with trimethylphosphine oxide and triphenylphosphine oxide.[14a-i] While the P-C bonds range in length from 1.73 to 1.85 Å, similar variations were found in the other compounds and probably are sterically induced.

In each TBPO molecule in the crystal, two butyl groups are anti in conformation and one is gauche. The torsion angles,[15] viewing the butyl groups from the P atom along the middle C-C bond, are as follows: ∠[C(1), C(2), C(3), C(4)] = -175 (1)°; ∠[C(5), C(6), C(7), C(8)] = -176(2)°; ∠[C(9), C(10), C(11), C(12)] = -67(3)°. The anti conformation in alkanes is of slightly lower energy;[16] in gaseous butane there is about a 3:2 mixture of anti and gauche forms at room temperature.[17] Mixtures of the two butyl conformations have also been observed in the solid, for example, in the tetrabutylammonium ion.[18] The C-C bond lengths found here scatter considerably, but there average is 1.48 Å. This appears foreshortened because of the large thermal motions which these atoms are executing; the root-mean-square amplitudes range from about 0.3 Å near the P atom to about 0.45 Å at the ends of the chains. If a correction for thermal motion is applied,[19] with the assumption that each atom rides on the next more central one, the average bond length increases to 1.51 Å, this agrees better with the values found in structures in which the C positions can be more precisely determined. the C-C-C angles in the three butyl groups average 114.3, 115.3, and 121.3°, respectively. In free butane, these are found to be 112.6°.[17]

Crystals have also been prepared by reacting $UO_2(NO_3)_2 \cdot 6H_2O$ with di-*n*-butylphosphoric acid (HDBP) and by a mixture of HDBP and TBPO. Analysis of these structures is in progress, and the results should make possibe a comparison of the roles enacted by the acidic, neutral, and combined extractants in complexing U(VI).

Acknowledgment. This research was sponsored by the Division of Chemical Sciences of the U.S. Department of Energy under Contract W-7405-eng-26 with the Union Carbide Corp. I thank C. F. Baes, Jr., W. D. Arnold, and F. J. Hurst for helpful discussions of solvent extraction chemistry.

Registry No. $UO_2(NO_3)_2(TBPO)_2$, 78821-60-0; $UO_2(NO_3)_2$, 36478-76-9.

Supplementary Material Available: A listing of observed and calculated structure amplitudes and a table of H atom parameters (7 pages). Ordering formation is given on any current masthead page.

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(15) Klyne, W.; Prelog, V. *Experientia* **1960**, *16*, 521.

(16) Kitaigorodsky, A. I. "Molecular Crystals and Molecules"; Academic Press: New York, 1973; p 398.

(17) Bartell, L. S.; Kohl, D. A. *J. Chem. Phys.* **1963**, *39*, 3097.

(18) Forrester, J. D.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1964**, *3*, 1500.

(19) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1964**, *17*, 142.

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Gas-Phase Structures of $(CF_3)_2S{=}O$, $(CF_3)_2S{=}NCl$, and $(CF_3)_2SF_2$. An Electron Diffraction Study

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The gas-phase structures of $(CF_3)_2S{=}O$, $(CF_3)_2S{=}NCl$, and $(CF_3)_2SF_2$, which have been determined via electron diffraction studies, reveal some interesting effects when compared with the totally fluorinated analogues. The S=O bond lengths and the XSX angles in $X_2S{=}O$ molecules increase with decreasing electronegativity of X (X = F 1.415_9 Å, 92.7_9 (0_4)°; X = CF_3 1.469 (4) Å, 94.2 (8)°). The increase in the XSX angle in $X_2S{=}NCl$ is even more enhanced (X = F 89.3 (6)°; X = CF_3 99.4 (9)°). The geometries of the S=NCl groups in $F_2S{=}NCl$ and $(CF_3)_2S{=}NCl$ are remarkably different with S=N and N—Cl shorter in $(CF_3)_2S{=}NCl$ (1.434 (8) Å, 1.676 (8) Å) than in $F_2S{=}NCl$ (1.477 (9) Å, 1.723 (4) Å) and with a larger S=NCl bond angle (138.2 (3.8)° vs. 120.0 (6)°) in $(CF_3)_2S{=}NCl$. The decrease of the equatorial bond angle from 101.5 (5)° in SF_4 to 97.3 (8)° in $(CF_3)_2SF_2$ is incompatible with the VSEPR model.

