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Weak hydrogen bonds: theoretical studies

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Hydrogen bonds A–H···A′, where A and A′ are electronegative atoms have been widely discussed. Weak hydrogen bonds involving such different arrangements as X–H···A, where X can be C; X–H···π, with phenyl rings, C≡C bonds; X–H···M, where M is a transition metal; X–H···H–M and X–H···H–B, have also been described in recent years. While the first types are typical of organic and inorganic compounds, as well as biological molecules, those involving transition metal atoms are special to organometallic chemistry. Theoretical calculations of different kinds and at several levels have been performed for many systems, revealing that a similar geometrical arrangement can hide another type of interaction. This happens for N–H···M close contacts which can be agostic interactions or hydrogen bonds, not so easily distinguishable for 16-electron complexes. M–H···H–X interactions also exhibit a different behavior, depending on whether the complexes are neutral or ionic. The AIM approach, by analysing the topological properties of the charge density with the determination of critical points, provides another way of looking for bonds, as discussed in several examples.

Introduction

Hydrogen bonds have been known since the beginning of this century, but were brought into the common body of knowledge by Pauling in 1939, in his book *The Nature of the Chemical Bond*.[1] Strong and weak hydrogen bonds are discussed by Jeffrey and Saenger, in *Hydrogen Bonding in Biological Structures*.[2] They consider as strong hydrogen bonds only those of the types F–H···F$^-$, O–H···O$^-$, and O$^+$–H···O, which are always two-center bonds, involving short distances and strongly directional, with typical energies higher than 41 kJ mol^{-1}. On the other hand, the normal or weak hydrogen bonds would be X–H···A, where the acceptor A is an electronegative atom. Multicentered bonds start to appear, directionality is lost, and the bond energies drop to below 20 kJ mol^{-1}. The common feature to all of these bonds is the presence of an electronegative atom A as acceptor. More recently, other types of hydrogen bonds were identified. The acceptor can be a π system, usually a ring, and these are denoted X–H···π hydrogen bonds.[3] More interesting for the inorganic chemist are those involving a transition metal, either directly in X–H···M interactions,[4] or as a metal hydride, to form X–H···H–M groups.[5] A similar environment can be found when boron takes the place of the transition metal, giving rise to X–H···H–B interactions.[6] This latter type, where the hydrogen attached to X acts as a proton and the other as a hydride, has been denoted the dihydrogen bond, emphasizing the proximity of the two hydrogen atoms (Scheme 1).[6]

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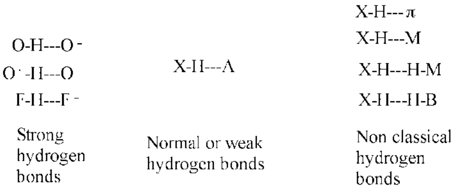

Scheme 1

As the hydrogen bonds become weaker, the difficulty of distinguishing between hydrogen bonds and van der Waals interaction becomes relevant and has been discussed.[7] The role of hydrogen bonds in supramolecular chemistry and solid design is extremely important, as well as in biochemical environments, namely in protein folding, and many publications deal with these themes.[8]

In this work, theoretical studies of the different types of weak interactions will be addressed, after a brief introduction to the computational methods that have been used for this purpose, with more or less success and limitations. Our interest lies mainly on the study of hydrogen bonds in systems containing transition metal organometallic complexes. They therefore constitute the main objective of this review, which is organized by type of bond, starting from weak X–H···A hydrogen bond, and moving on to X–H···π, X–H···M, and X–H···H–M(B). In some systems, the hydrogen bond takes place at the periphery of the molecules or ions, and the role of the metal is minimum. In such cases, results involving only main group elements are comparable. The X–H···H–B interaction also does not necessarily involve transition metals, but is very interesting to compare with X–H···H–M, in view of the differences between boron and a transition metal.

Computational methods

Many different approaches have been used to study weak hydrogen bonds, ranging from semiempirical calculations (extended Hückel,[4a,9] MNDO[10]) to *ab initio* studies (HF/MP2,[5c] B3LYP,[6,11] DFT[12]). These methods allow either a qualitative interpretation of the bond (extended Hückel), or geometry optimization, determination of binding energies, and calculation of charges and other relevant parameters. MP2 and B3LYP approaches are compared in a detailed study of formation of hydrogen bonded complexes of small molecules with water, where water can behave as donor or acceptor,

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depending on the type of molecule. B3LYP was found, by some authors,[11d] superior to MP2 in what concerns the quality of the results, and has the advantage of a much lower computational cost. In order to consider short-range, electrostratic, induction, and dispersion interactions, reliable quantitative calculations should include correlation effects, which are only taken into account by DFT and *n*th order Møller–Plesset methods, the lowest being MP2.[13a,b] Correlation determines dispersion interactions, and influences the others. There is much discussion about to what extent DFT methods can indeed be used when dispersion forces are significant, and the accepted view is that MP2 is better.[13] Another difficulty present in the determination of weak interaction energies is the basis set superposition error (BSSE). It can significantly reduce the magnitude of a weak interaction and eventually destroy it. Although its contribution should always be calculated, it has not been done, especially in less recent works and the results must be critically considered.[13a–c]

The theory of ‘atoms in molecules’ (AIM)[14] has been used to extract chemical bond information from wave functions (and therefore its ‘value’ depends on the theoretical calculations behind). An analysis of the topological properties of the charge density with the determination of critical points can help determine the presence of a bond and this reasoning has been applied to the study of hydrogen bonds.[15] Carroll and Bader studied, among others, the hydrogen bond formation between HF and a series of bases. They calculated critical points of the charge density, ρ, corresponding to open shell interactions (covalent bonds) and compared them with those resulting from closed shell interactions (Fig. 1).

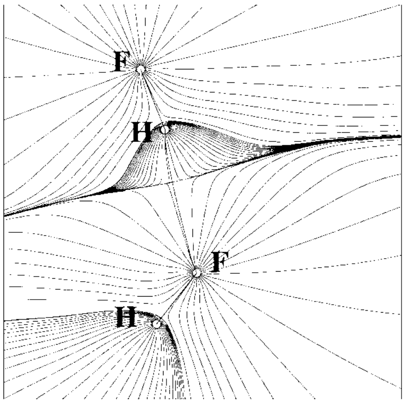


Fig. 1 Display of the gradient vector field of the charge density ρ for $(HF)_2$. Each line represents a trajectory of $\nabla\rho$. A nucleus acts as an attractor of the $\nabla\rho$ field, that is, all the trajectories in some open neighbourhood of a nucleus terminate at that nucleus. These trajectories are lines of steepest ascent through the charge density. An atom is the union of an attractor and its basin. Basins of neighbouring atoms are separated by trajectories that terminate at a bond critical point (denoted by a black dot). A pair of lines of steepest ascent (also shown as bold lines) originate at each critical point and terminate, one to each, at the neighbouring nuclei. They define the atomic interaction lines—lines along which ρ is a maximum with respect to any neighbouring line. If the system is at its equilibrium geometry, these lines are called bond paths.

