Reactions and Crystal and Molecular Structure of an Unsymmetrical Spirosulfurane: Manifestations of Hypervalent Bond Polarization in a Sulfurane[1]

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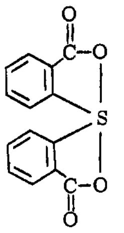
The regiospecificity evidenced in several of its reactions is correlated with the x-ray structure of unsymmetrically substituted diaryldialkoxyspirosulfurane **6**. Most impressive is the large difference (0.24 Å) between the lengths of the S–O bonds, 1.713 (2) and 1.955 (2) Å, from which we infer a high degree of polarization in the hypervalent O–S–O bond. The estimated S–O bond orders are 0.96 and 0.37, respectively. The crystals of **6** are monoclinic, the space group is $P2_1/c$, and there are four molecules in a unit cell of dimensions $a = 11.201$ (1), $b = 14.253$ (2), $c = 11.768$ (2) Å, $\beta = 114.08$ (1)°. The structure was refined to an R factor of 0.047. Reactions of **6** with methyl fluorosulfonate and trifluoromethanesulfonic acid reflect the relative nucleophilicities and basicities of the oxygens of **6**. The oxygen nearer the CF_3 substituents is more basic and more nucleophilic than that more distant from these electron-withdrawing groups, in a striking demonstration of the polarizability of the three-center four-electron bond. These chemical reactivities are consistent with what might be predicted from the x-ray data if one assumes the S and O separated by 1.955 Å to be essentially zwitterionic. The relevance of this work to earlier work on sulfuranes with polarized hypervalent bonds is discussed.

The x-ray structures of a number of symmetrically substituted sulfuranes, including **1** and **2**, have been reported.[2-6] A prominent feature of all these structures is the longer than usual S–O single bonds, identical in length to each other within experimental error. For example, the S–O bond lengths of **1** are both 1.83 Å,[2] and in **2** the S–O bond lengths are 1.82 and 1.83 Å.[3] Diazasulfurane **3** has S–N bond lengths of 1.899 and 1.897 Å.[6] Identical or nearly identical hypervalent bond lengths are expected for sulfuranes with identical apical ligands.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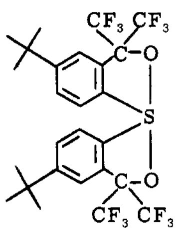
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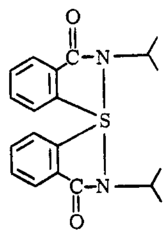
Evidence for the polarizability of the hypervalent bond in sulfuranes has recently been discussed.[7] The carbonyl-stretching frequency is found to be very responsive to variations in substituents (L, X, Y) in sulfuranes of type **4** and **5**. This has been postulated to be a result of the variable level of negative charge on the acyloxy group, reflecting a greater or lesser resemblance to a carboxylate anion in its carbonyl-stretching frequency.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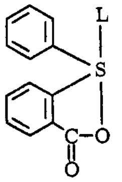
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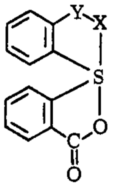
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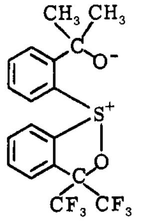
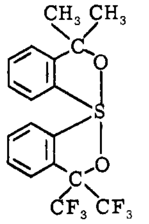
If sulfuranes with unsymmetrical apical substitution patterns have strongly polarized hypervalent bonds, then this should cause a significant difference in their bond lengths; i.e., the more electronegative apical ligand should have a longer S–X bond length and the less electronegative ligand should have a smaller S–X bond length.

We herein report the x-ray structure for unsymmetrical sulfurane **6** which reveals a large difference in S–O bond lengths. The three-center four-electron hypervalent bond[8] is not badly represented by resonance structures such as **6a** and **6b**. We might expect **6b** to contribute more to the structure than **6a** as a result of the inductive electron withdrawal of the CF_3 substituents. This expected polarization of the hypervalent three-center bond should be reflected in reactivity and in bond lengths. This work was undertaken to probe these predictions.


