Organic Chemistry

peri-Naphthylenediamines

29.* 1,8-Bis(dimethylamino)-3-nitro- and -3,6-dinitronaphthalenes and 5,6-bis(dimethylamino)-3-nitro- and -3,8-dinitroacenaphthenes as the first representatives of "proton sponges" *meta*-substituted relative to NMe_2 groups

*V. A. Ozeryanskii and A. F. Pozharskii**

Rostov State University,
7 ul. Zorge, 344090 Rostov-on-Don, Russian Federation.
Fax: +7 (863 2) 22 3958. E-mail: pozharsk@pozhar.rnd.runnet.ru

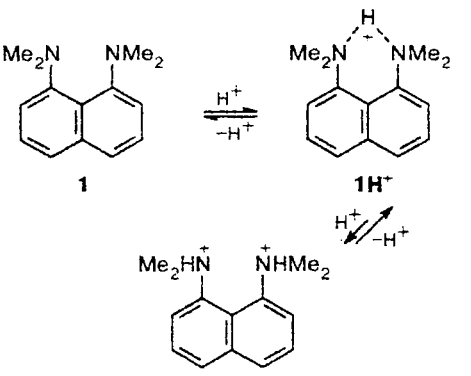
meta-Substituted "proton sponges" were prepared for the first time by the direct nitration of 5,6-bis(dimethylamino)acenaphthene under strong acidic conditions and by the selective reduction of 1,3,8-tri- and 1,3,6,8-tetranitronaphthalenes and subsequent alkylation of the compounds obtained. 4,5-Bis(dimethylamino)-1,2,3,6,7,8-hexanitronaphthalene was synthesized starting from 1,3,6,8-tetranitronaphthalene.

Key words: "proton sponge," 5,6-bis(dimethylamino)acenaphthene, 1,3,8-trinitronaphthalene, 1,3,6,8-tetranitronaphthalene, nitration, selective reduction, *N*-alkylation.

Electrophilic *meta*-substitution is well-known[2] to occur in strong acidic media, when the $NAlk_2$ group is converted to the dialkyl ammonium group and serves as a *meta*-orienting moiety. The chelated proton in 1,8-bis(dialkylamino)naphthalene cations (e.g., $\mathbf{1H^+}$) participates in the formation of an intramolecular hydrogen bond (IHB) and is located almost in the middle between the amine nitrogen atoms. Conversion of $\mathbf{1H^+}$ monocation to $\mathbf{1 \cdot 2H^+}$ dication (Scheme 1) is practically not realized ($\mathbf{1}$: pK_a^1 12.1, pK_a^2 −9.0 (H_2O)[3]). This above all can be explained by the reliability of the IHB that should be broken at the formation of $\mathbf{1 \cdot 2H^+}$.[4]

Thus, each dialkylamino group of the $\mathbf{1H^+}$ cation is only half-protonated even in strong mineral acids. This

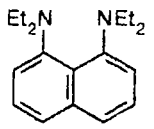
Scheme 1



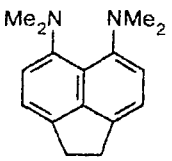
* For Part 28, see Ref. 1.

Published in *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1405—1411, August, 2000.

does cause the inactivation of positions 2 and 7, which is also favored by the steric hindrances to *ortho*-substitution. However, the *para*-positions (4 and 5) still remain rather active. Thus, it is not surprising that no case of *meta*-substitution towards the dialkylamino group has been observed in the studies on the chemistry of 1,8-bis(dimethylamino)naphthalene (**1**, the "proton sponge") during more than 20 years (see the previous communications of this series and also Ref. 5).

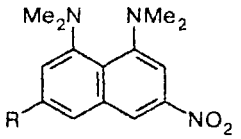


2



3

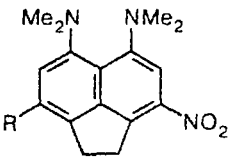
To continue the studies on the reactivity of 5,6-bis(dimethylamino)acenaphthene (**3**), we have supposed that this compound can appear to be the first substrate in the series of "proton sponges" capable of *meta*-substitution in acidic media and have studied its behavior in the nitrating mixture. Moreover, in this study we have carried out an indirect synthesis of the *meta*-derivatives of 1,8-bis(dialkylamino)naphthalene (**4**) and (**5**).



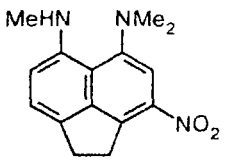
4: R = H
5: R = NO_2

Acenaphthene **3** was previously reported[6] to be obtained by multistage synthesis from aceperimidinium salts. However, for preparative needs this compound can be obtained more conveniently by direct *N*-alkylation of 5,6-diaminoacenaphthene with methyl iodide in KOH—DMSO. We decide to perform catalytic hydrogenation of 5,6-dinitroacenaphthene in DMF, which can further be used in the mixture with DMSO as a medium for alkylation of the resulting diamine. The number of steps is thus reduced to two, and the yield of "proton sponge" **3** from diaminoacenaphthene is increased to 98% (*cf.* Ref. 7).

