

# Molecular Structure of Bis(dimethylamino)difluorosulfurane. The First X-ray Crystal Structure of a Fluorosulfurane

A. H. Cowley,\* P. E. Riley, J. S. Szobota, and M. L. Walker

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. Received January 22, 1979

**Abstract:** The molecular structure of  $(\text{Me}_2\text{N})_2\text{SF}_2$  has been determined by single-crystal X-ray diffraction methods. The compound crystallizes in the monoclinic system, space group  $C2/c$ , with  $a = 11.00$  (2) Å,  $b = 5.693$  (6) Å,  $c = 12.24$  (3) Å,  $\beta = 92.79$  (10)°, and  $Z = 4$ . The symmetry of  $(\text{Me}_2\text{N})_2\text{SF}_2$  is  $C_2$ , and the structure is essentially trigonal bipyramidal with the fluorine and  $\text{Me}_2\text{N}$  ligands occupying axial and equatorial sites, respectively. The third equatorial site is occupied by the sulfur "lone pair" which lies along the  $C_2$  symmetry axis. The torsion angle formed about the S-N bond with the idealized dispositions of the S and N lone pairs is 120°. The N atoms lie 0.382 (2) Å from the plane formed by the three atoms to which each is bonded and the sum of the bond angles around the nitrogen atoms is 342.3°; hence the hybridization at these centers is approximately halfway between  $sp^2$  and  $sp^3$ . The S-F bonds are bent toward the sulfur lone pair by 5.3°, and the equatorial N-S-N' bond angle is 102.3 (1)°. The S-F and S-N bond distances are 1.770 (2) and 1.648 (2) Å, respectively.

## Introduction

The sulfuranes, which feature an unshared pair of electrons and a coordination number of four at the sulfur atom, are examples of a broader category of species for which Musher<sup>1</sup> coined the phrase "hypervalent molecules". Bonding models for such molecules have been advanced and discussed for several years.<sup>1,2</sup> In recent times molecular orbital (MO) calculations have provided useful insights into the nature of the bonding in the model system,  $\text{SH}_4$ ,<sup>3</sup> and the simplest known sulfurane,  $\text{SF}_4$ .<sup>4</sup>

Although X-ray crystallographic studies have been performed on several spirocyclic sulfuranes,<sup>5-9</sup> structural information on the acyclic sulfuranes is somewhat sparse. The molecular geometry of  $\text{SF}_4$  has been well established on the basis of microwave spectroscopic<sup>10</sup> and electron diffraction<sup>11</sup> data, and X-ray crystallographic data are available for  $(\text{C}_1\text{C}_6\text{H}_4)_2\text{SCl}_2$ <sup>12</sup> and  $(\text{C}_6\text{H}_5)_2\text{S}[\text{OC}(\text{CF}_3)_2\text{C}_6\text{H}_5]_2$ .<sup>13</sup> The present paper is concerned with an X-ray crystallographic investigation of  $(\text{Me}_2\text{N})_2\text{SF}_2$ ; as well as being the first fluorosulfurane to be studied by X-ray diffraction methods, the molecule is of special interest on account of the presence of three proximate lone pairs of electrons. As noted by Chen and Hoffmann,<sup>4a</sup> the structures of  $\text{R}_2\text{N}$ -substituted sulfuranes "would be of great interest" because of the operation of two competing effects, viz., the tendency of the sulfur and nitrogen lone pairs to avoid each other and the opposing tendency to maximize dative p-d  $\pi$  bonding. Additional structural information on sulfuranes is also pertinent to further refinements of the theoretical models to assist in understanding site preferences and bond-angle trends. Finally, we note that the structures of dialkylamino-substituted sulfuranes are of practical interest since these compounds are used as fluorinating agents<sup>14</sup> and as precursors to sulfonium cations.<sup>15</sup>

