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Theoretical Study of Dihydrogen Bonds between $(XH)_2$, X = Li, Na, BeH, and MgH, and Weak Hydrogen Bond Donors (HCN, HNC, and HCCH)

Ibon Alkorta,* Krzysztof Zborowski,[†] and Jose Elguero

Instituto de Química Médica (CSIC), Juan de la Cierva, 3, 28006 Madrid, Spain

Mohammad Solimannejad

Quantum Chemistry Group, Department of Chemistry, Arak University, Arak 38156-879, Iran

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The dihydrogen-bonded (DHB) complexes formed by $(XH)_2$, with X = Li, Na, BeH, and MgH, with one, two, and four protonic molecules (HCN, HNC, and HCCH) have been studied. These complexes have been compared to those of the XH monomers with the same hydrogen bond donor molecules. The energetic results have been rationalized based on the electrostatic potential of the isolated hydridic systems. The electron density properties have been analyzed within the AIM methodology, both at the bond critical points and the integrated values at the atomic basins. Exponential relationships between several properties calculated at the bond critical points (ρ,$\nabla^2\rho$, λ_i, G, and V) and variation of integrated properties (energy, charge, and volume) vs the DHB distance have been obtained.

Introduction

The hydrogen bond (HB) is, without discussion, the most important weak interaction. It is responsible for the 3-D shape of proteins, the double helix of DNA, and many other biological features.[1] In recent years, the chemical groups involved in HB interactions have been greatly expanded.[2] One of the most interesting cases corresponds to that where the electron donor moiety is a hydrogen atom. Thus, the two atoms directly involved in the interaction are hydrogens. This subtype of hydrogen bond has been named “dihydrogen bond” (DHB).[3,4] Several recent reviews have addressed the experimental and theoretical studies on this subject.[5−7]

Theoretically, the attractive interaction of $(H_3BNH_3)_2$ was proven using DFT methods and confirmed with a search of similar structures in the Cambridge Crystallographic Database.[8] Additional ab initio calculations of model compounds show that a number of metallic moieties could be involved in these interactions.[9,10] The crystal effect has been studied theoretically in the proton transfer of model DHB systems.[11] A thermodynamic study of the dissociation energy has been described for LiH and BeH_2 complexes.[12] Calculations that include anharmonic frequencies have shown to improve the agreement with the experimental data in DHB systems.[13] The DHB complex borane−dimethylamine was detected experimentally in supersonic jets and quantum chemical calculations were used to derive its structure.[14] The NMR properties along this interaction have been explored for one bond $^{(1d)}J(H-H)$ and three-bond $^{(3d)}J(X-M)$ spin−spin coupling constants.[15] The possibility to obtain these complexes with hydrogen atoms bonded to rare gas atoms and to other metals atoms has been theoretically proposed.[16−22] The electron density properties at the bond critical points (bcp) has been studied for three series of complexes[23−25] and a more detailed analysis has been carried out for the $(NH_3BH_3)_2$ complex.[26] The presence of bcp has been found in neutral complexes of iridium between H···H contacts while they where absent in cationic models.[27] The differences between standard HB and DHB with respect to the protonation have been studied using ELF analysis.[28]

The range of distances encountered in HB (from 1.2 to 3.0 Å) makes this interaction especially attractive to study the evolution of bonding properties along a broad range of interatomic distances.

The analysis of the electron density by means of the Atoms In Molecules (AIM) methodology provides tools to confirm the presence of HB interactions due to the existence of a bond path linking the two atoms involved in the interaction and its corresponding bond critical. In addition, this methodology allows defining of atomic regions, named atomic basins, where the integration of different properties provides the atomic contribution to the value of the whole system. While the analysis of the properties at the bond critical point has became a standard instrument in the study of HB, the difficulties of accurate integrations within the atomic basins has limited the study of the evolution of atomic properties within the AIM methodology. Most of the studies that carried out atomic integration in HB systems considered a small number of cases in their minimum configurations or the same complex with the two interacting molecules separated at different distances.[26,29,30]

To the best of our knowledge, no systematic study of the evolution of the electron density properties, in the bcp and integrated within the atomic basins, has been carried out in the minima configuration of DHB systems presenting a large range of interactions. In the present article, the dihydrogen bonds formed between $(XH)_2$, X = Li, Na, BeH, and MgH, and three weak hydrogen bond donors (HCN, HNC, and HCCH) have been calculated and compared with the corresponding ones obtained for the XH systems. The electron density derived properties at the bond critical point and those obtained from

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* To whom correspondence should be addressed. E-mail: ibon@iqm.csic.es. Fax: 34-91-564 48 53.

[†] On leave from the Faculty of Chemistry, Jagiellonian University, 3 Ingardena Street, 30-060 Kraków, Poland.

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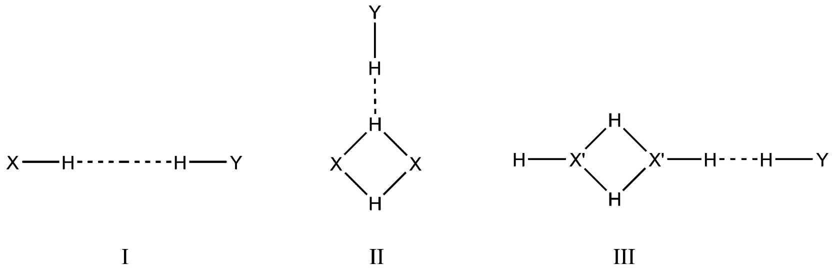
SCHEME 1: Schematic Representation of the Complexes Considered



Y = CN, NC, CCH
X = Li, Na, BeH, MgH
X' = Be, Mg

the integration within the atomic basins have been evaluated and analyzed for the minima configurations. Their relationship with the interatomic distance and with other calculated properties has been checked. In addition, the spectroscopic characteristics of these complexes have been calculated and analyzed.

