

scattering points at the positions of glob centers can be derived from the  $|F(\mathbf{s})|^2$ 's of the real crystal through dividing by  $G\langle I \rangle$  in the range  $2r_{ij} < d(hkl) < r_{gg}$ , provided that the globs in the crystal are 'spherical' and all alike. This raises the question of the existence of spherical globs in crystals.

One can say at once that the glob concept is useful only in connection with crystals with large unit cells as there must be a large number of interplanar spacings greater than 3 Å. The unit cells of such crystals contain a large number of atoms,\* which can be grouped into globs in many different ways. If, in interpreting the values of  $\langle I \rangle$ , it is assumed that the glob factors are spherical ( $F_g(\mathbf{s}) = F_g(s)$ ), the globs themselves must be (nearly) spherical globs and correspond to only certain ways of dividing the atoms in the cell into groups. It is probable that some structures do not provide any way of assigning the atoms to groups so as to make spherical globs, but it seems likely that many complex structures can provide nearly spherical globs by some method of subdivision. The assumption that  $\langle I \rangle = NF_g^2(s)$  corresponds to selecting a method of distributing the atoms into spherical globs, all with the same sets of interatomic distances.

When the structure of a crystal can be thought of as a set of similar globs in various positions and with different orientations, each of the structure factors is very probably near the value

$$F(s) = \sum_{j=1}^G \overline{F_g(\mathbf{s})} \exp [2\pi i s \cdot r_g] \quad (18)$$

\* In organic crystals, the number of reflections with  $d > 3$  Å is about ten times the number of atoms in the unit cell, not counting hydrogen.

obtained from formula (7) by replacing each  $F_g(\mathbf{s})$  by its average over all orientations. This statement is true, even if the globs are quite far from being spherical, provided enough different orientations of the globs are present. In such a case:

$$\langle I \rangle = \sum_{g=1}^N \overline{(F_g(\mathbf{s}))^2} = G \overline{(F_g(\mathbf{s}))^2}, \quad (19)$$

which is almost the same as (11), because

$$\frac{\overline{\sin 2\pi s r_{jj'}}}{2\pi s r_{jj'}} = \frac{\sin 2\pi s r_j}{2\pi s r_j} \cdot \frac{\sin 2\pi s r_{j'}}{2\pi s r_{j'}}, \quad (20)$$

where the bar over the left hand term indicates averaging  $r_{jj'}$  over all directions of  $\mathbf{r}_j$  and  $\mathbf{r}_{j'}$ . Consequently, a satisfactory approximation to a point-glob crystal is obtained by dividing the  $|F(\mathbf{s})|^2$ 's by  $G\langle I \rangle$  in this case also, which can occur quite frequently in complicated crystals.

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#### References

- WARREN, B. E. & GINGRICH, N. S. (1934). *Phys. Rev.* **46**, 368.  
 WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.  
 WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318.

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## The Structure of Diphenylene Naphthacene

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The unit cell of diphenylene naphthacene is monoclinic, with  $a = 11.0 \pm 0.05$ ,  $b = 5.15 \pm 0.03$ ,  $c = 19.6 \pm 0.10$  Å,  $\beta = 126^\circ$ . The space group is  $P2_1/c$ , and in the unit cell are two molecules, each lying on a centre of symmetry. The structure was solved by optical-transform methods, and the atomic positions were found with the aid of the (010) and (100) Fourier projections.

### Introduction

This compound is one of a number investigated largely by optical diffraction methods (Hanson, Taylor & Lipson, 1952). The procedure by which the approximate structure was determined is discussed elsewhere (Hanson, Lipson & Taylor, 1953), and will not be considered here.

### Unit cell and space group

The sample supplied consisted of a number of lath-like, blue, opaque crystals; although these were extremely thin, and showed a slight tendency to bend, no difficulty was experienced in selecting single crystals suitable for X-ray examination.

