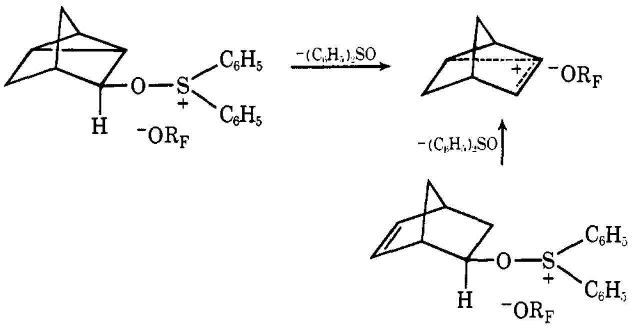
drated with **1** suggests that there is a common carbonium ion intermediate derived from the two isomers in this case.



The intramolecular kinetic isotope effect (k_H/k_D = 1.54) observed for the dehydration of *tert*-butyl alcohol with **1**, when considered in conjunction with our other evidence for the intermediacy of carbonium ions, supports a mechanism for dehydration of this tertiary carbinol near the E1 end of the mechanistic spectrum. The exothermic loss of a proton from something resembling the carbonium ion presumably proceeds through a transition state with little C–H bond breaking.[40] Other E1 eliminations show a similar kinetic isotope effect.[41]

Acknowledgment. We wish to acknowledge the partial support of this research by a National Institutes of Health Fellowship held by R. J. A. from 1967 to 1971, by National Science Foundation Grant No. GP 13331 and by a departmental equipment grant from the National Science Foundation which provided partial funding for a 220-MHz nmr spectrometer.

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Sulfuranes. VII. The Crystal and Molecular Structure of a Diaryldialkoxysulfurane[1,2]

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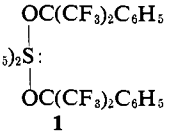
Received November 10, 1971

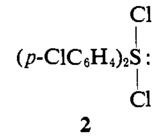
Abstract: The crystal structure for a diphenyldialkoxysulfurane, $(C_6H_5)_2S[OC(CF_3)_2C_6H_5]_2$, reveals an approximate trigonal bipyramidal geometry about sulfur, with a lone pair considered to occupy one equatorial position, the two phenyl ligands occupying the other two equatorial positions (C–S–O angles range from 86.4(2) to 91.2(2)°; the C–S–C angle is 104.4(3)°), and with the electronegative alkoxy ligands occupying apical positions (O–S–O angle is 175.1(2)° with the distortion from linearity in the direction of the equatorial phenyl rings). The S–O bond lengths (1.889(4) and 1.916(4) Å) are approximately 0.2 Å longer than the sum of the covalent radii as would be expected from an S–O bond order less than unity. The crystals are triclinic, the space group is $P\bar{1}$, and there are two molecules in a unit cell of dimensions a = 10.026(3), b = 14.268(3), c = 10.802(3) Å, α = 109° 50′(2′), β = 92° 52′(2′), and γ = 95° 20′(2′). The structure was solved by Patterson-heavy atom methods based on sulfur, and has been refined to a conventional R of 0.070 for 3364 nonzero reflections measured by counter methods. Some comparisons of the bonding scheme with those for tetracovalent sulfur compounds containing halogen ligands are made.

The first example of a stable, crystalline tetracoordinate sulfur(IV) compound lacking halogen atoms, sulfurane **1**, has been recently described.[3] Even more recently[4] Sheppard has reported low-temperature nmr and reactivity data which are interpreted in terms of a postulated tetraarylsulfurane structure. Other sulfuranes which have been studied include derivatives of SF_4,[5,6] molecules with S–Cl bonds,[7,8] and a compound postulated to have the structure of a spirodiacyloxysulfurane.[9] A preliminary X-ray investigation of the latter compound showed that in the crystal it had C_2 molecular symmetry, which would be consistent with a trigonal bipyramidal geometry. A complete crystal structure of $(p\text{-}ClC_6H_4)_2SCl_2$ (**2**) evidenced[7] a trigonal bipyramidal arrangement with the more electronegative chlorine atoms in the apical positions. In general it has been found[10] for trigonal bipyramidal compounds that



$$\begin{array}{c} OC(CF_3)_2C_6H_5 \\ | \\ (C_6H_5)_2S: \\ | \\ OC(CF_3)_2C_6H_5 \end{array}$$

1



$$\begin{array}{c} Cl \\ | \\ (p\text{-}ClC_6H_4)_2S: \\ | \\ Cl \end{array}$$

2

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[1] For Part VI in this series, see R. J. Arhart and J. C. Martin, *J. Amer. Chem. Soc.*, **94**, 5003 (1972).

[2] A preliminary account of this work has appeared; see I. C. Paul, J. C. Martin, and E. F. Perozzi, *ibid.*, **93**, 6674 (1971).

[3] J. C. Martin and R. J. Arhart, *ibid.*, **93**, 2341 (1971).

[4] W. A. Sheppard, *ibid.*, **93**, 5597 (1971).

[5] G. C. Demitras and A. G. MacDiarmid, *Inorg. Chem.*, **6**, 1903 (1967); D. T. Sauer and J. M. Shreeve, *Chem. Commun.*, 1679 (1970).

[6] W. A. Sheppard, *J. Amer. Chem. Soc.*, **84**, 3058 (1962).

[7] N. C. Baenziger, R. E. Buckles, R. J. Maner, and T. D. Simpson, *ibid.*, **91**, 5749 (1969).

[8] I. B. Douglass, K. R. Brower, and F. T. Martin, *ibid.*, **74**, 5770 (1952).

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

[10] E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966).

the more electronegative ligands tend to occupy apical positions leaving the less electronegative ligands in equatorial positions.

We have chosen to follow the widely accepted convention[10] which describes compounds such as SF_4 as trigonal bipyramidal in geometry, although there are only four ligands about sulfur. The four occupied coordination positions are very near the apices of a trigonal bipyramid, with one of the equatorial positions unoccupied. This emphasizes the resemblance to the geometry and bonding in pentacoordinate phosphorus compounds. We prefer, however, not to view the vacant equatorial position as being occupied by a phantom ligand when we specify coordination numbers. The sulfuranes discussed in this paper are therefore classed as tetracoordinate, rather than pentacoordinate.[10]

The evidence[7] for the trigonal bipyramidal structure of the analogous compound **2**, coupled with ^{19}F nmr evidence[3] that the alkoxy ligands of **1** occupy geometrically equivalent positions in solution indicated that a trigonal bipyramidal structure about sulfur, with the electronegative oxygen atoms in the apical positions, could be expected. A single crystal X-ray study was undertaken to confirm this hypothesis and to determine the lengths of the S–O bonds, quantities expected to shed some light on the bonding scheme in such species.

