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Hydrogen Bonds with π and σ Electrons as the Multicenter Proton Acceptors: High Level ab Initio Calculations

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π-Electrons of acetylene and σ-electrons of molecular hydrogen were investigated as Lewis bases in different complexes. Hence high level ab initio calculations were performed up to the MP2/6-311++G(3df,3pd) level of approximation. It was found that species analyzed possess characteristics typical for H-bonded systems. The Bader theory was additionally applied; bond paths between proton and π-electrons of acetylene or σ-electrons of molecular hydrogen were detected with the corresponding bond critical points attributed to the proton−acceptor interactions. Numerous correlations between topological, geometrical and energetic parameters were also found. For example, the H···π or H···σ interaction is stronger for the shorter corresponding distance between the proton and the middle of C≡C or H−H bond. It is connected with the greater elongation of C≡C or H−H bonds and the greater transfer of electron charge from the Lewis base to the Lewis acid.

Introduction

Hydrogen bonding is one of the most often investigated phenomena in chemistry since it is responsible for numerous processes. For example, it often steers chemical reactions, controls biochemical processes, influences the arrangement of molecules in crystal structures, influences the geometries of molecules, etc.[1]

There are different types of hydrogen bond interactions; those where the proton donor (X) and the proton acceptor (Y) centers are well defined and designated as X−H···Y[1] and those where such centers may be named as “multicenter” ones.[2] O−H···O, N−H···O, and N−H···N are examples of the former H-bonds with the proton donors and acceptors being electronegative atoms; they are well attributed to the early Pauling definition of hydrogen-bonding that “under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms, instead of only one, so that it may be considered to be acting as a bond between them. This is called the hydrogen bond.”[3] Pauling also pointed out that the hydrogen bond “is formed only between the most electronegative atoms” and that the proton acceptor should possess at least one free electron pair.[3] Some of the mentioned above X−H···Y systems with the well defined one-center atomic proton donor and one-center atomic proton acceptor may be attributed to the three center−four electron (3c−4e) hydrogen bonds described by Gilli and co-workers.[4] X and Y should be electronegative according to the definition of Pauling; however, Pimentel and McClellan considered also cases of C−H···Y interactions as hydrogen bonds.[5] The latter interactions were found and analyzed in crystal structures.[6] However the possibility that a C−H bond with a nonelectronegative carbon atom acts as a proton donor was first criticized and commonly accepted after the appearance of the study of Taylor and Kennard.[7] In the latter, the authors performed the statistical and refined analyses on the samples taken from the Cambridge Structural Database.[8] X−H···C or even C−H···C interactions have been also detected and classified as hydrogen bonds.[9]

It was found that the acidity of the C−H bond in hydrogen bonds increases in the following order: $C(sp^3)-H < C(sp^2)-H < C(sp)-H$, and hence, the strength of the C−H···Y hydrogen bonds increases in the same order; the corresponding calculations confirming that finding were performed for C−H···O systems[10] or for C−H···S and C−H···N ones.[11] It was found in numerous studies that the carbon atom may be involved in H-bonds (as X-donor or Y-acceptor) since it possesses an excess of negative charge. If the carbon atom is an acceptor center, thus, it does not possess the free electron pair as it was pointed out in the Pauling definition of hydrogen bonding. Hence the X−H···C interaction may not be classified as the 3c−4e system. The C−H···Y and X−H···C interactions were described and systematized in detail by Desiraju and Steiner,[9d] but the justification that they may be classified as H-bonds was presented early on, also by Pimentel and McClellan.[5] The existence of a C-atom as the proton acceptor was often the subject of discussions and controversy. Since the negatively charged carbon atom as the proton acceptor has sp or at least sp^2 hybridization, thus, it is often explained that π-electrons are acceptors of protons. Hence X−H···π or C−H···π systems are often considered as hydrogen bonds.[9d] However, they are not the three center H-bonds since the proton acceptors are multicenter ones. Simple X−H···π systems were investigated early both experimentally[12] and theoretically.[13] Spectroscopic studies are very well-known for C_2H_2···HF, C_6H_6···HF, and the other T-shaped complexes.[14] π-electrons, especially those of phenyl rings, are often acceptors of protons in crystal structures.[15] The crystal structure of $[H_3O.3C_6H_6]^+ [CHB_{11}Cl_{11}]^-$ C_6H_6[16] is one recent example where O−H···π hydrogen bonds exist since the H_3O^+ is surrounded by three benzene molecules. The calculations for that system were also carried out.[17]

There are also the other multicenter proton acceptors: those possessing σ-electrons. The molecular hydrogen is an example of such an acceptor. The calculations were carried out on a NH_4^+···H_2 complex[18] and further on the other complexes PH_4^+···H_2, AsH_4^+···H_2, SbH_4^+···H_2, and BiH_4^+···H_2 and also on larger clusters containing a greater number of H_2 molecules.[19] The latter may be named as charge assisted hydrogen bonds since the proton donors are positively charged. However also the HCCH···H_2 and FCCH···H_2 neutral complexes were

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TABLE 1: Classification of Hydrogen Bonds

