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- methylation (AlCl₃, CH₂Cl₂, room temperature, 1 h) in 74% overall yield.
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Crystal Structure of the Syn-Diaxial Conformer of 2,2-Diphenyl-1,3-dithiane *cis*-1,3-Dioxide

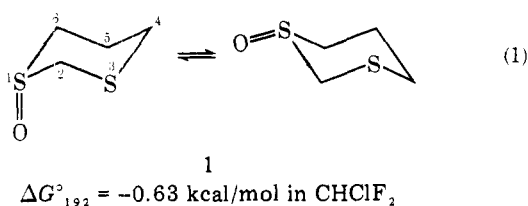
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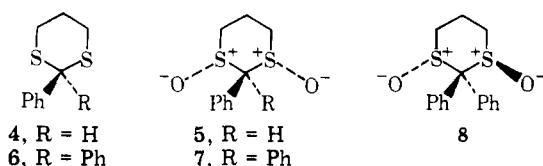
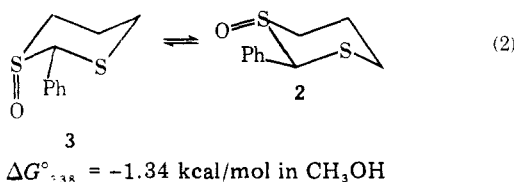
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The lower melting 1,3-dioxide of 2,2-diphenyl-1,3-dithiane has been determined to be the *cis* diastereomer by ¹H and ¹³C NMR spectroscopy and by single-crystal X-ray diffraction rather than *trans* as reported in the literature. The molecule exists in the conformation in the crystal which has both sulfoxide oxygens axial in spite of the significant electrostatic repulsions attending this conformation. The preference for the observed conformation appears to result from van der Waals interactions involving the two C(2)-phenyl substituents with each other and with the two oxygens. Crystals of the dioxide conform to space group *P*2₁/*n*, with *a* = 9.635 (2), *b* = 10.096 (3), *c* = 14.798 (4) Å, β = 98.86 (1)°, and *Z* = 4. The structure was solved by direct methods, and least-squares refinement gave *R* = 0.052 for 1680 independent significant reflections measured by counter diffractometry.

Our understanding of the factors which influence the conformational equilibrium in 1,3-dithiane 1-oxide (1) (eq 1) has



been aided by the systematic examination of the structural features of suitably substituted model compounds as revealed by X-ray crystallography.^{1,2} For example, the S(1)–C(2)–S(3) angle is significantly smaller (109.6° vs. 112.9°) in *trans*-2-phenyl-1,3-dithiane 1-oxide (2) than in the *cis* diastereomer 3, and this angle is smaller in both oxides than in the parent 2-phenyl-1,3-dithiane 4 (114.9°). We have attributed the bond angle contraction in the oxides to an electrostatic attraction between the positively polarized sulfoxide sulfur and S(3). This attraction is opposed in the axial oxide by a repulsive electrostatic interaction between oxygen and S(3), leading to a larger S(1)–C(2)–S(3) angle than in the equatorial oxide.³ An axial orientation of the sulfoxide group has been observed to be less stable than an equatorial one both in the conformational equilibrium of 1,3-dithiane 1-oxide (eq 1)⁴ and in the base-catalyzed equilibration of 2 and 3 (eq 2).⁵



The C(2) endocyclic angle responds in a predictable fashion toward introduction of a second sulfoxide oxygen. The S(1)-

...S(3) interaction becomes repulsive since both sulfurs are positively polarized, and the S(1)–C(2)–S(3) angle is observed to be 114.2° in the *cis*-1,3-dioxide (5) of 2-phenyl-1,3-dithiane.¹ We have extended our examination of 1,3-dioxides to include a 2,2-disubstituted derivative, thinking that the combination of a crowded environment and the proximity of like dipoles might cause the most stable conformation to be other than a chair. A crystal structure determination could then provide useful information concerning the distortion modes available to oxides of 1,3-dithiane. As will be seen in this paper, the conformation adopted by *cis*-2,2-diphenyl-1,3-dithiane 1,3-dioxide in the crystal was, in fact, a chair, but not the one expected on the basis of electrostatic considerations.

