Unusual Hydrogen Bonds: H···π Interactions

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We present theoretical proof that the nature of the interactions existent in the complexes formed between hydrogen fluoride and a series of π-systems (acetylene, ethylene, cyclopropene, cyclobutadiene, and benzene) and three-memebered-ring derivatives (cyclopropane and tetrahedrane) is that of a hydrogen bond between the hydrogen atom and the π-cloud. Geometric and energetic data and mainly the study of the topology of the electronic density within the frame of the theory of atoms in molecules established by Bader have been used for this analysis.

Introduction

It has been extensively shown from several experimental results that weak interactions can be established between triple and double bonds, aromatic and cyclopropane rings, and X−H compounds (hydrogen halides, O−H, N−H, C−H derivatives, etc.). These interactions, which possess the essential properties of hydrogen bonds (HB), are usually called "X-H···π hydrogen bonds".[1]

IR spectra have shown evidence of intramolecular hydrogen bonding involving double and triple bonds and cyclopropane rings as proton acceptors.[2,3] Microwave experiments have provided information about the spectrum and geometry of a series of HF or HCl complexes with cyclopropane, acetylene, ethylene, benzene, and propyne,[4] as well as the hydrogen bonding in the dimers of benzene with water or ammonia.[5] Several crystal structures have been determined where this kind of H···π interactions are observed intra-[6] or intermolecularly.[1,7] Besides, important studies have been done over the characteristics of the CH···π[8] and the CH···three-membered-ring[9] interactions.

At theoretical level, several quantum mechanical studies have been done over these H···π links. Some authors considered that "...The phenomenon of X−H···π hydrogen bonding is not yet well studied ... it is still questionable whether the individual C atoms or the electrons of the π-bond should be regarded as the acceptor ...",[10] whereas in the first neutron diffraction analysis of an O−H···π hydrogen bond, recently published, it is said that "... the O−H vector clearly directed toward the midpoint (X) of the triple bond ...".[11] Moreover, in a recent Density Functional Theory study done over H···π interactions[12] a T-shaped C−H···π-system is proposed, even though the hydrogen bonding is not mentioned, whereas in the ab initio study of the hydrogen bonding between pyrrole and hydrogen fluoride recently published[13] both H···C_3−C_4 pyrrole bond and H···C_2 interactions are proposed to explain this complex.

In 1990, Tang et al. reported a quantum chemical study (MP2/6-31G**//HF/6-31G*) on selected π-type hydrogen-bonded systems.[14] As HB donor they use HF and as HB acceptors a set consisting of acetylene, ethylene, cyclopropane and benzene. They were able to correctly describe a number of complexes previously identified by microwave spectroscopy; moreover, using Bader topological approach[15] they made a detailed description of these HBs. Due to the fact that much relevant experimental results have appeared in 1991−1996 and continuing with our interest in unusual HB,[16] we have decided to undertake a similar study, also using HF as HB donor but with two differences: a larger basis set (MP2 and B3LYP/6-311++G**) and a large number of HB acceptors (the four of Tang plus cyclopropene, cyclobutadiene and tetrahedrane). Tetrahedrane was selected since it is considered as a three-dimensional aromatic system and since it is a strong base (the cation $C_4H_5^+$ is much more stable than the base C_4H_4).[17]

We present theoretical evidence that the nature of these H···π interactions is that of a HB between the H atom and the π-cloud by means of the analysis of geometric and energetic data, and mainly by the study of the topology of the electronic density within the frame of the theory of atoms in molecules established by Bader.[15]

Computational Methods

The calculations have been performed using the Gaussian-94[18] program. All the molecular complexes have been fully optimized with the 6-31G**[19] and 6-311++G**[20] basis sets at the HF and MP2[21] levels of theory, respectively. Additionally, calculations using the density functional theory at the B3LYP[22] level have been carried out utilizing the largest basis set. All the complexes were characterized as minima by frequency calculations at HF/6-31G** level (all frequencies being positive). The interaction energies (at the MP2 and B3LYP levels of theory) have been corrected for the inherent basis set superposition error (BSSE) by using the full counterpoise method[23] and the following equation:

$$\mathrm{BSSE(A{-}B)} = E(\mathrm{A})_\mathrm{A} - E(\mathrm{A})_\mathrm{AB} + E(\mathrm{B})_\mathrm{B} - E(\mathrm{B})_\mathrm{AB} \quad (1)$$

where $E(\mathrm{A})_\mathrm{AB}$ represents the energy of the monomer A calculated using its geometry within the dimer and the complete set of basis functions used to describe the dimer; $E(\mathrm{A})_\mathrm{A}$ is the energy of the same molecule, but using only the basis functions centered on itself.