Introduction

Bis(*F*-alkyl)sulfur(IV) compounds are extremely interesting materials because of their chemical properties and because of the geometry at the sulfur center. Their syntheses and reaction chemistry have been examined in some detail.[2a] Earlier workers have suggested that the two fluorine atoms bonded to sulfur in $(R_f)_2SF_2$ undergo rapid exchange between axial and equatorial sites, and thus the ^{19}F NMR chemical shift observed is an average value.[2b] However, our infrared spectral studies support axial positions for these fluorine atoms in the gas-phase spectrum of $(CF_3)_2SF_2$.[3] The Raman study suggests an axial configuration for this molecule in the liquid phase. Unfortunately, no gas-phase ^{19}F NMR spectral data are available. In the present electron diffraction study, the axial positions of the S-F bonds are confirmed for the gas-phase molecule.

The isoelectronic molecules $(CF_3)_2S{=}O$ and $(CF_3)_2S{=}NCl$ differ markedly in stability due largely to the presence of the labile chlorine atom bonded to nitrogen in the latter. On the basis of Raman studies, the symmetry of $(CF_3)_2S{=}O$ is C_s.[4] The present study shows that a surprising difference in the geometries of the S=NCl groups in $F_2S{=}NCl$[5] and $(CF_3)_2S{=}NCl$ exists. It now has been possible to determine the structures of $(CF_3)_2SF_2$, $(CF_3)_2S{=}O$, and $(CF_3)_2S{=}NCl$ and

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(2) (a) Shreeve, J. M. *Acc. Chem. Res.* **1973**, *6*, 387; *Isr. J. Chem.* **1978**, *17*, 1; *Sulfur Org. Inorg. Chem.*, **1981**, *4*. (b) Muetterties, E. L.; Mahler, W.; Packer, K. J.; Schmutzer, R. *Inorg. Chem.* **1964**, *3*, 1298. Rosenberg, R. M.; Muetterties, E. L. *Ibid.* **1962**, *1*, 756.

(3) Coe, D. A.; Shreeve, J. M. *Spectrochim. Acta, Part A* **1977**, *33A*, 965.

(4) Carter, H. A.; Wang, C. S.-C.; Shreeve, J. M. *Spectrochim. Acta, Part A* **1973**, *29A*, 1479.

(5) Haase, J.; Oberhammer, H.; Zeil, W.; Glemser, O.; Mews, R. *Z. Naturforsch., A* **1970**, *25A*, 153.

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Table I. Details of Electron Diffraction Experiments

	$(CF_3)_2S{=}O$		$(CF_3)_2S{=}NCl$		$(CF_3)_2SF_2$	
camera dist/cm	50	25	50	25	50	25
sample temp/°C	−34	−34	−29	−29	−44	−44
nozzle temp/°C	10	10	10	10	10	10
camera press./10^{-5} torr	2.0	1.5	2.0	1.0	1.5	1.0
exposure times/s	14-25	45-75	20-30	45-80	13-25	40-70
electron wavelength/Å[a]	0.04876	0.04879	0.04877	0.04879	0.04876	0.04879
s range/Å^{-1} [b]	1.4-17	8-35	1.4-9	8-35	1.4-17	8-35

[a] Uncertainties in the wavelength are smaller than 1 in the last digit. [b] $s = (4\pi/\lambda)\sin(\vartheta/2)$; λ = electron wavelength, ϑ = scattering angle.

