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NITROGEN-14 NUCLEAR MAGNETIC RESONANCE OF AZOLES AND THEIR BENZO-DERIVATIVES

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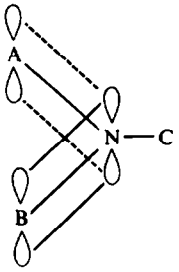
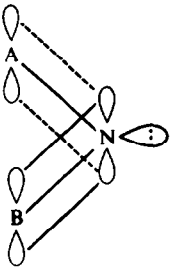
Abstract—The ^{14}N NMR spectra of some azoles, diazoles, triazoles, tetrazoles, oxazoles, thiazoles, and some bicyclic benzo-derivatives show a linear relationship between the chemical shifts and the SCF-PPP-MO π-charge densities. The resonances of the N-methyl nitrogen atoms are very characteristic of the type of ring system and may be used for distinguishing between tautomeric forms. The effects of tautomeric equilibria on the appearance of the ^{14}N spectra are considered. The average excitation energy approximation of the theory of chemical shifts is found to be reliable for the ^{14}N shifts of pyrrole-type nitrogen atoms in azole ring systems, even if the effect of polarisation in the σ-bonds is ignored.

INTRODUCTION

SO FAR there have been no systematic studies of the ^{14}N NMR spectra of five-membered aromatic or semi-aromatic rings containing one or more nitrogen atoms and, possibly, other hetero-atoms such as oxygen and sulphur. However, some data are available in the literature for the simplest representatives of this group.[1,2] We have recently reported[3] a relationship between the ^{14}N chemical shift and π-electron distribution in some six-membered hetero-aromatic rings. This shows that the nitrogen resonance moves to higher magnetic fields in a roughly parallel manner to the increase in π-charge density at the nitrogen atom. It is interesting from both the practical and theoretical point of view to examine the ^{14}N spectra of azoles since this group of molecules includes a large variety of nitrogen bonding states. The latter may be divided into two main types, type α in which the nitrogen atom is bonded to three atoms which are either in a plane or are very close to a plane, and the type β which contains examples of the nitrogen atom directly bonded to only two other atoms. In the approximation that divides the electron valence shell of a molecule into π and σ-orbital systems, the type-α nitrogen atom supplies two electrons to the π-orbital delocalized system whilst only one is supplied by each nitrogen atom of type-β.



type-α
(pyrrole-type
nitrogen atom)



type-β
(pyridine-type
nitrogen atom)

Both types of nitrogen bonding environment may be characterized in this approximation by the π-charge density at the nitrogen atom, q_N^π, by the mobile bond orders, p_{NA}^π and p_{NB}^π, and by a set of three σ-bonds as before.[3] We shall assume no σ-bond polarization. The nitrogen core in the π-orbital system of type-α is much more electron-attracting than that of type-β and the corresponding q_N^π values are higher for α from any sort of molecular orbital calculations, whereas the net charge on the nitrogen atom is positive for α and negative for type-β.

If there are nitrogen atoms of both types in a molecule and if C is a hydrogen atom, then a tautomeric equilibrium between two or more forms may exist. The resulting ^{14}N NMR spectrum should either be a dynamically averaged representation of the system or a superposition of the spectra of the individual tautomers.

Before proceeding into more theoretical aspects of the ^{14}N chemical shifts of azoles, it seems advisable to consider empirical relationships depending upon the structure of the ring system in this group of compounds. Such correlations may have a practical value independent of the possible success or failure of a theoretical explanation.

Empirical correlations

The experimental results of ^{14}N NMR measurements of some azoles are collected in Table 1. The molecules examined were chosen according to certain schemes in order to estimate the possible effects of tautomerism, to follow changes resulting from the introduction of another hetero-atom in various positions of the 5-membered ring system, from the extension of the aromatic system by additional benzene rings, etc.