## Experimental Section

The sample of  $(\text{Me}_2\text{N})_2\text{SF}_2$  was prepared according to the method of Middleton.<sup>14c</sup> In order to grow single crystals, small quantities of  $(\text{Me}_2\text{N})_2\text{SF}_2$  were sublimed into 30 capillaries, each of which was sealed off in vacuo. Sublimation was accomplished by heating one end of the capillary with a 60-W light bulb, while maintaining the other end at ambient temperature. From these samples one satisfactory crystal was obtained. It was transferred in its capillary to a goniometer head and then to a Syntex P2<sub>1</sub> diffractometer. During the course of all subsequent crystallographic experiments the crystal and its capillary were maintained at  $-35$  °C by a stream of cold  $\text{N}_2$ . Preliminary X-ray diffraction experiments indicated the monoclinic symmetry of

space group  $Cc$  (no. 9) or  $C2/c$  (no. 15). Crystal data and X-ray diffraction data collection details are summarized in Table I. Processing of the diffraction data (with  $p = 0.02$ ) was carried out as described previously.<sup>16</sup>

**Solution and Refinement of the Structure.** A calculated density of 1.38 g  $\text{cm}^{-3}$  (see Table I) is consistent with four molecules of  $(\text{Me}_2\text{N})_2\text{SF}_2$  per unit cell. Thus, while the molecules would have no crystallographically imposed symmetry in space group  $Cc$ , they would be required to reside at sites of either  $C_1$  or  $C_2$  symmetry in space group  $C2/c$ . Solution of the structure by standard heavy atom methods and satisfactory refinement by full-matrix least-squares procedures showed the space group to be  $C2/c$  and revealed that the molecules occupy sites of  $C_2$  symmetry. The function minimized in refinement is  $\sum w(|F_o| - |F_c|)^2$ , where the weight  $w$  is  $\sigma(|F_o|)^{-2}$ , the reciprocal square of the standard deviation of each observation,  $|F_o|$ . Neutral atom scattering factors for S, F, N, C,<sup>17</sup> and H<sup>18</sup> were used in these calculations, and the real ( $\Delta f'$ ) and imaginary ( $\Delta f''$ ) corrections<sup>17</sup> for anomalous scattering were applied to the sulfur scattering curve.

Least-squares convergence was attained using only those 656 data with  $I_o/\sigma(I_o) > 2.0$  for a structure in which nonhydrogen atoms were refined anisotropically and hydrogen atoms isotropically, with  $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.057$ ,  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.043$ , and a standard deviation of an observation of unit weight =  $[\sum w(|F_o| - |F_c|)^2 / (m - s)]^{1/2} = 1.56$ , for  $m = 652$  observations and  $s = 66$  variables. Examination of the data near the conclusion of refinement revealed that four reflections (002, 110, 200, and 11 $\bar{2}$ ) were apparently affected by secondary extinction. These reflections were deleted from the data set prior to final least-squares refinement.

In the final cycle of refinement all parameter shifts were less than 0.7% of a corresponding estimated standard deviation (esd) for nonhydrogen atoms and less than 1.7% of an esd for the hydrogen atoms. A final difference Fourier map showed no peak higher than 0.14 e  $\text{Å}^{-3}$ . For comparison, the heights of the carbon atoms from a previous Fourier map were 2.5 and 3.1 e  $\text{Å}^{-3}$ .

A listing of computer programs used in this work is provided elsewhere.<sup>16</sup> Atomic positional and thermal parameters with corresponding esd's as estimated from the least-squares inverse matrix are given in Table II. A tabulation of observed and calculated structure factor amplitudes is available.<sup>19</sup>

## Discussion

The structure of  $(\text{Me}_2\text{N})_2\text{SF}_2$  can be described as essentially trigonal bipyramidal. A stereoview of the molecule and a view approximately along the  $C_2$  symmetry axis are presented in Figures 1 and 2, respectively. The fact that both  $\text{Me}_2\text{N}$  groups occupy equatorial sites and both fluorine ligands occupy axial sites is anticipated on the basis of polarity rules<sup>20</sup> and confirms

