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peri-Naphthylenediamines
38.* Naphthalene and acenaphthene "proton sponges" with +M substituents in *ortho* positions with respect to *peri*-dimethylamino groups

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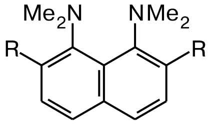
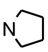
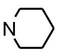
Previously unknown 4,5,6,7-tetrakis(dimethylamino)acenaphthene, which is the first acenaphthene derivative containing four vicinal dialkylamino groups, was synthesized based on 5,6-bis(dimethylamino)-4,7-dinitroacenaphthene. The total synthesis of 1,2,7,8-tetrakis(dimethylamino)naphthalene was carried out starting from 3,6-dinitronaphthalic anhydride. Other "proton sponges" of this type, *viz.*, 1,7,8-tris(dimethylamino)-2-methoxy- and 1,8-bis(dimethylamino)-2,7-dipiperidinonaphthalenes, were prepared by the nucleophilic substitution in 2,7-dimethoxy-1,8-dinitronaphthalene. In solutions, 1,2,7,8-tetrakis(dimethylamino)naphthalene and its analogs can form di- and trications in the presence of acids. The basicity constants pK_a^1 of the compounds measured in DMSO depend in a complex way on their structures but correlate with the basicity index *B*, which is determined by changes in the chemical shifts δ_H after the addition of the first proton. Due to low *C*-nucleophilicity of *ortho*-disubstituted "proton sponges" in combination with high basicity, these compounds hold considerable promise as reagents in organic synthesis.

Key words: acenaphthene, 1,8-dinitronaphthalene, nucleophilic substitution, catalytic hydrogenation, alkylation, "proton sponge", basicity, protonation, nitration, azo-coupling.

1,8-Bis(dimethylamino)naphthalene ("proton sponge," **1a**) and its 2,7-dimethoxy (**1b**) and 2,7-bis(dimethylamino) derivatives (**1c**) are of interest[2—5] because of their record high basicity (for example, pK_a for compounds **1a** and **1b** are 12.1 and 16.1, respectively, in the H_2O scale)[5—8] in combination with rather simple structures.



1a—e

R = H (**a**), OMe (**b**), NMe_2 (**c**), N (**d**), N (**e**)

Although the properties of the parent compound of this series, *viz.*, compound **1a**, have been investigated in considerable detail, derivatives **1b** and **1c** remain poorly studied, primarily, because they are difficultly accessible. Earlier, the properties of **1b** and **1c** have been considered only theoretically.[9—11] However, the nature of the unusually high basicity of compounds **1b** and **1c** is of interest from the viewpoint of the theory of acids and bases as well as from the standpoint of organic chemistry as such. In addition, protic salts of compound **1b** have recently been proposed as models for studying the types of intramolecular hydrogen bonds.[12] In the present study, we developed a convenient procedure for the synthesis of "proton sponges" **1b** and **1c** and some their close analogs, including the first derivative containing simultaneously the alkoxy and amino groups in the *ortho* positions. We also studied the characteristic features of protonation of these compounds, the relationship between their structure and basicity, and their behavior in nitration and azo-coupling reactions.

Synthesis. Earlier, we have demonstrated that the *o*-nitro group can be transformed into the *o*-NMe_2 group in 1,8-bis(dimethylamino)naphthalene derivatives by catalytic hydrogenation (Pd/C) followed by alkylation (MeI—KOH—DMF). In particular, this method was used for the preparation of triamine **2** in a total yield of 81%.[13] In the present study, we used this approach for the synthesis of diamine **3b** (100%) starting from rather readily accessible dinitroacenaphthene **3a** (see Ref. 14). Methylation of diamine **3b** in an MeI—KOH—DMF system afforded derivative **3c** (37%).

However, alkylation with dimethyl sulfate ($(MeO)_2SO_2$—Na_2CO_3—H_2O), which we have success-

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[*] For Part 37, see Ref. 1.

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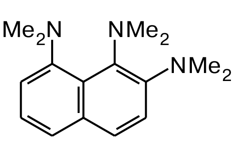

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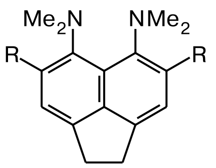


3a—c

R = NO_2 (**a**), NH_2(**b**), NMe_2 (**c**)

fully used earlier,[15—17] proved to be a method of choice for performing the transformation **3b** → **3c**. Since *N*-nucleophilicity of the amino groups at the C(4) and C(7) atoms in amine **3b** should be high, whereas *NH*-acidity, on the contrary, should be low, the use of superbasic systems, which generate readily oxidizable *N*-anions, is inefficient, whereas the reaction with the use of the $(MeO)_2SO_2$—Na_2CO_3—H_2O mixture afforded peralkylated polyamine **3c** in a yield of >63% through the successive quaternization—deprotonation steps (the details of the use of this alkylating system are reported for the first time in the present study; see the Experimental section).

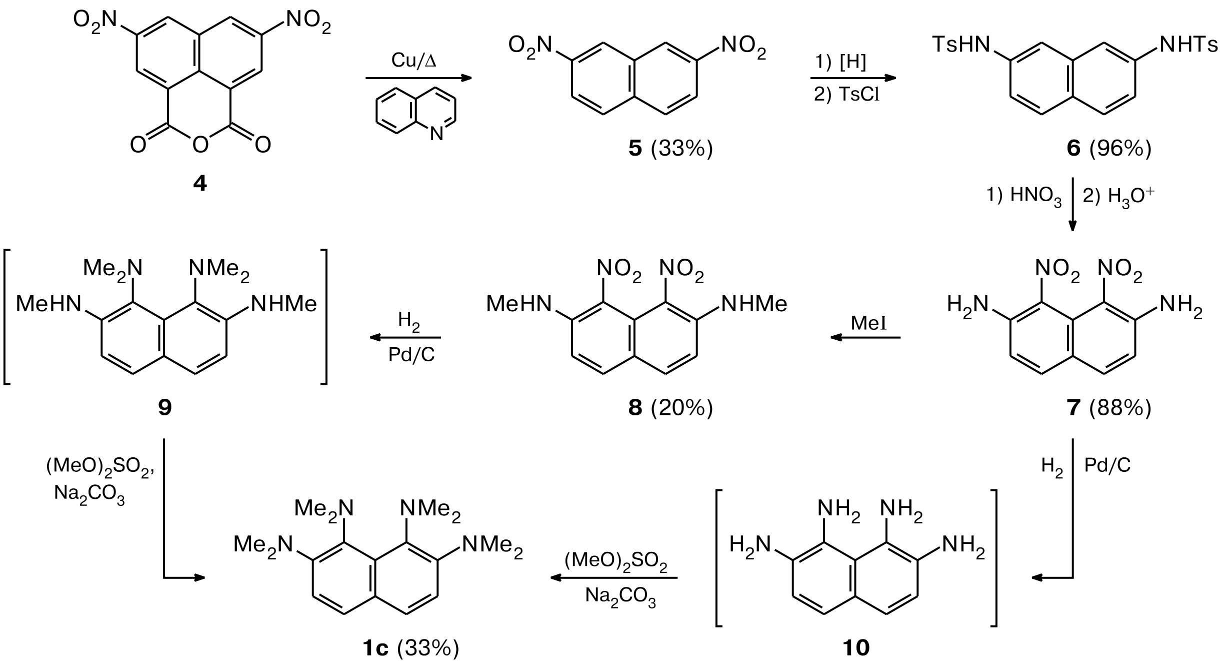
The evident precursor of "proton sponge" **1c**, *viz.*, 1,8-bis(dimethylamino)-2,7-dinitronaphthalene (analog of compound **3a**), is difficult to prepare.[14] Hence, we developed an alternative procedure for the preparation of compound **1c** from 3,6-dinitronaphthalic anhydride (**4**) (Scheme 1). In spite of the fact that this procedure involves many steps, it is characterized by high reliability and good yields (seven steps, the total yield is 10—15%).

