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X-ray Crystallographic Studies on a Sulfurane with a Diequatorial Four-Membered Ring and on a Fluorinated Cyclic Disulfoxide

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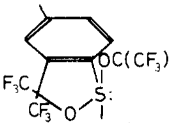
Abstract: The crystal and molecular structures of *F*-1,1-dibutoxy-1,3-dithiethane, $[(CF_3)_3CO]_2\overline{SCF_2SCF_2}$ (**5**), and of *F*-1,3-dioxo-1,3-dithiethane, $\overline{OSCF_2S(O)CF_2}$ (**6**), have been obtained from X-ray crystallographic studies. Compound **5** crystallizes in space group $P2_1/c$ of the monoclinic system with four molecules per unit cell having parameters a = 7.007 (3) Å, b = 12.038 (3) Å, c = 23.224 (8) Å, and β = 90.22 (15)°. The X-ray structure analysis (R = 0.133) shows distorted trigonal-bipyramidal geometry at sulfur with the four-membered ring in a diequatorial position. The axial S–O bond lengths are 1.811 (7) and 1.816 (7) Å while the equatorial S–C bond lengths are 1.887 (13) and 1.932 (13) Å. The equatorial C–S–C angle is 77.4 (6)° while the O–S–O angle is 168.6 (6)° distorted away from the sulfur lone pair. Compound **6** is a centrosymmetric molecule which crystallizes in the monoclinic space group $P2_1/n$ with two molecules per unit cell having parameters a = 6.090 (1) Å, b = 5.831 (1) Å, c = 8.060 (1) Å, and β = 105.33 (2)°. The X-ray structure analysis (R = 0.039) indicates pyramidal geometry at the sulfur atoms. The S–O bond length is 1.481 (3) Å, and the S–C bond lengths are 1.880 (4) and 1.890 (4) Å. The C–S–C angle of the four-membered ring is 79.4 (2)° while the O–S–C angles are 108.6 (2) and 107.0 (2)°.

Introduction

Over the past several years there has been considerable interest in the synthesis of and the geometry at sulfur in sulfuranes which contain one or two five-membered rings.[2] Several of these have been examined by using X-ray crystallographic techniques and have been found to exhibit roughly trigonal-bipyramidal geometry at sulfur.[3-6] With a single exception (**1**),[7] the five-membered rings have been observed to be bonded in axial–equatorial positions as in **2** or **3**. Arguments based on electronegativity rules have been used to rationalize their axial–equatorial orientation.



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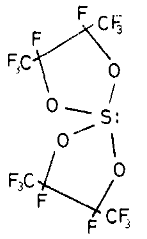

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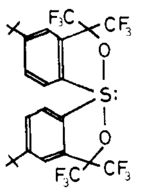

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However, although there are several sulfuranes which contain a four-membered ring, no X-ray crystallographic studies have been reported. Solely on the basis of nuclear magnetic resonance data and apicophility arguments, these sulfuranes were assumed to exist in a conformation with a diequatorial four-membered ring, e.g., ref 8–10.

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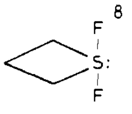

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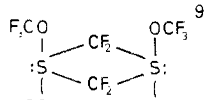

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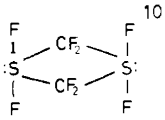
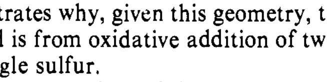


We have recently reported the synthesis of a solid *F*-di-*tert*-butoxysulfurane[11] which contains a four-membered ring. This compound is of particular interest because it is a stable material of moderate hydrolytic stability with a four-membered ring but it was not the product expected from the synthetic reaction, i.e., compare



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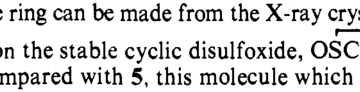
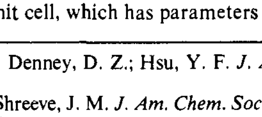


Compound **5** was the only product obtained regardless of the reaction stoichiometry. ^{19}F NMR suggests that the *F*-*tert*-butoxy groups are equivalent and thus, because of geometric constraints, are in axial positions. X-ray structure analysis confirms this and clearly demonstrates why, given this geometry, the only feasible product formed is from oxidative addition of two *F*-*tert*-butoxy groups to a single sulfur.