The electronic densities and their Laplacians at the critical points of the π···H interactions, the dipole moment enhancement, atomic charges, the mutual penetration of hydrogen and acceptor atom and the bond orders (within the frame of the theory of atoms in molecules—AIM—proposed by Bader[15]) have been computed at the MP2/6-311++G** and B3LYP/6-311++G** levels of calculation with the AIMPAC set of programs.[15]

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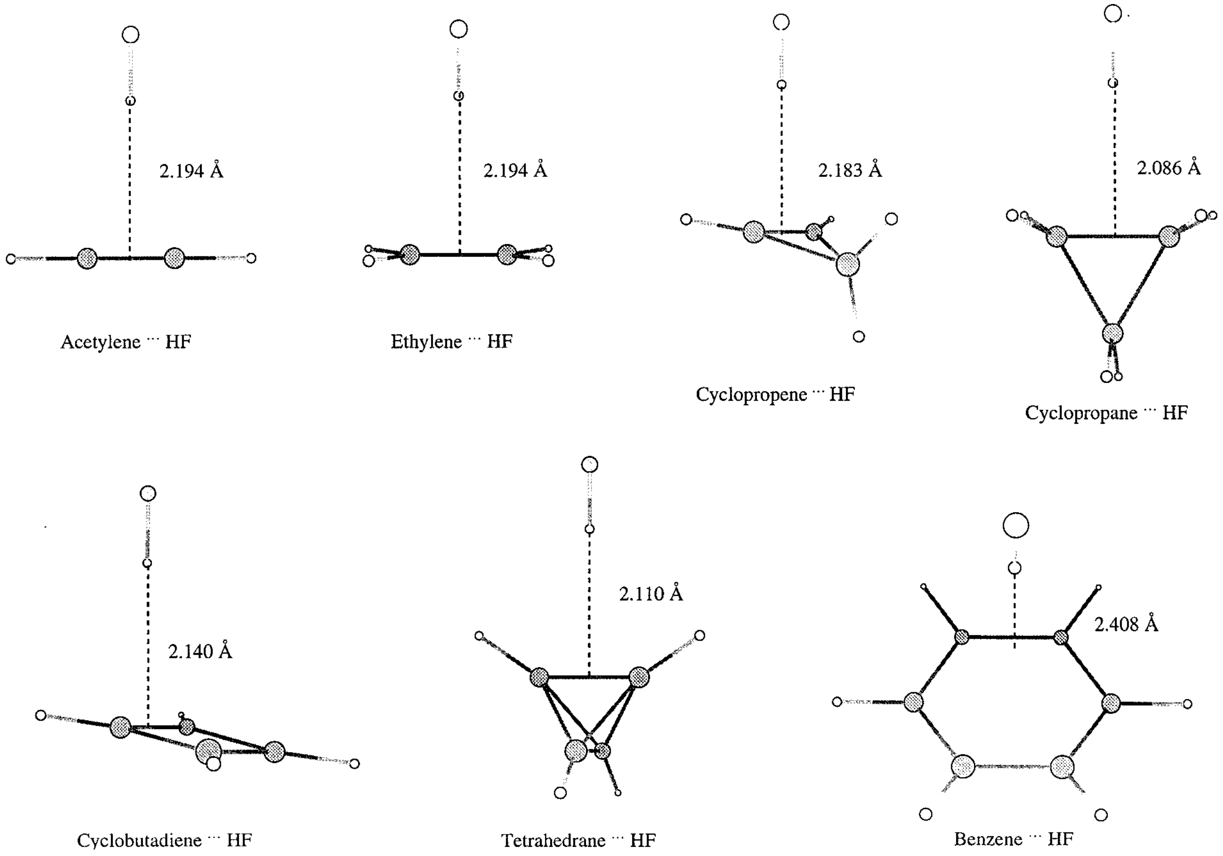

Figure 1. Minimum energy structures obtained for all the complexes studied at MP2/6-311++G** level of calculation. The H···π or H···(C−C) distances are shown.

TABLE 1: Distances (Å) between H and F Atoms to the π-centroid, in the Case of Unsaturated Compounds, or the Edge-centroid, in the Case of Cyclopropane and Tetrahedrane (⊗) and Angles (deg) Formed by the Axis along the HF Molecule and the Corresponding Molecular Plane of the H-acceptors of the Complexes Studied at Different Levels of Calculation. Experimental Data Is Also Included

	experimental *d*(F···⊗) *d*(H···⊗) *a*(F−H-plane)	HF/6-31-G** *d*(F···⊗) *d*(H···⊗) *a*(F−H-plane)	MP2/6-311++G** *d*(F···⊗) *d*(H···⊗) *a*(F−H-plane)	B3LYP/6-311++G** *d*(F···⊗) *d*(H···⊗) *a*(F−H-plane)
FH···acetylene	3.12[a]	3.257	3.109	3.084
	2.19[a]	2.352	2.194	2.151
	90.0° [e]	90.0° [e]	90.0° [e]	90.0° [e]
FH···ethylene	3.141[b]	3.295	3.119	3.107
		2.390	2.194	2.174
	90.0° [b]	90.0°	90.0°	90.0°
FH···cyclopropene		3.258	3.107	3.073
		2.371	2.183	2.140
		131.6°	109.6°	117.5°
FH···cyclopropane	3.021[c]	3.148	3.010	3.012
		2.244	2.086	2.080
	180.0° [c]	180.0°	180.0°	180.0°
FH···cyclobutadiene		3.236	3.065	3.067
		2.359	2.140	2.131
		133.3°	102.0°	106.2°
FH···tetrahedrane		3.176	3.036	3.021
		2.272	2.110	2.086
		90.0° [e]	90.0° [e]	90.0° [e]
FH···benzene	3.18[d]	3.390	3.298	3.526
	2.25[d]	2.507	2.408	2.627
		92.9°	89.3°	103.6°

[a] Legon, A. C.; Aldrich, P. D.; Flygare, W. H. *J. Chem. Phys.* **1981**, *75*, 625. [b] Ref 4c. [c] Ref 4a. [d] Ref 4d. [e] Angle formed by the FH molecule axis and one of the C of the interacting edge molecule.

