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CH-Anion *versus* anion-π interactions in the crystal and in solution of pentafluorobenzyl phosphonium salts†

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A series of phosphonium salts with pentafluorobenzyl substituents have been synthesized and were investigated in the crystal as well as in solution. The solid state structures of **1a**, **1b** and **2d** reveal the presence of anion-π as well as CH-anion interactions. The two attractive, yet competitive forces seem to act in concert and a directing effect of the CH interaction on the relative position between anion and π-system is observed. The search for anion-π interactions in solution failed. Only CH-anion interactions proved to be important in solution.

Introduction

Supramolecular Chemistry is commonly defined as the chemistry beyond the molecule. It deals with intermolecular interactions of molecules and with the self-assembly of molecular multicomponent aggregates.[1] Just recently anion-π interaction was recognized as an important weak force being present in ionic systems with electron deficient aromatics. However, the literature reveals a rapidly growing interest in anion-π interactions within the last 20 years.[2]

In the early 1990s, Schneider *et al.* described some experimental evidence for anion-π interactions by observing a weak attraction between a negatively charged part of the molecule and a polarized π-system.[3] This early study was followed by theoretical investigations by Mascal, Alkorta and Dèya. They explained the attractive nature of the interaction of the π-cloud of an electron-deficient arene with an anion.[4]

Subsequently several groups reported on anion-π interactions, mainly in the crystalline state.[5]

In 2008 we started systematic studies on anion-π interactions of ammonium and phosphonium salts, utilizing the pentafluorophenyl unit as an appropriate electron deficient aromatic moiety.[6] Initial results showed the versatility of the binding motifs between anions and electron-deficient aromatics which might be controlled by strong directing effects like CH- and NH-anion interactions between the anion and hydrogen atoms at the cation. An already reported example for a pentafluorophenyl phosphonium salt exhibiting an anion-π interaction in the solid phase is shown in Fig. 1. The CH_{phenyl}-anion interaction fixes the ion above the pentafluorophenyl unit in a η^2 type binding motif.

The role of anion-π interactions in solution is still an open question. Early studies gave indications for the presence of anion-π interactions in solution, but they did not reveal if they are relevant for binding.[7]

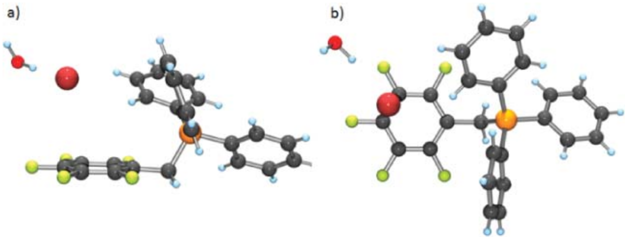

Fig. 1 Different views of the crystal structure of pentafluorobenzyl triphenyl phosphonium bromide showing anion-π interaction (η^2). One of the protons of the water is disordered and was removed for clarity (green: F, blue: H, black: C, yellow: P, brown: Br, red: O).[6]

In this manuscript, systematic investigations on anion-π interactions in the crystals of pentafluorobenzyl phosphonium salts with varying anions are described which are accompanied by NMR spectroscopic studies in solution.

Results and discussion

Based on the observation of the directing effects of substituents on the position of halide anions in the crystals of pentafluorobenzyl phosphonium and ammonium salts, phosphonium salts with different anions (halides, hexafluorophosphate, tetrafluoroborate or tetraphenylborate) were synthesized. The solid phase structures were investigated to show the presence of anion-π as well as CH-anion interactions. In addition, titration experiments were performed with the phosphonium salts of "noncoordinating" anions by adding *n*-tetrabutyl ammonium halides.

Synthesis of phosphonium compounds

The preparations of the phosphonium salts started from the corresponding phosphanes, which were reacted in a nucleophilic substitution with pentafluorobenzyl halides (**1a,b**, **2a**, **3a**). The phosphonium compounds with hexafluorophosphate, tetrafluoroborate or tetraphenylborate as anions **2b–2d** and **3b–3d** were obtained by salt metathesis from saturated, aqueous solutions.

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All compounds were characterized by standard analytical techniques. Crystals suitable for X-ray analysis were obtained for representative derivatives.

Solid state studies

Weak interactions are dominant intermolecular forces in crystals. They usually lead to well ordered arrays of molecules. In the following not the overall packing of the crystals will be described, but relevant anion-π and π–π interactions between neighbouring species (especially anions and cations) will be the focus of attention.

Pentafluorobenzyl-dimethylphenyl phosphonium bromide and iodide (1a,b). A part of the crystal structure of dimethylphenyl phosphonium bromide **1a**$\cdot\frac{1}{2}H_2O$ is shown in Fig. 2a. It reveals an asymmetric anion-π interaction between bromide and the pentafluorophenyl moiety which can be best described as "η^1" or maybe as "η^3". The closest anion-π contact is found between bromide and the 3-position of the arene ($C_{meta}\cdots Br = 3.451(5)$ Å, $C_{para}\cdots Br = 3.696(5)$ Å, $C_{ortho}\cdots Br = 3.895(5)$ Å). Additionally the anion forms CH-hydrogen bonds with the methyl (two molecules in asymmetric unit, $CH_{methyl}\cdots Br = 3.35(3)$ Å and 2.93(3) Å) and phenyl group ($CH_{phenyl}\cdots Br = 2.92(3)$ Å) and in every second case with cocrystallized water ($OH\cdots Br = 2.50(2)$ Å). The different types of CH-anion bonds determine the position of the bromide on top of the pentafluorophenyl system and lead to the observed asymmetric binding motif. The same structure controlling effect was described before for the corresponding ammonium salt.[6b] The cocrystallized water molecule forms a pair with another water by $OH\cdots O$ interaction ($O\cdots O$ distance 2.929(9) Å) leading to disordered H-atom locations. One hydrogen of four of this pair misses an H-bond acceptor, while another participates in an $OH\cdots O$ contact and the remaining two in $OH\cdots Br$ contacts.[6a]

