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Controlling the position of anions relative to a pentafluorophenyl group†

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The position of an anion above an electron-deficient arene can be controlled by the geometry of appended directing groups. Here a series of ammonium substituted pentafluorophenyl derivatives is investigated. The presented results are one step on the way to find the ideal structural features for an effective and superior receptor for anion– π studies.

Introduction

Supramolecular chemistry deals with non-covalent bonds,¹ which vary dramatically in their strength.² Both strong electrostatic attraction as well as weakly dispersive repulsion belong to supramolecular interactions. Even aromatic interactions like π – π stacking or cation– π interactions are in the focus of intense studies due to their relevance in biological and chemical processes.³ Recently the interaction between anions and electron-deficient arenes was identified as an attractive force based on computational as well as crystallographic results.⁴ Especially in the field of anion recognition and sensing this new interaction promises new applications and the development of novel anion receptors. However, the relevance of anion– π interactions in solution⁵ is debatable and gas phase⁶ studies are rare.

We started our work on anion– π interactions in 2008 by studying pentafluorophenyl ammonium and phosphonium salts in the solid state.⁷ First results showed that the position of an anion above the electron-deficient C_6F_5 -unit is flexible and can be controlled by directing substituents.⁸ Further studies were able to prove the dependence of anion– π interactions on the fluorination degree of the phenyl group.⁹ Through successive reduction of the number of fluorine atoms at the arene the electron-density was enhanced and the attractive anion– π interaction turns into a repulsive force. Moreover, we studied the effect of the anion geometry on the interaction of pentafluorophenyl ammonium cations with halides, nitrates, tetrafluoroborates and hexafluoroborates.¹⁰ Due to its strict electrostatic nature, the anion– π interaction shows no dependence on the geometry of the studied anion in the solid state.

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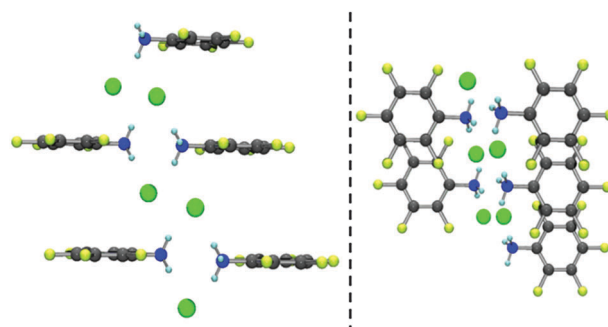


Fig. 1 Two different views of the crystal structure of **3a** (green: chloride, black: carbon, light-green: fluorine, blue: nitrogen, white: hydrogen).⁷

Anion– π interactions are relatively weak non-covalent interactions in solution and in the solid state and the central fixation of an anion above a π -system can easily be disturbed through packing effects. Substituents can support the position of an anion above the C_6F_5 unit by CH– or NH–anion bridges.^{8,11}

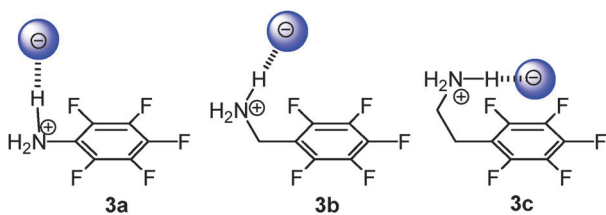
An already reported crystal structure of pentafluoroanilinium chloride⁷ showed the strong directing effect of the ammonium group on the position of the anion in the crystal lattice. The hydrogen atoms point away from the aromatic system and thereby the anion is fixed between four pentafluoroanilinium cations surrounded exclusively by NH–anion interactions (Fig. 1).

