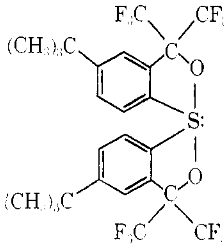
Crystal and Molecular Structures of a Spirodiaryldialkoxysulfurane Oxide and Its Parent Sulfurane[1,2]

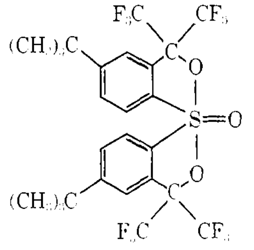
Edmund F. Perozzi, J. C. Martin,* and Iain C. Paul*

Contribution from the Department of Chemistry, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801. Received April 24, 1974

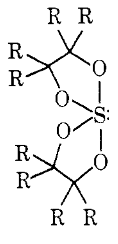
Abstract: Oxidation of the dipotassium salt of 2,2′-bis(1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl)-4,4′-di-*tert*-butyldiphenyl sulfide with bromine gives spirosulfurane, **1**. Oxidation of **1** with RuO_4 in carbon tetrachloride gives spirosulfurane oxide, **2**. The crystal structure of **1** reveals two independent molecules with distorted trigonal bipyramidal geometry about sulfur, with the lone pair considered to occupy one equatorial position, two phenyl ligands occupying the other two equatorial positions, and alkoxy ligands occupying the two apical positions. The exocyclic C–S–O angles range from 91.3 (3) to 92.4 (3)° and the endocyclic C–S–O angles from 85.8 (3) to 87.1 (3)° for the two molecules in refinement. The O–S–O angle is 177.1 (2)° (or, in the other molecule, 178.2 (2)°) with the distortion of the oxygen atoms from linearity being in the direction of the equatorial phenyl rings. The C–S–C angle is 108.1 (4)° (or 107.6 (3)° in the other molecule). The S–O bond lengths 1.832 (5) and 1.819 (5) Å (or 1.831 (5) and 1.816 (5) Å) are *ca.* 0.13 Å longer than the sum of the covalent radii, consistent with a bond order less than unity. The crystals of **1** are monoclinic, the space group is $P2_1/c$, and there are eight molecules in a unit cell of dimensions $a = 13.087$ (5) Å, $b = 19.975$ (9) Å, and $c = 22.330$ (9) Å, and $\beta = 94°15'$ (2′). The structure was refined to an R factor of 0.094 for 5517 nonzero reflections. The crystal structure of **2** shows less distortion from trigonal geometry in the equatorial plane than does **1**, with C–S–O (equatorial) angles of 120.7 (2) and 121.5 (3)° and a C–S–C angle of 117.7 (3)°, but more distortion from linearity of the apical O–S–O angle, to 172.3 (2)°. The exocyclic C–S–O (apical) angles are 88.8 (2) and 88.6 (2)° and the endocyclic ones are 87.2 (2) and 87.4 (2)°. The S–O apical bond lengths (1.780 (5) and 1.777 (5) Å) are *ca.* 0.08 Å longer than the sum of the covalent radii, and the S–O equatorial bond length (1.439 (4) Å) is similar to that found in sulfones. These crystals are monoclinic, the space group is $P2_1/c$, and there are four molecules in a unit cell of dimensions $a = 13.824$ (9) Å, $b = 12.231$ (5) Å, $c = 20.846$ (11) Å, $\beta = 126°55'$ (1′). The structure was refined to an R factor of 0.072 on 3005 nonzero reflections. A comparison of structural features for **1** and **2** with those of related compounds is discussed in terms of a number of factors important in determining the geometry of such species. High temperature nmr studies of spirosulfurane **1** show that geometric inversion about sulfur is slow on the nmr time scale at 200°.



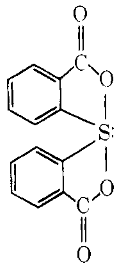
1



2

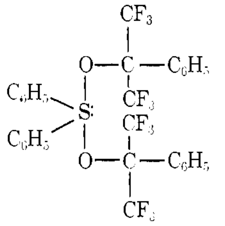


3, R = CF_3



4

The synthesis and characterization of a stable spirosulfurane, **1**, and of the first example of a pentacoordinate sulfur(VI) compound lacking halogen ligands, spirosulfurane oxide, **2**, have been recently described.[3,4] It has been reported[3,4] that spiro compounds **1** and **2** are stable toward hydrolysis; even in boiling aqueous acid or base no hydrolysis is observed. Other laboratories have reported[5,6] unreactivity toward hydrolysis for the spirosulfuranes **3** and **4**. For instance, **4** was hydrolyzed[6] to the sulfoxide by heating for 30 min in a 9:1 acetone–water solvent mixture. On the other hand, the acyclic sulfurane **5** is extremely water sensitive[7] and hydrolyzes instantly to diphenyl sulfoxide and hexafluoro-2-phenyl-2-propanol (R_FOH). Tetraphenoxysulfurane, **6**, is a hygroscopic solid which hydrolyzes[8] to phenol and diphenyl sulfite. The large differences in reactivity between spirosulfurane **1** and spirosulfurane oxide **2** on the one hand and acyclic



5

---

[1] Paper number XV in a series on sulfuranes. For paper XIV in this series see J. C. Martin, J. A. Franz, and R. J. Arhart, *J. Amer. Chem. Soc.*, **96**, 4604 (1974).

[2] A preliminary account of a portion of this work has appeared. See E. F. Perozzi, J. C. Martin, and I. C. Paul, *J. Amer. Chem. Soc.*, **96**, 578 (1974).

[3] J. C. Martin and E. F. Perozzi, *J. Amer. Chem. Soc.*, **96**, 3155 (1974).

[4] E. F. Perozzi and J. C. Martin, *J. Amer. Chem. Soc.*, **94**, 5519 (1972).

[5] M. Allan, A. F. Janzen, and C. J. Willis, *Can. J. Chem.*, **46**, 3671 (1968).

[6] I. Kapovits and A. Kálmán, *Chem. Commun.*, 649 (1971).

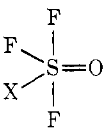
[7] (a) J. C. Martin and R. J. Arhart, *J. Amer. Chem. Soc.*, **93**, 2341 (1971); (b) R. J. Arhart and J. C. Martin, *ibid.*, **94**, 4997 (1972).

[8] J. I. Darragh and D. W. A. Sharp, *Angew. Chem., Int. Ed. Engl.*, **9**, 73 (1970).

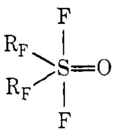
sulfuranes **5** or **6** on the other prompted us to look for structural features which might provide hints as to the origin of these striking differences in reactivity.

X-Ray crystal structures have previously been determined[9,10] for the spirosulfurane **4** and the acyclic sulfurane **5**. Both compounds exhibit approximate trigonal bipyramidal geometry about the sulfur atom with the third equatorial position presumably occupied by a lone pair of electrons. The most noteworthy difference between the two structures is in the length of the apical S–O bonds. For compound **5** these are reported[10] as 1.916 (4) and 1.889 (4) Å, whereas for compound **4** they are 1.83 (1) Å.[9]

The first reported sulfurane oxide, sulfur oxytetrafluoride, was obtained[11] by oxidation of sulfur tetrafluoride by nitrogen oxides, or by oxygen in the presence of nitrogen oxides at high temperatures, or by the reaction of thionyl fluoride (SOF_2) with elemental fluorine.[12–14] More recently, the sulfurane oxides **7a–c** have been obtained[15] by reaction of OSF_4 with appropriate silanes. The fluorination of perfluoroalkyl sulfoxides to produce difluorodialkylsulfurane oxides, **8**, has recently been reported.[16] The only structural data reported for any sulfurane oxides are from three electron diffraction studies on OSF_4.[17,18] These disagree as to finer structural details. An early study concluded[17a] that the axial fluorine atoms are bent from the collinear F–S–F geometry *in* the direction of the equatorial oxygen, *away* from the equatorial fluorines. Two more recent, and presumably more reliable, studies[17b,18] show that the direction of distortion from linearity is *away* from the equatorial oxygen. In all three studies the internal F–S–F equatorial angle (122.8 (1.8)°,[17a] 110.0 (7)°,[17b] or 110.1 (1.8)° [18]) is reported to be significantly larger than that in sulfur tetrafluoride as determined by microwave spectroscopy (101.6 (5)°)[19] or by electron diffraction (103.8 (6)°).[17a] In order to determine whether similar geometric changes might be observed in going from spirosulfurane **1** to spirosulfurane oxide **2**, full X-ray crystal structure determinations of these compounds were undertaken.



7a, $X = N(CH_3)_2$
b, $X = N(C_2H_5)_2$
c, $X = OC_6H_5$



8

Experimental Section

Synthesis. The syntheses of spirosulfurane **1** and spirosulfurane oxide **2** are reported in earlier papers.[3,4]

High Temperature Nuclear Magnetic Resonance Studies of Spirosulfurane 1. Spirosulfurane **1** in hexamethylphosphoramide (0.17 *M*) showed a decrease in separation of the ^{19}F peaks (56.4 MHz) for the two CF_3 quartets from 186 Hz at 42° to 170 Hz at 200°. The peaks were slightly broadened, but the ^{19}F spin–spin coupling multiplet structure (J_{FF} = 9 Hz) was still readily apparent at 200°. Similar chemical shift decreases were seen in solvent bromobenzene (from 183 Hz at 41° to 175 Hz at 130°) and in dibenzyl ether (from 298 Hz at 28° to 282 Hz at 122° in 96.5-MHz spectra) but without averaging out the 9 Hz spin–spin coupling between geminal CF_3 groups.

