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Cooperativity in Hydrogen-Bonded Interactions: Ab Initio and “Atoms in Molecules” Analyses

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The $H_2CO\cdots(HF)_n$ ($n = 1, ..., 9$) complexes were investigated using the MP2 method and the following basis sets: 6-311++G(d,p), aug-cc-pVDZ and aug-cc-pVTZ. It was found that the cooperativity effect enhances significantly the F−H···O hydrogen bond; in some of cases one can detect the covalent nature of hydrogen bonding. To deepen the nature of the interactions investigated, the scheme of decomposition of the interaction energy was applied; for stronger H-bonds where the coopearativity is more important, the delocalization energy term increases. The ratio of delocalization energy to electrostatic energy increases for stronger hydrogen bonds where the proton···acceptor distance is shorter. The Bader theory was also applied, and it was found that for stronger H-bonds the electronic energy density at the proton···acceptor bond critical point is negative and may be attributed to the partly covalent interaction.

Introduction

Hydrogen bonding is a well-known phenomenon and a steering factor in many physical, chemical and biochemical processes.[1,2] However, due to the variety of interactions classified as H-bonds, it is very difficult to indicate strictly their properties.[3] There are conventional X−H···Y H-bonds where X−H indicates the proton donating bond, Y is the proton acceptor, and both X and Y atoms are usually electronegative. Such meaning is in line with the definition of hydrogen bonding stated by Pauling.[4] There are also so-called unconventional H-bonds such as C−H···Y, X−H···C, X−H···π-electrons or even C−H···C.[3] In the case of those interactions it is often a subject of controversy whether they may be classified as H-bonds. One can also mention dihydrogen bonds,[5] a special kind of H-bond where the negative charged H-atom is a proton acceptor. The F−H···H−Li complex represents such an interaction.[6] The interaction energies related to H-bond strength may be also fixed within a broad range,[7] from 1 to 2 kcal/mol [8] for weak interactions such as C−H···O or C−H···C up to interaction energies of 40−60 kcal/mol for charge-assisted hydrogen bonds (CAHB). $[FHF]^-$ is an example.[6b]

The electrostatic-covalent hydrogen bond model (ECHB) was proposed by Gilli and co-workers[9] where the following statements concerning the nature of H-bonds were summarized: weak H-bonds are electrostatic in nature, and their covalency increases with increasing strength; very strong H-bonds may be characterized as three-center-four electron covalent bonds. The latter H-bonds are homonuclear and symmetrical because only for such cases two VB resonance forms X−H···X ⇔ X···H−X are isoenergetic, and their effective mixing is possible. The last statement may be expressed as the condition of minimum ΔPA (minimum proton affinity difference principle). Gilli and co-workers have also classified a few classes of H-bonds such as those which may be very strong: (a) CAHB(−) are negative, charge-assisted H-bonds ($[FHF]^-$ is an example of such interactions and has been mentioned above), CAHB(+) are positive, charge-assisted H-bonds ($H_2O\cdots H^+\cdots OH_2$ is an example), and RAHB are resonance-assisted H-bonds. In the case of RAHB, mainly intramolecular homonuclear O−H···O hydrogen bonds were investigated; for example, malonaldehyde and its derivatives where H-bond interaction closes the six-membered chelate ring and where both X−H and Y groups are coupled with a joint π-electron conjugated system. The intramolecular heteronuclear RAHBs were investigated and were found in crystal structures;[10] however, according to the ECHBM model, they are not as strong as homonuclear O−H···O H-bonds. Moreover, the covalent contribution for these heteronuclear interactions is not high. The intermolecular RAHBs are also known. Centrosymmetric acid dimers, formamide dimer, and DNA base pairs are examples among numerous others.[11]

It is worth mentioning that for the mentioned systems, CAHBs and RAHBs, the question if they are covalent in nature arises. The covalency of such interactions was discussed previously. Pauling claimed that $[FHF]^-$ is an example of covalent hydrogen bonding. He also estimated, by the use of the bond number idea, the covalent contribution for H-bonds in ice to be about 5%.[4] One can also mention the later experimental evidences concerning covalency of strong hydrogen bonds. A low temperature study of intramolecular hydrogen bonding in benzoylacetone was carried out with X-ray (8.4 K) and neutron diffraction data (20 K).[12] The charge density obtained from X-ray and neutron data have been analyzed by using multipolar functions and topological methods, which give evidence concerning π-electron delocalization in the keto−enol group. The covalent nature of hydrogen bonds has also been the subject of NMR[13] and Compton scattering[14] as well as theoretical investigations.[15]

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The question is, however, what does this mean that an H-bond is covalent in nature? Gilli stated that stronger H-bonds are more covalent in nature, and the weaker are mostly electrostatic interactions.[9] Desiraju has claimed that some hydrogen bonds have charge transfer characteristics and thus are partly covalent in nature.[16] The decomposition scheme of the interaction energy was applied in recent studies to get more detailed insight into the nature of H-bond interactions. It was pointed out that, for very strong, charge-assisted or resonance-assisted hydrogen bonds, the most important interaction energy term is the delocalization component, whereas for H-bonds which are typical, neutral and moderate in strength, the electrostatic term is dominant.[17] This is in line with the statements of Gilli. Very recent studies on intermolecular RAHBs have shown that, for carboxylic acids where homonuclear O−H···O H-bonds exist, the delocalization interaction energy term is more important than for the heteronuclear intermolecular RAHBs of formamide dimer and related systems.[18]

