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Monohydrazine analogues of naphthalene and acenaphthene 'proton sponges'

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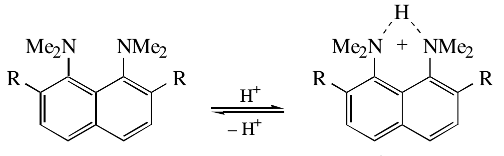
N-Amino derivatives (as picrates) of 1-dimethylamino-8-methylaminonaphthalene 5 and 5-dimethylamino-6-methylaminoacenaphthene 6 have been prepared by the electrophilic amination of 5 and 6 with *O*-picrylhydroxylamine.

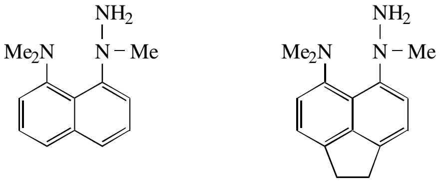
It is well known that exceptionally high basicity of 1,8-bis(dimethylamino)naphthalene ('proton sponge', **1**, pK_a 12.1, H_2O, 25 °C) is caused by the cooperative action of three main factors: (1) electrostatic repulsion of free nitrogen electron pairs; (2) purely steric repulsion of four methyl groups and (3) existence of strong intramolecular hydrogen bonding (IHB) in cation **1H$^+$**.[1] In particular, the role of the first factor is especially well displayed in 2,7-dimethoxy-1,8-bis(dimethylamino)naphthalene **2** (Scheme 1), whose basicity due to repulsion of four adjacent free electron pairs reaches a record value equal to 16.1 pK_a units (H_2O, 25 °C).[2] Therefore, it was interesting to prepare unknown hydrazine analogues of naphthalene 'proton sponges', the molecules of which also have additional possibilities for repulsive interactions of non-bonded electron pairs and thus can pretend for high basicity. The aim of this work was to synthesise and characterise monohydrazine 'proton sponges' **3** and **4** (Scheme 2).



1 R = H
2 R = OMe

1H$^+$ R = H
2H$^+$ R = OMe

Scheme 1



3

4

Scheme 2

Treatment of 1-dimethylamino-8-methylaminonaphthalene **5** and 5-dimethylamino-6-methylaminoacenaphthene **6** with *O*-picrylhydroxylamine in a $CHCl_3$–MeCN solution leads to desired compounds isolated as picrates **3H$^+$** and **4H$^+$** in 23 and 39% yield, respectively (Scheme 3).[†] For both of the salts, X-ray experiments were conducted and their results are depicted in Figures 1 and 2.[‡] The most important features of the molecular structures of picrates **3H$^+$** and **4H$^+$** are connected with protonation sites and hydrogen bonding. Analysis of X-ray data for salt **3H$^+$** indicated that an acidic proton is located on both α- and β-nitrogen atoms of the hydrazine group with relative probabilities of 77 and 23%, respectively.[§] It can be interpreted in favour of the coexistence of two tautomers **3H$^+$(b)** and **3H$^+$(c)** in a crystal lattice, the former being preferable. As for the other 'proton sponge' salts,[1] in **3H$^+$(b)** the IHB is formed. The hydrogen bond is rather asymmetrical and the NH proton lies much closer to the α-nitrogen atom of the hydrazine group (1.17 Å) than to the NMe_2 nitrogen (1.48 Å).[¶] The distance between the nitrogen atoms forming IHB in **3H$^+$(b)** equal 2.568 Å is typical of cations of naphthalene 'proton sponges' (*e.g.*, 2.55 Å in **1H$^+$**).[1] The coexistence of protonated forms **3H$^+$(b)** and **3H$^+$(c)** gives a ground to think that IHB in the former should be weakened. Indeed, in ^{1}H NMR spectra of picrate **3H$^+$** in a [$^2H_6$]DMSO or CD_3CN solution there is no signal of chelated NH proton, which is displayed for cations **1H$^+$** or **2H$^+$** in the region 18–20 ppm.[1] Instead, a broad three-proton signal of the NH_3^+ group is observed at 9.70 ppm testifying an exclusive presence of **3H$^+$(b)**. Unlike **3H$^+$**, acenaphthene picrate exists both in solution and in crystals only in β-protonated form **4H$^+$(a)**. As it follows from X-ray measurements in the solid state, this form [**4H$^+$(a)**] is stabilised by IHB closing a seven-membered cycle. Interestingly, a hydrogen bridge in **4H$^+$(a)** is almost symmetrical [N(3)–H(2N) 1.30 Å, N(1)–H(2N) 1.31 Å, angle N(3)–H(2N)–N(1) 161°]. We believe that the structural difference between salts **3H$^+$** and **4H$^+$** originates from the known difference between parent 'proton sponge' **1** and its acenaphthene analogue **7** (Scheme 4).[5] Whereas internitrogen distances in base **1** and cation **1H$^+$** are equal to 2.79 and 2.55 Å, in **7** and **7H$^+$** they are considerably enlarged (2.88 and 2.67 Å), providing for the latter cation a weaker IHB.[††] From this one can suggest that seven-membered chelate form **4H$^+$(a)** is energetically more favourable in comparison with its six-membered counterpart **4H$^+$(c)**. In accord with this in cation **4H$^+$** the N(1)···N(3) distance equal to 2.576 Å is much shorter than that between the atoms N(1) and N(2).

