The Structure of *N*-Aminoazoles: an Experimental (X-Ray and ^{15}N NMR) and Theoretical Study

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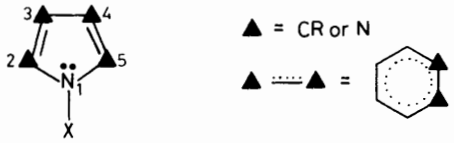
INDO calculations with complete optimization of the geometries (INDO‖INDO) have been carried out on the seventeen parent *N*-methyl and *N*-aminoazoles. The results are consistent with the available experimental evidence and provide a coherent picture of the conformation of the sp^3 amino group. The nitrogen-15 chemical shifts of eleven *N*-aminoazoles have been determined for the first time. Experimental determination of the geometry by X-ray crystallography has been carried out on 1-aminobenzimidazole: $P2_1/n$, a = 7.972 5(4), b = 11.041 1(4), c = 7.525 1(3) Å, β = 94.435(3)°, and on 2-aminobenzotriazole: $P2_1/c$, a = 11.590 0(5), b = 4.603 1(8), c = 12.559 1(8) Å, β = 109.914(4)°.

One of the most basic features of neutral heteroaromatic compounds is the azole N–X bond, which has no equivalent either in aromatic derivatives or in azines.



X = COR, azolides
X = azole, *N,N'*-biazoles
X = CH_3, *N*-methylazoles
X = NH_2, *N*-aminoazoles

For many years, we have focused our research on this bond, studying, for example, azolides,[1] *N,N'*-biazoles,[2] and many other functional groups.[3] From our previous work, we would like to stress two points. (i) In a theoretical study of *N*-methylazoles,[4,5] we discussed the effect of this substituent on the basicity of the azole and concluded that the difference between *C*-methyl and *N*-methyl substitution was the absence of hyperconjugation in the latter. (ii) When the effect of eighteen substituents (X) on the chemical shifts of carbon atoms at positions 2 and/or 5 were compared with SCS in benzenes (*ortho* C), two substituents, amino and methoxy, behaved abnormally, having much larger effects as *C*-substituents than as *N*-substituents.[6]

In order to obtain a better understanding of the structure of *N*-aminoazoles we decided to carry out (*a*) a theoretical study, within the INDO approximation, and (*b*) an experimental determination of the *N*-aminoazole properties, including two X-ray structures and the ^{15}N chemical shifts of eleven derivatives.

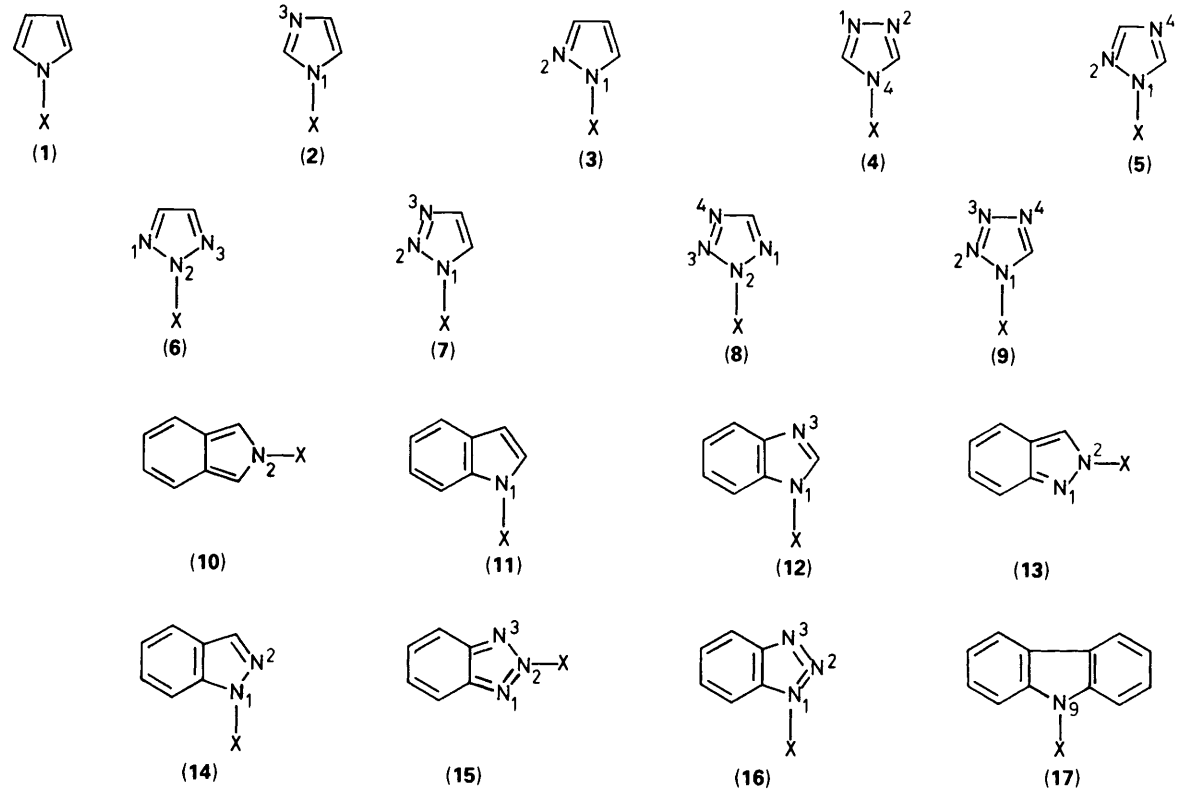
Experimental

1-Aminopyrrole (**1b**),[7] 1-aminoimidazole (**2b**),† 1-aminopyrazole (**3b**),[8] 1-amino-1,2,4-triazole (**5b**),[9] 1-aminobenzimidazole (**12b**),[9] 2-aminoindazole (**13b**),[10] 1-aminoindazole (**14b**),[10] 2-aminobenzotriazole (**15b**),[11] 1-aminobenzotriazole (**16b**),[11] and 9-aminocarbazole (**17b**)[12] were prepared according to literature procedures. 4-Amino-1,2,4-triazole (**4b**) is a commercial product. ^{15}N-labelled pyrazole was obtained from tetramethoxypropane and $^{15}NH_2$–$^{15}NH_2$ following a previously described synthesis.[13]

