Oxidation of 1-amino-4,5-bis(dimethylamino)naphthalene as a route to the double "proton sponges" based on dibenzo[*a*,*h*]phenazine and 1,1′-azonaphthalene

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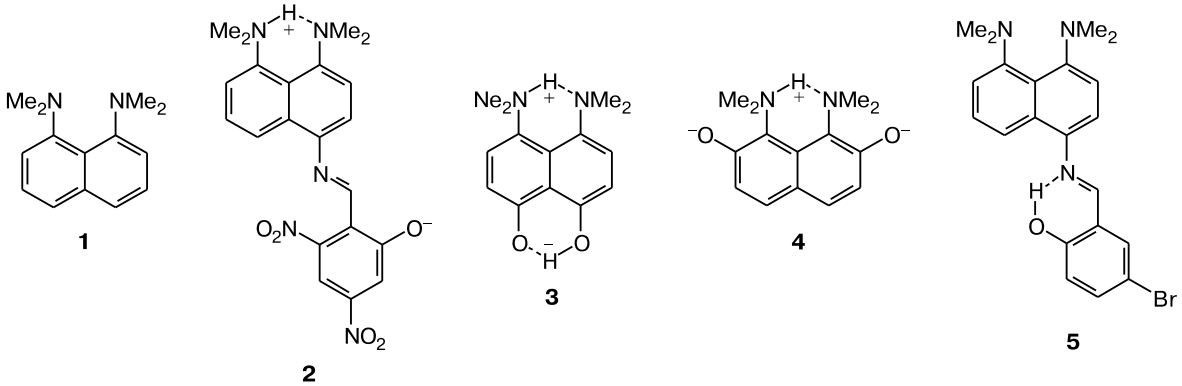
Behavior of 4-amino-1-dimethylamino- and 1-amino-4,5-bis(dimethylamino)naphthalenes sharply differs on their treatment with tosyl chloride and oxidation with the Bu^tOK/O_2 system. While the former upon the action of tosyl chloride in protic media is transformed to sulfonamide, the latter unexpectedly forms 4,5,11,12-tetrakis(dimethylamino)dibenzo[*a*,*h*]phenazine in ~20% yield as a product of the competitive reaction, which represents the earlier unknown type of double "proton sponges". In contrast to this, the oxidative dimerization of the indicated amines with Bu^tOK/O_2 leads to 5,12-bis(dimethylamino)dibenzo[*a*,*h*]phenazine and 4,5,4′,5′-tetrakis(dimethylamino)-1,1′-azonaphthalene, respectively. Possible mechanisms of these reactions were considered, as well as problems of coloring, solvatochromism, and protonation of the compounds obtained.

Key words: naphthylamines, "proton sponge", tosylation, oxidative dimerization, dibenzo[*a*,*h*]phenazine, 1,1′-azonaphthalene, protonation, solvatochromism.

It is known that 1,8-bis(dimethylamino)naphthalene derivatives ("proton sponge", **1**) containing phenol hydroxyls as substituents frequently exist in the chelated zwitterionic form, for example, compounds **2**—**4** (see Refs 1—4). If the proton of the OH group possesses reduced acidity, as in the case of compounds **5** (see Ref. 2), no its transfer to the *peri*-NMe_2 groups takes place. On the whole, however, the factors determining a possibility of the labile protons transfer in this series remain poorly studied.[5—7]

Taking into account this circumstance, the initial goal of the present work consisted in the studies of 1-tosylamino derivative **6**. We assumed that since the NH-acidity of benzenesulfonanilides (pK_a 9—11, H_2O)[8] is comparable with the basicity of the proton sponge (pK_a 12.1, H_2O),[1] the proton transfer from the amide nitrogen atom to the amine ones will be a possible process, too.

Compound **6** was obtained by treatment of amine **7** with tosyl chloride (1.1 equiv.) in boiling ethanol. This at first glance simple reaction unexpectedly led to the formation of a complex mixture of compounds, including resins, from which the target sulfonamide **6** was isolated in only 5% yield. More than 55% of the starting amine **7** was regenerated due to its protonation by the acid formed in the course of the reaction, whereas the major product (20% yield) was compound **8**, the earlier unknown double proton sponge of the dibenzo[*a*,*h*]phenazine series (Scheme 1).



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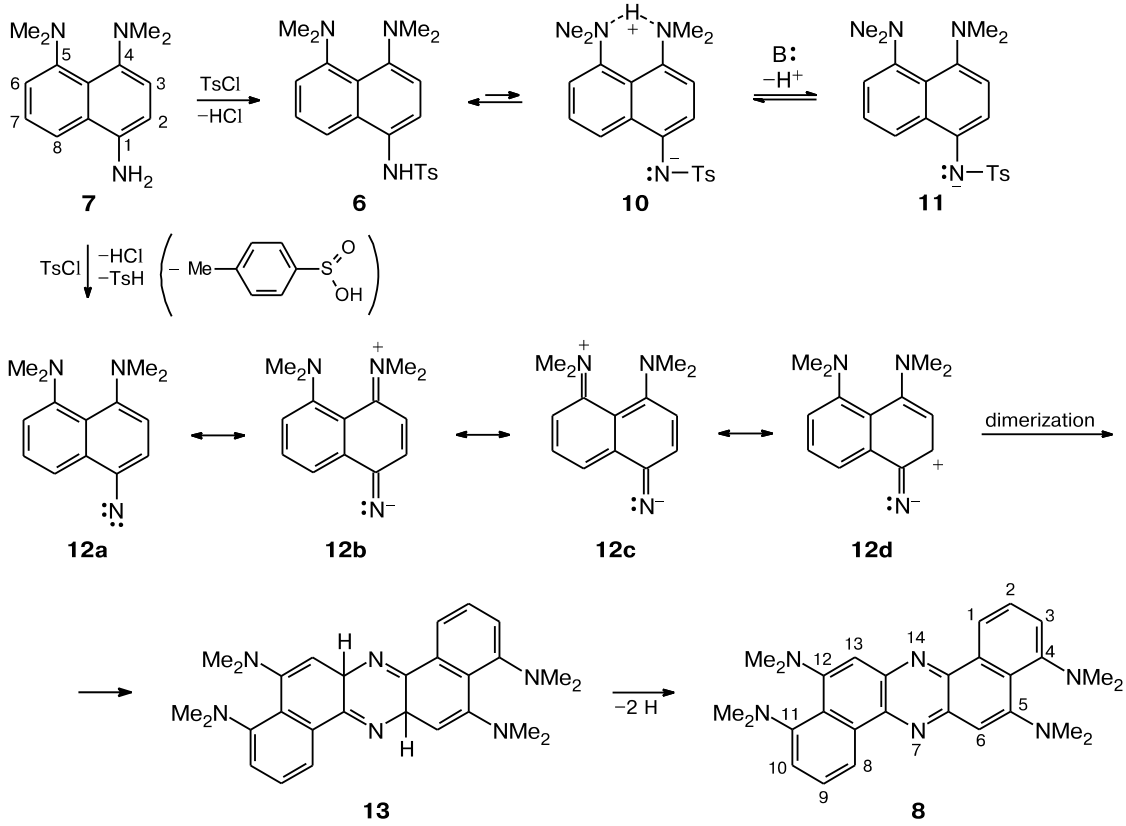
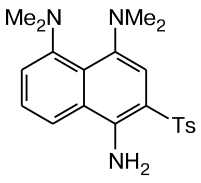
Scheme 1



Similar experiments with additions of external bases (AcONa, AcOK, pyridine), as well as with reduction of the temperature to ambient, also led to the formation of **8** in 15—18% yield; the yield of **8** decreases to 12% if the reaction is carried out under argon.

