peri-Naphthylenediamines.
28.* Nitration of 1,8-bis(dimethylamino)naphthalene and 5,6-bis(dimethylamino)acenaphthene in neutral and weakly acidic media. The first case of isolation of *o*-nitro and *o,o'*-dinitro derivatives of "proton sponges"

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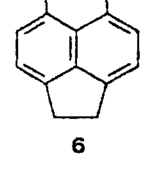
o-Nitro and *o,o'*-dinitro derivatives of 1,8-bis(dimethylamino)naphthalene and its acenaphthene analog were prepared for the first time by direct nitration with nitrogen dioxide or tetranitromethane. When 5,6-bis(dimethylamino)acenaphthene was treated with nitric acid in AcOH or MeCN or with nitronium tetrafluoroborate in MeCN, nitration was accompanied by partial demethylation of one of the NMe_2 groups.

Key words: 1,8-bis(dimethylamino)naphthalene, 5,6-bis(dimethylamino)acenaphthene, "proton sponge," nitronium tetrafluoroborate, tetranitromethane, nitration, *N*-demethylation, basicity.

Theoretically, the extremely high basicity of 1,8-bis(dimethylamino)naphthalene ("proton sponge," **1**, pK_a = 12.1, H_2O, 25 °C)[2] and, particularly, of its 2,7-dialkoxy derivatives **2** (pK_a ~16.1, DMSO : H_2O = 3 : 2, 25 °C)[3,4] should be even higher in the case of compounds containing *ortho*-dialkylamino groups. The previously unknown nitro derivatives, *viz*., 1,8-bis(dimethylamino)-2-nitronaphthalene (**3**) and 1,8-bis(dimethylamino)-2,7-dinitronaphthalene (**4**), could serve as their synthetic precursors.

Because of the peculiarities of the molecular structure of compound **1**, positions 2 and 7 in its molecule are substantially shielded by the methyl groups.[5] However, using chlorination with *N*-chlorobenzotriazole[6] and bromination with *N*-bromosuccinimide[7] as examples, we have recently demonstrated that regioselective *ortho*-substitution in 1,8-bis(dimethylamino)naphthalene can, in principle, occur. This gave promise that *ortho*-nitro derivatives **3** and **4** could be prepared. In previous studies[8,9] of nitration of diamine **1**, seven out of nine possible products of its nitration (**5a—g**; taking into account that the electrophilic substitution in this series never proceeds at *meta* positions[10]) were isolated. As part of continuing studies, in the present work we report the synthesis and properties of both missing *ortho*-isomers **3** and **4**. In addition, we performed *ortho*-nitration of 5,6-bis(dimethylamino)acenaphthene (**6**), whose reactivity has not been studied previously. To prevent deactivation of the *ortho* positions due to conversions of compounds **1** and **6** into protonated forms, all experiments associated with nitration were carried out in neutral or weakly acidic conditions.



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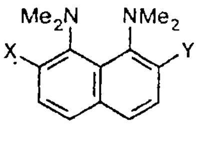
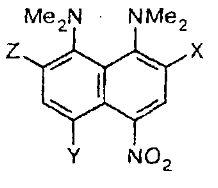


1—4

1: X = Y = H
2: X = Y = OMe, OEt
3: X = H, Y = NO_2
4: X = Y = NO_2



5a—g

5a: X = Y = Z = H
5b: X = Z = H, Y = NO_2
5c: Y = Z = H, X = NO_2
5d: X = Y = H, Z = NO_2
5e: Z = H, X = Y = NO_2
5f: Y = H, X = Z = NO_2
5g: X = Y = Z = NO_2

Previously, it has been demonstrated[9] that the reaction of compound **1** with nitrogen dioxide in $CHCl_3$ afforded a broad spectrum of nitro products. However, derivatives **3** and **4** were absent among these products. One would expect that nitration of diamine **1** in CCl_4, which involves substitution proceeding predominantly according to a radical mechanism,[11,12] would proceed even less selectively to form *ortho*-nitro derivatives **3** and **4** along with other nitration products. Actually, we succeeded in obtaining for the first time 1,8-bis(dimethylamino)-2-nitronaphthalene (**3**) in 9% yield along with nitro derivatives **5a—f** (which are generally formed) upon nitration of compound **1** with one equiva-

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* For Part 27, see Ref. 1.

