Molecular Orbital Theory of the Electronic Structure of Organic Compounds. XIII. Fourier Component Analysis of Internal Rotation Potential Functions in Saturated Molecules[1]

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Abstract: *Ab initio* molecular orbital theory is used to study internal rotation in ethane, methylamine, methanol, hydrazine, hydroxylamine, and hydrogen peroxide and each of the monomethyl and monofluoro derivatives of these molecules. Calculated energies are analyzed in terms of a Fourier-type expansion of the potential function. The separation into onefold (V_1), twofold (V_2), and threefold (V_3) components facilitates the interpretation of the results. It is found that the potential functions can be rationalized in terms of contributions from three principal effects. Firstly, staggered arrangements of bonds are preferred (reflected in the V_3 term). Secondly, the axis of a lone pair orbital prefers to be coplanar with an adjacent electron-withdrawing polar bond or orthogonal to an adjacent lone pair orbital (V_2 term). Finally, dipole moment components perpendicular to the internal rotation axis prefer to be opposed (V_1 term).

The way in which the energy of a molecule changes with rotation about its single bonds is of considerable interest. For the simplest case of a molecule in which internal rotation about one bond only is possible, the stable rotational isomers (local minima), their relative energies, and the energies required for their interconversion (potential barriers) may be obtained from the potential function for this rotation. Experimental data on rotational barriers, conformational energy differences, and, in some cases, full potential curves are becoming increasingly available and provide tests for the many theoretical approaches to the subject.[2]

Recently, *ab initio* molecular orbital theory has been shown by a number of workers to produce rotational barriers and conformational energy differences in moderate agreement with experiment.[3] Some of the most important bonds about which internal rotation can occur are C–C, C–N, C–O, N–N, N–O, and O–O and it is therefore not surprising that the parent molecules containing these bonds, ethane, methylamine, methanol, hydrazine, hydroxylamine and hydrogen peroxide, have been extensively studied.[4–20] In order to obtain further information concerning internal rotation about these bonds, we have also carried out *ab initio* calculations on the six parent molecules above. In addition, we have examined the effect of substituents on the potential functions by carrying out calculations on each of the monomethyl and monofluoro derivatives of these parent molecules. Some of these results have been reported in a previous paper[4a] in which we had the more limited objective of studying the relative energies of the stable conformational isomers (the local minima in the rotational potential function).

Internal rotation in ethane, methylamine, and methanol is adequately described by a simple threefold potential function

$$V(\phi) = \frac{1}{2}V_3(1 - \cos 3\phi) \qquad (1)$$

where V_3 is the threefold barrier and ϕ is a dihedral angle defining the molecular conformation. The potential functions for hydrazine, hydroxylamine, and hydrogen peroxide are more complicated. To a reasonable approximation, they may be written as truncated Fourier expansions

$$V(\phi) = \frac{1}{2}V_1(1 - \cos \phi) + \frac{1}{2}V_2(1 - \cos 2\phi) + \frac{1}{2}V_3(1 - \cos 3\phi) \qquad (2)$$

Finally, for asymmetric molecules such as the substituted hydrazines or N-substituted hydroxylamines, additional terms are necessary to reflect the lack of symmetry about $\phi = 180°$ as in (3).

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(1) This research was supported in part by National Science Foundation Grant GP-25617.

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(3) See, for example, L. C. Allen, *Annu. Rev. Phys. Chem.*, **20**, 315 (1969).

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$$V(\phi) = \frac{1}{2}V_1(1 - \cos\phi) + \frac{1}{2}V_2(1 - \cos 2\phi) + \frac{1}{2}V_3(1 - \cos 3\phi) + V_1' \sin\phi + V_2' \sin 2\phi \quad (3)$$

As we have mentioned, *ab initio* calculations have already been reported for all the parent molecules and their potential functions have been discussed in detail.[4-21] However, in only one of these studies[10] was a decomposition into onefold, twofold, and threefold components as in (2) attempted. We shall find that such a decomposition facilitates the interpretation of internal rotation potential functions.

The separation of $V(\phi)$ into components is not in itself new[22] but because of the very limited amount of experimental data currently available, little work of a comparative nature has been possible to this date. Some related theoretical work has been published.[12,23] By calculating detailed potential curves, we have been able to obtain theoretical values for the potential constants V_i and V_i' for all the molecules treated in this paper. We examine the values of V_1, V_2, V_3, V_1', and V_2' and attempt to relate them to physical effects contributing to the resultant potential functions.

Method and Results

Standard self-consistent field molecular orbital theory is used with the extended 4-31G basis set.[24] This has been described in detail previously.[24] Bond lengths and angles for all calculations are given the standard values listed by Pople and Gordon[25] unless otherwise noted. Full optimization of bond lengths and angles for each molecular conformation would be desirable but is currently too expensive to apply to a large set of molecules. Since we are interested here in obtaining a broad assessment of a Fourier decomposition of the potential function, we have sacrificed the additional accuracy that would accompany geometry optimization in order to be able to study a wide enough selection of molecules to make some general conclusions. However, the rigid rotor assumption will affect the quantitative results for individual molecules to varying degrees that depend on the extent of bond length and bond angle variation during the rotation process.

Maxima and minina in the potential curves have been determined by carrying out calculations at 5° intervals in the vicinity of the turning points, continuing until points on both sides are obtained. The theoretical uncertainty in the dihedral angles of the resultant potential maxima and minima is thus better than $\pm 2.5°$. Calculated total energies are listed in Table I. Only the maxima and minima for each molecule are quoted. The complete results are represented graphically[26,27] in Figures 1-5.

The potential constants V_i in (1)-(3) are obtained by inserting calculated total energies for the appropriate number of angles ϕ. For those molecules whose potential functions are described by (1), $V(0°)$ and $V(60°)$ have been taken; for (2), $V(0°)$, $V(60°)$, $V(120°)$, and $V(180°)$ have been used; and for (3), $V(0°)$, $V(60°)$, $V(120°)$, $V(180°)$, $V(240°)$, and $V(300°)$ have been used. The V_i are shown in Tables II and III.

An alternative procedure for obtaining the positions and values of the maxima and minima of the potential functions is to utilize the Fourier expansions (1)-(3) for $V(\phi)$ once the V_i have been determined. A comparison of results so derived with those from the direct optimization procedure then gives some measure of how well these expansions describe the calculated potential functions. They are therefore included in Table I. The agreement between the maxima and minima calculated by direct optimization and from the $V(\phi)$ is generally quite good indicating that the truncated Fourier expansions (1)-(3) give satisfactory descriptions of the detailed potential functions.

Discussion

Molecules with Simple Threefold Rotational Barriers. The potential functions for internal rotation in CH_3-CH_3, CH_3-NH_2, and CH_3-OH are given by (1) and are completely defined by a single parameter V_3 equal to the potential barrier. Calculated and experimental values of V_3 are included in Table II. In order to examine the effect of fluoro or methyl substitution on the barrier to rotation of the methyl groups in these molecules, we have included the appropriately substituted ethanes, methylamines, and methanols. The additional methyl group in these cases is taken to be staggered relative to the adjacent bonds. A full description of the rotation of methyl groups in propane, dimethylamine, and dimethyl ether requires a potential function with additional terms to describe the interaction between the two rotating methyl groups.[12,23] In this paper, however, we are only interested in the V_3 values and have obtained these using the simple threefold function (1). We should point out that these results for V_3 are nevertheless identical with those that would be obtained with a more complete potential function that includes coupling terms (as written in ref 12). Further, previous work on these interactions in propane has indicated that they are relatively small.[12,23]

The calculated barriers (Table II) are in moderately good agreement with experiment, all values being a little high. All the important trends are reproduced by the theory. Thus (a) the barriers for the sequence ethane, methylamine, and methanol are approximately in the ratio 3:2:1, (b) the barriers increase with methyl substitution, this effect being particularly marked for ethanol → dimethyl ether and methylamine → dimethylamine, and (c) there is a smaller increase in V_3 with fluoro substitution.

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(26) The zero values of energy in the potential curves correspond to the values in Table I except in the figures illustrating the decomposition of the potential function where $V(\phi = 0°)$ is taken to be zero.