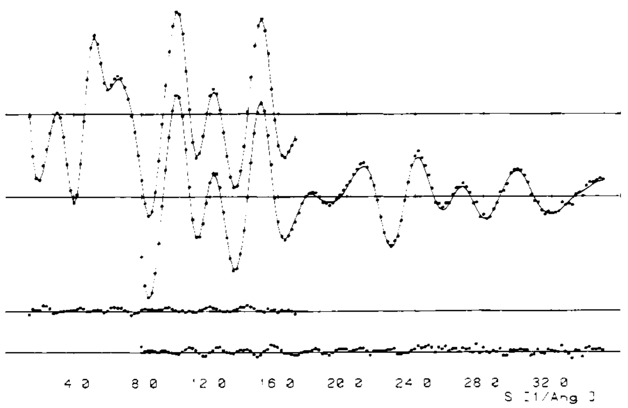

Figure 1. Experimental (•) and calculated (—) molecular intensities and differences for $(CF_3)_2S{=}O$.

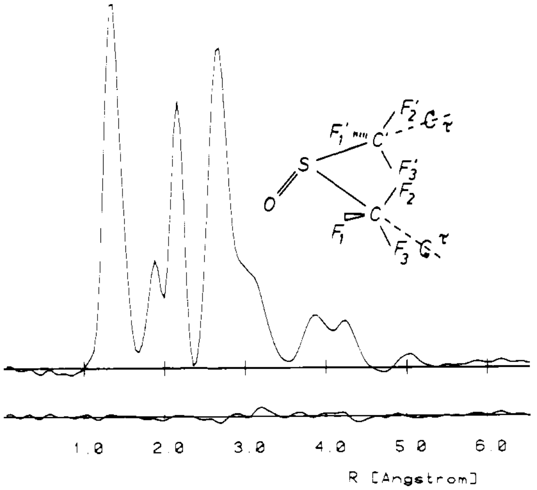

Figure 2. Experimental radial distribution function and difference curve for $(CF_3)_2S{=}O$.

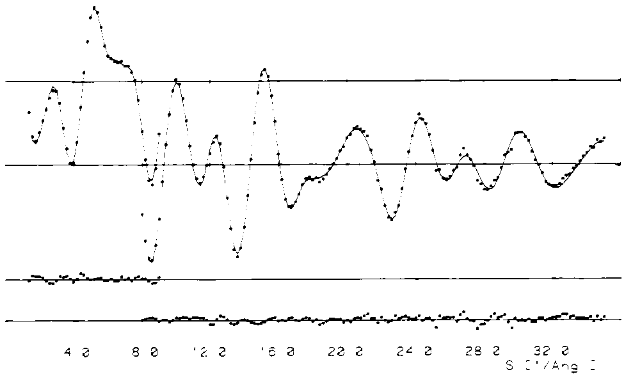

Figure 3. Experimental (•) and calculated (—) molecular intensities and differences for $(CF_3)_2S{=}NCl$.

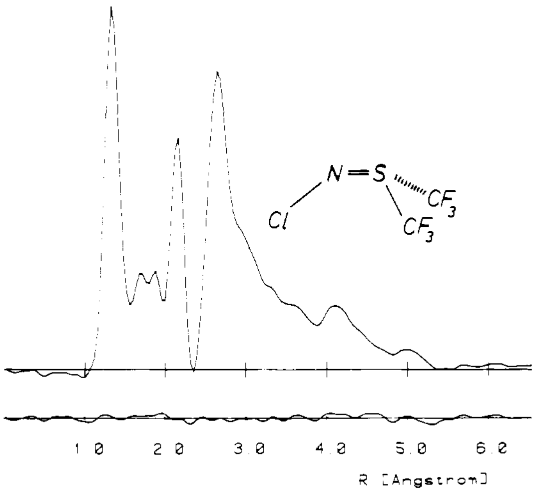

Figure 4. Experimental radial distribution function and difference curve for $(CF_3)_2S{=}NCl$.

to compare these data with those of their totally fluorinated analogues.

