The Crystal and Molecular Structure of 2-Methylhexahelicene*

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The crystal structure of 2-methylhexahelicene, $C_{27}H_{18}$, which is isomorphous with that of 2-bromohexahelicene, has been refined with diffractometer data. Crystals grown from the racemic mixture are optically pure and have orthorhombic symmetry. The space group is $P2_12_12_1$, with $a = 17.561$, $b = 13.285$, and $c = 7.733$ Å; $Z = 4$. Refinement was carried out by full-matrix least-squares and converged to an R value (on F_o) of 0.045. The hexahelicene nucleus has an approximate twofold axis normal to the helix axis. A number of unusually short C–C bonds are found around the periphery of the helix, while those in the helix core are lengthened, a pattern found in other fused aromatic molecules. The overall average bond length is 1.41 ± 0.02 Å. The medial rings are significantly distorted into a boat conformation, and the interplanar angle between the terminal rings is $54.8°$. Short intramolecular non-bonded contacts are found in the helix core, about 3 Å for carbon–carbon interactions and 2.5 Å for carbon–hydrogen interactions. The molecule shows rigid-body libration about the helix axis.

Introduction

Ever since the first synthesis of hexahelicene by New-man & Lednicer (1956), systems of six or more fused benzene rings have been of chemical interest because overcrowding in such molecules leads to inherent chirality and close intramolecular non-bonded contacts. Crystallographic evidence from the structure of 2-bromohexahelicene (Lightner, Hefelfinger, Powers, Frank & Trueblood 1972) demonstrated that the (−) enantiomorph of hexahelicene has the absolute molecular configuration of a left-handed helix. The structure of 2-bromohexahelicene indicates, moreover, that the molecular strain in such a helical molecule leads to intramolecular non-bonded carbon–carbon contacts of about 3 Å.

The predominance of the bromine atom as a scatterer of X-rays in 2-bromohexahelicene limits the precision with which the carbon atom positions can be measured. In crystals of 2-methylhexahelicene, whose structure turns out to be isomorphous with that of 2-bromohexahelicene (Frank, Hefelfinger, Trueblood & Lightner 1972), there are, on the contrary, no heavy atoms and the attainable precision in the determination of the molecular geometry of the hexahelicene moiety is consequently greater. In the crystal structure described below, the carbon positions have been found with significantly greater precision than that reported for 2-bromohexahelicene. The improved precision in

the anisotropic thermal parameters, moreover, has permitted an analysis of rigid-body thermal motion.

Experimental

Preparation of 2-*methylhexahelicene*

A sample of 2-bromohexahelicene, whose synthesis has been described by Lightner *et al.* (1972), was dissolved in anhydrous ethyl ether and treated with a 2 mole excess of n-butyllithium for thirty min, followed by treatment with dimethyl sulfate. The reaction mixture was washed with water and the contents of the ether layer were purified by preparative thin-layer chromatography. A mass spectrum of the product gave a molecular ion at $m/e = 342$, corresponding to the molecular weight of 2-methylhexahelicene. Several recrystallizations of the material from benzene–pentane mixtures gave yellow needles.

Collection of X-ray data

Data were collected from a needle-shaped crystal with approximate dimensions $0.5 \times 0.2 \times 0.1$ mm. The crystal was mounted about the needle axis (coincident with the crystallographic c axis). X-ray intensities were measured on a Picker FACS-1 automated four-circle diffractometer, with graphite crystal-monochromated Cu $K\alpha$ radiation. Collimators 1 mm in diameter were used on both incident and diffracted beams. The unit-cell parameters were refined by least-squares calculations from 2θ measurements at room temperature corresponding to the Cu $K\alpha_1$ (1.54051 Å) and Cu $K\alpha_2$ (1.54433 Å) peaks for eighteen independent high-angle reflections. Systematic absences for $h00$, h odd, $0k0$, k odd, and $00l$, l odd indicated $P2_12_12_1$ as the crystal space group. Crystal density was measured by flotation. The crystal data are presented in Table 1.

All reciprocal lattice points in the positive hkl octant were examined out to a maximum $(\sin \theta)/\lambda$ value of

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Table 1. Crystal data

Space group: $P2_12_12_1$; $Z=4$
$a=17\cdot561$ (2), $b=13\cdot285$ (2), $c=7\cdot733$ (1) Å
$V=1804$ Å^3; $d_{calc}=1\cdot26$ g cm^{-3}; $d_{exp}=1\cdot24$ g cm^{-3}

$0\cdot575$ Å^{-1} ($2\theta_{max}=125°$). Intensities of equivalent reflections in all octants of reciprocal space were sampled and found to be consistent to within 1%. Integrated intensities were measured with the θ–2θ scan technique using a 2θ scan rate of 1° per min, over a scan of about 2·3°. Left and right backgrounds were counted for a time interval equalling approximately one-half the peak scan time.

