Non-conventional hydrogen bonds

CHEMICAL SOCIETY REVIEWS

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Hydrogen bonds (HBs) are the most important 'weak' interactions encountered in solid, liquid and gas phases. The HB can be defined as an attractive interaction between two molecular moieties in which at least one of them contains a hydrogen atom that plays a fundamental role. Classical HBs correspond to those formed by two heteroatoms, A and B, with a hydrogen atom bonded to one of them and located approximately in between (A–H···B). Recently, knowledge of the number of functional groups which act as hydrogen bond donors or acceptors has increased considerably and most of these new groups are discussed.

1 Introduction

Hydrogen bonds (HBs) are the most important 'weak' interactions encountered in solid, liquid and gas phases. They define the crystal packing of many organic and organometallic molecules, the 3D structure of biological macromolecules, as well as modulate the reactivity of different groups within a molecule. Hydrogen bonds (HBs) can be defined as an attractive interaction between two molecular moieties (two molecules or two parts of the same molecule) in which at least one of them contains a hydrogen atom that plays a fundamental role in the interaction. In the rank of interactions among atoms, the HB falls between chemical bonds (as covalent bonds) and non-bonding interactions such as van der Waals interactions. In general, a HB is characterized by: (*i*) a weak to medium interaction energy;[1] (*ii*) a considerable interpenetration of the isolated electronic clouds of the two moieties involved; (*iii*) a certain electron transfer between the two moieties, and (*iv*) a preferred geometry.[2–4] Hibbert and Emsley[1] define three kinds of HBs depending on the interaction energy values obtained. Thus, HBs with energies between -2.4 and -12 kcal mol^{-1} (1 cal = 4.184 J) are defined as weak HBs, those with energies between -12 and -24 kcal mol^{-1} are defined as strong HBs and those with energies more negative than -24 kcal mol^{-1} are considered very strong HBs.

The classical HBs correspond to those formed by two heteroatoms, **A** and **B**, with a hydrogen atom bonded to one of them and located approximately in between (**A**–H··**B**). In general, there has been considered an electrostatic attraction between the positive end of the bond dipole of **A**–H and the centre of negative charge on **B** (generally a lone pair of electrons). Usually, the **A**–H moiety is defined either as an 'electron acceptor' or as a 'hydrogen bond donor (HBD)' and the **B** moiety as an 'electron donor' or a 'hydrogen bond acceptor (HBA)'. In this review we will use the hydrogen bond donor–acceptor nomenclature[5,6] except in Section 8. The previously mentioned classical requirements for HBDs and HBAs mean that both moieties come mainly from the same few groups of the periodic table: groups 15, 16 and 17. Therefore, most published works of HBs are the type O–H···B or N–H···B in which the HB acceptor 'B' posses N, O or F lone pairs responsible for the HB formation. These classical HBs have been generalized in other directions such as: (*i*) HBs with unconventional H donors such as C–H, (*ii*) HBs with unconven-

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tional H acceptors as π-bonded functional groups, halogens or C atoms, and (*iii*) dihydrogen bonds **A**–H···H–**B**.

Research over the years has widened the knowledge of groups acting as HBDs or HBAs, our understanding of which is reported in Table 1. The present review will not include 'classical' HBs (**A** and **B** both being heteroatoms), nor the 'non-conventional' case when **A** is a carbon atom (C–H as an HBD) because they have been reviewed in detail elsewhere.[7–9] From the point of view of the interaction energy, the HBs considered in the present review are within those considered weak by Hibbert and Emsley;[1] however, for a better understanding of these unconventional HBs we will estabish a new classification: HBs with interaction energies until $|-5|$ kcal mol^{-1} (interaction energy of the hydrogen bonded dimer of water)[1] will be considered as weak, those with energies between $|-5|$ and $|-10|$ kcal mol^{-1} will be defined as medium and those with energy values larger than $|-10|$ kcal mol^{-1} will be defined as strong or very strong.

Table 1 Non-conventional HBDs and HBAs—the object of the present review

	A–H··**B** Hydrogen bonds (HBs)	**A**–H···H–**B** Dihydrogen bonds (DHBs)
Protic	**B** = isonitriles[10] **B** = carbanions[11] **B** = carbenes[12] **B** = π-systems[10,13]	Ref. 14, 15
Solvent and electric field effects	$\mathbf{A}\text{–H}\cdot\cdot\mathbf{B} \rightarrow \overline{\mathbf{A}}\cdots\text{H–}\overset{+}{\mathbf{B}}$	$\mathbf{A}\text{–H}\cdots\text{H–}\mathbf{B} \rightarrow \overline{\text{A}}\cdots\text{H–H}\cdot\overset{+}{\mathbf{B}}$
	Ref. 16	Ref. 17
Hydric (inverese)	$\mathbf{A}\text{–H}\cdot\cdot\mathbf{B} \rightarrow \overset{+}{\mathbf{A}}\text{–H}\cdot\cdot\overline{\mathbf{B}}$ Ref. 18	

The development of new approaches to the treatment of electron density and its significance in the nature of chemical bonds have opened up new perspectives in the description of HBs making their definition more accurate and precise. Thus, according to Koch and Popelier,[4] and within the frame of the theory of atoms in molecules (AIM) proposed by Bader,[19] the new additional criteria for a more correct definition of a HB will be:

(*i*) Charge density (ρ_c) and the Laplacian of the charge density ($\nabla^2\rho_c$) at the bond critical points (BCPs, see Appendix). The values obtained for these two parameters (small ρ_c values and positive $\nabla^2\rho_c$ values) should correspond to what is defined as 'closed-shell' interactions[19] of the HB type (van der Waals complexes would have smaller ρ_c values).

