Supporting information

**Positively and negatively charged NHN hydrogen bonds in one molecule: synergistic strengthening effect, superbasicity and acetonitrile capture**

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Experimental Section

Spectroscopic Measurements and General Considerations

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker DPX-250 (250 MHz for $^1$H, 62.9 MHz for $^{13}$C) and Bruker Avance-400 (400 MHz for $^1$H, 100.6 MHz for $^{13}$C) spectrometers with the solvent residual peaks as the internal standard ($\delta$/ppm, $^\circ$J/Hz). Mass spectra were obtained from Bruker maXis mass spectrometer (electrospray ionization). Thin layer chromatography was carried out on Al$_2$O$_3$ and on silica gel (70–230 mesh, Aldrich). The progress of reactions and the purity of products were monitored by TLC on Al$_2$O$_3$; development with iodine vapor. The melting points were measured in sealed capillaries and are uncorrected. The solvents were purified and dried by standard methods. Commercial grade reagents were used in case of 1,8-bis(dimethylamino)naphthalene (1) (Alfa Aesar, 98+%), Pd/C 5% (Acros Organics).

Preparation of Starting Materials

Compound 9 was prepared as described previously [S1].

Tosylation was performed by analogy to a published method for 4,5-bis(dimethylamino)-1-(p-toluenesulfonamido)naphthalene [S2].

4,5-Bis(dimethylamino)-8-nitro-1-(p-toluenesulfonamido)naphthalene (10). Pyridine (0.24 mL, 3 mmol) and tosyl chloride (0.21 g, 1.1 mmol) were added to a solution of amine 9 (0.274 g, 1 mmol) in anhydrous chloroform (15 mL). The mixture was stirred for 36 h at r.t. in Ar-atmosphere until the starting amine disappeared and then neutralized with aq. KOH (1.1 mmol). The organic layer was separated, washed with the equal amount of water, dried with anhydrous Na$_2$SO$_4$ and concentrated to the minimum volume. Sulfonamide 10 was isolated by preparative thin-layer chromatography (Al$_2$O$_3$, CHCl$_3$) collecting the major fraction ($R_f$=0.42). Dark red crystals with mp 163–165 °C (from EtOAc). Yield 0.248 g (58%). $^1$H NMR (CDCl$_3$): $\delta = 2.28$ (s, 3H, Me), 2.81 (s, 6H, 4-NMe$_2$), 3.00 (s, 6H, 5-NMe$_2$), 6.48 (d, $J=9.0$, 1H, 6-H), 6.92 (d, $J=7.9$, 2H, 3′-H, 5′-H), 6.97 (d, $J=8.4$, 1H, 3-H), 7.08 (s, 1H, NH), 7.14 (d, $J=8.1$, 2H, 2′-H, 6′-H), 7.62 (d, $J=8.4$, 1H, 2-H), 7.74 (d, $J=9.0$, 1H, 7-H). $^{13}$C NMR (CDCl$_3$): $\delta = 42.8$ and 43.9 (NMe$_2$), 60.4, 106.2, 112.1, 115.8, 121.0, 126.7, 128.4, 128.9, 130.2, 132.8, 135.4, 136.1, 142.2, 151.3, 157.2. ESI-HRMS: MH$^+$ = 429.1598, calc: 429.1591. IR (MeCN), $\nu$/cm$^{-1}$: 3240 (NH), 3065 (CH), 2803, 1577 (asNO$_2$), 1481 (ring), 1379 (SO$_2$), 1304 (sNO$_2$), 1131 (SO$_2$).

8-Amino-4,5-bis(dimethylamino)-1-(p-toluenesulfonamido)naphthalene (11). A mixture consisting of nitroamide 10 (150 mg, 0.35 mmol), MeOH (10 mL) and 5% Pd/C (30 mg, about 0.2 if taken from the mass of the amide) was hydrogenated at room temperature with shaking until the starting nitroamide is consumed (controlled by TLC, Al$_2$O$_3$/MeCN). After that, the catalyst was filtered off and the solvent was removed to give amine 10 with quantitative yield as gray solid darkening in the air; mp 168–170 °C (MeCN). $^1$H NMR (CD$_3$CN): $\delta = 2.32$ (s, 3H, CH$_3$), 2.86 (d, $J=2.2$, 6H, 5-NMe$_2$), 2.90 (d, 3H, CH$_3$), 2.98 (s, 3H, Me).
J=2.6, 6H, 4-NMe₂), 6.35 (d, J=8.4, 1H, 7-H), 6.94 (d, J=8.4, 1H, 2-H), 7.21 (m, 4H, 3-H, 6-H, 3'-H, 5'-H), 7.73 (d, J=8.1, 2'-H, 6'-H), 19.28 (s, 1H, 4N···H···5N) and 2H (very br. s, NH₂); see Figure S3. 

**13C NMR (CD₃CN):** δ = 20.3 (Me), 45.3 (NMe₂), 45.5 (NMe₂), 106.2, 110.5, 121.1, 121.2, 122.5, 126.7, 128.7, 129.2, 130.9, 140.1, 143.6, 150.7, 150.9. ESI-HRMS: MH⁺ = 399.1865, calc: 399.1849.