X−H···Y H-bond	more detailed characterization	examples
one center proton and one center acceptor	Pauling type H−bond (3c−4e)	O−H···O, N−H···O, N−H···N
	nonelectronegative X (3c−4e)	C−H···O, C−H···N, C−H···S
	nonelectronegative Y	O−H···C, N−H···C
	nonelectronegative X and Y	C−H···C
	X−H...H−Y (dihydrogen bond)	N−H···H−Re, C−H···H−C, O−H···H−Be
multicenter Y or/and X	multicenter proton acceptor	X−H···π, X−H···σ
	multicenter proton donor and proton acceptor	$\pi\cdots H^+\cdots\pi$, $\pi\cdots H^+\cdots\sigma$, $\sigma\cdots H^+\cdots\sigma$

investigated; the calculations were carried out up to the MP2/6-311++G(3df,3pd) level of approximation indicating the binding energies for both complexes of −0.3 kcal/mol.[20] There are also the other, stronger bounded neutral X−H···σ complexes. For example, the F−H···H_2 T-shaped complex was investigated up to the MP2/aug-cc-pV5Z level of approximation showing the binding energy of −0.99 kcal/mol, the deformation energy as a result of complexation as well as the BSSE correction were included in these calculations.[2g] The calculations on $\pi\cdots H^+\cdots\pi$ interactions in $C_2H_2\cdots H^+\cdots C_2H_2$ and $C_2H_4\cdots H^+\cdots C_2H_2$ complexes were also carried out.[2f] For both complexes one $H^+\cdots\pi$ contact may be treated as a covalent interaction since it possesses the characteristics typical for covalent bonds, and the second $H^+\cdots\pi$ contact possesses the characteristics of intermolecular interaction.[2f] $\pi\cdots H^+\cdots\sigma$ and $\sigma\cdots H^+\cdots\sigma$ complexes were also analyzed since the calculations were carried out for the $C_2H_2\cdots H^+\cdots H_2$ and $H_2\cdots H^+\cdots H_2$ species.[2g] One can see that these species are the systems with multicenter acceptors as well as with multicenter donors. $C_2H_2\cdots H^+$, $C_2H_4\cdots H^+$, and $H_2\cdots H^+$ are multicenter donors (three center−two electron systems; 3c−2e). The latter species were investigated early on;[2] they exist in solar systems, and the experimental astrophysics investigations were performed on them;[21] they were also analyzed as the proton donors in H-bonded complexes.[2f,2g] Table 1 presents the new classification of hydrogen bonds proposed here which includes the above-mentioned multicenter systems.

Dihydrogen bonds (DHBs) have been investigated extensively since the mid 1990s by experimental[22] as well as the theoretical methods.[23] They were designated as $X{-}H^{+\delta}\cdots{}^{-\delta}H{-}Y$ systems where X−H is the typical proton donating bond and the second negatively charged hydrogen atom is the proton acceptor. The complexation leading to the formation of DHB causes changes similar as for conventional H-bonds. For example, the following complexes were investigated: $LiH\cdots H_2$, $LiH\cdots CH_4$, $LiH\cdots C_2H_6$, and $LiH\cdots C_2H_2$.[24] The authors found that the components of the interaction energy of the $LiH\cdots C_2H_2$ complex are similar to those of the water dimer; the main binding energy contributions come from the electrostatic energy, followed by the induction and dispersion energies, whereas for the other complexes, the partitioning is different. However, for the remaining complexes, the H···H interactions were not classified as dihydrogen bonds but as van der Waals interactions.[24] DHBs are also included within the classification presented in Table 1.

The aim of this study is to analyze different H-bonded systems with π-electrons and σ-electrons as proton acceptors. The same sample of proton donors was chosen for X−H···π and X−H···σ complexes to compare proton acceptor abilities of π-electrons and σ-electrons. Ab initio calculations for such complexes were performed, and the Bader theory[25] was applied to analyze H···π and of H···σ interactions.

Computational Details

The calculations have been performed with the *Gaussian 03*[26] set of codes on the following T-shaped complexes: $H^+\cdots C_2H_2$, $Li^+\cdots C_2H_2$, $Na^+\cdots C_2H_2$, $FH\cdots C_2H_2$, $C_2H_2\cdots C_2H_2$, $NH_4^+\cdots C_2H_2$, $H_2OH^+\cdots C_2H_2$, and $C_2H_2\cdots H^+\cdots C_2H_2$. The $H^+\cdots\pi$ intermolecular contacts exist for them, these are the contacts between the proton and the middle of the C≡C bond (π-electrons). The $Li^+\cdots\pi$ and $Na^+\cdots\pi$ interactions in $Li^+\cdots C_2H_2$ and $Na^+\cdots C_2H_2$ complexes are given for comparison. In other words, for these complexes, the acetylene molecule acts as the Lewis base and there are different Lewis acids. For the second sample of species analyzed here, the H_2 molecule acts as the Lewis base, and the Lewis acids are the same as for the first sample of complexes (with C_2H_2 Lewis base). The $H^+\cdots\sigma$, $Li^+\cdots\sigma$, and $Na^+\cdots\sigma$ intermolecular contacts for the latter complexes are analyzed. The molecular graphs of the selected moieties calculated here are given in Chart 1.

The calculations were carried out using the second-order Møller−Plesset perturbation method (MP2).[27] The Pople style 6-311++G(d,p), 6-311++G(2df,2pd) and 6-311++G(3df,3pd), basis sets[28,29,30,31] were used. Full optimizations have been performed, and all results of these optimizations correspond to energy minima since no imaginary frequencies were found. The binding energy for the analyzed complexes has been computed as the difference between the total energy of the complex and the energies of the isolated monomers and further has been corrected for the basis set superposition error (BSSE) using the counterpoise method.[32] It is worth mentioning that such an approach takes into account the deformation energy as a result of complexation since all complexes and their components (Lewis acids and Lewis bases separately) were optimized.