(27) The dihedral angles ϕ specifying molecular conformations are those given in Table I and Figures 1-5. For the threefold rotors, ϕ is taken as zero in an eclipsed conformation.

Table I. Calculated Total Energies (Hartrees) and Relative Energies (kcal mol^{-1})

		From direct calculations			Calculated from $V(\phi)$	
Molecule	Rotation axis	Conformation[a,b]	Total energy	Rel energy[c]	Conformation[a,b]	Rel energy[c]
Ethane	CH_3-CH_3	Eclipsed	−79.10965	3.26		
		Staggered	−79.11484	0		
Methylamine	CH_3-NH_2	Eclipsed	−95.06464	2.13		
		Staggered	−95.06803	0		
Methanol	CH_3-OH	Eclipsed	−114.86842	1.12		
		Staggered	−114.87020	0		
Propane	$CH_3-CH_2CH_3$	Eclipsed	−118.08622	3.70		
		Staggered	−118.09211	0		
Dimethylamine	CH_3-NHCH_3	Eclipsed	−134.02972	3.62		
		Staggered	−134.03549	0		
Dimethyl ether	CH_3-OCH_3	Eclipsed	−153.83095	2.98		
		Staggered	−153.83570	0		
Fluoroethane	CH_3-CH_2F	Eclipsed	−177.83576	3.63		
		Staggered	−177.84154	0		
N-Fluoro-*N*-methylamine	CH_3-NHF	Eclipsed	−193.72156	3.04		
		Staggered	−193.72640	0		
Methyl hypofluorite	CH_3-OF	Eclipsed	−213.48520	1.86		
		Staggered	−213.48817	0		
Ethylamine	$CH_3CH_2-NH_2$	CCN: = 0°	−134.04599	1.93	CCN: = 0°	1.93
		55°	−134.04906	0	57°	0
		120°	−134.04468	2.75	121°	2.76
		180°	−134.04823	0.52	180°	0.53
Fluoromethylamine	FCH_2-NH_2	FCN: = 0°	−193.79749	6.87	FCN: = 0°	6.87
		40°	−193.79798	6.56	39°	6.56
		95°	−193.79608	7.76	94°	7.73
		180°	−193.80844	0	180°	0
Ethanol	CH_3CH_2-OH	CCOH = 0°	−153.85082	2.06	CCOH = 0°	2.06
		65°	−153.85311	0.63	65°	0.64
		115°	−153.85198	1.34	116°	1.35
		180°	−153.85411	0	180°	0
Fluoromethanol	FCH_2-OH	FCOH = 0°	−213.60624	1.31	FCOH = 0°	1.31
		55°	−213.60832	0	57°	0
		180°	−213.59940	5.60	180°	5.60
Hydrazine	NH_2-NH_2	:NN: = 0°	−110.98255	12.27	:NN: = 0°	12.37
		100°	−111.00210	0	97°	0
		180°	−110.99640	3.58	180°	3.68
Methylhydrazine	CH_3NH-NH_2	:NN: = 95°	−149.97198	0	:NN: = 92°	0
		190°	−149.96679	3.26	182°	3.56
		265°	−149.97184	0.09	266°	0.66
		355°	−149.95299	11.92	359°	12.26
Fluorohydrazine	$FNH-NH_2$	:NN: = 15°	−209.64303	16.99	:NN: = 16°	17.04
		110°	−209.65872	7.14	106°	6.88
		185°	−209.65252	11.03	184°	10.90
		280°	−209.67010	0	280°	0
Hydroxylamine	NH_2-OH	:NOH = 0°	−130.78729	0	:NOH = 0°	0
		110°	−130.76861	11.72	112°	11.74
		180°	−130.77452	8.01	180°	8.01
O-Methylhydroxylamine	NH_2-OCH_3	:NOC = 0°	−169.75403	0	:NOC = 0°	0
		115°	−169.73714	10.60	116°	10.63
		180°	−169.74333	6.71	180°	6.71
O-Fluorohydroxylamine	NH_2-OF	:NOF = 0°	−229.40459	4.61	:NOF = 0°	4.61
		90°	−229.38481	17.02	89°	16.61
		180°	−229.41193	0	180°	0
N-Methylhydroxylamine	CH_3NH-OH	:NOH = 0°	−169.75941	0	:NOH = 357°	0
		110°	−169.74104	11.53	110°	11.43
		175°	−169.74834	6.95	180°	6.97
		245°	−169.74202	10.91	248°	11.00
N-Fluorohydroxylamine	$FNH-OH$	:NOH = 25°	−229.44907	0	:NOH = 25°	0
		115°	−229.43592	8.25	115°	8.24
		175°	−229.44104	5.04	175°	5.14
		270°	−229.42550	14.79	268°	14.98
Hydrogen peroxide	$HO-OH$	HOOH = 0°	−150.54120	7.94	HOOH = 0°	7.94
		120°	−150.55386	0	120°	0
		180°	−150.55283	0.65	180°	0.64
Methyl hydroperoxide	CH_3O-OH	COOH = 0°	−189.51301	7.99	COOH = 0°	7.96
		140°	−189.52574	0	140°	0
		180°	−189.52561	0.08	180°	0.06
Fluorine hydroperoxide	$FO-OH$	FOOH = 0°	−249.16166	3.33	FOOH = 0°	3.39
		75°	−249.16696	0	77°	0
		180°	−249.15518	7.39	180°	7.46

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[a] N: is used to denote the fourth tetrahedral direction in nitrogen. [b] The angles used to define conformations in this table are referred to as ϕ in the text. [c] Energies relative to that of the minimum energy conformation for the particular molecule.

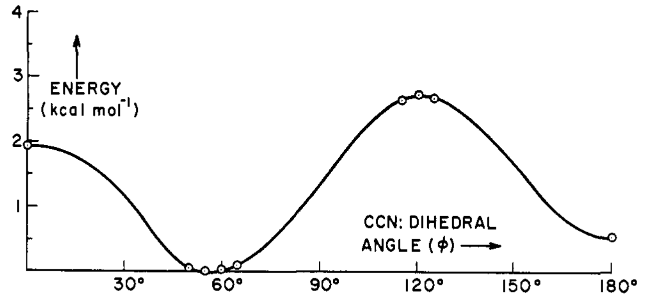


Figure 1a. Potential energy function describing internal rotation in ethylamine.

Ab initio calculations of the barriers in ethane,[4b-13] methylamine,[7,14] methanol,[6,7] and propane[12,23] have been reported previously and yielded similar results.

Table II. Threefold Rotational Barriers (V_3, kcal mol^{-1})

Molecule	Calcd	Exptl
CH_3-CH_3	3.26	2.93[a]
CH_3-NH_2	2.13	1.98[b]
CH_3-OH	1.12	1.07[c]
CH_3-CH_2CH_3	3.70	3.33[d]
CH_3-$NHCH_3$	3.62	3.22[e]
CH_3-OCH_3	2.98	2.72[f]
CH_3-CH_2F	3.63	3.30[g]
CH_3-NHF	3.04	
CH_3-OF	1.86	

[a] S. Weiss and G. E. Leroi, *J. Chem. Phys.*, **48**, 962 (1968). [b] D. R. Lide, *ibid.*, **27**, 343 (1957). [c] E. V. Ivash and D. M. Dennison, *ibid.*, **21**, 1804 (1953). [d] E. Hirota, C. Matsumura, and Y. Morino, *Bull. Chem. Soc. Jap.*, **40**, 1124 (1967). [e] J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, **54**, 532 (1971). [f] P. H. Kasai and R. J. Myers, *ibid.*, **30**, 1096 (1959). [g] D. R. Herschbach, *ibid.*, **25**, 358 (1956).