X-Ray Crystallography of Spirosulfurane 1. Spirosulfurane **1** was crystallized several times from petroleum ether to give white prisms. A single crystal of length 0.5 mm in the *b* direction and 0.2 × 0.3 mm in cross section was mounted along the *b* axis. No special precautions were needed to protect the crystal from moisture.

Crystal Data for 1. $C_{26}H_{24}F_{12}O_2S$; $M = 628.5$; monoclinic; $a = 13.087\ (5)$, $b = 19.975\ (9)$, $c = 22.330\ (9)$ Å; $\beta = 94°15'\ (2')$; $V = 5821$ Å^3; $Z = 8$; $\rho_{calcd} = 1.43$ g cm^{-3}, $F(000) = 2560$; space group $P2_1/c$ from systematic absences, $h0l$, when $l = 2n + 1$, $0k0$, when $k = 2n + 1$; nickel-filtered Cu Kα X-radiation; λ 1.54178 Å; μ (Cu Kα) = 19.2 cm^{-1}.

The cell parameters were determined by a least-squares fit to the settings of the angles for 12 hand-centered reflections on a Picker FACS-1 diffractometer. The reflections were measured by a scintillation counter, with attenuators being inserted when the count rate exceeded 10,000 counts sec^{-1}. All the symmetry-nonequivalent reflections in the 2θ range 0–130° were measured by a moving crystal–moving counter technique, with a 2θ scan rate of 2° min^{-1}. The base width of the scan was 2.0°, and a dispersion factor (0.285) was applied to allow for α_1–α_2 splitting. Background measurements were made for 10 sec at each limit of the scan.

Three standard reflections were monitored after every 50 measurements. There were some fluctuations of as much as ±10% in the intensities of the standards over the 15-day period of data collection. The changes appeared to be linear and continuous over fairly long time periods and were attributed to temperature fluctuations in the room and possibly to some attendant apparatus instabilities. The intensities of the reflections were normalized on the basis of a linear relationship between the periodic measurements of the standards. In all, 5517 symmetry-independent reflections were considered to be above background at the 2σ significance level based on counting statistics.[20] No correction was made for absorption or extinction. The maximum and minimum transmission coefficients (based on intensities) were estimated to be 0.68 and 0.50.

Solution and Refinement of the Structure of 1. The structure was solved by direct methods[21] using the series of programs SIGMA2, CONVERGE, and FASTAN[22] adjusted for centrosymmetric structures. Only data in the range 2θ = 0–100° were used to solve the structure. The *E* map based on the most consistent set of signs revealed the positions of 68 of the 82 nonhydrogen atoms in the two independent molecules in the crystal asymmetric unit. After we had completed a least-squares refinement of the positions and isotropic temperature factors for these 68 atoms, we obtained a Fourier map which revealed the positions of the remaining nonhydrogen atoms. Computer storage limitations necessitated carrying out the full-matrix least-squares refinement of anisotropic thermal parameters in four partial cycles. The first partial cycle consisted of the atoms S(1), O(1), F(1)–F(6), and C(1)–C(13), the second partial cycle consisted of the remaining atoms of the unprimed molecule, the third partial cycle consisted of the atoms S(1′), O(1′), F(1′)–F(6′), and C(1′)–C(13′), while the fourth partial cycle contained the remainder of the atoms of the primed molecule. The reflections were weighted using a program written by Dieterich[20] following the expression given by Corfield, Doedens, and Ibers.[23] One complete cycle of such refine-

---

[9] A. Kálmán, K. Sasvári, and I. Kapovits, *Acta Crystallogr., Sect. B*, **29**, 355 (1973); see also ref 6.

[10] I. C. Paul, J. C. Martin, and E. F. Perozzi, *J. Amer. Chem. Soc.*, **94**, 5010 (1972); **93**, 6674 (1971).

[11] W. C. Smith and V. A. Engelhardt, *J. Amer. Chem. Soc.*, **82**, 3838 (1960).

[12] W. Kwasnik, "F.I.A.T. Review of German Science (1936–1946), Inorganic Chemistry," Vol. 1, H. M. Stationery Office, London, 1948, pp 192–193.

[13] H. Jonas, *Z. Anorg. Allg. Chem.*, **265**, 273 (1951).

[14] F. B. Dudley, G. H. Cady, and D. F. Eggers, Jr., *J. Amer. Chem. Soc.*, **78**, 290 (1956).

[15] S. P. von Halasz and O. Glemser, *Chem. Ber.*, **103**, 594 (1970); S. P. von Halasz, O. Glemser, and M. F. Feser, *ibid.*, **104**, 1242 (1971).

[16] J. M. Shreeve, *Accounts Chem. Res.*, **6**, 387 (1973).

[17] (a) K. Kimura and S. H. Bauer, *J. Chem. Phys.*, **39**, 3172 (1963); (b) J. L. Hencher, D. W. J. Cruickshank, and S. H. Bauer, *ibid.*, **48**, 518 (1968).

[18] G. Gundersen and K. Hedberg, *J. Chem. Phys.*, **51**, 2500 (1969).

[19] W. M. Tolles and W. D. Gwinn, *J. Chem. Phys.*, **36**, 1119 (1962).

[20] Using a program written by D. A. Dieterich, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1973.

[21] J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

[22] G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. B*, **26**, 274 (1970).

[23] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

Table I. Final Coordinates for the Two Molecules of **1**. Estimated Standard Deviations in Parentheses

