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ELECTRONIC STRUCTURES AND GEOMETRIES OF N-O-F
COMPOUNDS: FLUORINATED HYDROXYLAMINES

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SUMMARY

STO-3G and 4-31G calculations have been carried out on hydroxylamine and its fluorinated derivatives with the hope of shedding some light on the electronic structures of these interesting molecules. The geometries of the hydroxylamines have been optimized using both computational methods and the resulting geometries predicted from the two methods are compared. We have also computed the atomization energies, the bond separation energies, the hydrogenation energies, the heats of formation and the isomerization energies. Whereas STO-3G theory is adequate for hydroxylamine, the introduction of fluorines in the molecule necessitates the use of a more flexible basis set (4-31G) for adequate description.

INTRODUCTION

We wish to report herein the results of our continuing investigations on the electronic structures of fluorinated compounds(1-3). Highly fluorinated organic compounds have unusual chemical and physical properties and this renders them

interesting systems for study. Substitution of fluorine for hydrogen in organic compounds is a useful way to change the electron-distribution pattern without substantially changing the shape or size of the molecule(4). For example, the effect of fluorine on the structure of the amine oxides is well known experimentally(5). Thus, while the trialkylamine oxides (and presumably the simplest but unknown H_3NO (2)) are salt-like in character, trifluoramine oxide has the properties of a covalent substance(5)

In this paper, we will examine a series of fluorinated hydroxyl amines together with a brief comparison with the isomeric amine oxides H_3NO and F_3NO . Compounds possessing N, O and F are of interest not only because of their somewhat unusual bonding properties but also because of their potential use as high-energy oxidizers(7). Of the substances examined in this study, the only known fluorinated species is trifluoramine oxide, F_3NO (6), although numerous efforts to prepare perfluorohydroxylamine, F_2NOF have been attempted(7). Although F_2NOF is unknown, there has been some recent synthetic success in preparing related substances such as FSO_2ONF_2 (8), SF_5ONF_2 (9) and CF_3ONF_2 (10).

The qualitative bonding theories of Linnett(11) and of Spratley and Pimentel(12) have been applied to H-N-O-F compounds while Ganguli and McGee(13) have applied the MINDO(14) semi-empirical molecular orbital method for the purpose of computing geometries and heats of formation of N-O-F compounds. Ab-initio calculations have been reported on hydroxylamine(14,15), and FHNOH and H_2NOF (16), using either experimental or standard geometries for the purpose of computing

torsional barriers. In the present study, we have used ab-initio molecular orbital theory to completely optimize the geometries of the fluorinated hydroxylamines. Ab-initio molecular orbital theory has been rather successful in reliably predicting molecular geometries(17). Pople's work on neutral molecules(18) and carbonium ions(19) has amply demonstrated that reliable geometry predictions are obtained at both the minimal and extended basis set levels. This paper reports on the results of the geometry optimizations and electronic structures of the H-N-O-F isomers related to hydroxylamine while the succeeding paper examines the conformational isomerism in these compounds.

COMPUTATIONAL METHODS

All of the calculations reported in this paper are of the SCF-LCAO-MO type with no empirical parameters being employed. The ab-initio calculations were carried out using the single-determinant theory of the Gaussian 70 series of programs(20). For calculations employing the minimal basis set, each Slater orbital was expanded as a linear combination of three Gaussian type orbitals (STO-3G)(21). In the extended or 4-31G basis set the inner (1s) shell of the first row atoms is represented by a linear combination of four s type Gaussians. The valence shell orbitals, on the other hand, are split into an inner part which is represented by a three Gaussian contraction, and an outer part which is represented by a single Gaussian(22).

