

An Attractive Interaction between the π -Cloud of C_6F_6 and Electron-Donor Atoms

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Received January 23, 1997[®]

A theoretical study of the possible interaction of the π -cloud of hexafluorobenzene (C_6F_6) with several small electron-donor molecules (FH, HLi, $:CH_2$, NCH, and CNH) has been carried out. The calculations have been performed using HF, MP2, and hybrid HF/DFT methods (B3LYP) with the 6-31G** and 6-311++G** basis sets. The topology of the electron density of the complexes has been characterized using the AIM methodology. The characteristics of the electron density and molecular electrostatic potential maps of benzene and hexafluorobenzene have been compared. Finally, the results obtained from a search in the Cambridge Structural Database system of this kind of interaction are shown.

Introduction

The ability of the π -cloud of benzene to act as an electron donor in the formation of hydrogen bonds has been shown both theoretical and experimentally.¹ In these cases, the π -electrons of the benzene interact with an electron-deficient atom, a hydrogen attached to an electronegative atom.

The presence of substituents in the aromatic ring should modulate this ability. In the extreme case in which the aromatic ring is substituted by six withdrawing groups, its electron-donor capabilities should be reversed. An example of this is suggested by the X-ray structure of hexafluorobenzene (C_6F_6) in which one of the fluorine atoms points to the center of another molecule of C_6F_6 .² This disposition in the crystal has been proposed to correspond to a local repulsion minimum.³

In this paper, we show a set of complexes in which the π -cloud of C_6F_6 interacts with electron donors, corresponding to local minima. The different behavior of C_6H_6 and C_6F_6 can be explained on the basis of their electron density and molecular electrostatic potential maps. In addition, a search in the Cambridge Structural Database system has been used to generalize this kind of interaction.

Methods

Five molecules have been selected, based on their small size and known capabilities as electron donors, to study the possible interaction between them and the π -electrons of C_6F_6 . In the linear molecules (FH, HLi, NCH, and CNH) a C_{6v} symmetry has been adopted (Chart 1). For the $C_6F_6 \cdots CH_2$ complex, the minimum found corresponds to a C_{2v} symmetry.

The geometry of the monomers and complexes has been fully optimized with the program Gaussian-94⁴ using the standard

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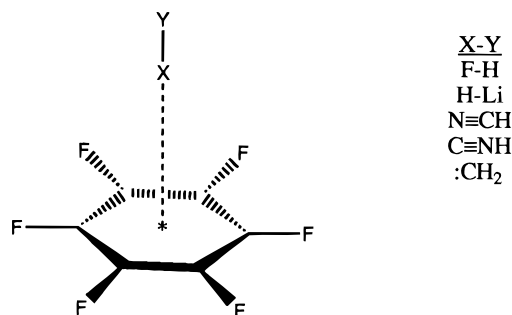
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Chart 1



6-31G**⁵ and 6-311++G**⁶ basis sets at the Hartree–Fock (HF) and Moller–Plesset⁷ (MP2) levels. In addition, a hybrid RHF-density functional method (Becke3LYP)⁸ has been used.

The fact that the complexes are minima at the RHF/6-31G** level has been confirmed by calculating the corresponding frequencies (no negative force constants). The interaction energies have been corrected for the inherent basis set superposition error (BSSE) using the Boys–Bernardi counterpoise technique.⁹

The topological properties of the electronic charge density have been characterized using the atoms in molecules methodology¹⁰ (AIM) with the AIMPAC program package.¹¹

A search in the Cambridge Structural Database¹² (CSD) has been carried out defining the C_6F_5 moiety with the CONNSER module, restricted to organic compounds without disorder and error free at 0.002 Å. All the situations where an atom is located at less than 4.0 Å of all the carbon atoms of the C_6F_5 moiety have been considered.

