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peri-Naphthylenediamines: XXXIX.* Synthesis and Structure of *N*,*N'*,*N'*-Trimethyl- *N*-nitroso-naphthalene-1,8-diamine Derivatives

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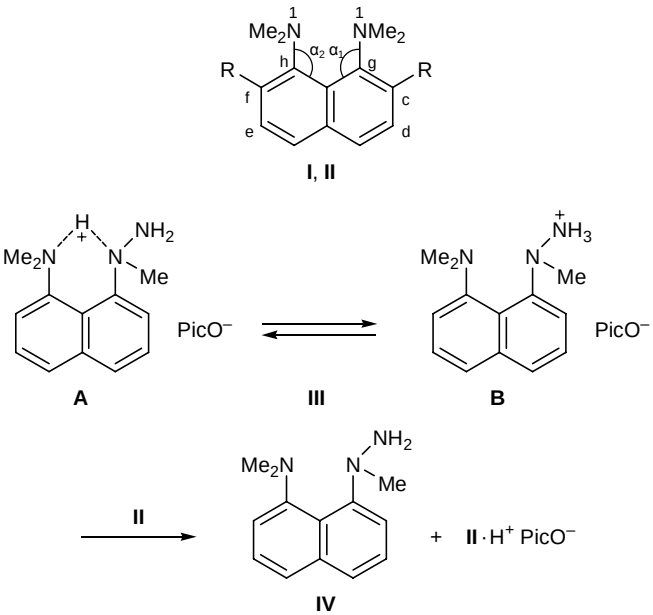
Abstract—The corresponding *N*-nitroso derivatives were synthesized by the action of nitrous acid on *N*,*N*,*N'*-trimethylnaphthalene-1,8-diamine, *N*,*N*,*N'*-trimethyl-5-nitronaphthalene-1,8-diamine, and *N*,*N*,*N'*-trimethylacenaphthene-5,6-diamine, and molecular structure of the products was studied.

An important factor responsible for the high basicity of 1,8-bis(dimethylamino)naphthalene (**I**, proton sponge) is electrostatic repulsion of lone electron pairs on the two nitrogen atoms in the *peri* positions; this repulsion is removed in going to the cation [2–4]. Therefore, an obvious way of further raising the basicity of proton sponges was to increase the number of lone electron pairs in the vicinity of the basic center. In fact, a sharp increase in pK_a was observed in going to 2,7-dimethoxy-1,8-bis(dimethylamino)naphthalene (**II**) (pK_a 16.1) which remains so far the strongest base in the series of naphthalene proton sponges [5]. Despite recent data [6] according to which rise in pK_a of compound **II** and some its analogs only partially results from repulsion of the four neighboring lone electron pairs, the contribution of this factor remains significant. In terms of the above concept we recently synthesized hydrazine analogs of proton sponge, e.g., compound **IV**, and studied the structure of the corresponding picrates [7]. Picrate **III** was found to exist in crystal as a mixture of tautomers **A** and **B** (Scheme 1), the latter being the first example of protonation of arylhydrazines at the α-nitrogen atom. It should be noted that free base **IV** was detected only by NMR spectroscopy when compound **II** was carefully added to picrate **III** in an NMR ampule and that deprotonation of **III** by the action of aqueous alkali or ammonia resulted in complete tarring. Probably, this result indirectly indicates repulsion of lone electron pairs on the three nitrogen atoms in **IV**, which leads to destabilization and favors its oxidation. Interestingly, the basicity of **IV** was approximately the same as that found for parent structure **I**; this is the maximal value for arylhydrazines.

Scheme 1.

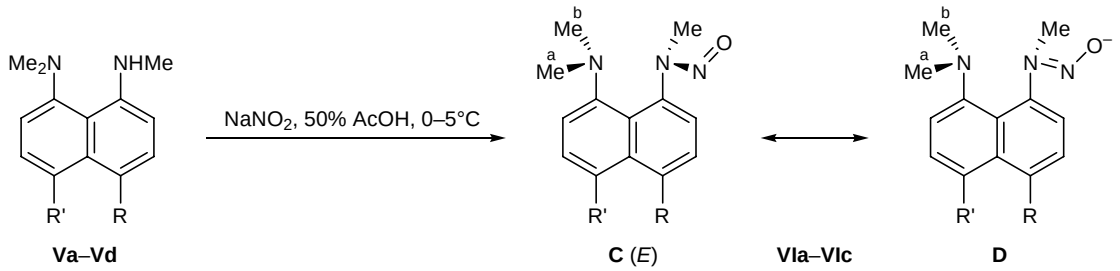


I, R = H; **II**, R = OMe.

While continuing studies in this line, in the present work we synthesized *N*-nitroso derivatives of *N*,*N*,*N'*-trimethylnaphthalene-1,8-diamines. Unlike hydrazine **IV**, *peri* interactions in *N*-nitroso-*N*,*N*,*N'*-trimethylnaphthalene-1,8-diamines can additionally involve lone electron pairs on the oxygen atom. *N*-Nitroso amines **VIa**–**VIc** were obtained in good yields by

* For communication XXXVIII, see [1].