Results and discussion

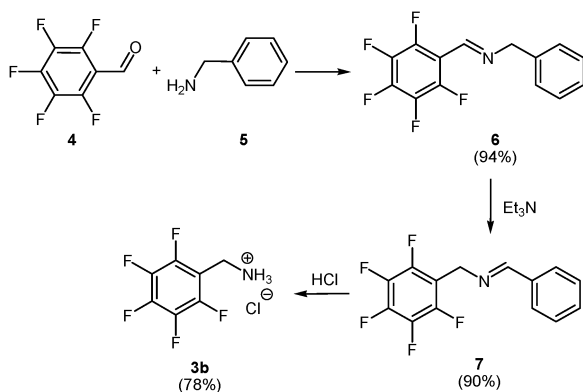
This observation inspired us to use the directing force of the ammonium group to study the influence of the spacer length between the ammonium group and the electron-deficient C_6F_5 unit. The length of the spacer is varied by stepwise insertion of CH_2 -groups. By lengthening the spacer between the ammonium group and the arene the anion should be forced to move closer to the centre of the pentafluorophenyl system (Scheme 1).

Synthesis of the pentafluorophenylammonium chlorides

While pentafluoroaniline is commercially available, the two ammonium chlorides containing a pentafluorophenyl group



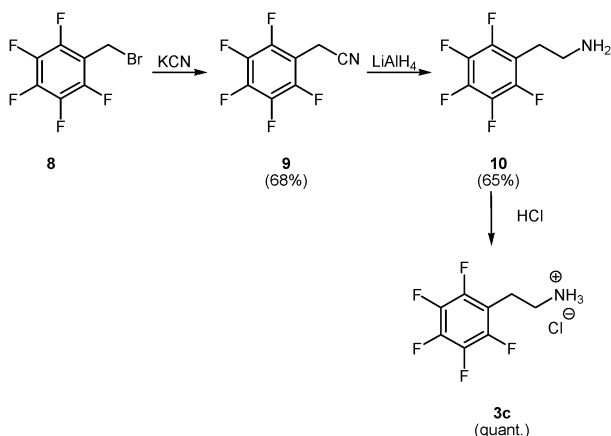
Scheme 1 Concept for studying the effect of the spacer length on the anion position in the solid state.



Scheme 2 Synthesis of 2,3,4,5,6-(pentafluoro)benzylammonium chloride **3b**.

(**3b** and **3c**) have to be synthesized. For 2,3,4,5,6-(pentafluoro)benzylammonium chloride (**3b**) the Schiff base was generated from pentafluorobenzaldehyde (**4**) and benzylamine (**5**). After rearrangement of **6** to **7** in triethylamine, the 2,3,4,5,6-(pentafluoro)benzylammonium salt was obtained by adding HCl (Scheme 2).

The 2-(pentafluorophenyl)ethylammonium chloride **3c** was generated from 2,3,4,5,6-(pentafluoro)benzylbromide (**8**). Substitution of the bromide with potassium cyanide leads to 2-(pentafluorophenyl)acetonitrile (**9**) and following reduction by lithium aluminium hydride gives the corresponding amine (**10**). By addition of HCl the final 2-(pentafluorophenyl)ethylammonium chloride **3c** was obtained (Scheme 3). For all three compounds crystal structures could be obtained.



Scheme 3 Synthesis of 2-(pentafluorophenyl)ethylammonium chloride **3c**.

Solid state investigations

As previously already mentioned hydrogen bond bridges from the ammonium groups to the chloride anions ($\text{NH}\cdots\text{Cl} = 2.843, 3.130$ (anions close to the π -system), $2.311, 2.164$ and 2.275 Å (anions in the far periphery)) are the dominating interaction in the crystal lattice of **3a**.⁷ The ammonium groups direct the anions away from the electron-deficient unit and bridge adjacent anions to each other. The fourth anion within the hydrogen bond distance from the ammonium group and also closest to an aryl ring is not hydrogen bonded to the ammonium group of the same molecule, because of the small $\text{NH}\cdots\text{Cl}$ angle (110°) and long $\text{NH}\cdots\text{Cl}$ distance (2.84 Å). Only two distances to the ring are within the sum of the van der Waals (vdW) radii of the involved atoms ($\text{C}^1/\text{C}^6\cdots\text{Cl} = 3.40$ and 3.41 Å) indicating anion- π contacts. Due to the fact that the anion is not positioned directly above the π -system (having a long distance to the center of the arene ($\text{centre}\cdots\text{Cl} = 4.06$ Å)) but rather over the outer periphery and due to the presence of strong $\text{NH}\cdots\text{Cl}$ interactions, no “intramolecular” anion- π interaction can be found in the solid state structure of **3a**.