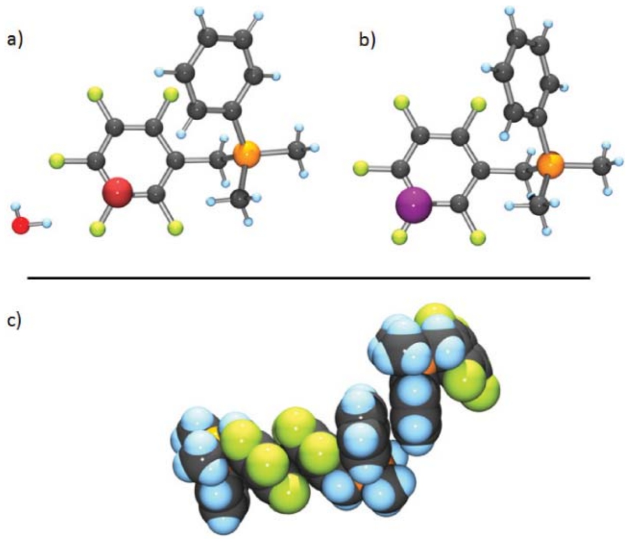

Fig. 2 (a) Part of the crystal structure of **1a**$\cdot\frac{1}{2}H_2O$ showing the η^1 type interaction between bromide and the pentafluorophenyl unit. One of the disordered protons of the water is omitted for clarity. (b) Part of the crystal structure of **1b**. (c) Molecular packing in the structure of **1b** showing the face-to-face orientation of homologous arenes (green: F, blue: H, black: C, yellow: P, brown: Br, magenta: I, red: O).

A structure very similar to that of **1a** is found for the dimethylphenyl phosphonium iodide **1b**. Here the solid phase structure again reveals a η^1 type binding motif for the iodide. In contrast to **1a**, structure **1b** (Fig. 2b) shows no cocrystallisation of water. The distances between the pentafluorophenyl group and the anion are longer in **1b** (two molecules in asymmetric unit, $C_{meta}\cdots I = 3.764(4)$ Å, $C_{para}\cdots I = 4.044(5)$ Å, $C_{ortho}\cdots I = 4.095(4)$ Å and $C_{meta}\cdots I = 3.657(4)$ Å, $C_{para}\cdots I = 3.675(5)$ Å, $C_{ortho}\cdots I = 4.322(4)$ Å) due to the larger van der Waals radius of iodide compared to bromide. The CH-anion interactions of the iodide **1b** (two molecules in asymmetric unit, $CH_{methyl}\cdots I = 2.93(3)$ Å and 3.10(3) Å, $CH_{phenyl}\cdots I = 3.21(3)$ Å and 3.28(4) Å) are very similar to those found in the bromide **1a**.

The observation of very similar structures for **1a** and **1b** in the solid state (despite the difference of cocrystallization of water in the case of **1a**) indicates that the cation-anion ensemble possessing anion-π as well as CH-anion interactions is a discrete building block in the crystal.

In both structures **1a** and **1b**, the molecular packing reveals face-to-face orientation of either two pentafluorophenyl or two phenyl groups, respectively (*e.g.* Fig. 2c). The distances between the centromers of the pentafluorophenyl groups (**1a**: c_1-c_2 = 3.829(7) Å, **1b**: c_1-c_2 = 3.611(6) Å) are in both complexes a bit shorter than the centromer distances in the electron-richer systems (**1a**: c_3-c_4 = 4.074(7) Å, **1b**: c_3-c_4 = 4.161(7) Å).

Pentafluorobenzyl triphenyl phosphonium tetraphenylborate 2d. Crystals of the salt **2d** were obtained from an aqueous solution of **2a** by adding a saturated solution of sodium tetraphenylborate in water. They formed within minutes. The analysis of **2d** regarding interactions between anion and cation is difficult due to the geometric requirement of the anion. It reveals several edge-to-face type orientations of the phenyl groups of the differently charged ions. The observation of a phenylic hydrogen atom pointing towards the center of the electron-deficient arene with a separation of only 2.95(2) Å is rather unexpected (Fig. 3b).

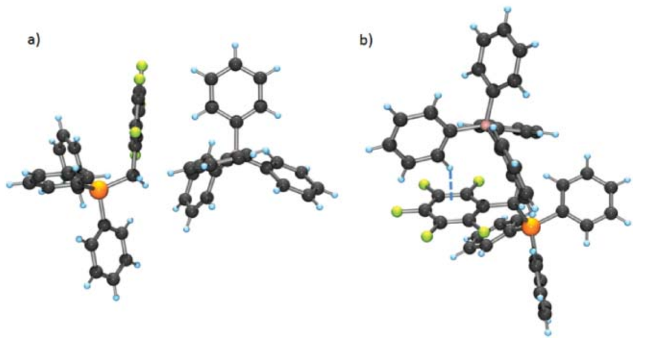

Fig. 3 X-ray structure of pentafluorobenzyl triphenyl phosphonium tetraphenylborate **2d** showing the anion cation pair (a) and CH-π interactions (b) (green: F, blue: H, black: C, yellow: P, pink: B).

