An E.S.R. Study of the Diborane Radical Anion in Solution

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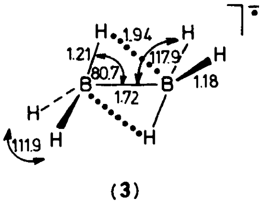
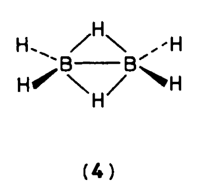
The e.s.r. spectrum of $B_2H_6^{\cdot -}$ in fluid ethereal solution indicates that this radical anion has an ethane-like structure with a one-electron B–B σ bond.

In 1969 Kasai and McLeod[1] reported that the e.s.r. spectrum of the diborane radical anion $B_2H_6^{\cdot -}$ could be observed at 4 K after u.v. photolysis of sodium atoms and diborane in an argon matrix. Experiments with B_2H_6, containing ^{11}B and ^{10}B in natural abundance,† and with $^{11}B_2D_6$ led these authors to a preliminary analysis of the poorly-defined spectra in terms of $A_{\parallel}(2^{11}B)$ 24.5 ± 0.5, $A_{\perp}(2^{11}B) \leq 2.5$, $a(6H) \leq 15$ G.‡ The proton and perpendicular boron splittings were not resolved but upper limits for these coupling constants were estimated by consideration of line widths. Subsequently, Claxton *et al.*[2] obtained a 'reasonable fit' to the published spectrum by assuming an isotropic splitting of 7 G from four or six equivalent protons. On the basis of *ab initio* molecular orbital (m.o.) calculations, these authors concluded that the most likely structure for $B_2H_6^{\cdot -}$ was the staggered D_{3d} species (**1**), which has a single B–B bonding σ electron. However, the geometries of (**1**) and of the alternative structures considered were not optimised and only planar BH_3 units ($\theta = 90°$) were considered for (**1**).

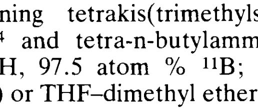
More recently, the e.s.r. spectrum of the isoelectronic ethane radical cation has been reported[3] and the unpaired electron is clearly associated principally with two of the six hydrogens [$a(2H)$ 152, $a(4H) \leq 10$ G at 4 K], although an exchange process renders all hydrogens magnetically equivalent [$a(6H)$ 50.4 G] by 77 K. Evidently, the unpaired electron is essentially confined to two C–H σ bonds, in accord with a C_{2h} structure of the type (**2**), and this was supported by the results of INDO m.o. calculations.[3]



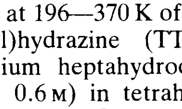
(**1**)



(**2**)



(**3**)



(**4**)

In view of the differences in the published e.s.r. spectra of $B_2H_6^{\cdot -}$ and $C_2H_6^{\cdot +}$, we set out to obtain an isotropic spectrum of the former species in solution.

An e.s.r. spectrum which we assign to $B_2H_6^{\cdot -}$ was recorded during continuous u.v. photolysis at 196—370 K of a solution containing tetrakis(trimethylsilyl)hydrazine (TTMH; *ca.* 0.4 M)[4] and tetra-n-butylammonium heptahydrodiborate[5,6] (TBAH, 97.5 atom % ^{11}B; *ca.* 0.6 M) in tetrahydrofuran (THF) or THF–dimethyl ether (2.5 : 1 v/v) [equations (1) and (2)]. 1,2-Dimethoxyethane (DME) was also used as solvent or co-solvent with dimethyl ether. The spectrum of $^{11}B_2H_6^{\cdot -}$ is shown in Figure 1(a) and the spectroscopic parameters are $a(2^{11}B)$ 10.88, $a(6H)$ 0.75 G, g 2.0024 at 243 K. When the TTMH was replaced by di-t-butyl peroxide, as a photochem-

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† The natural abundances of ^{11}B (I 3/2) and ^{10}B (I 3) are 81.2 and 18.8%, respectively; ($\gamma^{10}B/\gamma^{11}B$) is 0.335.

‡ 1 G = 10^{-4}T.

