Anion–π Interactions: Do They Exist?**

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Noncovalent interactions play a fundamental role in many areas of modern chemistry. In particular the interations of cations and π-electrons—cation–π interactions—are strong noncovalent binding forces of great importance in many systems.[1,2] Crystallographic studies provide much of the information on cation–π interactions and other nonbonding interactions that have attracted considerable attention in the last years such as anti-hydrogen bonds,[3] dihydrogen bonds,[4] and other unconventional hydrogen bonds.[5] These interactions have also been studied extensively by means of computational methods. Noncovalent interactions are usually characterized by Bader's theory of "atoms in molecules" (AIM),[6] which has been used successfully to understand conventional[7] and unconventional[8] hydrogen bonds and cation–π interactions.[9]

The cation–π interaction is in general dominated by electrostatic and cation-induced polarization.[10] The nature of the electrostatic component has been rationalized, emphasizing the function of the permanent quadrupole moment of benzene (see Figure 1).[11] The favorable interactions in the benzene–hexafluorobenzene complex have been studied, including the face-to-face stacking in its crystal structure.[12] A detailed analysis carried out by Williams stresses the important role of the large, permanent quadrupoles of the two molecules, which are similar in magnitude but of opposite sign.[13] The importance of the quadrupole moment for understanding intermolecular interactions of aromatic systems has been rationalized.[14]

Theoretical studies of the possible interaction of the π-electron cloud of C_6F_6 with several small electron donor molecules have been published previously.[15–17] In this communication we report a preliminary study of the interactions between anions and hexafluorobenzene. In these complexes the anion is positioned over the benzene ring along the C_6 axis. This study combines crystallographic and computational evidence to demonstrate that anion–π interactions exist and that they are energetically favorable. To the best of our knowledge this is the first study in which the term "anion–π interaction" is used to describe the interaction between the permanent quadrupole of C_6F_6 and anions.[18]

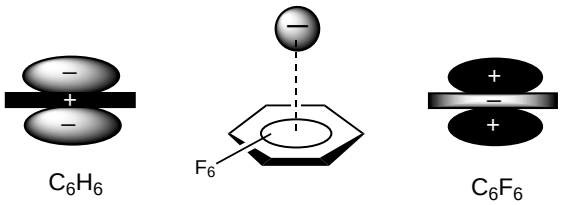

Figure 1. Representations of the quadrupole moments of benzene (left) and hexafluorobenzene (right) and the anion–π interaction (middle).

Initially the geometries of all the complexes included in this study were fully optimized at the Hartree–Fock (HF) level by using the 6-31++G** basis set.[19] The binding energies were calculated with and without correction for the basis set superposition error (BSSE) by using the Boys–Bernardi counterpoise technique[20] and zero-point energy (ZPE) corrections. Frequency calculations at the same level confirmed that the structures are at their energy minima. Furthermore, in all cases we extended our calculations to the MP2/6-31++G** level, assuming C_{6v} symmetry for complexes **1**–**5** and C_{3v} symmetry for complexes **6** and **7**. Unfortunately, the frequency calculations give either one or more imaginary frequencies for all complexes. To solve this

Table 1. Interaction energies with (E_{BSSE}, $E_{BSSE+ZPE}$ [kcal mol^{-1}]) and without (E [kcal mol^{-1}]) the basis set superposition error (BSSE) and zero-point energy correction (ZPE) and equilibrium distances (R_e [Å]) at HF/6-31++G** and MP2/6-31++G** (italics) levels of theory, and selected electron density topological properties for the complexes of hexafluorobenzene with anions.