**Table I.** Crystallographic Summary

Crystal Data at $-35\text{ }^{\circ}\text{C}^a$			
$a$ , Å	11.00 (2)	systematic	$hkl, h + k = 2n + 1$
$b$ , Å	5.693 (6)	absences	$h0l, l = 2n + 1$
$c$ , Å	12.24 (3)		$0k0, k = 2n + 1$
$\beta$ , deg	92.79 (10)	crystal	monoclinic
$V$ , Å <sup>3</sup>	766 (6)	system	
mol wt	158.22	space	$Cc$ (no. 9) or
$d_{\text{calcd.}}$ , g cm <sup>-3</sup>	1.38	group <sup>c</sup>	$C2/c$ (no. 15)
$Z$	4	empirical	$\text{C}_4\text{H}_{12}\text{F}_2\text{N}_2\text{S}$
$F(000)$ , electrons	336	formula	
Data Collection at $-35\text{ }^{\circ}\text{C}^d$			
radiation (Mo $K\alpha$ ), Å	0.710 69		
mode	$\omega$ scan		
scan range	symmetrically over $1.25^{\circ}$ about $K\alpha_{1,2}$ maximum		
background	offset $1.0$ and $-1.0^{\circ}$ in $\omega$ from $K\alpha_{1,2}$ maximum		
scan rate, deg min <sup>-1</sup>	variable, 2.0–5.0		
check reflections	four remeasured after every 96 reflections; analysis <sup>e</sup> of these data indicated a steady decline in intensity by ca. 9% at the conclusion of data collection. A correction for this effect was applied		
$2\theta$ range, deg	4.0–60.0		
total reflections measured	1112		

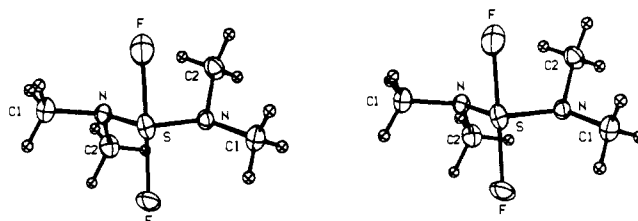
<sup>a</sup> Unit cell parameters were obtained by least-squares refinement of the setting angles of 41 reflections with  $13.0^{\circ} < 2\theta < 19.6^{\circ}$ .

<sup>b</sup> Owing to air sensitivity an experimental density was not determined.

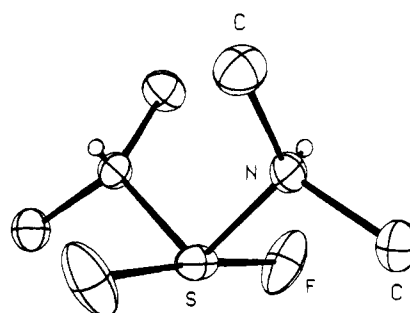
<sup>c</sup> Shown by successful refinement to be  $C2/c$  (see text). <sup>d</sup> Syntex P21 autodiffractometer equipped with a graphite monochromator and a Syntex LT-1 inert-gas low-temperature delivery system. <sup>e</sup> W. H. Henslee and R. E. Davis, *Acta Crystallogr., Sect. B*, **31**, 1511 (1975).

the structure suggested for this molecule from NMR spectroscopic evidence.<sup>21</sup> The third equatorial site can be considered to be occupied by the sulfur "lone pair" which is collinear with the  $C_2$  axis.<sup>22</sup> Significant aspects of the structure of  $(\text{Me}_2\text{N})_2\text{SF}_2$  are now discussed.

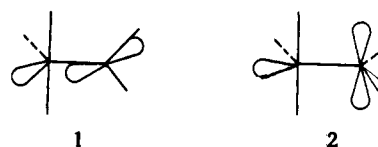
**1. Conformation of the  $\text{Me}_2\text{N}$  Groups.** Particular interest focuses on the nitrogen geometries and the stereochemical relationships between the  $\text{Me}_2\text{N}$  groups and the sulfur "lone pair". Chen and Hoffmann<sup>4a</sup> in their theoretical analysis of the model sulfurane,  $\text{H}_2\text{NSH}_3$ , have pointed out that dative  $\pi$  bonding from filled  $\text{N}(2p)$  orbitals favors conformation **1**,



**Figure 1.** Stereoview of the  $(\text{Me}_2\text{N})_2\text{SF}_2$  molecule, illustrating the atom numbering scheme. Nonhydrogen atoms are shown as ellipsoids of 30% probability and hydrogen atoms as spheres of radius 0.1 Å.