Owing to the high oxidizability of **3** by electrophilic agents,[1] its treatment with the nitrating mixture was performed with cooling to −25 °C. Moreover, taking into account the increased basicity of bis(dimethylamino)acenaphthene **3** (pK_a(**3**) = 18.3,[5] pK_a(**1**) = 18.2 (MeCN)[8]), it is clear that only the $3H^+$cation and not the neutral base **3** will interact with nitric acid in a medium of H_2SO_4. The results of the corresponding experiments yielding *meta*-nitroacenaphthenes **6**—**8** are given in Table 1.



6: R = H
7: R = NO_2



8

The nitronium cation generated in the nitrating mixture is oriented only to the *meta*-positions towards the dimethylamino groups, as the *ortho*-positions are deactivated and the *para*-positions are occupied. This is the first case of direct substitution in the *meta*-positions of the aromatic ring of "proton sponges."

Resulting *meta*-nitroacenaphthenes **6**—**8** can easily be detected in the ^{1}H NMR spectra from the down-field shift of the signals of the ethylene bridge protons (to δ 3.7—3.8). The same signals of the *ortho*-substituted derivatives of 5,6-bis(dimethylamino)acenaphthene are registered [1] in the region of δ 3.3.

In should be mentioned that "proton sponge" **6** still possesses noticeable reactivity. Its further interaction with HNO_3 probably follows two directions (see Table 1): (1) the second nitration to dinitro-substituted **7** and (2) oxidation resulting in the formation of demethylated product **8** (*cf.* Ref. 1). As the 6-NMe_2 group in compound **6** should be oxidized easier than the 5-NMe_2 group, the methylamino group in diamine **8** appears to be bound with the ring unsubstituted with a nitro group. The signal of the NH proton in the ^{1}H NMR spectrum of compound **8** appears at δ 8.0.

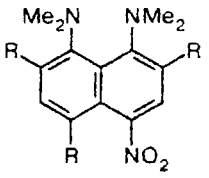
Treating acenaphthene "proton sponge" **3** with 2 equiv. of HNO_3 caused marked resinification of the reaction mixture. *meta*-Dinitroacenaphthene **7** (≤16%) was the only product isolated. Thus, in the case of compound **3** we succeeded in performing controlled nitration, and regulation of the medium acidity permitted us to change the orientation of the substituent introduced.[1]

Table 1. Nitration of acenaphthene "proton sponge" **3** with the nitrating mixture (−25 °C, 6 min)

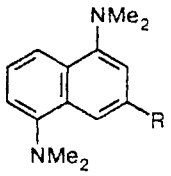
Entry	Amount	Composition of the reaction mixture (%)			
	HNO_3*/equiv.	**6**	**7**	**8**	Oxidation products
1	1	70	15	7	8
2	2	—	16	—	84

* d = 1.41 g cm^{-3}.

The use of >1 equiv. of HNO_3 while treating diamine **1** with the nitrating mixture was previously shown[9] to result instantaneously in tetranitro derivative **9**. The values of basicity of compounds **3** and **6** in DMSO we have measured turned out to be 7.7 and 6.0, whereas for compound **10** the pK_a value is only 3.5.[1] Thus, the *meta*-nitro group decreases the basicity of the product as compared to the starting substrate **3** not so effectively as the *para*-nitro group does as compared to "proton sponge" **1** (pK_a = 7.5 in DMSO[1]). This is the cause that mononitro derivative **6** is further nitrated in the form of the cation, in which the partially protonated NMe_2 groups direct the second substituent also in the *meta*-position (*cf.* with nitration[9] of compound **2**). On the contrary, the sharp decrease of the basicity at the conversion **1**→**10** due to the conjugation of nitro- and dimethylamino groups causes the appearance of neutral forms of substituted "proton sponges" in the nitrating mixture. The subsequent nitration of these structures proceeds quickly up to compound **9**.



9: R = NO_2
10: R = H



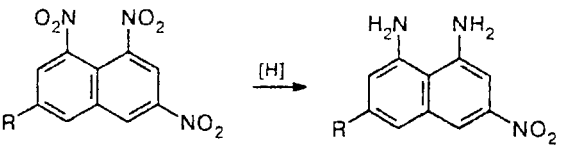
11: R = H
12: R = NO_2

The facts discussed above clarify the result of nitration of the 1,5-isomer of "proton sponge" **11**, which is easily converted to the **11** · $2H^+$ dication in acidic media because of the impossibility of IHB formation. *meta*-Nitro derivative **12** is the main product of treating this dication with the nitrating mixture.*

In order to obtain *meta*-nitro derivatives **4** and **5**, which are not generated at the direct nitration of compound **1**, we suggested the use of the relatively available 1,3,8-tri- (**13**) and 1,3,6,8-tetranitronaphthalenes (**14**) as their probable precursors. Reduction of compounds **13** and **14** to *peri*-diamines **15** and **16** (Scheme 2) and their exhaustive alkylation should result in the formation of the target "proton sponges" **4** and **5**.

