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AB-INITIO STUDIES OF FLUOROXYTRIFLUOROMETHANE GEOMETRY AND ELECTRONIC STRUCTURE

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SUMMARY

Ab-initio molecular orbital calculations using both minimal or STO-3G and extended or 4-31G basis sets have been applied to fluoroxytrifluormethane. Complete geometry optimizations using both basis sets have been applied to this molecule and the calculated structural parameters have been compared to the electron diffraction data. The extended basis set calculations are found to be in much better overall agreement with experiment although the minimal basis set does reproduce the angular parameters well, including the tilt angle. The barrier to the CF_3 torsion has been computed and it compares favorably with the microwave spectral value.

The electronic structure of CF_3OF and some related molecules have been examined by partitioning the electrons according to the method of Mulliken. The highest occupied orbital in CF_3OF is found to be largely an O-F π * orbital and the O-F bond is also found to be the least ionic and weakest bond in the molecule. The computed dipole moment of CF_3OF agrees well with the experimental value.

INTRODUCTION

Fluoroxytrifluoromethane (CF_3OF) is a reactive poisonous gas which was first prepared in 1948 by Kellogg and Cady (1). Although reactions of this molecule with organic substrates have been reported by a number of workers (2), its use as an organic reagent had not been fully realized However, this situation has been changed largely as a result of the studies of the Barton School (3) where these workers deomonstrated that CF_3OF is a powerful but yet a selective reagent for effecting electrophilic fluorination, addition and oxidation. Fluoroxytrifluoromethane can also undergo homolytic decompostion leading to fluorinations via the radical route (2d,4). Substitution of fluorine for hydrogen in organic compounds constitutes a useful way to change the electron-distribution pattern without substantially changing the shape or size of the molecule. Important and beneficial drugs could therefore be synthesized by the specific replacement of hydrogen by fluorine and the CF_3OF reagent serves admirably in this respect (4,5).

Recent structural studies including IR and Raman spectra (6-8), microwave spectra (9), and electron diffraction (10) results pointed to a C_s symmetry for fluoroxytrifluoromethane. The barrier to the CF_3 torsion has ranged from 1.13 kcal/mol, which was estimated by Wilt and Jones (7) with an assumed geometry, to 3.9 kcal/mol which was measured by Buckley and Weber (9). From Stark effect measurements these latter authors find CF_3OF to have a small dipole moment ($\sim 0.3D$).

In view of the current experimental interest in this molecule coupled with our current interest of the effects of fluorine substitution on the electronic structures of molecules (11), it was felt that a quantitative study of the electronic structure of CF_3OF would be highly desirable. It is well known that ab-initio molecular orbital methods have been quite successful in reliably predicting geometries of molecules (12), and we wish to report herein the results of minimal or STO-3G (13) and extended or 4-31G (14) basis set calculations on fluoroxytrifluoromethane.

COMPUTATIONAL METHODS

All of the calculations reported in this paper are of the SCF-LCAO-MO type with no empirical parameters being utilized. The ab-initio calculations were carried out using the single-determinant theory of the GAUSSIAN 70 series of programs (15). For calculations where the minimal basis set has been employed, each Slater orbital was expanded as a linear combination of three Gaussian-type orbitals (STO-3G). In the extended or 4-31G basis set the inner (1_s) 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. The split-valence shell or extended bases leads to increased flexibility over the minimal basis set description since it allows for a better description of anisotropic electron distribution(14). The 4-31G basis set is comparable to a double zeta basis set in accuracy (16) with typical discrepancies between optimized geometries at this level of theory and experiment being 0.01Å for bond distances and 4° for bond angles. We have not included any polarization functions in the basis set as it has previously been demonstrated (17) that the effect of d orbitals on the geometry of a number of fluorinated molecules is only modest. The number of basis functions in the STO-3G basis set for CF_3OF is 30 (25 of which are doubly occupied in the ground state) while this number increases to 54 for the extended basis set. Complete geometry optimizations have been carried out using both basis sets in this study.

