peri-Naphthylenediamines

24.* Double 1,1′-binaphthalene "proton sponge"

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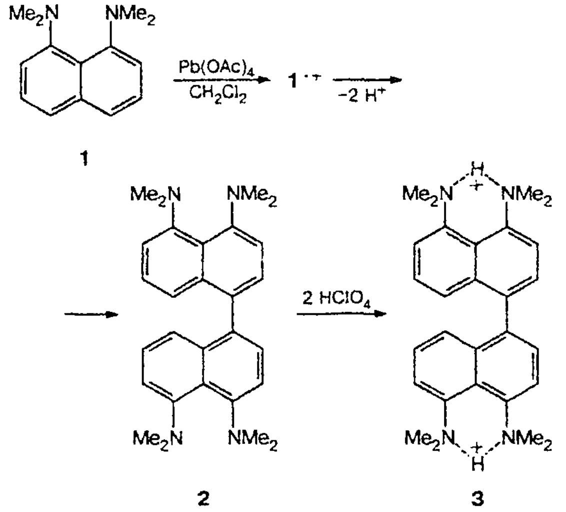
4,5,4′,5′-Tetrakis(dimethylamino)-1,1′-binaphthalene, unknown previously, was obtained in ~20% yield by the oxidation of 1,8-bis(dimethylamino)naphthalene with $Tl(OAc)_3$ or $Pb(OAc)_4$ at low temperatures. Treatment of the reaction product with excess Li and then with O_2 gave, depending on the reaction temperature, perylene or 4,4′-bis(dimethylamino)-1,1′-binaphthalene in good yields, instead of expected 3,4,9,10-tetrakis(dimethylamino)perylene.

Key words: 1,8-bis(dimethylamino)naphthalene, "proton sponge", oxidation, radical cation, radical anion, organic bases; 1,1′-binaphthalene; perylene; NMR spectra.

In order to synthesize sets of molecules based on 1,8-bis(dimethylamino)naphthalene ("proton sponge" (**1**)), we are developing methods for linking its naphthalene rings to each other. For example, recently,[2] 4,5,4′,5′-tetrakis(dimethylamino)dinaphthyl-1,1′-methane has been synthesized. In the present work, we report on the preparation and some properties of 4,5,4′,5′-tetrakis(dimethylamino)-1,1′-binaphthalene (**2**). It is known that compound **1** possesses a fairly low ionization potential[3,4] and readily undergoes electrochemical oxidation,[5] which occurs as two one-electron waves and yields radical cation $\mathbf{1}^{\cdot+}$ in the first step. Therefore, an oxidative method for binding together molecules of **1** that would include generation of radical cations and their dimerization seems especially promising.

Unlike 2-naphthol,[6] 1,8-bis(dimethylamino)naphthalene does not dimerize through the action of $FeCl_3$ in H_2O at 20—100 °C: the greater part of the initial compound **1** is recovered, and the rest is resinified. Apparently, this is due to the fact that the molecule binds HCl formed in the hydrolysis of $FeCl_3$ and is thus converted into a cation relatively inert with respect to oxidation. Binaphthalene **2** was obtained in ~20% yield by the oxidation of "proton sponge" **1** with $Pb(OAc)_4$ at −130 °C or with $Tl(OAc)_3$ at −35 °C (*cf.* Ref. 7) in a $Bu^tCl—CH_2Cl_2$ mixture.



The structure of compound **2** was confirmed by spectral methods. Unfortunately, we did not succeed in growing crystals suitable for X-ray diffraction analysis. According to the UV spectrum, the π-electronic interaction between the naphthalene rings in the molecule of **2** is insignificant; in fact, the positions of the absorption maxima in the spectra of compounds **1** and **2** are close to each other: λ_{max} = 341 and 350 nm, respectively. This is not surprising, because even in 1,1′-binaphthalene, both rings are rotated around the C(1)—C(1′) bond through 68° (see Ref. 8). In view of the pronounced structural distortions of the rings in the molecule of **1**, it can be assumed that in the case of binaphthalene sponge **2**, this angle is at least as large. The IR spectra of compounds **1** and **2** are also similar; even the "fingerprint" regions of these spectra resemble each other. According to our measurements, the basicity of compound **2** in MeCN (pK_a = 18.10) is only slightly lower than that of the "proton sponge" **1** (pK_a = 18.50); note that this value corresponds to the addition of two protons, *i.e.*, we were not able to separate pK_a^1 and pK_a^2