6a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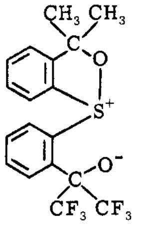

6b

Experimental Section

General. Chemical shifts for protons are reported on the δ scale, ppm downfield from the Me_4Si internal standard; fluorine chemical shifts are reported on the ϕ scale, ppm upfield from the $CFCl_3$ internal standard. The ^1H NMR and ^{19}F NMR integral ratios are rounded to the nearest whole number of nuclei. Melting points are uncorrected. Elemental analyses of new compounds are within 0.4% of theoretical values, unless otherwise noted.

Alkylation of 6 with Methyl Fluorosulfonate. Sulfurane **6** (81 mg, 0.198 mmol), synthesized by the published[9] method, was dissolved in ca. 1 mL of dry $CDCl_3$ and methyl fluorosulfonate (22.6 mg, 16 μL, 0.198 mmol) was added. The reaction, followed at 25 °C by ^1H NMR (disappearance of methyl singlet of $MeOSO_2F$), was complete after 12.5 days. The ^1H NMR spectrum of this solution showed methyl singlets at δ 2.04, 2.15, and 4.38 (OCH_3) for sulfonium salt **8**. Another small singlet (ca. 9% of the total OCH_3 singlet at 8 at 75% reaction completion) was seen at δ 3.98 which might be due to the methoxy group of sulfonium salt **7**. The solution was extracted with aqueous NaOH to give (^1H NMR) ca. 80% sulfoxide **9** and ca. 20% of an unidentified product. Chromatography on silica gel (6.2 g) with $CHCl_3$ gave 16.4 mg (20.3%) of sulfurane **6** and 66.1 mg (75.8%, 95% based on conversion) of sulfoxide **9**, mp 166–167 °C; ^{1}NMR (100 MHz, $CDCl_3$) δ 1.74 (s, 3, CH_3), 1.79 (s, 3, CH_3), 3.61 (m, 3, OCH_3, coupling to CF_3 groups, $J_{HF} = 1.1$ Hz), 4.54 (br s, 1, OH), 6.78 (br d, 1, ArH), 6.95–7.14 (m, 1, ArH), 7.20–7.40 (m, 2, ArH), 7.54–7.84 (m, 3, ArH), 8.28–8.46 (m, 1, ArH); ^{19}F NMR ($CDCl_3$) ϕ 68.13 (q, 3, CF_3, $J_{FF} = 8.5$ Hz), 70.64 (q, 3, CF_3, $J_{FF} = 8.5$ Hz); mass spectrum (70 eV) m/e (rel intensity) 440 (6.0, $M^{+\cdot}$), 425 (34.4, $M^{+\cdot} - CH_3$), 409 (3.9, $M^{+\cdot} - OCH_3$), 379 (7.2), 289 (4.0), 265 (4.2), 239 (4.7), 205 (12.8), 149 (44.6), 91 (15.6), 77 (17.0), 43 (100).

Anal. ($C_{19}H_{18}F_6O_3S$) C, H.