**IR (MeCN), ν/cm⁻¹:** 3438, 3363 (NH₂), 3202 (NH), 3096 (CH), 2788, 1130 (SO₂).

**4,5-Bis(dimethylamino)-1,8-bis(p-toluenesulfonamido)naphthalene, zwitterion (12).** Freshly prepared amine 11 (0.139 g, 0.35 mmol) was reacted with tosyl chloride (0.073 g, 0.385 mmol) dissolved in pyridine (2 mL). The mixture was stirred for 24 h at r.t. in Ar-atmosphere until the starting amine disappeared and then neutralized with aq. KOH (1.1 mmol). The organic layer was separated, washed with the equal amount of water, dried with anhydrous Na₂SO₄, and concentrated to the minimum volume. Target zwitterion 12 was isolated by preparative thin-layer chromatography (Al₂O₃, MeCN). Major fraction (Rf=0.9) gave 12 as a light beige solid (its solutions possess blue fluorescence under UV-light) with 60% yield (0.116 g); mp 219–220 °C (MeCN).

**1H NMR (CD₃CN):** δ = 2.32 (s, 6Н, two СH₃), 2.87 (d, J=2.6, 12H, 4-NMe₂, 5-NMe₂), 7.22 (d, J=8.0, 4H, 3'-H, 5'-H, 3''-H, 5''-H), 7.36 (m, 4H, 2-H, 3-H, 6-H, 7-H), 7.78 (d, J=8.2, 4H, 2'-H, 6'-H, 2''-H, 6''-H), 17.56 (br. d, 1H, 1N···H···2N), 19.11 (s, 1H, 4N···H···5N). 

**13C NMR (CD₃CN):** δ = 20.4 (Me), 45.4 (NMe₂), 111.4, 121.3, 126.9, 129.1, 134.6, 140.2, 142.2, 144.3. 

**1H NMR (DMSO-d₆):** δ = 2.53 (s, 6Н, two СH₃), 2.93 (br. s, 12H, 4-NMe₂, 5-NMe₂), 7.29 (m, 6H, 3'-H, 5'-H, 3''-H, 5''-H, 2-H, 3-H), 7.61 (d, J=8.5, 2H, 6-H, 7-H), 7.78 (d, J=7.6, 2'-H, 6'-H, 2''-H, 6''-H), 17.75 (br. s, 1H, 1N···H···2N), 18.88 (s, 1H, 4N···H···5N). 

**13C NMR (DMSO-d₆):** δ = 21.3 (Me), 46.0 (NMe₂), 111.2, 118.0, 122.0, 127.1, 129.7, 135.2, 140.3, 142.0, 144.0. ESI-HRMS: MH⁺ = 553.1962, calc: 553.1938. IR (nujol), ν/cm⁻¹: 3227 (NH), 1310, 1125 (SO₂).

**Tetrafluoroborate 12·HBF₄:** colorless crystals decomp. above 215 °C (from MeCN). **1H NMR (CD₃CN):** δ = 2.41 (s, 6H, CH₃), 2.87 (d, J=2.4, 12H, 4-NMe₂, 5-NMe₂), 7.13 (d, J=8.5, 2H, 3-H, 6-H), 7.32 (d, J=8.0, 4H, 3'-H, 5'-H, 3''-H, 5''-H), 7.59 (d, J=8.2, 4H, 2'-H, 6'-H, 2''-H, 6''-H), 7.70 (d, J=8.3, 2H, 2-H, 7-H), 9.63 (s, 2H, 1,2-NH), 19.14 (br. s, 1H, 4N···H···5N). 

**13C NMR (CD₃CN):** δ = 20.5 (Me), 45.6 (NMe₂), 121.8, 122.9, 127.9, 129.7, 133.2, 134.1, 142.5, 145.2.

**X-Ray Diffraction Analysis**

Crystals suitable for X-ray studies were grown up by slow evaporation from solutions of compounds in appropriate solvents: 12 (MeCN), 12·HBF₄ (MeOH). X-Ray measurements were conducted with Bruker APEX II diffractometer (Mo-Kα line, graphite monochromator, o-scanning) and SuperNova, Single source at offset/far, HyPix3000 (Cu-Kα line). Structure 12 was solved by direct method and refined by the full-matrix least-squares against F² in anisotropic (for non-hydrogen atoms) approximation. Structure 12·HBF₄ was solved with the ShelXT structure solution program using...
Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization. All hydrogen atoms were placed in geometrically calculated positions and were refined in isotropic approximation in riding model with the $U_{iso}(H)$ parameters equal to $n \cdot U_{eq}(C_i)$ (n = 1.2 for CH and CH$_2$ groups and n = 1.5 for CH$_3$ groups), where $U(C_i)$ are respectively the equivalent thermal parameters of the atoms to which corresponding H atoms are bonded. The main crystallographic data and some experimental details are given in Table S1. CCDC 1898534–1898535 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Table S1** Crystal data and structure refinement for compounds 12 and 12·HBF$_4$

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<th>12·HBF$_4$</th>
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<td>C$<em>{28}$H$</em>{33}$BF$_4$N$_4$O$_4$S$_2$</td>
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<td>Monoclinic</td>
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<tr>
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<td>11.09480(10)</td>
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<tr>
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**Figure S1.** $^1$H NMR spectrum of 10 (CDCl$_3$, 400 MHz).