Since β-protonation is a typical phenomenon for ordinary arylhydrazines,[6] one can conclude that compound **4** behaves normally in this sense. On the contrary, the behaviour of hydrazine **3** looks somewhat anomalous because along with formation of β-protonated form **3H$^+$(b)** its α-protonated tautomer **3H$^+$(a)** can exist at least in a solid state. To our knowledge, this is the first example of α-protonation in the arylhydrazine series.

[†] *Typical procedure for the synthesis of* **3H$^+$** *or* **4H$^+$**. To a stirred solution of **5** or **6**[3] (1.0 mmol) in $CHCl_3$ (5 ml), a solution of *O*-PicONH_2[4] (0.122 g, 0.5 mmol) in MeCN (3 ml) was added in portions at 20 °C. After stirring at room temperature for additional 1 h, the solid formed was filtered off and recrystallised from MeOH to afford **3H$^+$** or **4H$^+$** as yellow crystals.

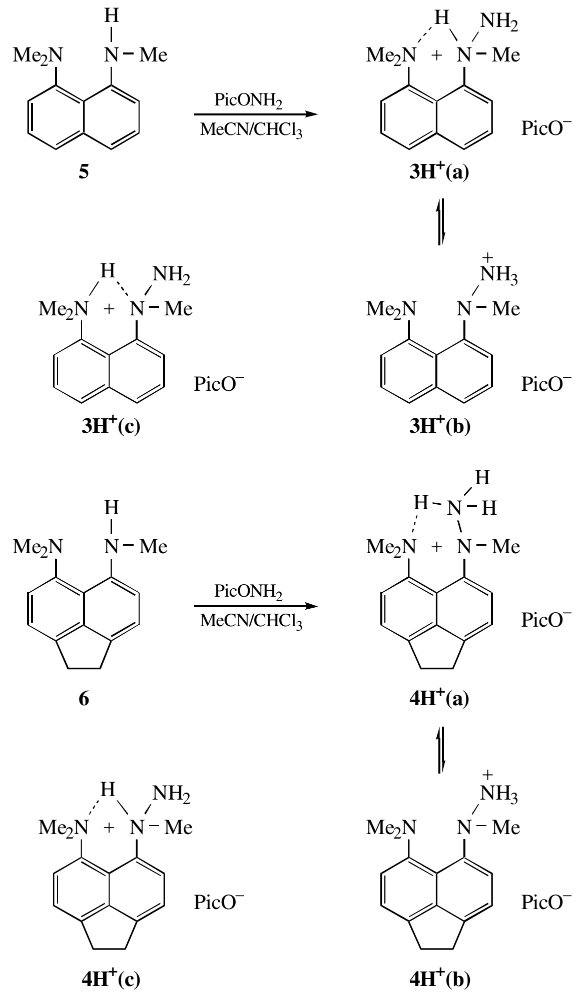
Compounds **3H$^+$** and **4H$^+$** gave analytical and spectral data in agreement with their structures.

For N*-methyl-*N*-(8-dimethylaminonaphthyl-1)hydrazinium picrate* **3H$^+$**: yield 0.051 g (23%), mp 133–134 °C. ^{1}H NMR (250 MHz, CD_3CN) δ: 3.23 (s, 3H, N–Me), 3.28 (s, 6H, NMe_2), 7.71 (m, 2H, 3,6-H), 8.01 (m, 4H, 2,4,5,7-H), 8.64 (s, 2H, Pic), 8.4–9.0 (br. s, 3H, NH_3^+). ^{1}H NMR (250 MHz, [$^2H_6$]DMSO) δ: 3.12 (s, 3H, NMe_2), 3.20 (s, 6H, NMe), 7.70 (m, 2H, 3,6-H), 7.96 (m, 2H, 2,4-H), 8.03 (m, 2H, 5,7-H), 8.59 (s, 2H, Pic), 9.70 (br. s, 3H, NH_3^+).