The earlier described crystal structure of **2a** with the same cation as in **2d** but with bromide instead of tetraphenylborate reveals anion-π interactions. The bromide is directed above two carbon atoms of the pentafluorophenyl unit ($C^4\cdots Br = 3.70$ Å, $C^4\cdots Br = 3.71$ Å) by CH-anion bonding to phenylic hydrogen atoms ($C^2H\cdots Br = 2.92$ Å, $C^3H\cdots Br = 3.14$ Å).[6a]

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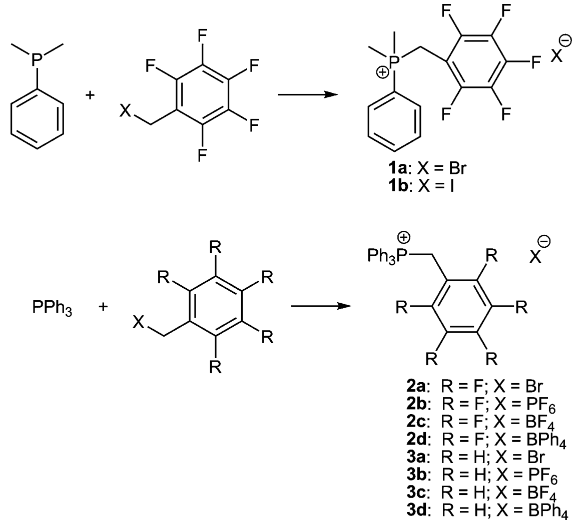
A literature search on the corresponding non-fluorinated benzyl triphenylphosphonium compounds does not reveal any anion-π interactions.[8] The results described herein show in addition to many reports in the literature[9] that anion-π interactions are commonplace in solids containing electron deficient aromatics as well as anions. The question remains whether anion-π interactions are important in solution as well.

Solution studies

As already mentioned in the introduction, some attempts were made to investigate anion-π interactions in solution.[7] Evidence was collected, but the existence of this weak interaction could not be finally proven. Strong solvation of the anions competes with the anion-π interaction and thus might suppress it.

In the present study we performed NMR titration experiments with the hexafluorophosphate **2b** and tetrafluoroborate **2c** salts and with the analogues **3b** and **3c** with phenyl instead of the electron deficient unit. *n*-Tetrabutyl ammonium halides (Cl, Br, I) were successively added to the PF_6 and BF_4 salts and differential binding constants were determined. Additionally, *n*-butylammonium hexafluorophosphate and tetrafluoroborate were added for comparison to exclude effects due to polarity changes of the medium and to show that no significant binding occurs between those “less-coordinating” anions and the cationsScheme 1.



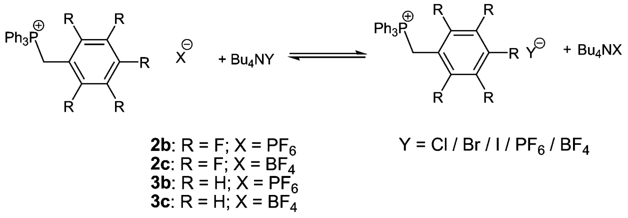
Scheme 1 Preparation of pentafluorobenzyl phosphonium salts **1–3**.

The corresponding tetraphenylborate **2d** could not be used in this study due to its low solubility in chloroform.

Scheme 2 summarizes the solution equilibria, assuming that contact ion pairs are present but solvent separated ion pairs are not. Shifting of proton NMR signals of the phosphonium cation during the titration reveals that some interactions between the cation and anion occur. The benzylic CH_2 group proved to be an appropriate NMR probe to follow this cation-anion interaction.

Initially Jobs method of continuous variation was used to show a 1 : 1 stoichiometry in the interaction of anions with cations (Fig. 4a).[10]

Following this, NMR-titrations were performed in $CDCl_3$ with a concentration of 0.01 M of **2b,c** or **3b,c**, respectively. The tetrabutylammonium halide was added as a solution in $CDCl_3$ (0.04 M). Titration curves (Fig. 4c) were obtained by following the abovementioned benzylic NMR signal (Fig. 4b) and were analyzed by standard methods of nonlinear regression.[10] The determined differential binding constants are summarized in Table 1.



Scheme 2 Anion-exchange equilibrium.

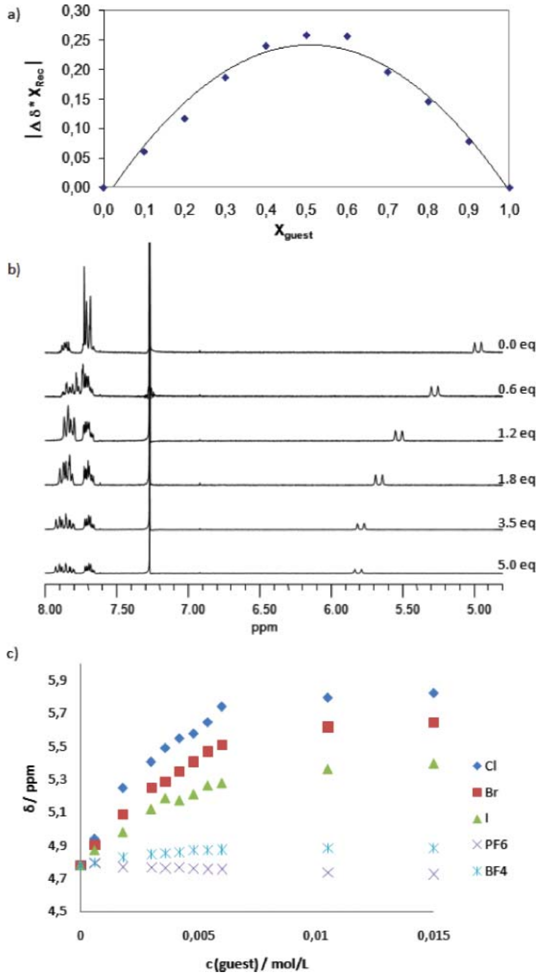


Fig. 4 (a) Representational Job-Plot for the titration of **2b** with *n*-Bu_4NCl. (b) Selected NMR spectra for the corresponding anion receptor system. *n*-Bu_4NCl (0.04 M solution) was successively added to a 0.01 M solution of **2b**. (c) Resulting ^1H NMR shift during the titration of **2b** with different tetrabutyl ammonium salts.

Reference experiments with *n*-Bu_4NPF_6 and *n*-Bu_4NBF_4 (Fig. 4c) did not show any significant shifting of the resonance of the benzylic protons, indicating no pronounced interaction of the complex anions with the CH_2 group.

