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

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The crystal structure of the title compound has been determined by means of X-ray diffraction. The space group is $P\bar{1}$ with $a=11.665(4)$, $b=8.775(4)$, $c=7.092(2)$ Å, $\alpha=95.73(3)$, $\beta=84.36(3)$, $\gamma=104.90(2)$°, and $Z=2$. The structure was refined to $R=0.048$ for 1770 reflections collected on a four-circle diffractometer. The thietane ring is puckered with dihedral angles, C(2)SC(4)/C(2)C(3)C(4) and SC(2)C(3)/SC(4)C(3), of 150.1° and 149.9° respectively. The conformation of the C–Cl bonds with respect to the thietane skeleton is (3e4e), consistent with that in solution derived from the dipole moments. The average distance of the two C–Cl bonds is 1.781 Å. The C(2)–S, C(4)–S, and C(2)–C(3) bond distances are 1.872(4), 1.811(5), and 1.545(6) Å respectively; agreeing well with the corresponding bond distances observed in the *cis* isomer of the compound; however, the C(3)–C(4) of 1.506(6) Å is much shorter. The bisector of the bond angle formed by the ring substituents at each of the ring atoms is tilted out of the corresponding CCC or CCS planes within the thietane ring so as to increase the staggering of the neighboring substituents. The angle of tilt at C_β is larger than those at the C_α's. The intermolecular S···S contact of 4.080(5) Å is normal in view of the usual van der Waals radii.

Thietane is an example of four-membered ring molecules including a hetero-atom and differs from cyclobutane in the factors governing the geometry of four-membered ring systems. Recently theoretical and experimental investigations[1)] on cyclobutane have indicated that the bisector of the methylene group is tilted out of the CCC plane of which the CH_2 group forms an apex and that the tilt of the CH_2 group appears to be an essential feature of bonding in the four-membered ring. Hence, detailed molecular geometries of thietane and its derivatives are required for comparative studies of the four-membered ring systems. The geometry of thietane itself was reported by Karakida and Kuchitsu;[2)] however, the angles of tilts exhibited by the methylene groups are still unknown. Thus far, the only paper describing the tilting angle of the methylene group in thietane derivatives explicitly has been a microwave study of thietane 1-oxide by Bevan, Legon, and Millen;[3)] the complete data of the molecular structure have not yet been presented. The present paper will describe a crystal-structure analysis of *trans*-2,2-diphenyl-3,4-dichlorothietane (abbreviated hereafter as *trans*-DCTE). The influence of the orientation of the ring substituents on the ring geometry is examined by comparing the molecular structure with that of *cis*-DCTE previously reported,[4)] while the tilts of the ring substituents and the deformation of the thietane skeletons will be discussed in terms of the CNDO/2 method.

Experimental

The title compound was synthesised by a cycloaddition of thiobenzophenone to *trans*-dichloroethylene.[5)] The crystals grown from a hexane solution are colorless plates. The lattice constants and intensity data were measured on a Philips PW 1100 automatic diffractometer, using Cu $K\alpha$ radiation monochromated by a graphite plate. The ω-2θ scan technique was employed with a scan speed of 4° min^{-1} in ω. The scan-width used was $(1.0+0.35 \tan\theta)$°. A total of 1806 non-zero reflections were measured up to $\theta=78$°. 1770 reflections with $|F_o|\geq 3\sigma(|F_o|)$ were used for the analysis. Three standard reflections, monitored every two hours, showed a steady decline in intensity; at the end of data collection, the maximum reduction reached to 29%. The intensity data were put on a common scale by reference to the standard reflections. Lorentz and polarization corrections were applied, but no absorption correction was made ($\mu r \lesssim 0.5$). The crystal data are listed in Table 1.