The number of independent reciprocal lattice points thus examined was 1700. Data were reduced using the following Lorentz–polarization factor:

$$Lp^{-1} = (\sin 2\theta_{cryst}/(\cos^2 2\theta_{mono} + \cos^2 2\theta_{cryst})$$

(after Azaroff, 1955) which is the expression appropriate for a geometry in which the respective θ–2θ planes of the monochromating and diffracting crystals are at right angles to each other. The crystal has a value of $\mu=5\cdot4$ cm.$^{-1}$. For the specimen used in data collection $\exp\,(-\mu R_{min}+\mu R_{max})=1\cdot25$. No correction for anisotropic absorption of X-rays was applied.

A value of $\sigma(F)$ based on counting statistics and other errors in measurement, such as coincidence errors, was calculated for each $|F_{hkl}|$ according to the expression:

$$\sigma(F) = \frac{Lp^{-1}}{2F_o}\ (\text{Scan intensity} + \text{Background} + 0\cdot04I_o)^{1/2}$$

Reflections for which $|F_{hkl}|$ was less than $2\sigma(F)$ were not used in the structure refinement. The number of reflections greater than $2\sigma(F)$ was 1566.

Structure refinement

Carbon-atom positions from the crystal structure of 2-bromohexahelicene (Lightner et al., 1972) provided a starting set for full-matrix least-squares refinement of the structural parameters in 2-methylhexahelicene. Carbon scattering factors were taken from International Tables for X-ray Crystallography (1962). Refinement of the carbon atom positions and anisotropic thermal parameters, each reflection's contribution weighted by $[1/\sigma(F)]^2$, converged to an R value, defined as

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|},$$

of 0·06.

At this stage, the positions of the hydrogen atoms on the hexahelicene helix were calculated, assuming trigonal arrangements around the carbon atoms and C–H bond lengths of 1·0 Å. A difference electron-density map phased on the carbon atoms showed fifteen large peaks corresponding to these hydrogen positions.

When these hydrogens atom were included in the structure-factor calculation, and a second difference electron-density map was computed, peaks corresponding to the methyl group hydrogen atoms were clearly seen. The positions of the methyl hydrogen atoms as located in this difference map, and the positions calculated on the basis of molecular geometry for the fifteen remaining hydrogen atoms, were not refined, but the hydrogen atoms were included in subsequent structure-factor calculations and are listed in Table 2. Hydrogen scattering factors used were those for bound hydrogen atoms (Stewart, Davidson & Simpson, 1965).

Table 2. Refined position parameters for carbon atoms, and hydrogen positions derived from molecular geometry

Estimated standard deviations are in parentheses

	x	y	z
C(1)	0·2126 (2)	0·2859 (2)	0·4187 (4)
C(2)	0·1389 (2)	0·2454 (2)	0·4196 (5)
C(3)	0·0980 (2)	0·2444 (3)	0·5752 (5)
C(4)	0·1297 (2)	0·2860 (3)	0·7216 (5)
C(5)	0·2300 (2)	0·3810 (3)	0·8684 (4)
C(6)	0·2940 (2)	0·4344 (3)	0·8642 (4)
C(7)	0·4017 (2)	0·5025 (3)	0·7018 (5)
C(8)	0·4404 (2)	0·5119 (2)	0·5483 (6)
C(9)	0·4665 (2)	0·4586 (3)	0·2512 (6)
C(10)	0·4560 (2)	0·3960 (3)	0·1147 (5)
C(11)	0·4082 (2)	0·2354 (3)	−0·0023 (5)
C(12)	0·3766 (2)	0·1456 (3)	0·0248 (5)
C(13)	0·3351 (2)	0·0116 (3)	0·2236 (5)
C(14)	0·3245 (2)	−0·0228 (3)	0·3865 (6)
C(15)	0·3341 (2)	0·0420 (2)	0·5325 (5)
C(16)	0·3511 (2)	0·1423 (2)	0·5025 (4)
C(17)	0·3600 (2)	0·1807 (2)	0·3324 (4)
C(18)	0·3553 (2)	0·1134 (2)	0·1936 (4)
C(19)	0·3808 (2)	0·2856 (2)	0·3004 (4)
C(20)	0·4148 (2)	0·3065 (3)	0·1381 (4)
C(21)	0·3756 (2)	0·3640 (2)	0·4258 (4)
C(22)	0·4281 (2)	0·4459 (2)	0·4074 (5)
C(23)	0·3217 (2)	0·3708 (2)	0·5672 (4)
C(24)	0·3404 (2)	0·4348 (2)	0·7119 (5)
C(25)	0·2468 (2)	0·3249 (2)	0·5682 (4)
C(26)	0·2024 (2)	0·3287 (2)	0·7246 (4)
C(27)	0·1043 (2)	0·2045 (3)	0·2585 (6)
H(1)	0·238	0·284	0·300
H(3)	0·046	0·210	0·600
H(4)	0·098	0·276	0·850
H(5)	0·198	0·384	0·990
H(6)	0·316	0·486	0·970
H(7)	0·426	0·552	0·800
H(8)	0·490	0·560	0·540
H(9)	0·500	0·520	0·240
H(10)	0·500	0·410	0·010
H(11)	0·430	0·260	−0·120
H(12)	0·370	0·090	−0·070
H(13)	0·330	−0·030	0·090
H(14)	0·306	−0·096	0·430
H(15)	0·322	0·000	0·660
H(16)	0·354	0·190	0·620
H(27a)	0·146	0·212	0·150
H(27b)	0·087	0·135	0·276
H(27c)	0·058	0·248	0·224