The other powerful method to study the nature of interactions is the "atoms in molecules" theory.[19] For atom−atom interactions such as intermolecular contacts or valence bonds, the characteristics of the corresponding bond critical point (BCP) are very important. These are the electron density at BCP (ρ_C) and its Laplacian ($\nabla^2\rho_C$). The energetic properties of BCPs are often considered such as the electron energy density at BCP (H_C) and its components: the kinetic electron energy density (G_C) and the potential electron energy density (V_C). There is a relation between these energetic characteristics, that is $H_C = G_C + V_C$. It is also known from the virial theorem that $^1/_4\nabla^2\rho_C = 2G_C + V_C$. The negative value of the Laplacian of the electron density at BCP designates the concentration of the electron charge in the region between the nuclei of the interacting atoms and is typical for covalent bonds−shared interactions. In the case of the positive value of $\nabla^2\rho_C$ there is a depletion of the electron charge between the atoms, which indicates that this is an interaction of closed-shell systems: ions, van der Waals interactions, or H-bonds. Hence one can see that the Bader theory arbitrarily provides the characteristics of BCPs depending on whether the interaction is covalent in nature. For a negative value of a Laplacian, there is no doubt of its covalency (from the AIM theory point of view). In some studies it is also stated that if $\nabla^2\rho_C > 0$ and $H_C < 0$, then the interaction may be classified as partly covalent in nature.[20] The crystal structure of benzylacetone mentioned above, where the O−H···O intramolecular RAHB system was found, is an example. The Bader theory was applied to the experimental electron density of that crystal structure, and it was found that both H···O interactions in an O−H···O H-bridge are characterized by negative values of the Laplacian at the corresponding BCPs.[12] It is strong experimental evidence concerning the covalent nature of the H-bond. For the MP2/6-311++G(d,p) calculations performed on centrosymmetric dimers of formic and acetic acids it was found that $\nabla^2\rho_C < 0$ for covalent OH bonds, whereas $\nabla^2\rho_C > 0$ and $H_C < 0$ for H···O contacts. It means that for these intermolecular RAHBs one may find the partially covalent H-bonds.[18]

Jeffrey has indicated that there are two kinds of cooperativity.[2] The first one is connected with π-electron delocalization, and RAHB systems are related to that effect. The second kind of cooperativity is related to σ-bonds connected to each other within a chain or a cycle. The chain of species connected through OH bonds, i.e., (R)OH···(R)OH···(R)OH···, is an example. Such a situation often occurs in crystals where the subsystem reduplicated within such a chain is in line with the translational symmetry required. The influence of the cooperative effects on the H-bond strength was investigated recently using the experimental microwave and ab initio techniques for H_3N···HF and H_3N···HF···HF complexes.[21] It was found that the addition of the second HF molecule causes a 0.21(6) Å contraction of the N···H hydrogen bond relative to that in the H_3N···HF complex. In other words, it is evident that the cooperativity effect exists in clusters where the monomer can participate concertedly as a donor and as an acceptor. There are also numerous theoretical investigations on the cooperativity effect.[22] For example, cooperativity in C−H···O and OH···O hydrogen bonds was compared.[23] The authors conclude in the latter case that the effect enhances the H-bond strength and also decreases the covalent nature of the proton donating bond because its elongation and a red-shift of the corresponding stretching mode are observed. In the case of C−H···O cooperativity blue shifting is detected for H-bonds of $(H_2CO)_n$ and $(HFCO)_n$ aggregates, but an increase in blue shifting is not related to the number of n-mers. However, there are other types of H-bonds, for example, CH···F where an enhancement of blue shift is observed as a result of cooperativity.[24] One can observe that cooperativity may exist for different kinds of hydrogen bonds, so-called conventional and unconventional ones. There is a very interesting case of πH-bonded interactions analyzed at the MP2/6-311++(2d,2p) level of approximation.[25] The other example where the H-bond cooperativity analyzed for chains of acetic acid molecules[26] is a very important contribution. The authors found that the cooperativity along the acetic acid molecules chain is rather small and amounts to 1.2 kcal/mol (the HF/6-31G(d,p) level of approximation).

The aim of this study is to investigate the cooperativity effect using the results of ab initio calculations as well as analyzing the characteristics of critical points derived from the Bader theory. The decomposition scheme of the interaction energy is also applied here[27] to deepen the nature of the cooperative H-bonding. Because topological parameters such as H_C and $\nabla^2\rho_C$ are useful to classify an interaction as covalent in nature, the topic of covalency for cooperative H-bonded interactions is also discussed here. The application of the decomposition of the interaction energy to study the effect of cooperativity seems to be interesting. To our knowledge such an attitude was not extensively applied to analyze that phenomenon. Very recently, the studies of water dimers, trimers and tetramers have appeared. The authors applied the NEDA (natural energy decomposition analysis) approach for DFT results and found that the cooperativity effect is connected with an increase in the value of the charge transfer energy and a decrease in the value of the electrostatic and polarization terms.[28]

The H_2CO···$(HF)_n$ complexes are considered here. Such species were analyzed earlier by Karpfen and Kryachko[24] up to $n = 4$. However, neither the Bader theory nor the decomposition of interaction energy scheme was applied to study F−H···O interactions. The authors analyzed additionally C−H···F blue-shifting H-bonds which are created for these fully optimized cyclic complexes.

Computational Details

The calculations have been performed with the GAMESS quantum chemistry package[29] of code. The complexes of H_2CO···HF, H_2CO···HF···HF and H_2CO···HF···HF···HF were considered. For these complexes there is the conventional F−H···O hydrogen bonding, and there are also the additional F−H···F interactions (except of the first case). Such species were chosen to analyze the cooperative hydrogen bonding effect that arises for the two latter complexes. There are different kinds of cooperativity and different determinations of this effect.[2] However, it is very often claimed that such an effect exists if the same species is involved in H-bonding as the proton donor and as the proton acceptor. This is fulfilled for the complexes mentioned above where HF molecules act as proton acceptors on one hand and as proton donors on the other hand. Additionally, for these complexes the Jeffrey definition of cooperativity may be applied because the chain of connected σ-bonds exists.[2] The calculations of these complexes were performed using the second-order Møller−Plesset perturbation method (MP2).[30] The Pople style basis set, 6-311++G(d,p),[31] as well as the Dunning type basis sets,[32,33] aug-cc-pVDZ and aug-cc-pVTZ, were applied. Full optimizations for these three complexes have been performed. The results of these optimizations correspond to energy minima because no imaginary frequencies were found.

