# The Structure of $[7,8\text{-}C_2B_9H_{12}]^-$; Correction of a Popular Misconception†

**Jill Buchanan, Ewan J. M. Hamilton, David Reed, and Alan J. Welch***
*Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ*

---

The $[7,8\text{-}C_2B_9H_{12}]^-$ ion has been shown, *via* n.m.r. spectroscopic and *X*-ray crystallographic study, to contain an *endo*-H atom bonded to B(10) and not, as generally thought, a B–H–B bridge. Four ion pairs of $[H(dmso)_2][C_2B_9H_{12}]$ (dmso = dimethyl sulphoxide) crystallise in a unit cell of dimensions $a$ = 8.2919(14), $b$ = 11.0802(21), $c$ = 18.128(5)Å, β = 100.135(18)°, and space group $P2_1/n$. The structure has been refined to $R$ = 0.0436, $R'$ = 0.0698 for 2 355 reflections measured at 185 ± 1 K. The presence of an *endo*-H atom in $[7,8\text{-}C_2B_9H_{12}]^-$ is rationalised by consideration of the form of the highest occupied molecular orbital of $[7,8\text{-}C_2B_9H_{11}]^{2-}$. Analysis of the results of extended-Hückel molecular orbital calculations confirms that the *endo*-H atom bonds to the cage *via* a four-centre two-electron bond, and allows the relative magnitudes of *endo* and *exo* B–H coupling constants to be understood as well as the observation of weak coupling between the *endo*-H atom and B(9) and B(11).

---

The $[7,8\text{-}C_2B_9H_{12}]^-$ ion (**1**), easily formed by partial cage degradation of $1,2\text{-}C_2B_{10}H_{12}$ in alcoholic solution,[1,2] has been known for very many years. Indeed, it is (following deprotonation with strong base) the precursor of the ubiquitous $[7,8\text{-}C_2B_9H_{11}]^{2-}$ ion that afforded the first carbametallaboranes nearly 25 years ago.[3,4]

Although it is well accepted[1,2] that (**1**) has a *nido*-icosahedral cage architecture, consistent with the Polyhedral Skeletal Electron Pair Theory,[5,6] its precise structure has never been determined, and in particular the exact nature of the twelfth H atom has never been demonstrated. In spite of the fact that Hawthorne *et al.*[2] considered a number of possible sites for this atom (including what turns out to be the correct one), later authors[7] almost invariably assume a bridge position on one of the two (otherwise symmetry-equivalent) B–B connectivities of the open pentagonal face.

Recent structural studies on *nido*-$[3,4\text{-}Et_2\text{-}3,4\text{-}C_2B_5H_6]^-$ (**2**)[8] and *nido*-$[B_{11}H_{14}]^-$(**3**)[9] have confirmed the presence of $\{BH_2\}$ units in *nido* boranes and carbaboranes, whereas such groups are more commonly associated with *arachno* and *hypho* polyboranes. This has prompted us to reconsider the possibility of a $\{BH_2\}$ group in (**1**), and to seek confirmation of the exact nature of this anion in both the solid state *via* single-crystal *X*-ray diffraction, and in solution *via* multinuclear, multidimensional n.m.r. spectroscopy.

## Experimental

N.m.r. spectra were recorded at room temperature as $CD_2Cl_2$ solutions on Bruker WP 200 SY or Bruker WH 360 spectrometers, the latter fitted with an Aspect 3000 computer. Techniques for recording $^1H\text{-}\{^{11}B\}$ and $^{11}B$ (correlation spectroscopy, COSY) spectra have been described previously.[10] Chemical shifts are quoted relative to external $SiMe_4$ ($^1H$) or $BF_3{\cdot}OEt_2$ ($^{11}B$), with positive values to high frequency. Microanalyses were performed by the departmental service.

