Tetrahedron Vol. 33, pp 3177 to 3180. Pergamon Press 1977. Printed in Great Britain

THE STRUCTURE OF HEXACYCLOPROPYLBENZENE

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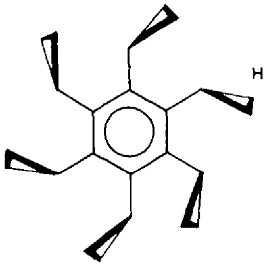
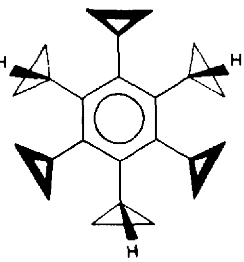
(*Received in the UK* 19 *April* 1977; *Accepted for publication* 26 *April* 1977)

Abstract—The title compound crystallizes in the orthorhombic system, space group *Pbnm*, $a = 9.933$ (2), $b = 11.068$ (2), $c = 17.134$ (3) Å, $z = 4$. The structure was solved by direct methods and refined via block-diagonal least squares to $R = 0.061$. The arrangement of the cyclopropyl rings with respect to the benzene ring approximates point symmetry D_{3d}. The crystallographic site symmetry is *m* with the mirror plane perpendicular to the benzene ring and passing through two of its vertices.

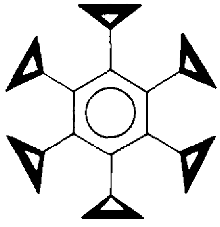
Usieli *et al.*[1] recently reported a facile preparation of hexacyclopropylbenzene (HCPB). Three possible conformations **1a–1c** were proposed for the molecule.



1a



1b



1c

Conformation **1a** was considered not favorable in solution on the basis of spectral data, even though such an arrangement is a favorable one on electronic grounds.[2] On the basis of the low solubility and high m.p. (266–270°) Usieli *et al.* suggested a highly ordered structure in the crystalline state. We undertook the determination of the crystal structure to establish the molecular structure in the solid.

EXPERIMENTAL

Crystals suitable for X-ray study were provided by Dr. Usieli. They were orthorhombic and the lattice constants $a = 9.933(2)$, $b = 11.068(2)$, $c = 17.134(3)$ Å were obtained from a least squares fit of $14\,2\theta$ values ranging between 24° and 53° (Cu-$K\bar{\alpha}$) as determined on a diffractometer. The systematic absences, $h0l$ with $h + l$ odd and $0kl$ with k odd, indicated the space groups *Pbnm* or $Pbn2_1$; the former was confirmed during the course of the study. The density of the crystal, as measured by flotation, is $D_m = 1.12\,\text{cm}^{-3}$. That calculated for 4 molecules in the unit cell is $D_c = 1.12\,\text{cm}^{-3}$, which requires molecular site symmetry *m* or $\bar{1}$ in space group, *Pbnm*. Both possibilities exist for HCPB but the second appeared unlikely from packing considerations.

Intensity data were collected on a Syntex diffractometer, using graphite monochromatized copper radiation. 1808 reflections were measured, and after Lorentz and polarization corrections, 209 of these having $F_0 < 2.5\sigma(F_0)$ were considered unobserved. No corrections were made for absorption or extinction. The structure was solved by direct methods by applying the SHELX[3] programs in an automatic phase determination process. 9 of 14 heavy atoms appeared in the *E* map based on the best set of signs in an orientation which requires molecular site symmetry *m*. The remaining five atoms in the asymmetric unit were subsequently located by Fourier methods. The structure was refined by block-diagonal least squares, first isotropic, then anisotropic, resulting in an *R* of 0.125. Hydrogen atoms were located from a difference map and included in the refinement which was continued by block-diagonal least squares to the final *R* 0.06 (0.67 including unobserveds).

Final atomic positional and thermal parameters along with their e.s.d.'s are given in Table 1. A stereo-view of the molecule, including numbering scheme, is given in Fig. 1.

