matographed on silica gel using benzene as eluent to give 0.1 g of isopropyl *p*-nitrobenzoate, mp 107–110 °C (lit. mp 108–110 °C), and 0.1 g of *p*-nitrobenzoylisopropoxy trisulfide: mp 77–79 °C; IR $\nu_{C=O}$ 1685 cm^{-1}; NMR ($CDCl_3$) δ 8.22 (q, 4 H), 4.23 (m, 1 H), 1.33 (d, 6 H). Anal. Calcd for $C_{10}H_{11}NO_4S_3$: C, 39.33; H, 3.63; S, 31.50. Found: C, 39.41; H, 3.65; S, 31.52.

Reaction of Dialkoxy Disulfides with Thiocarboxylic Acids. A solution of 3.8 g (0.05 mol) of thioacetic acid in 20 ml of CCl_4 was added to a stirred solution of 7.7 g (0.05 mol) of diethoxy disulfide in 30 ml of CCl_4 at room temperature, and then the temperature of the mixture was gradually raised to 60 °C during 1 h. Finally, the reaction mixture was refluxed for 1 h and EtOH was removed as its CCl_4 azeotrope by evaporation. The residual liquid was distilled to give 5.8 g of acetylethoxy trisulfide (**8b**), bp 60–61 °C (0.35 mm), yield 63%. Similarly, **8a, 8d,** and **8e** were obtained: yield of **8a,** 65%; **8d,** 69%; **8e,** 77%. *p*-Nitrobenzoylisopropoxy trisulfide was purified by recrystallization from *n*-hexane, mp 79 °C, yield 74%.

Reaction of 8b with Ethyl Mercaptan. A solution of 2.4 g (0.038 mol) of ethyl mercaptan in 20 ml of CCl_4 was added to a stirred solution of 7.0 g (0.038 mol) of **8b** in 30 ml of CCl_4 at room temperature for 1 h and then stirring was continued for an additional 3 h. The CCl_4 solution was then concentrated under reduced pressure and the residual liquid was distilled to give 3.0 g (47%) of acetylethyl tetrasulfide: bp 67–71 °C (0.3 mm); NMR δ 2.50 (s, 3 H), 2.93 (q, 2 H), 1.42 (t, 3 H). Anal. Calcd for $C_4H_8OS_4$: C, 23.98; H, 4.03; S, 64.01. Found: C, 24.06; H, 4.08; S, 63.98. IR $\nu_{C=O}$ 1730 cm^{-1}.

Reaction of 8b with Thiobenzoic Acid. A solution of 2.7 g (0.015 mol) of **8b** and 2.0 g (0.015 mol) of thiobenzoic acid in 50 ml of CCl_4 was stirred at 70 °C for 10 h and the solution became light yellow. The reaction mixture was cooled and the precipitate was collected and recrystallized from benzene to give 0.79 g (34%) of dibenzoyl trisulfide, mp 114–115 °C, IR $\nu_{C=O}$ 1690 cm^{-1}. Anal. Calcd for $C_{14}H_{10}O_2S_3$: C, 54.86; H, 3.29; S, 31.39. Found: C, 54.92; H, 3.30; S, 31.24. The filtrate was chromatographed on silica gel using CCl_4–chloroform (1:1) as eluent to give 0.45 g (11%) of dibenzoyl disulfide, mp 127–129 °C (lit.[12] mp 130 °C), and a small amount of diacetyl disulfide and trisulfide. Similarly, *p*-chlorothiobenzoic acid reacted with **8b** to give bis(*p*-chlorobenzoyl) trisulfide, mp 124–125 °C (lit.[4] 125–126 °C), and a small amount of diacetyl disulfide and trisulfide. Disulfide was formed during the operation of chromatography.

Registry No.—**7** (R′ = CH_3), 13165-72-5; **7** (R′ = Et), 6378-11-6; **7** (R′ = Pr), 22598-38-5; **7** (R′ = Pr-*i*), 22598-56-7; **7** (R′ = Ph), 13165-73-6; **7** (R′ = *p*-$CH_3C_6H_4$), 61268-28-8; **7** (R′ = *p*-$C_2H_5C_6H_4$), 61268-29-9; **7** (R′ = 2,4-$(CH_3)_2C_6H_3$), 61268-30-2; **9** (R′ = CH_3), 28752-21-8; **9** (R′ = Pr), 3359-05-5; **9** (R′ = Pr-*i*), 3359-04-4; **9** (R′ = Et), 28752-22-9; RCOSH (R = O_2N-*p*-C_6H_4), 39923-99-4; RCOSH (R = CH_3), 507-09-5; RCOSH (R = C_2H_5), 1892-31-5; RCOSH (R = C_3H_7), 3931-64-4; RCOSH (R = Ph), 98-91-9; *p*-nitrobenzoylisopropoxy trisulfide, 61268-31-3; ethyl mercaptan, 75-08-1; acetylethyl tetrasulfide, 61268-32-4; dibenzoyl trisulfide, 61268-33-5.

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An X-Ray Crystallographic Structural Study of Sulfoxides Derived from 2-Phenyl-1,3-dithiane

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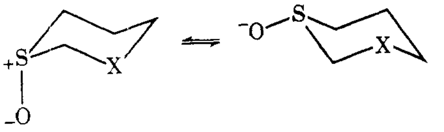
Single-crystal x-ray structure analyses have been carried out for *trans*-2-phenyl-1,3-dithiane 1-oxide (**5**), *cis*-2-phenyl-1,3-dithiane 1-oxide (**6**), and 2-phenyl-1,3-dithiane *trans*-1,*trans*-3-dioxide (**7**) to examine the effects of oxygen substitution on the geometry of the 1,3-dithiane ring. For **5**, a = 12.206 (2), b = 5.749 (1), c = 14.809 (2) Å, β = 97.11 (1)°; for **6**, a = 5.007 (1), b = 20.134 (4), c = 10.095 (3) Å, β = 98.76 (3)°; and for **7**, a = 12.315 (3), b = 5.851 (1), c = 14.829 (3) Å, β = 98.44 (2)°. The space group is $P2_1/c$ in each case with Z = 4. The dithiane rings have a chair conformation somewhat more puckered than that of cyclohexane with endocyclic torsion angles in the range 58–73°. The endocyclic C(2) valence angle shows a marked variation from compound to compound, being 109.6° in **5**, 112.9° in **6**, 114.2° in **7**, as compared to 114.9° in 2-phenyl-1,3-dithiane (**4**) itself. An argument accounting for the steric dependence of this angular variation is offered in terms of transannular dipolar interactions between the two sulfur atoms and oxygen and is discussed in relation to conformational equilibria in solution. Short C–H···O contacts indicative of significant dipolar interactions are found in all three crystal structures.