Also **3b** shows a strong dominance of hydrogen bridges ($\text{NH}\cdots\text{Cl} = 2.22(2), 2.28(2)$ and $2.48(2)$ Å) in the crystalline state and the adjacent anions are bridged by ammonium groups. As in **3a** there is a fourth anion within hydrogen bond distance from ammonium, but again with a rather small $\text{NH}\cdots\text{Cl}$ angle [$116(2)^\circ$] and long $\text{NH}\cdots\text{Cl}$ distance [$2.68(2)$ Å]. A closer view at an ion pair shows that the anion is fixed (by $\text{NH}\cdots\text{Cl}$ interaction) closer to the arene compared to **3a**. Due to the longer alkyl chain between the directing ammonium group and the pentafluorophenyl moiety the distance to the centre of the arene ($\text{centre}\cdots\text{Cl} = 4.37$ Å) is slightly longer in respect to **3a**. Like in **3a**, in **3b** only two carbon-anion distances are close to the sum of the vdW radii of the atoms ($\text{C}^1/\text{C}^6\cdots\text{Cl} = 3.897(3)$ and $3.663(3)$ Å). Consequently, neither **3a** nor **3b** structures match hard criteria for anion- π interactions in the solid state (Fig. 2).¹²

In contrast to that, the crystal structure of **3c** shows a chloride anion located above the π -system. The distance to the centre of the arene from the anion is 3.49 Å (3.51 Å for the second molecule in the asymmetric unit) the closest one in this series of solid state structures. The ammonium group fixes the anion [$\text{NH}\cdots\text{Cl} = 2.27(2)/2.29(3)$ Å] above the π -system.

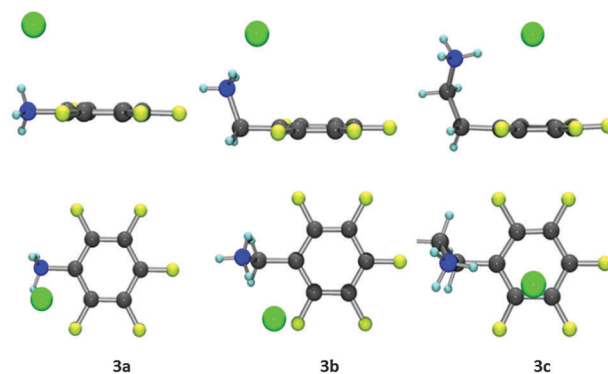


Fig. 2 Comparison of the crystal structures of **3a**, **3b** and **3c** (top: side-view; bottom: top-view; green: chloride, black: carbon, light-green: fluorine, blue: nitrogen, white: hydrogen).

Table 1 Summary of relevant NH/C...Cl⁻ binding distances [Å] of **3a**, **3b** and **3c**

	3a ⁷	3b	3c
NH...Cl ⁻	2.84	2.22(2)	2.27(2)/2.29(3)
C ¹ ...Cl ⁻	3.40	3.897(3)	3.711(6)/3.734(6)
C ² ...Cl ⁻	4.28	4.777(3)	3.359(6)/3.378(7)
C ³ ...Cl ⁻	5.02	5.356(3)	3.419(7)/3.428(7)
C ⁴ ...Cl ⁻	5.02	5.170(3)	3.800(7)/3.805(8)
C ⁵ ...Cl ⁻	4.29	4.374(3)	4.126(11)/4.105(11)
C ₆ ...Cl ⁻	3.41	3.663(3)	4.015(10)/4.112(11)
Centre _{aryl} ...Cl ⁻	4.06	4.37	3.49/3.51
Plane _{aryl} ...Cl ⁻	2.89	3.29	3.31/3.33

The anion is not placed above the center of the arene. This is due to the available void within the crystal packing, while the flexible spacer allows the shifting of the anion towards the rim of the aromatic unit. Three carbon–chloride distances are within the range of the vdW radii [C¹⁻³...Cl = 3.711(6), 3.359(6) and 3.419(7) Å and C¹⁻³...Cl = 3.734(6), 3.378(7) and 3.428(7) Å for the second molecule in the asymmetric unit]. So that at least the interaction between the pentafluorophenyl unit and the anion can be described as η³ anion–π interaction, although there are two additional NH...Cl contacts found from the ammonium group [2.24(3)/2.24(2) and 2.31(3)/2.24(2) Å]. The following table summarizes the measured distances in the solid state structures of **3a**, **3b** and **3c** (Table 1).

