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Novel Polyfunctional Tautomeric Systems Containing Salicylideneamino and Proton Sponge Moieties

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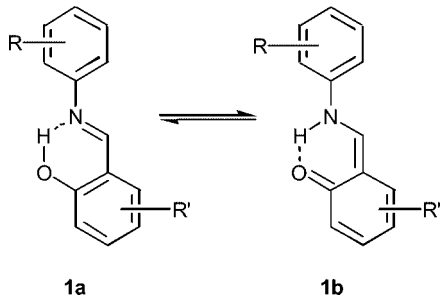
The first salicylidenearylamines containing a proton sponge residue with 5′-bromo (**6**), 5′-nitro (**7**), and 3′,5′-dinitro (**8**) substituents have been synthesized. X-ray diffraction and ^{1}H, ^{13}C, and ^{15}N NMR and infrared spectra revealed that **6** and **7** contain very strong OHN bridges typical of *o*-hydroxy Schiff bases. Additional π-electron coupling with the dimethylaminonaphthyl ring is manifested both in geometrical and infrared parameters. In the case of **7**, proton transfer to the imine nitrogen atom occurs in the solid state, accompanied by a remarkable shortening of the OHN bridge (2.553 Å). In dinitro derivative **8**, the OH proton jumps to the dimethylamino groups, giving a new tautomeric form with the formation of a homoconjugated $[NHN]^{+}$ cation. Protonation of **6** and **7**, affecting the (dimethylamino)naphthyl moiety, disrupts the π-coupling and makes these molecules, unlike common aromatic Schiff bases, highly sensitive to hydrolysis, while **8**, being already self-protonated, equilibrates in wet DMSO with the corresponding salicylaldehyde and arylamine in a ca. 1:1 ratio at room temperature.

Introduction

For the last few decades salicylidenearylamines (SAs) have attracted increasing attention because of their interesting ligand,[1] photochromic,[2] thermochromic,[3] and liquid crystalline[4] behavior. Ultimately, almost all the physicochemical peculiarities of SAs originate from the existence of intramolecular hydrogen bonding (IHB) in their molecules. Within this bonding the chelated proton can be localized at oxygen (OH form, **1a**) or nitrogen (NH form, **1b**) or it may occupy transient positions, reflecting the influence of both these tautomers (Scheme 1). In each case the exact location of the proton depends on variety of factors, including the natures of substituents, solvent, temperature, or other energetic stimuli.[2c,2d,3c,5] It should be noted, however, that the NH form is encountered only quite rarely and that no more than 6% of the available solid-state structures can be assigned to this form.[6] It is assumed that the proton transfer within the IHB in the ground state of a SA can be described in terms of an asymmetric double minimum potential well, whereas in the excited state the migration barrier disappears.[7] In fact, the azomethines **1** represent an excellent example of the coupling of electron and proton movements (resonance-assisted hydrogen bonds).[7b,8] Such molecules are known to have very short IHB,[5a,9] which is important for modeling of proton transfer in biological systems.[10]



1a **1b**

Scheme 1. Tautomerism in salicylidenearylamines.

In some respects there is a similarity between the properties of IHB in the compounds **1** and those in the cation of 1,8-bis(dimethylamino)naphthalene (proton sponge, DMAN) **2**. Though the $[NHN]^{+}$ hydrogen bonds in protonated proton sponges and the OH···N bonds in SAs differ markedly with respect to symmetry and charge distribution, there is a strong analogy between them. The main factor here is the barrier height to the proton transfer: in both cases we are dealing with so-called low-barrier hydrogen bonds (LBHBs). As can be deduced from the literature (see ref.[10] for review articles), such H-bridges are characterized

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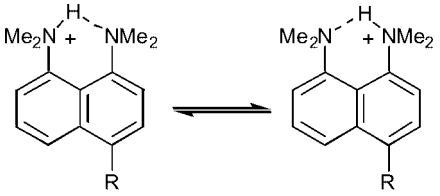
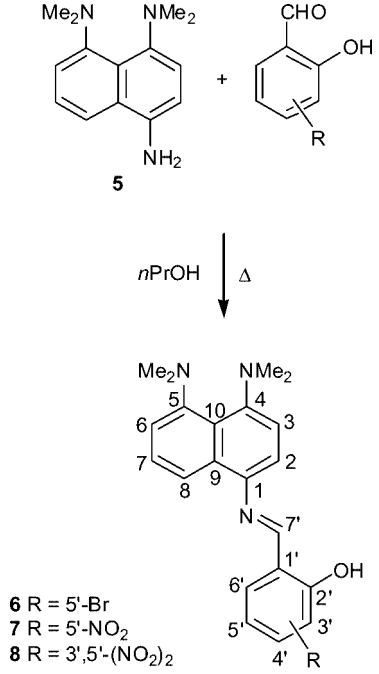
by high polarizability (i.e., strong susceptibility to the environment). It seems that such unusual polarizability of LBHBs is of great importance in biological processes.[10c,10d]

Although some data (e.g., NMR in solution) suggest symmetry of the IHB in **2**,[11] one current point of view based on quantum chemical calculations[12] and time-resolved spectroscopy including deuterium-induced effects[13] is that the NH proton equilibrates very rapidly near the plane of symmetry, so the best description of cationic structure **2** is perhaps interconversion of two equivalent tautomers **2a** and **2b** (Scheme 2). In the cations of monosubstituted proton sponges, the IHB becomes unsymmetrical and the NH proton, depending on the natures of the substituents, is preferably moved towards either the more distant (as in **3a**[11a,14]) or the nearer NMe_2 group (as in **4b**[11a]).



