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Macropolyhedral boron-containing cluster chemistry. An X-ray diffraction and nuclear magnetic resonance study of the double cluster 11-vertex:11-vertex tetracarbaborane $C_4B_{18}H_{22}$

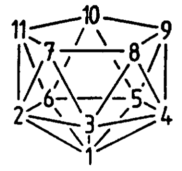
Zbyněk Janoušek,[a] Bohumil Štíbr,[a] Xavier L. R. Fontaine,[b] John D. Kennedy[b] and Mark Thornton-Pett[b]

[a] *Institute of Inorganic Chemistry, The Academy of Sciences of Czech Republic, 250 68 Řež near Prague, The Czech Republic*
[b] *School of Chemistry, The University of Leeds, Leeds LS2 9JT, UK*

The macropolyhedral compound '*neo*'-$C_4B_{18}H_{22}$ has been examined by single-crystal X-ray diffraction analysis and NMR spectroscopy, and compared with neutral 7,8-$C_2B_9H_{13}$ and the [7,8-$C_2B_9H_{12}$]$^-$ anion. Crystals (from hexane–chloroform) were orthorhombic, space group *Pbca*, with $Z = 16$, and with $a = 23.690(2)$, $b = 21.585(2)$ and $c = 12.3653(8)$ Å at 150 K. The structure was refined to a *wR*2 value of 0.1218 using all 4640 unique data. The molecular structure consists of two *nido*-type {7,8-$C_2B_9H_{11}$} units symmetrically conjoined at the 9,10 positions such that B(9)–B(9′) is *ca.* 1.65 Å and B(9)–B(10′) and B(10)–B(9′) are *ca.* 1.96 Å. Comparison is made with the previously established structure of [*nido*-7,8-$C_2B_9H_{12}$]$^-$. Multiple-element, multiple-resonance, and multidimensional NMR spectroscopy have been used to determine and assign the ^{11}B and ^{1}H chemical shifts and these are compared with those for neutral *nido*-7,8-$C_2B_9H_{13}$ and for [*nido*-7,8-$C_2B_9H_{12}$]$^-$.

Two adjacent elements in the Periodic Table, boron and carbon, are unique in forming extensive series of stable complex hydrides and related compounds. In this context it could perhaps be argued that the polyhedral chemistry of the boron hydrides and their derivatives is potentially as extensive as the chain and ring chemistry of the carbon hydrides and their derivatives. However, unlike that of the carbon hydrides, the subdiscipline of polyhedral boron hydride chemistry is relatively underdeveloped, and many of the structural and behavioural features that have so far been discovered are not yet well defined. This particularly applies to condensed intercluster fusions that result in 'macropolyhedral' molecules; a knowledge of these is crucial for the development of a borane-based chemistry to parallel, complement and extend the extensive oligomeric and macromolecular chemistry of carbon. In the development of this macropolyhedral chemistry it is of interest and importance to define particular building blocks by accurate structural work and by NMR spectroscopy so that their features and effects can be assessed and catalogued.

Over twenty years ago work in one of our laboratories revealed that the oxidation by chromic acid of the eleven-vertex anion [*nido*-7,8-$C_2B_9H_{12}$]$^-$ yielded two isomeric compounds of formulation $C_4B_{18}H_{22}$.[1–4] One of these, previously referred to as '*iso*'-$C_4B_{18}H_{22}$, was found by single-crystal X-ray diffraction analysis[3] to consist of a twelve-vertex *closo*-{1,2-$C_2B_{10}H_{11}$} unit and a ten-vertex *nido*-{5,6-$C_2B_8H_{11}$} unit conjoined by one direct two-electron two-centre interboron linkage, *exo* to *exo* between the B(3) position of the *closo* cluster and the B(8) position of the *nido* cluster. Although mechanistically interesting in that the product implies an intercluster transfer of a boron atom, in structural terms the two-electron two-centre linkage is a straightforward feature. The second compound, previously referred to as '*neo*'-$C_4B_{18}H_{22}$, consists of two *nido*-type eleven-vertex {7,8-$C_2B_9H_{11}$} clusters mutually conjoined at the 9,10 positions by a more interesting four-electron multicentre bonding link. However, only unassigned ^{11}B NMR data[2] and an approximate molecular structure[4] were reported. In view of the contemporaneously developing importance and consequent interest in 'big-cluster' macropolyhedral boron chemistry[5–9] there is merit in the assessment and description of the intercluster fusion mode in some detail.



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Here therefore we now report and briefly discuss a much more accurately determined molecular structure of this second $C_4B_{18}H_{22}$ isomer, together with more detailed NMR work that has enabled us fully to assign the ^{11}B and ^{1}H NMR spectra. The numbering scheme for the *nido* eleven-vertex clusters encountered in this work is in structure **I**.

Results and Discussion

Although $C_4B_{18}H_{22}$ can be recrystallized readily from a number of organic solvents to give large, beautiful, highly refractive crystals, the crystals obtained are very soft and, in our experience so far, generally adhere strongly to the interior surface of the vessel used for crystallization. Isolated single crystals suitable for diffraction work are therefore difficult to obtain. The crystal used in this work was ultimately obtained by overlayering a solution of $C_4B_{18}H_{22}$ in chloroform with hexane and allowing the solvents mutually to diffuse.