Scheme 2.



R = R' = H (**a**); RR' = $(CH_2)_2$ (**b**); R = H, R' = NO_2 (**c**); R = NO_2, R' = H (**d**).

treatment of *N*,*N*,*N'*-trimethylnaphthalene-1,8-diamines **Va**–**Vc** with an equivalent amount of sodium nitrite in 50% aqueous acetic acid (Scheme 2). No nitrosation occurred in hydrochloric acid, presumably because of protonation of the initial amine. However, we failed to effect nitrosation of amine **Vd**, regardless of the conditions. Presumably, the electron density on the amino nitrogen atom is reduced below a critical value due to the presence of an electron-acceptor group in *para* position.

We succeeded in obtaining crystals of **VIa** and **VIc** suitable for X-ray analysis. The results are given in Tables 1 and 2, and the molecular structures are shown in Figs. 1 and 2. These data led us to draw the following conclusions. The N^1 atoms of the nitrosoamine fragment in both compounds is sp^2-hybridized: the sum of bond angles at N^1 is 359.49° in compound **VIa** and 358.9° in **VIc** (hereinafter, for atom numbering in molecules **VIa** and **VIc**, see Figs. 1 and 2, respectively; atoms in the other compounds are numbered according to IUPAC recommendations). The MeNN(O) fragments are almost planar: the torsion angles $O^1N^2N^1C^{11}$ are 3.03 and 2.8° in molecules **VIa** and **VIc**, respectively. The MeNN(O) plane is turned with respect to the naphthalene system through a dihedral angle of 55.99 (**VIa**) or 52.5° (**VIc**), and the nitroso

Table 1. Bond lengths (*d*) and bond (ω) and torsion angles (φ) in the molecule of *N*,*N*,*N'*-trimethyl-*N'*-nitrosonaphthalene-1,8-diamine (**VIa**) according to the X-ray diffraction data

Bond	*d*, Å	Bond angle	ω, deg	Torsion angle	φ, deg
N^1–C^1	1.4304(17)	$N^2N^1C^{11}$	120.15(11)	$O^1N^2N^1C^1$	175.09(10)
N^1–N^2	1.3191(15)	$C^{11}N^1C^1$	122.71(10)	$N^2N^1C^1C^2$	–55.99(15)
N^1–C^{11}	1.4626(17)	$C^1N^1N^2$	116.63(11)	$N^2N^1C^1C^{10}$	127.76(13)
N^2–O^1	1.2452(16)	$O^1N^2N^1$	114.32(12)	$C^{11}N^1N^2O^1$	3.03(17)
N^3–C^9	1.4109(18)	$C^{13}N^3C^{12}$	111.89(11)	$C^{11}N^1C^1C^2$	115.85(14)
N^3–C^{13}	1.4546(17)	$C^{12}N^3C^9$	114.59(11)	$C^{11}N^1C^1C^{10}$	–60.40(16)
N^3–C^{12}	1.4572(18)	$C^{13}N^3C^9$	116.95(12)	$N^1C^1C^2C^3$	–177.97(11)

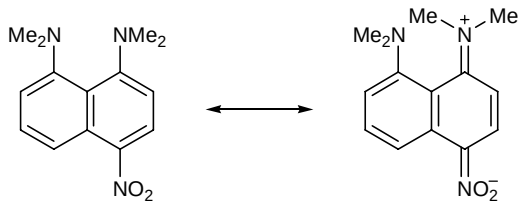
Table 2. Bond lengths (*d*) and bond (ω) and torsion angles (φ) in the molecule of *N*,*N*,*N'*-trimethyl-*N'*-nitroso-4-nitronaphthalene-1,8-diamine (**VIc**) according to the X-ray diffraction data

Bond	*d*, Å	Bond angle	ω, deg	Torsion angle	φ, deg
N^1–C^9	1.440(4)	$N^2N^1C^{11}$	121.3(3)	$O^1N^2N^1C^{11}$	2.8(4)
N^1-N^2	1.315(4)	$C^{11}N^1C^9$	122.1(3)	$N^2N^1C^9C^8$	–52.5(4)
N^1–C^{11}	1.459(4)	$C^9N^1N^2$	115.5(3)	$N^2N^1C^9C^{10}$	134.1(3)
N^2–O^1	1.253(4)	$O^1N^2N^1$	113.2(3)	$C^9N^1N^2O^1$	171.1(3)
N^3–C^1	1.372(4)	$C^{13}N^3C^{12}$	113.0(3)	$O^{3'}N^4C^4C^3$	–5(3)
N^3–C^{12}	1.461(4)	$C^{12}N^3C^1$	117.8(3)	$O^3N^4C^4C^3$	27.3(8)
N^3–C^{13}	1.464(4)	$C^1N^3C^{13}$	117.4(3)	$O^2N^4C^4C^3$	–143.7(6)
N^4–C^4	1.478(6)	$C^4N^4O^2$	119.5(6)	$O^{2'}N^4C^4C^3$	153.1(11)

group is oriented oppositely to the dimethylamino group (Fig. 3).

