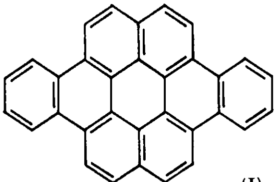
225. *Crystal-structure Studies of Polynuclear Hydrocarbons. Part V.*[1] 1,2:7,8-*Dibenzocoronene.*

By J. Monteath Robertson and James Trotter.

Crystals of 1,2:7,8-dibenzocoronene are monoclinic, with four molecules in a unit cell of dimensions $a = 22{\cdot}83$, $b = 5{\cdot}22$, $c = 15{\cdot}77$ Å, $\beta = 103{\cdot}9°$, space group $C2/c$. All the crystals examined have been twinned on (100). The structure has been determined from normal and generalised projections along the *b*-axis. The carbon skeleton of the molecule is completely planar, but there is evidence that some of the hydrogen atoms are displaced from this aromatic plane. Details of the molecular dimensions and of the intermolecular separations have been obtained.


(I)

A detailed *X*-ray investigation of the crystal and molecular structure of 1,2:7,8-dibenzocoronene (I) has been undertaken to obtain an accurate account of the dimensions of the molecule. Although partial three-dimensional data have been used to give an independent estimate of all three positional parameters for each carbon atom, the accuracy of the results is limited by the paucity of results obtained from the rather poor-quality twinned crystals. The bond lengths have nevertheless been determined with sufficient accuracy to allow some comparison to be made with the bond distances in related molecules.

Experimental

Crystals of 1,2:7,8-dibenzocoronene, obtained by crystallisation from 1-methylnaphthalene followed by sublimation in a high vacuum, were yellow needles elongated along the *b*-axis. The density was determined by flotation in aqueous potassium iodide. The unit-cell dimensions and space group were determined from rotation and oscillation photographs of a crystal rotating about the *b*-axis, and *h*0*l*, *h*1*l*, and *h*2*l* Weissenberg films. The Weissenberg photographs indicated clearly that the crystals were twinned on (100), and although several specimens were examined, a single crystal could not be obtained. However the photographs could be readily interpreted and indexed.

The crystal data were: 1,2:7,8-Dibenzocoronene, $C_{32}H_{16}$; *M*, 400·4; m. p. 496—499°. Monoclinic, $a = 22{\cdot}83 \pm 0{\cdot}06$, $b = 5{\cdot}22 \pm 0{\cdot}01$, $c = 15{\cdot}77 \pm 0{\cdot}05$ Å, $\beta = 103{\cdot}9° \pm 0{\cdot}3°$. Volume of the unit cell = 1824·3 Å^3. *d* calc. (with $Z = 4$) = 1·449, measured = 1·457 g. cm.$^{-3}$. Absorption coefficient for *X*-rays, $\lambda = 1{\cdot}542$ Å, $\mu = 7{\cdot}65$ cm.$^{-1}$. Total number of electrons per unit cell = $F(000) = 832$. Absent spectra: *hkl* when $(h + k)$ is odd, *h*0*l* when *l* is odd. Space group is Cc–C_s^4 or $C2/c$–C_{2h}^6.

The intensities of the *h*0*l* and *h*1*l* reflexions were recorded on Weissenberg films for a crystal rotating about the *b*-axis, with Cu-K_α radiation, the equi-inclination method being used for the *h*1*l* layer. The multiple-film technique [2] was used to correlate strong and weak reflexions. The range of intensities measured was about 2000 to 1 for the *h*0*l* reflexions and 7000 to 1 for the *h*1*l* reflexions, the estimates being made visually. There were only a few cases where reflexions from different parts of the twinned crystal overlapped on the films, so that indexing and intensity estimation were straightforward for most of the reflexions. In addition it was possible, by measuring intensities of reflexions from both parts of the twin, to obtain reliable values for the intensities even for those cases where overlap occurred.

The cross-section of the crystal normal to the *b*-axis was 0·11 × 0·09 mm., and no absorption corrections were considered necessary. The structure amplitudes were derived by the usual formulæ for a mosaic crystal, the absolute scale being established later by correlation with the calculated structure factors. 69 independent *h*0*l* reflexions and 188 *h*1*l* reflexions were observed, representing 30% and 44% respectively of the possible number observable under the experimental conditions.

