

An E.S.R. Study of the Triborane(7) Radical Anion

Jeremy R. M. Giles, Vernon P. J. Marti, and Brian P. Roberts*

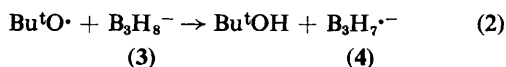
Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

The radical anion of triborane(7), $B_3H_7^{\cdot-}$, has been generated in solution by abstraction of hydrogen from $B_3H_8^-$ and studied by e.s.r. spectroscopy; MNDO-UHF calculations suggest that $B_3H_7^{\cdot-}$ has a cyclic C_{2v} structure with a single bridging hydrogen.

Although many stable complexes of triborane(7) (B_3H_7) with Lewis bases are known, the free borane is apparently highly reactive and has never been isolated. A number of theoretical studies of B_3H_7 have been reported¹⁻⁵ and both *ab initio* and semi-empirical molecular orbital calculations have been carried out with the aim of predicting its equilibrium geometry. Generally, the C_{2v} structure (1) (see Figure 1) has been predicted to be the most stable, although recent *ab initio* calculations by McKee and Lipscomb⁵ have indicated that the C_s structure (2) becomes slightly preferred (by *ca.* 18 kJ mol⁻¹) if polarisation functions are included in the basis set for boron and if account is taken of electron correlation. It would appear likely, therefore, that B_3H_7 is a fluxional molecule.

We have shown previously⁶ that hydrogen atom abstraction from H_4B^- provides an efficient route to $H_3B^{\cdot-}$ for e.s.r. studies of this radical anion in fluid solution. In an extension of this work, we have investigated hydrogen abstraction from the octahydrotriborate anion (3)⁷ as a potential route to the radical anion of triborane(7).

During continuous u.v. photolysis of di-*t*-butyl peroxide (DTBP) in the presence of $Bu^tNB_3H_8$ (TBAT)⁸ in a variety of solvents at 200–290 K, complex e.s.r. spectra which we ascribe to $B_3H_7^{\cdot-}$ (4) were observed [equations (1) and (2)].[†] Replacement of DTBP by tetrakis(trimethylsilyl)hydrazine,⁹ as a photochemical source of the hydrogen-abstracting radical $(Me_3Si)_2N^{\cdot-}$, also afforded e.s.r. spectra of (4).



The spectrum of (4) containing ¹⁰B and ¹¹B in natural abundance [18.8% (*I* 3) and 81.2% (*I* 3/2), respectively] is complicated by the presence of several radical anions which differ in

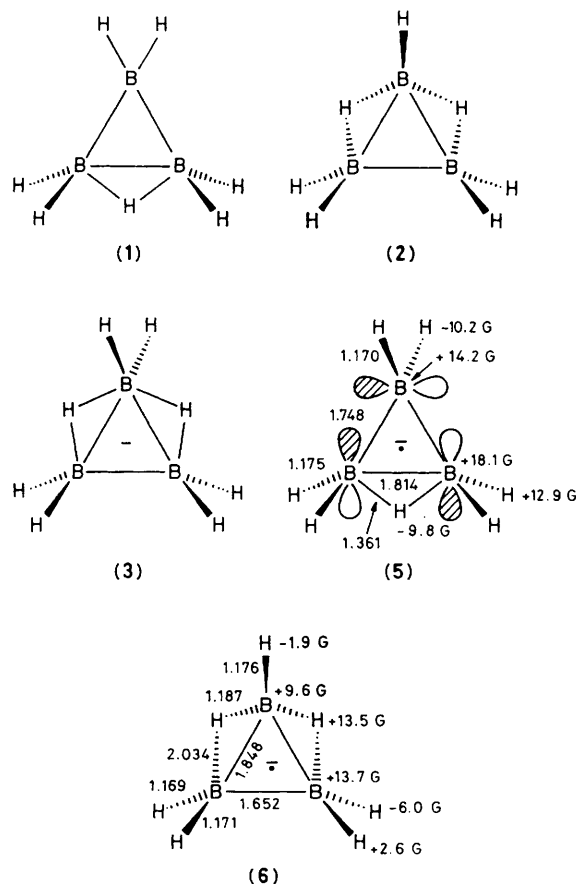


Figure 1. Structures of B_3H_7 , $B_3H_7^{\cdot-}$, and $B_3H_8^-$. Lines connecting atoms do not necessarily indicate two-electron bonds. For (5) and (6), optimised bond lengths (Å) and calculated coupling constants are shown.

