Conformational Properties of the Free and Methylated 2-Amino Group in Benzimidazole, Benzoxazole, and Benzothiazole. *X*-Ray Crystallographic Analysis and Nuclear Magnetic Resonance Study of the Internal Rotation

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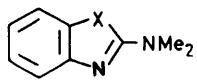
The conformational properties of the free and methylated 2-amino group in benzimidazole, 1-methylbenzimidazole, benzo-oxazole, and benzothiazole were studied, as well as the modifications induced by *N*-protonation and *N*-methylation at the heterocyclic ring. Both ^{1}H n.m.r. spectra and *X*-ray analysis show that in the ground state of the molecules examined the amino group is coplanar with respect to the plane of the rings. The *NN*-dimethylamino group tends to be distorted from coplanarity when a methyl group is present at the heterocyclic nitrogen: the degree of distortion determined experimentally compares satisfactorily with that corresponding to the energy minimum of the molecules calculated by semi-empirical methods. For the benzoxazole and benzothiazole derivatives it was also possible through ^{1}H dynamic n.m.r. measurements to determine the thermodynamic parameters for the internal rotation of the *NN*-dimethylamino group; and in the *N*-protonated forms the free energy of activation turns out to be higher than that in the free bases.

In previous studies[1,2] we have reported on the *N*-protonation and *N*-methylation of *NN*-dimethylaminopyridines and the internal rotation of the *NN*-dimethylamino group in several aromatic and heteroaromatic systems. Amino and *N*-methylamino derivatives of penta-atomic heterocyclic compounds are usually not sufficiently stable for protonation tests or for examining their thermodynamic properties in solution. A conformational study of 2-*NN*-dimethylaminothiazole has been reported.[3] Internal rotation of the *NN*-dimethylamino group has been mostly examined[4] in systems containing at least three heteroatoms, namely in derivatives of oxadiazole, thiadiazole, and thiatriazole. In particular, higher barriers for the *NN*-dimethylamino group are found[4] in the derivatives of heterocycles having one sulphur atom with respect to the corresponding oxygen compounds: this characteristic can probably be attributed to conjugation involving 3*d* orbitals of sulphur, increasing the double-bond character of the exocyclic C–N bond. The importance of conjugative effects on the barrier of the amino group has been stressed[5] in *para*-substituted anilines. Furthermore, in the heterocyclic derivatives of the azole series the barriers to rotation are[4] greater than in *NN*-dimethylaniline and *p*-nitro-*NN*-dimethylaniline.

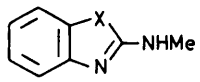
In 1-methylcytosine[6] and in pyridine derivatives[2] protonation at one of the ring nitrogens enhances the barrier to internal rotation and this is likely to occur in azole derivatives also. The exocyclic C–N bond ought to increase the double-bond character as a consequence of increased conjugation. On the other hand, one expects this barrier enhancement to be absent if protonation occurs at the nitrogen atom of the dimethylamino group. Thus the knowledge of the site of protonation in dimethylamino derivatives of azoles is clearly related to the study of the origin of the barrier for internal rotation in these compounds.

We report here the conformational behaviour of a number of *NN*-dimethylamino, *N*-methylamino, and amino derivatives of azoles with two heteroatoms, namely oxazole, thiazole, and imidazole, in their benzo-condensed forms, in order to enhance the stability of the molecules.

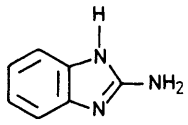
The internal rotation and geometry of the ground state of the amino group have been analysed in free bases and in mono-



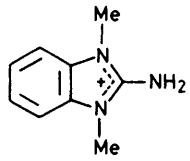
X
(1) NH
(2) O
(3) S
(4) NMe



X
(5) NH
(6) NMe



(7)



(8a)

protonated and monomethylated molecules, in order to examine the influence of heteroatoms on the barrier heights and the modifications induced by introducing a positive charge on the structure. The study is carried out by ^{1}H and ^{13}C n.m.r. spectroscopy and by *X*-ray analysis of the ionic species.

Results and Discussion

The compounds examined, which turned out to be sufficiently stable for carrying out n.m.r. measurements as free bases and for being converted into the corresponding *N*-protonated and *N*-methylated forms, are (1)—(7); in the case of 2-amino-1-methylbenzimidazole only the *N*-methylated form (8a) was considered.

(a) *N.m.r. Spectra.*—The more significant ^{1}H n.m.r. parameters are reported in Table 1. In compounds (1)—(4) the *NN*-dimethylamino group gives rise, at room temperature, to a singlet, which, in principle should indicate that rotation of the group around the C–N bond is fast (on the n.m.r. time scale). In

Table 1. ^{1}H Chemical shifts (δ values) of methyl groups[a] and protons bonded to nitrogen in the free bases and in the *N*-protonated[b] and *N*-methylated forms of the compounds examined. Coupling constants are in Hz

Solvent:	[$^2H_6$]DMSO			D_2O–$(CD_3)_2CO$ (1:2)	
Compound	N_S-Me	N_R-Me	N-H	N_S-Me	N_R-Me
(1)	3.03			3.15	
(2)	3.13			3.20	
(3)	3.14			3.20	
(4)	2.83	3.57		3.02	3.68
(5)	2.83(d, *J* 4.60)		6.44[c](b.b.)	3.01	
(6)	2.88(d, *J* 4.57)	3.41	6.60[c](b.b.)	3.06	3.52
(7)			6.27[c](b.b.) 4.30 (NH_2)		
(1a)[d] [(4b)]	3.19	3.71		3.43 (3.44)	3.93 (3.94)
(2a)	3.45	3.92		3.63	4.02
(3a)	3.50	3.98		3.65	4.13
(4a)	3.20	3.73		3.45	3.94
(5a)	2.98(d, *J* 4.69)	3.51	8.78(b.b.)	3.21	3.71
(6a)	3.23	3.71	8.27(b.b.)	3.48	3.99
(8a)					3.79
(1b)	3.24			3.37 (3.36)	
(2b)	3.29			3.49 (3.46)	
(3b)	3.36			3.54 (3.51)	
(5b)	2.93(d, *J* 4.40)		8.75(b.b.) 12.96(b.b.)	3.20 (3.18)	
(6b)	2.98(d, *J* 4.69)	3.51	8.78(b.b.)	3.24 (3.21)	3.71 (3.71)

[a] The S and R terms refer, in order, to the nitrogen atoms of the substituent and of the ring. The terms in parentheses stand for: d = doublet, b.b. = broad band. [b] Obtained by adding trifluoroacetic acid to the solutions of the corresponding bases; in parentheses are the values referred to the salts obtained by adding hydroiodic acid to the bases and isolating the crystalline compounds. [c] Refers to the amino substituent. [d] Compound (1a) [≡(4b)] is obtained exclusively from compound (4) by adding trifluoroacetic or hydroiodic acid.

compounds (5) and (6), the *N*-methyl group is a doublet in [$^2H_6$]DMSO solution with a coupling to the N–H proton of 4.6 Hz, while it collapses to a singlet in the D_2O–$(CD_3)_2CO$ solvent mixture owing to the fast exchange of the NH proton. The chemical shifts have a similar behaviour in the two solvents employed and they are all at lower field in water–acetone. The chemical shift of the NMe_2 group in compound (4) is at higher field with respect to compounds (1)—(3), which may indicate lower electronic conjugation of the nitrogen atom with the ring in the former compound, reflecting a lower degree of coplanarity of the NMe_2 substituent with the heterocyclic ring. Even the difference of 0.16 p.p.m. in the chemical shifts of the Me group bonded to the nitrogen atom of the heterocyclic ring in compounds (4) and (6) may reflect a different degree of coplanarity in the lowest-energy conformation of the NMe_2 and NHMe groups.