Scheme 2. Tautomerism in protonated naphthalene proton sponges.

In view of this, investigation of compounds containing both SA and DMAN moieties looks rather intriguing. If the abnormally high basicity of proton sponges[15] is taken into account, one might expect that in such compounds, besides the NH and OH forms **1a** and **1b**, a third tautomer



Scheme 3. Preparation of DMAN–SA molecules.

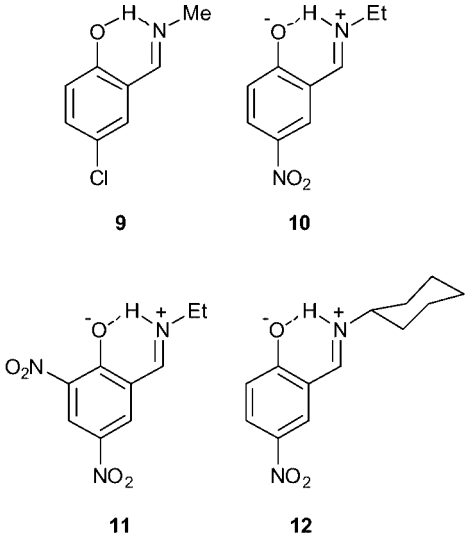
with the acidic proton chelated between the *peri*-NMe_2 groups could be produced. Polyfunctionality of this type would potentially be useful for designing molecular devices capable of serving as triple switchers. Here we report on the first representatives (**6**–**8**) of this kind. The compounds were prepared through reactions between 4-amino-1,8-bis(dimethylamino)naphthalene (**5**) and substituted salicylic aldehydes of widely ranging OH acidity (see Scheme 3, with atom numbering used uniformly in X-ray diffraction and spectral assignments). Below we describe the properties, low-temperature X-ray structures (for two azomethines), detailed analyses of ^1H, ^{13}C, and ^{15}N NMR spectra both in solution and in the solid state, and finally the solid state IR characteristics of these new molecules.

Results and Discussion

X-ray Diffraction Studies

The X-ray structures of molecules **6** and **7**, with atom labeling and thermal ellipsoids, are shown in Figure 1, while the main structural parameters are collected in Table 1.

In the case of **6**, very strong O–H···N hydrogen bonding with the proton localized at the oxygen atom is well reflected (Figure 1). With respect to the simple Schiff base 4-chloro-2-[(methylimino)methyl]phenol (**9**),[16] an essential structural difference is to be seen in the length of the C(1)–N(3) bond to the naphthyl ring. This bond is markedly shorter, reflecting considerable π-coupling of naphthalene and azomethine fragments. This coupling also causes some lengthening of the central C(7′)=N(3) double bond [1.284(4) vs. 1.269(2) Å in **9**]. The sum of these effects causes a noticeable difference in the O···N hydrogen bond lengths [2.610(4) vs. 2.553(2) Å in **9**].



The influence of the phenylimino group on the geometry of the DMAN part is rather weak. Nevertheless, one should note a slight shortening, in relation to unsubstituted DMAN,[17] of the C(2)–C(3) bond and an increasing in the

