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π-Systems as Simultaneous Hydride and Hydrogen Bond Acceptors

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A theoretical study of the hydride bond complexes with tetrafluoro- and tetracyanoethylene, C_2F_4 and $C_2(CN)_4$, has been carried out by means of density functional theory (DFT) and *ab initio* methods, up to the MP2/aug-cc-pVTZ computational level. In addition, the ternary complexes formed by an additional standard hydrogen bond donor, such as hydrogen fluoride, have been explored. The results show that the hydride bond complexes are stable and an electron transfer took place from the hydride to the C_2F_4 and $C_2(CN)_4$ molecules. While these molecules are not able to form stable complexes between the π-electrons and hydrogen bond donors, the presence of the hydrides in the opposite face of the π-system of C_2F_4 stabilizes the ternary complexes showing cooperativity effects.

Introduction

In the last years, a number of reports have described an increasing variety of groups that can be involved in hydrogen bond (HB) interactions.[1,2] The traditional idea that the hydrogen atom involved in the HB should be electron-deficient has been overcome with those cases where both interacting atoms were hydrogen, one positively charged and another negatively charged. This special kind of hydrogen bond has been designated as a dihydrogen bond.[3–16]

As an extension of this idea, hydride bond interactions, formerly named as inverse hydrogen bonds,[17] have been proposed where the unique hydrogen atom involved in the interaction is the one providing the needed electronic excess for the complex stabilization (Scheme 1).[17–20]

The π-systems are among the new groups able to act as HB acceptors. Following the seminal articles on the complexes between benzene and hydrogen fluoride, water, and ammonia,[21–23] many reports, both theoretical and experimental, have been published.[24–33]

Simultaneously, a large set of articles have shown the possibility of interaction between electron-rich groups and π-deficient systems.[34–44] Most of the π-deficient systems correspond to perfluorinated aromatic molecules.

In this article, we describe the possible formation of hydride bonds with two simple π-deficient systems, C_2F_4 and $C_2(CN)_4$. In addition, the interesting possibility of ternary complexes formed by hydric molecules, C_2F_4, and a protic HB donor have been explored.

Methods

Two density functional theory (DFT) based methods, B3LYP[45,46] and M05-2X,[47] with the 6-311++G(d,p) basis set[48] have been initially used to optimize the monomers and complexes. Further optimizations have been carried out with the MP2/6-311++G(d,p) computational method and, in selected cases, with the MP2/aug-cc-pVTZ one.[49,50] In all the cases, save the MP2/aug-cc-pVTZ method, frequency calculations at the corresponding computational level have been carried out to confirm whether the geometries obtained correspond to energetic minima. All the calculations have been carried out within the Gaussian03 package.[51]

SCHEME 1: Hydrogen Bond, Dihydrogen Bond, And Hydride Bond

A-H···B	A-H···H-M	X···H-M
δ+ δ–	δ+ δ–	δ+ δ–

The interaction energy has been calculated as the difference between the total energy of the complexes minus the sum of the energies of the isolated monomers. The basis sets used in this work are of sufficient quality that basis set superposition errors (BSSEs) should be rather small.[52] Moreover, it has been shown[53] that uncorrected MP2/aug-cc-pVTZ binding energies lie between corrected and uncorrected MP2/aug-cc-pVQZ energies. BSSE corrections may not always improve binding energies of hydrogen-bonded complexes, since in the counterpoise method[54] a monomer may utilize the valence and core functions of its partner, which are not available to the monomer in the complex.

The electron density topology and atomic properties have been evaluated within the AIM methodology[55] with the AIMPAC[56] and Morphy98 programs[57] using the using the M05-2X/6-311++G(d,p) wave function. The calculation of the atomic properties has been carried out by integration within the atomic basins using the default parameters except in those cases where the integrated Laplacian was larger than 1×10^{-3}, where more tight conditions have been used. Previous reports have shown small errors in the energy and charge for systems where all the values of the integrated Laplacian was smaller than the mentioned value.[58]

The orbital interactions have been analyzed within the natural bond orbital (NBO) framework[59] and the NBO 3.1 program.[60] This method allows analyses of the interactions between filled and empty orbitals and associates them to charge-transfer processes. These calculations have been carried out using the using the M05-2X/6-311++G(d,p) computational level.

