text{HH}}$  is 2.10 kcal/mole; thus such interactions account for almost all of the barrier. The change in interaction energy between a hydrogen on one methyl group and the three hydrogens on the other methyl (e.g.,  $\Delta E_{36} + \Delta E_{37} + \Delta E_{38}$ ) is 0.7 kcal/mole or one-third of the barrier. Breaking up these contributions to the barrier according to eq 7, it is found that  $\Delta E_{AB}^{(1)}$  is almost entirely responsible for the changes in the non-bonded energies; for example,  $\Delta E_{36}^{(1)} + \Delta E_{37}^{(1)} + \Delta E_{38}^{(1)} = 0.75$  kcal/mole in ethane. The contribution to the barrier of  $\Delta E_{AB}^{(2)}$  and  $\Delta E_{AB}^{(3)}$  are rather small in comparison.

The results are quite similar for methylamine and methyl alcohol. In the former molecule the total change in  $\text{H} \cdots \text{H}$  interactions is 1.52 kcal/mole (barrier = 1.57 kcal/mole), while for methanol it is 0.74 kcal/mole (barrier = 0.78). The net change in interaction energy between a hydrogen on the amino group and all methyl hydrogens is 0.76 kcal/mole, while the corresponding change for the hydroxyl hydrogen in methanol is 0.74. The corresponding values for  $\Delta E_{AB}^{(1)}$  are 0.67 and 0.73 kcal/mole, respectively. Thus the barriers in these three molecules (according to CNDO) may be explained almost entirely in terms of a net increase in antibonding between hydrogens across the axial bond as the molecule is rotated from the staggered to the eclipsed configuration. The similarity in

Table II. Contributions of Nonbonded H-H Interactions to Barriers in Ethane, Methylamine, and Methyl Alcohol

Ethane		Methylamine		Methyl alcohol	
A-B	$\Delta E_{AB}^a$ , kcal/mole	A-B	$\Delta E_{AB}^a$ , kcal/mole	A-B	$\Delta E_{AB}^a$ , kcal/mole
3-6	5.18 (S)	3-6	5.65 (S)	3-6	5.36 (S)
3-7	2.24 (E)	4-6	2.65 (E)	4-6	2.31 (E)
3-8	2.24 (E)	5-6	2.24 (E)	5-6	2.31 (E)
4-6	2.24 (E)	3-7	2.24 (E)	Total	0.74 (S)
4-7	2.24 (E)	4-7	2.65 (E)		
4-8	5.18 (S)	5-7	5.65 (S)		
5-6	2.24 (E)	Total	1.52 (S)		
5-7	5.18 (S)				
5-8	2.24 (E)				
Total	2.10 (S)				

<sup>a</sup> The letter S in parentheses in this column indicates the staggered configuration is preferred; E indicates eclipsed is preferred.

the values of these contributions to the barriers of all three molecules is noteworthy and indicates that the steady decrease in the barrier heights from ethane to methanol is simply due to the successive loss of a set of these interactions rather than the changes in inherent properties of the axial bond. It is found, as Pedersen and Morokuma<sup>5</sup> have observed, that those methyl hydrogens closest to the lone pairs on methylamine and methanol consistently have lower electron densities than do the other hydrogens in the methyl group; however, if these lone pairs play an important part in determining the barriers of these molecules it is not readily apparent from the present analysis.

$\text{H}_2\text{O}_2$ . Hydrogen peroxide is a nonplanar molecule with a dihedral angle,  $\omega$ , of  $111.5^\circ$  if  $\omega = 0^\circ$  is taken to be the configuration with the two hydrogens eclipsed.<sup>26</sup> Thus this molecule has barriers to internal rotation in both the *cis* ( $\omega = 0^\circ$ ) and *trans* ( $\omega = 180^\circ$ ) positions of 7.0 and 1.1 kcal/mole, respectively. Most *ab initio* calculations<sup>5-8</sup> fail to reproduce this geometry and, in fact, predict the molecule to be *trans* planar with only a *cis* barrier. Since the experimental geometry of hydrogen peroxide is quite different from the values used by MBLD, the CNDO calculations for this molecule were performed using the experimental values:  $R_{\text{OO}} = 1.475 \text{ \AA}$ ,  $R_{\text{OH}} = 0.95 \text{ \AA}$ , and  $\text{OOH angle} = 94.8^\circ$ . Using these values, the energy of  $\text{H}_2\text{O}_2$  was calculated at  $15^\circ$  intervals in the dihedral angle. The results are displayed graphically in Figure 2, and it is obvious that CNDO also fails to predict a *trans* barrier. The *trans* configuration is calculated to be more stable than the *cis* by 5.16 kcal/mole.

Because hydrogen peroxide has rather unusual bond lengths and angles as well as a nonplanar configuration, it is of interest to minimize the energy of this molecule with respect to all geometric parameters. The energy of both *cis*- and *trans*-hydrogen peroxide was minimized with respect to bond lengths and bond angles by the procedure outlined earlier.<sup>27</sup> Both configurations were then re-minimized for all geometric parameters including dihedral angle. In both cases a nonplanar equilibrium configuration was obtained with a dihedral angle of  $87.0^\circ$  and *cis* and *trans* barriers of 5.0 and 2.85 kcal/mole, respectively. The predicted bond lengths and OOH angle for all three configura-

(26) R. H. Hunt, R. A. Leacock, C. W. Peters, and K. T. Hecht, *J. Chem. Phys.*, **43**, 1931 (1965).

(27) M. Gordon and J. A. Pople, *ibid.*, **49**, 4643 (1968).

