518. *Crystal-structure Studies of Polynuclear Hydrocarbons. Part I.* 2 : 3-8 : 9-*Dibenzoperylene.*

By WILLIAM N. LIPSCOMB, J. MONTEATH ROBERTSON, and M. G. ROSSMANN.

Determination of the structure of crystalline 2 : 3-8 : 9-dibenzoperylene by *X*-ray diffraction has yielded bond lengths in good agreement with those predicted by molecular-orbital computations for a planar molecule. Deviations of individual atoms by as much as 0·07 Å from the mean plane of the molecule have been established, however. An intermolecular contact of 3·2 Å for a strictly planar model suggests that these distortions from planarity arise from packing.

FAVOURABLE comparisons of bond lengths as determined by *X*-ray diffraction with those predicted by molecular-orbital methods have led us to investigate the structure of 2 : 3-8 : 9-dibenzoperylene. The results, summarised below, of molecular-orbital discussions [1] are based on an empirical curve relating bond orders and bond lengths. We shall compare these predictions with experimental values.

The molecule was expected to be planar within experimental error, but significant nonplanarity has been discovered. This nonplanarity appears to have little effect on the bond lengths.

EXPERIMENTAL

The crystals, prepared by Clar,[2] were sublimed yellow needles showing {001} and, sometimes, {100} faces. The needle direction is along the monoclinic [010] axis. Unit-cell parameters are $a = 16{\cdot}51 \pm 0{\cdot}02$, $b = 5{\cdot}23 \pm 0{\cdot}01$, $c = 20{\cdot}52 \pm 0{\cdot}02$ Å, and $\beta = 107{\cdot}8° \pm 0{\cdot}2°$. The absences of (hkl) when $k + l$ is odd, of $(h0l)$ when h is odd and when l is odd, and of $(0k0)$ when k is odd, lead to C_{2h}^{6}–$A2/a$ or C_s^{4}–Aa as space-group possibilities. Assumption of four molecules of $C_{28}H_{16}$ in the unit cell leads to a calculated density of $1{\cdot}383 \pm 0{\cdot}007$ g. cm.$^{-3}$, in good agreement with the value of $1{\cdot}394 \pm 0{\cdot}002$ g. cm.$^{-3}$ determined by flotation.

Photographs were taken with the use of Cu-K_α radiation ($\lambda = 1{\cdot}542$ Å) of $(h0l)$ with a crystal 0·2 × 0·15 mm. in cross-section, of $(h1l)$ with a crystal 0·22 × 0·11 mm. in cross-section, and of $(0kl)$ with a crystal 0·43 mm. along b and 0·07 mm. along c. Absorption corrections [3] were made only for the $(0kl)$ data. Visual estimates were made of intensities with the aid of the multiple-film technique,[4] and the usual Lorentz and polarisation corrections were applied. A correction of the film factor was made in the case of $(h1l)$ for which the *X*-rays passed obliquely through the film.[5] The structure factors are listed in Table 8.

Structure Determination.—The short b axis led to a study of the projection along [010] as the first step. If the molecule were truly centrosymmetric, this projection would be the same

---

[1] D. G. Watson, B.Sc. Thesis, University of Glasgow, 1956; Goodwin and Watson, *J.*, 1959, 2625; Hall, *Trans. Faraday Soc.*, 1957, **53**, 573.

[2] Clar, *Ber.*, 1932, **65**, 846.

[3] Albrecht, *Rev. Sci. Instr.*, 1939, **10**, 221.

[4] Robertson. *J. Sci. Instr.*, 1943, **20** 175.

[5] Rossmann, *Acta Cryst.*, 1956, **9**, 819.

in $A2/a$ as in Aa. Moreover, the molecule was expected to be nearly resolved in this projection. Furthermore, the extraordinarily large (18,0,2), (18,0,4), (8,0,6), (6,0,16), (4,0,16), (6,0,$\overline{20}$), and (14,0,$\overline{12}$) reflections suggested that nearly all carbon atoms were in phase for each of these reflections. Hence, traces were made of these planes and, after a few trials, a lattice of hexagons (Fig. 1) was formed by superposition of these traces, with due regard for the centre of symmetry at the origin of this projection. These hexagons showed clearly that the molecule is tilted

