519. *Crystal-structure Studies of Polynuclear Hydrocarbons. Part II.** 1 : 9-5 : 10-*Diperinaphthyleneanthracene.*

By M. G. ROSSMANN.

A detailed *X*-ray structural investigation has been made of the overcrowded aromatic hydrocarbon 1 : 9-5 : 10-diperinaphthyleneanthracene. The monoclinic crystals, space group $P2_1$, have two molecules per unit cell. The distortion of the molecules was studied by means of difference-generalised projections of the ($h1l$) planes which were able to distinguish between the two possible modes of buckling. The molecules possess approximate twofold axes through their centres. The atoms in the overcrowded positions clear each other by 2·9—3·0 Å.

1 : 9-5 : 10- and 1 : 9-4 : 10-DIPERINAPHTHYLENEANTHRACENE, (I) and (II) respectively, were prepared by Clar and Kelly.[1] They observed electronic absorption bands near 6300 Å for (I) and 6435 Å for (II), and no other bands in the red region as far as 10,000 Å. One object of this *X*-ray diffraction study was to provide independent proof of the formula assigned to (I), because of Dewar's [2] prediction of absorption at 8430 Å for (I) as contrasted with an acceptable prediction of absorption at 6410 Å for (II).

A second object was that (I) can reasonably be expected to show nonplanar distortion owing to overcrowding near the atoms marked *. Similar studies on closely related

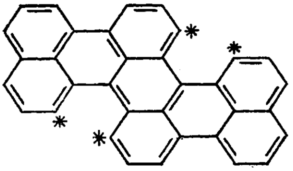
---

* Part I, preceding paper.

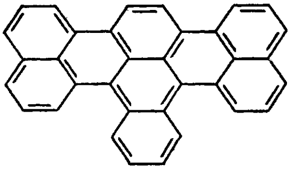
[1] Clar and Kelly, *J.*, 1954, 1108.

[2] Dewar, *J.*, 1952, 3539.

overcrowded molecules have appeared.[3] Unfortunately, none of these studies, including the present one, is sufficiently accurate to permit conclusions of the effects of overcrowding on bonded distances, but they do give significant and useful data on intramolecular and intermolecular non-bonded contacts and on intramolecular strain.



(I)



(II)

EXPERIMENTAL

The reciprocal lattice symmetry C_{2h} and extinction only of $(0k0)$ when k is odd led to a monoclinic cell with parameters $a = 11{\cdot}95 \pm 0{\cdot}03$, $b = 7{\cdot}83 \pm 0{\cdot}02$, $c = 11{\cdot}17 \pm 0{\cdot}03$ Å, and $\beta = 92° 18' \pm 20'$, having space-group symmetry $C_2{}^2$–$P2_1$ or $C_{2h}{}^2$–$P2_1/m$. Assumption of two molecules of $C_{34}H_{18}$ in the unit cell gives a calculated density of 1·356, in agreement with the measured density of 1·359. No molecular symmetry is required in the space group $P2_1$, but in $P2_1/m$ either a centre of symmetry or a mirror plane could occur. Weissenberg photographs were taken of the $(h0l)$, $(0kl)$, $(hk0)$, and (hll) nets in which 28%, 43%, 37%, and 28%, respectively, of all accessible reflections were recorded. Each of two crystals with dimensions 0·030 × 0·010 × 0·50 cm. and 0·010 × 0·006 × 0·50 cm. was used to photograph both the $(h0l)$ and (hll) reflections. For the $(hk0)$ zone a specimen with dimensions 0·017 × 0·072 cm. perpendicular to c was used, and for the $(0kl)$ zone one with 0·014 × 0·100 cm. perpendicular to a. Absorption corrections ($\mu = 6{\cdot}50$ cm.$^{-1}$) were made only to the $(hk0)$ and $(0kl)$ data. The multiple-film technique and Cu-K_α radiation ($\lambda = 1{\cdot}542$ Å) were used throughout, and visual estimates were made, after which the usual Lorentz-polarisation corrections were applied. The atomic scattering factors listed by McWeeny[4] were used.

Single crystals, prepared by sublimation, were pyramid-like needles, opaque and dark red. In quantity, or in powdered form, they appear dark blue. The presence of overgrowths and ease of bending produced difficulty in obtaining good specimens. The needles axis is along b.

