characteristics (extinctions) would be influenced noticeably.

An effort has been made to correlate data obtained from the 4-nitropyridine-*N*-oxide with X-ray studies carried out at present on other 4-substituted pyridine-*N*-oxides (Hayashi, 1950; McKeown, Ubbelohde & Woodward, 1951). These will be reported in more detail shortly.

The author is the recipient of a Fulbright Travel Grant and a George Ellery Hale Fellowship in the California Institute of Technology. He stands, moreover, in much obligation to Dr Linus Pauling, whose interest stimulated this research and who was good enough to read the manuscript. He is equally indebted to Drs Karst Hoogsteen, Edward W. Hughes and Robert Nathan for advice and discussions of some aspects of this project. He wishes especially to testify of his appreciation to Dr H. J. den Hertog of the Wageningen Agricultural Institute and to Dr Eiji Ochiai of the Pharmaceutical Institute of Tokyo University, whence most of the samples of pyridine-*N*-oxides have come.

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The Crystal and Molecular Structure of Bishydroxydurylmethane

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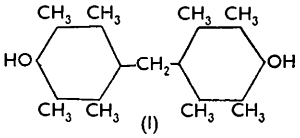
(*Received* 27 *February* 1956)

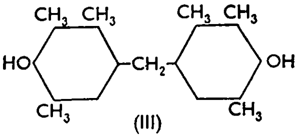
The structure of bishydroxydurylmethane has been fully determined. The crystals are monoclinic, with space group $C2$, and there are two molecules in a unit cell of dimensions $a = 22{\cdot}87$, $b = 4{\cdot}94$, $c = 7{\cdot}42$ Å and $\beta = 91° 0'$. Optical-transform methods have been used freely in the earlier stages of the structural analysis and the structure has been refined by two-dimensional Fourier syntheses. Steric repulsive interactions of the *o*-substituted methyl groups with the methylene group and of the *o*-substituted methyl groups with one another produce considerable strain in the molecule. Important features of the strain include a long $C_{Ar.}$–C_{CH_2} distance (1·60 Å), a wide angle (119°) between the two $C_{Ar.}$–C_{CH_2} linkages in each molecule and large displacements of the methylene carbon atom and the *o*-substituted methyl carbon atoms from the plane of the aromatic ring. The C–O distance is 1·35 Å.

1. Introduction

Bishydroxydurylmethane (I)



(I)



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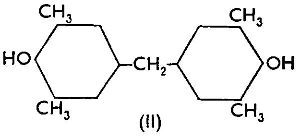
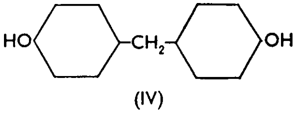


(II)



(IV)

can be hydrolysed and reduced with remarkable ease (Burawoy & Chamberlain, 1949); its behaviour in these respects is in marked contrast to that of bis-4-hydroxy-3:5-dimethylphenylmethane (II) and bis-4-hydroxy-2:3:5-trimethylphenylmethane (III), which often remain unchanged when subjected to similar chemical treatments. Burawoy & Chamberlain attribute the unusual activity of bishydroxydurylmethane to the weakening of the $C_{Ar.}$–C_{CH_2}–$C_{Ar.}$ linkages as a result of the intramolecular steric repulsive interaction of the *o*-substituted methyl groups with the methylene group and of the *o*-substituted methyl groups with one another. Because of the steric repulsion, it appears that any possible configuration of the bishydroxydurylmethane molecule must involve some

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deviations from normal bond distances and bond angles. The X-ray analysis of bishydroxydurylmethane has been undertaken to determine the nature of these deviations and to see if they support the explanation of the chemical behaviour of the material proposed by Burawoy & Chamberlain.

The importance of a structural investigation of the diphenylmethane derivatives is pointed out by Megson (1948) in connexion with the influence of molecular structure on the properties of phenolic resins with the phenol-methylene chain structure. A preliminary X-ray examination of some of the compounds in this series is described by Finn, Megson & Whittaker (1950), and the detailed analysis of the structure of one of the simplest members, 3:3′-dichloro-4:4′-dihydroxydiphenylmethane (IV), is discussed by Whittaker (1953).

2. Experimental data: the space group

Bishydroxydurylmethane crystallizes from ethyl alcohol in the form of very thin laths. The melting point is 213° C. The crystals are soft and cleave readily parallel to the lengths of the laths.

X-ray rotation, oscillation and Weissenberg photographs show that the crystals are monoclinic with the lengths of the laths parallel to the symmetry axis, and that the dimensions of the unit cell are

$$a = 22{\cdot}87,\ b = 4{\cdot}94,\ c = 7{\cdot}42\ \text{Å and } \beta = 91^\circ\, 0' .$$

It is estimated that the a, b and c dimensions are accurate to within $\pm 0{\cdot}4\%$ and that β is correct to $\pm 25'$.

There are two molecules in the unit cell (measured density 1·230 g.cm.$^{-3}$, calculated density 1·225 g.cm.$^{-3}$).

Reflexions $h0l$ and $hk0$, recorded on zero-layer-line Weissenberg photographs using unfiltered Cu $K\alpha$ radiation, provided the data from which the atomic positions were finally deduced. The intensities of the reflexions were measured by visual comparison with calibration spots of known relative exposure. The cross-sections of the crystal specimens used for taking both sets of Weissenberg photographs are rectangular in the plane perpendicular to the axis of oscillation; the cross-sectional dimensions are 0·14 mm.×0·02 mm. (b-axis specimen) and 0·32×0·02 mm. (c-axis specimen). No corrections have been made for absorption: it is estimated that errors in the structure amplitudes caused by neglecting the absorption corrections will not exceed 2% for the $h0l$ reflexions and 5% for the $hk0$ reflexions. Corrections for the spot-shape effect (Broomhead, 1948) have been applied to the intensities; they vary from unity to 0·87 for the $h0l$ reflexions and from unity to 0·76 for the $hk0$ reflexions. No attempt has been made to minimize or correct for extinction but the effect appears to be negligible for the specimens examined.

