peri-Naphthylenediamines

23.* Investigation of the intramolecular hydrogen bond in protonated 1,8-bis(dimethylamino)naphthalenes by ^1H NMR spectroscopy

A. F. Pozharskii and V. A. Ozeryanskii*

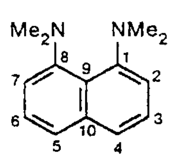
Rostov State University,
7 ul. Zorge, 344090 Rostov-on-Don, Russian Federation.
Fax: +7 (863 2) 28 5667. E-mail: pozharsk@pozhar.rnd.runnet.ru

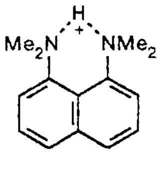
The ^1H NMR spectra of protonated 1,8-bis(dimethylamino)naphthalene cations ("proton sponges") containing substituents of various types in positions 2(7) and 4(5) were measured. To estimate the degree of asymmetry of the intramolecular hydrogen bridge in the cations studied, the spin-spin coupling constants of the NH proton with protons of nonequivalent Me_2N groups were suggested to be used. Bromination of the "proton sponge" into positions 2 and 7 by *N*-bromosuccinimide was carried out for the first time.

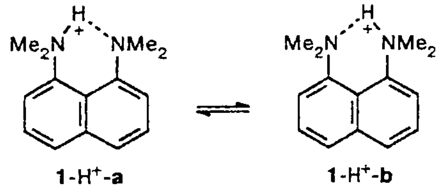
Key words: ^1H NMR spectra; 1,8-bis(dimethylamino)naphthalenes, "proton sponge", cations, intramolecular hydrogen bond, bromination.

It is known that one of the most important factors determining the unusually high basicity of 1,8-bis(dimethylamino)naphthalene (**1**), the "proton sponge", whose pK_a in water[2] and acetonitrile[3] is equal to 12.1 and 18.5, respectively, is the formation of a very strong intramolecular hydrogen bond (IHB) in the protonated form **1**-H^+.[4,5] In particular, an appreciable low-field shift of the signal of the chelated NH proton (δ 18 to 19) can serve as an indicator of this strength.[4–6] Numerous studies, mostly performed by X-ray analysis,[5] IR spectroscopy,[7,8] and NMR spectroscopy,[6,9] were dedicated to studying the nature and geometry of the hydrogen bridge in cation **1**-H^+. The crucial problem was the problem of the degree of symmetry of this bridge.

Theoretical calculations of the $H_3N...H^+...NH_3$ system showed that at the N...N distance (*R*) of approximately 2.50 Å the potential energy curve has one minimum (Fig. 1, *a*), *i.e.*, that the corresponding hydrogen bridge is symmetric.[5,11] An increase in the N...N distance results in a two-well potential and an increase in the energy barrier (Fig. 1, *b*, *c*). In the range of the *R* values from 2.55 to 2.75 Å this barrier is rather low (to 2.6 kcal mol^{-1}), but its value amounts to 10.2 kcal mol^{-1} at R = 3.00 Å. These calculations have been performed for the linear IHB; therefore, it is obvious that in the case of cation **1**-H^+, in which the N—H...N angle lies in the range from 140° to 160°, they must be corrected (which will hardly change the main tendency). It should be noted


1


1-H^+


1-H^+-**a** **1**-H^+-**b**

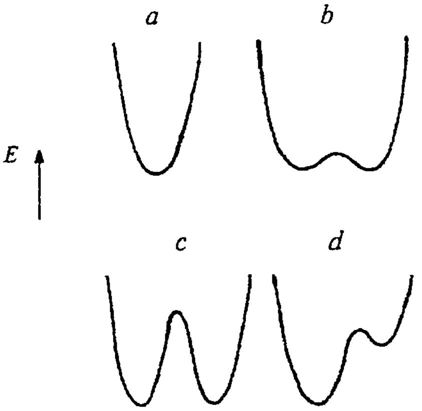


Fig. 1. Types of the potential energy curves for the IHB in the cations of symmetrically (*a*—*c*) and asymmetrically (*d*) substituted "proton sponges" at the *R*/Å = ~2.50 (*a*), 2.55 to 2.75 (*b*), and 3.0 (*c*).

---

* For Part 22, see Ref. 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 1, pp. 68—75, January, 1998.

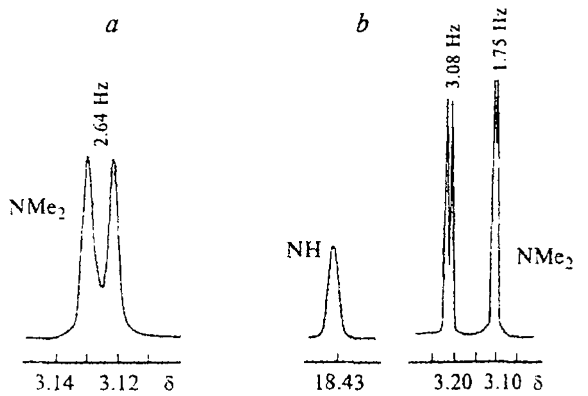


Fig. 2. Examples of spectral regions of Me_2N groups and the NH proton for the cations of "proton sponges" $1\text{-}H^+$ (*a*) and $15\text{-}H^+$ (*b*) in the ^1H NMR spectra obtained in DMSO-d_6.

that the formation of cation $1\text{-}H^+$ is accompanied by an appreciable shortening of the distance between the N atoms from 2.79 Å in the molecule of base **1** to 2.55 to 2.62 Å in the molecules of the salts.[5] Hence, the potential curve with pronounced tendency to symmetrization of the hydrogen bridge (Fig. 1, *b*) must correspond to the "proton sponge" cation, which is confirmed by experimental data.