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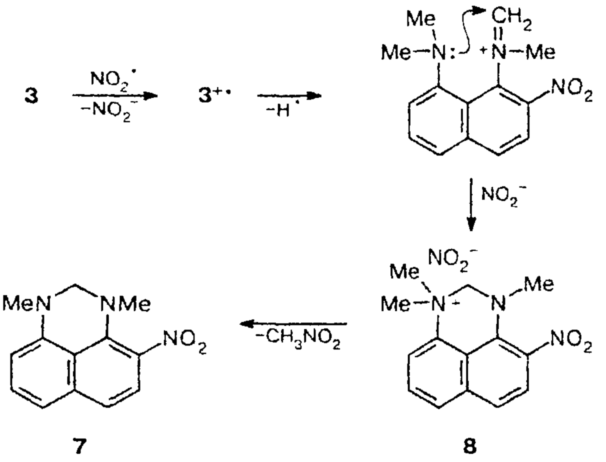
lent of NO_2 in CCl_4, whereas nitration with the use of two equivalents of NO_2 afforded 1,8-bis(dimethylamino)-2,7-dinitronaphthalene (**4**) (1%). As expected, a decrease in the selectivity of the reaction in CCl_4 was accompanied by a decrease in the total yield of nitration products by a factor of 1.5—2 due to substantial resinification (it is known[13] that CCl_4 is a stronger oxidizing agent than $CHCl_3$).

When nitration was performed in dichloroethane, the yield of *ortho*-dinitro derivative **4** increased to 2%. Further variations in the temperature (from −30 to +10 °C), concentration, and reaction time (10 min—6 h) as well as the use of different solvents (CH_2Cl_2 or MeCN) did not enhance the yield, which indicates that *ortho*-dinitration of 1,8-bis(dimethylamino)naphthalene (**1**) is extremely difficult.

It should be noted that nitration of compound **1** with nitrogen dioxide (1 equiv.) in dichloroethane or CH_2Cl_2 afforded the previously unknown 2,3-dihydro-1,3-dimethyl-4-nitroperimidine (**7**) (the yield was ≤1%) (Scheme 1). Analogous reactions have been observed previously for compound **1** [14] and 1,4,5,8-tetrakis(dimethylamino)naphthalene[15] under the action of particular transition metal complexes and iodine, respectively. Apparently, the process occurs according to Scheme 1, involving demethylation of intermediate 2,3-dihydroperimidinium quaternary salt **8** (see Ref. 16).

Scheme 1



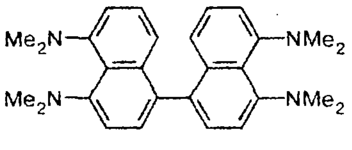
It is not inconceivable that compound **7** is also formed in other reactions with the participation of nitrogen dioxide. However, compound **7** often cannot be isolated due to a low yield and the tendency of dihydroperimidines to oxidize.

It is known[17,18] that in some cases tetranitromethane (TNM) can serve as a convenient nitrating agent for activated aromatic compounds. For example, its reaction with *N,N*-dimethyl-*p*-toluidine afforded *N,N*-dimethyl-2-nitro-*p*-toluidine in the cold, whereas this reaction at higher temperatures gave *N*-methyl-*N*-nitroso-*p*-toluidine.[19] Pyridine is commonly used for trapping nitroform that forms. It is believed[17,20] that nitration of *N,N*-dialkylanilines in solutions proceeds according to the ion-radical mechanism with the participation of the charge-transfer complex (CTC) in which the electron transfer occurs. This mechanism of nitration is also typical of TNM.[18]

We performed a series of experiments on nitration of compound **1** with TNM in various solvents (CCl_4, MeCN, dichloroethane, or CH_2Cl_2; the optimum conditions were as follows: 0 °C, reaction time 1 h). The highest yield of compound **3** (15%) was achieved in CCl_4.

