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Molecular structure of 5,6-bis(dimethylamino)acenaphthene, 5,6-bis(dimethylamino)acenaphthylene, and their monohydrobromides: a comparison with some naphthalene proton sponges

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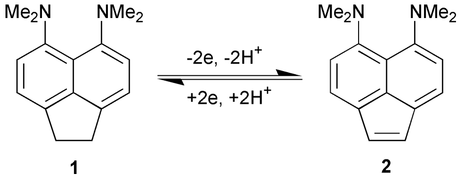
X-Ray study of the four title compounds has shown that the strong lowering in the basicity of the acenaphthylene proton sponge **2** in comparison with its acenaphthene counterpart **1** is due to pronounced conjugation between the NMe_2 groups and the π-electronic system of the molecule rather than to the nature of intramolecular hydrogen bonding in the protonated forms. The first X-ray structure of the acenaphthylene derivative is reported.

Introduction

Recently, we reported the synthesis of acenaphthene **1** and acenaphthylene **2** proton sponges, which easily interconvert as a result of the oxidation–reduction process.[1] An interesting feature of this redox system, which can be applied in molecular devices, consists of the sharp basicity change accompanying the interconversion **1** $\rightleftarrows$ **2**. Whereas the basicity of **1** ($pK_a = 18.3$, MeCN) is slightly greater than that for parent proton sponge **3** ($pK_a = 18.2$), the basicity of **2** ($pK_a = 14.1$) is decreased by nearly four powers of ten.[1] For a better understanding of the factors responsible for such a strong basicity change, we have studied the X-ray structures of bases **1** and **2** and of their conjugated acids as hydrobromides.



Experimental

Crystals of compounds **1** and **2** suitable for X-ray analysis were obtained by slow crystallisation of their melts. Hydrobromides **1**·HBr and **2**·HBr were prepared by addition of an equimolar quantity of 46% hydrobromic acid to a solution of the corresponding base in ethyl acetate. Samples of both salts for the X-ray study were further obtained by slow evaporation of their acetonitrile solutions at room temperature. At this time, the crystals of **2**·HBr were collected as solvate with one MeCN molecule. **1**·HBr: light-brown prisms with mp 265–266 °C (decomp.); **2**·HBr·MeCN: yellow crystals with mp 236–240 °C (decomp. above 260 °C).

Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD area detector at 200 K (for **1**·HBr, **2** and **2**·HBr·MeCN) and a CAD4 Enraf-Nonius diffractometer at 293 K (for **1**), using graphite monochromated Mo-Kα radiation. The absorption correlation for **1**·HBr and **2**·HBr·MeCN was carried out semiempirically from the equivalents using the SADABS program.[2] All structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 in anisotropic–isotropic approximation. The positions of the hydrogen atoms were located from the difference Fourier syntheses (for **1**·HBr, **2** and **2**·HBr·MeCN); for **1** all hydrogen atoms were placed in the geometrically calculated positions and included in the refinement using the riding model approximation with $U\text{iso}(H) = 1.2U\text{eq}(C)$ for acenaphthylene cycles and $U\text{iso}(H) = 1.5U\text{eq}(C)$ for methyl groups, where $U\text{eq}(C)$ is the equivalent isotropic temperature factor of the carbon atom bonded to the corresponding hydrogen atom. Crystal data, and experimental and refinement details are listed in Table 1. All calculations were made on an IBM PC with the help of SHELXTL software.[3]

Results and discussion

The main structural parameters of the title compounds and reference proton sponges **3**–**5** along with basicity values and the chemical shifts of the NH-proton in the corresponding salts are presented in Table 2. The atomic coordinates and equivalent isotropic displacement parameters for **1**, **2**, **1**·HBr, and **2**·HBr·MeCN, non-hydrogen atomic coordinates with anisotropic displacement parameters, hydrogen atom coordinates with isotropic displacement parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. CCDC reference numbers 168298–168301. See http://www.rsc.org/suppdata/p2/b1/b106725g/ for crystallographic files in .cif or other electronic format. The molecular structures with the atom numbering scheme are shown in Figs. 1 and 2. Some bond lengths and angles are given in Table 3; torsion angles are collected in Table 4.