[1] Part IV, *J.*, 1959, 2623.

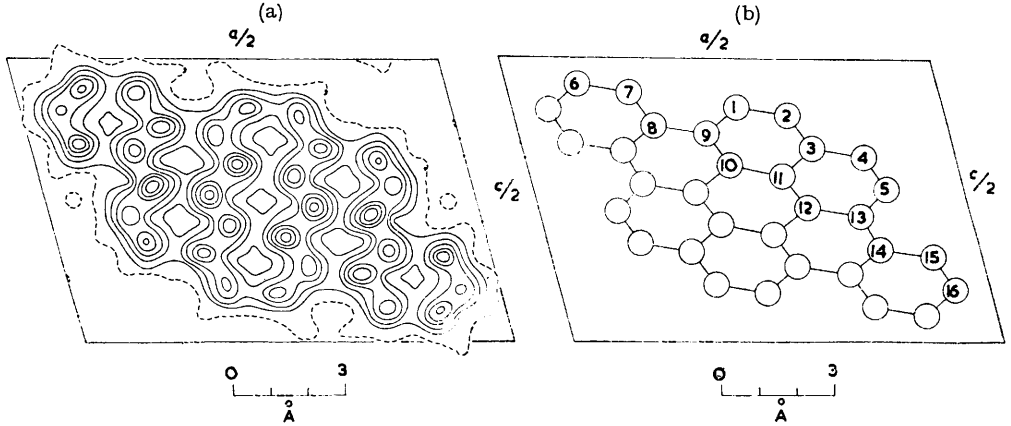
[2] Robertson, *J. Sci. Instr.*, 1943, **20**, 175.

Structure Analysis.—[010] *Projection.* Since it seemed probable that all the atoms in the molecule would be well resolved in the projection along the short *b*-axis, this projection was considered initially. Examination of the *h*0*l* weighted reciprocal lattice revealed regions of strong intensity among the higher-order reflexions, and the positions of these regions indicated clearly the hexagonal symmetry of the Fourier transform of the aromatic rings. The following high-order planes, which correspond approximately to the 1·2 Å spacings of the aromatic six-membered rings, have large structure amplitudes: (18,0,6), (18,0,4), $(\overline{14},0,14)$, $(\overline{14},0,12)$, (4,0,18), and (2,0,18). The orientation of one of the six-membered rings in the molecule was readily deduced by transforming this hexagon in the weighted reciprocal lattice into real space. This orientation was further checked by using a second set of intense reflexions, corresponding to the 2·1 Å spacings in the aromatic rings: $(\overline{10},0,2)$, $(\overline{12},0,2)$, $(\overline{10},0,4)$, $(\bar{4},0,10)$, $(\bar{2},0,10)$, (606), (608), (808). By assuming that all the rings in the molecule had similar dimensions, three possible orientations for the whole molecule were deduced.

A choice between these three orientations was then made from a consideration of the packing of the molecules in the unit cell. Since the cell contains four molecules, which are probably planar and centrosymmetrical, it seemed likely that the true space group was the centrosymmetrical one *C*2/*c*. When each molecule was placed on a centre of symmetry in this space group, only one of the three possible orientations could be fitted into the cell with the usual intermolecular separations. In addition the packing considerations also indicated that the molecule could not be accommodated on the centre of symmetry at (0,0,0), but was situated on the centre at $(\frac{1}{4},\frac{1}{4},0)$.

FIG. 1. (a) *Electron-density projection along the b-axis. Contours at intervals of* 1 eÅ^{-2}, *with the one-electron line broken.*

(b) *Projection of the structure on to* (010).



Structure factors were calculated for all the observed *h*0*l* reflexions, with the scattering curve for carbon of Berghuis *et al.*,[3] corrected for thermal vibration with $B = 4{\cdot}2$ Å^2 for all the atoms. The discrepancy between measured and calculated structure factors was 19·0%, so that there was no doubt that this structure, deduced from Fourier transform and packing considerations, was correct.