Structure Analysis.—Both a ratio test[5] and a distribution curve[6] failed to distinguish between $P2_1$ and $P2_1/m$, probably because of symmetry in the molecule itself.[7] Hence statistical methods were abandoned and a detailed examination of intensities was made. The strongest reflection (020) strongly suggested a layer structure, with at least roughly planar molecules perpendicular to b and spaced by $b/2$. The observation that (hll) reflections were in general greater in intensity than $(h0l)$ in a b axis rotation photograph clearly suggested that the molecular centres are not coincident with centres of symmetry in $P2_1/m$. Planar and roughly parallel molecules, if not tilted too much, require a b axis of almost 7 Å. But the observed $b = 7{\cdot}83$ Å is suggestive of an amount of nonplanarity, about 0·5 Å per molecule, similar to that observed in earlier studies of overcrowded molecules. This rules out the possibility of exactly planar molecules lying in mirror planes of $P2_1/m$. Thus these reasons, and also an expected buckling within the molecule, lead to the tentative conclusion, confirmed below, that the correct space group is $P2_1$, not $P2_1/m$.

Location of the centre of the molecule was then accomplished by a detailed comparison of $(h0l)$ and (hll) structure factors, as will now be described. Elementary packing considerations indicated that the long axis of the molecule must lie approximately along [101] or [$\bar{1}$01] in order to leave at least 3·4 Å between neighbouring molecules. Now we may choose the origin in the space group $P2_1$ at $x = z = 0$, and the y co-ordinate of the centre of the two molecules at $Y = \frac{1}{4}$ and $\frac{3}{4}$, with no loss of generality. Because the molecules lay approximately in layers

---

[3] McIntosh, Robertson, and Vand, *J.*, 1954, 1661; Herbstein and Schmidt, *J.*, 1954, 3302, 3314; Hirshfeld and Schmidt, *Acta Cryst.*, 1956, **9**, 233; Robertson and Trotter, following paper.

[4] McWeeny, *Acta Cryst.*, 1951, **4**, 513.

[5] Wilson, *Acta Cryst.*, 1949, **2**, 318.

[6] Howells, Phillips, and Rogers, *Acta Cryst.*, 1950, **3**, 210.

[7] Rogers and Wilson, *Acta Cryst.*, 1953, **6**, 439.

perpendicular to b, it was assumed at this stage that they are exactly planar and perpendicular to b, with corrections for nonplanarity to be introduced later. Thus, for the moment, we are assuming space group $P2_1/m$, with the origin at a centre of symmetry. Now, let x', y', z' be the co-ordinates of an atom relative to the molecular centre of symmetry at X, $\frac{1}{4}$, Z. Then the structure factor becomes, if we ignore hydrogen atoms,

$$F_{hkl}/f = 4(-1)^n \cos 2\pi\,(hX + lZ)\sum_{N/2} \cos 2\pi\,(hx' + lz')$$

when $k = 2n$, and a similar expression where $(-1)^n$ is replaced by $(-1)^{n+1}$ and $\cos 2\pi\,(hX + lZ)$ is replaced by $\sin 2\pi\,(hX + lZ)$ when $k = 2n + 1$. N is the number of atoms in one molecule and f is the atomic scattering factor. Thus we can show that

$$|\tan 2\pi hX| = \frac{|F_{h10}|f_{h00}}{|F_{h00}|f_{h10}} \text{ and } |\tan 2\pi lZ| = \frac{|F_{01l}|f_{00l}}{|F_{00l}|f_{01l}}$$

from which possible values of X and Z can be found from the observed reflections. Note that all distinct structures are covered if we examine only the ranges $0 \leqslant X \leqslant a/4$ and $-c/4 \leqslant Z \leqslant c/4$. The results, summarised in Tables 1 and 2, indicate that $X = 58°$ and $Z = \pm 14°$. Further comparison of $(h1l)$ and $(h0l)$ reflections, with the use of the equation

$$|\tan (h\,58° \pm l\,14°)| = \frac{|F_{h1l}|f_{h0l}}{|F_{h0l}|f_{h1l}}$$

indicated uniquely that the molecular centre is at $X = 58°$, $Z = 14°$, and by assumption, $Y = 90°$. Final values were later shown to be $X = 56°$ and $Z = 13°$ after refinement.

TABLE 1. *Application of the equation* $|\tan 2\pi hX| = |F_{h10}|f_{h00}/|F_{h00}|f_{h10}$.

Possible solutions for X are italicised. The mean value of $X = 58°$.

