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SEMIEMPIRICAL STUDIES ON THE STRUCTURE AND BONDING OF FLUORO-SULFURANES AND AMINOFLUOROSULFURANES

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SUMMARY

The structures of sulfur tetrafluoride, SF<sub>4</sub>, dimethylaminosulfur trifluoride, Me<sub>2</sub>NSF<sub>3</sub>, and bis(dimethylamino)sulfur difluoride, (Me<sub>2</sub>N)<sub>2</sub>SF<sub>2</sub> have been investigated using the PM3 semiempirical method. Full geometry optimizations do not agree with experimentally determined geometries. Constraining the F<sub>ax</sub>-S-F<sub>ax</sub> angle significantly improves the agreement.

INTRODUCTION

The sulfuranes are a class of hypervalent molecules with a coordination number of four and an unshared pair of electrons which have attracted a great deal of attention from both theoretical and structural chemists. Dimethylaminosulfur trifluoride (Me-DAST) and diethylaminosulfur trifluoride (DAST), which have found use as reagents for the transformation of alcohols to alkyl fluorides and carbonyls to geminal difluorides, are representative of the aminofluorosulfuranes [1]. Despite the scrutiny these compounds have endured, questions still remain concerning bonding and structure in both simple and more elaborate sulfuranes, axial versus equatorial disposition of the ligands, the interaction of the nitrogen and sulfur lone pairs, and the mechanism of their reactions. We have initiated our studies of these compounds by using the PM3 semiempirical method [2] to examine the bonding and structure in some simple sulfuranes.

Theoretical studies of structure and bonding in sulfuranes have been limited. The two seminal publications belong to Koutecky and Musher [3], who used CNDO/2 to describe the covalent and hypervalent bonds in  $SX_2$ ,  $SX_4$  and  $SX_6$ , and Chen and Hoffmann [4], who performed extended Huckel calculations on  $SX_4$  and  $RSX_3$  (where R = a donor or acceptor). Koutecky has concluded from the irregular effect of the inclusion of d orbitals in his calculations that these orbitals have negligible effect and modify only the first order Coulomb and exchange energies, although this may also be a deficiency in the method. More recent calculations by Hay [5] using a generalized valence bond (GVB) approach support the minimal necessity of including d orbitals. While d functions on sulfur improved the wave function and apparently do play a significant role in the geometry, Hay concluded that they were not crucial for a qualitative understanding of stability. Rather, charge transfer to the axial fluorines from the sulfur is the driving force. Chen's calculations were performed mainly without 3d orbitals on sulfur since these orbitals led to an exaggerated degree of mixing and a less clear cut interpretation.

A recent paper by Reed and Schleyer [6] provides an excellent review of bonding in hypervalent molecules as well as an in depth *ab initio* study of orbital participation. Their results clearly indicate the importance of negative hyperconjugation, that is, the electron donation from the n to  $\sigma^*$  orbital leading to partial  $\pi$  bond character. In addition, the  $\sigma$  bonding in the systems they studied was found to be significantly ionic. Back bonding from p type lone pairs into d orbitals of the hypervalent atom ( $dsp^3$  or  $d^2sp^3$  hybridization) contributes minimally to the  $\pi$  bonding of hypervalent species. The authors stress that d orbital polarization functions are essential for a qualitatively correct description of bonding, structure, and energy in hypervalent species, and that these orbitals function to provide orbital space at the central atom for back bonding. The resulting stabilization is sufficient to overcome ligand-ligand repulsion at the hypervalent atom.

This dichotomy of opinions regarding the participation and necessity for d orbitals or polarization functions in calculations on hypervalent species led us to question the applicability of semiempirical calculations using the MNDO [7], AM1 [8], or PM3 [2] methods, since none of these utilize d orbitals on third row elements, although they are parameterized to handle sulfur. These methods provide a relatively inexpensive means of studying larger, more interesting molecules and reactions than do *ab initio* methods. Given the interest in the structure, stability, and synthetic utility of aminofluorosulfuranes, we

decided to undertake a semiempirical study which would address these and other questions, including the importance of sulfur 3d orbitals to structure and bonding and the issue of apicophilicity.