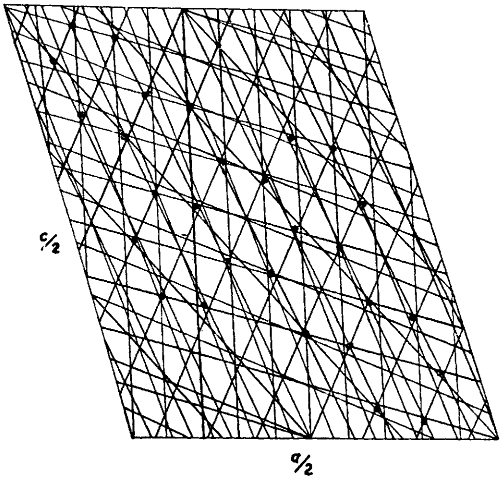


FIG. 1. *Prominent (h0l) reflections for dibenzoperylene.*

FIG. 2. *Projection of the dibenzoperylene structure on (010). Contour scale, one electron per Å², the first line being broken.*

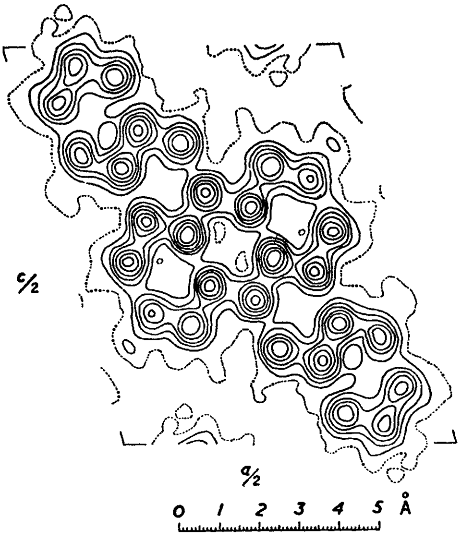
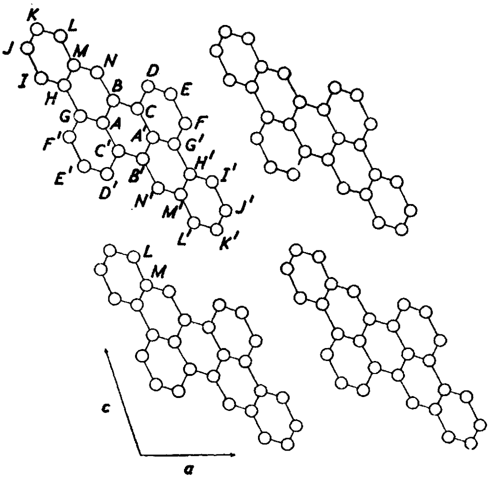


FIG. 3. *Atomic arrangement corresponding to the projection on (010).*



about 45° from the plane of projection; but there were at least six different ways of fitting the molecule to this array of hexagons. However, on account of the very intense (202) reflection, the long direction of the molecule was assumed along this direction, thus reducing the number of possible structures to two. The correct structure in this projection was then found by trial of these two possibilities, and three cycles of $F_o - F_c$ syntheses reduced the value of $R = \sum||F_o| - |F_c||/\sum|F_o|$ to 0·15. This refinement includes the contributions of hydrogen atoms and the anisotropic temperature factor $B = 2{\cdot}5 + 2{\cdot}7 \sin^2 (\phi - 160°)$, where ϕ is the angle between the c axis and the normal to a given plane. This variation of B between the limits

2·5 Å^2 and 5·2 Å^2 was indicated by the second $F_o - F_c$ synthesis, in which the direction of largest vibration appeared to be the long direction of the molecule in projection. The electron density projected along [010] is shown in Fig. 2, and the relation of the different molecules in the unit cell is shown in projection in Fig. 3.

When satisfactory x and z co-ordinates were obtained, attention was given to the ($0kl$) data to obtain the y co-ordinates. The assumption that the molecular centre of symmetry lay in the a glide plane of space group $A2/a$ gave good agreement for planes for which $k + l$ is even, but poor agreement for planes for which $k + l$ is odd. Hence, the molecular centre of symmetry was shifted by $(\vec{b} + \vec{c})/4$ so that it lay between the a glide planes. All ($0kl$) planes were then in satisfactory agreement, and a tentative assumption, later proved correct, was made that the space group was $A2/a$. The molecular arrangement, however, was basically correct at this stage, and the molecular packing strongly resembled that in similar aromatic molecules such as coronene and ovalene. Besides some remaining discrepancies between observed and calculated ($0kl$) reflections, there were some unusually long and short bond lengths, and a contact of only 3·2 Å between carbon atom L of one molecule and the corresponding atom L' of the molecule related by $(\vec{b} + \vec{c})/2$. A reinvestigation of the ($h0l$) data did not resolve these difficulties. Hence, the possibility of distortion of the molecule to nonplanar form, especially in the region of carbon atom L, was investigated with the use of the ($h1l$) data.