Methods

The geometry of the complexes has been optimized at the MP2/6-311++G(2d,2p)[31,32] computational level within the Gaussian-03 facilities.[33] The minimum nature of the complexes has been confirmed by frequency calculations for all the cases except for two complexes where $(HBeH)_2$ and HCN are involved and that will be discussed in the Results and Discussion section.

The interaction energy has been corrected of the inherent Basis Set Superposition Error (BSSE) using the "counterpoise" keyword in the Gaussian-03 package.

The absolute chemical shielding of the atoms has been calculated with the GIAO method[34] at the MP2/6-311++G(2d,2p) level.

The electron density obtained in the optimized structures at the MP2/6-311++G(2d,2p) level have been analyzed within the AIM methodology,[35] using the PROAIMV[36] and MORPHY98 programs.[26] The atomic integration has been carried out using the default parameters in the MORPHY program except for those atoms where the integrated Laplacian was larger than 1.0×10^{-3}. Ideally, the integrated Laplacian within an atomic basin should be equal to zero. However, previous studies have shown that systems in which all the atoms have an integrated Laplacian smaller than the mentioned value provide small errors in the total energy and charge partitions.[37,38]

Results and Discussion

Geometry and Energy. A schematic representation of the complexes formed by the monomers, XH, and dimers, $(XH)_2$, of the hydridic molecules and one of the protonic molecules, YH, is shown in Scheme 1. The minimum structures obtained present $C_{\infty v}$ symmetry for **I** and C_{2v} for the complexes **II** and **III**. In the case of the $(HBeH)_2$:HCN complex, structure **II** presents one imaginary frequency and all the attempts to obtain a minimum lead to structure **III**. The interatomic distances of the HB formed in these complexes have been gathered in Table 1. These distances ranges between 1.45 Å for the NaH:HNC complex to 2.50 Å for the $(HBeH)_2$:HCCH (**II**) complex. In all the cases, the interatomic distances of the complexes **II** is larger than the corresponding ones in **I**; besides those in **III** are the shortest ones for each hydridic and protonic molecules. The shortest DHB distances correspond to the complexes with HNC, followed by the HCN ones while the longest ones are those corresponding to the HCCH in each hydridic series.

TABLE 1: Interatomic Distance (Å) in the Dihydrogen Bonds Studied (Scheme 1)

X−H	H−Y	I	II	III
LiH	HCN	1.790	1.870	
LiH	HNC	1.487	1.538	
LiH	HCCH	1.995	2.070	
HBeH	HCN	2.055	2.411	2.008
HBeH	HNC	1.777	2.052[a]	1.735
HBeH	HCCH	2.225	2.501	2.178
NaH	HCN	1.770	1.812	
NaH	HNC	1.451	1.456	
NaH	HCCH	1.987	2.033	
HMgH	HCN	1.944	2.152	1.927
HMgH	HNC	1.652	1.779	1.640
HMgH	HCCH	2.126	2.302	2.113

[a] This structure presents one imaginary frequency.

TABLE 2: BSSE Corrected Interaction Energy (kJ/mol) of the Dihydrogen Bonds Studied (Scheme 1)

X−H	H−Y	I	II	III
LiH	HCN	−34.5	−25.4	
LiH	HNC	−55.7	−44.8	
LiH	HCCH	−16.6	−13.3	
HBeH	HCN	−7.9	−0.2	−10.1
HBeH	HNC	−13.5	−1.3	−16.8
HBeH	HCCH	−4.3	−0.6	−5.3
NaH	HCN	−37.7	−32.7	
NaH	HNC	−61.5	−57.6	
NaH	HCCH	−17.8	−16.6	
HMgH	HCN	−15.3	−4.6	−16.7
HMgH	HNC	−26.1	−11.2	−28.1
HMgH	HCCH	−7.9	−3.2	−8.5

The interaction energies of the complexes included in Scheme 1 are reported in Table 2. The evaluation of the interaction energy and BSSE correction for the complexes of the hydridic dimers, $(HX)_2$, has been carried out considering the latter systems as a monomer. The interaction energy expands from almost null values to −61.5 kJ/mol. The energetic results are in agreement with the geometric ones shown in Table 1. Thus, the shorter distances found in the complexes **III** and the longer ones in **II** when compared to those of **I** are associated to larger and smaller interaction energies for **III** and **II**, respectively, than those found in **I**. The representation of all the interaction energies vs the DHB distances (Figure 1) shows exponential relationships when compared to the complexes for the same proton donor molecule. It is significant that, for a given DHB distance, the strongest complex is that formed with HCCH, followed by the HCN one, and the weakest one is that of the HNC.

It has been reported that the minimum value of the molecular electrostatic potential (MEP) in the isolated hydrogen bond

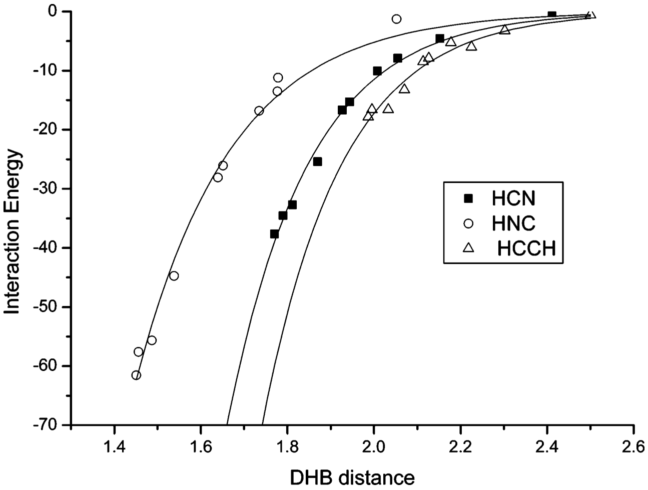


Figure 1. Interaction energy (kJ/mol) vs DHB distance (Å). The exponential relationships have square correlation coefficient, R^2, values of 0.99, 0.99, and 0.98 for the HCN, HNC, and HCCH complexes, respectively.

