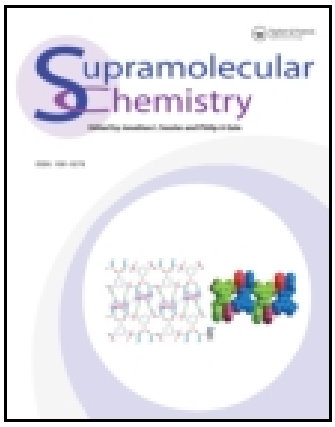

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Pentafluorophenyl salicylamine receptors in anion–π interaction studies

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A crystal structure analysis confirms the appropriateness of pentafluorophenyl salicylamine (**1a**) as a π-acceptor for anion–π interactions. Crystals of **1a**·HCl show that the OH-group fixes the anion in a η^2-type binding motif above the electron-deficient arene. Attempts to find some relevance for this weak intermolecular force in solution failed. Stronger CH–, NH– and OH–anion interactions are dominant over the weak anion–π interactions. Due to the hydrogen bonding, the non-fluorinated receptor exhibits the highest binding constants within this series.

Keywords: anion–π interaction; pentafluoro salicylamine; crystal structure; NMR titration

Introduction

Supramolecular chemistry relies on non-covalent bonds (*1*), which vary from strong electrostatic attraction to weakly dispersive. These intramolecular interactions control self-assembly processes of multicomponent systems (*2*). Recent investigations show that arenes are involved in natural as well as in synthetic self-organising systems by π–π-stacking or cation–π interactions (*3*). Within the last 20 years, an additional interaction between anions and electron-deficient arenes has achieved considerable attention (*4*). Earlier computational and structural studies on anion–π interactions suggest the attractive nature of the intermolecular force (*5*). Although the role of anion–π interactions in the solid state (*6*) seems to be understood, the relevance in solution (*7*) remains an open question.

In 2008, we started our work on anion–π interactions in pentafluorophenyl ammonium and phosphonium salts (*8*). First crystallographic results revealed a high flexibility of the anion position above the C_6F_5 unit. To describe the observed binding motifs, the hapticity (η) nomenclature for cation–π interactions was transferred to anion–π systems. Further investigations could show that the position of the anion above an electron-deficient arene can be controlled by directing substituent of the periphery (*9*). Therefore, CH– or NH–anion interactions were utilised. Moreover, the influence of the electron-density of the π-system in the interaction with anions was extensively studied, whereby the attraction in high-fluorinated systems (four to five fluorine atoms) turned to a repulsive force in low fluorinated arenes (three to two fluorine atoms) (*10*). Crystallographic studies on the role of the anions in anion–π interactions show no dependence on the geometry of the anion (*11*). However, serendipity leads to the remarkable stabilisation of the sensitive tetraiodid dianion (I_4^{2-}) by anion–π interactions (*12*). First attempts to find some relevance of anion–π interactions in solution by studying pentafluorobenzyl phosphonium salts show no evidence for this intermolecular force in chloroform (*13*).

Results and discussion

The idea

As mentioned in the 'Introduction' section, the role of anion–π interactions in solution is still unclear. First studies focused on the interaction of pentafluorobenzyl triphenyl phosphonium salts with anions in chloroform. The results of these studies gave no insight into the anion–π interaction in solution. The reason for that is the interplay of different non-covalent interactions in the examined system. To reduce the number of possible interactions, we searched for appropriate uncharged receptors with pentafluorophenyl units. By the support of simple force field calculations using Spartan 08 (MMFF), the pentafluorophenyl salicyl amine (**1a**) was identified as a promising candidate. We are well aware that force field calculations are not appropriate to describe anion–π interactions. The data obtained by this method are very rough but here they only act as a starting point to visualise promising systems to be synthesised. The phenolic OH-group should direct the anion above the electron-deficient moiety and support the anion–π interaction. Moreover, the OH-group can be used as reporter group during the NMR-titration experiments in order to determine the binding constants for the investigated anion–receptor complexes. A potential reference compound is the corresponding dichlorophenyl salicyl amine (**1b**).