A Fourier series was then summed, measured structure amplitudes with calculated signs being used as coefficients. On the resulting electron-density map (Fig. 1) all the carbon atoms were well resolved. Further refinement proceeded by computing successive difference syntheses, with $(F_o - F_c)$ as coefficients, and altering the positional and isotropic temperature parameters to minimise the slopes and difference electron-densities at the atomic centres. One cycle reduced the discrepany factor to 13·6%, and a second cycle to 11·9%. The final measured and calculated structure factors are listed in Table 3. Throughout the refinement there were no sign changes, so that Fig. 1 represents the final electron-density projection along the *b*-axis.

y-*Co-ordinates.* No resolution of the individual atoms in the molecule could be expected in

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[3] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

projections down the *a*- or *c*-crystal axes, and the problem of finding the *y*-co-ordinates was therefore approached by considering the *h*1*l* structure factors.

Approximate *y*-co-ordinates were easily deduced from a consideration of the bond lengths projected on (010), and these trial co-ordinates were then refined by use of difference generalised projections.[4] By using both cosine and sine series simultaneously it is possible to refine all three positional parameters *x*, *y*, *z*, and the isotropic temperature parameters, *B*, at the same time.

Structure factors were calculated for the *h*1*l* reflexions by using the *x*, *z*, and *B* parameters from the *h*0*l* refinement, and the trial *y*-co-ordinates. The discrepancy factor was 23·6%. Refinement proceeded by computing cosine and sine difference generalised projections. The resulting electron-density maps indicated that no significant changes in *x*, *z*, and *B* parameters were required. New *y*-co-ordinates (y_0) were obtained from the relation:

$$\sin 2\pi(y_0 - y_c) = \frac{1}{\sigma_{1,0}}\{S_1{}^D \cos 2\pi y_c - C_1{}^D \sin 2\pi y_c\}$$

where y_c are the co-ordinates used in the previous structure factor calculation, $S_1{}^D$ and $C_1{}^D$ are the values of the sine and cosine difference generalised projections at the atomic positions, and $\sigma_{1,0}$ is the generalised density (approximately equal to the electron density in the *h*0*l* projection). The maximum shift in *y*-co-ordinate was 0·05 Å. Structure factors were recalculated with the revised co-ordinates, and the discrepancy factor was 17·3%. A second set of difference generalised projections was calculated, but no further significant changes in *y*-co-ordinates were indicated. The final measured and calculated *h*1*l* structure factors are included in Table 3. Cosine and sine generalised projections, computed from measured structure amplitudes and calculated signs, are shown in Fig. 2. These maps represent projections of the structure on to (010) with the electron density in the *j*th atom multiplied by cos $2\pi y_j$ and sin $2\pi y_j$ respectively.

TABLE 1. *Final positional and temperature parameters, and deviations* (Δ) *from the mean plane.*

Atom *	*x*	*y*	*z*	*X′*	*Y*	*Z′*	*B* (Å²)	Δ (Å)
C 1	0·2604	0·775	0·1641	5·771	4·046	1·161	4·5	+0·009
2	0·3175	0·770	0·1504	7·036	4·019	0·632	4·5	+0·020
3	0·3351	0·607	0·0920	7·426	3·169	−0·386	4·5	−0·013
4	0·3929	0·600	0·0785	8·707	3·132	−0·915	4·5	+0·008
5	0·4098	0·430	0·0208	9·082	2·245	−1·918	4·5	+0·006
6	0·0837	0·769	0·2020	1·855	4·014	2·727	4·5	+0·004
7	0·1405	0·776	0·1884	3·114	4·051	2·201	4·5	−0·028
8	0·1589	0·601	0·1321	3·521	3·137	1·212	4·2	+0·007
9	0·2170	0·599	0·1170	4·809	3·127	0·656	4·2	−0·007
10	0·2341	0·430	0·0595	5·188	2·245	−0·345	4·0	−0·010
11	0·2919	0·427	0·0427	6·469	2·229	−0·926	4·0	−0·038
12	0·3099	0·248	−0·0135	6·868	1·295	−1·911	4·0	+0·009
13	0·3680	0·244	−0·0285	8·155	1·274	−2·466	4·2	+0·004
14	0·3842	0·077	−0·0862	8·514	0·402	−3·465	4·2	−0·010
15	0·4434	0·077	−0·0978	9·826	0·402	−3·972	4·5	+0·011
16	0·4598	−0·091	−0·1574	10·190	−0·475	−5·002	4·5	−0·020
Molecular centre	0·2500	0·250	0	5·540	1·305	−1·370	—	0

* Cf. Fig. 4.