Table III. Potential Constants (V_i, V_i' kcal mol^{-1}) for Internal Rotation

Molecule	V_1	V_2	V_3	V_1'	V_2'
CH_3-CH_3	0	0	−3.26		
CH_3CH_2-CH_3	0	0	−3.70		
FCH_2-CH_3	0	0	−3.63		
CH_3-NH_2	0	0	−2.13		
CH_3-$NHCH_3$	0	0	−3.62		
CH_3-NHF	0	0	−3.04		
CH_3CH_2-NH_2	0.89	0.21	−2.29		
FCH_2-NH_2	−4.86	4.28	−2.01		
CH_3-OH	0	0	−1.12		
CH_3-OCH_3	0	0	−2.98		
CH_3-OF	0	0	−1.86		
CH_3CH_2-OH	−0.93	−0.05	−1.14		
FCH_2-OH	+5.25	−2.20	−0.96		
NH_2-NH_2	−7.42	−7.92	−1.27		
CH_3NH-NH_2	−6.84	−7.56	−1.85	−0.34	−0.12
FNH-NH_2	−3.70	−9.50	−1.40	3.50	2.14
NH_2-OH	8.86	6.62	−0.84		
NH_2-OCH_3	8.47	5.65	−1.75		
NH_2-OF	−3.67	14.30	−0.94		
CH_3NH-OH	8.03	6.65	−1.08	0.35	0.16
FNH-OH	4.46	7.50	−0.83	−4.09	−1.40
HO-OH	−7.08	−3.51	−0.22		
CH_3O-OH	−7.53	−2.94	−0.37		
FO-OH	4.20	−5.17	−0.13		

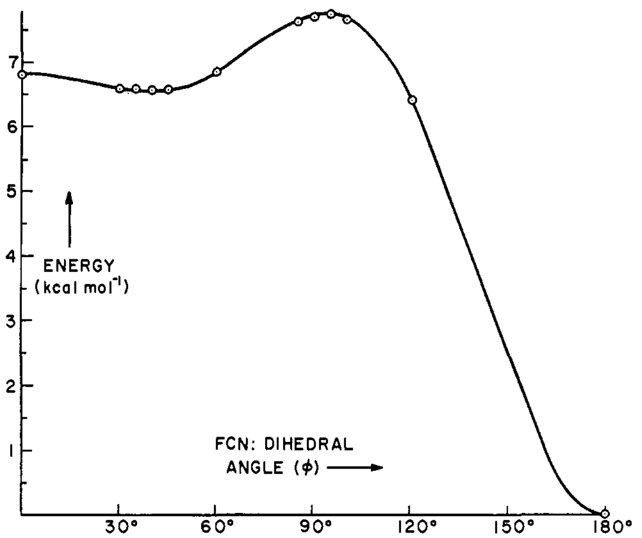


Figure 1b. Potential energy function describing internal rotation in fluoromethylamine.

Substituted Methylamines. Rotation about the C–N bond in substituted methylamines, XCH_2NH_2, may be described by the potential function (2). Calculated potential curves for ethylamine ($X = CH_3$) and fluoromethylamine ($X = F$) are given in Figures 1a and 1b, respectively, and the derived potential constants V_i are included in Table III. As an aid to understanding the decomposition of the potential function, the components $V_1(\phi) = {}^1/_2V_1(1 - \cos \phi)$, $V_2(\phi) = {}^1/_2V_2(1 - \cos 2\phi)$, and $V_3(\phi) = {}^1/_2V_3(1 - \cos 3\phi)$ are plotted along with the overall potential function $V(\phi)$ for fluoromethylamine in Figure 1c.

The substituted methylamines illustrate most of the important features which contribute to the potential functions for the molecules in this paper and we shall therefore discuss them in some detail. We begin by considering the potential constants V_i.

Firstly, V_3 is negative for ethylamine and fluoromethylamine just as for methylamine. This indicates a preference for staggered conformations (ϕ = 60, 180°)[27] over eclipsed conformations (ϕ = 0, 120°) and is, in fact, observed for all the other molecules examined in this paper as well. The values of V_3 in XCH_2NH_2 when X is H, CH_3, and F are similar, analogous to the result observed for the simple threefold rotation in the corresponding XCH_2CH_3 molecules.

The sign of the V_2 term may generally be predicted by considering a stabilizing mechanism we have previously postulated[4a] involving σ electron withdrawal and n electron donation. For example, in fluoromethylamine, withdrawal of electrons in the C–F bond partially empties the carbon 2p orbital and thus facilitates donation from the nitrogen lone pair in the FCN: trans (I) and cis (II) periplanar conformations. Such an interaction is a minimum in the perpendicular form (III). These qualitative ideas are reflected in the $2p_x$ populations on N (1.755, 1.750, and 1.775 in I, II, and III, respectively) and the π_x (C–N) overlap populations (0.0730, 0.0746, and −0.0354 in I, II, and III, respectively). Thus, on this basis, there should be a preference for the C–F bond to be coplanar with the axis of the lone pair orbital (I, II, ϕ = 180, 0°) rather than perpendicular to it (III, ϕ = 90°). Accordingly, we find that V_2 is large and positive for fluoromethylamine.

Finally, the V_1 term is large and negative for fluoromethylamine indicating a preference for the trans form (I) over the cis form (II). This is consistent with a

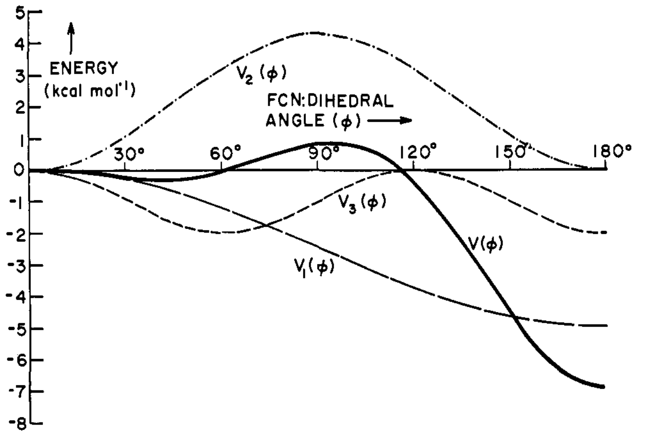
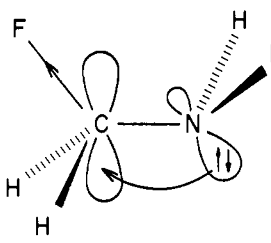


Figure 1c. Fourier decomposition of potential function for fluoromethylamine.

simple dipole–dipole argument which favors the trans form having opposed dipoles (I′, $\mu_{\text{calcd}} = 0.53$ D) over the cis form with reinforced dipoles (II′, $\mu_{\text{calcd}} = 4.12$ D). When X is CH_3, V_1 is small and positive indicating a slight preference for the cis over the trans conformation.



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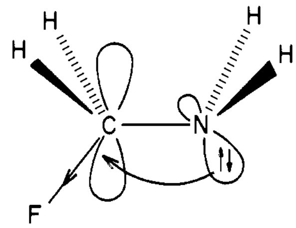

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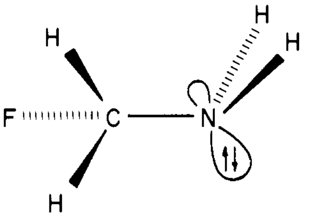
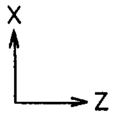
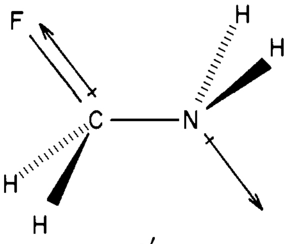
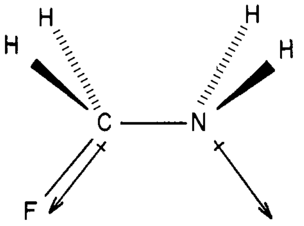


III





I′



II′

The onefold, twofold, and threefold components all contribute to the location of the resultant maxima and minima for the rotation. Conversely, the resultant potential function is more difficult to analyze than the components because it includes these contributions from several reinforcing or competing effects.

For ethylamine, the threefold component is dominant leading to minima for gauche ($\phi = 55°$) and trans ($\phi = 180°$) forms and, overall, a potential curve which looks very similar to that of methylamine. Because of the positive V_1, the gauche conformation is slightly favored (by 0.52 kcal mol⁻¹). The gauche → gauche and gauche → trans barriers are 1.93 and 2.75 kcal mol⁻¹, respectively. Spectroscopic evidence[28] suggests the presence of significant proportions of both gauche and trans forms, but the conformation of the more stable isomer has not yet been established.

