N-Aminoazoles. Part 3.[1] Molecular Structure and Multinuclear NMR Study of 1,3-Diaminobenzimidazolium Chloride Hydrate and 1-Amino-3-methylbenzimidazolium Iodide

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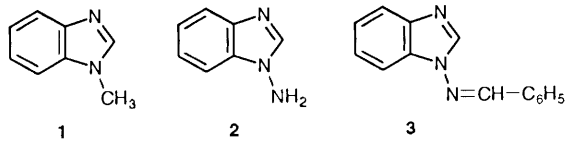
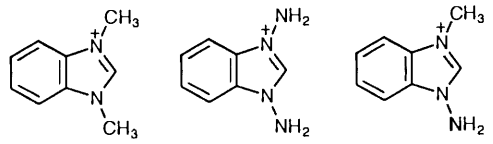
The crystal and molecular structures of the title compounds are reported. The chloride and iodide anions as well as the water molecule play an important role in the corresponding packing arrangements. Semiempirical (AM1) molecular orbital calculations on the cations lead to energy minima with geometries very similar to those observed in the crystal structures. The ^{1}H, ^{13}C and ^{15}N NMR spectra of these quaternary salts were measured and are discussed in comparison with experimental geometries and theoretical calculations.

In the two preceding papers of this series,[1,2] we have studied *N*-aminoazoles and their conjugate acids. We report here the study of *N*-aminobenzimidazoles, particularly their quaternary salts **5** and **6**. For the discussion, inclusion of data on some other derivatives is necessary; these derivatives include the already described 1-methylbenzimidazole **1** and 1-aminobenzimidazole **2**, the imine **3** and the 1,3-dimethylbenzimidazolium cation **4**.[3] The X-ray structures of **2** and its salt **7** (as a picrate) have previously been determined in the course of the study of *N*-aminoazoles.[1,2]



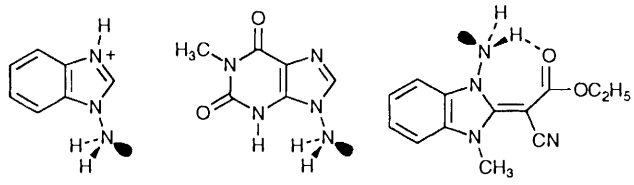
1 **2** **3**



4 **5** **6**

In the case of 1-aminobenzimidazole **2**[2] and its conjugate acid (protonated on N-3) **7**,[1] as well as in the case of 9-amino-3-methylxanthine **8**,[4] the *N*-amino group is pyramidal with the lone pair lying exactly in the ring plane. These structures indicate the absence of any significant conjugation between the amino group and the heteroaromatic π-system which is also consistent with other physico-chemical measurements.[5] Moreover, the hydrogen atoms of the amino group point out towards the benzene ring (**2** and **7**) or towards the uracil ring (**8**). 1-Amino-2-(1-cyano-1-ethoxycarbonylmethylene)-3-methylbenzimidazoline **9** presents the only exception to this rule.[6] In this last molecule, the orientation of the amino protons is inverted as a consequence of the hydrogen bond between one NH and the ethoxycarbonyl group.

Further studies of the molecular structure of *N*-aminoazoles and, in particular, of *N*-aminobenzimidazoles, are necessary to understand which non-covalent interactions play the predominant role in determining the hybridization and the conformation of *N*-amino groups. One possible approach would consist of the study of which structural and electronic modifications could make the amino group become more flat, *i.e.* more sp^2. For instance, it can be assumed that an increase in electron deficiency of the azole ring should favour such a tendency, as occurs in arylamines.[7] This was the reason to study the molecular structure and the NMR properties of *N*-aminobenzimidazolium salts **5** and **6**.



7 **8** **9**

Experimental

Compounds **3**,[8] **4** (an iodide)[3] and **6** (an iodide)[9] have already been reported. Compound **6** has been described recently as it was a new product.[10]

