1-Dimethylamino-2,7-dimethoxy-8-methylamino-3,5-dinitronaphthalene and 1,2,4-tribromo-6-dimethylamino-5-methylaminoacenaphthylene: first examples of N—H...N hydrogen bond contraction/expansion in neutral 1,8-diaminonaphthalenes

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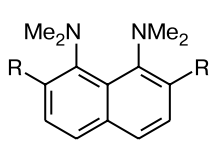
1-Dimethylamino-2,7-dimethoxy-8-methylamino-3,5-dinitronaphthalene and 1,2,4-tribromo-6-dimethylamino-5-methylaminoacenaphthylene containing the *N*,*N*,*N*′-trimethyl-1,8-diaminonaphthalene fragment with the substituted aromatic ring were studied by X-ray diffraction. Both systems are stabilized by an intramolecular hydrogen bond. The characteristics of the latter are determined by the influence of either the *ortho* substituents or the *peri*-annelated five-membered ring. In the former case, the intramolecular hydrogen bond is substantially shortened (N...N, 2.628(5) Å) due to the "buttressing effect" of the *o*-OMe groups, whereas the *peri*-dibromoethylene bridge and the Br substituent at position 4 cause a substantial elongation of the intramolecular hydrogen bond (N...N, 2.75(2) and 2.76(1) Å) in the latter case.

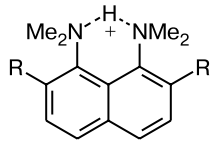
Key words: *N*,*N*,*N*′-trimethyl-1,8-diaminonaphthalenes, acenaphthylene, intramolecular hydrogen bond, crystal structure, "buttressing effect".

Among various manifestations of *peri* interactions in compounds of the naphthalene series (see, for example, Refs 1—4), intramolecular O—H...O, O—H...N, or N—H...N hydrogen bonds are of considerable importance. The ease of their formation is responsible for various conformational effects,[5] intramolecular acid catalysis,[6] and dramatic changes in the acid-base properties. For example, the surprisingly high basicity of compound **1a** (pK_a = 12.1, H_2O, 25 °C) is to a large extent determined by the formation of a strong intramolecular hydrogen bond in the cation of 1,8-bis(dimethylamino)naphthalene (**2a**, "proton sponge").[7] The low-barrier character of these hydrogen bonds and their geometry have attracted great interest both from the theoretical point of view and in the context of simulation of proton transfer processes in biological systems.[8]

The N...N distance in base **1a** is substantially longer than that in cation **2a** (2.792 [9] and 2.554 Å, respectively; Table 1), and the other geometric changes take place in the NMe_2 groups and the naphthalene ring.[2,3] Attempts to further contract the hydrogen bond in the cations of naphthalene "proton sponges," for example, by introducing bulky substituents in the *ortho* position almost failed. For example, the N...N distance in the cation of 2,7-di-



1a—c



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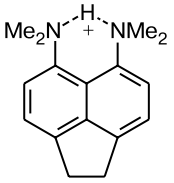

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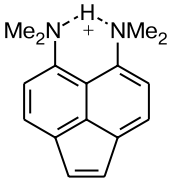

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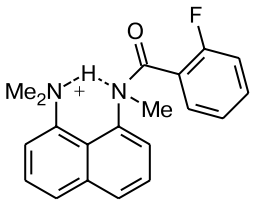

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R = H (**a**), OMe (**b**), Br (**c**)

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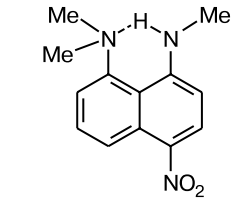
Table 1. Geometric parameters of intramolecular hydrogen bonds in cations of "proton sponges"

Compound	*d*/Å			N—H—N angle /deg	Reference
	N...N	N—H	H...N		
2a	2.554(4)	1.31(1)	1.31(1)	153(3)	10
2b	2.567(3)	1.303(7)	1.303(7)	160(3)	11
2c	2.547(3)	0.85(5)	1.73(5)	162(4)	12
3	2.666(2)	0.99(2)	1.72(2)	159(2)	13
4	2.671(3)	0.98(2)	1.75(2)	156(2)	13

methoxy derivative **2b** is even slightly longer (2.567 Å), and this distance remains virtually the same in the cation of 2,7-dibromide **2c** (2.547 Å). Apparently, this bond length is close to its lower limit.[12] By contrast, the N...N distances in the cations of acenaphthene (**3**) and acenaphthylene (**4**) "proton sponges" are, on the average, 2.67 Å (see Table 1) due to the "contracting" effect of the CH_2CH_2 and CH=CH bridges. In this class of compounds, the longest hydrogen bridge in the cation (2.90 Å) was found in amide **5**.[14]