	x	y	z		x	y	z
S(1)	0.5705 (2)	0.1569 (1)	0.3260 (1)	S(1′)	−0.0536 (1)	0.3197 (1)	0.2953 (1)
O(1)	0.6399 (4)	0.1724 (2)	0.3990 (2)	O(1′)	−0.1180 (3)	0.3395 (2)	0.3632 (2)
O(2)	0.4972 (4)	0.1450 (2)	0.2544 (2)	O(2′)	0.0129 (4)	0.2982 (3)	0.2294 (2)
C(1)	0.4575 (6)	0.1560 (4)	0.3664 (4)	C(1′)	0.0645 (6)	0.3368 (3)	0.3391 (3)
C(2)	0.3537 (7)	0.1544 (4)	0.3376 (4)	C(2′)	0.1620 (6)	0.3239 (3)	0.3195 (3)
C(3)	0.2730 (6)	0.1506 (4)	0.3753 (4)	C(3′)	0.2471 (6)	0.3458 (4)	0.3570 (4)
C(4)	0.2903 (7)	0.1462 (4)	0.4369 (4)	C(4′)	0.2332 (7)	0.3810 (4)	0.4106 (4)
C(5)	0.3932 (7)	0.1467 (4)	0.4652 (4)	C(5′)	0.1356 (7)	0.3733 (4)	0.4289 (3)
C(6)	0.4735 (6)	0.1518 (3)	0.4271 (3)	C(6′)	0.0533 (6)	0.3690 (3)	0.3930 (4)
C(7)	0.5865 (6)	0.1541 (4)	0.4480 (3)	C(7′)	−0.0584 (6)	0.3773 (4)	0.4049 (4)
C(8)	0.6222 (8)	0.0831 (5)	0.4678 (4)	C(8′)	−0.0897 (8)	0.4513 (5)	0.3979 (5)
C(9)	0.6111 (8)	0.2041 (6)	0.4977 (4)	C(9′)	−0.0820 (8)	0.3507 (5)	0.4683 (4)
C(10)	0.1984 (6)	0.1406 (5)	0.4777 (4)	C(10′)	0.3281 (7)	0.4106 (5)	0.4491 (4)
C(11)	0.2353 (10)	0.1361 (8)	0.5468 (5)	C(11′)	0.4292 (10)	0.3959 (10)	0.4212 (8)
M(11)[a]	0.1907 (25)	0.2152 (17)	0.5073 (14)	M(11′)	0.3809 (43)	0.3444 (28)	0.4819 (26)
C(12)	0.1280 (17)	0.2028 (11)	0.4660 (12)	C(12′)	0.3120 (10)	0.4897 (6)	0.4528 (6)
M(12)	0.0983 (26)	0.1560 (18)	0.4393 (14)	M(12′)	0.3987 (44)	0.4410 (26)	0.4073 (25)
C(13)	0.1461 (12)	0.0714 (9)	0.4630 (8)	C(13′)	0.3275 (13)	0.3816 (11)	0.5138 (7)
M(13)	0.1997 (33)	0.0783 (24)	0.5052 (20)	M(13′)	0.3066 (35)	0.4464 (29)	0.5014 (24)
C(14)	0.5922 (5)	0.2417 (4)	0.3024 (3)	C(14′)	−0.0800 (5)	0.2315 (3)	0.3020 (3)
C(15)	0.6363 (6)	0.2918 (4)	0.3385 (4)	C(15′)	−0.1264 (5)	0.2017 (4)	0.3504 (3)
C(16)	0.6475 (6)	0.3566 (4)	0.3119 (4)	C(16′)	−0.1429 (6)	0.1331 (4)	0.3483 (3)
C(17)	0.6190 (6)	0.3677 (4)	0.2503 (4)	C(17′)	−0.1147 (6)	0.0935 (4)	0.2985 (4)
C(18)	0.5777 (6)	0.3138 (4)	0.2146 (4)	C(18′)	−0.0745 (6)	0.1258 (4)	0.2498 (4)
C(19)	0.5637 (5)	0.2520 (4)	0.2419 (4)	C(19′)	−0.0564 (5)	0.1951 (4)	0.2528 (3)
C(20)	0.5165 (6)	0.1922 (4)	0.2112 (3)	C(20′)	−0.0116 (6)	0.2369 (4)	0.2044 (3)
C(21)	0.5923 (8)	0.1599 (5)	0.1688 (4)	C(21′)	−0.0890 (8)	0.2479 (6)	0.1507 (4)
C(22)	0.4130 (8)	0.2096 (5)	0.1763 (4)	C(22′)	0.0903 (8)	0.2035 (5)	0.1840 (5)
C(23)	0.6298 (8)	0.4381 (4)	0.2223 (5)	C(23′)	−0.1291 (8)	0.0172 (4)	0.2972 (5)
C(24)	0.7112 (15)	0.4283 (7)	0.1731 (8)	C(24′)	−0.2108 (15)	−0.0054 (5)	0.3389 (8)
M(24)	0.7449 (33)	0.4534 (22)	0.2278 (21)	M(24′)	−0.0747 (25)	−0.0083 (15)	0.3673 (14)
C(25)	0.5245 (12)	0.4594 (8)	0.1877 (9)	C(25′)	−0.1788 (15)	−0.0032 (6)	0.2297 (6)
M(25)	0.5822 (38)	0.4455 (22)	0.1649 (20)	M(25′)	−0.2333 (41)	−0.0017 (25)	0.2905 (24)
C(26)	0.6644 (14)	0.4909 (5)	0.2671 (6)	C(26′)	−0.0296 (12)	−0.0174 (6)	0.3035 (9)
M(26)	0.5561 (37)	0.4809 (22)	0.2574 (21)	M(26′)	−0.0808 (41)	−0.0176 (22)	0.2568 (22)
F(1)	0.6032 (4)	0.0393 (2)	0.4241 (2)	F(1′)	−0.0799 (4)	0.4720 (2)	0.3430 (2)
F(2)	0.7224 (4)	0.0802 (2)	0.4836 (2)	F(2′)	−0.1918 (4)	0.4603 (2)	0.4058 (2)
F(3)	0.5741 (4)	0.0604 (2)	0.5154 (2)	F(3′)	−0.0399 (4)	0.4924 (2)	0.4358 (2)
F(4)	0.5764 (4)	0.2656 (3)	0.4823 (2)	F(4′)	−0.0492 (4)	0.2892 (3)	0.4754 (2)
F(5)	0.5738 (4)	0.1882 (3)	0.5494 (2)	F(5′)	−0.0386 (4)	0.3868 (3)	0.5124 (2)
F(6)	0.7114 (5)	0.2129 (3)	0.5095 (2)	F(6′)	−0.1812 (4)	0.3500 (3)	0.4747 (2)
F(7)	0.6745 (4)	0.1390 (3)	0.1993 (2)	F(7′)	−0.1705 (4)	0.2788 (3)	0.1695 (2)
F(8)	0.5491 (4)	0.1047 (3)	0.1421 (2)	F(8′)	−0.0524 (4)	0.2842 (3)	0.1085 (2)
F(9)	0.6170 (4)	0.1995 (3)	0.1255 (2)	F(9′)	−0.1220 (4)	0.1903 (3)	0.1258 (2)
F(10)	0.3564 (4)	0.2454 (3)	0.2121 (2)	F(10′)	0.1505 (4)	0.1859 (3)	0.2319 (2)
F(11)	0.4236 (4)	0.2440 (3)	0.1268 (2)	F(11′)	0.0707 (4)	0.1493 (3)	0.1504 (2)
F(12)	0.3574 (4)	0.1548 (3)	0.1624 (2)	F(12′)	0.1419 (4)	0.2472 (3)	0.1524 (2)

[a] The sites referred to as M(11), etc., correspond to the minor sites for the atom C(11), etc. In the final structure factor calculation, the sites of C(11), C(12), and C(13) were given an occupancy of 0.67, those of M(11), M(12), and M(13) of 0.33, C(24), C(25), and C(26) had an occupancy of 0.69, M(24), M(25), and M(26) of 0.31, C(11′), C(12′), and C(13′) had an occupancy of 0.73, M(11′), M(12′), and M(13′) of 0.27, C(24′), C(25′), and C(26′) had an occupancy of 0.68, and M(24′), M(25′), and M(26′) of 0.32.

ment[24] gave an R factor of 0.158 and R_2 of 0.155.[25] At this stage a difference map revealed high electron density midway between the carbon atoms in all of the *tert*-butyl groups, indicating that the *tert*-butyl groups are disordered in the crystal. Together with refinement of the positional and anisotropic thermal parameters for the central carbon atoms of the *tert*-butyl groups, the occupancies and the positional parameters for the major and minor sites of the terminal carbon atoms were varied while their temperature factors were held constant (both sets of sites were given an average isotropic thermal parameter of 7.3 Å^2). This procedure gave an R factor of 0.139 and R_2 of 0.134, and the sums of the occupancies for the major and minor sites were reasonably near unity (0.95–1.13). The occupancies were scaled so that their sum equaled unity, and a further cycle of refinement on the *tert*-butyl carbon atoms was carried out. In this cycle, the positional and isotropic thermal parameters for the carbon atoms in the major and minor sites were varied while the occupancies were held constant, and the positional and anisotropic thermal parameters of the central carbon atoms in the *tert*-butyl groups were also refined. This procedure gave an R value of 0.133 and R_2 of 0.124. It was found that when both the temperature factors and occupancies were varied simultaneously, the results were unreasonable (*e.g.*, the sum of occupancies for major and minor sites was about 1.40 in some cases). In the final series of refinements, positional and anisotropic thermal parameters for all nonhydrogen atoms were varied, except in the cases of the terminal carbon atoms of the *tert*-butyl groups, where positions and anisotropic thermal parameters were varied for major sites, but positions and isotropic thermal parameters were varied for the minor sites. A single occupancy factor, the mean of those for the three methyl carbons, was given for each *tert*-butyl group. Once again the structure had to be divided into the four parts described previously, in order to carry out the refinement. The final R factor on all observed data was 0.094, and the final R_2 value was 0.088. A final difference map showed peaks corresponding to hydrogen atoms bonded to the phenyl rings, but the major and minor sites for the hydrogen atoms of the *tert*-butyl groups could not be discerned; there was no evidence for the presence of solvent molecules in the crystal. No attempt was made to include any hydrogen atoms in further calculations. The scattering curves were those compiled by

---

(24) Using a local modification of a program written by W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," Report ORNL-TM-305, Oak Ridge, Tenn., Aug 1962.

(25) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}$.

Cromer and Mann,[26] with appropriate corrections of the sulfur curve for anomalous dispersion,[27] and the one for hydrogen was that calculated by Stewart, *et al.*[28] The final coordinates are given in Table I. The temperature factors, as well as the observed and calculated structure factors, will appear in the microfilm edition.[29]

X-Ray Crystallography of Spirosulfurane Oxide 2. Spirosulfurane oxide **2** was recrystallized several times from petroleum ether to give needle-like white crystals. A single crystal of length 0.24 mm along the *b* direction and 0.21 × 0.07 mm in cross section was mounted along the *b* axis. No special precautions were necessary to protect the crystal from moisture.

Crystal Data for 2. $C_{26}H_{24}F_{12}O_3S$; M = 644.5; monoclinic; a = 13.824 (9), b = 12.231 (5), c = 20.846 (11) Å; β = 126°55′ (1′); V = 2818 Å^3; Z = 4; ρ_{calcd} = 1.52 g cm^{-3}, $F(000)$ = 1312; space group $P2_1/c$ from systematic absences, $h0l$, when $l = 2n + 1$, $0k0$, when $k = 2n + 1$; nickel-filtered Cu Kα X-radiation; λ 1.54178 Å; μ(Cu Kα) = 20.3 cm^{-1}.

The cell parameters were determined by a least-squares fit to the settings of the angles for 12 hand-centered reflections. All instrumental parameters were identical with those in the analysis of **1**. The intensities of the standards fell to about 90% of what they had been originally over the 7-day period of data collection. A total of 3005 symmetry-independent reflections was considered to be above background. Intensity data were normalized according to the periodic measurements of the standards. No correction was made for absorption or extinction.