(*ii*) Topology. By analyzing the bond paths between the H atom and the HBA it will be possible to determine the existence of an interaction such as a HB.

(*iii*) Mutual penetration of the H and the interacting bond. In order to estimate the mutual penetration of the H atom and the HBA (r^0_H and r^0_A) upon HB formation, the nonbonded radii of both parts have to be compared to the corresponding bonded radii (r_H and r_A, BCP radii). The nonbonded radius is defined as the distance of a nucleus to a 0.001 au charge density contour in the direction of the HB. Moreover, if all the penetrations are positive they can be designated as HBs.

(*iv*) Loss of charge and energetic destabilization of the H atom, and total charge transferred. A necessary criterion for the formation of a HB is the loss of charge of the H atom involved. This loss (ΔN) is computed by subtracting the electronic population of the H in the free monomer from the corresponding H in the complex, and should be negative. In addition, this H atom should be destabilized in the complex and the destabilization is given by the difference in total atomic energy between the complex and the monomer (ΔE) which should be positive. Finally, the total charge transferred in the formation of the HB should always be negative implying the donation of electrons from one molecule to another.

(*v*) Dipole moment enhancement. The electric charge rearrangement that accompanies the formation of a hydrogen bonded complex is an important characteristic of HBs. The difference between the dipole moment of the complex and the sum of those of the separate monomers provides some information of the electric rearrangement. These enhancements have contributions from the polarization of one monomer by the other and from the charge transferred in the formation of the HB. Thus, the dipole moment of the complexes should be larger than the vector sum of the dipole moment of the monomers as a consequence of the HB formation.

Taking into account all these conditions proposed to prove the existence of a HB, let us survey the different non-conventional hydrogen bonded systems that are the subject of the present review.

2 Isocyanides and carbon monoxide as HB acceptors

In 1962, Ferstanding[20] and Schleyer and Allerhand[21] both described the case of an HB of the type C–H···C. The experiments showed that the carbon atom of isocyanide **2a** R = Ph (also called isonitrile) acting as a HBA (HNC···H–**A**) was able to form strong HBs with a variety of HBDs including carbon derivatives such as phenylacetylene.

$\text{R–N}\equiv\text{C:}$

2a

$\text{H–N}\equiv\text{C:}\cdots\cdots\text{H–}\mathbf{A}$

2b

$[\text{H–N}\equiv\text{C–H}]^+$

2c

$\text{:O}\equiv\text{C:}$

2d

We have studied several HB complexes **2b** of hydrogen isocyanide (**2a**, R = H) as a HBA with five well known HBDs (HF, HOH, HNH_2, HCN) as well as with hydrogen isocyanide itself (HNC).[10] Calculations were carried out at the MP2/6-311++G** and B3LYP/6-311++G** levels (see Appendix) and one example of the results obtained with the help of the AIM methodology[19] is represented in Fig. 1. The main conclusions were: (*i*) concerning the geometry of the linear complex, there is a lengthening of the H–N bond and a shortening of the N≡C bond indicating for the isonitrile fragment of **2b** a geometry intermediate between **2a** and **2c** and justifying our view of HBs as intermediates in protonation reactions; (*ii*) the interaction energies are significant (E_{I+BSSE} = −5.4 kcal mol^{-1} for hydrogen isocyanide to compare with −3.3 kcal mol^{-1} for its isomer, hydrogen cyanide) making these HBs of a weak to medium strength; (*iii*) the calculated chemical shifts (GIAO)[22] are linearly correlated with the electron transfer in the complex; (*iv*) the X-ray structures found in the Cambridge Crystallographic Data Centre (CCDC),[23] although scarce, are well reproduced by the calculations.

