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UDC 547.654.1

Naphthalene 'proton sponges'

A F Pozharskii

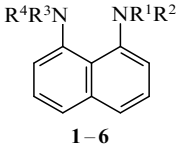
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Abstract. Methods of synthesis, physicochemical and structural characteristics, and reactivity of 1,8-bis(dialkylamino)naphthalenes and some of their close analogues pertaining to the class of so-called 'proton sponges' are considered. The bibliography includes 154 references.

I. Introduction

In 1968, Alder *et al.*[1] reported on a discovery of unusual changes in the variations of basicity in the series of *N*-methylated 1,8-diaminonaphthalenes (Table 1). It has been found that the pK_a values for the unsubstituted diamine **1** and its mono-, di-, and trimethyl derivatives **2** – **5** fall in the range typical of ordinary aryl amines, while that for 1,8-bis(dimethylamino)naphthalene **6** increases abruptly by nearly six orders. As a result, the basicity of compound **6** exceeds greatly that of both the known aromatic amines and practically all alkylamines. Further studies revealed that this feature is characteristic not only of aqueous solutions of the amine **6**, but also of solutions in non-aqueous solvents (*e.g.* acetonitrile[2]) and the gas phase.[3]



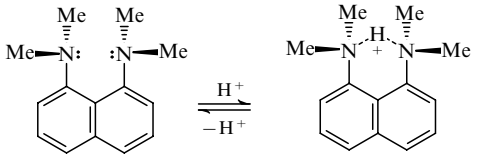
1 – **6**

Compound	R^1	R^2	R^3	R^4
1	H	H	H	H
2	Me	H	H	H
3	Me	H	Me	H
4	Me	Me	H	H
5	Me	Me	Me	H
6	Me	Me	Me	Me

It is believed that the abnormally high basicity of the compound **6** is caused by three main factors: (1) destabilisation of the base due to strong repulsion of unshared electron pairs of nitrogen atoms, (2) formation of a strong intramolecular hydrogen bond (IHB) in the protonated form, the cation (**6**-H^+), and (3) steric strain relief in the molecule upon the transition from a non-planar base to a planar cation.

A F Pozharskii Rostov State University, ul. Zorge 7, 344090 Rostov-on-Don, Russian Federation. Fax (7-863) 228 56 67. Tel. (7-863) 222 39 58. E-mail Pozharsk@pozhar.rnd.runnet.ru

Received 7 April 1997
Uspekhi Khimii **67** (1) 3 – 27 (1998); translated by R L Birnova



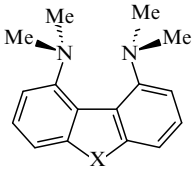
6 **6**-H^+

Another peculiar feature of the compound **6** is the slowness of proton addition – detachment due to the shielding of internitrogen space by four methyl groups. Thus, the high thermodynamic basicity of 1,8-bis(dimethylamino)naphthalene is associated with its rather low kinetic basicity. This circumstance made it possible to establish a similarity in the behaviour of the diamine **6** and genuine sponges, which slowly absorb water and retain it very strongly so that water is difficult to squeeze out. For this particular reason, the compound **6** has been named 'proton sponge',[4] which is generally accepted now and is further extended to all other compounds possessing this type of properties. At present, we can speak about the concept of 'proton sponges', which is based on the following principles: (1) the proper structural organisation of their molecule which provides rigid fixation of two nitrogen atoms at a sufficiently close distance from each other; (2) the existence in the molecule of a base of a destabilising repulsion effect of unshared electron pairs of the nitrogen atoms; (3) the occurrence of a strong IHB in the cation, which relieves steric and electronic strains characteristic of a base, and (4) the presence of a hydrophobic environment at the nitrogen atoms, most often in the form of alkyl groups, which actually accounts for the 'sponge' effect.

Table 1. Basicity constants, pK_a, of *N*-methyl derivatives of 1,8- diaminonaphthalene (25 °C).

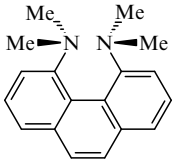
Compound	pK_a	
	in water[1]	in acetonitrile[2]
1	4.61	10.99
2	–	11.64
3	5.61	11.95
4	–	12.87
5	6.43	12.91
6	12.34	18.18

On the basis of this concept, the synthesis of a series of non-naphthalene proton sponges has been carried out since the mid-1980's. Thus, the research group headed by Staab *et al*. synthesised and analysed sponges of the fluorene **7**,[5] heterofluorene **8**,[6] and phenanthrene **9**[7] series and their analogues **10**[8,9] and **11**[10] with an sp^2-hybridised nitrogen heteroatom. The vinamidine sponges **12, 13** possessing even stronger basicity than compounds **6**–**11** were synthesised by Schwesinger *et al*.[11]

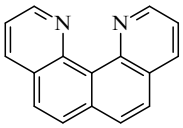


7, **8**

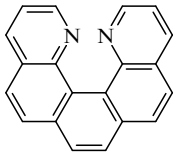
7: X = CH_2;
8: X = O, S, Se, Te.



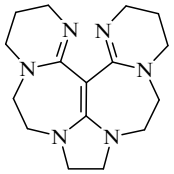
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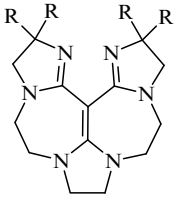
10



11



12



13
R = H, Me.

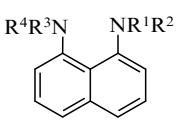
Until now, the main attention in the studies on 'proton sponges' has been given to their structural and physicochemical characteristics and bases and cations were considered from somewhat different points of view. Thus the following aspects have been studied for cations: (1) geometry of the intramolecular hydrogen bond (the distance between the amine nitrogen atoms, the N–H···N angle and, particularly, the position of the proton responsible for the IHB symmetry, (2) the ^{1}H NMR spectra (primarily, the chemical shift of the NH-proton and the constants of its spin-spin coupling with the NMe_2 groups), (3) kinetic NH-acidity (deprotonation rate).

Bases were analysed as regards: (1) their molecular geometry (the distance between the nitrogen atoms, distortion from the planar structure of the rings, conformational phenomena), (2) basicity, (3) the nature of interactions of unshared electron pairs of the nitrogen atoms with one another and with the π-system of the ring, and (4) reactivity.

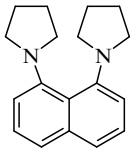
Several reviews survey exclusively structural and physicochemical aspects of the 'proton sponges'.[12–15] At the same time, a vast range of interesting information has been accumulated concerning methods of their synthesis and, especially, their reactivity. This review has been written with the aim of generalising the data on the methods of synthesis, reactivity, and physicochemical characteristics of 'proton sponges' of the naphthalene series. The literature cited herein includes the works published before 1997.

II. The types of naphthalene 'proton sponges'

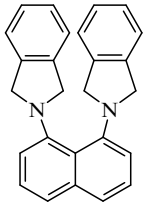
The types of naphthalene 'proton sponges' known to date are represented by the structures **14**–**30**.



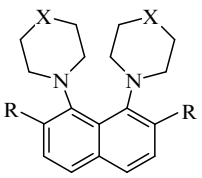
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15

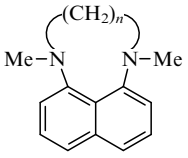


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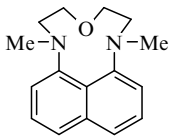


17, **18a**–**c**

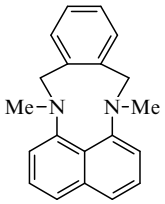
17: X = CH_2, R = H;
18a: X = O, R = H;
18b: X = O, R = OMe;
18c: X = O, R = OEt.



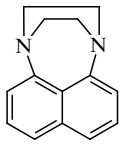
19a–**e**
n = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**), 5 (**e**).



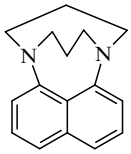
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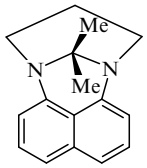
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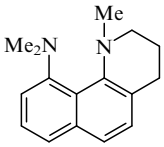
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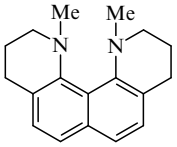
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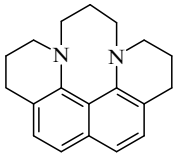
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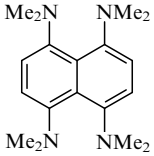
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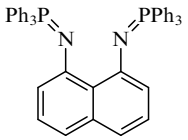
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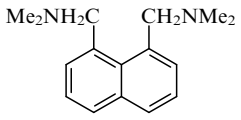
27



28



29



30

These include 1,8-bis(dialkylamino)naphthalenes **14** (the substituents R^1–R^4 can be identical or different), their analogues **15**–**18** in which the amine nitrogen atoms are incorporated into five- or six-membered rings, compounds **19**–**24** with bridgehead heteroatoms, compounds **25**–**27** with the nitrogen atoms incorporated in the fused rings, and the so-called double 'proton sponge' **28**. The properties of 'proton sponges' have also been found in iminophosphoranes **29** and 1,8-bis(dimethylamino-methyl)naphthalene **30**.

III. Synthesis of 1,8-bis(dialkylamino)-naphthalenes and their analogues

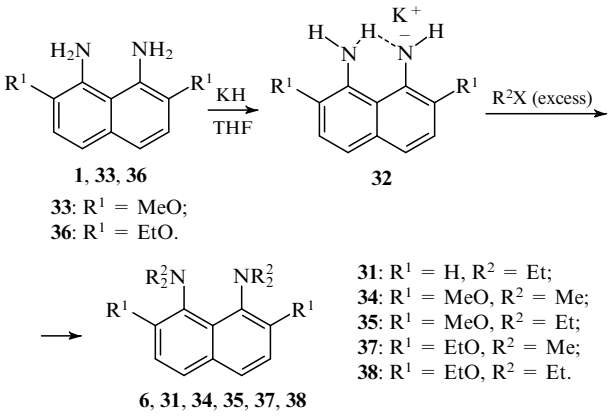
1. 1,8-Bis(dialkylamino)naphthalenes

There are two general approaches to the synthesis of these compounds which successfully complement each other. The first of them is based on the alkylation of 1,8-diaminonaphthalene or its partially alkylated derivatives. In the second, 1,1,3-trialkyl-2,3-dihydroperimidinium salts serve as the starting compounds.

a. Syntheses based on 1,8-diaminonaphthalenes

The first representative of naphthalene 'proton sponges' described in the literature was 1,8-bis(diethylamino)naphthalene **31**, which was obtained by heating the diamine **1** with an excess of ethyl bromide at 135 °C in the presence of alkali[16] (see also Ref. 17). Later, 1,8-bis(dimethylamino)naphthalene **6** was synthesised by treating the diamine **1** with dimethyl sulfate (the yield was not specified).[18] Initially, this compound was characterised as an oil,

although it is now known as a crystalline substance with m.p. 47–48 °C.[1]

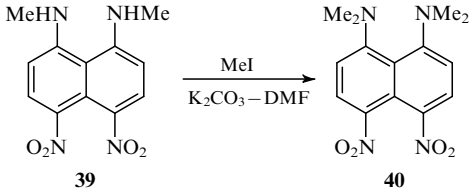


Two convenient procedures have been elaborated for exhaustive alkylation of the diamine **1**. Both of them entail the use of strong bases (sodium or potassium hydrides in anhydrous tetrahydrofuran [19] or potassium hydroxide in dimethyl sulfoxide) for the ionisation of N–H-bonds.[20]

Obviously, under these conditions it is the N-anions of the original diamine and intermediate substitution products that undergo alkylation. The ionisation is favoured by the very high (in comparison with ordinary arylamines) NH-acidity of the diamine **1** (pK_a = 24.5, DMSO, 25 °C), which is ascribed to the stabilisation of the N-anion **32** through IHB.[21] The yields of 'proton sponges' vary from high to satisfactory. Thus in the alkylation of the compound **6** in the presence of KH–THF or KOH–DMSO systems, the yields exceed 90%. To obtain good yields of the compound **31**, it is recommended to use hexametapol as a solvent instead of DMSO.[20] However, the alkylation of 1,8-diamino-2,7-dimethoxynaphthalene **33** gives compounds **34** and **35** in low yields (40% and 21%, respectively).[22] The yields of the 'proton sponges' **37**, **38** obtained by the alkylation of the diamine **36** are even lower.[23] The yield of the 'double sponge' **28** obtained by methylation of 4,5-diamino-1,8-bis(dimethylamino)naphthalene with dimethyl sulfate in an NaH–THF system was 31%.[24]

Depending on the length of the methylene chain, alkylation of the diamine **1** with α,ω-dihalogenoalkanes gives various types of 'proton sponges' (Table 2). If the halogens are separated by 4 or 5 atoms, compounds **15**–**18** are formed in which the amine nitrogen atoms are incorporated into five- or six-membered rings. With a closer arrangement of the halogen atoms, bridged sponges **22**–**24** are formed. Interestingly, the alkylation with 1,3-dibromopropane gives, along with compound **23**, a low yield of the pentacyclic compound **27**. Apparently, its precursor is naphtho[1,8-*b*,*c*]-1,5-diazacyclooctane (also isolated in low yield), which undergoes first *N*-, and then intramolecular *C*-alkylation with 1,3-dibromopropane.

In some cases, 1,8-bis(methylamino)naphthalene and its derivatives served as the starting compounds in the synthesis of 'proton sponges' by alkylation. Thus heating of 1,8-bis(methylamino)-4,5-dinitronaphthalene **39** with methyl iodide in DMF in the presence of potassium carbonate gave the compound **40** (yield 32%).[24]



Alder *et al.*[22] have synthesised a series of 'proton sponges' **19**–**21** by treating 1,8-bis(methylamino)naphthalene **3** with α,ω-dihalogenoalkanes (Table 3).

Table 3. 'Proton sponges' obtained by treatment of 1,8-bis(methylamino)-naphthalene with α,ω-dihalogenoalkanes and their analogues.[22]

'Proton sponge'	α,ω-Dihalide	Reaction conditions	Yield (%)
19b	$Br(CH_2)_2Br$	NaH–THF	80
19b	$Br(CH_2)_2Br$	$NaHCO_3$–DMF	25
19c	$Br(CH_2)_3Br$	$NaHCO_3$–$MeO(C_2H_4O)_2Me$, 190 °C	43
19c	$Br(CH_2)_3Br$	NaH–THF	1
19d [a]	$Br(CH_2)_4Br$	$NaHCO_3$–$MeO(C_2H_4O)_2Me$, reflux, 46 h	58
19e	$Br(CH_2)_5Br$	Na_2CO_3–$MeO(C_2H_4O)_2Me$	25
20	$O(CH_2CH_2Cl)_2$	Na_2CO_3–$MeO(C_2H_4O)_2Me$, reflux	77
21	α,α′-Dibromo-*o*-xylene	Na_2CO_3–DMF, reflux	13

[a] The compound was isolated and purified as a salt with the BF_4^- anion.

The alkylation of *N*,*N*,*N*′-trialkyl-substituted 1,8-diaminonaphthalenes proceeds very smoothly. The reaction is usually performed by heating the latter compounds with an excess of alkyl halide in an appropriate solvent or without any solvent. The proton sponge salt formed is converted into the base by treatment with an aqueous alkali.[25, 26]

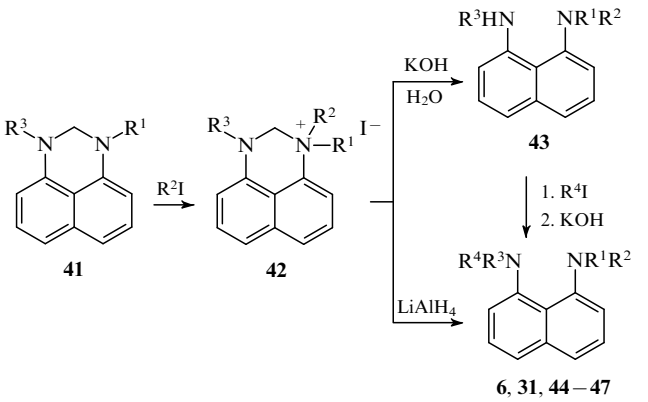
b. Syntheses based on 1,1,3-trialkyl-2,3-dihydroperimidinium salts

Far from all of the naphthalene 'proton sponges' can be obtained by alkylation of *peri*-diamines or by functionalisation of the unsubstituted compound **6**. Therefore, the author of this review with his coworkers have developed an alternative and practically versatile procedure for the synthesis of 1,8-bis(dialkylamino)-naphthalenes from 1,1,3-trialkyl-2,3-dihydroperimidinium salts. First, quaternisation of readily available 1,3-dialkyl-2,3-dihydroperimidines **41** gives the salts **42**, which are subjected to reductive scission with lithium aluminium hydride, resulting in the corresponding 'proton sponge' (in the ring-opening, the μ-methylene group is converted into the methyl group, *i.e.*, in this case R^4 = Me). However, sometimes this reaction does not proceed smoothly, *e.g.*, if the molecule of a salt contains halogens or other easily reducible groups. Better results are achieved when the salts **42** are treated with an aqueous alkali, which gives high yields of the corresponding *N*,*N*,*N*′-trialkyl-substituted 1,8-diaminonaphthalene **43**. Its alkylation and subsequent treatment of the quaternary salt with alkali give the target 'proton sponge'. This approach was used, in particular, in the synthesis of 1,8-bis(dialkylamino)-

Table 2. 'Proton sponges' obtained by treatment of 1,8-diaminonaphthalene with α,ω-dihalogenoalkanes and their analogues.[22]

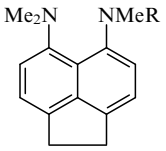
'Proton sponge'	α,ω-Dihalide	Reaction conditions	Yield (%)
15	$Br(CH_2)_4Br$	Na_2CO_3, refulx	60
16	α,α′-Dibromo-*o*-xylene	Na_2CO_3–DMF, refulx	5
17	$Br(CH_2)_5Br$	Na_2CO_3, refulx	60
18a	$O(CH_2CH_2Cl)_2$	Na_2CO_3, 150 °C	10
22	$BrCH_2CH_2Br$	Na_2CO_3–DMF, refulx	42
24	$Br(CH_2)_3Br$	Na_2CO_3–acetone, reflux	34
23	$Br(CH_2)_3Br$	DMF, diglyme or sulfolane, 150–200 °C	1–5
27	$Br(CH_2)_3Br$		1–2

naphthalenes **6**, **31**, and **44**–**47** with all possible combinations of the methyl and ethyl groups.[25]



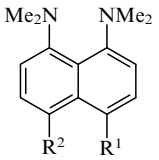
Compound	R^1	R^2	R^3	R^4
44	Me	Me	Me	Et
45	Me	Me	Et	Et
46	Me	Et	Me	Et
47	Et	Et	Et	Me

In a similar way, the acenaphthene 'sponges' **48**, **49**,[25] 4-halogeno- and 4,5-dihalogeno-1,8-bis(dimethylamino)naph-thalenes **50**–**53**,[27,28] and partially hydrogenated derivatives of 10-dimethylaminobenzo[*h*]quinoline **25** and quinolino[7,8:7′,8′]-quinoline **26** were synthesised.[29]



48, **49**

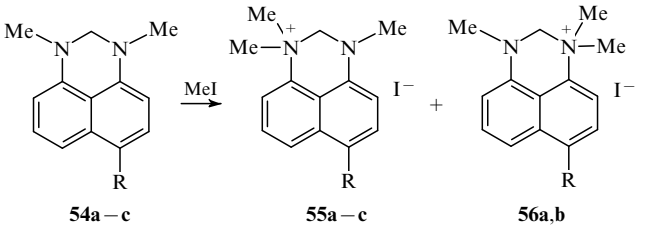
48: R = Me;
49: R = Et.