Solution and Refinement of Structure 2. The structure was solved by the symbolic addition procedure using the FAME-SYMPL-MAGIC series of programs[30] and refined initially by Fourier methods. Two cycles of full-matrix least-squares refinement, in which the positional and isotropic thermal parameters were varied, gave R of 0.16 and R_2 of 0.18. The weights were calculated as described previously. At this stage anisotropic temperature parameters were introduced for all the nonhydrogen atoms. Refinement was carried out in two partial cycles due to computer storage limitations. One partial cycle consisted of the atoms C(1)–C(13), O(1), O(3), F(1)–F(6), and the sulfur atom, while the other consisted of the remaining atoms and the sulfur atom. After one complete cycle, R was 0.122 and R_2 was 0.096. A difference map calculated at this stage allowed positions to be assigned to only 12 of the 18 *tert*-butyl hydrogen atoms. After another complete refinement cycle on all atoms, so far located, the R factor was reduced to 0.079 and R_2 was 0.080. Another difference map indicated that there was some disorder in the positions of the hydrogen atoms of the *tert*-butyl groups but allowed positions to be assigned to the major sites for these hydrogen atoms. No attempt was made to include minor sites for these hydrogen atoms in the final refinement cycles. There was no evidence from the difference map for the presence of solvent molecules in the crystal. Four complete cycles of full-matrix least-squares refinement of positional and anisotropic thermal parameters for the nonhydrogen atoms and of the positions of the hydrogen atoms, while holding their isotropic thermal parameters constant at 4.0 Å^2, gave final values of R and R_2 of 0.072 and 0.069 on all observed reflections.

The scattering curves were the same as those used in the analysis of **1**. The final coordinates for **2** are listed in Table II. The temperature factors, as well as observed and calculated structure factors, will appear in the microfilm edition.[29]

Table II. Final Coordinates for the Molecule of **2**. Estimated Standard Deviations in Parentheses

	x	*y*	*z*
S(1)	0.0425 (1)	0.3804 (1)	0.6340 (1)
O(1)	0.1648 (3)	0.3172 (3)	0.7240 (2)
O(2)	−0.0885 (3)	0.4257 (3)	0.5402 (2)
O(3)	0.0925 (3)	0.4887 (3)	0.6586 (2)
C(1)	0.0762 (4)	0.2931 (4)	0.5812 (3)
C(2)	0.0129 (5)	0.2823 (5)	0.4991 (3)
C(3)	0.0512 (5)	0.2082 (5)	0.4690 (3)
C(4)	0.1540 (5)	0.1433 (4)	0.5182 (3)
C(5)	0.2180 (5)	0.1578 (5)	0.6003 (3)
C(6)	0.1805 (4)	0.2304 (4)	0.6316 (3)
C(7)	0.2423 (4)	0.2527 (4)	0.7191 (3)
C(8)	0.3623 (5)	0.3143 (5)	0.7565 (4)
C(9)	0.2624 (6)	0.1480 (6)	0.7659 (4)
C(10)	0.1901 (5)	0.0617 (5)	0.4817 (3)
C(11)	0.3055 (8)	−0.0029 (7)	0.5455 (6)
C(12)	0.0973 (10)	−0.0200 (12)	0.4343 (9)
C(13)	0.2163 (12)	0.1230 (8)	0.4300 (7)
C(14)	−0.0576 (4)	0.3290 (4)	0.6549 (3)
C(15)	−0.0265 (5)	0.2642 (5)	0.7191 (3)
C(16)	−0.1146 (5)	0.2362 (5)	0.7278 (3)
C(17)	−0.2355 (4)	0.2714 (4)	0.6736 (3)
C(18)	−0.2622 (5)	0.3351 (5)	0.6106 (3)
C(19)	−0.1765 (4)	0.3628 (4)	0.6004 (3)
C(20)	−0.1957 (4)	0.4266 (4)	0.5326 (3)
C(21)	−0.2298 (5)	0.5463 (5)	0.5327 (4)
C(22)	−0.2919 (5)	0.3735 (5)	0.4504 (3)
C(23)	−0.3293 (5)	0.2384 (5)	0.6856 (3)
C(24)	−0.4490 (5)	0.2992 (6)	0.6295 (4)
C(25)	−0.3505 (7)	0.1168 (8)	0.6689 (6)
C(26)	−0.2815 (9)	0.2577 (10)	0.7708 (6)
F(1)	0.3439 (3)	0.4042 (3)	0.7158 (2)
F(2)	0.4127 (3)	0.3424 (3)	0.8315 (2)
F(3)	0.4427 (3)	0.2542 (3)	0.7569 (2)
F(4)	0.1606 (3)	0.0905 (3)	0.7306 (2)
F(5)	0.3428 (3)	0.0808 (3)	0.7708 (2)
F(6)	0.3010 (3)	0.1689 (3)	0.8396 (2)
F(7)	−0.1435 (3)	0.5936 (2)	0.6012 (2)
F(8)	−0.2469 (3)	0.6042 (3)	0.4733 (2)
F(9)	−0.3323 (3)	0.5528 (3)	0.5262 (2)
F(10)	−0.2658 (3)	0.2686 (3)	0.4519 (2)
F(11)	−0.4023 (3)	0.3777 (3)	0.4325 (2)
F(12)	−0.2976 (3)	0.4180 (3)	0.3912 (2)
H(2)	−0.053 (3)	0.331 (3)	0.465 (2)
H(3)	0.012 (3)	0.203 (3)	0.413 (2)
H(5)	0.286 (3)	0.109 (3)	0.636 (2)
H(11A)	0.338 (3)	−0.048 (3)	0.510 (2)
H(11B)	0.362 (3)	0.059 (3)	0.555 (2)
H(11C)	0.259 (3)	−0.046 (3)	0.562 (2)
H(12A)	0.024 (4)	0.001 (4)	0.408 (3)
H(12B)	0.114 (4)	−0.058 (3)	0.403 (2)
H(12C)	0.076 (5)	−0.038 (4)	0.466 (3)
H(13A)	0.281 (4)	0.104 (4)	0.481 (3)
H(13B)	0.148 (4)	0.162 (3)	0.390 (2)
H(13C)	0.252 (3)	0.078 (3)	0.409 (2)
H(15)	0.054 (3)	0.239 (3)	0.758 (2)
H(16)	−0.098 (3)	0.193 (3)	0.764 (2)
H(18)	−0.333 (3)	0.361 (3)	0.582 (2)
H(24A)	−0.501 (3)	0.272 (3)	0.642 (2)
H(24B)	−0.477 (3)	0.264 (3)	0.571 (2)
H(24C)	−0.432 (3)	0.372 (3)	0.643 (2)
H(25A)	−0.283 (4)	0.084 (3)	0.702 (2)
H(25B)	−0.409 (4)	0.100 (3)	0.679 (2)
H(25C)	−0.402 (4)	0.109 (4)	0.616 (2)
H(26A)	−0.211 (3)	0.229 (3)	0.807 (2)
H(26B)	−0.282 (3)	0.335 (3)	0.778 (2)
H(26C)	−0.345 (3)	0.260 (3)	0.773 (2)

Results

Spirosulfurane 1. Figures 1a and b show views of the two independent molecules of **1**. Table III contains a summary of the important bond lengths and angles in **1** and **2**. Complete lists will appear in the microfilm edition.[29]

Problems associated with handling a very large structure coupled with extensive disorder of the *tert*-butyl groups have resulted in a less well-refined structure for **1** than for **2**. The methyl carbon atoms of the *tert*-butyl groups occupy two sets of sites in the crystal, a major set occupied in 67–73% of the unit cells, and a minor one 27–33% of the cells. This disorder cor-

---

(26) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

(27) D. H. Templeton in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 213–216.

(28) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(29) See note at end of paper regarding supplementary material.

(30) (a) E. B. Fleisher, R. B. K. Dewar, and A. L. Stone, Abstracts American Crystallographic Association, Atlanta, Ga., Jan 1967, Paper A7, p 20; (b) R. B. K. Dewar, Ph.D. Thesis, University of Chicago, Chicago, Ill., 1968.

