The Molecular Structure of Hexaborane(12) in the Gas Phase as determined by Electron Diffraction

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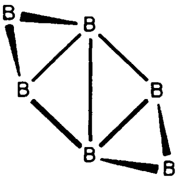
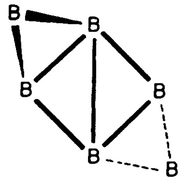
The structure of gaseous *arachno*-B_6H_{12}, the only simple binary borane for which crystallographic data are not available, has been determined by electron diffraction. The analysis showed unequivocally that the molecule has C_2 symmetry, with two BH_2 terminal groups, four other terminal hydrogen atoms, and four bridging hydrogen atoms, two of which are asymmetric. Models with C_i or C_s symmetries gave unsatisfactory R factors, and were rejected. The boron framework is a chiral six-atom fragment of a closed triangular dodecahedron from which two adjacent five-connected vertices have been removed. The results establish a clear structural relationship between the three *arachno* boranes B_4H_{10}, B_5H_{11}, and B_6H_{12}.

Hexaborane(12) is the only simple binary borane for which crystallographic data are not available, previous attempts to solve the structure by X-ray crystallography being thwarted because the compound forms a glass at low temperature.[1] N.m.r. evidence[2] and considerations based on geometrical and topological principles[3] are consistent with a (4212) structure of C_2 symmetry, (**I**), though alternative arrangements of C_i and C_s symmetry, (**II**) and (**III**) respectively, could not be entirely eliminated. An early electron diffraction study of the gaseous molecule failed to distinguish between the various formulations.[4] Geometrical parameters such as interatomic distances and angles are therefore entirely lacking, and for this reason we have undertaken a study of the molecular structure of the gaseous *arachno*-B_6H_{12} molecule by electron diffraction. The results establish that the molecule does indeed have C_2 symmetry and indicate a structural relationship between the three *arachno*-boranes B_4H_{10},[5] B_5H_{11},[6] and B_6H_{12}, all of which have now been studied by electron diffraction.



(**I**)



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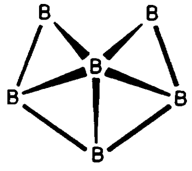

(**III**)

Experimental

Hexaborane(12) was prepared by the method of Shore and co-workers.[7] Pentaborane(9) was obtained from Dr. R. E. Williams (Chemical Systems Inc., California) and was used without further purification. Deprotonation was achieved with KH in a minimum amount of Me_2O at −78 °C. After addition of B_2H_6 to generate the $[B_6H_{11}]^-$ anion, care was taken to remove all traces of the solvent before the addition of HCl. Failure to do this resulted in loss of product by reaction with Me_2O to give B_5H_9. The B_6H_{12} was purified on a low-temperature fractional distillation column, with continuous monitoring of the distillate by mass spectrometry. Useful quantities of B_6H_{10} were also sometimes generated in the preparation, but with care it was possible to achieve an excellent separation of the two boranes. The final product was shown by i.r. and ^{11}B n.m.r. spectroscopy to be essentially free from impurities; its vapour pressure at 0 °C was 17.0 mmHg (*ca.* 2.26 kPa), in excellent agreement with the published value.[2b] The boranes were handled in conventional high-vacuum systems equipped with greaseless O-ring taps and spherical joints [J. Young (Scientific Glassware) Ltd.].

Electron diffraction scattering patterns were recorded photographically on Kodak Electron Image plates using the Edinburgh gas diffraction apparatus,[8] with nozzle-to-plate distances of 285.7 and 128.3 mm (three plates at each distance) and an accelerating voltage of *ca.* 44 kV. The sample was held at 0 °C and the nozzle was held at room temperature (17 °C) during the experiments. The plates were pumped for 24 h after completion of the experiment, before being developed, to minimise the effects of reaction between the sample and photographic emulsion. Calibration plates for benzene were also run at each camera distance, and we believe that by following this procedure systematic errors in the camera distance and electron wavelength are negligible (less than 1 part in 5 000).