50–**53**

50: R^1 = Cl, R^2 = H;
51: R^1 = Br, R^2 = H;
52: R^1 = R^2 = Cl;
53: R^1 = R^2 = Br.

It should be noted that quaternisation of 6-halogeno-1,3-dimethyl-2,3-dihydroperimidines **54a**,**b** gives a mixture of isomeric salts **55a**,**b** and **56a**,**b** in comparable amounts. Separation of this mixture is not required, since methylation of the isomeric *N*,*N*,*N*′-trialkyl-substituted 1,8-diaminonaphthalenes formed upon alkaline treatment give the same final product.[27,28]

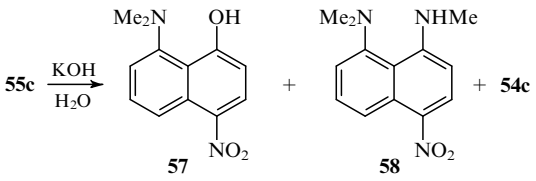


54a–**c** **55a**–**c** **56a**,**b**

R = Br (**a**), Cl (**b**), NO_2 (**c**).

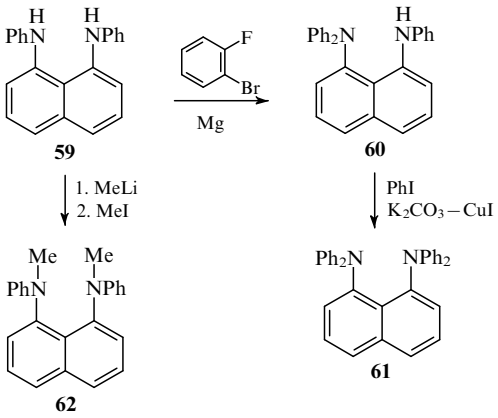
In some cases, however, alkylation of non-symmetrical dihydroperimidines occurs regioselectively. Thus if the nitrogen atoms have different substituents (*e.g.*, Me and Et), quaternisation affects only the nitrogen atom carrying the smallest group.[25] Analogously, but owing to electronic (rather than steric) factors, methylation of 1,3-dimethyl-6-nitro-2,3-dihydroperimidine **54c** gives exclusively the salt **55c**.[30]

The latter manifests an abnormal behaviour upon alkaline treatment. The main product of this reaction is the naphthol **57** formed in 65% yield. Dihydroperimidine **54c** was formed in a small amount (5%), whereas nitronaphthylenediamine **58** was present in only trace amounts.



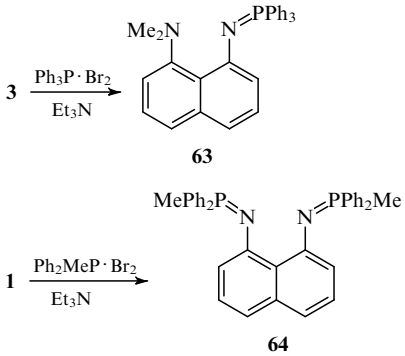
2. Analogues of 'proton sponges' with *N*-aryl groups

Two compounds of this type have been described thus far, *viz*., 1,8-bis(diphenylamino)- and 1,8-bis(methylphenylamino)-naphthalene,[31] which do not resemble classical 'proton sponges' in properties and molecular geometry. Fairly accessible 1,8-bis(phenylamino)naphthalene **59** served as the starting compound for their synthesis. Its sequential arylation (with dehydrobenzene generated from *o*-bromofluorobenzene and then with iodobenzene according to Ullman) has led, *via* the triphenyl-substituted compound **60**, to 1,8-bis(diphenylamino)naphthalene **61**. An attempted exhaustive Ullman arylation of the diamine **1** was unsuccessful. To synthesise 1,8-bis(methylphenylamino)-naphthalene **62**, the diamine **59** was converted into the dilithium salt, which was further subjected to methylation.



3. Iminophosphorane 'sponges'

In addition to iminophosphorane **29**, its analogues **63** and **64** were synthesised.[32,33] The general method for the synthesis of these compounds involves the reaction of a bromine–triphenylphosphine (diphenylmethylphosphine) complex with the corresponding amine in the presence of triethylamine. The yields are high, as a rule.



4. 1,8-Bis(dimethylaminomethyl)naphthalene

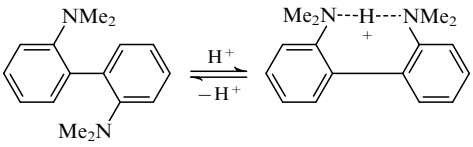
Compound **30** was obtained in 90% yield by reduction of 1,8-bis(dimethylcarbamoyl)naphthalene with lithium aluminium hydride.[34] In some features (see below), this can also be referred to as a 'proton sponge'.

IV. Physicochemical properties of naphthalene 'proton sponges'

1. Basicity

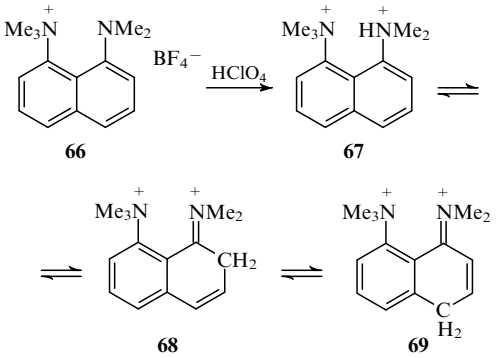
Unquestionably, high basicity is the main distinctive property of all the 'proton sponges'. The analysis of factors influencing this parameter sheds more light on both structural peculiarities of these compounds and their reactivity. We have already mentioned the three main reasons for the high basicity of 'sponges', namely, destabilisation of the base as a result of repulsion of unshared electron pairs of the proximal nitrogen atoms, steric strain relief upon the transition to the cation, and the formation of a strong IHB in the cation. The greatest importance is given to the latter factor, therefore the stability and geometry of IHB in cations of the 'proton sponges' have become objects of intense studies using ^{1}H NMR, IR spectroscopy, X-ray analysis, and other methods (see below).[13]

The contribution of IHB to the general increase in the basicity of a 'proton sponge' can be roughly estimated from the pK_a value of 2,2′-bis(dimethylamino)diphenyl **65**. This value is equal to 7.9, *i.e.*, the basicity of this compound is nearly three orders of magnitude higher than that of *N*,*N*-dimethylaniline.[35] Since the benzene rings in the compound **65** are turned at an angle of 135° relative to one another, this is free from both noticeable repulsion of unshared electron pairs of the nitrogen atoms and steric strain due to this repulsion. Thus this difference in basicity can be ascribed, with a fair degree of confidence, to the stabilising effect of the IBH in the cation **65**-H$^+$. Apparently, the energy contribution of the IBH in case of the 'proton sponge' is even higher, since the cation **6**-H$^+$ contains a six-membered ring, which is more stable than the seven-membered ring in the cation **65**-H$^+$.



65 **65**-H$^+$

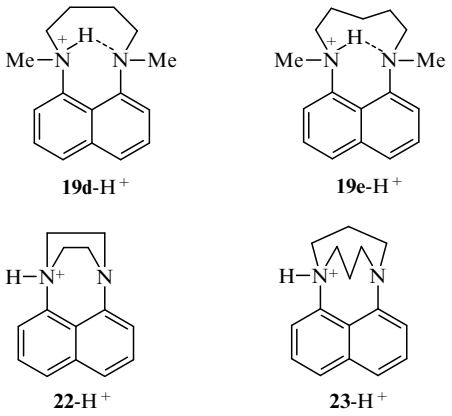
Of special note is the fact that the second ionisation constant of the 'proton sponge' measured in water (p$K_a^2 = -9.0$)[36] is much lower than the first one (p$K_a^1 = 12.1$). It is not surprising that in contrast to 1,8-diaminonaphthalene, which gives a stable crystalline dihydrochloride, the corresponding salts of the 'proton sponge' cannot be obtained. The reason is that the rupture of the IBH needed for the second *N*-protonation is energetically unfavourable even under the action of strong acids. Cations of other 1,8-bis(dialkylamino)naphthalenes behave in a similar way. At the same time, under the action of $HClO_4$ or CF_3SO_3H, the *N*-methylated cation of the 'proton sponge' **66** devoid of the IHB forms the dication **67**, which is partly isomerised into the *C*-protonated forms **68** and **69**.[37, 38]



66 **67**

68 **69**

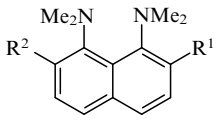
For the same reason, the chelated cations **19d**-H$^+$ and **19e**-H$^+$ do not undergo second *N*-protonation under analogous conditions, whereas the non-chelated cations **22**-H$^+$ and **23**-H$^+$ do form the N(1),N(8)-dications.[37]



19d-H$^+$ **19e**-H$^+$

22-H$^+$ **23**-H$^+$

Tables 4 and 5 present the values of the basicity constants, pK_a, of the naphthalene 'proton sponges' both without additional substituents in the naphthalene nucleus (**6**, **31**, **44**–**47**), and with substituents at *ortho*- (**25**, **26**, **70**–**73**) and *para*- (**48**–**53**, **74**–**86**) positions, as well as for one 2,4-disubstituted **87** and polynuclear compounds **88**–**93**. Only a few of the pK_a values have been measured in water or in mixtures of water with other solvents. Most of the data were obtained for acetonitrile; in some cases the measurements were performed in DMSO. The pK_a values of the compound **6** in acetonitrile (18.2), water (12.1, 12.3), and DMSO (7.5) indicate that the basicity of the 'sponge' drops by more than ten orders of magnitude as the proton-acceptor properties of a solvent increase.



70–**73**

70: R^1 = Cl, R^2 = H;
71: R^1 = Br, R^2 = H;
72: R^1 = R^2 = Cl;
73: R^1 = R^2 = Br.

Table 4. Basicity constants, pK_a, of naphthalene 'proton sponges' and some of their analogues in aqueous solvents.

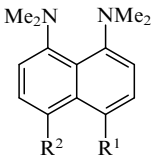
Compound	Solvent [a]	pK_a	Ref.
6	H_2O	12.3; 12.1	1, 17
6	 – H_2O (1 : 4)	11.5	17
31	DMSO – H_2O (3 : 7)	13.0	39
31	 – H_2O (1 : 4)	12.7	17
15	H_2O	10.0	40
18a	H_2O	7.5	23
34	DMSO – H_2O (3.5 : 6.5)	16.1	41
35	DMSO – H_2O (3.5 : 6.5)	16.3	41
37	DMSO – H_2O (3.5 : 6.5)	16.1	23
38	DMSO – H_2O (3.5 : 6.5)	16.1	23
18b	H_2O	13.0	23
18c	H_2O	12.5	23
19a	EtOH – H_2O (1 : 1)	3.8	42
19b	H_2O	4.6	40
19c	H_2O	10.3	40
19d	DMSO – H_2O (3 : 7)	13.6	40
19e	DMSO – H_2O (3 : 7)	13.0	40
20	DMSO – H_2O (3 : 7)	12.9	43

[a] Ratio of components is given in brackets (v/v).

Table 5. Basicity constants, pK_a, of naphthalene 'proton sponges' in acetonitrile.

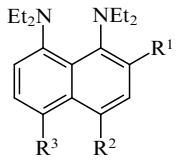
Compound	pK_a [a]	Ref.	Compound	pK_a [a]	Ref.
6	18.2; 18.5	2, 44	**79**	8.0 [b]	45
6	7.5 [b]	36	**28**	9.8 (4.9) [b]	24
31	18.95	25	**50**	17.4	44
44	18.5	25	**51**	17.3	44
45	18.7	25	**52**	16.1	44
46	18.7	25	**53**	16.4	44
47	18.9	25	**80**	14.9	44
48	18.3	25	**81**	12.3	44
49	18.6	25	**82**	16.8	44
25	17.5	29	**83**	14.9	44
26	17.6	29	**84**	14.1	46
70	18.35	44	**85**	15.3	46
71	18.20	44	**86**	11.8	46
72	17.8	44	**87**	15.5	46
73	17.45	44	**88**	18.6	44
74	17.8	44	**89**	14.6	44
75	14.45	44	**90**	18.1 (18.1)	44
76	9.8 [b]	45	**91**	18.3 (18.3)	44
77	18.35	44	**92**	18.4 (13.6)	44
78	10.1 [b]	45	**93**	18.5 (14.5)	44
79	19.15 (7.6)	44			

[a] The values in brackets relate to the second ionisation constant, pK_a^2.
[b] The pK_a values were measured in DMSO solution.



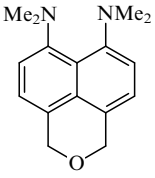
74–84

74: R^1 = CH=CH_2, R^2 = H;
75: R^1 = CH=$C(CN)_2$, R^2 = H;
76: R^1 = NH_2, R^2 = H;
77: R^1 = NHCOMe, R^2 = H;
78: R^1 = NHMe, R^2 = H;
79: R^1 = NMe_2, R^2 = H;
80: R^1 = CHO, R^2 = H;
81: R^1 = R^2 = CHO;
82: R^1 = COMe, R^2 = H;
83: R^1 = $COCF_3$, R^2 = H;
84: R^1 = NO_2, R^2 = H.

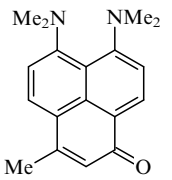


85–87

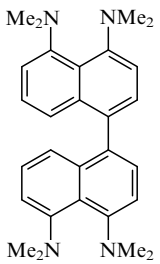
85: R^2 = NO_2, R^1 = R^3 = H;
86: R^1 = H, R^2 = R^3 = NO_2;
87: R^1 = R^2 = NO_2, R^3 = H.



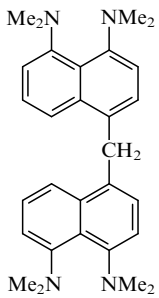
88



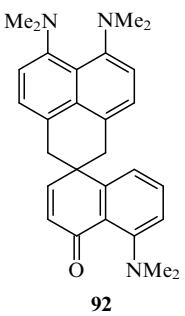
89



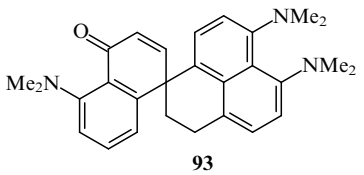
90



91



92



93

Measurements of the gas-phase basicity (that is the proton affinity) of the 'proton sponge' and other 1,8-diaminonaphthalenes have been carried out.[3] The corresponding values are given in Table 6 in comparison with analogous values for methylated derivatives of aniline and ammonia. The abrupt jump in basicity in both the gas phase and water is observed only for the transition from 1-dimethylamino-8-methylaminonaphthalene **5** to 1,8-bis-(dimethylamino)naphthalene **6**. This indicates that the abnormally high basicity of the 'proton sponge' in vapour and in water is due to the same factors. It is interesting to note that in the gas phase, all 1,8-diaminonaphthalenes are protonated at the nitrogen atom, whereas 1-aminonaphthalene and 1,3-diaminobenzene are protonated in the ring. It is believed that the stability of 1,8-diaminonaphthalene *N*-cations in the vapour is accounted for by the stabilising effect of the IHB.

Table 6. Effect of *N*-methylation on the gas-phase proton affinity (PA) and changes in free energy (ΔG_0^1) of protonation of the succeeding base in comparison with the preceding base in the gas phase and in water.[3,47]

Base	PA /kJ mol^{-1}	ΔG_0^1 /kJ mol^{-1}	
		gas phase	water
1	954.4	–	–
3	982.8	−28.5	−5.9
5	1000.8	−18.0	−4.6
6	1030.1	−29.3	−33.9
$PhNH_2$	895.0	–	–
PhNHMe	925.9	−31.0	−1.26
$PhNMe_2$	953.5	−27.6	−1.7
NH_3	866.1	–	–
$MeNH_2$	907.9	−4.2	−7.9
Me_2NH	939.3	−31.4	0
Me_3N	960.2	−20.9	+4.6

The dependence of gas-phase basicities of amines (including 1,8-diaminonaphthalenes) and core-bond energies of the σ-backbone has been studied.[47] It is linear for the bases the geometry of which is not changed significantly upon protonation. However, such a correlation was not found for compounds **3**, **5**, and **6**. It was suggested that for these compounds the degree of deviation from linearity can serve as a measure of steric strain relief upon the transition from the base to the cation. For the 'proton sponge' **6**, this value was estimated to be 62.8 kJ mol^{-1}, and for the amines **3** and **5**, 37.7 and 33.5 kJ mol^{-1}, respectively.