To increase accuracy the crystallographic data were collected at a crystal temperature of 150 K. The calculated cell dimensions thus obtained corresponded very closely with those for the original structure determination[4] (allowing for the difference in data-collection temperature) and the subsequent determination of the space group showed that the carbaborane had crystallized in exactly the same fashion. There are two independent molecules in the asymmetric part of the unit cell, and these are related by a pseudo two-fold axis parallel to the *y* axis. A drawing of the structure of one of the two molecules is given in Fig. 1. The two independent molecules have very similar structures that are

Table 1 Selected interatomic distances (Å) for $C_4B_{18}H_{22}$ together with those of [*nido*-7,8-$C_2B_9H_{12}$]$^-$ (data from ref. 10 for comparison), with estimated standard deviations (e.s.d.s) in parentheses

	$C_4B_{18}H_{22}$*				
	1A	**IB**	**IIA**	**IIB**	[7,8-$C_2B_9H_{12}$]$^-$
B(1)–B(2)	1.764(2)	1.762(2)	1.763(2)	1.763(2)	1.762(3)
B(1)–B(3)	1.809(2)	1.809(2)	1.815(2)	1.812(2)	1.768(3)
B(1)–B(4)	1.774(2)	1.773(2)	1.775(2)	1.776(2)	1.772(3)
B(1)–B(5)	1.759(2)	1.758(2)	1.755(2)	1.757(2)	1.794(3)
B(1)–B(6)	1.781(2)	1.774(3)	1.779(2)	1.785(2)	1.799(3)
B(2)–B(3)	1.766(2)	1.765(2)	1.766(2)	1.765(2)	1.759(3)
B(2)–B(6)	1.761(2)	1.769(2)	1.769(2)	1.764(2)	1.763(3)
B(2)–C(7)	1.689(2)	1.688(2)	1.692(2)	1.688(2)	1.717(3)
B(2)–B(11)	1.790(2)	1.793(2)	1.798(2)	1.795(2)	1.796(3)
B(3)–B(4)	1.771(2)	1.775(2)	1.769(2)	1.773(2)	1.764(3)
B(3)–C(7)	1.703(2)	1.699(2)	1.702(2)	1.701(2)	1.707(3)
B(3)–C(8)	1.694(2)	1.701(2)	1.698(2)	1.709(2)	1.726(3)
B(4)–B(5)	1.761(2)	1.758(2)	1.760(2)	1.756(2)	1.754(3)
B(4)–C(8)	1.738(2)	1.748(2)	1.737(2)	1.743(2)	1.711(3)
B(4)–B(9)	1.756(2)	1.759(2)	1.760(2)	1.755(2)	1.793(3)
B(5)–B(6)	1.794(2)	1.796(2)	1.789(2)	1.788(2)	1.816(3)
B(5)–B(9)	1.774(2)	1.774(2)	1.772(2)	1.772(2)	1.761(3)
B(5)–B(10)	1.885(2)	1.889(2)	1.877(2)	1.881(1)	1.775(3)
B(6)–B(10)	1.848(2)	1.851(2)	1.842(2)	1.847(2)	1.777(3)
B(6)–B(11)	1.820(2)	1.822(2)	1.829(2)	1.825(2)	1.771(3)
C(7)–C(8)	1.537(2)	1.540(2)	1.534(2)	1.538(2)	1.542(3)
C(7)–B(11)	1.647(2)	1.647(2)	1.647(2)	1.645(2)	1.613(3)
C(8)–B(9)	1.607(2)	1.604(2)	1.602(2)	1.601(2)	1.606(3)
B(9)–B(10)	1.772(2)	1.810(2)	1.817(2)	1.821(2)	1.817(3)
B(10)–B(11)	1.897(2)	1.900(2)	1.902(2)	1.897(2)	1.849(3)
B(9a)–B(9b)	1.652(5)		1.653(5)		
B(9a)–B(10b)	1.972(5)		1.964(5)		
B(9b)–B(10a)	1.959(5)		1.950(5)		

* **IA** = molecule 1, side a; **IB** = molecule 1, side b; **IIA** = molecule 2, side a; **IIB** = molecule 2, side b. See also footnote to Table 2.

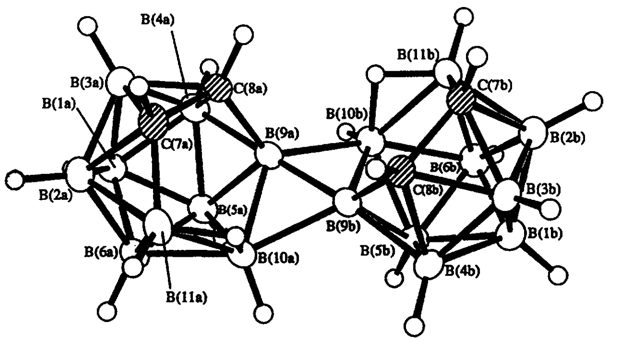


Fig. 1 An ORTEP drawing[10] of the crystallographically determined molecular structure of molecule 1 of $C_4B_{18}H_{22}$. Two crystallographically independent near-identical molecules occur in the unit cell. Boron and carbon atoms are represented as ellipsoids at the 50% probability level, and hydrogen atoms as circles, each with an arbitrary small radius. See footnote to Table 2 for additional information about numbering

