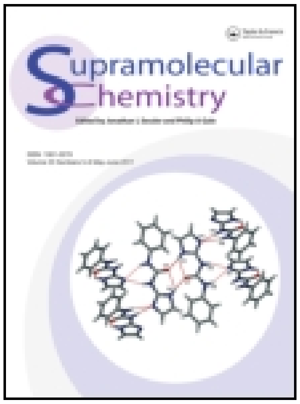

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Geometrically diverse anions in anion-π interactions

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Geometrically diverse anions in anion–π interactions

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The role of different anion geometries in anion–π interactions is discussed. The chemistry described herein is different to the interaction of spherical cations with aromatics. The influence of different geometries makes selective anion recognition more complicated than respective cation sensing. The present structural study reveals attractive interactions between pentafluorophenyl units and geometrically diverse anions (linear, trigonal planar, tetrahedral and octahedral). Due to the electrostatic nature of anion–π interactions, the anion geometry seems to be irrelevant. The size of the anion controls the relative orientation of the anion and the π system (e.g. in compounds **1–3**). The dimeric solid-state structure of ammonium tetrafluorophenolate betaine **4** shows π–π as well as anion–π interactions. In the solid-state structure of **5**, the linear BrIBr anion is panelled by three pentafluorophenyl units.

Keywords: anion–π interactions; anion geometry; ammonium salts

Introduction

Supramolecular chemistry is regarded as the chemistry of non-covalent bonding, which can vary dramatically from weak dispersive to strong electrostatic interactions (*1*). Aromatic systems are involved in weak non-covalent interactions such as π–π stacking and cation–π interactions and play a crucial role in chemical as well as in biological processes (*2*). Recently, an additional weak attractive interaction between electron-deficient arenes and anions has been identified – the anion–π interaction (*3*). Theoretical studies show the attractive nature between anions and electron-deficient aromatics (*4*). A large number of crystal structures give experimental evidence for this interaction (*5*). On the other hand, examples of anion–π interactions in solution (*6*) or in the gas phase (*7*) are rarely found in the literature.

Since 2008, our group has been performing systematic studies on anion–π interactions of purely organic pentafluorophenyl phosphonium and ammonium salts (*8*). The obtained crystal structures show a high variety in the relative position of the anion 'above' the electron-deficient π system. In this context, the hapticity (η) concept for cation–π interactions was transferred to anion–π systems. Due to the weak nature of anion–π attraction, a strong directing effect of NH– and CH–anion interactions on the positions of halide anions above the pentafluorophenyl unit could be observed. Moreover, we were able to show the dependence of anion–π interactions on the fluorination degree of the phenyl unit (*9*). Successive removal of fluoride enhances the electron density at the aromatic and thus turns the attractive into a repulsive interaction.

We identified 1-(pentafluorobenzylammonium)-4-aza-1-azoniabicyclo[2.2.2] octane (DABCO system) salts as appropriate system to investigate anion–π interactions. The rigid DABCO scaffold fixes the anion by CH–anion interactions near the centre of the pentafluorophenyl group. In the present study, we use the DABCO system to investigate geometrically different anions in anion–π interactions.

Results and discussion

In the literature, anion geometry is discussed as an influential factor for selective anion recognition (*3a*). In anion–π interactions with spherical anions, mainly the size and the polarisability of the anion are important. The question arises whether anions with other geometries interact in more complicated and versatile fashions with the earlier described pentafluorobenzyl ammonium cations. Taking this as starting point, a series of 1-(pentafluorobenzylammonium)-4-aza-1-azoniabicyclo[2.2.2] octane and pentafluorobenzyl triethyl ammonium salts with different anions (OH^-, NO_3^-, IBr_2^- BF_4^- and PF_6^-) were synthesised and the anion–π interactions were investigated in the solid phase (Scheme 1).

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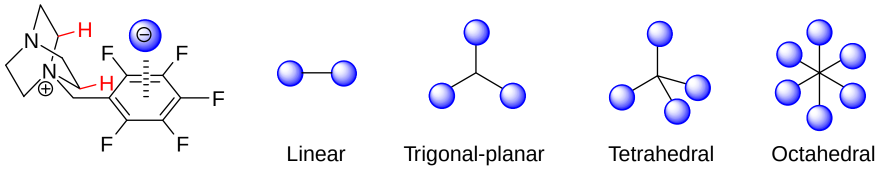
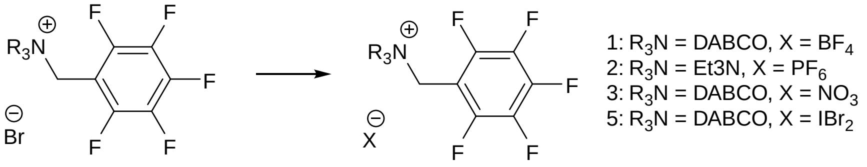
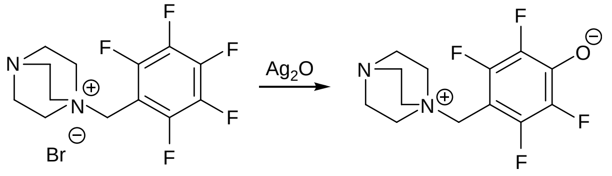


Scheme 1. Pentafluorobenzyl ammonium system and possible anion geometries.