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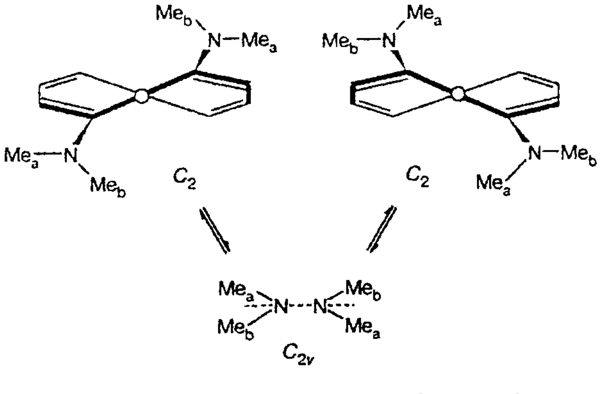
constants. This is additional evidence confirming that the mutual electronic influence of the naphthyl moieties is very weak. In this connection it is noteworthy that the attempt to prepare monoperchlorate of compound **2** by treating it with a half-equivalent quantity of $HClO_4$ gave only diperchlorate **3**.

The differences between compounds **1** and **2** are manifested most clearly in the NMR spectra, mostly in the region of signals for the Me_2N groups and the *peri*-protons. The ^1H NMR spectrum of "proton sponge" **1** under normal conditions contains a singlet corresponding to the Me_2N group; upon extensive cooling, this signal is broadened and at −120 °C (in CF_2Cl_2), it splits.[9] This is due to the fact that the molecule of **1** is "frozen" in a conformation containing two types of magnetically nonequivalent Me groups, namely, outer groups located approximately in the ring plane and inner groups, which appreciably project above the rings on their opposite sides. As shown by X-ray diffraction analysis[10] and MAS ^1H NMR spectroscopy,[11] the methyl groups in the crystals of the "proton sponge" fall into two types in exactly this way. Apparently, the signal for the inner Me groups is manifested in a higher field, because they should experience a stronger effect of the paramagnetic constituent of the ring current.[11]

It is believed that the methyl groups in the molecule of **1** undergo interconversion, which occurs in the "narcissistic manner" and involves a planar transition state of C_{2v} symmetry: $\Delta G^{\neq} = 7.5\pm0.2$ kcal mol^{-1}. In the case of sterically more hindered 1-benzylmethylamino-8-dimethylaminonaphthalene, the singlet corresponding to the Me_2N group splits at −38 °C; simultaneously, the singlet for the CH_2 group splits into a quadruplet ($\Delta G^{\neq}$ = 13.7±0.4 kcal mol^{-1}).[9]



Judging from the NMR spectra (Figs. 1—3), the conformational transition of the Me groups in the binaphthalene "sponge" **2** (structure **A**) occurs much more slowly than that in the molecule of **1**; besides, its rate for 4(4′)-NMe_2 groups is somewhat lower than that for the 5(5′)-NMe_2 groups. The Me_2N groups in the molecule of **2** are chemically nonequivalent; therefore, under the conditions of rapid exchange ($CDCl_3$, 50 °C), the spectrum exhibits two 12-proton singlets (see Fig. 2).

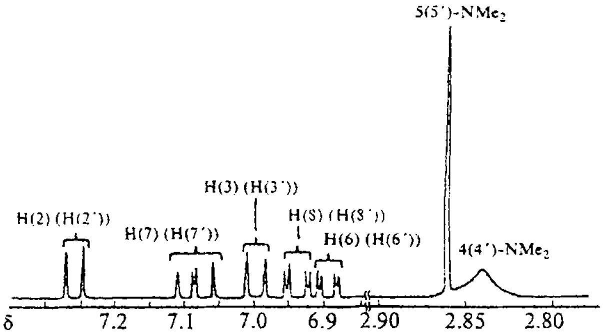
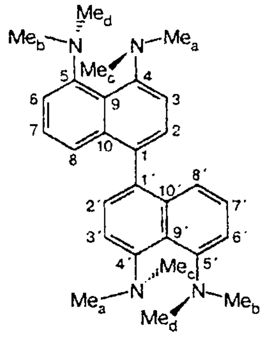


Fig. 1. General pattern of the ^1H NMR spectrum of compound **2** (in $CDCl_3$, 20 °C).



A

We attributed the higher-field signal (δ 2.86) to the 4(4′)-NMe_2 groups, because they can shield each other owing to the weak electron-donating effect through the inter-ring C—C bond. At 20 °C, this signal is markedly broadened, and upon further cooling, it splits; simultaneously, the lower-field signal (δ 2.88) corresponding to the 5(5′)-NMe_2 groups is also broadened and splits into two. At −40 °C, the spectrum contains four signals (6 H each). The signals were assigned, in order of moving downfield, to the Me$_c$, Me$_a$, Me$_d$, and Me$_b$ groups (see structure **A**). An even clearer picture can be followed in the dynamic ^{13}C NMR spectra (see Fig. 3). From the data of ^{13}C and ^1H NMR spectroscopy, the values $\Delta G^{\neq}_{298}$ = 13.6 and 14.8 kcal mol^{-1}, respectively, were found for this process.