**Figure S2.** $^{13}$C NMR spectrum of 10 (CDCl$_3$, 100.6 MHz).

**$^1$H and $^{13}$C NMR spectra of new compounds**

- **Me$_2$N**
- **NMe$_2$**
- **NO$_2$**
- **NHTs**

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Figure S4. $^3$C NMR spectrum of 11 (CD$_3$CN, 62.9 MHz).

Figure S3. $^1$H NMR spectrum of 11 (CD$_3$CN, 250 MHz).
**Figure S5.** $^1$H NMR spectrum of 12 (CD$_3$CN, 250 MHz).

**Figure S6.** $^{13}$C NMR spectrum of 12 (CD$_3$CN, 62.9 MHz).
Figure S7. $^1$H NMR spectrum of 12 (DMSO-d$_6$, 250 MHz).

Figure S8. $^{13}$C NMR spectrum of 12 (DMSO-d$_6$, 62.9 MHz).
**Figure S9.** $^1$H NMR spectrum of 12 + KOH (1 eq.) (anion 18) (DMSO-d$_6$, 250 MHz).

**Figure S10.** $^{13}$C NMR spectrum of 12 + KOH (1 eq.) (anion 18) (DMSO-d$_6$, 62.9 MHz).
**Figure S11.** $^1$H NMR spectrum of 12 + KOH (2 eq.) (dianion 19) (DMSO-d$_6$, 250 MHz).

**Figure S12.** $^{13}$C NMR spectrum of 12 + KOH (2 eq.) (dianion 19) (DMSO-d$_6$, 62.9 MHz).
**Figure S13.** $^1$H NMR spectrum of tetrafluoroborate 12-HBF$_4$ (CD$_3$CN, 250 MHz).

**Figure S14.** $^{13}$C NMR spectrum of tetrafluoroborate 12-HBF$_4$ (CD$_3$CN, 62.9 MHz).
**Figure S15.** $^1$H NMR spectrum of equimolar mixture of 12 and 1 (CD$_3$CN, 250 MHz).

**Figure S16.** $^1$H NMR spectrum of equimolar mixture of 12 and 16 (CD$_3$CN, 250 MHz).
**Figure S17.** $^1$H NMR spectrum of equimolar mixture of 12 and 17 (CD$_3$CN, 250 MHz).

**Figure S18.** $^1$H NMR spectrum of equimolar mixture of 12 and 17 (DMSO-d$_6$, 250 MHz).
Figure S19. CH/π interactions (the shortest distances are shown) in the crystal structure of inclusion compound 12·MeCN.

Figure S20. Mutual arrangement of the tosyl groups in X-ray structure of salt 12·HBF₄.
On the formation of zwitterion from mono-tosylated tetramine 11

Some time ago [S2] we described the 4-tosylamino derivative of DMAN 20 and found that it exists as such, without transferring the proton NH onto the NMe₂ groups. However, in the present work, when obtaining its close analogue 11, we noticed that in the 1H NMR spectrum of the substance recorded in CD₃CN, a signal of the chelated [NHN]⁺ proton appears at δ 19.28 ppm, which is consistent with the zwitterionic structure 11', but not 11 (Fig. S3, Scheme S1). The formation of 11' could be explained only by the internal proton transfer from the tosylamino group to the peri-NMe₂ groups in 11, since the latter was obtained in a neutral medium excluded the presence of external protons. Apparently, the stimulus for such proton transfer here might be the formation of the IHB of [NHN]⁻ type, which is impossible in compound 20. Regrettably, we could not perform an X-ray analysis of 20 due to its relative instability to air oxidation, resembling that of amine 21. Therefore, the main arguments in favor of real structure of 11 were based on the 1H NMR spectroscopy data and physical properties (e.g. 11 has rather high melting point and, similar to other protic salts of DMAN, is insoluble in Et₂O suggesting zwitterionic structure 11'). Thus, if the moderately widened signals of the NH₂ group in base 21 (in CDCl₃) and in perchlorate 21·HClO₄ (in MeCN) are located at 3.5 and 5.1 ppm, respectively, then in compound 11' it has a strongly diffuse appearance, extending between 6.5–8.5 ppm area (Fig. S3). This behavior is characteristic of weak and dynamically active hydrogen bonds [S3]. Based on this, we believe that zwitterion 11' actually equilibrates between the two forms 11'(a) and 11'(b) (Scheme S1). Obviously, accompanying and slowed in the NMR time scale rotation of the NH₂ group around the C₆–N bond causes a sharp paramagnetic shift of the NH₂ protons in 11' as compared with the chemical shift of the chelated [NHN]⁻ proton in the spectrum of zwitterion 12.

Scheme S1. Possible formation of the zwitterionic structure for compound 11.
References