Both *N*-nitroso amines **VIa** and **VIc** are *E* isomers. Such structure is typical of crystalline samples of most other *N*-alkyl-*N*-nitrosoanilines [8], except for sterically hindered compounds like *N-tert*-butyl-*N*-nitroso-2,3,5,6-tetrafluoro-4-trifluoromethylaniline [9], which exist mainly as *Z* isomers.

As in proton sponge **I**, the dimethylamino groups in molecules **VI** tend to arrange in the naphthalene ring plane to ensure conjugation with the π-electron system of the latter. The sum of the bond angles at the nitrogen atom of the dimethylamino group in compounds **I**, **VIa**, and **VIc** is 347.0, 343.4, and 348.2°, respectively. The larger value for **VIc** results from additional participation in conjugation of the nitro group [cf. the X-ray diffraction data for 1,8-bis(dimethylamino)-4-nitronaphthalene (**VII**), where the sums of the bond angles at the N^1 and N^8 atoms are 357 and 351.6°, respectively]. The nitro group in molecules **VIc** in crystal is disordered by two positions with different orientations with respect to the naphthalene ring (Fig. 3).



VII **VIII**

The character of *peri* interactions in compounds **VIa** and **VIc** should be noted (Table 3). Three main kinds of displacement of *peri* substituents relative to each other are generally distinguished in the naphthalene series (structures **E**–**G**) [10]. If one substituent is electrophilic and the other is nucleophilic, their interaction can lead to their displacement toward each other (**E**) or in one direction (**F**). If both substituents have similar electronic parameters, they usually repulse from each other; in this case, the substituents either reside in the naphthalene ring plane or decline from it in opposite directions (**G**). A typical example of type **G** is proton sponge **I**. The bond angles therein between the C_{arom}–N and C^1–C^9 (C^8–C^9) bonds (α_1 and α_2) slightly exceed 120°, but the main specificity of the molecular structure is that the nitrogen atoms deviate by 0.4 Å in opposite directions with respect to the mean-square plane of the ring [11]. This follows from a considerable angle (20°) between the C^1–N^1 and C^8–N^2 bonds, as well as from "twisting" of the naphthalene ring at the

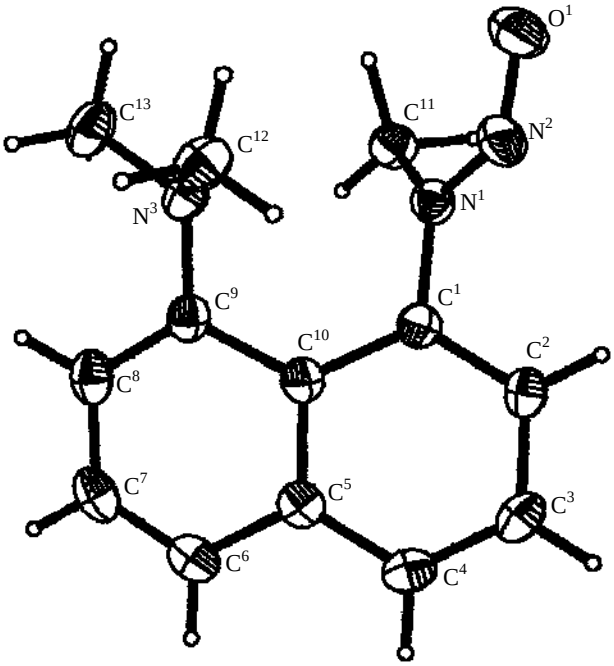


Fig. 1. Structure of the molecule of *N,N,N′*-trimethyl-*N′*-nitrosonaphthalene-1,8-diamine (**VIa**) with atom numbering.

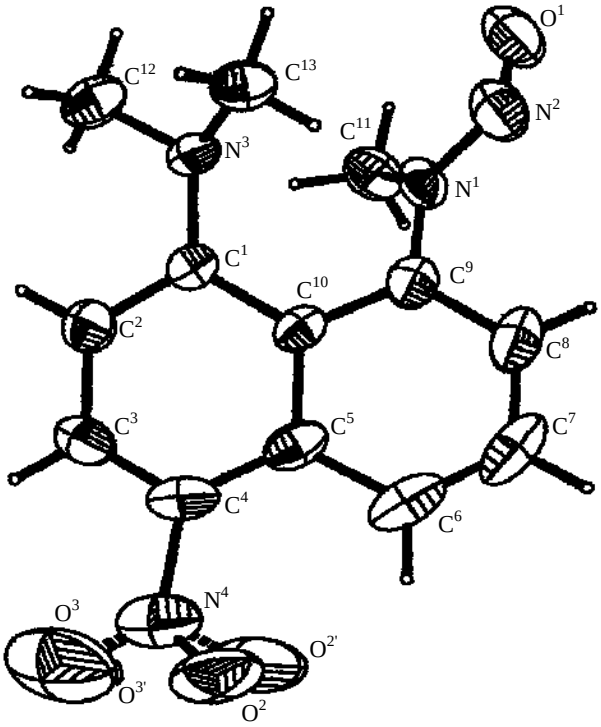


Fig. 2. Structure of the molecule of *N,N,N′*-trimethyl-*N′*-nitroso-4-nitronaphthalene-1,8-diamine (**VIc**) with atom numbering.

