making the four methyl groups magnetically equivalent at higher temperature. Sulfurane oxide diol **20** apparently undergoes similar topological isomerization processes via pathways similar to a and b, though the activation barrier is much higher for **20** than for its dipotassium salt (**45**). Three methyl singlets were seen in the ¹H NMR spectrum of **20** at room temperature, and coalescence of the three peaks into a singlet occurred only at 124 °C. This is in accord with the postulate that pathways a and b, Scheme VII, are associative processes, nucleophilic displacements on sulfur by an alkoxy ligand, more rapid for the alkoxide of **45** than for the alcohol oxygen of **20**.

The acylation of **46** to give persulfurane **47** provided a possible precursor to persulfurane **21** (Scheme VII). Unlike unsymmetrical persulfurane **7**, **21** is not very acid sensitive and undergoes fragmentation very slowly in solution under conditions which lead to rapid fragmentation of **7**. The symmetrically substituted three-center, four-electron bonds in persulfurane **21** are less polarized than those of persulfurane **7**.[21] Thus the protonation of the alkoxy ligands in **21** might not be as easy as protonation of the electron-rich acyloxy ligand of **7** (Scheme III). Furthermore, in the case of persulfurane **21**, the dissociation of a hypervalent bond in the first fragmentation step would generate an intermediate sulfurane oxide, which would be more stable to acid-catalyzed fragmentation (Scheme III).

## Conclusion

The successful synthesis of persulfurane **7** enables us for the first time to go beyond the limited scope of hexacoordinate sulfur(VI) chemistry involving the chemistry of mono- and disubstituted derivatives of SF₆. The results from the study of persulfurane **7** presented here have already given us a new insight into the syntheses of persulfuranes. The indirect method of cyclodehydration of sulfurane oxide diol **20** to give tetraalkoxypersulfurane **21** is one such example. It also demonstrates the fact that a sulfone bisketal, a 12-S-6 species such as **21**, can be prepared from the monoketal analogue of a sulfone, a 10-S-5 species such as **20**. We have found that sulfone monoketals can be obtained from their corresponding sulfones (8-S-4 species) by cyclodehydration. The chemistry of this ketalization of a sulfone will be reported in a later paper. A single-crystal X-ray structure determination on **7** has been completed. From its structural data, together with that of sulfurane **31a**, we shall learn more of the nature of the hypervalent bonding in persulfuranes and sulfuranes. These will be discussed in the following paper.

# A Comparison of Hypervalent Bond Polarizabilities in Sulfuranes (10-S-4 Species) and Persulfuranes (12-S-6 Species)

**William Y. Lam, Eileen N. Duesler, and J. C. Martin***

*Contribution from the Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois 61801. Received July 14, 1980*

**Abstract:** The crystal and molecular structures of bis[5-(1,1-dimethylethyl)-3-(1-hydroxy-1-methylethyl)benzoato(3–)-$C^2,O^1,O^3$](OC-6-22′)sulfur (persulfurane **1**), symmetrical spirosulfurane **9**, and unsymmetrical bicyclic sulfurane **10** were solved by X-ray crystallographic techniques. The X-ray structure analysis for **1** ($R$ = 0.203) confirms the approximate octahedral geometry around sulfur previously postulated. From the large difference (0.24 Å) between the S–O bond lengths, we infer a high degree of polarization in the hypervalent O–S–O bonds. The X-ray crystal structure analyses of both **9** ($R$ = 0.059) and **10** ($R$ = 0.063) reveal distorted trigonal-bipyramidal geometry about sulfur, similar to structures previously determined for other spirosulfuranes. The large difference (0.59 Å) between the lengths of the S–O bonds in **10**, 2.248 (2) and 1.662 (2) Å, clearly reflects the highly polarized nature of the hypervalent O–S–O bond, resulting from the difference in electronegativities of the apical ligands. Elements of the structure of bicyclic sulfurane **10** are compared with analogous elements in the structure of **1** and **9** and other spirosulfuranes. The postulated polarization of the hypervalent bonds is also reflected in the chemical shifts of the quaternary carbon in the alkoxy ligands in some unsymmetrically substituted sulfuranes of type **15** and **16**, as well as other model sulfuranes. The peak position for the quaternary carbon in the ¹³C NMR spectrum is found to be very responsive to the electronic nature of the ligand trans to an alkoxy group. Studies of structural data, carbonyl stretching frequencies, and carbon chemical shifts of the quaternary carbon in the alkoxy ligands agree that the O–S–O hypervalent bonds to sulfur(VI) in persulfurane **1** are less polarizable than the O–S–O hypervalent bond in sulfurane **10**.

## Introduction

Before our successful synthesis of a diarylbis(acyloxy)dialkoxypersulfurane, **1**,[1] hexacoordinate sulfur(VI) compounds (12-S-6



**1**



**2**
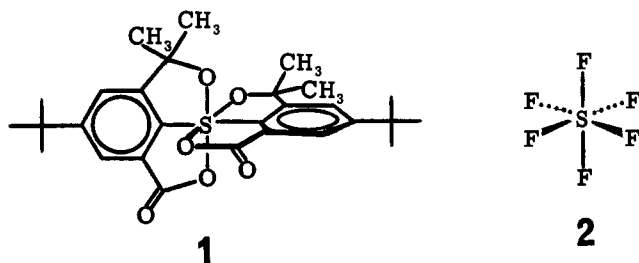
species) which had been reported included only sulfur hexafluoride (**2**) and its mono- and disubstituted derivatives, in which one or two fluorine ligands had been replaced with aryl, vinyl, ethynyl, perfluoroalkyl, and alkyl groups and various inorganic ligands.[2] Octahedrally symmetric[3] compound **2** has only a single ¹⁹F resonance as expected.[4] Complete structure determinations, by

(1) Lam, W. Y.; Martin, J. C., preceding paper in this issue.
(2) (a) Roberts, H. L. "Inorganic Sulfur Chemistry"; Nickless, G., Ed.; Elsevier: New York, 1968; Chapter 12. (b) Dresdner, R. D.; Hooper, T. R. *Fluorine Chem. Rev.* **1969**, *4*. (c) Sheppard, W. A.; Sharts, C. M. "Organic Fluorine Chemistry"; W. A. Benjamin: New York, 1969. (d) Denney, D. B.; Denney, D. Z.; Hsu, Y. F. *J. Am. Chem. Soc.* **1973**, *95*, 8191.
(3) (a) Brockway, L. O.; Pauling, L. *Proc. Natl. Acad. Sci. U.S.A.* **1933**, *19*, 68. (b) Braune, H.; Kuobe, S. *Z. Phys. Chem. Abt. B* **1933**, *21*, 297.

microwave spectroscopy and electron diffraction, on stable derivatives of **2** such as SF₅OF,[5] SF₅Cl,[5] and SF₅OSF₅[6] show only relatively small deviations from an octahedral arrangement of ligands around sulfur.

The X-ray structures of a number of sulfuranes, including spirosulfuranes **3–5** have been reported.[7–10] In all these cases,



**3**     **4**     **5** R = H
                     **6** R = CH₃
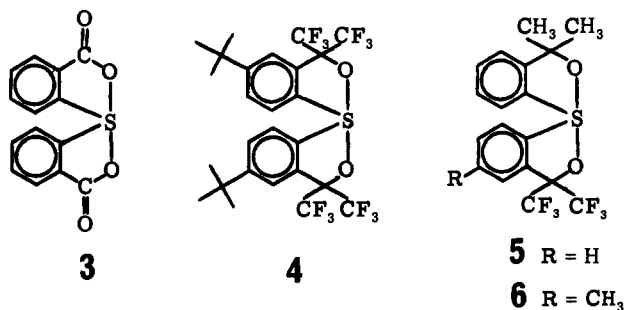
approximate trigonal-bipyramidal geometry is observed around the sulfur atom with the lone pair of electrons occupying one equatorial position. Sulfuranes in which the two apical ligands are identical such as **3** and **4** have identical or nearly identical hypervalent bond lengths. For example, the S–O bond lengths of **3** are both 1.83 (1) Å,[7] and in **4** the S–O bond lengths are 1.818 (5) and 1.832 (5) Å.[8] The large difference in S–O bond lengths (1.955 vs. 1.713 Å) seen for **5**[9a] has been explained to be a result of the polarization of the hypervalent O–S–O bonds, resulting from the unsymmetrical nature of the apical substitution.

Other evidence for the great polarizability of the hypervalent bond in sulfuranes is seen[11] in the wide range (~300 cm⁻¹) of carbonyl stretching frequencies determined for sulfuranes of type **7** and **8**. This has been postulated[11] to be a result of the variable level of negative charge on the acyloxy group, reflecting a greater or lesser resemblance to a carboxylate anion in its carbonyl stretching frequency.



**7**     **8**
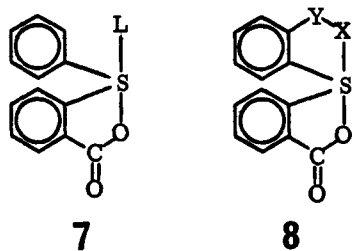
Since persulfurane **1** has unsymmetrically substituted apical positions, the three-center four-electron hypervalent bonds are expected to be polarized and its polarization might be reflected in bond lengths, as seen in the case of sulfurane **5**. We here report the X-ray structure of persulfurane **1**, which indeed reveals a large difference in S–O bond lengths. We also report a complete X-ray structure of symmetrical spirosulfurane **9**[12] and of unsymmetrical sulfurane **10**, a model compound closely related to persulfurane **1**.

