Eight-vertex Polyhedral Monocarbaborane Chemistry. Three *closo* Anions, $[CB_7H_8]^-$, $[CB_7H_7I]^-$ and $[CB_7H_6I_2]^-$. Preparation and Structural Studies *

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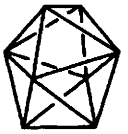
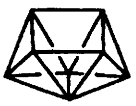
Salts of the eight-vertex [*closo*-1-CB_7H_8]$^-$ monoanion can be prepared from *arachno* nine-vertex ligand adducts *exo*-6-L-4-CB_8H_{12} by base-degradation reactions. Iodination of [*closo*-1-CB_7H_8]$^-$ with elemental iodine yields the [1-CB_7H_7-7-I]$^-$ and [1-CB_7H_6-7,8-I_2]$^-$ monoanions, characterised by single-crystal X-ray diffraction analysis. Crystals of [PPh_4][1-CB_7H_7-7-I] were triclinic, space group $P\bar{1}$, with $a = 7.4703(7)$, $b = 12.766(2)$, $c = 13.9102(12)$ Å, $\alpha = 100.973(10)$, $\beta = 92.886(7)$, $\gamma = 93.005(10)$° and $Z = 2$; structure refined for 3867 data collected at 150 K to $wR_2 = 0.0348$. Crystals of [PPh_4][1-CB_7H_6-7,8-I_2]$^-$ were triclinic, space group $P\bar{1}$, with $a = 7.8389(8)$, $b = 13.4489(11)$, $c = 13.6337(13)$ Å, $\alpha = 98.009(9)$, $\beta = 93.060(7)$, $\gamma = 92.939(7)$° and $Z = 2$; structure refined for 4284 data collected at 200 K to $wR_2 = 0.0504$. The {CB_7} cluster geometries of the two anions approximate closely to regular triangulated dodecahedral, with no sign of any opening. The three anions are fluxional to *ca.* 180 K; structures for the possible intermediates are briefly discussed.

The Williams–Wade cluster-geometry/electron-counting formalism,[1,2] and the consequent *closo–nido–arachno etc.* structural paradigm,[3] together often referred to as 'Wade's rules,' classically underpin much of polyhedral boron chemistry. However, there are exceptions to these formalisms, and it is also recognised that a number of classically structured species exhibit cluster fluxionalities. These last two factors show that alternative structure–energy minima are often readily available and that alternative 'non-Wadian' structures may therefore be isolatable, for example by variation of cluster constituent or substituent, or by modification of crystal-packing factors.[4]

Thus in ten-vertex chemistry the clusters of some classically *closo* species such as [$(PPh_3)_2HRhC_2B_7H_9$] are fluxional,[5] and corresponding open ten-vertex non-Wadian *isonido*[6] structures can be demonstrated. Alternative closed *isocloso*[7] structures also exist, and there are also indications of more open *isoarachno* geometry.[8] Similarly in eleven-vertex chemistry [*closo*-$B_{11}H_{11}$]$^{2-}$ itself is fluxional,[9] and more open *isonido* structures can be demonstrated,[10,11] again with indications of anomalous further opening to *isoarachno.*[12] In nine-vertex *closo* chemistry any propensity for fluxionality is not yet established, but nevertheless open *isonido*[13,14] geometries have been described, and again alternative closed *isocloso*[15] compounds are known. In twelve-vertex boron cluster chemistry open *isonido*[16] and alternative closed *isocloso*[17] shapes have been demonstrated, and some formally *closo* species are fluxional *via* more open *nido* and *isonido* types of structure.[18] These results in twelve-, eleven-, ten- and nine-vertex polyhedral boron chemistry have been taken to suggest[14] that there may well be an alternative *isocloso–isonido–isoarachno* structural paradigm to complement the classical *closo–nido–arachno* one. It is of interest to examine for this type of character in eight-vertex boron chemistry also.



I



II

In this eight-vertex area there have in fact long been interesting puzzles over aspects of the structures available to the formally *closo* $[B_8H_8]^{2-}$ anion.[19–22] The structure of $[B_8H_8]^{2-}$ approximates closely to D_{2d} dodecahedral (structure **I**) in [$Zn(NH_3)_4$][B_8H_8] in the solid state.[20] In solution, however, it is fluxional,[19,21] even at very low temperatures, indicating that other isomeric forms have similar energies.[22] Molecular-orbital calculations suggest that the D_{2d} structure **I** is most stable, but that a C_{2v} structure **II** is energetically very similar.[23,24] The C_{2v} *nido*-type structure **II** thereby constitutes a reasonable intermediate for the fluxionality *via* diamond–square–diamond processes.[19,22] In view of the very small energetic differences, it could well be that the appropriate choice of counter cation could favour one or other of **I** or **II** in the solid state: with the $[Zn(NH_3)_4]^{2+}$ counter cation, obviously structure **I** is preferred.

This reasonable picture is complicated in that NMR spectroscopy suggests that a third, non-fluxional, species, with an ^{11}B NMR relative intensity ratio of 4:2:2, exists under certain solution conditions.[21] This has not yet been accounted for in terms of $[B_8H_8]^{2-}$ isomers.[23,25]

The isoelectronic [1-CB_7H_8]$^-$ monoanion (schematic cluster structure **III**) is more readily synthesized[26] than the $[B_8H_8]^{2-}$ dianion. This is also fluxional, down to *ca.* 180 K in CD_2Cl_2 solution (see below), implying low-energy fluxional intermediates (*e.g.* **IV** and **V**) similar to those for $[B_8H_8]^{2-}$.