Molecular geometry. Bond lengths and angles are given in Table 2, together with averages for chemically equivalent features. The exocyclic C–C bonds are similar to those found in 1,1-dichloro-2,2-diphenylcyclopropane and the corresponding dibromo derivative[4] (1.500(5) Å and 1.502(6) Å), respectively and in 6,6-diphenyl-3,3-diethyl-3-azabicyclo[3.1.0] hexane[5] (1.503 Å) and is longer than the interring bond in bicyclopropyl[6] (1.487(4) Å).

Within the cyclopropyl rings the average length (1.503(3) Å) of the bonds adjacent to the exocyclic bond is the same as that found in bicyclopropyl[6] (1.501(3) Å) and in the present case is equal to the exocyclic bond. The average for the bond opposite the exocyclic bond is somewhat lower (1.494(8) Å) but due to the high scatter the significance of the difference is doubtful.

Again, in terms of average values the internal angles in the cyclopropyl rings are equal (60.2(2)° and 59.6(4)°); thus, the rings may be considered to be equilateral triangles within the precision of this determination.

Bond lengths of the benzene ring are slightly, but barely significantly, longer than the accepted value of 1.395(3).[7] Other features are quite normal.

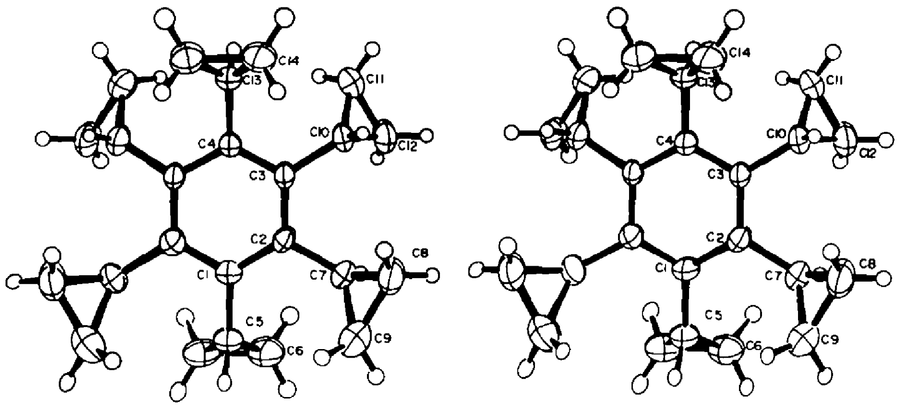


Fig. 1. ORTEP stereo plot of the molecule including numbering of the atoms. Hydrogens are numbered according to the carbon atom to which they are attached.

Table 1. Final positional and thermal parameters ($\times 10^4$) for non-hydrogen and ($\times 10^3$) for hydrogen atoms