TABLE 3: MEP Values (au) Minima along the Direction of the HB Formation and Distance (Å) to the Closest Hydrogen Atom

system	MEP values	distance
LiH	−0.1067	1.128
NaH	−0.1131	1.143
HBeH	−0.0217	1.367
HMgH	−0.0445	1.254
(LiH)$_2$	−0.0866	1.107
(NaH)$_2$	−0.1078	1.099
(HBeH)$_2$ (**III**)	−0.0275	1.336
(HMgH)$_2$ (**II**)	−0.0147	1.298
(HMgH)$_2$ (**III**)	−0.0480	1.249

acceptors provides a good estimation of the HB strength of the complexes formed.[39−42] The values of the minimum MEP along the direction of the formed HB have been calculated for the systems considered in Scheme 1 (Table 3). In the (HBeH)$_2$ system, no minimum has been found in the direction that corresponds to the complexes **II**. This result is in agreement with the small interaction energy obtained for the complexes in this configuration.

Linear dependencies have been found between the MEP values and the interaction energy for each hydrogen bond donor molecule, with a square correlation coefficient larger than 0.98 for each of the three HB donor molecules considered. The statistical parameters of the fitted linear relationship confirm that the MEP provides a good estimation of the interaction energy. These results are in agreement with the reports that show a good linear relationship between the MEP minima and the HB basicity, β^2_H, parameter.[42]

As an extension of the cases studied so far, some complexes with two and four protonic molecules have been considered (Scheme 2). The symmetry of all these complexes is D_{2h}. Similar to the previous results, the complex (BeH$_2$)$_2$:(HCN)$_2$ (**IV**) is not a minimum and presents two imaginary frequencies. In addition, complexes **VI** have been obtained only for (MgH$_2$)$_2$ since in the case of (BeH$_2$)$_2$ the two protonic molecules in a disposition similar to that of **IV** are not attracted by the hydridic atoms and tend to “fly” away. The energetic and geometric results of these complexes are collected in Table 4. In the case of the complexes with (BeH$_2$)$_2$ in disposition **IV**, the interaction energies are so weak that the inclusion of the BSSE correction provides positive values of the corrected E_I. In the rest of the cases, the interaction energies are slightly smaller than twice the corresponding ones shown for the complexes in Scheme 1. In the same way, the DHB distances are slightly longer in disposition **IV** and **V** compared to those of the analogues with one HB donor molecule, **II** and **III**, respectively. The complexes calculated with four molecules of HCN and HNC (configuration **VI**) provide interaction energies smaller in absolute value than the ones obtained for the (MgH$_2$)$_2$ in disposition **V**, which indicate that the system would prefer two DHBs instead of four, especially if the entropic term is considered.

SCHEME 2: Complexes with Two and Four Protonic Molecules

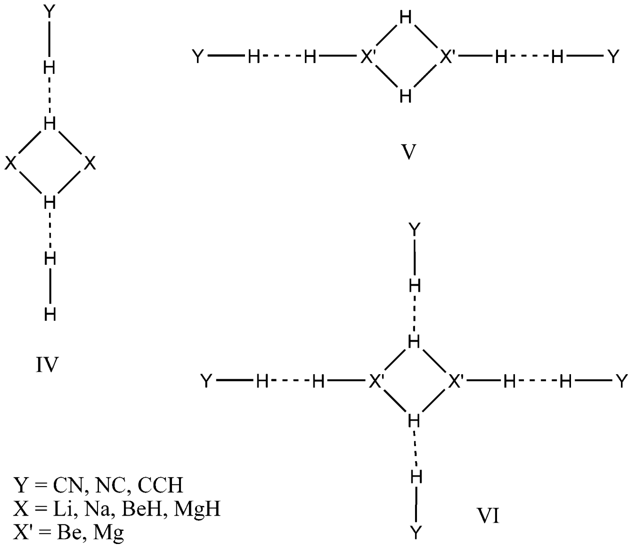


TABLE 4: DHB Distance (Å) and Corrected Interaction Energies (kJ/mol) of the Complexes Shown in Scheme 2

complex	disposition	DHB distance	E_I
(LiH)$_2$•••(HCN)$_2$	IV	1.894	−47.1
(LiH)$_2$•••(HNC)$_2$	IV	1.573	−82.0
(LiH)$_2$•••(HCCH)$_2$	IV	2.080	−26.0
(HBeH)$_2$•••(HCN)$_2$	IV	2.566[a]	1.5
(HBeH)$_2$•••(HNC)$_2$	IV	2.196	1.2
(HBeH)$_2$•••(HCCH)$_2$	IV	2.527	−0.9
(HBeH)$_2$•• (HCN)$_2$	V	2.032	−18.4
(HBeH)$_2$•• (HNC)$_2$	V	1.764	−30.3
(HBeH)$_2$•••(HCCH)$_2$	V	2.187	−10.3
(NaH)$_2$•••(HCN)$_2$	IV	1.836	−61.6
(NaH)$_2$•••(HNC)$_2$	IV	1.497	−107.5
(NaH)$_2$•• (HCCH)$_2$	IV	2.038	−32.6
(HMgH)$_2$•••(HCN)$_2$	IV	2.208	−6.1
(HMgH)$_2$••• (HNC)$_2$	IV	1.833	−16.3
(HMgH)$_2$•• (HCCH)$_2$	IV	2.308	−6.1
(HMgH)$_2$•••(HCN)$_2$	V	1.942	−31.7
(HMgH)$_2$•••(HNC)$_2$	V	1.658	−53.0
(HMgH)$_2$•••(HCCH)$_2$	V	2.119	−16.7
(HMgH)$_2$•••(HCN)$_4$	VI	2.290, 1.993	−28.6
(HMgH)$_2$•••(HNC)$_4$	VI	1.905, 1.716	−52.5
(HMgH)$_2$•••(HCCH)$_4$	VI	2.324, 2.133	−21.7

[a] This structure is not a minimum as indicated in the text.