1,3-*Diaminobenzimidazolium chloride* **5**.—To a solution of amine **2** (1.33 g, 0.01 mol) in dichloromethane (25 cm^3) and ethanol (5 cm^3), a suspension of *O*-picrylhydroxylamine (2.44 g, 0.01 mol) was added with stirring over a period of 2–3 min. An exothermic reaction was observed. Then the mixture was heated under reflux for 5 min. After cooling and standing for 30 min, a yellow-green solid of the picrate of **5** was filtered off, washed with dichloromethane and dried. The yield of crude product was 3.4 g (90%). The picrate was purified by crystallization from water, m.p. 204–206 °C (decomp.); ν_{max}(paraffin oil)/cm^{-1} 3310, 3240, 3216, 3162 (NH_2), 1633, 1615 and 1556 (ring) (Found: C, 41.5; H, 2.8; N, 25.9. Calc. for $C_{13}H_{11}N_7O_7$: C, 41.37; H, 2.91; N, 25.99%). The picrate (0.38 g) was transformed into a chloride by boiling it for 5 min with 18% hydrochloric acid (5 cm^3). After cooling, the crystals were collected and washed with ethanol. To remove the remaining picric acid, the crude product was boiled for 2 min with ethanol (20 cm^3), then cooled, filtered off and washed with ethanol and diethyl ether, to yield 0.16 g (82%).

Table 1 Crystal analysis parameters at room temperature

	5	**6**
Crystal data		
Formula	$C_7H_9N_4^+Cl^-\cdot H_2O$	$C_8H_{10}N_3^+I^-$
Crystal habit	Colourless prism	Colourless prism
Crystal size (mm)	0.13 × 0.17 × 0.40	0.07 × 0.13 × 0.18
Symmetry	Orthorhombic, $Pna2_1$	Triclinic, $P-1$
Unit cell determination	Least-squares fit from 72 reflections ($\theta < 45°$)	Least-squares fit from 68 reflections ($\theta < 45°$)
Unit cell dimensions (Å, °)	a = 16.5044(11)	a = 8.5922(8)
	b = 10.3433(5)	b = 8.5365(10)
	c = 5.2657(1)	c = 7.1551(6)
	90, 90, 90	105.417(9), 102.453(6), 86.458(10)
Packing: V (Å^3), Z	898.9(1), 4	494.0(1), 2
D_c (g cm^{-3}), M, F(000)	1.497, 202.64, 424	1.849, 275.09, 264
μ (cm^{-1})	35.52	31.58
Experimental data		
Technique	Four circle diffractometer: Philips PW1100, bisecting geometry Graphite oriented monochromator: $\omega/2\theta$ scans Detector apertures 1 × 1°. 1 min reflex^{-1}	
Radiation	Cu–Kα	Mo–Kα
Scan width (°)	1.4	1.6
θ_{max} (°)	65	35
Number of reflections:		
independent	859	4373
observed	837 [$3\sigma(I)$ criterion]	3429 [$3\sigma(I)$ criterion]
Standard reflections:	2 reflections every 90 min. No variation	
Max.–min. transmission factors	0.683–1.000	0.450–1.000
Solution and refinement		
Solution	Patterson	
Refinement: Least-squares on F_o	Full matrix	
Parameters:		
Number of variables	161	149
Degrees of freedom	676	3280
Ratio of freedom	5.2	23.0
Final shift/error	0.05	0.03
H atoms	From difference synthesis	
Weighting-scheme	Empirical as to give no trends in $\langle\omega\Delta^2F\rangle$ *vs.* $\langle\lvert F_{obs}\rvert\rangle$ and $\langle\sin\theta/\lambda\rangle$	
Max. thermal value (Å^2)	U22[O(1)] = 0.082(2)	U11[C(5)] = 0.118(5)
Final ΔF peaks (eÅ^{-3})	0.30	0.89 near I
Final R and R_w	0.034, 0.033	0.042, 0.060

After crystallization from ethanol, 1,3-diaminobenzimidazolium chloride **5** was obtained as a hydrate, colourless prisms with m.p. 170–171 °C (decomp.); ν_{max}(paraffin oil)/cm^{-1} 3468, 3429 (H_2O), 3257, 3192, 3151 (NH_2), 1667 (H_2O), 1649 and 1629 (ring) (Found: C, 41.8; H, 4.3; N, 27.8; Cl, 17.8. Calc. for $C_7H_7N_4Cl\cdot H_2O$: C, 41.89; H, 4.48; N, 27.93; Cl, 17.70%).

NMR Spectra.—These were recorded on a Bruker AC200 spectrometer using, for solution, the conditions described in our two preceding papers,[1,2] and, for the solid state (^{13}C CPMAS), those described in ref. 11.

