Structural and theoretical studies of intermolecular dihydrogen bonding in \([(C_6F_5)_2(C_6Cl_5)B]\)···H···H–[TMP]†

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The product of the intermolecular ‘frustrated Lewis pair’ (FLP) \(B(C_6F_5)_2(C_6Cl_5)/2,2,6,6\)-tetramethylpiperidine and \(H_2\) has been studied by single-crystal neutron diffraction. This is the first structurally characterised example of a geometrically unconstrained dihydrogen (H···H) bond within a hydrogenated FLP system.

In 2006, Stephan and co-workers uncovered the first metal-free system that reversibly splits \(H_2\). They succeeded in activating \(H_2\) using a frustrated Lewis pair (FLP), which is defined as a Lewis acid and a Lewis base that are unable to form a ‘classical’ donor–acceptor bond due to steric hindrance between the components. Since then FLPs have been used in a variety of small molecule activation reactions, including \(H_2\) heterolysis, CO2 sequestration, and to mediate the hydrogenation of \(CO_2\) to \(CH_3OH\). Recently we described the synthesis and characterisation of a series of electrophilic boranes, \(B(C_6Cl_5)_x(C_6F_5)_{3-x}\) \((x = 1-3)\). During the course of our studies into the heterolytic cleavage of \(H_2\) with the bimolecular FLP system \(B(C_6Cl_5)_x(C_6F_5)_{3-x}\)-TMP, we isolated large single crystals of \([(C_6F_5)_2(C_6Cl_5)B]\)···H–[TMP] (2, Fig. 1), which have been characterised by multinuclear NMR, elemental analysis and MS. The structure of 2 has been determined by single crystal X-ray diffraction studies and demonstrates that after splitting \(H_2\), the orientation of the ion pair in the salt is consistent with a possible dihydrogen bond (H···H = 1.844(2) Å) between the piperidinium and borohydride moieties. However, the precise location and bond

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Fig. 1 Crystallographically characterised products of FLP-mediated H2 cleavage which demonstrate dihydrogen bonds. Top: intramolecular example reported by Schulz et al.,\textsuperscript{17} bottom: synthesis of the intermolecular system, ([(C6F5)2(C6Cl5)B–H][H–TMP]). 2.

Fig. 2 Neutron structure of [(C6F5)2(C6Cl5)B–H][H–TMP] (2) at 100 K. Thermal ellipsoids at 50% probability. H atoms on the TMP molecule (except those bound to N atom) have been omitted for clarity.

distance between the hydrogen nuclei could not be adequately resolved by X-ray diffraction, and in order to accurately determine the geometry of B–H···H–N unit, we resorted to a single crystal neutron diffraction measurement (Fig. 2).

For comparative purposes, the electronic structure of 2 was also explored and optimised using density functional theory (DFT; B97D/TZVP), and pertinent metric data for all techniques are collated in Table 1.

In general, the neutron structure agrees well with the X-ray structure, displaying a four-coordinate boron atom which adopts a pseudo-tetrahedral coordination geometry. However, the H···H distance (1.8047(12) Å) is noticeably shorter than that determined by X-ray diffraction and DFT calculations, yet is substantially longer than the interhydrogen distance in free H2 (0.74 Å) or non-classical H2 transition metal complexes (ca. 0.82 Å).\textsuperscript{19} The geometry of the B–H···H–N fragment is also bent, as revealed by the B–H···H(N) bond angle. This is reported to be a common structural feature of dihydrogen bonding, and Crabtree has studied the solid-state structure of H3N-BH3, where it is reported that various intermolecular H···H contacts (range 1.7–2.2 Å) have N–H···H–B bond angles which are appreciably larger than B–H···H–N, which is also seen in the structure of 2.\textsuperscript{20}

Furthermore, calculations on the ammonia borane dimer have shown that the B–H–N bond strength is 6.1 kcal mol\textsuperscript{–1}, which would confer appreciable energetic stability to species containing this moiety. This could have an effect on the reversibility of FLP H2 heterolysis; interestingly, 2 shows no loss of H2 in the solid state upon heating in vacuo (18 hours, 110 °C, 10\textsuperscript{–2} mbar). Furthermore, X-ray data appreciably underestimate the N–H bond lengths, whereas the converse is true for B–H, relative to the neutron results. Overall, with respect to the B–H–N unit, DFT calculations for 2 correspond more closely with the experimental neutron structure than X-ray data. The Wiberg bond index for the dihydrogen bond in 2 of 0.011 (Table S1, ESI\textsuperscript{†}) is indicative of significant interaction between the two participating hydrogen atoms. This value is larger compared to the bond orders of the closest H···X interactions between fragments in the dimer. For comparison we calculate a bond index of 0.022 for the stronger H···H interaction in the ammonia borane dimer.

The B–H and N–H bond lengths (1.24 and 1.03 Å respectively)\textsuperscript{17} for 1 reported by Schulz et al. are comparable to those determined for 2. However, the distance between the H atoms for the former is significantly shorter than that seen in 2. One explanation for this observation could be that the bridge between the borate and N-base fragments in 1-N-TMPH–CH2–2[H(B(C6Cl5)3)C6H4] provides limited flexibility to accommodate the H···H interaction, which is supported by an internuclear B···N separation of 3.35 Å, compared to the significantly larger 3.829(3) Å seen in intermolecular 2.

The X-ray and neutron structure of [(C6F5)2(C6Cl5)B–H][H–TMP] show that the H atoms from FLP-mediated H2 cleavage are contained within a non-linear B-H···H(N) fragment. Single crystal neutron diffraction data allows the precise position of the H atoms to be determined, revealing the presence of a short B–H···H–N dihydrogen bond linking the ion pair. This is the first dihydrogen bond to be reported for the product of H2 cleavage by an intermolecular FLP.

