Is a $\pi \cdots H^+ \cdots \pi$ Complex Hydrogen Bonded?

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Received: September 16, 2003; In Final Form: December 1, 2003

π-proton-donor and π-acceptor systems were investigated by ab initio quantum-chemical calculations. $C_2H_2 \cdots H^+ \cdots C_2H_2$ and $C_2H_4 \cdots H^+ \cdots C_2H_2$ complexes were optimized using the MP2 level of theory; 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3d,3p), and aug-cc-pVDZ basis sets were applied. Their geometrical and energetic characteristics were compared with characteristics of the other systems with conventional and unconventional H bonds. Such a comparison indicates that $\pi \cdots H^+ \cdots \pi$ complexes may be classified as hydrogen bonded. The binding energies for $C_2H_2 \cdots H^+ \cdots C_2H_2$ and $C_2H_4 \cdots H^+ \cdots C_2H_2$ calculated at the MP2/aug-cc-pVDZ level are equal to 15.0 and 10.4 kcal/mol, respectively (basis set superposition error included), which correspond to medium or strong H bonds. The Bader theory was applied to characterize the bond-critical points (BCPs) of $H^+ \cdots \pi$ contacts. The electron densities at $H^+ \cdots \pi$ BCPs also indicate that such systems possess hydrogen bonds of medium strength. To obtain better insight into the nature of these interactions, the variation−perturbation approach was applied to evaluate components of the interaction energy.

Introduction

There is great diversity in the interactions that may be classified as hydrogen bonded.[1] From a classical point of view, an H bond represents an interaction usually designated as X−H···Y, where X and Y are electronegative atoms; X−H is named as a proton-donating bond, and Y is an acceptor center.[2] Hence O−H···O, N−H···O, N−H···N, O−H···Cl, etc. are known as the typical, conventional H bonds. However, the existence of different C−H···Y hydrogen bonds in crystal structures has been claimed early on by a number of workers.[3,4] Taylor and Kennard have shown[4] that for C−H···Y systems H bonds with the oxygen atom acceptor (Y = O) are of the most frequent occurrence. In addition, other C−H···Y hydrogen bonds are also possible as are, for example, intramolecular C−H···S bonds existing in the crystal structures of thiazolidine derivatives.[5] These unconventional H bonds with the C−H proton-donating bonds found in crystal structures[3] have been commonly admitted after the appearance of the work of Taylor and Kennard, where the statistical justification for the existence of hydrogen bonds with C−H donating bonds was given.[4] There are other kinds of hydrogen bonds that often are classified as unconventional ones, among them dihydrogen bonds[6,7] and blue-shifting hydrogen bonds.[8]

It is also known that π electrons may act as proton acceptors for H bonds, e.g., $X-H \cdots \pi$ interactions.[9−11] The existence of intramolecular $X-H \cdots \pi$ H bonds was detected using the IR spectroscopic technique.[12] Also microwave measurements have been performed on complexes of HF and HCl with cyclopropane, acetylene, ethylene, benzene, and propyne.[13] The $X-H \cdots \pi$ hydrogen bonds were also found within many crystal structures, for example, crystal structures of 2- and 3-aminophenols[14] or 2-ethynyladamantan-2-ol,[15] for which the neutron-diffraction analysis was applied. The $H \cdots \pi$ interactions were investigated theoretically by applying ab initio techniques;[16,17] they were also studied with the use of the Bader theory.[16,18]

The aforementioned unconventional hydrogen bonds often have similar properties to conventional bonds. For example, for another kind of unconventional H bond, $X-H^{+\delta} \cdots {}^{-\delta}H-Y$ dihydrogen bonds, a correlation between the H-bond energy and the H···H distance and the elongation of the proton-donating bond due to the dihydrogen bond formation was found.[19,20] Such dependencies are commonly known for conventional O−H···O bonds.[9,10]

Recent theoretical studies concern gas-phase proton-transfer reactions between π-proton-donor and π-acceptor systems.[21] Calculations have been performed at the B3LYP/6-31++G(d,p) level of theory for the following proton transfer (PT) reactions; $HC(H)CH^+ + C_2H_2 \rightarrow C_2H_2 + HC(H)CH^+$; $HC(H)CH^+ + C_2H_4 \rightarrow C_2H_2 + H_2C(H)CH_2^+$; and $H_2C(H)CH_2^+ + C_2H_4 \rightarrow C_2H_4 + H_2C(H)CH_2^+$. Single-point CCSD(T)/6-31++G(d,p) studies have been also carried out for these systems, and the results show the crucial role of the electron correlation for them. One can see the reactants and the products of the aforementioned reactions; and also their transition states contain $\pi \cdots H^+ \cdots \pi$ systems, which may be treated as unusual hydrogen bonds.

The aim of this study is to compare the $\pi \cdots H^+ \cdots \pi$ systems existing within $HC(H)CH^+ + C_2H_2$ and $H_2C(H)CH_2^+ + C_2H_2$ species with the other known H-bonded complexes. The Bader theory[22] is applied to characterize the bond-critical points (BCPs) of $H^+ \cdots \pi$ contacts. The geometrical[4] and topological criteria[23,24] of the existence of hydrogen bonding are conformed for the investigated complexes.

