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Interaction of Anions with Perfluoro Aromatic Compounds

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Received January 24, 2002

Abstract: The complexes formed by a variety of anions with perfluoro derivatives of benzene, naphthalene, pyridine, thiophene, and furan have been calculated using DFT (B3LYP/6-31++G**) and MP2 (MP2/6-31++G** and MP2/6-311++G**) ab initio methods. The minimum structures show the anion interacting with the π-cloud of the aromatic compounds. The interaction energies obtained range between −8 and −19 kcal mol^{-1}. The results obtained at the MP2/6-31++G** and MP2/6-311++G** levels are similar. However, the B3LYP/6-31++G** results provide longer interaction distances and smaller interaction energies than do the MP2 results. The interaction energies have been partitioned using an electrostatic, polarization, and van der Waals scheme. The AIM analysis of the electron density shows a variety of topologies depending on the aromatic system considered.

Introduction

The ability of the π-cloud of aromatic compounds to interact with positively charged atoms or the hydrogen of a hydrogen bond donor is well known.[1] However, in past years, several theoretical works have shown the possibility to invert this tendency in the case of hexafluorobenzene. The complexation of the π-cloud of C_6F_6 with the electron-rich moiety of simple molecules as FH, NCH, and OH_2 has been theoretically established.[2−5] More recently, the complexation of acetonitrile with C_6F_6 was first proposed by calculations and then proved by NMR experiments.[6] In a series of papers, Marder and Batsanov have explored the interactions of C_6F_6 and $C_{10}F_8$ with C_6H_6, $C_{10}H_8$, and several other aromatic hydrocarbons.[7]

The difference of the properties of C_6H_6 and C_6F_6 has been explained on the basis of the molecular electrostatic potential (MEP) of these molecules above the molecular plane. While in C_6H_6 a negative region of the MEP is observed, a positive region is obtained in the case of C_6F_6. A similar effect is expected for other aromatic compounds with a large number of withdrawing groups. Thus, Crabtree et al. have been able to obtain the X-ray structure of two complexes between perfluorophenanthrene and decamethylferrocene or ferrocene with [1:1] and [2:2] stoichiometries.[8,9] In contrast, a comparison of the supramolecular motifs present in the CSD database shows no major differences between those of perfluorinated and hydroaromatic compounds.[7,10]

To generalize these observations, three commercially available perfluoro-aromatic compounds (C_6F_6, C_5F_5N, and $C_{10}F_8$) and two additional highly reactive systems (C_4F_4O and C_4F_4S) have been considered in the present article (Figure 1). Their complexes with different anions (F^-, Cl^-, Br^-, H^-, CN^-, CNO^-, and CH_3^-) have been studied. DFT and MP2 ab initio methods have been used to characterize the geometry and interaction energies. The electron density of the complexes 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[11] program initially using the HF/6-31G**[12] computational level. These structures have been used as the starting point for the optimization at the B3LYP/6-31++G**[13,14] and MP2/6-31++G** levels.[15] In all of the cases, the minimum nature of

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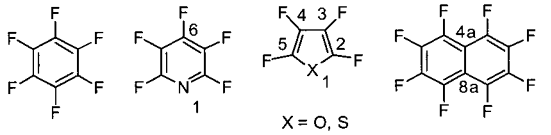

Figure 1. Schematic representation of the perfluoroaromatic compounds studied in the present work with their corresponding numbering.

the structures has been confirmed by frequency calculations at the HF/6-31G** level; otherwise, it has been mentioned in the text.

In several cases, calculations at the MP2/6-311++G** level have been carried out and used for comparative purposes with those at the B3LYP and MP2/6-31++G** levels.

The interaction energies have been calculated as the difference of the total energy of the complex and the sum of the isolated monomers. They have been corrected of the inherent basis set superposition error (BSSE) using the Boys−Bernardi counterpoise technique.[16]

The interaction energies have been analyzed using the general molecular interaction potential with polarization (GMIPp)[17] at the RHF/6-31+G** level. This method allows for the characterization of the electrostatic, polarization, and van der Waals[18] contributions to the interaction energy.