An interesting comparison of the geometry at sulfur(IV) and of the dithietane ring can be made from the X-ray crystal structure data obtained on the stable cyclic disulfoxide, $\overline{OSCF_2S(O)CF_2}$. When being compared with **5**, this molecule which results from the reaction of the sulfur difluoride with glass, viz.



demonstrates markedly the distortion of the ring which arises when the dithietane is unsymmetrically oxidized.

Experimental Section

Suitable crystals of **5** were obtained by sublimation and of compound **6** were obtained by recrystallization from anhydrous tetrahydrofuran/toluene in a desiccator over P_4O_{10}.

Crystal Data for 5. Crystals of **5** have monoclinic symmetry, space group $P2_1/c$. The unit cell, which has parameters a = 7.007 (3) Å, b =

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Table I. Positional Parameters of **5** (×10⁴)

	x/a	*y/b*	*z/c*
S(1)	2441 (4)	3811 (2)	8660 (1)
S(2)	1763 (7)	5856 (3)	9156 (2)
O(1)	2449 (12)	3343 (6)	9401 (3)
O(2)	2345 (12)	4550 (6)	7979 (3)
C(1)	2839 (18)	2262 (8)	9546 (4)
C(2)	2595 (21)	4056 (9)	7454 (4)
C(3)	361 (19)	4766 (10)	8888 (5)
F(31)	-777 (12)	5034 (9)	8455 (3)
F(32)	-636 (12)	4284 (7)	9286 (3)
C(4)	3725 (20)	5067 (10)	8956 (5)
F(41)	4776 (13)	5567 (6)	8545 (3)
F(42)	4964 (11)	4791 (7)	9374 (3)
C(11)	997 (39)	1559 (20)	9492 (11)
F(111)	1446 (15)	453 (8)	9463 (4)
F(112)	-4 (15)	1776 (9)	9000 (4)
F(113)	-267 (30)	1820 (14)	9885 (13)
C(12)	3436 (49)	2278 (20)	10187 (10)
F(121)	2435 (16)	3028 (7)	10490 (3)
F(122)	3063 (19)	1275 (8)	10437 (3)
F(123)	5156 (51)	2706 (26)	10311 (12)
C(13)	4385 (36)	1673 (21)	9182 (12)
F(131)	5338 (15)	912 (9)	9534 (4)
F(132)	5722 (16)	2434 (9)	9062 (5)
F(133)	3503 (43)	1309 (15)	8694 (7)
C(21)	1948 (34)	4873 (12)	7015 (6)
F(211)	2429 (19)	5913 (7)	7140 (3)
F(212)	2587 (16)	4636 (7)	6482 (3)
F(213)	27 (20)	4973 (15)	7020 (5)
C(22)	4707 (28)	3803 (14)	7373 (7)
F(221)	5033 (17)	3101 (9)	6916 (4)
F(222)	5626 (14)	4782 (9)	7292 (4)
F(223)	5512 (14)	3315 (9)	7842 (4)
C(23)	1508 (30)	2964 (14)	7364 (8)
F(231)	2539 (19)	2069 (6)	7625 (4)
F(232)	-81 (17)	3041 (9)	7639 (5)
F(233)	1206 (19)	2706 (9)	6818 (4)

12.038 (3) Å, *c* = 23.224 (8) Å, and β = 90.22 (15)°, contains four molecules, yielding a calculated density of 2.15 g/cm³.

As the crystals showed rapid decay in the X-ray beam (loss of more than 50% of the reflection intensity in 24 h), data of six crystals were collected on a Syntex P2₁ diffractometer by using graphite-monochromated Cu Kα radiation (λ = 1.541 78 Å) in the ω mode in the range 3.0° ≤ 2θ ≤ 135° at scan speeds of 2.93–29.30°/min, depending on the intensity of the reflection.

The data were corrected for crystal decay and Lorentz and polarization effects, but no absorption correction was made (μ = 43.31 cm^{-1} for Cu Kα radiation).

Scaling of the data of the different crystals was obtained by least-squares methods, yielding a consistency factor *R* = 0.088. After reduction of the data, 1831 unique reflections ($I \geq 2\sigma(I)$) were retained for the refinement of the structure.