Irrespective of the anion, both Me_2N groups in the ^1H NMR spectra of solutions of salts $1\text{-}H^+X^-$ are always equivalent and produce one doublet with the $^3J_{HN-CH_3}$ constant of approximately 2.6 Hz (Fig. 2, *a*).[6] We showed for the first time that the signal of the NH proton consists of 13 lines having the same spin-spin coupling constant (Fig. 3) (previously, this signal always has been considered as a broadened singlet). This points to the fact that the proton is bonded to both N atoms. Thus, the IHB is either symmetric and the NH proton lies in the symmetry plane of the cation, which passes through the C(9)—C(10) bond perpendicularly to the ring (structure $1\text{-}H^+$), or a tautomeric equilibrium between two asymmetric equivalent structures **1-H⁺-a** and **1-H⁺-b** takes place. The third possibility, fast vibrational motions of the NH proton in structure $1\text{-}H^+$ near the symmetry plane, is, obviously, an intermediate one between the first two cases. According to the X-ray analysis data,[11] the hydrogen bridge can be either symmetric or asymmetric depending on the anion and temperature,[12,13] and the degree of its asymmetry can vary in a wide range. Thus, the structure of cation $1\text{-}H^+$ is considered as either a tautomeric **1-H⁺-a** $\rightleftharpoons$ **1-H⁺-b** structure or a structure corresponding to fast motions of the NH proton in the vicinity of the symmetry plane.

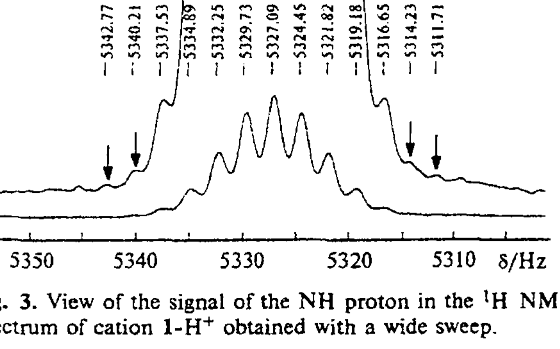
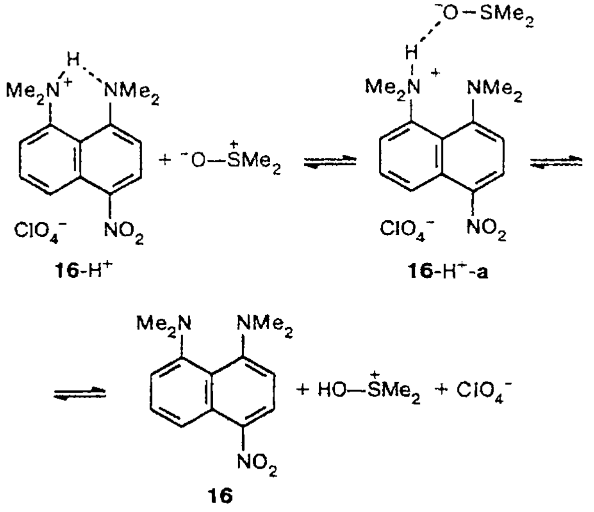


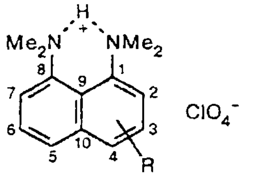
Fig. 3. View of the signal of the NH proton in the ^1H NMR spectrum of cation $1\text{-}H^+$ obtained with a wide sweep.

No data on the geometry of the hydrogen bridge in the cations of asymmetrically substituted "proton sponges" have been reported until recently (see Fig. 1, the potential energy curve *d*). Only a short time ago, X-ray and spectral investigations of the cation and base of 1,8-bis(dimethylamino)-4-nitronaphthalene (Table 1, compound **16**) have been carried out at our laboratory.[14] It has been established that in the corresponding cation $16\text{-}H^+$ the IHB is strongly asymmetric both in the crystalline state and in solution and the proton is mostly localized on the 8-N atom. Unequal constants of the spin-spin interaction between the NH proton and the Me_2N groups have been first observed for the "proton sponge" cations ($^3J_{1\text{-}HN-CH_3}$ = 1.72 Hz and $^3J_{8\text{-}HN-CH_3}$ = 3.19 Hz, in DMSO-d_6). In this case two doublets of the Me_2N groups with different spin-spin coupling constants and a broadened signal of the NH proton are present in the spectrum (see Fig. 2, *b*). The possibility of the cleavage of the hydrogen bridge and a partial deprotonation induced by DMSO appeared to be interesting properties of the above cation; because of this, we succeeded in observing simultaneously the chelated ($16\text{-}H^+$) and nonchelated (**16-H⁺-a**) cations and free base **16**.



To clarify the range of possible changes in the asymmetry of the IHB, the effect of solvents on the IHB, and the dependence between the degree of asymmetry of the IHB and the chemical shift of the NH proton, in this

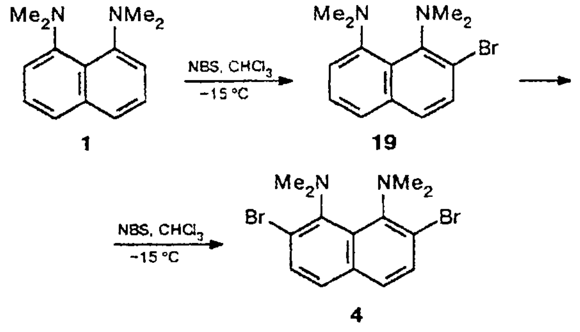
Table 1. Parameters of the ^{1}H NMR spectra for the groups participating in the formation of the hydrogen bridge in the cations of substituted "proton sponges" **1—19**



