Preparation and Structure of a Singly Hydrogen-bridged Organoborane Anion

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Summary The preparation and structure of an organoborane anion, $(C_4H_8)_2B_2H_3^-$, which contains a single transannular hydrogen bridge is described.

WE report the synthesis and structure (Figures 1 and 2) of a transannular single hydrogen-bridged anion which was prepared by reaction of compound (I) with potassium hydride. The hydrogen bridge of the anion (II), is remarkably resistant to nucleophilic displacement by additional hydride ion or amine bases at room temperature. This is

(I) (II)

in sharp contrast to (I) which reacts with amines at $-78°$.[1] Apparently the negative charge renders (II) resistant to nucleophilic attack.

In a mixed solvent the following metathesis reaction occurred.

$$[N(n\text{-}C_4H_9)_4^+]I^- + K^+[(C_4H_8)_2B_2H_3^-] \longrightarrow [N(n\text{-}C_4H_9)_4^+][(C_4H_8)_2B_2H_3^-] + KI$$

Crystals of $[N(C_4H_9)_4^+][(C_4H_8)_2B_2H_3^-]$ are stable at room temperature in the absence of moisture. They crystallize in the monoclinic space group $P2_1/c$. The dimensions of the unit cell were determined by a least-squares refinement of 16 reflections well-centred on a four-circle diffractometer; $a = 10{\cdot}065 \pm 0{\cdot}006$ Å, $b = 13{\cdot}951 \pm 0{\cdot}010$ Å, $c = 21{\cdot}734 \pm 0{\cdot}014$ Å, $\beta = 118{\cdot}48° \pm 0{\cdot}03°$. The intensities of 4168 unique reflections were measured using Cu-K_α scintillation counter data of which 2293 were greater than $3\sigma(I)$ and were regarded as observed. The positions of non-hydrogen atoms were determined by direct phasing techniques.[2] All hydrogen atom locations were determined from subsequent electron-density difference maps. Block-diagonal least-squares refinement with anisotropic temperature factors for heavy atoms and isotropic temperature factors for hydrogen atoms has led to a conventional R of 0·043.

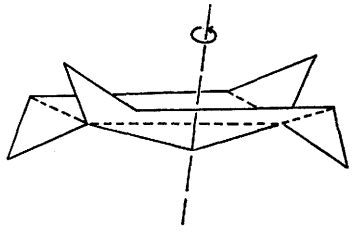

FIGURE 1. *Topography and symmetry of* $(C_4H_8)_2B_2H_3^-$.

No unusual features were noted for the n-tetrabutylammonium cations. Carbon–carbon bond lengths vary from 1·507 to 1·527 Å and carbon–nitrogen bond lengths

vary from 1·520 to 1·531 Å. The $(C_4H_8)_2B_2H_3^-$ ion has approximate C_2 symmetry. The rotation axis is normal to the *b*–*c* plane and passes through the bridging hydrogen. A simplified picture (Figure 1) shows the anion topography with double-chair conformation and an angle of *ca.* 120° between the planes of the fused chairs. An ORTEP[3] drawing is shown in Figure 2 with selected bond lengths. Small deviations from C_2 symmetry may be explained by the differences in packing around the anion. One branch of the $N(n\text{-}C_4H_9)_4^+$ cation lies in close proximity to the C(1)–C(4) group while the C(5)–C(8) group lies in comparatively free space.

The transannular singly hydrogen-bridged anion (II) is related to the $B_2H_7^-$ ion, the p.m.r. spectrum of which indicates the presence of a single hydrogen bridge[4] in the structure $H_3B\text{–}H\text{–}BH_3$. Although the structure of $B_2H_7^-$ is unknown in the solid state, Hall *et al.*[5] predict a B–H bond distance of 1·309 Å. The bridging B–H bond distances found in (II) agree well with this value. They are equivalent within one standard deviation. The bridge is nonlinear with a B–H–B angle of 140°. Attempts to increase the angle in models resulted in unreasonable contact distances for hydrogen atoms.

A final point of interest concerns the structural relationship between (II) and (I). The only reported evidence for

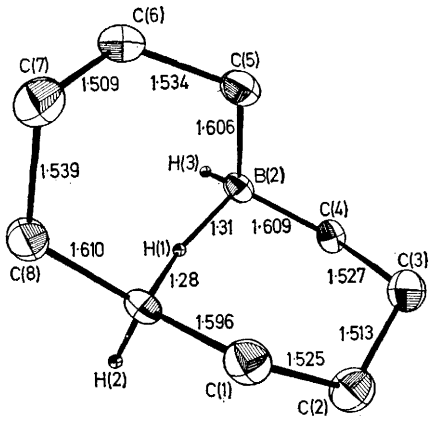

FIGURE 2. *Selected bond lengths of* $(C_4H_8)_2B_2H_3^-$.

structure (I) has been chemical in nature.[1,6,7] Structure (II) reinforces this work.

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