The comparison of the three solid state structures reveals the obvious influence of the spacer length on the position of the anion in the crystalline lattice. While in **3a** and **3b** the linkers are too short to fix the anion above the π-system, in **3c** the anion is located above the pentafluorophenyl unit and interacts with three carbon atoms. Moreover, the results show that a central binding of the anion above the electron-deficient moiety requires a more rigid receptor backbone.

Conclusions

The presented results show that it is possible to predict the relative position of an anion in respect to an electron-deficient arene and that in a connecting chain to the cation at least four σ-bonds between the directing hydrogen atom and the pentafluorophenyl group are necessary to fix an anion above the π-system. The chosen linker is too flexible for a fixation of the anion above the centre of the electron-deficient arene and allows shifting towards the rim. Probably, the presented results will help to design a superior receptor to study anion–π interactions in the solid phase, in solution and in the gas phase.

Experimental

Commercially available reagents were used as received. Solvents were distilled and used without further purification. The ¹H (300 MHz) and the ¹⁹F (282 MHz) NMR spectra were taken on Varian Mercury 300 in deuteriochloroform, DMSO or methanol. The mass spectrometric data were taken on Finnigan SSQ 7000 and Thermo Deca XP as EI (70 eV) or ESI. The infrared spectra were obtained on a PerkinElmer FTIR spectrometer Spektrum 100. The samples were measured in KBr (4000–650 cm⁻¹). The elemental analyses were done on a CHN-O-Rapid Vario EL from Heraeus. The melting points

were obtained on a Büchi B-540. Single crystal X-ray data of **3b** and **3c** were collected at 123(2) K using a Bruker-Nonius KappaCCD diffractometer with an APEX-II detector and graphite monochromatized Mo-Kα (λ = 0.71073 Å) radiation. COLLECT^{13a} software was used for the data collection (θ and ω scans) and DENZO-SMN^{13b} for the processing. The structures were solved by direct methods with SIR2004^{13c} and refined by full-matrix least-squares methods with WinGX-software,^{13d} which utilizes the SHELXL-97 module.^{13e} Lorentzian polarization and multi-scan absorption (SADABS^{13f}) corrections were applied on all data. All C–H hydrogen positions were calculated and refined as riding atom model. Ammonium H-atoms were found from Fourier maps and fixed (by DFIX) to a distance of 0.91 Å from the N atom. Thermal parameters for all H-atoms were set to 1.2 times that of the C/N atom parameter. Compound **3c** was found to be a racemic twin in the non-centrosymmetric polar space group and TWIN/BASF refinement was applied. Disorders in anisotropic parameters of aromatic carbons of **3c** were restrained by SIMU (s = 0.01) and ISOR (s = 0.01) in final refinement cycles.