Although we succeeded in increasing the yield of the key dinitrodiaminonaphthalene **7**, whose synthesis from diamide **6** has been described earlier (47% yield, see Ref. 18), to 88%, attempts to perform its exhaustive *N*-methylation failed. Diamine **7** remained intact under the action of $(MeO)_2SO_2$—K_2CO_3—DMF (100 °C, 50 h) or MeI—K_2CO_3—Me_2NAc (50—60 °C, 30 h) systems. The reactions with the use of MeI—KOH—DMSO (30 °C, 24 h) or MeI—K_2CO_3—MeOH (65 °C, 33 h) systems led to resinification of the starting diamine **7** due, apparently, to the competitive nucleophilic substitution of the nitro groups. Partially methylated product **8** was prepared in a yield of no higher than 20% only with the use of a MeI—K_2CO_3—DMF mixture (50—60 °C, 30 h). Product **8** is stabilized by an intramolecular hydrogen bond (ν_{NH} 3360 cm^{-1}, δ_H(NH) 8.0), which, along with increasing steric requirements, can hinder its further alkylation. We succeeded in obviating this problem by subjecting nitronaphthylamine **7** to hydrogenation followed by exhaustive alkylation of tetraamine **10** with the $(MeO)_2SO_2$—Na_2CO_3—H_2O system. Analogously, compound **1c** can also be prepared starting from methylamino derivative **8** without isolation of polyamine **9** (the yield was 33% with respect to dinitro derivative **8**).

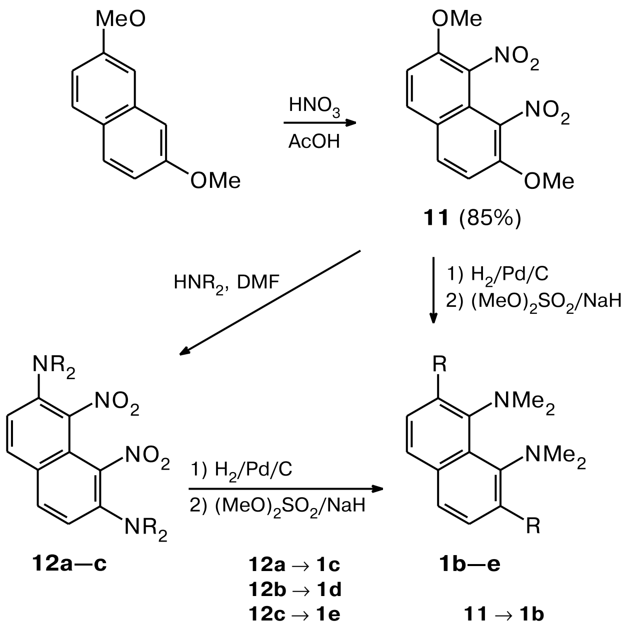
It should be emphasized that the four-step synthesis of 1,2,7,8-tetrakis(dimethylamino)naphthalene (**1c**) described earlier[3] afforded the target product in a yield of as low as 4% due, primarily, to complications in the methylation step (Scheme 2).

We demonstrated that the use of the $(MeO)_2SO_2$—Na_2CO_3—H_2O system instead of

Scheme 1



Scheme 2

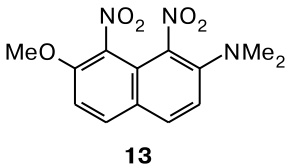


1: R = OMe (**b**), NMe_2 (**c**), $N(CH_2)_4$ (**d**), $N(CH_2)_5$ (**e**)
12: R = Me (**a**, 84%)[3]; $R_2 = (CH_2)_4$ (**b**, 90%)[3]; $(CH_2)_5$ (**c**, 32%)

$(MeO)_2SO_2$—NaH for methylation led to an increase in the total yield of compound **1c** from 5 to 40%. Moreover, the analogous transformation **11** → **1b** afforded the target product in a yield of up to 70% (earlier,[2] the efficiency of this transformation was lower than 20%).

Other "proton sponges" **1d,e** can be prepared by varying secondary alkylamine in the step of nucleophilic substitution of the methoxy groups in dinitronaphthalene **11**. Earlier,[3] this reaction was carried out with the use of dimethylamine and pyrrolidine. The results of the reactions of these and other dialkylamines with dimethoxy derivative **11** are presented in Table 1.

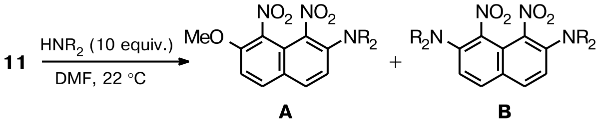
As can be seen from this table, the percentage of exhaustive substitution products decreases in the series pyrrolidine ≈ dimethylamine > piperidine (see Table 1, runs *2* and *4*). The latter reaction is accompanied by substantial resinification. We succeeded in preparing partial substitution product **13** containing the methoxy and dimethylamino groups in the *ortho* positions of the naphthalene system in high yield by decreasing the reaction time (see Table 1, run *1*).

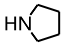
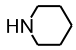


13

Nitronaphthylamines **12a—c** and **13** containing tertiary arylamino groups are sensitive to light. When exposed to UV light or sunlight, these compounds turn black both in solution and in the solid state within a few hours.

Table 1. Nucleophilic substitution in 2,7-dimethoxy-1,8-dinitronaphthalene (**11**) in the presence of secondary alkylamines

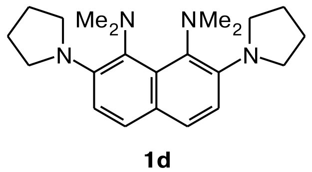


Run	HNR_2	τ /day	Composition of the reaction mixture (%)				Reference
			11	A	B	Resins*	
1	$HNMe_2$	**	7	90 (**13**)	0	3	***
2	$HNMe_2$	3	0	0	84 (**12a**)	16	3
3		4	0	0	90 (**12b**)	10	3
4		7	10	8	32 (**12c**)	50	***

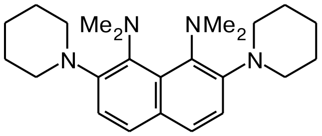
* Products of unknown composition.
** 3 h.
*** The present study.

Under the same conditions, 1,8-dinitronaphthalenes containing primary (**7**) or secondary (**8**) *o*-amino groups as well as dimethoxynaphthalene **11** remain intact.

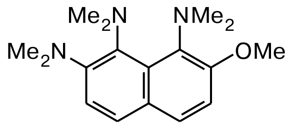
Dinitronaphthalenes prepared in this step were transformed into new "proton sponges" **14** and **1e** in 61 and 39% yields, respectively, by catalytic hydrogenation and alkylation with dimethyl sulfate. 2,7-Dipyrrolidine derivative **1d** has been characterized earlier[3] by X-ray diffraction analysis and its pK_a has been determined; however, the yield, spectroscopic characteristics, and physical properties of **1d** have not been reported. We prepared (in 48% yield) and completely characterized this compound (see the Experimental section).