X-Ray Structure Determination.—Crystals suitable for X-ray analysis were obtained by slow evaporation of saturated ethanol solutions. Crystal data and the main experimental details are given in Table 1. Both structures were solved by Patterson and refined by least-squares procedures. Empirical absorption corrections were applied.[12] Most calculations were performed using the XRAY80 System[13] on a VAX6410 computer. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography, vol. IV.[14]

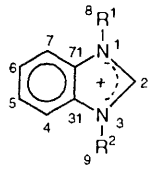
Results and Discussion

Crystal and Molecular Structure of 1,3-*Diaminobenzimidazolium Chloride* (**5**) *and* 1-*Amino*-3-*methylbenzimidazolium Iodide* (**6**).—The molecular structure of benzimidazole cations do not vary significantly,[15] either amongst themselves (Table 2) or when compared with those previously reported for the *N*-aminobenzimidazolium cation.[2] The conformation of the amino and methyl groups is staggered with respect to C(71) and C(31) as was the case for the amino substituent in **2H**$^+$.[1]

Full geometry optimizations using the semiempirical AM1 Hamiltonian[16] were performed on compounds **4**–**6** employing the X-ray coordinates as starting geometries. The calculated and observed molecular structures (Table 2) are very similar, but differ somewhat in the bond lengths involving the N(1) and N(3) atoms when an amino group is replaced by methyl. Moreover, for compound **4**, the conformation of the methyl group is twisted 9° with respect to the ideal staggered conformation.

The crystal packings shown in Figs. 1 and 2 are quite different. In compound **5**, the water molecule and the amino groups are involved in hydrogen bonds both as acceptor and as donor, creating a three-dimensional network in which the chlorine anion is also involved (Table 3). In the crystal lattice of compound **6**, the benzimidazolium skeleton is tilted 7.5(1)° with respect to the *ab* plane. Molecules related by unit translations along the *c* axis are linked together by hydrogen bonds through the iodine anion [H(81)···I···H(81) = 168(2)°]. Two of these centrosymmetrically related chains, Fig. 2, are intercalated in such a way that the molecules are located relative to each other in a head-to-tail manner. Within this stack, the interplanar spacing between the original molecule and those symmetrically related

Table 2 Selected bond distances (Å) and angles and torsion angles (°)[a]



	X-Ray		AM1		
	$R^1 = R^2 = NH_2$	$R^1 = NH_2$ $R^2 = Me$	$R^1 = R^2 = NH_2$	$R^1 = NH_2$ $R^2 = Me$	$R^1 = R^2 =$ Me
N(1)–C(2)	1.332(4)	1.328(5)	1.384	1.388	1.374
N(1)–C(71)	1.395(5)	1.387(4)	1.431	1.430	1.416
N(1)–N(8)/C(8)	1.411(4)	1.407(4)	1.361	1.360	1.436
C(2)–N(3)	1.321(3)	1.325(5)	1.384	1.369	1.374
N(3)–C(31)	1.392(4)	1.388(5)	1.431	1.418	1.416
N(3)–N(9)/C(9)	1.406(3)	1.470(6)	1.361	1.437	1.436
C(31)–C(71)	1.396(4)	1.390(5)	1.439	1.443	1.447
C(71)–N(1)–N(8)/C(8)	128.0(2)	128.7(3)	129.6	129.8	125.9
C(2)–N(1)–N(8)/C(8)	122.6(3)	122.4(3)	122.4	122.6	126.3
C(2)–N(1)–C(71)	109.2(2)	108.9(3)	108.0	107.5	107.9
N(1)–C(2)–N(3)	109.3(2)	109.7(3)	110.2	110.5	110.8
C(2)–N(3)–C(31)	109.4(2)	108.8(3)	108.0	108.4	107.9
N(3)–C(31)–C(71)	106.2(2)	106.4(3)	106.9	107.0	106.7
N(1)–C(71)–C(31)	105.8(3)	106.2(3)	106.9	106.6	106.7
C(2)–N(3)–N(9)/C(9)	122.7(2)	125.7(4)	122.4	126.1	126.3
C(31)–N(3)–N(9)/C(9)	127.8(1)	125.5(4)	129.6	125.5	125.9
C(71)–N(1)–N(8)–H(81)	−51(4)	−60(4)	−60	−60	—
C(71)–N(1)–N(8)–H(82)	71(3)	40(3)	60	60	—
C(31)–N(3)–N(9)–H(91)	56(3)	—	60	—	—
C(31)–N(3)–N(9)–H(92)	−61(3)	—	−60	—	—
C(71)–N(1)–C(8)–H(81)	—	—	—	—	−50
C(71)–N(1)–C(8)–H(82)	—	—	—	—	69
C(71)–N(1)–C(8)–H(83)	—	—	—	—	−171
C(31)–N(3)–C(9)–H(91)	—	54(7)	—	59	51
C(31)–N(3)–C(9)–H(92)	—	−40(13)	—	−61	−68
C(31)–N(3)–C(9)–H(93)	—	−176(17)	—	179	171

[a] The numbering scheme employed throughout the crystal structure discussion is as shown.