A distinguishing feature of nitration of 1,8-bis(dimethylamino)naphthalene (**1**) with the TNM/CCl_4 system is the formation of a brown precipitate, which was gradually transformed into soluble nitro products. We believe that this precipitate is actually a molecular complex of the substrate with TNM (it is known that compound **1** can form charge-transfer complexes even with weak π-acceptors[21]). Its formation accounts for the very low yield (of about 6%) of 2,7-dinitro derivative **4** (≤1%) and other dinitro compounds as well as for the complete absence of tri- and tetranitro derivatives.

Unlike NO_2 and TNM, nitronium tetrafluoroborate reacted with 1,8-bis(dimethylamino)naphthalene to give only compounds **5a,b,g** (Table 1). Apparently, nitration of compound **1** occurred primarily at positions 4 and 5 due to greater steric requirements (the NO_2^+ cation is linear, whereas the $NO_2^•$ radical has an angular structure). Interestingly, binaphthyl **9** is lacking among the reaction products. Small amounts of compound **9** (as evidence of radical processes) are always formed under the action of nitrogen dioxide, nitric acid, or even a nitrating mixture.[9]



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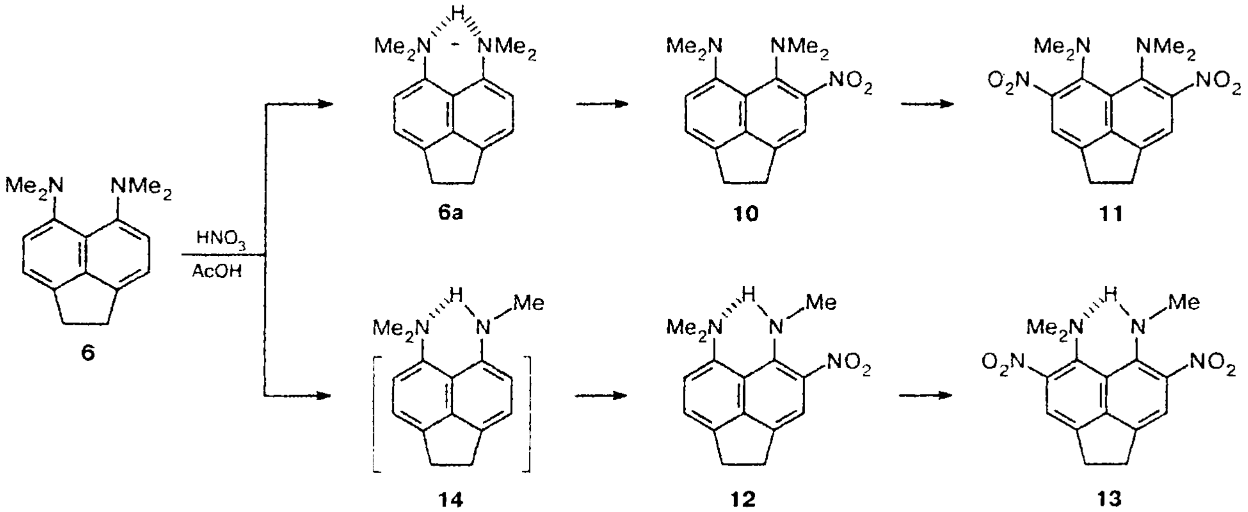
Previously, it has been demonstrated[8] that the reaction of compound **1** with the HNO_3/AcOH system (even when an insufficient amount of nitric acid was

Table 1. Results of nitration of 1,8-bis(dimethylamino)naphthalene (**1**) with nitronium tetrafluoroborate in acetonitrile (20 °C, 20 min)

NO_2BF_4 (equiv.)	Yield of products (%)				
	1	**5a**	**5b**	**5g**	Resin
1	6	58	5	6	25
2	—	25	8	17	50

