

The Crystal Structure of 4:4'-Dimethyldibenzyl

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The atomic and molecular arrangement in crystalline 4:4'-dimethyldibenzyl has been determined by X-ray diffraction. The unit cell dimensions are $a = 23.36$, $b = 6.10$, $c = 9.16$ Å; $\beta = 100.5^\circ$. The space group is $I2/a$. The shape of the molecule is similar to that of dibenzyl, and the relationship between the structures of the two substances is discussed. Bond lengths and inter-bond angles agree with standard values, but no attempt has been made to carry the determination to high accuracy because the unsuitable nature of the crystals and consequent unreliability of the intensities of the reflexions did not warrant the expenditure of further time and effort.

Introduction

In connexion with a chemical and X-ray investigation into the polymerization products obtained from *p*-xylene (Brown & Farthing, 1953), it was found that the α -form of the polymer gave a powder photograph which could be indexed on the basis of a unit cell remotely resembling that of dibenzyl. It was hoped to make use of this analogy in deriving a plausible structure for the polymer, but the resemblance was not sufficiently close. The powder photograph of the polymer was much more nearly like that of 4:4'-dimethyldibenzyl than that of dibenzyl, and it was therefore decided to work out an approximate structure for dimethyldibenzyl with a view to using the results in further work on the polymer.

Experimental

Crystals of 4:4'-dimethyldibenzyl were difficult to obtain in sizes suitable for X-ray single-crystal photographs. Although it is soluble in the majority of common organic solvents, in most cases the solubility curve rises very steeply with the temperature, and slow cooling produced only a powder. Slow evaporation was also fruitless on account of the high vapour pressure of the dimethyldibenzyl. The best crystals were obtained as thin plates on the cover of a vessel in which some residues containing 4:4'-dimethyldibenzyl had been left to stand at room temperature over a period of several months. These plates were large and clear, although only about 0.05 mm. thick, and they could readily be cut to shape with a sharp edge. Sections for *b*- and *c*-axis Weissenberg photographs were prepared in this way; they were far from ideal, but it was not practicable to obtain samples with more equi-dimensional cross-sections.

The dimensions of the unit cell were obtained by measurement of the layer lines on rotation photographs taken with Cu $K\alpha$ radiation. The monoclinic angle was

calculated from the unit lengths of a , b , c and that of $[111] = 12.13$ Å.

$$a = 23.36, b = 6.10, c = 9.16 \text{ \AA}; \beta = 100^\circ 33'.$$

The molecular weight (210) required, for four molecules per unit cell, a specific gravity of 1.086, while that observed by flotation was 1.084. Observed extinctions were $\{h0l\}$ for h odd and l odd and $\{hkl\}$ for $(h+k+l)$ odd, whence the space group is either Ia or $I2/a$. No pyroelectric effect was observed and the Wilson ratio favoured the centro-symmetrical space group, so $I2/a$ was adopted. The results of the structure determination confirmed this choice.

Weissenberg moving-film photographs were taken, also with Cu $K\alpha$ radiation, using batches of films in the usual way, about the zero layers of the b and c axes, and the first layer of b . The intensities of the reflexions were estimated by comparing the spots with those on a calibrated film strip. These values were corrected for polarization and angular velocity and placed on the absolute scale by comparison with sets of calculated structure amplitudes. No corrections were made for absorption or extinction.

The determination of the structure

The approximate structure was not difficult to deduce. On comparing the unit cell dimensions with those of dibenzyl, it was seen that, apart from the doubling of a occasioned by the body-centring, the only difference was an increase in the length of c , which might well be due to the additional methyl groups:

	$a \sin \beta$ (Å)	b (Å)	c (Å)
Dibenzyl	11.48	6.12	7.70
4:4'-Dimethyldibenzyl	2×11.48	6.10	9.16

Furthermore, the planes in dibenzyl which diffract most strongly are $(20\bar{2})$, (200) , (011) and $(21\bar{1})$, each