All binding constants for halide anions are found in the range of 960 to 1610 M^{-1}. There is no significant preference of the

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Table 1 Differential binding constants K_a [M^{-1}] for the 1 : 1 complex of phosphonium salts with various anions (Cl, Br and I added as tetrabutyl ammonium salts). The binding constants were determined by ^1H NMR titration experiments in $CDCl_3$. The proton signal of the benzylic group was observed. Errors are estimated to be lower than 20%

	Cl	Br	I
2b	1610	1050	1020
2c	1390	1120	1240
3b	1120	1140	1150
3c	1200	960	1180

cations for a specific anion and no preference of the anion for either fluorinated or non-fluorinated cations. In addition to the ^1H NMR spectra, a series of ^{19}F NMR spectra was collected. For significant interactions of the anions with the π-system a shifting of the fluoride signal should be expected. This was not observed.

These results indicate that the detected ^1H NMR shifting upon addition of halides to the tetrafluoroborate or hexafluorophosphate salts is not caused by anion-π interactions but rather by CH-anion interactions of the highly acidic benzyl phosphonium protons.

Conclusion

In conclusion, it was possible to observe anion-π interactions between pentafluorobenzylphosphonium salts and different anions in the solid phase. Hereby, directing influences of CH-anion interactions control the position of the anions above the electron-deficient systems. Anion-cation interactions in pentafluorobenzyltriphenyl phosphonium tetraphenylborate **2d** rely mainly on interactions between the π-systems of the aromatic groups.

NMR titrations give no indication of anion-π interactions in chloroform solutions of the investigated cations. Interactions appear to occur mainly between the most acidic benzylic protons and the anions. No significant differences could be detected for the benzylic or pentafluorobenzylic derivatives, which could be indicative for anion-π interactions.

Fig. 5 shows as a representative example a part of the crystal structure of **1b** depicting the anion-π interaction between iodide and the pentafluorophenyl moiety as well as CH-anion binding of the benzylic group with a second iodide. In solution the latter interaction seems to be dominant while the anion-π interactions are of minor importance or maybe not present at all.

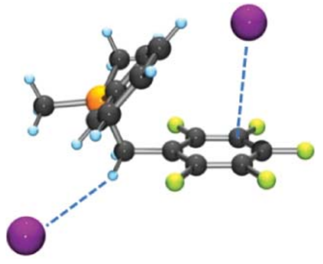

Fig. 5 Part of the crystal structure of **1b** showing the anion-π interaction between the cation and the anion as well as the competing CH-anion interaction of the benzylic unit.

The present study shows that weak anion-π interactions can be easily overridden in solution by other non-covalent interactions like CH-anion binding, solvent effects or electrostatic effects. While this interaction can be observed in many crystal structures, it is highly difficult to find clear evidence for it in solution.

Experimental

Commercially available reagents were used as received. The solvents were used after distillation without any further purification. NMR spectra were taken on a Varian Mercury 300 NMR spectrometer (^1H: 300 MHz, ^{19}F: 282 MHz) in deuteric chloroform. For mass spectrometric data, Finnigan SSQ 7000 and Thermo Deca XP were used as EI (70 eV) or ESI. IR spectra were obtained *via* a PerkinElmer FTIR spectrometer Spektrum 100. The samples were measured in KBr at 4000–650 cm^{-1}. CHN–O-Rapid Vario EL from Heraeus was used for elemental analysis. Melting points were measured on a Büchi B540 and are not corrected. Single crystal X-ray data of **1a**, **1b** and **2d** were collected at 123(2) K using a Bruker-Nonius KappaCCD diffractometer with APEX-II detector and graphite monochromatized Mo-Kα (λ = 0.71073 Å) radiation. COLLECT[11] software was used for the data collection (θ and ω scans) and DENZO-SMN[12] for the processing. The structures were solved by direct methods with SIR2004[13] and refined by full-matrix least-squares methods with WinGX-software,[14] which utilizes the SHELXL-97 module.[15] Lorentzian polarization correction was applied on all data and multi-scan absorption correction (SADABS[16]) for **1a** and **1b**. All C–H hydrogen positions were calculated and refined as riding atom model with 1.2 and 1.5 times the thermal parameter of the C atoms, respectively. Disordered H-atoms of the water molecule in **1a** were found from the electron density map and fixed (by DFIX) to a distance of 0.84 Å from the O atom and 1.4 Å from each other. Thermal parameters were set to 1.5 times that of the O atom parameter.

Synthesis of compounds

Synthesis of pentafluorobenzyl-dimethylphenyl phosphonium bromide 1a. Equimolar amounts of dimethylphenylphosphane (53 mg, 0.38 mmol) and pentafluorobenzyl bromide (100 mg, 0.38 mmol) were added to a round bottom flask and stirred for 24 h at room temperature. The resulting white block of solid was crushed and dried under vacuum.

Yield: 110 mg colorless solid (M = 397.99 g mol^{-1}, 0.28 mmol, 72%). - M.p.: 194 °C. - ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.92–7.79 (m, 3H, H_{aryl}), 7.70–7.62 (dt, ^3J = 8.5/3.2 Hz, 2H, H_{aryl}), 4.21 (d, ^2J = 15.8 Hz, 2H, H_{benz}), 2.39 (d, ^2J = 14.8 Hz, 6H, CH_3). - ^{19}F NMR ($CDCl_3$, 300 MHz): δ (ppm) = −139.3 (m, 2F, F_{meta}), −154.7 (m, 1F, F_{para}), −161.8 (m, 2F, F_{ortho}). - MS (EI): m/z (%) = 318.3 (63 $M–H^+$, $C_{15}H_{13}F_5P^+$). - IR (KBr): ν/cm^{-1} = 3054 (w), 2949 (m), 2915 (w), 2882 (m), 2803 (w), 2210 (w), 2165 (w), 2084 (w), 2034 (w), 1991 (w), 1952 (w), 1658 (w), 1588 (w), 1507 (vs), 1440 (m), 1412 (m), 1368 (w), 1346 (w), 1308 (m), 1243 (w), 1183 (w), 1121 (s), 1055 (w), 1034 (w), 994 (vs), 964 (vs), 948 (vs), 906 (m), 888 (m), 841 (w), 784 (m), 742 (s), 715 (m), 686 (s).- $C_{25}H_{17}BrF_5N$: C 45.14, H 3.28, found: C 45.33, H 3.30.