Scheme 2. Preparation of the ammonium compounds **1–3, 5** via salt metathesis.



4

Scheme 3. Synthesis of tetrafluorophenolate **4**.

Synthesis of the ammonium salts

The required ammonium compounds were obtained by salt metathesis from saturated aqueous solutions of 1-(pentafluorobenzylammonium)-4-aza-1-azoniabicyclo[2.2.2] octane bromide and solutions of the corresponding ammonium (NH_4BF_4, NH_4PF_6) or silver salts (Ag_2O, $AgNO_3$, Ag_2SO_4). The monoiododibromide (**5**) was obtained by treating a solution of 1-(pentafluorobenzylammonium)-4-aza-1-azoniabicyclo[2.2.2] octane bromide in water with a solution of iodobromide in dichloromethane (Scheme 2).

Attempts to obtain the hydroxide salt of the DABCO system in aqueous solution with silver(I)oxide led to the para-substituted phenolate **4** (Scheme 3).

The obtained compounds were characterised by standard analytical techniques (^{1}H NMR, ^{19}F NMR spectroscopy, mass spectrometry, infrared (IR) spectroscopy and elemental analysis). For investigation of anion–π interactions in the solid phase, the obtained single crystals were examined by X-ray analysis.

Crystallographic analysis of the ammonium salts

Molecular packing is the result of multiple non-covalent interactions, which result in extended networks. In the following, only the major interactions (CH–anion and anion–π) between neighbouring anions and cations, which are relevant here, are discussed in detail.

In previous work, a series of pentafluorobenzyl DABCO salts with halides and hexafluorophosphate anions were presented (*8b*). The analysis of the structures revealed that the spherical anions (Cl^-, Br and I^-) are located close to the centre of the electron-deficient unit. The structure of the corresponding hexafluorophosphate salt shows that the anion is shifted to the edge of pentafluorophenyl group of the cation. For comparison, the structural data for the pentafluorobenzyl DABCO bromide salt are given in Tables 1 and 2.

*1-(Pentafluorobenzylammonium)-4-aza-1-azoniabicyclo-[2.2.2]octane tetrafluoroborate (**1**) and pentafluorobenzyltriethylammonium hexafluorophosphate (**2**)*

The solid-state structure of **1** shows two different ion pairs per unit cell (**1a** and **1b**). Both subunits reveal short CH···FBF_3 contacts (**1a**: 2.982, 2.490 Å; **1b**: 2.522, 2.430 Å), which direct the tetrafluoroborate above the electron-deficient π system. The structure of subunit **1a** shows that one fluorine atom of tetrafluoroborate points directly to the centre of the pentafluorophenyl unit. The distances between the fluorine atom and the carbon atoms of the arene are between 2.879 and 3.399 Å, and the

Table 1. Comparison of the anion-carbon atom separations [Å] of the different anions.

		1a	**1b**	**2**
	A = Br^-	(A = BF_4[a])	(A = BF_4[a])	(A = PF_6[b])
C1···A	3.943	4.298	4.247	4.499
C2···A	3.839	4.417	4.147	4.552
C3···A	3.809	4.384	3.896	4.331
C4···A	3.872	4.224	3.764	4.031
C5···A	4.007	4.125	3.888	3.996
C6···A	4.046	4.153	4.110	4.223
Centr.···A	3.669	4.039	3.768	4.048

[a] Estimated vdW radius: 2.85 Å
[b] Estimated vdW radius: 3.07 Å.

centroid$\cdots$FBF$_3$ distance is 2.829 Å. The separations between the anion and the electron-deficient unit are shorter than the sum of the corresponding van der Waals radii (ΣvdW) and indicate an η^6 anion–π interaction. In the second subunit **1b**, the anion is located above the π system as well. The anion is rotated so that three fluorine atoms are next to the arene. The distances between the fluorine atoms and the centroid are between 3.314 and 3.885 Å (Figure 1).

The solid-state structure of the 1-(pentafluorobenzylammonium)-4-aza-1-azoniabicyclo-[2.2.2]octane hexafluorophosphate was described earlier. It revealed that the octahedral hexafluorophosphate is located off centre, displaced to one of the edges of the electron-deficient arene. In addition, we were able to synthesise the related pentafluorobenzyl triethylammonium hexafluorophosphate (**2**). Accordingly, the solid-state structure of **2** shows a displacement of the anion to one of the edges of the pentafluorophenyl unit. In contrast to the previously reported hexafluorophosphate, the anion of **2** is only slightly off centre. As in all of our structures, the anion shows close CH$\cdots$PF$_6$ contacts, which direct the anion close to the centre of the arene. The closest distances between the centroid of the pentafluorophenyl unit and the fluorine atoms of the hexafluorophosphate are 3.301 and 3.533 Å and can be described as η^6. In addition to the anion–π contacts, the crystal structure of **2** reveals anion–π interactions with the pentafluorophenyl group of another ammonium cation. The distance between the centroid and the nearest fluorine atom of the anion is 3.561 Å. The closest C$\cdots$FPF$_5$ contacts are 3.086 and 3.345 Å. The interaction can be described as η^2 anion–π interaction (Figure 2).