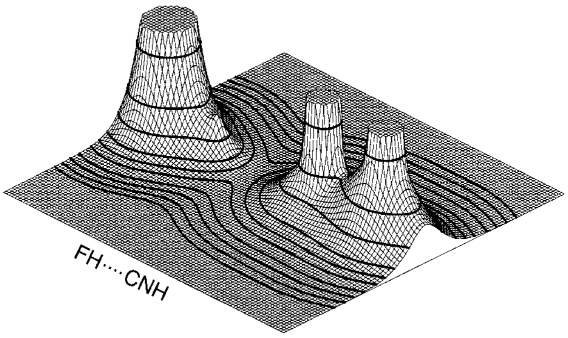
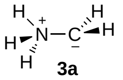


Fig. 1 Relief map of the electron density (ρ)[19] corresponding to the complex FH···:CNH

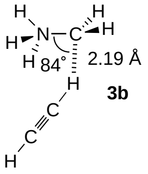
Concerning carbon monoxide **2d**, it has been established that the protonation in the gas phase occurs both on the carbon $[HCO]^+$ and on the oxygen $[COH]^+$.[24] When acting as a HBA, however, it uses the carbon and not the oxygen end[24,25] unless the carbon is coordinated to a metal.[26] Our calculations[10] show the existence of weak HB (from -0.5 to -3.4 kcal mol^{-1}) between carbon monoxide and different HBDs. In contrast, carbon monosulfide (CS) forms much stronger HBs (from -1.2 to -7.3 kcal mol^{-1}) which can be classified as weak to medium HBs. These differences can be explained based on the permanent dipole moment of both molecules.

3 Carbanions and zwitterions as HB acceptors

Theoretical work has proposed that carbanions could act as HBAs.[11] Thus, Platts *et al.* have shown that carbanions stabilized as zwitterionic species **3a** can form medium HBs with weak HBDs as acetylene ($E_{\mathrm{I+BSSE}} = -7.7$ kcal mol^{-1}) giving rise to complex **3b** containing one of the less studied types of HBs—the C–H···C bond.[11] The optimized geometry of **3b** at the MP2/6-311++G** level shows a short C···H distance and the possible existence of a secondary interaction between the hydrogen atoms on nitrogen and the triple bond of acetylene.



3a

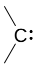


3b

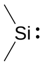
The strong basicity of the HBAs treated in the present section indicates that they would only be able to form HB with weak proton donors because more acidic donors would produce a spontaneous transfer of the hydrogen.

4 Carbenes and silylenes as HB acceptors

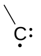
In this section we will discuss three related structures: (*i*) carbenes **4a**, (*ii*) silylenes **4b**, and (*iii*) carbynes **4c**.



4a

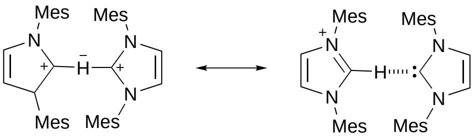


4b



4c

We previously discussed the case of carbenes **4a** and silylenes **4b** and here we summarize only the main conclusions.[12] Although carbenes are in general highly reactive species with short lifetimes, some examples are known of stable carbenes at room temperature.[27] Silylenes have similar structures and were reviewed recently.[28] Arduengo *et al.*[29] also reported an X-ray structure of a stable 'nucleophilic' carbene that shows a new type of intermolecular HB **4d**. It involves a carbonium and a carbene with an almost linear HB:



4d

In our paper,[12] a model (H_2C:···H–CH_2^+) of the structure reported by Arduengo was theoretically studied and this new type of HB was generalized in two ways: (*i*) other HBDs than C$^+$–H; and (*ii*) other HBAs than methylene. HBDs include CH_3^+, HCN, HF, H_2O and HBAs include CH_2: (singlet methylene), SiH_2: (singlet silylene) and CF_2: (singlet difluorocarbene). The highest level of calculations used was the MP2 or MP4/6-311++G**. Quantitatively, all the methods indicate the presence of HBs due to the short X:···H distances and interaction energies between -2 and -22 kcal mol^{-1}, depending on the complex studied. The values described by Arduengo [C:···H = 2.026(45) Å, C:···H–C = 172.5°, and H–C = 1.159(45) Å] for this new kind of HB are very similar to the ones obtained for the simplified model H_2C:···CH_3^+ (C:···H = 1.988, C:···H–C = 180.0°, and H–C = 1.102 Å). The model system shows a very strong HB (*ca.* -20 kcal mol^{-1}). For the strongest neutral complex (H_2C:···HF, Fig. 2) the interaction energy amounts to -10 kcal mol^{-1}.

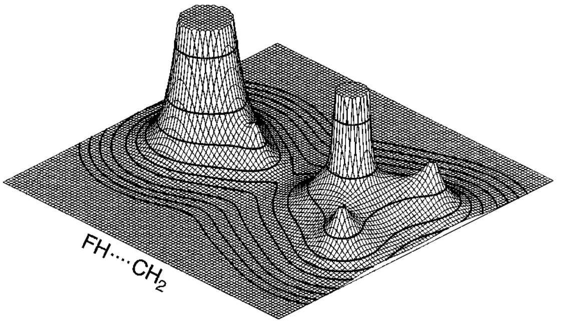


Fig. 2 Relief map of the electron density (ρ)[19] corresponding to the complex FH···:CH_2

The analysis of the charges, gathered in Table 2, shows a flow of electrons from the atoms attached to the carbene or silylene (X) that become more positive, to the more electronegative atom of the HBD (A).