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(4) (a) Muetterties, E. L.; Phillips, W. D. *J. Am. Chem. Soc.* **1959**, *81*, 1084. (b) Dunn, M. B.; McDowell, C. A. *Chem. Phys. Lett.* **1972**, *13*, 268.

(5) Laur, P. H. In "Sulfur in Organic and Inorganic Chemistry"; Senning, A., Ed.; Marcel Dekker: New York, 1972; Vol. 31, Chapter 24.

(6) Oberhammer, H.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 69.

(7) Kálmán, A.; Sasvári, K.; Kapovits, I. *Acta Crystallogr., Sect. B* **1973**, *B29*, 355.

(8) Perozzi, E. F.; Martin, J. C.; Paul, I. C. *J. Am. Chem. Soc.* **1974**, *96*, 6735.

(9) (a) Adzima, L. J.; Duesler, E. N.; Martin, J. C. *J. Org. Chem.* **1977**, *42*, 4001. (b) Adzima, L. J.; Chiang, C. C.; Paul, I. C.; Martin, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 953.

(10) (a) Baenziger, N. C.; Buckles, R. E.; Maner, R. J.; Simpson, T. D. *J. Am. Chem. Soc.* **1972**, *91*, 5749. (b) Hodges, K. C.; Schomburg, D.; Weiss, J. V.; Schmutzler, R. *Ibid.* **1977**, *99*, 6096.

(11) Livant, P.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 5761.

(12) Adzima, L. J.; Martin, J. C. *J. Org. Chem.* **1977**, *42*, 4006.

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**9**     **10** R = H
          **11** R = C(CH₃)₃
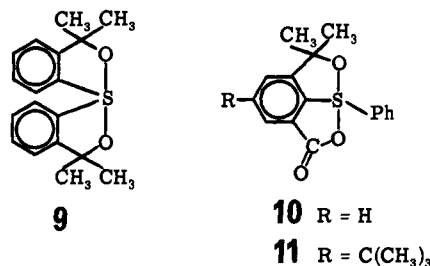
## Experimental Section

**General Remarks.** Carbon NMR spectra were taken on CDCl₃ solutions and chemical shifts are reported on the δ scale, ppm downfield from tetramethylsilane internal standard. Chemical shifts for ¹⁹F are reported in ppm upfield from CFCl₃.

**4-Methyl-3,3-bis(trifluoromethyl)-3′,3′-dimethyl-1,1′-spiro[3H-2,1-benzoxathiole] (6).** Diazomethane in ether was added to a solution of 4-methyl-2-(1-hydroxy-1-trifluoromethyl-2,2,2-trifluoroethyl)-2′-carboxydiphenyl sulfide[11] (351.6 mg, 0.85 mmol) in ether, and the solvent was removed. To the solution of the remaining solid in ether was added CH₃MgBr (1.4 mL of a 3 M solution in ether, 4.25 mmol). After 8 h, the solution was added to dilute aqueous HCl, the ether layer was separated and dried (Na₂SO₄), and the solvent was removed to give a solid, crude 4-methyl-2-(1-hydroxy-1-trifluoromethyl-2,2,2-trifluoroethyl)-2′-(1-hydroxy-1-methylethyl)diphenyl sulfide. From this sulfide diol, sulfurane **6** was synthesized by procedures described for **5**,[12] in 70% yield (295.4 mg, 0.7 mmol): mp 182–184 °C; ¹H NMR (CDCl₃) δ 8.39 (d, 1, J = 8 Hz, ArH ortho to S), 8.15 (d, 1, J = 8 Hz, ArH ortho to S), 7.55–7.2 (m, 5, ArH), 2.45 (s, 3, ArCH₃), 1.80 (s, 3, CH₃), 1.63 (s, 3, CH₃); ¹⁹F NMR (CDCl₃) –74.02 (q, 1), –77.03 (q, 1). Anal. (C₁₉H₁₆F₆O₂S): C, H, F, S.

**Crystal Growth.** Crystallization was induced for **1** by the slow diffusion of pentane into a solution of the material in toluene–pyridine and for **10** by the slow diffusion of ether into a solution in acetonitrile–toluene. Slow evaporation of a solution of **9** in chloroform–pentane gave good crystals. No special precautions proved necessary to protect any of these crystals from atmospheric moisture.

**Crystal Data of 1:** C₂₈H₃₄O₆S, mol wt = 498, orthorhombic, a = 25.782 (10) Å, b = 16.709 (5) Å, c = 16.472 (3) Å, V = 7096 Å³; systematic absences for 0kl, k = 2n + 1, h0l, l = 2n + 1, and hk0, h + k = 2n + 1, established the space group as *Pbcn*. Comparison of the calculated density, 0.93 g/cm³ (Z = 8), with the experimental density (1.21 g/cm³) indicated the incorporation of solvent molecules into the lattice. A Syntex P2₁ diffractometer equipped with a graphite monochromator, λ(Cu Kα₁) = 1.54178 Å, was used in obtaining the data set and the cell parameters.

**Solution and Refinement of the Structure of 1.** A crystal with dimensions ca. 0.4 × 0.2 × 0.1 mm was used for the data collection.[13] The unique octant hkl was collected in the 2θ:θ scan mode out to 2θ = 126° ((sin θ)/λ = 0.588). Out of the possible 5766 unique reflections collected, 2278 were observed by using a 1σ criterion based on counting statistics. The data were corrected for Lorentz and polarization effects but not for absorption.

Direct methods gave the basic persulfurane unit without difficulty.[14] However, attempts to locate the solvent molecules failed. A difference map shows no discrete solvent molecule or fragments, only large areas of diffuse electron density ranging from 0.5 to 1.5 hydrogen atoms. One of the *tert*-butyl groups shows a twofold disorder. The two sets of *tert*-butyl positions were refined and were constrained to be half-occupied. Positions for all the nonhydrogen atoms except for the disordered *tert*-butyl groups were refined anisotropically with the full-matrix least-squares program. None of the hydrogen atoms were included, and the refinements were stopped when the 313 parameters converged at R = 0.203, R_w = 0.23.[15] The final value of [Σw(|F_o| − |F_c|)²/(m − n)]^{1/2}, where m is the number of observations and n is the number of variables, was 4.14. The scattering factor tables were taken from the analytical expression used in ref 16. The final values of atomic coordinates for all nonhydrogen atoms are given in Table I (also see paragraph at end of

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(13) For the description of data collection, see that in ref 9a.

(14) The structure was solved by a version of the MULTAN program: Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368, that has been incorporated into the Syntex EXTL system, based on the Data General ECLIPSE computer. All crystallographic calculations were carried out on this system.

(15) R = Σ||F_o| − |F_c||/Σ|F_o|; R_w = [Σw||F_o| − |F_c||²/Σw|F_o|²]^{1/2}.

(16) Ibers, J. A., Hamilton, W. C., Eds. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; pp 99–102.

*Polarizabilities in Sulfuranes and Persulfuranes*

*J. Am. Chem. Soc., Vol. 103, No. 1, 1981* 129

Table I. Final Coordinates for Persulfurane 1[a]

| atom | x | y | z |
| --- | --- | --- | --- |
| S | 0.3220 (2) | 0.0225 (3) | 0.1504 (3) |
| O(1) | 0.3603 (6) | 0.0128 (8) | 0.2468 (8) |
| C(2) | 0.4038 (9) | -0.0238 (15) | 0.2355 (13) |
| C(3) | 0.4115 (8) | -0.0555 (12) | 0.1480 (12) |
| C(4) | 0.3703 (8) | -0.0348 (11) | 0.1012 (12) |
| C(5) | 0.3625 (8) | -0.0494 (12) | 0.0268 (10) |
| C(6) | 0.3110 (8) | -0.0182 (14) | -0.0025 (12) |
| O(7) | 0.2869 (5) | 0.0198 (8) | 0.0663 (7) |
| C(8) | 0.4512 (8) | -0.0989 (13) | 0.1145 (12) |
| C(9) | 0.4474 (9) | -0.1176 (12) | 0.0308 (13) |
| C(10) | 0.4021 (9) | -0.0922 (12) | -0.0143 (13) |
| O(2) | 0.4340 (6) | -0.0391 (10) | 0.2928 (9) |
| C6A | 0.2749 (9) | -0.0871 (16) | -0.0329 (16) |
| C6B | 0.3189 (10) | 0.0510 (15) | -0.0676 (13) |
| C9T | 0.4906 (8) | -0.1627 (16) | -0.0130 (13) |
| O(11) | 0.2890 (5) | -0.0760 (7) | 0.1859 (8) |
| C(12) | 0.2468 (10) | -0.0661 (15) | 0.2253 (13) |
| C(13) | 0.2335 (8) | 0.0232 (10) | 0.2409 (11) |
| C(14) | 0.2712 (8) | 0.0672 (11) | 0.2090 (11) |
| C(15) | 0.2755 (8) | 0.1502 (12) | 0.2074 (11) |
| C(16) | 0.3250 (9) | 0.1827 (13) | 0.1686 (14) |
| O(17) | 0.3509 (5) | 0.1098 (8) | 0.1316 (8) |
| C(18) | 0.1898 (8) | 0.0588 (12) | 0.2744 (13) |
| C(19) | 0.1930 (8) | 0.1471 (13) | 0.2706 (11) |
| C(20) | 0.2358 (8) | 0.1909 (13) | 0.2405 (12) |
| O(12) | 0.2196 (6) | -0.1189 (9) | 0.2508 (10) |
| C16A | 0.3128 (10) | 0.2384 (14) | 0.0936 (14) |
| C16B | 0.3610 (9) | 0.2148 (14) | 0.2348 (16) |
| C19T | 0.1415 (11) | 0.1899 (15) | 0.3070 (17) |
| C9TA | 0.5469 (11) | -0.1286 (18) | 0.0053 (17) |
| C9TB | 0.4795 (12) | -0.1715 (21) | -0.1065 (16) |
| C9TC | 0.4924 (16) | -0.2461 (19) | 0.0310 (29) |
| C19TA | 0.117 (2) | 0.251 (3) | 0.237 (3) |
| C19TB | 0.103 (2) | 0.136 (3) | 0.336 (4) |
| C19TC | 0.157 (3) | 0.257 (5) | 0.383 (4) |
| C19TD | 0.143 (3) | 0.174 (4) | 0.406 (4) |
| C19TE | 0.093 (2) | 0.152 (4) | 0.273 (4) |
| C19TF | 0.152 (3) | 0.289 (5) | 0.302 (5) |