In the first case, covalent bonds, the laplacian of the charge density, $\nabla^2\rho$, is negative at the critical point, while $\nabla^2\rho$ is positive for closed shell interactions, such as hydrogen bonds.[14b] The determination of critical points in the charge density and the signal of $\nabla^2\rho$ can therefore help in identifying bonds.

Weak hydrogen bonds of the type X–H···A

Weak hydrogen bonds, where X and A are not simultaneously very electronegative atoms, are important in organic and in organometallic chemistry, and a large group comprises C–H···A interactions, where A is an electronegative atom, such as oxygen. The use of the Cambridge Crystallographic Data Base (CSD)[16] has been of major importance in their detection. C–H···O short distances have been identified in organic[17] and organometallic compounds,[18] and also in nucleic acid molecules.[19]

The general properties of the C–H···O interactions were studied in detail, with an emphasis on the application of crystal correlation studies.[17] Calculated bond energies of organic C–H···O bonded dimers in vacuum led to values between *ca.* 2.1 and 15.8 kJ mol^{-1}, with an exceptionally high 38.9 kJ mol^{-1} for NH_3^+–CH_3···OH_2. Of course these values will be changed in solution, solvation being an important factor, but it is thought that the energies are essentially below 8.4 kJ mol^{-1}. The shortest contacts are *ca.* 3.0 Å (C···O) and *ca.* 2.0 Å (H···O).[17a]

C–H···O interactions are very much present in organometallic chemistry, namely in the crystal structures of carbonyl complexes simultaneously containing cyclopentadienyl, benzene, carbene, or any other group with a C–H group.[18] Electrostatic effects are determining in allowing the approach of C–H to an oxygen atom, and so the charges (positive in the hydrogen, negative in the oxygen) will play a major role. It is well known that the amount of back donation from metal centres to carbonyl ligands increases from terminal, to doubly bridging, to triply bridging carbonyls, leading to an increasing negative charge on the oxygen atom. Several families of compounds, obtained from a search in the CSD, were analysed in a molecular orbital study.[20] Triply bridging carbonyls should be the best at establishing strong hydrogen bonded networks in the solids. Would this effect overcome the natural preferences for carbonyl bonding in each complex? As a matter of fact, it does not, as covalent bonds are much stronger. Carbonyls bind in their preferred way to each metal, the trend being that the lighter the metal, the larger can be the number of bridging carbonyls. For instance, for the $(Cp^R)_3M_3(CO)_3$ clusters (M = Co, Rh, Ir), one finds, among other structures, $(Cp)_3Co_3(\mu_3\text{-}CO)_3(\mu\text{-}CO)_2$ and $(Cp)_3Ir_3(CO)_3$, bridges being observed for the lighter element clusters.[20b] Once the number and type of carbonyl is defined, the tendency to form stronger hydrogen bonds (defined here as having shorter distances and angles closer to 180°) lies with the triply bridging carbonyls.[20]

C–H···N hydrogen bonds with an estimated short H···N distance of 2.33 Å and an almost linear C-H···N arrangement are responsible for the packing in the crystals of bis(2,2′-dipyridylamido)cobalt(II).[7b] The authors question that many not so short C–H···X distances, along with not so linear C–H···X arrangements, are not indicative of hydrogen bonds, and sustain that most of them are indeed only classical van der Waals interactions. A reply has recently come out, giving more examples from the CSD.[7d]

A CSD search of hydrogen bonds to halides in organic and organometallic structures was recently reported, along with a statistical study, but no theoretical interpretations were attempted. One example of N–H···Cl interactions is found in 2,6-diphenylpyridinium tetrachloroaurate(III), where the Cl atom is coordinated to gold, and there is a bifurcated interaction between the N–H of the cation and two chlorides of the anionic complex.[21] The hydrogen bond between the chlorine atom in $OsHCl(CO)(PBu^t{}_2Me)_2$ and the hydrogen atom of alcohols was studied by NMR and computational methods (B3LYP and IMOMM, the integrated molecular orbital/molecular mechanics approach).[22] The bulk of the phosphines plays a significant role, preventing the formation of a Os←O bond, and only the IMOMM method, including a good basis set in the B3LYP part, provides a good reproduction of the experimental results. The role of fluorine in X–H···F hydrogen bonds has been discussed. Dunitz and Taylor demonstrated that, when covalently bound to carbon, fluorine does not participate in hydrogen bonds.[23] On the other hand, fluorine in the PF_6^- anion, a very popular ion in organometallic chemistry, is observed in many X–H···F–P interactions, believed to be hydrogen bonds.[8]

Hydrogen bonds of the X–H···π type

Suzuki *et al.* investigated the benzene–water dimer using MP2 calculations with BSSE corrections and found that the water molecule stood over the benzene ring, with its centre of mass on the sixfold symmetry axis. The ring acted as a hydrogen-bond acceptor toward the two hydrogens. The dissociation energy was calculated as 7.4 kJ mol^{-1}.[24a] A similar study of the ammonia–benzene dimer was also carried out. The ammonia molecule also preferred a position such that its centre of mass coincided with the sixfold symmetry axis, but in the lowest energy arrangement only one hydrogen pointed toward the benzene ring.[24b] The energy difference to the next arrangement with two hydrogen atoms pointing toward the ring was very small.