Table 1. Crystal data

$C_{15}H_{12}Cl_2S$, F.W.$=295.13$
Triclinic, Space group: $P\bar{1}$
$a=11.665(4)$ Å
$b=\ \ 8.775(4)$ Å
$c=\ \ 7.092(2)$ Å
$\alpha=95.73(3)$°
$\beta=84.36(2)$°
$\gamma=104.90(2)$°
$V=696.02$ Å
$D_x=1.408\ \text{Mg/m}^3$
$Z=2$
$\mu(\text{Cu}\ K\alpha)=5.345\ \text{mm}^{-1}$

Structure Analysis

The Cl and S positions were obtained from a sharpened Patterson map ($B=3.0$ Å^2). The positions of the remaining non-hydrogen atoms were determined by the heavy-atom method. A difference electron-density map computed at the stage of the R value of 0.07 revealed all the H atoms in plausible positions. Subsequent block-diagonal least-squares refinements including isotropic hydrogen atoms gave the final R value of 0.048. The weighting scheme of $w=1$ if $|F_o|\geq 10.0$ and $w=0.3$ otherwise was employed. The atomic scattering factors were taken from *International Tables for X-Ray Crystallography*.[6)] The final atomic parameters are listed in Table 2. The atomic parameters for H atoms, the temperature factors for non-hydrogen atoms, and the list of observed and calculated structure factors are kept as Document No. 8149 at the Chemical Society of Japan.

The calculations were carried out on a HITAC 8700/8800 computer at the Computer Center of the

TABLE 2. FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT THERMAL PARAMETERS (B_{eq}) FOR THE NON-HYDROGEN ATOMS, WITH e.s.d.'s IN PARENTHESES

	x	y	z	$B_{eq}/Å^2$
S	3295(1)	3658(1)	4876(2)	4.85
Cl(1)	3428(1)	2040(1)	−617(2)	4.68
Cl(2)	4945(1)	1504(2)	3726(2)	5.91
C(2)	2368(3)	3256(4)	2787(5)	3.70
C(3)	3146(4)	2148(5)	1896(6)	3.92
C(4)	4213(4)	2880(5)	3011(6)	4.44
C(11)	2458(3)	4729(5)	1721(6)	3.83
C(12)	3314(4)	6135(5)	2033(7)	4.89
C(13)	3352(4)	7432(5)	1011(8)	5.77
C(14)	2546(4)	7354(6)	−286(7)	5.66
C(15)	1701(4)	5949(6)	−629(7)	5.66
C(16)	1648(4)	4641(5)	376(6)	4.92
C(21)	1067(4)	2454(5)	3335(5)	3.88
C(22)	495(4)	1040(5)	2415(6)	4.53
C(23)	−714(4)	361(6)	2925(7)	5.18
C(24)	−1317(4)	1087(6)	4319(7)	5.74
C(25)	−756(5)	2507(6)	5278(7)	6.26
C(26)	459(4)	3178(5)	4768(7)	5.17

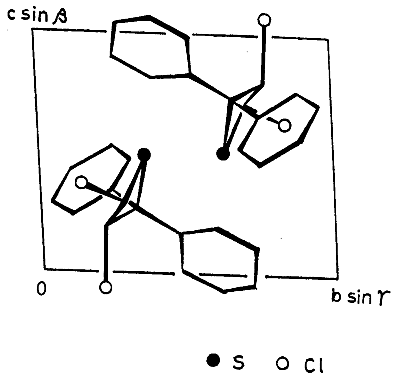

Fig. 1. A projection of the crystal structure along the a axis.

University of Tokyo and on a HITAC 8250 computer at Saitama University.

Description and Discussion of the Structure

The molecule is disymmetric, and both enantiomorphs exist in the crystal. A projection of the crystal structure viewed along the a axis is shown in Fig. 1. All the intermolecular contacts observed are normal in view of the usual van der Waals radii. The observed dipole moment of *trans*-DCTE (2.02 D) is close to that of *cis*-DCTE (2.16 D),7) although their directions in the molecules are different from each other. The closest intermolecular contact of S···S=4.080(5) Å seems to be normal in contrast to the case of *cis*-DCTE (3.32 Å).

