The Crystal and Molecular Structure of *cis*-2,2-Diphenyl-3,4-dichlorothietane 1,1-Dioxide

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The title compound crystallizes in the space group *C*2/*c* with a=18.85(2), b=6.15(1), c=27.94(2) Å, β=111.3(1)°, and Z=8. The structure was determined from the photographic X-ray data and was refined by the block-diagonal least-squares method to R=0.10 for 1006 observed reflections. Centrosymmetrically related molecules in the crystal form a dimer by means of weak intermolecular C–H···O hydrogen bonds. The thietane skeleton of the compound is bent with the dihedral angle, $C_\alpha SC_\alpha/C_\alpha C_\beta C_\alpha$, of 148.7°. The average distance of the C–S bonds is 1.87 Å, while that of the C–C's in the thietane ring is 1.58 Å. The conformation of the C–Cl bonds with respect to the thietane ring is (3a4e). The transannular S···Cl distance is 3.42 Å. The CNDO/2 calculation reveals that the 3*d*–3*p* bonding overlap is present between these atoms. The bond angles involving the ring substituents deviate greatly from those observed for *cis*-2,2-diphenyl-3,4-dichlorothietane. These deformations may be explained in terms of dipole-dipole interactions.

cis-2,2-Diphenyl-3,4-dichlorothietane 1,1-dioxide (abbreviated hereafter as *cis*-SO_2-DCTE) was prepared by the oxidation of *cis*-2,2-diphenyl-3,4-dichlorothietane (*cis*-DCTE) by using 30% H_2O_2 as an oxidizing agent.[1]

The crystal-structure analysis of *cis*-SO_2-DCTE was undertaken, and the molecular geometry was compared with that of *cis*-DCTE[2] in order to establish the geometry of the thietane ring and to know the effect of changing the ring substituents, which may alter the structure of the thietane ring.

Experimental

Single crystals of this compound grown from an ethanol solution are thin colorless plates with well-developed {001} planes and with a perfect {100} cleavage. The cell constants, determined from Weissenberg and oscillation photographs, are listed in Table 1, together with other crystal data.

TABLE 1. CRYSTAL DATA

Monoclinic
a= 18.85 (2) Å
b= 6.15 (1) Å
c= 27.94 (2) Å
β=111.3 (1)°
V=3018 Å^3
Formula $C_{15}H_{12}Cl_2SO_2$, F.W.=327.13
D_m=1.44 g/cm^3
D_x=1.440 g/cm^3
Z=8
μ=51.20 cm^{-1} (Cu$K\alpha$)
Possible space group: *Cc* or *C*2/*c*
(Absent spectra: *hkl* when $h+k$ is odd, and
*h*0*l* when *l* is odd.)

It was difficult to select a suitable crystal for the intensity measurements, because the crystals were thin, brittle plates. Specimens with dimensions of 0.05×0.07×0.2 mm, 0.05×0.1×0.08 mm and 0.1×0.1×0.05 mm were used for the collection of the intensity data around the *b*, *a*, and *c* axes respectively. Equi-inclination Weissenberg photographs were taken for *h*0*l*—*h*4*l*, 0*kl*, and *hk*0 using byCu$K\alpha$ radiation (λ=1.542 Å). The intensities of 1006 reflections were estimated visually and were corrected for the Lorentz, polarization, and spot-shape factors by the usual procedures. Absorption and extinction corrections were not applied.

Structure Analysis

The positions of the sulfur and chlorine atoms were determined from a Patterson synthesis, sharpened by a factor $\exp(B \sin^2\theta/\lambda^2)(B=3.0$ Å$^2)$, while the positions of the remaining non-hydrogen atoms were determined from the subsequent Fourier syntheses of the electron density. The space group, *C*2/*c*, is consistent with this structure. A block-diagonal least-squares refinement using anisotropic temperature factors reduced the R value ($R=\sum||F_o|-|F_c||/\sum|F_o|$) to 0.10. In the final cycles of the refinement, all the hydrogen atoms located by assuming a suitable geometry were included in the structure-factor calculations. The temperature factors of hydrogen atoms were assumed to be isotropic; the values of 3.0 Å^2 and 4.0 Å^2 were given for those atoms in the thietane skeleton and in the phenyl groups respectively. At every stage of the refinement, the scale factor, S, for F_0 was calculated for each layer-line data according to the following relation:

$$S \times \sum|F_o(hkl)| = \sum|F_c(hkl)|,$$

where the summation is taken over all the values of h and l for each k. A weighting scheme for the least-squares procedure, w=1 when $|F_o|\geq 5.0$ and 0.3 otherwise, was employed.

