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How To Determine Whether Intramolecular H···H Interactions Can Be Classified as Dihydrogen Bonds

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Different types of intramolecular H···H interactions have been analyzed using the MP2/6-311++G(d,p) level of approximation. These are C−H··· H−B, C−H···H−Al, C−H···H−C, C−H···H−O, O−H···H−Al and O−H···H−B contacts. Quantum theory of atoms in molecules and natural bond orbitals methods were applied to better understand the nature of these interactions. It was found that some of the species analyzed possess the characteristics of typical hydrogen bonds, such as the O−H···O ones. The electron charge transfer from the Lewis base to the antibonding X−H (for example O−H) orbital of the Lewis acid is one such characteristic. The NBO method may be considered decisive to classify any system as dihydrogen bonded.

Introduction

There are numerous studies on H···H interactions, their role in chemical processes and their impact on the stabilization of particular conformers.[1] The influence of such interactions on the arrangement of molecules in crystals is also meaningful.[2] Early studies concerning these topics were mostly connected with H···H steric repulsive interactions that disturb the molecular system or, in fact, it was assumed to be energetically destabilizing.[3] For example, the nonplanarity of the biphenyl molecule in the gas phase was explained as being the result of repulsive interaction of *ortho* hydrogen atoms. However, biphenyl molecules are planar in crystals (see CSD's BIPHEN refcode)[4] owing to the so-called packing forces. Another, more recent, example is the crystal structure of a pentacyclic half-cage compound measured by low-temperature neutron diffraction where a short H···H distance of 1.617(3) Å was detected and classified as a nonbonded repulsive interaction.[5]

The meaning and understanding of H···H contacts was changed and verified in the 1990s when a new type of interaction named dihydrogen bond[6] (DHB) was detected in different organometallic crystal structures.[7,8] This interaction was designated as X−H···H−M, where X−H denotes a typical proton donating bond such as O−H or N−H with the excess of positive charge on H-atom; the second hydrogen atom possessing a negative charge and connected with M (M is a transition metal or a boron atom) is the acceptor center. Other systems were also analyzed and classified as DHBs, even some C−H···H−C interactions were described as possessing the characteristics of dihydrogen bonds.[9] Numerous calculations on dihydrogen bonded systems were performed, it was found that binding energies for them in some cases exceed 10 kcal/mol.[10]

A more detailed analysis and classification of different interactions was performed,[1a] and it was pointed out that there are three kinds of HBs: typical hydrogen bonds, designated as X−H···Y, with the positive charge of H-atom; inverse (or hydride) bonds where a negatively charged H-atom is situated between electropositive atoms; and dihydrogen bonds X−H···H−Y containing both protic and hydric H-atoms.

What are the characteristics of DHBs? Generally, it seems that the properties of DHBs do not differ much from typical H-bonds.[11−13] The ab initio calculations (up to the MP4(SDQ)/6-311++G(d,p) and QCISD(T)/6-311++(d,p) levels of approximation) on dihydrogen bonded systems with hydrogen fluoride as the proton donor and hydrides of metals of the first and second groups of the periodic table as the acceptors have shown numerous correlations between geometrical, energetic and topological parameters.[12] For example, the elongation of the HF proton donating bond due to complexation is observed, and the H−F bond length correlates with the H-bond energy and the H···H distance. There are also other correlations, for instance those between the above-mentioned proton donating bond length and the donor−acceptor distance and the topological parameters (QTAIM parameters) derived from the Bader theory.[14]

The formation of DHB usually causes changes similar to those of conventional H-bonds. These are shifts of the proton donating X−H stretching bands to lower frequencies and an increase of their intensities, changes in the magnetic resonance shielding constants and changes in the QTAIM parameters.[15] There are the so-called blue-shifting H-bonds with the shift of X−H bands to higher frequencies; it is worth mentioning that blue-shifting DHBs were also detected.[16] The LiH···H_2, LiH···CH_4, LiH···C_2H_6 and LiH···C_2H_2 systems with H···H intermolecular contacts were analyzed[15c] with the perturbational IMPPT decomposition scheme.[17] The authors found that the components of the interaction energy of the LiH···C_2H_2 complex are similar to those of typical H-bonded systems (the main binding energy contributions come from the electrostatic energy, followed by the induction and dispersion energies), whereas for the remaining complexes the partitioning is different and these H···H interactions are not classified as dihydrogen bonds but as van der Waals complexes.