The salt $[H(dmso)_2][C_2B_9H_{12}]$ (**1a**) was afforded as a white solid by treatment of $K[C_2B_9H_{12}]$ (3g; *ca.* 10 mmol) in dimethyl sulphoxide (dmso)/water (5 $cm^3$) with concentrated $H_2SO_4$ (5 $cm^3$) and not stirring the product. Recrystallisation by slow diffusion of hexane into a $CH_2Cl_2$ solution at −30 °C yielded large colourless crystals (Found: C, 24.1; H, 8.55. $C_6H_{25}B_9O_2S_2$ requires C, 24.8; H, 8.65%). $^1H$ N.m.r; δ 6.5—7.0 (vbr, solvated $H^+$), 2.73 (12 H, $CH_3$), and 1.88 (br, 2H, cage CH).

*Crystallography.—Crystal data.* $C_6H_{25}B_9O_2S_2$, $M$ = 290.66, monoclinic, space group $P2_1/n$, $a$ = 8.291 9(14), $b$ = 11.080 2(21), $c$ = 18.128(5)Å, β = 100.135(18)°, $U$ = 1 639.5Å$^3$, from the least-squares refinement of 25 centred reflections (14 < θ < 15°) at 185 ± 1K, $Z$ = 4 ion pairs, $D_c$ = 1.177 g $cm^{-3}$, μ(Mo-$K_\alpha$) = 2.98 $cm^{-1}$, $F$(000) = 616.

*Data collection and processing.* CAD4 diffractometer, graphite-monochromated Mo-$K_\alpha$ *X*-radiation, λ(bar) = 0.710 69Å, ω—2θ scans in 96 steps, with ω scan width 0.8 + 0.34 tanθ. Variable scan speeds between 0.82 and 2.35° $min^{-1}$. 2 719 Unique data measured (1 < θ < 25°, $+h$ $+k$ $\pm l$) yielding 2 355 reflections with $F \geqslant 2.0\sigma(F)$. No measureable crystal decay or detectable movement.

*Structure solution and refinement.* All non-H atoms found by direct methods.[11] Hydrogen atoms from Δ$F$ syntheses following full-matrix least-squares refinement.[12] Empirical absorption correction[13] after isotropic convergence. Thereafter all non-hydrogen atoms allowed anisotropic thermal motion. Hydrogen atoms positionally refined but with common isotropic thermal parameter [$U_H$ = 0.046 2(16)Å$^2$ at convergence]. Weights applied according to $w^{-1} = [\sigma^2(F) + 0.008\,711F^2]$. $R$ = 0.043 6, $R'$ = 0.069 8, $S$ = 0.734. Maximum and minimum residues in final Δ$F$ map 0.38 and −0.62 e Å$^{-3}$ respectively. Scattering factors for neutral atoms as in SHELX 76.[12] Computer programs used in addition to those already referenced include CADABS,[14] CALC,[15] and EASYORTEP.[16] Co-ordinates of non-hydrogen atoms in Table 1.

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

## Results and Discussion

Recourse to the crystallographic and relatively sophisticated n.m.r. spectroscopic studies described herein is necessary because conventional spectroscopic techniques applied to anion (**1**) fail to define a unique structure. There is no evidence of a B–H–B bridge in its i.r. spectrum, but this is not conclusive

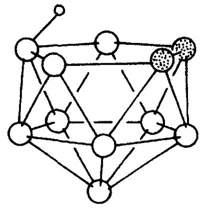
---

† Dodecahydro-7,8-dicarba-*nido*-undecaborate.

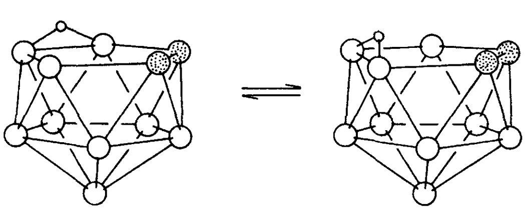
*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

