Journal of Fluorine Chemistry, 10 (1977) 197–218

Received: April 11, 1977

A COMPARATIVE AB-INITIO MOLECULAR ORBITAL STUDY OF AMMONIA OXIDE AND TRIFLUORAMINE OXIDE

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ABSTRACT

Geometry optimizations using various basis sets in the LCAO-SCF-MO method have been applied to F_3NO and H_3NO. Making use of the electronic wave-functions bonding is discussed in terms of donation from the oxygen lone pair into the N-F(H)σ* orbitals and d-type orbitals on the nitrogen. Participation of d orbitals in the bonding is of modest importance for F3NO but not H_3NO at least as far as the overlap population analysis is concerned.

INTRODUCTION

Among the electronic factors considered important in determining the geometries of molecules have been through-bond coupling (1,2), non-bonded attraction (3), hyperconjugation (4,5), and d orbitals lying above the valence shell (6,7). We wish to report on the role of d orbitals and hyperconjugation in the amine oxides,

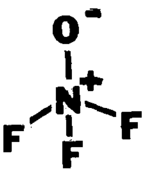
R_3NO. The concept of hyperconjugation or related ideas have been employed (4,5) to understand the rotational barriers in series of fluoro substituted molecules. The importance of the fluorine substitution presumably lies in reducing the energy of the σ^* orbitals and polarizing them so as to render them more available as electron acceptor orbitals. For this reason we have carried out a detailed comparison of H_3NO and F_3NO.

The significance of 'outer d orbitals' in the bonding of phosphorus and sulfur compounds has been a much debated question for a number of years (8,10). Until recently, it has been common practice to invoke sp^3d^2 hybridization around sulfur in SF_6, for example and sp^3d hybridization on phosphorus in PF_5 to account for the bonding in these molecules. In principle, however, even molecules of phosphorus and sulfur in high coordination states can be accomodated in bonding schemes which totally neglect 3d obitals (11).

The usual argument advanced for the lack of participation of outer d orbitals' in bonding descriptions of atoms of the 2nd and 3rd row of the periodic table is ascribed to their high energy and diffuseness (12). A number of workers (13-15) have however indicated that, for suitable valence shell electron configurations, the size andenergy of 3d orbitals may contract and drop, when under the influence of strongly electronegative ligands. Furthermore, Coulson (10) has distinguished two cases of d orbital participation. On the one hand, the d orbitals may simply be polarization functions with no net change occurring in the charge of the atom to which the d orbital has been admitted, since whatever electron density gained by the d orbitals would be lost by the s and p orbitals of the same atom. On the other hand, the d orbitals might be involved in the bonding by accepting charge from appropriate orbitals of neighboring atoms (p_π-d_π charge feedback) leaving the s, p-electron density on the atom which bears the d orbitals essentially unchanged.

Non-empirical molecular orbitals calculations (16-25) for a variety of phosphorus and sulfur compounds have demonstrated the importance of p_π-d_π type bonding interactions. However, some molecular orbital calculations on PF_5 and related molecules (21,24,25) indicate that the m.o. charge distribution obtained from an s,p,d basis set differs only moderately from a basis set where only s,p atomic orbitals were employed on the constituent atoms of the molecule. The shortness of the S-O bond in SO_4^{-2} and the P-O bond in F_3PO has been ascribed to the involvement of p_π-d_π bonding (6,7).

F_3NO which is valence isoelectronic to F_3PO has been shown to have (26) C_{3v} symmetry with a very short N-O distance, viz., 1.159 Å. This is 0.28 Å shorter than the sum of the Shomaker-Stevenson single-bond radii (corrected for electronegativity difference) (27), while the N-F distance at 1.432 Å is about 0.06 Å longer. The high IR stretching frequency (1690 cm^{-1}) of the N-O bond suggests a bond order of about two and raises the interesting question of whether the validity of the octet rule for first-row elements strictly holds for F_3NO (28). The following valence bond structures have been offered to account for the unusual bond lengths in F_3NO and the weakness of the N-F vs. the N-O bond:



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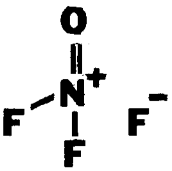
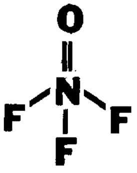