The choice of compounds **3**–**5** as reference ones is caused by the availability of X-ray information not only for the neutral bases but also for their hydrobromides. Besides, 2,7-dichloro derivative **5** represents the naphthalene proton sponge with a relatively rigid structure, in which the dimethylamino groups are brought together and fixed in a face-to-face conformation.[7] On the other hand, voluminous *peri*-substituents in tetramine **4** should strengthen an acoplanarity of the whole molecule.[6]

The most important structural change in molecules **1** and **2** and in their cations in comparison with proton sponges **3**–**5** (Table 2) is a strong increase in N ··· N distance which is

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Table 1 Crystal data and structure refinement for **1**, **2**, and their complexes

Compound	**1**	**1**·HBr	**2**	**2**·HBr·MeCN
Empirical formula	$C_{16}H_{20}N_2$	$C_{16}H_{21}BrN_2$	$C_{16}H_{18}N_2$	$C_{18}H_{22}BrN_3$
Formula weight	240.34	321.26	238.32	360.30
Crystal colour, habit	Light-yellow, needle	Light-brown, prism	Orange–red, plate	Yellow, needle
Crystal size/mm	0.2 × 0.1 × 0.1	0.4 × 0.4 × 0.3	0.5 × 0.4 × 0.2	0.3 × 0.2 × 0.15
Crystal system			Monoclinic	
Space group	$P2_1/c$	$C2/c$	$P2_1/n$	$C2/c$
a/Å	15.183(3)	19.0454(9)	9.0694(8)	28.400(2)
b/Å	8.656(2)	14.6856(7)	12.1429(11)	11.7675(10)
c/Å	11.822(2)	11.0912(5)	12.0763(11)	10.6404(9)
β/°	111.94(3)	101.788(1)	99.313(2)	94.721(2)
V/Å^3	1441.2(5)	3036.7(2)	1312.4(2)	3544.0(5)
Z	4	8	4	8
D_c/g cm^{-3}	1.108	1.405	1.206	1.351
Diffractometer	CAD4 Enraf-Nonius		Bruker SMART 1000 CCD	
T/K	293(2)		200(2)	
Radiation			MoKα ($\lambda = 0.71073$)	
Scan mode	θ-5/3θ		ω-scan with 0.3° step in ω and 10 s exposure per frame	
$2\theta_{max}$/°	53.94	60.08	60.08	60.14
Completeness of data set (%)	98.6	98.1	97.6	98.1
μ/mm^{-1}	0.065	2.697	0.071	2.320
Ranges: h	−19 to 17	−26 to 26	−12 to 10	−39 to 39
k	−11 to 0	−20 to 20	−16 to 17	−16 to 11
l	0 to 15	−15 to 15	−16 to 16	−14 to 14
Absorption correction	None		Semi-empirical from equivalents (SADABS)	
T_{max} and T_{min}	—	0.835, 0.624	0.924, 0.841	0.793, 0.657
Reflections collected	3418	22032	10340	18363
Reflections unique	3137	4356	3774	5145
With $[I > 2\sigma(I)]$	1045	3034	1926	1999
R (int)	0.0358	0.0363	0.0287	0.0801
F(000)	520	1328	512	1488
Goodness-of-fit on F^2	0.963	0.887	0.916	0.695
R_1, wR_2 $[I > 2\sigma(I)]$	0.0771, 0.2161	0.0262, 0.0525	0.0500, 0.1229	0.0368, 0.0498
R_1, wR_2 indices (all data)	0.2224, 0.3367	0.0467, 0.0553	0.0972, 0.1506	0.1283, 0.0700
Largest diff. peak/hole/eÅ^{-3}	0.296/−0.202	0.363/−0.430	0.232/−0.138	0.671/−0.297

Table 2 Main structural parameters, basicity constants, and δ_{NH} values for compounds **1**–**5** and their hydrobromides (for details see text)