**Table 1.** Positional parameters of non-hydrogen atoms in $[H(dmso)_2][7,8\text{-}C_2B_9H_{12}]$

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| S(1) | 0.675 15(6) | 0.317 81(4) | 0.389 41(3) |
| S(2) | 0.317 87(6) | 0.131 83(4) | 0.284 30(3) |
| O(1) | 0.528 07(19) | 0.387 38(13) | 0.344 18(10) |
| O(2) | 0.308 72(16) | 0.269 74(13) | 0.275 00(9) |
| C(11) | 0.694 4(3) | 0.379 84(22) | 0.479 88(13) |
| C(12) | 0.846 1(3) | 0.385 45(21) | 0.359 48(14) |
| C(21) | 0.114 5(3) | 0.090 26(25) | 0.290 71(14) |
| C(22) | 0.322 1(4) | 0.077 56(24) | 0.192 65(16) |
| B(1) | 0.350 11(24) | 0.281 74(18) | 0.589 54(12) |
| B(2) | 0.400 6(3) | 0.150 25(20) | 0.643 27(14) |
| B(3) | 0.422 2(3) | 0.152 21(19) | 0.548 49(14) |
| B(4) | 0.260 04(25) | 0.237 34(20) | 0.497 57(12) |
| B(5) | 0.132 1(3) | 0.284 14(18) | 0.559 51(13) |
| B(6) | 0.219 7(3) | 0.228 31(20) | 0.652 11(13) |
| C(7) | 0.321 46(22) | 0.036 77(17) | 0.583 13(11) |
| C(8) | 0.244 01(23) | 0.083 55(17) | 0.504 77(11) |
| B(9) | 0.075 8(3) | 0.156 04(19) | 0.503 37(13) |
| B(10) | 0.041 3(3) | 0.160 88(20) | 0.599 58(13) |
| B(11) | 0.215 0(3) | 0.068 71(20) | 0.646 94(13) |



**(I)**

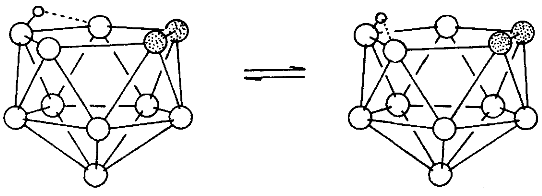


**(II)**

○ B—H$_{exo}$

● C—H$_{exo}$

o H



**(III)**

**Table 2.** Assignment of $^{11}B$ and $^{1}H$ n.m.r. chemical shifts of compound **(1b)**

| Position | δ($^{11}B$) | δ($^{1}H$) |
|---|---|---|
| 9,11 | −10.38 | 1.94 |
| 3(5,6) | −16.46 | 1.77 (1.24) |
| 2,4 | −21.29 | 1.26 |
| 10 | −32.54 | 0.11(*exo*), −2.80(*endo*) |
| 1 | −37.17 | 0.55 |

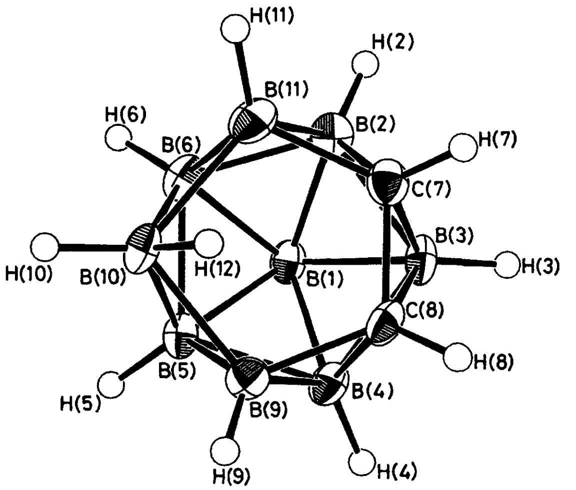


**Figure.** Plot of the $[7,8\text{-}C_2B_9H_{12}]^-$ anion (1) from above the open face; H(1) is totally obscured by B(1). All atoms drawn with 50% thermal ellipsoids, except H atoms which have been given an artificial radius of 0.1Å for clarity

evidence that such a bridge does not exist. Similarly, $^{11}B$ n.m.r. spectroscopy alone fails to distinguish between a $\{BH_2\}$-containing form (I) and rapidly interconverting hydrogen-bridged forms (II).