Optical densities were obtained from the plates using a computer-controlled Joyce-Loebl MDM6 microdensitometer at the S.E.R.C. Laboratory, Daresbury, using a scanning procedure described previously.[9] Calculations were carried out using our standard data-reduction[9] and least-squares refinement[10] programs, and the scattering factors of Schäfer *et al.*[11] Weighting points, used in setting up the off-diagonal weight matrices, are given in Table 1, together with other experimental details.

Structure Refinement.—As discussed earlier, there are good reasons for supposing, both on theoretical grounds[3] and by analysis of n.m.r. spectra,[2] that B_6H_{12} should have C_2 symmetry. However, as it is possible in principle that the molecules could have C_i or C_s symmetry (the latter would involve fortuitous coincidence of two chemical shifts), we thought it prudent to test models with each of these symmetries. These

Table 1. Camera heights, weighting functions, *etc.*

Camera height/mm	Electron wavelength/pm	Δs	$s_{min.}$	sw_1	sw_2	$s_{max.}$	Correlation parameter	Scale factor
		nm^{-1}						
285.7	5.685	2	20	40	122	144	0.488	0.647(12)
128.3	5.685	4	60	80	290	340	0.360	0.583(14)

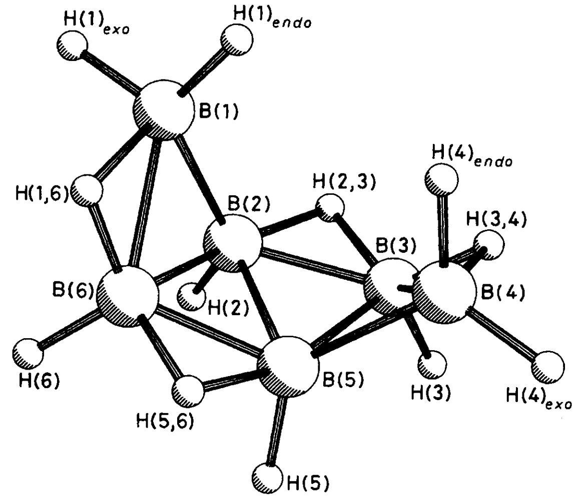

Figure 1. Perspective view of a molecule of B_6H_{12}

Table 2. Molecular parameters[a] (r_a, distances/pm, angles/°)

p_1	r(B–B) mean	179.5(1)
p_2	Δr(B–B) 1—6/2—6/5—6 minus 1—2/2—5	0.4(18)
p_3	Δr(B–B) 1—2 minus 2—5	−4.3(24)
p_4	Δr(B–B) 1—6/5—6 minus 2—6	2.8(17)
p_5	Δr(B–B) 1—6 minus 5—6	21.4(20)
p_6	Angle between planes 625 and 325	167.4(22)
p_7	Angle between planes 162 and 562	128.1(12)
p_8	r(B–H) (bridge) mean	130.8(14)
p_9	r(B–H) (terminal)	122.2(13)
p_{10}	H_tBH_t	112.0(fixed)
p_{11}	B(2)B(6)H(6)	110.0(fixed)
p_{12}	B(5)B(2)H(2)	110.0(fixed)
p_{13}	Δr B(1)–H(1,6) minus B(6)–H(1,6)	21.6(58)
p_{14}	B(1)H(1,6)B(6) dip[b]	0.0(fixed)[c]
p_{15}	Δr B(6)–H(5,6) minus B(5)–H(5,6)	0.0(fixed)[c]
p_{16}	B(5)H(5,6)B(6) dip[b]	0.0(fixed)[c]
p_{17}	B(1)H_2 wag[b]	0.0(fixed)[c]
p_{18}	B(1)H_2 rock[b]	0.0(fixed)[c]

[a] In the case of p_2, Δr(B–B) 1—6/2—6/5—6 minus 1—2/2—5 means the average of the first group of B–B distances minus the average of the second group, and likewise for p_3, p_4, p_5, p_{13}, and p_{15}. Errors, quoted in parentheses, are estimated standard deviations obtained in the least-squares refinements, increased to allow for systematic errors. [b] For definition see text. [c] See text.

tests showed quite unequivocally that C_2 symmetry is correct. With the other models, R factors were significantly worse (0.12 for C_s, 0.10 for C_i, compared with 0.08 for C_2), and even these values could only be obtained with highly unlikely distorted structures. Most refinements were therefore performed using the C_2 model, with two BH_2 terminal groups, four other terminal hydrogen atoms, and four bridging hydrogen atoms, as shown in Figure 1.