Let us now consider the effect of structural changes at the nitrogen atoms and in the ring on the basicity of 'sponges'. Successive substitution of the *N*-methyl groups by ethyl groups slightly increases the basicity, as a result of which the pK_a value of the 'tetraethyl sponge' **31** is 0.8–1.2 units higher than that of its tetramethyl analogue **6** (*cf.* Tables 4 and 5). More substantial changes in basicity are observed in those cases where the amine nitrogen atoms are incorporated into the rings. Thus, the basicity of 1,8-dipyrrolidino- and 1,8-dimorpholinonaphthalenes **15** and **18** is lower by 2.5 and 4.5 orders of magnitude, respectively, than that of the 'proton sponge' **6** (Table 4). The same tendency, although less pronounced, is manifested in compounds **25** and **26** (Table 5) the nitrogen atoms of which are incorporated into fused ring systems. It may be assumed that their structure is not optimum for the formation of a sufficiently strong IHB in the cation, *e.g.*, because the axes of unshared electron pairs of the nitrogen atoms can hardly be coplanar with the ring. This phenomenon was also noted for some non-naphthalene 'proton sponges'. Thus the basicity of benzo[1,2-*h*:4,3-*h*′]diquinoline **11** with a helicene structure is 2.5 orders of magnitude less[10] than that of the planar quino[7,8-*h*]quinoline **10** (Ref. 8) (pK_a = 10.3 and 12.8, respectively).

As can be inferred from Table 4, of a set of diamines **19**, only compounds **19c**–**e** can be regarded as 'proton sponges'. The basicity of the first two representatives of this series lies at a level characteristic of ordinary arylamines. It is understandable that the methylene and ethylene bridges in the molecules **19a**,**b** provide rigid fixation of the nitrogen atoms in the configuration where unshared electron pairs largely acquire *p*-character without any noticeable reciprocal repulsion; in addition, the IHB cannot be formed in their cations. Apparently, for this reason the bridged diamines **22**–**24**, which form the non-chelated cations **22**-H^+ and **23**-H^+, are not 'proton sponges'.

The effect of substituents in the nucleus on the basicity of 'proton sponges' is roughly as expected (Tables 4 and 5) for 2,7-dialkoxy derivatives **34**, **35**, **37**, and **38** the basicity of which is four orders of magnitude higher than that of the non-substituted 'sponges' (Table 4), and their salts are not significantly deprotonated by strong aqueous alkalis. Formerly, these compounds were considered to be the strongest of the known neutral bases. It is believed that the molecules of compounds **34**, **35**, **37**, and **38** manifest the so-called 'supporting effect' [Buttress effect. Ed.], in which *ortho*-substituents favour closer approach of unshared electron pairs of both dialkylamino groups to each other, enhancing electrostatic repulsion and, presumably, steric strain in the base. The 'supporting effect' was also observed in 2,7-dichloro- and 2,7-dibromo-1,8-bis(dimethylamino)naphthalenes **72** and **73**.[44, 48]

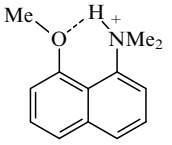
The attempts to separate the first and second ionisation constants for the binaphthyl **90** and binaphthylmethane **91** 'sponges' were unsuccessul.[44] Apparently, both their basic centers have little influence on each other.

The basicity of compounds **29**, **63**, and **64** could not be determined experimentally due to their poor solubility, slow rates of protonation, and hydrolysis of the iminophosphorane group. However, using complex extrapolations, the pK_a value for compound **29** in water was estimated to be equal to 15.6, which markedly exceeds the basicity of the classical 'proton sponges'.[49]

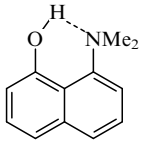
The basicity of 1,8-bis(dimethylaminomethyl)naphthalene **30** ($pK_a^1 = 18.3$, $pK_a^2 = 11.4$ in acetonitrile) is at a level typical of the 'naphthalene sponges'.[50] However, the fact that this compound binds two protons instead of one (as is the case with the classical 'proton sponges') testifies to the insufficiently strong IHB in the monocation; the latter finding was confirmed by ^1H NMR spectroscopic data.

2. The mechanism and rates of deprotonation of cations

As has already been mentioned, the high basicity of 'proton sponges' is combined with low rates of their protonation–deprotonation. The deprotonation rate constants for several 'sponges' are given in Table 7, which also contains data for the 1-dimethylamino-8-methoxynaphthalene cation **94**-H^+ and 8-dimethylaminonaphthol **95** for comparison.



94-H^+



95

Whereas the deprotonation rate for ordinary ammonium salts is limited by diffusion ($k \approx 3 \times 10^{10}$ litre mol^{-1} s^{-1}),[51] in the case of 'sponge' cations this process is much slower. Thus for the cation **6**-H^+ $k = 1.9 \times 10^5$ litre mol^{-1} s^{-1}, and for its tetraethyl analogue **31**-H^+ k is even one order of magnitude lower. Deprotonation of their 2,7-dimethoxy derivatives, **34**-H^+ and **35**-H^+, is especially slow, and in the latter case the reaction can even be followed spectrophotometrically. It is noteworthy that because of the high basicity of compounds **34** and **35**, the deprotonation of their cations is observed only in alkaline solutions of DMSO.

Table 7. Rate constants for the reaction of deprotonation of some 'proton sponge' cations.

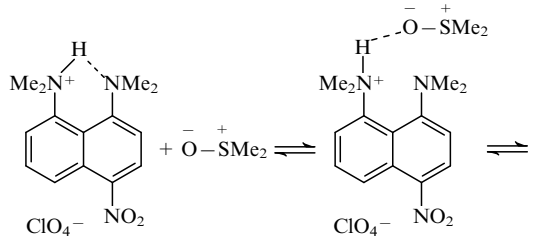
$$BH^+ + OH^- \overset{k}{\rightleftharpoons} B + H_2O.$$

Cation BH^+	Solvent [a]	k /litre mol^{-1} s^{-1}	Ref.
6-H^+	H_2O	1.9×10^5	17, 52
6-H^+	Dioxane–H_2O (1 : 4)	4.6×10^5	17
6-H^+	DMSO–H_2O (3 : 7)	6.1×10^5	14
31-H^+	Dioxane–H_2O (1 : 4)	1.6×10^4	17
31-H^+	DMSO–H_2O (3 : 7)	1.6×10^4	14
34-H^+	DMSO–H_2O (3 : 2)	4.4×10^2	41
35-H^+	DMSO–H_2O (3 : 2)	3.3	41
18a-H^+ (see [b])	H_2O	1.2×10^3	43, 53
20-H^+	DMSO–H_2O (3 : 7)	6.2×10^3	43
94-H^+ (see [b])	H_2O	0.4×10^7	54
95	DMSO–H_2O (4 : 1)	3.0×10^6	54

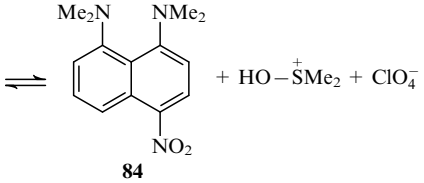
Note For more detailed information see Refs 23 and 40.
[a] Ratio of components is given in brackets (v/v). [b] HPO_4^{2-} was used as the base instead of OH^-.

It is reasoned that the low rates of cation deprotonation are mainly caused by the necessity of cleavage of a very strong IHB. Presumably, a certain role is played by steric factors: in the cation, the proton resides in a sort of hydrophobic 'pocket', therefore, access to a base must be hindered (especially in the case of tetraethyl 'sponges'). Compounds **94**-H^+ and **95** are also deprotonated very slowly, but still faster than the 'sponge' cations. It may be inferred from these data (Table 7) that the strength of the IHB decreases in the following order: **6**-H^+ > **95** > **94**-H^+.

Vivid debates in the current literature concern the mechanism of deprotonation of chelated species of 'proton sponge' cations.[14] Virtually all the data indicate that this process occurs in two steps: first, the IHB is cleaved under the influence of a base, and then deprotonation of the unchelated cation takes place. Apparently, the limiting step in this process is its first stage, therefore, the equilibrium concentration of the unchelated cation at each moment of time is low. However, we have recently observed for the first time in our laboratory all the three particles (both cations and the deprotonated base) in equilibrium, with 4-nitro-1,8-bis(dimethylamino)naphthalene **84** as an example.[55] It was found that the ^1H NMR spectrum of the cation **84**-H^+ in [$^2H_6$]-DMSO contained peaks not only of the chelated cation **84**-H^+-**a**, but also those of the free base **84** and of a third species the characteristics of which corresponded to those of the non-chelated cation **84**-H^+-**b**. At an initial concentration of the dissolved perchlorate **84**-H^+ of 5×10^{-2} mol litre^{-1}, the ratio **84**-H^+-**a** : **84**-H^+-**b** : **84** is 68 : 19 : 13, *i.e.*, under these conditions the chelated cation is predominant. If the concentration of the



84-H^+-**a** **84**-H^+-**b**



84

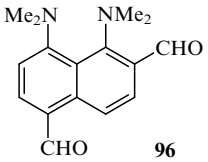
original salt decreases by one order, this ratio changes drastically (26 : 5 : 69) and the deprotonated base becomes the predominant form. The cation **84**-H^+-**a** does not undergo any noticeable changes in acetonitrile. Similarly, the cation of the 'proton sponge' **6**-H^+ is the only species that is present in [$^2H_6$]-DMSO.

Apparently, there are three reasons for the abnormal behaviour of the cation **84**-H^+: (1) considerable asymmetry of the IHB [according to X-ray and ^1H NMR data, the proton resides predominantly at the N(8) atom], (2) decreased (four orders of magnitude in comparison with compound **6**) basicity of the nitro-derivative **84**, and (3) the optimum moderate basicity of dimethyl sulfoxide sufficient to induce partial scission of the IHB and subsequent deprotonation, but at the same time insufficient for the complete shift of the equilibrium between the non-chelated cation and the base to the right.

3. Molecular and crystalline structure

a. Bases

The most important peculiarity of 'proton sponge' bases is a considerable distortion of the planar structure of their molecules due to the trend of the dialkylamino groups to maximally separate from one another. According to X-ray data, for compound **6**,[56] (1) the angle C(1)–C(9)–C(8) increases to 125.8°; (2) the distance C(1)–C(8) increases to 2.56 Å against 2.45 Å in naphthalene; (3) the distance N···N is rather large (2.79 Å) (*cf.* 2.72–2.74 Å in 1,8-diaminonaphthalene).[57] The mean plane of the naphthalene system is formed by C(2), C(3), C(9), C(10), C(6), and C(7) atoms, whereas the C(1)–C(9)–C(10)–C(4) and C(8)–C(9)–C(10)–C(5) fragments are symmetrically twisted relative to the central bond C(9)–C(10); the torsion angles are equal to 8.9° and 10.5°, respectively. Thus the two benzene rings begin to resemble two chairs put against each other so that the back of one chair is next to the legs of the other chair, and *vice versa*. As a consequence, the C(1) and C(8) atoms and, correspondingly, the nitrogen atoms deviate (the latter, by 0.4 Å) in opposite directions from the mean plane of the fused system (Fig. 1*a*). The orientation of the methyl groups is also different (Fig. 1*b*) as if one pair is directed inward towards the cyclic system, while the other is directed outward, the latter lying nearly in the mean plane of the ring. Obviously, the axes of the unshared electron pairs at the nitrogen atoms are also oriented in opposite directions to form an angle of about 40° with the axes of the aromatic *p*-electrons. The latter circumstance deserves special notice, since with such angles the conjugation of the dimethylamino groups with the π-system of the ring is still considerable.



96

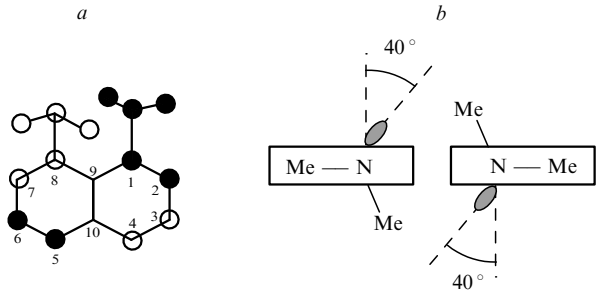


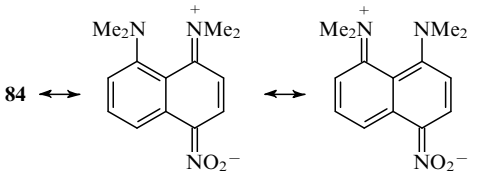
Figure 1. Structure of the 'proton sponge' molecule **6**: view from the top (*a*) and along the mean plane of the ring (*b*) (the empty and full circles belong to the atoms located on different sides of the mean plane).

Table 8. The distance between the nitrogen atoms, *r*(N···N), in some 1,8-diaminonaphthalenes.

Compound	*r*(N···N) /Å	Ref.	Compound	*r*(N···N) /Å	Ref.
1	2.72; 2.74[a]	57	**28**	2.75	24
6	2.79	56	**34**	2.76	60
17	2.89	58	**84**	2.86	55
18a	2.86	58	**81**	3.03	61
23	2.89	59	**96**	2.95	61
61	2.86	31			

[a] For two independent molecules.

An analogous pattern with some modification is also observed for other 'proton sponges' (Table 8). Thus in the 4-nitro-derivative **84**, as well as in 4,5- **81** and 2,5-dialdehydes **96**, the distance between the nitrogen atoms of the dimethylamino groups shows a tendency to increase, presumably, as a result of conjugation of the latter with π-acceptor substituents. This must be accompanied by flattening of bonds at the amine nitrogen atoms (due to the greater contribution of the structures of the type **84a** and **84b**), so that NMe_2 groups require larger space. Accordingly, the C(1)–N(1) and C(8)–N(2) bonds in compounds **84** (1.37–1.38 Å) and **81**, **96** (1.36 Å) become somewhat shorter than those in the 'proton sponge' **6** itself (1.40 Å).



84a **84b**

In compounds with electron-donor groups **28** and **35**, the lengths of C(1)–N(1) and C(8)–N(2) bonds are the same as in compound **6** (1.40 Å). The N···N distance remains virtually unchanged, although the distortions in the naphthalene ring structure become more pronounced. As expected, the N···N distance increases in the 'proton sponges' **61**, **17**, **18a**, and **23** having bulkier or less flexible substituents at the amine nitrogen atoms.

A characteristic feature of the molecular structure of 1,8-bis(dimethylaminomethyl)naphthalene **30** is the practically planar geometry of the naphthalene ring.[62]

b. Cations

A great number of X-ray studies have been carried out with the salts of the 'proton sponge' **6**-H^+ with various anions (Table 9). All these studies have demonstrated that the transition to the cation brings about drastic changes in the molecular structure. Owing to the formation of the hydrogen bridge, the dialkylamino groups rotate in such a way that the dihedral angle between them and the naphthalene system plane tends to reach 90°. This results in steric strain relief, flattening of the naphthalene fragment, and considerable approach of the nitrogen atoms. The N···N distance varies within the range of 2.55 to 2.65 Å, being, on the average, 2.58 Å. In the majority of salts, the naphthalene ring is virtually flat and both N atoms lie in the same plane. For some salts (X^- = $C_6Cl_5O^-$, BF_4^-, SCN^-), the twisting (by no more than 4–5°) of the planes of C(1)–C(9)–C(10)–C(4) and C(8)–C(9)–C(10)–C(5) around the central bond C(9)–C(10) still takes place. As a result, the molecule acquires a propeller shape, and the nitrogen atoms diverge in different directions from the mean plane (up to 0.25 Å). However, these deformations are much less than those observed in the 'proton sponge' base. The C(1)–N(1) and C(8)–N(2) distances in the cation **6**-H^+ increase up to 1.45 Å, which testifies to the lack of conjugation between the

Table 9. Geometric parameters of the hydrogen bridge in 'proton sponge' salts **6**-H^+X^-.

X^-	T/K	Distances /Å			Angle N···H—N /degree	Ref.
		N—H	N···H	N···N		
$[(hfac)_3^-Cu^{2+}]^-$ (see [a])	298	1.27	1.49	2.65	145	63, 64
$[(hfac)_3^-Mg^{2+}]^-$ (see [a])	298	1.25	1.58	2.60	134	63, 64
$Br^- \cdot 2H_2O$	298	1.30	1.30	2.55	153	65
BF_4^-	298	1.30	1.31	2.56	159	66
SCN^-	298	1.30	1.30	2.57	160	67
SCN^-	188	1.32	1.32	2.58	156	67
Tetrazolide $\cdot H_2O$	298	1.31	1.31	2.57	157	68
2,4-Dinitroimidazolide	298	1.18	1.47	2.61	160	69
1,8-Bis(tosylamido)-2,4,5,7-tetra-nitronaphthalene (monoanion)	298	1.05	1.63	2.61	152	70
1,8-Bis(trifluoroacetamido)-naphthalene (monoanion)	298	1.22	1.42	2.59	156	71
Pic_2N^- (see [b])	298	1.05	1.57	2.57	158	72
$[O(Ph)C_2B_{10}H_{10}]^-$	298	1.22	1.52	2.58	140	73
$OTeF_5^-$ (triclinic form)	167	1.17	1.46	2.57	159	74
$OTeF_5^-$ (orthorhombic form)	143	1.37	1.37	2.58	140	75
Squarate (monoanion)	150	1.08	1.55	2.58	157	76
Squarate (dianion) $\cdot 4H_2O$	100	0.94	1.69	2.57	156	77
The same [c]	100	0.97	1.66	2.59	162	77
$C_6Cl_5O^- \cdot 2C_6Cl_5OH$	100	1.11	1.47	2.56	162	78
$C_6F_5O^- \cdot 2C_6F_5OH$	100	1.07	1.56	2.57	154	79
The same [c]	100	0.86	1.84	2.57	141	79
Chloranilic acid dianion	298	1.14	1.51	2.59	155	80
	150	1.07	1.59	2.59	152	80
D-Hydrogen tartrate $\cdot 3H_2O$	100	0.91	1.75	2.61	157	81
The same [c]	100	0.84	1.86	2.61	149	81
3,4-Furandicarboxylate (monoanion)	298	1.06	1.62	2.62	155	82
Hemimellitate (monoanion) $\cdot \frac{1}{2}H_2O$	100	0.90	1.72	2.60	164	83
The same [c]	100	0.94	1.72	2.60	155	83
Maleate (monoanion)	298	1.17	1.49	2.61	157	84
1,2-Dichloromaleate (monoanion)	100	1.11	1.61	2.64	153	85

[a] hfac is hexafluoroacetonate. [b] Pic is picryl. [c] Data for two independent molecules obtained by differential Fourier synthesis are given.