The topological properties of the electron charge density have been studied using the atoms in molecules methodology[19] (AIM) with the AIMPAC program package.[20] The charge transfer of the complexes has been calculated by integrating the electron density of the anion within the complex.

A search in the Cambridge Structural Database (CSD)[21] has been carried out, exploring the presence of complexes between a perfluoroaromatic and anions. All of the structures that include any of the perfluoroaromatic molecules studied here have been retrieved and analyzed.

Results and Discussion

MEP maps have been used for long time as a tool to identify both nucleophilic and electrophilic regions in a molecule. The nucleophilic positions are associated to minima of the MEP.[22] On the other hand, the electrophilic areas can only be analyzed outside the molecular surface. In the case of the C_6F_6 molecule, the MEP map clearly shows positive regions above and below the aromatic ring. A similar picture is obtained for the isolated perfluoroaromatic systems considered here (Figure 2). On the basis of these maps, it is expected that electron-rich groups, as anions, should tend to interact with the electronically poor aromatic π-cloud where the positive region of the MEP is located.

Hexaflorobenzene:Anion Complexes. The corrected interaction energies of the complexes between C_6F_6 and a number of anions are reported in Table 1. In all cases, a C_{6v} symmetry has been assumed (except for the C_6F_6:CH_3^- complex where it is reduced to C_{3v}). In two cases (CN^- and CON^-), in which the two molecular ends can interact with the π-cloud of C_6F_6, both dispositions have been considered. All of the cases correspond to minimum structures, except for the C_6F_6:F^- complex that shows two degenerate imaginary frequencies (i40). The minimum structure corresponds to the nucleophilic attack of the fluoride anion on one of the carbon atoms. A similar result was previously reported on the basis of HF/3-21G calculations and pulsed electron-beam mass spectrometry.[23]

A subset of these complexes has been calculated at the MP2/6-311++G** level, providing results almost identical to those obtained at the MP2/6-31++G** level. In contrast, the B3LYP/6-31++G** calculations led to longer interaction distances than did the MP2 ones (average 0.15 Å) and, consequently, smaller interaction energies (average 2.15 kcal mol^{-1}). However, because the errors are almost systematic, B3LYP calculations can be used to obtain a qualitative description of the interaction, and thus it can be utilized for those systems in which the MP2 level is not feasible.

The calculated interaction energy values range between −18.7 and −11.4 kcal mol^{-1}, which is comparable to the interaction energy of some benzene:cation complexes (for example, the interaction energy of the benzene:K^+ complex is −18.3 kcal mol^{-1}).[24]

The interaction distance varies from 2.55 Å for the C_6F_6:F^- complex to 3.23 Å in the C_6F_6:Br^- complex. The calculated interaction distances of the C_6F_6:X^-, when X = F, H, and NC, are between 0.3 and 0.1 Å shorter than those calculated at the MP2 level on the corresponding neutral systems previously reported (FH, HLi, NCH).[2]

The effects of the complexation on the C_6F_6 molecule are a small shortening of the C−C bonds (0.004 Å) and a lengthening of the C−F bonds (0.006 Å). At the same time, the fluorine atoms move slightly toward the approaching anions, and thus the plane formed by the carbon atoms is about 0.02 Å further away from the anion than that formed by the fluorine atoms. The hexafluoro-benzene molecule adopts a "cup" conformation toward the anion; a similar effect is not observed for the benzene-cation complexes because the carbon−hydrogen bond distances are too short.