Experimental Section

Samples of $(CF_3)_2SF_2$,[6] $(CF_3)_2S{=}O$,[6] and $(CF_3)_2S{=}NCl$[7] were prepared and purified by using standard vacuum techniques. All samples were maintained at −78 °C when not being examined. The former two boil at 21.0 and 37.3 °C, respectively, and $(CF_3)_2S{=}NCl$ is a volatile liquid (~100 torr) at 25 °C.

The scattering intensities were recorded with the Balzers gas diffractograph KD-G2[8] at 50- and 25-cm camera distances and accelerating voltage of about 60 kV. Details of the experiments are listed in Table I (throughout this paper 1 Å = 100 pm and 1 torr = 101.325/760 kPa). For each compound and camera distance four plates were exposed, two of which were selected for the structure analysis. Due to the small amount of sample available in the case of $(CF_3)_2S{=}NCl$, only two plates could be obtained at the long camera distance. Unfortunately, both plates had defects in the emulsion at large scattering angles, and the data could be used only for $s < 9$ Å^{-1}. Processing of the plates and data reduction procedures are described elsewhere.[9] The averaged modified molecular intensities, interpolated

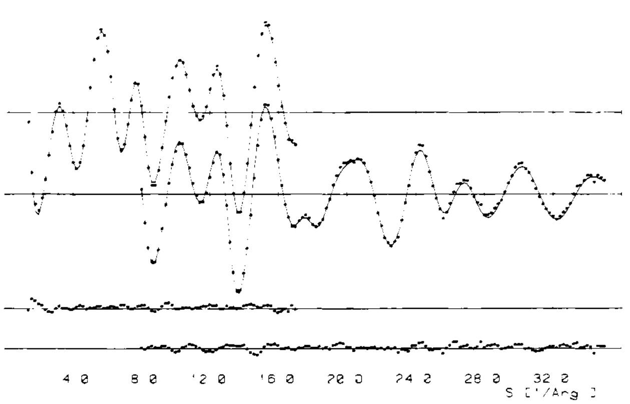

Figure 5. Experimental (•) and calculated (—) molecular intensities and differences for $(CF_3)_2SF_2$.

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(6) Saucer, D. T.; Shreeve, J. M. *J. Fluorine Chem.* **1971**, *1*, 1.
(7) Kumar, R. C.; Shreeve, J. M., submitted for publication.
(8) Oberhammer, H. "Molecular Structure by Diffraction Methods"; Chemical Society: London, 1976; Vol. 4, p 24.

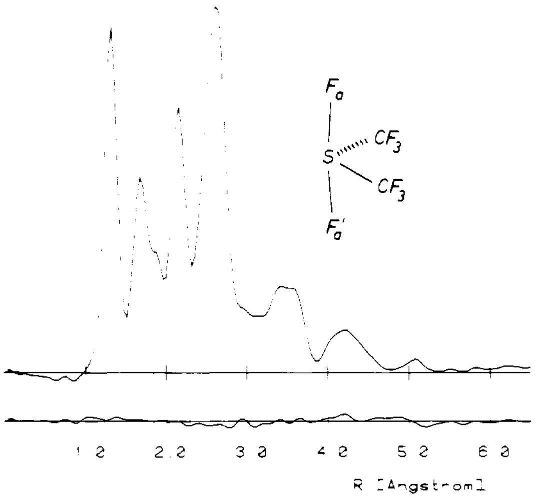

Figure 6. Experimental radial distribution function and difference curve for $(CF_3)_2SF_2$.