Table 2 Selected angles (°) between interatomic vectors for $C_4B_{18}H_{22}$ with e.s.d.s in parentheses*

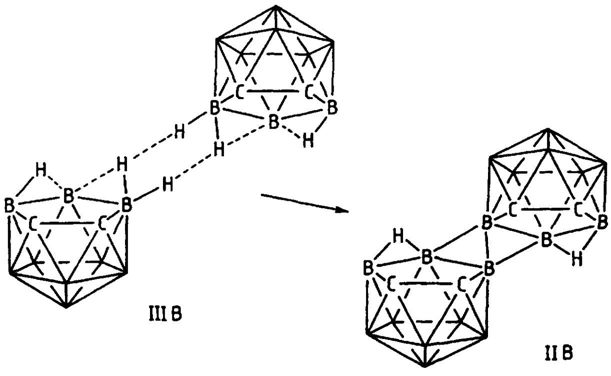
	IA	**IB**	**IIA**	**IIB**
C(7)–C(8)–B(9)	114.02(12)	113.89(12)	114.07(12)	114.15(12)
C(8)–B(9)–B(10)	108.12(12)	108.62(12)	108.36(11)	108.43(11)
B(9)–B(10)–B(11)	99.96(11)	99.34(11)	99.36(11)	99.01(10)
B(10)–B(11)–C(7)	104.83(11)	105.31(11)	104.97(11)	105.66(11)
B(11)–C(7)–C(8)	112.98(12)	112.73(12)	113.13(12)	112.59(12)
B(10′)–B(9)–B(4)	115.50(11)	114.80(11)	113.86(11)	112.78(11)
B(10′)–B(9)–B(5)	116.80(11)	116.58(11)	115.43(11)	114.85(11)
B(10′)–B(9)–C(8)	126.00(12)	125.46(12)	126.40(11)	126.21(11)
B(10′)–B(9)–B(10)	118.67(11)	119.10(11)	119.31(11)	119.79(11)
B(9)–B(9′)–B(4′)	173.35(13)	173.93(13)	170.43(13)	171.35(13)
B(9)–B(9′)–B(5′)	119.16(12)	118.98(12)	116.32(12)	116.37(12)
B(9)–B(9′)–C(8′)	123.31(12)	122.94(12)	126.49(12)	126.13(12)
B(9)–B(9′)–B(10)	59.24(9)	59.13(9)	59.89(9)	59.74(9)
B(9)–B(9′)–B(10′)	69.23(10)	68.83(10)	68.67(9)	68.24(9)
B(9′)–B(10)–B(5)	100.37(10)	99.92(11)	98.95(10)	98.34(10)
B(9′)–B(10)–B(6)	152.48(12)	151.97(12)	152.33(12)	151.76(12)
B(9′)–B(10)–B(9)	51.92(8)	51.64(8)	51.87(8)	51.60(8)
B(9′)–B(10)–B(11)	120.07(11)	119.79(11)	121.71(11)	122.13(11)

* Symbolism as in Table 1. Note the relationship between the primed numbering system and the a,b numbering system of Fig. 1: for example B(10′)–B(9)–B(4) will be B(10b)–B(9a)–B(4a) for side a and B(10a)–B(9b)–B(4b) for side b, and so on.

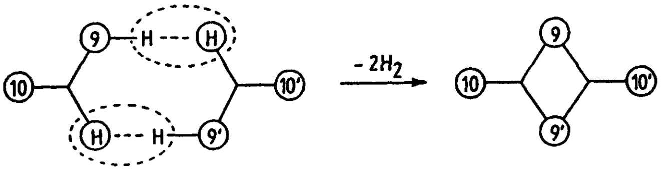
essentially identical within experimental error. Selected interatomic distances and angles for both are in Tables 1 and 2.

It can readily be seen that each molecule consists of two eleven-vertex *nido*-shaped {7,8-$C_2B_9H_{11}$} subunits linked (9,9′), (9,10′) and (9′,10) between the two atom pairs of B(9)B(10) and B(9′)B(10′). The B(9) positions do not have hydrogen atoms bound to them, and the intercluster B(9)–B(9′) distance is short, at 1.652(2) (molecule 1) and 1.653(2) Å (molecule 2), indicating much two-electron two-centre character to this linkage. All the other boron and carbon atoms have *exo*-terminal atoms bound to them, and, in addition, the B(10) and B(11) atoms in each cluster have a mutually bridging hydrogen atom associated with them. The B(10) atom is linked to the B(9′) atom in the other cluster [as is, conversely, B(9) to B(10′)] by a relatively long linkage of nearly 2 Å. The mutual orientation of the two clusters is such that, for each cluster, the disposition of the intercluster B(9)B(10)B(9′) linkage relative to the B(9)B(10) region is very similar to the disposition of the B(10)B(11)H(μ-10,11) bridging-hydrogen unit relative to the B(10)B(11) region, *i.e.* the B(9′) position of the opposing cluster takes up a position, relative to B(9)B(10), that would be equivalent to a bridging hydrogen atom[11,12] in the neutral single-cluster species 7,8-$C_2B_9H_{13}$.

