

# Aromatic Systems as Charge Insulators: Their Simultaneous Interaction with Anions and Cations

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A theoretical approach, using ab initio MP2(full)/6-31++G\*\* and MP2(full)/6-311++G\*\* levels, has been used to characterize the interaction of the  $\pi$ -cloud of C<sub>6</sub>F<sub>6</sub> with cations (Y<sup>+</sup> = Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>). In addition, the situation where C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>F<sub>6</sub> simultaneously interact with an anion (X<sup>-</sup> = F<sup>-</sup>, Cl<sup>-</sup>, and Br<sup>-</sup>) and a cation in opposite faces of the aromatic ring has been studied. For comparative purposes, other dispositions, such as those of the isolated cations and the anions and the complexes between neutral XY salts and the aromatic systems, have been considered. Complexes where the  $\pi$ -cloud of the aromatic ring interacts with a cation or, simultaneously, with a cation and an anion have been found to be minima structures. However, these complexes show high relative energies when compared to other minima of the potential hypersurface. The interaction energy has been decomposed into MEP, polarization and charge–charge interaction terms.

## Introduction

The ability of the  $\pi$ -cloud of aromatic compounds to interact with positively charged atoms or with the hydrogen of a hydrogen bond donor is well known.<sup>1</sup> The interaction of negatively charged atoms with benzene corresponds to the interaction of the former with the hydrogen of the latter.<sup>2</sup> However, the presence of electronegative atoms in the aromatic ring is able to reverse this general trend, and theoretical calculations have indicated that the complexes of hexafluorobenzene with several small molecules occur between the  $\pi$ -cloud of the first one and the electron donor atoms of the second.<sup>3–5</sup>

Further complexes between anions and hexafluorobenzene,<sup>6,7</sup> 2,4,6-trifluoro-1,3,5-triazine,<sup>8</sup> 1,3,5-trinitrobenzene,<sup>9</sup> and several perfluoroaromatic compounds<sup>6</sup> have been described using theoretical methods. X-ray and NMR data support the presence of these interactions.<sup>10,11</sup>

A comparison of the molecular electrostatic potential map (MEP) of benzene and several perfluoroaromatic derivatives shows, in the first case, a negative region above and below the aromatic ring, while in the second case there are positive regions, an indication of the favorable interaction with positively and negatively charged groups, respectively.<sup>3,6</sup>

In the present article, the complexes formed by isolated cations and C<sub>6</sub>F<sub>6</sub> by interaction either with the  $\pi$ -cloud or with the fluorine atoms have been studied. In addition, several dispositions where a cation and an anion interact with C<sub>6</sub>F<sub>6</sub> and C<sub>6</sub>H<sub>6</sub> have been considered, including those with an anion above the aromatic ring and the cation below it (“inverse sandwich”). The calculations have been carried out at the MP2(full)/6-31++G\*\* and MP2(full)/6-311++G\*\* levels. The partition of the interaction energies of the complexes was based on charge–charge interaction, molecular electrostatic potential, and polarization induced by a point charge in the same position where the ions are located in the aromatic systems. The electron

density has been analyzed using the atoms-in-molecules (AIM) methodology.

## Methods

The geometry of the monomers and complexes has been fully optimized with the Gaussian 98 program initially using the HF/6-31G\* computational level. These structures have been used as starting points for the optimization at the MP2(full)/6-31++G\*\* level. In all cases, the minimum nature of the structures has been confirmed by frequency calculations at the HF/6-31G\* and MP2/6-31++G\*\* levels; otherwise, it has been mentioned in the text.

Additional calculations at the MP2(full)/6-311++G\*\* level have been carried out for a number of cases and used for comparative purposes with those obtained at the MP2(full)/6-31++G\*\* level. As shown previously, the energetic and geometric results obtained are similar at both levels.<sup>6</sup>

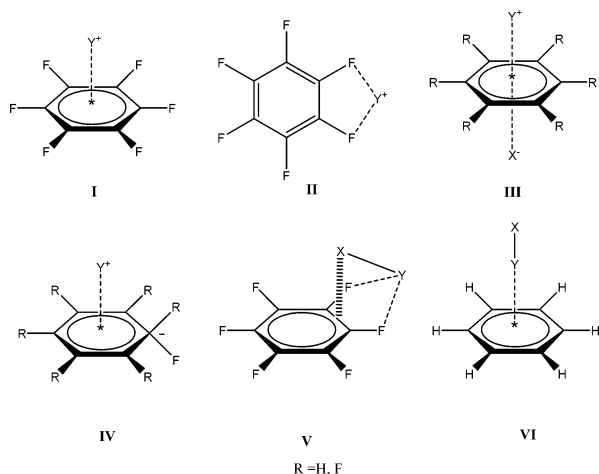
The interaction energies have been analyzed at the MP2(full)/6-31++G\*\* level by calculating the cation–anion electrostatic interaction and the electrostatic potential and polarization of the C<sub>6</sub>F<sub>6</sub> and C<sub>6</sub>H<sub>6</sub> due to the presence of different ions. The interaction energy of a molecule with an external charge  $q$  can be expressed as a perturbative expansion in terms of  $q$ . The coefficients of the expansion are the successive  $n$ th-order contributions to the interaction energy.