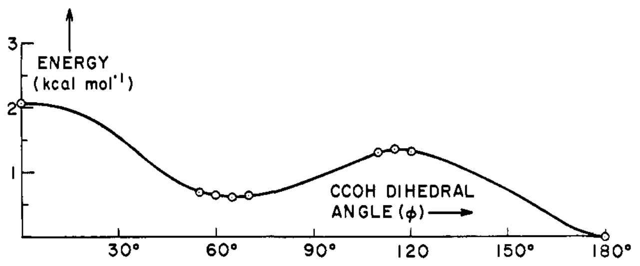


Figure 2a. Potential energy function describing internal rotation in ethanol.

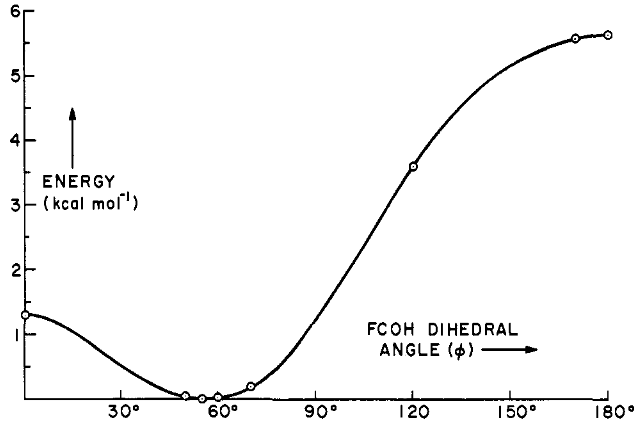


Figure 2b. Potential energy function describing internal rotation in fluoromethanol.

The way in which the V_1, V_2, and V_3 components contribute to the overall $V(\phi)$ for fluoromethylamine may be seen in Figure 1c. All of V_1, V_2, and V_3 favor the trans conformation (I, $\phi = 180°$) and it is the most stable form. The potential curve is fairly flat in the region $\phi = 0$–$60°$ due to opposing V_1, V_2, and V_3 terms. There is a slight minimum at $\phi = 40°$ lying approximately 6.56 kcal mol⁻¹ above the energy of the trans form. The trans → gauche barrier (at $\phi = 95°$) is 7.76 kcal mol⁻¹.

Substituted Methanols. Internal rotation about the C–O bond in substituted methanols XCH_2OH may also be described by the potential function (2). Calculated potential curves for ethanol (X = CH_3) and fluoromethanol (X = F) are given in Figures 2a and 2b, respectively, and the derived values of V_i in Table III.

Values of V_3 for X = H, CH_3, and F are again very similar, the negative values suggesting a preference for the staggered XCOH trans ($\phi = 180°$) and gauche ($\phi \sim 60°$) conformations. For ethanol, this is the dominant effect and there are potential minima for both gauche ($\phi = 65°$) and trans forms. The negative V_1 (which is possibly due to weak steric interaction in the cis form) leads to a slightly lower energy for the trans form. The gauche–trans energy difference is 0.63 kcal mol⁻¹ while the trans → gauche and gauche

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(28) T. Masamichi, A. Y. Hirakawa, and K. Tamagake, *Nippon Kagaku Zasshi*, **89**, 821 (1968).

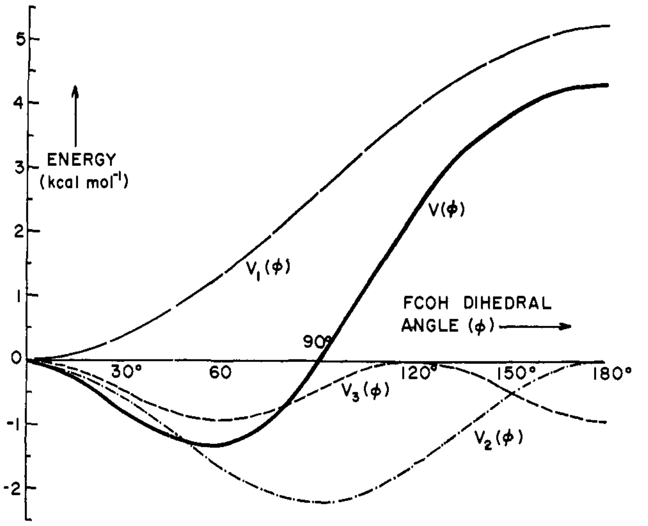
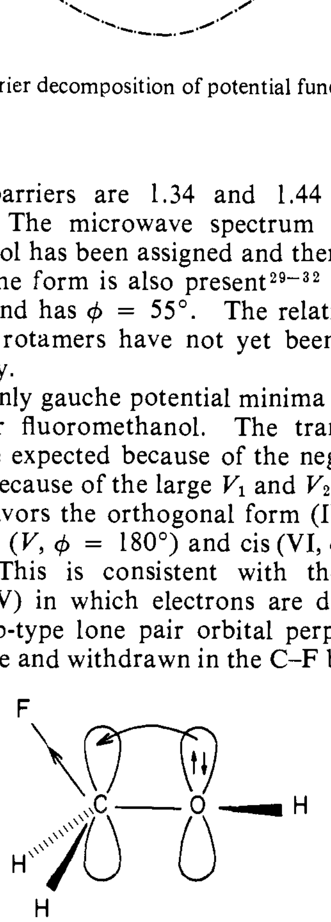


Figure 2c. Fourier decomposition of potential function for fluoromethanol.

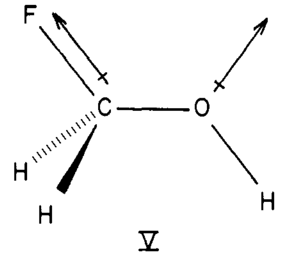
→ gauche barriers are 1.34 and 1.44 kcal mol^{-1}, respectively. The microwave spectrum of the trans form of ethanol has been assigned and there is evidence that the gauche form is also present[29-32] in significant proportions and has $\phi = 55°$. The relative stabilities of these two rotamers have not yet been determined experimentally.

There are only gauche potential minima in the potential curve for fluoromethanol. The trans minimum that would be expected because of the negative V_3 has disappeared because of the large V_1 and V_2 terms. The negative V_2 favors the orthogonal form (IV, $\phi = 90°$) over the trans (V, $\phi = 180°$) and cis (VI, $\phi = 0°$) conformations. This is consistent with the stabilizing interaction (IV) in which electrons are donated from the oxygen 2p-type lone pair orbital perpendicular to the COH plane and withdrawn in the C–F bond.

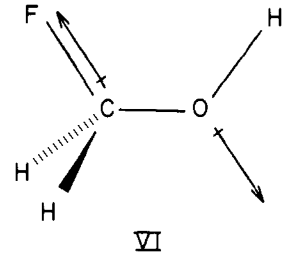


IV

This lone pair orbital on oxygen is the one from which electrons are most easily ionized (*e.g.*, in water) and therefore is the one from which donation is most likely to occur. The remaining lone pair orbital (lying in the COH plane) has a considerable amount of s character and is more tightly bound. It is therefore not likely to be effective in back donation. The large V_1 term leads to the trans form (V) being less favorable than the cis (VI) which is expected because of dipole interactions.



V



VI

The contributions of the V_1, V_2, and V_3 components to $V(\phi)$ for fluoromethanol are shown in full in Figure 2c and it is clear how the dominance of the V_1 term in the region near $\phi = 180°$ leads to a fairly flat maximum rather than a minimum. The lowest energy calculated is for the gauche form ($\phi = 55°$) with barriers at the cis and trans positions of 1.31 and 5.60 kcal mol^{-1}, respectively.

In a recent paper,[21] Wolfe, Rauk, Tel, and Csizmadia (WRTC) postulated a general rule for the prediction of the stereochemistry of systems containing adjacent lone pairs and polar bonds, *viz.*, "when electron pairs or polar bonds are placed or generated on adjacent pyramidal atoms, syn or anti periplanar orientations are disfavored energetically with respect to that structure which contains the maximum number of gauche interactions." They indicate that an apparent exception to the rule is that conformations which place a polar bond between two lone pairs are destabilized (the "anomeric effect") and give a detailed discussion of fluoromethanol as an example of this situation. Our results for fluoromethanol are in qualitative agreement with theirs in that both studies find only a single potential minimum with the trans form being a potential maximum. Their trans–cis energy difference (4.35 kcal mol^{-1}) is very similar to our value (4.29 kcal mol^{-1}) but they obtain a much lower relative energy for the gauche form (by *ca.* 7 kcal mol^{-1}) leading to substantially different calculated barriers. No explanation for this difference is apparent at this stage.