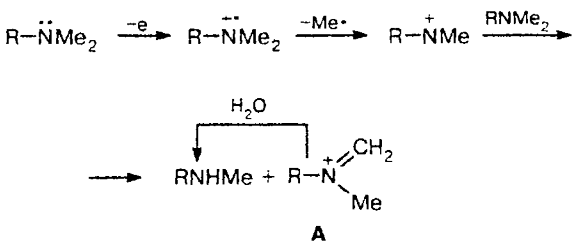
Scheme 2



used) afforded only tetranitro derivative **5g**. It is reasonable to expect that nitration of 5,6-bis(dimethylamino)acenaphthene (**6**) under these or analogous conditions will proceed exclusively at the *ortho* positions with respect to the NMe_2 groups. Actually, the reactions in AcOH afforded di- and mononitro derivatives (**11** and **12**, respectively; 3—12% yields, Table 2) in spite of the fact that mononitro compound **10** (Scheme 2) was detected in none of experiments. In this case, the formation of compound **12** was accompanied by elimination of the methyl group. The maximum yield of dinitroacenaphthene **11** was achieved in MeCN. However, the yield of **11** was only 10—12% (although this value is substantially higher than the yield of compound **4**), while the yield of compound **12** was 78%. In some cases, demethylated *o,o′*-dinitro-substituted derivative **13** was isolated from the reaction mixture in insignificant yields. Apparently, the absence of mononitro derivative **10** among the reaction products is attributable to the fact that nitration of compound **6** proceeds through its protonated form **6a**, whereas subsequent nitration of compound **10** proceeds through the nonprotonated form due to the sharp decrease in its basicity and, consequently, the latter process occurs substantially much more rapidly.

Apparently, demethylation is oxidative in character and proceeds with the participation of radical cation $\mathbf{6}^{+\bullet}$. Unlike radical cation $\mathbf{1}^{+\bullet}$, which reacts at activated and sterically slightly hindered *peri* positions (the reaction with $NO_2^{\bullet}$ to form 4-nitro derivative **5a** or dimerization to binaphthyl **9**), radical cation $\mathbf{6}^{+\bullet}$, whose *peri* positions are occupied, can lose the methyl group to form diamine **14** as an intermediate. In this case, either direct elimination of the CH_3 group (as the cation or radical initiated by a nucleophile or radical, respectively) or hydrolytic cleavage of immonium salt **A** can occur (Scheme 3).

Scheme 3



Apparently, the formation of compound **12** rather than its isomer in which the NHMe group is more remote from the nitro group is attributable to the fact that the NMe_2 group in *N,N′*-trimethyl-substituted *peri*-naphthylenediamines adopts a pyramidal configuration and cannot efficiently interact with the π-system of the ring.[21,22]

It is likely that oxidative destruction accompanied by nitration of compound **6** also proceeds through radical cation $\mathbf{6}^{+\bullet}$, especially, when an excess of nitric acid is used (*cf.* runs 1—4 or 6 and 7 in Table 2).

A sharp decrease in the acidity of the medium (the use of MeCN and NO_2BF_4 in place of AcOH and HNO_3, respectively) made it possible to suppress oxidation and to increase the yield of nitration product **12** to 70—80% (Table 2). The optimum procedure for its preparation involves gradual addition of 2—3 equiv. of a nitrating agent to the substrate.

We succeeded in preventing demethylation and terminating the reaction at the stage of introduction of one

Table 2. The composition of the reaction mixture formed upon nitration of 5,6-bis(dimethylamino)acenaphthene (**6**) with nitric acid (*d* 1.41) or nitronium tetrafluoroborate

Run	Medium	Nitrating agent (equiv.)	Time/min	*T*/°C	Composition of the reaction mixture (%)				
					6	**11**	**12**	**13**	Oxidation products
1	AcOH	HNO_3 (1)[a]	15	80	60	2	6	—	32
2	AcOH	HNO_3 (2)[a]	15	80	30	3	3	traces	64
3	AcOH	HNO_3 (3)[a]	15	80	—	—	12	—	88
4	AcOH	HNO_3 (4)[a]	15	80	—	—	—	—	100
5	MeCN	HNO_3 (1)[b]	5	82	30	10	27	2	31
6	MeCN	HNO_3 (1)[c]	5	82	10	12	29	1	48
7	MeCN	HNO_3 (2)[b]	5	82	10	10	15	5	60
8	MeCN	HNO_3 (2)[c]	5	82	2	4	47	—	47
9	MeCN	HNO_3 (3)[b]	5	82	—	—	60	traces	40
10	MeCN	HNO_3 (3)[c]	5	82	—	—	67	—	33
11	MeCN	HNO_3 (4)[a]	5	82	—	—	—	2	98
12	MeCN	NO_2BF_4 (1)[a]	5	82	35	—	52	4	9
13	MeCN	NO_2BF_4 (2)[a]	5	82	—	—	78	1	21

[a] The result is independent of the rate of addition.

