J. Phys. Chem. A **2007,** *111,* 13537−13543

π−H···O Hydrogen Bonds: Multicenter Covalent π−H Interaction Acts as the Proton-Donating System

Sławomir Janusz Grabowski

Department of Crystallography and Crystal Chemistry, University of Łódź,
Pomorska 149/153, 90-236 Łódź, Poland

Received: August 31, 2007; In Final Form: October 5, 2007

The MP2 method and the Pople-style basis sets 6-311++G(d,p), 6-311++G(2df,2pd), and 6-311++G(3df,3pd) were used to perform calculations on $H_3O^+\cdots C_2H_2$ and $C_2H_3{}^+\cdots C_2H_2$ complexes and related species. Hydrogen bonds existing for the analyzed complexes were investigated as well as related π−H···O → π···H−O and π−H···π → π···H−π proton-transfer processes. For some of the complexes analyzed the multicenter π−H interaction possessing the properties of a covalent bond acts as a proton donor; more generally it is classified as the Lewis acid. The quantum theory of "atoms in molecules" (QTAIM) was also applied to deepen the nature of these interactions in terms of characteristics of bond critical points. The π−H···O, O−H···π, and π−H···π interactions analyzed here may be classified as hydrogen bonds since their characteristics are the same as or at least similar to those of typical hydrogen bonds. H···π interactions are common in crystal structures of organic and organometallic compounds. The analyses performed here show a continuum of such interactions since there are H···π contacts possessing the characteristics of weak intermolecular interactions on the one hand and π−H multicenter covalent bonds on the other. Ab initio and QTAIM results support the latter statements.

Introduction

There are numerous examples of π-electron systems acting as Lewis bases for inter- and intramolecular interactions.[1] This is frequently observed in crystal structures of organic and organometallic compounds. The Cambridge Structural database (CSD)[2] is useful as a source of such observations since it collects all needed data on crystal structures, and so it is possible to analyze various interactions, ranging from weak van der Waals interactions to covalent bonds within molecules. Various types of H···π interactions are common in crystal structures, for example, X−H···π systems are often classified as hydrogen bonds since X−H acts as the proton donor and π-electrons as the proton acceptor.[1a] X is usually an electronegative atom such as O, N, F, etc., but not only, as there are also C−H···π interactions possessing the characteristics of hydrogen bonds.[3]

The X−H···π interactions were analyzed both experimentally and theoretically. The crystal structure of $[H_3O\cdot 3C_6H_6]^+[CHB_{11}Cl_{11}]^-$ C_6H_6[4] is a recent example where O−H···π hydrogen bonds exist since the H_3O^+ is surrounded by three benzene molecules. The calculations for that system and related ones were also carried out.[5] One can also mention early spectroscopic studies on such species such as $C_2H_2\cdots HF$, $C_6H_6\cdots HF$, and other T-shaped complexes.[6] Theoretical investigations into the latter species and related ones were also performed.[7]

The theoretical calculations up to MP2/6-311++G(d,p) and MP2/aug-cc-pVDZ levels of approximation were carried out for T-shaped complexes of acetylene acting as Lewis base.[8] It was found that the binding energies for these systems are not negligible since they amount to −3.1, −1.9, −1.8, and −1.1 kcal/mol if the following Lewis acids are taken into account: HF, HCl, HCN, and HCCH (MP2/6-311++G(d,p) level, basis set superposition error correction included). It was found that these complexes are connected through X−H···π contacts which may be attributed to hydrogen bonds since they possess typical characteristics of the latter interactions. For example, there is the electron transfer from the proton acceptor (acetylene) to the proton donor. Such a transfer is in the range of 33−56 millielectrons for the analyzed complexes. This is much more than a transfer of 23 millielectrons for the translinear water dimer calculated at the same MP2/6-311++G(d,p) level of approximation.[9] The T-shaped benzene dimer is an example of C−H···π interactions with the binding energy of about −1 kcal/mol. Certainly, the latter value depends on the level of approximation applied.[10] The results based on QTAIM theory (quantum theory of atoms in molecules)[11] show relatively low electron densities for bond critical points (BCPs) corresponding to H···π interactions if compared with the other hydrogen bonds like O−H···O ones. The values of Laplacians for BCPs of such H···π contacts are positive.[12]

The other complexes with the crucial role of π-electrons were also analyzed. These are, for example, $C_2H_2\cdots H^+\cdots C_2H_2$ and $C_2H_4\cdots H^+\cdots C_2H_2$ systems where the proton is closer to one of π-electron species.[13] In other words, for each of these complexes there are two H···π interactions, one of them is covalent and the other has the characteristic features of closed-shell interactions. Thus, the last-mentioned complexes may be designated as $C_2H_3{}^+\cdots C_2H_2$ and $C_2H_5{}^+\cdots C_2H_2$. For both of them the π−H···π interactions were classified as the unique, special type of hydrogen bond where π-electrons act as the proton donor and also as the proton acceptor. $C_2H_3{}^+$ and $C_2H_5{}^+$ are proton-donating multicenter systems (three-center−two-electron systems, 3c−2e). These species were investigated early on;[14] they exist in solar systems, and experimental astrophysics investigations were performed on them;[15] they were also analyzed as the proton donors in H-bonded complexes.[13] The π−H covalent interactions in $C_2H_3{}^+$ and $C_2H_5{}^+$ were analyzed and compared with the other covalent bonds.[16] Very recently the complexes

10.1021/jp076990t CCC: $37.00

with multicenter acceptors and donors were analyzed in detail.[17] Two classes of complexes were studied: with acetylene or with molecular hydrogen as the proton acceptors and with numerous proton donors. The following unique interactions, $\pi-\mathrm{H}\cdots\pi$, $\pi-\mathrm{H}\cdots\sigma$, and $\sigma-\mathrm{H}\cdots\sigma$, were also analyzed and classified as hydrogen bonds.[13b,17] Thus, it was justified to say that multicenter covalent interactions might act as the proton donors in hydrogen bonds if there were also multicenter acceptors.[17]