In terms of a model to describe the bonding between the two subclusters, these dimensions and orientations therefore tend to confirm the original[2] proposition that there are two two-

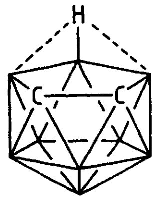


Scheme 1

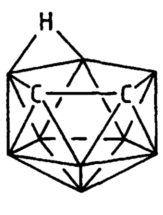


III A

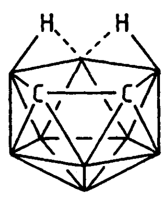
II A



IV



V



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electron three-centre bonds between the two subclusters. In this model B(9) is bound by a three-centre bond to B(9′) and B(10′) in the other cluster, and B(9′) is similarly bound to B(9) and B(10) (schematic structure **II**; see also Scheme 1). A consequence of this is a strong net bonding along the central B(9)–B(9′) vector, as also discussed in the following paragraph.

The oxidation in the preparative reaction,[1,2] starting notionally from neutral 7,8-$C_2B_9H_{11}$, can be visualized as a formal four-electron bis(dihydrogen) elimination from the (9,10) regions of the two $C_2B_9H_{13}$ molecules as in **III**. In valence-bond sum this engenders what is essentially a two-electron two-centre bond between the B(9) and B(9′) atoms, and bonding essentially of order 0.5 between B(9) and B(10′), and between B(10) and B(9′), in accord with the observed intercluster distances. This would leave the essential *nido* character of each subcluster unit little perturbed, in accord with the detailed intracluster dimensions and with the NMR properties as discussed below.

The constraints of the intracluster linkage engender a particular relative orientation of the two subclusters. The first point of interest here is that the relative positions of the two *nido* open faces constitute a *syn* configuration in that they are on the same side of the molecule. In this they may be compared with, for example, the well known macropolyhedral borane $B_{18}H_{22}$, which exhibits both *syn* and *anti* configurations.[13] It is interesting to speculate as to the nature of any mechanistic control for *syn*- *versus anti*-$C_4B_{18}H_{22}$ here, and also whether an *anti* form of $C_4B_{18}H_{22}$ may be isolatable. Another closely related isomeric possibility in this context is the one of fusion of the B(9)B(10) site with B(10′)B(11′) rather than B(9′)B(10′). These $(C_2B_9H_{11})_2$ configurations are of course different from the more evolved '*iso*'-$(C_2B_{10}H_{11})(C_2B_8H_{11})$ configuration[3] mentioned above. Mechanistically the *iso* configuration could evolve by the capping of the b subcluster (Fig. 1) with the B(9a) atom and severance of B(9b)–B(10a) and of all links of B(9a) to the a subcluster, except for B(9a)–B(5a).

A second point of interest is that the B(9)B(10)B(9′)B(10′) intercluster unit has a bent 'butterfly' configuration, with fold angles of 33.8(1) (molecule 1) and 32.5(1)° (molecule 2) that may by compared to typical[14,15] *arachno* four-vertex dihedral angles of *ca.* 30°. In this context it can be pointed out that, geometrically, the $C_4B_{18}H_{22}$ system is in fact a three-cluster fused system, with each of the two *nido* eleven-vertex clusters fused *via* two common boron atoms to a central *arachno* four-vertex cluster. However, the bent geometry does contrast to that of the equivalent four-boron region in the anion $[(B_{10}H_9)_2]^{2-}$, which is planar.[16] This could indicate that there may be an inherent symmetry to this type of linkage and that in $C_4B_{18}H_{22}$ it is perturbed by the lower symmetry of the *syn* disposition of the two $\{C_2B_9\}$ subclusters. In this regard non-bonded interactions could be important in determining the angular positions, the intercluster distances H(μ-10,11)···H(8′), H(4)···H(10′), and H(5)···H(10′) being 2.58(2), 2.75(2) and 2.94(2) Å respectively for molecule 1, and 2.65(2), 2.60(2) and 2.97(2) Å respectively for molecule 2, all comparable with typical hydrogen van der Waals radius sums[17] of 2.4–2.9 Å [note also that there is an NMR nuclear Overhauser effect (NOE) between ^{1}H(μ-10,11) and ^{1}H(8′); see footnote *h* in Table 3 below]. These non-bonded effects could also influence the intercluster distances as well as the angles. For example, in the $[(B_{10}H_9)_2]^{2-}$ anion the shorter intercluster link [equivalent to B(9)–B(9′) in $C_4B_{18}H_{22}$] is 1.72(1) Å, *versus* the longer one at 1.92(1) Å, so the difference of 0.20 Å is not nearly so great as that of 0.32 Å in $C_4B_{18}H_{22}$. Another factor here will be the differences in *intra*cluster bonding for the boron atoms involved in the *inter*cluster linkage {for example, the B(9)–B(10) linkage equivalent in $[(B_{10}H_9)_2]^{2-}$ is 1.68(1) Å *versus* 1.804(8) Å in $C_4B_{18}H_{22}$}. It would be of interest to see some rigorous theoretical treatments for this type of intercluster coupling.