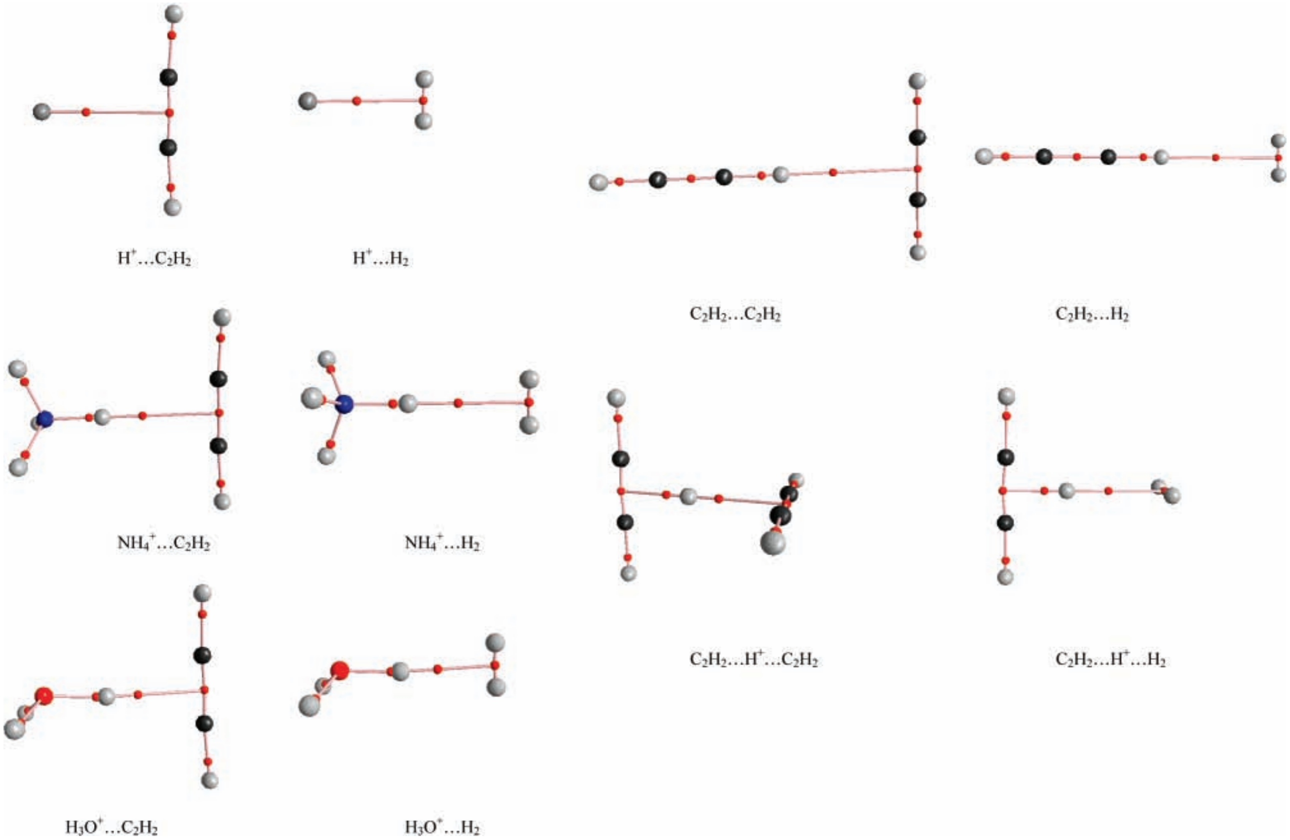
The CHelpG scheme[33] implemented within the Gaussian packages was also applied to calculate the atomic charges. The CHelpG procedure produces charges fitted to the electrostatic molecular potential (EMP) using a grid-based method. The application of the CHelpG method based on well-defined EMP expectation values yields much better estimates of intermolecular charge transfer than any arbitrary population analysis, where the corresponding relative error values were doubled reaching 50%.[34]

The quantum theory of atoms in molecules (QTAIM) of Bader[25] was applied to deepen the nature of the analyzed interactions. Hence critical points[35] of the above-mentioned $H^+(Li^+,Na^+)\cdots\pi$ and $H^+(Li^+,Na^+)\cdots\sigma$ contacts were found and analyzed in terms of electron densities and their Laplacians. The properties of BCPs were also studied in terms of local energy densities at BCPs: the local energy density at BCP ($H(r_{CP})$) and its components (the local kinetic energy density $G(r_{CP})$ and the local potential energy density $V(r_{CP})$). The AIM calculations were carried out using the AIM2000 program.[36]

Results and Discussion

Geometrical and Energetic Parameters. Table 2 presents some of geometrical parameters of the complexes analyzed here. MP2 results obtained with the use of 6-311++G(d,p), 6-311++G(2df,2pd), and 6-311++G(3df,3pd) basis sets are given. The $H^+\cdots\pi$ distances and C≡C bond lengths are presented for the species with acetylene as the Lewis base, and

CHART 1



correspondingly, the $H^+\cdots\sigma$ distances and H−H bond lengths are presented for the complexes with molecular hydrogen as the Lewis base. The corresponding distances of complexes with Li^+ and Na^+ are also included. Practically, for the first set of complexes, there is no difference between C≡C bonds calculated at MP2/6-311++G(2df,2pd) and MP2/6-311++G(3df,3pd) levels of approximation. For the $C_2H_2\cdots H^+\cdots C_2H_2$ moiety, this difference is the greatest one and is equal to 0.001 Å. The C≡C bond lengths calculated with the use of the 6-311++G(d,p) basis set differ more from the results calculated with the use of more saturated basis sets. In the case of $H^+(Li^+,Na^+)\cdots\pi$ distances the situation is more complicated; for complexes with H^+, Li^+, and Na^+ Lewis acids, there are not practically differences between MP2/6-311++G(2df,2pd) and MP2/6-311++G(3df,3pd) levels of approximation. The differences between the latter levels occur for the remaining complexes (Table 2).