The aim of this study was to analyze the proton located between the π-electronic system and the typical electronegative center which might act as an acceptor or as a donor of proton. The simple $\mathrm{H_3O^+\cdots C_2H_2}$ complex and its derivatives were analyzed. Generally, the aim of this study was to check whether or not the system possessing the multicenter proton donor and a typical acceptor exists, for example, if the $\pi-\mathrm{H}\cdots\mathrm{O}$ interaction exists at all. Such a system would be possible if acetylene or any of its derivatives were characterized by greater proton affinity than water or any of water derivatives. Hence, appropriate complexes were considered as well as the proton-transfer reactions investigated. The Bader theory was used to characterize $\pi-\mathrm{H}$ and $\mathrm{O-H}$ covalent bonds as well as $\mathrm{H}\cdots\pi$ and $\mathrm{H\cdots O}$ closed-shell interactions. Besides, it seemed interesting to deepen the nature of $\pi-\mathrm{H}$ and $\mathrm{H}\cdots\pi$ interactions since numerous important biochemical processes with π-electrons involved are known.[18]

Computational Details

The calculations were carried out with the Gaussian 03[19] set of codes on the following complexes: $\mathrm{H_2OH^+\cdots C_2H_2}$, $\mathrm{HFOH^+\cdots C_2H_2}$, $\mathrm{C_2H_3^+\cdots OFH}$, $\mathrm{C_2H_3^+\cdots OF_2}$, $\mathrm{C_2H_3^+\cdots C_2H_2}$, $\mathrm{C_2Li_2H^+\cdots C_2H_2}$, and $\mathrm{C_2H_3^+\cdots C_2F_2}$. For these complexes there are unconventional charge-assisted, CAHB(+), hydrogen bonds, which may be designated as $\mathrm{O-H^+}\cdots\pi$, $\pi-\mathrm{H^+\cdots O}$, and $\pi-\mathrm{H^+}\cdots\pi$. For the first $\mathrm{O-H^+}\cdots\pi$ case, there is the conventional proton-donating Lewis acid (hydronium ion, $\mathrm{H_2OH^+}$, or its derivative, $\mathrm{HFOH^+}$). In the second case of $\pi-\mathrm{H^+\cdots O}$, π-electrons are the donor of proton since the $\pi-\mathrm{H}$ 3c−2e covalent bond acts as a Lewis acid. In the latter $\pi-\mathrm{H^+}\cdots\pi$ case, π-electrons are the proton-donating system as well as such electrons being the proton acceptor. For convenience in further descriptions and discussions the above-mentioned hydrogen bonds are designated as $\mathrm{O-H}\cdots\pi$, $\pi-\mathrm{H\cdots O}$, and $\pi-\mathrm{H}\cdots\pi$. This is more justified since the proton designated as $\mathrm{H^+}$ is significantly devoid of positive charge in the systems analyzed here because of the electron charge transfer.

It can be seen that two pairs of tautomeric forms are analyzed here, and hence the transition states corresponding to the following proton-transfer processes are also taken into account: $\mathrm{HFOH^+\cdots C_2H_2} \Leftrightarrow \mathrm{HFO\cdots C_2H_3^+}$ and $\mathrm{C_2H_3^+\cdots C_2H_2} \Leftrightarrow \mathrm{C_2H_2\cdots C_2H_3^+}$.

All the calculations were performed by the MP2 method,[20] applying the Pople-style basis sets: 6-311++G(d,p), 6-311++G(2df,2pd), and 6-311++G(3df,3pd).[21] For seven complexes full optimizations were carried out leading to the minima since no imaginary frequencies were found; for the two above-mentioned cases the transition states corresponding to the processes of proton transfer were detected.

The binding energy for the analyzed complexes was computed as the difference between the total energy of the complex and the energies of the isolated monomers and were further corrected for the basis set superposition error (BSSE) using the counterpoise method.[22] It is worth mentioning that such an approach takes into account the deformation energy as a result of complexation[23] since all the complexes and their components (Lewis acids and Lewis bases separately) were optimized.

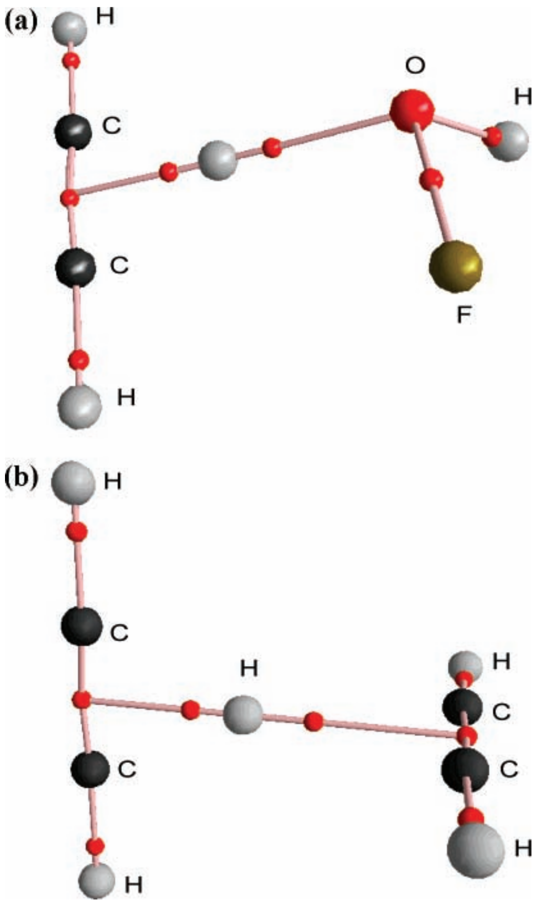

Figure 1. Molecular graphs of complexes with $\pi-\mathrm{H\cdots O}$ or $\pi-\mathrm{H}\cdots\pi$ hydrogen bonds, big circles correspond to attractors, small ones to bond critical points. (a) $\mathrm{C_2H_3^+\cdots OHF}$; (b) $\mathrm{C_2H_3^+\cdots C_2H_2}$.

