Synthetic routes to cyclic and unsymmetric diborane(4) compounds

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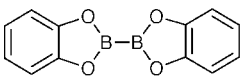
The reaction between 1,2-$B_2Cl_2(NMe_2)_2$ and disodium catecholate $Na_2[1,2\text{-}O_2C_6H_4]$ affords the cyclic diborane(4) compound 1,2-$B_2(NMe_2)_2$(cat) (cat = 1,2-$O_2C_6H_4$), whereas a similar reaction using dilithium thiocatecholate $Li_2[1,2\text{-}S_2C_6H_4]$ affords the 1,1-isomer 1,1-$B_2(NMe_2)_2$(thiocat) (thiocat = 1,2-$S_2C_6H_4$). Both compounds can be used to prepare unsymmetric diborane(4) species.

Diborane(4) compounds have recently been the focus of renewed interest in part because they are key reagents in transition metal catalysed diboration reactions[1] for which the most widely used are the diolate species $B_2(pin)_2$ (**1**) (pin = pinacolate) and $B_2(cat)_2$ (**2**) (cat = 1,2-$O_2C_6H_4$).[2] In addition to the boron(II) halides,[3] other well characterised and synthetically useful compounds include the amido species $B_2(NMe_2)_4$ [4] (**3**) and 1,2-$B_2Cl_2(NMe_2)_2$ [5] (**4**) and the thiocatecholate derivative $B_2(1,2\text{-}S_2C_6H_4)_2$ (**5**).[2b] From a structural perspective, it is noteworthy that compounds **1**, **2** and **5**, and almost all related species that have been structurally characterised, exist as 1,1-isomers,[6] as shown in the diagram for **2**, rather than as an alternative 1,2-isomer (*e.g.*, **2a**), although 1,2-isomers are known, as in the case of the binol derivative $B_2(O_2C_{20}H_{12})$ ($O_2C_{20}H_{12}$ = binaphthalenolate or binolate).[7] In fact, this topic of 1,1- *vs.* 1,2-isomers has a long history and was first addressed by Shore and co-workers[8] for a range of O, S and N substituted species and later by Nöth *et al.*,[9] although in most cases definitive structural data were lacking. We set out to determine whether a 1,2-isomer of **2** (*i.e.*, **2a**) could be prepared and describe some preliminary results herein.



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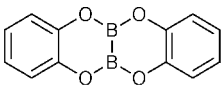
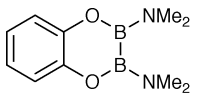


2a

The reaction between 1,2-$B_2Cl_2(NMe_2)_2$ (**4**) and disodium catecholate ($Na_2[1,2\text{-}O_2C_6H_4]$) in toluene afforded, after work-up, good yields of a colourless crystalline solid characterised as 1,2-$B_2(NMe_2)_2$(cat) (**6**).† The appearance of a single ^{11}B NMR chemical shift (δ_B 29.1)† was consistent with **6** being a 1,2-isomer [two signals close to the values for **2** (δ_B 29.0[2b]) and **3** (δ_B 34.9[2b,4]) would be expected for the inequivalent borons in a 1,1-isomer] and this was confirmed by X-ray crystallography (Fig. 1).‡ The molecules of **6** lie on a crystallographic C_2 axis and the B–B bond is bridged in a 1,2-fashion by the catecholate, with each boron carrying a terminal NMe_2 group. The B–O [1.411(3) Å] distance in **6** differs from those observed in **2** [B–O 1.382(2), 1.394(2) Å[6]], probably as a result of significantly less π-donation from oxygen to boron in **6**, due to the presence of a strongly π-donating NMe_2 group [B–N 1.391(3) Å]. The B–B bond is also longer than in **2** [B–B 1.707(4) Å, *cf.* 1.675(3) Å in **2**[6]], possibly as a result of its incorporation into a six-membered ring. That N → B π-donation is important is further established by the near coplanarity of all atoms associated with the BN unit, although this results in a marked twisting of the molecule in order to avoid unfavourable steric interactions between the C(5) methyl groups [torsion angle N(1)–B(1)–B(1A)–N(1A) 31.2°; angle between the mean planes O(1), B(1), N(1) and O(1A), B(1A), N(1A) 27.0°]. Separate methyl group resonances were also observed in the ^1H NMR spectrum of **6**, consistent with hindered rotation about the B–N bond. We note a related reaction between **4** and $K_2[1,2\text{-}(CH_2)_2C_6H_4]$ that also affords a 1,2-isomer, *viz.* 1,2-$B_2(NMe_2)_2[1,2\text{-}(CH_2)_2C_6H_4]$.[10]