The more in detail studies of the reaction mixture (^{1}H NMR, $CDCl_3$) showed that it contains, in addition to the starting amine **7**, sulfonamide **6**, phenazine **8**, and one more compound, to which was assigned the structure of 1-amino-4,5-bis(dimethylamino)-2-tosylnaphthalene (**9**).



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The ^{1}H NMR spectrum of compound **9** exhibits a broad two-proton singlet of the NH_2 group at δ 5.6, four signals for the protons of the naphthalene ring, and a standard set of peaks for the tosyl group. Unfortunately, we did not succeeded in the complete separation of sulfone **9** from phenazine **8** because of their close chromatographic lability, the small content in the reaction mixture (4%), and the tendency to oxidation. We assume that the formation of **9** is a result of electrophilic sulfonylation of position 2 activated with the amino group.

Sulfonamide **6**, unlike aminosulfone **9**, is stable in air and in solution. The proton of the NHTs group in compound **6** has characteristics usual for sulfonamides (ν_{NH} 3233 cm^{-1} (KBr), $\delta_{\underline{N}H}$ 6.47 ($CDCl_3$), 9.69 (DMSO-d_6)), that indicates the absence of the zwitterionic form **10** (see Scheme 1) and, consequently, the intramolecular proton transfer.

The polycyclic conjugated structure of phenazine **8** was confirmed by the NMR, IR, and UV spectroscopic data, as well as by mass spectrometry. Compound **8** possesses pronounced polymorphism, and orange needles and dark red plates are simultaneously formed under conditions of isothermic crystallization from ethyl acetate. X-ray diffraction studies were carried out for the both forms (Fig. 1, Table 1). The molecular structures of the polymorphic modifications differ insignificantly (the differences in bond lengths and nonvalent distances seldom exceed 1%), however, in the red polymorph, the NMe_2 groups are somewhat better conjugated with the aromatic π-system, which is in particular indicated by the shorter N(1)—C(1) and N(2)—C(9) bonds and the larger sum of the bond angles (ΣN) at the nitrogen atoms (see Table 1). This can be a consequence of more compact parallel arrangement of the orange polymorph molecules in the crystal, whereas a perpendicular arrangement is characteristic of the red polymorph molecules, that provides higher conformational lability for the amino groups to be conjugated (Fig. 2).

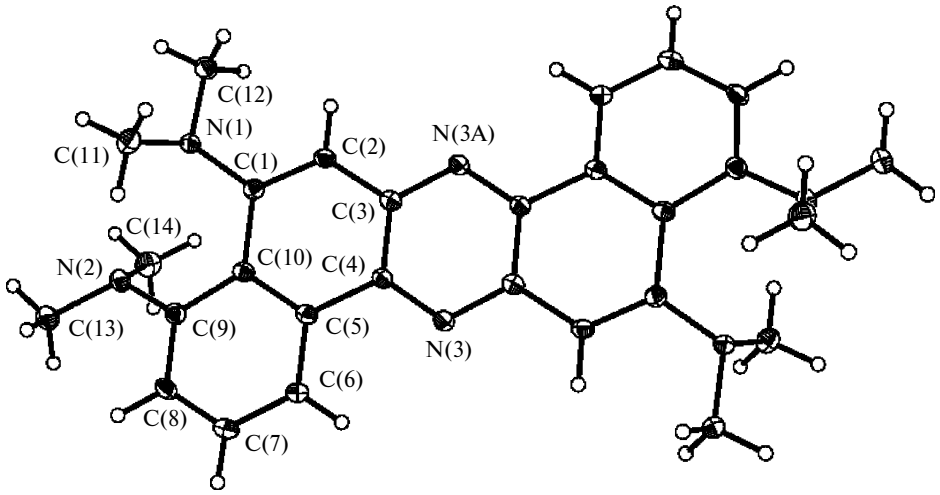


Fig. 1. The general view of the dibenzophenazine molecule **8** (triclinic orange polymorph). The ellipsoids of the atoms thermal movement are shown on the 30% level.

Apparently, the intermolecular charge transfer has lower effect on the coloring differences between the forms, since the stacking-interaction are absent in both polymorphs.

Though there are no examples of the formation of phenazines from arenesulfonamides in the literature,[9] initially we suggested that the reaction yet proceeds *via* sulfonamide **6**. Its deprotonation (with the starting substrate or by the intramolecular proton transfer) with subsequent fragmentation of the anion **11** with elimination of the tosyl anion could have give nitrene **12** stabilized, like 1-naphthylmethyl carbocations based on the proton sponge,[10,11] by the strong donor effect of the *peri*-NMe_2 group (see Scheme 1, structures **12a**—**d**). Nitrene **12** can be considered as a natural precursor of phenazine **8** formed through the cyclodimerization of the resonance structure **12d** and subsequent oxidation of dihydrophenazine **13** with the air oxygen or the nitrene itself (on the examples of transformation of nitrenes to phenazines see Refs 12—14).

However, it turned out that the amide **6** is not involved into the formation of **8**. In fact, we obtained sulfonamide **6** in about 40% yield upon treatment of amine **7** with tosyl chloride in aprotic medium ($CHCl_3$, pyridine, 0 °C, *cf.* Ref. 15), with the phenazine **8** forming under these conditions only in trace amounts. This result gave us an opportunity to carry out a number of special experiments with amide **6**. Thus, NMR monitoring of the solution of **6** in DMSO-d_6 (25 °C, 28 days) did not show any signs of its transformation to compound **8**. If a small excess of powdered KOH was added to the NMR tube, the amide proton of the NH group rapidly disappeared due to the for-

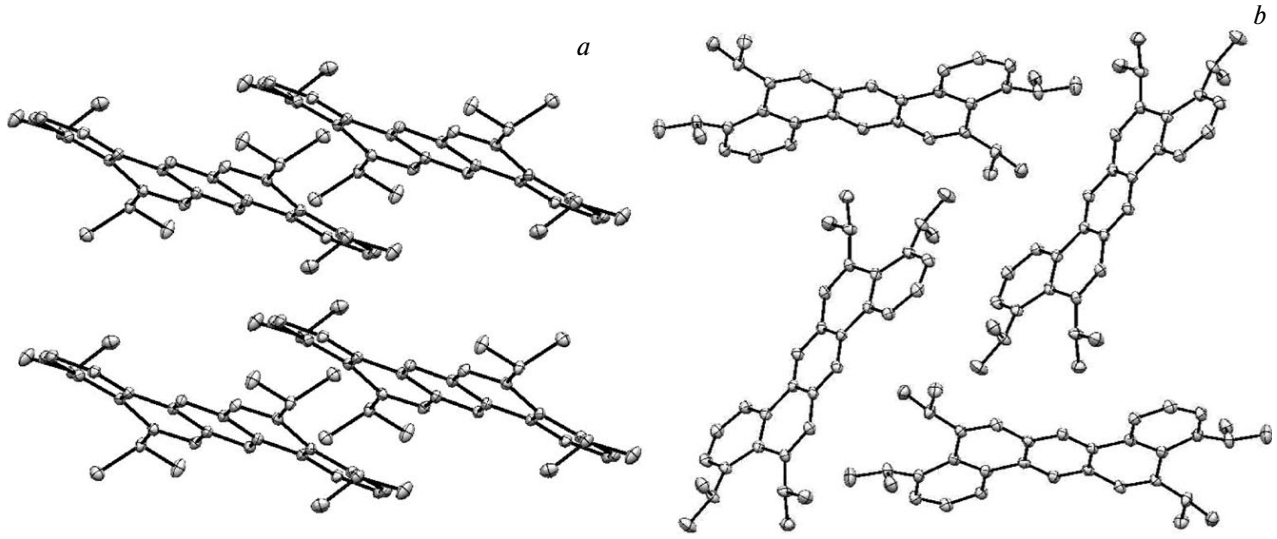


Fig. 2. The fragments of the crystal structure of orange (*a*) and red (*b*) polymorphs of dibenzophenazine **8**. Hydrogen atoms are not shown.