The CHelpG scheme[24] 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 the 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%.[25]

The quantum theory of atoms in molecules was applied to deepen the nature of the analyzed interactions. Hence, BCPs[26]- of the before-mentioned $\mathrm{H}\cdots\pi$, $\pi-\mathrm{H}$, $\mathrm{H\cdots O}$, and $\mathrm{O-H}$ contacts and covalent interactions were found and analyzed in terms of electron densities and their Laplacians. Additionally, BCPs for the corresponding contacts of transition states were analyzed. The properties of BCPs were also studied in terms of the local energy density at BCP (H_C) and its components: the local kinetic energy density, G_C, and the local potential energy density, V_C. The AIM calculations were carried out using the AIM2000 program.[27]

To my knowledge the systems with $\pi-\mathrm{H\cdots O}$ hydrogen bonds have not been analyzed yet; these are the complexes with 3c−2e proton-donating species possessing the characteristics of covalent bonds and one-center proton acceptors. Figure 1shows the molecular graphs of the complexes analyzed here and wherever such interactions exist. The other species investigated here are not illustrated since their molecular graphs are very similar to those presented, differing mainly in the proton position—closer to the oxygen center or to the π-electron system.

TABLE 1: Geometrical Parameters (in angstroms) and Electron Transfer (in Millielectrons) from the Neutral Species to the Protonated One[a]

	H···π distance				
complex	6-311++G(d,p) basis set	6-311++G(2df,2pd) basis set	6-311++G(3df,3pd) basis set	electron transfer	"proton" charge
$C_2H_3^+\cdots C_2H_2$	1.669	1.716	1.665	368	0.016
	1.298	1.267	1.288	621	
$H_3O^+\cdots C_2H_2$	1.738	1.74	1.729	308	0.184
$C_2H_3^+\cdots C_2F_2$	1.812	1.818	1.788	305	−0.003
	1.231	1.223	1.231	698	
$C_2Li_2H^+\cdots C_2H_2$	2.586	2.524	2.526	83	0.040
	1.092	1.088	1.087	877	
$C_2H_3^+\cdots OF_2$	1.138	1.138	1.14	773	0.077
$C_2H_3^+\cdots OHF$	1.188	1.207	1.225	658	0.109
$FH_2O^+\cdots C_2H_2$	1.468	1.496	1.463	472	0.127
$C_2H_2\cdots H^+\cdots C_2H_2$[b]	1.439	1.46	1.456	494	0.013
	1.462	1.46	1.457	493	
$C_2H_2\cdots H^+\cdots OHF$[b]	1.382	1.319	1.313	581	0.116

[a] The distance between the latter species is between the proton and the middle of the CC bond; the results were obtained by the MP2 method with the use of a Pople-style basis set; the results concerning electron transfer and "proton" charge were obtained at the MP2/6-311++G(3df,3pd) level. [b] Transition state corresponding to the proton-transfer reaction.

Results and Discussion

π−H and H···π Interactions. Table 1 presents π−H and H···π distances of the investigated complexes. The H···π (or π−H) distance is the one between the proton located within the system and the middle of the C≡C bond. Table 1 also presents the electron transfer from acetylene or its derivative (from C_2H_2, C_2F_2, or C_2Li_2) to the remaining part of the complex containing proton. There are also ChelpG net atomic charges of "proton" positioned within complexes—within the π···O or π···π area. As can be seen, these net charges are far from the unity positive charge expected for the proton. The greatest positive charge for such "middle-positioned proton" is found for the $H_3O^+\cdots C_2H_2$ complex, and it amounts to +0.184 au. This occurs for the complex which does not possess its tautomeric form corresponding to the proton-transfer reaction. The "proton" is attributed to H_3O^+ hydronium ion, and it is impossible to transfer it within the proximity of C_2H_2. Thus, the $C_2H_3^+\cdots OH_2$ form does not exist because of a much greater proton affinity of H_2O than of C_2H_2. A reverse situation occurs for $C_2H_3^+\cdots OF_2$: no existence of the other tautomeric form, $C_2H_2\cdots HOF_2^+$, since C_2H_2 has greater proton affinity than OF_2; additionally for the $C_2H_3^+\cdots OF_2$ complex the centrally situated "proton" is slightly negatively charged −0.003 au; this charge is the closest to zero if compared with the other species analyzed (see Table 1). It can be concluded that the "proton" located within the investigated complexes is close to being neutral; in fact it is the H-atom since it has almost one electron attributed.

As mentioned before, geometrical parameters collected in Table 1 were obtained using three types of the Pople-style basis sets. The parameters mentioned here correlate with each other since the stronger H···π interaction corresponds to the shorter distance and also to the greater electron transfer from the corresponding π-electron species (acetylene or its derivative). These characteristics are attributed to H-bonded complexes since it is known that the shorter proton-acceptor distance usually corresponds to the stronger hydrogen bonding and that the H-bond formation is connected with the transfer of electron charge from the proton acceptor to the proton donor.[28] More generally, there is the electron transfer from the Lewis base to the Lewis acid for such a pair of interacting moieties.[29] Figure 2 presents the relationship between the H···π distance and the electron transfer. It is the exponential relationship with the correlation coefficient close to unity ($R^2 = 0.9965$); this may mean that the electron transfer roughly corresponds to the strength of hydrogen bond. The results presented here indicate that the analyzed complexes possess the characteristics typical of hydrogen bonds. The electron transfer from the acetylene or its derivative leads to the elongation of the corresponding C≡C bond. Figure 3 presents the relationship between H···π distance and the C≡C bond length. The second-order polynomial regression was found for this relationship ($R^2 = 0.9331$). An analogous relationship was observed before for a series of complexes where different Lewis acids interacted with acetylene molecule acting as the Lewis base.[17]