The molecular conformation and the atomic-numbering scheme employed are shown in Fig. 2. The conformation observed can be described as (3e4e), based upon the orientations of the Cl substituents with respect to the thietane skeleton; this agrees with that deduced from the dipole-moment study.7) The two phenyl groups are planar; their orientations are illustrated in Fig. 3.

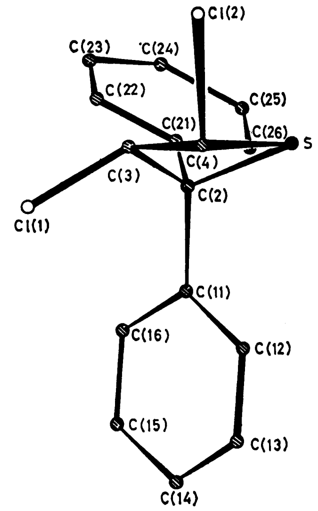

Fig. 2. The molecular conformation and the atomic numbering scheme.

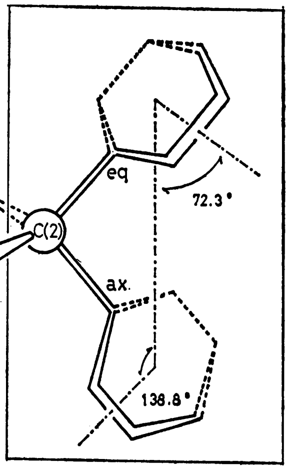

Fig. 3. Orientations of the equatorial and axial phenyl groups.

The bond lengths and angles are listed in Table 3, while the relevant non-bonded distances within the molecule are given in Table 4.

Ring Geometry. The thietane ring is puckered with the (C(2)SC(4)/C(2)C(3)C(4)) puckering angle of 29.9°(θ1) and the (SC(2)C(3)/SC(4)C(3)) puckering angle of 30.1°(θ2). All the inner angles within the thietane ring are much smaller than the values normally exhibited by the sp^3 carbon and the divalent sulfur respectively. The non-bonded S···C(3) and C(2)···C(4) distances are much smaller than the usual van der Waals contacts. The C(2)–S bond length of 1.872(4) Å is significantly longer than the C(4)–S bond length of 1.811(5) Å. The C(3)–C(4) of 1.506(6) Å is much shorter than the C(2)–C(3) (1.545(6) Å). The geometry of the thietane skeleton of *trans*-DCTE is compared with those of *cis*-DCTE, 3-cyano-3,5,7-trimethyl-6-oxo-1-thia-

TABLE 3. BOND LENGTHS (l) AND BOND ANGLES (ϕ)[a)]

Bond	l/Å	Bond	l/Å
S–C(2)	1.872(4)	C(13)–C(14)	1.364(7)
S–C(4)	1.811(5)	C(14)–C(15)	1.383(7)
C(2)–C(3)	1.545(6)	C(15)–C(16)	1.395(7)
C(3)–C(4)	1.506(6)	C(16)–C(11)	1.391(6)
C(2)–C(11)	1.536(6)	C(21)–C(22)	1.381(6)
C(2)–C(21)	1.529(6)	C(22)–C(23)	1.410(7)
C(3)–Cl(1)	1.778(4)	C(23)–C(24)	1.358(7)
C(4)–Cl(2)	1.784(5)	C(24)–C(25)	1.394(7)
C(11)–C(12)	1.387(6)	C(25)–C(26)	1.413(7)
C(12)–C(13)	1.398(7)	C(26)–C(21)	1.379(6)
Angle	**ϕ/°**	**Angle**	**ϕ/°**
C(2)SC(4)	76.6(2)	C(11)C(12)C(13)	120.2(4)
SC(2)C(3)	87.6(2)	C(12)C(13)C(14)	121.1(5)
C(2)C(3)C(4)	96.9(3)	C(13)C(14)C(15)	119.1(5)
C(3)C(4)S	91.0(3)	C(14)C(15)C(16)	120.7(5)
C(11)C(2)C(21)	110.6(3)	C(15)C(16)C(11)	120.2(4)
C(11)C(2)S	113.6(3)	C(16)C(11)C(12)	118.6(4)
C(11)C(2)C(3)	115.6(3)	C(21)C(22)C(23)	119.7(4)
C(21)C(2)S	111.9(3)	C(22)C(23)C(24)	120.3(5)
C(21)C(2)C(3)	115.9(3)	C(23)C(24)C(25)	121.0(5)
Cl(1)C(3)C(2)	117.4(3)	C(24)C(25)C(26)	118.4(5)
Cl(1)C(3)C(4)	115.5(3)	C(25)C(26)C(21)	120.6(5)
Cl(2)C(4)S	115.1(2)	C(26)C(21)C(22)	119.9(4)
Cl(2)C(4)C(3)	114.7(3)		

