Dihydrogen bonds (A–H···H–B)

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Theoretical calculations up to MP2/6-31G with BSSE correction are carried out on a series of A–H···H–B dihydrogen bonds (A = B, Li, Be; B = N, C).**

Classical hydrogen bonds (HBs) (**A**–H···**B**) where **A** and **B** are heteroatoms (generally F, O and N atoms)[1] have been generalized in three ways: HBs with unconventional donors (C–H);[2–4] HBs with unconventional acceptors (π-bonded functional groups,[3] Cl,[5] F,[6] C atoms[7]), and much more daring, dihydrogen bonds **A**–H···H–**B** (designated DHB).[8,9]

Crabtree and co-workers[8] reported 26 intermolecular DHBs of the type B–H···H–N with d_{HH} < 2.2 Å in 18 X-ray crystal structures from the Cambridge Structural Database (CSD);[10] in most cases, the N–H bonds correspond to N^+–H groups. These authors have studied the system $(H_3BNH_3)_2$ at the PCI-80/B3LYP level, finding that the Mulliken charges on the hydrogen involved in the DHB were +0.27 and −0.09 e for N–H and B–H respectively. Epstein and co-workers experimentally addressed the problem of *intermolecular* DHBs in solution.[9]

We report here a computational approach and the experimental verification of other DHBs. We started from the simple idea that these situations require two hydrogen atoms with opposite charges. Following Crabtree and Siegbahn, we will use as criteria to establish the existence of a DHB the interaction energy [$\Delta E = E(\mathbf{A}\text{–H}\cdots\text{H–}\mathbf{B}) - E(\mathbf{A}\text{–H}) - E(\mathbf{B}\text{–H})$] and the H···H distance. Crabtree and Siegbahn used, for the H···H distance, a limit of 2.4 Å as the sum of the van der Waals radii of two hydrogen atoms.[8] We prefer to use 2.7 Å which is the calculated value (RHF/6-311++G**) for H_3C–H···H–CH_3 [ΔE = 0.2 kcal mol^{-1} (cal = 4.184 J)].[11]

We have selected as compounds with 'acid' hydrogen atoms NH_4^+ (0.414 e) (Mulliken charges in parentheses), HCN (0.268 e) and H–C≡C–H (0.233 e); as representative compounds with 'basic' hydrogen atoms BH_4^- (−0.272 e), LiH (−0.193 e), BeH_2 (−0.109 e), and finally CH_4 (0.118 e) as an 'amphoteric compound'.[12]

The calculations have been performed using the Gaussian-92[13] and Gaussian-94[14] sets of programs. All the molecular complexes have been fully optimized with the 6-31G**[15] and 6-311++G**[16] basis sets at the HF and MP2[17] levels of theory. The frequencies of all complexes have been evaluated at the RHF/6-31G** level to confirm the minimum nature of the structures. The interaction energies have been corrected for the inherent basis set superposition error (BSSE) using the Boys–Bernardi counterpoise technique.[18] The DHBs have been characterized using the topological analysis of the electronic charge density[19] with the AIMPAC program package.[20]

The results are gathered in Tables 1 (energies) and 2 (geometries).

The theoretical results show two possible dispositions of dihydrogen bonds, nonlinear (**1** and **2**) in which three H···H interactions are present and linear (**3** and complexes with $C_{\infty v}$ symmetry). The linear arrangement for the systems of the first case has been optimized and yields structures, which are not minima of the potential surface, with shorter H···H distances (for instance 1.709 Å for BH_4^-···HCN, 2.121 Å for CH_4···NH_4^+ and 2.446 Å for BH_4^-···CH_4 calculated with the 6-31G** basis set).

We have tried some relationships between the interaction energies ΔE and the Mulliken populations of the hydrogen atoms of the isolated monomers (RHF/6-311++G**); for instance, $\Delta E = 45546\ (\pm 840)\ [(q_{\text{A–H}}) \times (q_{\text{B–H}})]^3$, $n = 7$, $r^2 = 0.998$ (excluding the CH_4···NH_4^+ complex). This equation predicts for the complex (BH_4^-···NH_4^+) a $\Delta E = -106.5$ kcal mol^{-1}.[21]

The charge density at the hydrogen bond critical points, ρ_c, shows large electronic densities and positive values of $\nabla^2\rho$ which indicate strong hydrogen bonds (Fig. 1 shows the plot of $\nabla^2\rho$ for the BeH_2···NH_4^+ complex). There is a rough relationship between ΔE and ρ_c: $\Delta E = 678.7\ \rho_c$, $n = 8$, $r^2 = 0.89$.