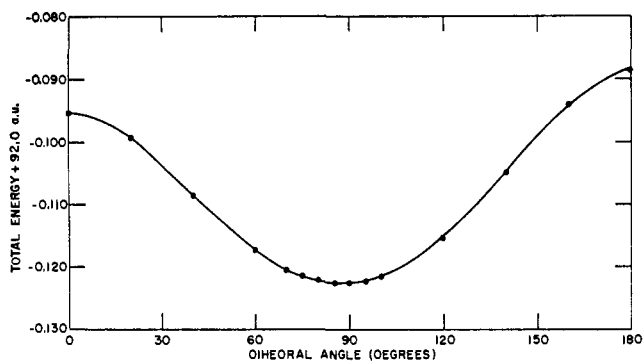


Figure 3. Total energy vs. dihedral angle for  $F_2O_2$  (experimental geometries).

tions are compared with the experimental values in Table III. Although the calculated values are considerably different from the experimental results, it is interesting to note that while the predicted bond lengths are virtually the same for all rotamers, the bond angles decrease consistently with increasing dihedral angle as one might intuitively expect.

Table III. Comparison of CNDO and Experimental Geometries for  $H_2O_2$

Dihedral angle, deg	$R_{OO}$ , Å	$R_{OH}$ , Å	$\angle OOH$ , deg
0	1.22	1.03	110.5
87	1.22	1.04	108.5
180	1.22	1.04	105.0
111.5 (exptl) <sup>a</sup>	1.475	0.95	94.8

<sup>a</sup> Reference 26 of text.

The energy breakup of hydrogen peroxide is rather different from the analysis of the previous molecules considered.  $\Delta E_{AB}$ <sup>b</sup> is not at all negligible for  $H_2O_2$ , and in fact the only term which favors the nonplanar configuration is the two-atom energy between the oxygens,  $\Delta E_{OO}$ . All other terms prefer to be in the *trans* position. Upon closer analysis it becomes apparent that, as before,  $\Delta E_{OO}$  is due almost exclusively to the "bonding" term  $\Delta E_{OO}^{(1)}$ . There is a substantial bond order (0.121) between the  $2p_y(\pi)$  orbitals on the oxygens in the nonplanar configuration, while the corresponding bond order is zero for both *cis* and *trans*. This is also indicated by the charge density on the  $2p_y$  orbital in oxygen which is 2.0 for both planar forms but only 1.979 for the nonplanar configuration. Thus, according to CNDO, the *trans* barrier in hydrogen peroxide is due to  $\pi$  bonding between the oxygens in the nonplanar configuration. The higher *cis* barrier is primarily the result of increased antibonding between the hydrogens.

$F_2O_2$ .  $F_2O_2$  is also a nonplanar molecule with a dihedral angle of  $87.5^\circ$ .<sup>28</sup> While the barriers have not been measured, they are expected to be higher than those for hydrogen peroxide. Using the experimental bond lengths and bond angle, CNDO calculations were performed on this molecule at  $15^\circ$  intervals in the dihedral angle (Figure 3). A nonplanar configuration,  $\omega = 88^\circ$ , is predicted to be the most stable with *cis* and *trans* barriers of 17.1 and 21.3 kcal/mole, respectively;

(28) R. H. Jackson, *J. Chem. Soc.*, 4585 (1962).

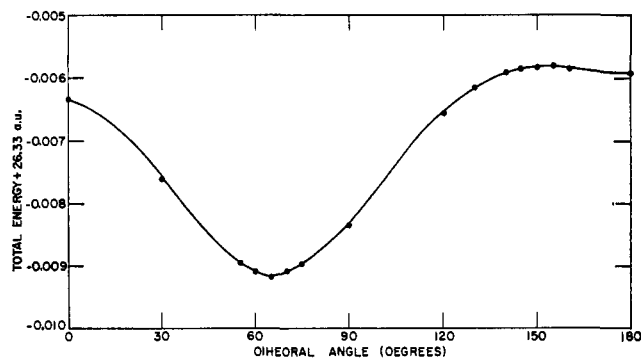


Figure 4. Total energy vs. dihedral angle for  $N_2H_4$  (standard geometries).

however, it is unusual that *cis* is predicted to be more stable than *trans*. An energy minimization analogous to that carried out for hydrogen peroxide was performed for  $F_2O_2$ , and again a nonplanar configuration was obtained ( $\omega = 86.5^\circ$ ). Now, however, *trans*- $F_2O_2$  is predicted to be more stable than *cis*, the barriers being 4.50 and 6.05 kcal/mole, respectively. The predicted geometries for the three configurations are listed in Table IV. The O-F bond length is rather small, but the geometry for the nonplanar configuration is otherwise in good agreement with experiment. Again, the bond lengths are invariant with respect to dihedral angle while the OOF angle decreases from *cis* to *trans*.

Table IV. Comparison of CNDO and Experimental Geometries for  $F_2O_2$

Dihedral angle, deg	$R_{OO}$ , Å	$R_{OF}$ , Å	$\angle OOF$ , deg
0	1.23	1.18	109.0
86.5	1.22	1.18	108.0
180	1.23	1.18	105.0
87.5 (exptl) <sup>a</sup>	1.217	1.575	109.5

<sup>a</sup> Reference 28 of text.

The barrier analysis of  $F_2O_2$  is similar to that for hydrogen peroxide.  $\Delta E_{AB}$ <sup>b</sup> is not negligible, the source of the *trans* barrier being bonding between the  $2p_y$  lone pairs on the oxygens (bond order = 0.127). The higher *cis* barrier is due to increased antibonding between the fluorines.