Results and Discussion

The formation of *cis*- (7) and *trans*-2,2-diphenyl-1,3-dithiane 1,3-dioxide (8) in approximately equal amounts on oxidation of 2,2-diphenyl-1,3-dithiane (6) with 2 equiv of hydrogen peroxide in acetic acid has been described by Neugebauer in collaboration with Kuhn⁶ and with Otting.⁷ Based on its infrared spectrum, the higher melting diastereomer (mp 189 °C) was assigned the *cis* stereochemistry 7 and the lower melting one (mp 177 °C) the *trans* structure 8.⁷ On repeating this work, we were able to obtain crystals suitable for X-ray work of one of the isomers much more easily than the other and directed our attention to that diastereomer. It melted at 173–175 °C and had an infrared spectrum identical with that reported for the *trans*-dioxide 8. Both ¹H and ¹³C NMR spectroscopy, however, indicated that the structural assignment in the literature was incorrect and that this compound was the *cis*-1,3-dioxide 7. In addition to multiplets for the four methylene protons at C(4) and C(6), the ¹H NMR spectrum exhibited separate one-proton multiplets centered at 1.9 and 2.8 ppm for the two C(5) protons. This is consistent with the *cis*-1,3-dioxide 7 where the C(5) protons are diastereotopic, but not with the *trans*-1,3-dioxide 8 where the C(5) protons are equivalent on the NMR time scale. Similarly, the ¹³C NMR spectrum contained six identifiable signals for aromatic carbons in the range 128–136 ppm. Because the phenyl groups are equivalent in the *trans*-1,3-dioxide 8 only four signals are possible for this compound, while the *cis*-1,3-dioxide 7 could

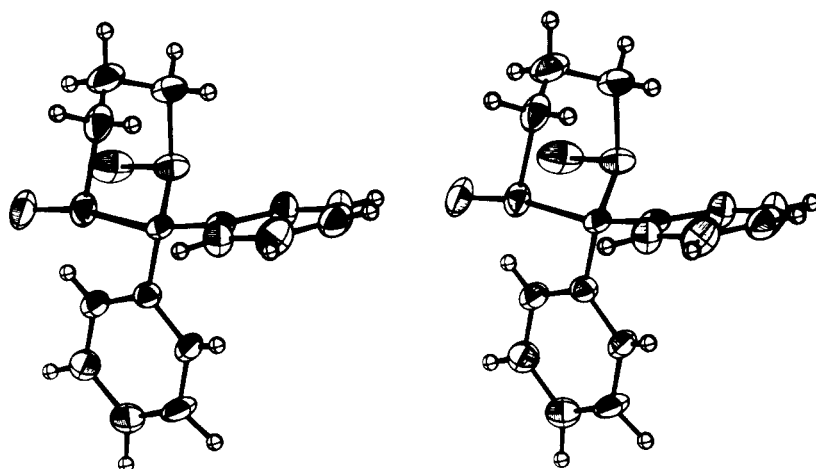


Figure 1. ORTEP stereoscopic view of the structure of *cis*-2,2-diphenyl-1,3-dithiane 1,3-dioxide (7). Thermal ellipsoids for the nonhydrogen atoms are drawn to the 50% probability level, and hydrogen atoms are represented by spheres of arbitrary radius.