Inspection of the differences $(|F_o| - |F_c|)$ revealed a number of large negative values associated with intense low-angle reflections; this was interpreted as evi-

dence of secondary extinction. All reflections were then corrected according to the formula:

$$|F_{corr}| = |F_o|[1 + \beta CI_o]^{1/2}$$

after Zachariasen (1967), where C was determined empirically to have the value 1.35×10^{-6}. The largest correction thus derived for any particular reflection was by a factor of 1.045. The final R value after addi-

Table 3. *Anisotropic thermal parameters for carbo atomsn*

Values are given in $\text{Å}^2 \times 10^3$ and correspond to the expression:
$$B = \exp\left[-2\pi^2 \left(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl\right)\right]$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	50 (1)	48 (1)	88 (2)	5 (1)	0 (2)	5 (2)
C(2)	58 (2)	54 (2)	99 (2)	2 (1)	−2 (2)	2 (2)
C(3)	68 (2)	67 (2)	104 (2)	−3 (2)	19 (2)	9 (2)
C(4)	85 (2)	74 (2)	97 (2)	8 (2)	30 (2)	12 (2)
C(5)	91 (2)	80 (2)	73 (2)	32 (2)	−2 (2)	−7 (2)
C(6)	97 (2)	68 (2)	82 (2)	33 (2)	−11 (2)	−15 (2)
C(7)	76 (2)	56 (2)	125 (3)	4 (2)	−32 (2)	0 (2)
C(8)	69 (2)	60 (2)	151 (3)	−4 (2)	−37 (2)	4 (2)
C(9)	50 (2)	87 (2)	135 (3)	−8 (2)	−8 (2)	35 (2)
C(10)	48 (2)	102 (2)	115 (3)	8 (2)	9 (2)	33 (2)
C(11)	71 (2)	121 (3)	71 (2)	32 (2)	6 (2)	6 (2)
C(12)	74 (2)	101 (2)	76 (2)	28 (2)	−9 (2)	−20 (2)
C(13)	71 (2)	75 (2)	102 (2)	6 (2)	−6 (2)	−17 (2)
C(14)	74 (2)	61 (2)	135 (3)	6 (2)	2 (2)	−9 (2)
C(15)	78 (2)	56 (2)	101 (2)	3 (2)	6 (2)	−6 (2)
C(16)	63 (2)	54 (1)	75 (2)	11 (2)	3 (2)	−1 (2)
C(17)	45 (1)	56 (1)	74 (2)	12 (1)	−3 (1)	−8 (2)
C(18)	56 (2)	80 (2)	74 (2)	18 (2)	−7 (2)	−6 (2)
C(19)	41 (1)	71 (2)	66 (2)	10 (1)	−1 (1)	14 (2)
C(20)	52 (2)	87 (2)	83 (2)	17 (2)	−2 (2)	15 (2)
C(21)	53 (1)	54 (2)	78 (2)	8 (1)	−8 (2)	9 (2)
C(22)	52 (2)	61 (2)	113 (2)	0 (2)	−12 (2)	13 (2)
C(23)	63 (2)	43 (1)	76 (2)	8 (1)	−13 (2)	4 (2)
C(24)	78 (2)	55 (2)	88 (2)	18 (2)	−25 (2)	−4 (2)
C(25)	56 (1)	46 (1)	74 (2)	15 (1)	−1 (2)	2 (2)
C(26)	70 (2)	58 (2)	81 (2)	18 (2)	6 (2)	8 (2)
C(27)	74 (2)	101 (3)	113 (3)	−11 (2)	−13 (2)	−12 (2)

