An imidazol-2-ylidene borane complex exhibiting *inter*-molecular [C–H$^{\delta+}$···H$^{\delta-}$–B] dihydrogen bonds†

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The structure of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene·BH$_3$, (1·BH$_3$) has been determined by X-ray crystallography; the high melting solid exhibits head-to-tail alignment of the molecular dipoles in the solid state, with the closest intermolecular contact being a simple well-defined example of an unconventional [C–H$^{\delta+}$···H$^{\delta-}$–B] dihydrogen bond.

The hydrogen bond is perhaps the most extensively studied "weak" *inter-* and *intramolecular* interaction, and this association often governs the structure of molecules in solids, liquids and gases.[1] Hydrogen bonding also plays a central role in the structure of biological molecules[2] and has been extensively used in the broad field known as "crystal engineering".[3]

It has only been recently accepted that the C–H fragment can act as a donor in the formation of a hydrogen bond.[4,5] Since this recognition, numerous examples have been identified, and perhaps the most extensively studied hydrogen bond to the C–H fragment has involved the [C–H···O] interaction.[5]

Nucleophilic carbenes have recently received attention due to their numerous applications in synthetic chemistry.[6–8] Our interest in hydrogen bonding interactions stems from the relationship between carbenes and imidazolium ions which are of great interest due to their application as ionic liquids.[9] Recently we reported the formation of extremely short [C–H···O] hydrogen bonds which result from protonation reactions of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (**1**) with phenols.[10] The shortness of these hydrogen bonds can, in part, be explained by "charge assistance"[11–14] between the cationic imidazolium ion [**1** − H] and the anionic phenoxide ion.

In the isolated C_2 symmetric imidazolium ion [**1** − H] three potentially acidic C–H sites exist. It has been observed that the shortest hydrogen bonds engage the C_2–H unit, whereas longer ones occur at $C_{4,5}$–H. These lengths are anticipated based on the relative acidity of the sites.

Non-conventional hydrogen bonds involving H centres as *both* the acceptor and donor have attracted interest lately.[1] These "dihydrogen" bonds are perhaps the weakest hydrogen bonds[15] with the best-studied example being the [NH$_3$–BH$_3$] interaction. In an elegant study Crabtree identified short *intermolecular* [N–H···H–B] dihydrogen bonds (1.82 Å) in samples of [NH$_3$–BH$_3$], and, noting these short distances, he could account for the higher melting point of [NH$_3$–BH$_3$] (104 °C) *versus* the low melting point of ethane (−181 °C).[16,17]

With respect to [C–H···H–B] dihydrogen bonds there is less structural data available. A series of amino boron hydrides have been reported and these show several *intramolecular* [H···H] bonds shorter than 2.65 Å, the sum of the van der Waals radius for the B–H/C–H fragment.[18,19] In a related study, the conformation of azocyclohexane–borane adducts were found to exhibit non-conventional hydrogen bonding between

[C–H···H–B].[20,21] Finally, the formation of [C–H···H–B] dihydrogen bonds has significant reactivity implications. It has been noted that hydroboration reactions occur slowly in CH$_2$Cl$_2$, and this has been explained by the formation of dipolar interactions between amine·borane adducts and the acidic hydrogen site of the solvent.[22]

In an attempt to probe the [C–H···H–B] dihydrogen bond we aimed to prepare complexes of the type [**1** − H][EH$_4$], E = B, Al, where charge assistance would shorten the [H···H] interaction *via* strong electrostatic attractions between the imidazolium cation [**1** − H]$^+$ and the hydridic anion. Ion exchange reactions were attempted by treating [**1** − H][Cl] with stoichiometric quantities of NaBH$_4$ or LiAlH$_4$ in THF solution. In all cases, evolution of gas was observed from these reaction mixtures, and **1**·BH$_3$ and the previously reported **1**·AlH$_3$[23] were identified from the complex reaction mixtures. These results suggest that the putative [H···H] bond in these systems is thermodynamically unstable with respect to hydrogen gas evolution. Indeed, [H···H] bonds are speculated to be important in reductive coupling reactions.[15]

Addition of BH$_3$·THF to **1** in THF followed by recrystallisation in CH$_2$Cl$_2$ affords colorless crystals of **1**·BH$_3$. The analytical data are consistent with the proposed structure.† A surprising feature is the high melting point of **1**·BH$_3$ (296–300 °C) which is significantly higher than crystalline **1** (150–155 °C)[24] or the related alane adduct **1**·AlH$_3$ (246–247 °C).[23] This data suggests strong *intermolecular* interactions in crystalline **1**·BH$_3$. In an attempt to shed light on this, the structure of **1**·BH$_3$ was determined by X-ray crystallography.‡

The result of the X-ray crystallographic study is shown in Fig. 1. The anticipated molecular structure for **1**·BH$_3$ is observed, and important bond lengths are included in the figure caption. The bond lengths and bond angles of **1**·BH$_3$ are consistent with the previously reported carbene·borane adduct, 2-borane-1,3-diethyl-4,5-dimethylimidazolidene.[25,26]

More interesting is the supramolecular structure of **1**·BH$_3$ shown in Fig. 1. This diagram clearly shows the head-to-tail alignment of **1**·BH$_3$ and this order is reminiscent of the [cation···anion···cation] linear arrays that are so often observed with the ionic salts containing imidazolium ions and anions such as OR, Cl and I.[10] The linear array of **1**·BH$_3$ is found to occur along the *b* axis.