Synthesis of compounds

N-(2,3,4,5,6-Pentafluorobenzylidene)benzylamine 6. Equimolar amounts of pentafluorobenzaldehyde (1.00 g, 5.1 mmol) and benzylamine (0.55 g, 5.1 mmol) were heated to 60 °C for 5 h. The obtained light-yellow solid was crushed and dried *in vacuo*. Yield: 1.37 g of light-yellow solid (4.8 mmol, 94%). Mp: 85 °C. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) = 8.49 (s, 1H, CHN), 7.26–7.34 (m, 5H, H_{aryl}), 4.91 (s, 2H, H_{benzyl}). ¹⁹F NMR (CDCl₃, 300 MHz): δ (ppm) = -142.62 (m, 2F, F_{ortho}), -150.94 (m, 1F, F_{para}), -161.92 (m, 2F, F_{meta}). MS (EI, 70 eV): m/z (%) = 285.0 (43, [M]⁺, C₁₄H₈F₅N⁺), 91.1 (100, C₇H₇⁺). IR (KBr) ν (cm⁻¹) = 3033 (w), 2901 (w), 2856 (w), 2652 (w), 2160 (w), 1826 (w), 1652 (m), 1555 (w), 1521 (s), 1491 (vs), 1453 (m), 1420 (w), 1377 (m), 1337 (w), 1311 (m), 1206 (w), 1180 (w), 1135 (m), 1078 (w), 1037 (w), 978 (vs), 926 (s), 857 (w), 820 (w), 789 (m), 750 (s), 701 (s), 681 (m). C₁₄H₈F₅N (285.21): C 58.96, H 2.83, N 4.91 (%); found: C 58.78, H 2.95, N 4.96 (%).

N-(Benzylidene)-2,3,4,5,6-(pentafluoro)benzylamine 7. 1.37 g of compound **6** were dissolved in 10 mL of triethylamine and stirred for 16 h. The solvent was removed under reduced pressure and the obtained solid was dried *in vacuo*. Yield: 1.23 g yellow solid (4.3 mmol, 90%). Mp: 55 °C. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) = 8.32 (s, 1H, CHN), 7.20–7.36 (m, 5H, H_{aryl}), 4.83 (s, 2H, H_{benzyl}). ¹⁹F NMR (CDCl₃, 300 MHz): δ (ppm) = -143.31 (m, 2F, F_{ortho}), -155.37 (m, 1F, F_{para}), -162.34 (m, 2F, F_{meta}). MS (EI, 70 eV): m/z (%) = 285.2 (91, [M]⁺, C₁₄H₈F₅N⁺), 91.1 (100, C₇H₇⁺). IR (KBr) ν (cm⁻¹) = 3030 (w), 2983 (w), 2873 (w), 2642 (w), 2182 (w), 2077 (w), 1974 (w), 1910 (w), 1826 (w), 1637 (m), 1579 (w), 1521 (s), 1497 (vs), 1450 (m), 1425 (w), 1382 (m), 1340 (m), 1299 (m), 1220 (m), 1124 (s), 1050 (s), 1003 (s), 983 (s), 955 (s), 927 (s), 851 (w), 791 (w), 759 (s), 693 (s), 673 (m). C₁₄H₈F₅N 0.5 H₂O (285.21): C 57.15, H 3.08, N 4.76 (%); found: C 56.97, H 3.27, N 4.78 (%).

2,3,4,5,6-(Pentafluoro)benzylammonium chloride 3b. To a solution of 1.2 g of compound **7** in 10 mL of diethylether

was added 10 mL aqueous HCl (36%). The aqueous layer was separated and the solvent was removed. After recrystallisation from acetone a yellow solid was obtained. The solid was dried *in vacuo*. Yield: 0.8 g yellow solid (3.4 mmol, 78%). Mp: 289 °C. ^1H NMR (MeOD, 300 MHz): δ (ppm) = 7.44 (s, 3H, NH), 4.30 (s, 2H, H_{benzyl}). ^{19}F NMR (MeOD, 300 MHz): δ (ppm) = -143.22 (m, 2F, F_{ortho}), -154.41 (m, 1F, F_{para}), -164.14 (m, 2F, F_{para}). MS (EI, 70 eV): m/z (%) = 197.0 (26, $[\text{M}]^+$, $\text{C}_7\text{H}_4\text{F}_5\text{N}^+$), 177.1 (100, $\text{C}_7\text{H}_3\text{F}_4\text{N}^+$). IR (KBr) ν (cm^{-1}) = 2877 (m), 2664 (w), 2628 (w), 2494 (w), 2400 (w), 2074 (w), 2000 (w), 1659 (m), 1593 (m), 1562 (m), 1504 (vs), 1436 (w), 1381 (m), 1309 (m), 1261 (w), 1155 (s), 1115 (s), 1060 (w), 984 (vs), 926 (vs), 886 (m), 799 (w), 749 (w), 700 (w), 664 (w). $\text{C}_7\text{H}_5\text{F}_5\text{NCl} \cdot 0.5 \text{H}_2\text{O}$ (233.57): C 37.48, H 2.47, N 6.24 (%); found: C 37.09, H 2.45, N 5.99 (%).

