

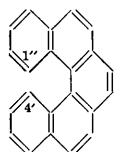
*The Crystal Structure and Molecular Shape of 3 : 4-5 : 6-Dibenzophenanthrene.*

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A detailed X-ray structural investigation has been made of 3 : 4-5 : 6-dibenzophenanthrene, the monoclinic crystalline modification which contains twelve molecules in the unit cell being used. Four of these molecules are found to display an exact two-fold axis of symmetry, while the other eight occupy general positions in the space group ( $C_{2h}^6$ ) which do not demand any molecular symmetry. The molecules are found to be severely distorted from the planar configuration, the two naphthalene wings being bent away from each other so as to achieve a clearance of about 3.0 Å between the non-bonded carbon atoms 4' and 1''. This bending is distributed over the five fused rings in such a manner as to cause no very severe buckling or angle distortion in any individual ring, and so the retention of aromatic properties can be understood. The two optical isomers are present in the unit cell, related to each other as required by the symmetry elements of the space group. Although approximate co-ordinates have been found for all the atoms, the accuracy is not high (about  $\pm 0.1$  to  $\pm 0.2$  Å) and no significant determinations of bond lengths within the molecule can be made.

THE structure of 3 : 4-5 : 6-dibenzophenanthrene (I) is of interest because it must depart considerably from the usual regularity of aromatic hydrocarbons (see, *e.g.*, Cook, *Ann. Reports*, 1942, **39**, 155, 173). To allow sufficient clearance between



two-fold axis

the non-bonded carbon atoms 4' and 1'', with their attached hydrogen atoms, there must be either a very severe distortion of the angles and bond lengths in the aromatic rings, or else the molecule must assume a non-planar form. That the second possibility is the one mainly operative appears to be established by the work of Bell and Waring (*J.*, 1949, 2689) who succeeded in isolating optically active forms of 2' : 2''-4' : 4''-tetramethyl-3 : 4-5 : 6-dibenzophenanthrene-9 : 10-dicarboxylic acid, and more recently by Hall and Turner (*Chem. and Ind.*, 1953, 1177) who have prepared optically active 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene.

We have now attempted to determine the exact nature of the molecular distortion in 3 : 4-5 : 6-dibenzophenanthrene by means of a detailed X-ray crystallographic investigation, and some preliminary results have been reported (McIntosh, Robertson, and Vand, *Nature*, 1952, **169**, 322). Unfortunately, the monoclinic modification of the compound which we have investigated is extremely complex, containing twelve molecules in the unit cell. In spite of repeated refinements by the double Fourier series method, in which the XRAC computer (Pepinsky, *J. Appl. Physics*, 1947, **18**, 601) has been employed, and by a large number of difference syntheses, the final accuracy is not high, although it is sufficient to establish the general features of the structure. It had been hoped to pursue this analysis further by means of the three-dimensional Fourier series method, but in the meantime a much simpler crystalline modification has been discovered by Harnick, Herbstein, and Schmidt (*Nature*, 1951, **168**, 158) which contains only four molecules in the monoclinic cell. It would therefore be more reasonable to conduct any further refinement of the molecular structure on this second and simpler modification.

*Crystal Data.*—3 : 4-5 : 6-Dibenzophenanthrene,  $C_{22}H_{14}$ ;  $M$ , 278.3; m. p. 177—178°;  $d$ , calc. 1.253, found 1.264. Monoclinic,  $a = 26.17 \pm 0.15$ ,  $b = 8.94 \pm 0.03$ ,  $c = 19.57 \pm 0.07$  Å,  $\beta = 105.1^\circ \pm 0.3^\circ$ . Absent spectra, ( $h0l$ ) when  $h$  is odd and when  $l$  is odd, ( $0k0$ ) when  $k$  is odd, ( $hkl$ ) when  $h + l$  is odd. Space group,  $C_2^4-Aa$  or  $C_{2h}^6-A2/a$ . The results of this analysis indicate  $C_{2h}^6$ . Twelve molecules per unit cell. Molecular symmetry, two-fold axis in four of the molecules. Volume of the unit cell = 4419 Å<sup>3</sup>. Absorption coefficient for X-rays ( $\lambda = 1.54$ )  $\mu = 6.6$  per cm. Total number of electrons per unit cell =  $F(000) = 1752$ .

