Chemistry of Heterocyclic Compounds, Vol. 44, No. 9, 2008

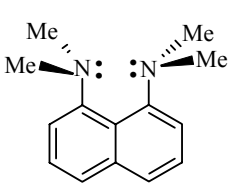
PROTON SPONGES-BASED (2-NAPHTHYL)PYRIDYLMETHANOL*

A. V. Degtyarev and A. F. Pozharskii

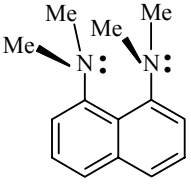
The action of 2-, 3-, and 4-pyridinecarboxaldehydes on 1,8-bis(dimethylamino)-2-lithium- and 1,8-bis(dimethylamino)-2,7-dilithiumnaphthalenes gave secondary mono- and dicarbinols containing pyridylcarbinol groups at C-2 and C-7 of the proton sponge. Spectral and X-ray diffraction structural data were used to study the molecular structure of these products.

Keywords: 1,8-bis(dimethylamino)naphthalene, (2-naphthyl)pyridylmethanols, proton sponge, intramolecular hydrogen bond.

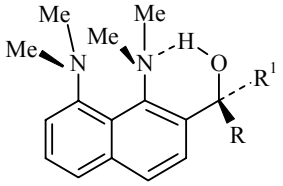
A major structural feature of all proton sponges, including 1,8-bis(dimethylamino)naphthalene (**1**), is that the axes of the unshared electron pairs of their nitrogen atoms are directed into the internitrogen space and approximately at each other (*in/in* conformation **1**), producing electrostatic repulsion [1-4], which destabilizes the base. As a result, protonation is accompanied by a considerable decrease in free energy reflected in a dramatic increase in the pK_a value. The alternative *in/out* conformation **2** is not found, probably due to steric



1

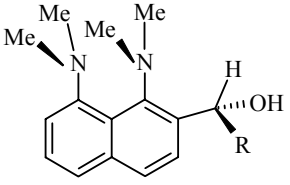


2



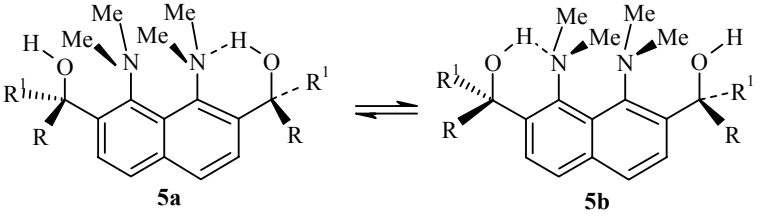
3

R, R^1 = Me, Ph



4

R = H, Me, Ph



5a **5b**

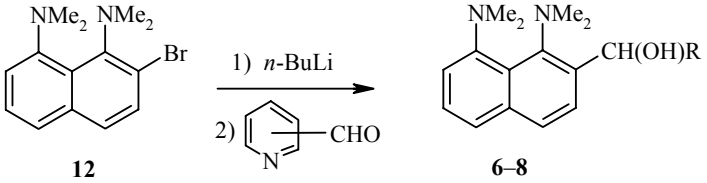
* Dedicated to Academician B. A. Trofimov, an outstanding organic chemist, who has made a major contribution to the chemistry of acetylenes and nitrogen heterocycles on the occasion of his seventieth jubilee.

South Federal University, 344090 Rostov-on-the-Don, Russia; e-mail: apozharzkii@rsu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1409-1417, September, 2008. Original article submitted April 29, 2008.

hindrance caused by the four N-methyl groups. The energy difference between conformers **1** and **2** calculated for the gas phase is ~4 kcal/mol [5]. We have recently shown that the *in/out* form can nevertheless be stabilized due to intramolecular hydrogen bonding between the *out*-inverted NMe_2 group and a suitable proton-donor substituent at C-2 [6, 7]. In particular, all tertiary alcohols are found in solution and in crystals exclusively in *in/out* form **3**, while the usual *in/in* conformation is found for secondary and primary alcohols **4**. It is interesting to note that 2,7-di-*tert* alcohols exist as rapidly interconverting nitrogen invertomers **5a** and **5b** in solution and in a monochelate form in crystals.