Results and Discussion

Isolated Monomers. The inclusion of four electron withdrawing substituents into the ethylene molecule, such as fluorine and cyano groups, reduces considerably the available electrons

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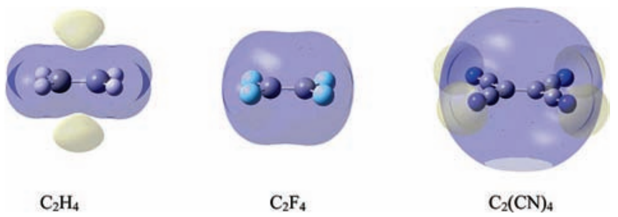
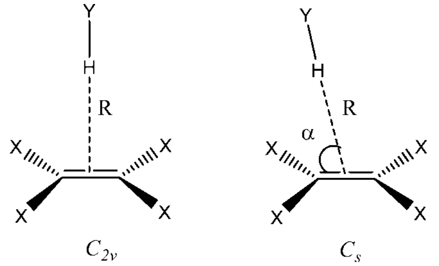


Figure 1. Molecular electrostatic potential at ±0.02 au. Isosurfaces using the M05-2X/6-311++G(d,p) wave function.

TABLE 1: Effect of the Partition Method in the Calculation of the Charges (e) at the M05-2X/6-311++G(d,p) Computational Level

	C_2H_4		C_2F_4		$C_2(CN)_4$	
partition method	C	H	C	F	C	CN
NBO	−0.380	0.190	0.634	−0.317	−0.125	0.062
AIM	−0.058	0.029	1.230	−0.615	0.181	−0.091
CHelpG	−0.281	0.1406	0.292	−0.146	−0.051	0.025

SCHEME 2: Schematic Representation of the Configurations Considered



X = F, CN Y = Li, Na, BeH, MgH, Be_2H_3, Mg_2H_3

in the π-double bond. Thus, the molecular electrostatic potential (MEP) does not present any negative region above/below the double bond but a positive region, especially in the case of the tetracyanoethylene molecule (Figure 1). The atomic derived charges with different methods have been gathered in Table 1. While the carbon atoms present negative charges in ethylene, they become positive for the tetrafluoroethylene in all the methods considered. In the case of the tetracyanoethylene, only the AIM partition provides positive charge for the central carbon atoms, in agreement with the electrostatic potential exhibited by this molecule.

The C_2F_4 and $C_2(CN)_4$ molecules present the quadrupole moments in the ZZ directions with opposite sign to that of C_2H_4 (−1.03, −1.36, and 1.25 D Å, respectively). An analysis on this property on C_6H_6, C_6F_6, and other related aromatic systems has been used to explain the preference of those systems with positive quadrupole to interact with cations, while the ones with negative quadrupole tend to form complexes with anions.[61]

As a counterpart of the π-deficient systems, molecules with electron-rich hydrogen atoms have been chosen based on their simplicity and on previous reports that show their suitability to act as electron donors in other interactions.[11]

Hydride Bonds with π-Systems. Initially, the complexes between C_2X_4 (X = F, CN) and the electron donors have been optimized with a C_{2v} symmetry (Scheme 2) by analogy with the experimental and calculated complexes of C_2H_4 with HB donors. However, the complexes obtained with this symmetry are not energetic minima. The minima configurations (C_s) of the C_2F_4 complexes present the electron donor systems slightly out of the C_{2v} symmetry axes (Figure 2) with the exception of the C_2F_4:HNa complex. In the case of the $C_2(CN)_4$ complexes with HLi and HNa, the hydride molecule is spontaneously dissociated, being the hydrogen covalently bonded to one of the carbon atoms and the metal to one of the nitrogens.

The intermolecular geometrical parameters of the calculated minima complexes have been gathered in Table 2, and the data of those with C_{2v} symmetry are included in the Supporting Information. In general, the longer distance for a given complex always corresponds to the B3LYP calculations and the shorter distance corresponds to the MP2/aug-cc-pVTZ, whereas the M05-2X and MP2/6-311++G(d,p) results are very similar. For a given hydride system, the distances for the $C_2(CN)_4$ complex are shorter than the corresponding C_2F_4 ones. In both series, the shorter distances correspond to those of the HLi and HNa complexes while the longer ones are those of the BeH_2 and Be_2H_4 ones. The distances obtained in these complexes are much larger than those found in the HB complexes of ethylene. For instance, the calculated C_2H_4:HF complex at the MP2/6-311++G(d,p) computational level presents a distance of 2.194 Å between the hydrogen and the center of the C−C bond.[25]

The lack of C_{2v} symmetry in the minima configuration could indicate a secondary interaction between the electron withdrawing moieties and the electropositive part of the metallic hydrides or that the electron donor molecules tried to avoid the residual electrons in the π-cloud. In any case, the energetic differences observed between the C_{2v} complexes and those of the true minima in most of the cases are very small.