The closest *intermolecular* contact occurs through a novel [C–H···H–B] hydrogen bond. These links, which happen between the hydridic borane B–H terminus and the alkenic C–H, are 2.24 Å in length. These interactions are *ca.* 0.4 Å shorter than 2.65 Å, the sum of the van der Waals radius.[18] Similarly, **1**·AlH$_3$,[23] and **1**·InH$_3$[27] also align in an analogous fashion, and the centroid–centroid distances are 7.70, and 8.00 Å, respectively, compared to 7.25 Å for **1**·BH$_3$.

The structural parameters for the [C–H···H–B] unit are consistent with the anticipated geometry for such an interaction. For example, the B–H···H angle is 113° and the H···H–C angle is 138.53°. Similar angles were observed in the [N–H···H–B] system.[17]

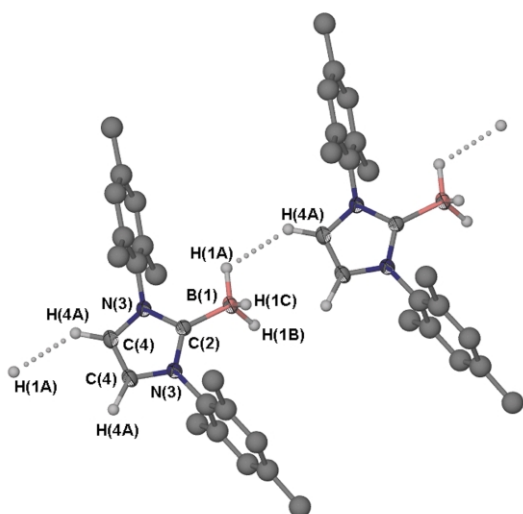We have also carried out a theoretical study on **1**·BH$_3$ and

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Fig. 1 Selected bond lengths (Å) and angles (°) for **1**·BH$_3$. Hydrogen atoms on the mesityl substituents are removed for clarity. Thermal ellipsoids are shown at 50% probability level: B(1)–C(2) 1.596(4), C(2)–N(3) 1.354(2), N(3)–C(4) 1.385(2), C(4)–C(4) 1.344(4), C(4)–H(4A) 1.09, B(1)–H(1) 1.210, H(1A)···H(4) 2.238; N(3)–C(2)–N(3) 104.55(17), N(3)–C(2)–B(1) 127.75(10), C(2)–N(3)–C(4) 111.03(16), C(4)–C(4)–N(3) 106.72(10), B(1)–H(1A)–H(4A) 138.46.

[NH$_3$–BH$_3$] to examine the partial charges on the C–*H*, N–*H*, and B–*H* components. All calculations were performed with the Gaussian 98 package of programs.[28] The geometry was optimised at the UB3LYP/6-31G level and partial atom charges were calculated using UB3LYP/6-311G*(2df,p) method. We have estimated the partial atom charges for the centres of interest, and the results for **1**·BH$_3$ are shown in Fig. 2.
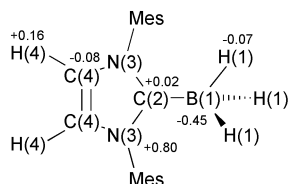

Fig. 2 Selected calculated partial atomic charges for **1**·BH$_3$. Selected bond lengths (Å) and angles (°): B(1)–C(2) 1.590, C(2)–N(3) 1.376, N(3)–C(4) 1.405, C(4)–C(4) 1.358, C(4)–H(4A) 1.09, B(1)–H(1) 1.215 and 1.229; N(3)–C(2)–N(3) 104.3, N(3)–C(2)–B(1) 127.9, C(2)–N(3)–C(4) 111.0, C(4)–C(4)–N(3) 106.9.

As shown, the hydrogen atom attached to boron possesses a partially negative charge, consistent with boranes' hydridic nature. The hydrogen atom attached to C$_4$ exhibits a partial positive charge. It is therefore unsurprising that the dipoles align in the observed fashion. In the [NH$_3$–BH$_3$] adduct, the charges on the hydrogens attached to boron and nitrogen are −0.07 and +0.31, respectively and these values are comparable to those obtained by Crabtree for the [NH$_3$–BH$_3$] dimer.[29] The larger partial charges on the amine proton in the [NH$_3$–BH$_3$] adduct, compared with H(4) of **1**·BH$_3$, lead to the [N–H···H–B] dihydrogen bond being shorter than the [C–H···H–B] dihydrogen bond. Finally, it is also noted that the estimated partial charge on the hydrogen atoms in CH$_2$Cl$_2$ is +0.2, and hence, in light of the observations in this study, [C–H···H–B] interactions likely form in halocarbon solvents used in hydroboration reactions.[22]

In conclusion, **1**·BH$_3$ has been synthesised and its structure confirmed using X-ray crystallography. Intermolecular [C–H$^{δ+}$···H$^{δ−}$–B] non-conventional dihydrogen bonds were observed with a head-to-tail alignment of **1**·BH$_3$ with the dihydrogen bonds being *ca.* 0.4 Å shorter than the sum of the van der Waals radii. A theoretical study was also carried out on **1**·BH$_3$ to determine the magnitude of the charge on the interacting C–H···B–H fragments, and the partial charge data

obtained are consistent with the hydrogen bonds in [NH$_3$–BH$_3$] being stronger and shorter than for **1**·BH$_3$.

Notes and references

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