The absent spectra do not permit an unambiguous determination of space group, and the possibilities,  $C_3^2$  or  $C_{2h}^6$ , must be distinguished by other means. The unusually large number of molecules in the unit cell suggests the group of higher symmetry. More direct confirmation was obtained by making a statistical survey of the intensities of the  $(h0l)$  and  $(hk0)$  zones, using the procedure of Howells, Phillips, and Rogers (*Acta Cryst.*, 1950, 3, 210). The distributions obtained were decisively in favour of a centrosymmetrical structure, as shown by Fig. 1, and thus pointed clearly to the space group  $C_{2h}^6$ .

The crystals of the present twelve-molecule modification of dibenzophenanthrene were obtained from ethyl alcohol solution and occur as well-developed bipyramids, the faces identified being (100), (101), (010), and (11 $\bar{1}$ ). When the compound is recrystallized from acetic acid, Harnick, Herbststein, and Schmidt's four-molecule monoclinic modification (*loc. cit.*) is obtained in the form of needles.

*Analysis of the Structure.*—A very unusual feature of this crystal structure, and one which greatly increases the complexity of the analysis, is the presence of twelve chemical

FIG. 1. Distribution of  $(h0l)$  and  $(hk0)$  intensities;  $z$  is a fraction of the local averaged intensity;  $N(z)$  is the fraction of the reflections with intensities equal to or less than  $z$ ; full curve is the theoretical distribution for a centrosymmetrical structure, broken curve for non-centrosymmetrical.

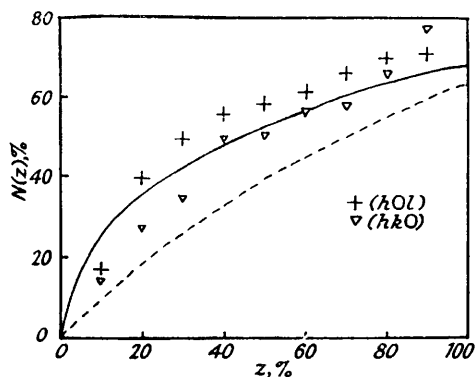
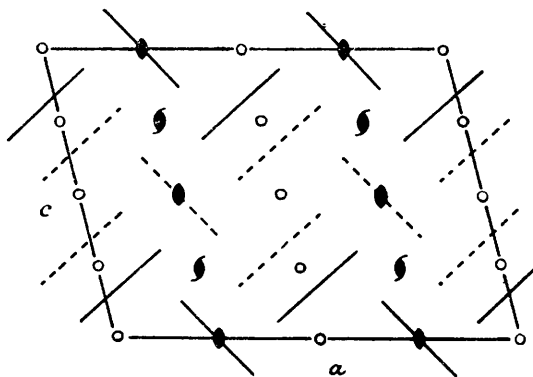


FIG. 2. Relative positions of the molecules in the unit cell, viewed along the two-fold axis. Broken lines represent molecules displaced  $\frac{1}{2}b$  with respect to the others. Small circles denote symmetry centres, ovals diad axes.



molecules in the unit cell. If the space group is assumed to be  $C_{2h}^6$  in accordance with the facts mentioned above, then the unit cell must contain eight equivalent asymmetric units. It follows that the asymmetric unit must consist of  $1\frac{1}{2}$  chemical molecules. Now, a molecule can only be shared between two equivalent asymmetric units if it contains an inherent element of symmetry required by the space group, that is, if it happens to coincide with one of the space-group symmetry elements. From the chemical formula (I) it is clear that the molecule cannot have a centre of symmetry, and thus the only possible symmetry is a two-fold axis, which must be parallel to the  $b$  crystallographic axis. This analysis therefore requires the four shared molecules to lie on the two-fold axes in the special positions  $\frac{1}{2}, y, 0$ ;  $\frac{3}{2}, \bar{y}, 0$ ;  $\frac{1}{2}, y + \frac{1}{2}, \frac{1}{2}$ ;  $\frac{3}{2}, \frac{1}{2} - y, \frac{1}{2}$ . The remaining eight molecules can then lie in the eight general positions of the space group. Taking an origin at a centre of symmetry, the co-ordinates of these positions are  $\pm(x, y, z)$ ;  $\frac{1}{2} - x, y, \bar{z}$ ;  $x, y + \frac{1}{2}, z + \frac{1}{2}$ ;  $\frac{1}{2} - x, y + \frac{1}{2}, \frac{1}{2} - z$ . Such a distribution of the molecules between both general and special positions is unusual, but a somewhat similar situation has been reported for diphenylene (Waser and Lu, *J. Amer. Chem. Soc.*, 1944, 66, 2035) and for bisdiphenyleneethylene (Fenimore, *Acta Cryst.*, 1948, 1, 295).