The $^{11}B$-$\{^1H\}$ n.m.r. spectrum of $[NMe_3(CH_2Ph)][C_2B_9H_{12}]$ (**1b**)* comprises five signals of relative area 2:3:2:1:1, and the $^{11}B$ n.m.r. spectrum confirms that all nine boron atoms in (**1**) carry *exo*-polyhedral H atoms since all five signals show clear doublet coupling, $J_{BH}$ 125—150(±5) Hz. In addition, the second lowest-frequency signal in the $^{11}B$ spectrum (δ −32.54 p.p.m.) shows a smaller coupling, 50 ± 5 Hz, thus appearing as a doublet of doublets [doublet of doublets, *apparent* triplet, is surely the correct description of the signal due to B(6) in anion (**2**)[8]]. The additional structure on this resonance was, in fact, noted in an early $^{11}B$ n.m.r. spectrum of anion (**1**) (Figure 3 of ref. 2).

An $^{11}B$(COSY) spectrum of (**1b**) allows assignment of the one-dimensional spectrum (Table 2). The signal with additional coupling in the $^{11}B$ n.m.r. spectrum arises from B(10), given a conventionally numbered *nido*-icosahedral anion in which the carbon atoms occupy positions 7 and 8. No other signal shows detectable coupling to the twelfth H atom.

A series of $^1H$ n.m.r. spectra with selective $^{11}B$ decoupling were obtained, and chemical shifts of the *exo*-polyhedral boron-bonded H atoms so determined are included in Table 2. In addition to these, a low-frequency H atom [δ −2.80, H(12)] is significantly enhanced by irradiation at −32.54 p.p.m. [B(10)] and very weakly enhanced by irradiation at −10.38 p.p.m. [B(9), B(11)]. Thus, at ambient temperature, H(12) is strongly bonded to B(10) but only weakly associated with the other (symmetry-equivalent) facial boron atoms, B(9) and B(11).

---

* Compound (**1b**) was precipitated by mixing aqueous solutions of $[NMe_3(CH_2Ph)]Br$ and $K[C_2B_9H_{12}]^2$ and recrystallised by slow diffusion of hexane into a $CH_2Cl_2$ solution at −30 °C (Found: C, 50.0; H, 10.00; N, 4.95. $C_{12}H_{28}B_9N$ requires C, 50.8; H, 9.95; N, 4.95%).

Evidently this latter association is sufficiently small that no additional structure or even broadening is seen on the doublet centred at −10.38 p.p.m. in the $^{11}$B n.m.r. spectrum.

No significant changes in the $^{11}$B or $^{11}$B-{$^{1}$H} n.m.r. spectra of compound (**1b**) are observed on cooling to −78 °C. Taken together with the aforementioned data, this implies that the structure of (**1**) is best represented either by the {$BH_2$}-containing form (**I**) [in which there is a small but detectable interaction between the *endo*-H atom and B(9) and B(11)] or by asymmetrically bridged forms (**III**) in rapid (and, within the limits of our experiment, unstoppable) interconversion.

In an attempt to gain additional information on this system we have studied anions (**1**) in the solid state by *X*-ray diffraction. Initial attempts were frustrated by disorder. Thus good single crystals of compound (**1b**) may be grown, but analysis of the diffraction data obtained* quickly revealed that the cage is randomly disordered, appearing as a closed icosahedron. Disorder of this kind is not uncommon for *nido*-icosahedral cages.[17] Very fortuitously, however, large single crystals of compound (**1a**) are afforded (following recrystallisation) if the synthesis of 9-$SMe_2$-7,8-$C_2B_9H_{11}$ [10,11] from K[7,8-$C_2B_9H_{12}$] is dmso/water and concentrated $H_2SO_4$ is attempted without sufficient stirring. The anion in this salt is *not* disordered, allowing the first structural characterisation of [7,8-$C_2B_9H_{12}$]$^-$.