RESULTS AND DISCUSSION

Both STO-3G and 4-31G geometry optimizations favor C_s symmetry for CF_3OF in agreement with experiment (6-10). We illustrate in Fig. 1 the C_s structure together with the axes and atom labelling used in this study.

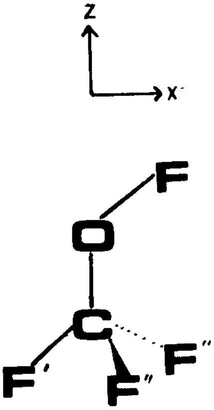


FIGURE 1

Table I compares the structural parameters found using STO-3G and 4-31G bases with the results found from electron diffraction (10). We have previously observed that the minimal basis set results deviate considerably from the experimental parameters for highly fluorinated molecules (11,17). STO-3G theory is also seen to perform poorly for CF_3OF at least as far as bond lengths are concerned. Bond angles at this level of theory are reproduced well however. The tilt angle, which corresponds to the movement of the C-O bond away from CF_3 symmetry axis (towards the - x direction of Figure 1), is also seen to be well reproduced at the STO-30 level.

TABLE I

CALCULATED AND EXPERIMENTAL STRUCTURAL PARAMETERS FOR CF_3OF

	METHOD		
PARAMETER*	STO-3G	4-31G	EXPERIMENT (Ref. 10)
C-O	1.445	1.392	1.395 ± 0.006
O-F	1.362	1.429	1.421 ± 0.006
C-F'	1.378	1.337	1.319 ± 0.003
C-F	2.223	2.224	2.230 ± 0.009
O-F'	2.262	2.229	2.160 ± 0.015
O-F"	2.327	2.229	2.244 ± 0.007
F'-F"	2.250	2.183	2.153 ± 0.008
F-F"	2.635	2.557	2.608 ± 0.010
F-F'	3.422	3.432	3.383 ± 0.010
∢ F'OC	109.4	109.5	109.4 ± 1.0
∢ OCF	104.5	105.	104.8 ± 0.6
Tilt Angle	3.5		4.1 ± 0.8

*Bond distances are given in Angstroms and bond angles are in degrees. See Figure 1 for atom labelling.

Unlike the minimal basis where the bond lengths are only in fair agreement with experiment, the extended basis reproduces the experimental parameters rather well. The C-O and C-F bond distances are predicted to shorten considerably (0.05 and 0.04Å, respectively) while the O-F bond distance increases by 0.07Å upon going from the STO-3G to the 4-31G basis. The C-F bond distance is only slightly longer than the experimental value (1.319Å) for this parameter. Optimizations at the 4-31G level applied to CF_3OH (17) yielded a C-F distance of 1.347Å and a C-O distance of 1.356Å which are similar to the values reported for CF_3OF. The C-O bond in these fluorinated molecules are considerably shorter than the corresponding bond in methanol (1.428Å). The structural parameters for CF_3OF and CF_3OH are consistent with the ideas of fluorine hyperconjugation (18).

The barriers for the CF_3 torsion have been estimated as: (a) 1.13 kcal/mol from IR (7) using an assumed geometry; (b) 2.5 ± 0.5 kcal/mol from electron diffraction data (10) and (c) 3.9 kcal/mol from the microwave data (9). Previous theoretical studies on CF_3OF using extended Hückel theory (10,19) reveal an energy difference between the staggered and eclipsed forms of about 1.5 kcal/mol with the staggered conformation being favored. CNDO calculations, on the other hand, predict the wrong conformer to be <u>more</u> stable by 5 kcal/mol (19). 4-31G calculations reveal an energy difference of 5.5 kcal/mol between the staggered and eclipsed conformations with the former being more stable. The barrier to the CF_3 torsion is thus predicted to be, according to present calculations, at least 5.5 kcal/mol which is somewhat higher than the microwave value. The low value estimated for this torsion from IR data presumably is due to the use of the geometry assumed by Wilt and Jones in their study (7).