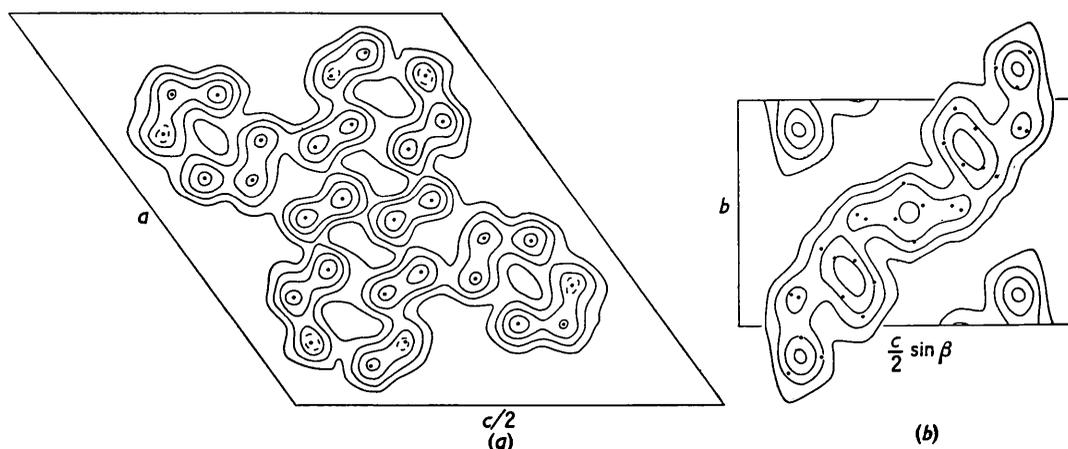


Fig. 1. (a) Electron-density map of (010) projection. Contours are drawn at intervals of  $1 \text{ e.}\text{\AA}^{-2}$ , the lowest being  $2 \text{ e.}\text{\AA}^{-2}$ . The contour at  $4\frac{1}{2} \text{ e.}\text{\AA}^{-2}$  has been drawn (as a broken line) where necessary to indicate atomic positions. (b) Electron-density map of (100) projection. Contours are drawn at intervals of  $2 \text{ e.}\text{\AA}^{-2}$ , the lowest being  $4 \text{ e.}\text{\AA}^{-2}$ .

Table 1. Atomic coordinates

	A			B		
	$x/a$	$y/b$	$z/c$	$X (\text{\AA})$	$Y (\text{\AA})$	$Z (\text{\AA})$
1	0.295	0.16	-0.130	2.62	0.82	-4.46
2	0.192	0.36	-0.174	1.70	1.85	-4.66
3	0.079	0.37	-0.163	0.70	1.91	-3.71
4	0.073	0.20	-0.110	0.64	1.03	-2.63
5	0.177	0.03	-0.065	1.57	0.15	-2.41
6	0.292	0.01	-0.077	2.59	0.05	-3.39
7	0.160	-0.13	-0.008	1.42	-0.67	-1.19
8	0.027	0.03	-0.021	0.24	0.15	-0.58
9	0.023	-0.21	0.081	0.20	-1.08	1.43
10	0.153	-0.37	0.097	1.36	-1.90	0.90
11	0.225	-0.55	0.160	2.00	-2.83	1.69
12	0.340	-0.71	0.179	3.02	-3.66	1.31
13	0.400	-0.64	0.129	3.56	-3.30	-0.05
14	0.338	-0.46	0.068	3.01	-2.37	-0.85
15	0.216	-0.31	0.052	1.93	-1.60	-0.39

A: Fractional coordinates, corresponding to crystal axes.

B: Coordinates in Ångström units, referred to orthogonal axes for which  $Y$  is parallel to  $b$ ,  $Z$  parallel to  $c$ .

The unit cell was shown by oscillation and Weissenberg photographs to be monoclinic, with

$$a = 11.0 \pm 0.05, \quad b = 5.15 \pm 0.03, \quad c = 19.6 \pm 0.10 \text{ \AA}, \\ \beta = 126^\circ.$$

A higher degree of accuracy is not claimed because no allowance was made for film shrinkage.

The measured density of the sample was  $1.37 \pm 0.03 \text{ g.cm.}^{-3}$ , and the calculated density, corresponding to two molecules in the unit cell, was  $1.39 \pm 0.02 \text{ g.cm.}^{-3}$ .

