Comparison of B–B π-bonding in singly reduced and neutral diborane(4) derivatives: isolation and structure of [{Li(Et_2O)$_2$}{MeO(mes)BB(mes)OMe}]

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A single-crystal X-ray diffraction study of [{Li(Et_2O)$_2$}{MeO(mes)BB(mes)OMe}] 1 (mes = $C_6H_2Me_3$-2,4,6) allows the first structural comparison between singly reduced and neutral diborane(4) species; compound 1 features a shortened B–B bond distance of 1.636(7) Å which may be compared to the 1.724(9) Å observed in the neutral precursor MeO(mes)BB(mes)OMe 2 and a distance of 1.62–1.64 Å observed in related doubly reduced $[R_2BBR_2]^{2-}$ species; the B–B bond in 1, which has a formal π-bond order of 0.5, is thus similar in length to that found in the doubly reduced diborane(4) dianions that possess a formal B–B π-bond order of unity.

Stable organosubstituted derivatives of diborane(4) have only been known since 1980.[1,2] It was shown that these compounds underwent one-electron reductions, and EPR spectroscopy indicated the presence of the radical anion $[R_2BBR_2]^{\cdot-}$ in solution.[3] Subsequent work has demonstrated that aryl substituted diborane(4) compounds had greater thermal stability.[4] Moreover, the tetraaryl diborane(4) compounds can be doubly reduced to give a substituted diborane(4) ethylene analogue such as $[mes_2BB(Ph)mes]^{2-}$ featuring a formal B–B double bond with a π-bond order of unity.[5] Unfortunately there are no structural data available for singly reduced $[R_2BBR_2]^{\cdot-}$ radical anion species which have a formal π-bond order of 0.5. Its structure would enable a unique comparison to be made with that of the doubly reduced diborane(4) dianion. Such a comparison is not possible anywhere else in the Group 13 element derivatives, since dianions of the type $[R_2MMR_2]^{2-}$ (M = Al, Ga, In, Tl) are currently unknown for the heavier element congeners. In this paper the isolation and first structural characterization of the singly reduced species [{Li(Et_2O)$_2$}{MeO(mes)BB(mes)OMe}] 1, which features a one-electron B–B π-bond, are now described.

$$\underset{\mathbf{2}}{\mathrm{MeO(mes)BB(mes)OMe}} \xrightarrow[\text{4 h, 25 °C}]{\text{Li, Et}_2\text{O}} \underset{\mathbf{1}}{[\{\mathrm{Li(Et_2O)_2}\}\{\mathrm{MeO(mes)BB(mes)OMe}\}]}$$

Reduction of MeO(mes)BB(mes)OMe 2[4] with Li in diethyl ether over *ca.* 4 h gave a dark purple solution from which 1 was obtained as dark blue, almost black, crystals.† The electronic absorption spectrum of 1 in diethyl ether has maxima at 589 and 307 nm which are attributable to π → π* transitions of the radical anion in 1. A single-crystal X-ray diffraction study‡ afforded the structure depicted in Fig. 1. The molecules of 1 possess a crystallographically required twofold rotation axis of symmetry defined by the Li atom and the midpoint of the B–B bond. Important structural data for both 1 and its neutral precursor 2[4] are given in Table 1. The most dramatic changes upon reduction are the closure of the angle between the boron planes from 74.9 to 2.5° and the shortening of the B–B distance from 1.724(9) to 1.636(7) Å. Thus the $B_2C_2O_2$ core atoms are essentially coplanar [max. deviation from the averaged plane = 0.031(1) Å]. In addition, the structure of 1 features a lengthened (by 0.09 Å) B–O distance and a narrower (by 5.0°) O–B–C angle than those observed for 2. The B–C distances [1.589(5) Å] in 1 and 2 [1.572(9) Å av.], however, are very similar. The lithium ion, which is solvated by two diethyl ethers and the oxygens from the methoxy groups, has distorted tetrahedral coordination. Both Li–O distances [Li–OMe 1.905(5) Å, Li–OEt$_2$ 1.968(5) Å] are similar to those observed in other organolithium compounds.[6] The closest Li···B contact observed in 1 is 2.734(8) Å.