TABLE 2. *Orientation of the molecule in the crystal.*

$\chi_L = 47^\circ\ 00'$ $\chi_M = 48^\circ\ 11'$ $\chi_N = 106^\circ\ 31'$
$\psi_L = 111^\circ\ 33'$ $\psi_M = 48^\circ\ 47'$ $\psi_N = 48^\circ\ 34'$
$\omega_L = 129^\circ\ 14'$ $\omega_M = 69^\circ\ 38'$ $\omega_N = 133^\circ\ 56'$

Co-ordinates, molecular dimensions, and orientation. The final positional and temperature parameters of the carbon atoms are listed in Table 1, *x*, *y*, and *z* being co-ordinates referred to the monoclinic crystal axes and expressed as fractions of the unit-cell edges, and *X′*, *Y*, and *Z′* co-ordinates in Ångström units referred to orthogonal axes *a′*, *b*, and *c*.

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

FIG. 2. (a) *Cosine and* (b) *sine generalised projections using the hl1 data. Contours at intervals of* 1 eÅ^{-2}, *negative contours broken, zero contours omitted.*

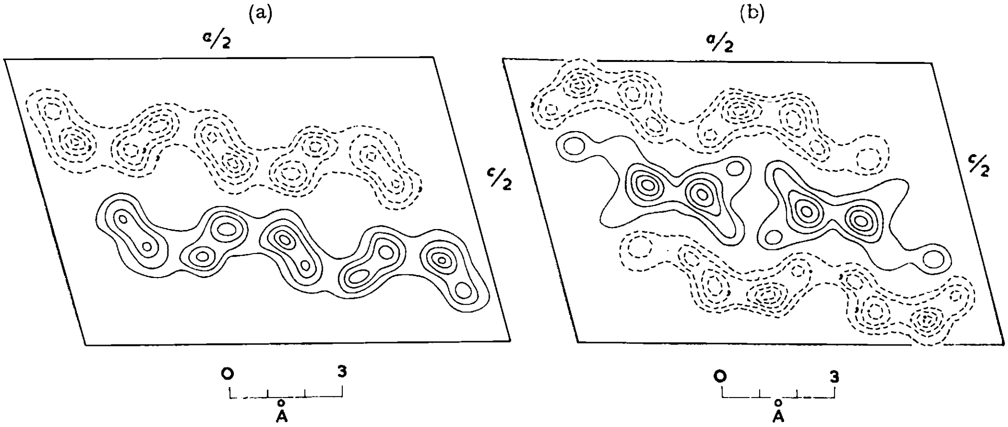


FIG. 3. (a) *Measured bond lengths* (Å) *and valency angles (degrees).* (b) *Mean bond lengths and valency angles.*

