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Boron–nitrogen analogues of the fluorenyl anion†‡

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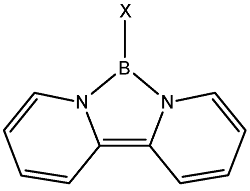
Received 25th February 2010, Accepted 16th April 2010
First published as an Advance Article on the web 29th April 2010
DOI: 10.1039/c0dt00028k

The synthesis and structural characterisation of [BPh(bipy)] and [BCl(bipy)] are described both of which contain a direduced bipy ligand (bipy = 2,2′-bipyridyl) and are analogues of the fluorenyl anion; DFT calculations highlight differences in the electronic structure of both species compared to the fluorenyl anion.

The substitution of pairs of carbon atoms with isoelectronic B–N units in polycyclic aromatic hydrocarbons leads to a series of compounds with similar structural features but subtly different electronic properties.[1,2] For example, analogues of pyrene with internal B–N substitution have recently been synthesised by Piers and coworkers,[3] and the effects of B–N substitution in benzene analogues have also been investigated both structurally with increasing unsaturation[4] and as a result of coordination to $Cr(CO)_3$.[5] These advances complement the recent characterisation of boron-substituted aromatic analogues, such as 9-boraanthracene[6] and also in a dithiophene species containing a B–B unit.[7] In comparison, BN analogues of aromatic hydrocarbons containing an excess of nitrogen atoms are comparatively underdeveloped, but highly fluorescent molecules have been synthesised which contain N–B–N moieties attached to perylene scaffolds.[8,9] In this context, we have recently described the 1,1- and 1,2-isomers of bis(diaminobenzene)diborane(4) compounds, which contain 20π electrons, and our investigations revealed electron partitioning which avoided the anti-aromatic state.[10] We sought to extend the scope of this family of compounds by probing the interactions between low-oxidation state boron units and bipyridyl (bipy) which resulted in the discovery of two novel N–B–N compounds, namely [BX(bipy)] (**1**, X = Cl; **2**, X = Ph), which are formally aromatic and analogues of the fluorenyl anion.



X = Cl (**1**), Ph (**2**)

Thus, we have recently discovered the synthesis of the persistent radical species $[BCl_2(bipy)]^{\bullet}$ (**3**) from the reaction of $B_2Cl_2(NMe_2)_2$ with bipy,[11] but during one particular experiment, we isolated a small crop of bright orange crystals rather than the intense purple/black coloured solid characteristic of **3**. Analysis of these orange crystals by X-ray crystallography showed them to be [BCl(bipy)] (**1**) (Fig. 1).§ Compound **1** is planar and formally contains the bipy ligand in its direduced state (*vide infra*). Inspired by this observation, we sought a more rational synthesis of **1** from Li_2[bipy] and BCl_3. However, whilst this reaction did indeed afford **1**, significant quantities of free bipy as well as a number of other unidentified products were also obtained. In turning our attention to related species, we found that the phenyl substituted analogue [BPh(bipy)] (**2**) could be readily prepared from the analogous reaction between Li_2[bipy] and $BPhCl_2$ in toluene, followed by filtration and recrystallisation giving a moderate yield of red crystals. ^{11}B NMR spectroscopy of a C_6D_6 solution of **2** showed a signal at 20.7 ppm whilst ^{1}H NMR spectroscopy revealed resonances at significantly lower frequency for the bipy unit (7.64, 7.19, 6.17, 5.92 ppm) compared to those observed in free bipy (8.75, 8.54, 7.20, 6.68 ppm).

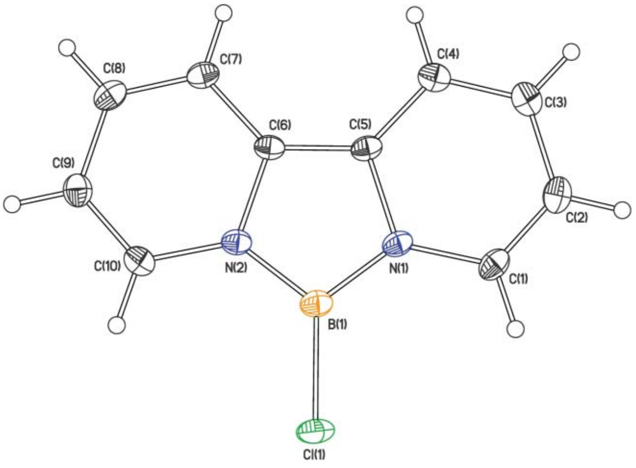


Fig. 1 Thermal ellipsoid plot (at 50% probability) of **1**. Selected bond distances and angles are presented in Table 1.