$h00$	$\lvert F_{h00}\rvert$	f_{h00}	$h10$	$\lvert F_{h10}\rvert$	f_{h10}	$\lvert\tan 2\pi hX\rvert$	$2\pi hX$	X(°)
100	23·3	4·95	110	36·5	4·26	1·815	61°	*61*
200	16·9	4·20	210	30·0	4·02	1·855	62°	31 *59*
300	11·8	3·60	310	0·7	3·39	0·079	5°	2 *59* *62*
400	7·7	3·00	410	5·0	2·85	0·680	34°	9 37 *56* 82
500	6·4	2·49	510	27·3	2·43	4·38	77°	15 20 51 *56* 87
600	29·2	2·07	610	19·4	2·01	0·685	34°	6 24 38 *54* 66 73
700	6·7	1·74	710	6·4	1·68	0·989	45°	6 19 32 45 *58* 71 83
11,00	4·6	0·78	11,10	5·5	0·78	1·040	46°	4 12 21 29 37 45 *53* *61* 70 78 87

The molecular centre is now located, and the approximate molecular orientation was found by comparing values of $R = \sum\big||F_o| - |F_c|\big|/\sum|F_o|$ for orientation of the long molecular axis along [101] or along [$\bar{1}$01]. Far better agreement was obtained with the long molecular axis along [$\bar{1}$01], that is, approximately parallel to the (101) planes.

TABLE 2. *Application of the equation* $|\tan 2\pi lZ| = |F_{01l}|f_{00l}/|F_{00l}|f_{01l}|$.

Possible solutions for Z are italicised. The mean value of $Z = 14°$.

$00l$	F_{00l}	f_{00l}	$01l$	F_{01l}	f_{01l}	$\lvert\tan 2\pi lZ\rvert$	$2\pi lZ$	Z(°)
001	64·2	4·83	011	22·7	4·26	0·401	22°	*22*
002	36·9	4·11	012	8·7	3·81	0·256	15°	*8* 82
003	14·7	3·39	013	11·0	3·18	0·798	39°	*13* 47 73
005	1·4	2·28	015	3·5	2·19	2·53	68°	*14* 22 50 58 86
006	1·6	1·89	016	2·7	1·83	1·74	60°	*10* *20* 40 50 70 80
008	4·1	1·26	018	8·7	1·23	2·17	65°	8 *14* 30 37 53 59 75 82
009	10·4	1·02	019	16·7	0·99	1·625	58°	6 *14* 26 34 46 54 66 74 86
00,10	2·2	0·81	01,10	6·9	0·81	3·14	72°	7 *11* 25 29 41 47 61 65 77 83

Refinement of the $(h0l)$ data was now carried through five cycles of $(F_o - F_c)$ syntheses. Both hydrogen and carbon atoms were included in the calculation of F_c in order to avoid obscuring required carbon-atom shifts in the already badly resolved projection. The hydrogen co-ordinates were obtained approximately by assuming their positions to be 1 Å from the corresponding carbon atoms. The final value of $R = 0{\cdot}19$ is about as satisfactory as can be expected, but the accuracy of the 68 position parameters is not high because only 99 ($h0l$) reflections were observed. The final electron-density projection is shown in Fig. 1 and explained in Fig. 2.

Distortion from Planarity.—While the assumption of a planar model yielded good agreement for the ($h0l$) data, a number of the ($h1l$) reflections, such as (211), (11$\bar{9}$), and (10,1,$\bar{3}$), showed calculated structure factors which were much too low. Two types of nonplanar distortion may reasonably be expected, the first (Model *A*) being centrosymmetric, and the second (Model *B*) having a twofold axis.

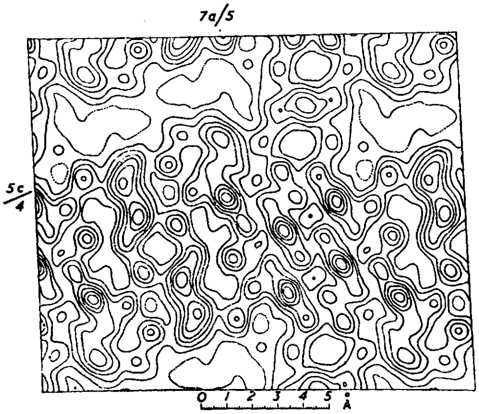


FIG. 1. *Electron density projection on* (010). *Contours at intervals of one electron per* Å², *the one-electron line being broken.*