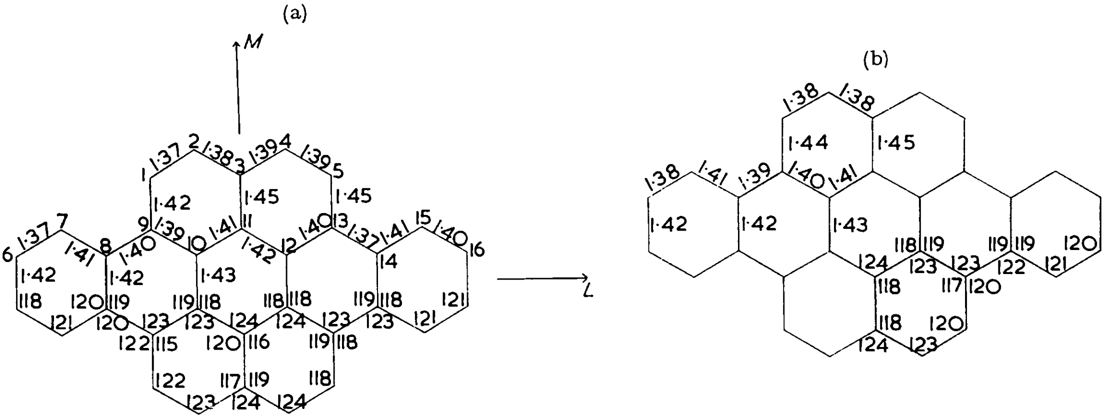


FIG. 4. *Normal projection of two parallel molecules.*

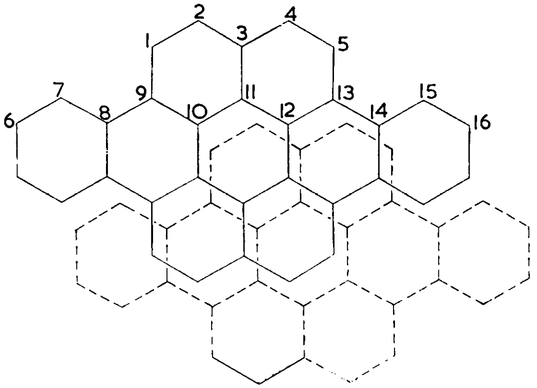
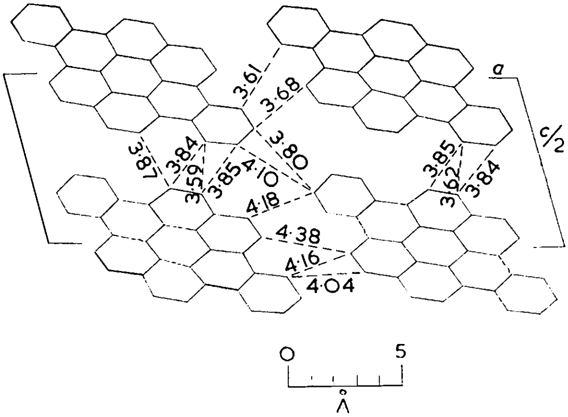


FIG. 5. *Projection of the structure on to* (010), *showing the shorter intermolecular distances.*



The equation of the mean molecular plane is

$$0{\cdot}2843X' - 0{\cdot}6615Y + 0{\cdot}6939Z' + 0{\cdot}2396 = 0$$

and the deviations of the atoms from this plane are listed in final column of Table 1.

The bond lengths and valency angles in the molecule, calculated from the co-ordinates of Table 1, are shown in Fig. 3(a). These values indicated that the symmetry of the molecule did not differ significantly from *mmm*, and the mean values of the bond lengths and valency angles are shown in Fig. 3(b).

The orientation of the molecule in the crystal is given in Table 2, where χ_L, ψ_L, ω_L; χ_M, ψ_M, ω_N; and χ_N, ψ_N, ω_N are the angles which the molecular axes *L*, *M* (see Fig. 3a), and the plane normal *N* make with the orthogonal axes *a′*, *b*, and *c*. *L* was taken through the molecular centre and the mid-point of bond 6′–16, and *M* through the molecular centre and atom 3 (for numbering used see Fig. 4). *L*, *M*, and *N* are thus not accurately mutually perpendicular, the angles being $\widehat{LM} = 90^\circ\ 25'$, $\widehat{MN} = 89^\circ\ 43'$, $\widehat{LN} = 89^\circ\ 53'$. The angle between the plane of the molecule and the (010) plane, which is expressed as ψ_N, the angle between the normal to the molecular plane and the *b*-axis, is 48·6°. For coronene [5] the corresponding angle is 43·7°.