Two distinct groups of ^{14}N chemical shifts are observed in the spectra. We exclude from consideration here systems where tautomerism might be present, and treat these in the next section. Type-α nitrogen atoms are characterized by a high field shift, usually about 200 ppm, relative to $MeNO_2$. In some cases, where a larger number of electron-attracting centres is present in the ring system, the shift may be reduced to about 100 ppm, but is always much higher than those for type-β nitrogen atoms. The half-height width of the ^{14}N resonance signal is usually much smaller for type-α, particularly for N–Me derivatives. The range of the shifts, +100 to +260 ppm in this group of nitrogen atoms is large enough for the resonance to constitute a valuable

TABLE 1. NITROGEN-14 MAGNETIC RESONANCE IN AZOLES (4·33 MHz)

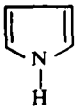
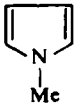
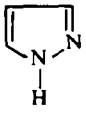
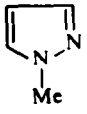
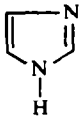
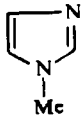
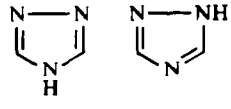
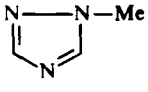
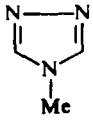
No.	Compound Formulae of possible tautomeric structures	Solvent Concentration (w/w)	^{14}N chemical shift [a] referred to internal $MeNO_2$ p.p.m.	Resonance half-height width Hz[b]
I	pyrrole 	neat	+235 ± 2	172 ± 5
		dioxan (1:1)	+232 ± 2	50 ± 5[c]
		methanol (1:1)	+233 ± 3	40 ± 5[c]
II	N-methylpyrrole 	neat	+231 ± 2	104 ± 5
		methanol (1:1)	+233 ± 1	90 ± 3
III	pyrazole 	dioxan (1:1)	+135 ± 3	730 ± 30
		methanol (1:1)	+133 ± 3	670 ± 20
IV	N-methylpyrazole 	CCl_4 (1:2)	+ 68 ± 2 (N)	325 ± 20
			+178 ± 2 (NMe)	142 ± 8
		methanol + CCl_4 (1:1:2)	+ 78 ± 3 (N)	385 ± 25
			+178 ± 2 (NMe)	185 ± 5
V	imidazole 	dioxan (satd.)	+171 ± 5	1200 ± 100
		methanol (1:1)	+171 ± 3	600 ± 30
VI	N-methylimidazole 	neat	+123 ± 2 (N)	325 ± 10
			+221 ± 1 (NMe)	150 ± 5
		CCl_4 (1:5)	+116 ± 3 (N)	300 ± 20
			+218 ± 1 (NMe)	125 ± 5
VII	1,2,4-triazole 	dioxan (satd.)	+134 ± 2	540 ± 30
		methanol (1:1)	+136 ± 3	940 ± 40
VIII	1-methyl-1,2,4-triazole 	neat	+126 ± 3 (N, N)	450 ± 50
			+170 ± 2 (NMe)	160 ± 10
		methanol (1:1)	+130 ± 5 (N, N)	550 ± 50
			+170 ± 1 (NMe)	170 ± 10
IX	4-methyl-1,2,4-triazole 	methanol (satd.)	+ 80 ± 4 (N, N)	600 ± 50
			+220 ± 2 (NMe)	190 ± 15