^{15}N NMR spectra were recorded on two instruments, a Bruker AC250 [compounds (**1b**), (**3b**), (**4b**), (**5b**), (**13b**), (**14b**), and (**17b**)] and a Bruker AC200 [compounds (**2b**), (**12b**), (**15b**), and (**16b**)], working at 25.35 and 20.29 MHz, respectively. As the experimental conditions are similar we will describe those used with the 250 MHz instrument with the data for the 200 MHz instrument in brackets when necessary. Samples were dissolved in [$^2H_6$]DMSO; the concentration was 10–25% (w/v) and the internal diameter of the tube was 10 mm. Nitromethane was used as an external standard and chemical shifts are expressed in ppm. No corrections for bulk differences were applied. Typical conditions were as follows: 90° pulse angle; spectral width 15.5 kHz; data points, 32K (16K), pulse repetition time for compounds (**1b**), (**2b**), (**3b**), (**4b**), (**5b**), (**12b**), and (**14b**), 20 s (10 s) and pulse repetition time in the presence of $Cr(acac)_3$ for compounds (**13b**), (**15b**), (**16b**), and (**17b**), 15 s (5 s); continuous broad-band proton decoupling. In all cases, it was necessary to accumulate 5 000–10 000 transients in order to obtain spectra with an acceptable signal-to-noise ratio.

^1H–^{15}N spin-coupling constants were determined with the aid of the polarization-transfer pulse sequence INEPT.[14] The width of a nitrogen 90° pulse was 25 μs (19 μs) and the width of a proton 90° pulse was 18 μs (14 μs). The delay time between the

† This compound was prepared according to the procedure described for 1-amino-1,2,4-triazole (**5b**) and 1-aminobenzimidazole (**10b**).[9] Using this method a 1:1 mixture of imidazole and 1-aminoimidazole (**2b**) was obtained. This difficult separation involves the preparation of the Schiff base (m.p. 114–115 °C), by reaction with benzaldehyde, and its subsequent hydrolysis with concentrated hydrochloric acid (6 h reflux). After purification by column chromatography (chloroform–ethanol, 9:1 on silica gel) the pure oily compound (**2b**) was obtained with a total yield of 21%.



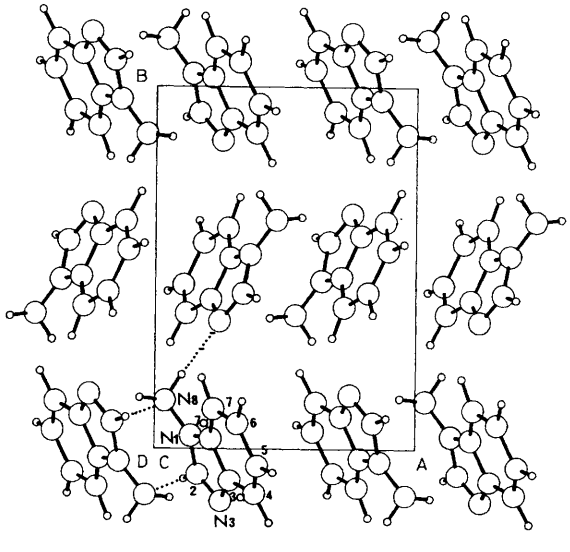


Figure 1. A view of the crystal structure of (**12b**) along the *c*-axis showing the atomic numbering and the independent part of the H-interaction network.

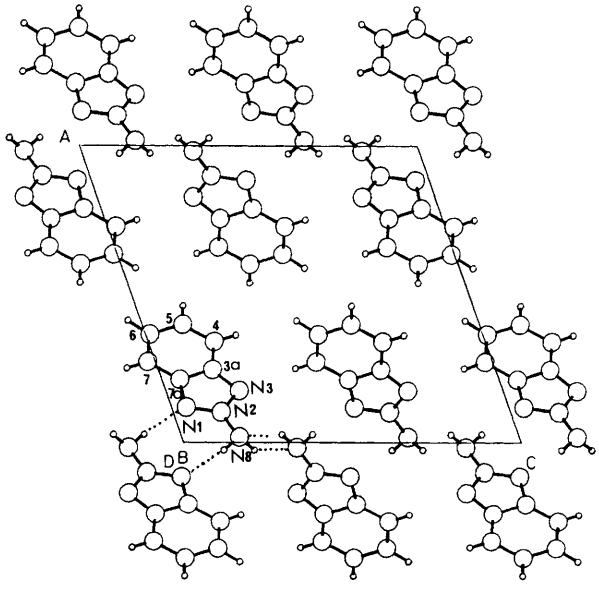


Figure 2. A view of the crystal structure of (**15b**) along the *b*-axis showing the atomic numbering and the independent part of the H-interaction network.

pulses was 0.003 ms which corresponds to a J value of about 80 Hz ($1/4\ J_{NH}$).[15]

Crystal Structure Determination.—The crystallography analysis is summarized in Table 1. Scattering factors were taken from ref. 16. The structures were solved by direct methods[17] and refined by full-matrix least-squares methods.[18] All hydrogen atoms were unambiguously obtained from difference synthesis and included isotropically in the final stages of refinement. Weights were chosen as to give no trends in $w\Delta^2F$ *vs.* $|F_{obs}|$ and

Table 1. Crystal analysis parameters at room temperature.