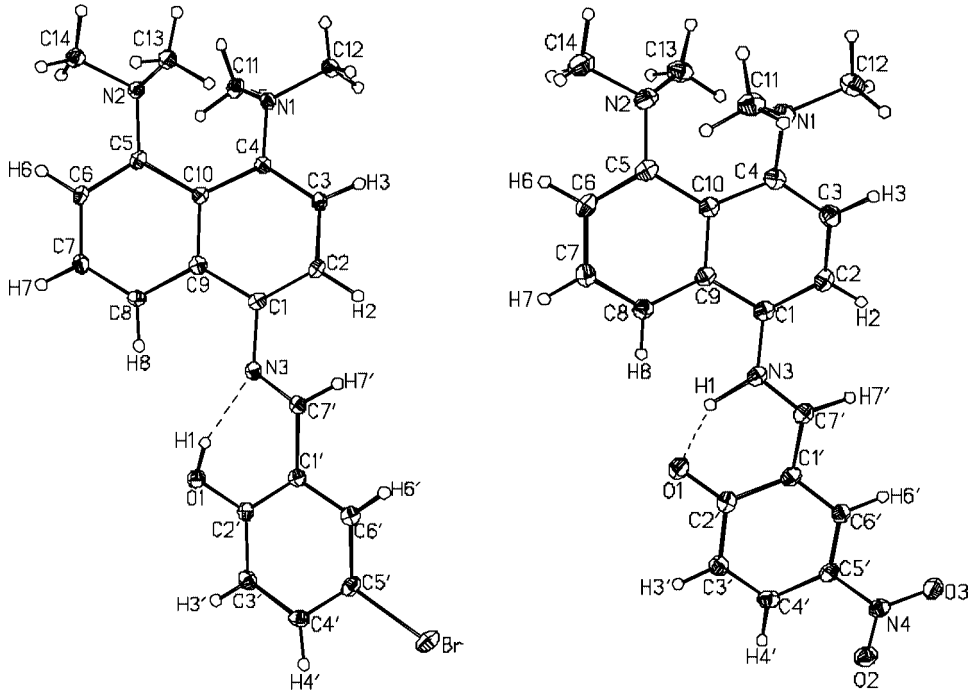


Figure 1. X-ray structures of **6** (left) and **7** (right) showing 50% probability displacement ellipsoids with atom numbering.

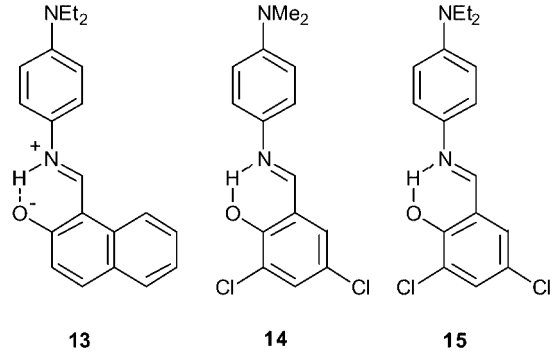
Table 1. Selected bond lengths (Å) for 5′-bromo (**6**) and 5′-nitro (**7**) derivatives (as in Scheme 3).

Compound	**6**	**7**
O(1)–C(2′)	1.350(4)	1.275(3)
N(1)–C(4)	1.402(4)	1.407(3)
N(3)–C(7′)	1.284(4)	1.303(3)
C(1′)–C(2′)	1.415(4)	1.453(3)
C(1′)–C(7′)	1.455(4)	1.421(3)
C(1)–N(3)	1.422(4)	1.416(2)
Hydrogen bond geometries		
O(1)–H(1)	0.77(4)	1.52(4)
N(3)–H(1)	1.92(4)	1.14(4)
O(1)···N(3)	2.610(4)	2.553(2)
< (OHN) [°]	149(4)	147(3)

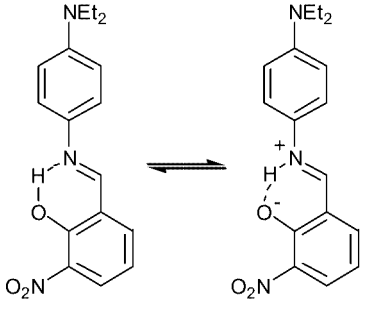
N(1)···N(2) distance due to the π-electron coupling discussed above extended over both parts of the molecule.

More spectacular geometrical effects are visible in the case of molecule **7**, existing in the NH form. The effect of proton transfer is clearly manifested in the C(2′)–O(1) bond length, which reaches a double character [see Table 1 and further ^{13}C NMR spectroscopic data for carbon C(2′)]. One should also note a considerable lengthening of the N(3)–C(7′) bond [from 1.284(4) Å in **6** to 1.303(3) Å in 7]. On the other hand, a marked elongation of the C(1′)–C(2′) bond takes place [from 1.415(4) Å to 1.453(3) Å]. This confirms a keto and less zwitterionic form of the proton transferred state.

From the available X-ray data on related systems (see Table 2) one can conclude that **7** is actually the first SA existing markedly as the NH form in the solid. The closest analogue of **7**, *N*-(3-nitrosalicylidene)-4-(diethylamino)aniline (**16**), has been reported to exist with disordered H-bonding in crystals at room temperature, which was interpreted in favor of equilibrium between the OH (**16a**) and the NH (**16b**) forms. All other instances of the NH forms have been registered for the salicylidenealkylamines **10**–**12**, containing strongly acidifying substituents – preferably nitro group(s) or two chlorine atoms – in their phenylimino parts.[20]



13 **14** **15**



16a **16b**

Table 2. Selected bond lengths (Å) for related azomethines **10**–**16**.

	Preferred form	*T* [K]	O···N	N···H	O···H	C–O	C=N	Ref.
7	NH	100	2.553	1.14	1.52	1.275	1.303	[a]
10	NH	r.t.	2.646	0.90	1.95	–	–	[18]
11	NH	100	2.638	1.03	1.85	1.257	1.295	[5a]
12	NH	100	2.667	1.03	1.87	1.263	1.297	[5a]
13	NH	r.t.	2.545	1.29	1.38	1.308	1.297	[19]
14	OH	r.t.	2.558	1.63	0.99	1.333	1.277	[19]
15	OH	r.t.	2.596	1.78	0.87	1.340	1.282	[19]
16a	OH[b]	r.t.	2.550	1.69	0.91	1.330	1.282	[19]
16b	NH[b]	r.t.	2.550	0.71	2.01	1.330	1.282	[19]

[a] This work. [b] Disordered H-bonding.