[b] Rapid addition of HNO_3 in the corresponding solvent (faster than 5 s).

[c] An HNO_3 solution was added dropwise over 1 min.

nitro group with the use of TNM as the nitrating agent. Thus, the reaction of 5,6-bis(dimethylamino)acenaphthene with 1 equiv. of $C(NO_2)_4$ in CCl_4 afforded mononitro derivative **10** in 64% yield. However, the use of 2 equiv. of TNM resulted in resinification.

From the preparative viewpoint, it is more convenient to synthesize compound **10** by alkylation of readily accessible trimethyl-substituted compound **12**. Prolonged refluxing of the latter with MeI afforded diamine **10** in a yield of higher than 85%.

All nitro derivatives of compounds **1** and **6** synthesized were obtained as crystalline substances, except for compound **3**, which formed as a red oil. It is worthy of note that the resulting nitro compounds are characterized by rather high chromatographic mobility (Table 3). It can be seen that *ortho*-nitro derivatives **3**, **4**, **10**, and **11** are characterized by the largest R_f values, which makes it possible to readily separate these derivatives from other nitroamines. On the whole, compounds of the acenaphthene series are more mobile than their naphthalene analogs.

Table 3. Chromatographic mobilities (R_f) of nitro compounds **3—5**, **10**, and **11** on Al_2O_3 (III, $CHCl_3$) and silica gel (C_6H_6)

Compound	Positions of nitro groups	Al_2O_3	Silica gel
4	2,7-$(NO_2)_2$	0.95	0.50
3	2-NO_2	0.88	0.25
5a	4-NO_2	0.83	0.17
5d	2,5-$(NO_2)_2$	0.80	0.10
5c	2,4-$(NO_2)_2$	0.64	[a]
5f	2,4,7-$(NO_2)_3$	0.64	[a]
5b	4,5-$(NO_2)_2$	0.33	[a]
5e	2,4,5-$(NO_2)_3$	0.25	[a]
5g	2,4,5,7-$(NO_2)_4$	0.20	[a]
10	4-NO_2	0.85[b]	0.38
11	4,7-$(NO_2)_2$	0.89[b]	0.80

[a] $R_f < 0.10$. [b] Al_2O_3-II.

We estimated the basicities of some of the synthesized nitro compounds by the competitive method using ^1H NMR spectroscopy in DMSO-d_6.[23] The following ionization constants pK_a were obtained: 4.1 (**3**), 3.5 (**5a**),[8] and 5.1 (**10**). Taking into account the fact that the pK_a values for *ortho*- and *para*-nitroanilines in water are −0.26 and 1.11, respectively,[24] the above pK_a values are indicative of the existence of the so-called "supporting effect" (high basicities of *ortho*-substituted "proton sponges") in *ortho*-nitro derivatives **3** and **10**. This effect has also been revealed previously in *ortho*-halogen derivatives,[25] but it is most pronounced in compounds **2**. Unfortunately, *o,o'*-dinitro derivatives **4** and **11** did not undergo protonation in dimethyl sulfoxide (pK_a = 0) even in the presence of an excess of mineral acid, which prevented us from determining their basicities by the concurrent method.

Experimental

The ^1H NMR spectra were recorded on Unity-300 (300 MHz) and Bruker DPX-250 (250 MHz) instruments with Me_4Si as the internal standard. The UV spectra were measured on a Specord M-40 spectrometer. The IR spectra were obtained on a Specord IR-71 spectrometer. Chromatography was carried out on Al_2O_3 (the activity is given in parentheses) and silica gel L 40/100 μm (Chemapol). The melting temperatures were measured on a PTP instrument in sealed tubes and were not corrected. Nitrogen dioxide was dried over $CaCl_2$ and P_2O_5. Tetranitromethane was synthesized according to a procedure reported previously[26] and dried with Na_2SO_4. Nitronium tetrafluoroborate (97% purity, Fluka) was used. The solvents were purified and dried according to standard procedures.