Computational Methods

Calculations have been performed with the use of the Gaussian 98 set of codes.[25] Two complexes were investi-

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10.1021/jp036770p CCC: $27.50

gated: $C_2H_2 + H^+ + C_2H_2$ and $C_2H_4 + H^+ + C_2H_2$. Their geometries were optimized at the MP2 level of theory; different basis sets were applied: 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3d,3p), and aug-cc-pVDZ. Similar optimizations were also applied for the proton-donating systems $C_2H_2 + H^+$ and $C_2H_4 + H^+$. For both complexes as well as for donating systems, minima were found as confirmed by the lack of imaginary frequencies. π electrons of the acetylene molecule may be treated as proton acceptors for both complexes. Hence optimizations were also performed for the acetylene molecule. For all species, optimizations were performed without any symmetry constraints. If for any species symmetry appears, it is the result of full geometry optimization and not of restrictions applied at the beginning of the calculations.

The H-bond energy was calculated as a difference between the energy of the optimized structure of the complex and the energies of the monomers as is commonly established.[26] $C_2H_2 + H^+$ and $C_2H_4 + H^+$ donating systems correspond to monomers in the present study. The interaction energies have been corrected for the inherent basis set superposition error (BSSE) by using the full counterpoise method.[27]

The Bader theory[22] was also applied to find critical points and to characterize them. The AIM2000 program[28] was applied here, and the critical points were analyzed in terms of electron densities and their Laplacians.

The BCPs are the most often used in studies of intermolecular interactions. It is well known that the characteristics of the BCPs may be useful to estimate the H-bond strength.[29−31] Another measure of the hydrogen-bonding strength is also applied in this study

$$\Delta_{com} = \{[(r_{X-H} - r_{X-H}{}^0)/r_{X-H}{}^0]^2 + [(\rho_{X-H}{}^0 - \rho_{X-H})/\rho_{X-H}{}^0]^2 + [(\nabla^2\rho_{X-H} - \nabla^2\rho_{X-H}{}^0)/\nabla^2\rho_{X-H}{}^0]^2\}^{1/2} \quad (1)$$

where r_{X-H}, ρ_{X-H}, and $\nabla^2\rho_{X-H}$ correspond to the parameters of the proton donating bond involved in H bonding, the bond length, electronic density at H−X BCP, and the Laplacian of that density, respectively; $r_{X-H}{}^0$, $\rho_{X-H}{}^0$, and $\nabla^2\rho_{X-H}{}^0$ correspond to the same parameters of the X−H bond not involved in H-bond formation. The Δ_{com} parameter was introduced to avoid problems connected with the heterogeneity of the analyzed sample[32] since all of its terms, geometrical and topological, are normalized regarding the proton-donating bonds not involved in H-bond formation ($r_{X-H}{}^0$, $\rho_{X-H}{}^0$, and $\nabla^2\rho_{X-H}{}^0$ values).

To get a more detailed insight into the nature of hydrogen bonds, the interaction energy decomposition scheme was applied. Among various decompositions the rigorously defined perturbational approach with basis sets approaching the Hartree−Fock limit (also known as the symmetry-adapted perturbation theory (SAPT))[33,34] gives the most accurate results. However, accurate results obtained from SAPT are only known for small systems such as He_2 and $(H_2O)_2$.[35] Hence the less resource demanding variation−perturbation decomposition approach[36] was applied here. It was compared with the other variational decompositions[37,38] implemented in the GAMESS program,[39] and the results show its best agreement with the benchmark SAPT results for He_2 and $(H_2O)_2$.[40]

According to the variation−perturbation approach mentioned above, the interaction energy can be decomposed in the following way

$$\Delta = \Delta E_{EL}{}^{(1)} + \Delta E_{EX}{}^{(1)} + \Delta E_{DEL}{}^{(R)} + \Delta E_{CORR} \quad (2)$$

where $\Delta E_{EL}{}^{(1)}$ is the first-order electrostatic term, $\Delta E_{EX}{}^{(1)}$ is the first-order exchange component, and $\Delta E_{DEL}{}^{(R)}$ and ΔE_{CORR} correspond to the higher order delocalization and correlation terms.

TABLE 1: Geometrical (in Å) and Topological (in au) Parameters of the Proton-Donating Bonds and of $H^+\cdots\pi$ Donating Contacts Analyzed Here[a]

donating molecule	donating bond (XH)	r_{XH}	ρ_{XH}	$\nabla^2\rho_{XH}$
HF	FH	0.917	0.371	−2.839
H_2O	OH	0.960	0.364	−2.515
C_2H_2	CH	1.064	0.284	−1.024
$C_2H_2\cdots H^+$	$\pi\cdots H^+$	1.124	0.199	−0.286
$C_2H_2\cdots H^+$ [b]	$\pi\cdots H^+$	1.118	0.198	−0.228
$C_2H_2\cdots H^+$ [c]	$\pi\cdots H^+$	1.121	0.200	−0.264
$C_2H_2\cdots H^+$ [d]	$\pi\cdots H^+$	1.132	0.196	−0.348
$C_2H_4\cdots H^+$	$\pi\cdots H^+$	1.114	0.186	−0.253
$C_2H_4\cdots H^+$ [b]	$\pi\cdots H^+$	1.111	0.182	−0.161
$C_2H_4\cdots H^+$ [c]	$\pi\cdots H^+$	1.113	0.182	−0.161
$C_2H_4\cdots H^+$ [c]	$\pi\cdots H^+$	1.123	0.183	−0.257

[a] The calculations were performed by the MP2 method; for all cases except where indicated, the 6-311++G(d,p) basis set was used. [b] 6-311++G(2d,2p) basis set. [c] 6-311++G(3d,3p) basis set. [d] aug-cc-pVDZ basis set.