Results and Discussion

Geometry and Energy. In all the minima obtained at the three levels of computation (see MP2 results in Figure 1) the H atom of the HF molecule is pointing toward the midpoint of one unsaturated bond in the case of the π-systems or one of the C−C bonds in the case of the three-membered rings. The

TABLE 2: C−C Bond Distances (Å) of the π- and Three-membered Ring Derivatives Isolated and Forming a Complex with the Hydrogen Fluoride Calculated at the B3LYP/6311++G and the MP2/6-311++G** Levels**

	B3LYP/6311++G**		MP2/6-311++G**	
	isolated	within complex	isolated	within complex
acetylene	1.200	1.201	1.216	1.217
ethylene	1.328	1.333	1.339	1.342
cyclopropene	1.291	1.296[a]	1.306	1.310[a]
	1.511	1.511	1.515	1.515
cyclopropane	1.509	1.529[a]	1.511	1.527[a]
		1.504		1.506
cyclobutadiene	1.333	1.338[a]	1.349	1.353[a]
	1.577	1.576	1.572	1.571
tetrahedrane	1.480	1.496[a]	1.485	1.498[a]
		1.478		1.484
		1.476		1.481
benzene	1.395	1.398[a]	1.400	1.402[a]
		1.397		1.402
		1.394		1.401
		1.395		

[a] C−C bond which interacts with the HF molecule.

TABLE 3: Interaction Energies (E_I, kcal/mol), BSSE (kcal/mol) and Corrected Interaction Energies (E_{I+BSSE}, kcal/mol) of the Complexes Studied

	E_I	BSSE	E_{I+BSSE}
	HF/6-31G**		
FH$\cdots$acetylene	−3.75	0.72	−3.03
FH$\cdots$ethylene	−3.94	0.85	−3.09
FH$\cdots$cyclopropene	−2.97	0.87	−2.10
FH$\cdots$cyclopropane	−2.92	0.75	−2.16
FH$\cdots$cyclobutadiene	−4.18	1.19	−2.99
FH$\cdots$tetrahedrane	−3.30	1.13	−2.16
FH$\cdots$benzene	−3.52	0.60	−2.92
	MP2/6-311++G**		
FH$\cdots$acetylene	−4.40	1.26	−3.14
FH$\cdots$ethylene	−4.39	1.03	−3.36
FH$\cdots$cyclopropene	−3.87	1.02	−2.86
FH$\cdots$cyclopropane	−4.45	1.17	−3.28
FH$\cdots$cyclobutadiene	−5.11	1.47	−3.64
FH$\cdots$tetrahedrane	−4.51	1.36	−3.15
FH$\cdots$benzene	−5.44	2.22	−3.22
	B3LYP/6-311++G**		
FH$\cdots$acetylene	−4.27	0.29	−3.97
FH$\cdots$ethylene	−4.44	0.37	−4.07
FH$\cdots$cyclopropene	−3.88	0.42	−3.46
FH$\cdots$cyclopropane	−3.96	0.47	−3.49
FH$\cdots$cyclobutadiene	−4.95	0.52	−4.42
FH$\cdots$tetrahedrane	−4.18	0.38	−3.80
FH$\cdots$benzene	−3.84	0.63	−3.21

TABLE 4: Electron Density ρ_c (e/a_0^3) and Laplacian $\nabla^2\rho_c$ (e/a_0^5) at the Bond Critical Point of the H$\cdots\pi$ Interaction of the Complexes Calculated at the MP2/6-311++G and B3LYP/6-311++G** Levels Using the AIM Methodology**

	MP2/6-311++G**		B3LYP/6-311++G**	
	ρ_c	$\nabla^2\rho_c$	ρ_c	$\nabla^2\rho_c$
F−H$\cdots$acetylene	0.0158	0.053	0.0181	0.054
F−H$\cdots$ethylene	0.0161	0.047	0.0176	0.046
F−H$\cdots$cyclopropene	0.0164	0.050	0.0189	0.052
F−H$\cdots$cyclopropane	0.0170	0.058	0.0175	0.057
F−H$\cdots$cyclobutadiene	0.0187	0.052	0.0201	0.049
F−H$\cdots$tetrahedrane	0.0179	0.054	0.0195	0.053
F−H$\cdots$benzene	0.0093	0.031	0.0123	0.036