There are two, more recent, communications that use molecular-orbital calculations on $[B_8H_8]^{2-}$ and related molecules to address further the above questions by matching proposed structures to NMR properties.[25,27] These tend to confirm the original[23] theoretical conclusions for the $[B_8H_8]^{2-}$

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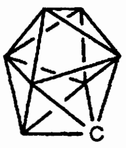
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

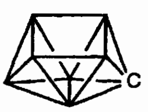
Table 1 Measured ^{11}B and ^{1}H NMR properties for $[PPh_4]^+$ salts of $[CB_7H_8]^-$, $[CB_7H_7I]^-$ and $[CB_7H_6I_2]^-$ in CD_2Cl_2 solution at 294–297 K

$[CB_7H_8]^-$			$[CB_7H_7I]^-$			$[CB_7H_6I_2]^-$		
Relative intensity	$\delta(^{11}B)$	$\delta(^{1}H)$	Relative intensity	$\delta(^{11}B)$	$\delta(^{1}H)$	Relative intensity	$\delta(^{11}B)$	$\delta(^{1}H)$
3	$+2.9^{e}$	$+2.84$	2	$+3.6^{a,b}$	$+3.17$	1	$+3.8^{c,d}$	$+3.21$
			1	$-1.4^{b,f,g}$	{I}	2	$-0.5^{d,g,h}$	{I}
4	-4.3^{i}	$+2.22$	4	$-3.3^{b,j}$	$+2.46$	4	$-2.4^{d,k}$	$+2.61$
1	{CH}	$+4.30$	1	{CH}	$+4.42$	1	{CH}	$+4.16$

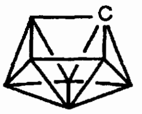
Footnotes[a–k]: approximate $w_{\frac{1}{2}}$ values in Hz at temperatures indicated. [a] 90 (297), 225 (220), 480 (200 K). [b] At 170 K, only one broad peak centred at $\delta(^{11}B)$ *ca.* −1, $w_{\frac{1}{2}}$ *ca.* 2000 Hz (128 MHz spectrum). [c] 115 (297), 400 (200 K). [d] At 180 K, only one broad peak, $w_{\frac{1}{2}}$ *ca.* 1700 Hz (128 MHz spectrum). [e] 55 (293), 510 (183 K). [f] 110 (297 K). [g] Resonance obscured by the overlapping resonance of relative intensity 4 at 220 K and below. [h] 120 (297 K). [i] 50 (293), 470 (183 K). [j] 75 (297), 180 (220), 390 (200 K). [k] 90 (297), 330 (220), 510 (200 K).



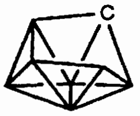
III



IV



V



VI

species **I** and **II**. However, there still remains the puzzle as to the nature of the '4:2:2' species,[21] and a protonated form of **I**, a $[B_8H_9]^-$ monoanion, has been suggested as a possible explanation here.[27] One of these two most recent papers[25] also addresses the $[CB_7H_8]^-$ monoanion and its fluxionality, and concludes that the closed structure represented in schematic **III**, with the carbon atom in a position of cluster connectivity four, is the most stable, and that the diamond–square–diamond fluxionality proceeds through the energetically similar open intermediate **IV** that does not have a carbon atom in the four-membered open face.

Throughout this history, there has been an emphasis that further experimental work would be of interest.

All these considerations have stimulated us to complete and report some of our own experimental findings on one known and two new species in this area. Specifically we describe details of the preparation and NMR properties of the $[1\text{-}CB_7H_8]^-$ monoanion (previously only reported in preliminary form),[26] and its mono- and di-iodo derivatives $[1\text{-}CB_7H_7\text{-}7\text{-}I]^-$ and $[1\text{-}CB_7H_6\text{-}7,8\text{-}I_2]^-$. We also report the results of single-crystal X-ray diffraction analysis on the $[PPh_4]^+$ salts of the two iodinated anions. Unfortunately, crystals of $[PPh_4][CB_7H_8]$ itself that we have been able to obtain have been subject to crystallographic disorder[28] so no useful information about the structure of $[CB_7H_8]^-$ has yet emerged from X-ray work on this compound.

Results and Discussion

Salts of the eight-vertex $[\textit{closo}\text{-}1\text{-}CB_7H_8]^-$ monoanion can be prepared in a variety of ways from *arachno* nine-vertex ligand (L) adducts *exo*-6-L-4-CB_8H_{12} in reaction systems that result in the loss of one boron vertex. Thus, in accord with the original preliminary work,[26] $[NMe_4][CB_7H_8]$ can be prepared from 6-(NMe_3)-*arachno*-4-CB_8H_{12} (prepared as in refs. 26 and 29), by treatment with NaH in refluxing tetrahydrofuran (thf); hydrolysis followed by addition of aqueous NMe_4Cl then results in the product in 65% yield [equation (1)].

$$6\text{-}(NMe_3)\text{-}4\text{-}CB_8H_{12} + H^- \longrightarrow [\textit{closo}\text{-}1\text{-}CB_7H_8]^- + BH_3(NMe_3) + H_2 \quad (1)$$