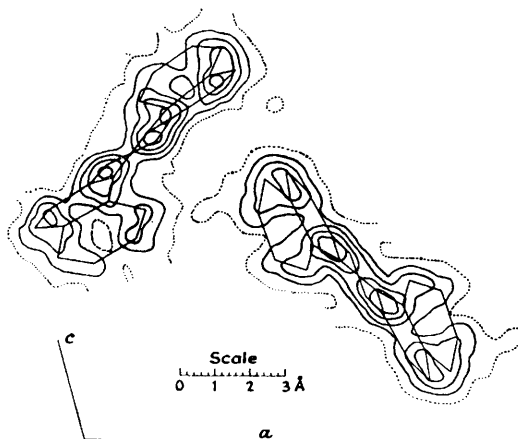
The distribution of the molecules as postulated above imposes certain limits on their possible arrangement and orientation. In particular, the two-fold symmetry axes (see I) of the molecules in special positions must be parallel to  $b$ , producing an end view of these molecules when viewed in projection on the (010) plane. The length of the  $b$  crystal axis (8.94 Å) is sufficient to accommodate a molecule in this position, and the great strength

of the (080) reflection ( $F = 97$ ) is explained because its period then corresponds approximately to the spacing between the rows of carbon atoms lying normal to the  $b$  axis.

When four molecules are placed in these special positions it is found that the sites of the remaining eight molecules are restricted by packing considerations. Although not required to display any exact two-fold axis, these molecules must be set up in a somewhat similar way so that they also appear in end view on the (010) projection. Further, it is observed that the ( $h0l$ ) reflections are on the average much stronger than those of the other two axial zones; and amongst the ( $h0l$ ) reflections the (402), (40 $\bar{4}$ ), (60 $\bar{4}$ ), (60 $\bar{6}$ ), (8,0, $\bar{10}$ ), (10,0,4), (10,0, $\bar{10}$ ), and (14,0,4) are very strong. These facts are consistent with the diagonal packing of the molecules illustrated in Fig. 2.

*Refinement of the Structure.*—Chemical considerations already mentioned show that the molecule of 3 : 4-5 : 6-dibenzophenanthrene cannot be planar, and so the end view along the two-fold axis cannot truly be represented by the simple lines in Fig. 2. Some direct X-ray evidence concerning the molecular distortion can be obtained from the (015) reflection, which is very strong. The form of the structure factor function for this reflection shows that it is not possible for any planar configuration of the carbon atoms to account for such a high value. The distortion required can be obtained by bending the two

FIG. 3. *Electron-density projection on (010) covering two molecules of 3 : 4-5 : 6-dibenzophenanthrene, with final co-ordinates superimposed. Contour interval,  $2 e \cdot \text{\AA}^{-2}$ , the two-electron line being dotted.*



naphthalene wings of the molecule in opposite directions out of the mean plane, which is represented by the short lines in Fig. 2. In this way, a reasonable trial model for the molecule was set up and adjusted until it yielded some measure of agreement between the observed and calculated structure factors.

An attempt was next made to refine the  $x$  and  $z$  co-ordinates of the atoms by the Fourier method, employing the ( $h0l$ ) structure factors and the projection along the relatively short  $b$  axis (8.94 Å). In the first synthesis 41 measured structure factors were employed, and although only vague groups of atoms could be distinguished it was at once clear that a distortion in the wrong direction had been applied to the molecules in the special positions. The sense of this distortion was then reversed, and further Fourier syntheses were computed.