2-(Pentafluorophenyl)acetonitrile 9. To a solution of 2,3,4,5,6-(pentafluoro)benzylbromide (500 mg, 2.4 mmol) in 7 mL of ethanol was added a solution of potassium cyanide (157 mg, 2.4 mmol) in 3 mL of water. After stirring for 5 h at 50 °C the mixture was extracted with 10 mL of diethylether (3 times). The organic layer was dried with magnesium sulfate. The solvent was removed under reduced pressure and a light-yellow liquid was obtained. Yield: 270 mg light-yellow liquid (1.3 mmol, 68%). ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) = 3.76 (s, 2H, H_{benzyl}). ^{19}F NMR (CDCl_3 , 400 MHz): δ (ppm) = -141.09 (m, 2F, F_{ortho}), -151.85 (m, 2F, F_{para}), -160.08 (m, 2F, F_{meta}). MS (ESI): m/z (%) = 230.2 (100, $[\text{M} + \text{Na}]^+$, $\text{C}_8\text{H}_2\text{F}_5\text{N} + \text{Na}^+$). IR (KBr) ν (cm^{-1}) = 3944 (w), 3727 (w), 3515 (w), 3327 (w), 3209 (w), 3062 (w), 2977 (m), 2883 (w), 2794 (w), 2634 (w), 2322 (m), 2237 (m), 2144 (w), 2182 (m), 2059 (m), 1981 (m), 1922 (w), 1856 (w), 1798 (w), 1718 (vs), 1589 (m), 1522 (vs), 1441 (m), 1380 (vs), 1269 (m), 1240 (s), 1167 (m), 1071 (w), 1013 (s), 864 (m), 829 (m), 784 (m), 761 (m), 718 (vs), 675 (m). $\text{C}_8\text{H}_2\text{F}_5\text{N} \cdot 0.25 \text{H}_2\text{O}$ (207.10): C 45.41, H 1.19, N 6.62 (%); found: C 45.78, H 1.12, N 5.91 (%).

2-(Pentafluorophenyl)ethylamine 10. The synthesis of compound **10** was performed under nitrogen atmosphere. To a solution of lithiumaluminium hydride (229 mg, 6.03 mmol) in 6 mL of THF a solution of aluminium trichloride (805 mg, 6.03 mmol, in 10 mL THF) was added. To this mixture 2-(pentafluorophenyl)acetonitrile (**9**, 500 mg, 2.41 mmol, 311 μL) was added. After stirring for 1 h the mixture was poured on ice. The aqueous layer was extracted with 15 mL of diethylether for three times. After evaporation of the solvent a yellow oil could be obtained. Yield: 330 mg yellow oil (1.6 mmol, 65%). ^1H NMR (CDCl_3 , 300 MHz): δ (ppm) = 2.88 (t, J = 6.7 Hz, 2H, CH_2), 2.77 (t, J = 6.7 Hz, 2H, CH_2). ^{19}F NMR (CDCl_3 , 300 MHz): δ (ppm) = -143.77 (m, 2F, F_{ortho}), -157.34 (m, 1F, F_{para}), -162.74 (m, 2F, F_{meta}). MS (EI, 70 eV): m/z (%) = 211.1 (8, $[\text{M}]^+$, $\text{C}_8\text{H}_6\text{F}_5\text{N}^+$), 195.1 (90, $\text{C}_8\text{H}_4\text{F}_5^+$). IR (KBr) ν (cm^{-1}) = 3353 (w), 2936 (w), 2641 (w), 2420 (w), 2114 (w) 1931 (w), 1623 (m), 1495 (vs), 1439 (m), 1372 (m), 1310 (m), 1286 (m), 1206 (w), 119 (s), 1073 (m), 978 (s), 942 (vs), 869 (m), 815 (m), 755 (w), 709 (m), 586 (s). $\text{C}_8\text{H}_6\text{F}_5\text{N} \cdot 0.5 \text{H}_2\text{O}$ (211.04): C 44.25, H 3.09, N 6.45 (%); found: C 44.15, H 3.01, N 5.91 (%).