Table 1. Principal crystallographic parameters of the dibenzophenazine **8** polymorphic modifications

Parameter	Polymorph	
	Needles	Plates
Bond	*d*/Å	
N(1)...N(2)	2.805(2)	2.785(2)
N(1)—C(1)	1.410(2)	1.393(2)
N(2)—C(9)	1.417(2)	1.400(3)
Angle	ω/deg	
N(1)Me_2—ring	36	32
N(2)Me_2—ring	39	40
ΣN(1)/ΣN(2)[a]	340.7/341.3	348.0/347.9
ΔN(1)/ΔN(2)[b]	0.395/0.592	0.434/0.638

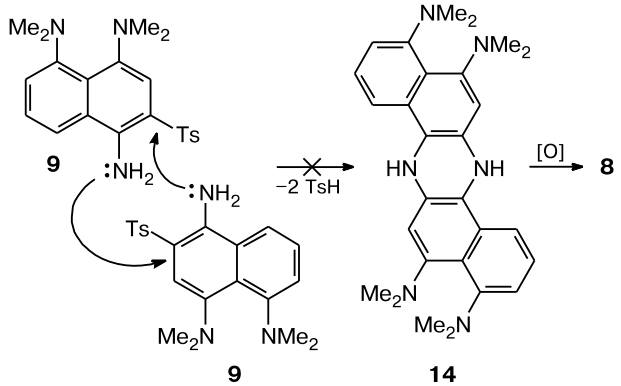
[a] The sum of the C—N—C angles at the corresponding nitrogen atoms.
[b] Deviation of the nitrogen atoms of the amino groups from the average plane of the pentacyclic dibenzophenazine system, Å.

mation of *N*-anion **11**, which did not change not only on reflux in DMSO, but also on bubbling oxygen through the solution over 1 h. Note that compound **6** remained unchanged after 48 h of stirring in the $KOBu^t/O_2$/PhMe system,[16] as well as on reflux in chloroform, ethanol, or ethanol in the presence of AcONa (1 equiv.), AcOH (1 equiv.), or concentrated HCl. Likewise for other arylsulfonamides, the quantitative detosylation of amide **6** to amine **7** occurred only in conc. H_2SO_4 (25 °C, 1 h); let us to note that the salts of amine **7**, for example **7** · HBF_4, do not react with tosyl chloride in boiling EtOH.

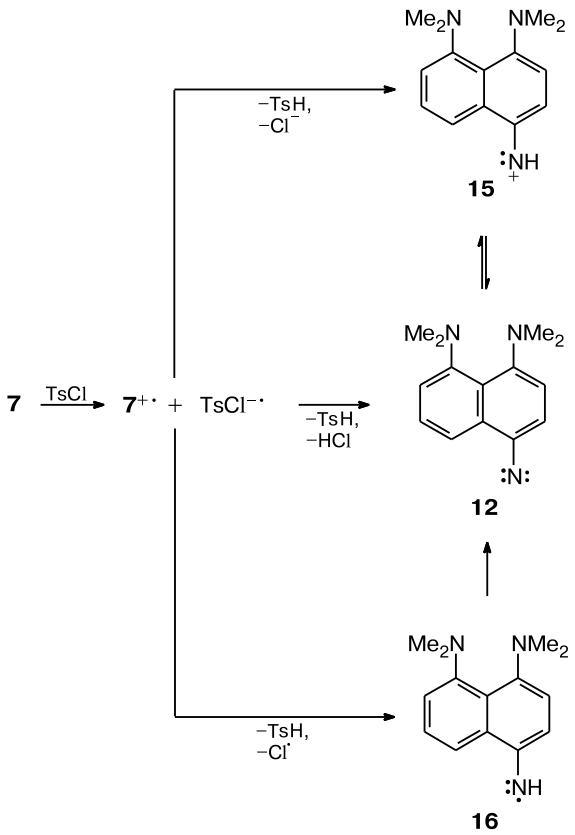
As yet another possible pathway for the formation of compound **8**, one can consider nucleophilic cyclodimerization of aminosulfone **9** with subsequent oxidation of dihydrophenazine **14** (Scheme 2). However, this possibility was excluded, since compound **9** isolated, as it was already mentioned above, with the admixture of **8**, did not change on heating in EtOH in air or chromatography on Al_2O_3 (only gradual resinification of **9** occurred).

Proceeding from the aforementioned, it seems the most probable that phenazine **8** is formed as a result of oxidation of amine **7** with tosyl chloride, with the radical cation $\mathbf{7}^{+\cdot}$ being generated in the first step, which further gives the aminyl cation **15**, radical **16**, or nitrene **12** (Scheme 3). Indirectly this is confirmed by three facts. First, no transformation **7** → **8** takes place at all in the absence of tosyl chloride. Second, sulfonyl halides have positive enough values of reducing potentials ($E_{red}^{1/2}$ = –0.13 V for $PhSO_2Cl$, 75% dioxane, saturated calomel electrode[17]), whereas the ionization potential of the proton sponge (IP_1 = 7.05 eV)[18] is very low and should be still lower for the easily oxidized in air amine **7**. Third, 4-amino-1-dimethylaminonaphthalene (**17**) upon treatment with tosyl chloride (1 equiv., ethanol) gives sulfonamide **18** as the major product (50%) (Scheme 4), that agrees with the significantly higher value of IP_1 = 7.50 eV for 1-dimethylaminonaphthalene.[18]

Scheme 2

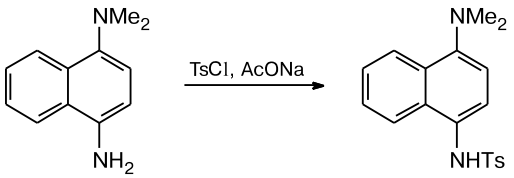


Scheme 3



The most difficult question to answer is which of the three species, **12**, **15**, or **16**, is the main precursor of phenazine **8**. Taking into account the aforementioned tendency of *peri*-NMe_2 groups to stabilize electron-deficient cen-

Scheme 4



17 **18**

ters, we give our preference to the cation **15** and in lower extent to the nitrene **12**. In fact, if the nitrene **12** would have been involved into the reaction, one should have expected[12—14,19] formation of the corresponding azo compound (see below) along with compounds **6** and **8**. Meanwhile, we did not observe even traces of its presence in the mixture during tosylation of amine **7** in EtOH or other solvents (chloroform, pyridine, acetonitrile). However, the situation significantly changed when amine **7** was treated with a four-fold excess of potassium *tert*-butoxide in toluene at room temperature with simultaneous bubbling oxygen through the solution (earlier,[16] this system has been recommended for the synthesis of various dibenzo[*a*,*h*]-phenazines). In our case, the earlier unknown 4,5,4′,5′-tetrakis(dimethylamino)-1,1′-azonaphthalene (**19**) was the major reaction product formed in 20% yield, while the yield of phenazine **8** did not exceed 5% (Scheme 5). Since formation of the aminyl cation **15** and partially nitrene **12** is very unlikely in the strong basic medium, we assume that the radical **16**, which is formed by the oxidation[16] of anion **20**, is the major intermediate in this case. Then, the formation of compounds **8** and **19** can be explained by the oxidative dimerization of the *N*-centered (**16a**) or *C*-centered (**16b**) forms of the radical **16**, respectively. It seems to us that the structure **16a** contributes more due to the strong +*M*-effect of the dimethylamino groups.

