Ab Initio Calculation of Structure and Inversion in Difluoramine and Dimethylamine

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Abstract: The fully optimized structures of both the equilibrium and the planar forms which are the transition states for inversion have been calculated for difluoramine and dimethylamine by the ab initio FORCE method. Even minor structural details in the equilibrium forms such as the asymmetric methyl groups and the methyl group tilt are very well reproduced. An explanation of the methyl group tilt is suggested, using localized orbitals and the valence shell electron pair repulsion theory. The inversion is accompanied by major changes in all the bond lengths and angles involving nitrogen. The calculated inversion barriers are: dimethylamine 2.6 kcal (exptl, 4.4 ± 1), difluoramine 34.4 kcal without and 41.7 kcal with d functions on nitrogen.

The inversion of nitrogen compounds has been studied extensively both theoretically and experimentally. The experimental results are usually interpreted assuming very few and very simple geometrical differences between the equilibrium geometry and that of the transition state for the inversion,[1] mainly because the latter form is not accessible to direct experimental study. This investigation is intended to examine the validity of such assumptions.

Difluoramine, F_2NH, and dimethylamine, $(CH_3)_2NH$, are isoelectronic and similar structurally, but there is a great difference in their behavior with respect to inversion around the nitrogen atom. The barrier to inversion in F_2NH is so large that no observable effects appear in the microwave spectrum,[2] while inversion splitting is readily observable for $(CH_3)_2NH$.[1] In addition to examining geometrical variations during the inversion motion, we wish to see if ab initio calculations can provide some interpretation for the large difference in the barriers of these two molecules. Further, we wish to examine whether such minor structural details as asymmetric methyl groups[1,3] and methyl group tilt[1] in dimethylamine are reproduced by ab initio SCF calculations with a limited basis set.

Method and Results

Ab initio SCF calculations have been made using the FORCE method of Pulay.[4] This procedure makes possible the simultaneous optimization of all geometrical parameters in a molecule and has been shown to reproduce even minor structural details satisfactorily.[5] The only nonoptimized parameter in our calculations was the methyl torsional angle for which the H atoms were constrained to lie in the CNC plane (see Figure 1). The resulting force calculated on this coordinate shows (within about 1°) that this restriction is correct, confirming the microwave result[1] that these hydrogens are in the plane within experimental error.

For the carbon, nitrogen, and fluorine atoms, a (7,3) Gaussian lobe basis set[6] contracted to (5,3) as ⟨3,1,1,1,1;3⟩ (see Johansen[7] for the nomenclature) was used. In order to investigate the effect of d orbitals, calculations were also done on difluoramine with a set of five d functions added to the basis set for the nitrogen atom.[8] Three uncontracted s functions were used for the hydrogen atoms. Orbital exponents were taken as 4.90, 0.82, and 0.18 as suggested by Pulay.[9] The optimized geometrical parameters resulting from the calculations are shown in Tables I and II and compared with experimental results where the latter exist.

The molecular orbitals obtained by the SCF procedure were transformed into localized orbitals corresponding to chemical bonds, inner shells, and lone pairs by the method of Boys.[10] Such localized orbitals provide an approach toward bringing together the results of molecular orbital calculations and the more qualitative valence bond language in which much chemical discussion is phrased.

Discussion

(1) Equilibrium Geometries. Table I shows that the geometry-optimized structure calculated for difluoramine agrees very well with the experimental structure obtained by microwave spectroscopy.[2] The experimental values shown correspond to an r_0 structure, so the equilibrium internuclear distances obtained from the calculation should be somewhat less than the experimental values, the effect being larger for the N–H distance than for the N–F distance.

Gordon and Pople[11] have reported a semiempirical calculation of the structure of NHF_2 using the INDO method, obtaining the following geometry: N–H = 1.09 Å, N–F = 1.25 Å, ∠FNF = 104.6°, and ∠HNF = 105.2°.

Experimental structures for dimethylamine are available both from the microwave studies of Wollrab and Laurie[1] and from the electron diffraction investigation by Beagley and Hewitt.[12] For most of the structure, the two studies agree within their experimental errors and the difference in definition between the r_s and r_g structural parameters. Differences are mainly in those parameters which involve the position of hydrogen atoms which are not well determined by electron diffraction, so for these parameters the microwave values would be preferred.