In essence, the structural parameters of 1 are consistent with the formation of a partial π-bond. The short B–B distance in 1 [1.636(7) Å, *cf.* 1.724(9) Å in the neutral precursor[4]] represents a *ca.* 5% contraction in the B–B bond length and may be compared to the dianion values of 1.636(11) Å in [{Li(Et_2O)$_2$}$_2${$mes_2BB(Ph)mes$}][5] and 1.627(9) Å av. in [{Li(Et_2O)$_2$}$_2${(Me_2N)PhBBPh(NMe_2)}].[7] Clearly, the B–B bond length scarcely changes upon the addition of the second electron in spite of the fact that the π-bond order formally doubles from 0.5 to 1.0. The lack of any appreciable change in the B–B bond length upon the second reduction may be attributed to an approximate balance between increased electrostatic repulsion between the two negative charges in the dianion, which tends to lengthen the bond, and the increased π-bond order which has the effect of shortening it.§

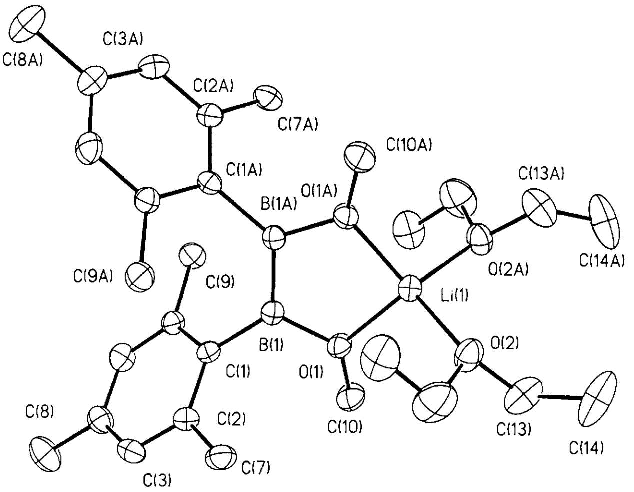

Fig. 1 Thermal ellipsoidal plot (30% probability) of 1; hydrogen atoms have been omitted for clarity

Table 1 Selected bond distances (Å) and angles (°) for 1 and 2

	1	2
B–B	1.636(7)	1.724(9)
B–O	1.454(4)	1.363(10 av.
B–C	1.589(5)	1.572(9) av.
O–B–C	117.5(3)	122.5(5) av.
O–B–B	114.0(2)	115.1(5) av.
C–B–B	128.4(2)	122.5(5) av.
Angle between B planes	2.5	74.9

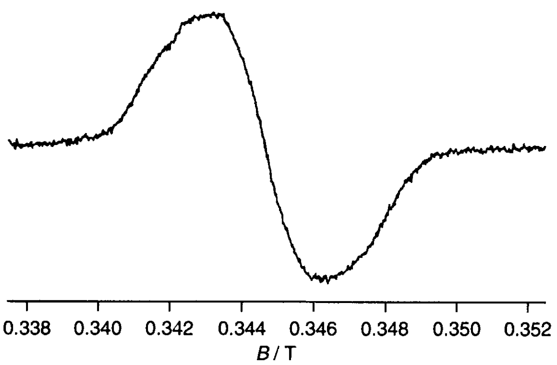

Fig. 2 Continuous wave EPR spectrum of 1; T = 5.2 K, microwave frequency = 9.67 GHz, microwave power = 0.20166 mW, modulation amplitude = 0.11 G, modulation frequency = 50 kHz, sweep time = 335 s, time constant = 82 ms

