The Structure of 3:3′-Dichloro-4:4′-dihydroxydiphenylmethane

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The structure of 3:3′-dichloro-4:4′-dihydroxydiphenylmethane is of interest on account of its relationship to phenol-formaldehyde polymers. It crystallizes with four molecules in a monoclinic cell with $a = 22\cdot3$, $b = 4\cdot93$, $c = 11\cdot76$ Å; $\beta = 112°\ 36'$. The space group is $C2/c$ and the molecules accordingly lie in special positions on the twofold axes. The projection down [010] was solved with the aid of a Patterson synthesis and refined by successive two-dimensional Fourier syntheses. The projection down [001] was then solved by trial-and-error methods and refined by two dimensional Fourier syntheses. The structure determination is not sufficiently accurate for a discussion of bond lengths, but it establishes the form of the molecule and shows that the C–C–C valency angle at the methylene group is appreciably in excess of the tetrahedral angle. The packing of the molecules is discussed and correlated with the cleavage of the crystal.

Introduction

The structure of the important group of high polymers prepared by the condensation of phenol and its derivatives with formaldehyde has not hitherto been investigated in any detail by X-ray methods. The phenol-formaldehyde resins themselves are liquids or amorphous solids in which no crystalline order can be induced, and therefore only radial distribution functions can be obtained from them by X-ray analysis. The interpretation of such results is hardly likely to be unique in the absence of some *a priori* knowledge of the geometry of the molecules, and it is therefore of interest to determine the structure of related low-molecular-weight compounds which can be crystallized. The information so obtained is relevant not only to the interpretation of the radial distribution functions, but also in purely chemical considerations of steric hindrance and cross-linking mechanisms in the resins.

A series of nine dihydroxydiphenylmethanes containing various substituents was kindly supplied for crystallographic study by Dr N. J. L. Megson and Mr S. R. Finn. Preliminary crystallographic data (unit cell and probable space group) were determined on the eight of these compounds which could be obtained in the form of suitable crystals. They have already been reported (Finn, Megson & Whittaker, 1950), together with the general findings on the form of the molecule of 3:3′-dichloro-4:4′-dihydroxydiphenylmethane which was chosen for the first detailed analysis. The present paper describes the structure determination in detail.

Description of the material

The material as received had been crystallized from a mixture of ether and petroleum, but was in the form of colourless polycrystalline aggregates. It was recrystallized by slow evaporation from aqueous alcohol and then gave fairly short monoclinic needles and laths without definite terminal faces but with cleavage faces perpendicular to the needle axis. The forms present were {100} (bright) and {001} (drusy) with the cleavage on {010} and also on {001}. The angle β was found to be $112°\ 36'$ by measurement on the optical goniometer. The melting point of the material is 104° C. The melting point of the recrystallized material agreed with that of the material as received, and its identity with the melting point of a mixture of the two served to confirm that solvation had not occurred during recrystallization.

Unit cell and space group

Oscillation photographs about each axis in turn showed the unit cell to have the dimensions

$$a = 22\cdot3,\ b = 4\cdot93,\ c = 11\cdot76 \text{ Å};\ \beta = 112°\ 36'.$$

Density (by flotation) = 1·51 g.cm.$^{-3}$. Number of molecules per unit cell = 4. The theoretical density for 4 molecules per cell is 1·50 g.cm.$^{-3}$.

Indexing of the photographs by standard methods showed that reflexions of the type hkl were present only with $(h+k)$ even and those of the type $h0l$ were present only with h and l both even. Hence possible space groups are Cc and $C2/c$. Tests were performed for both pyro- and piezo-electricity in an attempt to distinguish between these space groups, but both tests gave negative results. The space group was therefore assumed to be $C2/c$. The statistical tests for symmetry (Howells, Phillips & Rogers, 1950; Wilson, 1950) had not been published at this stage of the work, and the space group assumed was considered to be substantiated when it was found possible to refine the structure based on this assumption. After the completion of the structure analysis the statistical tests were applied in order to obtain further confirmation, but the results were inconclusive. The quantity $\langle I \rangle / \Sigma$ for reflexions $0k0$ should have the value 2 or 1