The conversion **14**→**16** was carried out previously[10] (the yield of diamine **16** was 50%) in the $SnCl_2$—AcOH—HCl system, which was specially suggested for the reduction of the α-nitro group and did not involve the nitro group at the β-position.[11] However, the selectivity of this method is rather low, especially in the case of several nitro groups. Besides the α-naphthylamines expected, β-naphthylamines and also all possible nitronaphthylamines are formed. Moreover, the starting

Scheme 2

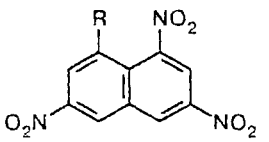


13: R = H
14: R = NO_2

15: R = H
16: R = NO_2

polynitronaphthalene is partially regenerated. For example, monoreduction of 1,3-dinitronaphthalene with the above reducing agent yields a mixture of 3-nitro-α-naphthylamine (33%), 4-nitro-β-naphthylamine (7%), 1,3-naphthylenediamine (3%), and the starting compound (21%). The remaining 36% of the substance is lost[11] in the isolation.

The detailed reproduction of the procedure described previously[10] permitted us to obtain diamine **16** in a yield no more than 7—10%, and almost without exception nitronaphthylamine (**17**) was the main product we succeeded in isolating. The subsequent alkylation of **17** with methyl iodide yielded derivative **18** (74%). Varying the amount of the reducing agent, temperature, and reaction time resulted only in the decrease of the yield of compound **16** and accumulation of α,β-diaminodinitronaphthalenes among the reaction products.



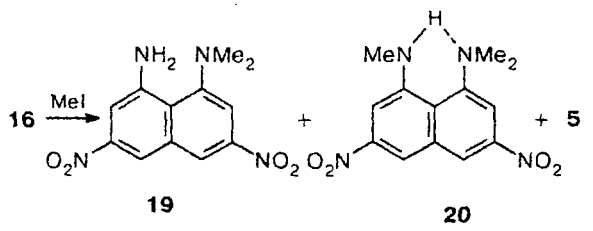
17: R = NH_2
18: R = NMe_2

The researchers who needed diamine **16** as the starting compound for the synthesis of heterocyclic compounds[12] faced the same difficulties. They obtained negative results using tin(II) chloride and phenylhydrazine. However, they succeeded in modifying the method[13] that used hydrazine solutions in the presence of $FeCl_3$ for the synthesis of compound **16**. Unfortunately, the authors[12] did not state the concentration of hydrazine hydrate used. We have found out that obtaining 1,8-diamino-3,6-dinitronaphthalene (**16**) with a yield up to 60% using 85% $N_2H_4 \cdot H_2O$ needs a more prolonged reflux (6 h).

Then compound **16** was *N*-alkylated with methyl iodide. Heating the components at 100 °C in the KOH—DMSO or the KOH—DMF system yielded complex mixtures with marked tarring even in an inert atmosphere. Methylation of diamine **16** with the MeI—KOH—DMF mixture at room temperature (24 h) also resulted in the formation of a complex mixture of

* Nitration of compound **11** under various conditions will be reported later.

Scheme 3

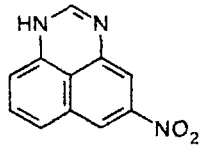


19 **20**

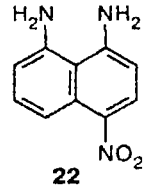
products. In this case we succeeded in isolation of intermediate products of alkylation **19** (2%) and **20** (18%) and also "proton sponge" **5** (3%) in low yields, trimethyl-substituted compound **20** (Scheme 3) stabilized by IHB being the dominant component.

We suppose the processes of nucleophilic substitution in the naphthalene ring activated by the nitro groups to be the probable cause of complications in alkylation in superbasic media. We appreciably succeeded in avoiding these difficulties by using potash as a basic agent (for the use of metal carbonates for exhaustive alkylation of aromatic polyamines see Refs. 14 and 15). For example, heating trimethyl derivative **20** with K_2CO_3 and MeI in DMF permits converting it quantitatively to compound **5**. Prolonged (several hours) reflux of naphthylenediamine **16** in the above mentioned system results in the formation of "proton sponge" **5** in 76% yield.

At the beginning of our study, there was practically no information on the selective reduction of the nitro groups in trinitronaphthalene **13**. The study reported in Ref. 16 can serve as the only example of such investigations. The authors performed the reduction of the β-nitro group with sodium sulfide and obtained 4,5-dinitro-β-naphthylamine in 25% yield. We have established that the use of $SnCl_2$ as a reducing agent gives mixtures of nitronaphthylamines, the share of diamine **15** being 20% and lower. The best results have been obtained using N_2H_4. The higher selectivity and efficiency of the reduction with hydrazine permit us to reach moderate yields of diaminonitronaphthalene **15** (50—55%). Heating diamine thus obtained with formic acid gives perimidine **21**. This proves the *peri*-location of the two amino groups.



21



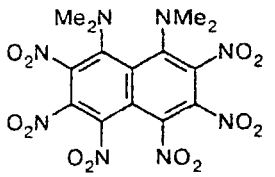
22

We also made an attempt to synthesize 1,8-diamino-3-nitronaphthalene (**15**) directly by nitration of 1,8-diaminonaphthalene in the HNO_3—H_2SO_4 system. However, we failed to detect even traces of the products of *meta*-substitution upon treating with nitrating mixture. Only 4,5-diamino-1-nitronaphthalene (**22**) was isolated (up to 17%). The major part of the starting diamine was oxidized.