TABLE 1—*Continued*

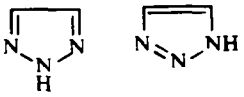
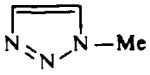
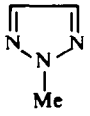
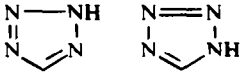
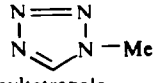
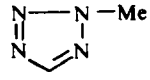
No.	Compound Formulae of possible tautomeric structures	Solvent Concentration (w/w)	^{14}N chemical shift [a] referred to internal $MeNO_2$ p.p.m.	Resonance half-height width Hz[b]
X	1,2,3-triazole 	neat	+ 60 ± 8 (N, N) +132 ± 4 (NH)	300 ± 50 150 ± 20
		methanol (1:1)	+ 60 ± 8 +128 ± 6	250 ± 50 200 ± 30
XI	1-methyl-1,2,3-triazole 	neat	+ 22 ± 1 (N, N) +143 ± 1 (NMe)	440 ± 10 120 ± 4
		methanol (1:1)	+ 28 ± 1 (N, N) +144 ± 1 (NMe)	480 ± 10 125 ± 4
XII	2-methyl-1,2,3-triazole 	neat	+ 51 ± 1 (N, N) +130 ± 1 (NMe)	235 ± 5 102 ± 4
		methanol (1:1)	+ 53 ± 2 (N, N) +132 ± 2 (NMe)	250 ± 5 105 ± 4
XIII	tetrazole 	acetone (satd.)	+ 15 ± 3 +106 ± 2	445 ± 25 300 ± 25
		methanol (satd.)	+ 25 ± 5 +106 ± 4	480 ± 30 350 ± 30
XIV	1-methyltetrazole 	$CHCl_3$ (1:1)	+ 17 ± 5 (N, N, N) +150 ± 2 (NMe)	600 ± 50 160 ± 10
XV	2-methyltetrazole 	CCl_4 (1:1)	+ 5 ± 6 (N-N)[d] + 44 ± 3 (-N-NMe)[d] +101 ± 1 (NMe)	300 ± 50 200 ± 50 115 ± 5
		methanol (2:1)	+ 10 ± 6 (N-N)[d] + 55 ± 4 (-N-NMe)[d] +103 ± 2 (NMe)	300 ± 50 200 ± 50 105 ± 5
XVI	oxazole 	CCl_4 (1:1) CCl_4 + methanol (1:1:1)	+124 ± 1 +125 ± 2	106 ± 4 170 ± 5
XVII	isoxazole 	neat DMF (1:1) methanol (1:1)	− 2 ± 1 − 4 ± 2 + 6 ± 2	220 ± 10 290 ± 20 335 ± 10
XVIII	thiazole 	neat methanol (1:1)	+ 56 ± 2 + 68 ± 2	150 ± 5 240 ± 10
XIX	isothiazole 	neat methanol (1:1)	+ 80 ± 1 + 85 ± 2	108 ± 4 135 ± 5

TABLE 1—*Continued*

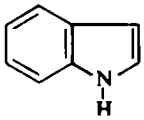
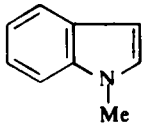
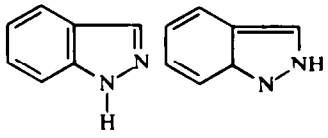
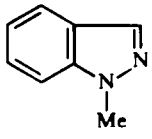
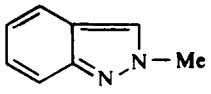
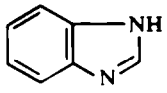
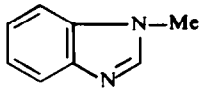
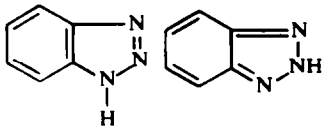
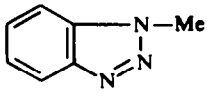
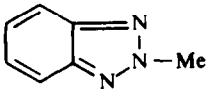
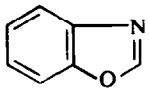
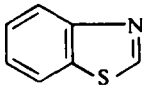
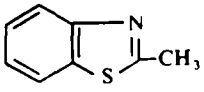
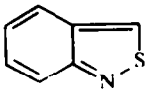
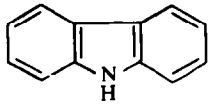
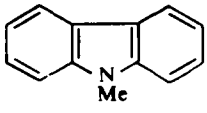
No.	Compound Formulae of possible tautomeric structures	Solvent Concentration (w/w)	^{14}N chemical shift [a] referred to internal $MeNO_2$ p.p.m.	Resonance half height width Hz[b]
XX	indole 	dioxan (satd.) methanol (satd.)	+251 ± 5 +246 ± 5	730 ± 30 380 ± 30
XXI	N-methylindole 	neat	+248 ± 5	900 ± 100
XXII	benzopyrazole 	acetone (satd.)	+ 75 ± 8 +197 ± 5	500 ± 70 360 ± 50
XXIII	1-methylbenzopyrazole 	acetone (satd.)	+ 71 ± 8 (N) +197 ± 5 (NMe)	500 ± 50 350 ± 50
XXIV	2-methylbenzopyrazole 	acetone (satd.)	+ 85 ± 5 (N) +162 ± 2 (NMe)	700 ± 100 350 ± 50
XXV	benzimidazole 	acetone (satd.) methanol (satd.)	+185 ± 5 +192 ± 5	400 ± 20 750 ± 50
XXVI	N-methylbenzimidazole 	acetone (satd.)	+130 ± 8 (N) +228 ± 5 (NMe)	350 ±50 300 ± 50
XXVII	benzotriazole 	dioxan (satd.) methanol (satd.)	+ 81 ± 7 + 89 ± 7	1500 ± 100 1600 ± 100
XXVIII	1-methylbenzotriazole 	acetone (satd.)	+ 40 ± 8 (N, N) +148 ± 5 (NMe)	600 ± 50 300 ± 50