Even with C_2 symmetry, a lot of parameters are required to define the molecular structure. For example, there are eight different B–H bonded distances, four terminal and four bridging, and ten angular parameters are also required to define the hydrogen atom positions. It was necessary to make a number of assumptions about the hydrogen positions, but no restrictions at all were placed on the boron atoms. The structure of the boron skeleton was thus defined by seven parameters, as listed in Table 2. Five of these describe the five different B–B 'bond' lengths, and these parameters were chosen to be the mean, and various differences. The remaining variables were angles between BBB planes. All seven of the cluster parameters were allowed to refine, even though the five B–B distances came within 15 pm of each other, but a single amplitude of vibration was refined for this group of distances.

The B–H bond lengths for the four distinct types of terminal hydrogen atom were refined as a single parameter, and the amplitude of vibration for this group was also refined, but tied to that for the bridging B–H bonds. For the terminal BH_2 groups the HBH angle was fixed at 112°, and it was initially assumed that the bisector of this angle coincided with the bisector of the angle B(2)B(1)B(6). At a later stage this restriction was relaxed, and the group was allowed to wag (*i.e.* to move in its own plane), or to rock (*i.e.* move perpendicular to its plane). The refined values for these parameters were 3.1(16)° (the displacement being *towards* the rest of the cluster) and −1.3(87)° [rocking *away* from B(2), *towards* B(6)]. Neither of these distortions was significant, so the parameters were subsequently fixed at zero again. The terminal hydrogen atom H(6) was assumed to lie in the plane bisecting the planes B(2)B(6)B(5) and B(1)B(6)B(2), and the remaining terminal atom H(2) was constrained to lie in the central plane of the molecule [bisecting B(3)B(2)B(5) and B(6)B(2)B(5)]. These two atoms were thus each located by the B–H bond length and one angle, but these angles could not be refined.

The bridging atoms, H(1,6) and H(5,6), were originally located by a single bridging B–H distance, and it was assumed that the bridge bonds lay in the local BBB planes [B(1)B(2)B(6) and B(5)B(2)B(6) respectively]. These restrictions were then relaxed by allowing asymmetry in each of the bridges, while continuing to refine a single mean bridge B–H distance, and by allowing displacement of the bridge atoms from the local BBB planes. For three of these four relaxations the refined parameters were not significantly different from zero, but for the B(1)H(1,6)B(6) bridge the bond to B(1) was found to be longer than that to B(6) by 21.6(58) pm.

The final refined geometrical parameters are listed in Table 2, and interatomic distances and amplitudes of vibration are given in Table 3. Errors quoted in these tables are estimated standard deviations obtained in the least-squares refinements. Table 4 gives the most significant elements of the least-squares correlation matrix, and Table 5 gives atom co-ordinates, from which interatomic distances, bond angles, and dihedral angles of interest may be computed. Figures 2 and 3 show the molecular scattering intensity curves and the radial distribution curve.

Discussion

A perspective view of the chiral *arachno*-B_6H_{12} molecule is shown in Figure 1. The boron framework can be thought of as being derived from a *closo*-dodecahedral B_8 cluster by removal of two adjacent five-connected boron atoms, consistent with the well known Williams–Wade cluster geometry and electron-counting rules.[12] In fact, the dihedral angles between adjacent triangular faces in B_6H_{12} are close to, but slightly greater than, the two internal dihedral angles characteristic of a regular triangular dodecahedron (157 and 120°): the observed angles are 167.4 ± 22° between the faces joined by B(2)–B(5), and

