

Simultaneous Interaction of Tetrafluoroethene with Anions and Hydrogen-Bond Donors: A Cooperativity Study

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Abstract: A computational study of the complexes formed by tetrafluoroethylene, C_2F_4 , with anions has been carried out by means of density functional theory (DFT) and second-order Möller–Plesset (MP2) computational methods, up to MP2/aug-cc-pVTZ level. In addition, the possibility of cooperativity in the interaction of anions and hydrogen-bond donors (FH, ClH, and H_2O) when interacting with different faces of the C_2F_4 molecule has been explored. Electron density of the complexes has been analyzed by means of atoms in molecules (AIM) methodology, while natural bond orbital (NBO) methodology has been used to characterize the orbital interaction. In addition, natural energy decomposition analysis (NEDA) has been applied to analyze the source of the interaction. The energetic results indicate that C_2F_4 is a weaker anion receptor than C_6F_6 , but in combination with the anions, it became a stronger hydrogen acceptor than C_2H_4 . Cooperativity effects are observed in $YH \cdot C_2F_4 \cdot X^-$ clusters. In $C_2F_4 \cdot X^-$ complexes the dominant attractive terms are the electrostatic and polarization ones, while in $YH \cdot C_2F_4 \cdot X^-$ complexes the charge transfer increases significantly, becoming the most important term for most of the FH and ClH complexes studied here.

Introduction

Noncovalent interactions play a crucial role in many areas of modern chemistry. They are important in deciding the conformation of many molecules.¹ They are also relevant in chemical reactions, molecular recognition, and regulation of biochemical processes.² These chemical processes are accomplished with specificity and efficiency by means of intricate combinations of weak intermolecular interactions of various sorts. Noncovalent interactions such as hydrogen bonding, anion– π , cation– π , and π – π interactions, and other weak forces govern the organization of multicomponent

supramolecular assemblies.³ A deep understanding of these interactions is of outstanding importance for the rationalization of effects observed in several fields, such as biochemistry and materials science. A quantitative description of these interactions can be performed by taking advantage of quantum chemical calculations on small model systems.⁴ In complex biological systems and in the solid state a multitude of these noncovalent interactions may operate simultaneously, giving rise to interesting cooperativity effects. For instance, it is well-known that hydrogen bonding shows highly cooperative behavior. The cumulative strength of networks of hydrogen bonds is larger than the sum of the individual bond strengths when they work simultaneously.⁵ Similar observations have been made for the interplay between stacking and hydrogen-bonding interactions. This

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combination is of great importance for the structural control in oligonucleotides.⁶ In addition, it has been recently demonstrated that there is interplay between ion- π and either π - π or hydrogen-bonding interactions, which can lead to strong cooperativity effects.⁷

In recent years, a number of reports have described an increasing variety of groups that can be involved in hydrogen-bond (HB) interactions.⁸ Among them, π -systems are able to act as hydrogen-bonding acceptors. In addition to pioneering works dealing with the complexation properties of benzene and hydrogen fluoride, water, and ammonia,⁹ several more recent studies have shed light on this topic from both theoretical and experimental views.¹⁰ Simultaneously, a large set of articles has shown the possibility of favorable interactions between electron-rich groups and π -deficient systems.¹¹ Among them, anion- π interactions¹² have attracted considerable attention in the last 5 years.¹³ There is a great deal of experimental¹⁴ and theoretical¹⁵ work that shows that anion- π interactions play a prominent role in several areas of chemistry, such as molecular recognition¹⁶ and transmembrane anion transport.¹⁷ Anion coordination is an important and challenging aspect of contemporary supramolecular chemistry. Recent investigations provided experimental evidence for the usefulness of anion- π interaction in a structurally directing role.¹⁸

Besides hydrogen bonds, the interactions between anions and π -systems are among the strongest noncovalent interactions in absolute terms. Obviously this depends on just how electron-deficient the π -system is. In the present paper we examine how these two interactions influence each other, using several criteria, that is, energetic and geometric features, an atoms-in-molecules (AIM) analysis, and a natural bond orbital (NBO) study. We describe the possible formation of anion- π complexes with a simple π -deficient system, C_2F_4 . In addition, the interesting possibility of formation of ternary complexes produced by the combination of several anions, C_2F_4 , and protic hydrogen-bonding donors has been explored.

Methods

The geometry of the systems has been initially optimized at the MP2/6-311++G(d,p)^{19,20} computational level. Frequency calculations at this computational level have been performed to confirm that the structures obtained correspond to energetic minima. Further optimization has been performed with the M05-2x/6-311++G(d,p)²¹ and MP2/aug-cc-pVTZ,²² computational methods. All these calculations have been carried out within the Gaussian-03 package.²³

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.²⁴ Moreover, it has been shown that uncorrected MP2/aug-cc-pVTZ binding energies lie between corrected and uncorrected MP2/aug-cc-pVQZ energies.²⁵ BSSE corrections may not always improve binding energies of weakly bonded complexes, since in the counterpoise method²⁶ a monomer may

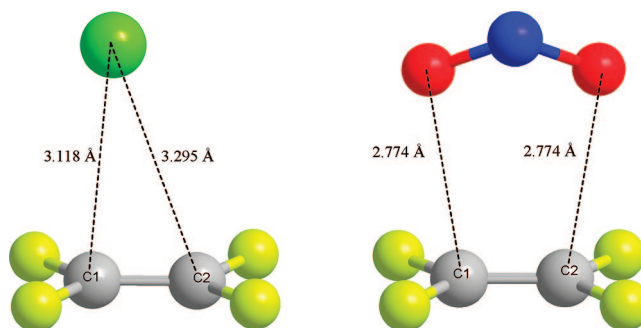


Figure 1. Optimized geometry of $C_2F_4 \cdot Cl^-$ and $C_2F_4 \cdot NO_2^-$ complexes at the MP2/6-311++G(d,p) computational level.

utilize the valence and core functions of its partner, which are not available to the monomer in the complex.

