# *Supplementary Information*

## A Polycyclic Borazine Radical Cation: [1,2-$B_2${1,2-$(MeN)_2C_6H_4$}$_2$]$^{\bullet+}$

**Xiaochen Xie,[a] Christopher J. Adams,[a] Muhsen A. M. Al-Ibadi,[b, c] John E. McGrady,[b] Nicholas C. Norman[a],* and Christopher A. Russell[a],***

[a] *University of Bristol, School of Chemistry, Bristol, BS8 1TS, UK*
[b] *Department of Chemistry, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR, UK*
[c] *Present address: Department of Chemistry, University of Kufa, Najaf, Iraq.*

### General Experimental

$B_2(NMe_2)_4$[1], 1,2-$B_2${1,2-$(NH)_2C_6H_4$}$_2$[2] and Ag[Al{OC$(CF_3)_3$}$_4$][3] were prepared according to literature procedures. All other chemicals used were purchased from commercial sources and used as supplied. Elemental compositions (C, H and N) were determined by sealing samples in air-tight aluminium boats in a glove-box and recorded on a Carlo Erba EA1108 CHN elemental analyser. Solution NMR spectroscopy samples were prepared using dry and degassed deuterated solvent in air-tight NMR tubes sealed with a Young's tap; $^{11}B$ NMR spectra were run on a Jeol Eclipse and/or Lambda 300 MHz spectrometers and referenced to external samples of $BF_3.OEt_2$. $^1H$ and $^{13}C$ NMR spectra were referenced to the internal solvent peaks.

Electrochemical studies were performed on an EG&G model 273A potentiostat with a three-electrode cell: platinum wire auxiliary electrode, silver wire pseudo-reference electrode and a platinum disc working electrode. Solutions were comprised of $1\times10^{-3}$ M test compound and 0.1 M [$^n$Bu$_4$N][PF$_6$] as the supporting electrolyte in 5 cm$^3$ of dry, deoxygenated solvent. All $E_{1/2}$ values were referenced internally to $Cp_2Fe$ ($E_{1/2}$ = 0.47 V in $CH_2Cl_2$ (vs. SCE)).

EPR spectra were recorded on a Bruker ESP300E spectrometer at room temperature using 1 mm thick quartz flat cells. The potentiostat (Autolab, Type II) was controlled via a PC running General Purpose Electrochemical System software, version 4.9 (Eco Chemie BV, Utrecht). Simulations were performed using EasySpin software.

## Single Crystal X-ray Crystallography

Experiments were performed on **2** and $\mathbf{2}^{\bullet+}[\mathrm{Al}\{\mathrm{OC}(\mathrm{CF}_3)_3\}_4]^-$ using a Bruker-AXS SMART APEX three circle diffractometer employing Mo-$K_\alpha$ radiation ($\lambda = 0.71073$ Å). Intensities were integrated from several series of exposures, each exposure covering 0.3° in $\omega$. Absorption corrections were applied based on multiple and symmetry-equivalent measurements.

**Preparation of 2:** To a solution of $1,2\text{-}B_2\{1,2\text{-}(NH)_2C_6H_4\}_2$ (0.107 g, 0.46 mmol) in THF (20 $cm^3$), a *n*-hexane solution of $Bu^nLi$ (1.6 M, 1.15 $cm^3$, 1.8 mmol) was added dropwise at -78 °C resulting in a pale yellow coloured solution which was then allowed to warm to room temperature with stirring. After 30 min, the reaction mixture was brought briefly to reflux and then left to stir for a further 5 h. A solution of iodomethane (0.260 g, 1.83 mmol) in THF (5 $cm^3$) was then added to the reaction mixture via syringe and the reaction mixture was stirred for another 16 h. After this time, the solvent was removed under reduced pressure and the residue was extracted with toluene (3 × 5 $cm^3$). After storage for 16 h, compound **2** was isolated as colourless crystals and dried in vacuo (0.077 g, 57 %). Single crystals of **2** were grown from a saturated toluene solution stored at 5 °C for 16 h.

**Melting Point:** 133-134 °C, decomposed 194-198 °C to a grey solid.

**NMR data for 2:** $^{11}B\text{-}\{^1H\}$ NMR (96 MHz, 25 °C, $CDCl_3$) $\delta = 34.2$ (br, s); $^1H$ NMR (300 MHz, 25 °C, $CDCl_3$) $\delta = 7.08$ (m, 4H, $C_6H_4$), 6.98 (m, 4H, $C_6H_4$), 3.37 (s, 12H, $CH_3$); $^{13}C\text{-}\{^1H\}$ NMR (100 MHz, 25 °C, $CDCl_3$) $\delta = 139.8$ (s, $C_6H_4$), 120.2 (s, $C_6H_4$), 115.1 (s, $C_6H_4$), 37.0 (s, $CH_3$).

**Elemental Analysis:** Calculated for $C_{16}H_{20}B_2N_4$: C, 66.27; H, 6.95; N, 19.32; found C, 66.12; H, 7.06; N, 19.23%.

**X-ray crystallography:** Crystals of **2** were mounted in inert oil and transferred to the cold gas stream of the diffractometer. Crystal data: $C_{16}H_{20}B_2N_4$, $M = 289.98$, Monoclinic, space group $P2_1/c$, $a = 10.1884(4)$, $b = 7.2885(3)$, $c = 9.9017(4)$ Å, $\beta = 96.650(2)°$, $U = 730.33(5)$ Å$^3$, $Z = 2$, $D_c = 1.319$ Mg/m$^3$, $\lambda = 0.71073$ Å, $\mu(\text{Mo-K}_\alpha) = 0.079$ mm$^{-1}$, $F(000) = 308$, $T = 100(2)$K, $R_1 = 0.0396$ [for 1404 reflections with $I > 2\sigma(I)$]. $wR_2 = 0.11156$ [for all 1689 reflections]. CCDC 945386.