according as a twofold axis is present or absent. The value found was 1·3, but as only three reflexions were available for calculating it and the standard deviation of the value was 0·6 the result is not significant. The distribution test for centrosymmetry was also applied to the $h0l$ zone. The result is shown in Fig. 1, and it
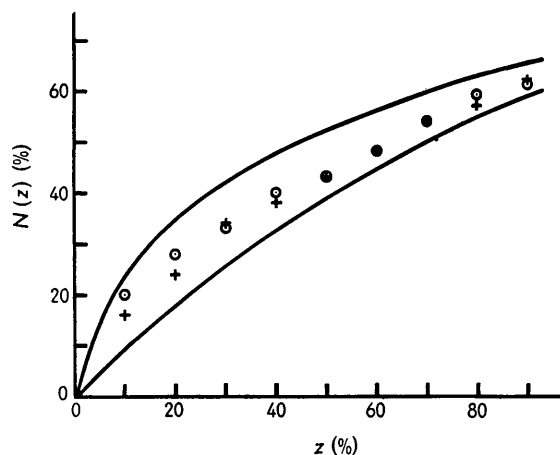

Fig. 1. Distribution test for centro-symmetry. Crosses: experimental points; circles: points derived from the calculated intensities.

will be seen that the experimental points lie mid-way between the two theoretical curves. This could be due to pseudo-symmetry, but the low-angle reflexions taken alone actually give points nearer to the acentric curve than those shown, whereas the reverse should be true for a pseudo-symmetric structure. Also, the intensities calculated from the structure adopted give points only a little nearer to the centric curve than the experimental points. It is therefore concluded that the structure does not satisfy the assumptions underlying the statistical theory of intensity distribution. The validity of the assumed space group must therefore continue to rest on the agreement between observed and calculated intensities and on the verisimilitude of the electron-density maps obtained with its aid.

Determination of the structure

(a) Intensity determination

The intensities of the $h0l$ and $hk0$ reflexions were determined visually from two sets of oscillation photographs with overlapping 15° oscillation ranges, using a 3 cm. radius camera and filtered Cu $K\alpha$ radiation. Additional 5° oscillation photographs were used to check the indices of reflexions which were indexed ambiguously from the 15° oscillation photographs. The intensities of the $hk0$ reflexions were also re-determined, and their indices checked, from a Weissenberg photograph when a Weissenberg goniometer became available. The observed intensities were corrected for the polarization and Lorentz factors. The crystals used for the intensity determinations had dimensions less than 0·1 mm. in the equatorial plane. Absorption

corrections were evaluated graphically for a few reflexions covering a wide range of positions with respect to the crystal, but were found to show a negligible variation with direction. Absorption was therefore neglected. The number of non-zero reflexions observed was 116 out of a possible 157 for the zone $h0l$, and 56 out of a possible 73 for the zone $hk0$.

The absolute scale of the observed structure factors was determined by comparison with the calculated values when the structure determination had been completed. The calculated structure factors were also corrected by an empirical temperature factor determined at the same stage.

(b) Patterson synthesis

From the intensity data for the $h0l$ reflexions a Patterson synthesis was calculated and is shown in Fig. 2. There exists no peak value in the Patterson
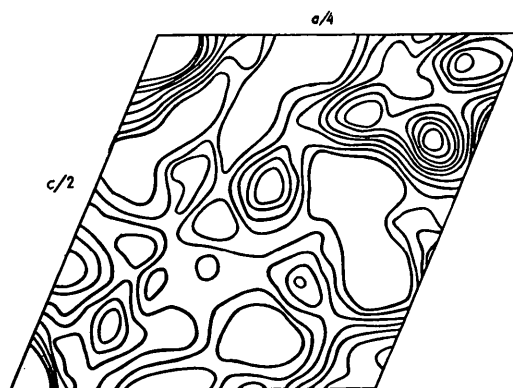

Fig. 2. Patterson synthesis projected down [010]. One asymmetric unit (one-eighth of the unit cell) is shown. Contours at equal arbitrary intervals except at the origin peaks.

synthesis with so great an intensity that it can be immediately identified as due to the Cl–Cl vector; each must be due to the superposition of a number of vectors. However, it was possible to show from packing considerations and from the usual values of bond lengths that a chemically and spatially reasonable structure could be postulated which would give the Cl–Cl vector at the position of the highest Patterson peak and which would give superpositions of vectors to account for the other main features of the Patterson synthesis. Other identifications of the Cl–Cl vector led to difficulties. The structure deduced from the Patterson synthesis was used to calculate a set of structure factors, which were in reasonable agreement with the observed values.

