True Nature of the '*nido*-2,6-$C_2B_7H_{11}$' Dicarbaborane. Correction of an Error Persisting for Fifteen Years

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A complex n.m.r. study has proved that '*nido*-2,6-$C_2B_7H_{11}$' is in fact the *arachno*-4,5-$C_2B_7H_{13}$ dicarbaborane.

We report that the compound previously described as '*nido*-2,5-$C_2B_7H_{11}$,' reported several times since its discovery[1] in 1971 under this formula with varying numbering and structure,[1—3] is not in fact of this formulation, and the relevant sections of papers dealing with it[1—4] will have to be reassessed in the light of its true formula and structure.

Our recent multinuclear n.m.r. investigation has shown unequivocally that the compound is in reality the 4,5-dicarba-*arachno*-nonaborane(13), 4,5-$C_2B_7H_{13}$, (**1**). The two additional hydrogens (as compared with '$C_2B_7H_{11}$') have now been found in the ^1H n.m.r. spectrum in C_6D_6 (Figure 1a): one in the H(C) signal of intensity 2 at δ 0.44 p.p.m. and the second one in the hydrogen bridge of intensity 2 at δ -2.15 p.p.m. The ^{13}C n.m.r. spectrum has identified the CH and CH_2 signals unambiguously (Figure 1b). The ^{11}B n.m.r. spectrum (Figure 1c), after line narrowing, has shown two B–H vertices (A, B) influenced by the coupling with adjacent B–H–B bridges and a triplet of a BH_2 group (F). The B–H–B coupling expected with the boron C is hidden in the C, D, E envelope.

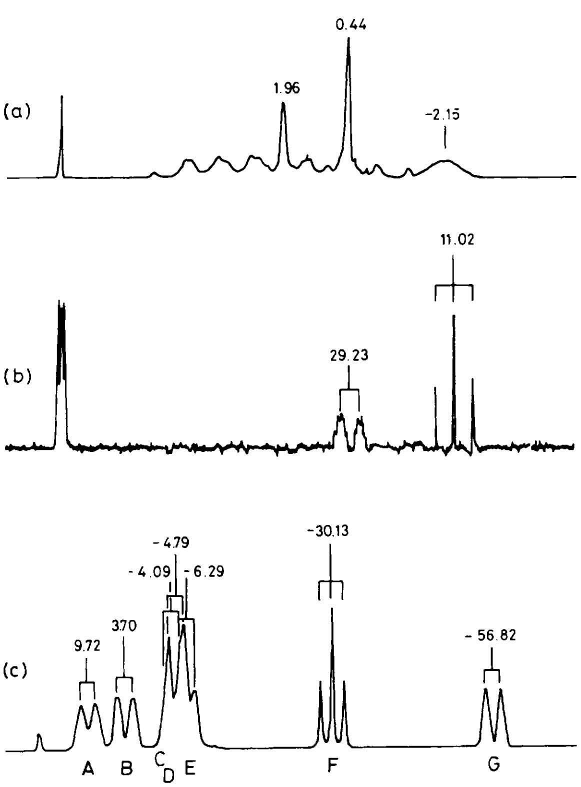


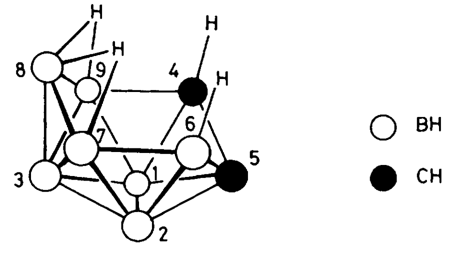
Figure 1. N.m.r. spectra of $4,5\text{-}C_23_7H_{13}$ (**1**): (a) ^1H; (b) ^{13}C; (c) ^{11}B.

On the basis of new findings, the mass spectra of (**1**) have been re-measured using all three main techniques. The results (electron impact, 70 eV: *m/z* 113, *P* -1; chemical ionisation *m/z* 115, *P* $+1$; negative ion: *m/z* 114, parent) are consistent with the formula $^{12}C_2{}^{11}B_7{}^1H_{13}$.

These facts cannot be interpreted otherwise than in terms of the structure (**1**). The two-dimensional ^{11}B–^{11}B spectrum fully supports structure (**1**), showing nine of the ten expected cross peaks, namely A = B (7) interacting with: E^4, F^1, G^1; B = B (9): D^3, G^4; C = B (8): G^5; D = B (1): B^3, G^3; E = B (2): A^4, F^1, G^1; F = B (6): A^1, E^1; G = B (3): A^1, B^4, C^5, D^3, E^1 (the indexes denote intensities of the interactions). The missing E–D cross peak is in the overlap area.

The species (**1**) has thus a conventional nine-vertex *arachno* framework with $2n + 6 = 24$ skeletal electrons, two vicinal hydrogen bridges, one BH_2 group, and the CH and CH_2 groups within the open hexagonal face of 4,5-$C_2B_7H_{13}$, being thus an isoskeletal and isotopological counterpart of the long known 4,6-$C_2B_7H_{13}$ dicarbaborane.[5] The two isomers differ only in the positions 5 and 6, respectively, where skeletal atoms are interchanged.

Three main errors were responsible for the persistence of this error for fifteen years: (a) unsuspected dehydrogenation under the conditions of the mass spectrometric experiment



(**1**)

indicated the erroneous $C_2B_7H_{11}$ formula; (b) the original ^1H spectra[1,2] were not re-measured, and published intensities of the two CH and one B–H–B signals were not previously doubted; (c) the conclusive ^{13}C n.m.r. spectrum had not previously been recorded.

Having been involved in the chemistry of '$C_2B_7H_{11}$' for a long time, we feel some responsibility for the persistence of this error, and we apologize for this to the community of borane chemists.

A full paper on this subject is now in preparation.

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