Table 2 Atomic charges (|e|) of the carbene and sylylene monomers and the HB complexes at the MP2/6-311++G** level using the AIM methodology

HBAs	X	**B**:	HBDs	H	**A**
H_2C:	0.008	−0.016	HF	0.712	−0.712
H_2Si:	−0.726	1.453	HCN	0.204	0.817
F_2C:	−0.648	1.297	H_2O	0.567	−1.133
			H_3N	0.348	−1.043
			H_3C^+	0.275	0.176

HB complexes[a]

	Δ*X*	Δ**B**:	Δ*H*	Δ**A**	Electron transfer
H_2C:···HF	0.045	−0.010	−0.007	−0.073	0.080
H_2C:···HCN	0.026	−0.024	0.065	−0.047	0.028
H_2C:···H_2O	0.069[b]	−0.100	−0.010	−0.018	0.038
H_2C:···H_3N	0.012	−0.006	0.040	−0.037	0.018
H_2C:···H_3C^+	0.084	−0.084	0.098	−0.093	0.084
H_2Si:···HF	0.008	0.046	−0.021	−0.041	0.062
H_2Si:···HCN	0.006	0.014	0.018	0.022	0.026
F_2C:···HF	0.012	0.024	−0.002	−0.046	0.048
F_2C:···HCN	0.007	0.000	0.030	−0.023	0.014

[a] The atomic charges are relative to the monomers values. [b] Average of the two protons.

In addition, several relationships between the parameters that define these HBs (such as HB distance, electron transfer, electron density on the HB critical point and interaction energy) were found. Finally, although the case of carbynes **4c** was examined, their multiplet nature complicates the calculations considerably.[10]

5 π Acceptors

There has been much interest in hydrogen bonds where the HBA is a π-system, especially acetylenes and benzenes.[8] Thus, Mingos *et al.*[30] have characterized by X-ray crystallography the T-shaped intermolecular Cl_3C–H··π (C≡C) interactions present in chloroform solvates of gold(I) ethyne complexes. Recently, Chandra *et al.*[31] reported theoretical studies of diacetylene···HF and allene···HX (X = Cl, F) complexes at the MP2 level of the theory and Chandra and Nguyen explored the possibilities of the same diacetylene as an HBA towards HCl and announced a similar study for the complex acetylene···HCl.[31] The information about benzenes as π-HBAs is abundant: microwave experiments have provided information about the spectrum and geometry of a series of HF or HCl complexes with benzene.[32] Several crystal structures have been determined where these kinds of H··π interactions are observed intra-[33] or intermolecularly.[34,35] Tang *et al.* have reported a quantum chemical study (MP2/6-31G**//6-31G*) on a selection of π-type hydrogen-bonded systems.[13] They used hydrogen fluoride as HBD and a set consisting of acetylene, ethylene, cyclopropane and benzene as HBAs. They were able to correctly describe a number of complexes previously identified by microwave spectroscopy. Moreover, using the Bader topological approach,[19] they made a detailed description of the HBs.

Due to a multitude of relevant experimental results appearing between the years 1991–1996, we decided to undertake a similar study[10] also using HF as HBD, but with two differences: namely, we used a 6-311++G** basis set and a large number of HBAs (the four of Tang plus cyclopropene, cyclobutadiene and tetrahedrane). Tetrahedrane was selected because it is not only considered a three-dimensional aromatic system but also a strong base (the cation $C_4H_5^+$ is much more stable than the base C_4H_4).[36]

For all these complexes, we have carried out the electron density analysis proposed by Koch and Popelier described previously[4] representing in Fig. 3 the structure of two of these complexes: Fig. 3(*a*) corresponds to the benzene···HF complex and Fig. 3(*b*) to the tetrahedrane···HF complex. In the case of the benzene complex [Fig. 3(*a*)], our minimum energy structure is different from that of Tang *et al.* (point symmetry C_{6v})[13] and is more in agreement with experimental results.[10,13]

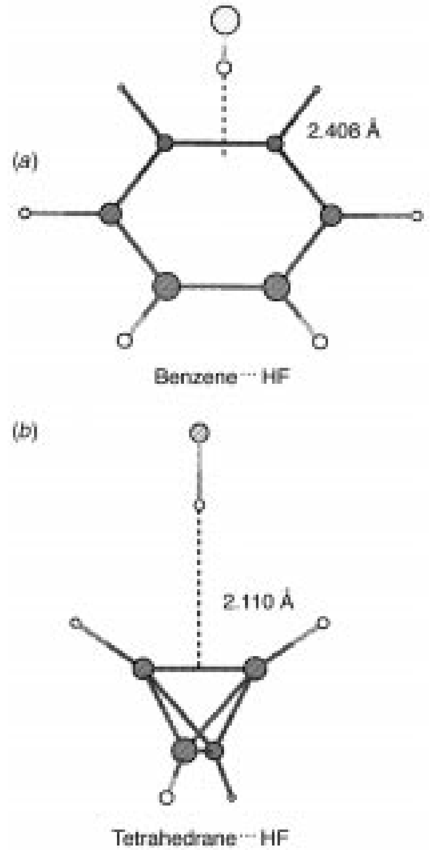
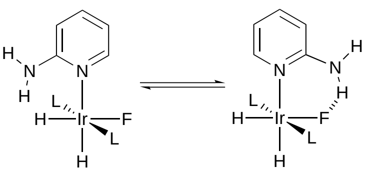


Fig. 3 Geometries obtained at the MP2/6-311++G** level for the minimum energy H··π complexes formed between hydrogen fluoride and (*a*) benzene, (*b*) tetrahedrane. Also shown are the distances between the H atom and (*a*) the π cloud, (*b*) the C–C bond critical point.