The calculated interaction energies of the minima complexes are shown in Table 3. The statistical analysis of these results (eqs 13) shows that the MP2/6-311++G(d,p) values are the most similar to the MP2/aug-cc-pVTZ values, with the largest correlation coefficient, slope close to unity, and small intercept. Between the two DFT methods considered, the M05-2X method is clearly better than the B3LYP one. However, the former DFT method is not able to locate two of the minima present at the MP2 level.

$$\mathrm{Ei(MP2/aug\text{-}cc\text{-}pVTZ)} = -3.44 + 1.47 \times \mathrm{Ei(B3LYP/6\text{-}311{+}{+}G(d,p))}, \quad r^2 = 0.980 \tag{1}$$

$$\mathrm{Ei(MP2/aug\text{-}cc\text{-}pVTZ)} = -0.15 + 1.18 \times \mathrm{Ei(M05\text{-}2X/6\text{-}311{+}{+}G(d,p))}, \quad r^2 = 0.988 \tag{2}$$

$$\mathrm{Ei(MP2/aug\text{-}cc\text{-}pVTZ)} = -0.17 + 1.04 \times \mathrm{Ei(MP2/6\text{-}311{+}{+}G(d,p))}, \quad r^2 = 0.999 \tag{3}$$

The NBO analysis does not show any significant orbital interactions between the interacting molecules which indicates the main electrostatic nature of the interaction.

The energetic results obtained can be qualitatively explained based on the electronic characteristics of the two interacting systems. Thus, the complexes with HLi and HNa should be dominated by a dipole−quadrupole interaction, while in the rest the dominant term should be the quadrupole−quadrupole one. Thus, the interaction energy of the complexes with HNa are always slightly more stable than the ones with HLi, being the relationship of those energies is almost identical to that of the dipole moment of the isolated hydrides. In the same way, the energetic values obtained for the Be and Mg hydrides follow the same ordering of their calculated quadrupole moments. Regarding the quadrupole of the C_2X_4 molecules, the values obtained for the two isolated molecules in the interaction direction are not able to explain the large differences in the stability of their complexes as an indication that other effects such as proton transfer and electronic

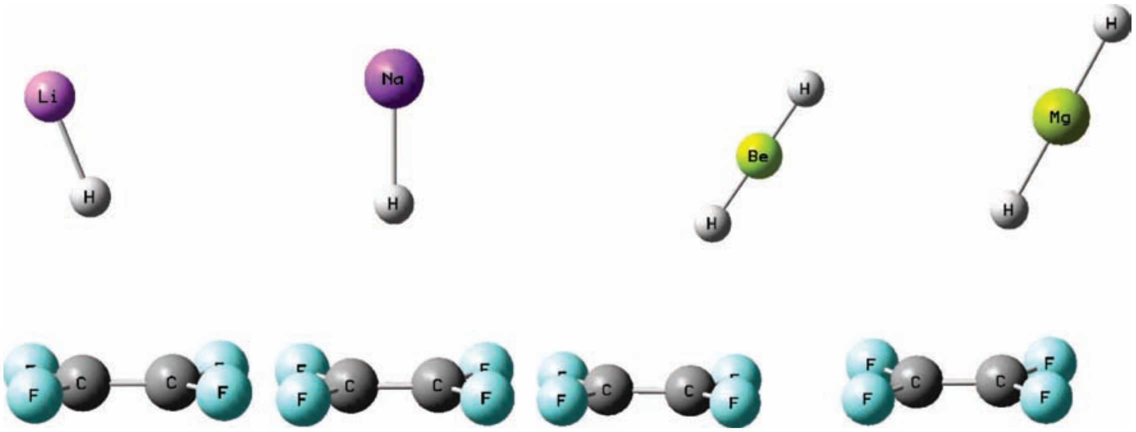


Figure 2. Optimized geometries of some of the minima complexes studied at the MP2/aug-cc-pVTZ computational level.

TABLE 2: Geometrical Intermolecular Parameters of the Calculated Minima Complexes

	B3LYP/6-311++G(d,p)		M05-2X/6-311++G(d,p)		MP2/6-311++G(d,p)		MP2/aug-cc-pVTZ	
complex	R	α	R	α	R	α	R	α
C_2F_4:HLi	2.996	80.6	2.889	75.5	2.890	80.9	2.804	79.0
C_2F_4:HNa	2.979	90.0	2.869	90.0	2.865	90.0	2.779	90.0
C_2F_4:BeH_2	3.247	75.7	–[a]	–	3.030	74.8	2.907	70.1
C_2F_4:MgH_2	3.138	76.3	–[a]	–	2.974	76.9	2.875	73.1
C_2F_4:Be_2H_4	3.170	79.1	3.082	66.7	2.971	78.6	n.c.[b]	
C_2F_4:Mg_2H_4	3.112	79.1	2.960	72.4	2.951	78.1	n.c.[b]	
$C_2(CN)_4$:BeH_2	3.156	74.1	2.952	69.0	2.885	74.1	n.c.[b]	
$C_2(CN)_4$:MgH_2	3.011	65.9	2.887	64.2	2.829	69.0	n.c.[b]	
$C_2(CN)_4$:Be_2H_4	3.078	72.3	3.075	62.2	2.928	69.1	n.c.[b]	
$C_2(CN)_4$:Mg_2H_4	2.988	66.3	2.876	64.2	2.824	70.3	n.c.[b]	

[a] The minimum found does not correspond to the interaction of the hydride with the π-system. [b] n.c. stands for not calculated.