**Figure 2.** A view of the  $(\text{Me}_2\text{N})_2\text{SF}_2$  molecule showing the idealized dispositions of the lone pairs of electrons of the nitrogen atoms. The lone pairs, indicated as small blank spheres, have been placed along the axes which pass through the N atoms and are normal to the S, C, C planes.

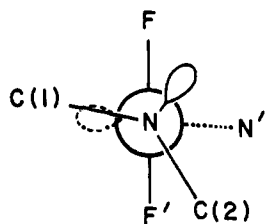


while repulsion between the nitrogen and sulfur lone pairs favors conformation **2**. However, in the case of  $(\text{Me}_2\text{N})_2\text{SF}_2$  the hybridization of the nitrogen atoms is not  $sp^2$  as in **1** and **2** but is, as indicated by the displacement of the N atoms by 0.382 (2) Å from the planes of the three atoms to which each is bonded and by the sum of the bond angles around N of  $342.3^{\circ}$ , between  $sp^2$  and  $sp^3$ . That is, the N atoms are pyramidal. This observation may be rationalized by appeal to our theoretical studies of other systems containing two or more lone pairs, such as the aminophosphines.<sup>23</sup> For example, in the case of  $\text{H}_2\text{NPH}_2$  it was demonstrated that the nitrogen geometry

**Table II.** Fractional Coordinates and Anisotropic ( $\times 10^4$ ) and Isotropic Thermal Parameters for the Atoms of  $(\text{Me}_2\text{N})_2\text{SF}_2^a$ 

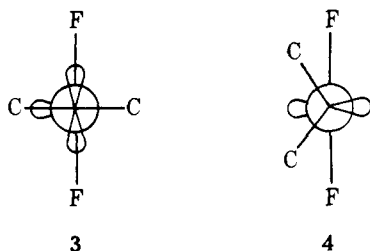
atom	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
S	0	-0.0273 (2)	$\frac{1}{4}$	76 (1)	167 (4)	50 (1)	0	-19 (1)	0
F	0.0977 (2)	-0.0417 (4)	0.1395 (2)	103 (2)	653 (12)	64 (2)	126 (4)	-5 (2)	-95 (4)
N	0.0965 (2)	0.1542 (4)	0.3133 (2)	51 (2)	203 (9)	44 (2)	-4 (4)	-4 (2)	-10 (3)
C(1)	0.2013 (3)	0.0240 (8)	0.3632 (3)	63 (3)	297 (14)	70 (3)	6 (6)	-12 (3)	0 (6)
C(2)	0.0476 (4)	0.3311 (7)	0.3868 (3)	91 (4)	271 (13)	56 (3)	14 (7)	-6 (3)	-32 (5)
atom <sup>b</sup>	$x$	$y$	$z$	$B, \text{Å}^2$					
H (1, 1)	0.264 (3)		0.135 (7)	0.372 (3)					
H (1, 2)	0.186 (3)		-0.068 (6)	0.428 (3)					
H (1, 3)	0.232 (3)		-0.103 (7)	0.312 (3)					
H (2, 1)	0.103 (4)		0.434 (7)	0.394 (3)					
H (2, 2)	-0.028 (4)		0.410 (7)	0.354 (3)					
H (2, 3)	0.030 (3)		0.258 (7)	0.464 (3)					

<sup>a</sup> See Figure 1 for identity of the atoms. Numbers in parentheses throughout the table are the estimated standard deviations in the units of the least significant digits for the corresponding parameter. The anisotropic temperature factor is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . <sup>b</sup> The sequence number of a hydrogen atom corresponds to that of the carbon atom to which it is bound.