Treatment with methyl iodide afforded the *N*-methylated compounds (1a)—(6a).* The ^{1}H n.m.r. spectra of derivatives (1a)—(3a) show two methyl signals, in 1:2 ratio, while in derivative (4a) two 1:1 methyl signals are observed. In derivatives (5a) and (6a) in [$^2H_6$]DMSO solution the signal corresponding to the methyl group of the substituent show a coupling with the NH proton. These data favour exclusive alkylation at the nitrogen atom of the ring. The chemical shift of the NMe_2 group is at higher field in compounds (1a) and (4a) with respect to those, (2a) and (3a), which could be connected to a different degree of planarity of this substituent. Even for the methyl group bonded to the heterocyclic ring, the chemical shifts indicate that, probably, a different conformational situation is present in compounds (2a) and (3a) with respect to compounds (1a), (4a)—(6a), and (8a). These features will be re-examined in the section dedicated to the conformational properties of these molecules.

* In the case of compounds (1), (5), and (7) both mono- and di-methylation at the heterocyclic ring were observed.

Table 2. ^{13}C Chemical shifts (δ values) of methyl groups[a] bonded to nitrogen in the free bases and in the *N*-protonated[b] and *N*-methylated forms of the compounds examined [the solvent is a 1:2 mixture of D_2O and $(CD_3)_2CO$]

Compound	N_S-Me	N_R-Me
(1)	38.44, 37.77[c]	
(2)	37.61	
(3)	40.29, 39.6[e]	
(4)	41.92	31.27
(5)	29.94	
(6)	29.58	28.28
(1a)[d] [(4b)]	41.14 (41.48)	30.64 (33.57)
(2a)	40.82	34.02
(3a)	45.47	38.10
(4a)	41.73	33.03
(5a)	29.94	31.58
(6a)	31.47	31.58
(8a)		30.16
(1b)	38.93 (39.37)	
(2b)	38.43 (38.86)	
(3b)	42.51 (42.63)	
(5b)	29.73[f] (29.66)	
(6b)	29.65 (30.75)	29.15 (30.37)

[a,b,d] See footnotes of Table 1. [c] Ref. 8: solvent CH_3OH. [e] Ref. 9: solvent [$^2H_6$]DMSO. [f] This signal overlaps with those of $(CD_3)_2CO$ carbons.

By adding trifluoroacetic acid to the free bases the protonated forms (1b)—(7b) were obtained: the solutions were directly examined by n.m.r. and no attempt to isolate the protonated molecules was carried. The same ions (1b)—(7b) were nevertheless obtained in the form of iodide salts and their n.m.r. spectra recorded in D_2O–$(CD_3)_2CO$ solvent. The ^{1}H chemical shifts reported in parentheses in Table 1 are close to those of the derivatives obtained by adding trifluoroacetic acid to the solutions of the free bases.

For the ions (5b) and (6b) the methyl group on the amino substituent shows a coupling with the NH proton in [$^2H_6$]-

DMSO solution. Even in the case of these molecules no doubling was observed of the *N*-methyl signal which could indicate the presence of 'frozen' conformations at room temperature concerning rotation around the exocyclic C–N bond. In compound (**3b**) the NMe_2 group shows a broadening which may be related to a slowing of internal rotation frequency.

The ^{13}C chemical shifts of the Me groups in the molecules examined are reported in Table 2. With regard to the free bases (**1**)—(**6**), it was observed that the chemical shifts of Me groups cover two distinct ranges for the NMe_2 and NHMe groups, as also occurs in other classes of compounds.[7] This difference is maintained even in the *N*-protonated and *N*-methylated forms. All the proton-decoupled signals are singlets showing no doubling related to the presence of 'frozen' conformations at room temperature. *N*-Protonation does not result in appreciable changes of the chemical shifts of the methyl groups, while *N*-methylation of (**2**) and (**3**) determines appreciable low-field shifts of these groups. These results seem to indicate that the carbon shifts are affected by electronic and anisotropy effects and the *N*-methylation and the *N*-protonation changes these contributions to different extents. The changes observed for ^1H chemical shifts as a consequence of *N*-protonation and *N*-methylation are not correlated with those for the corresponding ^{13}C chemical shifts.

In the case of compounds (**1**)—(**3**) the ^1H n.m.r. spectra were recorded for different ratios of compound–trifluoroacetic acid, and the chemical shifts of the NMe_2 group examined as a function of the pH of the solution. It was thus observed that as a function of pH the chemical shift changes within a range of 0.2 p.p.m. in the compounds examined. This change in chemical shift is not an indication of the protonation site since the same order of magnitude is found in compounds differing in the protonation site, such as *NN*-dimethylaniline and *NN*-dimethylaminopyridines[1] (the latter compounds are protonated at the heterocyclic nitrogen). Further, by following the change in chemical shift of *N*-methyl protons in compounds (**1**)—(**3**) as a function of the pH of the solution, it is seen that the strongest variation occurs in a narrow pH range, which should be located in the neighbourhood of the p*K* value of the group which is being protonated. Thus the strongest variations of chemical shifts occur for the different compounds in the following pH ranges: 6.5—7.5 for compound (**1**), 2.5—3.5 for compound (**2**), and 4.0—5.0 for compound (**3**). These values should be compared with the pK_a values[10] of 2-aminobenzimidazole (7.51), 2-aminobenzoxazole (3.70), and 2-aminobenzothiazole (4.48), which are usually associated with protonation of the heterocyclic nitrogen.

