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Synthesis and Properties of 5,6-Bis(dimethylamino)acenaphthylene: The First Proton Sponge with Easily-Modified Basicity

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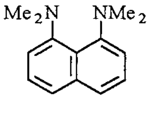
Introduction

Some N-peralkylated aromatic diamines with unusually high basicity, due to repulsion of the nitrogen lone-pairs which is relieved by enforced hydrogen bonding on protonation, are called proton sponges.[1] The first member of the proton sponge family is 1,8-bis(dimethylamino) naphthalene (**1**, $\mathrm{p}K_a$ 18.2 in MeCN,[1c] 7.5 in DMSO[2]). Besides the high basicity, the repulsion between two amine sites in molecule **1** causes steric strain, which is particularly evident in the considerable twisting of the naphthalene system.[3] As a result, neighboring *peri*-carbon atoms, especially those linked to the NMe_2 groups, are found on opposite sides of the mean ring plane. This tendency is greatly enhanced in the 1,4,5,8-tetrasubstituted naphthalenes (e.g., **2**).[4]

It is obvious that proton sponge **1** will retain such properties, even with molecular bridges of different lengths, which will fuse its *peri*-positions to form a cycle. Changing the size of the cycle can influence the "proton sponge" properties of the compounds. The extent of this influence can be followed by an analysis of basicity values and chemical shifts of the NH proton in the ^{1}H NMR spectra of the corresponding cations. It is known that in such cations, the NH proton is involved in a strong intramolecular hydrogen bond (IHB) between two NMe_2 groups, and is normally observed at an extremely low field (δ_{NH} 18−21 ppm).[1c,5] As the IHB is weakened, the NH signal proportionally moves to a higher field.

Until now, only proton sponges with six- (e.g., **3**)[6] and formally eight-membered *peri*-condensed rings **4** have been described.[7] Their protonation, basicity constants, and other properties show that both compounds retain the structure of the proton sponge fragment close to **1**.[7,8] This is quite understandable, since the introduction of *peri*-cycles of such a size should not significantly affect the ring strain. However, the situation can be changed in the case of smaller rings (four- and five-membered ones are possible). It should be stressed that in these derivatives the deforming influence of short bridges greatly planarize the naphthalene core, simultaneously changing the *peri*-distances in the main plane of their molecules.[9] Most likely, induced strain in such compounds will result in increasing the distance between the NMe_2 groups that will lead to decreasing their basicity and weakening of the IHB in its cations. To study this point, and as part of our ongoing research program on *peri*-condensation in **1**, in the present Note we report a simple synthesis and some properties of acenaphthene **6** and acenaphthylene **7** proton sponges—the first proton sponges with easily modified basicity.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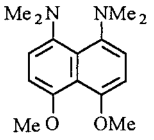
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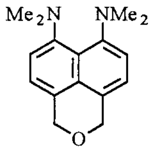
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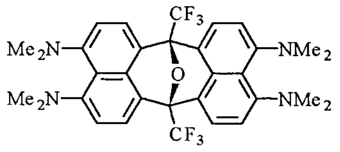
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Results and Discussion

Compound **6** was obtained in nearly quantitative yield by methylation of 5,6-diaminoacenaphthene (**5**) with an excess of methyl iodide in DMSO−KOH.[10,11] Subsequent dehydrogenation of **6** with chloranil (in boiling benzene, 30 min) gave compound **7** also in high yield (Scheme 1).

Unlike other similar acenaphthenes,[13] dehydrogenation of **6** by activated MnO_2 in dry xylene (boiling for 6 h) proceeds slowly and results in the formation of **8** at 10% yield, along with the proton sponge **7** (20% yield).[11,12,14] The fact that **8** is derived from **7** is partly confirmed by transformation of **7** into **8** (xylene, reflux, MnO_2, 6 h). The ratio **7**:**8** is equal to 2:1 and is quite constant, even when the reaction time is extended beyond 6 h and both compounds start to degrade significantly.