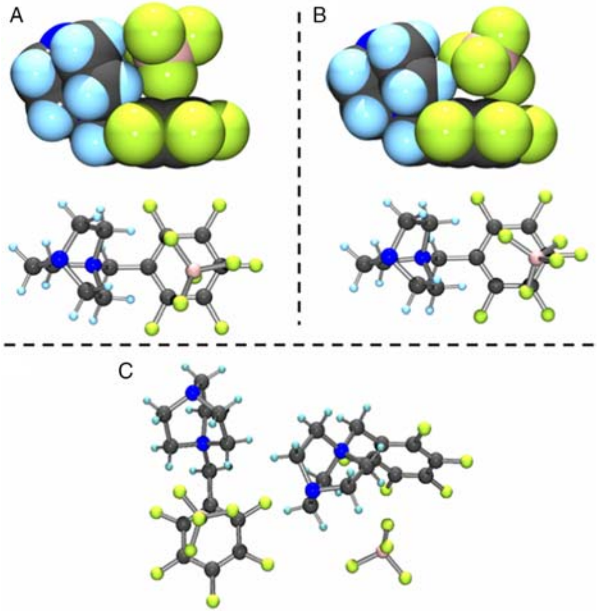


Figure 1. Part of the crystal structure of **1** showing the two different ion pairs in the unit cell (side and top view; A: **1a**, B: **1b**). C: molecular packing in the unit cell.

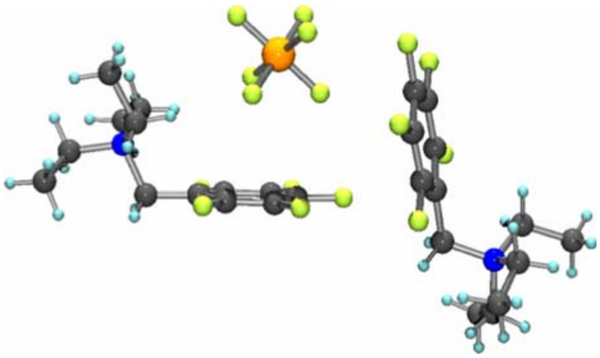


Figure 2. Part of the crystal structure of **2** showing anion–π contacts to two different pentafluorophenyl units (η^6 and η^2).

Comparison of the bromide, tetrafluoroborate and the hexafluorophosphate ammonium salts

Due to the different geometries of the anion bromide, tetrafluoroborate and hexafluoroborate, the comparison of distances is difficult. Therefore, the structures are compared by treating all anions as idealised spheres. The distances between the centre of the anions and the carbon atoms of the arene are listed. To discuss the hapticity of the different anion–π interactions, vdW radii of the tetrafluoroborate and the hexafluorophosphate were estimated. Therefore, the distance of the B—F or P—F bond from the crystallographic data was used and the vdW radius of fluorine was added.

By using the estimated vdW radii for tetrafluoroborate and hexafluorophosphate for the analysis of the distances between the carbon atoms of the arene and the centre of the anion, it becomes clear that all solid-state structures show close anion–π contacts. The comparison of the distances of tetrafluoroborate **1**, hexafluorophosphate **2** and the previously discussed bromide indicates an increase in the distance between the centroid and the anion, due to the increasing vdW radius of the corresponding anion. All C$\cdots$anion distances are within the range of the ΣvdW radii and can be described as η^6 anion–π interactions.

Moreover, the solid-state structure of tetrafluoroborate **1** reveals no directionality in the anion–π attraction. This is due to the fact that the anion–π interaction is caused by the electrostatic attraction between the anion and the positively polarised π system.

1-(Pentafluorobenzylammonium)-4-aza-1-azoniabicyclo-[2.2.2]octane nitrate (3)

The crystal structure of **3** shows two different anion–cation pairs in the unit cell (**3a** and **3b**). In one ion pair, the nitrate is located in a nearly parallel fashion with respect to the electron-deficient arene. The angle between the arene and the nitrate plane is about 4.52°. In the other ion pair, the nitrate plane is tilted with one oxygen atom pointing to the edge of the electron-deficient unit (angle between the planes: 45.03°). In both structures, the anion is fixed by short CH···anion contacts near the arene centre (CH···ONO_2: **3a**: 2.319, 2.415 Å, **3b**: 2.465, 2.474 Å). The distances between the carbon atoms of the C_6F_5 unit and the nitrogen atom of the nitrate are between 4.004 and 4.302 Å for **3a** and between 3.964 and 4.261 Å for **3b**. The distances from centromer to the nitrate anions are 3.924 Å (**3a**) and 3.876 Å (**3b**), which are clearly longer than the sum of vdW radii of the corresponding atoms. The closest contacts between the anion and the electron-deficient arene can be observed for **1b** between the carbon atoms in positions 5 and 6 and one oxygen atom of the nitrate (C_5···ONO_2: 3.145 Å, C_6···ONO_2: 3.297 Å). Those contacts are within the range of the sum of the vdW radii and can be described as η^2 anion–π interaction (Figure 3).