The first-order contribution, known as the molecular electrostatic potential (MEP), includes the Coulomb term to the interaction energy and represents the energy of the interaction of a static distribution of charges with the external charge  $q$ . Second- and higher-order terms include the induction and dispersion contributions to the interaction energy due to the polarization of the charge distribution by the presence of  $q$ . As a first approximation, it can be considered that only the first two terms, MEP and polarization, are important to characterize the interaction energy.<sup>12</sup>

The polarization has been calculated using a probe charge of 0.1 e, and scaled to the corresponding of 1.0 e, as developed previously.<sup>13</sup> In this scheme, no charge transfer, polarization,

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## SCHEME 1



or other effects associated with the ions are considered. The energy partition used here is similar to the general molecular interaction potential with potential (GMIPp) developed by Orozco and Luque<sup>14</sup> that evaluates the MEP and polarization at the HF level and, in addition, includes a van der Waals contribution by means of a molecular mechanics force field.

In the case of the complexes where the aromatic systems simultaneously interact with an anion in one face and a cation in the opposite, the interaction of the two point charges across the space has been calculated using eq 1.

$$E_{q_1q_2} = \frac{q_1q_2}{4\pi\epsilon_0R} = -\frac{3.322 \times 10^2}{R} \text{ kcal/mol} \quad (1)$$

The interaction energies have been corrected from the inherent basis set superposition error (BSSE) using the full counterpoise method of Boys and Bernardi (eq 2).<sup>15</sup>

$$E_{\text{BSSE}}(\text{ABC}) = E(\text{A})_{\text{A}} - E(\text{A})_{\text{ABC}} + E(\text{B})_{\text{B}} - E(\text{B})_{\text{ABC}} + E(\text{C})_{\text{C}} - E(\text{C})_{\text{ABC}} \quad (2)$$

where  $E(\text{A})_{\text{ABC}}$  represents the energy calculated for monomer A using its geometry in the complex and the complete set of basis functions used to describe the complex, and  $E(\text{A})_{\text{A}}$  is the energy for monomer A using its geometry in the complex and its basis set.

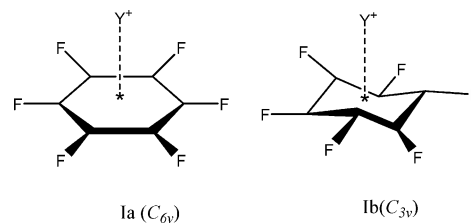
The atomic charges and the corresponding charge transfer within the complexes have been calculated with the NBO-5 method<sup>16</sup> at the MP2(full)/6-31++G\*\* computational level. This procedure has shown to produce similar charges independently of the basis set used.

The topological properties of the electron charge density have been studied using the atoms-in-molecules methodology<sup>17</sup> (AIM) with the AIMPAC program package.<sup>18</sup>

## Results and Discussion

This section has been divided in four parts. Part one studies the complexes formed by single cations with  $\text{C}_6\text{F}_6$  (structures **I** and **II** in Scheme 1) and compares the results with those obtained for similar complexes of  $\text{C}_6\text{H}_6$ . The second one considers the complexes of  $\text{C}_6\text{F}_6$  and  $\text{C}_6\text{H}_6$  with a cation in one face and an anion in the other one (**III**). The third part describes the complexes resulting from the attack of the fluoride anion to  $\text{C}_6\text{F}_6$  and  $\text{C}_6\text{H}_6$  in the presence of the cation (**IV**). Finally the last one reports those of the aromatic systems and the neutral molecule XY formed by the anion and the cation (**V** and **VI**).

## SCHEME 2



Other configurations have been explored but they are not reported since they do not correspond to minima configurations in any of the complexes, for instance, those with the XY molecule in the molecular plane of the aromatic ring.

**$\text{C}_6\text{F}_6$ :Cations.** Two different configurations of the interaction of a series of cations ( $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$ ) with  $\text{C}_6\text{F}_6$  have been initially studied (Scheme 1). The first one corresponds to the interaction of the cations with the  $\pi$ -cloud of  $\text{C}_6\text{F}_6$  **I** while in the second one, the interaction of the cations is with the fluorine atoms **II**.

For the two smallest cations,  $\text{Li}^+$  and  $\text{Na}^+$ , minimum complexes with  $C_{6v}$  symmetry (**Ia**) at the HF/6-31G\* level have been found. However, at the MP2(full)/6-31++G\*\* level the  $C_{6v}$  structures show an imaginary frequency and the minimum, with  $C_{3v}$  symmetry (**Ib**), correspond to a system where the planarity of the aromatic ring is lost with three alternated carbon atom in a plane and the other three defining a different plane (a flattened "chair", Scheme 2). The energetic differences between these two structures is very small, 0.18 and 0.27 kcal/mol for the  $\text{Li}^+$  and  $\text{Na}^+$  complexes, respectively.

