

**Effect of 2-Triphenylsilyl Substitution on the Molecular Geometry
of 1,3-Dithianes.¹ Crystal Structures of
2-Methyl-2-triphenylsilyl-1,3-dithiane and
trans-2-Triphenylsilyl-1,3-dithiane 1-Oxide**

Robert F. Bryan,* Francis A. Carey,* Oscar Hernandez, and Ivan F. Taylor, Jr.

Chemistry Department, University of Virginia, Charlottesville, Virginia 22901

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The crystal structures of 2-methyl-2-triphenylsilyl-1,3-dithiane (1) and *trans*-2-triphenylsilyl-1,3-dithiane 1-oxide (2) have been determined to establish their conformations and the effect upon ring geometry of a 2-triphenylsilyl substituent. Crystals of 1 conform to space group $C2/c$, with $a = 28.780$ (6), $b = 11.901$ (3), $c = 15.909$ (3) Å, $\beta = 130.93$ (3)°, and $Z = 8$. For 2, the space group is $P2_1/c$, with $a = 10.390$ (3), $b = 9.988$ (3), $c = 20.207$ (12) Å, $\beta = 97.61$ (3)°, and $Z = 4$. The endocyclic C(2) valence angle in 2, 106.0 (3)°, is 5.4° smaller than in 1, but each of these angles is, respectively, 3.6° smaller than the corresponding angles in *trans*-2-phenyl-1,3-dithiane 1-oxide (4), 109.6 (2)°, and in 2-phenyl-1,3-dithiane (3), 115°. This additional contraction is attributed to the electron-releasing character of silicon, an effect known in phenylsilanes, but not previously noted in silyl-substituted alicyclic systems. The crystal structure of 2 contains a short intramolecular CH...O contact, which is diagnosed as a strong dipolar interaction both by virtue of the conformational change induced about the C(2)-Si bond and the valence angle distortion produced at the phenyl-ring carbon involved.

In the course of synthetic work involving dithiane oxides,² *trans*-2-triphenylsilyl-1,3-dithiane 1-oxide (2) was prepared. Its structure was determined by single-crystal x-ray analysis so as to establish the orientation of oxygen, but showed significant and interesting variations in dithiane ring geometry associated with the triphenylsilyl group, which are the subject of this paper. For purposes of comparison, and to check the validity of our conclusions, a structure determination was also carried out for 2-methyl-2-triphenylsilyl-1,3-dithiane (1).³

Our understanding of conformational effects in sulfoxides derived from 1,3-dithiane has been substantially enhanced by x-ray crystallographic structural studies. The crystal structures of a diastereomeric pair, *trans*-2-phenyl- and *cis*-2-phenyl-1,3-dithiane 1-oxide, 4 and 5, respectively, have been described and used as models to probe the effect of equatorial vs. axial orientation of oxygen on bond distances and on valence and torsion angles.⁴ The significant difference observed in the S(1)-C(2)-S(3) valence angle from one to the other has been ascribed to electrostatic interactions between the sulfoxide group and S(3).⁵ The results obtained for additional examples, the equatorial oxide 6⁶ and the axial oxide 7,⁷ may be interpreted in the same way. Besides the effect upon the C(2) valence angle, oxygenation leads to different patterns of ring puckering as compared to the parent compounds, and variations in the C-S bond distances, which have been correlated to substitution patterns in the ring.⁶

Additional information on all of these effects is provided by the analyses reported here, and, in addition, evidence is presented pointing to electron transfer from silicon to the dithiane ring as a contributory factor in the changes in the

C(2) valence angle. There is also evidence for the conformational importance of an intramolecular C-H...O interaction in 2, and further examples of intermolecular C-H...O interactions are found.⁴

Results and Discussion

Atomic parameters defining the crystal structures of 1 and 2 are given in Table I, and stereoscopic ORTEP⁸ drawings of the two structures are shown in Figures 1 and 2. Selected bond lengths and angles are given in Table II, and torsion angles for the dithiane rings of 1-4 are given in Table III.

Both rings adopt puckered chair conformations with the triphenylsilyl group equatorial at C(2), but the form of the puckering in each is different. In 1, the presence of the axial methyl group at C(2) leads to interactions between the methyl proton H(7) and the axial hydrogen atoms on C(4) and C(6). Conformational distortion at the C(2) apex is inhibited by the quaternary substitution pattern, and these syn-axial interactions are accommodated with an increase in the torsion angles about the C(4)-C(5) and C(5)-C(6) bonds. The observed proton separations are H(7)...H(4a) 2.49 Å and H(7)...H(6a) 2.65 Å. In 2, although the C(2) axial hydrogen atom, H(2a), is 2.66 Å from H(4a) and 2.56 Å from H(6a), these interactions are possible with a flattening of the dithiane ring at the C(5) apex relative to 1 and also to *trans*-2-phenyl-1,3-dithiane 1-oxide, 4. Thus, although the syn-diaxial contacts between hydrogens in 2 are nearly identical to those found in 4, 2.55 and 2.66 Å, the C(4)-C(5) and C(5)-C(6) endocyclic torsion angles are 57° and 59° in 2 compared to 64° and 67° in 4. This difference is a direct result of the replacement of a 2-phenyl substituent by the triphenylsilyl group, which has the effect of removing a buttressing interaction in 4 between H(2a) and a phenyl-ring proton [H(2a)...H(12), 2.38 Å] that prevents movement of H(2a) in a direction away from the dithiane ring center. The combination of the buttressing interaction in 4 with the puckering induced at the C(2) apex by oxygen substitution means that syn-diaxial strain can only be relieved torsionally by increased puckering at the C(5) apex. In 2, by contrast, with the buttressing interaction removed, H(2a) is more able to move away from H(4a) and H(6a), leaving the C(5) apex comparatively unstrained. This same movement of H(2a) is presumably also responsible for the somewhat larger than usual puckering at C(2) in 2.