The crystal structure of **2**§ (Fig. 2) is similar to that of **1** in most respects (Table 1) with the boron atom in each case chelated by a direduced bipy ligand, with the phenyl group tilted with respect to the B(bipy) plane (dihedral angles of −38.3 and −39.4° for each of the two independent molecules in the asymmetric unit).

A comparison of **1** and **2** reveals a number of interesting features (Table 1). Within the pyridyl units, the C–C bond lengths may be grouped into those with more single-bond character [1.437(2) to 1.414(2) Å] and those with greater double-bond character [1.345(2) to 1.359(2) Å]. Most strikingly, the

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† Dedicated to Professor David W. H. Rankin on the occasion of his retirement.

‡ Electronic supplementary information (ESI) available: Syntheses and experimental data for **1** and **2** and the UV-vis spectrum of **2**. Packing diagrams for both structures in the solid state. Computed dimensions for **A** and **B**. CCDC reference numbers 767737 and 767738. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00028k

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Table 1 A structural comparison of bond lengths (Å) and angles (°) in [BCl(bipy)] (**1**), [BPh(bipy)] (**2**) and their calculated structures

	1	**2**[a]	Calculated **1**	Calculated **2**
B(1)–Cl(1)	1.7650(15)		1.776	
B(1)–N(1), B(1)–N(2)	1.4193(19), 1.4202(19)	1.443(2), 1.442(2) 1.444(2), 1.438(2)	1.430, 1.430	1.445, 1.445
N(1)–C(1), N(2)–C(10)	1.3927(18), 1.3930(18)	1.3979(18), 1.3933(18) 1.3941(18), 1.3944(19)	1.388, 1.388	1.387, 1.387
C(1)–C(2), C(10)–C(9)	1.348(2), 1.346(2)	1.345(2), 1.348(2) 1.345(2), 1.348(2)	1.357, 1.357	1.358, 1.358
C(2)–C(3), C(9)–C(8)	1.437(2), 1.4372(19)	1.431(2), 1.437(2) 1.434(2), 1.433(2)	1.438, 1.438	1.437, 1.437
C(3)–C(4), C(8)–C(7)	1.358(2), 1.359(2)	1.357(2), 1.358(2) 1.355(2), 1.358(2)	1.368, 1.368	1.368, 1.368
C(4)–C(5), C(7)–C(6)	1.4161(18), 1.4183(19)	1.416(2), 1.414(2) 1.421(2), 1.417(2)	1.417, 1.417	1.418, 1.418
C(5)–N(1), C(6)–N(2)	1.4273(16), 1.4252(16)	1.4208(17), 1.4185(17) 1.4192(17), 1.4185(17)	1.427, 1.427	1.424, 1.424
C(5)–C(6)	1.3785(19)	1.380(2), 1.379(2)	1.389	1.389
N(1)–B(1)–N(2)	106.10(11)	103.38(12), 103.55(12)	105.72	103.67
N(1)–C(5)–C(6), N(2)–C(6)–C(5)	108.10(11), 108.29(11)	108.19(12), 108.08(12) 108.15(12), 108.08(12)	108.18, 108.18	108.06, 108.06
N(1)–B(1)–C(11)–C(16)		−38.3, −39.4		−45.9

[a] Two independent molecules in the asymmetric unit.