Even though, the MEP map of  $\text{C}_6\text{F}_6$  indicates that favorable interactions will be possible only with negatively charged groups, positively charged groups could polarize the  $\text{C}_6\text{F}_6$  molecule to generate a stable complex similar to those obtained for the  $\text{C}_6\text{H}_6$ :cation complexes. The partition of the interaction energy in MEP and polarization terms (Table 1) shows that the second term is of the same magnitude as the first one but with opposite sign. Other contributions, not considered here, as those involved in the electronic rearrangement of the ions, the charge transfer and the molecular deformation, should slightly increase the attraction between the cations and  $\text{C}_6\text{F}_6$ . In the case of the  $\text{C}_6\text{F}_6/\text{Na}^+$  the complex formed is very weak and its interaction energy is only  $-0.4$  kcal/mol at the MP2/6-31++G\*\* level [ $-1.15$  at the MP2(full)/6-31++G\*\* one] that became positive with the inclusion of the BSSE correction. Caution should be taken with the BSSE corrected energies since in some cases the correction provided nonphysical results, as in this case, or badly reproduced larger calculation, for instance the interaction energy of the  $\text{C}_6\text{F}_6:\text{Li}^+$  and  $\text{C}_6\text{F}_6:\text{Na}^+$  complexes calculated at the MP2/6-31++G(2d,2p) are  $-9.33$  and  $-2.42$  kcal/mol, respectively. Thus, the  $\text{C}_6\text{F}_6$  molecule shows similar minima complexes for the interaction of the  $\pi$ -cloud with isolated cations and anions. On the other hand, the complexes with anions are much stronger than with cations.<sup>6</sup>

Configuration **II** corresponds to a simultaneous interaction of the cations with two fluorine atoms adopting a complex of  $C_{2v}$  symmetry. These complexes are more stable than those of configuration **I** (Table 1).

The calculated  $\text{C}_6\text{F}_6:\text{Li}^+$  and  $\text{C}_6\text{F}_6:\text{Na}^+$  complexes with  $C_{6v}$  symmetry show the cation atoms at 2.16 and 2.66 Å above the aromatic ring, respectively. For comparative purposes, the corresponding complexes with benzene have been calculated; at the MP2(full)/6-31++G\*\*, the distances between the cations ( $\text{Li}^+$  and  $\text{Na}^+$ ) and the center of the aromatic ring are 1.91 and 2.39 Å, respectively, which corresponds to a difference of 0.25

**TABLE 1: Interaction Energies (kcal/mol) of the C<sub>6</sub>F<sub>6</sub>:Cation Complexes Calculated at the MP2/6-31++G\*\* and MP2/6-311++G\*\* (in parentheses) Levels<sup>a</sup>**

system	Structure <b>Ia</b>				Structure <b>Ib</b>		Structure <b>II</b>	
	<i>E</i> <sub>I</sub>	<i>E</i> <sub>I+BSSE</sub>	MEP	Polar	<i>E</i> <sub>I</sub>	<i>E</i> <sub>I+BSSE</sub>	<i>E</i> <sub>I</sub>	<i>E</i> <sub>I+BSSE</sub>
C <sub>6</sub> F <sub>6</sub> :Li <sup>+</sup>	-5.72 (-8.21)	-1.41	18.93	-19.59	-5.90 (-8.38)	-1.70	-24.14 (-22.45)	-20.14
C <sub>6</sub> F <sub>6</sub> :Na <sup>+</sup>	-0.42 (-0.80)	3.32	13.61	-11.28	-0.68 (-1.15)	2.94	-15.53 (-14.15)	-12.43
C <sub>6</sub> F <sub>6</sub> :K <sup>+</sup>							-11.10	-8.50

<sup>a</sup> The contribution of the MEP and polarization (kcal/mol) to the interaction energy of structures **Ia** is included (Scheme 1).

and 0.27 Å shorter than those obtained for the corresponding C<sub>6</sub>F<sub>6</sub> complexes. In the same way, important differences are found in the interaction energies: while in the C<sub>6</sub>H<sub>6</sub> complexes they are -40.1 and -28.0 kcal/mol, respectively, with C<sub>6</sub>F<sub>6</sub> they are -5.7 and -0.4 kcal/mol at the MP2(full)/6-31++G\*\* computational level.

In complexes **Ia** and **Ib**, the geometrical effect on the C<sub>6</sub>F<sub>6</sub> molecule of the interaction with the cation is a small lengthening of the C-C distances, up to 0.01 Å, and a shortening of the C-F distances, up to 0.02 Å. In addition, in **Ia** the fluorine atoms move in opposite direction to the position of the cation, and thus the plane formed by the carbon atoms is about 0.02 Å closer to the cation than that formed by the fluorine atoms. All of these results are opposite to those found for the interaction of anions with C<sub>6</sub>F<sub>6</sub>.<sup>6</sup> In the **Ib** complexes, the planes defined by the two sets of carbon atoms of the aromatic ring distance 0.02 and 0.04 Å for the Li<sup>+</sup> and Na<sup>+</sup> complexes, respectively.

The complexes with C<sub>2v</sub> symmetry (**II**), where the cations interact with two fluorine atoms, show a lengthening of the interacting C-F bonds up to 0.04 Å and a small shortening of the closest C-C bond with respect to the isolated C<sub>6</sub>F<sub>6</sub> molecule.

The analysis of the electron density of the complexes with structure **Ia** shows six degenerate bond critical points situated between the cation and the carbon atoms of the C<sub>6</sub>F<sub>6</sub> molecule as in the case of the C<sub>6</sub>H<sub>6</sub>:cation complexes.<sup>19</sup> In addition, and due to topological reasons, six new ring critical points and a cage critical point are found for all the complexes. The value of the electron density and its laplacian at the bcp and rcp are almost identical for each of the C<sub>6</sub>F<sub>6</sub>:Li<sup>+</sup> and C<sub>6</sub>F<sub>6</sub>:Na<sup>+</sup> complexes, showing small and positive values for the electron density (0.010 and 0.007 au, respectively) and its laplacian (0.045 and 0.030 au, respectively) characteristic of weak ionic interactions. The **Ib** complexes show only three bcp's between the cations and the closest carbon atoms of the aromatic ring, with values similar to the **Ia** complexes. In the case of the complexes with structure **II**, only new bond critical points are found between the cation and the interacting fluorine atoms and the corresponding ring critical point. In these cases, the electron density at the bcp is 2.5 times larger than that of the corresponding complexes with structure **I** an indication that the interaction is stronger.