It is known that the "proton sponge" forms only a single-charged cation **1**-H$^+$ with a strongly chelated NH proton, whose signal occurs at 18.5—19.0 ppm, depending on the solvent.[12] The NMe_2 groups in this cation are strictly pyramidal and are rotated through ~90° in relation to the ring; this ensures the formation of the strongest intramolecular hydrogen bond (IHB). The hydrogen bridge in the **1**-H$^+$ cation is virtually symmetrical as indicated by the fact that the four *N*-methyl groups are manifested in the ^1H NMR spectrum as one doublet with the spin-spin coupling constant $^3J_{HN-CH_3}$ ≈ 2.6 Hz. In the case of monosubstituted "proton sponges", the IHB becomes asymmetrical, and the nonequivalent dimethylamino groups are responsible for two doublets (6 H each) with different spin-spin coupling constants; the larger $^3J_{HN-CH_3}$ constant corresponds to the Me_2N group located closer to the NH proton.[1] Evidently, the binaphthalene "sponge" **2** also belongs formally to this type of compounds; therefore, it is reasonable to expect that the ^1H NMR spectrum of

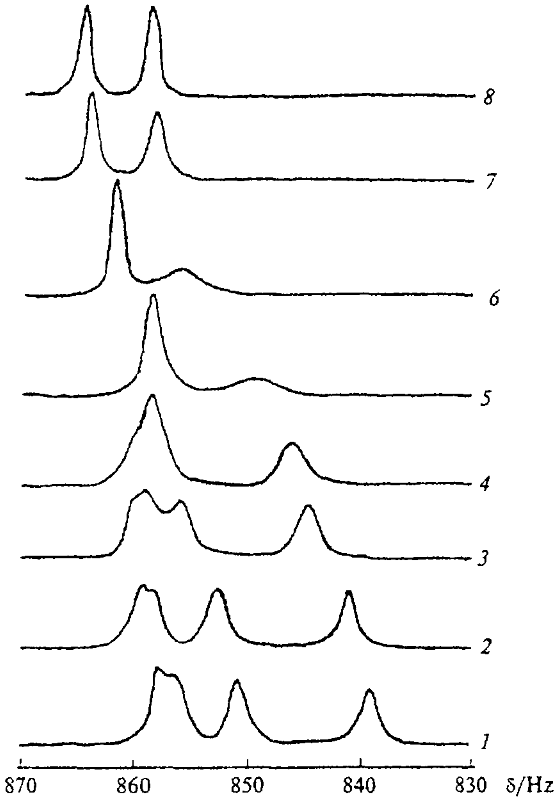


Fig. 2. Signals for the *N*-methyl groups in the ^{1}H NMR spectrum of compound **2** (in $CDCl_3$) at various temperatures: *T*/°C = −60 (*1*); −40 (*2*); −20 (*3*); −10 (*4*); 0 (*5*); 20 (*6*); 40 (*7*); 50 (*8*).

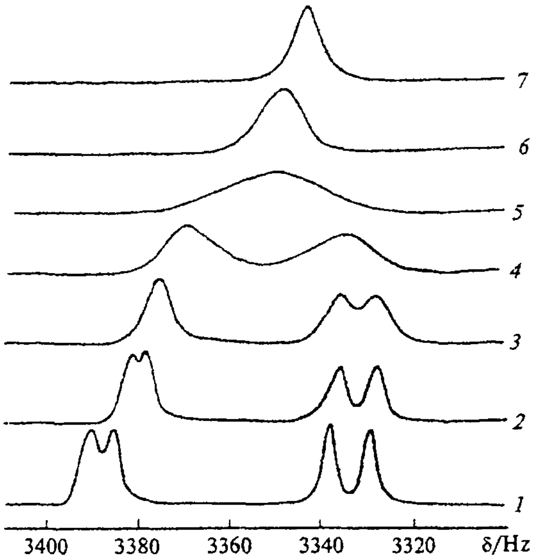


Fig. 3. Signals for the *N*-methyl groups in the ^{13}C NMR spectrum of compound **2** (in $CDCl_3$) at various temperatures: *T*/°C = −40 (*1*); −20 (*2*); −10 (*3*); 0 (*4*); 10 (*5*); 20 (*6*); 30 (*7*).