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	10211(3)	1228(3)	2500	249(13)	306(19)	348(15)	0	0	−5(14)
C2	9508(2)	1276(2)	3212(1)	297(11)	314(13)	279(10)	8(9)	−39(8)	8(9)
C3	8096(2)	1332(2)	3211(1)	285(10)	315(12)	249(10)	−2(9)	5(8)	22(9)
C4	7398(3)	1430(3)	2500	250(14)	318(19)	275(13)	0	0	15(13)
C5	11723(3)	1102(4)	2500	253(15)	438(24)	447(19)	0	0	−15(16)
C6	12403(3)	88(3)	2935(2)	314(13)	599(21)	756(21)	121(17)	−27(14)	64(15)
C7	10267(3)	1295(3)	3971(1)	361(12)	463(17)	323(12)	21(11)	−98(10)	−1(12)
C8	9989(3)	2236(3)	4583(2)	576(17)	595(22)	367(14)	−85(14)	−106(13)	0(16)
C9	11274(3)	2276(3)	4136(2)	536(18)	661(22)	475(16)	−41(15)	−142(14)	−156(17)
C10	7304(2)	1241(3)	3958(1)	356(12)	478(17)	272(11)	27(10)	39(9)	42(12)
C11	6252(3)	272(3)	4041(2)	467(15)	713(23)	432(15)	157(15)	62(13)	−93(16)
C12	205(3)	7522(4)	4507(2)	541(16)	624(22)	359(13)	159(13)	40(13)	57(17)
C13	5910(3)	1656(4)	2500	274(17)	454(24)	331(16)	0	0	47(17)
C14	5319(3)	2702(3)	2939(2)	425(15)	651(23)	518(17)	−105(15)	0(13)	208(16)
	x	y	z	U_{iso}		x	y	z	U_{iso}
H5	1224(4)	196(4)	250	50(4)	H10	704(3)	208(2)	422(2)	44(8)
H6a	1184(4)	−56(3)	322(2)	86(12)	H11a	620(3)	−32(3)	360(2)	59(10)
H6b	1321(3)	17(3)	323(2)	74(11)	H11b	545(3)	41(3)	434(2)	66(10)
H7	1055(3)	44(3)	420(2)	48(8)	H12a	815(3)	−39(3)	441(2)	69(12)
H8a	925(3)	289(3)	449(2)	62(10)	H12b	747(3)	37(3)	508(2)	59(9)
H8b	1006(3)	202(3)	509(2)	50(2)	H13	539(5)	87(4)	250	62(14)
H9a	1138(3)	2192(3)	375(2)	56(10)	H14a	591(3)	328(3)	319(2)	60(10)
H9b	1212(3)	207(3)	440(2)	66(10)	H14b	449(4)	266(3)	323(2)	95(13)

Esd's in parenthesis are in units of least significant digit. Hydrogen atoms are numbered according to the carbon atoms to which they are bonded. Anisotropic temperature factors are in the form exp − $(2\pi^2(a_1^{*2}h^2U_{11}^2 + \cdots a_1^* a_2^* hkU_{12}^2 + \cdots)$.

Deviations of C atoms from the best plane of the benzene ring are given in Table 3. The ring itself is planar to within 0.036 Å. The deviations of the ring atoms from planarity do not exhibit any significant pattern. On the other hand the alternating pattern of out-of-plane deviations for the phenyl-bonded cyclopropyl carbons (C3, C7, C10, C13) is typical of other hexasubstituted benzenes with large substituents (e.g. hexaiodobenzene,[8] hexanitrobenzene[9] and hexaphenylbenzene[10]) but the magnitude (Ave. = 0.123 Å) is greater than for these three compounds (0.039 Å, 0.03 Å and 0.083 Å, respectively).

The normals to the planes of the 3-membered rings designated by C5, C7, C10 and C13 make angles of −55.1, 56.7, −60.7 and 59.2° with the plane of the benzene ring. Torsion angles about exocyclic bonds are given in Table 4. It is seen that the molecular conformation is essentially that represented by **1b**. However, in addition to the slight displacements of the 3-membered rings from the benzene plane, there is a suggestion of a "windmill" effect due to small rotations about the exocyclic bonds. Thus the elevation of C9 is greater than that of C8 with respect to the benzene plane (Table 3) and likewise for C12 and C11. The rotations may be described as clockwise about the exocyclic bond when the direction of view is along the bond towards the benzene ring. Much larger rotations are found in the hexaphenylbenzene,[10] hexanitrobenzene[9] and mellitic acid[11] structures.

DISCUSSION

This structure provides another fairly convincing validation of the molecular orbital description of cyclopropane based on the Walsh model[12] and recently discussed in terms of crystallographic studies by Lauher and Ibers.[4] Very briefly summarized, when the cyclo-

Table 2. Geometric features of the molecule[a]

A. *Cyclopropyl rings*

b——c a Ph	C6——C6 C5	C8——C9 C7	C11——C12 C10	C14——C14 C13	Average (scatter)[b]
a–Ph	1.508(4)	1.504(3)	1.506(3)	1.499(4)	1.504(5)
a–b	1.507(5)	1.503(4)	1.504(4)	1.500(5)	1.503(3)
a–c	[1.507(5)]	1.503(4)	1.499(4)	[1.500(5)]	
b–c	1.489(7)	1.489(5)	1.494(5)	1.505(6)	1.494(8)
b–a–Ph	121.0(3)	121.4(2)	119.4(2)	121.0(3)	120.7(8)
	[121.0(3)]	120.4(2)	120.6(2)	[121.0(3)]	
a-b–c	60.3(2)	60.3(2)	60.0(2)	59.9(2)	60.2(2)
a–c–b	[60.3(2)]	60.3(2)	60.3(2)	[59.9(2)]	
b–a–c	59.3(2)	59.4(2)	59.7(2)		59.6(4)