The analogous findings are detected for complexes with molecular hydrogen. The differences for H−H bond lengths are not observed if 6-311++G(2df,2pd) and 6-311++G(3df,3pd) basis sets' results are compared. The results for 6-311++G(d,p) are different than those for the other basis sets. There are greater differences between $H^+(Li^+,Na^+)\cdots\sigma$ distances obtained with the use of different basis sets than such differences for H−H bonds.

The $H^+\cdots\pi$ ($H^+\cdots\sigma$) distance correlates with the elongation of the C≡C (H−H) bond length; the shorter contact, thus, the greater elongation. This is connected with the transfer of electron charge from the Lewis base to the Lewis acid as a result of complexation. Such a transfer of electron charge is a well-known phenomenon for H-bonded systems: from the proton acceptor (Lewis base) to the proton donor (Lewis acid).[37] All systems analyzed here may be treated as H-bonded ones except for the complexes with Li^+ and Na^+ ions. The transfer of electrons presented in Table 2 was calculated with the use of the ChelpG method at the MP2/6-311++G(3df,3pd) level of approximation. The greatest transfer of electron charge is observed for $H^+\cdots H_2$ and for $H^+\cdots C_2H_2$ Lewis acids. There is the great electron transfer for NH_4^+ and H_3O^+ Lewis acids. Generally the electron transfer is greater for acetylene Lewis base than for the H_2 molecule if the same Lewis acids are considered. One can expect that this transfer is connected with the strength of interaction since for the shorter $H^+\cdots\pi$ ($H^+\cdots\sigma$) distances the greater part of electronic charge is transferred. Figure 1 presents such relationships for two samples of complexes analyzed here, the first sample concerns complexes with C_2H_2, for the second sample, the H_2 molecule is the Lewis base. The second-order polynomial relationships were found for both samples. The species which may be classified as H-bonded are considered here since they contain a H^+ ion, and the systems with Li^+ and Na^+ ions are presented only for comparison but not included within regression lines.

One can expect that the transfer of electron charge from the proton acceptor is connected with the elongation of the corresponding bond, C≡C for acetylene and H−H for molecular hydrogen. Figure 2 shows the relationship between electron transfer and such an elongation. The elongation is related to the C≡C or H−H bonds not disturbed by complexation since it is estimated as $(r - r_0)/r_0$, where r_0 is the reference (C≡C or H−H) bond length not involved in any interaction and r is that bond length within the complex considered. The elongations are systematically greater for molecular hydrogen than for acetylene since for the latter the triple C≡C bond is less sensitive to the external agents than the single H−H bond.

Table 3 presents the binding energies of the complexes analyzed here. The results with and without the inclusion of the correction for BSSE are given. The BSSE error is usually less than 1 kcal/mol: only in few cases it exceeds 1 kcal/mol,

TABLE 2: Geometrical Parameters (in Å) of Complexes Analyzed Here[a]

C_2H_2 Lewis base	$H^+\cdots\pi$ distance			$C\equiv C$ bond length			electron transfer
	b	*c*	*d*	*b*	*c*	*d*	
$H^+\cdots C_2H_2$	1.123	1.117	1.117	1.235	1.228	1.228	744
$Li^+\cdots C_2H_2$	2.233	2.241	2.242	1.222	1.215	1.215	173
$Na^+\cdots C_2H_2$	3.157	3.165	3.165	1.220	1.214	1.214	127
$FH\cdots C_2H_2$	2.188	2.129	2.117	1.218	1.212	1.212	87
$C_2H_2\cdots C_2H_2$[e]	2.697	2.666	2.636	1.217	1.211	1.211	15
$NH_4^+\cdots C_2H_2$	2.104	2.073	2.074	1.220	1.214	1.214	182
$H_3O^+\cdots C_2H_2$	1.738	1.740	1.729	1.221	1.216	1.216	308
$C_2H_2\cdots H^+\cdots C_2H_2$	1.669	1.716	1.665	1.223	1.217	1.218	368

H_2 Lewis base	$H^+\cdots\sigma$ distance			H−H bond length			electron transfer
	b	*c*	*d*	*b*	*c*	*d*	
$H^+\cdots H_2$ (H_3^+)	0.757	0.754	0.754	0.874	0.871	0.871	667
$Li^+\cdots H_2$	2.010	2.011	2.011	0.747	0.746	0.745	69
$Na^+\cdots H_2$	2.439	2.464	2.470	0.743	0.742	0.741	42
$FH\cdots H_2$	2.115	1.994	1.983	0.740	0.739	0.739	46
$C_2H_2\cdots H_2$[e]	2.603	2.603	2.573	0.739	0.738	0.737	1
$NH_4^+\cdots H_2$	1.990	1.952	1.971	0.743	0.742	0.741	62
$H_3O^+\cdots H_2$	1.588	1.590	1.590	0.749	0.748	0.747	139
$C_2H_2\cdots H^+\cdots H_2$	1.958	1.900	1.899	0.744	0.733	0.743	99