The anion is viewed, from a position above the centre of the open face, in the Figure, and Table 3 lists interatomic distances and important interbond angles derived†. Anion (**1**) has the expected *nido*-icosahedral geometry with an *exo*-polyhedral H atom terminal to each cage atom (B or C). The open face is *not* planar, but is folded into an envelope conformation about the B(9)···B(11) vector such that both B(10) and the C(7)–C(8) edge dip towards the B(2)B(3)B(4)B(5)B(6) lower pentagonal belt. This *is* planar ($\sigma$ = 0.012 6Å) and, with respect to it, the aforementioned three- and four-atom portions of the upper pentagonal face (the latter of which is planar to within 0.004 4Å) make fold angles[19] ($\varphi$ and $\theta$) of 2.34 and 1.88° respectively. Folding of the upper face in this way is commonly observed in metal complexes of [$C_2B_9H_{11}$]$^{2-}$ and related ligands.[19]

In the solid state the twelfth H atom of (**1**) clearly occupies a symmetric *endo*-terminal position on B(10), affording the entire anion effective $C_s$ molecular symmetry. We have tested the fact the H(12) is ordered in the crystal [and not, say, disordered about B(9)–B(10) and B(10)–B(11) bridging sites] by a least-squares refinement with H(12) and, for comparison, H(10) omitted from the final model. The two highest maxima in the resultant $\Delta F$ synthesis correspond to H(10) (0.83e Å$^{-3}$) and H(12) (0.53e Å$^{-3}$) respectively. The next peak [0.39e Å$^{-3}$, *ca.* 1 Å from S(2)] is assigned to a S lone pair, and all further peaks have an electron density < 0.3e Å$^{-3}$.

**Table 3.** Interatomic Distances (Å) and selected interbond angles (°) in [H(dmso)$_2$][7,8-$C_2B_9H_{12}$]

(*a*) Anion

| | | | |
|---|---|---|---|
| B(1)–B(2) | 1.762(3) | B(5)–B(6) | 1.816(3) |
| B(1)–B(3) | 1.768(3) | B(5)–B(9) | 1.761(3) |
| B(1)–B(4) | 1.772(3) | B(5)–B(10) | 1.775(3) |
| B(1)–B(5) | 1.794(3) | B(5)–H(5) | 1.09(3) |
| B(1)–B(6) | 1.799(3) | B(6)–B(10) | 1.777(3) |
| B(1)–H(1) | 1.122(23) | B(6)–B(11) | 1.771(3) |
| B(2)–B(3) | 1.759(3) | B(6)–H(6) | 1.07(3) |
| B(2)–B(6) | 1.763(3) | C(7)–C(8) | 1.542(3) |
| B(2)–C(7) | 1.717(3) | C(7)–B(11) | 1.613(3) |
| B(2)–B(11) | 1.796(3) | C(7)–H(7) | 0.95(3) |
| B(2)–H(2) | 1.01(3) | C(8)–B(9) | 1.606(3) |
| B(3)–B(4) | 1.764(3) | C(8)–H(8) | 0.96(3) |
| B(3)–C(7) | 1.707(3) | B(9)–B(10) | 1.817(3) |
| B(3)–C(8) | 1.726(3) | B(9)–H(9) | 0.94(3) |
| B(3)–H(3) | 1.09(3) | B(10)–B(11) | 1.849(3) |
| B(4)–B(5) | 1.754(3) | B(10)–H(10) | 1.10(3) |
| B(4)–C(8) | 1.716(3) | B(10)–H(12) | 1.15(3) |
| B(4)–B(9) | 1.793(3) | B(11)–H(11) | 1.08(3) |
| B(4)–H(4) | 1.09(3) | | |