Table 3 Intermolecular interactions[a]

	Interatomic distances (Å)			Angle (°)
X–H···Y	X–H	X···Y	H···Y	X–H···Y
Compound **5**[b]				
O(1)–H(11)···Cl[1]	1.01(12)	3.322(5)	2.33(12)	169(9)
O(1)–H(12)···Cl	0.90(9)	3.349(5)	2.45(9)	178(6)
N(8)–H(81)···O(1)	0.83(4)	3.061(3)	2.24(4)	173(5)
N(8)–H(82)···N(9)[2]	0.91(4)	3.195(5)	2.42(4)	143(3)
N(8)–H(82)···Cl[3]	0.91(4)	3.262(2)	2.77(4)	115(3)
N(9)–H(91)···Cl[4]	0.93(4)	3.274(2)	2.35(4)	171(4)
N(9)–H(92)···N(8)[5]	0.93(4)	3.101(5)	2.18(5)	168(3)
C(2)–H(2)···Cl[6]	0.97(4)	3.478(4)	2.54(4)	162(3)
C(6)–H(6)···O(1)[7]	0.97(4)	3.487(5)	2.73(4)	136(3)
C(5)–H(5)···C(31–71)[8]	0.99(4)	3.619(3)	2.95(4)	126(3)
C(31–71)···C(1–71)[7]		3.789(2)		
Compound **6**[c]				
N(8)–H(81)···I	1.14(7)	3.633(4)	2.70(8)	139(6)
N(8)–H(82)···I[9]	0.91(6)	3.754(4)	2.95(6)	147(4)
C(4)–H(4)···I[10]	0.87(7)	3.923(6)	3.06(7)	168(6)
C(2)–H(2)···I[11]	1.04(9)	3.923(4)	3.04(11)	143(7)
C(9)–H(91)···C(31–71)[11]	1.13(12)	3.625(6)	2.72(12)	136(8)

[a] Numbers refer to symmetry operations and C(1–71) and C(31–71) to the centroids of the corresponding rings. [b] 1: $x, y, -1 + z$; 2: $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; 3: $-x, 1 - y, -\frac{1}{2} + z$; 4: $-x, -y, -\frac{1}{2} + z$; 5: $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} + z$; 6: $\frac{1}{2} + x, \frac{1}{2} - y, -1 + z$; 7: $x, y, 1 + z$; 8: $-x, -y, \frac{1}{2} + z$. [c] 9: $x, y, -1 + z$; 10: $1 - x, -y, 1 - z$; 11: $-x, -y, 1 - z$.

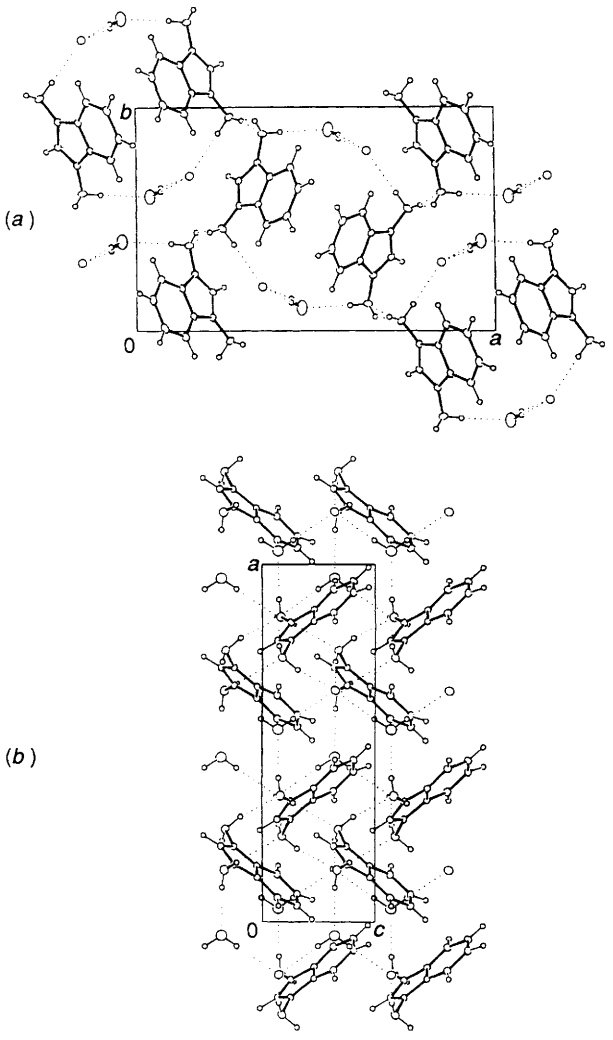


Fig. 1 The crystal packing of compound **5** viewed down (*a*) *c* and (*b*) *b* axes. Hydrogen bonds are represented by dotted lines. Thermal ellipsoids are plotted at 30% probability level.