II



III

Valence bond structures I and II maintain the valence shell octet at nitrogen with I corresponding to a typical amine oxide dative bond structure while II is a double bond-no bond resonance structure presumably arising from donation of oxygen lone-pair electron density into N-F antibonding σ^* orbitals. Structures I and II would be expected to employ d orbitals merely as polarization functions. Structure III, which is considered to be important for F_3PO (19,23), has also been advanced for F_3NO to account for the short N-O bond (29). It is in this structure where the d orbitals are accepting electron density from the oxygen lone pairs and the nitrogen is formally exceeding its octet of electrons. The importance of 3d orbitals in the bonding of F_3NO May at first be hard to accept since these orbitals lie approximately 300 kcal/mol above the ground state of the nitrogen atom (26). As mentioned previously, however, the presence of the large number of very electronegative ligands may have the effect of contracting the nitrogen d orbitals and lowering their energies, sufficiently enough perhaps to permit substantial bonding. Of course, the N-F σ^* would be made more available as well. We note that semiempirical calculations by Frost, et al (29) give as a conclusion "these calculations do nevertheless indicate strongly that minimum basis sets of Slater-type orbitals with free-atom exponents will need the addition of 3d orbitals for application to to F_3NO, F_3PO, and related molecules."

It is the object of the present investigation to hopefully shed further light on the question of the importance of d and σ^* orbitals in the bonding of F_3NO and H_3NO by carrying out non-empirical molecular orbital calculations on these species.

COMPUTATIONAL DETAILS

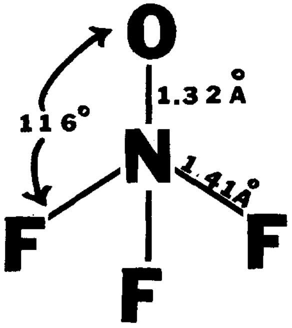
The Ab-initio calculations were performed using the single-determinant theory of the GAUSSIAN 70 series of programs (30). For calculations using the minimum basis set, each Slater function was expanded as a linear combination of three Gaussians (STO-3G) (31). In addition, calculations were performed using extended basis sets at three levels of approximation: (1) The 4-31G basis is the comutational recipe for which most calculations reported herein were carried out (32). It is comparable to double zeta (33) in accuracy with one basis function for each core orbital (represented by a linear combination of four s-type gaussians) and two functions for each atomic valence orbital a three-gaussian contraction for the inner part and a single gaussian for the outer part; (2) The 4-31G basis is improved by adding two additional gaussians to the description of the core orbitals, giving rise to the 6-31G basis; (34) (3) Finally, the 4-31G basis is improved by adding a set of five pure d-type functions $(3z^2-r^2, xz, yz, xy, x^2-y^2) \exp(\alpha_d r^2)$ herein referred to as the 4-31G(d) basis. The value of α_d used in these calculations is 0.8 which has been suggested by Hariharan and People (35). For F_3NO with d orbitals the full basis set consists of 106 primitive Gaussian functions, contracted to 51 basis functions. The calculations with d-orbitals on nitrogen (utilizing the POLYATOM (36) program) proved to be quite costly compared with calculations done in the 4-31G or 6-31G bases.

RESULTS AND DISCUSSION

F_3NO

Geometry optimizations employing the STO-3G basis favored a C_{3v} structure for F_3NO consistent with experimental observations

(26). The STO-3G optimized structure is given as IV, where the molecule is seen to be close to tetrahedral.



IV

The N-F bond distance and the value of the ONF angle (pyramidal angle) Θ are in good agreement with the experimental (26) values of 1.432Å and 117.1° but the N-O bond distance is predicted to be much too long, by about 0.16Å. We have therefore repeated the geometry optimization employing both the 4-31G and the 4-31G (d) basis. The results of these optimizations are (4-31G(d) in parentheses): r(NO) = 1.187 Å (1.156Å); r(NF) = 1.412 Å and Θ = 117.2°. Because of the expense involved with d orbitals in the basis set only N-O optimizations were carried out in the 4-31G (d) basis. The results are now seen to be in much better agreement with experiment, with a satisfactory N-O bond length being produced by the split valence shell basis set, d orbitals not being necessary. This can be compared to the results of Schaefer et al (37) for ClF_4^+ and SF_4 where polarization functions were found to be necessary to achieve reasonable agreement with experiment for these second row molecules.

For comparative purposes it was decided to carry out the following calculations on F_3NO using the electron-diffraction (26) geometry. In Table I we record the energies of the occupied orbi-

TABLE I.