The observation of X–H···π hydrogen bond has become frequent in recent years, as more examples of their presence in organic and organometallic crystals have been reported.[25] The first neutron diffraction study of an O–H···π hydrogen bond appeared in 1996.[25c]

A statistical study of these bonds, taking as donors O–H, N–H, N–H^+, sp^2 C–H, sp C–H, and S–H, and as acceptors phenyl or substituted phenyl rings, used the April 1996 version of the CSD and led to 1537 occurrences, in 530 of which the C_6H_5 ring participated.[10] The X–H approaches to the ring were classified in six groups. In group I, the hydrogen atom pointed at the centre and the X–H bond was perpendicular to the ring, while in group II X–H was no longer vertical. The other four groups included X–H bonds more or less near a carbon atom, rather than the centre, and more or less vertical. Types III and V were preferred by almost all donors, type I being significant for only N–H^+···C_6H_5. The authors performed semiempirical calculations (AM1, PM3) in a wide range of systems and *ab initio* calculations [HF with MP2, BSSE, ZPE (zero point energy) corrections] in a few. The interactions were always found to be attractive, with binding enthalpies decreasing in the order N–H^+ > O–H > N–H > sp^2 C–H > sp C–H. The interactions are described by shallow potentials allowing many binding arrangements (for instance, ammonia pointing with one, two, or three hydrogen atoms at the centre of the ring) and exhibit a long range nature.[10]

Theoretical calculations (GAUSSIAN92/DFT) were also performed on 5-ethynyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol, a molecule which dimerizes in the solid (Fig. 2) and exhibits C–H···π and O–H···π interactions.

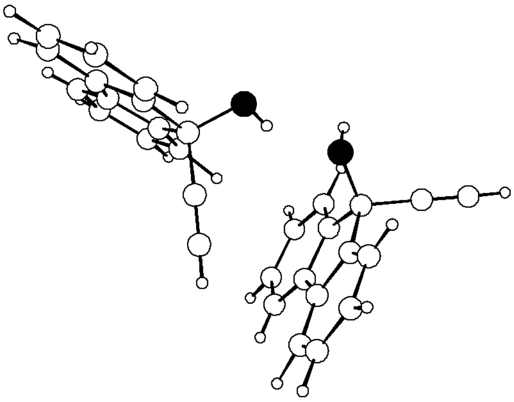


Fig. 2 The dimer of 5-ethynyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (the black circle represents the oxygen). Hydrogen bonds are intermolecular and not seen.

In C–H···π, the hydrogen is close to the centre of the ring and almost vertical, while the O–H in O–H···π is much closer to one of the carbon atoms. The interaction energies were calculated at *ca.* 1.3 kcal mol^{-1} for both types.[25a] The authors also point out the softness of the interaction, which allows many different geometric arrangements with similar energies, although the minimum energy is observed for the face-on bonds.

Other π bonds have been shown to participate in hydrogen bonding.[26] Philp and Robinson[26a] searched the occurrence of C≡C–H···π(C≡C) short contacts in the CSD (October 1997) and found 37 hits. They performed *ab initio* calculations (MP2) in order to determine cooperative effects when hydrogen bond networks were found. The energy determined for a C–H···π(C≡C) interaction was 1 kcal mol^{-1}, close to that of an O–H···π(C≡C) interaction (1.5 kcal mol^{-1}). Cooperative effects turned out not to be significant, while the 'independence' of the interaction energy from the interaction geometry was again noted, as well as the poor capabilities of the C≡C bond as a hydrogen bond acceptor. Mingos and coworkers[26b] also studied theoretically, using different approaches, the interactions between HC donors (HCN, $C_{4-n}H_n$) and C_2R_2 acceptors (R = H, Na, H_3PAu) in a T shaped geometry. They are very weak for ethyne (< 10 kJ mol^{-1}), but become much stronger (stronger than most hydrogen bonds) in the gold derivative (10 kJ mol^{-1}) and in C_2Na_2. Another conclusion of the study was that DFT methods, of the best quality, always underestimated weak interaction energies by failing to describe accurately the dispersion force,[26b] as pointed out above.[13]

X–H···π hydrogen bonds with X = Cl, F and the π bond a C=C or a C≡C bond, were studied using the formalism of AIM,[14] and HF/MP2 calculations.[27] Their energies ranged from 3.09 kcal mol^{-1} for Cl–H···π(HC≡CH), to 4.87 kcal mol^{-1} in other systems (HF with MP2 corrections) and the values of $\nabla^2\rho$ at the hydrogen bond critical point were all negative, reflecting an interaction between closed shells.[27]

The participation of a pyrazole ring as a hydrogen bond acceptor was reported for the first time recently and was observed in the $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-pz})(CO)_9(Hpz)]^-$ complex. In the crystal structure, one N–H bond points perpendicularly toward the centre of the ring, and NMR data show that this interaction remains in solution.[25d]

Recently, we came across C–H···π intramolecular hydrogen bonds involving fluorenyl rings. One example is given by $[(C_{13}H_9)_2ZrCl_2]$, where Zr exhibits the pseudo tetrahedral coordination environment typical of bent metallocenes. The two rings are coordinated in a rather asymmetric fashion, one of them being a characteristically η^5 bound ring, while the second is slipped to an extent that made the authors call it a η^3-fluorenyl, as two Zr–C bonds are 2.8 Å long (the others range between *ca.* 2.39 and 2.64 Å).[28] There is considerable steric crowding around the metal. The slippage of the ring can be compensated by more π-donation from the chlorine atoms to the metal, and a small stabilization is in principle gained by the formation of the C–H···π hydrogen bond (Fig. 3).

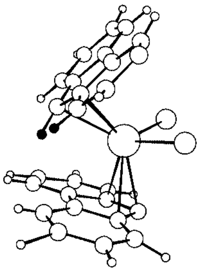


Fig. 3 The C–H···π hydrogen bonds in $[(C_{13}H_9)_2ZrCl_2]$.

A similar interaction is observed in $[(C_{13}H_9)(C_9H_7)_2Mo(CO)_2]$, a complex having one η^3-fluorenyl and one η^5-indenyl ring. Both in the experimentally determined structure and in the optimized geometry (DFT calculations, ADF program, with nonlocal and correlations corrections included in the calculation of gradients),[29] C–H groups from the indenyl are involved in intramolecular hydrogen bonds with carbon atoms of the fluorenyl groups.[30]