(b) *Activation Parameters for the Internal Rotation of Amino Groups.*—In substituted anilines and in *NN*-dimethylaniline derivatives[5,11] rotation around the Ar–N bond is hindered and examples have been also reported for nitrogen heterocyclic derivatives.[3,4,12] In the internal rotation process the ground state is that corresponding to a planar or nearly planar disposition of the amino group with respect to the aromatic ring, while the transition state corresponds to a 90° rotation of the amino group. In nitrogen heterocyclic derivatives this barrier should be enhanced when *N*-protonation or *N*-alkylation of the ring nitrogen occurs, as a result of conjugative effects.[2,13]

For compounds (**2**)—(**4**) and for their protonated derivatives, dynamic n.m.r. experiments were performed in order to measure the thermodynamic parameters for the internal rotation process around the exocyclic C–N bond. Measurements were carried out in $(CD_3)_2CO$ or CF_2Cl_2 solution. In compounds (**2**) and (**3**) coalescence broadening followed by doubling of the *N*-methyl resonance was observed at low temperature, while for compound (**4**) the spectrum did not show significant changes down to 123 K. The solubility of the ionic compounds, both *N*-protonated and *N*-methylated derivatives, is very low, especially at low temperature, and the dynamic n.m.r. behaviour could be followed only on samples obtained by adding trifluoroacetic acid to the solutions of the free bases in $(CD_3)_2CO$. According to this procedure, only for (**2b**) and (**3b**) could changes of the spectra be followed, enabling their activation parameters to be determined. Total line-shape simulation[14] was employed in order to calculate the thermodynamic parameters. The separation between the peaks of the methyl group at low temperature is usually small and for compound (**2**) restricted within 2—3 Hz (at 60 MHz): the experimental free energy of activation is thus not determined to better than 4—5 kJ mol^{-1}. By employing an approximate formulation[15] which makes use of the chemical shift between the separate signals of the methyl group and of the rate constant at the coalescence point, the ΔG^* values reported in parentheses in Table 3 are also obtained: these values are close to those obtained from total line-shape analysis.

Table 3. Activation parameters (at 298 K) obtained from dynamic n.m.r. in $(CD_3)_2CO$

Compound	ΔG^*/ kJ mol^{-1}	ΔH^*/ kJ mol^{-1}	ΔS^*/ JK^{-1} mol^{-1}	T_c/K	E_a/ kJ mol^{-1}
(**2**)	50.39 (47.92)[a]	42.53	−26.37	212	45.01
(**3**)	47.46 (46.37)[a]	41.78	−19.07	209	44.26
(**2b**)	62.46 (64.36)[a]	92.71	102.78	274	95.19
(**3b**)	63.69 (65.62)[a]	89.22	85.71	287	91.73

[a] Values obtained by employing the approximate formalism given in Ref. 15.

For the ionic compounds (**2b**) and (**3b**) the entropy of activation is higher than normal, since it is generally accepted that for hindered internal rotation the ΔS^* values should be negligible.[16,17] We deem that, owing to the small chemical-shift separation between the signals of anisochronous methyl groups, the ΔS^* values may be affected by a larger error than the ΔG^* values. Further, proton exchange, solvent effects, and ion-pair formation should also lie at the origin[18] of the large values of the entropy of activation of these molecules.

The activation parameters reported in Table 3 show that in compounds (**2**) and (**3**) almost equal energy barriers are present, both in terms of entropy and enthalpy of activation. These values indicate that no substantial difference exists between oxygen and sulphur compounds, differences which, on the other hand, were found in other series of heterocyclic derivatives.[3] Furthermore, the values are higher than those found for *NN*-dimethylamino derivatives[2] of benzene and pyridine, but similar to those of oxatriazole and thiatriazole derivatives.[2] In addition, the ΔG^* value of compound (**3**) is significantly higher than that of 2-*NN*-dimethylaminothiazole,[3] where the presence of a nitro substituent on the heterocyclic ring increases[3] the energy barriers to values close to those of derivative (**3**). The condensed benzene ring should thus act as an electron-withdrawing group enhancing the Ar-N double-bond character. This effect also appears to operate on the basic character of these molecules since the 1-amino-1,3-thiazole derivative is more basic (pK_a 5.36;[19] 5.32[20]) than the benzo-condensed derivative (pK_a 4.48;[10] 4.23[21]).

For the ionic compounds (**2b**) and (**3b**) the energy barriers increase in comparison with their bases (**2**) and (**3**), in agreement with previous experimental findings[2,6] and with theoretical predictions.

(c) *Crystal and Molecular Structures.*—In order to acquire definite information on *N*-protonation and *N*-methylation sites in the compounds here examined and to have more precise

Table 4. Bond distances (Å) and angles (°) in the organic cation, with estimated standard deviations in parentheses

Compound:	(1a) X = N(2)	(2a) X = O	(3a) X = S	(4a) X = N(2)	(6a) X = N(2)	(8a) X = N(2)
(a) Bond distances						
N(1)–C(1)	1.365(8)	1.339(7)	1.335(4)	1.343(7)	1.353(10)	1.349(14)
N(1)–C(7)	1.391(7)	1.389(7)	1.397(6)	1.380(5)	1.396(9)	1.380(15)
N(1)–C(8)	1.473(10)	1.461(7)	1.458(6)	1.479(6)	1.459(11)	1.440(15)
X–C(1)	1.368(7)	1.345(6)	1.739(4)	1.329(6)	1.346(9)	1.339(14)
X–C(2)	1.364(7)	1.378(7)	1.738(4)	1.375(7)	1.407(9)	1.365(16)
X–C(9)				1.498(7)	1.457(10)	1.466(16)
N(3)–C(1)	1.311(8)	1.301(8)	1.318(4)	1.358(7)	1.330(9)	1.341(24)
N(3)–C(10)	1.466(14)	1.448(9)	1.457(7)	1.469(11)	1.438(12)	
N(3)–C(11)	1.461(12)	1.468(9)	1.457(6)	1.460(8)		
C(2)–C(3)	1.386(9)	1.347(8)	1.381(6)	1.393(7)	1.391(10)	1.405(18)
C(2)–C(7)	1.407(9)	1.376(7)	1.383(5)	1.384(6)	1.364(11)	1.405(16)
C(3)–C(4)	1.392(11)	1.397(9)	1.374(6)	1.375(9)	1.371(11)	1.362(21)
C(4)–C(5)	1.378(15)	1.386(10)	1.377(7)	1.408(11)	1.364(14)	1.452(21)
C(5)–C(6)	1.402(13)	1.358(11)	1.383(7)	1.366(10)	1.405(11)	1.375(21)
C(6)–C(7)	1.355(10)	1.377(9)	1.364(6)	1.387(7)	1.389(10)	1.380(16)
(b) Bond angles						
C(1)–N(1)–C(7)	110.2(6)	107.6(5)	112.8(3)	108.8(4)	107.2(6)	108.2(8)
C(1)–N(1)–C(8)	128.5(6)	129.4(5)	126.4(4)	126.1(4)	129.8(7)	125.6(10)
C(7)–N(1)–C(8)	121.2(6)	122.5(5)	119.7(4)	123.5(4)	123.0(7)	126.2(10)
C(1)–X–C(2)	110.4(6)	106.9(4)	89.7(2)	109.5(4)	108.2(6)	109.1(9)
C(1)–X–C(9)				126.3(4)	124.5(7)	124.9(10)
C(2)–X–C(9)				123.5(4)	127.3(6)	125.9(10)
C(1)–N(3)–C(10)	122.0(8)	124.8(6)	124.4(4)	119.9(5)	128.9(8)	
C(1)–N(3)–C(11)	120.9(8)	118.0(5)	119.0(4)	122.2(5)		
C(10)–N(3)–C(11)	114.8(8)	116.7(6)	116.6(4)	117.8(6)		
N(1)–C(1)–X	106.3(5)	110.6(5)	113.2(3)	108.6(5)	109.7(6)	109.3(10)
N(1)–C(1)–N(3)	129.5(7)	131.7(5)	127.5(3)	124.9(5)	128.2(7)	124.2(12)
X–C(1)–N(3)	123.7(7)	117.7(5)	119.3(3)	126.5(5)	122.1(7)	126.4(11)
X–C(2)–C(3)	132.2(7)	127.3(5)	127.2(3)	132.1(5)	130.3(7)	131.9(11)
X–C(2)–C(7)	107.2(6)	108.4(4)	111.3(4)	106.5(4)	106.5(6)	106.8(10)
C(3)–C(2)–C(7)	120.6(6)	124.4(5)	121.6(4)	121.4(5)	123.2(7)	121.3(11)
C(2)–C(3)–C(4)	116.5(8)	114.8(5)	117.6(4)	116.8(5)	115.4(8)	116.7(12)
C(3)–C(4)–C(5)	122.7(8)	121.6(6)	120.9(5)	121.2(6)	122.5(8)	121.8(14)
C(4)–C(5)–C(6)	118.5(7)	121.8(7)	121.1(4)	121.8(6)	122.2(8)	120.7(14)
C(5)–C(6)–C(7)	118.8(9)	116.9(7)	118.4(4)	116.9(6)	115.3(7)	117.2(11)
N(1)–C(7)–C(2)	105.7(5)	106.6(5)	112.7(4)	106.6(4)	108.5(6)	106.6(9)
N(1)–C(7)–C(6)	132.8(8)	133.0(6)	126.8(4)	131.5(5)	130.1(7)	131.2(10)
C(2)–C(7)–C(6)	121.4(7)	120.4(6)	120.5(4)	121.8(5)	121.4(7)	122.2(11)