[a] $H^+\cdots\pi$ (π, the middle of C−C bond), $H^+\cdots\sigma$ (σ, the middle of the H−H bond). Distances are given as well as $C\equiv C$ and H−H bond lengths. The corresponding distances for the complexes with Li^+ and Na^+ are included, MP2 method applied and the Pople-style basis sets. The last column present the electron transfer from C_2H_2 or H_2 molecules (in me) to the Lewis acid (6-311++G(3df,3pd) basis set). The H_2 length for isolated molecule amounts to 0.739, 0.737, and 0.737 Å for 6-311++G(d,p), 6-311++G(2df,2pd), and 6-311++G(3df,3pd) basis sets, respectively. The $C\equiv C$ bond length in the C_2H_2 isolated molecule amounts to 1.216, 1.211, and 1.211 Å for 6-311++G(d,p), 6-311++G(2df,2pd), and 6-311++G(3df,3pd) basis sets, respectively. [b] 6-311++G(d,p) basis set. [c] 6-311++G(2df,2pd) basis set. [d] 6-311++G(3df,3pd) basis set. [e] T-shaped complex.

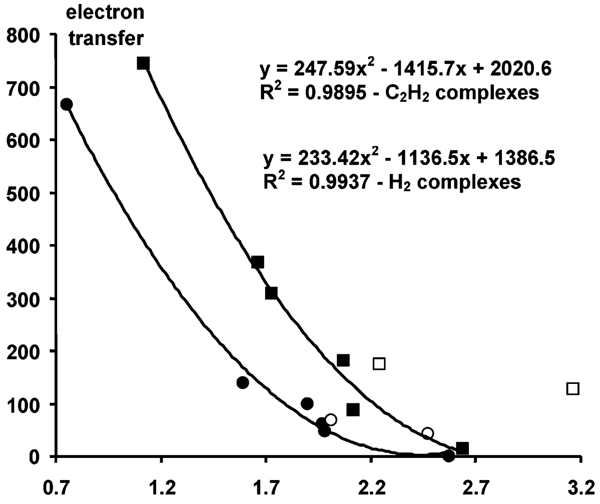


Figure 1. Relationships between H(Li, Na)$\cdots\sigma$ and H(Li, Na)$\cdots\pi$ distances (in Å) and the transfer of electron charge from the Lewis base to the Lewis acid (in milielectrons), squares correspond to complexes with C_2H_2 and circles to complexes with H_2. Black figures are attributed to $H\cdots\sigma$ and $H\cdots\pi$ interactions and white figures to complexes with Li^+ and Na^+ ions.

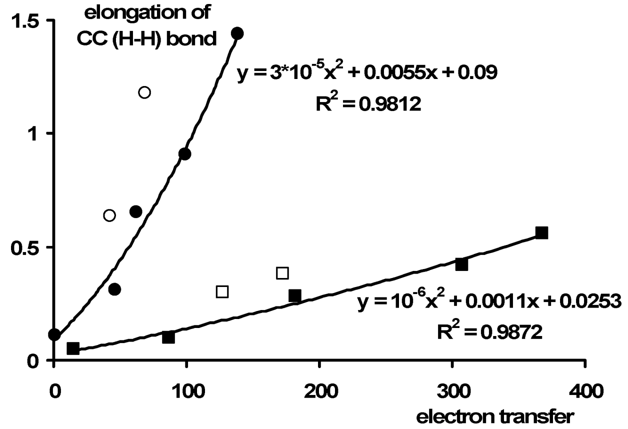


Figure 2. Relationships between the transfer of electron charge (in milielectrons) from the Lewis base to the Lewis acid and the elongation of the $C\equiv C$ or H−H bond (see the text), squares correspond to complexes with C_2H_2 and circles to complexes with H_2. Black figures are attributed to $H\cdots\sigma$ and $H\cdots\pi$ interactions and white figures to complexes with Li^+ and Na^+ ions. $H^+\cdots C_2H_2$ and $H^+\cdots H_2$ complexes are excluded from these relationships since the values corresponding to these species are out of the values' ranges of the other systems (see Table 2).

for $H^+\cdots C_2H_2$ and $H_3O^+\cdots C_2H_2$ complexes. However, for the $H^+\cdots C_2H_2$ complex, the percentage contribution of BSSE to the binding energy is less than 1%. This is because the binding energy in this case corresponds to covalent bonds' energies. For $H^+\cdots C_2H_2$ and $H^+\cdots H_2$, there are so-called three center−two electron systems (3c−2e) investigated both experimentally and theoretically and possessing the properties of typical covalent bonds.[38] There are meaningful $K^+\cdots\pi$ and $K^+\cdots\sigma$ (K = Li and Na) interactions which are greater for acetylene complexes since the proton affinity of acetylene is greater than of molecular hydrogen. The results of Table 3 show that the acidity of the Lewis acid increases in the following order: $C_2H_2 < FH < NH_4^+ < Na^+ \approx C_2H_2\cdots H^+ < H_3O^+ < Li^+ < H^+$; only the order of Na^+ and $C_2H_2\cdots H^+$ depends if acetylene or molecular hydrogen is the Lewis base. Figure 3 presents the second-order polynomial relationship between binding energies of two sub-samples of complexes considered here showing that the Lewis base properties are stronger for C_2H_2 than for H_2.