Electron Density. In all the dihydrogen bonds formed, the topological analysis of the electron density shows the presence of a bond critical point (bcp). The electron density, its Laplacian, curvatures, and kinetic, potential, and total energies per electron density have been calculated at the bcp (see Supporting Information). The small values of the electron density and the positive ones of the Laplacian are characteristic of this kind of interaction. The combined analysis of the Laplacian and the total energy per electron density, H, at the bcp of the HB has shown

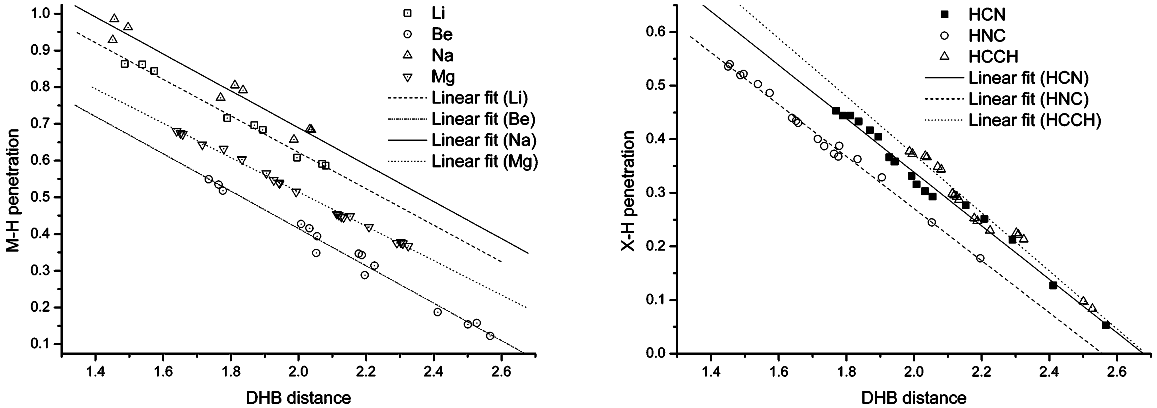


Figure 2. Penetration (Å) of the hydric hydrogen (a) and protic hydrogen (b) vs the DHB distance.

to be a useful tool for characterizing the strength of the contact.[43] Thus, those cases with negative H and positive Laplacian correspond to the largest interaction energies of the systems studied here, being stronger than 25 kJ/mol. These cases have been considered by some authors as an indication of the partial covalent nature of the hydrogen bonds.

From a study of CH···O hydrogen bonds, Popelier proposed a set of rules to define hydrogen bond interactions based on the electron density properties.[29] These rules where later confirmed for the DHB found in the (BH_3NH_3) dimer.[26] The seven rules proposed are fulfilled by the DHB found here. However, some exceptions are found and thus the electron density and Laplacian values (0.041−0.003 and 0.046−0.010 au, respectively) are out of the ranges proposed by Popelier (0.035−0.002 and 0.139−0.024 au, respectively for the electron density and the Laplacian.

To check the penetration of the electronic cloud of the two hydrogens involved in the DHB, a surface contour value of 0.001 e/au^3 has been used for reference in the isolated monomers since it has been found that this surface encloses a volume similar to the experimental molecular volume of the molecules. The penetration can be up to 0.99 and 0.54 Å in the hydric and protic hydrogens, respectively. In addition, linear relationships, with correlation coefficient larger than 0.97 in all cases (Figure 2), are obtained when the data are divided based on the metal atom, for the hydric hydrogen penetration, and hydrogen bond donors molecule, for the protic hydrogen penetration vs the DHB distance. These correlations indicate the possibility to obtain DHB complexes with long interatomic distances and no penetration of the atoms.

The uniform and large variation in the HB distances of the minimum complexes described in this paper provides an excellent data set to analyze the variation of the properties derived from the electron density at the bond critical point. A number of exponential relationships have been found between the different properties calculated at the bond critical point and the distance (Table 5). More importantly, the evolution of the Laplacian with the distance shows a maximum at short distances (about 1.6 Å, Figure 3). This maximum precludes the negative values of the Laplacian for smaller distances within the open shell regime.[44] Considering only those cases with positive total energy density, the values of the Laplacian present a good exponential relationship with the distance. In addition, excellent linear correlations have been found between the sum of perpendicular curvatures, λ_1 and λ_2, vs the potential energy density, *V*, and between the curvature in the direction of the HB, λ_3, vs the kinetic energy density, *G* (Table 6), analogous to those found for theoretical F··H contacts[44] and experimental H···O HB.[45] The empirical equation (eq 1) proposed by Abramov[46] to evaluate the kinetic energy that in the bond critical points only depends on the electron density and its Laplacian has been applied to experimental values and tested versus theoretical standard H···F and H···O hydrogen bonds.[47,48] In the present case the % relative error = $[100^*(G - G_{\text{Abramov}})/G]$ has been plotted vs the DHB distance (Figure 4). The tendency of the error indicates that the equation proposed by Abramov underestimates the *G* values for long distances and overestimates for the shorter ones. Similar findings have been reported for NH···N HBs.[49]