Table II. Results of Least-Squares Analysis for $(CF_3)_2S{=}O^a$

(a) Geometric Parameters (r_a Values) (Å or Deg)			
C–F	1.328 (3)	CSC	94.2 (8)
S=O	1.469 (4)	CSO	104.5 (1.1)
S–C	1.885 (4)	δ^c	3.6 (5)
FCF	109.0 (2)	τ^d	5.2 (4.0)
(b) Vibrational Amplitudes (Å)^b			
C–F	0.047 (2)	$C\cdots F_2'$	0.157 (10)
S=O	0.039 (6)	$O\cdots F_1$	
S–C	0.055 (5)	$O\cdots F_3$	
$F_1\cdots F_2$	0.056 (3)	$F_1\cdots F_2'$	0.115 (57)
$S\cdots F$	0.084 (5)	$F_2\cdots F_2'$	0.210^e
$C\cdots C'$	0.080^e	$F_2\cdots F_3'$	0.296 (101)
$C\cdots O$	0.074 (12)	$O\cdots F_2$	0.074 (14)
$C\cdots F_1'$	0.081 (23)	$F_1\cdots F_1'$	0.090^e
(c) Agreement Factors (%)			
R_{50}	3.7	R_{25}	7.5

[a] Error limits are 3σ values (see text). [b] For atom numbering see Figure 2. [c] Tilt angle of CF_3 groups (see text). [d] Torsional angle of the CF_3 groups (see Figure 2). [e] Value fixed in least-squares analysis.

Table III. Results of Least-Squares Analysis for $(CF_3)_2S{=}NCl^a$

(a) Geometric Parameters (r_a Values) (Å or Deg)			
C–F	1.317 (2)	CSC	99.4 (9)
S=N	1.434 (8)	CSN	108.8 (2.5)
S–C	1.878 (6)	SNCl	138.2 (3.8)
N–Cl	1.676 (8)	δ^c	2.8 (2.0)
FCF	109.5 (3)	τ^d	6.4 (1.3)
(b) Vibrational Amplitudes (Å)^b			
C–F	0.046 (3)	$C\cdots F_2'$	0.192 (26)
S=N	0.042^e	$N\cdots F_1$	
S–C	0.056 (8)	$N\cdots F_3$	
N–Cl	0.039 (10)	$F_1\cdots F_1'$	0.090^e
$F_1\cdots F_2$	0.054 (3)	$F_1\cdots F_2'$	0.117 (35)
$S\cdots F$	0.084 (6)	$F_2\cdots F_2'$	0.200^e
$S\cdots Cl$	0.130 (20)	$F_2\cdots F_3'$	0.340^e
$C\cdots C'$	0.080^e	$C\cdots Cl$	0.243 (54)
$C\cdots N$	0.080^e	$Cl\cdots F_1$	0.458 (151)
$C\cdots F_1'$	0.085^e	$Cl\cdots F_3$	
$N\cdots F_2'$		$Cl\cdots F_2$	0.230 (49)
(c) Agreement Factors (%)			
R_{50}	4.9	R_{25}	7.4

[a] Error limits are 3σ values (see text). [b] For atom numbering of the CF_3 group see Figure 2. [c] See Table II, footnote *c*. [d] See Table II, footnote *d*. [e] Value fixed in least-squares analysis.

Table IV. Results of Least-Squares Analysis for $(CF_3)_2SF_2{}^a$

(a) Geometric Parameters (r_a Values) (Å or Deg)			
C–F	1.317 (2)	CSC	97.3 (8)
$S–F_a$	1.681 (3)	F_aSF_a'	173.9 (8)
S–C	1.888 (4)	δ^c	1.4 (8)
FCF	109.3 (2)		
(b) Vibrational Amplitudes (Å)^b			
C–F	0.047 (2)	$C\cdots F_2'$	0.326 (68)
$S–F_a$	0.057 (4)	$F_1\cdots F_1'$	0.090^d
S–C	0.051 (5)	$F_1\cdots F_2'$	0.178 (27)
$F_1\cdots F_2$	0.062 (3)	$F_2\cdots F_2'$	0.400^d
$S\cdots F$	0.079 (4)	$F_2\cdots F_3'$	0.500^d
$C\cdots C'$	0.080^d	$F_1\cdots F_a$	0.188 (28)
$C\cdots F_a$	0.079 (9)	$F_2\cdots F_a$	0.151 (17)
$F_a\cdots F_a'$	0.060^d	$F_3\cdots F_a$	0.122 (13)
$C\cdots F_1'$	0.096 (30)		
(c) Agreement Factors (%)			
R_{50}	4.2	R_{25}	7.9

