

Crystal Structure of 2,4,6,8,9,10-Hexamethyl-2,4,6,8,9,10-hexaboro-adamantane

By Ivan Rayment and Harrison M. M. Shearer,* Department of Chemistry, Durham University, South Road, Durham DH1 3LE

Crystals of the title compound are orthorhombic, with $a = 16.184(1)$, $b = 13.251(1)$, $c = 6.999(1)$ Å, $Z = 4$, space group $Pnma$. The structure was solved by the symbolic-addition procedure and refined by the method of least squares to R 0.06 for 639 observed reflections. The molecules have an adamantane-like structure with four carbon atoms lying near the corners of a tetrahedron and the six BMe groups lying above the edges. The molecular symmetry approximates to $\bar{4}3m$ and the mean B-C distance is 1.564 Å.

THE title compound was prepared,¹ in 25% yield, by the pyrolysis of trimethylborane at 450 °C. N.m.r. studies (¹H, ¹¹B, and ¹³C) showed that the six BMe groups were magnetically equivalent as were the four CH groups and an adamantane-like structure was suggested. This structure may be contrasted with the *nido*-decaborane type structure² which might have been expected by analogy with boranes and carboranes of the general formula $(CH)_x(BR)_y$ and the present work was undertaken to provide further information about this compound.

EXPERIMENTAL

Crystals were grown by sublimation *in vacuo* at room temperature and were obtained as prisms, elongated along c , with well developed {110} faces. The crystal used for data collection had dimensions $0.4 \times 0.3 \times 0.2$ mm and was sealed in a thin-walled capillary.

Crystal Data.— $C_{10}H_{22}B_6$, $M = 207.02$, Orthorhombic, $a = 16.184(1)$, $b = 13.251(1)$, $c = 6.999(1)$ Å, $U = 1501$ Å³, $D_m = 0.87$, $Z = 4$, $D_c = 0.905$ g cm⁻³, $\mu = 3.2$ cm⁻¹ for Cu- K_α radiation, $\lambda = 1.5418$ Å. Space group $Pnma$.

Intensity data were collected on a Hilger and Watts Y 290 four-circle diffractometer by use of Ni-filtered Cu radiation and a θ — 2θ scan. Two sets of equivalent reflections were measured within the range $0 < \theta \leq 55^\circ$; of the 993 independent reflections 639 were considered observed having net counts $\geq 3\sigma$. Intensities were corrected for Lorentz and polarisation effects but not for absorption.

The compound is very volatile at room temperature and the standard reflections, measured at intervals of 40 ordinary reflections, showed a general decrease during data collection. To correct for any movement of the crystal within the capillary the orientation of the crystal was redetermined whenever the intensities of the standard reflections fell by 15%. Unit-cell dimensions were obtained by a least-squares treatment of the positions of 12 high-order reflections.

Structure Determination and Refinement.—The structure was solved by the symbolic-addition procedure, the E map calculated on 126 phased reflections showing the positions of all non-hydrogen atoms. The atomic parameters were refined by the method of least squares and with anisotropic thermal parameters for all the atoms R was 0.13. A

† See Notice to Authors No. 7, in *J.C.S. Dalton*, 1976, Index issue (items less than 10 pp. are supplied as full-size copies).

¹ M. P. Brown, A. K. Holliday, and G. M. Way, *J.C.S. Dalton*, 1975, 148.

² R. E. Williams, *Inorg. Chem.*, 1971, **10**, 210.

difference-Fourier synthesis gave the positions of the hydrogen atoms attached to the cage carbon atoms and also showed annuli of electron density adjacent to the methyl carbon atoms indicating that the methyl groups were rotating about the B-C bonds.

Hydrogen atoms were placed at the positions observed for those atoms attached to the cage carbon atoms. Allowance for the rotation of the methyl groups was made by placing six hydrogen atoms, each with an occupation factor of one-half, at equal intervals on a circle calculated by assuming normal bond lengths and angles. Hydrogen atoms were included in the structure-factor calculations but their parameters were not refined. Further refinement using full-matrix least-squares methods caused R to converge to its final value of 0.06, for the 639 observed reflections. The inclusion of the hydrogen atoms led to significant changes in the lengths of the B-C bonds, both terminal and within the cage, and again shows their importance in the structure analysis of such light-atom compounds. A difference map, calculated at the end of the refinement, showed no peaks > 0.2 eÅ⁻³.