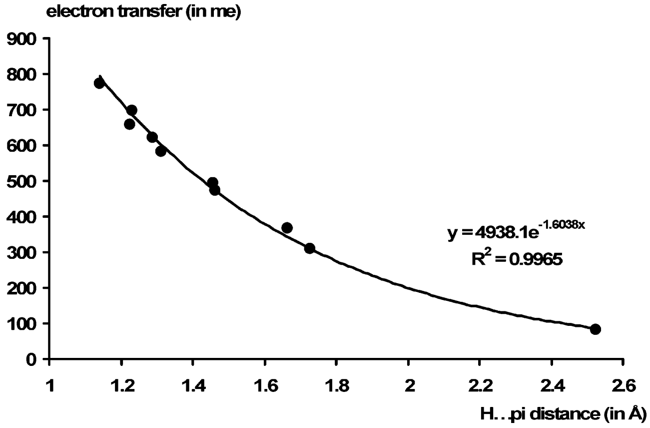

Figure 2. Relationship between H···π distance (in angstroms) and the electron transfer (in millielectrons) from the π-electron system.

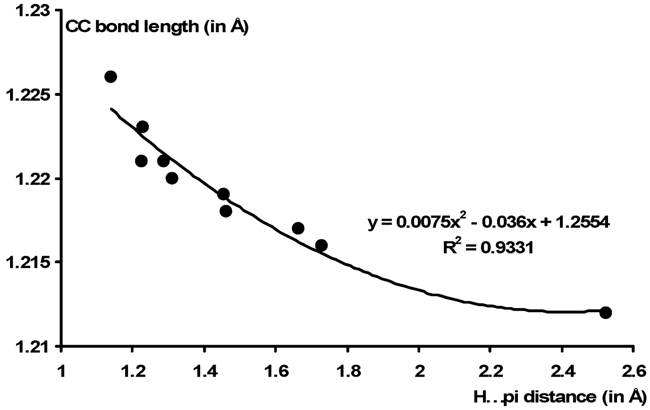

Figure 3. Relationship between H···π distance and the C≡C bond length (in angstroms).

TABLE 2: Topological Parameters of BCPs (in au), Corresponding H$\cdots\pi$ Distances Given in Table 1[a]

complex	ρ_C	$\nabla^2\rho_C$	G_C	V_C	H_C
$C_2H_3^+\cdots C_2H_2$	0.0639	0.0149	0.0286	−0.0534	−0.0248
	0.1454	−0.2059	0.0478	−0.1472	−0.0994
$H_3O^+\cdots C_2H_2$	0.0534	0.0278	0.0265	−0.0461	−0.0196
$C_2H_3^+\cdots C_2F_2$	0.0524	0.0341	0.0247	−0.0409	−0.0162
	0.164	−0.2486	0.0548	−0.1717	−0.1169
$C_2Li_2H^+\cdots C_2H_2$	0.0105	0.0287	0.0061	−0.005	0.0011
	0.2073	−0.2631	0.0942	−0.2541	−0.1599
$C_2H_3^+\cdots OF_2$	0.1979	−0.3298	0.0697	−0.2217	−0.1521
$C_2H_3^+\cdots OHF$	0.1667	−0.2842	0.0523	−0.1756	−0.1233
$FH_2O^+\cdots C_2H_2$	0.0989	−0.0782	0.0368	−0.0932	−0.0564
$C_2H_2\cdots H^+\cdots C_2H_2$[b]	0.1015	−0.0747	0.0376	−0.094	−0.0564
	0.1015	−0.0747	0.0376	−0.094	−0.0564
$C_2H_2\cdots H^+\cdots OHF$[b]	0.1377	−0.1998	0.0441	−0.1381	−0.094

[a] These are the following: electron density, ρ_C; Laplacian of the electron density, $\nabla^2\rho_C$; the kinetic electron energy density at BCP, G_C; the potential electron energy density at BCP, V_C; the total electron energy density at BCP, H_C; the results were obtained at the MP2/6-311++G(3df,3pd) level. [b] Transition state corresponding to the proton-transfer reaction.

Table 2 presents the topological parameters of the H$\cdots\pi$ (or π−H) interactions; the following parameters are taken into account: electron density at H$\cdots\pi$ BCP, ρ_C, its Laplacian, $\nabla^2\rho_C$, the electron energy density at BCP, H_C, and the components of the latter value, the kinetic electron energy density at BCP, G_C, and the potential electron energy density at BCP, V_C. It can be seen that different types of interactions are taken into account here; those corresponding to typical covalent ones since the Laplacian values for them are negative indicating the concentration of electronic charge between the interacting atoms. There are well-known relationships between the energetic topological parameters and Laplacian at critical point (eqs 1 and 2).[11c]

$$^1/_4\nabla^2\rho_C = 2G_C + V_C \tag{1}$$

$$H_C = V_C + G_C \tag{2}$$

For some of the interactions $\nabla^2\rho_C$ is positive and H_C is negative, which indicates the kind of interaction partly covalent in nature.[30] G_C is always positive and V_C is negative. Almost for all $\pi\cdots$H interactions at least H_C is negative. There is only one exception for the $C_2Li_2H^+\cdots C_2H_2$ complex, where the shorter $\pi\cdots$H contact corresponds to the multicenter covalent interaction and to the $C_2Li_2H^+$ proton-donating moiety; the other longer $\pi\cdots$H contact is between the proton and the C_2H_2 acceptor. And for the latter one both $\nabla^2\rho_C$ and H_C are positive indicating a weaker interaction attributed to closed-shell interactions.