The conformational preferences exhibited by six-membered cyclic sulfoxides are strongly dependent upon the nature of the other ring atoms, especially those which bear a 1,3 relationship to the sulfoxide group (eq 1).[1] The more stable chair conformation of thiane 1-oxide (**1**) has the oxygen axial.[2] This conformation appears to be the more stable for 1,3-oxathiane 3-oxide (**2**) as well.[3] In 1,3-dithiane 1-oxide (**3**), however, it is the conformation with the sulfoxide oxygen equatorial which is the more stable.[3a,4] The reasons for these differences in conformational preference are not completely understood. It has been suggested that the axial conformation of **1** is stabilized by an attractive van der Waals interaction between the sulfoxide oxygen and the syn-axial C–H bonds.[2a,b] Electrostatic interactions between the polar sulfoxide group and the cross-ring heteroatom are expected to make important contributions to the conformational energies of **2** and **3**. Indeed, molecular mechanics calculations indicate that most of the



(1)

1, X = CH_2 $\Delta G°$ = +0.17 to 1.3 kcal/mol
2, X = O $\Delta G°$ = +0.6 kcal/mol
3, X = S $\Delta G°$ = −0.6 kcal/mol

Table I. Atomic Parameters Defining the Crystal Structures of 2-Phenyl-1,3-dithiane 1-Oxides[a]