1—19

Cation	R	Solvent	1-NMe$_2$	8-NMe$_2$	NH$^+$	Δδ	J/Hz		Degree of localization of the proton (%)	
			ppm			/Hz	$^3J_{1\text{-HN-CH}_3}$	$^3J_{8\text{-HN-CH}_3}$	*PL*-1	*PL*-8
1-H$^+$	H	DMSO-d$_6$	3.12	3.12	18.33	0	2.63	2.63	50	50
		CD$_3$CN	3.11	3.11	18.69	0	2.64	2.64	50	50
2-H$^+$	2,7-Cl$_2$	DMSO-d$_6$	3.37	3.37	19.91	0	2.41	2.41	50	50
3-H$^+$	4,5-Cl$_2$	DMSO-d$_6$	3.10	3.10	19.14	0	2.52	2.52	50	50
4-H$^+$	2,7-Br$_2$	DMSO-d$_6$	3.40	3.40	20.09	0	2.41	2.41	50	50
		CD$_3$CN	3.41	3.41	20.33	0	2.64	2.64	50	50
5-H$^+$	4,5-Br$_2$	DMSO-d$_6$	3.10	3.10	19.12	0	2.41	2.41	50	50
6-H$^+$	4-NHMe	DMSO-d$_6$	3.11	2.98	18.31	−36	3.40	1.21	74	26
7-H$^+$	4-NH$_2$	DMSO-d$_6$	3.09	2.99	18.26	−31	3.23	1.21	73	27
		CD$_3$CN	3.10	3.02	18.64	−26	3.41	1.87	65	35
8-H$^+$	4-NMe$_2$	DMSO-d$_6$	3.11	3.06	18.48	−13	2.86	2.20	57	43
		CD$_3$CN	3.10	3.07	18.84	−10	2.97	2.31	56	44
9-H$^+$	4-NHAc	DMSO-d$_6$	3.12	3.11	18.55	−4	2.86	2.24	56	44
		CD$_3$CN	3.12	3.11	18.90	−3	2.75	2.63	51	49
10-H$^+$	4-CH=CH$_2$	DMSO-d$_6$	3.12	3.13	18.64	2	2.30	2.30	~50	~50
11-H$^+$	4-Cl	DMSO-d$_6$	3.11	3.14	18.52	8	2.42	2.64	48	52
12-H$^+$	4-Br	DMSO-d$_6$	3.11	3.14	18.56	8	2.31	2.53	48	52
13-H$^+$	4-COMe	DMSO-d$_6$	3.10	3.17	18.58	19	1.97	2.86	41	59
14-H$^+$	4-CN	DMSO-d$_6$	3.09	3.21	18.15	37	1.88	2.97	39	61
15-H$^+$	4-CHO	DMSO-d$_6$	3.10	3.21	18.43	33	1.75	3.08	36	64
		CD$_3$CN	3.10	3.20	18.75	30	1.98	3.30	38	62
16-H$^+$	4-NO$_2$	DMSO-d$_6$	3.17	3.29	18.50	33	1.72	3.19	35	65
		CD$_3$CN	3.08	3.19	18.72	31	2.13	3.36	39	61
17-H$^+$	4-COCF$_3$	DMSO-d$_6$	3.09	3.23	18.34	42	1.44	3.15	31	69
		CD$_3$CN	3.10	3.22	18.67	37	1.86	3.41	35	65
18-H$^+$	2-Cl	DMSO-d$_6$	3.18	3.32	18.02	42	0.77	4.06	16	84
		CD$_3$CN	3.25	3.27	18.80	5	1.54	3.84	29	71
19-H$^+$	2-Br	DMSO-d$_6$	3.22	3.33	18.09	33	~0.5	3.95	11	89
		CD$_3$CN	3.27	3.26	18.87	3	1.65	3.84	30	70

work a widespread investigation of the cations of substituted "protonated sponges" (**1—19**) by the ^{1}H NMR spectroscopy was carried out. Compounds containing both acceptor and donor substituents in position 4 were used as subjects of investigation. A number of derivatives containing Cl and Br atoms in positions 2 and 7 (*ortho*) was also studied. Recently,[15] we have performed a regioselective chlorination of compound **1** into positions 2 and 7 using 1-chlorobenzotriazole. In this work, we synthesized the previously unknown 2-bromo (**19**) and 2,7-dibromo derivatives (**4**) by bromination of base **1** by *N*-bromosuccinimide (NBS) in $CHCl_3$ at low temperature. Only bromination of the "proton sponge" **1** into position 4 has been reported up to the present.[16] In addition, symmetrically substituted "proton sponges", 2,7- and 4,5-dihalo derivatives, were studied.



The parameters of the ^{1}H NMR spectra and properties of the cations of substituted "proton sponges" (for all salts, the ClO_4^- anion was the counterion) are listed in Tables 1—3. The degree of localization of the NH proton

Table 2. Parameters of the ^1H NMR spectra of the cations of "proton sponges" (the region of aromatic protons and other functional groups)