C^9–C^{10} bond. This deformation is also characterized by an angle of 11.3° between the *cd* and *ef* bonds. The corresponding deviations in 4-nitro derivative **VII** are

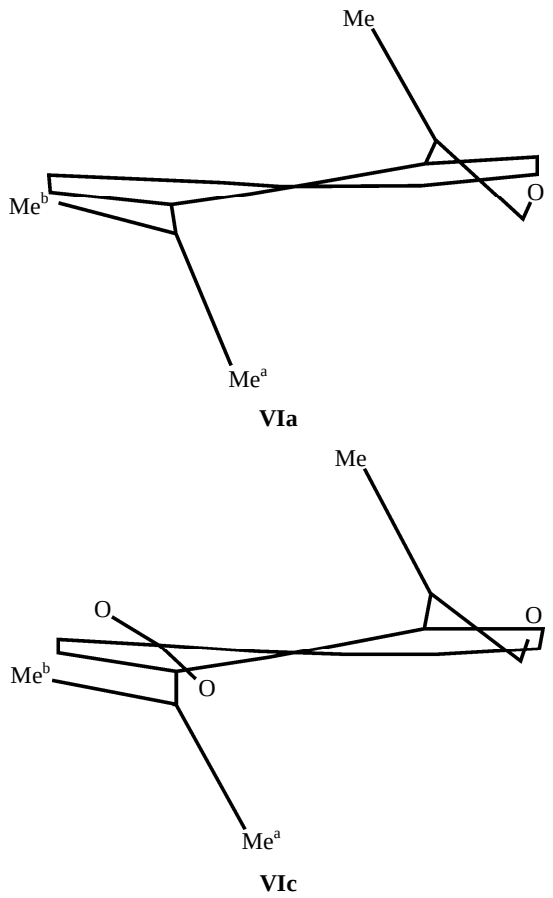
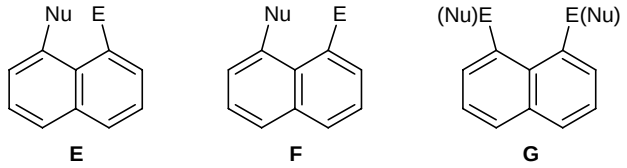


Fig. 3. Relative orientations of the *peri* substituents in *N*,*N*,*N'*-trimethyl-*N'*-nitrosonaphthalene-1,8-diamines **VIa** and **VIc** (one of the two possible orientations of the nitro group in molecule **VIc** is shown).

even stronger, for the dimethylamino groups in molecule **VII** require more space to ensure their coplanar orientation due to conjugation with the nitro group [12]. As a result, the distance between the amino nitrogen atoms in **VII** increases to 2.86 Å (against 2.79 Å in proton sponge **I**; Table 3).



Despite similar distortion of the naphthalene ring as in molecule **I**, the *peri* substituents in *N*-nitroso amine **VIa** are appreciably inclined. This follows both from α_1 and α_2 angles and from considerably shortened distance between the amino nitrogen atoms. Here, the *peri* interaction looks like attack by the N(NO)Me group on the dimethylamino group. The reason is obvious: conjugation within the *N*-methyl-*N*-nitrosoamino group induces a partial positive charge on the amino nitrogen atom (structure **D**), and the latter is attracted by the lone electron pair on the dimethylamino nitrogen atom due to electrostatic forces. A more complex pattern is observed for compound **VIc** whose structure is likely to reflect a combination of interactions typical of molecules **VIa** and **VII**.

There are reasons to believe that compounds **VIa**–**VIc** in solution also exist in a single form. The ^{1}H NMR spectra of all *N*-nitroso amines **VIa**–**VIc** in $CDCl_3$ contain only one signal from methyl protons of the N(NO)Me group at δ 3.31, 3.37, and 3.23 ppm, respectively. It is known that such compounds as *N*-nitroso-*N*-ethyl- and *N*-nitroso-*N*-isopropylanilines which exist as mixtures of *E* and *Z* isomers (but not *N*-methyl-*N*-nitrosoaniline which is *E* isomer [13]) give rise to double sets of signals from the *N*-alkyl groups [14]. We believe that *N*-nitroso amines **VIa** and **VIb** in solution occur in the less sterically hindered *E* form. This is confirmed by both X-ray diffraction data and quantum-chemical calculations. According to the results of *ab initio* calculations (using STO 3-21G basis set), the *E* isomer of **VIa** is by 8 kJ/mol more stable than the *Z* isomer. The total energy of *E*-**VIa** is –1935231 kJ/mol, the total energy of isomer *Z*-**VIa** is –1935223 kJ/mol, and the barrier to rotation about the N–N(O) bond in molecule **VIa** is 88 kJ/mol.