Except for the complexes mentioned above the other series of systems was also investigated. The linear $H_2CO\cdots(HF)_n$ systems are considered where the number of HF molecules ranges from 1 to 9. The linear means $C{=}O\cdots(HF)_n$ atoms are positioned on the same line. In other words the species of this series are characterized by C_{2v} symmetry. Such an approach is connected partly with the aim of this study: how far does the cooperative hydrogen bonding effect range? In the case of fully optimized systems such an investigation is not possible because additional intermolecular contacts are formed, except for O···H−F and F···H−F. Additionally, the approach applied for the second series, with C_{2v} symmetry constraints, corresponds to the situation found in crystal structures where cooperativity often exists and it is most likely a result of the translational symmetry. It is worth mentioning that systems of the second series analyzed here do not correspond to minima. However, such a situation is usual in crystal structures where the single molecular moiety or even the complex taken from the crystal and considered separately does not correspond to the minimum; the C_{2v} systems analyzed here are finite aggregates. The calculations for the linear complexes were performed at the MP2/aug-cc-pVDZ level of approximation.

The variation-perturbation approach[27] was applied to perform the decomposition of the interaction energy and to deepen the nature of interactions within the analyzed complexes. The starting wave functions of the subsystems are obtained in this approach in the dimer-centered basis set (DCBS).[34] Hence the total interaction energy as well as all of its components are free of basis set superposition error (BSSE) due to the full counterpoise correction.[34,35]

The following interaction energy components can be obtained in this way:

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

where $E_{EL}^{(1)}$ is the first-order electrostatic term describing the Coulomb interaction of static charge distributions of both molecules, $E_{EX}^{(1)}$ is the repulsive first-order exchange component resulting from the Pauli exclusion principle, and $E_{DEL}^{(R)}$ and E_{CORR} correspond to higher order delocalization and correlation terms. The delocalization term contains all classical induction, exchange-induction, etc., from the second order up to infinity. The charge transfer term, which is strongly basis set dependent, is included in the delocalization contribution, which is much less basis set sensitive.[27] The corresponding software has been implemented[36] within the GAMESS package.[29] It is worth mentioning that in the most often applied energy partitioning technique, namely the Kitaura−Morokuma scheme,[37] there are the following interaction energy components: electrostatic, exchange, polarization and charge transfer. The two latter terms correspond approximately to the delocalization term. However, in the Kitaura−Morokuma approach the total energy and its components are not free of basis set superposition error. The polarization interaction energy in this scheme may be approximately described as connected with the internal redistribution of electron charge, whereas the charge transfer term is connected with the density shifts from one molecule to the other. Both schemes of the interaction energy partitioning are applied here for comparison.

TABLE 1: Geometrical Parameters (Å) of $H_2C{=}O\cdots(HF)_n$ Complexes (n = 1, 2, ..., 9), MP2/aug-cc-pVDZ Results

N	r(HF)	r(CO)	r(H···O)
1	0.9315	1.2222	1.8393
2	0.9368	1.2227	1.7496
3	0.9393	1.2229	1.7146
4	0.9405	1.2230	1.7023
5	0.9411	1.2231	1.6956
6	0.9414	1.2232	1.6928
7	0.9418	1.2231	1.6827
8	0.9417	1.2232	1.6899
9	0.9419	1.2232	1.6848

The "atoms in molecules" (AIM) theory of Bader[19] was also applied in this study to find the critical points[38,39] and to analyze them in terms of electron densities and their Laplacians. The properties of BCPs and hence the interatomic and intermolecular interactions were also studied in terms of the local electron energy density at BCP ($H(r_{CP})$) and its components (the local kinetic energy density $G(r_{CP})$ and the local potential energy density $V(r_{CP})$). The AIM calculations were carried out using the AIM2000 program.[40]

Results and Discussion

Geometrical Parameters. The analyses performed here are mainly related to the H···O intermolecular interaction, i.e., the F−H···O hydrogen bond. And the other F−H···F hydrogen bonds influencing the H···O interaction are not analyzed here in detail. Such an attitude is connected with the investigation of the cooperativity effect. This is indicative of how the number of hydrogen fluoride molecules affects the strength of the F−H···O=C interaction. The linear systems are taken into account to mimic the situation existing in crystals where the translational symmetry connected with the cooperativity effect enhances the strength of the interactions, among them hydrogen bonds. Additionally, fully optimized systems are considered, with up to three hydrogen fluoride molecules. Table 1 presents the geometrical parameters of the linear systems. The geometries of the F−H···O hydrogen bonds obtained at the MP2/aug-cc-pVDZ level of approximation are presented. One can observe the following tendencies revealing the increase in the strength of the F−H···O hydrogen bond if the number of HF molecules increases: the elongation of the proton donating bond (HF), the elongation of the C=O accepting bond and the shortening of the H···O intermolecular distance. The changes are not meaningful in the case of the HF bond length. For the linear $H_2CO\cdots HF$ complex this bond length equals 0.932 Å; for $H_2CO\cdots(HF)_9$ it amounts to 0.942 Å. Hence there is the range of 0.01 Å. Such a range for the C=O bond is only 0.001 Å because the double accepting bond is less sensitive to the intermolecular interactions in comparison with the donating single H−F bond. There are greater changes for the H···O distances: 1.84 Å for the $H_2CO\cdots HF$ complex and 1.68 Å for $H_2CO\cdots(HF)_9$. One can also observe the meaningless changes for a number of HF molecules greater than five. The tendencies mentioned above