Studies of C−H···H−C interactions in organoammonium tetraphenylborates were performed,[9] the Bader theory[14] was applied to the experimental electron density,[18] and the authors

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concluded that the transition from H···H contacts in DHBs to contacts in van der Waals complexes is continuous without borders. Other calculations on model dihydrogen bonded systems ranging from weak to strong ones have been investigated.[15a,b] For example, the authors predicted the binding energy for the $LiNCH^+$···HLi complex (at the MP2/aug'-cc-pVTZ level) to be 27.1 kcal/mol. Similarly, strong dihydrogen bonds were analyzed where the hydronium ion or its derivatives act as the proton donating system and the BeH_2 molecule or its derivative is a proton acceptor because it has the negatively charged, hydric Lewis base center.[19] It was found that for the latter complexes the delocalization interaction energy term is the most important attractive one whereas the electrostatic energy was dominant for medium strength or even strong H-bonds. It was found that the delocalization energy is attributed to covalency of interactions, and hence very strong H-bonds and DHBs are covalent in nature.[20]

Very recently another kind of H···H interaction was analyzed; these are the so-called H−H stabilizing interactions that are different in nature if compared with DHBs. The detailed topological analysis of such H···H intramolecular interactions in biphenyls and other similar systems was performed by Matta et al.[21] and also the comparison of the latter interactions with typical DHBs was performed.

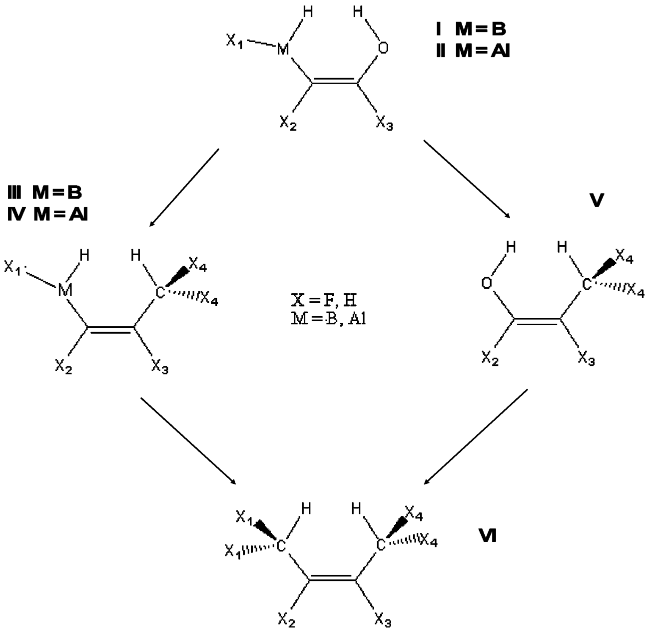
One can see a broad spectrum of H···H interactions, those arising from sterically overcrowded molecular structures, dihydrogen bonds and finally H−H stabilizing interactions analyzed in recent studies. In the case of intermolecular interactions the decision whether they may be attributed to DHBs may be based on the analysis of binding energies and the other characteristics, including those derived from the decomposition schemes of the interaction energy. Such investigations were performed and briefly described above. The situation is much more complicated for intramolecular interactions because the estimation of the H-bond energy is not univocal.[22] The studies on the intramolecular H···H interactions are not common[23] and do not explain their nature in detail. Hence, the aim of this study is to analyze such interactions for the greater sample of species and, what is most important here, to explain which factors decide whether any system may be classified as an intramolecular dihydrogen bond.

Computational Details

The calculations were carried out using the Gaussian 03[24] set of codes. The systems possessing H···H intramolecular contacts were taken into account and fully optimized. These are the species presented in Scheme 1 and classified into six classes: (I) there is the proton donating O−H bond acting as a Lewis acid and the hydric group (BH_2) where the H-atom is the Lewis base center; (II) this class is similar to the previous one because the $-AlH_2$ group interacts with the OH bond; (III) and (IV) hydric H-atoms of BH_2 and AlH_2 groups interact with the methyl group, which may be treated as a weak Lewis acid, especially if it is substituted by F-atoms (CF_2H), because in such a case the more polarized C−H bond is a stronger Lewis acid than in the case of an unsubstituted CH_3 methyl group; (V) OH acts as Lewis acid and CH_3 is suspected to be a very weak Lewis base center; (VI) these are C−H···H−C intramolecular interactions.

The calculations were performed using the second-order perturbation Møller−Plesset method (MP2)[25] and the Pople type 6-311++G(d,p) basis set was used.[26] The "atoms in molecules" (AIM) theory of Bader was applied, and the critical points found were further analyzed in terms of electron densities and their Laplacians. The AIM calculations were performed with the use of the AIM2000 program.[27] To deepen into the nature of intramolecular interactions considered here, the natural bond orbitals (NBO) method was also applied (B3LYP/6-311++G (d,p) approximation to apply NBO method).[28]