Reflexions hkl are absent when $(h+k)$ is odd; since there are no other systematic absences the space group must be $C2/m$, $C2$ or Cm. The space group $C2/m$ is ruled out by a test for pyroelectricity, which shows that the crystals are polar. The pyroelectric test appears to indicate that the crystals are polar along the b axis; if this can be established firmly the space group Cm is also eliminated. The choice between the space groups $C2$ and Cm is confirmed by a statistical analysis of the intensities of the $h0l$ reflexions (Wilson, 1949; Howells, Phillips & Rogers, 1950; Lipson & Woolfson, 1952). The experimental distribution curve (Fig. 1) lies very close to the hypercentric distribution curve, indicating that the [010] projection is centrosymmetric and that what is usually called the 'asymmetric unit' of the structure (in this case half the bishydroxydurylmethane molecule) is itself centrosymmetric; the half-molecule can, in fact, be regarded as centrosymmetric if the difference in scattering power of the hydroxyl group and half the methylene group is ignored. The [010] projection is centrosymmetric in the space group $C2$ and non-centrosymmetric in the space group Cm; the correct space group is therefore $C2$.

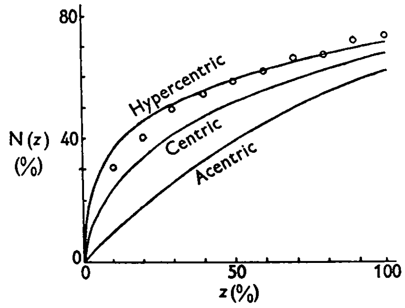


Fig. 1. Comparison of the experimental distribution of the intensities of the $h0l$ reflexions (open circles) and the theoretical acentric, centric and hypercentric distributions (full lines).

3. Determination of the structure

(i) *Preliminary considerations*

The two molecules in the unit cell must lie on rotation axes, since these are the only special positions in the space group $C2$. Without loss of generality the methylene carbon atoms at the centres of the molecules may be fixed at (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, 0)$ on the pair of rotation axes $[0, y, 0]$ and $[\frac{1}{2}, y, 0]$. Initially it was assumed that the atoms in each aromatic ring are coplanar with the attached groups, that the bond distances and bond angles are those to be expected in a molecule free from strain caused by steric hindrance, and that the two aromatic rings in each molecule are linked to the methylene carbon atom by bonds which make an angle of 109° with each other. The problem of finding an approximate structure is then reduced to the determination of (a) the mutual orientations of the aromatic rings, which can be varied by rotations about the $C_{\text{Ar.}}$–C_{CH_2} linkages, (b) the orientation of the molecule as a whole about the axis [010]. The latter was determined from packing considerations, which indicate that the molecules lie with their longest dimension along a direction approximately parallel to the [100] axis. The mutual orientations of the aromatic rings were obtained by considering the weighted reciprocal lattice.

(ii) *The weighted reciprocal lattice: optical transforms*

The determination of the shape and orientation of projections of benzene rings from weighted reciprocal-lattice sections is discussed in detail by Hanson, Lipson & Taylor (1953). The $h0l$ section of the weighted reciprocal lattice of bishydroxydurylmethane is shown in Fig. 2; the weights are proportional to the unitary structure factors. The six groups of strong reflexions —shown by broken rings—near the benzene circle correspond to strong characteristic peaks in the transform of the benzene ring; their positions indicate that the planes of the benzene rings are inclined to the (010) plane at an angle of about 40°; only one set of six peaks is observed because in the [010] projection the two benzene rings in the unit of pattern have parallel orientations.

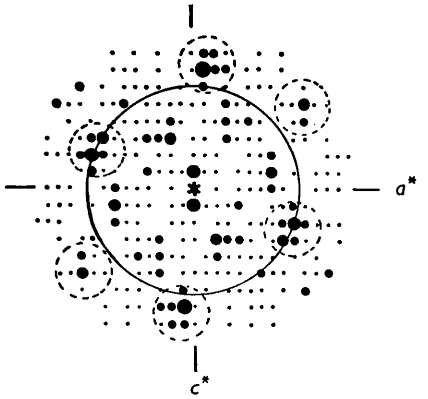


Fig. 2. The $h0l$-section of the weighted reciprocal lattice of bishydroxydurylmethane.