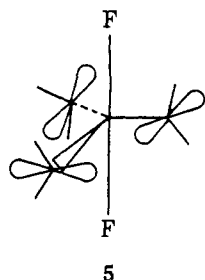


**Figure 3.** View along a S-N bond in which the idealized dispositions of the sulfur lone pair (SLP) and nitrogen lone pair (NLP) are represented by broken and closed lobes, respectively. Selected torsion angles: F-S-N-NLP = 33.9°, SLP-S-N-C(1) = 8.0°, SLP-S-N-C(2) = -124.6°, SLP-S-N-NLP = 119.9°, N'-S-N-NLP = -60.2°, F'-S-N-NLP = -150.2°. The sign of the torsion angle A-B-C-D is positive if A must be rotated clockwise to eclipse D. Coordinates of primed atoms are related to those of the corresponding unprimed atoms of Table II by the operation  $-x, y, \frac{1}{2} - z$ .

is trigonal planar when the nitrogen and phosphorus lone pairs occupy orbitals which are orthogonal, but approximately tetrahedral when the lone pairs are eclipsed. Applying these principles to  $(\text{Me}_2\text{N})_2\text{SF}_2$  one would anticipate a trigonal planar nitrogen geometry in conformation **3** and an approximately tetrahedral conformation in **4**. However, the confor-



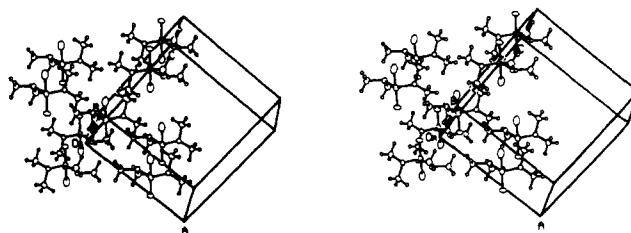
mation which the molecule adopts differs from **3** or **4** and is shown in Figure 3. The torsion angles about the S-N bond formed with the idealized positions of the lone pairs of S and N in **3** and **4** are 90 and 180°, respectively. The value observed in  $(\text{Me}_2\text{N})_2\text{SF}_2$  is 120°. Clearly, the fact that  $(\text{Me}_2\text{N})_2\text{SF}_2$  adopts a conformation between **3** and **4** implies that the response of nitrogen geometry to inter-lone-pair angle is monotonic. The deduction that the nitrogen geometry in  $(\text{Me}_2\text{N})_2\text{SF}_2$  is influenced by the sulfur lone pair rather than other structural features is supported by the observation that in the closely analogous fluorophosphorane  $(\text{Me}_2\text{N})_3\text{PF}_2$  (**5**), the



nitrogen geometries are, within experimental error, trigonal planar.<sup>25</sup>

The two shortest intermolecular methyl...methyl distances in this crystal structure are 3.571 (6) and 3.963 (6) Å. The van der Waals methyl...methyl contact distance is 4.00 Å.<sup>26</sup> However, since all intermolecular H...H distances are greater than 2.60 Å and since the van der Waals H...H contact distance is ~2.0 Å,<sup>27</sup> there are no methyl...methyl interactions in this crystal structure which have a significant effect upon the geometry of the  $\text{Me}_2\text{N}$  groups.

**2. Axial (Hypervalent) Bonds.** The fact that the S-F bonds are bent toward the sulfur lone pair (by 5.3°) is noteworthy. To our knowledge, the only other cases where this occurs are

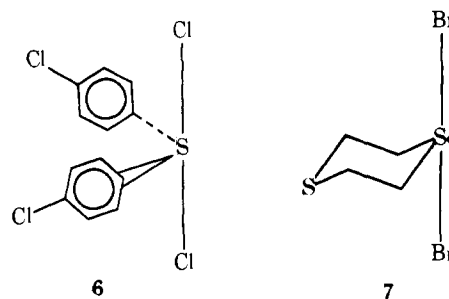


**Figure 4.** Stereoview of the immediate environment of a  $(\text{Me}_2\text{N})_2\text{SF}_2$  molecule. Each molecule is surrounded by eight other molecules at nonhydrogen contact distances of 3.6-3.85 Å in an approximately square antiprismatic arrangement of molecules. Nonhydrogen atoms are shown as ellipsoids of 30% probability and hydrogen atoms as spheres of radius 0.1 Å.