TABLE 1—*Continued*

No.	Compound Formulae of possible tautomeric structures	Solvent Concentration (w/w)	^{14}N chemical shift [a] referred to internal $MeNO_2$ p.p.m.	Resonance half-height width Hz[b]
XXIX	2-methylbenzotriazole 	neat	+ 50 ± 8 (N, N) +118 ± 2 (NMe)	500 ± 50 250 ± 30
XXX	benzoxazole 	neat	+140 ± 3	400 ± 30
XXXI	benzothiazole 	neat	+ 60 ± 2	700 ± 20
XXXII	2-methylbenzothiazole 	neat	+ 63 ± 5	750 ± 50
XXXIII	benzisothiazole 	neat	+119 ± 2	640 ± 30
XXXIV	carbazole 	acetone (satd.)	+260 ± 5	1500 ± 100
XXXV	N-methylcarbazole 	acetone (satd.)	+260 ± 4	1000 ± 100

[a] positive sign denotes high-field direction
[b] apparent width if there is more than one resonance in the signal
[c] a doublet, $J(^{14}N–H) = 58 \pm 1$ Hz
[d] tentative assignments; see text

means of identification of azole ring systems, especially of tautomeric forms, e.g.

1-methyltetrazole (XV)	+150 ppm
2-methyltetrazole (XVI)	+103 ppm
1-methyl-1,2,4-triazole (VIII)	+170 ppm
4-methyl-1,2,4-triazole (IX)	+220 ppm
1-methyl-1,2,3-triazole (XI)	+143 ppm
2-methyl-1,2,3-triazole (XII)	+130 ppm
1-methylbenzotriazole (XXVIII)	+148 ppm
2-methylbenzotriazole (XXIX)	+118 ppm

In general, the chemical shifts in this group may be classified according to the number of nitrogen atoms in the 5-membered ring:

azoles	230 — 260 ppm
diazoles	160 — 230 ppm
triazoles	120 — 220 ppm
tetrazoles	100 — 150 ppm

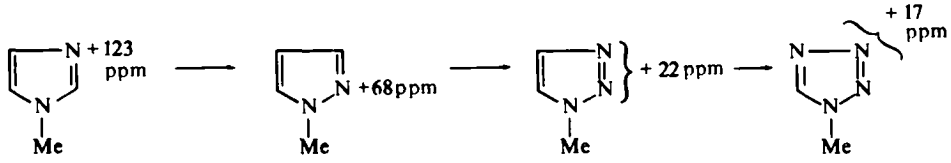
where the shifts are all to high field with respect to $MeNO_2$ as reference.

An expansion of the aromatic system of an azole by condensed benzene rings usually results in a high-field shift of the ^{14}N resonance signal of the N–Me group, or indeed of a β-type nitrogen (II→XXI→XXXV; IV→XXIII; VI→XXVI; XVI→XXX; XIX→XXXIII) except for cases where the resulting structure is of a quinoid character (XXIV, XXIX). This is similar to the trend observed in the ^{14}N NMR spectra of six-membered hetero-aromatic rings.[3]

The effect of methyl-substitution at the nitrogen atom, on its ^{14}N chemical shift, does not seem to be very significant. It is close to zero for pyrrole (I, II) and certainly not larger than solvent effects. It is also within the range of the experimental error for indole (XX, XXI), and carbazole (XXXIV, XXXV), but the range is larger because of the considerable width of the resonances.