Synthesis of pentafluorobenzyl iodide. To a solution of pentafluorobenzyl bromide (2.5 g, 9.62 mmol) in 20 ml acetone was added sodium iodide (2.88 g, 19.24 mmol). The suspension

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was stirred for 48 h at room temperature in the dark. Then 5 mL water was added. The organic layer was dried over sodium sulfate and the solvent was removed under reduced pressure.

Yield: 1.70 g brown solid (M = 307.91 g mol^{-1}, 5.52 mmol, 57%). - M.p.: 58 °C. - ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 4.36 (t, J (HF) = 1.5 Hz, 2H, H_{benz}). - ^{19}F NMR ($CDCl_3$, 300 MHz): δ (ppm) = −142.25 (m, 2F, F_{ortho}), −154.05 (m, 1F, F_{para}), −161.4 (m, 2F, F_{meta}). - MS (EI): m/z (%) = 307.9 (5 M$^+$, $C_7H_2F_5I^+$), 181.0 (100, $C_7H_2F_5^+$). - IR (KBr): ν/cm^{-1} = 3043 (w), 2962 (w), 2655 (w), 2325 (w), 2087 (w), 1713 (w), 1656 (m), 1589 (w), 1569 (w), 1500 (vs), 1425 (m), 1389 (w), 1313 (w), 1286 (w), 1260 (w), 1159 (m), 1130 (m), 1116 (s), 1045 (w), 1021 (w), 963 (vs), 842 (w), 800 (w), 736 (w), 660 (w).- $C_7H_2F_5I$: C 27.30, H 0.65, found: C 27.18, H 0.70.

Synthesis of pentafluorobenzyl-dimethylphenyl phosphonium iodide 1b. To a solution of dimethylphenyl phosphine (90 mg, 0.65 mmol) in 15 mL of toluene a solution of pentafluorobenzyl iodide (200 mg, 0.65 mmol) in 5 mL of toluene was added dropwise. The mixture was heated to 120 °C for 3 h. The solvent was removed under reduced pressure and the light-yellow solid was dried.

Yield: 150 mg light yellow solid (M = 445.97 g mol^{-1}, 0.24 mmol, 52%). - M.p.: 254 °C. - ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.85–7.63 (m, 5H, H_{aryl}), 2.77 (d, ^{2}J = 13.2 Hz, 2H, H_{benz}), 1.75 (d, ^{2}J = 13.2 Hz, 6H, CH_3). - ^{19}F NMR ($CDCl_3$, 300 MHz): δ (ppm) = −137.2 (m, 2F, F_{meta}), −150.0 (m, 1F, F_{para}), −158.8 (m, 2F, F_{ortho}). - MS (EI): m/z (%%) = 318.2 (3 M–H$^+$, $C_{15}H_{13}F_5P^+$). - IR (KBr): ν/cm^{-1} = 3058 (w), 2952 (m), 2883 (m), 2801 (w), 2257 (w), 2084 (w), 1902 (w), 1658 (w), 1588 (w), 1508 (vs), 1440 (m), 1409 (m), 1346 (w), 1309 (m), 1244 (w), 1182 (w), 1121 (s), 1034 (w), 994 (vs), 964 (vs), 946 (s), 886 (m), 837 (w), 784 (w), 742 (s), 715 (m), 685 (s).- $C_{25}H_{17}BrF_5P$: C 40.38, H 2.94, found: C 40.39, H 3.00.

Synthesis of pentafluorobenzyl 2a and benzyl triphenylphosphonium bromide 3a. Equimolar amounts of triphenyl phosphane and pentafluorobenzyl bromide were dissolved in toluene. The mixture was heated to 120 °C for 3h. Then the precipitate was filtered off and dried in vacuum.

2a: Yield: 0.9 g colorless solid (M = 522.02 g mol^{-1}, 1.70 mmol, 45%). - M.p.: 244 °C. - ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.99–7.95 (m, 3H, H_{aryl}), 7.84–7.76 (m, 12H, H_{aryl}), 5.30 (d,^{2}J = 14.1 Hz, 2H, H_{benz}). - ^{19}F NMR ($CDCl_3$, 300 MHz): δ (ppm) = −137.9 (m, 2F, F_{ortho}), −152.3 (m, 1F, F_{para}), −161.4 (m, 2F, F_{meta}). - MS (EI): m/z (%) = 442.3 (80, $C_{25}H_{16}F_5P^+$). - IR (KBr): ν/cm^{-1} = 3061 (m), 3009 (w), 2952 (w), 2849 (w), 2764 (w), 2212 (w), 2108 (w), 2006 (w), 1813 (w), 1656 (w), 1586 (w), 1520 (m), 1503 (s), 1435 (m), 1392 (w), 1309 (w), 1251 (w), 1191 (w), 1160 (w), 1110 (s), 1033 (w), 973 (vs), 865 (w), 838 (w), 753 (s), 725 (s), 686 (s).- $C_{25}H_{17}BrF_5P$: C 57.38, H 3.26, found: C 58.11, H 3.59.

3a: Yield: 953 mg colorless solid (M = 434.33 g mol^{-1}, 2.19 mmol, 95%). - M.p.: 241 °C. - ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.81–7.71 (m, 9H, H_{aryl}), 7.67–7.61 (m, 6H, H_{aryl}), 7.25–7.19 (m, 1H. H_{aryl}), 7.16–7.08 (m, 4H, H_{aryl}) 5.42 (d, ^{2}J = 13.7 Hz, 2H, H_{benz}). - MS (ESI): m/z (%) = 353.17 (100 M$^+$, $C_{25}H_{22}P^+$). - IR (KBr): ν/cm^{-1} = 3662 (w), 3374 (w), 3051 (w), 2984 (w), 2853 (m), 2774 (w), 2260 (w), 2103 (w), 1986 (w), 1907 (w), 1602 (w), 1585 (w), 1484 (m), 1455 (w), 1435 (s), 1333 (w), 1316 (w), 1250 (w), 1187 (w), 1162 (m), 1109 (s), 1072 (m), 1030 (w), 994 (m), 921 (w), 873 (m), 823 (w), 790 (m), 751 (s), 718 (s), 688 (vs).- $C_{25}H_{22}P$: C 69.29, H 5.12, found: C 69.13, H 5.45.