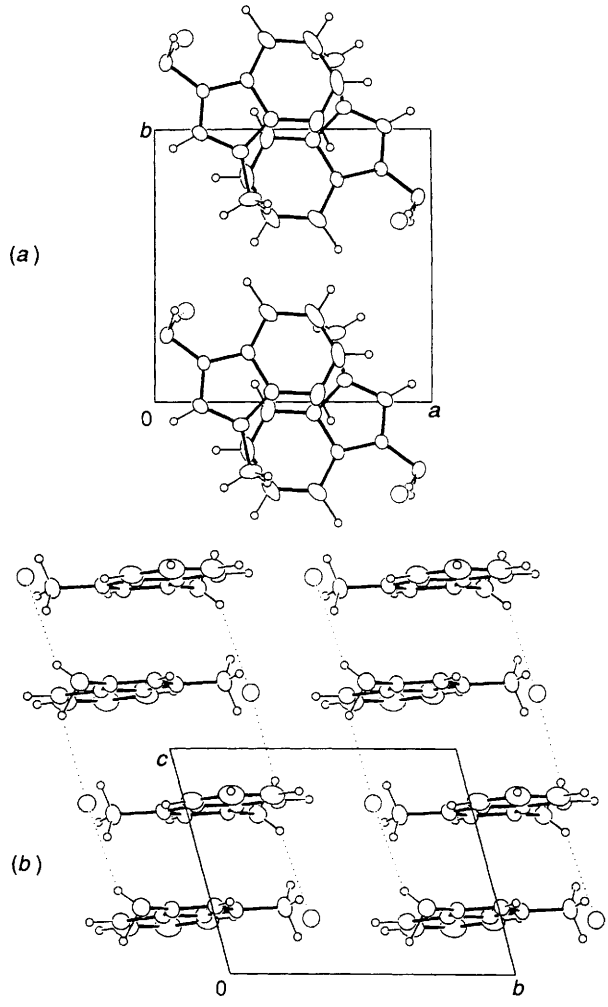


Fig. 2 A view of the crystal packing of compound **6** showing (*a*) the overlap between the cations in the stack and (*b*) the piles of intercalated chains of cations joined through the iodide ion by hydrogen bonds

$(1 - x, -y, -z; 1 - x, -y, 1 - z)$ are 3.507(1) and 3.477(1) Å respectively. Two intermolecular C–H · · · I weak interactions, Table 3, contribute to the stability of this double chain.

The local packing coefficients, defined as $C_k = V_{guest}/V_{hole}$, are 0.83 and 0.60 for compounds **5** and **6** respectively, the total packing coefficients ($C_{all} = V_{host+guest}/V_{unit\ cell\ volume}$) being 0.74 and 0.67. The water molecules and the chloride anions are located into channels along the *c* axis while the iodide anions are located in pocket cavities (Figs. 1 and 2, respectively).

Supplementary structural data consisting of lists of atomic coordinates and thermal components for the non-hydrogen atoms, hydrogen parameters and bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC).*

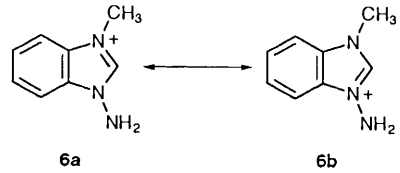
NMR Spectroscopy.—The new results of the NMR study are reported in Tables 4 (^{1}H), 5 (^{13}C) and 6 (^{15}N) (DMSO = dimethylsulfoxide).