a) The C–H bond lengths are in the range of 0.98—1.14 Å.

TABLE 4. RELEVANT INTRAMOLECULAR NON-BONDED CONTACTS (l)

	l/Å		l/Å
S···C(3)	2.376(4)	Cl(1)···C(16)	3.442(5)
C(2)···C(4)	2.283(6)	Cl(1)···C(2)	2.841(4)
S···C(11)	2.857(4)	Cl(1)···C(4)	2.782(5)
S···C(12)	3.104(5)	Cl(1)···Cl(2)	3.824(2)
S···C(21)	2.825(4)	Cl(2)···C(3)	2.775(4)
S···C(26)	3.233(5)	Cl(2)···S	3.033(2)
Cl(1)···C(11)	3.134(4)		

5,7-diazaspiro[3.5]nonane (CTMTN),[8)] 2-(2,6-dimethylphenylimino)-3,3-dimethyl-4,4-diphenylthietane (DDDTE),[9)] and thietane itself[2)] in Table 5. The puckering angles of *trans*-DCTE are slightly larger than those of *cis*-DCTE. The values of both compounds are larger than the others listed in the table. Significant deviations between the ring geometries of *trans*- and *cis*-DCTE's are found only for the C(3)–C(4) bond distances, the C(2)–S–C(4) angles, and the non-bonded C(2)···C(4) distances. The shortening of the C(3)–C(4) bond (0.074 Å in *trans*-DCTE) brings about a decrease in the C(2)–S–C(4) angle by 2.7° and a contraction of the C(2)···C(4) distance (0.077 Å); it also increases

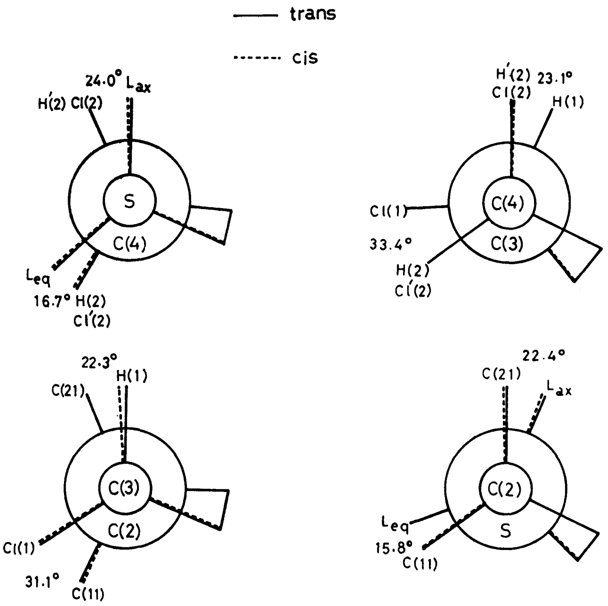

Fig. 4. Newman projections of *trans*- and *cis*-DCTE's along their ring bonds. L_{eq} and L_{ax} represent the directions of lone pairs on sulfur assumed to be in the tetrahedral disposition. H′ and Cl′ mean the atoms in the *cis* isomer.