| | | | |
|---|---|---|---|
| B(2)–B(1)–B(3) | 59.76(13) | B(9)–B(5)–B(10) | 61.84(13) |
| B(2)–B(1)–B(6) | 59.34(12) | B(1)–B(6)–B(2) | 59.27(12) |
| B(3)–B(1)–B(4) | 59.77(12) | B(1)–B(6)–B(5) | 59.50(12) |
| B(4)–B(1)–B(5) | 58.90(12) | B(2)–B(6)–B(11) | 61.09(13) |
| B(5)–B(1)–B(6) | 60.73(12) | B(5)–B(6)–B(10) | 59.20(12) |
| B(1)–B(2)–B(3) | 60.31(13) | B(10)–B(6)–B(11) | 62.82(13) |
| B(1)–B(2)–B(6) | 61.40(13) | B(2)–C(7)–B(3) | 61.82(13) |
| B(3)–B(2)–C(7) | 58.80(12) | B(2)–C(7)–B(11) | 65.18(13) |
| B(6)–B(2)–B(11) | 59.68(13) | B(3)–C(7)–C(8) | 63.93(13) |
| C(7)–B(2)–B(11) | 54.61(12) | B(3)–C(8)–B(4) | 61.68(12) |
| B(1)–B(3)–B(2) | 59.93(13) | B(3)–C(8)–C(7) | 62.68(13) |
| B(1)–B(3)–B(4) | 60.23(12) | B(4)–C(8)–B(9) | 65.22(13) |
| B(2)–B(3)–C(7) | 59.38(13) | B(4)–B(9)–B(5) | 59.13(12) |
| B(4)–B(3)–C(8) | 58.89(12) | B(4)–B(9)–C(8) | 60.35(12) |
| C(7)–B(3)–C(8) | 53.39(11) | B(5)–B(9)–B(10) | 59.47(12) |
| B(1)–B(4)–B(3) | 60.00(12) | B(5)–B(10)–B(6) | 61.50(13) |
| B(1)–B(4)–B(5) | 61.18(12) | B(5)–B(10)–B(9) | 58.69(12) |
| B(3)–B(4)–C(8) | 59.43(12) | B(6)–B(10)–B(11) | 58.42(12) |
| B(5)–B(4)–B(9) | 59.53(12) | B(9)–B(10)–H(12) | 65.8(13) |
| C(8)–B(4)–B(9) | 54.43(12) | B(11)–B(10)–H(12) | 64.5(13) |
| B(1)–B(5)–B(4) | 59.93(12) | H(10)–B(10)–H(12) | 109.7(19) |
| B(1)–B(5)–B(6) | 59.77(12) | B(2)–B(11)–B(6) | 59.24(13) |
| B(4)–B(5)–B(9) | 61.34(12) | B(2)–B(11)–C(7) | 60.21(13) |
| B(6)–B(5)–B(10) | 59.30(12) | B(6)–B(11)–B(10) | 58.75(12) |

(*b*) Cation

| | | | |
|---|---|---|---|
| S(1)–O(1) | 1.549 8(17) | C(11)–H(113) | 1.00(3) |
| S(1)–C(11) | 1.759 4(24) | C(12)–H(121) | 0.97(3) |
| S(1)–C(12) | 1.770 8(25) | C(12)–H(122) | 0.84(3) |
| S(2)–O(2) | 1.537 7(16) | C(12)–H(123) | 0.96(3) |
| S(2)–C(21) | 1.771(3) | C(21)–H(211) | 0.94(3) |
| S(2)–C(22) | 1.773(3) | C(21)–H(212) | 1.04(3) |
| O(1)–H(O) | 0.95(4) | C(21)–H(213) | 0.91(3) |
| O(2)···H(O) | 1.45(4) | C(22)–H(221) | 0.73(3) |
| C(11)–H(111) | 0.91(3) | C(22)–H(222) | 0.94(3) |
| C(11)–H(112) | 0.95(3) | C(22)–H(223) | 1.00(3) |

| | | | |
|---|---|---|---|
| O(1)–S(1)–C(11) | 103.45(10) | C(21)–S(2)–C(22) | 98.58(13) |
| O(1)–S(1)–C(12) | 103.01(10) | S(1)–O(1)–H(O) | 113.4(21) |
| C(11)–S(1)–C(12) | 100.03(11) | S(2)–O(2)···H(O) | 115.2(14) |
| O(2)–S(2)–C(21) | 103.67(11) | O(1)–H(O)···O(2) | 172.2(35) |
| O(2)–S(2)–C(22) | 104.06(11) | | |