Reaction of Unsymmetrical Spirosulfurane 6 with Trifluoromethanesulfonic Acid. To a solution of sulfurane 6 (230 mg, 0.563 mmol) in 25 mL of ether was added 51 μL (86.2 mg, 0.574 mmol) of trifluoromethanesulfonic acid at 25 °C. In a few seconds a white precipitate formed. The mixture was stirred for 15 min and filtered. The crystals were washed with ether to give 256 mg (81.4%) of crystalline sulfonium triflate 12: mp 200–202 °C; IR (KBr) 3450 (w, br, OH), 3000 (w), 1475 (w), 1447 (w), 1320–1120 (s, five or more strong peaks), 1030 (m), 975 (m), 965 (m), 948 (m), 831 (m), 765 (m), 704 (m), 640 (m); ^1H NMR (220 MHz, CH_2Cl_2) δ 1.932 (s, 3, CH_3), 2.205 (s, 3, CH_3), 7.468 (d, 1, ArH, J = 8 Hz), 7.627 (t, 1, ArH, J = 8 Hz), 7.705–7.932 (m, 5, ArH), 8.09 (d, 1, ArH, J = 8 Hz), 11.40 (br s, 1, OH); ^{19}F NMR (90 MHz, CH_2Cl_2) ϕ 73.51 (q, 3, CF_3, J_{FF} = 8.5 Hz), 74.73 (q, 3, CF_3, J_{FF} = 8.5 Hz), 78.9 (s, 3, $^-OSO_2CF_3$).

Anal. ($C_{19}H_{15}F_9O_5S_2$) C, H, F, S.

Treatment of Sulfurane 6 with HCl. (a) Sulfurane 6 (132.2 mg, 0.32 mmol), dissolved in 3 mL of CH_2Cl_2, was shaken with 1 mL of concentrated HCl. The CH_2Cl_2 layer was separated and the aqueous layer was extracted twice with CH_2Cl_2. The CH_2Cl_2 extracts were combined and dried ($MgSO_4$), and solvent was removed, leaving a white solid (120 mg, 91.8% recovered) identified as 6 by melting point and ^1H NMR: ^1H NMR of 6 ($CDCl_3$) δ 1.62 (s, 3, CH_3), 1.80 (s, 3, CH_3) 7.15–7.80 (m, 6, ArH), 8.15–8.47 (m, 2, ArH, protons ortho to S).

(b) A solution of sulfurane 6 (242 mg, 0.59 mmol) in 10 mL of dry ether was saturated with HCl gas. No precipitate formed. The ether was removed by N_2 stream and the product was analyzed by ^1H NMR ($CDCl_3$): δ 1.83 (s, 3, CH_3), 2.10 (s, 3, CH_3), 7.40–7.87 (m, 6, ArH), 7.93–8.14 (m, 1, ArH), 8.35 (d, 1, ArH, J = 8 Hz). The product was recrystallized from $CHCl_3$–hexane (181 mg, 75% recovered) and was identified as 6 (^1H NMR).

(c) A solution of 6 in $CDCl_3$, saturated with HCl, gave the following ^1H NMR: δ 1.92 (s, 3, CH_3), 2.22 (s, 3, CH_3), 7.43–8.06 (m, 7, ArH), 8.30 (d, 1, ArH, J = 8 Hz), 9.13 (s, 2.2, HCl, excess). The downfield shifts of the methyl groups in the presence of HCl suggest some sort of interaction with HCl but no chlorosulfurane (14) could be isolated.

X-Ray Crystallography of Spirosulfurane 6. Crystals of 6 were grown by slowly evaporating a chloroform solution of 6. No special precautions were needed to protect the crystal from moisture.

Crystal Data for 6: $C_{18}H_{14}F_6O_2S$ mol wt = 408.4; monoclinic, a = 11.201 (1), b = 14.253 (2), c = 11.768 (2) Å, β = 114.08 (1)°, V = 1715.4 Å, Z = 4, ρ_c = 1.58 g/cm^3, $\mu(CuK_\alpha)$ = 23.6 cm^{-1}, $F(000)$ = 832, systematic absences for $0k0$ when $k = 2n + 1$ and for $h0l$ when $l = 2n + 1$ establish the space groups as $P2_1/c$. The cell dimensions were obtained by a least-squares fit to the automatically centered setting for 15 reflections on a Syntex P2$_1$ diffractometer equipped with a graphite monochromator, $\lambda(CuK_{\bar\alpha})$ = 1.54178 Å.