[†] Approximately second-order decay of (4) was observed when photolysis was interrupted. In DME at 235 K, the first half-life was *ca.* 3 s for an initial concentration of *ca.* 10^{-6} mol l⁻¹.

isotopic composition. To avoid this problem, we synthesised TBAT starting from ¹¹B-enriched F_3B-OMe_2 containing only 2.5 atom % ¹⁰B, using the route outlined in Scheme 1.

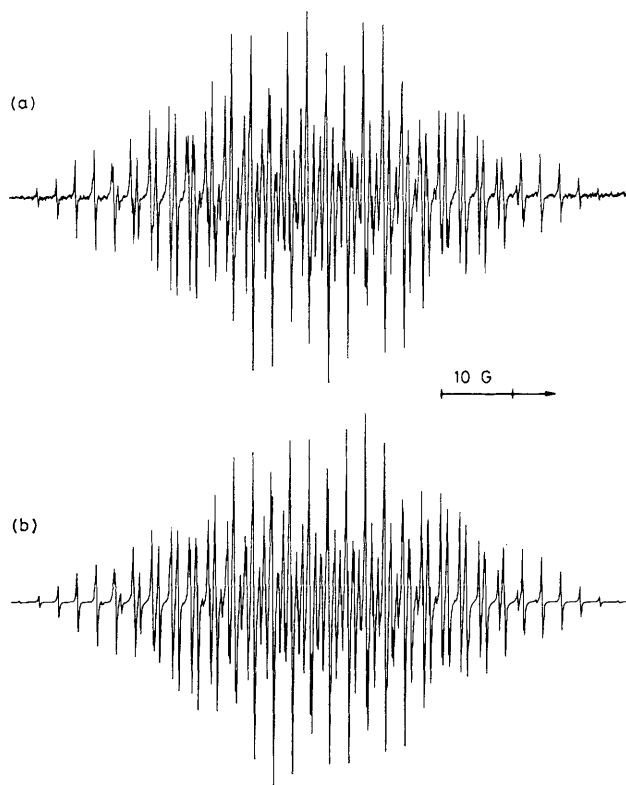
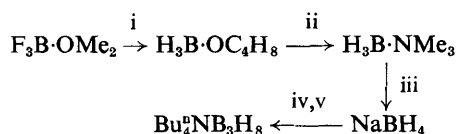


Figure 2. (a) E.s.r. spectrum of $B_3H_7^-$ in DME- Me_2O -MeOH at 245 K. (b) Computer simulation obtained using the coupling constants given in the text.



Scheme 1. i, $LiAlH_4$ -DME, B_2H_6 passed into tetrahydrofuran; ii, Me_3N ; iii, NaOMe; iv, I_2 ; v, Bu_4^+NI .

The e.s.r. spectrum of (4) (g 2.0025) obtained from ^{11}B -enriched TBAT in 1,2-dimethoxyethane (DME)- Me_2O -MeOH solvent (1 : 7 : 2 v/v) at 245 K is shown in Figure 2, along with a computer simulation based on $a(^{11}B)$ 7.97, $a(^{21}B)$ 2.72, $a(1H)$ 10.69, $a(2H)$ 11.59, and $a(4H)$ 2.72 G.[‡] In this mixed solvent $a(^{21}B)$ and $a(4H)$ are fortuitously equal within the linewidth, but in other solvents these splittings are different, resulting in more complex spectra [e.g. see Figure 3(a)]. In DME- Me_2O - NH_3 (5 : 4 : 2 v/v) the e.s.r. parameters are $a(^{11}B)$ 7.89, $a(^{21}B)$ 2.91, $a(1H)$ 10.79, $a(2H)$ 11.60, $a(4H)$ 2.61 G, and g 2.0025 at 230 K. Wing regions of the spectra obtained from natural abundance- and ^{11}B -enriched-TBAT are shown in Figure 3 and comparison with the computer simulations, obtained by assuming a statistical distribution of boron isotopes, confirms the presence of two equivalent borons and one different boron in the radical anion (4).