(c) Fourier refinement of the b-axis projection

The molecular orientation thus found was such as to give appreciable resolution in a one-dimensional projection on the a axis. Such a projection was therefore calculated and showed good agreement with expectation both as regards peak positions and relative

electron densities, but indicated that small changes in the x coordinates of the chlorine and oxygen atoms were required. A similar projection on the c axis was also calculated, and in spite of low resolution it showed a satisfactory density distribution and suggested a small change in the z coordinate of the chlorine atom. Permutation of the signs of two terms which were in doubt gave obviously less probable results. Recalculation of the structure factors with the modified oxygen and chlorine coordinates gave improved agreement with the observed values, and the signs so derived were used in the first two-dimensional Fourier synthesis projected down the b axis.

The x and z coordinates were refined in three stages by two-dimensional Fourier methods. The third Fourier synthesis (Fig. 3) was used to derive the best fitting molecule, assuming a 'regular' benzene ring, i.e. a ring whose projection has opposite sides of the hexagon equal in length and the peripheral bonds directed radially. Structure factors calculated on this basis (including the contribution of hydrogen) gave sign changes for two terms which were very small and whose

calculated values were smaller than the observed ones. As shifts of the atoms within the experimental error could reverse these signs, and as their change tended
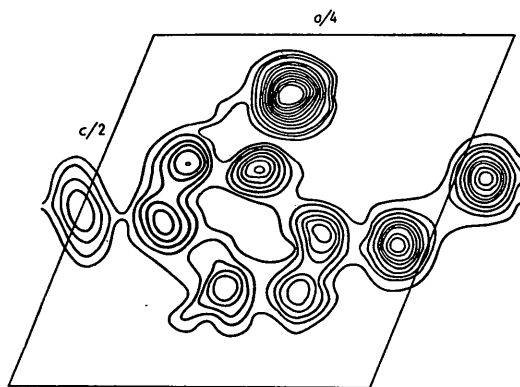

Fig. 3. Electron density projected down [010]. Contours at intervals of 1 e.Å^{-2} except on the chlorine atom where the odd contours above the 6th are omitted. The 1-electron line is also omitted. The asymmetric unit, which is one-eighth of the unit cell and contains half a molecule, is outlined.

Table 1. *Observed and calculated structure factors*

hkl	F_o	F_c		hkl	F_o	F_c		hkl	F_o	F_c
200	1·2	1·2		730	0	1·1		20,0,2	1·6	− 1·7
400	18·9	−23·5		930	2·3	3·3		22,0,2	1·7	− 1·6
600	11·1	−12·2		11,3,0	0	− 0·5		24,0,2	1·7	1·3
800	12·8	13·8		13,3,0	3·5	− 4·4		004	4·1	− 3·4
10,0,0	5·2	6·7		15,3,0	0	− 0·9		204	7·3	− 7·2
12,0,0	5·3	− 5·8		17,3,0	2·6	2·8		404	10·1	10·2
14,0,0	8·8	− 9·0		19,3,0	0	0·7		604	3·0	2·6
16,0,0	6·9	8·0		21,3,0	1·8	− 1·7		804	0	0·3
18,0,0	14·9	13·3		23,3,0	0·6	− 0·7		10,0,4	5·4	− 6·2
20,0,0	3·7	− 2·6		040	4·7	− 5·1		12,0,4	0	0·5
22,0,0	2·4	− 3·1		240	2·0	1·4		14,0,4	1·0	2·3
24,0,0	1·8	− 1·0		440	3·8	3·8		16,0,4	2·0	2·7
26,0,0	0·8	1·1		640	0	0·7		18,0,4	1·6	− 1·7
110	0·8	− 0·7		840	6·3	− 6·1		20,0,4	0	− 0·1
310	12·2	11·6		10,4,0	4·7	− 4·4		22,0,4	0·9	0·7
510	8·6	8·5		12,4,0	1·4	1·3		006	4·9	− 5·0
710	0	0·3		14,4,0	3·0	2·8		206	3·5	− 3·9
910	19·4	−17·5		16,4,0	0	− 0·1		406	2·5	2·6
11,1,0	3·5	4·4		18,4,0	1·2	− 1·6		606	4·1	4·0
13,1,0	3·7	3·8		150	4·3	3·6		806	3·5	− 3·6
15,1,0	5·9	6·1		350	0	− 0·6		10,0,6	2·2	− 2·4
17,1,0	3·3	− 2·4		550	4·9	− 4·8		12,0,6	0	− 0·5
19,1,0	0	− 0·3		750	0·9	− 1·2		14,0,6	3·0	2·8
21,1,0	1·3	1·2		950	3·1	3·8		16,0,6	0	− 0·7
23,1,0	1·6	1·7		11,5,0	2·5	− 2·2		18,0,6	0	− 1·0
25,1,0	1·1	− 0·9		13,5,0	1·7	− 1·6		008	3·3	− 3·4
020	7·9	7·7		15,5,0	0	0·2		208	3·1	4·4
220	3·5	− 3·7		060	1·7	− 1·5		408	3·0	2·4
420	4·6	− 2·3		260	0	0·7		608	1·6	− 2·0
620	8·5	− 6·8		460	1·3	0·5		808	3·3	− 3·1
820	6·1	5·4		660	0	0·4		10,0,8	0·9	2·2
10,2,0	2·0	1·5		860	0·5	0·5		12,0,8	2·8	3·2
12,2,0	4·1	− 3·3		002	11·2	−14·9		14,0,8	0	− 0·4
14,2,0	0	− 0·9		202	3·7	− 3·6		16,0,8	0	− 0·4
16,2,0	0	0·6		402	14·7	−17·0		0,0,10	2·5	2·7
18,2,0	1·4	1·7		602	7·3	8·7		2,0,10	4·0	3·2
20,2,0	0	− 0·7		802	7·2	6·5		4,0,10	0	− 0·2
22,2,0	0	− 0·8		10,0,2	0	0·1		6,0,10	2·2	− 2·1
24,2,0	0	− 0·4		12,0,2	5·2	− 5·7		8,0,10	0	0·4
130	5·3	5·6		14,0,2	2·5	1·3		10,0,10	0·7	0·4
330	5·4	5·1		16,0,2	0	− 0·1		12,0,10	0	0·2
530	5·4	− 6·2		18,0,2	0	− 0·5		0,0,12	0	0·8