Experimental Section

Sulfurane **1**, previously obtained in this laboratory,[3,11] was recrystallized several times from ether-pentane under high vacuum ($<10^{-4}$ Torr). An apparatus having two 50-ml bulbs connected through a tube containing a fritted glass disk (see Figure 1) was constructed to carry out the crystallization. The impurities were concentrated in bulb A by filtering the mother liquors into this bulb while the pure material was crystallized repeatedly in bulb B. The solvents used in the crystallization were outgassed prior to use by standard freeze–thaw techniques. The transparent, colorless, prismatic crystals of **1**, so obtained, were found to react with or dissolve in the solvents in every glue used to mount crystals. Consequently, the crystals were wedged in 0.5-mm thin-walled glass capillaries which were sealed under a dry nitrogen atmosphere.

Crystal Data. $C_{30}H_{20}O_2F_{12}S$, $M = 672.1$, triclinic, $a = 10.026(3)$, $b = 14.268(3)$, $c = 10.802(3)$ Å, $\alpha = 109° 50'(2')$, $\beta = 92° 52'(2')$, $\gamma = 95° 20'(2')$, $V = 1447$ Å^3, $Z = 2$, $\rho_{calc} = 1.54$ g cm^{-3}, $F(000) = 680$, μ(Cu Kα) = 19.8 cm^{-1}. The space group is either $P1$ or $P\bar{1}$, with the latter choice being established by the results of the analysis. Owing to the extreme reactivity of the compound, no density measurement was attempted.

The cell parameters were determined by a least-squares fit to the settings for the 4 angles for 12 reflections on a Picker FACS-1 diffractometer (Cu Kα, $\lambda = 1.54178$ Å). Because of crystal decomposition, two crystals (approximately equidimensional prisms, *ca.* 0.5 mm) had to be used to collect the data on the diffractometer (Cu Kα radiation). The crystals were mounted about the *b* and *c* crystal axes, respectively. The reflections were measured by a scintillation counter, with attenuators being inserted when the count rate exceeded 10,000 counts sec^{-1}. All the symmetry-nonequivalent reflections in the 2θ range 0–130° were measured by a moving crystal moving counter technique, with a 2θ scan rate of 2° min^{-1}. The base width of the scan was 2.0°, and a dispersion factor was applied to allow for the α_1–α_2 splitting. Background measurements were made at each limit of the scan.

A total of 2818 reflections containing some symmetry-related pairs was measured on the first crystal and a total of 3436 reflections was measured on the second crystal. To allow a good estimate of a scaling factor between crystals, 259 common reflections were measured on both crystals. Three standard reflections were monitored after every 50 measurements. A significant decrease in intensity was noted, together with a developing yellow color and some liquefaction on the crystal surfaces during the 5- and 6-day periods in which data were collected for each crystal. During these periods, the intensities of the standards for the two crystals fell approximately linearly to between 80 and 85% of their original values. The intensities of the reflections were then corrected by assuming a linear fall-off between the periodic measurements of the standards and by scaling to a normalized value for the intensity of the standards. In addition to the long term drop in intensity, there were irregular, short term drops in the intensity of the standards. These corresponded to movements of the crystal within the glass capillary, after which crystal realignment was necessary. This realignment had to be carried out approximately 20 times throughout the entire data collection procedure. Data obtained after crystal movement was detected were discarded and new intensity data were collected.

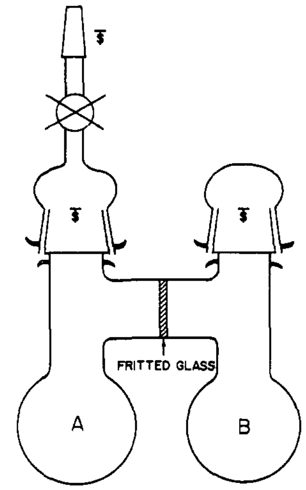

Figure 1. Apparatus used to crystallize sulfurane.

In all, 3365 symmetry-independent reflections (about 70% of available data within the 130° sphere) were considered significantly above 0 at the 2σ significance level based on counting statistics. In view of the frequent and large changes in position of the crystal with respect to the instrumental geometry, and the gradual accumulation of liquid around the crystal, absorption corrections were considered impractical.

Solution and Refinement of the Structure. The structure was solved by Patterson–heavy atom methods based on the sulfur atom. The initial location of the sulfur atom was apparent from a point-atom sharpened Patterson map. A Fourier map based on the sulfur atom (10% of the scattering) revealed a major portion of the structure. Nineteen atoms were chosen from the map and were refined by least-squares methods[12] varying positional and isotropic thermal parameters to obtain an *R* factor of 0.45. Another Fourier map at this stage revealed the positions of all the nonhydrogen atoms in the molecule. Four additional cycles of full-matrix least-squares refinement, varying the positional and isotropic temperature factors of the nonhydrogen atoms, gave an *R* factor of 0.178 and R_2, defined as $[\Sigma w(||F_o| - |F_c||)^2/\Sigma w|F_o|^2]^{1/2}$ of 0.249. The refinement was based on 3365 nonzero reflections which were given estimated standard deviations, $\sigma(F)$, as 1.1, 1.0, or 1.2, depending on whether σ(counting statistics)/$|F_o|$ was in the range 0–0.03, 0.03–0.10, or greater than 0.10, and weighted accordingly. At this stage, anisotropic temperature parameters were introduced for all the nonhydrogen atoms. Refinement was continued in two partial cycles owing to computer storage limitations, one cycle consisting of the atoms S(1), O(1), C(1)–C(9), C(25)–C(30), and F(1)–F(6), and the other consisting of S(1) and the remainder of the atoms. One complete cycle of such refinement reduced the *R* to 0.135 and R_2 to 0.223. At this stage it was noted that one reflection ($\bar{3}10$) was grossly incorrect due to an error in paper tape punching. The reflection was removed and a second complete cycle of refinement on the remaining 3364 nonzero reflections gave an *R* of 0.107 and R_2 of 0.107. As all the hydrogen atoms could not be located unambiguously from a difference map, they were positioned assuming C–H bond lengths of 0.95 Å and trigonal C–C–H angles. Three additional complete cycles of refinement on the positions of the hydrogen atoms, while holding their isotropic thermal parameters

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[11] We would like to thank R. J. Arhart and J. A. Franz for supplying generous quantities of the sulfurane.

[12] Using a local modification of the program written by W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS, A Fortran Crystallographic Least-Squares Program," Report ORNL-TM-305, Aug 1962.