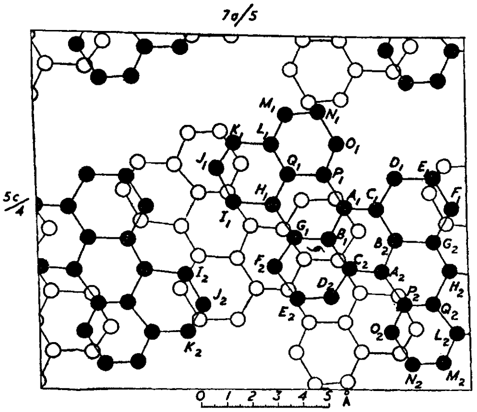


FIG. 2. *Atomic arrangement corresponding to the projection on* (010), *showing overlapping molecules at different levels.*

TABLE 3. *The signs of the quantities* sin 2π ($hx + lz$) *for certain* ($h1l$) *structure factors expected to have large imaginary parts. When* sin 2π ($hx + lz$) $< 0{\cdot}25$, *a zero appears in the Table.*

$h1l$	A_1	B_1	C_1	D_1	E_1	F_1	G_1	H_1	I_1	J_1	K_1	L_1	M_1	N_1	O_1	P_1	Q_1
+(21$\underline{1}$)	+	+	−	−	0	+	−	−	−	−	−	+	+	0	0	+	+
+(11$\bar{9}$)	+	+	+	0	−	+	−	−	−	−	+	+	+	+	+	+	+
−(10,1$\bar{3}$)	0	+	−	−	+	+	+	+	−	−	+	0	−	−	−	0	+

$h1l$	A_2	B_2	C_2	D_2	E_2	F_2	G_2	H_2	I_2	J_2	K_2	L_2	M_2	N_2	O_2	P_2	Q_2
+(21$\underline{1}$)	+	−	+	−	−	−	−	−	+	+	−	−	+	+	+	+	−
+(11$\bar{9}$)	+	0	+	+	0	−	−	−	−	−	−	−	0	0	+	−	−
−(10,1$\bar{3}$)	+	0	+	0	−	−	−	−	0	−	−	0	+	+	+	+	+

Consideration of the trigonometric parts of the structure factors of the ($h1l$) reflections,

$$A = -2 \sin 2\pi\,(hx + lz) \sin 2\pi y$$

and

$$B = 2 \sin 2\pi\,(hx + lz) \cos 2\pi y$$

suggests a method for establishing which distortion is correct. Remember that x and z are known for all atoms, and note that since y is near 90° the value of $\sin 2\pi y$ changes only slowly. Hence the A part changes only very little as y is displaced from 90°. Hence those structure factors ($h1l$) which disagree with the planar model must have relatively large imaginary parts, and, in order to make B large, the contributions of all or nearly all atoms must have the same sign. Since the signs of $\sin 2\pi\,(hx + lz)$ are already known, it is possible to find the sign of $\cos 2\pi y$ so that the product, $\sin 2\pi\,(hx + lz) \cos 2\pi ky$, has the same sign for every atom. It is immaterial whether B is made positive or negative, because reversal of the sign simply gives

TABLE 4. *Atomic co-ordinates. The x and z co-ordinates, expressed as ratios of the cell lengths, are those obtained after the completion of the fifth difference synthesis of the (h0l) planes, except for atoms M_2 and O_2, which have been adjusted to give better agreement with the final electron-density map.*

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
A_1	0·095	0·286	0·147	M_1	−0·093	0·411	0·472	G_2	0·387	0·186	0·028
B_1	0·040	0·286	0·037	N_1	0·015	0·350	0·483	H_2	0·440	0·128	−0·075
C_1	0·200	0·261	0·142	O_1	0·073	0·422	0·370	I_2	0·570	0·147	−0·093
D_1	0·263	0·225	0·252	P_1	0·030	0·342	0·263	J_2	0·623	0·181	−0·202
E_1	0·388	0·242	0·255	Q_1	−0·088	0·325	0·262	K_2	0·575	0·161	−0·298
F_1	0·448	0·197	0·145	A_2	0·215	0·250	−0·080	L_2	0·459	0·219	−0·298
G_1	−0·070	0·242	0·038	B_2	0·260	0·233	0·033	M_2	0·412	0·219	−0·402
H_1	−0·138	0·242	0·155	C_2	0·108	0·242	−0·070	N_2	0·307	0·303	−0·410
I_1	−0·267	0·203	0·163	D_2	0·045	0·217	−0·170	O_2	0·242	0·283	−0·297
J_1	−0·322	0·197	0·282	E_2	−0·067	0·208	−0·178	P_2	0·287	0·239	−0·197
K_1	−0·265	0·261	0·370	F_2	−0·138	0·244	−0·065	Q_2	0·382	0·214	−0·192
L_1	−0·141	0·258	0·367								

TABLE 5. *Agreement factors at different stages of refinement of the (h1l) planes.*

Structure	Centrosymmetrical	Twofold axis
Planar	0·500	0·500
Trial	0·424	0·386
After 1st difference-generalised cosine projection...	0·400	0·324
After 2nd difference-generalised cosine projection...	—	0·304

TABLE 6. *Intermolecular distances* (Å).