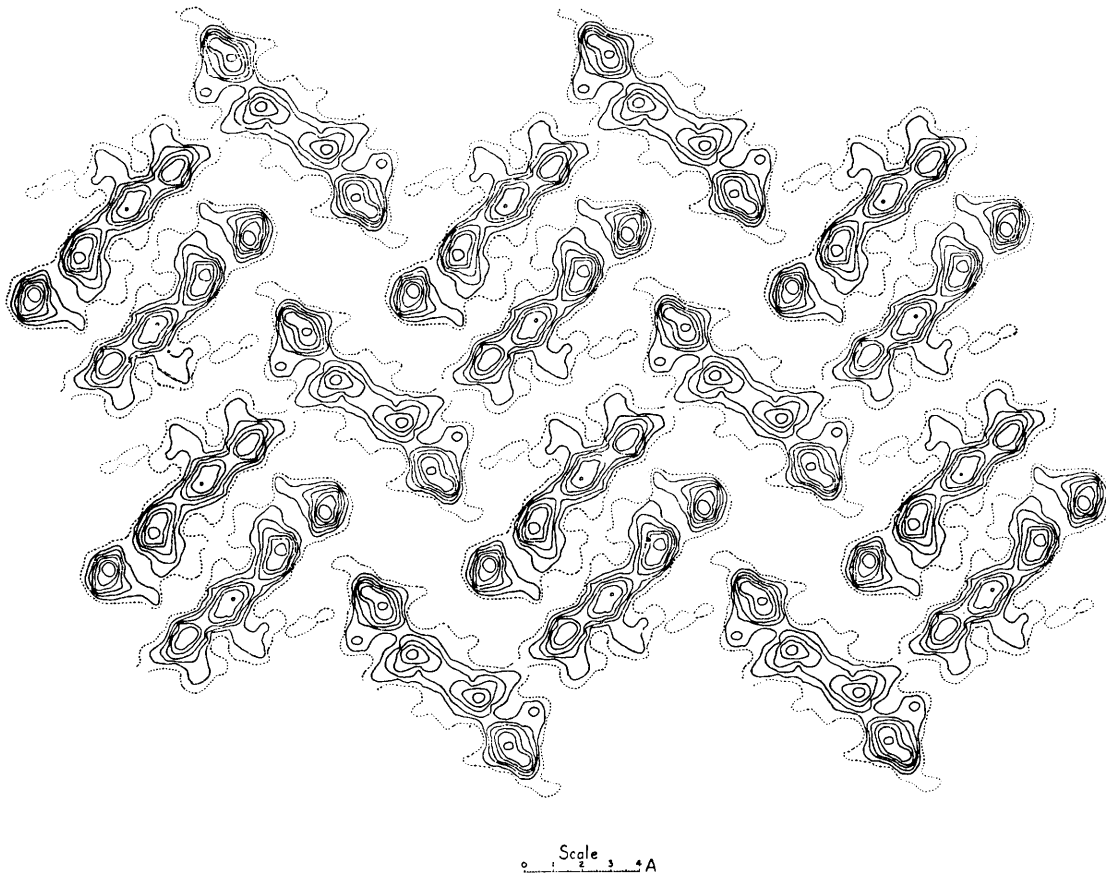
At this point it became possible through the courtesy of Professor Pepinsky to employ the X-Ray Analogue Computer (XRAC) at Pennsylvania State College on the refinement process (Pepinsky, *J. Appl. Physics*, 1947, **18**, 601). In this work background criteria were employed to indicate the probable signs of some of the smaller structure factors, but the refinement process was greatly hampered by the fact that few separately resolved atoms can be expected in any projection of the structure owing to the complex interleaving of the molecules. The final projection from the computer had well-developed detail in the outspread parts of the molecule which indicated the general form of the distortion but still left considerable latitude in choosing atomic co-ordinates.

Further refinement of the co-ordinates was achieved by means of difference syntheses.

After the computation of 13 of these the discrepancy between the observed and calculated structure factors of the 146 ( $h0l$ ) planes employed had decreased to 27%. At this stage the structure appears to be reasonably certain, although not sufficiently precise to permit significant calculations of all the individual C-C bond lengths within the molecule. A final electron-density projection on (010) showing the two crystallographically independent molecules is shown in Fig. 3, and Fig. 4 shows on a smaller scale the mutual arrangement of all the molecules in the unit cell.

*Co-ordinates.*—The  $x$  and  $z$  co-ordinates were obtained from the above Fourier syntheses and from the difference syntheses, while the  $y$  co-ordinates were adjusted mainly by trial

FIG. 4. *Electron-density projection on (010) covering whole unit cell. (This map is based on an earlier and less refined Fourier synthesis than Fig. 3.)*



and error, the ( $hk0$ ) and ( $0kl$ ) reflections being used. The final values of the co-ordinates for the 33 carbon atoms in the asymmetric unit are given in Table 1. The origin is taken at a centre of symmetry. Atoms lettered  $A$  to  $K$  refer to one-half of the molecule lying on the diad axis (see Fig. 2 and Fig. 5), the co-ordinates of the atoms forming the other half of this molecule being given by  $(\frac{1}{2}a - x, y, -z)$ . Atoms lettered  $A'$  to  $K'$  and  $A''$  to  $K''$  refer to the two corresponding halves of the other molecule lying in the general position.  $x, y, z$  are monoclinic co-ordinates expressed as fractions of the axial lengths;  $X, Y, Z$  are in Ångstrom units, and  $X'$  and  $Z'$  are orthogonal co-ordinates in Ångstrom units, referred to the  $a$  and  $b$  crystal axes and their perpendicular  $c'$ .