The final difference map is flat within the range of ±0.2 eÅ^{-3}. The final atomic and thermal parameters are listed in Table 2. A list of the observed and calculated structure factors has been deposited with the Chemical Society of Japan.[3]

The atomic scattering factors were taken from the International Tables for X-ray Crystallography, Vol. III.

The calculations were carried out on a HITAC 5020E computer at the Computer Center of the University of Tokyo and on a TOSBAC 3400 of Saitama University.

Description and Discussion of the Structure

Figure 1 shows the molecular conformation, the bond distances, the bond angles, and the atomic numbering scheme. The molecule is dissymmetric, but both

Table 2. Atomic parameters

Positional parameters for the atoms in the asymmetric unit with their standard deviations (× 10^4)

	x/a	y/b	z/c
S	−114 (2)	−1223 (9)	796 (2)
Cl (1)	−1486 (2)	1760 (10)	369 (2)
Cl (2)	−528 (2)	2470 (10)	1569 (1)
O (1)	−593 (6)	−2415 (24)	1001 (5)
O (2)	168 (6)	−2375 (23)	444 (4)
C (2)	630 (8)	505 (29)	1276 (5)
C (3)	18 (9)	2392 (33)	1163 (5)
C (4)	−487 (9)	1550 (30)	612 (7)
C (11)	1267 (9)	930 (33)	1072 (6)
C (12)	1296 (7)	2891 (30)	808 (6)
C (13)	1910 (11)	3305 (34)	646 (7)
C (14)	2471 (9)	1637 (36)	747 (6)
C (15)	2399 (8)	−274 (32)	994 (6)
C (16)	1809 (8)	−591 (29)	1159 (6)
C (21)	978 (8)	−3 (32)	1860 (6)
C (22)	1498 (10)	1360 (40)	2174 (6)
C (23)	1821 (10)	914 (44)	2702 (7)
C (24)	1591 (12)	−960 (49)	2887 (7)
C (25)	1088 (14)	−2468 (52)	2561 (7)
C (26)	777 (12)	−1876 (39)	2045 (6)

Thermal parameters (× 10^3)

The temperature factor is of the form:

$$T=\exp[-2\pi^2(U_{11}a^{*2}h^2+U_{22}b^{*2}k^2+U_{33}c^{*2}l^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+2U_{23}b^*c^*kl)]$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	48	77	76	2	60	12
Cl (1)	51	117	64	42	12	−9
Cl (2)	57	102	52	27	48	−50
O (1)	46	102	116	10	27	34
O (2)	79	86	71	11	62	191
C (2)	53	73	45	36	33	4
C (3)	84	91	52	−123	77	−189
C (4)	76	56	113	71	144	212
C (11)	82	87	53	−29	79	−133
C (12)	15	71	95	−50	28	−192
C (13)	112	64	116	−50	138	12
C (14)	59	111	86	−49	76	−174
C (15)	34	81	86	2	28	−272
C (16)	33	71	76	48	30	−68
C (21)	44	85	65	74	62	141
C (22)	70	163	50	−40	8	−289
C (23)	74	176	76	9	11	−147
C (24)	98	200	76	80	−4	17
C (25)	192	199	79	18	152	400
C (26)	138	106	74	63	92	76

enantiomers are present in the crystal because the requirement of the space group.

The thietane ring is bent with a dihedral angle, C(2)SC(4)/C(2)C(3)C(4), of 148.7°. The average length of the C–S bonds is 1.87 Å, while that of the ring C–C's is 1.58 Å. The mean value of the S–C–C bond angles and the C–C–C in the ring are 88.8° and 95.3° respectively. The C–S–C of 77.6(8)° is much smaller than that of dimethyl sulfone (103.0°).[4] The average distance of the S=O bonds is 1.45 Å, and the O–S–O angle is 117.2°. These values agree with those observed for dimethyl sulfone (1.445(15) Å and 117.9(8)°). The C(3)–Cl(2) and C(4)–Cl(1) bond distances are 1.79(2) Å and 1.76(2) Å respectively. The directions of these bonds are axial and equatorial respectively, as is shown in Fig. 1, and differ from those, (3e4a), observed for *cis*-DCTE. This fact suggests an inversion of the thietane ring by the oxidation of *cis*-DCTE in the course of the preparation of *cis*-SO_2-DCTE. The non-bonded S······Cl(2) distance in the *cis*-SO_2-DCTE molecule is 3.42 Å, significantly shorter than the usual van der Waals contact (3.65 Å). If the *cis*-SO_2-DCTE molecule could retain the conformation observed for *cis*-DCTE in its crystalline state, it would take the (3e4a) conformation, in which the transannular S······Cl(2) distance would be 4.07 Å. Hence, the (3a4e) conformer seems not to be favored in view of the non-bonded repulsions between the Cl atom and the sulfonyl group. In order to explain the ring inversion, a molecular orbital calculation using the CNDO/2 method was carried out for the model molecules assumed for both the conformers.[5] It was found that the (3a4e) conformer may be more stable than the (3e4a) conformer. The electronic energy mainly participates in stabilizing the (3a4e) conformer. The ring inversion can be explained in terms of this contribution. It is noteworthy that the 3*d*-3*p* interaction between the S and Cl(2) atoms is bonding, while that in the (3e4a) conformer is approximately non-bonding.