The ab initio calculated structure (Table II) for dimethylamine agrees remarkably well with the experimental structure, the major discrepancies being the H_iNC and CNC angles, both of which are overestimated by about 3°. Especially interesting is the asymmetry of the methyl groups. The electron diffraction method is not sensitive to this minor structural detail, and the interpretation of the experiment assumed symmetry. The microwave experiment shows the asymmetry clearly (especially in the three NCH angles), but lack of data on the ^{13}C isotope made it necessary to assume that C–H′ = C–H″ and that ∠HCH′ = ∠HCH″. This produces a methyl group with two long C–H bonds. The theoretical result shows that there are two short bonds with one long bond trans to the nitrogen lone pair. The latter result is in accord with infrared measurements on partially deuterated dimethylamine.[3] This experiment yielded r_0 values for the C–H bonds of 1.095, 1.098, and 1.108 Å (two short, nearly equal bonds, and one about 0.01 Å longer). The same lengthening by about 0.01 Å of a C–H bond trans to a lone pair has been observed experimentally in dimethyl ether,[13] and theoretically in methylamine.[9b]

A related structural detail is the tilt of the methyl groups in the direction of the nitrogen lone pair. The tilt observed ex-

Table I. Experimental and Calculated Parameters for Difluoramine[a]

	Equilibrium structure			Transition state	
		Theoretical[c]		Theoretical[c]	
	Exptl[b]	sp[d]	spd[e]	sp[d]	spd[e]
N-H	1.026 ± 0.002	1.011	1.007	0.990	0.990
N-F	1.400 ± 0.002	1.428	1.389	1.387	1.357
∠FNF	102.9 ± 0.2	102.8	103.0	114.1	113.6
∠HNF	99.8 ± 0.2	101.4	100.6	122.9	123.2
E_T[f] + 253		−0.3746142	−0.4088940	−0.3198374	−0.3424537
ΔE_I[g]				34.4	41.7
μ[h]	1.93	2.53	2.32	2.49	2.39

[a] Bond lengths in Å, angles in deg. [b] Microwave structure of Lide.[2] An apparently less accurate electron diffraction study (O. L. Hersh, *Diss. Abstr.*, 24, 2286 (1963)) gave N-H = 1.08 ± 0.1, N-F = 1.367 ± 0.004, ∠FNF = 104.3 ± 0.7, ∠HNF = 103.5 ± 2.7. [c] Internal accuracy better than 0.001 Å and 0.1°. [d] Ab initio result with only s and p functions. [e] Ab initio result with d functions added to nitrogen. [f] Total energy in atomic units. [g] Inversion barrier in kcal/mol. [h] Dipole moment in Debye.

Table II. Experimental and Calculated Results for Dimethylamine

	Equilibrium structure			
	Exptl			
Parameter	ED[a]	MW[b]	Theoretical	Theoretical transition state
N-H_i	1.00 ± 0.02	1.019 ± 0.007	0.999[d]	0.988
N-C	1.455 ± 0.002	1.462 ± 0.005	1.461	1.440
C-H	1.106 ± 0.003[c]	1.084 ± 0.005	1.080	1.080
C-H'	1.106 ± 0.003	1.098 ± 0.004[c]	1.081	1.088
C-H"	1.106 ± 0.003	1.098 ± 0.004	1.090	1.088
∠H_iNC	107 ± 2	108.9 ± 0.3	112.3	119.8
∠CNC	111.8 ± 0.6	112.2 ± 0.2	115.1	120.4
∠NCH	112.0 ± 0.8[c]	109.7 ± 0.3	109.4	109.6
∠NCH'	112.0 ± 0.8	108.2 ± 0.3	109.2	112.2
∠NCH"	112.0 ± 0.8	113.8 ± 0.3	114.0	112.2
∠HCH'	106.8 ± 0.8[c]	109.0 ± 0.2[c]	108.0	107.7
∠HCH"	106.8 ± 0.8	109.0 ± 0.2	108.5	107.7
∠H'CH"	106.8 ± 0.8	107.2 ± 0.3	107.6	107.3
E_T + 134[e]			−0.0611546	−0.0570488
ΔE_I[f]		4.4 ± 1		2.6
μ[g]		1.01	1.15	0.44

[a] Electron diffraction structure of Beagley and Hewitt.[12] [b] Microwave structure of Wollrab and Laurie.[1] [c] Brackets indicate values assumed equal. [d] Internal accuracy better than 0.001 Å and 0.1°. [e] Total energy in atomic units. [f] Inversion barrier in kcal/mol. [g] Dipole moment in Debye.

