Synthesis and Properties of 1,3,5-Tris(dimesitylboryl)benzene and 1,3-Bis(dimesitylboryl)benzene

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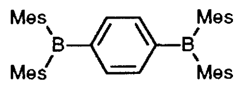
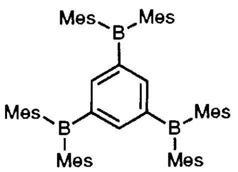
1,3,5-Tris(dimesitylboryl)benzene and 1,3-bis(dimesitylboryl)benzene were synthesized and their conformational analysis including X-ray structure determination of the former was studied; electrochemical properties of these compounds were also examined.

Benzenes substituted with more than two diarylboryl groups are interesting compounds because of their multiple propeller structures[1] owing to the triarylborane units, as well as their electron-accepting ability[2] being perturbed by the boryl substituents. Hitherto, only a few compounds of this type are known. 1,4-Bis(dimesitylboryl)benzene **1** and its biphenyl analogue are such limited examples and their reduction potentials have been reported.[3] Conformational study of these compounds has not been reported. We now report synthesis of 1,3,5-tris(dimesitylboryl)benzene **2** and 1,3-bis(dimesitylboryl)benzene **3**, conformational studies including X-ray structural analysis of **2**, and their reduction potentials.

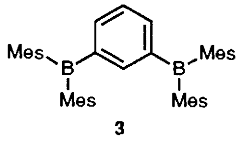
Synthesis of **2** was achieved by a simple one-pot procedure; into a Grignard solution prepared from 1,3,5-tribromobenzene (1 equiv.) and magnesium (3.2 equiv.) in tetrahydrofuran (THF), dimesitylfluoroborane (3.2 equiv.) was added and the solution was refluxed for 2 days. The separation with chromatography (SiO_2) provided the desired **2** in 2% yield along with **3** (2%) and dimesitylphenylborane (23%). Compound **3** was obtained in higher yield (15%) from *m*-dibromobenzene under similar conditions. These boranes are stable toward moisture and air.†



1



2



3

In view of the propeller conformation of triarylboranes,[1] a structure having a three propeller conformation (D_3-symmetry in an ideal case) can be expected for **2**. Fig. 1 shows a temperature-dependent ^1H NMR (500 MHz) spectrum of *o*-methyl protons of **2**. A singlet owing to the *o*-methyl protons at 30 °C splits into more than six singlets at −105 °C through a coalescence signal at −85 °C. The observed spectrum cannot be explained by D_3-symmetry, because only two singlets of the *o*-methyl protons are expected in the conformer of this high symmetry. A conformer of lower C_2-symmetry has six kinds of methyl protons. Provided that the signal observed at δ 1.68 is a pure singlet of conformer of C_2-symmetry, the integration indicates that this singlet occupies about 75% of the conformers. Similarly, the signal of the *o*-methyl protons of **3** splits into more than four singlets with intensities of about 6 : 1.5 : 1.5 : 1 from the lower field at −95 °C.

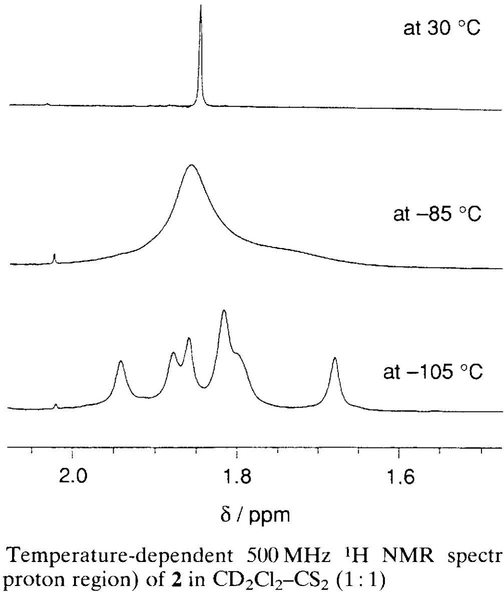


Fig. 1 Temperature-dependent 500 MHz ^1H NMR spectrum (*o*-methyl proton region) of **2** in CD_2Cl_2–CS_2 (1 : 1)

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† *Spectral and physical data* for **2** and **3**: **2**; colourless prisms, m.p. 237 °C, ^1H NMR (400 MHz, CD_2Cl_2) δ 1.89 (s, 36H), 2.25 (18H, s), 6.71 (s, 12H), 7.51 (s, 3H). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 21.2, 23.3, 128.0, 138.4, 140.48, 140.54 (br), 145.4, 146.2 (br). **3**; colourless prisms, m.p. 169 °C, ^1H NMR (400 MHz, CD_2Cl_2) δ 1.94 (s, 24H), 2.27 (s, 12H), 6.77 (s, 8H), 7.32 (td, 1H, *J* 7.3, 0.7 Hz), 7.50 (br s, 1H), 7.53 (dd, 2H, *J* 7.3, 1.3 Hz). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 21.2, 23.3, 127.7, 128.1, 138.6, 139.1, 140.7, 141.9 (br), 142.8, 146.4 (br).