Table I. Final Atomic Coordinates in Fractions of the Unit Cell Edge, with Estimated Standard Deviations in Parentheses[a]

	x	y	z
S(1)	0.2197 (1)	0.2490 (1)	0.2215 (1)
O(1)	0.2104 (4)	0.3699 (3)	0.1828 (4)
O(2)	0.2235 (4)	0.1237 (3)	0.2443 (4)
C(1)	0.3087 (6)	0.4525 (4)	0.2346 (6)
C(2)	0.2972 (8)	0.4987 (5)	0.3888 (7)
C(3)	0.4476 (7)	0.4265 (5)	0.2039 (9)
C(4)	0.2765 (7)	0.5324 (4)	0.1721 (7)
C(5)	0.3337 (8)	0.6317 (5)	0.2267 (8)
C(6)	0.3047 (10)	0.7014 (6)	0.1676 (10)
C(7)	0.2195 (11)	0.6702 (6)	0.0531 (10)
C(8)	0.1627 (10)	0.5710 (6)	−0.0030 (8)
C(9)	0.1924 (8)	0.5020 (5)	0.0562 (8)
C(10)	0.2530 (6)	0.1233 (4)	0.3739 (6)
C(11)	0.4080 (7)	0.1435 (5)	0.4022 (7)
C(12)	0.2112 (9)	0.0124 (5)	0.3596 (8)
C(13)	0.1778 (7)	0.1944 (4)	0.4803 (6)
C(14)	0.0391 (8)	0.1791 (6)	0.4707 (7)
C(15)	−0.0329 (9)	0.2422 (7)	0.5673 (9)
C(16)	0.0354 (10)	0.3198 (7)	0.6711 (9)
C(17)	0.1716 (10)	0.3364 (6)	0.6800 (8)
C(18)	0.2436 (8)	0.2740 (5)	0.5878 (7)
C(19)	0.0385 (6)	0.2327 (4)	0.2037 (6)
C(20)	−0.0311 (7)	0.3094 (5)	0.2711 (7)
C(21)	−0.1688 (8)	0.2921 (7)	0.2677 (9)
C(22)	−0.2384 (8)	0.2016 (8)	0.1968 (9)
C(23)	−0.1678 (9)	0.1263 (7)	0.1272 (10)
C(24)	−0.0310 (7)	0.1398 (5)	0.1291 (8)
C(25)	0.2671 (6)	0.1876 (4)	0.0564 (6)
C(26)	0.3855 (6)	0.1440 (4)	0.0452 (7)
C(27)	0.4267 (8)	0.1028 (5)	−0.0791 (8)
C(28)	0.3509 (9)	0.1024 (5)	−0.1902 (8)
C(29)	0.2334 (9)	0.1446 (5)	−0.1762 (7)
C(30)	0.1886 (7)	0.1890 (5)	−0.0533 (6)
F(1)	0.4537 (4)	0.3849 (3)	0.0738 (5)
F(2)	0.5444 (4)	0.5052 (3)	0.2458 (6)
F(3)	0.4883 (4)	0.3593 (3)	0.2552 (5)
F(4)	0.3028 (5)	0.4281 (3)	0.4435 (4)
F(5)	0.1807 (5)	0.5344 (3)	0.4118 (4)
F(6)	0.3949 (5)	0.5704 (3)	0.4502 (4)
F(7)	0.4539 (4)	0.2369 (3)	0.4111 (4)
F(8)	0.4732 (4)	0.0840 (3)	0.3113 (4)
F(9)	0.4494 (4)	0.1339 (3)	0.5178 (4)
F(10)	0.2217 (6)	0.0017 (3)	0.4789 (4)
F(11)	0.0844 (5)	−0.0179 (3)	0.3128 (5)
F(12)	0.2832 (6)	−0.0505 (3)	0.2822 (5)
H(5)	0.409 (7)	0.657 (5)	0.312 (7)
H(6)	0.362 (7)	0.773 (6)	0.217 (7)
H(7)	0.194 (7)	0.715 (6)	0.010 (7)
H(8)	0.073 (7)	0.541 (5)	−0.102 (7)
H(9)	0.149 (7)	0.438 (6)	0.019 (7)
H(14)	−0.026 (7)	0.117 (5)	0.392 (7)
H(15)	−0.139 (8)	0.222 (5)	0.548 (7)
H(16)	−0.019 (7)	0.371 (6)	0.718 (7)
H(17)	0.220 (7)	0.394 (6)	0.746 (7)
H(18)	0.341 (7)	0.290 (5)	0.592 (7)
H(20)	0.009 (7)	0.369 (6)	0.300 (7)
H(21)	−0.216 (8)	0.336 (6)	0.285 (8)
H(22)	−0.346 (7)	0.196 (5)	0.205 (7)
H(23)	−0.210 (8)	0.075 (6)	0.087 (8)
H(24)	0.014 (8)	0.098 (6)	0.087 (8)
H(26)	0.465 (7)	0.159 (5)	0.130 (7)
H(27)	0.512 (7)	0.081 (5)	−0.084 (7)
H(28)	0.381 (7)	0.064 (5)	−0.276 (7)
H(29)	0.178 (8)	0.140 (6)	−0.241 (8)
H(30)	0.106 (7)	0.224 (5)	−0.042 (7)

[a] Hydrogen atoms are numbered with the corresponding carbon atom number.