Attempts to synthesise 1-(pentafluorobenzylammonium)-4-aza-1-azoniabicyclo-[2.2.2]octane hydroxide failed. Instead of anion exchange, a nucleophilic substitution at the *para*-position of the pentafluorophenyl unit occurs and tetrafluorophenolate **4** in its betaine form was obtained. Betaine **4** was crystallised from methanol by slow diffusion of ethylacetate into the solution. The solid-state structure of **4** shows cocrystallisation with one molecule of methanol, which is hydrogen bonded to phenolate oxygen with OH···O distance of 2.646(2) Å and angle of 167(3)°. The phenolate oxygen of one molecule is in close contact (2.387 and 2.364 Å) to the CH groups of the second molecule. This leads to a stacked arrangement of the electron-deficient arenes with a π–π distance of 3.327 Å. Due to the strong directing effect of the CH–anion interaction and the electrostatic attraction between the ammonium nitrogen and the phenolate oxygen, the anionic terminus of betaine is not located above the centre of the pentafluorophenyl unit. The distances between the carbon atoms and the phenolate oxygen are within the range of 3.516–4.353 Å and significantly longer than the ΣvdW = 3.22 Å. However, two of the C···O distances are short enough to describe this interaction as an η^2 anion–π interaction (Figure 4).

1-(Pentafluorobenzylammonium)-4-aza-1-azoniabicyclo-[2.2.2]octane dibromoiodide (5)

The treatment of 1-(pentafluorobenzylammonium)-4-aza-1-azoniabicyclo-[2.2.2]octane bromide with BrI leads to the dibromoiodide salt, which could be crystallised from a mixture of methanol and ethylacetate. The crystal structure of interhalide **5** reveals that the linear Br(1)–I–Br(2)$^{-}$ anion (angle: 173.59°; Br(1)–I: 2.772 Å, Br(2)–I: 2.762 Å) is panelled by three pentafluorophenyl units which all show anion–π contacts with the interhalide. Moreover, the crystal structure reveals disordered interhalogen and additional bromide ions for charge compensation, which show no anion–π interactions in the solid state. The iodine atom of BrIBr– is centred above the π unit of the central pentafluorophenyl ammonium cation (C···I:

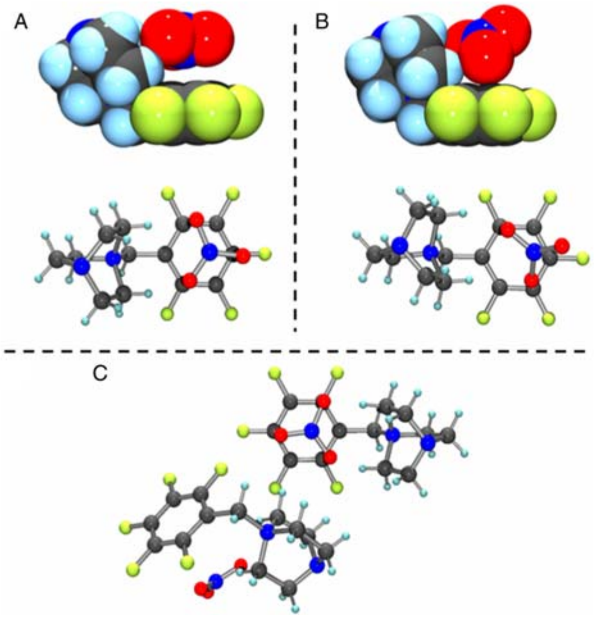


Figure 3. Part of the crystal structure of **3** showing a side and a top view of the two different ion pairs in the unit cell (A: **3a**, B: **3b**). C: molecular packing of the two different ion pairs in the unit cell.

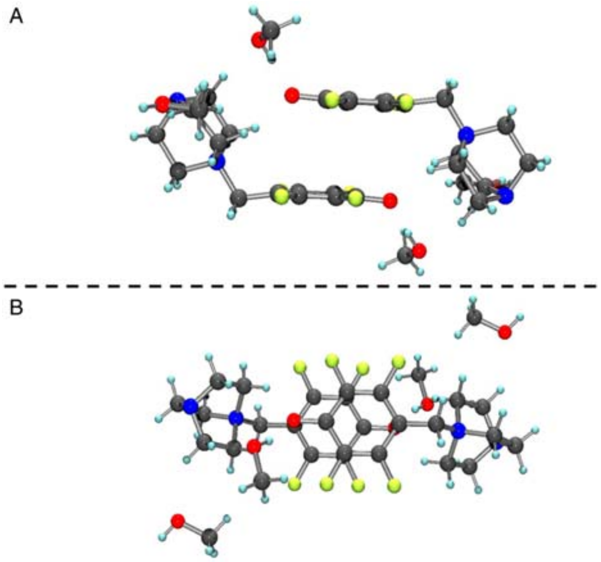


Figure 4. Part of the crystal structure of **4** showing a top (A) and a side view (B) of the betaine dimer with stacked arene units.