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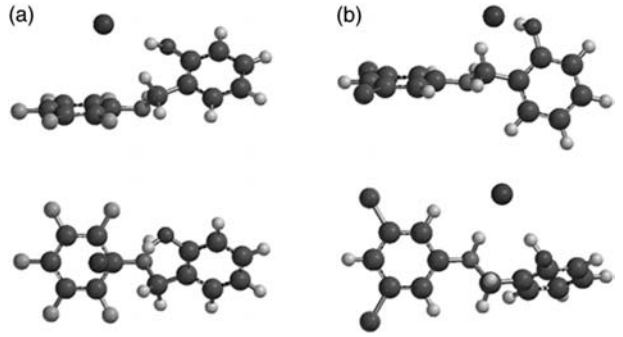


Figure 1. Predicted interactions for receptors **1a** and **1b** with bromide by molecular modelling (force field calculations).

For this no cooperative forces of the hydrogen-bridges (from OH or NH) and the anion–π interaction were predicted (Figure 1).

Synthesis of the phenyl salicylamines

In order to perform solution studies, the desired phenyl salicylamines **1a** and **1b** have to be synthesised (Scheme 1). Therefore, salicyl aldehyde (**2**) was reacted in an imine condensation with the corresponding aniline derivatives (**3a** or **3b**). The resulting imines (**4a** and **4b**) can be reduced by mixture of sodium borohydride and silicon dioxide to the desired amines **1a** and **1b**. All compounds and intermediates were fully characterised by standard analytical methods (^{1}H, ^{19}F NMR, MS, IR and CHN).

X-ray structural analysis

Crystal structures are the result of the interplay of various non-covalent interactions and steric effects. In the following discussion only the relevant anion interactions of the ion pairs are taken into account.

Intense attempts to co-crystallise the phenyl salicylamines with tetra-alkyl ammonium salts failed. However, diffusion of gaseous HCl into a solution of pentafluorophenyl salicylamine **1a** in ethylacetate resulted in colourless crystals. Hydrochloride **1a**·HCl crystallises in the monoclinic space group $P2_1/n$. The solid-state structure of **1a** shows that the anion is fixed above the C_6F_5 unit (Figure 2) by a hydrogen-bridge of the OH-group [O···Cl = 3.086(2) Å, O—H···Cl = 174(3)°]. Two of the carbon–chloride distances are close to the sum of the van der Waals (vdW) radii of the involved atoms [$C^{3/4}$···Cl = 3.506(3), 3.533(3) Å]. A wider look on the crystalline packing of the ion pairs reveals that the anion position is further fixed by two N—H···Cl hydrogen-bridges from neighbouring cations [N···Cl = 3.055(2), 3.074(2) Å; N—H···Cl = 170(2), 152(2)°, respectively].

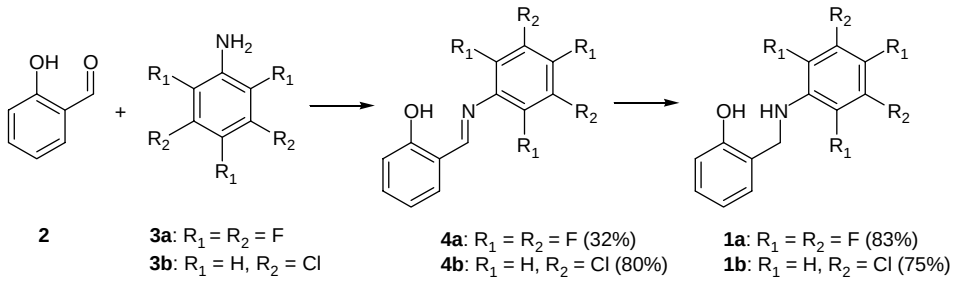
It should be noted that due to the protonation of the amine, the nitrogen is constrained to an sp^3-hybridised fashion. In the following solution studies, the free amine is used, which is frequently inverted. Both results are not directly comparable. But the crystal structure of **1a**·HCl shows that the phenolic OH-group is able to direct an anion above the electron-deficient arene regardless of the existent synergetic intermolecular hydrogen-bridges and that the chosen receptor geometry is appropriate for anion–π studies in solution.

Solution studies

In order to determine the binding constants for the anion–receptor complexes, NMR-titration experiments were performed in chloroform. Therefore, a 0.01 M stock solution of the phenyl salicyl amines **1a** and **1b** and a 0.04 M guest solution of the tetrabutylammonium halides were prepared. To exclude polarity effects, additional titrations with tetrabutylammonium hexafluorophosphate were carried out. The studied association equilibria are summarised in Scheme 2.