This small distortion from planarity can be made in space group $A2/a$ in which the molecule would remain centrosymmetric, or in Aa, in which a noncentrosymmetric distortion could occur. A simple method of testing the correctness of the centrosymmetric distortion is, then, to compare the y co-ordinates and R values for ($h1l$) reflections for h odd with the R value for reflections for h even. Separate refinement of these two classes of reflection by the use of difference-generalised projections [6] gave final values of $R = 0{\cdot}15$ for the 132 ($h1l$) planes for h odd and $R = 0{\cdot}17$ for the 128 planes for h even, the ($31\bar{1}$) plane, thought to be subject to extinction, being omitted. The y co-ordinates obtained from these two independent sets of data agreed remarkably well, and thus confirmed the centrosymmetric type of slight out-of-plane distortion of the molecule.

A final series of refinements was carried out at the University of Minnesota with the aid of the Univac Scientific 1103 high-speed digital computer. Five cycles of least-squares refinement of all ($h0l$), ($h1l$), and ($0kl$) data were carried out with the use of six independent thermal parameters for each carbon and one isotropic thermal parameter for each hydrogen atom. Weighting factors described elsewhere [7] were used with $F_{\text{min.}}$ chosen as 3. The final values of $R = 0{\cdot}12$ and $r = 0{\cdot}086$ were obtained.[7]

Results and Accuracy.—The final co-ordinates, expressed as ratios of the cell lengths, after the least-squares refinements, are shown in Table 1. Standard deviations of 0·00054 (0·009 Å) for x, 0·00364 (0·019 Å) for y, and 0·00044 (0·009 Å) for z were computed from the diagonal terms only of the least-squares matrix, and lead to standard deviations of 0·032 Å in the C–C bond lengths, or 0·023 Å in the position of a carbon atom. On the average, these final co-ordinates differ but little from those obtained from the earlier Fourier refinement, but maximum differences are 0·037 Å for the x co-ordinate of atom G, 0·062 Å for the y co-ordinate of atom J, and 0·045 Å for the z co-ordinate of atom K. We feel that even these maximum differences are not significant and that the least-squares results are the more accurate. An estimate of 0·015 for standard deviations of x and z was obtained from the curvature of the electron density

TABLE 1. *Atomic co-ordinates.*

Atom	x	y	z	Atom	x	y	z
A	−0·05966	0·44047	0·26584	*H*	−0·12793	0·61287	0·34780
B	−0·01311	0·24868	0·31648	*I*	−0·18169	0·79004	0·36520
C	0·04540	0·06190	0·30068	*J*	−0·19180	0·78966	0·43109
D	0·09155	−0·11296	0·34916	*K*	−0·14999	0·59927	0·47697
E	0·14692	−0·28317	0·33368	*L*	−0·09760	0·41830	0·46137
F	0·16079	−0·28890	0·27035	*M*	−0·08665	0·43382	0·39584
G	−0·11545	0·61235	0·28045	*N*	−0·02978	0·26269	0·37960

---

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

[7] Dickerson, Wheatley, Howell, and Lipscomb, *J. Chem. Phys.*, 1957, **27**, 200.

of the ($h0l$) projection by the Fourier method [8,9] of assessing errors, but this method does not yet include a proper weighting scheme or corrections for convergence, and, in this example, does not include all the data.

The anisotropic thermal motion was treated by means of the factor [10]

$$q(h,k,l) = \exp - (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{23}kl + b_{13}hl)$$

where $b_{11} = 2\pi^2a^{*2}U_{11}$, $b_{12} = 2 \times 2\pi^2a^*b^*U_{12}$, etc., U_{ij} being the components of the symmetric tensor which characterises the anisotropic vibrations of each atom. The final parameters obtained as a result of the least-squares refinement are given in Table 2, and apply to the co-ordinates given in Table 1. No complete analysis of the thermal motion as defined by these parameters has been attempted, but it appears that on the average the values of the Debye temperature factor (B) along the a, b, and c axes are roughly 3·5, 6·0, and 3·5 Å^{-2}.

TABLE 2. *Values of b_{ij} which apply to the co-ordinates as defined in Table* 1.