**Anions: C<sub>6</sub>R<sub>6</sub>(R=F, H): Cations.** All the complexes studied in this section present the ions along the original C<sub>6</sub> symmetry axis of the aromatic ring (structure **III** in Scheme 1). At the HF/6-31G\* level, the C<sub>6</sub>F<sub>6</sub> complexes with C<sub>6v</sub> symmetry (**IIIa**) correspond to a minimum configuration, with the exception of the fluoride complexes which show two degenerate imaginary frequencies in agreement with previous studies that have shown similar results for fluoride complexes with perfluoroaromatic derivatives.<sup>6-8</sup> At the MP2(full)/6-31++G\*\* level, an additional imaginary frequency is present in all these complexes as indication that the minima at this level correspond to a C<sub>3v</sub> symmetry structures (**IIIb**), similar to what was observed in

configuration **I**. Regarding the C<sub>6</sub>H<sub>6</sub> series, only the bromide complexes are minima. The corresponding minima of the fluoride derivatives correspond to a nucleophilic attack of the aromatic ring and will be treated in detail later.

The only significant difference between the **IIIa** and **IIIb** complexes corresponds to the lack of planarity of the aromatic system in the last cases, since the distance between ions to the geometrical center of the aromatic ring is almost the same for each given complex. The distance between the two planes defined by the two set of alternating carbon atoms in the **IIIb** structures ranges between 0.04 Å in the F<sup>-</sup>:C<sub>6</sub>H<sub>6</sub>:Li<sup>+</sup> complex to 0.07 Å in the Br<sup>-</sup>:C<sub>6</sub>F<sub>6</sub>:K<sup>+</sup> complex.

The interaction energy and the decomposition of the electrostatic interaction of the complexes are gathered in Table 2. The most important contribution comes from the attraction of the anion and the cation, which represents between a 60 to 70% of the interaction energy. The aromatic ring acts as insulator of the two charges, avoiding the formation of the corresponding salt. In general, the sum of the contributions considered here is able to account for more than 90% of the interaction energy obtained for these complexes. The calculated value of charge transfer, calculated with the NBO method and the MP2(full)/6-31++G\*\* wave function, seems to be small in all these complexes (the largest value is 0.1 e in some lithium complexes). The cooperative effect in these complexes, evaluated as the gain in interaction energy of the trimer relative to the addition of the two-body interaction energies, reaches values of between 8 and 11 kcal/mol in these complexes.

The geometrical evidence of the interaction of the anion and the cation comes from their distances to the center of the aromatic ring that are closer than those obtained when the interaction is between the isolated cation, or anion, with C<sub>6</sub>F<sub>6</sub> or C<sub>6</sub>H<sub>6</sub>. Thus, differences up to 0.3 and 0.4 Å are found for the cations and anions, respectively.

The simultaneous interaction of the cation and the anion produces a cooperative effect in the movement of the fluorine and hydrogen atoms out of the molecular plane toward the anions in the **IIIa** complexes of C<sub>6</sub>F<sub>6</sub> and C<sub>6</sub>H<sub>6</sub>, respectively. The maximum effect in the complexes with C<sub>6</sub>F<sub>6</sub> corresponds to those complexes with Na<sup>+</sup>, and in the case of C<sub>6</sub>H<sub>6</sub> with those with K<sup>+</sup>, reaching a maximum value of 0.07 and 0.11 Å for the Br<sup>-</sup>:C<sub>6</sub>F<sub>6</sub>:Na<sup>+</sup> and Br<sup>-</sup>:C<sub>6</sub>H<sub>6</sub>:K<sup>+</sup> complexes, respectively.

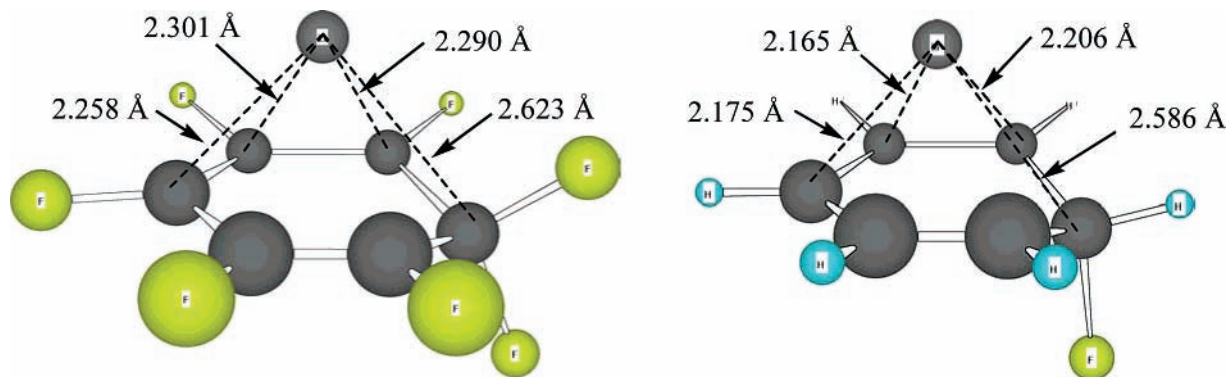
In contrast, the effect on the C-C and C-R distances of C<sub>6</sub>R<sub>6</sub> (R = F and H) due to the simultaneous interaction with a cation and an anion are partially compensated due to the opposite effects of both ions. In addition, the cations produce a lengthening of the C-C distance in C<sub>6</sub>H<sub>6</sub> and a shortening of the C-H one, while the opposite happens for the C<sub>6</sub>F<sub>6</sub> molecule as mentioned before. Since the interaction with the cation is stronger, the final results correspond to a geometrical variation modulated by the effect of the anions.