Electron density topology and atomic properties have been evaluated within the AIM methodology²⁷ with AIMPAC,²⁸ Morphy98,²⁹ and AIMAll programs³⁰ using the M05-2x/6-311++G(d,p) wave function. Calculation of the atomic properties has been carried out by integration within the atomic basins by use of 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 energy and charge for systems where all values of the integrated Laplacian were smaller than the mentioned value.³¹

Orbital interactions have been analyzed within the NBO³² framework and the NBO 5.0G program³³ at the M05-2x/6-311++G(d,p) computational level. This method allows analyses of the interaction between filled and empty orbitals and associates them with charge-transfer processes. In addition, natural energy decomposition analysis (NEDA)^{34,35} has been carried out to obtain insights into the source of the interactions. These calculations have been performed within the Gamess program.³⁶

Results and Discussion

C_2F_4 ·Anion Complexes. Geometrical characteristics of the obtained minimum-energy complexes are shown in Figure 1 and Table 1. For other anions, such as F^- and OH^- , a spontaneous attack of these systems on the C_2F_4 molecules is obtained with formation of covalent bond and will not be considered here. In general, the interacting atom of the anionic system is closer to one of the carbon atoms of C_2F_4 than the other. However, in the complexes with Br^- , NNN^- , HCO_2^- , and NO_2^- , the interaction with the two carbon atoms of C_2F_4 is the same, presenting C_{2v} symmetry in the first three cases and C_s symmetry in the last one. The distances obtained are very similar for the two computational methods used here; the longest distance is for the $C_2F_4 \cdot Br^-$ complex (3.34 Å at MP2/aug-cc-pVTZ computational level) and the shortest is that for $C_2F_4 \cdot O_2^-$ (2.50 Å), followed by those of the $C_2F_4 \cdot NCO$, $C_2F_4 \cdot HCO_2^-$, and $C_2F_4 \cdot NO_2^-$ complexes (2.71, 2.77, and 2.73 Å, respectively).

Interaction energies have been gathered in Table 2. The values range from $-62.6 \text{ kJ mol}^{-1}$ for the $C_2F_4 \cdot O_2^-$ complex to $-32.4 \text{ kJ mol}^{-1}$ for the $C_2F_4 \cdot CN^-$ one obtained at the MP2/aug-cc-pVTZ computational level. The interaction

Table 1. Interatomic Distances between the Closest Atom of the Anion and the Two Carbon Atoms of C₂F₄^a

complex	MP2/6-311++G(d,p)		M05-2x/6-311++G(d,p)		MP2/aug-cc-pvtz	
	X–C1	X–C2	X–C1	X–C2	X–C1	X–C2
C ₂ F ₄ •Cl [–]	3.118	3.295	3.130	3.336	3.118	3.294
C ₂ F ₄ •Br [–]	3.415	3.415	3.429	3.429	3.340	3.340
C ₂ F ₄ •CN ^{–b}	3.011	3.381	2.912	3.395	2.921	3.357
C ₂ F ₄ •NC ^{–b}	2.851	3.124	2.707	3.203	2.804	3.098
C ₂ F ₄ •NNN [–]	2.847	2.847	2.873	2.873	2.824	2.824
C ₂ F ₄ •NO ₂ [–]	2.774	2.774	2.733	2.733	2.732	2.732
C ₂ F ₄ •HCO ₂ [–]	2.779	2.779	2.726	2.726	2.772	2.772
C ₂ F ₄ •CCH [–]	2.988	3.124	2.845	3.175	2.884	3.103
C ₂ F ₄ •OCN ^{–b,c}	2.875	3.046	2.838	3.043	2.856	3.012
C ₂ F ₄ •NCO ^{–b}	2.774	3.154	2.684	3.187	2.709	3.152
C ₂ F ₄ •O ₂ [–]	2.481	2.481	2.524	2.524	2.497	2.497

^a All distances are given in angstroms. ^b The first atom after C₂F₄ indicates the one pointing toward this molecule. ^c The oxygen is closer to C1, while the nitrogen is closer to C2.

Table 2. Interaction Energies of Calculated Complexes

complex	E _i (kJ mol ^{–1})		
	MP2/ 6-311++G(d,p)	M05-2x/ 6-311++G(d,p)	MP2/ aug-cc-pvtz
C ₂ F ₄ •Cl [–]	–39.01	–35.92	–35.16
C ₂ F ₄ •Br [–]	–34.76	–30.65	–34.18
C ₂ F ₄ •CN ^{–a}	–31.34	–32.71	–32.42
C ₂ F ₄ •NC ^{–a}	–36.00	–36.05	–35.69
C ₂ F ₄ •NNN [–]	–46.02	–40.82	–45.34
C ₂ F ₄ •NO ₂ [–]	–43.77	–47.44	–42.93
C ₂ F ₄ •HCO ₂ [–]	–48.49	–50.90	–46.76
C ₂ F ₄ •CCH [–]	–40.99	–39.04	–39.55
C ₂ F ₄ •OCN ^{–a}	–40.39	–37.17	–38.93
C ₂ F ₄ •NCO ^{–a}	–36.74	–37.86	–37.33
C ₂ F ₄ •O ₂ [–]	–62.37	–70.87	–62.55

^a The first atom after C₂F₄ indicates the one pointing toward this molecule.

energies are smaller than those reported for complexes of the same anions with hexafluorobenzene^{12b} [for instance, interaction energies of C₆F₆•Cl[–] and C₆F₆•CN[–] complexes at MP2/6-311++G(d,p) computational level are –51.0 and –52.2 kJ mol^{–1}, respectively] and are similar to those complexes with triazine.^{12a} Thus, it can be considered that the C₂F₄ molecule is a weak anion acceptor. The interaction energies computed at the M05-2x/6-311++G** level of theory are in good agreement with those computed at the MP2/aug-cc-pVTZ level. The largest differences are observed in the strongest complex (8.32 kJ mol^{–1}), C₂F₄•O₂[–], followed by C₂F₄•Br[–] (4.53 kJ mol^{–1}) and C₂F₄•NNN[–] (4.52 kJ mol^{–1}).