TABLE 3. *Measured and calculated structure factors (one-half absolute scale).*

k l	$\lvert F_o\rvert$	F_c	h k l	$\lvert F_o\rvert$	F_c	h k l	$\lvert F_o\rvert$	F_c	h k l	$\lvert F_o\rvert$	F_c	h k l	$\lvert F_o\rvert$	F_c	h k l	$\lvert F_o\rvert$	F_c
2 0 0	79·4	−79·2	$\bar{6}$ 0 8	6·2	+6·3	5 1 1	19·6	−18·2	1 1 4	90·1	+91·6	7 1 7	2·7	+6·1	$\overline{11}$ 1 11	4·4	−6·5
4	48·3	−50·2	$\bar{4}$	9·4	−6·1	7	7·5	+9·7	3	1·4	−4·4	17	5·5	−8·2	$\bar{3}$	8·3	+5·8
6	21·7	−21·0	$\bar{2}$	6·6	−6·7	9	2·1	+3·9	5	11·5	+6·3	19	4·8	+7·5	1	4·6	+6·8
8	7·5	−5·8	0	9·6	−9·3	11	23·8	−20·5	7	39·7	−39·3	$\overline{21}$ 1 8	5·9	+10·6	3	2·5	−5·4
10	5·6	−3·5	4	8·5	+9·0	13	19·3	+22·5	9	3·4	−4·5	$\overline{17}$	3·7	+4·2	7	15·2	−13·0
12	2·8	−4·7	6	32·9	+27·7	15	13·7	+10·6	11	3·5	−3·3	$\overline{15}$	11·2	−14·3	9	10·0	+10·6
$\overline{14}$ 0 2	13·9	−10·8	8	37·5	−40·3	17	21·8	−27·4	17	6·0	−6·7	$\bar{9}$	8·4	+7·3	13	4·3	+4·7
$\overline{12}$	41·1	−46·5	$\overline{14}$ 0 10	7·4	+9·0	19	2·7	+4·4	19	4·6	+8·4	$\bar{7}$	3·7	−6·3	$\overline{13}$ 1 12	6·5	+9·3
$\overline{10}$	53·6	+56·0	$\bar{4}$	45·8	−41·9	$\overline{21}$ 1 2	2·7	−5·6	$\overline{13}$ 1 5	7·4	−6·3	$\bar{5}$	20·1	−17·0	$\bar{9}$	3·6	+6·2
$\bar{8}$	11·7	+14·6	$\bar{2}$	25·9	+22·6	$\overline{17}$	3·5	+7·3	$\overline{11}$	28·9	−29·6	$\bar{3}$	20·7	+17·8	$\bar{3}$	6·4	−11·9
$\bar{4}$	17·3	+21·2	0	6·5	+5·4	$\overline{11}$	6·4	+10·3	$\bar{9}$	18·5	+12·6	1	14·3	−10·2	7	5·9	+4·3
$\bar{2}$	10·2	+10·4	8	8·4	−5·5	$\bar{9}$	5·1	−5·9	$\bar{7}$	6·5	+3·8	3	6·5	+5·0	9	7·0	−6·3
0	79·1	+78·1	$\overline{18}$ 0 12	9·3	+10·0	$\bar{7}$	13·0	−14·3	$\bar{5}$	11·6	+9·2	7	2·3	+3·2	13	4·6	+3·9
2	77·2	−76·7	$\overline{16}$	13·4	+16·5	$\bar{5}$	12·9	−12·4	$\bar{3}$	11·6	+9·6	17	5·0	+4·4	$\overline{15}$ 1 13	3·7	−5·6
4	55·7	−51·8	$\overline{14}$	37·8	−36·5	$\bar{3}$	30·3	−34·3	$\bar{1}$	5·7	+7·3	19	10·5	−11·7	$\overline{13}$	3·8	+3·6
6	14·4	−14·6	$\bar{6}$	11·5	−2·4	$\bar{1}$	63·5	−62·6	1	30·7	−30·1	$\overline{21}$ 1 9	4·5	+7·7	$\bar{5}$	5·2	+2·9
8	10·5	−11·6	$\bar{4}$	15·3	−8·4	1	98·5	+96·2	3	23·4	+23·4	$\overline{19}$	7·1	−11·2	$\bar{3}$	15·1	−9·7
12	9·5	+13·6	$\bar{2}$	20·5	+16·4	3	20·3	+13·0	5	34·3	+28·5	$\overline{17}$	3·7	−9·3	$\bar{1}$	9·1	+9·1
$\overline{16}$ 0 4	6·9	−9·7	0	5·2	+5·0	5	15·2	+10·3	7	34·5	−28·2	$\overline{15}$	21·4	+27·3	1	5·0	−4·4
$\overline{12}$	11·0	−11·1	2	7·5	−4·8	9	2·2	+5·2	9	4·7	+8·1	$\overline{13}$	2·5	−5·1	3	5·7	+5·5
$\overline{10}$	48·5	+50·4	$\overline{14}$ 0 14	29·6	−30·9	11	18·8	+15·6	11	3·6	+3·7	$\bar{9}$	3·1	−4·8	$\overline{15}$ 1 14	6·3	+6·6