COMPARISON OF ORBITAL ENERGIES (au) of F_3NO (C_{3v}) FOR VARIOUS BASIS SETS

Symmetry	STO-3G	4-31G	4-31G*	Δ‡	6-31G
$1a_1$	-26.0446	-26.3756	-26.3628	+0.013	-26.4253
1e	-26.0445	-26.3755	-26.3627	+0.013	-26.4253
$2a_1$	-20.2806	-20.6528	-20.6527	+0.000	-20.6926
$3a_1$	-15.8053	-16.0344	-16.0214	+0.013	-16.0618
$4a_1$	-1.6978	-1.8462	-1.8270	+0.019	-1.8507
2e	-1.5367	-1.6771	-1.6665	+0.011	-1.6816
$5a_1$	-1.4570	-1.6287	-1.6130	+0.016	-1.6317
$6a_1$	-0.9412	-1.0844	-1.0725	+0.012	-1.0879
3e	-0.7672	-0.9170	-0.9044	+0.013	-0.9189
$7a_1$	-0.6723	-0.8487	-0.8422	+0.007	-0.8503
4e	-0.5744	-0.7685	-0.7619	+0.007	-0.7712
$8a_1$	-0.5378	-0.7377	-0.7332	+0.005	-0.7405
$1a_2$	-0.5257	-0.7137	-0.7019	+0.012	-0.7161
5e	-0.5233	-0.7052	-0.6953	+0.010	-0.7079
6e	-0.3615	-0.5639	-0.5697	-0.006	-0.5653
$9a_1$	+0.3615	-0.0951	0.1147	--	-0.0920
$2\Sigma_i e_i$	-254.956	-263.874	-263.495	+0.352	-264.395
E_T	-421.4339	-426.7270	-426.8169	-0.090	-427.1437

*with d

‡Changes due to the inclusion of d-orbitals on nitrogen

tals, the lowest virtual orbital, twice the sum of the orbital energies and the total energy as found by the various basis sets. Comparing the results of the 4-31G basis both with and without d orbitals confirms the analysis of Nakatsuji and Musher (38) where these authors have shown that inclusion of polarization functions should have a first-order effect of raising all the orbital energies save those showing large participation of polarization functions such as the 6e orbitals for F_3NO. We note that the addition of d orbitals to the 4-31G basis improves the total energy by only 0.09 hartrees while the addition of the two gaussians to the core to give the 6-31G basis is seen to substantially lower the total energy (by 0.42 hartrees).

Examination of the coefficients comprising the various molecular orbitals produced the symmetry labels given in Table I and a comparison of the m.o. coefficients with the a.o. coefficients together with the orbital energies allows one to readily identify the $1a_1$ - $3a_1$ levels as the core orbitals with the $3a_1$ m.o., for example, being largely a 1s nitrogen orbital. The remaining sixteen filled valence orbitals describe the bonding as well as the lone pairs on the oxygen and the fluorine ligands. We will return to a more detailed examination of the description of the valence orbitals below.

In Table II we compare the calculated vertical ionization potentials as found using INDO theory and 4-31G(d) theory with the corresponding experimental quantities (29). The INDO entries of Table II have been empirically corrected by lowering all INDO orbital energies by 4 eV; a correction that has been found useful when comparing ionization potentials with calculated orbital energies (29). It is seen that even with this correction the first ionization potential predicted by INDO is too low by 1.9 eV. The

TABLE II

IONIZATION POTENTIALS (ev) AND ORBITAL ENERGIES (ev) FOR F_3NO

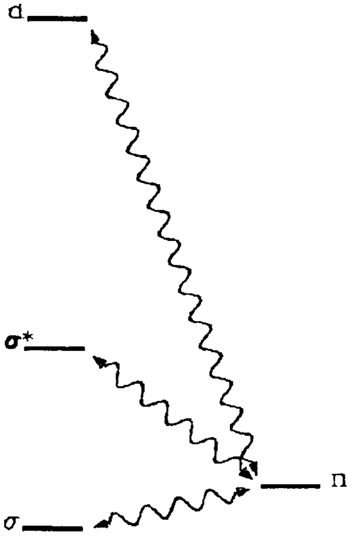
Adiabatic[a]	Vertical[a]	INDO[a]	4-31G(d)
13.5	14.3	12.4 (e)	15.5 (e)
15.1	15.1	16.6 (a_1)	18.9 (e)
16.5	17.3	17.4 (e)	19.1 (a_2)
20.0	20.3	18.0 (a_2)	19.9 (a_1)

[a] Reference 29

4-31G(d) basis on the other hand is seen to be too high by 1.2 eV. The INDO method is slightly better correlated with experiment than our ab initio results; however, neither theoretical method can be said to provide satisfactory agreement with experiment. There is also seen to be a discrepancy between the ab initio results and the INDO semi-empirical results with regards to the ordering of the molecular orbitals. We are inclined to believe that our ordering is correct based on the known inadequacies of the semiempirical methods.