Topological analysis of the electron density shows three different patterns (Figure 2): (i) For those cases where one of the atoms of the anion is closer to C1 than C2, a unique bond critical point (bcp) is found between the anion and C1, with the exception of the C₂F₄•OCN[–] complex. (ii) For C₂F₄•Br[–], a bifurcated bond path is found connecting the bromine atom to the center of the CC bond, similar to the one found in the hydrogen-bonded C₂H₄•HF complex.³⁷ (iii) For C₂F₄•HCO₂[–], C₂F₄•NO₂[–], C₂F₄•OCN[–], and C₂F₄•O₂[–], two bond critical points between the C1 and C2 atoms and the anions are found. The bcp's present small values of the electron density, ρ , between 0.029 and 0.010 au and small and positive values of the Laplacian, $\nabla^2\rho$, between 0.083 and 0.029 au, which corresponds to a closed-shell interaction

similar to those found in other weak interactions such as hydrogen bonds.³⁸

A summary of the calculated properties obtained by integration within the atomic basins has been gathered in Table 3. A charge transfer from the anion to the C₂F₄ is observed, up to 0.138 e for the C₂F₄•O₂[–] complex. A representation of the electron shift (Figure 3) shows that the charge gained by the C₂F₄ molecule is concentrated in the face opposite the position of the anion, increasing the nucleophilic character of the C₂F₄ molecule in this region.

The calculated energy of the anions within the complex with AIM methodology indicates an energy destabilization for all the anions except Cl[–], Br[–], NO₂[–], and O₂[–]. In closely related systems, a linear relationship has been observed between these two parameters but in the present case, the diverse nature of the anions prevents observation of a similar relationship.³⁹

NBO analysis shows an interaction of the lone pair of the anion with the antibonding C–C orbital (Table 4) with the corresponding charge transfer between them. The stabilization provided for this interaction ranges from 2.1 kJ mol^{–1} for the C₂F₄•Br[–] complex to 19.4 kJ mol^{–1} in the case of the two interactions obtained for the C₂F₄•HCO₂[–] cluster.

Natural energy decomposition analysis (NEDA) is a method for partitioning molecular interaction energies including charge transfer (CT), electrostatic (ES), polarization (POL), exchange (XC), and core repulsion contributions (DEF). The charge transfer term is based on the interaction of filled orbitals, donor, with empty ones, acceptor, of the species involved. For the complexes studied here, the electrostatic and polarization terms are the most important ones in all cases. For the complexes where a nitrogen atom is directly interacting with the C₂F₄ molecule (C₂F₄•NC[–], C₂F₄•NNN[–], and C₂F₄•NCO[–]), the polarization term is the dominant one, while in those cases where a carbon or a halogen is interacting with C₂F₄, the electrostatic term is the largest one. In the complexes where oxygen is involved in the interaction, the electrostatic term is the dominant one in the three cases where a double interaction is observed (C₂F₄•HCO₂[–], C₂F₄•NO₂[–], and C₂F₄•O₂[–]) while the polarization term is more important in the C₂F₄•OCN[–] case. In addition, the charge transfer and exchange terms have large values. In fact, several complexes can each contribute up to 20% of the total stabilization energy.

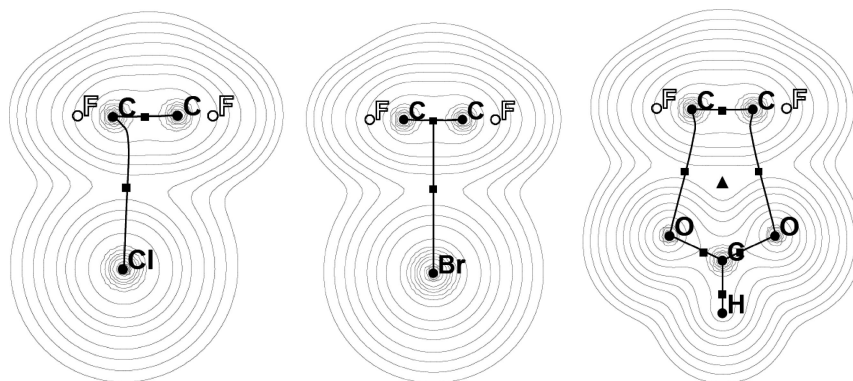


Figure 2. Electron density maps of $\text{C}_2\text{F}_4 \cdot \text{Cl}^-$, $\text{C}_2\text{F}_4 \cdot \text{Br}^-$, and $\text{C}_2\text{F}_4 \cdot \text{HCO}_2^-$ complexes. The outer contour line corresponds to 0.001 au and the next ones correspond to values increasing according to the pattern 2×10^n , 4×10^n , and 8×10^n , where n varies from -3 to 2 . (■) Bond critical points (bcp); (▲) ring critical points. Lines connecting the atoms correspond to bond paths. Atoms in the represented plane are shown in black, and those out of the plane are in white.

Table 3. Properties of Intermolecular Bond Critical Points and Variation of Integrated Charge and Energy of Anions^a

	ρ (au)	$\nabla^2\rho$ (au)	charge transfer (e)	energy variation (kJ mol ⁻¹)
$\text{C}_2\text{F}_4 \cdot \text{Cl}^-$	0.013	0.038	0.057	-109.8
$\text{C}_2\text{F}_4 \cdot \text{Br}^-$	0.010	0.029	0.052	-1261.6
$\text{C}_2\text{F}_4 \cdot \text{CN}^-$	0.015	0.038	0.060	94.2
$\text{C}_2\text{F}_4 \cdot \text{NC}^-$	0.017	0.056	0.043	86.9
$\text{C}_2\text{F}_4 \cdot \text{NNN}^-$ ^b	0.014	0.040	0.074	77.0
$\text{C}_2\text{F}_4 \cdot \text{NO}_2^-$ ^b	0.016	0.050	0.051	-62.9
$\text{C}_2\text{F}_4 \cdot \text{HCO}_2^-$ ^b	0.016	0.050	0.054	51.3
$\text{C}_2\text{F}_4 \cdot \text{CCH}^-$	0.016	0.040	0.076	154.8
$\text{C}_2\text{F}_4 \cdot \text{OCN}^-$	0.013 ^c	0.042	0.047	95.6
$\text{C}_2\text{F}_4 \cdot \text{OCN}^-$	0.012 ^d	0.039		
$\text{C}_2\text{F}_4 \cdot \text{NCO}^-$	0.018	0.059	0.043	97.7
$\text{C}_2\text{F}_4 \cdot \text{O}_2^-$ ^b	0.029	0.083	0.138	-176.3

^a Obtained by use of the M05-2x/6-311++G(d,p) wavefunction.