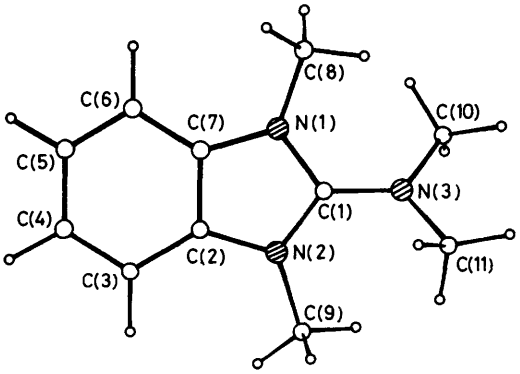


Figure Projection of cation (**4a**) on the benzimidazolium plane, showing the nomenclature system adopted in the crystal analysis

molecular geometries for energy calculations, the molecular structure of a number of molecules was also determined. For these measurements the ionic compounds were used, the anion A^- being chosen in order to have crystalline forms appropriate for *X*-ray analysis: (**1a**; $A^- = ClO_4^-$); (**2a**; $A^- = I^-$); (**3a**; $A^- = I^-$); (**4a**; $A^- = ClO_4^-$); (**6a**; $A^- = ClO_4^-$); (**8a**; $A^- = ClO_4^-$).

Bond distances and angles obtained for the compounds are reported in Table 4 and the arbitrary numbering scheme employed in crystal analysis is shown in the Figure. The intramolecular bond lengths and angles in the benzimidazole part of compounds (**1a**), (**4a**), (**6a**), and (**8a**) are in line with the hybridization expected for the atoms involved and are also in a reasonable agreement with those of benzimidazole.[22] For the benzothiazole system too, compound (**3a**), bond lengths and angles are close to those found for similar systems:[23] the short S–C single bonds, 1.739(4) and 1.738(4) Å, indicate that the sulphur atom is involved in a partial π delocalization, as has also been pointed out elsewhere.[23] Crystal analysis of compound (**2a**) represents, to the best of our knowledge, the first example of a structural study on a benzoxazole system. The substitution of N(2) in a benzoxazole ring with an oxygen atom does not appreciably influence the geometrical parameters of the molecular skeleton.

Apparently the two-ring fused system is planar, within the limits of experimental error, for all the compounds examined. Some small, but significant, deviations from planarity are nevertheless observed, concerning the benzene ring of compound (**1a**) and the thiazole ring in compound (**3a**); in these

cases the planarity of the molecule is influenced as shown in Supplementary Publication No. SUP 56275 (11 pp.).*

The averaged angle around the nitrogen atoms was found to have the following values: for N(1) 120.0° (**1a**), 119.8° (**2a**), 119.6° (**3a**), 119.5° (**4a**), 120.0° (**6a**), 120.0° (**8a**); for N(2) 119.8° (**4a**), 120.0° (**6a**), 120.0° (**8a**); and for N(3) 119.5° (**1a**), 119.8° (**2a**), 120.0° (**3a**), 120.0° (**4a**). These results indicate that the nitrogen atoms of the compounds should be considered close to an sp^2 hybridization state. On the other hand, a comparison in terms of pyramidality of N atoms indicate that N(1) lies in the plane containing the three atoms attached to it only in compounds (**6a**) and (**8a**), while the distance from this plane in compounds (**1a**)—(**4a**) is, in order, −0.030(16), 0.059(5), 0.088(3), 0.103(5) Å. For N(2) these distances are 0.069(5) and −0.022(9) Å in compounds (**4a**) and (**8a**), while full planarity is found only in compound (**6a**).

Since the configuration of the N atom is derived from the position of the surrounding atoms, the planar trigonal arrangement of the substituents bonded to N(3) in compounds (**6a**) and (**8a**) found by structure analysis has some degree of uncertainty. In fact, though the co-ordinates of the hydrogen atoms bonded to nitrogen were refined, the resulting parameters suggest that the position of the hydrogens is highly uncertain. As regards N(3) we may thus conclude that only in compound (**3a**) does it lie in the plane of C(1), C(10), and C(11), while in derivatives (**1a**)—(**3a**) it is distant from this plane by 0.125(18), 0.059(6), and −0.023(5) Å, respectively. The high sp^2 character of C(1) is observed in all the structures, except in compound (**1a**), where a low but significant deviation from the trigonal planar arrangement is found, the distance of C(1) from the plane determined by N(1), N(2), and N(3) being 0.052(18) Å.

The plane determined by C(10), N(3), C(11) of the *NN*-dimethylamino group shows a very similar situation with respect to the mean plane of the molecule in compounds (**1a**)—(**3a**), the dihedral angle between these planes being 15.6, 8.0, and 11.8°, respectively. This angle increases in compound (**4a**) to 40.4°, and this may be interpreted in terms of steric interactions with the methyl substituents at N(2).

The geometry of the perchlorate anion for compounds (**1a**), (**4a**), (**6a**) and (**8a**) has the oxygen atoms with large vibrational freedom, as reflected in the thermal parameters. As a consequence, the observed Cl–O distances and O–Cl–O angles are not in agreement with those expected from tetrahedral geometry. Furthermore, ClO_4^- of compound (**4a**), which is not involved in hydrogen bonding, has the largest static disorder with respect to the other compounds. In particular O(2), O(3), and O(4) are present as two half-atoms generated by rotation of the tetrahedron around the Cl–O(1) direction.

