The Structure of the *arachno*-$[B_{10}H_{13}CN]^{2-}$ Anion; an Example of *endo* Substitution in the Decaborane(14) Framework

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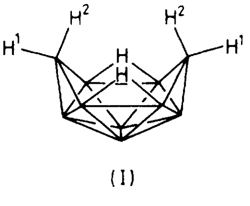
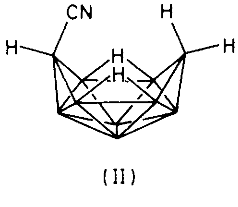
The cyano group in $[B_{10}H_{13}CN]^{2-}$ occupies an *endo*-position with respect to the cage in both solution (n.m.r.) and solid (*X*-ray crystallography) states, indicating a general pathway for the formation of heteroboranes.

The mechanism of formation of carbaborane cage compounds from the boron hydrides remains obscure in spite of many studies on such systems.[1–3] For example, in the conversion of a B_{10} to a $B_{10}C$ cage a vital intermediate is the simple anion $[6\text{-CN-B}_{10}H_{13}]^{2-}$.[4–6] There is no definitive evidence on the structure of such species, and the substituent can occupy either the *exo* (H^1) or *endo* (H^2) positions with respect to the B_{10} cage, structure (I). *exo*-Substitution has been established for other decaborane(14) derivatives such as $B_{10}H_{12}L_2$ (L = MeCN,[7] Me_2S[8]), and while intermediates with *endo*-like configurations have been suggested[2,3,9,10] for some compounds, these suggestions have not been substantiated. Two recent studies have also dealt with general aspects of the substitution process. Thus, the formation of 6,9-$(PMe_2Ph)_2$-*arachno*-$B_{10}H_{12}$ under controlled conditions results in a mixture of *endo–exo* (85%) and *exo–exo* (15%) isomers from n.m.r. studies, although the former is converted rapidly into the latter on heating in $C_6D_5CD_3$ solution.[11] Also the *arachno* anion $[B_{10}H_{12}(PPh_2)]^-$ has been shown to have the PPh_2 group bridging the 6,9-boron atoms of the cage, corresponding effectively to *endo*-substitution.[12]

We now report results for the *arachno*-$[6\text{-CN-B}_{10}H_{13}]^{2-}$ anion which establish that the simple cyano substituent occupies uniquely the *endo*-position in both the solution and solid states. The cyano derivative (II) was obtained from the action of sodium cyanide on decaborane(14) in aqueous solution, as previously described.[4] The ^{11}B n.m.r. spectrum of (II) (Cs salt) in D_2O exhibits the expected six doublets with relative intensities 1:1:2:2:2:1 at −0.84 [B(2)], −1.90 [B(4)], −17.38 [B(8,10)], −18.47 [B(5,7)], −37.12 [B(1,3)], and −38.54 p.p.m. [B(6)], with one triplet of relative intensity 1 at −32.53 [B(9)] p.p.m. The resonances were assigned on the basis of the results of ^{11}B-COSY spectroscopy, and are consistent with the cyano substituent being located at B(6). The location of the cyano group in the *endo*-position was confirmed by the results of $^{1}H\{^{11}B\}$ and especially $^{1}H\{^{11}B\}$ nuclear Overhauser enhancement (n.O.e) broad-band decoupled n.m.r. spectra. The $^{1}H\{^{11}B\}$ n.m.r. spectrum of (II) (Cs salt) in D_2O shows seven singlets (rel. intens. 1:1:4:1:3:1:2), and, on the basis that *endo* (but not *exo*) H atoms on B(6,9) will show significant dipolar interaction with the bridging H atoms between B(7,8) and B(5,10), these singlets may be assigned as follows: δ 2.42 [H(4)], 2.35 [H(2)], 1.51 [H(8,10)],[a] 1.50 [H(5,7)],[a] 0.77 [H(6)], 0.44 [H(1,3)],[b] 0.42 [H(9)*exo*],[b] −0.23 [H(9)*endo*], and −4.78 [H bridge (7,8)(5,10)]. ([a,b] Indicate overlapping resonances; the individual shifts were obtained by ^{11}B selective decoupling.) The $^{1}H\{^{11}B\}$ n.O.e. spectra on the same (not deoxygenated) sample show that irradiation of the bridge resonance at δ −4.78 gives significant enhancement (2.5%) only for the resonance at δ −0.23 p.p.m., and not for those at either δ 0.42 or 0.77 (≤1%). Such enhancement of the *endo*-H atom on B(9), but not for the H atom on B(6), clearly indicates that it is the cyano group which is occupying the *endo*-position on B(6). We have found that this general pattern of n.O.e. intensities in (II) also occurs in $B_{10}H_{14}$ (fully coupled) where significant interactions between bridge and face (B-5,6,7,8,9,10) terminal H atoms are observed, while the interactions are smaller or negligible between the H atoms of B–H(terminal) groups. A more detailed study of these and related $^{1}H\{^{11}B\}$ n.O.e. spectra will be published in the near future.