*a* Estimated standard deviations in parentheses.

Table II. Final Coordinates for Spirosulfurane 9[a]

| atom | x | y | z |
| --- | --- | --- | --- |
| S | 0.48426 (9) | 0.06599 (7) | 0.38454 (4) |
| O(1) | 0.3466 (3) | -0.0178 (2) | 0.3246 (1) |
| C(2) | 0.4135 (4) | -0.1222 (3) | 0.2825 (2) |
| C(3) | 0.5987 (4) | -0.1079 (3) | 0.2900 (2) |
| C(4) | 0.7150 (4) | -0.1754 (4) | 0.2511 (2) |
| C(5) | 0.8816 (5) | -0.1474 (5) | 0.2597 (2) |
| C(6) | 0.9309 (4) | -0.0536 (5) | 0.3067 (2) |
| C(7) | 0.8170 (4) | 0.0135 (4) | 0.3483 (2) |
| C(8) | 0.6500 (4) | -0.0178 (3) | 0.3396 (1) |
| C(9) | 0.3568 (6) | -0.2591 (4) | 0.3061 (2) |
| C(10) | 0.3600 (5) | -0.0961 (5) | 0.2078 (2) |
| O(1)' | 0.6235 (3) | 0.1440 (2) | 0.4438 (1) |
| C(2)' | 0.6331 (5) | 0.0935 (3) | 0.5135 (2) |
| C(3)' | 0.4965 (4) | -0.0060 (3) | 0.5188 (1) |
| C(4)' | 0.4469 (5) | -0.0700 (4) | 0.5793 (2) |
| C(5)' | 0.3097 (6) | -0.1507 (4) | 0.5784 (2) |
| C(6)' | 0.2186 (5) | -0.1669 (4) | 0.5181 (2) |
| C(7)' | 0.2674 (5) | -0.1063 (4) | 0.4574 (2) |
| C(8)' | 0.4086 (4) | -0.0274 (3) | 0.4581 (1) |
| C(9)' | 0.6001 (9) | 0.2118 (5) | 0.5616 (2) |
| C(10)' | 0.8007 (6) | 0.0293 (6) | 0.5275 (3) |
| H(4) | 0.691 (5) | -0.229 (4) | 0.219 (2) |
| H(5) | 0.961 (5) | -0.176 (4) | 0.236 (2) |
| H(6) | 1.050 (6) | -0.023 (4) | 0.397 (2) |
| H(7) | 0.850 (6) | 0.101 (5) | 0.370 (2) |
| H9A | 0.384 (5) | -0.271 (3) | 0.351 (2) |
| H9B | 0.405 (5) | -0.329 (4) | 0.281 (2) |
| H9C | 0.238 (6) | -0.260 (4) | 0.307 (2) |
| H10A | 0.404 (5) | -0.158 (4) | 0.184 (2) |
| H10B | 0.399 (5) | -0.029 (4) | 0.189 (2) |
| H10C | 0.236 (5) | -0.112 (3) | 0.199 (2) |
| H(4)' | 0.502 (5) | -0.047 (4) | 0.618 (2) |
| H(5)' | 0.284 (6) | -0.200 (4) | 0.620 (2) |
| H(6)' | 0.118 (6) | -0.228 (5) | 0.517 (2) |
| H(7)' | 0.212 (5) | -0.117 (4) | 0.421 (2) |
| H9'A | 0.475 (6) | 0.249 (4) | 0.549 (2) |
| H9'B | 0.678 (7) | 0.259 (6) | 0.547 (3) |
| H9'C | 0.616 (6) | 0.181 (4) | 0.609 (3) |
| H10'A | 0.820 (6) | -0.043 (4) | 0.491 (2) |
| H10'B | 0.801 (6) | -0.009 (4) | 0.574 (2) |
| H10'C | 0.883 (7) | 0.076 (5) | 0.528 (3) |

*a* Estimated standard deviations in parentheses.

paper regarding supplementary material).

**Crystal Data of 9**: $C_{18}H_{20}O_2S$, mol wt = 300.4, orthorhombic, $a$ = 8.102 (2) Å, $b$ = 10.115 (2) Å, $c$ = 19.231 (5) Å, $V$ = 1576.0 Å$^3$, $F(000)$ = 640, $\rho_c$ ($Z$ = 4) = 1.27 g/cm$^3$, $\mu$(Mo K$\alpha$) = 2.1 cm$^{-1}$. Systematic absences for $h00$, $h$ = $2n$ + 1, $0k0$, $k$ = $2n$ + 1, and $00l$, $l$ = $2n$ + 1, establish the space group as $P2_12_12_1$. The cell dimensions were obtained by a least-squares fit to the automatically centered settings for 15 reflections on a Syntex P2$_1$ automated diffractometer equipped with a graphite monochromator $\lambda$(Mo K$\alpha$) = 0.7107 Å.

**Solution and Refinement of the Structure of 9.** A crystal of dimensions 0.38 × 0.55 × 0.67 mm was used for the $2\theta$:$\theta$ scan data collection. The variable scan option was used between 4–29°/min. The background count time/total scan time was set at 0.5. Data in the *hkl* octant were collected out to $2\theta$ = 70°. Three reflections were monitored every 57 reflections; an examination of these at the end of the data collection showed no signs of crystal decomposition. The data were corrected for Lorentz and polarization effects. Of the 3917 unique reflections collected, 2748 were considered observed at the $1.96\sigma(I)$ level.

The structure was solved by the MULTAN program.[14] After anisotropic refinements on the nonhydrogen atoms, all of the hydrogen atom positions were observed in difference maps. Final full-matrix least-squares refinements on all positional parameters and anisotropic thermal parameters of the nonhydrogen atoms and isotropic thermal parameters of the hydrogen atoms converged to agreement factor $R$ and $R_w$ of 0.059 and 0.065, respectively.[15] The final value of $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where $m$ is the number of observations (2748) and $n$ is the number of variables (270), was 1.76. A final difference map showed no peak greater than 0.34 e/Å$^3$. The scattering curves for the neutral atoms were taken from the analytical expression used in ref 16. The final values of atomic coordinates of **9** are given in Table II (also see paragraph at end of paper regarding supplementary material).

**Crystal Data for 10**: $C_{16}H_{14}O_3S$, mol wt = 286.4, triclinic, $P1$, $a$ = 7.747 (3) Å, $b$ = 8.065 (1) Å, $c$ = 22.781 (7) Å, $\alpha$ = 88.14 (2)°, $\beta$ = 95.57 (3)°, $\gamma$ = 95.68 (2)°, $V$ = 1409.3 Å$^3$, $Z$ = 4, $\rho_c$ = 1.35 g/cm$^3$, $\mu$(Mo K$\alpha$) = 2.3 cm$^{-1}$, $F(000)$ = 600; no systematic absences. The cell dimensions were obtained by a least-squares fit to the automatically

centered settings for 15 reflections on a Syntex P2$_1$ diffractometer equipped with a graphite monochromator, $\lambda$(Mo K$\alpha$) = 0.7107 Å.

