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Ultrashort $H^{\delta+} \cdots H^{\delta-}$ intermolecular distance in a supramolecular system in the solid state

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Herein we report experimental evidences for the shortest intermolecular distance reported for two electronically-different hydrogen atoms in the solid state. The $H^{\delta+} \cdots H^{\delta-}$ non-covalent interaction was studied by theoretical calculations indicating that electrostatic and dispersion forces are of paramount importance.

The understanding of chemical bonding is of fundamental importance for the advancement of chemical sciences.¹ In this regard, the origin and consequences of chemical interactions play a central role in fields as diverse as inorganics, biochemistry, solid matter as well as physical and organic chemistry.² The last years has witnessed a renewed interest to explore the limits of a certain type of interactions less common than classical hydrogen bonding or ion pairing.³ In particular, recent reports dealing with ultrashort $H \cdots H$ non-covalent interactions (i.e. $d_{H \cdots H} < 3.08$ Å) have shown their relevance from an structural and theoretical point of view.⁴ By means of unique, purely-organic molecular designs, Pascal, Jr. and co-workers reported a number of small cage-shaped molecules featuring extremely short intramolecular $H \cdots H$ distances ranging from 1.89 to 1.76 Å for physicochemically identical hydrogen atoms (A and B, Fig. 1).⁵ Further computational studies point out that even shorter distances up to 1.56 Å might be feasible.^{5,6} Bullock and co-workers reported the shortest intramolecular $H \cdots H$ distance found for an organometallic complex.^{7,8}

The quest for ultrashort intermolecular $H \cdots H$ distances is more challenging because the systems are prone to display higher degrees of freedom, resulting in longer distances compared to the intramolecular versions. In this respect, the seminal work from Schreiner and co-workers is of paramount importance as they reported the shortest intermolecular $H^{\delta+} \cdots H^{\delta+}$ distance of 1.57 Å (C, Fig. 1).⁹ This was found between two electronically-identical hydrogen atoms in a dimeric species comprising extremely bulky trityl moieties with *tert*-butyl groups behaving as dispersion energy donors, thus featuring attractive London dispersion interactions. On the other hand,

electronically-different, short intermolecular $H^{\delta+} \cdots H^{\delta-}$ distances (up to 1.66 Å) have been observed for purely ionic, highly charged molecular entities containing BH_4^- anions.¹⁰ Following our interest on weak interactions,¹¹ we herein report the discovery of the shortest $H^{\delta+} \cdots H^{\delta-}$ intermolecular distance found for two electronically-different hydrogen atoms (D, Fig. 1).

Fig. 1 Non-ionic chemical systems featuring the shortest intramolecular $H^{\delta+} \cdots H^{\delta-}$ (A) and $H^{\delta+} \cdots H^{\delta+}$ (B) distances as well as intermolecular $H^{\delta+} \cdots H^{\delta+}$ (C) and $H^{\delta+} \cdots H^{\delta-}$ (D, current contribution) distances. NRD = neutron diffraction data.

In the course of our studies on ligand design for supramolecular catalysis,¹² we synthesized the phosphine-phenol **1** and the corresponding borane adduct **2** (Scheme 1) following a modified procedure from the literature (see ESI).¹³ Both compounds delivered single crystals suitable for analysis by X-ray diffraction studies.¹⁴ In the solid state, compound **1** was organized in a supramolecular polymeric chain stabilized by classical hydrogen bonding involving the hydroxyl groups (see Fig. S1 in the ESI).

Scheme 1 Synthesis of phosphine **1** and borane adduct **2**.