(I)



(II)

In 'open' boron clusters it is not uncommon for solution and solid state structures to differ since H atoms, and sometimes ligands, can exchange positions on the open face.[10,12,13] In the present case an *X*-ray crystal structure analysis of (II) confirms the *endo*-substitution and substantiates the high stability of this configuration for the *arachno*-$[6\text{-CN-B}_{10}H_{13}]^{2-}$ anion. The structure (Figure 1) was obtained for the $[PhMe_3N]_2^+$ $[6\text{-CN-B}_{10}H_{13}]^{2-}$ salt, and crystals were obtained from aqueous solution.

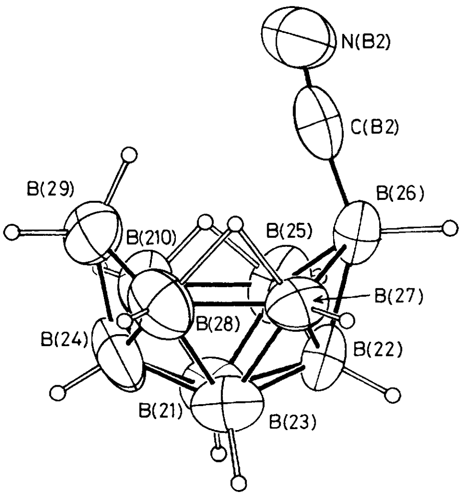


Figure 1. View of one $[6\text{-CN-B}_{10}H_{13}]^{2-}$ ion. All atoms, including H, were located and refined. Average values for the B–C and C–N distances are 1.576(11) and 1.143(10) Å, and the B–C–N angle is 175.0(1.0)°. *Crystal data*: triclinic, space group $P\bar{1}$, a = 9.765(3), b = 17.178(12), c = 17.303(9) Å, α = 114.10(4), β = 90.49(3), γ = 90.47(4)°, U = 2649(2) Å^3; Z = 4, R = 0.083 for 2194 unique observed $[I/\sigma(I) \geq 2.0]$ reflections. The two independent anions are indistinguishable. The atomic numbering corresponds to the chemical numbering with the addition of a prefixed 2 (for anion 2). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographc Data Centre. See Notice to Authors, Issue No. 1.

This first fully determined *endo*-configuration for the ligand attached to an *arachno*- ten-vertex polyhedron allows a clearer insight into the pathway for the formation of the monocarbon carbaborane cage ($B_{10}C\text{-}NH_3$). This must occur *via* protonation of the CN group, removal or transfer of the bridging B–H–B atoms, and concomitant facile insertion of the carbon atom into the open face.[3,14] These results also suggest the possibility of a similar configuration for the S_x^{2-} and NO_2^- ligands in $[B_{10}H_{13}S_x]^{3-}$ (ref. 15) and $[6\text{-}NO_2\text{-}9\text{-tetrahydrofuran-}B_{10}H_{12}]^-$ (ref. 16) respectively, which are themselves precursors to cage B_9S and B_9N heteroboranes. Orbital interactions may well favour the initial *endo*-approach by several ligands,[17,18] and the present results suggest that this type of stereochemistry is probably more common than has hitherto been suspected.

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