An interesting pattern is observed in the ^{1}H NMR spectra in the region of NMe_2 signals (Table 4, Fig. 4). The dimethylamino groups in compounds **VIa** and **VIb** give rise to two signals at δ ~2.8 and 2.4 ppm, indicating restricted rotation of these groups about the C_{arom}–N bond. In keeping with the X-ray diffraction data, the observed signals were assigned, respectively, to the equatorial (Me^b) and axial (Me^a) methyl groups. Presumably, shielding of the Me^a protons (the strongest in the series of known proton sponges) is caused by paramagnetic constituent of the ring current, while the Me^b signal is located in the region typical of most naphthalene proton sponges, including parent compound **I**. It should be noted that protons of the methyl group in compound **I** become nonequivalent only below –100°C and that the difference in the chemical shifts is a few Hertz [15].

Taking into account a strong similarity in the molecular structures of compounds **VIa** and **VIc** (Fig. 3), we expected the Me^a and Me^b groups to be nonequivalent in the ^{1}H NMR spectrum of the latter. Surprisingly, this was not the case: The ^{1}H NMR

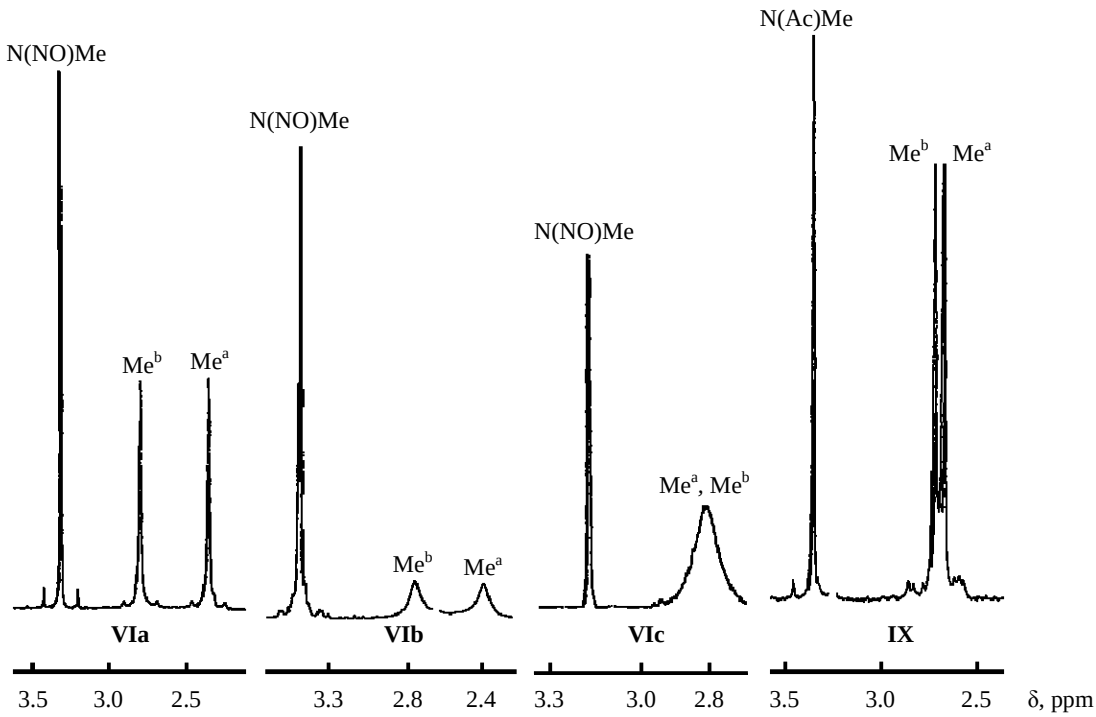


Fig. 4. Signals from protons of the dimethylamino groups in the ^{1}H NMR spectra of compounds **VIa**–**VIc** and **IX** (17°C, $CDCl_3$).

spectrum of **VIc** at room temperature contained only one singlet at δ 2.72 ppm. In fact, this means that the Me^a group in **VIc** is not shielded by the ring; therefore, its signal appears in the region typical of proton sponges. Several factors may be proposed to be responsible for the observed pattern; these include weakening of the ring current due to greater rigidity of the endocyclic bonds as a result of conjugation between the NO_2 and NMe_2 groups; additional planarization of the NMe_2 group, which eliminates shielding of the axial methyl group; freer rotation of the NMe_2 group; and considerable change in conformation of the methylnitrosoamino group, which affects the Me^a group. On the basis of the X-ray diffraction data and general considerations (for example, it is difficult to presume that the presence of a nitro group in molecule **VIc** facilitates free rotation of the dimethylamino group) we are inclined to believe that the first two factors are crucial.

From the viewpoint of electronic structure, *N*-acyl derivatives of 1-dimethylamino-8-methylaminonaphthalene can be regarded as analogs of the *N*-nitroso amines under study. Therefore, it was interesting to compare their ^{1}H NMR spectra. We found that methyl protons in the dimethylamino group of 1-(*N*-acetyl-*N*-methylamino)-8-dimethylaminonaphthalene (**IX**) are also nonequivalent; in the spectrum recorded in $CDCl_3$, they give signals at δ 2.72 (Me^b) and 2.68 ppm (Me^a). Carbonyl group is a weaker acceptor than nitroso group, and the difference in the chemical shifts of the Me^b and Me^a protons in the spectrum of **IX** is smaller (Δδ 0.04 ppm) than the corresponding difference for compound **VIa** (Δδ 0.44 ppm).

