Jeffrey, G. A., Koch, H. P. & Nyburg, S. C. (1948). *J. Chem. Soc.* pp. 1118–1122.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
North, A. M., Pethrick, R. A. & Wilson, A. D. (1974). *Spectrochim. Acta Part A*, **30**, 1317–1327.
Schmonsees, W. (1974). Thesis, Ch. 1 and Appendix I, Wayne State Univ.
Taylor, I. F. & Amma, E. L. (1975). *Acta Cryst.* B**31**, 598–600.
Zalkin, A. (1974). *A Fortran Program for the Calculation of Idealized Hydrogen Positions*, local program version.

Acta Cryst. (1979). B**35**, 203–205

The Structure of *p,p'*-Dichlorodiphenyl Disulphide [Bis(4-chlorophenyl) Disulphide]

By M. R. Spirlet, G. Van den Bossche, O. Dideberg and L. Dupont

Laboratoire de Cristallographie, Institute de Physique B5, Université de Liège au Sart Tilman, B-4000 Liège, Belgium

(*Received* 12 *May* 1978; *accepted* 26 *September* 1978)

Abstract. $C_{12}H_8Cl_2S_2$, orthorhombic, *Pbcn*, a = 7·659 (2), b = 5·973 (2), c = 27·175 (5) Å, Z = 4. The structure was determined by three-dimensional X-ray analysis. Positional and temperature-factor parameters have been refined for all atoms by Fourier and block-diagonal least-squares methods to a final R value of 0·0479 for 988 observed reflections. The molecule, which has a non-planar conformation is centred on the twofold axis. The intramolecular S–S and Cl–C distances are respectively 2·039 (1) and 1·744 (3) Å. The planes of the benzene rings make an angle of 126·5° and the value of the dihedral angle C–S–S/S–S–C is 103·6°.

Introduction. The structure determination of the title compound was undertaken in order to make a comparative study of molecular conformations of diphenyl disulphur analogues and derivatives whose general formula may be written $Y\text{–}C_6H_4\text{–}X\text{–}X\text{–}C_6H_4\text{–}Y$ with X = S, Se, Te and Y = H, CH_3, Br, Cl.

Crystal structures for only seven compounds in this series have been previously determined: Ph–S–S–Ph (Lee & Bryant, 1969; Sacerdoti & Gilli, 1975), Br–Ph–S–S–Ph–Br (Toussaint, 1945), CH_3–Ph–S–S–Ph–CH_3 (Vorontsova, Zvonkova & Zhdanov, 1967), Ph–Se–Se–Ph (Marsh, 1952), Cl–Ph–Se–Se–Ph–Cl (Kruse, Marsh & McCullough, 1957), Ph–Te–Te–Ph (Llabrès, Dideberg & Dupont, 1972), Cl–Ph–Te–Te–Ph–Cl (Kruse, Marsh & McCullough, 1957). Cl–Ph–S–S–Ph–Cl does not appear to be isostructural with any of these compounds.

Single crystals were prepared by room-temperature evaporation of solutions of *p,p'*-dichlorodiphenyl disulphide in *n*-hexane. Preliminary Weissenberg and precession photographs displayed systematic absences ($0kl$ absent for k odd, $h0l$ for l odd and $hk0$ for $h + k$ odd) and symmetry uniquely consistent with the orthorhombic space group *Pbcn*. The cell dimensions were established by the least-squares method from angle data recorded at 293 ± 1 K for 12 reflections (Cu $K\alpha$, λ = 1·5418 Å). Integrated intensities of a total of 1098 unique reflections were measured with a four-circle Hilger diffractometer. The intensities for all observed reflections were corrected for Lorentz and polarization effects. No corrections were made for absorption or extinction. The structure was solved by the direct method using the program *MULTAN* described by Main, Lessinger, Woolfson, Germain & Declercq (1977). The E map showed well resolved maxima for all atoms other than H.