All components of interaction energy are calculated in the dimer basis set to eliminate the BSSE. The electrostatic term, $\Delta E_E{}^{(1)}$, is further decomposed into the long-range multipole component, $\Delta E_{EL-MTP}{}^{(1)}$, and the short-range penetration term, $\Delta E_{EL-PEN}{}^{(1)}$

$$\Delta E_{EL}{}^{(1)} = \Delta E_{EL-MTP}{}^{(1)} + \Delta E_{EL-PEN}{}^{(1)} \quad (3)$$

This decomposition approach was also applied for the $C_2H_2\cdots H^+\cdots C_2H_2$ and $C_2H_4\cdots H^+\cdots C_2H_2$ systems mentioned above.

Results and Discussion

Topological and Geometrical Parameters. It is possible to assume H-bond interactions if selected geometrical criteria are fulfilled.[4] For such systems the H···Y distance should be less than the sum of the corresponding H and Y sum of van der Waals radii; the elongation of the proton donating X−H bond and, hence, the red-shift of the X−H stretching vibration should be detected, etc. These criteria are controversial since the hydrogen bonding is mainly an electrostatic interaction and functions far beyond the aforementioned sum of van der Waals radii.[9,41] Additionally, the blue-shifting H bonds for which there is a shortening of the proton-donating bond were recently analyzed.[8]

The main problem related to $\pi\cdots H^+\cdots\pi$ systems existing within the $HC(H)CH^+ + C_2H_2$ and $H_2C(H)CH_2^+ + C_2H_2$ complexes and analyzed here is that there is no typical covalent proton-donating bonds. One may label them as the proton-donating $C_2H_2 + H^+$ and $C_2H_4 + H^+$ species. They all were optimized at the MP2 level of theory with the basis sets mentioned in the previous section, revealing the C_{2v} symmetry structure. For both donating systems, the 2-fold axis of symmetry passes through H^+ and the middle of the CC bond. For both of them, the mirror plane contains carbon atoms and H^+. The second mirror plane containing H^+ and the midpoint of the CC bond is perpendicular to the first one.

Table 1 shows the parameters of the $C_2H_2 + H^+$ and $C_2H_4 + H^+$ species and the parameters of the typical OH, FH, and CH proton-donating bonds. In addition, Table 1 presents also the topological characteristics of the BCPs of the XH-bonds:

TABLE 2: Geometrical (Å) and Topological (au) Parameters of π-Proton-Donor and π-Acceptor Systems Investigated Here and Parameters of Some H-Bonded Complexes, H-Bond Energies, and BSSE Corrections (kcal/mol)[a]

complex	r_{XH}	$r_{H\cdots Y}$	E_{HB}	BSSE	ρ_{XH}	$\nabla^2\rho_{XH}$	$\rho_{H\cdots Y}$	$\nabla^2\rho_{H\cdots Y}$
$(F\cdots H\cdots F)^-$	1.138	1.138	−39.87	4.51	0.174	−0.349	0.174	−0.349
$FH\cdots OCH_2$	0.923	1.869	−5.43	0.80	0.359	−2.787	0.022	0.107
$FH\cdots HLi$	0.950	1.399	−12.62	0.72	0.323	−2.327	0.041	0.057
$FH\cdots\pi$	0.923	2.186	−3.15	1.26	0.36	−2.755	0.016	0.053
$(H_2O)_2$	0.966	1.95	−4.45	1.65	0.356	−2.512	0.023	0.091
$HCCH\cdots OH_2$	1.070	2.198	−2.45	1.38	0.283	−1.033	0.014	0.052
$HCCH\cdots\pi$	1.067	2.697	−1.05	0.95	0.284	−1.029	0.007	0.019
$C_2H_2\cdots H^+\cdots C_2H_2$	1.298	1.667	−13.12	2.77	0.140	−0.179	0.064	0.026
$C_2H_2\cdots H^+\cdots C_2H_2$[b]	1.280	1.707	−14.60	1.81	0.143	−0.164	0.058	0.033
$C_2H_2\cdots H^+\cdots C_2H_2$[c]	1.269	1.720	−14.93	1.82	0.149	−0.197	0.056	0.042
$C_2H_2\cdots H^+\cdots C_2H_2$[d]	1.308	1.672	−15.03	2.42	0.138	−0.217	0.062	0.051
$C_2H_4\cdots H^+\cdots C_2H_2$	1.167	2.051	−8.73	2.17	0.172	−0.256	0.028	0.057
$C_2H_4\cdots H^+\cdots C_2H_2$[b]	1.174	2.024	−10.25	1.11	0.165	−0.177	0.030	0.054
$C_2H_4\cdots H^+\cdots C_2H_2$[c]	1.173	2.023	−10.51	1.40	0.169	−0.226	0.030	0.059
$C_2H_4\cdots H^+\cdots C_2H_2$[d]	1.186	2.018	−10.39	1.90	0.166	−0.265	0.030	0.058

[a] The calculations were performed by the MP2 method; for all cases except where indicated, the 6-311++G(d,p) basis set was used. [b] 6-311++G(2d,2p) basis set. [c] 6-311++G(3d,3p) basis set. [d] aug-cc-pVDZ basis set.

