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Gas-Phase Structure of $(CF_3)_2S(O)F_2$

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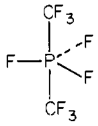
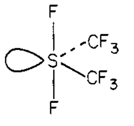
The geometric structure of $(CF_3)_2S(O)F_2$ has been studied by gas electron diffraction. In the distorted trigonal-bipyramidal structure the CF_3 groups and the double bond occupy the equatorial positions, in agreement with VSEPR theory. The following geometric parameters have been obtained (r_a values with 3σ uncertainties including a possible scale error of 0.1% for bond lengths): C—F = 1.314 (3) Å, S═O = 1.422 (7) Å, S—F_a = 1.641 (4) Å, S—C = 1.891 (5) Å, CSC = 97.8 (8)°, F_aSF_a = 173.1 (6)°, FCF = 109.4 (3)°. The results are discussed in connection with SF_4, OSF_4, and $(CF_3)_2SF_2$, and an attempt is made to explain variations in the bond angles by nonbonded fluorine–fluorine interactions.

Introduction

On the basis of the VSEPR model,[1] the most electronegative substituents occupy the axial positions in trigonal-bipyramidal molecules. An exception to this rule has been observed for the (trifluoromethyl)fluorophosphoranes CF_3PF_4 and $(CF_3)_2PF_3$ (I).[2] While the former compound exists in the gas phase as a mixture of axial and equatorial conformers (i.e. with the axial or equatorial position being occupied by the CF_3 group), the latter compound occurs only as the conformer with both CF_3 groups in axial positions. However, $(CF_3)_2SF_2$ (II), which we can formally consider isoelectronic with $(CF_3)_2PF_3$ with one equatorial fluorine substituted by the sulfur lone pair, obeys the electronegativity rule;[3] i.e., both CF_3 groups occupy equatorial positions.[4] This different stereochemistry can be rationalized by different steric requirements of a single bond and a lone pair. Since the VSEPR model considers a double bond intermediate between a single bond and a lone pair with respect to steric activity, we were interested in the stereochemistry and geometric structure of $(CF_3)_2S(O)F_2$, where the lone pair in II is replaced by the S═O double bond. Furthermore, this compound completes our previous structural studies of trifluoromethyl sulfur compounds with sulfur in different oxidation states: $(CF_3)_2$,[5] $(CF_3)_2SO$,[4] $(CF_3)_2SF_2$,[4] and $(CF_3)_2SO_2$.[6]



I



II

Experimental Section

Samples. $(CF_3)_2S(O)F_2$ was prepared according to the literature method.[7] The sample was purified by trap to trap fractionation, and its purity was checked by MS, IR, and NMR spectroscopy. The compound was transferred from Idaho to Germany in dry ice.

Electron Diffraction. The electron diffraction intensities were recorded with a Balzers KD-G2 gas diffractograph[8] at two camera distances (50 and 25 cm) and an accelerating voltage of about 60 kV. The sample temperature was −46 °C, and the inlet system and nozzle were at room temperature. The camera pressure never exceeded 2×10^{-5} torr during the experiment. Kodak electron image plates (13 × 18 cm) were exposed for 8–12 and 20–40 s at the long and short camera distances, respectively. The electron wavelength was determined from ZnO diffraction patterns. Two plates for each camera distance were analyzed by the usual procedures.[5] Background scattering, recorded without gas, was subtracted from the 25-cm data. The averaged molecular intensities for the s ranges 3.4–17 and 8–35 $Å^{-1}$ in steps of $\Delta s = 0.2$ $Å^{-1}$ are presented in Figure 1.