Compound[a]	**1**	**1**·HBr	**2**	**2**·HBr ·MeCN	**3**	**3**·HBr	**4**	**4**·2HBr	**5**	**5**·HBr
N ··· N distance/Å	2.877(5)	2.666(2)	2.955(2)	2.671(3)	2.792(8)	2.554(4)	2.745(1)	2.567(5)	2.768(4)	2.561(3)
Shortening of N ··· N on protonation (%) (Å)	7.3 (0.211)		9.6 (0.284)		8.5 (0.238)		6.5 (0.178)		7.5 (0.207)	
N–H distance/Å	—	0.99(2)	—	0.98(2)	—	1.31(1)	—	1.22(1)	—	1.29(1)
H ··· N distance/Å	—	1.72(2)	—	1.75(2)	—	1.31(1)	—	1.39(1)	—	1.29(1)
∠ NHN/°	—	159(2)	—	156(2)	—	153(3)	—	158(3)	—	165(2)
NHN/N$^+$ ··· N	—	**59.6**	—	**58.4**	—	**59.9**	—	**61.6**	—	**64.4**
δ_{NH}, [D$_6$]DMSO (ppm)	—	**16.35**	—	**15.77**	—	**18.33**	—	**18.80**	—	**19.91**
pK_{a1}, DMSO	7.7		5.7		7.5		9.8		7.0	
pK_{a1}, MeCN	18.3		14.1		18.2		—[b]		17.8	
∠ NMe$_2$–aromatic ring[c]/°	43	87	36	84	40	~90	~53	~90	71	~90
C$_{arom}$–N distance[c]/Å	1.408	1.461	1.395	1.460	1.402	1.465	1.408	1.457	1.404	1.458
Sum of CNC angles at N[c]/°	339.1	337.2	348.3	336.9	347.1	337.8	344.5	336.1	353.0	342.7
∠ C(1)–C(9)–C(8)/°	130.4(3)	128.5(1)	129.8(1)	129.1(2)	125.8(3)	125.9(3)	123.6(1)	124.4(3)	124.5(2)	124.9(2)
∠ C(4)–C(10)–C(5)/°	110.7(4)	112.4(1)	109.7(1)	110.9(2)	119.5(3)	122.3(3)	123.6(1)	124.4(3)	117.5(2)	119.6(2)
C(1) ··· C(8) distance/Å	2.588(5)	2.567(2)	2.619(2)	2.580(3)	2.562(8)	2.528(5)	2.544(1)	2.504(7)	2.573(4)	2.543(3)
C(4) ··· C(5) distance/Å	2.317(6)	2.342(2)	2.306(2)	2.326(3)	2.443(8)	2.476(6)	2.544(1)	2.504(7)	2.419(4)	2.439(3)
Deviations of N atoms from mean ring plane[c]/Å	0.184	0.058	0.411	0.041	0.400	0.019	0.120	0.018	0.054	0.004

[a] For all the compounds (base or cation) in this Table a general atom numbering system is adopted as represented by structure **3**, treating molecules **1** and **2** as naphthalene derivatives. Data for proton sponge **3** were accepted from ref. [4], **3**·HBr from [5], **4** and **4**·2HBr from [6], **5** and **5**·HBr from [7], and **1** and **2** (pK_a and δ_{NH} values) from [1]. Bolded parameters in the Table are in a qualitative correlation. [b] Absence of data. [c] Average values.

especially marked for acenaphthylene **2** (2.955 Å). Undoubtedly, this is a result of the "tightening" influence of the CH_2CH_2 and CH=CH bridges which draw together the C(4) and C(5) atoms, and at the same time pull apart the NMe_2 groups. Protonation induces the reduction of the N ··· N distance (up to ~10% in the case of **2**), but even in the form of a cation the hydrogen bridge length for **2**·HBr seems to be a record in its longitude among other naphthalene type proton sponge cations studied up to now (see literature survey at [8,9]). Moreover, the absolute value of N ··· N distance reduction for **2** (0.284 Å) is the largest reported so far for all kinds of proton sponges.[8]

In both cations **1**·H$^+$ and **2**·H$^+$ the intramolecular hydrogen bridges are asymmetrical at 200 K, with an almost equal extent of asymmetry judging by the N ··· H bond lengths. Unlike cations **3**·H$^+$, **4**·2H$^+$ and **5**·H$^+$ with practically symmetrical

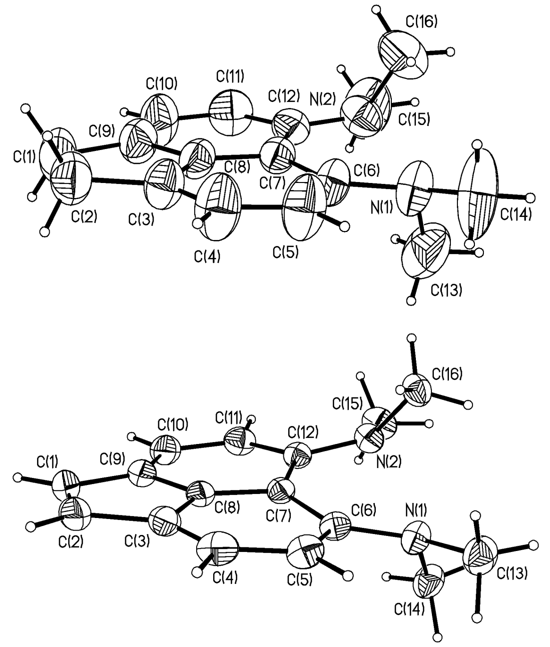


Fig. 1 Structures of molecules **1** (above) and **2** (below) showing 30% probability ellipsoids of thermal motion and the atom numbering scheme.