Exhaustive methylation of compound **15** was performed with heating in the MeI—K_2CO_3—DMF system. The yield of "proton sponge" **4** reached 42% after heating for 30 h. Interestingly, this compound is the most basic nitro derivative of "proton sponge" **1** because of the absence of mesomeric interaction of nitro group and the amino groups (pK_a in DMSO is 5.2).

The ^{1}H NMR spectrum of 1,8-bis(dimethylamino)-3,6-dinitronaphthalene (**5**) (in $CDCl_3$) is its important peculiarity, because the signals of aromatic protons at room temperature appear as very broad singlets taking the form of doublets with heating. This reflects the slow (according to the NMR time scale) dynamic processes probably connected with the rotation of the *meta*-nitro groups but not of the NMe_2 groups. To a small extent the same phenomenon is observed for compound **4** and even for acenaphthene analogs **6** and **7** with more rigid molecules.

Thus, "proton sponges" **4** and **5** turned to be the first *meta*-substituted 1,8-bis(dimethylamino)naphthalenes synthesized. Such compounds are still highly reactive and can be used for the synthesis of multifunctional "proton sponges" and polysubstituted naphthalenes. Really, compound **5** undergoes further nitration by treating with nitric acid in neutral medium in spite of the presence of two nitro groups. This permits us to substitute the rest of the free positions of the naphthalene ring. The yield of 4,5-bis(dimethylamino)-1,2,3,6,7,8-hexanitronaphthalene (**23**) reaches 73%.



23

The relatively easy accessibility of naphthalenes completely substituted by this approach using 1,8-bis(acetamido)hexanitronaphthalene as example was also mentioned previously.[12] In our opinion, compound **23**, which is probably the naphthalene "proton sponge" with the lowest basicity, can offer promise for the synthesis of "polydentate" organic bases.

Experimental

^{1}H NMR spectra were registered on a Bruker DPX-250 (250 MHz) instrument using Me_4Si as the internal standard. UV spectra were taken on a Specord M-40 spectrometer in

methanol. IR spectra were recorded on a Specord IR-71 spectrometer in Nujol. Chromatography was performed on Silica gel L 40/100 (Chemapol) using $CHCl_3$ as the eluent. Hydrazine hydrate (85%) was obtained by the procedure reported earlier.[17] Melting points were measured in a sealed capillary on a PTP instrument and were uncorrected.

Caution: polynitronaphthalenes are dangerously explosive!

5,6-Diaminoacenaphthene. The catalyst (2% Pd/C, 4 g) was added to a solution of 11 g (0.045 mol) of 5,6-dinitroacenaphthene (obtained according to the reported procedure[18]) in 50 mL of DMF, and the resulting mixture was hydrogenated for 14 h at 40 °C (~6 L of H_2 was absorbed). Then the catalyst was filtered off, and the filtrate was poured out into water (250 mL) and extracted with diethyl ether (6×100 mL). Ether was removed to give 7.6 g (92%) of practically pure **5,6-diaminoacenaphthene**, m.p. 154—155 °C (*cf.* Ref. 19: m.p. 160 °C). ^{1}H NMR (DMSO-d_6), δ: 3.11 (br.s, 4 H, CH_2CH_2); 5.14 (br.s, 4 H, 2 NH_2); 6.49 and 6.86 (both d, both 2 H, H-4(7), H-3(8), $J_{3,4}$ = 7.29 Hz). The product was used in the next step without additional purification.

5,6-Bis(dimethylamino)acenaphthene (3). Dimethylsulfoxide (13 mL) was added to 2.0 g (0.011 mol) of 5,6-diaminoacenaphthene (or to 14 mL of its solution in DMF, see above), and the mixture was stirred for 5 min under argon. Then 2.84 g (0.051 mol) of powdered KOH was added, and after 5 min 3.26 mL (0.052 mol) of cooled CH_3I was added portionwise (if heat was evolved significantly, the reaction mixture was cooled with ice-cold water). The mixture was stirred for 2 h at ~20 °C and for another 2 h at 100 °C. Then heating was stopped and another 1.08 g (0.019 mol) of KOH was added. After the reaction mixture was cooled, it was poured onto 60 g of ice. The precipitate was filtered off to yield 2.56 g (98%) of dark brown crystalline substance (compound **3**), which was dissolved in ethanol (100 mL). Perchloric acid (1 equiv., 70%) was added, and the resulting perchlorate (**3**·$H^+ClO_4^-$) was recrystallized from ethanol with charcoal to yield 3.4 g (94%) of light cream-colored crystals, m.p. 270—271 °C (decomp.). Found (%): C, 56.20; H, 6.35; Cl, 10.07. $C_{16}H_{21}ClN_2O_4$. Calculated (%): C, 56.39; H, 6.21; Cl, 10.40. It is more convenient to store the substance as perchlorate. For further synthesis the needed amount of the salt was decomposed with an equimolar amount of aqueous KOH. That is, 1 g (2.9 mmol) of perchlorate was dissolved with heating in the mixture of 27 mL of MeOH and 8 mL of water; then 8.5 mL of 10% KOH was added to the hot solution up to an alkaline reaction. After 2 min the emulsion was diluted with water to 100 mL, and **5,6-bis(dimethylamino)acenaphthene (3)** generated was extracted with benzene to give a light yellow oil that crystallized upon storing in quantitative yield. M.p. 42—43 °C (*cf.* Ref. 6: m.p. 39—40 °C). ^{1}H NMR ($CDCl_3$), δ: 2.83 (s, 12 H, NMe_2); 3.31 (s, 4 H, CH_2CH_2); 6.96 and 7.17 (both d, both 2 H, H-4(7), H-3(8), $J_{3,4}$ = 7.47 Hz).