The *ca.* 5% shortening in **1** may also be compared to those observed in the single reduction of the related aluminium and gallium compounds $[Trip_2MMTrip_2]^{\cdot-}$ [Trip = $C_6H_2Pr^i{}_3$-2,4,6; M = Al (6.7%),[8] Ga (6.8%)[9]] and $[R_2MMR_2]^{\cdot-}$ [R = $CH(SiMe_3)_2$; M = Al (4.9%),[10] Ga (5.5%)[11]]. The significantly greater shortening in the heavier element aryl derivatives may be attributed to the neutralization of the partial $\delta+$ charge on the electropositive metals (Al, Ga) that occurs upon reduction. In the case of the neutral boron precursors the partial positive charge on boron is not nearly as great owing to the less electropositive nature of this element. For the aluminium and gallium alkyl species the percentage shortening is not as large, possibly as a result of the very large size of the $CH(SiMe_3)_2$ substituents. It has been proposed, however, that hyperconjugative interactions between the H–C–Si bonds of the substituents and the unsaturated Al and Ga centres give rise to a weak electronic delocalization across the Al–Al and Ga–Ga bonds[11] thus reducing the bond shortening effects of the one electron reduction. The lengthening of the B–O distance from 1.363(10) Å av. to 1.454(4) Å probably occurs for two major reasons. First, the coordination number of oxygen is increased upon solvation of the lithium ion. In addition, the ionic contribution to B–O bonding is reduced owing to a competitive attraction of the oxygen electron density by the Li^+ ion. It is, however, possible to argue that some of the increase in B–O bond length is due to a diminution of the B–O π-bonding owing to the formation of the B–B π-bond.

The CW EPR spectrum of **1** at 5.2 K is shown in Fig. 2. The absence of resolved hyperfine coupling is, perhaps, its most notable feature. Though unresolved, it is probable that proton hyperfine couplings of the same order of magnitude as ^{11}B or ^{10}B coupling broaden the spectrum to the extent that the boron hyperfine couplings can not be determined precisely.¶

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Footnotes

† All manipulations were conducted under anaerobic and anhydrous conditions. Compound **1** was synthesized by the addition of MeO(mes)BB(mes)OMe **2**[4] (0.35 g, 1.1 mmol) in diethyl ether (20 ml) to a suspension of lithium powder (0.09 g, 13.5 mmol) in diethyl ether (10 ml) cooled in a solid CO_2–acetone bath. After stirring for 1 h the solution was allowed to warm to room temp. and stirred for a further 3 h (longer reaction times result in a significantly reduced yield of the product owing to decomposition). After filtering through a frit, hexane (10 ml) was added and the volume of the solution was reduced to *ca.* 15 ml. Slow cooling in a −20 °C freezer overnight yielded dark blue–black crystals of **1** (0.11 g, 0.2 mmol, 21% based on boron); mp 69–69.5 °C. IR (Nujol): ν/cm^{-1} 1610ms, 1410s, 1320s, 1260vs, 1150s (sh), 1100vs (br), 1015vs, 975ms, 940mw, 875m, 850ms, 800vs, 740w, 720mw, 690mw, 550w, 480mw (br), 395mw, (br). UV–VIS (Et_2O): λ/nm 307 (sh) 589. EPR (Et_2O, 5.2 K): g = 2.0046(10).

‡ *Crystal data* for **1** with Cu-Kα radiation (λ = 1.54178 Å), T = 212 K, $C_{14}H_{24}BLi_{0.5}O_2$, monoclinic, space group $I2/a$, a = 15.562(3), b = 11.578(2), c = 17.106(3) Å, β = 95.509(9)°, Z = 8, R = 0.067 for 1496 [$I > 2\sigma(I)$] data. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/210.

§ It is unlikely that the association of alkali-metal counter cations with an $[R_2BBR_2]^{-\cdot}$ ion would have any major effect on the B–B bond length. Although calculations[13] on the doubly reduced hypothetical species $Li_2H_2BBH_2$ show that the B–B distance increases when the Li^+ ions are removed, a partial crystal structure[14] of the solvent separated ion pair species $[\{K(18\text{-crown-}6)(thf)_2\}\{mes_2BB(mes)Ph\}]$ shows that the B–B distance is 1.65(1) Å which is just over one standard deviation longer than the B–B distance observed in **2**.

¶ Proton coupling constants (*ca.* 0.4 mT) and ^{11}B coupling constants (*ca.* 0.8 mT); for example, see ref. 3(*a*).

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