TABLE 5: Exponential Relationship Found in the Properties Evaluated at the Bond Critical Point ($P_1 = a_1{*}e^{a_2{*}P_2}$); Distances in Å and the Rest of the Properties in au

P_1	P_2	a_1	a_2	r^2	no. of cases
r	H···H dist.	1.01	−2.24	0.972	54
λ_1	H···H dist.	−4.33	−2.97	0.988	54
λ_2	H···H dist.	−4.37	−2.98	0.988	54
λ_3	H···H dist.	3.06	−2.04	0.996	54
G	H···H dist.	0.29	−1.90	0.994	54
V	H···H dist.	−1.35	−2.71	0.988	54
$\nabla^2\rho$	H···H dist.	0.74	−1.64	0.994	36[a]
$\lambda_1 + \lambda_2$	λ_3	−0.011	15.81	0.977	54

[a] Only the cases with positive *H* values are considered. For an explanation, see the discussion.

$$G(r)_{[\text{Abramov}]} = \left(\frac{3}{10}\right)(3\pi^2)^{2/3}\rho(r)^{5/3} + \left(\frac{1}{72}\right)\frac{[\nabla\rho(r)]}{\rho(r)} + \left(\frac{1}{6}\right)\nabla^2\rho(r) \tag{1}$$

TABLE 6: Linear Relationship between the Curvatures and the Energies (au) ($P_1 = b_1 + b_2{*}P_2$)

P_1	P_2	b_1	b_2	r^2	no. of cases
V	$\lambda_1 + \lambda_2$	−0.0007	0.225	0.998	54
G	λ_3	−0.0042	8.598	0.998	54

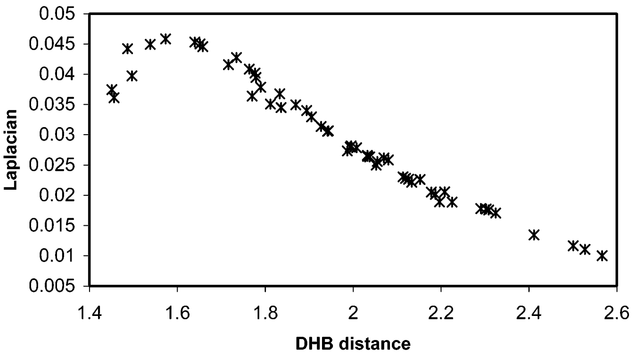


Figure 3. Plot of the Laplacian vs the DHB distance (in Å).

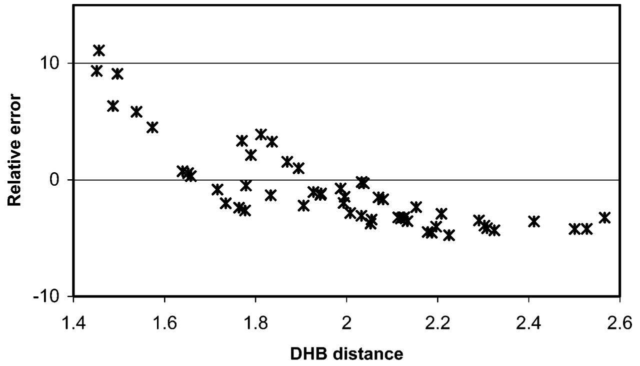


Figure 4. Relative error between the kinetic energy per electron density calculated with the Abramov equation, G_{Abramov} [eq 1, $G(r)$] and that calculated with the wave function vs the DHB distance.

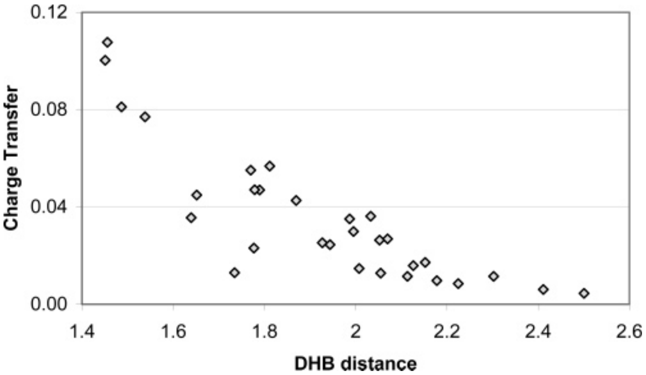


Figure 5. Charge transfer (e) vs DHB distance (Å).