**Preparation of $\mathbf{2}^{\bullet+}$:** To a solid sample of $Ag[Al\{OC(CF_3)_3\}_4]$ (0.070 g, 0.069 mmol), a solution of **2** (0.020 g, 0.069 mmol) in dichloromethane (10 $cm^3$) was added at room temperature resulting in a green-black solution. This solution was stirred for 16 h in the absence of light and then filtered through Celite, washed with dichloromethane (3 × 5 $cm^3$) and then concentrated to *ca.* 5 $cm^3$ and cooled to 0 °C overnight which afforded dark green crystals of $\mathbf{2}^{\bullet+}$ (0.021 g, 23%).

**Melting Point:** decomposed 286-293 °C to a black solid.

**Elemental Analysis:** Calculated for $C_{32}H_{20}AlB_2F_{36}N_4O_4$: C, 30.57; H, 1.60; N, 4.46; found: C, 30.42; H, 1.82; N, 4.36%.

**X-ray crystallography:** Crystals of $\mathbf{2}^{\bullet+}[Al\{OC(CF_3)_3\}_4]^-$ were mounted in inert oil and transferred to the cold gas stream of the diffractometer. Crystal data: $C_{32}H_{20}AlB_2F_{36}N_4O_4$, $M$ = 1257.12, Monoclinic, space group $P2_1/c$, $a$ = 15.4396(11), $b$ = 14.1144(9), $c$ = 20.1020(12) Å, $\beta$ = 94.047(4)°, $U$ = 4369.7(5) Å$^3$, $Z$ = 4, $D_c$ = 1.911 Mg/m$^3$, $\lambda$ = 0.71073 Å, $\mu$(Mo-K$_\alpha$) = 0.246 mm$^{-1}$, $F$(000) = 2476, $T$ = 100(2)K, $R_1$ = 0.0516 [for 11269 reflections with $I>2\sigma(I)$]. w$R_2$ = 0.1251 [for all 15725 reflections]. CCDC 945387.

## Computational methods

Calculations were carried out using the B3LYP functional[4] implemented in Gaussian03.[5] Both structural optimization and the calculation of hyperfine coupling constants, *a*, was performed using the N07D basis set developed by Barone and co-workers[6] which contains core-valence s functions optimised for the computation of *a*. The computed bond lengths are in excellent agreement with experiment, both for $\mathbf{2}^{\bullet+}$ and its one-electron reduced precursor, **2**.

## Table of optimised bond lengths

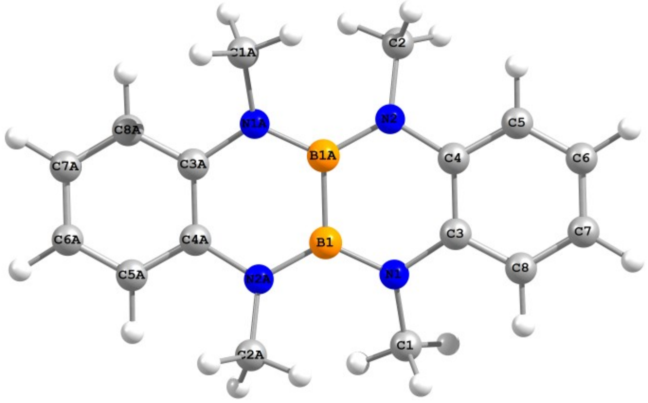

**Table S1.** Selected X-ray and computed bond lengths (Å) for **2** and $\mathbf{2}^{\bullet+}$ (labelled according to figure above).

| | **2** | | $\mathbf{2}^{\bullet+}$ | |
|---|---|---|---|---|
| | **X-ray** | **Computed** | **X-ray** | **Computed** |
| B-B | 1.650(2) | 1.65 | 1.643(3) | 1.65 |
| B-N | 1.426(2), 1.430(2) | 1.44 | 1.427(7), 1.423(7) | 1.44 |
| C(1)-N(1) | 1.470(1) | 1.47 | 1.467(3) | 1.48 |
| C(3)-N(1), C(4)-N(2) | 1.417(2), 1.417(2) | 1.42 | 1.396(3), 1.392(3) | 1.40 |
| C(3)-C(4) | 1.429(2) | 1.43 | 1.435(3) | 1.44 |
| C(3)-C(8), C(4)-C(5) | 1.400(2), 1.398(2) | 1.41 | 1.386(3), 1.410(3) | 1.40 |
| C(5)-C(6), C(7)-C(8) | 1.389(2), 1.387(2) | 1.39 | 1.410(3), 1.370(3) | 1.38 |
| C(6)-C(7) | 1.379(2) | 1.39 | 1.386(3) | 1.40 |

**Table S2.** Comparison of computed isotropic hyperfine values for **2**$^{\bullet+}$ (G) with the final values from the simulation.

| | **DFT** | **Simulation** |
|---|---|---|
| B | 2.48 | 2.12 |
| N | 3.34 | 3.87 |
| C(3)/C(4) | -0.67 | |
| C(5)/C(8) | -0.75 | |
| C(6)/C(7) | 0.77 | |
| C(1)/C(2) | -1.80 | |
| H(5)/H(8) | -0.16 | -0.32 |
| H(6)/H(7) | 1.40 | -1.49 |
| H(Me) | 3.57 | 3.58 |

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