The systematic absences were  $h0l$  for  $l$  odd, and  $0kl$  for  $k$  odd. These indicated the space group  $P2_1/c$ , with molecules lying on centres of symmetry.

### Determination of the structure

The X-ray intensities for the  $h0l$  and  $0kl$  zones were estimated by visual comparison of each Weissenberg spot with a density wedge on similar film. Very long exposures, limited ultimately by background scattering, were required for the Weissenberg photographs,

and it is felt that the effect of the reflexions which were too weak to be observed might not have been negligible. Moreover, the tendency of the crystals to bend resulted in spots which differed appreciably in shape and size, some being more diffuse than others. It is feared therefore that the intensity data may not be altogether reliable.

The structure amplitudes were derived by using the usual trigonometrical factor, and, since the absorption coefficient of the compound was small, it was felt that further corrections were unnecessary.

The (010) projection was readily solved by what might now be called conventional optical-transform methods. It was refined by successive sign determinations and correction syntheses; the calculation involved in determining signs was very much reduced by the use of a form of the procedure for the optical derivation of structure amplitudes (Hanson, 1953). The electron-density map of the projection is given in Fig. 1(a).

The (100) projection was obtained largely by stereo-

Table 2. Observed and calculated structure amplitudes for  $h0l$  zone

$h0l$	$F_o$	$F_c$	$h0l$	$F_o$	$F_c$	$h0l$	$F_o$	$F_c$
002	50.3	62.8	302	6.3	2.8	6,0,18	< 6.4	- 1.2
004	58.0	-60.0	304	5.0	- 8.4	700	< 6.1	- 3.1
006	7.8	4.8	306	22.4	-27.4	702	< 7.9	8.8
008	15.8	-15.4	308	24.5	-23.8	704	< 6.4	0.9
0,0,10	< 5.2	- 2.0	3,0,10	< 4.5	- 0.7	702	< 5.8	4.4
0,0,12	13.5	13.9	3,0,12	8.0	- 7.7	704	< 5.5	3.9
0,0,14	< 6.3	1.6	3,0,14	< 5.9	- 3.4	706	12.5	-12.1
0,0,16	< 6.4	3.8	3,0,16	9.7	11.2	708	< 5.3	2.8
100	72.0	67.0	3,0,18	< 6.4	- 1.7	7,0,10	< 5.4	1.7
102	28.2	29.8	3,0,20	13.4	-11.3	7,0,12	< 5.7	- 0.8
104	7.6	4.4	400	7.3	- 2.2	7,0,14	11.9	14.1
106	< 4.2	- 2.2	402	27.0	21.6	7,0,16	< 6.3	- 1.7
108	< 5.0	- 0.4	404	6.5	6.4	7,0,18	14.1	-15.9
1,0,10	12.8	9.3	406	13.6	-16.9	7,0,20	< 6.1	- 4.5
1,0,12	9.0	9.3	408	< 6.3	- 1.4	800	< 8.6	- 8.7
1,0,14	< 5.0	- 1.0	402	27.4	-19.2	802	< 6.3	1.8
102	30.4	40.5	404	< 3.7	2.7	804	< 5.9	3.8
104	5.7	5.1	406	25.7	34.1	802	< 6.3	- 3.7
106	5.1	8.2	408	14.3	-11.9	804	< 6.1	0.7
108	< 4.2	0.5	4,0,10	33.6	-33.0	806	13.2	-16.4
1,0,10	8.6	4.4	4,0,12	< 5.1	- 0.9	808	8.8	- 7.3
1,0,12	11.2	9.0	4,0,14	< 5.8	2.2	8,0,10	< 5.9	5.2
1,0,14	< 6.2	- 5.0	4,0,16	< 6.3	- 3.6	8,0,12	< 6.0	2.2
1,0,16	9.2	- 8.7	4,0,18	< 6.4	3.2	8,0,14	< 6.2	3.3
1,0,18	< 6.3	- 1.7	4,0,20	< 5.9	- 0.7	8,0,16	9.1	- 9.2
200	52.6	-47.0	500	20.5	12.7	8,0,18	9.7	-12.3
202	31.0	31.0	502	15.6	16.0	8,0,20	< 6.1	- 1.7
204	7.1	- 3.8	504	< 5.7	5.1	900	< 6.2	- 2.1
206	8.3	4.0	506	< 6.3	0.3	902	< 7.1	- 8.1
208	26.2	23.0	502	6.7	- 3.8	904	< 4.8	1.2
2,0,10	6.3	4.4	504	16.3	12.2	902	< 8.0	7.2
2,0,12	< 6.2	- 0.5	506	12.1	17.3	904	< 6.4	3.1
202	35.2	-41.7	508	6.5	1.4	906	< 6.2	- 0.4
204	28.4	35.5	5,0,10	6.4	- 7.0	908	17.7	-17.2
206	14.1	-14.6	5,0,12	13.2	-12.0	9,0,10	22.4	-22.2
208	5.9	3.4	5,0,14	< 5.7	- 2.8	9,0,12	< 6.3	0.4
2,0,10	18.5	20.0	5,0,16	< 6.2	4.3	9,0,14	< 6.4	0
2,0,12	7.7	- 7.6	600	15.0	13.3	9,0,16	< 6.4	- 5.8
2,0,14	< 6.1	- 2.5	602	< 6.0	0.6	9,0,18	< 6.2	2.5
2,0,16	< 6.4	- 3.8	604	< 6.3	2.3	10,0,0	< 5.4	1.1
2,0,18	10.8	-10.3	602	32.0	28.5	10,0,2	< 4.3	- 6.6
2,0,20	< 5.2	- 4.1	604	21.7	22.6	10,0,2	11.9	7.3
300	11.9	10.8	606	10.5	-13.1	10,0,4	< 6.3	- 1.9
302	< 4.0	- 3.2	608	14.6	-18.6	10,0,6	< 6.4	1.2
304	14.9	-12.8	6,0,10	< 5.0	8.3	10,0,8	< 6.4	1.2
306	< 5.3	- 0.4	6,0,12	< 5.4	- 1.4	10,0,10	16.8	-16.8
308	16.1	7.9	6,0,14	< 5.8	- 0.9	10,0,12	12.3	-10.1
3,0,10	< 6.4	0.5	6,0,16	11.4	12.7	10,0,14	< 6.4	2.6