TABLE 2: Geometrical Parameters (Å) of the Fully Optimized $H_2CO\cdots(HF)_n$ Systems ($n = 1-3$)

n	r(CO)	r(H···O)	r(HF)
	MP2/6-311++G(d,p)		
1	1.2178	1.7556	0.9319
2	1.2219	1.6412	0.9466
3	1.2213	1.5731	0.9563
	MP2/aug-ccpVDZ		
1	1.2280	1.7222	0.9425
2	1.2325	1.6079	0.9606
3	1.2320	1.5412	0.9729
	MP2/aug-ccpVTZ		
1	1.2185	1.7034	0.9405
2	1.2231	1.5907	0.9596
3	1.2228	1.5206	0.9730

clearly show the increase of the H-bond strength if the number of HF molecules increases and that the number of HF molecules considered in this study (up to 9) is sufficient to mimic the situation existing in crystals.

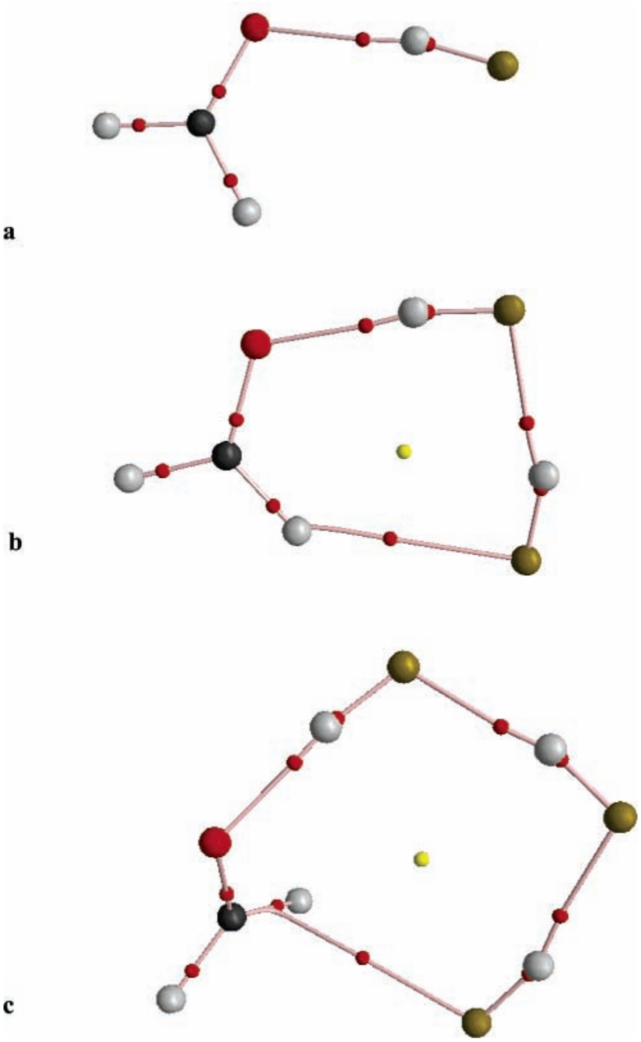

Figure 1. Molecular graphs of the fully optimized systems: (a) $H_2CO\cdots HF$, (b) $H_2CO\cdots HF\cdots HF$, and (c) $H_2CO\cdots HF\cdots HF\cdots HF$. Graphs were obtained at the MP2/aug-cc-pVTZ level. Big circles correspond to attractors and small ones to critical points.

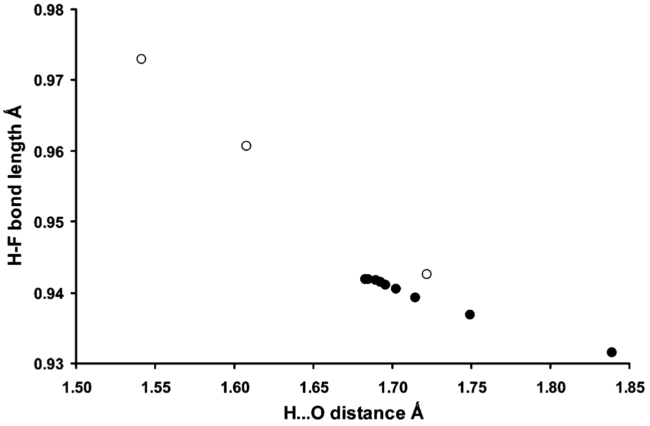

Figure 2. Relationship between H···O distance (Å) and the OH bond length (Å) for the linear (C_{2v} symmetry) systems (full circles) and the fully optimized systems (open circles); MP2/aug-cc-pVDZ level of approximation.

TABLE 3: Decomposition Interaction Energy Terms (kcal/mol), Eq 1

n	$\Delta E^{(1)}$	$E_{EL}^{(1)}$	$E_{EX}^{(1)}$	$E_{DEL}^{(R)}$	ΔE_{SCF}	E_{CORR}	ΔE_{MP2}
1	−3.02	−8.65	5.63	−3.01	−6.03	0.42	−5.62
2	−3.90	−11.41	7.50	−4.73	−8.63	0.72	−7.91
3	−4.21	−12.64	8.43	−5.60	−9.81	0.84	−8.97
4	−4.42	−13.19	8.77	−5.99	−10.41	0.90	−9.51
5	−4.52	−13.48	8.97	−6.20	−10.72	0.93	−9.79
6	−4.59	−13.64	9.05	−6.31	−10.90	0.95	−9.95
7	−4.51	−13.91	9.40	−6.55	−11.06	0.96	−10.10
8	−4.66	−13.80	9.14	−6.41	−11.07	0.96	−10.11
9	−4.61	−13.92	9.32	−6.53	−11.14	0.97	−10.17