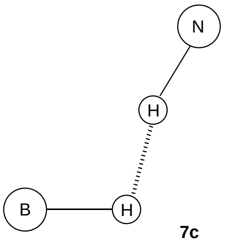
6 Dihydrogen bonds and electric field effects on dihydrogen bonds

We[14] and others[15,37,38] have devoted some effort to the understanding of dihydrogen bonds (DHBs). These bonds, mainly present in transition metal compounds, are of the type 'proton-hydride', *i.e.* between an **A**–H$^{\delta+}$ and a **B**–H$^{\delta-}$.

The main characteristics of the **M**–H···H–**A** systems (**M** = metal such as Ir or Re, **A** = O, N) are: (*i*) close H···H contacts (1.75–1.90 Å) (*ii*) interaction energies in the range of weak conventional HBs (−3 to −7 kcal mol^{-1}) (*iii*) large couplings ($^1J_{HH'}$ = 2–4) between the **A**H (**A** = O) and the **M**H (**M** = Ir) protons, and (*iv*) abnormally low minimum T_1 values in the ^{1}H NMR spectra. Experiments using complex **7** reveal that the N–H···F–Ir bond (−5.2 kcal mol^{-1}) is a little stronger than the N–H···H–Ir DHB (−5.0 kcal mol^{-1}).[38]



7a **7b**



7c

These bonds were first generalized to the system B–H···H–N (**7c**).[37] Theoretical calculations (PCI-80/B3LYP) sustained by structures found in the CSD show these bonds to be of medium strength (−6.1 kcal mol^{-1} for H_3BNH_3) and directional (H···H–N almost linear and B–H···H bent, in the range 95–120°). The B–H···N bending is due to an attractive Coulombic interaction between the strongly negatively charged B and the protonic NH$^{\delta+}$. We showed that DHBs are more general and that not only B–H···H–N (**7c**) but also several other systems present interaction energies E_{I+BSSE} (in kcal mol^{-1}), charge densities at the hydrogen bond critical points ρ_c (in $e\ a_0^{-3}$) and geometries which are consistent with the existence of a HB.[14] The systems studied were $BH_4^-\cdots HCN$, $BH_4^-\cdots CH_4$, $LiH\cdots NH_4^+$, $LiH\cdots HCN$, $LiH\cdots HCCH$, $BeH_2\cdots NH_4^+$, $BeH_2\cdots HCN$ and $CH_4\cdots NH_4^+$. An empirical model, relating E_{I+BSSE} to Mulliken populations, predicts a E_{I+BSSE} = −106.5 kcal mol^{-1} for the complex H_3B^-–H···H–NH_3^+. The situation is not stable because when the structure is minimized it evolves to $H_3B + H_2 + NH_3$. Contreras *et al.*[38] have described experimental results (X-ray for the solid state and ^{1}H NMR for the solution) consistent with the existence of 'protic–hydric' C–H$^{\delta+}\cdot\cdot{}^{\delta-}$H–B and protic–fluoride C–H$^{\delta+}\cdot\cdot{}^{\delta-}$F–B interactions (here C and B stand for carbon and boron).

As a logical consequence of two of our lines of research (that on DHBs and that on the effect of electric fields[16]) and in order to investigate the hydrogen transfer within a crystal (by means of the crystal field), we studied the effect of an external field over three different proton equilibria with *ab initio* methods (HF/6-31G**).[17] The equilibria chosen were eqn. (1)–(3).

$$\mathrm{Li{-}H\cdots H{-}F \rightleftharpoons Li^+\cdots H{-}H\cdots F^-} \qquad (1)$$

$$\mathrm{H_3N\cdots H{-}H\cdots BH_3 \rightleftharpoons H_3N^+{-}H\cdots H{-}BH_3^-} \qquad (2)$$

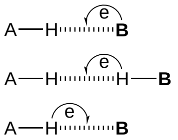
$$\mathrm{HBe{-}H\cdots H{-}NH_3^+ \rightleftharpoons HBe^+\cdots H{-}H\cdots NH_3} \qquad (3)$$

An electric field, in positive and negative directions, was applied along the molecular axis increasing from 0.00557 to 0.03342 au in steps of 0.00557 au. In the absence of an external field, structures in the left side of the equilibria were stationary points [with two negative frequencies in equilibria (1) and (2) and zero negative frequencies in equilibrium (3)].