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
A. *trans*-2-Phenyl-1,3-dithiane 1-Oxide (5)									
S(1)	8809.5 (4)	3325.4 (9)	2084.5 (3)	48.3 (4)	175 (1)	21.0 (2)	−10.4 (6)	1.4 (2)	−0.6 (5)
S(3)	7064.3 (5)	1099.8 (13)	785.8 (4)	50.1 (4)	471 (3)	22.6 (3)	−30.8 (9)	−1.2 (3)	−14.5 (7)
C(2)	7864 (2)	854 (4)	1899 (2)	48 (2)	202 (7)	25 (1)	−10 (3)	3 (1)	−2 (2)
C(4)	8151 (2)	905 (5)	63 (2)	64 (2)	388 (10)	23 (1)	−21 (3)	6 (1)	−23 (3)
C(5)	8993 (2)	2821 (4)	234 (2)	60 (2)	308 (9)	24 (1)	−2 (3)	10 (1)	10 (2)
C(6)	9636 (2)	2738 (4)	1180 (2)	47 (2)	252 (8)	25 (1)	−13 (3)	4 (1)	11 (2)
C(11)	7086 (2)	920 (4)	2610 (1)	43 (2)	224 (7)	24 (1)	−17 (3)	−1 (1)	−1 (2)
C(12)	7063 (2)	−883 (4)	3231 (2)	62 (2)	248 (8)	32 (1)	−7 (3)	4 (1)	16 (2)
C(13)	6326 (2)	−808 (5)	3875 (2)	82 (2)	369 (10)	32 (1)	−31 (4)	11 (1)	31 (3)
C(14)	5613 (2)	1039 (5)	3898 (2)	63 (2)	435 (11)	33 (1)	−28 (4)	13 (1)	−4 (3)
C(15)	5637 (2)	2829 (5)	3289 (2)	51 (2)	370 (10)	42 (1)	15 (3)	8 (1)	−12 (3)
C(16)	6370 (2)	2774 (4)	2652 (2)	54 (2)	287 (8)	31 (1)	4 (3)	4 (1)	13 (2)
O	9539 (1)	2774 (3)	2946 (1)	70 (1)	314 (6)	26 (1)	−22 (2)	−7 (1)	4 (2)
H(2a)	830 (2)	−58 (4)	194 (2)	3.2 (5)					
H(4a)	856 (2)	−65 (4)	18 (2)	4.0 (6)					
H(4e)	779 (2)	96 (5)	−54 (2)	3.8 (6)					
H(5a)	859 (2)	429 (4)	16 (2)	3.4 (5)					
H(5e)	953 (2)	274 (5)	−17 (2)	3.8 (6)					
H(6a)	997 (2)	115 (4)	131 (2)	3.4 (5)					
H(6e)	1021 (2)	389 (4)	127 (2)	3.6 (5)					
H(12)	755 (2)	−244 (4)	320 (2)	3.6 (5)					
H(13)	633 (2)	−211 (5)	430 (2)	4.7 (6)					
H(14)	509 (2)	109 (5)	436 (2)	4.2 (6)					
H(15)	517 (2)	401 (5)	328 (2)	4.5 (6)					
H(16)	639 (2)	406 (4)	224 (2)	3.6 (5)					
B. *cis*-2-Phenyl-1,3-dithiane 1-Oxide (6)									
S(1)	3430 (2)	623.3 (4)	6336 (1)	299 (3)	17.0 (2)	94 (1)	0 (1)	14 (1)	−5.9 (4)
S(3)	2917 (2)	2109.8 (4)	6727 (1)	704 (5)	16.2 (2)	106 (1)	−1 (1)	−9 (2)	−3.9 (4)
O	6278 (4)	746 (1)	6246 (2)	275 (8)	38 (1)	165 (3)	8 (2)	42 (4)	−19 (1)
C(2)	2234 (5)	1297 (1)	7327 (3)	269 (11)	20 (1)	90 (4)	3 (3)	25 (5)	−4 (1)
C(4)	1036 (7)	2057 (2)	5054 (3)	609 (19)	22 (1)	105 (4)	8 (4)	−6 (7)	10 (2)
C(5)	2043 (6)	1518 (2)	4224 (3)	455 (17)	30 (1)	94 (4)	−7 (3)	14 (7)	1 (2)
C(6)	1552 (6)	827 (2)	4719 (3)	365 (14)	26 (1)	85 (4)	−6 (3)	20 (6)	−6 (2)
C(11)	3439 (6)	1200 (2)	8773 (3)	284 (12)	22 (1)	84 (4)	6 (3)	26 (5)	−5 (1)
C(12)	5686 (7)	1532 (2)	9358 (4)	486 (19)	35 (1)	123 (5)	−40 (4)	−48 (7)	11 (2)
C(13)	6711 (7)	1437 (2)	10676 (4)	569 (20)	42 (2)	118 (5)	−34 (5)	−97 (8)	2 (2)
C(14)	5596 (7)	997 (2)	11441 (3)	542 (19)	39 (1)	89 (4)	27 (4)	−3 (7)	−3 (2)
C(15)	3409 (8)	660 (2)	10877 (4)	741 (22)	53 (2)	116 (5)	−63 (6)	24 (8)	19 (2)
C(16)	2305 (7)	765 (2)	9551 (4)	553 (18)	47 (2)	96 (4)	−75 (4)	−3 (7)	5 (2)
H(2a)	36 (5)	120 (1)	721 (3)	3.0 (6)					
H(4a)	−82 (6)	198 (2)	521 (3)	5.6 (8)					
H(4e)	121 (6)	248 (2)	462 (3)	5.7 (8)					
H(5a)	399 (5)	157 (1)	422 (3)	4.7 (3)					
H(5e)	110 (6)	157 (1)	335 (3)	4.9 (7)					
H(6a)	−35 (5)	75 (1)	480 (3)	3.5 (6)					
H(6e)	208 (5)	48 (1)	405 (3)	4.7 (7)					
H(12)	659 (7)	181 (2)	881 (4)	7.7 (10)					
H(13)	836 (4)	162 (2)	1109 (3)	7.1 (9)					
H(14)	636 (6)	89 (2)	1236 (3)	5.8 (8)					
H(15)	244 (7)	43 (2)	1133 (4)	10.2 (12)					
H(16)	76 (6)	55 (2)	906 (3)	6.8 (9)					
C. 2-Phenyl-1,3-dithiane *trans*-1,*trans*-3-Dioxide (7)									
S(1)	8833 (1)	3588 (3)	2098 (1)	54 (1)	172 (4)	30.3 (6)	−21 (2)	1.3 (6)	7 (2)
S(3)	7097 (1)	976 (3)	785 (1)	52 (1)	563 (8)	28.6 (7)	−57 (3)	2.5 (7)	−28 (2)
O(1)	9556 (3)	3090 (7)	2979 (2)	71 (3)	283 (17)	36 (2)	−30 (6)	−6 (2)	1 (4)
O(3)	6608 (3)	−1311 (10)	734 (2)	135 (3)	825 (28)	50 (2)	−238 (11)	33 (3)	−104 (8)
C(2)	7930 (4)	1088 (9)	1915 (3)	41 (3)	182 (18)	31 (2)	−4 (8)	4 (2)	−7 (7)
C(4)	8210 (4)	904 (13)	135 (3)	80 (5)	541 (33)	26 (3)	−30 (12)	8 (3)	2 (9)
C(5)	8938 (4)	2996 (10)	270 (3)	72 (5)	330 (26)	34 (3)	−39 (9)	9 (3)	32 (7)
C(6)	9633 (4)	2984 (9)	1200 (3)	60 (4)	211 (22)	37 (2)	−44 (7)	12 (3)	26 (6)
C(11)	7149 (3)	1164 (10)	2616 (3)	33 (3)	188 (18)	30 (2)	17 (8)	−7 (2)	−5 (7)
C(12)	7099 (4)	−642 (10)	3216 (3)	59 (4)	239 (22)	32 (3)	7 (8)	7 (3)	16 (7)
C(13)	6354 (4)	−578 (11)	3822 (3)	66 (5)	365 (27)	34 (2)	−16 (9)	2 (3)	28 (8)
C(14)	5671 (4)	1235 (13)	3849 (3)	55 (5)	453 (27)	36 (3)	−5 (11)	16 (3)	−9 (9)
C(15)	5696 (4)	2993 (11)	3259 (4)	46 (4)	378 (27)	47 (3)	21 (9)	−4 (3)	−14 (7)
C(16)	6450 (4)	2979 (10)	2637 (3)	61 (4)	242 (23)	38 (3)	−2 (8)	0 (3)	29 (6)
H(2a)	841 (3)	−15 (7)	196 (2)	1.1 (8)					

Table I (*Continued*)

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
H(4a)	862 (3)	−53 (8)	36 (3)	3.1 (11)					
H(4e)	793 (3)	105 (8)	−38 (2)	3.9 (10)					
H(5a)	943 (3)	304 (9)	−20 (3)	4.3 (12)					
H(5e)	845 (3)	458 (8)	13 (3)	3.3 (11)					
H(6a)	1004 (4)	137 (10)	144 (3)	6.4 (14)					
H(6e)	1009 (3)	419 (6)	122 (2)	1.0 (8)					
H(12)	755 (3)	−213 (8)	313 (3)	2.9 (11)					
H(13)	645 (3)	−162 (8)	429 (2)	2.6 (10)					
H(14)	517 (3)	134 (8)	424 (3)	2.9 (10)					
H(15)	530 (4)	429 (10)	319 (3)	6.7 (15)					
H(16)	647 (3)	423 (8)	228 (2)	2.1 (9)					

[a] Positional parameters are given as fractions of the unit cell edges (C, O, and S × 10^4, H × 10^3) and anisotropic thermal parameters as coefficients to conform to the exponent $-[\beta_{ii}h_i^2 + \cdots 2\beta_{ij}h_ih_j + \cdots]$. Isotropic thermal parameters for hydrogen are given as B (Å^2). Estimated standard deviations are given, on the same scale, in parentheses.