The AIM analysis of these complexes (Table 2) indicates the formation of six degenerate bond critical points (bcp) between the anions and each of the carbon atoms of the C_6F_6 molecule in a similar way to what was observed for the C_6F_6:XY neutral complexes[2] and the C_6H_6:Na^+ complex.[25] In addition, six ring critical points (rcp) and a cage critical point (ccp) are generated. It is worth mentioning that the values of electron density of the new bcp and its corresponding rcp are almost the same (the differences are less than 1×10^{-4} au). The positive and small value of the Laplacian of the bcp's indicates the closed shell nature of the interaction similar to those found in hydrogen bonds and ionic interactions.

Perfluoropyridine:Anion Complexes. The interaction energies obtained for the three C_5F_5N:X^- complexes studied range from −13.2 to −14.1 kcal mol^{-1} (Table 3). In all of the cases, they are slightly stronger than the corresponding C_6F_6:X^- anion complexes by 1 kcal mol^{-1}. It is well known in heterocyclic chemistry that pyridines are π-electron-deficient aromatic compounds that can be assimilated to nitrobenzene.[26,27] There-

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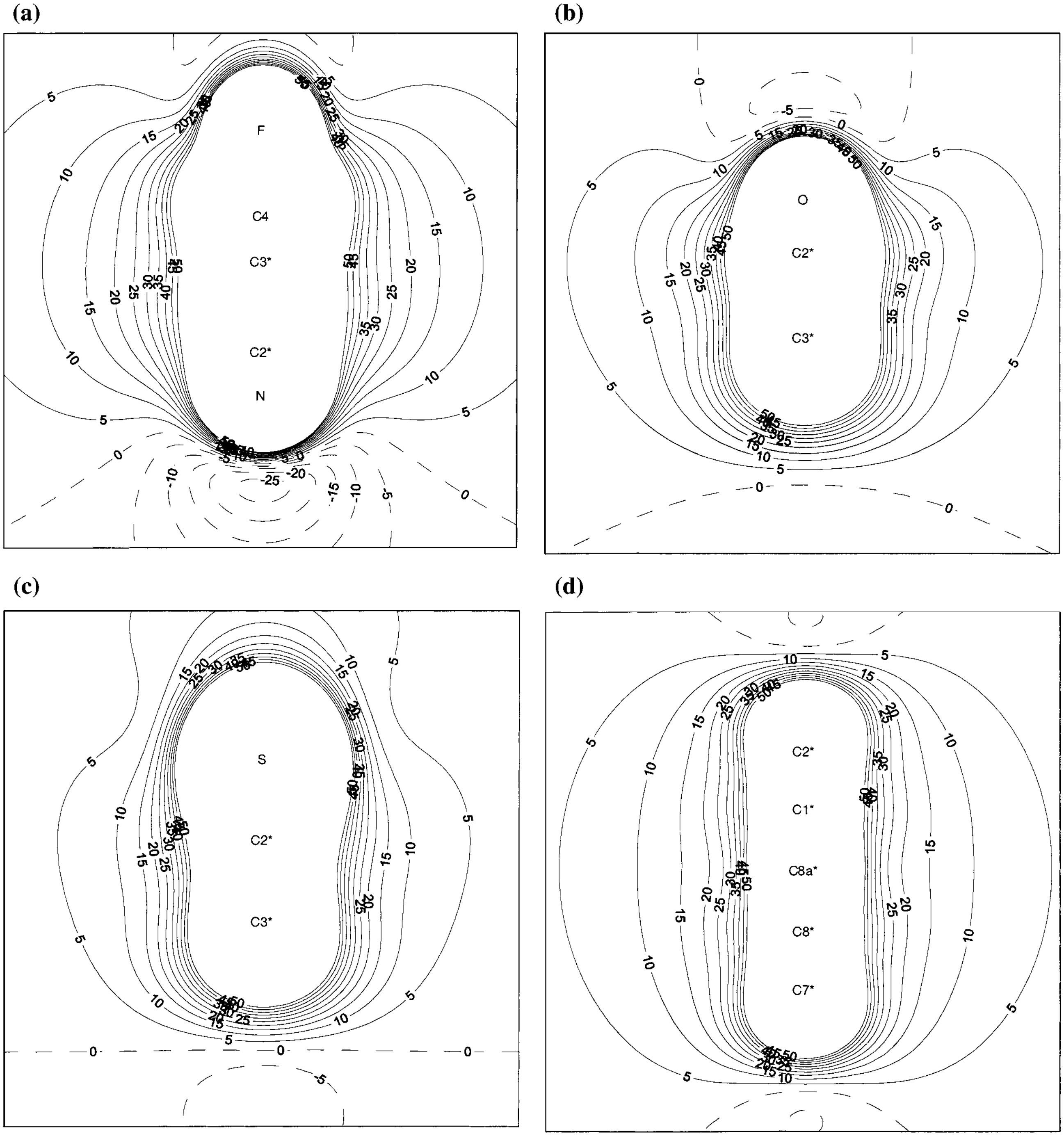