TABLE 3: Interaction Energy (kJ/mol) of the Minima Complexes Studied

complex	B3LYP/ 6-311++ G(d,p)	M05-2X/ 6-311++ G(d,p)	MP2/ 6-311++ G(d,p)	MP2/ aug-cc-pVTZ
C_2F_4:HLi	−9.63	−14.62	−14.99	−15.01
C_2F_4:HNa	−9.86	−15.28	−16.26	−16.17
C_2F_4:BeH_2	−2.13	–[a]	−6.20	−7.02
C_2F_4:MgH_2	−4.28	–[a]	−9.19	−9.50
C_2F_4:Be_2H_4	−2.99	−7.82	−7.82	n.c.[b]
C_2F_4:Mg_2H_4	−4.77	−8.80	−10.21	n.c.[b]
$C_2(CN)_4$:BeH_2	−5.84	−11.46	−15.08	n.c.[b]
$C_2(CN)_4$:MgH_2	−12.97	−20.40	−25.09	n.c.[b]
$C_2(CN)_4$:Be_2H_4	−8.44	−15.71	−19.75	n.c.[b]
$C_2(CN)_4$:Mg_2H_4	−14.37	−22.09	−27.12	n.c.[b]

[a] The minimum found does not correspond to the interaction of the hydride with the π-system. [b] n.c. stands for not calculated.

polarization are important. Thus, the complexes with $C_2(CN)_4$ are up to three times more stable than the corresponding ones with C_2F_4.

The representation of the MEP values of the isolated C_2X_4 molecules in the position of the interacting hydrogen versus the corresponding interaction energy, for the C_{2v} symmetry complexes, shows a clear relationship between these two parameters (Figure 3).

The topology of the electron density shows a T shape path between the hydrides and the C_2X_4 molecules in the complexes with C_{2v} symmetry, while in the minima configuration the bond path links the hydride with the closest carbon atom (Figure 4). These results are an indication of a catastrophic topological description for the C_{2v} configuration as previously shown for the analogous hydrogen-bonded complexes.[25] The characteristics of the intermolecular bond critical points have been gathered in Table 4. In all cases, the electron density is small and presents a positive value of the Laplacian, similar to that found in weak interactions such as standard hydrogen bonds.[62] The important curvature of most of the intermolecular bond paths prevents the presence of good correlations between the electron density at the bond critical point or its Laplacian versus the interatomic distances as have been found for other cases.[63–67]

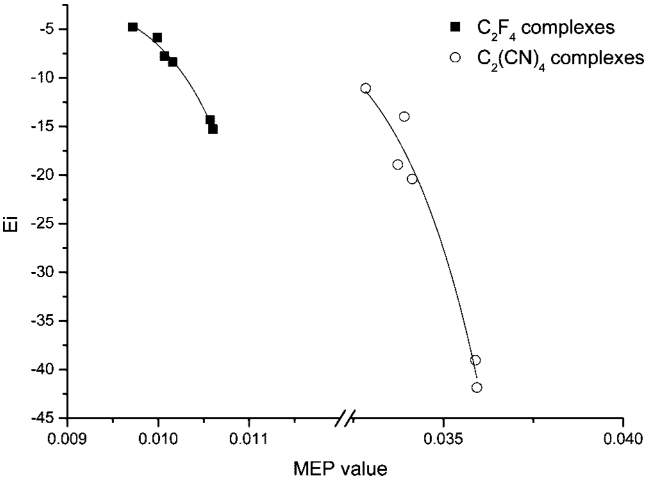


Figure 3. Interaction energy (kJ/mol) versus MEP value (au) in the position of the interacting hydrogen obtained at the M05-2X/6-311++G(d,p) computational level.

The integration of the atomic properties within the AIM methodology (Table 5) of the minima configurations at the M05-2X/6-311+G(d,p) computational level shows an energetic stabilization of the C_2X_4 molecule except for those complexes with magnesium hydrides. As expected, the hydride transfers

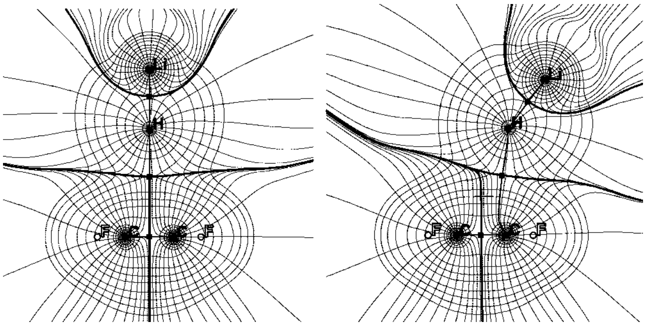


Figure 4. Electron density map of the C_2F_4:HLi complexes using the M05-2X/6-311++G(d,p) wave function. The position of the atoms is indicated with circles, and the bond critical points are indicated with squares. The atomic interaction lines are shown.