tional cycles of refinement was 0.045, based on the 1566 reflections used in refinement, and 0.050 for the entire set of 1700 measured reflections. The refined values for the atomic coordinates, and anisotropic thermal parameters are given in Tables 2 and 3 respectively. The quoted estimated standard deviations are derived from the inverse of the least-squares matrix. Values of F_o and F_c are listed in Table 4.

Description of the structure

Bond distances and angles

The bond distances and angles involving only carbon atoms are shown in Fig. 1; they have estimated standard deviations of 0.006 Å and 0.3° respectively. There is a pattern of shortened bonds along the periphery of the helix and a lengthening of bonds around the inner 'core' of the molecule. The average bond length for the six inner core C–C bonds is 1.44 ± 0.02 Å, and that for the six outermost bonds parallel to the inner core bonds is 1.36 ± 0.02 Å. The overall C–C bond length average is 1.41 ± 0.02 Å. This is similar to the pattern found in analogous systems of three or four fused benzene rings, for example in phenanthrene (Trotter, 1963), benzophenanthrene and dimethylbenzophenanthrene (Hirschfeld, Sandler & Schmidt, 1963).

Unsubstituted hexahelicene should have a twofold axis normal to the helix axis and passing through the bond between carbon atoms 21 and 22. This feature is found approximately in 2-methylhexahelicene as well, and may be seen in the molecule viewed along the C(21)–C(22) bond in Fig. 2. If bonds in corresponding positions on the left and right branches of the molecule are compared, the r.m.s. average difference between such pairs of bonds is 0.021 Å, with a maximum discre-
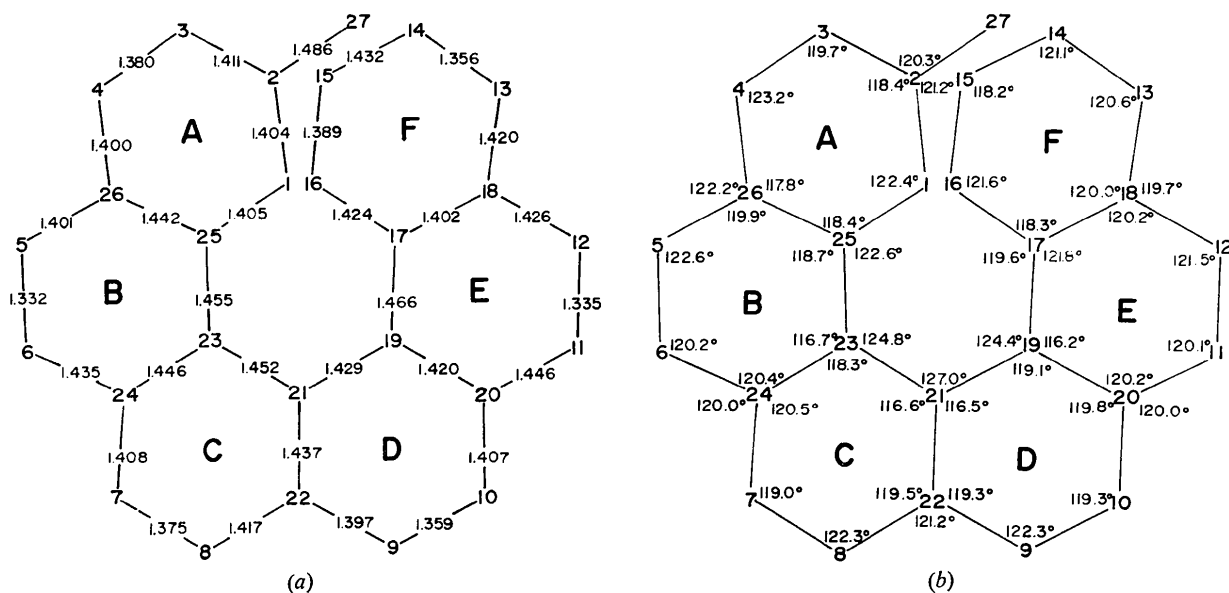

Fig. 1. (a) Bond lengths. (b) Bond angles.

pancy of 0·040 Å, seen between the C(25)–C(26) and C(17)–C(18) bonds. The r.m.s. average difference between corresponding angles is 1·4°.