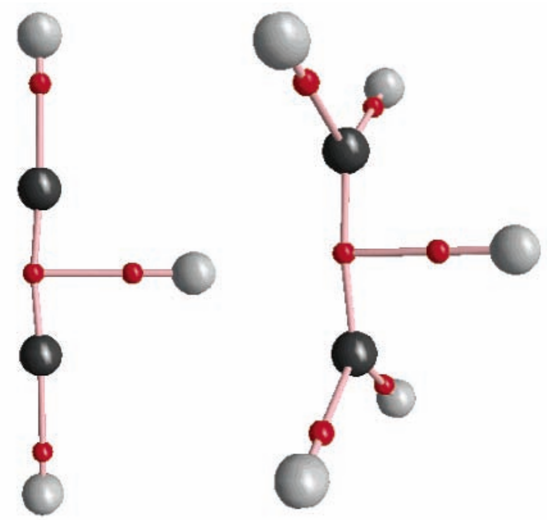

Figure 1. Molecular graphs of the $C_2H_2\cdots H^+$ and $C_2H_4\cdots H^+$ complexes.

electron densities, ρ_{XH}, and their Laplacians, $\nabla^2\rho_{XH}$. It should be mentioned that for $C_2H_2 + H^+$ and $C_2H_4 + H^+$ the proton-donating bond may be roughly attributed to the distance between H^+ and the middle of the $C\equiv C$ (or $C{=}C$) bond, simply, the $H^+\cdots\pi$ contact. Such meaning is in line with the Bader theory since the bond path connects two critical points, the attractor of H^+ and the BCP of the $C\equiv C$ ($C{=}C$) bond. Figure 1 presents molecular graphs of $C_2H_2 + H^+$ and $C_2H_4 + H^+$, the positions of the attractors corresponding to atomic nuclei are visible (big circles) as well as the positions of BCPs (small circles).

Table 2 displays the geometrical and topological parameters of the $C_2H_2 + H^+ + C_2H_2$ and $C_2H_4 + H^+ + C_2H_2$ complexes. Also, for comparison, Table 2 presents the geometrical and topological parameters of different typical, simple H-bonded complexes. The results for the presented systems were obtained within the MP2/6-311++G(d,p) level of theory, one of the levels that was applied for the $\pi\cdots H^+\cdots\pi$ systems analyzed here. One can see that the $\pi\cdots H^+\cdots\pi$ systems have features analogous to the other H bonds presented in Table 2. There is the elongation of the $H^+\cdots\pi$ (the CC midpoint) distance within both complexes, for $C_2H_2\cdots H^+$ from 1.124 Å for a donating species to 1.298 Å within the complex and for $C_2H_4\cdots H^+$ from 1.114 to 1.167 Å (the MP2/6-311++G(d,p) level).

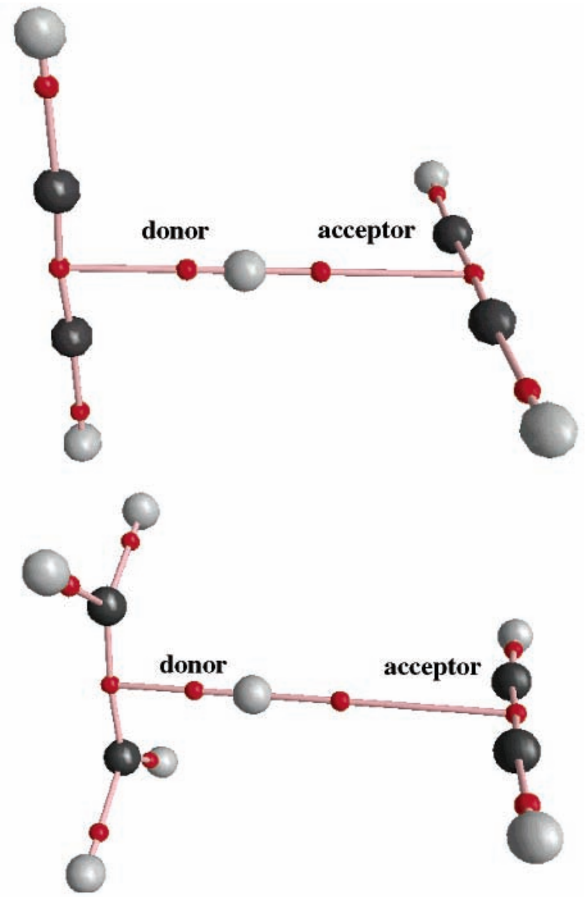

Figure 2. Molecular graphs of the $C_2H_2\cdots H^+\cdots C_2H_2$ and $C_2H_4\cdots H^+\cdots C_2H_2$ complexes.

Figure 2 presents the molecular graphs of the $C_2H_2\cdots H^+\cdots C_2H_2$ and $C_2H_2\cdots H^+\cdots C_2H_4$ complexes. For the $C_2H_2\cdots H^+\cdots C_2H_2$ complex, the C_2H_2 species are perpendicular and similar for the $C_2H_2\cdots H^+\cdots C_2H_4$ complex; the olefin CC bond is perpendicular to the acetylene molecule. The BCPs corresponding to the donor and to the acceptor are indicated (Figure 2); one can see that the first one is closer to the hydrogen atom than the second one, similarly as for the other types of H-bonds. For the $C_2H_2\cdots H^+\cdots C_2H_4$ complex, the proton is closer to C_2H_4 moiety; the $C_2H_4\cdots H^+$ is the proton-donating system as it was pointed out earlier. This is in line with the values of gas basicities for ethylene and ethyne of 155.7 and 147.4 kcal/mol, respectively.[42] Figure 3 shows the contour electron density maps for $C_2H_2\cdots H^+$ and its complex with acetylene, $C_2H_2\cdots H^+\cdots$

