Boron-centred Diradical Dianion: a New Triplet State Molecule

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Sodium reduction of bis(dimesitylboron)-1,3-phenylene **1** in 2-methyltetrahydrofuran–tetrahydrofuran gives the corresponding diradical dianion, a new triplet state molecule.

New organic triplet diradicals, with strong intramolecular ferromagnetic coupling, good thermal stability, and a potential for complexation of metals, may serve as building blocks for molecular magnets.[1] Such diradicals are prerequisites for the design and preparation of new very high-spin molecules, especially relevant to the study of magnetism on the mesoscopic scale.[2] Only a few examples of such diradicals, even partially satisfying the above criteria, have been reported.[3]

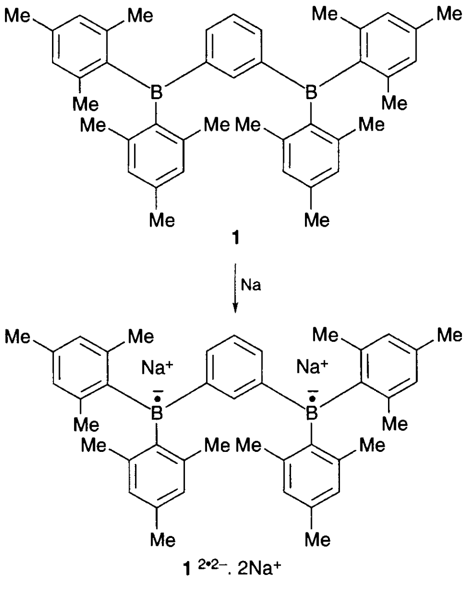
Here we report a new triplet state molecule, diradical dianion $\mathbf{1}^{2\cdot 2-}.2Na^+$, which was prepared by reduction of the corresponding diborane **1** with sodium metal in tetrahydrofuran–2-methyltetrahydrofuran (THF–2MeTHF).

The diradical dianion $\mathbf{1}^{2\cdot 2-}.2Na^+$ can be viewed as two stable 'monoradicals' (triarylborane radical anions) linked with a 'ferromagnetic coupling unit' (1,3-phenylene);[2a,4] an analogous design, with π-isoelectronic triarylmethyl 'monoradicals', was used for polyarylmethyl di- and poly-radicals.[2a,5,6]

Diborane **1** was obtained by addition of the di-Grignard reagent, 1,3-bis(bromomagnesium)phenylene, to dimesitylboron fluoride.[†,7] CV of **1** in THF/TBAP (TBAP = tetrabutylammonium perchlorate) revealed two reversible waves at peak potentials E_p = −2.02 and −2.64 V, with identical peak currents.[8,9] Controlled potential bulk electrolysis at a potential exceeding that corresponding to the less negative CV wave gave a deep blue solution; for this solution, an intense ESR spectrum corresponding to a spin S = 1/2 species was obtained. For comparison, dimesitylphenylborane in THF/TBAP shows only one CV wave at E_p = −2.10 V, which, in triarylboranes, was assigned to one-electron reductions to radical anions.[4c,9] Therefore, the two CV waves for **1** most likely correspond to one-electron transfers, *i.e.* radical anion and diradical dianion (or dianion) of **1**.

It has been reported that Na metal in THF cleanly produced the radical anion of dimesitylphenylborane and only sluggishly led to its diamagnetic dianion.[10] Thus, the diradical dianion of **1** might be generated under comparable conditions and the overreduction of **1** to the higher charged anions (corresponding to dianions of monoborane) can be avoided.

The reaction of 0.014 mol dm^{-3} **1** in 2-MeTHF–THF (1 : 1) with excess sodium metal at ambient temperature was followed by ESR spectroscopy. At the initial reaction stage, the ESR spectrum of the deep purple–blue reaction mixture was identical to that obtained from the product of the bulk electrolysis. Upon further reduction the reaction mixture slowly changed to deep green; the corresponding X-band ESR spectra of the frozen reaction mixture at 80 K showed a replacement of the centre peak (the S = 1/2 radical anion) with a broad four-line symmetrical spectrum with a spectral width of *ca.* 300 G, which was assigned to a triplet state (S = 1) with the zero field splitting (zfs) parameters, $|D/hc|$ = 0.0103 and $|E/hc|$ *ca.* 0.001 cm^{-1} (see Fig. 1). Also, a weak Δm_s = 2 resonance was observed. The values of the zfs parameters are comparable to those for the π-isoelectronic polyarylmethyl diradicals,[5] suggesting analogous spin density distributions.[11] Upon dilution with THF, the UV–VIS spectrum revealed a broad band at λ_{max} 530 nm (sh 700 nm). Furthermore, following ESR spectroscopy, oxidation of the deep green reaction mixture with iodine gave a colourless solution, from which diborane **1** was recovered. Thus, the S = 1 ESR spectrum was assigned to the diradical dianion $\mathbf{1}^{2\cdot 2-}.2Na^+$.



