105400-01-9; **16**, 105400-02-0; **17**, 90633-87-7; **18**, 105400-03-1; **19**, 105400-04-2; **20**, 79495-97-9; **21**, 100330-77-6; **21a**, 105400-05-3; **22**, 105400-06-4; **23**, 105400-07-5; **24**, 105400-08-6; **25**, 60742-69-0; **26**, 100330-78-7; **27**, 105400-09-7; **28**, 93000-67-0; **29**, 105400-10-0; **29**·KSCN, 105400-18-8; **30**, 69930-74-1; **31**, 72911-99-0; **32**, 105400-12-2; **33**, 62871-83-4; **34**, 69703-25-9; **35**, 90633-85-5; **36**, 88104-28-3; **37**, 93000-66-9; **38**, 105400-14-4; **39**, 94978-65-1; **40**, 105400-15-5; **41**, 105400-16-6; **42**, 105399-86-8; **43**, 33051-25-1; **44**, 105399-89-1; bisCIEE, 112-26-5; 1,8-DAOO, 929-59-9; DGACL, 21062-20-4; DCIE, 111-44-4; DIE, 34270-90-1; bisIEE, 36839-55-1; A15, 105399-87-9; 1,5-DAOP, 2752-17-2; B15, 66582-25-0; C15, 105399-91-5; D15, 105399-95-9; A18, 86577-64-2; B18, 105399-99-3; C18, 105400-11-1; D18, 66582-26-1; E18, 105400-13-3; Ca, 7440-70-2; Na, 7440-23-5; K, 7440-09-7; 1,2-bis(2-azidoethoxy)ethane, 59559-06-7; diglycolic acid, 110-99-6; 2-methoxyethylamine, 109-85-3; ethyl bromoacetate, 105-36-2; *o*-methoxybenzylamine, 6850-57-3; 1,7-bis(2-methoxybenzyl)-2,6-dioxo-4-oxa-1,7-diazaheptane, 105399-90-4; furfurylamine, 617-89-0; 1,7-difurfuryl-2,6-dioxo-4-oxa-1,7-diazaheptane, 105399-93-7; 2-furoyl chloride, 527-69-5; 1,7-bis(2-furylcarbonyl)-4-oxa-1,7-diazaheptane, 105399-94-8; tetraethyleneglycol diiodide, 36839-56-2; 1-aminohexane, 111-26-2; 1-bromohexane, 111-25-1; octanoyl chloride, 111-64-8; 1-chlorononane, 2473-01-0; 1-aminononane, 112-20-9; nonanoyl chloride, 764-85-2; decanoyl chloride, 112-13-0; dodecylamine, 124-22-1; myristic acid, 544-63-8; myristoyl chloride, 112-64-1; 1-bromohexadecane, 112-82-3; stearoyl chloride, 112-76-5; 2-cyanobenzyl bromide, 22115-41-9; dodecanoic acid, 143-07-7; 2-hydroxybenzyl bromide, 58402-38-3.

Structure of 1-Chloro-1,1-dihydro-1-phenyl-3,3-dimethyl-3*H*-2,1-benzoxathiole, a Chlorosulfurane. Structural Manifestations of an Electronically Unbalanced Hypervalent Bond

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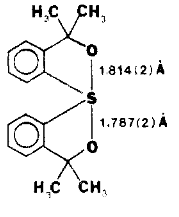
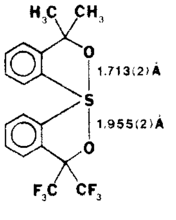
Received June 16, 1986

The X-ray crystal structure of 1-chloro-1,1-dihydro-1-phenyl-3,3-dimethyl-3*H*-2,1-benzoxathiole, chlorosulfurane **5**, is reported ($R = 0.030$). The axial S–Cl bond of **5** is extremely long (2.747 (1) Å), and the axial S–O bond is the shortest axial S–O bond of any reported sulfurane having the 3,3-dimethyl-3*H*-2,1-benzoxathiole moiety (1.639 (2) Å). The axial three-center four-electron bond of **5** is thus remarkably polarized. There is a good linear correlation between the electronegativity/apicophilicity of an axial ligand and the length of the S–O bond of a 3,3-dimethyl-3*H*-2,1-benzoxathiole moiety trans to it along a three-center four-electron array. The O–S–Cl bond angle of **5** (measured in an arc which includes the sulfur lone pair) of 173.6 (1)° is unusual in being less than 180°, but is similar to the axial angles of previously reported dichlorosulfuranes. The compressed endocyclic C–C–O angle of **5** (103.0 (2)°) is not due to the *gem*-dimethyl group, since 2-[(2-phenylsulfinyl)phenyl]-2-propanol (**6**) exhibits an analogous C–C–O angle of 110.6 (2)°. The X-ray crystal structure of **6** is also reported ($R = 0.058$).