It is useful in this context to compare the detailed dimensions of the two *nido* eleven-vertex subclusters of $C_4B_{18}H_{22}$ with those of equivalent non-conjoined $\{7,8\text{-}C_2B_9\}$ cluster compounds. Neutral 7,8-$C_2B_9H_{13}$ would be the ideal comparison in view of the proposed bonding scheme (structure **II** and ref. 2), but structural data for this compound, which would be important for structural comparison in the vast field of twelve-vertex $\{MC_2B_9\}$ cluster chemistry, are surprisingly not available. However, data for the closely related [7,8-$C_2B_9H_{12}]^-$ anion are available,[11] and these are included in Table 1 for comparison. This anion has an *endo*-type hydrogen atom at B(10) (structure **IV**), as opposed to a bridging one at B(10)B(11) (structure **V**) (which would perhaps be the more appropriate model for neutral $C_2B_9H_{13}$), but nevertheless some informative comparison can be made.

Thus, inspection of the data of Table 1 shows that equivalent distances in $[C_2B_9H_{12}]^-$ and $C_4B_{18}H_{22}$ are largely very similar, with the principal deviations being in the B(9)B(10) region directly associated with the cluster linkage and in the bonding to B(5), which, uniquely, is bonded to both B(9) and B(10). In these regions differences of up to more than 0.1 Å occur. There are also noticeable changes in the distances to B(11) which will be associated with the difference between the non-bridged structure **IV** for the anion as opposed to the H(μ-10,11) bridged structure of $C_4B_{18}H_{22}$. The cluster NMR properties also show their principal changes in these areas, indicating that the effects of the linkage are quite localized (compare **II** and **III** above), leaving the essential eleven-vertex *nido* character of the subclusters little perturbed.

The measured NMR data for $C_4B_{18}H_{22}$ are summarized in Table 3 (see also Figs. 4 and 5 below). The ^{11}B NMR spectrum showed eight resonance positions (Fig. 2), with one, at δ(^{11}B)

Table 3 Measured NMR parameters for $C_4B_{18}H_{22}$ in CD_2Cl_2 solution at 294–297 K

Assignment[a]	δ(^{11}B)	^1J(^{11}B–^{1}H)/Hz	Observed [^{11}B–^{11}B] COSY correlations[b,c]	δ(^{1}H)[d]	Observed [^{1}H–^{1}H] COSY correlations[c,e]
1	−29.5	153	2s, 3s, 4s, 5s, 6s	+1.53	2s, 3m, 4s, 5s, 6s, 7vw?^{4}
2	+0.8	*f*	1s, 3w, 6m	+2.96	3s, 6m, 7m, 11w
3	−14.4	175	1s, 2w, 4m	+2.29	1m, 2mw, 4m, 7s, 8s
4	−0.5	*f*	1s, 3m, 5s, 9m	+3.12	1vs, 3s, 5m, 8vs
5	+6.2	156	1s, 4s, 6m, 9m, 10w[g]	+2.72	1s, 4m, 6s, 8vw^4, 10s
6	−5.3	157	1s, 2m, 5m, (10/11)s[g]	+2.40	1s, 2m, 5s, 7w?^{4}, 10s, 11w?, μvw
7	[C]	—	—	+3.50	1vw?^{4}, 2m, 3s, 6w?^{4}, 8vs, 11vw
8	[C]	—	—	+3.38	3vs, 4vs, 5vw^4, 7vs
9	+4.2	—	4m, 5m, 10s[g]	—	—
10	−26.3[g]	*f*	{5w, 6s, 9s}[g]	+2.22[h]	5s, 6s, μs^2
11	−26.3[g]	*f*		+1.49[h,i]	2w, 6w?, 7vw, μs^2
μ(10,11)	—	—	—	−4.10[h,j]	6vw, 10s^2, 11vs^2

[a] Assignments by COSY correlations; see also text and note *h*. [b] Carried out under conditions of complete {^{1}H} decoupling. [c] s = Strong, m = intermediate, w = weak, v = very, ? = uncertain. [d] Related to directly bound B positions by ^{1}H-{^{11}B(selective)} experiments; see also note *h*. [e] Carried out under conditions of complete {^{11}B} decoupling; correlations arise from couplings ^3J(^{1}H–^{1}H) except where superscript *n* indicates ^nJ pathway. [f] Not accurately measurable because of peak overlap. [g] Note ^{11}B(10) and ^{11}B(11) are resonances accidentally coincident. [h] Note that in ^{1}H-{^{11}B(broad-band noise), ^{1}H(selective)} triple-resonance experiments decoupling of ^{1}H[μ(10,11)] gave marked sharpening of ^{1}H(11) together with some sharpening of ^{1}H(10) resonances and also suggested an NOE enhancement of the ^{1}H(8) resonance. This NOE effect (of *ca.* 0.5%) was confirmed in a NOE difference experiment. [i] Doublet structure, splitting *ca.* 14 Hz, in the ^{1}H-{^{11}B} NMR spectrum. [j] Doublet of doublets, splittings *ca.* 14 and 4.5 Hz, in the ^{1}H-{^{11}B} NMR spectrum.