Synthesis of the phosphonium hexafluorophosphates 2b, 3b, tetrafluoroborates 2c, 3c and tetraphenylborates 2d, 3d. To saturated solutions of the phosphonium bromides, solutions of ammonium hexafluorophosphate, ammonium tetrafluoroborate or sodium tetrafluoroborate were added dropwise until precipitation stopped. The white solids were filtered off and dried under reduced pressure.

2b: Yield: 743 mg colorless solid (M = 588.33 g mol^{-1}, 1.26 mmol, 74%). - M.p.: 215 °C. - ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.90–7.83 (m, 3H, H_{aryl}), 7.74–7.59 (m, 12H, H_{aryl}), 4.78 (d, ^{2}J = 13.6 Hz, 2H, H_{benz}). - ^{19}F NMR ($CDCl_3$, 300 MHz): δ (ppm) = −72.91 (d, ^{2}J = 756 Hz, 6F, PF_6), −137.14 (d, ^{2}J = 18.13 Hz, 2F, F_{meta}), −150.18 (t, ^{2}J = 21.151 Hz, F, F_{para}), −159.52 (t, ^{2}J = 18.130 Hz, 2F, F_{ortho}). - MS (ESI): m/z (%) = 443.2 (100 M$^+$, $C_{25}H_{16}P^+$). - IR (KBr): ν/cm^{-1} = 2928 (w), 1660 (w), 1588 (w), 1507 (m), 1440 (m), 1403 (w), 1310 (w), 1195 (w), 1112 (m), 974 (s), 830 (vs), 749 (m), 724 (m), 686 (m).- $C_{25}H_{17}F_5PPF_6$: C 51.04, H 2.91, found: C 50.95, H 2.82.

3b: Yield: 685 mg colorless solid (M = 498.38 g mol^{-1}, 1.36 mmol, 69%). - M.p.: 234 °C. - ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.83–7.76 (m, 3H, H_{aryl}), 7.68–7.61 (m, 6H, H_{aryl}), 7.55–7.47 (m, 6H, H_{aryl}), 7.28–7.26 (m, 1H, H_{aryl}), 7.16 (t, ^{3}J = 7.8 Hz, 2H, H_{aryl}), 6.91 (d, ^{3}J = 7.8 Hz, 2H, H_{aryl}), 4.58 (d, ^{2}J = 13.8 Hz, 2H, H_{benz}). - ^{19}F NMR ($CDCl_3$, 300 MHz): δ (ppm) = −72.61 (d, ^{2}J = 759 Hz, 6F, PF_6). - MS (EI): m/z (%) = 353.17 (14 M$^+$, $C_{22}H_{22}P$). - IR (KBr): ν/cm^{-1} = 3066 (w), 1590 (w), 1489 (w), 1440 (m), 1413 (w), 1337 (w), 1238 (w), 1191 (w), 1164 (w), 1143 (w), 1113 (m), 1069 (w), 1033 (w), 998 (w), 925 (w), 876 (w), 824 (vs), 785, (m), 747 (m), 720 (m), 700 (m), 686 (s).- $C_{25}H_{22}PPF_6$: C 60.25, H 4.45, found: C 60.15, H 4.41.

2c: Yield: 608 mg colorless solid (M = 530.17 g mol^{-1}, 1.15 mmol, 61%). - M.p.: 198 °C. - ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.88–7.83 (m, 3H, H_{aryl}), 7.72–7.65 (m, 12H, H_{aryl}), 4.95 (d, ^{2}J = 13.8 Hz, 2H, H_{benz}). - ^{19}F NMR ($CDCl_3$, 300 MHz): δ (ppm) = −136.80 (m, 2F, F_{meta}), −150.50 (m, 1F, F_{para}), −152.23 (m, ^{2}J = 12.1 Hz, 4F, BF_4), −159.66 (m, 2F, F_{ortho}). - MS (ESI): m/z (%) = 443.25 (100 M$^+$, $C_{25}H_{16}F_5P^+$). - IR (KBr): ν/cm^{-1} = 3642 (w), 3556 (w), 3070 (w), 2975 (w), 2909 (w), 2079 (w), 1987 (w), 1937 (w), 1656 (w), 1619 (w), 1587 (w), 1506 (s), 1439 (m), 1403 (m), 1371 (w), 1322 (w), 1286 (w), 1248 (w), 1194 (w), 1111 (s), 1054 (vs), 980 (vs), 968 (vs), 850 (m), 754 (s), 726 (s), 691 (s).- $C_{25}H_{17}F_5PBF_4$: C 55.63, H 3.31, found: C 55.42, H 3.36.

3c: Yield: 853 mg colorless solid (M = 440.22 g mol^{-1}, 1.94 mmol, 85%). - M.p.: 215 °C. - ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.88 (t, ^{3}J = 8.3, 3H, H_{aryl}), 7.68–7.50 (m, 12H, H_{aryl}), 7.25–7.20 (m, 1H, H_{aryl}), 7.14 (t, ^{3}J = 7.9 Hz, 2H, H_{aryl}), 6.93 (d, ^{3}J = 7.9 Hz, 2H, H_{aryl}), 4.77 (d, ^{2}J = 14.3 Hz, 2H, H_{benz}). - ^{19}F NMR ($CDCl_3$, 300 MHz): δ (ppm) = −151.99 (d, ^{2}J = 12.1 Hz, 4F, BF_4). - MS (ESI): m/z (%) = 353.84 (14 M$^+$, $C_{25}H_{22}P^+$). - IR (KBr): ν/cm^{-1} = 3068 (w), 3030 (w), 2973 (w), 2931 (w), 2219 (w), 2084 (w), 1982 (w), 1740 (m), 1587 (w), 1487 (w), 1455 (w), 1438 (s), 1418 (w), 1367 (w), 1286 (w), 1230 (w), 1216 (w), 1193 (w), 1166 (w), 1110 (s), 1058 (vs), 925 (w), 857 (m), 821 (w), 788 (m), 749 (s), 719 (s), 688 (vs).- $C_{25}H_{22}PBF_4$: C 68.21, H 5.04, found: C 67.89, H 4.68.