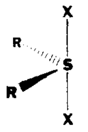
The axial three-center four-electron bond of sulfuranes[1] is remarkably pliable, responding to subtle electronic changes in the axial ligands with large changes in bond length. For example, the symmetrical O–S–O system of **1**[2] becomes grossly distorted in the related sulfurane **2**.[3]



1

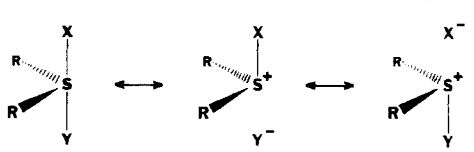


2



3

Such electronic elasticity is expected theoretically: Musher's[4] MO view of the X–S–X system of **3** results in a bond order of 1.0 for the three-atom array, or 0.5 per S–X bond. More rigorous theoretical treatments[5] confirm this view, which may be summarized in a familiar way by writing resonance structures a–c. For $X \neq Y$, structures b and c will contribute unequally, and even if $X = Y$, structures b and c will contribute heavily relative to structure a.



a b c

Recently we reported[6] that chlorosulfurane **4** hydrolyzed roughly 2000 times faster than **5**, even though the electronic effect of the cyclopropyl group would tend to stabilize **4** relative to **5**. A tentative explanation was advanced based on expansion (in the case of **4**) or com-

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[1] (a) Hayes, R. A.; Martin, J. C. *Studies in Organic Chemistry*; Elsevier, Amsterdam, 1985; Vol. 19, Chapter 8, p 408. (b) Bond distortions similar to those discussed here for the 10-S-4 sulfuranes have been reviewed for the 10-S-3 trithiapentalenes and related 10-S-3 compounds: Gleiter, R.; Gygax, R. In *Topics in Current Chemistry*; Boschke, F., Managing Ed.; Springer-Verlag: Berlin, Heidelberg, New York, 1976; Vol. 63, pp 49–88.

[2] Lam, W. Y.; Duesler, E. N.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 127.

[3] Adzima, L. J.; Duesler, E. N.; Martin, J. C. *J. Org. Chem.* **1977**, *42*, 4001.

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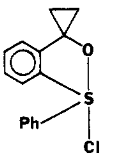
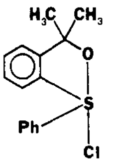
[6] Datta, A. K.; Livant, P. *J. Org. Chem.* **1983**, *48*, 2445.

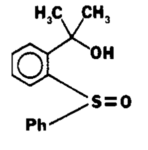
0022-3263/86/1951-5384$01.50/0



4



5



6

pression (in the case of 5) of the endocyclic C–C–O angle in the five-membered ring containing sulfur: This would result in an S–O bond longer in 4 than in 5, in effect placing 4 closer to the transition state in any hydrolysis reaction coordinate involving S–O bond lengthening. In this, as in many explanations of the so called "five-membered ring effect",[7] it is desirable to know the detailed geometry of the five-membered ring. Therefore the X-ray crystal structure of 5 was obtained and is discussed herein. Suitable crystals of 4 have not yet been obtained; comparisons of 4 and 5 therefore must be left to the future. An X-ray crystal structure determination of 6 (the hydrolysis product of 5) was performed in order to compare various structural features of 5 to a nonhypervalent analogue.

Experimental Section

Crystals of 5, prepared by literature methods,[8] were obtained by crystallization from CH_2Cl_2–pentane at -20 °C.

Crystal data for 5: $C_{15}H_{15}OSCl$, mol wt = 278.80, orthorhombic, a = 8.388 (2) Å, b = 10.148 (2) Å, c = 16.551 (3) Å, V = 1408.8 (6) Å^3, Z = 4, space group $P_{na}2_1$. Cell dimensions were obtained by least-squares refinement using 15 computer-centered reflections on a Nicolet four-circle autodiffractometer equipped with a graphite monochromator λ(Mo K$\bar{\alpha}$) = 0.71073 Å.

Solution and Refinement of the Structure of 5. A crystal of dimensions 0.35 × 0.55 × 0.60 mm was used for ω scan data collection at T = 20 ± 1 °C. The ratio of background counting time to net scanning was 0.5. Six reflections were monitored every 300 reflections. Fifteen steps were taken, of which 11 were used in intensity calculation. Scan rate varied from 3.0°/min to 6.0°/min, and 1987 reflections were collected. The data were corrected for Lorentz and polarization effects.

The structure was solved using the SHELXTL Direct Methods programs. The two methyl groups were treated as rigid rotors of sp^3 geometry with a C–H bond length of 0.96 Å. Other hydrogen atoms were included in the structure factor calculations as idealized atoms assuming sp^2 carbons and a C–H bond length of 0.96 Å. The isotropic thermal parameters of each hydrogen atom was fixed at 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which it was bonded. After the final least-squares cycle there were no peaks present in the difference Fourier above the noise level (0.17 e$^-$/Å^3). The final values of the agreement factors R_1 and R_2 were 0.030 and 0.031, respectively.[9] The final goodness-of-fit defined as $\{\sum w(|F_o| - |F_c|)^2/(NO - NV)\}^{1/2}$ where NO is the number of observations and NV is the number of variables was 1.54.

Crystal data for 6: $C_{15}H_{16}O_2S$, mol wt 260.35, triclinic, a = 8.470 (3) Å, b = 8.642 (3) Å, c = 10.943 (4) Å, α = 98.40 (3)°, β = 106.47 (3)°, γ = 114.44 (3)°, V = 666.7 (4) Å^3, Z = 2, space group $P\bar{1}$. Cell dimensions were obtained by least-squares refinement of 15 reflections on a Nicolet P3 diffractometer equipped with graphite monochromator, λ(CuK$\bar{\alpha}$) = 1.54178 Å.

