Supplementary material for

Cooperativity of H-bonding and anion-π interactions in the binding of anions to neutral π-acceptors

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Experimental Details

Synthesis of *N*-phenylbenzamides 2a and 2b: To a solution of aniline (1.0 eq.) in dichloromethane 1.0 eq. pyridine and 1.0 eq. pentafluorobenzoyl chloride or 3,5-dichlorobenzoyl chloride was added. The solution was stirred for 3 h. The organic layer was washed with a saturated, aqueous solution of sodium bicarbonate (2 times) and a solution of sodium chloride (1 time). After drying the organic solution with Na_2SO_4 and removing the solvent, the obtained white solid was purified by column chromatography (silica, hexane:EE = 3:1). After removing the solvent the remaining solid was dried in vacuo.

2a: yield: 148 mg (M = 287.18 g/mol, 0.51 mmol, 59%), Mp.: 189 °C. - ^{1}H-NMR (300 MHz, $CDCl_3$, a0121391): δ (ppm) = 7.54 (d, J = 7.9 Hz, 2H, H_{aryl}), 7.51 (t, J = 7.9 Hz, 2H, H_{aryl}), 7.36 (t, J = 7.9 Hz, 1H, H_{aryl}). - ^{19}F-NMR (300 MHz, $CDCl_3$): δ (ppm) = −139.95 (m, 2F, F_{ortho}), −149.70 (m, 1F, F_{para}), −159.45 (m, 2F, F_{meta}). - MS (EI, 70 eV): m/z (%) = 287.0 (51, $[M]^+$, $C_{13}H_6F_5NO^+$), 194.9 (100, $C_7F_5O^+$). - IR (KBr): ν (cm^{-1}) = 3245 (w), 3201 (w), 3144 (w), 3076 (w), 3049 (w), 2961 (w), 2871 (w), 2824 (w), 2621 (w), 2162 (w), 2077 (w), 1872 (w), 1658 (s), 1605 (m), 1560 (m), 1493 (vs), 1446 (s), 1421 (m), 1340 (m), 1262 (m), 1213 (w), 1177 (w), 1096 (s), 1026 (m), 985 (vs), 907 (w), 859 (w), 801 (m), 748 (s), 689 (m). – Elemental analysis (%): calc. $C_{13}H_6F_5NO \cdot 1/2\ H_2O$: C 52.72, H 2.38, N 4.73; found: C 52.95, H 2.48, N 4.61.

2b: yield: 489 mg (M = 266.12 g/mol, 1.84 mmol, 38%), Mp.: 150 °C. - ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.74 (d, J = 1.8 Hz, 2H, H_{aryl}), 7.69 (s, 1H, NH), 7.61 (d, J = 7.8 Hz, 2H, H_{aryl}), 7.54 (t, J = 1.8 Hz, 1H, H_{aryl}), 7.39 (t, J = 7.8 Hz, 2H, H_{aryl}), 7.19 (t, J = 7.8 Hz, 1H, H_{aryl}). - MS (EI, 70 eV): m/z (%) = 266.1 (65, $[M]^+$, $C_{13}H_9Cl_2NO$). - IR (KBr): ν (cm^{-1}) = 3315 (s), 3131 (w), 3065 (m), 2962 (w), 2854 (w), 2793 (w), 2660 (w), 2325 (w), 2083 (w), 1994 (w), 1945 (w), 1869 (w), 1755 (w), 1647 (vs), 1598 (m), 1563 (s), 1527 (vs), 1434 (vs), 1316 (vs), 1255 (vs), 1177 (w), 1101 (m), 1025 (m), 931 (w), 905 (m), 873 (m), 847 (w), 799 (s), 758 (s), 736 (s), 686 (vs). – elemental analysis (%): calc.: $C_{13}H_9Cl_2NO$: C 58.67, H 3.41, N 5.26; found: C 58.18, H 3.32, N 5.15.

Synthesis of *N,N'*-(1,2-phenylene)bis(2,3,4,5,6-pentafluorobenzamide) 2c: A mixture of 1,2-phenylen diamine (101 mg, 0.93 mmol) and pentafluorobenzoyl chloride (430 mg, 1.87 mmol) in dichloromethane was stirred for 12 h at ambient temperature. The precipitating white solid was filtered off and recrystallized from methanol. The remaining solid was dried in vacuo.