$N_2H_4$ . The dihedral angle in an  $A_2B_4$  molecule may be defined as the angle between the bisectors of the two BAB angles. Thus  $\omega = 0^\circ$  corresponds to the all-eclipsed configuration,  $\omega = 180^\circ$  to the all-staggered configuration, and  $\omega = 120^\circ$  to the configuration in which one pair of B atoms is eclipsed and the other pair is staggered. It has been established from the microwave spectrum of hydrazine<sup>29</sup> that this molecule has a dihedral angle of  $90$ – $95^\circ$ . Assuming equal *cis* and *trans* barriers, the experimental barrier height is 3.14 kcal/mole.<sup>29</sup> A number of *ab initio* calculations have been performed on hydrazine,<sup>5,9,10</sup> each of which yields a dihedral angle near  $90^\circ$ . Allen, *et al.*,<sup>10</sup> predict *cis* and *trans* barriers of 11.88 and 3.70 kcal/mole, respectively. Veillard's<sup>9</sup> results are 11.5 and 4.7 kcal/mole, and Pedersen and Morokuma<sup>5</sup> obtain 11.05 and 6.21 kcal/mole. Using the MBLD geometries, the

(29) T. Kasuya and T. Kojima, *J. Phys. Soc. Japan*, **18**, 364 (1963).

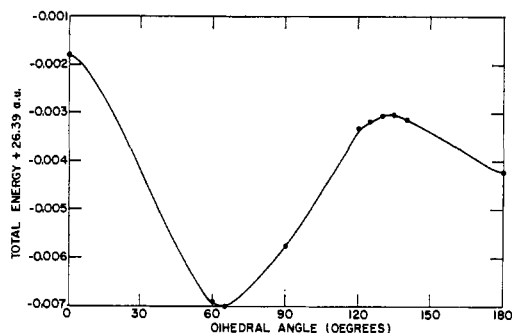


Figure 5. Total energy vs. dihedral angle for  $N_2H_4$  (calculated geometries).

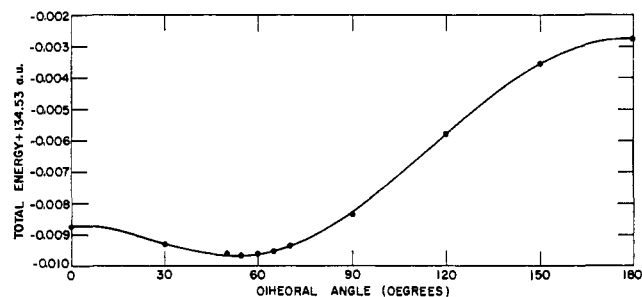


Figure 6. Total energy vs. dihedral angle for  $N_2F_4$  (standard geometries).

energy of hydrazine was calculated by CNDO as a function of dihedral angle with the results displayed in Figure 4. The most stable configuration is correctly predicted to be skewed ( $\omega = 65.0^\circ$ ) but with a somewhat smaller dihedral angle than observed experimentally. However, the eclipsed configuration is calculated to be more stable than *trans* in disagreement with the *ab initio* results and a very slight maximum in the energy curve is found at  $\omega = 155^\circ$ .

The energy of hydrazine was minimized with respect to bond length and bond angles for a number of dihedral angles with the results shown in Figure 5. The dihedral angle of the most stable configuration is  $66.0^\circ$  with a barrier of 3.3 kcal/mole at  $\omega = 0^\circ$ ; however, the energy curve is quite different from the standard model in other respects. The *trans* configuration is now more stable than *cis* by 1.9 kcal/mole, in qualitative agreement with the *ab initio* results. However, the *trans* rotamer is predicted to be a second minimum with a skew to *trans* barrier of 2.5 kcal/mole occurring at a dihedral angle of  $133^\circ$ . The occurrence of the second minimum is probably questionable; however, this situation is found to occur in the related molecule  $N_2F_4$ .<sup>30</sup>

The predicted geometries of the extrema in hydrazine are compared with experimental values in Table V. The CNDO results are in fair agreement with experiment, and the HNN bond angle is predicted to decrease from eclipsed to staggered.

The energy breakup of hydrazine is not so easily analyzed as it was for  $H_2O_2$  and  $F_2O_2$ ; however, it is interesting that  $\Delta E_{NN}^{(1)}$  is large and that one cannot simply sum all bonded terms to give a negligible contribution to the barrier. Most of the  $\Delta E_{NN}$  lies in the bonding

(30) C. B. Colburn, F. A. Johnson, and C. Haney, *J. Chem. Phys.*, **43**, 4526 (1965).

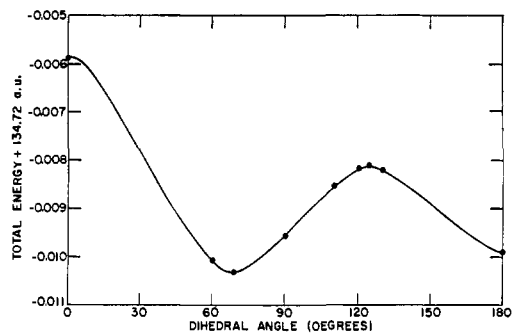


Figure 7. Total energy vs. dihedral angle for  $N_2F_4$  (calculated geometries).

term  $\Delta E_{NN}^{(1)}$ ; thus it seems that in hydrazine, as in  $H_2O_2$  and  $F_2O_2$ , the lone pairs on the axial atoms play an important role in determining the barriers.

Table V. Comparison of CNDO and Experimental Geometries for  $N_2H_4$

Dihedral angle, deg	$R_{NN}$ , Å	$R_{NH}$ , Å	$\angle NNH$ , deg	$\angle HNH$ , deg
0	1.33	1.07	110.6	102.5
66	1.33	1.07	109.0	103.0
133	1.34	1.07	107.5	102.5
180	1.34	1.07	106.5	102.5
90-95 (exptl) <sup>a</sup>	1.45	1.20	112.0	105.8

<sup>a</sup> A. Yamaguchi, I. Schishima, T. Shimanouchi, and S. Mizushima, *Spectrochim. Acta*, **16**, 1471 (1960).