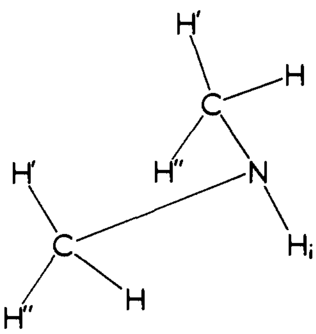

Figure 1. Designation of atoms in dimethylamine. Atoms C-N-C-H are coplanar.

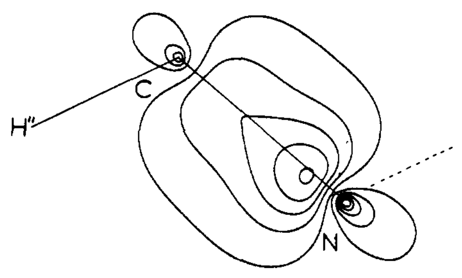

Figure 2. Density of localized orbital corresponding to the C-N bond of dimethylamine in the H"CN plane. The dashed line shows the approximate direction of the lone pair. Contour values from 0.035 to 0.435 in steps of 0.1 electron/bohr^3. Only the position of the atoms in the plane are shown.

perimentally is 3.4° while the calculated value is 3.2°. Pulay and Török also found that the ab initio structure correctly reproduced the similar tilt in methylamine.[9b] The origin of the tilt can be interpreted in terms of the valence shell electron pair repulsion theory.[14] The C-N bonding orbital is assumed to be repelled more strongly by the nitrogen lone pair than it is by the N-H bonding orbital. This bends the C-N bond slightly in the direction away from the lone pair, as seen in the localized molecular orbital corresponding to the C-N bond shown in Figure 2. Figure 3 shows that the orbital is bent away from the lone pair. The bent C-N bond will repel the C-H" bond more strongly than it does the other two C-H bonds, thus increasing the NCH" angle and tilting the whole methyl group in the direction of the lone pair. The direction of the tilt, both calculated and experimental, indicates that it is not caused by methyl group repulsion, as suggested for dimethyl ether.[13] In fact, an ab initio study[15c] of the internal rotation has found evidence for an attractive interaction between the methyl groups in both dimethyl ether and in dimethylamine.

An ab initio calculation of the CNC angle by Genson and Christoffersen[16] using molecular fragments yielded 102°. Semiempirical calculations by Bingham, Dewar, and Lo[17] using the MINDO/3 method yielded C-H = 1.122 Å, N-H = 1.021 Å, C-N = 1.393 Å, and ∠CNC = 129.4°.

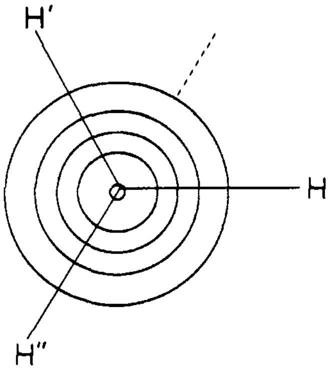

Figure 3. Density of localized orbital corresponding to the C-N bond of dimethylamine in a plane perpendicular to and bisecting the bond. The dashed line shows the approximate direction of the lone pair. Contour values from 0.05 to 0.25 in steps of 0.05 electron/bohr^3. Only the positions of the methyl hydrogens are shown.

(2) **Transition State Geometries.** Many of the geometrical parameters of the two molecules studied show considerable change as the molecules pass through the planar configurations corresponding to the transition states for inversion. The bonds to nitrogen are shortened by 0.01 to 0.04 Å. This strengthening of the bonds corresponds to the change in hybridization from about sp^3 to about sp^2. The increased s character of the bonds in the transition state leads to better bonding overlap[18] and thus to shorter bonds. The changes are larger for difluoramine which has smaller equilibrium bond angles corresponding to more p character.