Complex	E	E_{BSSE}	$E_{BSSE+ZPE}$	R_e	CP[a]	n	$10^2\rho$	$10^2\nabla^2\rho$
$C_6F_6\cdots H^-$	−11.2	−11.1	−10.2	3.034	(3, −1)	6	0.578	1.135
1	*−17.5*	*−14.3*	*−13.4*	*2.706*	(3, +1)	6	0.576	1.139
					(3, +3)	1	0.426	1.611
$C_6F_6\cdots F^-$	−18.8	−18.1	−17.8	2.669	(3, −1)	6	1.001	4.200
2					(3, +1)	6	0.996	4.226
					(3, +3)	1	0.702	4.106
$C_6F_6\cdots Cl^-$	−11.0	−10.8	−10.6	3.404	(3, −1)	6	0.572	1.637
3	*−18.0*	*−13.2*	*−12.9*	*3.155*	(3, +1)	6	0.571	1.637
					(3, +3)	1	0.450	1.820
$C_6F_6\cdots Br^-$	−13.2	−9.3	−9.5	3.479	(3, −1)	6	0.618	1.612
4	*−20.7*	*−12.4*	*−11.9*	*3.214*	(3, +1)	6	0.616	1.613
					(3, +3)	1	0.480	1.887
$C_6F_6\cdots CN^-$	−11.9	−11.3	−10.9	3.020	(3, −1)	6	0.701	2.276
5					(3, +1)	6	0.700	2.290
					(3, +3)	1	0.534	2.543
$C_6F_6\cdots NO_3^-$	−9.7	−8.4	−8.2	3.325	(3, −1)	3	0.535	1.089
6	*−18.7*	*−12.4*	–[b]	*2.922*	(3, +1)	3	0.324	1.477
					(3, +3)	1	0.234	1.308
$C_6F_6\cdots CO_3^{2-}$	−28.4	−26.9	−26.6	3.011	(3, −1)	3	1.043	3.385
7					(3, +1)	3	0.598	2.588
					(3, +3)	1	0.401	2.147

[a] The electron density (ρ) and its Laplacian ($\nabla^2\rho$) in atomic units at the critical points (CP) originating upon complexation are given, as well as the total number (n) of each CP in the complex. [b] Unfortunately, the frequency calculation of complex **6** was impossible to carry out since the program stops with an error message.

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issue, we carried out the geometry optimizations without imposing any symmetry constraints. As a result, complexes **1**, **3**, **4**, and **6** have been successfully optimized and the minimum-energy nature of the structures has been confirmed, except for complex **6** (see footnote of Table 1). For the other complexes—**2**, **5**, and **7**—the minimum-energy structures correspond to the nucleophilic attack of the anion at one of the carbon atoms. Topological analysis of the charge density $\rho(r)$ distribution and properties of critical points (CP) were determined by using the AIM method, which provides an unambiguous definition of chemical bonding,[21] by means of the program AIMPAC[22] using the HF/6-31++G** wavefunction.

Table 1 reports the energies and equilibrium distances calculated at both HF and MP2 levels of theory corresponding to the interaction of hexafluorobenzene with a series of anions. In general, the MP2-computed binding energies are more negative than the HF ones and the equilibrium distances are shorter. For complexes **1**–**5** exploration of the CPs revealed the presence of six $(3,-1)$ and six $(3,+1)$ CPs symmetrically distributed. The bond CPs connect the anion with the carbon atoms, and the ring CPs connect the anion with the middle of the C–C bond (see Figure 2). The Laplacian of the $(3,-1)$ CPs is positive which indicates a depletion of the electron density, as is common in closed-shell interactions.[6] Finally, the interaction is further described by the presence of a cage CP located over the hexafluorobenzene molecule along the C_6 axis, connecting the anion with the center of the ring. Quantitative values for $\rho(r)$ and $\nabla^2\rho(r)$ at the CPs give hints on the character and strength of the interaction. The values obtained for complexes **1**–**7** (see Table 1) are similar to those found for cation–π interactions.[9] The pattern of CPs that appears upon complexation is altered in the complexes **6** and **7** (NO_3^- and CO_3^{2-}). Only three bond and three ring CPs are found as a result of the geometry of the optimized complexes, in which the anion is placed parallel over the ring and the nitrogen (or carbon) atom is located along the C_6 axis (see Figure 2). In these complexes the interaction can be also viewed as a face-to-face parallel stacking interaction in which one component is electron deficient and the other is electron rich.