Thus, when applying an electric field (positive or negative) over the system on the right in equilibrium (1), this equilibrium is displaced to the left yielding a DHB system. Reciprocally, when an increasing positive field is applied over the DHB system on the right of the equilibrium (2) we obtained the system on the left. In the complexes with coordinated hydrogen molecules of equilibria (2) and (3), the H–H bonds were broken by the field effect resulting in two molecules in each case that moved to the infinite. Further, by applying an increasing electric field it was possible to keep connected an unstable DHB complex [right side of equilibrium (2)] or an unstable hydrogen coordinated complex [right side of equilibrium (3)]. In conclusion, we found that by applying an external electric field, the transfer of H atoms between two heavy atoms is possible as it occurs within the crystal due to internal forces. Recently, a situation corresponding to the right side of eqn. (1) has been described, namely CsF(H_2) and KF(H_2).[39]

7 Inverse HB complexes

In all the unusual HBs mentioned above, the H atom plays the role of electron acceptor, with the exception of the DHBs where one of the H atoms accepts the electrons while the other provides them. Following this sequence we studied a new class of unconventional HBs where the H atom provides electrons and another non-hydrogen atom accepts them.[18]



In order to obtain these 'inverse' HBs we should consider a particular set of molecules formed by 'donors' and 'acceptors' of electrons. On one hand, LiH, BeH_2 and BH_4^- with very electron deficient heavy atoms will be electron donors ('e-donors'). On the other, electron acceptors ('e-acceptors') will be the Li or Be hydrides because these alkaline atoms would accept the electrons easily and without any steric restriction. Besides, other Li and Be derivatives with methyl or fluoride groups have been included in the 'e-acceptors'. The complexes studied were:

(*i*) Those formed by 'linear approximation' between a Li, Be or B hydride ('e-donors'), and a Li derivative ('e-acceptors').

(*ii*) Those formed by 'multiple approximation' between Li and Be hydrides and fluorides where the metal, hydrogen and/or fluorine atoms form a larger number of linkages than their corresponding valence. This group has been studied only for comparative purposes because the interactions involved cannot be properly considered as HBs.

Many of the structures discussed in ref. 18, both monomers and complexes, have not been observed, but compounds of Li, Be and B that are experimentally known span a wide range of structural types.[18] Some of these complexes were previously calculated. For example, in the case of the linear $(LiH)_2$ dimer, some authors termed the interaction 'lithium bond' and other authors considered these aggregates as bounded binary complexes. None, however, suggest these interactions to be inverse HBs.[18]

Given the basically accepted definition of a HB—a bond distance d(H$\cdots$**A**) shorter than the sum of the atomic van der Waals radii of H and **A**; a bond angle α(**B**–H$\cdots$**A**) almost linear; a certain transfer of charge among these three atoms and an energy around -2 to -22 kcal mol^{-1}—our study suggested that linear complexes fulfil all the conditions, and, therefore, should be considered as inverse HBs. The computation of the atomic charges of the linear complexes showed that there is an electron transfer from fragments defined as 'e-donors' to the 'e-acceptors' in all the complexes studied as can be seen in Table 3. Therefore, and contrary to classical HBs, the charge and the H atom flow in the same direction from the acid to the basic fragment. This makes these inverse HBs unique.

Within the frame of the AIM theory,[19] the electronic distribution in these inverse HBs shows a hydrogen atom bound to both the 'e-donor' and the 'e-acceptor' by closed-shell interactions, both of which are closed-shell interacting fragments. The bond critical points obtained in these interactions reflect all the characteristics associated with HBs: low ρ_c values and $\nabla^2\rho_c > 0$.

The energy results showed that the inclusion of correlation effects, diffuse functions, and ZPE and BSSE corrections are significant in the description of these particular HB complexes. Linear complexes of BeH_2 showed interaction energies within -5 to -10 kcal mol^{-1} whereas the LiH dimer and the BH_4^- complex exhibited interaction energies around -25 to -50 kcal mol^{-1}.

8 Conclusions

(*i*) Although much of our contribution is related to calculations of small systems, that is, to idealized 'gas-phase' simple situations, according to ref. 5, 'The study of HB interactions in the gas-phase is relevant because it provides direct information on the structure and stability of these complexes in the absence of the perturbations induced by the solvent'. In the solid-state (mostly X-ray structures), care should be taken not to define HBs only in geometrical terms, following Dunitz's advice it is important not to confuse attractive–repulsive interaction forces with stabilizing–destabilizing interaction energies.[40] Moreover, a short distance (H$\cdots$**B** or H$\cdots$H) alone is not proof of the existence of a HB or DHB.