Table 1 (*cont.*)

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
2,0,12	0	0	$40\bar{6}$	6·5	8·0	$10,0,\bar{10}$	0	0·2
4,0,12	1·2	− 1·6	$60\bar{6}$	4·2	− 3·6	$12,0,\bar{10}$	3·3	− 3·0
6,0,12	0	− 0·4	$80\bar{6}$	3·9	− 2·5	$14,0,\bar{10}$	0	0
$20\bar{2}$	5·0	5·2	$10,0,\bar{6}$	4·0	− 5·8	$16,0,\bar{10}$	4·4	3·5
$40\bar{2}$	4·6	4·8	$12,0,\bar{6}$	5·7	5·4	$18,0,\bar{10}$	0	− 0·1
$60\bar{2}$	8·6	− 8·7	$14,0,\bar{6}$	1·5	− 1·0	$20,0,\bar{10}$	4·0	− 3·8
$80\bar{2}$	1·0	0·5	$16,0,\bar{6}$	1·5	− 1·2	$22,0,\bar{10}$	0	− 0·6
$10,0,\bar{2}$	9·5	8·6	$18,0,\bar{6}$	3·5	− 3·4	$24,0,\bar{10}$	0	0
$12,0,\bar{2}$	1·0	1·3	$20,0,\bar{6}$	0	0·7	$26,0,\bar{10}$	1·1	1·1
$14,0,\bar{2}$	7·2	− 7·7	$22,0,\bar{6}$	1·2	1·5	$2,0,\bar{12}$	2·5	3·5
$16,0,\bar{2}$	3·2	− 3·2	$24,0,\bar{6}$	0	− 0·1	$4,0,\bar{12}$	0·9	− 0·5
$18,0,\bar{2}$	3·9	− 3·1	$26,0,\bar{6}$	0	− 0·9	$6,0,\bar{12}$	2·0	− 1·9
$20,0,\bar{2}$	4·5	4·5	$28,0,\bar{6}$	0	− 0·5	$8,0,\bar{12}$	2·1	2·1
$22,0,\bar{2}$	0	0	$20\bar{8}$	3·5	− 2·8	$10,0,\bar{12}$	0	1·2
$24,0,\bar{2}$	0·8	− 1·5	$40\bar{8}$	0	− 0·5	$12,0,\bar{12}$	1·6	− 1·5
$26,0,\bar{2}$	0	0·1	$60\bar{8}$	9·9	11·7	$14,0,\bar{12}$	1·9	− 2·2
$20\bar{4}$	8·6	9·3	$80\bar{8}$	0·9	− 0·6	$16,0,\bar{12}$	0	− 0·8
$40\bar{4}$	6·4	5·4	$10,0,\bar{8}$	6·3	− 5·3	$18,0,\bar{12}$	2·1	2·1
$60\bar{4}$	4·1	− 3·4	$12,0,\bar{8}$	2·8	− 2·8	$20,0,\bar{12}$	2·5	2·7
$80\bar{4}$	10·8	−10·1	$14,0,\bar{8}$	5·0	5·0	$22,0,\bar{12}$	1·4	− 1·7
$10,0,\bar{4}$	1·0	2·3	$16,0,\bar{8}$	1·7	2·4	$24,0,\bar{12}$	0	− 0·4
$12,0,\bar{4}$	6·4	6·3	$18,0,\bar{8}$	2·0	− 2·2	$2,0,\bar{14}$	0	0·1
$14,0,\bar{4}$	7·1	6·9	$20,0,\bar{8}$	1·7	− 2·2	$4,0,\bar{14}$	1·3	− 1·5
$16,0,\bar{4}$	5·4	− 6·5	$22,0,\bar{8}$	2·1	− 1·6	$6,0,\bar{14}$	0	− 0·5
$18,0,\bar{4}$	2·1	1·2	$24,0,\bar{8}$	3·3	3·3	$8,0,\bar{14}$	0	0·1
$20,0,\bar{4}$	1·9	2·5	$26,0,\bar{8}$	0	− 0·9	$10,0,\bar{14}$	1·4	1·4
$22,0,\bar{4}$	1·0	1·1	$28,0,\bar{8}$	1·2	− 0·9	$12,0,\bar{14}$	0	0·6
$24,0,\bar{4}$	0	− 1·7	$2,0,\bar{10}$	5·7	− 6·6	$14,0,\bar{14}$	1·0	− 0·9
$26,0,\bar{4}$	0	− 1·0	$4,0,\bar{10}$	1·7	− 2·3	$16,0,\bar{14}$	0·8	− 1·3
$28,0,\bar{4}$	0	0·5	$6,0,\bar{10}$	1·7	− 0·1	$18,0,\bar{14}$	0·9	0·8
$20\bar{6}$	1·2	− 1·1	$8,0,\bar{10}$	2·6	2·9			