Table 1. *Experimental and calculated structure amplitudes*

hkl	$F(\text{exp.})$	$F(\text{calc.})$	hkl	$F(\text{exp.})$	$F(\text{calc.})$	hkl	$F(\text{exp.})$	$F(\text{calc.})$
000	—	+456	710	47	+37	15,1,2	6	-8
200	51	+47	11,1,0	25	-19	17,1,2	9	-12
400	93	-92	19,1,0	9	-12	18,1,3	3	+4
600	14	+21	21,1,0	15	-13	16,1,3	8	+12
800	27	-34	23,1,0	5	+4	14,1,3	5	-5
10,0,0	15	-14	020	57	+59	12,1,3	7	-10
14,0,0	7	+1	220	4	+5	10,1,3	2	+1
20,0,0	3	+1	420	5	-6	813	27	-33
22,0,0	11	-10	820	13	+13	613	14	-22
24,0,0	4	-3	10,2,0	31	+28	413	35	+40
22,0,2	3	+1	12,2,0	17	-19	213	13	+19
16,0,2	10	+6	14,2,0	18	-14	013	2	+4
14,0,2	19	-16	18,2,0	7	-7	213	11	-16
12,0,2	46	-44	130	5	+3	413	9	+11
10,0,2	6	+8	330	7	+18	613	33	+26
802	23	-41	730	12	+18	10,1,3	3	-5
602	9	-13	11,3,0	20	-21	12,1,3	3	-2
402	144	+170	13,3,0	4	-2	14,1,3	21	-14
202	54	+56	040	18	-9	16,1,3	14	-9
002	46	-46	440	6	+7	18,1,3	8	+6
402	3	+1	840	9	+7	20,1,3	3	+3
602	11	+3	10,4,0	13	+18	21,1,4	5	0
10,0,2	19	+16	12,4,0	8	-10	17,1,4	3	+3
14,0,2	17	+12	14,4,0	9	-9	15,1,4	7	-7
16,0,2	13	+9	060	5	+6	11,1,4	10	-13
18,0,2	27	-25	12,6,0	6	+3	914	48	-58
20,0,2	11	-11	22,1,1	3	-3	714	10	+12
20,0,4	8	+7	16,1,1	3	-4	514	55	+51
18,0,4	7	-6	14,1,1	9	+14	114	7	-3
16,0,4	18	-22	12,1,1	17	+20	314	21	+20
12,0,4	6	-8	10,1,1	19	-17	514	18	+16
10,0,4	7	-10	811	18	-12	714	3	-5
804	8	+23	611	7	-9	914	3	+4
204	12	-4	411	118	-102	13,1,4	8	+3
404	4	0	211	15	-19	15,1,4	3	+1
604	29	+33	011	101	-106	17,1,4	5	-4
804	3	+4	211	17	-28	215	4	+5
10,0,4	20	+20	411	8	-1	215	16	+20
12,0,4	26	+22	611	23	-25	415	3	+4
14,0,4	27	-28	811	20	+21	615	3	-6
16,0,4	14	-18	10,1,1	33	+24	815	3	0
18,0,4	4	+4	12,1,1	4	-5	10,1,5	8	-9
12,0,6	14	-8	14,1,1	4	-3	12,1,5	10	-10
10,0,6	13	-12	18,1,1	13	-11	14,1,5	3	+4
206	15	-13	20,1,1	6	-5	16,1,5	3	+4
006	4	-6	22,1,1	5	+5	23,1,6	4	+4
206	18	+25	25,1,2	5	+3	21,1,6	4	+6
406	4	+5	23,1,2	4	-6	19,1,6	4	-6
606	7	+8	15,1,2	11	-16	17,1,6	3	-4
806	14	+24	13,1,2	3	-4	15,1,6	3	-3
10,0,6	6	-10	11,1,2	3	+8	13,1,6	11	-23
12,0,6	6	-9	712	18	-15	916	7	+12
16,0,8	4	-5	512	80	-67	516	3	0
14,0,8	9	-7	312	58	+48	316	3	-4
608	6	-6	112	131	+94	116	3	+8
408	6	-6	112	1	-5	116	3	+4
208	6	+10	312	42	+31	316	3	0
008	4	+3	712	23	+7	916	17	+15
110	12	+14	912	24	+10	11,1,6	6	+5
310	38	+41	11,1,2	6	-8	13,1,6	7	-6
510	2	-2	13,1,2	7	+6			

of which, allowing for the doubling of h , gives a strong reflexion in dimethyldibenzyl, namely $(40\bar{2})$, (400) , (011) and $(41\bar{1})$.