Before the association constants can be determined, the stoichiometries of the investigated anion–receptor complexes have to be checked by the method of Job. Hereby, the curves for the complexes of **1a** show a 1:1 ratio. In contrast to this, **1b**·I and **1b**·PF_6 deviate strongly from the 1:1 ratio towards a 2:1 ratio (see Figure 3(a)).

Unfortunately, it was not possible to follow the OH-proton in the ^{1}H NMR. The titration's curves of **1a** were obtained by following the fluorine signals and for **1b** the



Scheme 1. Synthesis of the phenyl salicylamines **1a** and **1b**.

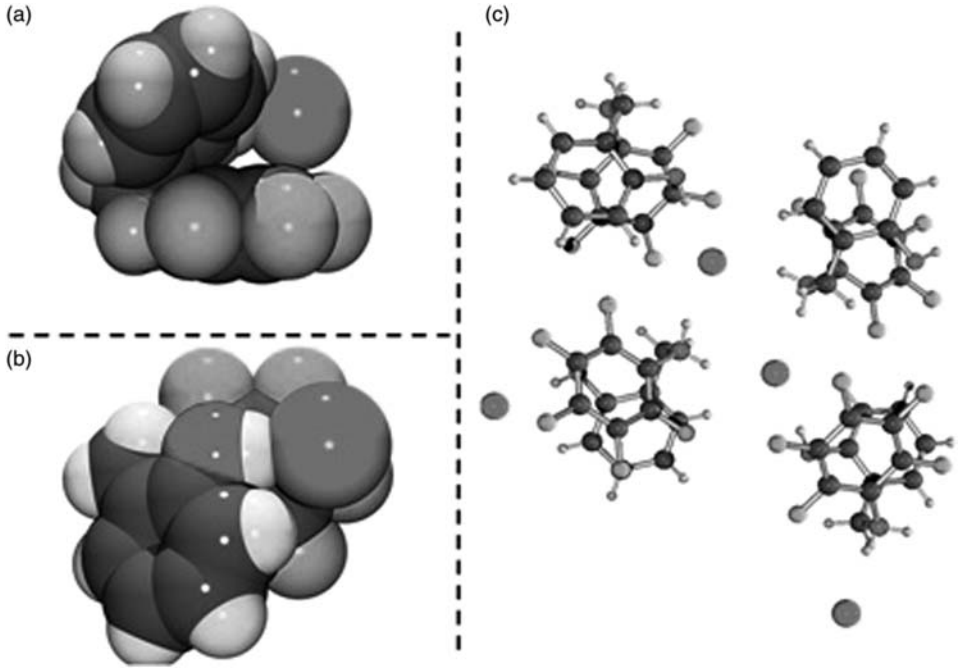


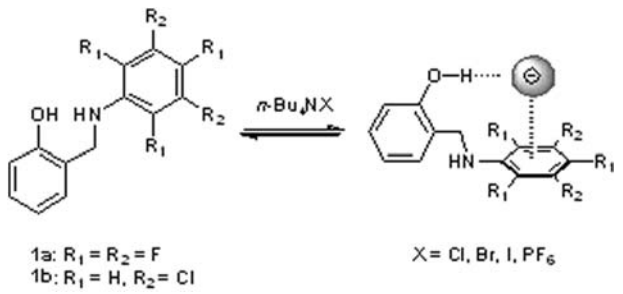
Figure 2. Part of the crystal structure of **1a**·HCl: (a) side-view and (b) top-view of the ion pair as well as the molecular packing as observed in the crystal structure of **1a**·HCl.

benzylic protons were used as probe. The binding constants result from a standard method of nonlinear regression and are summarised in Table 1.

The binding constants for **1a** vary slightly from 275 to 81 M^{-1}. Hereby, the following of the different fluorine signals (*ortho*, *meta* or *para*) in the ^{19}F NMR result in the same association constants. A comparison of the determined values reveals a decreasing binding strength from chloride, bromide to iodide. The association constant for **1a**·PF_6 is with 94 M^{-1}, somewhat higher than the **1a**·I binding constant. The reason for that might be the dependence of the anion–receptor stability from the polarizability of the anions.