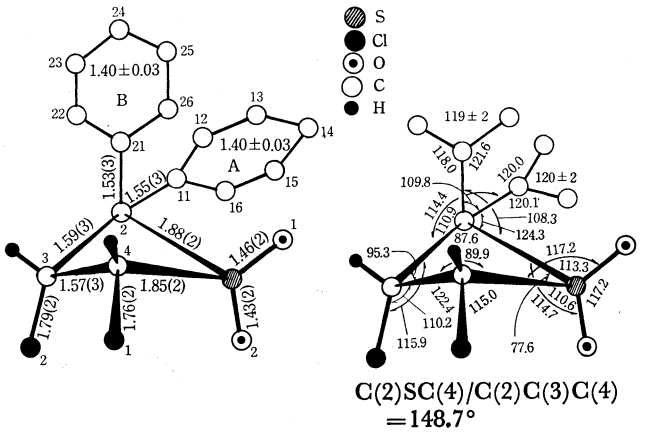

Fig. 1. Bond lengths (Å). E.s.d.'s are shown in parentheses. Bond angles (°). The e.s.d.'s of the bond angles involving Cl and S atoms are ±0.8 °∼1.3 ° and those of the others are ±1.4 °∼1.8 °.

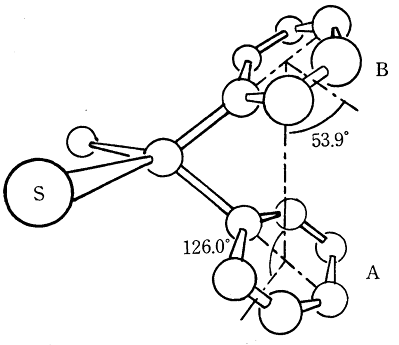

Fig. 2. Orientations of the phenyl groups.

The phenyl groups, A and B, are practically planar; their orientations are shown in Fig. 2. The non-bonded distances, O(1)······C(26), S······C(26), O(2)······C(16), and S···C(16), are 3.21 Å, 3.41 Å, 3.13 Å, and 3.30 Å respectively. Non-bonded repulsions caused by these close contacts might play an important role in determining the phenyl orientations.

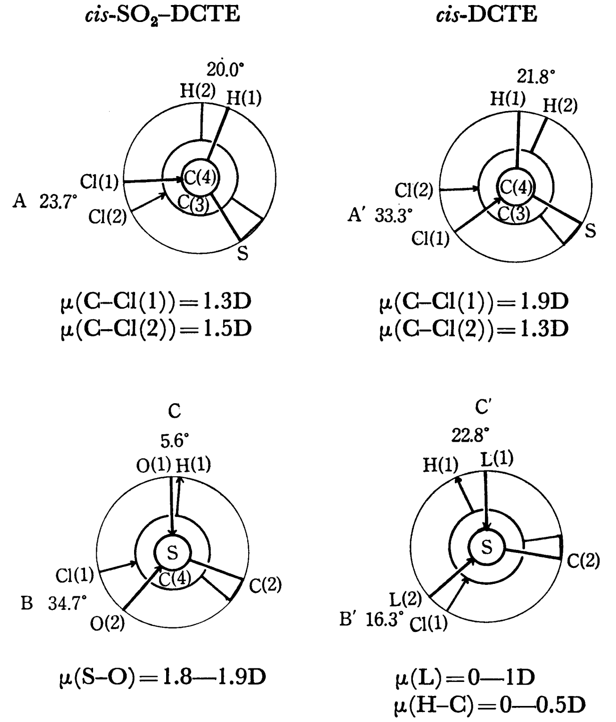

Fig. 3. Newman projections of the torsion angles involving the thietane-ring atoms in *cis*-SO₂-DCTE and in *cis*-DCTE. L(1) and L(2) represent the lone pairs in the axial and equatorial directions, respectively.