X–H···M interactions

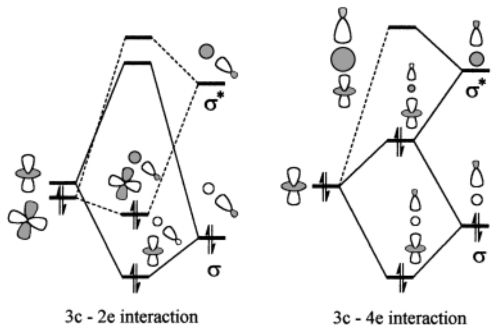
Short distances between a hydrogen atom attached to nitrogen or carbon and a metal have been known for a while, but were often interpreted as a manifestation of agostic hydrogens.[31] They were mainly observed in square planar Group VIII complexes, formally 16-electron species, where the X–H bond approached the metal from one of the axial positions.[32] Brammer *et al.* were among the first to assign X–H···M short contacts as intermolecular hydrogen bonds, in the study of $[NPr^n_4][PtCl_4][PtCl_2(NH_2Me)_2]$.[4a] The structure of this compound was determined at 4 K by neutron diffraction and showed a short N–H···Pt distance of 2.262(11) Å, with an N–H···Pt angle of 167.1(9)°. NMR evidence did not agree with the typical behavior of agostic hydrogens. As similar X–H···M distances had also been observed in d^{10} 18-electron complexes,[33] and agostic hydrogens were not expected, they were thought to be ideal systems worth further study. $[NHEt_3][Co(CO)_4]$ was chosen,[33a] and a neutron diffraction study at 15 K revealed a Co···H–N distance of 2.613 Å, C–H 1.054 Å, and an angle N–H···Co 180°.[4b] The authors performed EH calculations, but the results were not conclusive.[4b] Previous EH calculations on a related model $[NH_4][Ni(CO)(PPh_3)_3]^+$, had indicated a weak attractive interaction, made possible by mixing N–H σ* in the otherwise four-electron repulsive interaction between Ni d_{z^2} and N–H σ.[33b] The strength of the N–H···Co hydrogen bonds was further investigated by modifying ligands (to modify the basicity of the metal centre) or the cation. Indeed, replacing $[NHEt_3]^+$ by protonated DABCO (1,4-diazobicyclooctane), a less bulky cation, favouring the approach to the metal, the N···Co distance is reduced from 3.648 to 3.437 Å. Substitution of a carbonyl by a phosphine in the *trans* position relative to the N–H bond, leads to an N···Co distance of 3.294 in (DABCO)-$H^+Co(CO)_3(PPh_3)$. The authors performed *ab initio* calculations (HF) on these systems, and found that transfer of hydride to cobalt was energetically preferred. The energy minimum for $(DABCO)[HCo(CO)_3(PPh_3)]$ was deeper than the minimum for $(DABCO)H^+Co(CO)_3(PPh_3)$, a result understandable by the fact that solvent effects were not considered.[34]

These weak X–H···M interactions are thus important in the context of metal protonation and reactivity, especially when square planar metal centres are involved.[35] The complex [*trans*-$Rh(CO)(8\text{-methylquinoline})(PPh_3)_2][BF_4]$, for instance, is a 16-electron complex containing a square planar d^8 species and exhibits a short C–H···Rh distance 2.21 Å. The authors were looking for agostic hydrogens, but the weak interaction detected between the axial methyl and the metal was not unambiguously an agostic hydrogen.[36]

In a typical agostic interaction, the metal centre is electron deficient and receives electrons from a C–H σ bond, back donation from the metal to the σ* C–H bond being possible. As a result, the C–H bond becomes weaker and relatively short metal···hydride (though much longer than metal–hydride) distances develop. Such bonds can be described as three-centre–two-electron bonds (C–H→M), as sketched in the left of Scheme 2.[37]

The agostic bond was theoretically studied using the AIM formalism,[38] and it was found that the criteria used to define hydrogen bonds did not apply in the systems studied ($CH_3TiCl_2^+$, $C_2H_5TiCl_2^+$, $C_3H_7TiCl_2^+$), emphasizing the difference between the two types of bonds. Indeed, in a hydrogen bond, the metal is not necessarily electron deficient, and the interaction is a three-centre–four-electron one (Scheme 2, right).[35]

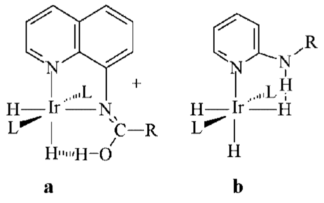
NMR was used to distinguish between agostic and hydrogen bond interactions in 16-electron square planar complexes, as the proton resonance was shifted upfield for the first case, and downfield for the second, compared to the free ligand.[35] More recently, the CSD was searched for examples of complexes containing the X–H···M arrangement.[4c] The 50 hits included d^8 square planar complexes, d^6 square pyramidal complexes (the sixth position of the octahedron being taken by the H–X) and other systems. Only N–H and C–H bonds were found to interact with d^8 square planar centres. All the N–H groups were oriented perpendicularly to the plane of the complex, so that the orbitals of the metal which can overlap are d_{z^2} and p_z. As this last orbital has a very high energy, the interaction belongs to the three-centre–four-electron type (Scheme 2, right), namely a hydrogen bond, as in the 18-electron systems. The C–H···M arrangements were not so clearly cut, as many were not perpendicular and a final conclusion was not reached. The doubt remains as to whether a hydrogen or an agostic bond is present, but a weak hydrogen bond is favored.[4c]



Scheme 2

The dihydrogen bond: X–H···H–M and X–H···H–B

The term dihydrogen bond was introduced by Crabtree and coworkers[6] to describe X–H···H–M bonds, where X is an electronegative atom and the metal–hydride σ bond behaves as an acceptor. The complex *cis*-$[IrH(OH)(PMe)_4][PF_6]$[39] was the compound where such an arrangement was seen for the first time in 1986.[39a] A low temperature neutron diffraction study was carried out later,[39b] showing a short O–H···H–Ir distance of 2.40(1) Å and a short Ir–O–H angle of 104.4(7)°. This weak interaction was assigned to a dipole–dipole interaction.[5e] Another O–H···H–Ir interaction was discovered by Crabtree and coworkers[5a] in the iridium complex **a** shown in Scheme 3, based on NMR evidence, as no hydrogen atoms could be detected in the X-ray crystal structure. The H···H distance was estimated as *ca.* 1.8 Å from the NMR data. Other related complexes were prepared and the first N–H···H–Ir (Scheme 3, **b**) interaction was observed.[5b]