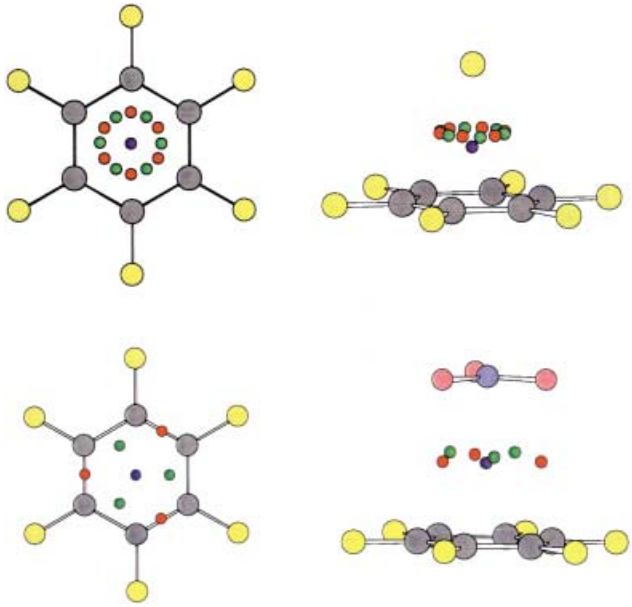

Figure 2. Representations of the location of the $(3,-1)$ CPs (red circles), the $(3,+1)$ CPs (green circles), and the $(3,+3)$ CP (blue circle) originating from the interaction of hexafluorobenzene with fluoride (top) and nitrate (bottom) ions. On the left-hand side the complexes are viewed perpendicular to the benzene ring; for clarity, the anions have been omitted in these representations. On the right-hand side the complexes are viewed side-on.

It is quite clear that without the results of crystallographic experiments molecular modeling would be a highly speculative activity at best. Crystal structures are so rich in information and often reveal effects that had not been noticed by the original authors. The Cambridge Structural Database (CSD) appeared to us to be a convenient and reliable storehouse for geometrical information. The utility of small-