^b Two identical bcp's are found in these complexes. ^c Values of $\text{O} \cdots \text{C}$ interaction. ^d Values of $\text{N} \cdots \text{C}$ interaction.

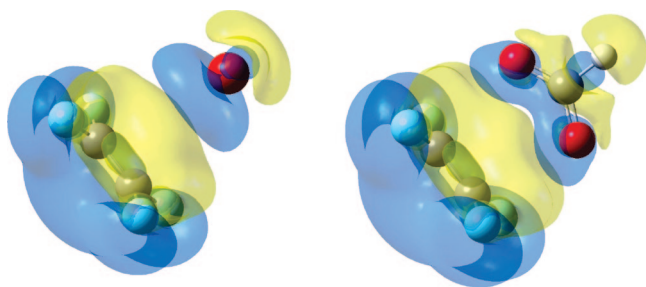


Figure 3. Electron density difference maps of $\text{C}_2\text{F}_4 \cdot \text{Br}^-$ and $\text{C}_2\text{F}_4 \cdot \text{HCO}_2^-$ complexes. Blue and yellow isosurfaces represent gain and loss of electron density upon complex formation, relative to the isolated subunits. Contours shown are ± 0.0002 e/au³ calculated at the M05-2x/6-311++G(d,p) level.

Anion·C₂F₄·HY Complexes. The isolated C_2F_4 system is not able to form a stable complex with hydrogen-bond donors, such as FH, ClH, and H_2O , while interacting with the π -cloud of the former. However, the presence of electron donors in one face of the C_2F_4 molecule has been shown to allow its interaction with electron-deficient groups acting as hydrogen-bond acceptor.⁴⁰ In this section the cluster formed by an anion interacting with C_2F_4 on one face and a hydrogen-bond donor on the opposite will be discussed.

Interactions between FH and all the complexes studied in the previous section have been considered, while only four cases have been chosen for the complexes with ClH and H_2O . In the case of the $\text{FH} \cdot \text{C}_2\text{F}_4 \cdot \text{CCH}^-$ system, the CCH^- and O_2^- anions spontaneously tend to form a covalent bond with one of the carbon atoms of the C_2F_4 molecule. $\text{FH} \cdot \text{C}_2\text{F}_4 \cdot \text{CN}^-$ and $\text{FH} \cdot \text{C}_2\text{F}_4 \cdot \text{NC}^-$ became the same, being better described as the latter one (Figure 4). In the rest of the cases, stable clusters are obtained. The same symmetries obtained for the corresponding $\text{C}_2\text{F}_4 \cdot \text{X}^-$ complexes are observed for $\text{FH} \cdot \text{C}_2\text{F}_4 \cdot \text{X}^-$ and $\text{ClH} \cdot \text{C}_2\text{F}_4 \cdot \text{X}^-$, except for the $\text{FH} \cdot \text{C}_2\text{F}_4 \cdot \text{Br}^-$ case, which now adopts C_s symmetry. The complexes studied with H_2O adopt C_s symmetry in all cases.

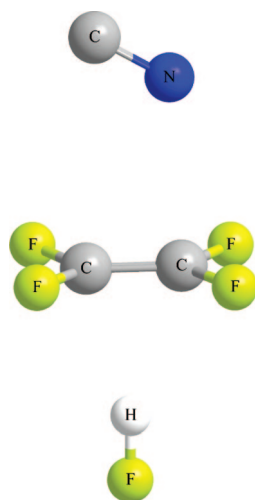
The intermolecular distances are gathered in Table 5. The $\text{X} \cdots \text{C1}$ distances obtained in these clusters are in all the cases shorter than the corresponding ones of the $\text{C}_2\text{F}_4 \cdot \text{X}^-$ complexes. For a given cation, in general, the longest distance is obtained in the complexes with H_2O . Of the four anions considered for all the hydrogen bond donors, two of the complexes present the shortest distance with ClH and another two with FH at MP2/aug-cc-pVTZ computational level. These results indicate that another effect in addition to the expected amount of positive charge of the interacting hydrogen at the hydrogen bond donors ($\text{FH} > \text{ClH} > \text{H}_2\text{O}$), can be important for the final geometry of the complex. The individual larger difference in the $\text{X} \cdots \text{C1}$ distance between the $\text{C}_2\text{F}_4 \cdot \text{X}^-$ complexes and the corresponding $\text{YH} \cdot \text{C}_2\text{F}_4 \cdot \text{X}^-$ ones is obtained in the $\text{ClH} \cdot \text{C}_2\text{F}_4 \cdot \text{Cl}^-$ case where the difference at the MP2/aug-cc-pVTZ computational level is 0.24 Å.