(*ii*) Another point worthy of consideration is that HBs can be viewed as intermediates in protonation processes.[16] For instance, DHBs may lie on the pathway whenever a hydride undergoes protonation[14,37] eqn. (4).

$$\mathbf{M}\text{–H}^- + \text{H}^+\text{–}\mathbf{A} \rightarrow \mathbf{M}\text{–H}\cdots\text{H–}\mathbf{A} \rightarrow \text{M} + \text{H}_2 + \text{A} \tag{4}$$

The problem of the relation between HBs and protonation is very general, being found in the three states of matter: in the solid state where a continuum of situations between **A**–H$\cdots$**B** and **A**$^-\cdots$H–**B**$^+$ is observed in X-ray crystallography and in solid state NMR by slightly modifying the nature of **A** and **B**;[16] in the gas-phase where linear relationships between thermodynamic proton affinities and HBs have been reported;[6] and in solution where the study of the complex relations between both properties is the most developed.[5]

Table 3 Atomic charges (|e|) s of the inverse HB linear complexes at the MP2/6-311++G** level using the AIM methodology

	$\Delta X_{(1,2)}$[a]	ΔH	ΔLi	$\Delta Y_{(1,2)}$[b]	Electron transfer
Li–H$\cdots$Li–H	0.022	0.009	−0.021	−0.010	0.031
H–Be–H$\cdots$Li–H	0.011, 0.013	−0.010	−0.011	−0.003	0.014
H–Be–H$\cdots$Li–CH_3	0.010, 0.013	−0.010	−0.009	0.020, −0.008[c]	0.013
H–B≡$(H)_3\cdots$Li–H	0.160, −0.015	−0.036[c]	−0.015	−0.022	0.037

[a] Atoms attached to the H atom in order from the nearest to the farthest. [b] Atoms attached to the Li atom in order from the nearest to the farthest. [c] Average of the three protons.

(*iii*) In 1970 Abboud and Bellon and Sherry and Purcell simultaneously proposed models of the form $E_{HB} = \alpha\,\beta$, α and β being parameters related to HB acidity and basicity.[5] We have reported in Table 4 some values of $-E_{I+BSSE}$ from our publications.[10,12]

Table 4 Matrix of energies of different complexes ($-E_{I+BSSE}$ at the B3LYP/6-311++G** level) in kcal mol^{-1}

	HBA:	CNH	CO	CS	$:CH_2$	$\cdot CH_3$
HBD:						
	FH	5.763	3.356	7.253	12.070	3.061
	NCH	3.891	1.253	3.450	5.458	1.205
	H_2O	2.849	1.324	3.254	5.921	1.367
	NH_3	1.148	0.454	1.236	2.055[a]	0.488
	HC≡CH	1.813	0.568	1.551	2.681	0.485

[a] Value estimated from the model $E = \alpha\,\beta$ (see Table 5).

We have deconstructed these and other $-E_{I+BSSE}$ values into a product of two terms, one characterizing the HBD (α) and the other the HBA (β) (assuming that the value of β for the methyl radical is 1). The results are reported in Table 5 and constitute a scale of α and β values for the gas-phase, the largest values corresponding to the strongest HBDs (FH) and HBAs ($:CH_2$).

Table 5 α and β values corresponding to the HB energies of Table 4

HBD (α)		HBA (β)	
FH	2.773	CNH	2.564
NCH	1.285	CO	1.038
H_2O	1.256	CS	2.649
NH_3	0.459	$:CH_2$	4.477
HC≡CH	0.579	$\cdot CH_3$	1
		HC≡CH	1.432
		$CH_2{=}CH_2$	1.475
		Cyclopropene	1.251
		Cyclopropane	1.248
		Cyclobutadiene	1.598
		Tetrahedrane	1.358
		Benzene	1.145

(*iv*) In this review we have tried to present an integrated view of hydrogen bonds. Using the 'protic'/'hydride' nomenclature,[37,38] HBs can be classified in three groups: protic HBs, hydric HBs and protic-hydric DHBs. In the case of protic HBs, non-conventional HBDs correspond, for instance, to the case when **A** is a carbon atom (C–H··**B**, **B** = O, N),[7–9] while several non-conventional HBAs have been reviewed here (isonitriles, carbanions, carbenes and π-systems). We have summarized the results concerning protic–hydric DHBs and those of the new class of hydric inverse HBs. A simple picture, seen below, could represent the situation of hydrogen bonded complexes today. Obviously, if the area were proportional to the importance (or the number of references), then, protic HBs would cover more than 99.9% of the pie surface (Fig. 4); we expect that this situation will become more balanced in the future. This review has tried to demonstrate that non-conventional hydrogen bonds, although in some cases weak, are still one of the most important of the non-covalent interactions.

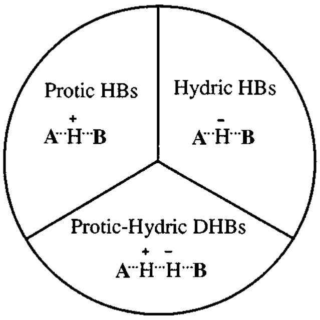


Fig. 4

9 Appendix

In this section, the technical terms used to describe the calculations performed over the systems reviewed here will be defined to aid understanding.

9.1 Molecular orbital *ab initio* calculations

This approximate treatment of electron distribution and motion assigns individual electrons to one-electron functions. These contain a product of spatial functions termed molecular orbitals $\psi_1(x,y,z)$, $\psi_2(x,y,z)$ . . . (MOs). In the simplest version of the theory, a single assignment of electrons to orbitals is made. These orbitals form a many-electron wavefunction Ψ which is the simplest MO approximation to the solution of the Schrödinger equation. In practical calculations, the molecular orbitals ψ_1, ψ_2 . . . are considered as a linear combination of a set of N known one-electron functions $\phi_1(x,y,z)$, $\phi_2(x,y,z)$ . . . eqn. (5).

$$\Psi_i = \sum_{\mu=1}^{N} c_{\mu_i}\,\phi_\mu \tag{5}$$

The ϕ_1, ϕ_2 . . . functions are known as one-electron basis functions and they constitute the basis set. When these basis functions are the atomic orbitals for the atoms of the molecule, eqn. (5) is described as the linear combination of atomic orbitals (LCAO) approximation.