Structure Analysis

Radial distribution functions calculated for models with equatorial and axial CF_3 groups are shown in Figure 2 (curves B and C). Thereby, the final geometric parameters derived for the equatorial conformer were used for both models, interchanging the FSF and CSC angles. Variation of these angles for the axial conformer within a reasonable range does not change the basic characteristics of curve C. Comparison of the calculated curves B and C with the experimental radial distribution (curve A) demonstrates clearly that the CF_3 groups occupy equatorial positions, and contributions from other conformers >10% can certainly be excluded. A preliminary molecular model based on the radial distribution function was refined by a least-squares analysis of the molecular intensities. A diagonal-weight matrix was applied to the intensities, and the scattering amplitudes and phases of Haase were used.[9] The CF_3 groups were constrained to C_{3v} symmetry with a possible tilt angle between the symmetry axis and the S–C bond direction. Preliminary calculations with various rotational positions of the CF_3 groups indicated that one C—F bond eclipses the S═O double bond or is very close to this position. Thus, C_{2v} overall symmetry was assumed in the final least-squares analysis. With these geometric constraints and assumptions for the vibrational amplitudes, which are evident from Table I, 8 geometric parameters and 11 vibrational amplitudes were refined. Only three correlation coefficients had values larger than 0.6: CS/FCF = −0.73, tilt/F_aSF_a = 0.84, and tilt/l(S···F) = 0.77. The final results of the analysis are summarized in Table I.

Discussion

In the series $(CF_3)_2PF_3$, $(CF_3)_2SF_2$, and $(CF_3)_2S(O)F_2$ only the phosphorane with the CF_3 groups in axial positions is an exception to the electronegativity rule, whereas the S(IV) and S(VI) compounds confirm this rule. The exceptional stereochemistry of $(CF_3)_2PF_3$ can possibly be rationalized by considering nonbonded F···F interactions. According to Stölevik et al.,[10] nonbonded F···F distances in the range 2.6–3.0 Å are strongly attractive. F···F distances shorter than 2.3 Å are repulsive, and distances longer than 3.0 Å are less attractive. Applying this argument to $(CF_3)_2PF_3$ shows that nonbonded F···F interactions favor the axial conformer by about 5 kcal/mol with respect to equatorial position of the CF_3 groups, thus replacing electronegativity considerations as the dominant

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Table I. Results of Least-Squares Analysis

(A) Geometric Parameters (r_a Values) in Å and deg[a]

C–F	1.314 (3)	$S-F_a$	1.641 (4)	CSC′	97.8 (0.8)	FCF	109.4 (0.3)
S=O	1.422 (7)	S–C	1.891 (5)	F_aSF_a'	173.1 (0.6)	tilt[b]	1.5 (1.1)

(B) Interatomic Distances and Vibrational Amplitudes in Å[c]

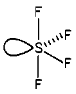
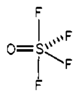
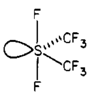
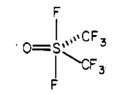
atom pair	m^d	r	l	atom pair	m^d	r	l
C–F	6	1.31	0.048 (3)	$C\cdots C'$	1	2.85	0.090^e
S=O	1	1.42	0.040^e	$O\cdots C$	2	3.02	
$S-F_a$	2	1.64	0.055 (4)	$C\cdots F_2'$	4	3.05	0.195 (63)
S–C	2	1.89	0.046 (5)	$F_1\cdots F_a$	4	3.11	0.150^e
$F_1\cdots F_2$	6	2.15	0.066 (3)	$F_a\cdots F_a'$	1	3.28	0.060^e
$O\cdots F_a$	2	2.23	0.065^e	$O\cdots F_1$	2	3.30	0.120^e
$C\cdots F_a$	2	2.46		$C\cdots F_1'$	2	4.06	
$F_2\cdots F_a$	4	2.38	0.077 (16)	$F_2\cdots F_3'$	2	3.42	0.149 (42)
$S\cdots F_1$	2	2.66	0.074 (4)	$F_3\cdots F_a$	4	3.57	0.071 (7)
$S\cdots F_2$	4	2.63		$O\cdots F_2$	4	3.82	0.126 (28)
$F_2\cdots F_2'$	2	2.66	0.170^e	$F_1\cdots F_2'$	4	4.29	0.148 (26)
				$F_1\cdots F_1'$	1	5.18	0.120^e

(C) Agreement Factors

$R_{50} = 5.6\%$ $R_{25} = 10.0\%$

[a] Error limits are 3σ values and include a possible scale error of 0.1% for bond lengths. [b] Tilt of CF_3 group away from S=O bond. [c] Error limits are 3σ values. [d] Multiplicity of distance. [e] Not refined.

