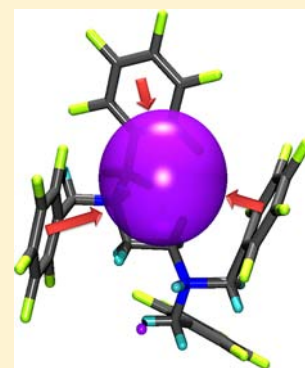


Di-, Tri-, and Tetra(pentafluorophenyl) Derivatives for Oligotopic Anion- π InteractionsMichael Giese,[†] Markus Albrecht,^{*,†} Simon Steike,[†] Anton Ackermann,[†] Arto Valkonen,[‡] and Kari Rissanen[‡][†]Institut für Organische Chemie, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany[‡]Nanoscience Center, Department of Chemistry, University of Jyväskylä, P.O. Box 35, FIN-40014, Jyväskylä, Finland

Supporting Information

ABSTRACT: The present study describes a series of pentafluorobenzyl ammonium salts with two, three, or four C₆F₅ units in order to investigate simultaneous interactions of several perfluorinated arenes with anions in the crystalline state. Most of the structures show multiple anion- π contacts. However, only **6·2HI** reveals an effective encapsulation of the iodide ion by the aromatic units. For comparison, the structure of **4b** is investigated because it offers two π -systems with inverse charge distribution to a bromide anion. Only the electron-deficient π -system of the pentafluorophenyl group interacts with the anion.



INTRODUCTION

Supramolecular chemistry, the chemistry of the noncovalent (or reversible) bond, deals with molecular self-assembly and recognition processes driven by weak intermolecular interactions.¹ These may vary dramatically in strength, from strong electrostatic to weakly dispersive attraction.² Because of their crucial role in biological and chemical processes, interactions of arenes like π - π stacking or cation- π interactions have attracted considerable attention.³ Intuitively, the interaction between anions and aromatics should be repulsive. However, anion- π interactions recently were identified for appropriate systems to be an attractive force. Computational as well as crystallographic results prove the existence of this new kind of intermolecular interaction.⁴ Especially in the field of anion recognition and sensing, the anion- π interaction promises new applications and the development of novel anion receptors. Nevertheless, the relevance of anion- π interactions in solution⁵ or in the gas phase⁶ is debatable.

In 2008, we started our work on anion- π interactions in the solid state utilizing pentafluorophenyl ammonium and phosphonium salts⁷ as electron-deficient π -acceptors. First results showed the appropriateness of pentafluorophenyl groups for anion- π investigations in the solid state and revealed a large variation of the anion position with respect to the electron-deficient C₆F₅ unit. Our studies showed that the position strongly depends on the directing substituents close to the π -system.⁸ Moreover, the dependence of anion- π interactions on the fluorination degree of the phenyl group proved to be important.⁹ Successive reduction of the number of fluorine atoms at the arene moiety reduced the electron

deficiency, and the net attractive anion- π interaction turns into a repulsive force. Additionally, the effect of the size and shape of the anion have been investigated in the crystals of pentafluorophenyl ammonium cations with halides, nitrate, tetrafluoroborate, and hexafluoroborate.¹⁰ However, because of its electrostatic nature, the geometry of the anions seems not to be relevant in the solid-state structures of the investigated anion- π complexes.

In 2005, Frontera, Deyà, and co-workers reported additive behavior of anion- π interactions between trifluoro-1,3,5-triazine (TFZ) and chloride anions (Figure 1).¹¹ They calculated the binding energies of the complexes of chloride with one, two, or three TFZ units in chloroform and water, as well as in the gas phase. Their results show a strict dependence of the binding energy on the number of involved electron-deficient π -systems. In 2008, Ghosh et al. described the crystal

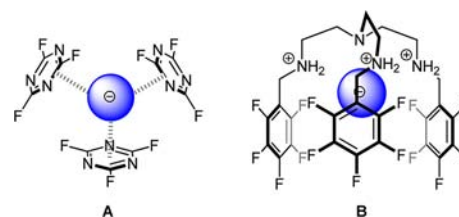


Figure 1. System of Frontera, Deyà, and co-workers (A) to investigate the additivity of anion- π interactions and the Ghosh derivative (B).

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structure of tris(pentafluorobenzyl-2-aminoethyl)ammonium chloride and bromide.¹² Unfortunately, the anion is fixed by strong NH–anion interactions in the cap of the ammonium salt and does not show η^6 -anion– π interaction with the central anion. Similar results were obtained for the corresponding urea compounds.¹³ Inspired by these studies, we started our investigations of interactions of oligo pentafluorophenyl derivatives with anions in the solid state. The present paper reports investigations of concerted anion– π interactions of the pentafluorophenyl groups with various anions in the solid state.

EXPERIMENTAL SECTION

Commercially available reagents were used as received, and solvents were distilled and used without further purification. The ¹H (300 MHz) and ¹⁹F (282 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer in deuterated solvents. Mass spectrometric data were recorded on a Finnigan SSQ 7000 and Thermo Deca XP as electron ionization (EI, 70 eV) or electrospray ionization (ESI). Infrared spectra were taken on a PerkinElmer Spektrum 100 FTIR spectrometer. All samples were measured in KBr (4000–650 cm⁻¹). The elemental analysis was performed on a CHN-O-Rapid Vario EL from Heraeus, and melting points were obtained on a Büchi B-540.

