The Structure of CsB_9H_{14}: *X*-Ray and Proton and Boron-11 Nuclear Magnetic Resonance Studies

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Summary The *X*-ray crystal structure of CsB_9H_{14} shows the presence of three BH_2 groups and two B–H–B groups in the open face of the B_9 cluster: in solution, the ^{11}B(28·87 MHz) and ^1H(220 MHz) n.m.r. spectra indicate pseudo-threefold symmetry with nine terminal B–H bonds and five more labile hydrogen atoms.

THE structure of the $B_9H_{14}^-$ anion has been predicted[1] on the basis of the known structure of the isoelectronic adduct $MeCNB_9H_{13}$, but no definitive evidence has been presented for its structure, although n.m.r. data have been reported.[2] This paper gives the results of a single-crystal *X*-ray structure determination of CsB_9H_{14} and relates this to the ^{11}B and ^1H n.m.r. spectra of the $B_9H_{14}^-$ anion in various solvents over a range of temperature.

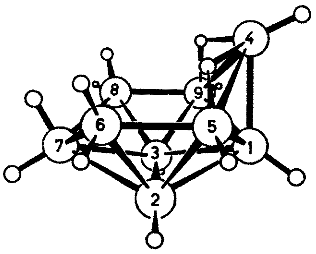

FIGURE 1. *The solid-state structure of* $B_9H_{14}^-$.

Air-stable, colourless, prismatic crystals of CsB_9H_{14} of high quality were prepared by degradation of $B_{10}H_{14}$[3] and subsequent recrystallisation from hot water. Preliminary optical and *X*-ray examination did not reveal any crystal symmetry and so a triclinic cell was defined: a = 5·686(4) Å, b = 8·780(6) Å, c = 10·690(10) Å, α = 88·32(5)°, β = 113·80(5)°, γ = 97·47(5)°: space group $P\bar{1}$ by successful refinement of the structure: D_m (flotation) 1·66; D_c 1·70 gcm^{-3}, $Z = 2$. The intensities of 2817 independent reflections were measured using a Hilger–Watts automated 4-circle diffractometer; 2716 of these were classed as observed and used in refinement. The co-ordinates of all non-hydrogen atoms were derived from the Patterson function and refined with anisotropic temperature factors by full-matrix least-squares procedures to a conventional *R*-factor (on $|F|$) of 8·9%. The extinction coefficient was then allowed to refine to give an *R*-factor of 6·9%. A difference Fourier was then calculated and this unequivocally showed the positions of all fourteen hydrogen atoms. These were included (with isotropic temperature factors) in a further set of least-squares calculations and the *R*-factor converged to a final value of 6·5% for the observed reflections.

The crystal structure of CsB_9H_{14} consists of the packing of Cs^+ cations with monomeric $B_9H_{14}^-$ anions. The inter-ion distances are sufficiently large to preclude any significant covalent bonding: the shortest contacts are those between caesium and hydrogen and these are all longer than 2·95 Å. The structure of the $B_9H_{14}^-$ ion is shown in Figure 1 and the derived 2613 topological structure is in Figure 2a. It is seen to be related to decaborane by removal of the B-6(9) boron atom and the formation of BH_2 groups on the three adjacent boron atoms. The boron-atom arrangement is thus as predicted but the arrangement of the hydrogen atoms differs from that predicted (Figure 2b). The B–B bond lengths vary between 1·69 Å (B-1–B-4) and 1·99 Å (B-8–B-9) and the B–H bond lengths are approximately 1·1 Å for the terminal hydrogens and 1·3 Å for bridge hydrogens, although these latter lengths are rather inaccurate.

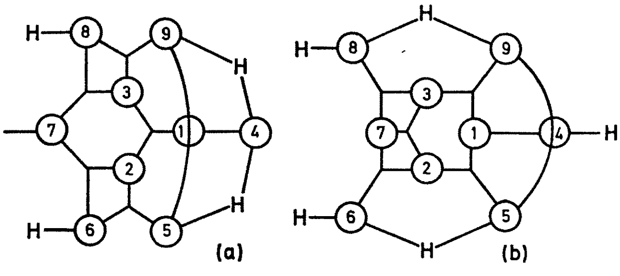

FIGURE 2. *The topology of* $B_9H_{14}^-$ (a) *found*; (b) *predicted*.