$N_2F_4$ . Tetrafluorohydrazine has a dihedral angle of  $65^\circ$ , and the barriers are estimated to be greater than 3 kcal/mole.<sup>31</sup> Colburn, *et al.*,<sup>30</sup> suggest two minima at dihedral angles of 60 and  $180^\circ$  with the latter more stable by 0.1-0.2 kcal/mole. Durig and Clark<sup>32</sup> also find two isomers (*gauche* and *trans*) with a very small energy difference. Using CNDO, the energy of  $N_2F_4$  was calculated as a function of dihedral angle with the results shown in Figure 6. Only one minimum is found at  $\omega = 55^\circ$  with *cis* and *trans* barriers of 0.53 and 4.30 kcal/mole, respectively. The corresponding energy vs. dihedral angle curve for energy-minimized bond lengths and angles is displayed in Figure 7 and is rather different from Figure 6. The most stable structure has a dihedral angle of  $69.0^\circ$  in good agreement with experiment. In addition, a second minimum is found at the *trans* position and is 0.25 kcal/mole less stable than the lowest energy configuration. The occurrence of the second minimum is in agreement with the experimental evidence.<sup>30,32</sup> The barrier in the *cis* position is calculated to be 2.75 kcal/mole, while the second maximum at  $\omega = 124^\circ$  is 1.40 kcal/mole lower in energy than *cis*. The predicted geometries for the extrema in the energy vs. dihedral angle curve for  $N_2F_4$  are listed in Table VI, the results for the predicted equilibrium configuration being in fair agreement with experiment.

As for hydrazine the energy breakup for  $N_2F_4$  is rather inconclusive since there are many contributing terms of similar order of magnitude; however,  $\Delta E_{NN}^{(1)}$  is again important and  $\Delta E_{AB}^b$  is not negligible.

(31) D. R. Lide and D. E. Mann, *ibid.*, **31**, 1129 (1959).

(32) J. R. Durig and J. W. Clark, *ibid.*, **48**, 3217 (1968).

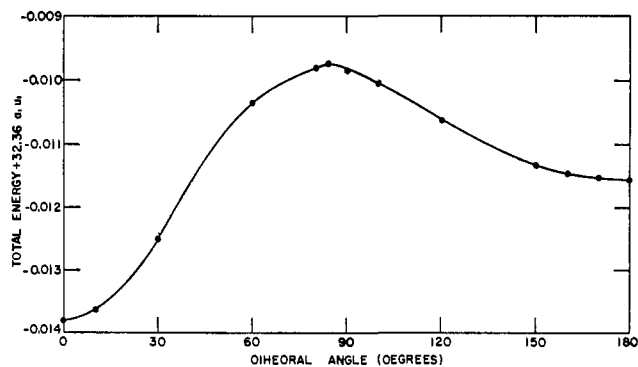


Figure 8. Total energy vs. dihedral angle for  $\text{NH}_2\text{OH}$  (standard geometries).

**$\text{NH}_2\text{OH}$ .** The dihedral angle in hydroxylamine may be defined as the angle between the O-H bond and the bisector of the HNH angle. It is thought that the most stable configuration is either *cis* staggered ( $\omega = 0^\circ$ ) or *trans* staggered ( $\omega = 180^\circ$ ).<sup>33,34</sup> Allen, *et al.*,<sup>10</sup>

Table VI. Comparison of CNDO and Experimental Geometries for  $\text{N}_2\text{F}_4$

Dihedral angle, deg	$R_{\text{NN}}$ , Å	$R_{\text{NF}}$ , Å	$\angle \text{NNF}$ , deg	$\angle \text{FNF}$ , deg
0	1.36	1.25	107.5	105.0
69	1.36	1.25	106.0	105.0
124	1.36	1.25	106.0	104.5
180	1.36	1.25	105.0	105.0
65 (exptl) <sup>a</sup>	1.47	1.37	104.0	108.0

<sup>a</sup> Reference 31 of text.

predict minima at both configurations with *trans* staggered more stable by 10.79 kcal/mole and a *trans* to *cis* barrier of 11.95 kcal/mole. The barrier is predicted to occur at a dihedral angle of  $53.5^\circ$ . Pedersen and Morokuma<sup>5</sup> predict *trans* staggered to be more stable than *cis* by 7.37 kcal/mole with a *trans* to *cis* barrier of 9.90 kcal/mole at  $\omega = 60^\circ$ . The energy vs. dihedral angle curve calculated by CNDO for standard MBLD geometries is shown in Figure 8. While minima are predicted at both *cis*- and *trans*-staggered configurations, the former is more stable by 1.43 kcal/mole in disagreement with the more exact calculations. The calculated *cis* to *trans* barrier is 2.5 kcal/mole at a dihedral angle of  $84^\circ$ .

The geometry minimization for hydroxylamine was run with the simplifying assumption that the two N-H bonds and the HNO angles are equal (Figure 9). *cis* staggered is again predicted to be more stable than *trans*, the energy difference being 1.10 kcal/mole. The calculated *cis* to *trans* barrier is 3.60 kcal/mole, the maximum-energy configuration occurring at a dihedral angle of  $74^\circ$ . Thus the CNDO results are still in disagreement with the *ab initio* calculations. The predicted geometries for the maximum and minima of hydroxylamine are compared with the experimental values in Table VII. The agreement is fair, and again the bond angles are seen to vary considerably with the dihedral angle.

(33) E. A. Myers and W. N. Lipscomb, *Acta Cryst.*, **8**, 583 (1955).

(34) P. A. Giguere and I. D. Liu, *Can. J. Chem.*, **30**, 948 (1952).

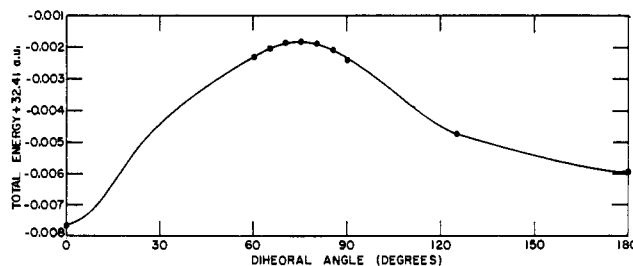


Figure 9. Total energy vs. dihedral angle for  $\text{NH}_2\text{OH}$  (calculated geometries).

