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 threecenter, 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 SF_6 . 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.

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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



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 symmetric³ compound 2 has only a single ¹⁹F resonance as expected.⁴ Complete structure determinations, by

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Lam, W. Y.; Martin, J. C., preceding paper in this issue.
 (a) Roberts, H. L. "Inorganic Sulfur Chemistry"; Nickless, G., Ed.; (2) (a) Roberts, H. L. "Inorganic Sultur 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 SF₅OSF₅⁶ 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,



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 seen¹¹ in the wide range ($\sim 300 \text{ cm}^{-1}$) of carbonyl stretching frequencies determined for sulfuranes of type 7 and 8. This has been postulated¹¹ 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.



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 912 and of unsymmetrical sulfurane 10, a model compound closely related to persulfurane 1.

- (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, 1070 17
- (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.



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-2,1benzoxathiole] (6). Diazomethane in ether was added to a solution of 4-methyl-2-(1-hydroxy-1-trifluoromethyl-2,2,2-trifluoroethyl)-2'-carboxydiphenyl sulfide¹¹ (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. $(C_{19}H_{16}F_6O_2S): C, H, F, S.$

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: $C_{28}H_{34}O_6S$, 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 + 1k = 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/cm^3) indicated the incorporation of solvent molecules into the lattice. A Syntex P21 diffractometer equipped with a graphite monochromator, $\lambda(Cu K\alpha_1) = 1.54178$ 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. $0.4 \times 0.2 \times 0.1$ mm was used for the data collection.¹³ The unique octant hkl was collected in the $2\theta:\theta$ scan mode out to $2\theta = 126^{\circ}$ $((\sin \theta)/\lambda = 0.588)$. 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 tertbutyl positions were refined and were constrained to be half-occupied. Positions for all the nonhydrogen atoms except for the disordered tertbutyl groups were refined anisotropically with the full-matrix leastsquares 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 $[\sum w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$, where m is the number of observations and n is the number of variables, was 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

⁽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⁾ $R = \sum_{i} ||F_0| - |F_0|| / \sum_{i} |F_0|; R_w = \sum_{i} ||F_0| - |F_0||^2 / \sum_{i} ||F_0|^2 ||^{1/2}.$ (16) Ibers, J. A., Hamilton, W. C., Eds. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; pp 99-102.

Table I. Final Coordinates for Persulfurane 1^a

atom	x	У	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)
С9Т	0.4906 (8)	-0.1627 (16)	-0.0130 (15)
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.

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 Å³, F(000) = 640, ρ_c (Z = 4) = 1.27 g/cm³, μ (Mo K α) = 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 P2₁ automated diffractometer equipped with a graphite monochromator λ (Mo K α) = 0.7107 Å.

Solution and Refinement of the Structure of 9. A crystal of dimensions $0.38 \times 0.55 \times 0.67$ mm was used for the 2θ : θ scan data collection. The variable scan option was used between $4-29^{\circ}$ /min. The background count time/total scan time was set at 0.5. Data in the *hkl* octant were collected out to $2\theta = 70^{\circ}$. 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 nonhydrogen atoms converged to agreement factor R and R_w of 0.059 and 0.065, respectively.¹⁵ The final value of $[\sum w(|F_0| - |F_c|)^2/(m - n)]^{1/2}$, 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/A^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: C₁₆H₁₄O₃S, mol wt = 286.4, triclinic, *P*1, *a* = 7.747 (3) Å, *b* = 8.065 (1) Å, *c* = 22.781 (7) Å, *α* = 88.14 (2)°, *β* = 95.57 (3)°, γ = 95.68 (2)°, *V* = 1409.3 Å³, *Z* = 4, *ρ_c* = 1.35 g/cm³, μ (Mo K α) = 2.3 cm⁻¹, *F*(000) = 600; no systematic absences. The cell dimensions were obtained by a least-squares fit to the automatically

Table II. Final Coordinates for Spirosulfurane 9^a

		E	
atom	x	У	Z
S	0.48426 (9)	0.06599 (7)	0.38454 (4)
0(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)
HIU B	0.801 (6)	-0.009 (4)	0.574 (2)
HIUC	0.883 (7)	0.076 (5)	0.528 (3)

^a Estimated standard deviations in parentheses.

centered settings for 15 reflections on a Syntex P2₁ diffractometer equipped with a graphite monochromator, λ (Mo K α) = 0.7107 Å.

