248. *Crystal-structure Studies of Polynuclear Hydrocarbons. Part VI.*[1] 1,12:2,3:4,5:6,7:8,9:10,11-*Hexabenzocoronene.*

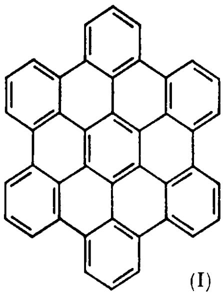
By J. Monteath Robertson and James Trotter.

Crystals of hexabenzocoronene are monoclinic, with two molecules in a unit cell of dimensions $a = 18{\cdot}42$, $b = 5{\cdot}11$, $c = 12{\cdot}86$ Å, $\beta = 112{\cdot}5°$, space group $P2_1/a$. All the crystals examined have been twinned on (001). The structure has been determined from normal and generalised projections along the *b*-axis. The carbon skeleton of the molecule is completely planar, but some of the hydrogen atoms are possibly displaced from the aromatic plane. Details of the molecular dimensions and of the intermolecular separations have been obtained.

A detailed *X*-ray investigation of the crystal and molecular structure of 1,12:2,3:4,5:6,7:8,9:10,11-hexabenzocoronene (I) has been undertaken to obtain an account of the dimensions of the molecule. The extreme stability of this hydrocarbon is indicated by its very high melting point. Unfortunately all the crystals available for examination were twinned and gave rather poor *X*-ray photographic records, so that, 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 rather limited.

Experimental

Crystals of hexabenzocoronene, obtained by crystallisation from boiling pyrene, followed by sublimation in a high vacuum, were yellow needles elongated along the *b*-axis. The density, unit-cell dimensions, and space group were determined as recorded in Part V[1] The several crystals examined were twinned on (001), and no single crystal could be obtained. It was not too difficult however to interpret and index the films, and the analysis proceeded satisfactorily with the data collected using the twinned crystals. The crystal data were: 1,12:2,3:4,5:6,7:8,9:10,11-hexabenzocoronene, $C_{42}H_{18}$; *M*, 522·6; m. p. >700°. Monoclinic, $a = 18{\cdot}42 \pm 0{\cdot}05$, $b = 5{\cdot}11 \pm 0{\cdot}01$, $c = 12{\cdot}86 \pm 0{\cdot}03$ Å, $\beta = 112{\cdot}5° \pm 0{\cdot}3°$. Volume of the unit cell = 1118·2 Å^3. *d* calc. (with $Z = 2$) = 1·542, measured = 1·544 g. cm.$^{-3}$. Absorption coefficient for *X*-rays, $\lambda = 1{\cdot}542$ Å, $\mu = 8{\cdot}13$ cm.$^{-1}$. Total number of electrons per unit cell = $F(000) = 540$. Absent spectra: *h*0*l* when *h* is odd, 0*k*0 when *k* is odd. Space group is uniquely determined as C_{2h}^5–$P2_1/a$.


(I)

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 3000 to 1 for the *h*0*l* reflexions and 2000 to 1 for the *h*1*l* reflexions, the estimates being made visually. On the *h*0*l* zone photographs there were only a few cases where reflexions from different parts of the twinned crystal overlapped, 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. On the *h*1*l* zone films, since reflexions with *h* both even and odd were present, indexing was a little more difficult, but reliable estimates of the intensities were obtained for most of the reflexions. There were, however, a few *h*1*l* reflexions for which it was considered that either the indexing or intensities might not be reliable, and these were omitted from the *h*1*l* zone refinement. These reflexions were all very weak.

The cross-section of the crystal normal to the *b*-axis was 0·14 × 0·09 mm., and no absorption corrections were applied. The structure amplitudes were derived by the usual formulæ for a mosaic crystal, the absolute scale being established later by correlation with the calculated

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[1] Part V, *J.*, 1961, 1115.

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

structure factors. 106 independent *h*0*l* reflexions and 99 *hll* reflexions were observed representing 37% and 18% respectively of the possible number observable under the experimental conditions.