[a] Error limits are 3σ values (see text). [b] For atom numbering of the CF_3 group see Figure 2. [c] See Table II, footnote *c*. [d] Value fixed in least-squares analysis.

in steps of $\Delta s = 0.2$ Å^{-1}, are shown in Figures 1, 3, and 5 (numerical values of the total intensities are available as supplementary data).

Structure Analysis

Preliminary molecular models, derived from the radial distribution functions (Figures 2, 4, and 6) were refined by a least-squares analysis based on the molecular intensities. A diagonal weight matrix was used with elements increasing exponentially from 0.25 to 1 for $s < 3$ Å^{-1} and $s < 9$ Å^{-1} of the 50- and 25-cm data, respectively, and decreasing exponentially from 1 to 0.1 for $s > 16$ Å^{-1} (8 Å^{-1} in the case of $(CF_3)_2S{=}NCl$) and $s > 30$ Å^{-1}. All other elements were chosen to be 1. The theoretical intensities were calculated with the scattering amplitudes and phases of ref 10.

The following assumptions were made in the least-squares analyses: (1) C_s symmetry was assumed for $(CF_3)_2S{=}O$ and $(CF_3)_2S{=}NCl$ and C_{2v} symmetry for $(CF_3)_2SF_2$ with CF_3 groups in the equatorial positions of the distorted trigonal bipyramid. Model calculations clearly show that a conformation with axial CF_3 groups is incompatible with the electron diffraction intensities. (2) Local C_{3v} symmetry was assumed for the CF_3 groups. A tilt angle between the C_3 axis and the S–C bond direction was introduced. For all three molecules the tilt angle lies in the CSC plane and the direction indicates repulsion of the two CF_3 groups. (3) Vibrational amplitudes that caused large correlations with other parameters or that were poorly determined in the electron diffraction experiment were constrained (see Tables II–IV). In the analysis of $(CF_3)_2S{=}O$ and $(CF_3)_2S{=}NCl$, some amplitudes between the two CF_3 groups are constrained to the respective values obtained for $(CF_3)_2S$.[9] This assumption is justified by refined C···F and F···F amplitudes, which agree within the error limits with the values for $(CF_3)_2S$. Furthermore, the same torsional frequencies (75 cm^{-1}) were observed in the Raman spectra of $(CF_3)_2S$ and $(CF_3)_2S{=}O$.[4] In $(CF_3)_2SF_2$, refined vibrational amplitudes for torsion-dependent distances are considerably larger, and thus larger values were assumed for amplitudes that could not be refined. These larger vibrational amplitudes in $(CF_3)_2SF_2$ can be rationalized by the V_6 potential for internal rotation as compared to the V_3 potential for the other compounds. It should be pointed out, however, that assumptions for these nonbonded vibrational amplitudes have a negligible effect on bond lengths and angles derived from the electron diffraction data. With these constraints the following correlation coefficients had values >0.6: $(CF_3)_2S{=}O$ S–C/C–F = 0.65, S–C/FCF = 0.71, C–F/FCF = 0.70, $\delta/l(S\cdots F) = 0.61$; $(CF_3)_2S{=}NCl$ C–F/FCF = 0.70, SNCl/CSO = 0.88, CSO/$l(C\cdots F_2') = 0.75$, SNCl/$l(C\cdots F_2') = 0.76$, $\delta/l(S\cdots F) = 0.88$; $(CF_3)_2SF_2$ S–C/FCF = 0.65, $\delta/l(S\cdots F) = 0.69$. The results of the least-squares analyses for the three molecules are listed in Tables II–IV. Error limits are in general 3σ values. For bond distances a possible scale error of 0.1% has been added. For $(CF_3)_2S{=}NCl$, an uncertainty of ±0.005 Å for the S=N vibrational amplitude is included in the error limit for the S=N bond length.