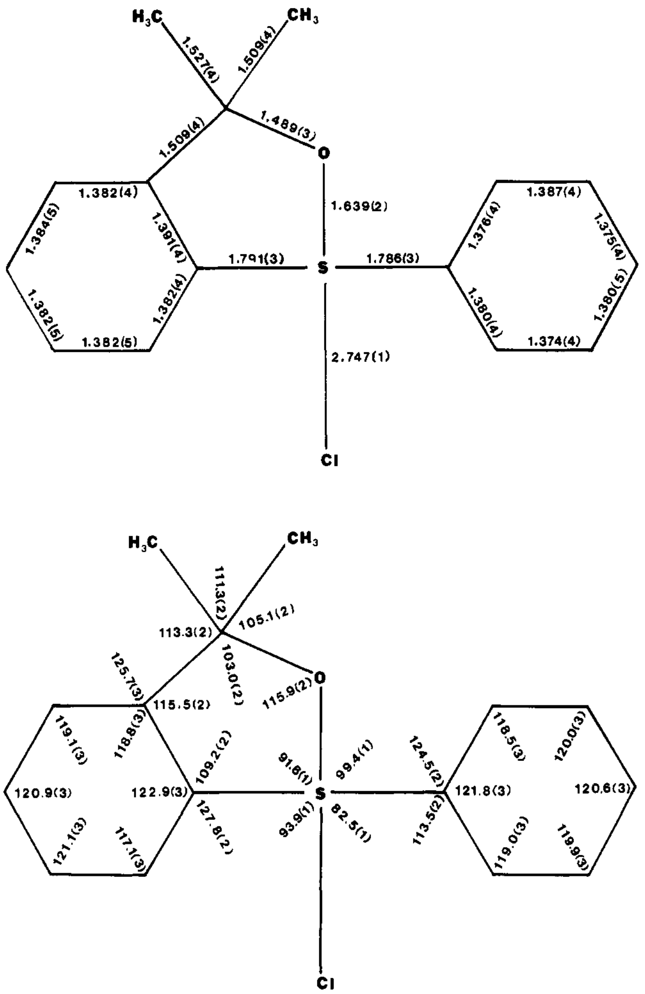


Figure 1. Structural parameters for chlorosulfurane 5. The numbers in parentheses are estimated standard deviations in the last significant digit. Top drawing gives bond lengths and bottom drawing gives bond angles.

Table III. Structural Parameters Not Shown in Figures 1 and 3[a]

	molecule	
parameter	5	6
Cl–S–O(1)	173.6 (1)°	
C(1)–S–C(10)	104.0 (1)°	
O(1)–C(7)–C(8)	109.9 (2)°	109.0 (3)°
C(2)–C(7)–C(9)	113.6 (2)°	110.5 (3)°

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.

Solution and Refinement of the Structure of 6. Two reflections were monitored every 46 reflections. Scan rate was 4.9°/min and 2045 reflections were collected, of which 1755 unique reflections were used in calculations. The data were corrected for Lorenz and polarization effects. The two methyl groups were treated as rigid rotors of sp^3 geometry and C–H bond length of 0.96 Å. Other hydrogen atoms were treated as idealized atoms assuming sp^2 carbons and a C–H bond length of 0.96 Å. Solution by the SHELXTL direct methods program resulted in agreement factors R_1 and R_2 of 0.058 and 0.077, respectively. The goodness of fit, defined above was 3.08.

Results

Fractional atomic coordinates for all non-hydrogen atoms are given for 5 and 6 in Tables I and II, respectively, which are available in the microform edition. (See paragraph at the end of this article concerning Supplementary

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[7] (a) Eberhard, A.; Westheimer, F. H. *J. Am. Chem. Soc.* **1965**, *87*, 253. (b) Hudson, R. F.; Brown, C. *Acc. Chem. Res.* **1972**, *5*, 204. (c) Usher, D. A.; Dennis, E. A.; Westheimer, F. H. *J. Am. Chem. Soc.* **1965**, *87*, 2320. (d) Aksnes, G.; Bergesen, K. *Acta Chem. Scand.* **1965**, *19*, 931. (e) Cremer, S. E.; Trivedi, B. C.; Weitl, F. L. *J. Org. Chem.* **1971**, *36*, 3226. (f) Davis, R. E. *J. Am. Chem. Soc.* **1962**, *84*, 599. (g) Britos, P. A.; Tillett, J. G.; Wiggins, D. E. *J. Chem. Soc. B* **1968**, 1360. (h) Pagdin, N.; Pine, A. K.; Tillett, J. G.; van Woerden, H. F. *J. Chem. Soc.* **1962**, 3835. (i) de la Mare, P. B. D.; Tillett, J. G.; van Woerden, H. F. *Chem. Ind. (London)* **1961**, 1533. (j) Westheimer, F. H. *Acc. Chem. Res.* **1968**, *1*, 70. (k) Kumamoto, J.; Cox, J. R., Jr.; Westheimer, F. H. *J. Am. Chem. Soc.* **1956**, *78*, 4858. (l) de la Mare, P. B. D.; Tillett, J. G.; van Woerden, H. F. *J. Chem. Soc.* **1962**, 4888. (m) Kaiser, E. T.; Katz, I. R.; Wulfers, T. F. *J. Am. Chem. Soc.* **1965**, *87*, 3781.

[8] Martin, J. C.; Balthazor, T. M. *J. Am. Chem. Soc.* **1977**, *99*, 152.