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2d: Yield: 120 mg colorless solid ($M = 762.59$ g mol^{-1}, 0.16 mmol, 60%). - M.p.: 183 °C. - ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.74–7.69 (m, 3H, H_{aryl}), 7.52–7.43 (m, 6H, $H_{aryl, cation}$), 7.30–7.23 (m, 6H, H_{aryl}), 7.06–6.97 (m, 4H, H_{aryl}), 6.83–6.73 (m, 16H, H_{aryl}), 3.32 (d, $^2J = 13.1$ Hz, 2H, H_{benz}). - ^{19}F NMR ($CDCl_3$, 300 MHz): δ (ppm) = −135.88 (m, 2F, F_{meta}), −150.38 (m, 2F, F_{para}), −159.52 (m, 2F, F_{ortho}). - MS (ESI): m/z (%) = 443.1 (100 M$^+$, $C_{25}H_{16}F_5P$). - IR (KBr): ν/cm^{-1} = 3620 (w), 3371 (w), 3201 (w), 3053 (w), 2932 (w), 2869 (w), 2784 (w), 2210 (w), 2095 (w), 1994 (w), 1940 (w), 1828 (w), 1656 (w), 1583 (w), 1505 (vs), 1437 (s), 1314 (w), 1262 (w), 1197 (w), 1110 (s), 1032 (w), 976 (vs), 847 (m), 751 (s), 725 (vs), 690 (vs)- $C_{25}H_{17}F_5PBC_{24}H_{20}$: C 77.17, H 4.89, found: C 77.05, H 4.76.

3d: Yield: 90 mg colorless solid ($M = 672.64$ g mol^{-1}, 0.13 mmol, 45%). - M.p.: 231.2 °C. - ^{1}H NMR (DMSO, 300 MHz): δ (ppm) = 7.94–7.86 (m, 3H, H_{aryl}), 7.78–7.61 (m, 12H, H_{aryl}), 7.32–7.12 (m, 12H, H_{aryl}), 7.00–6.88 (m, 10H, H_{aryl}), 6.82–6.74 (m, 3H, H_{aryl}), 5.13 (d, $^2J = 15.9$ Hz, 2H, H_{benz}). - MS (ESI): m/z (%) = 353.2 (100 M$^+$, $C_{25}H_{22}P^+$). - IR (KBr): ν/cm^{-1} = 3053 (m), 3001 (w), 2941 (w), 2899 (w), 2165 (w), 1949 (w), 1582 (m), 1480 (m), 1437 (m), 1401 (w), 1339 (w), 1269 (w) 1184 (w), 1146 (w), 1111 (m), 1068 (w), 1031 (m), 997 (w), 922 (w), 849 (m), 833 (m), 786 (m), 732 (s), 704 (vs).- $C_{25}H_{22}PBC_{24}H_{20}$: C 87.49, H 6.29, found: C 87.07, H 6.27.

X-ray structural analysis

Crystaldata

1a: Colorless rods from MeOH, $(C_{15}H_{13}F_5P)_2Br_2\cdot H_2O$, F.W. = 816.28, crystal size 0.17 × 0.07 × 0.06 mm, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.8147(4)$, $b = 12.0612(3)$, $c = 14.5634(5)$ Å, $\alpha = 94.048(2)$, $\beta = 110.887(2)$, $\gamma = 118.155(2)°$, $V = 1636.05(9)$ Å^3, $Z = 2$, $D_c = 1.657$ Mg m^{-3}, $\mu = 2.656$ mm^{-1}, $F(000) = 812$, 19069 collected reflections ($\theta_{max} = 25.00°$) of which 5722 independent [$R_{int} = 0.0611$], $T_{max} = 0.8569$, $T_{min} = 0.6609$, full-matrix least-squares on F^2 with 8 restraints and 415 parameters, GOF = 1.062, $R_1 = 0.0481$ [$I > 2\sigma(I)$], wR_2 (all data) = 0.0947, largest peak/hole = 0.509/−0.383 e$^-$Å^{-3}.

1b: Colorless plates from CH_3CN, $(C_{15}H_{13}F_5P)I$, F.W. = 446.12, crystal size 0.20 × 0.18 × 0.05 mm, monoclinic, space group $P2_1/c$ (no. 14), $a = 12.6682(3)$, $b = 18.0617(4)$, $c = 14.3740(3)$ Å, $\beta = 90.972(2)°$, $V = 3288.43(13)$ Å^3, $Z = 8$ ($Z' = 2$), $D_c = 1.802$ Mg m^{-3}, $\mu = 2.087$ mm^{-1}, $F(000) = 1728$, 41227 collected reflections ($\theta_{max} = 25.02°$) of which 5799 independent [$R_{int} = 0.0653$], $T_{max} = 0.9028$, $T_{min} = 0.6803$, full-matrix least-squares on F^2 with 0 restraints and 397 parameters, GOF = 1.094, $R_1 = 0.0343$ [$I > 2\sigma(I)$], wR_2 (all data) = 0.0670, largest peak/hole = 0.480/−0.461 e$^-$Å^{-3}.