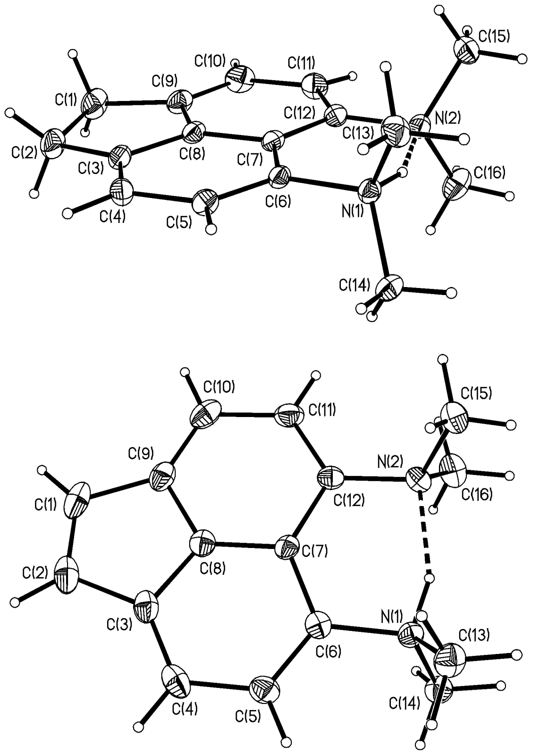
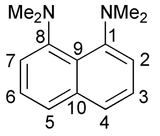


Fig. 2 Structures of cations **1**·H$^+$ (above) and **2**·H$^+$ (below) showing 30% probability ellipsoids of thermal motion and the atom numbering scheme.

H-bridges, hydrogen bond asymmetry in **1**·H$^+$ and **2**·H$^+$ is apparently due to enlargement of the N ··· N distance. In accordance with theoretical estimations[8] (at the MP2/6-31G* level), the proton in a cation, beginning from r(N ··· N) > 2.72 Å, is placed in a double minimum potential well that signifies its asymmetrical disposition between the nitrogen atoms. As the N ··· N distance enlarges, the intramolecular hydrogen bond (IHB) weakens and makes the NHN-bridge more asymmetrical (see Table 2).

The angle N ··· H–N$^+$ in **1**·HBr and **2**·HBr·MeCN salts (156–159°) is somewhat bigger than in unsubstituted proton sponge cation **3**·HBr (153°). Nevertheless, as seen in Table 2, the highest extent of linearity of the IHB among all studied cations of naphthalene proton sponges is observed for **5**·HBr (165°).



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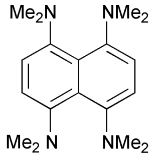

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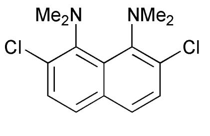

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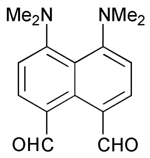


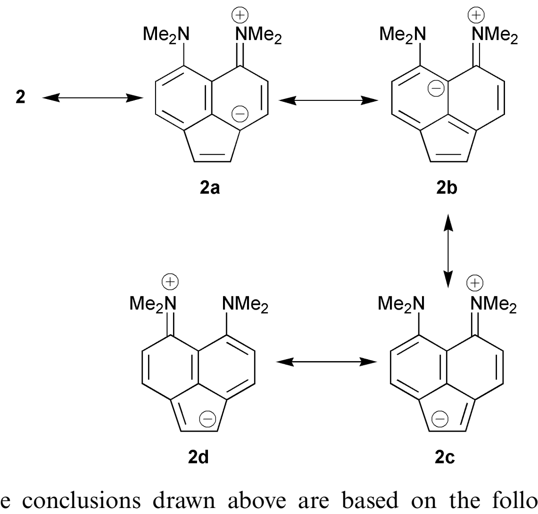
6

It is generally assumed[10] that for series of compounds with similar structure, the strength of the IHB is changed in one direction with the chemical shift value of the bridging proton, δ_{NH}.