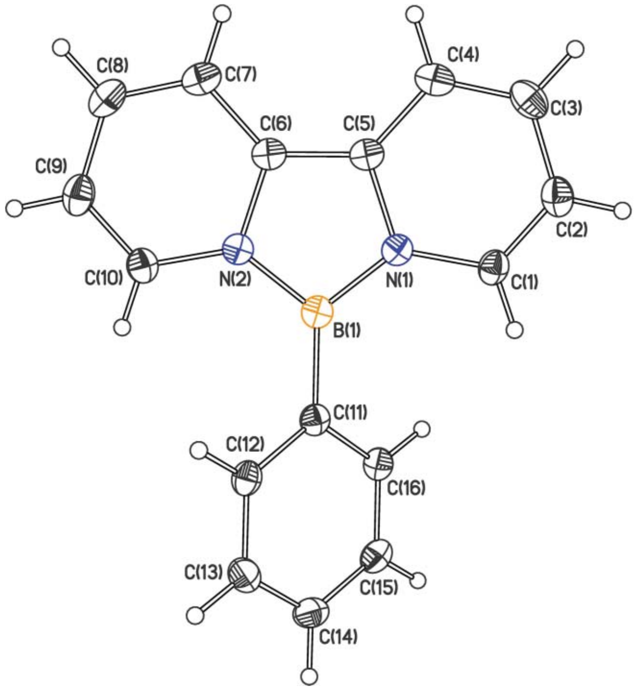

Fig. 2 Thermal ellipsoid plot (at 50% probability) of one of the two crystallographically independent molecules of **2**. Selected bond distances and angles are presented in Table 1.

C–C bond linking the two pyridyl groups are relatively short [1.379(2) to 1.380(2) Å, *cf.* 1.488 Å in free bipy[12]], clearly demonstrating multiple-bond character. Whilst it is tempting to describe **1** and **2** as bipy stabilised B(I) species, this bond length analysis is indicative of bipy in its direduced form which implies a boron atom in its usual +3 oxidation state. Another striking feature is the bending that the bipy group has undergone in order to chelate to the boron atom as evidenced by the angles N(1)–C(5)–C(6) and N(2)–C(6)–C(5): 108.08(12) to 108.29(11)°, compared with 116.26° in free bipy.[12] The B–N bond lengths [1.419(2) to 1.444(2) Å] are similar to those seen in other B–N compounds.[10] We note also that in the structure of **1**, the [BCl(bipy)] molecules stack parallel to each other with an inter-bipy distance of 3.43 Å, whilst slightly shorter distances of 3.27 and 3.30 Å between parallel molecules of **2** are observed (see ESI‡).

Compounds containing the bipy ligand in either its mono- or di-reduced forms are rare compared to the very many examples of bipy acting as a neutral bidentate ligand. However, a few examples have been reported such as [Li(thf)$_4$][Al(bipy)$_2$] (**4**)[13] and [Si(bipy)$_2$] (**5**)[14] which have been characterised by X-ray crystallography and have been assigned as having the aluminium and silicon centres in oxidation states +3 and +4 respectively. In addition, predominantly ionic species have also been structurally characterised including the disodium salt Na$_2$[bipy] (**6**)[15] and the dirubidium salt Rb$_2$[bipy] (**7**).[16] The structural features in all of these species mimic those in **1** and **2**; in particular the diagnostic inter-ring distances [*i.e.*, analogous to C(5)–C(6) in **1** and **2**] show significant multiple bond character [varying between 1.35(1) and 1.34(1) Å in **5**,[14] 1.36 and 1.37 Å in **4**,[13] 1.375 and 1.376 Å in **6**[15] and 1.399(6) Å in **7**;[16] *cf.* 1.488 Å in free bipy[12]]. We also note the syntheses of the related boron-containing species [B(bipy)$_2$]$^•$ and [B(NMe$_2$)(bipy)] using di-reduced and/or mono-reduced bipy with suitable boron substrates. Both species are air-sensitive and interestingly, [B(bipy)$_2$]$^•$ was shown to be a persistent radical, although no solid-state structures were obtained for either species.[17]

DFT calculations were employed in order to further investigate the electronic structures of **1** and **2**.¶ The calculated HOMO for **2** is shown in Fig. 3 and the calculated bond lengths and angles for both **1** and **2** (Table 1) coincide well with what is observed in the solid-state structures. Nucleus-independent chemical shifts (NICS-1)[18] which measure the absolute chemical shielding of ghost atoms placed 1 Å above the centres of rings has emerged as a useful means of estimating aromaticity in molecules.[10] Calculated NICS-1 values for **1**, **2**, the fluorenyl anion, 2,2′-bipy and model compounds based