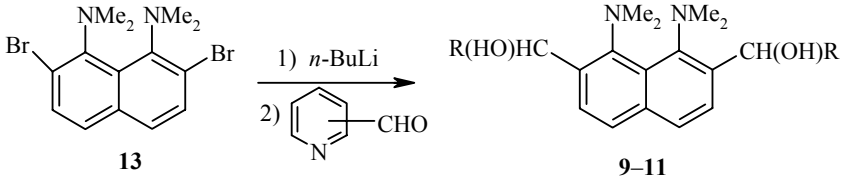
In the present work, we synthesized isomeric (2-naphthyl)pyridylmethanols and studied the structures of these products. We might have expected that some increase in the acidity of the OH group due to the electron-withdrawing effect of the pyridine ring would lead to stabilization of the *in/out* form even for secondary alcohols. Furthermore, in the case of 2-naphthyl(2-pyridyl)methanols, the aza group and NMe_2 moiety may compete for the OH group proton. This competition holds independent interest.

Monobromide **12** and dibromide **13** were taken as the starting compounds for the preparation of alcohols **6-11** as in similar cases [7, 8]. Bromides **12** and **13** were converted to the corresponding proton sponge lithium derivatives and then treated with pyridinealdehydes. The alcohol yields were only moderate since the reaction is complicated by the addition of the lithiumnaphthalenes to the pyridine ring to give very unstable dihydropyridines. Pyridylcarbinol **7** was also isolated in a small amount in the preparation of diol **10**, which may be attributed to partial protolysis of the corresponding dilithium derivative (see our earlier work [8]).



12 **6–8**

6 R = 2-Py (45%); **7** R = 3-Py (29%); **8** R = 4-Py (26%)



13 **9–11**

9 R = 2-Py (60%); **10** R = 3-Py (21%); **11** R = 4-Py (35%)

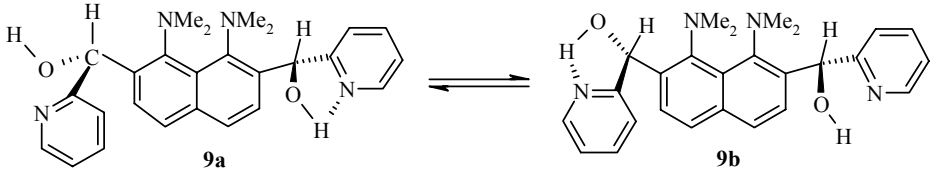
Monoalcohols **6-8** are light-brown oils, while diols **9-11** are yellow crystalline compounds. ^{1}H NMR and IR spectroscopy focusing on the OH group bands was used to analyze the conformation of these compounds in solution (when solubility was sufficient). We took into consideration that chelation involving the NMe_2 group shifts the OH signal to 10.5-10.7 ppm [6, 7], while chelation involving the 2-aza group shifts this signal to 6.0-7.7 ppm [9, 10]. In the absence of chelation due to the formation of aggregated species, within which the proton is rapidly exchanged, the OH group peak in $CDCl_3$ solution, as a rule, is not seen or is found at δ 3.5-4.5 ppm; the OH group gives a doublet at δ 5.1-5.7 ppm in DMSO-d_6 due to decomposition of the aggregated species [6, 7, 11].

The ^{1}H NMR spectra of monocarbinols **6** and **7** with 2- or 3-pyridyl groups taken in $CDCl_3$ lack a signal for the OH group, while this signal in DMSO-d_6 appears as a one-proton doublet in the vicinity of 5.9 ppm due to coupling with a CH proton. As a consequence of the poor solubility of alcohol **8**, the ^{1}H NMR spectrum of this compound could be recorded only in DMSO-d_6, where the OH group gives a doublet at δ 5.99 ppm. The

position of the OH group signal and its shape in $CDCl_3$ and DMSO-d_6 unequivocally indicate the lack of any chelation for alcohols **6-8** in solution. This conclusion may be extended to dicarbinols **10** and **11** with 3- and 4-pyridyl groups. Dicarbinol **10** acts as a typical secondary *ortho* alcohol proton sponge. For example, the ^{1}H NMR spectrum of this compound in $CDCl_3$ lacks an OH proton peak, while this peak is seen in DMSO-d_6 as a two-proton doublet at δ 6.0 ppm. As a result of the poor solubility of dicarbinol **11** in chloroform, its ^{1}H NMR spectrum was recorded only in DMSO-d_6, where the OH signal is found at δ 6.07 ppm.