**Solution and Refinement of the Structure of 10.** A crystal with dimensions ca. 0.80 × 0.53 × 0.28 mm was used for data collection. The $2\theta$:$\theta$ scan mode was used with a variable scan (4.0–20.0°/min) with the total background time/scan time set at 0.5. Three standards from different parts of the reciprocal space were monitored every 57 reflections. Examination of these showed no crystal deterioration during data collection. The quadrants $\pm h,k,\pm l$ were collected out to $2\theta$ = 65°. Out of a possible 10 259 unique reflections 5676 were considered observed at the $1.96\sigma(I)$ level. The data were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct methods using the MULTAN program.[14] The hydrogens were located from difference maps. Full-matrix least-squares refinements on the positional and anisotropic thermal parameters for the nonhydrogen atoms and the positional and isotropic thermal parameters for the hydrogen atoms converged to agreement factors $R$ and $R_w$ of 0.063 and 0.062, respectively.[15] The final value of $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where $m$ is the number of observations and $n$ is the number of variables, was 1.58. The scattering curves were taken from the analytical expression used in ref 16. A final difference map showed no peak greater than 37% of an ideal hydrogen atom. The highest 4 peaks from the last difference map were <1 Å from the sulfur atoms. The final values of atomic coordinates are given in Table III (also see paragraph at end of paper regarding supplementary material).

## Results

**Persulfurane 1.** Our failure to locate solvent molecules included in the crystals of **1** has resulted in a less well-defined structure for **1** than one might have desired. The basic structural features of the molecules are, however, easily discerned and the uncertainties in the positional parameters for the central sulfur atom and its surrounding atoms were relatively small. Figure 1 sum-
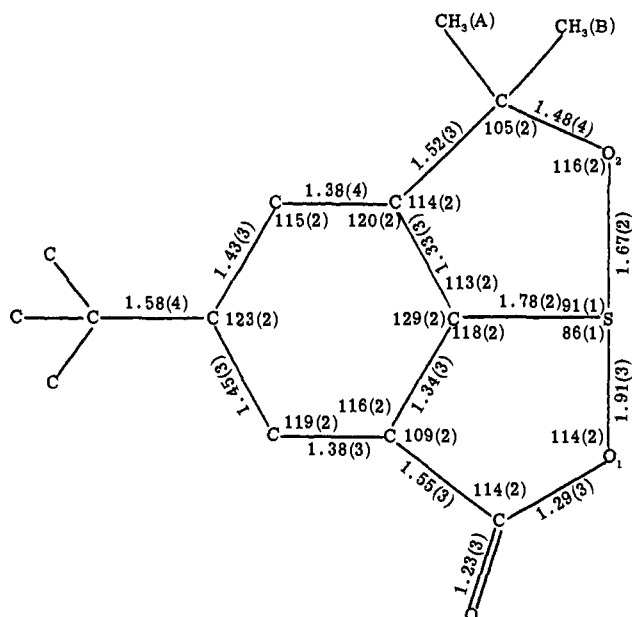
**Figure 1.** Averaged (assuming a $C_2$ symmetry for the two halves of the molecule) bond lengths (Å) and bond angles (deg) in **1** with estimated standard deviations in parentheses. The values in half of the molecule are within three standard deviations of those in the other half. Not shown on the figure are values for the following angles: O(1)–S–O(2) = 173 (1)°, C–S–C = 171 (1)°, O(1)–S–O(1)' = 84 (1)°, and O(2)–S–O(2)' = 96 (1)°.

marizes the basic persulfurane geometry. The S–O$_1$ bond is very obviously elongated with respect to the S–O$_2$ bond. The angle between the normals to the two halves of the persulfurane unit is 89° (with use of the best planes calculated for the two halves). A stereoview of the single molecule of **1** is given in Figure 2. A stereoview of the packing in one unit cell is depicted in Figure 3. The large volume containing the disordered solvent molecules is easily discernible in Figure 3.

**Symmetrical Spirosulfurane 9.** The crystal structure of **9** reveals an approximate trigonal-bipyramidal geometry about sulfur. Figure 4 shows the selected bond lengths and bond angles while Figures 5 and 6 are stereoscopic views of a single molecule and the packing in one unit cell.

**Unsymmetrical Sulfurane 10.** The crystal structure of **10** reveals two independent molecules with distorted trigonal-bipyramidal geometry about sulfur. Figure 7 shows a stereoview of the unprimed molecule of **9**, and Figure 8 shows a stereoview of the
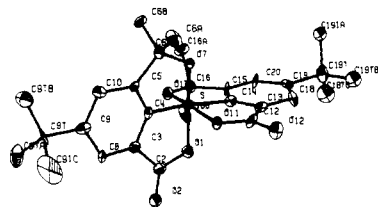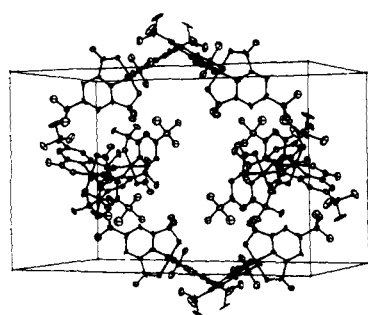
packing in one unit cell. Some selected bond lengths and bond angles are given in Figure 9. The dihedral angles between the two planes containing the phenyl rings is 94.5° (and 96.2°) for the two independent molecules. (In this discussion values for the unprimed molecule of **10** will be followed, in parentheses, by values for the primed molecule.) The apical positions of the trigonal-bipyramidal structure are occupied by the two oxygen atoms with O–S–O angles of 170.1 (1)° (170.8 (1)°). The distortion from linearity of the oxygen atoms is in the direction of the ring-fused phenyl (away from the sulfur lone pair of electrons and the free equatorial phenyl ring). The S–O(1) bond is significantly longer than the S–O(9) bond. The carbon atoms adjacent to sulfur in the phenyl rings occupy the equatorial plane with C–S–C angles of 107.6 (1)° (108.3 (1)°), and the S–C(10) bond is slightly shorter than the S–C(14) bond.
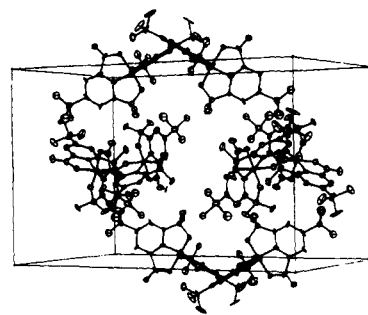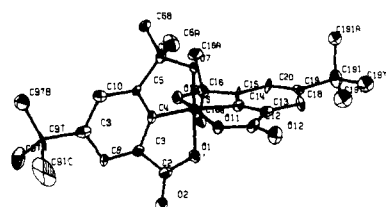
**Discussion**

**Polarization of Hypervalent O–S–O Bonds.** The ionization of 10-S-4 species (sulfuranes) to give sulfonium salts (8-S-3 species) is at least partially understood (eq 1). The heterolysis of the S–X

$$ \begin{array}{c} R \diagdown \\ R' \diagup \end{array} \!\!\! \overset{\displaystyle Y}{\underset{\displaystyle X}{\big|}} \!\!\! S \quad \longrightarrow \quad \begin{array}{c} R \diagdown \\ R' \diagup \end{array} \!\!\! \overset{\displaystyle Y}{\underset{\displaystyle }{\big|}} \!\!\! S_+ \qquad X^- \tag{1} $$

$$ \left( \begin{array}{c} \text{10-S-4} \\ \text{species} \end{array} \right) \qquad\qquad \left( \begin{array}{c} \text{8-S-3} \\ \text{species} \end{array} \right) $$
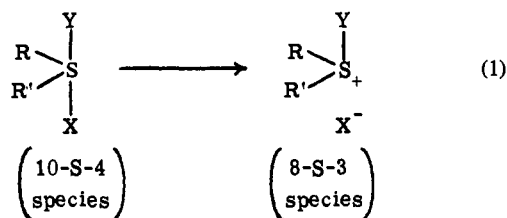
bond in the pictured sulfurane is favored by σ-electron releasing ability in Y. The inclusion of Y and R in a five-membered ring favors the trigonal-bipyramidal structure of the sulfurane over the sulfonium structure and makes the S–X heterolysis more difficult. Ground-state geometries and charge distributions are skewed, in unsymmetrically substituted sulfuranes (X ≠ Y) in a manner which reflects the magnitudes of the barriers to reactions in the various heterolytic modes; e.g., if S–X heterolysis is favored over S–Y heterolysis, the S–X bond is expected to be longer in the ground state than the S–Y bond with more negative charge on X than on Y. This has already been observed to be the case for spirosulfurane **5**,[9a] in which the S–O bond to the fluoroalkoxy ligand (X) is 0.24 Å longer than to the unfluorinated alkoxy ligand (Y). Methylation of **5** occurs preferentially at the oxygen of the fluoroalkoxy group. We postulate that a similar rationalization holds for the dissymmetry of the S–O bonds seen in persulfurane **1**.