With respect to FH and ClH molecules acting as hydrogen-bond donors, in those cases where they are not symmetrically oriented with respect to C1 and C2, they tend to be closer to C2 than to C1, except in the $\text{FH} \cdot \text{C}_2\text{F}_4 \cdot \text{OCN}^-$ complex. In any case, the difference between these distances is always smaller than 0.22 Å. Intermolecular distances obtained for the FH complexes (between 2.11 and 2.33 Å) are in general shorter than those obtained for the $\text{FH} \cdot \text{C}_2\text{F}_4$ complex calculated at the MP2/6-311++G(d,p) computational level ($\text{FH} \cdots \text{C1/C2}$ distance of 2.30 Å).³⁷ In complexes with H_2O , in general, the interacting hydrogen is closer to C1 than C2 with the exception of the $\text{H}_2\text{O} \cdot \text{C}_2\text{F}_4 \cdot \text{NC}^-$ complex, probably

Table 4. Orbital Interaction Energies and Natural Energy Decomposition Analysis^a

complex	lp (X ⁻) → σ* CC	NEDA					
		CT	ES	POL	XC	DEF (C ₂ F ₄)	DEF (X ⁻)
C ₂ F ₄ •Cl ⁻	4.4	-13.4	-52.8	-42.5	-30.7	65.0	39.8
C ₂ F ₄ •Br ⁻	2.1	-10.1	-44.2	-35.5	-27.2	57.2	29.9
C ₂ F ₄ •CN ⁻	10.2	-32.3	-57.7	-50.2	-31.6	60.5	79.0
C ₂ F ₄ •NC ⁻	11.0	-39.6	-52.8	-85.9	-40.9	92.4	91.6
C ₂ F ₄ •NNN ⁻	23.0	-53.3	-58.5	-61.6	-46.7	81.9	96.9
C ₂ F ₄ •NO ₂ ⁻	2 × 3.8	-46.7	-73.1	-54.1	-44.0	66.3	108.4
C ₂ F ₄ •HCO ₂ ⁻	2 × 9.7	-45.1	-76.7	-71.0	-49.2	82.8	111.3
C ₂ F ₄ •CCH ⁻	10.8	-37.8	-71.3	-55.6	-42.2	87.6	80.4
C ₂ F ₄ •OCN ⁻	10.3	-38.4	-48.5	-57.7	-41.0	77.2	72.5
C ₂ F ₄ •NCO ⁻	10.8	-35.6	-53.1	-71.8	-36.4	72.7	87.3
C ₂ F ₄ •O ₂ ⁻	2 × 14.3	-109.9	-133.9	-91.0	-66.4	114.1	215.1

^a Calculated at the M05-2x/6-311++G(d,p) computational level. All energies are given in kilojoules per mole.

**Figure 4.** Optimized geometry of FH•C₂F₄•NC⁻ complex at the MP2/6-311++G(d,p) computational level.

due to secondary interactions of the additional hydrogen of this molecule with the fluorine atoms of C₂F₄.

Calculated interaction energies of the cluster (Table 6) range between -54.5 kJ mol⁻¹ for the weakest complex, H₂O•C₂F₄•Br⁻, and -80.3 kJ/mol for the strongest one, FH•C₂F₄•HCO₂⁻, at the MP2/aug-cc-pVTZ computational level. For a given cation, the strongest complex is the one formed with FH, followed by ClH, being and those obtained with H₂O are the weakest ones. This order follows the expected charge of hydrogen atoms involved in the interaction (FH > ClH > H₂O). In general, a similar stabilization order to that obtained for the C₂F₄•X⁻ complexes is obtained here, showing square correlation coefficients with the data reported in Table 2 of 0.95, 0.995, and 0.997 for FH, ClH, and H₂O complexes obtained at the MP2/aug-cc-pVTZ computational level.

In order to evaluate the possible existence of cooperativity in these complexes, the attractive interaction between FH and the anions in the disposition of the cluster has been evaluated. Thus, the cooperativity has been calculated by use of eq 1:

$$\text{coop} = E_i(\text{YH}\cdot\text{C}_2\text{F}_4\cdot\text{X}^-) - E_i(\text{C}_2\text{F}_4\cdot\text{X}^-) - E_i(\text{YH}\cdot\text{X}^-) \quad (1)$$

where $E_i(\text{YH}\cdot\text{C}_2\text{F}_4\cdot\text{X}^-)$ and $E_i(\text{C}_2\text{F}_4\cdot\text{X}^-)$ correspond to interaction energies of the corresponding minima structures,

which are gathered in Tables 6 and 2, respectively. $E_i(\text{YH}\cdot\text{X}^-)$ is the attractive interaction of these two molecules as they stand in the YH•C₂F₄•X⁻ cluster. As indicated previously, the YH•C₂F₄ complex where YH points toward the π-cloud of C₂F₄ system is not attractive, and thus it has not been considered to calculate the cooperativity. The values found for this parameter are always negative, as indicative of true cooperativity. The cooperativity values obtained are much larger at the MP2/aug-cc-pVTZ computational level (between -15.2 and -5.4 kJ mol⁻¹) than those obtained with the 6-311++G(d,p) basis set at MP2 or M05-2x levels (between -9.6 and -3.0 kJ mol⁻¹). These results are due to a slightly larger interaction energy obtained at the MP2/aug-cc-pVTZ computational level in the trimers and a smaller stabilization in the YH•X⁻ pair that favor, in both, cases larger cooperativities. With respect to the HB donors, larger cooperativities are obtained in the ClH complexes than in the FH ones, with the smallest values in the H₂O cases for a given anion. This tendency can be associated with the strength of the interaction in the first place and with the polarization of the HB donor in the second.

Electron density maps show that while the anions tend to form a bond path with C1, the FH and ClH molecules do so with C2 and H₂O with C1, in agreement with the closer proximity of these molecules to the corresponding carbon atoms of C₂F₄ (Figure 5). Values of the electron density and Laplacian at the X...C bcp (Table 7) are larger than those found in the corresponding C₂F₄•X⁻, as expected due to the shorter interatomic distance found in these complexes.^{41,42}

Integrated electron density within the atomic basins shows that in FH and ClH most of the charge lost by the anionic systems goes to the YH molecule, while the electronic gain of the C₂F₄ molecule is here smaller than in the C₂F₄•X complexes. In contrast, in the H₂O complexes the electronic gain of this molecule is very small due to the long interatomic distances obtained between this molecule and the C₂F₄ one. The electron density difference for two FH•C₂F₄•X⁻ complexes (Figure 6) clearly shows, again, how the electron gain tends to be shifted further away from the position of the anion.