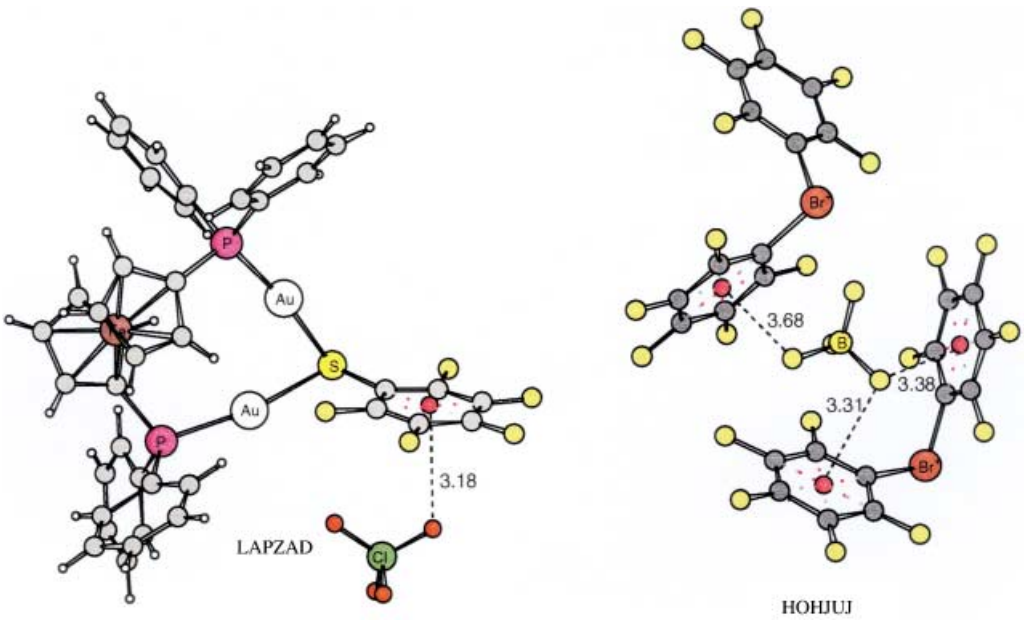

Figure 3. X-ray crystal structures of $[(Ph_2PC_5H_4)_2FeAu_2SC_6F_5][ClO_4]$ (LAPZAD)[31] and $[(C_6F_5)_2Br][BF_4]$ (HOHJUJ); distances in Å.

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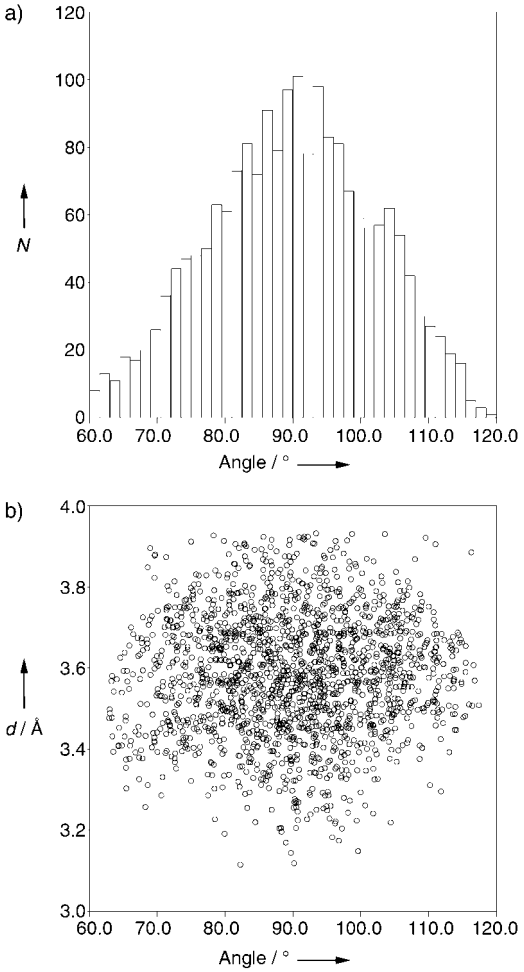

Figure 4. Plots obtained directly from analysis of the CSD database for structures in which noncovalent interactions are present between an electronegative atom (X) such as F, Cl, Br, O, S, and N and a perfluorobenzene fragment. a) Histogram showing the number of structures *N* obtained at an angle defined by the electronegative atom X, the ring centroid, and one carbon atom of the ring. b) Scatterplot for the structures in which the same angle and the average of all six X–C_{ring} distances are plotted. Both plots were obtained directly from the CSD database software.

molecule crystallography and the CSD in analyzing geometrical parameters and nonbonding interactions has been clearly established.[23] In exploring the CSD we found 1944 fragments in which noncovalent π interactions are present between lone-pair electrons of electronegative atoms such as F, Cl, Br, O, S, and N and perfluorobenzene derivatives. Twenty-seven of those were π interactions between anions and pentafluorobenzene derivatives.[24] In Figure 3 we show two selected examples and the CSD reference codes of crystal structures in which the anion–π interaction is evident. It is remarkable that the HOHJUJ[25] structure in which the tetrafluoroborate anion is surrounded by three pentafluorophenyl moieties and two fluorine atoms of the anion clearly interact with the π-electron cloud of the aromatic rings. In order to validate the crystallographic study, we provide in Figure 4 an angle histogram and an angle–distance scatterplot, in which the angle used for the histogram and the scatterplot is defined by the interacting atom (X), the ring centroid, and one carbon atom of the ring, and the distance used for the scatterplot is the average of all six X–C_{ring} distances. The major number of hits in the search corresponds to angles close to 90° (see histogram) and the concentration of data are at angles close to perpendicular to the aromatic ring and interaction distances closer than the van der Waals contact (see scatterplot).