Table II. Final Anisotropic Thermal Parameters ($\times 10^4$)[a]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	79 (1)	33 (1)	77 (2)	4 (1)	11 (1)	10 (1)
O(1)	87 (4)	32 (2)	99 (5)	−5 (2)	−4 (4)	18 (3)
O(2)	134 (5)	33 (2)	84 (5)	7 (3)	15 (4)	12 (3)
C(1)	88 (7)	39 (3)	113 (8)	−4 (4)	−7 (6)	18 (4)
C(2)	189 (12)	43 (4)	111 (9)	−6 (6)	−32 (8)	20 (5)
C(3)	84 (7)	56 (4)	196 (12)	−6 (5)	2 (8)	35 (6)
C(4)	128 (8)	36 (3)	129 (9)	9 (4)	25 (7)	25 (4)
C(5)	158 (11)	45 (4)	188 (12)	−4 (5)	−10 (9)	33 (6)
C(6)	226 (15)	51 (5)	209 (14)	6 (7)	27 (12)	52 (7)
C(7)	259 (16)	66 (6)	191 (14)	49 (8)	74 (12)	72 (8)
C(8)	270 (16)	70 (6)	145 (11)	27 (8)	2 (11)	48 (6)
C(9)	193 (12)	45 (4)	127 (10)	14 (6)	1 (9)	24 (5)
C(10)	137 (8)	40 (3)	84 (7)	11 (4)	15 (6)	22 (4)
C(11)	140 (9)	69 (5)	95 (8)	27 (5)	10 (7)	27 (5)
C(12)	210 (13)	45 (4)	136 (10)	10 (6)	17 (9)	31 (5)
C(13)	128 (8)	45 (4)	85 (7)	12 (4)	26 (6)	27 (4)
C(14)	130 (10)	84 (5)	123 (9)	11 (6)	31 (8)	47 (6)
C(15)	145 (11)	112 (7)	152 (12)	30 (7)	54 (9)	66 (8)
C(16)	202 (14)	82 (6)	151 (12)	50 (8)	77 (11)	39 (7)
C(17)	193 (13)	62 (5)	141 (11)	6 (6)	59 (10)	4 (6)
C(18)	149 (10)	63 (5)	122 (9)	2 (6)	38 (8)	24 (5)
C(19)	90 (7)	50 (4)	87 (7)	−2 (4)	14 (5)	24 (4)
C(20)	110 (9)	69 (5)	111 (9)	11 (5)	21 (7)	27 (5)
C(21)	116 (10)	117 (8)	140 (11)	34 (7)	33 (8)	50 (8)
C(22)	90 (9)	135 (9)	189 (13)	−8 (8)	11 (9)	77 (9)
C(23)	116 (10)	101 (7)	207 (14)	−47 (7)	−28 (9)	70 (9)
C(24)	104 (8)	54 (4)	145 (10)	−15 (5)	−2 (7)	29 (5)
C(25)	110 (7)	42 (3)	71 (7)	1 (4)	20 (6)	15 (4)
C(26)	99 (7)	51 (4)	101 (8)	9 (4)	25 (6)	17 (4)
C(27)	128 (9)	59 (4)	127 (10)	23 (5)	50 (8)	20 (5)
C(28)	196 (12)	67 (5)	101 (9)	33 (6)	53 (9)	25 (5)
C(29)	190 (12)	70 (5)	75 (8)	26 (6)	18 (8)	29 (5)
C(30)	132 (9)	53 (4)	100 (8)	19 (5)	19 (7)	26 (5)
F(1)	142 (6)	83 (3)	197 (7)	25 (3)	74 (5)	43 (4)
F(2)	103 (5)	68 (3)	345 (10)	−25 (3)	−12 (5)	55 (4)
F(3)	118 (5)	67 (3)	230 (7)	11 (3)	−16 (5)	55 (4)
F(4)	289 (8)	56 (3)	102 (5)	6 (4)	−30 (5)	19 (3)
F(5)	239 (8)	76 (3)	112 (5)	51 (4)	42 (5)	11 (3)
F(6)	271 (8)	63 (3)	149 (6)	−42 (4)	−70 (6)	12 (3)
F(7)	119 (5)	70 (3)	133 (5)	−7 (3)	5 (4)	36 (3)
F(8)	165 (6)	94 (3)	148 (6)	61 (4)	53 (5)	27 (3)
F(9)	173 (6)	105 (3)	134 (5)	31 (4)	−6 (5)	60 (4)
F(10)	336 (10)	77 (3)	158 (6)	1 (4)	8 (6)	73 (4)
F(11)	210 (7)	62 (3)	228 (8)	−35 (4)	−20 (6)	52 (4)
F(12)	311 (10)	45 (3)	238 (8)	50 (4)	85 (7)	29 (4)

[a] Expressed as exp $-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$.

constant at 4.0 Å^2, together with refinement on the positional and anisotropic thermal parameters for other atoms gave a final R of 0.070 and R_2 of 0.077 on all observed reflections.

The scattering curves were taken from ref 13. The final coordinates and temperature factors are listed in Tables I and II. The final values of observed and calculated structure factors are published in the microfilm edition.[14] A final difference map revealed two electron density maxima of *ca.* 0.5 e/Å^3 in the vicinity of the S(1)–O(2) bond, but no chemical significance can reasonably be attached to these peaks.

Results and Discussion

Figures 2 and 3 show the molecular dimensions found in the analysis while Figure 4 is a stereoscopic view of a single molecule. The root mean square deviation among the 24 C–C (aromatic) bond lengths is 0.013 Å, which is only slightly above the average standard deviation from least squares for these lengths (0.012 Å); this good agreement indicates that the effect of systematic errors, such as absorption, in the data is not very important. The root mean square deviation among the 12 C–F bond lengths is 0.016 Å. This is considerably

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(13) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, 1962, pp 201-209.

(14) This table will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-5010. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

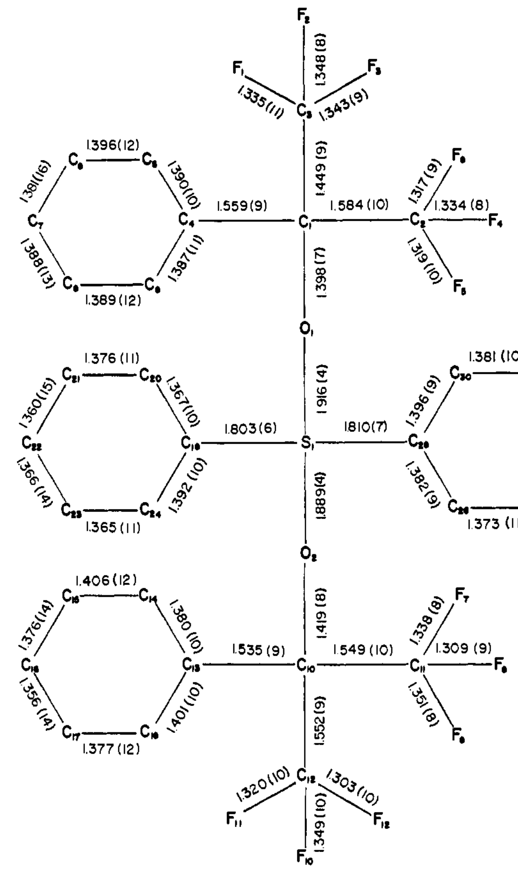

Figure 2. Bond lengths (Å) with estimated standard deviations in parentheses.