A molecular disposition was therefore adopted for the trial structure which corresponded with that of dibenzyl. Good agreement was at once obtained for a

set of $\{h0l\}$ structure amplitudes, and the atomic coordinates for this zone were refined in the usual way by means of successive Fourier syntheses. The approximate y coordinates were found by calculation, assuming standard bond lengths and angles, and knowing x and z from the b -axis projection. Good

agreement was also obtained for the $\{hk0\}$ structure amplitudes, and the refinement of the c -axis projection proceeded without difficulty. The final b - and c -axis projections are shown in Figs. 1 and 2.

When these two projections were finished, the $\{h1l\}$ structure amplitudes were calculated and compared with the experimental values. This was done to ensure that the two projections had been combined in the

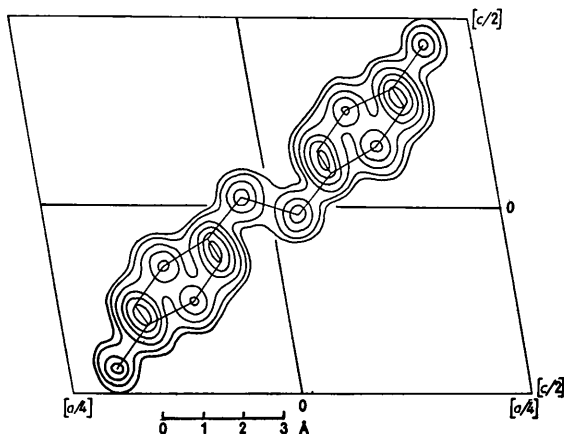


Fig. 1. Electron-density map of 4:4'-dimethyldibenzyl; $[b]$ projection.

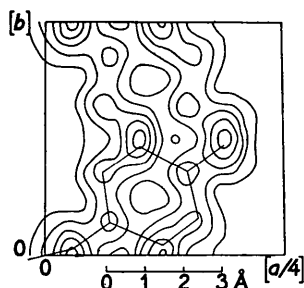


Fig. 2. Electron-density map of 4:4'-dimethyldibenzyl; $[c]$ projection on to (001).

correct way with the corresponding centres of symmetry as origin. These $\{h1l\}$ structure amplitudes were not used in any of the refining syntheses.

The value of B in the temperature factor which gave the best agreement between the calculated and experimental structure amplitudes was $8 \times 10^{-16} \text{ \AA}^2$. The discrepancies given by the usual formulae are

$$R(h0l) = 0.21; R(hk0) = 0.18; R(h1l) = 0.26.$$

The values of the calculated and experimental structure amplitudes are given in Table 1; planes where $F(\text{exp.}) = 0$ are omitted for the sake of economy of space: in all cases these give small calculated values.

Description of the structure

The structure of 4:4'-dimethyldibenzyl is a simple molecular one, the discrete molecules being packed in

a centred monoclinic cell with their centres lying on centres of symmetry. This requires that the two benzene rings of a molecule must be parallel; they are not co-planar, but are arranged step-wise, as in dibenzyl. The nearest contacts between molecules are between pairs of C_3 atoms related by a twofold axis, at 3.69 Å. There are also contacts between C_7 of one molecule and C_4 of the neighbouring molecule along the b axis at 3.77 Å. The terminal methyl groups (C_8) lie equidistant from two other terminal methyl groups of neighbouring molecules at 4.05 Å. There are also several distances in the region of 4.08 Å between the carbon atoms of a benzene ring and neighbouring CH_2 and CH_3 groups.

The atomic coordinates derived from the two projections and the corresponding bond lengths are listed in Table 2.