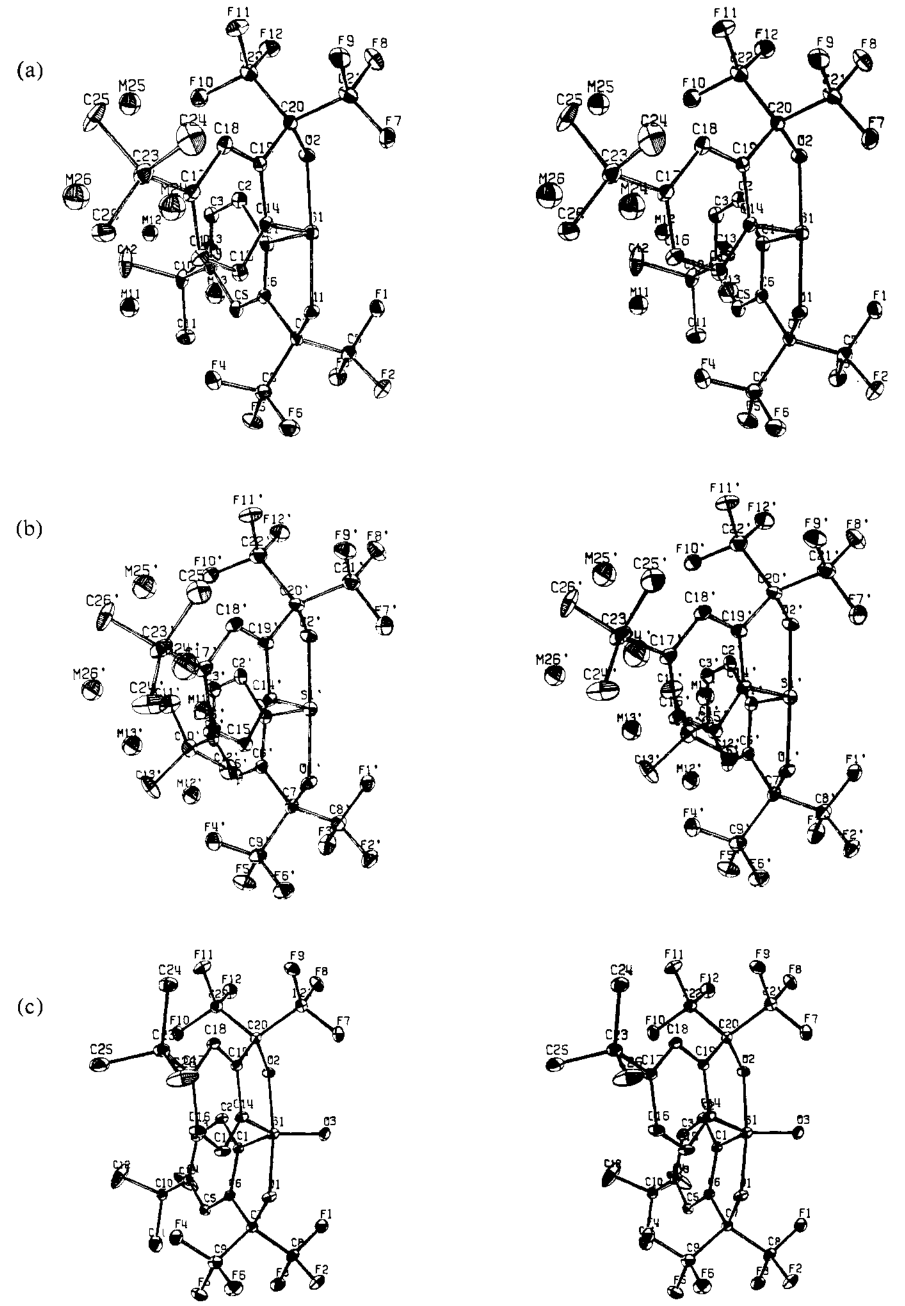


Figure 1. Stereoscopic views of the two crystallographically independent molecules of **1** and **2**: (a) the unprimed molecule of **1**, (b) the primed molecule of **1**, (c) the sulfurane oxide **2**. In no case are hydrogen atoms shown. Both major and minor sites are shown for **1**, but the bonds are joined only for the major sites.

responds to rotation about the C(phenyl)–C(*tert*-butyl) bond. These figures were based on the refinement of occupancies by the least-squares method. However, a final difference synthesis indicates significant electron density between major and minor sites, possibly arising from several other minor sites for the methyl carbon atom. The root mean square deviation among the 24 C–C(aromatic) bond lengths in **1** is 0.023 Å (*cf.* average esd from least squares of 0.012 Å), while the rms deviation among the 24 C–F bond lengths is 0.017 Å (*cf.* average esd from least squares of 0.012 Å).

The configuration about the sulfur atom in spirosulfurane **1** may be thought of as a distorted trigonal bipyramid. The carbon atoms adjacent to sulfur in the phenyl rings occupy the equatorial plane with C–S–C angles of 107.6 (3)° (and 108.1 (4)°) for the two independent molecules. (In this discussion values for the unprimed molecule of **1** will be followed, in parentheses, by values for the primed molecule.) The six carbon atoms making up each of the phenyl rings are coplanar with the accuracy of the analysis and these planes make angles of 110°36′ (108°42′) with each other. The sulfur atom does not lie in the phenyl ring planes but is displaced 0.093 (2) and 0.021 (2) Å (0.10 (2) and 0.184 (2) Å) on the side of the plane occupied by the lone pair of electrons. The apical positions of the trigonal bipyramid are occupied by the two oxygen atoms with O–S–O angles of 177.1 (2)° (178.2 (2)°). The distortion from linearity of the oxygen atoms is in the direction of the equatorial phenyl rings and away from the lone pair. The O–S–C angles range from 85.8 (3) to 92.4 (3)°. The plane drawn through the O–S–O atoms was found to inter-

Table III. A Summary of Some of the Important Bond Lengths (Å) and Angles (deg) in the Molecules of **1** and **2**

	1		
	Unprimed	Primed	**2**
Bonds Endocyclic to the Five-Membered Ring			
S–O (apical)	1.832 (5)	1.831 (5)	1.780 (5)
	1.819 (5)	1.816 (5)	1.777 (5)
S–C (equatorial)	1.787 (8)	1.798 (8)	1.784 (5)
	1.803 (8)	1.803 (7)	1.796 (6)
C(aromatic)–C(aromatic)	1.359 (11)	1.383 (11)	1.396 (8)
	1.390 (11)	1.373 (11)	1.385 (8)
C(aromatic)–C(sp^3)	1.518 (11)	1.513 (12)	1.504 (8)
	1.489 (11)	1.517 (11)	1.492 (8)
C–O	1.390 (9)	1.392 (9)	1.382 (7)
	1.385 (9)	1.375 (10)	1.392 (7)
Other Bonds			
S–O (equatorial)			1.439 (4)
C–F (av)	1.33 ± 0.01	1.33 ± 0.02	1.33 ± 0.01
C(phenyl)–C(phenyl) av	1.41 ± 0.04	1.41 ± 0.04	1.38 ± 0.01
Bond Angles			
O(apical)–S–O(apical)	177.1 (2)	178.2 (2)	172.3 (2)
O(apical)–S–O(equatorial)			94.3 (2)
			93.4 (2)
C–S–O (endo)	85.8 (4)	86.5 (3)	87.4 (2)
	87.2 (3)	86.7 (3)	87.2 (2)
C–S–O (exo)	91.3 (3)	92.2 (3)	88.6 (2)
	92.2 (3)	92.4 (3)	88.8 (2)
C–S–C	108.1 (4)	107.6 (3)	117.7 (3)
C–O–S	114.2 (4)	113.7 (3)	117.2 (3)
	114.2 (4)	115.3 (5)	116.1 (3)
C–C–O (endo)	107.5 (4)	108.9 (6)	107.0 (3)
	108.5 (6)	107.0 (4)	108.4 (4)
S–C–C (endo)	115.5 (7)	114.8 (5)	113.5 (3)
	112.8 (3)	113.3 (3)	113.8 (3)

sect the plane drawn through the C–S–C atoms at an angle of 86°49′ (86°30′).

There are no short (≤3.6 Å) intermolecular contacts involving the sulfur atom (see microfilm edition for complete listing). The closest sulfur to sulfur contact is 5.979 (3) Å. The S···F intramolecular distances S(1)···F(1) and S(1)···F(8) are 3.219 (5) and 3.248 (5) Å, respectively, which are slightly longer than the sum of the appropriate van der Waals radii (3.20 Å)[31a] indicating little bonding interaction between sulfur and fluorine.

Spirosulfurane Oxide 2. Figure 1c shows a stereoscopic view of the molecule of **2** in the same orientation as spirosulfurane **1**. Certain bond lengths and angles are listed in Table III.

It was found in the latter stages of the analysis that several of the hydrogen atoms around the *tert*-butyl groups were disordered. The hydrogen atoms were refined at the major sites, and no attempt was made to include minor sites for the hydrogen atoms in any calculations.

The configuration about the sulfur atom in spirosulfurane oxide **2** closely approaches a trigonal bipyramid. The carbon atoms in the equatorial plane make a C–S–C angle of 117.7 (3)° and make O–S–C angles with the oxygen in the equatorial plane of 121.5 (3) and 120.7 (2)°. The four atoms C(1), C(10), S(1), and O(3) form a plane within the accuracy of the analysis. This plane intersects the plane formed by the oxygens O(1) and O(2) at the apices of the trigonal bipyramid and the sulfur atom at an angle of 89°12′. The phenyl rings are planar within the accuracy of the analysis and these planes intersect at an angle of 118°40′. The sulfur atom does not lie in the planes of the phenyl rings but is displaced from them by 0.039 (2) and 0.086 (1) Å in the general direction away from the equatorial oxygen, O(3), and toward the phenyl ring C(10)–C(15).

There are no short intermolecular contacts involving the sulfur atom and in neither **1** nor **2** is there any indication of any specific intermolecular interaction. Both **1** and **2** appear to exist as molecular crystals. Each apical oxygen atom is involved in four short O···F intramolecular contacts. The range of distances (2.68–2.80 Å) is virtually equal to the sum of the appropriate van der Waals radii (2.75 Å),[31a] possibly indicating a very weak nonbonded interaction.

The apical S–O bond lengths, 1.780 (5) and 1.777 (5) Å, in **2** are identical within the standard deviations from the least-squares refinement. The equatorial S–O bond length in **2** is 1.439 (4) Å.