Distances	d	Distances	d
$J_1(S)\ldots F_1(S\bar{a})$	3·09	$I_1(S)\ldots A_2(S_1)$	3·72
$F_2(S)\ldots J_2(S\bar{a})$	3·22	$I_2(S)\ldots G_2(S_1a)$	3·72
$A_1(S)\ldots E_2(S')$	3·34	$B_1(S)\ldots F_2(S')$	3·79
$K_2(S)\ldots E_1(S_1a)$	3·35	$J_2(S)\ldots F_1(S_1a)$	3·82
$I_1(S)\ldots F_1(S\bar{a})$	3·40	$K_1(S)\ldots O_2(S_1)$	3·84
$I_2(S)\ldots F_1(S_1a)$	3·45	$N_2(S)\ldots D_1(S\bar{c})$	3·84
$J_1(S)\ldots E_1(S\bar{a})$	3·47	$M_2(S)\ldots E_1(S\bar{c})$	3·84
$J_2(S)\ldots E_1(S_1a)$	3·49	$J_1(S)\ldots P_2(S_1)$	3·87
$J_1(S)\ldots O_2(S_1)$	3·51	$H_1(S)\ldots D_2(S')$	3·88
$F_2(S)\ldots I_2(S\bar{a})$	3·57	$N_2(S)\ldots E_1(S\bar{c})$	3·93
$M_1(S)\ldots N_1(S'\bar{c})$	3·59	$C_1(S)\ldots F_2(S')$	3·94
$K_1(S)\ldots N_2(S_1)$	3·65	$N_1(S)\ldots N_1(S'\bar{c})$	3·95
$A_1(S)\ldots F_2(S')$	3·66	$M_1(S)\ldots N_1(S_1\bar{c})$	3·95
$I_1(S)\ldots P_2(S_1)$	3·66	$G_1(S)\ldots C_2(S')$	3·96
$G_1(S)\ldots B_1(S_1)$	3·69	$G_1(S)\ldots C_2(S_1)$	3·96
$E_2(S)\ldots J_2(S\bar{a})$	3·71		

Code:

Molecule	Related to	By Operation
S	Sc	c
S	Sa	a
S	$S\bar{c}$	$-c$
S	$S\bar{a}$	$-a$
S'	S	2_1 along b
S'	$S'c$	c
S'	$S'a$	a
S_1	S	2_1 along $-b$
S_1	S_1c	c
S_1	S_1a	a

the other optical isomer which is not usually distinguishable by X-ray methods. The results, summarized for these three planes in Table 3, indicate that the determination of the sign of $\cos 2\pi y$ is reasonably unambiguous for many of the atoms. Since $y < b/4$ if $\cos 2\pi ky$ is positive, and $y > b/4$ if $\cos 2\pi ky$ is negative, the distortion is clearly shown to be that of model B, in which a twofold axis occurs.

The $(h1l)$ reflections were then refined by means of difference-generalised projections,[8] with results which leave no reasonable doubt of the correctness of the molecular distortion. The

[8] Rossmann and Shearer, *Acta Cryst.*, 1958, **11**, 829.