1d



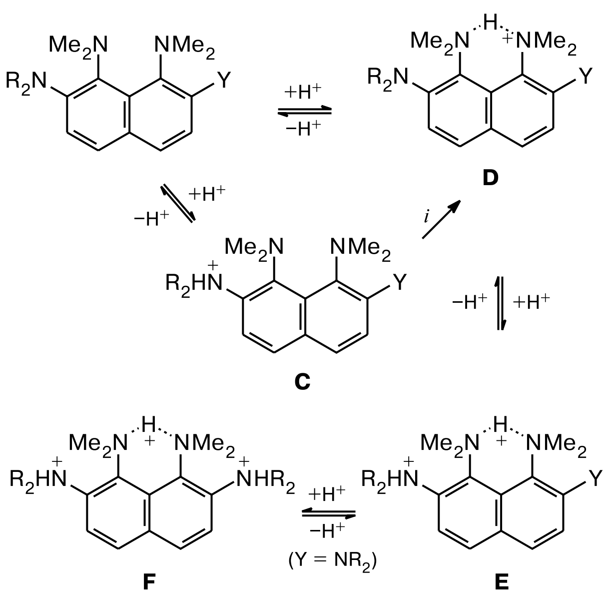
1e



14

Protonation. "Proton sponges" **1a—d**, **3b,c**, and **14** are polyacidic bases, which can add several protons (concentrated HBr, $HClO_4$, and HBF_4 were used). The first proton is coordinated to the *peri*-NMe_2 groups (Scheme 3) to form the cation **D** with an intramolecular hydrogen bond. This cation is classical for "proton sponges".[5] For the cations **D**, the signals of the *peri*-NMe_2 groups are shifted downfield by 0.4—0.5 ppm and turn into doublets due to spin-spin coupling with the proton of the NH group; the latter appears in the ^1H NMR spectrum as a broadened singlet or a multiplet (depending on the symmetry of the cation) at δ 18—20 (see the Experimental section and Table 2).[19]

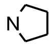
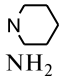
Scheme 3



i. Proton transfer

There are grounds to suppose that in the reactions of acids with *ortho*-amino-substituted "proton sponges," the first proton rapidly adds to the more accessible β-amino group to form the cation **C**. In solution, the latter is irreversibly rearranged into the thermodynamically more stable cation **D**. This assumption is confirmed by the following observations. Under homogeneous conditions (MeCN, MeOH, or DMF), a monoprotonated salt of the type **D** can be prepared in the individual form by adding one equivalent of mineral acid to the "proton sponges" under study followed by careful removal of the solvent. By contrast, under heterogeneous conditions (hexane, benzene, or Et_2O), the addition of even one equivalent of acid led to the rapid formation of a precipitate, which virtually completely consisted of diprotonated salt **E**.

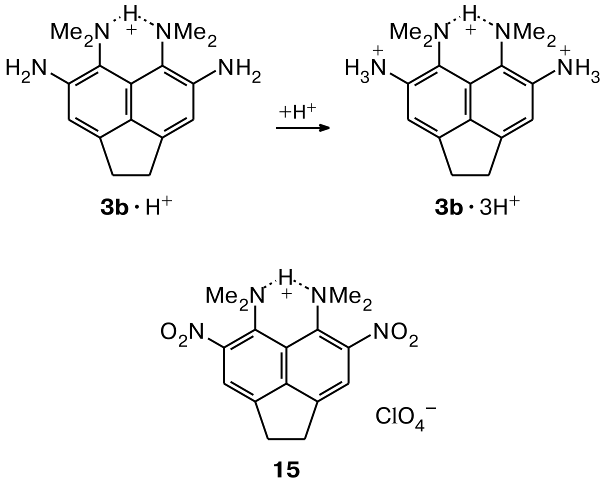
Table 2. Chemical shifts (δ_H) of selected fragments of *ortho*-disubstituted "proton sponges" in the neutral and protonated* forms (DMSO-d_6)

Compound	R	NMe_2	H_o	N—H...N
1b	OMe	2.82 (3.18)	7.16 (7.53)	(19.38)
1c	NMe_2	2.91 (3.30)	7.20 (7.85)	(19.81)
1d		2.83 (3.25)	7.11 (7.79)	(19.82)
1e		2.92 (3.29)	7.28 (7.84)	(19.88)
3b	NH_2	2.80 (3.14)	6.45 (6.55)	(18.48)
3c	NMe_2	2.88 (3.25)	7.04 (7.65)	(18.53)

* The spectroscopic data for the protonated form are given in parentheses.

In the presence of an excess of acid, protonation of compound **14** afforded the dication **E** (R = Me, Y = OMe) as the final product. The other "proton sponges" gave the trications **F** (see Scheme 3). It is noteworthy that the ^1H NMR spectroscopic characteristics of the trication $\mathbf{3b} \cdot 3H^+$, unlike those of the monocation $\mathbf{3b} \cdot H^+$, are similar to those of salt **15** (Scheme 4, Table 3).

Scheme 4



Another distinguishing feature of "proton sponges" containing *ortho*-amino substituents is that the constant $J_{NH,NMe}$ gradually decreases with increasing amount of the acid added to solutions of the "proton sponges" in acetonitrile. In the course of this process, the chemical shift of the chelated proton δ_{NH} first sharply decreases

Table 3. Spectroscopic characteristics of solutions of salts $\mathbf{3b} \cdot HClO_4$ and **15** (δ_H, CD_3CN)

Compound	$HClO_4$ (equiv.)	δ				$J_{NH,NMe}$ /Hz
		NMe_2	CH_2CH_2	H_{arom}	N...H—N	
3b	1	3.22	3.29	6.87	17.69	2.72
3b	2	3.27	3.36	7.12	17.01	2.71
3b	4	3.27	3.38	7.16	17.17	2.69
3b	10	3.28	3.41	7.24	17.46	2.66
3b	20	3.28	3.41	7.28	17.65	2.62
15	—	3.29	3.59	7.86	18.65	2.58

Table 4. Protonation of tetraamines **1c** and **3c** in CD_3CN according to ^1H NMR spectroscopic data

Compound	$HClO_4$ (equiv.)	δ			$J_{NH,NMe}$ /Hz
		α-NMe_2	β-NMe_2	N...H—N	
1c	1	3.30	2.74	20.08	2.61
1c	2	3.40	2.85	16.97	—*
1c	3	3.43	3.22	17.26	2.52
1c	4	3.43	3.23	17.33	2.51
3c	1	3.28	2.74	18.80	2.56
3c	3	3.39	3.15	15.53	2.20

* The constant was not determined because of overlapping of the signal of the α-dimethylamino groups with the common signal of the water molecule and the acidic protons (except for the chelated proton in the N—H...N bridge); in this case, the signal of the bridging proton does not have a multiplet structure and appears as a broadened singlet.

Table 5. Constants pK_a for selected "proton sponges" (24 °C, DMSO)

Compound	pK_a	Compound	pK_a
1a	7.47±0.04 [20]	**1e**	11.31±0.04[a]
1b	11.50±0.05 [3,6]	**3b**	11.38±0.17
1c	11.23±0.04[b]	**3c**	11.11±0.05[a]
1d	10.97±0.04[c]	**14**	11.27±0.04

[a] The constant was determined at 70 °C due to poor solubility of the compound in DMSO and extrapolated to ~20 °C.

[b] *Cf.* lit. data[3]: 11.20.

[c] *Cf.* lit. data[3]: 10.90.

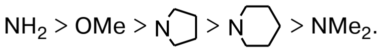
and then slowly increases. The minimum chemical shift δ_{NH} was observed in the presence of 2—3 equiv. of monobasic acid (see Tables 3 and 4). Protonation of the monocations **D** in DMSO, as opposed to that in acetonitrile, was virtually undetectable, because this basic solvent successfully competes with these monocations for subsequent protons.

It should be noted that all cationic species, which are generated in the reactions of acids with symmetrical polyamines **1a—e** and **3b,c**, are symmetrical in solutions on the NMR time scale. Only triamine **14** forms the true unsymmetrical mono- and dications, the chelated NH proton in its monocation being shifted by 60% toward the β-dimethylamino group and only by 40% toward the β-methoxy group (the degree of asymmetry of intramolecular hydrogen bonds in such cations was determined according to a procedure described in the literature[19]).

Structure—basicity relationship. Evidently, the overall electronic effect of the *ortho* substituents in "proton sponges" should depend substantially on the solvation effects. Apparently, that is the reason why the constants pK_a of compounds **1a—e** and **3b,c** change in a very complex way (Table 5).

As expected, all *ortho*-amino-substituted "proton sponges" are much more basic than parent compound **1a**, although their pK_a are no higher than the record value of 11.5 (in DMSO) for dimethoxy derivative **1b**. The evident reason for this fact is that the mesomeric interactions of the β-dialkylamino groups, which are substantially twisted relative to the ring, with the aromatic π system, are weaker compared to those of the methoxy groups in compound **1b** (see below). At the same time, the conjugation of the *o*-NH_2 groups in amine **3b** should be stronger, which corresponds to higher basicity of this compound compared to **3c**. The latter compound is also somewhat less basic than its naphthalene analog **1c** due, apparently, to poorer solvation of the cation **3c**·H^+ in DMSO because of the presence of the ethylene bridge. In the basicity, "hybrid" **14** (pK_a is 11.3 in DMSO) is intermediate between compounds **1b** and **1c** (pK_a are 11.5 and 11.2, respectively), being more similar to the latter. This fact is probably attributable to the presence of an asymmetric and, hence, weaker intramolecular hydrogen bond in the cation **14**·H^+ (see above).