C–H (average): on "outer" carbons 0.98(4); on "inner" carbons 1.06(3)
H–C–H (average): on "outer" carbons 111.3(4.2); H–C–C on "inner" carbons 113.8(2.8)

B. *Phenyl ring*

								Average (scatter)[b]
C1–C2	1.407(3)	C2–C3	1.404(3)	C3–C4	1.405(3)			1.405(2)
C2–C1–C2	120.3(3)	C1–C2–C3	119.7(2)	C2–C3–C4	119.8	C3-C4–C3	120.1	120.0(3)
C5–C1–C2	119.8(1)	C7–C2–C1	120.1(2)	C7–C2–C3	120.1(2)			120.0(7)
C10–C3-C4	119.0(2)	C13–C14–C3	119.9(1)	C10–C3–C2	121.2(2)			

[a] Bond lengths in Å; bond angles in degrees; e.s.d.'s in parenthesis. Bracketed entries are symmetry equivalents.
[b] Scatter $= [\Sigma_i(\bar{r} - r_i)/(n-1)]^{1/2}$.

Table 3. Plane of benzene ring. Equation of Plane: $0.5943x + 1.4487y + 0.0z - 2.0430 = 0$. Deviations from plane (Å)

C1	0.002	C8	1.100
C2	0.008	C9	1.231
C3	−0.026	C10	−0.180
C4	0.036	C11	−1.321
C5	−0.035	C12	−1.309
C6	−1.109	C13	0.185
C7	0.080	C14	1.300

Table 4. Torsion angles about exocyclic bonds (°)

C4–C3–C10–C11	54.5	C1–C2–C7–C8	128.6
C4–C3-C10–C12	124.6	C1–C2–C7–C9	58.1
C2–C3-C10–C11	−123.2	C2–C1–C5–C6	54.2
C2–C3–C10–C12	−53.1		
C3-C2–C7–C8	−50.0	C3–C4–C13–C14	53.8
C3–C2–C7–C9	−120.6		

propane ring is bonded to a group which can participate in π interactions, the interaction between the ring and the substituent is favored for the "bisecting" orientation of the ring, as represented, say, by **1a**. In such cases the resulting bond lengths in the cyclopropyl ring are not equal,[4] the bond opposite the substituted atom being shorter than the other two. On the other hand, interactions via π overlap are absent in the "perpendicular" orientation as represented by the structure found in this study, essentially **1b**, and all the internal cyclopropyl bond lengths are expected to be equivalent as is found here.

An earlier attempt to prepare a charge-transfer complex between hexacyclopropylbenzene and tetracyanoethylene (TCNE) was unsuccessful.[1] If the conformation in solution is similar to that here then it is clear that the close plane-to-plane approach of *ca.* 3.3 Å required by π-complex formation (again based on solid-state studies)[13] is severely hindered. In solution hexaethylbenzene forms only a very weak ($K = 5.11$)[14] complex with TCNE compared to hexamethylbenzene ($K = 301.7$)[15] and the increased bulkiness of the cyclopropyl group over the Et groups would make complex formation even more difficult.