The principal difference in bond angles, within the dithiane

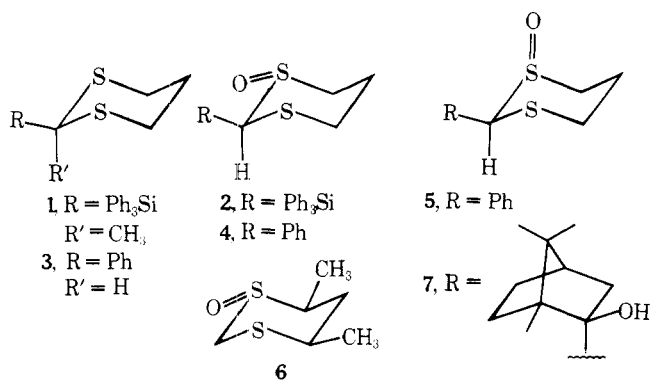


Table I. Atomic Parameters Defining the Crystal Structures

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i>
S(1)	4281.1 (5)	1294.4 (8)	4528.4 (8)	3.1	5138 (2)	4718 (2)	2872 (1)	5.3
S(3)	4627.4 (5)	3664.0 (8)	4487.2 (8)	3.4	4201 (2)	3170 (2)	3919 (1)	5.4
Si	3654.9 (4)	2420.8 (8)	2349.2 (8)	2.0	7163 (2)	3377 (2)	3958 (1)	3.1
C(2)	4432 (2)	2272 (3)	3857 (3)	2.7	5527 (5)	3310 (6)	3424 (3)	3.5
C(4)	5279 (2)	3351 (4)	5946 (3)	4.7	2897 (7)	2754 (8)	3292 (5)	7.5
C(5)	5133 (2)	2529 (4)	6458 (3)	4.9	2623 (8)	3748 (9)	2740 (5)	9.9
C(6)	4986 (2)	1364 (4)	5977 (3)	4.2	3730 (9)	4061 (9)	2368 (4)	7.5
C(7)	4939 (2)	1827 (4)	3864 (3)	3.9				
O					6168 (6)	4844 (6)	2437 (2)	8.2
C(11)	3564 (2)	1177 (3)	1524 (3)	2.7	8364 (5)	2400 (6)	3532 (3)	3.8
C(12)	3541 (2)	85 (3)	1804 (3)	3.2	8400 (7)	2593 (7)	2842 (3)	5.2
C(13)	3451 (2)	-823 (3)	1179 (3)	3.7	9286 (7)	1840 (8)	2524 (4)	6.7
C(14)	3389 (2)	-665 (4)	248 (3)	4.1	10 108 (7)	969 (8)	2875 (4)	7.4
C(15)	3412 (2)	395 (4)	-47 (3)	4.2	10 108 (7)	749 (8)	3554 (5)	7.3
C(16)	3496 (2)	1310 (3)	570 (3)	3.5	9214 (6)	1510 (7)	3886 (3)	5.2
C(21)	3676 (2)	3762 (3)	1758 (2)	2.7	6964 (5)	2579 (6)	4772 (3)	3.2
C(22)	4112 (2)	3935 (3)	1633 (3)	3.8	6726 (6)	1196 (6)	4801 (3)	4.4
C(23)	4131 (2)	4903 (4)	1190 (4)	4.2	6566 (7)	571 (6)	5402 (3)	5.4
C(24)	3715 (2)	5742 (4)	847 (3)	4.1	6605 (7)	1139 (7)	5975 (3)	5.4
C(25)	3277 (2)	5606 (3)	952(3)	4.1	6807 (7)	2694 (7)	5955 (3)	5.2
C(26)	3257 (2)	4632 (3)	1393 (3)	3.3	6990 (6)	3304 (6)	5356 (3)	4.3
C(31)	3002 (1)	2436 (3)	2352 (3)	2.7	7650 (5)	5156 (5)	4100 (3)	3.3
C(32)	2520 (2)	1671 (3)	1716 (3)	3.4	8920 (6)	5589 (7)	4093 (3)	4.9
C(33)	2036 (2)	1676 (4)	1726 (4)	4.4	9288 (6)	6895 (8)	4230 (4)	6.2
C(34)	2033 (2)	2442 (4)	2361 (3)	4.4	8365 (7)	7811 (7)	4392 (4)	5.9
C(35)	2502 (2)	3213 (3)	2989 (3)	4.1	7108 (6)	7424 (6)	4397 (3)	5.0
C(36)	2984 (2)	3211 (3)	2984 (3)	3.3	6757 (6)	6098 (6)	4261 (3)	4.1
H(2a)					554 (4)	252 (4)	318 (2)	1.2 (9)
H(4a)	564 (2)	303 (4)	593 (3)	5.7 (10)	303 (5)	189 (6)	309 (3)	6.2 (15)
H(4e)	538 (2)	421 (4)	626 (4)	8.4 (14)	214 (6)	279 (6)	351 (3)	7.2 (17)
H(5a)	479 (2)	286 (4)	642 (4)	7.3 (12)	217 (6)	452 (7)	300 (3)	8.9 (19)
H(5e)	549 (2)	251 (4)	727 (4)	6.6 (12)	191 (6)	352 (7)	240 (3)	8.7 (19)
H(6a)	533 (2)	97 (3)	605 (3)	4.8 (9)	406 (6)	328 (7)	214 (3)	8.5 (19)
H(6e)	487 (2)	79 (4)	634 (3)	5.3 (10)	351 (6)	470 (7)	195 (3)	9.3 (20)
H(7)	529 (2)	168 (3)	453 (3)	5.1 (10)				
H(7')	504 (2)	248 (3)	356 (3)	5.3 (10)				
H(7'')	482 (2)	104 (3)	342 (3)	5.3 (10)				
H(12)	358 (2)	-3 (3)	246 (3)	3.3 (8)	776	331	256	<i>b</i>
H(13)	345 (2)	-159 (3)	142 (3)	8.0 (13)	931	196	199	
H(14)	334 (2)	-128 (3)	-11 (3)	6.9 (12)	1079	42	262	
H(15)	340 (2)	57 (4)	-69 (3)	4.8 (9)	1076	3	382	
H(16)	351 (2)	205 (3)	35 (3)	4.5 (9)	920	139	442	
H(22)	438 (2)	331 (4)	179 (3)	5.9 (11)	666	61	435	
H(23)	445 (2)	481 (4)	112 (4)	7.2 (13)	641	-50	542	
H(24)	374 (2)	646 (3)	57 (3)	3.6 (8)	648	87	644	
H(25)	300 (2)	628 (4)	74 (4)	6.5 (11)	682	329	640	
H(26)	295 (2)	453 (3)	148 (3)	4.8 (9)	718	431	520	
H(32)	251 (2)	110 (3)	124 (3)	3.6 (8)	964	488	398	
H(33)	170 (2)	104 (4)	131 (4)	3.5 (8)	1028	721	421	
H(34)	171 (2)	242 (4)	241 (4)	3.2 (8)	865	883	451	
H(35)	250 (2)	384 (3)	342 (3)	5.9 (11)	639	814	451	
H(36)	334 (2)	377 (3)	350 (3)	4.1 (9)	577	579	428	