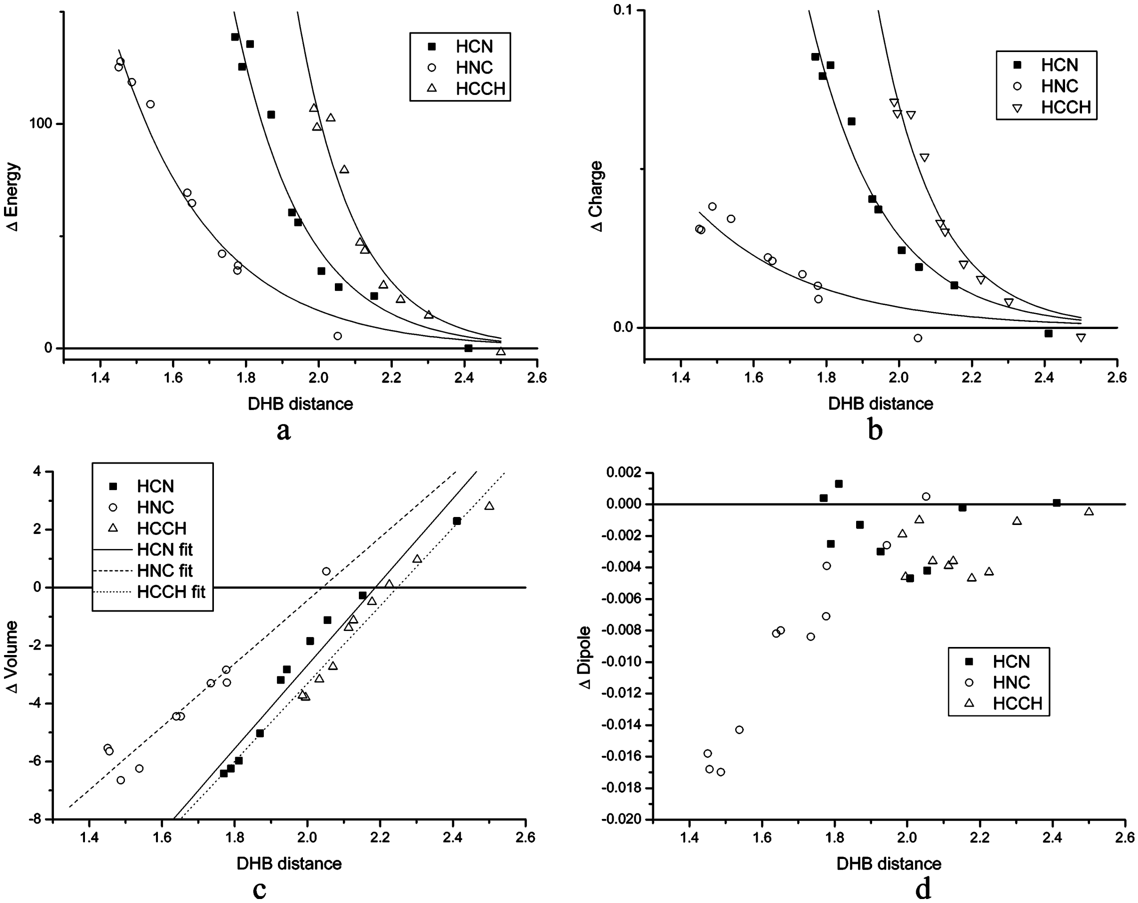
TABLE 7: Statistical Analysis of the Error in the Total Energy and Charge of the Systems Due to the Integration in the Atomic Basins

	energy (kJ/mol)	charge (e)
maximum unsigned error	1.67	0.0037
average error	0.04	0.0001
average unsigned error	0.38	0.0006

In addition, several integrated properties (energy, charge, volume, and dipole moment) have been calculated within the AIM methodology for the 30 complexes with only one protic molecule and in the isolated monomers, for comparative purposes. The error due to the integration in the energy and total charge when compared to the MP2 ab initio results are gathered in Table 7.

The numerical values of the redistribution of the energy, charge, and volume at a molecular level from the isolated monomers to the complexes has been included in the Supporting Information. An energy destabilization is observed for most of the hydric molecules, except for all the $(LiH)_2$ and LiH complexes and the NaH:HNC and BeH_2:HNC one. In the case of the protic molecule an energy stabilization that corresponds to the complexation energy plus the destabilization of the hydric molecules is observed, except for two complexes of LiH that present a larger stabilization of this molecule.

In the case of the charge variation, an electronic loss in the hydric molecule and a gain in the protic one is obtained without any exception in the complexes considered, which indicate that the electron transfer always goes from the hydric system to the



a

b

c

d

Figure 6. Variation of the atomic properties (energy, kJ/mol; charge, volume, and dipole, au) of the protic hydrogen due to the complex formation vs the DHB distance (Å). (a) The R^2 values for the fitted exponential relationships are 0.96, 0.98, and 0.95 for the HCN, HNC, and HCCH correlations, respectively. (b) The R^2 values for the fitted exponential relationships are 0.97, 0.84, and 0.96, respectively. (c) The R^2 values for the linear relationships are 0.95, 0.93, and 0.96, respectively.