A greater part of the structure could be determined by direct methods (MULTAN).[12] During completion of the structure by difference maps a molecular disorder of one of the OC(CF$_3$)$_3$ groups was noticed that corresponds to a rotation of 35° around one of the O–C axes. This molecular disorder leads to a new position only for the carbon atoms and one fluorine atom per CF$_3$ group. The residual two fluorine atoms per CF$_3$ group approximately coincide with original atoms. Occupation factors for the two parts of the disordered group are near 50% (54 (1):46 (1)%). After anisotropic temperature factors were introduced, the refinement converged to a final value of *R* = 0.133. This high value can be explained by the rapid decay of the crystals and different absorption effects for different crystals.

In the last cycle of refinement the shifts of all parameters divided by their standard deviations were smaller than 0.03. A final difference map displayed no electron density higher than 0.44 e Å^{-3}.

Crystal Data for 6. Crystals of **6** have monoclinic symmetry, space group $P2_1/n$. The unit cell, which has the parameters *a* = 6.090 (1) Å, *b* = 5.831 (1) Å, *c* = 8.060 (1) Å, and β = 105.33 (2)°, contains two molecules, yielding a calculated density of 2.36 g/cm³.

Data of a crystal of the dimensions 0.4 × 0.2 × 0.1 mm were measured on a Syntex P2₁ diffractometer by using graphite-monochromated Cu Kα radiation in the θ–2θ mode in the range 3° ≤ 2θ ≤ 135° at scan speeds of 2.93–29.30°/min, depending on the intensity of the reflection.

Table II. Positional Parameters of **6** (×10⁴)

	x/a	*y/b*	*z/c*
S	3027 (1)	1482 (1)	4452 (1)
C	5921 (6)	1043 (6)	4084 (4)
F(1)	7260 (4)	2834 (4)	4552 (3)
F(2)	5755 (4)	537 (4)	2445 (2)
O	1287 (5)	596 (5)	2939 (4)

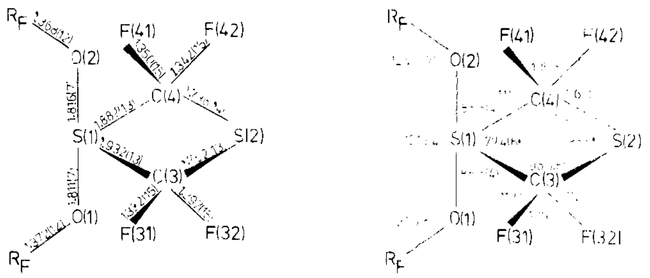

Figure 1. Bond lengths and angles of **5**. Noncited standard deviations of bond angles are 0.8–1.0°. Values of the parameters not shown: O(2)–S(1)–C(3) = 85.5 (4)°, O(1)–S–C(4) = 84.5 (4)°, F(41)–C(4)–S(2) = 112.4 (9)°, F(42)–C(4)–S(1) = 111.8 (8)°, F(31)–C(3)–S(2) = 115.0 (9)°, F(32)–C(3)–S(1) = 109.8 (8)°. Mean values of the residual parameters: C–C = 1.53 Å, C–F = 1.35 Å, C–C–O = 110°, C–C–C = 109°, C–C–F = 111°, F–C–F = 108°.

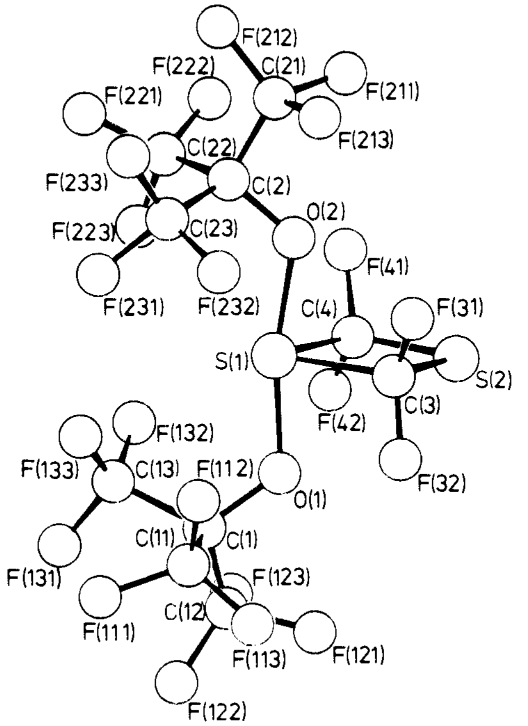

Figure 2. View of a molecule of 5. The C(CF$_3$)$_3$ group at O(1) shows rotational disorder.