The ^{1}H NMR chemical shifts show a smooth variation to the point that it is possible to assign 4- and 7-H of compound **6** by comparison with the data for compounds **4** and **5**. The chemical shift of 2-H in compound **2** (δ 8.07) indicates significant shielding, probably due to the amino group since the chemical shift of 2-H is further downfield in the imine **3** (δ 8.98). If the signals of the amino groups are considered, it is observed than from **2** (δ 6.13) to **5** (δ 7.14), the quaternization produces a deshielding of δ 1.0 while between **2** and **6** (δ 6.92), the effect is only δ 0.8. We assign this difference to the fact

Table 4 ^{1}H NMR spectra of *N*-aminobenzimidazoles and benzimidazolium salts in [$^2H_6$]DMSO

Compound	2-H	4-H/7-H	5-H/6-H	NH_2	CH_3
1[a]	8.40	7.87/7.77	7.40/7.48	—	3.96
2[b]	8.07	7.62/7.49	7.12/7.30	6.13	—
3[c]	8.98	7.73/7.82	7.29/7.37	—	—
4	9.64	7.99–8.03	7.67–7.72	—	4.07
5	9.86	7.89–7.94	7.62–7.67	7.14	—
6	9.71	7.95–8.03 (4-H) 7.86–7.92 (7-H)	7.64–7.75	6.92	4.04

[a] 1-Methylbenzimidazole: DMSO.[17] [b] 1-Aminobenzimidazole: the spectrum in $CDCl_3$ has been described.[18] [c] 9.21 (CH), 7.93–7.98 (H_o), 7.53–7.56 (H_m and H_p); $J_{4,5} = 7.1$, $J_{4,6} = 0.9$, $J_{5,6} = 7.2$, $J_{5,7} = 1.1$, $J_{6,7} = 7.2$.



6a 6b

* For details of the CCDC deposition Scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, 1994, issue 1.

Table 5 ^{13}C NMR spectra of *N*-aminobenzimidazoles and benzimidazolium salts[a]

Compd.	Solvent	C-2	C-4	C-5	C-6	C-7	C-3a	C-7a	CH_3
3[b]	[$^2H_6$]DMSO	136.8 ^1J = 219.9	119.9 ^1J = 159.1	122.6 ^1J = 157.1 ^3J = 7.7	123.7 ^1J = 159.2 ^3J = 7.8	110.7 ^1J = 163.8	141.8	133.2	
4	[$^2H_6$]DMSO	143.1 [0.0] ^1J = 225.0	113.4 [−6.3] ^1J = 171.0	126.4 [+4.9] ^1J = 165.0	126.4 [+4.0] ^1J = 165.0	113.4 [+4.5] ^1J = 171.0	131.6 [−11.6]	131.6 [−2.6]	33.2 ^1J = 145.0
5	[$^2H_6$]DMSO	141.8 ^1J = 224.0	113.1 ^1J = 173.8 ^3J = 5.0	126.3 ^1J = 165.1 ^3J = 7.6	126.3 ^1J = 165.1 ^3J = 7.6	113.1 ^1J = 173.8 ^3J = 5.0	130.9	130.9	
	CPMAS	142.8	114.1	125.6	125.6	114.1	131.8	131.8	
6	[$^2H_6$]DMSO	142.4 ^1J = 221.9	113.3 ^1J = 171.1 ^3J = 7.5	126.3 ^1J = 165.2 ^3J = 6.5	126.4 ^1J = 165.5 ^3J = 6.5	113.0 ^1J = 171.4 ^3J = 7.5	131.7	130.4	33.4 ^1J = 143.8 ^3J = 1.0
	CPMAS	141.3	113.9	127.6	127.6	113.9	132.0	130.1	33.6

[a] Data corresponding to compounds **1** and **2** have already been published.[1,19] [b] δ(C-1′) = 132.1; δ(C-2′) = δ(C-6′) = 128.0, ^1J = 161.8; δ(C-3′) = δ(C-5′) = 129.0, ^1J = 159.4; δ(C-4′) = 131.4, ^1J = 161.8. ^3J = ^3J = 8.0.

Table 6 ^{15}N NMR spectra of *N*-aminobenzimidazoles and benzimidazolium salts[a]

Compound	N-1	N-3	NH_2	Solvent
3[b]	−183.1 (^2J = 14.5)	−76.4 (^2J = 3.2)	−137.2[c] (^2J = 11.5)	[$^2H_6$]DMSO
4[d]	−228.3 (^2J = 7.2)	−228.3 (^2J = 7.2)	—	[$^2H_6$]DMSO
5[e]	−212.5 (^2J = 4.3)	−212.5 (^2J = 4.3)	−308.6 (^1J = 70.7)	[$^2H_6$]DMSO
	−225.4	−225.4	−308.7	H_2SO_4
6[f]	−209.0 (^2J = 4.6)	−232.4 (^2J = 7.0)	−308.9 (^1J = 72.2)	[$^2H_6$]DMSO
	−220.1	−232.7	−312.1	H_2SO_4