Topological Parameters. Table 4 presents the topological parameters derived from the Bader theory[25] and concerning bond critical points of $H^+(Li^+,Na^+)\cdots\pi$ and $H^+(Li^+,Na^+)\cdots\sigma$ contacts. It was found in numerous studies that the properties of BCP of intermolecular contact reflect the strength of interaction.[39] The characteristics of BCPs mentioned in the previous section and presented in Table 4 should correspond to the strength of interaction. The following parameters are shown in the table: the electron density at BCP (ρ_C), its Laplacian ($\nabla^2\rho_C$), the kinetic electron energy density at BCP (G_C), the potential electron energy density at BCP (V_C), and the total electron energy density at BCP (H_C). The total electron energy density H_C may be expressed by eq 1.[25]

$$H_C = G_C + V_C \tag{1}$$

The relationship between Laplacian and components of the local energy density H_C is given by the following equation (2):[25]

$$(h^2/4m)\nabla^2\rho(r_{BCP}) = 2G_C + V_C \tag{2}$$

This expression given in atomic units has the following form (3):

$$(1/4)\nabla^2\rho(r_{BCP}) = 2G_C + V_C \tag{3}$$

The sign of the Laplacian determines whether the negative potential energy or the positive kinetic energy is in excess of the virial ratio amounting to 2. In negative regions of Laplacian, the potential energy dominates, whereas in the positive regions,

TABLE 3: Binding Energies (in Kcal/mol) of the Complexes Analyzed Here

	without BSSE correction			with BSSE correction		
	a	*b*	*c*	*a*	*b*	*c*
C_2H_2 Lewis base						
$H^+\cdots C_2H_2$	−156.06	−155.72	−155.94	−153.71	−154.23	−154.45
$Li^+\cdots C_2H_2$	−20.64	−20.2	−20.23	−18.95	−19.52	−19.68
$Na^+\cdots C_2H_2$	−12.75	−12.71	−12.75	−11.48	−12.06	−12.16
$FH\cdots C_2H_2$	−4.41	−4.69	−4.89	−3.15	−3.89	−3.91
$C_2H_2\cdots C_2H_2$[d]	−1.97	−1.71	−1.85	−1.02	−1.36	−1.43
$NH_4^+\cdots C_2H_2$	−10.54	−11.21	−11.56	−9.22	−10.55	−10.74
$H_3O^+\cdots C_2H_2$	−19.57	−20.46	−20.65	−17.48	−19.22	−19.39
$C_2H_2\cdots H^+\cdots C_2H_2$	−15.87	−16.42	−16.96	−13.1	−15.2	−15.46
H_2 Lewis base						
$H^+\cdots H_2$	−105.78	−105.99	−105.97	−105.22	−105.76	−105.74
$Li^+\cdots H_2$	−5.69	−5.77	−5.75	−5.41	−5.69	−5.68
$Na^+\cdots H_2$	−2.79	−3	−3.03	−2.59	−2.9	−2.94
$FH\cdots H_2$	−0.84	−1.02	−1.14	−0.58	−0.82	−0.84
$C_2H_2\cdots H_2$[d]	−0.31	−0.3	−0.34	−0.15	−0.24	−0.28
$NH_4^+\cdots H_2$	−2	−2.4	−2.55	−1.78	−2.28	−2.34
$H_3O^+\cdots H_2$	−4.95	−5.57	−5.53	−4.51	−5.19	−5.19
$C_2H_2\cdots H^+\cdots H_2$	−2.36	−2.86	−3.02	−1.99	−2.49	−2.76

[a] 6-311++G(d,p) basis set. [b] 6-311++G(2df,2pd) basis set. [c] 6-311++G(3df,3pd) basis set. [d] T-shaped complex.

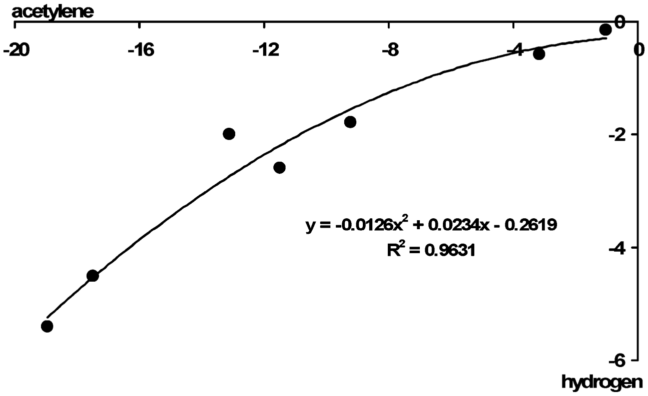


Figure 3. Relationship between the binding energy of the complex with C_2H_2 and the corresponding binding energy of the complex (the same Lewis acid) with H_2 (energies in kcal/mol). Even the better second-order polynomial correlation is detected if $H^+\cdots C_2H_2$ and $H^+\cdots H_2$ pair of complexes is included; however, the binding energies for the latter pair are out of the range of the remaining energies. Hence, the latter pair of systems is excluded.

there is the domination of the kinetic energy. The negative values of the Laplacian indicate covalent interactions in the shared systems, whereas positive values of the Laplacian are attributed to closed-shell interactions such as ionic and van der Waals interactions as well as typical, not strong hydrogen bonds.[25] Sometimes the negative V_C value outweighs G_C, but the Laplacian is still positive; this is often attributed to interactions which are at least partially covalent.[40] In such cases H_C is negative (eq 1). Sometimes the Laplacian is negative for H-bond interaction indicating its covalent character.[41] However systems with the negative H_C value and positive $\nabla^2\rho(r_{BCP})$ are more common, and they are often analized.[42]