The crystal structure is shown in Fig. 2. There are no unusually short intermolecular distances and the packing

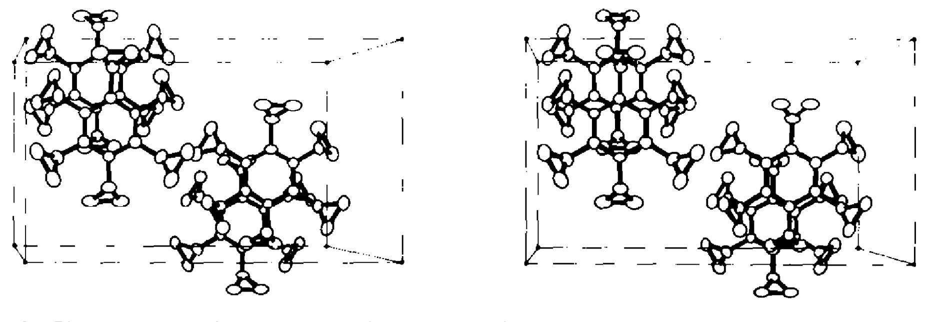


Fig. 2. ORTEP stereo plot of the structure as viewed down the *b* axis; the *c* axis is horizontal and the *a* axis vertical.

Table 5. Molecular point groups and crystallographic site symmetries of hexasubstituted benzenes

Substituent	Molecular symmetry[a]	Crystallographic Site symmetry	Space group	Ref.
H	D_{6h}	C_i	*Pbca*	16*a*
H[f]	D_{6h}	C_i	$P2_1/n$	16*b*
F	D_{6h}	C_i	$P2_1/c$	17
F[b]	D_{6h}	C_i	$R\bar{3}m$	18
F[c]	D_{6h}	C_i	$P\bar{1}$	19
F[d]	D_{6h}	C_i	$C2/m$	20
CH_3[b]	D_{6h}	C_i	$R\bar{3}m$	18
CH_3[c]	D_{6h}	C_i	$P\bar{1}$	19
CH_3[e]	D_{6h}	C_i	$P\bar{1}$	14
CH_3[f]	D_{6h}	C_i	$I2/m$	21
CH_3[h]	D_{6h}	C_i	$P2_1/n$	25
CH_3	D_{6h}	C_i	$P\bar{1}$	22
Cl	D_{6h}	C_i	$P2_1/c$	28
Br[g]	D_{6h}	C_i	$P2_1/c$	23
I	D_{6h}	C_i	$P2_1/c$	8
CH_2Br	D_{3d}	D_{3d}	$R\bar{3}$	24
NO_2	D_{6h}	C_2	$I2/c$	9
CO_2H	D_{6h}	C_2	Pccn	11
C_6H_5	D_{6h}[i]	C_1	$Pna2_1$	10
C_3H_5	D_{3d}	$C_s(\sigma)$	Pbnm	This study

[a] Highest possible point symmetry not considering hydrogens on substituents.
[b] In π-molecular complex hexamethylbenzene: hexafluorobenzene.
[c] As in note b, triclinic form.
[d] In π-molecular complex durene: hexafluorobenzene.
[e] In π-molecular complex with tetracyanoethylene.
[f] In π-molecular complex with tetracyanoquinodimethane.
[g] In complex with 1,2,4,5 tetrabromobenzene.
[h] In π-molecular complex with 1,2,4,5-tetracyanobenzene.
[i] With all phenyl substituents perpendicular to ring.

is governed by van der Waals forces. The very ordered alignment of the molecules dictated by the space group and site symmetry is in accordance with the predictions of Usieli *et al.*[1] which were based on the high m.p. and low solubility of the compound.

Of all the hexasubstituted benzenes studied to date, this is the first to have site symmetry $C_s(\sigma)$ (Table 5). In general, crystallographic site symmetry is lower than molecular point symmetry, and in accordance with Kitaigorodskii's generalization,[26] centrosymmetric molecules generally retain only the center of symmetry in the crystal. Bel'skii[27] has surveyed the literature for axially symmetric molecules and has noted that if the molecule contains more than one two-fold axis (D_2, D_3, D_4 or D_6) then for 80% of the cases surveyed only one of the 2-fold axes is retained in the crystal. Again, the present structure provides an exceptional example where a mirror plane is retained rather than a center of symmetry or a 2-fold axis.

Acknowledgements—We are grateful to Sylvia Schreiber for technical assistance, and to Dr. Usieli for providing the crystals.

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