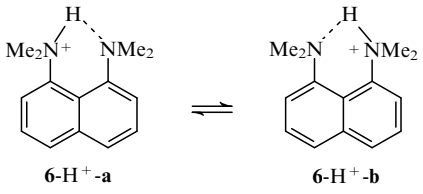
dimethylamino groups and the aromatic π-system. This conclusion is confirmed by a variety of other data.

In contrast to 1,8-bis(dialkylamino)naphthalene cations, the naphthalene ring in cations of the iminophosphorane 'sponges' **29**, **63**, and **64**, is strongly distorted, but the distance between the nitrogen atoms is smaller (2.52 – 2.60 Å).[32, 33]

The main attention in the studies of 'proton sponge' cations has been paid to the symmetry and geometric characteristics of the hydrogen bridge. This problem was comprehensively discussed in a number of reviews,[13, 86] therefore we shall confine ourselves to a mere statement of the central issues. Theoretically, four types of potential energy curves for the N···H—N system are possible (Fig. 2).

The profile *a* having one minimum corresponds to a completely symmetrical bridge, whereas the profile *b*, which has a low activation barrier, reflects the rapid tautomeric equilibrium between two equivalent asymmetric structures. It is the question as to which of these two profiles is realised in the cation of the 'proton sponge' **6**-H^+ that has been discussed in most detail.

Theoretical calculations of an $[H_3N \cdots H \cdots NH_3]^+$ system have shown that when the distance between the nitrogen atoms is 2.75 Å, the potential curve has two minima with a barrier of 10.9 kJ mol^{-1}; with a decrease in the distance down to 2.50 Å, the barrier disappears.[13] In terms of the data listed in Table 9, these results may indicate that the energy profile for the cation **6**-H^+ corresponds to type *b* with a low barrier of transition between the structures **6**-H^+-**a** and **6**-H^+-**b**.



6-H^+-**a** ⇌ **6**-H^+-**b**

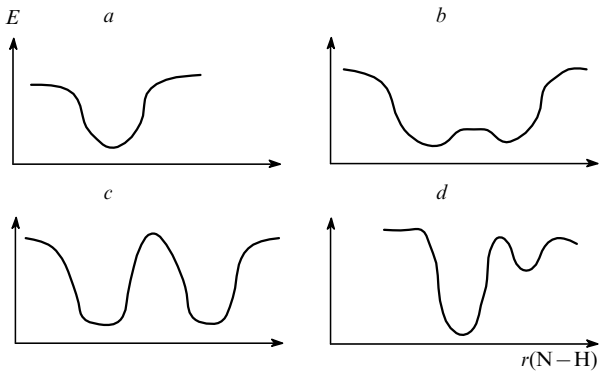


Figure 2. Types of potential energy curves for the IHB in 'proton sponge' cations; for *a* – *d*, see text.

Indeed, in some cases it was shown that the proton NH lies in the plane of symmetry of the cation **6**-H^+ not only at room temperature, but even at low temperatures; the length of the N—H bond is averaged ($\sim$ 1.3 Å). In those salts (which constitute the majority), where the hydrogen bridge is asymmetrical, the N—H bond is much longer than the standard value ($\sim$ 0.9 Å). In the case of the salt **6**-H^+ with the dianion of the chloranilic acid, a decrease in the temperature from 300 to 150 K results in the shortening of this bond from 1.14 to 1.07 Å. This is indirect evidence that the elongation of the N—H bond is due to the disordered position of the NH-proton oscillating between the nitrogen atoms and the plane of symmetry. Obviously, the anion influences the mode of these oscillations and, correspondingly, the geometry of the hydrogen bridge both through the electric field induced by it and due to the changes in the crystal lattice. The formation of a weak bifurcated hydrogen bond involving the anion and the NH-proton was recorded both for the **6**-H^+ salt with hydrosquarate and squarate anions. Thus at present the majority of researchers tend to accept that the cation **6**-H^+ exists in a position of fast tautomerism

6-H^+-**a** $\rightleftharpoons$ **6**-H^+-**b**.

An asymmetrical hydrogen bridge was observed in crystals of the 'double sponge' dication **28**-($2H^+$) as well as in cations of the bisiminophosphorane **29** and the compound **30**. It is probable that the energy curve profile of the type *c* corresponds to these bridges. As expected, in cations of unsymmetrical bases, *e.g.*, **84**-H^+ or **63**-H^+, the proton practically completely resides on the more basic of the two N atoms: on N(8) and the imine nitrogen, respectively (type *d* curve, Fig. 2) (Table 10).

It should be mentioned in conclusion that in cations of all the 'proton sponges' the hydrogen bridge is non-linear and the N—H···N angle lies within the range of 150–160° with only few exceptions. The neutronographic method, which is considered to be more precise for establishing the molecular structure than X-ray structural analysis (as was shown with the **6**-H^+ salt with the dichloromaleic acid anion), gives basically the same results.[85, 87]

Table 10. Geometric parameters of the hydrogen bridge in cations of some 'proton sponges' at 298 K.

Cation	Anion	Distances /Å			Angle N···H—N, /degree	Ref.
		N···N	N—H	H···N		
84-H^+	ClO_4^-	2.57	0.99	1.64	153	55
28-($2H^+$)	$2Br^-$	2.57	1.22	1.39	158	24
29-H^+	Br^-	2.58	0.85	1.78	159	32
63-H^+	Br^-	2.52	1.20	1.38	154	33
30-H^+	NO_3^-	2.64	1.28	1.39	164	34
30-H^+	NO_3^-	2.63 [a]	0.83 [a]	1.83 [a]	161 [a]	88
30-H^+	NO_3^-	2.63 [a]	1.04 [a]	1.61 [a]	165 [a]	88
30-H^+	$PicO^-$	2.72	1.07	1.68	162	89
30-H^+	ClO_4^-	2.68	1.18	1.51	167	90

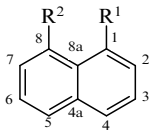
[a] At 100 K.

4. NMR spectra

^1H, ^{13}C, and ^{15}N NMR spectra of the 'proton sponges' and their cations were investigated both for solutions and solid state. NMR spectroscopy was used to establish structural characteristics, π-electron distribution, and the ease of proton exchange between the cations and bases.

a. Bases

As expected, the signals for all the aromatic protons in the ^1H NMR spectrum of compound **6** (Table 11) are at higher field than those for naphthalene (δ 7.46 and 7.81 ppm for α- and β-protons, respectively). The greatest shielding is of the protons at positions 2 and 7, then H3(6) and H4(5), the difference in the chemical shifts between *meta*- and *para*-protons being very small.



94, **97**–**99**

94: R^1 = OMe, R^2 = NMe_2;
97: R^1 = R^2 = OMe;
98: R^1 = NMe_2, R^2 = H;
99: R^1 = OMe, R^2 = H.

If one assumes that the degree of proton shielding is proportional to the $+M$-effect of the substituents, the following conclusion can be made: the electron donor capacity of the NMe_2 groups in the molecule of compound **6** is somewhat lower than that of the *peri*-substituents in 1-dimethylamino-8-methoxy- **94** and 1,8-di-methoxynaphthalenes **97** (Table 12). Even in 1-methoxynaphthalene **99**, the donor effect of the substituent seems to be higher than in 1-dimethylaminonaphthalene **98**. This conclusion is confirmed by analysis of ^{13}C NMR spectra (Table 13). Since in benzene derivatives the shielding effects of NMe_2 and MeO groups are opposite and correspond to the Hammett σ-constants, it is reasonable to conclude that the decreased electron donor capacity of the NMe_2 groups in 1-dimethylamino- and 1,8-bis-(dimethylamino)naphthalenes is a

Table 11. ^1H NMR spectra of 1,8-bis(dimethylamino)naphthalene **6** and its cations **6**-H^+.[91]

Compound [a]	Solvent	δ /ppm					J /Hz			
		H(2), H(7)	H(3), H(6)	H(4), H(5)	CH_3	$(NHN)^+$	$J_{H(2)-H(3)}$	$J_{H(3)-H(4)}$	$J_{H(2)-H(4)}$	J_{NH-CH_3}
6	$CDCl_3$ [92]	6.96	7.33	7.39	2.82	—	7.3	8.2	1.5	—
6	CD_2Cl_2	6.92	7.27	7.32	2.77	—	7.2	8.1	1.5	—
6	CCl_4 [1]	6.76	7.09	7.18	2.71	—	7.6	7.9	1.2	—
6	CD_3CN	6.90	7.23	7.30	2.70	—	7.2	8.1	1.5	—
6	CD_3NO_2	6.91	7.24	7.30	2.73	—	7.2	8.1	1.5	—
6-H^+	CF_3CO_2H [1]	8.04	7.71	7.83	3.21	19.51	8.3	7.6	0.9	2.0
6-H^+Cl^-	CD_3CN	8.00	7.70	8.04	3.20	18.58	7.5	8.4	0.9	2.7
6-$H^+Br^- \cdot H_2O$	CD_3CN	7.96	7.71	8.05	3.17	18.66	7.8	8.4	0.9	2.7
6-$H^+NO_3^-$	CD_3CN	7.94	7.70	8.04	3.14	18.92	7.8	8.4	0.9	2.7
6-$H^+BF_4^-$	CD_3CN	7.92	7.71	8.05	3.12	18.67	7.5	8.4	0.9	2.7
6-$H^+ClO_4^-$	CD_3CN	7.91	7.70	8.05	3.11	18.66	7.8	8.4	1.2	2.7
6-$H^+ClO_4^-$	CD_3NO_2	7.98	7.75	8.08	3.25	19.08	7.8	8.4	0.9	2.7
6-$H^+ClO_4^-$	$(CD_3)_2SO$ [93]	8.08	7.73	8.09	3.12	18.33	7.7	8.2	1.1	2.6

[a] The ^1H NMR spectra of 'proton sponge' salts with the following anions: I^-, NCS^-, PF_6^-, Ph_4B^- were also recorded in CD_3CN.[94] The values of chemical shifts in these salts are very close to those cited above.

Table 12. ^{1}H NMR spectra of some close analogues of the 'proton sponge' in $CDCl_3$.[92]

Compound	δ /ppm							
	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)	CH_3
94	6.89	7.45	7.38	7.38	7.45	7.02	–	4.01 (MeO); 2.87 (NMe_2)
97	6.86	7.36	7.40	7.40	7.36	6.86	–	3.99
98	7.18	7.50	7.60	7.60	7.60	7.94	8.38	3.00
99	6.88	7.47	7.56	7.56	7.56	7.90	8.40	4.06

Table 13. ^{13}C NMR spectra of the 'proton sponge' and some of its close analogues.

Compound	Solvent	δ/ppm										Ref.
		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(8a)	C(4a)	CH_3	
6	$CDCl_3$	150.70	112.70	125.40	121.70	121.70	125.40	112.70	150.70	120.60	137.80	44.40	92
6	$CDCl_3$	151.26	113.47	126.02	122.49	122.49	126.02	113.47	151.26	121.37	138.66	–	95
6	CD_3CN	151.33	113.57	126.30	122.28	122.28	126.30	113.57	151.33	121.13	138.58	44.68	91
6	CD_3NO_2	152.03	113.92	126.78	122.65	122.65	126.78	113.92	152.03	121.65	139.12	44.99	91
6	see [a]	119.80	112.10	124.60	120.90	122.10	123.90	113.30	121.80	149.70	136.50	41.0; 41.8 44.2; 45.1	96
1	$CDCl_3$	144.20	111.30	126.00	119.40	119.40	126.00	111.30	144.20	116.80	136.70	–	57
94	$CDCl_3$	156.10	106.40	126.00	122.00	121.60	125.60	113.30	150.70	120.30	137.60	56.3; 45.6	92
97	$CDCl_3$	157.10	106.30	126.30	120.80	120.80	126.30	106.30	157.10	117.60	137.40	56.40	92
6-H$^+$$ClO_4^-$	CD_3CN	145.12	122.36	127.86	130.04	130.04	127.86	122.36	145.12	120.02	136.19	46.73	91
6-H$^+$$BF_4^-$	see [a]	117.40	120.70	128.30	126.50	126.50	128.30	120.70	117.40	143.40	134.80	43.6; 46.4	96

[a] Spectrum for solid compound.

result of their considerable non-coplanarity with the nucleus caused by *peri*-interactions. It is noteworthy in this respect that the chemical shift of the *N*-methyl groups (δ 2.8 ppm) in the 'proton sponge' is lower than that of 1-dimethylaminonaphthalene (δ 3.0 ppm), which testifies to an increased contribution of the *s*-component in the *n*-orbital of the amine nitrogen.

Evidence for the effects of substituents in the nucleus on the parameters of the ^{1}H NMR spectra can be inferred from Table 14. As can be seen, *ortho*- (Cl, Br) and $-M$-substituents at position 4 (CHO, $COCF_3$, NO_2) cause a down-field shift of the *N*-methyl signals (by $\sim$ 0.2 ppm). In addition, $-M$-substituents produce a strong deshielding effect on H(5) [to a lesser degree, on H(3)]. This is accompanied by reduction of the spin-spin coupling constant $J_{H(5)-H(7)}$ and marked increase in the spin-spin coupling constant $J_{H(2)-H(3)}$ (presumably, due to an increased contribution of structures of the type **84a**,**b**).

Recent measurements of MAS ^{1}H NMR and ^{13}C NMR spectra of a solid sample of the 'proton sponge' **6** gave quite unexpected results:[96] they revealed strong asymmetry of its molecule. It was found that all four methyl groups, like all ten ring carbon atoms, resonate as separate peaks, *i.e.*, they are non-equivalent (Table 13). This has been interpreted in terms of electrostatic interactions between the neighbouring molecules in the crystal lattice and has led to partial revision of the previously established [56] results of X-ray studies of the 'proton sponge'.

^{1}H NMR spectra have been used to study the ease of the proton exchange between the bases of the 'proton sponge' **6** and its tetraethyl analogue **34**, on the one hand, and the corresponding cations, on the other.[97] The ^{1}H, ^{13}C, and ^{15}N NMR spectra of compound **30** have also been recorded.[34, 98]

Table 14. ^{1}H NMR spectra of 'proton sponge' derivatives in $CDCl_3$ (300 MHz, 298 K).

Compound	δ /ppm								J /Hz					Ref.
	1-NMe_2	8-NMe_2	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	$J_{H(2)-H(3)}$	$J_{H(3)-H(4)}$	$J_{H(5)-H(6)}$	$J_{H(6)-H(7)}$	$J_{H(5)-H(7)}$	
70	3.03	2.78	–	7.32	7.39	7.37	7.29	7.05	–	8.71	7.91	7.62	1.33	28
71	3.02	2.75	–	7.30	7.51	7.37	7.30	7.07	–	8.71	7.99	7.39	1.39	93
72	2.98	2.98	–	7.33	7.45	7.45	7.33	–	–	8.71	8.71	–	–	28
73	2.96	2.96	–	7.35	7.51	7.51	7.35	–	–	8.70	8.70	–	–	93
50	2.78	2.80	6.80	7.38	–	7.80	7.41	6.98	8.21	–	8.35	7.62	1.03	28
51	2.82	2.84	6.79	7.63	–	7.84	7.45	7.02	8.20	–	8.20	7.61	1.17	27
52	2.76	2.76	6.74	7.37	–	–	7.37	6.74	8.28	–	–	8.28	–	28
53 [a]	2.74	2.74	6.62	7.60	–	–	7.60	6.62	8.35	–	–	8.35	–	27
74 [b]	2.82	2.80	6.98	7.51	–	7.64	7.35	6.98	7.98	–	8.20	8.20	< 1.0	109
79	2.79	2.79	6.86	6.97	–	7.85	7.30	6.90	8.13	–	8.35	7.62	1.02	45
80	2.97	2.78	6.84	7.72	–	8.89	7.48	6.97	8.20	–	8.21	7.62	0.88	131
83 [c]	3.00	2.72	6.84	7.90	–	8.64	7.45	6.94	9.08	–	8.43	7.77	0.88	110
84	2.99	2.78	6.70	8.30	–	8.43	7.49	6.95	9.08	–	8.49	7.62	0.88	55

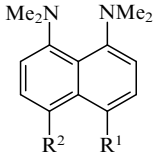
[a] At -55 °C. [b] In [$^2H_6$]-acetone. [c] In [$^2H_6$]-DMSO.

b. Cations

On going from the base **6** to the cation **6**-H^+, the signals for all the protons are shifted down-field: H[2(7)], by +1.1 ppm, H[3(6)], by +0.4 ppm, H[4(5)], by +0.7 ppm, and CH_3, by +0.3 ppm. Although it would be logical to expect that the signals of *ortho*-protons were at the lowest field, it is not always the case (Table 11). For example, in a solution of the perchlorate **6**-H^+ in [$^2H_6$]-DMSO, the signals of *ortho*- and *para*-protons overlap; however, in CD_3CN and CD_3NO_2, the doublet of doublets of H[4(5)] are at lower field. The signals of the both types of protons can be distinguished by larger values of the *ortho*-constants, $J_{H(3)-H(4)}$ and $J_{H(5)-H(6)}$ in comparison with $J_{H(2)-H(3)}$ and $J_{H(6)-H(7)}$. The nature of the anion in 'proton sponge' salts has practically no effect on their NMR spectra (Table 11).

Yet, the main peculiarity of the ^1H NMR spectra of 'proton sponge' cations is the unusually high chemical shift of the NH-proton (δ 18–20 ppm), which is indicative of strong chelation. For the cations of symmetrical 'proton sponges' including **6**-H^+, the NH signal in high-resolution spectra has thirteen lines due to spin-spin coupling with the protons of the methyl groups. The signal of the latter is split into a doublet with an intensity of 12 proton units with a spin-spin coupling constant of about 2.5 Hz. Thus the NMR method has permitted recording of a symmetrical IHB for these cations at room temperature, which probably reflects rapid (on the NMR time scale) deviations of the NH-proton relative to the plane of symmetry. The same is observed in the spectra of the symmetrical iminophosphorane 'sponges' **29** and **64**.[32,49] Although, as has been shown earlier, the hydrogen bridge has an asymmetrical shape in crystals of their cations, according to NMR data both tautomeric forms are in fast equilibrium and the NH-proton is shared equally by both nitrogen atoms.