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}
A	0·00307	0·00100	0·00269	−0·00422	−0·00270	0·00138
B	0·00401	0·01969	0·00276	−0·00306	−0·00718	0·00142
C	0·00326	0·06038	0·00254	−0·00301	0·00354	0·00110
D	0·00347	0·06211	0·00286	0·00241	0·00163	0·00120
E	0·00430	0·09716	0·00301	−0·00115	0·00125	0·00248
F	0·00360	0·03725	0·00327	0·00397	0·00235	0·00181
G	0·00321	0·04328	0·00297	0·00991	0·00016	0·00238
H	0·00454	0·01661	0·00282	−0·00257	0·00334	0·00281
I	0·00402	0·12417	0·00384	−0·00793	0·00335	0·00242
J	0·00466	0·08452	0·00379	−0·00445	0·00931	0·00199
K	0·00430	0·08820	0·00371	−0·00082	−0·00510	0·00242
L	0·00506	0·09480	0·00292	0·00145	0·00330	0·00261
M	0·00398	0·04631	0·00297	0·00107	0·00300	0·00249
N	0·00516	0·07393	0·00307	−0·00985	0·00193	0·00224

The hydrogen atom positions were included in the least-squares refinement, with isotropic temperature factors, and the final values obtained are given in Table 3. These figures are subject to large errors, the standard deviation in position being about 0·25 Å and in C–H bond length about 0·35 Å. These bond lengths vary between 0·8 and 1·3 Å, the mean value being 1·00 Å.

TABLE 3. *Hydrogen parameters.*

Atom	x	y	z	B	Atom	x	y	z	B
O(*I*)	−0·229	0·912	0·338	5·4	*S*(*N*)	0·011	0·095	0·423	6·6
P(*J*)	−0·234	0·879	0·441	2·9	*T*(*D*)	0·087	−0·179	0·397	4·5
Q(*K*)	−0·165	0·599	0·525	0·8	*U*(*E*)	0·177	−0·338	0·373	0·5
R(*L*)	−0·061	0·314	0·498	0·1	*V*(*F*)	0·207	−0·323	0·264	0·7

The mean plane of the molecule is $Y = -1{\cdot}0513X - 0{\cdot}5110Z + 2{\cdot}1599$, where $X = x + z\cos\beta$, $Y = y$, and $Z = z\sin\beta$ is a conversion to an orthogonal system described by a, b, and c' orthogonal to a and b. The deviations of each atom from this plane are listed in Table 4.

TABLE 4. *Distances* (Å) *of atoms from mean plane.*

Atom	Distance	Atom	Distance	Atom	Distance
A	−0·006	*F*	−0·024	*K*	0·008
B	0·009	*G*	0·007	*L*	0·067
C	0·019	*H*	−0·002	*M*	0·035
D	−0·014	*I*	−0·036	*N*	0·011
E	−0·026	*J*	−0·066		

Atoms *L* and *J* appear to be significantly off the mean plane. In our less accurate Fourier results, atom *L* was 0·080 Å and atom *J* was −0·039 Å away from the molecular plane, and the average of all of the differences between the Fourier and least-squares final values was only 0·016 Å.

---

[8] Hughes and Lipscomb, *J. Amer. Chem. Soc.*, 1946, **68**, 1970.
[9] Cruickshank, *Acta Cryst.*, 1949, **2**, 65.
[10] Cruickshank, *Acta Cryst.*, 1956, **9**, 747.

The perpendicular distance between molecular planes is 3·42 Å, almost identical with the value of 3·40 Å for graphite. The nature of the contacts perpendicular to the molecular planes is shown in Fig. 4, in which the carbon atoms in contact tend to avoid direct overlap.

Bond lengths are shown in Table 5 where they are compared with the values computed by the molecular-orbital method. The agreement is remarkably good, with an average deviation of 0·016 Å and a maximum deviation of 0·05 Å. The strictly planar model shows an average deviation of 0·037 Å and a maximum deviation of 0·12 Å from the least-squares model of Table 5. The model obtained from the earlier Fourier refinements is not shown here, but it shows an average deviation of 0·032 Å and a maximum deviation of 0·07 Å from the least-squares model, and an average deviation of 0·042 Å and a maximum deviation of 0·07 Å from the molecular-orbital model. Of all of these comparisons, the best by far is between the least-squares model and the molecular-orbital model, as shown in Table 5.