Table II. Comparison of Geometric Parameters of Related Compounds

				
$S-X_e$,[a] Å	1.545 (3)[b]	1.539 (3)[c]	1.888 (4)[d]	1.891 (5)[e]
$S-F_a$, Å	1.646 (3)	1.596 (3)	1.681 (3)	1.641 (4)
S=O, Å		1.409 (3)		1.422 (7)
X_eSX_e, deg	101.5 (5)	112.8 (4)	97.3 (8)	97.8 (8)
F_aSF_a,[f] deg	173.1 (5)	164.6 (2)	173.9 (8)	173.1 (6)
F_aSX_e, deg	87.8 (3)	85.7 (1)	88.0 (4)	87.7 (3)

[a] X_e = F or C. [b] r_0 values from ref 14. [c] r_a values from ref 15. [d] r_a values from ref 4. [e] r_a values from this study. [f] Axial fluorine atoms are bent away from lone pair or double bond.

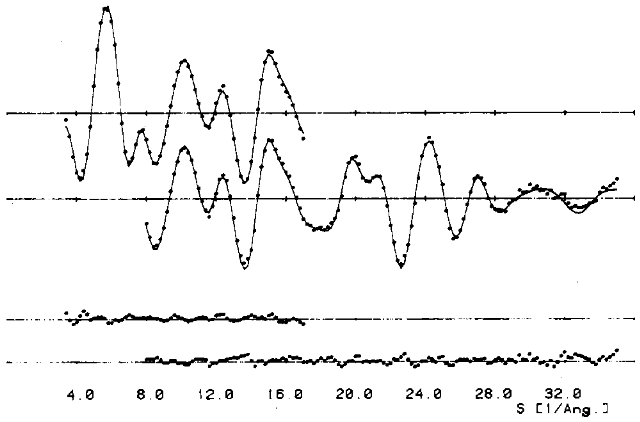


Figure 1. Experimental (···) and calculated (—) molecular intensities and differences.

effect. Nonbonded interactions in the sulfur compounds are different, because of the presence of a lone pair or a double bond to oxygen, and on the basis of the experimental results, these interactions do not override the electronegativity effect. For these interactions no potential functions are available in the literature that would allow a quantitative estimate.

Table II compares geometric parameters of sulfur tetrafluoride and thionyl(VI) tetrafluoride with the corresponding CF_3 substituted compounds. Within experimental error limits the equatorial bond lengths ($S-F_e$ and S–C) are not affected by increasing the sulfur oxidation number, while the axial S–F bonds in the S(VI) compounds are shorter by 0.04–0.05 Å than those in the S(IV) compounds. Substitution of the equatorial fluorine atoms by CF_3 groups causes lengthening of the $S-F_a$ bonds by about 0.04 Å in both cases. The S=O bond lengthens slightly upon substitution of the equatorial fluorine atoms by CF_3 groups. This trend is in agreement with ob-