Discussion

For $(CF_3)_2SF_2$ the equatorial position of the CF_3 groups as predicted from NMR[11] and vibrational[3] spectra is confirmed

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(9) Oberhammer, H.; Willner, H.; Gombler, W. *J. Mol. Struct.* **1981**, *70*, 273.

(10) Haase, J. *Z. Naturforsch., A* **1968**, *23A*, 1000.

Table V. Geometric Parameters for Some Related Molecules (Å or Deg)

	S–F	S–F_a	S–C	S=O or S=N	XSX[a]	XSO or XSN
SF_2[d]	1.592_1 (0_1)				98.2_0 (0_2)	
SF_4[b,e]	1.545 (3)	1.646 (3)			101.5 (5)	
$F_2S{=}O$[f]	1.586_8 (0_4)			1.415_9 (0_6)	92.7_9 (0_4)	106.6_6 (0_6)
$F_2S{=}NCl$[g]	1.596 (6)			1.476 (9)	89.3 (6)	111.2 (3)
$(CH_3)_2S$[h]			1.802 (2)		98.8 (2)	
$(CH_3)_2S{=}O$[i]			1.808 (4)	1.485 (5)	96.6 (2)	106.6 (2)
$(CF_3)_2S$[j]			1.819 (3)		97.3 (8)	
$(CF_3)_2S{=}O$[k]			1.885 (4)	1.469 (4)	94.2 (8)	104.5 (1.1)
$(CF_3)_2S{=}NCl$[k]			1.878 (6)	1.434 (8)	99.4 (9)	108.8 (2.5)
$(CF_3)_2SF_2$[c,k]		1.681 (3)	1.888 (4)		97.3 (8)	

[a] X = F or C. [b] F_aSF_a = 173.1 (5)°. [c] F_aSF_a = 173.9 (8)°. [d] r_z structure from ref 12. [e] r_0 structure from ref 13. [f] r_z structure from ref 14. [g] r_a structure from ref 5. [h] r_s structure from ref 15. [i] r_z structure from ref 16. [j] $r_\alpha{}^\circ$ structure from ref 9. [k] r_a structure from this work.

by the electron diffraction experiment. A comparison of bond lengths and angles for some related molecules (Table V) reveals some interesting effects upon variation of substituents and/or variation of the oxidation state of the central sulfur atom.

(1) For the S–C bond lengths we observe a small increase upon CH_3/CF_3 substitution in S(II) compounds (1.802 (2) Å in $(CH_3)_2S$ vs. 1.819 (3) Å in $(CF_3)_2S$), while this substitution effect is very strong for S(IV) compounds (1.808 (4) Å in $(CH_3)_2S{=}O$ vs. 1.885 (4) Å in $(CF_3)_2S{=}O$). The S–CH_3 and S–F bond lengths are rather insensitive toward increase in the sulfur oxidation number (S–F = 1.592_1 (0_1) Å in SF_2 vs. 1.586_8 (0_4) Å in $F_2S{=}O$ or 1.596 (6) Å in $F_2S{=}NCl$ and S—C = 1.802 (2) Å in $(CH_3)_2S$ vs. 1.808 (4) Å in $(CH_3)_2S{=}O$). The S—CF_3 bond lengths, however, increase considerably with increasing sulfur oxidation number (1.819 (3) Å in $(CF_3)_2S$ vs. 1.885 (4) Å in $(CF_3)_2S{=}O$ or 1.878 (6) Å in $(CF_3)_2S{=}NCl$ or 1.888 (4) Å in $(CF_3)_2SF_2$).