The data were corrected for Lorentz, polarization, and absorption effects by using an empirical absorption program written by D.S. (μ = 88.67 cm^{-1} for Cu Kα radiation). After reduction of the data 461 unique reflections ($I \geq 3\sigma(I)$) were retained for the refinement of the structure.

The position of the sulfur atom was determined by Patterson methods whereas the other atoms could be found in a difference map. After anisotropic temperature factors were introduced, the refinement converged to a final value of *R* = 0.039. In the last cycle of refinement the shifts of all parameters divided by their standard deviation were smaller than 0.001. A final difference map displayed no electron density higher than 0.55 e Å^{-3}.

Results

The X-ray analysis of compound **5** unequivocally supports diequatorial geometry of the four-membered ring at sulfur. Some

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[12] MULTAN: Germain, G.; Main, P.; Woolfson, M. *Acta Crystallogr. Sect. A* **1971**, *27A*, 368.

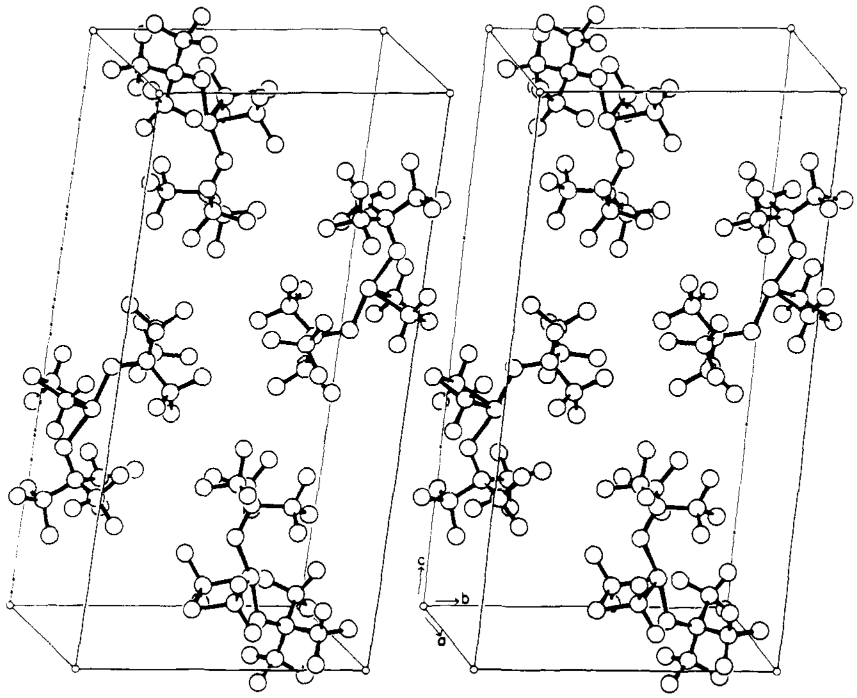


Figure 3. Unit cell of **5**.

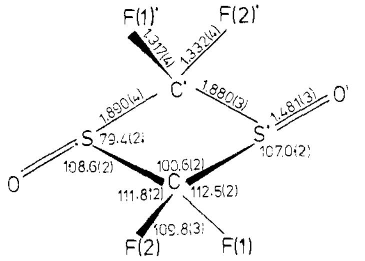


Figure 4. Bond lengths and angles of **6**. Angles not shown: S–C–F(1) = 112.5 (2)° and S′–C–F(2) = 111.8 (2)°.

selected bond lengths and angles are given in Figure 1. Figure 2 provides a view of the molecule. The configuration about the sulfur atom is a highly distorted trigonal bipyramid. The carbon atoms of the ring occupy two of the equatorial positions, and the lone pair on the sulfur fills the remaining equatorial position. The axial positions are occupied by the R_FO ligands. All sulfur–ligand bonds are bent away from the lone pair if the direction S(1) → lone pair is assumed to be exactly opposite to S(1) → S(2). (The angle between the direction S(1)···S(2) and S(1)–O(1) is 83.2° and between S(1)···S(2) and S(1)–O(2) is 85.4° and O(1)–S(1)–O(2) = 168.6°.) The least-squares plane of the four-membered ring (maximum deviation 0.007 Å) is approximately perpendicular to the plane formed by O(1), S(1), and O(2) (dihedral angle 89.1°). While the S–C–S angles are considerably distorted from tetrahedral or idealized 90° expected for planar four-membered rings, the angle at S(2) is also decreased from its ideal value but still 9° larger than that at S(1). Because of the steric demands of the ring the OR_F groups are rotated in the direction of the lone pair (torsional angles O(1)–S(1)–O(2)–C(2) = 179.4° and O(2)–S–O(1)–C(1) = 176.8°).