SCHEME 1



Results and Discussion

Geometrical and Topological Parameters. According to an early criterion of existence of hydrogen bonding, the proton−acceptor distance should be smaller than the corresponding sum of van der Waals radii.[29] Such a criterion is often applied for the hydrogen bonds occurring in crystals where geometrical parameters are very often the only information on the characteristics of moieties constituting crystal structures. That was questioned because hydrogen bonding, like most electrostatic interactions, acts far beyond the van der Waals cutoff;[30] thus this criterion may be applied only as a first rough classification into any type of interaction. Because the dihydrogen bond may be treated as a special kind of hydrogen bond, this criterion may be applied here for intramolecular H···H distances. Table 1 shows that generally H···H distances are close to the sum of van der Waals radii (2.2−2.4 Å) or they are even greater. However, there are distances meaningfully smaller than 2 Å; the shortest one is 1.885 Å. The shortest H···H distances are observed for B−H···H−O systems (the mean H···H distance for this class amounts to 1.990 Å) whereas the longest ones are observed for Al−H···H−C systems (the mean value is equal to 2.498 Å).

Table 1 also presents QTAIM parameters, electron density at H···H bond critical point), its Laplacian ($\nabla^2\rho_C$), kinetic electron energy density at bond critical point (BCP) (G_C) and potential electron energy density at BCP (V_C). For some of the species presented in Table 1 the H···H bond paths with BCPs were not found. Compounds **V** have been considered only with C_s symmetry, even though in several cases there are no minima, because none of the C_1 minima present has a H···H BCP. The lack of H···H BCPs corresponds in a few cases to the greater H···H distance (in two cases H···H is greater than 2.5 Å); however, for two O−H···H−C interactions the H···H distance is about 2.07 Å and a BCP is not observed. The latter situation is connected with the interaction of protic hydrogen with H−C,

TABLE 1: H···H Distance between Protic and Hydric H-Atoms (in Å); Ratio between the Hydric H-Atom Radius (H-atom···BCP Distance) and the Protic H-Atom Radius (Protic H-atom···BCP Distance)[a]; and QTAIM (in au) Characteristics of the Species Analyzed Here

compound	H···H distance	γ ratio	ρ_c	$\nabla^2\rho_c$	G_c	V_c	N_{im}[b]	compound	H···H distance	γ ratio	ρ_c	$\nabla^2\rho_c$	G_c	V_c	N_{im}[b]
I	1.935	1.292	0.0155	0.0484	0.0109	−0.0097	0	**II**	2.265	1.399	0.0096	0.0262	0.0057	−0.0049	0
I (X_3 = F)	1.885	1.294	0.0169	0.0516	0.0118	−0.0107	0	**II** (X_3 = F)	2.086	1.375	0.0124	0.0325	0.0072	−0.0064	0
I (X_1 = F)	2.066	1.279	0.0119	0.0416	0.0118	−0.0107	0	**II** (X_1 = F)	2.517	*d*					0
I (X_2 = F)	1.992	1.271	0.0138	0.0443	0.0098	−0.0085	0	**II** (X_2 = F)	2.278	1.375	0.0091	0.0250	0.0054	−0.0046	0
I ($X_{1,2,3}$ = F)	2.016	1.260	0.0129	0.0427	0.0094	−0.0081	0	**II** ($X_{1,2,3}$ = F)	2.289	1.386	0.0089	0.0253	0.0054	−0.0047	0
I ($X_{2,3}$ = F)	1.927	1.279	0.0155	0.0483	0.0109	−0.0097	0	**II** ($X_{2,3}$ = F)	2.105	1.367	0.0119	0.0312	0.0069	−0.0060	0
I ($X_{1,2}$ = F)	2.103	1.256	0.0110	0.0385	0.0083	−0.0070	0	**II** ($X_{1,2}$ = F)	2.470	*d*					0
I ($X_{1,3}$ = F)	1.993	1.277	0.0135	0.0451	0.0100	−0.0087	0	**II** ($X_{1,3}$ = F)	2.317	*d*					0
mean	1.990	1.276	0.0139	0.0451	0.0104	−0.0091		mean	2.291	1.380	0.0104	0.0280	0.0061	−0.0053	
III	2.174	1.125	0.0106	0.0358	0.0075	−0.0061	0	**IV**	2.507	1.287	0.0073	0.0204	0.0044	−0.0036	0
III (X_1 = F)	2.239	1.128	0.0094	0.0329	0.0069	−0.0055	0	**IV** (X_1 = F)	2.592	*d*					0
III (X_2 = F)	2.199	1.122	0.0101	0.0346	0.0072	−0.0058	0	**IV** (X_2 = F)	2.511	1.273	0.0071	0.0199	0.0042	−0.0035	0
III (X_3 = F)	2.178	1.119	0.0105	0.0359	0.0075	−0.0060	0	**IV** (X_3 = F)	2.476	1.256	0.0073	0.0208	0.0044	−0.0036	0
III ($X_{2,3}$ = F)	2.181	1.119	0.0104	0.0358	0.0075	−0.0060	0	**IV** ($X_{2,3}$ = F)	2.462	1.260	0.0075	0.0209	0.0044	−0.0037	0
III (X_4 = F)	2.138	1.133	0.0110	0.0386	0.0080	−0.0064	0	**IV** (X_4 = F)	2.439	1.284	0.0079	0.0220	0.0047	−0.0039	0
mean	2.185	1.124	0.0104	0.0356	0.0074	−0.0060		mean	2.498	1.272	0.0074	0.0208	0.0044	−0.0037	
V*	1.976	1.142	0.0122	0.0453	0.0097	−0.0080	1	**VI**	2.078	1.000	0.0110	0.0387	0.0080	−0.0064	0
V (X_2 = F)[c]	1.992	1.140	0.0119	0.0452	0.0096	−0.0079	1	**VI** (X_1 = F)	2.081	1.015	0.0106	0.0396	0.0081	−0.0063	0
V (X_3 = F)[c]	2.068	*d*					1	**VI** (X_2 = F)	2.124	1.003	0.0101	0.0364	0.0075	−0.0059	0
V ($X_{2,3}$ = F)	2.067	*d*					0	**VI** ($X_{2,3}$ = F)	2.146	1.000	0.0098	0.0357	0.0073	−0.0057	0
V (X_4 = F)[c]	2.044	1.116	0.0104	0.0434	0.0090	−0.0072	1	**VI** ($X_{1,2,3,4}$ = F)	2.054	1.000	0.0108	0.0411	0.0083	−0.0064	0
mean	2.029	1.133	0.0115	0.0446	0.0094	−0.0077		mean	2.097	1.004	0.0104	0.0383	0.0079	−0.0061	