distances obtained with the three methods of calculation and the experimental data available are gathered in Table 1. The distances at HF level are the longest and MP2 distances are longer than those obtained with the B3LYP method. At these two levels the results obtained are in good agreement with the experimental data. Looking at each method separately we observe that the calculated distances between the H atom and the centroid of the π-bond or the C−C bond are very similar, within a range of 0.1 Å except for the case of the benzene complex (see Table 1). In general, these distances correspond to those expected for a HB interaction (<2.5 Å). When the π-system studied has a localized unsaturation (acetylene, ethylene, cyclopropene, and cyclobutadiene) the HF molecule points toward the middle point of such a bond in a T-shape interaction. In the case of the structure of minimum energy of the benzene complex (Figure 1), the HF molecule points toward the middle point of one of the C−C bonds being different from that of Tang et al. (point symmetry C_{6v})[14] and agreeing better with the experimental results[4d] in which two equilibrium HF orientations are suggested consistent with the spectroscopic results. In one possible equilibrium structure the fluorine atom is placed over the benzene ring close to the C_6 symmetry axis of benzene, the HF then oscillates about its center of mass (which is close to the F atom) to produce a symmetric cone of all possible HF orientations. In the other possible structure the HF axis is placed at some angle to the C_6 axis pointing at a C atom.[4d]

Regarding the interacting C−C bonds, all of them increase the distance when forming a complex with the HF molecule (see MP2 and B3LYP results in Table 2). In the case of cyclopropene, cyclobutadiene and benzene the formation of the π$\cdots$HB with HF produces the expansion of the whole ring, being larger the increment in the interacting bond.

The results obtained for the interaction energies (E_I), BSSEs, and corrected interaction energies (E_{I+BSSE}) of all the complexes studied at the three levels of calculation are gathered in Table 3. The computed E_{I+BSSE} values are between −2.1 to −4.4 kcal/mol which corresponds to the presence of weak HBs. At the three levels of calculation, the interaction in the case of the HF$\cdots$ethylene and HF$\cdots$cyclobutadiene complexes seems to be stronger since their E_Is are the highest for each computational method (HF/6-31G**: −3.1, −3.0 kcal/mol; B3LYP/6-311++G**: −4.1, −4.4 kcal/mol and MP2/6-311++G**: −3.4, −3.6 kcal/mol respectively). For each method, the E_{I+BSSE} calculated are within a range of 1 kcal/mol, and the values increase from those obtained at the HF level to those at MP2 level being the highest the values resulting from B3LYP calculations, except for the case of the benzene complex. A parallelism is found between these energy results and those obtained for the distances between the H atom and the π-centroid. It should be noticed that the B3LYP method provides very small BSSE errors being the smallest from the three methods of calculation used what makes this method a useful tool for the calculation of this kind of systems.

Charge Density and AIM. According with Bader et al.[24] the theory of atoms in molecules (AIM) offers a self-consistent way of partitioning any system into its atomic fragments considering the gradient vector field of its electronic density ρ. By means of a topological analysis, features such as critical points and paths of maximum electron density (atomic interaction lines) can be studied since AIM provides a “molecular graph” which is a representation of the bonding interactions. Thus, the HB can be also apparent in the charge density by an atomic interaction line between the proton and the acceptor atom, and for that reason we have chosen AIM to analyze the H$\cdots\pi$ interactions of the hydrogen fluoride complexes from the B3LYP/6-311++G** and MP2/6-311++G** results. For the discussion we will follow the scheme of criteria for hydrogen bonding proposed by Koch and Popelier.[25]

TABLE 5: Electron Density ρ_c (e/a$_0^3$) at the Bond Critical Point and Bond Order n of the Interacting Bond (C−C) of the Monomers within the Complexes with HF and that of the Isolated Monomers Calculated at the MP2/6-311++G Levels Using the AIM Methodology**

	ρ_c (within complex)	ρ_c (isolated)	**n** (within complex)	**n** (isolated)
	MP2/6-311++G**			
acetylene	0.389	0.389	3.1	3.1
ethylene	0.333	0.334	2.0	2.0
cyclopropene	0.334 (0.227)[a]	0.337 (0.227)[a]	2.0 (0.9)[a]	2.1 (0.9)
cyclopropane	0.223 (0.235)[a]	0.233	0.9 (1.0)[a]	0.9
cyclobutadiene	0.327 (0.220)[a]	0.330 (0.220)[a]	1.9 (0.9)[a]	2.0 (0.9)
tetrahedrane	0.226 (0.237)[a]	0.236	0.9 (1.0)[a]	1.0
benzene	0.302 (0.302)[a]	0.278	1.6 (1.6)[a]	1.3
	B3LYP/6-311++G**			
acetylene	0.411	0.412	3.0	3.0
ethylene	0.341	0.344	1.9	2.0
cyclopropene	0.348 (0.229)[a]	0.352 (0.229)[a]	2.0 (0.9)[a]	2.1 (0.9)[a]
cyclopropane	0.222 (0.236)[a]	0.234	0.9 (1.0)[a]	1.0
cyclobutadiene	0.341 (0.218)[a]	0.344 (0.217)[a]	1.9 (0.9)[a]	2.0 (0.9)[a]
tetrahedrane	0.227 (0.241)[a]	0.239	0.9 (1.0)[a]	1.0
benzene	0.306 (0.307)[a]	0.308	1.5 (1.5)[a]	1.6

[a] Values corresponding to the C−C bonds of the ring which are adjacent to that involved in the interaction with the HF molecule.