The structure was refined by block-diagonal least-squares methods (Ahmed, Hall, Pippy & Huber, 1966) on the 988 reflections for which $I > 2\sigma(I)$. In the first stages Cl, S and C atom parameters, including anisotropic temperature factors for Cl and S, were refined to an R value of 0·0773. Then H atoms were included in calculated positions assuming C–H bond lengths of 1·087 Å. Refinement was completed varying atomic coordinates for all atoms, anisotropic temperature

Table 1. *Atomic positional parameters with standard deviations in p,p'-dichlorodiphenyl disulphide*

	x	y	z
S	0·6010 (1)	0·2884 (1)	0·2255 (1)
C(1)	0·5369 (4)	0·1119 (5)	0·1760 (1)
C(2)	0·5824 (4)	0·1847 (6)	0·1294 (1)
C(3)	0·5479 (5)	0·0536 (7)	0·0887 (1)
C(4)	0·4649 (5)	−0·1494 (6)	0·0953 (1)
C(5)	0·4165 (4)	−0·2229 (6)	0·1411 (1)
C(6)	0·4536 (4)	−0·0932 (5)	0·1820 (1)
Cl	0·4234 (2)	−0·3193 (2)	0·0444 (1)

0567-7408/79/010203-03$01.00

factors for Cl, S and C atoms and isotropic temperature factors for H atoms. A Cruickshank (1961) type of weighting scheme was used. The final value of the conventional discrepancy factor R is 0·0479 for the 988 observed reflections. The final atomic coordinates are given in Table 1.*

Discussion. In the unit cell, the twofold axis parallel to b is common to the molecule and the crystal.

The molecular structure is shown in Fig. 1, each atom being represented by its 50% probability ellipsoid (*ORTEP* II, Johnson, 1971). Bond lengths, bond angles and packing distances together with their standard deviations are given in Tables 2, 3 and 4.

The equations of the best least-squares planes through the benzene rings calculated by the method of Schomaker, Waser, Marsh & Bergman (1959) are reported in Table 5. Distances of atoms from the planes show that the benzene rings are planar within 0·004 Å (standard deviation maximum).

In Table 6, some characteristic results are compared with those reported for diphenyl disulphide, dibromodiphenyl disulphide and ditolyl disulphide.

Interatomic distances S–S^{i} (2·039 Å) and S–C(1) (1·778 Å) in Cl–Ph–S–S–Ph–Cl compare favourably with the values found in diphenyl disulphide. The larger values, 2·15 Å and 2·07 Å, reported for the S–S^{i} distance in Br–Ph–S–S–Ph–Br and CH_3–Ph–S–S–Ph–CH_3, are apparently due to the inaccuracy of the data in these structure determinations.

Comparison of the dihedral angles C(1)–S–S^{i}/S–S^{i}–C(1^{i}) and of the angles of relative rotation of the different molecular planes shows that the *para* substitution on the diphenyl disulphide molecule considerably changes its conformation. CH_3–Ph–S–S–Ph–CH_3 appears to adopt the most stable conformation since a dihedral angle C–S–S^{i}/S–S^{i}–C^{i} of 90°

Table 2. *Bond lengths* (Å) *with standard deviations in parentheses*

The superscript (i) refers to the coordinates $1-x$, y, $0{\cdot}5-z$ relative to the reference set in Table 1.