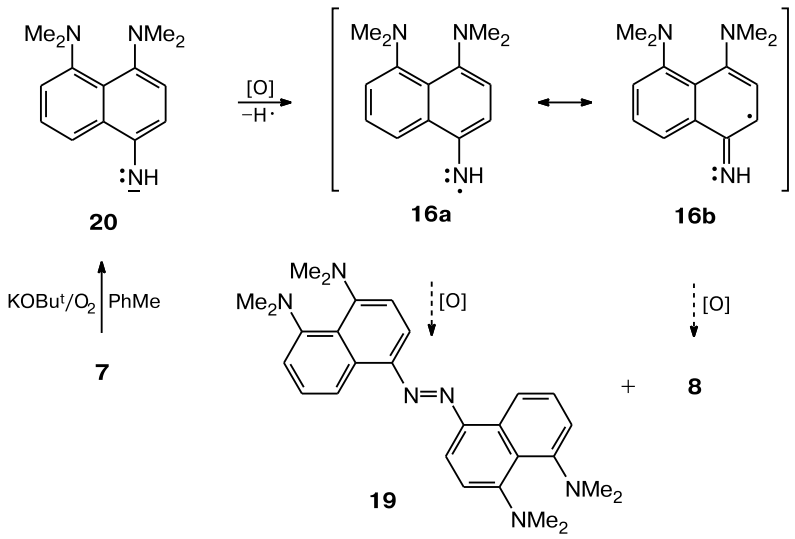
According to the data obtained in the present work, oxidation of amine **17** in the $KOBu^t/O_2$/PhMe system gives 28% of phenazine **21**, whereas the literature[16] reports that α-naphthylamine **22** under the same conditions gives dibenzo[*a*,*h*]phenazine **23** in 79% yield (Scheme 6). In our opinion, the change in the degree of conversion of arylamine to the corresponding phenazine in the order **22** > **17** > **7** reflects not so much a regular decrease in the NH-acidity of these amines, as a decrease in the spin density on the naphthalene ring of the aminyl radical as the NMe_2 groups are accumulated on the ring. From this point of view, it becomes more clear why the oxidation of amines **17** and **22**, in contrast to **7**, proceeded more selectively and is not accompanied by the formation of azo compounds. In this respect, amine **7** resembles more simple anilines than naphthylamines **17** and **22** (see Ref. 16,20).

Usually oxidation of 1- and 2-naphthylamines to dibenzo[*a*,*h*]phenazines* involving anionic and radical intermediates is a very long process, which takes 24—48 h.[16,23,24] In our case, formation of **8** takes about 1 h, that agrees with the involvement into the reaction of more stabilized and, apparently, more rapidly formed electrophilic intermediates **12** or **15**.

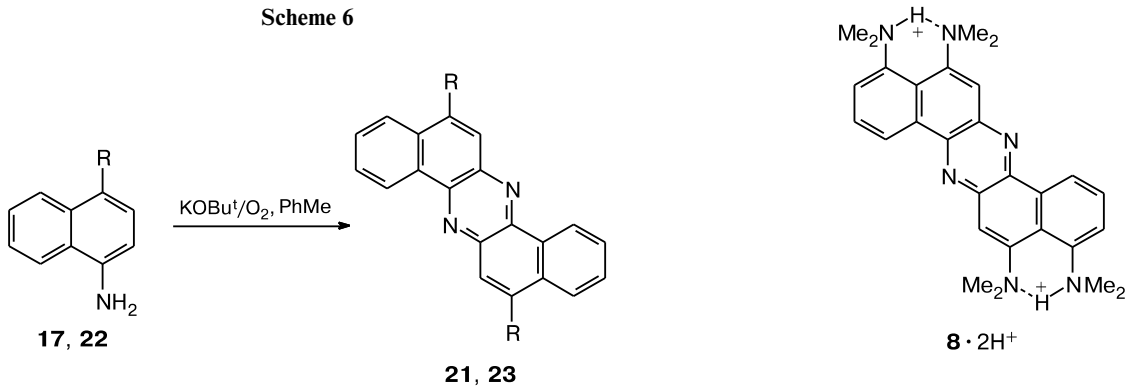
As to the detection in the reaction leading to phenazines their partially hydrogenated precursors of the type **14**, it seems improbable because of the antiaromatic character of 1,4-dihydropyrazines and their extremely easy aromatization.[9,25—27] No wonder that attempts to reduce

* On specificities of the transformation of 4-R-1,2-naphthylenediamines to dibenzophenazines see Refs 21 and 22.

Scheme 5



Scheme 6



R = NMe_2 (**17**, **21**), H (**22**, **23**)

phenazine **8** to the dihydro form **14** with zinc in boiling AcOH were unsuccessful, whereas its catalytic hydrogenation (H_2/Pd—C/MeOH, 1 atm, 25 °C) led to elimination of two NMe_2 groups in positions 4 and 11 and formation of diamine **21** in the quantitative yield (it is interesting that the dication **8**·$2H^+$ under the same conditions remains unchanged).

Since the nitrogen bases **8**, **19**, and **21** synthesized in the present work are deeply colored and some are acid indicators, solvatochroms, and photochroms, we studied the questions of their coloring in more details. Solution of dibenzophenazine **8** in neutral organic solvents has a crimsonish red color (Table 2), while in acidic medium compound **8** gives the dication **8**·$2H^+$ colored in yellow (λ_{max} = 427 nm). In the dication, the dimethylamino groups are protonated, which excludes them from the conjugation, approximating its UV spectrum to that of unsubstituted dibenzo[*a*,*h*]phenazine (λ_{max} = 414 nm, MeOH).[28] The pyridine nitrogen atoms of phenazine **8** in acidic medium (a five-fold excess of $HClO_4$ in MeCN) cannot be protonated or quaternized, for example, with excess of MeI (25 °C, 1 month or 110—120 °C, 2 h in a sealed tube).

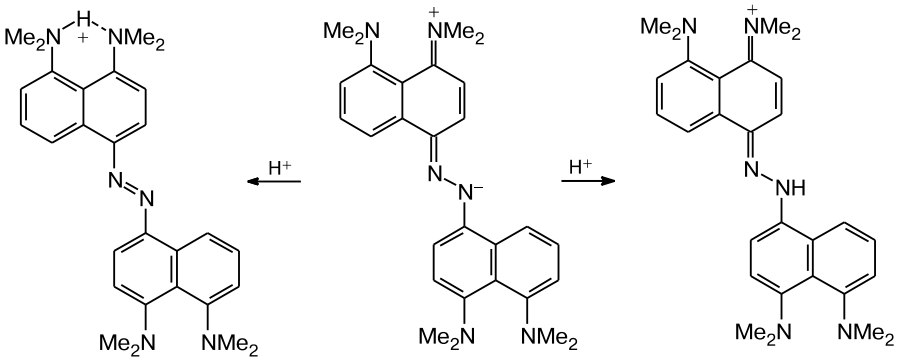
Solutions of dibenzophenazine **8** possess orange fluorescence, in $CHCl_3$ the maxima are λ^{fl}_{max} = 616 nm and λ^{abs}_{max} = 520 nm, the Stokes shift is 96 nm. The corresponding values for compound **21** having yellow fluorescence are 563, 460, and 103 nm. In acidic medium, the fluorescence disappears for both compounds.