Cation	R	Solvent	δ							J/Hz				
			H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	R	$J_{H(2)-H(3)}$	$J_{H(3)-H(4)}$	$J_{H(5)-H(6)}$	$J_{H(6)-H(7)}$	$J_{H(5)-H(7)}$
1-H$^+$	H	DMSO-d$_6$	8.08	7.73	8.09	8.09	7.73	8.08	—	7.69	8.24	8.24	7.69	1.05
		CD$_3$CN	7.91	7.71	8.05	8.05	7.71	7.91	—	7.69	8.13	8.13	7.69	1.05
2-H$^+$	2,7-Cl$_2$	DMSO-d$_6$	—	7.83	8.20	8.20	7.83	—	—	—	8.95	8.95	—	—
3-H$^+$	4,5-Cl$_2$	DMSO-d$_6$	8.15	8.02	—	—	8.02	8.15	—	8.40	—	—	8.40	—
4-H$^+$	2,7-Br$_2$	DMSO-d$_6$	—	7.98	8.09	8.09	7.98	—	—	—	8.90	8.90	—	—
		CD$_3$CN	—	7.89	7.96	7.96	7.89	—	—	—	8.90	8.90	—	—
5-H$^+$	4,5-Br$_2$	DMSO-d$_6$	8.28	8.04	—	—	8.04	8.28	—	8.35	—	—	8.35	—
6-H$^+$	4-NHMe	DMSO-d$_6$	7.86	6.55	—	8.18	7.58	7.94	2.86 (NMe); 6.83 (NH)	8.50	—	8.46	7.91	0.99
7-H$^+$	4-NH$_2$	DMSO-d$_6$	7.76	6.79	—	8.15	7.54	7.92	6.26	8.50	—	8.40	7.65	1.07
		CD$_3$CN	7.64	6.90	—	8.00	7.61	7.83	5.14	8.35	—	8.57	7.58	0.99
8-H$^+$	4-NMe$_2$	DMSO-d$_6$	7.97	7.28	—	8.25	7.70	8.03	2.82	8.35	—	8.57	7.58	1.04
		CD$_3$CN	7.79	7.28	—	8.35	7.69	7.87	2.90	8.35	—	8.57	7.58	1.10
9-H$^+$	4-NHAc	DMSO-d$_6$	8.06	7.82	—	8.19	7.75	8.10	2.19 (Me); 10.15 (NH)	8.35	—	8.57	7.58	0.88
		CD$_3$CN	7.90*	7.90*	—	8.18	7.75	7.94	2.19 (Me); 8.64 (NH)	—	—	8.57	7.69	0.99
10-H$^+$	4-CH=CH$_2$	DMSO-d$_6$	8.07	7.87	—	8.30	7.77	8.11	5.59, 5.90, 7.55	8.02	—	8.47	7.64	<1
11-H$^+$	4-Cl	DMSO-d$_6$	8.10	7.98	—	8.34	7.92	8.24	—	8.30	—	8.57	7.69	1.00
12-H$^+$	4-Br	DMSO-d$_6$	8.16	8.03	—	8.30	7.91	8.23	—	8.20	—	8.50	7.69	0.88
13-H$^+$	4-COMe	DMSO-d$_6$	8.24	8.15	—	8.51	7.82	8.18	2.74	8.02	—	8.57	7.69	0.88
14-H$^+$	4-CN	DMSO-d$_6$	8.23	8.44	—	8.27	8.02	8.33	—	8.02	—	8.46	7.69	0.99
15-H$^+$	4-CHO	DMSO-d$_6$	8.30	8.40	—	9.31	7.96	8.26	10.44	7.91	—	8.46	7.69	1.10
		CD$_3$CN	8.10	8.30	—	9.39	7.93	8.05	10.42	7.80	—	8.67	7.69	1.04
16-H$^+$	4-NO$_2$	DMSO-d$_6$	8.37	8.52	—	8.32	8.06	8.40	—	8.60	—	8.10	7.60	0.90
		CD$_3$CN	8.02	8.30	—	8.42	7.94	8.10	—	8.24	—	8.70	7.63	1.07
17-H$^+$	4-COCF$_3$	DMSO-d$_6$	8.22	8.33	—	8.55	7.96	8.31	—	8.20	—	8.60	7.91	<1
		CD$_3$CN	8.05	8.36	—	8.70	7.93	8.09	—	8.20	—	8.69	7.72	0.88
18-H$^+$	2-Cl	DMSO-d$_6$	—	7.74	8.13	8.17	7.79	8.23	—	—	8.90	8.13	7.69	1.00
		CD$_3$CN	—	7.67	8.04	8.10	7.76	7.99	—	—	8.90	8.35	7.69	1.05
19-H$^+$	2-Br	DMSO-d$_6$	—	7.88	8.03	8.17	7.81	8.23	—	—	8.90	8.23	7.69	1.00
		CD$_3$CN	—	7.84	7.94	8.09	7.77	7.98	—	—	8.90	8.24	7.69	1.10

* The signals coalesce and degenerate into a singlet.

Table 3. Some properties of "proton sponge" perchlorates

Cation	M.p./°C (decomp., from EtOH)	Found/Calculated (%)				Empirical formula
		C	H	N	Hal	
1-H$^+$	296—298[a]	53.40 53.42	6.12 6.09	8.87 8.90	11.82 11.86	$C_{14}H_{19}ClN_2O_4$
2-H$^+$	260—261	43.86 43.83	4.46 4.47	7.27 7.30	27.64 27.72	$C_{14}H_{17}Cl_3N_2O_4$
4-H$^+$	260—261	35.64 35.58	3.59 3.63	5.92 5.93	41.27 41.32	$C_{14}H_{17}Br_2ClN_2O_4$
5-H$^+$	233—234	35.47 35.58	3.60 3.63	5.90 5.93	41.26 41.32	$C_{14}H_{17}Br_2ClN_2O_4$
9-H$^+$	268—271[b]	51.73 51.69	5.92 5.96	11.28 11.30	9.46 9.53	$C_{16}H_{22}ClN_3O_5$
12-H$^+$	242—243[b]	42.68 42.71	4.64 4.61	7.13 7.12	29.25 29.30	$C_{14}H_{18}BrClN_2O_4$
13-H$^+$	195—196[b,c]	53.81 53.86	5.88 5.93	7.86 7.85	9.91 9.94	$C_{16}H_{21}ClN_2O_5$
14-H$^+$	240—241	53.10 53.02	5.31 5.34	12.40 12.37	10.38 10.43	$C_{15}H_{18}ClN_3O_4$
15-H$^+$	238—239[b]	52.57 52.56	5.64 5.59	8.14 8.17	10.31 10.34	$C_{15}H_{19}ClN_2O_5$
17-H$^+$	176—178[c]	46.85 46.78	4.39 4.42	6.80 6.82	22.47 22.51	$C_{16}H_{18}ClF_3N_2O_5$
18-H$^+$	275—276	48.11 48.15	5.23 5.20	8.02 8.02	20.23 20.30	$C_{14}H_{18}Cl_2N_2O_4$
19-H$^+$	263—264	42.64 42.71	4.65 4.61	7.11 7.12	29.30 29.30	$C_{14}H_{18}BrClN_2O_4$