S–S^{i}	2·039 (1)	C(4)–C(5)	1·372 (5)
S–C(1)	1·778 (3)	C(5)–C(6)	1·384 (4)
C(1)–C(2)	1·385 (4)	C(6)–C(1)	1·391 (4)
C(2)–C(3)	1·381 (6)	Cl–C(4)	1·744 (3)
C(3)–C(4)	1·381 (5)		

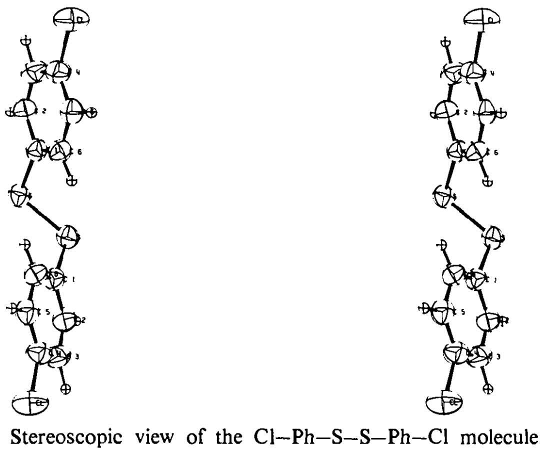

Fig. 1. Stereoscopic view of the Cl–Ph–S–S–Ph–Cl molecule looking down the crystallographic twofold axis.

Table 3. *Bond angles* (°) *with standard deviations in parentheses*

C(1)–S–S^{i}	106·5 (1)	C(4)–C(5)–C(6)	119·6 (3)
S–C(1)–C(2)	115·9 (2)	C(5)–C(6)–C(1)	119·6 (3)
S–C(1)–C(6)	124·1 (2)	C(6)–C(1)–C(2)	119·8 (3)
C(1)–C(2)–C(3)	120·5 (3)	Cl–C(4)–C(3)	119·5 (3)
C(2)–C(3)–C(4)	118·8 (3)	Cl–C(4)–C(5)	118·9 (3)
C(3)–C(4)–C(5)	121·6 (3)		

Table 4. *Packing distances* (Å): *shortest intermolecular* S···S, C···S, C···C, *and* Cl···Cl *distances* (Å) *with standard deviations in parentheses*

Key to symmetry operations relating designated atoms to reference atoms at (x,y,z):

(ii)	$\frac{3}{2}-x,$	$\frac{1}{2}+y,$	z	(v)	$\frac{1}{2}-x,$	$-\frac{1}{2}+y,$	z
(iii)	$\frac{1}{2}-x,$	$\frac{1}{2}+y,$	z	(vi)	$1-x,$	$-1-y,$	$-z$
(iv)	$x,$	$1-y,$	z				

S···S^{ii}	3·759 (1)	C(2)···C(4^{ii})	3·723 (5)
S···C(1^{ii})	3·638 (3)	C(2)···C(5^{iv})	3·773 (5)
S···C(6^{ii})	3·680 (3)	C(5)···C(6^{v})	3·763 (5)
C(1)···C(5^{iii})	3·732 (4)	Cl···Cl^{vi}	3·444 (1)
C(2)···C(3^{ii})	3·754 (5)	Cl···Cl^{v}	3·997 (2)

Table 5. *Best least-squares planes*

Plane I: C(1), C(2), C(3), C(4), C(5), C(6)

$-0{\cdot}8875x+0{\cdot}4504y-0{\cdot}0972z+3{\cdot}8106=0 \quad \chi^2=13{\cdot}62$

Plane II: C(1^{i}), C(2^{i}), C(3^{i}), C(4^{i}), C(5^{i}), C(6^{i})

$-0{\cdot}8875x-0{\cdot}4504y-0{\cdot}0972z+4{\cdot}3072=0 \quad \chi^2=13{\cdot}62$

Distances (Å) of atoms from planes

	Distance ($\times 10^4$)	$\sigma(\times 10^4)$		Distance ($\times 10^4$)	$\sigma(\times 10^4)$
C(1)	−27	30	C(4)	−32	35
C(2)	69	34	C(5)	73	33
C(3)	−40	40	C(6)	−43	32

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33929 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 6. *Characteristic results compared with those for diphenyl disulphide, dibromophenyl disulphide and ditolyl disulphide*