An alternative route, sometimes more convenient, and with a higher yield, is a similar reaction using $NaBH_4$ as a hydride source, in 1,2-dimethoxyethane at 80 °C for 12 h; hydrolysis and precipitation with NMe_4Cl then results in the product in 83.5% yield. A third, simpler, one-boron dismantling route, is the treatment of 6-(SMe_2)-*arachno*-4-CB_8H_{12} with aqueous hydroxide base (2 h at room temperature), which results in a 67% yield of $[NMe_4][CB_7H_8]$ after crystallisation [equation (2)].

$$6\text{-}(SMe_2)\text{-}4\text{-}CB_8H_{12} + [NMe_4]OH + 2H_2O \longrightarrow [NMe_4][CB_7H_8] + SMe_2 + B(OH)_3 + 3H_2 \quad (2)$$

The ^{11}B NMR behaviour of $[1\text{-}CB_7H_8]^-$ shows a 3:4 fluxionality at room temperature (Table 1) as pointed out initially,[26] and as more recently discussed elsewhere.[22,25,27] The ^{1}H NMR behaviour is also in accord with fluxional behaviour. In this regard we have now examined the ^{11}B NMR spectrum of this anion down to *ca.* 180 K in CD_2Cl_2 solution, and find no sign of any definitive emergence of a 2:2:1:1:1:1 relative intensity ratio that would be expected for static **III**. There is, however, considerable broadening at these low temperatures [$w_{\frac{1}{2}}(^{11}B)$ = *ca.* 510 (3 B) and *ca.* 470 Hz (4 B) at 183 K] (see also compounds below), but it is not clear whether this is due to solution-induced relaxation broadening or a slowing down of the fluxionality, or incipient equilibration between **III** and fluxional intermediates such as **IV**. The difference in energy, ΔH, between the $[CB_7H_8]^-$ structures **III** and **IV** has been calculated to be *ca.* 12 (ref. 25), < *ca.* 17 (ref. 23) and *ca.* 21 kJ mol^{-1} (ref. 27). A mean value of ΔH of 18 kJ mol^{-1} and an assumption of an arbitrary value for ΔS of 100 J K^{-1} mol^{-1} would then predict a 50:50 concentration ratio of **III**:**IV** at 180 K, so that a weighted mean time-averaged ^{11}B spectrum with contributions from both **III** and **IV** could perhaps be expected at this temperature.

We surmised that if an open structure such as **IV** were a possibility, then there was a chance that this might manifest itself in a solid-state structural analysis. However, single-crystal X-ray diffraction studies of the $[PPh_4]^+$ salt of $[1\text{-}CB_7H_8]^-$ have been beset by problems of severe disorder which have so far made it impossible to distinguish between the closed dodecahedral *closo* configuration **III** and the tetragonally faced open structure **IV**. The possibility of some opening to give something like **VI** also cannot be excluded on the basis of the X-ray work.[28] It is of interest that this last structure **IV** would on time-average give the observed mysterious 4:2:2 intensity ratio if applied to a similarly open-structured $[B_8H_8]^{2-}$ anion in dynamic equilibrium as in **VIIa** and **VIIb**. In this context it would be of interest to see the results of *ab initio*/NMR/IGLO calculations as applied to **VI** and **VII**.

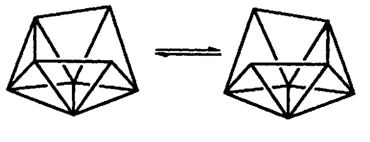
For this $[CB_7H_8]^-$ anion it is likely that crystallographic work using an alternative counter cation will be more informative, and we are working on routes to generate and crystallize suitable compounds.

An alternative strategy is to make substituted derivatives of the $[CB_7H_8]^-$ anion. These may be less prone to disorder, and/or the nature and position of the substituent might electronically favour and thereby fix individual structures among **III–VI**. We have started to explore this possibility by the synthesis of the mono- and di-iodo-substituted species $[CB_7H_7I]^-$ and $[CB_7H_6I_2]^-$, by the examination of their NMR properties, and by the examination of their crystal and molecular structures by single-crystal X-ray diffraction analysis.

We have found that both these compounds result from the straightforward iodination of the unsubstituted $[CB_7H_8]^-$ anion. A slight excess of diiodine in dichloromethane solution is discoloured by $[PPh_4][CB_7H_8]$ after 2 h at room temperature. Chromatographic separation then yields $[PPh_4][1\text{-}CB_7H_7\text{-}7\text{-}I]$ (73%) and $[PPh_4][1\text{-}CB_7H_6\text{-}7,8\text{-}I_2]$ (27%) as white crystalline solids.

The NMR properties (Table 1) indicate fluxionality, with similar characteristics to those discussed above for the unsubstituted species (also included in Table 1), suggesting similar structural ambiguity in solution. Again there is considerable broadening in the ^{11}B spectrum at lower temperatures (< *ca.* 180 K), perhaps suggesting some equilibration, or a slowing of the exchange process.