[a] *Cf.* Ref. 7: m.p. 292—294 °C.
[b] From water.
[c] Without decomposition.

on each of the N atoms (indicated in Table 1) is in fact a characteristic of the asymmetry of the IHB. The following fact was taken into account in these calculations. It is known that the $^3J_{HN-CH_3}$ spin-spin coupling constant observed in the ^{1}H NMR spectra of *N*-protonated dimethylaminoarenes (for instance, in that of the *N,N*-dimethylanilinium cation) is approximately equal to 5.2 Hz.[17] As in the case of cation **1**-H$^+$, its value is approximately halved by chelation, likely due to the distribution of the proton between the N atoms and, hence, to the increase in the statistical mean value of the N—H distance (*cf.* ^{1}H NMR spectra of ^{15}N-labeled porphyrins).[18] The same regularity also persists for the cations of asymmetric "proton sponges". In this case, the mean value of the sum of the $^3J_{1\text{-}HN-CH_3}$ and $^3J_{8\text{-}HN-CH_3}$ spin-spin coupling constants is equal to 4.83 and 5.34 Hz in DMSO-d$_6$ and MeCN-d$_3$, respectively, which is close to the above value. On this basis the degree of localization of the NH proton on the 1-N and 8-N atoms (or the *PL*-1 and *PL*-8 indices, respectively) can be calculated using the following formula:

$$PL = \frac{^3J_{HN-CH_3}}{^3J_{1\text{-}HN-CH_3} + {}^3J_{8\text{-}HN-CH_3}} \cdot 100\%.$$

The *J* values obtained for each concrete measurement were used in calculations of the *PL* indices, *i.e.*, in each case the sum of the spin-spin coupling constants differs from its mean value. Data for symmetric (*PL* = 50%) and asymmetric cations in descending order of the *PL*-1 value (in DMSO) are listed in Table 1. If the *J* values are rounded off to the first decimal place, the calculation error is ±0.4%, which is in fact the accuracy of determination of the *PL* indices

Asymmetry of the hydrogen bridge. In estimating the asymmetry of the IHB the question arises first as to which of the two *peri* nitrogen atoms the NH proton is shifted. It is logical to assume that in the cations containing electron-acceptor groups including halogens having, as is known, positive Hammet σ constants, the NH proton is shifted toward the 8-N atom, which is the most distant from the above groups and, hence, has the highest basicity. This is confirmed by the X-ray data[14] for cation **16**-H$^+$. As can be seen in Table 1, the degree of asymmetry of the IHB in cations with the $-M$-substituents in position 4 changes in the following sequence (the *PL*-8 index is given in parentheses): $COCF_3$ (69) > NO_2 (65) > CHO (64) > CN (61) > COMe (59) (all data for DMSO-d$_6$). The fact that these values do not change rigorously in parallel with the values of the σ_p constants of the substituents equal to 0.80, 0.81, 0.47, 0.70 and 0.47, respectively,[19] is not surprising, since the known steric interaction between these groups and the H(5) atom[20] orients them differently with respect to the mean plane of the ring, which should also affect the change in the geometry of the whole molecule including the hydrogen bridge. Noteworthy also is the increased degree of asymmetry of the IHB in cation **15**-H^+ despite the fact that the σ constant of the CHO substituent is appreciably smaller than, for instance, that of CN group.

It is evident that in the cations of 4-amino derivatives **6**-H^+—**8**-H^+ the proton is to a greater extent shifted toward the 1-N atom. Among these three, the cation containing the 4-methylamino group has the most asymmetric hydrogen bridge (*PL*-1 = 74%); it is followed by the cations of 4-NH_2 and 4-NMe_2 derivatives (the *PL*-1 values of 73 and 57%, respectively, data for solutions in DMSO-d_6). This sequence exactly corresponds to the effect of the same groups on the increase in the basicity of the "proton sponge".[1] The weakened +*M*-effect of the Me_2N group is explained by its increased noncoplanarity with the ring as compared to the NH_2 and NHMe groups.

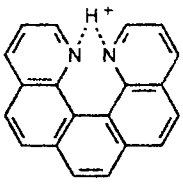
Cations of 2-chloro- (**18**-H^+) and 2-bromo-1,8-bis(dimethylamino)naphthalenes (**19**-H^+) are characterized by the most asymmetric IHBs. Since the *ortho*-Hal substituents decrease the basicity of aromatic amines by ~2 orders of magnitude,[21] it is likely that the NH proton must be located in the vicinity of the 8-N atom. The degree of asymmetry of the hydrogen bridge in cations **18**-H^+ and **19**-H^+ is so high (*PL*-8 = 84 and 89%, respectively) that even the possibility of existence of an H-bridge in such a proton-acceptor solvent as DMSO seems to be surprising. Nevertheless, this fact was unambiguously proved, since the signal of the NH proton in the ^{1}H NMR spectra of both cations is observed in the region of δ 18.