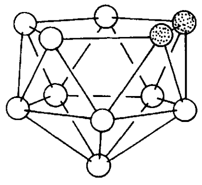
---

* *Crystal data.* $C_{12}H_{28}B_9N$, $M$ = 283.65, triclinic, space group $P\bar{1}$, $a$ = 11.833(5), $b$ = 11.915(5), $c$ = 13.723(7)Å, $\alpha$ = 110.692(15), $\beta$ = 91.954(13), $\gamma$ = 93.480(13)°, $U$ = 1 803.5Å$^3$, by the least-squares refinement of 25 centred reflections, $11 < \theta < 12°$, $Z$ = 4 ion pairs, $D_c$ = 1.045 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 0.49 cm$^{-1}$, $F$(000) = 608.

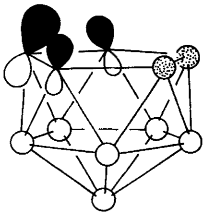
*Data collection and processing.* As for compound (**1a**) except scan speeds between 1.37 and 5.49° min$^{-1}$. 3 578 Unique data measured ($1 < \theta < 20°$, $+h \pm k \pm l$) yielding 2 190 with $F \geqslant 2.0\ \sigma(F)$. No measureable crystal decay or detectable movement.

*Structure solution.* All non-H atoms found by direct methods[11] and refined with individual isotropic thermal parameters by full-matrix least squares.[12] Atoms of both crystallographically independent [$NMe_3(CH_2Ph)$]$^+$ ions ordered. However, in both [$C_2B_9H_{12}$]$^-$ ions disorder noted over all 12 vertices of approximate icosahedra. Impossible satisfactorily to model disorder and unambiguously identify cage carbon atoms (all cage atoms modelled as B). Refinement terminated at $R$ = 0.157 5, unit weights. Co-ordinates of refined atoms deposited as Supplementary Data.

† The cation consists of an O-protonated dmso molecule to which a second dmso is hydrogen bonded *via* the O(1)–H(O)···O(2) bridge. The hydrogen bond is of a conventional type[18] with O(1)–H(O) 0.95(4), O(2)···H(O) 1.45(4)Å, and O(1)–H(O)···O(2) 172(4)°. There is a small (0.01Å) but statistically significant difference in the S–O bond lengths, that to the protonated oxygen being the longer. Overall, the cation has effective $C_s$ molecular symmetry.



**(IV)**



**(V)**

Consistent with other studies,[8,9] the *endo* B–H bond appears to be a little longer than *exo* B–H bonds involving similarly connected boron atoms, but even though the present study is an accurate one the estimated standard deviations (e.s.d.s) on B–H distances are sufficiently high to preclude further comment. The H(10)–B(10)–H(12) angle, 109.7(19)°, is, within experimental error, the tetrahedral ideal, and H(12) is evenly distanced from B(9) and B(11), 1.71(3)Å in each case. The lengths of the B(9)–B(10) and B(10)–B(11) edges are typical of those of unbridged connectivities.[20]

Thus, the key result from the crystallographic study is that anion (**1**) has the $\{BH_2\}$-containing structure (**I**), and therefore by implication that this, and not forms (**II**) or (**III**), is the preferred, ground-state structure, at least in the solid.*