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The reaction between **6** and catechol in Et_2O, followed by addition of 2 equiv. of HCl, was carried out with the expectation, by analogy with the reaction between **3** and catechol,[2b,§] of forming $B_2(cat)_2$ as the 1,2-isomer **2a**. However, although the reaction proceeded cleanly, the compound isolated was found to be the 1,1-isomer **2** as confirmed by spectroscopic[2b] and X-ray crystallographic methods.[6] The fact that **2** rather than **2a** was formed indicates that the 1,1-isomer is probably thermodynamically favoured and results from a catecholate group rearrangement process in solution {similar isomeric rearrangements have been suggested by Nöth and co-workers for the compounds $B_2(NR_2)_2[N(Me)CH_2CH_2N(Me)]$

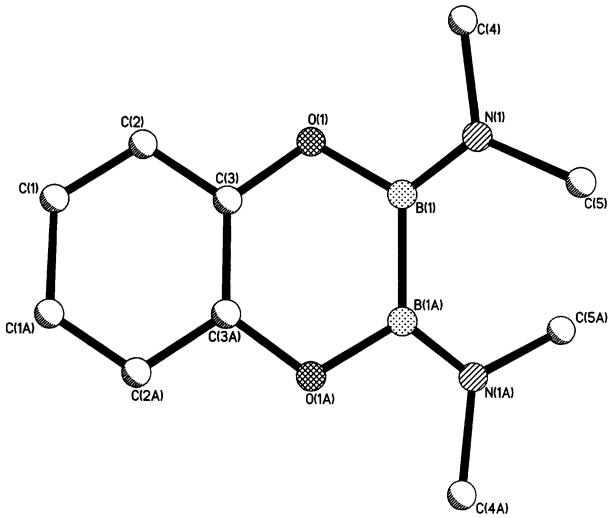
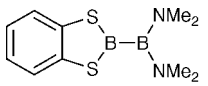


Fig. 1 A view of the molecular structure of **6** showing the atom numbering scheme. Atoms are drawn as spheres of arbitrary radius. Selected bond lengths (Å) and angles (deg) include B(1)–B(1A) 1.707(4), B(1)–N(1) 1.391(3), B(1)–O(1) 1.411(3), O(1)–C(3) 1.373(2), B(1A)–B(1)–N(1) 131.52(13), B(1A)–B(1)–O(1) 113.73(11), N(1)–B(1)–O(1) 114.68(18).

(R = Me, Et) based on spectroscopic data[9b]. However, this observation indicated that reactions between **6** and other diols might afford unsymmetrical diborane(4) compounds (an aim originally envisaged though not realised by Welch and Shore[8a]). Thus, B_2(cat)(pin) (**7**)¶ (probably as a 1,1-isomer¶) was the major product in the reaction between **6** and pinacol although appreciable amounts of **1** and **2** were also formed. The reaction between **6** and tetrachlorocatechol also afforded mixtures of **2**, $B_2(1,2\text{-}O_2C_6Cl_4)_2$ [13] and B_2(cat)$(1,2\text{-}O_2C_6Cl_4)$ (**8**) as evidenced by mass spectrometry.¶ Both reactions indicate that intermolecular (and possibly intramolecular) diolate group rearrangement is occurring (see also ref. 9*b*), possibly catalysed by any excess HCl present.