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	0·0389	−0·178	0·4053	0·662	−0·910	4·938	4·2	+0·065
2	0·0965	0·002	0·4773	1·642	0·010	5·458	4·2	+0·019
3	0·1289	0·172	0·4221	2·194	0·879	4·520	4·2	+0·008
4	−0·1379	−0·690	0·2093	−2·347	−3·526	3·664	4·2	−0·002
5	−0·0794	−0·513	0·2739	−1·351	−2·621	4·082	4·2	−0·006
6	−0·0483	−0·348	0·2198	−0·822	−1·778	3·167	4·2	−0·020
7	0·0097	−0·175	0·2874	0·165	−0·894	3·628	4·2	−0·024
8	0·0467	0·008	0·2387	0·795	0·041	2·740	4·2	−0·035
9	0·1051	0·173	0·3030	1·789	0·884	3·156	4·2	+0·002
10	0·1397	0·350	0· 2507	2·377	1·789	2·239	4·2	−0·012
11	0·1976	0·519	0·3159	3·363	2·652	2·670	4·2	+0·003
12	0·2316	0·698	0·2672	3·941	3·567	1·804	4·2	−0·036
13	−0·1636	−0·695	0·0946	−2·784	−3·551	2·370	4·2	−0·025
14	−0·1302	−0·520	0·0342	−2·216	−2·657	1·358	4·2	−0·026
15	−0·0680	−0·344	0·1058	−1·157	−1·758	1·840	4·2	+0·005
16	−0·0374	−0·175	0·0470	−0·636	−0·894	0·868	4·2	−0·017
17	0·0232	0·000	0·1166	0·395	0·000	1·336	4·2	+0·001
18	0·0582	0·169	0·0675	0·990	0·864	0·458	4·2	+0·012
19	0·1159	0·343	0·1331	1·972	1·753	0·895	4·2	+0·005
20	0·1519	0·516	0·0832	2·585	2·637	−0·001	4·2	+0·019
21	0·2072	0·697	0·1451	3·526	3·562	0·405	4·2	−0·035
Molecular centre	0	0	0	0	0	0	—	0

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

$\chi_L = 48° 42'$
$\psi_L = 43° 18'$
$\omega_L = 100° 46'$

$\chi_M = 73° 15'$
$\psi_M = 89° 54'$
$\omega_M = 16° 44'$

$\chi_N = 134° 36'$
$\psi_N = 47° 03'$
$\omega_N = 78° 05'$

Structure Analysis.—[010] *Projection*. The cell dimensions, although greater, are strikingly similar to those found in the coronene structure,[3] and the general arrangement of the molecules is likely to be similar. It was therefore decided to approach the complete solution by a preliminary study of the short *b* axis projection. There are two molecules of hexabenzocoronene in the unit cell and the space group is $P2_1/a$, so that the molecules must be centrosymmetrical and situated on the centres of symmetry at (0,0,0) and ($\frac{1}{2},\frac{1}{2}$,0). In addition it seemed likely that the molecule might conform, at least approximately, to the much higher symmetry 6/*mmm*, so that the whole structure could be established by locating, on the *h*0*l* weighted reciprocal lattice, regions of high intensity corresponding to the 1·2 Å and 2·1 Å spacings of the regular aromatic hexagons. The orientation of the whole molecule was thus easily established from the following outstanding reflexions: (i) corresponding to 1·2 Å spacings, $(22,0,\bar{4})$, $(22,0,\bar{5})$, (10,0,6), (10,0,7), (807), $(12,0,\overline{10})$, $(12,0,\overline{11})$, $(14,0,\overline{11})$; (ii) corresponding to 2·1 Å spacings, (005), (006), $(20\bar{6})$, (10,0,0), (10,0,1), (12,0,0), $(10,0,\bar{5})$, $(12,0,\bar{5})$, $(12,0,\bar{6})$.

Structure factors were calculated for all the observed *h*0*l* reflexions, by using the scattering curve for carbon of Berghuis *et al.*,[4] corrected for thermal vibration with $B = 4{\cdot}2$ Å² for all the atoms. The discrepancy between measured and calculated structure factors was 24·1%. Refinement of the structure proceeded by computing successive difference syntheses, with $(F_o - F_c)$ as coefficients, and shifting the atoms to minimise the slopes at the atomic centres. No significant changes in temperature parameters were indicated, and *B* was retained at 4·2 Å² for all the atoms. After three cycles the discrepancy factor had been reduced to 13·1%, and a final $(F_o - F_c)$ synthesis indicated no further changes in positional or temperature parameters. Measured and calculated structure factors are listed in Table 3, and a final F_o synthesis, computed with measured structure amplitudes and calculated signs, is shown in Fig. 1.

y-*Co-ordinates*. No resolution of the individual atoms in the molecule could be expected in projections down the *a*- or *c*-crystal axes, and the problem of finding the *y*-co-ordinates was