For compounds **8**, **19**, and **21**, the change of hexane for DMSO (or chloroform) leads to a bathochromic shift of the long-wave absorption band by $\Delta\lambda^{abs}_{max}$ = 28, 48, and 11 nm, respectively. As it is seen, solvatochromism is

Table 2. The UV spectroscopic data of dibenzophenazines **8** and **21** and azo compounds **19** and **28**

Compound	Solvent	λ^{abs}_{max}/nm (logε)	Terminal absorption to/nm
8	*n*-Hexane	242 (4.43), 274 (4.45), 326 (4.30), 360 (4.06), 492 (4.05)	550
	MeOH	273 (4.23), 328 (3.99), 509 (3.67)	610
	MeCN	328 (4.01), 380 (3.81), 513 (4.01)	600
	DMSO	520 (3.91)	640
	$CHCl_3$	241 (4.41), 277 (4.46), 330 (4.33), 382 (4.11), 520 (4.10)	640
	4% HCl	224 (4.81), 248 (4.60), 294 (4.77), 404 (4.25), 427 (4.40)	—
19	*n*-Hexane	279 (4.54), 500 (4.54)	590
	MeOH	528 (4.00)	660
	DMSO	548 (4.31)	650
	$CHCl_3$	532 (4.22)	680
	4% HCl	222 (4.83), 266 (4.45), 402 (4.36)	—
	50% H_2SO_4	248 (4.72), 286 (4.34), 328 (4.32), 485 (3.76)	—
	95% H_2SO_4	224 (4.84), 253 (4.58), 282 (4.51), 673 (4.11)	750
21	*n*-Hexane	261 (4.46), 284 (4.25), 307 (4.30), 319 (4.30), 444 (4.11)	495
	MeOH	262 (4.01), 287 (3.79), 322 (3.86), 452 (3.61)	520
	MeCN	263 (4.31), 287 (4.06), 323 (4.14), 454 (3.91)	510
	$CHCl_3$	266 (4.59), 290 (4.36), 326 (4.45), 455 (4.24)	520
28	EtOH	272 (4.17), 481 (4.39)	590
	4% HCl	271 (4.31), 374 (4.27), 513 (3.99)	640
	50% H_2SO_4	565 (4.07)	620
	95% H_2SO_4	223 (4.82), 255 (4.57), 295 (4.67), 547 (3.88)	610

Scheme 7

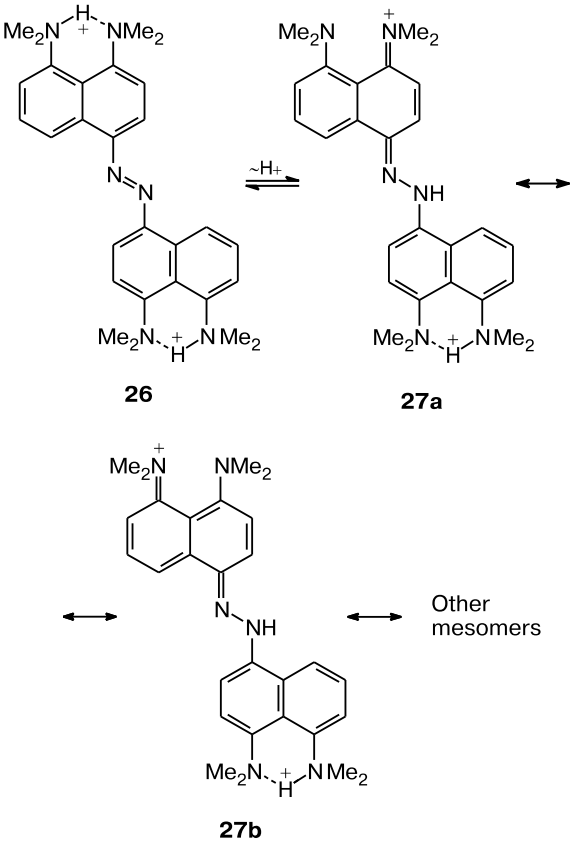


more pronounced in the azo compound **19** than in dibenzo[*a*,*h*]phenazines **8** and **21**, which can be explained by the longer chain of conjugation and more efficient charge transfer from the NMe_2 groups to the acceptor center (see, for example, structure **19´**, Scheme 7). The effect of chloroform on solvatochromism looks unexpected, however, the similar pattern of the change in λ^{abs}_{max} (*n*-hexane < Bu^tOH < MeCN < $CHCl_3$) has been observed recently for another proton sponge derivative, as well.[29]

Since DMSO is characterized by stabilization of the polar forms (in our case, **19´**), a question arises: is the base **19** able, like common azo compounds,[30,31] to form a cation of the type **24**? The ^1H NMR spectroscopic data show that addition of weighed portions of $HClO_4$ to a solution of **19** in DMSO-d_6 initially gives the monocation **25** and then the dication **26** (Scheme 8). They are represented, respectively, by a one-proton and a two-proton signals of the chelated protons of the NH groups[32] at δ 18.55 and 18.45; the transformation from **25** to **26** is accompanied by a noticeable simplification of the NMR spectrum due to the symmetrization of the structure. In this case, the reddish violet color of solution of the base **19** (λ^{abs}_{max} = 548 nm) turns yellowish brown, whereas the electron absorption spectrum of the dication **26** approximates to that for the unsubstituted 1,1´-azonaphthalene (λ^{abs}_{max} = 397 nm (logε 4.22), cyclohexane).[33] Further increase in the acidity of the medium (from 4% HCl to 95% H_2SO_4) again leads to the deepening the color right to the indigo blue ($\Delta\lambda_{max}$ > 270 nm; *cf.* Ref. 31: $\Delta\lambda^{abs}_{max}$ = 104 nm for 4-dimethylaminoazobenzene on going from MeCN to the MeCN—HCl mixture) (see Table 2). We assume that in the strongly acidic medium, the dication **26** isomerizes to the hydrazone-imine form **27**, which provides much more efficient delocalization of the positive charge (see Scheme 8).

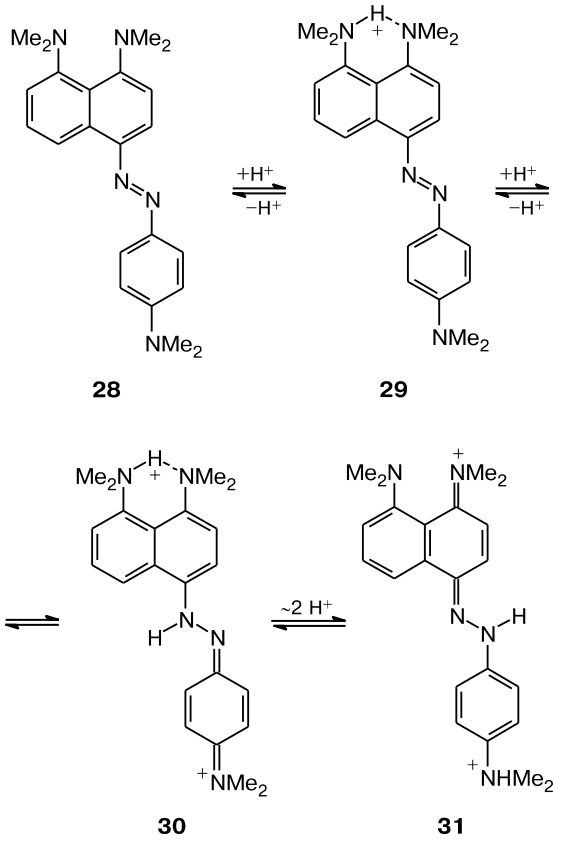
Behavior of 1,1´-azonaphthalene itself can serve as a confirmation of this fact, since it is protonated in acidic medium at the azo group (λ^{abs}_{max} = 596 nm (logε 4.46), EtOH—70% $HClO_4$, 1 : 4),[33] as well as behavior of the model azo compound **28** (Scheme 9) synthesized by us by the coupling of the corresponding diazonium salt with the "proton sponge" **1** according to the analogous method given in the work.[34] The base **28** due to the presence of only one fragment of the "proton sponge" is protonated at the azo group easier than compound **19** and *via* the series of protolytic equalibriums initially gives the chelated

Scheme 8



monocation **29** ($\delta_{N\underline{H}}$ 18.48, DMSO-d_6—$HClO_4$) and then a dication of the type **30**, which in the sizable amount is formed already in 4% HCl (*cf.* $\lambda^{abs}{}_{max}$ = 515 nm (MeCN—HCl) for 4-dimethylaminoazobenzene[31] with the data for compounds **19** and **28** in 4% HCl, Table 2). The latter, undergoing a partial isomerization, can exist in the mixture with the dication **31** (Scheme 9), whose content, obviously, increases on going from HCl to H_2SO_4.