TABLE 4: Electron Density and Laplacian (au) at the Intermolecular Bond Critical Points Calculated at the M05-2X/6-311++G(d,p) Computational Level

complex	conf	ρ	$\nabla^2\rho$
C_2F_4:HLi	C_{2v}	0.0082	0.0170
C_2F_4:HLi	min	0.0089	0.0184
C_2F_4:HNa	C_{2v}/min	0.0085	0.0170
C_2F_4:BeH_2	C_{2v}	0.0055	0.0125
C_2F_4:MgH_2	C_{2v}	0.0067	0.0143
C_2F_4:Be_2H_4	C_{2v}	0.0059	0.0135
C_2F_4:Be_2H_4	min	0.0067	0.0186
C_2F_4:Mg_2H_4	C_{2v}	0.0068	0.0146
C_2F_4:Mg_2H_4	min	0.0073	0.0167
$C_2(CN)_4$:HLi	C_{2v}	0.0100	0.0214
$C_2(CN)_4$:HNa	C_{2v}	0.0103	0.0214
$C_2(CN)_4$:BeH_2	C_{2v}	0.0065	0.0152
$C_2(CN)_4$:BeH_2	min	0.0074	0.0189
$C_2(CN)_4$:MgH_2	C_{2v}	0.0077	0.0170
$C_2(CN)_4$:MgH_2	min	0.0102	0.0238
$C_2(CN)_4$:Be_2H_4	C_{2v}	0.0071	0.0169
$C_2(CN)_4$:Be_2H_4	min	0.0080	0.0221
$C_2(CN)_4$:Mg_2H_4	C_{2v}	0.0080	0.0176
$C_2(CN)_4$:Mg_2H_4	min	0.0106	0.0248

TABLE 5: Variation of the Molecular Properties (Energy (kJ/mol), Charge (e), and Volume (au)) Calculated by Integration Within the AIM Methodology Using the M05-2X/6-311++G(d,p) Wave Function

complex	Δ energy (C_2X_4)	Δ charge (C_2X_4)	Δ vol (C_2X_4)	Δ vol total
C_2F_4:LiH	−140.86	−0.039	4.40	−8.38
C_2F_4:NaH	−41.17	−0.039	4.89	−9.89
C_2F_4:Be_2H_4	−355.31	−0.019	2.78	−5.05
C_2F_4:Mg_2H_4	13.29	−0.021	2.91	−4.14
$C_2(CN)_4$:BeH_2	−131.27	−0.015	2.52	−0.57
$C_2(CN)_4$:MgH_2	338.39	−0.040	1.50	−12.50
$C_2(CN)_4$:Be_2H_4	−296.06	−0.021	−7.55	−17.01
$C_2(CN)_4$:Mg_2H_4	513.13	−0.042	−4.57	−22.06

charge to the C_2X_4 molecule, which has been associated with a gain of the molecular volume.[68] However, in this case, two of the complexes increase their electron charge but lose volume. Finally, a loss of the volume with respect to the sum of the isolated monomers is observed for all the cases considered.

Another interesting feature observed in the complexes associated to the charge transfer and molecular polarization corresponds to the dipole moment enhancement when compared to the sum of those of the isolated interacting molecules. The values of the dipole moment enhancement are larger for the $C_2(CN)_4$ complexes (between 0.30 and 1.24 debyes) than those of the C_2F_4 complexes (between 0.13 and 0.63 debyes). In both series, the larger enhancement corresponds to the HNa complexes. In addition, the representation of this parameter versus the interaction energy for the C_{2v} complexes shows that both are related (Figure 5).

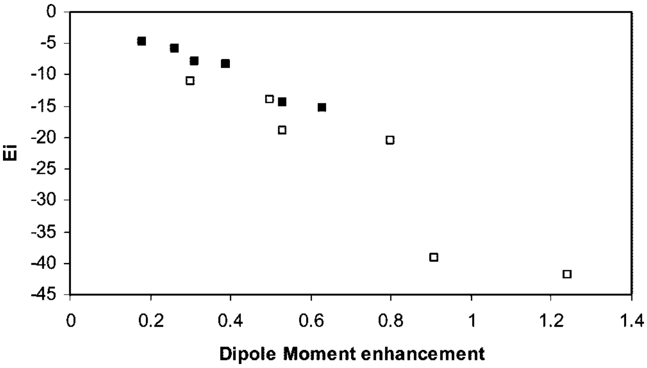
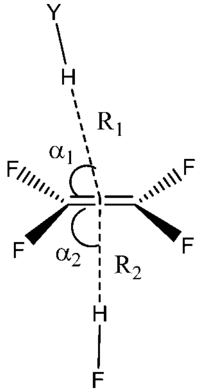


Figure 5. Dipole moment enhancement (debye) versus interaction energy (kJ/mol) of the complexes in C_{2v} symmetry calculated at the M05-2X/6-311++G(d,p) computational level. Black and white squares represent the C_2F_4 and $C_2(CN)_4$ complexes, respectively.