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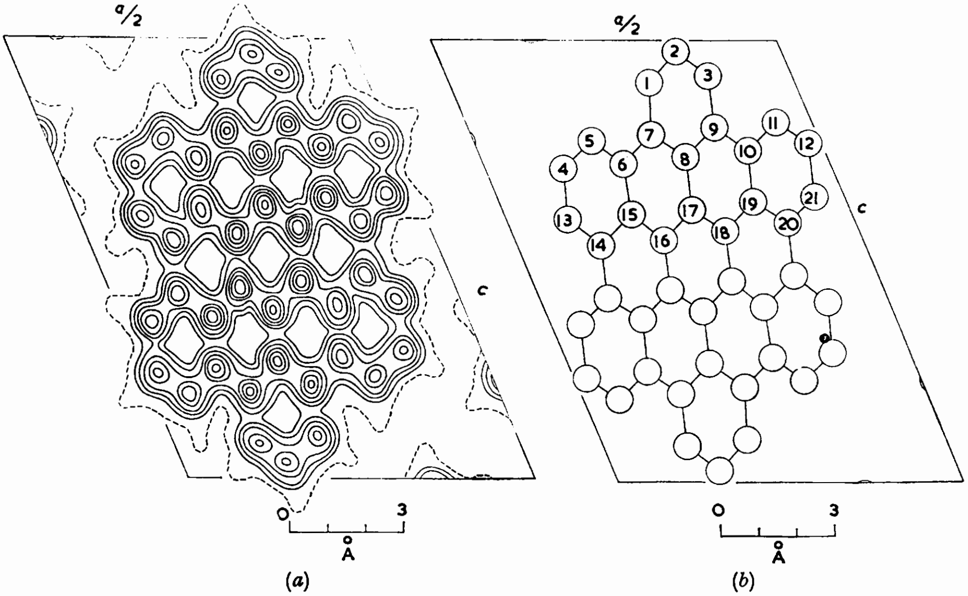
[3] Robertson and White, *J.*, 1945, 607.

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

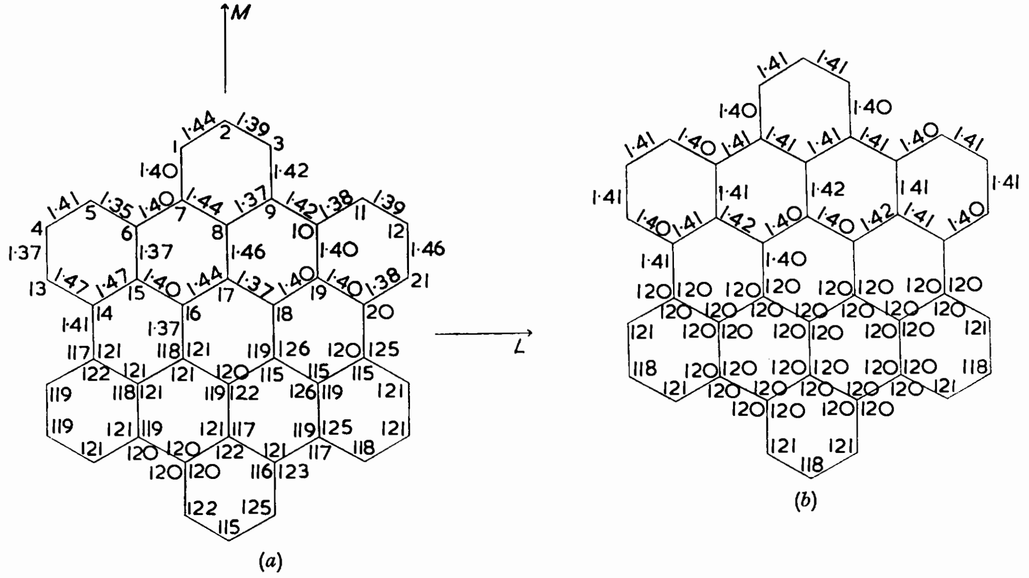
therefore approached by considering the hll structure factors. Approximate y-parameters were easily deduced from a consideration of the bond lengths projected on (010). Structure factors were calculated for the observed hll reflexions, by using these trial y-co-ordinates and the x, z, and B parameters from the $h0l$ refinement. The discrepancy factor was 19·2%. Refinement proceeded by computing cosine and sine difference generalised projections.[5] By this

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).