Analysis of the influence of the *ortho* substituents in the *ortho*-disubstituted "proton sponges" on the ^1H NMR spectroscopic parameters (*cf.* the chemical shifts of the H_o protons and the dimethylamino groups in the neutral and monoprotonated compounds, see Table 2) shows that their electron-donating effect changes in the following series:*



The changes in pK_a are, on the whole, consistent with this series, except for compound **1d**, which is characterized by a somewhat lower basicity. This fact is to a certain extent explained by the results of X-ray diffraction analysis, which are presented in Table 6 along with analogous data for amines **1b**, **1c**, and **3c**. X-ray diffraction analysis of the latter compound was carried out in the present study. The overall view of one of two crystallographically independent molecules **3c** is shown in Fig. 1.

As can be seen from Table 6, the pyrrolidine groups in base **1d** are twisted with respect to the naphthalene system by only 36°. This fact should be favorable for their strong steric interactions with the *peri*-NMe_2 groups. To reduce repulsions, all amino groups in molecule **1d** deviate from the mean plane of the naphthalene ring in different directions and the ring undergoes distortions. The torsion angle between the C(4)—C(5) and C(10)—C(11) bonds in-

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* This series differs substantially from the analogous series for the sterically unhindered methoxy and amino groups in benzene derivatives[21]

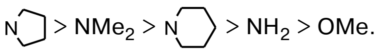


Table 6. Selected structural characteristics of molecules **1b,c,d** and **3c**

Compound	R	N...N[a] /Å	Angle/deg		Sum of C—N—C angles[d] /deg	p[e] (%)	*T*/K	Reference
			NMe_2—ring[b]	R—ring[c]				
1b	OMe	2.756	74	6	346.2	90	190	23
1c	NMe_2	2.770	55	64	356.2	97	298	3
1d		2.848	61	36	357.6	98	298	3
3c	NMe_2	2.824[f]	63	68	352.4	95	120	[g]

[a] The nonbonded distance between the *peri*-nitrogen atoms.

[b] The average angles of rotation of the *peri*-NMe_2 groups with respect to the aromatic ring.

[c] The average angles between the substituents R and the aromatic ring.

[d] The average sums of the angles at the nitrogen atoms of the *peri*-NMe_2 groups.

[e] The p character of the lone electron pairs of the nitrogen atoms of the *peri*-NMe_2 groups was evaluated (%) from the C—N—C bond angles as described in the study.[22]

[f] The average value for two crystallographically independent molecules in the unit cell.

[g] The present study.

creases to 19° as opposed to 3° in compounds **1b** and **3c** and 14° in molecule **1c** (see Fig. 1). Apparently, the conformationally more rigid pyrrolidine groups in the cation $\mathbf{1d} \cdot H^+$ are virtually perpendicular to the plane of the aromatic system, as evidenced by the largest changes in the chemical shifts of the dimethylamino groups ($\Delta\delta(NMe_2)$ 0.42) and the aromatic H_o protons ($\Delta\delta(H_o)$ 0.68) for a pair of the species $\mathbf{1d}$—$\mathbf{1d} \cdot H^+$ in the series of the compounds under consideration (see Table 2). Taking into account that the chemical shift of the chelated proton $\delta_H(NH)$ is determined by the effective volume of the *ortho* substituent,[24] the data presented in Table 2 allow one to easily calculate the dimensionless basicity index *B*, which we propose as the following expression

$$B = \delta_H(NH)/(\Delta\delta(NMe_2) + \Delta\delta(H_o)).$$

Since this index deals with the chemical shifts, it takes into account the influence of the solvent (DMSO), the electronic interactions between the substituents, and the steric effects and depends qualitatively on the constant pK_a. For example, the indices *B* for compounds **1c**, **1d** and **3c** are 19.0, 18.0, and 18.9, respectively.

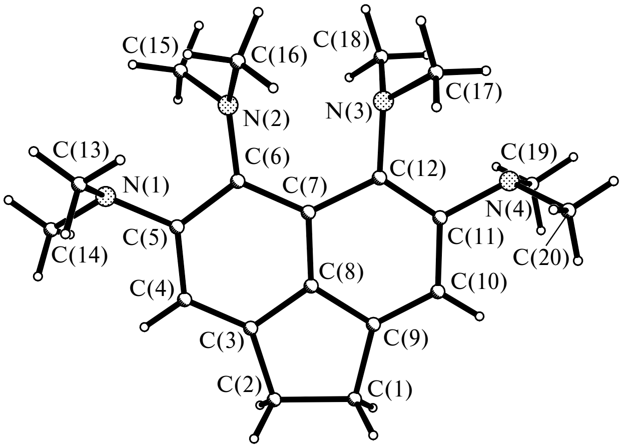
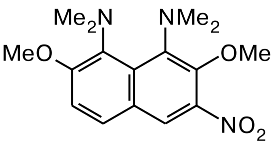


Fig. 1. Overall view and the atomic numbering scheme for one of crystallographically independent molecules of compound **3c**.

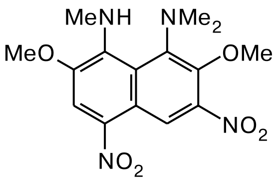
The ethylene bridge in compound **3c** is responsible for a series of structural changes, which are unfavorable for an increase in the constant pK_a compared to that of "proton sponge" **1c**. Among these changes are: 1) an increase in the N...N distance from 2.77 to 2.82 Å resulting in the formation of a more elongated and weak hydrogen bridge in the cation $\mathbf{3c} \cdot H^+$ (see Tables 2 and 4); 2) an increase in acoplanarity of the *o*-dimethylamino groups and the naphthalene ring (68° compared to 64° for tetraamine **1c**), which reduces their electron-donating effect; 3) an increase in the distance between the *ortho* substituents and the *peri*-NMe_2 groups and, consequently, a decrease in their mutual repulsion (the degree of pyramidality of the bonds at the nitrogen atoms of the *peri*-NMe_2 groups increases). The latter fact leads to a decrease in the sum of the bond angles at the *peri*-nitrogen atoms and a decrease in the p-character of their lone electron pairs, which is virtually equivalent to a decrease in basicity (see Table 6).[25] Nevertheless, all these factors are to a certain extent compensated by the $+I$ effect of the CH_2CH_2 fragment.[26]

Reactivity. Earlier studies demonstrated that, in spite of the virtually complete absence of *N*-nucleophilicity, "proton sponge" **1a** possesses high *C*-nucleophilicity and readily reacts with numerous electrophiles.[5,27] For example, the reaction of compound **1a** with dilute HNO_3 in AcOH immediately afforded the 2,4,5,7-tetranitro derivative regardless of the substrate : HNO_3 ratio. Until recently, analogous data on *ortho*-disubstituted "proton sponges" were lacking. However, this problem is of considerable interest due to high basicity of these compounds and the sharply different geometry of their *peri*-dimethylamino groups, which are substantially twisted (by 55—74°) with respect to the naphthalene ring (see Table 6). These facts should lead to a decrease in the activity of compounds of types **1b** and **1c** in electrophilic substitution reactions, even despite the presence of additional activating groups. The results of our study on the behavior of compounds **1b** and **1c** in nitration and azo-coupling reactions confirmed this assumption.