Table 2 presents the MP2 results obtained with the use of Pople-style and Dunning basis sets (6-311++G(d,p), aug-cc-pVDZ and aug-cc-pVTZ) for fully optimized systems, up to three HF molecules included. Figure 1 presents molecular graphs for these systems (obtained within the MP2/aug-ccpVTZ level of approximation). The results collected in Table 2 show that the geometrical changes are much greater here than in the case of C_{2v} symmetry systems. The MP2/aug-cc-pVTZ results show the HF bond length equal to 0.941 Å in the case of one HF molecule and 0.973 Å for three HF molecules. The C═O bond elongation amounts to 0.004 Å if one compares the complex with one and three HF molecules. Hence one can observe that in the case of nonlinear complexes the enhancement of H-bond strength due to cooperativity is greater. MP2/aug-cc-pVDZ results, as was mentioned earlier, show an HF bond length of 0.932 Å for linear $H_2CO\cdots HF$ complexes, whereas for nonlinear complexes bond length is equal to 0.943 Å. Other geometrical parameters also confirm the stronger cooperativity effect for nonlinear systems. This is probably the effect of the additional, mainly electrostatic, interactions. There are also additional C−H···F interactions for nonlinear complexes which may be classified as weak H-bonds, especially if the number of HF molecules amounts to two or three. Figure 2 shows the dependence between H···O distance and HF bond length. Full circles correspond to linear systems. In these results the linear correlation coefficient amounts to 0.996. The results for nonliner systems are also included (Figure 2).

Hydrogen Bond Energy and the Decomposition of the Interaction Energy. Table 3 shows the energetic results for linear systems. The MP2 binding energies calculated within the supermolecular approach[41] are included. This means that such energies were calculated for the fixed positions of nuclei. In the studies performed here, the energy of the H···O interaction is analyzed. It is the difference between the energy of the whole complex and the energies of two species. One is the H_2CO molecule, and the second is the remaining part of the complex, all HF molecules. In other words, as was mentioned above, all HF molecules within the complex analyzed are treated as the donating system. It was mentioned earlier that the aim of this

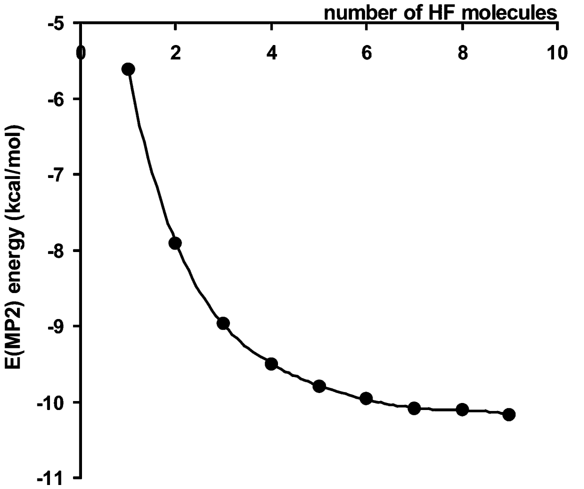

Figure 3. Dependence between the number of HF molecules and the binding energy (MP2/aug-cc-pVDZ level, in kcal/mol). The linear systems are taken into account.

TABLE 4: Decomposition Interaction Energy Components (kcal/mol) for Fully Optimized Systems, Eq 1

N	$\Delta E^{(1)}$	$E_{EL}^{(1)}$	$E_{EX}^{(1)}$	$E_{DEL}^{(R)}$	ΔE_{SCF}	E_{CORR}	ΔE_{MP2}
			MP2/6-311++G(d,p)				
1	−2.28	−13.19	10.91	−5.12	−7.41	0.80	−6.61
2	−3.11	−20.14	17.03	−9.52	−12.63	1.40	−11.23
3	−1.94	−23.95	22.01	−13.05	−14.99	1.70	−13.28
			MP2/aug-cc-pVDZ				
1	−1.58	−14.03	12.45	−6.09	−7.67	−0.01	−7.68
2	−2.10	−21.80	19.70	11.47	−13.56	0.23	−13.34
3	−0.30	−26.35	26.05	−16.07	−16.37	0.18	−16.19
			MP2/aug-cc-pVTZ				
1	−1.05	−14.32	13.27	−6.51	−7.57	−0.80	−8.26
2	−1.42	−22.26	20.84	−12.17	−13.59	−0.80	−14.39

study is mainly to analyze the H···O interaction and the interrelation between the number of HF molecules and the F−H···O H-bond strength. In other words, the influence of cooperativity on the H···O contacts is analyzed. Such a situation exists in crystals. For example it was pointed out early on that H···O distances in centrosymmetric dimers of carboxylic acids are shorter than the same distances in the gas phase.[42] The enhancement of H-bond strength in solid carboxylic acids is connected with various effects: disorder, mesomeric effect of carboxylic groups[43] and with cooperativity.[42] Table 3 shows the increase of the binding energy (the H···O interaction) for linear systems if the number of HF molecules increases. This is also presented in Figure 3. For the $H_2CO\cdots HF$ complex the binding energy amounts to 5.6 kcal/mol, whereas for $H_2CO\cdots(HF)_9$ it is equal to 10.2 kcal/mol. If one assumes that 10.2 kcal/mol is the energetic limit (the additional HF molecules do not change the binding energy), then the “linear” cooperativity effect is equal to 4.6 kcal/mol. This is quite reasonable because the binding energy practically does not change for hydrogen fluoride molecules where $n = 7$, 8, or 9. Table 4 shows the results for fully optimized systems, and one can see that the cooperativity in such a case is stronger because the binding energy for the system with three HF molecules is equal to 16.2 kcal/mol (the same as for the linear complexes level of approximation, MP2/aug-cc-pVDZ). This may be partly connected with the additional C−H···F interaction. However, one should remember also that H···O distances are shorter for nonlinear systems (see the previous section). This means that H···O interactions in nonlinear systems are stronger than for the corresponding linear systems (with the same number of HF molecules).