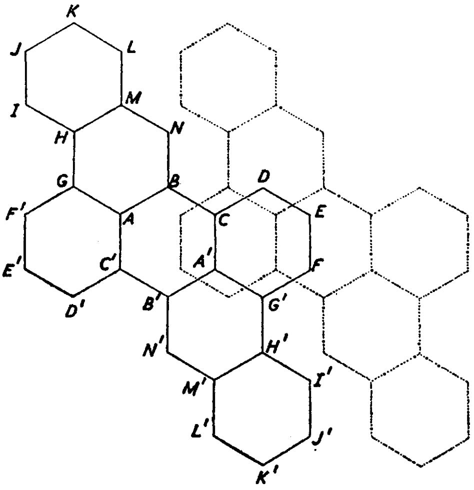


FIG. 4. *Normal projection of two parallel molecules.*

Bond angles are shown in Table 6. The maximum variations from 120° are 5·7° for angle *MNB* and 6·0° for *NBA*, which are associated with the buckled region of the molecule.

The short intermolecular contact between atom *L* on the standard molecule and atom *L′* on the molecule translated by $\overrightarrow{b}/2 + \overrightarrow{c}/2$ from the standard molecule remained short, even after further refinement of the y co-ordinates by use of the generalised-projection technique. It was

TABLE 5.

Bond	X-Ray	M.O.	Bond	X-Ray	M.O.	Bond	X-Ray	M.O.	Bond	X-Ray	M.O.
AB	1·48	1·45	*FG′*	1·42	1·41	*HI*	1·40	1·41	*LM*	1·41	1·42
BC	1·48	1·47	*CA′*	1·45	1·43	*IJ*	1·41	1·38	*MN*	1·41	1·43
CD	1·39	1·40	*AG*	1·38	1·42	*JK*	1·40	1·40	*NB*	1·41	1·38
DE	1·38	1·39	*GH*	1·46	1·46	*KL*	1·38	1·38	*MH*	1·38	1·43
EF	1·39	1·38									

TABLE 6. *Bond angles computed from final parameters.*

Angle		Angle		Angle		Angle		Angle	
C′AB	117·1°	*DEF*	122·7°	*F′GH*	119·9°	*GHM*	119·6°	*HIJ*	120·8°
ABC	121·9	*EFG′*	118·2	*GHI*	121·8	*HMN*	118·8	*IJK*	117·8
BCA′	121·0	*FG′A′*	119·9	*NML*	118·5	*MNB*	125·7	*JKL*	123·1
BCD	121·9	*G′A′C*	121·2	*BAG*	121·7	*NBA*	114·0	*KLM*	116·9
A′CD	117·0	*CBN*	124·2	*AGH*	120·2	*MHI*	118·7	*LMH*	122·7
CDE	121·0								

TABLE 7. *Intermolecular distances* (Å) *according to Fourier refinement.*

S–SIII	Distance	S–SII	Distance	SI–SII	Distance	SII–SIII	Distance
L...L′	3·26	*E...I*	3·66	*F...I*	3·82	*K...K′*	3·68
K...N′	3·52	*F...I*	3·70	*E...I*	3·83	*J...K′*	3·77
L...K′	3·94	*E...J*	3·81	*E...J*	3·90	*J...J′*	3·90

TABLE 8. *Observed and calculated structure factors for* 2 : 3-8 : 9-*dibenzoperylene.*