The molecular packing is determined by hydrogen bonds of the type NH • • • O, in which an oxygen atom of the ClO_4^- ion is bonded to a hydrogen-substituted N atom. For compound (**1a**) N(2) • • • O(2)^{i} 2.87, H(2) • • • O(2)^{i} 2.25 Å; N(2)–H(2) • • • O(2)^{i} 146.7°; i = $x, y, 1 + z$; for compound (**6a**) N(3) • • • O(1)^{ii} 2.83, H(30) • • • O(1)^{ii} 2.12 Å, N(3)–H(30) • • • O(1)^{ii} 143.4°; ii = $1 + x, y, z$; for compound (**8a**) N(3) • • • O(2)^{iii} 2.97, H(32) • • • O(2)^{iii} 1.99 Å; N(3)–H(32) • • • O(2)^{iii} 149.3°; iii = $x - \frac{1}{2}, \frac{1}{2} - y, z$. Other contacts are consistent with van der Waals interactions.

(d) *Energy Calculations and Conformational Conclusions.*— Quantum mechanical calculations were performed on a number of the compounds examined, in order to analyse the energy behaviour as a function of the angle of rotation around the exocyclic C–N bond in the light of the experimental trends shown by these molecules.

The calculations were performed in the framework of the semi-empirical CNDO/2 method,[24] which has been proved[1,2] to give reasonable understanding of the internal rotation of the *NN*-dimethylamino group in derivatives of heterocyclic compounds. More sophisticated methods were not employed, owing to the large molecular sizes involved.

For compounds (**1**)—(**7**) and for their *N*-protonated forms, calculations were performed by employing fictitious geometries constructed from standard bond lengths and angles,[25] while for ions (**1a**)—(**4a**), (**6a**), and (**8a**) experimental geometries were employed. In the experimental geometries the atoms of the heterocyclic ring deviate significantly from coplanarity, as pointed out in the previous section, while fictitious geometries were assumed to be perfectly planar.

The results of calculations are collected in Table 5.

For compounds (**1**)—(**3**) the energy pattern shows a minimum corresponding to the planar disposition of the *NN*-dimethylamino group lying in the same plane of the heteroaromatic ring, while the transition state corresponds to a 90° rotation. The calculated energy barrier ΔE, as also found previously in similar systems,[2] turns out to be underestimated with respect to the experimental ΔG^* values.

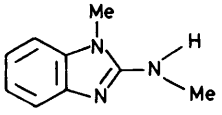
The approximate free energy of activation, $\Delta G^*(1)$ and $\Delta G^*(2)$, may be calculated by employing empirical equations[2] correlating the π-bond order in the exocyclic C–N bond referred

Table 5. Energy barriers ΔE for the rotation of the *NN*-dimethylamino or *N*-methylamino group and π-bond orders η for the exocyclic C–N bond calculated by employing the CNDO/2 method; energy of activation $\Delta G^*(1)$ calculated by the empirical expression reported in ref. 2 and experimental values of free energy of activation (298 K), where measured. Energy values are in kJ mol^{-1}

Compound	$\Delta G^*_{exp.}$	$\Delta G^*(1)$	η_{min} [a]	$\eta_{90°}$ [b]	ΔE [c]
(**1**)		34.36	0.3346 (0°)	0.1975	26.70
(**2**)	50.39	46.78	0.3660 (0°)	0.2081	30.76
(**3**)	47.46	48.64	0.3707 (0°)	0.2014	52.14
(**4**)			0.2747 (40°)	0.1973	13.49
(**5**) [d]		34.84	0.3358 (0°)	0.2062	31.73
		33.89	0.3334 (0°)		29.89
(**6**) [e]		34.24	0.3343 (0°)	0.2060	31.15
(**7**) [f]		34.32	0.3345 (0°)	0.2151	35.73
(**1a**) [g,h]			0.5330 (30°)	0.3164	49.33
[≡(**4b**)]					
(**2a**) [g]		144.19	0.6123 (0°)	0.3294	84.27
(**3a**) [g]		149.41	0.6255 (0°)	0.3141	126.00
(**4a**) [g]			0.3826 (41.3°)	0.2642	19.48
(**5a**) [e]		69.88	0.4244 (0°)	0.2332	57.12
[≡(**6b**)]					
(**6a**)			0.2925 (55°)	0.2303	18.43
(**8a**) [g,h]			0.3557 (16.5°)	0.2348	14.35
(**1b**)		78.17	0.4453 (0°)	0.2326	42.85
(**2b**)	62.46	107.37	0.5192 (0°)	0.2590	59.30
(**3b**)	63.69	120.31	0.5519 (0°)	0.2602	85.67
(**5b**)		73.91	0.4346 (0°)	0.2366	45.56

[a] Referred to the energy minimum of the rotational path: in parentheses is reported the corresponding angle of rotation relative to the planar conformation. [b] Referred to the perpendicular conformation. [c] Referred to the energy difference between the minimum and the perpendicular conformation. [d] Referred to the NHMe group: the results in the first line correspond to the planar ground state having the proton on the amino group and that on the heterocyclic ring in a *syn* configuration while the second line corresponds to the *anti* configuration. [e] Referred to the NHMe group: the minimum refers to the planar conformation having the methyl of the amino group and that on the heterocyclic ring in an *anti* configuration. [f] Referred to the NH_2 group. [g] Calculations of energy differences and bond orders are performed with the experimental geometry. [h] The atoms of the penta-atomic ring are distorted from planarity.

* For details of Supplementary Publications see Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1985, Issue 1.



(9)

to the planar ground state, [$\Delta G^*(1)$], or calculated ΔE values [$\Delta G^*(2)$], to the experimental ΔG^* values. From Table 5 it appears that the $\Delta G^*(1)$ values are close to the experimental values even if they show an increasing order from compound (**1**) to (**3**): the difference between compounds (**2**) and (**3**) is small and contrary to the experimental trend, but we believe that the experimental results referred to these compounds should be considered practically coincident within experimental error. By employing the calculated energy barriers ΔE, $\Delta G^*(2)$ values thus obtained turn out to be greatly overestimated and they will not be included in our discussion.

For compound (**4**) the energy minimum does not correspond to the planar conformation and the plane of the *NN*-dimethylamino group is twisted by 40° with respect to the plane of the heteroaromatic ring, while the all-planar conformation has the highest energy content. This situation is in line with the conclusions drawn on the basis of ^{1}H chemical shifts. The lower stability of the all-planar conformation should be due to steric interactions between one of the methyl groups on the amino nitrogen and that bonded to the heterocyclic nitrogen. One may thus expect that the energy barrier for this molecule is lower than in compounds (**1**)—(**3**), owing to the increased energy content of the ground state: this may be at the origin of the lack of any change in the n.m.r. spectrum in the range of temperatures examined.

For compound (**5**) two energy minima are found corresponding to the all-planar conformations having the proton on the amino group *syn* or *anti* with respect to that on the heterocyclic ring: the former conformation is slightly more stable. The calculated $\Delta G^*(1)$ values indicate that the internal barrier should be not too different from that present in compound (**1**).