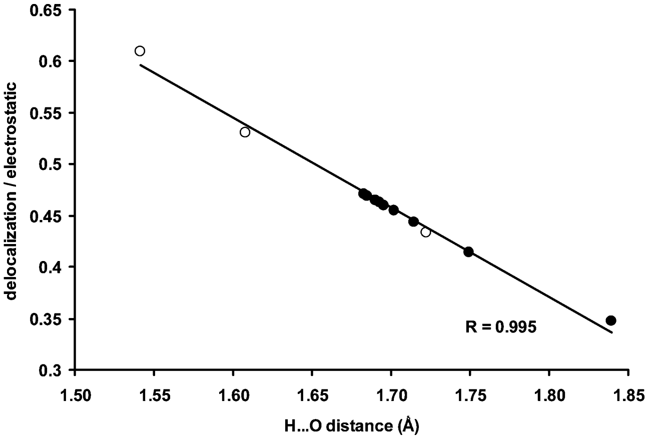

Figure 4. Linear correlation between H···O distance (Å) and the ratio of the interaction energy terms (electrostatic and delocalization). Full circles correspond to linear systems and the open circles correspond to those fully optimized systems: the decomposition scheme according to eq 1; MP2/aug-cc-pVDZ level of approximation.

The results of Tables 3 and 4 indicate that the importance of all main interaction energy terms increases (their absolute values increase) if n, the number of HF molecules, increases. These are the electrostatic, delocalization, and exchange interaction energy terms. The correlation energy also increases, but if n is equal to 6−7, it does not change. The same tendencies are observed for nonlinear complexes that binding energy increases if n increases.

Because there is a shortening of the H···O distance if n increases, the covalency of F−H···O hydrogen bond also increases. This is in line with the statement of Pauling[4] who claimed that for the shorter interatomic distances there is a greater bond number for the corresponding interaction and its greater covalency. It was pointed out very recently[17,44] that covalency is connected to an increase in the value of the exchange energy term as well as the most important attractive terms: the electrostatic and delocalization terms. However, the latter term increases more rapidly than the electrostatic term if the proton···acceptor distance decreases (covalency increases). In other words the ratio, the delocalization/electrostatic energies, correlates with the proton···acceptor distance. Such a correlation for the complexes analyzed here is presented in Figure 4. Full circles correspond to linear systems, and the open circles correspond to nonlinear systems. The linear correlation coefficient for those MP2/aug-cc-pVDZ results is equal to 0.995 despite the fact that linear and nonlinear systems are considered together. This also shows that cooperativity enhances the covalency of interaction. The decomposition of the interaction energy results correspond to eq 1.[27] It is worth mentioning that these ΔE_{MP2} energies and energy components are free of the BSSE error because the starting wave functions of the subsystems are obtained in the dimer-centered basis set (DCBS).[34] This is the reason the SCF binding energies presented in Tables 5 and 6 are different from those of Tables 3 and 4. In the case of previous values (Tables 5 and 6) they are not free of BSSE error.

The results of Tables 5 and 6 show also the interaction energy components calculated within the Morokuma−Kitaura scheme.[37] These results are presented for comparison because such a decomposition scheme is most often applied and also to check the well-known statements that the covalency is connected with the charge transfer interaction energy term.[16] Because the delocalization energy term analyzed in Figure 4 is composed of the charge transfer and polarization energies, the following

TABLE 5: Decomposition Interaction Energy Terms (kcal/mol) According to the Kitaura−Morokuma Scheme

N	EL	EX	PL	CT	MIX	ΔE_{SCF}
1	−8.95	5.64	−2.26	−1.74	1.01	−6.30
2	−11.76	7.47	−3.77	−2.70	1.81	−8.95
3	−13.01	8.37	−4.56	−3.20	2.25	−10.15
4	−13.57	8.71	−4.92	−3.42	2.44	−10.75
5	−13.87	8.90	−5.11	−3.53	2.55	−11.07
6	−14.03	8.98	−5.21	−3.59	2.60	−11.25
7	−14.30	9.33	−5.44	−3.75	2.76	−11.41
8	−14.19	9.07	−5.31	−3.64	2.65	−11.42
9	−14.32	9.25	−5.42	−3.72	2.73	−11.49

TABLE 6: Decomposition Interaction Energy Components (kcal/mol) for Fully Optimized Systems, the Kitaura−Morokuma Approach[a]

N	EL	EX	PL	CT	MIX	ΔE_{SCF}
			MP2/6-311++G**			
1	−13.74	10.62	−3.36	−3.39	1.98	−7.89
2	−20.97	16.75	−6.48	−6.04	3.46	−13.28
3	−25.00	21.77	−8.89	−8.57	4.97	−15.73
			MP2/aug-cc-pVDZ			
1	−14.38	12.29	−5.01	−4.11	3.20	−8.01
2	−22.22	19.49	−9.89	−7.62	6.16	−14.09
3	−26.85	25.89	−14.87	−11.30	10.10	−17.02
			MP2/aug-cc-pVTZ			
1	−14.38	13.30	−10.48	−9.70	13.61	−7.64
2	−22.27	20.86				−13.70

[a] There were problems with the convergence of some of energy components within the Morokuma−Kitaura scheme for $n = 2$ and 3 and the aug-cc-pVTZ basis set.