+4.2, showing no coupling to ^{1}H and thereby assigning it to B(9), and another, at δ(^{11}B) *ca.* −26.3, having a relative intensity of 2 indicating accidental equivalence of chemical shift. This latter coincidence was confirmed by ^{1}H-{^{11}B(selective)} experiments that showed that there are two separate ^{1}H resonances associated with δ(^{11}B) *ca.* −26.3 and therefore two separate {BH} units as expected from the cluster asymmetry. These selective measurements also assigned the other ^{1}H resonances to their respective boron positions. [^{11}B–^{11}B] Correlation spectroscopy (COSY) then enabled assignment of the ^{11}B NMR spectrum, with ambiguities arising from the overlap at δ(^{11}B) *ca.* −26.3 being resolved by the results of [^{1}H–^{1}H] COSY work (Fig. 3) which also assigned the two cluster CH protons between C(7) and C(5). The assignment of H(8) was confirmed by the observation of an NOE effect when ^{1}H(μ-10,11) was irradiated, the positions of these two protons being very close in space as discussed above.

Fig. 4 presents some of these NMR data in graphical form, and includes selected data from neutral *nido*-7,8-$C_2B_9H_{13}$ and the [*nido*-7,8-$C_2B_9H_{12}$]$^-$ anion for comparison. The most striking comparison occurs with the neutral species, *nido*-$C_2B_9H_{13}$, and there is a clear correspondence of the ^{11}B shielding pattern, with the marked exception of the B(9) position centrally involved in the linkage, which is shifted by some 30 ppm to lower shielding. The other main differences, less marked, are for B(10) which is also involved in the linkage and which is shifted upfield by some 10 ppm, and for B(5) which, uniquely, is bonded to both linkage atoms B(9) and B(10), and which is shifted downfield by a similar amount. In this respect it was noted above that the major geometrical structural changes were also associated largely with these three positions. The overall ^{11}B cluster shielding is very similar for both species, averaging at δ(^{11}B) −12.5 for *nido*-7,8-$C_2B_9H_{13}$ *versus* −10.1 for $C_4B_{18}H_{22}$, the 2.4 ppm difference arising principally from the large difference for the B(9) position. The proton shielding pattern is also very similar for both species (Fig. 4), with {δ(^{11}B),δ(^{1}H)} chemical-shift data points for individual BH(*exo*) units in $C_4B_{18}H_{22}$ lying close to the (anomalously shallow) slope of δ(^{1}H) : δ(^{11}B) 1 : 28 previously drawn[12] for $C_2B_9H_{13}$, again emphasizing the electronic similarities. Even the proton shielding of H(10), which is directly associated with a boron atom involved in the intercluster linkage, shows no significant departure from this correlation.

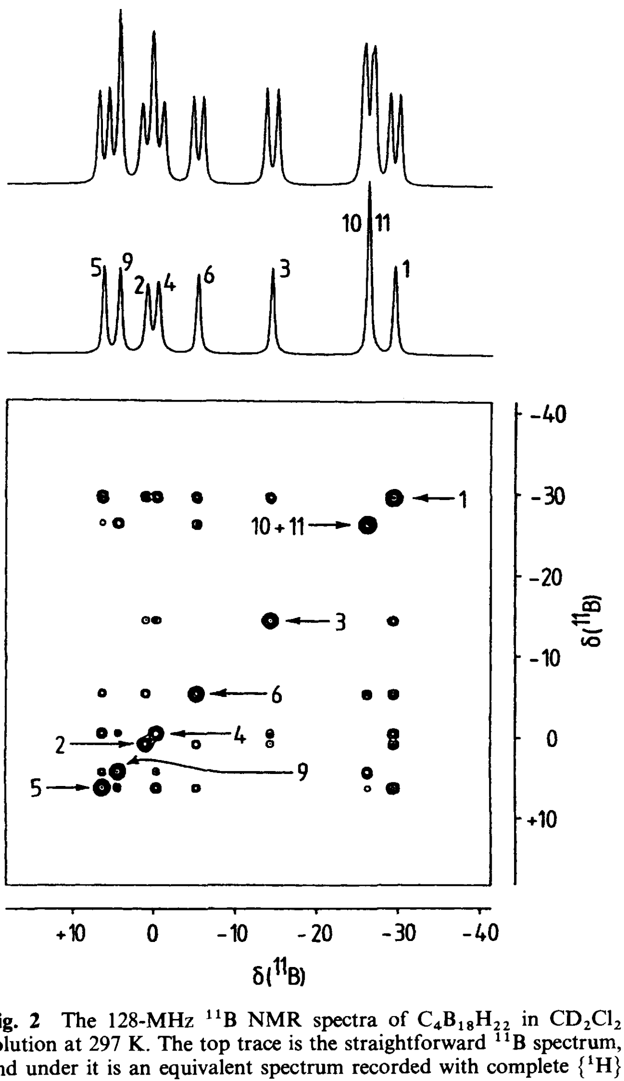

Fig. 2 The 128-MHz ^{11}B NMR spectra of $C_4B_{18}H_{22}$ in CD_2Cl_2 solution at 297 K. The top trace is the straightforward ^{11}B spectrum, and under it is an equivalent spectrum recorded with complete {^{1}H} decoupling. The bottom diagram is a 'two-dimensional' contour plot arising from a [^{11}B–^{11}B] correlation spectroscopy (COSY) experiment, also conducted with complete {^{1}H} decoupling