For N*-methyl-*N*-(4-dimethylaminoacenaphthenyl-5)hydrazinium picrate* **4H$^+$**: 0.092 g (39%), mp 152 °C. ^{1}H NMR (250 MHz, CD_3CN) δ: 3.20 (s, 3H, N–Me), 3.27 (s, 6H, NMe_2), 3.34 (s, 4H, CH_2CH_2), 7.46 (m, 2H, 2,3-H), 7.59 (d, 1H, 7-H, *J* 7.59 Hz), 7.79 (d, 1H, 6-H, *J* 7.62 Hz), 8.1–8.4 (br. s, 3H, NH_3^+), 8.62 (s, 2H, Pic). ^{1}H NMR (250 MHz, [$^2H_6$]DMSO) δ: 2.96 (s, 6H, NMe_2), 3.20 (s, 3H, NMe), 3.34 (s, 4H, CH_2CH_2), 7.42 (m, 3H, 2,3,7-H), 7.59 (d, 1H, 6-H, *J* 7.57 Hz), 8.58 (s, 2H, Pic), 9.95 (br. s, 3H, NH_3^+).

Unfortunately, we did not succeed in the isolation of free bases **3** and **4** since at addition of aqueous alkalies or ammonia to salts **3H$^+$** or **4H$^+$** a complete tarring occured. Possibly, both these bases are very air-sensitive as many other arylhydrazines with electron-donor substituents. Nevertheless, we could register ^{1}H NMR spectra of compounds **3** and **4**. When to a [$^2H_6$]DMSO solution of picrate **3H$^+$** or **4H$^+$**, placed in an NMR ampoule, an equimolar amount of base **2** was added full deprotonation took place and both formed species **3** (or **4**) and **2H$^+$** could be clearly distinguished. For example, the peaks of the terminal amino group in **3** and **4** resonate at 5.12 and 4.68 ppm, respectively.[‡‡]

Finally, we have estimated the basicity of compounds **3** and **4** in [$^2H_6$]DMSO solution by a competetive protonation method based on ^{1}H NMR spectroscopy.[7] As it was just mentioned, salts **3H$^+$** and **4H$^+$** are fully deprotonated by base **2** (pK_a 11.5 in DMSO, 25 °C). At the same time no deprotonation occurs with acenaphthylene 'proton sponge' **8** (pK_a 5.7 in DMSO, 25 °C).[5] These facts mean that basicities of the studied hydrazines are somewhere in an interval between 6 and 10 pK_a units. Indeed, when equimolar quantites of **3H$^+$** or **4H$^+$** and 'proton sponge' **1** (pK_a 7.5 in DMSO, 25 °C) were mixed in an NMR ampoule we