[a] This ratio is designated as γ. [b] N_{im} is the number of imaginary frequencies detected. [c] C_s symmetry has been imposed to these molecules. [d] No BCP found.

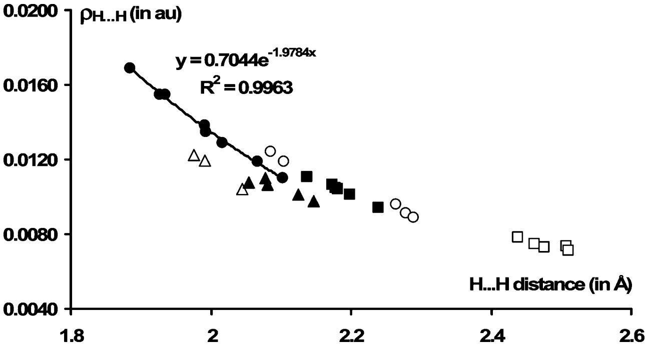


Figure 1. Relationship between H···H distance (in Å) and the electron density at the corresponding BCP (in au): full circles, B−H···H−O interactions; open circles, Al−H···H−O interactions; full squares, C−H···H−B; open squares, C−H···H−Al; full triangles, C−H···H−C systems; open triangles, O−H···H−C contacts. Exponential regression is presented for B−H···H−O interactions.

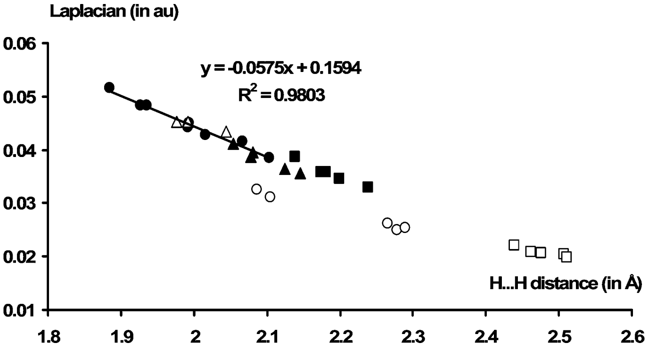


Figure 2. Relationship between H···H distance (in Å) and $\nabla^2\rho_{H...H}$ (in au), designations of subsamples are the same as in Figure 1, the regression line for B−H···H−O is included.

which, in the case of intermolecular hydrogen bonds, usually acts as the proton donating bond. This may be the reason why BCPs were not found. One can see that there is no consistency between H···H distances and QTAIM parameters because the lack of BCPs, usually interpreted as the lack of stabilizing interactions, does not correspond to the greatest H···H distances. However, one can observe some relationships.

Figure 1 presents the poor dependence between the H···H distance and the electron density at the corresponding BCP ($\rho_{H\cdots H}$). There is a rough exponential correlation concerning all the systems analyzed here. However, if subsamples (those designated in Scheme 1) are analyzed separately, then a good exponential correlation for B−H···H−O systems is observed (R^2 = 0.996). It seems that such a dependence is not observed for the other subsamples considered here. Only in the case of Al−H···H−O interactions does the exponential correlation exist (R^2 = 0.990), but only six systems of that type are analyzed because for the other two Al−H···H−O species BCPs were not found (Table 1). Similarly, a linear correlation between the H···H distance and the Laplacian of the electron density at the corresponding BCP is observed only for the species with B−H···H−O interactions; the latter correlation is rather poor for the other subbsamples (Figure 2).