**Table III.** Selected Geometric Parameters for  $(\text{Me}_2\text{N})_2\text{SF}_2$ <sup>a</sup>

Bond Lengths (Å)			
S-F	1.770 (2)	N-C(1)	1.479 (5)
S-N	1.648 (2)	N-C(2)	1.470 (5)
Bond Angles (deg)			
F-S-F'	174.7 (1)	S-N-C(1)	110.6 (2)
N-S-N'	102.3 (1)	S-N-C(2)	118.1 (2)
N-S-F'	94.1 (1)	C(1)-N-C(12)	113.1 (3)
N-S-F	89.2 (1)		
Dihedral Angles (deg)			
C(1)-N-C(2) and N-S-N' planes		48.2°	
N-S-N' and F-S-F' planes		86.9°	
C(1)-N-C(2) and F-S-F' planes		105.2°	

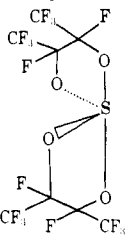
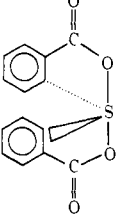
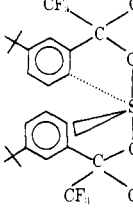
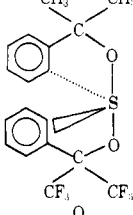
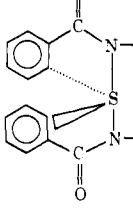
<sup>a</sup> Estimated standard deviations are in parentheses. Coordinates of primed atoms are related to the coordinates of the corresponding unprimed atoms of Table II by the operation  $-x, y, \frac{1}{2} - z$ .



in the chlorosulfurane **6**<sup>12</sup> and in  $\text{C}_4\text{H}_8\text{SSeBr}_2$  (**7**).<sup>28</sup> Since short intermolecular S...Cl and S-Cl...Cl-S contacts were observed in the crystal structure, the distortion in **6** seems best attributed to crystal packing effects. In **7**, however, these distortions have been ascribed to intramolecular repulsions between the large axial Br atoms and the equatorial  $\text{CH}_2$  groups. This rationale is supported by the structural results obtained with the corresponding Te species,  $\text{C}_4\text{H}_8\text{STeBr}_2$ .<sup>29</sup> Because of the greater size of the Te atom, the Te-Br and Te-C bonds are longer than the Se-Br and Se-C bonds and consequently the intramolecular repulsions in  $\text{C}_4\text{H}_8\text{STeBr}_2$  are diminished.

That the bending of S-F bonds toward the lone pair of electrons of the sulfur atom in  $(\text{Me}_2\text{N})_2\text{SF}_2$  is due to intermolecular interactions rather than electronic effects has been considered. Two rather short F...C contacts of 3.319 (5) and 3.524 (5) Å (from two neighboring molecules) occur, with corresponding F...H distances of 2.40 (4) and 2.56 (4) Å. These values may be compared to the sums of the van der Waals radii of 3.35 Å for F and C atoms<sup>26</sup> and 2.35 Å for F and H atoms.<sup>26,27</sup> (It must be remembered that intermolecular distances involving hydrogen atomic positions obtained from X-ray diffraction data may be substantially overestimated.<sup>30</sup>) The C-H...F angles are 167 (3) and 152 (2)° (close to linear-