Scheme 3

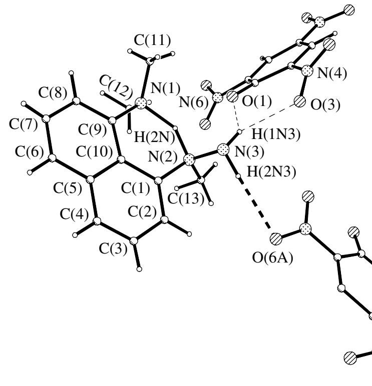


Figure 1 General view of **3H$^+$** (*S*-enantiomer). Selected bond lengths and distances (Å): N(1)–C(9) 1.456(2), N(1)–H(2N) 1.48(3), N(2)–H(2N) 1.17(3), N(2)–N(3) 1.461(2), N(2)–C(1) 1.462(2), N(3)–H(1N3) 0.92(2), N(3)–H(2N3) 1.03(3), selected bond angles (°): C(9)–N(1)–C(12) 111.7(2), C(9)–N(1)–C(11) 114.1(1), C(12)–N(1)–C(11) 110.8(2), C(9)–N(1)–H(N2) 101(1), C(12)–N(1)–H(N2) 106(1), C(11)–N(1)–H(N2) 113(1), N(3)–N(2)–C(1) 110.7(1), N(3)–N(2)–C(13) 112.9(2), C(1)–N(2)–C(13) 113.3(1), N(3)–N(2)–H(N2) 105(1), C(1)–N(2)–H(N2) 105(1), C(13)–N(2)–H(N2) 101(1), N(2)–N(3)–H(2N3) 105(2), H(1N3)–N(3)–H(2N3) 110(2), N(1)–H(N2)–N(2) 151(2); torsion angles (°): N(1)–C(9)–C(10)–C(1) 5.1(2), N(2)–C(1)–C(10)–C(9) 5.0(2); interatomic distance N(1)···N(2) 2.568(2) Å; Σ angles N(1) 336.6°, N(2) 336.77°, N(3) 324.8°.

[‡] *Crystal data for* **3H$^+$**: at 110 K crystals of $C_{19}H_{20}N_6O_7$ (M = 444.41) are monoclinic, space group $P2_1/n$, a = 9.806(1) Å, b = 9.501(1) Å, c = = 21.769(3) Å, β = 101.093(3)°, V = 1990.3(5) Å^3, Z = 4, d_{calc} = 1.483 g cm^{-3}, μ(MoKα) = 0.116 mm^{-1}, F(000) = 928. Intensities of 22807 reflections were measured with a Bruker SMART diffractometer at 110 K and 5730 independent reflections (R_{int} = 0.0325) were used in a further refinement. The structures were solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic approximation for non-hydrogen atoms. All hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. The refinement converged to wR_2 = 0.1567 and GOF = 0.859 for all independent reflections [R_1 = 0.0580 was calculated against F for 3410 observed reflections with $I > 2\sigma(I)$].

Crystal data for **4H$^+$**: at 120 K crystals of [$C_{15}H_{20}N_3^+$][$C_6H_2N_3O_7^-$] (M = 470.45) are monoclinic, space group $P2_1/n$, a = 14.552(2) Å, b = = 7.953(1) Å, c = 18.435(3) Å, β = 105.131°, V = 2059.6(5) Å^3, Z = 4, d_{calc} = 1.517 g cm^{-3}, μ(MoKα) = 0.117 mm^{-1}, F(000) = 984. Intensities of 14119 reflections were measured with a Bruker SMART diffractometer at 120 K and 4484 independent reflections (R_{int} = 0.0386) were used in a further refinement. The structures were solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic approximation for non-hydrogen atoms. The hydrogen atoms (except ones in the NH and NH$_2$ groups) were placed in geometrically calculated positions and included in the final refinement using the 'riding' model with the U_{iso}(H) parameters equal to 1.2U_{eq}(C$_i$) or 1.5U_{eq}(C$_{ii}$), where U(C$_i$) and U(C$_{ii}$) are the equivalent thermal parameters of the methyne and methylene carbon atoms, respectively, to which corresponding H atoms are bonded. The hydrogen atoms of NH and NH$_2$ groups were located from the Fourier synthesis and refined in the isotropic approximation. The refinement converged to wR_2 = 0.1638 and GOF = 0.977 for all independent reflections [R_1 = 0.0731 was calculated against F for 4484 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL (Version. 5.1) software on an IBM PC.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 210485 and 210486. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2003.

[§] The site occupancy factors (s.o.f.) for H$_2$N and H$_3$N$_3$ atoms were obtained by the refinement of corresponding values of s.o.f. with the constraints: their sum was equal to 1 and the isotropic temperature factors of H$_2$N and H$_3$N$_3$ were fixed upon the refinement. (The s.o.f. were expressed in terms of a free variable, FVAR 0.5, 21.0000 and –21.0000 for H$_2$N and H$_3$N$_3$, respectively).

[¶] Contrary to this, the proton affinity values, PA, for **3** calculated by B3LYP/6-31+G**//HF/6-31G** level of theory, turned to be equal to 1024.7, 923.9 and 1025.0 kJ mol^{-1} for protonated species **3H$^+$(a)**, **3H$^+$(b)** and **3H$^+$(c)**, respectively. Thus, they predict almost the same stability for forms **3H$^+$(a)** and **3H$^+$(c)** but ignore protonation at the β-nitrogen atom of the hydrazine functionality. Since these quantum chemical calculations refer to gas phase, one can suggest that these disagreements are due to crystal field and solvation effects.