(i) Charge density (ρ_c) and the Laplacian of the charge density ($\nabla^2\rho_c$) at the bond critical points (BCPs). For each complex several BCPs have been found but only those related to the H···π link (see Table 4) and the C−C interacting bond (see Table 5) will be discussed. In all the cases studied a BCP has been found between the H atom of the hydrogen fluoride and the C−C π bond in the cases of acetylene, ethylene, cyclopropene, cyclobutadiene, and benzene and one C−C single bond in the cases of cyclopropane and tetrahedrane. The ρ_c found in all these BCPs are shown in Table 4 being quite small ($\sim 10^{-2}$ au) and the values obtained for the $\nabla^2\rho_c$ at these H···π BCPs are positive in all the complexes studied (see Table 4). The values obtained for these two parameters correspond to "closed-shell" interactions of the HB type (van der Waals complexes would have even smaller ρ_c values, $\sim 10^{-3}$ au) confirming the proposed HB nature for these H···π interactions.

In the case of the C−C interacting bonds the ρ_c values found at the corresponding BCP are high ($>10^{-1}$ au) and with negative Laplacian values which indicates that these bonds are "shared" interactions, which means depending on the cases, unsaturated or covalent bonds. The BCPs have been also determined in the isolated molecules and the ρ_c values obtained (see Table 5) are very similar to those obtained within the hydrogen fluoride complexes which confirms the nature of these bonds. For C−C bonds, Bader[26] define a bond order (**n**) in terms of the values of ρ_c using the following equation:

$$\mathbf{n} = \exp\{A(\rho_c - B)\}$$

where $B = \rho_c$ for ethane, and A is adjusted for the cases of $\mathbf{n}_{\text{ethene}} = 2.0$, $\mathbf{n}_{\text{ethine}} = 3.0$, and $\mathbf{n}_{\text{benzene}} = 1.6$ (at MP2 level: $A = 7.542$ and $B = 0.2396$, and at B3LYP level: $A = 6.319$ and $B = 0.2378$). Thus, the corresponding C−C bond orders have been calculated for the C−C interacting bonds of each molecule and the results for the isolated molecules and those within the hydrogen fluoride complexes are gathered in Table 5. In the case of the localized unsaturated derivatives (acetylene, ethylene, cyclopropene, and cyclobutadiene), the ρ_c and **n** values corresponding to the interacting C−C bonds slightly increase from the isolated molecule to the complex, meaning that the interaction with the HF molecule produces a small concentration of density in the point which interacts with the H atom. In the case of the saturated C−C bond derivatives (cyclopropane and tetrahedrane) both ρ_c and **n** values diminish very slightly, maybe because some electron density is lost in favor of the interaction with the HF molecule. Regarding benzene a lost in the symmetry of the aromatic ring is observed in the ρ_c values as well as in the bond distances (see Tables 2 and 5).

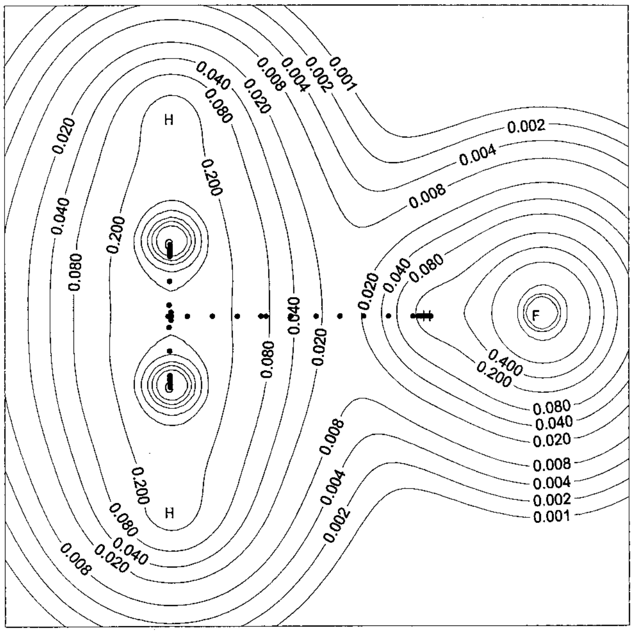

Figure 2. Contour plot of ρ and the bond path of both π···H and C−C bonds for the FH···acetylene complex.