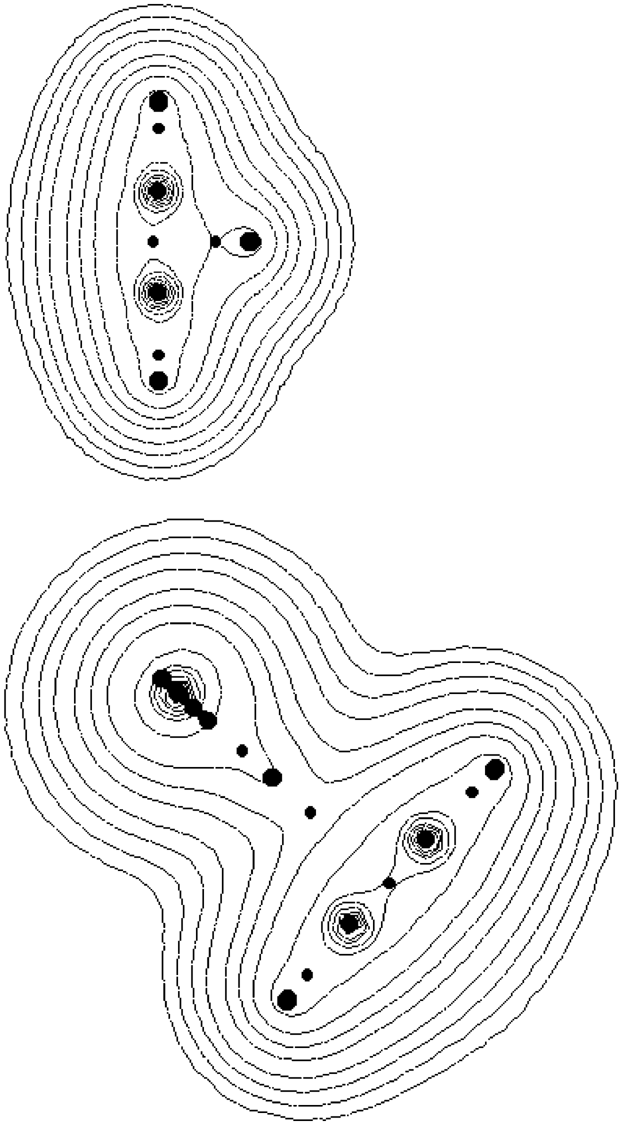

Figure 3. Contour maps of the electron density for (a) the $C_2H_2\cdots H^+$ proton-donating system and (b) the $C_2H_2\cdots H^+\cdots C_2H_2$ complex. The accepting moiety is visible at the right side of the picture; for both pictures, big circles correspond to attractors, while the small ones correspond to the BCPs.

C_2H_2. Again, big circles correspond to attractors and small ones to BCPs showing the existence of $\pi\cdots H^+$ donating and accepting contacts.

Table 2 presents the characteristics of these critical points. One can see that BCPs related to the $\pi\cdots H^+$ donors are similar to the BCPs of the conventional donating bonds such as OH, CH, and FH; there are the negative values of Laplacians for $C_2H_2\cdots H^+$ and $C_2H_4\cdots H^+$ (Table 1) and relatively high values of electron densities. There is a decrease in electron density after complexation. The same trend is observed for the other H-bonded systems (Tables 1 and 2).

It is usual that the increase in the values of the Laplacian due to complexation is observed for the proton-donating bond (Laplacian has a negative value; hence its modulus decreases due to the complexation). One notices it for typical H-bonds, except for the $HCCH\cdots OH_2$ complex (Tables 1 and 2) for which there is only a small reduction of electron density at C−H BCP and a decrease in the corresponding Laplacian. There is also an increase in Laplacian for $C_2H_2\cdots H^+$ and a decrease for $C_2H_4\cdots H^+$.

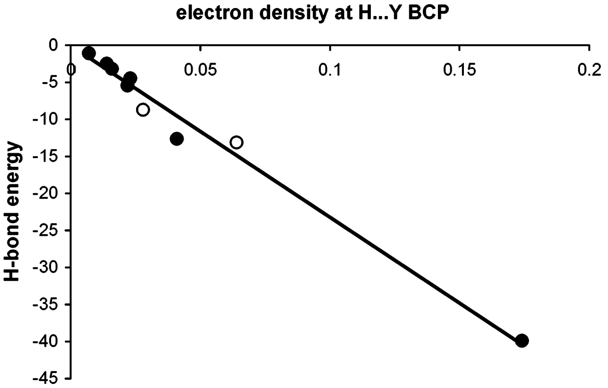

Figure 4. The relationship between the electron density at H···Y BCP (in au) and the H-bond energy (in kcal/mol). Calculations were performed at the MP2/6-311++G(d,p) level of theory.

For BCPs of $H^+\cdots\pi$ contacts within complexes, lower values of electron densities are predicted than the corresponding values for the BCPs of $H^+\cdots\pi$ donors. The positive values of the BCP Laplacians corresponding to accepting contacts indicate the existence of the closed-shell system interactions, similarly as for the other H-bonded systems. It is worth mentioning that the designations "contact" and "donor" are not considered here only conventionally. For the investigated systems, a proton is located between two π-electron systems. From a geometrical point of view, if the proton is closer to a given molecule, one can consider it as the donating system. The molecule that is farther away may be designated as an acceptor. Such designations could be controversial since there are not the typical covalent bonds for $\pi\cdots H^+\cdots\pi$ systems. However the values of Laplacians unequivocally indicate which interactions are for the closed-shell systems and which are not. For longer $H^+\cdots\pi$ contacts, there are the positive values of Laplacians, typical for van der Waals interactions. For shorter H-bonded contacts, there are negative Laplacian values, which are common for covalent bonds.