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Table 1. Total Energy (Hartree), Interaction Energy with the BSSE Correction (kcal/mol), E_{I+BSSE} , and Distance between the Interacting Atom to the Center of the Aromatic Ring (Å) ($X\cdots*$ in Scheme 1)

system	RHF/6-31G**			B3LYP/6-31G**			MP2/6-31G**		
	total energy (hartrees)	E_{I+BSSE} (kcal/mol)	distance $X\cdots*$ (Å)	total energy (hartrees)	E_{I+BSSE} (kcal/mol)	distance $X\cdots*$ (Å)	total energy (hartrees)	E_{I+BSSE} (kcal/mol)	distance $X\cdots*$ (Å)
$C_6F_6\cdots FH$	-923.768 171	-0.85	3.076	-928.028 060	-0.30	2.858	-925.714 957	-0.88	2.814
$C_6F_6\cdots HLi$	-831.740 738	-2.76	3.012	-835.684 216	-1.89	2.925	-833.524 919	-3.02	2.746
$C_6F_6\cdots CH_2$	-862.633 784	-1.49	3.596	-866.732 380	-0.90	3.355	-864.508 415	-1.78	3.255
$C_6F_6\cdots NCH$	-916.633 997	-1.47	3.419	-921.024 293	-0.82	3.255	-918.687 590	-2.10	3.023
$C_6F_6\cdots CNH$	-916.616 085	-1.08	3.584	-920.999 949	-0.64	3.351	-918.655 997	-1.93	3.132

system	RHF/6-311++G**			B3LYP/6-311++G**		
	total energy (hartrees)	E_{I+BSSE} (kcal/mol)	distance $X\cdots*$ (Å)	total energy (hartrees)	E_{I+BSSE} (kcal/mol)	distance $X\cdots*$ (Å)
$C_6F_6\cdots FH$	-924.043 607	-1.28	3.298	-928.353 973	-1.23	3.127
$C_6F_6\cdots HLi$	-831.979 667	-3.66	3.117	-835.961 776	-3.78	2.933
$C_6F_6\cdots CH_2$	-862.880 535	-1.86	3.669	-867.019 900	-1.82	3.394
$C_6F_6\cdots NCH$	-916.892 805	-1.81	3.416	-921.326 891	-1.65	3.267
$C_6F_6\cdots CNH$	-916.875 325	-1.45	3.638	-921.303 627	-1.52	3.427

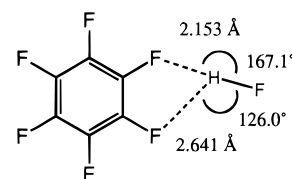
Table 2. Total Energy (Hartree), Zero Point Energy Correction (kcal/mol), and Interaction Energies of the Two $C_6F_6\cdots FH$ Complexes Found at the RHF/6-31G** Level

system	total energy (hartree)	zero point energy (kcal/mol)	rel energy (kcal/mol)	rel energy with zero point corr (kcal/mol)
$C_6F_6\cdots FH$ (Chart 1)	-923.768 171	42.00	0.00	0.00
$C_6F_6\cdots HF$ (Figure 1)	-923.768 723	42.46	-0.35	0.11

Results and Discussion

The total energy, interaction energy, and distance between the interacting atom center of the aromatic ring in the optimized complexes are gathered in Table 1. Both the energetic and geometric results show some dependence of the theoretical methods used. However, the relative strength of the interaction energy of the complexes is not altered by the different basis sets or levels of calculation used here: $C_6F_6\cdots HLi \gg C_6F_6\cdots CH_2 > C_6F_6\cdots NCH > C_6F_6\cdots CNH > C_6F_6\cdots FH$. In the interaction distances a shortening effect is observed by the inclusion of electron correlation (MP2 and B3LYP methods), the shortest distances being the ones corresponding to the FH and HLi complexes. The results obtained with the two methods, which include electron correlation (MP2 and B3LYP) and the largest basis set, are more reliable due to the difficulties to reproduce weak interactions at the HF level.