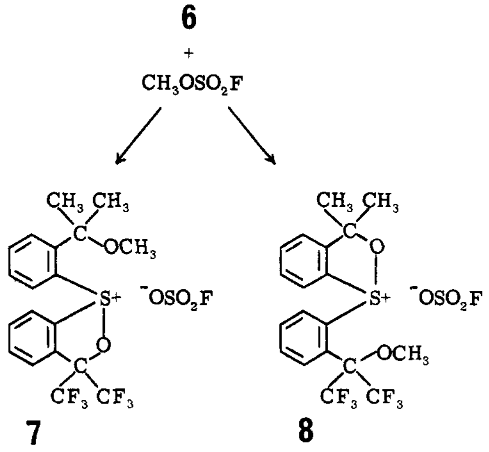
Solution and Refinement of the Structure of 6. A crystal with dimensions ca. 0.4 × 0.3 × 0.2 mm was used for data collection. The data collection was performed in the $2\theta{:}\theta$ scan mode. The variable scan option was employed (2.0–10.0°/min) with the total background time/scan time set at 0.25. Three standards from different parts of the reciprocal space were monitored every 50 reflections. Examination of these reflections showed no crystal deterioration. The hkl and $\bar{h}kl$ octants were collected out to 2θ = 126° ($\sin\theta/\lambda$ = 0.588). Out of the possible 3075 unique reflections collected, 2556 were observed using a 2σ criterion based on counting statistics. The data were corrected for Lorentz and polarization effects, but not for absorption; the maximum and minimum transmission factors were estimated to be 0.45 to 0.62.[10]

The structure was solved by direct methods using the programs supplied by Syntex.[11] The hydrogens were located from difference maps. Full-matrix, least-squares refinement of positional and anisotropic thermal parameters for the nonhydrogen and of positional and isotropic thermal parameters for the hydrogen atoms converged with values for R and R_w of 0.047 and 0.057, respectively.[12] The final value of $[\Sigma w(|F_{obsd}| - |F_{calcd}|)^2/(m - n)]^{1/2}$, where m is the number of observations and n is the number of variables, was 1.91. The scattering curves were taken from the analytical expression used in the "International Tables for X-Ray Crystallography".[13] A final difference map showed a peak, 60% of an average hydrogen, between C(18) and C(16); the rest were less than 50% of an average hydrogen. The final values of the atomic coordinates[14] are given in Table I.

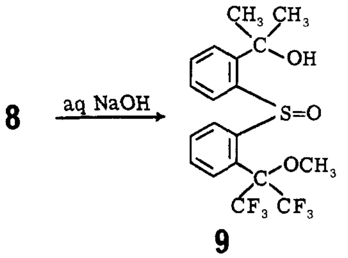
Results

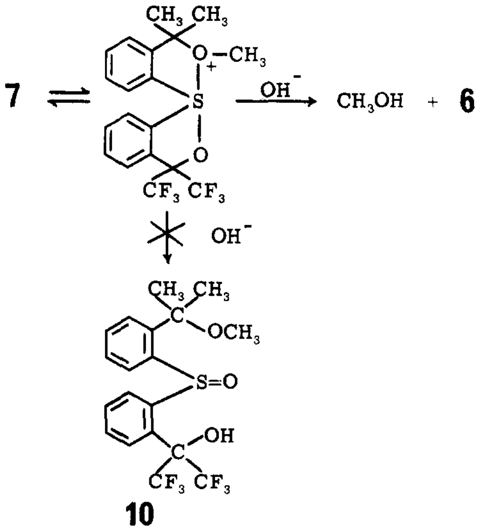
The synthesis and some properties of spirosulfurane 6 have been reported.[9] It is found to be inert toward hot aqueous acid or base, a property which it shares with sulfurane 2.[15] Pyrolysis of 6 occurs only at temperatures above ca. 350 °C, which reflects an unusually high thermal stability for 6, compared to other spirosulfuranes[9,16] substituted with less electronegative ligands. Sulfurane 6 is only weakly basic as evidenced by interactions with a chiral alcohol and with Eu(fod)$_3$.[9] The oxidation of 6 to the sulfurane oxide has also been reported.[17] Oxidation is the only reaction seen for 2.[15]