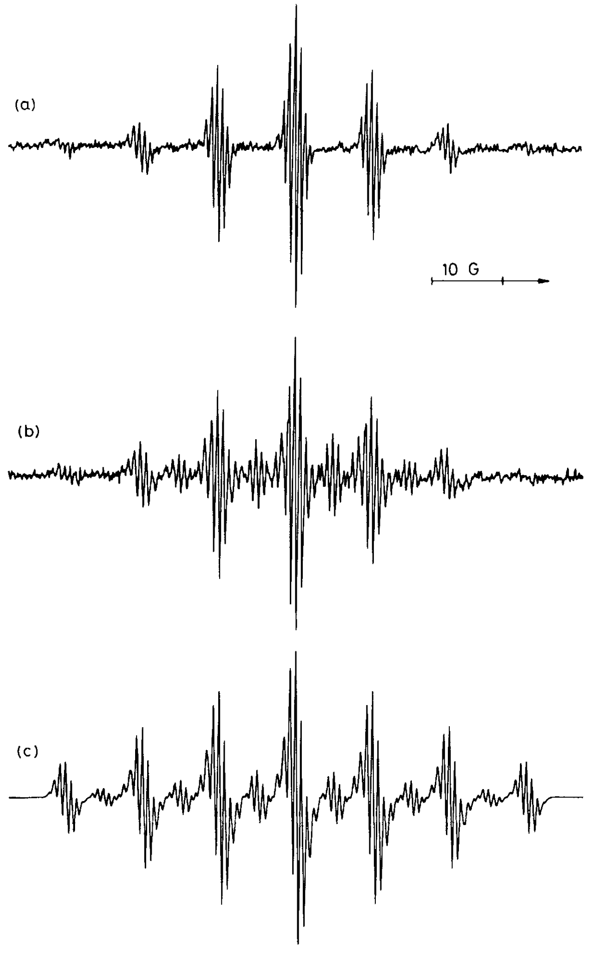

Figure 1. (a) E.s.r. spectrum of $B_2H_6^{\bullet -}$ derived from ^{11}B-enriched TBAH in THF–Me_2O (2.5 : 1 v/v) at 243 K. (b) E.s.r. spectrum of $B_2H_6^{\bullet -}$ containing ^{11}B and ^{10}B in natural abundance in THF–Me_2O (2.5 : 1 v/v) at 244 K. (c) Computer simulation of (b) using the coupling constants and relative concentrations of isotopic species given in the text; to within the limits of experimental error, $a(^{10}B)$ is equal to $(\gamma^{10}B/\gamma^{11}B) \times a(^{11}B)$. The outer lines of the experimental spectra are broadened as a result of incomplete averaging of the boron hyperfine anisotropy.

ical source of hydrogen abstracting t-butoxyl radicals, a stronger spectrum of $B_2H_6^{\bullet -}$ could be observed, but only below *ca.* 220 K when there is pronounced broadening of the outer lines as a result of incomplete averaging of the ^{11}B hyperfine anisotropy. Above this temperature the TBAH is very rapidly consumed, probably in a chain reaction involving attack of $B_2H_6^{\bullet -}$ on the peroxide.

$$(Me_3Si)_2NN(SiMe_3)_2 \xrightarrow{h\nu} 2(Me_3Si)_2N^\bullet \qquad (1)$$

$$(Me_3Si)_2N^\bullet + B_2H_7^- \longrightarrow B_2H_6^{\bullet -} + (Me_3Si)_2NH \qquad (2)$$

Comparison of Figure 1(a) with the spectrum [Figure 1(b)] obtained from TBAH containing the natural distribution of ^{11}B and ^{10}B confirms the presence of two equivalent borons in the radical anion, since the latter spectrum can be simulated [see Figure 1(c)] as a superposition of $^{11}B_2H_6^{\bullet -}$, $^{11}B^{10}BH_6^{\bullet -}$, and $^{10}B_2H_6^{\bullet -}$ in the predicted relative concentrations (65.9, 30.5, and 3.5%, respectively).

In an attempt to relate our results to the previously published[1] spectrum attributed to $B_2H_6^{\bullet -}$ at 4 K, we determined the temperature dependence of the boron and proton splittings over the widest possible range. In DME or DME–Me_2O (the latter for temperatures below 240 K), the value of $a(2^{11}B)$ (10.88 ± 0.02 G) did not vary significantly between 196 and 370 K, whilst $a(6H)$ increased from 0.68 to 1.03 G. To assess further the size of the vibrational contribution to the hyperfine splittings, we generated $B_2D_6^{\bullet -}$ containing the naturally occurring distribution of boron isotopes (see Figure 2). At 309 K in DME the spectroscopic parameters are $a(2^{11}B)$ 10.38, $a(6D)$ 0.11 G, g 2.0025, and the deuterium splitting corresponds to a proton splitting of 0.72 G;§ under the same conditions $a(6H)$ for $B_2H_6^{\bullet -}$ is 0.94 G. These results suggest that only the ground states of vibrational modes which involve large changes in the hyperfine splittings are appreciably populated in the temperature range studied.