In spite of the large experimental error in the bond lengths and bond angles found for **1**, the structure determination confirmed
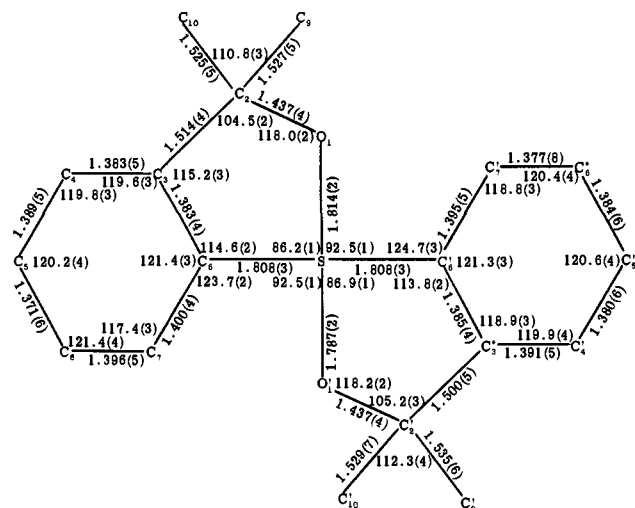


**Figure 2.** Stereoscopic view of the single molecule of persulfurane **1**.



**Figure 3.** Stereoscopic view of the crystal structure of **1**.

**Figure 4.** Selected bond lengths (Å) and bond angles (deg) in **9** with estimated standard deviations in parentheses. Two angles around the sulfur atom which are not shown on the figure are O(1)–S–O(1)' = 178.2 (1)° and C(8)–S–C(8)' = 112.4 (1)°.

the gross structure which had been postulated on the basis of chemical and infrared and NMR spectroscopic studies of this compound.[1] We will comment on a few structural features which are obvious despite the relatively large uncertainties in the structure determination. Persulfurane **1** is clearly shown to have approximate octahedral geometry about sulfur, similar to the geometry seen for $SF_6$ and some of its monosubstituted derivatives.[5,6] The O–S–O bonds are bent ca. 7° from collinearity, bending in each case in the direction to make the endocyclic C–S–O angles smaller than the exocyclic C–S–O angles. The angle between the two alkoxy O–S bonds [O(7)–S(1)–O(17) = 96 (1)°] is larger than the angle between the two acyloxy O–S bonds [O(1)–S(1)–O(11) = 84 (1)°]. This distortion may be the result of a greater steric interaction between the two alkoxy ligands. The closest intramolecular contact distance between alkoxy oxygens (shorter S–O bonds) in the two halves of the molecule is 2.48 Å, whereas the intramolecular contact distance between acyloxy oxygens (longer S–O bonds) is 2.57 Å. Both contact distances are well within the sum of van der Waals radii of two oxygen atoms (2.80 Å).[17]

The most striking feature of **1** is the large difference in the lengths of the S–O bonds (S–O$_1$ = 1.91 (3), S–O$_2$ = 1.67 (2) Å; Figure 1). Their difference (0.24 Å) reflects polarization of the hypervalent O–S–O bond resulting from the difference in electronegativities of the unsymmetrical ligands. The short S–O$_2$ distance in **1** is slightly shorter than a "normal" S–O single bond (1.70 Å),[18] whereas the S–O$_1$ bond distance is 0.21 Å longer than this "usual" distance.

The acyloxy ligand in persulfurane **1** is effectively more electronegative than the alkoxy ligand. Electron density is expected[11]

(17) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, N.Y., 1960; p 260.

(18) This "normal" S–O bond length (1.70 Å) is the sum of the covalent radii of S and O; see ref 17, p 224. The X-ray structures of monocyclic compounds **14**,[19] **25**,[20] and **26**,[21] which may be regarded as model compounds, reveal the S–O bond lengths to be 1.684 (3), 1.711 (3), and 1.680 (6) Å, respectively, very close to the "normal" length.
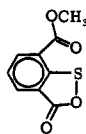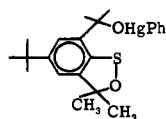


**25**     **26**

(19) Walter, W.; Krische, B. *Justus Liebigs Ann. Chem.* **1980**, 14.
(20) Walter, W.; Krische, B.; Adiwidjaja, G.; Voss, J. *Chem. Ber.* **1978**, *111*, 1685.
(21) Lau, P. H. W. Ph.D. Thesis, University of Illinois, Urbana, Illinois, 1979.

**Table III.** Final Coordinates for Sulfurane **10**[a]

| atom | x | y | z |
|------|------|------|------|
| S(1) | 0.85772 (8) | 0.20381 (7) | 0.405 73 (3) |
| S(1)' | 0.25726 (8) | 0.54950 (8) | 0.097 54 (3) |
| O(1) | 0.6653 (2) | 0.3937 (2) | 0.393 74 (8) |
| C(2) | 0.7392 (3) | 0.5405 (3) | 0.404 20 (11) |
| C(3) | 0.9336 (3) | 0.5404 (3) | 0.418 27 (10) |
| C(4) | 1.0549 (3) | 0.6746 (3) | 0.432 80 (11) |
| C(5) | 1.2305 (3) | 0.6488 (3) | 0.442 78 (12) |
| C(6) | 1.2894 (3) | 0.4942 (3) | 0.437 76 (12) |
| C(7) | 1.1694 (3) | 0.3589 (3) | 0.423 98 (10) |
| C(8) | 1.2007 (3) | 0.1804 (3) | 0.417 27 (13) |
| O(9) | 1.0246 (2) | 0.0891 (2) | 0.419 43 (8) |
| C(10) | 0.9968 (3) | 0.3876 (3) | 0.415 54 (10) |
| O(11) | 0.6696 (2) | 0.6709 (2) | 0.403 32 (9) |
| C(12) | 1.2706 (5) | 0.1500 (5) | 0.359 49 (18) |
| C(13) | 1.3123 (6) | 0.1165 (4) | 0.470 42 (21) |
| C(14) | 0.8127 (3) | 0.1740 (3) | 0.327 99 (11) |
| C(15) | 0.7322 (4) | 0.0199 (4) | 0.312 68 (15) |
| C(16) | 0.7018 (5) | −0.0173 (5) | 0.253 44 (17) |
| C(17) | 0.7509 (5) | 0.0969 (5) | 0.210 73 (16) |
| C(18) | 0.8284 (5) | 0.2517 (5) | 0.226 63 (15) |
| C(19) | 0.8597 (4) | 0.2908 (4) | 0.285 63 (13) |
| O(1)' | 0.4484 (2) | 0.7806 (2) | 0.097 39 (8) |
| C(2)' | 0.6000 (4) | 0.7429 (3) | 0.088 58 (11) |
| C(3)' | 0.6019 (3) | 0.5591 (3) | 0.078 12 (10) |
| C(4)' | 0.7390 (3) | 0.4762 (3) | 0.063 17 (12) |
| C(5)' | 0.7176 (4) | 0.3053 (3) | 0.057 17 (13) |
| C(6)' | 0.5633 (3) | 0.2107 (3) | 0.067 20 (12) |
| C(7)' | 0.4240 (3) | 0.2908 (3) | 0.082 03 (10) |
| C(8)' | 0.2463 (3) | 0.2158 (3) | 0.097 09 (12) |
| O(9)' | 0.1442 (2) | 0.3632 (2) | 0.096 06 (9) |
| C(10)' | 0.4484 (3) | 0.4616 (3) | 0.085 89 (10) |
| O(11)' | 0.7357 (3) | 0.8361 (2) | 0.088 93 (10) |
| C(12)' | 0.1544 (4) | 0.0990 (4) | 0.050 96 (17) |
| C(13)' | 0.2544 (5) | 0.1345 (5) | 0.158 28 (16) |
| C(14)' | 0.2647 (4) | 0.5950 (3) | 0.173 76 (12) |
| C(15)' | 0.3909 (5) | 0.5475 (4) | 0.215 84 (15) |
| C(16)' | 0.3814 (9) | 0.5896 (6) | 0.273 99 (18) |
| C(17)' | 0.2497 (11) | 0.6775 (6) | 0.287 51 (25) |
| C(18)' | 0.1254 (9) | 0.7239 (5) | 0.246 12 (24) |
| C(19)' | 0.1303 (5) | 0.6832 (4) | 0.187 90 (17) |
| H(4) | 1.015 (3) | 0.783 (3) | 0.436 5 (11) |
| H(5) | 1.316 (3) | 0.743 (3) | 0.452 4 (12) |
| H(6) | 1.401 (3) | 0.476 (3) | 0.443 5 (11) |
| H12A | 1.199 (5) | 0.193 (4) | 0.324 7 (16) |
| H12B | 1.382 (5) | 0.214 (4) | 0.354 0 (15) |
| H12C | 1.280 (4) | 0.037 (4) | 0.355 7 (13) |
| H13A | 1.321 (4) | 0.011 (5) | 0.467 5 (14) |
| H13B | 1.428 (4) | 0.173 (4) | 0.466 3 (13) |
| H13C | 1.278 (6) | 0.138 (6) | 0.507 8 (22) |
| H(15) | 0.709 (4) | −0.056 (4) | 0.342 0 (13) |
| H(16) | 0.645 (4) | −0.125 (4) | 0.244 1 (15) |
| H(17) | 0.728 (4) | 0.062 (4) | 0.171 5 (16) |
| H(18) | 0.863 (4) | 0.333 (4) | 0.198 7 (14) |
| H(19) | 0.903 (4) | 0.391 (4) | 0.294 5 (12) |
| H(4)' | 0.840 (3) | 0.539 (3) | 0.056 5 (10) |
| H(5)' | 0.803 (4) | 0.257 (3) | 0.046 8 (12) |
| H(6)' | 0.550 (3) | 0.101 (3) | 0.063 3 (11) |
| H12'A | 0.044 (4) | 0.062 (4) | 0.064 0 (13) |
| H12'B | 0.142 (4) | 0.159 (4) | 0.011 2 (14) |
| H12'C | 0.219 (4) | 0.007 (4) | 0.048 7 (12) |
| H13'A | 0.326 (4) | 0.041 (4) | 0.158 5 (14) |
| H13'B | 0.139 (5) | 0.093 (4) | 0.165 5 (15) |
| H13'C | 0.314 (4) | 0.209 (4) | 0.187 1 (15) |
| H(15)' | 0.475 (3) | 0.499 (3) | 0.206 1 (12) |
| H(16)' | 0.468 (5) | 0.552 (5) | 0.293 9 (19) |
| H(17)' | 0.250 (7) | 0.707 (6) | 0.321 4 (24) |
| H(18)' | 0.035 (5) | 0.795 (5) | 0.255 7 (18) |
| H(19)' | 0.045 (4) | 0.715 (4) | 0.153 7 (15) |