Synthesis of Di-, Tri-, and Tetra(pentafluorophenyl)-ammonium Salts. *Dimethyl Bis(pentafluorobenzyl)ammonium Bromide 1.* Equimolar amounts of pentafluorobenzyl bromide (400 mg, 1.54 mmol, 230 μ L) and dimethyl amine (40% aqueous solution, 180 mg, 1.54 mmol, 180 μ L) were dissolved in 10 mL of acetonitrile and stirred for 48 h at ambient temperature. The solvent was removed, and the remaining white solid was twice recrystallized from methanol. We were not able to separate both salts quantitatively, but during the crystallizations we isolated crystals of **1** as well as of H₂N(CH₂)₂Br. Yield of **1**: 367 mg colorless solid (0.6 mmol, 40%). mp: 213 °C. ¹H NMR (MeOD, 300 MHz): δ 4.74 (s, 4H, H_{benzyl}), 3.08 (s, 6H, CH₃), 2.60 (s, 6H, H₂N(CH₂)₂⁺). ¹⁹F NMR (MeOD, 300 MHz): δ -137.35 (m, 4F, F_{ortho}), -150.77 (m, 2F, F_{para}), -162.55 (m, 4F, F_{meta}). MS (ESI): m/z 406.2 (100, [M]⁺, C₁₆H₁₀F₁₀N⁺). IR (KBr): ν (cm⁻¹) 3448 (w), 3010 (w), 2773 (w), 2437 (w), 1740 (w), 1658 (m), 1506 (vs), 1425 (m), 1392 (m), 1310 (m), 1261 (w), 1227 (w), 1135 (vs), 1060 (m), 1042 (m), 979 (vs), 958 (vs), 918 (s), 904 (m), 870 (s), 802 (m), 748 (w), 693 (w), 671 (m). Anal. Calcd for C₁₆H₁₀F₁₀NBr·NH₂(CH₂)₂Br (612.14): C 35.22, H 2.96, N 4.58. Found: C 35.66, H 2.39, N 4.28.

Tetramethyl Bis(pentafluorobenzyl)ethylenediammonium Dibromide 2a. To begin, 2.0 equiv of pentafluorobenzyl bromide (400 mg, 1.54 mmol, 230 μ L) was dissolved in 10 mL of acetonitrile; 1.0 equiv of TMEDA (89 mg, 0.77 mmol, 115 μ L) was added. After the mixture was stirred for 48 h at ambient temperature, the precipitated white solid was filtered off and washed with ethyl acetate. The remaining white solid was dried in a vacuum. Yield: 392 mg colorless solid (0.6 mmol, 80%). mp: 205 °C. ¹H NMR (MeOD, 300 MHz): δ 4.80 (s, 4H, H_{benzyl}), 4.20 (s, 4H, CH₂), 3.19 (s, 12H, CH₃). ¹⁹F NMR (MeOD, 300 MHz): δ -136.45 (m, 2F, F_{ortho}), -146.86 (m, 1F, F_{para}), -159.68 (m, 2F, F_{meta}). MS (EI, 70 eV): m/z 559.0 (100, [M + Br]⁺, C₂₀H₂₀BrF₁₀N₂⁺). IR (KBr): ν (cm⁻¹) 3007 (w), 2954 (w), 2049 (w), 1982 (w), 1663 (m), 1508 (vs), 1476 (m), 1443 (m), 1403 (w), 1381 (w), 1357 (w), 1331 (w), 1308 (m), 1234 (w), 1135 (s), 1035 (s), 969 (vs), 924 (w), 904 (m), 892 (m), 876 (m), 816 (m), 766 (w), 721 (m), 682 (m). Anal. Calcd for C₂₀H₂₀BrClF₁₀N₂ (628.06): C 37.64, H 3.16, N 4.39. Found: C 37.60, H 3.25, N 4.38.

Tetramethyl Bis(pentafluorobenzyl)ethylenediammonium Sulfate 2b. To a solution of 200 mg (1.0 equiv, 0.31 mmol) of tetramethyl bis(pentafluorobenzyl)ethylenediammonium dibromide (**2a**) in 30 mL of water was added a solution of 97 mg (1.0 equiv, 0.31 mmol) of silver(I) sulfate in 20 mL of water. The precipitating white solid was filtered off, and the solvent was removed under reduced pressure. The remaining white solid was dried in a vacuum. Yield: 167 mg colorless solid (0.3 mmol, 90%). mp: 193 °C. ¹H NMR (D₂O, 300 MHz): δ 4.93 (s, 4H, H_{benzyl}), 4.43 (s, 4H, CH₂), 3.28 (s, 12H, CH₃). ¹⁹F NMR (CDCl₃, 300 MHz): δ -137.3 (m, 4F, F_{ortho}),

-150.8 (m, 2F, F_{para}), -162.6 (m, 4F, F_{meta}). MS (EI, 70 eV): m/z 239.2 (100, [M]²⁺, C₂₀H₂₀F₁₀N₂²⁺). IR (KBr): ν (cm⁻¹) 3387 (m), 3029 (s), 2975 (s), 2657 (s), 2321 (s), 2156 (s), 2156 (s), 2081 (s), 2001 (s), 1657 (m), 1527 (w), 1501 (w), 1426 (m), 1396 (s), 1369 (s), 1314 (m), 1233 (s), 1076 (w), 969 (w), 908 (m), 870 (m), 815 (s), 771 (s), 725 (s), 687 (m). Anal. Calcd for C₂₀H₂₀F₁₀N₂O₄S·2H₂O (574.10): C 39.35, H 3.96, N 4.59. Found: C 39.38, H 4.13, N 4.56.