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
000	—	736	6,0,12	15	+14	$1,1,\overline{13}$	9	−12	$4,1,\overline{19}$	9	−12	$8,1,\overline{19}$	10	+11	13,1,9	10	−5
200	82	+94	6,0,10	14	+15	$1,1,\overline{15}$	10	+8	$4,1,\overline{21}$	5	+6	9,1,17	12	+15	13,1,5	10	+2
400	141	−142	606	66	+61	$1,1,\overline{19}$	7	+8	5,1,15	8	+4	917	5	+2	13,1,3	6	−2
600	36	+42	604	15	−12	$1,1,\overline{21}$	10	+6	5,1,11	6	−3	915	9	−7	13,1,1	10	+14
800	19	−10	602	38	−42	2,1,21	4	−3	519	6	+4	913	9	−12	$13,1,\bar{1}$	14	+11
020	46	−60	$60\bar{2}$	20	+18	2,1,19	4	+4	517	46	+38	911	18	+21	$13,1,\bar{3}$	22	−19
060	22	−22	$60\bar{4}$	14	+10	2,1,17	22	+23	515	56	−65	$91\bar{3}$	35	−36	$13,1,\bar{5}$	5	+5
002	102	−102	$60\bar{6}$	22	−26	2,1,15	22	−25	513	34	−34	$91\bar{5}$	9	−17	$13,1,\bar{7}$	6	+5
004	36	−34	$60\bar{8}$	14	−10	2,1,13	4	−1	511	60	+71	$91\bar{7}$	17	−18	$13,1,\bar{9}$	8	+11
006	34	+34	$6,0,\overline{10}$	26	−29	2,1,11	28	−25	$51\bar{1}$	22	+15	$91\bar{9}$	10	−10	$13,1,\overline{11}$	8	+6
008	27	+28	$6,0,\overline{12}$	8	−9	219	18	−18	$51\bar{3}$	38	+42	$9,1,\overline{11}$	11	+1	$13,1,\overline{15}$	6	−5
0,0,10	31	−28	$6,0,\overline{18}$	27	+24	217	22	−22	$51\bar{5}$	33	+30	$9,1,\overline{13}$	11	−16	$13,1,\overline{17}$	6	−8
0,0,12	17	−12	$6,0,\overline{20}$	19	−25	215	40	−51	$51\bar{7}$	10	+2	$9,1,\overline{15}$	22	+25	14,1,5	8	+3
0,0,16	14	−13	8,0,16	18	−18	213	4	−1	$51\bar{9}$	26	+22	$9,1,\overline{17}$	14	+17	14,1,3	26	−24
			808	54	−38	211	102	−109	$5,1,\overline{11}$	17	−20	$9,1,\overline{19}$	12	−18	14,1,1	19	+11
011	74	+80	806	90	+73	$21\bar{1}$	152	+142	$5,1,\overline{13}$	18	−17	10,1,17	2	−4	$14,1,\bar{1}$	7	−3
013	41	+31	$80\bar{8}$	14	+18	$21\bar{3}$	30	+27	$5,1,\overline{15}$	6	+11	10,1,13	9	−6	$14,1,\bar{3}$	20	+18
015	26	+16	$8,0,\overline{12}$	13	+7	$21\bar{5}$	14	−16	$5,1,\overline{19}$	7	−6	10,1,11	5	+6	$14,1,\bar{7}$	7	+8
017	6	−14	$8,0,\overline{14}$	14	−19	$21\bar{7}$	6	+12	6,1,17	13	−11	10,1,7	26	−21	$14,1,\bar{9}$	6	+5
019	44	+35	$8,0,\overline{18}$	20	+22	$21\bar{9}$	42	+49	6,1,15	18	+18	10,1,5	4	+6	$14,1,\overline{11}$	10	+10
0,1,11	30	−23	10,0,2	11	+11	$2,1,\overline{11}$	4	+7	6,1,13	6	+4	10,1,3	6	+6	$14,1,\overline{13}$	10	+11
0,1,13	8	+5	$10,0,\overline{12}$	22	−22	$2,1,\overline{13}$	10	+11	619	6	+5	10,1,1	10	−7	$14,1,\overline{19}$	5	−4
0,1,15	38	−41	$10,0,\overline{14}$	9	+12	$2,1,\overline{19}$	9	−14	617	32	+34	$10,1,\bar{3}$	9	−6	15,1,5	10	+6
0,1,17	10	+6	12,0,2	14	−23	$2,1,\overline{21}$	10	+9	615	9	+9	$10,1,\bar{5}$	7	−7	15,1,3	33	−36
022	17	+24	$12,0,\bar{2}$	54	+59	3,1,21	4	−3	613	26	+27	$10,1,\bar{7}$	10	−12	15,1,1	14	+14
024	50	+50	$12,0,\bar{4}$	16	−10	3,1,19	8	+6	611	4	−9	$10,1,\bar{9}$	8	+6	$15,1,\bar{1}$	5	+15
026	16	−17	$12,0,\overline{12}$	22	+11	3,1,17	13	+14	$61\bar{1}$	13	−18	$10,1,\overline{11}$	16	+9	$15,1,\bar{3}$	12	−10
0,2,16	16	−18	$12,0,\overline{14}$	54	−44	3,1,15	6	−3	$61\bar{3}$	43	−51	$10,1,\overline{13}$	38	−42	$15,1,\bar{7}$	6	+5
0,2,20	14	+19	$12,0,\overline{16}$	10	−12	3,1,13	6	−4	$61\bar{5}$	40	+37	$10,1,\overline{15}$	18	+14	16,1,9	3	−3
035	25	−29	14,0,12	10	−13	3,1,11	8	−7	$61\bar{7}$	14	+12	$10,1,\overline{19}$	10	+12	16,1,7	3	+3