Compound	(12b)	(15b)
Formula	$C_7H_7N_3$	$C_6H_6N_4$
Crystal habit	Transparent prism	
Crystal size/mm	0.33 × 0.10 × 0.17	0.30 × 0.10 × 0.07
Symmetry	$P2_1/n$	$P2_1/c$
Unit cell determination:	Least-squares fit from 58 and 70 reflections ($\theta < 45°$)	
a/Å	7.972 5(4)	11.590 0(5)
b/Å	11.041 1(4)	4.603 1(8)
c/Å	7.525 1(3)	12.559 1(8)
β/°	94.435(3)	109.914(4)
V/Å^3	660.4(1)	630.0(1)
Z	4	4
D_c/g cm^{-3}	1.339	1.414
M	133.15	134.14
F(000)	280	280
Technique	Four-circle diffractometer, Philips PW1100, bisecting geometry graphite oriented monochromator: Cu-K_α ω/2θ scans, scan width: 1.6°, detector apertures 1.0 × 1.0°	
Total measurements	Up to 65° in θ	
Speed	1 min per reflec.	
Independent reflections	1 123	1 076
Observed reflections [$3\sigma(I)$]	841	888
Standard reflections:	2 reflections every 90 minutes, no variation	
Number of variables	119	115
Final shift/error	0.03	0.02
Final ΔF peaks (e Å^{-3})	0.18	0.25
Final R *and* R_w	0.052, 0.059	0.056, 0.056

Table 2. Final atomic co-ordinates for (**12b**).

Atom	x	y	z
N(1)	0.137 5(3)	0.035 6(2)	0.291 1(3)
C(2)	0.164 1(3)	−0.070 9(2)	0.205 9(3)
N(3)	0.253 3(3)	−0.147 7(2)	0.306 0(3)
C(3A)	0.287 6(3)	−0.088 0(2)	0.467 4(3)
C(4)	0.381 3(3)	−0.124 7(2)	0.622 4(4)
C(5)	0.392 5(4)	−0.046 2(3)	0.765 6(4)
C(6)	0.315 1(4)	0.067 4(3)	0.756 1(4)
C(7)	0.226 1(3)	0.106 9(2)	0.603 6(3)
C(7A)	0.213 4(3)	0.026 8(2)	0.459 8(3)
N(8)	0.038 3(3)	0.130 2(2)	0.214 0(3)

Table 3. Final atomic co-ordinates for (**15b**).

Atom	x	y	z
N(1)	0.116 8(2)	0.742 6(4)	0.042 2(1)
N(2)	0.101 4(2)	0.715 4(4)	0.141 0(1)
N(3)	0.172 7(2)	0.536 2(4)	0.216 1(1)
C(3A)	0.244 7(2)	0.425 5(5)	0.159 9(2)
C(4)	0.339 5(2)	0.218 7(5)	0.194 1(2)
C(5)	0.397 8(2)	0.156 6(6)	0.119 3(2)
C(6)	0.363 8(2)	0.289 1(7)	0.011 7(2)
C(7)	0.271 1(2)	0.486 3(6)	−0.023 6(2)
C(7A)	0.210 9(2)	0.554 6(4)	0.052 8(2)
N(8)	0.017 6(2)	0.886 8(5)	0.169 1(2)

sin θ/λ. The final atomic co-ordinates are presented in Table 2 and 3 according to the numbering system given in Figures 1 and 2.[19]*

Table 4. Bond lengths/Å and bond angle/° for compounds (**12b**) and (**15b**).

(12b)		(15b)	
N(1)–C(2)	1.363(3)	N(1)–N(2)	1.319(3)
N(1)–C(7A)	1.367(3)	N(1)–C(7A)	1.363(3)
N(1)–N(8)	1.408(3)	N(2)–N(3)	1.312(2)
C(2)–N(3)	1.308(3)	N(2)–N(8)	1.386(3)
N(3)–C(3A)	1.390(3)	N(3)–C(3A)	1.363(3)
C(3A)–C(4)	1.396(4)	C(3A)–C(4)	1.406(3)
C(3A)–C(7A)	1.398(3)	C(3A)–C(7A)	1.399(3)
C(4)–C(5)	1.380(4)	C(4)–C(5)	1.362(4)
C(5)–C(6)	1.397(4)	C(5)–C(6)	1.410(4)
C(6)–C(7)	1.373(4)	C(6)–C(7)	1.360(4)
C(7)–C(7A)	1.395(3)	C(7)–C(7A)	1.401(4)
N(8)–H(10)	0.97(4)		
C(7A)–N(1)–N(8)	129.0(2)	N(3)–N(2)–N(8)	119.9(2)
C(2)–N(1)–N(8)	123.3(2)	N(1)–N(2)–N(8)	121.1(2)
C(2)–N(1)–C(7A)	107.6(2)	N(3)–N(2)–N(1)	118.8(2)
N(1)–C(2)–N(3)	112.7(2)	N(2)–N(1)–C(7A)	102.0(2)
C(2)–N(3)–C(3A)	104.9(2)	N(1)–C(7A)–C(3A)	108.5(2)
N(3)–C(3A)–C(7A)	109.9(2)	C(7A)–C(3A)–N(3)	108.6(2)
C(3A)–C(7A)–N(1)	104.9(2)	C(3A)–N(3)–N(2)	102.1(2)
N(1)–N(8)–H(9)	107(2)	N(2)–N(8)–H(9)	109(2)
N(1)–N(8)–H(10)	107(2)	N(2)–N(8)–H(10)	110(2)
H(9)–N(8)–H(10)	109(3)	H(9)–N(8)–H(10)	115(3)
N(8)–H(9)···N(3)[a]	170(2)	N(8)–H(9)···N(8)[c]	146(2)
N(8)···N(3)[a]	2.973(3)	N(8)···N(8)[c]	3.188(3)
N(8)–H(9)	0.95(3)	N(8)–H(9)	0.90(3)
H(9)···N(3)[a]	2.04(3)	H(9)···N(8)[c]	2.40(3)
C(2)–H(2)···N(8)[b]	174(3)	N(8)–H(9)···N(3)[d]	117(2)
C(2)···N(8)[b]	3.496(3)	N(8)···N(3)[d]	3.096(3)
C(2)–H(2)	0.99(3)	N(8)–H(9)	0.90(3)
H(2)···N(8)[b]	2.51(3)	H(9)···N(3)[d]	2.58(3)
		N(8)–H(10)···N(1)[e]	173(3)
		N(8)···N(1)[e]	3.092(2)
		N(8)–H(10)	0.91(3)
		N(8)···N(1)[e]	2.19(3)

[a] $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$. [b] $-x, -y, -z$. [c] $-x, -\frac{1}{2} + y, \frac{1}{2} - z$. [d] $-x, \frac{1}{2} + y, \frac{1}{2} - z$. [e] $-x, 1 - y, -z$.