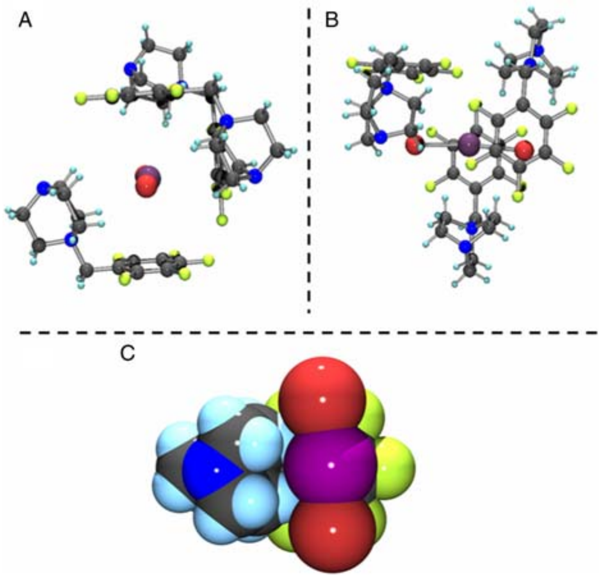


Figure 5. Crystal structure of **5** showing the Br–I–Br interhalide in a channel surrounded by pentafluorophenyl groups (A: side view; B: top view). C: central anion–cation pair showing the interhalide above the electron-deficient π system. The disordered interhalogen and the bromide anion for charge compensation were removed for clarity.

Table 2. Comparison of the anion-carbon atom separations [Å] of the different anions.

	A = Br	A = I	**5** (A = Br_1)	**5** (A = I)	**5** (A = Br_2)
C1···A	3.943	4.105	4.156	4.131	4.025
C2···A	3.839	3.898	3.976	4.141	3.798
C3···A	3.809	3.883	3.917	4.120	3.686
C4···A	3.872	3.942	4.037	4.032	3.770
C5···A	4.007	4.131	4.232	4.017	4.003
C6···A	4.046	4.207	4.287	4.071	4.129
Centr.···A	3.669	3.777	3.865	3.846	3.655

4.017–4.141 Å, centr.···I: 3.846). Also both bromine atoms show short distances to the electron-deficient arenes of the neighbouring cations (C···Br(1): 3.917–4.287 Å, centr.···Br(1): 3.865; C–Br(2): 3.686–4.129 Å, centr.···Br(2): 3.655). In comparison with the structural data from 1-(pentafluorobenzylammonium)-4-aza-1-azoniabicyclo-[2.2.2]octane bromide and iodide, it can be concluded that all three atoms of the interhalide show anion–π interactions, which can be described with η^3–η^6 (Figure 5).

Conclusion

The present structural study shows attractive interactions between spherical, linear, trigonal planar, tetrahedral and octahedral anions and pentafluorophenyl-ammonium cations. Hereby, the geometry of the anion seems to be less influential than the size of the anion. This matches excellently to the fact that the anion–π interaction is mainly based on the electrostatic attraction between the negatively charged anion and the positively polarised π system. Thus, no directed binding is expected. The big BF_4 and PF_6 anions as well as the spherical halide anions show short anion–π contacts. In contrast, the flat nitrate anion in **3** is fixed too far from the arene to show a symmetric η^6 anion–π interaction.

In addition, we were able to observe intermolecular anion–π interactions in the dimeric structure of ammonium tetrafluorophenolate betaine **6**. This might be a starting point for investigation on intramolecular anion–π interactions in betaine structures.

Moreover, a pentafluorophenyl panelled interhalide (**5**) was obtained.

We conclude that the presented structural results help to understand the nature and directionality of anion–π interactions with geometrically diverse anions. A final challenge will be to utilise this knowledge to design superior anion receptors for sensing, separation, stabilisation or catalysis.

Experimental section

Commercially available compounds were used as received. The solvents were used after distillation without further purification. NMR spectra were recorded in deuteric methanol by using a Varian Mercury 300 (^{1}H: 300 MHz, ^{19}F: 282 MHz). The mass spectrometric data were taken from Thermo Deca XP used as electrospray ionisation mass spectrometry (ESI). The IR spectra were obtained via PerkinElmer FT–IR spectrometer Spektrum 100 in KBr at 4000–650 cm^{-1}. The elemental analysis was carried out on CHN-O-Rapid Vario EL from Heraeus and the melting points were measured on a Büchi B540. X-ray data were collected at 123.0 ± 2 K with Bruker-Nonius KappaCCD diffractometer equipped with APEXII detector, using graphite monochromatised MoK_α radiation ($\lambda = 0.71073$ Å). COLLECT (*10a*) software was used for data collection and data were processed with DENZO-SMN (*10b*). The structures were solved by direct methods, using SIR-2004 (*10c*) and refined on F^2, using SHELXL-97 (*10d*). The multi-scan absorption correction [SADABS (*10e*)] was enabled to all data. The H atoms bonded to C atoms were calculated to their idealised positions with isotropic temperature factors (1.2 or 1.5 times the C atom temperature factor) and refined as riding atoms. The H atom bonded to O atom in **4** was found from electron density map and fixed to a distance of 0.84 Å from O atom (DFIX) with isotropic temperature factor (1.5 times the O atom temperature factor). The figures for publication were drawn with ORTEP-3 (*10f*), MERCURY (*10f*) and POV-RAY (*10h*).