Figure 2. MEP maps (kcal/mol) of (a) C_5F_5N, (b) C_4F_4O, (c) C_4F_4S, (d) $C_{10}F_8$ in the perpendicular plane to the aromatic rings. The stars indicate that the position of the atom is projected to the plane studied. For the MEP map of C_6F_6, see ref 2.

fore, in perfluoropyridine, the positive region of the MEP should be reinforced as compared to that of hexafluoro-benzene.

The location of the anions in the complexes is closer to the C(4) than to the N(1) to avoid the negative MEP generated by the nitrogen atom. Regarding the distances to the molecular plane, they range between 2.0 and 2.2 Å, being slightly shorter (approximately 0.05 Å) than those in the corresponding C_6F_6: X^- complexes (Table 3).

The AIM analysis of the structures shows only one bcp between the anion and the C(4) of the pyridine ring (Table 4). The electron density and Laplacian values are slightly larger than those of the C_6F_6:X^-. These results are in agreement with recent theoretical and experimental reports that have shown a relationship between the electron density and the interaction distance.[28]

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Table 1. Corrected Interaction Energies (kcal/mol) and C_6F_6 Centroid−Anion Distances (*···X) (Å), Calculated at the B3LYP/6-31++G** and MP2/6-31++G** Levels (Results Calculated at the MP2/6-311++G** Level Are in Parentheses)

	B3LYP/6-31++G**		MP2/6-31++G** (MP2/6-311++G**)	
system	$E_{\mathrm{I+BSSE}}$	*···X	$E_{\mathrm{I+BSSE}}$	*···X
C_6F_6:Cl^-	−10.97	3.31	−12.76	3.159
			(−12.19)	(3.106)
C_6F_6:Br^-	−9.42	3.37	−12.19	3.230
C_6F_6:CN^- [a]	−10.36	3.15	−12.80	2.991
			(−12.52)	(2.954)
C_6F_6:NC^- [a]	−10.85	2.96	−13.14	2.801
C_6F_6:CCH^- [a]	−12.23	3.11	−15.07	2.935
C_6F_6:ONC^- [a]	−9.42	2.80	−11.42	2.654
C_6F_6:CNO^- [a]	−9.61	3.12	−12.43	2.941
C_6F_6:F^-	−17.44	2.65	−18.63	2.554
			(−17.31)	(2.559)
C_6F_6:H^-	−14.82	2.81	−14.22	2.709
			(−13.98)	(2.663)
C_6F_6:CH_3^-	−16.12	3.36	−14.55	3.125

[a] The first atom after the C_6F_6 is the one pointing toward this molecule.