to increase rather than decrease spurious detail in the electron-density map it was concluded that they should not be changed, and that no further refinement was practicable. The final value of $\Sigma||F_o|-|F_c|| \div \Sigma|F_o|$ was 0·18 including as zero all reflexions not observed. If these reflexions are omitted the value is 0·14, and the various other possible ways of treating unobserved reflexions lead to values between these limits.

(d) Fourier refinement of the c-axis projection

The inclinations of the various bonds to the (010) plane were calculated from the x and z coordinates and standard bond lengths. The derivation of the y coordinates was then treated as a one-parameter problem and a first trial structure was based on packing considerations. The $hk0$ structure factors were calculated from the atomic positions thus obtained, but the agreement with observation was not very good. The corresponding Fourier synthesis was calculated and gave the expected degree of resolution of C_7 and O, and the expected superposition of two C_1 atoms from different molecules and of the C_3 atom on the chlorine atom of another molecule, but only very vague indications of the positions of C_2, C_4, C_5 and C_6 could be observed. A probable shift of the molecule as a whole was deduced from the positions of the resolved peaks, and a further set of structure factors was calculated. These were in better agreement with observation at moderate angles but in worse agreement at high angles, and in the corresponding Fourier synthesis the vaguely

indicated C_4 atom disappeared and split into two low ridges with a trough between them at the expected peak position. An attempt to use this Fourier synthesis as the basis of further adjustment led to still worse agreement between the observed and calculated values of F_{h50} and had to be abandoned.

In view of the non-convergence of the refinement process, the position of the molecule (treated as a single parameter) was explored over the whole range in order to find the best agreement for the reflexions 310, 330, 350, 370, 020, 220 and 14,2,0. This exploration showed that no position of the molecule was satisfactory, and in particular that no position would give a large enough value for F_{020}. It was concluded that the shape of the molecule must be adjusted as well as its position. Relatively minor relaxations in the assumed bond lengths and x and z coordinates were found to permit considerable changes in the y coordinates (0–0·15 Å for the carbon atoms and 0·25 Å for the chlorine atom) which were sufficient to make the agreement between calculated and observed structure factors much better and to change the calculated signs of ten structure factors. These changes in atomic position corresponded to a small rotation of the benzene ring, with the chlorine atom, about the C_1–C_4 axis. The Fourier synthesis calculated with the new signs gave good resolution of all the atoms which should be resolved. After two further stages of refinement, and including the effect of the hydrogen atoms, the reliability factor $\Sigma||F_o|-|F_c|| \div \Sigma|F_o|$ was reduced to 0·16 with unobserved reflexions considered as zero,