With reference to the stereochemical rule of WRTC, we confirm that fluoromethanol is an apparent exception. However, we find that another exception to the rule occurs for molecules in which a polar bond is adjacent to a single lone pair. This is the situation, for example, in fluoromethylamine where the FCN: trans periplanar conformation is strongly favored (see above). We suggest that the anomeric effect is not a special case and that exceptions to the *rule as stated*[21] will be found generally for molecules containing an electron-withdrawing polar bond adjacent to lone pairs.

Substituted Hydrazines. Potential curves for substituted hydrazines $XNHNH_2$ are given in Figure 3. The appropriate potential function when X = CH_3 or F is (3) while for hydrazine itself (X = H), (2) may be used since V_1' and V_2' are zero by symmetry (Figure 3a). The V_i, V_i' values are listed in Table III.

V_3 is negative for each of the substituted hydrazines suggesting a preference for a staggered arrangement of bonds and lone pairs. There is an increase in V_3 with methyl and fluoro substitution analogous to the sequence CH_3NH_2, CH_3NHCH_3, CH_3NHF. The large negative values of V_2 indicate that the lone pair or-

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(29) Ch. O. Kadzhar, I. D. Isaev, and L. M. Imanov, *Zh. Strukt. Khim.*, **9**, 445 (1968).

(30) M. Takano, Y. Sasada, and T. Satoh, *J. Mol. Spectrosc.*, **26**, 157 (1968).

(31) Y. Sasada, M. Takano, and T. Satoh, *ibid.*, **38**, 33 (1971).

(32) J. Michielsen-Effinger, *Bull. Cl. Sci., Acad. Roy. Belg.*, **53**, 226 (1967).

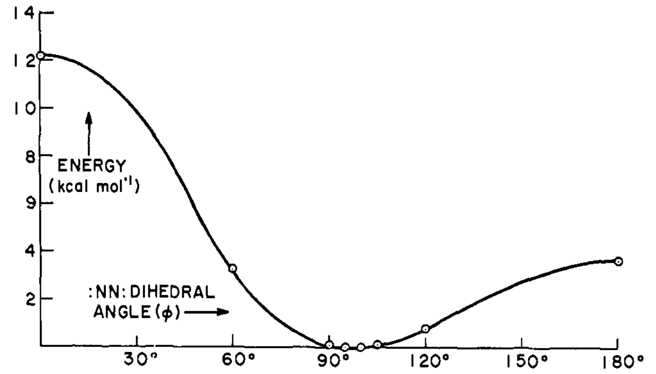
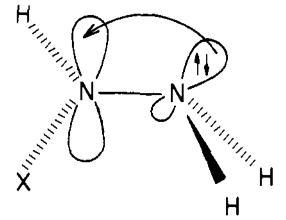
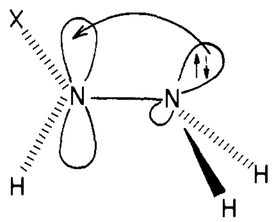


Figure 3a. Potential energy function describing internal rotation in hydrazine.

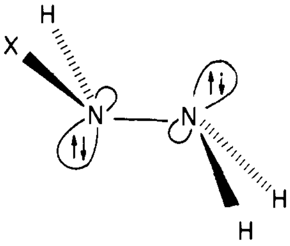
bitals prefer to be orthogonal (VII, VIII) rather than coplanar (IX, X) facilitating delocalization.



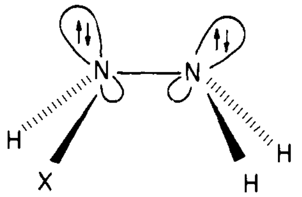
VII



VIII

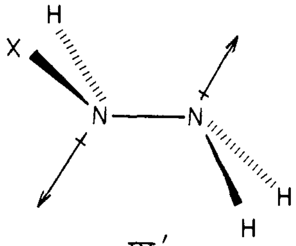


IX

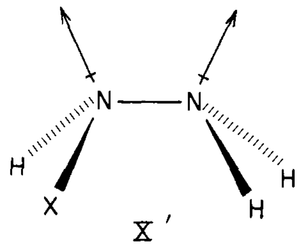


X

Finally the V_1 values are all large and negative showing that there is a strong preference for a trans (IX′) rather than cis (X′) arrangement of lone pairs. This result is consistent with the optimization of dipole–dipole interactions, the magnitude of V_1, of course, depending on the dipolar properties of the N–X bond.



IX′



X′

The contributions of the components $V_i(\phi)$ for hydrazine to the resultant $V(\phi)$ are shown in Figure 3b. The V_2 and V_1 terms are seen to be most important. There is a potential minimum when $\phi = 100°$ with a large barrier (12.27 kcal mol^{-1}) at the cis position (unfavorable V_1, V_2, and V_3 terms) and a smaller barrier (3.58 kcal mol^{-1}) at the trans position. Previous *ab initio* calculations on hydrazine have yielded similar results.[7,14,15]

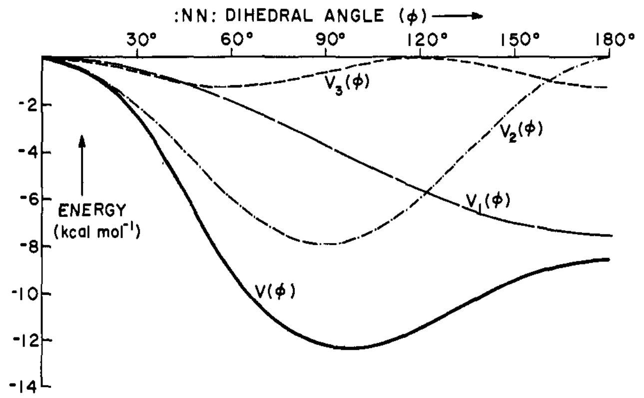


Figure 3b. Fourier decomposition of potential function for hydrazine.

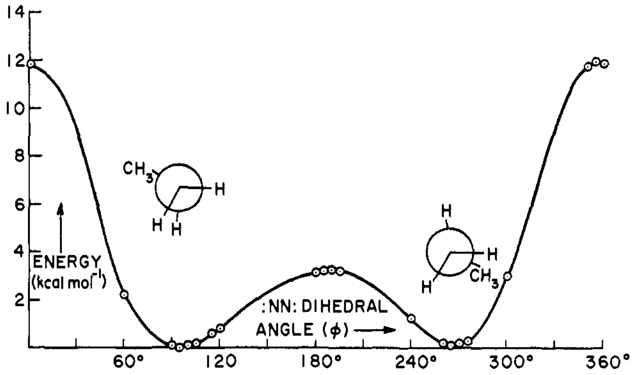
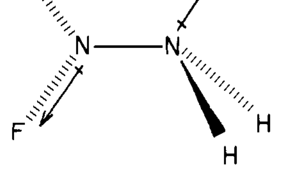


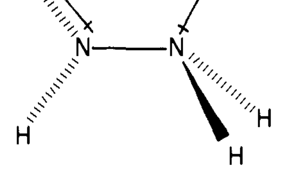
Figure 3c. Potential energy function describing internal rotation in methylhydrazine.

The potential function for methylhydrazine (Figure 3c) is very similar to that for hydrazine. Values of V_1' and V_2' are very small so the curves in the 0–180° and 180–360° regions are almost mirror images. There are potential minima for $\phi = 95°$ (CNNH external) and 265° (CNNH internal), the energy difference being only 0.09 kcal mol^{-1}. Barriers[33] at near-cis ($\phi = -5°$) and near-trans ($\phi = 190°$) positions are 11.87 and 3.26 kcal mol^{-1}, respectively. An infrared study[34] suggested that approximately 90% of the molecules exist in the external form with 10% in the internal form. However, in a recent microwave study[35] the internal form is found to be favored by 0.84 kcal mol^{-1}.