TABLE 1
OPTIMIZED GEOMETRIES OF X₂NOX and X₃NO

Molecule	Basis	r(N-O) ^a	r(N-X) ^a	r(O-X) ^a	XON ^b	XNX ^b	∅ ^c	Energy(hartrees)
H ₃ NO	4-31G	1.54	1.00	-	-	108.	-	-130.7601
H ₂ NOH	4-31G	1.44	1.00	0.95	106.1	106.	0	-130.7918
	Exptl. d	1.46	1.02	0.96	103.	106.	0	-
FHNOH	4-31G	1.39	1.39 ^e	0.95 ^e	106.7	107.7	30	-229.4518
			1.00			108.9		
H ₂ NOF	4-31G	1.38	1.00 ^e	1.46 ^e	106.4	108.7	180	-229.4145
FHNOF	4-31G	1.34	1.35 ^e	1.47	107.6	110.	180	-328.0654
			1.00			112.		
F ₂ NOH	4-31G	1.35	1.40	0.96	112.	108.	180	-328.1079
F ₂ NOF	4-31G	1.345	1.377	1.45	108.4	109.5	180	-426.7115
F ₃ NO	4-31G f	1.19	1.41	-	-	117.	-	-421.7287
	Exptl. f	1.16	1.43	-	-	117.	-	-

a= Bond distance in Angstroms

b= Bond Angles in Degrees.

c= ∅ corresponds to the: NOX dihedral angle

d= Reference 24 of text.

e= Assumed parameters, not optimized

The split-valence shell or extended basis leads to increased flexibility over the minimal basis set description since it allows for a better description of anisotropic electron distributions(22). The 4-31G basis set is comparable to a double zeta basis set in accuracy(23) with typical discrepancies between optimized geometries at this level of theory and experiment being 0.01\AA for bond distances and 4° for bond angles.

RESULTS AND DISCUSSION

1. Geometries

We record in Table 1 the optimized geometries of the $X_2\text{NOX}$ and $X_3\text{NO}$ molecules as predicted by the 4-31G level of theory together with the experimental parameters of the known molecules: H_2NOH (24) and F_3NO (6). The angle ϕ in Table 1 corresponds to the :NOX dihedral angle for hydroxylamine and its derivatives. The change in energy vs. dihedral angle ϕ for hydroxylamine and its fluorinated derivatives will be discussed in the following paper. An examination of Table 1 reveals that the N-O bond length shortens as a result of fluorination according to the extended 4-31G basis with the largest change occurring for the first fluorine substitution ($0.05\text{-}0.06\text{\AA}$) with a bond length reduction of about 0.1\AA in the fully fluorinated hydroxylamine. STO-3G, on the other hand, predicts a slight lengthening ($\sim 0.01\text{\AA}$) of the N-O bond upon fully fluorinating hydroxylamine. The O-F bond is also predicted to be too short, by about 0.1\AA , according to the minimal basis set results. A finding similar to that presented here has been reported previously(1) where 4-31G theory gave an optimized structure for CF_3OF very close to experiment

while STO-3G was found to be rather poor for bond length predictions. Palke(25) has pointed out the shortcomings of a minimal basis set in computing rotational barriers in fluorinated ethanes.

Table 1 reveals that certain structural trends are apparent in addition to the bond length variations alluded to above. In the hydroxylamines, O-fluorination leads to somewhat shorter (0.01\AA) N-O bonds than the corresponding N-fluorination. It is also apparent from the entries recorded in Table 1 that certain bond parameters are predicted to be relatively constant from molecule to molecule. Thus, the N-H bond distance consistently optimizes around 1.00\AA , the C-H bond around 0.95\AA and the O-F bond around 1.46\AA .

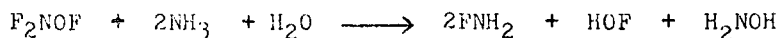
As far as the bond angles are concerned 4-31G theory generally leads to angles larger than experimentally found for molecules consisting of first row atoms(26). This is indeed the case for hydroxylamine where the experimentally determined HON angle is 103° but it is predicted to be 106° according to 4-31G theory. The XON bond angle for the other members of the series X_2NOX are also seen to be similar to the 106° predicted value in hydroxylamine with a slight broadening as a result of fluorination. The 4-31G optimized HON angle in F_2NOH is however predicted to be much larger (112°). A similar situation having been found for CF_3OH (3), where 4-31G theory predicts an HOC bond angle of about 116° . It should however be pointed out that the potential curve for bending of the HON angle around the minimum in F_2NOH is rather flat. Thus, the structure having an HON angle of 108° for instance is only 0.3 kcal/mol higher in energy than

the minimum energy structure. The ONX angles are according to the results of Table 1 rather close to tetrahedral for the hydroxylamines. For F_3NO this angle is more pyramidal(2,6).