[9] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

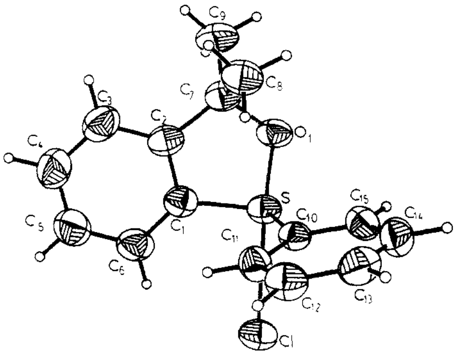


Figure 2. ORTEP plot of chlorosulfurane 5. Non-hydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the atom's electron density. Hydrogens are presented as spheres of arbitrary size conveying no information about thermal motion.

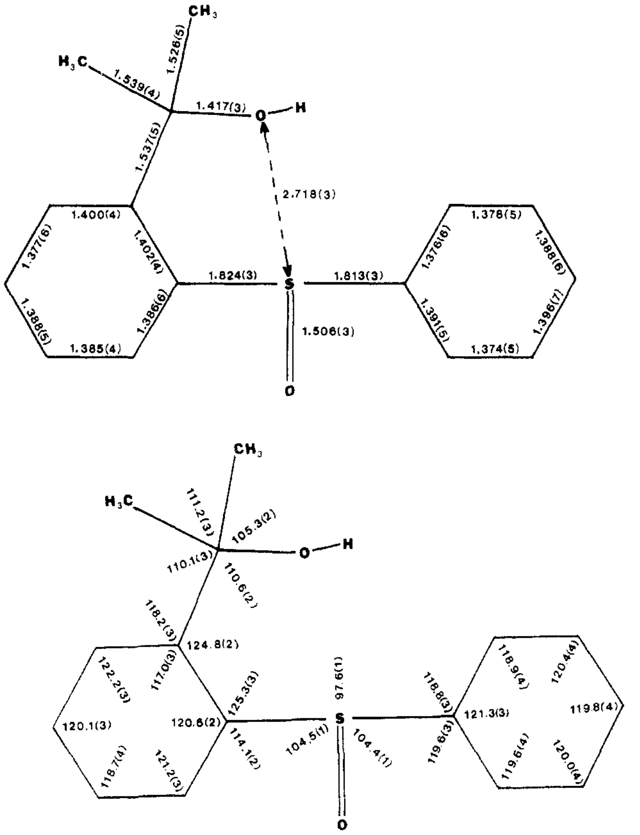
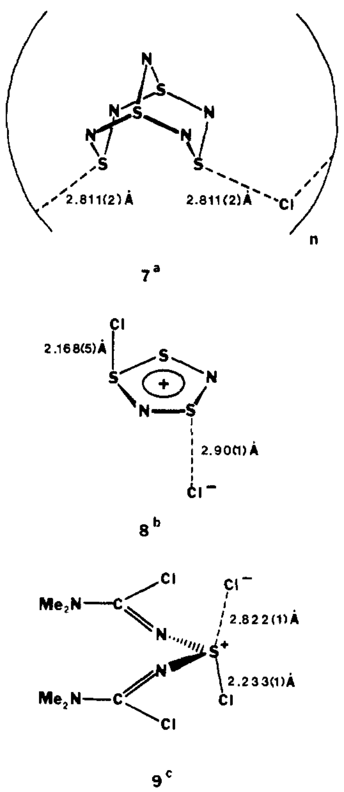


Figure 3. Structural parameters for sulfoxide alcohol 6. The numbers in parentheses are estimated standard deviations in the last significant digit. Top drawing gives bond lengths, and bottom drawing gives bond angles.

Chart I. Structures of Compounds with Formally Ionic S^+-Cl^- Bonds



[a] Reference 16. [b] Reference 13. [c] Reference 18.

Material). Selected bond lengths and angles for 5 are given in Figure 1, and those parameters not shown explicitly there are listed in Table III. Figure 2 is an ORTEP plot of 5, with atom numbering indicated. Atom numbering for 6 corresponds to that for 5, with the sulfoxide oxygen designated O(2). Selected bond lengths and angles for 6 are given in Figure 3, and those parameters not shown explicitly there are listed in Table III.

Discussion

The length of the S–Cl bond in 5 is striking. One expects[10] a S–Cl covalent single bond length of 2.03 Å, and, for example, one finds S–Cl distances for a series of sulfonyl chlorides to range between 1.985 and 2.064 Å,[11] for S_2Cl_2 2.07 Å,[12] for $\{S_3N_2Cl\}^+$ 2.168 Å,[13] for $S_3N_3Cl_3O_3$ 1.996 and 2.004 Å,[14] and for $S_3N_3Cl_3$ 2.084 and 2.150 Å,[15] to cite several examples. With this in mind, one might well ask whether the S–Cl bond in 5 is instead ionic. Unfortunately, a bondafide example of an ionic sulfonium chloride in which chloride does not participate in a bridging interaction is unavailable for comparison. However an estimation of the S^+ Cl^- interionic distance using Pauling's method gives 3.6 Å,[16] and the sum of van der Waals radii for these atoms is 3.59 Å[17] or 3.65 Å.[15] Several sulfonium chlorides have been reported (Chart I) but the authors of these reports note that chlorine is bonded partially covalently to sulfur since the S^+–Cl^- distances are well below the value expected for purely ionic interaction. Further, Minkwitz et al.[19] extrapolated a Cl_3S^+—Cl^- distance of 2.90 Å from consideration of a series of trichlorosulfonium salts. These

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[10] Pauling, L. *The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry*, 3rd ed.; Cornell: Ithaca, NY, 1960, p 229.