TABLE 5. A COMPARISON OF RING-GEOMETRIES IN *cis*- AND *trans*-DCTE'S, CTMTN, DDDTE, AND THIETANE

	cis-DCTE	*trans*-DCTE	CTMTN[a)]	DDDTE[b)]	Thietane
Bond length l/Å					
S–C(2)	1.89(1)	1.872(4)	1.844(3)	1.868(5)	1.846(2)
S–C(4)	1.81(1)	1.811(5)	1.817(3)	1.777(5)	1.846(2)
C(2)–C(3)	1.55(2)	1.545(6)	1.597(4)	1.591(7)	1.548(3)
C(3)–C(4)	1.58(2)	1.506(6)	1.541(4)	1.524(7)	1.548(3)
Non-bonded distance l/Å					
S···C(3)	2.38(1)	2.376(4)	2.432	2.455	2.421(3)
C(2)···C(4)	2.36(2)	2.283(6)	2.331	2.270	2.294(6)
Bond angle ϕ/°					
C(2)SC(4)	79.3(5)	76.6(2)	79.0(1)	77.0(2)	76.8(3)
SC(2)C(3)	86.7(7)	87.6(2)	89.6(2)	90.1(3)	90.6(3)
C(2)C(3)C(4)	98.1(9)	96.9(3)	95.8(2)	93.5(4)	95.6(4)
SC(4)C(3)	88.8(7)	91.0(3)	92.6(2)	95.8(3)	90.6(3)
Puckering angle ϕ/°					
$\theta 1$	28.9	29.9	18.3	20.0	26
$\theta 2$	28.1	30.1	18.7	21.2	

a) The C(2) is defined as the C_α linked to the spiro substituent. b) The C(2) is defined as the C_α linked to two phenyl groups.

TABLE 6. TILTING (γ), BENDING (δ), AND TWISTING (χ) ANGLES OF RING-SUBSTITUENTS IN *cis*- AND *trans*-DCTE'S AND CTMTN

	cis-DCTE			*trans*-DCTE			CTMTN		
	C(2)	C(3)	C(4)	C(2)	C(3)	C(4)	C(2)	C(3)	C(4)
$\gamma/°$	1.2	5.0	0.5	0.5	4.4	1.4	0.5	4.8	1.1
$\delta/°$	4.7	0.5	2.0	3.5	4.1	0.9	2.9	0.7	3.1
$\chi/°$	0.7	1.4	0.6	0.8	2.1	1.7	2.6	0.0	1.1

the puckering angle, $\theta 2$. Newman projections of the ring substituents in *trans*-DCTE are shown in Fig. 4, where those of *cis*-DCTE are superimposed. There are no significant deviations between them, although the *trans* arrangement of the substituted Cl atoms with the Cl(1)···Cl(2) contact of 3.824 Å seems to be stereochemically more favorable than that of the *cis* (3.25 Å). These observations indicate that the shortening of the C(3)–C(4) bond in *trans*-DCTE is a consequence of releasing a steric interaction between the Cl substituents on going from *cis* to *trans*. Furthermore, this C(3)–C(4) bond length is significantly shorter than the usual value for C(sp^3)–C(sp^3). This provides an interesting contrast to the longer bond observed for most cases of the four-membered ring systems, for example, thietane (C–C=1.548(3) Å)[2)] and cyclobutane (C–C=1.548(3) Å).[10)] A CNDO/2 calculation of the model molecules for *cis*- and *trans*-DCTE's[11)] shows that the observed contraction of the C(3)–C(4) bond in the *trans* isomer may be attributed not only to the alleviation of steric hindrance between the Cl substituents, but also to an increased contribution of the 2s AO on C(4) to the C(3)–C(4) bonding. The C(2)–C(3) bond length in *trans*-DCTE is in good agreement with those in *cis*-DCTE, thietane, and CTMTN. The S–C(2) bond lengths in *cis*- and *trans*-DCTE's may be compared with the value in DDDTE, but they are longer than that in thietane. The carbon atoms at the ends of the longer C–S bonds are linked to two phenyl groups. These longer bonds may be a consequence of the lengthening effect due to the two phenyl groups at C_α. The C(4)–S bond length in *trans*-DCTE is in good agreement with those in *cis*-DCTE and CTMTN, but significantly shorter than that in thietane.