Figure 4 presents the relationships between H$\cdots\pi$ distance and the topological parameters at the corresponding bond critical point. Empty squares and empty circles correspond to the G_C and V_C values, respectively, as written before, the former being always positive, the latter always negative. Full circles (H_C) and full triangles ($\nabla^2\rho_C$) illustrate the observations described above that $\pi\cdots$H interactions analyzed in this study are usually very strong or at least strong possessing characteristics of covalent bonds since H_C's are negative, except in the case of the $C_2Li_2H^+\cdots C_2H_2$ complex described earlier.

Figure 5 shows the dependence between the $\pi\cdots$H distance and the electron density at the corresponding bond critical point. The latter dependence is well approximated by the exponential relationship with a high value of the correlation coefficient (R^2 = 0.9995). It was checked in numerous studies that the shorter atom−atom contact which may be the rough measure of the strength of interaction corresponds to the greater electron density at the related bond critical point.[31] The latter correlation is in agreement with the exponential relation between the bond order and the electron density at the bond critical point.[11c]

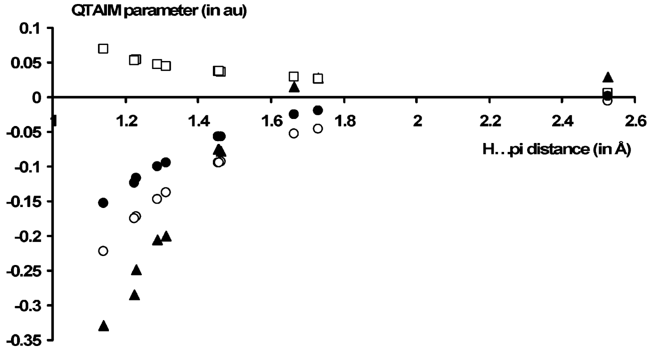

Figure 4. Relationships between H$\cdots\pi$ distance (in angstroms) and the topological parameters at the corresponding bond critical point (in au); empty squares (G_C), empty circles (V_C), full circles (H_C), and full triangles ($\nabla^2\rho_C$).

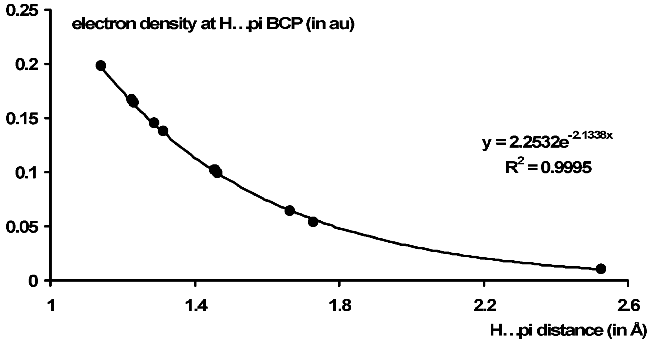

Figure 5. Relationship between H$\cdots\pi$ distance (in angstroms) and the electron density at the corresponding bond critical point (in au).

Figures 4 and 5 show the continuum of $\pi\cdots$H interactions ranging from covalent ones to weak closed-shell interactions. The latter case is poorly represented in those figures (only one complex of $C_2Li_2H^+\cdots C_2H_2$) because of specific and unique features of the complexes analyzed there. However, as briefly described in the introduction to this paper, weak $\pi\cdots$H interactions with both $\nabla^2\rho_C$ and H_C being positive are the most common, for example, in crystal structures. Such a continuum of $\pi\cdots$H contacts is well-known for the other interactions. For example, H$\cdots$F ones were considered and their continuum was detected since the F−H covalent bond is known, which may be weaker owing to the H-bond formation, and then the closed-shell H$\cdots$F intermolecular nonbonded interactions are possible.[32] A similar continuum was detected for H$\cdots$O[1d] or H$\cdots$H interactions.[33] It was also analyzed for a broad spectrum of various interactions, not only H-bonds, existing in a few crystal structures where the experimental electron density distribution was analyzed.[34] The latter investigations, especially those concerning hydrogen bonds, are in line with the statement given by Desiraju who claimed that hydrogen bonding is an interaction without borders since there is no "sharp" and noncontinuous passage from covalent bonds to hydrogen bonds on the one hand and from the hydrogen bonds to the van der Waals interactions on the other.[35]

O−H and H$\cdots$O Interactions. For some of the complexes analyzed here the oxygen atom center acts as a proton acceptor for $C_2H_3^+\cdots OF_2$ and $C_2H_3^+\cdots OHF$ species, and also oxygen is the proton donor for the $H_3O^+\cdots C_2H_2$ and $FH_2O^+\cdots C_2H_2$ complexes. Thus O−H covalent bonds and H$\cdots$O intermolecular contacts are analyzed as well as H$\cdots$O interactions of transition states. As mentioned in the previous section, the continuum of

TABLE 3: Geometrical Parameters (in angstroms) and Electron Transfer (in Millielectrons) from the Neutral Part of the Complex (H_2O, F_2O, or OHF) to the Remaining One[a]

	O−H or H···O			
complex	6-311++G(d,p) basis set	6-311++G(2df,2pd) basis set	6-311++G(3df,3pd) basis set	electron transfer
$H_3O^+\cdots C_2H_2$	1.044	1.043	1.046	508
$C_2H_3^+\cdots OF_2$	2.015	1.91	1.878	150
$C_2H_3^+\cdots OHF$	1.637	1.565	1.521	233
$FH_2O+\cdots C_2H_2$	1.201	1.18	1.204	401
$C_2H_2\cdots H^+\cdots OHF$[b]	1.284	1.36	1.367	303

[a] The distance between the latter part concerns the O−H covalent bond or H···O contact; the results were obtained by the MP2 method with the use of a Pople-style basis set; the results concerning electron transfer were obtained at the MP2/6-311++G(3df,3pd) level. [b] Transition state corresponding to the proton-transfer reaction.