Yield: 356 mg (M = 496.26 g/mol, 0.72 mmol, 39%), Mp.: 249 °C. - ^{1}H-NMR (300 MHz, DMSO-d6): δ (ppm) = 10.36 (s, 2H, NH), 7.58 (m, 2H, H_{aryl}), 7.41 (m, 2H, H_{aryl}). - ^{19}F-NMR (300 MHz, DMSO-d6): δ (ppm) = -141.12 (m, 4F, F_{ortho}), -151.98 (m, 2F, F_{para}), -161.41 (m, 4F, F_{meta}). - MS (EI, 70 eV): m/z (%) = 496.4 (19, $[M]^+$, $C_{20}H_6F_{10}N_2O_2^+$), 195.1 (100, $C_7HF_5O^+$). - IR (KBr): ν (cm^{-1}) = 3255 (m), 3024 (w), 2325 (w), 2084 (w), 1664 (vs), 1493 (vs), 1418 (m), 1330 (m), 1264 (m), 1232 (m), 1102 (m), 991 (vs), 894 (w), 812 (w), 789 (m), 751 (s), 726 (m), 678 (w). – elemental analysis (%): calc. $C_{20}H_6F_{10}N_2O_2$: C 48.41, H 1.22, N 5.64; found: C 48.43, H 1.72, N 5.63.

NMR spectroscopic investigations

Table S1. Binding constants K_a [M^{-1}] for the 1:1 complexes of **2a** and **2b** with various anions (*n*-Bu_4NCl, Br, I, PF_6). The binding constants were determinded by following the signals in the $^1H/^{19}F$ NMR spectra in $CDCl_3$. (Errors are estimated to be lower than 20%).

	Signal	Cl	Br	I	BF_4**	PF_6
2a	**NH**	237	173	99	135	89
	CH_{ortho}	217	208	67	144	96
	CH_{meta}	348	203	111	133	107
	CH_{para}	302	224	113	153	115
	F_{ortho}	154	63	168	123	114
	F_{meta}	262	203	101	145	97
	F_{para}	236	193	94	149	98
2b	**NH**	163	114	82	102	74
	DCP-H_{ortho}	173	126	88	143	*
	DCP-H_{para}	209	100	119	*	*
	H_{ortho}	170	119	82	148	*
	H_{meta}	222	75	87	*	*
	H_{para}	255	*	106	*	*

* no systematic behaviour
** determinded for a 1:1 complex

The NMR spectrometric data for the low-temperature investigations are shown in figure S1.

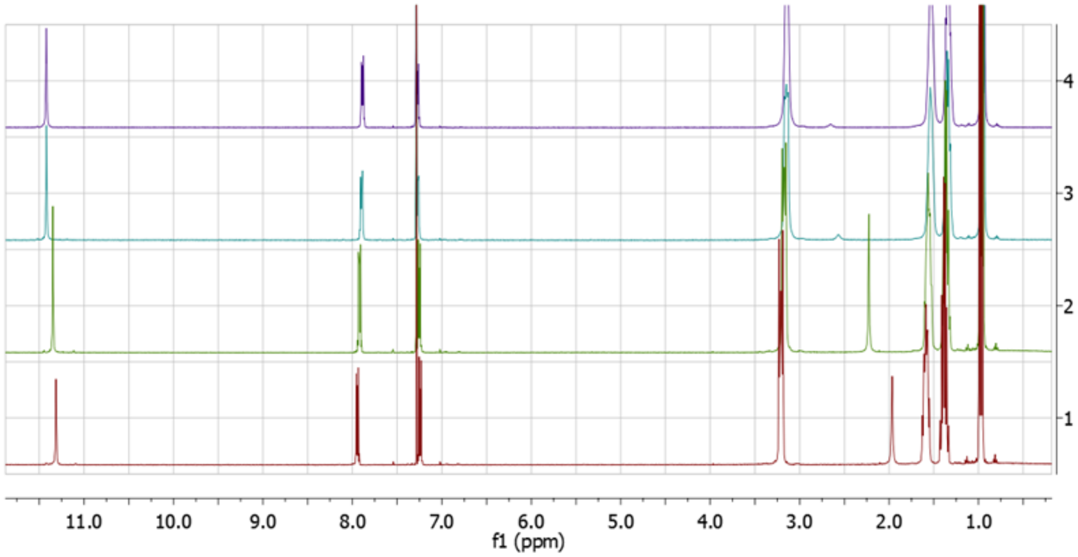

Figure S1. Selected ^1H NMR spectra of **3c**·$BrNBu_4$ in CD_3CN at -60, -50, -10 and 25°C.