The electron density map of these complexes shows twelve new bcp for the **IIIa** complexes, corresponding to the bonds of

**TABLE 2: Interaction Energy and Contribution of the MEP, Polarization and Anion–Cation Electrostatic Interaction (kcal/mol), and Distances of the Ions to the Center of the Aromatic Rings Calculated at the MP2(full)/6-31++G\*\* and MP2(full)/6-311++G\*\* (in parentheses) Levels of the Complexes with Structure III**

system	structure IIIa		structure IIIb		cations		anions		anion–cation	sum of contribut.	cation: <sup>a</sup> distance	anion: <sup>a</sup> distance
	$E_I$	$E_{I+BSSE}$	$E_I$	$E_{I+BSSE}$	MEP	POL	MEP	POL				
F <sup>-</sup> :C <sub>6</sub> F <sub>6</sub> :Li <sup>+</sup>	-113.67 (-116.21)	-102.93	-113.92 (-116.45)	-103.54	22.53	-25.05	-17.45	-17.43	-78.87	-116.27	1.938 (1.879)	2.274 (2.275)
F <sup>-</sup> :C <sub>6</sub> F <sub>6</sub> :Na <sup>+</sup>	-100.00 (-98.70)	-89.33	-100.28 (-99.06)	-89.88	16.34	-15.66	-17.07	-16.82	-70.99	-104.20	2.373 (2.402)	2.307 (2.309)
F <sup>-</sup> :C <sub>6</sub> F <sub>6</sub> :K <sup>+</sup>	-90.34	-81.42	-90.77	-81.94	12.23	-9.39	-16.63	-16.13	-64.04	-93.97	2.842	2.345
Cl <sup>-</sup> :C <sub>6</sub> F <sub>6</sub> :Li <sup>+</sup>	-101.27 (-105.94)	-88.76	-101.56 (-106.25)	-89.40	21.69	-23.87	-12.29	-9.48	-68.97	-92.92	1.983 (1.902)	2.833 (2.809)
Cl <sup>-</sup> :C <sub>6</sub> F <sub>6</sub> :Na <sup>+</sup>	-89.29	-76.65	-89.62	-77.07	15.98	-15.09	-12.08	-9.18	-63.05	-83.41	2.407	2.863
Cl <sup>-</sup> :C <sub>6</sub> F <sub>6</sub> :K <sup>+</sup>	-80.51	-69.42	-81.03	-69.97	12.02	-9.11	-11.76	-8.74	-57.49	-75.08	2.870	2.908
Br <sup>-</sup> :C <sub>6</sub> F <sub>6</sub> :Li <sup>+</sup>	-104.41	-86.88	-105.18	-87.43	21.68	-23.85	-11.62	-8.55	-67.62	-89.96	1.984	2.929
Br <sup>-</sup> :C <sub>6</sub> F <sub>6</sub> :Na <sup>+</sup>	-92.72	-74.86	-93.43	-75.29	16.01	-15.13	-11.48	-8.37	-62.06	-81.04	2.404	2.949
Br <sup>-</sup> :C <sub>6</sub> F <sub>6</sub> :K <sup>+</sup>	-83.53	-67.86	-84.53	-68.20	12.00	-9.07	-11.19	-7.99	-56.63	-72.88	2.873	2.993
F <sup>-</sup> :C <sub>6</sub> H <sub>6</sub> :Li <sup>+</sup>	-123.30 (-124.92)	-113.28			-14.01	-28.84	12.98	-15.12	-79.66	-124.64	1.769 (1.738)	2.401 (2.399)
F <sup>-</sup> :C <sub>6</sub> H <sub>6</sub> :Na <sup>+</sup>	-103.10 (-101.11)	-92.84			-13.78	-17.84	12.65	-14.22	-70.65	-103.84	2.239 (2.256)	2.463 (2.452)
F <sup>-</sup> :C <sub>6</sub> H <sub>6</sub> :K <sup>+</sup>	-87.42 (-89.99)	-79.74			-11.22	-10.97	12.38	-13.52	-63.56	-86.89	2.715 (2.659)	2.511 (2.492)
Cl <sup>-</sup> :C <sub>6</sub> H <sub>6</sub> :Li <sup>+</sup>	-114.90 (-118.59)	-103.75			-14.19	-27.89	9.78	-8.40	-69.47	-110.16	1.804 (1.754)	2.978 (2.966)
Cl <sup>-</sup> :C <sub>6</sub> H <sub>6</sub> :Na <sup>+</sup>	-96.12 (-96.09)	-84.80			-13.66	-17.41	9.60	-8.13	-62.93	-92.52	2.266 (2.267)	3.013 (3.001)
Cl <sup>-</sup> :C <sub>6</sub> H <sub>6</sub> :K <sup>+</sup>	-81.30 (-85.22)	-72.64			-11.13	-10.72	9.34	-7.71	-57.30	-77.52	2.733 (2.673)	3.065 (3.040)
Br <sup>-</sup> :C <sub>6</sub> H <sub>6</sub> :Li <sup>+</sup>	-117.49 (-116.01)	-102.53			-14.20	-27.84	9.20	-7.68	-67.82	-108.34	1.805 (1.757)	3.093 (3.130)
Br <sup>-</sup> :C <sub>6</sub> H <sub>6</sub> :Na <sup>+</sup>	-98.64 (-93.98)	-83.86			-13.65	-17.38	9.07	-7.33	-61.69	-90.98	2.268 (2.278)	3.117 (3.164)
Br <sup>-</sup> :C <sub>6</sub> H <sub>6</sub> :K <sup>+</sup>	-83.62 (-83.50)	-71.79			-11.12	-10.76	8.91	-7.10	-56.44	-76.50	2.735 (2.682)	3.151 (3.204)