TABLE 4: Topological Parameters of BCPs (in au), Corresponding O−H/H···O Distances Given in Table 3[a]

complex	ρ_C	$\nabla^2\rho_C$	G_C	V_C	H_C
$H_3O^+\cdots C_2H_2$	0.2715	−2.0808	0.0674	−0.655	−0.5876
$C_2H_3^+\cdots OF_2$	0.0317	0.0837	0.0238	−0.0267	−0.0029
$C_2H_3^+\cdots OHF$	0.0758	0.0698	0.0495	−0.0815	−0.032
$FH_2O^+\cdots C_2H_2$	0.1762	−0.6283	0.0738	−0.3021	−0.2283
$C_2H_2\cdots H^+\cdots OHF$[b]	0.1128	−0.0451	0.0639	−0.139	−0.0751

[a] These are the following: electron density, ρ_C; Laplacian of the electron density, $\nabla^2\rho_C$; the kinetic electron energy density at BCP, G_C; the potential electron energy density at BCP, V_C; the total electron energy density at BCP, H_C; the results were obtained at MP2/6-311++G(3df,3pd) level. [b] Transition state corresponding to the proton-transfer reaction.

TABLE 5: Binding Energies (kcal/mol): E_{bin}'s of the Systems Analyzed Here (including BSSE Correction)

	E_{bin}		
complex	6-311++G (d,p) basis set	6-311++G (2df,2pd) basis set	6-311++G (3df,3pd) basis set
$C_2H_3^+\cdots C_2H_2$	−13.1	−15.2	−15.46
$H_3O^+\cdots C_2H_2$	−17.48	−19.22	−19.39
$C_2H_3^+\cdots C_2F_2$	−2.9	−7.44	−7.81
$C_2Li_2H^+\cdots C_2H_2$	−2.9	−3.19	−3.72
$C_2H_3^+\cdots OF_2$	−1.8	−3.18	−3.93
$C_2H_3^+\cdots OHF$	−11.54	−12.92	−13.3
$FH_2O^+\cdots C_2H_2$	−24.87	−26.67	−27.06

H···O interactions was found; this was for the C−O−H···O═C ⇔ C═O···H−O−C proton-transfer reaction where O−H covalent bonds, H···O contacts, and the mid-in-length H···O distances of transition states were analyzed.[1d,36] That was detected from experimental neutron diffraction results on crystal structures. Table 3 presents such distances for the species analyzed here; there are two covalent bonds amounting to 1.046 and 1.204 Å, two intermolecular contacts of 1.878 and 1.521 Å; the H···O distance of 1.367 Å corresponds to the transition state. Table 3 also shows the transfer of electron charge from the species containing the oxygen atom to the one containing the hydrogen atom; the transfer concerns the H···O (or O−H) analyzed interaction. This means that H···O or O−H may be treated as a "channel" through which the electron transfer takes place. There is the dependence between H···O (O−H) distance and the amount of the electron charge transferred (Table 3). This is the exponential dependence with a high value of the correlation coefficient ($R^2 = 0.9941$). This may indicate that for very strong interactions, like those considered here, being similar in nature to hydrogen bonds and being at least partly covalent in nature the charge transfer is a driving force steering the geometry and behavior of the complexes. A similar relationship was observed in the previous section for $\pi\cdots$H interactions. The topological parameters collected in Table 4 support the findings concerning the strength of H···O interactions since the H_C's values of the corresponding BCPs are negative. There is the exponential dependence between O−H (H···O) distance (Table 3) and the electron density at the corresponding BCP (Table 4). The correlation coefficient for the latter relationship amounts to 0.9991.

Proton Transfer and Binding Energies. Table 5 presents the binding energies (BSSE correction included) of the analyzed complexes. It can be seen that the interactions considered here may be classified as very strong hydrogen bonds. For example, for the $FH_2O^+\cdots C_2H_2$ complex, the binding energy is equal to −27.1 kcal/mol (MP2/6-311++G(3df,3pd) level of approximation). For the corresponding tautomeric form of the proton-transfer reaction, $C_2H_3^+\cdots OHF$, the binding energy at the same level of approximation amounts to −13.3 kcal/mol. It seems that for both forms the strong H-bonds are detected because of similar proton affinity of OHF and C_2H_2 moieties. This is in line with the proton affinity principle that for lower values of ΔPA (the proton affinity difference between the H-bond donor and the acceptor) the two VB tautomeric forms may mix to a great extent.[1d,37] Actually, it is shown later that both $FH_2O^+\cdots C_2H_2$ and $C_2H_3^+\cdots OHF$ are very close to the corresponding transition state.

Two weakest interactions are detected for $C_2Li_2H^+\cdots C_2H_2$ and $C_2H_3^+\cdots OF_2$; the binding energies for them are equal to −3.7 and −3.9 kcal/mol, respectively. For the first complex the proton affinity for C_2Li_2 is larger than for C_2H_2 since the Li electron-donating substituent causes that C_2Li_2 is a stronger base than C_2H_2. Similarly, for the second complex the proton affinity is larger for C_2H_2 than for OF_2 since the electronegative fluorine atoms withdraw electron charge from oxygen making the latter a weaker base center. Considerable differences between the proton affinities of the donor and the acceptor are the reason why for the latter two complexes the tautomeric forms corresponding to the proton-transfer reaction do not exist. Initial calculations of $C_2H_3^+\cdots C_2Li_2$ and $C_2H_2\cdots HOF_2^+$ lead to a situation where both species collapse into $C_2Li_2H^+\cdots C_2H_2$ and $C_2H_3^+\cdots OF_2$, respectively.