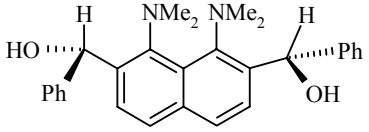
The behavior of diol **9** with 2-pyridyl groups is unique. This compound is only secondary *ortho* alcohol proton sponge presently known [6, 7], whose ^{1}H NMR spectrum in $CDCl_3$ has a two-proton OH group signal at δ 5.72 ppm. We should note that this shift is similar to the average chemical shift of OH groups in chelated (δ 6.5-7.7 ppm) [9,10] and nonchelated pyridylcarbinols (δ 3.25-4.45 ppm) [11]. Both these findings suggest that alcohol **9** exists in solution as a pair of degenerate forms **9a** and **9b**, which rapidly interconvert on the NMR time scale. The molecular models and X-ray diffraction structural analysis data (see below) indicate that such an interconversion requires only a rotation of the OH groups relative to the C_α–OH bond by 69°; the rotational barrier about a C_{sp^3}–O bond is only 1.1 kcal/mol [12].

In complete accord with these findings, the ^{1}H NMR spectrum of diol **9** in $CDCl_3$ is extremely simple and corresponds to a symmetrical structure (Table 1). The NMe_2 groups give a 12-proton singlet at δ 3.18 ppm, while the naphthalene ring protons give doublets at δ 6.95 and 7.41 ppm with coupling constants $J_{3,4} = J_{5,6} = 8.5$ Hz. This spectrum also has four two-proton signals corresponding to the pyridine rings, indicating their equivalence. The ^{1}H NMR spectrum of diol **9** in DMSO-d_6 also corresponds to a symmetrical structure (Table 1).



An X-ray diffraction structural analysis was carried out for diol **9**. Some of these results along with the analogous data [7] for related diol **14** with phenyl groups instead of 2-pyridyl groups are given in Table 2. Diol **9** exists in the *in/in* form with the pyridine rings pointing in opposite directions from the plane of the naphthalene system, strongly reminiscent of its analog **14** (Fig. 1). We should note that both the pyridine nitrogen atoms are oriented toward the hydroxyl groups but only the proton of one of these groups, O(1)–H, lies in the plane of the heterocycle and is primed for chelation with N(3) (Fig. 1*a*, here and subsequently, we give the crystallographic numbering of the atoms). The geometry of the five-membered ring thereby formed is similar to the analogous ring of similar chelates [9, 10, 13-15]. The O(2)-H group is rotated relative to the plane of the adjacent pyridine ring by 69° and efficient chelation with this group is impossible.

The molecular packing for **9** in the crystal lattice (Fig. 2) differs strongly from the packing for diol **14** due to chelation. While the molecules of **14** are packed in a complex network [7], the molecules in diol **9** form simpler hydrogen-bonded zigzag chains. The oxygen atom in the chelated O(1)–H group in these chains acts as a proton acceptor, while the nonchelated O(2)-H hydroxyl group is a proton donor.



14

IR spectra in $CDCl_3$ could be recorded only for **7** and **10** due to the poor solubility of carbinols **6-11**. These spectra show a broad band for the bound hydroxyl group at 3463-3035 cm^{-1} in addition to a narrow band for the free OH group at 3600 cm^{-1} (for **7**) and 3590 cm^{-1} (for **10**). The spectra for solid samples of **6-11** show only the short-wave length band at 3463-3035 cm^{-1} (Table 1).

Thus, there is no chelation of the hydroxyl proton with the NMe_2 group in any of the 2-hydroxypyridylmethyl and 2,7-dihydroxypyridylmethyl derivatives. On the other hand, hydrogen bonding involving one of the pyridine nitrogen atoms occurs in the crystals of the diol with a 2-pyridyl group. Evidence was obtained that this alcohol exists as an equilibrium of two degenerate O-H···N conformers due to rapid rechelation at the aza group.

TABLE 1. Hydroxyl Group Stretching Vibrations in the IR Spectra of Pyridylcarbinols **6-11** and **14**

Diol	Solvent	ν_{OH}*, cm^{-1}
6	Vaseline oil	3396, br
7	Film	3300, br
	$CHCl_3$	3600, sh; 3270, br
8	Vaseline oil	3333, br
9	Vaseline oil	3400, br
10	Vaseline oil	3270, br
	$CHCl_3$	3590, sh; 3230, br
11	Vaseline oil	3149, br
14	Vaseline oil	3350, br

* Abbreviations: sh – sharp, br – broad; only the centers of the broad bands are indicated.