Parameter shifts in the final cycle of refinement were all

TABLE 1

Final positional (fractional) parameters for non-hydrogen atoms, with estimated standard deviations in parentheses

	x	y	z
B(1)	0.012 9(3)	0.25(—)	-0.170 8(9)
B(2)	0.191 6(3)	0.25(—)	0.115 2(8)
B(3)	0.147 5(2)	0.157 6(3)	-0.173 5(6)
B(4)	0.057 9(2)	0.155 8(3)	0.117 1(5)
C(1)	0.007 1(3)	0.25(—)	0.051 3(7)
C(2)	0.101 1(3)	0.25(—)	-0.261 8(6)
C(3)	0.149 3(2)	0.149 4(2)	0.050 5(5)
C(4)	-0.067 1(3)	0.25(—)	-0.296 0(9)
C(5)	0.273 5(3)	0.25(—)	0.234 5(8)
C(6)	0.018 7(3)	0.071 6(3)	0.246 1(6)
C(7)	0.194 2(2)	0.079 1(3)	-0.301 3(6)

$< 0.15\sigma$. The weighting scheme was: $\sqrt{w} = 1/\{5.5 + |F_o| + 0.015|F_o|^2 + 0.002|F_o|^3\}$. Unobserved reflections were given zero weight in the refinement. Scattering factors were taken from ref. 3, apart from those of hydrogen which were obtained from ref. 4. The atomic positional parameters of the non-hydrogen atoms are shown in Table 1 and those of the hydrogen atoms in Table 2. Structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21892 (7 pp., 1 microfiche).†

³ 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

⁴ R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1966, **42**, 3175.

RESULTS

As originally suggested,¹ the molecules have an adamantane-like structure (Figure 1). Four carbon atoms lie near the corners of a tetrahedron with the six boron atoms lying above the edges of the tetrahedron in an almost octahedral arrangement. Thus the boron atoms are

TABLE 2
Positional (fractional) parameters * for hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>
H(1) †	-0.050	0.25	0.125
H(2) †	0.092	0.25	-0.417
H(3) †	0.183	0.083	0.083
H(41)	-0.054	0.25	-0.450
H(42)	-0.123	0.25	-0.198
H(43)	-0.106	0.182	-0.261
H(44)	-0.071	0.182	-0.387
H(51)	0.326	0.25	0.135
H(52)	0.309	0.182	0.199
H(53)	0.275	0.182	0.325
H(54)	0.258	0.25	0.388
H(61)	0.068	0.014	0.274
H(62)	0.054	0.067	0.381
H(63)	-0.003	0.104	0.381
H(64)	-0.046	0.088	0.274
H(65)	-0.033	0.035	0.168
H(66)	0.025	-0.002	0.168
H(71)	0.257	0.108	-0.331
H(72)	0.212	0.116	-0.438
H(73)	0.160	0.070	-0.438
H(74)	0.153	0.015	-0.331
H(75)	0.197	0.007	-0.225
H(76)	0.250	0.054	-0.225

* B 8.0 Å². † Occupation factor 1.0, all others 0.5.

attached to two carbon atoms in the cage and to a terminal methyl group whereas the cage carbon atoms are bound to three boron atoms and to a terminal hydrogen atom. The molecules lie across mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$ with the atoms B(1), B(2), C(1), and C(2) of the molecular framework situated on the mirror plane at $y = \frac{1}{4}$. The overall molecular symmetry approximates to $\bar{4}3m$.

The B-C distances (Table 3) are the same, mean

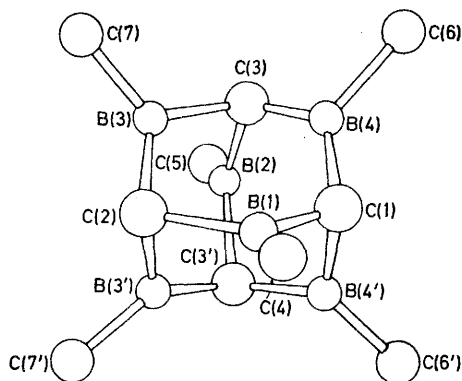


FIGURE 1 A perspective view of the molecule; hydrogen atoms are not shown

1.564(2) Å. This is similar to the value⁵ [1.578(1) Å] in BMe_3 , but is shorter than that [1.590(3) Å] in $B_2H_2Me_4$,⁶ presumably as a consequence of the change from three- to four-fold co-ordination at boron. In the present case, sufficient valence electrons are available to allow the atoms to bond by normal two-electron two-centre bonds. In

⁵ L. S. Bartell and B. L. Carroll, *J. Chem. Phys.*, 1965, **42**, 3076.

contrast, the B-C distances in carboranes are normally longer than such single bonds and are associated with co-ordination numbers at boron greater than three, e.g. the B-C distance⁷ is 1.710 Å in $B_{10}C_2H_{12}$, which has a co-ordination number of six at both boron and carbon.