Table 6 presents energy differences between the transition state of the proton-transfer reaction and the tautomeric form corresponding to local minima. The highest level MP2/6-311++G-(3df,3pd) results show that these differences are equal to 0.11, 0.04, and 0.08 kcal/mol for $C_2H_3^+\cdots C_2H_2$, $C_2H_3^+\cdots OHF$, and $FH_2O^+\cdots C_2H_2$ complexes, respectively. If the ZPVE correction is taken into account, there is no proton-transfer reaction barrier for these complexes at all. This means that for some of the species the equilibrium between π−H···O and O−H···π interactions exist in such a sense that proton moves freely between oxygen and π-electron base centers. The same concerns π−H···π systems; protons may move without any energetic barriers between π-electron moieties.

TABLE 6: Energy Differences (in kcal/mol) between the Transition State of the Proton-Transfer Reaction and the Tautomeric Form Corresponding to the Local Minima

complex	6-311++G (d,p) basis set	6-311++G (2df,2pd) basis set	6-311++G (3df,3pd) basis set
$C_2H_3^+\cdots C_2H_2$[a]	0.106	0.224	0.105
$C_2H_3^+\cdots OHF$	0.424	0.109	0.043
$FH_2O^+\cdots C_2H_2$	0.025	0.188	0.0845
difference[b]	0.398	−0.079	−0.042

[a] Both tautomers of the proton-transfer reaction are equivalent. [b] The energy difference between $C_2H_3^+\cdots OHF$ and $FH_2O^+\cdots C_2H_2$ tautomeric forms.

TABLE 7: Classification of Hydrogen Bonds

X−H···Y H-bond	more detailed characterization	examples
one-center proton donor 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 X or/and Y	multicenter proton acceptor	X−H···π, X−H···σ
	multicenter proton donor and proton acceptor	π−H···π, π−H···σ, σ−H···σ
	multicenter proton donor	π−H···O

Summary. π−H···O, O−H···π, and π−H···π interactions were analyzed here; it was found that energetic, geometrical, and QTAIM parameters indicate that they may be classified as hydrogen bonds. Besides, those interactions are rather strong since for almost all the complexes analyzed the total electron energy density at the proton···acceptor bond critical point, H_C, is negative.

It is worth mentioning that π−H···O hydrogen bonds were not analyzed before; generally speaking, such interactions are uncommon since there are multicenter proton-donating moieties for them and typical proton acceptors. Thus, it is very difficult to find systems where the proton affinity of π-electrons is greater than the proton affinity of a typical electronegative center. For some of the complexes analyzed here $C_2H_3^+$ is the proton donor and OF_2 or OHF are the proton acceptors; for such systems π−H···O hydrogen bonds exist. Hence, since a new kind of hydrogen bond is analyzed, the classification of different types of hydrogen bonds proposed recently[17] may be slightly modified; Table 7 presents this modified classification. There is a subclass of hydrogen bonds with multicenter proton donors and multicenter proton acceptors; such interactions were investigated recently.[17]

Additionally, the proton-transfer processes were discussed: π−H···O ⇔ O−H···π and π−H···π ⇔ π···H−π. For both reactions there are low barrier heights of the PT process: even if the ZPVE correction is included there is no barrier; this means that for such systems one can observe the free movement of proton within the π···O or π···π area.

Acknowledgment. Support has been provided by Grant No. 505/706 2007 (University of Łódź). I would also like to thank the Cracow Supercomputing and Networking Center as well as ICM for a generous allotment of computer time.

References and Notes

(1) (a) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press, Inc.: New York, 1999. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley & Sons: Hoboken, New Jersey, 2005. (c) *Hydrogen Bonding*—*New Insights*; Grabowski, S. J., Ed.; Springer, 2006. (d) Sobczyk, L.; Grabowski, S. J.; Krygowski, T. M. *Chem. Rev.* **2005**, *105*, 3513.

(2) Allen, F. H.; Davies, J. E.; Galloy, J. E.; Johnson, J. J.; Kennard, O.; Macrave, C. F.; Mitchel, E. M.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci*. **1991**, *31*, 187.

(3) Nishio, M.; Hirota, M.; Umezawa, Y. *The CH/π Interaction, Evidence, Nature, and Consequences*; Wiley-VCH, 1998.

(4) (a) Stoyanov, E. S.; Hoffmann, S. P.; Kim, K.-C.; Tham, F. S.; Reed, C. A. *J. Am. Chem. Soc*. **2005**, *127*, 7664. (b) Stoyanov, E. S.; Kim, K.-C.; Reed, C.A. *J. Am. Chem. Soc.* **2006**, *128*, 1948.

(5) Parthasarathi, R.; Subramanian, V.; Sathyamurthy, N.; Leszczynski, J. *J. Phys. Chem. A* **2006**, *111*, 2.

(6) (a) Legon, A. C.; Aldrich, P. D.; Flygare, W. H. *J. Chem. Phys*. **1982**, *76*, 2238. (b) Read, W. G.; Flygare, W. H. *J. Chem. Phys*. **1982**, *76*, 2238. (c) Shea, J. A.; Flygare, W. H. *J. Chem. Phys*. **1982**, *76*, 4857. (d) Rodham, D. A.; Suzuki, S.; Suenram, R. D.; Lovas, F. J.; Dasgupta, S.; Goddard, W. A., III; Blade, G. A. *Nature* **1993**, *362*, 735.

(7) (a) Tarakeshwar, P.; Choi, H. S.; Lee, S. J.; Lee, J. Y.; Kim, K. S. *J. Chem. Phys.* **1999**, *111*, 5838. (b) Kim, K. S.; Tarakeshwar, P.; Lee, J. Y. *Chem. Rev*. **2000**, *100*, 4145.

(8) Scheiner, S.; Grabowski, S. J. *J. Mol. Struct*. **2002**, *615*, 209.

(9) Domagała, M.; Grabowski, S. J.; Urbaniak, K.; Mlostoñ, G. *J. Phys. Chem. A* **2003**, *107*, 2730.

(10) (a) Hobza, P.; Havlas, Z. *Chem. Rev*. **2000**, *100*, 4253. (b) Lee, E. C.; Kim, D.; Jurečka, P.; Tarakeshwar, P.; Hobza, P.; Kim, K. S. *J. Phys. Chem. A* **2007**, *111*, 3446.