2. Bond Separation Energies and Isomerization Energies

Table 2 records the bond separation energies and heats of formation at 298K⁰ in kcal/mol for hydroxylamine and its fluorinated derivatives.

Although single determinant molecular orbital theory is inadequate for describing atomization energies, recent studies have suggested that bond separation energies and hydrogenation energies may be satisfactorily described at this level of theory(16,27). In a bond separation reaction, a molecule with three or more heavy atoms is converted into molecules with two heavy atoms and the same types of formal bonds. For example, the bond separation reaction for perfluorohydroxylamine is:



and the corresponding heat will be the heat of bond separation. Computing the 4-31G energies of the reactants and products allows us then to compute the bond separation energies recorded in Table 2. These theoretical bond separation energies should rightly be compared with experimental heats of reaction at 0⁰K corrected for zero-point vibrations. However we have followed Pople's(16) philosophy and have assumed that the corrections should be small and that the calculated bond separation energies may be applied without adjustment to reactions at 298⁰K.

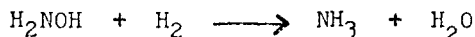
TABLE 2

BOND SEPARATION ENERGIES AND HEATS OF FORMATION OF X₂NOX

COMPOUND	BOND SEPARATION ENERGIES (KCAL/MOL)	$\Delta H^{25^{\circ}}$ (KCAL/MOL)
	4-31G	4-31G
H ₂ NOH	-	-9.3 ^a
FHNOH	10.9	-12.6
H ₂ NOF	11.7	+7.8
F ₂ NOH	13.8	+28.2
FHNOF	12.3	+10.1
F ₂ NOF	13.5	+13.3

^aReference 36 of text.

The bond separation energies are all seen to be positive with a mean value of 12.4kcal/mol. The positive values of the bond separation energy corresponds to a stabilization of the larger molecule. The values of the bond separation energy reported in Table 2 are not much different from that found(16) for CH₂F₂(11.5kcal/mol) but are substantially less than the value computed for CF₄(40.5kcal/mol). Apparently, perfluorination has less of a strengthening effect for substitution at nitrogen or oxygen than at carbon. In addition to bond separation energies, one can also compute hydrogenation energies. The hydrogenation of hydroxylamine corresponds to the reaction:



Since the theoretical hydrogenation energies are for fixed nuclei they also should be compared with experimental heats of hydrogenatic

at 0°K corrected for zero-point vibrations(27). As with the bond separation energies we assume a comparison with 298°K is acceptable. The theoretical hydrogenation energy for hydroxylamine is computed to be -59.2kcal/mol which is in good agreement with the experimental value of -59.5kcal/mol at 298°K(16). In general, Pople(16) has found the 4-31G hydrogenation energies to be more negative than the experimental results. The corresponding STO-3G value of -25.2kcal/mol is seen as perhaps expected, to be in much poorer agreement with experiment. That minimal basis set theory is inadequate for the calculation of hydrogenation energies has been previously noted by Pople, et al.(27). The theoretical 4-31G complete hydrogenation energy of F₂NOF is -286kcal/mol while STO-3G places the value at -124kcal/mol.

Also recorded in Table 2 are the theoretical heats of formation. These were computed using the theoretical bond separation energies together with the heats of formation of molecules with two heavy atoms. The heats of formation of HOF and H₂NF have been estimated(16) and accordingly the heats of formation recorded in Table 2 should be viewed with caution as they may be in error by several kcal/mol. F₂NOF was predicted to have marginal stability according to the semi-empirical MINDO calculations(13), this being consistent with the present estimation of 13kcal/mol.