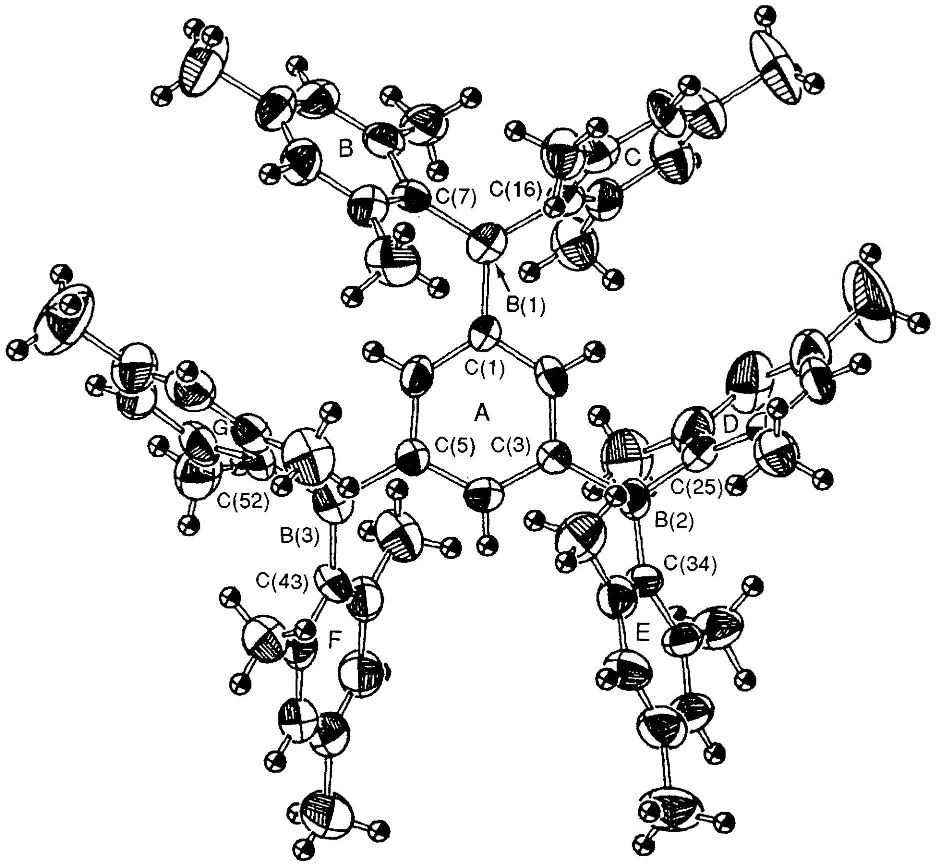

Fig. 2 ORTEP view of **2** showing 50% thermal ellipsoids. Incorporated recrystallization solvent (C_6H_6) is omitted. Bond distances (Å) including B(1), B(2) and B(3) are as follows: B(1)–C(1) 1.56(1), B(1)–C(7) 1.58(1), B(1)–C(16) 1.59(1), B(2)–C(3) 1.57(1), B(2)–C(25) 1.56(1), B(2)–C(34) 1.58(1), B(3)–C(43) 1.57(1), B(3)–C(52) 1.55(1). Dihedral angles between mesityl (plane *B–G*) and central benzene (plane *A*) rings are as follows: *B–A* 66.3, *C–A* 71.2, *D–A* 74.3, *E–A* 69.9, *F–A* 66.6, *G–A* 71.0°.

In order to obtain a definitive insight into the conformation of **2**, X-ray structural analysis was performed.‡ Fig. 2 shows an ORTEP drawing of **2**. Boron and three sp^2 carbons bound to it are almost coplanar in all the three triarylborane units. Six mesityl groups rotate out from the central benzene ring to the extent of 66–75°. Two mesityl groups bound to the same boron make a propeller conformation with the central benzene ring and three propeller structures were observed. However, one of the propellers has a different helicity from the other two and the molecule lies almost on a C_2-axis. These results with the above temperature-dependent ^1H NMR spectral data indicate that compounds **2** and **3** in solution, exist as an equilibrium mixture of conformers, which have a different helicity in the propeller structure of the triarylborane units. The major isomer in Fig. 1 can be a conformer similar to the X-ray structure.

Kaim and Schulz reported the reduction potential of **1** and estimated the electron-withdrawing ability of the dimesitylboryl group to be comparable with the cyano group.[3] However, the reduction potential [$E_{\frac{1}{2}}$; V *vs.* SCE (saturated calomel electrode) in DMF (dimethylformamide)] of **2** (−1.95) was unexpectedly low compared to the *p*-analogue **1** [$E_{\frac{1}{2}}(1) = -1.55$, $E_{\frac{1}{2}}(2) = -2.25$], almost the same with that of **3** (−1.98) and a little higher than trimesitylborane (−2.18).§ The second reduction peak for **2** and **3** was lower than −2.4 V (limit of measurement under the conditions).

Acknowledgement is made to the Itoh Science Foundation for partial financial support.

Received, 13th August 1991; Com. 1/04240H

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‡ *Crystal data* for **2**: $C_{60}H_{69}B_3{\cdot}C_6H_6$, monoclinic, space group $P2_1/c$ (No 14), $a = 12.097(9)$, $b = 20.947(4)$, $c = 21.497(6)$ Å, $\beta = 96.72(4)°$, $V = 5410(4)$ Å^3, $Z = 4$, $D_c = 1.106$ g cm^{-3}; Rigaku AFC5R; Mo-Kα radiation [$\lambda(K\alpha) = 0.71069$ Å]; $3° < 2\theta < 50°$; 7553 unique reflections, of which 2339 were treated as observed [$F_o^2 > 3\sigma(F_o^2)$]; an absorption correction was not applied; $R = 0.060$, $R_w = 0.061$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ The reduction potentials were determined by cyclic voltammetry in DMF containing tetrabutylammonium perchlorate (0.1 mol dm^{-3}) with a sweep rate of 100 mV s^{-1} at 20 °C. Slightly different values have been reported for **1** and trimesitylborane by Kaim *et al.*[3]