In non-symmetrically substituted cations, the dimethylamino groups are non-equivalent, they are observed as two doublets with different spin-spin coupling constants (Table 15). It has been suggested to use the relationship between the coupling constants for estimating the degree of IHB asymmetry in a particular cation.[93] The most asymmetrical is the hydrogen bridge in the cations of 2-halogeno-1,8-bis(dimethylamino)naphthalene **70**-H^+ and **71**-H^+; in [$^2H_6$]-DMSO, the NH-proton belongs to the N(8) atom by more than 80%. The asymmetry of IHB in the cations of 4-amino- **76**-H^+ and 4-methylamino derivatives **78**-H^+ is very strong [in these cases, the NH-proton is closer to the N(1) atom] and it is somewhat less in the cations having $-M$-substituents at position 4: **80**-H^+, **82**-H^+ – **84**-H^+, and **100**-H^+. The least asymmetrical is the IHB in the cations of 4-vinyl- **74**-H^+, 4-acetamido- **77**-H^+, and 4-halogeno-derivatives **50**-H^+ and **51**-H^+. It was established that the transition from [$^2H_6$]-DMSO to a less proton-accepting solvent, acetonitrile, favours the symmetrisation of the hydrogen bridge, which is especially pronounced in the cations of 2-halogeno- and 4-amino-1,8-bis(dimethylamino)-naphthalenes.



100–**102**

100: R^1 = CN, R^2 = H;
101: R^1 = PhCO, R^2 = H;
102: R^1 = R^2 = PhCO.

Table 15. Parameters of ^1H NMR spectra of the groups involved in hydrogen bridge formation in 'proton sponge' cations.[93]

Cation	Solvent	δ /ppm			J /Hz		Proton localisation (%) [a]	
		1-NMe_2	8-NMe_2	NH^+	$J_{NH-1\text{-}NMe_2}$	$J_{NH-8\text{-}NMe_2}$	1-NMe_2	8-NMe_2
6-H^+	[$^2H_6$]-DMSO	3.12	3.12	18.33	2.63	2.63	50	50
6-H^+	CD_3CN	3.11	3.11	18.69	2.64	2.64	50	50
70-H^+	[$^2H_6$]-DMSO	3.18	3.32	18.02	0.77	4.06	16	84
70-H^+	CD_3CN	3.25	3.27	18.80	1.54	3.84	29	71
71-H^+	[$^2H_6$]-DMSO	3.21	3.33	18.09	< 1	4.06	16	84
71-H^+	CD_3CN	3.27	3.26	18.87	1.65	3.84	30	70
72-H^+	[$^2H_6$]-DMSO	3.37	3.37	19.91	2.41	2.41	50	50
73-H^+	[$^2H_6$]-DMSO	3.40	3.40	20.09	2.41	2.41	50	50
73-H^+	CD_3CN	3.41	3.41	20.33	2.64	2.64	50	50
50-H^+	[$^2H_6$]-DMSO	3.11	3.14	18.52	2.42	2.64	48	52
51-H^+	[$^2H_6$]-DMSO	3.11	3.14	18.56	2.31	2.53	48	52
52-H^+	[$^2H_6$]-DMSO	3.10	3.10	19.14	2.52	2.52	50	50
53-H^+	[$^2H_6$]-DMSO	3.10	3.10	19.12	2.41	2.41	50	50
74-H^+	[$^2H_6$]-DMSO	3.12	3.12	18.64	2.30	2.30	~50	~50
76-H^+	[$^2H_6$]-DMSO	3.09	2.99	18.26	3.23	1.21	73	27
76-H^+	CD_3CN	3.10	3.02	18.64	3.41	1.87	65	35
77-H^+	[$^2H_6$]-DMSO	3.12	3.11	18.55	2.86	2.24	56	44
77-H^+	CD_3CN	3.12	3.11	18.90	2.75	2.63	51	49
78-H^+	[$^2H_6$]-DMSO	3.11	2.98	18.31	3.40	1.21	74	26
79-H^+	[$^2H_6$]-DMSO	3.11	3.06	18.48	2.86	2.20	57	43
79-H^+	CD_3CN	3.10	3.07	18.84	2.97	2.31	56	44
80-H^+	[$^2H_6$]-DMSO	3.10	3.21	18.43	1.75	3.08	36	64
80-H^+	CD_3CN	3.10	3.20	18.75	1.98	3.30	38	62
82-H^+	[$^2H_6$]-DMSO	3.10	3.17	18.58	1.97	2.86	41	59
83-H^+	[$^2H_6$]-DMSO	3.09	3.23	18.35	1.44	3.15	31	69
83-H^+	CD_3CN	3.10	3.22	18.67	1.86	3.41	35	65
84-H^+	[$^2H_6$]-DMSO	3.17	3.28	18.50	1.72	3.19	35	65
84-H^+	CD_3CN	3.08	3.19	18.72	2.13	3.36	39	61
100-H^+	[$^2H_6$]-DMSO	3.09	3.21	18.15	1.88	2.97	39	61

[a] Indices of proton localisation at each of the dimethylamino groups (PL) were calculated by the formula:
$PL = [J_{NH-1(8)\text{-}NMe_2} / (J_{NH-1\text{-}NMe_2} + J_{NH-8\text{-}NMe_2})] \cdot 100\%$.

For a series of compounds of the same type, there is no apparent correlation between the stability of the IHB and the chemical shift of the NH-proton. It is therefore sufficient to compare the cation **6**-H^+ and its 4-nitro-derivative **84**-H^+. Although in the latter case, the signal of the NH-proton is shifted down-field by 0.4 ppm relative to the analogous signal in the spectrum of the cation **6**-H^+, its hydrogen bridge is partly cleaved by DMSO and other dipolar solvents (see section IV. 2), whereas in the cation **6**-H^+, no signs of its cleavage were observed. Apparently, the stability of the IHB is largely determined by the basicity of the corresponding 'proton sponge', while the δ_{NH} value depends on the distance between the nitrogen atoms and the degree of NH-proton expulsion from the plane of the ring as a result of which it experiences the effect of the diamagnetic component of the magnetic field of the naphthalene π-system. The unusually high chemical shift of the NH-proton ($\delta \sim 20.0$ ppm) in the spectra of cations of 2,7-dihalogeno-derivatives of the 'proton sponge' is indirect evidence in favour of this explanation. It is unlikely that in these compounds the NH-proton lies in the plane of the ring. More probably, the nitrogen atoms become closer to each other pushed by the halogens, so that this proton is out of the plane and undergoes strong deshielding in the cation **11**-H^+ (δ_{NH} 24.0 ppm).[10] On the whole, the factors influencing the magnitude of the chemical shift of the NH-proton in 'proton sponge' cations have ben studied insufficiently. For example, it is still unclear why the signals of the NH-protons in the cations **25**-H^+ (δ 16.56 ppm), **26**-H^+ (δ 14.90 ppm),[29] **29**-H^+, **64**-H^+ ($\delta \sim$ 16.5 ppm),[32,49] and **30**-H^+ ($\delta \sim$ 15.8 ppm)[34] are at much higher fields than those in the cations of 1,8-bis(dialkylamino)naphthalenes.

^{13}C and ^{15}N NMR spectra of salts of **6**-H^+ (with tetrazolide,[99] 1-methyltetrazole-5-thiolate, and hydrogen squarate[100] anions) were recorded for solutions in MeCN and in the solid state. As expected, the signals of C(2) and C(4) nuclei are more sensitive to salt formation: they shift 4–5 ppm down-field. However, the largest changes in the chemical shifts (by 6 ppm for solutions in MeCN and by 10 ppm in solid state) are observed in the ^{15}N NMR spectra upon transition from the base to the cation. It is ^{15}N NMR spectroscopy that is recognised as being the most appropriate for the study of the structure of cations in solution and in the crystalline state. Recent ^1H and ^{13}C NMR spectral data of solid samples of **6**-H^+ with thiocyanate and tetrafluoroborate revealed two types of *N*-methyl groups, presumably located close to the plane of the ring and remote from it. At the same time, unlike the base, the naphthalene ring of the cation **6**-H^+ itself did not reveal any signs of asymmetry.[96]

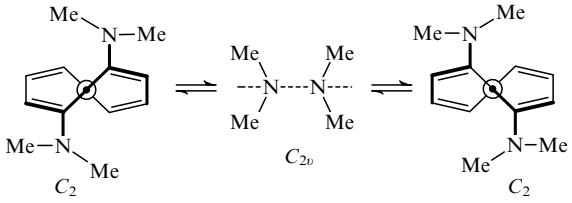
^{13}C (Ref. 49) and ^{31}P MAS (Ref. 101) NMR spectra of cations of the iminophosphorane 'proton sponges' **29**, **63**, and **64**, and ^{13}C and ^{15}N NMR spectra of the salts **30**-H^+ have been analysed.[98]

c. NMR spectra and molecular dynamics

The majority of the naphthalene 'proton sponges' are sterically strained, therefore, many of them exist in different conformations due to hindered rotation of dialkylamino groups around the $C_{Ar}-N$ bonds, distorted ring shape, inversion of nitrogen, *etc.* The corresponding transitions can most effectively be followed by NMR spectroscopy. Sometimes, dynamic processes manifest themselves even at room temperature as a widening (sometimes, rather prominent) of peaks of the *N*-alkyl groups and aromatic protons.

Although the solution ^1H and ^{13}C NMR spectra of the 'proton sponge' **6** demonstrate the equivalence of all the four *N*-methyl groups at room temperature, this was shown to result from rapid reversible transitions that average the respective conformations on the NMR time-scale.[26] It was found that the singlet of the methyl groups in the ^1H NMR spectrum of compound **6** in CF_2Cl_2 splits into a doublet upon cooling down to −120 °C. The free energy of activation ($\Delta G^{\neq}$) for the conformational transition was estimated as 31.4±0.8 kJ mol^{-1}. It was assumed that the interconversion of the methyl groups is of a 'narcissistic' type and occurs *via* a planar transition state with C_{2v} symmetry (Scheme 1).

Scheme 1



In the case of sterically more hindered 1-benzylmethylamino-8-dimethylaminonaphthalene, the conversion of the NMe_2 group singlet into the doublet occurs at −38 °C; simultaneously, the methylene group singlet splits into a quartet. In this case, the $\Delta G^{\neq}$ value is equal to 57.3±1.7 kJ mol^{-1}.[26] Similar dynamic processes were observed in the ^1H NMR spectra of compounds **62**,[31] **53**,[27] and **90**.[102]

5. Nuclear quadrupole resonance spectra

Contrary to the original interpretation of the ^{14}NQR spectrum, with cross-relaxation, of the base **6**,[103] recent measurements revealed the presence in this spectrum of four (rather than two) resonance peaks from two nitrogen atoms.[104] This finding unambiguously testifies to their non-equivalence and thus correlates with NMR data on the asymmetry of the 'proton sponge' molecule in crystals.

6. Electron spectroscopy for chemical analysis

According to Hasselbach *et al.*,[105] neither NMR nor X-ray diffraction analysis can give an unequivocal answer to the question about the IHB symmetry in the 'proton sponge' cation. This can be done only with the help of 'faster' methods, such as electron spectroscopy for chemical analysis (ESCA). Here, the ionisation of core electrons takes about 10^{-16} s, therefore the non-equivalent atoms can be distinguished even at fast equilibrium. The ESCA spectrum recorded for the salt **6**-H^+ BF_4^- in the N1s energy region revealed two maxima of identical height, which points to the non-equivalence of nitrogen atoms in the cation **6**-H^+. However, the splitting of the two peaks was relatively low. This points to the fact that the hydrogen bridge in the cation **6**-H^+ is nevertheless nearly symmetrical. ESCA studies of a number of other 'proton sponge' salts have also been carried out.[106,107]

7. Electronic absorption spectra, colour, and solvatochromism

Perhaps the most valuable information about the electron interaction of dialkylamino groups and the naphthalene π-system in 'proton sponges' can be derived from UV spectra. The longwave absorption band in the UV spectra of 1,8-diaminonaphthalene and its *N*-alkyl derivatives including compound **6** lies in the region 340–350 nm (Table 16). As in the case of other aryl amines, it is ascribed to the transfer of electron density from the *n*-orbital of the nitrogen atoms to the π-antibonding orbital of the naphthalene system ($p-\pi^*$ transition). The intensity of this band strongly depends on steric factors influencing the rotation of the amino group around the $C_{Ar}-N$ bond. We used this circumstance[2] to determine the value of the dihedral angle (φ) between the plane passing through the $C_{Ar}-N$ bond perpendicularly to the aromatic system and the plane passing through the same bond and the symmetry axis of the unshared electron pair of the nitrogen atom. The angle φ was determined from the known ratio, $\varepsilon/\varepsilon_0 = \cos^2\varphi$, where ε is the extinction coefficient at the absorption maximum for the amine under study, and ε_0 is the same for a planar model, in which $\varphi = 0$, *i.e.*, the conjugation is a maximum. 1,3-Dimethyl-2,3-dihydroperimidine **19a** was used as a model for which the longwave absorption band did have the maximum intensity. The experimental values of φ are listed in Table 16. For the 'proton

Table 16. The position of longwave absorption bands (λ_{max}, ε) and magnitudes of dihedral angles (φ) in UV spectra of 1,8-diaminonaphthalenes.[2]

Compound	λ_{max} /nm	$10^{-3}\varepsilon$ /litre mol^{-1} cm^{-1}	φ /deg
1	337	10.40	42
2	339	8.96	46
3	351	6.07	55
4	341	8.72	90; 14
5	351	9.50	81; 0
6	341	12.40	35
19a	344	18.60	0

sponge' **6**, $\varphi = 35°$, which agrees well with the X-ray data ($\varphi = 40°$)[56] and other estimates.[1] The not very high value of the angle φ points to the possibility of significant conjugation of the dimethylamino groups with the naphthalene system in the base **6**, which is confirmed by all its physicochemical properties and reactivity.

The π-donor effect of the dimethylamino groups is especially prominent in the derivatives of the 'proton sponge' containing $-M$-substituents at position 4. In contrast to the colourless compound **6**, these compounds give different colours from yellow to violet depending on the electron-acceptor properties of the substituent (Table 17). As expected, the longwave absorption band, which is determined by direct polar conjugation, is very sensitive to the solvent polarity. Thus in the case of the 4-nitro-derivative **84**, the λ_{max} in hexane, benzene, methanol, and DMSO is 411, 444, 463, and 484 nm.[55] Such a solvatochromism may be due to the different solvation of the excited state, which can be represented by bipolar structures of the type **84a**,**b**. Evidently, the more polar the solvent, the stronger the solvation, the smaller the electron transfer energy, and the deeper the colour.

Table 17. Position of the longwave absorption band in UV spectra and colour of some 'proton sponge' derivatives (in methanol).

Compound	λ_{max} /nm	lg ε	Colour	Ref.
74	353	3.62	Pale yellow	109
75	516	4.02	Dark violet	110
80	407	3.84	Yellow	61
81	449	3.52	Brown	61
82	389	3.68	Yellow	110
83	431	3.68	Red	110
84	463	4.02	Dark red	55
89	521	4.00	Claret	110
96	403	3.67	Yellow	61
101	405	3.57	"	110
102	413	3.82	"	110

Since chelation of the NH-proton takes the dimethylamino groups completely out of conjugation with the ring, the absorption spectra of 'proton sponge' cations closely resemble the spectra of appropriate naphthalenes devoid of dimethylamino groups. Thus, the λ_{max} of the longwave absorption band for the cations **6**-H$^+$ and **84**-H$^+$ are equal to 288 nm (lg $\varepsilon = 3.85$)[108] and 334 nm (lg $\varepsilon = 3.50$)[55] (in 0.1 M HCl), whereas the corresponding values for naphthalene and 1-nitronaphthalene are 297 nm (lg $\varepsilon = 2.82$) and 342 nm (lg $\varepsilon = 3.59$).

An interesting variety of solvatochromism was observed for the cation **84**-H$^+$.[55] When the colourless perchlorate is dissolved in DMSO, DMF, or pyridine, the solution immediately turns deep red or red-orange (for DMF); in the majority of other solvents, colourless, yellowish, or pink solutions are formed. The reason for solvatochromism is the decreased basicity of 1,8-bis(dimethylamino)-4-nitronaphthalene **84** and IHB asymmetry in its cation, so that the solvents with high proton-acceptor capacity disrupt the IHB, thereby releasing the dimethylamino groups for the conjugation. Practical applications of solvatochromism of the perchlorate **84**-H$^+$ are proposed.[55]

8. Infrared spectra

The most important in the IR spectrum of the base **6** are the bands at 2780, 2830, 2870, and 1580 cm^{-1} (Refs 86, 111). The first three of them, known as Bolman bands, are associated with stretching vibrations of the C—H bonds of the methyl groups *trans*-oriented with respect to the unshared electron pairs of the nitrogen atoms. The band at 1580 cm^{-1} is associated with stretching vibrations of the ring. Its high intensity is the consequence of the asymmetry of the naphthalene system. Indeed, the intensity of this band sharply decreases upon protonation, and the band slightly shifts towards high frequencies. The Bolman bands also practically disappear upon transition to the cation or, in the case of partial protonation, decrease in intensity. These changes can be used for the quantitative estimation of the degree of protonation of the base **6** by different acids including phenols. However, the most interesting feature is the appearance of stretching vibration bands of the hydrogen bridge ν_s(NHN) in the IR spectra of **6**-H$^+$ salts. The dependence of the position of this band on pressure,[112] counterion structure,[113] deuteration [the isotope ratio, ν(NHN)/ν(NDN) was determined],[114] and the change in the aggregate state[115] was studied. In solution (the measurements were performed in acetonitrile, dichloromethane, and dichloroethane), the band manifests itself as a very broad 'continuum' at the background level extending from 3000 to about 300 cm^{-1}. In the crystalline state, the type of absorption changes drastically; the band shifts towards 800–250 cm^{-1} and acquires fine structure. This phenomenon is typical of very stable hydrogen bridges having a short N···N distance ($\sim$ 2.55–2.65 Å). It is assumed that the band structure can be explained in detail only by taking into account the superposition of δ- and γ-deformation oscillation, their overtones, and internal oscillations causing modulation of the hydrogen bridge geometry.[111] These data are consistent with the abnormally high isotope ratio, which in some cases reaches 1.8–2.05 (in the case of weak IHBs, it is less than 1.45).[114] There is a tendency to broadening of the ν_s(NHN) band, and its shift towards higher frequencies with an increase in the proton-acceptor capacity of the anion.[113, 114] Thus, in the case of the anions Ph_4B^- and F^-, the centre of the band is at 463 and 583 cm^{-1}, respectively. The effect of the anion was explained by its bifurcation interaction with the NH-proton of the cation. It should be recalled, however, that X-ray studies of numerous salts of the 'proton sponge' allowed one to reveal reliably the bifurcation effect only in two cases (Section IV. 3. b).