Table 2. Electron Densities and Their Laplacian for the Electron Density Critical Points Found in the Complexes (au) Calculated at the MP2/6-31++G** Level

	bond cp		ring cp	cage cp
C6F6:X	ρ	$\nabla^2\rho$	ρ	ρ
C_6F_6:Cl^-	0.0080	0.0238	0.0080	0.0061
C_6F_6:Br^-	0.0087	0.0240	0.0086	0.0065
C_6F_6:CN^-	0.0087	0.0249	0.0087	0.0066
C_6F_6:NC^-	0.0097	0.0313	0.0097	0.0072
C_6F_6:CCH^-	0.0098	0.0277	0.0098	0.0073
C_6F_6:ONC^-	0.0097	0.0358	0.0096	0.0067
C_6F_6:CNO^-	0.0090	0.0268	0.0089	0.0067
C_6F_6:F^-	0.0118	0.0470	0.0117	0.0082
C_6F_6:H^-	0.0080	0.0170	0.0080	0.0064
C_6F_6:CH_3^-	0.0088	0.0192	0.0087	0.0066

Table 3. Corrected Interaction Energies (kcal/mol) and Interaction Distances (Å) of the Pentafluoropyridine Complexes at the MP2/6-31++G** Computational Level (Results in Italics Correspond to the B3LYP/6-31++G** Calculations)

system	$E_{\mathrm{I+BSSE}}$	X···N(1)	X···C(4)	X···plane
C_5F_5N:Cl^-	−14.08	3.660	3.198	3.092
	−12.69	4.220	3.064	3.075
C_5F_5N:Br^-	−13.23	3.814	3.292	3.182
	−10.12	4.435	3.006	2.999
C_5F_5N:CN^-	−13.90	3.344	3.184	2.937
	−11.24	3.601	3.273	3.119

Table 4. Electron Density Properties of the bcp Formed between the Interacting Anion and the C(4) Atom in the C_5F_5N:X^- Complexes Calculated at the MP2/6-31++G** Level

system	ρ	$\nabla^2\rho$
C_5F_5N:Cl^-	0.0115	0.0361
C_5F_5N:Br^-	0.0118	0.0351
C_5F_5N:CN^-	0.0102	0.0308

Perfluorofuran and Perfluorothiophene Complexes with Anions. The complexes of tetrafluorofuran and tetrafluorothiophene with the anions here studied show interaction energies smaller than those of the corresponding C_6F_6 complexes. The approximate average differences are 4.7 and 3.4 kcal mol^{-1}, respectively (Table 5).

In the case of the tetrafluorofuran complexes, the anions are located closer to the oxygen than to any other atom in the ring.

Table 5. Corrected Interaction Energies (kcal/mol) and Interaction Distances (Å) of the Tetrafluorothiophene and Tetrafluorofuran Complexes at the MP2/6-31++G** Computational Level (Results in Italics Correspond to the B3LYP/6-31++G** Calculations)

	$E_{\mathrm{I+BSSE}}$	X···O/S(1)	X···C(2)	X···C(3)	X···plane
C_4F_4O:Cl^-	−9.04	3.235	3.276	3.440	3.106
	−7.87	3.401	3.445	3.599	3.283
C_4F_4O:Br^-	−8.57	3.322	3.359	3.533	3.198
	−6.52	3.413	3.479	3.687	3.321
C_4F_4O:CN^-	−9.82	3.239	3.459	3.849	3.225
	−7.69	3.193	3.261	3.462	3.089
C_4F_4S:Cl^-	−8.06	3.537	3.487	3.492	3.252
	−6.57	3.782	3.689	3.646	3.455
C_4F_4S:Br^-	−7.68	3.692	3.564	3.483	3.311
	−5.17	4.106	3.779	3.462	3.389
C_4F_4S:CN^-	−8.12	3.425	3.270	3.317	3.058
	−5.96	3.770	3.531	3.322	3.211