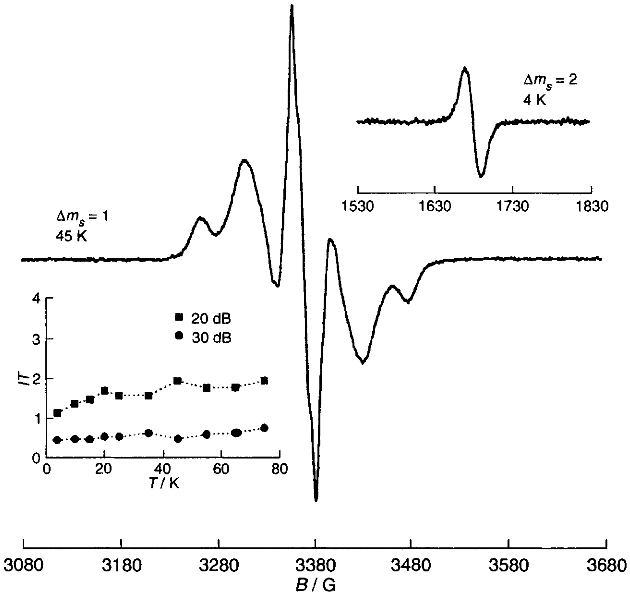


Fig. 1 The ESR spectra of 0.014 mol dm^{-3} diradical dianion $1^{2\cdot 2-}.2Na^+$ in 2-MeTHF/THF (1 : 1). Main spectrum and upper insert: the Δm_s = 1 and Δm_s = 2 regions at T = 45 and 4 K, respectively; computer simulation (not shown) of the Δm_s = 1 region gives the following parameters for an S = 1 state: $|D/hc|$ = 0.0103 cm^{-1}, $|E/hc|$ = *ca.* 0.001 cm^{-1}, Gaussian line width of 20 G. Lower insert: plot of the product (IT) of the intensity (I) for the Δm_s = 2 resonance and the temperature (T) *vs.* T at two settings of microwave power attenuation 30 and 20 dB (the third setting, 10 dB, is not shown); no detectable microwave saturation was found at the lowest power (30 dB). The values of I are obtained by numerical double integration of the Δm_s = 2 region.

The ESR spectra in the both $\Delta m_s = 1$ and 2 regions at 4 K (with some loss of intensity due to microwave saturation) was very intense. The plot of the product (IT) of the intensity (I) for the $\Delta m_s = 2$ resonance and temperature (T) *vs.* T was constant in the 4–75 K range (Fig. 1); similarly, the Curie plot (I *vs.* $1/T$) was linear in this temperature range. Because no detectable change in relative thermal population of the triplet and singlet states in the 4–75 K range was found, the singlet–triplet energy gap (ΔE_{ST}) was approximately either smaller or greater than RT in this temperature range. In the first case, the singlet and triplet states are near degenerate; in the second case, the triplet state has to be the ground state. The triplet ground state, *i.e.* intramolecular ferromagnetic coupling between the two 'unpaired' electrons, is tentatively considered more likely.[12]

When diborane **1** was reacted with Na in 2-MeTHF or 2-MeTHF–THF (4 : 1), more complex and broader (spectral width of 470 and 370 G) X-band ESR spectra for $S = 1$ states of $\mathbf{1}^{2\cdot 2-}$;$2Na^+$ were obtained. When the sample of diradical dianion $\mathbf{1}^{2\cdot 2-}.2Na^+$, prepared in 2-MeTHF, was diluted with an approximately equal volume of THF, the ESR spectrum changed to that obtained for $\mathbf{1}^{2\cdot 2-}.2Na^+$, prepared in 2-MeTHF–THF (1 : 1).[13] Similar solvent dependence of the ESR spectra for the $S = 1$ states of selected carbodianions was assigned to ion pairing effects.[14,15]

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Footnote

† Selected data for **1**: white solid, mp 168–169 °C. HR EIMS: M^+ 574.39411 (0.6%, −0.19 ppm dev. for $^{12}C_{42}{}^{1}H_{48}{}^{11}B_2$); $(M - C_9H_{12})^+$ 454.30025 (24.0%, −0.15 ppm dev. for $^{12}C_{33}{}^{1}H_{36}{}^{11}B_2$), 453.30253 (11.3%, −3.1 ppm dev. for $^{12}C_{33}{}^{1}H_{36}{}^{11}B_1{}^{10}B_1$); $(M - C_{18}H_{24})^+$ 334.20806 (100.0%, 4.9 ppm dev. for $^{12}C_{24}{}^{1}H_{24}{}^{11}B_2$), 333.21119 (45.6%, 3.4 ppm dev. for $^{12}C_{24}{}^{1}H_{24}{}^{11}B_1{}^{10}B_1$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.54 (dd, $J = 7$ and 1 Hz, 2 H), 7.52 (br s, 1 H), 7.29 (t, $J = 7$ Hz, 1 H), 6.74 (s, 8 H), 2.26 (s, 12 H) and 1.94 (s, 24 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 146.4 (br), 142.9, 142.0 (br), 140.7, 139.1, 138.6, 128.1, 127.6, 23.3 and 21.1.

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