Scheme I



The alkylation of 6 with methyl fluorosulfonate provides insight into the relative nucleophilicities of the two oxygens of 6. Two possible methylation products are sulfonium salts 7 and 8 (Scheme I). The addition of 1 equiv of methyl fluorosulfonate to a chloroform solution of 6 at 25 °C initially gives sulfonium salt 8 as the only detectable product. The ^1H NMR spectrum of 8 shows two methyl singlets at δ 2.04 and 2.15. The methoxy signal is a broad multiplet (J_{HF} = 1.1 Hz) at δ 4.38. Upon treatment with aqueous NaOH, sulfonium salt 8 is converted to sulfoxide alcohol 9. During the course of the methylation, another singlet at δ 3.98 begins to grow until, when the reaction is 75% complete, the new singlet is ca. 9% of the area of the methoxyl singlet of 8. We suspect that this singlet might be the methoxyl peak of sulfonium salt 7. Our failure to isolate the corresponding sulfoxide 10 upon hydrolysis of the reaction mixture may be the result of de-





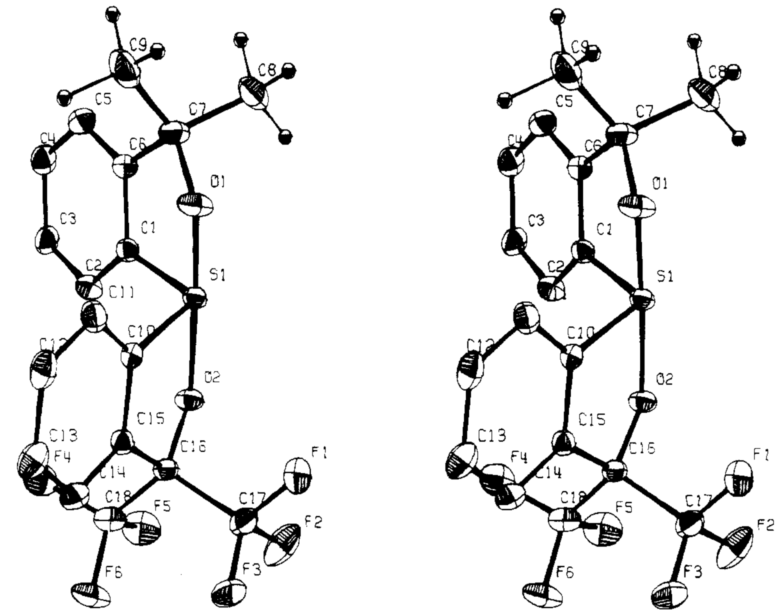
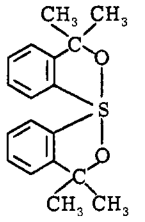


Figure 1. Stereoscopic view of spirosulfurane **6**.

methylation of **7** to regenerate **6** under these conditions. The ether function in **9** is probably less prone to demethylation because the electron-withdrawing trifluoromethyl groups lower the Lewis basicity of the adjacent oxygen and hence decrease the importance of S–O bonding analogous to that giving oxonium character to **7** in the pictured route to **6**. In any case, methylation on the perfluoroalkoxy oxygen is the kinetically preferred reaction. Clearly, the oxygen adjacent to the CF_3 groups is the more nucleophilic of the two. It is interesting to note that methylation[9] of spirosulfurane **11** is much slower than methylation of **6** (12.5 days for **6** vs. 11 h for **11**).[18]