Table II. Torsion Angles of Dithiane Ring Portion of 2-Phenyl-1,3-dithiane and Related Sulfoxides

	Endocyclic torsion angles, deg			
Central bond	4[a]	5	6	7
S(1)–C(2)	−57	−63	−59	−61
C(2)–S(3)	57	63	61	60
S(3)–C(4)	−56	−61	−62	−61
C(4)–C(5)	63	64	68	72
C(5)–C(6)	−61	−67	−67	−73
C(6)–S(1)	54	63	58	62

[a] Values of Kalff and Romers (ref 6).

Table III. Bond Angles of Dithiane Ring Portion of 2-Phenyl-1,3-dithiane and Related Sulfoxides[a]

	Valence angle, deg			
	4[b]	5	6	7
S(1)–C(2)–S(3)	115.2	109.6 (2)	112.9 (2)	114.2 (3)
C(2)–S(3)–C(4)	99.2	100.5 (2)	99.2 (2)	97.0 (2)
S(3)–C(4)–C(5)	116.1	113.0 (2)	112.6 (2)	113.4 (4)
C(4)–C(5)–C(6)	116.5	113.3 (2)	113.0 (3)	111.2 (4)
C(5)–C(6)–S(1)	114.9	114.0 (2)	114.6 (2)	112.0 (3)
C(6)–S(1)–C(2)	100.9	98.2 (2)	98.7 (2)	96.9 (2)
C(6)–S(1)–O		105.4 (1)	106.9 (2)	106.7 (2)
C(2)–S(1)–O		105.2 (1)	108.4 (2)	104.1 (2)
C(2)–S(3)–O				104.5 (3)
C(4)–S(3)–O				107.0 (3)

[a] Standard deviations indicated in parentheses. [b] Values of Kalff and Romers (ref 6). Esd's ~1.5°.

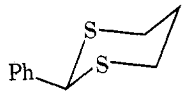
energy difference between the equatorial and axial conformations of **3** arises from dipole–dipole interactions.[5] The conformation of **3** which has the oxygen axial is less stable than the conformation with the oxygen equatorial largely because of the closer proximity of the two sites of high electron density, the sulfoxide oxygen and the cross-ring sulfur. Dipolar interactions are presumed to be significant in **2** as well, but variations in other nonbonded interactions brought about by the reduced C–O bond length (relative to C–C and C–S) make the net effect difficult to assess.

In order to understand the dynamic processes represented by eq 1, reliable structural information is required. This paper describes a detailed investigation, using single-crystal x-ray diffraction techniques, of a series of oxides of 2-phenyl-1,3-dithiane (**4**). A structure determination had been reported for **4** earlier by Kalff and Romers.[6] We have prepared *trans*-2-phenyl-1,3-dithiane 1-oxide (**5**) and *cis*-2-phenyl-1,3-dithiane 1-oxide (**6**) in connection with another aspect of this work, and have assigned configurations on chemical and spectroscopic grounds.[7] These compounds seemed appropriate models for an equatorial oxide of 1,3-dithiane and an axial oxide, respectively, so their structures were determined crystallographically. The postulated importance of dipole–dipole interactions in **3** suggested that a structure determination of 2-phenyl-1,3-dithiane *trans*-1,*trans*-3-dioxide (**7**) would also be useful.[8]

Table IV. Bond Distances of Dithiane Ring Portion of 2-Phenyl-1,3-dithiane and Related Sulfoxides[a]

	Bond distance, Å			
Bond	4[b]	5	6	7
S(1)–C(2)	1.79	1.830 (2)	1.843 (2)	1.834 (5)
C(2)–S(3)	1.80	1.814 (2)	1.797 (3)	1.833 (4)
S(3)–C(4)	1.83	1.808 (2)	1.812 (3)	1.787 (5)
C(4)–C(5)	1.46	1.506 (3)	1.508 (4)	1.513 (8)
C(5)–C(6)	1.51	1.519 (2)	1.512 (4)	1.513 (6)
C(6)–S(1)	1.81	1.806 (2)	1.808 (3)	1.803 (5)
S(1)–O		1.497 (1)	1.484 (2)	1.498 (3)
S(3)–O				1.465 (3)
C(2)–Ph	1.52	1.503 (2)	1.506 (3)	1.518 (6)

[a] Standard deviations indicated in parentheses. [b] Values of Kalff and Romers (ref 6). Esd's ~0.03 Å.



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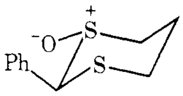

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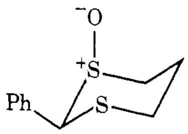

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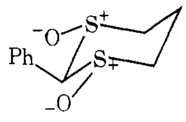

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Results and Discussion

The atomic parameters which define the crystal structures of **5**, **6**, and **7** are recorded in Table I, and torsion angle, bond angle, and bond distance data for the dithiane ring portions of **4–7** are collected in Tables II–IV. The structures of **5**, **6** and **7** are depicted by the ORTEP[9] drawings shown in Figures 1–3, respectively. The stereochemical assignments of **5** and **6** are confirmed by the x-ray structure determinations. The dithiane

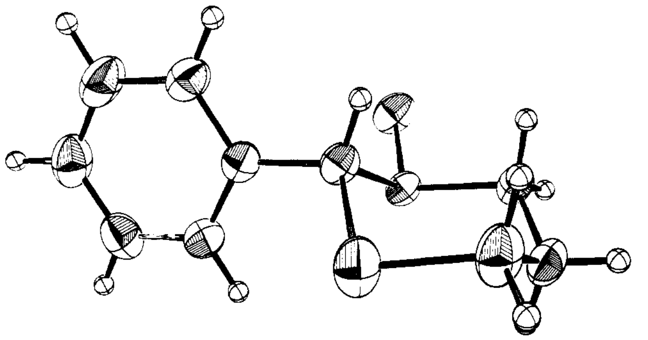


Figure 1. ORTEP drawing of the structure of **5**. Thermal ellipsoids for S, O, and C are drawn with the 50% probability level as boundary surface. Hydrogen atoms are represented by spheres of arbitrary radius.