An interesting exception is the naphthalene counterpart of SA, **13**, in which the NH form has also been claimed to be preferred. This example, however, is less instructive than that of azomethine **7**, as the O–H and N–H bond lengths in **13** are quite similar and the C–O bond is rather long (Table 2). We believe that production of the NH form in **7** is a consequence of joint action of two factors: the presence of a nitro group in the salicylidene fragment and the strongly electron-donating effect of two NMe_2 groups in the DMAN moiety.[14,15e] Clear-cut evidence for this is the increases in the N···N distances (2.840 Å against 2.812 Å in **6** and 2.804 Å in DMAN itself[17]) and the decreases in the dihedral angles between the planes of the NMe_2 groups and the naphthalene ring systems (ranges are 34–35°, 36–38°, and 39–40° for **7**, **6**, and DMAN, respectively).

Lastly, some comments regarding the mutual arrangements of the naphthyl and phenyl rings through the azomethine linkages with assistance of the O–H···N bridges are needed. Firstly, the naphthyl rings are not entirely planar. Thus, in 7, an envelope conformation is expressed in a small angle of 9.9(1)° between two moieties, flipped onto the opposite sides of the mean ring plane. This deviation from planarity, caused by the 4- and 5-NMe_2 groups due to their trend to conjugate with phenylimino group, is additional evidence of the π-electron coupling between the two parts of the molecule. Some deviation from coplanarity should also be noted with respect to the central part, represented by the C(1), N(3), C(7′) and C(1′) atoms and the phenyl ring. The angle between these planes in **7** is 3.4(8)°. Furthermore, the H(1)···H(8) and H(2)···H(7′) interactions would not allow the 2′-hydroxybenzylidene and 4,5-bis(dimethylamino)-1-naphthyl groups to be entirely coplanar in any of the azomethines, though more pronounced π-coupling in **7** makes this molecule, unlike **6**, almost flat overall. Indeed, the angles between the naphthalene and benzene rings are 32.3(1)° and 7.5(1)° in **6** and **7**, respectively.

NMR Spectra

The NMR spectroscopic data collected for the studied compounds are presented in Table 3. The protonated carbon atom signals were identified by 2D GHSQC experiments, and the remaining quaternary signals were assigned by long-range correlation experiments (GHMBC). The nitrogen signals in solution were recorded by 2D GHMBC measurements, two-bond correlation with the proton in position 6. The data collected in Table 3 enabled us to draw the following conclusions with respect to the structures of the compounds studied here.

The first compound, the 5′-Br derivative **6**, exists in both phases in the OH form with hydrogen bonds to the imine nitrogen atom. The hydrogen-bonded imine proton chemical shift (in the range about 13–15 ppm) and the corresponding nitrogen chemical shifts in chloroform solution and in the solid state (about –80 ppm) are both typical for this structure.[21] The chemical shifts of C(2′) in both phases are located very close to ca. 155–160 ppm, in the range characteristic of OH structures.

The second derivative – 5′-NO_2 (**7**) – exists in solution as the OH structure but with stronger hydrogen bonding than in the 5′-Br compound: the OH signal is shifted downfield, nitrogen upfield, and C(2′) downfield. In the solid state, the proton in the bridge is shifted strongly towards the nitrogen atom: a large upfield shift in the nitrogen signal (to –152.7 ppm) and a downfield shift in the C(2′) signal (δ =173.3 ppm) are manifested. At 223 K in chloroform solution the nitrogen signal is shifted slightly upfield in relation to room temperature experiments, indicating some tautomeric equilibrium shift towards the NH form on cooling.

The third compound, the 3′,5′-di-NO_2 derivative **8**, shows a quite different structure and behavior. First of all it is unstable in solution. In chloroform, nitromethane, DMF, and acetonitrile containing traces of water, more than one structure is observed. In all the above solvents an additional downfield NH signal at ca. 18 ppm – typical for cations of proton sponges – was observed. Simultaneously, a characteristic peak at ca. 10 ppm and obviously belonging to the aldehyde proton appeared (in the ^{13}C NMR spectrum the CHO signal is detected near 190 ppm). This means that partial decomposition due to hydrolysis of the imine moiety occurs in solution, resulting in the salt of 4-amino-DMAN and the anion of 3,5-dinitrosalicylic aldehyde (see Scheme 4 below). The imine nitrogen atom signal of the DMAN Schiff base **8** is typical of the non-hydrogen-bonded

Table 3. ^{1}H, ^{13}C and ^{15}N NMR spectroscopic data for **6**–**8** (atom numbering as in Scheme 1 and Figure 1).