In this connection, it is of interest to consider the properties of intramolecular hydrogen bonds in neutral *peri*-diamines, particularly, in *N*,*N*,*N*′-trimethyl-1,8-diaminonaphthalenes. Recently, we have studied the first representatives of this class of compounds, *viz.*, nitro derivatives **6** and **7**, by X-ray diffraction. It was found that, although hydrogen bonds in these compounds are very weak (N...N, 2.65 and 2.71 Å; N—H...N, 139 and 128°, respectively),[15] they have a substantial effect on the orientation of the amino groups relative to the naphthalene moiety. For example, the NHMe group is virtually coplanar with the ring in compound **6**, whereas the NHMe group in compound **7** is twisted with respect to the plane of the naphthalene ring by 26.2° (Table 2). In continuation of these observations, in the present study we performed X-ray diffraction analysis of the first representatives of this series, in which either the "buttressing effect" (**8**) or the "contracting effect" of the bridge in the *para* positions (**9**) occurs. These examples provide an insight into the possible range of hydrogen bridge contraction and expansion in neutral *peri*-diamines.



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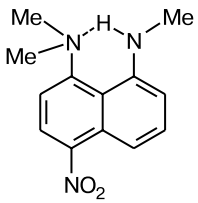

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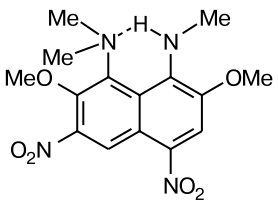

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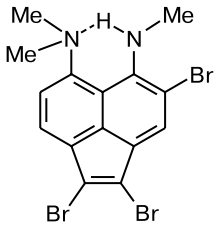

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Table 2. Principal geometric parameters of *N*,*N*,*N*′-trimethyldiaminonaphthalenes **6—9**

Parameter	**6** [a]	**7** [a]	**8** [b]	**9** [b]
Bond			*d*/Å	
N(1)...N(2)	2.650(2)	2.706(2)	2.628(5)	2.75(2); 2.76(2)
N(2)—H	0.90(2)	0.89(3)	0.93(5)	0.90; 0.90
H...N(1)	1.91(2)	2.06(3)	1.79(5)	2.13; 2.09
N(1)—C(arom.)	1.441(2)	1.407(2)	1.449(6)	1.45(2); 1.45(1)
N(2)—C(arom.)	1.341(2)	1.359(3)	1.327(6)	1.37(1); 1.37(1)
Angle			ω/deg	
N(2)—H...N(1)	139(2)	128(2)	149(5)	125; 129
NHMe ring	7.8	26.2	16.5	35.7; 30.5
NMe_2 ring	74.7	62.4	83.9	70.2; 68.3
Sum of angles[c]			ω_Σ/deg	
ΣN(1)	337.3	342.4	344.3	338.1; 336.4
ΣN(2)	359.8	355.9	359.0	360.0; 360.0

[a] The results of the study.[15]
[b] The present study.
[c] The sum of the C—N—C or C—N—H angles at the corresponding nitrogen atoms.

Experimental

X-ray diffraction data sets were collected from crystals of **8** and **9** on a KM-4 KUMA DIFFRACTION diffractometer (ω/2θ scanning technique, Mo-Kα radiation, graphite monochromator) at room temperature. The crystal structures were solved by direct methods followed by calculations of Fourier syntheses with the use of the SHELXS-97 program package.[16] The structures were refined by the full-matrix least-squares method with anisotropic displacement parameters for all non-hydrogen atoms using the SHELXL-97 program package.[16] For the structure of **9**, an absorption correction was applied using the DIFABS program.[17] The coordinates of the hydrogen atoms were calculated geometrically, except for the coordinates of the H(2) atom at the N(2) atom in compound **8**, which were determined experimentally. The main bond lengths and bond angles are given in Table 2. The crystallographic data and characteristics of X-ray diffraction study are listed in Table 3.