An attempt was made to find an explanation for the differences between the lengths of some pairs of corresponding bonds. It can be seen that the bond pairs showing the best agreement are C(10)–C(20) and C(7)–C(24), C(5)–C(6) and C(11)–C(12), C(17)–C(19)

Table 4. *Values of F_o and F_c*

Reflections marked by asterisk not included in least-squares refinement.

and C(23)–C(25). These pairs are very nearly parallel to each other in the molecule and any systematic errors which might be a function of bond orientation probably cancel when comparing the bonds. Bonds showing large discrepancies, such as C(26)–C(25) and C(18)–C(17), C(19)–C(20) and C(23)–C(24), C(5)–C(26) and C(12)–C(18), on the other hand, have quite different orientations. The three latter bond pairs also have large components along the crystallographic c axis, and the estimated standard deviations in the z coordinates of the atoms were slightly higher than those for the x and y coordinates. However, no systematic pattern could be discerned in these differences, nor is there any obvious correlation between these differences and those seen in pairs of bonds of 2-bromohexahelicene (Lightner et al., 1972). Since the crystal is elongated along the c axis, there is a maximum absorption of X-rays for optical paths in this direction. However, it would seem that any effect on the bond

lengths would be in the same direction for each bond of the three pairs in question

Deviations from planarity

It is to be expected that as substituent chemical groups on fused aromatic systems become bulkier, or when the shape of the molecule brings such substituents into close proximity, steric interference will cause deviations from the planarity that would obtain in the absence of such strains. In phenanthrene (Trotter, 1963), interaction between the two hydrogen atoms that point into the medial portion of the molecule and thus toward each other is not so great as to force a bending of the molecule out of planarity, at least not significantly in terms of the precision quoted for the atomic positions. However, in the four-ring systems, benzophenanthrene and dimethylbenzophenanthrene (Hirschfeld et al., 1963), the interference of two hydrogen atoms directed toward each other in the

Table 5. *Least-squares molecular planes (after Schomaker et al.,* 1959)

| Symbol | Atom nos.* | Deviations (Å) | | Equation of plane coefficients§ | | | |
		r.m.s.†	Max.‡	A	B	C	D
A	1, 2, 3, 4, 25, 26	0·017	0·027 (25)	0·3758	−0·8956	0·2379	0·760
B	5, 6, 23, 24, 25, 26	0·048	0·079 (23)	0·4697	−0·8071	0·3577	0·656
C	7, 8, 21, 22, 23, 24	0·078	0·126 (21)	0·6413	−0·6539	0·4014	0·269
D	9, 10, 19, 20, 21, 22	0·076	0·118 (21)	0·7970	−0·4825	0·3633	−0·297
E	11, 12, 17, 18, 19, 20	0·064	0·106 (19)	0·9200	−0·3191	0·2276	−0·778
F	13, 14, 15, 16, 17, 18	0·020	0·029 (18)	0·9739	−0·2202	0·0549	−0·907
A'	1, 3, 4, 25	0·013	−0·012 (2)	0·3731	−0·8984	0·2318	0·750
			−0·042 (26)				
B'	6, 24, 25, 26	0·004	+0·044 (5)	0·4843	−0·8073	0·3374	0·744
			+0·147 (23)				
C'	8, 22, 23, 24	0·025	+0·071 (7)	0·6348	−0·6770	0·3725	0·399
			+0·230 (21)				
D'	9, 19, 20, 22	0·032	−0·216 (21)	0·8134	−0·4772	0·3332	−0·419
			−0·072 (10)				
E'	11, 17, 18, 20	0·004	−0·195 (19)	0·9178	−0·3405	0·2043	−0·890
			−0·064 (12)				
F'	13, 14, 16, 17	0·010	+0·020 (15)	0·9749	−0·2176	0·0480	−0·893
			+0·052 (18)				
I	7, 8, 9, 10, 21, 22	0·009	0·016 (8)	0·7389	−0·5847	0·3350	−0·019
II	7, 21, 23, 24	0·040	0·051 (24)	0·5460	−0·6993	0·4614	0·310
II'	10, 19, 20, 21	0·042	0·054 (20)	0·8347	−0·3781	0·4004	−0·342
III	1, 2, 3, 4, 5, 23, 25, 26	0·048	0·086 (5)	0·3833	−0·8827	0·2719	0·758
III'	12, 13, 14, 15, 16, 17, 18, 19	0·056	0·101 (12)	0·9702	−0·2217	0·0977	−0·895