Actually, for all proton sponge cations considered here, δ_{NH} and the *ratio* of the angle NHN to the distance N$^+$ ··· N are of some qualitative correlation (see Table 2).

At the same time, there is no dependence between the δ_{NH} and the basicity values of proton sponges **1**–**5**, which are given in Table 2 for solution in DMSO or MeCN. In particular, hydrogen bonding characteristics for cations **1**·HBr and **2**·HBr are very similar, though pK_a values of compounds **1** and **2** differ by 2–4 orders of ten (depending on the solvent). From these data it follows that the relative basicity of both proton sponges is mainly determined by the electronic influence of substituents and possibly, to some extent, by steric relief on protonation (*e.g.* shortening of the N ··· N distance, planarization of the naphthalene moiety; see below).[11]

We believe that in molecule **2** there exists a rather strong resonance interaction between both NMe$_2$ groups and the naphthalene system with a considerable contribution of bipolar structures like **2a** and **2b** in the resonance hybrid. The participation of the CH=CH bridge in through-conjugation with the NMe$_2$ groups, and the contribution of structures **2c** and **2d**, on the other hand, are relatively small.† Thus, the vinylene and the naphthalene π-systems in solid **2** are quite isolated from each other.



The conclusions drawn above are based on the following structural data. 1) The dihedral angle between the plane of each

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† Such through-conjugation is the most effective in *peri*-dialdehyde **6**. In this molecule[12] the N ··· N distance is equal to 3.033 Å and the dihedral angle between the plane of each NMe$_2$ group and the naphthalene plane is diminished to 27°.

Table 3 Selected bond lengths (Å) and angles (°) for **1**, **2**, **1**·HBr and **2**·HBr·MeCN

	1	**2**	**1**·HBr	**2**·HBr·MeCN
N(1)–C(6)	1.422(5)	1.399(2)	1.4742(16)	1.473(3)
N(1)–C(13)	1.495(7)	1.450(2)	—	—
N(1)–C(14)	1.428(6)	1.455(2)	—	—
N(2)–C(12)	1.394(5)	1.391(2)	1.4484(18)	1.447(3)
C(1)–C(2)	1.495(7)	1.339(3)	1.537(3)	1.333(4)
C(2)–C(3)	1.501(6)	1.461(2)	1.518(2)	1.462(4)
C(3)–C(8)	1.405(5)	1.413(2)	1.413(2)	1.406(3)
C(1)–C(9)	1.531(6)	1.464(2)	1.511(2)	1.476(3)
C(3)–C(4)	1.332(6)	1.363(2)	1.363(2)	1.365(3)
C(4)–C(5)	1.386(6)	1.395(2)	1.420(2)	1.408(3)
C(7)–C(8)	1.419(5)	1.404(2)	1.4056(18)	1.389(3)
C(1)–C(2)–C(3)	105.6(4)	109.0(2)	105.31(13)	109.4(3)
C(4)–C(3)–C(2)	132.7(4)	136.1(2)	133.26(14)	136.4(3)
C(8)–C(3)–C(2)	109.7(4)	106.0(2)	108.04(13)	105.5(2)
C(5)–C(6)–N(1)	120.7(4)	120.3(1)	120.98(12)	122.0(2)
N(1)–C(6)–C(7)	120.0(4)	121.1(1)	117.39(12)	117.1(2)
C(8)–C(7)–C(6)	114.0(3)	114.8(1)	115.13(12)	114.6(2)
C(3)–C(8)–C(7)	125.5(3)	125.2(1)	123.84(13)	125.1(2)
C(6)–N(1)–H	—	—	100.7(10)	102.4(12)

Table 4 Selected torsion angles (°) for **1**, **2**, **1**·HBr and **2**·HBr·MeCN and deviations of N atoms (ΔN) from the planes C(6)–C(13)–C(14), C(12)–C(15)–C(16)