Table I. Atomic Parameters Defining the Crystal Structure of 2,2-Diphenyl-1,3-dithiane *cis*-1,3-Dioxide^a

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i>
S(1)	3578 (1)	3801 (1)	3606.3 (7)	3.10
S(3)	4403 (1)	724 (1)	3762.1 (7)	3.05
O(1)	2227 (3)	3525 (4)	3540 (2)	4.05
O(3)	2879 (3)	432 (4)	3685 (2)	4.65
C(2)	4762 (4)	2423 (4)	4273 (3)	2.13
C(4)	4769 (5)	1015 (5)	2615 (3)	3.75
C(5)	3834 (5)	2082 (6)	2132 (3)	4.57
C(6)	4243 (5)	3455 (6)	2483 (3)	4.13
C(11)	4235 (4)	2406 (4)	5208 (3)	2.30
C(12)	2842 (4)	2100 (4)	5293 (3)	2.83
C(13)	2393 (5)	2065 (5)	6135 (3)	3.58
C(14)	3303 (5)	2300 (5)	6929 (3)	3.89
C(15)	4669 (5)	2619 (5)	6842 (3)	3.58
C(16)	5129 (4)	2655 (4)	5986 (3)	2.74
C(21)	6312 (4)	2715 (4)	4302 (3)	2.45
C(22)	6831 (4)	3989 (4)	4261 (3)	3.21
C(23)	8251 (5)	4232 (5)	4304 (3)	4.05
C(24)	9189 (5)	3206 (6)	4378 (3)	3.97
C(25)	8705 (5)	1961 (5)	4459 (3)	4.21
C(26)	7294 (5)	1675 (5)	4422 (3)	3.30

^a Positional parameters are given as fractions of the unit cell edges ($\times 10^4$), and equivalent isotropic *B* values are given in \AA^2 . Anisotropic thermal parameters for S, O, and C are given in the supplementary material together with positional and thermal parameters for H atoms.

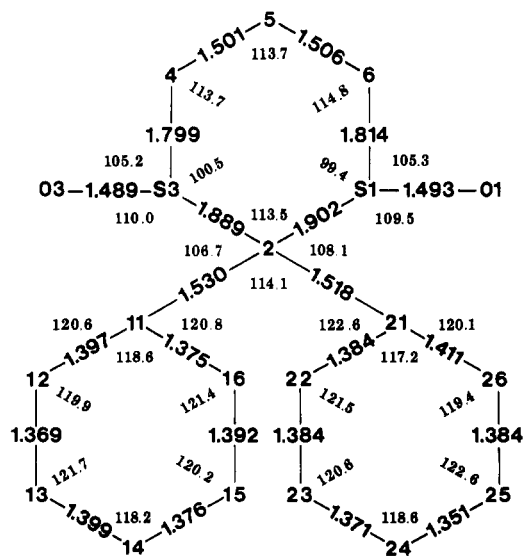


Figure 2. Bond distances (\AA), bond angles (deg), and numbering scheme for 7.

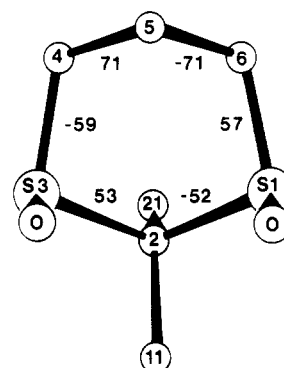
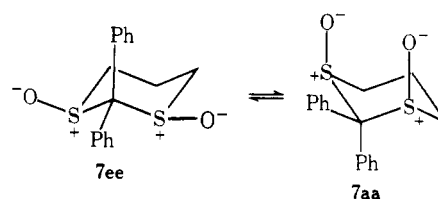


Figure 3. Torsion angles (deg) in the dithiane ring portion of 7.

have, barring accidental coincidence of chemical shifts, eight signals for the two diastereotopic aromatic rings.

Conclusive evidence in support of the structural assignment came from a single-crystal X-ray diffraction determination which clearly established that the sulfoxide oxygens were *cis*. The positional parameters defining the crystal structure are given, together with their associated estimated standard deviations, in Table I. A stereoscopic drawing of the molecule is shown in Figure 1. Bond distances and angles are shown in Figure 2, which also gives the numbering scheme. Torsion angles in the dithiane ring are shown in Figure 3, and a view of the molecular packing in the crystal is shown in Figure 4. The dithiane ring exists in a chair conformation, slightly flattened at the C(2) end.