Synthesis of 1-(pentafluorobenzylammonium)-4-aza-1-azoniabicyclo[2.2.2] octane tetrafluoroborate (1) and pentafluorobenzyltriethylammonium hexafluorophosphate (2)

Saturated solution of the pentafluorobenzylammonium bromide was treated with saturated aqueous solutions of ammonium tetrafluoroborate and hexafluorophosphate. The precipitated white solid was filtered off and washed three times with cold water (ca. 1–2 ml). The product was dried in vacuum.

Compound **1**

Yield: 54 mg of colourless solid, $M = 380.06$ g/mol, 0.70 mmol, 97%. M.p. 221.9°C; ^{1}H NMR (300 MHz, CD_3OD): δ (ppm) = 4.64 (m, 2H, H_{benz}); 3.45 (t, $^3J = 7.4$ Hz, 6H, CH_2); 3.20 (t, $^3J = 7.5$ Hz, 6H, CH_2); ^{19}F NMR (300 MHz, CD_3OD): δ (ppm) = –137.2 (m, 2F, F_{ortho}); – 151.2 (m, 1F, F_{para}), – 154.7 (m, 4F, BF_4^-), – 162.9 (m, 2F, F_{meta}); MS (EI, 70 eV): *m/z* (%) = 293.1 (10, $[M]^+$, $C_{13}H_{14}F_5N_2^+$), 181.1 (100, $C_7H_2F_5^+$); IR (KBr): ν (cm^{-1}) = 3036 (s), 1966 (s), 2898 (s), 2198 (s), 2165 (s), 2049 (s), 1993 (s), 1659 (m), 1530 (m), 1504 (w), 1470 (m), 1431 (s), 1408 (s), 1375 (m), 1309 (m), 1189 (s), 1137 (m), 1060 (w), 983 (m), 945 (m), 890 (m), 846 (m), 795 (m), 752 (s), 697 (s), 697 (s); elemental analysis calcd (%) for $C_{13}H_{14}N_2F_5BF_4$: C 41.08, H 3.71, N 7.37; found: C 41.09, H 3.62, N 7.39.

Compound **2**

Yield: 100 mg of colourless solid, $M = 427.09$ g/mol, 0.24 mmol, 88%. M.p. 171°C; ^{1}H NMR (300 MHz, CD_3OD): δ (ppm) = 4.66 (s, 2H, H_{benzyl}); 3.39 (q, $^3J = 7.2$ Hz, 6H, CH_2); 1.43 (t, $^3J = 7.2$ Hz, 9H, CH_3); ^{19}F NMR (300 MHz, CD_3OD): δ (ppm) = –74.86 (d, $^2J = 707.8$ Hz, PF_6); – 137.52 (m, 2F, F_{ortho}); – 151.31 (m, 1F, F_{para}); – 162.84 (m, 2F, F_{meta}); MS (ESI): *m/z* (%) = 282.20 (100, M^+, $C_{13}H_{17}F_5N^+$); IR (KBr): ν (cm^{-1}) = 3006 (w), 1660 (w), 1529 (m), 1510 (m), 1461 (w), 1405 (w), 1382 (w), 1308 (w), 1134 (w), 1016 (m), 981 (w), 938 (m), 827 (vs), 747 (w), 671 (w); elemental analysis calcd (%) for $C_{13}H_{17}F_5NPF_6$: C 36.55, H 4.01, N 3.28; found: C 36.61, H 3.75, N 3.30.

Synthesis of 1-(pentafluorobenzylammonium)-4-aza-1-azoniabicyclo[2.2.2] octane nitrate (3)

1-(Pentafluorobenzylammonium)-4-aza-1-azoniabicyclo[2.2.2] bromide (200 mg, 0.53 mmol, 1 eq.) was dissolved in 5 ml water and treated with a saturated solution of silver nitrate. The precipitated solid was filtered off. The desired compound (3) was obtained by evaporation of the water under reduced pressure. Yield: 149 mg of colourless solid, $M = 355.26$ g/mol, 0.42 mmol, 79%. M.p. 250.9°C, under decomposition; ^{1}H NMR (300 MHz, CD_3OD): δ (ppm) = 4.65 (s, 2H, H_{benz}); 3.45 (t, $^3J = 7.4$ Hz, 6H, CH_2); 3.19 (t, $^3J = 7.4$ Hz, 6H, CH_2); ^{19}F NMR (300 MHz, CD_3OD): δ (ppm) = –137.1 (m, 2F, F_{ortho}); – 151,1 (s, 1F, F_{para}), – 162.8 (m, 2F, F_{meta}); MS (ESI): *m/z* (%) = 293.2 (100, $[M]^+$, $C_{13}H_{14}F_5N_2^+$), 417.4 (100, $[M(NO_3)_2]^-$, $C_{13}H_{14}F_5N_4O_6^-$); IR (KBr): ν (cm^{-1}) = 3024 (s), 2970 (s), 2894 (s), 2386 (s), 2217 (s), 2167 (s), 2050 (s), 1974 (s), 1748 (s), 1659 (m), 1528 (m), 1504 (w), 1467 (m), 1409 (m), 1344 (w), 1314 (w), 1189 (s), 1134 (m), 1058 (m), 985 (m), 948 (w), 893 (m), 847 (m), 795 (m), 751 (s), 696 (m), 670 (m); elemental analysis calcd (%) for $C_{13}H_{14}F_5N_2NO_3$: C 43.95, H 3.97, N 11.83; found: C 43.83, H 3.35, N 11.75.