Results and Discussion

Crystal and Molecular Structure of 1-*Aminobenzimidazole* (**12b**) *and* 2-*Aminobenzotriazole* (**15b**).—Selected geometrical parameters for compounds (**12b**) and (**15b**) are given in Table 4. It is worth noticing the sp^3 character of the N8 atom and the localization of the double bond character at C4–C5, C6–C7, for both compounds and at C2–N3 in (**12b**) while delocalization is observed in the triazole ring of (**15b**).[20] Moreover, the substituted nitrogen atoms, N1 and N2, in (**12b**) and (**15b**), although planar, are quite different, N2 in (**15b**) being more symmetrical (as indeed is the whole molecule). Not considering the amino hydrogen atoms, both molecules are quite planar, with the NH_2 group making angles of 89(2) and 51(2)° with the imidazole and the triazole rings respectively. Whereas for (**12b**) these hydrogen atoms are staggered with respect to the C7A atom [C7A–N1–N8–H9/H10 = −59(2)/58(2)°],[21] for (**15b**)

* Tables of thermal parameters, hydrogen atom co-ordinates and full lists of bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre. For details see 'Instructions for Authors (1990),' *J. Chem. Soc., Perkin Trans. 2*, in the January issue.

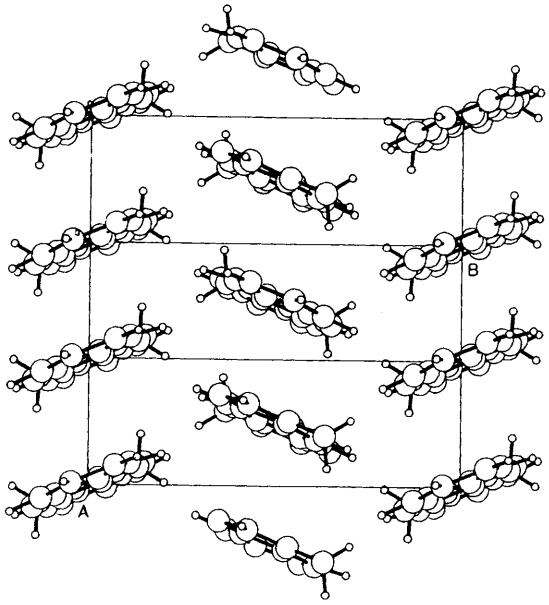


Figure 3. The herring backbone packing of (**12b**) seen along the *c*-axis, then rotated about *OB* to show the molecular planes.

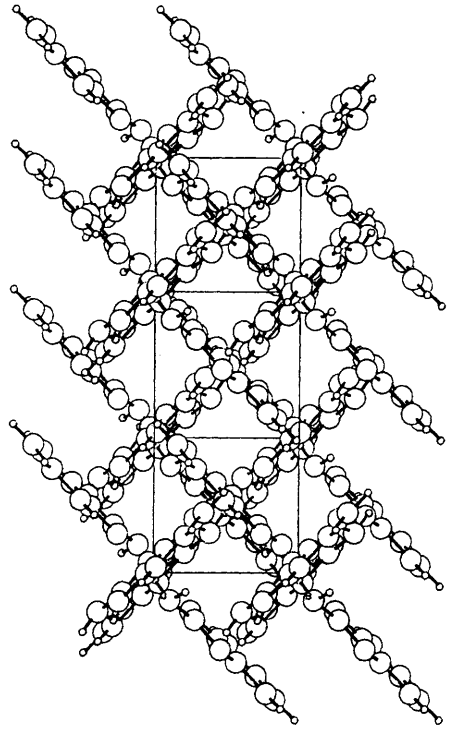


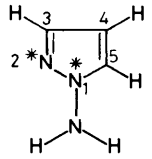
Figure 4. The molecular intercross packing of (**15b**) seen along the *a*-axis, then rotated about *OB* to show the molecular planes.

of the amino hydrogen atoms is almost coplanar with the N1 atom [N1–N2–N8–H9/H10 = 135(2)/8(2)°].[22] Crystals are built by chains with hydrogen interactions along the twofold axis. These chains are also linked by hydrogen interactions which form dimers through symmetry centres (see Figures 1 and 2 and Table 4). The differences are that in (**12b**) the dimers involve a CH hydrogen atom;[23,24] besides, one hydrogen of the NH_2 group is not involved in any bond: for (**15b**), only the NH_2 hydrogen atoms form the network. These networks give rise to the packing schemes shown in Figures 3 and 4.

This is the first time that the structures of simple *N*-aminoazoles are reported. Complexes of 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole with nickel(II) and rhodium(I) have been described.[21,22]

Nitrogen-15 *Chemical Shifts and* $^1J(^{15}N–^1H)$ *Coupling Constants of* N-*Aminoazoles in DMSO Solution.*—We have reported in Table 5 not only the present results on *N*-aminoazoles (**b**), but the relevant data of the corresponding *N*-methylazoles (**a**): ^{13}C chemical shifts of the *N*-methyl group,[6] their corresponding $^1J(^{13}C–^1H)$ coupling constants,[6] and ^{15}N chemical shifts of the nitrogen atoms (pyrrole-like, directly bonded to the methyl group, and pyridine-like).[25]

In addition to these data, the study of the labelled *N*-aminopyrazole (**3b′**) [$^{15}N(1)$, $^{15}N(2)$] in $CDCl_3$ provided some additional coupling constants [N(1) signal is broad, probably due to the interaction with the $^{14}NH_2$, and some coupling constants are lost].