Interestingly, the binding constant for **1b**·Cl is significantly higher than that for **1a**·Cl. The corresponding **1b**·Br complex shows with 143 M^{-1} a comparable binding affinity like **1a**·Br. Due to the deviation of the **1b**·I and **1b**·PF_6 complexes from a 1:1 ratio, the corresponding binding constants were not calculated.

The comparison of the obtained binding constants for **1a** and **1b** shows no hint for the relevance of anion–π interactions in the association of the receptor–anion complexes in chloroform. The higher binding constant for **1b**·Cl might be due to the cooperativity of OH–, NH– and CH–anion interactions in **1b** (Scheme 3(a)). In contrast to this, the OH– hydrogen bridge in **1a** can cooperate with the NH-anion (Scheme 3(b)) or the anion–π interaction (Scheme 3(c)). Furthermore, the binding constants of **1a** and **1b** were determined by the following different NMR signals (^{19}F and ^{1}H).



Scheme 2. Investigated association equilibria.

Conclusion

In conclusion, the presented results show that anion–π interactions of **1a**·HCl can be observed in the solid state. Due to the η^2-hapticity of these complexes, it can be deduced that the structural features of the receptor are not finally optimised for a fixation of the anion above the centre of the electron-deficient arene. Although only the charged aggregate **1a**·HCl could be observed in the solid, NMR spectroscopic titrations show that the neutral compound **1a** is an appropriate anion receptor in solution. The structure of the receptors in solution is flexible and the pentafluoro salicylamine is a promising candidate for anion–π studies with a neutral receptor.