While the dimethylamine transition state has nearly equal angles of 120°, there is a marked asymmetry in difluoramine. The HNF angles are nearly 10° larger than the FNF angle. The reason for this difference may be related to the fact that carbon has nearly the same electronegativity as hydrogen whereas fluorine is considerably more electronegative.

(3) **Dipole Moments.** The calculated dipole moments are 15-25% higher than the observed, as is usual for this type of calculation. The directions of the dipole moments, however, agree within a few degrees with experiment.[1,2] The dipole moment is much smaller in the transition state for dimethylamine, showing that the main contributor in the equilibrium structure is the nitrogen lone pair. The dipole moment in difluoramine is nearly unchanged during the inversion; in this case, the polar N-F bonds play the dominant role in determining the dipole moment.

(4) **Inversion Barriers.** The calculations predict a very large difference in the barriers to inversion in the two molecules. The value for difluoramine of 30-40 kcal explains why no effects of the inversion have been experimentally observed. It is apparent from our results that difluoramine undergoes much greater geometry changes during inversion than does dimethylamine. While the bond lengths in the transition state can each attain its most stable value independently, the bond angles around nitrogen are forced to expand to an average value of 120° even though the most favorable values are far smaller, particularly for difluoramine. A rough, semiquantative estimate of the difference in inversion barriers can be obtained by calculating the energy required to increase the bond angles from the equilibrium to the transition state values, using the experimental force constants[19,20] for the various angles. This simple procedure yields 27 kcal for difluoramine and 2.2 kcal for dimethylamine, giving the right order of magnitude in both cases. The angles involving hydrogen, which have the smallest force constants, change by the largest amounts in both cases.

The substitution of the strongly electronegative fluorine atoms for the methyl groups tends to increase the s character of the nitrogen lone pair.[21] The sum of the squares of the nitrogen s-orbital coefficients in the localized orbital corresponding to the nitrogen lone pair divided by the sum of the squares of the p-orbital coefficients is 0.38 in dimethylamine and 1.16 in difluoramine, showing the greater lone pair s character in the latter molecule. In the planar transition state, the lone pair is calculated to be in a pure p orbital in both cases. Even though this solution may only be a saddle point, as Kaldor has shown for NH_3,[22] the true lone pair localized orbital in NH_3 was an almost pure p orbital. The change in the lone pair is thus much larger in difluoramine, leading to a larger barrier.

A semiempirical calculation of the inversion barrier in dimethylamine by the MINDO method has given a value of 6.7 kcal.[23]

(5) **Influence of d Orbitals.** Calculations with d functions added to the basis set for the nitrogen atoms were done only on difluoramine because of the prohibitive cost of similar calculations on dimethylamine. It is interesting to note that inclusion of d orbitals has very little influence on the computed bond angles, the principal effect being to shrink the N-F bond length by about 0.03 to 0.04 Å. In the equilibrium conformation, this change puts the bond length in better agreement with the experimental value.

The inversion barrier is calculated to be about 7 kcal larger with the spd basis set. That nitrogen inversion barriers are highly dependent on d orbitals has also been observed for ammonia.[24] It has been suggested[25] that this is due to the fact that one of the filled orbitals in the transition state has a symmetry that prohibits d orbital participation. The present results on difluoramine do not support this hypothesis, since the transition state has C_{2v} symmetry which permits d orbital participation in all symmetry species. The calculated inversion barrier for dimethylamine is lower than the experimental, presumably because no d functions were used. Lehn and Munsch[21b] obtained a barrier of 8.6 kcal using a $\langle 9,5,1 \rangle$ basis set.

Conclusion

The most important result of the present study has been the demonstration that inversion of trivalent nitrogen compounds is accompanied by major structural changes in all bond lengths and angles involving nitrogen, not just in those involving hydrogen, as is usually assumed in interpreting experimental results.[1] Furthermore, it has been shown that even minor structural details such as methyl group asymmetry and tilt can be very well reproduced using the FORCE method and a limited basis set. Since the calculated equilibrium ab initio geometries for these molecules are very close to those obtained by experiment, the method may confidently be expected to give reliable information about intermediate states in the inversion process.