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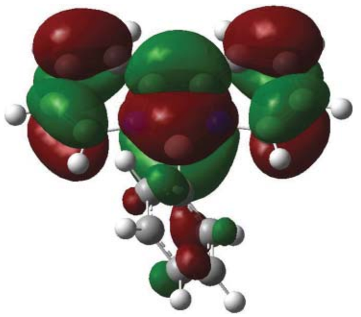

Fig. 3 A view of the HOMO calculated for **2**.

on the related boracycles, 2,3-dihydro-1*H*-1,3,2-diazaboroles[19] (**B**), and 1,2-dihydro[1,3,2]diazaborolopyridines[20] (**A**) are shown in Fig. 4. These results suggest that the boron-containing five-membered rings in **1** and **2** display a similar and substantial degree of aromaticity. Interestingly, removing the fused pyridyl ring(s) to form **A** and **B** results in a decrease in aromaticity in the diazaboracycle. The NICS-1 values of the central ring in **1** and **2** are in fact higher than the corresponding ring of the fluorenyl anion calculated using the same methodology. However, for **1**, **2** and the model 1,2-dihydro[1,3,2]diazaborolopyridine, the values for the adjacent 6-membered pyridyl ring(s) are much reduced compared to those in free bipy and the equivalent rings in the fluorenyl anion, suggesting that the aromaticity in **1** and **2** is largely localised on the central ring at the expense of the pyridyl rings, whereas it is delocalised over the entire framework in the fluorenyl anion.

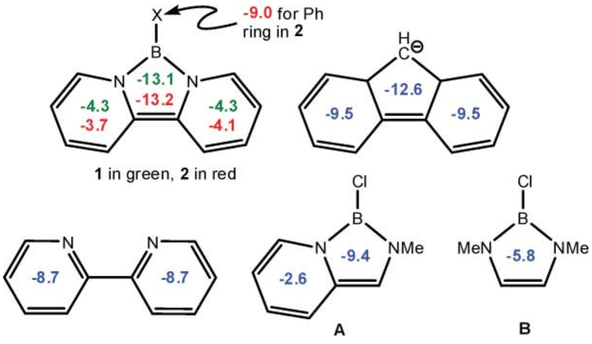

Fig. 4 NICS-1 values for **1**, **2**, the fluorenyl anion, 2,2′-bipy and model compounds based on related diazaboracycles.

In summary, two BN-containing analogues of the fluorenyl anion have been prepared. The pattern of bond lengths in both species point to bipy in its direduced form and DFT calculations suggest a shift in electronic structure compared to the fluorenyl anion with the central BN_2-containing five-membered ring showing appreciable aromatic character and the two pyridyl rings conversely showing less aromaticity.

Notes and references

§ Single crystals of **1** and **2** were obtained from saturated solutions of *n*-hexane and toluene respectively stored at −20 °C. Data were collected for crystals mounted in inert oil and transferred to the cold gas stream of the diffractometer. Structures were solved using SHELXS and refined using SHELXL.[21] Crystal Data for **1**: $C_{10}H_8BClN_2$, $M = 202.44$, monoclinic, space group $P2_1/c$, $a = 3.84030(10)$, $b = 14.0971(4)$, $c = 16.9200(5)$ Å, $\beta = 90.269(2)°$, $U = 915.99(4)$ Å^3, $Z = 4$, $D_c = 1.468$ Mg m^{-3}, $\lambda = 0.71073$ Å, μ(Mo-Kα) = 0.368 mm^{-1}, $F(000) = 416$, $T = 100(2)$ K, $R_1 = 0.0298$ [for 1799 reflections with $I > 2\sigma(I)$], w$R_2 = 0.0761$ [for all 2072 reflections], CCDC = 767737. Crystal Data for **2**: $C_{16}H_{13}BN_2$, $M = 244.09$, monoclinic, space group $P2_1/c$, $a = 20.144(2)$, $b = 17.3230(19)$, $c = 7.1036(7)$ Å, $U = 2474.0(5)$ Å^3, $Z = 8$, $D_c = 1.311$ Mg m^{-3}, $\lambda = 0.71073$ Å, μ(Mo-Kα) = 0.077 mm^{-1}, $F(000) = 1024$, $T = 100(2)$ K, $R_1 = 0.0414$ [for 4049 reflections with $I > 2\sigma(I)$], w$R_2 = 0.1055$ [for all 5645 reflections], CCDC = 767738.
¶ Calculations were carried out using the Gaussian03 package[22] with the structures of **1** and **2** optimised at the B3LYP/6-31g* level. Single point calculations using B3LYP/6-311g**+ and the GIAO methodology[23] were used to predict the NICS values of ghost atoms 1 Å above the centroid of each ring being studied.