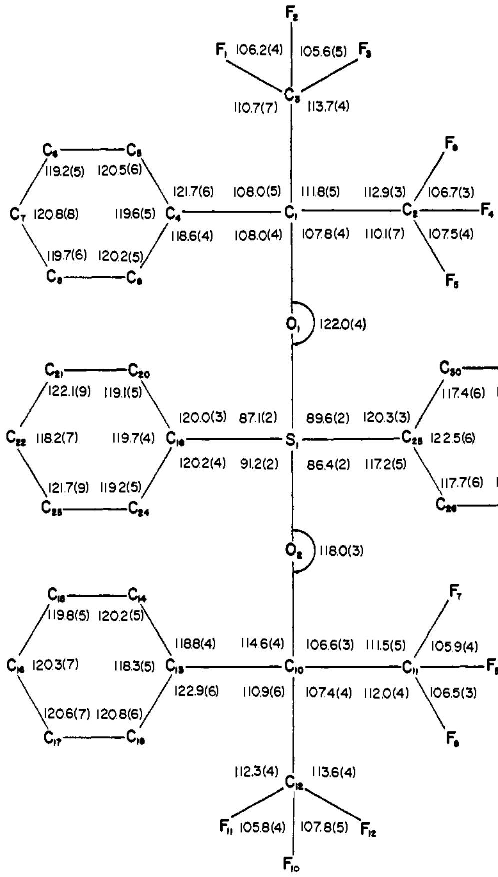

Figure 3. Bond angles (degrees) with estimated standard deviations in parentheses. Angles not shown on figure are as follows: F(2)-C(3)-C(1), 114.6(5)°; F(1)-C(3)-F(3), 105.4(5)°; C(3)-C(1)-O(1), 112.8(3)°; C(2)-C(1)-C(4), 108.2(5)°; F(4)-C(2)-C(1), 110.3(7)°; F(5)-C(2)-F(6), 109.1(7)°; O(1)-S(1)-O(2), 175.1(2); C(19)-S(1)-C(25), 104.4(3)°; C(12)-C(10)-O(2), 103.0(6)°; C(11)-C(10)-C(13), 113.5(4)°; F(8)-C(11)-C(10), 114.0(4)°; F(7)-C(11)-F(9), 106.3(3)°; F(10)-C(12)-C(10), 110.1(7)°; F(11)-C(12)-F(12), 106.8(3)°.

greater than the average standard deviation from least squares for the C–F lengths (0.009 Å) and probably indicates significant oscillation of the CF_3 groups in the crystal.

The configuration about the sulfur atom in sulfurane **1** is an approximate trigonal bipyramid. The phenyl rings occupy two of the equatorial positions with the C–S–C angle between them being 104.4(3)°. The third equatorial position is considered to be occupied by the lone pair of electrons.[10,15] The apical positions are occupied by the two more electronegative alkoxy ligands. The O–S–O angle is 175.1(2)°, with the distortion from linearity in the direction of the equatorial phenyl rings, and away from the lone pair, while the O–S–C angles range from 86.4(2)° to 91.2(2)°.

The six carbon atoms making up each of the phenyl rings are coplanar within the accuracy of the analysis. The sulfur atom was found to be significantly (0.178(2) and 0.095(2) Å) displaced from the planes through the atoms of the two equatorial phenyl rings, C(19)–C(24) and C(25)–C(30), respectively, and in the general direction of the shorter S–O bond. The equatorial phenyl rings make angles of 32° 22′ and 42° 31′ with the plane defined by the atoms C(19), S(1), and C(25).

There are no short (<3.80 Å) intermolecular contacts involving the sulfur atom (Table III). Three S---F intramolecular distances (S(1)---F(4), 2.867(5) Å; S(1)---F(3), 2.929(4) Å; and S(1)---F(7), 3.094(4) Å) are shorter than the sum of the appropriate van der Waals radii (3.20 Å),[16] leading to speculation regarding a possible weak nonbonded interaction between the fluorine atoms and the sulfur atom. A stereoscopic view of the unit cell packing is shown in Figure 5.

S–O Bonds. The S–O bond lengths for **1** are 1.889(4) and 1.916(4) Å. The 0.027 Å difference between them, while numerically significant, probably results from crystal packing requirements. These lengths are considerably greater than the sum of the covalent radii for sulfur and oxygen (1.70 Å),[17] than the S–O single bond lengths of 1.533–1.616 Å reported for organic sulfates,[18] or than the lengths of 1.594–1.627 Å found for sulfonates.[19] S---O contacts ranging from 2.034 to 2.65 Å have been reported[20,21] in several compounds, *e.g.*, **3**. In many of these cases the oxygen atom lies along the extension of an S–S vector. The fusion product **4** of captan and resorcinol[22,23] provides an interesting com-

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(16) L. Pauling, "The Nature of the Chemical Bond," 3rd Edition, Cornell University Press, Ithaca, New York, 1960, p 260.

(17) Reference 16, pp 221–228.

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(21) P. L. Johnson, K. I. G. Reid, and I. C. Paul, *J. Chem. Soc. B*, 946 (1971).

(22) I. Pomerantz, L. Miller, E. Lustig, D. Mastbrook, E. Hansen, R. Barron, N. Oates, and J. Y. Chen, *Tetrahedron Lett.*, 5307 (1969).

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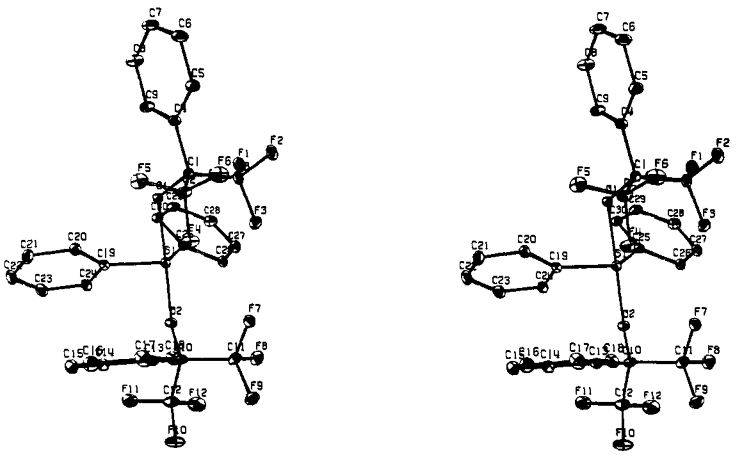


Figure 4. Stereoscopic view of a single molecule of **1**.

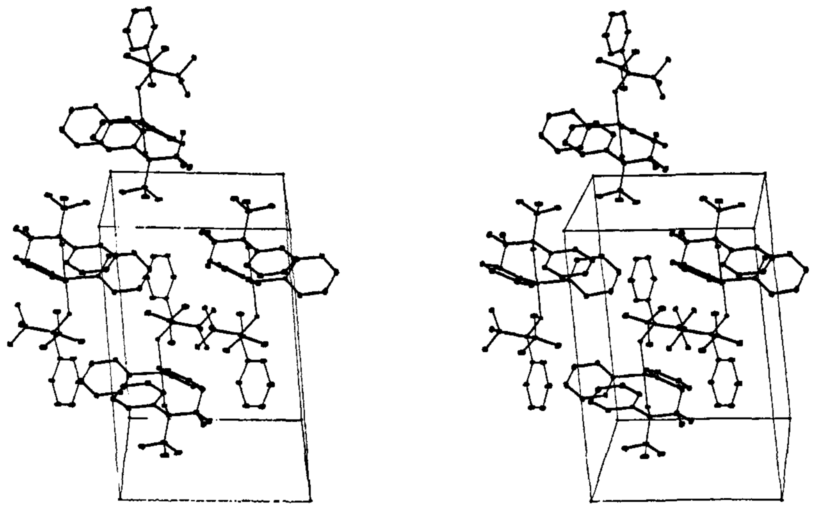


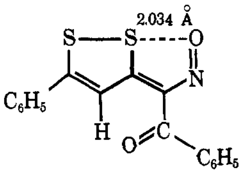
Figure 5. Stereoscopic view of the molecular packing viewed down the $-c$ axis.