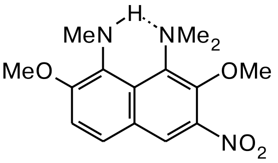
It was found that the reaction of 2,7-dimethoxy derivative **1b** with one equivalent of HNO_3 (d = 1.41) in concentrated H_2SO_4 (20 °C, 45 min) afforded only traces of 3-nitro derivative **16**. The yield of the latter was increased to 81% in the presence of four equivalents of HNO_3. This is the first example of the *meta* substitution with respect to the NMe_2 groups in a series of naphthalene "proton sponges" devoid of substituents in the *peri* positions (*cf.* lit. data[28]). This fact is quite understandable. In an acidic medium, compound **1b** occurs completely in the cationic form due to its high basicity. In this cation, the charged dimethylamino groups cannot activate the *ortho* and *para* positions of the ring due to which the direction of the attack of the electrophile is determined by the methoxy groups.



16

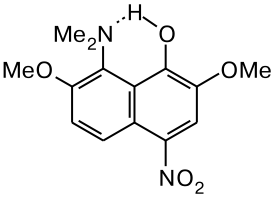


17



18

Interestingly, this reaction at 0 °C afforded dinitro derivative **17** as virtually the only product, although in a low yield (~18%). Apparently, the transformation **16** → **17** proceeds through demethylated intermediate **18**, in which the methylamino group is efficiently conjugated with the naphthalene ring due to the presence of an intramolecular hydrogen bond. As a result, the second nitro group is attached at position 5 (*cf.* lit. data[14]). The remarkable feature of the ^1H NMR spectrum of compound **17** is strong deshielding of the H(4) proton (δ_H 9.51) due to the presence of the adjacent *ortho*- and *peri*-nitro groups.



19

Unlike compound **1a**, compound **1b** is not nitrated by nitronium salts (NO_2BF_4—MeCN and NO_2BF_4—Py—MeCN systems were examined) as well as by HNO_3 in AcOH. It should be noted that the latter reaction performed on heating afforded naphthol **19** in ~3% yield. Its structure was confirmed by ^1H NMR spectroscopy (δ_{OH} 18.6) and mass spectrometry (m/z 292 $[M]^+$).

Compound **1c** appeared to be completely inactive with respect to nitrating agents. Under all the above-mentioned conditions, this compound remained intact. This is consistent with the data on the geometry of base **1c** as well as with the fact that in acidic media this compound forms the trication **F** in which all positions of the naphthalene ring are strongly deactivated. The resistance of tetraamine **1c** to electrophiles (see also below) correlates with the analogous behavior of 1,2-bis(dimethylamino)benzene, which, unlike the 1,3- and 1,4-isomers, does not undergo nitrosation and azo coupling with diazonium salts.[29]

We examined the possibility of the reactions of compounds **1a—c** with diazonium tetrafluoroborates[30] in a neutral medium (MeCN). It was demonstrated for the first time that compound **1a** readily reacts with diazonium salts to form azo dyes (for example, **20**) in 15—55% yields.* By contrast, 2,7-disubstituted naphthalenes **1b,c**, like their tetrafluoroborates, are inert to the diazonium cations under study both at room temperature and on heating to 60—80 °C.

This fact can be used for synthetic purposes. It is known[5] that in some cases, acid HX eliminated in electrophilic substitution reactions of "proton sponge" **1a** is trapped by the starting substrate, thus removing one-half of the compound from the reaction. This trapping occurs also in the azo-coupling reaction of diamine **1a** with diazonium tetrafluoroborates due to which a two-fold excess of the substrate is required. We demonstrated that in the reaction of one equivalent of the diazonium salt with an equimolar mixture of compounds **1a** and **1b** (or **1c**), "proton sponges" **1b,c** only trap a proton, whereas 1,8-bis(dimethylamino)naphthalene (**1a**) is completely transformed into an azo dye. One of examples is illustrated in Scheme 5.

Compound **20** is easily separated from the salt $\mathbf{1b} \cdot HBF_4$ with diethyl ether, and base **1b** can be regenerated and used repeatedly.

Evidently, the introduction of *ortho* substituents into molecule **1a** substantially passivates the naphthalene system with respect to electrophiles, due to which many reactions are either hindered or do not proceed at all. Only 2,7-dimethoxy derivative **1b** was successively subjected to nitration, which proceeded with an anoma-

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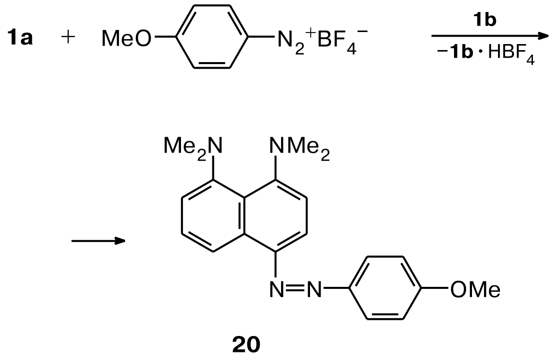
* The results of detailed investigation of this problem will be published elsewhere.

Scheme 5



lous orientation and was accompanied by oxidative demethylation.

* * *

To summarize, we developed convenient preparative procedures for the synthesis of both new (**1e**, **3b,c**, and **14**) and previously known (**1b,c,d**) *ortho*-disubstituted "proton sponges." The characteristic features of their protonation and the dependence of the basicity on the structural factors were revealed. It was demonstrated that these compounds tend to act as strong bases rather than to be subjected to the electrophilic attack. As a resut, *ortho*-disubstituted "proton sponges" are more convenient auxiliary reagents in organic synthesis compared to parent compound **1a** in reactions, which require the use of a strong but low-nucleophilic base.[31—33]

Experimental

The ^{1}H NMR spectra were recorded on Bruker DPX-250 (250 MHz) and Varian Unity-300 (300 MHz) instruments with $SiMe_4$ as the internal standard. The UV spectra were measured on a Varian Cary 100 spectrophotometer in 96% EtOH. The IR spectra were recorded on a Specord IR-75 spectrometer in Nujol mulls. The mass spectra were obtained on a Perkin—Elmer PE-5MS RX instrument. Chromatography was carried out on silica gel L (40—100 μm; Chemapol). The course of the reactions and the purities of the reaction products were monitored by TLC on Al_2O_3 and Silufol plates; visualization was carried out with iodine vapor. The melting points were measured in sealed capillaries and are uncorrected. Commercial 5% Pd/C (Lancaster) and 1,8-bis(dimethylamino)naphthalene (**1a**, Aldrich) were used.

The basicities of amines **1d,e**, **3b**,**c**, and **14** were measured by the competitive method using ^{1}H NMR spectroscopy in DMSO-d$_6$; the concentration of each compound was $4.10 \cdot 10^{-2}$ mol L^{-1}; "proton sponges" **1b** and **1c** were used as the reference compounds. The results of measurements (the first ionization constants characterizing the neutral base $\rightleftharpoons$ monocation equilibrium) are given in Table 5. The constants pK_a of compounds **1c** and **1d** were refined in the present study. Since acenaphthene **3b** containing free *o*-amino groups is readily oxidized in solution, its pK_a was estimated with a low accuracy.

Table 7. Crystallographic data and details of X-ray diffraction study of compound **3c**

Parameter	Characteristic
Molecular formula	$C_{20}H_{30}N_4$
Molecular weight	326.48
T/K	120(2)
λ/Å	0.71073
Diffractometer	«Bruker SMART 1000 CCD»
Crystal dimensions/mm	0.35×0.40×0.60
Space group	Monoclinic, $P2(1)/n$
a/Å	10.626(5)
b/Å	26.575(13)
c/Å	13.527(6)
β/deg	98.600(10)
V/Å^3	3777(3)
Z	8
d_{calc}/g cm^{-3}	1.148
μ/mm^{-1}	0.069
F(000)	1424
θ_{max}/deg	2.08—27.87
Number of measured reflections	28191
Number of independent reflections (R_{int})	8952 (0.1951)
R factors for all reflections	
R_1	0.2191
wR_2	0.2076
GOOF	0.821

Orange crystals of tetraamine **3c** suitable for X-ray diffraction analysis were grown by concentraing its saturated solution in *n*-hexane under isothermal conditions at +5 °C. The crystallographic characteristics and main details of X-ray diffraction study are given in Table 7. The atomic coordinates, bond lengths, bond angles, and torsion angles for the structure of **3c** were deposited with the Cambridge Structural Database (CCDC 216764).