2d: Colourless blocks from MeOH–EtOH, $(C_{25}H_{17}F_5P)$-$(C_{24}H_{20}B)$, F.W. = 762.57, crystal size 0.25 × 0.25 × 0.14 mm, monoclinic, space group $C2/c$ (no. 15), $a = 32.7210(7)$, $b = 14.0835(3)$, $c = 17.1709(3)$ Å, $\beta = 102.5470(10)°$, $V = 7723.8(3)$ Å^3, $Z = 8$, $D_c = 1.312$ Mg m^{-3}, $\mu = 0.131$ mm^{-1}, $F(000) = 3168$, 13235 collected reflections ($\theta_{max} = 25.00°$) of which 6792 independent [$R_{int} = 0.0435$], full-matrix least-squares on F^2 with 0 restraints and 505 parameters, GOF = 1.031, $R_1 = 0.0511$ [$I > 2\sigma(I)$], wR_2 (all data) = 0.1110, largest peak/hole = 0.443/−0.434 e$^-$Å^{-3}.

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Notes and References

1 (*a*) J.-M. Lehn, *Supramolecular Chemistry – Concepts and Perspectives*, VCH: Weinheim, 1995; (*b*) J. Steed, J. L. Atwood, *Supramolecular Chemistry*, John Wiley: New York, 2009.

2 P. de Hoog, P. Gamez, H. Mutikainen, U. Turpeinen and J. Reedijk, *Angew. Chem.*, 2004, **116**, 5939, (*Angew. Chem., Int. Ed.*, 2004, **43**, 5815).

3 (*a*) H.-J. Schneider, F. Werner and T. Blatter, *J. Phys. Org. Chem.*, 1993, **6**, 590; (*b*) for some earlier studies in the gas phase see: K. Hiraoka, S. Mizuse and S. Yamabe, *J. Phys. Chem.*, 1987, **91**, 5294.

4 (*a*) I. Alkorta, I. Rozas and J. Elguero, *J. Am. Chem. Soc.*, 2002, **124**, 8593; (*b*) M. Mascal, A. Armstrong and M. D. Bartberger, *J. Am. Chem. Soc.*, 2002, **124**, 6274; (*c*) A. Frontera, F. Saczewski, M. Gdaniec, E. Dziemidowicz-Borys, A. Kurland, P. M. Deya, D. Quinonero and C. Garau, *Chem.–Eur. J.*, 2005, **11**, 6560; (*d*) C. Garau, D. Quinonero, A. Frontera, P. Ballester, A. Costa and P. M. Deya, *J. Phys. Chem. A*, 2005, **109**, 9341; (*e*) D. Quinonero, C. Garau, A. Frontera, P. Ballester, A. Costa and P. M. Deya, *Chem. Phys. Lett.*, 2002, **359**, 486; (*f*) C. Garau, A. Frontera, D. Quinonero, P. Ballester, A. Costa and P. M. Deya, *J. Phys. Chem. A*, 2004, **108**, 9423; (*g*) C. Garau, A. Frontera, P. Ballester, D. Quinonera, A. Costa and P. M. Deya, *Eur. J. Org. Chem.*, 2005, 179.

5 (*a*) A. Bianchi, K. Bowman-James and E. Garcia-Espana, *Supramolecular Chemistry of Anions*, Wiley-VCH: New York, 1997; (*b*) B. L. Schottel, H. T. Chifotides and K. R. Dunbar, *Chem. Soc. Rev.*, 2008, **37**, 68; (*c*) B. P. Hay and V. S. Bryantsev, *Chem. Commun.*, 2008, 2417.

6 (*a*) M. Albrecht, C. Wessel, M. de Groot, K. Rissanen and A. Lüchow, *J. Am. Chem. Soc.*, 2008, **130**, 4600; (*b*) M. Albrecht, M. Müller, O. Mergel, A. Valkonen and K. Rissanen, *Chem.–Eur. J.*, 2010, **16**, 5062.

7 For example: (*a*) H. Maeda, A. Osuka and H. Furuta, *J. Inclusion Phenom. Macrocyclic Chem.*, 2004, **49**, 33; (*b*) H. Maeda and H. Furuta, *J. Porphyrins Phthalocyanines*, 2004, **8**, 67; (*c*) Y. S. Rosokha, S. V. Lindeman, S. V. Rosokha and J. K. Kochi, *Angew. Chem.*, 2004, **116**, 4750, (*Angew. Chem., Int. Ed.*, 2004, **43**, 4650); (*d*) O. B. Berryman, F. Hof, M. J. Hynes and D. W. Johnson, *Chem. Commun.*, 2006, 506; (*e*) M. Staffilani, K. S. B. Hancock, J. W. Steed, K. T. Holman, J. L. Atwood, R. K. Juneja and R. S. Burkhalter, *J. Am. Chem. Soc.*, 1997, **119**, 6324; (*f*) R. M. Fairchild and K. T. Holman, *J. Am. Chem. Soc.*, 2005, **127**, 16364.

8 (*a*) A. C. Skapski and F. A. Stephens, *J. Cryst. Mol. Struct.*, 1974, **4**, 77; (*b*) S. J. Archer, T. A. Modro and L. R. Nassimbeni, *Phosphorus Sulfur Relat. Elem.*, 1981, **11**, 101; (*c*) M. N. Ponnuswamy and E. W. Czerwinski, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1986, **42**, 1019.

9 Structural Database analysis: D. Quinonero, C. Garau, C. Rotger, A. Frontera, P. Ballester, A. Costa and P. M. Deyà, *Angew. Chem.*, 2002, **114**, 3539, (*Angew. Chem., Int. Ed.*, 2002, **41**, 3389).

10 (*a*) K. A. Connors, *Bindung Constants: The measurement of Molecular Complex Stability*, Wiley, New York, 1987; (*b*) C. S. Wilcox, in *Frontiers in Supramolecular Chemistry and Photochemistry* (ed.: H.-J. Schneider and H. Dürr), Wiley-VCH, Weinheim, 1991, p. 123.

11 *COLLECT*, Bruker AXS, Inc., Madison, Wisconsin, USA, 2008.

12 Z. Otwinowski, W. Minor, in *Methods in Enzymology* 1997, 276, Macromolecular Crystallography, Part A, 307–326.

13 M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 2005, **38**, 381–388.

14 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837–838.

15 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.

16 G. M. Sheldrick, *SADABS*, University of Göttingen, Germany, 1996.

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