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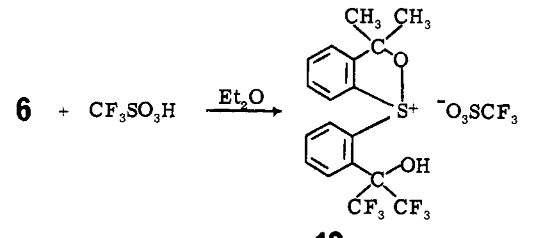
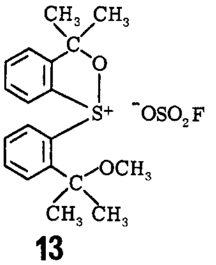
The addition of trifluoromethanesulfonic (triflic) acid to an ether solution of **6** gave a precipitate of sulfonium triflate **12**. The structure assigned to **12** is based on chemical-shift



12

comparisons of the methyl groups of **12** with sulfonium salts **8** (δ 2.04 and 2.15) and **13** (δ 1.78, 1.87, 1.98, and 2.17).[9] The methyl peaks of **12** at δ 1.93 and 2.21 are similar in chemical shifts to those of **8** and to two of the peaks of **13** (δ 1.98 and 2.17), and very different from the chemical shifts of the *gem*-dimethyl peaks for the ether function of **13** (δ 1.78 and 1.87) and of the *gem*-dimethyl peaks for the product of hydrolysis of **8**, sulfoxide **9** (δ 1.74 and 1.79), which serve as models for the isomer of **12** which would result from protonation at the other oxygen.



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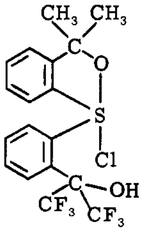
Since **12** is the product of a rapid protonation equilibrium, one expects both O-protonated species to be present in a solution of **12**. The chemical-shift arguments presented above suggest that the equilibrium strongly favors protonation on the fluoroalkoxy oxygen. The more basic site is, therefore, the same as the more nucleophilic site which was methylated in the reaction forming **8**.

An attempt to prepare chlorosulfurane **14** by the procedure[9] used to prepare chlorosulfurane **15** failed. However, when a



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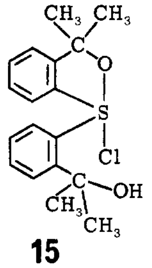


15

$CDCl_3$ solution of **6** is saturated with HCl the methyl groups shift downfield. A similar shift is also seen in **15**.[9] The interaction of **6** with HCl appears to be quite weak with the equilibrium lying in the direction of **6**.

$$\mathbf{6} \rightleftharpoons \mathbf{14}$$

The final coordinates for spirosulfurane **6** are listed in Table I.[14] The important bond lengths and bond angles of **6** are found in Tables II and III.[14] The important bond lengths and bond angles of **2** and **6** are compared in Table IV.[14] Figure 1 shows a stereoscopic view of the molecular structure of **6** and Figure 2 shows its crystal structure.

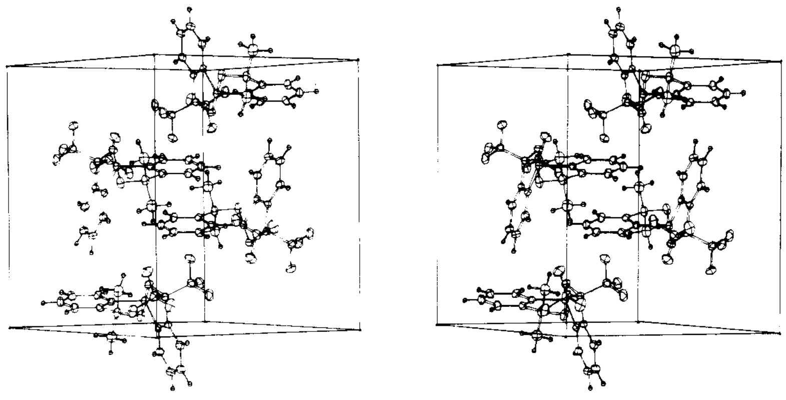


Figure 2. Stereoscopic view of the crystal structure of 6.