In compound (**6**) the planar conformation having the methyl group on the amino substituent *anti* with respect to that on the heterocyclic nitrogen (**9**) corresponds to the minimum of the energy pattern while the other planar conformation corresponds to the highest value. Thus, for this molecule the planar conformation described above should prevail almost entirely. The presence of this conformation in a large amount with respect to the situation of the other derivatives, where the two planar conformations have identical or almost identical [compound (**5**)] energy content, could be at the origin of the higher ^{1}H chemical shift of the N_R-Me group with respect to the other compounds. The $\Delta G^*(1)$ value predicts a barrier close to that of derivative (**1**), even if, from the calculated energy pattern, one would expect that once the molecule has reached the perpendicular transition state it would return to the same planar conformation (**9**). Attempts to measure the internal dynamic behaviour of this molecule were carried out in CF_2Cl_2 solution, but the ^{1}H n.m.r. spectrum did not show appreciable changes down to 143 K: this finding does not contradict the theoretical predictions.

In compound (**7**) the calculated energy pattern resembles that of compound (**1**) and even the $\Delta G^*(1)$ values for the two molecules are very close.

For the *N*-methylated molecules, the calculated ground state corresponds to all-planar conformations in compounds (**2a**), (**3a**), and (**5a**) [≡(**6b**)]: for compound (**5a**) the planar conformation having the methyl group on the amino nitrogen *anti* to that on the nitrogen atom of the heterocyclic ring corresponds to an energy minimum, while the highest energy content corresponds to the other planar conformation. This situation resembles that encountered in derivative (**6**). For compounds (**1a**), (**4a**), (**6a**), and (**8a**) the ground state corresponds to a conformation where the amino group is twisted with respect to the plane of the heterocyclic ring. These features should be related to the differences in ^{1}H chemical shifts found for the Me groups, which could thus be attributed to peculiarities in the conformational properties of these molecules.

Table 6. Experimental and calculated[a] angles of twist (absolute values) between the plane of the amino group and the plane of the heterocyclic ring

Compound	Calculated	Experimental
(**1a**)	30.3	24.0
(**2a**)	0.0	1.3
(**3a**)	0.0	11.5
(**4a**)	41.3	41.3
(**6a**)	0.0	7.7
(**8a**)	16.5	6.9

[a] Corresponding to the minimum of the CNDO/2 total energy calculated in function of the angle of rotation of the *NN*-dimethylamino, *N*-methylamino, and amino group

The angles of twist in the conformations of minimum energy are reported in Table 6 together with the experimental geometries determined for the compounds in the solid state: the agreement may be considered satisfactory when it is borne in mind that the results refer to physical states which are not comparable. Further, within a range of 10—12° of this angle a molecule may still be considered very near to an all-planar situation.

For the *N*-methylated derivatives dynamic n.m.r. experiments could not be performed owing to the low solubility of the compounds in the solvents employed for low-temperature measurements.

The energy barriers estimated from π-bond orders, $\Delta G^*(1)$, in compounds (**2a**) and (**3a**), where the ground state seems to be planar, are higher than in the corresponding bases, but the values are probably overestimated, as occurs for the corresponding protonated molecules (**2b**) and (**3b**).

In the protonated molecules the calculated ground state corresponds to the all-planar situation, except in derivative (**4b**) [≡(**1a**)]. These features still agree with the conclusions from ^{1}H chemical shifts. For derivatives (**1b**)—(**3b**), and (**5b**), the estimated $\Delta G^*(1)$ values show that for these molecules the energy barriers are higher than in the corresponding bases, even if they are probably overestimated. This may be confirmed for compounds (**2b**) and (**3b**), where the comparison with experimental values is possible. Also in previous work [2] we have verified that calculated energy barriers for ionic derivatives with respect to the free bases are largely overestimated both by semi-empirical and *ab initio* methods; and this is probably due either to an improper extension of correlations obtained from neutral molecules to ionic compounds, or to effects due to solute–solvent interactions. These interactions should in fact tend to diffuse the charge of the cation on the solvent lattice, especially in the case of polar solvents, with consequent lowering of the effect of internal charge delocalization on the energy barrier.

Experimental

M.p.s were obtained on a Büchi apparatus (uncorrected). Mass spectra were recorded on a Varian Mat 112 using g.l.c. or direct insertion. Physical and analytical data of new compounds are reported in Table 7. N.m.r. spectra were recorded in [$^2H_6$]-DMSO solution or in D_2O–$(CD_3)_2CO$ (1:2) solvent mixture, at 200 MHz for ^{1}H and 50.3088 MHz for ^{13}C, employing a Varian

Table 7. Physical and analytical data of compounds

Compound	M.p. (°C)	Found (%) C	H	N	S	Formula	Required (%) C	H	N	S	*m/z* (fragment, % rel. intensity)
(1)	260 (decomp.)	67.2	6.7	26.2		$C_9H_{11}N_3$	67.05	6.9	26.1		161 (*M*, 100); 146 (*M*–Me, 73); 132 (*M*–NMe, 62)
(2)	88—89	66.7	6.4	17.0		$C_9H_{10}N_2O$	66.6	6.2	17.3		162 (*M*, 100); 147 (*M*–Me, 88); 133 (*M*–NMe, 28); 120 (*M*–NMe_2, 36)
(3)	86—88	60.5	5.4	15.9	18.1	$C_9H_{10}N_2S$	60.6	5.65	15.7	18.0	178 (*M*, 100); 163 (*M*–Me, 49); 149 (*M*–NMe. 85); 136 (*M*–NMe_2, 47)
(4)	(*a*)	68.6	7.6	23.7		$C_{10}H_{13}N_3$	68.5	7.5	24.0		175 (*M*, 4); 160 (*M*–Me, 23); 146 (*M*–NMe, 96); 131 (*M*–NMe_2, 100)
(5)	165—167	65.2	6.3	28.5		$C_8H_9N_3$	65.3	6.2	28.55		147 (*M*, 55); 132 (*M*–Me, 8); 118 (*M*–NMe, 67)
(6)	180—181	67.1	7.0	25.9		$C_9H_{11}N_3$	67.05	6.9	26.1		161 (*M*, 100); 146 (*M*–Me, 24); 131 (*M*–2Me, 56)
(1a; $A^- = I^-$)	195—197	39.5	4.7	13.8		$C_{10}H_{14}IN_3$	39.6	4.65	13.9		175 (*M*–HI, 60); 160 (*M*–HI–Me, 74); 142 (MeI, 100)
(2a; $A^- = I^-$)	201—202	39.6	4.2	9.1		$C_{10}H_{13}IN_2O$	39.5	4.3	9.2		162 (*M*–MeI, 100); 147 (*M*–MeI–Me, 88); 142 (MeI, 98)
(3a; $A^- = I^-$)	184—185	37.7	4.2	8.6	9.9	$C_{10}H_{13}IN_2S$	37.5	4.1	8.75	10.0	178 (*M*–MeI, 100); 163 (*M*–MeI–Me, 72); 149 (*M*–MeI–NMe, 89)
(4a; $A^- = I^-$)	234—235	41.6	5.2	13.1		$C_{11}H_{16}IN_3$	41.65	5.1	13.25		175 (*M*–MeI, 79); 160 (*M*–MeI–Me, 80); 146 (*M*–MeI–NMe, 60); 142 (MeI, 100)
(5a; $A^- = I^-$)	217—218	37.2	4.0	14.6		$C_9H_{12}IN_3$	37.4	4.2	14.5		161 (*M*–HI, 53); 146 (*M*–HI–Me, 21); 131 (*M*–HI–2Me, 40); 128 (HI, 100)
(6a; $A^- = I^-$)	212—213	39.8	4.55	13.6		$C_{10}H_{14}IN_3$	39.6	4.6	13.9		161 (*M*–MeI, 48); 146 (*M*–MeI–Me, 19); 128 (HI, 100)
(1a; $A^- = ClO_4^-$)	270—271	43.8	5.3	15.25		$C_{10}H_{14}ClN_3O_4$	43.6	5.1	15.2		175 (*M*–$HClO_4$, 91); 160 (*M*–$HClO_4$–Me, 100); 146 (*M*–$HClO_4$–NMe, 82)
(4a; $A^- = ClO_4^-$)	212—214	45.7	5.8	14.6		$C_{11}H_{16}ClN_3O_4$	45.6	5.6	14.5		189 (*M*–$HClO_4$, 18); 175 (*M*–$MeClO_4$, 88); 160 (*M*–$MeClO_4$–Me, 100); 146 (*M*–$MeClO_4$–NMe, 71)
(6a; $A^- = ClO_4^-$)	198—199	43.6	5.0	15.4		$C_{10}H_{14}ClN_3O_4$	43.6	5.1	15.2		175 (*M*–$HClO_4$, 88); 160 (*M*–$HClO_4$–Me, 100); 146 (*M*–$HClO_4$–NMe, 55)