Scheme 3

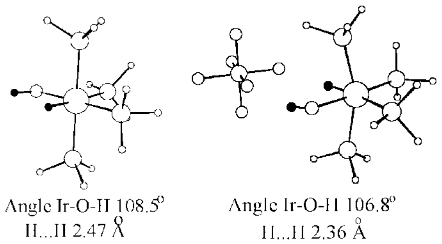
Calculations (HF, GAUSSIAN92) were performed on a model of complex **b**.[5c] The energy of the model $IrH_3(PH_3)_2(HNCHNH_2)$ was lower by 60.3 kJ mol^{-1} when the N–H group was in the same plane as IrH_3, as in **b**, showing a barrier to rotation due to breaking the N–H···H–Ir interaction. This value was corrected to 41.5 kJ mol^{-1} to account for the difference between formamidine (model) and 2-aminopyridine, in good agreement with the experimental value of 45.1 kJ mol^{-1}. The strength of the hydrogen bond was estimated as 29.7 kJ mol^{-1}. The ligand *trans* to the hydride participating in the hydrogen bond may affect the bond; a poorer σ donor will cause a less negative charge on the hydride, decreasing the electrostatic interaction between the H$^-$ and the H$^+$, and therefore leading to a weaker hydrogen bond.[5c]

Another interesting system, dealing also with N–H···H–Ir interactions, was reported in 1994. Morris and coworkers synthesized iridium hydride complexes containing aminothiolate ligands and exhibiting N–H···H(Ir)···H–N[5g] or two N–H···H–Ir interactions.[5h] The H···H interactions were detected by NMR experiments, as the position of the hydrogen atoms could not be located in the X-ray crystal structures. Liu and Hoffmann studied [Ir{H(η^1-SC$_6$H$_4$NH)(PH$_3$)}$_2$] (PH$_3$ instead of PCy$_3$, in the model) using EH calculations,[9] starting by locating the two hydrides. They found a positive, though small, overlap population for the H···H interaction and also noticed the increase in energy upon rotation of the aminothiolate and consequent disruption of the hydrogen bond. The bond was found to be weakly attractive and with a significant electrostatic contribution. Smaller related systems, where similar interactions could arise from intermolecular approaches, such as H–F···H–Li and H–F···HMn(CO)$_5$, were also studied (HF calculations). For H–F···HMn(CO)$_5$, an energy minimum (27.4 kJ mol^{-1}) at a distance of 1.683 Å was determined.

The search for H···H intermolecular dihydrogen bonds[40] had the first result in the cocrystallization of the complex ReH$_5$(PPh$_3$)$_3$ with indole. A neutron diffraction structure showed that two of the hydrides were interacting with the N–H bond of the indole (H···H distances 1.75 and 2.25 Å). B3LYP calculations led to a relatively good reproduction of the geometrical features (H···H distances 1.92 and 2.48 Å) and gave an interaction energy of 33.4 kJ mol^{-1}.[40a] Reaction of the Re precursor with imidazole afforded ReH$_5$(PPh$_3$)$_2$(imidazole), where two of the hydrides were involved in hydrogen bonding with the N–H of a free imidazole molecule (H···H distances 1.68 and 1.99 Å).[40b] The strength of the interaction was estimated from IR data to be 22.6 kJ mol^{-1}.

The related derivatives containing pyridine[40c] and *o*- or *p*-NHR substituted pyridine, were prepared and the hydride fluxionality studied by NMR[40d] and theoretically (B3LYP).[40e] The rate was accelerated with the introduction of the *o*-NHR substituent in pyridine, and ascribed to intramolecular dihydrogen bond formation. Comparisons were made with the *p*-NHR derivative as this substituent cannot form intramolecular hydrogen bonds but electronic substituent effects are similar. The turnstile mechanism, with simultaneous rotation of three hydrides, was found to be the preferred both from experimental and theoretical results, leading to comparable barriers. A detailed study of the reaction mechanism showed that, for the 2-aminopyridine complex, strong hydrogen bonding was found in an intermediate along the reaction pathway. There was a barrier before reaching the transition state, owing to repulsion between two hydrides, and this prevented more powerful consequences of hydrogen bond toward lowering the activation barrier for hydride rotation.

Reviews about these non-classical hydrogen bonds appeared[5d–f] and several searches in the CSD for crystals exhibiting short intra- and inter-molecular H···H contacts were made.[12,41,42] Many of the examples refer to intramolecular interactions involving X–H···H–M, where X is an electronegative atom (O, N, S), starting with the already mentioned *cis*-[IrH(OH)(PMe$_3$)$_4$][PF$_6$].[39] Other cationic mononuclear complexes belong to this group, such as [IrH$_2$(CO)(PPh$_3$)$_2$(pzH-*N*)][BF$_4$]·C$_6$H$_5$Me with H···H 1.998 Å,[43] [IrH(Cl)(L)][PF$_6$] (L = 7-methyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene) with H···H 2.335 Å,[44] as well as the neutral compounds IrH(Cl)(PEt$_3$)$_2$[NHPh(C$_7$H$_{10}$)] with H···H 2.242 Å,[45] Ru(H)$_2$(CO)$_2$(PHPh$_2$)(PPr$^i{}_3$)$_2$, with H···H 2.63 Å, and the *cis*-dicarbonyl [OsH(CO)$_2$(PHPh$_2$)(PPr$^i{}_3$)$_2$][BF$_4$] with H···H 3.04 and 2.83 Å.[46] Spectroscopic evidence suggested the presence of M–H···H–N interactions in Ru complexes (NMR),[47] although no crystals of the product could be obtained. Polynuclear complexes and clusters also exhibit short H···H distances between a hydride and a X–H hydrogen. Examples are given by Cp$_2$Zr(NHAr)(μ-H)(μ-NBu^t)IrCp*, with an H···H distance of 1.717 Å,[48] the two related complexes [Rh$_2$H$_2$(μ-SH$_2$)$_2${MeC(CH$_2$PPh$_2$)$_3$}][BPh$_4$]·HCONMe$_2$[49] and [(μ-H)$_2$Ir$_2$(μ-NH$_2$)$_2$(PEt$_3$)$_4$(NH$_3$)$_2$]·Me$_2$CO,[50] with H···H 1.891 Å and 2.260, 2.189 Å, respectively for the Rh and the Ir complex, (μ-H)Ru$_3$(CO)$_9$(μ-C$_6$H$_2$-1-NH-2-NH$_2$-4,5-Me$_2$), with H···H 2.383 Å,[51] [Ru$_6$(μ-H)$_6$(μ^3-η^2-ampy)(CO)$_{14}$] (ampy = 2-aminopyridine), with H···H 2.064 Å.[52] N–H···H–M interactions have also been detected in compounds without structural characterization, such as OsH(NH$_3$)(CO)$_9$,[53a] and [{η^5-C$_5$H$_4$CH(CH$_2$)$_4$NMe}Ir(PPh$_3$)H$_2$].[53b] The observation of these interactions in the polynuclear complexes containing bridging hydrides is particularly interesting, as these hydrides often behave like acids. A close observation of the structure, however, suggests that steric constraints are responsible for the observed short H···H contacts.[12a] The M–H bond can also participate in M–H···O hydrogen bonding,[18a] as seen from many structures, but most of the hydrides involved are doubly or triply bridging hydrides which are very likely to carry a positive charge, so that the situation is not so surprising from an electrostatic point of view. Theoretical studies (DFT) were performed on some of the complexes, the most interesting results relating to the two cationic species, *cis*-[IrH(OH)(PMe$_3$)$_4$][PF$_6$] and [IrH$_2$(CO)(PPh$_3$)$_2$(pzH-*N*)][BF$_4$].[12] The geometries of the cations were optimised (using PH$_3$ instead of PMe$_3$ or PPh$_3$) and the agreement with the experimental structures was not particularly good. Introduction of the counter ion (PF$_6{}^-$ or BF$_4{}^-$) in the calculations led to a better geometry. The charge distribution in these complexes is compatible with an electrostatic interaction between the negatively charged hydride and the positive hydrogen attached to N or O. The relevant geometric features can be seen in Scheme 4 for *cis*-[IrH(OH)(PH$_3$)$_4$][PF$_6$].