1-Dimethylamino-2,7-dimethoxy-8-methylamino-3,5-dinitronaphthalene (8) was prepared according to a known procedure[18] and crystallized from methanol.

1,2,4-Tribromo-6-dimethylamino-5-methylaminoacenaphthylene (9). A solution of NBS (0.71 g, 4 mmol) in DMF (5 mL) was added with vigorous stirring to a solution of 5,6-bis(dimethylamino)acenaphthylene[19] (0.24 g, 1 mmol) in DMF (5 mL) at 15 °C for 30 min. Then cooling was terminated, the mixture was diluted with water (10 mL) containing several drops of aqueous ammonia and extracted with *n*-hexane (4×4 mL), and the solvent was removed. The residue was puri-

Table 3. Crystallographic data and characteristic of X-ray diffraction study for naphthalene **8** and acenaphthylene **9**

Parameter	**8**	**9**
Molecular formula	$C_{15}H_{18}N_4O_6$	$C_{15}H_{13}Br_3N_2$
Molecular weight	350.33	461.00
T/K	293(2)	293(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	14.343(3)	11.469(2)
b/Å	7.729(2)	11.820(2)
c/Å	14.882(3)	13.164(3)
α/deg	90	78.97(3)
β/deg	99.00(3)	67.53(3)
γ/deg	90	71.77(3)
V/Å^3	1629.5(6)	1561.1(5)
Z	4	4
d_{calc}/g cm^{-3}	1.43	1.96
μ/mm^{-1}	0.112	7.743
Number of reflections: observed/independent	974/2858	4510/4309
Number of reflections with $[F_0 > 4\sigma(F_0)]$	781	1849
Number of parameters	227	362
$(2\theta)_{max}$/deg	50.12	46.10
R Factor	0.055	0.055

Note: the CCFC refcodes are 263260 (**8**) and 263261 (**9**).

fied by chromatography on silica gel ($CHCl_3$ as the eluent), and the major red fraction was collected. Tribromide **9** (0.10 g, 22%) was obtained as a red oily compound, which crystallizes from *n*-hexane during slow evaporation, m.p. 113—114 °C. Found (%): C, 39.20; H, 2.92; Br, 51.91. $C_{15}H_{13}Br_3N_2$. Calculated (%): C, 39.08; H, 2.84; Br, 52.00. IR (film), ν/cm^{-1}: 3245 (NH); 3060, 3040, 3000, 2930, 2870 (CH); 1600, 1580, 1560, 1500, 1465 (C=C + ring). ^{1}H NMR (250 MHz, $CDCl_3$), δ: 2.80 (s, 6 H, 6-NMe_2); 3.25 (s, 3 H, 5-NMe); 7.20 and 7.52 (both d, 1 H each, H(7) and H(8), $J_{7,8}$ = 7.71 Hz); 7.66 (s, 1 H, H(3)); 8.93 (br.s, 1 H, NH).

Results and Discussion

The crystal structure of **8** consists of crystallographically identical molecules $C_{15}H_{18}N_4O_6$ (Fig. 1, see Tables 2 and 3). The dihedral angle between the planes of the six-membered rings of the naphthalene fragment is 4.9°. The maximum deviation of the carbon atoms from the plane of the bicyclic fragment C(1)C(2)...C(10) (0.11 Å) is observed for the C(7) atom. The crystal structure of **9** contains two crystallographically independent molecules $C_{15}H_{13}Br_3N_2$ (hereinafter, **A** and **B**). The tricyclic fragments of molecules **A** and **B** are virtually planar; the maximum deviations of the carbon atoms from the mean plane of the acenaphthylene system are 0.09 Å (C(12A) atom of molecule **A** and C(12B) atom of molecule **B**). The maximum deviation of the bromine atom from this plane is 0.19 Å for molecule **A** (Br(1A) atom) and 0.17 Å for molecule **B** (Br(3B) atom).