Compounds **4** and **5** were synthesized according to procedures described earlier.[34,35]

4,7-Diamino-5,6-bis(dimethylamino)acenaphthene (3b). A suspension of dinitroacenaphthene **3a** (see Ref. 14) (0.1 g, 0.3 mmol) in MeOH (80 mL) was hydrogenated in the presence of 5% Pd/C (0.025 g). After separation of the catalyst and removal of MeOH under a stream of argon, diamine **3b** was prepared in a yield of 0.081 g (~100%) as pale-gray crystals, which turned dark on storage in air, m.p. 172—174 °C (from 96% EtOH). Found (%): C, 71.22; H, 8.03. $C_{16}H_{22}N_4$. Calculated (%): C, 71.08; H, 8.20. IR, ν/cm^{-1}: 3450, 3360 (br., NH_2). ^{1}H NMR ($CDCl_3$), δ: 2.92 (s, 12 H, NMe_2); 3.14 (s, 4 H, CH_2CH_2); 3.90 (br.s, 4 H, NH_2); 6.54 (s, 2 H, H_{arom}). **Perchlorate 3b · HClO$_4$**, colorless needle-like crystals (from MeOH), which turned dark on storage in sunlight or air; the compound does not melt up to 300 °C, gradually turns black, and decomposes. IR, ν/cm^{-1}: 3492, 3395, 3240, 1630 (NH_2); 1100 (ClO_4^-).

Perchlorate 15 was prepared from compound **3a** according to a known procedure[19] as pale-cream-colored crystals, m.p. 214—215 °C (with decomp., from MeCN). Found (%): C, 44.60; H, 4.32; Cl, 8.41. $C_{16}H_{19}ClN_4O_8$. Calculated (%): C, 44.61; H, 4.45; Cl, 8.23.

2,7-Di(*p*-toluenesulfonamido)naphthalene (6) was synthesized by catalytic hydrogenation of dinitronaphthalene **5** (*cf.* lit. data[36]) followed by tosylation of 2,7-diaminonaphthalene.[37] Compound **6** was prepared as greenish needle-like crystals, m.p. ~190 °C (from 50% EtOH; *cf.* lit. data[37]: 198 °C). IR, ν/cm^{-1}: 3260, 1650 (NH); 1600, 1525 (ring). ^{1}H NMR (DMSO-d$_6$), δ: 2.28 (s, 6 H, Me); 7.16 (dd, 2 H, H(3), H(6)); 7.31, 7.34, 7.65, and 7.70 (all d, 4 H, 2 H, 2 H and 4 H, H(3´), H(1), H(8), H(4), H(5), H(2´)); 10.51 (s, 2 H, NH); $J_{1,3}$ = 1.9 Hz, $J_{3,4}$ = 8.9 Hz, $J_{2´,3´}$ = 8.2 Hz.

2,7-Diamino-1,8-dinitronaphthalene (7). A solution 70% HNO_3 (6.22 mL, 97 mmol) was added dropwise with vigorous stirring to a solution of disulfonamide **6** (3.11 g, 6.7 mmol) in AcOH (30 mL) at a temperature of no higher than 30 °C for 10 min. After 10—15 min, crystals began to precipitate. The suspension was stirred for 12 h and then poured into water (200 mL). The orange-brown precipitate that formed was washed with water and dried in air at 120 °C to prepare a dinitro derivative, which was dissolved in cold concentrated H_2SO_4 (45 mL) and kept at ≈20 °C for 16 h. Then the resulting dark solution was poured into ice water (450 g), which gave rise to a precipitate of compound **7**. The latter was separated, washed with water, and dried in air at 120 °C. Small orange-red crystals were prepared in a yield of 1.46 g (88%), m.p. 282 °C (decomp., from acetone; *cf.* lit. data[18]: t.decomp. 302 °C). IR, ν/cm^{-1}: 3480, 3395, 3375, 1625 (NH_2); 1530, 1350 (NO_2). ^{1}H NMR (DMSO-d$_6$), δ: 6.94 (d, 2 H, H(3), H(6)); 7.40 (br.s, 4 H, NH_2); 7.65 (d, 2 H, H(4), H(5)); $J_{3,4}$ = 8.9 Hz.

2,7-Bis(methylamino)-1,8-dinitronaphthalene (8). A mixture of diamine **7** (0.248 g, 1 mmol), K_2CO_3 (0.690 g, 5 mmol), DMF (8 mL), and MeI (2.5 mL, 40 mmol) was refluxed for 30 h and diluted with water (150 mL). The reaction products were extracted with 1,2-dichloroethane (DCE) (3×10 mL). After removal of the solvent and traces of DMF *in vacuo*, the residue was dissolved in a minimum amount of DCE and purified by chromatography on silica gel (DCE). The main dark-orange fraction was collected. Methylamino derivative **8** was prepared in a yield of 0.055 g (20%) as red prismatic crystals, m.p. 265—266 °C (decomp., from $CHCl_3$ or DCE); a powder of **8** is orange in color. Found (%): C, 52.29; H, 4.15. $C_{12}H_{12}N_4O_4$. Calculated (%): C, 52.17; H, 4.38. IR, ν/cm^{-1}: 3360 (NH); 1540, 1350 (NO_2). ^{1}H NMR ($CDCl_3$), δ: 3.07 (d, 6 H, Me); 6.83 and 7.60 (both d, 2 H each, H(3), H(6), H(4), H(5)); 7.99 (br.s, 2 H, NH); $J_{NH,NMe}$ = 5.1 Hz, $J_{3,4}$ = 9.1 Hz.

2,7-Dimethoxy-1,8-dinitronaphthalene (11) was prepared according to a procedure described in the literature.[38] Red-brown crystals, t.decomp. 270 °C (from Py) (*cf.* lit. data[38]: 286 °C); m.p. 235—245 °C reported in the study[12] is, apparently, erroneous. ^{1}H NMR (DMSO-d$_6$), δ: 4.05 (s, 6 H, OMe); 7.67 and 8.33 (both d, 2 H each, H(3), H(6), H(4), H(5)); $J_{3,4}$ = 9.3 Hz.

2,7-Bis(dimethylamino)-1,8-dinitronaphthalene (12a) was synthesized according to a known procedure[3] (see Table 1, run *2*) in 84% yield. The properties of compound **12a** are identical to those published in the literature.[3] ^{1}H NMR ($CDCl_3$), δ: 2.96 (s, 12 H, NMe_2); 7.19 and 7.66 (both d, 2 H each, H(3), H(6), H(4), H(5)); $J_{3,4}$ = 9.0 Hz.

7-Dimethylamino-2-methoxy-1,8-dinitronaphthalene (13) (see Table 1, run *1*) was prepared analogously to compound **12a**, the reaction time being decreased from 3 days to 3 h. Red platelet-like crystals, m.p. 223—224 °C (from acetone). Found (%): C, 53.55; H, 4.54. $C_{13}H_{13}N_3O_5$. Calculated (%): C, 53.61; H, 4.50. ^{1}H NMR ($CDCl_3$), δ: 2.98 (s, 6 H, NMe_2); 3.98 (s, 3 H, OMe); 7.16, 7.21, 7.72, and 7.82 (all d, 1 H each, H(6), H(3), H(4), H(5)); $J_{3,4}$ = 9.2 Hz, $J_{5,6}$ = 9.0 Hz.