Scheme 4

The energy increases by 20.8 kJ mol^{-1} when the torsion angle H–Ir–O–H changes from 0 to 180° in the cation. As the angle varies, the H···H interaction vanishes. The corresponding energy difference is 44.1 kJ mol^{-1} when the PF$_6{}^-$ anion is present. The relevant conclusion is of a non-negligible role of the counter ion in helping to stabilize the short H···H arrangements. In order to understand more about these interactions, the AIM approach was used to detect the hydrogen bonds.[54] *cis*-[IrH(OH)(PH$_3$)$_4$][PF$_6$][39] and the neutral complex IrH$_3$(PH$_3$)$_2$(HNCHNH$_2$), theoretically studied by Eisenstein and coworkers,[5c] were chosen, to allow a direct comparison between neutral and charged species. These two complexes have iridium as the metal, which is also an advantage, as all the calculations can be done under the same conditions. The gradient vector fields and the bond critical points (black circles) are shown in Fig. 4, in the plane containing the X–H···H–Ir bonds.

For the neutral IrH$_3$(PH$_3$)$_2$(HNCHNH$_2$) there is a critical point between the hydride and the N–H hydrogen. The values

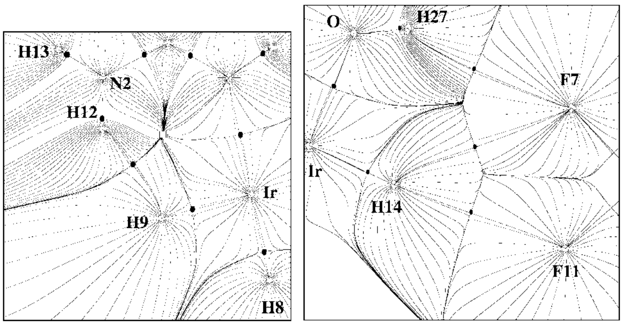


Fig. 4 The gradients of charge density and the critical points (black dots) along bonds in the Ir–H···H–N plane for $IrH_3(PH_3)_2(HNCHNH_2)$ (left) and *cis*-$[IrH(OH)(PMe_3)_4][PF_6]$ (right).

shown in Table 1 for the density ρ and the laplacian $\nabla^2\rho$ are typical for hydrogen bonds,[15] with positive $\nabla^2\rho$. For comparison, the critical points describing some relevant covalent bonds are also given. $\nabla^2\rho$ is now negative and the different values indicate, for instance, how the participation of H12 in the hydrogen bond with the hydride modifies the N2–H12 bond relative to N2–H13.

The cationic complex is different, because no critical point exists between the two hydrogen atoms. Instead, there are hydrogen bonds to the fluorine atoms in the PF_6^- anion. The H27(O) atom makes one hydrogen bond with F7, while the hydride is involved in hydrogen bond with the two fluorines, F7 and F11. The first hydrogen bond, H27–F7 is not surprising, as H27 carries a positive charge and F7 is negative. On the other hand, both the hydride H14 and the two fluorines F7 and F11 are negative. The values of $\nabla^2\rho$ and ρ for the bonds given in Table 1 are characteristic of covalent bonds (N–H, O–H) and hydrogen bonds (H···F). If this interpretation is indeed correct, the role of the counter ion is even greater than was thought.

The effect of charges in hydrogen bonds has also been assessed in the study of $O–H^-\cdots O^-$ interactions in chains of oxalate anions (UHF). These are repulsive interactions. The reason why the atoms hold together is that they simultaneously participate in attractive interactions with the counter ion, K^+.[55] This is a situation where a short $O–H^-\cdots O^-$ distance does not indicate a hydrogen bond.[18e] The point is controversial,[56] and brings forward the question whether distances by themselves provide an answer to the existence of a bond. As the previous example shows, short distances in $O–H^-\cdots O^-$ chains can coexist with repulsive interactions, because a stronger cation–anion electrostatic attraction holds all ions in their place. A similar effect seems to take place in *cis*-$[IrH(OH)(PH_3)_4][PF_6]$.

Besides the previous examples, which include the oldest known systems, other intramolecular and intermolecular hydrogen bonds have been studied. Sometimes, they may be considered as the first step in the formation of a H–H bond, to give $M–H_2$ complexes, for instance. The $ReH_5(PPh_3)_3\cdot$indole$\cdot C_6H_6$ compound,[40] where two hydrides approach the N–H bond of indole, has already been mentioned. More recently, an equilibrium between the $Ir–H_2$ complex of $IrH(L)_2(bq\text{-}NH_2)$ (L = phosphine, bq-NH_2 = 2-amino-10-methylbenzo[*h*]quinoline) and the Ir–H···H_3N species was found to take place, its extent depending on the phosphine. Theoretical calculations (B3PW91) reproduce the trend: more basic phosphines lead to formation of the $Ir–H_2$ complex. An accurate modeling of the phosphine was critical and surprisingly PH_3 was not a good model for PPh_3.[5i]