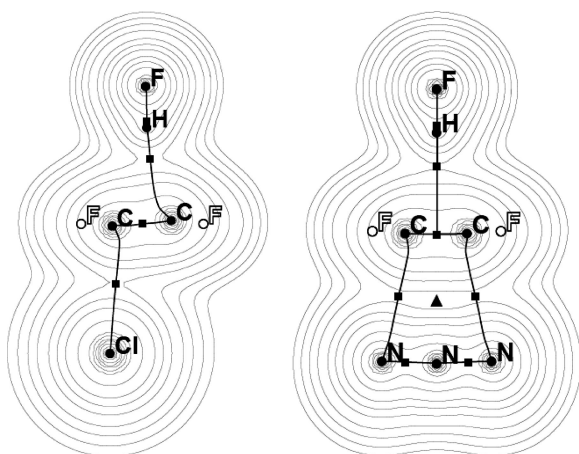
The calculated energy variation per molecule shows different patterns depending on the hydrogen-bond donor and anionic systems studied. As in the case of the C₂F₄•X⁻ complexes, those complexes with Cl⁻, Br⁻, and NO₂⁻ present

Table 5. Intermolecular Distances from Anions and Hydrogen-Bond Donor Molecules to $C_2F_4^a$

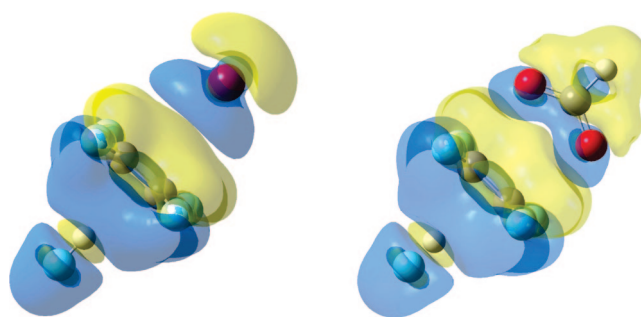
	MP2/6-311++G(d,p)				M05-2x/6-311++G(d,p)				MP2/aug-cc-pVTZ			
	X...C1	X...C2	YH...C1	YH...C2	X...C1	X...C2	YH...C1	YH...C2	X...C1	X...C2	YH...C1	YH...C2
FH·C ₂ F ₄ ·Cl [−]	2.810	3.267	2.329	2.110	2.859	3.275	2.305	2.145	2.894	3.236	2.274	2.138
FH·C ₂ F ₄ ·Br [−]	3.282	3.287	2.259	2.259	3.260	3.267	2.253	2.251	3.215	3.220	2.219	2.217
FH·C ₂ F ₄ ·NC [−]	2.734	2.996	2.275	2.219	2.574	3.034	2.296	2.167	2.668	2.993	2.245	2.168
FH·C ₂ F ₄ ·HCO ₂ [−]	2.685	2.685	2.219	2.219	2.628	2.628	2.199	2.199	2.663	2.663	2.195	2.195
FH·C ₂ F ₄ ·NNN [−]	2.765	2.765	2.253	2.253	2.764	2.764	2.248	2.248	2.739	2.739	2.215	2.215
FH·C ₂ F ₄ ·NO ₂ [−]	2.685	2.685	2.226	2.226	2.658	2.658	2.216	2.216	2.649	2.649	2.202	2.202
FH·C ₂ F ₄ ·OCN [−]	2.801	2.939	2.251	2.264	2.751	2.956	2.235	2.247	2.794	2.898	2.212	2.237
FH·C ₂ F ₄ ·NCO [−]	2.253	3.047	2.323	2.172	2.549	3.047	2.302	2.160	2.541	3.046	2.286	2.123
CIH·C ₂ F ₄ ·Cl [−]	2.831	3.293	2.172	2.388	2.955	3.280	2.427	2.301	2.875	3.255	2.288	2.119
CIH·C ₂ F ₄ ·Br [−]	3.305	3.305	2.353	2.353	3.293	3.293	2.409	2.409	3.227	3.227	2.234	2.234
CIH·C ₂ F ₄ ·NC [−]	2.741	3.027	2.369	2.299	2.599	3.065	2.425	2.304	2.650	3.009	2.270	2.183
CIH·C ₂ F ₄ ·HCO ₂ [−]	2.674	2.674	2.267	2.267	2.632	2.632	2.275	2.275	2.687	2.687	2.267	2.267
HOH·C ₂ F ₄ ·Cl [−]	2.951	3.339	2.754	3.054	2.990	3.348	2.661	2.963	2.956	3.317	2.470	2.562
HOH·C ₂ F ₄ ·Br [−]	3.299	3.389	2.462	2.624	3.238	3.441	2.647	3.022	3.146	3.407	2.455	2.592
HOH·C ₂ F ₄ ·NC [−]	2.816	3.046	3.126	2.718	2.734	3.065	3.072	2.605	2.759	3.016	2.649	2.441
HOH·C ₂ F ₄ ·HCO ₂ [−]	2.707	2.740	2.653	2.983	2.665	2.684	2.590	2.914	2.678	2.731	2.444	2.674

^a Intermolecular distances are given in angstroms.**Table 6.** Total Interaction Energy, Attractive Energy between FH and X[−], and Cooperativity^a

