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

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The crystal structure of *cis*-2,2-diphenyl-3,4-dichlorothietane has been determined from three-dimensional X-ray data collected by the photographic method. The compound forms monoclinic crystals with $a=9.94(1)$, $b=12.56(1)$, $c=12.96(1)$ Å, $\beta=120.66(8)°$, and $Z=4$ in the space group of $P2_1/c$. The structure has been refined by the block-diagonal least-squares method to a final R value of 0.10, based on 1578 observed reflections. The conformation of the C–Cl bonds with respect to the thietane ring is (3e4a), consistent with that in solution derived from the dipole moments. The thietane skeleton of the compound is puckered, with a dihedral angle of 151.1°. The two C–S distances are 1.81 Å and 1.89 Å, and the average distance between the C–Cl bonds is 1.785 Å. The C–S and C–Cl bond characters are discussed in terms of the CNDO/2 method. The intermolecular S···S contact of 3.32 Å is remarkably short; it may be explained as a consequence of an attractive interaction between the dipole moments of the molecules.

cis-2,2-Diphenyl-3,4-dichlorothietane (abbreviated hereafter as *cis*-DCTE) was synthesised by the cycloaddition of thiobenzophenone to *cis*-dichloroethylene.[1] A study of the dipole moment of a series of thietane derivatives including this compound has revealed an unusually large bond moment for the C_α–Cl bond in *cis*-DCTE.[2] This X-ray study was undertaken in order to establish the geometry of the thietane ring and to shed light on the bond character of the C_α–Cl bond.

Experimental

The crystals of *cis*-2,2-diphenyl-3,4-dichlorothietane grown from an *n*-hexane solution are colorless plates. The cell dimensions and the space group were determined from oscillation and Weissenberg photographs taken around the *b* and *a* axes, using Cu$K\alpha$ radiation ($\lambda=1.542$ Å). They are listed in Table 1, together with other crystal data.

Two specimens with dimensions of $0.05\times0.05\times0.30$ mm and $0.05\times0.06\times0.20$ mm were used for the collection of the intensity data around the *b* and *a* axes respectively. Equi-inclination Weissenberg photographs were taken for *h*0*l*—*h*9*l* and for 0*kl*—7*kl*. The intensities of 1578 reflections were estimated visually and were corrected for the usual Lorentz, polarization, and spot shape factors. The absorption effect was neglected in view of the small size of the specimen.

TABLE 1. CRYSTAL DATA

Monoclinic
$a=9.94(1)$ Å
$b=12.56(1)$ Å
$c=12.96(1)$ Å
$\beta=120.66(8)°$
$V=1392$ Å^3
Formula $C_{15}H_{12}Cl_2S$, F.W.$=295.13$
$D_x=1.408$ g/cm^3
$D_m=1.41$ g/cm^3
$Z=4$
$\mu=53.45$ cm^{-1} (Cu$K\alpha$)
Space group: $P2_1/c$
(Absent spectra: *h*0*l* when *l* is odd, and 0*k*0 when *k* is odd.)

Structure Analysis

The positions of the sulfur and chlorine atoms were deduced from a three-dimensional Patterson synthesis sharpened by a factor of $\exp(B\sin^2\theta/\lambda^2)$ ($B=3.0$ Å^2). The positions of the lighter atoms except for hydrogen were determined by the routine application of the heavy-atom method. Block-diagonal least-squares refinement using anisotropic temperature factors reduced the R value to 0.10. The positions of all the hydrogen atoms were given from the suitable geometry, but were not refined. The temperature factors for hydrogen were assumed to be isotropic, with the same values as those of the carbon atoms to which the hydrogen atoms are bonded. The following weighting scheme was employed for the least-squares refinement:

$$1.0 \text{ for } |F_o|\geq 5.0$$

and

$$0.3 \text{ for } |F_o|<5.0.$$

The final difference map was flat within the range

TABLE 2. ATOMIC PARAMETERS

Positional parameters for the atoms in the asymmetric unit with their standard deviations ($\times10^4$).

	x/*a*	*y*/*b*	*z*/*c*
S	258(3)	932(2)	995(2)
Cl(1)	3647(3)	357(3)	2639(3)
Cl(2)	2500(4)	492(2)	4574(2)
C(2)	368(10)	1546(7)	2367(9)
C(3)	1073(11)	472(8)	3008(8)
C(4)	1660(12)	56(8)	2158(9)
C(11)	1494(11)	2539(7)	2827(8)
C(12)	2135(13)	2993(8)	2184(9)
C(13)	3073(13)	3897(9)	2603(10)
C(14)	3335(11)	4394(7)	3655(9)
C(15)	2707(11)	3966(8)	4294(9)
C(16)	1719(11)	3057(8)	3877(9)
C(21)	−1171(10)	1858(8)	2196(8)
C(22)	−2274(12)	2358(9)	1143(10)
C(23)	−3732(13)	2637(11)	953(13)
C(24)	−4082(11)	2390(9)	1844(12)
C(25)	−2971(14)	1885(11)	2910(13)
C(26)	−1519(12)	1594(10)	3113(10)

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Thermal parameters.