The interaction energy of these complexes, except for the $C_6F_6\cdots HLi$ complex that is clearly stronger than the rest, is similar to the ones observed in weak hydrogen bonds.¹³ Thus, this interaction could compete with weak interactions when no other stronger interactions are possible. An example of this hypothesis is confirmed by the comparison of the energy of the two possible minima found in the $C_6F_6\cdots FH$ dimmers. The energy of the complex between the C_6F_6 and HF through a standard HB between one of the F atom of C_6F_6 and the hydrogen of HF (Table 2 and Figure 1) is only 0.35 kcal/mol more stable than the new complex shown here (Chart 1). In addition, when the zero point energy of both complexes is included in the energetic comparison the relative energy of both systems is reversed favoring the electron donor- π cloud interaction by 0.11 kcal/mol. These

**Figure 1.** Optimized $C_6F_6\cdots HF$ complex formed through a standard hydrogen bond at the HF/6-31G* level.

results are in agreement with recent reports that indicate the poor capabilities of organic fluorines as hydrogen-bond acceptors.¹⁴⁻¹⁶

The atom in molecules (AIM) analysis of the complexes shows small electron density in the bond critical points (BCPs) found between the two interacting systems, and a small effect is shown in the electronic characteristic of the molecules in the complexes when compared with the isolated monomers (Table 3). The interacting BCPs found here are situated in the bond path that directly connects the electron-donor atoms and the aromatic carbons, in contrast to the BCP found in hydrogen bonds between π -systems and proton donors where the description of the electron density corresponds to a conflict catastrophe point of the bifurcate type. In the latter case, the same BCP is shared by the two bond paths of the hydrogen to the two carbon atoms that holds the π -cloud, and the bond paths go from the hydrogen to the center of the C-C bond and then bifurcate to each one of the carbon atoms.¹⁷

In this case, a cage critical point is defined between the center of the aromatic ring and the electron-donor atom, again with a small electron density. As an example of the location of the critical points, the $C_6F_6\cdots HLi$ electron density with the position of the corresponding critical points is shown in Figure 2.

The extent of overlap of the electronic clouds of the monomers in the complexes provides another measure of the interaction strength. The 0.001 e/au^3 electron density isodensity surface has been considered as the one defining the molecular volume. The atomic radii in the interaction direction, $r_{0.001}$, can be defined as the distance

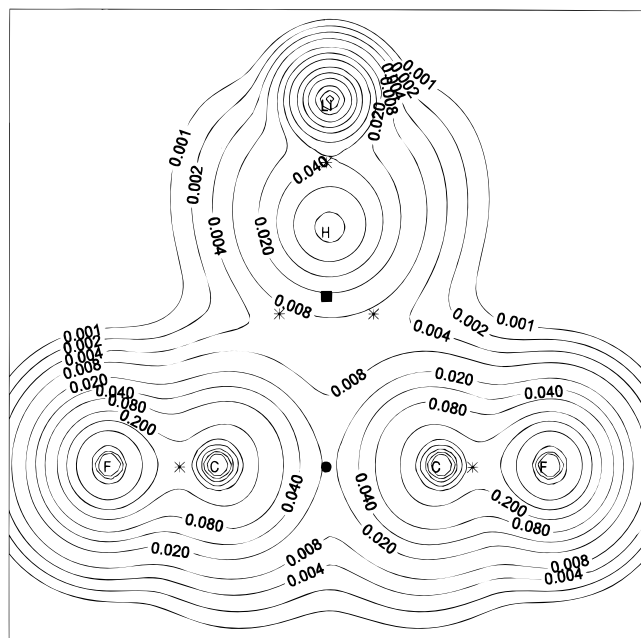
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Table 3. Electron Density at the Critical Points Calculated at the B3LYP/6-311++G Level**

system	C-C	C-F	C-X	*(center of C_6F_6)	cage critical point	others
C_6F_6	0.3165	0.2645		0.0184		
$C_6F_6 \cdots CH_2$	0.3176	0.2627	0.0050	0.0187	0.0041	0.2738 (C-H)
$C_6F_6 \cdots CNH$	0.3173	0.2630	0.0040	0.0188	0.0034	0.4352 (C \equiv N) 0.3322 (N-H)
$C_6F_6 \cdots FH$	0.3171	0.2633	0.0035	0.0187	0.0029	0.3672 (F-H)
$C_6F_6 \cdots HLi$	0.3181	0.2615	0.0048	0.0188	0.0041	0.0397 (H-Li)
$C_6F_6 \cdots NCH$	0.3173	0.2629	0.0042	0.0187	0.0035	0.4845 (N=C) 0.2866 (C-H)