Inspection of Figure 1 shows an interesting difference in the two crystallographically independent molecules of **1**. The primed molecule has almost exact C_2 symmetry, whereas in the unprimed molecule this symmetry is prevented by the relationship of the major sites for the terminal carbon atoms of the *tert*-butyl groups. The sulfurane oxide **2** also has almost exact C_2 symmetry.

Discussion

The Apical S–O Bonds. Sulfuranes **1**, **4**, and **5** and sulfurane oxide **2** all have distorted trigonal bipyramidal geometry about sulfur with apical S–O bonds significantly longer than the sum of the sulfur and oxygen covalent radii (1.70 Å).[31b] The S–O bonds in acyclic sulfurane **5** are *ca.* 1.90 Å in length,[10] in spirosulfurane **1**, *ca.* 1.82 Å, and in spirosulfurane oxide **2**, *ca.* 1.78 Å. Bond orders, calculated from Pauling's[32] equation relating bond order and bond length, for the apical S–O bonds of **5**, **1**, and **2** are 0.46, 0.62, and 0.74.

The geometric features enumerated above are consistent[10] with a bonding scheme in which the apical ligands are considered to be attached to sulfur by four-electron three-center (hypervalent) bonds.[10,33–35] Earlier papers in this series[1,3,4,7,10] have discussed the chemistry and geometry of sulfuranes with reference to this bonding scheme, so we will not discuss the idea in detail here. The suggestion that d orbitals or other high-energy atomic orbitals on the central atom (sulfur in this case) are not extensively involved in the apical bonding of this class of compounds has received experimental support from several quarters,[36] including studies using nuclear quadrupole resonance,[37] photoelectron spectroscopy,[38] and Mössbauer spectroscopy.[39] Theoretical studies have generally supported the same

---

(31) (a) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260; (b) *ibid.*, pp 221–228.

(32) L. Pauling, *J. Amer. Chem. Soc.*, **69**, 542 (1947).

(33) R. E. Rundle, *Surv. Progr. Chem.*, **1**, 81 (1963).

(34) (a) J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969); (b) J. I. Musher, *Advan. Chem. Ser.*, **No. 110**, 44 (1972); (c) J. I. Musher, *Science*, **141**, 736 (1963).

(35) For a general discussion of trigonal bipyramidal molecules see E. L. Muetterties and R. A. S. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966).

(36) J. G. Malm, H. Sellig, J. Jortner, and S. A. Rice, *Chem. Rev.*, **65**, 199 (1965).

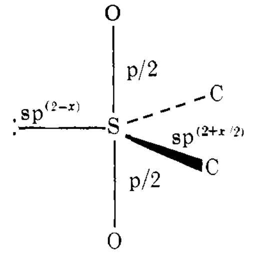
(37) C. D. Cornwell and R. S. Yamasaki, *J. Chem. Phys.*, **27**, 1060 (1957).

(38) B. Brehm, M. Menzinger, and C. Zorn, *Can. J. Chem.*, **48**, 3193 (1970).

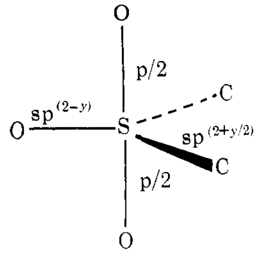
(39) B. S. Ehrlich and M. Kaplan, *J. Chem. Phys.*, **54**, 612 (1970).

viewpoint.[40,41] Charge distribution[42,43] in hypervalent molecules might be expected[40] to be the molecular property most sensitive to contributions from higher atomic orbitals. This has been discussed in an earlier paper in this series.[42]

The bonding in sulfuranes can then be described in a zero-order approximation by a bonding model (**9**) which pictures the equatorial C–S bond as sp^2 hybridized, on the average, with the lone pair of electrons occupying one of the orbitals while the apical S–O bonds are best described as p/2. A similar description (**10**) is advanced for the sulfurane oxides, substituting oxygen for the lone pair of electrons.

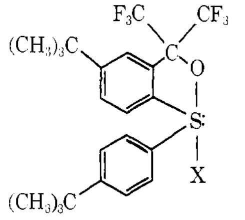


9



10

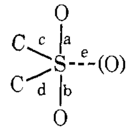
The order, based on length, found for the S–O bonds of **1** and **5** is consistent with that inferred from the relative reactivities of cyclic and acyclic sulfuranes in dissociative apical ligand exchange reactions.[1,3,42] The stabilizing effect of a five-membered ring which includes an electronegative apical oxygen ligand and a relatively electropositive equatorial ligand to sulfurane sulfur is reflected not only in shorter S–O bond lengths but also in the great hydrolytic stability of **1**. The slowing by several orders of magnitude of the rates of exocyclic apical ligand exchange in monocyclic sulfuranes of type **11** is presumably attributable to the same or closely related factors.[3]



11

It is of interest to examine, in Table IV, a partial representation of the known molecular geometries of compounds of hypervalent sulfur which contain apical oxygen ligands, with an eye for structural features which might lead to a better understanding of this five-membered ring effect, which so dramatically stabilizes cyclic sulfuranes.

Table IV. A Comparison of Bond Lengths and Bond Angles about Sulfur in Sulfuranes and Sulfurane Oxides



	Compound				
	1[a]	**1**[b]	**2**	**5**[c]	**4**[d]
a (Å)	1.819	1.816	1.777	1.916	1.83
b (Å)	1.832	1.831	1.780	1.889	1.83
c (Å)	1.803	1.803	1.796	1.810	1.82
d (Å)	1.787	1.798	1.784	1.803	1.82
e (Å)			1.439		
∠ab (deg)	182.9[e]	181.8	187.7	184.9	181.5
∠cd (deg)	108.1	107.6	117.7	104.4	107.8
∠ae (deg)			94.3		
∠be (deg)			93.4		

[a] Unprimed molecule in the unit cell. [b] Primed independent molecule. [c] Reference 10. [d] Reference 9. [e] In this table the angle *ab* is defined as including either the equatorial oxygen atom or the sulfur lone pair of electrons.

The apical S–O bonds of these hypervalent sulfur species are not exactly collinear. In each case[45] the O–S–O angle is bent *away* from the lone pair (or equatorial oxygen), *toward* the equatorial phenyl rings. Magnitudes of the deviations from linearity are in the order **2** (7.7°) > **5** (4.9°) > **1** (2.9 or 1.8°). These deviations can be rationalized by considering the repulsive interactions[40c,46] between π-donor ligands and the apical ligand bonding electrons in **2** and between the sulfur lone pair and the apical ligand bonding electrons

---

(40) (a) A. Rauk, L. C. Allen, and K. Mislow, *J. Amer. Chem. Soc.*, **94**, 3035 (1972); (b) J. B. Florey and L. C. Cusachs, *ibid.*, **94**, 3040 (1972); (c) R. Hoffmann, J. M. Howell, and E. L. Muetterties, *ibid.*, **94**, 3047 (1972); (d) J. I. Musher, *ibid.*, **94**, 1370 (1972); (e) P. C. Van Der Voorn and R. S. Drago, *ibid.*, **88**, 3255 (1966); (f) for a somewhat different view, see I. Ugi and F. Ramirez, *Chem. Brit.*, 198 (1972). See also R. Gleiter and R. Hoffmann, *Tetrahedron*, **24**, 5899 (1968).

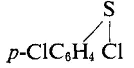
(41) (a) Discussed by F. A. Cotton and G. Wilkinson in "Advanced Inorganic Chemistry—A Comprehensive Text," Interscience, New York, N. Y., 1962, p 412; (b) D. P. Craig and E. A. Magnusson, *Discuss. Faraday Soc.*, **No. 26**, 116 (1958); (c) see, however, D. W. J. Cruickshank, B. C. Webster, and D. F. Mayers, *J. Chem. Phys.*, **40**, 3733 (1964).

(42) L. J. Kaplan and J. C. Martin, *J. Amer. Chem. Soc.*, **95**, 793 (1973).

(43) Microwave techniques have been used[44a] to determine the molecular quadrupole moment of SF_4, showing the apical fluorines to be negatively charged and the equatorial ones positively charged, as predicted by hypervalent bonding theory. Results of an X-ray photoelectron study[44b] have sketched out patterns of charge distribution in PF_5, SF_4, and ClF_3 parallel to those from the microwave study. It is interesting that the amount of negative charge on the apical fluorines does not change in the series PF_5, SF_4, ClF_3, leading to the conclusion[44b] that ". . . the PF_3, SF_2 and ClF fragments, in which the bonds are all two-center, two-electron bonds, appear to the axial fluorines as pseudoargon centers; hence the axial fluorines bond to these centers with nearly the same redistribution of charge."

(44) (a) R. G. Stone, H. L. Tigelaar, and W. H. Flygare, *J. Chem. Phys.*, **53**, 3947 (1970); (b) R. W. Shaw, Jr., T. X. Carroll, and T. D. Thomas, *J. Amer. Chem. Soc.*, **95**, 5870 (1973).