Discussion

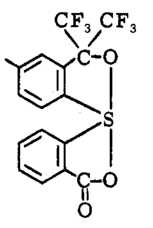
Unsymmetrical spirosulfurane 6 has approximate trigonal bipyramidal geometry about sulfur, like the geometry seen for other sulfuranes.[2-6] The most striking feature of 6 is the large difference in the lengths of the S–O bonds (*a*, 1.713 (2); *b*, 1.955 (2) Å; see Table IV). Their difference (0.24 Å) reflects polarization of the hypervalent O–S–O bond resulting from the difference in electronegativities of the apical ligands. The average S–O bond length of 6 (1.83 Å) is nearly equal to the S–O bond lengths of sulfurane 2 (1.825 Å). The short S–O distance in 6 is only slightly longer than a normal S–O bond (1.70 Å),[19] whereas the other S–O bond distance is 0.26 Å longer. Respective bond orders of 0.96 and 0.37 are calculated for these bonds, using the Pauling[20] correlation of bond order with bond length. The only other significant difference between the bond lengths and bond angles of 2 and 6 are the C–O bonds of 6 (*e*, 1.436; and *f*, 1.369; Table IV) which differ by 0.07 Å. This difference may be in part ascribed to the electronegativity differences of the alkoxy ligands, since bond *f* in 6 is slightly shorter than the average C–O bond length of 2 with the shorter C–O bond in 6 being associated with a longer S–O bond to the same oxygen atom.

The C–S–C angles of 2 and 6 are identical. This is somewhat surprising because the C–S–C angle of 6 might have been expected to be larger than that of 2, in view of a previously noted trend[4,21] which relates a decrease in the electronegativity of the apical ligands to an increase in the angle. On going from 2 to 6 one apical ligand decreases in electronegativity. The large difference in the S–O bond lengths does not affect the O–S–O angle of 6, which is nearly equal to that of 2.

The x-ray structure of 6 shows that the hypervalent O–S–O bond in sulfur is strongly distorted by the introduction of structural features expected to result in polarization of this three-center bond. The fluoroalkoxy ligand in 6 is significantly more electronegative than the unfluorinated alkoxy ligand. Electron density is removed from the dimethylalkoxy ligand toward the fluoroalkoxy ligand. The observations of a long S–O bond *b* and a short S–O bond *a* in 6 are consistent with the idea that resonance structure **6b** is quite important in describing the resonance hybrid which is 6.

The overall effect of the CF_3 groups is to decrease the basicity and nucleophilicity of 6 compared to the unfluorinated analogue 11. The inductive electron-withdrawing effect of this substitution of CF_3 for CH_3 is shown by the results of this paper to be greater at the oxygen more remote from the CF_3 substituent of 6 than at the adjacent oxygen. The reactions of 6 with methyl fluorosulfonate and triflic acid occur preferentially at the oxygen of the fluoroalkoxy group consistent with the postulated large contribution of resonance structure **6b**. Electrophilic attack at the fluoroalkoxy oxygen places the positive charge of the product alkoxysulfonium ion adjacent to the less electronegative alkoxy group in 8 and 12. The resemblance of the transition state for methylation to the product can be used to rationalize the greater nucleophilicity of the oxygen nearer the CF_3 substituents.

The carbonyl-stretching frequencies of sulfuranes 1, 16, and 17 are 1724, 1708, and 1647 cm^{-1}. The hypervalent bond is symmetrically substituted in sulfurane 1. The lower carbonyl-stretching frequency seen (16) has been interpreted[7] in terms of an increase in carboxylate anion character for 16 in relation to 1. In 16 there is more electron density on the acyloxy ligand than on the fluoroalkoxy ligand. The acyloxy ligand is effectively more electronegative than the fluoroalkoxy ligand. The considerably lower carbonyl-stretching frequency seen in 17 points to an even higher degree of carboxylate anion character in this unsymmetrical sulfurane, a result of the lesser electronegativity of the alkoxy ligand compared to the fluoroalkoxy ligand.