Single crystal X-ray analysis

The crystals suitable for single crystal X-ray diffraction analyses were obtained by diffusing diethyl ether into a solution of **1** in methanol or by slow evaporation of acetonitrile solution of **2c**. The structural data were collected at 123.0 ± 1 K with Bruker-Nonius KappaCCD diffractometer equipped with APEXII detector, using graphite monochromatized MoK$_\alpha$ radiation (λ = 0.71073 Å). COLLECT[S1] software was used for data collection and data were processed with DENZO-SMN.[S2] The structures were solved by direct methods, using SIR-2004[S3] and refined on F^2, using SHELXL-97.[S4] The multi-scan absorption correction (SADABS[S5]) was enabled to all data. The H atoms bonded to C atoms were calculated to their idealized positions with isotropic temperature factors (1.2 times the C atom temperature factor) and refined as riding atoms. The H atoms bonded to N atoms were found from electron density map and fixed to distances of 0.91 Å from N atom (DFIX) with isotropic temperature factor (1.2 times the N atom temperature factor). The figures for the article and supplementary material were drawn with ORTEP-3[S6], MERCURY[S7] and POV-RAY[S8].

Crystal data of 1: Colourless plates, $C_{15}H_{22}BrF_5N_2O$, F.W. = 421.26, crystal size 0.18 x 0.09 x 0.07 mm^3, monoclinic, space group $P2_1/n$ (no. 14), a = 7.39080(10), b = 10.8170(2), c = 22.6232(4) Å, β = 97.6370(10) °, V = 1792.60(5) Å^3, Z = 4, D_{calc} = 1.561 g/cm^3, μ = 2.346 mm^{-1}, $F(000)$ = 856, 5933 collected reflections (θ_{max} = 25.25°) of which 3237 independent [R_{int} = 0.0283], T_{max} = 0.8530, T_{min} = 0.6774, full-matrix least-squares on F^2 with 2 restraints and 223 parameters, GOF = 1.062, $R1$ = 0.0351 [$I > 2\sigma(I)$], w$R2$ (all data) = 0.0734, largest peak/hole = 0.365/-0.343 e$^-$Å^{-3}.