	6			**7**			**8**				
Position	Solution $CDCl_3$		CP MAS[a]	Solution $CDCl_3$		CP MAS[a]	Solution CD_3CN		Solution DMSO		CP MAS[a]
	^{1}H	$^{13}C/^{15}N$	$^{13}C/^{15}N$	^{1}H	$^{13}C/^{15}N$	$^{13}C/^{15}N$	^{1}H	$^{13}C/^{15}N$	^{1}H	$^{13}C/^{15}N$	$^{13}C/^{15}N$
1	–	138.7		–	136.7		–	149.2	–	149.7	148.7
2	7.09	114.1		7.19	114.4		7.88	122.2	7.36	114.5	
3	6.91	111.9		6.93	111.7		7.35	114.0	8.09	122.7	
4	–	150.8	148.1[b]	–	150.9	150.5[b]	–	141.5	–	141.9	
5	–	150.6	149.1[b]	–	151.2	148.2[b]	–	144.3	–	145.3	
6	7.00	113.6		7.01	114.4		7.92	122.0	8.12	122.7	
7	7.39	126.5		7.42	126.9		7.72	121.7	7.77	127.2	
8	7.80	115.9		7.77	115.3		8.47	125.0	8.25	124.5	
9	–	132.6		–	132.3		–	131.3	–	130.9	
10	–	119.6		–	119.7		–	119.7	–	119.4	
N(1)[b]			–336.0			–331.4				–346.6[c]	–343.7
N(2)[b]			–337.8			–335.1				–347.4[d]	–346.7
											–348.7
CH_3 (4)	2.81	44.1	47.0[b] 46.1[b]	2.82	44.0	47.4[b]	3.11 [e]	45.8	3.15 [f]	45.8	45.7 broad
CH_3 (5)	2.84	44.1	42.8[b]	2.86	44.0	41.1[b]	3.09 [g]	45.7	3.12 [h]	46.1	45.7 broad
1′	–	121.3		–	118.8		–	127.6	–	128.1	
2′	–	160.2	155.5	–	167.2	173.3	–	168.7	–	169.8	170.4
3′	6.95	119.1		7.11	118.4		–		–		
4′	7.43	135.0		8.25	127.7		8.86	127.7[b]	8.65[b]	126.3[b]	
5′	–	110.4		–	139.8		–		–		
6′	7.52	133.6		8.39	127.8		8.71	126.2[b]	8.79[b]	127.0[b]	
7′	8.57	158.3	159.8	8.72	157.3	156.1	9.03	160.5	–	159.7	156.7 154.7
OH/NH	13.7			15.1							
N–**H**–N							18.7		18.4		
N(3)		–83.1	–87.9		–89.8	–152.7		–75.7[i]		[j]	–64.6 –75.6

[a] The remaining ^{13}C signals in CPMAS spectra are not assigned, due to overlapping. The ^{13}C signals of carbon atoms bonded to the Br or NO_2 group(s) are not recorded in 2D experiments, probably due to significant signal broadening. [b] Signal assignment may be reversed. [c] $1J_{N,H}$ = 34 Hz. [d] $1J_{N,H}$ = 29 Hz. [e] $3J_{H,H}$ = 2.5 Hz. [f] $3J_{H,H}$ = 2.5 Hz. [g] $3J_{H,H}$ = 2 Hz. [h] $3J_{H,H}$ = ca. 1 Hz. [i] In DMF solution. [j] Not recorded, due to strong signal broadening.

structure region[22] and the C(2′) signal is shifted downfield as is normal in phenolate anions (near 170 ppm).[23] The decomposition process in chloroform, DMF, and acetonitrile solutions is much stronger than in DMSO, so the measurement of nitrogen signals of the NMe_2 groups can only be performed in DMSO solution. The results presented in Table 3 unambiguously confirm the proton transfer from the Schiff base site to the DMAN part, resulting in a nonsymmetrical $[NHN]^+$ structure: the nitrogen signals are shifted about 10 ppm upfield in relation to compounds **6** and **7** and two different $^{1}J_{N,H}$ coupling values are observed.[13d] In the solid state, the corresponding CPMAS spectra provide evidence for the undecomposed compound. The only difference is that **8** exists in the crystalline state as a mixture of two forms, presumably rotamers with different conformations around the C(1′)–C(7′) bond: two nitrogen signals in the imine region, two signals assigned to the C(7′) position, and three amine signals were found in this case. The amine signals in solid **8** are shifted upfield in relation to with those in **6** and **7**, also indicating protonation of the proton sponge moiety.

Mass Spectrometric Data

Some MS information for the 3′,5′-dinitro derivative **8** was obtained. In the electron impact spectrum, the molecular peak of m/z = 423 (23% of intensity) was recorded, confirming that this compound is stable in the gas phase. In the electrospray spectrum taken from the methanol solution, the 424 peak of the monoprotonated form (i.e., **8**·H^+) was observed. No decomposition of the parent compound was found under these conditions.