* Includes only those atoms used to determine best plane.
† Based only on plane determining atoms.
‡ Atom no. given in parentheses.
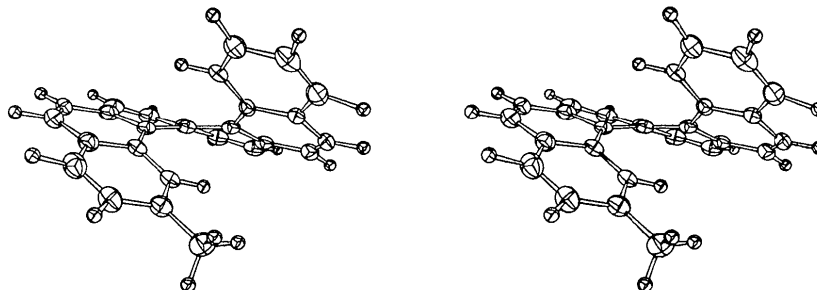§ Equation has the form: $AX + BY + CZ = D$.

Fig. 2. Stereo *ORTEP* view along molecular twofold axis.

former molecule is sufficient to result in deviations of up to 0·4 Å from the mean molecular plane, while such interactions between two methyl groups in the latter molecule result in deviations of up to 1·5 Å. In the crystal structure of 3:4-5:6-dibenzophenanthrene (McIntosh, Robertson & Vant, 1954), with five fused benzene rings, the molecule is inherently chiral, with atoms in the terminal rings deviating several Å from the mean plane through the medial rings.

In the six ring hexahelicene molecule one can no longer refer to a mean molecular plane. Indeed, the bending back of the branches of the molecule results in an angle of 54·8° between normals to the best planes of the two terminal rings, A and F. Moreover, the medial rings B, C, D and E, taken individually, show severe distortions from planarity, as can be seen from the r.m.s. average deviations for these rings listed in Table 5. The significance of the amount of distortion in rings A and F is difficult to assess. However, in each of the six rings the distortion from planarity may be best characterized as being a boat conformation The planes designated as A', B', C', D', E', and F' in Table 5 have each been fixed by four carbon atoms which form two parallel bonds in a ring. In all six rings the fifth and sixth *para* carbon atoms are bent toward the same side of the 4-carbon plane.

Although the combination of folding and twist in the molecule defies simple description, it should be noted that the regions of greatest distortion from planarity are not along the bonds which form the border between adjacent rings. Rather, the helix may be described in terms of five relatively planar regions, designated in Table 5 and in Fig. 3 as I, II, II', III, and III', with each region of the helix bending progressively away from plane I. The angles between normals to the various planes of interest are given in Table 6.

Table 6. *Interplanar angles*

Planes	II	II'	III	III'	F
I	14·8°	−13·6°	27·1°	−28·4°	–
II		−25·2	17·2	−43·1	–
II'			40·1	−21·1	–
III				53·5	–
A					54·8

Torsional angles

Atom sequence	Angle	Atom sequence	Angle
H(1)–C(1)–C(25)–C(23)	2°	C(23)–C(21)–C(19)–C(17)	30°
H(1)–C(25)–C(23)–C(21)	13	C(21)–C(19)–C(17)–C(16)	16
C(25)–C(23)–C(21)–C(19)	26	C(19)–C(17)–C(16)–H(16)	6

The 'pitch' of the inner core of the helix may also be described in terms of the torsional angles about the long carbon–carbon bonds bordering this core. These are listed in Table 6, and it can be seen that the principal twisting occurs about the C(21)–C(23) and C(21)–C(19) bonds. Because of this twist, C(19), C(21), and C(23) show much greater distortion in the expected

trigonal arrangement of bonds radiating from these atoms, as compared with other carbons in the molecule.

Non-bonded intramolecular contacts

The above-described distortion of 2-methylhexahelicene from planarity arises, obviously, from the overlapping of rings A and F. This induces a strain in the molecule, such that certain atoms of rings A and F are brought closer together than normally found for atoms of neighboring molecules in crystal structures where packing is determined mainly by van der Waals-type forces. Indeed, if one takes the van der Waals radii for carbon and hydrogen to be about 1·8 and 1·2 Å respectively, then in the structure of 2-methylhexahelicene itself, no intermolecular contacts are to be found shorter than the sums of the van der Waals radii for the atoms in question.