Figure 3 shows the torsion angles around the thietane rings observed for *cis*-SO₂-DCTE and *cis*-DCTE as Newman projections, where the arrows superposed on the projected bonds indicate the directions of the bond moments assigned to the respective bonds. The direction of the lone pairs of the sulfur atom in *cis*-DCTE is deduced by assuming a tetrahedral disposition around the sulfur atom. A comparison of the two molecules reveals that the bond angles in *cis*-SO₂-DCTE deviate greatly from the corresponding angles of *cis*-DCTE. The torsion angle, A, is smaller than A′; B is larger than B′; and C smaller than C′. These deformations can be explained qualitatively in terms of dipole-dipole interactions between the ring substituents by taking into account the values of the bond moments⁶⁾ given in Fig. 3.

The crystal structure viewed along the *b* axis is illustrated in Fig. 4. The relevant intermolecular contacts are listed in Table 3. These distances are all normal except for the C(4$^{\text{i}}$)···O(2) of 3.26 Å, which is found in a pair of enantiomers. Using the calculated position of the hydrogen atom, H(1$^{\text{i}}$), attached to C(4$^{\text{i}}$), it is found that this atom is on a line connecting O(2) and C(4$^{\text{i}}$) and that the distance between O(2) and H(1$^{\text{i}}$) is 2.23 Å, much smaller than the usual van der Waals contact (2.6 Å). These facts suggest a weak C–H···O hyhrogen bond between O(2) and C(4$^{\text{i}}$). Similar hydrogen bonds have been found in the crystal of di-(*p*-chlorophenyl) sulfone.⁷⁾ The enantiomers in the crystal of *cis*-SO₂-DCTE form a dimer by this hydrogen bond, as is shown in Fig. 4.

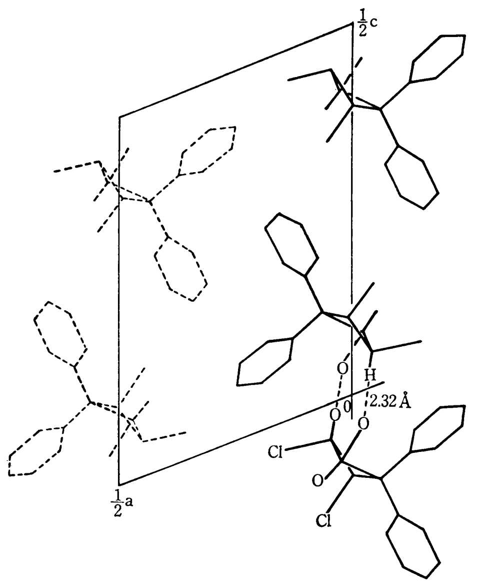

Fig. 4. Projection of the crystal structure viewed along the *b* axis.

Table 3. Relevant intermolecular contacts

S···O(2$^{\text{i}}$)	4.08 Å
S···C(13$^{\text{i}}$)	4.41
Cl(1)···O(2$^{\text{i}}$)	3.95
Cl(2)···C(24$^{\text{ii}}$)	3.60
O(2)···O(2$^{\text{i}}$)	3.74
O(2)···C(4$^{\text{i}}$)	3.26

i=$-x$, $-y$, $-z$ ii=$-x$, $1/2+y$, $1/2-z$

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References ane Notes

1) A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *Tetrahedron Lett.*, **1969**, 161.

2) S. Kumakura and T. Kodama, This Bulletin, to be published.

3) The table of the F_o-F_c values is kept as a document at the office of the Bulletin of the Chemical Society of Japan. (Document No. 7515).

4) D. E. Sands, *Z. Krist.*, **119**, 245 (1963).

5) A CNDO/2 calculation has been carried out by using a published program (J. A. Pople and D. L. Beveridge, "*Approximate Molecular Orbital Theory*," McGraw-Hill, New York, 1970) on a HITAC 8700/8800 computer at the Computer

Center of the University of Tokyo. For great savings in computer time, the phenyl groups in *cis*-SO_2–DCTE were ignored. Calculations were made for the model molecules, that is, for *cis*-2,3-dichlorothietane 1,1-dioxide taking either the (2a3e) conformation or the (2e3a), the skeletal dimension of which is assumed to be equal to that of *cis*-SO_2-DCTE (3a4e) observed in its crystalline state. The (2e3a) conformer, corresponding to the *cis*-SO_2-DCTE (3a4e), is found to be more stable by 5.1 kcal/mol than the (2a3e).

6) The values of the bond moments for *cis*-DCTE were cited from Ref. 2. The values for *cis*-SO_2-DCTE were obtained from the results of an analysis carried out on the dipole moments of *cis*- and *trans*-SO_2-DCTE molecules by using the molecular dimensions observed for the *cis*-compound in its crystalline state.

7) D. J. Sutor, *J. Chem. Soc.*, **1963**, 1105.