Table 1 The charge density and the laplacian of the charge density at some critical points between bonds in model complexes $IrH_3(PH_3)_2(HNCHNH_2)$ and *cis*-$[IrH(OH)(PH_3)_4][PF_6]$

$IrH_3(PH_3)_2(HNCHNH_2)$			*cis*-$[IrH(OH)(PH_3)_4][PF_6]$		
Bond	ρ	$\nabla^2\rho$	Bond	ρ	$\nabla^2\rho$
N2–H12	0.352	−0.2129	H27···F7	0.193	0.714
N2–H13	0.366	−0.2175	H14···F11	0.252	0.782
H9···H12	0.168	0.4251	O1–H27	0.376	−0.234
			Ir2–H14	0.169	0.344

A hydrogen bond between the H–O group in acidic alcohols and W hydrido complexes $WH(CO)_2(NO)L_2$ (L = phosphine) was detected by IR and NMR data and the H···H distance estimated as 1.77 Å, for L = PMe_3.[57] $Ru(dppm)_2H_2$ interacts with PhOH or 1,1,1,3,3,3-hexafluoroisopropyl alcohol, *via* Ru–H···H–O hydrogen bonds and forms the dihydride complex.[58] $ReH_2(CO)(NO)L_2$ (L = phosphine) also interacts with alcohols,[59] but both O–H···H–Re and O–H···O–N–Re hydrogen bonds may be formed, the latter becoming predominant when the phosphine is bulky (PPr^i_3). Theoretical calculations (DFT) were performed in the model compound $ReH_2(CO)(NO)(PH_3)_2\cdots OH_2$, allowing both types of approach to take place (to the M–H or to the O–N bond). The O–H···H–Re bond type is electronically favoured by 12.5–14.6 kJ mol^{-1}, but forces the OH carrying molecule to be very close to the metal, and this becomes difficult when two bulky axial phosphines are present. O–H···O–N–Re hydrogen bonds are then formed for steric reasons.[59]

Orlova and Scheiner performed calculations of different types (HF/3-21G, B3LYP, BLYP, B3PW91) to study the intermolecular bonding of molybdenum and tungsten hydrides with HR (R = F, OH, H_2O^+) complexes.[11a] The study of the interaction of HF with $Mo(CO)_2(NO)(PH_3)H$ led to the conclusion that the DFT/B3PW91 method was the best, even taking into account that all DFT methods tend to afford distances that were too long, and it was chosen for most studies. The Mo–H···H–F hydrogen bond energy was estimated as *ca.* 46 kJ mol^{-1}. Substitution of the *cis* ligand PH_3 by the better σ donor NH_3 increases the strength of the hydrogen bond, while changing the metal to W does not afford any major change. A greater acidity of the HR species also leads to a stronger hydrogen bond and formation of H_2-complexes, while, as expected, bulkier ligands have the opposite effect. The authors notice the inadequacy of Mulliken charges to adequately describe the system, but they rely on a Mulliken-type analysis (overlap populations) to interpret relative trends. The competition of formation of other bonds, such as F–H···O–N–Mo was investigated,[11a] as done previously for Re complexes.[59]

Orlova and Scheiner[11b] also addressed the interactions of CpReH(CO)(NO), $CpReH(NO)(PH_3)$ and $CpRuH(CO)(PH_3)$ with several proton donors (H_2O, $HOCF_3$, H_3O^+) with B3PW91 methods. The formation of H_2-complexes as a result of H···H hydrogen bonding and the alternative protonation at the metal to form dihydride complexes are discussed. $CpReH(NO)(PH_3)$ has a very strong nucleophilic centre at the metal and only the dihydride forms, while for $CpRuH(CO)(PH_3)$ only the H_2-complex forms with strongly acidic HR. When a weaker acid such as CF_3OH is considered, the R–H···H–Ru interaction also becomes a minimum on the potential energy surface. For the third complex, CpReH(CO)(NO), the three species (the dihydrogen complex, the dihydride complex and the hydrogen bonded complex with R–H··H–M) can be obtained from the calculations. The basicity of the metal is therefore an important factor in determining the formation of hydrogen bonds where the M–H bond behaves as acceptor.[11b]

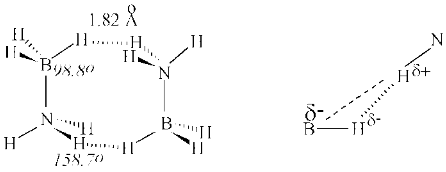
The C–H bond can also engage in weak intra- and intermolecular hydrogen bonds of the type C–H···H–M. They were seen in some of the complexes referred to above, such as $[(\mu\text{-}H)_2Ir_2(\mu\text{-}NH_2)_2(PEt_3)_4(NH_3)_2]\cdot Me_2CO$,[50] with H···H 2.105 Å, and $ReH_5(PPh_3)_3\cdot$indole,[40] with H···H 1.903, 1.929 Å. These and other complexes were hits in a CSD search for short C–H···H–M distances and the observation of the data suggested a new mechanism for cyclometallation.[60] Some other examples have been reported since then and structurally characterized.[61]

Intermolecular C–H···H–M hydrogen bonds are very weak and normally coexist with other types of not so weak hydrogen bonds involving N–H or O–H, especially if they are intramolecular. Intermolecular C–H···H–M hydrogen bonds are sometimes alone in holding together two molecules, as seen in many of the examples taken in CSD search (October 1996).[41]

$[N(PPh_3)_2]_2[W_2H_2(CO)_8]$ offers an interesting situation, where one C–H bond of a phenyl group approaches a bridging hydride on each side of the molecule.[62] EH calculations[41] indicate that the bridging hydride carries a negative charge, owing to the large electron richnness of the metal centres. Therefore, an electrostatic interaction between the negative hydride and the positively charged H–C is responsible for the short H···H distances. Only a very small positive overlap population of 0.01 is found between the hydrogen atoms. In *mer*-$[(Me_3P)IrH(Cl)(C_5H_4N)]$,[63] each hydride enters an interaction with a C–H bond of the pyridine ring of the adjacent molecule. These two Ir–H···H–C bonds hold together the dimer (data taken from CSD). Rotating the pyridine out of the plane disrupts the bond and increases the energy by *ca.* 58 kJ mol^{-1}.[41] In the other representative compounds of the group,[64] small positive overlap populations were found, and a charge distribution consistent with an electrostatic interaction.[41]