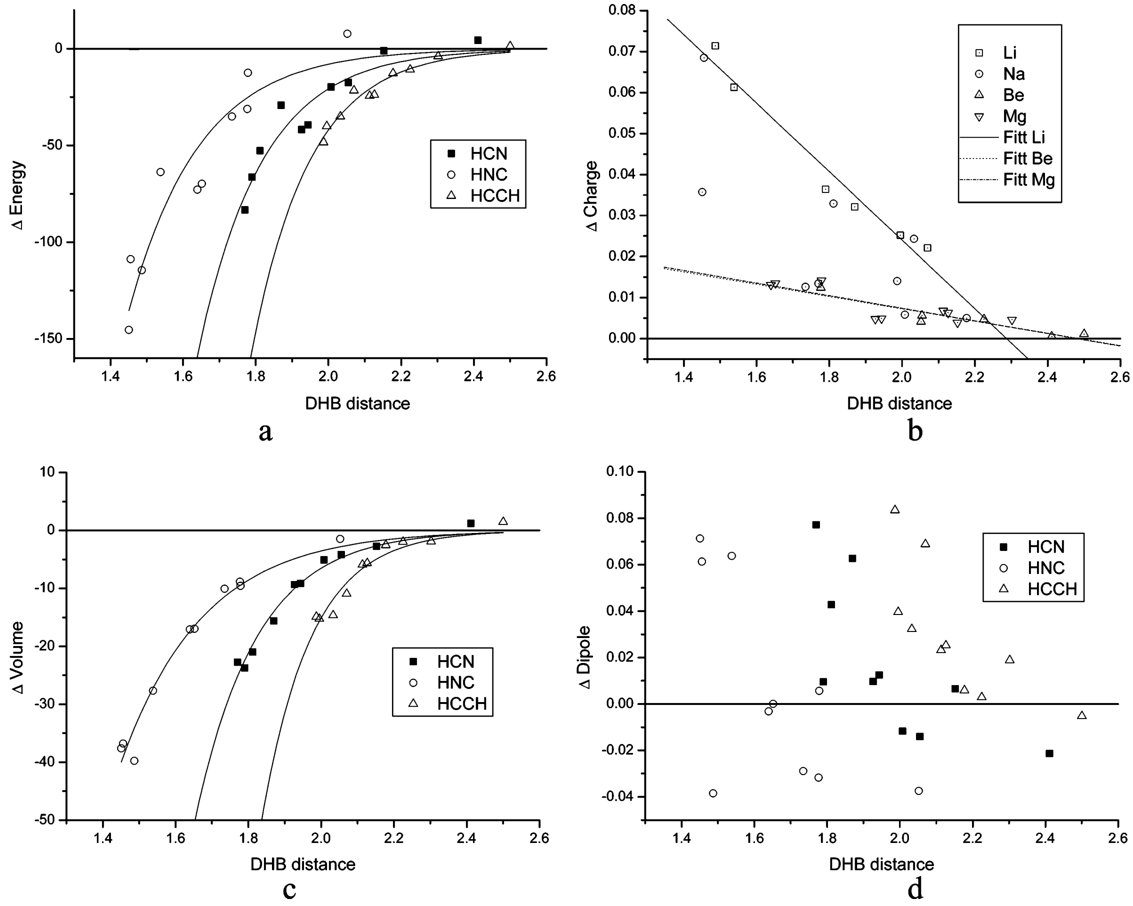


Figure 7. Variation of the atomic properties (energy, kJ/mol; charge, volume, and dipole, au) of the hydric hydrogen due to the complex formation vs the DHB distance (Å). (a) The R^2 values for the fitted exponential relationships are 0.91, 0.89, and 0.96 for the HCN, HNC, and HCCH correlations, respectively. (b) The R^2 values for the fitted exponential relationships are 0.96, 0.86, and 0.84, for the Li, Be, and Mg correlations, respectively. (c) The R^2 values for the exponential relationships are 0.98, 0.97, and 0.94 for the HCN, HNC, and HCCH correlations, respectively.

protic one, as expected. A clear attenuation of the electron transfer is observed as the DHB distance increases (Figure 5).

The reduction of the volume is observed for the hydric molecules, except for the two complexes with the longest DHB distances in the data set [$(BeH_2)_2$:HCN and $(BeH_2)_2$:HCCH]. In the protic molecules, a small increment of the volume is obtained within exceptions. A good linear correlation (with a square correlation coefficient of 0.95) has been obtained between the charge and volume variation within the hydric molecules.

In addition, the variations observed in the integrated properties of the two hydrogen atoms involved in the interaction have been considered when compared to the values of the corresponding isolated monomers (Figures 6 and 7). It should be noted that the rules proposed by Popelier include the energy destabilization, loss of charge, and reduction of the volume and dipolar moment of the protic hydrogen atom.

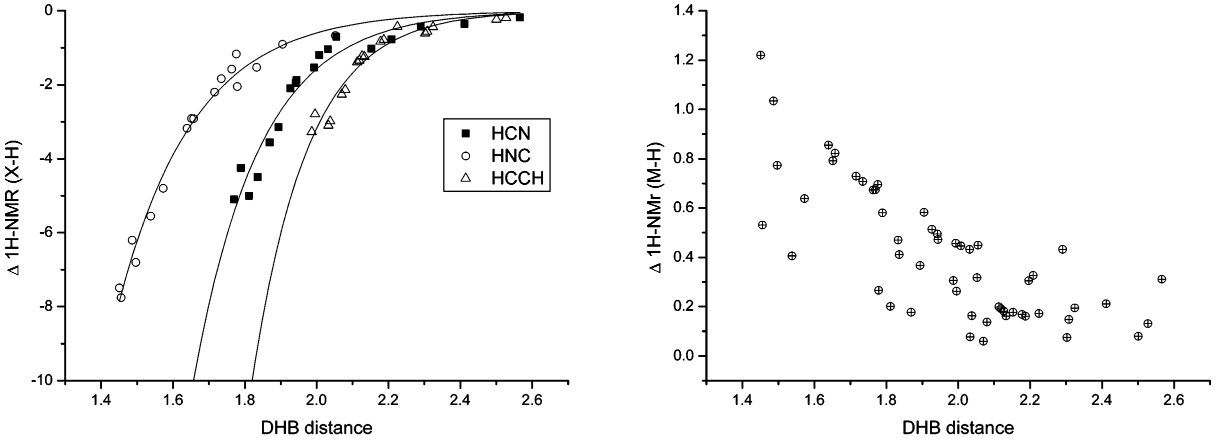
An energetic destabilization, up to 139 kJ/mol, is found in the protic hydrogen atom (Figure 6a) for all the cases, except for the complex with the longest DHB, which corresponds to the $(BeH_2)_2$:HCCH (**II**). Exponential relationships have been found between the value of the energy variation and the DHB distance for each series of proton donor complexes. For a given DHB distance, the effect is more pronounced in the HNC complexes than in the HCN ones, being the ones with HCCH where the difference is smaller.

In the charge analysis of the protic hydrogens (Figure 6b), a loss of charge is observed for all the cases (up to 0.071 e). As previously noted, exponential relationships can be found for the charge variation for each family of HB donors. The magnitude of the charge loss follows the same trend as the one observed in the energy variation. In fact, good linear relationships have been found for the charge vs energy variations for each hydrogen bond donor molecule with square correlation coefficient values, R^2, of 0.996, 0.90, and 0.998 for the HCN, HNC, and HCCH complexes, respectively. Similar correlations between the charge and energy variations has been described in a more general example.[50]

The volume variation of the protic hydrogen (Figure 6c) shows a rough linear relationship for each proton donor molecule. Thus, the complexes with the longer distances for each case present positive variations. Other studies have already shown that, in the case of long HB distances, the volume variation can be positive.[30,39] As pointed out by Koch and Popelier, who found an exception to the volume reduction rule,[29] this feature cannot be considered as a necessary condition in the HBs.