	1	**2**	**1**·HBr	**2**·HBr·MeCN
C(3)–C(2)–C(1)–C(9)	−5.6(5)	−0.9(2)	5.0(2)	0.9(4)
C(1)–C(2)–C(3)–C(8)	5.3(5)	1.0(2)	−3.2(2)	−0.7(3)
C(2)–C(3)–C(4)–C(5)	178.9(5)	175.2(2)	176.3(2)	178.0(3)
C(4)–C(3)–C(8)–C(9)	179.4(4)	179.2(1)	−178.7(1)	179.0(2)
N(1)–C(6)–C(7)–C(12)	−6.4(6)	−9.9(2)	−1.1(2)	−2.0(4)
N(2)–C(12)–C(7)–C(6)	−4.0(6)	−10.9(2)	2.5(2)	−1.0(4)
N(1)–C(6)–C(7)–C(8)	174.7(3)	170.3(1)	178.6(1)	177.9(2)
N(2)–C(12)–C(7)–C(8)	175.0(3)	169.0(1)	−177.1(1)	179.2(2)
ΔN/Å	0.387[a]	0.286[a]	0.416[a]	0.418[a]

[a] Average value.

dimethylamino group and the mean plane of the naphthalene system in molecule **2** (equal to 36°) is less than the similar angle for any other compounds presented in Table 2. 2) The bond lengths C_{arom}–N (1.395 Å) in diamine **2** are somewhat shorter than in compounds **1**, **3**–**5**. 3) The sum of valence angles at the nitrogen atoms in **2** (348.3°) is greater than in molecules **1**, **3**, and **4** (an exception is compound **5** where the NMe_2 groups under the influence of two *ortho*-chlorine atoms adopt an even more planar (353.0°) conformation). 4) The bond lengths C(2)–C(3) and C(1)–C(9) (~1.46 Å, Table 3) are practically unchanged at transition **2** ⟶ $\mathbf{2}\cdot H^+$. 5) The multiplicity of the formal double bond C=C in base **2** (1.339 Å, see Table 3) only slightly differs from similar bonds in pyracylene (1.346 Å), for which, also, only minor conjugation between the vinylene groups and the aromatic part of the molecule was established.[13] Unfortunately, our search in the CCDC has shown that at present there is no reliable information on the geometry of acenaphthylene itself (*cf.* [14]).

The main contribution of the vinylene bridge in proton sponge **2** to falling basicity seems to be the increase of the N ··· N distance that assists the NMe_2 groups in being flatter and thus more effectively conjugate with the naphthalene system and the vinylene group itself (see ref. [1]). In contrast to the solid state (see above) the contribution of canonical structures **2c** and **2d** in such polar solvents as DMSO and MeCN, used for basicity measurements, seems to be significant. Another minor influence of the CH=CH bridge may be its moderate −*I*-effect (*cf.* small decrease of the basicity of 1,8-bis(dimethylamino)-4-vinylnaphthalene (pK_a 17.5, MeCN) in comparison with unsubstituted **3**).[1,15] Since the NMe_2 groups in compound **2** occupy a comparatively large space volume, the molecular distortions in this case are more significant than, for instance, in **1**. Formally, these distortions are displayed in the turning back of the benzene ring halves carrying nitrogens on opposite sides of the plane C(1)–C(2)–C(3)–C(4)–C(7)–C(8)–C(9)–C(10) (Fig. 3).

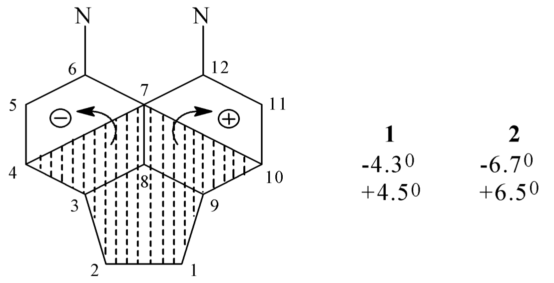

Fig. 3 Schematic representation of plane distortions and their values in molecules **1** and **2**.

As in the case of compound **2**, the fixing effect of the CH_2CH_2 bridge in acenaphthene proton sponge **1** does not permit the whole molecule to adopt a propeller-like shape with the twisting along the bond common for two benzene rings, which is observed[4] for parent sponge **3**. As a result, the extent of p,π-interaction between the NMe_2-groups and the aromatic ring in **3** is the average among compounds **1** and **2**. The relative basicity of diamines **1**–**3** (Table 2) agrees qualitatively with these geometry changes, although the purely electronic influence of the substituents, especially pronounced for compounds **4** and **5**, should also be taken into consideration.