To analyze the physical nature of the anion–π interaction and determine whether polarization is important, we computed its contribution to the total interaction energy with the recently developed Molecular Interaction Potential with polarization (MIPp),[26] which is a powerful tool for predicting the binding properties of aromatic compounds.[10,27] MIPp is an improved generalization of the molecular electrostatic potential (MEP), in which three terms contribute to the interaction energy: 1) an electrostatic term identical to the MEP,[28] 2) a classical dispersion–repulsion term, and 3) a polarization term derived from perturbational theory.[29] Therefore, it provides a natural partitioning of the interaction energy into intuitive components.

Calculation[30] of the MIPp of hexafluorobenzene interacting with F^- (see Table 2) was performed with the HF/6-311 + G** geometries and wavefunctions. In the calculations the F^- ion was considered as a classical nonpolarizable particle. We explored the electrostatic (E_e), polarization (E_p), van der Waals (E_{vw}), and total (E_t) interacting energies when a fluoride ion approaches an hexafluorobenzene molecule perpendicular to the center of the aromatic ring. The results in Table 2 point out the importance of the polarization component, which is similar to the electrostatic one in the 2.0–3.0 Å range.

Table 2. Contributions to the total interaction energy [kcal mol^{-1}] calculated with MIPp for hexafluorobenzene interacting with F^- at several distances [Å] from the center of the ring.

Distance	E_e	E_p	E_{vw}	E_t
1.5	−36.59	−43.84	1047.82	967.38
2.0	−22.44	−24.89	119.05	71.72
2.5	−16.39	−13.93	13.44	−16.89
3.0	−12.66	−7.96	−0.50	−20.12
3.5	−9.90	−4.74	−0.83	−15.48

In summary, the results derived from crystallographic structures and theoretical calculations reported in this study reveal the existence of anion–π interactions. This new nonbonding interaction has been studied by using a topological analysis of the electron density and MIPp calculations. The interaction of anions with other benzene derivatives with positive quadrupole moments such as 1,3,5-trinitrobenzene is under study.

Note added in proof: Since submission of this manuscript, a publication has appeared that includes relevant work. It describes the interaction of π-electron deficient 1,3,5-triazine ring and several anions by ab initio calulations at the MP2 level of theory.[32] We are grateful to the editor for bringing this to our attention.

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A Springlike 3D-Coordination Network That Shrinks or Swells in a Crystal-to-Crystal Manner upon Guest Removal or Readsorption**

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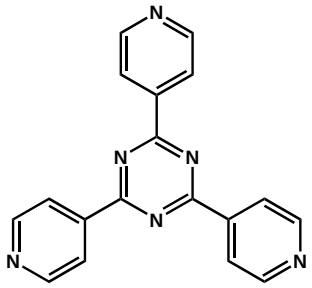
The recent upsurge in the crystal engineering of coordination nets is caused by their several useful functional properties such as porosity, use in separation and catalysis, and magnetism.[1] Particularly, some metal–organic 3D networks were shown to be porous: the networks and their crystalline nature are intact after the guest removal and the emptied network had the ability to reabsorb and desorb guest molecules.[2] Here we show another class of compounds in which a 3D network contracts after guest removal and expands after a guest is readsorbed; this class of molecules can also exchange guest molecules without affecting the 3D network or its crystalline nature. Linear and rigid bifunctional ligands (1D) such as 4,4′-bipyridine form several networks with various properties.[3] However, its 3D analogue, 2,4,6-tris(4-pyridyl)triazine (TPT, **1**), has not been explored to that extent.[4] In solution chemistry we have already shown that panel-like ligands such as **1** self-assemble into 3D polyhedra upon reaction with



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