On the basis of the IR spectral data of proton sponge salts, most authors concluded that the potential energy curve for the hydrogen bridge corresponded either to a potential with two minima and a very low barrier, or to a potential with one minimum and a flat bottom (Fig. 2*a*, *b*).

Because of the nearly planar structure of the naphthalene system in compound **30**, its IR spectrum differs substantially from that of the 'proton sponge' **6**.[62]

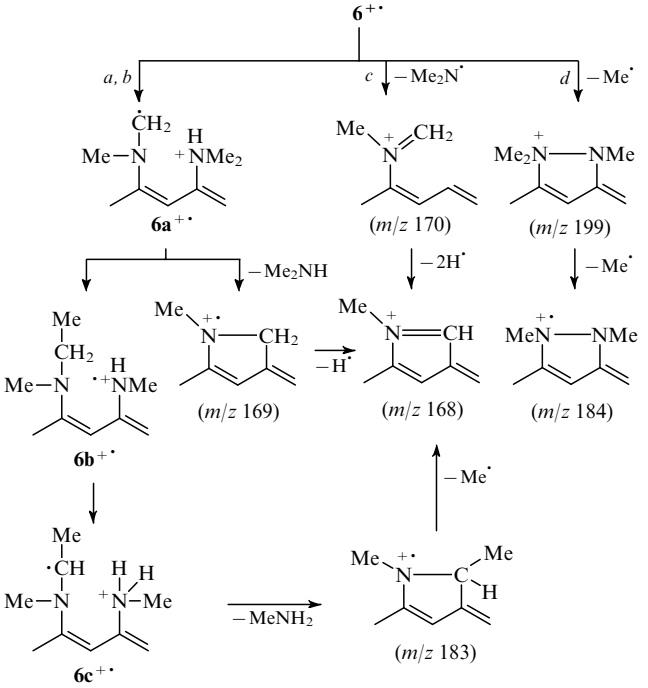
9. Mass spectra

Mass spectra of sterically hindered bis(dimethylamino)arenes including various types of 'proton sponges' were studied in most detail.[116, 117] In all cases, the fragmentation of the molecular ion which is the most intense, as a rule, is determined by the proximity of dimethylamino groups (the so-called 'proximity effect') and at early stages involves practically only these groups. The fragmentation processes include isomerisation and elimination of the $MeNH_2$, Me_2NH, and H$^\bullet$ fragments giving rise to stable heterocyclic ions.

Four main pathways of fragmentation of the molecular ion of the base **6** under electron impact are shown in Scheme 2.[116] The first pathway (*a*) is a stepwise counterflow intramolecular transfer

of H$^{\bullet}$ and Me$^{\bullet}$ species from one nitrogen atom to another resulting in the ions **6a**$^{+\bullet}$, **6b**$^{+\bullet}$, and **6c**$^{+\bullet}$, respectively.

Scheme 2



The latter eliminates $MeNH_2$, which accounts for the presence in the spectrum of an intense peak with m/z 183; this peak was assigned to the 1,2-dimethyl-1,2-dihydrobenzo[*c*,*d*]indolium ion. Its subsequent aromatisation gives the 1-methylbenzo[*c*,*d*]indolium ion (m/z 168). The peak of this ion is second in intensity after the peak of M$^{+\bullet}$ and in some 'proton sponge' derivatives it is the most abundant. The second pathway of fragmentation (*b*), which also gives the 1-methylbenzo[*c*,*d*]indolium ion, consists in the elimination of Me_2NH from the **6a**$^{+\bullet}$ ion. The third (*c*) and the fourth (*d*) pathways represent direct fragmentation of the molecular ion **6**$^{+\bullet}$ consisting in the loss of $Me_2N^{\bullet}$ or Me$^{\bullet}$ species. In the latter case, methyl derivatives of the benzo[*c*,*d*]indazolium ion with m/z 199 and 184 are formed.

The above fragmentation features are observed in the mass spectra of other derivatives of the 'proton sponge' and, which is the most interesting, in the spectrum of 1,8-bis(diphenyl-amino)-naphthalene **61**.[117]

10. Dipole moments

Dipole moments in benzene were measured for three compounds of the given series: the 'proton sponge' **6**, its 4-formyl- **80**, and 4,5-diformyl derivatives **81**.[61] The dipole moment of compound **6** (μ = 1.19 D) is precisely equal to that of 1-dimethylamino-naphthalene. This is lower than the expected value, since the π-conjugation of both dimethylamino groups with the ring would result in the summation of the vectors of the corresponding dipole moments. Apparently, due to the high non-coplanarity of the molecule **6**, both vectors are directed at a considerable angle to each other. In contrast, the dipole moments of the aldehyde **80** (μ = 5.44 D) and the dialdehyde **81** (μ = 9.21 D) appeared to be unexpectedly high. This suggests that the conjugation of the aldehyde and the NMe_2 groups in them is very efficient. The additional moment of the π-interaction, μ^{π}, in compounds **80** and **81** is equal to ~ 1.4 and 2.3 D, which is higher than in 4-dimethylaminonaphthalene-1-carbaldehyde (μ^{π} = 0.35 D) and even in *p*-dimethylaminobenzaldehyde ($\mu^{\pi} \approx 1$ D). These data are in good agreement with the X-ray data for compound **81**. The high dipole moment makes this compound closer to ionic substances; it is therefore not incidental that in contrast to many other derivatives of the 'proton sponge', the dialdehyde **81** is rather soluble in water and has a high melting point (162 – 164 °C).

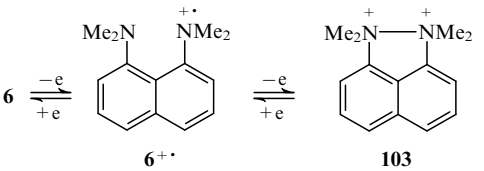
11. Donor-acceptor properties

a. Gas-phase ionisation potentials

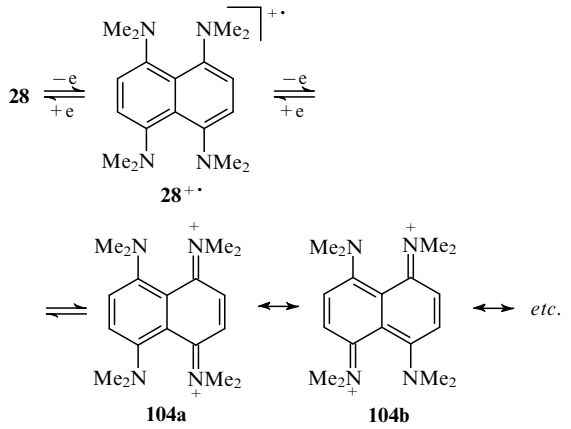
The gas-phase ionisation potentials, IP_1, of the 'proton sponge' **6** and its partially *N*-methylated precursors **1** – **5** measured by electron impact were strikingly similar, from 7.38 to 7.47 eV (see Table 18).[2] This could indicate that the first electron is ejected from the π-orbital of compounds **1** – **6**. Indeed, if these values characterised the ejection of an *n*-electron, then, taking into account significant differences in the basicity of these compounds, the ionisation potential of the 'proton sponge' would be much lower in comparison with that of the diamines **1** – **5**. However, Maier,[118] who used photoelectron spectroscopy to measure the ionisation potentials of compounds **1** and **6**, came to a somewhat different conclusion. The IP_1 value for the diamine **1** (7.10 eV) was also assigned to the π-ionisation potential, while for the 'proton sponge' **6** (IP_1 = 7.05 eV) it was ascribed to electron ejection from the *n*-orbital. This conclusion was made on the basis of calculations using perturbation theory, which revealed that the highest occupied π-MO for compound **6** correlated better with the second ionisation potential, IP_2 = 7.47 eV. It is hardly probable that this argument is self-explanatory. It will be recalled once again that according to UV spectroscopy data, the conjugation of the nitrogen atoms with the naphthalene ring and, correspondingly, the π-donor capacity of compound **6** is at least no less than that of 1,8-diaminonaphthalene.

b. Anodic oxidation potentials. Radical cations

Electrochemical oxidation of the 'proton sponge' **6** on a platinum disc electrode in MeCN gives two reversible one-electron waves with $E_{ox}^{1/2}$ = 0.36 and 1.02 V.[119] Presumably, the radical cation **6**$^{+\bullet}$ is formed at the fist step, and the dication **103**, at the second; the structure with a σ-bond between the nitrogen atoms was ascribed to the latter. The radical cation **6**$^{+\bullet}$ was also generated by oxidation of compound **6** with PbO_2. Its EPR spectrum represents an unresolved singlet with a width ΔH of 23 Œ (g = 2.0043). On the basis of these data, it was concluded that the conjugation of the dimethylamino groups with the naphthalene ring in compound **6** is significant and according to its electron-donor properties it occupies a position between *N*,*N*-dimethylaniline ($E_{ox}^{1/2}$ = 0.68 V) and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine ($E_{ox}^{1/2}$ = 0.015 V).



The oxidation of compound **23** occurs in an analogous way, but more easily.[120] Its radical cation can be conserved unchanged in acetonitrile over a period of many months. The UV spectrum of this radical cation (λ_{max} = 480 nm, lg ε = 3.1) is very similar to that of compound **23** itself, which has led to a conclusion that the naphthalene fragment of the molecule does not take part in the oxidation. In contrast to compounds **6** and **23**, the 'double proton sponge' **28** is oxidised in one two-electron wave with $E_{ox}^{1/2}$ = −0.50 V (relative to Fc/Fc^{+} = 0.0 V, Fc is ferrocene).[24] Apparently, the driving force of this process is the formation of the resonance-stabilised dication **104**, which was isolated in the form of black crystals and thoroughly characterised.[24, 121] The radical cation **28**$^{+\bullet}$ giving the EPR spectrum with hyperfine structure can be obtained by chemical oxidation of compound **28**.[24]



c. The formation of π-complexes

All 1,8-diaminonaphthalenes, including the 'proton sponge' **6** can easily form molecular complexes (MC) in which they act as donors. An attempt has been made to use the complexes with 1,3,5-trinitrobenzene (1 : 1, the complex formation constants K_c lie in the range 2.0 – 3.4 litre mol^{-1}) for estimating their electron-donor capacity.[2] Presumably, stronger donors would produce MC with an absorption maximum of the charge transfer band shifted to longer wavelengths. However, measurements revealed (Table 18) the lack of correlation between the basicity of 1,8-diaminonaphthalenes and the ease of formation of MC by these compounds. Morever, the most basic compound (the 'proton sponge' itself) gives a MC having the lowest value of λ_{max} (500 nm). It was therefore concluded that compounds **1** – **6** behave as π-donors in the formation of MC, whereas the differences in the ease of formation and stability of MC are determined predominantly by steric factors and inductive effects of the methyl groups.

Table 18. Ionisation potentials, IP_1, and electrochemical oxidation potentials ($E_{ox}^{1/2}$) of 1,8-diaminonaphthalenes and the long-wave absorption maximum (UV spectra) of their molecular complexes with 1,3,5-trinitrobenzene.

Compound	IP_1 /eV		$E_{ox}^{1/2}$ /V (in MeCN)	λ_{max} /nm (in $CHCl_3$)[2]
	EI[2]	PS[118]		
1	7.47	7.10	–	530
2	7.40	–	–	560
3	7.43	–	–	575
4	7.38	–	–	540
5	7.40	–	–	580
6	7.38	7.05	0.36, 1.02[119]	500
23	–	–	0.11, 0.72[120]	–

d. The formation of H-complexes

In some cases, IR and NMR methods were used to investigate the interaction of compound **6** with phenols,[113, 122–124] carboxylic acids,[123] and SH-acids.[125] An unexpected finding was that phenol (pK_a = 9.99) hardly protonated the 'proton sponge', although its basicity exceeded that of the phenolate anion by more than two orders of magnitude. Distinct protonation is observed only with phenols having $pK_a < 8.4$. This reaction gives two types of salts having the composition of 1 : 1 and 1 : 2, the latter being much more stable. This is rationalised by formation of homoconjugated anions, $ArOH\cdots{}^{-}OAr$. Evidence for their stability can be derived from the fact that the salt of the base **6** with pentachlorophenol (1 : 1) disproportionates in acetonitrile to give a 1 : 2 salt and a non-protonated 'proton sponge':[113]

$$\mathbf{6}\text{-}H^+C_6Cl_5O^- \rightleftharpoons \mathbf{6} + \mathbf{6}\text{-}H^+C_6Cl_5O^-\cdots HOC_6Cl_5 .$$

e. Electron acceptor properties. Radical anions

There is only one study concerned with the ability of 'proton sponges' to undergo one-electron reduction.[126] It has been shown that treatment of compound **6** with sodium in 1,2-dimethoxyethane gives a stable radical anion; its EPR spectrum was recorded at −20 °C. The hyperfine splitting constants (HFS) for the unpaired electron with cyclic protons are: $a_{H(4),H(5)}$ = 4.46, $a_{H(3),H(6)}$ = 1.77, and $a_{H(2),H(7)}$ = 1.39 Gs, *i.e.*, they are somewhat smaller than the corresponding values for the naphthalene radical anion. At the same time, the HFS constants with the protons of the methyl groups and ^{14}N nuclei are very small. This was interpreted as a result of non-coplanarity of the dimethylamino groups and the naphthalene ring. The magnitude of the dihedral angle between the axes of unshared electron pairs of the nitrogen and the $2p_\pi$-orbitals of cyclic C-atoms in the radical anion $\mathbf{6}^{-\cdot}$ was estimated to be 60 – 70 °.

12. Quantum-mechanical calculations

Using the *ab initio* method with optimisation of geometry, the optimum structures of the 'proton sponge' **6** and its protonated form **6**-H^+ were calculated.[127] The following main conclusions were made: (1) in the gas phase, the molecule of compound **6** has C_2 symmetry and the fragment $N(C_{10}H_6)N$ is essentially non-planar; (2) the degree of non-planarity in the isolated molecule of the base is lower than in the crystals; (3) increased orders of the $N-C_{Ar}$ bonds attest to a significant conjugation of the nitrogen atoms with the π-system of the ring; (4) in protonation, the molecule becomes practically planar and its symmetry approximates the C_{2v} type; (5) the hydrogen bridge in the isolated cation **6**-H^+ is symmetrical; its optimum parameters are as follows: $r[N(1)-H]$ = 1.05 Å, $r[N(2)\cdots H]$ = 1.64 Å, the angle $N(1)-H-N(2)$ = 156.8 °.

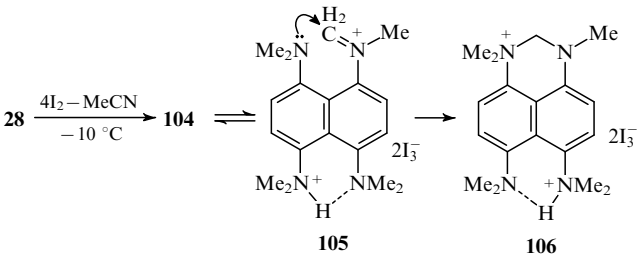
Semi-empirical simulations of the optimum structures of the base **6** and the cation **6**-H^+ were made[13, 84] using the AM1 and PM3 methods; the enthalpies of protonation for compounds **1**, **3**, **5**, and **6** and some hypothetical aza-derivatives of the 'proton sponge' were also estimated.[128]

V. Reactivity of naphthalene 'proton sponges'

Naphthalene 'proton sponges' are typical electron-rich compounds. In addition to high basicity, they are characterised by significant π-donor capacity and the presence of a negative π-charge on the cyclic carbon atoms. It is not surprising that electrophilic substitution and oxidative conversions are the most typical reactions for these compounds. A few examples of nucleophilic substitution are reported, only for compounds with electron-acceptor groups in the ring. It is probable that some reactions of the 'proton sponge', *e.g.*, chlorination with *N*-chlorobenzotriazole (CBT) or bromination with *N*-bromosuccinimide (NBS) occur through a radical mechanism, as can be judged from their unusual orientation. However, convincing evidence for this mechanism is absent, and the corresponding transformations are discussed in Section V. 2 dealing with reactions with electrophiles.

1. Oxidation

As has been mentioned above, electrochemical or chemical oxidation of 'proton sponges' results first in the formation of radical cations and then of dications. Thus treatment of the 'double sponge' **28** with an excess of iodine at −10 °C gave black needles of the salt **104** (with the I_3^- anion), which could be studied by the X-ray method.[121] It is noteworthy that increase in temperature to 25 °C or heating of the salt **104** results in its isomerisation, presumably *via* the immonium cation **105**, into the dication **106**.[121] The 'proton sponge' undergoes similar conversions under the action of certain complexes of Rh^{3+}, Ru^{3+}, and Ru^{2+}, which result in the formation of the 1,1,3-trimethyl-2,3-dihydroperimidinium cation **42** (R^1-R^3 = Me).[129]



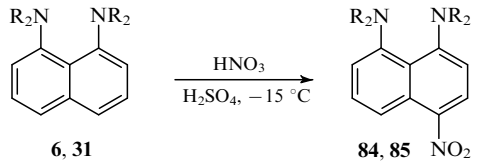
Oxidation of compound **6** with thallium triacetate or lead tetraacetate in dichloromethane at low temperature [102] or, which is better, with iodine in boiling acetonitrile [130] gives the 1,1′-binaphthyl 'sponge' **90** in moderate yields. The latter is also formed as a by-product (yield 10%) in the nitration of compound **6**.[130] Apparently, in all these cases it is the intermediate radical cation $\mathbf{6}^{+\bullet}$ that undergoes dimerisation.