[11] Hargittai, I.; Bliefert, C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1053.

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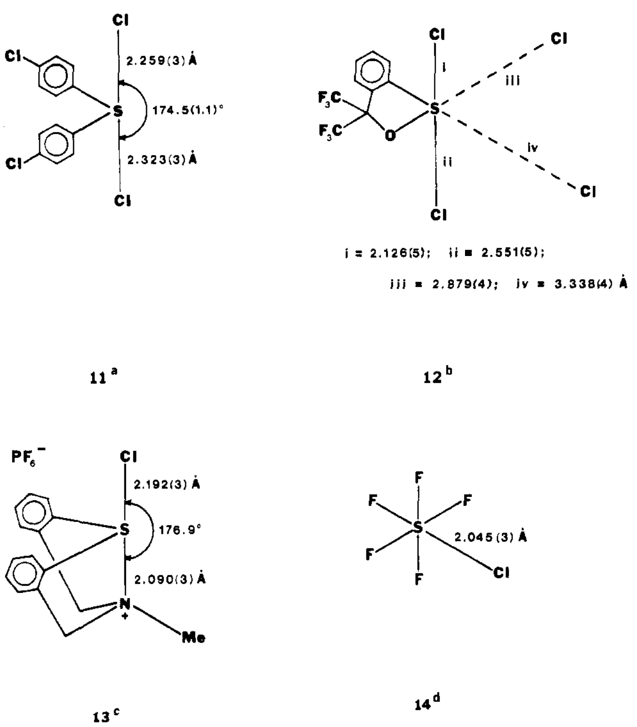
[21] Martin, L. D.; Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 3595.

[22] (a) Iwasaki, F.; Akiba, K. *Acta Crystallogr., Sect B: Struct. Sci.* **1985**, *B41*, 445. (b) Akiba, K.; Takee, K.; Ohkata, K.; Iwasaki, F. *J. Am. Chem. Soc.* **1983**, *105*, 6965.

[23] Marsden, C. J.; Bartell, L. S. *Inorg. Chem.* **1976**, *15*, 3004.

Chart II. Structures of Chlorosulfuranes

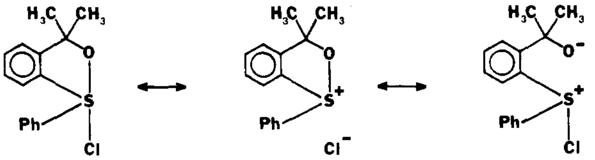


11[a] **12**[b] **13**[c] **14**[d]

[a]Reference 20. [b]Reference 21. [c]Reference 22. [d]Reference 23.

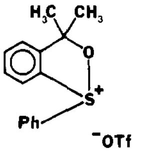
workers too have referred to this bond as "appreciably covalent." Compound **9** (Chart I) is especially interesting. Although characterized as pyramidal about sulfur by the authors,[18] the geometry at sulfur might also be viewed as a distorted trigonal bipyramid (TBP), with the nearly linear Cl–S–Cl (160.9° measured through the sulfur lone pair) defining the axial direction. This is discussed further below.

It is clear that the S–Cl bond in **5** is quite polar. This may be rationalized by invoking a very heavy contribution of resonance structure **5b** in the overall description of **5**.



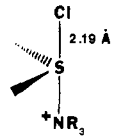
5a **5b** **5c**

To say that **5** *is* ionic would be in error, however. In methylene chloride solution, the average proton chemical shift of the two methyl singlets of **5** is 1.48 ppm, while for the unquestionably ionic sulfonium triflate **10**, it is 1.76 ppm.

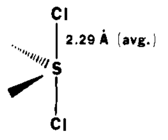


10

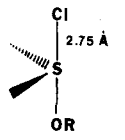
Structural data for some chlorosulfuranes do exist, and are shown in Chart II. Comparison with **12** however is difficult because the geometry at sulfur is essentially octahedral; **12** is tetrameric and two cis octahedral sites are involved in bridging interactions with two neighboring molecules of the tetramer. Too, **14** is a 12-S-6 species and not strictly comparable to the 10-S-4 sulfuranes under discussion here. Sulfuranes **13**, **11**, and **5** form an interesting series, summarized below.



13



11

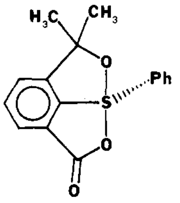


5

As the group opposite chlorine on the three-center four-electron bond (call it Y) changes from being more electronegative/apicophilic than chlorine (**13**) to being less electronegative/apicophilic than chlorine (**5**), the S–Cl bond exhibits bond length changes of −4% to +20% of its value in the symmetrical sulfurane **11**. Such changes are significant when one recalls that the change from a carbon–carbon single bond to a carbon–carbon double bond, certainly a major change in bonding, involves a bond length change of −13%. Taking as a standard S–Cl single bond length 2.03 Å,[10] the S–Cl bonds in **13**, **11**, and **5** correspond to Pauling bond orders of 0.60, 0.43, and 0.10, respectively. This is equivalent to saying that for **13**, resonance structure b (X = Cl, Y = R_3N^+) is the major contributor, but as we move to **11**, structures b and c contribute equally (X = Y = Cl), and finally in **5** the reverse polarization is achieved and c (X = Cl, Y = OR) is the major contributor.