Scheme 9



In conclusion, in the present work 4,5,11,12-tetrakis(dimethylamino)dibenzo[*a*,*h*]phenazine and 4,5,4′,5′-tetrakis(dimethylamino)-1,1′-azonaphthalene were synthesized based on 1-amino-4,5-bis(dimethylamino)-naphthalene and using two independent methods (oxidation in the aprotic or tosylation in the protic medium). These compounds are two new representatives of the double "proton sponges" possessing properties of polyfunctional nitrogen bases. It was shown that no intramolecular proton transfer takes place in 4,5-bis(dimethylamino)-1-(*p*-toluenesulfonamido)naphthalene.

Experimental

^{1}H NMR spectra were recorded on a Bruker DPX-250 spectrometer (250 MHz) using $SiMe_4$ as an internal standard. Mass spectra (EI, 70 eV) were recorded on a Finnigan MAT INCOS 50 instrument using direct injection of the samples. IR spectra were recorded on a FSM-1202 IR Fourier-spectrometer. UV spectra were recorded on a Varian Cary-50 spectrophotometer, fluorescence spectra, on a Varian Cary Eclipse instrument. Chemapol L 40/100 silica gel was used for chromatography. The reaction progress and purity of obtained compounds were monitored by TLC on Al_2O_3 and Silufol plates, visualizing in the iodine vapors. Melting points were determined in sealed capillary tubes and were not corrected. Oxygen with the content of the main substance more than 98% was used in the work.

Orange and red crystals of tetraamine **8** suitable for X-ray crystallography were obtained by isothermic evaporation of its saturated solution in ethyl acetate at 20 °C. The crystals of **8** were studied at 100 K on a Bruker APEX II diffractometer (ω/θ-scanning, Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator). The crystal structures were solved by the direct methods and subsequent Fourier-syntheses using the SHELXS-97 program. The structures were refined by the least squares method in the anisotropic full-matrix approximation for all the nonhydrogen atoms using the SHELXL-97 program. Crystallographic characteristics and principal details of the experiments are given in Table 3. The atom coordinates, bond distances, bond and dihedral angles for the two polymorphs of the structure **8** were deposited with the Cambrige Structural Database under the numbers CCDC 809934 (orange polymorph, needles) and CCDC 809935 (red polymorph, plates).

Compounds **7** and **17** were synthesized according to the known methods.[35,36]

Tosylation of naphthylamines in protic medium (general procedure). Tosyl chloride (0.20 g, 0.11 mmol) was added to a solu-

Table 3. Crystallographic data and parameters of the X-ray diffraction experiment for the dibenzophenazine **8** polymorphic modifications

Polymorph	Needles	Plates
Molecular formula	$C_{28}H_{32}N_6$	
Molecular weight	452.60	
T/K	100(2)	
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	6.5492(15)	6.7491(11)
b/Å	7.1734(16)	14.074(2)
c/Å	12.875(3)	12.457(2)
α/deg	83.058(5)	90
β/deg	77.409(5)	95.704(4)
γ/deg	81.497(5)	90
V/Å^3	581.4(2)	1177.4(3)
Z	1	2
d_{calc}/g cm^{-3}	1.293	1.277
μ//mm^{-1}	0.079	0.078
Number of reflections: total/independent	6883/3062	10031/2286
Number of reflections with $I > 2\sigma(I)$	2135	1260
Number of refined parameters	158	158
R-factor	0.0444	0.0483

tion of the corresponding amine (0.10 mmol) in ethanol (20 mL) and the reaction mixture was refluxed until complete consumption of the starting amine (1—1.5 h). Then, KOH (0.12 g) was added, followed by reflux for another 5 min, EtOH (12 mL) was evaporated. The reaction mixture was diluted with water (10 mL) and the products were extracted with chloroform or dichloromethane. After the extragent was removed, the residue was subjected to chromatography, collecting the major labile fractions.

4,5-Bis(dimethylamino)-1-(*p*-toluenesulfonamido)naphthalene (6). The sorbent was Al_2O_3, the eluent was ethyl acetate. The yield was 5%. Light cream needles, m.p. 173—175 °C (from ethyl acetate). Found (%): C, 65.82; H, 6.51; N, 10.89; S, 8.30. $C_{21}H_{25}N_3O_2S$. Calculated (%): C, 65.77; H, 6.57; N, 10.96; S, 8.36. IR (KBr), ν/cm^{-1}: 3233 (NH); 2931, 2825, 2778 (CH); 1577, 1481 (ring); 1326, 1155 (SO_2). ^{1}H NMR ($CDCl_3$), δ: 2.34 (s, 3 H, C—Me); 2.74 (s, 6 H, C(5)NMe_2); 2.75 (s, 6 H, C(4)NMe_2); 6.47 (br.s, 1 H, NH); 6.72 (d, 1 H, H(3), J = 8.2 Hz); 6.85 (br.d, 1 H, H(6), J = 7.3 Hz); 7.09 (d, 1 H, H(2), J = 8.2 Hz); 7.16 (m, 3 H, H(3′), H(5′), H(7)); 7.30 (br.d, 1 H, H(8), J = 8.2 Hz); 7.61 (d, 2 H, H(2′), H(6′), J = 8.2 Hz). ^{1}H NMR (DMSO-d_6), δ: 2.36 (s, 3 H, C—Me); 2.69 (s, 6 H, C(5)NMe_2); 2.70 (s, 6 H, C(4)NMe_2); 6.75 (d, 1 H, H(3), J = 8.3 Hz); 6.82 (d, 1 H, H(2), J = 8.3 Hz); 6.90 (br.d, 1 H, H(6), J = 7.3 Hz); 7.22 (t, 1 H, H(7), J = 7.7 Hz); 7.33 (d, 2 H, H(3′), H(5′), J = 8.2 Hz); 7.53 (br.d, 1 H, H(8), J = 8.2 Hz); 7.60 (d, 2 H, H(2′), H(6′), J = 8.2 Hz); 9.69 (br.s, 1 H, NH). ^{1}H NMR of anion **11** (DMSO-d_6—KOH), δ: 2.24 (s, 3 H, C—Me); 2.56 (s, 6 H, C(5)NMe_2); 2.67 (s, 6 H, C(4)NMe_2); 6.60 (d, 1 H, H(2), J = 8.3 Hz); 6.81 (m, 2 H, H(3), H(6)); 7.08 (m, 3 H, H(7), H(3′), H(5′)); 7.60 (d, 2 H, H(2′), H(6′), J = 8.2 Hz); 8.21(dd, 1 H, H(8), J = 8.2 Hz, J = 1.2 Hz). MS, m/z (I_{rel} (%)): 383 [M]$^+$ (3), 228 (7), 115 (7), 91 (39), 65 (30), 58 (100), 44 (14).