The values of electron density and its Laplacian for the BCP of the $H^+\cdots\pi$ (acceptor) contact are equal to (Table 2), 0.064 and 0.026 au for $C_2H_2\cdots H^+\cdots C_2H_2$ and 0.028 and 0.057 au for $C_2H_4\cdots H^+\cdots C_2H_2$, respectively (the MP2/6-311++G(d,p) level). These values are within the ranges of electron density and Laplacian proposed by Koch and Popelier[23] for the existence of hydrogen bonding. The typical range of the electron density at the H···Y BCP $\rho_{H\cdots Y}$ for the H bond is 0.002−0.035 au and 0.024−0.139 au for its Laplacian $\nabla^2\rho_{H\cdots Y}$.[23,24] The topological parameters may be treated as measures of H-bond strength since they correlate with H-bond energy and the other geometrical parameters. The electron density at H···Y BCP ($\rho_{H\cdots Y}$) is the most often used topological parameter correlating to H-bond strength.

Figure 4 presents the relationship between $\rho_{H\cdots Y}$ and the H-bond energy (E_{HB}) for the sample of various H bonds presented in Table 2. The $\pi\cdots H^+\cdots\pi$ systems are also included (designated in Figure 4 as open circles). The linear correlation for this dependence was found despite the inclusion of the $\pi\cdots H^+\cdots\pi$ systems varying significantly from the others (eq 4)

$$E_{HB}\ (\text{kcal/mol}) = -228.68\ \rho_{H\cdots Y}\ (\text{au}) - 0.2127 \qquad (R = 0.99) \quad (4)$$

The correlation shows that $\rho_{H\cdots Y}$ is a good H-bond strength descriptor even for heteregenous samples of complexes analyzed

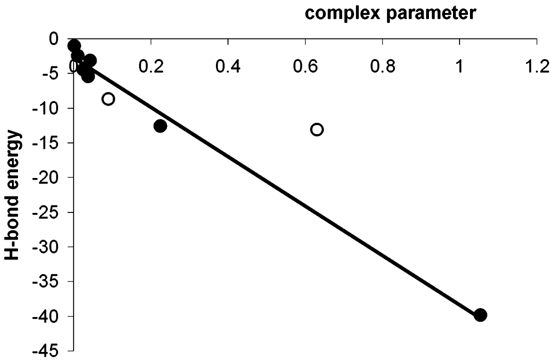

Figure 5. The relationship between the complex parameter and the H-bond energy (in kcal/mol). Calculations were performed at the MP2/6-311++G(d,p) level of theory.

here. This correlation indicates also that $\pi\cdots H^+\cdots\pi$ systems are of a similar nature to the other H bonds.

Figure 5 presents the correlation between the H-bond energy and the complex parameter (eq 1) introduced to describe the H-bonding strength.[43] The correlation coefficient for all systems is equal to 0.94, and if the $\pi\cdots H^+\cdots\pi$ bonds are excluded from this correlation, it is equal to 1.00. Equation 5 presents the linear regression for this dependence

$$E_{HB}\ (\text{kcal/mol}) = -30.779\ \Delta_{com} - 2.7424\ (R = 0.94) \quad (5)$$

One may explain the improvement of the correlation after the exclusion of $\pi\cdots H^+\cdots\pi$ systems in the following way. The complex parameter is based on the proton-donating bond characteristics, and for the $\pi\cdots H^+\cdots\pi$ complex, there are no typical covalent bonds. Additionally, there is unusual behavior of Laplacian for the BCP of the $H^+\cdots\pi$ donating contact for the $C_2H_4\cdots H^+\cdots C_2H_2$ complex as was mentioned earlier. However, correlation is very good even after the inclusion of these systems.

It is worth mentioning that the other characteristics of $\pi\cdots H^+\cdots\pi$ systems analyzed in this study are similar to those of typical H-bond interactions. For example, it is known that the formation of hydrogen bonds causes the transfer of the electron charge density from the acceptor to the proton-donating system.[26] At the MP2/6-311++G(d,p) level of theory, this transfer for a water dimer amounts to 19 me; for $C_2H_2\cdots H^+\cdots C_2H_2$, the transfer is equal to 381 me, and for $C_2H_4\cdots H^+\cdots C_2H_2$ it is 127 me. The greater electron transfers for π acceptors may be the common feature. For example, for the T-shaped configuration of the dimer of acetylene, this transfer is equal to 38 me (the MP2/6-311++G(d,p) level) despite the weak H bond for this complex.

For the $C_2H_2\cdots H^+\cdots C_2H_2$ complex, one of the acetylene molecules that connects more strongly with H^+ creates the donating moiety; the second acetylene molecule is an acceptor. Figure 6 presents the molecular graph of a transition state for the proton-transfer reaction for this complex. One can see that the $H^+\cdots\pi$ critical points are equivalent. The distances between the middle of the C≡C bonds and the proton are equal to each other; for both BCPs, the electron densities are equal to 0.099 au, and their Laplacians are equal to −0.058 au. The potential barrier height for the proton-transfer reaction calculated at the MP2/6-311++G(d,p) level is equal to 0.11 kcal/mol. The transition-state system has C_{2v} symmetry; acetylene molecules within are perpendicular to each other.

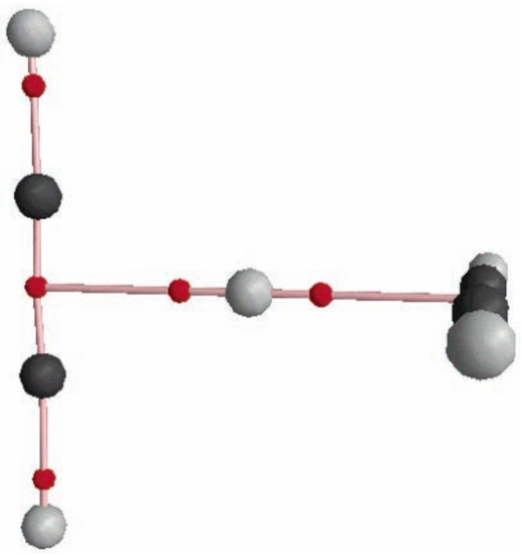

Figure 6. Molecular graph of the transition state of the $C_2H_2\cdots H^+\cdots C_2H_2$ complex.