The S–Cl bond is unquestionably extraordinarily long. What prediction may be made, then, about the S–O bond of **5**? Is it expected to be long or short? The kinetic data for hydrolysis of **4** vs. **5** suggested that the S–O bond of **5** ought to be short, as discussed above. Also, in **2**, the axial bond distortion is such that the bond to the more electronegative/apicophilic ligand (–C(CF$_3$)$_2$–O–) lengthens and the bond to the less electronegative/apicophilic ligand (–C(CH$_3$)$_2$–O–) shortens. Therefore we expect the long S–Cl bond of **5** to be accompanied by a short S–O bond. Indeed the S–O bond of **5** *is the shortest apical S–O bond of any 10-S-4 species having an apical S-O bond.*[1] Sulfurane **5** has perhaps the most electronically unbalanced hypervalent three-center four-electron bond yet studied. Further, several sulfuranes for which structural data exist also have the same 3,3-dimethyl-3*H*-2,1-benzoxathiole moiety as does **5**, and a detailed comparison of five-membered ring geometry, in particular the S–O bond length, may be made.

The sulfuranes in this series are **1**, **2**, **15**,[2] and **5**. The bond lengths between sulfur and the cumyloxy oxygen in this series are **1**, 1.80 Å (av); **2**, 1.71 Å; **15**, 1.66 Å; **5**, 1.64 Å. The contraction of the cumyloxy S–O bond is in precise response to the increase in the electronic tug of the ligand opposite. This qualitative statement may be made semiquantitative in the following way. A sensitive index of the electronegativity/apicophilicity of a group has been shown to be the value of the carbonyl stretching frequency of a spiroannelated benzoate group, as in **16** or **17**.[24] Groups A–B in **16** or L in **17** less electronegative/apicophilic than –C(O)–O– engender distortion of the hypervalent bond toward the sulfonium carboxylate extreme. The –C(O)–O– group is thus more $-CO_2^-$-like and $\nu^{C=O}$



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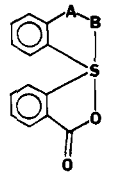

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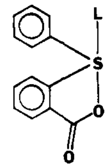

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(24) Livant, P.; Martin, J. C. *J. Am. Chem. Soc.* 1977, *99*, 5761.

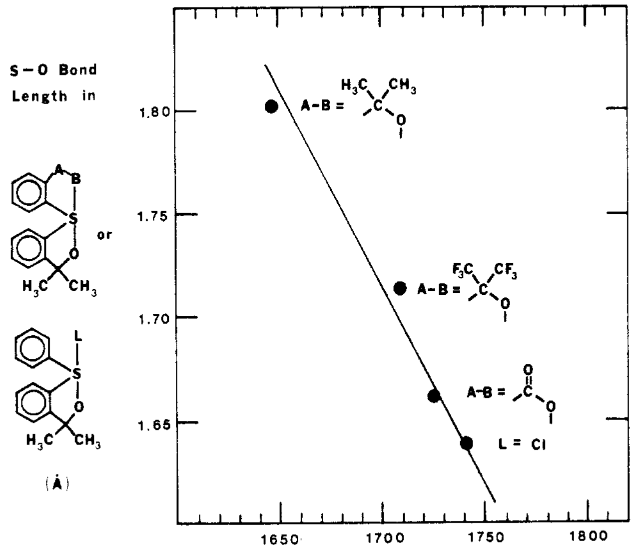
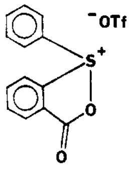


Figure 4. Response of sulfurane axial S–O bond length (Å) to electronegativity/apicophilicity of the axial ligand opposite it.

moves toward the region typical for carboxylate salts, 1600–1620 cm^{-1}. Groups A–B or L more electronegative/apicophilic than –C(O)–O– engender distortion toward the other extreme, namely carboxysulfonium L$^-$ or carboxysulfonium –A–B$^-$ and $\nu^{C=O}$ moves toward the value observed[24] for the ionic carboxysulfonium triflate **18**, 1832 cm^{-1}, or **19**, 1828 cm^{-1}.[25] Therefore the carbonyl stretching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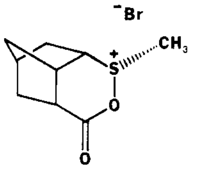
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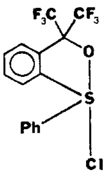
frequencies of sulfuranes like **16** or **17** are reporting the electronegativity/apicophilicity of A–B or L. Figure 4 shows a plot of ligand electronegativity/apicophilicity (as monitored by $\nu^{C=O}$) vs. the effect of the ligand on the S–O bond length of a spiroannelated cumyloxy group. The correlation is remarkably good. (r^2 = 0.986)