2,7-Dipiperidino-1,8-dinitronaphthalene (12c) (see Table 1, run *4*). A solution of dinitronaphthalene **11** (0.278 g, 1 mmol) and piperidine (2 mL, 20 mmol) in DMF (5 mL) was kept in the dark for one week. Then the solution was poured into water (50 mL). The precipitate was separated, washed with water, dried in air, and purified by chromatography on silica gel ($CHCl_3$). The main orange zone was collected. The solvent was removed. The oily residue was triturated with *n*-pentane to prepare yellow-orange crystals in a yield of 0.123 g (32%), m.p. 183—184 °C (from acetone or MeOH). Found (%): C, 62.32; H, 6.17. $C_{20}H_{24}N_4O_4$. Calculated (%): C, 62.49; H, 6.29. ^{1}H NMR (DMSO-d$_6$), δ: 1.56 (m, 12 H, H(3´), H(4´), H(5´)); 3.01 (m, 8 H, H(2´), H(6´)); 7.66 and 8.18 (both d, 2 H each, H(3), H(6), H(4), H(5)); $J_{3,4}$ = 9.0 Hz.

1,8-Bis(dimethylamino)-2,7-dimethoxynaphthalene (1b). A mixture of dinitronaphthalene **11** (1.39 g, 5 mmol), MeOH (60 mL), and Pd/C (0.4 g) was hydrogenated until the calculated amount of hydrogen was absorbed. The catalyst was filtered off and the methanol was removed on a rotary evaporator under a stream of argon. Dimethyl sulfate (3.79 mL, 40 mmol), $Na_2CO_3 \cdot 10H_2O$ (11.44 g, 40 mmol), and water (30 mL) were added to the residue of **1,8-diamino-2,7-dimethoxynaphthalene**. The suspension was vigorously stirred under argon at 20 °C for 5 h and then extracted with benzene (25 mL). The extract, which contained oxidation products and resins, was discarded. Potassium hydroxide (10 g) was added with cooling and stirring to the aqueous phase. After dissolution of KOH, the reaction product was extracted with benzene (5×25 mL). The organic phase was dried with anhydrous K_2CO_3 and then 60% aqueous HBF_4 (0.575 mL, 5 mmol)* was added. The reaction mixture was vigorously stirred for 1 h to prepare a precipitate of **1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene tetrafluoroborate (1b·HBF$_4$)** (1.27 g, 70%), which was separated, washed with Et_2O, and crystallized from aqueous EtOH or water. Pale-gray needle-like crystals were obtained, m.p. 228 °C (*cf.* lit. data[2]: 227—230 °C). ^{1}H NMR (CD_3CN), δ: 3.19 (d, 12 H, NMe_2); 4.07 (s, 6 H, OMe); 7.41 and 7.96 (both d, 2 H each, H(3), H(6), H(4), H(5)); 19.61 (m, 1 H, NH); $J_{NH,NMe}$ = 2.6 Hz, $J_{3,4}$ = 9.3 Hz. Free base **1b** was prepared as follows. The required amount of tetrafluoroborate (100—250 mg) was dissolved in a minimum volume of MeCN. The resulting solution was shaken with 35% aqueous KOH (10 mL) and compound **1b** was extracted with *n*-hexane (5×10 mL). Compound **1b** with m.p. 68 °C was prepared in nearly quantitative yield. The properties of **1b** are identical to those of the sample described in the literature.[2]

Compounds **1c,d,e**, **3c**, and **14** and their tetrafluoroborates were synthesized analogously.

1,2,7,8-Tetrakis(dimethylamino)naphthalene (1c), pale-yellow needle-like crystals, m.p. 78—80 °C (from MeOH) (*cf.* lit. data[3]: 78—80 °C); does not decompose up to 250 °C. The yield

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* In the synthesis of "proton sponges" **1c,d,e**, **3c**, and **14**, which contain the β-amino groups and, hence, can form bis(tetrafluoroborates) (see the text), this amount was doubled.

from compound **12a** was 57%; the yield from compound **8** was 33%. **Tetrafluoroborate 1c · HBF$_4$**, colorless platelet-like crystals, m.p. 255—257 °C (decomp., from water) (*cf.* lit. data[3]: 254—256 °C).

1,8-Bis(dimethylamino)-2,7-dipyrrolidinonaphthalene (1d), pale-cream-colored needle-like crystals, m.p. 109—111 °C (from Et_2O). The yield from compound **12b** was 48%. Found (%): C, 75.02; H, 9.09. $C_{22}H_{32}N_4$. Calculated (%): C, 74.96; H, 9.15. ^{1}H NMR ($CDCl_3$), δ: 1.92 (m, 8 H, H(3´), H(4´)); 2.90 (s, 12 H, NMe_2); 3.04 (m, 8 H, H(2´), H(5´)); 7.12 and 7.38 (both d, 2 H each, H(3), H(6), H(4), H(5)); $J_{3,4}$ = 8.5 Hz. **Tetrafluoroborate 1d · HBF$_4$**, colorless crystals, m.p. 204—206 °C (decomp., from water). ^{1}H NMR (CD_3CN), δ: 2.07 and 3.12 (both m, 8 H each, H(3´), H(4´), H(2´), H(5´)); 3.27 (d, 12 H, NMe_2); 7.72 and 8.02 (both d, 2 H each, H(3), H(6), H(4), H(5)); 20.09 (br. m, 1 H, NH); $J_{NH,NMe}$ = 2.6 Hz, $J_{3,4}$ = 9.0 Hz.

1,8-Bis(dimethylamino)-2,7-di(piperidino)naphthalene (1e), pale-yellow rhombic crystals, without well-defined m.p. (138—147 °C, from *n*-pentane). The yield from compound **12c** was 39%. Found (%): C, 75.67; H, 9.60. $C_{24}H_{36}N_4$. Calculated (%): C, 75.74; H, 9.54. ^{1}H NMR ($CDCl_3$), δ: 1.56 (m, 4 H, H(4´)); 1.73 (m, 8 H, H(3´), H(5´)); 2.79 (m, 8 H, H(2´), H(6´)); 2.96 (s, 12 H, NMe_2); 7.23 and 7.41 (both d, 2 H each, H(3), H(6), H(4), H(5)); $J_{3,4}$ = 8.7 Hz. **Tetrafluoroborate 1e · HBF$_4$**, colorless needle-like crystals, m.p. 245—246 °C (decomp., from water). ^{1}H NMR (CD_3CN), δ: 1.49, 1.80, and 2.91 (all m, 4 H, 8 H, 8 H, H(4´), H(3´), H(5´), H(2´), H(6´)); 3.30 (d, 12 H, NMe_2); 7.74 and 8.02 (both d, 2 H each, H(3), H(6), H(4), H(5)); 20.11 (br.m, 1 H, NH); $J_{NH,NMe}$ = 2.5 Hz, $J_{3,4}$ = 8.9 Hz.

4,5,6,7-Tetrakis(dimethylamino)acenaphthene (3c), yellow-brown platelet-like crystals, m.p. 123—124 °C (from *n*-hexane). The yield from compound **3a** was 63%. Found (%): C, 73.65; H, 9.33. $C_{20}H_{30}N_4$. Calculated (%): C, 73.58; H, 9.26. ^{1}H NMR ($CDCl_3$), δ: 2.66 (s, 12 H, 4,7-NMe_2); 2.93 (s, 12 H, 5,6-NMe_2); 3.22 (s, 4 H, CH_2CH_2); 7.02 (s, 2 H, H_{arom}). **Tetrafluoroborate 3c · HBF$_4$**, pale-cream-colored needle-like crystals, m.p. 241—242.5 °C (decomp., from water). ^{1}H NMR (CD_3CN), δ: 2.74 (s, 12 H, 4,7-NMe_2); 3.28 (d, 12 H, 5,6-NMe_2); 3.42 (s, 4 H, CH_2CH_2); 7.58 (s, 2 H, H_{arom}); 18.80 (br.s, 1 H, NH); $J_{NH,NMe}$ = 2.6 Hz.