The problem of localization of the NH proton in cations characterized by a low degree of asymmetry of the hydrogen bridge and containing such substituents as 4-NHCOMe (**9**-H^+), 4-CH=CH_2 (**10**-H^+), 4-Cl (**11**-H^+), and 4-Br (**12**-H^+) is more complicated. *A priori*, it is logical to assume that in cations with asymmetric IHB the *ortho*-proton adjacent to the Me_2N group, toward which the NH proton is shifted and on which, hence, the largest portion of the positive charge is localized, will be more deshielded. In all above mentioned salts the signals of the H(7) protons are observed in a lower field as compared to those of the H(2) protons (see Table 2). This difference is most pronounced for the 4-halogen derivatives. Positive values of σ_p constants of the Cl and Br atoms show beyond a doubt that in salts **11**-H^+ and **12**-H^+ the chelated proton is actually shifted toward the 8-N atom, though the asymmetry of the IHB is insignificant. The issue of the asymmetry of the IHB in salts **9**-H^+ and **10**-H^+ calls for further investigation since the σ constants of the acetamide and vinyl groups are close to zero.[19] Moreover, not for all studied salts the degree of deshielding of the *ortho*-proton changes in parallel with the direction of the shift of the signal of the NH proton in the ^{1}H NMR spectra. Thus, in the case of cations **6**-H^+—**8**-H^+, where the largest portion of positive charge must be localized on the 1-N atom, the signal of the H(7) proton appears to be the low-field one rather than that of the H(2) proton. This is likely due to the shielding of the latter because of the strong +*M*-effect of the amino groups. A similar picture is also observed for the cations containing the 4-CHO and 4-COMe groups, in which the H(2) proton is deshielded more strongly than the H(7) proton.

In the cations of the "proton sponge" itself and its formally symmetric 2,7-dihalo- (**2**-H^+ and **4**-H^+) and 4,5-dihalosubstituted derivatives (**3**-H^+ and **5**-H^+), the hydrogen bridge is strictly symmetric in solution (the spectrum of type *a* in Fig. 2). However, there are several essential differences between these cations and they will be discussed below.

There is an approximately parallel dependence between the degree of asymmetry of the IHB and the difference between the chemical shifts of the protons of the Me_2N groups: $\Delta\delta = \delta(8\text{-}NMe_2) - \delta(1\text{-}NMe_2)$. The larger this difference, the more asymmetric the hydrogen bridge. For instance, the Δδ values (in Hz) for cations **6**-H^+—**8**-H^+ change as follows: −36 (4-NHMe), −31 (4-NH_2), and −13 (4-NMe_2), which is in agreement with decreasing the *PL*-1 index in this series.

The signal of the NH proton. The chemical shift of the NH proton in the ^{1}H NMR spectra of the studied salts is dependent on the nature, number, and positions of the substituents (see Table 1). The strong deshielding of chelated protons is known to be due to the totality of a number of electrostatic interactions.[22] At the same time, the anisotropic effect of the π-electron fragment of the molecule can also make an appreciable contribution to the deshielding. The cation of 1,14-diaza[5]helicene (**20**-H^+) can serve as the most dramatic example.[23] In the ^{1}H NMR spectrum of this cation obtained in DMSO-d_6 the signal of the NH proton is observed in the unusually low field at δ 24. This is explained by a helical arrangement of benzene rings; as a result, the chelated proton experiences an increased effect of the diamagnetic component of the magnetic field produced by the circular electron current.



20-H^+

It can be assumed that in the case of cations of "proton sponges" a similar effect can occur due to deviation of the NH proton out of the ring plane. First of all this must be favored by steric factors disturbing the optimal orientation of the Me_2N groups upon the formation of IHB, for instance, in the case of 2,7-dihalo derivatives **2**-H$^+$ and **4**-H$^+$. In fact, they are characterized by record values of the chemical shifts of the NH proton among the cations of naphthalene "proton sponges" (δ 19.9 to 20.3). The increased volumes of the substituents in position 4 (or 5) also favor the deshielding of the NH proton. For instance, the δ(NH) values increase in the sequence 4-NH_2 < 4-NHMe < 4-NMe_2 < 4-NHCOMe for the donor substituents and in the sequence 4-CN < 4-CHO < 4-NO_2 < 4-COMe for the acceptor substituents. This tendency is most clearly seen in the spectra of the cations of 4,5-dihalo derivatives 3-H$^+$ and **5**-H$^+$, where the δ(NH) value exceeds 19 ppm. It is likely that the *peri*-interaction between the substituents in positions 4 and 5 produces additional distortions of the ring in the cation and deviation of the N atoms out of the mean plane (according to X-ray analysis data, for some salts of composition **1**-H$^+$X$^-$ such deviations amount to 0.25 Å).[13] This can result in a change in the geometry of the hydrogen bridge and increase in the deshielding of the NH proton.

At the same time, unexpectedly low values of δ(NH) are observed in the ^{1}H NMR spectra of 2-chloro- and 2-bromo-1,8-bis(dimethylamino)naphthalene perchlorates obtained in DMSO-d_6 (18.02 and 18.09 ppm, respectively). This can be due to the strong weakening of the IHB characterized by a marked asymmetry. A more accurate conclusion will be drawn after performing an X-ray study of these salts.

It is of interest that there is no explicit relationship between the basicity of the "proton sponges" and the δ(NH) value. For instance, despite the fact that the pK_a values of compound **1** and its 4-trifluoroacetyl derivative **17** obtained in MeCN differ by more than three orders of magnitude,[24] the δ(NH) values for their cations are nearly equal.