Infrared Spectra

Detailed analyses of the infrared spectra of Schiff bases have recently been reported in papers by Filarowski and Koll,[24] while similar treatment of DMAN and its protonated form is reported in in the literature[12d,25].

For the compounds studied in this paper, we analyzed a characteristic band located a little above 1600 cm^{-1} and marked as ν(CN). Depending on the substituents and on the protonation of the DMAN group it changes only in the

range between 1608–1619 cm^{-1}; nevertheless, one can draw certain conclusions from the observed trends. Thus, in the cases of **6** and **7** we observe very low ν(CN) frequencies (i.e., 1608–1609 cm^{-1}), which, as in results from ref.[24a], correspond to very strong hydrogen bonds with the proton markedly shifted towards the nitrogen atom. Simultaneously, such low values of the ν(CN) frequencies are obviously due to coupling with the 4,5-bis(dimethylamino)-1-naphthyl group. As has been shown recently,[24a] these values are close to those calculated for the proton transfer state. For strong hydrogen bonds (e.g., as in the dichloro derivative mentioned in the literature[20]), ν(CN) equals ca. 1620 cm^{-1}. The most convincing evidence of the π-electron coupling with the naphthyl group comes from the results obtained for the protonated DMAN group; for the transition **7** → **7**·HBr, for example, the shift reaches 9 cm^{-1} (from 1610 to 1619 cm^{-1}), which implies interaction between the lone electron pair at the NMe_2 nitrogen atom and the C=N group through the π-electron system of the naphthalene ring.

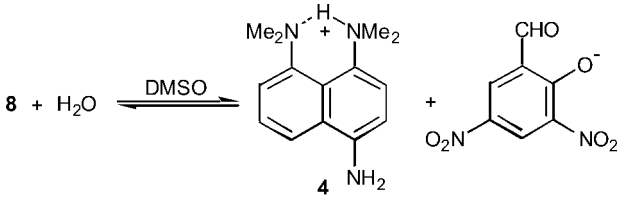
Very important infrared spectral findings are connected with the ν(OH) band. It is well known that the intensities of these band in SAs are markedly lower than those in analogous Mannich bases in which the OH groups are isolated from the π-electron systems.[8a] This phenomenon is ascribed to the coupling of electrons and proton motions and is regarded as one of the main characteristics of resonance-assisted hydrogen bonds. In the case of *N*-naphthyl derivatives of Schiff bases we observe further substantial drops in the intensities of ν(OH) bands. The bands are so weak and broad that it is hardly possible to localize them with sufficient precision. Generally, their shape is similar to those presented in ref.[8a], but with much lower intensity and a lack of any broad absorption in the fingerprint region. Importantly, however, the absorption intensity in the ν(OH) region increases slightly after protonation of the DMAN moiety, and for compound **7** one can distinguish two submaxima at ca. 2700 (stronger) and ca. 2000 cm^{-1} (much weaker). This finding confirms coupling between the imine group and the amino group of DMAN through the naphthalene system as concluded from the behavior of the ν(CN) band.

In all three cases (**6**–**8**) there are excellent reflected Bohlmann bands[26] attributable to ν(CH) vibrations of the *N*-methyl groups with frequencies around 2767–2780 cm^{-1}, while these disappear after DMAN protonation (see ref.[27]). The nitro groups in positions 3′ and 5′ of **8** are well reflected in $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ modes located at 1478 and 1334 cm^{-1}, respectively, indicating considerable coupling between these groups and the overall π-electron system.

The behavior of the $\nu(NHN)^+$ band in the protonated DMAN group should also be mentioned. In all three monoprotonated compounds this band is located at very low frequencies in the 500–600 cm^{-1} region. When the NHN^+ bridge is symmetrical, the band displays a maximum at ca 500 cm^{-1} with a halfwidth of ca. 350 cm^{-1}.[12e] Consistently with previous studies on protonated 4-amino derivatives of DMAN,[28] this band becomes much broader and shifted to higher frequencies. This can be interpreted as the result of desymmetrization of the double minimum potential for the proton motion.