The most striking, and unexpected, feature of 7, however, is that the chair conformation observed is **7aa**, having the



oxygen atoms syn diaxially disposed to one another rather than the diequatorial dioxide conformer **7ee**. In adopting conformation **7aa**, the molecule incorporates a substantial electrostatic energy, resulting from the syn-diaxial alignment of like dipoles. This energy has been calculated by molecular mechanics to be 8.0 kcal/mol (in vacuum) for 1,3,5-trithiane *cis*-1,3-dioxide.⁸

In order to understand why 7 adopts the diaxial dioxide conformation in the crystal, it is necessary to consider the various steric interactions which involve the C(2)-phenyl

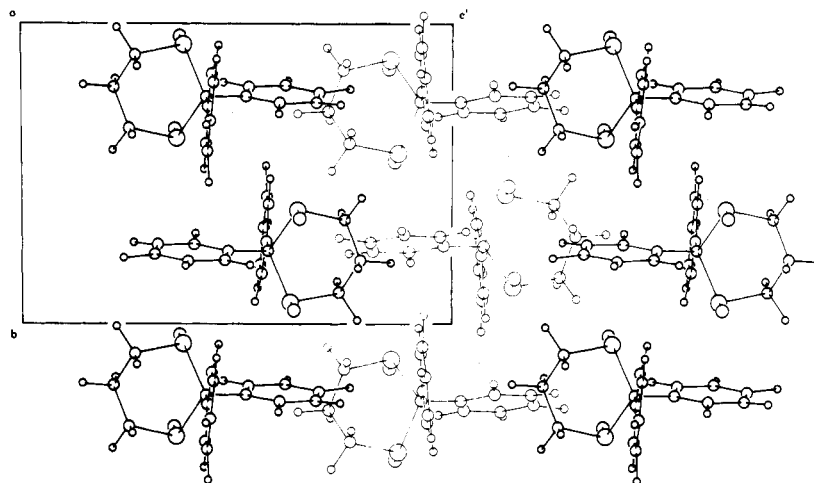


Figure 4. View in *a* axis projection of the molecular packing in 7.

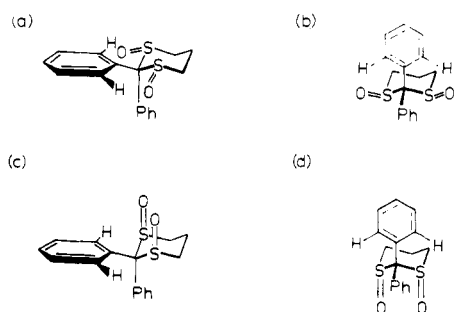


Figure 5. Relationships between ortho hydrogens of a "perpendicular" phenyl substituent and sulfoxide oxygens for various conformations of 7 (for clarity only one of the phenyl groups is shown): (a) diequatorial dioxide-equatorial phenyl; (b) diequatorial dioxide-axial phenyl; (c) diaxial dioxide-equatorial phenyl; (d) diaxial dioxide-axial phenyl.

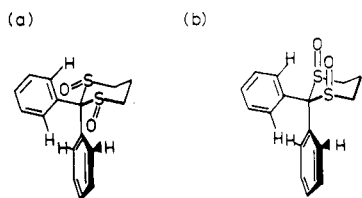


Figure 6. Diequatorial dioxide (a) and diaxial dioxide (b) conformations of 7 with equatorial phenyl "parallel" and axial phenyl "perpendicular".

substituents with each other and with the sulfoxide oxygens. Using the terminology of Allinger,⁹ the limiting rotamers available to the phenyl substituents may be defined as "perpendicular" or "parallel" according to the relationship between the plane of the aromatic ring and the symmetry plane of the dithiane ring. The ortho hydrogens of a "perpendicular" phenyl group, either axial or equatorial, will experience greater gauche van der Waals repulsions with equatorial than with axial sulfoxide oxygens (Figure 5). Since an axial phenyl group compresses the C(4) and C(6) syn-axial hydrogens when it is "parallel", the best arrangement of phenyl groups in 7 is expected to be equatorial phenyl "parallel" and axial phenyl "perpendicular" (Figure 6). Conformation 7ee, with the phenyl groups arranged in this way, remains strained because of the serious van der Waals repulsion between the equatorial oxygens and the ortho hydrogens of the axial phenyl. Conformation 7aa becomes more stable than 7ee because it minimizes the gauche repulsions involving the sulfoxide oxygens and the phenyl groups. The crystal structure of 7 has