(**3b′**)

$^1J[N(1)–N(2)] = 14.0$ Hz
$^1J[C(5)–N(1)] = 16.5$ Hz
$^1J[C(3)–N(2)] = 1.9$ Hz
$^2J[C(4)–N(1)] = 6.4$ Hz
$^3J[H(4)–N(1)] = 7.2$ Hz

The values of Table 5 can be discussed in several ways. Here are the most relevant conclusions:

(i) There is a linear relationship between the ^{15}N chemical shift of the amino group and the ^{13}C chemical shift of the methyl group for the eleven azoles of Table 5: $\delta^{15}N(NH_2) = -422.4 + 3.37\ \delta^{13}C(CH_3)$, $n = 11$, $r^2 = 0.983$. The goodness of fit is indicative that an *N*-azole as a substituent can be described by empirical parameters of the Hammett kind. The aniline ($\delta^{15}N = -320$ ppm)/toluene [$\delta^{13}C(CH_3) = 21.3$ ppm] pair does not belong to the above family. Thus, with regard to the methyl, the amino group acts differently on benzenes than in *N*-azoles (see Introduction) and reciprocally, the *N*-azole does not affect the amino group in the same manner as the phenyl group.

(ii) There is no relationship between the ^1J coupling constants of amino ($^{15}N–^1H$) and methyl groups ($^{13}C–^1H$) ($r^2 = 0.09$). It is known[15,25] that $^1J(^{15}N–^1H)$ coupling constants in aniline are very sensitive to medium effects. We have observed this behaviour for 1-aminopyrazole (**3b**) (Table 5). The absence of correlation between both ^1J coupling constants is probably due to the erratic nature of the $^1J(^{15}N–^1H)$ values in Table 5 (solvent, solute, and concentration effects).

(iii) Figure 5 represents the chemical shifts of ring nitrogen atoms of *N*-amines *vs.* *N*-methylazoles. Several correlations are found, all of them excellent, but the fact remains that the different kinds of nitrogens (pyrrole- and pyridine-like) are not in the same line.

Semiempirical Calculations.—Semiempirical calculations were carried out within the INDO approximation[26] with complete optimization of the geometry.[27] The 34 *N*-methyl and *N*-aminoazoles, (**1a**)–(**17b**), have been calculated. The corresponding NH derivatives either have been found in the literature,[28,29] or have been calculated for this work. When no indication is given about the conformation of the *N*-methyl and *N*-amino groups, the calculated properties correspond to the most stable conformer. The analysis of charge distribution is based on the Mulliken population analysis. Recently,[30] a 3-21G calculation of *N*-aminopyrrole (**1b**) has been published (see Table 7).

Geometries.—Ring geometries. The comparison of the calculated geometries for the benzimidazole ring, compound (**12b**), and for the 2*H*benzotriazole ring, compound (**15b**), with the

Table 5. Carbon-13 and nitrogen-15 NMR parameters (δ and ^1J) of *N*-methyl- and *N*-amino-azoles.

	N-Methylazoles (**a**)					*N*-Aminoazoles (**b**)				
Azole	CH_3	$^1J_{CH}$	$N(CH_3)$	N pyridine-like		NH_2	$^1J_{NH}$	$N(NH_2)$	N pyridine-like	
Pyrrole (**1**)	35.2	137.6	−230.1	—	—	−306.4	70.0	−209.8	—	—
Imidazole (**2**)	32.9	139.1	−218.5	−118.1[a]	—	−311.4	*k*	−198.7	−126.8[a]	—
Pyrazole (**3**)	38.4	139.1	−180.8	−73.7[b]	—	−295.1[g]	71.0[h]	−162.1[i]	−72.4[b,j]	—
4*H*-1,2,4-Triazole (**4**)	31.4	141.6	−217.8	−59.8[c]	—	−315.5	70.0	−198.2	−66.1[c]	—
1*H*-1,2,4-Triazole (**5**)	35.0	140.5	−171.3	−81.9[b]	−124.7[d]	−303.0	72.2	−155.7	−79.8[b]	−131.6[d]
Benzimidazole (**12**)	30.4	139.4	−236.4	−136.3[a]	—	−317.8	71.9	−215.8	−143.6[a]	—
2*H*-Indazole (**13**)	39.7	140.0	−162.1	−92.3[e]	—	−289.1	70.5	−145.5	−94.8[e]	—
1*H*-Indazole (**14**)	35.2	138.0	−203.8	−57.6[b]	—	−305.9	72.7	−184.6	−56.3[b]	—
2*H*-Benzotriazole (**15**)	42.8	143.1	−117.0	−62.6[f]	—	−275.3	73.4	−99.9	−83.6[f]	—
1*H*-Benzotriazole (**16**)	33.7	140.5	−161.5	−1.1[b]	−41.0[a]	−307.7	73.4	−148.2	−2.3[b]	−50.8[a]
Carbazole (**17**)	29.7	137.5	−272.7	—	—	−322.9	*k*	−249.2	—	—

[a] N(3). [b] N(2). [c] N(1) and N(2). [d] N(4). [e] N(1). [f] N(1) and N(3). [g] In $CDCl_3$: −295.5. [h] In $CDCl_3$: ^1J = 69.2 Hz. [i] In $CDCl_3$: −162.7. [j] In $CDCl_3$: −72.7. [k] Not measurable (NH signal too large).