1,8-Bis(dimethylamino)naphthalene was a commercially available reagent (Merck).

Nitration of 1,8-bis(dimethylamino)naphthalene* (1). *A. With nitrogen dioxide (1 equiv.). A solution of NO_2 (46 μL, 1.5 mmol) in dry CCl_4 (10 mL) precooled to 0 °C was added portionwise (over 30 min) with stirring to a solution of compound **1** (320 mg, 1.5 mmol) in dry CCl_4 (30 mL) cooled to 0 °C. The reaction mixture immediately turned dark cherry. The mixture was kept at 0 °C for 4 h. Then the precipitate that formed was filtered off, refluxed with 10% KOH (10 mL) for 1 min, and extracted with benzene (3×4 mL). The extract was passed through a column with Al_2O_3 (III; $CHCl_3$ as the eluent) and the starting compound **1** was recovered in a yield of 0.170 g (45%).

The filtrate was concentrated and compounds **3** and **5a** were isolated from the residue by preparative TLC on silica gel (benzene as the eluent) in yields of 0.034 g (9%) and 0.072 g (19%), respectively.

1,8-Bis(dimethylamino)-2-nitronaphthalene (**3**), a red oil soluble in acids and organic solvents. Found (%): C, 64.72; H, 6.68. $C_{14}H_{17}N_3O_2$. Calculated (%): C, 64.85; H, 6.61. ^1H NMR ($CDCl_3$), δ: 2.79 (s, 6 H, 8-NMe_2); 2.90 (s, 6 H, 1-NMe_2); 7.02 (dd, 1 H, H(7), $J_{6,7}$ = 7.62 Hz); 7.31 (dd, 1 H, H(5), $J_{5,6}$ = 7.91 Hz, $J_{5,7}$ = 1.17 Hz); 7.32 (d, 1 H, H(4), $J_{3,4}$ = 8.79 Hz); 7.39 (t, 1 H, H(6)); 7.53 (d, 1 H, H(3)). UV (MeOH), λ_{max}/nm (lg ε): 225 (4.41), 250 (sh, 4.20), 320 (sh, 3.91), 438 (3.53), terminal absorption to 610 nm.

1,8-Bis(dimethylamino)-4-nitronaphthalene (5a), dark-cherry crystals, m.p. 134—135 °C. A mixture with the authentic sample[8] did not give a melting point depression.

B. With nitrogen dioxide (2 equiv.). The reaction was carried out analogously to method *A*. The reaction mixture was stirred at 0 °C for 4 h and the resinous precipitate that formed was filtered off and discarded. The filtrate was concentrated to the minimum volume and passed through a column with silica gel (benzene as the eluent). The first red-orange fraction was collected. **1,8-Bis(dimethylamino)-2,7-dinitronaphthalene (4)** was obtained as pale-brown crystals in a yield of 4 mg (1%), m.p. 175—176 °C (from MeOH). Found (%): C, 55.33; H, 5.39. $C_{14}H_{16}N_4O_4$. Calculated (%): C, 55.26; H, 5.30. ^1H NMR ($CDCl_3$), δ: 2.92 (s, 12 H, NMe_2); 7.37 (d, 2 H, H(4), H(5), $J_{3,4}$ = 8.79 Hz); 7.62 (d, 2 H, H(3), H(6)). UV (MeOH), λ_{max}/nm (lg ε): 249 (4.27), 295 (sh, 3.84), 384 (3.71), 516 (sh, 3.34), terminal absorption to 560 nm.

When the reaction was carried out in dichloroethane (−30 °C, 6 h), compounds **7** and **4** were isolated in yields of 4 mg (1%) and 10 mg (2%), respectively.