Before proceeding further we present in Scheme I an interaction diagram for the interplay of the oxygen lone pairs with the N-F(H) σ and σ^* bonds as well as the d orbitals on the nitrogen. Donation into the nominally empty σ^* and d orbitals is a stabilizing interaction which will increase the strength of the N-O bond and allow for charge drift towards the nitrogen. Electronegative substituents such as fluorine will lower the energy of the σ^* orbitals and polarize them so as to favor interaction with the adjacent oxygen lone pairs. Additionally, such substituents will have the effect of decreasing the energy of the d orbitals making them also more available for accepting electron density.

Scheme I



We present in Table III the results of a Mulliken population analysis (39) for F_3NO (experimental geometry) for each occupied m.o. as found using the 4-31G(d) basis. The effect of including d orbitals in the basis set can be seen by comparing the total population figures presented at the bottom of Table III. There is seen to be a remolding of electron density with a drift of electronic charge from oxygen toward nitrogen giving rise to a less extreme charge distribution and a strengthening of both the N-O and N-F bonds. Of the total electron density centered on the nitrogen atom, 0.3 e resides in d orbitals, which is comparable to the d orbital population of 0.5 e in PF_3O as found by Serafini, et al (40). The d orbital participation is also apparent from the overlap populations. The contribution of the nitrogen 3d orbitals to the overlap for the N-O bond is 0.21 (53% of the total N-O overlap population) which is similar to the value of 0.23 found (40) for the P-O bond in

TABLE III

MULLIKEN PUPULATION ANALYSIS OF F_3NO ACCORDING TO 4-31G* BASIS

Orbital	N	O	F1	N-O	N-F1
$1a_1$	0.004	0.001	0.673	0.000	0.002
1e	0.002	0.000	1.32	0.000	0.002
$2a_1$	0.005	1.995	0.000	0.008	0.000
$3a_1$	1.995	0.002	0.001	0.004	0.001
$4a_1$	0.630	0.235	0.378	0.179	0.123
2e	0.212	0.006	1.260	0.002	0.093
$5a_1$	0.534	0.860	0.202	0.515	-0.027
$6a_1$	0.752	0.296	0.318	-0.323	-0.091
3e	1.484	0.468	0.683	0.282	0.080
$7a_1$	0.303	0.996	0.234	-0.679	0.062
4e	0.068	0.116	1.272	0.026	0.018
$8a_1$	0.164	0.458	0.459	0.066	-0.008
$1a_2$	0.000	0.000	0.667	0.000	0.000
5e	0.122	0.042	1.280	0.026	0.002
6e	0.182	2.610	0.402	0.298	-0.011
Total	6.458 (6.137)	8.083 (8.282)	9.153 (9.194)	0.399 (0.198)	0.243 (0.120)

The parenthetic values are the populations obtained from the 4-31G wavefunctions without d orbitals in the basis set.

PF_3O. The d orbitals on nitrogen make their presence felt to the greatest extent in the degenerate pair of 6e orbitals where about 50% of the 6e overlap comes from p_π-d_π bonding. The d_σ bonding, which is substantial (33% of the total d overlap), arises primarily within the $8a_1$ orbital with a smaller contribution from the $5a_1$ orbital.