(45) Indeed this is general for sulfuranes containing apical halogens as well, with the apparent exception of dichlorosulfurane **12** which, in the crystal, has its Cl–S–Cl axis bent toward the lone pair (in an X-ray crystallographic structure determined by N. C. Baenziger, R. E. Buckles, R. J. Maner, and T. D. Simpson, *J. Amer. Chem. Soc.*, **91**, 5749 (1969)). Evidence for possible weak intermolecular interactions between a sulfur atom and a chlorine atom in an adjacent molecule in the unit cell is provided by some short intermolecular contacts. Intermolecular chlorine–chlorine interactions also appear to be possible contributors to the anomalous geometry of **12** in the crystal.

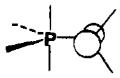


12

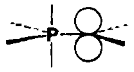
(46) (a) S. C. Peake and R. Schmutzler, *Chem. Commun.*, 1662 (1968); (b) *J. Chem. Soc. A*, 1049 (1970); (c) M. A. Landau, V. V. Sheluchenko, G. I. Drozd, S. S. Dubov, and S. Z. Ivin, *Zh. Strukt. Khim.*, **8**, 1097 (1967); (d) V. V. Sheluchenko, M. A. Sokal'skii, M. A. Landau, G. I. Drozd, and S. S. Dubov, *ibid.*, **10**, 142 (1969); (e) M. A. Sokal'skii, G. I. Drozd, M. A. Landau, and S. S. Dubov, *ibid.*, **10**, 1113 (1969); (f) J. S. Harman and D. W. A. Sharp, *Inorg. Chem.*, **10**, 1538 (1971); (g) G. M. Whitesides and H. L. Mitchell, *J. Amer. Chem. Soc.*, **91**, 5384 (1969); (h) E. L. Muetterties, P. Meakin, and R. Hoffmann, *ibid.*, **94**, 5674 (1972).

in sulfuranes **1**, **4**, and **5**, following the suggestion of Gillespie.[47]

Experimental[40c] and theoretical[40] bases exist for the assertion that equatorial π-donor ligands in phosphoranes have a preferred orientation with the donor p orbital in the equatorial plane, as in **13**. This has been explained[41c] in terms of angular dependence of the destabilizing interactions between a filled p orbital of the π-donor ligand and filled orbitals of the phosphorane σ-bond skeleton. These repulsive interactions are more important in the conformation in which the p-orbital axis is parallel with the apical axis of the molecule, as in **14**.



13



14

The apical F–S–F angle is more nearly linear for SF_4O (184.4°) than for SF_4 (186.1°); the angle is defined to include the equatorial oxygen atom (see Table IV). In contrast, sulfurane oxide **2** has a more bent O–S–O angle (187.7°) than does its sulfurane analog **1** (182.4°). Two geometric features of these molecules might be invoked to explain this curious inversion.

(a) If the bending of the apical F–S–F angle away from the equatorial oxygen of SF_4O reflects the relief of repulsive interactions between the apical σ-bond electrons and the oxygen lone pair in a parallel p orbital, the distortion which relieves this repulsive interaction must simultaneously increase the analogous interaction between the apical σ-bond electrons and lone pairs on equatorial fluorine atoms, thus opposing the distortion.

The analogous distortion of the sulfurane oxide to relieve interactions with lone pairs on the equatorial oxygen is larger because the equatorial phenyl ligands are constrained to a geometry in which the p orbitals of the π-system are perpendicular to the apical axis (Figure 1c), thus minimizing the repulsive interaction with the apical bonds. The exocyclic C–S–O apical angles (88.8 and 88.6°) are larger than the endocyclic ones (87.2 and 87.4°) but both are smaller than 90°, reflecting the reduction of repulsive interactions which results from the favorable angles of twist of the phenyl rings in this compound. The inclusion of two trigonal carbons, with their associated ideal 120° angles (the S–C–C and the C–C–C angles), in the five-membered ring also tends to compress the endocyclic C–S–O angle.

(b) Another geometric feature of **2** which allows a greater deviation from linearity for the apical bonds than is found for spirosulfurane **1** is related to the larger C–S–C angles found in the sulfurane oxide (117.7° *vs.* 107.6 or 108.1°). The resulting greater separation between the five-membered rings of **2** allows the deformation of the trigonal bipyramid which accompanies O–S–O bending to be accomplished without incurring prohibitive repulsive interactions between the endo-CF_3 groups and the aromatic protons ortho to sulfur (*e.g.*, H(2)···F(10) and F(12)). Such interactions are clearly important in **1**. The relevant intramolecular H···F contacts are 2.63 and 2.59 Å, approximately the same as the sum of the appropriate van der Waals radii (2.55 Å).[31a] The values of the C–C–F angles in the two molecules of **1** are larger for the endo-CF_3 groups (111.7, 112.3, 111.6, and 113.2°) than for the exo-CF_3 groups (110.5, 109.9, 110.4, and 109.0°), supporting the importance of these interactions in **1**.

The π-donor equatorial phenyl ligands of **1** and one of the phenyl rings of **11** are constrained to the geometry, represented by **13** in the phosphorane series, which minimizes the repulsions between apical ligand σ-bonding electrons and the phenyl π-system. In acyclic sulfurane **5**, however, steric interactions between ortho protons of the equatorial phenyl rings and the apical ligands[48] force a twisting of the two phenyl rings to within 32.4 and 42.5° of the equatorial plane.[10] This geometry greatly increases the repulsive interactions between the phenyl π-electrons and the apical bonding electrons, an interaction relieved in part by an elongation, with concomitant weakening, of the S–O bonds. This steric factor, in combination with other steric factors, with the entropy factors which favor associations involving bidentate ligands, and with the possible influences of angle strain discussed elsewhere,[2] is expected to contribute to the greatly enhanced stabilities of the cyclic sulfuranes of this study.

The sixfold barrier for internal rotation about the apical bond joining a π-donor apical ligand to phosphorane phosphorus is expected[40c] to be low in energy. The lower symmetry about sulfurane sulfur necessitates a consideration of the possibility that the existence of a twofold barrier of appreciable size, analogous to that in the hydrogen peroxide molecule,[49] for rotation about the apical S–O bonds of our sulfuranes might provide a major determinant of bond strength in molecules of fixed geometry. In Table V we list values of a torsion angle, θ, the angle between a C–S–O plane and a plane determined by C, S, and the sulfur lone pair (assumed to lie along the C–S–C bisector) for the sulfuranes of this study and **5**. One might expect an energy maximum for conformations with θ approximately 90°, a geometry analogous to the high energy coplanar conformations of hydrogen peroxide.[49] The observation that the geometry of **1** appears to coincide more nearly with that of this probable energy maximum than does that of **5** renders unlikely an explanation for the greater S–O bond strength of **1** based on this sort of angular dependent electron–electron repulsion.

The S–O (Equatorial) Bond of Spirosulfurane Oxide 2. This S–O bond (1.439 (4) Å) is slightly longer than that reported for OSF_4 (1.422 (8),[17a] 1.413 (1),[17b] or 1.403 (3)[18] Å). It is, however, considerably shorter than the S–O bond lengths found in sulfoxides, for example, diphenyl sulfoxide (1.473 (16) Å),[50] *cis*-9-methylthioxanthene 10-oxide (1.492 (3) Å),[51] *trans*-thioxanthen-9-ol

---

[47] (a) R. J. Gillespie, *J. Chem. Phys.*, **37**, 2498 (1962); (b) *Inorg. Chem.*, **5**, 1634 (1966); (c) *Can. J. Chem.*, **39**, 318 (1961); (d) *ibid.*, **38**, 818 (1960); (e) see, however, A. W. Searcy, *J. Chem. Phys.*, **31**, 1 (1959).

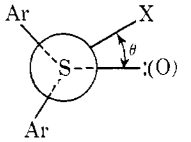
[48] A high barrier for rotation about the S-phenyl bond of (pentafluorophenyl)sulfur trifluoride has been deduced from nmr studies. W. A. Sheppard and D. W. Ovenall, *Org. Magn. Resonance*, **4**, 695 (1972).

[49] R. Curci and J. O. Edwards in "Organic Peroxides," Vol. I, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1970, p 201.

[50] S. C. Abrahams, *Acta Crystallogr.*, **10**, 417 (1957).

[51] J. Jackobs and M. Sundaralingam, *Acta Crystallogr., Sect. B*, **25**, 2487 (1969).

Table V. Torsion Angles, θ, for Acyclic Sulfurane **5**, Spirosulfurane **1**, and Spirosulfurane Oxide **2**



where $X = -C(CF_3)_2-$ for 1 and **2**
$X = -C(CF_3)_2C_6H_5$ for **5**

Compound	θ (deg)	Plane 1[a]	Plane 2[a]
5	21.9	C(1)–O(1)–S(1)	O(1)–S(1)–lone pair[b]
5	24.2	C(10)–O(2)–S(1)	O(2)–S(1)–lone pair
1	107.4[c]	C(20)–O(2)–S(1)	O(2)–S(1)–lone pair[b]
1	105.5[c]	C(7)–O(1)–S(1)	O(1)–S(1)–lone pair
1	107.2[d]	C(20′)–O(2′)–S(1′)	O(2′)–S(2′)–lone pair
1	106.0[d]	C(7′)–O(1′)–S(1′)	O(1′)–S(1′)–lone pair
2	106.7	C(20)–O(2)–S(1)	O(2)–S(1)–O(3)
2	109.1	C(7)–O(1)–S(1)	O(1)–S(1)–O(3)

[a] Atom numbering schemes for **1** and **2** are shown in Figure 1. Those for sulfurane **5** may be found in ref 10. [b] Lone pair positions are calculated by assuming the lone pair to lie along the equatorial C–S–C bisector. [c] Unprimed molecule. [d] Primed molecule.