This conclusion is fully consistent with the form of the highest occupied molecular orbital (h.o.m.o.) of $[7,8\text{-}C_2B_9H_{11}]^{2-}$. The frontier orbitals of $[C_2B_9H_{11}]^{2-}$, as given by extended-Hückel m.o. calculation, have been reported previously.[21] For the present purposes we have repeated this calculation using the $\{C_2B_9H_{11}\}$ fragment derived crystallographically above [by removal of H(12), line diagram (**IV**)] and performing the calculation, using the ICON8 program[22] and the weighted $H_{ij}$ formula,[23] with full charge iteration (including Madelung correction) on all atoms. The h.o.m.o., an *a′* m.o., is localised on B(10) (41%) and B(9) and B(11) (13% on each), and these contributions are sketched in (**V**). The components from these atoms are *s*–*p* hybrids, outward pointing from the open face. Clearly, the preferred site of protonation of $[7,8\text{-}C_2B_9H_{11}]^{2-}$ is above B(10), slightly inside the upward projection of the pentagonal face, to afford the *endo*-H atom revealed by the crystallographic study.

In addition to affording an understanding of the experimental finding of an *endo*-H atom in anion (**1**), we find that the results of extended-Hückel m.o. calculations also allow some rationalisation of the relative magnitudes of *endo* and *exo* B–H coupling constants. Thus, a calculation on $[C_2B_9H_{12}]^-$ reveals < B(2*s*)/*exo*-H(1*s*) > overlap integrals in the range 0.520—0.605, whereas that between B(10)(2*s*) and H(12)(1*s*) is only 0.506. Moreover, significant overlap integrals (0.277) are calculated between B(9,11)(2*s*) and H(12)(1*s*), in keeping with the small but real interaction between H(12) and B(9) and B(11) that was detected by the $^1H\text{-}\{^{11}B$, selective$\}$ n.m.r. experiments.

## Acknowledgements

We thank the S.E.R.C. and the S.E.D for support, and Dr. S. G. D. Henderson for some spectra.

## References

1 R. A. Wiersboeck and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1964, **86**, 1642.

2 M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 862.

3 M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, 1965, **87**, 1818.

4 M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, jun., and P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 879.

5 K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.

6 R. E. Williams, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 67.

7 For example; T. P. Onak, 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982; N. N. Greenwood and A. Earnshaw, 'Chemistry of the Elements,' Pergamon, Oxford, 1984.

8 J. S. Beck, W. Quintana, and L. G. Sneddon, *Organometallics*, 1988, **7**, 1015.

9 T. D. Getman, J. A. Krause, and S. G. Shore, *Inorg. Chem.*, 1988, **27**, 2398.

10 G. B. Jacobsen, D. G. Meina, J. H. Morris, C. Thomson, S. J. Andrews, D. Reed, A. J. Welch, and D. F. Gaines, *J. Chem. Soc., Dalton Trans.*, 1985, 1645.

11 G. M. Sheldrick, University of Göttingen, 1986.

12 G. M. Sheldrick, University of Cambridge, 1976.

13 N. G. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

14 R. O. Gould and D. E. Smith, University of Edinburgh, 1986.

15 R. O. Gould and P. Taylor, University of Edinburgh, 1986.

16 P. D. Mallinson and K. W. Muir, *J. Appl. Crystallogr.*, 1985, **18**, 51.

17 See, for example, G. K. Barker, N. R. Godfrey, M. Green, H. E. Parge, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1983, 277.

18 J. Emsley, *Chem. Soc. Rev.*, 1980, **9**, 91.

19 D. E. Smith and A. J. Welch, *Acta Crystallogr., Sect. C*, 1986, **42**, 1717 and refs. therein.

20 G. F. Mitchell and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1987, 1017.

21 D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1977, 602.

22 J. Howell, A. Rossi, D. Wallace, K. Haraki, and R. Hoffmann, Quantum Chemistry Program Exchange, University of Indiana, 1977, no. 344.

23 J. H. Ammeter, H-B. Burgi, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, 1982, **100**, 3686.

*Received 24th April 1989; Paper 9/01707K*

---

* *Note added in proof*: The *endo* terminal position of H(12) in $[7,8\text{-}C_2B_9H_{12}]^-$ has been independently determined (see following paper), *via* n.m.r. spectroscopic studies.