^a Positional parameters are given as fractions of the unit cell edges (C, O, and S $\times 10^4$, H $\times 10^3$. Equivalent isotropic *B* values (\AA^2) are given for the heavy atoms and actual *B* values for H atoms whose parameters were allowed to refine in the least-squares treatment. Where applicable, estimated standard deviations are given on the same scale in parentheses. ^b In the refinement, *B* values equal to those given for the carbon atom of attachment were used for the phenyl H atoms of **2**. Positional parameters for these atoms were held fixed.

rings, between **1** and **2** is in the endocyclic C(2) valence angle which is 111.4° in **1** and 106.0° in **2**. This difference, 5.4° , is identical to that found for this same angle when 2-phenyl-1,3-dithiane, **3**, and *trans*-2-phenyl-1,3-dithiane 1-oxide, **4**, are compared,^{4,9} so that it may reasonably be attributed to the effects of equatorial oxygen substitution at S(1). The same dipolar mechanism invoked to explain the difference in angles between **3** and **4** may be applied. However, there remains the observation that the differences in this C(2) angle between **1** and **3**, and between **2** and **4**, are both equal to 3.6° . This difference is attributed to the electron-releasing property of silicon with respect to carbon. Domenicano, Vaciago, and

Coulson¹⁰ have related the electronegativities of second-row elements, and the changes induced by σ -electron-density transfer, to endocyclic valence angles in phenyl rings to which these atoms are attached. In the case of silicon, the angle α , at the carbon of attachment of the phenyl ring, is decreased, and the angles β , at the flanking carbon atoms, are increased. These effects may be rationalized using arguments based on changes in orbital hybridization, or on the basis of VSEPR theory. Considering only a model involving changes in orbital hybridization, and assuming silicon to act as an electron-releasing substituent, the p character of the Si-C bond is reduced and that of the two adjacent C-C bonds is increased.

