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o,o′-Dibromodibenzyl [1,2-Bis(2-bromophenyl)ethane]

BY EUGENE R. COREY

Department of Chemistry, University of Missouri–St. Louis, St. Louis, Missouri 63121, *USA*

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Abstract. $C_{14}H_{12}Br_2$, $M_r = 340\cdot1$, orthorhombic, *Pbca*, $a = 14\cdot628\ (7)$, $b = 13\cdot234\ (6)$, $c = 6\cdot668\ (3)$ Å; $Z = 4$, $D_m = 1\cdot73\ (2)$, $D_c = 1\cdot75$ Mg m^{-3}; $U = 1291\ (1)$ Å^3; μ(Mo $K\alpha$) = 6·62 mm^{-1}. Molecules of *o,o′*-dibromodibenzyl are located on crystallographically required centers of symmetry. The phenyl moieties are *trans* and parallel to one another but not coplanar. The dihedral angle between the plane of the C atoms of the phenyl substituent and the plane of the three central bonds of the molecule is 89°.

Introduction. During the course of structural investigations of 10,11-dihydrodibenzosilepin derivatives (Corey, Corey & Glick, 1977), the crystal structure of *o,o′*-dibromodibenzyl has been determined. This 1,2-disubstituted ethane is the organic precursor for the synthesis of dibenzosilepin compounds (Corey & Farrell, 1978) and is the first *ortho*-substituted dibenzyl whose crystal structure has been studied.

Solid-state structures of three related disubstituted ethanes have been reported: dibenzyl (Jeffrey, 1947, and references therein); 4,4′-dimethyldibenzyl (Brown, 1954); and 1,2-diphenyltetrafluoroethane (Cruickshank, Jeffrey & Nyburg, 1959). Preliminary X-ray crystallographic data and space-group symmetry arguments have been applied to a series of diethyldibenzyl compounds (Carlisle & Crowfoot, 1941) and divinyldibenzyl compounds (Jeffrey, Koch & Nyburg, 1948). The structure of the aromatic π-complex of dibenzyl and $AgClO_4$ has also been studied (Taylor & Amma, 1975).

An approximately spherical crystal with maximum and minimum radii 0·25 and 0·29 mm was mounted on a Syntex $P2_1$ diffractometer and a total of 1362 intensities were counted using Mo $K\alpha$ (graphite monochromator) radiation ($\lambda = 0\cdot71069$ Å). All reflections with $2\theta \le 50°$ were measured with a θ–2θ scan speed of 2·0° min^{-1}. Backgrounds were measured at each end of the scan (2θ scan range: 2θ Mo $K\alpha_1 - 1\cdot0°$ to 2θ Mo $K\alpha_2 + 1\cdot0°$) for a total time equal to one half the scan time. During data collection, the intensities of three standard reflections were measured every 97 reflections with no significant variation in intensity observed. The data were reduced to F^2 and $\sigma(F^2)$ and a spherical absorption correction was made [μ(Mo $K\alpha$) = 6·62 mm^{-1}] (Schmonsees, 1974). Standard deviations were assigned as follows: $\sigma(I) = [\sigma_{\text{counter}}(I)^2 + (0\cdot04I)^2]^{1/2}$, where $\sigma_{\text{counter}} = (I + K^2B)^{1/2}$, I = net intensity, B = total background counts and K = ratio of scan time to background time. The 410 data with $F_o^2 \ge 3\sigma(F_o^2)$ were used in the structure solution and refinement.

Half a molecule constitutes the asymmetric unit of the structure; the Br-atom positional coordinates were determined from a Patterson map. The remaining nonhydrogen atoms were located from an electron density map calculated with phases determined by the Br atom. Atomic scattering factors and both anomalous-dispersion components were taken from *International Tables for X-ray Crystallography* (1974). Least-squares refinement (Busing, Martin & Levy, 1962) was completed with anisotropic thermal parameters for nonhydrogen atoms and inclusion of H atoms at fixed positions (Zalkin, 1974) with fixed isotropic thermal parameters; the H atoms were relocated after each cycle of refinement with C—H distances of 1·0 Å. The largest positional parameter and thermal parameter shifts in the final cycle of refinement were 10% and 25% of their standard deviations, respectively. The final discrepancy values were $R_1 = \sum ||F_o| - |F_c||/\sum |F_o| = 0\cdot050$ and $R_2 = [\sum (w|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0\cdot059$; the error of fit was 2·42. The highest residual electron density in the final difference map was 0·39 e Å^{-3}. Final positional parameters are given in Table 1.*

Discussion. A perspective drawing of the structure is given in Fig. 1 with associated bond distances (Å) and angles (°) (Johnson, 1965; Busing, Martin & Levy, 1964). The molecule possesses a crystallographically required center of symmetry located at the midpoint of the ethano C—C bond. The phenyl moieties are *trans* and parallel to one another but not coplanar with one