Effect of the solvent. The ^{1}H NMR spectra of most of the cations were measured in both DMSO-d_6 and CD_3CN. The latter solvent has a much lower proton-acceptor power than DMSO: the pK_a value for DMSO and MeCN is equal to 0 and −10.1, respectively.[25]

The major conclusion is that acetonitrile favors symmetrization of the hydrogen bridge in all asymmetric cations. This effect is most clearly seen for the 2-halo and 4-amino derivatives, while for the cations containing $-M$-substituents in *para*-position it manifests itself to a lesser extent. For instance, a rather symmetrical IHB in cation **9**-H$^+$ becomes so symmetrized on going from DMSO (*PL*-1 = 56%) to MeCN (*PL*-1 = 51%) that the signal of the NH proton appears as a complex multiplet (see Fig. 3); however, the Me_2N groups are still nonequivalent (see Fig. 2, *b*, the Me_2N region). In parallel, an increase in the ($^3J_{1\text{-HN—CH}_3}$ + $^3J_{8\text{-HN—CH}_3}$) sum and δ(NH) is observed on going from DMSO to MeCN. It is likely that the NH proton in DMSO enters into a bifurcate interaction with the solvent resulting in the stretch of the N—H bond, weakening of the IHB, and a decrease in the δ(NH) value. The greater the asymmetry of the corresponding cation, the more pronounced this tendency. In addition, a similar bifurcation predetermines the possibility of a further cleavage of the IHB for the cations of relatively low-basic derivatives of the "proton sponge". Such a cleavage was mentioned above in the case of cation **16**-H$^+$. In this work, the cleavage of the IHB was also observed in the case of 1,8-bis(dimethylamino)-4-trifluoroacetylnaphthalene perchlorate **17**-H$^+$ in DMSO. It should be noted that symmetrization of the IHB on going from one solvent to another is accompanied by a decrease in the difference of the chemical shifts of the protons of Me_2N groups (see Table 1).

Noteworthy is that the sum of the spin-spin coupling constants ($^3J_{1\text{-HN—CH}_3}$ + $^3J_{8\text{-HN—CH}_3}$) in CD_3CN is nearly constant and for most cations is equal to 5.28 Hz. Only in a few cases does its value increase by no more than 0.2 Hz. This indicates the absence of a noticeable interaction between acetonitrile and the NH proton. The scatter of this value observed in DMSO points to appreciable interaction between the solvent and the NH proton, which varies over a wide range on going from one cation to another. This interaction is the least observed in the cation of the "proton sponge" itself.

Thus, the analysis of the constants of the spin-spin coupling between the NH proton and the Me_2N groups in the ^{1}H NMR spectra of the cations of asymmetrically substituted "proton sponges" is a convenient method for estimating the asymmetry of the IHB. The latter changes over a wide range: from strictly symmetric bonds to such bonds in which the proton belongs to one of the N atoms by more than 80%. Going from DMSO to a less proton-acceptor solvent, acetonitrile, favors symmetrization of the hydrogen bridge, which is most pronounced in the case of the cations of 2-halo- and 4-amino-1,8-bis(dimethylamino)naphthalenes. Judging by the extremely large values of the chemical shifts of the NH protons for the cations of 2,7-dihalo derivatives, the retention of the symmetry of the IHB in these cations is accompanied by considerable changes in the geometry of the hydrogen bridge. For this reason, an X-ray structural investigation of these salts would seem to be timely.

Experimental

^{1}H NMR spectra were recorded on a Unity-300 spectrometer (300 MHz) at 20 °C with $SiMe_4$ as the internal standard. The concentrations of the samples were $4 \cdot 10^{-2}$ mol L^{-1}. The signal of the NH proton of the **1**-H$^+$ perchlorate was recorded at a concentration of 0.12 mol L^{-1} using an integrator.

2-Bromo-1,8-bis(dimethylamino)naphthalene (19). A solution of NBS (0.14 g, 0.79 mmol) in $CHCl_3$ (10 mL) was added dropwise over a period of 30 min with intense stirring to a solution of compound **1** (0.16 g, 0.75 mmol) in $CHCl_3$ (7 mL) cooled to −15 °C. The dark-brown reaction mass was stirred an additional 30 min at ~20 °C, concentrated to 2 mL, and chromatographed on a column with Al_2O_3 (Brockmann III activity, d = 1.7 cm, l = 25 cm, with $CHCl_3$ as the eluent). Compound **19** was obtained as a colorless fraction with R_f 0.23. The yield was 80 mg (36%), a thick pale-yellow oil, highly soluble in most organic solvents and water-insoluble. Found (%): C, 57.41; H, 5.90; Br, 27.14. $C_{14}H_{17}BrN_2$. Calculated (%): C, 57.35; H, 5.84; Br, 27.25. ^1H NMR ($CDCl_3$), δ: 2.75 (s, 6 H, 8-NMe_2); 3.02 (s, 6 H, 1-NMe_2); 7.07 (dd, 1 H, H(7), $J_{H(5)-H(7)}$ = 1.34 Hz); 7.30 (d+t, 2 H, H(3), H(6), $J_{H(3)-H(4)}$ = 8.67 Hz, $J_{H(6)-H(7)}$ = 7.39 Hz); 7.37 (dd, 1 H, H(5), $J_{H(5)-H(6)}$ = 7.99 Hz); 7.51 (d, 1 H, H(4)).

2,7-Dibromo-1,8-bis(dimethylamino)naphthalene (4). A solution of NBS (0.31 g, 1.74 mmol) in $CHCl_3$ (20 mL) was added over a period of 30 min with stirring to a solution of compound **1** (0.16 g, 0.75 mmol) in $CHCl_3$ (7 mL) cooled to −15 °C. The reaction mass was stirred an additional 30 min at 20 °C, concentrated to 3 mL, and chromatographed on a column with Al_2O_3 (Brockmann III activity, d = 1.7 cm, l = 25 cm, with $CHCl_3$ as the eluent). Compound **4** was collected as a yellow fraction with R_f 0.54. Yield 145 mg (52%), yellow needles, m.p. 75—76 °C (from MeOH). Found (%): C, 45.01; H, 4.47; Br, 43.17. $C_{14}H_{16}Br_2N_2$. Calculated (%): C, 45.19; H, 4.33; Br, 42.95. ^1H NMR ($CDCl_3$), δ: 2.96 (s, 12 H, 1-NMe_2 and 8-NMe_2); 7.35 (d, 2 H, H(3), H(6), $J_{H(3)-H(4)}$ = 8.68 Hz); 7.51 (d, 2 H, H(4), H(5), $J_{H(5)-H(6)}$ = 8.68 Hz).