Table II. Selected Bond Lengths (Å) and Bond Angles (Deg) with Their Estimated Standard Deviations

Bond	1	2
S(1)-C(2)	1.815 (3)	1.807 (5)
S(3)-C(2)	1.824 (3)	1.811 (5)
S(1)-C(6)	1.819 (4)	1.793 (8)
S(3)-C(4)	1.828 (4)	1.778 (8)
C(4)-C(5)	1.497 (6)	1.492 (13)
C(5)-C(6)	1.505 (6)	1.488 (12)
C(2)-C(7)	1.545 (5)	
S(1)-O		1.478 (5)
Si-C(2)	1.938 (4)	1.890 (5)
Si-C(11)	1.882 (3)	1.881 (5)
Si-C(21)	1.873 (3)	1.864 (5)
Si-C(31)	1.879 (3)	1.859 (5)

Angle	1	2
S(1)-C(2)-S(3)	111.4 (2)	106.0 (3)
S(1)-C(2)-Si	105.1 (2)	115.8 (3)
S(3)-C(2)-Si	106.7 (2)	112.3 (3)
S(1)-C(2)-C(7)	111.4 (3)	
S(3)-C(2)-C(7)	111.0 (3)	
Si-C(2)-C(7)	111.0 (3)	
C(2)-S(1)-O		108.2 (3)
C(6)-S(1)-O		107.0 (4)
C(2)-S(1)-C(6)	102.6 (2)	99.5 (3)
C(2)-S(3)-C(4)	101.7 (2)	100.8 (3)
S(3)-C(4)-C(5)	113.9 (3)	115.4 (6)
S(1)-C(6)-C(5)	113.3 (3)	114.6 (6)
C(4)-C(5)-C(6)	114.3 (3)	115.7 (7)
C(2)-Si-C(11)	108.2 (3)	108.7 (3)
C(2)-Si-C(21)	108.0 (3)	107.0 (3)
C(2)-Si-C(31)	110.0 (3)	109.4 (2)
C(11)-Si-C(21)	110.8 (2)	109.9 (3)
C(11)-Si-C(31)	109.1 (2)	112.3 (3)
C(21)-Si-C(31)	110.7 (2)	109.1 (3)
C(12)-C(11)-C(16)	116.7 (3)	120.0 (6)
C(22)-C(21)-C(26)	116.0 (3)	117.6 (5)
C(32)-C(31)-C(36)	117.9 (3)	117.1 (5)
C(11)-C(12)-C(13)	122.0 (4)	118.8 (6)
C(11)-C(16)-C(15)	121.1 (4)	120.5 (7)
C(21)-C(22)-C(23)	122.3 (4)	121.2 (5)
C(21)-C(26)-C(25)	121.7 (3)	121.6 (6)
C(31)-C(32)-C(33)	120.9 (3)	122.1 (6)
C(31)-C(36)-C(35)	121.1 (4)	121.7 (6)

It has been shown¹⁰ that, whereas, because of thermal effects, the C-C bond distances are not sensitive indicators of such effects, the angles α and β are. The mean value found for α from a survey of phenylsilanes is 116.98°, a reduction from the canonical value of 120° of just over 3°.

Given that the ipso effect¹¹ is dependent on σ -electron-density transfer, it seems reasonable to assume that the 3.6° diminution in each of the C(2) angles in **1** and **2**, relative to **3** and **4**, arises from similar causes consequent upon a diminution in the relative p character of the Si-C(2) bond. In the absence of a planar ring system, there is no direct need for a compensatory increase in the β angles at sulfur, but it is observed that, whereas in **3** the endocyclic valence angles at S(1) and S(3) are 99.2° and 100.9°, in **1** they are 101.7° and 102.6°. In the same way, whereas in **4** these angles are 98.2° and 100.5°, in **2** they are 99.5° and 100.8°. It seems possible that enhanced s character in the two C(2)-S bonds may also be reflected at the sulfur atoms.

Comparable ipso effects are found in five of the six phenyl rings of **1** and **2**. The mean contraction in these five angles is 2.9° and the mean expansion in β angles is 1.6°, comparable to earlier observations.¹⁰ The exception involves the phenyl ring in **2**, one of whose β protons is involved in a short intramolecular C-H...O interaction which appears to override in

Table III. Endocyclic Torsion Angles (Deg) in the Dithiane Rings of 1-4

Angle	Compound			
	1	2	3 ^a	4
S(1)-C(2)	-56	-66	-57	-63
C(2)-S(3)	56	65	57	63
S(3)-C(4)	-58	-59	-56	-61
C(4)-C(5)	66	57	63	64
C(5)-C(6)	-66	-59	-61	-67
C(6)-S(1)	58	62	57	63

^a Values of Kalf and Romers (ref 10).

importance the effect of silicon substitution. This interaction is described in more detail below.

Within the dithiane ring, the valence angles at C(4), C(5), and C(6) in **2** have an average value of 115.2° compared to 113.9° in **1**, an effect associated with the flattening of the C(5) apex in **2**. The remaining important difference in valence angles between **1** and **2** involves the S-C(2)-Si angles. In **1**, the presence of the sterically bulky C(2)-methyl substituent prevents any opening of these angles to minimize 1,3-interactions between sulfur and silicon, and leads to compressed values of 106.7° and 105.1° for these two angles. In **2**, by contrast, the absence of an axial substituent allows relaxation of the S...Si interactions and leads to expanded values of 115.8° and 112.3°. This opening, coupled with increased puckering at C(2) in **2**, places C(2) 0.99 Å below the least-squares mean plane through the four central atoms of the dithiane ring in **2**, compared to a displacement of 0.84 Å in **1**, but places Si 1.54 Å below that plane in **2** compared to only 0.64 Å in **1**.