Table 1 also presents G_C and V_C values; one can see that for all the cases considered here $G_C > |V_C|$. Because it was pointed out in earlier studies that H_C ($H_C = G_C + V_C$) is negative for rather strong H-bonds,[31] all the interactions considered here may be classified as only medium strength or weak ones. The ratios between the distance of the BCP to the hydric and protic H-atoms are also included in Table 1, the greatest ratios occur for B(Al)−H···H−O interactions whereas for C−H···H−C they are the smallest and close or even equal to unity. This is connected with symmetry of the systems analyzed: 2,3-butene is symmetrical with equivalent C−H interacting bonds (ratio equal to 1); for the remaining C−H···H−C interactions the polarization of C−H bonds is weak, resulting in negligible differences between the volumes of contacting H-atoms.

Figure 3 presents relationships between the electron density at H···H BCP and the radii of protic and hydric H-atoms. One can see linear correlations for B−H···H−O interactions, which indicates a decrease of both atomic radii with an increase of

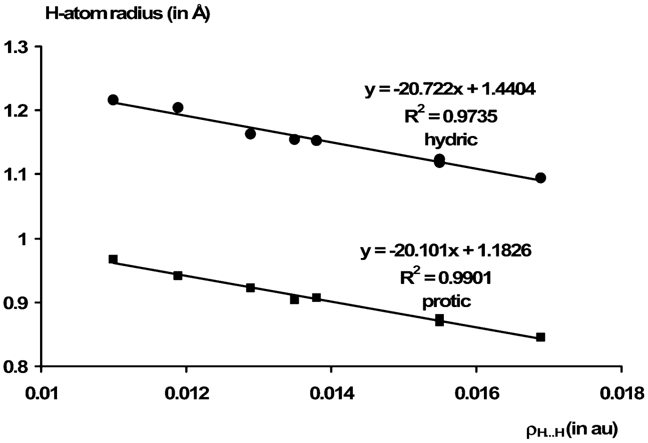


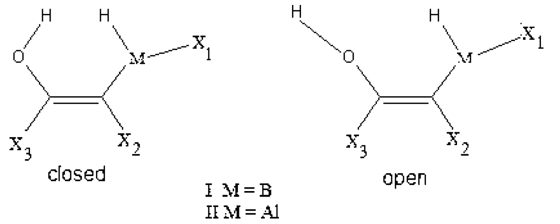
Figure 3. Dependence between electron density at H···H BCP (in au) and the hydric and protic H-atoms' radii (in Å), the radius of atom is the distance between its attractor and H···H BCP.

TABLE 2: Differences in Energies (in kcal/mol) between the Open and Closed Forms (Scheme 2)[a]

compound	energy difference	compound	energy difference
I	4.93	**II**	2.27
I (X_3 = F)	3.83	**II** (X_3 = F)	1.26
I (X_1 = F)	2.90	**II** (X_1 = F)	0.27
I (X_2 = F)	3.56	**II** (X_2 = F)	1.29
I ($X_{1,2,3}$ = F)	0.66	**II** ($X_{1,2,3}$ = F)	−2.07
I ($X_{2,3}$ = F)	2.64	**II** ($X_{2,3}$ = F)	−0.01
I ($X_{1,2}$ = F)	1.74	**II** ($X_{1,2}$ = F)	−0.68
I ($X_{1,3}$ = F)	1.85	**II** ($X_{1,3}$ = F)	−0.82

[a] Positive values indicate that the closed form is more stable.

SCHEME 2



$\rho_{H\cdots H}$. For the other subsamples these dependences are not well correlated. Generally, the geometrical and topological results presented here show the strong systematic interrelations for B−H···H−O species and to a lesser degree for Al−H···H−O interactions. This may indicate that for these subsamples there are attractive and stabilizing interactions whereas for the other subsamples such interactions may be only accepted in the limit.

Energy Dependencies. Table 2 presents the energy differences (ΔE) between the so-called closed and open configurations (Scheme 2). Such a difference is often treated as a rough measure of hydrogen bond strength.[32,33] Only B−H···H−O and Al−H···H−O contacts are included because for these species good correlations were observed in the previous section. Additionally, for **III**, **IV** and **VI** subsamples the so-called open configurations do not exist. One can see that for all the species of subsample **I** the closed conformation is more stable than the open one. This is in agreement with the short interatomic distances and the presence of BCPs, which indicate the attractive H···H interaction for B−H···H−O contacts. For subsample **II**, with an Al−H Lewis base center, for some of the species the open configuration is energetically favorable and for others the closed one is more stable. The above-mentioned energy difference (ΔE) for subsample **I** is in the range +0.66/+4.93 kcal/mol whereas such a difference for **II** is in the range −2.07/+2.27 kcal/mol. It was analyzed, in early and recent studies, that ΔE is only the rough estimation of H-bond strength and hence there are more refined proposals to calculate the intramolecular H-bond energy.[34] This may be the reason why ΔE does not correlate with any topological or geometrical parameters. It seems that the application of the more refined techniques is not advisable here, especially for Al−H···H−O systems where ΔE energy differences are not meaningful.