No one term in the energy breakup comparison stands out as being primarily responsible for the greater stability of the *cis*-staggered configuration; however, as for the other molecules with lone pairs on both ends of the axial bonds,  $\Delta E_{\text{NO}}^{(1)}$  is quite large and  $\Delta E_{\text{AB}}^b$  is not negligible.

Table VII. Comparison of CNDO and Experimental Geometries for  $\text{NH}_2\text{OH}$

Dihedral angle, deg	$R_{\text{NO}}$ , Å	$R_{\text{NN}}$ , Å	$R_{\text{OH}}$ , Å	$\angle \text{HNO}$ , deg	$\angle \text{NOH}$ , deg	$\angle \text{HNH}$ , deg
0	1.28	1.08	1.04	109.0	110.0	103.0
74	1.29	1.08	1.03	108.0	108.5	101.5
180	1.28	1.08	1.04	107.0	106.0	103.0
Exptl <sup>a</sup>	1.41	1.02	0.96	106.0	103.0	107.0

<sup>a</sup> Reference 34 of text.

Since geometry optimization has been shown to have a rather substantial effect on the energy curve of small molecules, it is of interest to investigate the barriers of geometry-optimized ethane, methylamine, and methanol. For the latter two molecules, the methyl groups were restrained to  $\text{C}_{3v}$  and the tilting of the methyl groups was not taken into account. In addition, the  $\text{NH}_2$  group in methylamine was restrained to  $\text{C}_{2v}$  symmetry. The resulting barriers for these three molecules are 2.25, 2.07, and 1.25 kcal/mole, while  $\Delta E$  due to hydrogen interactions across the axial bond are 2.25, 1.78, and 0.96 kcal/mole, respectively. Thus, although the 3:2:1 ratio of these barriers is no longer reproduced, they are still interpreted by CNDO as mainly arising from an increase in  $\text{H}\cdots\text{H}$  antibonding upon internal rotation. One would suspect that since CNDO does not predict the geometric parameters of all three molecules with the same degree of accuracy (Table VIII), the earlier interpretation of the relative barriers of these molecules may very well still be correct. A further argument in this direction is the experimental fact that the barriers do occur in a 3:2:1 ratio.

**Fluoro-Substituted Ethanes.** The internal rotation barriers calculated by CNDO for the fluoroethanes are compared with the experimental results in Table IX. In all cases, the staggered configuration is correctly predicted to be most stable; however, the observed trends in the barriers for this group of molecules are obviously not reproduced.  $\Delta E_{\text{AB}}^b$  is approximately zero for all of these molecules, indicating that the failure of CNDO to reproduce the observed trends may be due to an underestimation of nonbonded H-F and F-F inter-

**Table VIII.** Comparison of Calculated and Experimental Geometries for C<sub>2</sub>H<sub>6</sub>, CH<sub>3</sub>NH<sub>2</sub>, and CH<sub>3</sub>OH<sup>a</sup>

Molecule	R <sub>CX</sub> , Å	R <sub>CH</sub> , Å	R <sub>XH</sub> , Å	θ(HCX), deg	θ(HCH), deg	θ(CXH), deg	θ(HXH), deg	ω, <sup>b</sup> deg
C <sub>2</sub> H <sub>6</sub>	1.46	1.12	...	...	106.0	112.5	...	0
	1.46	1.12	...	...	106.5	112.0	...	180
	1.536	1.108	...	...	108.8	110.1	...	180 (expt <sup>c</sup> )
CH <sub>3</sub> NH <sub>2</sub>	1.41	1.12	1.07	112.0	106.8	108.7	103.8	0
	1.41	1.12	1.07	111.7	107.0	107.5	104.2	180
	1.474	(1.093)	1.011	(109.5)	(109.5)	112.3	105.8	180 (expt <sup>d</sup> )
CH <sub>3</sub> OH	1.37	1.12	1.03	110.9	108.0	106.6	...	0
	1.37	1.12	1.03	110.7	108.2	105.0	...	180
	1.434	(1.093)	0.937	109.5	109.5	109.5	...	180 (expt <sup>e</sup> )

<sup>a</sup> X = C for C<sub>2</sub>H<sub>6</sub>, N for CH<sub>3</sub>NH<sub>2</sub>, and O for CH<sub>3</sub>OH. Experimental values in parentheses are assumed values. <sup>b</sup> ω is the dihedral angle: 0° for eclipsed, 180° for staggered. <sup>c</sup> W. J. Lafferty and E. K. Plyler, *J. Chem. Phys.*, **37**, 2688 (1962). <sup>d</sup> T. Nishikawa, T. Itoh, and K. Shimoda, *ibid.*, **23**, 1735 (1955). <sup>e</sup> E. V. Ivash and D. M. Dennison, *ibid.*, **21**, 1804 (1953).

**Table IX.** Comparison of CNDO and Experimental Barriers for the Fluoroethanes

Molecule	CNDO barrier, kcal/mole	Exptl barrier, kcal/mole
CH <sub>3</sub> -CH <sub>3</sub>	2.18	2.875 <sup>a</sup>
CH <sub>3</sub> -CH <sub>2</sub> F	2.00	3.30 <sup>b</sup>
CH <sub>3</sub> -CHF <sub>2</sub>	1.88	3.18 <sup>b</sup>
CH <sub>3</sub> -CF <sub>3</sub>	1.76	3.48 <sup>c</sup>
CF <sub>3</sub> -CH <sub>2</sub> F	1.46	4.58 <sup>d</sup>
CF <sub>3</sub> -CHF <sub>2</sub>	1.22	3.51 <sup>e</sup>
CF <sub>3</sub> -CF <sub>3</sub>	1.07	3.92 <sup>f</sup>

<sup>a</sup> Reference 22 of text. <sup>b</sup> D. R. Herschach, *J. Chem. Phys.*, **25**, 358 (1956). <sup>c</sup> H. T. Minden and B. P. Dailey, *Phys. Rev.*, **82**, 338 (1951). <sup>d</sup> C. R. Ward and C. H. Ward, *J. Mol. Spectry.*, **12**, 289 (1964). <sup>e</sup> A. B. Tipton, C. O. Britt, and J. E. Boggs, *J. Chem. Phys.*, **46**, 1606 (1967). <sup>f</sup> D. E. Mann and E. K. Plyler, *ibid.*, **21**, 1116 (1953).

actions. A more detailed analysis of these molecules is probably not justified due to the poor agreement.