McPhail⁶ has suggested that differences in the C-S bond lengths in 1,3-dithianes and their oxides depend only on the pattern of substitution of the ring, shorter bonds being associated with methylene groups, and we have offered additional evidence in support of this view.⁷ The observed C-S distances in **2** conform to this pattern, the longer distances involving C(2), the site of substitution, and the shorter bonds being to C(4) and C(6). This is not the case, however, in **1** where all four bonds are of equivalent length and all are longer than the distances found in **2**. Inasmuch as lengthening of these bonds is thought to depend on steric factors, it is likely that the observed lengthening and the equivalence of all four distances arise principally from the steric effects of the axial methyl group.

The mean Si-C_{sp²} bond distance is 1.873 Å, and individual variations from this mean value probably have little significance. There is, however, a significant difference in the length of the Si-C(2) bond distance of 1.938 (4) Å in **1** and 1.890 (5) Å in **2**, which is to be correlated with the large differences in valence angles at C(2) in the two compounds.

The relative orientations of the dithiane ring and the triphenylsilyl moiety in **1** and **2** are illustrated by the Newman projections shown in Figure 3. The two conformations are markedly different, and neither is a completely staggered arrangement about C(2)-Si. The mean rotation of the two fragments in **1** is 40° and in **2** is only 25°. The diminished rotation in **2** is to be attributed to the H(12)...O interaction described below.

The dihedral angles between the three phenyl groups and the central plane of the dithiane ring are 129°, 70°, and 91° in **1** and 75°, 128°, and 90° in **2**. The 90° orientation seems to favor interaction between a β proton on the phenyl ring and the S(3) axial lone pair, whereas a 129° orientation favors an interaction between a β proton and the S(1) equatorial lone pair of **1**.

Nonbonded C-H...O interactions. In our earlier report,⁴

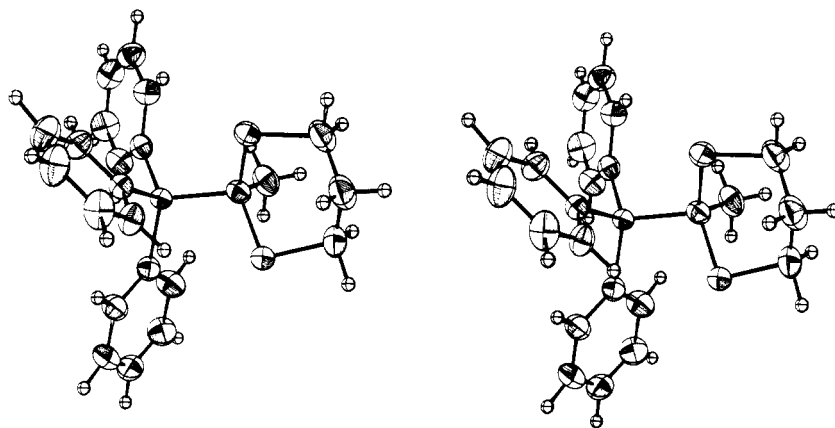


Figure 1. ORTEP stereoscopic view of the structure of **1**. Thermal ellipsoids for the nonhydrogen atoms are drawn to the 50% probability level and hydrogen atoms are represented by spheres of arbitrary radius.

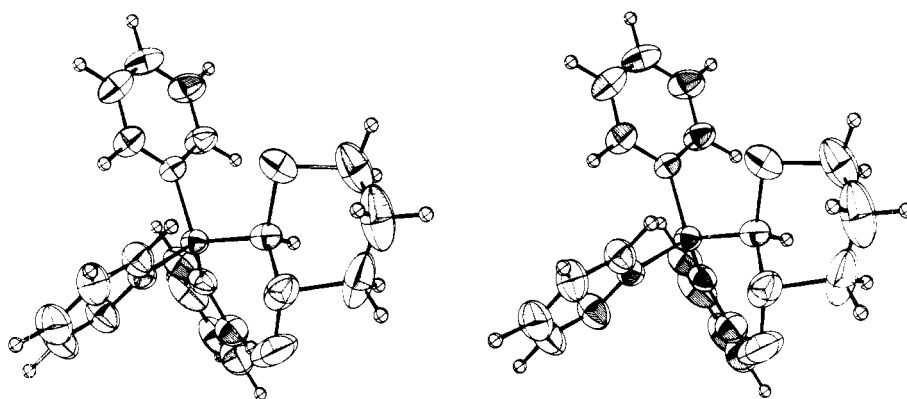


Figure 2. ORTEP stereoscopic view of **2**.

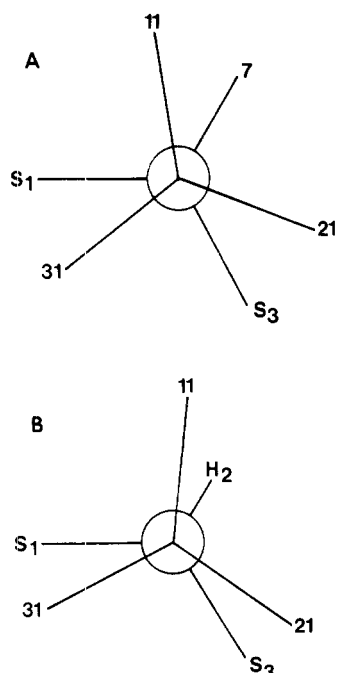


Figure 3. Newman projection down the Si-C(2) bond in **1** (A) and **2** (B). Atoms are carbon unless otherwise labeled.