1 Z. Q. Liu and T. B. Marder, *Angew. Chem., Int. Ed.*, 2008, **47**, 242–244.
2 M. J. D. Bosdet and W. E. Piers, *Can. J. Chem.*, 2009, **87**, 8–29.
3 M. J. D. Bosdet, W. E. Piers, T. S. Sorensen and M. Parvez, *Angew. Chem., Int. Ed.*, 2007, **46**, 4940–4943.
4 E. R. Abbey, L. N. Zakharov and S. Y. Liu, *J. Am. Chem. Soc.*, 2008, **130**, 7250–7252.
5 A. J. V. Marwitz, M. H. Matus, L. N. Zakharov, D. A. Dixon and S. Y. Liu, *Angew. Chem., Int. Ed.*, 2009, **48**, 973–977.
6 T. K. Wood, W. E. Piers, B. A. Keay and M. Parvez, *Angew. Chem., Int. Ed.*, 2009, **48**, 4009–4012.
7 A. Wakamiya, K. Mori, T. Araki and S. Yamaguchi, *J. Am. Chem. Soc.*, 2009, **131**, 10850–10851.
8 T. Riehm, G. De Paoli, H. Wadepohl, L. De Cola and L. H. Gade, *Chem. Commun.*, 2008, 5348–5350.
9 T. Riehm, H. Wadepohl and L. H. Gade, *Inorg. Chem.*, 2008, **47**, 11467–11469.
10 M. A. M. Alibadi, A. S. Batsanov, G. Bramham, J. P. H. Charmant, M. F. Haddow, L. MacKay, S. M. Mansell, J. E. McGrady, N. C. Norman, A. Roffey and C. A. Russell, *Dalton Trans.*, 2009, 5348–5354.
11 S. M. Mansell, C. J. Adams, G. Bramham, M. F. Haddow, W. Kaim, N. C. Norman, J. E. McGrady, C. A. Russell and S. J. Udeen, *Chem. Commun.*, in press.
12 F. E. Kuhn, M. Groarke, E. Bencze, E. Herdtweck, A. Prazeres, A. M. Santos, M. J. Calhorda, C. C. Romao, I. S. Goncalves, A. D. Lopes and M. Pillinger, *Chem.–Eur. J.*, 2002, **8**, 2370–2383.
13 G. B. Nikiforov, H. W. Roesky, M. Noltemeyer and H. G. Schmidt, *Polyhedron*, 2004, **23**, 561–566.
14 R. Morancho, P. Pouvreau, G. Constant, J. Jaud and J. Galy, *J. Organomet. Chem.*, 1979, **166**, 329–338.
15 H. Bock, J. M. Lehn, J. Pauls, S. Holl and V. Krenzel, *Angew. Chem., Int. Ed.*, 1999, **38**, 952–955.
16 E. Gore-Randall, M. Irwin, M. S. Denning and J. M. Goicoechea, *Inorg. Chem.*, 2009, **48**, 8304–8316.
17 M. A. Kuck and G. Urry, *J. Am. Chem. Soc.*, 1966, **88**, 426–431.
18 P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. J. Jiao and N. Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317–6318.
19 L. Weber, M. Schnieder, T. C. Maciel, H. B. Wartig, M. Schimmel, R. Boese and D. Blaser, *Organometallics*, 2000, **19**, 5791–5794.
20 L. Weber, M. Schnieder, R. Boese and D. Blaser, *J. Chem. Soc., Dalton Trans.*, 2001, 378–382.
21 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.
22 *Gaussian 03, Revision D.02*, Gaussian, Inc., Wallingford CT, 2004.
23 K. Wolinski, J. F. Hilton and P. Pulay, *J. Am. Chem. Soc.*, 1990, **112**, 8251–8260.

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