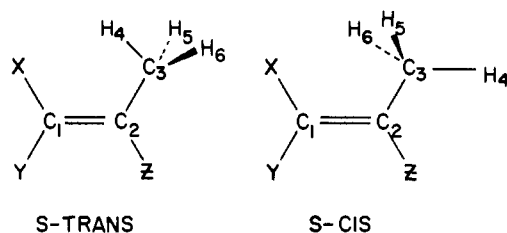


Figure 10. Configurations of substituted propenes: X, Y, Z = H or F.

A related molecule of interest is 1,2-difluoroethane which is thought to have stable *trans* and *gauche* isomers,<sup>35</sup> although no accurate measurements of the relative stabilities of these rotamers have been made. Klaboe and Nielsen<sup>35</sup> have estimated the enthalpies to be approximately equal in the gas phase. CNDO predicts the *gauche* isomer to be more stable by 0.1 kcal/mole; however, in light of the results for other molecules of this type, this agreement must be regarded as fortuitous. In addition, the barriers in the eclipsed positions of F<sub>2</sub>O<sub>2</sub> and N<sub>2</sub>F<sub>4</sub> are probably somewhat underestimated.

**Fluoro-Substituted Propenes.** The barrier to internal rotation in propene and its fluoro derivatives have received a great deal of interest from microwave spectroscopists in recent years.<sup>36-41</sup> The most stable ro-

(35) P. Klaboe and J. R. Nielsen, *J. Chem. Phys.*, **33**, 1764 (1960).

tamer of each molecule considered here is the *s-trans* configuration (Figure 10); thus the barrier is the energy difference between *s-trans* and the highest energy configuration, *s-cis* (Figure 10). The CNDO barriers calculated for these molecules are compared with the experimental values in Table X. In agreement with experiment, the configurations of lowest and highest energy are *s-trans* and *s-cis*, respectively. Although the calculated barriers are somewhat too small, the trends are correctly reproduced except in the case of 2-fluoropropene. It is especially interesting to note that CNDO reproduces the observed drop in the barriers of *cis*-1-fluoropropene and 1,1-difluoropropene relative to the parent molecule although the calculated reduction in barrier height is too small.

**Table X.** Calculated and Observed Barriers for Substituted Propenes

Molecule	Calcd barrier, kcal/mole	Obsd barrier, kcal/mole
Propene	1.16	1.978 <sup>a</sup>
<i>trans</i> -1-Fluoropropene	1.30	2.200 <sup>b</sup>
<i>cis</i> -1-Fluoropropene	0.93	1.057 <sup>b</sup>
2-Fluoropropene	0.88	2.430 <sup>d</sup>
1,1-Difluoropropene	0.96	1.252 <sup>e</sup>

<sup>a</sup> Reference 36. <sup>b</sup> Reference 37. <sup>c</sup> Reference 38. <sup>d</sup> Reference 39. <sup>e</sup> Reference 40.

Upon analysis of the energy break-up of these molecules, it becomes clear that, as was noted for ethane, methylamine, and methyl alcohol,  $\Sigma_A \Delta E_A$  and  $\Delta E_{AB}$ <sup>b</sup> are quite small for the fluoropropenes. Thus the barriers are due primarily to the nonbonded interactions,  $\Delta E_{AB}$ <sup>n</sup>. Further, in each propene derivative the only terms which contribute significantly to the barrier are the interactions between the methyl group and atoms C<sub>1</sub>, Z, and X (see Figure 10 for notation). The values for these  $\Delta E_{AB}$ 's are listed in Table XI where the letter in parentheses in the last column indicates the configuration preferred (T for *s-trans* and C for *s-cis*). H<sub>4</sub> is the in-plane hydrogen and H<sub>5,6</sub>'s are the out-of-plane hydrogens of the methyl group. It should be noted that if one sums the contributions of each of the

(36) D. R. Lide and D. E. Mann, *ibid.*, **27**, 868 (1957).

(37) S. Siegel, *ibid.*, **27**, 989 (1957).

(38) R. A. Beaudet and E. B. Wilson, Jr., *ibid.*, **37**, 1133 (1962).

(39) L. Pierce and J. M. O'Reilly, *J. Mol. Spectry.*, **3**, 536 (1959).

(40) V. W. Weiss, P. Bak, and W. H. Flygare, *J. Chem. Phys.*, **46**, 981 (1967).

(41) R. G. Stone, S. L. Srivastava, and W. H. Flygare, *ibid.*, **48**, 1890 (1968).