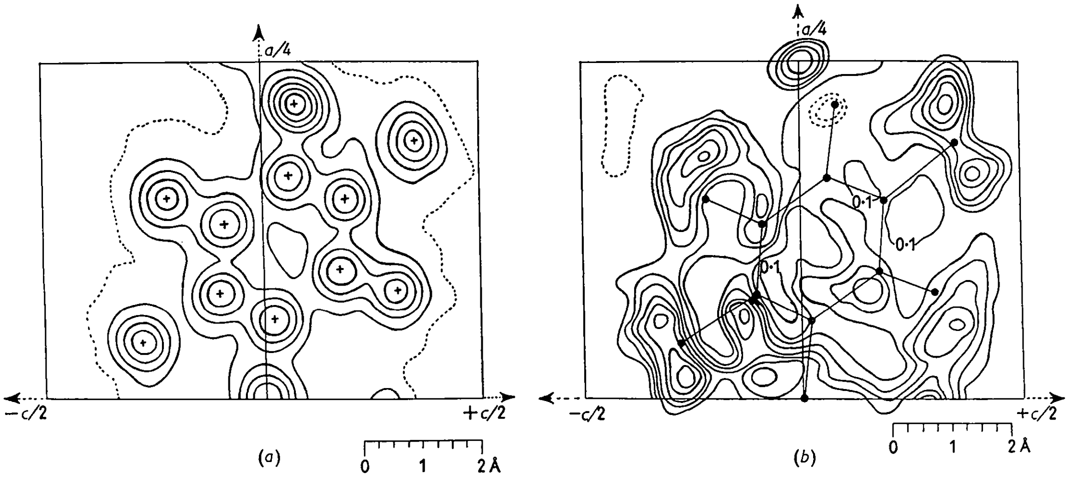
At this stage the trial structure was tested by comparing its optical transform (Hanson *et al.*, 1953) with the $h0l$ section of the weighted reciprocal lattice. A reasonable agreement was obtained; the agreement was improved by minor alterations in the positions of the methyl carbon atoms.

The [010] projection of the structure was refined by Fourier methods. For the first two syntheses the phase angles were deduced from optical transforms (Hanson *et al.*, 1953): this method of determining the phase angles permitted the inclusion of 80 reflexions in the first synthesis and 131 reflexions in the second synthesis.

(iii) *The* [010] *projection*

The final (third) $F_o(h0l)$ synthesis included all of the 155 experimentally observed $h0l$ reflexions; the phase angles were determined from calculated structure factors. The electron density was evaluated at intervals of $a/128$ and $c/64$, using the Manchester University Electronic Digital Computer; the distribution of electron density is shown in Fig. 3(*a*). No changes in phase angle were obtained on re-calculation of the structure factors using the atomic coordinates deduced from this projection.

An (F_o-F_c) synthesis was now computed using all the observed $h0l$ reflexions. The resulting $(\varrho_o-\varrho_c)$ map (Fig. 3(*b*)) has been interpreted as follows: (*a*) Series-termination errors in the final F_o synthesis are small; corrections for these errors (Cochran, 1951) give shifts of 0·015, 0·008 and 0·020 Å in the positions of atoms C_2, C_5 and C_6 respectively and negligible shifts in the positions of the other atoms. (*b*) The thermal vibra-



(*a*) (*b*)

Fig. 3. (*a*) Projection of the electron density along [010]. Contours are drawn at intervals of 1 e.Å^{-2}, the 1 e.Å^{-2} contour being broken. (*b*) (F_O-F_C) synthesis, showing the hydrogen atoms, projected along the [010] axis. Contours are drawn at intervals of 0·1 e.Å^{-2}, negative contours being broken. An outline of the molecule is superimposed on the contour diagram.

tions of the atoms are very nearly isotropic in the [010] projection. (*c*) Peaks are observed which may be attributed to the hydrogen atoms.

(iv) *The hydrogen atoms*

Each half-molecule of bishydroxydurylmethane contains one hydrogen atom of the methylene group; this atom is represented in Fig. 3(*b*) by a well-resolved peak. The hydrogen atom of the hydroxyl group lies so close to the twofold screw axis at [$\frac{1}{4}$, y, 0] that it overlaps in projection with the corresponding hydrogen atom from the other molecule in the unit cell; the two overlapping hydrogen atoms are represented by a single peak.

The groups of hydrogen atoms attached to the four methyl carbon atoms in each half-molecule are clearly represented in Fig. 3(*b*) by four ridges of high electron density. Two of the ridges have two peaks and the other two only one peak, and, because of the poor resolution, it is difficult to deduce the positions of the three hydrogen atoms associated with each ridge. The poor resolution may be caused by free or restricted rotation of the methyl groups, overlapping of the hydrogen atoms in projection, or errors in the visually estimated intensities. Free or restricted rotation is unlikely because of the strong steric repulsive interactions between the methyl groups; even in 1:4-dimethoxybenzene (Goodwin, Przybylska & Robertson, 1950), where the methyl groups are much less restricted by intramolecular contacts, there is evidence that the hydrogen atoms in the methyl groups are localized. Various configurations of localized hydrogen atoms were therefore tested, using a modified version