[a] b.p. 110—112 °C/2 × 10^{-4} mmHg

XL 200 spectrometer. The concentration was 0.2M for derivatives (**2**)—(**4**), while saturated solutions were employed for the other derivatives, owing to the low solubility of the compounds. The *N*-protonated compounds were obtained both by adding trifluoroacetic acid directly to the solutions of the free bases in the n.m.r. sample tubes and by treating the free bases with hydroiodic acid. In the latter case the salts were isolated, purified, and then dissolved in the selected solvents for n.m.r. analysis. Tetramethylsilane was added to the samples as internal standard.

Variable-temperature measurements were carried out on a JEOL JNM-C60-HL spectrometer (60 MHz for ^1H) equipped with a JNM-NT-C60-HL variable-temperature unit. The temperature reading was calibrated from the difference in chemical shifts between the OH proton and the methylene protons of ethylene glycol for the measurements above room temperature, and from the difference in the chemical shifts of the OH proton and the methyl protons of methanol for those below room temperature (estimated error in temperature reading ± 0.5 °C). Band-shape calculations were performed on a Cyber 76 CDC computer.

2-Methylamino (**5**) *and* (**6**) *and 2-Dimethylamino* (**1**)—(**4**) *Derivatives.—General preparation procedure.* The corresponding (known or commercial) 2-chloro heterocyclic compound (5 mmol) was dissolved in a Carius tube with either 30% aqueous $MeNH_2$ or 30% aqueous Me_2NH (10 ml). After 15 h at 160 °C, the mixture was cooled, diluted with H_2O (100 ml), and then extracted with CH_2Cl_2 (3 × 20 ml). The organic phase was dried over Na_2SO_4 and then evaporated under reduced pressure. The product was isolated (62—88% yield) and purified by distillation [(**4**), b.p. 110—112 °C at 2 × 10^{-4} mmHg] or by crystallization from H_2O–$(CH_3)_2CO$ (1:1) [(**1**) and (**5**)], C_6H_6 [(**6**)], or n-hexane [(**2**) and (**3**)].

Methiodides (**1a**)—(**4a**) *and* (**6a**).—*General preparation procedure.* These were obtained from the corresponding base (5 mmol) and CH_3I (5.5 mmol) in C_6H_6 (30 ml) at reflux for 24 h. Cooling and filtration afforded the salt derivative, which was purified by crystallization [H_2O–$(CH_3)_2CO$, 1:1], yields 72—91%.

Methiodide (**5a**).—This was prepared by treating the base (**6**) (6 mmol) with HI (6.5 mmol) in C_6H_6 (30 ml) for 5 min. The solid was filtered and purified by repeated crystallization [H_2O–$(CH_3)_2CO$, 1:1], yield 83%.

Perchlorate Salts (**1a**), (**4a**) *and* (**6a**).—*General preparation procedure.* The corresponding methiodide (3 mmol) was dissolved in H_2O–$(CH_3)_2CO$ (1:1, 10 ml) and treated with solid $AgClO_4$ for 1 h with stirring. After filtration of AgI, the mother liquid afforded on slow evaporation crystalline material suitable for *X*-ray analysis.

Crystal Structure of 1-Methyl-2-dimethylaminobenzimidazolium Perchlorate (**1a**).—The compound was recrystallized from methanol as tabular prisms elongated on [010]. Lattice constants were determined using the program CTDIF[26] which repeatedly rectifies on the diffractometer the values of $(\theta,\chi,\varphi)_{hkl}$ angles of 29 reflections to have the maximum of the peak when the angles are moving not more than 0.01°.

Crystal data. $C_{10}H_{14}ClN_3O_4$, M = 275.7. Monoclinic, a = 19.081(5), b = 6.760(2), c = 9.765(3) Å, β = 103.6(1)°, U = 1 224.3 Å^3; Z = 4; D_c = 1.50 g cm^{-3}, Cu-K_α radiation; μ(Cu-K_α) = 29.2 cm^{-1}. Space group $C2$ from structure determination.

Intensity data were collected on a Siemens AED single-crystal diffractometer up to θ 70°. To collect every reflection the angles were determined on the basis of the orientation matrix and a measuring scan, along the θ circle, was made collecting the outline of the peak. 1 330 Independent reflections were measured, of which 1 048 were used in the crystal analysis, having intensities $> 2[\sigma^2(I) + 10^{-4}I^2]^{\frac{1}{2}}$, where I is the relative intensity and $\sigma^2(I)$ its variance. The dimensions of the crystal roughly in the x,y,z directions were 0.05, 0.71, and 0.19 mm. No absorption correction was applied.

Structure analysis and refinement. The structure was solved by direct methods by use of the system of computer programs written by Sheldrick.[27] The structure was refined by cycles of full-matrix anisotropic least-squares (hydrogen atoms isotropically) up to R = 0.074, R_w = 0.077. The hydrogen atoms of the phenyl ring and of N(2) were located in a difference-Fourier map.

Crystal Structure of 3-Methyl-2-dimethylaminobenzoxazolium Iodide (**2a**).—Crystals were prisms elongated on [010]. Cell parameters were derived as before and lattice parameters were refined from 25 $(\theta,\chi,\varphi)_{hkl}$ measurements.