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(10) (a) This alkylation procedure has been formerly adopted for the synthesis of parent compound **1** and seems to be the best one for an exhaustive alkylation of *peri*-diamines (Kurasov, L. A.; Pozharskii, A. F.; Kuz'menko, V. V. *Zh. Org. Khim.* **1981**, *17*, 1944−1947). (b) Compound **6** has been earlier prepared from 1-methylaceperimidine via multistaged synthesis, but its spectral properties were not characterized (Pozharskii, A. F.; Kurasov, L. A.; Kuz'menko, V. V.; Popova, L. L. *Zh. Org. Khim.* **1981**, *17*, 1005−1013). **6**: yellowish solid, mp 42−43 °C; ^{1}H NMR (300 MHz, $CDCl_3$): 2.83 (s, 12 H, NMe_2), 3.31 (s, 4 H, H-1, H-2), 6.96 (d, 2 H, H-4, H-7, $J_{3,4}$ = 7.47 Hz), 7.17 (d, 2 H, H-3, H-8); ^{13}C NMR (75 MHz, $CDCl_3$), δ (^1J, Hz): 29.9 (131.7, CH_2-CH_2), 45.2 (134.2, CH_3), 115.0 (155.3, C-4), 119.2 (158.4, C-3), 120.9 (C-2a), 139.3 (C-5a), 142.7 (C-8b), 147.9 (C-5); UV/vis (MeOH), λ_{max} (lgϵ): 235 (4.43), 320 (4.12), 410 (sh., 2.25) nm; IR (CCl_4), ν: 3035, 2940, 2860, 2830, 2780 (CH), 1592, 1510, 1480, 1455 ($C{=}C_{arom}$) cm^{-1}.

(11) All new compounds gave correct data for C, H, N, and Cl (if any) in combustion analyses.

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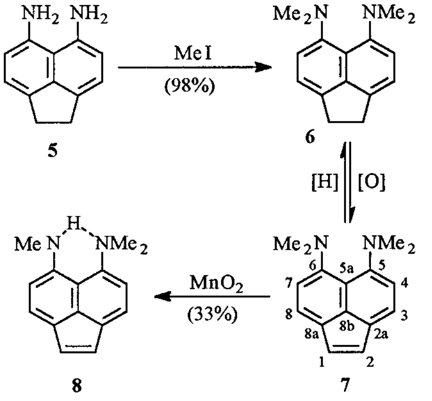
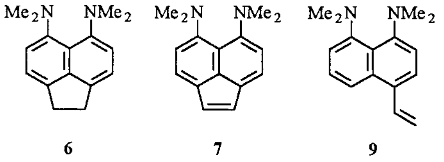
Scheme 1



Interestingly, acenaphthylene **7** is formed in small yield (<5%) even on recrystallization of **6** from alcohol in the presence of charcoal. Evidently the oxidation–reduction process is easily reversible, but under these conditions the equilibrium is shifted toward **6**. At the same time, catalytic hydrogenation of **7** (H_2, 2% Pd–C, 20 °C, 10 min) afforded **6** in a quantitative yield. Using potentiometric titration in MeCN and a competitive protonation method based on ^{1}H NMR spectroscopy,[5a] we have measured pK_a values for compounds **6**, **7**, and **9** at room temperature (Table 1). The basicity constants for compounds **6** and **7** are found to be quite different.

Table 1. Basicity Values (pK_a) of the Key Proton Sponges in Two Solvents (DMSO and MeCN) at 25 °C



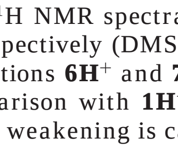
pK_a	6	7	9
DMSO	7.7	5.7	7.3
MeCN	18.3[a]	14.1	17.5[b]

[a] See reference 1c. [b] See reference 8.