## METHODS

The semiempirical program MOPAC [9], developed originally by Dewar and currently being maintained by Stewart, was used to calculate the optimized structures of fluorosulfuranes 1-3. The MNDO method is known to have several deficiencies [8] which can lead to incorrect geometries, while sulfur parameters have never been published for the AM1 method. We therefore chose to use the relatively untested PM3 Hamiltonian and parameters [2]. Calculations were run on both an Apollo DN4500 workstation and a DECstation 3100 using MOPAC 5.0 [10]. Full geometry optimizations were performed for SF<sub>4</sub>, Me<sub>2</sub>NSF<sub>3</sub>, and (Me<sub>2</sub>N)<sub>2</sub>SF<sub>2</sub>. Constrained geometry optimizations were performed by holding the F<sub>ax</sub>-S-F<sub>ax</sub> bond angle at 174°, the experimentally determined angle in Me<sub>2</sub>NSF<sub>3</sub> [11]. All stationary points were confirmed by a force constant calculation.

## RESULTS AND DISCUSSION

### Applicability of the PM3 computational method for the structural study of hypervalent sulfur

The structures of sulfur tetrafluoride, 1, dimethylaminosulfur trifluoride, 2, and bis(dimethylamino)sulfur difluoride, 3, were optimized without geometrical or symmetry constraints. The results are summarized in Table 1. These semiempirical calculations failed to adequately reproduce the experimental geometries of both SF<sub>4</sub> and Me<sub>2</sub>NSF<sub>3</sub> because the PM3 parameters calculations do not provide for a difference between the axial and equatorial positions on sulfur. This supports the conclusions by Hay [5] and Reed [6] that sulfur 3d orbitals are essential to the geometry of these systems. The calculated bond lengths in SF<sub>4</sub> are in reasonable agreement with those measured by electron diffraction [12] and microwave spectroscopy [13], although the first ionization potential of 11.84 eV is too low. Me<sub>2</sub>NSF<sub>3</sub> minimizes to give the trigonal bipyramidal structure with one axial fluorine, two fluorines and the amine equatorial, and the lone pair occupying the other axial site. The first ionization potential of 9.56 eV agrees well with the experimentally determined value of 9.92 eV, which has been assigned to the nitrogen lone pair [14].

TABLE 1

PM3 and Experimental Geometric Parameters of Sulfuran<sup>a,b</sup>

	SF <sub>4</sub> <sup>c</sup>	Me <sub>2</sub> NSF <sub>3</sub> <sup>d</sup>	(Me <sub>2</sub> N) <sub>2</sub> SF <sub>2</sub> <sup>e</sup>
<b>Bond Lengths</b>			
S-F <sub>ax</sub>	1.622 <i>1.619</i> (1.648)	1.652 <i>1.660, 1.642</i> (1.670)	1.687, 1.691 <i>1.700, 1.667</i> (1.770)
S-F <sub>eq</sub>	1.596 <i>1.552</i> (1.545)	1.609 <i>1.567</i> (1.563)	
S-N		1.777 <i>1.792</i> (1.639)	1.800 <i>1.802, 1.794</i> (1.648)
<b>Bond Angles</b>			
F <sub>ax</sub> -S-F <sub>ax</sub>	142.4 <i>177.0</i> (177)		179.8 <i>174.7</i> (174.7)
F <sub>ax</sub> -S-F <sub>eq</sub>	80.9 <i>89.0</i> (87.8)	79.7 <i>87.2, 86.9</i> (88.5)	
F <sub>eq</sub> -S-F <sub>eq</sub>	121.2 <i>100.7</i> (101.5)	124.3	
F <sub>ax</sub> -S-N		90.5 <i>92.4</i> (92.9)	87.6, 92.1 <i>90.2, 86.5</i> (89.2, 94.1)
F <sub>eq</sub> -S-N		115.6 <i>107.2</i> (104.6)	
N-S-N			116.1 <i>112.0</i> (102.3)
<b>Ionization Potential<sup>f</sup></b>			
	11.84 <i>10.24</i> (12.85)	9.56 <i>9.91</i> (9.92)	8.33 <i>9.49</i> (8.83)

<sup>a</sup> fully optimized results in normal text, constrained optimization results in italics, experimental values in parentheses.

<sup>b</sup> bond lengths in angstroms, angles in degrees, and ionization potentials in electron Volts.