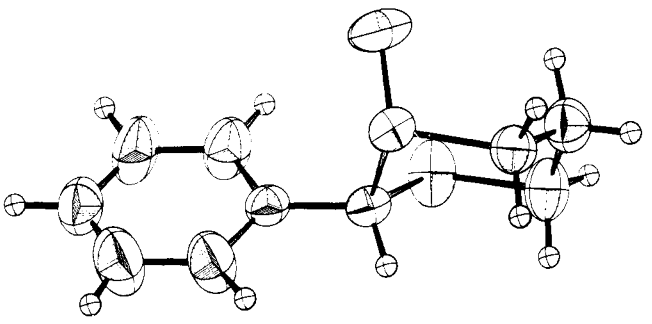


Figure 2. ORTEP drawing of the structure of **6**.

ring portions of all of the compounds adopt chair conformations in the crystal with the phenyl group occupying an equatorial site. A chair conformation in solution has been inferred for **4** from NMR and dipole moment measurements.[10] The 1,3-dithiane rings are all more highly puckered than cyclohexane (for which the torsion angles are 56°), with the puckering most pronounced in the C(4)–C(5)–C(6) region. This puckering is quite apparent in the disulfoxide **7** where the ring torsion angles involving C(5) average 72.5°.

The most significant structural difference observed among the compounds is the large variation in the S(1)–C(2)–S(3) valence angle (Table III). This angle is larger in **4** (114.9°) than in either of the corresponding monosulfoxides **5** and **6**, but almost identical with that of the disulfoxide **7** (114.2°). The amount of bond angle contraction between **4** and the monosulfoxides is stereochemically dependent, being more pronounced in the equatorial oxide **5** (109.6°) than in the axial oxide **6** (112.9°). These observations support the view that transannular dipolar interactions are important determinants of structure in the 1,3-dithiane 1-oxide system. The smaller S(1)–C(2)–S(3) angles in **5** and **6** are reasonably attributed to a more favorable electrostatic interaction between the sulfur atoms. The sulfur of the sulfoxide group is positively polarized and an attractive interaction with S(3) compresses the C(2) valence angle in **5** and **6**. The effect is smaller in **6** than in **5** because it is opposed by repulsion between the negatively polarized axial oxygen and S(3). In the disulfoxide **7**, the attractive interaction is replaced by a dipolar repulsion between two positively polarized sulfur atoms and the bond angle is increased.[11]

The endocyclic bond angles around C(4), C(5), and C(6) are all smaller in the oxides **5**–**7** than in **4**. These angles average 115.8° in **4**, but only 113.4° in **5** and **6** and 112.2° in **7**. These differences are related to the increased puckering in this region mentioned earlier, and may indicate additional attractive interactions in which the sulfoxide sulfur is involved. Interaction of the sulfoxide sulfur with the electrons in the γ-C–C bond would be capable of producing such a distortion, and is consistent with the effect being most pronounced in the disulfoxide **7**. The C–S–C angles are similar to those reported for *trans*-1,4-dithiane 1,4-dioxide (**8**, 97.9°)[12] and *cis*-1,4-dithiane 1,4-dioxide (**9**, 96.6 and 97.6°).[13] The C–S–O angles

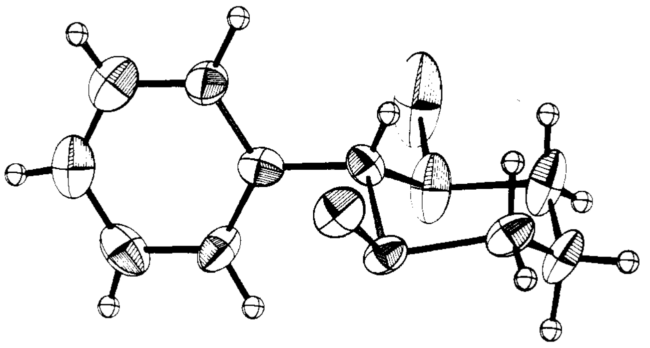


Figure 3. ORTEP drawing of the structure of **7**.

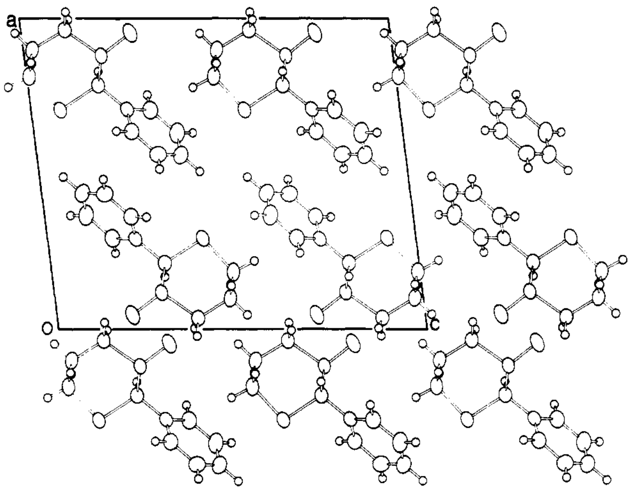
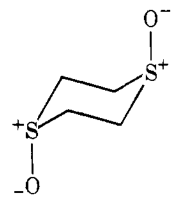


Figure 4. View in *b*-axis projection of the molecular packing in **5**.



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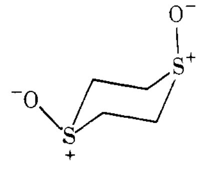

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in the equatorial sulfoxides **5** and **7** are slightly smaller than those in the axial sulfoxide **6**. These angles average 105.3° in **5**, 105.6° in **7**, and 107.6° in **6**. A similar effect has been observed in **9** where the C–S–O angles around the equatorial sulfoxide are 109.4° while those around the axial sulfoxide are 111.4°.