On the other hand the distance between C(1) and C(16) in the same molecule is 3·16 Å, and Fig. 5(a) shows other carbon–carbon contacts of about 3 Å.
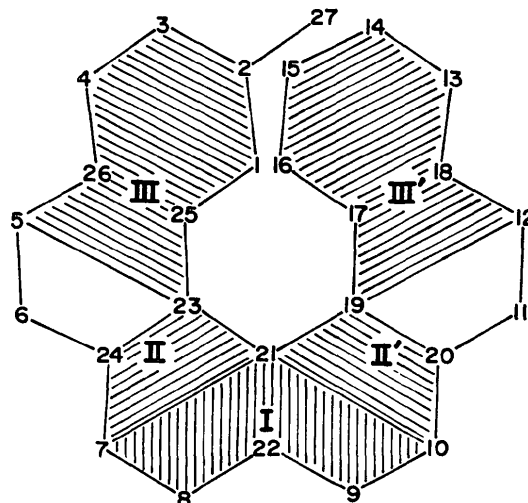

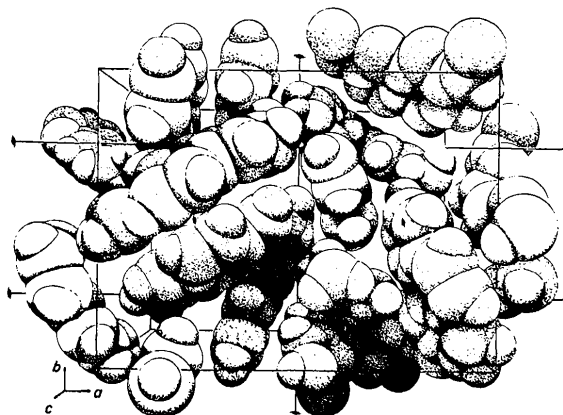Fig. 3. Molecular planes.

Fig. 4. Packing diagram. Four full molecules shown with portions of adjacent molecules in neighboring cells.

Distances between carbons atoms of the inner core of the helix and the positions of H(1) and H(16), which were calculated from the molecular geometry, assuming a C–H bond of 1·1 Å, are shown in Fig. 5(b). These are also seen to be several tenths of an Å less than the sum of the van der Waals radii. C(2) and C(15), however, are not closer to any other atoms of the same molecule than the sum of the appropriate van der Waals radii. It may be inferred from this that groups no more bulky than a bromine atom or a methyl group when substituted onto C(2) and C(15) do not significantly alter the geometry of the helix by steric interaction. This concurs with spectroscopic studies on helicene derivatives by Laarhoven & Veldhuis (1972).

The packing diagram in Fig. 4 illustrates the staggered herring-bone type packing of 2-methylhexahelicene molecules. In spite of the bulkiness of the helices, the packing is efficient. A 'molecular volume', understood to be that volume enclosed by the van der Waals spheres around the atoms, was estimated with the aid of scaled space-filling models to be about 340 Å³. When this volume was divided by the volume of the asymmetric unit (¼ of the unit-cell volume), the molecular packing coefficient, *i.e.* the volume density, was determined to be 0·76. Such a value corresponds to relatively dense packing for an organic molecular crystal and is similar to values found in other fused ring molecules (Kitaigorodsky, 1955).

Molecular thermal motion

Inspection of the *ORTEP* drawings of the molecule in Fig. 6 suggests that the molecule is librating about a point close to its centroid. Rigid-body thermal motion analysis was carried out according to the 21-element tensor model of Schomaker & Trueblood (1968). A comparison of the observed U_{ij} values listed in Table 3 with those calculated on the basis of the rigid-body tensors, whose principal axes are given in Table 7, gives a r.m.s. average difference of 0·0049 Å². This is based on the 26 carbon atoms of the helix, excluding the methyl carbon. When the methyl carbon is included, the differences between its observed U_{ij} values and

those calculated on the basis of the rigid-body model are large, indicating that this atom 'wags' considerably with respect to the rest of the molecule. The 0·0049 Å² value is less than twice as large as the r.m.s. average standard deviation for these parameters, which was derived from least-squares refinement and has the value 0·0027 Å². While this indicates some 'floppiness' in the molecular thermal motion, it is felt that the **T, L**, and **S** tensors as calculated give a fair representation of the correlated rigid-body motion of the entire molecule.