**Table IV.** Equatorial Bond Angles ( $\theta_1$ ) and Axial Bond Lengths for Sulfuranes

sulfurane	$\theta_1$ , deg <sup>a</sup>	axial bond lengths, Å
SF <sub>4</sub>	101.6 <sup>b</sup>	1.64 <sup>b</sup>
(Me <sub>2</sub> N) <sub>2</sub> SF <sub>2</sub>	102.3 <sup>c</sup>	1.77 <sup>c</sup>
Ph <sub>2</sub> S[OC(Ph)(CF <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	104.4 <sup>d</sup>	1.889, 1.916 <sup>d</sup>
	104.6 <sup>e</sup>	1.754, 1.756 <sup>e</sup>
	107.8 <sup>f</sup>	1.83 <sup>f</sup>
	107.6, 108.1 <sup>g,h</sup>	1.832, 1.819 <sup>g,h</sup> 1.831, 1.816 <sup>g,h</sup>
	108.1 <sup>i</sup>	1.713, 1.955 <sup>i</sup>
	104.7 <sup>j</sup>	1.897, 1.899 <sup>j</sup>
(C <sub>10</sub> H <sub>8</sub> ) <sub>2</sub> SCl <sub>2</sub>	108.6 <sup>k</sup>	2.259, 2.323 <sup>k</sup>

<sup>a</sup>  $\theta_1$  is defined in 7. <sup>b</sup> Reference 10. <sup>c</sup> Present work. <sup>d</sup> Reference 13. <sup>e</sup> Reference 8. <sup>f</sup> Reference 5. <sup>g</sup> Reference 6. <sup>h</sup> Two crystallographically independent molecules per unit cell. <sup>i</sup> Reference 7. <sup>j</sup> Reference 9. <sup>k</sup> Reference 12.

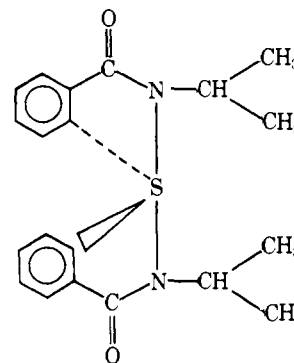
ity); hence, these C-H...F interactions appear to be attractive rather than repulsive. Thus, the possibility that the small bending of the S-F bonds toward the lone pair of the sulfur atom is due partially or wholly to weak attractive intermolecular forces cannot be dismissed. The packing of the (Me<sub>2</sub>N)<sub>2</sub>SF<sub>2</sub> molecules in the crystal is shown in Figure 4.

From an electronic standpoint, it would be reasonable to ascribe the observed F<sub>a</sub>-S-F<sub>a</sub> angle to repulsions between the

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fluorine ligands and the nitrogen lone pairs. Alternatively, Chen and Hoffmann<sup>4a</sup> have presented a perturbational MO argument to the effect that at a fixed equatorial bond angle  $\theta_1$  (see 8) the axial bond angle,  $\theta_2$ , will increase with increasing disparity in electronegativity between the axial and equatorial ligands. This argument is consistent with the fact that for SF<sub>4</sub>  $\theta_2 = 173.1^\circ$ , while for (Me<sub>2</sub>N)<sub>2</sub>SF<sub>2</sub>  $\theta_2 = 185.3^\circ$ .

**3. Equatorial Bonds.** The S-N bond distances (equal by symmetry) for (Me<sub>2</sub>N)<sub>2</sub>SF<sub>2</sub> are 1.648 Å and thus substantially less than the sum of the covalent radii for sulfur and nitrogen (1.75 Å) (see Table III).<sup>26</sup> This is perhaps not surprising since the covalent radius for nitrogen is predicated on the assumption of tetrahedral geometry. Furthermore, expansion of the C-N-C angle is expected to impart more N(2s) character to the bonds, thereby shortening them. The only other crystal-

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lographically characterized sulfurane with S-N bonds is the interesting spirocyclic species, 9.<sup>9</sup> Obviously, here the nitrogen atoms are in axial positions and, as expected, these hypervalent S-N bonds are considerably longer (average 1.898 Å) than the equatorial S-N bonds in (Me<sub>2</sub>N)<sub>2</sub>SF<sub>2</sub>.

Chen and Hoffmann<sup>4a</sup> and Paul, Martin, and Perozzi<sup>13</sup> have independently suggested that, for sulfurane substitution by more electronegative ligands at the axial sites, a smaller equatorial bond angle,  $\theta_1$ , is probable. The available structural data bearing on this point are summarized in Table IV. It is clear that, while the relatively small  $\theta_1$  value for (Me<sub>2</sub>N)<sub>2</sub>SF<sub>2</sub> is understandable on this basis, the general correlation between  $\theta_1$  and the electronegativity of the atoms at axial positions is poor.