In fact, such a correlation might have predictive value: if the effect of a ligand on a trans S–O bond length is directly proportional to its electronegativity/apicophilicity index, as is indeed the case in Figure 4, then its effect on a trans S–Cl bond length might also be expected to vary linearly with electronegativity/apicophilicity. Using this notion, one may interpolate between the S–Cl bond length of **11** ($\nu^{C=O}$ for **17** (L = Cl) = 1740 cm^{-1}) and that of **5** ($\nu^{C=O}$ for **16** (A–B = –C(CH$_3$)$_2$–O–) = 1647 cm^{-1}) to predict the S–Cl bond lengths of the chlorosulfuranes **20** and **21** as 2.45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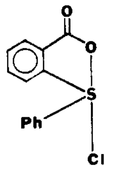
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Å and 2.37 Å, respectively ($\nu^{C=O}$ for **16** (A–B = –C(CF$_3$)$_2$–O–) = 1708 cm^{-1}; $\nu^{C=O}$ for **16** (A–B = –C(O)–O–) = 1724 cm^{-1}). (See Figure 5.) Structural data are not available for either of these compounds. Taking this idea one step further, one might use a known S–Cl bond length to assess the electronegativity/apicophilicity of a trans ligand L or A–B and thus predict the $\nu^{C=O}$ for the **16** or **17** having that ligand A–B or L. For example, in **13** the 2.19 Å S–Cl bond length would lead to the prediction that $\nu^{C=O}$ for (the unreported) sulfurane **22** should be 1760 cm^{-1} (Figure 5).

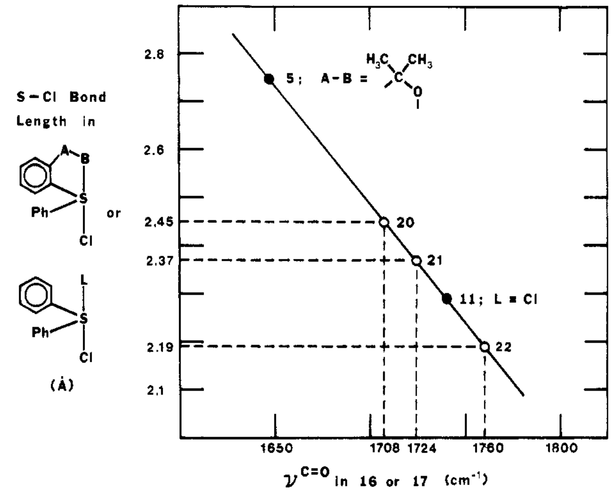
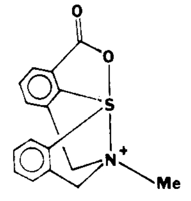


Figure 5. Response of sulfurane axial S–Cl bond length (Å) to electronegativity/apicophilicity of the axial ligand opposite it. Filled circles represent experimental data. Open circles are interpolations between the experimental points.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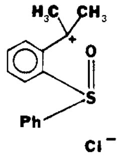
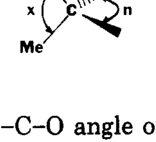
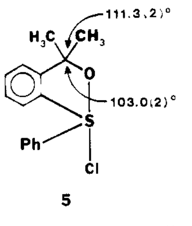

5d

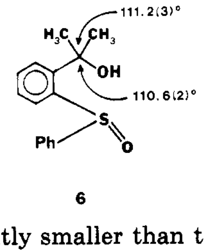
Before leaving the discussion of the S–O bond of **5**, it should be noted that the Pauling bond order for this bond is 1.22, which should be compared to the 0.5 predicted by crude MO theory, and the 0.5–1.0 expected from consideration of resonance structures **5a–5c**. That the bond appears to have partial double bond character compels one to consider adding resonance structure **5d** to **5a–5c** in order to portray the molecule more faithfully. This point is discussed further below.

It might be expected that the presence of a *gem*-dimethyl moiety would engender a compression of the bond angle opposite it, i.e., x > 109° > n below. At first glance, **5** would seem to confirm this suggestion; the endocyclic





5



6

C–C–O angle of 103.0° is significantly smaller than the ideal tetrahedral angle. However, while the Me–C–Me angle in **6** is the same as in **5**, the angle opposite is not at all compressed in **6**; indeed, it is a little bigger than 109°. This comparison suggests that the *gem*-dimethyl moiety in and of itself does not cause a diminution of the opposite angle. If it did, the effect would show up in **6**. However,

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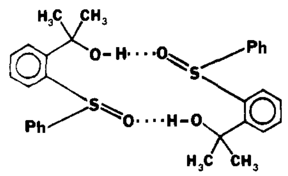
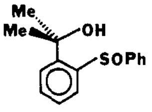
(25) Glass, R. S.; Hojjatie, M.; Petsom, A.; Wilson, G. S.; Göbl, M.; Mahling, S.; Asmus, K. D. *Phosphorus Sulfur* 1985, *23*, 143.

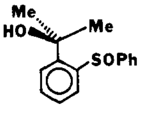


6

the situation is complicated by the fact that crystalline **6** is a hydrogen-bonded dimer having an O–H—O distance of 2.81 Å. This leads to two possibilities: (i) the effect of the hydrogen bonding on the C_{Ph}–C–O angle is negligible, and the conclusion just suggested (that the *gem*-dimethyl has no effect on the opposite bond angle) remains valid, or (ii) the hydrogen bonding does affect the C_{Ph}–C–O angle, and the conclusion in that case is that the *gem*-dimethyl effect must be weaker than the hydrogen-bonding effects since the angle is slightly expanded. In either case, the effect of the *gem*-dimethyl on the opposite bond angle is probably small. It should be noted that the absence of a direct relation between the exocyclic Me–C–Me bond angle and the angle opposite it is not related to the Thorpe–Ingold effect,[26] which merely would favor rotamer **6a** over rotamer **6b**. Also, the suggestion that the expansion of a Me–C–Me angle doesn't cause the compression of the angle opposite it in no way invalidates the proposal that a cyclopropyl ring causes an expansion of the angle opposite it and in this way may be responsible for the increased reactivity of **4** vs. **5**.