The temperature factor ($\times 10^3$) is of the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2+U_{22}b^{*2}k^2+U_{33}c^{*2}l^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+2U_{23}b^*c^*kl)]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	47	32	36	−3	50	−15
Cl (1)	48	58	97	18	87	14
Cl (2)	82	56	40	22	46	15
C (2)	28	34	59	12	56	16
C (3)	43	38	46	14	48	9
C (4)	53	38	46	23	54	0
C (11)	37	31	51	−15	62	3
C (12)	74	29	53	−43	93	−26
C (13)	61	51	77	−57	89	−3
C (14)	46	22	64	7	54	16
C (15)	46	41	47	4	41	−25
C (16)	38	38	56	−25	56	−25
C (21)	33	37	46	9	39	−14
C (22)	48	48	59	13	54	14
C (23)	43	77	99	53	32	46
C (24)	36	42	112	−19	74	−56
C (25)	59	87	105	−31	110	−46
C (26)	48	70	61	−51	82	−26

of ±0.3 eÅ^{-3}. The final positional and thermal parameters are listed in Table 2. A list of the observed and calculated structure factors is preserved by the Chemical Society of Japan.[3]

The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[4]

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

Description of the Structure and Discussion

The molecular conformation, bond lengths, bond angles, and their standard deviations are shown in Fig. 1, together with the atomic numbering scheme. The molecule is dissymmetric, and both enantiomorphs are present in the crystal.

The thietane ring is not planar. The dihedral angle (θ) between the planes, (C(2), C(3), C(4)) and (C(2), S, C(4)), is 151.1°. The C(2)–C(3)–C(4) angle and the average inner C–C–S angle are 98.1° and 87.8° respectively. The average distance of the C–C bonds in the ring is 1.565 Å. The C(2)–S of 1.89(1) Å is much longer than 1.812 Å, the mean of the 11 experimental values in the compounds containing the C–S single bonds.[5] Such lengthening has also been observed for the bonds of thietane rings in the following compounds: thietane itself (1.847(2) Å),[6] 2-isopropylidene-1,1,7,7,9,9-hexamethyl-3,5,10,11-tetrathiadispiro[3,1,3,2]undecane-8-thione (1.834(5) Å),[7] and *N*-(*p*-bromophenylcarbamoyl)thiamine anhydride (1.843(11) Å).[8] The longer bonds appear to be a common feature of such a strongly strained system. Thus, it might be unusual that the C(4)–S of 1.81(1) Å is much shorter than the C(2)–S. The C(4)–Cl of 1.78(1) Å is in agreement with the C(3)–Cl of 1.79(1) Å. This fact is in contrast to the unusually large bond moment of the C(4)–Cl.[9] In order to gain a better understanding of the C(4)–Cl and C(4)–S bond characters, a CNDO/2 calculation[10] was carried out for a model (*cis*-2,3-dichlorothietane) with skeletal dimensions assumed to be the same as those of *cis*-DCTE in the crystalline state. The lower electronic energy (−0.730 au) of the valence electrons for the C(2)–S bond of the model in comparison with that of C(4)–S (−0.660 au) may account for the shortening of the C(4)–S bond in *cis*-DCTE. A closer examination of the electronic energy matrix of the valence electrons reveals that this shortening may be attributed to increases in the π bond order and in the s character of the valence orbital of C(4). The atomic charge on Cl(1) in *cis*-DCTE is predicted to be slightly lower than that on Cl(2) (−0.121 e and −0.169 e for the respective atoms in the model), in contrast with the large value of the C(4)–Cl bond moment. The large C(4)–Cl bond dipole might be a consequence of additional contributions of the atomic polarization of component atoms in the molecule and the skeletal dipole due to the point-charge distribution. Here, it is noteworthy that a perturbation of the lowest vacant orbital to the ground-state electronic distribution could cause an increase in the ionic character of the C(2)–Cl bond (corresponding to the C(4)–Cl in *cis*-DCTE) and a decrease in that of the C(3)–Cl (corresponding to the C(3)–Cl) as a result of decreasing the electronic population in the lone pairs of sulfur.