TABLE 2. Some Bond Lengths (*l*) and Valence Angles for Alcohols **9** and **14**

Diol	*l*, Å				Angles, deg.		
	N(1)···N(2)	O(1)···N(3)	O–H	N(3)···H	ΣN(1)*	1-NMe_2–ring*[2]	N(3)···H–O
9	2.746	2.600	0.900*[3]	1.941	353.5 (352.7)	69 (70)	129
14*[4]	2.747	—	—	—	352.4 (352.9)	72 (72)	—

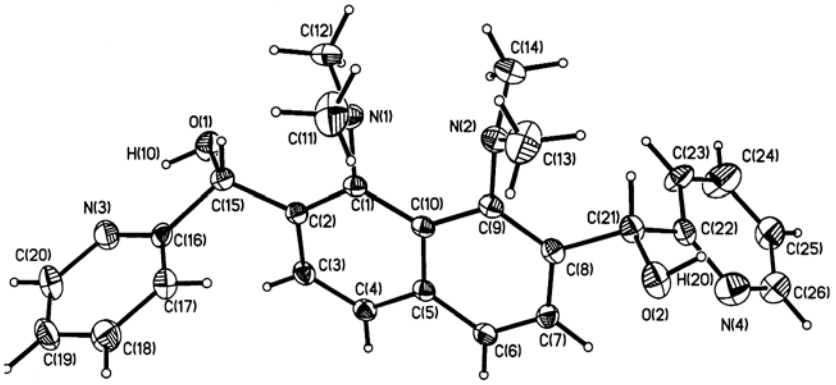
* The sum of the CNCValence angles at the nitrogen atoms. The data for the 2-NMe_2 group are given in parentheses.

*[2] Calculated at the C(2)–C(1)–N(1)–C and C(8)-C(9)-N(2)-C torsion angles, respectively. The data for the 2-NMe_2 group are given in parentheses.

*[3] For the chelated OH group.

*[4] Averaged data for the two independent molecules.

a



b

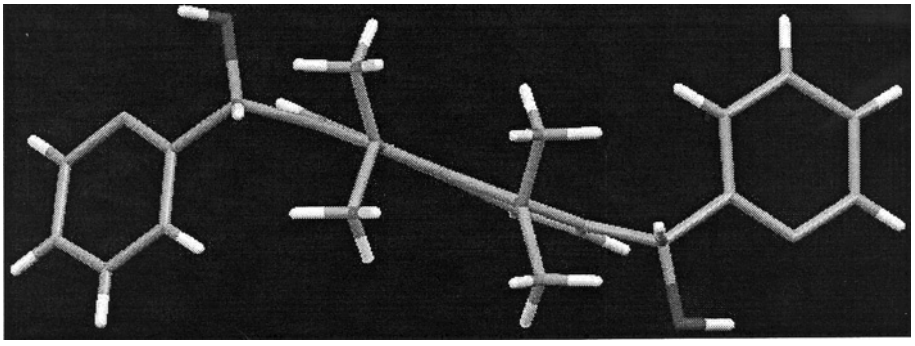


Fig. 1. Molecular structure of diol **11**: (*a*) ellipsoid model along with crystallographic numbering of the atoms, (*b*) steric model.