[a] Data corresponding to compounds **1** and **2** have already been published.[1,2,19] [b] INEPT, *D*1 = 2.0, *D*2 = 0.05 and 0.025, Hz/pt = 0.576. [c] This signal belongs to an N=CHAr nitrogen atom. [d] INEPT. *D*1 = 2.0, *D*2 = 0.025, Hz/pt = 0.954. [e] INEPT, *D*1 = 1.0, *D*2 = 0.05 and 0.0036, Hz/pt = 0.576. [f] INEPT, *D*1 = 2.0, *D*2 = 0.025 and 0.0025, Hz/pt = 0.576.

that the positive charge is more localized on the *N*-methyl, N-3, than on the *N*-amino, N-1. In other words, the resonance form **6a** predominates over **6b**. We will come back to this point.

There is nothing unusual in the ^{13}C NMR solution data of Table 5. The chemical shifts obtained in the solid state using the Cross Polarization Magic Angle Spinning (CPMAS) technique for compounds **5** and **6** are very similar to the values in DMSO solution. The absence of splitting in any signal is consistent with the presence of only one independent molecule in the unit cell in both compounds.

Concerning the ^{15}N NMR results, we have already described that 1-aminobenzimidazole **2**, like all other *N*-aminoazoles, shows very different chemical shifts in trifluoroacetic and in sulfuric acid [$\Delta\delta(NH_2)$ = +5.3, $\Delta\delta$(N-1) = −19.9 and $\Delta\delta$(N-3) = +9.3].[1] We decided to record the spectra of compounds **5** and **6** to determine if sulfuric acid is strong enough to diprotonate compound **2** (on N-3 and NH_2). The results obtained (Table 6) show the following shifts between DMSO and sulfuric acid: **5**, $\Delta\delta(NH_2)$ = −0.1, $\Delta\delta$(N-1 and N-3) = −12.9; **6**, $\Delta\delta(NH_2)$ = −3.2, $\Delta\delta$(N-1) = −11.1, $\Delta\delta$(N-3) = −0.7. Although the $\Delta\delta$ values are difficult to compare, at least a large and negative effect on N-1 is observed for compounds **2**, **5** and **6** in sulfuric acid, pointing to a partial protonation on the amino group.

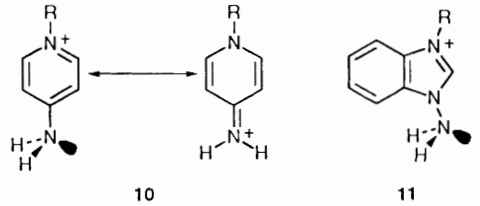
Coming back to the question of the resonance between **6a** and **b**, the AM1 calculations (Table 2) can be used in two ways. Firstly, the N–C bond lengths for compounds **4** [N(1)–C(2) = C(2)–N(3) = 1.374 Å], **5** [N(1)–C(2) = C(2)–N(3) = 1.384 Å] and **6** [N(1)–C(2) = 1.388 and C(2)–N(3) = 1.369 Å] point out that in compound **6** resonance form **6a** is more important since C(2)–N(3) is shorter than in compound **4** and N(1)–C(2) is longer than in compound **5**. The second approach uses the total charges on N(1) and N(3). These charges are −0.1015 for compound **4**, −0.0807 for compound **5** and −0.0781 (*N*-amino) and −0.1046 (*N*-methyl) for compound **6**. Here again, the charges in compound **6** slightly deviate with regard to symmetrical compounds **4** and **5**; *N*-methyl by 0.031 (from −0.1015 to −0.1046) and *N*-amino nitrogens by −0.026 (from −0.0807 to −0.0781). These opposite differences are consistent with the predominance of form **6a**.

This result corresponds to the fact that *N*-methylazoles are more basic than *N*-aminoazoles,[1] *i.e.* the *N*-methyl group stabilizes the positive charge better than the *N*-amino group.

Conclusions

The transformation of an azole into an azolium cation is not sufficient a driving force to modify either the hybridization or the conformation of the *N*-amino group. Even in the case of the 1,3-diamino derivative **5**, both amino groups have the same conformation as in all *N*-aminobenzimidazoles (lone pair in the plane of the ring and pointing towards 2-H).