SCHEME 3: Ternary Complexes Studied[a]



[a] The parameters used in Table 6 are indicated.

Cooperativity with HB Donors. The reduction of the π-electrons of the C_2X_4 molecule due to the presence of the four electron withdrawing substituents prevents the formation of complexes analogous to those obtained between ethylene and HB donors, such as hydrogen fluoride. However, we found that ternary complexes with an electron donor in one face of the π-cloud of the C_2F_4 molecule and HF in the opposite one are stable (Scheme 3). As previously, the C_{2v} and C_s configurations have been explored, with the C_{2v} complex minima only in the NaH:C_2F_4:HF case and C_s in the rest. For the complex with BeH_2, no minima has been found with the hydride atom pointing toward the C−C bond.

The distances (Table 6) obtained between the hydric hydrogen and the C_2F_4 are shorter than the corresponding ones obtained in the dimeric complexes studied before, with the larger differences for the HLi and HNa complexes having differences up to 0.14 Å at the MP2/6-311++G(d,p) computational level. In addition, it is noteworthy the almost perfect C_{2v} disposition of the HF:C_2F_4 atoms in all the complexes considered as indicated by an α_2 angle very close to 90°. The distances of the interacting hydrogens to the center of the C−C bonds for the hydride atoms are larger (between 2.73 to 2.94 Å) than those of the protic ones (between 2.36 to 2.64 Å) at the MP2/6-311++G(d,p) computational level. These differences confirm the larger electron density of the hydride atoms versus the protic ones.

The interaction energies of the trimeric structures have been gathered in Table 7. Even though these results seem to indicate

TABLE 6: Intermolecular Geometrical Parameters of the Ternary Minima Complexes

	B3LYP/6-311++G(d,p)				M05-2X/6-311++G(d,p)				MP2/6-311++G(d,p)				MP2/aug-cc-pVTZ			
complex	R_1	α_1	R_2	α_2	R_1	α_1	R_2	α_2	R_1	α_1	R_2	α_2	R_1	α_1	R_2	α_2
FH:C_2F_4:HLi	2.820	90.0	2.369	90.0	2.737	101.8	2.297	89.3	2.757	97.5	2.367	89.7	2.680	82.7	2.233	90.4
FH:C_2F_4:HNa	2.820	90.0	2.369	90.0	2.712	90.0	2.324	90.0	2.728	90.0	2.357	90.0	2.660	90.0	2.222	90.0
FH:C_2F_4:MgH_2	2.997	98.1	2.537	90.0	2.856	105.1	2.441	90.0	2.872	99.4	2.536	89.4				
FH:C_2F_4:Be_2H_4	3.052	80.0	2.600	89.6	2.841	76.3	2.421	90.2	2.889	78.9	2.600	90.2				
FH:C_2F_4:Mg_2H_4	3.052	79.9	2.595	89.7	2.895	72.3	2.484	90.2	2.849	79.9	2.488	89.6				

TABLE 7: Interaction Energy and Cooperativity (kJ/mol) of the Ternary Minima Complexes

	B3LYP/6-311++G(d,p)			M05-2X/6-311++G(d,p)			MP2/6-311++G(d,p)			MP2/aug-cc-pVTZ		
complex	E_I	DHB[a]	coop	E_I	DHB[a]	coop	E_I	DHB[a]	coop	E_I	DHB[a]	coop
FH:C_2F_4:HLi	−14.70	−5.01	−0.10	−21.47	−5.69	−1.17	−22.18	−5.53	−1.67	−26.57	−5.71	−5.86
FH:C_2F_4:HNa	−15.30	−5.14	−0.30	−23.14	−6.09	−1.78	−24.48	−6.22	−2.00	−28.98	−6.45	−6.35
FH:C_2F_4:MgH_2	−4.16	−1.51	1.62	−9.54	−1.78	2.91	−11.33	−1.88	−0.31	−15.40	−1.97	−3.95
FH:C_2F_4:Be_2H_4	−2.14	−1.05	1.87	−6.93	−1.22	2.06	−9.22	−1.31	−0.12			
FH:C_2F_4:Mg_2H_4	−4.97	−1.67	1.41	−10.50	−2.06	0.32	−12.88	−2.25	−0.47			

[a] Interaction energy of the FH and hydride molecule as they stand in the ternary complex.