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In stark contrast, compound **2** led to a supramolecular polymeric chain featuring O-H...H-B very close contacts (Fig. S2 in the ESI).¹⁵ In the unit cell, two crystallographically independent molecules were present, each one being connected with each other *via* different type of O-H...H-B weak interactions (see ESI for atom labelling details). In one case, two borane protons lie at 1.78 Å [$d_{\text{B-H(1B)}\cdots\text{H(52)-O(52)}}$] and 1.85 Å [$d_{\text{B-H(1C)}\cdots\text{H(1)-O(1)}}$], respectively, from the hydroxyl protons from the other molecule (Fig. S3-S4 in the ESI).¹⁶ Due to a slight disorder in the hydroxyl groups around the three phenyl groups (i.e. the population of O(52) and O(1) is 33% and 22%, respectively), such O-H...H-B distances might not be fully reliable nor representative of the system. Interestingly, in the other case, a single O-H...H-B interaction as short as 1.61 Å [$d_{\text{B-H(51C)}\cdots\text{H(2)-O(2)}}$] was unambiguously detected (Fig. 2). Importantly, the O(2) atom linked to the hydrogen atom involved in this short distance is the most populated one by far (61.8%). To the best of our knowledge, this is the shortest intermolecular $\text{H}^{\delta+}\cdots\text{H}^{\delta-}$ distance between electronically-different hydrogen atoms ever reported for non-ionic species.¹⁷ Unfortunately, attempts to obtain large crystals of a size suitable to collect low-temperature neutron diffraction data, which is well capable of determining the exact hydrogen positions (as it was the case for **1**, Fig. 1), failed so far. IR spectroscopy studies were performed on **1** and **2** and compared to pure phenol and $\text{Ph}_3\text{P-BH}_3$ (Fig. S5 and Table S1 in the ESI). The main OH vibration (3221 cm^{-1}) of compound **2** is shifted *ca.* 118 cm^{-1} to lower wavenumbers compared to **1** (3339 cm^{-1}). This observation points out to a sort of interaction in the solid state between the O-H group and the borane group of **2** similar to what has been found in the gas phase of a phenol-borane system elsewhere.¹⁸ The appearance of a shoulder at 3401 cm^{-1} in **2** also suggests a loss of symmetry of the vibration mode. As expected, the B-H vibration signal appears at 2378 cm^{-1} and additional peaks with maxima at 2346 and 2260 cm^{-1} . Multinuclei NMR was not conclusive, hereby suggesting that the observed phenomenon is not likely in solution.

Fig. 2 Molecular structure of phosphine-borane adduct **2** displayed as ORTEP drawing with thermal ellipsoids at 50% probability. Non-relevant hydrogen atoms have been removed for the sake of clarity.

A theoretical density-functional theory (PBE0¹⁹-D3²⁰/def2-TZVP²¹) study was performed in order to rationalize the $\text{H}^{\delta+}\cdots\text{H}^{\delta-}$ short distance in **2** (see ESI for computational

details and Fig. S6). First, the molecular electrostatic potential (MEP) minima and maxima surfaces of species **2** was calculated (Fig. S6 in the ESI). As expected, the MEP maximum ($+57.1\text{ kcal/mol}$) is located at the phenolic hydrogen atom ($\text{H}^{\delta+}$). On the other hand, the MEP minimum is not located at the extension of the B-H bond, but rather along the P-B bond (-35.1 kcal/mol). The MEP value at the borane-connected hydrogen atom ($\text{H}^{\delta-}$) is slightly more positive (-31.4 kcal/mol).

Next, we combined the quantum theory of atoms in molecules (QTAIM)²² with the non-covalent interaction (NCI) plot index analysis to further study the $\text{H}^{\delta+}\cdots\text{H}^{\delta-}$ interaction in **2** (Fig. 3).²³ In the dimer of **2**, the $\text{H}^{\delta+}\cdots\text{H}^{\delta-}$ interaction is characterized by a bond critical point (red sphere) and bond path interconnecting the hydrogen atoms. Importantly, a blue NCI isosurface is located between both $\text{H}^{\delta+}$ and $\text{H}^{\delta-}$ atoms in **2**, thus revealing a moderately strong, attractive interaction. In fact, the BSSE-corrected dimerization energy was calculated to be -6.0 kcal/mol (BSSE correction: 0.3 kcal/mol). The value of the Laplacian and total energy density at the bond critical point are both positive ($\nabla^2\rho = 0.0814\text{ a.u.}$ and $\text{Hr} = 0.0024\text{ a.u.}$), thus confirming the non-covalent nature of the interaction.²⁴ The NCI plot index analysis reveals the existence of additional green isosurfaces between both monomers, thus suggesting the existence of ancillary long range van der Waals forces (vdW in Fig. 3). We have estimated the contribution of the $\text{H}^{\delta+}\cdots\text{H}^{\delta-}$ interaction by using the potential energy density (V_r) predictor, using the expression developed by Espinosa and co-workers ($E = \frac{1}{2}V_r$).²⁵ The resulting energy for the $\text{H}^{\delta+}\cdots\text{H}^{\delta-}$ contact is -4.9 kcal/mol and, consequently, the contribution of the long range van der Waals forces can be estimated by difference, i.e. -1.1 kcal/mol .