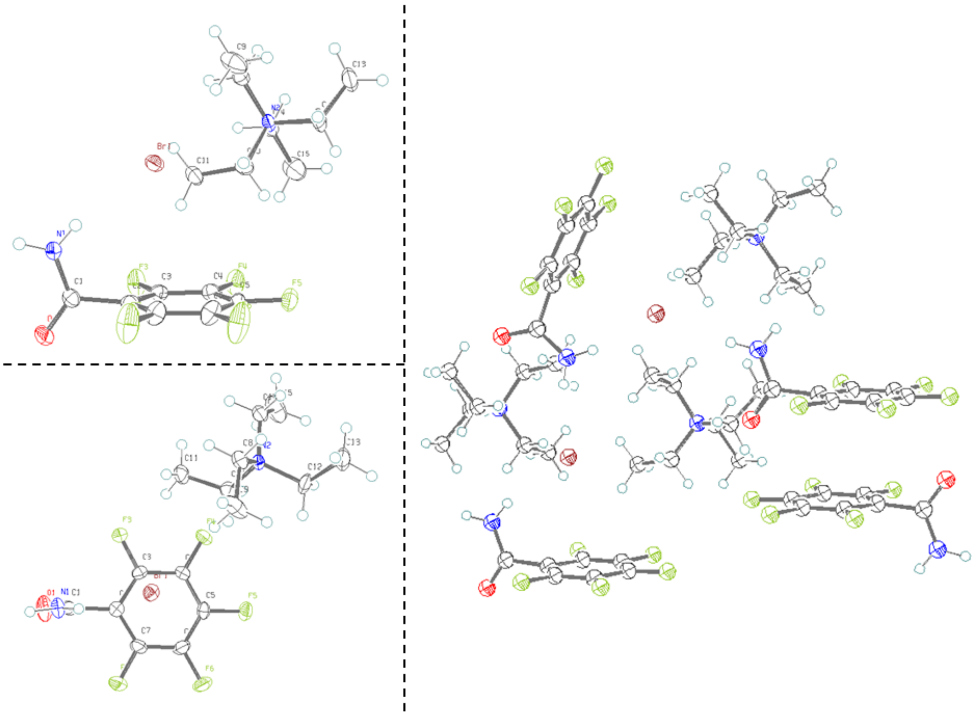

Figure S2. Part of the crystal structure of **1** showing the molecular packing.

Crystal data of 2c: Colourless sticks, $C_{20}H_6F_{10}N_2O_2$, F.W. = 496.27, crystal size 0.25 x 0.07 x 0.02 mm^3, triclinic, space group *P*-1 (no. 2), a = 4.9394(2), b = 10.5985(5), c = 17.8123(8) Å, α = 101.134(3), β = 97.114(2) °, γ = 91.720(3), V = 906.49(7) Å^3, Z = 2, D_{calc} = 1.818 g/cm^3, μ = 0.188 mm^{-1}, $F(000)$ = 492, 11489$^{\#}$ collected reflections (θ_{max} = 25.25°) of which 3248 independent [R_{int} = 0.0738$^{\#}$], T_{max} = 0.9962, T_{min} = 0.9545, full-matrix least-squares on F^2 with 2 restraints and 314 parameters, GOF = 1.065, $R1$ = 0.0612 [I>2σ(I)], w$R2$ (all data) = 0.1375, largest peak/hole = 0.337/-0.297 e$^-$Å^{-3}.

The crystals of **2c** were found to be non-merohedrically twinned with two domains. The data were refined with HKLF5 method type reflection file (.hkl) and with BASF parameter, which obtained a value of 0.16285 in the final refinement. The parameter values marked with $^{\#}$ above are given as prior to HKLF5 refinement.