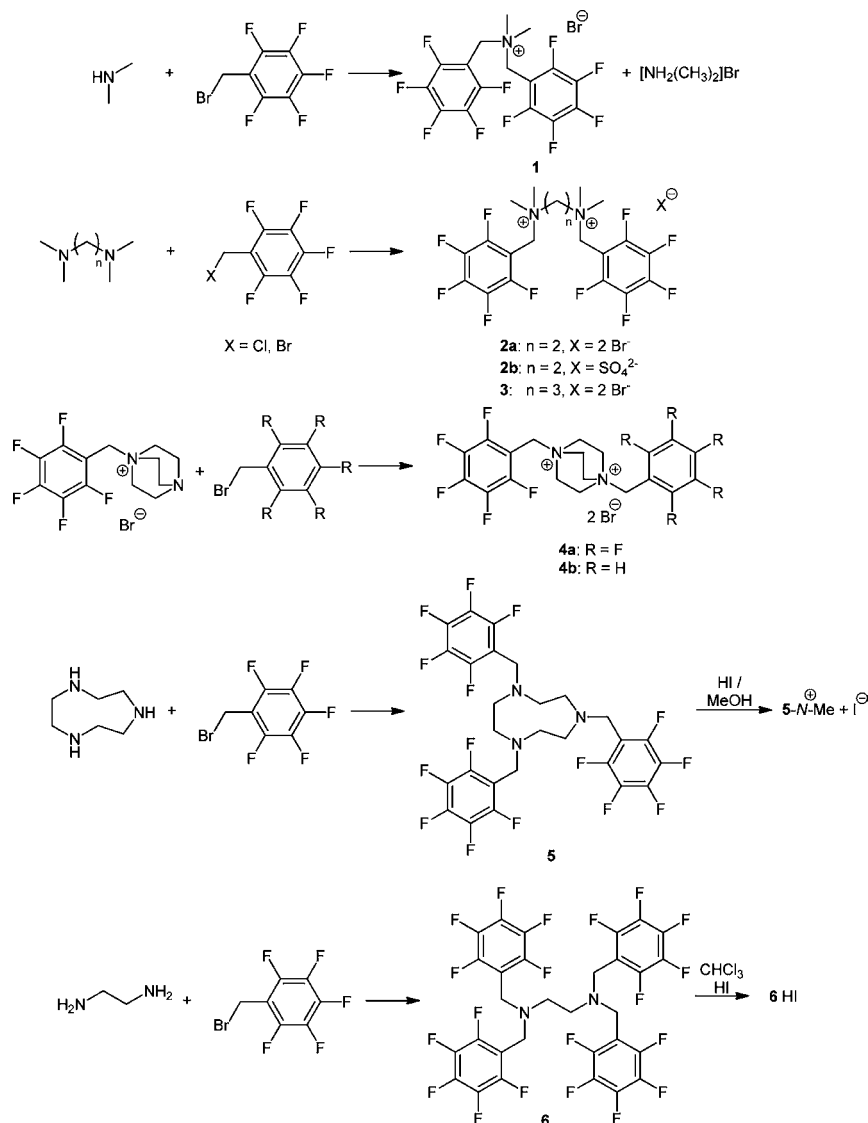
Tetramethyl Bis(pentafluorobenzyl)propylenediammonium Dibromide 3. A solution of 200 mg (2.0 equiv, 0.77 mmol, 116 μ L) of pentafluorobenzyl bromide in 10 mL of acetonitrile was mixed with 44 mg (1.0 equiv, 0.38 mmol, 64 μ L) of tetramethyl propylene diamine. The mixture was stirred for 20 h at ambient temperature. The precipitating white solid was filtered off and washed with ethyl acetate. The remaining white solid was dried in a vacuum. Yield: 210 mg colorless solid (0.3 mmol, 84%). mp: 200 °C. ¹H NMR (MeOD, 300 MHz): δ 4.84 (s, 4H, H_{benzyl}), 3.65 (m, 4H, CH₂), 3.27 (s, 12H, CH₃), 2.60 (m, 2H, CH₂). ¹⁹F NMR (CDCl₃, 300 MHz): δ -137.80 (m, 4F, F_{ortho}), -150.72 (m, 2F, F_{para}), -162.50 (m, 4F, F_{meta}). MS (EI, 70 eV): m/z 571.1 (100, [MBr]⁺, C₂₁H₂₂BrF₁₀N₂⁺). IR (KBr): ν (cm⁻¹) 3401 (m), 3322 (m), 3207 (w), 3013 (w), 2981 (w), 2660 (w), 2323 (w), 2198 (w), 2182 (w), 2120 (w), 1992 (w), 1659 (m), 1527 (s), 1505 (vs), 1470 (s), 1440 (m), 1425 (m), 1380 (m), 1364 (m), 1312 (m), 1233 (w), 1184 (w), 1137 (s), 1075 (w), 1043 (s), 1028 (s), 977 (s), 960 (vs), 922 (m), 903 (m), 853 (s), 773 (w), 754 (m), 719 (w), 692 (w), 677 (w). Anal. Calcd for C₂₁H₂₂Br₂F₁₀N₂·H₂O (650.00): C 37.63, H 3.61, N 4.18. Found: C 37.62, H 3.63, N 4.21.

1-Pentafluorobenzylammonium-4-benzylammonium-bicyclo[2.2.2]octanedibromide 4b. To a solution of 200 mg (1.0 equiv, 0.54 mmol) of pentafluorobenzyl-1,4-diazoniabicyclo[2.2.2]octanbromide in 5 mL of ethanol was added 91 mg (1.0 equiv, 0.54 mmol, 64 μ L) of benzyl bromide, and the solution was stirred for 24 h at ambient temperature. The precipitating white solid was filtered off and dried in a vacuum. Yield: 282 mg colorless solid (0.5 mmol, 97%). mp: 252 °C, under decomposition. ¹H NMR (MeOD, 300 MHz): δ 7.61 (m, 5H, H_{aryl}), 5.04 (s, 2H, H_{benzyl}), 4.89 (s, 2H, H_{benzyl}), 4.05 (m, 6H, CH₂), 3.12 (m, 6H, CH₂). ¹⁹F NMR (MeOD, 300 MHz): δ -137.49 (m, 2F, F_{ortho}), -149.72 (m, 1F, F_{para}), -162.06 (m, 2F, F_{meta}). MS (ESI): m/z 465.33 (90, [MBr]⁺, C₂₀H₂₁F₅N₂Br). IR (KBr): ν (cm⁻¹) 3638 (w), 3478 (w), 3413 (m), 3350 (m), 2997 (m), 2902 (w), 2085 (w), 1661 (m), 1584 (w), 1527 (s), 1508 (vs), 1458 (m), 1426 (m), 1396 (m), 1356 (w), 1310 (m), 1213 (w), 1139 (s), 1095 (m), 1055 (m), 1004 (m), 963 (vs), 905 (m), 855 (vs), 772 (s), 710 (s), 659 (m). Anal. Calcd for C₂₀H₂₁F₅N₂Br·H₂O (543.00): C 42.73, H 4.12, N 4.98, N 4.18. Found: C 42.83, H 4.45, N 4.77.