Figure 1 shows that the conformation of *cis*-DCTE can be described as (3*e*4*a*). This conformation agrees

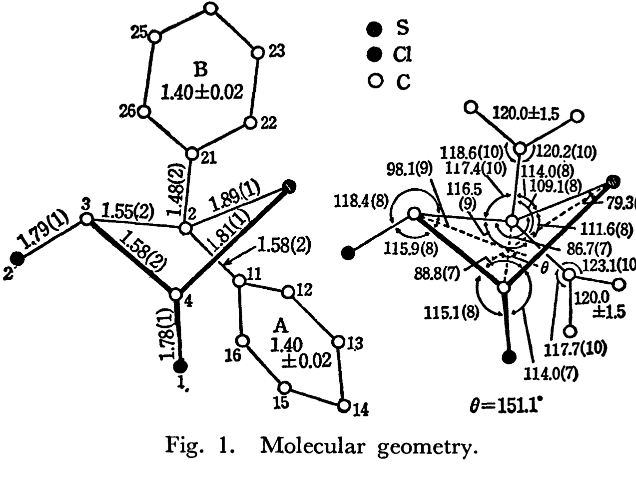

Fig. 1. Molecular geometry.

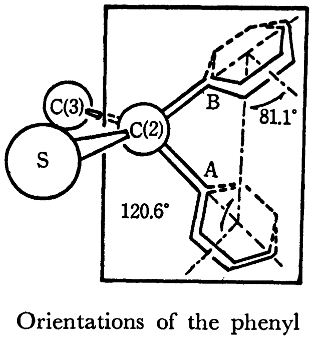

Fig. 2. Orientations of the phenyl groups.

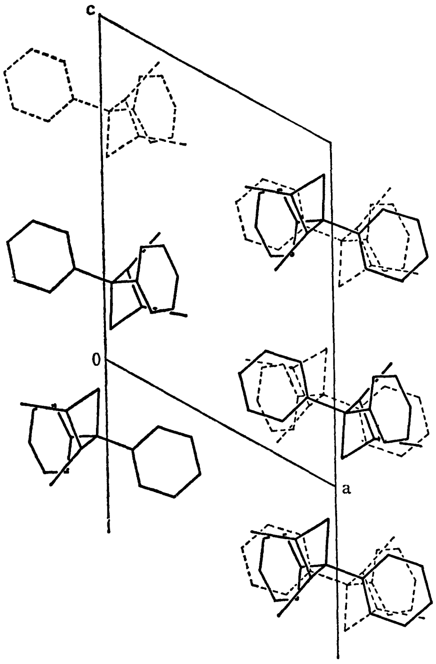

Fig. 3. Projection of the crystal structure of *cis*-DCTE viewed along the *b* axis.

TABLE 3. CLOSEST INTERMOLECULAR CONTACTS

$\mathrm{S\cdots S^{i}}$	3.32 Å
$\mathrm{S\cdots C(15^{ii})}$	3.72
$\mathrm{C(14)\cdots C(26^{ii})}$	3.45
$\mathrm{Cl(2)\cdots C(13^{iii})}$	3.75

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

with the results of the measurement of dipole moments in a benzene solution.

The phenyl groups, A and B, are practically planar. Their orientaions are shown in Fig. 2. The non-bonded distances of S$\cdots$C(22), S$\cdots$C(12), and Cl(2)$\cdots$C(16) are 3.17, 3.10, and 3.33 Å respectively. Steric interactions between these non-bonded atoms play an important role in determining the orientations of the phenyl groups.

A projection of the crystal structure viewed along the *b* axis is presented in Fig. 3. The closest intermolecular contacts are listed in Table 3. They are normal except for that between S and S$^{\rm i}$, which is significantly shorter than the usual contact of 3.70 Å.[11] The closest approach between the sulfur atoms is across a center of inversion. The dipole moments of the molecules involving these sulfurs are arranged in an antiparallel orientation. The dipole-dipole interaction energy was computed for the molecular pair related by a center of symmetry by rotating the component molecules around their respective centers of mass so as to alter their relative orientation and by placing the C–Cl and C–S bond moments on the centers of the corresponding bonds as a point dipole. The relative arrangement observed was found to be at the energy minimum, with a value of −5 kcal/mol. Therefore, the closest contact of the sulfur atoms might be explained as a consequence of attractive interaction between the molecular dipoles.

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9) Another analysis of the dipole moments of *cis*- and *trans*-DCTE was carried out by using the molecular dimensions of the *cis*-compound observed in its crystalline state; there was only an insignificant deviation from the results previously obtained—*i.e.* $\mu(\mathrm{C_\alpha{-}Cl}) = 1.9$ D and $\mu(\mathrm{C_\beta{-}Cl}) = 1.3$ D.

10) A CNDO/2 calculation was carried out on a HITAC 8700/8800 computer at the Computer Centre of the University of Tokyo by using a published program (J. A. Pople and D. J. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, 1970)) partly modified for the SP and SPD′ calculations (D. P. Santry, *J. Amer. Chem. Soc.*, **90**, 3309 (1968)). Only the SP calculation gives reasonable predictions with respect to the dipole moment and the conformation of the model. The calculated dipole moment of 2.19 D is in good agreement with the value of 2.16 D observed for *cis*-DCTE in a benzene solution.

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