*Discussion of Results.*—The refinement of the structure has not proceeded far enough to enable the carbon-carbon bond lengths within the molecule to be determined with any

TABLE 1. Co-ordinates.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>X'</i>	<i>Z'</i>
<i>A</i>	0.247	0.636	0.031	6.46	5.68	0.61	6.30	0.59
<i>B</i>	0.233	0.498	0.061	6.10	4.45	1.20	5.79	1.16
<i>C</i>	0.220	0.498	0.126	5.76	4.45	2.46	5.12	2.38
<i>D</i>	0.201	0.358	0.158	5.26	3.20	3.09	4.46	2.98
<i>E</i>	0.198	0.222	0.114	5.18	1.98	2.23	4.60	2.15
<i>F</i>	0.176	0.089	0.144	4.61	0.80	2.82	3.88	2.72
<i>G</i>	0.158	0.965	0.094	4.13	8.62	1.83	3.65	1.77
<i>H</i>	0.163	0.975	0.022	4.27	8.71	0.42	4.16	0.41
<i>I</i>	0.196	0.095	0.006	5.12	0.85	0.12	5.09	0.12
<i>J</i>	0.210	0.225	0.044	5.49	2.01	0.86	5.27	0.83
<i>K</i>	0.234	0.358	0.022	6.12	3.20	0.43	6.01	0.42
<i>A'</i>	0.008	0.114	0.162	0.22	1.02	3.17	-0.61	3.06
<i>B'</i>	-0.014	0.253	0.132	-0.38	2.26	2.58	-1.05	2.49
<i>C'</i>	-0.066	0.253	0.095	-1.74	2.26	1.85	-2.22	1.79
<i>D'</i>	-0.088	0.392	0.067	-2.29	3.51	1.30	-2.63	1.26
<i>E'</i>	-0.056	0.525	0.069	-1.45	4.69	1.35	-1.80	1.30
<i>F'</i>	-0.071	0.645	0.022	-1.86	5.76	0.43	-1.97	0.42
<i>G'</i>	-0.033	0.765	0.014	-0.87	6.84	0.27	-0.94	0.26
<i>H'</i>	0.019	0.765	0.050	0.49	6.84	0.97	0.24	0.94
<i>I'</i>	0.038	0.637	0.093	1.00	5.69	1.83	0.52	1.77
<i>J'</i>	0.000	0.522	0.107	0.00	4.66	2.10	-0.55	2.03
<i>K'</i>	0.012	0.392	0.142	0.31	3.51	2.78	-0.41	2.68
<i>A''</i>	0.067	0.117	0.198	1.76	1.05	3.87	0.75	3.74
<i>B''</i>	0.092	0.253	0.234	2.40	2.26	4.58	1.21	4.42
<i>C''</i>	0.148	0.253	0.277	3.87	2.26	5.42	2.46	5.23
<i>D''</i>	0.175	0.392	0.307	4.58	3.51	6.00	3.02	5.79
<i>E''</i>	0.145	0.531	0.298	3.79	4.75	5.83	2.27	5.63
<i>F''</i>	0.166	0.665	0.339	4.34	5.94	6.63	2.61	6.40
<i>G''</i>	0.136	0.793	0.342	3.56	7.09	6.69	1.82	6.46
<i>H''</i>	0.085	0.790	0.301	2.21	7.06	5.89	0.68	5.69
<i>I''</i>	0.061	0.656	0.257	1.60	5.86	5.03	0.29	4.86
<i>J''</i>	0.091	0.533	0.249	2.38	4.77	4.87	1.11	4.70
<i>K''</i>	0.060	0.395	0.211	1.58	3.53	4.13	0.50	3.99

accuracy. The co-ordinates in Table 1 yield values for these bond lengths which vary from 1.3 to 1.6 Å. They are not reported individually because they are subject to errors of between  $\pm 0.1$  and  $\pm 0.2$  Å at the present stage of the analysis. The actual bond-length variation in a molecule of this type is likely to be from 1.35 to 1.50 Å, as in ovalene (Donaldson and Robertson, *Proc. Roy. Soc.*, 1953, *A*, **220**, 157) and perylene (Donaldson, Robertson, and White, *ibid.*, p. 311). In the present structure some of the longest bonds appear to be those connecting the two naphthalene wings of the molecule in the general position (*A'A''* and *K'K''*); these are the bonds which are probably subject to the greatest twisting strain and distortion. This result cannot be confirmed for the other molecule, however, because the resolution is here too poor to enable any conclusions to be drawn.