1,4,7-Tris(pentafluorobenzyl)-1,4,7-triazacyclononane 5. 1,4,7-Triazacyclononanhydrochloride was obtained by the procedure described in the literature.¹⁴ To a solution of 300 mg (1.0 equiv, 1.26 mmol) of 1,4,7-triazacyclononane hydrochloride in 5 mL of dry toluene was added 282 mg (4.0 equiv, 5.03 mmol) of potassium hydroxide. Then a solution of 985 mg (3.0 equiv, 3.77 mmol, 572 μ L) of pentafluorobenzyl bromide dissolved in 1 mL of dry toluene was slowly added. The suspension was heated for 7 h to 110 °C and then cooled to ambient temperature. Then 71 mg (1.0 equiv, 1.26 mmol) of potassium hydroxide and 328 mg (1.0 equiv, 1.26 mmol, 190 μ L) of pentafluorobenzyl bromide were added, and the mixture was stirred for an additional 12 h at 110 °C. After the mixture was cooled to room temperature, the precipitating salts were filtered off and the solvent was slowly removed. Yield: 574 mg colorless solid (0.9 mmol, 68%). mp: 90 °C, under decomposition. ¹H NMR (CDCl₃, 300 MHz): δ 3.71 (s, 6H, H_{benzyl}), 2.70 (s, 12H, CH₂). ¹⁹F NMR (CDCl₃, 300 MHz): δ -142.35 (m, 2F, F_{meta}), -155.57 (m, 1F, F_{para}), -162.38 (m, 2F, F_{ortho}). MS (EI, 70 eV): m/z 669.3 (6, [M]⁺, C₂₇H₁₈F₁₅N₃⁺), 181.1 (100, C₇H₇F₅⁺). IR (KBr): ν (cm⁻¹) 2930 (w), 2870 (w), 2827 (w), 2795 (w), 1656 (w), 1497 (s), 1454 (m), 1364 (m), 1315 (m), 1298 (m), 1241 (w), 1126 (s), 1019 (s), 992 (s), 962 (s), 935 (s), 904 (m), 877 (w), 797 (w), 741 (w), 669 (w). Anal. Calcd for C₂₇H₁₈F₁₅N₃·H₂O (669.43): C 47.17, H 2.93, N 6.11. Found: C 47.49, H 3.04, N 6.00.

Tetrakis(pentafluorobenzyl)ethylene Diamine 6. To begin, 46 mg (1.0 equiv, 0.81 mmol, 60 μ L) of ethylene diamine, 458 mg (4.25

Scheme 1. Synthesis of the Pentafluorobenzyl Ammonium Salts



equiv, 3.43 mmol) of potassium carbonate, and 870 mg (4.25 equiv, 3.43 mmol, 505 μL) of pentafluorobenzyl bromide were dissolved in 30 mL of acetonitrile and stirred for 48 h at ambient temperature. The precipitating salts were filtered off, and the solvent was removed under reduced pressure. The remaining white solid was recrystallized from methanol and dried in a vacuum. Yield: 108 mg colorless solid (0.1 mmol, 25%). mp: 116 $^\circ\text{C}$, under decomposition. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 3.61 (s, 8H, H_{benzyl}), 2.51 (s, 4H, CH_2). $^{19}\text{F NMR}$ (CDCl_3 , 300 MHz): δ -142.9 (m, 4F, F_{ortho}), 154.3 (m, 2F, F_{para}), 162.0 (m, 4F, F_{meta}). MS (EI, 70 eV): m/z 390.1 (100, $\text{C}_{15}\text{H}_6\text{F}_{10}\text{N}^+$). IR (KBr): ν (cm^{-1}) 2987 (w), 2925 (w), 2850 (w), 2103 (w), 1657 (m), 1497 (vs), 1428 (w), 1377 (w), 1335 (m), 1297 (m), 1236 (m), 1127 (s), 1013 (s), 964 (m), 930 (m), 914 (m), 850 (m), 802 (w), 763 (m), 740 (m), 691 (m), 664 (w). Anal. Calcd for $\text{C}_{30}\text{H}_{12}\text{F}_{20}\text{N}_2 \cdot 2\text{H}_2\text{O}$ (780.40): C 44.13, H 1.98, N 3.43, Found: C 44.26, H 1.80, N 3.18.