we noted the occurrence of striking intermolecular interactions in the crystal structures of **4** and of the two oxides *cis*-2-phenyl-1,3-dithiane 1-oxide, **5**, and 2-phenyl-1,3-dithiane *trans*-1, *trans*-3-dioxide. These involved C-H...O contacts, with potentially acidic hydrogen atoms attached to carbons

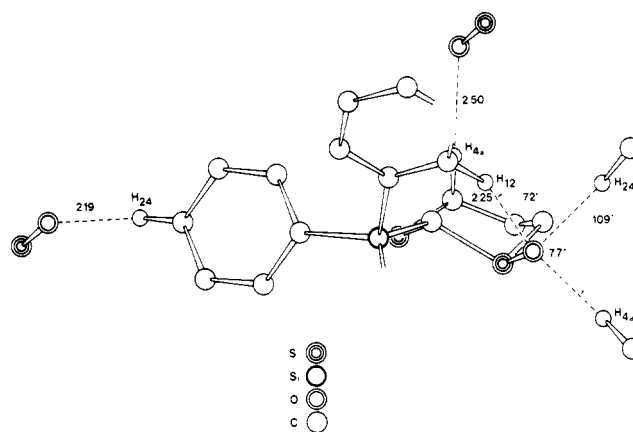


Figure 4. View of the short C-H...O interactions in the crystal structure of **2**. Distances are given in Å and angles in deg.

adjacent to sulfur, which were markedly shorter than the sum of the accepted van der Waals radii of O and H, 2.60 Å. A similar observation has been made by McPhail for the crystal structure of the oxide **6**, and in the axial oxide **7** the oxygen atom acts as an acceptor in an O-H...O intramolecular hydrogen bond. Typically, O...H separations between 2.13 and 2.58 Å have been noted, those at the shorter end of the range being attributed to strong dipolar interactions.

In the crystal structure of **2** there are three further examples of such nonbonded interactions, two intermolecular and one intramolecular. These are illustrated in Figures 4 and 5. The intermolecular interaction involving H(4a) is of the general type previously described.⁴ The other, involving H(24), the *p* proton of a phenyl ring, and with O...H 2.19 Å, is clearly a

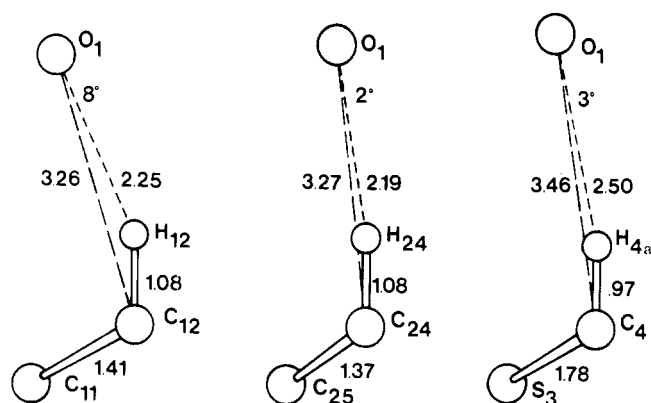


Figure 5. The individual short C-H...O interactions in **2** seen in projection onto the plane of the three atoms. The C-O-H angles are given as well as the interatomic separations (Å).

strong interaction, presumably of an induced-dipole type. The most interesting interaction, however, is the intramolecular contact between the phenyl proton H(12) and oxygen, with O...H only 2.25 Å. There seems no doubt that this contact arises from a powerful dipolar attraction between the two atoms, not only from the shortness of the interaction, but also from the effects produced on conformation about the C(2)-Si bond, described above, and on valence angle patterns in this phenyl ring. The ring involved is the only one of the six phenyl rings not to show an ipso effect of silicon substitution. Instead, the endocyclic valence angle at C(11) has a normal value of 120.0°, whereas C(12) subtends an angle of 118.8°. By the same arguments advanced to account for the angle contraction induced by silicon substitution, it seems that the interaction allows a pathway for transmission of electron density from oxygen to the phenyl ring of a magnitude comparable to that arising from silicon substitution. The widespread occurrence of such interactions in these compounds, and in other sulfoxides,¹² suggests that neutron-diffraction studies should be carried out in order to unambiguously define the exact hydrogen positions in these quasi hydrogen bonds.

Other intermolecular contacts in the crystal structures are of normal van der Waals type. Selected approach distances are listed in the Supplementary Material.

Experimental Section

NMR spectra were recorded on a Varian HA-100 spectrometer with CDCl₃, and chemical shifts are reported in ppm (δ) from internal tetramethylsilane. Infrared spectra were measured on a Perkin-Elmer 337 grating instrument as KBr disks. Melting points are corrected and were determined on a Thomas-Hoover apparatus. Mass spectra were obtained using a Hitachi-Perkin-Elmer RMU-6E spectrometer at an ionizing potential of 70 eV. Microanalyses were performed by Alfred Bernhardt, Engelskirchen, West Germany.