Solution and Refinement of the Structure of 10. A crystal with dimensions ca. $0.80 \times 0.53 \times 0.28$ mm was used for data collection. The $2\theta:\theta$ scan mode was used with a variable scan $(4.0-20.0^{\circ}/\text{min})$ 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 $2\theta = 65^{\circ}$. 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 $[\sum w(|F_0| - |F_a|)^2/(m-n)]^{1/2}$, 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



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



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

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 trigonalbipyramidal 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



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 $(X \neq Y)$ 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 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 SF₆ 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 $[O(7)-S(1)-O(17) = 96 (1)^{\circ}]$ 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-O₂ distance in 1 is slightly shorter than a "normal" S-O single bond (1.70 Å),¹⁸ whereas the S–O₁ 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 expected¹¹

(17) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell

(17) Fading, L. The Nature of the chemical bond, side call, content 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.



- (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 10⁴

		s for Suffarance 10	
atom	x	у	Ζ
S(1)	0.85772 (8)	0.20381 (7)	0.405 73 (3)
$\tilde{s}(1)'$	0.25726 (8)	0.54950 (8)	0.097 54 (3)
0(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)	1.1094(3) 1 2007(3)	0.3389(3) 0.1804(3)	0.425 98 (10) 0.417 27 (13)
0(9)	1.0246(2)	0.1804(3)	0.41943(8)
C(10)	0.9968(3)	0.3876(3)	0.41554(10)
0(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)	-0.01/3(5)	0.25344(17) 0.21072(16)
C(17)	0.7309 (3)	0.0909(3) 0.2517(5)	0.21073(10)
C(19)	0.8597(4)	0.2908(4)	$0.225\ 63\ (13)$
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(n)	0.4240(3) 0.2463(3)	0.2908(3) 0.2158(3)	0.08203(10) 0.09709(12)
	0.2403(3) 0.1442(2)	0.2138(3) 0.3632(2)	0.09709(12)
C(10)'	0.1442(2) 0.4484(3)	0.3032(2) 0.4616(3)	0.085 89 (10)
O(11)'	0.7357 (3)	0.8361(2)	0.08893(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) 0.1254(9)	0.0773(0)	0.28751(25) 0.24612(24)
C(19)'	0.1234(5) 0.1303(5)	0.7239(3) 0.6832(4)	0.24012(24) 018790(17)
H(4)	1.015 (3)	0.783(3)	0.4365(11)
H(5)	1.316 (3)	0.743 (3)	0.4524 (12)
H(6)	1.401 (3)	0.476 (3)	0.443 5 (11)
H1 2A	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)
HI 3A UI 2D	1.321 (4)	0.011(5) 0.172(4)	0.4675(14)
H13C	1.428 (4)	0.173(4) 0.138(6)	0.4003(13) 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)	0.0468(12)
H12'A	0.330(3)	0.101(3) 0.062(4)	0.0035(11) 0.064 0.(13)
H1 2'B	0.142 (4)	0.159 (4)	0.011 2 (14)
H1 2'C	0.219 (4)	0.007 (4)	0.048 7 (12)
H13'A	0.326 (4)	0.041 (4)	0.158 5 (14)
H1 3'B	0.139 (5)	0.093 (4)	0.165 5 (15)
H13'C	0.314 (4)	0.209 (4)	0.187 1 (15)
$H(15)^{\prime}$	0.475 (3)	0.499 (3)	0.206 1 (12)
H(17)	0.400 (3)	0.332 (3)	0.293 9 (19)
H(18)'	0.035 (5)	0.707 (0)	0.321 4 (24)
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.









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



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°, $\angle cd$) 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 fusedring 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 $(\angle ab)$ 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.



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 (Å) and Bond Angles (Deg) about Sulfur $% \mathcal{A}$



	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)
с	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	3.9 00	3.66	3.58
c + d	3.596	3.605	3.616	3.536	3.64	3.56
∠ab ^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)
∠bc				79.4 (1)		86 (1)
Lađ				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	¹³ C(quaternary)		
compd	L (in 15)	X-Y (in 16)	ppm (CDCl ₃)	
19 9 6 13 17 18 10 11 11 + CF₃COOH 1 20	-Cl -OSO₂CF₃ ^b	-C(CH ₃) ₂ O- -C(CH ₃) ₂ O- -C(CF ₃) ₂ O- -COO-	79.11 80.92 86.16 92.03 98.81 104.81 95.57 95.19 103.18. 88.00 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.

¹³C 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 frequencies¹¹ is also reflected in ¹³C 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 \oplus) of $\nu_{C=0}$ in acyloxysulfuranes, 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 \blacksquare is the value of $\nu_{C=0}$ 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 alkoxypersulfurane $20.^{1}$ The quaternary carbon chemical shift for 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



(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 possibility that sulfurane oxide diol 22 has the alternative structure 24.¹





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 \neq Y) bond.

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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.