Crystallography. Single-crystal X-ray data were collected at 123.0(1) K using a Bruker-Nonius KappaCCD diffractometer with an APEX-II detector and graphite-monochromatized $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. COLLECT^{15a} software was used for the data collection (θ and ω scans) and DENZO-SMN^{15b} for the processing. The structures were solved by direct methods with SIR2004^{15c} and refined by full-matrix least-squares methods with WinGX software,^{15d} which utilizes the SHELXL-97 module.^{15e} Lorentzian polarization

correction was applied on all data, and absorption effects were corrected with the multiscan method (SADABS^{15f}). All C–H hydrogen positions were calculated and refined as riding atoms. Hydrogen atoms bonded to O (in **2b**, **3**, and **4b**) or N (**6-2HI**) were found from Fourier maps and restrained (by DFIX, $s = 0.02$) to a distance of 0.84 Å from O or 0.91 Å from N atoms. Thermal parameters of hydrogen atoms were set to 1.2 times those of the parent C and N atoms or 1.5 times those of parent O atoms. In **2a**, the disordered positions for Br^- and Cl^- were constrained to be equal (EXYZ) and the anisotropic displacement parameters were equalized (EADP) for Br^- and Cl^- . Anisotropic displacement parameters restraints (SIMU, $s_1 = 0.01$, $s_2 = 0.02$; DELU, $s = 0.01$; ISOR, $s = 0.01$) were also applied for few atoms in structures **2a**, **2b**, **4b**, and **5-N-Me⁺I⁻**. The bond distances in disordered solvents were restrained to be more equal in **2b** (SADI, $s = 0.02$). Crystallographic data and parameters for nine structures (Table S1) and for a second structure related to **2a** (Table S2) are summarized in the Supporting Information.

RESULTS AND DISCUSSION

Synthesis of Ammonium Compounds. The bis-(pentafluorobenzyl)ammonium bromides **1**, **2a**, and **3** were obtained by reaction of the corresponding pentafluorobenzyl bromide with diethyl amine or the corresponding tetramethyl

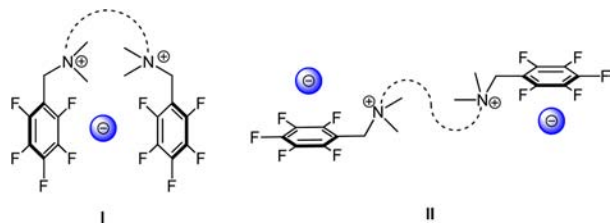
amines via nucleophilic substitution (Scheme 1). Compound **2b** is available by salt metathesis from **2a** and silver sulfate in aqueous solution. Compounds **4a** and **4b** were synthesized by reacting 1-(pentafluorobenzylammonium)-4-aza-1-azoniabicyclo[2.2.2]octane bromide with equimolar amounts of pentafluorobenzyl and benzyl bromide, respectively. The tris(pentafluorobenzyl)triaminocyclononane (**5**) was synthesized from 1,4,7-triaminocyclononane¹⁴ in toluene in the presence of potassium hydroxide. Crystals of **5** were obtained by diffusion of HI into a solution of **5** in methanol. During the crystallization process, **5** was methylated and the crystal structure of the corresponding ammonium iodide (**5-N-Me⁺I⁻**) was obtained.

The tetrakis(pentafluorobenzyl)ethylene amine (**6**) was obtained by reacting pentafluorobenzyl bromide with ethylene diamine in the presence of potassium carbonate in acetonitrile (Scheme 1). The corresponding hydroiodide (**6·2HI**) was crystallized by diffusion of HI into a solution of **6** in chloroform.

All isolated compounds except **5-N-Me⁺I⁻** and **6·2HI** are characterized by standard analytical methods (¹H and ¹⁹F NMR, IR, MS, and elemental analysis). For **1–5**, as well as for **5-N-Me⁺I⁻**, **6**, and **6·2HI**, suitable crystals for X-ray analysis could be obtained.

Solid-State Studies. Crystals are the result of the interplay of inter- and intramolecular forces, which may have a significant influence on how the molecules or complexes pack into a crystal lattice. In the following, the focus will be the analysis of the relevant interactions between the π -systems and anions present in the crystal. In systems with multiple electron-deficient arenes, the anion– π interaction can occur as simultaneous interactions of two π -systems by paneling the anion (Scheme 2, I) or as two separate anion– π interactions (separated interactions, Scheme 2, II).

Scheme 2. Binding Motifs for the Interaction of Electron-Deficient Arenes with Anions



Di- and Tetramethyl Bis(pentafluorobenzyl)ammonium Salts (1–3). Crystals of dimethyl bis(pentafluorobenzyl)ammonium bromide (**1**) were obtained from a mixture of methanol and diethyl ether. Compound **1** (Figure 2) crystallizes in the monoclinic space group $P2_1/c$ with two ion pairs (**A** and **B**) per asymmetric unit. In both ion pairs, the anion is not centered above a π -system. However, the bromide is fixed in both cases close to two carbon atoms of the electron-deficient arenes (η^2 -binding motif: **A**, $C^2\cdots Br = 3.624$ Å, $C^3\cdots Br = 3.528$ Å; **B**, $C^4\cdots Br = 3.558$ Å, $C^5\cdots Br = 3.417$ Å). The second electron-deficient arene unit of the cation in **A** shows an additional short (η^1 type) contact to a neighboring bromide ($C^3\cdots Br = 3.459$ Å). Moreover, the anions are embedded in various CH–anion interactions with the protons of the methyl or the benzyl group ($CH\cdots Br = 2.683$ – 3.025 Å).

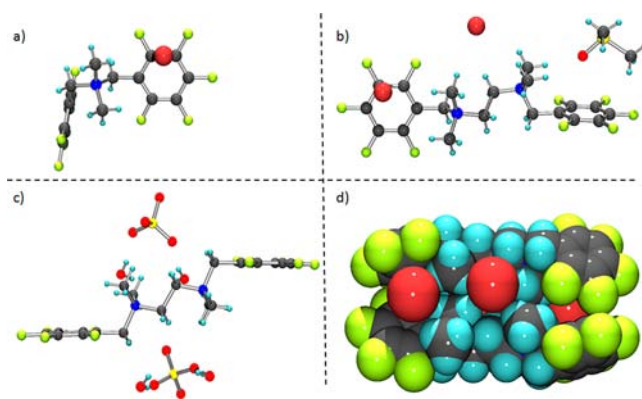


Figure 2. (a) View of one ion pair as observed in the crystal structure of **1**. (b) Solid-state structure of **2a** showing the anion– π and lone-pair– π interactions. (c) Representative part of the crystal structure of **2b**. The sulfate anions show exclusively CH–anion binding to the alkyl groups and hydrogen bonding to the cocrystallized water (disordered solvent molecules were omitted for clarity). (d) Molecular packing of **3** reveals that one bromide anion is interacting with two pentafluorobenzyl units of different dications (gray, carbon; light blue, hydrogen; dark blue, nitrogen; light green, fluorine; dark red, bromide; light red, oxygen; yellow, sulfur).