Hydrolytic Stability

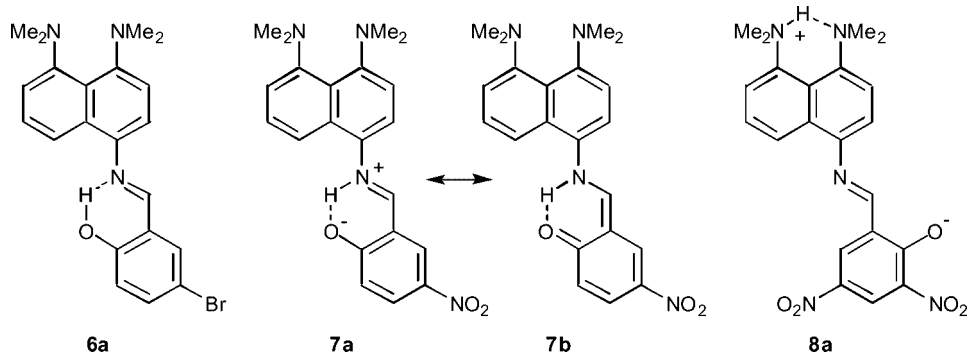
A particular feature of monoprotonated **6** and **7** (e.g. **6**·HBr and **7**·HBr) is that, when dissolved in wet DMSO, they are partially hydrolyzed to form the corresponding salicylaldehyde and 4-amino-DMAN hydrobromide. In its turn, the self-protonated azomethine **8**, as mentioned above, reacts with water even more easily and without any addition of acid (Scheme 4). This may be connected with known stabilizing ability of the IHB on reactivity of the CH=N bond, which is absent in **8**.[29] At the same time, the NMe_2 groups in **8** are decoupled from the conjugation, since they are protonated, which also accelerates the hydrolysis.[29] In fact, at 20 °C and a concentration of 3.3×10^{-2} M, 26% of **6**·HBr, 37% of **7**·HBr, and ca. 50% of **8** are hydrolyzed in DMSO after ca. 0.5 h of standing. On heating to 140 °C the hydrolysis of **8** is practically complete, but on returning to ambient temperature the initial equilibrium is restored. Obviously, the vulnerability of azomethines **6**–**8** to hydrolysis under the indicated conditions is a consequence of the violation of the π-conjugation between the two parts in these polyfunctional molecules. This is in contrast with common arylidenearylamines (aromatic Schiff bases), which are quite stable in wet media.[29]



Scheme 4. Reversible interaction of **8** with water.

Conclusions

In summary, the first three representatives of salicylidenearylamines containing proton sponge moieties have been obtained. Their structures have been shown by X-ray, NMR, and IR measurements to be strongly dependent both on the natures of the substituents on the benzene rings and the presence of the proton sponge fragment. Thus, in two out of three investigated samples the influence of DMAN part is clear. In one case (the NH form of **7**) it is connected with the known strongly electron-donating ability of the NMe_2 groups, and in the other case (zwitterionic structure of **8**) with the high basicity of DMAN. Finally, compounds **6**–**8** should be best represented in the manner depicted in Scheme 5, reflecting all proton transfer states possible in this series. Thus, in the case of weakly acidifying groups (5′-Br), the corresponding Schiff base exists as a common chelated OH form. However, on changing to more strongly



Scheme 5. Dominant forms of molecules **6**–**8**.

electron-withdrawing substituents, the acidic proton can jump to the azomethine nitrogen (with 5′-NO_2) or even to the NMe_2 groups [3′,5′-$(NO_2)_2$] with the generation of chelated (**7a**, **7b**) or betaine (**8a**) structures. Obviously, further studies on the ligand and photochromic behavior of the prepared azomethines could be of interest.

Experimental Section

X-ray diffraction studies were performed with a Kuma KM4CCD κ-axis four-circle diffractometer fitted with an Oxford Cryosystem Cooler, with use of graphite monochromated MoK_α radiation. The data were corrected for Lorentz and polarization effects. For **6**, analytical correction for absorption was applied.[30] Both structures were solved by direct methods by use of SHELXA-97[31a] and refined on F_2 by full-matrix least-square methods with the aid of the SHELXL-97[31b] program. Non-hydrogen atoms were refined with anisotropic thermal parameters. The H atoms in **6** were found by difference synthesis and refined with isotropic displacement parameters; only H atoms of the methyl groups were refined as riding atoms with isotropic displacement parameters. All H atoms in **7** were also found by difference synthesis and refined as riding models with isotropic displacement parameters, except for H(1), which was refined. The crystal data and structure refinement are summarized in Table 4. The XP package[32] was used to generate the molecular drawings. Unfortunately, we have not yet been able to grow crystals of compound **8** of sufficient quality and size.

CCDC-268508 to -268509 contain the supplementary crystallographic data for this paper. These data can be obtained free of

Table 4. Crystal data and structure refinement for 5′-bromo (**6**) and 5′-nitro (**7**) derivatives.