Although no definite results can be obtained regarding individual bond-length variations, the nature of the molecular distortion can be ascertained with some certainty from this analysis. Its general form will be clear from a study of the projection of the molecules along the direction of the two-fold axis (Fig. 5).

In a coplanar, undistorted molecule the distance between the non-bonded carbon atoms *I'* and *I''* would be about 1.4 Å. For the molecule in the general position we find this distance to be 3.1 Å, and for the molecule in the special position, 2.9 Å. These measurements are subject to a maximum error of about  $\pm 0.2$  Å, and the mean value of 3.0 Å may be taken as indicating the magnitude of the displacement. This distortion is achieved without any very great change in the carbon valency angles or severe buckling of any individual benzene ring. Instead, the bending is distributed over the five fused rings in a manner similar to that which occurs when a rigid molecular model is forcibly distorted by bending the two wings apart. Such a distortion, which does not greatly disturb the trigonal symmetry of the bonds about any particular carbon atom, is compatible with the observed retention of aromatic character.

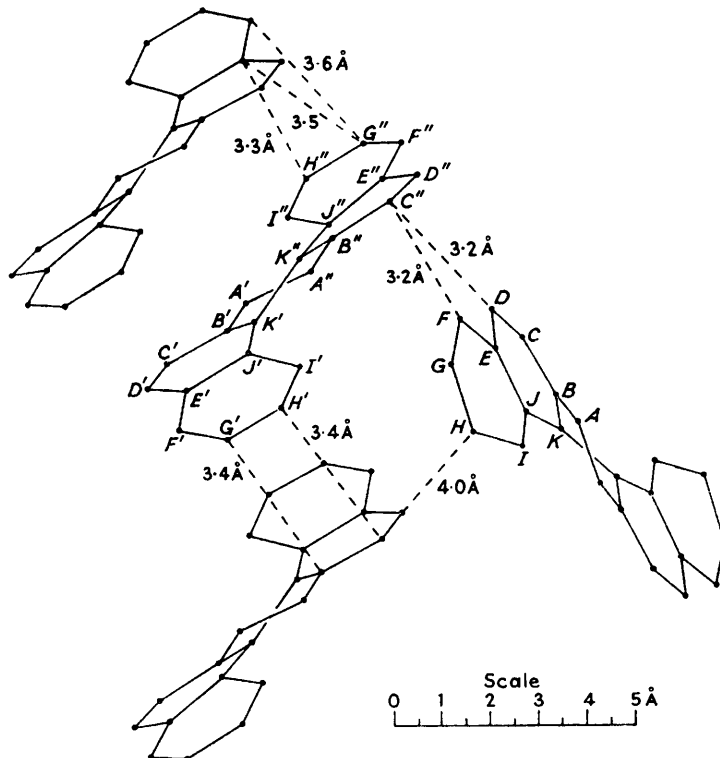
As required by the symmetry of the space group, the molecule in the special position lies with its two-fold axis perpendicular to the (010) plane, and in Fig. 5 this molecule (on

the right) shows an exact centre of symmetry in the projection. The other molecules in the general positions probably also have an exact two-fold symmetry axis, but in this case the axis appears to be tilted a few degrees away from the perpendicular position.

The compound, being a synthetic product, contains the expected two possible optical isomers in equal proportions. The two isomers present in the unit cell are related as demanded by the symmetry elements (Fig. 2)—the centres of symmetry, for example, requiring the axes of alternate molecules to be directed up and down respectively.

Intermolecular approach distances are indicated in Fig. 5. Again these are subject to possible errors of up to  $\pm 0.2$  Å, but within these limits they are found to conform to the minimum distances usual for aromatic hydrocarbon structures. For the pair of

FIG. 5. *Projection of part of the unit cell on (010), showing intermolecular contacts.*



molecules related by a centre of symmetry and lying in the general position the distance between carbon atom *G* of one and *B* of the other is 3.4 Å. Between *H* and *G* of the same pair of molecules the distance is also 3.4 Å. Between *F* and *D* of a molecule in the special position and *C* of the nearest one in the general position the distances are both 3.2 Å. Between *H* (special) and *D* (general) the distance is 4.0 Å. Between the other pair of molecules in the general position approaches of 3.5 Å (*G* . . . *E*), 3.6 Å (*G* . . . *F*), and 3.5 Å (*H* . . . *E*) are found.