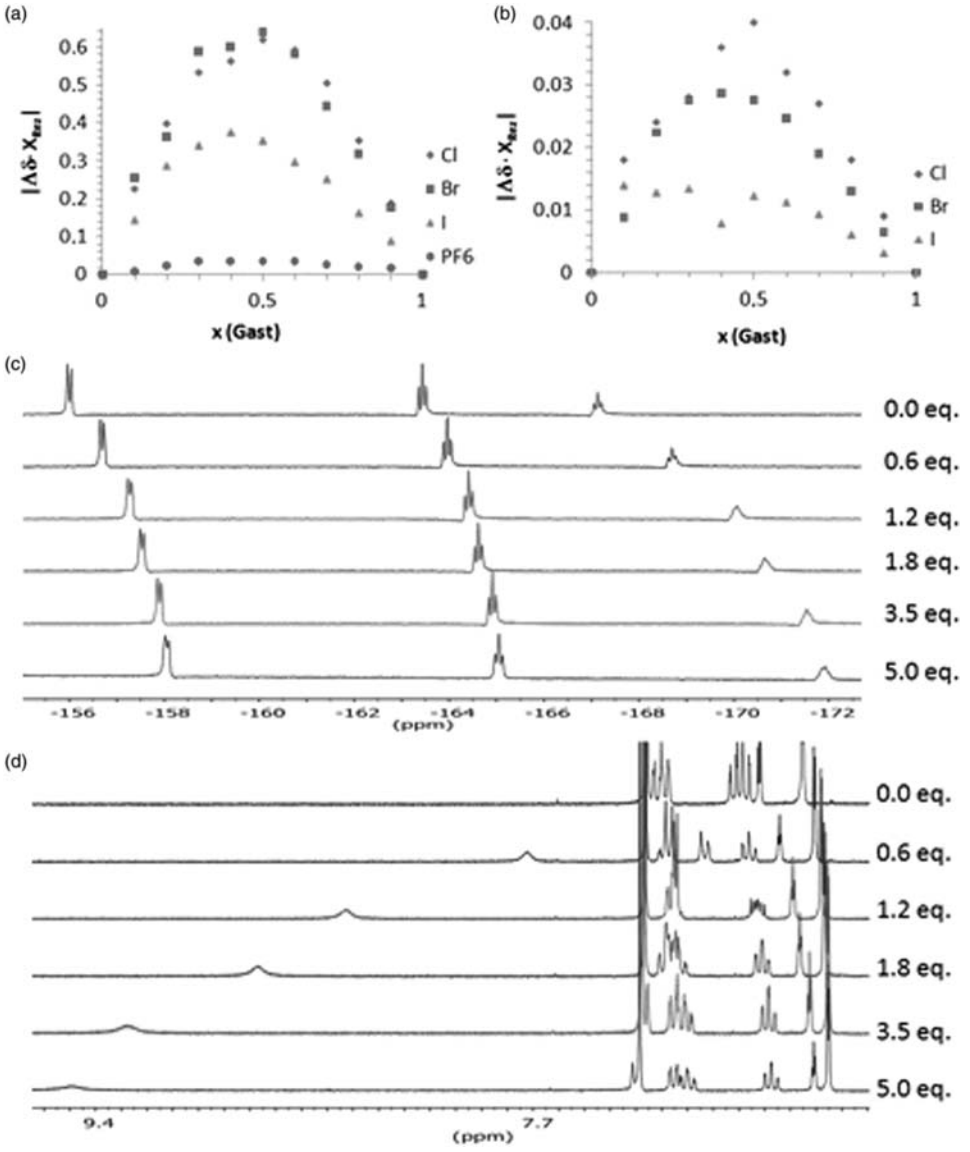


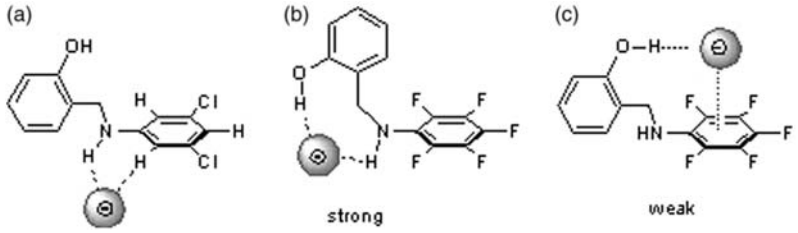
Figure 3. (a) Representative Job plots for receptor **1a** with various anions (Cl, Br, I, BF_4, PF_6 added as *n*-Bu_4N-salts) in deuteric chloroform; (b) corresponding Job plots for receptor **1b**; (c) selected ^{19}F NMR spectra for a 0.01 M solution of **1a**. A solution of *n*-Bu_4NCl in $CDCl_3$ was successively added; (d) selected ^{1}H NMR spectra for a 0.01 M solution of **1b**. A solution of *n*-Bu_4NCl in $CDCl_3$ was successively added.

Table 1. Binding constants K_a (M^{-1}) for the complexes of the phenyl salicylamines **1a** and **1b** with various anions (Cl, Br, I and PF_6 added as tetrabutyl ammonium salts).

		Cl	Br	I	PF_6
1a	F_{ortho}	275	161	81	96
	F_{meta}	256	159	82	94
	F_{para}	256	146	81	96
1b	H_{benzyl}	478	143	[a]	[a]

Notes: The binding constants were determined by $^{1}H/^{19}F$ NMR titration experiments in $CDCl_3$. Errors are estimated to be lower than 20%.
[a] Not calculated due to the deviation from a 1:1 ratio.

The NMR studies in deuteric chloroform give no indication for the relevance of anion–π interactions in the investigated receptors. In contrast to our expectations, the non-fluorinated anion receptor **1b** shows a significant higher affinity to chloride than to **1a**. Since binding constants are averages over all non-covalent interactions of the system (competing and cooperative), in solution the observed results become explainable. Due to the weakness of the anion–π interaction, it can easily be covered by other intermolecular effects. Further attempts have to exclude these effects to find conclusive evidence for anion–π interaction in solution.



Scheme 3. Competing and cooperating interactions with the anion.

Experimental

The commercially available reagents were used as received without further purification. The solvents were used after distillation. For NMR spectra, a Varian Mercury 300 NMR spectrometer (^{1}H: 300 MHz, ^{19}F: 282 MHz) was used. The samples were solved in deuteric chloroform. Mass spectrometric data were obtained via a Finnigan SSQ 7000 and Thermo Deca XP as EI (70 eV) or ESI. IR spectra were measured on a PerkinElmer FT-IR spectrometer Spektrum 100. All 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 determined on a Büchi B540 without further correction. X-ray data were collected at 123(2) K with Bruker-Nonius KappaCCD diffractometer equipped with APEXII detector, using graphite monochromatised Mo Kα radiation ($\lambda = 0.71073$ Å). COLLECT (*14a*) software was used for data collection and data were processed with DENZO-SMN (*14b*). The structure was solved by direct methods, using SIR-2004 (*14c*) and refined on F^2, using SHELXL-97 (*14d*). The multi-scan absorption correction (SADABS (*14e*)) was applied to data. The H atoms bonded to C atoms were calculated to their idealised positions with isotropic temperature factors (1.2 times the C atom temperature factor) and refined as riding atoms. The H atoms bonded to N or O atoms were found from electron density map and restrained to distances of 0.91 (N) or 0.84 Å from N/O atom (DFIX, $s = 0.02$) with isotropic temperature factors [1.2 (N) or 1.5 (O) times the parent atom temperature factor].