[††] The analysis of the Fourier difference map, calculated without H(2)N hydrogen, unambiguously have showed that there is only one maxim in the interatomic N···N region in both **3H$^+$** and **4H$^+$**, thus indicating that there is no disordered of the corresponding hydrogen atoms.

[‡‡] ^{1}H NMR (250 MHz, [$^2H_6$]DMSO) for **3**, δ: 2.79 (s, 6H, NMe$_2$), 2.94 (s, 3H, NMe), 5.12 (br. s, 2H, NH$_2$), 7.10–7.47 (m, 6H, 2,7-H).

^{1}H NMR (250 MHz, [$^2H_6$]DMSO) for **4**, δ: 2.77 (s, 6H, NMe$_2$), 2.94 (s, 3H, NMe), 3.27 (s, 4H, CH$_2$CH$_2$), 4.68 (br. s, 2H, NH$_2$), 6.95–7.21 (m, 4H, 3,4,7,8-H).

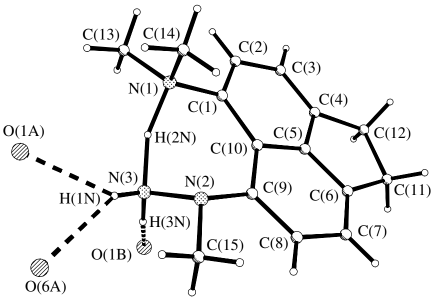
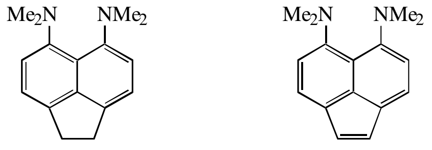


Figure 2 General view of cation **$4H^+$** (*S*-enantiomer). Selected bond lengths (Å): N(1)–C(1) 1.461(3), N(2)–N(3) 1.457(3), N(2)–C(9) 1.438(3), N(2)–C(15) 1.464(3), N(3)–H(1N) 0.83(3), N(3)–H(2N) 1.30(3), N(3)–H(3N) 0.99(3), N(1)–H(2N) 1.31(3); selected bond angles (°): C(1)–N(1)–C(13) 116.0(2), C(1)–N(1)–C(14) 112.7(2), C(13)–N(1)–C(14) 109.3(2), C(9)–N(2)–N(3) 110.3(2), C(9)–N(2)–C(15) 116.7(2), N(3)–N(2)–C(15) 110.3(2), C(2)–C(1)–N(1) 119.4(2), C(10)–C(1)–N(1) 119.4(2), C(10)–C(1)–N(1) 119.5(2), C(8)–C(9)–N(2) 118.6(2), N(2)–C(9)–C(10) 122.3(2), N(3)–H(N2)–N(1) 161(1); torsion angles (°): N(3)–N(2)–C(9)–C(10) 52.4(3), N(1)–C(1)–C(10)–C(9) 3.4(4); interatomic distances N(1)···N(2) 2.971(2) Å; N(1)···N(3) 2.576(3) Å; Σ angles N(1) 338.01°, N(2) 337.23°, N(3) 329.14°.

observed at an equilibrium state exactly equal amounts of all possible protonated and deprotonated species: **$3H^+$** or **$4H^+$**, **3** or **4**, as well as **1** and **$1H^+$**. Hence, the pK_a values of hydrazines **3** and **4** can be evaluated as being equal ~7.5. At extrapolation to water solution this value corresponds to ~12 pK_a.

Thus, our study has demonstrated that substitution of one Me group in ‘proton sponge’ **1** for the NH_2 group actually does not lead to any basicity changes. However, this result in our opinion can be considered as purely accidental. The matter is that compounds **3** and **4** are protonated in solution at terminal amino groups, in other words, behave as arylhydrazines, not ‘proton sponges’. From such a point of view estimated for them pK_a value looks unprecedentally high for arylhydrazines [$PhNHNH_2$: pK_a 5.27, H_2O, 25 °C.[9] It is surprising, but we did not found any other information concerning the basicity of other simple arylhydrazines (SciFinder system was used for this search)]. The reason for the high basicity of compounds **3** and **4** is apparently a field effect of the 8-NMe_2 group (actually electrostatic repulsion), which destabilises the 1-(α-methyl)hydrazine group and gives an additional stimulus for its protonation.[§§]



7 **8**

Scheme 4

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[§§] Similar field effect of peri-substituents was found in 3-(8-halogen-1-naphthyl)propiolic acids.[8]