	MP2/6-311++G(d,p)			M05-2x/6-311++G(d,p)			MP2/aug-cc-pvtz		
	E _i	YH·X ^{−b}	coop	E _i	YH·X ^{−b}	coop	E _i	YH·X ^{−b}	coop
FH·C ₂ F ₄ ·Cl [−]	−66.30	−20.11	−7.18	−63.00	−20.20	−6.89	−66.13	−18.75	−12.22
FH·C ₂ F ₄ ·Br [−]	−58.61	−18.19	−5.66	−55.23	−18.56	−6.02	−63.67	−17.89	−11.60
FH·C ₂ F ₄ ·NC [−]	−61.06	−18.80	−6.26	−62.68	−19.24	−7.40	−65.44	−18.11	−11.64
FH·C ₂ F ₄ ·HCO ₂ [−]	−77.56	−21.69	−7.38	−82.99	−22.61	−9.47	−80.32	−20.74	−12.83
FH·C ₂ F ₄ ·NNN [−]	−71.32	−18.01	−7.29	−66.14	−18.27	−7.04	−74.27	−17.30	−11.63
FH·C ₂ F ₄ ·NO ₂ [−]	−70.99	−20.77	−6.46	−77.89	−22.01	−8.43	−74.04	−19.57	−11.54
FH·C ₂ F ₄ ·OCN [−]	−64.18	−17.84	−5.36	−61.64	−18.17	−4.44	−66.99	−17.13	−10.31
FH·C ₂ F ₄ ·NCO [−]	−61.83	−18.23	−3.20	−64.59	−18.56	−8.86	−66.41	−17.38	−10.10
CIH·C ₂ F ₄ ·Cl [−]	−62.91	−15.43	−8.47	−56.79	−15.00	−5.87	−63.21	−13.85	−14.20
CIH·C ₂ F ₄ ·Br [−]	−55.89	−13.83	−7.29	−49.46	−13.77	−5.03	−60.93	−13.29	−13.45
CIH·C ₂ F ₄ ·NC [−]	−58.21	−14.28	−7.93	−56.45	−14.35	−6.05	−62.56	−13.31	−13.56
CIH·C ₂ F ₄ ·HCO ₂ [−]	−74.80	−16.71	−9.61	−76.36	−17.31	−8.15	−77.54	−15.60	−15.19
HOH·C ₂ F ₄ ·Cl [−]	−59.86	−17.27	−3.58	−56.47	−17.58	−2.98	−55.11	−14.58	−5.36
HOH·C ₂ F ₄ ·Br [−]	−51.71	−13.85	−3.09	−49.93	−15.94	−3.34	−54.52	−13.76	−6.57
HOH·C ₂ F ₄ ·NC [−]	−55.18	−15.20	−3.98	−55.50	−15.43	−4.02	−55.49	−13.22	−6.58
HOH·C ₂ F ₄ ·HCO ₂ [−]	−70.64	−17.84	−4.31	−74.69	−18.77	−5.02	−69.42	−15.88	−6.78

^a All values are given in kilojoules per mole. ^b In the geometrical disposition of the FH·C₂F₄·X[−] cluster.**Figure 5.** Electron density maps of FH·C₂F₄·Cl[−] and FH·C₂F₄·NNN[−] clusters. Contour levels, symbols, and atoms are represented as in Figure 2.

important destabilization of the C₂F₄ molecule. For the rest of the anions, in the complexes with FH, a gain of electronic charge is associated with an energy stabilization of the C₂F₄ and FH molecules similar in value. In the complexes with

**Figure 6.** Electron density difference maps of FH·C₂F₄·Br[−] and FH·C₂F₄·HCO₂[−] complexes. Blue and yellow isosurfaces represent gain and loss of electron density upon complex formation, relative to the isolated subunits. The contours shown are ±0.0002 e/au³ calculated at the M05-2x/6-311++G(d,p) level.

CIH, this molecule is stabilized while the C₂F₄ one is destabilized. Finally, the H₂O molecule, which shows a small gain of electron density, presents an energy destabilization due to complex formation, while the C₂F₄ present significant stabilization energies.

Table 7. Properties of Intermolecular Bond Critical Points and Variation of Integrated Charge and Energy of C₂F₄ and Hydrogen-Bond Donor Molecules upon Complexation

complex	X...C		YH...C		charge		Δ energy	
	ρ (au)	$\nabla^2\rho$ (au)	ρ (au)	$\nabla^2\rho$ (au)	C ₂ F ₄ (e)	YH (e)	C ₂ F ₄ (kJ mol ⁻¹)	YH (kJ mol ⁻¹)
FH·C ₂ F ₄ ·Cl ⁻	0.0205	0.0524	0.0226	0.0538	-0.045	-0.054	104.9	-29.4
FH·C ₂ F ₄ ·Br ⁻	0.0138	0.0393	0.0199	0.0510	-0.027	-0.049	1201.0	205.3
FH·C ₂ F ₄ ·NC ⁻	0.0224	0.0696	0.0218	0.0534	-0.012	-0.051	-63.6	-67.8
FH·C ₂ F ₄ ·NNN ^{-a}	0.0173	0.0482	0.0193	0.0527	-0.061	-0.039	-63.4	-64.4
FH·C ₂ F ₄ ·NO ₂ ^{-a}	0.0183	0.0574	0.0220	0.0535	-0.017	-0.054	43.6	-43.5
FH·C ₂ F ₄ ·HCO ₂ ^{-a}	0.0191	0.0601	0.0228	0.0552	-0.018	-0.055	-52.0	-66.5
FH·C ₂ F ₄ ·OCN ⁻	0.0150 ^b , 0.0139 ^c	0.0492, 0.0450	0.0199	0.0531	-0.019	-0.042	-76.7	-69.8
FH·C ₂ F ₄ ·NCO ⁻	0.0229	0.0744	0.0220	0.0536	-0.010	-0.051	-78.5	-72.0
ClH·C ₂ F ₄ ·Cl ⁻	0.0173	0.0471	0.0182	0.0417	-0.040	-0.042	124.37	-81.70
ClH·C ₂ F ₄ ·Br ⁻	0.0131	0.0372	0.0159	0.0378	-0.034	-0.037	1095.12	-3085.97
ClH·C ₂ F ₄ ·NC ⁻	0.0213	0.0666	0.0181	0.0419	-0.018	-0.040	33.83	-184.41
ClH·C ₂ F ₄ ·HCO ₂ ⁻	0.0191	0.0597	0.0216	0.0479	-0.020	-0.051	43.75	-198.14
HOH·C ₂ F ₄ ·Cl ⁻	0.0261	0.0442	0.0080	0.0233	-0.068	-0.006	36.12	66.94
HOH·C ₂ F ₄ ·Br ⁻	0.0129	0.0347	0.0079	0.0236	-0.061	-0.005	1179.60	250.42
HOH·C ₂ F ₄ ·NC ⁻	0.0166	0.0542	0.0085	0.0253	-0.044	-0.004	-165.57	32.67
HOH·C ₂ F ₄ ·HCO ₂ ⁻	0.0179	0.0562	0.0092	0.0261	-0.056	-0.008	-135.29	35.18

^a Two identical X...C bcp's are found in these complexes. ^b Values of O...C1 interaction. ^c Values of N...C1 interaction.