The potential function for fluorohydrazine (Figure 3d) is considerably more complicated but we shall comment on some of the main features. Electron withdrawal in the N–F bond leads to a large negative V_2 (see VII and VIII) and smaller negative V_1 (see IX′ and X′) as expected. The positive V_1' means that conformations with $\phi > 180°$ are preferred to cor-



XI



XII

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[33] Barriers quoted in this paper all refer to the energy required to convert the *more* stable conformational isomer to the *less* stable form.

[34] J. R. Durig, W. C. Harris, and D. W. Wertz, *J. Chem. Phys.*, 50, 1449 (1969).

[35] R. P. Lattimer and M. D. Harmony, *ibid.*, 53, 4575 (1970).

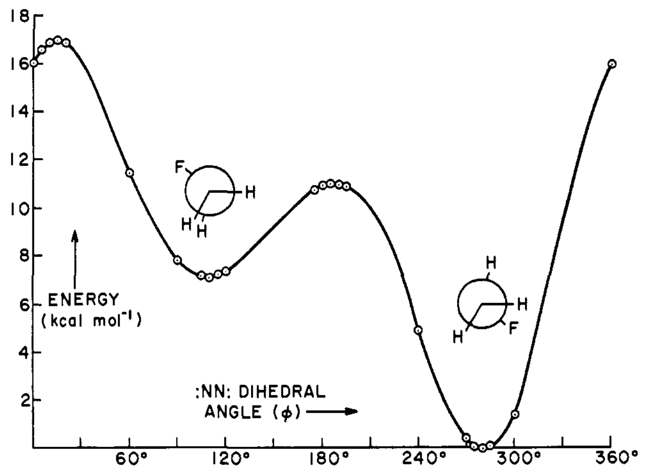


Figure 3d. Potential energy function describing internal rotation in fluorohydrazine.

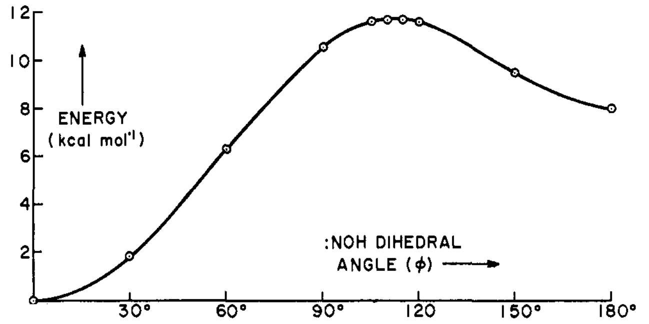


Figure 4a. Potential energy function describing internal rotation in hydroxylamine.

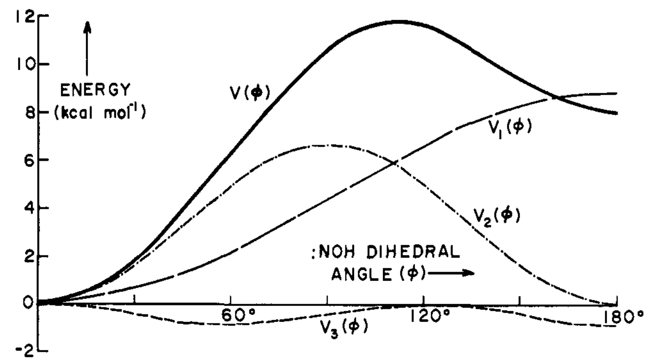


Figure 4b. Fourier decomposition of potential function for hydroxylamine.

responding (360° − ϕ) forms. For example, XI ($\phi = 270°$) is preferred to XII ($\phi = 90°$).

The large V_2 term leads to minima in $V(\phi)$ for ϕ = 110 and 280°, the latter having the lower energy (by 7.14 kcal mol^{-1}) because of the large V_1' and V_2' terms. The barriers at the near-trans ($\phi = 185°$) and near-cis ($\phi = 15°$) positions are 11.03 and 16.99 kcal mol^{-1}, respectively.

Substituted Hydroxylamines. Potential curves for hydroxylamine (NH_2OH), O-substituted hydroxylamines (NH_2OX, X = CH_3, F), and N-substituted hydroxylamines (NHXOH, X = CH_3, F) are shown in Figure 4. The potential constants V_i from (2) for the NH_2OX and V_i, V_i' from (3) for NHXOH are listed in Table III.

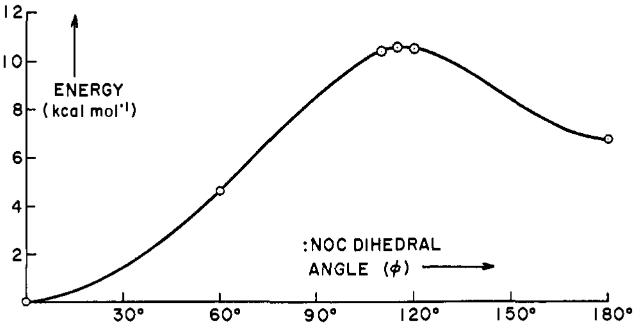


Figure 4c. Potential energy function describing internal rotation in O-methylhydroxylamine.

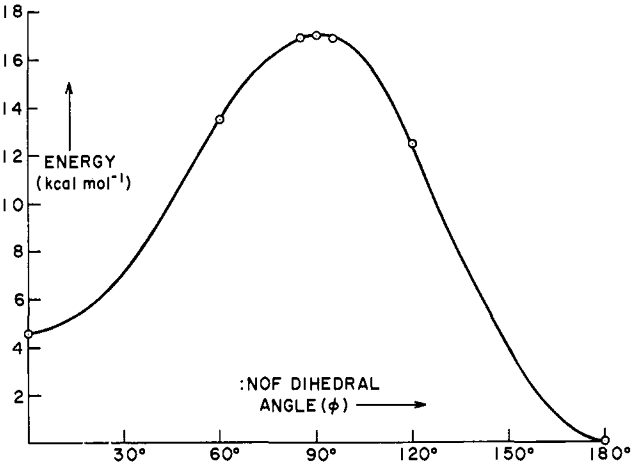
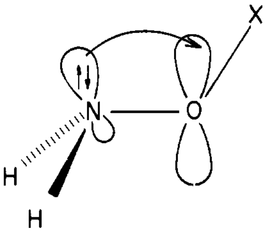
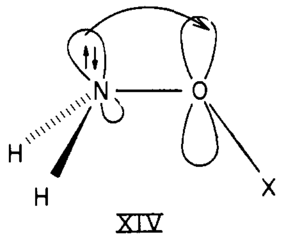


Figure 4d. Potential energy function describing internal rotation in O-fluorohydroxylamine.

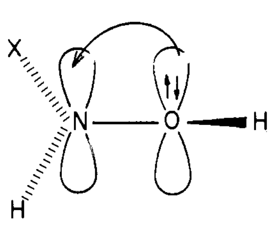
V_3 is small and negative in all cases indicating a preference for staggered bonds. The increased V_3's for NH_2OCH_3 and NH_2OF (compared with NH_2OH) are analogous to the increase for CH_3OCH_3 and CH_3OF compared with CH_3OH. V_2 is always large and positive thus favoring :NOX or :NOH cis and trans forms consistent with the interactions shown in XIII–XVI.



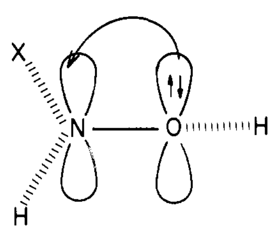
XIII



XIV



XV



XVI

The electron-withdrawing fluoro substituent leads to an increased V_2, this effect being particularly marked for NH_2OF. As expected on the basis of dipole–dipole interactions (see XVII, XVIII), V_1 is large and

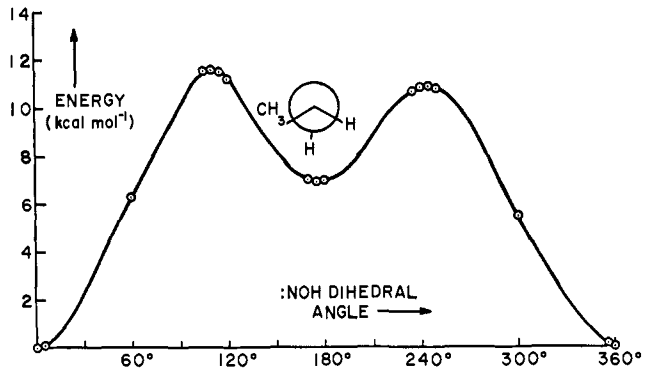


Figure 4e. Potential energy function describing internal rotation in *N*-methylhydroxlamine.