1,3-Dimethyl-4-nitro-2,3-dihydroperimidine (7), R_f 0.65 (silica gel, benzene), pale-red needles, m.p. 93—94 °C (from hexane), poorly soluble in dilute mineral acids and readily soluble in organic solvents. Found (%): C, 64.52; H, 5.17. $C_{13}H_{13}N_3O_2$. Calculated (%): C, 64.19; H, 5.39. ^1H NMR ($CDCl_3$), δ: 3.01 (s, 3 H, 1-NMe); 3.05 (s, 3 H, 3-NMe); 4.29 (s, 2 H, H(2)); 6.60 (dd, 1 H, H(9), $J_{8,9}$ = 7.77 Hz); 7.17 (dd, 1 H, H(7), $J_{7,8}$ = 8.07 Hz); 7.28 (d, 1 H, H(6), $J_{5,6}$ = 9.20 Hz); 7.47 (t, 1 H, H(8), $J_{8,9}$ = 7.77 Hz); 7.95 (d, 1 H, H(5)).

C. With tetranitromethane. A solution of TNM (178 μL, 1.5 mmol) in dry CCl_4 (20 mL) was added dropwise with vigorous stirring to a solution of compound **1** (320 mg, 1.5 mmol) in dry CCl_4 (20 mL) cooled to 0 °C. The reaction mixture rapidly turned dark red and a brown precipitate formed. The mixture was vigorously stirred for 1 h (taking into account the time of addition of TNM). After cooling to −20 °C, 10% KOH (10 mL) was added to the mixture, and the mixture was refluxed with stirring for 1 min. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic extracts were concentrated and the residue was chromatographed on silica gel (benzene as the eluent). Compounds **4**, **3**, and **5a** were successively isolated in yields of 4 mg (1%), 58 mg (15%), and 70 mg (18%), respectively. The samples are identical in physicochemical properties to those obtained previously.

D. Nitronium tetrafluoroborate (1 equiv.). A solution of NO_2BF_4 (0.132 g, 1 mmol) in anhydrous MeCN* (140 mL) was rapidly added with stirring to a solution of compound **1** (0.214 g, 1 mmol) in anhydrous MeCN (10 mL). The color of the reaction mixture changed from pale yellow to pale brown. Then MeCN was evaporated. The residue was treated with concentrated NH_3 (3 mL) and concentrated to dryness. The resulting mixture was treated with $CHCl_3$ (4×4 mL). The chloroform extracts were combined and chromatographed on Al_2O_3 (II, $CHCl_3$). Compound **5a**, the starting compound **1**, and **1,8-bis(dimethylamino)-4,5-dinitronaphthalene** (**5b**) were obtained in the order of elution in yields of 150 mg (58%), 13 mg (6%), and 16 mg (5%), respectively. The latter compound was obtained as a dark-red finely crystalline powder, m.p. 277—280 °C (with decomp., from $CHCl_3$).[9]

The residue of the reaction mixture undissolved in chloroform was crystallized from acetone. Yellow-brown crystals of **1,8-bis(dimethylamino)-2,4,5,7-tetranitronaphthalene** (**5g**) were obtained in a yield of 22 mg (6%), t.decomp. >250 °C.[9]

Nitration of 5,6-bis(dimethylamino)acenaphthene (6). A. With nitric acid *(Table 2, run 7).* A solution of 70% HNO_3 (102 μL, 1.6 mmol) in MeCN (40 mL) was added to a boiling solution of compound **6**[22] (0.192 g, 0.8 mmol) in MeCN (40 mL) over 5 s. The red-brown solution was refluxed for 5 min, cooled to −60 °C, treated with concentrated NH_3 (5 mL), and concentrated to dryness. The residue was chromatographed on a column with silica gel ($CHCl_3$ as the eluent). Compounds **11**, **13**, and **12** were obtained in the order of elution in yields of 26 mg (10%), 0.013 g (5%), and 0.033 g (15%), respectively.

5,6-Bis(dimethylamino)-4,7-dinitroacenaphthene (11), R_f 0.77, pale-orange needles, m.p. 266—268 °C (from EtOH). Found (%): C, 58.02; H, 5.40. $C_{16}H_{18}N_4O_4$. Calculated (%): C, 58.18; H, 5.49. ^1H NMR ($CDCl_3$), δ: 2.86 (s, 12 H, NMe_2); 3.32 (s, 4 H, H(1), H(2)); 7.42 (s, 2 H, H(3), H(8)). UV (MeOH), λ_{max}/nm (lg ε): 258 (4.18), 295 (sh, 3.76), 400 (3.62), terminal absorption to 520 nm.