**Table XI.**  $\Delta E_{AB}$  for Major Contributing Terms to Barriers in Propenes

Interaction	Molecule	X	Y	Z	$\Delta E_{AB}$ , kcal/mole <sup>a</sup>
$H_{4,5,6}-C_1$	Propene	H	H	H	1.484 (T)
	<i>cis</i> -1-Fluoropropene	F	H	H	1.437 (T)
	<i>trans</i> -1-Fluoropropene	H	F	H	1.499 (T)
	2-Fluoropropene	H	H	F	1.505 (T)
	1,1-Difluoropropene	F	F	H	1.349 (T)
$H_{4,5,6}-Z$	Propene	H	H	H	0.389 (T)
	<i>cis</i> -1-Fluoropropene	F	H	H	0.376 (T)
	<i>trans</i> -1-Fluoropropene	H	F	H	0.402 (T)
	2-Fluoropropene	H	H	F	0.157 (T)
	1,1-Difluoropropene	F	F	H	0.376 (T)
$C_3-X$	Propene	H	H	H	0.439 (C)
	<i>cis</i> -1-Fluoropropene	F	H	H	0.809 (C)
	<i>trans</i> -1-Fluoropropene	H	F	H	0.407 (C)
	2-Fluoropropene	H	H	F	0.489 (C)
	1,1-Difluoropropene	F	F	H	0.784 (C)

<sup>a</sup> The letter in parentheses indicates the favored configuration: T for *s-trans*; C for *s-cis*.

terms listed in Table XI for each molecule the barriers are not exactly reproduced although the trends are intact. This means that the other terms in  $\Delta E_{AB}$ <sup>n</sup> do make small contributions to the barriers; however, the terms listed are by far the dominant ones.

From Table XI it is apparent that CNDO predicts the most important term contributing to the barriers to be the interaction of the methyl hydrogens with the terminal carbon on the double bond,  $C_1$ , rather than atom Z. The near-invariance of this term upon fluorine substitution is particularly striking. The interaction of each methyl hydrogen with  $C_1$  is listed in Table XII, where it is again noteworthy that these terms vary little

**Table XII.** Methyl Group Two-Atom Energies for the Fluoropropenes

Molecule	Interaction	$\Delta E_{AB}$ , kcal/mole <sup>a</sup>
Propene	$H_4-C_1$	4.850 (C)
	$H_5-C_1$	3.167 (T)
	$H_6-C_1$	3.167 (T)
	$H_4-Z$	3.727 (T)
	$H_5-Z$	1.669 (C)
	$H_6-Z$	1.669 (C)
<i>cis</i> -1-Fluoropropene	$H_4-C_1$	4.963 (C)
	$H_5-C_1$	3.200 (T)
	$H_6-C_1$	3.200 (T)
	$H_4-Z$	3.752 (T)
	$H_5-Z$	1.688 (C)
	$H_6-Z$	1.688 (C)
<i>trans</i> -1-Fluoropropene	$H_4-C_1$	4.725 (C)
	$H_5-C_1$	3.112 (T)
	$H_6-C_1$	3.112 (T)
	$H_4-Z$	3.789 (T)
	$H_5-Z$	1.694 (C)
	$H_6-Z$	1.694 (C)
2-Fluoropropene	$H_4-C_1$	4.041 (C)
	$H_5-C_1$	2.773 (T)
	$H_6-C_1$	2.773 (T)
	$H_4-Z$	2.215 (T)
	$H_5-Z$	1.029 (C)
	$H_6-Z$	1.029 (C)
1,1-Difluoropropene	$H_4-C_1$	4.939 (C)
	$H_5-C_1$	3.143 (T)
	$H_6-C_1$	3.143 (T)
	$H_4-Z$	3.777 (T)
	$H_5-Z$	1.700 (C)
	$H_6-Z$	1.700 (C)

<sup>a</sup> The letter in parentheses indicates the favored configuration: T for *s-trans* and C for *s-cis*.

from molecule to molecule. As one might expect, in all cases the in-plane hydrogen,  $H_4$ , favors the *s-cis* configuration due to this interaction while  $H_5$  and  $H_6$  favor *s-trans*. The sum of the latter two terms is greater; therefore the net interaction of the methyl hydrogens with  $C_1$  favors the *s-trans* configuration. This is primarily due to a net increase in antibonding between these hydrogens and  $C_1$  upon rotation; that is,  $\Delta E_{AB}$ <sup>(1)</sup> is again the dominant term in the energy breakup.

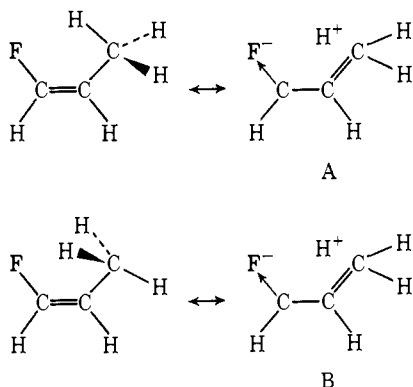
According to CNDO, the interaction of the methyl hydrogens with the atom (Z) attached to the adjacent carbon (H or F) is of secondary importance in determining the barriers of these molecules. It would appear, then, that this is the reason that CNDO successfully predicts the trends in the propene barriers in spite of the poor results for the fluoroethanes. In this context, it is interesting to note that when Z is a fluorine (2-fluoropropene), the interaction between  $H_{4,5,6}$  and Z is much smaller than for the other molecules in this series (Table XI) and that this is just the type of interaction which is underestimated in the fluoroethanes. It is not unlikely, therefore, that the underestimation of this contribution is the major cause of the poor prediction of the barrier in 2-fluoropropene by CNDO. The interaction of each hydrogen in the methyl group with atom Z is listed in Table XII. Here the in-plane hydrogen prefers the *s-trans* configuration, while the out-of-plane hydrogens favor *s-cis*, the former term being dominant in all cases. Again, the principle contribution to these terms is  $\Delta E_{AB}$ <sup>(1)</sup>, indicating a net increase in antibonding between the methyl hydrogens and atom Z upon rotation from *s-trans* to *s-cis*.

Due to the interaction with atoms  $C_1$  and Z, the in-plane hydrogen,  $H_4$ , prefers to be in the *s-cis* configuration, while the out-of-plane hydrogens prefer *s-trans*. Since the latter pair of interactions is larger, the series of propene derivatives favor the *s-trans* configuration. It should be mentioned here that the propene calculations were performed using the standard model of the MBLD program,<sup>21</sup> which assigns a value of 120° to the CCC angle, whereas the experimental angle in propene is 124.6°. Using the experimental value may to some extent increase the importance of the  $H_{4,5,6}-Z$  contribution to the barrier with respect to  $H_{4,5,6}-C_1$ , but the sum of the two interactions should not be much affected. As seen earlier for  $H_2O_2$ ,  $F_2O_2$ , etc., bond angles vary considerably upon internal rotation; however, experimentally the propene geometry is known only for the equilibrium configuration. In addition, the CCC angles for the fluoro derivatives of propenes are not known. For these reasons, the use of the MBLD geometries is reasonable for the present qualitative analysis.