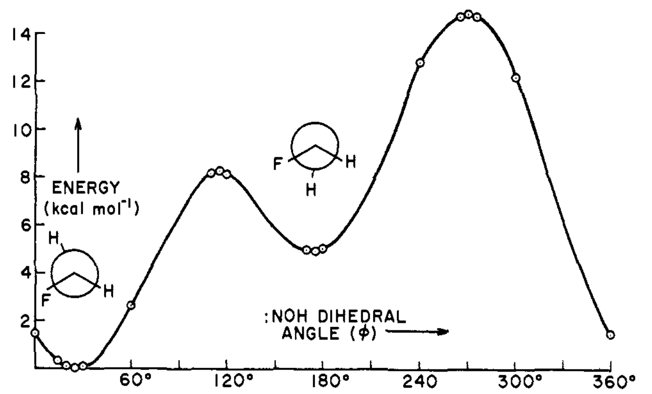
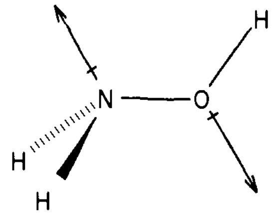
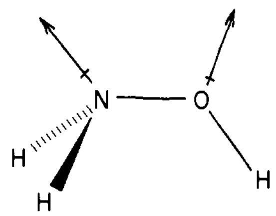


Figure 4f. Potential energy function describing internal rotation in *N*-fluorohydroxylamine.

positive for hydroxylamine and the methylhydroxylamines.



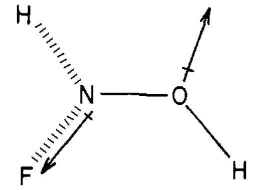
XVII



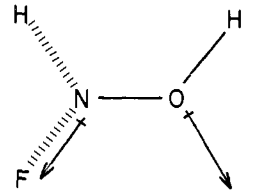
XVIII

V_1 becomes decreased positive when an amino hydrogen is replaced by fluorine and negative when the hydroxyl hydrogen is replaced by fluorine.

The negative value of V_1' for NHFOH shows that conformations with ϕ between 0 and 180° are preferred to the corresponding $(360° - \phi)$ conformations. For example, XIX ($\phi = 120°$) is favored over XX ($\phi = 240°$)



XIX



XX

The contributions of the $V_i(\phi)$ to $V(\phi)$ for hydroxylamine are shown in Figure 4b. Because of the large positive V_2 term, hydroxylamine has minima for cis ($\phi = 0°$) and trans ($\phi = 180°$) conformations, the former being favored (positive V_1) by 8.01 kcal mol^{-1}. There is a large cis → trans barrier (11.72 kcal mol^{-1}) at $\phi = 110°$. Similar results have been obtained from previous *ab initio* calculations.[7,16] Experimental evidence[36] suggests that hydroxylamine has potential minima for :NOH cis and trans.

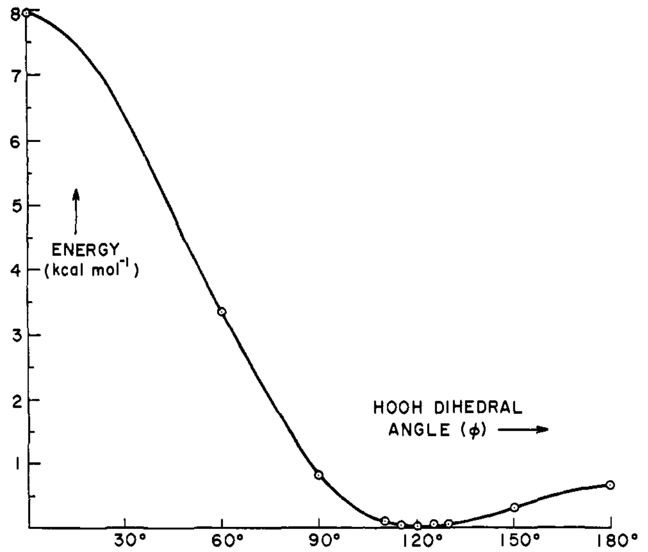


Figure 5a. Potential energy function describing internal rotation in hydrogen peroxide.

The curves for *O*-methylhydroxylamine and *N*-methylhydroxylamine are very similar to that for hydroxylamine itself. For *O*-methylhydroxylamine, the trans–cis energy difference is 6.71 kcal mol^{-1} and the cis → trans barrier is 10.60 kcal mol^{-1} at $\phi = 115°$. For *N*-methylhydroxylamine, the near-trans ($\phi = 175°$)–near-cis ($\phi = 0°$) energy difference is 6.95 kcal mol^{-1} and the barriers[33] at $\phi = 110$ and 245° are 11.53 and 10.91 kcal mol^{-1}, respectively.

O-Fluorohydroxylamine also has minima for cis and trans forms with a large barrier (17.02 kcal mol^{-1}) between them. However, in this case, the trans form is favored (negative V_1) by 4.61 kcal mol^{-1} and the barrier occurs at $\phi = 90°$ (larger positive V_2). The large negative V_1' for NHFOH leads to the minima in this molecule being displaced slightly from the cis ($\phi = 0°$) and trans ($\phi = 180°$) forms. They occur at $\phi = 25$ and 175°, the former being favored by 5.04 kcal mol^{-1}. There is a large barrier (14.79 kcal mol^{-1}) at $\phi = 270°$ and a somewhat smaller barrier (8.25 kcal mol^{-1}) at $\phi = 115°$.

Substituted Peroxides. Potential curves for internal rotation in peroxides XOOH (X = H, CH_3, F) are shown in Figure 5. Potential constants V_i derived from (2) are listed in Table III.

For all three molecules, V_3 is very small and negative indicating a slight preference for staggered conformations. Lone pair electron delocalization occurs most easily in the orthogonal (XXI) conformation rather than in the coplanar (XXII, XXIII) conformations. This is reflected in negative V_2 values and, as expected, V_2 is most negative for FOOH. V_1 is negative for HOOH (see XXIV, XXV) and CH_3OOH while it is positive in FOOH (see XXVI, XXVII), consistent with the dipole interactions.

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

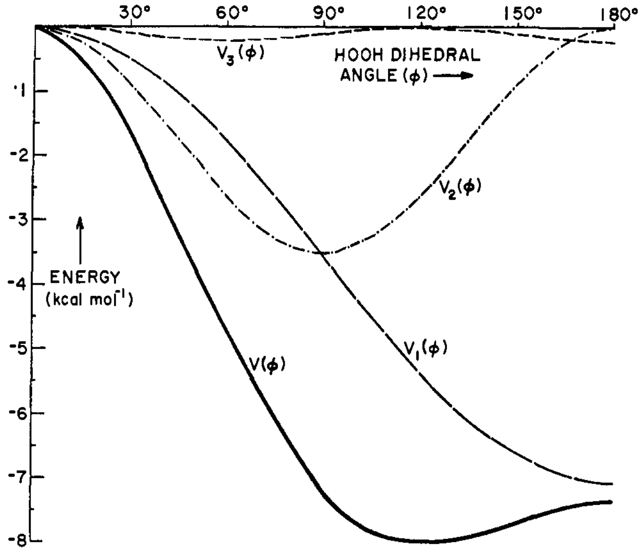
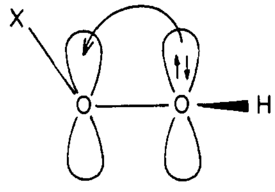
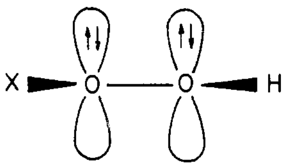


Figure 5b. Fourier decomposition of potential function for hydrogen peroxide.