There are no systematic trends evident in bond distances among the various molecules though the C–C bond distances in all are significantly shorter than the standard C_{sp^3}–C_{sp^3} bond length of 1.54 Å, an effect consistent with the opened valence angles at the carbon atoms involved. The wide variation in S–O bond distances is more apparent than real with all the distances subject to error owing to the pronounced thermal anisotropy of the oxygen atoms. The pattern of motion observed and the mass difference between sulfur and oxygen suggest that the oxygen rides on sulfur and when a correction for this motion is applied a good consistency of values results: 1.512 Å in **5**; 1.509 Å in **6**; and 1.507 and 1.510 Å in **7**. Thermally uncorrected S–O bond distances reported

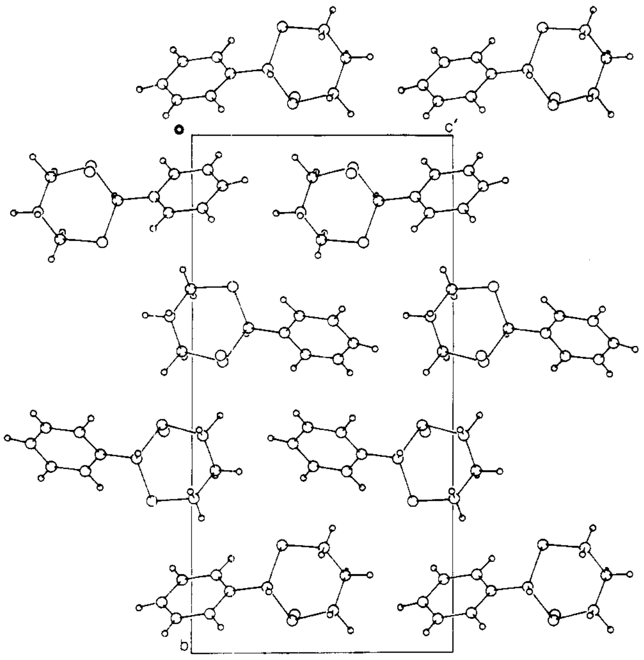

Figure 5. View in *a*-axis projection of the molecular packing in **6**.

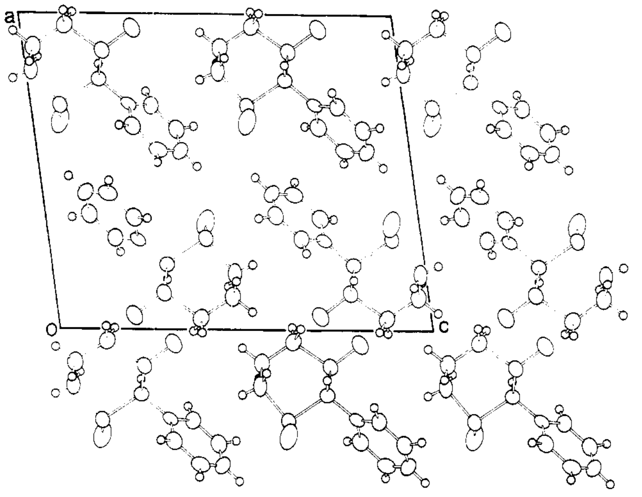

Figure 6. View in *b*-axis projection of the molecular packing in **7**. Note the similarity to Figure 4.

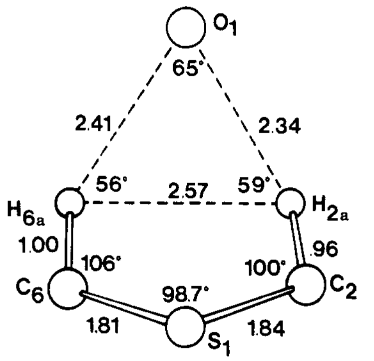

Figure 7. C–H⋯O approaches in the axial oxide **6**. Distances are given in Å.

in the literature show wide variations. The 1,4-diaxial oxide **8** has S–O 1.48 Å, and that determined for dimethyl sulfoxide by electron diffraction[14a] is 1.47 Å, by x-ray diffraction[14b] 1.499 Å. Smaller S–O distances have been reported for both the axial (1.43 Å) and equatorial (1.40 Å) sulfoxide groups in **9**.

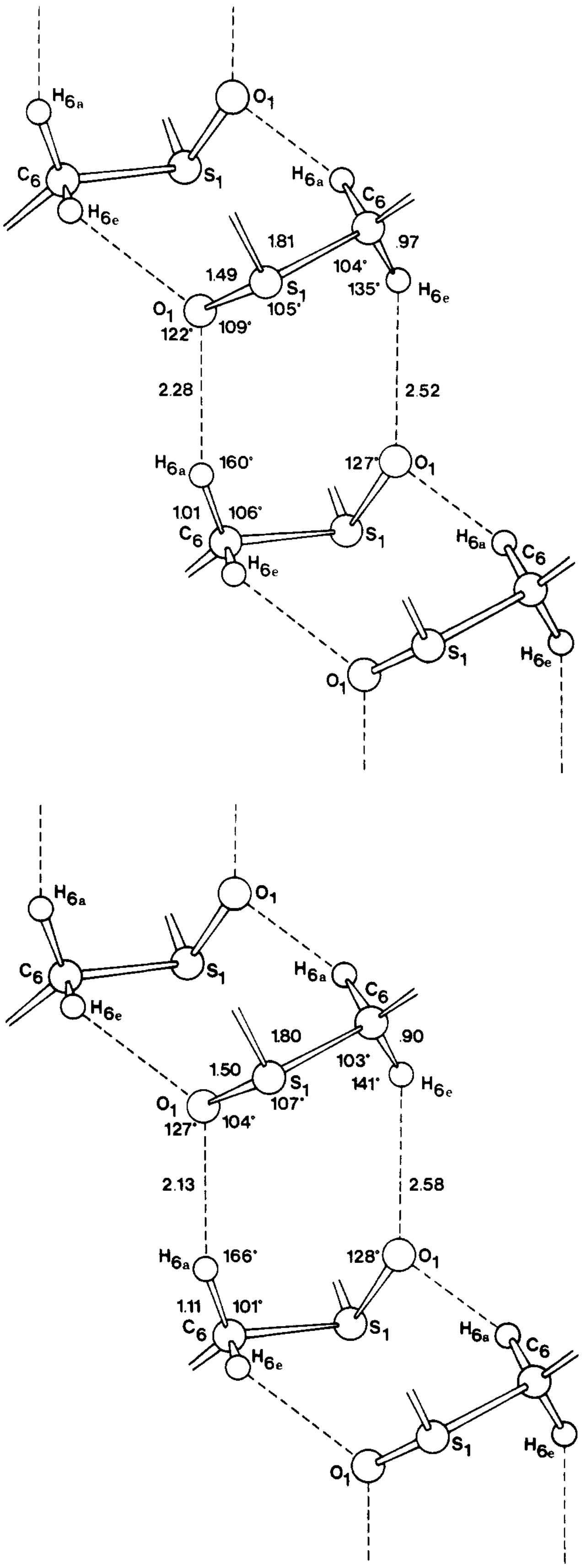

Figure 8. C–H⋯O approaches in (a) the equatorial oxide **5** and (b) dioxide **7**. Distances are given in Å.