The relationship of the ^{11}B NMR behaviour of $C_4B_{18}H_{22}$ with that of the [7,8-$C_2B_9H_{12}$]$^-$ anion is at first sight less straightforward (Fig. 4) because the visual comparison within

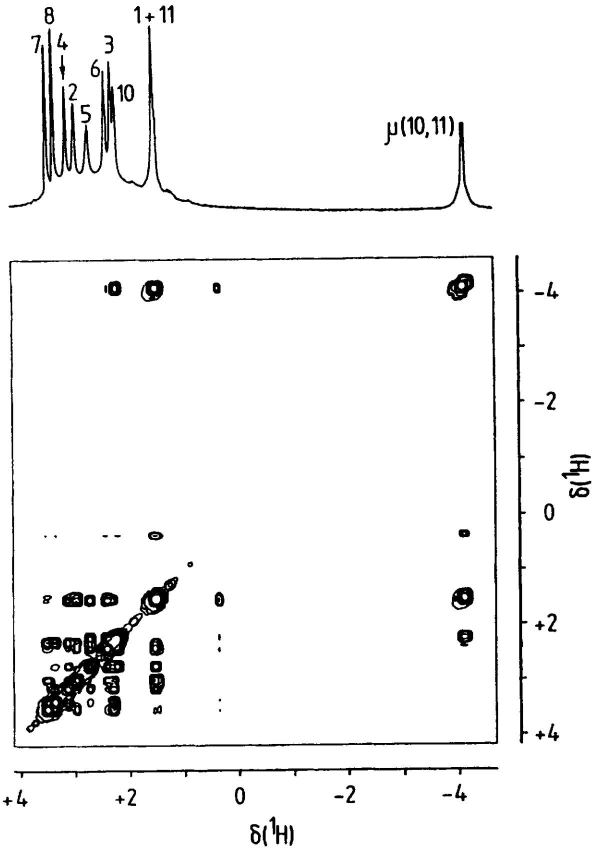

Fig. 3 The 400-MHz ^1H NMR spectra of $C_4B_{18}H_{22}$ in CD_2Cl_2 solution at 297 K, both recorded with complete {^{11}B} decoupling. The top trace is the straightforward ^1H spectrum, and the bottom diagram is a 'two-dimensional' contour plot arising from a [^1H–^1H] COSY experiment

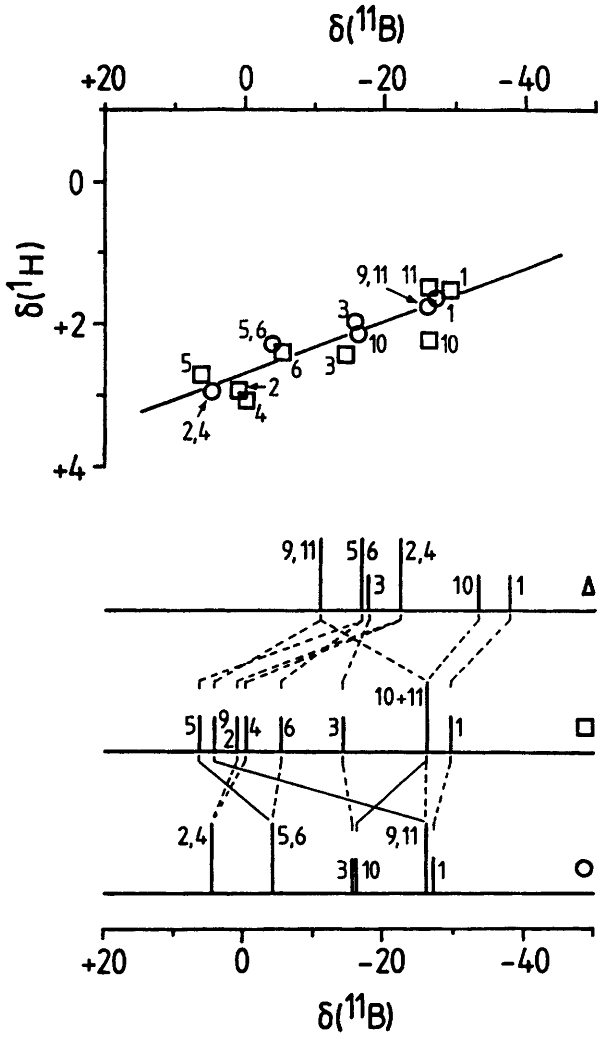

Fig. 4 Boron-11 and ^1H NMR data for $C_4B_{18}H_{22}$ (□) together with those for 7,8-$C_2B_9H_{13}$ (○, data from ref. 12) and [7,8-$C_2B_9H_{12}$]$^-$ (Δ, data from ref. 12) for comparison. The top diagram is a plot of $\delta(^1H)$ *versus* $\delta(^{11}B)$ for directly bound {BH(exo)} units, the line drawn having slope $\delta(^1H)$: $\delta(^{11}B)$ 1 : 27.5, with intercept +2.7 in $\delta(^1H)$. The bottom diagrams are stick representations of the chemical shifts and relative intensities in the ^{11}B spectra, with lines joining equivalent positions in the *nido* eleven-vertex clusters