The variation of the atomic dipole moment of the protic hydrogen (Figure 6d) presents negative variations with values up to −0.017 and four cases with small positive ones. In addition, no correlation has been found between these values and the DHB distance for the complexes studied.

Regarding the hydric hydrogen atom, correlation has been attempted dividing the systems based on the hydrogen bond donor or the metal atom present in the complex. Only those correlations with square correlation coefficient, R^2, larger than 0.85 have been included in the figures or will be mentioned in the text.



a b

Figure 8. ^{1}H chemical shielding variation due to the complexation. The fitted exponential relationships have R^2 values of 0.95, 0.98, and 0.94 for the HCN, HNC, and HCCH molecules, respectively.

An energy stabilization (Figure 7a) is found for the hydric hydrogens with a maximum value of −145 kJ/mol. The exceptions correspond to the three complexes with $(BeH_2)_2$ in disposition **II** that show a small destabilization. Exponential relationships have been found when the data have been divided taking into account the different hydrogen bond donor molecules. In this case, the larger effect is observed in the HCCH complexes followed by the HCN and the smallest being the ones with HNC, in contrast to the results obtained for the protic hydrogens.

Regarding the charge variation (Figure 7b), a loss is observed in all the hydric hydrogens (up to 0.085), with the exceptions of the $(BeH_2)_2$ complexes in disposition **II** where the hydric hydrogen gains a small amount of charge. In this case, rough linear correlations are found when the systems have been divided based on the metal atom present. The larger effect corresponds to the lithium complexes while the effect for the beryllium and magnesium are very similar.

The volume variation observed in the hydric hydrogen (Figure 7c) is much larger than the one observed in the protic counterpart, the largest variation being 39.8 a.u. In this case, an exponential relationship based on the hydrogen bond donor system (shown in Figure 7c) and, in addition, linear relationship vs the DHB distance has been obtained for each set of complexes of a given metal atom. The square correlation coefficients, R^2, for the linear correlations are 0.88, 0.99, 0.89, and 0.90 for the Li, Na, Be, and Mg complexes, respectively.

The atomic dipole polarization (Figure 7d) of the hydric hydrogen increases in 21 cases and decreases in 9. The last ones corresponds mostly to the beryllium complexes.

Spectroscopic Properties. The ^{1}H NMR chemical shielding and the harmonic frequency shift in the HB donor have been explored. Positive variations have been obtained in the hydric hydrogens while they are negative in the protic hydrogens. The effects are much larger in the protic cases than in the hydric ones, the maximum differences being −7.8 ppm [$(NaH)_2$:HNC] and 1.22 ppm (NaH:HNC), respectively. For the variation found in the protic hydrogens, exponential relationships have been found for each hydrogen bond donor molecule (Figure 8). In the case of the hydric hydrogens (Figure 8b), no significant variation has been found grouping the data for each metal atom or hydrogen bond donor molecule, although an inverse trend to that represented in Figure 8a is observed.

The calculated frequency shift in the HB donor molecules is always negative with values that range between −2 and −1000. The larger variations correspond to the HNC complexes and the smaller to the HCCH ones. The representation of this variation vs ρ at the BCP (Figure 9) shows a clear relationship between these two parameters for all the cases considered in the present work.

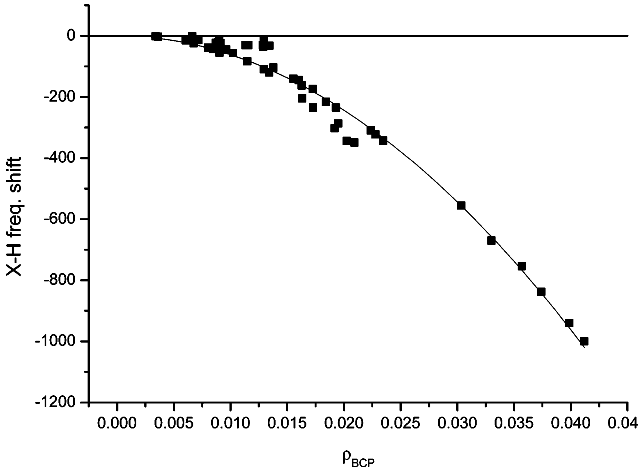


Figure 9. X−H frequency shift (cm^{-1}) vs ρ at the bond critical point (au). The fitted curve has a square correlation coefficient of 0.98.

Conclusion

Theoretical calculations of the DHB complexes among (XH), $(XH)_2$ (X = Li, Na, BeH, and MgH), and three hydrogen-bonding donors (HCN, HNC, and HCCH) have been carried out at the MP2/6-311++G(2d,2p) computational level. The energetic results have been rationalized based on the molecular electrostatic potential of the isolated HB donor molecules. The analysis of the electron density properties at the bond critical point and integrated properties within the atomic basins agree with the rules defined by Popelier to consider the interactions as HB, with a small number of borderline exceptions. Exponential relationships have been found for most of the properties vs the DHB distances, especially when the complexes for each hydrogen bond donor molecule have been considered separately.

The similitude of the present results with those obtained in the study of the electron density and other properties for standard HB interactions reinforces the belief that the DHB is just another type of HB.

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Supporting Information Available: Tables with the properties derived from the electron density at the bond critical point, variation of the molecular energy, charge, and volume due to the complexation. Coordinates of the complexes calculated at the MP2/6-311++G(2d,2p) computational level. This material is available free of charge via the Internet at http://pubs.acs.org.

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