Compound **2a** cocrystallizes with one molecule of DMSO from a DMSO/diethyl ether mixture. Because one of the two electron-deficient moieties shows lone-pair– π interactions with the oxygen atom of the cocrystallized DMSO ($C\cdots O = 3.325$ – 3.602 Å; center $\cdots O = 3.170$ Å), only the second pentafluorophenyl group is able to interact with anions. A closer look at the packing of **2a** reveals that one bromide is sandwiched between two pentafluorophenyl groups of adjacent cations. Hydrogen-bonding interaction of the methyl groups directs the anion between the π -systems ($CH\cdots Br = 2.986$ Å). However, the anion is shifted off center ($C^{2-4}\cdots Br = 3.527, 3.724, 3.782$ Å; $C^{3-5}\cdots Br = 3.608, 3.620, 3.771$ Å) because of the cocrystallized solvent molecule showing an η^3 type anion– π interaction with both arenes. The second anion does not show interactions with electron-deficient moieties and is surrounded exclusively by CH–anion contacts ($CH\cdots Br = 2.677$ – 3.343 Å). A wider view of the crystal packing reveals the T-shaped orientation of the perfluorinated arenes ($CF\cdots center = 3.046$ Å). A second solid-state structure related to **2a** was obtained by a substitution reaction of TMEDA and pentafluorobenzyl chloride and bromide. The solid-state structure was obtained by crystallization from DMSO/diethyl ether and cocrystallizes with one molecule of DMSO. The crystal structure reveals features similar to those of the bromide structure with disordered (1:1) bromide/chloride content over two equal positions (1, $0.6Br^-/0.4Cl^-$; 2, $0.4Br^-/0.6Cl^-$; see Supporting Information, Table S2).

So far, not one of the described structures shows simultaneous interaction of two pentafluorophenyl groups in order to capture the anion in an electron-deficient cavity. Because the described ammonium salts have the opportunity to interact with two anions and/or lone pairs of cocrystallized solvent molecules, we synthesized tetramethyl bis(pentafluorobenzyl)ethyleneammonium sulfate (**2b**) by salt metathesis. Unfortunately, **2b** crystallizes with two molecules of water and disordered solvent molecules (additional water, methanol, and ethyl acetate). The pentafluorophenyl units of **2b** do not show anion– π interactions with the sulfate. The sulfate anions of adjacent ion pairs are bridged by water

molecules ($\text{HOH}\cdots\text{OSO}_3 = 1.920\text{--}1.930 \text{ \AA}$) and embedded in various $\text{CH}\cdots\text{anion}$ interactions from the benzyl or alkyl groups ($\text{CH}\cdots\text{OSO}_3 = 2.322\text{--}2.718 \text{ \AA}$). One of the two π -systems interacts with the oxygen atom of a cocrystallized disordered solvent molecule (H_2O , ethyl acetate; for H_2O , $\text{C}\cdots\text{O} = 3.210\text{--}3.373 \text{ \AA}$; $\text{center}\cdots\text{O} = 2.992 \text{ \AA}$).

Again, no simultaneous intramolecular anion– π interactions of the pentafluorobenzyl groups with one anion are observed in the solid state. Therefore, the spacer distance between the two electron-deficient arenes was elongated in order to create a more flexible backbone and allow wrapping around the anion. In **3**, the pentafluorobenzyl groups are linked by a propylene chain. The longer chain enables a higher adaptability and should be more appropriate for “intramolecular” anion– π interactions in the sense of **1**. However, the solid-state structure of **3** shows that one bromide anion is fixed by the methyl groups ($\text{CH}\cdots\text{Br} = 2.923, 3.178 \text{ \AA}$) above the π -system in an η^3 -binding motif ($\text{C}^{4-6}\cdots\text{Br} = 3.880, 3.615, 3.642 \text{ \AA}$). The molecular packing shows that a second pentafluorophenyl unit is close to the anion. The distances of 4.081 and 4.102 \AA are a little too long for showing attractive anion– π interactions. A second bromide anion is surrounded by several $\text{CH}\cdots\text{anion}$ interactions ($\text{CH}\cdots\text{Br} = 2.828\text{--}2.993 \text{ \AA}$). Anions are connected via the cocrystallized water molecule ($\text{HOH}\cdots\text{Br} = 2.415, 2.423 \text{ \AA}$).

A more rigid linker between the two pentafluorobenzyl units was reported earlier.⁸ The 1,4-bis(pentafluorobenzylammonium)-1,4-bisazoniabicyclo[2.2.2]octane dibromide (**4a**) crystallized with three molecules of methanol per asymmetric unit. The oxygen atom of the methanol interacts with the electron-deficient arene ($\text{C}\cdots\text{OHCH}_3 = 3.503\text{--}4.078 \text{ \AA}$; $\text{center}\cdots\text{OHCH}_3 = 3.537 \text{ \AA}$) and forces the anion away from the position above the π -system. Only an η^2 -anion– π interaction with one of two pentafluorobenzyl moieties ($\text{C}^{5/6}\cdots\text{Br} = 3.416, 3.411 \text{ \AA}$) is observed in the crystal structure. Starting from this and inspired by our study on the dependence of the anion position above arenes with various electron densities,⁹ we were interested in investigating the direct competition of an electron-rich and an electron-deficient arene in the solid state. Therefore, the bis(pentafluorobenzyl)ammonium derivative **4b** with a pentafluorobenzyl as well as a benzyl group was synthesized (Figure 3). While the electron-deficient C_6F_5 unit should interact attractively with an anion, the benzyl group should be repulsive with respect to anions.