A view of the unit cell packing is shown in Figure 3.

Bond lengths and angles of **6** are shown in Figure 4. Figure 5 provides a view of the molecule. As was the case in compound **5**, all endocyclic angles had to be decreased considerably from their ideal values to form the planar four-membered ring. The geometry at the sulfur is pyramidal with the electron pair occupying the apical position. Figure 6 shows the unit cell packing of 6.

Discussion

As is the case for other sulfuranes, the ligand geometry at the tetracoordinate sulfur atom in compound **5** may be described as a markedly distorted trigonal bipyramid with the lone electron pair being found in an equatorial position. The axial positions are occupied by R_FO groups and the remaining two equatorial positions by the planar four-membered ring. The fact that both ring atoms occupy equatorial positions is quite surprising in small four- or five-membered rings which, because of reduced ring strain, usually are found in an axial–equatorial geometry. The C–S–C angle of 77.4 (6)° deviates greatly from the 120° required for the ideal trigonal-bipyramidal structure and appears to be less

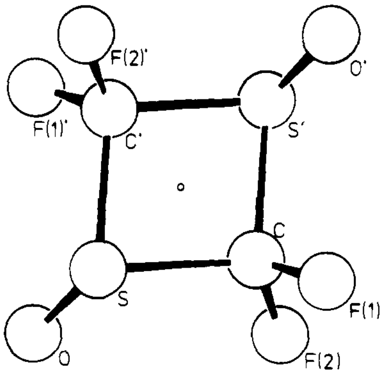


Figure 5. View of a molecule of **6**.

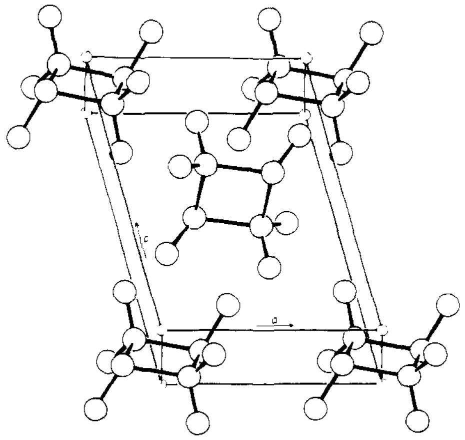
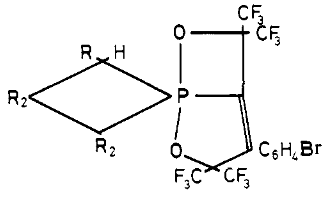


Figure 6. Unit cell of **6**.

than the smallest angle reported in the only other known sulfurane with a diequatorial ligand where the angle in a five-membered ring is 95°. In acyclic sulfuranes, the equatorial angles range between 101.6–108.6°.[7a,b,13] The angle at the dicoordinate sulfur atom is 9° larger than that at S(1). As the ideal values for both angles are roughly the same (see above and compare C–S–C of 105° in $(CH_3)_2S$[14]), this difference demonstrates clearly the much higher flexibility of the diequatorial angle at sulfur(IV) compared with the angle at sulfur(II). In compound **6**, where the geometry at sulfur is roughly pyramidal, the C–S–C angle is 79.4 (2)° and the S–C–S angles of 100.6 (2)° are somewhat larger than those in compound **5** which have a mean value of 98.1°. In each case the endocyclic angles at the bridging carbon atoms have decreased considerably from that expected for tetrahedral.

Although there are several compounds in which pentacoordinate phosphorus is claimed to be bonded to diequatorial rings, there is little X-ray structural data available. In the only published case known to us, a four-membered P–C–C–C ring is forced into the diequatorial position by the planarity of the sp^2 carbon bonded to the phosphorus atom (**7**).[15] The diequatorial angle, C–P–C, is 82.9°, a somewhat smaller distortion from the trigonal-bipyramidal geometry or from 90° than in our case.