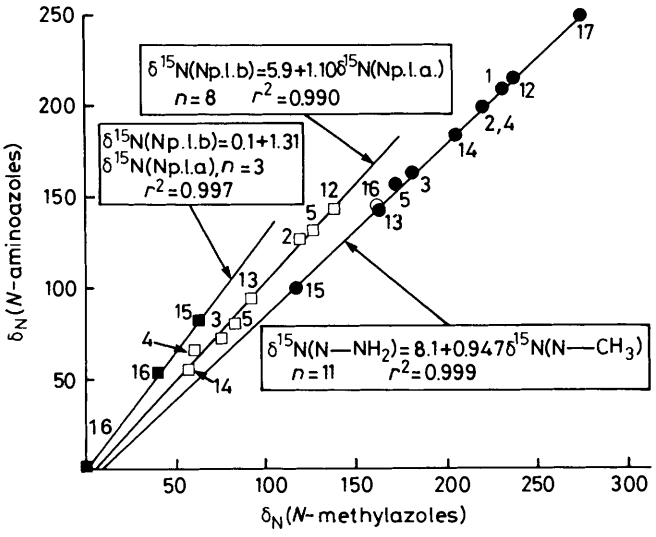


Figure 5. Relationships between the ^{15}N chemical shifts of *N*-aminoazoles [series (**b**)] and *N*-methylazoles [series (**a**)].

experimental geometries (Table 4), shows excellent agreement with the exception of the C–H bond lengths. It is well known that the INDO method affords too long C–H and N–H distances,[28] whereas the opposite is true for X-ray crystallography X–H bond lengths.[31] In the case of compounds (**12b**) and (**15b**), averaged C–H and N–H distances are 1.12 and 1.07 Å (INDO) and 0.98 and 0.93 Å (X-ray) (scaling factor, 0.87), whereas the standard neutron diffraction distances are 1.083 and 1.009 Å, respectively.[20] Considering only the bond lengths and bond angles involving heavy atoms, we found for compound (**12b**) an averaged deviation of +0.013 Å [maximum deviation: 0.039 Å for the C(1)–C(7a) bond] and 1° [maximum deviation 3.35° for the C(1)–N(2)–C(3) angle] and for compound (**15b**), 0.012 Å [0.026 Å for the C(4)–C(5) bond] and 0.8° [(1.73° for the N(1)–C(7a)–C(7) angle], respectively.

For the remaining derivatives, we have compared the geometries of the *N*-unsubstituted azoles (which, generally, agree with the experimental ones)[28] with those of the *N*-methyl-, series (**a**), and *N*-amino-azoles, series (**b**). The only differences concern the bond lengths and bond angles of the nitrogen atom carrying the substituent. The X–N (pyrrole-like) lengths increase by about 0.007 Å (*N*-methylation) and 0.005 Å (*N*-amination) and the X–N–Y angles decrease by about 2.3° (*N*-methylation) and 1.0° (*N*-amination).

Amino group geometries. The calculated geometries of the amino groups for compounds (**12b**) and (**15b**) are reported in Table 6, together with the experimental values of Table 4.

The exocyclic N–N bond length shows a difference (0.06 Å) between the experimental and the calculated value which is larger than in the ring geometry. The angles between heavy atoms are correct but the lengths and angles implying H atoms deviate. The bond lengths are too long and, as a consequence, the HNH angle is too closed (*ca.* 6°), since the H–H repulsion is underestimated.

Conformation of the amino group. Recently a publication by Dyall[32] reported the IR study of several *N*-aminoazoles: (**1b**), (**13b**), (**14b**), (**15b**), (**16b**), and (**17b**). From the N–H stretching band, he draws conclusions about the conformation of the amino group in the vapour phase and in CCl_4 solution (Table 7).

To define the conformation of the amino group we used the following criteria: (i) α is the dihedral angle between the lone pair of the amino group and the perpendicular to the ring plane; (ii) for the sp^3 hybridization, α = 90° corresponds to the conformation in which the lone pair eclipses the *Z* part of the ring, in the case of rings of C_s symmetry (α = 90°′ for the opposite conformation). In Figure 6 are represented some situations.

Table 7 deserves some comment:

(i) The agreement between experimental and semiempirical results is excellent. It is reasonable to be confident in the theoretically preferred conformations when there is not experimental evidence.

(ii) The sp^3 hybridization is always favoured, but in the case of aniline the planar form is only 1.5 kcal mol^{-1} higher, whereas in 1-aminopyrrole (**1b**) the difference is about 10 kcal mol^{-1}. In the case of 2-aminobenzotriazole (**15b**), the difference reduces to 5.9 kcal mol^{-1}.

(iii) For monocyclic azoles, (**1b**)–(**9b**), parallel conformations (α = 90° or 90°′) are always the most stable. The perpendicular ones (α = 0°) lie between 0.1 (**6b**) and 1.6 kcal mol^{-1} higher (**3b**), and (**5b**). The presence of nitrogen atoms in the β-position stabilizes the perpendicular conformer [*cf.* (**2b**), (**4b**), (**3b**), (**7b**), and (**9b**)], but the most important effect is that of α-nitrogens: none (**1b**), (**2b**), and (**4b**), one (**3b**), (**5b**), (**7b**), and (**9b**), or two (**6b**), and (**8b**). One α-nitrogen favours a 90°′ conformation, with both lone pairs on opposite sides. Two α-nitrogens destabilize the parallel conformation and the perpendicular one becomes very close in energy.

Table 6. Theoretical and experimental geometries of the amino groups for 1-aminobenzimidazole (**12b**) and 2-aminobenzotriazole (**15b**).

Bond lengths/Å	Calc.	Exp.	Bond angles/°	Calc.	Exp.
(12b)					
N(1)–N(8)	1.339	1.408	C(7a)–N(1)–N(8)	130.5	129.0
N(8)–H(9)	1.077	0.966	C(2)–N(1)–N(8)	124.6	123.3
N(8)–H(10)	1.077	0.945	N(1)–N(8)–H(9)	109.9	106.8
			N(1)–N(8)–H(10)	109.9	107.4
			H(9)–N(8)–H(10)	104.0	108.8
(15b)					
N(2)–N(8)	1.337	1.386	N(1)–N(2)–N(8)	119.5	121.1
N(8)–H(9)	1.072	0.897	N(3)–N(2)–N(8)	119.5	119.9
N(8)–H(10)	1.072	0.905	N(2)–N(8)–H(9)	110.8	109.0
			N(2)–N(8)–H(10)	110.8	110.1
			H(9)–N(8)–H(10)	107.9	115.2

Table 7. Experimental and theoretical study of the amino group conformation (theoretical energies in kcal mol^{-1} with regard to the most stable conformation).