Treating 5,6-bis(dimethylamino)acenaphthene with the nitrating mixture (see Table 1, experiment *1*). A solution of compound **3** (0.48 g, 20 mmol) in 20 mL of concentrated H_2SO_4 was cooled to −25 °C. Then a solution of 0.127 mL (20 mmol) of 70% HNO_3 (d = 1.41 g·cm^{-3}) in 20 mL of concentrated H_2SO_4 was added dropwise with stirring. The yellowish-green mixture was stirred for 6 min at −25 °C and then was poured onto 40 g of ice and quenched with concentrated NH_4OH (200 mL). The reaction products were extracted with chloroform (3×50 mL). The extract was evaporated to the minimum volume and chromatographed. A dark claret fraction with R_f 0.73 was the first to be gathered. The solvent was removed to give dark claret crystals of **5-dimethylamino-6-methylamino-3-nitroacenaphthenes (8)** (39 mg, 7%), m.p. 118—119 °C (from *n*-octane). Found (%): C, 66.10; H, 6.27. $C_{15}H_{17}N_3O_2$. Calculated (%): C, 66.40; H, 6.32. ^{1}H NMR ($CDCl_3$), δ: 2.76 (s, 6 H, NMe_2); 2.96 (s, 3 H, NMe); 3.31, 3.74 (both m, both 2 H, 2 H-1, 2 H-2, $J_{1,2}$ = 5.89 Hz); 6.63 (d, 1 H, H-7, $J_{7,8}$ = 7.79 Hz); 7.29 (dt, 1 H, H-8, $J_{1,8}$ = 1.30 Hz); 7.74 (s, 1 H, H-4); 8.0 (br.s, 1 H, NH). IR, ν/cm^{-1}: 3333 (NH); 1540, 1380 (NO_2). Then the dark brown fraction with R_f 0.45 was isolated to give 98 mg (15%) of reddish-brown needles of **5,6-bis(dimethylamino)-3,8-dinitroacenaphthene (7)**, m.p. 235—236 °C (decomp., from 1 : 1 ethanol—acetone). Found (%): C, 58.11; H, 5.15. $C_{16}H_{18}N_4O_4$. Calculated (%): C, 58.18; H, 5.49. ^{1}H NMR ($CDCl_3$), δ: 2.86 (s, 12 H, NMe_2); 3.82 (s, 4 H, CH_2CH_2); 7.80 (s, 2 H, H-4(7)). UV, λ_{max}/nm (lg ε): 255 (4.14), 296 (4.07), 480 (3.62), terminal absorption up to 650 nm. The third fraction isolated (R_f 0.28) gave 400 mg (70%) of **5,6-bis(dimethylamino)-3-nitroacenaphthene (6)** as dark cherry-colored needles, m.p. 111—113 °C (from ethanol), readily dissolved in diluted mineral acids. Found (%): C, 67.75; H, 6.30. $C_{16}H_{19}N_3O_2$. Calculated (%): C, 67.35; H, 6.71. ^{1}H NMR ($CDCl_3$), δ: 2.79 and 2.84 (both s, both 6 H, 6- and 5-NMe_2); 3.34 and 3.74 (m and t, both 2 H, 2 H-1, 2 H-2, $J_{1,2}$ = 5.58 Hz); 7.15 and 7.30 (both d, both 1 H, H-7, H-8, $J_{7,8}$ = 7.76 Hz); 7.56 (s, 1 H, H-4). UV, λ_{max}/nm (lg ε): 350 (3.79), 485 (3.56), terminal absorption up to 580 nm.

Polynitronaphthalenes 13 and 14 were obtained by the method[10] described earlier.

1,3,8-Trinitronaphthalene (13). ^{1}H NMR (DMSO-d_6), δ: 8.10 (t, 1 H, H-6, $J_{6,7}$ = 7.69 Hz); 8.69, 8.89 (both dd, both 1 H, H-7, H-5, $J_{5,6}$ = 8.24 Hz, $J_{5,7}$ = 0.88 Hz); 9.02, 9.62 (both d, both 1 H, H-2, H-4, $J_{2,4}$ = 2.25 Hz).

1,3,6,8-Tetranitronaphthalene (14). ^{1}H NMR (DMSO-d_6), δ: 9.22, 9.91 (both d, both 2 H, H-2(7), H-4(5), $J_{2,4}$ = 2.20 Hz).