Table 3 records the isomerization energies of the hydroxylamines and amine oxides. Both the minimal and extended basis set calculations predict hydroxylamine to be thermodynamically more stable than H₃NO. A similar conclusion having been reached earlier by Hart(28) and Trindle and Shillady(29). With the fully fluorinated analogs however, the minimal basis prefers

TABLE 3

Isomerization Energies (kcal/mol) of X_2NOX and X_3NO

<u>REACTION</u>	<u>Basis</u>	
	<u>STO-3G</u>	<u>4-31G</u>
$H_2NOH \longrightarrow H_3NO$	56.8	19.9
$F_3NO. \longrightarrow F_2NOF$	-49.8	10.8
$F_2NOH \longrightarrow FHNOF$	-	26.6
$FHNOH \longrightarrow H_2NOF$	-	23.4

perfluorohydroxylamine to trifluoramine oxide contrary to the extended basis set results and to experiment.

In the case of the N-fluorinated vs. the O-fluorinated hydroxylamines, 4-31G theory is seen to favor the N-F compounds over the O-F compounds. A similar finding having been reported earlier by Pople, et al.(16) for the $FHNOH-H_2NOF$ pair where standard geometries were employed. FNO and FON are the simplest isomers of this type and recent calculations by Peslak, et al.(30) reveal that FNO is more stable by 46.7kcal/mol. FON however, has recently been observed experimentally(31).

3. Population Analysis

Table 4 records the 4-31G gross charges, bond overlap populations and dipole moments for the geometry optimized species considered in this study. The charges and bond populations were computed using the Mulliken partitioning scheme(32). The 4-31G dipole moments are generally too large (17) and this is illustrated

TABLE 4
 Gross Charges and Bond Overlap Populations for Optimized X_2NOX' and X_3NO

Molecule	Basis	Gross Charge					Bond Overlaps				μ
		X	N	O	X'	N-O	N-X	O-X'	μ		
H_3NO	4-31G	0.39	-0.67	-0.48	-	-0.15	0.61	-	-	5.38	
H_2NOH	4-31G	0.34	-0.51	-0.60	0.43	0.17	0.64	0.51	0.51	0.94	
$FHNOH$	4-31G	-0.32(F) 0.38(H)	0.05	-0.56	0.44	0.14	0.12(N-F) 0.63(N-H)	0.52	0.52	2.66	
H_2NOF	4-31G	0.36	-0.39	-0.08	-0.25	0.14	0.65	0.05	0.05	2.90	
$FHNOF$	4-31G	-0.29(F) 0.40(H)	0.15	-0.06	-0.20	0.10	0.13(N-F) 0.62(N-H)	0.07	0.07	2.65	
F_2NOH	4-31G	-0.28	0.41	-0.49	0.44	0.15	0.11	0.48	0.48	2.49	
F_2NOF	4-31G	-0.24	0.64	-0.03	-0.14	0.03	0.14	0.06	0.06	0.38	
F_3NO	4-31G	-0.19	0.86	-0.28	-	0.20	0.12	-	-	0.51	

by a comparison of the value in Table 4 with the only known experimental value, that of 0.04D for F_3NO (33). The dipole moment calculated for H_3NO is consistent with an amineoxide dative bond ($H_3\overset{+}{N}-\bar{O}$) formulation. F_2NOH has been postulated as an intermediate in the basic hydrolysis of NF_3 but like CF_3OH it is predicted to rapidly lose HF (34). The 4-31G charges on the OH proton together with the OH bond overlaps are rather similar for both H_2NOH and F_2NOH . There is however a small positive overlap population (0.005) for the nonbonded fluorine and hydrogen in F_2NOH . Other than this positive F-H overlap, there does not appear to be anything unusual about the electronic structure of F_2NOH to account for its apparent instability. The O-F bond overlaps recorded in Table 4 are similar to the 4-31G value of 0.08 computed for F_2O at its experimental geometry(35). The 4-31G N-O overlaps in the hydroxylamines are seen to be around 0.12 except for the rather small value of 0.03 computed for F_2NOF . The π component for this bond in F_2NOF is 0.09 so that there is a weak σ antibonding component leading to the low total N-O bond order and weak bond(12).

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