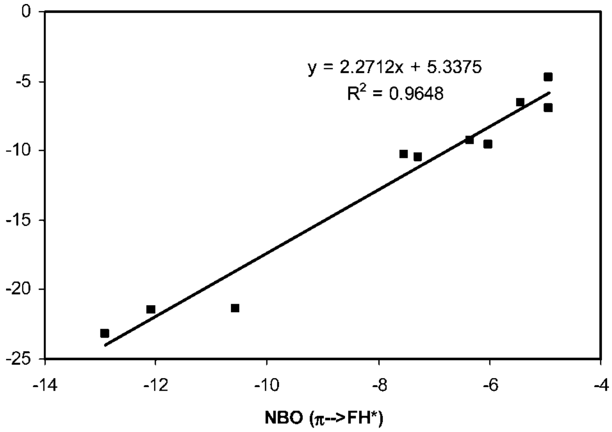


Figure 6. Interaction energy versus the $\pi \rightarrow$ FH antibonding orbital interaction (kJ/mol) of the complexes obtained at the M05-2X/6-311++G(d,p) computational level.

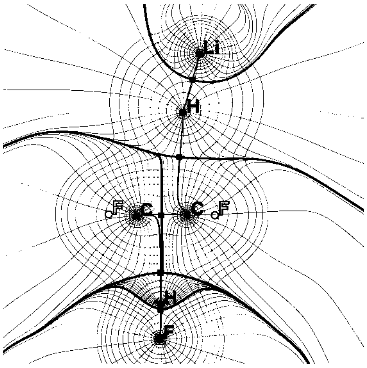


Figure 7. Electron density map of the LiH:C_2F_4:HF complex with indications of the bond critical point, bond path, and interatomic lines obtained with the M05-2X/6-311++G(d,p) wave function.

a cooperativity effect, we should consider that the interaction between the hydric and protic systems can play and important role in these trimeric complexes. Thus, we have evaluated the interaction energy of the pseudo-DHB complex by simply removing the C_2F_4 molecule. The results obtained show, indeed, that an important stabilizing interaction is established between these two systems with values over 6 kJ/mol in the complex where HNa and HF are involved.

Thus, the cooperativity values listed in Table 7 correspond to the difference of interaction energy of the trimer and the three possible dimers. In the case of the complex between the π-cloud of C_2F_4 and the HB donor, since no stable complex is obtained, a null interaction energy has been considered. The interaction between protic and the hydric systems has been evaluated as indicated above. Finally, the interaction energy between the C_2F_4 molecule and the electron donors has been taken from those obtained in the previous section of this article and listed in Table 3. The results obtained are highly dependent on the computational methods used. The MP2 calculations indicate the existence of a positive cooperative (the trimer is more stable than the sum of the three separated pairs), while the opposite is found with the DFT methods, with the exception of the HLi and HNa complexes.

The NBO analysis of these trimers presents an interaction between the π-cloud of the C_2F_4 molecule with the antibonding of the HF one. The energetic value of this orbital interaction ranges between −12.9 kJ/mol for the HNa:C_2F_4:HF complex

TABLE 8: Electron Density and Laplacian at the Intermolecular Bond Critical Points Using the M05-2X/6-311++G(d,p) Wave Function

		metal−H···π		F−H···π	
complex	conf.	ρ	$\nabla^2\rho$	ρ	$\nabla^2\rho$
FH:C_2F_4:HLi	C_{2v}	0.0100	0.0228	0.0127	0.0367
FH:C_2F_4:HLi	min	0.0105	0.0230	0.0137	0.0398
FH:C_2F_4:HNa	C_{2v}/min	0.0104	0.0229	0.0130	0.0373
FH:C_2F_4:BeH_2	C_{2v}	0.0062	0.0152	0.0088	0.0257
FH:C_2F_4:MgH_2	C_{2v}	0.0076	0.0178	0.0100	0.0293
FH:C_2F_4:MgH_2	min	0.0082	0.0191	0.0098	0.0287
FH:C_2F_4:Be_2H_4	C_{2v}	0.0068	0.0168	0.0093	0.0273
FH:C_2F_4:Be_2H_4	min	0.0072	0.0183	0.0088	0.0258
FH:C_2F_4:Mg_2H_4	C_{2v}	0.0078	0.0184	0.0103	0.0302
FH:C_2F_4:Mg_2H_4	min	0.0083	0.0192	0.0102	0.0300