The net atomic charges on H···H interacting atoms were calculated and compared. Table 3 presents such charges calculated within the CHelpG scheme as well as using the NBO method; the charge differences between protic and hydric H-atoms are included. The CHelpG scheme,[35] implemented within the Gaussian packages, produces charges fitted to the electrostatic molecular potential (EMP) using a grid based method. It was found that the application of the CHelpG method yields much better estimates of intermolecular charge transfer than any other arbitrary population analysis.[36] One can see that meaningful negative and positive charges for contacting H-atoms are observed for **I** and **II** classes of the analyzed species, for such moieties the charge differences are the greatest ones. For C−H···H−B(Al) interactions the differences are also meaningful, indicating a possible attractive interaction, for these systems the net positive charge is on the H(C) atom. One can see that for C−H···H−C interactions these differences are close to zero and even in a few cases both H-atoms possess a positive charge. The results for C−H···H−O species are very interesting, almost all these species are transition states because imaginary frequencies were detected for them (Table 1). CHelpG charges for that subsample are positive for H(O) atoms and negative for H(C) centers. This means that C−H bonds act here as Lewis bases, the situation being similar to C−H···M (M−metal) agostic interactions where the M center is the Lewis acid and C−H is the Lewis base.[37,38] However, one can observe that NBO charges calculated for the O−H···H−C species are positive for both contacting H-atoms (Table 3).

The results collected in Table 3 may indicate that B(Al)−H···H−O interactions are attractive ones and can be attributed to DHBs because charge differences on contacting H-atoms are meaningful and the greatest ones of all. The results for the remaining samples (**III**−**VI**) are not so clearly conclusive.

To delve further into the nature of intramolecular interactions, an NBO analysis was performed. Table 3 also presents the energies connected with the transfer of electronic charge from the filled σ_{YH} orbital to the antibond σ_{XH}^*. YH denotes the Lewis base center, and XH is the Lewis acid (proton donating bond in hydrogen bonding). This is the second-order energy lowering which in SCF MO theory may be expressed as

$$\Delta E_{\sigma\sigma^*}{}^{(2)} = -2\frac{\langle\sigma|\hat{F}|\sigma^*\rangle}{\epsilon_{\sigma^*}-\epsilon_{\sigma}} \tag{1}$$

where $\hat{F}$ is the Fock operator and ϵ_{σ^*} and ϵ_{σ} are the NBO orbital energies. It is worth mentioning that in the case of typical hydrogen bonding a two-electron $n_Y \rightarrow \sigma_{XH}^*$ intermolecular donor−acceptor interaction is considered where electron density from the lone pair n_Y of the Lewis base Y delocalizes into the unfilled σ_{XH}^* antibonding orbital of the Lewis acid. It was pointed out that $n_Y \rightarrow \sigma_{XH}^*$ orbital overlap is the general characteristic of hydrogen bonding.[28] In other words, such an overlap may be treated as a criterion of the existence of the H-bond. For the systems analyzed here the role of the n-lone pair is replaced by the bonding orbital of base, i.e., the Y−H bond. This was earlier observed for the other simple models of intermolecular dihydrogen bonds.[28b] The $\sigma_{YH} \rightarrow \sigma_{XH}^*$ is also observed here for all B(Al)−H···H−O interactions and for a

TABLE 3: Atomic Charges on H-Atoms, Hydric and Protic (in au),[a] and Orbital Interaction Energy $\Delta E_{\sigma\sigma^*}{}^{(2)}$ (kcal/mol)