Samples of the $[PPh_4]^+$ salts suitable for single-crystal X-ray diffraction were obtained from solutions in dichloromethane that had been overlayered with hexane. The structures of both compounds (Figs. 1 and 2) were readily determined *via* heavy-atom techniques. Here it was interesting to note no disorder of the iodine atom(s), particularly in the case of the monoiodide. In both cases the data were collected at low temperatures (150 K for the monoiodo, and 200 K for the diiodo compound) and we were able to locate and to refine freely all the hydrogen atoms associated with the cages. Interatomic distances for both compounds are listed together in Table 2 for comparative purposes, and interatomic angles in Table 3.



VIIA **VIIB**

Table 2 Comparative interatomic distances (Å) for the $[PPh_4]^+$ salts of the $[1\text{-}CB_7H_7\text{-}7\text{-}I]^-$ and $[1\text{-}CB_7H_6\text{-}7,8\text{-}I_2]^-$ anions, with estimated standard deviations (e.s.d.s) in parentheses

	$[1\text{-}CB_7H_7\text{-}7\text{-}I]^-$	$[1\text{-}CB_7H_6\text{-}7,8\text{-}I_2]^-$
I(7)–B(7)	2.180(3)	2.161(3)
I(2)–B(8)		2.165(3)
C(1)–B(2)	1.517(4)	1.517(5)
C(1)–B(6)	1.596(4)	1.591(4)
C(1)–B(4)	1.699(4)	1.706(5)
C(1)–B(3)	1.701(4)	1.705(5)
B(2)–B(3)	1.817(4)	1.803(5)
B(2)–B(4)	1.817(4)	1.804(5)
B(2)–B(5)	1.693(4)	1.687(5)
B(3)–B(5)	1.918(4)	1.904(5)
B(3)–B(6)	1.900(4)	1.915(5)
B(3)–B(7)	1.687(4)	1.689(4)
B(4)–B(5)	1.903(4)	1.930(5)
B(4)–B(6)	1.896(4)	1.908(5)
B(4)–B(8)	1.706(4)	1.689(4)
B(5)–B(7)	1.800(4)	1.813(4)
B(5)–B(8)	1.827(4)	1.824(4)
B(6)–B(7)	1.803(4)	1.804(4)
B(6)–B(8)	1.823(4)	1.805(4)
B(7)–B(8)	1.602(4)	1.590(4)
C(1)–H(1)	0.96(3)	0.98(3)
B(2)–H(2)	1.07(3)	1.11(3)
B(3)–H(3)	1.08(3)	1.02(4)
B(4)–H(4)	1.08(3)	1.32(3)
B(5)–H(5)	1.11(3)	1.08(3)
B(6)–H(6)	1.08(3)	1.08(3)
B(8)–H(8)	1.38(2)	

Both anions (Figs. 1 and 2) have straightforward eight-vertex closed polyhedral structures, as seen for the parent $[B_8H_8]^{2-}$ anion,[19,20] and their cluster geometries approximate to an ideal

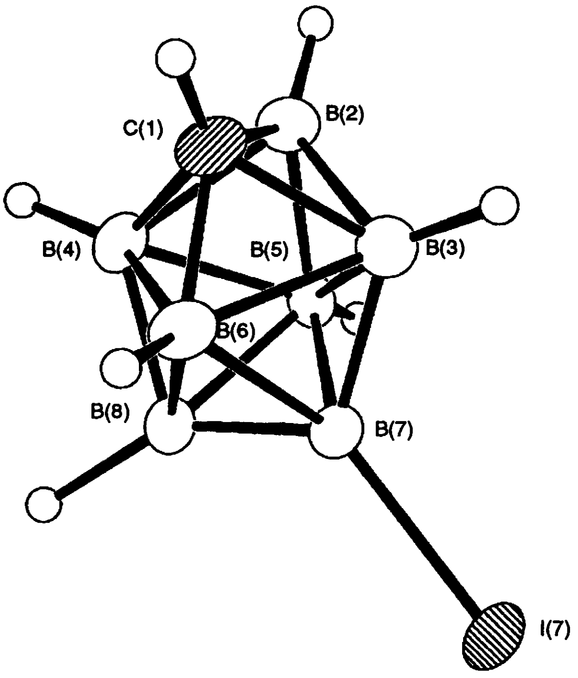


Fig. 1 ORTEP representation of the crystallographically determined molecular structure of the $[\textit{closo}\text{-}1\text{-}CB_7H_7\text{-}7\text{-}I]^-$ anion. Ellipses are shown at the 50% probability level and hydrogen atoms are drawn with an arbitrary small radius

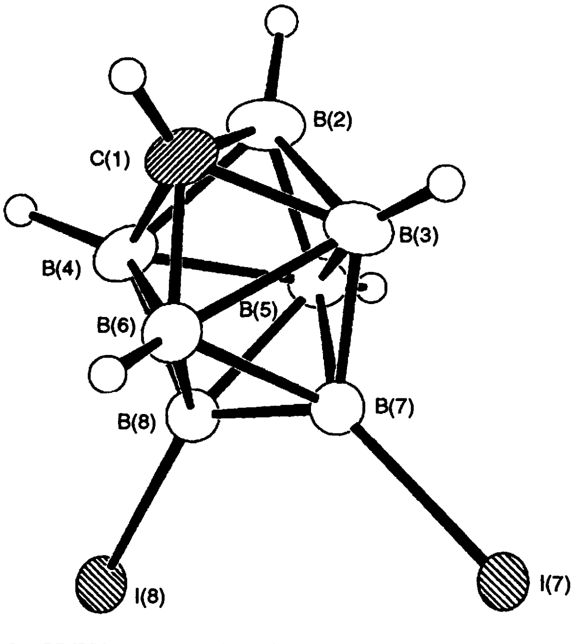
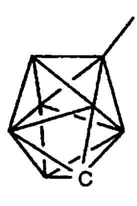