9.2 Hartree–Fock (HF) approximation

Imposes two constrains in the resolution of the Schrödinger equation and to obtain the energy: (*i*) the use of a limited basis set in the orbital expansion and (*ii*) the use of a single assignment of electrons to orbitals.

9.3 Møller–Plesset (MP) perturbation energy

This is an alternative approach to the correlation problem. Within a given basis set it tries to solve the full Hamiltonian matrix (within the Schrödinger equation). The approach is to treat the matrix as the sum of two parts, the second being a perturbation of the first.

9.4 MP2, MP4

By carrying out MP2, MP4, the energy can be expressed as series and practical correlation methods may be formulated by truncation of the series to various orders. We refer to the methods by the highest-order energy term allowed, thus, MP2 means that the truncation has been made after the second-order and MP4 after the fourth-order.

9.5 Differential functional theory (DFT)

In DFT, the exact exchange of the Hartree–Fock method for a single determinant is replaced by a more general expression, the exchange-correlation function, which can include terms accounting for both exchange energy and the electron correlation expressed as a function of the density matrix, which is omitted from the HF theory.

9.6 B3LYP

B3LYP is a hybrid method which includes a mixture of the HF exchange with DFT exchange-correlation. This functional described as Becke3 (B3) is the three-parameter exchange functional containing Slater exchange functional, HF and Becke's 1988 gradient correction and the LYP (Lee–Young–Parr) correlation functional.

9.7 6-31G* and 6-31G**

These are commonly used split-valence plus polarization basis sets which contain inner-shell functions each written as a linear combination of six gaussians, and two valence shells represented by three and one gaussian primitives respectively (represented by 6-31G). In addition, a set of six d-type gaussian primitives has been added to each heavy atom (represented by *) and a single set of gaussian p-type functions to each hydrogen atom (represented by **).

9.8 6-311++G**

This is a split-valence basis set plus polarization and diffuse functions. It comprises an inner shell of six s-type gaussians, and an outer (valence) region, which has been split into three parts, represented by three, one, and one primitives, respectively (represented by 6-311G). The basis is supplemented by a single set of five d-type gaussian functions for first-row atoms, and a single set of uncontracted p-type gaussians for hydrogen (represented by **). In addition, it incorporates two sets of diffuse gaussian s- and p-type functions (represented by ++).

9.9 Mulliken population analysis

This is an analysis of the electron population of how a molecule distributes electrons according to the atomic orbital occupancy, and the overlap population between two atoms is arbitrarily divided evenly between both of them, without taking into account possible differences in coefficients, atom types, electronegativities, and other aspects.

9.10 E_{I+BSSE}

With this expression is defined the interaction energy of a HB complex corrected by the basis set superposition error (BSSE). BSSE refers to vacant orbitals on one atomic centre being used to make up for a basis set deficiency on a neighboring atom. The interaction energies of all the complexes are calculated as the difference between the total energy of the complex and the total energy of the isolated monomers ($E_I = E_{AB} - \{E_A + E_B\}$). Because the computed interaction energies will be affected by the basis set superposition error (BSSE), the latter has been estimated using the full counterpoise method and eqn. (6) where

$$\text{BSSE (A–B)} = E(\text{A})_\text{A} - E(\text{A})_\text{AB} + E(\text{B})_\text{B} - E(\text{B})_\text{AB}$$

$E(\text{A})_\text{AB}$ represents the energy of the monomer A calculated using its geometry within the dimer and the complete set of basis functions used to describe the dimer; and $E(\text{A})_\text{A}$ is the energy of the same molecule, but using only the basis functions centred on it.

9.11 Gauge independent atomic orbital (GIAO)

It represents the eigenfunctions of the one-electron system that have been perturbed by an external magnetic field.

9.12 AIM methodology

According to Bader *et al.*[19] the theory of atoms in molecules (AIM) offers a self-consistent way of partitioning any system into its atomic fragments considering the gradient vector field of its electron density ρ. By means of a topological analysis, features such as critical points and paths of maximum electron density (atomic interaction lines) can be studied since AIM provides a 'molecular graph' which is a representation of the bonding interactions.

9.13 Electron density function (ρ)

EDF is a three-dimensional function defined such that ρ(r) *dr* is the probability of finding an electron in a small volume element, *dr*, at some point in the space, *r*.

9.14 ρ_c

This is the electron density found at the bond critical point (BCP, which represents the point between two atoms with a minimum in the path of maximum electron density).

9.15 $\nabla^2\rho_c$

This is the Laplacian of the electron density found at the bond critical point.

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