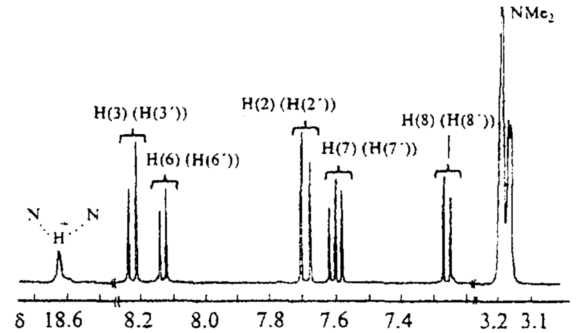
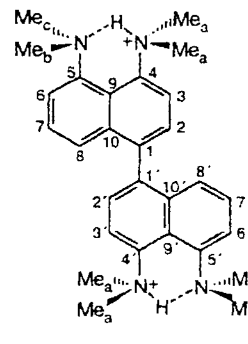


Fig. 4. General pattern of the ^{1}H NMR spectrum of diperchlorate **3** ($DMSO-d_6$, 20 °C).

its diperchlorate would exhibit two doublets (12 H each) for the nonequivalent Me_2N groups. However, in reality, the spectrum contains a doublet at δ 3.19 (6 H) and a multiplet at δ 3.22 (18 H) (Fig. 4). This indicates that the Me_2N substituents in cation **3** are rotated with respect to the ring through an angle much smaller than 90°; as a consequence, the Me groups in each of these substituents, like those in the base, are magnetically nonequivalent (structure **B**). Probably, the six-proton doublet at δ 3.19 is due to the Me groups that extend more substantially above the plane of the ring and experience the influence of the paramagnetic constituent of the ring current. It is difficult to unambiguously assign this doublet to particular groups; however, some assumptions can be made.



B

Previously,[1] it has been found that the sum of spin-spin coupling constants ($^3J_{1\text{-HN-CH}_3} + {}^3J_{8\text{-HN-CH}_3}$) for the cations of all asymmetrical "proton sponges" is close to 5.2 Hz. In the ^{1}H NMR spectrum of salt **3**, the signal at δ 3.19 is split into a doublet with a spin-spin coupling constant of 2.2 Hz (*i.e.*, less than half of this sum). Therefore, it can be assumed that the corresponding Me groups are attached to the N atoms that are more remote from the NH proton. Apparently, these are the N atoms at C(5) and C(5′) in those benzene rings that are not joined by the inter-ring bond. In fact, the doublet for H(3) and H(3′) is observed at a lower field (δ 8.24) than the doublet for the other pair of *ortho*-protons H(6) and H(6′) (δ 8.13). It would be reasonable to explain the increased deshielding of the H(3) and H(3′) atoms by the fact that the Me_2N groups located near them are more positive due to the close contact with the NH proton. Thus, it can be assumed that the 4-NMe_2 and 4′-NMe_2 groups in diperchlorate **3** are rotated through ~90° with respect to the plane of the naphthalene system to which they are attached, whereas