Parameter	**6**	**7**
Empirical formula	$C_{21}H_{22}BrN_3O$	$C_{21}H_{22}N_4O_3$
Fw	412.33	378.28
Temperature [K]	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	orthorhombic	triclinic
Space group	*Pbca*	$P\bar{1}$
a [Å]	7.5427(3)	6.620(2)
b [Å]	12.3083(2)	8.820(2)
c [Å]	40.045(1)	16.100(3)
α [°]		90.91(3)
β [°]		95.12(3)
γ [°]		103.33(3)
V [Å^3]	3717.7(2)	910.4(4)
Z	8	2
d_c [Mg·m^{-3}]	1.473	1.380
μ [mm^{-1}]	2.226	0.095
Crystal size [mm]	0.34×0.30×0.10	0.35×0.30×0.05
θ range [°]	27.5	30
Index ranges		
h	–9 to 9	–9 to 9
k	–15 to 14	–12 to 12
l	–51 to 50	–22 to 22
No. of refl. collected/unique	34240/4191	16331/5286
R(int.)	0.053	0.046
Absorption correction	analytical	none
$T_{max.}$,$T_{min.}$	0.818 and 0.518	
Data [$F>4\sigma(F)$]/parameters	3467/291	3486/285
Goodness-of-fit on F^2	1.125	1.10
R_1, wR_2 [$F>4\sigma(F)$]	0.0436, 0.0758	0.0445, 0.0720
R_1, wR_2 indices (all data)	0.0577, 0.0885	0.0585, 0.0997
Δρ [e·Å^{-3}]	0.680/–0.275	0.310/–0.254

charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Infrared Spectra: Infrared Spectra in the 400–4000 cm^{-1} range were recorded at room temperature in Nujol or Fluoroluble suspensions, as well as in KBr discs, with a Bruker IF S66 spectrophotometer.

Solution NMR: Solution NMR experiments were performed with a Bruker DRX 500 Avance spectrometer fitted with a 5 mm inverse, Z-gradient, variable-temperature probehead. For acquisition and processing of the spectra, standard Bruker software was applied. About 10 mg samples were used for solution experiments. Internal TMS and external nitromethane were employed as standards for proton, carbon, and nitrogen measurements.

Solid-State NMR: Solid-state NMR studies were performed by the CPMAS technique with a Bruker 4 mm probehead. The typical acquisition parameters for nitrogen spectra were: spectral width 28 kHz, acquisition time 40 ms, relaxation delay 10–120 s, spin rate 6–12 kHz, contact time for spin locking 5 ms. The appropriate parameters for carbon measurements were: spectral width 31 kHz, acquisition time 20 ms, contact time 2 ms, spin rate 12 kHz. Additionally, to distinguish protonated and quaternary carbon atoms, SCT (short contact time) experiments were performed (contact time 40 μs). In this experiment only protonated carbon atoms were detected. The solid-state spectra were originally with reference to a glycine sample, and the chemical shifts were then recalculated to TMS and nitromethane scales, respectively.

Mass Spectrometry: Mass spectrometric investigation of **8** (EI and ES) was carried out with an AMD 604 spectrometer.

Materials: 5-Bromo-, 5-nitro, and 3,5-dinitrosalicylaldehydes were purchased from Aldrich. 4-Amino-DMAN **5** was prepared by Pd/C hydrogenation of 4-nitro-DMAN in propanol as described previously.[33]

General Procedure for the Condensation of 4-Amino-DMAN 5 with Salicylaldehydes: A solution consisting of **5** (0.23 g, 1 mmol), the corresponding salicylaldehyde (1 mmol), and *n*-PrOH (20 mL) was heated at reflux for the time indicated below. The solvent was then removed under reduced pressure and the residue was recrystallized to give pure compounds with the yields specified below.

1-[(5′-Bromo-2′-hydroxybenzylidene)amino]-4,5-bis(dimethylamino)-naphthalene (6): Time of heating 30 min. Yield 0.33 g, 80%. Golden-brown, lustrous plates with m.p. 114–115 °C (from EtOH). Elemental analysis calcd. (%) for $C_{21}H_{22}BrN_3O$: C 61.2, H 5.4; found C 61.3, H 5.2. Hydrobromide **6**·HBr: white-greenish crystals with m.p. 205–207 °C (decomp., from EtOH). Poorly soluble in MeCN, decomposes in DMSO.

4,5-Bis(dimethylamino)-1-[(2′-hydroxy-5′-nitrobenzylidene)amino]-naphthalene (7): Time of heating 20 min. Yield 0.30 g, 79%. Dark-red needles with m.p. 160–161 °C (from *n*-octane). Elemental analysis calcd. (%) for $C_{21}H_{22}N_4O_3$: C 66.65, H 5.9; found C 66.5, H 5.6. Hydrobromide **7**·HBr: light-yellow crystals with m.p. 226–227 °C (decomp., from EtOH). Poorly soluble in MeCN, decomposes in DMSO.

4,5-Bis(dimethylamino)-1-[(2′-hydroxy-3′,5′-dinitrobenzylidene)-amino]naphthalene, Zwitterionic Form (8): Time of heating 10 min. Yield 0.33 g, 78%. Small, brown needles decomposing at 236–237 °C (from MeCN). Elemental analysis calcd. (%) for $C_{21}H_{21}N_5O_5$: C 59.6, H 5.0; found C 59.6, H 5.1. Insoluble in $CHCl_3$ and hydrocarbons, sparingly soluble in water (with decomposition), decomposes in DMSO. MS (70 eV, EI): *m*/*z* (%): 423 (23) $[M]^+$, 406 (8), 393 (16), 243 (12), 213 (9), 198 (28), 183 (45), 168 (17), 58 (13).

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