# Electronic Supplementary Data

## Structural and Theoretical Studies of *Inter*molecular Dihydrogen Bonding in $[(C_6F_5)_2(C_6Cl_5)B]–H\cdots H–[TMP]$

**Hasna Zaher,[a] Andrew E. Ashley,*[b] Mark Irwin,[a] Amber L. Thompson,[a] Matthias J. Gutmann,[c] Tobias Krämer[a] and Dermot O'Hare*[a]**

---

### Experimental Details of the Computational Methods

The quantum chemical calculations have been performed with the Gaussian 09 package.[S1] The geometry of $[(C_6F_5)_2(C_6Cl_5)B{-}H][H{-}TMP]$ has been fully optimized without symmetry constraints ($C_1$ symmetry), using tight convergence criteria (keyword *opt=tight* in combination with *int=ultrafine*). These calculations were done at the DFT level using Grimme's B97-D functional, which includes an empirical correction for intramolecular dispersion interactions.[S2] Ahlrich's triple-ζ valence basis set extended by one polarization function (TZVP) was used on all atoms.[S3] The presence of the crystal environment was approximated by embedding the FLP pair into a polarizable continuum model (in the default integral equation formalism variant, IEF-PCM).[S4] The chosen dielectric constant ($\varepsilon$ = 78.4) corresponds to that of water. Subsequent calculation of the Hessian at the geometry of the optimized stationary point and using the same level of theory (B97D/TZVP/PCM) confirmed the presence of a true minimum (no imaginary frequencies). Initial coordinates were taken from the single-crystal neutron diffraction experiment.

[S1] Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.;

Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

**S2** Grimme, S. *J. Comput. Chem*. **2006**, *27*, 1787.

**S3** Schäfer, A.; Huber, C; Ahlrichs, R. *J. Chem. Phys*. **1994**, *100*, 5829.

S4 Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev*. **2005**, *105*, 2999