<sup>a</sup> \*Represents the centroid of the aromatic ring.

**Figure 1.** Optimized geometries of the C<sub>6</sub>F<sub>7</sub><sup>-</sup>:Li<sup>+</sup> (structure IV) and C<sub>6</sub>H<sub>6</sub>F<sup>-</sup>:Li<sup>+</sup> (structure IV) complexes calculated at the MP2(full)/6-31++G\*\* level.

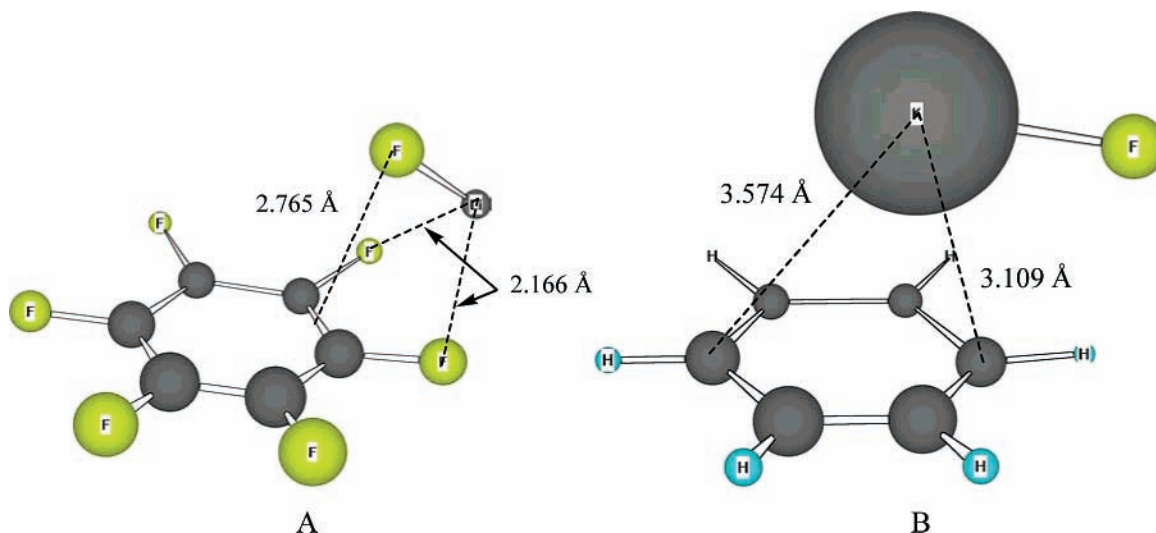
the cation and the anion with each of the carbon atoms of the aromatic ring, and six bcp for the IIIb complexes, similar to the isolated complexes of the anions or the cations with C<sub>6</sub>F<sub>6</sub> and C<sub>6</sub>H<sub>6</sub>. The values of the electron densities at the new bcp are larger than those found in the corresponding complexes of the isolated ion with the aromatic rings because the ions are closer to the aromatic ring, in agreement with a recent report that correlates the electron density with the bond distance.<sup>20</sup>

Experimental examples of similar complexes can be found in the work of Atwood et al., who have shown complexes with simultaneous interactions of metallic cation and anions in calixarene cavities.<sup>21</sup> In addition, Dougherty et al. have synthesized carboxylate derivatives of cyclophanes with affinity toward charged arginine derivatives.<sup>22</sup>

**C<sub>6</sub>R<sub>6</sub>F<sup>-</sup>:Y<sup>+</sup> (R = F and H) Complexes.** As indicated previously, the fluoride complexes with C<sub>6v</sub> symmetry show

two degenerate imaginary frequencies. All these systems evolved following the initial attack of one of the carbon atoms of the aromatic ring by the fluoride atom, forming the complexes with structure IV (Scheme 1). The three C<sub>6</sub>H<sub>6</sub>F<sup>-</sup>:Y<sup>+</sup> complexes are minimum structures, while for the hexafluorobenzene only the C<sub>6</sub>F<sub>7</sub><sup>-</sup>:Li<sup>+</sup> is. For the other two systems (Y<sup>+</sup> = Na<sup>+</sup> and K<sup>+</sup>), the process continues with the abstraction by the cations of one of the fluorine atoms of the CF<sub>2</sub> group, yielding the minimum structure V (Scheme 1) without energetic barrier.

