Lewis and Brønsted multifunctionality: an unusual heterocycle from the reaction of bis(pentafluorophenyl)borinic acid with nitriles†

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**The combination of Lewis and Brønsted acidity as well as Lewis basicity in $(C_6F_5)_2BOH$ results in a remarkable reactivity towards organonitriles to give novel heterocyclic compounds containing a BOBOCN six-membered ring.**

Bis(pentafluorophenyl)borinic acid, $(C_6F_5)_2BOH$ (**1**), is an intriguing example of multifunctionality in terms of chemical reactivity, due to the presence of both relatively strong Lewis and Brønsted acidity as well as a Lewis basic site within the same molecule. It was first prepared more than 40 years ago,[1] but has found renewed interest recently due to applications as a catalyst in organic synthesis,[2,3] as a co-catalyst in olefin polymerisation[4–7] and in battery electrolytes.[8] The presence of both Lewis acidic and basic sites leads to the formation of a trimer in the solid state which, in solution, is in equilibrium with a monomeric form (Eq. 1).[9] The position of this equilibrium was found to be strongly solvent dependent and the rate of inter-conversion affected by the presence of water.[10]
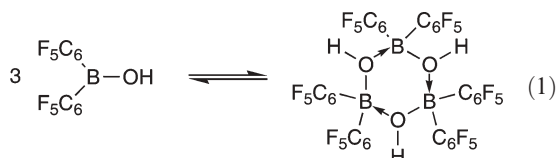

In the course of our investigations on the Lewis acidic properties of perfluorinated borinic and boronic esters such as $(C_6F_5)_2BO(C_6F_5)$,[11] we found that these Lewis acids readily form adducts with nitriles such as acetonitrile, as indicated by a characteristic shift in the ^{11}B NMR spectrum, for example from 41.2 to 22.1 ppm in the case of $(C_6F_5)_2BO(C_6F_5)$. Tris(pentafluorophenyl)borane $B(C_6F_5)_3$ displays a similar reactivity with a change in chemical shift from 59 to −10.3 ppm.[12] In contrast, we found that $(C_6F_5)_2BOH$ does not appear to form an adduct when dissolved in CD_3CN, as indicated by the ^{11}B NMR chemical shift of 38.8 ppm (*cf.* 42.2 ppm in toluene-d_8).[9] However, during the course of a day this signal at 38.8 ppm slowly decreases and two new sharp peaks of equal intensity appear at 1.2 and −3.4 ppm (in CD_3CN). In the ^{19}F NMR spectrum, two new sets of signals due to the *ortho*, *meta* and *para* fluorine atoms are formed, while those corresponding to $(C_6F_5)_2BOH$ slowly decrease. It appears therefore that a new compound is formed containing two similar but inequivalent $(C_6F_5)_2B$ units. After removal of the acetonitrile solvent, the new compound was

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† Electronic supplementary information (ESI) available: X-ray crystallography. See DOI: 10.1039/b516262a

isolated as a white solid in 92% yield, which was recrystallised from pentane. Single crystal X-ray analysis revealed the formation of a rather unusual six-membered heterocyclic compound **2a**, containing two boron and two oxygen atoms, one carbon and one nitrogen atom, obviously made from two $(C_6F_5)_2BOH$ and one acetonitrile molecules (see Fig. 1). Similar reactions are observed with other nitriles such as propionitrile or benzonitrile, yielding the corresponding ring compounds **2b** and **2c** (Eq. 2).‡ No reaction was observed when using the less Lewis and Brønsted acidic diphenylborinic acid $(C_6H_5)_2BOH$. When the reaction was carried out in non-dried acetonitrile, the formation of **2a** was considerably faster (< 1 day). We believe that water plays an important role in the rate of the formation of **2a**, as it does in the trimerisation process shown in Eq. 1.[10]

R = Me: **2a**
R = Et: **2b**
R = Ph: **2c**
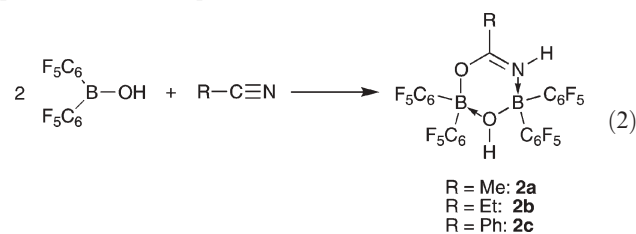
The only example of a similar compound reported previously is compound **I**, prepared by a different route from diphenylborinic acid and 2-hydroxypyridine.[13] The resulting borinic ester forms an adduct with $(C_6H_5)_2BOH$ to give the heterocyclic compound **I**. Also related is compound **II**, which was prepared from $(F_2BOMe)_3$ and acetic anhydride. This compound can be viewed as an adduct between the mixed anhydride of difluoroborinic acid and acetic acid together with the methyl difluoroborinic ester.[14] The variety in the substituents in these examples suggests substantial scope in this unexplored class of compounds.