TABLE 7. *Observed and calculated structure factors.*

hkl	F_o	F_c	α	*hkl*	F_o	F_c	α	*hkl*	F_o	F_c	α	*hkl*	F_o	F_c	α
000	—	444	—	601	34·6	32·8	180	106	7·8	8·2	0	712	6·4	5·0	143
100	30·4 §	27·8	0	501	3·2	2·2	0	$10\bar{6}$	9·6	11·8	0	412	8·6	15·4	179
200	20·8	19·4	0	401	7·2	4·4	0	$40\bar{6}$	6·4	7·6	0	312	4·2	6·2	66
300	14·8	16·2	0	301	44·2	44·6	180	$80\bar{6}$	3·4	1·2	180	212	14·8	10·2	355
400	10·8	13·0	180	201	4·0	8·2	0	407	3·2	4·2	0	112	26·2	27·4	51
500	8·2	5·6	180	101	30·8	32·6	0	107	2·8	5·6	180	$11\bar{2}$	33·0	29·8	359
600	42·6	44·6	180	$10\bar{1}$	24·8	27·6	180	$40\bar{7}$	3·0	2·0	0	$21\bar{2}$	6·2	7·6	93
700	7·2	9·2	0	$30\bar{1}$	17·0	15·6	0	$50\bar{7}$	2·6	1·2	180	$31\bar{2}$	10·4	16·6	326
11,00	5·6 *	1·4	0	$40\bar{1}$	20·2	21·1	180	108	3·0	6·0	0	$41\bar{2}$	4·6	5·2	166
020	187·0	212·4	174	$50\bar{1}$	12·6	12·8	0	$60\bar{8}$	3·4	2·6	0	$51\bar{2}$	3·0	9·2	201
040	31·9	51·2	328	$70\bar{1}$	4·6	7·8	180	109	11·0	13·4	180	$71\bar{2}$	5·6	2·4	141
060	12·4	12·8	142	$11,0\bar{1}$	2·8	1·0	180	$50\bar{9}$	3·8	7·2	0	813	4·2	4·6	124
080	3·8	2·8	306	902	2·6	5·0	0	$60\bar{9}$	3·8	4·2	0	713	5·0	12·4	350
001	59·4 §	63·6	0	602	9·0	11·2	0	1,0,10	13·6	13·2	180	613	6·4	4·8	155
002	30·2	34·4	180	402	7·6	10·8	0	110	50·0	46·2	188	513	5·6	4·8	202
003	13·4	9·8	180	302	19·6	16·0	180	210	42·4	39·0	357	413	9·6	10·8	202
005	2·2	2·0	180	202	30·4	26·4	0	310	5·0	4·6	18	313	4·0	3·8	333
008	3·2	3·4	180	$10\bar{2}$	48·6	51·2	0	410	7·0	15·8	313	213	7·8	9·2	280
009	13·4	16·4	180	$30\bar{2}$	6·8	4·2	180	510	40·5	37·4	187	113	12·0	7·0	189
				$40\bar{2}$	9·2	10·8	180	610	28·5	20·8	197	$11\bar{3}$	5·4	8·4	168
011	23·2	36·2	249	$50\bar{2}$	2·2 *	0·8	0	710	9·9	5·8	237	$21\bar{3}$	9·6	7·6	157
012	8·6	9·0	5	$60\bar{2}$	4·4	5·8	180	11,10	7·6	8·4	175	$31\bar{3}$	15·8	11·2	101
013	10·9	13·4	325	$70\bar{2}$	3·0	5·6	0	12,10	2·8	2·0	168	$41\bar{3}$	9·4	10·6	157
014	2·6	1·2	323	703	4·0	3·6	180	120	105·4	78·0	264	$51\bar{3}$	4·8	5·6	51
015	4·0	4·6	282	503	8·6	5·2	0	220	18·4	17·6	357	$81\bar{3}$	5·4	2·6	173
016	2·8	5·6	2	403	2·6	1·6	0	320	14·6	10·0	217	$91\bar{3}$	19·0	9·6	337
017	3·6	3·0	353	303	3·4	3·6	180	420	4·0	10·8	282	$10,1\bar{3}$	6·0	2·2	28
018	9·3	12·8	158	203	16·6	17·4	180	520	38·6	15·4	83	10,14	4·4	1·4	234
019	18·4	28·2	180	$10\bar{3}$	28·8	25·0	180	620	14·4	23·0	339	914	8·4	5·4	262
01,10	7·0	4·6	126	$20\bar{3}$	4·4	3·8	0	11,20	5·4	1·0	340	814	13·6	10·6	178
021	89·4	78·8	140	$30\bar{3}$	2·8	8·4	180	130	48·8	27·8	20	714	7·0	16·4	323
022	19·2	35·2	336	$40\bar{3}$	6·4 *	0·6	0	230	5·0	23·0	170	414	11·6	5·0	12
023	8·8	5·8	322	$50\bar{3}$	3·2	2·8	180	330	4·2	5·8	230	314	17·8	28·6	158
024	8·8	9·0	291	$70\bar{3}$	4·2	5·0	0	430	10·2	16·2	124	214	12·0	6·2	31