The interaction energy of C<sub>6</sub>F<sub>7</sub><sup>-</sup>:Li<sup>+</sup> complex of structure IV (Figure 1) is very large (-119 kcal/mol) as expected for the interaction of a cation (Li<sup>+</sup>) with an anion (C<sub>6</sub>F<sub>7</sub><sup>-</sup>). However, its relative energy vs. that of the corresponding structure V is 46 kcal/mol, which could explain the reason similar minima for the remaining C<sub>6</sub>F<sub>7</sub><sup>-</sup>:Y<sup>+</sup> systems are not found. In the case of the C<sub>6</sub>H<sub>6</sub>F<sup>-</sup>:Y<sup>+</sup> complexes, the interaction energy cannot be



**Figure 2.** Optimized geometries of the  $C_6F_6:FLi$  (structure **V**) and the corresponding minimum of the  $C_6H_6:KLi$  complexes calculated at the MP2(full)/6-31++G\*\* level.

**TABLE 3: Interaction and Relative Energy (kcal/mol) of the  $C_6F_6:XY$  Complexes (**V**) with Respect to the Corresponding Structure III Complexes and Representative Distances (Å) at the MP2(full)/6-31++G\*\* and MP2(full)/6-311++G\*\* (in parentheses) Levels**

system	$E_I$	$E_{I+BSSE}$	$E_{rel}$	$X\cdots^a$ distance <sup>a</sup>	$Y\cdots F$ distance
$C_6F_6:FLi$	-12.56 (-11.37)	-7.00	-80.42 (-78.21)	2.765 (2.728)	2.166 (2.221)
$C_6F_6:FNa$	-13.85	-8.99	-65.14	2.623	2.530
$C_6F_6:FK$	-15.17	-10.28	-57.27	2.589	2.882
$C_6F_6:CLi$	-13.07 (-10.71)	-5.57	-64.90 (-61.84)	<i>b</i>	1.999 (2.086)
$C_6F_6:CLiNa$	-14.13	-7.67	-56.14	3.173	2.525
$C_6F_6:ClK$	-16.17	-8.27	-46.23	3.186	2.884
$C_6F_6:BrLi$	-17.32	-7.40	-61.31	3.239	2.171
$C_6F_6:BrNa$	-17.38	-7.71	-54.15	3.261	2.531
$C_6F_6:BrK$	-19.36	-8.37	-46.00	3.277	2.877

<sup>a</sup> \*Indicates the center of the C–C bond. <sup>b</sup> This complex shows  $C_{2v}$  symmetry.

calculated because  $C_6H_6F^-$  is not stable when isolated as a molecule evolving to the complex where the fluoride atom interacts with the hydrogens of  $C_6H_6$  in the molecular plane. The relative energies of these complexes when compared with that corresponding to structure **VI** are between 43 and 57 kcal/mol less stable than the latter.

The geometry of all these complexes shows the cation approximately above the center of the aromatic ring at distance similar to that of the C–R groups. The average distances between the cation and the carbon atoms of the aromatic systems are 2.18, 2.60, and 2.98 Å for the  $C_6H_6F^-:Y^+$  complexes ( $Y^+ = Li^+, Na^+, \text{ and } K^+$ ), respectively. In the case of  $C_6F_7^-:Li^+$ , the cation is in a similar disposition at 2.6 Å of the carbon atom of the  $CF_2$  group and approximately at 2.3 Å of the rest of the carbon atoms of the aromatic ring.

**$C_6R_6:XY$  (R = F and H) Complexes.** The complexes between the XY molecules and the aromatic systems provide two different complexes (**V** and **VI**). On one hand, the  $C_6F_6:XY$  complexes (**V**) adopt a disposition where the electronegative atom of the XY molecule is above one of the C–C bonds of the aromatic ring and the electropositive atom interacts simultaneously with two fluorine atoms of  $C_6F_6$  (Figure 2a). The only exception corresponds to the  $C_6F_6:CLi$  complex where the  $CLi$  molecule is in the molecular plane with only the lithium atom interacting with the fluorine atoms. The  $C_6H_6:XY$  complexes

**TABLE 4: Interaction and Relative Energy (kcal/mol) of the  $C_6H_6:YX$  Complexes (**VI**) with Respect to the Corresponding Structure III Complexes and Representative Distances (Å) at the MP2(full)/6-31++G\*\* and MP2(full)/6-311++G\*\* (in parentheses) Levels**

	$E_I$	$E_{I+BSSE}$	$E_{rel}$	$Y\cdots^a$	elongation of XY bond
$C_6H_6:LiF$	-19.52 (-17.51)	-10.81	-77.75 (-75.65)	2.055 (2.056)	0.007 (0.017)
$C_6H_6:NaF$	-14.20	-8.23	-62.39	2.491	0.008
$C_6H_6:KF^b$	-8.95 (-9.32)	-6.05	-53.97 (-54.96)	3.051 (3.003)	0.022 (0.024)
$C_6H_6:LiCl$	-22.21 (-21.16)	-13.17	-60.42 (-59.63)	2.021 (1.982)	-0.004 (0.014)
$C_6H_6:NaCl$	-15.66 (-14.77)	-9.33	-50.85 (-50.86)	2.459 (2.488)	0.012 (0.011)
$C_6H_6:KCl^b$	-10.93 (-11.34)	-7.17	-40.21 (-40.42)	2.989 (2.947)	0.021 (0.026)
$C_6H_6:LiBr$	-24.43 (-21.33)	-13.95	-55.35 (-53.52)	2.003 (1.973)	-0.020 (0.020)
$C_6H_6:NaBr$	-18.78 (-14.82)	-9.68	-49.63 (-47.00)	2.457 (2.492)	0.013 (0.015)
$C_6H_6:KBr$	-12.64 (-11.64)	-7.45	-39.20 (-37.62)	2.996 (2.936)	0.029 (0.029)