$\bar{8}$	5·1	−3·2	$\overline{12}$	17·3	+14·0	13	6·3	−6·8	17	2·7	+4·8	$\bar{3}$	15·4	−11·5	$\overline{13}$	5·9	−4·6
$\bar{4}$	31·4	−34·4	$\overline{10}$	10·9	+8·5	15	6·5	−3·8	$\overline{15}$ 1 6	5·0	+8·1	$\bar{1}$	4·2	−4·5	$\bar{3}$	15·4	−11·2
$\bar{2}$	20·3	−19·8	4 0 16	9·5	+5·4	17	22·1	−25·1	$\overline{13}$	3·1	+0·4	1	6·8	−7·5	1	2·7	−0·9
0	44·2	−50·6	2 0 18	11·8	−4·5	19	5·3	+9·7	$\overline{11}$	16·6	−14·8	3	5·0	+6·0	3	17·9	+15·4
2	37·8	+39·1	4	23·9	+18·7	21	2·6	+3·1	$\bar{9}$	27·6	+23·9	7	3·5	−6·8	5	3·2	−3·5
4	7·4	+6·7				$\overline{21}$ 1 3	6·5	+11·1	$\bar{5}$	27·6	−22·2	9	6·3	−0·5	$\overline{15}$ 1 15	4·9	+7·5
6	22·5	−23·3	1 1 0	16·6	−17·1	$\overline{11}$	7·4	+6·1	$\bar{3}$	17·2	+13·3	17	4·1	−2·2	$\bar{3}$	5·6	−2·7
8	5·3	+8·7	3	17·3	−15·2	$\bar{9}$	3·7	−2·4	3	6·1	−6·4	19	10·0	+10·9	$\bar{1}$	7·4	+6·6
14	12·3	+16·5	5	22·3	−22·0	$\bar{5}$	18·6	−15·7	7	29·2	−24·2	$\overline{21}$ 1 10	2·5	+5·2	1	6·3	−3·0
16	18·8	+16·7	11	36·7	+35·7	$\bar{3}$	25·3	−25·4	11	3·4	+3·2	$\overline{19}$	2·6	−2·0	3	22·6	+17·1
18	31·0	−34·9	15	2·8	+4·0	$\bar{1}$	64·6	−63·3	17	5·0	+6·5	$\overline{15}$	20·3	−25·6	5	5·9	−6·9
$\overline{20}$ 0 6	12·2	−16·9	17	12·7	−13·9	1	132·8	−137·0	19	3·6	−4·6	$\overline{13}$	10·1	+9·8	$\overline{15}$ 1 16	3·2	+5·2
$\overline{16}$	5·0	+5·9	$\overline{23}$ 1 1	3·1	−7·5	3	18·7	+21·6	$\overline{15}$ 1 7	3·9	−7·2	$\overline{11}$	5·4	+5·8	$\overline{13}$	13·7	−12·3
$\bar{6}$	5·3	−11·6	$\overline{17}$	2·5	+7·1	5	30·4	+30·3	$\overline{11}$	8·5	−8·3	$\bar{7}$	3·2	+3·5	3	11·8	+9·5
$\bar{2}$	3·2	−4·7	$\overline{13}$	2·9	+4·4	7	14·3	−12·6	$\bar{9}$	23·6	+22·1	$\bar{5}$	2·2	+1·4	5	5·7	−6·2
0	15·8	+15·5	$\overline{11}$	11·1	−9·0	17	13·5	−15·0	$\bar{7}$	8·3	+7·5	1	4·0	+4·5	$\overline{15}$ 1 17	2·4	+2·3
2	13·1	−14·3	$\bar{9}$	11·7	+10·6	19	5·3	+11·6	$\bar{5}$	37·2	+30·8	3	5·9	−6·9	$\overline{13}$	12·4	−11·9
4	13·3	+13·6	$\bar{5}$	13·2	+15·5	21	3·1	+3·8	$\bar{3}$	35·6	−31·1	7	11·5	+8·9	$\overline{11}$	4·5	+4·2
6	30·9	+30·7	$\bar{3}$	15·6	−14·7	$\overline{11}$ 1 4	15·4	−15·7	$\bar{1}$	9·9	−8·6	9	6·5	−8·9	$\bar{9}$	5·7	+6·1
8	12·1	−15·9	$\bar{1}$	10·5	−17·2	$\bar{9}$	9·3	+10·4	1	20·3	+16·6	19	3·5	−4·6	$\bar{7}$	4·7	−5·3
18	28·6	−29·5	1	16·8	+16·3	$\bar{3}$	14·5	−13·0	3	10·4	−10·7	$\overline{15}$ 1 11	12·5	+14·6	$\overline{13}$ 1 18	4·9	−4·9
$\bar{8}$ 0 8	7·1	+10·6	3	3·1	+1·2	$\bar{1}$	26·7	−20·7	5	2·0	−4·6	$\overline{13}$	12·8	−14·0	$\bar{7}$	5·9	+7·0