or 0·13 omitting them. The final electron-density map is shown in Fig. 4. This does not take account of the change in sign of $F_{1\bar{1}0}$ which occurred in the final set
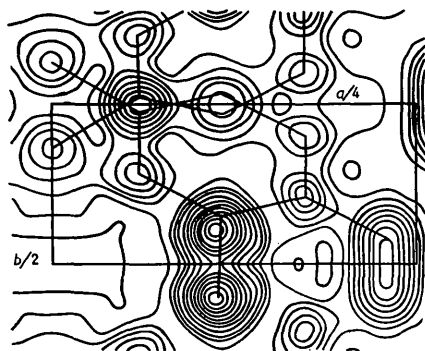

Fig. 4. Electron density projected down [001]. Contours as in Fig. 3. The asymmetric unit is outlined, and parts of two overlapping molecules are drawn in.

of calculated structure factors. In view of the long periodicity of this term in the electron-density projection and also its small value and relatively large rounding off errors in two-figure Beevers–Lipson strips, it was considered that any changes in atomic position to which it might lead would not be significant.

The whole set of observed and calculated structure factors is given in Table 1.

(e) Atomic positions and accuracy

The atomic positions adopted finally are shown in Table 2 (the positions given are those within one molecule).

Table 2. *Final coordinates*

	x (Å)	y (Å)	z (Å)
C₁	1·37	0·12	3·10
C₂	1·32	1·07	2·16
C₃	2·57	1·72	2·30
C₄	3·86	1·43	3·39
C₅	3·89	0·48	4·35
C₆	2·65	−0·16	4·21
C₇	0	−0·66	2·94
O	5·13	2·07	3·56
Cl	2·52	2·96	0·99

For the purpose in hand high accuracy is not required, and the ultimate refinements of correcting for termination-of-series errors and statistical treatment of the random errors were not applied. It is believed that the former would be small in any case, as the intensities of the high-angle reflexions are already very low. Some idea of the likely errors may however be obtained as follows:

(i) In the final stage of refinement of the *b*-axis projection the mean change in the *x* coordinates was 0·01 Å and in the *z* coordinates 0·005 Å.

(ii) The corresponding figures for the *c*-axis projection were 0·02 Å for the *x* coordinates and 0·04 Å for the *y* coordinates.

(iii) The mean discrepancy between the final *x* coordinates from the two projections was 0·02 Å.

(iv) The mean discrepancy between the positions of the peaks of the electron density and the positions required to give a 'regular molecule' in each of the final projections was 0·03 Å.

It is concluded that the atomic positions are not likely to be in error by more than about 0·05 Å.

The positions of the hydrogen atoms used in calculating the final structure factors are shown in Table 3, where H_i denotes the hydrogen atom attached to C_i.

Table 3. *Final coordinates of hydrogen atoms*

	x (Å)	y (Å)	z (Å)
H₂	0·32	1·29	1·27
H₅	4·92	0·26	5·23
H₆	2·64	0·89	4·96
H₇	0·27	1·32	3·90

These positions were determined graphically on the projections. For H_2, H_5, and H_6 the C–H bonds were assumed to be radial to the benzene ring and of length 1·10 Å. They were constructed to have a projected length in proportion to the parallel C–C bonds of the benzene ring taken as 1·40 Å. The C_7–H_7 bond was assumed to lie in a plane perpendicular to the plane of the C_1–C_7–C_1' bonds and to make an angle of 53° with it. The positions cannot be considered more than approximate. No attempt was made to locate the hydrogen of the hydroxyl group, and its contribution to the scattering was included with that of the oxygen atom.

Discussion of the structure

(a) The form of the molecule

The best fit plane through the atoms of the benzene ring was determined analytically by the method of least squares. Referred to orthogonal axes parallel to *a*, *b*, and *c** it has the equation

$$-0.443x + 0.690y + 0.572z - 1.655 = 0 .$$

The atoms of the ring all lie within 0·02 Å of this plane. The non-ring atoms lie at the following distances from it:

$$C_7: \ -0.05 \text{ Å}; \quad O: \ -0.02 \text{ Å}; \quad Cl: \ -0.03 \text{ Å} .$$

The plane through the symmetry axis, C_7 and O has the equation

$$-0.111x + 0.994z - 2.829 = 0 .$$

The atoms C_1 and C_4 both lie within 0·01 Å of this plane, and the plane of the benzene ring makes an angle of 52° with it.