Synthesis of perchlorates (general procedure). Perchloric acid (70%, 0.4 mmol) was added to a solution of corresponding base (0.04 mmol) in ethyl acetate (2 mL), and after 1 min the mixture was diluted with ether (3 mL). The precipitate was filtered off, washed with ether, dried in air, and recrystallized. The yields were quantitative. All perchlorates are colorless substances. Properties of perchlorates of **6**-H^+—**8**-H^+, **3**-H^+ and **11**-H^+, **10**-H^+, and **16**-H^+ have been described previously (see Refs. 1, 15, 26, and 14, respectively); characteristics of other salts are given in Table 3.

The authors express their gratitude to N. V. Vistorobskii for kindly submitting several bases of 1,8-bis(dimethylamino)naphthalenes.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-32153a). NMR spectra were recorded at the RFBR Center of Collective Use at the Institute of Physical and Organic Chemistry of the Rostov State University.

References

1. V. A. Ozeryanskii and A. F. Pozharskii, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1501 [(*Russ. Chem. Bull.*, 1997, **46**, 1437 (Engl. Transl.)].
2. F. Hibbert, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1862.
3. A. F. Pozharskii, A. N. Suslov, N. M. Starshikov, L. L. Popova, N. A. Klyuev, and V. A. Adanin, *Zh. Org. Khim.*, 1980, **16**, 2216 [*J. Org. Chem. USSR*, 1980, **16** (Engl. Transl.)].
4. H. A. Staab and T. Saupe, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 865.
5. A. L. Llamas-Saiz, C. Foces-Foces, and J. Elguero, *J. Mol. Struct.*, 1994, **328**, 297.
6. Z. Dega-Szafran, B. Nowak-Wydra, and M. Szafran, *Magn. Res. Chem.*, 1993, **31**, 726.
7. Z. Malarski, L. Sobczyk, and E. Grech, *J. Mol. Struct.*, 1988, **177**, 339.
8. B. Brzezinski, E. Grech, Z. Malarski, and L. Sobczyk, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 1777.
9. B. Brycki, B. Brzezinsky, E. Grech, Z. Malarski, and L. Sobczyk, *Magn. Res. Chem.*, 1991, **29**, 558.
10. L. Jaroszewski, B. Lesyng, J. J. Tanner, and J. A. McCammon, *Chem. Phys. Lett.*, 1990, **175**, 282.
11. A. F. Pozharskii, *Usp. Khim.*, 1998, **67**, 3 [*Russ. Chem. Rev.*, 1998, **67**, 1 (Engl. Transl.)].
12. J. A. Kanters, A. Schouten, A. J. M. Duisenberg, T. Glowiak, Z. Malarski, L. Sobczyk, and E. Grech, *Acta Crystallogr., C*, 1991, **47**, 2148.
13. J. A. Kanters, E. H. ter Horst, J. Kroon, and E. Grech, *Acta Crystallogr., C*, 1992, **48**, 328.
14. A. F. Pozharskii, V. V. Kuz'menko, G. G. Aleksandrov, and D. V. Dmitrienko, *Zh. Org. Khim.*, 1995, **31**, 570 [*Russ. J. Org. Chem.*, 1995, **31** (Engl. Transl.)].
15. V. A. Ozeryanskii, A. F. Pozharskii, and N. V. Vistorobskii, *Zh. Org. Khim.*, 1997, **33**, in press [*Russ. J. Org. Chem.*, 1997, **33**, in press (Engl. Transl.)].
16. N. V. Vistorobskii and A. F. Pozharskii, *Zh. Org. Khim.*, 1989, **25**, 2154 [*J. Org. Chem. USSR*, 1989, **25** (Engl. Transl.)].
17. S. Toppet, K. Platteborze, and T. Zeegers-Huyskens, *J. Chem. Soc., Perkin Trans. 2*, 1995, 831.
18. H. J. G. Yah, M. Soto, and I. Morishima, *J. Magn. Reson.*, 1977, **26**, 365.
19. *Correlation Analysis in Chemistry: Recent Advances*, Eds. N. B. Chapman and J. Shorter, Plenum Press, New York—London, 1978.
20. V. Balasubramaniyan, *Chem. Rev.*, 1966, **66**, 567.
21. *The Chemistry of the Amino Group*, Ed. S. Patai, Interscience Publ., London—New York—Sydney, 1968, 161.
22. B. I. Ionin, B. A. Ershov, and A. I. Kol'tsov, in *YaMR-spektroskopiya v organicheskoi khimii* [*NMR Spectroscopy in Organic Chemistry*], Khimiya, Leningrad, 1983, 56 (in Russian).
23. H. A. Staab, M. A. Zirnstein, and C. Krieger, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 86.
24. A. F. Pozharskii, N. L. Chikina, N. V. Vistorobskii, and V. A. Ozeryanskii, *Zh. Org. Khim.*, 1997, **33**, in press [*Russ. J. Org. Chem.*, 1997, **33**, in press (Engl. Transl.)].
25. E. M. Arnett, in *Progress in Physical Organic Chemistry*, Eds. S. G. Cohen, A. Streitwieser, and R. W. Taft, Interscience Publ., New York—London, 1963.
26. N. V. Vistorobskii and A. F. Pozharskii, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2297 [*Russ. Chem. Bull.*, 1996, **45**, 2181 (Engl. Transl.)].

Received March 31, 1997;
in revised form June 6, 1997