	Ph–S–S–Ph[a]	Cl–Ph–S–S–Ph–Cl[b]	Br–Ph–S–S–Ph–Br[c]*	CH$_3$–Ph–S–S–Ph–CH$_3$[d]
Bond lengths (Å)				
S–S^{i}	2·023	2·039	2·15	2·07
S–C(1)	1·788†	1·778	1·80	1·79*
Bond angles (°)				
S–C(1)–C(2)	115·4†	115·9	–	117†
S–C(1)–C(6)	124·4†	124·1	–	121·7†
C(1)–S–S^{i}	106·2†	106·5	107	106·5†
Dihedral angle (°)				
C(1)–S–S^{i}/S–S^{i}–C(1^{i})	83·8	103·6	–	90·2
Angle of relative rotation of benzene rings (°)	102·7	126·5	–	94·0
Angle of rotation of the benzene ring relative to the C(1)–S–S^{i} plane (°)	9·0†	40·0	–	13·5†

(*a*) Sacerdoti & Gilli (1975). (*b*) This work. (*c*) Toussaint (1945). (*d*) Vorontsova, Zvonkova & Zhdanov (1967).

* Two-dimensional structure analysis.
† Average value, the molecule having no symmetry element.

corresponds to a minimum repulsion between the lone pairs of electrons on the adjacent S atoms (Pauling, 1949). The larger value of the dihedral angle in Cl–Ph–S–S–Ph–Cl would result from some displacement of these lone pairs of electrons. We also assume that partial conjugation of the S atom with the benzene ring with which it is linked is responsible for the deformation of the exterior angles at C(1) [S–C(1)–C(2) = 115·90°; S–C(1)–C(6) = 124·14°] in *p,p′*-dichlorodiphenyl disulphide as well as in diphenyl disulphide.

No intermolecular distance (Table 4) less than 3·40 Å between non-bonded atoms was found in *p,p′*-dichlorodiphenyl disulphide. Hence it appears that only van der Waals forces are present between molecules in the crystal.

The distance between Cl atoms of two different molecules packed along *c* (Cl···Cl = 3·444 Å) is shorter than the sum of the van der Waals radii (3·60 Å). Repulsion between Cl atoms explains the cleavage along the (001) plane. Br–Ph–S–S–Ph–Br crystals also show a (001) cleavage plane (Toussaint, 1945).

The authors wish to thank Professor J. Toussaint for his interest in this work, Mr M. Vermeire for technical assistance and Mr J. P. Piette (Laboratoire de Chimie Organique de l'Université de Liège, Service du Professeur Renson) for preparing the *p,p′*-dichlorodiphenyl disulphide.

References

AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. National Research Council, Ottawa, Canada.

CRUICKSHANK, D. W. J. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, edited by R. PEPINSKY, J. M. ROBERTSON & J. C. SPEAKMAN. Oxford: Pergamon Press.

JOHNSON, C. K. (1971). *ORTEP* II. Report ORNL-3794 revised. Oak Ridge National Laboratory, Tennessee.

KRUSE, F. M., MARSH, R. E. & MCCULLOUGH, J. D. (1957). *Acta Cryst.* **10**, 201–209.

LEE, J. D. & BRYANT, M. W. R. (1969). *Acta Cryst.* **B25**, 2094–2101.

LLABRÈS, G., DIDEBERG, O. & DUPONT, L. (1972). *Acta Cryst.* **B28**, 2438–2444.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1977). *MULTAN 77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univ. of York, England.

MARSH, R. E. (1952). *Acta Cryst.* **5**, 458–462.

PAULING, L. (1949). *Proc. Natl Acad. Sci. USA*, **35**, 495–510.

SACERDOTI, M. & GILLI, G. (1975). *Acta Cryst.* **B31**, 327–329.

SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600–604.

TOUSSAINT, J. (1945). *Bull. Soc. Chim. Belg.* **54**, 346–359.

VORONTSOVA, L. G., ZVONKOVA, Z. V. & ZHDANOV, G. S. (1967). *Sov. Phys. Dokl.* **12**, 7–10.