Crystal data. $C_{10}H_{13}IN_2O{\cdot}H_2O$, M = 322.3. Monoclinic, a = 24.307(5), b = 6.891(1), c = 14.347(2) Å, β = 90.7(1)°; U = 2 402.9 Å^3; Z = 8; D_c = 1.78 g cm^{-3}; Mo-K_α radiation, λ = 0.710 69; μ(Mo-K_α) = 26.2 cm^{-1}. Space group $C2/c$ from structure determination.

Intensity data were collected as before. Of 3 258 independent reflections measured, 2 017 were used in the crystal analysis. The dimensions of the crystal used were 0.38, 0.47, and 0.15 mm. No absorption correction was applied.

Structure analysis and refinement. The structure was solved by use of the same program routine as before and refined by cycles of full-matrix anisotropic least-squares (hydrogen atoms isotropically) up to R = 0.047, R_w = 0.049. The hydrogen atoms of the phenyl ring were located in a difference-Fourier map. The hydrogen atoms of the water molecule could not be located from a final difference map and therefore were not included in the refinement.

Crystal Structure of 3-Methyl-2-dimethylaminobenzothiazolium Iodide (**3a**).—Crystals were prisms elongated on [010]. Cell parameters were derived as before and lattice parameters were refined from 29 $(\theta,\chi,\varphi)_{hkl}$ measurements.

Crystal data. $C_{10}H_{13}IN_2S$, M = 320.2. Monoclinic, a = 14.423(4), b = 7.434(3), c = 10.869(2) Å, β = 98.8(1)°; U = 1 151.7 Å^3; Z = 4; D_c = 1.85 g cm^{-3}. Mo-K_α radiation; μ(Mo-K_α) = 28.9 cm^{-1}. Space group $P2_1/n$ from systematic absences.

Intensity data were collected as before. Of 3 141 independent reflections collected, 2 027 were used in the crystal analysis. The dimensions of the crystal used were 0.24, 0.33, and 0.24 mm. No absorption correction was applied.

Structure analysis and refinement. The structure was solved by use of the same program routine as before and refined by cycles of full-matrix anisotropic least-squares (hydrogen atoms isotropically) up to R = 0.031, R_w = 0.032. The hydrogens of the phenyl ring were located in a difference-Fourier map.

Crystal Structure of 1,3-Dimethyl-2-dimethylaminobenzimidazolium Perchlorate (**4a**).—Crystals were prisms elongated along [100]. Preliminary cell dimensions and space group were obtained from rotation and Weissenberg photographs. Lattice parameters were refined by least-squares from eighteen $(\theta,\chi,\varphi)_{hkl}$ measurements taken on a Siemens single-crystal diffractometer.

Crystal data. $C_{11}H_{16}ClN_3O_4$, M = 289.7. Monoclinic, a = 6.898(5), b = 18.845(7), c = 11.127(6) Å, β = 109.5(1)°, U = 1 363.5 Å^3; Z = 4; D_c = 1.41 g cm^{-3}; Cu-K_α radiation; μ(Cu-K_α) = 26.5 cm^{-1}. Space group $P2_1/c$ from systematic absences.

Intensity data were collected up to θ 70° by use of the ω–2θ scan method and the five-points technique[28] with nickel-filtered Cu-K_α radiation on the same single-crystal diffractometer. Of

2 688 independent reflections measured, 1 377 were used in the crystal analysis. The dimensions of the crystal used were 0.52, 0.14, and 0.19 mm. No absorption correction was applied.

Structure analysis and refinement. The structure was solved by use of the same program routine as before and refined by cycles of full-matrix anisotropic least-squares (hydrogen atoms isotropically) up to R 0.060, $R_w = 0.069$.

Crystal Structure of 1,3-*Dimethyl*-2-*methylaminobenzimidazolium Perchlorate* (**6a**).—The compound was recrystallized from methanol as prisms elongated on [010]. Cell parameters were derived as before and lattice parameters refined from twenty-two $(\theta,\chi,\varphi)_{hkl}$ measurements.

Crystal data. $C_{10}H_{14}ClN_3O_4$, $M = 275.7$. Monoclinic, $a = 6.238(2)$, $b = 8.333(3)$, $c = 11.751(4)$ Å, $\beta = 95.9(1)°$, $U = 607.6$ Å^3; $Z = 2$; $D_c = 1.51$ g cm^{-3}, Cu-K_α radiation; μ(Cu-K_α) = 29.5 cm^{-1}. Space group Pn from structure determination.

Intensity data were collected as before. Of 1 307 independent reflections measured, 871 were used in the crystal analysis. The dimensions of the crystal used were 0.13, 0.52, and 0.15 mm. No absorption correction was applied.

Structure analysis and refinement. The structure was solved by use of the same program routine as before and refined by cycles of full-matrix anisotropic least-squares (hydrogen atoms isotropically) up to R 0.059, R_w 0.058. Only the hydrogen of N(3) was located in the difference-Fourier map.

Crystal Structure of 1,3-*Dimethyl*-2-*aminobenzimidazolium Perchlorate* (**8a**).—Crystals, obtained from acetone–water (1:1) solution, were tabular plates elongated on [001]. Cell parameters were derived as for compound (**1a**) and were refined from 20 $(\theta,\chi,\varphi)_{hkl}$ measurements.

Crystal data. $C_9H_{12}ClN_3O_4$, $M = 261.7$. Orthorhombic, $a = 10.069(5)$, $b = 19.449(6)$, $c = 5.892(3)$ Å; $Z = 4$; $D_c = 1.51$ g cm^{-3}; $U = 1\,153.8$ Å^3; Cu-K_α radiation, $\lambda = 1.5418$ Å, μ(Cu-K_α) = 30.7 cm^{-1}. Space group $Pna2_1$ from structure determination.

Intensity data were collected as for (**1a**). Of 1 327 independent reflections measured, 659 were used in the crystal analysis. The dimensions of the crystal used were 0.14, 0.04, and 0.57 mm. No absorption correction was applied.

Structure analysis and refinement. The structure was solved by use of the same program routine as before and refined by a few cycles of full-matrix anisotropic least-squares up to R 0.084. A difference-Fourier synthesis computed at this stage revealed significant residual peaks near the positions where the hydrogen atoms were expected to occur only for N(3) atom. So the other hydrogen atoms were included in refinement with geometrically calculated positional parameters. The hydrogens in the methyl groups were refined as rigid groups. The weighting function was of the form $1/w = \sigma^2(F_0) + 0.005F_0^2$. The final agreement factor R was 0.065, $R_w = 0.072$.

For all compounds atomic scattering factors were from ref. 29 for non-hydrogen atoms and from ref. 30 for hydrogen. Thermal parameters and other data are in SUP 56275. All calculations relating to the crystal structure were carried out on the CDC Cyber 76 computer of Consorzio per la Gestione del Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Casalecchio, Bologna, Italy. Bibliographic searches were carried out using the Cambridge Crystallographic Data Files through the Servizio Italiano di Diffusione dei Dati Cristallografici, Parma, Italy.

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