The angles at boron within the cage are all equal, mean 117.2°, whereas those at carbon lie in the range 103.1–106.4°. All these angles are smaller than those expected for atoms in sp^2 and sp^3 hybrid states respectively and this feature is dictated by the structure itself. In a molecule of

TABLE 3

(a) Bond lengths (Å), with estimated standard deviations in parentheses

B(1)-C(1)	1.557(8)	B(3)-C(3)	1.571(5)
B(1)-C(2)	1.563(7)	B(3)-C(7)	1.566(5)
B(1)-C(4)	1.564(8)	B(4)-C(1)	1.565(5)
B(2)-C(3)	1.566(4)	B(4)-C(3)	1.552(5)
B(2)-C(5)	1.566(7)	B(4)-C(6)	1.570(6)
B(3)-C(2)	1.564(5)		

(b) Bond angles (°), with estimated standard deviations in parentheses

C(1)-B(1)-C(2)	117.5(4)	C(3)-B(2)-C(5)	121.6(3)
C(3)-B(2)-C(3')	116.8(3)	C(2)-B(3)-C(7)	121.7(3)
C(2)-B(3)-C(3)	117.2(3)	C(3)-B(3)-C(7)	121.0(3)
C(1)-B(4)-C(3)	117.1(3)	C(1)-B(4)-C(6)	121.6(3)
C(1)-B(1)-C(4)	120.6(4)	C(3)-B(4)-C(5)	121.3(3)
C(2)-B(1)-C(4)	121.9(4)		
B(1)-C(1)-B(4)	105.2(3)	B(2)-C(3)-B(3)	103.8(3)
B(4)-C(1)-B(4')	105.9(3)	B(2)-C(3)-B(4)	106.4(3)
B(1)-C(2)-B(3)	106.1(3)	B(3)-C(3)-B(4)	106.2(3)
B(3)-C(2)-B(3')	103.1(3)		

(c) Some intramolecular non-bonding contacts (Å)

B(1) ... B(3)	2.499(6)	C(2) ... C(3)	2.676(5)
B(1) ... B(4)	2.480(7)	C(3) ... C(3')	2.667(4)
B(2) ... B(3)	2.468(6)	C(3) ... C(6)	4.681(7)
B(2) ... B(4)	2.497(6)	C(4) ... C(7)	4.797(6)
B(3) ... B(4)	2.497(5)	C(5) ... C(7)	4.754(6)
B(3) ... B(3')	2.450(5)	C(5) ... C(7)	4.564(6)
B(4) ... B(4')	2.497(6)	C(6) ... C(6')	4.728(6)
C(1) ... C(2)	2.667(6)	C(6) ... C(7)	4.770(6)
C(1) ... C(3)	2.660(5)	C(7) ... C(7')	4.529(5)

(d) Intermolecular contacts (Å) < 4.25 Å between methyl carbon atoms

C(1) ... C(5 ^{II})	4.068	C(5) ... C(7 ^{VI})	2.163
C(3) ... C(7 ^{III})	4.082	C(6) ... C(6 ^{VII})	3.979
C(4) ... C(5 ^V)	4.009	C(6) ... C(6 ^{VIII})	4.074
C(4) ... C(6 ^{IV})	4.218	C(6) ... C(7 ^{VIII})	4.001

Roman numeral superscripts refer to the following equivalent positions with respect to the molecule at x, y, z :

I	$x, \frac{1}{2} - y, z$	V	$-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} - z$
II	$-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$	VI	$x, y, 1 + z$
III	$\frac{1}{2} - x, -y, \frac{1}{2} + z$	VII	$-x, -y, -z$
IV	$x, y, -1 + z$	VIII	$-x, -y, 1 - z$

ideal $\bar{4}3m$ symmetry an angle of 120° at boron necessitates an angle of 103° 12' in the cage at carbon, whereas an angle of 109° 28' at carbon requires the angles at boron also to be tetrahedral. The angles observed represent a compromise between these limits. The C-B-C (methyl) angles vary from 120.6 to 121.9°.

Departure from $\bar{4}3m$ symmetry occurs throughout the molecule (Table 4) but is most evident in the distances (Table 3) between methyl carbon atoms which vary from 4.529 to 4.797 Å. The effect is greatest for C(7) which appears displaced towards C(7') across the mirror plane at $y = \frac{1}{4}$ and towards C(5). This distortion increases the separation between C(7) and C(6) in the molecule at $\bar{x}\bar{y}\bar{z}$ to 4.001 Å, so that the shortest intermolecular contacts are

⁶ B. L. Carroll and L. S. Bartell, *Inorg. Chem.*, 1968, **7**, 219.