Standard deviations. The standard deviations of the atomic positions were calculated from Cruickshank's formulæ.[6] The mean values for all the atoms are $\sigma(x) = \sigma(y) = \sigma(z) = 0{\cdot}012$ Å, so that the standard deviation of the individual bond distances is 0·017 Å. This value may be compared with the root-mean-square deviation of the individual bond lengths from the mean values, for those bonds for which two independent measurements have been made, this value being 0·012 Å. The standard deviations of the mean bond distances are 0·017 Å for those bonds where there is only one measured value, and $0{\cdot}017/\sqrt{2} = 0{\cdot}012$ Å for those bonds where two independent measurements are available.

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[5] Robertson and White, *J.*, 1945, 607.

[6] Cruickshank, *Acta Cryst.*, 1949, **2**, 65.

Intermolecular distances. All the intermolecular distances correspond to normal van der Waals interactions. The perpendicular distance between the aromatic planes of molecules related by translation *b* is 3·45 Å, but the carbon atoms in contact tend to avoid direct overlap as can be seen from Fig. 4, which shows the normal projection of two parallel molecules. The corresponding perpendicular distance in coronene is 3·40 Å. The shorter lateral contacts are illustrated in Fig. 5.

DISCUSSION

The carbon skeleton of the molecule of 1,2:7,8-dibenzocoronene is completely planar within the limits of experimental error, the maximum deviation of the atoms from the mean plane being 0·038 Å, and the root-mean-square deviation 0·016 Å. There is, however, some indication on the electron-density map (Fig. 1), and on the corresponding difference synthesis, that the hydrogen atoms in the "overcrowded" positions (those bonded to carbons 7, 1, 5, and 15) deviate from the ring diagonals in a manner which suggests that H(7) and H(1) are pushed out of the aromatic plane in opposite directions, and similarly H(5) and H(15). This evidence is of course not very definite, but the possible deviations are in accord with the displacements which might be expected in order to increase non-bonded H • • • H separations of about 1·7 Å in a completely planar model to the usual van der Waals distances.

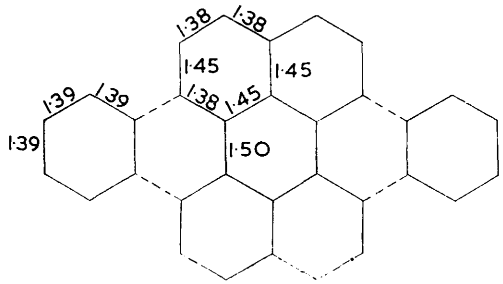

FIG. 6. *Bond lengths in perylene and an o-phenylene group.*

The bond distances in the central portion of the 1,2:7,8-dibenzocoronene molecule (Fig. 3b) are very similar to the corresponding lengths in perylene[7] (Fig. 6), suggesting that, to a first approximation, the molecule might be considered as being built up from perylene by the addition of two *o*-phenylene groups. A shortening of the *peri*-bond from 1·50 to 1·43 Å indicates an increase in aromatic character in that part of the dibenzocoronene molecule in comparison with perylene, but the fact that this distance is not reduced as far as the aromatic value (1·39 Å) supports the molecular formulation suggested by Clar[8] from spectroscopic evidence.

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CHEMISTRY DEPARTMENT, UNIVERSITY OF GLASGOW. [*Received, September 8th,* 1960.]

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[7] Donaldson, Robertson, and White, *Proc. Roy. Soc.*, 1953, *A*, **220**, 311.

[8] Clar, Ironside, and Zander, *Tetrahedron*, 1959, **6**, 358.