			sp^3 (α values)			sp^2	
Compound	X-ray [Σ°][a]	IR[27]	0°	90°	90°′	0°	90°
(1b)[b]	—	sp^3, α = 90°	1.2	0	—	11.8	9.7
(2b)	—	—	1.3	0	0.4	—	—
(3b)	—	—	1.6	1.2	0	—	—
(4b)	—	—	0.5	0	—	—	—
(5b)	—	—	1.6	1.4	0	—	—
(6b)	—	—	0.1	0	—	8.1	8.4
(7b)	—	—	1.3	0.7	0	—	—
(8b)	—	—	0.4	0	0.3	8.7	8.5
(9b)	—	—	0.9	0	1.0	—	—
(10b)	—	—	0	0.4	—	—	—
(11b)	—	—	2.4	0.5	0	—	—
(12b)	sp^3 [Σ = 323(2)°], α = 90°,[c]	—	2.3	0.7	0	—	—
(13b)	—	sp^3, α = 90° or 90°′	0	1.7	0.4	—	—
(14b)	—	sp^3, α = 90° or 90°′	2.6	0.7	0	—	—
(15b)	sp^3 [Σ = 334(2)°], α = 30°,[c]	sp^3, α = 0°	0	2.6	—	5.9	11.4
(16b)	—	sp^3, α = 90° or 90°′	2.2	0.3	0	—	—
(17b)	—	sp^3, α = 90°	11.6	0	—	—	—
Aniline[d]	sp^2/sp^3 [Σ = 340–345°], α = 0°	sp^3, α = 0°	0	6.7	—	1.5	13.5

[a] Sum of the bond angles around the amino nitrogen. [b] 3-21G calculations[30] led to the following order of decreasing stability: sp^3 (α = 90°) > sp^2 (α = 90°) ≃ sp^3 (α = 0°) ≫ sp^2 (α = 0°). [c] This work. [d] From ref. 33.

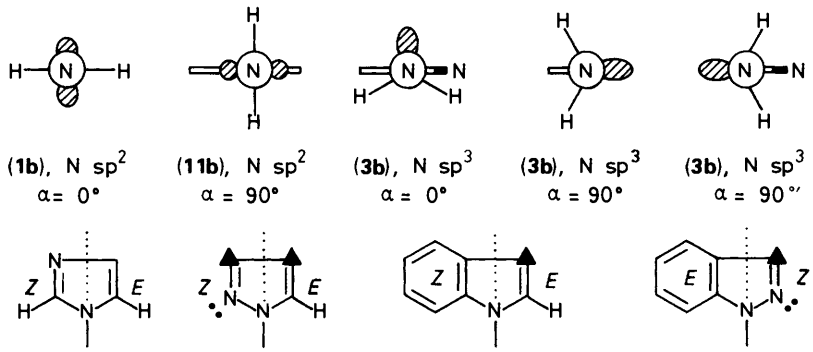
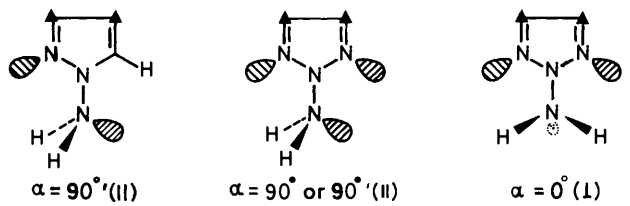


Figure 6. Definition of the dihedral angle with regard to the *E*- and *Z*- parts of the molecule.



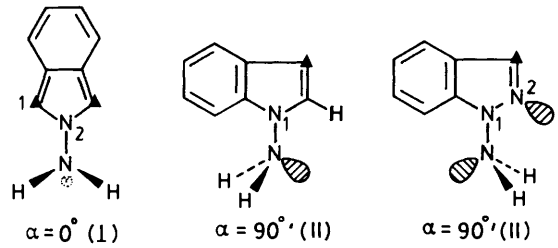
(iv) For bicyclic azoles, benzazoles (**10b**)–(**17b**), perpendicular conformations (⊥, α = 0 °) are the most stable in the case of the 2-substituted compounds (**10b**), (**13b**), and (**15b**). For (**15b**), the parallel conformation (∥, α = 90 °) is 2.6 kcal mol^{-1} less stable, due to the accumulated effect of lone-pair repulsion and extended conjugation. For 1-substituted compounds, the α = 90 °′ conformations are the most stable with the lone-pair directed towards the five-membered ring when there is a C–H in

Table 8. Total charge of carbon (q_{CH_3}) and nitrogen atoms in the most stable conformations of *N*-methyl- and *N*-amino-azoles.

	N-Methylazoles (**a**)					*N*-Aminoazoles (**b**)				
Azole	q_{CH_3}	$q_{N(CH_3)}$	$q_{N(pyridine\text{-}like)}$			q_{NH_2}	$q_{N(NH_2)}$	$q_{N(pyridine\text{-}like)}$		
Pyrrole (**1**)	3.82	5.03	—	—	—	5.12	4.94	—	—	—
Imidazole (**2**)	3.82	5.04	5.24[a]	—	—	5.12	4.96	5.23[a]	—	—
Pyrazole (**3**)	3.85	4.93	5.18[b]	—	—	5.14	4.84	5.20[b]	—	—
4*H*-1,2,4-Triazole (**4**)	3.83	5.04	5.15[c]	—	—	5.12	4.95	5.14[c]	—	—
1*H*-1,2,4-Triazole (**5**)	3.84	4.95	5.21[b]	5.25[d]	—	5.14	4.86	5.22[b]	5.25[d]	—
2*H*-1,2,3-Triazole (**6**)	3.87	4.82	5.17[f]	—	—	5.15	4.73	5.19[f]	—	—
1*H*-1,2,3-Triazole (**7**)	3.85	4.95	5.05[b]	5.12[a]	—	5.14	4.86	5.07[b]	5.12[a]	—
2*H*-Tetrazole (**8**)	3.87	4.85	5.18[e]	5.06[a]	5.14[d]	5.15	4.76	5.20[e]	5.06[a]	5.15[d]
1*H*-Tetrazole (**9**)	3.85	4.95	5.08[b]	5.03[a]	5.16[d]	5.14	4.86	5.10[b]	5.03[a]	5.16[d]
Isoindole (**10**)	3.84	4.98	—	—	—	5.13	4.87	—	—	—
Indole (**11**)	3.82	5.08	—	—	—	5.11	5.00	—	—	—
Benzimidazole (**12**)	3.82	5.09	5.26[a]	—	—	5.11	5.01	5.26[a]	—	—
2*H*-Indazole (**13**)	3.86	4.87	5.23[e]	—	—	5.15	4.76	5.25[e]	—	—
1*H*-Indazole (**14**)	3.84	4.99	5.14[b]	—	—	5.13	4.90	5.15[b]	—	—
2*H*-Benzotriazole (**15**)	3.89	4.75	5.22[f]	—	—	5.16	4.63	5.25[f]	—	—
1*H*-Benzotriazole (**16**)	3.84	5.01	5.01[b]	5.14	—	5.13	4.92	5.03[b]	5.14[a]	—
Carbazole (**17**)	3.81	5.12	—	—	—	5.11	5.03	—	—	—