Since semi-empirical MNDO molecular orbital calculations have proved quite successful for predicting the structures of polyboranes and derived diamagnetic anions,⁴ we have

carried out MNDO-UHF calculations¹⁰ for (4) with optimisation of all geometrical variables within reasonable symmetry constraints. The only stable structure located on the potential energy surface was (5). The C_s structure (6) was less stable by 22 kJ mol⁻¹ and diagonalisation of the Hessian matrix^{4,10} resulted in one negative normal vibrational frequency, suggesting that (6) could be a transition state for exchange of bridging and terminal hydrogens in (5) by rotation of a basal BH_3 fragment. However, bearing in mind the reversal in stabilities of (1) and (2),⁵ mentioned above, on going from MNDO to *ab initio* methods and the reported⁴ tendency of MNDO calculations to underestimate the strength of 3-centre bonds, it is possible that more sophisticated calculations might predict a C_s structure of the type (6) to be the more stable. However, if such a C_s structure is the equilibrium geometry, the *cis*- and *trans*-basal terminal protons must be exchanging rapidly on the e.s.r. time scale at all temperatures examined, without simultaneous exchange of the remaining three protons.

Although we favour (5), whichever of (5) or (6) is the equilibrium structure of $B_3H_7^-$, the other could serve as a transition state in an exchange process that, upon repetition, would ultimately render the three borons equivalent and the seven hydrogens equivalent. However, although the spectrum of (4) broadened at about room temperature, it did not sharpen again at higher temperatures up to 375 K [in DME with $(Me_3Si)_2NN(SiMe_3)_2$ as primary radical source], when only a broad absorption of width similar to that of the low temperature spectrum was observed. Thus, it appears that the barrier to exchange in (4) is larger than that calculated by the MNDO method.

The SOMO of (5) is principally composed of in-plane B-2p orbitals, as indicated in Figure 1. $B_3H_7^-$ is isoelectronic with $C_3H_7^{2+}$, which would be formed by removal of an electron from protonated cyclopropane. Corner-protonated cyclopropane, analogous to (6), has been calculated to be 26 kJ mol⁻¹ more stable than the edge-protonated structure analogous to (5).¹¹

The hyperfine splitting constants, calculated from the valence s-orbital populations before quartet annihilation,^{8,10} for the structures (5) and (6) are shown in Figure 1. The calculated splittings for (5) are in tolerable¹⁰ agreement with experiment, although the predicted values of $a(^{21}B)$ and $a(4H)$ are much too large. However, the latter splittings should be rather sensitive to the positions of the terminal basal protons (H_{tb}) and this was confirmed by fixing $\angle H_{tb}BB_{apleal}$ (θ ; optimised value 113.9°) and optimising all other variables. With θ fixed at 108 and 103°, $a(4H)$ decreased to +8.3 and +2.6 G, respectively; the corresponding values of $a(2B)$ were +10.8 and +7.8 G. All calculations refer, of course, to free anions in the gas phase at 0 K and solvent- and cation-association effects and the effects of vibrational averaging on hyperfine splittings could easily account for the discrepancies between calculation and experiment.

The triborane(7) radical anion appears to be appreciably less reactive than H_3B^- ,⁶ as might be expected for a delocalised species of higher ionisation potential. As judged by e.s.r. spectroscopy, there was no evidence for addition of (4) to benzene, ethylene, or acetonitrile up to 270 K in DME- Me_2O solvent (up to 250 K with ethylene). Neither was there any evidence for abstraction of bromine from Pr^+Br^- or Bu^+Br^- .

We are indebted to Dr. J. E. Parkin for his invaluable help in modifying and running the computer programs for MNDO

[‡] 1 G = 10⁻⁴ T.

[§] 1H -1s and ^{11}B -2s spin populations were multiplied by 504.5 G¹⁰ and 725 G,¹² respectively, to give the hyperfine splittings.