(11) (a) Bader, R. F. W. *Acc. Chem. Res*. **1985**, *18*, 9. (b) Bader, R. F. W. *Chem. Rev*. **1991**, *91*, 893. (c) Bader, R. F. W. *Atoms in Molecules, A Quantum Theory*; Oxford University Press: Oxford, 1990. (d) *Quantum Theory of Atoms in Molecules: Recent Progress in Theory and Application*; Matta, C., Boyd, R. J., Eds.; Wiley-VCH, 2007.

(12) Grabowski, S. J. *J. Phys. Chem. A* **2001**, *105*, 10739.

(13) (a) Grabowski, S. J.; Sokalski, W. A.; Leszczynski, J. *J. Phys. Chem. A* **2004**, *108*, 1806. (b) Grabowski, S. J.; Sokalski, W. A.; Leszczynski, J. *Chem. Phys. Lett*. **2006**, *432*, 33.

(14) (a) Lammertsma, K.; Ohwada, T. *J. Am. Chem. Soc*. **1996**, *118*, 7247. (b) Lischka, H.; Köhler, H.-J. *J. Am. Chem. Soc*. **1978**, *100*, 5297. (c) Vager, Z.; Zajfman, D.; Graber, T.; Kanter, E. P. *Phys. Rev. Lett*. **1993**, *71*, 4319. (d) Knoll, L.; Vager, Z.; Marx, D. *Phys. Rev. A* **2003**, *67*, 22506. (e) del Rio, E.; López, R.; Sordo, T. L. *J. Phys. Chem. A* **1998**, *102*, 6831.

(15) Glassgold, A. E.; Omont, A.; Guélin, M. *Astrophys. J.* **1992**, *396*, 115.

(16) Grabowski, S. J. *Chem. Phys. Lett*. **2007**, *436*, 63.

(17) Grabowski, S. J. *J. Phys. Chem. A* **2007**, *111*, 3387.

(18) (a) Burley, S. K.; Petsko, G. A. *Science* **1985**, *229*, 23. (b) McGaughey, G. B.; Gagne, M.; Rappe, A. K. *J. Biol. Chem*. **1998**, *273*, 15458. (c) Gazit, E. *FASEB J.* **2002**, *16*, 77.

(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vrevenrban, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2003.

(20) Møller, C.; Plesset, M. S. *Phys. Rev*. **1934**, *46*, 618.

(21) (a) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys*. **1984**, *80*, 3265. (b) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys*. **1980**, *72*, 650. (c) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. V. R. *J. Comput. Chem*. **1983**, *4*, 294.

(22) Boys, S. F.; Bernardi, F. *Mol. Phys*. **1970**, *19*, 553.

(23) (a) Grabowski, S. J. *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* **2006**, *102*, 131−165. (b) Grabowski, S. J.; Sadlej, A. J.; Sokalski, W. A.; Leszczynski, J. *Chem. Phys*. **2006**, *327*, 151.

(24) Breneman, C. M.; Wiberg, K. B. *J. Comp. Chem.* **1990**, *11*, 361.

(25) Szefczyk, B.; Sokalski, W. A.; Leszczynski, J. *J. Chem. Phys*. **2002**, *117*, 6952.

(26) Bader, R. F. W.; MacDougall, P. J.; Lau, C. D. H. *J. Am. Chem. Soc*. **1984**, *106*, 1594.

(27) Biegler- König, F. *AIM2000*; University of Applied Sciences: Bielefeld, Germany.

(28) Scheiner, S. *Hydrogen Bonding: A Theoretical Perspective*; Oxford University Press: New York, 1997.

(29) Lipkowski, P.; Grabowski, S. J.; Leszczynski, J. *J. Phys. Chem. A* **2006**, *110*, 10296.

(30) (a) Cremer, D.; Kraka, E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 627. (b) Rozas, I.; Alkorta, I.; Elguero, J. *J. Am. Chem. Soc.* **2000**, *122*, 11154.

(31) (a) Mó, O.; Yánez, M.; Elguero, J. *J. Chem. Phys*. **1992**, *97*, 6628. (b) Mó, O.; Yánez, M.; Elguero, J. *J. Mol. Struct. (THEOCHEM)* **1994**, *314*, 73. (c) Espinosa, E.; Molins, E.; Lecomte, C. *Chem. Phys. Lett*. **1998**, *285*, 170. (d) Grabowski, S. J. *J. Phys. Org. Chem*. **2004**, *17*, 18.

(32) Espinosa, E.; Alkorta, I.; Elguero, J.; Molins, E. *J. Chem. Phys.* **2002**, *117*, 5529.

(33) Grabowski, S. J.; Sokalski, W. A.; Leszczynski, J. *Chem. Phys*. **2007**, *337*, 68.

(34) Dominiak, P. M.; Makal, A.; Mallison, P. R.; Trzcinska, K.; Eilmes, J.; Grech, E.; Chruszcz, M.; Minor, W.; Wozniak, K. *Chem. Eur. J.* **2006**, *12*, 1941.

(35) Desiraju, G. R. *Acc. Chem. Res*. **2002**, *35*, 565.

(36) Grabowski, S. J.; Krygowski, T. M. *Chem. Phys. Lett.* **1999**, *305*, 247.

(37) (a) Malarski, Z.; Rospenk, M.; Sobczyk, L.; Grech, E. *J. Phys. Chem.* **1982**, *86*, 401. (b) Sobczyk, L. *Ber. Bunsen-Ges. Phys. Chem*. **1998**, *102*, 377. (c) Reinhardt, L. A.; Sacksteder, K. A.; Cleland, W. W. *J. Am. Chem. Soc*. **1998**, *120*, 13366. (d) Gilli, P.; Bertolasi, V.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc*. **2000**, *122*, 10405.