**Figure 2.** Electron density (e/au^3) of the $C_6F_6 \cdots HLi$. The position of bond critical points are indicated with asterisks, the ring critical point with a circle, and the cage with a square.**Table 4. Distance from the X Atom to the 0.001 e Isoelectronic Surface in the Direction of the Interaction, $r_{0.001}$, and Extent of the Overlap of the Electronic Clouds (Å) in the Corresponding Complex with C_6F_6 at the B3LYP/6-311++G** Level**

	$r_{0.001}$	overlap extent
FH	1.613	0.273
LiH	1.713	0.566
:CH ₂	2.221	0.613
HNC	2.044	0.403
NCH	1.894	0.413
C_6F_6	1.786 ^a	

^a This value corresponds to the distance from the center of the aromatic ring through the C_6 axes to the 0.001 e isoelectronic surface.

between the atomic coordinate, centroid in the case of C_6F_6 , and the isosurface. The difference between the interaction distance (distance between the C_6F_6 centroid and the interacting atom in the complex) and the sum of the atomic radii provides the electronic cloud overlap. The results (Table 4) show a small overlap of the electronic clouds of the monomers in the complex similar to the ones described for van der Waals complexes.¹⁸ The calculated value of overlap has been found to correlate with the electron density at the C \cdots X bonds and cage critical points ($r^2 = 0.992$ and 0.982 , respectively), which indicates the almost null electron transfer between the two interacting systems.

Several aspects of the molecular characteristics of benzene and hexafluorobenzene have already been compared in the literature, especially to account for the different behavior in the aromatic interactions of these two compounds using theoretical and experimental techniques.^{19–23} Thus, a similar quadrupole moment but with opposite sign^{24,25} has been considered as the guiding force in these interactions. Other differences found between these two compounds correspond to the aromatic solvent-induced NMR shifts when used as solvents,²⁶ the collisional energy transfer in highly excited molecule,²⁷ and the nuclear reorganization energies and solvation dynamics.²⁸ However, some recent calculations of the ring currents and aromaticity²⁹ and aromatic shielding³⁰ of these molecules do not show significant differences between them.

In the present paper, the molecular electrostatic potential (MEP) and electron density of C_6F_6 and C_6H_6 have been compared in order to understand the different behavior of these molecules regarding their interactions above the aromatic plane. The analysis of the MEP (Figure 3) shows the effects of the fluorine atoms above the aromatic plane. While in benzene, this region has negative values of MEP, and the C_6F_6 molecule shows positive values. These results indicate that C_6H_6 would interact with positively charged atoms such as lithium and hydrogens bonded to electronegative atoms. The opposite would happen in the case of C_6F_6 were the interaction with negatively charged species as the one shown here or the π -cloud of benzene in the (1:1) complex $C_6H_6:C_6F_6$ ³¹ would be preferred.

The results obtained for the electron density (Figure 4) confirmed those obtained for the MEP of both molecules. Thus, the corresponding maps as well as the electron density at the ring critical points located in the center of the aromatic rings (0.0187 in C_6F_6 and 0.0215 e/au^3 in C_6H_6 , which are similar to the values described by Laidig²⁴) indicate a reduction of this property in the