We measured ^{1}H NMR spectra of compounds **VIa**, **VIb**, and **IX** in DMSO-d_6 at different temperatures. As expected, raising the temperature leads to broadening of the NMe^a and NMe^b signals which coalesce at 60°C for compound **VIa**, 35°C for **VIb**, and 33°C for **IX**; here, signals from the other protons did not change their shape. On cooling, the original pattern is restored. Using the ^{1}H NMR data, we estimated the barrier to rotation about the C–NMe_2 bond in molecules **VIa**, **VIb**, and **IX** at 66.3, 61.4, and 58.4 kJ/mol, respec-

Table 3. Some geometric parameters of proton sponges, reflecting interactions between *peri* substituents in their molecules

Comp. no.	α_1, deg	α_2, deg	$N^1\cdots N^8$, Å	*cd*–*ef* angle, deg	C^1N^1–C^8N^8 (*gh*) angle, deg
I [11]	120.1	120.8	2.79	11.3	20
VIa	118.1	121.3	2.73	13.9	20
VIc	120.6	121.6	2.76	13.7	27
VII [12]	122.4	120.2	2.86	14.7	31

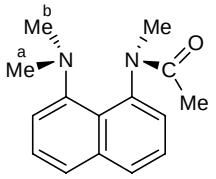
Table 4. Chemical shifts of the methyl protons (δ, ppm) in the 1H NMR spectra of compounds **VIa**–**VIc** and **IX** and barriers to rotation about the C–NMe_2 bond ($\Delta G^{\neq}$, kJ/mol)

Comp. no.	Solvent	N–Me[a]	N–Me[b]	N(NO)Me	$\Delta G^{\neq}$
VIa	$CDCl_3$	2.36	2.80	3.31	–
	DMSO-d_6	2.25	2.76	3.25	66.3
VIb	$CDCl_3$	2.38	2.76	3.37	–
	DMSO-d_6	2.26	2.71	3.29	61.4
VIc	$CDCl_3$	2.77	2.77	3.22	–
	DMSO-d_6	2.68	2.68	3.26	–
IX	$CDCl_3$	2.68	2.72	3.35[a]	–
	DMSO-d_6	2.59	2.64	3.23[a]	58.4

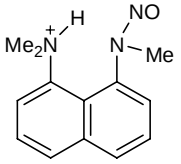
[a] N(COMe)**Me**.

tively (Table 4). Presumably, the lower barrier to rotation about the C_{arom}–NMe_2 bond in **VIb** is explained by longer distance between the N^1 and N^3 atoms, which is typical of 5,6-bis(dimethylamino)acenaphthene [16].

Unfortunately, we failed to measure the basicities of the prepared compounds, for they readily underwent denitrosation by the action of acids. For example, our attempt to obtain tetrafluoroborate **X** by treatment of nitroso compound **VIa** with an equimolar amount of tetrafluoroboric acid in diethyl ether at 25°C resulted in formation of a mixture consisting (according to the ^{1}H NMR data, DMSO-d_6) of protonated *N*,*N*,*N'*-trimethylnaphthalene-1,8-diamine (**Va**), base **VIa**, and probably salt **X** at a ratio of 3.9:9.6:1. The only evidence in favor of the latter was a signal located at δ 15.3 ppm which could be assigned to chelated NH proton (in the spectrum of protonated species **Va** in DMSO-d_6, the NH proton appears at δ 6.10 ppm [17]).



IX



X

The reduction of *N*-nitroso amines **VIa**–**VIc** with hydrogen over 5% Pd/C, with $LiAlH_4$ in Et_2O under argon, or with zinc in acetic acid gave only the corresponding denitrosation products **Va**–**Vc** in 29–35% yield. Taking into account the poor yield, the process may be accompanied by formation of hydrazines **IV**; the latter are unstable, and they decompose during the reaction or isolation.

EXPERIMENTAL

The ^{1}H NMR spectra were measured on a Bruker-250 spectrometer at 250 MHz. The mass spectra were recorded on Kratos MS-30 (electron impact, 70 eV; compounds **VIa** and **VIb**) and Finnigan MAT INCOS 50 spectrometers (electron impact, 50 eV; **VIc**). The IR spectra were obtained on a Specord 75IR spectrometer from samples dispersed in mineral oil. The progress of reactions and the purity of products were monitored by TLC on aluminum oxide (Brockman activity grade III–IV); development with iodine vapor.