(*a*) (*b*)

FIG. 2. (a) *Measured bond lengths* (Å) *and valency angles* (*degrees*).
(b) *Mean bond lengths and valency angles.*



(*a*) (*b*)

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

method it is possible to refine all three positional parameters x, y, z, and the isotropic temperature parameters, B, simultaneously, but the maps indicated that no significant changes in x, z, and B parameters were required. New y-co-ordinates were obtained, the maximum shift being 0·04 Å, and structure factors were recalculated. The discrepancy factor was 11·7%. A second set of difference generalised projections was calculated, but no further significant changes in y-co-ordinates were indicated. The measured and calculated hll structure factors are included in Table 3.

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.

FIG. 3. *Normal projection of two parallel molecules.*

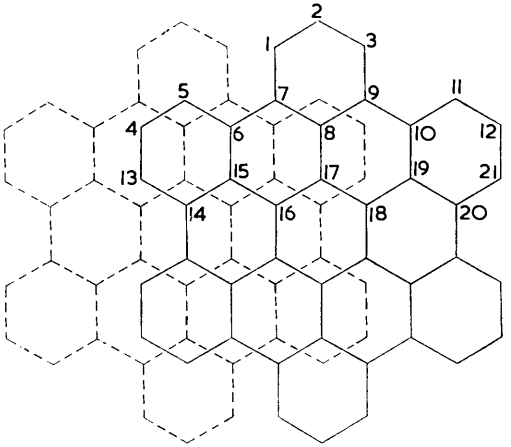
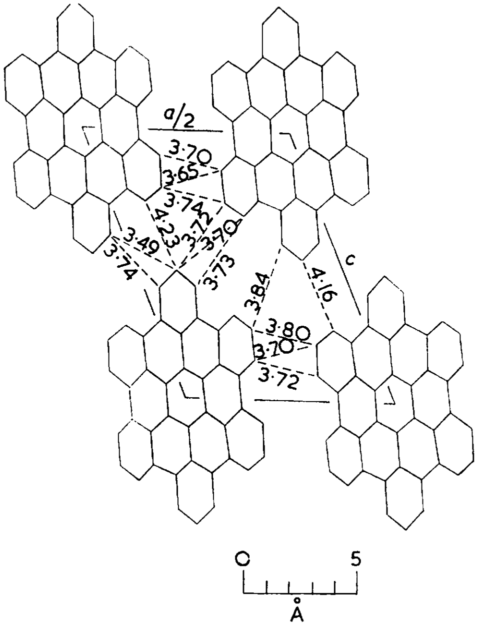


FIG. 4. *Projection of the structure on to* (010), *showing the shorter intermolecular distances.*



The equation of the mean molecular plane is

$$0{\cdot}7022X' - 0{\cdot}6814Y - 0{\cdot}2065Z' = 0$$

and the deviations of the atoms from this plane are listed in the 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. 2(a). The mean values, assuming symmetry $6/mmm$, are shown in Fig. 2(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_M; and χ_N, ψ_N, ω_N are the angles which the molecular axes L, M [see Fig. 2(a)], 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 14′—20 (for numbering used see Fig. 3), and M through the molecular centre and atom 2. L, M, and N are thus not accurately mutually perpendicular, the angles being $L\wedge M = 89° 17'$, $M\wedge N = 90° 05'$, $L\wedge N = 90° 21'$. The angle between the plane of the molecule and the (010) plane, ψ_N, is 47·0°. For coronene[3] the corresponding angle is 43·7°.

Standard deviations. The standard deviations of the atomic positions were calculated from Cruickshank's[6] formulæ. The mean values for all the atoms are $\sigma(x) = \sigma(y) = \sigma(z) = 0{\cdot}020$ Å, so that the standard deviations of the individual bond distances are 0·028 Å. This value may be compared with the root-mean-square deviation of the individual bond lengths from the mean

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

values, 0·032 Å. The standard deviations of the mean bond distances are $0{\cdot}028/\sqrt{3} = 0{\cdot}016$ Å where three independent estimates are available, and $0{\cdot}028/\sqrt{6} = 0{\cdot}011$ Å where six independent measurements have been made. These accuracy calculations reflect the measure of agreement that we have been able to obtain with the available data. As the amount of these data is small, owing to poor-quality crystals, the actual errors in the bond length estimates may be greater than is indicated by these standard calculations.