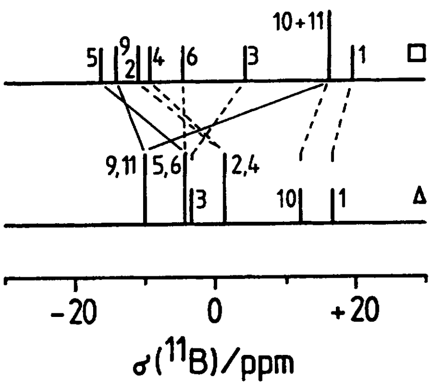

Fig. 5 Stick diagrams of the chemical shifts and relative intensities in the ^{11}B NMR spectra of $C_4B_{18}H_{22}$ (□) and the [7,8-$C_2B_9H_{12}$]$^-$ anion (Δ) (data from ref. 12). The scale is in ppm of the nuclear shielding with the origin taken as the weighted mean chemical shift [$\delta(^{11}B)$ −10.1 and −20.9, respectively] in each case

the diagram is complicated by the upfield shift of the anion, which has an average $\delta(^{11}B)$ value of −20.9 compared to −10.1 for $C_4B_{18}H_{22}$. However, allowance can be made for this 10.8 ppm difference by considering the relative ordering of the nuclear shielding, rather than an absolute shift comparison. This permits a simpler comparison (Fig. 5). The principal difference is then a large shift of the B(10) resonance position arising from a conversion of the *endo*-H(1) unit in [7,8-$C_2B_9H_{12}$]$^-$ into the H(μ-10,11) bridge position. Interesting in these terms is that the shielding of B(9) is not much affected, the *endo*-bridge change of about 25 ppm in the $\delta(^{11}B)$ ordering sequence being compensated for by the 30 ppm lower shielding induced by the boron–boron intercluster linkage.

Experimental

Samples of *neo*-$C_4B_{18}H_{22}$ were prepared according to the previously reported procedure.[2] Crystals suitable for single-crystal X-ray diffraction analysis were obtained by crystallizing the carbaborane from a chloroform–hexane (1 : 1 v/v). The NMR spectroscopy was carried out on a Bruker AM400 instrument operating at *ca.* 9.35 T, with the basic techniques as described in other recent papers from our laboratories.[18–20] Chemical shifts δ are given in ppm to high frequency (low field) of Ξ 100 MHz ($SiMe_4$) for ^1H (quoted ± 0.05 ppm) and of 32.083971 MHz (nominally $F_3B{\cdot}OEt_2$ in $CDCl_3$) for ^{11}B (quoted ± 0.5 ppm), Ξ being defined as in ref. 21.

Crystallography

All crystallographic measurements were carried out on a Stoe STADI-4 diffractometer operating in the ω–θ scan mode using an on-line profile-fitting method[22] and graphite-monochromated Cu-Kα X-radiation (λ = 1.54184 Å). The crystal was maintained at 150 K throughout. The structure was determined by direct methods using SHELXS 86[23] and was refined (on F^2) by full-matrix least squares with SHELXL 93.[24] All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located on a Fourier-difference synthesis and freely refined with individual isotropic displacement parameters. Refinement included an isotropic extinction parameter x so that $F_c' = kF_c[1 + 0.001xF_c^2\lambda^3]^{-\frac{1}{4}}$ where k is the overall scale factor. The weighting scheme $w = [\sigma^2(F_o^2) + (0.0662P)^2 + 1.816P]^{-1}$ was used where $P = (F_o^2 + 2F_c^2)/3$. The final Fourier-difference synthesis was flat and showed no features of chemical significance (maximum and minimum residual densities $+0.214$ and -0.164 e Å^{-3} respectively).

Crystal data. $C_4H_{22}B_{18}$, $M = 264.80$, $0.64 \times 0.38 \times 0.25$ mm, orthorhombic, space group *Pbca*, $a = 23.690(2)$, $b = 21.585(2)$, $c = 12.3653(8)$ Å, $U = 6323.0(9)$ Å^3, $Z = 16$, $D_c = 1.113$ Mg m^{-3}, $\mu = 0.284$ mm^{-1}, $F(000) = 2176$.

Data collection. $4.0 < 2\theta < 120.0°$, each scan divided into 30 steps, scan widths and step sizes calculated from a learnt profile, scan speeds 1.0–8.0° min^{-1}. Number of data collected = 5228, number of unique data (n) = 4640, number with $I > 2.0\sigma(I)$ = 3915, $R_{int}[=\Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2] = 0.0193$; $R_{sig}(=\Sigma\sigma F_o^2/\Sigma F_o^2) = 0.0206$.

Structure refinement. Number of parameters (p) = 574, $R1$ $(=\Sigma||F_o| - |F_c||/\Sigma|F_o|) = 0.0400$, $wR2$ $\{=[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}\} = 0.1218$, isotropic extinction parameter $x = 0.00083(8)$, goodness of fit s $\{=[\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}\} = 1.050$, maximum $\Delta/\sigma = 0.002$ [in y/b of H(6b) of molecule 1], mean $\Delta/\sigma = 0.000$.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/167.

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