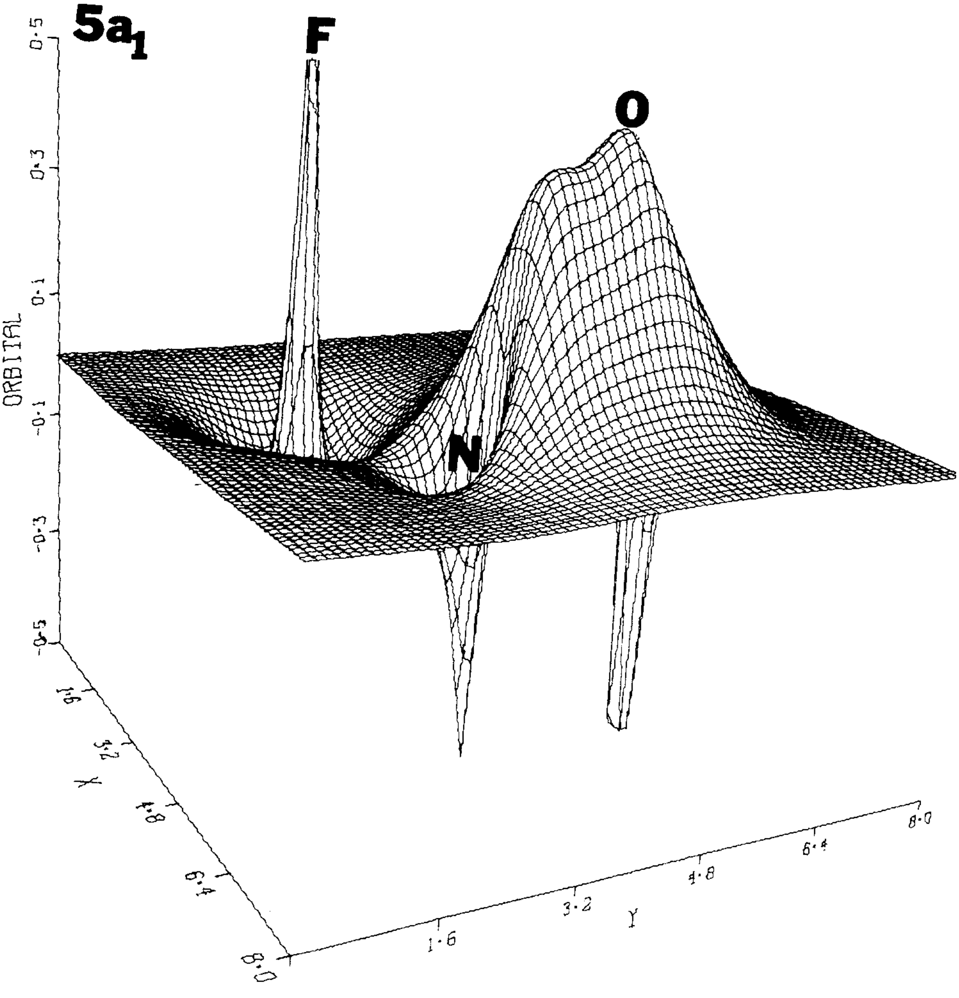
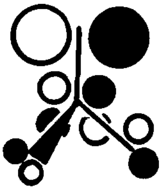


Figure 1. A three dimensional plot of the $5a_1$ molecular orbital of F_3NO (including d orbitals on the nitrogen) evaluated in a plane containing the nitrogen, oxygen and one of the fluorines. The distance of the plotted surface from the reference plane is proportional to the value of the molecular orbital in the plane.

We present in Figures 1 and 2 the three dimensional plots of two of the more interesting valence shell molecular orbitals of F_3NO (evaluated in a plane containing the oxygen, nitrogen and one of the fluorines) as obtained from the 4-31G(d) basis. As seen from Figures 1 and 2 and the results of Table III the $5a_1$ orbital constitutes, in large measure, the N-O sigma bonding in this molecule. The 6e orbital set is seen to be largely oxygen lone pair but it is also seen to be N-O π bonding. The following schematic picture for one of the 6e orbitals shows how the d orbital on nitrogen can interact with the orbitals on both oxygen and fluorine to strengthen these bonds:



6e

The influence of the d orbitals is clearly seen by examining the difference plot for the 6e level (d - no d magnified three times). The difference plot clearly illustrates the double-lobe character of the orbital along the threefold N-O bond axis. Additionally, it can be seen that when d orbitals are allowed, electron density is shifted from the lone pairs on the oxygen into the N-O bonding region giving rise to the $p_\pi - d_\pi$ bond.

H_3NO

Ammonia oxide, although a hypothetical molecule (only the tautomeric form hydroxylamine is known) should exhibit classical dative bonding ($\equiv \overset{+}{N} - \overset{-}{O}$). The influence of d orbitals would be expected to