(2) The S=O bond lengths in $X_2S{=}O$ molecules increase with decreasing electronegativity of the substituent X (from 1.415_9 (0_6) Å in $F_2S{=}O$ to 1.469 (4) Å in $(CF_3)_2S{=}O$ to 1.485 (5) Å in $(CH_3)_2S{=}O$). The S=N bond lengths, however, show the opposite trend (1.479 (9) Å in $F_2S{=}NCl$ vs. 1.434 (8) Å in $(CF_3)_2S{=}NCl$).

(3) The axial S—F bond lengths increase by about 0.04 Å with substitution of the equatorial fluorine atoms of SF_4 by CF_3 groups.

(4) The XSX angle in $X_2S{=}O$ increases with decreasing electronegativity of the X substituent (92.7_9 (0.0_4)° in $F_2S{=}O$, 94.2 (8)° in $(CF_3)_2S{=}O$, and 96.6 (2)° in $(CH_3)_2S{=}O$). This effect is even stronger for $F_2S{=}NCl$ (89.3 (6)°) and $(CF_3)_2S{=}NCl$ (99.4 (9)°). While these trends are in qualitative agreement with predictions based on the VSEPR model,[17] the decrease of the equatorial bond angle from 101.5 (5)° in SF_4 to 97.3 (8)° in $(CF_3)_2SF_2$ is incompatible with this model. The axial bond angles in these two molecules are equal within their error limits.

(5) XSN bond angles are by about 4–5° larger than XSO angles, and both are quite insensitive toward the substituent X (note the large error limit for CSN in $(CF_3)_2S{=}NCl$).

(6) The geometries of the S=NCl groups in $F_2S{=}NCl$[5] and $(CF_3)_2S{=}NCl$ are remarkably different: in the latter molecule we observe shorter S=N and N—Cl bond lengths (N—Cl = 1.676 (8) Å in $(CF_3)_2S{=}NCl$ vs. 1.723 (4) Å in $F_2S{=}NCl$) and a larger SNCl bond angle (138.2 (3.8)° vs. 120.0 (6)°). The trends in these three parameters are consistent with partial delocalization of the nitrogen lone pair with the consequence of partial double and triple bond contributions to the N—Cl and S=N bonds and opening of the SNCl angle. It is not obvious, however, why such delocalization should occur in $(CF_3)_2S{=}NCl$ and not in $F_2S{=}NCl$.

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Registry No. $(CF_3)_2S{=}O$, 30341-37-8; $(CF_3)_2S{=}NCl$, 77386-73-3; $(CF_3)_2SF_2$, 30341-38-9.

Supplementary Material Available: Listings of total molecular scattering intensities (6 pages). Ordering information is given on any current masthead page.

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(11) Sauer, D. T.; Yu, S. L.; Shepard, W. N.; Magnuson, J. A.; Porter, R. A.; Shreeve, J. M. *Inorg. Chem.* **1975**, *14*, 1229.
(12) Kirchhoff, W. H.; Johnson, D. R.; Powell, F. X. *J. Mol. Spectrosc.* **1973**, *48*, 157.
(13) Tolles, M. W.; Gwinn, W. G. *J. Chem. Phys.* **1962**, *36*, 1119.
(14) Lucas, N. J. D.; Smith, J. G. *J. Mol. Spectrosc.* **1972**, *43*, 327.
(15) Dreizler, H.; Rudolph, H. D. *Z. Naturforsch., A* **1962**, *17A*, 712.
(16) Typke, V. *Z. Naturforsch., A* **1978**, *33A*, 842.
(17) Gillespie, R. J. "Molecular Geometry"; Van Nostrand-Reinhold: London, 1972.