Hence, changing the carbon–carbon bridge length results in a proton sponge which is either more or less basic than **1**, by a factor of 10^2 (basic scale in DMSO) or 10^4 (in MeCN)! This unique behavior, which is the first reported case for a proton sponge, might find application in molecular electronics where easily switchable redox systems are sought. It seems possible that the slightly elevated pK_a values for compound **6** are due to an electron-donating effect of the CH_2CH_2 fragment. On the other hand, the relatively low basicity of **7** indicates that the influence of *peri*-CH═CH bridge is not limited by its weak acceptor properties. Perhaps instead the rigid five-membered cycle significantly changes the geometry of the naphthalene moiety, leading to a considerable weakening of IHB in the cation (see below) and also minimizing the steric interaction of the NMe_2 groups in this compound. This could result in lowering of the basicity because the activity of the nitrogen lone-pairs is diminished by more effective conjugation between the NMe_2 groups and the naphthalene π-system in **7** compared to **6** (cf., ^{1}H and ^{13}C NMR data for the NMe_2, H-4, C-2a, C-4, and C-5a atoms). Indeed, according to the preliminary quantum chemical calculations (see below), the acenaphthylene moiety of molecule **7** is essentially planar.

At the same time, proton sponge **9** may be treated as acyclic analogue of **7** with a nonrigid substituent. As a consequence of the steric *peri*-interaction between H-5 and CH_2═CH fragments of **9**, relatively high pK_a values are observed for this vinyl derivative.

Both **6** and **7** form symmetrical chelated monocations **6H**$^+$ and **7H**$^+$ when treated with acids. The NH protons in their ^{1}H NMR spectra are observed at 16.4 and 15.8 ppm, respectively (DMSO solutions).[11,15] Thus the IHB in the cations **6H**$^+$ and **7H**$^+$ are considerably weakened by comparison with **1H**$^+$ (δ_{NH} 18.3 ppm).[5b] We believe that this weakening is caused by the "tightening" influence of the CH_2CH_2 or CH═CH bridges that brings C-2a and C-8a closer while simultaneously causing the C-5···C-6 distance to increase. This view is supported by the observation that in the cation of 5,6-bis(dimethylamino)-4,7-dinitroacenaphthene [16] **10H**$^+$, in which *o*-nitro groups due to their "buttressing effect" should decrease the distance between NMe_2 groups (cf., data for 2,7-dihalogeno derivatives of **1**),[1c,5b] the signal of the NH proton is observed at 18.7 ppm.[11,15]



6H$^+$ R=H, X= CH_2CH_2
7H$^+$ R=H, X= CH=CH
10H$^+$ R=NO_2, X= CH_2CH_2

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(12) Compound **7**: orange solid, mp 38.5–39.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): 2.91 (s, 12 H, NMe_2), 6.85 (s, 2 H, H-1, H-2), 6.89 (d, 2 H, H-4, H-7, $J_{3,4}$ = 7.58 Hz), 7.53 (d, 2 H, H-3, H-8); ^{13}C NMR (75 MHz, $CDCl_3$), δ (^1J, Hz): 44.3 (135.1, CH_3), 113.2 (155.6, C-4), 117.7 (C-2a), 124.7 (158.0, C-3), 125.4 (167.4, C-1), 131.5 (C-5a), 132.5 (C-8b), 152.0 (C-5); UV/vis (MeOH), λ_{max} (lgϵ): 237 (4.13), 267 (4.09), 325 (3.45), 418 (3.91) nm; IR (in film), ν: 3095, 3030, 2945, 2860, 2840, 2790 (CH), 1620, 1605, 1595, 1530, 1510, 1490 (C═C + C═C_{arom}) cm^{-1}. Though acenaphthylene polymerization is out of the present work, we have noticed that prolonged manipulations with **7** in the presence of Al_2O_3, light, or elevated temperatures come to the formation of a high-melting (darkened at 280 °C, dec at 350 °C) yellow-brown powder which keeps its ability to dissolve in $CHCl_3$, C_6H_6, or acids, but it is insoluble in alcohols, MeCN, and hydrocarbons. This is a typical behaviour for polymers or oligomers, and this process is accelerated in the salts of **7** (spontaneous polymerization in crystals giving the same yellow-brown powder on basification did not enable us to grow a good quality pattern for an X-ray analysis). An attempt to alkylate **8** by MeI did not give **7**, but led only to the "polymer", which probably arises from oligomerization of **7·HI** (cf., with difficulty of polymerization of 1,8-bis-(dimethylamino)-4-vinylnaphthalene (**9**): Vistorobskii, N. V.; Pozharskii, A. F. *Russ. Chem.* Bull. **1996**, *45*, 2297–2300).