Fig. 2 ORTEP representation of the crystallographically determined molecular structure of the $[\textit{closo}\text{-}1\text{-}CB_7H_6\text{-}7,8\text{-}I_2]^-$ anion. Ellipses are shown at the 50% probability level and hydrogen atoms are drawn with an arbitrary small radius

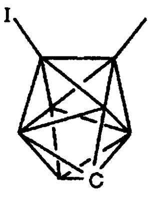
Table 3 Selected comparative angles (°) between interatomic vectors for the $[PPh_4]^+$ salts of $[1\text{-}CB_7H_7\text{-}7\text{-}I]^-$ and $[1\text{-}CB_7H_6\text{-}7,8\text{-}I_2]^-$ with e.s.d.s in parentheses

	$[1\text{-}CB_7H_7\text{-}7\text{-}I]^-$	$[1\text{-}CB_7H_6\text{-}7,8\text{-}I_2]^-$
(*i*) Boron–carbon–boron		
B(2)–C(1)–B(3)	68.5(2)	67.8(2)
B(2)–C(1)–B(4)	68.5(2)	67.8(2)
B(2)–C(1)–B(6)	115.6(2)	115.3(3)
B(3)–C(1)–B(6)	70.3(2)	70.9(2)
B(3)–C(1)–B(4)	97.2(2)	97.1(2)
B(4)–C(1)–B(6)	70.2(2)	70.6(2)
(*ii*) Carbon–boron–boron		
C(1)–B(2)–B(3)	60.6(2)	61.1(2)
C(1)–B(2)–B(4)	60.5(2)	61.1(2)
C(1)–B(2)–B(5)	101.3(2)	102.4(2)
C(1)–B(3)–B(2)	51.0(2)	51.1(2)
C(1)–B(3)–B(5)	86.5(2)	87.5(2)
C(1)–B(3)–B(6)	52.3(2)	51.8(2)
C(1)–B(3)–B(7)	106.3(2)	105.8(2)
C(1)–B(4)–B(2)	51.0(2)	51.1(2)
C(1)–B(4)–B(5)	87.0(2)	86.6(2)
C(1)–B(4)–B(6)	52.4(2)	51.9(2)
C(1)–B(4)–B(8)	107.3(2)	105.9(2)
C(1)–B(6)–B(3)	57.4(2)	57.3(2)
C(1)–B(6)–B(4)	57.5(2)	57.5(2)
C(1)–B(6)–B(7)	105.6(2)	105.6(2)
C(1)–B(6)–B(8)	106.5(2)	105.7(2)
(*iii*) Boron–boron–boron		
B(3)–B(7)–B(8)	107.9(2)	106.6(2)
B(3)–B(7)–B(5)	66.6(2)	65.7(2)
B(3)–B(7)–B(6)	65.9(2)	66.4(2)
B(5)–B(7)–B(6)	89.9(2)	90.5(2)
B(5)–B(7)–B(8)	64.7(2)	64.4(2)
B(6)–B(7)–B(8)	64.4(2)	63.9(2)
B(4)–B(8)–B(5)	65.1(2)	66.5(2)
B(4)–B(8)–B(6)	64.9(2)	66.1(2)
B(4)–B(8)–B(7)	104.6(2)	106.6(2)
B(5)–B(8)–B(6)	88.5(2)	90.1(2)
B(5)–B(8)–B(7)	62.9(2)	63.7(2)
B(6)–B(8)–B(7)	63.2(2)	63.8(2)
B(2)–B(3)–B(7)	109.0(2)	109.2(2)
B(2)–B(4)–B(8)	110.2(2)	109.0(2)
B(2)–B(5)–B(7)	109.4(2)	108.8(2)
B(2)–B(5)–B(8)	110.3(2)	108.2(2)
Other B–B–B	52.5(2)–66.1(2) 83.7(2)–91.2(2)	51.8(2)–67.1(2) 83.6(2)–90.3(2)
(*iv*) Boron–boron–iodine		
B(3)–B(7)–I(7)	124.2(2)	122.9(2)
B(5)–B(7)–I(7)	131.8(2)	133.7(2)
B(6)–B(7)–I(7)	138.3(2)	135.7(2)
B(8)–B(7)–I(7)	127.9(2)	130.5(2)
B(4)–B(8)–I(8)		123.4(2)
B(5)–B(8)–I(8)		134.9(2)
B(6)–B(8)–I(8)		135.0(2)
B(7)–B(8)–I(8)		130.0(2)

triangulated dodecahedron of D_{2d} symmetry. In both cases the cluster carbon atom is located in the cluster 1 position, of cluster connectivity four, and the iodide substituents are β to this in the 7 position (monoiodide, Fig. 1) and 7- and 8-positions (diiodide, Fig. 2) (schematics **VIII** and **IX** respectively). These iodinated 7- and 8-positions are also of lower cluster connectivity four. Although 'long' interboron distances (> 190 pm) are observed for some connectivities in both compounds, these seem to be more a feature of the dodecahedral geometry than of any cluster-opening towards *nido* or *isonido*. Comparable distances are also observed in $[B_8H_8]^{2-}$ experimentally,[20] and also emerge from high-level *ab initio* calculations.[22,24,27]