[a] N(3). [b] N(2). [c] N(1) and N(2). [d] N(4). [e] N(1). [f] N(1) and N(3).

the α-position [(**11b**), (**12b**)] or towards the six-membered ring when there is a N-atom in α-position [(**14b**), (**16b**)].



Charges. No experimental values for the diple moments are available; the calculated ones are as follows (in D*): (**1b**) 2.21, (**2b**) 4.26, (**3b**) 0.56, (**4b**) 5.47, (**5b**) 2.38, (**6b**) 1.81, (**7b**) 2.54, (**8b**) 3.36, (**9b**) 4.19, (**10b**) 3.50, (**11b**) 1.58, (**12b**) 3.79, (**13b**) 3.42, (**14b**) 0.30, (**15b**) 2.16, (**16b**) 2.00, and (**17b**) 1.88.

Relationships between total charge densities and ^{15}N *chemical shifts.* The total charge densities necessary for the following discussion are gathered in Table 8. There exist some correlations between these values that parallel those described previously for the chemical shifts. Thus, there is a linear relationship between the charges of the amino group and the methyl group for the seventeen azoles of Table 8: $qN(NH_2) = 2.47 + 0.69\ qC(CH_3), n = 11, r^2 = 0.924$. Another relationship which corresponds to Figure 5 (○) relates the charges of pyrrole-like nitrogens in *N*-methyl and *N*-aminoazoles: $qN\text{-}(N\text{–}NH_2) = -0.44 + 1.07\ qN(N\text{–}CH_3)$, $n = 17$, $r^2 = 0.994$. The charges of pyridine-like nitrogen atoms do not change between *N*-methyl- and *N*-amino-azoles.

The existence of linear relationships between chemical shifts (for instance, nitrogen-15)[15,22] is a well-established fact. A comparison of the data of Tables 5 and 8, led to the equations (1)–(6).

N-methylazoles

$$^{13}C(N\text{–}CH_3) = -590.8 + 163.0\ q(\pi + \sigma), \quad n = 11, r^2 = 0.843 \quad (1)$$

$$^{15}N(N\text{–}CH_3) = 1\,746.8 - 391.1\ q(\pi + \sigma), \quad n = 11, r^2 = 0.950 \quad (2)$$

[without compound (**16**)]

$$^{15}N(\text{N pyridine-like in } \alpha\text{-position}) = 2\,505.8 - 499.0q(\pi + \sigma), n = 8, r^2 = 0.934 \quad (3)$$

[without compound (**15**)]

N-aminoazoles

$$^{15}N(N\text{–}NH_2) = -4\,503.2 + 818.5\ q(\pi + \sigma), \quad n = 11, r^2 = 0.923 \quad (4)$$

$$^{15}N(N\text{–}NH_2) = 1\,466.5 - 337.3\ q(\pi + \sigma), \quad n = 10, r^2 = 0.939 \quad (5)$$

[without compound (**16**)]

$$^{15}N(\text{N pyridine-like in } \alpha\text{-position}) = 2\,634.4 - 523.8\ q(\pi + \sigma), n = 8, r^2 = 0.840 \quad (6)$$

[without compound (**15**)]

The slopes (ppm per electron) are in the range of expected values save in the case of equations (1) and (4), both concerning sp^3 atoms, where the slopes have inverted sign.[25,34]

Conclusions

Theoretical calculations at the INDO ‖ INDO level are feasible for both quite complicated molecules and large series of compounds. In the case of *N*-aminoazoles, the calculated geometries are accurate (when experimental data are available) and consistent. The amino group is always pyramidal and its rotation about the N–N bond takes place more easily than does nitrogen inversion (through a planar sp^2 transition state).

The electronic distribution, as far as the chemical shifts are concerned, seems reasonable although the benzotriazole derivatives (**15**) and (**16**) show somewhat different behaviour.

Finally, concerning the interaction between the amino group and the azole, some facts have emerged: (i) the α-nitrogen atoms determine the preferred conformation; (ii) in the case of com-

* 1 D = *ca.* 3.335 × 10^{-30} C m.

pounds with two α-nitrogen atoms, the perpendicular conformation and the sp^2 hybridization are stabilized; and (iii) an aromatic ring in the β,β′ position stabilizes the perpendicular conformation. This picture corresponds to a positive interaction between the hydrogen atoms of the NH_2 group and pyridine-like nitrogens in the α-position (IMHB: intramolecular hydrogen-bond) and to some conjugative interaction between the amino group and the azole which favours the perpendicular conformation in 2-substituted benzazoles.

The sum of the three angles around the amino nitrogen (INDO, α = 0°) also reflects this situation, increasing with the sp^2 character from 1-aminopyrrole (**1b**) and 9-aminocarbazole (**17b**) (Σ = 324.3°), to 2-aminobenzotriazole (**15b**) (Σ = 329.5°) and to aniline (Σ = 341.4°). The experimental Σ values (Table 7) are very similar to the calculated ones.

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