Table 3. Observed and calculated structure amplitudes for  $0kl$  zone

$0kl$	$F_o$	$F_c$	$0kl$	$F_o$	$F_c$	$0kl$	$F_o$	$F_c$
002	53.4	64.0	019	19.8	17.5	033	< 6.7	- 4.2
004	54.8	-53.8	0,1,10	< 7.1	- 6.6	034	< 6.9	- 2.1
006	10.4	5.0	020	5.1	2.5	035	< 7.1	5.3
008	18.4	-16.5	021	< 4.9	3.9	036	< 7.3	7.2
0,0,10	< 6.9	- 2.3	022	13.9	17.6	037	< 7.6	- 5.8
0,0,12	19.3	15.8	023	< 5.3	6.7	038	< 7.9	0.7
011	8.1	11.9	024	18.4	13.3	039	10.0	-11.7
012	38.2	53.1	025	16.9	-11.0	040	< 8.0	- 3.2
013	54.7	56.0	026	< 6.1	- 3.8	041	< 8.0	- 3.1
014	36.2	35.1	027	8.7	-14.4	042	< 8.0	6.2
015	< 4.7	- 1.9	028	8.5	- 7.0	043	< 8.1	- 2.8
016	6.7	- 3.2	029	9.7	8.0	044	< 8.1	5.2
017	< 5.7	- 5.5	031	17.3	12.4	045	< 8.3	5.0
018	15.3	- 9.8	032	< 6.5	4.2	046	12.7	-10.6

chemistry, and approximately confirmed by the electron-density map of Fig. 1(b). No individual atoms are

resolved, and the atomic positions indicated must be regarded as tentative.