X-Ray diffraction study of compounds VIa and VIc. Single crystals of compounds **VIa** and **VIc** were obtained by slow evaporation of their solutions in methanol at room temperature. Experimental reflections (10214 for compound **VIa** and 3788 for **VIc**) were measured on a Bruker SMART 1000 CCD Area Detector diffractometer at 110 K and on an Enraf–Nonius CAD-4 diffractometer at 295 K. The acquired data were processed using SAINT [18] and SADABS programs [19]. The structures were solved by the direct method, and all non-hydrogen atoms were localized by the difference synthesis of electron density and were refined in anisotropic approximation. Hydrogen atoms were localized and refined in isotropic approximation using the *rider* model with $U(H) = nU(C)$, where $n = 1.2$ for CH groups, $n = 1.5$ for CH_3 groups, and $U(S)$ is the equivalent temperature factor of the carbon atom to which the corresponding hydrogen atom is attached. The calculations were performed using SHELXTL PLUS 5 software package [20].

Principal crystallographic parameters for compounds VIa and VIc. Compound **VIa**: monoclinic crystals; M 229.29; unit cell parameters: a = 6.2623(11), b = 10.3711(18), c = 18.382(3) Å; α = 90, β = 98.264(4), γ = 90°; V = 1181.5(4) Å^3; Z = 4; d_{calc} = 1.790 mg/mm^3; space group $P2(1)/n$; μ = 0.085 mm^{-1}; $F(000)$ = 488; crystal habit 0.2×0.4×0.5 mm; 3079 independent reflections (R_{int} = 0.0315); 154 refined parameters; final divergence factors R_1 = 0.0595, wR_2 = 0.1483 [for 2205 reflections with $I > 2\sigma(I)$], R_1 = 0.0778, wR_2 = 0.1625 (for all independent reflections); reliability 98.0%. Compound **VIc**: orthorhombic crystals: M = 274.28; a = 10.412(2), b = 9.5960(19), c = 26.730(5) Å; α = β = γ = 90°; V = 2670.7(9) Å^3, Z = 8, d_{calc} = 1.364 mg/mm^3; space group $Pbca$; μ = 0.100 mm^{-1}; $F(000)$ = 1152; crystal habit 0.5×0.3×0.3 mm; 3788 independent reflections (R_{int} = 0.000); 199 refined parameters; final divergence factors R_1 = 0.0536, wR_2 = 0.0980 [for 2205 reflections with I >

$2\sigma(I)$], R_1 = 0.3301, wR_2 = 0.1708 (for all independent reflections); reliability 97.4%. The coordinates of atoms and their temperature factors, bond lengths, and bond angles, are deposited to the Cambridge Crystallographic Data Center [CCDC, entry nos. 233636 (**VIa**) and 233637 (**VIc**)].

The barrier to rotation about the C–NMe_2 bond ($\Delta G^{\neq}$, kJ/mol) in compounds **VIa**, **VIb**, and **IX** was calculated by the equation $\Delta G^{\neq} = 19.14\,T_c[9.97 + \log(T_c/\Delta\nu)]\times 10^{-3}$. Here, $\Delta\nu$ is the maximal distance between the signals of the *N*-methyl protons in the absence of exchange, and T_c is the coalescence temperature; **VIa**: $\Delta\nu$ = 125 Hz, T_c = 333 K; **VIb**, $\Delta\nu$ = 111 Hz, T_c = 308 K; **IX**, $\Delta\nu$ = 11 Hz, T_c = 306 K.

***N*-Nitroso amines VIa–VIc (*general procedure*).** A solution of 1 mmol of compound **Va**, **Vb** [21], or **Vc** [22] in 5 ml of 50% aqueous acetic acid was cooled to 0–5°C, and a solution of 0.069 g (1 mmol) of sodium nitrite in 0.5 ml of water was added dropwise at such a rate that the temperature of the mixture did not exceed 5°C. The mixture was stirred for 30 min at that temperature and neutralized with a concentrated ammonia solution to pH 7–8, and the resulting dispersion was treated with chloroform. The chloroform extract was subjected to column chromatography on Al_2O_3 using chloroform as eluent, a fraction with R_f 0.4–0.6 being collected. Crystalline compounds **VIa**–**VIc** were stored at –25°C; however, they underwent complete tarring in a month.

***N,N,N′*-Trimethyl-*N′*-nitrosonaphthalene-1,8-diamine (VIa).** Yield 70%, colorless crystalline substance, mp 53–55°C (from hexane). IR spectrum, ν, cm^{-1}: 1592, 1599, 1605. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.36 s (3H, NMe^a), 2.80 s (3H, NMe^b), 3.31 s [3H, N(NO)Me], 7.22 m (1H, 7-H), 7.34 d.d (1H, 5-H, ^3J = 7.33, ^4J = 1.46 Hz), 7.48 m (2H, 3-H, 6-H), 7.62 d.d (1H, 2-H, ^3J = 8.06, ^4J = 1.10 Hz), 7.92 d.d (1H, 4-H, ^3J = 8.43, ^4J = 1.10 Hz). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.25 s (3H, NMe^a), 2.76 s (3H, NMe^b), 3.25 s [3H, N(NO)Me], 7.38 m (2H, 5-H, 7-H), 7.58 m (2H, 3-H, 6-H), 7.77 d (1H, 2-H, ^3J = 8.09 Hz), 8.06 d (1H, 4-H, ^3J = 8.46 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 229 (2) $[M]^+$, 199 (66) $[M - NO]^+$, 185 (8) $[M - NMe_2]^+$, 184 (45) $[M - NOMe]^+$, 183 (100) $[M - NOMe - H]^+$. Found, %: C 68.02; H 6.65; N 18.24. $C_{13}H_{15}N_3O$. Calculated, %: C 68.12; H 6.55; N 18.34.