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 3·48 Å, but the individual atoms are not vertically over each other. Indeed there is a pronounced tendency to avoid such overlap, as can be seen from Fig. 3, which shows the normal projection of two parallel molecules separated by translation *b*. The corresponding perpendicular distance in coronene is 3·40 Å. The shorter lateral contacts are illustrated in Fig. 4.

TABLE 3. *Measured and calculated structure factors.*

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	*h k l*	$\lvert F_o\rvert$	F_c
0 0 1	85·0	+91·5	1	19·0	+19·2	0	28·8	−23·8	$\bar{4}$	21·9	+23·3	$\bar{6}$	24·0	+22·5	1	28·7	−27·4
2	60·6	−61·1	2	15·0	−14·9	1	69·0	−60·4				$\bar{4}$	8·2	+7·9	2	34·8	−38·8
3	3·7	−4·4	3	6·2	−10·5	2	5·6	−4·5	0 1 1	5·1	+3·2	$\bar{3}$	20·2	+26·7	3	11·6	+8·0
4	18·3	+20·2	4	6·2	+8·7	5	5·6	−12·9	2	8·1	−8·5	$\bar{1}$	170·9	−171·0	7	33·4	+30·8
5	61·5	−60·1	5	6·0	−4·1	6	45·7	+47·9	3	8·0	−9·5	0	75·3	−77·7	8 1 $\bar{10}$	41·3	+42·2
6	58·7	−60·3	8	8·9	+9·4	7	32·5	+35·0	5	5·9	−4·0	1	25·4	+30·4	$\bar{9}$	10·9	+9·2
7	10·5	+10·9	6 0 $\bar{10}$	7·6	+8·1	8	5·3	−5·0	8	8·1	+14·4	5	31·6	+35·0	$\bar{5}$	21·3	−16·5
11	11·9	−11·3	$\bar{7}$	7·0	−6·1	12 0 $\bar{11}$	45·7	+55·3	1 1 $\bar{5}$	18·6	+19·2	7	9·7	+2·8	$\bar{4}$	48·9	−51·0
2 0 $\bar{12}$	15·3	−23·8	$\bar{4}$	16·7	−18·4	$\bar{10}$	24·4	+26·4	$\bar{4}$	8·1	−15·9	8	17·7	+13·7	$\bar{3}$	8·5	+11·7
$\bar{11}$	12·3	−19·7	$\bar{3}$	5·1	−2·4	$\bar{9}$	7·8	−10·0	$\bar{2}$	22·2	+21·3	5 1 $\bar{7}$	25·6	−23·0	$\bar{2}$	9·8	+13·9
$\bar{8}$	10·8	+10·4	$\bar{2}$	12·5	+9·7	$\bar{7}$	9·4	+8·0	$\bar{1}$	33·8	−41·2	$\bar{6}$	29·4	−34·6	$\bar{1}$	14·0	+16·5
$\bar{7}$	11·5	−14·6	$\bar{1}$	49·0	+46·5	$\bar{6}$	28·8	−19·9	0	Not	+7·9	$\bar{3}$	9·6	−8·3	1	29·7	−29·2
$\bar{6}$	77·3	−75·7	2	5·1	+3·8	$\bar{5}$	62·7	−54·4		observed		$\bar{1}$	101·0	+91·3	9 1 $\bar{10}$	32·9	+35·6
$\bar{5}$	6·1	−3·7	3	6·9	+10·1	$\bar{4}$	2·7	−0·6	1	36·0	−33·7	0	12·2	+7·0	$\bar{6}$	8·3	+6·9
$\bar{3}$	26·1	+26·3	4	14·2	−20·6	$\bar{3}$	3·9	+5·3	2	25·2	+27·5	1	8·3	−6·8	$\bar{5}$	28·7	−31·7
$\bar{2}$	33·0	−34·4	5	6·7	+10·3	$\bar{1}$	7·5	+8·8	3	14·5	−15·2	2	25·0	−24·9	$\bar{4}$	10·8	−9·7
$\bar{1}$	70·5	+76·5	6	8·4	−10·4	0	36·4	−28·1	4	10·7	+13·1	5	8·6	−2·0	1	14·3	−13·0
0	86·0	+93·3	7	6·3	−5·0	1	20·9	−18·2	5	18·0	−20·2	7	22·5	+24·1	10 1 $\bar{10}$	12·8	+11·4
1	42·5	−40·0	8	9·2	−10·0	6	11·0	+9·3	6	7·9	−8·8	8	23·5	+18·1	$\bar{2}$	21·3	−21·5