I   II
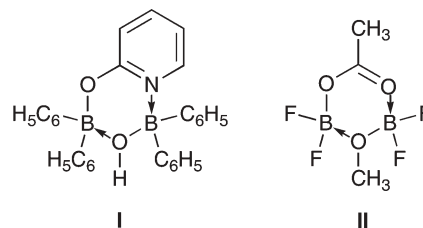
The X-ray analysis of a crystal of **2a** revealed the presence of two independent molecules (**A** and **B**) with different conformations for the central BOBOCN six-membered ring. In both cases the ring has a slightly distorted sofa conformation, but whereas in molecule **A** (Fig. 1) the oxygen atom O(5) lies *ca.* 0.52 Å out of the plane of the other five atoms (which are coplanar to within *ca.* 0.06 Å), in molecule **B** (Fig. S1 in the supporting information) it is
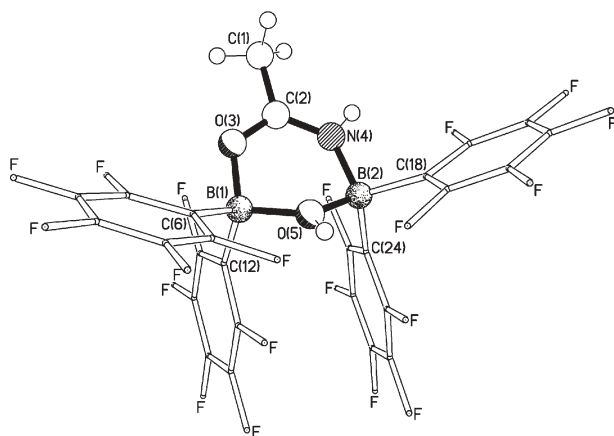
Fig. 1 The molecular structure of one (A) of the two independent molecules present in the crystals of **2a**.
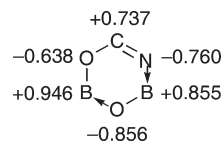

Fig. 2 Computed atomic charges in **2a′**.

In conclusion, we have shown that the reaction between $(C_6F_5)_2BOH$ and organonitriles leads to the formation of heterocyclic compounds with a BOBOCN ring, the atoms being held together by a combination of covalent and dative bonds. This discovery is an exciting manifestation of the multi-functionality of $(C_6F_5)_2BOH$, *i.e.* Lewis and Brønsted acidity as well as Lewis basicity, which allows a multitude of reactions, such as protonations, Lewis acid–base interactions, H-bonding and the formation of covalent bonds. We are currently investigating the mechanism of formation of these heterocycles and their reactivity.

We are grateful to the EPSRC for support (GR/R92042/01).

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the boron atom B(1′) that lies *ca.* 0.64 Å out of the plane of the other five atoms (which are again coplanar to within *ca.* 0.06 Å). There are no statistically significant differences in the equivalent bond lengths within the central six-membered rings of the two independent molecules, and the pattern of bonding is similar to that seen in the related compound **I** (Table 1).[13] The bonds in **I** are all longer than in **2a** (on average, by *ca.* 0.03 Å), presumably a consequence of the change from phenyl to pentafluorophenyl groups and the increased Lewis acidity of the boron centres in **2a**. The amide C–O and C–N distances seen here in **2a** are the same as each other (at *ca.* 1.30 Å) in contrast to the *ca.* 0.1 Å difference [C–O *ca.* 1.23 Å, C–N *ca.* 1.33 Å] seen in simple acyclic amides, indicating a significant contribution from the canonical form as shown in Eq. 2.

In order to obtain further insight into the type of bonding in this unusual heterocycle, the formation of **2a** was modelled with DFT calculations.§ As can be seen in Table 1, the bond lengths of the optimised structure **2a′** are in very good agreement with the experimental data. Irrespective of the starting geometry for the calculations, **A** or **B**, the optimised structure **2a′** has geometry **B**, which indicates that this geometry is probably thermodynamically favoured whereas geometry **A** arises from crystal packing effects in the solid state (F⋯π interactions). Natural bond orbital analysis (NBO)[15–19] reveals a C=N double bond, a covalent polarised C–O bond and highly ionic B–O and B–N bonds.

The computed atomic charges, as shown in Fig. 2, are consistent with a highly ionic mode of bonding and confirm the proposed bonding description with significant positive charge on the carbon and boron centres and negative charge on the oxygen and nitrogen centres.

Table 1 Selected bond lengths in **2a**, **I** and **2a′**

	2a	I	2a′
C=N	1.296(3)	1.342(7)	1.308
N→B	1.539(3)	1.612(8)	1.562
B–O	1.523(2)	1.553(7)	1.527
O→B	1.529(2)	1.558(8)	1.542
B–O	1.503(2)	1.532(7)	1.499
O–C	1.295(2)	1.325(6)	1.293

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