025	8·8	8·2	165	$90\bar{3}$	4·2 *	1·2	0	530	17·0	15·6	7	114	16·0	21·8	131
026	3·2	1·8	148	$10,0\bar{3}$	7·8	4·0	180	630	7·8	8·6	29	$11\bar{4}$	4·4	6·0	24
028	6·8	9·4	296	904	9·2	5·0	180	730	6·4	7·8	134	$21\bar{4}$	14·6	15·6	233
029	11·0	11·4	0	804	8·0	9·6	180	10,30	3·2	4·2	90	$31\bar{4}$	48·0	59·8	179
031	29·4	25·2	84	704	7·0 *	1·8	180	11,30	4·6	5·0	356	$41\bar{4}$	10·8	9·0	279
032	12·2	15·0	41	504	6·8	6·4	0	140	27·2	23·2	66	$51\bar{4}$	5·6	4·0	345
033	8·4	3·8	250	404	4·6 *	0·0	—	240	10·0	23·8	247	$81\bar{4}$	13·8	16·2	24
034	8·6	9·2	353	304	33·6	29·8	0	340	5·0	6·4	202	$91\bar{4}$	19·8	23·2	3
035	5·6	4·6	144	204	25·4	25·4	0	440	11·8	9·8	96	$10,1\bar{4}$	4·6	4·6	117
036	4·4	1·0	148	$10\bar{4}$	14·8	13·2	0	540	6·8	7·0	203	815	8·2	5·8	150
038	6·8	7·8	330	$20\bar{4}$	5·6	7·8	180	740	6·8	0·6	262	715	6·6	7·6	343
03,10	3·2	5·0	318	$30\bar{4}$	24·4	29·4	0	150	17·4	11·4	198	515	5·8	0·8	289
041	35·8	23·2	332	$40\bar{4}$	5·8	7·6	0	250	7·8	10·0	324	415	11·2	15·2	197
042	14·4	11·4	138	$70\bar{4}$	6·0	8·0	180	350	4·6	3·8	97	315	31·4	37·0	181
043	22·8	7·2	77	$80\bar{4}$	25·4	22·8	0	650	3·4	2·6	176	215	13·6	12·8	282
044	2·8	7·8	173	$90\bar{4}$	7·2 *	0·4	180	160	8·0	7·6	199	115	4·4	9·0	186
045	3·0	10·6	335	10,05	5·0 *	1·0	180	260	7·4	7·4	12	$11\bar{5}$	3·0	3·2	198
046	7·2	6·4	293	905	24·0	25·8	180	460	4·4	1·4	335	$21\bar{5}$	23·2	32·8	180
048	9·4	4·2	119	805	14·8	14·6	180	170	5·4	2·8	349	$31\bar{5}$	23·8	22·6	171
049	3·6	5·0	162	705	5·4 *	1·4	0					$51\bar{5}$	6·2	9·6	187
051	17·0	5·0	117	605	2·8	3·4	180	811	7·0	4·6	101	$81\bar{5}$	5·8	6·8	335
052	3·2	4·6	279	505	5·4 *	0·4	180	711	11·2	7·0	55	$91\bar{5}$	6·0	2·8	289
053	10·0	5·8	133	405	5·6	6·0	180	611	19·0	11·8	128	616	4·0	3·6	357
056	5·0	3·8	234	305	34·2	37·0	0	511	9·2	7·0	354	516	3·8	0·8	137
058	5·2	1·6	160	205	4·2 *	0·4	0	411	7·4	8·0	244	416	4·0	9·4	179
061	14·2	3·8	154	$10\bar{5}$	7·0	7·0	0	311	12·8	8·8	342	316	3·8	1·8	240
062	6·6	5·8	238	$20\bar{5}$	21·2	21·2	180	211	43·2	42·4	289	216	3·8	2·0	165
063	12·4	5·4	257	$40\bar{5}$	5·0	5·4	180	111	— †	70·6	187	116	8·2	10·0	3
064	5·4	6·0	40	$70\bar{5}$	7·2	5·4	180	$11\bar{1}$	— †	20·8	117	$21\bar{6}$	3·6	4·4	69
071	7·0	0·6	359	$80\bar{5}$	24·4	21·0	0	$21\bar{1}$	31·6	30·8	324	$31\bar{6}$	4·8	7·6	352
072	3·4	3·2	183	$90\bar{5}$	4·4	1·8	0	$31\bar{1}$	10·0	2·4	213	$41\bar{6}$	4·4	10·0	181
081	3·8	2·4	336	10,06	3·8*	0·4	180	$41\bar{1}$	4·6	12·0	127	$11\bar{8}$	6·2	3·2	228
				906	8·8	6·0	180	$51\bar{1}$	17·4	23·4	345	219	4·8	3·2	163
12,01	3·2	5·0	180	806	4·0	5·4	0	$61\bar{1}$	9·4	6·2	83	119	10·6	5·6	257
801	4·6	2·0	180	706	3·8	2·0	180	912	4·4	2·2	300	$11\bar{9}$	13·0	6·8	270