The valency angle C_1–C_7–C_1' calculated from the positions of C_1 and C_7 alone is 119°, subject to an uncertainty of about ±6° corresponding to the assumed uncertainty of ±0·05 Å in the atomic positions, but if it is assumed that the atoms C_7, C_1, C_4 and O are

really collinear then the angle may be derived most accurately from the positions of the oxygen atoms. This gives the angle $O–C_7–O'$ as 122° with an uncertainty of ±2°.

The form of the molecule may therefore be defined in terms of the hypothetical planar configuration shown in Fig. 5, if the benzene rings are rotated about
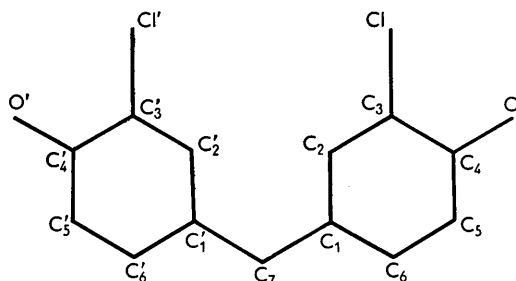

Fig. 5. The molecule of 3 : 3'-dichloro-4 : 4'-dihydroxydiphenyl-methane. The actual configuration is obtained from this by rotating the benzene rings through 52° in opposite senses about the $C_7–O$ axes.

the $C_7–O$ axes by 52° in opposite senses. There could exist two configurations of the molecule which would both have the same angle between the planes of the rings. The alternative configuration to the one found would be obtained by rotating the rings through 128° from the planar configuration of Fig. 5. The two configurations differ in their intramolecular Cl–Cl distance; in the form actually observed this is 7·5 Å; in the alternative hypothetical form it would be 10·8 Å.

It may be further observed that the molecule occurs in the structure in two enantiomorphic configurations which are symmetrically related to one another by means of the glide plane. There is of course no evidence that the two forms are not freely interconvertible in solution, but the existence of this enantiomorphy does suggest that analogous compounds with substituent groups adjacent to the C_7 carbon atom might be resolvable into optical isomers if sufficient hindrance to rotation were introduced by the substituents. This has been pointed out previously by Megson (1948).

(b) Interatomic distances and molecular packing

The distance between bonded atoms are shown in Table 4.

Table 4. Interatomic distances

$C_1–C_2$	1·32 Å	$C_6–C_1$	1·33 Å
$C_2–C_3$	1·37	$C_7–C_1$	1·53
$C_3–C_4$	1·37	$C_3–Cl$	1·77
$C_4–C_5$	1·35	$C_4–O$	1·38
$C_5–C_6$	1·38		

The bond lengths are all normal within the experimental error discussed above. No significance can be attached to the variation in the aromatic C–C bonds reported; rather they serve to confirm the magnitude of the errors in the investigation.

The closest non-bonded interatomic contacts within the molecule are

$C_1 \cdots C_1'$	2·64 Å
$C_2 \cdots C_2'$	3·55
$O \cdots Cl$	3·00

The closest intermolecular contacts are between the oxygen atoms of adjacent molecules, which are 2·97 Å apart. The other closest contacts are

$C_6 \cdots C_3''$	3·54 Å
$Cl \cdots C_1''$	3·46
$O \cdots C_4''$	3·30

The rather short $O \cdots O$ distance is interpreted as evidence of a weak intermolecular hydrogen bonding which links the molecules into layers parallel to (001). There are no hydrogen bonds between these layers of molecules. The weakness of the hydrogen bonds is evidenced by two facts in addition to their length:

(i) There is a good cleavage of the crystal parallel to (010) which involves breaking hydrogen bonds.