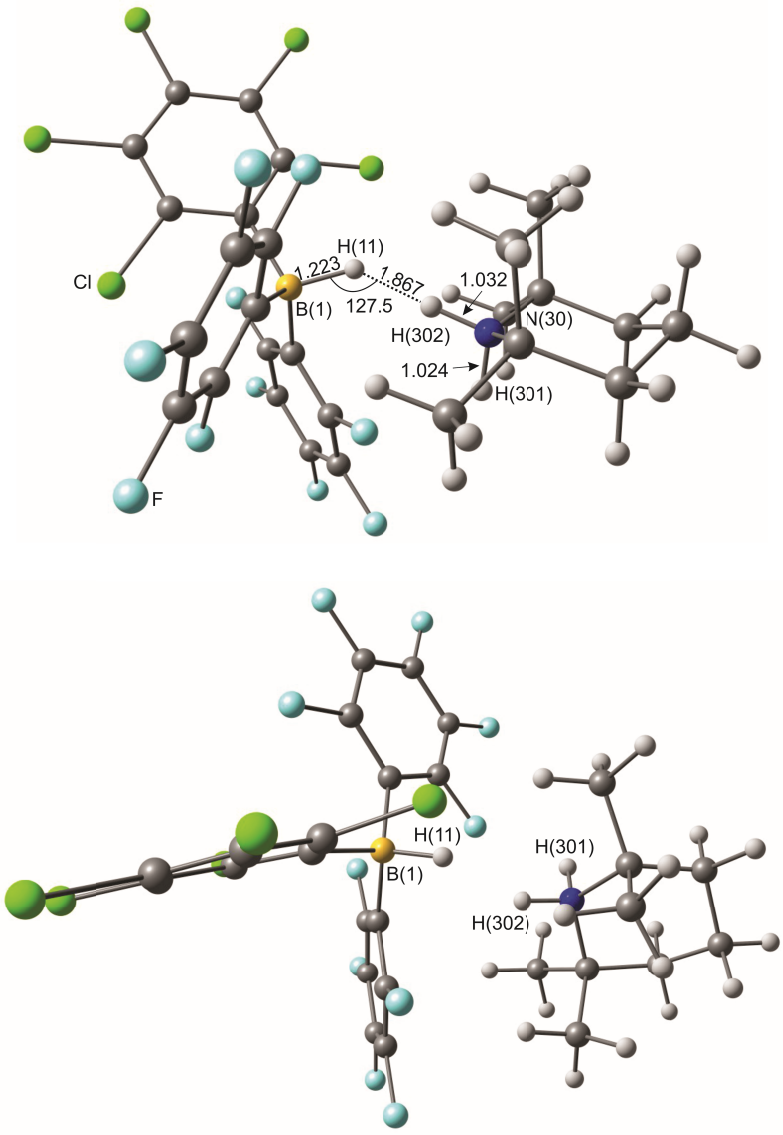


**Figure S1**. Optimized geometry of $[(C_6F_5)_2(C_6Cl_5)B{-}H][H{-}TMP]$ in sideview (top) and rotated view (bottom), including selected bond lengths (Å) and angles (deg) as well as the crystallographic labels.

The Wiberg bond index for the dihydrogen bond in **2** of 0.011 (Table S3) 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. The bond index can also be compared to the $(H_3NBH_3)_2$ dimer, a prototypical example for dihydrogen bonding interactions (see *J. Am. Chem. Soc.*, **1995**, *117*, 12875 and *J. Phys. Chem. A*, **1998**, *102*, 1873), schematically shown in Figure S2. For the latter we calculate a bond index of 0.022 for the stronger (H–H 1.72 A) of two interactions present in this dimer, using a MP2-optimised geometry with $C_s$ symmetry. The dihydrogen bond in **2** therefore is of the same order of magnitude as in the dimer.

**Table S1**. Wiberg Bond Indices for selected bonds / interactions omparing both gas phase and solution phase optimised geometries.

| Bond | Wiberg Bond Order |
|---|---|
| *[(C$_6$F$_5$)$_2$(C$_6$Cl$_5$)B−H][H−TMP]* | |
| B–H(11) | 0.8955 |
| N–H(301) | 0.7713 |
| N–H(302) | 0.7361 |
| H(11)···H(302) | 0.0109 |
| shortest H···X contacts | 0.0030 – 0.0500 |
| | |
| *(H$_3$BNH$_3$)$_2$* | |
| H···H | 0.0220 |
| H*···H* | 0.0036 |

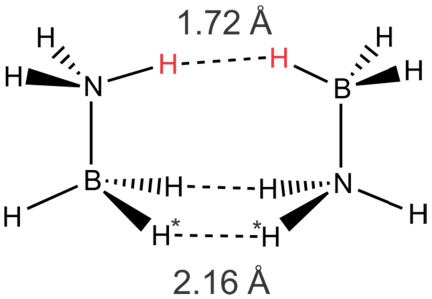


**Figure S2**. Schematic structure of the $(H_3NBH_3)_2$ dimer (with $C_s$ symmetry). Bond distances are given for the geometry obtained from a MP2/TZVP optimisation. Bond metric data are identical to the ones reported by Popelier (*J. Phys. Chem. A*, **1998**, *102*, 1873). Dihydrogen bonds are highlighted.

**Table S2**. Selected bond metric data of the optimized product complex (B97–D/TZVP), comparing both gas phase and solution phase optimised geometries.

| | [$(C_6F_5)_2(C_6Cl_5)$B−H][H−TMP] | | | |
|---|---|---|---|---|
| ***Distances* / Å** | **exp (X–ray)** | **exp (neutron)** | **PCM(water)** | **gasphase** |
| H(11)−H(302) | 1.844(2) | 1.8047(12) | 1.867 | 1.698 |
| N−H(301) | 0.897 | 1.030(8) | 1.024 | 1.025 |
| N−H(302) | 0.882 | 1.038(9) | 1.032 | 1.040 |
| B−H(11) | 1.353 | 1.203(9) | 1.223 | 1.228 |
| | | | | |
| *Angles* / ° | | | | |
| B−H(11)−H(302) | 136.43(5) | 139.5(8) | 127.5 | 127.1 |
| N−H(302)−H(11) | 174.95(5) | 174.4(9) | 152.1 | 147.7 |