In both these compounds, the bonds at the N(2) atom have the trigonal configuration, whereas the bonds at the N(1) atom assume the tetrahedral configuration (see Table 2). In molecule **8**, the methoxy groups in the *ortho* positions with respect to the nitrogen atoms exhibit the "buttressing effect,"[20] and the *peri*-nitrogen atoms approach each other to a distance of 2.628(5) Å, which is favorable for the formation of an intramolecular hydrogen bond. This bond in compound **8** is, apparently, stronger than those in compounds **6** and **7**. Taking into account the deshielding of the proton of the NH group in the ^{1}H NMR spectrum of diamine **8** (δ_H (NH) 11.33)[18]

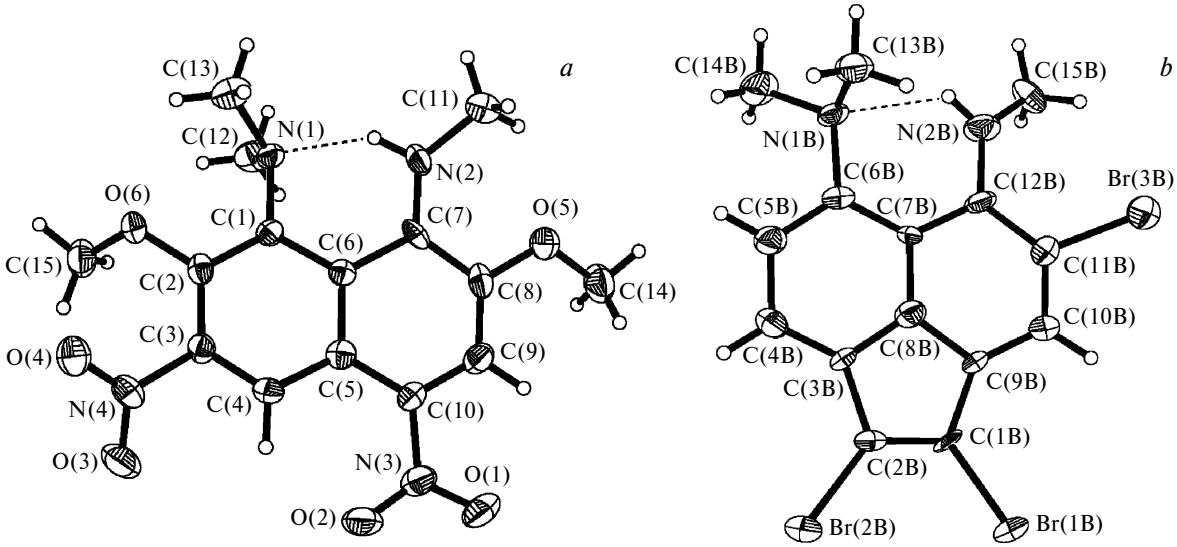

Fig. 1. Overall view of molecule **8** (*a*) and one of two independent molecules (**B**) of compound **9** (*b*) with displacement ellipsoids drawn at the 30% probability level.

and a substantially lowered N—H stretching frequency (ν(NH) 3120 cm^{-1}),[18] this conclusion can be extended to solutions as well. At the same time, as expected, the presence of the 1,2-dibromoethylene bridge in **9** leads to an increase in the distance between the N(1) and N(2) atoms to 2.75(2) and 2.76(2) Å, thus weakening the hydrogen bond compared to those in compounds **6—8**. In addition, the methylamino group in both independent molecules **9** is twisted about the N(2)—C(arom) bond by an angle of larger than 30°, resulting in weaking of the steric interaction between the C(15) and Br(3) atoms (see Table 2). This leads to the deviation of the hydrogen atom involved in the intramolecular hydrogen bond from the mean plane of the ring by 0.30 Å. As a result, not only the NH...N distance increases to 2.09—2.13 Å, but also the linearity of the N—H···N bridge substantially decreases (N—H—N, 125 and 129°). These observations are also consistent with the data for solutions. For example, the signal for the proton NH in the ^{1}H NMR spectrum of compound **9** (δ_H (NH) 8.93) is strongly shielded, and ν(NH) is shifted to higher frequencies (3245 cm^{-1}).

To summarize, we demonstrated for the first time that the parameters of the intramolecular N—H...N hydrogen bond in neutral *peri*-diamines can be changed by varying the substituents in the naphthalene ring of *N*,*N*,*N*′-trimethyl-1,8-diaminonaphthalenes, thus facilitating, in particular, hydrogen bond contraction or expansion, at least, in the range of 2.63—2.76 Å.

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