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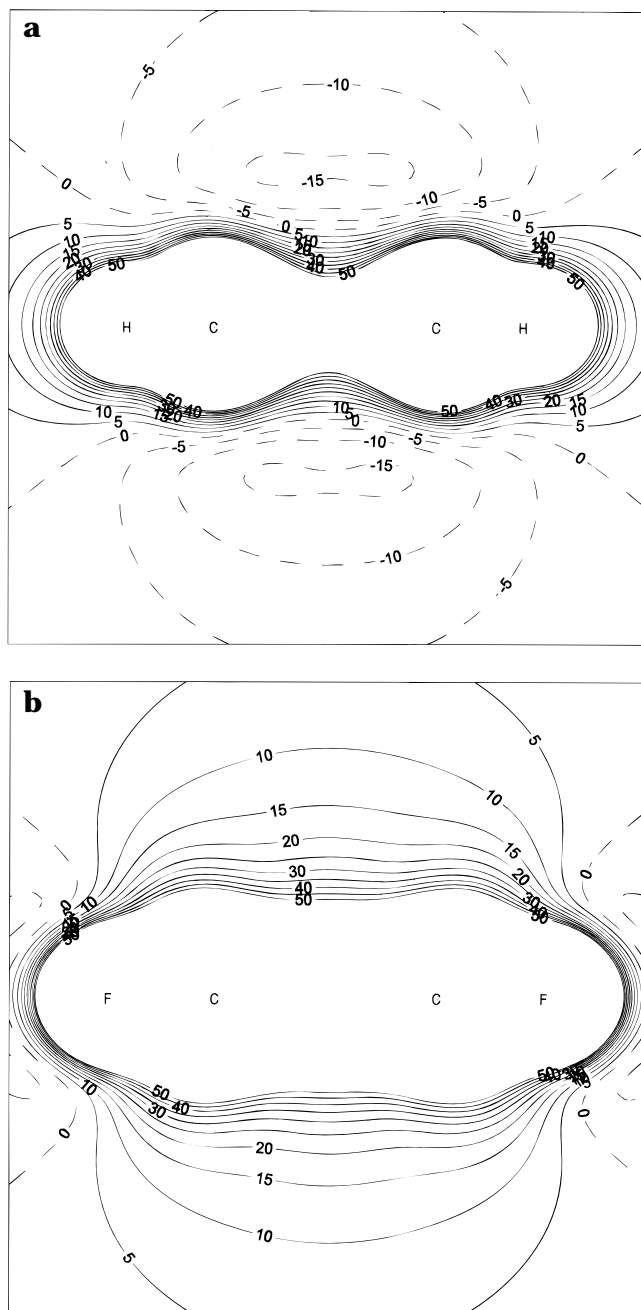


Figure 3. Molecular electrostatic potential (kcal/mol) of (a) benzene and (b) hexafluorobenzene above and below the aromatic plane.

plane above the aromatic ring by the effect of the fluorine atoms, a reduction that correspond to more positive MEP regions.

In order to confirm the possible existence of this kind of interaction in a more general way, a search in the CSD system has been carried out. All of the crystals with the C_6F_6 molecule or the C_6F_5 moiety that do not include organometallic atoms have been retrieved, and all the atoms that are in the crystal simultaneously at less than 4 Å of all the carbons of the electron-deficient aromatic ring (C_6F_6 or C_6F_5X) have been tabulated. The results obtained show 53 interactions of this kind in 30 crystals. In most of the interactions, the atoms interacting with the C_6F_5 moiety correspond to a fluorine atom attached to another aromatic ring in a manner similar to the case of the C_6F_6 crystal described previously. In addition, other atoms such as oxygen in carbonyl (BICCAR)(CSD