2	57·7	+50·3	8 0 $\bar{9}$	8·4	−11·7	7	5·1	−4·6	2 1 $\bar{3}$	27·6	−25·9	6 1 $\bar{7}$	29·6	+29·6	13 1 0	16·0	−13·1
3	18·3	−19·1	$\bar{8}$	6·8	+7·4	14 0 $\bar{12}$	9·9	+9·5	0	26·0	−40·0	$\bar{4}$	35·0	−34·8	14 1 0	19·6	+16·7
4	17·9	+16·4	$\bar{7}$	8·2	−13·9	$\bar{11}$	23·5	+25·7	1	12·8	+14·1	$\bar{1}$	30·2	−33·1	15 1 $\bar{12}$	8·4	+8·6
6	11·0	+11·9	$\bar{5}$	14·3	+17·6	$\bar{3}$	10·2	−8·8	2	11·9	−8·3	0	21·8	+23·0	$\bar{11}$	14·5	+14·3
7	3·9	−1·8	$\bar{4}$	13·6	+13·9	$\bar{2}$	3·1	−4·9	3	6·9	+3·1	1	45·8	−43·5	$\bar{6}$	21·0	−17·9
8	5·9	−4·4	$\bar{2}$	16·6	−15·6	$\bar{1}$	3·1	+5·7	5	25·4	+22·4	2	35·0	−31·2	0	16·9	−15·3
4 0 $\bar{12}$	8·1	−8·0	$\bar{1}$	16·8	−20·8	0	3·2	+4·3	6	16·4	+19·2	5	7·8	−9·9	16 1 $\bar{12}$	14·5	−14·7
$\bar{9}$	13·0	−14·5	0	7·5	+6·4	1	10·3	+8·1	7	12·8	−12·0	7	41·4	+38·3	$\bar{11}$	12·2	−14·0
$\bar{7}$	9·0	+5·1	2	7·7	+6·9	16 0 $\bar{11}$	7·6	−6·7	3 1 $\bar{6}$	24·0	−30·1	8	15·1	+15·9	$\bar{6}$	15·8	+17·9
$\bar{6}$	12·3	+11·7	7	26·2	+29·5	$\bar{3}$	6·5	+9·7	$\bar{2}$	17·8	−19·0	7 1 $\bar{10}$	17·8	+14·1	17 1 $\bar{12}$	13·6	+13·5
$\bar{5}$	12·3	+7·8	12	5·9	−5·8	18 0 $\bar{3}$	7·9	−5·5	$\bar{1}$	110·8	+135·3	$\bar{8}$	6·3	−5·0	18 1 $\bar{12}$	9·0	−8·3
$\bar{4}$	27·2	−26·3	10 0 $\bar{5}$	39·3	−38·8	20 0 $\bar{4}$	10·0	+8·6	0	101·4	+102·2	$\bar{7}$	7·2	−7·1	$\bar{4}$	25·6	+20·6
$\bar{3}$	53·6	+54·4	$\bar{4}$	17·0	−12·6	1	6·9	−3·3	1	15·5	−18·0	$\bar{6}$	7·8	+8·5	$\bar{3}$	18·0	+17·2
$\bar{2}$	39·5	−46·1	$\bar{3}$	7·6	+6·6	2	9·9	−6·3	3	16·8	+19·9	$\bar{5}$	20·3	−21·1	19 1 $\bar{4}$	20·4	+19·3
$\bar{1}$	34·0	−35·6	$\bar{2}$	3·4	−5·6	22 0 $\bar{10}$	10·5	−8·9	5	39·4	−39·3	$\bar{4}$	37·1	−30·5			
0	48·1	−54·4	$\bar{1}$	13·1	+10·6	$\bar{5}$	17·5	+16·2	4 1 $\bar{7}$	22·8	+23·6	$\bar{1}$	9·0	−7·2			

Discussion.—The carbon skeleton of hexabenzocoronene is probably planar within the limits of experimental error, the maximum deviation of the atoms from the mean plane being 0·065 Å, and the root-mean-square deviation 0·024 Å. The indications for the "overcrowded" positions (1 and 5, 3 and 11, 13 and 21) are very similar to those for 1,2:7,8-dibenzocoronene.[1]

The mean bond distances show little variation over the molecule. The bonds radiating from the central ring are the longest in the molecule, but none of the differences is really significant. Better crystals would be required to define the bond distances with greater precision.

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