**Table S3.** Cartesian coordinates of the optimized geometry of [$(C_6F_5)_2(C_6Cl_5)$B−H][H−TMP]

| | | | |
|---|---|---|---|
| H | 1.576638000 | 9.123361000 | 4.745273000 |
| C | 2.439331000 | 7.451301000 | 3.370016000 |
| C | 2.237060000 | 6.344847000 | 2.522200000 |
| C | 3.123003000 | 5.986007000 | 1.490987000 |
| C | 4.300904000 | 6.731212000 | 1.307137000 |
| C | 4.590033000 | 7.787993000 | 2.187474000 |
| C | 3.671048000 | 8.111547000 | 3.204505000 |
| C | 1.233326000 | 7.156457000 | 5.863540000 |
| C | 2.100901000 | 6.128048000 | 6.249533000 |
| C | 2.082811000 | 5.531784000 | 7.516348000 |
| C | 1.171760000 | 5.969851000 | 8.475090000 |
| C | 0.289543000 | 6.999831000 | 8.146332000 |
| C | 0.350020000 | 7.556391000 | 6.871007000 |
| C | -0.154321000 | 8.155859000 | 3.626812000 |
| C | -1.366334000 | 7.503090000 | 3.870132000 |
| C | -2.542087000 | 7.764855000 | 3.160621000 |
| C | -2.532225000 | 8.706437000 | 2.131549000 |
| C | -1.342657000 | 9.370022000 | 1.831426000 |
| C | -0.198136000 | 9.081014000 | 2.576637000 |
| B | 1.280942000 | 7.977696000 | 4.435632000 |
| F | 3.035491000 | 5.640174000 | 5.392988000 |
| F | 2.944733000 | 4.538286000 | 7.824730000 |
| F | 1.143266000 | 5.410805000 | 9.700142000 |
| F | -0.598608000 | 7.441976000 | 9.062332000 |
| F | -0.544412000 | 8.559368000 | 6.617629000 |
| F | 0.925874000 | 9.774862000 | 2.241801000 |
| F | -1.318485000 | 10.288055000 | 0.842245000 |
| F | -3.655318000 | 8.973459000 | 1.439433000 |
| F | -3.686423000 | 7.108268000 | 3.448045000 |
| F | -1.452967000 | 6.539142000 | 4.820016000 |
| Cl | 0.844631000 | 5.294057000 | 2.805185000 |
| Cl | 2.785423000 | 4.622307000 | 0.437327000 |
| Cl | 5.407041000 | 6.331930000 | 0.007237000 |
| Cl | 6.088977000 | 8.683780000 | 1.998268000 |
| Cl | 4.146341000 | 9.376212000 | 4.348774000 |

| | | | |
|---|---|---|---|
| H | -0.317610000 | 10.776823000 | 6.624877000 |
| H | 0.414609000 | 10.514998000 | 5.193765000 |
| C | -1.072542000 | 12.044627000 | 5.164994000 |
| C | -1.433481000 | 13.197326000 | 6.115203000 |
| H | -1.905559000 | 12.778041000 | 7.015400000 |
| H | -2.186558000 | 13.812313000 | 5.609154000 |
| C | -0.220587000 | 14.042199000 | 6.530230000 |
| H | -0.549219000 | 14.835272000 | 7.211318000 |
| H | 0.220407000 | 14.536476000 | 5.656069000 |
| C | 0.825241000 | 13.169271000 | 7.238046000 |
| H | 1.698557000 | 13.762858000 | 7.532371000 |
| H | 0.385916000 | 12.757327000 | 8.157779000 |
| C | 1.334595000 | 12.007536000 | 6.371464000 |
| C | -0.671590000 | 12.534870000 | 3.771450000 |
| H | -0.015520000 | 13.405906000 | 3.804902000 |
| H | -0.182065000 | 11.745956000 | 3.193783000 |
| H | -1.587400000 | 12.823747000 | 3.244902000 |
| C | -2.219102000 | 11.032751000 | 5.056281000 |
| H | -2.498750000 | 10.644037000 | 6.043164000 |
| H | -3.089234000 | 11.535918000 | 4.622458000 |
| H | -1.943288000 | 10.195132000 | 4.408198000 |
| C | 2.220504000 | 12.472551000 | 5.213638000 |
| H | 2.382266000 | 11.665317000 | 4.491597000 |
| H | 1.813992000 | 13.343473000 | 4.697141000 |
| H | 3.193311000 | 12.752990000 | 5.631716000 |
| C | 2.075247000 | 10.962939000 | 7.217048000 |
| H | 2.390590000 | 10.113522000 | 6.600270000 |
| H | 2.964587000 | 11.431496000 | 7.651137000 |
| H | 1.441445000 | 10.600712000 | 8.036696000 |
| N | 0.091321000 | 11.265472000 | 5.823531000 |