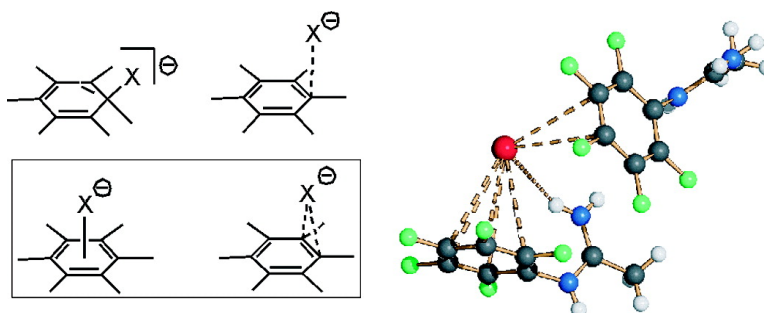


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Structural Versatility of Anion– π Interactions in Halide Salts with Pentafluorophenyl Substituted Cations

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Supramolecular chemistry relies on noncovalent interactions which can be of different natures.¹ Only recently it was commonly accepted that anion– π interactions are attractive noncovalent interactions if electron-deficient aromatics are present.² However, the systematic study of purely organic “receptors” without coordination of a metal ion to the aromatic unit is rare.^{3,4}

As pointed out by Hay et al., there are several possible modes of interaction between an anion and a π -system. In **A** (Chart 1) covalent binding occurs between the anion X^- and the aromatic unit. This represents the Meisenheimer intermediate of the S_NAr reaction. In **B** anion-donor– π -acceptor interactions occur between X^- and only one position of the aromatic ring, while **C** represents an “ η^6 ” anion– π complex with the anion located above the center of the π -system.⁵

For systematic investigations we attached a cationic moiety (ammonium, iminium, amidinium) to a pentafluorophenyl ring and introduced a halide as a counteranion. Crystals of **1–3** were obtained by diffusion of HCl, HBr, or HI into an acetone or acetonitrile solution of pentafluoroaniline. Using acetonitrile as the solvent, two different kinds of crystals (small cubes **1a** and plates **3a**) were formed with HCl, while HBr yielded only the amidinium salt (**3b**). Acetone as solvent resulted in the iminium salts **2b** and **2c**.⁶

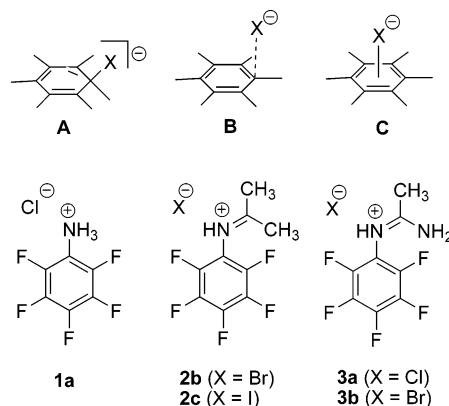
The main interactions between the anion and the cation in **1a** (Figure 1a) occur by hydrogen bonding. Cl^- is situated close to the C_6F_5 -ring leading to short C–Cl contacts of 3.41, 3.40, and 3.78 Å. However, for effective anion– π interactions too many H-bond competitors for the anion coordination are present at the aryl- NH_3^+ unit.

The salts **2b** and **2c** crystallize isostructurally (Figure 1b, only **2b** is shown). Due to the reduced number of hydrogen bond donors, anion– π interactions of type **B** take place with short Hal–C³ contacts of 3.44 (Br) and 3.61 Å (I). In addition, the anions are binding to the electrophilic C-atom of the iminium ions ($C^{imin}-Br = 3.65$ Å, $C^{imin}-I = 3.63$ Å).⁷

The most interesting interactions in this series are observed in the amidinium salts **3a** and **3b** (Figure 1c, only **3b** is shown). In both, the anion is surrounded by four neighboring cations: two bind by NH hydrogen bonds (not shown in Figure 1) and one binds by “ η^2 ”-type π -anion coordination (**3a**: C–Cl = 3.34, 3.41 Å; **3b**: C–Br = 3.66, 3.73 Å). The interaction with the fourth cation (Figure 1c) takes place by a NH-hydrogen bond which fixes the anion on top of the aromatic system close to its center ($C_{arom}-Hal = 3.52-3.98$ Å (**3a**) or 3.65–3.83 Å (**3b**), Table 1). Halogen–centroid distances are 3.50 Å (**3a**) or 3.48 Å (**3b**) with Hal–centroid–aromatic plane angles of 79.5° (**3a**) and 85.7° (**3b**), respectively.

Our results show that anion– π interaction can occur in the crystals of salts with pentafluorophenyl substituted cations. The

Chart 1. Interactions between Anions and Aromatic π -Systems (Top) and Salts Investigated in This Study (Bottom)



interactions become more prominent by reduction of hydrogen bonding to the anions. Mainly interactions of type **B** are observed. Only the fixation of the anion on top of the π -system of **3a/b** leads to the stabilization of an “ η^6 ” anion– π -complex like shown in **C**.