2-Triphenylsilyl-1,3-dithiane and 2-methyl-2-triphenylsilyl-1,3-dithiane were prepared as described in the literature.¹³

Preparation of *trans*-2-Triphenylsilyl-1,3-dithiane 1-Oxide (2). A solution containing 3.78 g (10 mmol) of 2-triphenylsilyl-1,3-dithiane in 50 mL of dichloromethane was cooled to -15 °C and *m*-chloroperoxybenzoic acid (2.03 g, 10 mmol) in 75 mL of dichloromethane was added dropwise. After standing overnight at -20 °C the solution was washed with 10% aqueous sodium carbonate and brine, dried (Na₂SO₄), and evaporated. The crude product (3.64 g) was a single isomer and was free of starting material, as evidenced by its NMR spectrum. Recrystallization from dichloromethane-ether gave pure **2** (2.28 g, 58%): mp 174.5-177 °C; IR (KBr) 1640, 1120, 1040 (S=O), 795, 748, 700, 630, 510, and 500; NMR (CDCl₃) δ 7.8-7.2 (m, 15, arom), 3.98 (s, 1, C-2 H), 3.5-3.2 (m, 1, C-6 eq H), and 2.9-2.2 (m, 5, ring H); mass spectrum (70 eV) *m/e* (rel intensity) 259 (100), 227 (30), 199 (70), 181 (30), 167 (35).

The analytical sample, mp 177.5-178.5 °C, was obtained by recrystallization from dichloromethane-ether.

Anal. Calcd for C₂₂H₂₂OS₂Si: C, 66.97; H, 5.62; S, 16.25. Found: C, 66.75; H, 5.53; S, 16.44.

Table IV. Crystal Data for 1 and 2

	1	2
Space group	C2/c	P2 ₁ /c
<i>a</i> , Å	28.780 (6)	10.390 (3)
<i>b</i> , Å	11.901 (3)	9.988 (3)
<i>c</i> , Å	15.909 (3)	20.207 (12)
β , deg	130.93 (3)	97.61 (3)
ρ_{obsd} , g cm ⁻³	1.27	1.23
ρ_{calcd}	1.27	1.26
<i>U</i> , Å ³	4117	2079
<i>Z</i>	8	4
<i>F</i> (000)	1664	832
μ (Cu K α), cm ⁻¹	28	28
Crystal size, mm ³	0.3 × 0.3 × 0.4	0.4 × 0.5 × 0.2
Significant reflns	2182	2386
$2\theta_{\text{max}}$, deg	110	120

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 K α radiation. For **1**, reflections occur only for *hkl*: *h* + *k* = 2*n*; *h0l*: *l* = 2*n* (*h* = 2*n*); and *0k0*: (*k* = 2*n*); consistent with space groups *Cc* and *C2/c*. The distribution of intensity as a function of scattering angle indicates the presence of a center of symmetry and, hence, space group *C2/c*. With eight molecules in the unit cell, no molecular symmetry is implied. For **2**, the limiting conditions are *h0l*: *l* = 2*n*, and *0k0*: *k* = 2*n*, uniquely defining the space group as *P2₁/c*. Again, no molecular symmetry is implied. Accurate unit-cell dimensions were obtained by a least-squares fit to the diffractometer values of $\pm 2\theta$ for 20 strong general reflections from carefully centered crystals (λ = 1.5418 Å). Relevant data for the two compounds are presented in Table IV.

Intensity Data. Measurements of intensity for **1** and **2** were made using a Picker four-circle diffractometer controlled by an XDS Sigma 2 computer. Cu K α radiation was used, made monochromatic by Bragg reflection from a highly oriented graphite crystal, with scintillation counting and pulse-height analysis. The θ - 2θ scan method was used with a scan range of 2.5° and a scan speed of 2° min⁻¹. Background intensities were measured for 10 s at the beginning and end of each scan with the crystal and counter stationary. Measurements were made, in each case, for a single quadrant of reciprocal space with the symmetry equivalent *0k \bar{l}* reflections also measured to provide a check on crystal alignment. The deviation from the mean in these averaged intensities was typically <2%. Stability of the experimental conditions was monitored by measurement of three reference reflections after every 50 scans. The rms deviations about the mean intensities were 2.5%, fluctuations being random. Scattered intensity in a scan was taken as significantly above background at the 3 σ level. No absorption corrections were applied, and intensities were converted to structure amplitudes in the usual way.

Structure Determination and Refinement. For **1**, the locations of the three heavy atoms (2S + Si) were determined from a sharpened three-dimensional Patterson function, and the phase problem was solved by the heavy-atom method using phases calculated for these three atoms (*R* = 0.54). Preliminary least-squares refinement of the parameters for Si, S, O, and C atoms (*R* = 0.08) enabled positions for the hydrogen atoms to be calculated [except for those of the C(7) methyl group which were located by a general-plane difference electron-density synthesis]. Continued refinement (3 × 3, 6 × 6 blocks) of all positional and anisotropic thermal parameters for all atoms other than H, for which isotropic *B* values were adopted, gave at convergence [$\Delta(p)$ < 0.2 $\sigma(p)$] conventional unweighted and weighted residuals of 0.041 and 0.048, respectively, for the observed reflections.