Table 4 shows the negative values of Laplacians for $H^+\cdots\sigma$ and $H^+\cdots\pi$ contacts of $H^+\cdots H_2$ and $H^+\cdots C_2H_2$ complexes, respectively. These are multicenter 3c−2e bonds described previously, and as it was justified recently, they possess the features of typical covalent bonds.[38] For some of the complexes, Laplacians are positive but H_C values are negative (Table 4), indicating partly covalent interactions. In the case of acetylene acting as the Lewis base, the complexes with the following Lewis acids possess negative H_C's: NH_4^+, H_3O^+, and $C_2H_2\cdots H^+$. In the case of the second sub-sample, with the H_2 molecule as the Lewis base the H_C value at $H^+\cdots\sigma$ BCP is negative for the $H_3O^+\cdots H_2$ complex. If one excludes the H_3^+ 3c−2e species as the unique one possessing covalent interactions, thus, the results of $H_3O^+\cdots H_2$ are surprising since the H_2 molecule is a rather weak Lewis base. Additionally, the binding energy of 5.2 kcal/mol (MP2/6-311++G(3df,3pd) level of approximation, Table 3) for that complex is the value for which the positive $\nabla^2\rho(r_{BCP})$ and H_C values are typical.

TABLE 4: Topological Parameters (in au) of the Systems Analyzed Here[a]

	ρ_C	$\nabla^2\rho_C$	G_C	V_C	H_C
C_2H_2 Lewis base					
$H^+\cdots C_2H_2$	0.2059	−0.3220	0.0776	−0.2357	−0.1581
$Li^+\cdots C_2H_2$	0.0192	0.0907	0.0198	−0.0169	0.0029
$Na^+\cdots C_2H_2$	0.0124	0.0581	0.0118	−0.0091	0.0027
$FH\cdots C_2H_2$	0.0199	0.0532	0.0127	−0.0122	0.0005
$C_2H_2\cdots C_2H_2$[b]	0.0077	0.0235	0.0047	−0.0036	0.0011
$NH_4^+\cdots C_2H_2$	0.0251	0.0554	0.0147	−0.0156	−0.0009
$H_3O^+\cdots C_2H_2$	0.0534	0.0278	0.0265	−0.0461	−0.0196
$C_2H_2\cdots H^+\cdots C_2H_2$	0.0651	0.0126	0.0289	−0.0546	−0.0257
H_2 Lewis base					
$H^+\cdots H_2$	0.1380	−0.2458	0.0021	−0.0656	−0.0635
$Li^+\cdots H_2$	0.0126	0.0685	0.0141	−0.0110	0.0031
$Na^+\cdots H_2$	0.0075	0.0401	0.0079	−0.0058	0.0021
$FH\cdots H_2$	0.0109	0.0079	0.0381	−0.0062	0.0319
$C_2H_2\cdots H_2$[b]	0.0033	0.0124	0.0024	−0.0016	0.0008
$NH_4^+\cdots H_2$	0.0131	0.0406	0.0088	−0.0074	0.0014
$H_3O^+\cdots H_2$	0.0307	0.0536	0.0185	−0.0235	−0.005
$C_2H_2\cdots H^+\cdots H_2$	0.0167	0.0428	0.0100	−0.0094	0.0006

[a] The characteristics of $H^+(Li^+, Na^+)\cdots\pi$ (σ) BCP: the electron density at BCP (ρ_C), its Laplacian ($\nabla^2\rho_C$), the potential electron energy density (V_C), the kinetic electron energy density (G_C), and the total electron energy density at BCP (H_C). The results obtained at MP2/6-311++G(3df,3pd) level of approximation. [b] T-shaped complex.

Some correlations between topological and energetic parameters as well as geometrical ones were found for the complexes analyzed here. Figure 4 presents exponential relationships between the $H^+\cdots\pi$ ($H^+\cdots\sigma$) distance and the electron density at the corresponding BCP. The correlation coefficients for two sub-samples (one with C_2H_2 and the second one with H_2 as the proton acceptor) are very close to unity (Figure 4). The species containing Li^+ and Na^+ ions are excluded from these relationships but are presented in the figure for comparison. These correlations are not surprising since the proton−proton acceptor

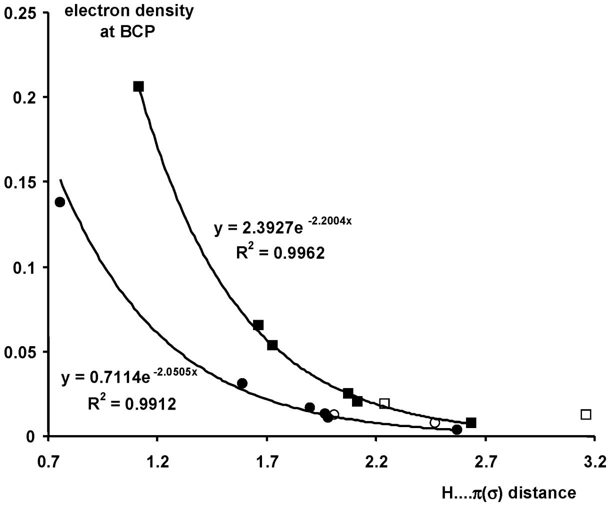


Figure 4. Relationships between the H(Li, Na)···σ and H(Li, Na)···π distances (in Å) and the electron density at the corresponding bond critical point (in au). Squares correspond to complexes with C_2H_2 and circles to complexes with H_2. Black figures are attributed to H···σ and H···π interactions and white figures to complexes with Li^+ and Na^+ ions.