<sup>a</sup> \*Represents the centroid of the aromatic ring. <sup>b</sup> These complexes shows two degenerate imaginary frequencies.

present  $C_{6v}$  symmetry with the electropositive atoms pointing toward the aromatic  $\pi$ -cloud. Two of these complexes present two degenerate imaginary frequencies,  $C_6H_6:KF$  and  $C_6H_6:KCl$ . The corresponding minimum structure of these complexes corresponds to a disposition where the potassium atom is above the center of the aromatic ring and the fluoride or chloride extremity is over one of the aromatic carbon atoms (Figure 2b).

An energy comparison of the  $C_6R_6:XY$  complexes (**V** and **VI**) with the  $X^-:C_6R_6:Y^+$  ( $R = F$  and  $H$ ) complexes shows that the former are between 80 and 33 kcal/mol more stable than the latter (Tables 3 and 4). The largest differences in each series correspond to the  $C_6R_6:FY$  complexes, which are not minima configurations in structure **II**.

In  $C_6F_6:XY$  complexes, the distance between the middle of the C–C bond and the anion shows different tendencies for the alkali fluoride salts, on one hand, and the chloro and alkali bromide salts on the other (Table 3). While in the first case, the distance reduces as the size of the alkali atom increases, it increases in the latter. Regarding the distances between the

cation and the fluorine atoms of the  $C_6F_6$  molecule, they show small variations for each cation independently of the attached anion, with the exception of the  $C_6F_6:CLi$  which shows a different disposition from the rest of the complexes.

The  $C_6H_6:YX$  complexes with structure **VI** show the cations less than 0.2 Å apart from the center of the aromatic ring when compared to the corresponding  $C_6H_6:Y^+$  as a clear indication of the highly polar nature of the XY molecules (Table 4). In general, the XY bond tends to elongate when interacting with the  $C_6H_6$  molecule in a manner similar to what happened with the hydrogen bond donor.<sup>23</sup>

The electron density map of complexes with structure **V** shows a bifurcated bond between the anion and one of the aromatic C–C bonds, similar to the maps found for the interaction of hydrogen bond donors and  $C_6H_6$ . In addition, two bond critical points are found between the cations and each one of the two closer fluorine atoms. The only exception corresponds to the  $C_6F_6:CLi$  complex, which as indicated previously has a  $C_{2v}$  symmetry, with two bcp between the  $Li^+$  and the fluorine atoms.

The electron density map of the  $C_6H_6:XY$  complexes shows, as previously, six new bond critical points between the X atom and each of the carbon atoms of the aromatic ring.

Using the electron density in all the complexes studied here with  $C_{6v}$  symmetry, good exponential correlations are found between the electron density or its laplacian at the bond critical point versus the bond distance for the  $C\cdots X^-$  and  $C\cdots Y^+$  interactions. These relationships are especially good for the anions where, in all the cases, the value of the square correlation coefficient is over 0.99.

While this article was in the editorial process, Deyà et al. published a study of ternary complexes between sodium,  $C_6H_6$  or  $C_6F_6$  and the three halogen anions, which corresponds to complex **IIIa** of the present article with  $C_{6v}$  symmetry.<sup>24</sup> The importance of the polarization term in the interaction energy has been shown using the MIPp method to evaluate it. In addition, some examples extracted from the CSD, where this interaction has been found, are mentioned.

## Conclusion

The potential complexes of  $C_6F_6$  and isolated cations and  $C_6R_6$  ( $R = F$  and  $H$ ) simultaneously with a cation and an anion in different faces, forming a kind of inverse sandwich complex, have been studied using ab initio MP2(full)/6-31++G\*\* and MP2(full)/6-311++G\*\* levels. The comparison of the frequency calculation at the HF/6-31G\* and MP2(full)/6-31++G\*\* levels has shown that, with the latter method, additional imaginary frequencies are encountered that indicate the lack of planarity of the aromatic ring in some of the complexes.

Several of the complexes where the ions interact with the  $\pi$ -cloud of  $C_6R_6$  correspond to minima structures. However, more stable configurations are obtained in all the studied cases. Thus, those complexes where an aromatic ring is intercalated between a cation and an anion will only be possible for systems that cannot evolve kinetically like those that have been reported for encapsulated cations<sup>25</sup> and anions<sup>26</sup> inside fullerenes.

The partition of the interaction energy in electrostatic terms (MEP, polarization and charge–charge interaction) is able to explain more than 90% of the obtained values. In the case of the complexes where a cation is located in one face and the anion in the other, the most important term corresponds to the charge–charge interaction, the aromatic molecules acting as a charge insulator.

The AIM analysis shows bond critical points between the anions or cations and the carbon atoms of the aromatic ring when the former are located in its  $C_6$  axis. In other configurations, the bond critical points show the interaction between the ions and the different component of the aromatic molecules.

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**Supporting Information Available:** Total energy and Cartesian coordinates of the complexes calculated at the MP2(full)/6-31++G\*\* level. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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