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* Lists of anisotropic thermal parameters for the nonhydrogen atoms, fractional coordinates for the hydrogen atoms and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33909 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final atomic coordinates* ($\times 10^3$) *for o,o'-dibromodibenzyl with e.s.d.'s in parentheses*

	x	*y*	*z*
Br	83·0 (1)	152·4 (1)	126·2 (3)
C(1)	−12 (1)	−20 (1)	399 (2)
C(2)	71 (1)	−48 (1)	276 (2)
C(3)	105 (1)	−145 (1)	291 (2)
C(4)	182 (1)	−179 (1)	190 (2)
C(5)	225 (1)	−109 (1)	62 (2)
C(6)	195 (1)	−13 (1)	45 (2)
C(7)	120 (1)	15 (1)	154 (2)

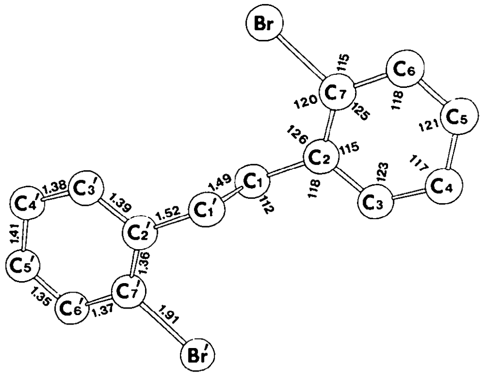

Fig. 1. A perspective drawing of *o,o'*-dibromodibenzyl. Estimated standard deviations: bond angles, 1°; C–C distances, 0·02 Å; C–Br distance, 0·01 Å.

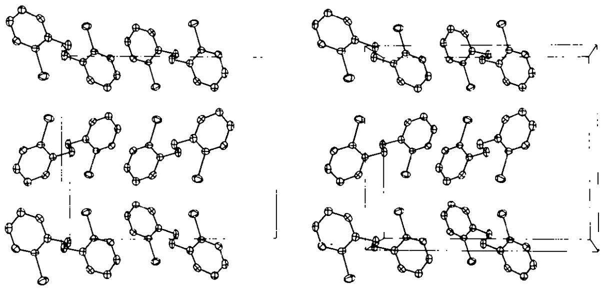

Fig. 2. Packing of the *o,o'*-dibromodibenzyl molecules viewed down *c*; atoms are drawn with 25% probability anisotropic thermal ellipsoids. The *a* axis is across the page.

another. This antiperiplanar conformation has been found for each of the four related compounds that have been studied in the solid state; in each case the asymmetric unit of the structure is half a molecule located about a crystallographically required center of symmetry. Preference for the observed conformation has been demonstrated by potential-energy calculations (Bereznitskaya, Kitaigorodskii, Kozhin, Kozlova & Mirskaya, 1972) and the same conformation has been used for interpretation of infrared and Raman spectra in the solid state (Chiu, Huang & Chia, 1972; North, Pethrick & Wilson, 1974). Rotational isomerism in solution (Chiu, Huang & Chia, 1972; North, Pethrick & Wilson, 1974) and in the gas phase (Ivanov, Pojarlieff & Tyutyulkov, 1976) indicates the presence of *gauche* rotamers of dibenzyl and its derivatives.

The plane of the C atoms in the phenyl substituent of *o,o'*-dibromodibenzyl forms a dihedral angle of 89° (perpendicular within experimental error) to the best plane of the central bonds of the molecule. Values for the analogous angle in related structures are 85°, 1,2-diphenyltetrafluoroethane (Cruickshank, Jeffrey & Nyburg, 1959); 73°, dibenzyl (Jeffrey, 1947); 72°, 4,4'-dimethyldibenzyl (Brown, 1954). The perpendicular orientation of phenyl groups in the title compound is probably favored because of the *ortho* substituents. The packing of the molecules is illustrated in Fig. 2. The shortest intermolecular distance that involves a nonhydrogen atom and a H atom is 2·96 Å between C(6) and the H atom on C(6) related by the screw axis in the *c* direction. The largest displacement of an atom from the best plane of the eight atoms in the asymmetric unit [C(1)—C(7) and Br] is 0·03 Å.

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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

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Abstract. $C_{12}H_8Cl_2S_2$, orthorhombic, *Pbcn*, $a = 7{\cdot}659$ (2), $b = 5{\cdot}973$ (2), $c = 27{\cdot}175$ (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 $Y—C_6H_4—X—X—C_6H_4—Y$ 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 (0*kl* absent for *k* odd, *h*0*l* for *l* odd and *hk*0 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 $K\alpha$, $\lambda = 1{\cdot}5418$ 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)

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