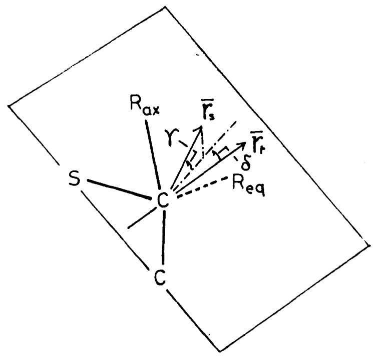

Fig. 5. A definition of the tilting, bending, and twisting angles (γ,δ,χ) exhibited by the ring substitutens. R_{ax} and R_{eq} represent the axial and equatorial substituents, respectively. The vectors, $\bar{r}_s$ and $\bar{r}_r$, are the bisectors of R_{ax}–C–R_{eq} and S–C_α–C_β angles, respectively. The angle, χ, stands for the angle of anticlockwise rotation of the $R_{ax}CR_{eq}$ plane around the vector $\bar{r}_s$.

Orientation of the Ring Substituents. The tilting, bending, and twisting angles (γ,δ,χ) exhibited by the ring substituents are defined as in Fig. 5. Table 6 lists these angles in *cis*- and *trans*-DCTE's and in CTMTN. Their e.s.d.'s are in the range of 0.3°—2°. It is commonly observed for all the compounds that the γ values are positive and that the γ at the C_β is larger than those at the C_α's. Although the puckering angles of *cis*- and *trans*-DCTE's are much larger than those of CTMTN, the γ values at the C_β's in the compounds are approximately equal to each other and agree well with the value of 4° predicted by Pasternak *et al.*[1c)] based upon a geometrical model of cyclobutane composed of sp^3 carbons at the puckering angle of 30°. The γ's at the C_α's with the substituents are, however, much smaller than the predicted value. The CNDO/2 energies (E_t) for thietane and the model molecules assumed for *cis*- and *trans*-DCTE's[12)] were calculated by varying the tilting angles, γ_1 and γ_2, at C_α and C_β in the range of 0°—6°. The values of γ_1 and γ_2 giving a minimum E_t value for thietane were found to be 1.5° and 3° respectively, while those for the model molecule of *cis*-DCTE were 1° and 5° respectively. The calculated values of these angles approximately agree with those observed for *cis*-DCTE and CTMTN. The tilting of the ring substituents is mainly caused by the resonance energy[13)] in the electronic energy calculated; hence, it may be due to the nature of bonding in the thietane ring. On the other hand, the calculated values of γ_1 and γ_2 for the *trans* isomer were about 2°. Both these angles are positive, in accordance with those observed for *trans*-DCTE; however, this relative magnitude does not agree with that observed.

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11) In order to save computer time, the phenyl groups in *cis*- and *trans*-DCTE's were ignored. Calculations were made for the model molecules, *cis*- and *trans*-2,3-dichlorothietanes, the skeletal dimensions of which are assumed to be equal to those of *cis*- and *trans*-DCTE's. The dipole moments calculated by employing the (*sp*) basis sets are 2.19 D and 1.83 D, which are in good agreement with the observed values of the corresponding DCTE's.

12) The skeletal geometry of thietane observed was employed in the CNDO/2 calculations of thietane itself and of *cis*- and *trans*-2,3-dichlorothietanes. The tilting angles of the methylene groups calculated for thietane agree well those obtained by an *ab initio* calculation (P. N. Skancke, G. Fogarasi, and J. E. Boggs, *J. Mol. Struct.*, **52**, 259 (1980)).

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