#### EXPERIMENTAL

Copper radiation ( $\lambda = 1.542$  Å) and photographic methods were used throughout this study. Visual estimates of intensities were made from moving-film records, the multiple film technique being used (Robertson, *J. Sci. Instr.*, 1943, **20**, 175). The crystal specimens employed were small bipyramids about 0.5 mm. by 0.4 mm. in cross section, although some slightly larger specimens were used to record the fainter reflections. The crystals were completely bathed in a uniform X-ray beam, and absorption corrections were not applied because of the approximately square cross section. The mosaic crystal formula was assumed, and the resulting

structure factors are given in Table 2 ( $F_0$ ). The absent reflections and a few very weak ones are omitted from this table.

TABLE 2. *Measured and calculated structure factors.*

<i>hkl</i>	$F_0$	$F_c$	<i>hkl</i>	$F_0$	$F_c$	<i>hkl</i>	$F_0$	$F_c$	<i>hkl</i>	$F_0$	$F_c$
000	—	1752	16,0,6	38	30	10,0, $\bar{1}\bar{2}$	10	-2	20,2,0	24	12
200	66	91	14,0,6	43	-22	12,0, $\bar{1}\bar{2}$	40	-47	21,2,0	30	1
400	84	110	12,0,6	18	15	14,0, $\bar{1}\bar{2}$	34	-50	22,2,0	31	27
600	60	44	10,0,6	33	-17	18,0, $\bar{1}\bar{2}$	23	-26	340	29	-26
800	138	-112	806	34	50	20,0,14	16	10	440	51	-31
10,0,0	26	-16	606	69	99	14,0,14	9	-19	540	10	15
12,0,0	107	119	406	9	-3	12,0,14	25	-37	640	34	33
14,0,0	72	91	206	8	-33	6,0,14	25	31	740	10	61
30,0,0	16	12	206	174	-173	4,0,14	9	8	840	45	59
020	56	-56	406	117	87	2,0,14	16	6	940	37	27
040	39	41	606	203	171	2,0, $\bar{1}\bar{4}$	14	15	10,4,0	42	8
060	12	-29	806	51	-4	4,0, $\bar{1}\bar{4}$	12	-39	11,4,0	21	-19
080	97	99	10,0, $\bar{6}$	61	74	6,0, $\bar{1}\bar{4}$	8	-4	13,4,0	22	-9
002	27	27	12,0, $\bar{6}$	13	14	8,0, $\bar{1}\bar{4}$	8	-3	14,4,0	39	43
004	15	23	14,0, $\bar{6}$	23	-8	10,0, $\bar{1}\bar{4}$	15	-28	15,4,0	23	-26
006	16	30	16,0, $\bar{6}$	21	15	12,0, $\bar{1}\bar{4}$	58	38	16,4,0	65	-72
008	25	35	18,0, $\bar{6}$	43	27	14,0, $\bar{1}\bar{4}$	42	42	17,4,0	14	-32
0,0,10	16	-10	32,0, $\bar{6}$	20	-16	18,0, $\bar{1}\bar{4}$	38	-27	20,4,0	25	10
0,0,12	18	-5	18,0,8	31	-17	30,0, $\bar{1}\bar{4}$	24	-14	21,4,0	15	28
0,0,20	32	24	16,0,8	25	-18	10,0,16	29	40	22,4,0	26	10
0,0,22	23	-28	14,0,8	16	-23	8,0,16	22	-18	23,4,0	14	-16
16,0,2	18	2	10,0,8	21	32	4,0,16	13	-11	25,4,0	13	3
14,0,2	41	-51	808	35	28	6,0,16	42	-43	26,4,0	13	1
12,0,2	59	-75	608	55	6	12,0,16	40	-36	30,4,0	13	-7
10,0,2	83	-87	408	91	102	14,0,16	26	-20	260	38	-48
802	44	70	208	7	-10	20,0,16	24	3	560	22	4
602	193	-167	208	6	16	28,0,16	18	-25	660	13	-35
402	284	341	408	73	-34	10,0,18	16	17	960	14	27
202	137	-93	608	74	78	6,0,18	44	50	10,6,0	29	-43
20 $\bar{2}$	121	-124	10,0,8	67	85	4,0,18	30	32	11,6,0	14	-35
40 $\bar{2}$	124	97	12,0,8	15	-5	18,0,18	24	-7	12,6,0	14	-3
60 $\bar{2}$	155	161	16,0,8	23	22	10,0,20	9	12	15,6,0	25	-1
80 $\bar{2}$	7	-6	30,0,8	21	22	8,0,20	10	-1	17,6,0	25	-2
10,0, $\bar{2}$	69	88	16,0,10	25	27	2,0,20	19	25	18,6,0	14	29
12,0, $\bar{2}$	15	3	14,0,10	21	2	4,0,20	14	-16	180	15	18
14,0, $\bar{2}$	55	-45	10,0,10	22	-16	8,0,20	13	-31	280	25	21
26,0, $\bar{2}$	23	37	8,0,10	8	-4	10,0,20	18	12	380	31	-28
18,0,4	16	-15	6,0,10	11	-13	12,0,20	18	1	480	44	42
16,0,4	28	1	4,0,10	8	2	16,0,20	31	10	580	25	4
14,0,4	80	-84	2,0,10	19	-31	18,0,20	19	19	980	15	-24
12,0,4	23	27	2,0, $\bar{1}\bar{0}$	58	68	120	6	-32	11,8,0	30	12
10,0,4	149	-133	4,0, $\bar{1}\bar{0}$	97	-81	220	62	-88	011	95	-95
804	82	-117	6,0, $\bar{1}\bar{0}$	12	24	320	64	-22	013	51	-46
604	148	-127	8,0, $\bar{1}\bar{0}$	112	-121	420	7	-5	015	134	124
404	153	115	10,0, $\bar{1}\bar{0}$	122	-97	520	25	-26	017	33	29
204	88	-87	12,0, $\bar{1}\bar{0}$	11	-17	620	33	19	022	24	30
20 $\bar{4}$	22	46	26,0, $\bar{1}\bar{0}$	44	65	720	14	-17	024	33	-36
40 $\bar{4}$	294	-334	16,0,12	21	5	820	22	16	026	35	-24
60 $\bar{4}$	272	-265	14,0,12	12	-6	920	16	14	033	35	42
80 $\bar{4}$	26	26	12,0,12	14	23	10,2,0	24	-34	044	30	-14
10,0,4	14	1	8,0,12	24	-37	11,2,0	10	-2	046	94	-110
14,0,4	61	52	6,0,12	13	20	12,2,0	31	43	055	39	-8
16,0,4	20	-48	2,0, $\bar{1}\bar{2}$	33	35	15,2,0	12	18	066	49	-7
18,0,4	60	-68	4,0, $\bar{1}\bar{2}$	33	-57	18,2,0	66	75			
18,0,6	37	-37	8,0, $\bar{1}\bar{2}$	36	-5	19,2,0	29	30			