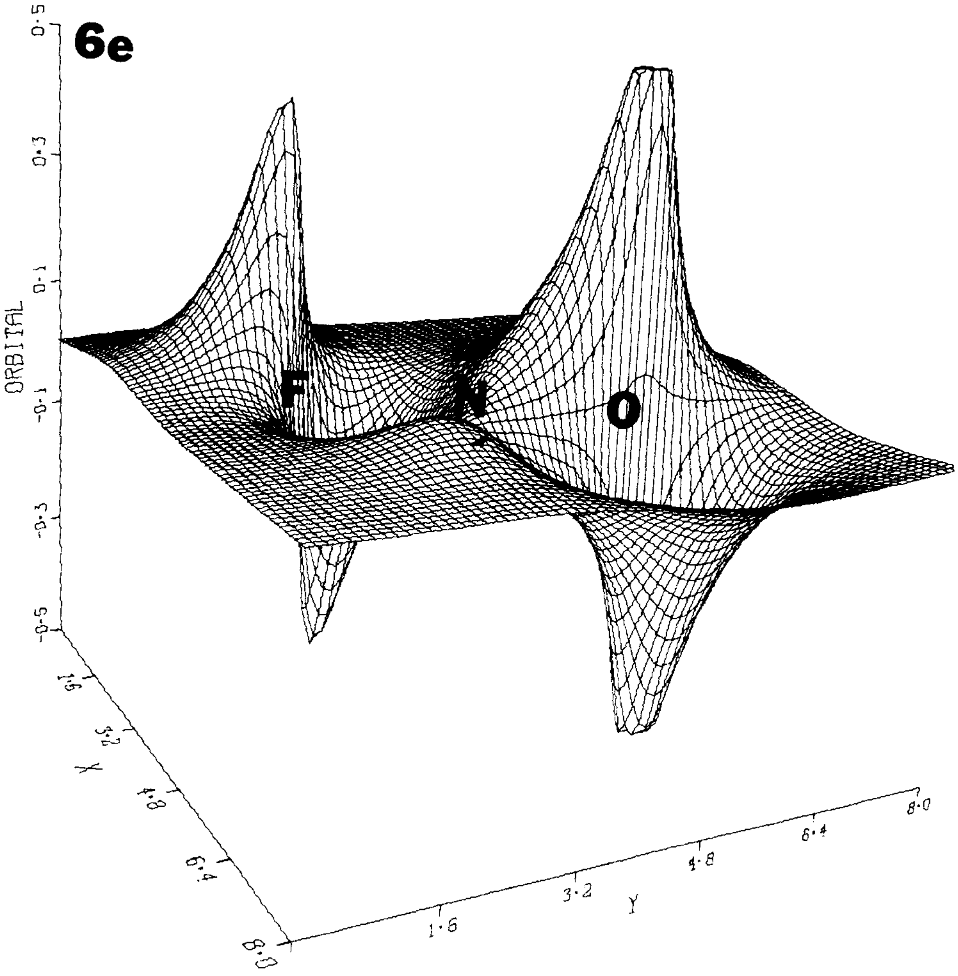


Figure 2. (a) A three dimensional plot of one of the 6e moleculear orbitals of F_3NO (including d orbitals on the nitrogen) evaluated in a plane containing the nitrogen, oxygen, and one of the fluorines. The distance of the plotted surface from the reference plane is proportional to the molecular orbital in the plane.

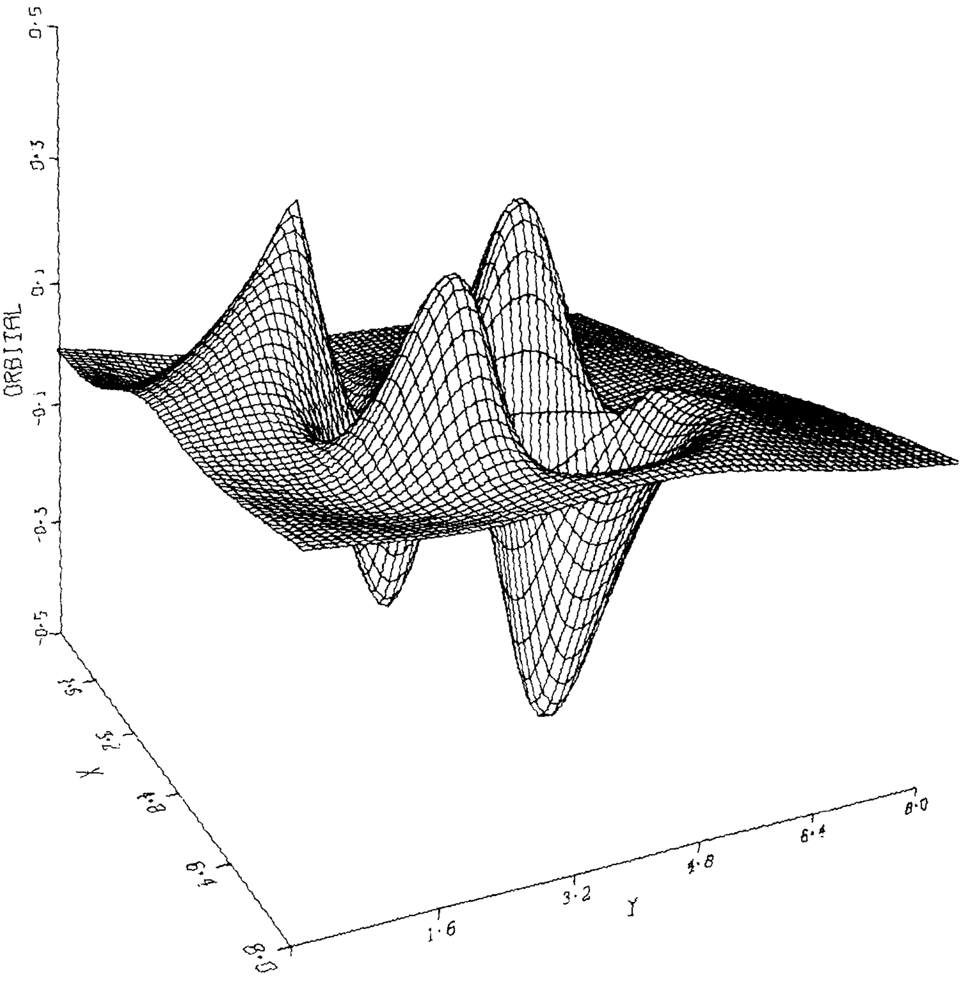
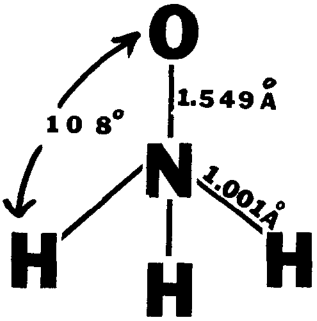