Attempts to prepare $B_2(NMe_2)_2$(pin) (**9**), the pinacolate analogue of **6**, by the reaction of **4** with disodium pinacolate $Na_2[O_2C_2Me_4]$ (the dilithium salt reacts similarly) afforded a mixture of **1** and **3** although ^{11}B NMR data were consistent with the presence of small amounts of 1,1-$B_2(NMe_2)_2$(pin) (δ_B 38.8, 29.7; *cf.* **3** δ_B 34.9, **1** δ_B 28.5); the possibility that a 1,2-isomer is present in solution cannot be ruled out. The reaction between **4** and the dilithium salt of dithiocatechol in toluene–THF, however, proceeded much more cleanly, affording high yields of 1,1-$B_2(NMe_2)_2$(thiocat) (**10**) (thiocat = $1,2\text{-}S_2C_6H_4$) identified unambiguously as the 1,1-isomer by the disparate ^{11}B NMR chemical shifts (δ_B 61.6, 31.8, *cf.* **5** δ_B 57.9,[2b] **3** δ_B 34.9).‖ The reason why **6** is formed as a 1,2-isomer whereas **10** is observed as a 1,1-isomer is unclear although the fact that **6** is not very stable in solution,† together with the diolate rearrangements referred to above, indicate that the 1,2-isomeric forms might be kinetic products whereas the 1,1-isomers are thermodynamically more stable. To shed light on this matter *ab initio* electronic structure calculations on the 1,1- and 1,2-isomers of **2**, **5**, **6** and **10** were carried out. Geometries were optimised at the HF/6-31G level of theory with **2** and **5** having D_{2h} symmetry and **6** and **10** having C_2 symmetry.[14] Single point B3LYP/6-31G*//HF/6-31G calculations were carried out to obtain reliable energies. These results are in good agreement with the experimental observations: the 1,1-isomers of **2**, **5** and **10** are the more stable (by 3.0, 19.3 and 6.0 kcal mol^{-1}, respectively) whereas the 1,2-isomer of **6** is the more stable by 7.7 kcal mol^{-1}.**

Treatment of **10** in THF with either pinacol and HCl or catechol and HCl afforded B_2(thiocat)(pin) (**11**) or B_2(thiocat)(cat) (**12**), respectively (presumably as 1,1-isomers), identified by mass spectrometry, albeit as mixtures with the respective symmetrical species **1** and **5** or **2** and **5**.††



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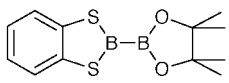

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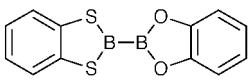

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In conclusion, these preliminary results reveal that although cyclic 1,2-species such as **6** can be formed, facile rearrangement of diolate or dithiolate groups in solution allows access to favoured 1,1-isomers with an unsupported B–B bond. In most cases, the formation of mixtures of unsymmetrical and symmetrical products is synthetically undesirable although **6** and **10** can be prepared and isolated in high yields.

Acknowledgements

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Notes and references

† Equimolar quantities of **4** (3.518 g, 19.5 mmol) and $Na_2[1,2\text{-}O_2C_6H_4]$ (3.00 g, 19.5 mmol) were stirred in toluene for 3 h. Filtration, reduction of the filtrate volume and cooling afforded colourless crystals of **6** (66%). Recrystallisation from MeCN and cooling to −26 °C afforded X-ray quality crystals. Traces of **4** (δ_B 35.7) and B(NMe$_2$)(cat) (δ_B 23.8) were observed by ^{11}B NMR. Spectroscopic data for **6**: NMR (CD_2Cl_2) ^{1}H δ 6.98 (m, 2H, $1,2\text{-}O_2C_6H_4$), 6.85 (m, 2H, $1,2\text{-}O_2C_6H_4$), 2.90 (s, 6H, NMe_2), 2.83 (s, 6H, NMe_2); ^{13}C-{^{1}H} δ 145.0 (C–O), 121.5 (cat CH), 119.3 (cat CH), 40.9 (NMe_2), 35.4 (NMe_2); ^{11}B-{^{1}H} δ 29.1 (br s). $C_{10}H_{16}B_2N_2O_2$ requires C, 55.15; H, 7.40; N, 12.85. Found C, 53.40; H, 6.35; N, 12.65.

‡ Crystal data for **6**: $C_{10}H_{16}B_2N_2O_2$, M = 217.86, monoclinic, space group $C2/c$, a = 11.931(7), b = 11.105(11), c = 8.929(5) Å, β = 90.96(4)°, U = 1182.8(15) Å^3, Z = 4, λ = 0.710 73 Å, μ = 0.082 mm^{-1}, T = 173(2) K, D_{calc} = 1.223 Mg m^{-3}, $F(000)$ = 464, 930 unique data, R_1 = 0.0402. CCDC reference number 440/162. See http://www.rsc.org/suppdata/nj/a9/a909645k/ for crystallographic files in .cif format.