4,5,11,12-Tetrakis(dimethylamino)dibenzo[*a*,*h*]phenazine (8). The sorbent was silica gel, the eluent was ethyl acetate. The yield was 20%. Reddish orange needles with m.p. 276—278 °C or dark red plates with m.p. 279—280 °C (from ethyl acetate). The orange fluorescence is observed upon irradiation of the substance solutions with the UV light. Found (%): C, 74.25; H, 7.09; N, 18.56. $C_{28}H_{32}N_6$. Calculated (%): C, 74.30; H, 7.13; N, 18.57. IR (Nujol), ν/cm^{-1}: 1602, 1588, 1453 (ring); (KBr) 2932, 2829, 2781 (CH); 1600, 1586, 1447 (ring). Fluorescence spectrum ($CHCl_3$), λ_{max}/nm: 520 (excit.), 616 (fluor.). ^{1}H NMR ($CDCl_3$), δ: 2.86 (s, 12 H, C(4)NMe_2, C(11)NMe_2); 2.93 (s, 12 H, C(5)NMe_2, C(12)NMe_2); 7.24(dd, 2 H, H(3), H(10), J = 7.4 Hz, J = 1.0 Hz); 7.34 (s, 2 H, H(6), H(13)); 7.59 (t, 2 H, H(2), H(9), J = 7.8 Hz); 9.00(dd, 2 H, H(1), H(8), J = 8.1 Hz, J = 1.0 Hz). MS, m/z (I_{rel} (%)): 453 [M + 1]$^+$ (31), 452 [M]$^+$ (96), 437 [M – Me]$^+$ (14), 408 [M – NMe_2]$^+$ (17), 378 (20), 377 (29), 376 (31), 375 (29), 363 (25), 361 (23), 195 (31), 188 (33), 181 (28), 58 (62), 44 (100), 42 (52).

Di(hydrochloride) 8·2HCl, light yellow needles with decomp. point above 300 °C (from conc. HCl). ^{1}H NMR (CD_3CN), δ: 3.25 (br.s, 12 H, C(5)NMe_2, C(12)NMe_2); 3.30 (d, 12 H, C(4)NMe_2, C(11)NMe_2, J = 2.6 Hz); 8.17 (t, 2 H, H(2), H(9), J = 7.9 Hz); 8.30 (br.d, 2 H, H(3), H(10), J = 7.7 Hz); 8.57 (s, 2 H, H(6), H(13)); 9.65 (br.d, 2 H, H(1), H(8), J = 8.1 Hz); 18.58 (br.s, 2 H, NH).

1-Amino-4,5-bis(dimethylamino)-2-tosylnaphthalene (9). The sorbent was Al_2O_3, the eluent was ethyl acetate. The substance was isolated as a light yellow caramel mass in the mixture with a small admixture of phenazine **8**, which cannot be separated. ^{1}H NMR ($CDCl_3$), δ: 2.35 (s, 3 H, C—Me); 2.67 (s, 6 H, C(4)NMe_2); 2.76 (s, 6 H, C(5)NMe_2); 5.58 (br.s, 2 H, NH_2); 7.02(dd, 1 H, H(6), J = 6.4 Hz, J = 1.3 Hz); 7.24 (m, 3 H, H(3′), H(5′), H(3)); 7.33 (m, 2 H, H(7), H(8)); 7.83 (d, 2 H, H(2′), H(6′), J = 8.4 Hz).

4-Dimethylamino-1-(*p*-toluenesulfonamido)naphthalene (18) was obtained according to the general procedure in the presence of anhydrous AcONa (1 equiv.). The sorbent was Al_2O_3, the eluent was CH_2Cl_2. The yield was 46%, colorless crystals, m.p. 275—277 °C (from acetone). Found (%): C, 67.05; H, 5.80; N, 8.31; S, 9.53. $C_{19}H_{20}N_2O_2S$. Calculated (%): C, 67.03; H, 5.92; N, 8.23; S, 9.42. ^{1}H NMR ($CDCl_3$), δ: 2.34 (s, 3 H, C—Me); 2.84 (s, 6 H, NMe_2); 6.60 (br.s, 1 H, NH); 6.89 (d, 1 H, H(3), J = 8.2 Hz); 7.15 (m, 3 H, H(2), H(3′), H(5′)); 7.40 (m, 2 H, H(6), H(7)); 7.60 (d, 2 H, H(2′), H(6′), J = 8.5 Hz); 7.80(dd, 1 H, H(8), J = 7.6 Hz, J = 1.6 Hz); 8.17(dd, 1 H, H(5), J = 7.9 Hz, J = 1.3 Hz).

Tosylation of amine 7 in aprotic medium. Pyridine (3 equiv., 0.25 mL) and tosyl chloride (0.2 g, 0.1 mmol) were added to a cooled to 0 °C solution of amine **7** (0.23 g, 0.1 mmol) in anhydrous chloroform (5 mL). The mixture that obtained was stirred for 4 h at 0 °C until the starting amine disappeared, neutralized with aqueous ammonia (3 mL). The organic layer was separated, washed with the equal amount of water, dried with anhydrous Na_2SO_4, concentrated to the minimum volume, and sulfonamide **6** was isolated by preparative thin-layer chromatography (the sorbent was Al_2O_3, the eluent was ethyl acetate). The yield was 0.14 g (36%). When the reaction was carried out without pyridine, the yield decreased to 14—18%.

4,5,4′,5′-Tetrakis(dimethylamino)-1,1′-azonaphthalene (19) was obtained in the mixture with compound **8** upon oxidation of amine **7** according to the described procedure.[16] After the reaction reached completion, the solvent was evaporated, the products were isolated by column chromatography (the sorbent was silica gel, the eluent was ethyl acetate), sequentially collecting a pink light fraction of dibenzophenazine **8** (5%; the properties are similar to those of the sample described above) and the reddish violet fraction of the azo compound **19** (20%). Azo compound **19**: claretish violet crystals, m.p. 228—230 °C (from EtOAc). Found (%): C, 74.02; H, 7.47; N, 18.51. $C_{28}H_{34}N_6$. Calculated (%): C, 73.97; H, 7.54; N, 18.49. ^{1}H NMR ($CDCl_3$), δ: 2.80 (s, 12 H, C(5)NMe_2, C(5′)NMe_2); 2.91 (s, 12 H, C(4)NMe_2, C(4′)NMe_2); 6.98 (m, 4 H, H(3), H(3′), H(6), H(6′)); 7.43 (t, 2 H, H(7), H(7′), J = 7.9 Hz); 7.87 (d, 2 H, H(2), H(2′), J = 8.5 Hz); 8.70 (br.d, 2 H, H(8), H(8′), J = 8.2 Hz). ^{1}H NMR of dication **26** (DMSO-d_6—$HClO_4$), δ: 3.18 (br.s, 12 H, C(4)NMe_2, C(4′)NMe_2); 3.25 (br.s, 12 H, C(5)NMe_2, C(5′)NMe_2); 7.99 (t, 2 H, H(7), H(7′), J = 8.1 Hz); 8.26 (m, 6 H, H, naphthyl); 9.16 (br.d, 2 H, H(8), H(8′), $J_{2,3}$ = 8.4 Hz); 18.45 (br.s, 2 H, NH). MS, m/z (I_{rel} (%)): 454 [M]$^+$ (4), 168 (7), 154 (5), 58 (100), 44 (53), 42 (29).

5,12-Bis(dimethylamino)dibenzo[*a*,*h*]phenazine (21). ***A.*** The products were obtained from amine **17** according to the published procedure[16] and isolated by chromatography (the sorbent was silica gel, the eluent was ethyl acetate) collecting the bright yellow fraction. The yield was 28%, yellow needles with m.p. 245—245 °C or yellowish orange plates with m.p. 246—248 °C (from ethyl acetate). Found (%): C, 78.75; H, 6.09; N, 15.21. $C_{24}H_{22}N_4$. Calculated (%): C, 78.66; H, 6.05; N, 15.29. IR (KBr), ν/cm^{-1}: 2939, 2918, 2774 (CH); 1617, 1601, 1475 (ring). Fluorescence spectrum ($CHCl_3$), λ_{max}/nm: 460 (excit.), 563

(fluor.). ^{1}H NMR ($CDCl_3$), δ: 3.06 (s, 12 H, NMe_2); 7.60 (s, 2 H, H(6), H(13)); 7.77 (m, 4 H, H(2), H(3), H(9), H(10)); 8.30 (m, 2 H, H(4), H(11)); 9.44 (m, 2 H, H(1), H(8)).