2-(Pentafluorophenyl)ethylammonium chloride 3c. To a solution of compound **10** (500 mg, 2.4 mmol) in 10 mL of methanol 1 mL of aqueous HCl (36%) was added. After stirring the mixture for

20 min the solvent was removed and the obtained solid was dried *in vacuo*. Yield: 590 mg colorless solid (2.4 mmol, quant). Mp: 240 °C. ^1H NMR (MeOD, 300 MHz): δ (ppm) = 3.16 (dt, J = 6.2/6.8 Hz, 4H, CH_2). ^{19}F NMR (MeOD, 300 MHz): δ (ppm) = -145.31 (m, 2F, F_{ortho}), -158.72 (m, 1F, F_{para}), -165.10 (m, 2F, F_{meta}). MS (EI, 70 eV): m/z (%) = 210.2 (20, $[\text{M}-\text{H}]^+$, $\text{C}_8\text{H}_6\text{F}_5\text{N}$), 181.1 (100, $\text{C}_7\text{H}_2\text{F}_5$). IR (KBr) ν (cm^{-1}) = 2953 (m), 2895 (m), 2612 (w), 2014 (w), 1659 (w), 1590 (w), 1500 (vs), 1295 (w), 1123 (s), 1043 (m), 994 (s), 966 (s), 935 (s), 857 (m), 787 (w), 718 (w), 669 (w). $\text{C}_8\text{H}_7\text{F}_5\text{NCl}$ (247.59): C 38.81, H 2.85, N 5.66 (%); found: C 39.59, H 2.91, N 5.52 (%).

X-Ray structural analysis

Crystal data. 3b: Colorless plates from EtOH–EtOAc, $\text{C}_7\text{H}_5\text{NF}_5\text{Cl}$, F.W. = 233.57, crystal size 0.36 \times 0.25 \times 0.04 mm³, monoclinic, space group $P2_1/c$ (no. 14), a = 12.1722(7), b = 6.1586(3), c = 12.0356(6) Å, β = 90.762(3)°, V = 902.15(8) Å³, Z = 4, D_{calc} = 1.720 g cm⁻³, μ = 0.461 mm⁻¹, $F(000)$ = 464, 4987 collected reflections (θ_{max} = 25.02°) of which 1594 independent [R_{int} = 0.0386], T_{max} = 0.9818, T_{min} = 0.8517, full-matrix least-squares on F^2 with 3 restraints and 136 parameters, GOF = 1.026, $R1$ = 0.0366 [$I > 2\sigma(I)$], $wR2$ (all data) = 0.0895, largest peak/hole = 0.290/−0.253 e⁻ Å⁻³.

3c: Colorless plates from DMF–Et₂O, $\text{C}_8\text{H}_7\text{NF}_5\text{Cl}$, F.W. = 247.60, crystal size 0.30 \times 0.12 \times 0.08 mm³, orthorhombic, space group $Pca2_1$ (no. 29), a = 14.8569(5), b = 5.4919(3), c = 23.4876(10) Å, V = 1916.41(15) Å³, Z = 8 (Z' = 2), D_{calc} = 1.716 g cm⁻³, μ = 0.439 mm⁻¹, $F(000)$ = 992, 7988 collected reflections (θ_{max} = 25.24°) of which 3161 independent [R_{int} = 0.0416], T_{max} = 0.9657, T_{min} = 0.8796, full-matrix least-squares on F^2 with 91 restraints and 290 parameters, GOF = 1.048, $R1$ = 0.0462 [$I > 2\sigma(I)$], $wR2$ (all data) = 0.1201, absolute structure parameter (BASFL) = 0.2(2), largest peak/hole = 0.459/−0.264 e⁻ Å⁻³.

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