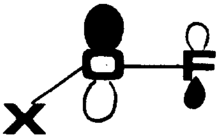
In Table II we tabulate the orbital energies, electronic energy (Vee), nuclear repulsion energy (Vnn), total molecular energy (E_T) and the atomization energy (E_A) for the STO-3G and 4-31G optimized structures (<u>vide infra</u>). The atomization energy was computed by subtracting from the molecular energy for CF_3OF, the sum of the total energies of the corresponding set of isolated neutral atoms in their ground states using the same basis sets for atomic and molecular calculations (13,14). The molecular orbitals are labelled according to the irreducible representations

TABLE II
ONE ELECTRON ENERGY LEVELS (HARTREES) OF CF_3OF

SYMMETRY	STO-3 G	4-31G
1a'	-26.046	-26.376
2a'	-26.014	-26.365
3a'	-26.008	-26.352
1a"	-26.007	-26.352
4a'	-20.407	-20.738
5a'	-11.339	-11.620
6a'	- 1.639	- 1.816
7a'	- 1.593	- 1.720
8a'	- 1.533	- 1.700
2a"	- 1.532	- 1.698
9a'	- 1.246	- 1.425
10a'	- 0.840	- 1.005
11a'	- 0.712	- 0.894
3a"	- 0.702	- 0.891
12a'	- 0.697	- 0.884
4a"	- 0.609	- 0.796
13a'	- 0.580	- 0.768
14a'	- 0.550	- 0.748
5a"	- 0.539	- 0.743
15a'	- 0.529	- 0.715
6a"	- 0.516	- 0.710
7a"	- 0.497	- 0.703
16a'	- 0.495	- 0.708
17a'	- 0.436	- 0.647
8a"	- 0.417	- 0.612
18a'	+ 0.403	0.093
V(ee)	-775.7995	-787.7477
V(nn)	272.4403	278.0647
E_T	-503.3592	-509.6830
E_A		- 0.2821

of the C_s point group. The 1a' - 5a' orbitals are the core orbitals for this molecule with the 1a' MO being largely the hypofluorite fluorine 1_s orbital and the 5a' orbital being primarily the carbon 1_s orbital. The bonding and the unshared pairs of electrons in this molecule are described by the 6a' - 8a" orbitals while orbital 18a' is the lowest unoccupied orbital. The orbital energies may prove useful in interpreting the photoelectron spectra of this molecule. The Koopmans' theorem first ionization potential is predicted to be 11.3ev according to STO-3G while

4-31G theory places it at 16.6ev. We are unaware of the experimental values for CF_3OF but it would be expected to be similar to that found is F_2O since the CF_3 group often acts similar to a fluorine atom (20). The 4-31G basis places the homo of F_2O at a similar energy (-0.600au) to that found in CF_3OF, while the homo in HOF is significantly higher in energy (-0.545au). The homo in these three molecules is similar being largely an antisymmetric combination (n_-) of the n_O orbitals on oxygen and fluorine, viz.,



The final entry in Table II is the atomization energy of CF_3OF which is 177 kcal/mol according to 4-31G theory. This value, although having the correct sign for a stable compound, is probably considerably smallest than the experimental value since it is well known that single determinant theory is inadequate for computing binding energies since atomization involves the change from singlets to states of higher multiplicity and correlation effects are expected to be large. Thus the value estimated for the molar heat of formation at 298°K from the gaseous atoms was calculated as -481.4 kcal(2b).

Table III summarizes the electron populations of CF_3OF and related molecules. The electron populations have been computed using the procedure of Mulliken (21). The wavefunctions used to compute population and overlaps for CF_3OF and CF_3OH correspond to the optimized geometries computed for these species. For F_2O the same OF bond length as in CF_3OH was employed while for HOF since the experimental OF distance (1.44Å) is similar to that found herein for the OF bond in CF_3OF we employed the experimental geometry of HOF (22).