Synthesis of 1-(tetrafluorobenzyl-4-oxolate-ammonium)-4-aza-1-azoniabicyclo[2.2.2] octane (4)

To a solution of 1-(pentafluorobenzylammonium)-4-aza-1-azoniabicyclo[2.2.2] bromide (100 mg, 0.26 mmol, 1 eq.) in 40 ml of water was added silver(I)-oxide (93 mg, 0.40 mmol, 1.5 eq.). The suspension was stirred for 24 h in the darkness. The black solid was filtered off and the solvent was removed under reduced pressure. The remaining solid was recrystallised from methanol. Yield: 68 mg of pink solid, $M = 290.10$ g/mol, 0.23 mmol, 90%. M.p. 193°C; ^{1}H NMR (300 MHz, CD_3OD): δ (ppm) = 4.43 (s, 2H, H_{benzyl}); 3.37 (t, $^3J = 7.4$ Hz, 6H, CH_2); 3.16 (t, $^3J = 7.4$Hz, 6H, CH_2); ^{19}F NMR (300 MHz, CD_3OD): δ (ppm) = –146.93 (m, 2F, F_{ortho}); – 167.72 (m, 2F, F_{meta}); MS (ESI): *m/z* (%) = 291.7 (100, M^+, $C_{13}H_{15}F_4N_2O^+$); IR (KBr): ν (cm^{-1}) = 3221 (m), 3024 (m), 2975 (m), 2583 (s), 2274 (s), 2119 (s), 1994 (s), 1649 (w), 1502 (w), 1419 (m), 1370 (m), 1326 (s), 1288 (w), 1242 (m), 1169 (w), 1042 (w), 989 (w), 940 (w),884 (m), 848 (m), 800 (m), 737 (s), 676 (m); elemental analysis calcd (%) for $C_{13}H_{14}F_5N_2 \cdot 1.5\ H_2O$: C 49.21, H 5.40, N 8.83; found: C 49.71, H 5.52, N 8.94.

Synthesis of 1-(pentafluorobenzylammonium)-4-aza-1-azoniabicyclo[2.2.2] octane dibromoiodide (5)

To a solution of BrI (166 mg, 0.81 mmol, 1 eq.) in 10 ml dichloromethane was added a solution of 1-(pentafluorobenzylammonium)-4-aza-1-azoniabicyclo[2.2.2] bromide (300 mg, 0.81 mmol, 1 eq.) in 5 ml of water. The mixture was stirred for 30 min at room temperature. The organic layer was separated and dried over $MgSO_4$. The solvent was removed under reduced pressure and the light-brown solid was dried in vacuum. Yield: 70 mg of light-brown solid, $M = 579.97$ g/mol, 0.12 mmol, 15%. ^{1}H NMR (300 MHz, CD_3OD): δ (ppm) = 4.56 (s, 2H, H_{benz}); 3.36 (t, $^3J = 7.5$ Hz, 6H, CH_2); 3.11 (t, $^3J = 7.5$ Hz, 6H, CH_2); ^{19}F NMR (300 MHz, CD_3OD,): δ (ppm) = –137.1 (m, 2F, F_{ortho}); – 151.0 (m, 1F, F_{para}); – 162.7 (m, 2F,

F_{meta}); MS (EI, 70 eV): m/z (%) = 293.2 (100, $[M]^+$, $C_{13}H_{14}F_5N_2^+$); IR (KBr): ν (cm^{-1}) = 2963 (m), 2085 (s), 1997 (s), 1659 (m), 1527 (m), 1505 (w), 1460 (s), 1432 (s), 1407 (s), 1374 (m), 1319 (s), 1259 (m), 1187 (s), 1134 (m), 1054 (w), 1019 (w), 985 (m), 949 (m), 892 (m), 843 (m), 796 (w), 693 (m), 670 (m); elemental analysis calcd (%) for $C_{13}H_{14}Br_2F_5IN_2{\cdot}2H_2O$: C 25.35, H 2.95, N 4.55; found: C 25.97, H 3.04, N 3.94.

Crystal data

Compound **1**

Colourless plates from DMF/Et_2O, $C_{13}H_{14}BF_9N_2$, F.W. = 380.07, crystal size 0.16 × 0.15 × 0.11 mm, monoclinic, space group Pc (no. 7), $a = 14.0139(5)$, $b = 7.7727(3)$, $c = 14.9162(5)$ Å, $\beta = 114.846(2)°$, $V = 1474.37(9)$ Å^3, $Z = 4$ ($Z' = 2$), $D_{calc} = 1.712$ mg/m^3, $\mu = 0.181$ mm^{-1}, $F(000) = 768$, 17,984 collected reflections ($\theta_{max} = 25.25°$) of which 2663 are independent [$R_{int} = 0.0496$], $T_{max} = 0.9804$, $T_{min} = 0.9716$, full-matrix least-squares on F^2 with 8 restraints and 451 parameters, GOF = 1.093, $R_1 = 0.0355$ [I > 2σ(I)], wR_2 (all data) = 0.0822, largest peak/hole = 0.342/−0.174 e$^-$Å^{-3}. Two floating origin restraints were generated. Six more restraints were applied with SIMU (s = 0.01, st = 0.02) to equalise the U_{ij} parameters of B14 and F15. Friedel pairs were merged. Poor data/parameter ratio B level alert in CHECKCIF report appeared after merging the Friedel pairs.