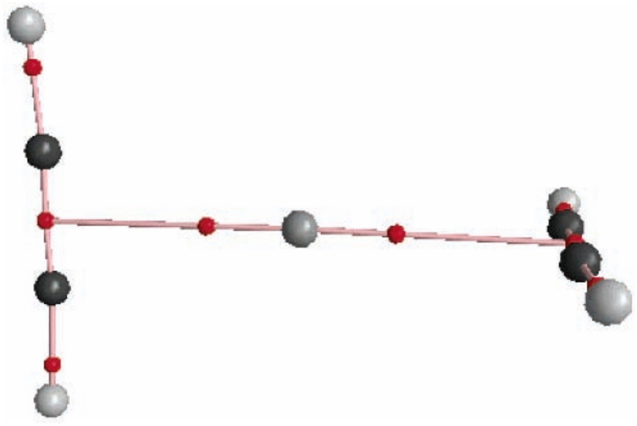

Figure 7. Molecular graph of the $C_2H_2\cdots Li^+\cdots C_2H_2$ complex.

Figure 7 presents, for comparison, the molecular graph of the similar complex of the lithium ion with two acetylene molecules, $C_2H_2\cdots Li^+\cdots C_2H_2$. The lithium ion is located exactly between two acetylene molecules, and the complex has C_{2v} symmetry. The distance between the middle of the C≡C bond and Li^+ is equal to 2.235 Å; two $Li^+\cdots\pi$ BCPs are equivalently arranged at the lithium ion; the electron density at the $Li^+\cdots\pi$ BCPs amounts to 0.019 au, and their Laplacians are equal to 0.091 au. This system is similar to the transition state of $C_2H_2\cdots H^+\cdots C_2H_2$; however, in this case, the complex represents a minimum-energy structure, no imaginary frequencies. Additionally, the $\pi\cdots Li^+\cdots\pi$ complex is similar to the typical H-bond or van der Waals interactions; Laplacians for both BCPs are positive, while for the transition state of $C_2H_2\cdots H^+\cdots C_2H_2$ for $H^+\cdots\pi$ interaction, the Laplacian at BCP is negative as for covalent bonds.

These findings are in line with ab inito and DFT results concerning transition states of resonance-assisted O−H···O, N−H···O, and O−H···N intramolecular H bonds, which were analyzed very recently.[44,45] For transition states of these systems, the negative values of Laplacians were also observed. Such situation was explained by Gilli and co-workers[44] in the following way. The hydrogen bond is mostly considered as an ionic or electrostatic interaction. However, for very strong H bonds, the evidence of covalent forces cannot be neglected, for some very strong O−H···O bonds, one should consider three-center-four-electron covalent bonds.[41] Hence H-bonds can be classified as shared interactions (mostly covalent) and closed-shell interactions (mostly electrostatic) according to the value

TABLE 3: Interaction Energy Terms (kcal/mol) for Complexes Analyzed in This Study

energy component[a]	$C_2H_2\cdots H^+\cdots C_2H_2$	$C_2H_4\cdots H^+\cdots C_2H_2$
$\Delta E^{(1)}$	22.473	6.718
$\Delta E_{EL}^{(1)}$	−24.456	−13.140
$\Delta E_{EL-MTP}^{(1)}$	−18.512	−9.504
$\Delta E_{EL-PEN}^{(1)}$	−5.994	−3.636
$\Delta E_{EX}^{(1)}$	46.929	19.858
$\Delta E_{DEL}^{(R)}$	−33.196	−11.154
ΔE_{SCF}	−10.722	−4.436
ΔE_{CORR}	−8.383	−5.254
ΔE_{MP2}	−19.106	−9.689

[a] $\Delta E_{MP2} = \Delta E_{SCF} + \Delta E_{CORR}$ and $\Delta E^{(1)} = \Delta E_{EL}^{(1)} + \Delta E_{EX}^{(1)}$.

TABLE 4: Interaction Energy Components of Selected Complexes According to Morokuma's Definition, Energy (kcal/mol)

energy component	$HOH\cdots OH_2$[a]	$F_3CH\cdots OH_2$[a]	$FH\cdots C_2H_2$[b]	$HCCH\cdots C_2H_2$[b]
electrostatic	−7.58	−7.06	−6.4	−2.2
exchange	4.24	4.14	6.3	2.1
polarization	−0.71	−0.69	−1.5	−0.3
charge transfer	−0.93	−0.97	−2.2	−0.5
correlation	−0.30	−0.25	−0.4	−0.5

[a] Reference 47. [b] Reference 17.

of the Laplacian of H···Y (Y is an acceptor for X−H···Y H-bond) BCP, negative for former and positive for the latter cases. Transition states of the resonance-assisted hydrogen bonds (RAHBs) according to the suggestion of Gilli can be classified as shared interactions for which negative values of Laplacians are common. One can see the similar situation of negative Laplacian of $H^+\cdots\pi$ for the transition state of $C_2H_2\cdots H^+\cdots C_2H_2$ system. On the other hand, for $C_2H_2\cdots Li^+\cdots C_2H_2$ with a Li^+ ion in the center of the system, there is the energy minimum and the positive Laplacian values of electron density at $Li^+\cdots\pi$ BCPs indicate the closed-shell interactions.