To understand the differences between an amino group linked through the carbon to a pyridinium ring, for instance **10**, and an amino group linked through the nitrogen to an azolium



10

11

ring, for instance **11** [R = H(7),[2] R = NH_2(5), R = CH_3(6)], a simple discussion based on resonance forms will be useful. It is clear that quaternization of the pyridine ring will stabilize a planar sp^2 amino group.* On the other hand, such effects cannot be observed in structure **11**. The azole nitrogen prevents this possibility and *N*-aminoazoles resemble more aliphatic than aromatic amines, being sensitive to inductive effects but scarcely to resonance effects.

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* A search in the Cambridge Structural Database (CSD, version April 1993)[20] for 4-amino (**10**) and 4-dimethylaminopyridinium salts yields two 4-amino derivatives (codenames CUTBUO and SODCUJ) and eight 4-dimethylamino derivatives (DMAPYC, GASVIF, JOJXUB, JUBJOF, JUBJUL, JUBKAS, VEKMON and VIPCUS). Amino derivatives have both sp^2 nitrogen atoms (sum of angles around nitrogen 359.6–359.8°) and planar geometries (torsion angles −0.6 to −1.1°). Dimethylamino derivatives have sp^2 nitrogen atoms (358.7–360.0°) and geometries ranging from planar (−0.9°) to a little twisted (torsion angles up to 9.2°).

References

1 Part 2. R. M. Claramunt, D. Sanz, J. Catalán, F. Fabero, A. García, C. Foces-Foces, A. L. Llamas-Saiz and J. Elguero, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1687.
2 C. Foces-Foces, F. H. Cano, R. M. Claramunt, D. Sanz, J. Catalán, F. Fabero, A. Fruchier and J. Elguero, *J. Chem. Soc., Perkin Trans. 2*, 1990, 237.
3 R. M. Claramunt and J. Elguero, *An. Quim.*, 1986, **82C**, 162.
4 V. V. Kuz'menko, T. A. Kuz'menko, G. G. Alexandrov, A. F. Pozharskii and A. V. Gulevskaya, *Khim. Geterotsikl. Soedin.*, 1987, 836.
5 V. V. Kuz'menko and A. F. Pozharskii, *Adv. Heterocycl. Chem.*, 1992, **53**, 85 and references therein.
6 T. A. Kuz'menko, V. V. Kuz'menko, A. F. Pozharskii, O. V. Kryshtaluk and G. G. Alexandrov, *Khim. Geterotsikl. Soedin.*, 1992, 205.
7 D. B. Adams, *J. Chem. Soc., Perkin Trans. 2*, 1993, 567.
8 R. A. Abramovich and K. Schofield, *J. Chem. Soc.*, 1955, 2326.
9 V. V. Kuz'menko, T. A. Kuz'menko and A. M. Simonov, *Khim. Geterotsikl. Soedin.*, 1986, 346.
10 T. Kaiya, M. Ohta and K. Kohda, *Tetrahedron*, 1993, **49**, 8795.
11 P. Molina, A. Arques, R. Obón, A. L. Llamas-Saiz, C. Foces-Foces, R. M. Claramunt, C. López and J. Elguero, *J. Phys. Org. Chem.*, 1992, **5**, 507.
12 M. Walker and D. Stuart, Difabs, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
13 J. M. Stewart, P. A. Machin, C. W. Dickinson, H. L. Ammon, H. Heck and H. Flack, The X-ray System, Technical Report TR-446, Computer Science Centre, Univ. of Maryland, USA, 1976.
14 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham (present distributor D. Reidel, Dordrecht), 1974, vol. IV.
15 G. A. Abrahams and E. T. Keve, *Acta Crystallogr., Sect. A*, 1971, **27**, 157.
16 J. J. P. Stewart, MOPAC6.0, Frank J. Seiler Research Laboratory, United States Air Force Academy, CO 80840, USA, 1990.
17 J. de Mendoza, M. L. Castellanos, J. P. Fayet, M. C. Vertut and J. Elguero, *J. Chem. Res.*, 1980, 50 (M 514).
18 M. Somei, M. Matsubara, Y. Kanda and M. Nasume, *Chem. Pharm. Bull.*, 1978, **26**, 2522.
19 R. M. Claramunt, D. Sanz, G. Boyer, J. Catalán, J. L. G. de Paz and J. Elguero, *Magn. Reson. Chem.*, 1993, **31**, 791.
20 F. H. Allen, J. E. Davies, J. J. Galloy, O. Johnson, O. Kennard, C. F. Macrae, E. M. Mitchell, G. F. Mitchell, J. M. Smith and D. G. Watson, *J. Chem. Inf. Comp. Sci.*, 1991, **31**, 187.

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