Table 3. Interatomic distances and amplitudes of vibration (pm)*

		Distance	Amplitude			Distance	Amplitude
r_1	B(1)–B(2)	177.8(18)	5.0(10)	r_{21}	B(1)···H(2,3)	257.7(21)	8.9(15)
r_2	B(2)–B(5)	182.1(13)		r_{22}	B(2)···H(1)	261.9(17)	
r_3	B(2)–B(6)	177.7(16)		r_{23}	B(2)···H(1,6)	239.0(20)	
r_4	B(1)–B(6)	191.3(7)		r_{24}	B(2)···H(6)	247.8(19)	
r_5	B(5)–B(6)	169.9(14)		r_{25}	B(2)···H(3)	255.8(17)	
r_6	B–H(terminal)	122.2(13)	7.9(5)	r_{26}	B(2)···H(5)	251.6(14)	
r_7	B–H(5,6)	130.8(14)	8.5(tied to u_6)	r_{27}	B(6)···H(2)	241.9(17)	
r_8	B(1)–H(1,6)	141.6(25)		r_{28}	B(6)···H(5)	233.5(20)	
r_9	B(6)–H(1,6)	120.0(38)		r_{29}	B(1)···H(5)	381.2(23)	13.6(31)
r_{10}	B(1)···B(5)	282.5(22)	16.4(53)	r_{30}	B(1)···H(3,4)	348.8(23)	
r_{11}	B(1)···B(3)	305.1(16)	9.4(11)	r_{31}	B(1)···H(3)	416.0(21)	
r_{12}	B(3)···B(6)	294.4(29)		r_{32}	B(2)···H(4)$_{endo}$	324.7(30)	
r_{13}	B(1)···B(4)	335.3(39)	31.0(122)	r_{33}	B(2)···H(4)$_{exo}$	392.1(21)	
r_{14}	B(1)···H(2)	273.9(20)	12.0(18)	r_{34}	B(6)···H(3,4)	363.8(24)	
r_{15}	B(1)···H(5,6)	296.8(20)		r_{35}	B(6)···H(3)	380.0(26)	
r_{16}	B(1)···H(6)	276.3(13)		r_{36}	B(6)···H(4)$_{endo}$	333.7(28)	
r_{17}	B(2)···H(5.6)	258.1(22)		r_{37}	B(6)···H(4)$_{exo}$	408.8(21)	
r_{18}	B(2)···H(3,4)	264.1(33)		r_{38}	B(1)···H(4)$_{endo}$	311.5(54)	20.0(fixed)
r_{19}	B(6)···H(1)	271.2(12)		r_{39}	B(1)···H(4)$_{exo}$	457.3(46)	
r_{20}	B(6)···H(2,3)	305.0(21)					

* Non-bonded H···H atom pairs were also included in the refinement but are not listed here.

Table 4. Least-squares correlation matrix (× 100)*

p_3	p_4	p_7	p_9	u_1	u_{10}	u_{11}	u_{14}	k_2	
−63	−76				−70		60		p_2
	51								p_3
							−57		p_4
				−90					p_5
	−52	−68			−66	−53	76		p_6
			−82						p_8
			83						p_{13}
						56	−62		u_{10}
						58			u_{21}
						75			u_{29}
								54	k_1

* u_n Represents the amplitude of vibration for distance r_n in Table 3, and k_2 represents a scale factor; only elements with absolute values > 50 are included.

Table 5. Atomic co-ordinates/pm

Atom	x	y	z
B(1)	−102.87	132.35	139.02
B(2)	0.00	91.03	0.00
B(3)	147.03	7.49	16.23
B(4)	102.87	−132.35	139.02
B(5)	0.00	−91.03	0.00
B(6)	−147.03	−7.49	16.23
H(1)$_{endo}$	−69.41	101.10	252.35
H(1)$_{exo}$	−171.00	233.82	137.73
H(1,6)	−202.33	34.67	114.06
H(6)	−220.64	11.16	−79.55
H(5,6)	−122.15	−135.90	13.49
H(2)	0.00	132.84	−114.86
H(4)$_{endo}$	69.41	−101.10	252.35
H(4)$_{exo}$	171.00	−233.82	137.73
H(3,4)	202.33	−34.67	114.06
H(3)	220.64	−11.16	−79.55
H(2,3)	122.15	135.90	13.49
H(5)	0.00	−132.84	−114.86