[a] Estimated standard deviations in parentheses.

to be removed from the alkoxy ligand toward the acyloxy ligand. The carbonyl stretching frequencies of sulfuranes **3**, **12**, and **13** are 1724, 1708, and 1647 cm⁻¹, respectively. The considerably lower carbonyl stretching frequency seen in **13** relative to **3** points to a high degree of carboxylate anion character in this sulfurane,
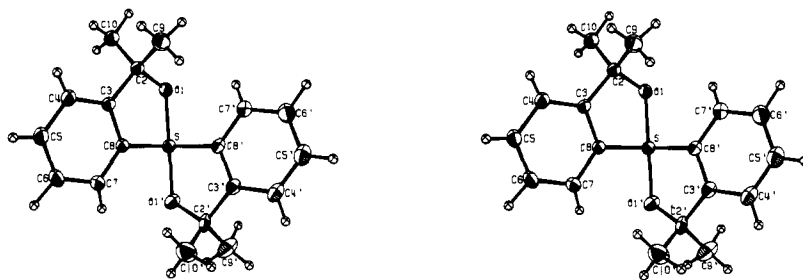
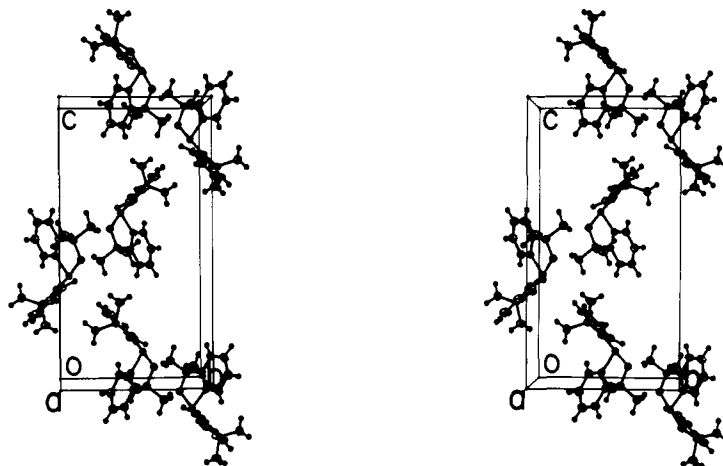**Figure 5.** Stereoscopic view of the single molecule of spirosulfurane **9**.



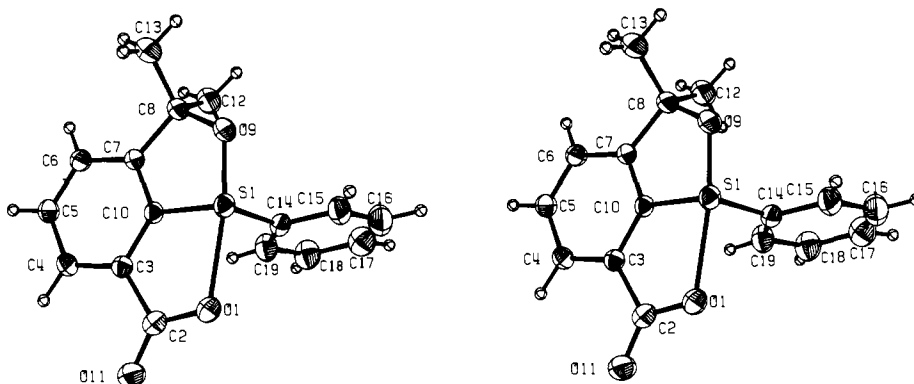**Figure 6.** Stereoscopic view of the packing in one unit cell of **9**.



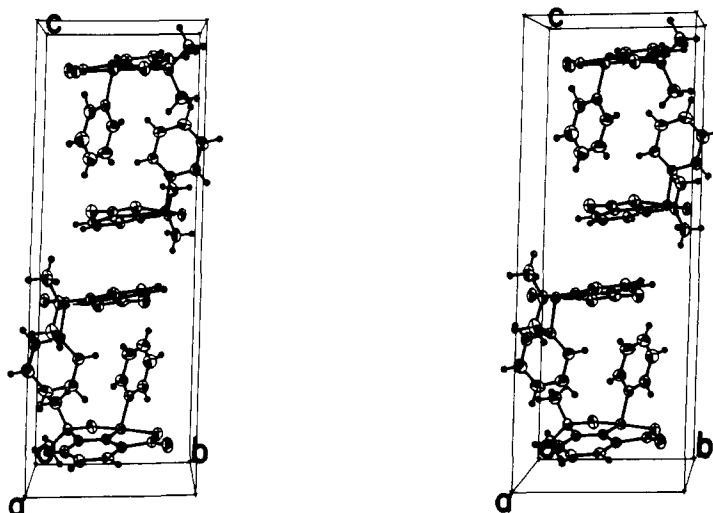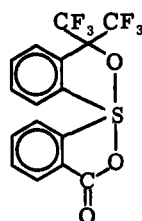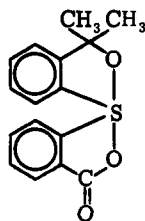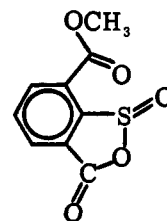**Figure 7.** Stereoscopic view of the single molecule of sulfurane **10**.
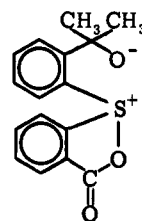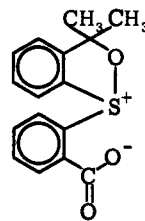


**Figure 8.** Stereoscopic view of the crystal structure of **10**.

*Polarizabilities in Sulfuranes and Persulfuranes*

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**12**          **13**



**13a**          **13b**

since resonance form **13b** is expected to contribute more to the structure than **13a**. Bicyclic sulfuranes **10** and **11**, which are structurally more closely related to persulfurane **1** than is **13**, show carbonyl stretching frequencies at 1639 and 1645 cm⁻¹, respectively, very similar to that seen for **13** (the contributions of resonance structures are in the order **10b** > **10a**; **11b** > **11a**). The
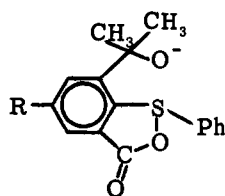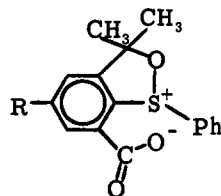


**10a** R = H          **10b** R = H
**11a** R = C(CH₃)₃    **11b** R = C(CH₃)₃

carbonyl stretching frequency in persulfurane **1** is 1712 cm⁻¹, much higher than that seen in sulfuranes **10** and **11**. This suggests that the persulfurane with its expected greater concentration of positive charge on sulfur will be less polarizable along the three-center four-electron bonds than is the case for sulfuranes **10** and **11**. This decreases the importance of structures analogous to **10b** or **11b** and shifts the carbonyl stretching frequency higher in **1** than in **10** or **11**.

The suggestion that polarization of the hypervalent O–S–O bonds in unsymmetrical sulfuranes and persulfuranes is reflected both in the carbonyl stretching frequencies of the acyloxy apical ligands and in the difference of the S–O bond lengths in the hypervalent bonds allows us to predict that sulfurane **10** or **11** would show a greater degree of dissymmetry in S–O bond lengths than persulfurane **1**. The X-ray structure of **10** indeed reveals a large difference in the lengths of the S–O bonds [averaged S–O(1) = 2.248 (2) Å, S–O(9) = 1.662 (2) Å]. Their difference (0.59 Å) clearly reflects the highly polarized nature of the hypervalent O–S–O bond resulting from the difference in electronegativities of the apical ligands. The greater resemblance of the acyloxy ligands in **10** to a carboxylate anion is also well illustrated by the close correspondence of C=O [C(2)–O(11) = 1.229 (3) Å] and C–O [C(2)–O(1) = 1.28 (3) Å] bond lengths. The C=O bond length of **10** is slightly longer than that seen for sulfurane **3** and for cyclic sulfinylcarboxylate **14**,[19] a tricoordinate sulfur(IV) compound (by ca. 0.02 and 0.045 Å, respectively), whereas the C–O bond length of **10** is shorter (by 0.06 and 0.1 Å, respectively). The difference (0.05 Å) in C=O and C–O bond lengths for **10** is much smaller than that for **3** and **14** (0.13 and 0.2 Å, respectively). Bond orders for the C–O bonds in **10** are therefore very similar, with the electron density being almost evenly dis-

tributed between the two C–O bonds, as would be the case for a carboxylate anion. On the basis of the structural and infrared data for **10**, **1**, and **3**, we might assume in general that the longer the S–O bonds attached to the carboxy ligand (2.248, 1.91, and 1.83 Å for **10**, **1**, and **3**, respectively), the lower would be the carbonyl frequencies (1639, 1712, and 1724 cm⁻¹ for **10**, **1**, and **3**, respectively).