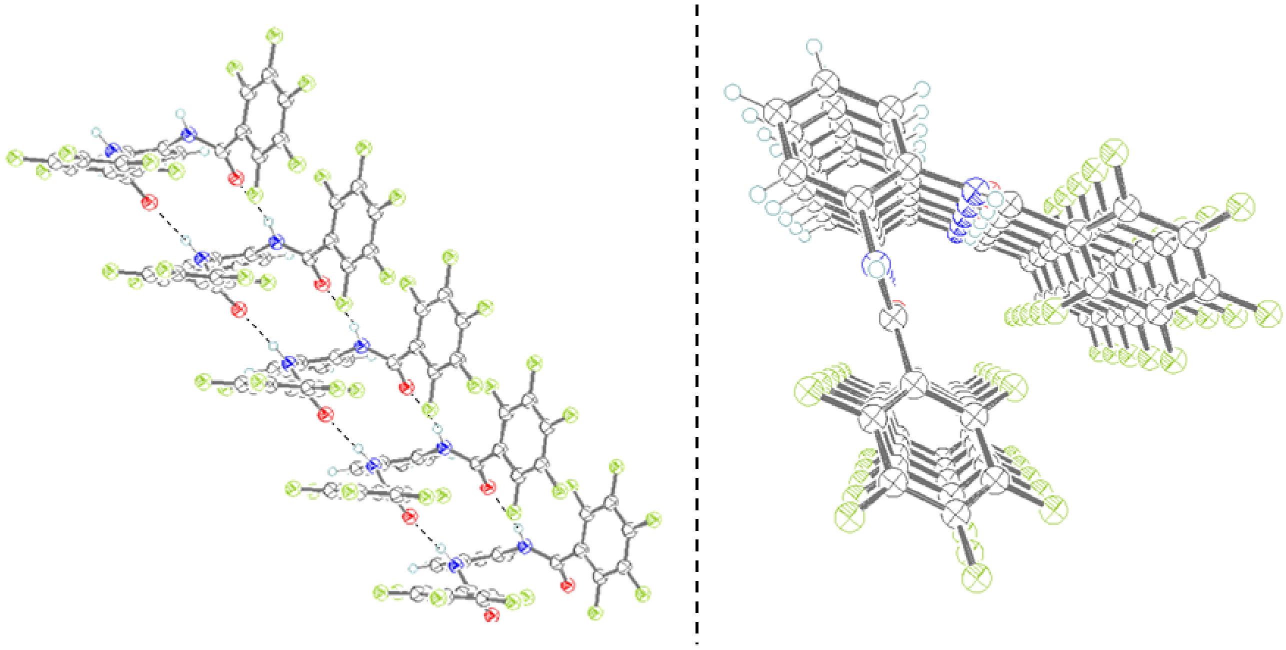

Figure S3. Two different views of as well as from the molecular packing of **2c** as observed in the solid phase.

Table S2. Hydrogen bonding interactions in **1** and **2c**.

Compound	D-H···A	Distance D-H in Å	Distance H···A in Å	Distance D···A in Å	Angle D-H···A in °
1	N1-H1B···Br1	0.89(2)	2.57(2)	3.431(3)	163(3)
1	N1-H1A···Br1*	0.89(2)	2.51(2)	3.392(3)	169(3)
2c	N1-H1···O7**	0.91(2)	2.16(2)	3.044(4)	163(4)
2c	N2-H2N···O14	0.90(2)	1.93(3)	2.722(4)	147(4)

Symmetry operations: * -x+1/2, y-1/2, -z+1/2; ** x-1, y, z

Computational studies

Figure S4 shows the geometrically optimized structures of both conformers **A** and **B** of compound **2c** with bromide. The energetically favoured conformer has been optimized on the MP2/6-311++g** level as well.[S1]

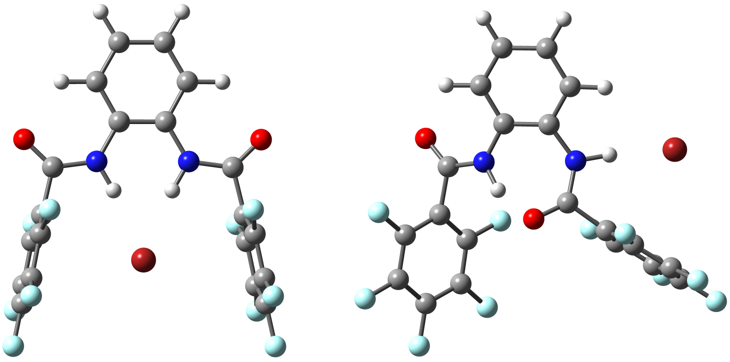

Figure S4. With MP2/6-31g* geometrically optimized conformers A and B of **2c** with bromide.

Table S3. Comparison of conformer **A** of complex **2c** with different anions attached, level of theory: MP2/6-311++g**, * the energy of the anion is subtracted.

Anion	Distance to C_6F_5 in Å	Distance to N-H in Å	Energy in a.u.	Energy* in a.u.
Cl	3.224	2.065	-2479.563790	-2019.860220
Br	3.377	2.321	-4592.368950	-2019.800585

Comparison of the geometrically optimized structure with chloride and bromide (Table S3) reveals different distances between the C_6F_5 group and the anion and the N-H group and the anion. In both cases, the distance is bigger with bromine as an anion due to its bigger ionic radius (Cl: 181 pm Br: 196 pm).

To compare the energies of the two complexes, the energy of both anions has been calculated. For bromide the energy results in -2572.568365 a.u. and for chloride in -459.703570 a.u. on the MP2/6-311++g** level of theory. The energy difference is about 37.42 kcal/mol. Therefore, the complex with chloride (Figure S5) is energetically favoured.

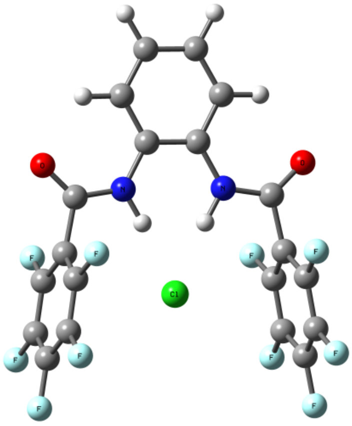

Figure S5. With MP2/6-311++g** geometrically optimized conformer A of **2c** with chloride.

References

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