Table 1. *Observed and calculated structure factors for the h0l reflexions*

h 0 l	$\|F_o\|$	F_c
2 0 0	11·8	12·5
4 0 0	39·6	−31·1
6 0 0	—	0·1
8 0 0	24·2	−21·4
10 0 0	11·3	−10·0
12 0 0	6·9	4·0
14 0 0	20·8	21·4
16 0 0	7·7	−6·5
18 0 0	2·5	−1·1
20 0 0	2·2	1·8
22 0 0	4·8	4·0
24 0 0	2·0	1·2
26 0 0	2·3	2·4
0 0 1	100·6	94·7
0 0 2	16·4	−12·8
0 0 3	20·4	21·1
0 0 4	5·0	−2·4
0 0 5	8·9	−8·1
0 0 6	—	−1·6
0 0 7	4·4	−5·1
0 0 8	3·7	−3·9
2 0 1	19·6	−22·0
4 0 1	12·3	8·5
6 0 1	13·0	−12·8
8 0 1	43·9	43·0
10 0 1	3·2	2·8
12 0 1	—	0·0
14 0 1	7·9	7·2
16 0 1	5·7	−6·2
18 0 1	11·2	10·7
20 0 1	3·3	−3·6
2 0 2	—	−3·5
4 0 2	30·0	32·4
6 0 2	11·0	−14·5
8 0 2	3·3	−2·4
10 0 2	7·8	−7·8
12 0 2	6·2	5·7
14 0 2	6·2	−6·0
16 0 2	18·7	20·2
18 0 2	23·2	24·3
20 0 2	11·4	−11·8
22 0 2	3·4	−3·0
24 0 2	2·8	−2·1
26 0 2	3·1	−2·5
2 0 3	4·4	1·9
4 0 3	53·2	53·6
6 0 3	22·6	−18·9
8 0 3	26·2	−21·3
10 0 3	6·2	−4·6
12 0 3	2·0	0·8
14 0 3	5·9	−4·0
16 0 3	19·8	20·3
18 0 3	11·1	11·8
20 0 3	6·1	−6·5
22 0 3	—	−1·6
24 0 3	—	1·0
26 0 3	2·0	2·2
2 0 4	14·9	13·8
4 0 4	22·1	21·8
6 0 4	8·5	−8·7
8 0 4	9·1	8·5
10 0 4	6·0	−7·2
12 0 4	5·2	6·7
14 0 4	3·5	−3·6
16 0 4	—	0·4
18 0 4	2·5	2·5
20 0 4	—	−0·4
22 0 4	1·8	1·3
2 0 5	6·6	6·4
4 0 5	4·3	−2·6
6 0 5	5·6	4·4
8 0 5	4·7	4·9
10 0 5	—	−2·6
12 0 5	9·6	8·9
14 0 5	3·2	−3·0
16 0 5	3·9	3·5
18 0 5	—	−0·1
20 0 5	3·0	2·9
22 0 5	2·3	2·1
24 0 5	6·1	−5·0
2 0 6	3·3	−2·4
4 0 6	—	−1·0
6 0 6	6·9	−5·7
8 0 6	8·3	−5·4
10 0 6	5·7	4·5
12 0 6	5·3	4·2
14 0 6	—	0·0
16 0 6	4·3	4·6
18 0 6	—	−0·8
20 0 6	6·1	4·0
2 0 7	2·0	−0·5
4 0 7	—	−0·8
6 0 7	4·5	−4·1
8 0 7	1·8	−1·6
10 0 7	5·3	4·3
12 0 7	3·3	3·0
14 0 7	3·0	−3·2
2 0 8	—	−1·2
4 0 8	—	−0·3
6 0 8	4·6	4·1
8 0 8	—	−0·6
10 0 8	3·0	2·9
12 0 8	—	1·0
14 0 8	2·5	−1·6
16 0 8	1·0	1·2
2 0 $\bar{1}$	21·6	21·3
4 0 $\bar{1}$	32·2	−30·5
6 0 $\bar{1}$	5·4	5·9
8 0 $\bar{1}$	24·6	−24·2
10 0 $\bar{1}$	21·0	−18·6
12 0 $\bar{1}$	8·6	6·4
14 0 $\bar{1}$	27·7	26·5
16 0 $\bar{1}$	—	−3·0
18 0 $\bar{1}$	7·3	7·4
20 0 $\bar{1}$	—	0·0
22 0 $\bar{1}$	2·5	2·6
24 0 $\bar{1}$	3·3	2·8
26 0 $\bar{1}$	3·3	−3·7
2 0 $\bar{2}$	17·2	−18·8
4 0 $\bar{2}$	15·8	10·1
6 0 $\bar{2}$	7·9	4·0
8 0 $\bar{2}$	4·3	2·9
10 0 $\bar{2}$	15·7	17·3
12 0 $\bar{2}$	7·8	−6·8
14 0 $\bar{2}$	14·3	14·0
16 0 $\bar{2}$	2·2	−1·8
18 0 $\bar{2}$	—	0·9
20 0 $\bar{2}$	—	1·0
22 0 $\bar{2}$	—	−0·4
24 0 $\bar{2}$	4·7	5·8
26 0 $\bar{2}$	3·7	−4·6
28 0 $\bar{2}$	2·4	−2·9
2 0 $\bar{3}$	17·6	16·3
4 0 $\bar{3}$	—	−1·0
6 0 $\bar{3}$	26·6	26·5
8 0 $\bar{3}$	8·3	−10·2
10 0 $\bar{3}$	7·8	10·4
12 0 $\bar{3}$	7·2	−7·1
14 0 $\bar{3}$	—	0·8
16 0 $\bar{3}$	—	1·3
18 0 $\bar{3}$	3·1	−4·6
20 0 $\bar{3}$	3·0	2·4
22 0 $\bar{3}$	—	1·6
24 0 $\bar{3}$	3·3	3·7
2 0 $\bar{4}$	12·7	15·8
4 0 $\bar{4}$	9·1	−10·6
6 0 $\bar{4}$	25·1	26·1
8 0 $\bar{4}$	4·7	−4·7
10 0 $\bar{4}$	16·4	−19·5
12 0 $\bar{4}$	3·9	−4·8
14 0 $\bar{4}$	2·0	2·8
16 0 $\bar{4}$	1·8	−0·9
18 0 $\bar{4}$	6·2	6·0
20 0 $\bar{4}$	9·7	10·0
2 0 $\bar{5}$	5·4	−3·7
4 0 $\bar{5}$	3·4	−6·4
6 0 $\bar{5}$	14·3	14·1
8 0 $\bar{5}$	3·7	3·9
10 0 $\bar{5}$	5·7	−5·8
12 0 $\bar{5}$	—	−1·5
14 0 $\bar{5}$	—	1·6
16 0 $\bar{5}$	3·3	−2·6
18 0 $\bar{5}$	4·0	3·8
20 0 $\bar{5}$	10·7	14·1
22 0 $\bar{5}$	2·2	−3·1
24 0 $\bar{5}$	4·0	−3·8
2 0 $\bar{6}$	13·8	12·0
4 0 $\bar{6}$	2·3	−0·1
6 0 $\bar{6}$	3·7	4·5
8 0 $\bar{6}$	—	0·1
10 0 $\bar{6}$	3·1	3·7
12 0 $\bar{6}$	2·5	4·7
14 0 $\bar{6}$	3·4	−4·0
16 0 $\bar{6}$	—	0·4
18 0 $\bar{6}$	—	−2·0
20 0 $\bar{6}$	4·5	4·1
2 0 $\bar{7}$	23·7	21·5
4 0 $\bar{7}$	9·7	9·2
6 0 $\bar{7}$	7·7	−7·0
8 0 $\bar{7}$	—	−1·3
10 0 $\bar{7}$	2·8	−3·4
12 0 $\bar{7}$	2·5	−1·5
14 0 $\bar{7}$	—	−0·8
16 0 $\bar{7}$	2·8	3·4
2 0 $\bar{8}$	6·9	6·1
4 0 $\bar{8}$	6·9	7·2
6 0 $\bar{8}$	4·7	−4·8
8 0 $\bar{8}$	—	−0·6
10 0 $\bar{8}$	—	−1·3
12 0 $\bar{8}$	3·0	−3·3
14 0 $\bar{8}$	—	0·2
16 0 $\bar{8}$	3·7	4·6