Finally, one other trend predicted by Chen and Hoffmann<sup>4a</sup>—namely, that  $\theta_1$  should decrease as the axial bond distances increase—is not borne out by the available data in Table IV.

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**Supplementary Material Available:** Observed and calculated structure factors for [(CH<sub>3</sub>)<sub>2</sub>N]<sub>2</sub>SF<sub>2</sub> (6 pages). Ordering information is given on any current masthead page.

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## EXAFS Studies of Proteins and Model Compounds Containing Dimeric and Tetrameric Iron-Sulfur Clusters

Boon-Keng Teo,\*<sup>1a</sup> R. G. Shulman,\*<sup>1a</sup> G. S. Brown,<sup>1b</sup> and A. E. Meixner<sup>1a</sup>

Contribution from Bell Laboratories, Murray Hill, New Jersey 07974.

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**Abstract:** Proteins and model compounds containing dimeric and tetrameric iron-sulfur clusters have been studied by extended X-ray absorption fine structure (EXAFS) spectroscopy in fluorescence and transmission modes. Iron-sulfur and iron-iron distances have been obtained for both proteins and models. Debye-Waller factors, accurate to within 10%, provide an indirect but reliable measure of the spread of these distances. Detailed comparisons of these molecular parameters (average interatomic distances and Debye-Waller factors) are made between (1) proteins and models (which provides direct structural evidence that Holm's model compounds are excellent representations of the active sites of the proteins); (2) solid and solution states (which shows no drastic structural changes at the active site upon dissolution of the proteins); (3) oxidized and reduced states (which reveals small but significant structural changes upon redox). Thus, the present study bridges the two reservoirs of structural information on these important nonheme iron-sulfur proteins—the intact protein on one hand and the bare inorganic clusters on the other. It also provides strong evidence that structural changes at the active site(s) are energetically insignificant as judged by comparing the protein structures with those of the model compounds.

### Introduction

The class of nonheme iron-sulfur proteins has been shown to be involved in a variety of biological reactions including photosynthesis, nitrogen fixation, and mammalian steroid hydroxylation. These metalloproteins function as electron carriers via their redox reactions. There are four prototypes of the nonheme iron-sulfur proteins containing one, two, four, or eight iron atoms. The corresponding prosthetic groups are Fe(SR)<sub>4</sub> in rubredoxins; Fe<sub>2</sub>S<sub>2</sub>\*(SR)<sub>4</sub> for plant, mammalian, and certain bacterial ferredoxins (Fd); Fe<sub>4</sub>S<sub>4</sub>\*(SR)<sub>4</sub> for photosynthetic "high-potential" iron proteins (HIP) and non-photosynthetic bacterial ferredoxins; and two Fe<sub>4</sub>S<sub>4</sub>\*(SR)<sub>4</sub> units for bacterial ferredoxins where S\* and SR refer to sulfide and cysteinyl moieties, respectively.<sup>2</sup>

Extensive chemical and physical data have been obtained for these metalloproteins. X-ray protein crystallography<sup>3,4</sup> has provided structural information on several of the iron-sulfur

proteins. The resolution, generally about 2.0 Å, has not been good enough to evaluate accurately the structural changes of the iron-sulfur clusters upon reduction. On the other hand, Holm and co-workers have synthesized a class of organometallic analogues of the active sites of the four types of iron-sulfur proteins which can serve as detailed structural models.<sup>5-7</sup> We consider it of the utmost importance to bridge these two reservoirs of structural information on iron-sulfur proteins: the intact protein on one hand and the bare inorganic cluster models on the other. Such a linkage would be highly significant by allowing a detailed assessment on the extent to which the intrinsic properties, and hence the biological functions, of the active sites are modified by the proteins.

Recently we have reported comprehensive extended X-ray absorption fine structure (EXAFS) studies on rubredoxin and its model compounds in the oxidized and reduced states.<sup>8</sup> Rubredoxin is a particularly favorable compound for EXAFS