VIII



IX

As expected, the interatomic distances to the carbon cluster atom in the 1 position are significantly shorter than the distances to boron on the otherwise equivalent 2 position, and they are also shorter than the comparable distances in $[B_8H_8]^{2-}$ itself (see Table 2). Thus, for example, the short B(1)–B(2) distance of 1.56(2) Å in $[B_8H_8]^{2-}$ has shortened to 1.517(4) and 1.517(5) Å for C(1)–B(2) in the mono- and di-iodo derivatives respectively. The electronic effects of the iodine substituents produce slight but significant lengthening of the connectivities to the substituted boron vertices in both of the species. The effect is most conveniently seen by comparison between distances to the substituted 7 position and the unsubstituted 8 position of the monoiodide anion (see Table 2). A similar but less significant effect is noted when comparing distances to the substituted vertices of both iodo derivatives with the relevant otherwise equivalent distances in $[B_8H_8]^{2-}$. Above all, it is apparent that there is no marked cluster opening as could possibly be the case with unsubstituted $[CB_7H_8]^-$ (**V** and **VI** above).

We are at present continuing this approach by the synthesis of neutral ligand species CB_7H_7L, where L = NMe_3, PPh_3 *etc.*, which may be prepared from the $[1\text{-}CB_7H_8]^-$ anion by treatment with suitable ligands L under oxidizing conditions. Preliminary results indicate that these generally have static structures at room temperature in solution, and we hope to be able to report fully on these species in the future.

Experimental

Preparation of $[NMe_4][CB_7H_8]$ *from* 6-(NMe_3)-4-CB_8H_{12} *and* NaH.—Sodium hydride (300 mg of a 50% suspension in oil, *ca.* 6.25 mmol) was added to a solution of 6-(NMe_3)-4-CB_8H_{12} (1.0 g, 5.89 mmol; prepared as in ref. 29) in thf (20 cm^3) and the mixture then heated at 60 °C for 8 h. The excess sodium hydride was removed by filtration (Schlenk apparatus), the filtrate was evapoated and the residue dried at 20 °C (oil-pump vacuum) for 2 h. Water (*ca.* 30 cm^3) was then added carefully, the residual thf was evaporated (rotary evaporator) and the remaining aqueous solution filtered in air. Addition of NMe_4Cl (647 mg, 5.89 mmol) to the filtrate precipitated a white solid, which was filtered off and recrystallised from boiling 35% aqueous EtOH, and then dried *in vacuo* at 20 °C for 6 h to give $[NMe_4][CB_7H_8]$ (651 mg, 65%). A second product, *arachno*-4-CB_8H_{14} (150 mg, 22%), readily identified as such by NMR spectroscopy, was isolated after acidification (with Me_3CO_2H) of the mother-liquor after crystallisation, followed by extraction with hexane.

Preparation of $[NMe_4][CB_7H_8]$ *from* 6-(NMe_3)-4-CB_8H_{12} *and* $NaBH_4$.—The compound 6-(NMe_3)-4-CB_8H_{12} (300 mg, 1.75 mmol) was dissolved in 1,2-dimethoxyethane (20 cm^3) and $NaBH_4$ (500 mg, 13.2 mmol) added. The mixture was heated (80 °C) and stirred for 12 h, cooled, treated with water (40 cm^3), and the 1,2-dimethoxyethane then removed (rotary evaporator, water-pump pressure). Treatment of the resulting aqueous solution with aqueous NMe_4Cl (5 mol dm^{-3}, 1 cm^3) gave a white precipitate, which was filtered off, washed with water and recrystallised from acetone–ethanol to give $[NMe_4][CB_7H_8]$ as a white crystalline air-stable solid (249 mg, 146 mmol, 83.5%). The $[PPh_4]^+$ salt is prepared similarly by the use of PPh_4Cl instead of NMe_4Cl.

Table 4 Crystallographic data[a] for the $[PPh_4]^+$ salts of $[1\text{-}CB_7H_7\text{-}7\text{-}I]^-$ and $[1\text{-}CB_7H_6\text{-}7,8\text{-}I_2]^-$

Compound	$[PPh_4][1\text{-}CB_7H_7\text{-}7\text{-}I]$	$[PPh_4][1\text{-}CB_7H_6\text{-}7,8\text{-}I_2]$
Formula	$C_{25}H_{27}B_7IP$	$C_{25}H_{26}B_7I_2P$
M	561.00	686.94
Crystal dimensions/mm	0.5 × 0.4 × 0.3	0.42 × 0.30 × 0.19
Crystal system	Triclinic	Triclinic
a/Å	7.4703(7)	7.8389(8)
b/Å	12.766(2)	13.4489(11)
c/Å	13.9102(12)	13.6337(13)
α/°	100.973(10)	98.009(9)
β/°	92.886(7)	93.060(7)
γ/°	93.005(10)	92.939(7)
U/Å^3	1298.1(2)	1418.8(2)
Space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
D_c/g cm^{-3}	1.44	1.61
$F(000)$	560	664
μ/mm^{-1}	1.308	2.286
T/K	150	200
Max., min. transmission factors	0.6061, 0.7648	0.5041, 0.6189
No. of data collected	4651	5150
No. of unique data, n	4561	4996
No. of observed data[b]	3867	4284
R_{sig}[c]	0.0267	0.0179
ρ_{max},ρ_{min}/e Å^{-3}	0.46, −0.42	0.47, −0.49
Δ/σ_{max}	0.001	0.001
wR_2[d]	0.0348	0.0504
R_1[e]	0.0226	0.0208
Weighting parameters x,y[f]	0.0272, 0.7201	0.0238, 1.4147
No. of parameters, p	335	340
Goodness of fit[g]	1.032	1.026