just this arrangement of the two phenyl groups. Some close contacts remain in 7aa, including one between an ortho hydrogen of the equatorial phenyl and the two axial oxygens. This distance averages 2.33 Å and is considerably less than the sum of the van der Waals radii of H and O, 2.6 Å. For comparison, the corresponding O...H contact in the monophenyl axial monosulfoxide 3, where the plane of the phenyl group has rotated 55.8° away from the "parallel" orientation to escape this interaction, is 3.43 Å.¹⁰

The other ortho hydrogen of the equatorial phenyl compresses the carbon of the axial phenyl bonded to C(2). Since the interaction would exist as well in conformer 7ee, it does not contribute to the question of conformational preference.

Previous structural studies of oxides of 1,3-dithiane have related gauche repulsions to increases in S-C bond distances when the carbon atom adjacent to a sulfoxide group bears an alkyl or aryl substituent.^{1,2} The discussion above emphasized the importance of gauche repulsions in 7, and it is not surprising that the C(2)-S bonds are quite long (1.889 and 1.902 Å) compared to those of dioxide 5 (1.833 and 1.834 Å)¹ and dithiane 4 (1.79 and 1.80 Å).¹¹

The crystal structures of other dithiane oxides^{1,2} are characterized by one or more unusually short C-H...O contacts in which the H...O separations are significantly less than the commonly accepted sum of the van der Waals radii of these atoms, 2.6 Å, but yet not so short as the H...O separations found in O-H...O hydrogen bonds. These contacts normally involve axial protons of the dithiane ring, and a similar short contact, 2.14 Å, is found in the crystal of 7 between O(3) and the axial C(6) proton of a neighboring molecule. We have characterized these contacts as strong dipolar interactions. As in the other examples, the C-H...O system is nearly linear with the C-H...O angle 170°. Neutron diffraction studies are planned to more fully describe these contacts.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer 337 grating spectrometer as KBr disks. Melting points are uncorrected and were measured on a Thomas-Hoover apparatus. The nuclear magnetic resonance spectrometers used were a Varian Instruments EM-390 for proton NMR and a JEOL PS 100 P/EC-100 Fourier transform spectrometer for ¹³C NMR. All NMR spectra were measured in Silanor C, and chemical shifts are given in ppm downfield from internal tetramethylsilane.

2,2-Diphenyl-1,3-dithiane *cis*-1,3-Dioxide (7). Oxidation of 2,2-diphenyl-1,3-dithiane (6) with hydrogen peroxide in acetic acid was carried out as described by Kuhn and Neugebauer.⁶ A solution containing 2.72 g (10 mmol) of 6 and 2.38 g (21 mmol) of 30% hydrogen peroxide solution in 200 mL of acetic acid was allowed to stand for 3

days at room temperature. Water (1 L) was added and the solution extracted with 100 mL of chloroform. After the chloroform was evaporated, the crude product was chromatographed on 150 g of Woelm activity I acidic alumina and eluted with 6% acetone in chloroform previously saturated with water. The early fractions (1.20 g) were a mixture of mono- and disulfoxides. There was then eluted 1.035 g (34%) of material which was recrystallized from ethanol to give 422 mg of **7** as hard white crystals: mp 171–172 °C; ¹H NMR (CDCl₃) δ 8.20–8.0 (m, 2, aromatic), 7.4 (s, 8, aromatic), 3.6–2.9 (m, 4, CH₂CH₂CH₂), 2.9–2.6 (m, 1, C-5 axial H), 2.1–1.7 (m, 1, C-5 equatorial H); ¹³C NMR (CDCl₃) δ 9.37 (C-5), 45.09 (C-4, C-6), 77.71 (C-2), 128.63, 129.11, 129.30, 129.40, 134.69, and 135.42 (aromatic carbons). Four further recrystallizations from ethanol provided a sample for single-crystal X-ray diffraction studies, mp 173–175 °C. The infrared spectrum of this material was identical with that of the product reported by Otting and Neugebauer⁷ to which they assigned the *trans*-1,3-dioxide structure (mp 177 °C). As is evident from the NMR and X-ray diffraction data, however, this compound is the *cis*-1,3-dioxide **7**. (see Results and Discussion).