5-Dimethylamino-6-methylamino-4,7-dinitroacenaphthene (13), R_f 0.60, dark-brown crystals, m.p. 180—182 °C (from EtOH). Found (%): C, 57.15; H, 5.08. $C_{15}H_{16}N_4O_4$. Calculated (%): C, 56.96; H, 5.10. ^1H NMR ($CDCl_3$), δ: 2.82 (s, 3 H, 6-NMe); 2.89 (s, 6 H, 5-NMe_2); 3.28 (m, 2 H, H(1), H(2), $J_{1,2}$ = 4.69 Hz); 7.44 (br.s, 1 H, H(3)); 7.76 (t, 1 H, H(8), $J_{1,8}$ = 1.41 Hz); 9.77 (br.s, 1 H, NH). IR (Nujol mulls), ν/cm^{-1}: 3420 (NH), 1550, 1325 (NO_2).

5-Dimethylamino-6-methylamino-7-nitroacenaphthene (12), R_f 0.40, red needles with a golden luster, m.p. 141—143 °C (from EtOH). Found (%): C, 66.12; H, 5.99. $C_{15}H_{17}N_3O_2$. Calculated (%): C, 66.40; H, 6.32. ^1H NMR ($CDCl_3$), δ: 2.76 (s, 6 H, 6-NMe_2); 2.82 (s, 3 H, 5-NMe); 3.24 (m, 4 H, H(1), H(2), $J_{1,2}$ = 5.61 Hz); 7.21 (d, 1 H, H(7), $J_{7,8}$ = 7.60 Hz); 7.30 (br.d, 1 H, H(8)); 7.65 (t, 1 H, H(3), $J_{2,3}$ = 1.54 Hz); 10.17 (br.s, 1 H, NH). IR (Nujol mulls), ν/cm^{-1}: 3400 (NH), 1550, 1330 (NO_2).

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* NO_2BF_4 very slowly dissolves in acetonitrile. It is better to prepare a solution at 50 °C followed by cooling to room temperature.

B. With nitronium tetrafluoroborate *(Table 2, run 12).* The reaction was carried out analogously to nitration of compound **1**, except that a solution of NO_2BF_4 was added to a boiling solution of compound **6** and the red-brown reaction mixture was refluxed for 5 min. Dinitroacenaphthene **13** (4%) and compound **12** (52%) were successively isolated by chromatography on silica gel ($CHCl_3$ as the eluent). The properties of the resulting compound are identical to those of the authentic samples. Further elution made it possible to recover up to 35% of the initial acenaphthene **6**.

C. With tetranitromethane. The reaction was carried out analogously to nitration of compound **1**. **5,6-Bis(dimethylamino)-4-nitroacenaphthene (10)** was isolated by chromatography on silica gel ($CHCl_3$ as the eluent) as a red-brown oil in 64% yield. The oil gradually crystallized to form red-brown needles (m.p. 45—46 °C) soluble in dilute mineral acids. Found (%): C, 67.58; H, 6.59. $C_{16}H_{19}N_3O_2$. Calculated (%): C, 67.35; H, 6.71. ^1H NMR ($CDCl_3$), δ: 2.78 (s, 6 H, 6-NMe_2); 2.86 (s, 6 H, 5-NMe_2); 3.28 (br.s, 4 H, H(1), H(2)); 7.06 (d, 1 H, H(7), $J_{7,8}$ = 7.62 Hz); 7.26 (br.d, 1 H, H(8)); 7.32 (br.s, 1 H, H(3)). UV (MeOH), λ_{max}/nm (lg ε): 225 (4.43), 256 (sh, 4.11), 310 (sh, 3.95), 442 (3.46), terminal absorption to 530 nm.

Alkylation of compound 12 (the procedure was optimized). A solution of compound **12** (0.027 g, 0.1 mmol) in MeI (3 mL) was refluxed for 50 h (should be protected from light!). Then an excess of MeI was distilled off to dryness. The residue was refluxed with 10% KOH (2 mL) for 1 min, cooled to −20 °C, extracted with benzene, and chromatographed (silica gel, $CHCl_3$). The starting compound **12** (3—5%) and compound **10** (85—88%) were successively isolated. Their physicochemical characteristics are identical to those of the samples described above.

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