0,4,16	14	+15	$14,0,\bar{4}$	28	+23	319	6	+6	$61\bar{9}$	48	−49	11,1,15	6	+2	16,1,5	11	+8
			$14,0,\overline{12}$	87	+95	317	27	+24	$6,1,\overline{11}$	13	+10	11,1,13	6	−3	16,1,3	16	−18
2,0,14	26	−19	$14,0,\overline{14}$	35	−46	315	59	−53	$6,1,\overline{13}$	17	+15	11,1,11	10	+10	16,1,1	2	−1
2,0,12	17	−19	$14,0,\overline{16}$	9	−8	313	10	−14	$6,1,\overline{15}$	6	−7	11,1,9	9	−4	$16,1,\bar{1}$	11	−11
2,0,10	10	−8	16,0,6	9	−6	311	251	+239	7,1,19	6	−2	11,1,7	26	+26	$16,1,\bar{9}$	5	+2
206	6	−9	16,0,4	13	0	$31\bar{1}$	102	−134	7,1,17	17	+22	11,1,5	8	−6	$16,1,\overline{11}$	10	−8
204	95	−111	16,0,2	8	−19	$31\bar{3}$	35	−38	7,1,15	16	−18	11,1,3	6	+6	$16,1,\overline{13}$	23	+22
202	156	−162	$16,0,\overline{10}$	9	−11	$31\bar{5}$	4	−9	7,1,13	4	−8	$11,1,\bar{1}$	6	+5	$16,1,\overline{19}$	4	+4
$20\bar{2}$	23	+21	$16,0,\overline{12}$	30	+26	$31\bar{7}$	5	−1	715	9	+5	$11,1,\bar{3}$	18	+14	$16,1,\overline{21}$	6	+5
$20\bar{4}$	96	+98	$16,0,\overline{14}$	10	+11	$31\bar{9}$	24	−30	713	3	−2	$11,1,\bar{5}$	8	−3	17,1,7	3	+6
$20\bar{6}$	34	+32	$16,0,\overline{16}$	20	+20	$3,1,\overline{15}$	6	−11	711	42	−43	$11,1,\overline{11}$	11	+12	17,1,5	6	+6
$2,0,\overline{10}$	98	+97	18,0,4	41	+45	$3,1,\overline{19}$	11	−18	$71\bar{1}$	4	+4	$11,1,\overline{13}$	66	−58	17,1,3	6	−5
$2,0,\overline{12}$	14	−11	18,0,2	24	−34	$3,1,\overline{21}$	10	+9	$71\bar{3}$	54	−52	$11,1,\overline{15}$	10	+13	17,1,1	5	−5
$2,0,\overline{14}$	23	−26	$18,0,\overline{12}$	22	−26	4,1,17	9	+13	$71\bar{5}$	43	+46	$11,1,\overline{17}$	12	+11	$17,1,\bar{1}$	3	−4
4,0,18	18	−8				4,1,15	12	+11	$71\bar{7}$	10	−15	$11,1,\overline{19}$	5	−5	$17,1,\bar{3}$	6	+4
4,0,16	78	+66	1,1,17	22	+20	4,1,13	7	+8	$71\bar{9}$	50	+55	12,1,13	13	−8	$17,1,\bar{7}$	9	−12
4,0,14	26	−22	1,1,15	55	−61	4,1,11	5	+7	$7,1,\overline{13}$	17	+18	12,1,11	7	+6	$17,1,\overline{11}$	24	+23
4,0,12	21	−12	1,1,13	8	+8	419	10	−13	8,1,19	5	+1	12,1,9	7	+7	$17,1,\overline{13}$	24	−24
406	33	−38	1,1,11	37	+42	417	26	+28	8,1,17	19	+20	12,1,7	12	−13	$17,1,\overline{15}$	3	−2
404	6	−10	119	17	−26	415	44	−40	8,1,15	6	+8	12,1,1	9	+7	18,1,3	6	+6
402	8	+14	117	7	−18	413	12	+11	8,1,11	7	−8	$12,1,\bar{3}$	20	+18	$18,1,\bar{3}$	6	−6
$40\bar{2}$	17	−24	115	26	+30	411	156	−161	817	6	−3	$12,1,\bar{5}$	8	−7	$18,1,\bar{7}$	9	−10
$40\bar{4}$	36	−40	113	14	−11	$41\bar{1}$	34	+45	815	10	+10	$12,1,\bar{7}$	6	−9	$18,1,\overline{11}$	21	−17
$40\bar{6}$	19	−28	111	46	−42	$41\bar{5}$	21	−20	811	30	+33	$12,1,\bar{9}$	4	+6	$18,1,\overline{13}$	9	+7
$40\bar{8}$	94	−94	$11\bar{1}$	36	−33	$41\bar{7}$	2	−5	$81\bar{3}$	44	−42	$12,1,\overline{11}$	12	+16	$19,1,\bar{5}$	7	+5
$4,0,\overline{10}$	106	+93	$11\bar{3}$	43	−32	$41\bar{9}$	6	−13	$81\bar{5}$	29	+30	$12,1,\overline{13}$	26	−26	$19,1,\bar{7}$	8	−11
$4,0,\overline{14}$	13	+11	$11\bar{5}$	18	+14	$4,1,\overline{11}$	14	+15	$81\bar{7}$	18	+18	$12,1,\overline{17}$	11	−13	$19,1,\overline{11}$	14	+10
$4,0,\overline{20}$	10	−28	$11\bar{7}$	7	+9	$4,1,\overline{15}$	9	+10	$81\bar{9}$	26	−23	$12,1,\overline{19}$	4	−4	$20,1,\bar{5}$	6	+6
6,0,18	18	−18	$11\bar{9}$	43	+38	$4,1,\overline{17}$	6	+4	$8,1,\overline{15}$	11	+14	13,1,13	6	−9	$20,1,\overline{11}$	3	−3
6,0,16	31	+22	$1,1,\overline{11}$	32	−31												