compound	H-protic	H-hydric	charge difference	$\Delta E_{\sigma\sigma^*}{}^{(2)}$	compound	H-protic	H-hydric	charge difference	$\Delta E_{\sigma\sigma^*}{}^{(2)}$
I	+0.4595	−0.2537	0.7132	1.95	**II**	+0.4327	−0.3789	0.8116	1.26
	+0.4867	−0.1182	0.6049			+0.4768	−0.4029	0.8797	
I (X_3 = F)	+0.4439	−0.2411	0.6850	2.46	**II** (X_3 = F)	+0.4176	−0.3685	0.7861	2.33
	+0.5057	−0.1190	0.6247			+0.4979	−0.4086	0.9065	
I (X_1 = F)	+0.4298	−0.2370	0.6668	1.18	**II** (X_1 = F)	+0.4018	−0.3762	0.7780	0.57
	+0.4793	−0.1491	0.6284			+0.4691	−0.4256	0.8947	
I (X_2 = F)	+0.4331	−0.2017	0.6348	1.36	**II** (X_2 = F)	+0.4025	−0.3503	0.7528	1.07
	+0.4870	−0.1018	0.5888			+0.4776	−0.3983	0.8759	
I ($X_{1,2,3}$ = F)	+0.3902	−0.1764	0.5666	1.42	**II** ($X_{1,2,3}$ = F)	+0.3645	−0.3372	0.7017	1.10
	+0.5000	−0.1411	0.6411			+0.4923	−0.4264	0.9187	
I ($X_{2,3}$ = F)	+0.4143	−0.1779	0.5922	1.91	**II** ($X_{2,3}$ = F)	+0.3878	−0.3388	0.7266	2.06
	+0.5069	−0.1028	0.6097			+0.4986	−0.4037	0.9023	
I ($X_{1,2}$ = F)	+0.4038	−0.1939	0.5977	0.95	**II** ($X_{1,2}$ = F)	+0.3769	−0.3500	0.7269	0.59
	+0.4810	−0.1378	0.6188			+0.4719	−0.4217	0.8936	
I ($X_{1,3}$ = F)	+0.4109	−0.2222	0.6331	1.62	**II** ($X_{1,3}$ = F)	+0.3863	−0.3623	0.7486	1.04
	+0.4984	−0.1513	0.6497			+0.4910	−0.4303	0.9213	
III	+0.0874	−0.2357	0.3231		**IV**	+0.0449	−0.3575	0.4024	
	+0.2182	−0.1032	0.3216			+0.2095	−0.3934	0.6029	
III (X_1 = F)	+0.0618	−0.2091	0.2709		**IV** (X_1 = F)	+0.0337	−0.3526	0.3863	
	+0.2141	−0.1333	0.3474			+0.2041	−0.4185	0.6226	
III (X_2 = F)	+0.1042	−0.1988	0.3030		**IV** (X_2 = F)	+0.0630	−0.3398	0.4028	0.5
	+0.2192	−0.0887	0.3079			+0.2110	−0.3893	0.6003	
III (X_3 = F)	+0.1578	−0.2280	0.3858		**IV** (X_3 = F)	+0.1267	−0.3582	0.4849	
	+0.2339	−0.0998	0.3337			+0.2248	−0.3914	0.6162	
III ($X_{2,3}$ = F)	+0.1865	−0.1906	0.3771		**IV** ($X_{2,3}$ = F)	+0.1498	−0.3382	0.4880	0.53
	+0.2352	−0.1020	0.3372			+0.2265	−0.3872	0.6137	
III (X_4 = F)	+0.0716	−0.2139	0.2855	0.7	**IV** (X_4 = F)	+0.0353	−0.3313	0.3666	0.98
	+0.1541	−0.0850	0.2391			+0.1476	−0.3876	0.5352	
V	+0.4411	−0.1041	0.5452		**VI**	−0.0060	−0.0060	0	
	+0.4629	+0.1802	0.2827			+0.1987	+0.1987	0	
V (X_2 = F)	+0.4329	−0.0708	0.5037	0.52	**VI** (X_1 = F)	+0.0312	−0.0225	0.0537	
	+0.4791	+0.1780	0.3011			+0.1993	+0.1353	0.0640	
V (X_3 = F)	+0.4140	+0.0063	0.4077		**VI** (X_2 = F)	+0.0766	+0.0011	0.0755	
	+0.4626	+0.1966	0.2660			+0.2129	+0.1995	0.0134	
V ($X_{2,3}$ = F)	+0.4095	+0.0546	0.3549		**VI** ($X_{2,3}$ = F)	+0.0940	+0.0940	0	
	+0.4795	+0.1951	0.2844			+0.2114	+0.2114	0	
V (X_4 = F)	+0.4288	−0.0869	0.5157		**VI** ($X_{1,2,3,4}$ = F)	+0.0940	+0.0940	0	0.53
	+0.4632	+0.1171	0.3461			+0.1482	+0.1482	0	

[a] Upper value corresponds to ChelpG charge and lower one to NBO charge.

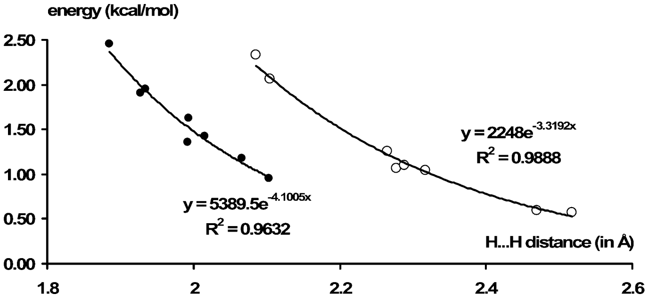


Figure 4. Relationship between H···H distance (in Å) and the second-order energy lowering energy (eq 1, in kcal/mol); black circles, B−H···H−O; open circles, Al−H···H−O.