For **2**, the phase problem was solved using the FAME-MAGIC¹⁴ direct-methods program. Reflections 340, 473, and 734 were given plus signs to determine the origin, and symbols were assigned to 14, 1, 4, 863, and 943. Of the top 400 *E(hkl)*, 393 were phased with *p* > 0.98, and the resulting *E* map correctly indicated the positions of 24 of the 26 heavy atoms in the molecule. The remaining atoms were found in the standard way from difference electron-density maps. The refinement proceeded in the same way as for **1**, save that the hydrogen atoms of the phenyl rings were included in the least-squares treatment in fixed positions with isotropic *B* values set equal to the equivalent isotropic *B* for the carbon of attachment. For the observed reflections, both the unweighted and weighted *R* values were 0.064. The higher

residual in this structure is probably associated with the generally higher level of thermal vibration in **2** than in **1**.

In each case, a conventional weighting scheme was used.¹⁵ Scattering curves for the nonhydrogen atoms were taken from Hanson, Herman, Lea, and Skillman,¹⁶ and allowance was made for the real part of the anomalous dispersion terms for Si, S, and O.¹⁷ For hydrogen, the curve of Stewart, Davidson, and Simpson was used.¹⁸ Programs used, other than FAME-MAGIC and ORTEP for which a CDC 6400 computer was used, were written in this laboratory for the Sigma 2 computer.

Registry No.—**1**, 13433-56-2; **2**, 63883-55-6; **4**, 60349-76-0; 2-triphenylsilyl-1,3-dithiane, 13433-53-9.

Supplementary Material Available. Anisotropic thermal parameters, selected nonbonded intramolecular contact distances, intermolecular contacts, and information on least-squares mean planes of interest (3 pages). Ordering information is given on any current masthead page.

References and Notes

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Optically Active 1,3-Dithiane 1-Oxide: Optical Resolution and Absolute Configuration

Robert F. Bryan,* Francis A. Carey,* Oliver D. Dailey, Jr., Robert J. Maher, and Richard W. Miller

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

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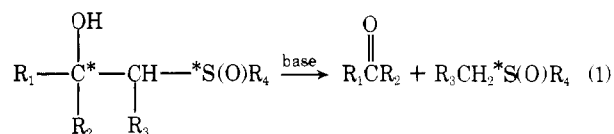
1,3-Dithiane 1-oxide (**1**) has been resolved into its enantiomers by two methods, both based on separation of D(+)-camphor adducts followed by base-catalyzed cleavage back to **1** and camphor. Reaction of the lithio derivative of (±)-**1** with D(+)-camphor gives a mixture of diastereomeric adducts **2** and **3**, either of which may be isolated depending on the temperature at which the reaction is carried out and the isolation procedure adopted. Diastereomer **2** was cleaved to (–)-**1** on treatment with potassium hydroxide in *tert*-butyl alcohol, whereas similar treatment of **3** yielded (+)-**1**. Oxidation of (2*R*)-2-(1,3-dithian-2-yl)isoborneol (**4**) with *m*-chloroperoxybenzoic acid gave a mixture of diastereomeric sulfoxides from which **3** could be isolated. The absolute configuration of (–)-**1** is *S* as determined by x-ray crystallographic characterization of its precursor **2**. Crystals of **2** conform to space group *P*₂₁₂₁ with *a* = 23.890 (7), *b* = 9.336 (4), *c* = 6.727 (3) Å, and *Z* = 4. The valence angle of 112.8° found for S–C–S in the dithiane moiety of **2** is identical with that found in *cis*-2-phenyl-1,3-dithiane 1-oxide.

The stereochemical properties of 1,3-dithiane 1-oxide (**1**) and its derivatives are receiving much attention. Questions of conformation have been studied experimentally^{1–3} and probed by molecular mechanics.⁴ These investigations, together with x-ray crystallographic studies,⁵ have revealed significant structural effects associated with cross-ring electrostatic interactions. The stereoselectivity of formation of diastereomeric derivatives of **1** by oxidation of 2-substituted 1,3-dithianes^{1,6} and by the reaction of the 2-lithio derivative of **1** with electrophilic reagents has been determined.⁷

Since **1** is a chiral molecule, other aspects of stereochemistry may be explored as well. Asymmetric synthesis, for example, would use optically active **1** as a chiral carbonyl equivalent group. The synthetic value of carbonyl equivalents in nucleophilic acylation reactions is well established.⁸ Many useful transformations involving 1,3-dithiane⁹ and methyl methylthiomethyl sulfoxide¹⁰ have been described which embody this concept. Considerable success in asymmetric synthesis has also been achieved by Meyers using (4*S*,5*S*) 2-substituted

4-methoxymethyl-5-phenyl-2-oxazolines as chiral carbonyl equivalents.¹¹

A number of techniques have been developed for the preparation of optically active sulfoxides.¹² Sulfinyl-group transfers from optically active sulfinate esters on reaction with organometallic reagents have proven particularly useful¹³ but are not appropriate for **1**. Oxidations of unsymmetrical sulfides with optically active peroxy acids have been reported, but normally with low optical yields.¹² We envisioned generation of optically active **1** by base-catalyzed cleavage of a single stereoisomer of a β-hydroxyalkyl sulfoxide (eq 1). The process



is then one of resolution whereby separation of a mixture of diastereoisomers and subsequent cleavage lead to optically