2. Electrophilic substitution reactions

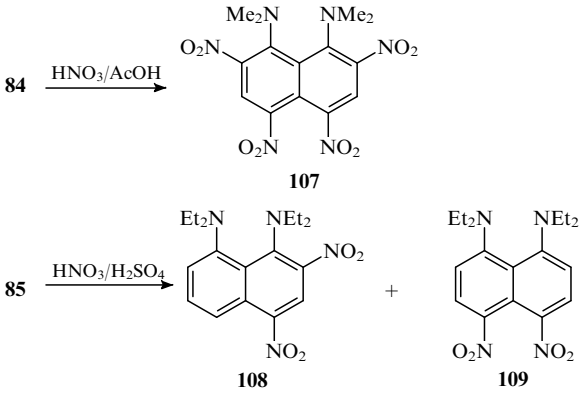
'Proton sponges' manifest unusually high activity in reactions of electrophilic substitution. To avoid resinification and to ensure desired regioselectivity, the syntheses are usually carried out at low temperatures (< 0 °C). In some cases (the Friedel–Crafts acylation), the substrate should be passivated by being converted into a salt. It should be noted that such catalysts as $AlCl_3$ or BF_3 do not give *n*-complexes with 'proton sponges'. As a rule, the first substituent enters only at positions 4 and 5 (for exceptions see Section V. 2. b). The second and subsequent substituents can occupy both the *para*- and *ortho*-positions. The specific orientation is determined by the nature of the substituent already present and, consequently, by the pK_a of the substrate and the degree of symmetry of the IHB in the corresponding cation. There is good reason to believe that some reactions of naphthalene 'proton sponges' with electrophiles occur through a radical cation mechanism, where the radical cation generated first undergoes further nucleophilic attack by the anion present in the reaction mixture (see Section V. 2. b).

a. Nitration

Nitration of the 'proton sponges' **6** and **31** in acetic acid gives directly the 2,4,5,7-tetranitro-derivative of the type **107** irrespective of the amount of nitric acid.[46] This was explained by the fact that due to the decrease in basicity of each subsequent substitution product and the increase in the concentration of the corresponding free base the rate of each successive nitration increases. Mononitration, which gives the 4-nitro-derivatives **84** and **85** in 50%–70% yields, can be carried out only in concentrated sulfuric acid with one equivalent of HNO_3[46, 55] (as mentioned above, the binaphthyl 'sponge' **90** is also formed as a by-product). Obviously, in strongly acidic media, compounds **84** and **85** are present exclusively in the form of cations, and the reaction does not proceed further. However, an attempt at subsequent nitration of compound **84** gave only the tetranitro-derivative **107**. In the case of the ethyl analogue **85**, dinitration could be accomplished with one equivalent of HNO_3 to give the 2,4- and 4,5-dinitro-derivatives **108** and **109** in yields 32% and 28%, respectively.[46] The nitration of compound **6** can be controlled to a greater extent when nitrogen dioxide is used as a nitrating agent.[130]



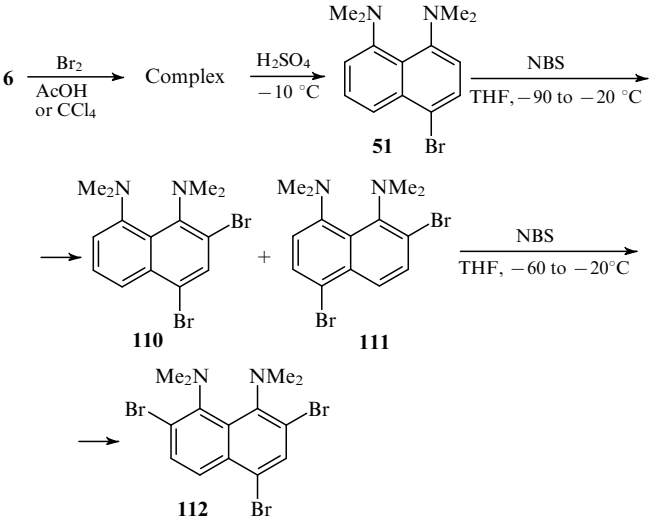
R = Me (**6**, **84**), Et (**31**, **85**).



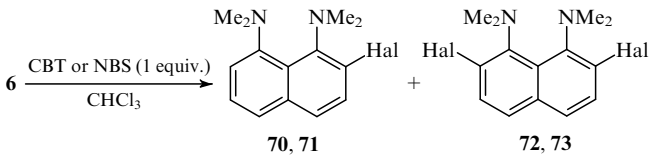
Nitration of 4-bromo-1,8-bis(dimethylamino)naphthalene **51** with one equivalent of HNO_3 in concentrated H_2SO_4 gave 4-bromo-5-nitro- and 4-bromo-2-nitro-derivatives (yields 27% and 15%, respectively).[27]

b. Halogenation

On treatment of the 'proton sponge' **6** with one equivalent of bromine in acetic acid or CCl_4, a crimson-coloured complex of an unknown structure precipitates, and gradually resinifies. Treatment of the complex with concentrated H_2SO_4 converts it into 4-bromo-1,8-bis(dimethylamino)naphthalene **51** in good yield. Subsequent bromination could be achieved only with NBS.[27] First, with 1 equiv. of NBS, a mixture of 2,4- and 2,5-dibromo-derivatives **110** and **111** is formed in a 54 : 46 ratio. Further bromination of this mixture (1 equiv. of NBS) gives 2,4,7-tribromo-1,8-bis(dimethylamino)naphthalene **112** as the only product. An attempt to convert it into a tetrabromo-derivative was unsuccessful. Thus unlike nitration, acylation, and formylation (see below), *peri*-dibromination in naphthalene 'proton sponges' does not take place, presumably due to larger steric hindrances exerted by bromine atoms.

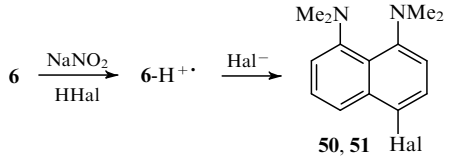


It is noteworthy that bromination of the 'proton sponge' **6** with NBS (1 equiv.) in chloroform occurs in quite a different way.[93] In this case, 2-bromo- **71** and 2,7-dibromo-derivatives **73** are formed in 36% and 52% yields, respectively. *ortho*-Substitution occurs nearly quantitatively in the chlorination of compound **6** with *N*-chlorobenzotriazole (CBT) to give 2-chloro- **70** and 2,7-dichloro-derivatives **72**.[28] Probably, these reactions proceed with the participation of the 'sponge' base (rather than the cation) in which the π-electron density at positions 2 and 7 is greater than at positions 4 and 5. At the same time, one should not rule out the radical mechanism of substitution.



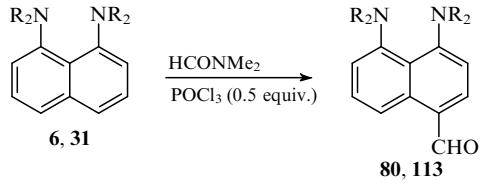
Hal = Cl (**70**, **72**), Br (**71**, **73**).

Recently, in our laboratory we have established that treatment of compound **6** with sodium nitrite in hydrochloric acid gives 4-chloro-1,8-bis(dimethylamino)naphthalene **50** in a nearly quantitative yield. If hydrobromic acid is used instead of hydrochloric acid, the yield of the 4-bromo-derivative **51** is much lower (~ 20%).[130] The formation of these somewhat unusual products is a convincing proof of the radical-cation mechanism of halogenation. Obviously, at the first stage the 'proton sponge' is oxidised with nitrous acid to the radical cation, which is subjected to nucleophilic attack by the halide anion at position 4, where the highest positive charge is accumulated.

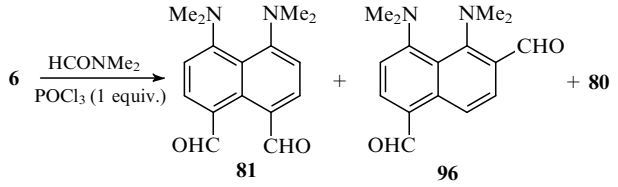


c. Formylation and acylation

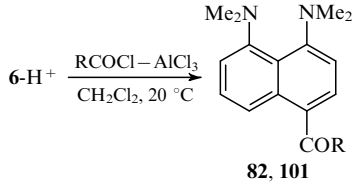
Formylation of the 'proton sponges' **6**[131] and **31**[132] under conditions of the Vilsmeier reaction in a deficiency of $POCl_3$ (0.5 equiv.) gives the corresponding 4-formyl-derivative **80** and **113** in moderate yields. When an equimolar amount of $POCl_3$ is used, compound **6** gives the 4,5-dialdehyde **81** and small amounts of the 2,5-dialdehyde **96** along with the monoaldehyde **80**.[131]



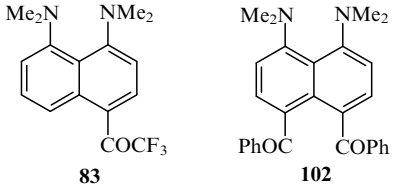
R = Me (**80**), Et (**113**).



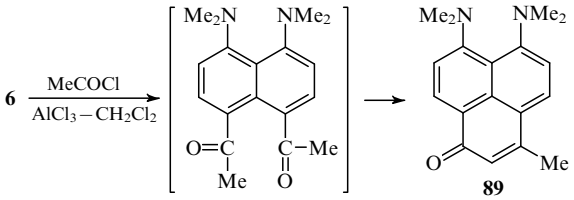
1,8-Bis(dimethylamino)naphthalene **6** does not undergo the Vilsmeier–Haack acylation or acylation with carboxylic acids in polyphosphoric acid (as takes place in the series of perimidones, 2,3-dihydroperimidines, and perimidines).[133] At the same time, under conditions of the Friedel–Crafts reaction in the presence of $AlCl_3$ or $AlBr_3$, acyl chlorides acylate the 'sponge' base even at −90 °C.[110] The reaction is not very smooth, therefore it is more convenient to perform it with the salt **6**-H^+. The yields of the ketones **82** and **101** are virtually quantitative.

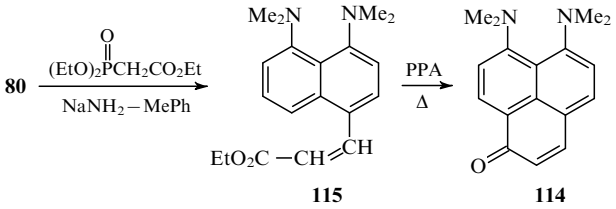


The reaction of the base **6** with trifluoroacetic anhydride does not require a catalyst and proceeds at −30 °C. This results in the formation of the 4-trifluoroacetyl derivative **83** in moderate yield.



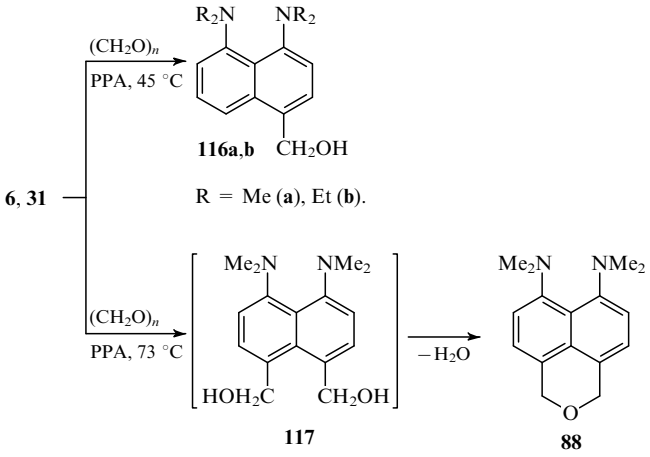
Treatment of the base **6** with an excess of benzoyl chloride gave the 4,5-benzoyl derivative **102** (yield 7%). Under the same conditions, the reaction with excess acetyl chloride gives phenalenone **89** (yield 27%), presumably as a result of intramolecular aldol condensation of the intermediate, the 4,5-diacetyl derivative. The progenitor of this phenalenone series (**114**) was synthesised (yield 15%) by intramolecular acylation of ethyl acrylate **115** upon heating in polyphosphoric acid (PPA).[110]





d. Hydroxymethylation

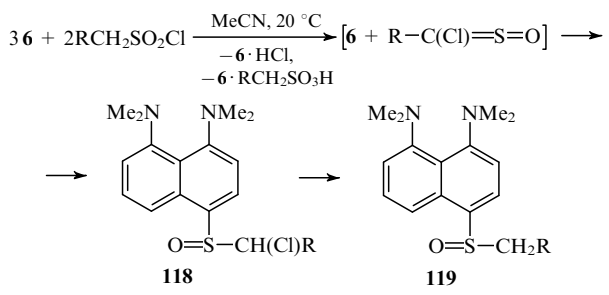
'Proton sponges' undergo hydroxymethylation with paraformaldehyde in polyphosphoric acid at 45 °C to give the alcohols **116a**,**b**.[132,134] At higher temperatures, compound **6** is converted into naphthopyran **88** in good yield, apparently as a result of dehydration of the intermediate 4,5-bishydroxymethyl derivative **117**. The alcohols **116** were also obtained by reduction of the aldehydes **80** and **113** with $LiAlH_4$.[132]



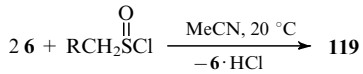
e. Miscellaneous reactions

The 'proton sponge' **6** reacts with alkanesulfonyl chlorides to give the 4-alkylsulfinyl derivatives **118** and **119**.[135] It was established that the active species, which directly interacts with compound **6**, is the corresponding chlorosulfine generated *in situ*. Compounds

119 can be also obtained by the reaction of the 'proton sponge' **6** with alkanesulfinyl chlorides.

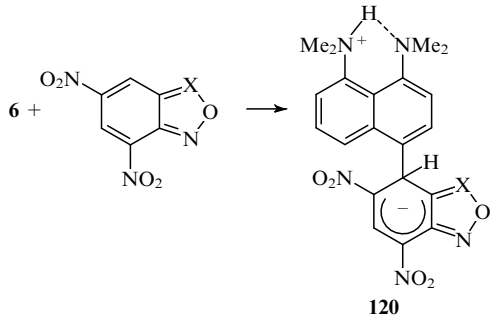


R = H, Me, $PhCH_2$.



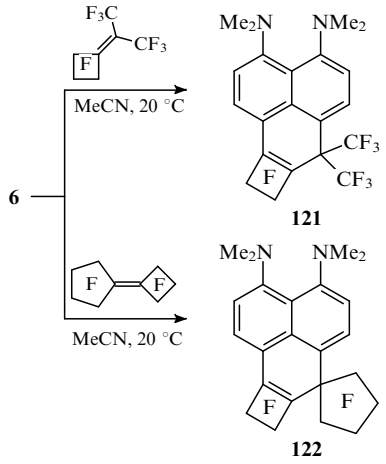
R = H, Me, CF_3, F, Cl.

Compound **6** behaves as a strong CH-nucleophile with respect to 4,6-dinitro-derivatives of benzofuroxan and benzofurazan to give the corresponding adducts **120**.[136]



X = N, N→O.

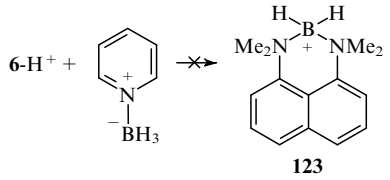
The 'proton sponge' easily adds to perfluorocycloalkanes with exocyclic double bonds. This reaction involves both *peri*-positions and the phenalene derivatives are formed **121**,**122**.[137]



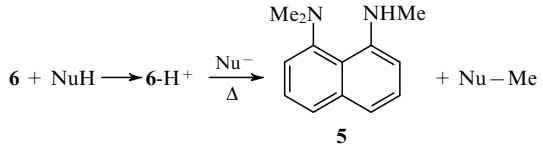
3. Reactions involving dialkylamino groups

The following four types of these reactions are known: (1) quaternisation, (2) dealkylation, (3) substitution of the dialkylamino groups, and (4) oxidative conversions. The latter have already been described in Section V. 1. Here, only the first three types will be considered. Practically all these reactions have been performed with compound **6**.

Only one example of quaternisation of the 'proton sponge' is known. Contrary to the original report,[1] it was established that its treatment with methyl fluorosulfate gives the non-crystalline salt **68** (as the SO_3F^- anion), which is converted into the crystalline tetrafluoroborate **67** under the action of $NaBF_4$.[37] An attempt to synthesise the borate complex **123** by treating the cation **6**-H^+ with pyridine–borane was unsuccessful.[138] At the same time, complexes of this type are easily formed with tetramethyl-*o*-phenylenediamine and 2,2′-bipyridyl. This circumstance can be regarded as additional proof of the extremely low nucleophilicity of the 'proton sponge'.

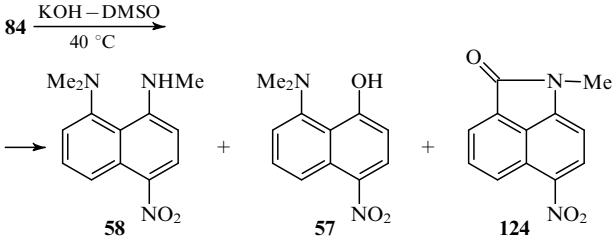


Heating of 'proton sponge' salts containing mild nucleophiles, such as thiocyanate,[26] phenylmercaptide, and phenylselenide [139] leads to demethylation and the formation of 1-dimethylamino-8-methylaminonaphthalene **5**. This reaction proceeds especially smoothly with selenophenol; the yield of the amine **5** is close to quantitative. It is of note that if the 'sponge' **6** is heated with thiophenol and selenophenol, the formation of the cation **6**-H^+ proceeds at a very low rate (> 1 h).

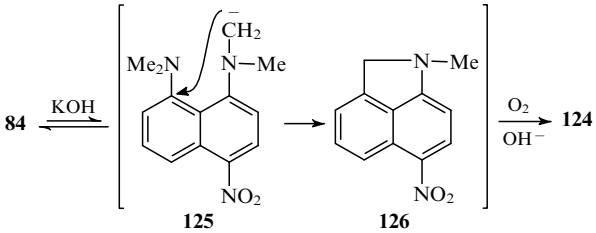


Nu^- = SCN^-, PhS^-, $PhSe^-$.