Synthesis of the phenyl salicylimines

Equimolar amounts of salicylaldehyde and the corresponding aniline derivative (pentafluoroanilin or 3,5-dichloroanilin) were stirred at 100°C for 6–8 h. The resulting solid was washed sparely with cold hexane and dried under *vacuo*.

Pentafluorophenyl salicylimine ***4a***

Yield: 410 mg yellow solid ($M = 287.18$ g/mol, 1.40 mmol, 32%). m.p.: 140°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 12.24 (s, 1H, OH), 8.83 (s, 1H, CHN), 7.47 (dt, $J = 8.0/1.4$ Hz, 1H, H_{aryl}), 7.41 (dd, $J = 8.0/1.4$ Hz, 1H, H_{aryl}), 7.06 (d, $J = 8.0$ Hz, 1H, H_{aryl}), 6.99 (dt, $J = 8.0/1.4$ Hz, 1H, H_{aryl}). ^{19}F NMR ($CDCl_3$, 300 MHz): δ (ppm) = −151.91 (m, 2 F, F_{ortho}), −158.08 (m, 1 F, F_{para}), −162.32 (m, 2 F, F_{meta}). MS (EI, 70 eV): *m/z* (%) = 286.8 (100, $[M]^+$, $C_{13}H_6F_5NO^+$). IR (KBr): ν (cm^{-1}) = 3424 (m), 3334 (m), 3138 (m), 2654 (w), 2477 (w), 2325 (w), 2201 (m), 2145 (m), 1926 (w), 1705 (w), 1611 (s), 1573 (w), 1503 (vs), 1367 (m), 1274 (m), 1205 (m), 1151 (m), 1112 (m), 975 (vs), 901 (m), 759 (vs), 665 (w). $C_{13}H_6F_5NO$: C 54.35, H 2.09, N 4.84, found: C 54.49, H 1.93, N 4.94.

3,5-Dichlorophenyl salicylimine ***4b***

Yield: 871 mg colourless solid ($M = 266.12$ g/mol, 3.27 mmol, 80%). m.p.: 87°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 12.55 (s, 1H, OH), 8.58 (s, 1H, CHN), 7.41 (d, $J = 3.2$ Hz, 1 H_{aryl}), 7.27 (t, $J = 1.8$ Hz, 1H, H_{aryl}), 7.26 (s, 1H, H_{aryl}), 7.17 (d, $J = 1.7$ Hz, 1H, H_{aryl}), 7.05 (s, 1H, H_{aryl}), 7.02 (s, 1 H, H_{aryl}), 6.97 (dt, $J = 8.0/11.2$ Hz, 1H, H_{aryl}). MS (ESI): *m/z* (%) = 264.0 (100, $[M - H]^-$, $C_{13}H_8Cl_2NO$). IR (KBr): ν (cm^{-1}) = 3129 (w), 3079 (m), 2988 (w), 2722 (w), 2653 (w), 2328 (m), 2098 (m), 1996 (w), 1948 (w), 1675 (m), 1618 (s), 1563 (s), 1494 (m), 1455 (s), 1422 (m), 1362 (s), 1278 (s), 1235 (m), 1192 (s), 1150 (s), 1104 (s), 1031 (w), 991 (w), 942 (s), 850 (s), 802 (s), 748 (s), 669 (s). $C_{13}H_9NCl_2O$: C 58.62, H 3.41, N 5.26, found: C 58.50, H 3.30, N 5.30.

Synthesis of the phenyl salicylamines

Imine **4a** or **4b** was mixed with 5.0 equiv. of sodium borhydride, 1.00 g silica gel and a few drops of chloroform. The slurry was grounded five times for 15 min. In between the slurry was rested for 20 min. To the mixture was added 30 mL of chloroform and the non-soluble solid was filtered off. After removing the solvent the obtained white solid was dried *in vacuo*.