(ii) Topology. By analyzing the bond paths corresponding to these π···HBs between the H atom and the perpendicular C−C interacting bond, a particular situation is found in all the complexes studied: there is an interaction line between the H of the HF molecule and the BCP at the midpoint of the C−C interacting bond of the other molecule, that is, all the configurations found correspond to "conflict catastrophe structures".[27] In these T-shaped HF complexes the (3,−1) BCP in the interacting C−C bond is the attractor for the bond path linking the H of the hydrogen fluoride molecule to that C−C bond. The bond path associated with the π···HB has a (3,−1) BCP that intersects nontransversally the interatomic surface of the C−C (3,−1) BCP. Examples of these conflict catastrophe configurations are shown in Figures 2, 3 and 4 where the contour plots of ρ_c and the bond path of both π···H and C−C bonds are represented for the FH···acetylene, FH···cyclopropane, and FH···benzene complexes, respectively. As it has been stated above, all the complexes studied presented zero negative frequencies, they are minima on the potential energy surface. However, from the point of view of the electron density these π···H bonded configurations are unstable because a small displacement of the HF molecule in the molecular axes of the acetylene from the conflict catastrophe configurations causes the molecular graphs to change radically. A break in the symmetry of the system seems to be the generator of such a change, thus, if a fluoro group is introduced in one of the extremes of the acetylene molecule the complex with the HF molecule does not exhibit a conflict catastrophe configuration but a bond path with a BCP between the H atom and the C(−H) atom of the fluoroacetylene molecule independent of the bond path and BCP of the C≡C as can be observed in the molecular graph of Figure 5.

(iii) Mutual penetration of H and the interacting bond. To estimate the mutual penetration of the H atom and the H acceptor

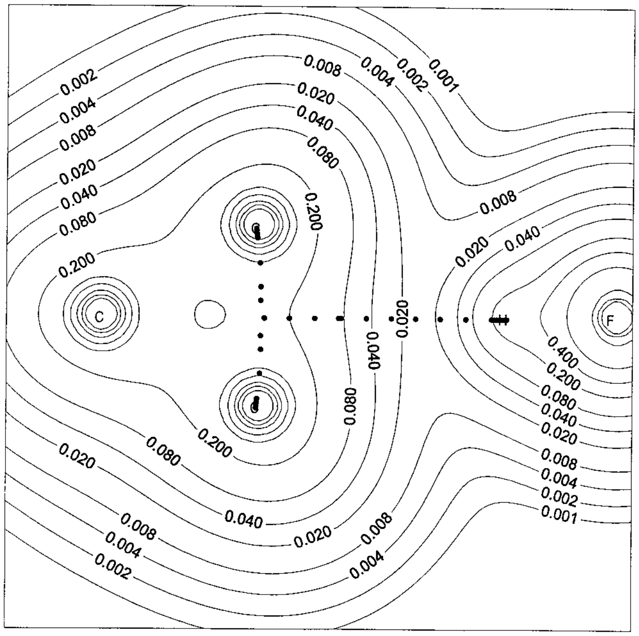

Figure 3. Contour plot of ρ and the bond path of both π···H and C−C bonds for the FH···cyclopropane complex.

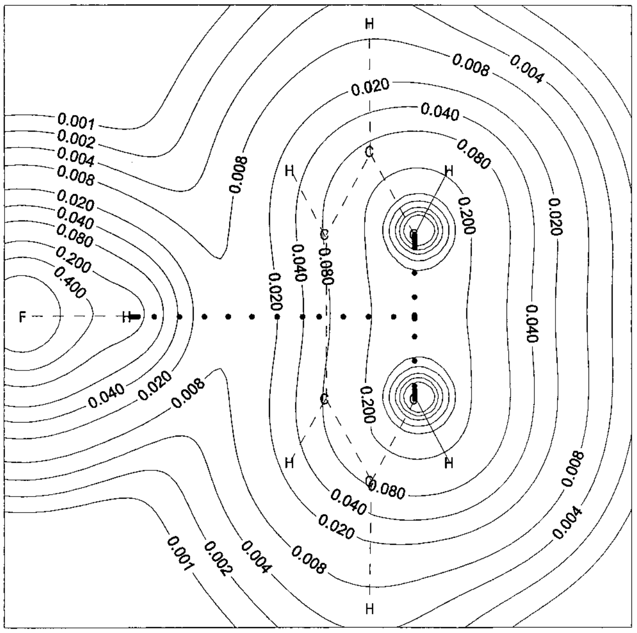

Figure 4. Contour plot of ρ and the bond path of both π···H and C−C bonds for the FH···benzene complex.

($r^0{}_H$ and $r^0{}_\pi$) upon HB formation, the nonbonded radii of both parts have to be compared to the corresponding bonded radii (r_H and r_π, BCP radii). The nonbonded radius is defined as the distance of a nucleus to a 0.001 au charge density contour in the direction of the HB, and in these cases it has been measured from the BCP of each interacting bond. The distances obtained at both levels of calculation are gathered in Table 6 where it can be seen that in all the cases studied the C−C bond (π or σ) is penetrated more than the H atom which is in agreement with the hard acid nature of HF proposed by Carroll and Bader.[28] Moreover, all the penetrations for π···HB are positive and therefore they can be designated as HBs.