<sup>c</sup> experimental values from Ref. 12.

<sup>d</sup> experimental values from Ref. 11.

<sup>e</sup> Cowley, A. H., Riley, P. E., Szobota, J. S., Walker, M. L., *J. Am. Chem. Soc.* 1979, 101, 5620.

<sup>f</sup> experimental values from Ref. 14.

The calculated structure of  $(\text{Me}_2\text{N})_2\text{SF}_2$  is in much better agreement with experiment. As predicted by EHT (extended Huckel theory), the more electronegative substituents prefer the axial positions and the ionization potential is reasonably correct. Interestingly, in going from  $\text{SF}_4$  to  $\text{Me}_2\text{NSF}_3$  to  $(\text{Me}_2\text{N})_2\text{SF}_2$ , bond angles become more accurate than bond lengths, possibly due to the steric factors becoming more important relative to orbital considerations.

We next ran the geometry optimizations for each molecule with the  $\text{F}_{\text{ax}}\text{-S-F}_{\text{ax}}$  angle constrained to the experimentally observed value. ORTEP plots of  $\text{Me}_2\text{NSF}_3$  and  $(\text{Me}_2\text{N})_2\text{SF}_2$  are shown in the Figure. As can be seen from Table 1, this constraint dramatically improved the agreement between calculated and observed geometry for  $\text{Me}_2\text{NSF}_3$  with the exception of the nitrogen to sulfur bond length, which remains almost ten percent too long. The bond angles and ionization potential are significantly closer to their measured values. Similar improvements are seen in the  $\text{SF}_4$  geometry but not the ionization potential. The major effect for both compounds is manifested in all geometric parameters involving the equatorial fluorines; in particular, the sulfur to fluorine bond shortens and the  $\text{F}_{\text{eq}}\text{-S-F}_{\text{eq}}$  angle decreases, while the  $\text{F}_{\text{ax}}\text{-S-F}_{\text{eq}}$  angle increases. These changes are reflected in a charge transfer from the equatorial to axial fluorines, as observed by Hay [5] and Reed [6]. Regardless of similar changes in charge distribution observed in  $(\text{Me}_2\text{N})_2\text{SF}_2$ , there is little geometric change about this more sterically hindered hypervalent sulfur (relative to  $\text{SF}_4$  and  $\text{Me}_2\text{NSF}_3$ ) indicating once again the relative importance of steric and electronic versus orbital effects.

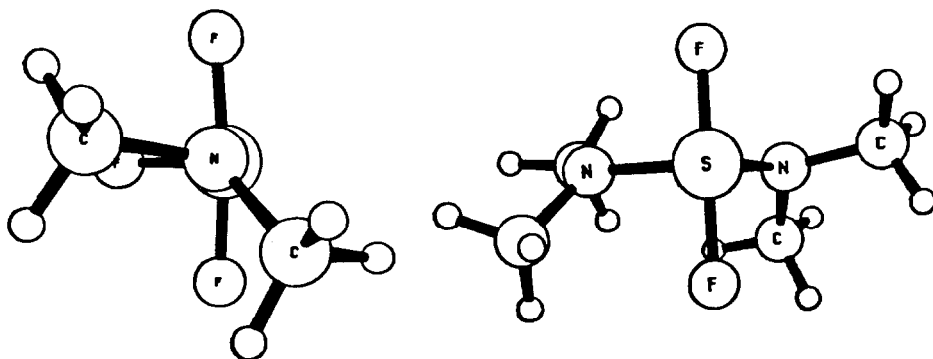


Fig. ORTEP plots of  $\text{Me}_2\text{NSF}_3$  (2) and  $(\text{Me}_2\text{N})_2\text{SF}_2$  (3) calculated with the  $\text{F}_{\text{ax}}\text{-S-F}_{\text{ax}}$  angle constrained to the experimentally observed value.

## CONCLUSIONS

In conclusion, the sulfur 3d orbitals do appear to be important in determining molecular geometry of uncongested sulfuranes, but not of sterically crowded aminosulfuranes such as  $(\text{Me}_2\text{N})_2\text{SF}_2$ . Bond lengths and angles, and electronic factors such as ionization potential and charge densities, can be reasonably calculated using the semiempirical PM3 method.

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