Table 7. *Molecular rigid-body tensors*

	Eigenvalues	Direction cosines referred to crystal axes		
Translational	0·072 Å	−0·3513	−0·0150	0·9451
Tensor, **T***	0·056	0·5649	0·7990	0·1749
	0·044	−0·7487	0·6056	−0·2611
Librational	16·2 deg²	−0·7941	0·6071	−0·0293
tensor, **L**	4·9	−0·0884	−0·0506	0·9948
	3·7	0·6042	0·7954	0·0467
Correlation	0·0024 rad Å	0·5994	0·7440	0·2592
tensor, **S***	0·0011	−0·0893	−0·3120	0·9544
	−0·0036	−0·7881	0·6045	−0·1287
Moment of	137	0·4252	−0·4999	−0·7546
inertia	117	0·7178	−0·6941	−0·0554
tensor†	30	0·5514	−0·5180	0·6539

	x	*y*	*z*
Mass centroid	0·3158	0·2837	0·4362
Center of libration	0·2981	0·2893	0·4031

* Reduced after symmetrization of S tensor.
† Eigenvalues on arbitrary scale.

The **T** tensor describing the translational oscillations of the molecule shows only a small degree of anisotropy. The libration tensor **L**, on the other hand, has one eigenvalue much larger than the other two (the tensor is thus representable as a prolate ellipsoid). This librational axis is nearly parallel to what might be called the helix axis [approximately along the vector joining C(1) to C(16)]. In Fig. 6, the molecule has been drawn as it would appear viewed along this li-
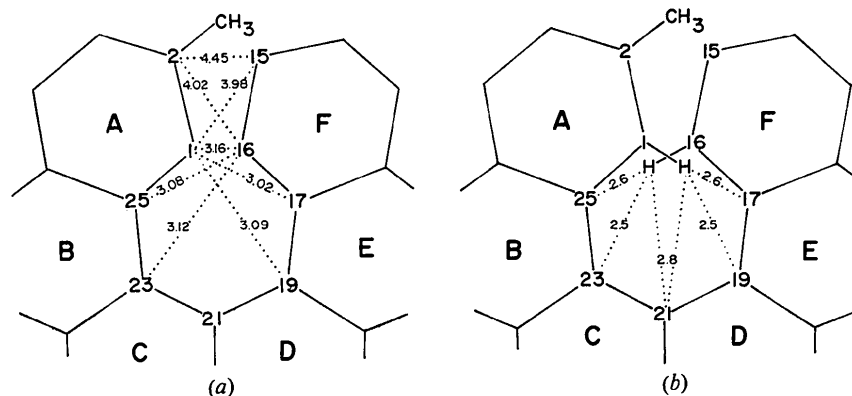

Fig. 5. (a) Intramolecular C–C contacts. (b) Intramolecular C–H contacts.
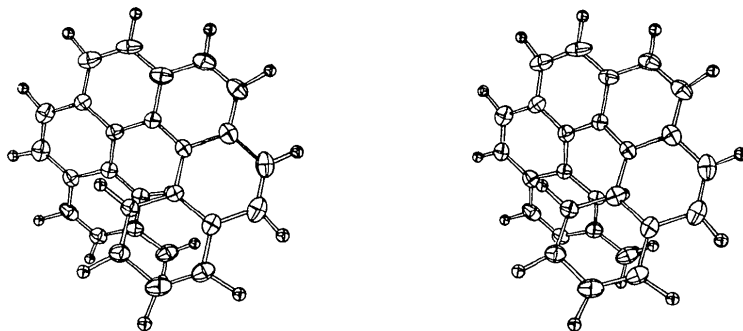
Fig. 6. Stereo *ORTEP* view along helix axis.

bration axis. The apparent foreshortening of bond lengths due to this libration was computed after Cruickshank (1961). The largest such correction to a carbon–carbon bond length is 0·004 Å, and the distances given in Fig. 1(*a*) are the corrected values.

Symmetrizing the correlation tensor S determines a unique point in space, which has been referred to as the center of libration (Willis & Pawley, 1970). The coordinates of this point, as well as those of the mass centroid of the molecule are listed in Table 7. The two points are only 0·28 Å apart. Table 7 also gives the eigenvalues and eigenvectors for the tensor of moment of inertia of the molecule. These do not seem to bear any special relationship to the principal axes of the T and L tensors. However, an inspection of the direction cosines for the L, T, and symmetrized S tensors indicates that their respective principal axes are more or less parallel, and each has one principal axis nearly parallel to the short crystallographic *c* axis.

Full-matrix least-squares refinement was carried out with the computer program of P. K. Gantzel, R. A. Sparks and K. N. Trueblood (*UCLA-LS* 1) and stereoscopic drawings were made using the *ORTEP* program written by C. K. Johnson (ORNL Report 3794, revised). The authors wish to express gratitude for the criticisms and suggestions of Professor K. N. Trueblood, and to thank Thomas W. Powers, who synthesized the sample of 2-bromohexahelicene. John D.

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