Pentafluorophenyl salicylamine ***1a***

Yield: 286 mg colourless solid ($M = 289.20$ g/mol, 1.00 mmol, 83%). m.p.: 78°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.22 (dt, $J = 7.6/1.6$ Hz, 1H, H_{aryl}),

7.14 (dt, $J = 7.6/1.6$ Hz, 1H, H_{aryl}), 6.92–6.84 (m, 2H, H_{aryl}), 6.42 (s, 1H, OH), 4.44 (s, 2H, H_{benzyl}), 4.05 (s, 1H, NH). ^{19}F NMR ($CDCl_3$, 300 MHz): δ (ppm) = −156.02 (m, 2F, F_{ortho}), −163.45 (m, 2F, F_{meta}), −167.08 (m, 1F, F_{para}). MS (EI, 70 eV): *m/z* (%) = 289.1 (17, $[M]^+$, $C_{13}H_8F_5NO^+$). IR (KBr): ν (cm^{-1}) = 3333 (m), 3151 (w), 3026 (w), 2963 (w), 2877 (w), 2092 (w), 2007 (w), 1948 (w), 1697 (w), 1656 (w), 1593 (m), 1511 (vs), 1459 (s), 1356 (m), 1299 (w), 1246 (s), 1184 (w), 1152 (w), 1108 (w), 1057 (m), 1016 (vs), 987 (s), 956 (s), 892 (w), 870 (m), 850 (w), 819 (m), 780 (m), 756 (s), 729 (m), 662 (w). $C_{13}H_8F_5NO$: C 53.99, H 2.79, N 4.84, found: C 53.88, H 2.73, N 4.85.

Single crystals of **1a**·HCl were obtained by slow diffusion of HCl into a solution of **1a** in ethylacetate.

*3,5-Dichlorophenyl salicylamine **1b***

Yield: 374 mg colourless solid ($M = 268.14$ g/mol, 1.40 mmol, 75%). m.p.: 74°C. ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 7.23–7.18 (m, 2H, H_{aryl}), 6.92 (dd, $J = 9.0/1.2$ Hz, 1H, H_{aryl}), 6.88 (dd, $J = 8.0/0.9$ Hz, 1H, H_{aryl}), 6.82 (t, $J = 1.8$ Hz, 1H, H_{aryl}), 6.66 (s, 1H, H_{aryl}), 6.65 (s, 1H, H_{aryl}), 4.35 (s, 2 H, H_{benzyl}). MS (EI, 70 eV): *m/z* (%) = 268.0 (100, $[M]^+$, $C_{13}H_{11}Cl_2NO$). IR (KBr): ν (cm^{-1}) = 3407 (s), 3327 (m), 3043 (w), 2921 (w), 2871 (w), 2697 (w), 2324 (w), 2105 (w), 1991 (w), 1949 (w), 1913 (w), 1695 (w), 1586 (s), 1490 (s), 1449 (s), 1407 (m), 1353 (m), 1317 (m), 1267 (m), 1235 (s), 1181 (m), 1105 (s), 1068 (s), 1037 (m), 982 (m), 925 (m), 856 (m), 824 (s), 792 (s), 755 (s), 706 (w), 663 (s). $C_{13}H_{11}NCl_2O$: C 58.23, H 4.13, N 5.22, found: C 57.98, H 4.05, N 5.18.

Crystal data

*Compound **1a**·HCl*

Colourless prisms from EtOAc, $C_{13}H_9ClF_5NO$, F.W. = 325.66, crystal size 0.38 × 0.36 × 0.16 mm, monoclinic, space group $P2_1/n$ (no. 14), $a = 9.9652(3)$, $b = 13.1330(3)$, $c = 10.4590(3)$ Å, $\beta = 97.193(2)°$, $V = 1358.03(6)$ Å^3, $Z = 4$, $D_{calc} = 1.593$ g/cm^3, $\mu = 0.337$ mm^{-1}, $F(0\,0\,0) = 656$, 4767 collected reflections ($\theta_{max} = 25.25°$) of which 2454 are independent [$R_{int} = 0.0316$], full-matrix least-squares on F^2 with 3 restraints and 199 parameters, GOF = 1.046, $R_1 = 0.0400$ [$I > 2\sigma(I)$], wR_2 (all data) = 0.1036, largest peak/hole = 0.321/−0.252 e Å^{-3}.

Crystal data CCDC-883887 (**1a**·HCl) without structure factors can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html.

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