Demethylation of 'proton sponge' bases occurs only if the ring contains strong electron-acceptor groups and if the reaction is carried out in a superbasic medium.[30] Thus, treatment of the 'nitro sponge' **84** with a solution of KOH in DMSO (40 °C, 24 h) gave the trimethyl-substituted compound **58** (yield 40%). The two other reaction products were naphthol **57** (yield 7%) and, which is especially unexpected, lactam **124** (yield 11%).



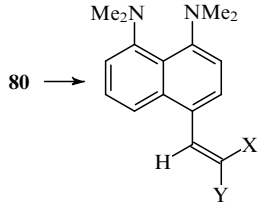
The formation of naphthol **57** seems to be a result of nucleophilic substitution of the dimethylamino group in the more activated position 1. Some complex reactions also entail hydrolytic substitution of the dimethyamino group by the carbonyl group (see Section V. 5). The mechanism of formation of the lactam **124** is not known with certainty. Presumably, this reaction begins with the generation of an equilibrium amount of the carbanion **125** in which intramolecular nucleophilic substitution of the 8-NMe_2 group takes place. The 1-methyl-6-nitro-1,2-dihydrobenzo[*c*,*d*]indole **126** formed undergoes further autooxidation, which is also characteristic of other compounds of this kind.



It is known that the 8-NMe_2 group can be substituted by hydrogen in the catalytic hydrogenation of the 'nitro sponge' **84** (see Section V. 4).

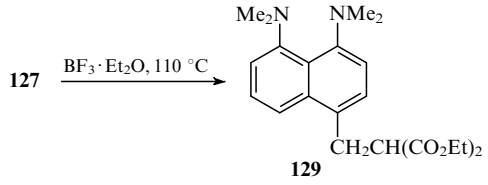
4. Reactions of functional groups

The greatest number of 'proton sponge' derivatives (azomethines, hydrazones, oxime, nitrile, *etc*.) were synthesised from the 4-aldehyde **80**.[129] The latter was also converted by the Wittig reaction into 4-vinyl-1,8-bis(dimethylamino)naphthalene **74**[109] and compound **115**.[131] A number of other 4-vinyl derivatives (**75**, **127**, **128**) were synthesised by condensation of the aldehyde **91** with the corresponding CH-acids. The conditions for polymerisation of the vinyl 'sponge' were investigated.[109] It was found that heating of compound **127** with boron trifluoride etherate results in the reduction of the exocyclic C=C bond and the concomitant formation of the naphthylmethyl derivative of diethyl malonate **129** instead of the expected intramolecular cyclisation into the corresponding phenalenone.[131] It was assumed that the ethyl groups of the etherate play the role of a hydride donor, and the reaction can be realised due to polarisation of the C=C bond, which is enhanced by the donor effect of the dimethylamino groups.



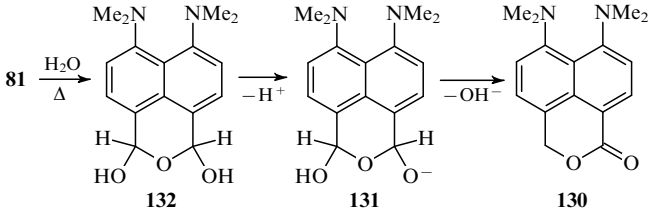
74: X = Y = H;
75: X = Y = CN;
115: X = CO_2Et, Y = H;
127: X = Y = CO_2Et;
128: X = CO_2Et, Y = CN.

74, **75**, **115**, **127**, **128**



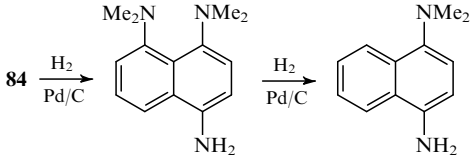
129

Upon boiling in water, the dialdehyde **81** undergoes the intramolecular Cannizzaro reaction to give the naphtho[1,8-*c*,*d*]-pyranone derivative **130** in 36% yield.[131] The unusual feature of this reaction is that it does not require any alkali. Apparently, the alkalinity of the medium sufficient for the formation of the anion **131** is created by the 'proton sponge' itself. It should be noted that unlike the naphthalene-1,8-dicarbaldehyde, which exists under ordinary conditions only in the form of a cyclic hydrate, the dialdehyde **81** is stable. This may be ascribed to the stabilising effect of the dimethylamino groups, which, when entering into conjugation, reduce the partial positive charge on the carbonyl carbon atoms and thus hamper the hydration. However, the formation of the hydrate **132** which is needed for the Cannizzaro reaction, does take place upon boiling of the dialdehyde **81** in water.



132 **131** **130**

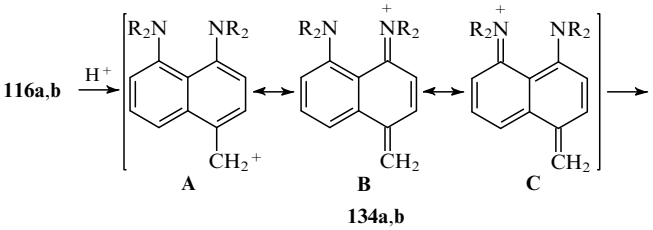
Catalytic hydrogenation of the 'sponge' **84** gave the amine **76**,[45] which is extremely unstable and oxidisable in air. 4,5-Diamino-1,8-bis(dimethylamino)naphthalene was obtained by hydrogenation of the dinitro-derivative **40**.[24] Subsequent hydrogenation of compound **76** is accompanied by elimination of the 8-NMe_2 group and the formation of 1-dimethylamino-4-aminonaphthalene **133**. The amine **76** gives azomethine with *p*-nitrobenzaldehyde and the *N*-acetyl derivative **77**; the latter was methylated to give quite stable 4-methylamino- **78** and 4-dimethylamino-derivatives **79** of the 'proton sponge'.[45] The latter can be regarded as a kind of a 'sesqui-sponge'.



76 **133**

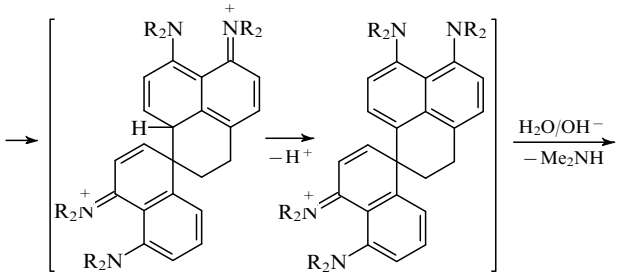
5. Transformations of naphthylmethyl carbocations derived from the 'proton sponge'

It has recently been established in our laboratory that treatment of the alcohol **116a** with concentrated hydrochloric or phosphoric acid gave unexpectedly the spiro compound **93** containing two fragments of the 'proton sponge' in a nearly quantitative yield.[134, 140]

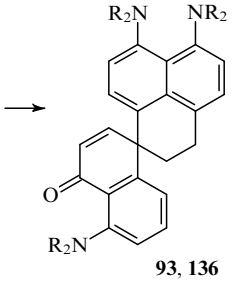


A **B** **C**

134a,**b**



135a, **b**



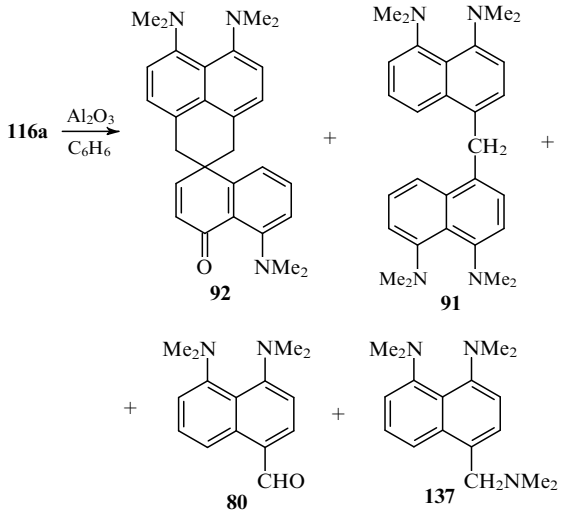
93, **136**

R = Me (**116a**, **93**), Et (**116b**, **136**).

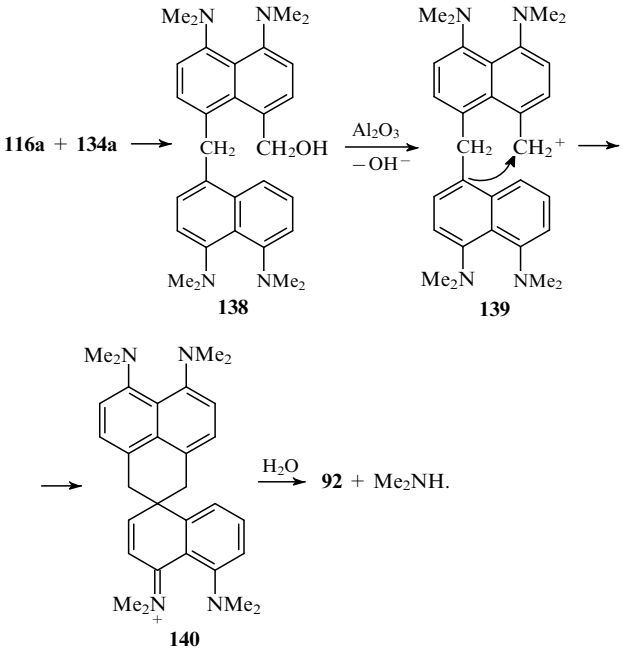
There are reasons to assume that the key intermediate in this synthesis is the naphthylmethyl carbocation **134a** (structure **A**) in which strong resonance stabilisation involving both dimethylamino groups provides the fixation of the diene system containing the *exo*- and *endo*-cyclic bonds CH_2=C and C(4a)=C(5) (structures **B** and **C**). In the subsequent [4π + 2π]-cycloaddition, one molecule of the carbocation behaves as a diene, whereas the second one plays the role of a dienophile; this reaction occurs in a 'head-to-head' mechanism as shown in the scheme. An analogous spiro compound (**136**) is obtained from the alcohol **116b**; however, this reaction is much slower and the yield is lower (~ 22%).[132] This may evidently be due to insufficient stabilisation of the carbocation **134b** due to the more pronounced non-coplanarity of the ring and the diethylamino groups.

The cycloaddition reaction observed when the alcohol **116a** was heated in benzene in the presence of solid acidic adsorbents (Al_2O_3, SiO_2, or TiO_2) occurs in a different direction.[132, 141] In this

case, the main reaction product is the isomeric spiro compound **92** of the 'head-to-tail' type (yield 23%). This reaction also gives dinaphthylmethane **91** (10%), the aldehyde **80** (19%), and the 4-dimethylaminomethyl derivative of the 'proton sponge' **137** (22%) (all the yields are given for Al_2O_3; for other supports they vary somewhat).



Most probably, all these compounds are the products of transformation of the carbocation **134a**. Thus the formation of the aldehyde **80** can be explained by the well-established ability of carbenium ions to oxidise alcohols to aldehydes through elimination of the hydride ion. The formation of the dinaphthylmethane derivative **91** seems to be due to the *ipso*-substitution of the CH_2OH group in the original alcohol **116a** by the carbocation **134a**. An attack by the carbocation at the second possible direction of the free *peri*-position 5 in the molecule of compound **116a** should lead to the formation of the alcohol **138**, which further generates the carbocation **139**. Subsequent intramolecular *ipso*-attack by the carbenium centre on the other residue of the 'proton sponge' at position 4 gives ultimately the spiro product **92** *via* the immonium salt **140**. The dimethylamine liberated in the hydrolysis of the immonium group reacts with the carbocation **134a** to give compound **137**.

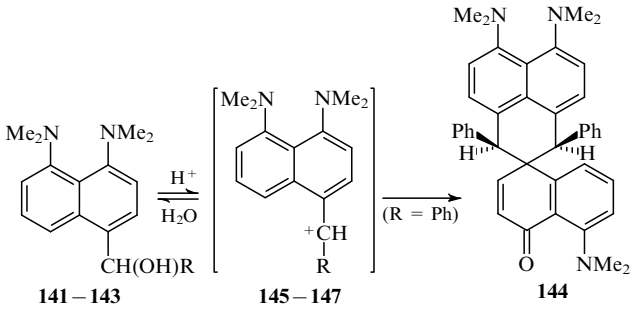


The different direction of cycloaddition reactions in protic media and in the presence of Lewis catalysts is explained in the following way. In a strongly acidic protic medium favouring the formation of the non-symmetrical spiro compounds **93** and **136**, the original alcohol appears to be fully protonated due to the high basicity of the 'proton sponge'. It is therefore hardly likely that it will easily interact with the carbocation **134a**. As a result, the [4π + 2π]-cycloaddition remains the only possible reaction of the carbocation, especially when its concentration is high enough. At the same time, on the surface of an adsorbent the carbocation **134a** is formed in a low concentration. Being surrounded by an excess of the original alcohol, it will primarily react with the latter to give the symmetrical spiro compound **92**, or with another strong nucleophile. Thus for naphthyl carbocations derived from 'proton sponges' there exist two different cycloaddition reactions, which follow different mechanisms and give spiro compounds of two different types.

The most surprising feature in the formation of the spiro compounds **93** and **136** is that contrary to electrostatic laws, the positively charged carbon atoms from two methylene groups combine. Quantum mechanical calculations [140, 142, 143] suggest that this process is favoured by the symmetry of their boundary orbitals. This process may not be synchronous and occurs *via* the formation of a biradical intermediate.

The secondary alcohols **141 – 143** behave differently in the presence of acids. Whereas the two former do not change even on prolonged heating in concentrated HCl or CF_3CO_2H, their phenyl analogue forms the spiro compound **144** in 87% yield.[140] At first, this compound was erroneously identified as **93**; however, subsequent X-ray analyses confirmed the validity of the symmetrical structure.[144] At present, it still remains obscure whether compound **144** is formed by a mechanism of two-step electrophilic substitution, as is the case with the spiro adduct **92**, or as a result of a [4π + 2π]-cycloaddition of two molecules of the cation **147** and its abnormal direction is due to steric factors.

The behaviour of the alcohols **141 – 143** with respect to Al_2O_3 is also different. When boiled in benzene in the presence of Al_2O_3, compound **141** underwent dehydration, presumably, by a mechanism of *E*1-elimination *via* the carbocation **145**. This reaction gives the 4-vinyl derivative **74** in good yield. The alcohols **142** and **143** do not change under these conditions.[109] The inertness of the alcohol **142** in both protic media and in the presence of Al_2O_3 might be due to stabilisation of the cation **146** by the electron-acceptor group CF_3, so that it is not formed at a steady-state concentration that is sufficient for this reaction.

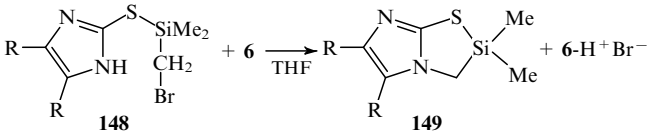


R = Me (**141**, **145**); CF_3 (**142**, **146**), Ph (**143**, **147**).

Apparently, the specific reactivity of naphthalene 'proton sponges', which is ultimately due to the potent + *M*-effect of two dimethylamino groups, is manifested in cycloaddition reactions to a far greater degree than in any other conversion. Indeed, although these reactions have been later discovered in alcohols derived from 1,8-dimethoxy-, 1-dimethylamino-8-methoxy-,[145] and even 1-dimethylaminonaphthalene,[92] they proceeded with considerable difficulty and gave spiro compounds in low yields and of only one specific type.

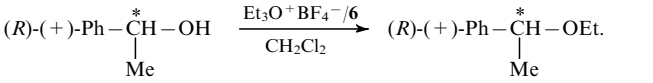
VI. Applications of the 'proton sponges' in organic syntheses

There are numerous indications of the use of 'proton sponge' in organic syntheses, mostly as a strong but low-nucleophilic base. Its application is useful in those cases where it is necessary to ionise the acidic X—H bond or to bind an acid liberated in the course of the reaction without any effect on other base-sensitive groups. A typical example is the cyclisation of the imidazoles **148** in 2-dimethylsila-3*H*-imidazo[2,1-*b*]thiazoles **149**, which occurs in the presence of the 'proton sponge' **6** and in more than 80% yield. Substitution of compound **6** by ordinary bases (OH^-, MeO^-, *etc*.) leads to the cleavage of the S—Si bond.[146]

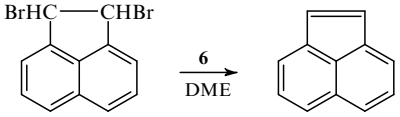


R = H, Ph.

In reactions of chiral compounds requiring the use of a base, the 'proton sponge' hardly causes any racemisation and favours the retention of high optical purity.[147–149] An example is the conversion of optically active alcohols into ethers under the action of triethyloxonium tetrafluoroborate:[147]



Quite unexpected was the use of the 'proton sponge' as a debrominating agent in the conversion of *vic*-dibromides into alkenes.[150] Thus, heating of compound **6** with dibromoacenaphthene in dimethoxyethane gives acenaphthylene in a nearly quantitative yield. Dibromides of coumarin, isocoumarin, chalcone, *etc*., enter into this reaction. However, the fate of the 'proton sponge' in this conversion could not be followed.



Other applications of the 'proton sponge' in organic syntheses are documented in several publications.[151–154]

VII. Conclusion

The discovery of the high basicity of 1,8-bis(dialkylamino)-naphthalenes has given a strong impetus to the search for other, still stronger neutral organic bases. Developments in this field have led to the appearance of an interesting branch of organic chemistry, namely, the chemistry of 'proton sponges'. Although naphthalene 'proton sponges' are no longer record holders among neutral bases, their potential in the design of novel compounds possessing unusual physicochemical properties has by no means been exhausted. Of substantial interest are *inter alia* combined (*e.g*., proton-hydride) 'sponges', the synthesis and study of their hydroxy derivatives, and the development of organometallic chemistry based on them. Finally, it may be expected that the naphthalene 'proton sponges' will be effective building blocks in the construction of supramolecular structures manifesting specific receptor properties.

This review has been written with the financial support of the Russian Foundation for Basic Research (Project No. 96-03-32153a).

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