Notes and references

‡ Synthesis of [(C6F5)2(C6Cl5)B–H][H–TMP] (2): a 50 ml thick-walled glass ampoule was charged with a magnetic stir bar, B(C6Cl5)3(C6F5)2 [ref. 18] (0.30 g, 0.84 mmol), TMP [118 mg, 0.84 mmol] and anhydrous

### Table 1 Comparison of selected bond lengths and angles for 2, as determined by single crystal X-ray and neutron diffraction, and calculated data (B97-D/TZVP).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Experimental X-ray</th>
<th>Experimental neutron</th>
<th>Calculated\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(11)···H(302) (Å)</td>
<td>1.844(2)</td>
<td>1.8047(12)</td>
<td>1.867</td>
</tr>
<tr>
<td>N–H(301) (Å)</td>
<td>0.897</td>
<td>1.030(8)</td>
<td>1.024</td>
</tr>
<tr>
<td>N–H(302) (Å)</td>
<td>0.882</td>
<td>1.038(9)</td>
<td>1.032</td>
</tr>
<tr>
<td>B–H(11) (Å)</td>
<td>1.353</td>
<td>1.203(9)</td>
<td>1.223</td>
</tr>
<tr>
<td>B–H(11)···H(302) (°)</td>
<td>136.43(5)</td>
<td>139.5(8)</td>
<td>127.5</td>
</tr>
<tr>
<td>N–H(302)···H(11) (°)</td>
<td>174.95(5)</td>
<td>174.4(9)</td>
<td>152.1</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Performed using a polarisable continuum model (PCM) with the dielectric constant corresponding to that of water (ε = 78.4), in order to mimic the electric field within the crystalline lattice.
The reaction was freeze-pump-thaw degassed three times with 

He (1 atm), sealed at room temperature, and then heated (110 °C) for 7 days with stirring. The solvent was removed under vacuum and the residue was washed with pentane (2 x 10 ml), the solids collected and dried under vacuum (10⁻² mbar) at 80 °C to afford 2 as a colourless solid (284 mg, 76%, 0.38 mmol). ¹H NMR (CDCl₃, 300 MHz): δ = 6.21 (t (1:1:1), 2H, J=51 Hz, NH); 3.81 (q (1:1:1:1), 1H, J=90 Hz, BF); 1.73 (m, 2H, CH₃; TMP); 1.63 (m, 4H, CH₂; TMP); 1.39 (s, 12H, CH₃; TMP). ¹³B NMR (CDCl₃, 128 MHz): δ = –9.8 (d, J=90 Hz). ¹³C¹H¹N MRM (CDCl₃, 75 MHz): δ = 149.5 (dm, J_CB = 234 Hz, ortho-CF₃); 145.0 (br s, iso-CF₃Cl); 139.3 (s, iso-CF₂Cl₂); 139.0 (dm, J_CB = 242 Hz, para-CF₃); 137.90 (dm, J_CB = 243 Hz, meta-CF₃); 131.3 (s, para-CF₂Cl); 129.8, 126.2 (both s, meta-CF₂Cl₃ and ortho-CF₃Cl); 126.16 (br s, iso-CF₂Cl₃); 39.76 (s, NC(CH₃)₂CH₃); 35.73 (s, NC(CH₃)₂CH₂); 27.68 (s, NC(CH₃)₂CH₂); 17.01 (s, NC(CH₃)₂CH₂); iso-CF₃Cl was not observed. ¹⁹F NMR (CDCl₃, 282 MHz): δ = –134.5 (d, 4F, J_CF = 22 Hz, ortho-CF₃Cl); –165.3 (t, 2F, J_CF = 19 Hz, para-CF₃Cl); –168.4 (m, 4F, meta-CF₃Cl). HRMS (ESI⁺, m/z): for C₁₈H₁₇BCl₅F₁₀N: calc’d: 592.8471. Found: 592.8471. IR (cm⁻¹): 2959 (w), 2262 (w), 1639 (w), 1573 (s), 1512 (s), 1452 (s), 1384 (w), 1327 (w), 1301 (s), 1259 (s), 1076 (m), 958 (s), 893 (s), 785 (s). Anal.caled for C₁₂H₁₃BCl₁₀N: C 43.97; H 2.87; N 1.90. Found: C 44.07; H 2.78; N 2.04.

§ Single crystals for both X-ray and neutron diffraction were grown from a saturated toluene solution of 2, which was layered with pentane (298 K). Single crystal X-ray diffraction data were collected at 100 K with an Oxford Diffraction (Agilent) SuperNova diffractometer. Data collection, unit cell refinement, integration, interfame scaling and absorption corrections were carried out using CrysAlisPro. The structure was solved with SuperFlips and refined with CRYSTALS. Neutron diffraction data were collected at 100 K using the time-of-flight Laue diffractometer SXD at the ISIS spallation neutron source. The structure from the X-ray solution was refined against the neutron diffraction data, using SHELXL. Full refinement details for both datasets are given in the ESI. CCDC 953644 and 953645. Single crystal diffraction data: C₁₂H₁₃BCl₁₀N, Mᵣ = 737.52, monoclinic, P₂₁/c, α = 47.3, β = 114.9580(17), V = 2949.53(8) Å³, data/restraints/parameters = 6171/0/397, R₁ = 0.029, final R₁ = 0.0270, wR₂ = 0.0668 ([I > 3σ(I)]). Neutron refinement – a = 14.011(3) Å, b = 17.334(4) Å, c = 13.332(3) Å, β = 115.030(15)°, V = 3035.8(11) Å³, data/restraints/parameters – 143550/0/596, final R₁ = 0.0928, wR₂ = 0.2584 (all data).