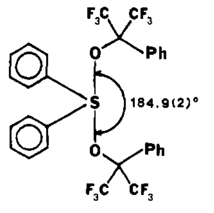


6a



6b

The O–S–Cl angle in **5**, measured in an arc which includes the sulfur lone pair, is 173.6 (1)°. The vast majority of 10-S-4 species exhibit an axial angle (defined, following Martin,[1] as the angle between axial ligands measured in an arc which includes the sulfur lone pair) greater than 180°. Many of those sulfuranes however are spirobicyclic, which might constrain an axial angle to be greater than 180° against its "will". The "will" of the axial angle was considered theoretically by Hoffmann and Chen[5e] who concluded that equatorial and axial substituents more nearly equal to each other in electronegativity would favor axial angles >180°, and equatorial and axial substituents more disparate in electronegativity would tend to favor axial angles <180°. In **5**, Cl and O are obviously more electronegative than the equatorial phenyls, and the axial angle is <180°, so the prediction would appear to be validated, but the axial oxygens of **23**[27] are also obviously more electronegative than the equatorial phenyls, but the axial angle is bent the other way. In accord with prediction, the electronegativity of the equatorial and axial substituents are more similar in **24**[28] than in **23**, and the axial angle increases. However on going from **11** to **12** (a transformation similar to **23** → **24**), the axial angle decreases from 174.5 (1.1)° to 167.6 (2)°. (Compound **12** however is roughly octahedral, as mentioned.) The next member in the series **11** → **12** → ? would be a dichlorosulfurane having two electronegative equatorial substituents, and we would expect the axial angle to be further contracted. (Also the asymmetry in the S–Cl bond lengths evident in **11** is accentuated in **12** and would be expected to be even more pronounced in the next member of the series.) We assert that **9** should be viewed as the next dichlorosulfurane in the series **11** → **12** → **9**. The axial angle indeed contracts to 160.9°, and the asymmetry in the S–Cl bond lengths is even more pronounced. Whether **9** is a chlorosulfonium chloride or a dichlorosulfurane is at this point a debatable question, but when viewed in the context of successive replacement of sulfurane phenyl equatorial substituents by σ-acceptor/π-donor heteroatoms, **9** appears to be a 10-S-4 species whose geometry is entirely reasonable.



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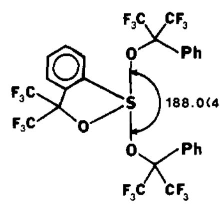

24

Finally, it was suggested above that resonance form **5d** was a significant contributor to the correct description of **5**. This was in order to explain the "short" S–O bond. If this suggestion is correct, resonance form **5d** is telling us that the C–O bond ought to be long. Taking as a normal C–O single bond length 1.43 Å,[10] the C–O bond length in **5** of 1.489 (3) Å is indeed significantly lengthened. The C–O bond lengths in related sulfuranes are **1**, 1.437 (4) Å; **2**, 1.436 (4) Å; **15**, 1.489 (3) Å. The first two have normal C–O bond lengths, while **15** exhibits a long C–O bond. It would appear that when the two apical ligands are the same or similar in electronegativity (i.e., **1** or **2**), resonance forms such as **5d**, having no C–O bond, are not important. However, when the hypervalent bond is exceedingly unsymmetrically polarized, as in **15** or **5**, resonance forms such as **5d** contribute in a nontrivial way. In **5**, resonance form **5c** is absolutely unimportant. If it were important, the C–O bond length would contract (cf. C–O bond length of 1.40–1.41 Å in *tert*-butoxide[29]).

Against the background of the unusual structure of **5** reported here, it will be particularly intriguing to obtain the structure of **4**. Work in that direction is in progress.

Acknowledgment. Crystal structure determination of **5** was performed by Dr. Cynthia Day (Crystalytics, Inc.). Crystal structure determination of **6** was performed by Dr. Charles Campana (Nicolet XRD Corp.). Support in the form of an Auburn University Intramural Grant-In-Aid (ER 83-03) is gratefully acknowledged.

Supplementary Material Available: Final atomic coordinates for **5** (Table I) and **6** (Table II) and thermal parameters for **5** (Table IV) and **6** (Table V) (4 pages). Ordering information is given on any current masthead page.

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(26) (a) Thorpe, J. F.; Ingold, C. K.; Beesley, *J. Chem. Soc.* **1915**, *107*, 1080 (b) Ingold, C. K. *Ibid.* **1921**, *119*, 305.

(27) (a) Paul, I. C.; Martin, J. C.; Perozzi, E. F. *J. Am. Chem. Soc.* **1972**, *94*, 5010; (b) **1971**, *93*, 6674.

(28) Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 1155.

(29) Greiser, Th.; Weiss, E. *Chem. Ber.* **1977**, *110*, 3388.