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An ab Initio Molecular Orbital Study of Polyoxides. 2. Fluorine and Alkyl Polyoxides (F_2O_3, F_2O_4, $(CH_3)_2O_3$, $(CF_3)_2O_3$)

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Abstract: Ab initio molecular orbital theory (STO-2G and STO-4G) is used to study equilibrium geometries, dipole moments, charge distribution, and molecular energetics of polyoxides of the type YO_nY (Y = F, CH_3, CF_3; n = 2, 3, 4). All compounds investigated have been found to possess a zigzag skew chain structure, and are stable molecular species with respect to decomposition products.

Ab initio calculations have been found to be a reliable tool for determination of equilibrium geometries and relative energies of molecules.[1,2]

We have recently reported the results of the ab initio study on hydrogen polyoxides.[2] Two recent reports, one on the theoretical[4] and the other on the experimental[5] aspect of the same subject, are in good agreement with our results.

We wish to present in this paper the results of our extended study on other polyoxides of the type YO_nY (Y = F, CH_3, CF_3). The existence of fluorine polyoxides is still a controversial issue.[6] On the other hand, two trioxides, i.e., CF_3OOOCF_3[7] and $(CH_3)_3COOOC(CH_3)_3$,[8] have recently been isolated and their spectroscopic data reported.

We have used in the present study the ab initio method to solve the Roothaan equation. Owing to the size of molecules, minimal STO-2G basis set was used to calculate molecular geometries of compounds under investigation.[9] The experience with this basis set (each Slater orbital is expanded into only two Gaussian ones) shows that such an expansion gives the same geometry parameters as STO-3G. Unless otherwise stated (see Tables I and II) complete structure minimization was undertaken subject only to the imposed symmetry (C_2 point-group symmetry for YO_4Y). Since a chain of six atoms in tetroxides would require three dihedral angles for complete specification, the problem was simplified by assuming dihedral angles $\angle Y_a\text{–}O_1\text{–}O_2\text{–}O_3$ and $\angle Y_b\text{–}O_4\text{–}O_3\text{–}O_2$ to be 180°. The dihedral angle $\angle Y_b\text{–}O_3\text{–}O_2\text{–}O_1$ in trioxides was taken to be 180°.[3] Tetrahedral arrangement of atoms in CH_3 and CF_3 groups was also assumed.

The calculation of dipole moments, charge distribution, and molecular energetics was performed with STO-4G basis set. Attempts to use the extended 4-31G (split-valence) basis set were frustrated (for larger molecules) by the limited capability of our computer facilities (CDC CYBER 72).

Results and Discussion

The results and experimental values, where available, are summarized in Tables I–III. A zigzag chain with a dihedral angle, Φ, is again the most characteristic feature of all polyoxides investigated. The equilibrium conformations have O–Y groups on the opposite sides of the O–O plane (anti-form). In polyoxides with Y = CH_3 or CF_3, a staggered conformation has been found to have the lowest energy.

The difficulties in obtaining satisfactory values for bond lengths, especially for F–O bonds, by using minimal basis set, have already been reported.[10] Particularly short O–O and particularly long F–O bonds are not accounted for by calculations at this level of approximation. It is interesting to note that bonds in F_2O_2 are also in serious error by using the extended 4-31G basis set (up to 0.2 Å).[4] However, good agreement with experiment has been obtained for the dihedral angle in F_2O_2 and for other compounds investigated.

The characteristic feature of charge distribution in fluorine compounds (Y = F) is dispersion of charge from oxygen atoms bonded to fluorine. All these oxygens bear a positive charge. The effect is most pronounced in the case of fluorine trioxide where oxygen bonded to fluorine, which is located out of the plane of the molecule, bears higher positive charge than the oxygen atom bonded to fluorine oriented in the plane. The alternating charges observed in these molecules were already encountered in theoretical studies on other fluorocarbons.[11,12]

In hydrogen polyoxides, the inner oxygen atoms bear relatively more positive charge compared to oxygens bonded to hydrogen atoms. A similar pattern is observed also in alkyl and fluorine substituted trioxides. Both groups, i.e., CH_3 and CF_3, are electron donating with the effect of the latter being more pronounced. All hydrogen atoms in alkyl polyoxides are positive and their net charges are approximately 0.06. In fluorine substituted alkyl compounds, all fluorine atoms are charged negatively (~ -0.13).

The calculated values for dipole moments of H_2O, H_2O_2, $(CH_3)_2O$, and F_2O are in fair agreement with experimental values. Exception is the calculated value for the dipole mo-

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