B–H bonds can replace M–H as hydrogen bond acceptors. This was recognized in 1995 and confirmed with a CSD search which gave 22 structures with H···H distance < 2.2 Å. The average H···H distance was 1.96 Å, in a range between 1.7 and 2.2 Å.[6]

The B–H···H–X bond was studied (PCI-80/B3LYP method) in the $[H_3BNH_3]_2$ dimer (Scheme 5, left) and although there is no available structure of this compound, the features seen in the optimized geometry are typical of other boron compounds.[6]



Scheme 5

A particularly interesting aspect of these bonds with boron is that a linear B–H···H–X arrangement is an exception. In $[H_3BNH_3]_2$, the calculated B–H–N angle is 98.8° and N–H–H is 158.7°. Although bent bonds were observed in other cases for weak bonds, here they seem to be rule. An explanation lies in the large negative charge carried by the boron atom, compared to the small negative charge carried by the hydrogen. In order to take advantage of the charge distribution, the H–N points toward the B–H bond rather than toward H (Scheme 5, right).[6]

Epstein *et al.*[65] studied these interactions theoretically (HF) and spectroscopically, using as models $BH_4^+\cdots OH_2$, $BH_4^+\cdots HOCH_3$, $H_3NBH_3\cdots HOCH_3$, $[H_3BNH_3]_2$. They determined minima for the approach of the B–H bond to the donor, for distances 1.836–2.209 Å, always smaller than the sum of van der Waals radii (2.4 Å), and small positive overlap populations between the hydrogen atoms. Contrary to the results of Siegbahn and coworkers,[6] a positive charge is assigned to boron.

Alkorta *et al.*[66] studied dihydrogen bonds for a variety of combinations of acid hydrogen atoms (NH_4^+, HCN, HC≡CH), basic hydrogen atoms (BH_4^-, LiH, BeH_2), and an amphoteric (CH_4), using several methods (HF, MP2) and correcting for BSSE. Frequency calculations were used to check the minima. The charge density at the critical points and the positive values of $\nabla^2\rho$, within the AIM approach, indicated strong hydrogen bonds. The geometries obtained were compared with structures taken from the CSD, which included B–H···H–N, B–H···H–O, B–H···H–C, Al–H···H–C, besides the ones described earlier in ref. 6.

The homonuclear dihydrogen bond?

The CSD searches for short H···H distances also afforded structures not belonging to any of the previous type, namely dimeric species, where both hydrogens must have the same charge and the electrostatic features of hydrogen bonds are not present.[41] The prototype is the dimer of $HMn(CO)_5$.[67] The structure has been determined both by X-ray and neutron diffaraction,[67a] and later by electron diffraction in the gas phase.[67b] There are two polymorphs in the solid, α and β, differing in the packing. In α, the hydride was not located. β-$HMn(CO)_5$ contains dimers with an H···H distance of 2.292 Å, approaching each other in a non linear way, as seen in Fig. 5.

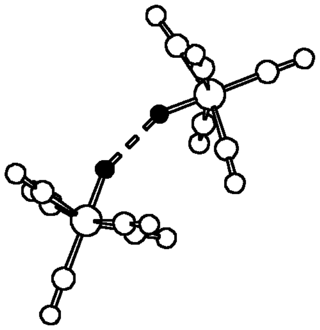
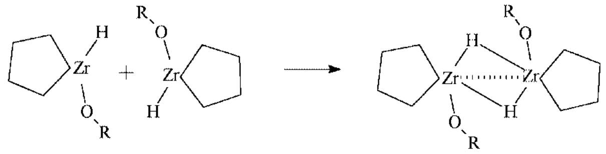


Fig. 5 The $HMn(CO)_5$ dimer, showing the short H···H distance.

The monomer, which exhibits a distortion of the equatorial carbonyls toward the hydride, had been the object of an earlier theoretical study.[68] The approach geometry of the dimer was optimized using DFT calculations.[41] The H···H distance was found to be 2.008 Å, the Mn–H 1.559 Å and the angle between Mn–H bonds 147°. The experimental values are 2.292 Å, 1.601(16) Å, and 155.8°, respectively. The interaction energy was calculated as 0.4 kcal mol^{-1}. A qualitative EH analysis showed that there was some residual bonding character between the two hydrogens, as if an activated H_2 molecule was bridging the two manganese atoms. This same interaction has been suggested by other authors.[5d] A BSSE correction should be performed before giving a final answer to this problem.

The other example of M–H···H–M interaction is provided by the dimer $[(\eta^5\text{-}C_5H_5)_2Zr(\mu\text{-}H)(OSO_2CF_3)]_2\cdot 0.5THF$ with an H···H separation of 2.122 Å.[69] EH calculations indicated a repulsive interaction between the hydrogens. The monomer would be $[(\eta^5\text{-}C_5H_5)_2Zr(H)(OSO_2CF_3)]$, a 16-electron bent metallocene (Scheme 6).



Scheme 6

Two monomers interlock, allowing the hydride of each unit to engage in a bond with the other Zr atom. Although this is a longer bond, it is a covalent bond. The interaction can be termed agostic, as one Zr–H bond donates electrons into the empty orbital of the other Zr.[41]

C–H···H–C interactions in the methane dimer were studied at several levels of theory. MP2 provided the best method to study the approach of two methane molecules. All possible H···H contact arrangements were atractive, and the stabilization energy increases with the number of H···H contacts.[70]

Attractive interactions between identical hydrogen atoms can therefore exist in different contexts, either in organic molecules involving C–H bonds, or in organometallic complexes through M–H bonds.

Conclusions

Theoretical calculations of different types have been performed to study weak hydrogen bonds. Small attractive energies were determined in many cases, but owing to the size of the systems, BSSE corrections were not performed routinely, especially for organometallic systems. On the other hand, many studies rely on DFT (rather than MP2) calculations, which appear to lead to long distances and weak bonds, in spite of consideration of correlation effects. There is still much to be done to reproduce quantitatively these weak interactions: good models, high levels of theory and good basis sets are required. In ionic systems, the role of the counter ion is determining, therefore making calculations even larger and more difficult. The dihydrogen bond M–H···H–X in cationic complexes is one of such systems where the interaction appears to be dependent on the counter ion, as its introduction in the calculation leads to a better geometrical agreement with experimentally determined structures. The 'atom in molecules' approach appears to be very promising to study these weak bonds and to determine their origin, allowing one to distinguish between agostic and hydrogen bonds in some ambiguous situations. The quality of the results depends, however, on the level of theory used in calculating the electron density.

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