B. The product was obtained by the catalytic hydrogenation (H_2, 5% Pd/C) of phenazine **8** in methanol for 2 h at 25 °C. The yield was quantitative. The physicochemical characteristics and spectral data of the substance agree with those for the sample obtained above upon oxidation of amine **17**.

4,5-Bis(dimethylamino)-1-(*p*-dimethylaminophenylazo)naphthalene (28) was obtained from the "proton sponge" **1** and *p*-dimethylaminophenyldiazonium tetrafluoroborate according to the known procedure.[34] The product was isolated by chromatography on Al_2O_3 (the eluent was $CHCl_3$) collecting a bright red light fraction. The yield was 78%, reddish claret crystals, m.p. 162—163 °C (from MeOH). Found (%): C, 73.45; H, 7.14; N, 19.29. $C_{22}H_{27}N_5$. Calculated (%): C, 73.10; H, 7.53; N, 19.37. ^{1}H NMR ($CDCl_3$), δ: 2.79 (s, 6 H, C(5)NMe_2); 2.88 (s, 6 H, C(4)NMe_2); 3.06 (s, 6 H, C(4′)NMe_2); 6.77 (d, 2 H, H(3′), H(5′), J = 9.1 Hz); 6.95 (m, 2 H, H(3), H(6)); 7.42 (t, 1 H, H(7), J = 7.9 Hz); 7.72 (d, 1 H, H(2), J = 8.5 Hz); 7.92 (d, 2 H, H(2′), H(6′), J = 9.1 Hz); 8.59 (br.d, 1 H, H(8), J = 8.2 Hz).

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References

1. A. F. Pozharskii, V. A. Ozeryanskii, *Proton sponges*, in *The Chemistry of Anilines*, Ed. Z. Rappoport, J. Wiley and Sons, Chichester, 2007, Part 2, Ch. 17, p. 931.
2. V. A. Ozeryanskii, A. F. Pozharskii, W. Schilf, B. Kamieński, W. Sawka-Dobrowolska, L. Sobczyk, E. Grech, *Eur. J. Org. Chem.*, 2006, 782.
3. H. A. Staab, C. Krieger, G. Hieber, K. Oberdorf, *Angew. Chem., Int. Ed.*, 1997, **36**, 1884.
4. V. A. Ozeryanskii, A. A. Milov, V. I. Minkin, A. F. Pozharskii, *Angew. Chem., Int. Ed.*, 2006, **45**, 1453.
5. S. J. Schmidtke, D. F. Underwood, D. A. Blank, *J. Am. Chem. Soc.*, 2004, **126**, 8620.
6. A. J. Kirby, N. Dutta-Roy, D. da Silva, J. M. Goodman, M. F. Lima, C. D. Roussev, F. Nome, *J. Am. Chem. Soc.*, 2005, **127**, 7033.
7. H. E. Zimmerman, J. Cheng, *J. Org. Chem.*, 2006, **71**, 873.
8. E. S. Petrov, *Usp. Khim.,* 1983, 1974 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1983, **52**, 1144].
9. A. E. A. Porter, *Pyrazines and their Benzo Derivatives*, in *Comprehensive Heterocyclic Chemistry*, Eds A. R. Katritzky, C. W. Rees, Pergamon Press, Oxford, 1984, **3**, p. 157; N. Sato, in *Comprehensive Heterocyclic Chemistry II*, Eds A. R. Katritzky, C. W. Rees, E. F. V. Scriven, Pergamon Press, Oxford, 1996, **6**, p. 233; N. Sato, in *Comprehensive Heterocyclic Chemistry III*, Eds A. R. Katritzky, C. A. Ramsden, E. F. V. Scriven, R. J. K. Taylor, Elsevier Science, New York, 2008, **8**, p. 273.
10. N. V. Vistorobskii, A. F. Pozharskii, S. V. Shorshnev, A. I. Chernyshev, *Mendeleev Commun.*, 1991, **1**, 10.
11. O. V. Vinogradova, E. A. Filatova, N. V. Vistorobskii, A. F. Pozharskii, I. V. Borovlev, Z. A. Starikova, *Zh. Org. Khim.*, 2006, **42**, 355 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2006, **42**, 338].
12. P. Walker, W. A. Waters, *J. Chem. Soc.*, 1962, 1632.
13. B. Nay, E. F. V. Scriven, H. Suschitzky, D. R. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 1980, 611.
14. R. Abdayem, G. Baccolini, C. Boga, M. Monari, S. Selva, *Tetrahedron Lett.*, 2003, **44**, 2649.
15. N. E. Briffett, F. Hibbert, *J. Chem. Soc., Perkin Trans. 2*, 1989, 765.
16. L. Horner, J. Dehnert, *Chem. Ber.*, 1963, **96**, 786.
17. L. Horner, H. Nickel, *Chem. Ber.*, 1956, **89**, 1681.
18. J. P. Maier, *Helv. Chim. Acta*, 1974, **57**, 994.
19. A. Reiser, F. W. Willets, G. C. Terry, V. Williams, R. Marley, *Trans. Faraday Soc.*, 1968, **64**, 3265.
20. G. Crank, M. I. H. Makin, *Aust. J. Chem.*, 1984, **37**, 845.
21. F. Kehrmann, I. Safar, *Helv. Chim. Acta*, 1925, **8**, 668.
22. L. B. Volodarskii, V. A. Koptyug, *Zh. Obshch. Khim.*, 1964, **34**, 3046 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1964, **34**, 3083].
23. K. H. Pausacker, *J. Chem. Soc.*, 1953, 1989.
24. K. H. Pausacker, J. G. Scroggie, *J. Chem. Soc.*, 1954, 4003.
25. G. A. Swan, D. G. I. Felton, *Phenazines*, Intersci. Publ., New York—London, 1957, p. 28.
26. I. N. Borukhova, V. F. Gryazev, I. A. Yarysheva, Z. V. Pushkareva, *Khim. Geterotsikl. Soedin.*, 1976, 548 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1976, **12**, 458].
27. L. Bemi, M. T. Thomas, V. Snieckus, *Synthesis*, 1979, 130.
28. Y. Kosugi, K. Itoho, H. Okazaki, T. Yanai, *J. Org. Chem.*, 1995, **60**, 5690.
29. C. D. Swor, L. N. Zakharov, D. R. Tyler, *J. Org. Chem.*, 2010, **75**, 6977.
30. P. F. Gordon, P. Gregory, *Organic Chemistry in Colour*, Springer-Verlag, Berlin—Heidelberg—New York, 1983, 322 pp.
31. D. R. C. Matazo, R. A. Ando, A. C. Borin, P. S. Santos, *J. Phys. Chem. A*, 2008, **112**, 4437.
32. P. Chmielewski, V. A. Ozeryanskii, L. Sobczyk, A. F. Pozharskii, *J. Phys. Org. Chem.*, 2007, **20**, 643.
33. J. Schulze, F. Gerson, J. N. Murrell, E. Heilbronner, *Helv. Chim. Acta*, 1961, **44**, 428.
34. V. A. Ozeryanskii, V. I. Sorokin, A. F. Pozharskii, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 388 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 404].
35. V. A. Ozeryanskii, A. F. Pozharskii, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1501 [*Russ. Chem. Bull.* (*Engl. Transl.*), 1997, **46**, 1437].
36. A. Corma, S. Iborra, I. Rodriguez, F. Sanchez, *J. Catal.*, 2002, **211**, 208.

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