(iv) Loss of charge and energetic destabilization of the H atom and total charge transferred. Another necessary criterion for the formation of a HB is the loss of charge of the H atom involved. This loss (Δ*N*) is computed by subtracting the electronic population of the H in the free monomer from the corresponding H in the complex, and should be negative. The results here obtained at MP2 level are shown in Table 7. In addition, this particular H atom should be destabilized in the complex what is measured by the difference in total atomic energy between the complex and the monomer (see Δ*E* in Table 7) which should be positive.

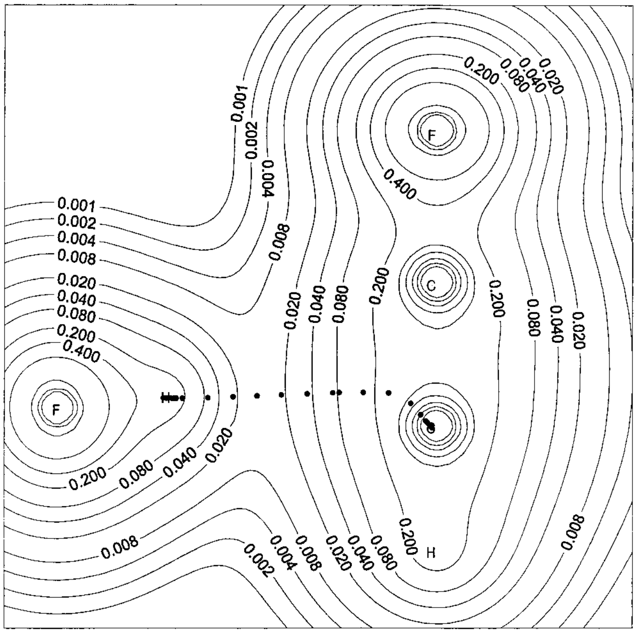

Figure 5. Contour plot of ρ and the bond path of the HF···1-fluoroacetylene complex which does not exhibit a conflict catastrophe structure.

TABLE 6: Mutual Penetration (in Bohr) of the Monomers of the Complexes Studied in Terms of Nonbonded Radii ($r^0{}_X$) and BCP Radii (r_X), Where X Is the BCP of the Interacting Bond, Calculated at B3LYP/6-311++G and MP2/6-311++G** Levels**

	$r^0{}_\pi$	r_π	Δr_π	$r^0{}_H$	r_H	Δr_H	$\Delta r_\pi + \Delta r_H$
	MP2/6-311++G**						
FH···acetylene	3.95	2.73	1.22	2.13	1.41	0.72	1.94
FH···ethylene	4.05	2.72	1.33	2.13	1.43	0.70	2.03
FH···cyclopropene	3.98	2.68	1.30	2.13	1.41	0.72	2.02
FH···cyclopropane	3.79	2.48	1.31	2.13	1.39	0.74	2.05
FH···cyclobutadiene	4.07	2.65	1.42	2.13	1.39	0.74	2.16
FH···tetrahedrane	3.91	2.46	1.45	2.13	1.39	0.74	2.19
FH···benzene	3.90	2.92	0.98	2.13	1.64	0.49	1.47
	B3LYP/6-311++G**						
FH···acetylene	3.97	2.68	1.29	2.14	1.39	0.75	2.04
FH···ethylene	4. 05	2.69	1.36	2.14	1.43	0.71	2.52
FH···cyclopropene	3.94	2.61	1.33	2.14	1.39	0.75	2.08
FH···cyclopropane	3.76	2.46	1.30	2.14	1.40	0.74	2.04
FH···cyclobutadiene	4.08	2.63	1.45	2.14	1.39	0.75	2.20
FH···tetrahedrane	3.89	2.43	1.46	2.14	1.38	0.76	2.20
FH···benzene	3.90	2.79	1.29	2.14	1.54	0.60	1.89

The total charge transferred in the formation of the π···HB is always negative what implies a donation of electrons from the π cloud to the HF molecule. This electronic transfer is larger in the cases of cyclobutadiene and tetrahedrane. Surprisingly, in the case of benzene the transfer is the smallest, what could be explain considering that electrons in localized π-systems are easier to be polarized than those in delocalized current ring π-systems.

Dipole Moment Enhancement. The electric charge rearrangement that accompanies the formation of a hydrogen bonded complex is an important characteristic of these HBs. The difference between the dipole moment of the complex and those

TABLE 7: Atomic Populations and Total Atomic Energies of the HB Hydrogen Atom in the Complexes Calculated at MP2/6-311++G Level. The Total Charge Transferred (Δ*Q*, e) in the Formation of the Complexes Is Also Gathered**

	$N(H)_{complex}$	ΔN^{a}	$E(H)_{complex}$	ΔE^{b}	$N(F)_{complex}$	ΔQ^{c}
F**H**···acetylene	0.710	−0.002	−0.2924	0.0033	−0.742	−0.032
F**H**···ethylene	0.702	−0.010	−0.2919	0.0038	−0.744	−0.042
F**H**···cyclopropene	0.704	−0.008	−0.2936	0.0021	−0.739	−0.035
F**H**···cyclopropane	0.710	−0.002	−0.2911	0.0046	−0.741	−0.031
F**H**···cyclobutadiene	0.700	−0.012	−0.2942	0.0015	−0.745	−0.045
F**H**···tetrahedrane	0.702	−0.010	−0.2925	0.0032	−0.745	−0.043
F**H**···benzene	0.711	−0.001	−0.2917	0.0040	−0.735	−0.024

[a] $N_{FH}(H) = +0.712$. [b] $E_{FH}(H) = -0.2957$. [c] $N_{FH}(F) = -0.712$.