TABLE 9: Variation of the Molecular Properties versus Those of the Isolated Molecules (kJ/mol and e) within the AIM Methodology Using the M05-2X/6-311++G(d,p) Wave Function

	energy			charge		
	C_2F_4	HF	hydride system	C_2F_4	HF	hydride system
FH:C_2F_4:HLi	−83.5	−67.5	129.5	−0.016	−0.029	0.045
FH:C_2F_4:HNa	−9.3	−49.7	35.9	−0.017	−0.030	0.048
FH:C_2F_4:H_2Mg	38.7	−38.3	−14.4	−0.006	−0.017	0.024
FH:C_2F_4:H_4Be_2	−259.4	−103.0	355.5	−0.005	−0.015	0.020
FH:C_2F_4:H_4Mg_2	38.5	−41.3	−7.8	−0.006	−0.019	0.025

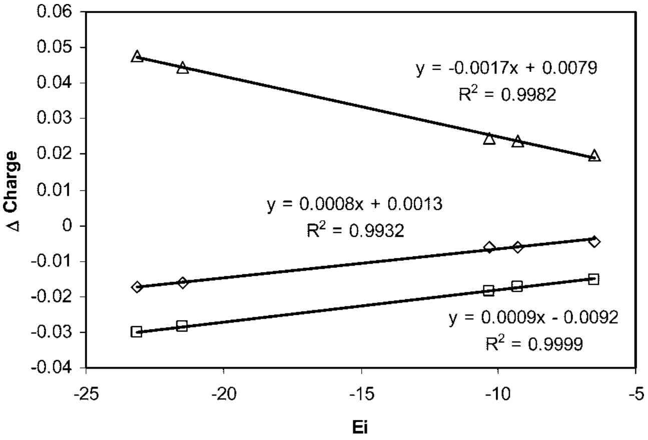


Figure 8. Charge variation (e) in the C_2F_4 (tilted squares), HF (triangles), and hydride molecules (squares) versus the interaction energy (kJ/mol) using the M05-2X/6-311++G(d,p) wave function.

to −4.9 kJ/mol for the corresponding one with the BeH_2 molecule. The representation of the total interaction energy of the trimers versus the orbital interaction shows that both are linearly related (Figure 6), in a similar way to what has been described for other hydrogen-bonded complexes.

The topological analysis of the electron density of the minima configurations shows that while the hydride atom is bonded to one of the carbon atoms of C_2F_4, the HF molecule is bonded to the other one as shown for the LiH:C_2F_4:HF complex in Figure 7. In the C_{2v} configurations, the bond path goes directly from the hydrogen atoms to the center of the C−C bond, in a similar way to that represented in Figure 4 (left side).

Both interactions present small values of the electron density at the bond critical point and positive values of the Laplacian (Table 8). However, if similar electron density values are compared, the value of 0.0100 e/bohr^3 is obtained for the hydric interaction in the FH:C_2F_4:HLi complex and, for the protic one in the FH:C_2F_4:MgH_2 complex, the hydric interactions present much larger interatomic distances than the protic ones, like if the former atom presents a more effective charge than the latter.[69,70]

The variations of molecular properties obtained by atomic integration within the AIM methodology are gathered in Table 9. Energetically, the hydrogen fluoride molecule is stabilized in all the complexes. As in the case of the dimer previously discussed, the C_2F_4 molecule is stabilized except for the complexes with magnesium. The opposite is observed for the metal hydride systems. A charge transfer is observed from the hydride molecule to the two other ones, presenting in all the cases the HF molecule the larger negative charge. The C_2F_4 molecule gains electronic charge in all the systems considered but less charge than hydrogen fluoride in the same complex. The charge variations for each molecule of the trimers are highly correlated with the corresponding interaction energy obtained (Figure 8).

Conclusion

A theoretical study of the suitability of hydride bond formation between the π-region of the C_2F_4 and $C_2(CN_4)$ molecules and systems with electron-rich hydrogen atoms has been carried out by means of DFT, B3LYP/6-311++G(d,p) and M05-2X/6-311++G(d,p), and *ab initio* methods, MP2/6-311++G(d,p) and MP2/aug-cc-pVTZ. The calculated interaction energies are related to the value of the electrostatic potential in the position of the interacting hydrogen of the isolated C_2X_4 molecules as well as the dipole moment enhancement due to the complex formation. The AIM analysis has allowed us to study the topology of the electron density and the evolution of the energy transfer at the molecular level.

In addition, the ternary complexes formed by a hydride molecule, C_2F_4, and a hydrogen bond donor system have been found to be stable, presenting cooperativity effects. The simultaneous presence in these complexes of hydrides and protons makes them possible models for studying transfer processes of both kinds that are of fundamental importance in biological systems.[71,72]

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Supporting Information Available: Geometrical and energetic parameters of the nonminima C_{2v} complexes. Cartesian coordinates of the complexes obtained at the MP2/6-311++G(d,p) computational level. This material is available free of charge via the Internet at http://pubs.acs.org.

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