Table 2. *Observed and calculated structure amplitudes and calculated phase angles for the $hk0$ reflexions*

$h\ k\ 0$	$\|F_o\|$	$\|F_c\|$	α_c (°)	$h\ k\ 0$	$\|F_o\|$	$\|F_c\|$	α_c (°)	$h\ k\ 0$	$\|F_o\|$	$\|F_c\|$	α_c (°)
2 0 0	13·8	12·5	0	17 1 0	—	3·3	55	9 3 0	7·1	9·2	244
4 0 0	40·8	31·6	180	19 1 0	—	0·9	90	11 3 0	7·3	4·8	29
6 0 0	—	0·0	180	21 1 0	10·9	10·0	34	13 3 0	10·2	10·6	326
8 0 0	26·2	22·8	180	23 1 0	5·8	5·9	194	15 3 0	7·5	8·7	267
10 0 0	13·5	10·6	180	2 2 0	20·5	22·2	268	17 3 0	5·4	3·9	162
12 0 0	8·0	4·7	0	4 2 0	14·2	14·0	20	19 3 0	—	2·3	93
14 0 0	24·6	24·2	0	6 2 0	9·4	10·1	183	21 3 0	—	1·0	64
16 0 0	8·2	7·6	180	8 2 0	15·6	11·8	29	23 3 0	—	2·3	114
18 0 0	—	1·2	180	10 2 0	15·0	13·6	38	25 3 0	6·3	4·6	27
20 0 0	—	2·4	0	12 2 0	11·3	9·9	235	2 4 0	10·8	11·7	199
22 0 0	6·5	5·4	0	14 2 0	—	2·2	90	4 4 0	8·0	9·6	94
0 2 0	4·3	4·1	346	16 2 0	—	3·3	199	6 4 0	15·9	15·7	334
0 4 0	11·9	14·0	270	18 2 0	8·1	9·3	29	8 4 0	14·2	12·5	34
1 1 0	39·4	44·0	97	20 2 0	11·3	13·8	138	10 4 0	9·6	8·7	105
3 1 0	35·6	37·6	354	22 2 0	6·3	3·4	30	12 4 0	5·0	4·9	211
5 1 0	20·2	23·1	194	24 2 0	12·7	14·1	318	14 4 0	5·0	5·3	15
7 1 0	16·2	17·3	245	26 2 0	7·1	5·5	245	1 5 0	—	2·6	286
9 1 0	24·3	20·4	262	1 3 0	8·1	6·8	147	3 5 0	6·9	6·8	316
11 1 0	36·5	30·2	10	3 3 0	13·6	13·4	22	5 5 0	8·6	8·5	16
13 1 0	4·1	4·3	252	5 3 0	9·1	9·8	262	7 5 0	10·4	12·2	105
15 1 0	6·9	6·9	12	7 3 0	8·8	12·2	45	9 5 0	5·2	4·9	227

of the optical transform technique described by Pinnock & Lipson (1954). A wire model of the methyl group was used to suggest possible configurations of each of the four groups of hydrogen atoms; the model was constructed with tetrahedral angles, possible distortions caused by steric repulsive interaction being ignored. The orientation of the model was varied until its configuration, in projection, appeared to be reasonably compatible with the appropriate ridge in the $(\varrho_o-\varrho_c)$ map. The most probable of a number of possible configurations was then deduced by comparing the optical transforms of the hydrogen atoms alone, for each of these configurations, and a reciprocal-lattice section weighted with values of $|F_o-F_c|$. The reciprocal-lattice section used for the comparison incorporates only 13 reflexions, all with low values of θ and high values of $|F_o-F_c|$; the F-values for these 13 reflexions are the ones most likely to be influenced by hydrogen atoms. Inclusion of the hydrogen atoms in the calculated structure factors reduces the agreement residual ($R = \Sigma|F_o-F_c| \div \Sigma|F_o|$) from 0·24 to 0·08 for the 13 selected reflexions and from 0·16 to 0·12 for the whole zone of $h0l$ reflexions; in evaluating R accidentally absent reflexions are excluded.

The final values of F_c, including the contributions from the hydrogen atoms, may be compared with the values of F_o for the whole zone of $h0l$ reflexions in Table 1. A plot of log (F_o/F_c) against $\sin^2\theta/\lambda^2$ was used to put the values of F_o on an absolute scale and to derive the temperature factor applied to the atomic scattering factors; the latter were taken from *International Tables* (1935).