The curves in Figure 5b show how the delicate balance between the V_1 and V_2 terms in HOOH leads to a very flat region in the potential curve between ϕ = 90 and 180°. Accordingly, the *position* of the potential minimum in this region may be sensitively dependent on the choice of basis set and molecular geometry.



XXI



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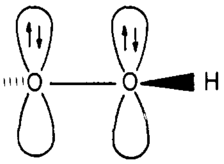

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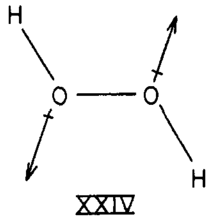

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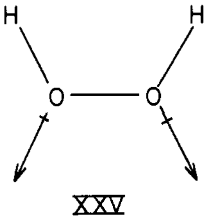

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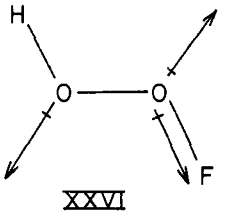
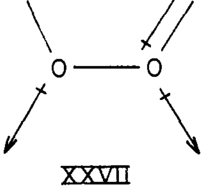


XXVI



XXVII

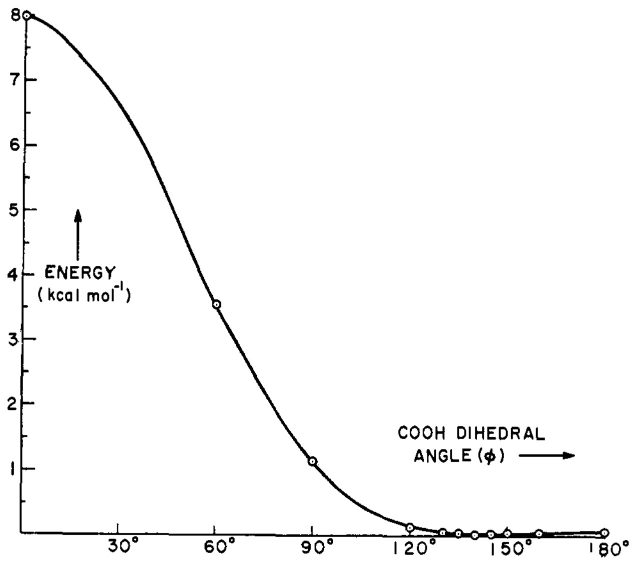


Figure 5c. Potential energy function describing internal rotation in methyl hydroperoxide.

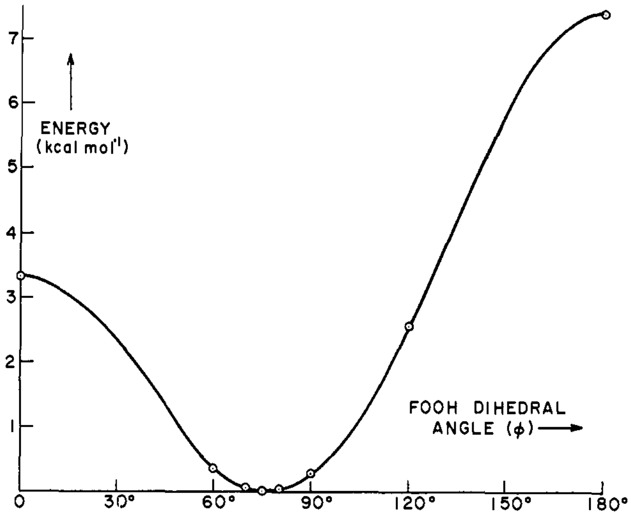


Figure 5d. Potential energy function describing internal rotation in fluorine hydroperoxide.

We obtain a slight minimum for ϕ = 120° with a large barrier (7.94 kcal mol^{-1}) at the cis position and a very small barrier (0.65 kcal mol^{-1}) at the trans position. An infrared spectroscopic study[22c] gave an HOOH dihedral angle of 111.5° and cis and trans barriers of 7.0 and 1.1 kcal mol^{-1}, respectively, while a microwave determination[37] yielded a dihedral angle of 120.0°. This quantitative agreement with experiment is somewhat fortuitous and due partly to the use of fixed, standard bond lengths and bond angles. Full geometry optimization with the 4-31G basis set leads to a trans structure.[38] If the calculations are carried out with optimized HOO angles for each conformation (but using standard bond lengths), the trans structure is again found to have the lowest energy (energy −150.55980 hartrees) and the derived potential constants are $V_1 = -11.26$, $V_2 = -3.14$, and $V_3 = -0.23$ kcal mol^{-1}. Thus V_1 is altered considerably but V_2 and

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(37) W. C. Oelfke and W. Gordy, *J. Chem. Phys.*, **51**, 5336 (1969).

(38) W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, unpublished results.

V_3 are only slightly changed from the values in Table III. There have been a number of previous *ab initio* calculations on hydrogen peroxide.[6,7,10,11,16,17,19,20] Most of these considerably underestimate or fail to find any trans barrier.[6,7,10,11,16,19,20] However, it is found that the result is generally improved by inclusion of polarization functions.[6,7,10,20] The most extensive study reported to date is that of Veillard[10] who finds that use of polarization functions accompanied by optimization of bond angles and lengths leads to a theoretical description of the internal rotation in hydrogen peroxide in close agreement with experiment.

For methyl hydroperoxide, the principal change in the potential function is that the minimum has been shifted to $\phi = 140°$ (V_2 decreased negative, V_1 increased negative) and the trans barrier is close to zero (0.1 kcal mol^{-1}). Finally, for fluorine hydroperoxide, V_1 is positive and the minimum occurs at $\phi = 75°$ with a large trans barrier (7.39 kcal mol^{-1}) and a smaller cis barrier (3.33 kcal mol^{1-}).

Conclusions

In concluding this survey of rotation potential functions, it is useful to summarize the results in terms of three principal effects which we have found to interpret many of the known experimental facts in a reasonable manner and which can be usefully separated by Fourier components.

(1) The first effect is some form of bond–bond repulsion which is sufficiently peaked to lead to a (negative) V_3 component in the Fourier expansion. The magnitudes of V_3 for the six parent molecules are displayed in Table IV. The decrease in V_3 for the sequence CH_3–CH_3, CH_3–NH_2, CH_3–OH in the approximate ratio 3:2:1 is well known. The results in Table IV show that this is a general effect; *i.e.*, there is a decrease in V_3 for *all* the sequences X–CH_3, X–NH_2, X–OH (X = CH_3, NH_2, OH) and the values are seen to be approximately proportional to the number of bond–bond interactions. This suggests that it is not necessary to invoke any V_3 components involving lone pair interactions to explain the data. A consequence of this bond–bond interaction is a preference for staggered conformations in molecules with a methyl group at one end.

Table IV. Magnitudes of V_3 (kcal mol^{-1}) for Molecules X–Y[a]

X	Y: CH_3	NH_2	OH
CH_3	3.26 (9)	2.13 (6)	1.12 (3)
NH_2	2.13 (6)	1.27 (4)	0.84 (2)
OH	1.12 (3)	0.84 (2)	0.22 (1)

[a] Values in parentheses are the number of bond–bond interactions.

(2) The second effect is the stabilizing influence of back donation from lone pair orbitals at one end of the molecule into antibonding σ orbitals at the other. Such an interaction is greatest if the effective axis of the lone pair orbital is coplanar with the bond into which electrons are being transferred. It is also strongly accentuated if this bond is polar and electron withdrawing. The lone pair back-donation effect leads to large V_2 terms in the total potential with important stereochemical consequences. This is particularly the case in fluorine-substituted molecules (such as FCH_2-OH). If there are lone pair orbitals at both ends of the molecules (as in H_2NNH_2, H_2NOH, and HOOH), their axes tend to be in perpendicular to each other so that such back donation can occur more effectively.

(3) The third effect is the interaction of local dipoles at the two ends of the molecule. This leads to lower energies for conformations in which the dipole components perpendicular to the bond are antiparallel to each other and is reflected in a V_1 term which may also be an important factor determining the equilibrium conformation. The V_1 term may also be influenced by steric interactions. This is likely to become more important in larger molecules (*e.g.*, *n*-butane[12]).