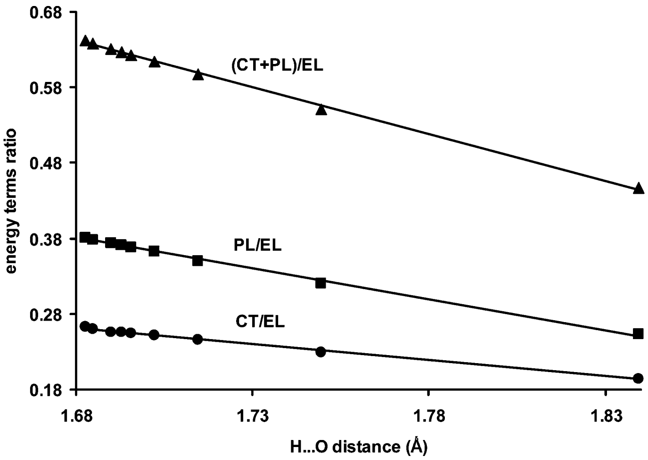

Figure 5. Linear correlation between H···O distance (Å) and the ratio of the interaction energy terms: charge transfer/electrostatic (CT/EL), polarization/electrostatic (PL/EL) and polarization and charge transfer/electrostatic ((CT+PL)/EL). Linear systems are taken into account; the Kitaura−Morokuma decomposition scheme; MP2/aug-cc-pVDZ level of approximation.

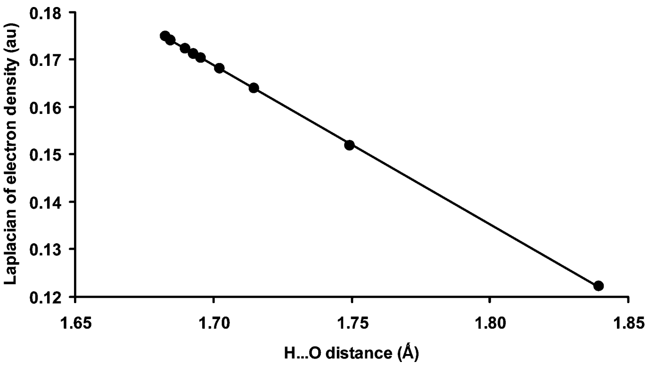

Figure 6. Linear dependence between H···O distance (Å) and the Laplacian of electron density at the corresponding H···O bond critical point. The linear systems are taken into account; MP2/aug-cc-pVDZ level of approximation.

ratios are analyzed here, CT/El, PL/EL and (CT + PL)/EL and their correlations with H···O distance are presented (Figure 5). The linear correlation coefficients for these three dependencies are equal to 0.999. One can see that not only the charge transfer energy depends on the proton···acceptor distance (covalency) but also the polarization energy term. The second term depends on the proton···acceptor distance even more because the polarization/electrostatic ratio increases more than the charge transfer/electrostatic ratio if the H···O distance decreases. However, one should also know that the results of Tables 5 and 6 are mostly qualitative because the results presented herein are not free of the BSSE error. Additionally there is the MIX interaction energy term within the Morokuma-Kitaura scheme which is the result of nonseparated components.

These findings show the σ-cooperativity effect enhances H-bond interaction and hence the covalency of this interaction. The covalency is related to the greater importance of the delocalization energy (polarization and charge transfer) and less importance of electrostatic energy. That may be supported if one relates to the recent statements that the electrostatic interaction is overestimated as computed at the Hartree−Fock level at which there is a too stabilizing electrostatic interaction at the cost of covalency.[45]

Topological Parameters. The Bader theory is applied here to analyze the characteristics of the H···O bond critical point (BCP). It is worth mentioning that in the equilibrium geometry an interatomic interaction line is referred to as a bond path.[46] For such equilibrium molecular structure, for each bond path of interacting atoms there is the virial path.[46,47] These statements were questioned from time to time because for equilibrium structures the steric repulsion hydrogen−hydrogen interactions were detected with bond paths and corresponding BCPs.[48] However, it was also found recently that hydrogen−hydrogen interactions known usually as those steric ones make the stabilizing energy contribution.[47] Such H−H interactions are recently the subject of disputes.[49]

However, in the case of relatively strong F−H···O interactions analyzed here there are the corresponding bond paths and critical points (CPs) within the equilibrium structures. And such H···O BCPs are characterized here. It was found and indicated in numerous studies that the characteristics of proton···acceptor BCPs are very useful to estimate the strength of hydrogen bonding.[50] Such parameters as electron density at the proton···acceptor BCP (ρ_C) and its Laplacian ($\nabla^2\rho_C$) often correlate with the H-bond energy or other parameters, among them the proton···acceptor distance, the proton donating bond length, etc. Such relationships are often well fulfilled, especially for homogeneous samples of complexes.[51] Figure 6 shows the dependence between the H···O distance and the Laplacian of electron density at the corresponding BCP. The linear systems investigated here are presented. It is worth mentioning that the linear correlation coefficient is equal to 1.000.

The parameters derived from the Bader theory also indicate the type of interaction. The negative value of Laplacian of electron density at BCP indicates that there is a shared interaction as is the covalent bond. The positive $\nabla^2\rho_C$ concerns the interaction of the closed-shell systems: ionic interaction, van der Waals or hydrogen bonding. In the latter case the negative $\nabla^2\rho_C$ shows that the H-bond is covalent in nature. It was found for the experimental electron density that $\nabla^2\rho_C$ for

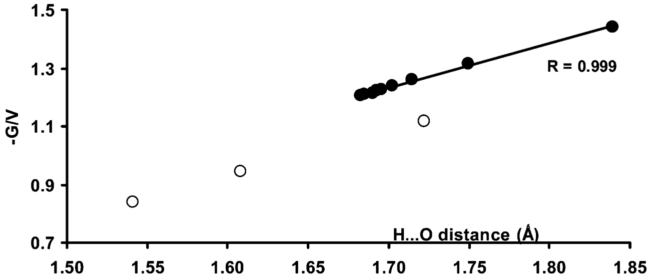

Figure 7. Relationship between H···O distance (Å) and the $-G/V$ ratio (G, the kinetic electron energy density at BCP; V, the potential electron energy density at BCP); MP2/aug-cc-pVDZ level of approximation.