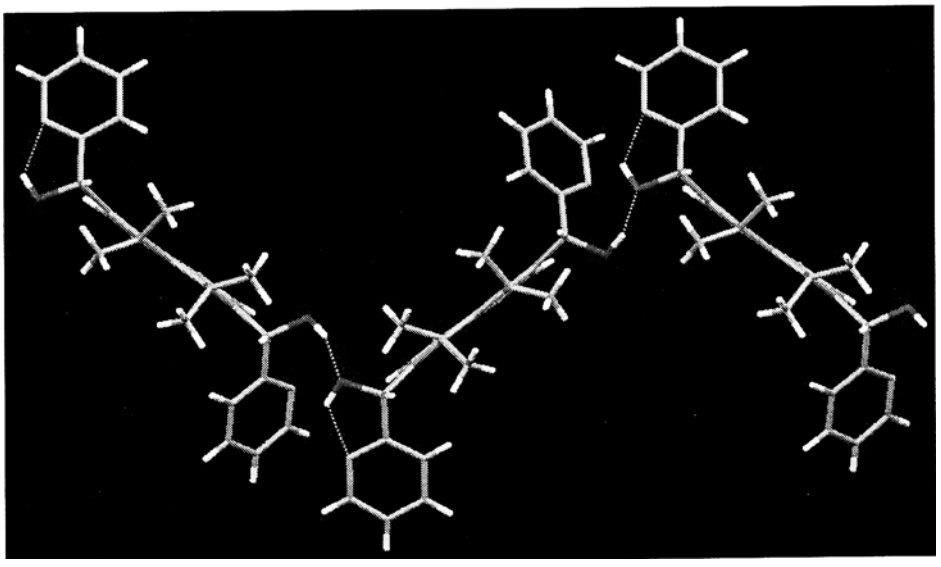


Fig. 2. Crystal structure of diol **11** showing the intramolecular and intermolecular hydrogen bonds involving the OH groups and nitrogen heteroatoms (view along the diagonal between the *a* and *c* axes from the side of the dimethylamino groups).

EXPERIMENTAL

The ^{1}H NMR spectra were taken on a Bruker DPX-250 spectrometer at 250 MHz with TMS as the internal standard. The IR spectra were taken on a Varian 1000 FT-IR spectrometer. The melting points were determined in sealed capillaries on a PTP instrument and were not corrected. The reaction course and purity of the products were monitored by thin-layer chromatography on Brockmann Grade III Activity alumina using acetonitrile as the eluent. Commercial samples of 1,8-bis(dimethylamino)naphthalene (from Aldrich, Merck, and Fluka), *n*-BuLi (1.6 M solution in hexane, from Fluka), 4-pyridinecarbaldehyde (98%, from Acros), and 3-pyridinecarbaldehyde (99%, Lancaster) were used.

X-ray Diffraction Study. Monoclinic crystals of alcohol **9** were grown slowly by evaporation of a solution in acetonitrile. The unit cell parameters at -173°C: a = 13.7706(11), b = 8.9181(7), c = 19.0787(15) Å, β = 103.889(2)°, V = 2274.5(3) Å^3, M_r = 428.52, Z = 4, space group $P2_1/c$, d_{calc} = 1.25 g/cm^3, μ(MoKα) = 0.05 mm^{-1}, F(000) = 976. The unit cell parameters and intensities of 22,886 reflections (4902 independent reflections, R_{int} = 0.0453) were measured on a Bruker SMART 1000 diffractometer using MoKα radiation, a CCD detector, graphite monochromator, and ω-scanning, $2\theta_{max}$ =54°.

The structure was solved by the direct method using the SHELXL-97 program package [16]. The positions of the hydroxyl group hydrogen atoms were found in the electron density map and refined isotropically using the riding model with $U_{iso} = nU_{eq}$ for the non-hydrogen atom bound to the given hydrogen atom (n = 1.5 for methyl groups and n =1.2 for the other hydrogen atoms). The structure was refined anisotropically relative to the F^2 map using the full-matrix method of least squares for the non-hydrogen atoms to wR_2 = 0.0923 for 3574 reflections with $I > 2\sigma(I)$. The complete crystallographic data were deposited at the Cambridge Crystallographic Data Center, No. CCDC 685190.

2-[Hydroxy(2-pyridyl)methyl]-1,8-bis(dimethylamino)naphthalene (6). A solution of *n*-BuLi (0.64 ml, 1.02 mmol) was added in an argon atmosphere with stirring and cooling to a solution of bromide **12** (0.3 g, 1.02 mmol) in dry ether (5 ml). The mixture was stirred for 15 min at -20°C and then 2-pyridinecarbaldehyde (0.09 ml, 1.02 mmol) was added. The reaction mixture was maintained with cooling for 24 h and then cooling was terminated. The mixture was brought to room temperature and decomposed by adding water (10 ml). The ethereal layer was separated and the aqueous layer was extracted with five portions (5 ml) chloroform. The extracts were combined and evaporated. The residue was separated by preparative thin-layer chromatography to give alcohol **6** (0.147 g, 45) as a light-brown oil, R_f 0.11 (acetonitrile). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): 2.68 (3H, s, 8-N(CH_3)$_2$); 2.84 (3H, s, 8-N(CH_3)$_2$); 3.06 (6H, s, 1-N(CH_3)$_2$); 6.3 (1H, s, C<u>H</u>(OH)-2Py); 6.96 (1H, br. d, J = 7.9, H-7); 7.08 (1H, d, J = 8.53, H-3); 7.13-7.18 (2H, m, H-5, H$_{Py}$-4); 7.29 (1H, t, J = 7.58, H-6); 7.37-7.43 (2H, m, H-4, H$_{Py}$-3); 7.53 (1H, td, J = 1.74, J = 7.66, H$_{Py}$-5); 8.58 (1H, d, J = 4.9, H$_{Py}$-6). ^{1}H NMR spectrum (DMSO–d_6), δ, ppm (J, Hz): 2.68 (6H, br. s, 8-N(CH_3)$_2$); 2.87 (6H, s, 1-N(CH_3)$_2$); 5.89 (1H, d, J = 4.74, CH(O<u>H</u>)-2Py); 6.19 (1H, d, J = 4.74, C<u>H</u>(OH)-2Py); 7.11 (1H, dd, J = 1.1, J = 7.43, H-7); 7.16-7.21 (1H, m, H$_{Py}$-4); 7.28 (1H, t, J = 7.74, H-6); 7.37-7.43 (3H, m, H-3,5, H$_{Py}$-3); 7.48 (1H, d, J = 8.53, H-4); 7.74 (1H, td, J = 1.9, J = 7.75, H$_{Py}$-5); 8.43 (1H, d, J = 4.74, H$_{Py}$-6). Found, %: C 74.71; H 7.2; N 13.09. $C_{20}H_{23}N_3O$. Calculated, %: C 74.74; H 7.21; N 13.07.