To check if these DHBs correspond to real situations we have explored the CSD.[10] We have retrieved those of type B–H···H–N reported previously;[8] moreover other situations have been found: B–H···H–O, B–H···H–C where C is an aliphatic sp^3 C atom or an aromatic ring (Mulliken population for benzene q_H = 0.148 e) and Al–H···H–C where C belongs to the CH_2 of tetraethylammonium cation (Mulliken population for the CH of CH_3–NH_3^+ q_H = 0.222 e). To illustrate these findings we have selected four examples (CSD refcode and name in parentheses): B–H···H–O, H···H 2.19 Å, B–H···H 151°, H···H–O 125°, B–H···H–O torsion −109° [KUMFED, tetrapotassium 7,6-bidecaboryl(18) dihydrate]; B–H···H–C(sp^3), H···H 2.02 Å, B–H···H 128°, H···H–C(sp^3) 159°, B–H···H–C(sp^3) torsion 130° [BORMUQ01, bis(triphenylphosphine)iminium heptahydroborate dichloromethane solvate]; B–H···H–C(ar), H···H 1.75 Å, B–H···H 159°, H···H–C(ar) 155°, B–H···H–C(ar) torsion −62° {WAGBAH, (*R*)-(−)-*N*-methyl, *N*-[1*R*,2*S*)-1-(alphahydroxybenzyl)ethyl]amino(methyl)phenylphosphine borane]; Al–

Table 1 Interaction energies, ΔE (kcal mol^{-1}), and values of the charge density at the hydrogen bond critical point ρ_c (e a_0^{-3})

System	6-31G**[a]	6-31G**[b]	6-311++G**[b]	MP2/6-31G**[b]	ρ_c[c]
BH_4^-···HCN	−18.50	−18.02	−17.02	−18.03	0.018
BH_4^-···CH_4	−1.80	−1.37	−1.20	−1.88	0.007
LiH···NH_4^+	−46.35	−38.60	−38.08	—	0.046[d]
LiH···HCN	−7.72	−7.42	−7.42	−7.28	0.017
LiH···HCCH	−3.36	−3.04	−3.14	−3.32	0.011
BeH_2···NH_4^+	−17.36	−8.07	−7.88	−9.26	0.025
BeH_2···HCN	−1.57	−1.42	−1.45	−1.53	0.008
CH_4···NH_4^+	−11.62	−2.46	−2.52	−3.51	0.013

[a] Without BSSE correction. [b] With BSSE correction by the counterpoise method. [c] MP2/6-31G** calculations. [d] RHF/6-31G** calculation.

H···H–C, H···H 1.91 Å; Al–H···H 143°, H···H–C 155°, Al–H···H–C torsion 95° (TEAMAL, tetraethylammonium tetrahydroaluminate).

An additional proof of the reliability of our calculations is provided by the ΔH value of the equilibrium $NH_4^+ + CH_4 \rightleftharpoons [NH_4{\cdot}CH_4]^+$ in the gas phase: experimental value 3.59 ± 0.11,[22] calculated value 3.51 kcal mol^{-1} (Table 1).

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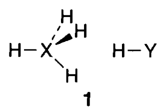
Table 2 H···H (Å) distance, symmetry and structure of the complexes



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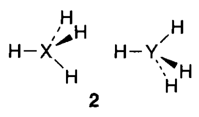

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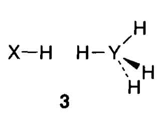

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System	6-31G**	6-311++G**	MP2/6-31G**	Symmetry	Structure	X	Y
BH_4^-···HCN	2.184	2.227	2.101	C_{3v}	**1**	B	C≡N
BH_4^-···CH_4	2.797	2.929	2.583	C_{3v}	**2**	B	C
LiH···NH_4^+	1.390	1.391	—	C_{3v}	**3**	Li	N
LiH···HCN	1.970	1.981	1.866	$C_{\infty v}$			
LiH···HCCH	2.233	2.430	2.080	$C_{\infty v}$			
BeH_2···NH_4^+	1.722	1.744	1.591	C_{3v}	**3**	HBe	N
BeH_2···HCN	2.248	2.306	2.115	$C_{\infty v}$			
CH_4···NH_4^+	2.237	2.357	2.226	C_{3v}	**2**	C	N

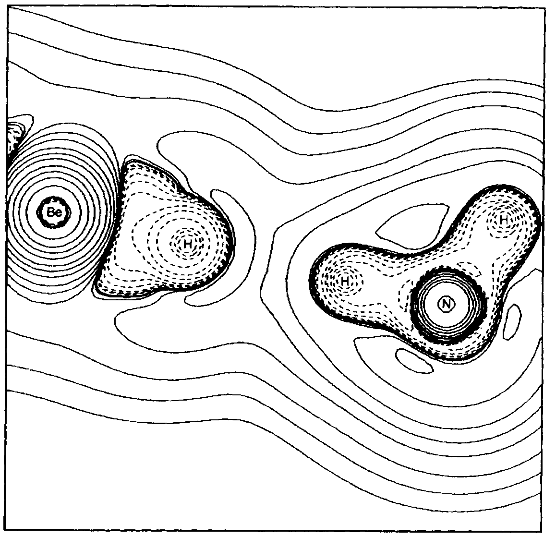

Fig. 1 Plot of $\nabla^2\rho$ in H–Be–H···H–N$^+$–H_3

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