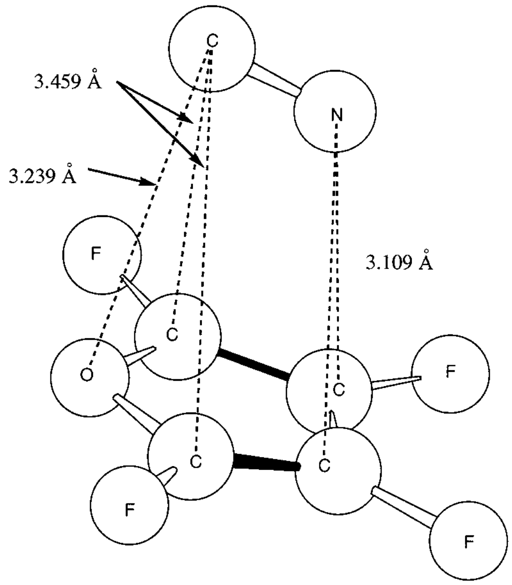

Figure 3. Optimized structure of the C_4F_4O:CN^- complex at the MP2/6-31++G** level.

In contrast, in the tetrafluorothiophene complexes, they are closer to the carbon atoms than to the sulfur one, probably because of the larger size of the sulfur atom. A special case is the C_4F_4O:CN^-, where the CN anion is almost parallel to the molecular ring (Figure 3), interacting the carbon atom with the oxygen and the nitrogen end with the C(3) and C(4) atoms. The distance of the anions to the molecular plane is slightly shorter for the tetrafluorofuran complexes than for the corresponding C_6F_6:X^- cases and slightly longer than for the tetrafluorothiophene cases (Table 6).

The electron density of the C_4F_4O:Cl^- and C_4F_4O:Br^- complexes shows bcp's between the anions and the O(1), C(2), and C(5) (Table 7). In addition, three rcp's and one ccp are obtained. The C_4F_4O:CN^- complex shows a bcp between the O(1) and the carbon atom of CN, and two more bcp's between the N atom of CN and C(3) and C(4). In the case of the C_4F_4S complexes, a bcp between the anion and S(1) is found in all the cases. In addition, in the Cl^- complex, as well as in the CN complex, bcp's are found with C(2) and C(5). In contrast, the Br^- complex shows two bcp's with C(3) and C(4).

Perfluoronaphthalene Complexes with Anions. The interaction energy of these complexes is the largest of all those

Table 6. Electron Densities and Their Laplacian for the Electron Density Bond Critical Points Found in the C_4F_4O:X and C_4F_4S:X Complexes (au) Calculated at the MP2/6-31++G** Level

	X···O(1)/S(1)		X···C(2/3)	
system	ρ	$\nabla^2\rho$	ρ	$\nabla^2\rho$
$C_4F_4O:Cl^-$	0.0096	0.0337	0.0098[a]	0.0314
$C_4F_4O:Br^-$	0.0100	0.0324	0.0104[a]	0.0299
$C_4F_4O:CN^-$	0.0077	0.0262	0.0098[b]	0.0304
$C_4F_4S:Cl^-$	0.0087	0.0267	0.0077[a]	0.0227
$C_4F_4S:Br^-$	0.0082	0.0233	0.0090[b]	0.0250
$C_4F_4S:CN^-$	0.0088	0.0261	0.0085[b]	0.0241

[a] The data correspond to the X···C(2) bond. [b] The data correspond to the X···C(3) bond.

Table 7. Corrected Interaction Energies (kcal/mol) and Interaction Distances (Å) of the Octafluoronaphthalene Complexes at the MP2/6-31++G** Computational Level (Results in Italics Correspond to the B3LYP/6-31++G** Calculations)

	B3LYP/6-31++G**		MP2/6-31++G**	
system	E_{I+BSSE}	*···X[a]	E_{I+BSSE}	*···X[a]
$C_{10}F_8:Cl^-$	−14.25	3.226	−17.31	3.056
$C_{10}F_8:Br^-$	−12.25	3.256	−16.70	3.147
$C_{10}F_8:CN^-$	−12.55	3.159	−16.51	2.988

[a] "*" represents the centroid of the C(4a)−C(8a) bond.