2-[Hydroxy(3-pyridyl)methyl]-1,8-bis(dimethylamino)naphthalene (7) was obtained analogously to naphthalene **6** from bromide **12** (0.3 g, 1.02 mmol) and 3-pyridinecarbaldehyde (0.09 ml, 1.02 mmol) as a light-brown oil. The yield of **7** was 29% (0.095 g), R_f 0.03 (acetonitrile). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): 2.62 (3H, s, 8-N(CH_3)$_2$); 2.74 (3H, s, 8-N(CH_3)$_2$); 2.83 (6H, s, 1-N(CH_3)$_2$); 6.29 (1H, s, C<u>H</u>(OH)-Py); 7.20-7.71 (7H, m, H-3,4,5,6,7, H$_{Py}$-4,5); 8.47 (1H, br. d, J = 3.47, H$_{Py}$-6); 8.62 (1H, br. s, H$_{Py}$-2). ^{1}H NMR spectrum (DMSO–d_6), δ, ppm (J, Hz): 2.59 (6H, s, 8-N(CH_3)$_2$); 2.78 (6H, s, 8-N(CH_3)$_2$); 5.95 (1H, d, J = 3.86, CH(O<u>H</u>)-3Py); 6.2 (1H, J = 3.86, C<u>H</u>(OH)-3Py); 7.14-7.75 (7H, m, H-3,4,5,6,7, H$_{Py}$-4,5); 8.07-8.44 (2H, m, H$_{Py}$-2,6). Found, %: C 74.72; H 7.19; N 13.1. $C_{20}H_{23}N_3O$. Calculated, %: C 74.74; H 7.21; N 13.07.

2-[Hydroxy(4-pyridyl)methyl]-1,8-bis(dimethylamino)naphthalene (8) was obtained analogously to naphthalene **6** from bromide **12** (0.3 g, 1.02 mmol) and 4-pyridinecarbaldehyde (0.09 ml, 1.02 mmol) as a light-brown oil. The yield of **8** was 26% (0.085 g), R_f 0.16 (acetonitrile). ^{1}H NMR spectrum (DMSO–d_6), δ, ppm (*J*, Hz): 2.57-2.88 (12H, m, 1-N(CH_3)$_2$; 8-N(CH_3)$_2$); 5.99 (1H, d, *J* = 4.54, CH(O<u>H</u>)-4Py); 6.12 (1H, d, *J* = 4.54 (C<u>H</u>(OH)-4Py); 7.12 (1H, dd, *J* = 1.18, *J* = 7.41, H-7); 7.17 (2H, d, *J* = 5.99, H_{Py}-3,5); 7.26 (1H, t, *J* = 7.89, H-6); 7.31 (1H, d, *J* = 8.59, H-3); 7.39 (1H, dd, *J* = 0.96, *J* = 8.53, H-5); 7.47 (1H, d, *J* = 8.59, H-4); 8.38 (1H, d, *J* = 5.99, H_{Py}-2,6). Found, %: C 74.72; H 7.22; N 13.06. $C_{20}H_{23}N_3O$. Calculated, %: C 74.74; H 7.21; N 13.07.