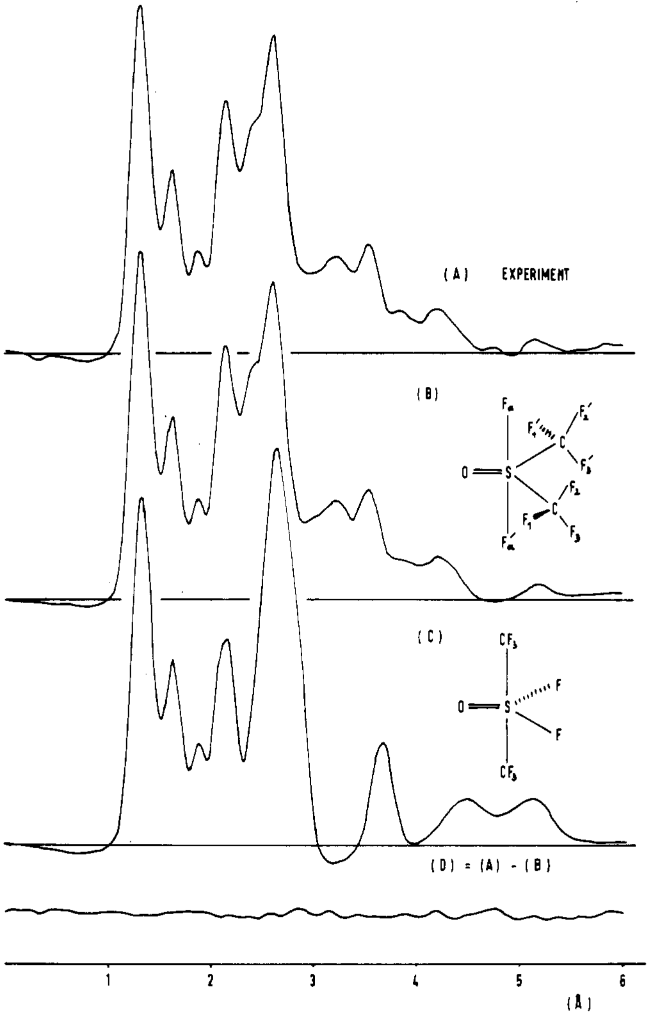


Figure 2. Radial distribution functions: (A) experimental curve; (B) calculated curve for final molecular model; (C) calculated curve for model with axial CF_3 groups; (D) difference curve between experiment and final model.

servations for F_2SO and $(CF_3)_2SO$ (1.416 (1) Å[11] vs. 1.469 (4) Å[4]) and F_2SO_2 and $(CF_3)_2SO_2$ (1.397 (2) Å[12] vs. 1.424 (4) Å[6]).

A more marked effect is observed for the bond angles at the sulfur atom, when the oxidation number is increased or F substituted by CF_3. Replacing the lone pair in SF_4 by a sulfur–oxygen double bond causes an increase in the F_eSF_e angle by about 11°, while the axial bond angle decreases. This indicates that the steric requirement of the S═O bond is smaller in equatorial direction and larger in axial direction as compared to that of the lone pair. Such direction-dependent steric effects of double bonds have been pointed out previously by Christe et al.[13] The situation is quite different in the CF_3-substituted compounds. Here, the sulfur bond angles do not change upon replacing the lone pair by the sulfur–oxygen double bond and the equatorial angle (CSC) in $(CF_3)_2S(O)F_2$ is smaller by 15° than the F_eSF_e angle in OSF_4. A very similar trend in the equatorial bond angles has been observed between $O{=}SF_4$ and $H_2C{=}SF_4$ (112.8° vs. 97.0° [16]). On the basis of ab initio calculations, these strong variations in the sulfur bond angles were rationalized by different "shapes" of the S═O and S═C π bonds.[17] While the S═O π bond is nearly symmetric (i.e. similar electron densities in axial and equatorial direction), the S═C π bond is strongly asymmetric with much higher electron density in the equatorial direction. Since we do not expect a drastic change of the S═O π bond upon F/CF_3 substitution in the equatorial plane, it is unlikely that the above argument can be applied in explaining the different bond angles in OSF_4 and $(CF_3)_2S(O)F_2$. An alternative explanation for the equal CSC bond angles in $(CF_3)_2SF_2$ and $(CF_3)_2S(O)F_2$ is based on the nonbonded F···F interactions mentioned above. The shortest F···F distances between CF_3 groups ($F_2 \cdots F_2'$) are 2.66 Å, i.e. just in the range of energetically favored distances. Thus, increasing the CSC angle in $(CF_3)_2S(O)F_2$ as compared to that in $(CF_3)_2SF_2$ would not lower the total energy, although the reduced steric requirement of the double bond as compared to that of the lone pair would allow such an increase of this angle. Stölevik's F···F interaction potential can explain the small CSC angles in $(CF_3)_2S$ (97.3° [5]), $(CF_3)_2SF_2$ (97.3° [4]), and $(CF_3)_2S(O)F_2$ (97.8°). These CSC angles are smaller than the FSF angles in the totally fluorinated compounds (98.2° for SF_2,[18] 101.5° for SF_4, and 112.8° for OSF_4), in contradiction to the VSEPR model. This indicates that the increased repulsion between bonding electron pairs is overcompensated by attractive F···F interactions in the CF_3 compounds. In the totally fluorinated compounds the F···F distances are shorter and repulsive. The angle between the axial fluorine atoms is constant, except in OSF_4, where F_aSF_a is about 9° smaller. This apparently large effect on the F_aSF_a angle, however, corresponds to a variation of only about 2° in the angle between axial and equatorial bonds. Such small effects can certainly not be accounted for by the crude bonding model discussed for these compounds.

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Registry No. $(CF_3)_2S(O)F_2$, 33716-15-3.

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