Table 8. Electron Density Properties of the bcp Formed between the Interacting Anion and the C(4a) and C(8a) Atoms in the $C_{10}F_8:X^-$ Complexes Calculated at the MP2/6-31++G** Level

	bond cp		ring cp	
system	ρ	$\nabla^2\rho$	ρ	$\nabla^2\rho$
$C_{10}F_8:Cl^-$	0.0131	0.0428	0.0131	−0.0073
$C_{10}F_8:Br^-$	0.0134	0.0403	0.0134	−0.0101
$C_{10}F_8:CN^-$	0.0125	0.0346		

Table 9. Electrostatic, Polarization, and van der Waals Contributions (kcal/mol) to the Interaction Energy Calculated Using the GMIPp Method (Corresponding Values of the Geometry Relaxation (kcal/mol) and Eletron Transfer (e) Not Included in the GMIPp Model Are also Reported)

system	electrostatic (MEP)	polarization	VdW	geometry relaxation	electron transfer
$C_6F_6:Cl^-$	−11.8	−6.6	5.2	0.17	0.053
$C_4F_4O:Cl^-$	−8.6	−5.8	7.4	0.31	0.062
$C_4F_4S:Cl^-$	−6.1	−6.3	5.1	0.19	0.051
$C_5F_5N:Cl^-$	−13.9	−7.0	8.0	0.23	0.062
$C_{10}F_8:Cl^-$	−14.3	−9.8	9.4	0.34	0.071

studied in the present work, approximately −4.5 kcal/mol more than the corresponding $C_6F_6:X^-$ energies (Table 8). The anions are located over the C(4a)−C(8a) bond, giving the whole complex a C_{2v} symmetry. In the optimized structure, the naphthalene system became bent toward the anion with an angle between the two aromatic rings of 2.4, 4.5, and 5.2° for the complexes with Cl^-, Br^-, and CN^-, respectively. Thus, in this case, instead of the "cup" of C_6F_6, $C_{10}F_8$ adopts a "book" conformation pointing toward the anion.

The AIM analyses of these systems show the generation of two bcp's between the anions and the C(4a) and C(8a) atoms and the corresponding rcp (Table 9) for the $C_{10}F_8:Cl^-$ and $C_{10}F_8:Br^-$ complexes. In contrast, the electron density map of the $C_{10}F_8:CN^-$ complex corresponds to a conflict catastrophic configuration where a small perturbation modifies the topological description of the electron density, similar to those found for HBs with π-systems.[29]

All of the Complexes. To compare the properties obtained for the perfluoroaromatic molecules, the distance and energy of the complexes with Cl, Br, and CN anions have been averaged (distances in Å and interaction energies E_{I+BSSE} in kcal mol^{-1} from Tables 1, 3, and 5): C_5F_5N (3.070, 13.74), C_6F_6 (3.127, 12.58), C_4F_4O (3.176, 9.14), and C_4F_5S (3.214, 7.95). These properties are linearly related ($r^2 = 0.95$): the shorter the distance, the stronger the interaction. The octafluoronaphthalene has not been considered because in their complexes the anions interact with one bond, while, in the rest of the cases, the interaction is with the aromatic ring.

It is tempting to see if one of these properties, for instance, E_{I+BSSE}, is related to some aromaticity criteria. These indexes are known only for the parent compounds (H instead of F), like ISE (isodesmic stabilization energy),[26] HHSE (hyperhomodesmotic stabilization energy),[27] Chesnut and Davis's DB(n) (the energy of the homomolecular differential bond separation energy involving a system with n double bonds), and H(n) (the homomolecular homodesmotic reaction),[27,30] as well as some magnetic properties such as Schleyer's NICS.[31−33]

All of the energy values for the four parent compounds are related ($r > 0.94$), and most of them correspond to the aromaticity order pyridine ≥ benzene ≫ furan ≥ thiophene (there are some inversions between pyridine and benzene and between furan and thiophene), which is similar to the order of average E_{I+BSSE} values: $13.74 > 12.58 > 9.14 > 7.95$. For instance, $E_{I+BSSE} = (3.0 \pm 0.9) + (0.16 \pm 0.2)$ ISE, $n = 4$, $r^2 = 0.977$.