(v) *The* [001] *projection*

The structure of the [001] projection was deduced approximately, using a wire model of the bishydroxydurylmethane molecule constructed with normal bond distances and bond angles. The model was oriented so that its shadow, cast on the [010] electron density map (Fig. 3(a)) by a beam of light parallel to the [010] axis, superimposed fairly closely on the projected molecule observed in Fig. 3(a). The shadow produced by a second beam of light parallel to the [001] axis was then used to deduce the y co-ordinates of the atoms in the molecule.

Refinement of the non-centrosymmetric [001] projection by Fourier methods must necessarily be slow; the initial stages of refinement were therefore effected by testing various slight modifications of the structure, using the relatively rapid optical-transform method. At all stages of refinement the x co-ordinates adopted were those obtained from the [010] projection. An agreement residual of 0·21 was obtained for the structure finally deduced from the optical transforms. The residual was reduced to 0·18 after the first Fourier synthesis and to 0·17 after two more syntheses. Small changes in the absolute scale of the observed structure amplitudes and in the temperature factor of the calculated structure amplitudes gave a further reduction in the residual to 0·16.

At this stage the calculated structure amplitudes did not include the contributions of the hydrogen atoms. An attempt to determine the positions of the hydrogen atoms in the [001] projection, using the objective method of a difference synthesis, was unsuccessful; this may be attributed to the fact that in the non-centrosymmetric [001] projection the difference synthesis loses much of its power because all calculated phase angles suffer from errors due to non-inclusion of the contributions of the hydrogen atoms. The y co-ordinates of the hydrogen atoms were therefore calculated from their x and z coordinates, as obtained from the [010] projection, assuming normal bond lengths and bond angles for the linkages to the hydrogen atoms; the assumption is not completely justified since the molecule is in a state of strain (§ 4) which may be expected to cause considerable deviations in the positions of the hydrogen atoms. On including the hydrogen atom parameters in the calculations of structure amplitude the agreement residual fell immediately to 0·13. This fall in the residual, using hydrogen atom parameters deduced from the [010] projection, offers further evidence that the positions of the hydrogen atoms postulated in the [010] projection are approximately correct.

The inclusion of the hydrogen atoms in the structure-factor calculations made appreciable alterations in the phase angles of most of the *hk*0 reflexions. A final Fourier synthesis was therefore computed, using the modified phase angles; the projected electron density is shown in Fig. 4. The atomic positions deduced from Fig. 4 show shifts of about 0·01 Å from the positions obtained in the previous synthesis. No significant change is obtained in the agreement residual on re-calculation of the structure amplitudes. The observed and calculated structure amplitudes and the calculated phase angles for the *hk*0 reflexions are given in Table 2. There are some indications of thermal anisotropy in the structure but the only allowance made for it in the structure-factor calculations is the adoption of different average temperature factors for the [010] and [001] projections; this accounts for the discrepancies in the values of $F_c(h00)$ associated with the *h*0*l* and *hk*0 reflexions respectively.

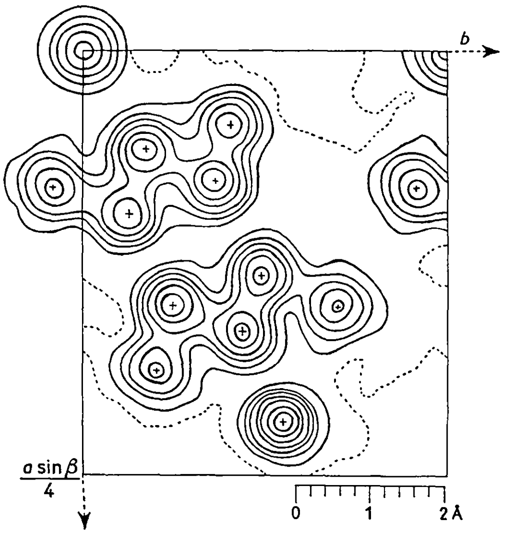


Fig. 4. Projection of the electron density along [001]. Contours are drawn at intervals of 1 e.Å^{-2}, the 1 e.Å^{-2} contour being broken.

It is observed in both Fig. 3(*a*) and 4 that the peak values of the electron densities of the methyl carbon atoms are smaller than those of the carbon atoms in the aromatic ring; in Fig. 3(*a*) the peak values (in electrons/Å^2) range from 5·3 to 5·8 (average 5·6) for the methyl carbon atoms and from 5·9 to 6·0 (average 6·0) for the aromatic carbon atoms, whilst in Fig. 4 the corresponding values are 6·0 to 6·5 (average 6·1) and 6·7 to 7·8 (avergge 7·3). The effect may be attributed to thermal vibration. Oscillation of the molecule as a whole about its centre or of each half of the molecule about the C_{CH_2}–$C_{Ar.}$ linkage would lower peak heights to the greatest extent at the outer parts of the molecule occupied by the methyl groups. Similar effects have been observed in durene (Robertson, 1933) and geranylamine hydrochloride (Jeffrey, 1945).

(vi) *Atomic co-ordinates: accuracy*

The atomic co-ordinates used in the final calculations of structure factors, bond lengths and bond angles are given in Table 3. The [001] projection is less reliable than the [010] projection because (*a*) the experimental data include only 52 values of $F_o(h0l)$ as compared with 155 values of $F_o(hk0)$, (*b*) in refinement by the method of successive Fourier syntheses the error in atomic positions is twice as great for non-centrosymmetric as for centrosymmetric projections (Luzzati, 1951). The *x* and *z* coordinates in Table 3 are therefore those obtained from the [010] projection. The *y* co-ordinates are derived from the [001] projection and must be regarded as less accurate than the *x* and *z* co-ordinates.