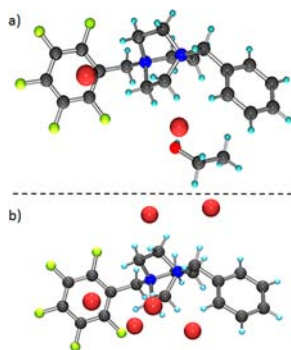


Figure 3. Two representative views of the ammonium cation in **4b** showing the asymmetric unit (a) as well as all anionic neighbors of the cation (b); cocrystallized ethanol molecule was omitted for clarity (gray, carbon; light blue, hydrogen; dark blue, nitrogen; light green, fluorine; dark red, bromide; light red, oxygen).

The solid-state structure of **4b** was obtained from ethanol and supports this suggestion. One molecule of ethanol cocrystallizes per asymmetric unit. The two methyl groups direct the bromide ($\text{CH}\cdots\text{Br} = 2.891, 2.866 \text{ \AA}$) above the center of the pentafluorobenzyl unit (η^6 -binding motif: $\text{C}\cdots\text{Br} = 3.791\text{--}3.864 \text{ \AA}$; $\text{center}\cdots\text{Br} = 3.571 \text{ \AA}$). The anion also accepts $\text{CH}\cdots\text{anion}$ interactions from the neighboring cation ($\text{CH}\cdots\text{Br} = 2.792, 2.883 \text{ \AA}$; $\text{CH}_{\text{benzyl}}\cdots\text{Br} = 3.009 \text{ \AA}$). The second anion shows a hydrogen bridge to the OH group of the cocrystallized ethanol ($\text{OH}\cdots\text{Br} = 2.469 \text{ \AA}$). The 1,4-diazabicyclo[2.2.2]octane unit of the cation binds the second anion by $\text{CH}\cdots\text{anion}$ interactions ($\text{CH}\cdots\text{Br} = 2.659, 2.822 \text{ \AA}$), and the anion forms similar contacts to two neighboring cations ($\text{CH}\cdots\text{Br} = 2.832, 2.882, 2.839 \text{ \AA}$; $\text{CH}_{\text{aryl}}\cdots\text{Br} = 2.851 \text{ \AA}$). A wider look at the crystal packing of **4b** reveals that each cation is surrounded by six anions, whereby only one shows anion– π interactions. This crystal structure is an important argument in the discussion of anion– π interactions in the solid state because it clearly shows that the position above an electron-deficient arene is favored for an anion while the electron-rich benzyl group is not able to interact.

N,N,N-Tris(pentafluorobenzyl)triaminocyclononane (**5**) and Its Methylated Ammonium Salt (*5-N-Me⁺I⁻*). Crystals of **5** could be obtained from toluene by slow evaporation of the solvent. The pentafluorobenzyl groups of **5** show inter- and intramolecular aryl–aryl contacts. Whereas for the intramolecular interactions the arenes are oriented in a T-shaped fashion ($\text{CF}\cdots\text{center} = 2.933 \text{ \AA}$), the intermolecular interactions show a shifted face-to-face ($\text{center}\cdots\text{center} = 3.551 \text{ \AA}$; $\text{plane}\cdots\text{plane} = 3.276 \text{ \AA}$) as well as a T-shaped orientation of the electron-deficient C_6F_5 moieties ($\text{CF}\cdots\text{center} = 3.475 \text{ \AA}$).

The methylated ammonium iodide *5-N-Me⁺I⁻* could be obtained by diffusing HI into a solution of **5** in methanol. Compound **5** crystallizes in the orthorhombic space group *Pbca* with disordered water molecules (Figure 4). The anion is fixed above the C_6F_5 unit by $\text{CH}\cdots\text{anion}$ interactions ($\text{CH}\cdots\text{I} = 3.289, 3.127 \text{ \AA}$) and shows short distances to three carbon

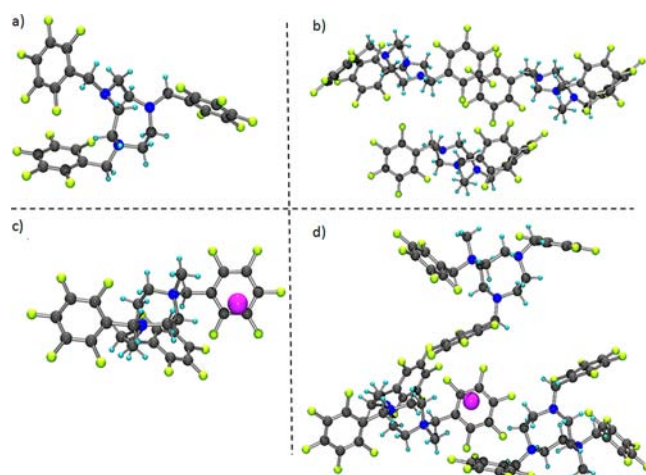


Figure 4. Two representative views of **5** showing the intramolecular π – π interactions (a) as well as a view of the crystalline packing exhibiting the intermolecular π – π interactions (b). The interactions of the iodide in the solid-state structure of *5-N-Me⁺I⁻* with the surrounding pentafluorophenyl units are shown in (c) and (d). (Disordered water molecules were omitted for clarity; gray, carbon; light blue, hydrogen; dark blue, nitrogen; light green, fluorine; violet, iodide.)

atoms of the electron-deficient arene (η^3 , $C^{4-6}\cdots I = 4.138, 3.982, 4.040$ Å; center $\cdots I = 3.942$ Å). The remaining pentafluorobenzyl units of the ion pair are oriented away from the iodide. However, the pentafluorobenzyl groups of neighboring cations exhibit further anion– π contacts (η^2 , $C^{2/3}\cdots I = 3.969, 3.865$ Å; center $\cdots I = 4.175$ Å; η^2 , $C^{5/6}\cdots I = 4.029, 3.960$ Å; center $\cdots I = 4.480$ Å).