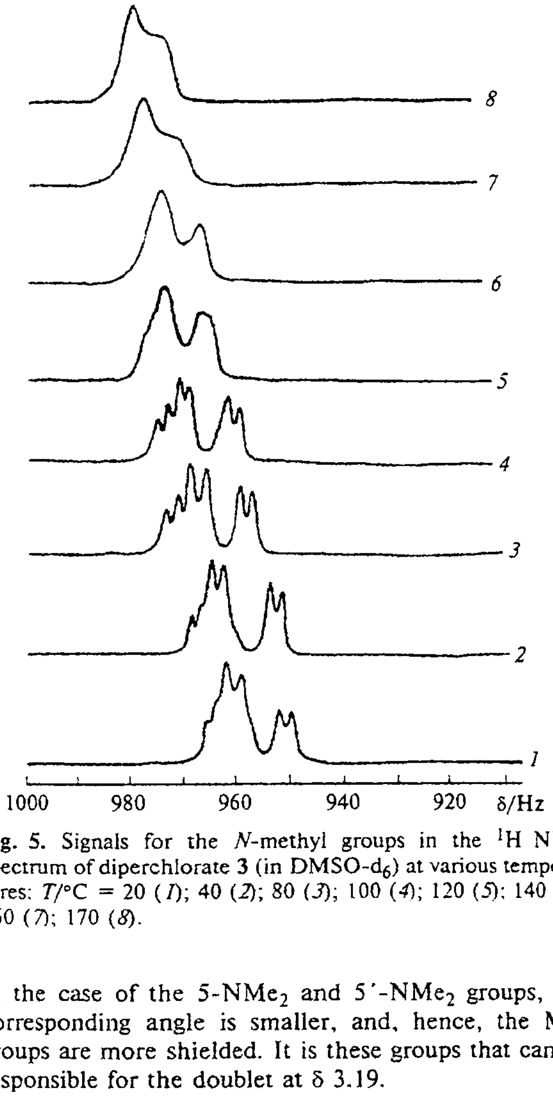


Fig. 5. Signals for the *N*-methyl groups in the ^{1}H NMR spectrum of diperchlorate **3** (in DMSO-d_6) at various temperatures: *T*/°C = 20 (*1*); 40 (*2*); 80 (*3*); 100 (*4*); 120 (*5*); 140 (*6*); 160 (*7*); 170 (*8*).

in the case of the 5-NMe$_2$ and 5′-NMe$_2$ groups, the corresponding angle is smaller, and, hence, the Me$_b$ groups are more shielded. It is these groups that can be responsible for the doublet at δ 3.19.

In the ^{1}H NMR spectrum of diperchlorate **3** (Fig. 5) recorded at 170 °C, the signals for the Me-group protons are substantially broadened and shifted closer together; however, they do not coalesce, and their relative intensity (1 : 3) does not change. This provides additional evidence for the high strength of the IHB in proton sponge cations, which hampers conformational changes.

The signal for the H(8) and H(8′) atoms (δ 7.37) in the ^{1}H NMR spectrum of diperchlorate **3** is exhibited in a markedly higher field than the signal for the H(4) and H(5) *peri*-protons (δ 8.08) in the cation derived from "proton sponge" **1** ($\Delta\delta_{peri}$ = −0.71). Apparently, this is due to the fact that the naphthyl groups are rotated with respect to each other around the C(4)—C(4′) bond, and consequently, the H(8) and H(8′) protons fall in the area of the paramagnetic constituent of the ring current. A similar although a somewhat smaller shift ($\Delta\delta_{peri}$ = −0.45) is also observed in the spectrum of base **2** (δ 6.94) with respect to that of base **1** (δ 7.39). This can be interpreted as an indication that the non-coplanarity of the naphthalene groups in the molecule of perchlorate **3** is more pronounced than that in binaphthalene **2**.

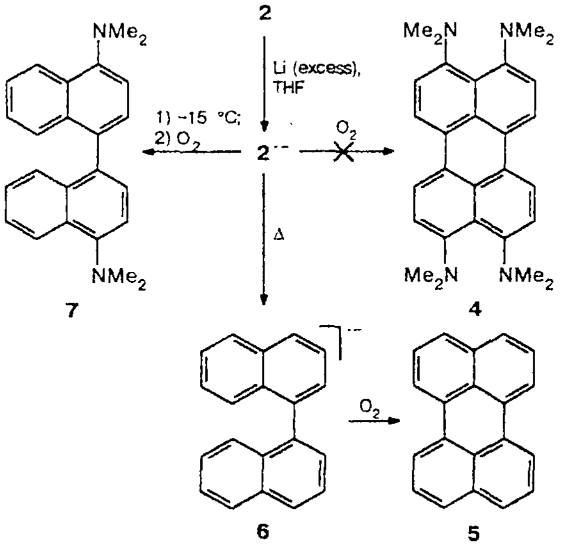
The synthesis of the binaphthalene "proton sponge" was of interest in view of its possible transformation into previously unknown double perylene "sponge" **4**. Perylenes are known to be yellow-colored and to exhibit strong luminescence. During isolation of compound **2**, not even traces of any compounds with these properties were detected on chromatograms. Nevertheless, we undertook several attempts to prepare compound **4**.

When binaphthalene **2** was treated with Pb(OAc)$_4$ in CH$_2$Cl$_2$ at −20 °C, in addition to some initial compound recovered, a yellow amorphous powder was isolated. Judging from the NMR spectrum, it was a complex mixture consisting apparently of oligomers and destruction products. The same reaction at −70 °C afforded a colorless product manifested on a thin-layer chromatogram as a single spot with an R_f value equal to that of the initial binaphthalene **2**. However, GC/MS analysis showed that this product consisted of three substances: initial binaphthalene **2** (43%), a compound having the same molecular weight (426) as binaphthalene **2** (38%), and a compound whose molecular weight, equal to 424, corresponded to perylene "sponge" **4** (16%). Unfortunately, we have not yet succeeded in separating and identifying these products (these studies are in progress). The second compound is presumably a product of isomerization of binaphthalene **2**. It is relatively unlikely that the third compound has a perylene structure, because it is colorless and does not exhibit specific fluorescence.