Table 3. *Atomic co-ordinates*

Atom	x (Å)	y (Å)	z (Å)
$C_0(CH_2)$	0·000	0·000	0·000
C_1	1·335	0·860	0·150
C_2	2·187	0·600	1·281
C_3	3·387	1·220	1·412
C_4	3·775	2·160	0·450
C_5	2·962	2·395	−0·655
C_6	1·771	1·780	−0·772
$C_7(CH_3)$	1·800	−0·420	2·262
$C_8(CH_3)$	4·375	0·990	2·612
$C_9(CH_3)$	3·407	3·440	−1·617
$C_{10}(CH_3)$	0·950	1·985	−2·075
O(OH)	5·000	2·710	0·595
$H_1(C_0)$	0·33	−0·81	−0·66
$H_2(C_7)$	0·82	−0·75	1·97
$H_3(C_7)$	1·37	0·23	3·00
$H_4(C_7)$	2·45	−1·06	2·85
$H_5(C_8)$	3·95	1·45	3·50
$H_6(C_8)$	4·90	0·00	2·45
$H_7(C_8)$	5·35	1·50	2·57
$H_8(O)$	5·72	3·30	0·00
$H_9(C_9)$	4·35	3·45	−2·32
$H_{10}(C_9)$	4·25	4·16	−1·32
$H_{11}(C_9)$	3·02	4·35	−2·20
$H_{12}(C_{10})$	1·37	1·40	−2·90
$H_{13}(C_{10})$	0·40	2·95	−2·20
$H_{14}(C_{10})$	0·05	1·36	−2·12

The values of the final agreement residuals—0·12 for the *h*0*l* reflexions and 0·13 for the *hk*0 reflexions—are quite low considering that the intensities have been estimated visually, that no detailed allowance has been made for thermal anisotropy, and that the postulated positions of the hydrogen atoms must be subject to considerable error. It is unlikely, therefore, that there are large errors in the positions determined for the carbon and oxygen atoms.

A quantitative estimate of the accuracy of the atomic co-ordinates is obtained from an examination of the planarity of the aromatic ring. The equation of the best plane through the six atoms in the aromatic ring, calculated by the method of least squares, is

$$-3{\cdot}639x+6{\cdot}020y+4{\cdot}182z = 1\,.$$

The displacements of all atoms in the molecule (except hydrogen atoms) from this plane are given in Table 4;

Table 4. *Perpendicular distances of the atoms from the mean plane through the aromatic carbon atoms*

Atom	Distance (Å)	Atom	Distance (Å)
C_1	0·007	$C_0(CH_2)$	−0·122
C_2	0·001	$C_7(CH_3)$	−0·075
C_3	−0·009	$C_8(CH_3)$	−0·004
C_4	0·018	$C_9(CH_3)$	0·066
C_5	−0·012	$C_{10}(CH_3)$	−0·144
C_6	−0·005	O(OH)	−0·048

the mean displacement is $0{\cdot}008_7$ Å and the maximum displacement 0·018 Å. The least accurate co-ordinates —the y co-ordinates—are given a fair weighting in the least-squares analysis since the plane of the aromatic ring is inclined to the (010) plane at an angle of 43°. It is reasonable to assume, therefore, that the probable error in the co-ordinates of the atoms in the aromatic ring is of the order of 0·01 Å and the probable error in the aromatic-ring bond lengths about $\sqrt{2}$ times larger than this value. The y co-ordinates of the methyl carbon atoms may be considerably less accurate because of the uncertain influence of the attached hydrogen atoms.

4. Discussion of the structure

The configuration of the bishydroxydurylmethane molecule and the arrangement of the molecules in the crystal are indicated in Fig. 5: the twofold symmetry axis is normal to the plane of the diagram and passes through the methylene carbon atom C_0. The planes of the two aromatic rings in each molecule are inclined to the (010) plane at an angle of 43° and are therefore mutually inclined at an angle of 86°. The magnitudes of the bond lengths and bond angles are given in Fig. 6 whilst the intermolecular distances and non-bonded intramolecular distances are shown in Fig. 5.

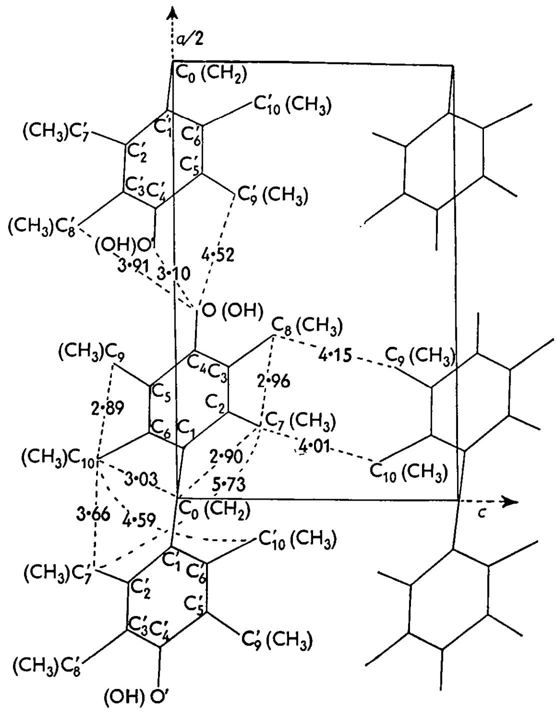


Fig. 5. The structure of bishydroxydurylmethane viewed along the [010] axis; intermolecular and non-bonded intramolecular distances are given in Ångström units.