Figure 2. (b) A difference plot (d - no d) of the 6e orbital. The vertical scale in the difference plot is magnified three times relative to the plot at the top.

be small in this molecule since the electronegative fluorine ligands of F_3NO have been replaced by hydrogens. Consequently, the N-O bond in these molecules would be expected to be rather 'normal' with a distance of about 1.4 Å. (The N-O bond distance in trimethylamine oxide for example is 1.39Å) (41).

To examine the electronic structure of this molecule we have carried out 4-31G optimizations with the constraint of C_{3v} symmetry. For H_3NO the 4-31G optimized form corresponds to structure V:



V

The 4-31G method is seen to predict a rather long N-O bond distance. The N-O stretching potential curve, however, is predicted to be rather flat around the minimum; for example, a structure corresponding to V with an N-O distance of 1.39Å is only 5 kcal/mol higher in energy. While this work was in progress Hart (42) reported Gaussian lobe calculations (no d orbitals on N) on H_3NO where he also finds a rather long N-O bond distance (1.69Å). Lathan, et al. (43), using the minimal basis STO-3G method also find a long N-O distance of 1.58Å. We interpret the long N-O bond length of H_3NO relative to F_3NO, in the without d calculations as being due to the higher energy and less favorable polarization of the N-Hσ^* relative to the N-F σ^* orbitals.

When H_3NO was examined in the 4-31G(d) basis the optimized N-O bond distance found to shorten by 0.10 Å. The minimum energy structure resembles V but with an N-O distance of 1.45 Å. As when using the 4-31G basis the N-O potential curve is found to be rather flat. A structure similar to V but having an N-O distance of 1.39Å is now only 1.2 kcal/mol higher in energy than the minimum energy structure. The N-O stretching potential curve in F_3NO, on the other hand, is an order of magnitude larger. The effect of adding d orbitals to the basis set has only a modest effect (0.02 hartrees) in lowering the total energy. In agreement with Hart (42) we find the $^1A_1$ electronic ground state of H_3NO to be thermodynamically stable by 53 kcal/mol with respect to dissociation into NH_3 ($^1A_1$) and an oxygen atom (^1D), according to 4-31G theory. However, H_3NO is predicted to be about 16 kcal/mol higher in energy (4-31G theory) than its tautomeric form hydroxylamine (H_2NOH), a similar finding having been reported earlier by Trindle (44).

Table IV compares the results of a Mulliken population analysis for H_3NO and related species as obtained from the 4-31G wavefunctions. The parenthetic values for H_3NO and F_3NO were obtained from the 4-31G basis with d orbitals on nitrogen. The following geometries were adopted for the molecules presented in Table IV: H_3N (r_{NH}= 1.001Å, θ = 116°); F_3N (r_{NF}= 1.385Å, θ = 116°); for H_3NO structure V was employed and for F_3NO the experimental geometry was adopted. The angle θ is the pyramidal angle referred to earlier (see Structure IV).