8-Amino-1,3,6-trinitronaphthalene (17). The procedure[10] reported for obtaining compound **16** was reproduced. The product was twice crystallized from PhMe—AcOH (1 : 1) to give 64% of compound **17** as very small reddish-brown crystals, m.p. 224 °C (decomp.). Found (%): C, 43.07; H, 2.26. $C_{10}H_6N_4O_6$. Calculated (%): C, 43.18; H, 2.17. ^{1}H NMR (DMSO-d_6), δ: 6.75 (br.s, 2 H, NH_2); 7.54, 8.00, 8.45, and 9.12 (all d, all 1 H, H-7, H-5, H-2, H-4, $J_{2,4}$ = 2.17 Hz, $J_{5,7}$ = 2.32 Hz). IR, ν/cm^{-1}: 3480, 3380 (NH_2).

8-Dimethylamino-1,3,6-trinitronaphthalene (18). A mixture of compound **17** (0.056 g, 0.2 mmol), MeI (0.25 mL, 4 mmol), K_2CO_3 (0.138 g, 1 mmol), and 1.5 mL of DMF was refluxed. After 4 h the reaction mixture was diluted with 10 mL of water, and the precipitate was separated and washed with ethanol. Compound **18** (0.046 g, 74%) was obtained as small brownish-red crystals, m.p. 197—200 °C (from ethanol). Found (%): C, 47.14; H, 3.40. $C_{12}H_{10}N_4O_6$. Calculated (%): C, 47.06; H, 3.29. ^{1}H NMR (DMSO-d_6), δ: 3.16 (s, 6 H, NMe_2); 7.79, 8.12, 8.49, and 9.18 (all d, all 1 H, H-7, H-5, H-2, H-4, $J_{2,4}$ = 2.22 Hz, $J_{5,7}$ = 2.74 Hz).

1,8-Diamino-3,6-dinitronaphthalene (16) was synthesized as described earlier[12] using 85% hydrazine hydrate. The reaction mixture was refluxed for 6 h and then diluted ten-fold with water. The residue was filtered off and recrystallized from pyridine to give 60% of diamine **16**. IR, ν/cm^{-1}: 3470, 3375 (NH_2); 1525, 1350 (NO_2).

Alkylation of 1,8-diamino-3,6-dinitronaphthalene. *A.* The mixture of diamine **16** (0.22 g, 0.88 mmol), MeI (2 mL, 32 mmol), and powdered KOH (0.50 g, 8.8 mmol) in 20 mL of DMF was stirred for 24 h at ~20 °C. During the reaction time the reaction mixture changed its color from purple-violet to dark grayish brown. The mixture was diluted with 200 mL of

water and extracted with chloroform (4×14 mL). The extract was evaporated *in vacuo* to remove the traces of DMF and chromatographed. The reddish-orange fraction with R_f 0.72 was gathered first to yield 47 mg (18%) of **1-dimethylamino-8-methylamino-3,6-dinitronaphthalene (20)** as light red crystals with golden play, m.p. 170—171 °C (from ethanol). Found (%): C, 53.76; H, 4.91. $C_{13}H_{14}N_4O_4$. Calculated (%): C, 53.79; H, 4.86. ^{1}H NMR ($CDCl_3$), δ: 2.80 (s, 6 H, 1-NMe_2); 3.04 (d, 3 H, 8-NMe, $J_{NH,NMe}$ = 4.91 Hz); 7.22, 7.98, 8.02, and 8.52 (all d, all 1 H, H-7, H-2, H-5, H-4, $J_{2,4}$ = 2.34 Hz, $J_{5,7}$ = 2.26 Hz); 9.07 (br.s, 1 H, NH). IR, ν/cm^{-1}: 3180 (NH); 1530, 1330 (NO_2). The next was a yellowish-brown fraction with R_f 0.62 that was a mixture of compounds **5** and **19**. It was additionally separated by chromatography on Al_2O_3 (II degree of activity) using $CHCl_3$ as the eluent. Under these conditions "proton sponge" **5** had a shorter retention time than naphthylamine **19**. **1,8-Bis(dimethylamino)-3,6-dinitronaphthalene (5)** (9 mg, 3%) was isolated as brownish-red crystals with m.p. 177—178 °C (from ethanol), easily soluble in diluted mineral acids. Found (%): C, 55.35; H, 5.28. $C_{14}H_{16}N_4O_4$. Calculated (%): C, 55.26; H, 5.30. ^{1}H NMR ($CDCl_3$, 45 °C), δ: 2.94 (s, 12 H, NMe_2); 7.80 and 8.37 (both d, both 2 H, H-2(7), H-4(5), $J_{2,4}$ = 1.77 Hz). UV, λ_{max}/nm (lg ε): 252 (4.41), 291 (4.29), 444 (3.65), terminal absorption up to 570 nm.

Then **8-amino-1-dimethylamino-3,6-dinitronaphthalene (19)** (5 mg, 2%) was isolated as red crystals, m.p. 192—193 °C (from ethanol). Found (%): C, 52.10; H, 4.45. $C_{12}H_{12}N_4O_4$. Calculated (%): C, 52.17; H, 4.38. ^{1}H NMR ($CDCl_3$), δ: 2.75 (s, 6 H, NMe_2); 6.44 (br.s, 2 H, NH_2); 7.32, 7.87, 8.01, and 8.43 (all d, all 1 H, H-7, H-2, H-5, H-4, $J_{2,4}$ = 2.24 Hz, $J_{5,7}$ = 2.26 Hz). IR, ν/cm^{-1}: 3435, 3360 (NH_2).