2,7-Di[hydroxy(2-pyridyl)methyl]-1,8-bis(dimethylamino)naphthalene (9). A solution of *n*-BuLi (1.07 ml, 1.6 mmol) was added with stirring and cooling in an argon atmosphere to a solution of dibromide **13** (0.3 g, 0.81 mmol) in dry ether (5 ml). The mixture was stirred for 15 min at -20°C and then, 2-pyridinecarbaldehyde (0.15 ml, 1.62 mmol) was added. The reaction mixture was maintained with cooling for 24 h and then, cooling was terminated. The mixture was brought to room temperature and decomposed by adding 10 ml water. The ethereal layer was separated and the aqueous layer was extracted with five portions (5 ml) chloroform. The extracts were combined and evaporated. The residue was separated by preparative thin-layer chromatography to give 0.207 g (60%) alcohol **9** as yellow crystals, mp 235-236°C (acetonitrile), R_f 0.01 (acetonitrile). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.18 (12H, br. s, 1-N(CH_3)$_2$, 8-N(CH_3)$_2$); 5.72 (2H, d, *J* = 3.28, CH(O<u>H</u>-2Py); 6.21 (2H, d, *J* = 3.28, C<u>H</u>(OH)-2Py); 6.95 (4H, m, H-3,6, H_{Py}-3,3'); 7.20 (2H, m, H_{Py}-4,4'); 7.41 (2H, d, *J* = 8.48, H-4,5); 7.56 (2H, td, *J* = 1.54, *J* = 7.14, H_{Py}-5,5'); 8.66 (2H, d, *J* = 4.76, H_{Py}-6,6'). ^{1}H NMR spectrum (DMSO–d_6); δ, ppm (*J*, Hz): 2.98 (12H, br. s, 1-N(CH_3)$_2$, 8-N(CH_3)$_2$); 5.95 (2H, br. s, CH(O<u>H</u>)-2Py); 6.15 (2H, br. s, C<u>H</u>(OH)-2Py); 7.18-7.24 (4H, m, H-3,6, H_{Py}-4,4'); 7.47 (2H, d, *J* = 8.42, H-4,5); 7.57 (2H, d, *J* = 7.74, H_{Py}-3,3'); 7.79 (2H, td, *J* = 1.85, *J* = 7.48, H_{Py}-5,5'); 8.42 (2H, d, *J* = 3.87, H_{Py}-6,6'). Found, %: C 72.85; H 6.60; N 13.03. $C_{26}H_{28}N_4O_2$. Calculated, %: C 72.87; H 6.59; N 13.07.

2,7-Di[hydroxy(3-pyridyl)methyl]-1,8-bis(dimethylamino)naphthalene (10) was obtained analogously to naphthalene **9** from dibromide **13** (0.3 g, 0.81 mmol) and 3-pyridinecarbaldehyde (0.15 ml, 1.62 mmol) as yellow crystals, mp 140-142°C (acetonitrile). The yield was 21% (0.073 g), R_f 0.01 (acetonitrile). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.93 (12H, s, 1-N(CH_3)$_2$, 8-N(CH_3)$_2$); 6.33 (2H, s, C<u>H</u>(OH)-3Py); 7.22-7.33 (4H, m, H-3,6, H_{Py}-5,5'); 7.6 (2H, d, *J* = 8.49, H-4,5); 7.71 (2H, d, *J* = 8.1, H_{Py}-4,4'); 8.48 (2H, d, *J* = 5.02, H_{Py}-6,6'); 8.59 (2H, br. s, H_{Py}-2,2'). ^{1}H NMR spectrum (DMSO–d_6), δ, ppm (*J*, Hz): 2.85 (12H, s, 1-N(CH_3)$_2$, 8-N(CH_3)$_2$); 6.0 (2H, d, *J* = 4.63, CH(O<u>H</u>)-3Py); 6.14 (2H, d, *J* = 4.63, C<u>H</u>(OH)-3Py); 7.26-7.34 (4H, m, H-3,6, H_{Py}-5,5'); 7.53-7.59 (4H, m, H-4,5, H_{Py}-4,4'); 8.37-8.49 (4H, m, H_{Py}-2,2',6,6'). Found, %: C 72.89; H 6.57; N 13.03. $C_{26}H_{28}N_4O_2$. Calculated, %: C 72.87; H 6.59; N 13.07.