The 28·87 MHz ^{11}B n.m.r. spectrum of CsB_9H_{14} in Me_2SO at room temperature (Figure 3) comprises a doublet 8·17 p.p.m. upfield from $Et_2O{\cdot}BF_3$ (J_{B-H} = 140 Hz) and an apparent triplet of twice this intensity; this triplet collapses to an unsymmetrical doublet at lower field strengths and can be resolved using an electronic curve analyser into two overlapping doublets of equal intensity at 20·37 and 23·69 p.p.m. upfield from $Et_2O{\cdot}BF_3$ (J_{B-H} 132, 140 Hz respectively). This spectrum is consistent with a structure involving three groups of three equivalent boron atoms, each boron atom being coupled to only one hydrogen atom; the coupling constants suggest normal two-centre B–H

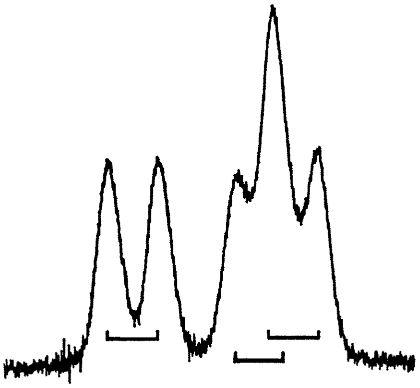

FIGURE 3. *The* 28·87 *MHz* ^{11}B *n.m.r. spectrum of* CsB_9H_{14} (*in* Me_2SO).

bonds. The five other hydrogen atoms do not couple with boron and must be labile. The solid-state structure has an approximate threefold axis of symmetry for the boron positions (which can be seen in Figure 2a for B-1B-2B-3, B-5B-7B-9, and B-4B-6B-8), but there are three BH_2 units and two bridge hydrogen atoms. Whilst this may be the instantaneous structure in solution, there must also be rapid exchange between one hydrogen atom from each BH_2 unit and the bridge hydrogen atoms so that the molecule has effective C_{3v} symmetry on the n.m.r. time-scale. It is not necessary to invoke the recently suggested[2] topological structure 5340 to explain the ^{11}B n.m.r. spectrum. In an attempt to slow down the exchange the 28·87 MHz ^{11}B n.m.r. spectrum of CsB_9H_{14} was measured at −90° in aqueous Me_2CO; the high field triplet collapsed to an unsymmetrical doublet and the low field doublet broadened to a complex envelope, but even at this low temperature the protons were still partially labile.

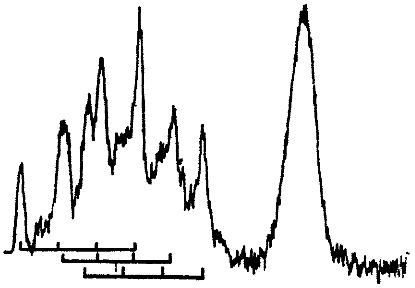

FIGURE 4. *The* 220 *MHz* ^{1}H *n.m.r. spectrum of* CsB_9H_{14} (*in* D_2O).

This interpretation of the ^{11}B n.m.r. spectrum was confirmed by the 90 and 220 MHz ^1H n.m.r. spectra of CsB_9H_{14} in D_2O solution. The 220 MHz spectrum (Figure 4) was kindly obtained for us by I.C.I. Ltd., Petrochemical and Polymer Division; it comprises a broad singlet, 6·02 p.p.m. upfield from water, of relative intensity 5 (due to the five labile hydrogen atoms) and three overlapping quartets each of intensity 3 (due to the coupled protons on the three sets of three boron atoms—^{11}B has $I = \frac{3}{2}$). These three quartets, centred at 2·43, 3·05, and 3·52 p.p.m. upfield from water, have J_{B-H} = 136, 124, and 140 Hz respectively and overlay a much weaker complex resonance presumably due to the unresolved triplet of septets arising from protons coupled to the 19% abundant ^{10}B ($I = 3$).

The solution behaviour of $B_9H_{14}^-$ is reminiscent of that of $B_{11}H_{14}^-$ in which a delocalised triangle of hydrogen atoms has been suggested.[4] Certainly, on the n.m.r. time-scale, the nett configuration in $B_9H_{14}^-$ involves an exchanging (delocalised) set of five hydrogen atoms, but whether the instantaneous configuration in solution has 5340 or 2613 topology cannot be decided on the basis of the present evidence. In the solid state, however, the topology is unequivocally 2613.

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