X-ray Crystallographic Measurements. Crystal Data. The unit cell symmetry was established from 25° precession photographs taken with Mo K α radiation. The crystal system is monoclinic, and systematic absences $h0l$ with $h + l$ odd and $0k0$ with k odd uniquely define the space group as $P2_1/n$, a nonstandard setting of space group $P2_1/c$. Accurate unit cell dimensions were established by a least-squares fit to the diffractometer values of $\pm 2\theta$ for 20 strong general reflections measured from a carefully centered crystal and are ($\lambda = 1.5418$ Å) $a = 9.635$ (2), $b = 10.096$ (3), $c = 14.798$ (4) Å, and $\beta = 98.86$ (1)°. With four molecules in the unit cell, the calculated density of 1.421 g cm⁻³ is in good agreement with that measured by flotation, 1.41 g cm⁻³. $F(000)$ is 640, and the absorption coefficient, μ , for Cu K α radiation is 32.5 cm⁻¹. No absorption corrections were made, and most of the residual errors are attributable to this neglect.

Intensity Data. Measurements of intensity were made using a crystal 0.13 × 0.30 × 0.45 mm parallel to the cell edges and mounted so as to rotate about a^* on a Picker four-circle diffractometer operated under the control of an XDS Sigma 2 computer. Cu K α radiation was used, made monochromatic by Bragg reflection of the direct beam from a graphite crystal. A single quadrant of reciprocal space was measured to $2\theta = 120^\circ$. Intensity significantly above background [$I > 3\sigma(I)$] was measured at 1680 of the 2129 independent reflections examined. Scintillation counting was used with pulse height analysis. The θ - 2θ scan technique was used with a scan range of 2° in 2θ and a scan speed of 2°/min. Background measurements were made for 15 s before and after each scan with crystal and counter at rest. Stability of the experimental conditions was monitored by measurement of the intensities of two symmetry equivalent reflections after every 50 scans. With a mean intensity of about 5300 counts, the root mean square radiation about the mean was 5.7% for one reflection and 3.5% for the other, but no systematic trends were evident. Crystal alignment was checked by measurement of symmetry equivalent $0kl$ and $0k\bar{l}$ reflections. The residual between the two sets of observed structure amplitudes was 4.1%. Structure amplitudes and normalized structure amplitudes were derived in the usual ways.

Structure Determination and Refinement. The structure was solved routinely by use of the program MULTAN¹² and refined by block-diagonal least-squares methods using a conventional weighting scheme.¹³ Anisotropic thermal parameters were adopted for S, C, and O atoms. All hydrogen atoms were identified from difference electron density maps and included in the refinement with isotropic B values. Convergence was assumed when the largest calculated parameter shift was less than one-fifth the corresponding calculated esd. The final conventional unweighted and weighted residuals were 0.052 and 0.065. The scattering factors used were taken from ref 15.

With the exception of MULTAN and ORTEP,¹⁴ for which a CDC Cyber 172 computer was used, all programs used were written in this laboratory for the XDS Sigma 2 computer.

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Registry No.—**6**, 10359-08-7; **7**, 69401-66-7; **8**, 69401-67-8.

Supplementary Material Available: Refined and calculated coordinates for hydrogen atoms, anisotropic thermal parameters for S, C, and O atoms, and isotropic B values for H atoms, information on least-squares mean planes of interest, selected shorter intramolecular and intermolecular approach distances, and a list of observed and calculated structure amplitudes (6 pages). Ordering information may be found on any current masthead page.

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