Heating binaphthalene **2** with anhydrous AlBr$_3$ (100—300 °C) is accompanied by resinification. It is known that perylenes can be obtained[13] by heating 1,8-diiodo- or 1,8-dibromonaphthalenes with Pd(OAc)$_2$ in DMF in the presence of K$_2$CO$_3$ and Bu$_4$NBr. We found that under these conditions (100 °C, 100 h), 4,5-dibromo-1,8-bis(dimethylamino)naphthalene[14] is slowly debrominated to give a mixture consisting of the initial compound (39%), 4-bromo-1,8-bis(dimethylamino)naphthalene (27%), "proton sponge" **1** (6%), and a resinous residue.

Yet another general method for the synthesis of perylenes[15] consists of the reaction of binaphthalenes with Li in THF followed by oxidative coupling of the arising radical anions by O$_2$. The good prospects for using this method in this particular case are supported by the following: treatment of "proton sponge" **1** with Na in dimethoxyethane gives a radical anion fairly stable at −20 °C;[16] according to ESR spectroscopy, the spin density in this radical anion is localized predominantly in positions 4 and 5.

However, contrary to expectations, we found that refluxing binaphthalene **2** with excess Li in dry THF followed by bubbling O$_2$ through the reaction mixture yields perylene **5** in a good yield. The elimination of the Me$_2$N groups may occur either after the formation of compound **4** or at the step of generation of the binaphthalene-sponge radical anion **2**$^{\cdot -}$, which is converted into perylene **5** *via* radical anion **6**. The latter version is more likely, because under milder conditions (−15 °C), the reaction affords 4,4′-bis(dimethylamino)-1,1′-binaphthalene **7** (yield 58%), whose structure has been confirmed by spectroscopy. To elucidate the reasons for this highly selective elimination of the Me_2N groups from positions 5 and 5′, further investigation is required. When the reaction temperature decreases to −50 °C, the process leads only to the recovery of the initial compound (up to 92%), although, judging from the black-green color of the reaction mixture, radical anions are generated under these conditions.



When "proton sponge" **1** was treated with excess Li in THF (2 h at −50 °C) and then O_2 was bubbled through the reaction mixture for a short period (~10 s) at the same temperature, the following products were identified by GC/MS analysis: 1-dimethylaminonaphthalene (26%), 1,1′-binaphthalene (17%), naphthalene (12%), 1-isocyanonaphthalene (6%), and, with high probability, 4-dimethylamino-1,1′-binaphthalene (9%), dimethylaminonaphthol (16%), and dihydronaphthalene (2%); no binaphthalene "proton sponge" **2** was detected. Thus, under the action of oxygen, the radical anions derived from "proton sponges" **1** and **2** undergo the same type of transformations, among which deamination processes predominate.

It should be noted that 1-dimethylaminonaphthalene does not tend to undergo extensive transformations under similar conditions. Treatment of this compound with excess Li in THF (2 h, at −50 °C) followed by bubbling O_2 resulted in the recovery of 78% of the initial compound. GC/MS analysis showed the presence of naphthalene (1%), two isomeric dimethylaminodihydronaphthalenes (2.5 and 0.5%), and dimethylaminotetrahydronaphthalene (2%). 1-Dimethylaminonaphthalene is resistant to $Pb(OAc)_4$ at various temperatures; only in some experiments were traces (~1—2%) of the expected binaphthalene **7** detected, while the bulk of the initial compound was recovered unchanged.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Unity-300 instrument (300 and 75.4 MHz, respectively) using $SiMe_4$ as the internal standard. UV spectra were measured on a Specord M40 spectrophotometer, and IR spectra were run on a UR-20 spectrometer. Mass spectra were obtained on an MX-1321A instrument with direct sample injection at a temperature in the ionization chamber of 50—100 °C and at an ionizing voltage of 70 eV. GC/MS studies were carried out on a Perkin—Elmer Q-Mass 910 instrument (a PE-2 capillary column with a methylsilicone phase (l = 25 m, d = 0.32 mm), initial temperature 120 °C, heating rate 10 °C min^{-1}, final temperature 270 °C, duration of chromatography 45 min, helium as the carrier gas, pressure ~1 atm). Melting points were determined in sealed glass capillaries on a PTP instrument and were not corrected.