Alkylation of trimethyl derivative **20** by the method described above for compound **18** resulted in "proton sponge" **5** in quantitative yield (refluxing for 10 h).

B. A mixture of compound **16** (0.17 g, 0.68 mmol), MeI (2 mL, 32 mmol), and potash (0.94 g, 6.8 mmol) in 6 mL of DMF was refluxed for 30 h. After cooling the suspension was diluted with 180 mL of water and treated as described in method ***A***. Compound **5** (0.16 g, 76%) was obtained with properties identical to those of the sample described above.

1,8-Diamino-3-nitronaphthalene (15) was obtained from trinitronaphthalene **13** analogously to diamine **16** by the method described above[12] using 85% hydrazine hydrate. The mixture was refluxed for 7 h, diluted ten-fold with water, and extracted with diethyl ether until the ether layer remained colorless. Ether was removed, and the dark red residue was chromatographed. The main orange-brown zone with R_f 0.27 was gathered. Starting from compound **13** (0.526 g, 2 mmol) diamine **15** (0.207 g, 51%) was obtained as black-claret needles, m.p. 208—210 °C (from pyridine). Found (%): C, 59.21; H, 4.32. $C_{10}H_9N_3O_2$. Calculated (%): C, 59.11; H, 4.46. ^{1}H NMR ($CDCl_3$, 50 °C), δ: 4.71 (br.s, 4 H, 2 NH_2); 6.78 (dd, 1 H, H-7); 7.26 (d, 1 H, H-2, $J_{2,4}$ = 2.25 Hz); 7.28 (t, 1 H, H-6, $J_{6,7}$ = 7.28 Hz); 7.37 (dd, 1 H, H-5, $J_{5,6}$ = 8.24 Hz, $J_{5,7}$ = 1.20 Hz); 8.05 (d, 1 H, H-4). IR, ν/cm^{-1}: 3400, 3310 (NH_2); 1525, 1330 (NO_2).

5-Nitroperimidine (21). A yellow solution of diamine **15** (0.01 g, 0.05 mmol) in 1 mL of 85% HCOOH was refluxed for 40 min and evaporated to dryness. The residue was crystallized from ethanol to give rhombic dark red crystals in quantitative yield, m.p. 284—285 °C (decomp.). Found (%): C, 62.06; H, 3.40. $C_{11}H_7N_3O_2$. Calculated (%): C, 61.97; H, 3.31. ^{1}H NMR (DMSO-d_6), δ: 6.71 (br.s, 1 H, H-9, $J_{8,9}$ = 6.71 Hz); 6.99 (d, 1 H, H-4, $J_{4,6}$ = 2.00 Hz); 7.38 (m, 2 H, H-7, H-8, $J_{7,8}$ = 8.31 Hz); 7.56 (s, 1 H, H-2); 8.02 (d, 1-H, H-6); 11.1 (br.s, 1 H, NH).

Nitration of 1,8-diaminonaphthalene. 1,8-Diaminonaphthalene (0.158 g, 1 mmol) was dissolved in 2 mL of concentrated H_2SO_4, and a nitrating mixture containing 0.0638 mL (1 mmol) of 70% HNO_3 and 1 mL of concentrated H_2SO_4 was added gradually (over 1—2 min) at 0 °C. The grayish brown reaction mixture was stirred for another 1 h at 0 °C and poured out onto 10 g of ice. After quenching with 18 mL of concentrated NH_4OH the mixture was extracted with $CHCl_3$ (3×10 mL) and chromatographed. The starting diamine (R_f 0.40, 47 mg, 30%) and **4,5-diamino-1-nitronaphthalene (22)** (R_f 0.22, 35 mg, 17%) were subsequently isolated. Compound **22**: reddish-brown crystals, m.p. 176—177 °C (from pyridine). Found (%): C, 59.07; H, 4.38. $C_{10}H_9N_3O_2$. Calculated (%): C, 59.11; H, 4.46. ^{1}H NMR ($CDCl_3$, 50 °C), δ: 4.2 (br.s, 4 H, 2 NH_2); 6.45 (d, 1 H, H-3); 7.79 and 7.41 (both dd, both 1 H, H-6, H-7, $J_{6,7}$ = 7.50 Hz, $J_{6,8}$ = 1.04 Hz, $J_{7,8}$ = 8.82 Hz); 8.22 (d, 1 H, H-2, $J_{2,3}$ = 8.70 Hz); 8.42 (dd, 1 H, H-8). IR, ν/cm^{-1}: 3490, 3390 (NH_2); 1520, 1350 (NO_2).

Alkylation of 1,8-diamino-3-nitronaphthalene (15) was performed as described for diamine **16** (method ***B***). The reaction mixture was refluxed for 30 h, alkalized with aqueous ammonia, and treated as described above. The main pink-brown fraction with R_f 0.21 was isolated by chromatography. Yield: 42% of **1,8-bis(dimethylamino)-3-nitronaphthalene (4)** as red oil readily soluble in diluted mineral acids. Found: (%): C, 64.93; H, 6.57. $C_{14}H_{17}N_3O_2$. Calculated (%): C, 64.85; H, 6.61. ^{1}H NMR ($CDCl_3$), δ: 2.79 and 2.84 (both s, both 6 H, 8- and 1-NMe_2); 7.08 (d, 1 H, H-7); 7.43 (m, 2 H, H-5, H-6, $J_{5,6}$ = 7.80 Hz, $J_{6,7}$ = 7.50 Hz); 7.56 (br.s, 1 H, H-2); 8.22 (br.s, 1 H, H-4). UV, λ_{max}/nm (lg ε): 226 (4.43), 292 (4.09), 340 (pl, 3.68), 444 (3.33), terminal absorption up to 550 nm.