Interaction Energy Decomposition. It is well known that for hydrogen bond interactions the electrostatic term plays the most important role.[26] These characteristics were analyzed for the $C_2H_2\cdots H^+\cdots C_2H_2$ and $C_2H_4\cdots H^+\cdots C_2H_2$ systems. The components of interaction energy were calculated according to the scheme presented in the previous section (eqs 2 and 3). Table 3 presents the components of interaction for both complexes (according to the designations of eqs 2 and 3). One can see (Table 3) the crucial role of the higher-order attractive energy components ($\Delta E_{DEL}^{(R)}$ and ΔE_{CORR}) for both systems. It is also worth mentioning that the first-order term ($\Delta E^{(1)} = \Delta E_{EL}^{(1)} + \Delta E_{EX}^{(1)}$) is positive (repulsive) due to the high value of exchange energy. It is the consequence of the ionic character of the investigated systems.

These results may be compared with the other complexes. Several complexes linked by conventional and unconventional H bonds were investigated using the interaction energy decomposition proposed by Morokuma and co-workers.[46] Table 4 presents the results for different complexes.[17,47] For the trans-linear conformation of a water dimer with the O−H···O conventional H-bond, there is the dominant role of the electrostatic term (−7.58 kcal/mol) and a much smaller share of the other attractive energy contributions; the first-order energy is negative since the electrostatic term outweighs the exchange energy term. A similar situation is observed for the $CF_3H\cdots OH_2$ complex, which is connected through an unconventional C−H···O hydrogen bond. For T-shaped complexes with π electrons as proton acceptors, $FH\cdots\pi$ (C_2H_2) and $HCCH\cdots\pi$ (C_2H_2), the exchange and electrostatic terms are comparable; the remaining, second-order terms are smaller.

Interesting results were obtained very recently for dihydrogen bonds with the same acceptor, lithium hydride (LiH), $LiH\cdots H_2$, $LiH\cdots CH_4$, $LiH\cdots C_2H_6$, and $LiH\cdots C_2H_2$.[48] For these cases, the interaction energy was partitioned according to another intermolecular Møeller−Plesset perturbation theory scheme.[49] The main qualitative conclusions are as follows. For weaker H-bonded complexes with H_2, CH_4, and C_2H_6 donors, there is the large repulsive exchange term that outweighs the attractive electrostatic term; hence the first-order energy component is positive. For the stronger H-bonded $LiH\cdots C_2H_2$ complex, the energy partitioning is similar to complexes with typical H bonds as for the water dimer; the electrostatic term outweighs the exchange one. These results for dihydrogen bonds were obtained at the MP2/aug-cc-pVDZ(aD) and MP2/aug-cc-pVTZ(aT) levels of theory.[48]

Because of different partitioning schemes, it is difficult to compare quantitatively the previous results with those presented for the $C_2H_2\cdots H^+\cdots C_2H_2$ and $C_2H_4\cdots H^+\cdots C_2H_2$ systems, but one may point out qualitative conclusions. For $\pi\cdots H^+\cdots\pi$ systems, there is the positive first-order term (because of the great exchange energy term within) and the meaningful contribution of the correlation energy. These systems are similar to weak dihydrogen bonds. However, for $\pi\cdots H^+\cdots\pi$ systems, the exchange energy term is significantly greater than the electrostatic term. Additionally, there are significant higher-order attractive terms. It makes the $\pi\cdots H^+\cdots\pi$ H bonds at least of medium strength, while dihydrogen bonds with H_2, CH_4, and C_2H_6 donors are weak.

Additionally if we compare the total interaction energies presented in Table 3 with those of Table 2 (E_{HB}), one can see significant differences; it is connected with the positive deformation energy not included for the results of Table 3. For partitioning schemes, it is usual to calculate the interaction energy terms for the connection between rigid species. Hence a comparison of the results of Tables 2 and 3 shows that deformation energies for $\pi\cdots H^+\cdots\pi$ systems are of great importance; one can see the meaningful changes of donors (Table 1) due to the process of complexation (Table 2).

Summary

We conclude that $\pi\cdots H^+\cdots\pi$ complexes analyzed here may be treated as hydrogen bonded since their features are similar to other H bonds such as O−H···O, F−H···O, F−H···π, dihydrogen bonds, etc. Despite the lack of typical proton-donating covalent bonds for these systems, one may consider them as species that possess features of donors. The geometrical and topological parameters of $\pi\cdots H^+\cdots\pi$ systems change similarly as for typical H-bonds and correlate well with the H-bond energy. For both cases of complexes analyzed, π electrons of the acetylene molecule may be treated as acceptors. An analysis of the topological parameters confirms that statement. The characteristics of $H^+\cdots\pi$ BCPs (middle of C≡C bond) show that some of them have the same properties as covalent bonds; others are similar to typical closed-shell systems interactions. Hence, from a topological point of view, there are typical donors and typical acceptors for $\pi\cdots H^+\cdots\pi$ systems.

Additionally, the decomposition of the interaction energy performed indicates the unique nature of the $\pi\cdots H^+\cdots\pi$ interactions in comparison with the other H-bonded systems where usually the electrostatic term plays a crucial role in interactions.

Acknowledgment. The support from Grant No. 505/675 2003 (University of Łódź), NSF CREST No. 9805465, NSF EPSCoR 94475601, and ONR Grant N00014-98-1-0592 is gratefully acknowledged. Calculations have been partly carried out in Academic Computer Center—Cyfronet AGH Kraków.

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