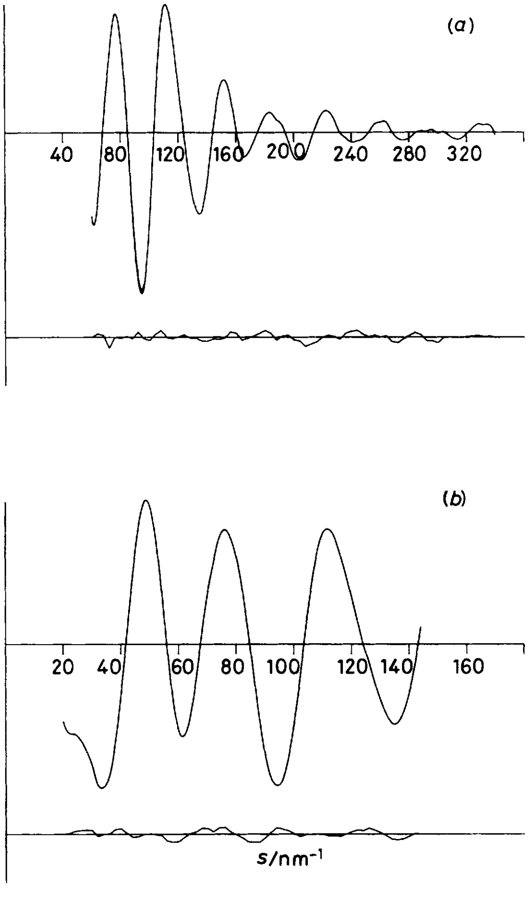

Figure 2. Observed and final weighted difference molecular electron scattering intensity curves at nozzle-to-plate distances of (*a*) 128 and (*b*) 286 mm

128.1 ± 12° between the faces joined by B(2)–B(6) and by B(3)–B(5), respectively. The only other comparable compound for which structural data are available is the *hypho* adduct $B_6H_{10}(PMe_3)_2$, which has been described as a fragment of the equatorial belt of an icosahedron.[13] The dihedral angles calculated from data for this *hypho* adduct are 140° at the central 'hinge' and 154° at the two outer hinges; the former is indeed very close to the regular icosahedral angle of 138.2° (*i.e.*

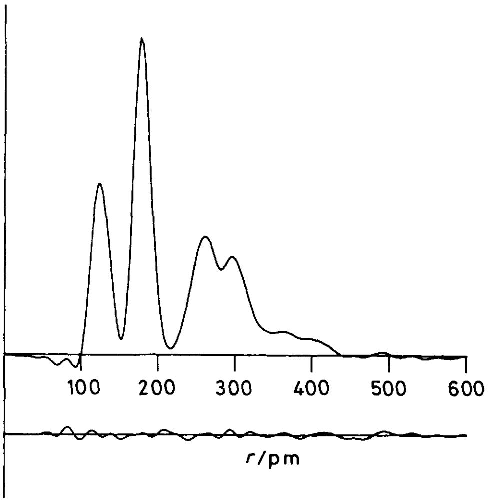

Figure 3. Observed and final difference radial distribution curves, $P(r)/r$. Before Fourier inversion the data were multiplied by $s\cdot\exp[-0.000\,02s^2/(Z_P - f_P)(Z_N - f_N)]$