**Comparisons of Symmetrical and Unsymmetrical Sulfuranes.** We may observe some effects of various apical ligands (in this case, perfluoroalkoxy, alkoxy, and acyloxy) on the structure of sulfuranes by comparing the bond lengths and angles about sulfur in the species of Table IV. All the sulfuranes have approximate trigonal-bipyramidal geometry about sulfur. Sulfuranes with symmetrically substituted apical ligand positions, **4**, **9**, and **3**, are clearly shown to have identical or nearly identical S–O bond lengths (*a* and *b*), whereas unsymmetrical sulfuranes **5** and **10** have large differences in their S–O bond lengths attributed to polarization of the hypervalent O–S–O bonds. The persulfurane, though unsymmetrically substituted, has a smaller difference in the two types of S–O bonds than does the similarly substituted **10**. That the sum of S–O bond lengths (*a* + *b*) in **9** is significantly less than in sulfuranes **4** and **3** is somewhat surprising in view of the great unreactivity of **4** relative to **9**. The hydrolysis of **9** in aqueous methanol is relatively facile,[12] while **4** is greatly favored at equilibrium over its hydrolysis product. The greater length of the S–O bonds to the more electronegative apical ligands of the less reactive **4** is seen to be offset by shorter equatorial S–C bonds in **4** relative to **9**. Since the alkoxy ligands of **9** are effectively less electronegative than either the perfluoroalkyl or the acyloxy ligands, less positive charge is concentrated on the central sulfur of **9**.

The lower electronegativity of the apical alkoxy ligands may also be reponsible for the observed large C–S–C angle (112.4°, ∠ *cd*) in **9**, as compared to those in the other sulfuranes of Table IV (~107.9°) which have more electronegative apical ligands. The postulated greater effective positive charge on the sulfur atoms of sulfuranes having more electronegative apical ligands could accentuate the 3s–3p energy difference for the sulfur atom,[8,22] thus increasing s character in the lone-pair orbital and decreasing the C–S–C angles. This observation is consistent with that seen for acyclic sulfuranes,[8,22] in which the C–S–C angle decreases with increasing electronegativity of apical ligands.

Because of its unique structure, a direct comparison of fused-ring sulfurane **10** with spirosulfuranes **4**, **5**, **9**, and **3** is difficult. Nevertheless, it is of particular interest to point out certain significant differences between the structural features around sulfur in **10** and in these spirosulfuranes (Table IV). The most noticeable difference is the smaller O–S–O angle (∠ *ab*) in **10** relative to that in **3**, **4**, **5**, and **9**. This greater deviation from linearity may be in part ascribed to the unusually long and hence easily deformable hypervalent O–S–O bond (*a* + *b*). Another major difference is the greater degree of dissymmetry in C–S bond lengths (*c* and *d*) in **10** in comparison to other spirosulfuranes. The two C–S bond lengths in **3**, **4**, **5**, and **9** are identical or nearly identical. Furthermore, the "short" C–S bond (*c*) in **10** is significantly shorter than the C–S bonds in **3**, **4**, **5**, and **9**. This may be in part due to the fact that this C–S bond is the common bridge for the two nonequivalent five-membered heterocyclic rings in the bicyclic

(22) Paul, I. C.; Martin, J. C.; Perozzi, E. F. *J. Am. Chem. Soc.* **1972**, *94*, 5010.
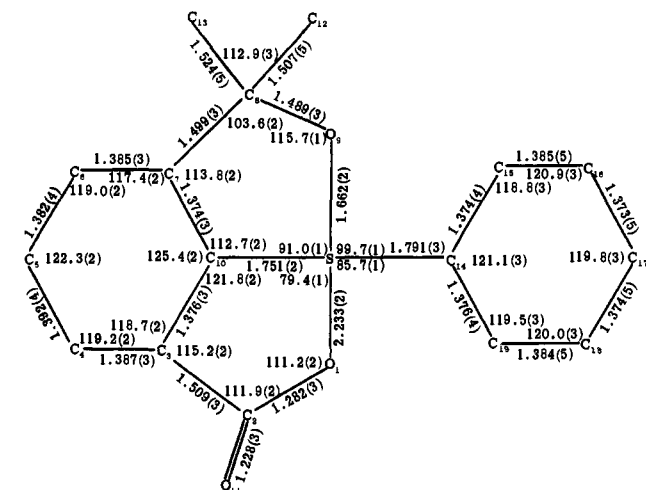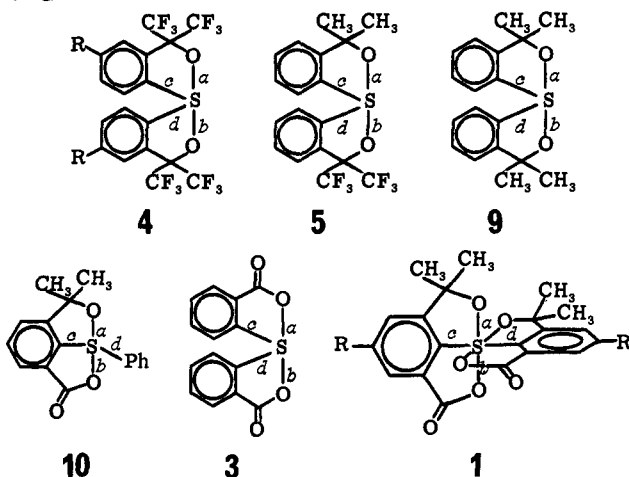
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**Figure 9.** Selected bond lengths (Å) and bond angles (deg) in **10** with estimated standard deviations in parentheses. Two angles around the sulfur atom which are not shown in the figure are O(1)-S-O(9) = 170.1 (1)° and C(10)-S-C(14) = 107.6 (1)°.

**Table IV.** A Comparison of Bond Lengths (A) and Bond Angles (Deg) about Sulfur



| | | compds | | | | |
|---|---|---|---|---|---|---|
| | $4^a$ | $5^b$ | 9 | $10^c$ | $3^d$ | $1^e$ |
| a | 1.818 (5) | 1.713 (2) | 1.787 (2) | 1.662 (2) | 1.83 (1) | 1.67 (1) |
| b | 1.832 (5) | 1.955 (2) | 1.814 (2) | 2.248 (2) | 1.83 (1) | 1.91 (3) |
| c | 1.803 (8) | 1.806 (3) | 1.808 (3) | 1.750 (2) | 1.82 (2) | 1.78 (2) |
| d | 1.793 (8) | 1.799 (3) | 1.808 (3) | 1.786 (2) | 1.82 (2) | 1.78 (2) |
| a + b | 3.650 | 3.668 | 3.601 | 3.900 | 3.66 | 3.58 |
| c + d | 3.596 | 3.605 | 3.616 | 3.536 | 3.64 | 3.56 |
| $Lab^f$ | 177.6 (2) | 177.3 | 178.2 (1) | 170.5 (1) | 178.5 | 173 (1) |
| Lcd | 107.9 (4) | 107.9 (1) | 112.4 (1) | 107.9 (1) | 107.8 | 171 (1) |
| Lac | 86.2 (3) | 89.2 (1) | 86.2 (1) | 91.2 (1) | 88.7 | 91 (1) |
| Lbd | 87.0 (3) | 84.3 (1) | 86.9 (1) | 83.9 (1) | 88.7 | 88 (1) |
| Lbc | | | | 79.4 (1) | | 86 (1) |
| Lad | | | | 100.2 (1) | | 93 (1) |

$^a$ Reference 8. $^b$ Reference 9a. $^c$ Listed here are the averaged values for the unprimed and primed molecules in the unit cell. $^d$ Reference 7. $^e$ Listed here are the averaged values of the two halves (assuming a $C_2$ symmetry). $^f$ In this table the angle *ab* is defined as bending away from the lone pair of electrons on sulfur.

system. Indeed the five-membered ring containing the alkoxy oxygen of **10** is remarkably similar in its dimensions to the analogously constituted ring in **1** (compare Figures 1 and 9). The principal difference in the bicyclic fused-ring system containing the two oxygens in **1** and **10** lies in the greater S–O bond distance to the carboxylate oxygen of **10** than is found for the two analogous S–O bonds in **1**. The greater S–O bond distance in **10** increases the resemblance to a sulfonium carboxylate zwitterion (resonance

**Table V.** Chemical Shifts of the Quaternary Carbon in Alkoxy Ligands in Some Alkoxysulfuranes

| | trans ligand | | $^{13}$C(quaternary) chem shifts,$^a$ |
|---|---|---|---|
| compd | L (in 15) | X-Y (in 16) | ppm (CDCl$_3$) |
| 19 | | -C(CH$_3$)$_2$O- | 79.11 |
| 9 | | -C(CH$_3$)$_2$O- | 80.92 |
| 6 | | -C(CF$_3$)$_2$O- | 86.16 |
| 13 | | -COO- | 92.03 |
| 17 | -Cl | | 98.81 |
| 18 | -OSO$_2$CF$_3$$^b$ | | 104.81 |
| 10 | | | 95.57 |
| 11 | | | 95.19 |
| 11 + CF$_3$COOH | | | 103.18. |
| 1 | | | 88.00 |
| 20 | | | 82.44 |

$^a$ Full spectral data are listed in Table XVIII (see note concerning supplementary material). $^b$ Probably the ionic sulfonium triflate.

structure **10b**) and increases the positive charge on sulfur. Even though the S–O (carboxylate) bonds of **1** are shorter, which suggests less charge polarization, there are two such S–O bonds on a single sulfur. This may mean that the positive charges on sulfur in **1** and **10** are very similar. The S–C bond lengths and the geometry of the five-membered ring containing the alkoxy oxygen could then be largely determined by the magnitude of the positive charge on sulfur. The explanation for these features of the geometry must await the results of further structural studies.