The NICS criteria (in ppm, the more negative the more aromatic) correspond to a very different picture of aromaticity, at least for the compounds in question: thiophene (−13.80)[33] > furan (−12.31)[33] > benzene (−9.70).[31] We have recalculated these values (pyridine was missing) at the B3LYP/6-31++G** level and found thiophene (−13.09) > furan (−12.06) > benzene > (−8.21) > pyridine (−6.91). With these values, the following equation is found: $E_{I+BSSE} = (20.1 \pm 0.3) + (0.92 \pm 0.02)$ NICS, $n = 4$, $r^2 = 0.999$.

To analyze the contribution of the electrostatic and polarization terms, the GMIPp partition has been calculated for all of the complexes with chlorine (Table 9). The results indicate that the polarization energy is between 50 and 100% of the electrostatic energy. Other interaction terms not accounted for by the GMIPp method, such as the geometry relaxation or the charge transfer, show small energetic values. In fact, the sum of the three terms calculated with the GMIPp method provides an energetic value very close to the corrected interaction energy obtained at the MP2 level. In general, the results shown here are analogous to those found for the cation−π interactions.[17]

The calculated electron density properties for all of the complexes here with Br^-, Cl^-, and CN^- at both the MP2/6-31++G** and the B3LYP/6-31++G** level have been found to show exponential relationships between the electron density and its Laplacian at the bond critical point versus the distance of the interacting atoms.[28] The correlation coefficient of these relationships ranges between 0.90 and 0.98.

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A search of the polyfluoro compounds studied in the present article in the CSD has provided 22 crystal structures with C_6F_6, two with C_5F_5N and two with $C_{10}F_8$. Several of the structures including C_6F_6 show interactions between the π-cloud with neutral electron-rich groups (JOCRIC, JOCRIC01). In those with C_5F_5N, the nitrogen atom is complexed to metals. Using other experimental techniques, such as pulsed electron-beam mass spectrometry, it was proposed the presence of complexes between C_6F_6 and Cl^-, Br^-, and I^-, such as those studied here.[34]

Conclusions

The present study has explored the structure and electronic properties of the complexes formed by several perfluoroaromatic compounds with a number of anions. Ab initio MP2 and B3LYP methods have been used. While the results obtained at the MP2/6-31++G** level are almost identical to those from MP2/6-311++G**, the B3LYP/6-31++G** level provides longer interaction distances and smaller interaction energies which indicate that this last method can only be used to obtain a qualitative description of these interactions.

In all of the cases, minimum complexes have been found between the anions and the π-cloud of the perfluoroaromatic derivatives. The formation of these complexes has been rationalized on the basis of the MEP maps of the isolated perfluoroaromatic compounds that show positive regions above the molecular plane susceptible to an interaction with negatively charged molecules.

The interaction energies obtained range between -19 and -8 kcal mol^{-1}, and the distance between the anions and the molecular plane of the aromatic derivatives ranges from 2.5 to 3.3 Å depending on the size of the approaching atom. The AIM analysis has allowed us to characterize the new bcp generated in the complexes.

Relationships have been found between a criteria of aromaticity of the perfluoroaromatic compounds and their relative interaction energy with anions.

Acknowledgment. The present article is dedicated to the memory of our friend and colleague Prof. Manfred Stud. We are most grateful to Dr. F. J. Luque (Barcelona, Spain) for stimulating comments and providing a copy of the MOPETE program. The authors thank the Ministerio de Ciencia y Tecnología (Project No. BQU-2000-0906) for financial support.

Supporting Information Available: Tables with absolute energies and Cartesian coordinates of the calculated geometry of all of the monomers and complexes at the MP2/6-31++G** computational level (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA025693T

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