Table 2. Atomic coordinates and bond lengths

	x/a	y/b	z/c
C_1	0.028	0.04	0.976
C_2	0.072	0.15	0.095
C_3	0.060	0.36	0.144
C_4	0.100	0.46	0.252
C_5	0.152	0.36	0.310
C_6	0.163	0.15	0.263
C_7	0.124	0.05	0.156
C_8	0.195	0.48	0.428

$C_1-C_1' = 1.53 \text{ \AA}$	$C_4-C_5 = 1.37 \text{ \AA}$
$C_1-C_2 = 1.51$	$C_5-C_6 = 1.39$
$C_2-C_3 = 1.39$	$C_6-C_7 = 1.36$
$C_3-C_4 = 1.37$	$C_7-C_2 = 1.38$
	$C_5-C_8 = 1.52$

All the angles within the molecule are $120^\circ \pm 1^\circ$, except $C_1C_1'C_2$ which is 116° (in dibenzyl this angle is 115°). The angle between the plane containing $C_2C_1C_1C_2$ and the benzene rings is 113° (in dibenzyl this angle is $108^\circ 24'$). No estimate of accuracy is given; it is obviously not very high since only two-dimensional methods were used, and the experimental structure amplitudes may be subject to some error on account of the platy form of the crystals. The self-consistency of the molecular dimensions and the level of structure amplitude agreement do, however, indicate that the structure is essentially correct. Fig. 3 shows the dimensions of a molecule of 4:4'-dimethyldibenzyl, and Fig. 4 the packing of molecules in the unit cell compared with that of dibenzyl.

Discussion

It appears from the previous section that 4:4'-dimethyldibenzyl and dibenzyl are closely related not only in their unit-cell dimensions, but also in their molecular configurations: the step-wise arrangement and the angular inclinations of the central bonds are almost identical in the two cases. The essential difference between the two structures is in their mode of packing. This is partly necessitated by the addition

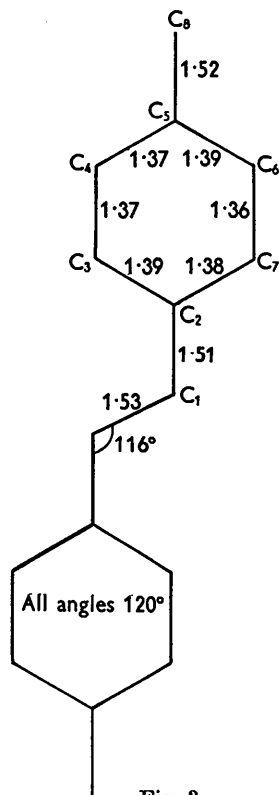


Fig. 3.

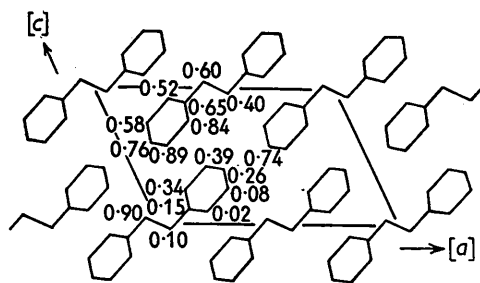


Fig. 4.

Fig. 3. Molecule of 4:4'-dimethyldibenzyl, showing bond lengths and inter-bond angles.

Fig. 4. Diagram of contents of unit cells of dibenzyl and 4:4'-dimethyldibenzyl, to show difference in packing.

of the methyl group to the end of the benzene rings, but it is not immediately obvious, even when taking this into consideration, why the two substances should not be completely isomorphous. From Fig. 4 it can be seen that in both cases the end of each molecule is separated from its nearest neighbour by approximately $\frac{1}{2}b$, and in both cases each benzene ring has other benzene rings packing approximately at right angles as its nearest neighbours; but the relative positions of adjacent molecules in the two structures are different. If the $(20\bar{2})$ planes in dibenzyl are considered, it would appear that the gap between two molecules in one plane is spanned by a molecule in the next plane. In 4:4'-dimethyldibenzyl this is not so in the case of the corresponding $(40\bar{2})$ planes. Presumably the addition of the methyl groups causes the distance between the benzene rings of adjacent molecules to be

come too great for another molecule to span, and an alteration in the packing system becomes imperative. Again, all molecules in any one $(20\bar{2})$ plane in dibenzyl all point in the same direction, but in a $(40\bar{2})$ plane in dimethyldibenzyl they point alternately up and down, giving a zigzag appearance. The general effect of this is that in dibenzyl the molecules may be regarded as forming layers in the (xy) plane, with a possible (001) cleavage, but in dimethyldibenzyl the layers are in the (yz) plane, with a possible (100) cleavage. The change is accompanied by a slight reduction in density from 1.12 to 1.08 g.cm.⁻³.

References

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