$^{13}$**C NMR Evidence.** It is perhaps not surprising that the polarization of hypervalent bonds in sulfuranes of type **7** and **8** which is reflected in the carbonyl stretching frequencies[11] is also reflected in $^{13}$C NMR chemical shifts. The chemical shift of the quaternary carbon in the alkoxy ligands of sulfuranes of type **15** and **16** is
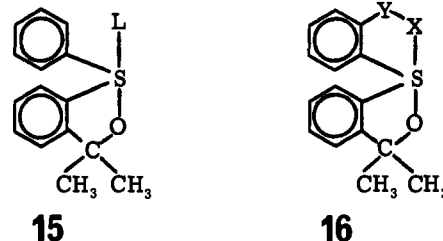


found to be very reponsive to the change of the nature of trans apical substituents (L, X, Y) (Table V). Examples of sulfurane type **15** are chlorosulfurane **17**[23] and sulfonium triflate **18**,[23]
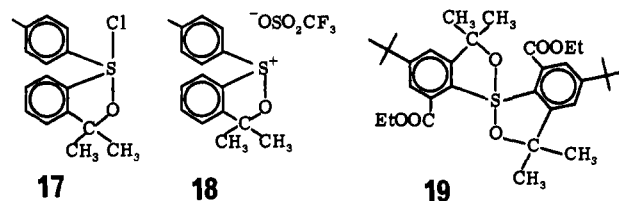


whereas examples of sulfurane type **16** include **6, 9, 13,** and **19**.[1] The peak positions for these quaternary carbons of the alkoxy ligands shift markedly to lower field with increasing electronegativities of the trans apical ligands. Alkoxysulfuranes bearing identical apical ligands such as **9, 19,** and **10, 11** have very similar quaternary carbon chemical shifts (Table V), in spite of the presence of different substituents in the aryl rings.

Polarization of the O–S–O′ or O–S–X hypervalent bond evidenced by this carbon chemical shift is closely parallel to that evidenced by carbonyl stretching frequencies of the acyloxy ligands. Figure 10 shows the correlation of carbonyl stretching frequencies for acyloxysulfurane type **7** and **8** with the quaternary carbon chemical shifts for alkoxysulfurane type **15** and **16**, responding to the same apical ligands.
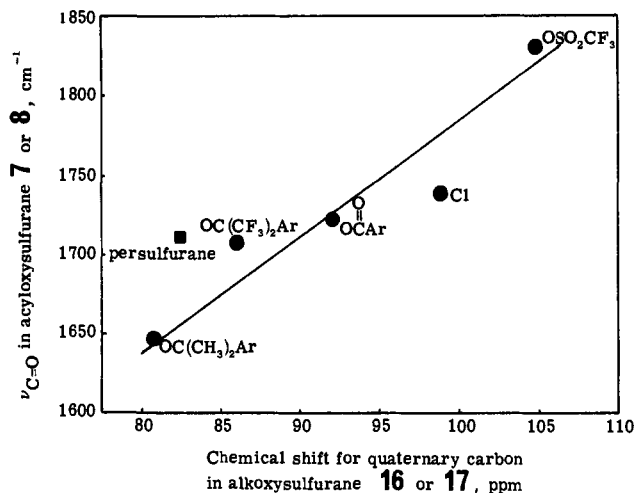
(23) Figuly, G. D.; Martin, J. C., unpublished work.

**Figure 10.** Plot of values (represented by ●) of $\nu_{C=O}$ in acyloxy-sulfuranes, in order of increasing frequency: **13, 12, 3, 7** (L = Cl), and **7** (L = OSO₂CF₃) against values of quaternary carbon chemical shift in the closely analogous alkoxysulfuranes in order of increasing shift: **9, 6, 13, 17,** and **18.** The point represented by ■ is the value of $\nu_{C=O}$ in persulfurane **1** plotted against the value of quaternary carbon chemical shift in persulfurane **20.**

This correlation is, however, apparently not applicable to persulfuranes. The carbonyl stretching frequency for persulfurane **1** (1712 cm⁻¹) would, according to Figure 10, have correlated to the quaternary carbon chemical shift of ca. 90 ppm for alkoxy-persulfurane **20.**[1] The quaternary carbon chemical shift for **20**



**20**
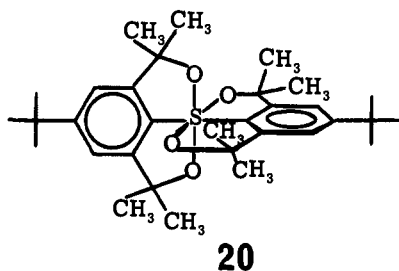
was found to be 82.44 ppm, much lower than the predicted value. Furthermore, the peak position of the quaternary carbon in the alkoxy ligand of persulfurane **1** (88.00 ppm) is at higher field than that of its structure-related sulfurane **11** (95.19 ppm). These indicate that the O–S–O hypervalent bonds in persulfuranes are less polarizable, consistent with the conclusion reached earlier.

Like the carbonyl stretching frequencies, the quaternary carbon chemical shifts are also correlated well with the S–O bond lengths to the alkoxy ligands in sulfuranes. For compounds **9, 5, 1,** and **10,** the longer the S–O bonds to the alkoxy ligand (see Table IV), the more upfield the peak position for quaternary carbons in the alkoxy ligand would be (see Table V).

It is interesting to note that the chemical shifts of the quaternary carbon in the alkoxy ligands in sulfurane oxides **21, 22,** and **23**
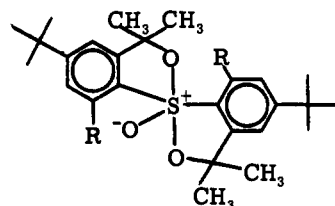


**21** R = COOEt
**22** R = CH₂OH
**23** R = C(CH₃)₂OH

(79.34, 80.46, and 80.81 ppm, respectively), 10-S-5 species, are not significantly different from those of the 10-S-4 sulfuranes (see Table V). In sulfurane oxide **23,** the peak position for the quaternary carbons in the free tertiary alcohol substituents (74.3 ppm) is at higher field than that for those in the apical alkoxy ligands (80.8 ppm). Based on these observations, we may at least tentatively rule out the possiblity that sulfurane oxide diol **22** has the alternative structure **24.**[1]
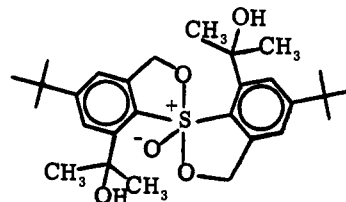


**24**

### Conclusion

The large difference in the S–O bond lengths revealed in the X-ray structure of **1** clearly indicates the polarization of the three-center four-electron hypervalent bonds in this 12-S-6 (persulfurane) species. These O–S–O hypervalent bonds to sulfur(VI) in persulfurane **1** are, however, shown to be less polarizable than the O–S–O hypervalent bond in the closely related unsymmetrical 10-S-4 (sulfurane) species **10.** This conclusion is based on studies of structural data, carbonyl stretching frequencies, and ¹³C chemical shifts for the quaternary carbons in the alkoxy ligands of **1, 10,** and related species. It is interesting to speculate that the hypervalent bonds in 10-S-5 (sulfurane oxide) species would be polarizable, perhaps intermediate between 10-S-4 and 12-S-6 species. No unsymmetrical sulfurane oxides are yet known, however; hence there is no test of the polarizability of this type of X–S–Y (X ≠ Y) bond.

**Supplementary Material Available:** A listing of the thermal parameters for **1** (Table VI), **9** (Table IX), and **10** (Table XII), bond lengths and angles for **1** (Tables VII and VIII), **9** (Tables X and XI), and **10** (Tables XIII and XIV), observed and calculated structure factor amplitudes for **1** (Table XV), **9** (Table XVI), and **10** (Table XVII), and full ¹³C NMR spectral data of most compounds in this paper (Table XVIII) (128 pages). Ordering information is given on any current masthead page.