1,7,8-Tris(dimethylamino)-2-methoxynaphthalene (14), pale-yellow crystals, m.p. 47—48.5 °C (from *n*-pentane). The yield from compound **13** was 61%. Found (%): C, 71.18; H, 8.65. $C_{17}H_{25}N_3O$. Calculated (%): C, 71.04; H, 8.77. ^{1}H NMR ($CDCl_3$; the assignment was made by comparing with the spectra of compounds **1b,c**), δ: 2.68 (s, 6 H, 7-NMe_2); 2.90 (s, 6 H, 1-NMe_2); 2.94 (s, 6 H, 8-NMe_2); 3.87 (s, 3 H, OMe); 7.06, 7.13, 7.40, and 7.46 (all d, 1 H each, H(3), H(6), H(5), H(4)); $J_{3,4}$ = 9.0 Hz, $J_{5,6}$ = 8.7 Hz. **Tetrafluoroborate 14 · HBF$_4$**, colorless needles, m.p. 158—159.5 °C (from water). ^{1}H NMR (CD_3CN), δ: 2.74 (s, 6 H, 7-NMe_2); 3.17 (d, 6 H, 1-NMe_2); 3.33 (d, 6 H, 8-NMe_2); 4.09 (s, 3 H, OMe); 7.56, 7.62, 8.01, and 8.02 (all d, 1 H each, H(3), H(6), H(5), H(4)); 19.78 (br.s, 1 H, NH); $J_{NH,1\text{-}NMe}$ = 2.1 Hz, $J_{NH,8\text{-}NMe}$ = 3.0 Hz, $J_{3,4}$ = 9.2 Hz, $J_{5,6}$ = 8.9 Hz.

Compounds **1c** and **3c** and their analogs can be additionally purified by vacuum sublimation (100 °C, 0.2 Torr)[2] or elution with Et_2O through a small layer of deactivated Al_2O_3 (main fractions).

1,8-Bis(dimethylamino)-2,7-dimethoxy-3-nitronaphthalene (16). A solution of 70% HNO_3 (0.126 mL, 2.0 mmol) in concentrated H_2SO_4 (5 mL) cooled to 0 °C was added with stirring to a solution of compound **1b** (0.137 g, 0.5 mmol) in concentrated H_2SO_4 (10 mL) cooled to 0 °C. The reaction solution immediately turned dark-red. Then cooling was stopped and the reaction mixture was kept at 20 °C for 45 min, after which the solution was poured onto ice (200 g), neutralized with concentrated NH_3 until a steady ammonia odor appeared, and extracted with $CHCl_3$ (5×5 mL). The extract was concentrated to a minimum volume and the residue was purified by chromatography on a column with Al_2O_3 ($CHCl_3$ as the eluent), the brown fraction with R_f 0.46 being collected. Nitronaphthalene **16** was obtained in a yield of 0.129 g (81%) as small brown crystals, m.p. 118—120 °C (from MeOH—H_2O, 1 : 1). Found (%): C, 60.01; H, 6.75. $C_{16}H_{21}N_3O_4$. Calculated (%): C, 60.17; H, 6.63. UV, λ_{max}/nm (logε): 240 (4.62), 303 (4.14), 415 sh (3.59), absorption tail to 560 nm. ^{1}H NMR ($CDCl_3$), δ: 2.93 and 2.97 (both s, 6 H each, 1- and 8-NMe_2); 3.83 and 3.95 (both s, 3 H each, 2- and 7-OMe); 7.22 (d, 1 H, H(6)); 7.35 (d, 1 H, H(5)); 8.20 (s, 1 H, H(4)); $J_{5,6}$ = 8.8 Hz.

1-Dimethylamino-2,7-dimethoxy-8-methylamino-3,5-dinitronaphthalene (17) was prepared and isolated as described above but the starting dark-red solution was kept at 0 °C for 30 min. Compound **17** was obtained as dark-claret needle-like crystals in a yield of 0.030 g (18%), m.p. 172—174 °C (from MeOH), R_f 0.49 (Al_2O_3—$CHCl_3$). Found (%): C, 51.58; H, 5.15. $C_{15}H_{18}N_4O_6$. Calculated (%): C, 51.42; H, 5.18. UV, λ_{max}/nm (logε): 280 (4.74), 323 sh (4.51), 417 (4.46), 503 (4.79). IR, ν/cm^{-1}: 3120 (NH); 1600, 1560, 1525, 1500 (ring). ^{1}H NMR ($CDCl_3$), δ: 2.91 (s, 6 H, 1-NMe_2); 3.30 (d, 3 H, 8-NMe); 3.86 and 3.90 (both s, 3 H each, 2- and 7-OMe); 8.21 and 9.51 (both s, 1 H each, H(6) and H(4)); 11.33 (br.s, 1 H, NH).

8-Dimethylamino-2,7-dimethoxy-4-nitronaphthalen-1-ol (19). A 70% HNO_3 solution (0.252 mL, 4.0 mmol) was added with stirring to a solution of compound **1b** (0.274 g, 1.0 mmol) in AcOH (20 mL). The reaction mixture was stirred at 50 °C for 2 h, poured into H_2O (100 mL), neutralized with 20% NaOH to pH 7, and extracted with $CHCl_3$ (5×5 mL). After removal of the solvent, the residue was chromatographed on Al_2O_3 ($CHCl_3$ as the eluent), and the orange fraction with R_f 0.41 was collected. Naphthol **19** was obtained in a yield of 0.005 g (2.5%) as orange-brown crystals, m.p. 146—147 °C (from MeOH). Found (%): C, 57.69; H, 5.25. $C_{14}H_{16}N_2O_5$. Calculated (%): C, 57.53; H, 5.52. UV, λ_{max}/nm (logε): 241 (4.13), 436 (3.68). IR, ν/cm^{-1}: 2720, 1570, 1525, 1485, strong absorption in the region lower than 650 cm^{-1} with the center at 500 cm^{-1}. ^{1}H NMR ($CDCl_3$), δ: 3.00 (d, 6 H, 8-NMe_2); 4.01 and 4.02 (both s, 3 H each, 2- and 7-OMe); 7.33 (d, 1 H, H(6)); 8.24 (s, 1 H, H(3)); 8.94 (d, 1 H, H(5)); 18.58 (br.s, 1 H, OH); $J_{OH,NMe}$ = 1.2 Hz, $J_{5,6}$ = 10.0 Hz. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 293 $[M + 1]^+$ (11), 292 $[M]^+$ (100), 277 $[M - Me]^+$ (67), 262 $[M - 2\ Me]^+$ (31), 260 $[M - Me - OH]^+$ (34), 231 (29), 188 (24), 144 (26), 115 (24), 102 (22).

4,5-Bis(dimethylamino)-1-(4-methoxyphenylazo)naphthalene (20). A solution of *p*-methoxyphenyldiazonium tetrafluoroborate[30] (0.022 g, 0.1 mmol) in anhydrous MeCN (0.6 mL) was added in one portion to a solution of "proton sponge" **1a** (0.021 g, 0.1 mmol) and compound **1b** (0.027 g, 0.1 mmol) in anhydrous MeCN (0.6 mL) at 0 °C. The solution immediately turned dark-red. The reaction mixture was kept at 0 °C for 1 h, the solvent was removed, and the residue was treated with Et_2O (2×2 mL). After removal of Et_2O and crystallization of the residue from MeOH, azo dye **20** was prepared in a yield of 0.031 g (89%) as black-claret crystals, m.p. 115—117 °C. Found (%): C, 72.14; H, 7.08. $C_{21}H_{24}N_4O$. Calculated (%): C, 72.39; H, 6.94. UV, λ_{max}/nm (logε): 283 (4.16), 482 (4.22), absorption tail up to 595 nm. ^1H NMR ($CDCl_3$), δ: 2.80 and 2.91 (both s, 6 H each, 4- and 5-NMe_2); 3.88 (s, 3 H, OMe); 7.00 (m, 4 H, H(3), H(3´), H(5´), H(6)); 7.44 (br.t, 1 H, H(7)); 7.77 (d, 1 H, H(2)); 7.95 (d, 2 H, H(2´), H(6´)); 8.58 (br.d, 1 H, H(8)); $J_{2,3}$ = 8.5 Hz, $J_{2´,3´}$ = 8.9 Hz, $J_{7,8}$ = 7.8 Hz. A gray crystalline precipitate was washed with diethyl ether to prepare tetrafluoroborate of compound **1b** (0.035 g, 97%), from which free amine **1b** can be isolated as described above.

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