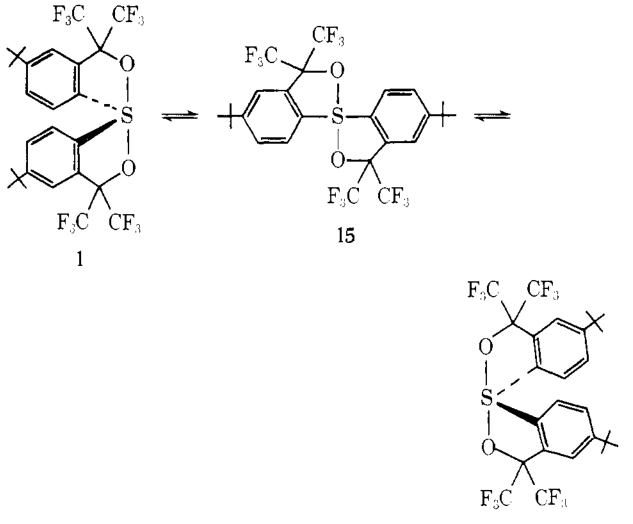
oxide (1.484 (8) Å),[52] and β-thianthrene dioxide (1.479 (16) and 1.474 (16) Å).[53] It is close in length to the S–O bond lengths in bis(p-chlorophenyl)sulfone (1.432 (5) Å),[54] bis(p-aminophenyl)sulfone (1.44 and 1.45 Å),[55,56] bis(p-iodophenyl)sulfone (1.43 Å),[57] and dimesitylsulfone (1.413 (10) and 1.410 (6) Å).[58] This similarity suggests pπ–dπ bonding between sulfur and oxygen similar to that usually invoked[59] for sulfones. On the other hand, the change in hybridization in the σ-bond from sulfur to oxygen from *ca.* sp^3 in the sulfone to *ca.* sp^2 in **2** might have been expected[60] to result in some bond shortening.

The C–S–C Angle. The C–S–C angles for acyclic sulfurane **5** and spirosulfuranes **4** and **1** (104.4 (3), 107.8 (8), and 108.1 (4)°, respectively) are smaller than the equatorial angle of 120° in a regular trigonal bipyramid. If the unshared electrons on sulfur tend to utilize a higher proportion of the lower energy s orbitals[61] at the expense of the p orbitals (in **9**, $x > 0$), the resulting increase in p character in the two equatorial bonds of a sulfurane is expected to decrease the angle between the equatorial bonds. When an equatorial oxygen replaces the lone pair, on going to the sulfurane oxide, this influence on geometry is removed (in **9** and **10**, $x > y$) and the C–S–C angle opens out toward 120° (to 117.7°) as expected.

As the electronegativity of the apical substituents bonded to the sulfur atom increases in acyclic sulfuranes, the C–S–C angle decreases[10] toward 90°. For example, in examining the series of compounds $(p\text{-}BrC_6H_4)_2S$,[62] the chlorosulfurane **12**,[45] and the acyclic sulfurane **5**,[10] the C–S–C angle decreases from 109.5 (5) to 108.6 (4) to 104.4 (3)°.

This trend has been explained[10] in terms of an increase in effective nuclear charge on sulfur with increasing electronegativity of the apical substituents accentuating the preference for s character in the lone pair orbital. It must be pointed out that the C–S–C angles of spirosulfurane **1** (108.1 (4)°) and **4** (107.8 (8)°) do not fit in this regular progression. However, the gross geometrical differences in these molecules, with the equatorial phenyl rings held rigidly perpendicular to the C–S–C plane makes direct comparisons with the acyclic sulfuranes of doubtful validity.

High Temperature Studies of Spirosulfurane 1. The stability of chiral sulfurane **1** toward inversion was demonstrated by observing a solution of sulfurane **1** in hexamethylphosphoramide by ^{19}F nmr over the temperature range 42–200°. The ^{19}F–^{19}F spin–spin coupling was still observable at 200° (two quartets with J = 9 Hz, only slightly broadened at 200°). Inversion of spirosulfurane **1** to give its enantiomer through planar transition state **15** must proceed with a rate constant[63] less than 20 sec^{-1} ($\Delta G^* > 25.3$ kcal/mol) at 200°. Similar results were obtained in solvents bromobenzene or dibenzyl ether (over smaller temperature ranges).



1 15 1

These data may be compared with data for inversion of sulfonium ions. Sulfonium salt **16** was found[64] to undergo inversion with a coalescence temperature of 200 ± 5° in benzophenone. Andersen, *et al.*,[64] calculated a rate of 17.8 sec^{-1} for the process and a free energy of activation of 25.4 kcal/mol. Scartazzini and Mislow[65] found a ΔH^* for racemization of 1-adamantylethylmethylsulfonium perchlorate of 26 kcal/mol and a ΔS^* of 8 eu, and ruled out mechanisms other

---

(52) A. L. Ternay, Jr., D. W. Chasar, and M. Sax, *J. Org. Chem.*, **32**, 2465 (1967).

(53) S. Hosoya, *Acta Crystallogr.*, **21**, 21 (1966).

(54) J. G. Sime and S. C. Abrahams, *Acta Crystallogr.*, **13**, 1 (1960).

(55) C. Dickinson, J. M. Stewart, and H. L. Ammon, *Chem. Commun.*, 920 (1970).

(56) Similar values may be calculated from the data of M. Alleaume and J. Decap, *C. R. Acad. Sci.*, **261**, 1693 (1965).

(57) C. Keil and K. Plieth, *Z. Kristallogr.*, **106**, 388 (1955).

(58) S. A. Chawdhury and A. Hargreaves, *Acta Crystallogr., Sect. B*, **27**, 548 (1971).

(59) (a) H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951); (b) J. R. Van Wazer and I. Absar, *Advan. Chem. Ser.*, **No. 110**, 20 (1972).

(60) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 150.

(61) See, for example, H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

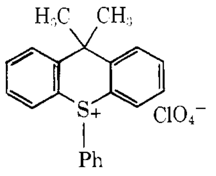
(62) J. Toussaint, *Bull. Soc. Chim. Belg.*, **54**, 319 (1945).

(63) (a) R. S. Drago, "Physical Methods in Inorganic Chemistry," Van Nostrand-Reinhold, New York, N. Y., 1965, pp 281–285; (b) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 223.

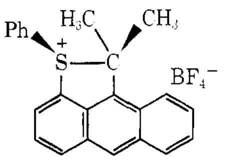
(64) K. K. Andersen, M. Cinquini, and N. E. Papanikolaou, *J. Org. Chem.*, **35**, 706 (1970).

(65) R. Scartazzini and K. Mislow, *Tetrahedron Lett.*, 2719 (1967).

than inversion for the process. Darwish and Tourigny[66] reported the racemization rate for *tert*-butylethylmethylsulfonium perchlorate in ethanol ($k = 4.7 \times 10^{-4}$ sec^{-1} at 50°), which is postulated to involve simple pyramidal inversion. Darwish and Tomilson[67] made reference to unpublished results in which ΔH^* values of 25–29 kcal/mol for trialkylsulfonium salts (compounds not specified) were found by measuring rates of racemization of resolved compounds. Martin and Basalay[68] found that coalescence of the two methyl groups of sulfonium ion **17** was nearly but not quite complete at 200°. These data suggest that the free energy of activation of the inversion of spirosulfurane **1** (greater than 25.3 kcal/mol) is at least comparable to, and perhaps greater than, the 25–29 kcal/mol for the inversion of the sulfonium ions. The resolution of compounds such as **1** and **2** into their optical antipodes is presently being attempted in this laboratory.

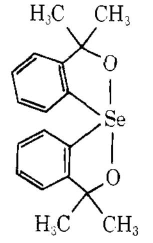


16



17

Spiroselenurane **18**, like spirosulfurane **1**, is stable toward hydrolysis and nonpolar and can be chromatographed on silica gel. Reich has reported[69] that the methyl groups of **18** remain diastereotopic up to 200°, reflecting a free energy of activation for inversion greater than 27 kcal/mol.



18

Acknowledgments. Support for this research was provided by Grant No. GP 30491X from the National Science Foundation and a grant for computing from the University of Illinois Research Board.

Supplementary Material Available. A listing of final thermal parameters, complete bond lengths and angles, intermolecular contacts, and observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $12.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-6735.

---

(66) D. Darwish and G. Tourigny, *J. Amer. Chem. Soc.*, **88**, 4303 (1966).

(67) D. Darwish and R. L. Tomilson, *J. Amer. Chem. Soc.*, **90**, 5938 (1968).

(68) J. C. Martin and R. J. Basalay, *J. Amer. Chem. Soc.*, **95**, 2572 (1973).

(69) H. J. Reich, *J. Amer. Chem. Soc.*, **95**, 964 (1973).