(ii) The melting point of the compound (104° C.) is rather low compared with analogous compounds, as shown below.

m.p. 158° C.

m.p. 126° C.

m.p. 104° C.

m.p. 119° C.

m.p. 126° C.

m.p. 178° C.
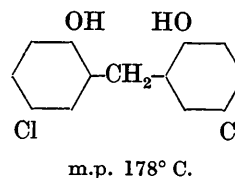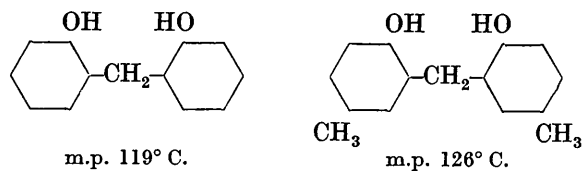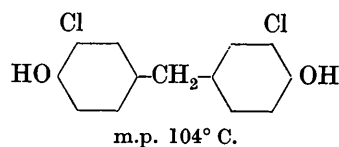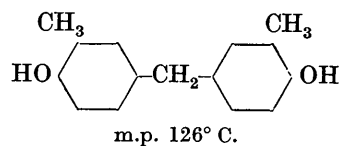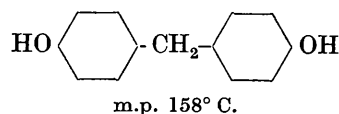
It may be noted that adjacent molecules are linked in the a and b directions by hydrogen bonds, and that in the c direction the chlorine atom of one molecule lies in almost the same plane as the benzene ring of its

neighbour, whereas in the b direction the chlorine atom of one molecule lies near to the axis of the benzene rings of both its neighbours. It seems possible that some polarization effect associated with this arrangement may be responsible for the orientation of the (010) cleavage plane which cuts across the network of hydrogen bonds.

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electric tests, and the Directors of Ferodo Ltd for permission to publish this paper.

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The Crystal Structure of Zinc Acetate Dihydrate, $Zn(CH_3COO)_2.2H_2O$

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Crystals of zinc acetate dihydrate, $Zn(CH_3COO)_2.2H_2O$, are monoclinic with space group $C2/c$. The unit cell, of dimensions $a = 14\cdot50$, $b = 5\cdot32$, $c = 11\cdot02$ Å, $\beta = 100° 0'$, contains only four formula units. The zinc atoms lie on twofold axes.

Projections of the structure on two crystallographic planes are given. The six nearest neighbours of a zinc atom are four oxygen atoms and two water molecules which form a badly distorted octahedron around the zinc atom. The acetate groups have normal bond distances and angles.

The formula units are firmly linked by strong hydrogen bonds to form 'two-dimensional' sheets. Only feeble van der Waals forces exist between such sheets. This sheet-like nature of the structure accounts for such physical properties as the mosaic character, softness and ready cleavage of the crystals.

Introduction

Direct X-ray evidence for the existence of metal-to-metal bonds in the structures of cupric and chromous acetate (van Niekerk & Schoening, 1953a, b; van Niekerk, Schoening & de Wet, 1953) has raised the question whether the acetates of the other transition elements have similar or related structures. The present investigation was therefore undertaken as part of a systematic X-ray examination of the structural features of such compounds.

Crystal data and space group

Crystals of zinc acetate dihydrate, $Zn(CH_3COO)_2.2H_2O$, are colourless and generally crystallize in the form of needles. They are extremely soft and split very readily along the needle direction (b axis). Good single crystals are the exception, as the crystals usually assume the form of thin, elongated plates which are stacked together to form prismatic needles. The prism faces are the (100) and (001) faces, the angle between them being $80° 0'$.

The crystals are monoclinic and the unit-cell dimensions, as determined from rotation photographs and goniometer measurements, are

$$a = 14\cdot50, \ b = 5\cdot32, \ c = 11\cdot02 \text{ Å}, \ \beta = 100° 0'.$$

The axial ratios

$$a:b:c = 2\cdot726:1:2\cdot071$$

agree well with the values

$$3c:b:3a = 2\cdot713:1:2\cdot069, \ \beta = 80° 0'$$

given by Rammelsberg (1881).

Systematic extinctions occur only for hkl with $h+k$ odd, $h0l$ with h odd and l odd and $0k0$ with k odd. The space group is therefore either Cc or $C2/c$. In order to distinguish between the two possible space groups a statistical $N(z)$ test, in which all the hkl spectra were used, was made. The result was, however, not decisive. The crystals were also tested for pyro-electricity, following methods described by Bunn (1946). The results were negative, so that these experiments, although not conclusive, at least do not contradict the $C2/c$ space group. The successful structural analysis probably gives the best evidence that the space group is $C2/c$.

Assuming four formula units in the unit cell, the calculated density is $1\cdot76$ g.cm.$^{-3}$, in good agreement with the measured density $1\cdot77$ g.cm.$^{-3}$.