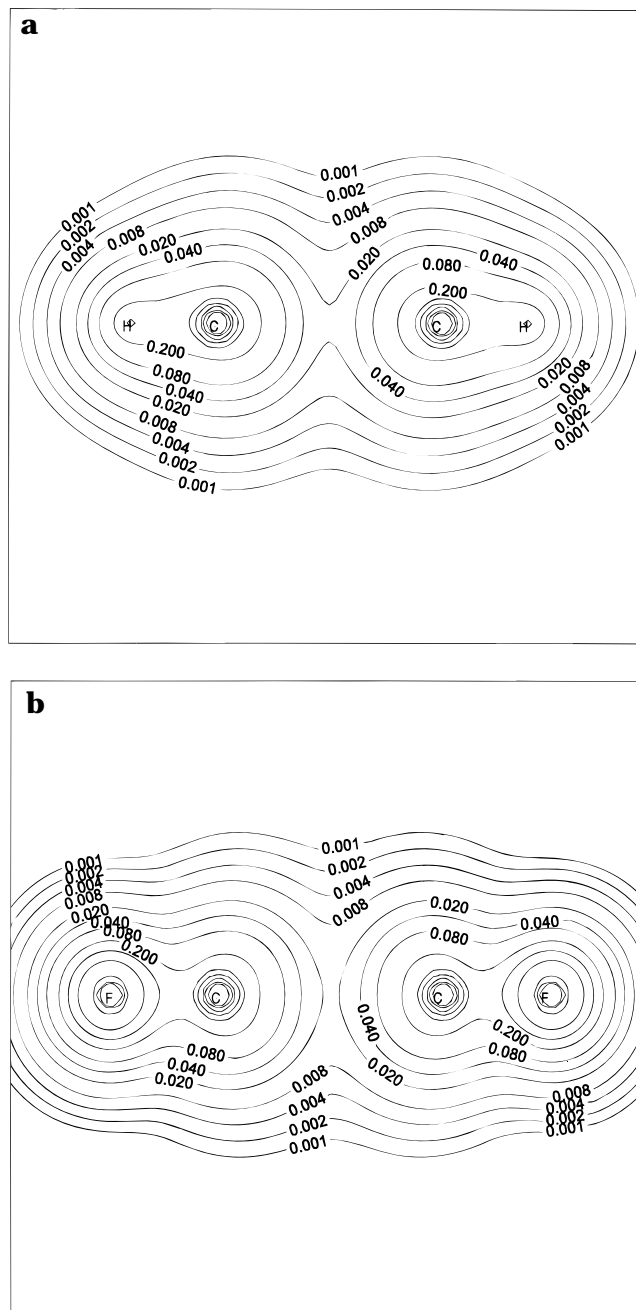


Figure 4. Electron density ($e/a.u.^3$) of (a) benzene and (b) hexafluorobenzene above and below the aromatic plane.

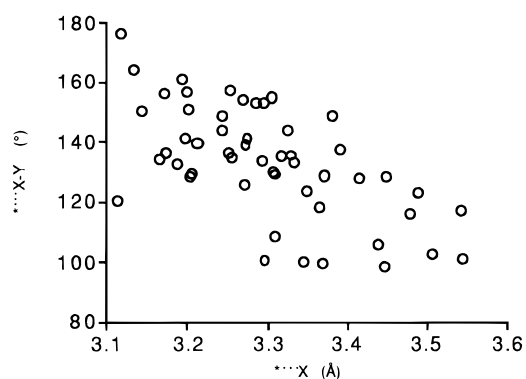


Figure 5. Distribution of the interaction distance (*...X in Scheme 1) versus the interaction angle (*...X-Y in Scheme 1) in the CSD system search.

Refcode in parenthesis), ester (FUMBUK), phosphate (DPFPRO), and ether groups (HALZUP), nitrogens in amines (KUYUYU), fluorine in fluorosulfones (FIYYAN), and carbons in isocyanates (KUMXOF) have been found in the search. As expected for a weak interaction like this one, the representation of the interaction distance ($X\cdots*$ in Chart 1) *versus* the angle formed by the center of the aromatic ring (*), the interacting atom (X) and the atom attached to the later one (Y), shows a large dispersion (Figure 5). However, it can be observed that shorter interaction distances correspond larger angles.

Conclusion

The interaction studied here shows the extreme case of modulating effect of substituent on the reactivity of the aromatic ring. The inclusion of a large number of electron-withdrawing atoms, six fluorine atoms in this case, inverts the electronic properties of the π -cloud in aromatic rings. This new interaction could be considered similar to that recently described between ClF and electron donor,³² in which the strong electronegativity of the fluorine atom inverts the natural electron-donor characteristics of the chlorine atom.

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In the present paper, the geometry, energy, and electron density properties of a series of complexes formed by in C_6F_6 and several small electron-donating molecules have been studied by means of *ab initio* HF, MP2, and hybrid HF/DFT methods with the 6-31G** and 6-311++G** basis sets. The calculations have shown that all the complexes studied are minima of the potential energy surface.

The effects of the fluorine atoms on the aromatic ring have been studied by comparing the MEP and electron density maps of the benzene and hexafluorobenzene.

Finally, a search on the CSD system has been used to generalize this interaction.

Acknowledgment. Thanks are given to the EU for the network Location and Transfer of Hydrogen (No. CHRX CT 940582).

Supporting Information Available: List of Refcodes, interacting distances, angles, and atom labels found in the CSD search (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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