4,5,4′,5′-Tetrakis(dimethylamino)-1,1′-binaphthalene (2). ***A.*** A solution of $Pb(OAc)_4$ (2.50 g, 5.5 mmol) in 20 mL of CH_2Cl_2 was added dropwise with intense stirring to a solution of compound **1** (2.14 g, 10 mmol) in a mixture of 50 mL of Bu^{i}Cl and 15 mL of CH_2Cl_2 cooled to −130 °C. Then the cooling bath was removed and the dark-brown mixture was stirred until its temperature increased to ~20 °C. After that, 50 mL of H_2O was added, the mixture was alkalified with a 10% aqueous solution of KOH to pH 14, the layers were separated, and the aqueous layer was extracted with $CHCl_3$ (3×15 mL). The extract was combined with the organic layer, concentrated on a rotary evaporator to a small volume, and passed through a Schott filter with Al_2O_3 of Brockman activity III ($h = d$ = 3.0 cm) using hexane as the eluent to give unchanged "proton sponge" **1** (R_f 0.16, yield 0.52 g, 24%) and binaphthalene **2** (R_f 0.05, yield 0.34 g, 16%). With allowance for the recovered initial compound, the yield of **2** was 21%. Colorless powder, m.p. 186—187 °C (from heptane). Found (%): C, 78.79; H, 8.02; N, 13.07. $C_{28}H_{34}N_4$. Calculated (%): C, 78.82; H, 8.04; N, 13.14. UV (MeOH), λ_{max}/nm (logε): 243 sh (4.52), 284 sh (3.98), 303 sh (4.06), 350 (4.14). IR (Vaseline oil), ν/cm^{-1}: 2820, 2766 (C—H); 1595 sh, 1570, 1510 (ring). ^1H NMR (20 °C, $CDCl_3$), δ: 2.85 (br.s, 12 H, 5-NMe_2, 5′-NMe_2); 2.87 (s, 12 H, 4-NMe_2, 4′-NMe_2); 6.89 (dd, 2 H, H(6), H(6′), $J_{H(6)-H(7)} = J_{H(6')-H(7')}$ = 7.44 Hz, $J_{H(6)-H(8)} = J_{H(6')-H(8')}$ = 1.28 Hz); 6.94 (dd, 2 H, H(8), H(8′), $J_{H(8)-H(7)} = J_{H(8')-H(7')}$ = 8.31 Hz, $J_{H(8)-H(6)} = J_{H(8')-H(6')}$ = 1.28 Hz); 6.99 (d, 2 H, H(3), H(3′), $J_{H(3)-H(2)} = J_{H(3')-H(2')}$ = 7.77 Hz); 7.09 (dd, 2 H, H(7), H(7′), $J_{H(7)-H(6)} = J_{H(7')-H(6')}$ = 7.44 Hz, $J_{H(7)-H(8)} = J_{H(7')-H(8')}$ = 8.31 Hz); 7.26 (d, 2 H, H(2), H(2′), $J_{H(2)-H(3)} = J_{H(2')-H(3')}$ = 7.77 Hz). ^{13}C NMR (20 °C, $CDCl_3$), δ: 44.40 (Me); 112.02 (C(6), C(6′)); 112.26 (C(3), C(3′)); 120.27 (C(1), C(1′)); 120.64 (C(8), C(8′)); 124.92 (C(2), C(2′)); 127.73 (C(7), C(7′)); 132.63 (C(9), C(9′)); 137.38 (C(10), C(10′)); 149.95 (C(5), C(5′)); 150.58 (C(4), C(4′)). MS, m/z (I_{rel} (%)): 426 $[M]^+$ (100), 411 $[M-Me]^+$ (10), 382 $[M-NMe_2]^+$ (4), 351 (7), 213 (7).

B. A solution of $Tl(OAc)_3$ (2.1 g, 5.5 mmol) in 20 mL of CH_2Cl_2 was added dropwise with intense stirring to a solution of compound **1** (2.14 g, 10 mmol) in a mixture of 50 mL of Bu^{i}Cl and 15 mL of CH_2Cl_2 cooled to −35 °C. Then the reaction was carried out and the products were isolated as described in procedure *A* to give 0.61 g (28%) of unreacted "proton sponge" **1** and 0.36 g (17%) of binaphthalene **2** (23.5% with allowance for the recovered initial compound).