Tetrakis(pentafluorobenzyl)ethylene Amine (6) and Its Hydroiodide (6·2HI). Compound **6** crystallizes in the monoclinic space group $P2_1/c$ from chloroform. Various π – π contacts can be observed in the crystalline packing of the tetrakis(pentafluorobenzyl)ethylene amine (**6**). The most prominent arene–arene interaction is the intramolecular edge-to-face interaction of adjacent C_6F_5 units ($CF\cdots center = 3.196$ Å; $\angle = 83.71^\circ$).

After HI is diffused into a solution of **6** in chloroform, the corresponding hydroiodide **6·2HI** was obtained with one molecule of chloroform per asymmetric unit (Figure 5). One

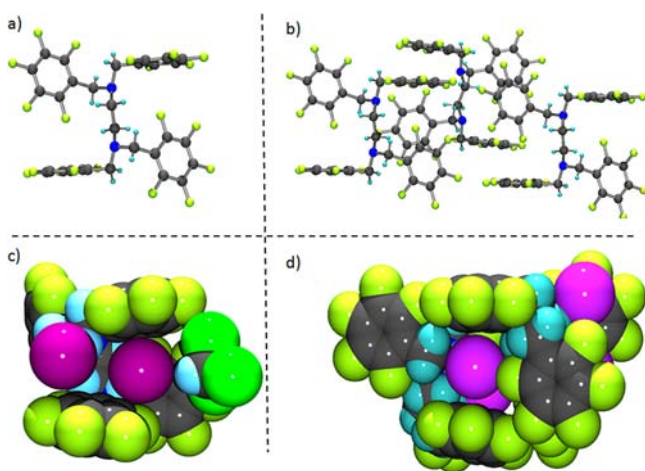


Figure 5. Part of the crystal structure of **6** indicating the intramolecular π – π interactions (a) and the intermolecular π – π interactions (b). The representative parts of the crystal structure (c and d) show the inter- and intramolecular interactions of the arenes and their anion– π contacts as observed in the solid-state structure of **6·2HI**. (Disordered water molecules were omitted for clarity; gray, carbon; light blue, hydrogen; dark blue, nitrogen; light green, fluorine; dark green, chlorine; violet, iodide.)

of the two iodides is bound to the protons of the ammonium group as well as of the alkyl chain ($NH\cdots I = 2.517$ Å; $CH\cdots I = 3.115$ Å) and is paneled by three pentafluorobenzyl moieties ($aryl^1$, $C\cdots I = 3.748$ – 4.377 Å, center $\cdots I = 3.838$ Å (η^4); $aryl^2$, $C\cdots I = 3.654$ – 5.131 Å, center $\cdots I = 4.219$ Å (η^3); $aryl^3$, $C\cdots I = 3.669$ – 5.266 Å, center $\cdots I = 4.318$ Å (η^3)). The remaining open sides around the anion are covered by a benzylic group of an adjacent cation and one molecule of cocrystallized $CHCl_3$ interacting by CH –anion interactions with the iodide ($CH_{benzyl}\cdots I = 3.248$ Å; $Cl_3CH\cdots I = 3.433$ Å). The second iodide anion is also bound to an ammonium group ($NH\cdots I = 2.546$ Å) and to two methylene protons of the adjacent cation ($CH_{benzyl}\cdots I = 3.102$ Å, $CH\cdots I = 3.176$ Å). In addition, it shows an η^2 type interaction with one pentafluorobenzyl unit ($C^{5/6}\cdots I = 3.930, 4.121$ Å) and two anion– π contacts to C_6F_5 units of the neighboring cations ($C^{3-5}\cdots I = 3.898, 4.135, 4.173$ Å (η^3); $C^{2/3}\cdots I = 3.988, 4.001$ Å (η^2)).

The crystal structure of **6·2HI** shows that a simultaneous involvement of several pentafluorophenyl groups in anion– π

interactions with only one anion is possible. Because of the insufficient preorganization and rigidity of the backbone, an efficient electron-deficient cavity could not be observed.

CONCLUSION

This study shows examples for both failure and success of a concept. On the basis of previous results, a series of solid-state structures of pentafluorobenzyl ammonium salts with two, three, or four electron-deficient arenes was presented. Not one of the structures creates a perfect electron-deficient cavity to shield anions effectively from the surroundings. In the solid-state structure of **6·2HI**, three sides around the anion are paneled by C_6F_5 units. Therefore, **6** is the most promising anion– π capsule. Further investigations on more rigid scaffolds have to be performed to find an ideal π -acceptor for anion– π investigations in the crystal as well as in solution. An interesting structure described within this work is the solid-state structure of **4b** because it directly provides an electron-deficient as well as an electron-rich moiety. In the solid state, only the attractive interactions between bromide and the pentafluorobenzyl group are observed.

The results of the present study are a further step toward understanding the nature of anion– π interactions as a basis for the development of superior anion receptors.

ASSOCIATED CONTENT

Supporting Information

Crystal data for **1**, **2a**, **2b**, **3**, **4b**, **5**, $5-N-Me^+I^-$, **6**, and **6·2HI**, and crystallographic data for the structure related to **2a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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