⁷ R. K. Bohn and M. D. Bohn, *Inorg. Chem.*, 1971, **10**, 350.

close to 4 Å which is normally accepted as the closest distance of approach between rotating methyl groups. The movement of C(7) towards the mirror plane is accompanied by a similar but smaller movement of B(3) so that the B(3)···B(3^I) separation is smaller than the other B···B distances. In addition, B(3) lies 0.024 Å above the plane of its three attached carbon atoms whereas the

atoms. This structure is predicted⁸ by comparison with other boranes and carboranes but is also compatible with a two-centre bond description.⁹ Thus the B-C distance [1.556(2) Å] is appropriate for a normal single bond and the B-B distance [1.853 Å] is longer than those usually found in carboranes, *e.g.* 1.720 Å in C₂B₄H₆.⁹

TABLE 4

Equations of some weighted least-squares mean planes where X , Y , Z are in Å with respect to the orthogonal axes a , b , c . Deviations (Å) of atoms from the mean plane are given in square brackets

Plane (1): B(3), B(3^I), B(4), B(4^I), C(6), C(6^I), C(7), C(7^I)
 $-0.8053X + 0.0Y - 0.5928Z + 1.2461 = 0$

[B(3) 0.043, B(4) 0.005, C(6) -0.019, C(7) -0.035]

Plane (2): B(1), B(2), B(3^I), B(4), C(4)-(6), C(7^I)
 $0.3916X - 0.7164Y - 0.5774Z + 1.5884 = 0$

[B(1) -0.013, B(2) -0.036, B(3^I) -0.026, B(4) 0.004, C(4) -0.014, C(5) 0.001, C(6) 0.033, C(7^I) 0.042]

Plane (3): B(1), B(2), C(3)-(5), C(3^I)

$0.5622X + 0.0Y - 0.8270Z - 1.0841 = 0$

[B(1) 0.022, B(2) -0.08, C(3) -0.018, C(4) 0.018, C(5) 0.047]

other boron atoms are coplanar with their attached carbon atoms. The distortion also accounts for the angles B(3)-C(2)-B(3^I) and B(2)-C(3)-B(3) being less than the other angles in the cage at carbon. The arrangement of the molecules in the projection along c is shown in Figure 2.

DISCUSSION

Carboranes have been defined⁸ as mixed hydrides of carbon and boron in which both carbon and boron atoms participate in the electron-deficient molecular framework so that the compound described here is strictly not a carborane. The boron-carbon ratio is 3 : 2 and sufficient valence electrons are available for the atoms to be joined by single bonds. It is of interest that the compound adopts a classical adamantane-like structure in preference to the electron-deficient decaborane-type skeleton.

One other compound is known with this boron-carbon ratio, namely C₂B₃H₅. Its structure,⁹ determined by electron diffraction methods, is based on a trigonal bipyramid with the apical positions occupied by carbon

⁸ R. Snaith and K. Wade, 'MTP International Reviews of Science,' Ser. I, vol. I, Butterworths, 1972.

⁹ E. A. McNeill, K. L. Gallaher, F. R. Scholer, and S. H. Bauer, *Inorg. Chem.*, 1973, **12**, 2108.

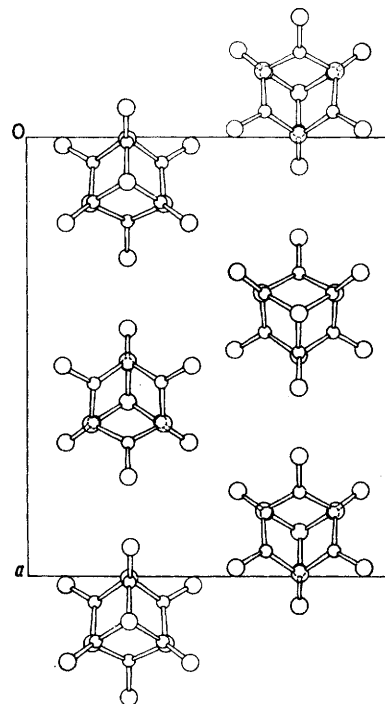


FIGURE 2 The packing of the molecules in the projection along c

This boron-boron separation was not thought to preclude B···B interaction but did suggest it is weaker than in normal carboranes.

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¹⁰ F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Huber, N.R.C. Crystallographic Programs for the IBM 360 system, World List of Crystallographic Computer Programs, 2nd edn., Appendix, p. 52.