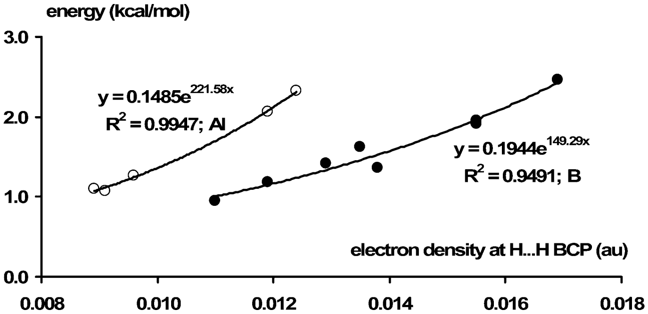


Figure 5. Relationship between the electron density at H···H BCP (in au) and the second-order energy lowering energy (eq 1, in kcal/mol): black circles, B−H···H−O; open circles, Al−H···H−O.

few other systems (Table 3) with the corresponding lowering energy described by eq 1. This is in line with the other results earlier described that the existence of DHBs is more probable for series **I** and **II**. It is worth mentioning that the above-mentioned overlap is observed even for those Al−H···H−O interactions where BCPs were not found. Table 3 also shows the systems from the other series where $\sigma_{YH} \rightarrow \sigma_{XH}{}^*$ delocalization is observed: they are those species where the hydric B(Al)H_2 group exists or where C−H bond polarization is enhanced. This electron transfer is observed owing to the influence of F-substituents. There is one strange case of C−H···H−C interaction for the symmetrical species of **VI** ($X_{1,2,3,4}$ = F); however, in this case there are two symmetrical and equivalent mutually existing overlaps.

One can find a few interesting correlations between the energy described by eq 1 and the other parameters usually attributed to H-bonding. Figures 4−6 present the dependences between parameters usually analyzed as good descriptors of H-bond strength and the charge-transfer energy (eq 1). The following descriptors are taken into account: H···H distance, electron density at H···H BCP ($\rho_{H\cdots H}$) and the Laplacian of the electron density. One can observe very good exponential correlations between $\Delta E_{\sigma\sigma^*}{}^{(2)}$ and these descriptors. Two series of compounds were analyzed: those connected through B−H···H−O

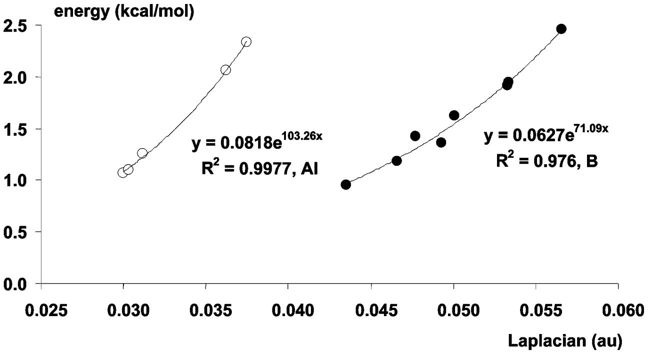


Figure 6. Relationship between the Laplacian of electron density at H···H BCP (in au) and the second-order energy lowering energy (eq 1, in kcal/mol): black circles, B−H···H−O; open circles, Al−H···H−O.

contacts and those interacting through Al−H···H−O. For both series correlations are good; both kinds of Lewis base centers, i.e., AlH_2 and BH_2, are well separated because the correlations are observed for **I** and **II** subsamples separately. Similar correlations between $\Delta E^{(2)}$ and the electron density were reported for the complexes formed between guanidine and formate with RNA bases through hydrogen bond interactions.[39]

Conclusions

The results of ab initio calculations performed on the species where intramolecular H···H contacts exist were analyzed. Additionally, the observations and findings were supported by AIM and NBO results. It was found that neither geometrical nor QTAIM characteristics are decisive if H···H contacts are attractive and stabilizing interactions, or whether they may be classified as dihydrogen bonds.

However, NBO results show that for some types of H···H contacts, the electron charge transfer from Lewis base to Lewis acid, the so-called $\sigma \rightarrow \sigma^*$ lowering energy, correlates well with a few other parameters usually treated as descriptors of H-bond strength. It is worth mentioning that such energy lowering exists for H···H interactions between a typical Lewis acid (OH bond) and typical Lewis base (BH_2 and AlH_2) even if the appropriate bond path with BCP was not detected. This shows that NBO could be very helpful to deepen the nature and to classify any interaction.

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