Fig. 3 Distribution of bond and ring critical points CPs and bond paths for the dimer of **2**. The NCI plot isosurface is also represented using the $\text{RDG} = 0.5\text{ a.u.}$ isosurface and $p = 0.04$ cut-off for noncovalent interactions. The colour range is $-0.035\text{ a.u.} \leq \text{sign}(\lambda_2)\rho \leq 0.035\text{ a.u.}$ This dimer corresponds to the X-ray geometry. The value of p at the bond CP is given in italics (a.u.). The BSSE-corrected interaction energy is also indicated.

To further analyze the energetic features of the dimer of compound **2**, the interaction energy was decomposed by means of the symmetry adapted perturbation theory (SAPT)²⁶ calculations (see ESI for details). The SAPT terms are grouped into four chemically relevant categories: electrostatics, exchange-repulsion, induction and dispersion. The total SAPT energy (-5.7 kcal/mol) is similar to the BSSE-corrected dimerization energy (-6.0 kcal/mol), thus giving reliability to the partition method. The examination of the individual contributions to the interaction energy (Fig. 4) reveals that

electrostatic and dispersion terms are similar, being the latter the largest attractive term (in green). The large contribution of the electrostatic term is quite intuitive, due to the opposite electronic nature of the hydrogen atoms involved in the interaction. The large contribution of dispersion is lesser intuitive, though it agrees well with previous investigations that have demonstrated the decisive role of dispersion interactions to explain the attractive nature of very short C–H...H–C interactions in hydrocarbons.⁹ The SAPT results also show that the contribution of induction is important (28.7 % of the attractive terms). As usual, the largest magnitude is the exchange-repulsion (+16.7 kcal/mol). Charge transfer effects have been also investigated using two different methods (NPA and Merz-Kollman) to derive atomic charges (see ESI for details). Both methods suggest a similar net charge transfer from the BH₃ group to the phenolic H-atom (i.e., 0.021 e and 0.019 e for NPA and M-K charges, respectively).

Fig. 4 SAPT decomposition of the interaction energy (in kcal/mol) for the dimer of **2** (X-ray geometry). The contribution of exchange (repulsion), electrostatic, induction and dispersion terms are indicated.

To investigate the role of packing effects, the dimer of **2** was computed in the gas phase at the same level of theory (see ESI for details). The corresponding optimized dimer (PBE0-D3/def2-TZVP level of theory) elongates the H^{δ+}...H^{δ-} distance contact to 1.789 Å with additional π-π stacking (see ESI for details), a feature that is not found in the solid state (Fig. 2). The dependence of the O–H...H–B distance upon the choice of functional and basis set gives minimal differences (see ESI for details). Further theoretical studies (MARIJ-PB86-D3/def2-SVP level of theory, see ESI for details) focused on a pentamer of **2** (Fig. 5) that structurally resembles the supramolecular polymeric chain observed in the solid state of **2**. In contrast to the computed dimeric species, no π-π stacking was observed which is line with the findings in the solid state of **2** (*vide supra*). Interestingly, besides the presence of several common O–H...H–B distances,¹⁶ one very short O–H...H–B distance of 1.66 Å was found (Fig. 5). Although this value is again longer than the experimental value of 1.61 Å, it is much shorter than the value computed in the gas phase for the dimeric species (*vide supra*). Therefore, crystal packing is, in contrast to compound **C** (Fig. 1), decisive for stabilizing the observed short H^{δ+}...H^{δ-} distance of 1.61 Å in the supramolecular polymeric chain of **2** (Fig. 2).

Fig. 5 Optimized geometry of the pentameric assembly **2**₅ at the MARIJ-PB86-D3/def2-SVP level of theory, distances (blue color) are indicated in Å. Only the B/O-bonded H-atoms are shown for the sake of clarity.

In summary, we have demonstrated that the shortest H^{δ+}...H^{δ-} intermolecular distance for two electronically-different hydrogen atoms can reach values as low as 1.61 Å, which was so far unknown to date for non-ionic species. In silico thorough calculations evidenced the non-covalent nature of the interaction and that electrostatic and dispersion forces are equally important as attraction forces between both electronically different hydrogen atoms. Overall, trivial molecules such as **2** can display unexpected physical properties as it is here discussed. These findings provide a fundamental understanding for ultrashort, electronically-different H...H non-covalent interactions and they are expected to pave the way towards further studies in view to disclose the limits for uncommon chemical bonding phenomena.

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Conflicts of interest

There are no conflicts to declare.

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