TABLE 7: Topological Parameters for the C_{2v} Symmetry Systems Analyzed Here[a]

n	ρ_C	$\nabla^2\rho_C$	G_C	V_C	H_C	$-G_C/V_C$
1	0.0214	0.1222	0.0234	−0.0162	0.0072	1.444
2	0.0270	0.1520	0.0306	−0.0233	0.0073	1.313
3	0.0297	0.1640	0.0340	−0.0270	0.0070	1.259
4	0.0297	0.1681	0.0353	−0.0285	0.0068	1.239
5	0.0297	0.1703	0.0360	−0.0293	0.0066	1.229
6	0.0297	0.1712	0.0363	−0.0297	0.0066	1.222
7	0.0324	0.1750	0.0374	−0.0311	0.0064	1.203
8	0.0318	0.1722	0.0366	−0.0301	0.0065	1.216
9	0.0322	0.1741	0.0372	−0.0308	0.0064	1.208

[a] Electron density at H...O BCP is included as well as its Laplacian and the energetic parameters of H...O BCP; all values in au.

both H···O interactions within O−H···O bridge are negative, showing the covalent nature of hydrogen bonding.[12] There are other theoretical studies where the covalent nature of H-bonding was detected.[17] It was detected for very strong dihydrogen bonds,[17] for resonance-assisted hydrogen bonds[18] or for proton sponges.[52] It was also claimed that, if $\nabla^2\rho_C$ is positive but H_C is negative, then the interaction, as for hydrogen bonding, is partly covalent in nature.[20] H_C is the electron energy density at BCP and is the sum of the kinetic electron energy density (G_C) and the potential electron energy density (V_C). The latter value is negative, and the previous one is positive. The balance between those two values determines the kind of interaction. Hence the $-G_C/V_C$ may show the regions belonging to covalent or noncovalent interactions. If such a ratio is greater than 1, then the interaction is noncovalent. In the case of the ratio between 0.5 and 1, the interaction is partly covalent in nature and where $-G_C/V_C$ is less than 0.5; thus interaction is a shared interaction because $\nabla^2\rho_C$ is negative. Figure 7 shows the relationship between the H···O distance and the ratio mentioned above. One can see that for all linear systems H_C values are positive (Table 7); hence, $-G_C/V_C$ is greater than 1 and belongs to noncovalent interactions. In the linear systems one can observe all tendencies, indicating the role of the cooperative effect: an increase of F−H···O interaction if the number of HF molecules increases: there is the increase of ρ_C, $\nabla^2\rho_C$, G_C and a decrease of V_C and H_C. The same tendencies are observed for nonlinear systems (Table 8). However, in the latter case some H···O interactions may be treated as partly covalent in nature because the H_C values are negative, that is, when $n = 2$ and 3. Even at the MP2/aug-cc-pVTZ level of theory all fully optimized complexes show negative H_C values for H···O interactions. This is confirmed in Figure 7 where for $n = 2$ and 3 and the nonlinear complexes belong to the region of $H_C \in (0.5;1)$.

TABLE 8: Topological Parameters for the Fully Optimized Systems Analyzed Here[a]

n	ρ_C	$\nabla^2\rho_C$	G_C	V_C	H_C	$-G_C/V_C$
MP2/6-311++G(d,p)						
1	0.0333	0.1391	0.0334	−0.0320	0.0014	1.044
2	0.0453	0.1648	0.0447	−0.0481	−0.0035	0.929
3	0.0545	0.1794	0.0531	−0.0614	−0.0083	0.865
MP2/aug-cc-pVDZ						
1	0.0362	0.1610	0.0365	−0.0327	0.0038	1.116
2	0.0491	0.1846	0.0490	−0.0519	−0.0029	0.944
3	0.0593	0.1862	0.0578	−0.0691	−0.0113	0.836
MP2/aug-cc-pVTZ						
1	0.0410	0.1085	0.0353	−0.0434	−0.0082	0.813
2	0.0552	0.1236	0.0468	−0.0626	−0.0159	0.748
3	0.0665	0.1272	0.0554	−0.0790	−0.0236	0.701

[a] Electron density at H...O BCP is included as well as its Laplacian and the energetic parameters of H...O BCP; all values in au.

Summary

The influence of the cooperativity effect on the strength of hydrogen bonding was investigated for $H_2CO\cdots(HF)_n$ complexes. It was found that the additional HF molecules acting as proton donors as well as proton acceptors enhance the F−H···O H-bond strength. This is confirmed by geometrical, energetic and topological parameters; the H···O distances are shorter and the H-bond energies as well as the ρ_C and $\nabla^2\rho_C$ values are greater if the number of HF molecules increases.

The decomposition of the interaction energy shows that, for stronger H-bonds, the delocalization energy term becomes more important because the ratio (delocalization energy)/(electrostatic energy) increases if the H···O distance decreases. In other words, the cooperativity effect enhances the covalent nature of the H-bond interaction. The Morokuma−Kitaura decomposition scheme was also applied, and it was found that the values of well-known interaction energy terms such as “polarization” and “charge transfer” increase when the cooperativity effect is stronger. This verifies slightly the previous findings because until now it was stated that for very strong H-bonds the charge transfer energy is the most important. Our studies indicate that the polarization interaction energy term is even more important than the charge transfer term.

The topological parameters derived from the Bader theory are in line with the considerations based on the energetic and geometrical parameters. For nonlinear systems the inclusion of additional hydrogen fluoride molecules enhances the H-bond and even causes this interaction to become partly covalent in nature.

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(8) The binding energy is usually computed as the difference between the total energy of the complex (E_{AB}) and the energies of the isolated monomers (E_A and E_B); for stable complexes in minima such values are negative; for the convenience of discussion the absolute positive values of binding energies are presented ($-E_{AB}$) in the text, and E_{AB} values and the terms of the decomposition of the interaction energies are given in tables.

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