In all proton sponge cations, the NMe_2 group planes have become practically perpendicular to the naphthalene system. Nevertheless, it is interesting that for hydrobromide complexes of **1** and **2**, this angle *does not reach* 90° (Table 2). In the case of compound **5**, where the position of the NMe_2 substituents is fixed rather hard by the *ortho*-chlorine atoms, alteration of the dihedral angle on protonation is negligible. The C_{arom}–N bond lengths in all the cations increase strongly, and the nitrogen atoms' hybridisation becomes closer to the sp^3 type after coordination with a proton (check the degree of pyramidalization of the nitrogen atoms in Tables 2 and 4).

The angle C(1)–C(9)–C(8), during the complexation of the proton sponges with a proton, changes in a different manner depending on the compound's type (Table 2), but most often it is decreased. In contrast to that, the distance between the *peri*-carbon atoms C(1) ··· C(8) becomes smaller in all cases (especially on protonation of compounds **2** and **4**, ~0.04 Å). Like other proton sponges, the formation of cations $\mathbf{1}\cdot H^+$ and $\mathbf{2}\cdot H^+$ is accompanied by increases in both the angle C(4)–C(10)–C(5) and the C(4) ··· C(5) distance (apart from **4**·2HBr, where two cationic centres appear).

The coplanarity of the hydrocarbon moiety in **1** and **2**, when they are protonated, gets a more pronounced character, and that is the situation for all the other molecules collected in Table 2. For example, average deviations of the main torsion angles (Table 4) forming the N,C-skeleton of the **2**·HBr·MeCN complex do not exceed 1.3° from 0 or 180°, whereas they equal approximately 6.1° for base **2** (for salt **1**·HBr and proton sponge **1** these values are 2.6 and 4.2°, respectively).

In both the salts studied there are Br ··· H(Ar) and Br ··· H(Me) contacts ranging within 2.80–3.17 Å for **1**·HBr and 2.91–3.05 Å for **2**·HBr·MeCN. Most of the contact distances are shorter than the sum of the H and Br van der Waals radii (3.02 Å)[16] and, therefore, can be considered as weak hydrogen bonds. The Br ··· H(Ar) distances (2.80–2.82 Å) are especially short in complex **1**·HBr, for which these, as well as Br ··· H(Me) contacts, are depicted in Fig. 4. Molecular packing of cations $\mathbf{1}\cdot H^+$ and $\mathbf{2}\cdot H^+$ in crystals occurs to form layers with antiparallel stacking of the cations, so that the positively charged NHN-bridge of one molecule is located above the naphthalene π-system of another (see, for example, Fig. 4). This situation is a particular feature of many other proton sponge acid complexes.[5,7,9]

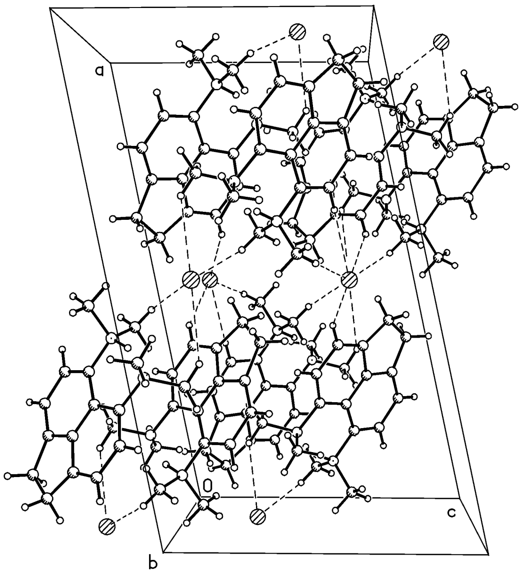

Fig. 4 Projection of the structure of the **1**·HBr complex along the *b* axis showing the hydrogen bonds Br ··· H.

It is worth noticing that for acenaphthene **1** and its hydrobromide the C(3)–C(4) (C(9)–C(10)) bond in the carbon skeleton of their molecules is the shortest one (1.33–1.36 Å, Table 3). A similar situation was earlier revealed for unsubstituted acenaphthene[17] (1.38 Å) in which this bond also has almost a pure double but not aromatic character.

In conclusion, the X-ray data have confirmed preceding assumptions[1] made on the basis of NMR spectra and quantum-chemical calculations about the tightening effect of the CH_2–CH_2 and CH=CH bridges on the structure of proton sponges **1** and **2**. At the same time, they have revealed considerable p,π-electron interaction existing between the NMe_2 groups and the naphthalene moiety in molecule **2**, responsible for a sharp decrease of its basicity. This tendency is displayed well in the reactivity of proton sponge **2** which is currently under investigation.

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