(7)

There is a striking difference in the bond lengths between the two bridging carbons and the two sulfur atoms in compound **5**. The sulfur–carbon bonds to the tetracoordinate sulfur are about 0.1–0.15 Å longer than the S–C sp^2 bonds in compound **1** and other sulfuranes.[3,4,13] The sulfur–carbon bonds in compound **6** in which the sulfur is tricoordinate and approximately pyramidal are roughly the same as the analogous distances associated with the tetracoordinate sulfur in compound **5**.

The two sulfur–oxygen bonds in **5** are comparable to values found in dioxy–diaryl spirocyclic sulfuranes[3,4,13] and to the acyclic S–O bonds in compound **1**. However, they are siginificantly longer than the cyclic S–O bond in compound **1** (0.25 Å) and in the tetraoxysulfurane (**2**).[6] The analogous bonds in $Ph_2S(OR_F)_2$[16] are longer (0.1 Å). The fact that the bond distance between sulfur and its axial ligands depends upon the electronegativity of the equatorial substituents is very remarkable and finds a parallel in phosphorane chemistry. In every case the S–O bond is bent away from the lone pair.

The answer to the question of why only two *F-tert*-butoxy groups were added to one sulfur of the dithietane ring and no two such groups were added to each sulfur as is the case when *F*-methoxy groups are the reactants is now clear. Since the distances of several fluorine atoms from the plane perpendicular to the ring, which goes through C(3) and C(4), are smaller than their van der Waals radii, addition of two more $OC(CF_3)_3$ groups would lead to very close contacts between several fluorine atoms of the cis standing $OC(CF_3)_3$ groups and therefore cause rather large distortions. Addition probably would be possible, however, if the ring occupied an axial–equatorial position at the second sulfur atom. This seems to be very unfavorable.

Monocyclic or spirocyclic sulfuranes tend to be more stable with respect to hydrolysis and less likely to undergo other reactions. For example, the first of the spirosulfuranes, the perfluoropinacol derivative, is extremely stable[17] and compound **3** does not hydrolyze even under reflux with HCl or NaOH in 9:1 THF–H_2O solution.[18,19] Monocyclic sulfuranes usually exhibit an hydrolytic reactivity intermediate between the acyclic and the spiro compounds.[19] However, in the case of compound **5** hydrolysis occurs much more rapidly than with an acyclic analogue, e.g.

$$\mathbf{5} \xrightarrow[\text{few hours}]{\text{moist air}} (CF_3)_3COH$$

whereas

$$S(OC(CF_3)_3)_4{}^{11} \xrightarrow[\text{1 week}]{\text{moist air}} (CF_3)_3COH \text{ (very slow)}$$

While compound **4** and $(CF_3)_2S(OCF_3)_2$ are readily hydrolyzed,[9] the monocyclic $R'R\overline{SOS(CF_3)_2N{=}C}(R)O$ is hydrolyzed only slowly in the presence of water.[20] Compound **5** appears to be an exception to the usual hydrolytic stability of monocycles. This must arise from the greater accessibility of the electron pair to nucleophilic attack arising from a rather major distortion from trigonal-bipyramidal geometry especially in the equatorial plane because of the small diequatorial angle and rather large deviation (11°) from linearity of the O–S–O angle away from the lone pair.

Compound **6**, the first fluorinated cyclic disulfoxide, not only is useful as a standard for comparison with the *F*-dialkoxy cyclic sulfurane but also is an interesting compound in its own right. Whereas dithietane derivatives usually are planar,[21] the ring becomes puckered when one of the sulfur atoms is oxidized as in $S(CH_2)_2SO$.[22] As mentioned earlier in the disulfoxide (**6**), the ring is planar again as it is in $O_2S(CH_2)_2SO_2$.[22]

The decrease in the C–S–C bond angle from the ideal value of 98.2° found in $(CH_3)_2SO$[23] is accompanied by a remarkable increase in the C–S bond length (1.885 compared to 1.796 Å). A similar but less dramatic increase is observed in the puckered ring $OS(CHPh)_2CH_2$[24] where an average S–C bond length of 1.859 Å is found whereas in $S(CH_2)_2SO$ no significant increase is noticed.

The S=O double bond in **6** is shortened with respect to $(CH_3)_2SO$ (1.481 compared to 1.521 Å).

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Supplementary Material Available: Tables of temperature factors, full bond lengths and angles, and observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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