***N,N,N′*-Trimethyl-*N′*-nitrosoacenaphthene-5,6-diamine (VIb).** Yield 80%, dark brown oily substance. IR spectrum, ν, cm^{-1}: 1597, 1600, 1605. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.38 br.s (3H, NMe^a), 2.76 br.s (3H, NMe^b), 3.37 s [3H, N(NO)Me], 3.39 s (4H, CH_2CH_2), 7.18 d (1H, 2-H, ^3J = 7.69 Hz), 7.26 m (3H, 3-H, 7-H, 8-H). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.26 br.s (3H, NMe^a), 2.71 br.s (3H, NMe^b), 3.29 s [3H, N(NO)Me], 3.36 s (4H, CH_2CH_2), 7.26–7.40 m (4H, 2-H, 3-H, 7-H, 8-H). Mass spectrum, *m*/*z* (I_{rel}, %): 255 (1) $[M]^+$, 227 (1) $[M - (CH_2)_2]^+$, 211 (4) $[M - NMe_2]^+$, 210 (100) $[M - NNO - Me]^+$. Found, %: C 70.39; H 6.77; N 16.37. $C_{15}H_{17}N_3O$. Calculated, %: C 70.59; H 6.67; N 16.47.

***N,N,N′*-Trimethyl-*N′*-nitroso-4-nitronaphthalene-1,8-diamine (VIc).** Yield 40%, light yellow crystals, mp 138–139°C (from ethanol). IR spectrum, ν, cm^{-1}: 1596, 1600, 1605. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.72 br.s (6H, NMe_2), 3.23 s [3H, N(NO)Me], 7.05 d (1H, 7-H, ^3J = 8.79 Hz), 7.49 d.d (1H, 7-H, ^3J = 7.33, ^4J = 1.10 Hz), 7.74 m (1H, 6-H), 8.30 d (1H, 3-H, ^3J = 8.80 Hz), 8.83 d.d (1H, 5-H, ^3J = 7.70, ^4J = 1.10 Hz). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.68 br.s (6H, NMe_2), 3.26 s [3H, N(NO)Me], 7.23 d (1H, 2-H, ^3J = 8.74 Hz), 7.61 d.d (1H, 7-H, ^3J = 8.09, ^4J = 1.00 Hz), 7.88 m (1H, 6-H), 8.40 d (1H, 3-H, ^3J = 8.74 Hz), 8.72 d.d (1H, 5-H, ^3J = 9.71, ^4J = 1.00 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 274 (7) $[M]^+$, 244 (100) $[M - NMe_2]^+$, 229 (6) $[M - NNO - Me]^+$. Found, %: C 56.83; H 5.01; N 20.54. $C_{13}H_{14}N_4O_3$. Calculated, %: C 56.93; H 5.11; N 20.44.

***N*-Acetyl-*N,N′,N′*-trimethylnaphthalene-1,8-diamine (IX).** Compound **Va**, 0.150 g (0.8 mmol), was dissolved in 1 ml of acetic anhydride, the mixture was kept for 30 min, and the resulting dispersion was diluted with water and extracted with chloroform (2×5 ml). The solvent was evaporated to leave 0.140 g (80%) of compound **IX**. Colorless crystals, mp 70°C (from octane). IR spectrum, ν, cm^{-1}: 1592, 1600. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.84 s (3H, COMe), 2.68 s (3H, N–Me^a), 2.72 s (3H, N–Me^b), 3.35 s [3H, N(CO)Me], 7.25 m (2H, 7-H, 5-H), 7.42 m (2H, 3-H, 6-H), 7.60 d (1H, 2-H, ^3J = 7.71 Hz), 7.80 d (1H, 4-H, ^3J = 7.72 Hz). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.68 s (3H, COMe), 2.59 s (3H, N–Me^b), 2.64 s (3H, N–Me^a), 3.23 s [3H, N(CO)Me], 7.30 m (1H, 7-H), 7.43 m (3H, 3-H, 5-H, 6-H), 7.54 m (1H, 2-H), 7.69 m (1H, 4-H). Found, %: C 74.28; H 7.54; N 11.47. $C_{15}H_{18}N_2O$. Calculated, %: C 74.38; H 7.44; N 11.57.

Reaction of *N,N,N′*-trimethyl-*N′*-nitrosonaphthalene-1,8-diamine (VIa) with tetrafluoroboric acid. Compound **VIa**, 0.115 g (0.5 mmol), was dis-

solved in 5 ml of diethyl ether, 0.06 ml (0.5 mmol) of 60% HBF_4 was added, the mixture was vigorously shaken over a period of 2 min, and the precipitate was filtered off and washed with diethyl ether (2×2 ml). We thus obtained 0.03 g (25%) of salt **X** which quickly turned dark on exposure to air.

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