Table 8. Intermolecular Orbital Interaction Energies and Natural Energy Decomposition Analysis^a

complex	X lp \rightarrow σ^*CC	$\pi CC \rightarrow \sigma^*HF$	NEDA						
			CT	ES	POL	XC	DEF (C ₂ F ₄)	DEF (X ⁻)	DEF (HF)
FH·C ₂ F ₄ ·Cl ⁻	24.6	33.3	-94.0	-94.6	-48.9	-55.4	118.6	81.5	28.0
FH·C ₂ F ₄ ·Br ⁻	4.1	27.9	-67.6	-73.0	-39.0	-46.3	98.7	49.7	24.9
FH·C ₂ F ₄ ·NC ⁻	17.5	32.5	-108.4	-83.6	-98.1	-63.0	142.0	121.0	28.9
FH·C ₂ F ₄ ·HCO ₂ ⁻	2 \times 14.3	34.6	-117.3	-110.9	-85.4	-73.9	126.1	153.4	30.5
FH·C ₂ F ₄ ·NNN ⁻	36.0	24.5	-112.3	-85.4	-84.2	-70.8	126.9	133.8	26.9
FH·C ₂ F ₄ ·NO ₂ ⁻	2 \times 8.0	32.8	-114.3	-108.8	-58.4	-65.0	100.9	145.6	29.5
FH·C ₂ F ₄ ·OCN ⁻	14.1	26.8	-92.6	-70.3	-72.2	-61.5	115.7	96.2	26.5
FH·C ₂ F ₄ ·NCO ⁻	19.8	32.4	-106.7	-83.6	-90.3	-58.7	119.9	126.9	29.1
ClH·C ₂ F ₄ ·Cl ⁻	0.7	31.4	-71.80	-81.13	-51.71	-53.56	114.52	58.70	25.19
ClH·C ₂ F ₄ ·Br ⁻	3.6	25.8	-54.77	-67.40	-45.15	-47.36	101.71	21.55	44.89
ClH·C ₂ F ₄ ·NC ⁻	15.7	31.1	-95.40	-78.12	-99.33	-63.64	142.34	113.14	27.03
ClH·C ₂ F ₄ ·HCO ₂ ⁻	2 \times 14.0	41.7	-116.11	-109.70	-88.99	-78.70	137.36	151.84	33.51
HOH·C ₂ F ₄ ·Cl ⁻	12.6	2.0	-41.13	-76.57	-56.44	-46.82	90.42	57.40	19.71
HOH·C ₂ F ₄ ·Br ⁻	4.6	1.8	-33.10	-65.73	-49.79	-42.59	82.89	42.76	19.46
HOH·C ₂ F ₄ ·NC ⁻	6.7	2.4	-50.79	-66.90	-84.64	-51.71	105.23	77.24	20.54
HOH·C ₂ F ₄ ·HCO ₂ ⁻	13.0/11.4	2.9	-71.92	-100.29	-90.75	-66.40	108.32	130.88	21.55

^a Calculated at the M05-2x/6-311++G(d,p) computational level. All energies are given in kilojoules per mole.

Analysis of the orbital interaction in the FH and ClH complexes shows a strong interaction between the π -electrons of C₂F₄ and the σ antibonding orbital of the YH molecule (Table 8). The value of this interaction is able to account for the difference in stability between C₂F₄·X⁻ and YH·C₂F₄·X⁻ complexess. In addition, reinforcement of the interaction between the anion lone pair and the antibonding CC orbital is found in the trimeric structures when compared to the dimeric ones. In the NEDA analysis, a significant increment of the charge-transfer term due to the presence of the HB with the π -systems is observed. These results are in agreement with previous reports that have indicated the preponderance of charge transfer in HB complexes.

In contrast, in the H₂O complexes, a small interaction is observed between π -electrons of C₂F₄ and the OH antibonding orbital. These results are in agreement with the long distances of the hydrogen bonds formed in these cases. Due to this effect, the NEDA analysis indicates that

in these complexes the electrostatic and polarization terms are the most important stabilization forces.

Conclusion

A theoretical study of the complexes formed by tetrafluoroethylene (C₂F₄) with anions has been carried out by means of ab initio, MP2, and DFT, M05-2x, methods. In several complexes obtained, the position of the anions avoids the center of the C=C bond. However, several complexes are symmetric around the CC middle point, providing a similar environment to both carbon atoms of C₂F₄. The interaction energy of the complexes indicates that C₂F₄ is a weaker acceptor of anions than C₆F₆. Natural energy decomposition analysis shows that electrostatic and polarization terms are the most important attractive forces in these complexes.

In addition, possible cooperativity in the interaction of anions and hydrogen-bond donors (FH, ClH, and H₂O) in opposite faces of C₂F₄ has been explored. The minima complexes obtained show a shortening of the intermolecular distance between the anions and C₂F₄. In addition, the FH

molecule is located, in general, at shorter distances than in the $\text{FH} \cdot \text{C}_2\text{H}_4$ complex, indicating that the $\text{C}_2\text{F}_4 \cdot \text{X}^-$ is a more effective hydrogen-bond acceptor than C_2H_4 . Cooperativity values between -15.2 and -5.4 kJ mol^{-1} have been obtained for all the systems studied here. Finally, the presence of hydrogen bonding increases significantly the charge-transfer attractive term in the NEDA analysis for the FH and ClH complexes, becoming the most important term in most cases.

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Supporting Information Available: Optimized geometries of the complexes at the MP2/6-311++G(d,p) computational level. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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