X-Ray Crystal and Molecular Structure of the *nido*-Carborane $B_7C_2H_9Me_2$

By J. C. HUFFMAN* and W. E. STREIB

(*Department of Chemistry, Indiana University, Bloomington, Indiana* 47401)

Summary The *nido*-carborane $B_7C_2H_7Me_2$ occurs as a bicapped Archimedean antiprism with the 6 position missing, methylated carbon atoms in the 1 and 2 cage positions, and bridging hydrogen atoms between the 7–10 and 9–10 positions.

RIETZ AND SCHAEFFER[1] recently reported the characterization of a new *nido*-carborane $B_7C_2H_{11}$ and its dimethyl derivative $B_7C_2H_9Me_2$. Based on the ease of formation and low symmetry implied by the ^{11}B and ^1H n.m.r. spectra they tentatively suggested an open B_7C_2 icosahedral fragment analogous to the structure known[2] for the isoelectronic species $B_9H_{13}{\cdot}MeCH$. We felt that a definitive structure determination was needed and our *X*-ray diffraction study of the dimethyl derivative has established a somewhat different arrangement.

The compound was prepared as described previously[1] and purified on a high-vacuum low-temperature fractionation column.[3] Samples were then distilled into thin-walled glass capillaries of 0·5 mm diameter and sealed under vacuum. A Picker automatic diffractometer equipped with a graphite monochromator and a nitrogen vapour cooling system[4] was used to collect the diffraction data. A single crystal was grown at *ca.* −9 °C and, once grown, cooled to −170 °C. A systematic search of a limited hemisphere located reflections which could be indexed in a monoclinic cell of dimensions $a = 5{\cdot}570(4)$, $b = 13{\cdot}136(9)$, $c = 12{\cdot}998(10)$ Å, and $\beta = 104{\cdot}43(10)°$. Systematic absences uniquely indicated the space group $P2_1/c$. Four molecules per unit cell gives a calculated density of 0·849 g cm^{-3}, a reasonable value for compounds of this type.

Redundant data collected by the moving crystal–moving counter technique were averaged to a unique set of 627 reflections, of which 522 were considered observed $[I_{\text{net}} > \sigma(I)]$. All non-hydrogen atoms were located by direct methods and hydrogen atoms were located in a difference Fourier map after isotropic refinement of the non-hydrogen atoms. Further least-squares refinement in which non-hydrogen atoms were given anisotropic thermal parameters and hydrogen atoms were given isotropic thermal parameters gave a final residual of 0·058. Electron density and difference maps based on the final parameters revealed no anomalies, with the largest peak corresponding to 0·25 e Å^{-3}.

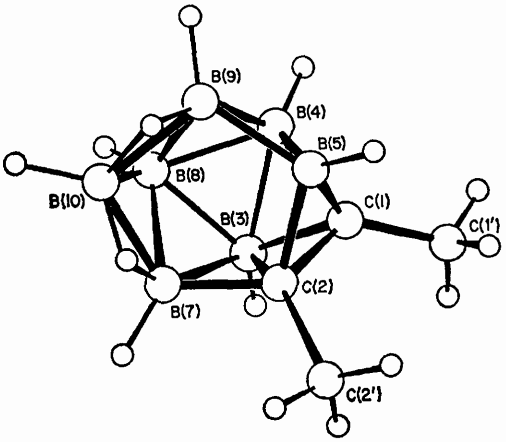

FIGURE. *The structure of* $B_7C_2H_9Me_2$. *Bond distances, in* Å, are 1–2 = 1·55; 1–1′ = 1·47; 2–2′ = 1·53; 1–3, 4, 5 = 1·60; 2–3 = 1·67; 2–5 = 1·75; 2–7 = 1·65; 8–10 = 1·69; 4–9 = 1·75. *All other* B–B *single bonds are* 1·78—1·81. *Average* $B–H_t$ = 1·15, $B–H_{br}$ = 1·25; *and* C–H = 1·00. *Errors are* ±0·01 *for non-hydrogen and* ±0·03 *for hydrogen distances.*

The molecular geometry and the numbering system used[5] are shown in the Figure. The structure is essentially a bicapped Archimedean antiprism with the 6 position removed. The distance across the open face B(7)–B(9) = 2·63 Å, is not significantly different from the similar B(2)–B(4) distance, 2·59 Å, in the fully closed 1,6-dicarba-*closo*-decaborane(10) cage.[6] The 2–3–4–5 positions describe a plane which is parallel within experimental error to the plane defined by the 7–8–9 positions, and bridging hydrogen atoms occur between the 7–10 and 9–10 positions. No appreciable lengthening of B–B bonds adjacent to cage carbon atoms is observed.[7] $B_7C_2H_9Me_2$ possesses no molecular symmetry, and therefore occurs as a racemic mixture in the centrosymmetric crystal structure.

Although 70·6 MHz ^{11}B n.m.r. spectra suggest that the parent compound $B_7C_2H_{11}$ may be structurally different[8] from the dimethyl derivative reported here, single crystals prepared to date have been unsuitable for *X*-ray work.

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[1] R. Rietz and R. Schaeffer, *J. Amer. Chem. Soc.*, 1971, **93**, 1263.
[2] F. Wang, P. Simpson, and W. Lipscomb, *J. Chem. Phys.*, 1961, **35**, 1335.
[3] J. Dobson and R. Schaeffer, *Inorg. Chem.*, 1970, **9**, 2183.
[4] J. C. Huffman, J. M. Mueller, and W. E. Streib, unpublished work.
[5] R. M. Adams, *Inorg. Chem.*, 1968, **7**, 1945.
[6] T. Koetzle and W. N. Lipscomb, *Inorg. Chem.*, 1970, **9**, 2279.
[7] (a) H. Hart and W. N. Lipscomb, *Inorg. Chem.*, 1968, **7**, 1070; (b) H. Hart and W. N. Lipscomb, *ibid.*, 1967, **6**, 874.
[8] R. R. Rietz, Ph.D. Thesis, Indiana University, 1971.