Table III. Intermolecular Contacts <3.80 Å for Nonhydrogen Atoms[a]

$F(11)\cdots C(29^{I})$	3.50	$F(10)\cdots C(29^{IV})$	3.58
$F(8)\cdots C(22^{II})$	3.68	$F(8)\cdots C(27^{V})$	3.26
$F(3)\cdots C(21^{II})$	3.66	$F(8)\cdots C(28^{V})$	3.26
$F(3)\cdots C(22^{II})$	3.65	$F(12)\cdots C(27^{V})$	3.71
$C(6)\cdots F(12^{III})$	3.36	$C(21)\cdots C(7^{VI})$	3.70
$C(17)\cdots C(29^{IV})$	3.66	$C(22)\cdots C(7^{VI})$	3.74
$C(18)\cdots C(29^{IV})$	3.62	$C(8)\cdots C(9^{VI})$	3.58
$F(9)\cdots C(28^{IV})$	3.51	$C(14)\cdots F(10^{VII})$	3.69
$F(10)\cdots C(28^{IV})$	3.50	$C(15)\cdots F(10^{VII})$	3.67

[a] The Roman numerals as superscripts refer to the equivalent positions, relative to the reference molecule at x, y, z: I = $-x, -y, -z$; II = $1 + x, y, z$; III = $x, 1 + y, z$; IV = $x, y, 1 + z$; V = $1 - x, -y, -z$; VI = $-x, 1 - y, -z$; VII = $-x, -y, 1 - z$.

parison with **1**, as it has S–O bond lengths of 1.878(2) and 1.879(2) Å. Compound **4** appears formally as a tricoordinate sulfur(IV) compound, but if one considers the equivalent orbital representation in which the C═S double bond is represented as two equivalent bent bonds,[24,25] the similarity to **1** is apparent. In compounds **4** and **1** the S–O bonds are elongated by *ca.* 0.2 Å. The two S–Cl bonds in **2** were also somewhat unequal and were 0.23 and 0.29 Å longer than the sum of the S and Cl covalent radii.[7] A tendency for sulfur to form additional weak interactions with an oxygen and sulfur atom and thus form a distorted trigonal bipyramid was noted in the case of 1-acetonyl-1-thionia-5-thiacyclooctane perchlorate (**5**).[26] A bonding scheme



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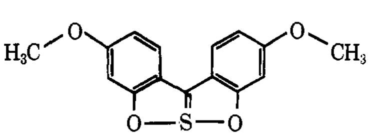

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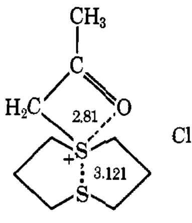

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consistent with these observations follows from ideas of Pimentel,[27] Rundle,[28] and Havinga and Wiebenga,[29] as

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(27) G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

(28) (a) R. J. Hach and R. E. Rundle, *J. Amer. Chem. Soc.*, 73, 4321

applied to interhalogen compounds,[28c] sulfur tetrafluoride[30] and its analogs,[6,31] phosphoranes,[32] and the fluorides of xenon,[33] all types of compounds with bonding which Musher[34] has called hypervalent. More attention has been given the description of the bonding in the rare gas fluorides than to that in the other types of compounds on this list. Several quantum mechanical studies of XeF_2 have been summarized[33b] in the statement that "very small mixing of the Xe(5s), Xe(4d), Xe(6s), and Xe(5d) orbitals was obtained." A similar conclusion was reached for the SF_4 molecule.[30] We will discuss the bonding of the apical ligands to the sulfur of sulfuranes in terms of this approximate theory. The involvement of other sulfur orbitals of the proper symmetry must, of course, improve the wave function but is not expected to make any major contribution for the same reasons that the analogous atomic orbitals of xenon contribute only slightly to the bonding in XeF_2.

The apical bonds are, in this picture, constructed from three atomic orbitals, the sulfur p_z orbital and one from each of the oxygen ligands, which are used to form three molecular orbitals to describe a three-center four-electron bond. Two electrons are in the bonding MO, distributed over all three atoms, and two are in the approximately nonbonding MO, with electron density only on oxygen (Figure 6). This results in formal negative charge on the apical oxygen ligands and positive charge on the sulfur. Such compounds are expected to be most stable when the apical ligands are more electronegative than the central atom, as here. The S–O bond order in such a description is 0.5. The correlation[35] of bond length and bond order proposed by Pauling suggests that such a bond should be 0.18 Å longer than the bond of order 1.0 joining the same two atoms. The observed S–O bond elongations of 0.19 and 0.22 Å in **1** are in good agreement with this prediction.

This picture, which ignores the contributions of sulfur 3d orbitals in the trigonal bipyramidal bonding, receives experimental support from several quarters.[33b] For example, the results of nuclear quadrupole resonance studies of the closely related interhalogen compounds ICl_4^- and ICl_2^-[36a] provide evidence for only minimal d character in the I–Cl bonds in these analogs of **1**. The photoelectron spectrum of XeF_2 is reported[36b] to be consistent with the above ideas. On the other hand, Gleiter and Hoffmann[37] have reported the results of extended Hückel calculations on related systems in which centers with six valence electrons are stabilized through electron-rich three-center bonding to two ligands. The calculations showed a definite stabilization of the symmetrical three-center four-electron system when d orbitals were included. Although some such d orbital involvement in the bonding about sulfur in **1** is likely, an sp^{3}d description of the hybridization probably overstates this involvement. For a discussion of the use of outer d orbitals in bonding see ref 38.

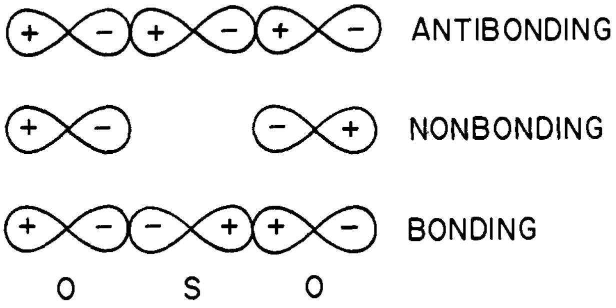
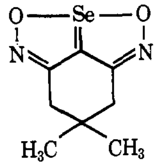


Figure 6. Molecular orbital diagram of bonding in sulfurane **1**.

Tolles and Gwinn[39] summarize the preceding ideas of orbital mixing in their study of SF_4 by stating that "the structure of SF_4 appears to be intermediate between that formed by using four of the sp^{3}d orbitals and the structure formed by using only the three sulfur p orbitals to form four bonds. This latter extreme might be described as p^2(p/2)^2 bonding for sulfur."