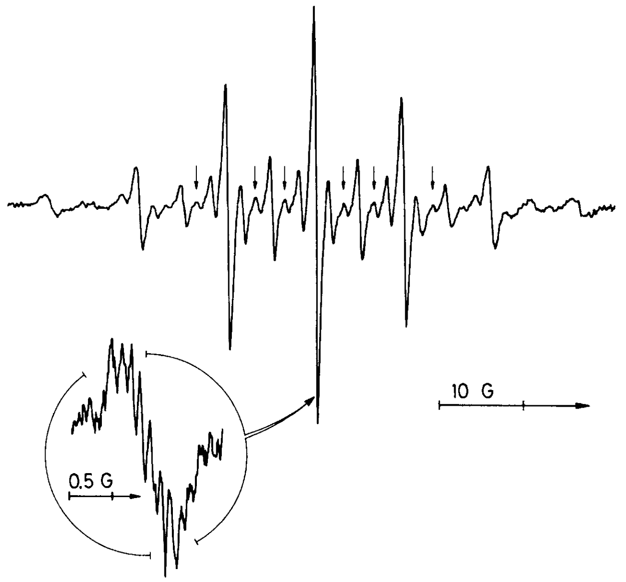

Figure 2. E.s.r. spectrum of $B_2D_6^{\bullet -}$ containing ^{11}B and ^{10}B in natural abundance in THF at 243 K; an expansion of the central line at 309 K is shown inset. Some of the lines (labelled with arrows) from $^{10}B_2D_6^{\bullet -}$ are clearly visible.

It is rather difficult to reconcile our e.s.r. data for $B_2H_6^{\bullet -}$ with those reported by Kasai and McLeod,[1] although we cannot eliminate the possibility that temperature and/or matrix effects could account for the differences. However, the D_{3d} structure (**1**), proposed by Claxton *et al.*[2] on the basis of Kasai and McLeod's results, is the only reasonable geometry consistent with our data. The value of θ, averaged over the populated vibrational states, must be such that the positive contribution to $a(6H)$, arising because of the H-1s component in the SOMO, is almost cancelled by the negative contribution resulting from spin-polarisation of the B–H σ bonding electron pairs. The proton hyperfine splitting would therefore be expected to be strongly dependent on the value of $\theta_{av.}$. The ^{11}B splitting for $B_2H_6^{\bullet -}$ is somewhat greater than half that (19.9 G) for $H_3B^{\bullet -}$,[7] as expected since the B-2s orbital can contribute directly to the SOMO of (**1**), even if the H_3B units are planar.

The structure of $B_2H_6^{\bullet -}$ is thus similar to that proposed by Hudson and Williams[8] for the radical anion of the trimethyl borate dimer. The ^{11}B splitting for $[(MeO)_3B{\cdot}B(OMe)_3]^-$ is 46.3 G, substantially greater than that for $B_2H_6^{\bullet -}$ and indicates that the $(MeO)_3B$ groups in the former are more

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§ Obtained by multiplying $a(6D)$ by (γ_H/γ_D) (= 6.514).

pyramidal than the H_3B groups in the latter, as expected from consideration of the ligand electronegativities.

In order to gain further insight into the structure of the *diborane* radical anion, we have carried out semi-empirical MNDO-UHF m.o. calculations,[9] which have previously proved successful for the triborane(7) radical anion.[10] Interestingly the C_{2h} structure (**3**), analogous to (**2**), corresponded to the only minimum which could be located on the potential energy surface; the computed bond lengths (Å) and bond angles (°) are indicated. The calculated coupling constants (before quartet annihilation) for this structure, which can be thought of as derived from that of diborane (**4**) by stretching of two bridge bonds and tipping of the terminal BH_2 groups, are a(2H) +109.7, a(4H) −5.5, and $a(2^{11}B)$ +20.5 G.

Geometry optimisation for $B_2H_6^{\bullet -}$ within the constraint of D_{3d} symmetry gave a structure of the type (**1**) with r(B–B) 1.88, r(B–H) 1.17 Å, and θ 102.9°, but showing two negative vibrational frequencies. However, this D_{3d} structure was only 13.6 kJ mol^{-1} less stable than (**3**) and high level *ab initio* calculations could well reverse the stability order. Before quartet annihilation, the computed coupling constants for the D_{3d} structure are $a(2^{11}B)$ +16.3 and a(6H) +10.1 G, but a series of calculations with fixed values of θ between 110 and 90° showed that as this angle decreases so a(6H) decreases rapidly, passes through zero (θ *ca.* 95°), and then becomes increasingly negative (−9.6 G when θ = 90°).

Preliminary results indicate that $B_2H_6^{\bullet -}$ is less reactive and more selective than $H_3B^{\bullet -}$.[7]¶ Thus, we found no e.s.r. evidence for addition of $B_2H_6^{\bullet -}$ to benzene (*ca.* 2 M) below 312 K. However, $B_2H_6^{\bullet -}$ reacts rapidly with alkyl bromides in THF at 244 K to give the corresponding alkyl radicals and Bu^tBr is 1.7 ± 0.1 times more reactive than Pr^nBr (the relative reactivity is 1.2 towards $H_3B^{\bullet -}$ under the same conditions).

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¶ At 243 K in THF, $B_2H_6^{\bullet -}$ decayed within the fall time of the spectrometer (0.3 s) when photochemical generation ceased.