4,5-Bis(dimethylamino)-1,2,3,6,7,8-hexanitronaphthalene (23). Nitric acid (70%, 0.05 mL, 0.8 mmol) was added in one stage to a solution of compound **5** (0.030 g, 0.1 mmol) in 0.8 mL of Ac_2O at 0 °C. The clear solution was kept at ~20 °C. Just after 40 min small lustrous crystals of hexanitro derivative began separation. After 2 h the reaction mixture was diluted with 2 mL of Pr^iOH and cooled to 0 °C. The precipitate was filtered off on a glass filter and washed with cold Pr^iOH to yield small yellowish-orange crystals of hexanitronaphthalene **23** (0.019 g, 40%). The mother liquid was concentrated *in vacuo* to give another 0.016 g (33%) of crude product (total yield 73%). The substance is moderately soluble in acetone and reacts with DMF and DMSO (especially with heating). It can be crystallized from Ac_2O; it is nonmelting, decomp.p. >240 °C. *Do not mix with reducing agents! Explosion hazard!* Found (%): C, 34.50; H, 2.61. $C_{14}H_{12}N_8O_{12}$. Calculated (%): C, 34.72; H, 2.50. ^{1}H NMR, δ: 3.31 (s, DMSO-d_6); 3.58 (s, acetone-d_6). UV (acetone), λ_{max}/nm (lg ε): 360 (4.13), 428 (pl, 4.22), 453 (4.35).

The work was financially supported by the Russian Foundation for Basic Research (Project No. 99-03-33133a).

References

1. V. A. Ozeryanskii, A. F. Pozharskii, and N. V. Vistorobskii, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 1215 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 1212 (Engl. Transl.)].
2. M. Brickman, J. H. P. Utley, and J. H. Ridd, *J. Chem. Soc.*, 1965, 6851.
3. R. L. Benoit, D. Lefebvre, and M. Frechette, *Can. J. Chem.*, 1987, **65**, 996.
4. R. W. Alder, *Chem. Rev.*, 1989, **89**, 1215.

5. A. F. Pozharskii, *Usp. Khim.*, 1998, **67**, 3 [*Russ. Chem. Rev.*, 1998, **67**, 1 (Engl. Transl.)].
6. A. F. Pozharskii, L. A. Kurasov, V. V. Kuz'menko, and L. L. Popova, *Zh. Org. Khim.*, 1981, **17**, 1005 [*J. Org. Chem. USSR*, 1981, **17** (Engl. Transl.)].
7. L. A. Kurasov, A. F. Pozharskii, and V. V. Kuz'menko, *Zh. Org. Khim.*, 1981, **17**, 1944 [*J. Org. Chem. USSR*, 1981, **17** (Engl. Transl.)].
8. A. F. Pozharskii, A. N. Suslov, N. M. Starshikov, L. L. Popova, N. A. Klyuev, and V. A. Adanin, *Zh. Org. Khim.*, 1980, **16**, 2216 [*J. Org. Chem. USSR*, 1980, **16** (Engl. Transl.)].
9. L. A. Kurasov, A. F. Pozharskii, V. V. Kuz'menko, N. A. Klyuev, A. I. Chernyshev, S. S. Goryaev, and N. L. Chikina, *Zh. Org. Khim.*, 1983, **19**, 590 [*J. Org. Chem. USSR*, 1983, **19** (Engl. Transl.)].
10. H. H. Hodgson, E. R. Ward, and J. S. Whitehurst, *J. Chem. Soc.*, 1945, 454.
11. H. H. Hodgson and H. S. Turner, *J. Chem. Soc.*, 1943, 318.
12. V. L. Zbarskii, A. P. Goncharuk, and V. P. Fedosov, *Zh. Org. Khim.*, 1994, **30**, 453 [*Russ. J. Org. Chem.*, 1994, **30**, 487 (Engl. Transl.)].
13. Jpn. Pat. 52-456995, 1977.
14. H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, 1953, **75**, 24.
15. A. Zweig, A. Maurer, and B. G. Roberts, *J. Org. Chem.*, 1967, **32**, 1322.
16. H. H. Hodgson and E. R. Ward, *J. Chem. Soc.*, 1945, 794.
17. *Organicum*, Ed. K. Schwetlick, VEB Deutscher Verlag der Wissenschaften, Berlin, 1976.
18. M. M. Dashevskii, *Zh. Prikl. Khim.*, 1959, **32**, 2749 [*J. Appl. Chem. USSR*, 1959, **32** (Engl. Transl.)].
19. F. Sachs and G. Mosebach, *Ber.*, 1911, **44**, 2852.

Received January 24, 2000;
in revised form, May 3, 2000