It is interesting to note that increases of approximately 0.2 Å over the sum of the covalent radii occur in a number of halide complexes of selenium and tellurium (for a listing, see ref 7). If similar arguments can be invoked in the cases where there is a C=S or a C=Se double bond instead of the C–S–C or C–Se–C fragment, then increases of 0.27 Å over twice the covalent radius for sulfur (2.08 Å) in symmetrical thiathiophthenes,[40] and 0.19 Å over the sum of the selenium and oxygen radii (1.83 Å) in **6**[41,41a] have been noted in addition to the previously discussed example of **4**.



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O–S–O Angle. All of the ligands to the sulfur atom in **1** lie on the same side of a plane through the sulfur atom. A similar arrangement is found in SF_4 in the gas phase for which a microwave study[39,42] showed an equatorial F–S–F angle of 101° 33′(30′) and an apical F–S–F (measured along an arc bisecting the internal equatorial F–S–F angle) of 173° 4′(30′).[39]

(1951); (b) R. E. Rundle, *ibid.*, **85**, 112 (1963); (c) R. E. Rundle, *Surv. Progr. Chem.*, **1**, 81 (1963).

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(38) (a) K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969); (b) see also E. L. Rozenberg and M. E. Dyatkina, *Zh. Strukt. Khim.*, **11**, 323 (1970); (c) see, however, C. R. Brundle and G. R. Jones, *Chem. Commun.*, 1198 (1971).

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(40) F. Leung and S. C. Nyburg, *Chem. Commun.*, 137 (1969).

(41) R. J. S. Beer, J. R. Hatton, E. C. Llaguno, and I. C. Paul, *ibid.*, 594 (1971); E. C. Llaguno and I. C. Paul, *J. Chem. Soc., Perkin Trans. 2*, in press.

(41a) Note Added in Proof. The sulfur analog of 6 has recently been shown to have S–O lengths of 1.88 and 1.89 Å, E. C. Llaguno and I. C. Paul, submitted for publication.

(42) Somewhat similar results were obtained from an electron diffraction study: K. Kimura and S. H. Bauer, *J. Chem. Phys.*, **39**, 3172 (1963).

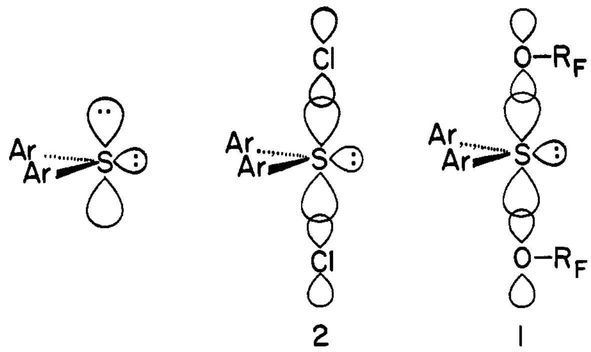

Figure 7. Molecular orbital representations of a diaryl sulfide and sulfuranes **1** and **2** (R_F = $C(CF_3)_2C_6H_5$).

Compound **2**, at least in the crystal, is apparently an exception in that the deformation of the Cl–S–Cl axis is toward the lone pair. Evidence for possible weak interactions between a sulfur atom and a chlorine atom in an adjacent molecule in the unit cell is provided by some short intermolecular contacts.[7] The authors attribute some of the distortion from the ideal trigonal-bipyramidal geometry to these interactions. There is also a nearly linear S–Cl·····Cl–S array (Cl·····Cl, 3.31 Å) with appreciable interactions between chlorine atoms which may also affect the geometry of **2** in the crystal.

It is possible to explain the deviation from linearity of the O–S–O atoms by considerations which have been advanced to explain analogous distortions seen for other molecules. These focus upon repulsion between the sulfur lone pairs and other sulfur valence shell electrons.[15,43] The strongest repulsion will be between the equatorial lone pair and the electrons in the apical bonds, which are directed away from sulfur by 90° angles. An alternative approach[44] using MO theory with inclusion of the outer s orbitals also predicts the direction of this distortion of the apical ligands away from collinearity with the central atom.

C–S–C Angle. Table IV contains data on bond lengths and angles in various sulfur compounds. In the sulfides, the two S–C bonds may be viewed (Figure 7) as involving two equivalent hybrids of the s, p_x, and p_y atomic orbitals on sulfur with one lone pair occupying the third hybrid orbital in the C–S–C plane, and one lone pair in the p_z orbital normal to this plane. The three in-plane orbitals are not equivalent; the two sulfur orbitals used in bonding to carbon have more p character than does the in-plane orbital containing the lone pair, as the unshared electrons tend to utilize a higher proportion of the lower energy s orbital at the expense of the higher energy p orbitals.[45] The C–S–C angle is thus less than the 120° predicted for equivalent sp^2 orbitals by an amount which depends on the magnitude of the 3s–3p energy level separation, among other factors.

Table IV. Comparison of S–C Bond Lengths and C–S–C Bond Angles for Various Sulfur Compounds

	S–C length, Å	C–S–C angle, deg	Ref
$(p\text{-}CH_3C_6H_4)_2S$	1.76 (4) 1.74 (4)	109 (1.9)	*a*
$(p\text{-}BrC_6H_4)_2S$	1.75 (3)	109.5 (5)	*b*
2	1.767 (7) 1.797 (9)	108.6 (4)	7
1	1.803 (6) 1.810 (7)	104.4 (3)	This work
$(C_6H_5)_2SO$	1.763 (21) 1.756 (21)	97.3 (1.0)	*c*
$(p\text{-}ClC_6H_4)_2SO_2$	1.765 (6)	104.8 (4)	*d*

[a] W. R. Blackmore and S. C. Abrahams, *Acta Crystallogr.*, **8**, 329 (1955). [b] J. Toussaint, *Bull. Soc. Chim. Belg.*, **54**, 319 (1945). [c] S. C. Abrahams, *Acta Crystallogr.*, **10**, 417 (1957). [d] J. G. Sime and S. C. Abrahams, *ibid.*, **13**, 1 (1960).

This picture (Figure 7) of bonding in sulfides can be extended to compounds **1** and **2**. The hypervalent bonding scheme[34] as applied to **1** and **2** predicts positive charge on the central sulfur atom and negative charge on the electronegative apical ligands. This charge polarization is expected to be more pronounced for the alkoxy ligands of **1** than for the less electronegative chloro ligands of **2**. The postulated greater effective nuclear charge on the sulfurane sulfur atom (when compared to the sulfide sulfur atom), with the attendant increase in the 3s–3p energy level separation,[46] could accentuate the preference for s character in the lone pair orbital, thus decreasing the C–S–C angle. These arguments would lead one to expect the order of the angles to be sulfide > **2** > **1**, as is observed. With the use of simple geometric and hybridization arguments,[47] the percentages of s character in the S–C bonds in sulfides, **2**, and **1** are calculated to be 25, 24, and 20%, respectively.[48,49] These calculations assume no bond bending, *i.e.*, that the interorbital angle is equal to the angle between internuclear vectors.