The structural features associated with the 2-phenyl substituents appear normal and do not require comment.[15]

Some striking intermolecular interactions are found in the crystal structures of the oxides which may be of significance

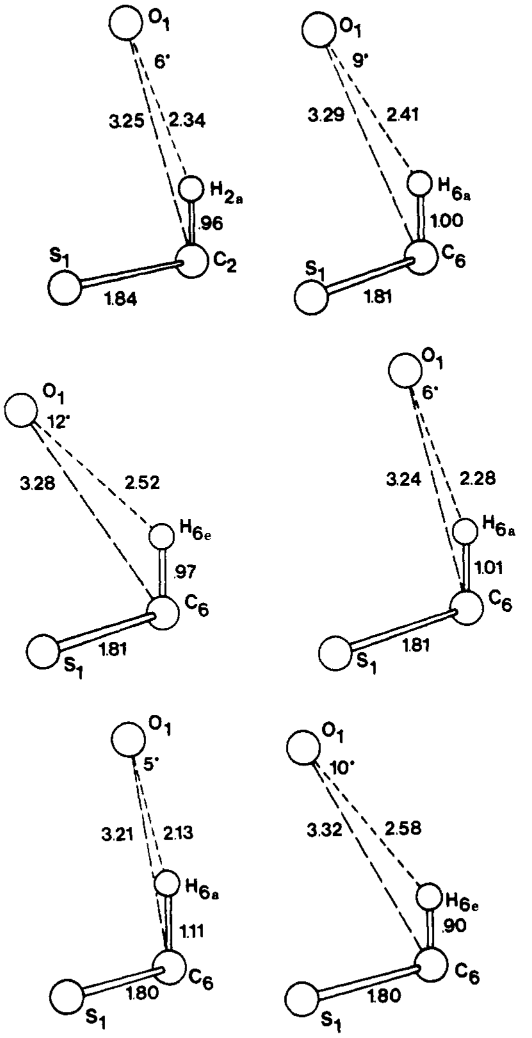

Figure 9. View of C–H···O contacts projected onto the C–H···O plane, (a) in the axial oxide **6**, (b) in the equatorial oxide **5**, (c) in the dioxide **7**.Note that the shorter O···H separations are associated with smaller C···O···H angles. Distances are given in Å.

Table V

Compd	**5**	**6**	**7**
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	12.206 (2)	5.007 (1)	12.315 (3)
b	5.749 (1)	20.134 (4)	5.851 (1)
c	14.809 (2)	10.095 (3)	14.829 (3)
β, deg	97.11 (1)	98.76 (3)	98.44 (2)
ρ_{obsd}, g cm^{-3}	1.37	1.37	1.42
ρ_{calcd}	1.37	1.38	1.43
U, Å^3	1031	1020	1057
Z	4	4	4
$F(000)$	448	448	480
μ(Mo Kα), cm^{-1}	4.6	4.6	4.6
Crystal size, mm^3	0.6 × 0.4 × 0.1	0.25 × 0.25 × 0.25	0.25 × 0.05 × 0.1
Significant reflns ($2\theta_{max}$ 60°)	1589	1446	953

in relation to intramolecular and intermolecular interactions in solution. Packing diagrams for **5, 6** and **7** are presented in Figures 4–6. Interactions involving the sulfoxide oxygen and certain axial C–H bonds are suggested by the occurrence of several C–H···O contacts markedly less than the sum of the normal van der Waals radii of oxygen and hydrogen (2.48 Å), and detailed views of these contacts are shown in Figures 7 and 8. The equatorial oxide **5** and dioxide **7** are isostructural and a similar pattern of contacts involving O(1) is found in each with the axial hydrogen of C(6) of a neighboring molecule 2.28 Å distant from O(1) in **5** and 2.13 Å distant in **7**. By contrast, the contact between the equatorial hydrogen of C(6) and O(1) of a neighbor is of normal length in both **5** and **7**, 2.52 and 2.58 Å, respectively. In the axial sulfoxide **6**, the closest intermolecular contacts of the sulfoxide group involve the oxygen atom and the axial hydrogens at C(2) and C(6) of a neighbor with O···H separations of 2.34 and 2.41 Å. The structural similarity of all these close C–H···O contacts is shown by Figure 9 in which the near linearity of the C–H···O system is clearly seen in each case.

Although these contacts involve hydrogen atoms in observed positions and are hence subject to the fairly large esd's associated with such quantities (ca. 0.05 Å), the same pattern of short contact distances persists if hydrogen atoms are assumed in plausible calculated positions. Indeed the effects are even more pronounced if, in these calculations, the C–H bond distance is taken at its internuclear value, 1.08 Å, rather than at the shorter x-ray values found.

Contacts between sulfur and oxygen of sulfoxide groups of neighboring molecules in the crystal appear normal. The normal S···O van der Waals separation of 3.22 Å[16] is similar to that observed in **5** (3.26 Å) and **7** (3.31 Å). The separation is somewhat larger in the axial oxide **6**, where it is 3.63 Å. Thus, orientation of the S–O dipoles in an antiparallel fashion with respect to each other does not play as significant a role in crystal packing as do S–O···H–C interactions. Inasmuch as these interactions involve hydrogen atoms on carbon bonded to sulfinyl groups, it is tempting to interpret them as electrostatic effects. A sulfinyl group will strongly polarize an adjacent C–H bond so that the hydrogen is more positive than a C–H bond in, for example, a hydrocarbon allowing for effective electrostatic interactions with the sulfoxide oxygen of a neighboring molecule.