It has been suggested<sup>42</sup> that the unusually low barriers found for *cis*-1-fluoropropene and 1,1-difluoropropene relative to the parent molecule may be due to a hyperconjugative effect of the type shown below. Since there are two such forms B for *s-cis* and only one (A) for *s-trans*, the former would be lowered in energy relative to the latter and the barrier reduced. The corresponding effect in *trans*-1-fluoropropene would be small. The prediction of relative charge distribution by CNDO has been rather successful;<sup>16</sup> thus an interest-

(42) R. A. Beudet, *J. Chem. Phys.*, **40**, 2705 (1964).





ing test of this hyperconjugative hypothesis is a comparison of the charge density on the fluorovinyl group in vinyl fluoride with that on the same molecular fragment in *cis*-1-fluoropropene. Since these charge densities are  $-0.036$  and  $-0.033$  in vinyl fluoride and *cis*-1-fluoropropene, respectively, there is little charge migration from methyl to vinyl and hence little hyperconjugation.

It may be, however, that some type of interaction between the methyl group and atom X is the cause of the lowering of the barriers. According to Table XI,  $\Delta E_{X-C_3}$  consistently favors the *s-cis* configuration; however, for *cis*-1-fluoropropene and 1,1-difluoropropene this term is much larger than for the other molecules in the series and gives rise to the drop in the barriers. While CNDO predicts the  $C_3-X$  interaction to be the cause of the barrier-lowering rather than the interaction between X and the methyl hydrogens, it seems likely that the lowering does ultimately stem from these hydrogens.

Finally Flygare and coworkers<sup>38,39</sup> have noted that the barriers in the halopropenes are approximately additive. In particular, the barrier in 1,1-difluoropropene may be approximated as the propene barrier plus the increase in the propene barrier due to the *trans*-fluoro substitution minus the decrease due to *cis*-fluoro substitution on carbon 1. Applying this formula to the experimental barriers of propene and *cis*- and *trans*-1-fluoropropene, one obtains a barrier of 1.279 kcal/mole for 1,1-difluoropropene while the observed barrier is 1.252 kcal/mole. It has been mentioned above that the various terms contributing the calculated barriers of these molecules are rather constant; thus CNDO should predict similar barrier additivity. Applying the formula given above, one obtains a barrier of 0.97 kcal/mole for the 1,1-difluoropropene while the calculated barrier is 0.96. Although the close agreement is probably fortuitous, CNDO does qualitatively reproduce the observed additivity.

## Conclusions

From the foregoing results it appears that CNDO will be applicable to the study of internal rotation only so long as nonbonded interactions between highly electronegative atoms are unimportant. The results for ethane, methylamine, methyl alcohol, and most of the

propenes reproduce the observed trends, and the simplicity of the method facilitates an extension to more complicated systems such as molecules containing two rotors. The failure to reproduce the correct trends in the fluoroethane barriers as well as 2-fluoropropene, however, suggests that the application of CNDO to other molecules in which similar interactions with electronegative atoms are important may be equally uncertain. It is not unlikely that the failure to reproduce the proper trends in these molecules is due to the underestimation of the vicinal interactions involving the electronegative atoms.

Optimization of the geometry improved the major features of the internal rotation-energy curves of  $H_2O_2$ ,  $F_2O_2$ ,  $N_2H_4$ , and  $N_2F_4$ . The most notable improvements occurred for hydrogen peroxide and tetrafluorohydrazine, although the remaining geometrical features of the former molecule are rather poorly predicted. The barriers in ethane, methylamine, and methyl alcohol were improved to some extent with respect to the standard geometries, but their 3:2:1 ratio is no longer reproduced. The internal rotation curve for hydroxylamine was little changed by optimization, and the predicted equilibrium dihedral angle is in disagreement with the *ab initio* results.<sup>19,29</sup>

One would hope that as *ab initio* calculations approach the Hartree-Fock limit the calculated geometries would approach the experimental values. The usefulness of geometry optimization would then depend on how greatly the bond lengths and bond angles change during internal rotation.<sup>43</sup> The present results indicate that the bond angles in the small molecules (e.g.,  $H_2O_2$ ,  $NH_2OH$ ) change more rapidly with dihedral angle than in the other molecules considered. In this context it would be interesting to perform an *ab initio* calculation on hydrogen peroxide allowing relaxation of geometry since this is a rather simple molecule for which the *ab initio* results are generally in disagreement with experiment.

The results of the CNDO energy breakup analyses imply a division of the molecules considered into two types. Those having lone pairs on (at most) one end of the axial bond (ethane) have barriers which may be explained primarily in terms of nonbonded interactions between atoms on either end of this bond. However, if lone pairs occur at both ends of the axial bond ( $H_2O_2$ ), the interaction of these lone pairs seems to be at least as important as nonbonded interactions. In all cases CNDO predicts the barriers to be primarily a result of changes in the bonding term,  $\Delta E_{AB}^{(1)}$ . It would be most interesting to see if such two-center interactions are indeed of primary importance in exact barrier calculations.

**Acknowledgments.** The author is indebted to Professor J. A. Pople for many discussions and continuous encouragement during the course of this work. This work was supported by grants from the U. S. Army and the National Institutes of Health.

(43) O. Sovers and M. Karplus, *J. Chem. Phys.*, **44**, 3033 (1966), have suggested that small geometry changes on internal rotation may have a significant effect on a barrier.