* Terms not included in final electron density map of Fig. 1.
† Cut off by beam stop.
§ Cut off by beam stop (estimated from oscillation photograph).

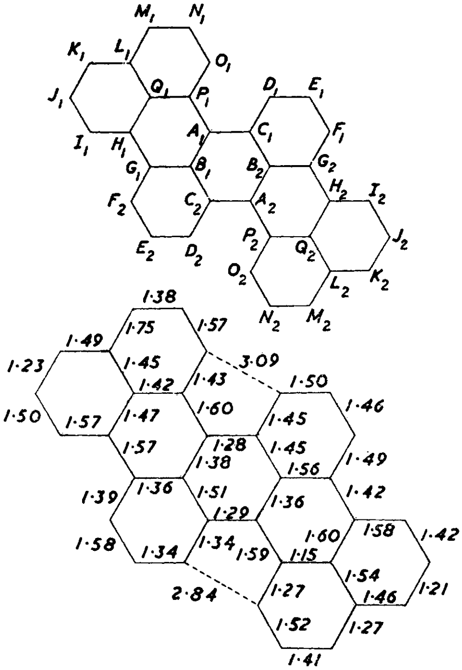
final atomic co-ordinates are shown in Table 4. The results of refinements of both models *A* and *B*, summarised in Table 5, clearly favour *B*. Finally, the *R* value for the (*hk*0) reflections fell from 0·59 to 0·28, and the *R* value for the (0*kl*) reflections fell from 0·60 to 0·28 as the centrosymmetric model was distorted into model *B* having the twofold axis.

RESULTS AND DISCUSSION.

The behaviour of the temperature factor was somewhat unusual in that the best fit of experimental and calculated structure factors required $B = 7·0$ Å,^{2} as compared with an average value of about $B = 3·5$ Å^2 found for other overcrowded molecules. In circumanthracene[9] an abnormally high temperature factor appears to be produced by the presence of impurities. In addition, the indication of 4—8% of impurity of molecular masses less than the expected values near 426·5 in a mass-spectroscopic study, and the observation that the melting point (333—334°) is below its expected value, all make reasonable the assumption that the apparently high temperature factors are due to impurities in the crystal.

Owing to a combination of the apparently large temperature factor and the limited amount of X-ray data, the bond lengths (Fig. 3) are not very precisely determined. However, some of the trends may be interesting, even though the root mean-square deviations among chemically equivalent bond lengths average to about 0·15 Å. The average C–C bond distance is 1·43 Å. The average of the bonds G_1H_1, G_2H_2, A_1P_1, and A_2P_2 is 1·54 Å; these should be single bonds in the ground-state Kekule resonance hybrid, but are probably to be expected to be rather shorter than the single-bond C–C length of 1·54 Å in a molecular-orbital description. The non-bonded distances $O_1D_1 = 3{\cdot}09$ and $O_2D_2 = 2{\cdot}84$ average to 2·97 Å for the closest non-bonded contacts in the overcrowded region of the molecule. In the studies referred to on p. 2607, the range expected for similar distances in other molecules is 2·9 to 3·0 Å.

FIG. 3. *Bond lengths* (Å).



The list of all intermolecular contacts less than 4·0 Å shown in Table 6 shows that only four are less than 3·40 Å, and that the smallest of the four is 3·09 Å. Since the estimated internal consistency of chemically equivalent distances suggests that the standard deviation is about 0·15 Å, no significant conclusion should be drawn, but it is interesting that Herbstein and Schmidt [3] have also observed comparable short intermolecular distances in overcrowded hydrocarbon molecules.

I am indebted to Dr. E. Clar and Mr. W. Kelly who prepared the crystals. I thank Professors J. M. Robertson and W. N. Lipscomb for the opportunity to do this work, and for help and encouragement.

CHEMISTRY DEPARTMENT, UNIVERSITY OF GLASGOW. [*Received, December* 29*th*, 1958.]

[9] Clar, Kelly, Robertson, and Rossmann, *J.*, 1956, 3878.