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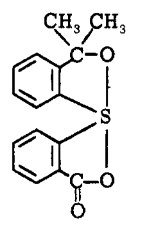
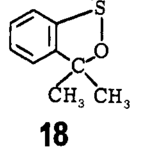


17

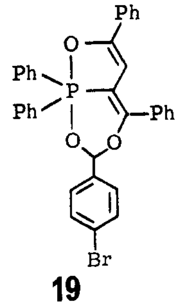
Chemical shift evidence for polarization of the hypervalent bond has been reported[7] for monocyclic sulfuranes of structure 18. The average of the peak positions for the two methyl groups shift to lower field with increasing electronegativity of X. Extension of this argument to bicyclic sulfuranes is possible. The average positions of the methyl groups of 11, 6, and 17 are δ 1.62, 1.74, and 1.82. The increasing downfield shift parallels the expected order of increasing polarization of the O–S–O bond.



18

The order of increasing polarization of the hypervalent bond for known spirosulfuranes is inferred from an examination of both infrared and ^1H NMR evidence, to be as follows: 1, 2, 11 (symmetrical) $< 16 < 6 < 17$.

Similar distortions of the hypervalent bond are reported for phosphoranes. The crystal structures of unsymmetrical phosphoranes 19 and 20 have been determined.[22,23] The P–O



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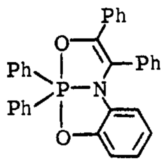

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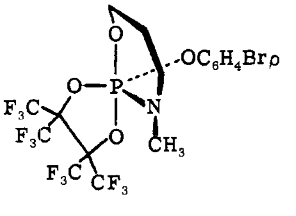
bond lengths of **19** differ by 0.05 Å and those of **20** by 0.06 Å. The differences in apical bond lengths are not nearly as large as those found in **6** (0.24). Compound **21** provides an even closer analogue of **6** in that one apical substituent is an α,α-bis(trifluoromethyl)alkoxy group and the other an "ordinary" alkoxy group. The difference in the two apical P–O bond lengths[24] is 0.10 (1) Å, a deviation from the ideal TBP geometry, with equal bond lengths, which is in the same direction as the deviation from ideality seen for **6**, but less than half as large. The smaller differences in P–O bond lengths seen for **19**, **20**, and **21** reflect a smaller polarizability, or at least a smaller deformability, of a hypervalent bond with a central phosphorus than is seen for one with a central sulfur. A similar reduction in polarizability is reflected in carbonyl-stretching frequencies of iodinanes[25] when compared to sulfuranes. Further work will be required to probe the generality of this observation and to establish a probable rationalization.



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Registry No.—**2**, 38195-99-2; **6**, 63731-54-4; **8**, 63731-56-6; **9**, 63731-57-7; **12**, 63765-59-3; **13**, 63731-59-9; methyl fluorosulfonate, 421-20-5; trifluoromethanesulfonic acid, 14993-13-6.

Supplementary Material Available: A listing of final thermal parameters (Table I), complete bond lengths and angles (Tables II and III), and a comparison of bond lengths and angles (Table IV) (6 pages). Ordering information is given on any current masthead page.

References and Notes

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(10) Four high-intensity reflections suffered noticeably from absorption; however, since the molecular geometry is in agreement with expected bond lengths and angles, these data were not omitted in the refinements.

(11) The structure was solved by a version of the MULTAN program, G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971), 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.

(12) $R = \Sigma||F_{obsd}| - |F_{calcd}||/\Sigma|F_{obsd}|$; $R_w = [\Sigma w||F_{obsd}| - |F_{calcd}||^2/\Sigma w|F_{obsd}|^2]^{1/2}$.

(13) "International Tables of X-Ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Ed., Kynoch Press, Birmingham, England, 1974, pp 99–102.

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

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(18) The different solvents used (ether for **11** and $CDCl_3$ for **6**) may be responsible for some of the rate difference, since the reaction product of **11** precipitated out of ether, whereas the product **8** of the methylation of **6** was soluble in $CDCl_3$.

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