Except for the work carried out on the XRAC computer, most of the Fourier syntheses were evaluated numerically. For some of the difference syntheses a mechanical Fourier synthesizer was employed (Vand, *ibid.*, 1950, 27, 257); others were calculated by numerical methods. In the structure-factor calculations, an empirical scattering curve for carbon was used (Robertson, *Proc. Roy. Soc.*, 1935, A, 150, 106), without any allowance for hydrogen atoms. Owing to the large unit cell and the complex arrangement of atoms, most of the structure factors attain only a very small fraction of their possible maximum values. At first the value for the average discrepancy between calculated and observed structure factors (expressed as a sum of all the discrepancies divided by the total of the observed F values) was far from encouraging, but it improved steadily as the refinement proceeded. The structure factors

calculated from the final co-ordinates are given in Table 2 ( $F_o$ ), and the overall discrepancy is 29%. For the  $(h0l)$  zone, which was most intensively studied, the value is 26.6%. In the  $(hk0)$  zone the reflections are mostly very weak, and here the discrepancy is about 40%. The  $(0kl)$  zone was not completely calculated, but the agreements found are reasonable. The above discrepancy figures are rather poor and indicate that considerable further refinement should be possible. This would be difficult to achieve, however, without a full three-dimensional investigation; at the present stage it may be concluded that the main outlines of the structure are well established, but that the individual atomic positions are subject to errors of between 0.1 and 0.2 Å.

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