Compound **2**

Colourless plates from DMF/EtOAc, $C_{13}H_{17}F_{11}NP$, F.W. = 427.25, crystal size 0.31 × 0.18 × 0.06 mm, orthorhombic, space group $Pca2_1$ (no. 29), $a = 19.9919(3)$, $b = 9.4637(2)$, $c = 17.5495(3)$ Å, $V = 3320.32(10)$ Å^3, $Z = 8$ ($Z' = 2$), $D_{calc} = 1.709$ mg/m^3, $\mu = 0.279$ mm^{-1}, $F(000) = 1728$, 40,557 collected reflections ($\theta_{max} = 25.25°$) of which 5956 are independent [$R_{int} = 0.0580$], $T_{max} = 0.9835$, $T_{min} = 0.9186$, full-matrix least-squares on F^2 with 1 restraints and 470 parameters, GOF = 1.034, $R_1 = 0.0378$ [I > 2σ(I)], wR_2 (all data) = 0.0894, largest peak/hole = 0.250/−0.273 e$^-$Å^{-3}. The crystal is a racemic twin and refined BASF parameter is 0.31(11). One floating origin restraint was generated.

Compound **3**

Colourless blocks from DMF/EtOAc, $C_{13}H_{14}F_5N_3O_3$, F.W. = 355.27, crystal size 0.40 × 0.33 × 0.26 mm, monoclinic, space group Pc (no. 7), $a = 13.9690(3)$, $b = 7.6105(2)$, $c = 14.9287(4)$ Å, $\beta = 115.581(2)°$, $V = 1431.51(6)$ Å^3, $Z = 4$ ($Z' = 2$), $D_{calc} = 1.648$ mg/m^3, $\mu = 0.160$ mm^{-1}, $F(000) = 728$, 17,286 collected reflections ($\theta_{max} = 25.25°$) of which 2563 are independent [$R_{int} = 0.0403$], full-matrix least-squares on F^2 with 2 restraints and 434 parameters, GOF = 1.077, $R_1 = 0.0292$ [I > 2σ(I)], wR_2 (all data) = 0.0720, largest peak/hole = 0.267/−0.168 e$^-$Å^{-3}. The crystal is a racemic twin and refined BASF parameter was 0.082(8) before merging the Friedel pairs. Two floating origin restraints were generated. Poor data/parameter ratio B level alert in CHECKCIF report appeared after merging the Friedel pairs.

Compound **4**

Colourless plates from MeOH/EtOAc, $C_{14}H_{18}F_4N_2O_2$, F.W. = 322.30, crystal size 0.22 × 0.19 × 0.06 mm, orthorhombic, space group $Pbca$ (no. 61), $a = 7.04490(10)$, $b = 16.4303(3)$, $c = 24.1718(4)$ Å, $V = 2797.88(8)$ Å^3, $Z = 8$, $D_{calc} = 1.530$ mg/m^3, $\mu = 0.138$ mm^{-1}, $F(000) = 1344$, 4682 collected reflections ($\theta_{max} = 25.25°$) of which 2525 are independent [$R_{int} = 0.0194$], full-matrix least-squares on F^2 with 1 restraint and 203 parameters, GOF = 1.093, $R_1 = 0.0411$ [I > 2σ(I)], wR_2 (all data) = 0.1056, largest peak/hole = 0.210/−0.230 e$^-$Å^{-3}.

Compound **5**

Red prisms from MeOH/EtOAc, $C_{78}H_{84}Br_9F_{30}I_7N_{12}$, F.W. = 3367.06, crystal size 0.19 × 0.10 × 0.07 mm, monoclinic, space group $P2/c$ (no. 13), $a = 14.2731(3)$, $b = 9.4406(2)$, $c = 39.3115(8)$ Å, $\beta = 103.7940(10)°$, $V = 5144.3(2)$ Å^3, $Z = 2$ ($Z' = 0.5$), $D_{calc} = 2.174$ mg/m^3, $\mu = 5.709$ mm^{-1}, $F(000) = 3184$, 16,033 collected reflections ($\theta_{max} = 25.25°$) of which 9247 are independent [$R_{int} = 0.0385$], full-matrix least-squares on F^2 with 0 restraint and 652 parameters, GOF = 1.028, $R_1 = 0.0493$ [I > 2σ(I)], wR_2 (all data) = 0.1208, largest peak/hole = 1.738/−0.928 e$^-$Å^{-3}.

CCDC-831302 (**1**), CCDC-831303 (**2**), CCDC-831304 (**3**), CCDC-831305 (**4**) and CCDC-831306 (**5**) can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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