[a] Common to both structures: Mo-Kα radiation, λ = 0.710 69 Å, ω–θ scan mode, scan speeds 1.5–8.0° min^{-1}, scan widths 1.05 + α-doublet splitting, $4.0 < 2\theta < 50.0°$. [b] Criterion for observed reflection, $|F_o| > 4.0\sigma(|F_o|)$, used only in calculation of R_1. [c] $R_{sig} = \Sigma[\sigma(F_o^2)]/\Sigma(F_o^2)$. [d] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$. [e] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [f] Weighting scheme used $w = [\sigma^2(F_o^2) + (xP)^2 + yP]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$. [g] Goodness of fit $= \Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{\frac{1}{2}}$.

Preparation of $[NMe_4][CB_7H_8]$ *from* $6\text{-}(SMe_2)\text{-}4\text{-}CB_8H_{12}$ *and* $[NMe_4]OH$.—The compound $6\text{-}(SMe_2)\text{-}4\text{-}CB_8H_{12}$ (500 mg, 2.87 mmol; prepared as in ref. 29) was dissolved in benzene (30 cm^3) and an aqueous solution of $[NMe_4]OH$(10%, 10 cm^3) added. The mixture was stirred for 2 h and the resulting precipitate filtered off, washed with benzene and water, and recrystallised from acetone–ethanol as above to yield $[NMe_4][CB_7H_8]$ (330 mg, 193 mmol, 67%).

Preparation of $[PPh_4][CB_7H_7I]$ *and* $[PPh_4][CB_7H_6I_2]$ *from the Reaction of* $[PPh_4][CB_7H_8]$ *with* I_2.—The compound $[PPh_4][CB_7H_8]$ (700 mg, 1.60 mmol) was dissolved in dichloromethane (20 cm^3), a slight excess of I_2 (420 mg, 1.65 mmol) was added and the solution stirred until colourless (*ca.* 2 h). Column chromatography (silica gel 1.5 × 20 cm; CH_2Cl_2) gave two fractions: R_f (CH_2Cl_2) 0.38 (A) and 0.25 (B) [analytical TLC was performed on foil-backed silica-gel G sheets (supplier: Kavalier)]. Removal of solvent (rotary evaporator, water-pump pressure) gave $[PPh_4][CB_7H_7I]$ from fraction A (650 mg, 1.15 mmol, 73%) and $[PPh_4][CB_7H_6I_2]$ from fraction B (300 mg, 0.43 mmol, 27%), both as white crystalline solids. Crystalline samples suitable for single-crystal X-ray work were grown from dichloromethane–hexane.

NMR Spectroscopy.—Nuclear magnetic resonance spectroscopy was carried out by standard techniques;[30] chemical shifts δ are quoted in ppm, ±0.5 to low field (high frequency) of Ξ 32.083 971 MHz (nominally $BF_3\cdot OEt_2$ in $CDCl_3$) for ^{11}B and ±0.05 to low field (high frequency) of Ξ 100 MHz ($SiMe_4$) for ^1H, Ξ being defined as in ref. 31.

Single-crystal X-ray Diffraction Analysis.—All crystallographic measurements were carried out on a Stoe STADI4 diffractometer operating in the ω–θ scan mode using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). Crystal data are listed in Table 4 together with details of data collection and structure refinement. Both data sets were corrected for absorption semi-empirically using azimuthal ψ-scans.

Both structures were solved by direct methods using SHELXS 86[32] and refined by full-matrix least squares (based on F^2) using SHELXL 93.[33] Refinement was essentially the same for all compounds such that all non-hydrogen atoms were refined with anisotropic displacement parameters. Geometrical restraints were applied to the phenyl groups such that each group remained flat with overall C_{2v} symmetry. In both structures the phenyl hydrogen atoms of the $[PPh_4]^+$ cation were constrained in calculated positions (C–H 0.93 Å) and were assigned a fixed isotropic thermal parameter of $1.2U_{eq}$ of the parent carbon atom. Fractional atomic coordinates for $[PPh_4][1\text{-}CB_7H_7\text{-}7\text{-}I]$ and $[PPh_4][1\text{-}CB_7H_6\text{-}7,8\text{-}I_2]$ are listed in Tables 5 and 6 respectively. Figs. 1 and 2 were drawn using ORTEP.[34]