When one compares H_3N with H_3NO there is seen to be a σ charge transfer of 0.45 e to oxygen from the nitrogen with a corresponding π-back donation of 0.27 e. The donation of electrons from the protons is seen to be greater in H_3NO compared to H_3N, with a corre-

TABLE IV

4-31G POPULATION ANALYSIS FOR H_3NO AND RELATED SPECIES

		H_3N	H_3NO	F_3N	F_3NO
N:	2s	1.746	1.658	1.648	1.336
	$2p_\sigma$	1.782	1.412	1.360	0.931
	$2p_\pi$	2.342	2.608	1.224	1.874
	Total	7.865	7.674 (7.703)	6.229	6.137 (6.458)
H:	1s	0.712	0.615 (0.588)	--	--
O:	2s	--	2.001	--	2.019
	$2p_\sigma$	--	0.525	--	0.973
	$2p_\pi$	--	3.958	--	3.294
	Total	--	8.480 (8.516)	--	**8.282** (8.083)
F:	2s	--	--	2.014	2.012
	2p	--	--	5.248	5.186
	Total	--	--	9.257	9.194 (9.153)
N-H		0.648	0.610 (0.609)	--	--
N-O		--	-0.148 (-0.166)	--	0.198 (0.399)
N-F		--	--	0.120	0.120 (0.243)
exp (D)		1.47[a]	--	0.24[b]	0.04[c]
calc (D)		2.54	5.38	0.44	0.51

[a] D.K. Coles, W.E. Good, J.K. Bragg and A.H. Sharbaugh, Phys. Rev. 82, (1951) 877.

[b] P. Kisliuk, J. Chem Phys., 22, (1954) 86.

[c] W.H. Kirchhoff and D.R. Lide, J. Chem. Phys., 51, (1969) 467.

sponding weakening of the N-H bond. The bond overlap populations for the N-O bond in H_3NO are predicted to be negative according to Mulliken analysis of the 4-31G wavefunction both with and without d-orbitals on nitrogen. This problem is occasionally encountered and not much meaning should be attached to this and is presumably due to the use of the split valence shell. STO-3G calculations, for instance, on the geometries reported in Table IV for F_3NO and H_3NO yield N-O bond overlap populations of 0.59 and 0.13, respectively. Extended Hückel calculations (45) also reveal a similar overlap analysis with the N-O bond in F_3NO being considerably stronger than the corresponding bond in H_3NO.

The effect of adding d orbitals to the basis set for H_3NO is seen to be small and, in fact, instead of electrons being drawn away from oxygen, the effect of d orbitals is to increase the charge on oxygen.

It appears that the effect of adding d orbitals is simply to polarize the sp^3 hybrid, housing the lone pair in NH_3 to make it a better donor. The major orbital which has a positive d orbital occupation is $5a_1$ which is a σ orbital. The 2e set of highest occupied orbitals are primarily oxygen lone-pair orbitals (with 3.78 e on oxygen). That back donation in H_3NO is unimportant can also be gleaned from the computed dipole moments of H_3NO and F_3NO reported in Table IV.

Comparing F_3N with F_3NO there is seen to be a σ-charge transfer of 0.74 e with a corresponding π-back donation of 0.65 e. The relatively large positive charge on nitrogen in F_3N compared to that found in H_3N makes the former molecule a much better acceptor of electrons resulting in the larger π-back donation. If the N-F distance in F_3N is taken to be identical to that in F_3NO, the N-F overlap population then rises from 0.12 to 0.15. The N-H and N-F overlap population changes upon forming the oxides are consistent with electron density on oxygen being donated into N-F and N-H antibonding orbitals.

Summary

Ab initio SCF calculations on F_3NO and H_3NO indicate that the involvement of d orbitals in the bonding of these molecules is more important for the former molecule. In F_3NO the effect of the highly electronegative fluorine ligands is to lower the energy of the d - orbital manifold and the N-Fσ^* levels so as to allow their effective interaction with the oxygen lone pairs resulting in a stronger and shorter N-O bond and a longer N-F bond. In H_3NO, on the other hand, the d orbitals lie quite high in energy so that there is no tendency for the lone pairs on oxygen to be donated to the nitrogen d functions. The d orbitals in F_3NO cannot be dismissed as trivial, as their presence is important in shaping the electron distribution in this molecule leading to less extreme charges and a stronger N-O bond. However, they do not have as dramatic an effect on the N-O shortening and total energy lowering as is found in F_3PO (46).

Acknowledgement

We are grateful to the support provided by the CUNY Computer Center. One of us (JMH) is appreciative of a Faculty Research Award Grant from CUNY.

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