TABLE 8: Dipole Moment Ehancement (DME) Calculated as the Difference between the Sum of the Dipole Moment of Monomers and that of the Complexes at MP2/6-311++G and B3LYP/6-311++G** Level**

	$\bar{\mu}$ complex	$\bar{\mu}$ FH	$\bar{\mu}$ monomer	DME
	MP2/6-311++G**			
FH···acetylene	2.5307	1.9682	0.0	0.5625
FH···ethylene	2.5953	1.9682	0.0	0.6271
FH···cyclopropene	2.6146	1.9682	0.4466	0.8061
FH···cyclopropane	2.7269	1.9682	0.0	0.7587
FH···cyclobutadiene	2.6744	1.9682	0.0	0.7062
FH···tetrahedrane	2.8494	1.9682	0.0	0.8812
FH···benzene	2.4717	1.9682	0.0	0.5035
	B3LYP/6-311++G**			
FH···acetylene	2.6799	1.9818	0.0	0.6981
FH···ethylene	2.7374	1.9818	0.0	0.7556
FH···cyclopropene	2.6088	1.9818	0.4651	0.8324
FH···cyclopropane	2.8358	1.9818	0.0	0.8540
FH···cyclobutadiene	2.8457	1.9818	0.0	0.8639
FH···tetrahedrane	3.0140	1.9818	0.0	1.0322
FH···benzene	2.7135	1.9818	0.0	0.7317

of the separate monomers provides some information of the electric rearrangement. These enhancements have contributions from the polarization of one monomer by the other and from the charge transferred in the formation of the HB. Thus, the enhancement of the electric dipole moment over the vector sum of the monomer dipole moments have been evaluated at both MP2 and B3LYP levels and the results are shown in Table 8. In all the cases the dipole moment of the complexes is larger than the vector sum of the dipole moment of the monomers as a consequence of the $\pi\cdots$HB formation.

Conclusions

The nature of the $\pi\cdots$HB has been theoretically investigated. According with the results obtained, the complexes formed by unsaturated derivatives and three-membered ring-derivatives as proton acceptors and hydrogen fluoride are stabilized by HBs. In general, the interaction energies are around −3 kcal/mol which implies the formation of weak HBs but, in the case of the complexes with ethylene and cyclobutadiene this energy goes up to −4.1 and −4.4 kcal/mol respectively at B3LYP level and −3.4 and −3.6 kcal/mol respectively at MP2 level, implying stronger HBs.

Considering the aromatic character of the family of compounds here studied we can order them as follows: benzene (aromatic) > cyclopropane and tetrahedrane (both manifest σ-aromaticity) > acetylene, ethylene, and cyclopropene (they are not aromatic) > cyclobutadiene (antiaromatic). Because aromaticity is directly related to the stability of the compounds, it could be said that the interaction energy (E_{I+BSSE}) of the corresponding HF complexes should be inversely related to the aromatic character of the monomers. This is only observed in the B3LYP results (see Table 3) with the exception of cyclopropene since the E_{I+BSSE} values obtained are in the order cyclobutadiene < ethylene < acetylene < tetrahedrane < cyclopropane < cyclopropene < benzene. This results manifest the suitability of the DFT methods in the evaluation of interaction energies in HB complexes.

All the configurations of minimum energy found correspond to conflict catastrophe structures of the electron density in which there is an interaction line between the H of the HF molecule and the midpoint of the interacting C−C bond of the other molecule. Yet, the ρ_c ($\sim10^{-2}$ au) and $\nabla^2\rho_c$ (>0) values obtained for the BCPs of these $\pi\cdots$HBs are those corresponding to a “closed-shell” interaction. These values are in agreement with the HB nature that we proposed for these interactions. It has been found that the formation of a $\pi\cdots$HB between HF and benzene is strong enough to modify the π-delocalization in the aromatic ring.

According to Koch and Popelier[24] in all the data collected so far, the mutual penetration criterion has never been violated by what is generally accepted as being a HB. Therefore, the results obtained for this criterion in the present set of complexes enables one to confirm the presence of HBs. Likewise, the criteria of loss of charge and energetic destabilization of the H atom involved in the $\pi\cdots$HB and that of overall charge transfer in the formation of a HB are fulfilled. Moreover, the dipole moment enhancements observed for these $\pi\cdots$HB complexes correspond to the already known increment of the polarization of the molecules that formed H bonded complexes.

It has been theoretically proved that in hydrogen fluoride complexes the interaction between the H atom and the π-cloud of unsaturated molecules, as well as the interaction between a H atom and a σ-bond of three-membered rings (cyclopropane and tetrahedrane), can be classified as a class of HBs namely $\pi\cdots$HBs.

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