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(14) 5-Dimethylamino-6-methylaminoacenaphthylene (**8**): dark-yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): 2.79 (s, 6 H, 5-NMe_2), 3.01 (d, 3 H, 6-NMe, $J_{NH, NMe}$ = 5.17 Hz), 6.34 (d, 1 H, H-7, $J_{7,8}$ = 7.80 Hz), 6.76 (d, 1 H, H-1, $J_{1,2}$ = 5.05 Hz), 6.98 (d, 1 H, H-2), 7.20 (d, 1 H, H-4, $J_{3,4}$ = 7.47 Hz), 7.55 (d, 1 H, H-8), 7.60 (d, 1 H, H-3), 8.57 (bs, 1 H, NH); UV/vis (MeOH), λ_{max} (lgϵ): 247 (4.11), 308 (sh., 3.53), 355 (3.67), 390 (sh., 3.48), 445 (sh., 3.25), end absorption up to 520 nm; IR ($CHCl_3$), ν: 3300 (NH), 2950, 2840, 2790 (CH), 1645, 1600, 1540, 1490, 1460, 1435 cm^{-1}.

(15) Data for perchlorates are given. **3H**$^+$: colorless plates with mp 275–277 °C (dec at 300 °C, from EtOH); ^{1}H NMR (300 MHz, DMSO-d_6): 3.08 (d, 12 H, NMe_2, $J_{NH, NMe}$ = 2.42 Hz), 5.00 (s, 4 H, H-1, H-3), 7.49 (d, 2 H, H-4, H-9, $J_{4,5}$ = 7.49 Hz), 8.02 (d, 2 H, H-5, H-8), 18.16 (m, 1 H, NH); **6H**$^+$: brownish needles with mp 270–271 °C (dec, from EtOH); ^{1}H NMR (DMSO-d_6): 3.09 (d, 12 H, NMe_2, $J_{NH,NMe}$ = 2.41 Hz), 3.39 (s, 4 H, H-1, H-2), 7.49 (d, 2 H, H-3, H-8, $J_{3,4}$ = 7.58 Hz), 7.95 (d, 2 H, H-4, H-7), 16.35 (m, 1 H, NH); **7H**$^+$: yellow crystals with mp 293–295 °C (dec, from EtOH); ^{1}H NMR (DMSO-d_6): 3.15 (d, 12 H, NMe_2, $J_{NH,NMe}$ = 2.31 Hz), 7.21 (s, 2 H, H-1, H-2), 7.93 (d, 2 H, H-3, H-8, $J_{3,4}$ = 7.58 Hz), 8.04 (d, 2 H, H-4, H-7), 15.77 (m, 1 H, NH); **10H**$^+$: brownish crystals with mp 214–215 °C (dec, from MeCN); ^{1}H NMR (CD_3CN, completely deprotonated in DMSO): 3.29 (d, 12 H, NMe_2, $J_{NH,NMe}$ = 2.58 Hz), 3.59 (d, 4 H, H-1, H-2, $J_{1,8}$ = 0.8 Hz), 7.86 (t, 2 H, H-3, H-8), 18.65 (m, 1 H, NH). The NH proton chemical shift is slightly increased (~0.3 ppm) when acetonitrile is used instead of DMSO.[5b]

11 **12**

11		12
10.9	pK_a (H_2O)	11.5
16.50	δ_{NH}, ppm [D$_6$]DMSO	18.37

Figure 1.