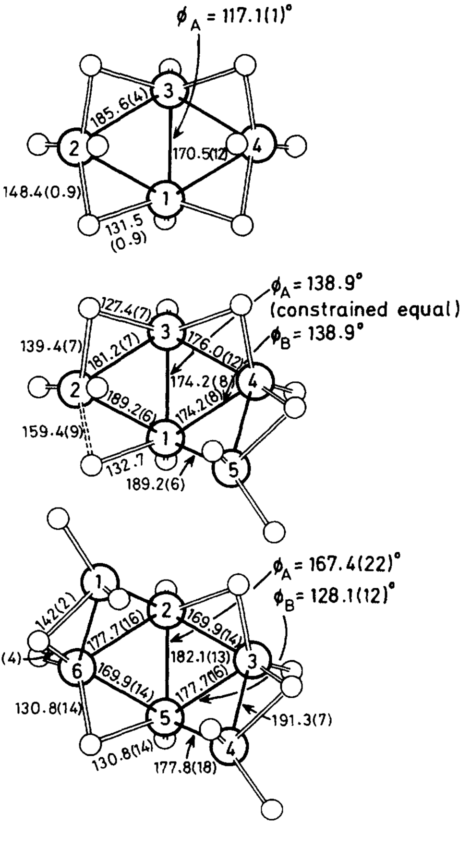

Figure 4. Structural relationship between the *arachno* boranes B_4H_{10}, B_5H_{11}, and B_6H_{12} (see text for discussion); distances in pm

$\pi - \sin^{-1}\frac{1}{3}$), whereas the latter two are somewhat more open. In further comparing the detailed structures of *arachno*-B_6H_{12} and *hypho*-$B_6H_{10}(PMe_3)_2$, it is apparent that the notional replacement of two terminal hydrogen atoms in *arachno*-B_6H_{12} by the phosphine ligands induces substantial re-arrangement of the remaining hydrogen atoms. In particular, in B_6H_{12} all the peripheral B–B contacts apart from B(1)–B(2) and B(4)–B(5) are bridged by hydrogen atoms, whereas in $B_6H_{10}(PMe_3)_2$ these are the only pairs which *do* carry hydrogen bridges. Despite these differences, many of the interatomic B–B distances are remarkably similar in the two molecules.

Of greater interest, because of its possible relevance to the mechanisms of borane interconversion reactions,[14] is the clear relationship which is established as a result of this work, between the structures of the three *arachno* binary boranes B_4H_{10}, B_5H_{11}, and B_6H_{12}.[2c] This is emphasized in Figure 4, which indicates that B_5H_{11} is related to B_4H_{10} by replacement of a hydrogen bridge by a BH_2 group, with the simultaneous conversion of a terminal hydrogen on B(4) into a bridging position between atoms B(4) and B(5). Hexaborane(12) is then derived from B_5H_{11} by a similar modification to the opposite side of the molecule. It should be pointed out that the hydrogen atom bridging B(1) and B(2) of B_5H_{11} is sometimes viewed as a terminal hydrogen atom attached to B(1). However, both low-temperature *X*-ray diffraction data[15] and our own recent gas-phase electron diffraction measurements[6] indicate that the hydrogen is asymmetrically disposed above the B(1)B(2)B(5) face and can therefore be regarded as having at least partial bridging character between atoms B(1) and B(2). When the structure of B_5H_{11} is viewed in relation to that of B_4H_{10} it becomes easier to understand why this should be. Further confirmation that this is a useful way of viewing the relationship between these molecules comes from a comparison of their actual dimensions. There is, for example, a regular increase in the 'hinge' B–B internuclear distance from 170.5(12) pm in B_4H_{10}, through 174.2(8) pm in B_5H_{11}, to 182.1(13) pm in B_6H_{12}, and this is accompanied by a progressive decrease in the 'unsubstituted' B–B interatomic distance from B(3)–B(2) 185.6(4) pm in B_4H_{10}, through B(3)–B(4) 176.0(12) pm in B_5H_{11}, to B(2)–B(3) 169.9(14) pm in B_6H_{12}. There is also a systematic opening of the dihedral angle of the 'butterfly' structure from 117.1(7), through 138.9, to 167.4(22)°. For comparison, values ranging from 115 to 119° have been found in a series of six metallaborane derivatives with the MB_3 framework,[16] and a value of 127° in [$(OC)_4MnB_3H_7$-Br-4(*exo*)];[17] interestingly the value found in B_5H_{11} (138.9°) is close to that (138.2°) calculated for a regular icosahedron.

A final point worthy of mention is that the B(1)HB(6) bridge has been found to be distinctly asymmetric, the two halves differing by some 21.6 pm. The nature of this asymmetry in B_6H_{12} is consistent with that found in other binary boranes[6] where the distance from a bridging H atom to the boron atom of a BH_2 group is generally longer than that to a BH group.

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