TABLE III

POPULATION ANALYSIS FOR CF_3OF AND RELATED MOLECULES

MOLECULE:		CF_3*OF		CF_3*OH	FOF$^+$	HOF$^\pm$
		BASIS				
Atom	**Orbital**	STO-3G	4-31G	4-31G	4-31G	4-31G
C:	2s	1.113	0.703	0.709	----	----
	2pσ	1.590	1.246	1.285	----	----
	$2p_{\pi}$	0.780	0.611	0.591	----	----
	TOTAL	5.476	4.553	4.578	----	----
O:	2s	1.864	1.992	1.908	1.937	1.909
	2pσ	2.300	2.319	2.895	1.823	2.364
	$2p_{\pi}$	1.956	1.938	1.921	2.006	2.003
	TOTAL	8.119	8.247	8.720	7.760	8.271
F:	2s	1.964	2.003	----	2.000	1.998
	2pσ	3.055	3.115	----	3.127	3.188
	$2p_{\pi}$	2.000	1.997	----	1.997	1.997
	TOTAL	9.018	9.112	----	9.120	9.179
H:	1s	----	----	0.537	----	0.550
F*	2s	1.948	2.026	2.022	----	----
	2p	5.189	5.338	5.361	----	----
	TOTAL	9.129	9.359	9.378	----	----
Bond	**Overlap**					
C-O	TOTAL	0.444	0.226	0.436	----	----
O-F	TOTAL	0.276	0.092	----	0.076	0.140
O-H	TOTAL	----	----	0.522	----	0.460
C-F*	TOTAL	0.414	0.438	0.427	----	----
μ (Debyes)		0.34	0.31	2.67	0.44	2.63

*The three fluorine charges and three C-F bonds were averaged to a single value.

+Same OF bond length as in CF_3OF. Angle 100 deg.

±Experimental geometry.

Perhaps the most glaring feature of the electron populations presented in Table III is the large charge polarization upon going from the minimum to the extended basis. Thus carbon, for example, is predicted to become more positive by a loss of 0.93e (total carbon electron population is 5.476e in STO-3G and 4.553e in 4-31G). Most of the polarization resulting from a change of basis is due to the fluorines of the CF_3 group, with each fluorine withdrawing 0.23e. Although there is predicted to be considerable charge polarization between the two bases the dipole moment is nearly identical for these two bases and the computed dipole moment is in excellent agreement with the microwave value (9). This is perhaps somewhat fortuitous, especially at the 4-31G level, since this method frequently overestimates electronic dipole moments (14).

The populations (4-31G) computed for CF_3OF and CF_3OH are seen to be rather similar with the major difference being the larger C-O overly population found in CF_3OH. This is consistent with the shorter optimize C-O bond found in CF_3OH (1.36Å). The larger double bond character of the C-O bond in CF_3OH is compensated for by the weaker and longer CF bonds. The $2p_y$ oxygen populations are instructive. In F_2O or HOF the population is 2.00e while the corresponding population in methanol is 1.97e reflecting a small amount of back-bonding into the C-H σ * orbital of appropriate symmetry. In CF_3OF and CF_3OH the $2p_y$ AO populations are 1.94 and 1.92e^-, respectively, indicating a substantially larger back-donation into the more polarized and accessible C-F σ * orbitals.

The O-F bond in CF_3OF is predicted to be the weakest bond in the molecule using overlaps as a guide. This is consistent with the experimental observations (2b,23). The OF bond in CF_3OF is seen to have an overlap population which lies between the OF populations computed for F_2O and HOF. The OF bond in CF_3OF is predicted to be the least ionic while the C-F bond is most ionic. The weakness of the OF bond and the nature of the homo in CF_3OF is consistent with the chemical reactions of this molecule. Finally, it is interesting to note the similarity in the electronic structures of CF_3OH and FOH. This is reflected in the nearly identical dipole moments computed for these species. CF_3OH is of course unknown but we have previously presented theoretical arguments for its thermodynamic existence (17).

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