To provide more insight into the nature of the “ η^6 ” anion– π interactions quantum chemical calculations were performed for **3a/b**. All calculations have been carried out with the Turbomole program package^{8a} and include the Boys–Bernardi basis set superposition error correction. At the B3LYP/TZVP level of theory we have been able to obtain structures of the isolated neutral salts **3a/b** close to the X-ray structures. The anion–H distances are smaller due to the missing attraction to the other neighboring cations, and thus the anion is slightly displaced from a central position toward the N–H group. The $C_{arom}-Hal$ distances are 3.64–3.82 Å for **3a** and 3.67–3.92 Å for **3b** in excellent agreement with the X-ray data. Strong binding energies of 470 (**3a**) and 435 kJ/mol (**3b**) have been calculated at the MP2/TZVPP level with the B3LYP structures. The fraction of the binding energy due to the anion– π interaction has been estimated by replacing the cation with hexafluorobenzene such that the pentafluorophenyl system and the anion retain their positions. The binding energy at the MP2/TZVPP level is 56 kJ/mol for the chloride system and 52 kJ/mol for the bromide, indicating a strong anion– π interaction. These values agree well with interaction energies obtained for the optimized hexafluorobenzene-halide system by Alkorta et al.^{4a} Although the anion– π interaction is small compared to the hydrogen bond-like interaction H–Hal, it is sufficiently strong to determine the structure if, as sterically possible in **3a/b**, the two interactions favorably add.

Inspired by those results we prepared compound **4**, in which no strongly acidic protons are present, and determined its X-ray structure. **4** cocrystallized with a disordered molecule of water.

In **4** only the electron-poor pentafluorophenyl unit undergoes anion– π interactions. One of the C_6H_5 groups interacts by two

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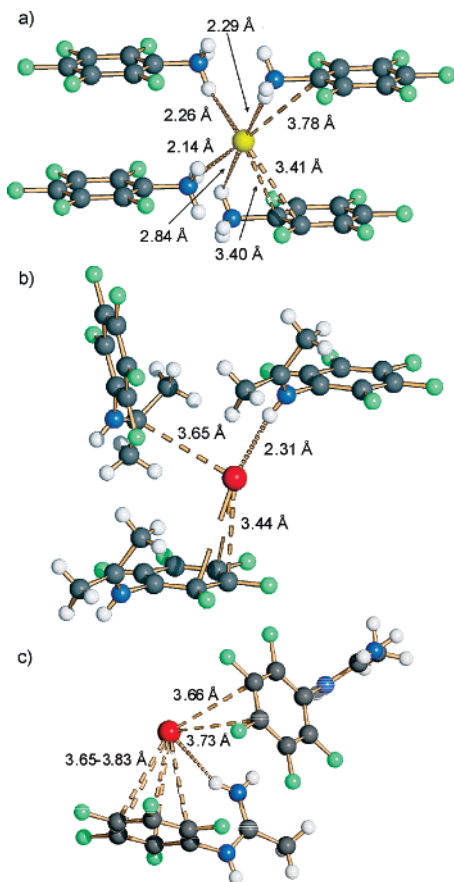


Figure 1. X-ray structure analyses of **1a** (a) and **2b** (b) showing the bonding interactions between the anion and its neighbors. Part of the crystal structure of **3b** (c). **2c** and **3a** are not shown (black, C; white, H; green, F; blue, N; yellow, Cl; red, Br).

Table 1. Comparison of the X–H and X–C Contacts [Å] within the “ η^6 ” Bonded Part of **3a** and **3b**

	C ¹ –X	C ² –X	C ³ –X	C ⁴ –X	C ⁵ –X	C ⁶ –X
3a	3.77	3.98	3.98	3.75	3.52	3.53
3b	3.74	3.65	3.65	3.74	3.83	3.82

C–H \cdots Br hydrogen bonds with the anion in addition to H-bonding of a water molecule.⁹ In the crystal, the bromide is shifted toward the rim of the pentafluorophenyl unit showing only two short close to equidistant contacts Br–C of 3.70 and 3.71 Å. This interaction represents neither the anion-donor– π -acceptor structure **B** nor the “ η^6 ” anion– π -complex **C**. The observed interaction should be described as an “ η^{2*} ”-type as it is shown in **D** (Figure 2) and as it also was observed in the crystal structures of **3a** and **3b** (see Figure 1c).

In conclusion, we presented a systematic approach to “metal-free” salts, which contain pentafluorophenyl as a substituent and which exhibit extensive anion– π interactions. According to the investigations by Hay, we also observe anion-donor– π -acceptor **B** as well as “ η^6 ” anion– π -complex **C** type interactions. The latter kind was also investigated by high level quantum chemical calculations of our compounds and showed the strong attraction due to anion– π interaction in addition to hydrogen binding. Similar results were observed with isocyanuric acid derivatives.^{4c}

Based on our studies we would like to add the “ η^{2*} ”-type binding mode **D** (Figure 2) as an additional alternative in which the anion is not located above the center of an aromatic ring and does not interact with only one specific carbon atom of the π -system.

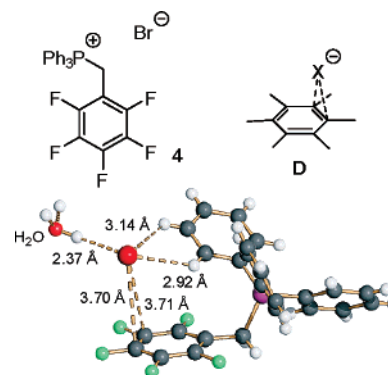


Figure 2. X-ray structure analyses of **4**·H₂O. The water molecule shows disorder (black, C; white, H; green, F; pink, P; red, Br, O).

It is concluded that an anion– π interaction can lead to structurally highly flexible relative orientations of the aromatic moiety and the anion, which probably is due to the mainly electrostatic and dispersive nature of the bonding.

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Supporting Information Available: CIF files of the X-ray structural investigations of **1a**, **2b**, **2c**, **3a**, **3b**, and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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