Bent[45] has used related arguments to explain bond angle variation among the H–O–H, H–S–H, and F–O–F molecules, and reached the conclusion that *increase* of the electronegativity of the central atom would lead to an *increase* in the angle. He based his arguments on the variation in p character in the O–H, S–H, and O–F bonds. At first sight, this result seems to contradict the correlation obtained for sulfides and sulfuranes, but in fact a direct comparison is invalid since the nature of the atoms forming the bonds and the bond lengths are changing in the H_2O, H_2S, F_2O series, whereas these are essentially invariant in the sulfide and sulfurane series. The major change in the latter series is in the effective electronegativity of the central atom as induced by changing substituents bonded to the central atom by a bond involving a sulfur $3p_z$ orbital.

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(43) (a) R. J. Gillespie, *J. Chem. Phys.*, 37, 2498 (1962); (b) R. J. Gillespie, *Inorg. Chem.*, **5**, 1634 (1966); (c) R. J. Gillespie, *Can. J. Chem.*, **39**, 318 (1961); (d) see, however, A. W. Searcy, *J. Chem. Phys.*, **31**, 1 (1959).

(44) L. S. Bartell, *Inorg. Chem.*, **5**, 1635 (1966).

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

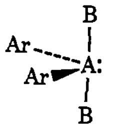
(46) The energy separation between 3s and 3p levels of sulfur does in fact increase as one goes from atomic sulfur ($3s^2$, $3p^4$) to the monocation ($3s^2$, $3p^3$). See C. E. Moore, National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington, D. C.

(47) See, for example, K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, pp 24–42.

(48) The C–S–C angle for sulfoxides (Table IV) is smaller (97.3°) than those for the sulfides and sulfuranes. If similar arguments can be applied, then there will be a still greater effective nuclear charge on the sulfoxide sulfur atom, thus inducing more s character in the lone pair. The sulfone, lacking a lone pair on sulfur, does not show this effect and the C–S–C angle (104.8°) is larger than that for the sulfoxide.

(49) The possibility that the small C–S–C angle in **1** as compared to that in **2** is a result of steric forces has been considered. Were that the case, however, one might anticipate that the S(1)–C(25)–C(26) and S(1)–C(19)–C(20) angles would also be so influenced and be larger than the corresponding S(1)–C(25)–C(30) and S(1)–C(19)–C(24) angles. Such an effect is not observed (Figure 3).

Additional observations which are consistent with these ideas are provided by studies of other hypervalent derivatives of group VI elements of the general type Ar_2AB_2 (7). The Ar–A–Ar(C–A–C) angles in



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$(p\text{-}CH_3C_6H_4)_2SeCl_2$ and $(p\text{-}CH_3C_6H_4)_2SeBr_2$ are 106.5(1.0) and 108(1)°,[50] respectively, while in $(C_6H_5)_2TeBr_2$[51] and $(p\text{-}ClC_6H_4)_2TeI_2$,[52] they are 96.3(1.2) and 101.1(1.0)°. The more electronegative the B ligand the smaller the C–A–C angle as long as A is constant. The variation in C–A–C angles (S > Se > Te) as A is changed is that predicted by the rule given by Bent.[45]

Acknowledgment. We thank the U. S. National Science Foundation for partial support of this research through grant number GP 13339.

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Synthesis of Substituted Five-Membered Ring Halonium Ions and Their Reactions with Nucleophiles

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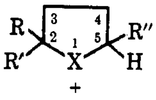
Received December 11, 1971

Abstract: 3-Chlorotetramethylene-, 3-methyltetramethylene-, *cis*-cyclohexane-1,2-dimethylene-, *cis*-3,4-dichlorotetramethylenechloronium, and 3-bromotetramethylenebromonium ions were formed by ionization of 1,2,4-trichlorobutane, 1,4-dichloro-2-methylbutane, *cis*-1,2-bis(chloromethyl)cyclohexane, *meso*-1,2,3,4-tetrachlorobutane, and 1,2,4-tribromobutane, respectively, in antimony pentafluoride–sulfur dioxide solution at −65 to −78°. Reaction of 3-chloro- and 3-methyltetramethylenechloronium ions with dimethyl ether, methanol, acetic acid, and trifluoroacetic acid in each case gave the expected two products whose ratio is presumed to reflect the steric and inductive effects of the substituent.

In previous investigations[3–5] it has been shown that cyclic five-membered ring halonium ions can be prepared by the ionization of 1,4-dihaloalkanes in antimony pentafluoride–sulfur dioxide at low temperatures. Depending on the starting alkane various alkyl and/or haloalkyl substituents can be incorporated into the ring structure **1**.



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The first five-membered ring ions prepared were the tetramethylene- (unsubstituted, R = R′ = R″ = H; X = Cl, Br, I), 2-methyltetramethylene- (primary–secondary, R = CH_3; R′ = R″ = H; X = Cl, Br, I), and the 2,5-dimethyltetramethylene- (disecondary, R = R″ = CH_3; R′ = H; X = Cl, Br, I) halonium ions.[3] Reaction of the 2-methyltetramethylenehalonium ions with methanol gave secondary ether products, indicating the preference for SN1 type ring opening. The 2,2-dimethyltetramethylenehalonium ions (R = R′ = CH_3; R″ = H; X = Cl, Br, I) similarly gave a tertiary ether product[4] upon reaction with methanol.

Presently the only halo-substituted five-membered halonium ions which have been prepared are the 2-chloromethyltetramethylenechloronium ion (R = CH_2Cl; R′ = R″ = H; X = Cl) and the 2-bromomethyltetramethylenebromonium ion (R = CH_2Br; R′ = R″ = H; X = Br).[5] On reaction with methanol, these ions gave ethers derived from both possible ring opening reactions, with the SN2 like opening product predominating,[5] in contrast with the results cited above for other ions. This result presumably reflects the inductive influence of the haloalkyl substituent.

The predominantly qualitative results cited above indicate that halonium ion reactions are open for quantitative exploration of the role of such factors as inductive substituent effects, delocalization of charge in transition states, and the effect of reactant nucleophilicity and/or basicity. Such studies are, in part, analogous to those involving solvolytic reactions of substrates such as tosylates, chlorides, and, particularly, sulfonium salts $[R'S(R)_2]^+X^-$. The relatively unstudied chloronium ion substrates, however, possess possibly the most reactive leaving group, $[RCl]^+$, of any compound yet obtained as a stable species, permitting studies of reactions in "inert" solvents (*e.g.*, SO_2) where the influence of reactant nucleophilicity can be studied without concomitant variation of ionizing power. As in solvolytic studies, competition experiments and direct measurement of rates of reaction may be envisioned. The present paper utilizes the former method (competition) to explore the interaction of inductive substituent effects in the halonium ion with the nucleophilic-

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