The chemical shift of the same signal for compound **9** is 18.65 ppm (DMSO).[12] Actually, as mentioned above, the through-space repulsion between the proton H-5 and the 4-vinyl group places this proton sponge in a very similar category to **2** or **1** with regard to IHB properties. It is also worth noting that, in the case of phenanthrene proton sponges **11** and **12**, the appearance of an ethylenic bridge results in an increase of basicity and IHB strength that is quite contrary to that found for the acenaphthene–acenaphthylene pair (Figure 1).[5a] although the reason for this is quite clear.[17]

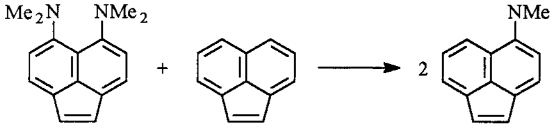
Quantum Chemical Calculations

It is of interest to see if the trends in pK_a reported here are reflected in the intrinsic (gas phase) basicities of these proton sponges and whether they might be correlated with other electronic properties such as strain energy. Using the methodology described recently,[18] we have carried out ab initio Hartree–Fock and density functional calculations using GAUSSIAN98.[19] Structures of **6**, **7**, and their associated cations were first optimized at the HF/3-21G level, with harmonic frequency calculations to confirm stability and estimate thermal energies (scaling the HF/3-21G result by the empirical correction factor 0.89).[20] The structures were further optimized at the HF/6-31G** level, with B3-LYP/6-31+G** single point energy calculations at these geometries to obtain an estimate of the correlation energies. Strain energies for **6** and **7** have been calculated from isodesmic reaction schemes such as the one illustrated below (applying identical computational methods to obtain the structures and energies of the extra compounds required). The distances r(N···N) between nitrogens in both the unprotonated base and in the cation (in parentheses), and also the displacement d of the nitrogens from the mean plane in the unprotonated base, are reported in Table 2. The results for the parent proton sponge **1** are taken from ref 18.

Table 2. Selected Results from Quantum Chemical Calculations on Proton Sponges 1, 6, and 7. Proton Affinities and Strain Energies in kJ/mol; Distances in Å

	1	6	7
PA HF/6-31G**	1056.3	1062.8	1044.3
B3-LYP/6-31+G**	1030.7	1038.7	1013.1
STRAIN HF/6-31G**	36.4	26.1	22.8
B3-LYP/6-31+G**	26.9	20.6	17.7
d HF/6-31G**	0.139	0.088	0.091
r(N···N) HF/6-31G**	2.791 (2.684)	2.879 (2.751)	2.914 (2.774)

Scheme 2



The three protonated cations (**1H**$^+$, **6H**$^+$, and **7H**$^+$) are completely planar (although the geometries were optimized without symmetry constraints). The strain energy is largest for parent proton sponge **1** (which, it may be recalled, also showed the largest δ_{NH}) and is also the most "twisted" (largest value of d, the displacements of the nitrogens from the mean plane). The gas-phase basicity of compound **6** is marginally greater than for **1**, and both **1** and **6** proton sponges are markedly more basic than the acenaphthylene sponge **7**, which is in complete agreement with the solution pK_a measurements. Since **7** has the longest intramolecular hydrogen bond and the least strain to be released on protonation, its relatively low basicity is easily understood. The slightly enhanced basicity of **6** over **1**, despite the greater strain energy and strongest hydrogen bond of the latter (**1** has by far the smallest r(N···N) in the cation), has two possible explanations we can infer now. Either the nitrogens have a higher intrinsic basicity in **6** compared to **1**; or there is more complete release of the strain energy in **6** when it is protonated. More detailed calculations along with the lines carried out in[18] could determine which of these two hypotheses is correct, but this is beyond the scope of this Note. The apparent correspondence of the strain energy in the unprotonated base with the chemical shift of the bridging proton in the cation is an intriguing result which clearly deserves further investigation in a wider range of compounds.

In summary: the systems presented appear to represent the first pair of proton sponges with easily reversible basicity **6** ↔ **7**. It seems likely that this property could be optimized by the study of various derivatives, and this is under investigation. In particular, given the possible materials applications for a fixed proton sponge with adjustable properties, our future attention will be paid to the copolymerization of **7** and to other reactions of the double bond of this accessible compound.

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(16) Compound **10** is one of the nitration products of acenaphthene proton sponge **6**. Its preparation and properties will be described elsewhere.

(17) Note, that the difference between the basicity values of **11**, **12** (which are both lower than that for **1**) is much smaller than in our case. Moreover, the interconvertion **11**↔**12** is impossible in a one-stage mode (5a).

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