An examination of Figs. 5 and 6 and Table 4 reveals that there is a considerable amount of strain in the molecule. The strains follow closely the pattern predicted by Burawoy & Chamberlain (1949), who suggested that the steric repulsive interaction of the methylene group and the o-substituted methyl groups should produce a lengthening of the $C_{Ar.}$–C_{CH_2} linkages and a widening of the angle between them and a displacement of the methylene carbon atom from the planes of the aromatic rings. The value of 1·60 Å for the $C_{Ar.}$–C_{CH_2} distance is significantly longer than the normal single-bond C–C distance of 1·54 Å; since the position of the methylene carbon atom is fixed by symmetry the probable error in this bond length is particularly small and is estimated to be 0·010 Å. The angle of 119·2° between the two $C_{Ar.}$–C_{CH_2} linkages is 10° more than the normal bond angle. It is interesting to note that Whittaker (1953) observed that the $C_{Ar.}$–C_{CH_2} distance is normal (1·53 Å) in 3:3′-dichloro-4:4′-dihydroxydiphenylmethane (IV) which has a similar configuration to bishydroxyduryl-

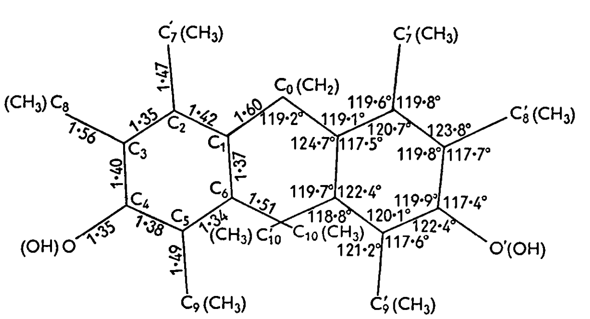


Fig. 6. Simplified diagram of the bishydroxydurylmethane molecule giving bond lengths and bond angles. In the true molecular configuration the aromatic rings are rotated out of the plane of the diagram about the C_0–C_1 and C_0–C_1' linkages.

methane but which is without one of the elements—the *o*-substituted methyl groups—presumed to cause the strain; however, Whittaker quotes a widened valency angle $C_{Ar.}$–C_{CH_2}–$C_{Ar.}$ of the same order of magnitude as that now observed in bishydroxydurylmethane. Unusually long C–C linkages have been reported in two electron diffraction studies: Kitaĭgorodskiĭ (1949) claims that in acenaphthene the distance between the CH_2 groups is 1·64±0·4 Å whilst Lemaire & Livingstone (1950) estimate that the C–C bond lengths in octafluorocyclobutane lie within the limits 1·57 and 1·62 Å; in each case the increase in the bond length is attributed to intramolecular strain. The methylene carbon atom is displaced by 0·12 Å from the mean plane through the atoms in the aromatic ring so that instead of lying in the plane of the ring the C_{CH_2}–$C_{Ar.}$ linkage is inclined to it at an angle of 4·4°; the direction in which the aromatic ring bends away from the C_{CH_2}–$C_{Ar.}$ linkage is such that it tends to reduce the stresses caused by steric repulsion.

The positions of the methyl carbon atoms provide further evidence of the existence of considerable steric repulsion within the molecule. The atoms C_7 and C_{10} are displaced by 0·075 and 0·144 Å respectively from the plane of the aromatic ring. The atom C_7 lies at distances of 2·90 Å from the methylene carbon atom C_0 and 2·96 Å from the neighbouring methyl carbon atom C_8; C_{10} is 3·03 Å from C_0 and 2·89 Å from the nearest methyl carbon atom C_9. In contrast, the distance between methyl carbon atoms in opposite halves of the molecule is relatively large—3·66 Å—whilst the smallest distances between methyl carbon atoms in different molecules are normal at about 4·0 Å.

The observed interactions between the carbon atoms of the methyl and methylene groups must take place indirectly through the attached hydrogen atoms. It is unfortunate that the *y* co-ordinates of the hydrogen atoms could not be determined directly since details of the strains in the linkages to the hydrogen atoms would give a fuller picture of the steric interactions. The [010] difference synthesis (Fig. 3(*b*)) does, however, show certain features which indicate that the hydrogen atoms may be displaced by very considerable amounts from the positions they would normally occupy. For example, the line joining the two symmetrically related hydrogen atoms of the methylene group should be at right angles to the line joining the carbon atoms C_0 and C_1 if the bonds from the methylene carbon atom follow the usual tetrahedral arrangement; instead the two lines are mutually inclined at an angle of about 60°, the deviation from a right angle being in such a direction that it increases the very short distance which separates each hydrogen atom from the nearest methyl group.

The length of the C_4–O bond (1·35 Å) is significantly less than the normal single-bond distance of 1·42 Å. Short $C_{Ar.}$–O distances are observed in other structures, e.g. 1·36 Å in resorcinol (Robertson, 1936) and 1·36 Å in 1:4-dimethoxybenzene (Goodwin *et al.*, 1950); the C–O distance observed by Whittaker (1953) in 3:3′-dichloro-4:4′-dihydroxydiphenylmethane is 1·38 Å.

We wish to thank Dr A. Burawoy for drawing our attention to this interesting problem and for supplying suitable crystals of bishydroxydurylmethane. We are also indebted to Prof. H. Lipson for his interest and encouragement, to Dr M. M. Qurashi for some preliminary data and to Dr F. Fowweather and Mr F. Foster for performing some of the final computational work on the Manchester University Electronic Digital Computer. One of us (B. C.) acknowledges with thanks a maintenance grant from the Government of Assam, India.

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