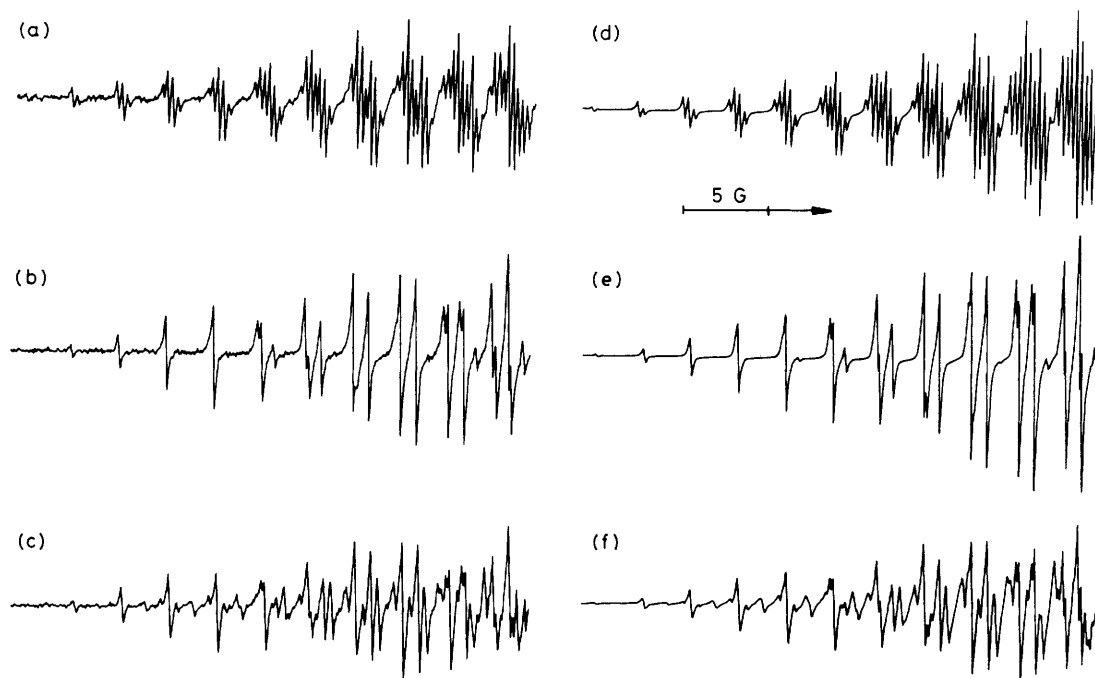


Figure 3. Low field sections of the e.s.r. spectrum of $B_3H_7^{\bullet-}$; (a) from ^{11}B -enriched TBAT in DME- Me_2O - NH_3 at 230 K; (b) from ^{11}B -enriched TBAT in DME- Me_2O - $MeOH$ at 244 K; (c) from natural abundance TBAT in DME- Me_2O - $MeOH$ at 246 K; (d) computer simulation of (a) obtained using the coupling constants given in the text; (e) computer simulation of (b) obtained using the coupling constants given in the text; (f) computer simulation of (c) as a superposition of the spectra of three radicals containing three ^{11}B atoms, one basal ^{10}B , and one apical ^{10}B , respectively, present in the statistical molar proportions (0.535:0.248:0.124). It was assumed that $a(^{10}B) = 0.335a(^{11}B)$.

calculations and for simulation of spectra and we are grateful to Dr. T. Clark for providing a copy of the MNDO program.¹⁰

Received, 31st March 1983; Com. 418

References

- 1 D. R. Armstrong, *Inorg. Chim. Acta*, 1976, **18**, 13.
- 2 L. D. Brown and W. N. Lipscomb, *Inorg. Chem.*, 1977, **16**, 1.
- 3 I. M. Pepperberg, T. A. Halgren, and W. N. Lipscomb, *Inorg. Chem.*, 1977, **16**, 363.
- 4 M. J. S. Dewar and M. L. McKee, *Inorg. Chem.*, 1978, **17**, 1569.
- 5 M. L. McKee and W. N. Lipscomb, *Inorg. Chem.*, 1982, **21**, 2846.
- 6 J. R. M. Giles and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1981, 360; *J. Chem. Soc., Perkin Trans. 2*, 1982, 1699.
- 7 C. R. Peters and C. E. Nordman, *J. Am. Chem. Soc.*, 1960, **82**, 5758.
- 8 G. R. Ryschkewitsch and K. C. Naiman, *Inorg. Synth.*, 1974, **15**, 111.
- 9 J. C. Brand, B. P. Roberts, and J. N. Winter, *J. Chem. Soc., Perkin Trans. 2*, 1983, 261.
- 10 P. Bischof and G. Freidrich, *J. Comput. Chem.*, 1982, **3**, 486.
- 11 P. C. Hariharan, L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1974, **96**, 599.
- 12 P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967.