Additional material available from the Cambridge Crystallographic Data Centre comprises remaining H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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Table 5 Non-hydrogen fractional atomic coordinates (× 10^4) together with borane–hydrogen fractional atomic coordinates (× 10^3) for $[PPh_4][1\text{-}CB_7H_7\text{-}7\text{-}I]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
I(7)	7 988.1(2)	8 317.57(15)	9 002.64(11)
P(1)	9 533.8(8)	7 580.1(4)	12 210.1(4)
C(11)	10 890(3)	7 405(2)	11 168(2)
C(12)	12 298(3)	8 173(2)	11 164(2)
C(13)	13 358(3)	8 081(2)	10 368(2)
C(14)	13 045(3)	7 234(2)	9 586(2)
C(15)	11 660(3)	6 469(2)	9 590(2)
C(16)	10 579(3)	6 549(2)	10 383(2)
C(21)	11 048(3)	7 794(2)	13 281(2)
C(22)	11 084(3)	8 745(2)	13 964(2)
C(23)	12 332(4)	8 922(2)	14 760(2)
C(24)	13 521(4)	8 157(2)	14 874(2)
C(25)	13 498(3)	7 210(2)	14 194(2)
C(26)	12 271(3)	7 026(2)	13 392(2)
C(31)	8 189(3)	8 707(2)	12 241(2)
C(32)	8 511(3)	9 476(2)	11 674(2)
C(33)	7 392(4)	10 321(2)	11 729(2)
C(34)	5 982(3)	10 401(2)	12 243(2)
C(35)	5 675(3)	9 638(2)	12 910(2)
C(36)	6 763(3)	8 787(2)	12 865(2)
C(41)	7 965(3)	6 451(2)	12 149(2)
C(42)	8 035(3)	5 786(2)	12 835(2)
C(43)	6 690(3)	4 979(2)	12 790(2)
C(44)	5 297(3)	4 841(2)	12 081(2)
C(45)	5 221(3)	5 504(2)	11 397(2)
C(46)	6 548(3)	6 312(2)	11 428(2)
C(1)	9 513(4)	6 326(2)	5 912(2)
B(2)	7 529(4)	5 977(3)	5 786(2)
B(3)	8 603(4)	6 360(2)	7 013(2)
B(4)	8 277(4)	7 272(3)	5 540(2)
B(5)	6 637(4)	7 029(2)	6 490(2)
B(6)	10 017(4)	7 460(2)	6 609(2)
B(7)	8 260(4)	7 653(2)	7 456(2)
B(8)	8 065(4)	8 248(2)	6 544(2)
H(1)	10 453(43)	5 915(25)	5 610(23)
H(2)	6 944(37)	5 238(23)	5 366(20)
H(3)	8 862(36)	5 756(22)	7 439(20)
H(4)	8 177(38)	7 371(23)	4 783(21)
H(5)	5 169(34)	7 048(20)	6 567(18)
H(6)	11 407(39)	7 764(22)	6 751(20)
H(8)	8 205(26)	9 212(16)	6 237(14)

Table 6 Non-hydrogen fractional atomic coordinates (× 10^4) and borane–hydrogen fractional atomic coordinates (× 10^3) for $[PPh_4]$-$[1\text{-}CB_7H_6\text{-}7,8\text{-}I_2]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
I(7)	1933.8(2)	4228.76(13)	3738.00(13)
I(8)	1952.2(2)	3806.70(13)	491.66(13)
P(1)	−250.4(8)	2562.2(5)	−2812.1(5)
C(1)	528(4)	947(2)	2024(2)
B(2)	2440(5)	818(3)	2091(3)
B(3)	1551(4)	1460(2)	1124(3)
B(4)	1543(4)	1700(3)	3017(3)
B(5)	3262(4)	2007(2)	2124(3)
B(6)	−10(4)	2072(2)	2024(2)
B(7)	1735(4)	2861(2)	2683(2)
B(8)	1729(4)	2713(2)	1505(2)
C(11)	−1544(3)	2590(2)	−1767(2)
C(12)	−2776(3)	3309(2)	−1655(2)
C(13)	−3856(4)	3320(2)	−885(2)
C(14)	−3726(4)	2617(2)	−238(2)
C(15)	−2519(3)	1904(2)	−348(2)
C(16)	−1414(3)	1890(2)	−1110(2)
C(21)	−1722(3)	2468(2)	−3833(2)
C(22)	−3237(3)	1868(2)	−3906(2)
C(23)	−4446(4)	1835(2)	−4685(2)
C(24)	−4154(4)	2397(2)	−5445(2)
C(25)	−2638(4)	2970(2)	−5439(2)
C(26)	−1422(4)	3014(2)	−4657(2)
C(31)	1084(3)	1512(2)	−2893(2)
C(32)	2423(3)	1531(2)	−2171(2)
C(33)	3526(3)	757(2)	−2230(2)
C(34)	3316(4)	−23(2)	−3009(2)
C(35)	2000(4)	−47(2)	−3725(2)
C(36)	875(3)	721(2)	−3672(2)
C(41)	1202(3)	3652(2)	−2720(2)
C(42)	2521(4)	3637(2)	−3371(2)
C(43)	3698(4)	4450(2)	−3292(2)
C(44)	3575(4)	5268(2)	−2568(2)
C(45)	2271(4)	5291(2)	−1933(2)
C(46)	1067(3)	4484(2)	−2001(2)
H(1)	−32(4)	38(2)	201(2)
H(2)	306(4)	10(2)	211(2)
H(3)	140(5)	114(3)	40(3)
H(4)	155(4)	141(2)	390(2)
H(5)	463(4)	216(2)	218(2)
H(6)	−135(4)	221(2)	195(2)

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