distance (H···Y) is often treated as a measure of hydrogen bond strength.[1] The same holds for the electron density at BCP ($\rho_{H\cdots Y}$); it was shown in numerous studies that such density also expresses the H-bond strength since it correlates very well with the binding energy.[39] This is in line with the general statement that the distance between two interacting atoms (H-bonded, covalent bond, ionic interaction etc.) correlates with the corresponding electron density at BCP.[25c] Additionally, at least for H-bonds, $\rho_{H\cdots Y}$ is less sensitive to the diversity of the sample considered than the H···Y distance. It means that $\rho_{H\cdots Y}$ is a more universal parameter of the strength of interaction than any other geometrical descriptor. For example, for the relationship between the H···N distance and the binding energy if R—C≡N···H—X (X = F and Cl) complexes are considered two linear relationships are observed; one concerning the sub-sample with HF proton donor and the second sub-sample concerns HCl proton donor.[43] In the case of the relationship between $\rho_{H\cdots Y}$ and binding energy, the linear correlation coefficient is very close to unity, and it concerns the whole sample containing both HF and HCl proton donors. For sub-samples considered here, the correlations between the $H^+\cdots\pi(\sigma)$ distance and the binding energy were not detected; even if H_2 and C_2H_2 complexes are analyzed separately.

Figure 5 shows relationships (second-order polynomial regressions) between $\rho_{H\cdots Y}$ and the electron charge transferred from the Lewis base to the Lewis acid. The species containing Li^+ and Na^+ ions are also included in these correlations. The transfer of electrons from the proton acceptor to the proton donor is a typical feature of hydrogen-bonded systems.[37] Generally, for different kinds of interactions, the electron transfer is observed from the Lewis base to the Lewis acid.[44] That phenomenon is also observed for the complexes analyzed here and similarly as for the other H-bonds, it reflects here the strength of the interaction.

It was explained before that for covalent bonds and for very strong H-bonds the Laplacian of the electron density is negative. Sometimes the Laplacian value is positive but H_C is negative indicating H-bond interactions which are at least partly covalent in character. The potential electron energy density V_C is the negative component of Laplacian (and H_C); hence one may say that it is responsible for covalency. Figure 6 presents correlations between the electron transfer from the electron donor moiety to the Lewis acid and the V_C value. These are not linear relationships but the second-order polynomial correlations. This is in agreement with previous predictions that the covalency and consequently the strength of hydrogen bonding are attributed to the charge-transfer energy.[45] Further, it was calculated in detail that the delocalization interaction energy term (approximately the sum of polarization and charge-transfer energies) is attributed to covalency of interaction.[46]

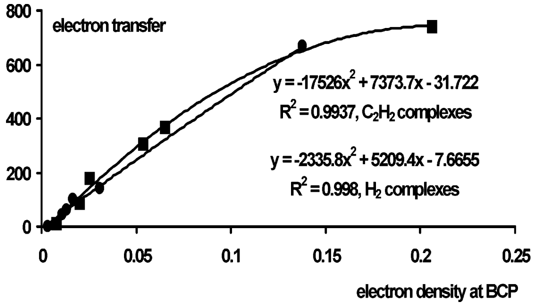


Figure 5. Relationships between the electron density at the H···σ and H···π bond critical point (in au) and the transfer of electron charge from the Lewis base to the Lewis acid (in milielectrons). Squares correspond to complexes with C_2H_2 and circles to complexes with H_2. Complexes with Li^+ and Na^+ ions are excluded from these correlations.

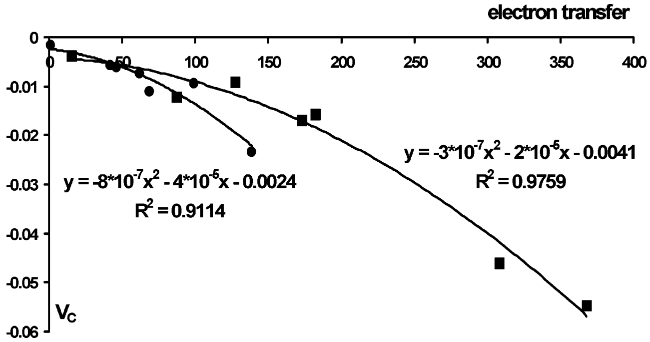


Figure 6. Relationships between the transfer of electron charge from the Lewis base to the Lewis acid (in milielectrons) and the potential electron energy density at the H(Li, Na)···σ or H(Li, Na)···π BCP (in au). Squares correspond to complexes with C_2H_2 and circles to complexes with H_2. $H^+\cdots C_2H_2$ and $H^+\cdots H_2$ complexes are excluded from these relationships since the values corresponding to these species are out of the values' ranges of the other systems (see Tables 2 and 4).

Summary

Different complexes with σ- and π-electrons of molecular hydrogen and acetylene, respectively, acting as Lewis bases, are investigated. It was found that if Lewis acids are the proton donating systems thus for these complexes stabilizing interactions designated as H···..σ and H···π may be classified as hydrogen bonds. The strength of these interactions correlates with the proton-acceptor distance and with the other topological and energetic parameters such as for example the electron density at H···σ or H···π bond critical point or their Laplacians. Additionally, the transfer of the electron charge from acetylene or molecular hydrogen to the Lewis acid is observed. That is accompanying by the elongation of C≡C or H—H bond. It was found here that some of interactions possess characteristics typical for covalent bonds or at least the partial covalency is observed. Even in the case of σ-electrons acting as Lewis base there is the $H_3O^+\cdots H_2$ complex with the partially covalent $H^+\cdots\sigma$ interaction.

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