2,7-Di[hydroxy(4-pyridyl)methyl]-1,8-bis(dimethylamino)naphthalene (11) was obtained analogously to naphthalene **9** from dibromide **13** (0.3 g, 0.81 mmol) and 4-pyridinecarbaldehyde (0.15 ml, 1.62 mmol) as yellow crystals, mp 212-215°C (acetonitrile), R_f 0.03 (acetonitrile). The yield of **11** was 35% (0.121 g). ^{1}H NMR spectrum (DMSO–d_6), δ, ppm (*J*, Hz): 3.0 (12H, s, 1-N(CH_3)$_2$, 8-N(CH_3)$_2$); 6.07 (2H, d, *J* = 4.6, CH(O<u>H</u>)-4Py); 6.11 (2H, d, *J* = 4.6, C<u>H</u>(OH)-4Py); 7.16 (2H, d, *J* = 8.42, H-3,6); 7.28 (4H, d, *J* = 5.68, H_{Py}-3,3', 5,5'); 7.54 (2H, d, *J* = 8.42, H-4,5); 8.48 (4H, d, *J* = 5.68, H_{Py}-2,2',6,6'). Found, %: C 72.84; H 6.57; N 13.1. $C_{26}H_{28}N_4O_2$. Calculated, %: C 72.87; H 6.59; N 13.07.

This work was carried out with the financial support of the Russian Basic Research Fund (Grants Nos. 05-03-32110a and 08-03-00028-a). The X-ray diffraction investigation was carried out by Z. A. Starikova at the Institute of Organoelement Compounds of the Russian Academy of Sciences, to whom the authors express their gratitude.

REFERENCES

1. A. F. Pozharskii and V. A. Ozeryanskii, *Proton Sponges*, in: Z. Rappoport (editor), *The Chemistry of Anilines,* J. Wiley & Sons, Chichester (2007), Part 2, Chap. 17.
2. A. F. Pozharskii, *Usp. Khim.*, **67**, 3 (1998).
3. H. Einspahr, J.-B. Robert, R. E. Marsh, and J. D. Roberts, *Acta Crystallogr.*, **B29**, 1611 (1973).
4. P. R. Mallinson, K. Wozniak, C. C. Wilson, K. I. McCormack, and D. S. Yufit, *J. Am. Chem. Soc.*, **121**, 4640 (1999).
5. A. Szemik-Hojniak, J. M. Zwier, W. J. Buma, R. Bursi, and J. H. Van der Waals, *J. Am. Chem. Soc.*, **120**, 4840 (1998).
6. A. V. Pozharskii, O. V. Ryabtsova, V. A. Ozeryanskii, A. V. Degtyarev, Z. A. Starikova, L. Sobczyk, and A. Filarowski, *Tetrahedron Lett.*, **46**, 3973 (2005).
7. A. V. Pozharskii, A. V. Degtyarev, O. V. Ryabtsova, V. A. Ozeryanskii, M. E. Kletskii, Z. A. Starikova, L. Sobczyk, and A. Filarowski, *J. Org. Chem.*, **72**, 3006 (2007).
8. A. F. Pozharskii, O. V. Ryabtsova, V. A. Ozeryanskii, A. V. Degtyarev, O. N. Kazheva, G. G. Alexandrov, and O. A. Dyachenko, *J. Org. Chem.*, **68**, 10109 (2003).
9. H. Kotsuki, H. Hayakawa, H. Tateishi, M. Wakao, and M. Shiro, *Tetrahedron: Asymmetry*, **9**, 3203 (1998).
10. J. J. Görlitz, P. Nielsen, H. Toftlund, and A. D. Bond, *Acta Crystallogr.*, **E60**, 1319 (2004).
11. F. Rahm, A. Fisher, and C. Moberg, *Eur. J. Org. Chem.*, 4205 (2003).
12. E. V. Anslyn and D. A. Dougherty, *Modern Physical Organic Chemistry*, University Science Books, Sausalito, California, 2006, p. 97.
13. G. Ferguson, C. D. Carrol, C. Glidewell, C. H. Zakaria, and A. J. Lough, *Acta Crystallogr.*, **B51**, 367 (1995).
14. F. R. Keene, M. R. Snow, and R. T. Tiekink, *Acta Crystallogr.*, **C44**, 937 (1988).
15. E. Skrzypczak-Jankun and Z. Kaluski, *Acta Crystallogr.*, **B37**, 768 (1981).
16. G. M. Sheldrick, SHELXTL*, Structure Determination Software Suite, Bruker AXS*, V. 5.10, Madison, Wisconsin, 1998.