found to be 3·26 Å, while the least-squares refinement gives a molecular contact of 3·24 Å. All other molecular contacts are greater than 3·40 Å. The closest approach between atoms in molecules related by the translation *b* is 3·49 Å.

Molecular contacts less than 4·0 Å, apart from molecules related by translation *b*, are given in Table 7. S refers to the standard molecule; SI, SII, and SIII are molecules related to the standard by the translation $\vec{b}$, $(\vec{a} + \vec{b})/2$, and $(\vec{b} + \vec{c})/2$, respectively. The relative arrangement of the molecules as viewed down the *b* axis is seen in Fig. 3. The hydrogen atom attached to atom *L* and the symmetry-related hydrogen on *L′* clear each other by 2·9 Å.

DISCUSSION

This is not the first time that an apparently planar molecule has been found slightly buckled. In anthracene [11] the distortion is very small and almost certainly due to packing effects. In chrysene [12] there are small displacements in the end rings similar to those found in the present investigation. In every case there appears to be a very good logical explanation for the production of slight buckling. If the molecule takes on a slightly

---

[11] Cruickshank, *Acta Cryst.*, 1956, **9**, 915.

[12] Iball, personal communication.

distorted shape, then the atoms of neighbouring molecules—generally hydrogen atoms—are able to pack into slight cavities, leaving less empty space elsewhere. There cannot be any doubt that in certain cases the energy of strain in distorted molecules is less than the energy gained by closer packing. It appears that such is the case here. Two molecules have come excessively close together, presumably to reduce empty spaces in the crystal structure. There are other crystals in which similar short distances have been observed.[13]

The reasons which have accrued to give very strong evidence of out-of-plane distortion in this case are: (i) Atom L is furthest from the mean plane, and its displacement (between 0·07 and 0·08 Å) is significant. It is the same atom which approaches a symmetry-related atom on another molecule to within 3·26 Å. (ii) The displacements of the other atoms from the mean plane of the molecule are sensible. Atom L and its neighbour, M, are both above the mean plane, while the two opposite atoms, J and I, are both below the mean plane. The remaining two atoms, which act as a kind of axis of rotation for the ring, are almost exactly on the mean plane. (iii) The atoms, apart from those in the ring containing atom L, are displaced far less from the mean plane. (iv) The bond lengths in the ring containing atom L become more sensible on assumption of a buckled, rather than planar, molecule.

There is no significant difference between the results of the molecular-orbital calculations and the X-ray work. The former had to be based on the assumption of a planar molecule, but this does not appear to have affected the validity of the results to any great extent.

We thank Dr. E. Clar for the crystal sample.

CHEMISTRY DEPARTMENT, UNIVERSITY OF GLASGOW.
SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA,
MINNEAPOLIS 14.

[*Received, December 29th*, 1958.]

---

[13] Herbstein and Schmidt, *J.*, 1954, 3302, 3314; Rossmann, following paper.