§ The reaction between **4** and 2 equiv. of either catechol or pinacol provides an alternative synthetic route to **2** and **1**, respectively, although it offers no particular advantage over published procedures starting from **3**.[2,11] The complex $[B_2Cl_4(NHMe_2)_2]$[2b,12] may also be employed as the boron source.

¶ Compound **6** was generated *in situ* in THF, which was followed by addition of 1 equiv. of pinacol and a slight excess of HCl in Et_2O (>2 equiv.) at −78 °C. Filtration, removal of all volatiles from the filtrate and extraction in hexane afforded **1** and **7**; subsequent extraction in benzene afforded **2**. Spectroscopic data for **7**: NMR (C_6D_6) ^{1}H δ 7.03 (m, 2H, $1,2\text{-}O_2C_6H_4$), 6.78 (m, 2H, $1,2\text{-}O_2C_6H_4$), 1.04 (s, 12H, pin); ^{11}B-{^{1}H} δ 29.3 (br s) [although only one ^{11}B NMR signal was seen for **7**, the chemical shifts of **1** (28.5) and **2** (29.0) are very similar, making it difficult to distinguish between possible 1,1- and 1,2-isomers]. HRMS calculated for $C_{12}H_{16}B_2O_4$ 246.123 470. Found 246.122 677. Compound **8** was prepared by generating **6** in toluene and adding tetrachlorocatechol. All volatiles were then removed and the white solid dissolved in Et_2O to which HCl was added. Extraction in toluene afforded mostly **2**, leaving a mixture of **8** and $B_2(1,2\text{-}O_2C_6Cl_4)_2$ as a white solid. Spectroscopic data for **8**: LRMS m/z 376 (M^+).

‖ A solution of **4** (0.470 g, 2.60 mmol) in toluene (20 cm^3) was added *via* syringe to a solution of $Li_2[1,2\text{-}S_2C_6H_4]\cdot$THF in THF (0.576 g, 2.25 mmol) cooled to 0 °C. After stirring overnight and warming to room temperature, a white precipitate was removed by filtration and all volatiles removed from the filtrate. Extraction into hexane, further filtration and vacuum pumping afforded an oily solid comprising **10** (90%). Spectroscopic data for **10**: NMR ($CDCl_3$) ^{1}H δ 7.85 (m, 2H, $1,2\text{-}S_2C_6H_4$), 7.29 (m, 2H, $1,2\text{-}S_2C_6H_4$), 2.72 (s, 12H, NMe_2); ^{11}B-{^{1}H} δ 61.6, 31.8 (br s).

** To calibrate and validate this computational approach, further calculations were carried out on models of **2**, **5**, **6** and **10**. The models differ from the structures discussed in the text in that the 1,2-disubstituted benzene rings are replaced with *cis*-1,2-disubstituted ethene units and the dimethylamino fragments are replaced by amino groups. For the model systems, B3LYP/6-31G*//HF/6-31G energies were calculated as above, yielding similar results as for the full compounds; full geometry optimisation at the B3LYP/6-31G* level was also performed. The geometries were very similar to the HF/6-31G values and the relative energies were essentially identical. The effects of larger basis sets and other methods for treating electron correlation were explored by performing full B3LYP/6-311+G* optimisations as well as single point MP2/6-31G*//HF/6-31G calculations. All of these calculations were in very close agreement with the B3LYP/6-31G*//HF/6-31G results.

†† Spectroscopic data for **11**: NMR (C_6D_6) ^{1}H δ 7.53 (m, 2H, $1,2S_2C_6H_4$), 6.93 (m, 2H, $1,2\text{-}S_2C_6H_4$), 1.10 (s, 12H, pin); ^{11}B-{^{1}H} δ 55.5, 29.7 (br s). HRMS calculated for $C_{12}H_{16}B_2O_2S_2$ 278.077 784. Found 278.077 507. Spectroscopic data for **12**: NMR (C_6D_6) ^{1}H δ 7.51 (m, 2H, $1,2\text{-}S_2C_6H_4$), 7.08, (m, 2H, $1,2\text{-}O_2C_6H_4$), 6.90 (m, 2H, $1,2S_2C_6H_4$), 6.82, (m, 2H, $1,2\text{-}O_2C_6H_4$); ^{11}B-{^{1}H} δ 53.2, 28.8 (br s). HRMS calculated for $C_{12}H_8B_2O_2S_2$ 270.015 184. Found 270.014 923.

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