Diperchlorate 3. 60% $HClO_4$ (0.1 mL) was added to a solution of base **2** (0.13 g, 0.3 mmol) in 12 mL of EtOH. The precipitated white crystals were filtered off, washed with cold EtOH (~3 mL), and dried in a vacuum desiccator. Yield 0.18 g (95%). Upon heating above 345 °C, the salt turns dark and explodes. ^{1}H NMR (20 °C, DMSO-d_6), δ: 3.19 (d, 6 H, NMe_2); 3.22 (br.d, 18 H, 3 NMe_2); 7.37 (d, 2 H, H(8), H(8′)); 7.60 (dd, 2 H, H(7), H(7′)); 7.70 (d, 2 H, H(2), H(2′)); 8.14 (d, 2 H, H(6), H(6′)); 8.24 (d, 2 H, H(3), H(3′)); 18.70 (br.s, 2 H, 2 NH, $J_{H(2)-H(3)} = J_{H(2')-H(3')}$ = 7.80 Hz, $J_{H(6)-H(7)} = J_{H(6')-H(7')}$ = 7.47 Hz, $J_{H(7)-H(8)} = J_{H(7')-H(8')}$ = 8.46 Hz).

Perylene (5). Finely cut Li (7 mg, 1 mmol) was added under argon to a solution of compound **2** (43 mg, 0.1 mmol) in 4 mL of anhydrous THF. The reaction mixture was stirred for 2.5 h at gentle boiling and cooled to ~20 °C. Dry O_2 was bubbled through the mixture, and the dark violet mixture became almost immediately bright yellow. Then the THF was completely distilled off, and the residue was chromatographed on Al_2O_3 of Brockman activity III (*h* = 4 cm, *d* = 1 cm) using $CHCl_3$ as the eluent. A bright yellow fluorescing fraction with R_f 0.95 consisting of perylene was isolated. Yield 17 mg (72%). Lustrous golden yellow plates, m.p. 273—274 °C (from xylene). ^{1}H NMR ($CDCl_3$), δ: 7.46 (dd, 4 H, H(2), H(5), H(8), H(11), $J_{H(2)-H(1)}$ = 7.47 Hz, $J_{H(2)-H(3)}$ = 8.27 Hz); 7.66 (dd, 4 H, H(3), H(4), H(9), H(10), $J_{H(3)-H(2)}$ = 8.27 Hz, $J_{H(3)-H(1)}$ = 1.10 Hz); 8.17 (dd, 4 H, H(1), H(6), H(7), H(12), $J_{H(1)-H(2)}$ = 7.47 Hz, $J_{H(1)-H(3)}$ = 1.10 Hz).

4,4′-Bis(dimethylamino)-1,1′-binaphthalene (7). Finely cut Li (7 mg, 1 mmol) was added under argon to a solution of compound **2** (43 mL, 0.1 mmol) in 4 mL of anhydrous THF. The reaction mixture was stirred at 50 °C and then, when it began to turn dark, it was cooled at −15 °C and stirred for ~40 min; after that, dry O_2 was bubbled. After ~20 s, the dark green reaction mixture completely decolorized. Then excess Li was filtered off, the filtrate was concentrated, the residue was dissolved in a small amount of $CHCl_3$, and the solution was passed through a chromatographic column with Al_2O_3 of Brockman activity III (*h* = 10 cm, *d* = 1 cm) using hexane as the eluent. A colorless fraction with R_f 0.23 was collected to give 20 mg of compound **7** (58%). Small crystals, m.p. 140—143 °C (from hexane) (lit. data:[17] m.p. 130 °C). Found (%): C, 84.12; H, 7.04; N, 8.09. $C_{24}H_{24}N_2$. Calculated (%): C, 84.66; H, 7.11; N, 8.23. ^{1}H NMR (DMSO-d_6), δ: 2.87 (s, 12 H, 4-NMe_2, 4′-NMe_2); 6.82 (d, 2 H, H(3), H(3′), $J_{H(3)-H(2)} = J_{H(3')-H(2')}$ = 8.50 Hz); 7.09 (dd, 2 H, H(5), H(5′), $J_{H(5)-H(6)} = J_{H(5')-H(6')}$ = 7.40 Hz, $J_{H(5)-H(7)} = J_{H(5')-H(7')}$ = 0.88 Hz); 7.22 (m, 2 H, H(6), H(6′)); 7.42 (dd, 2 H, H(8), H(8′), $J_{H(8)-H(7)} = J_{H(8')-H(7')}$ = 7.03 Hz, $J_{H(8)-H(6)} = J_{H(8')-H(6')}$ = 1.0 Hz); 7.62 (m, 2 H, H(7), H(7′)); 8.27 (d, 2 H, H(2), H(2′), $J_{H(2)-H(3)} = J_{H(2')-H(3')}$ = 8.50 Hz). MS, *m/z* (I_{rel} (%)): 340 $[M]^+$ (100), 325 $[M-Me]^+$ (16.5), 296 $[M-NMe_2]^+$ (5.3), 295 (10.9).

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