Experimental Section

The preparations of 2-phenyl-1,3-dithiane (**4**),[17] *trans*-2-phenyl-1,3-dithiane 1-oxide (**5**),[7a] and *cis*-2-phenyl-1,3-dithiane 1-oxide (**6**)[7a] have been previously described. Stereochemical assignments to **5**, mp 145–147 °C, and **6**, mp 163.5–165.5 °C, made on the basis of chemical behavior, synthesis, and NMR spectra were confirmed by the x-ray crystallographic determinations. Treatment of **4** with 2 equiv of *m*-chloroperoxybenzoic acid in dichloromethane (−18 to −30 °C) gives 2-phenyl-1,3-dithiane *trans*-1,*trans*-3-dioxide (**7**, mp 187–188 °C) as the major product in 71% yield.[18] The NMR spectrum was suggestive of the stereochemistry shown, but rigorous structure proof required the x-ray determination described here.

X-Ray Crystallographic Measurements. Crystal Data. Unit cell symmetry and preliminary cell dimensions were derived from observations of systematic absences and measurements made on 25° precession photographs taken with Mo Kα radiation. Accurate cell dimensions were obtained by a least-squares fit to carefully measured diffractometer values of $\pm 2\theta$ for 17–25 strong general reflections (λ = 0.71069 Å). Relevant data for compounds **5–7** are summarized in Table V.

Intensity Data. Measurements of intensity for the three compounds were made using a Picker four-circle diffractometer controlled by an XDS Sigma 2 computer. Mo Kα radiation, made monochromatic by Bragg reflection from a highly oriented graphite crystal, was used with scintillation counting and pulse-height analysis with θ–2θ scans at a scan rate of 2°/min. Background intensity was determined either by direct measurement with both crystal and counter stationary at either end of the scan ranges or by interpolation from a carefully predetermined curve of scattered background intensity vs. diffractometer angle. Measurements were made for the appropriate nonredundant section of reciprocal space, but an additional symmetry-related zone of reflections was included in each case to check crystal alignment. The deviation from the mean in these averaged reflections was typically <3%. Stability of the experimental conditions during the course of the data collection was monitored by measurement of two or three reference reflections after every 50 scans. A similar variation in intensity was noted in these standards but no systematic trends were evident. Scattered intensity in a scan was assumed significant at the 3σ level. No absorption corrections were applied and the data were converted to structure amplitudes in the usual way.

Structure Determination and Refinement. For **5**, the positions of the two sulfur atoms were found from a sharpened three-dimensional Patterson function and the structure solved by the heavy atom method. Compound **7** is isostructural with **5** and parameters for the atoms of **5** were used to phase the reflections of **7**. The additional oxygen atom was found from a difference map. The program MULTAN[19] was used to solve the structure of **6** in a routine way.

Hydrogen atoms were located in all cases from difference electron-density maps and included in the block-diagonal least-squares refinement. A conventional weighting scheme was used,[20] and anisotropic thermal parameters were assigned to S, O, and C atoms, isotropic B values to H. Damping factors were applied to assure smooth convergence and refinement continued until no calculated shift in any parameter exceeded one-tenth of the corresponding esd. The final conventional unweighted and weighted residuals were 0.044 and 0.040 for **5**, 0.045 and 0.032 for **6**, and 0.047 and 0.036 for **7**. The scattering curves used for S, O, and C were taken from Hanson et al.[21] and for hydrogen from Stewart et al.[22] Programs used, other than MULTAN and ORTEP, were written in this laboratory for the XDS Sigma 2 computer.

Registry No.—**4**, 5425-44-5; **5**, 60349-76-0; **6**, 60349-79-3; **7**, 61158-78-9.

Supplementary Material Available. Listings of observed and calculated structure amplitudes, complete bond length and angle calculations, and information on least-squares mean planes of interest and on intermolecular contacts (35 pages). Ordering information is given on any current masthead page.

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Chemistry of the Sulfur–Nitrogen Bond. 12.[1] Metal-Assisted Synthesis of Sulfenamide Derivatives from Aliphatic and Aromatic Disulfides

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The metal-assisted synthesis of sulfenamide derivatives **1** and **2** from aliphatic and aromatic disulfides and amines was explored. This method is more convenient and results in higher yields and a less reactive product than sulfenamides prepared from sulfenyl chlorides. Sulfenamides containing reactive functional groups, not accessible from sulfenyl chlorides, can be prepared using this procedure. With ammonia and aromatic disulfides this method yields bis(arenesulfen)imides **4** when the groups attached to sulfur are more electron donating than a 3,4-dichlorophenyl group. Alkanesulfenamides of ammonia ($RSNH_2$) cannot be isolated, but are trapped with aromatic aldehydes and ketones to yield N-alkylidenealkanesulfenamides **2**.

Sulfenamides **1** and N-alkylidenesulfenamides **2** are important intermediates in organic synthesis and have proven useful in investigations of lone pair interactions ("α effect"), bond polarization effects, and (p–d) π conjugation.[2] Sulfenamides have also found important industrial applications.

R-S-NR′R″
1a, R = alkyl
b, R = aryl

R-S-N=CR′R″
2, R′, R″ = alkyl, aryl

Sulfenamides (**1**) are used as sulfenyl-transfer reagents in the synthesis of sulfides,[3] disulfides,[4] trisulfides,[4b] sulfenate esters,[5] sulfenamides,[6] alkyl (aryl) dialkylaminosuccinimidosulfonium salts,[7] and aminecarbotrithioates.[8] N-Alkylidenearenesulfenamides, **2b**, can be oxidized to 2-arenesulfonyl-3-phenyloxaziridines[9a] and sulfinamides.[9b] The latter compounds are useful in the synthesis of sulfenic acids.[9b,10]

The possibility that interactions between the lone pairs of electrons on sulfur and nitrogen may destabilize the S–N