One should note that the ^{14}N resonances for pyrrole (I) in dioxan and MeOH appear as resolved doublets spaced at 58 ± 1 Hz. This indicates that there is no rapid exchange of protons at the pyrrole rings under the specified conditions. The spacing is smaller than the recently reported value of the ^{14}N–H coupling constant of $69{\cdot}5 \pm 1$ Hz in pyrrole and $68{\cdot}6 \pm 1$ Hz in tetradeuteropyrrole[4] calculated from the proton resonance spectra. It is much closer to the previously reported values of 55 ± 5 Hz[5] and about 60 Hz[6] for pyrrole, but this may also be an effect of quadrupole relaxation.[4]

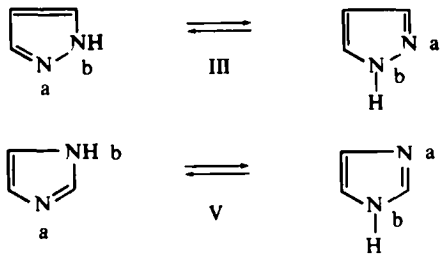
Type-β nitrogen atoms in azole rings are characterized by lower values of the ^{14}N chemical shift ranging from zero to +140 ppm relative to $MeNO_2$. In many instances, if there are two or more such atoms in the ring system, only one signal is observed for them due to overlap. However, some general trends may be discerned. If there are two or more adjacent nitrogen atoms, a low-field shift is observed relative to the case in which the nitrogen atoms are separated. The same effect is found with oxygen atoms, but not with sulphur.



Sulphur-containing ring systems are different in this respect, since the resonances of thiazoles (XVIII, XXXI, XXXII) occur at lower fields than those of isothiazoles (XIX, XXXIII). In all cases, however, there is a considerable relative shift for each pair of 1,2- and 1,3-diazoles, oxazoles and thiazoles which is advantageous from the point of view of spectral identification.

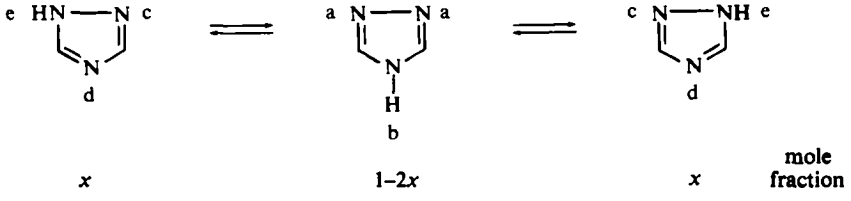
Effects of tautomerism in some labile azole systems

Some of the ring systems examined here, such as diazoles, triazoles, and tetrazoles, may exhibit tautomerism which should be reflected in the appearance of their ^{14}N NMR spectra. The simplest cases are pyrazole (III) and imidazole (V) where the possible tautomers are energetically equivalent.



If there is fast proton migration, the ^{14}N resonance signal is expected to occur at (a + b)/2, where a and b refer to the positions of the signals of the a and b type nitrogen atoms indicated above. The corresponding N–Me derivatives (IV, VI) should provide close estimates of the respective a and b chemical shifts. Table I indicates that the single signals in the ^{14}N spectra of III and V are located, within experimental error and possible solvent effects, at positions corresponding to the mean values of the signals of IV and VI, respectively.

The 1,2,4- and 1,2,3-triazole systems (VII, X) involve more complicated equilibria, e.g. for VII



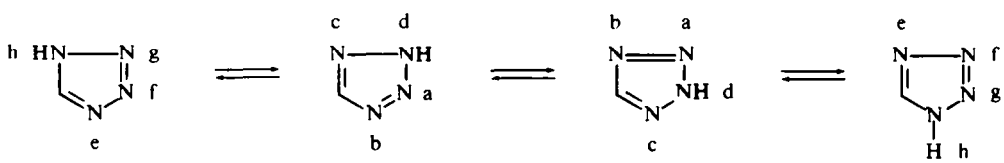
with an analogous situation for the 1,2,3-triazole (X) system. In this case even fast proton exchange must lead to at least two resonances, one at $A = (1 - 2x)a + x(c + e)$ and the other at $B = (1 - 2x)b + 2xd$. The value of x may be expressed in terms of the shifts as:

$$x = \frac{(2A + B) - (2a + b)}{2[(c + d + e) - (2a + b)]} \tag{1}$$

For 1,2,4-triazole (VII) only one resonance is observed due to overlap of the resonance signals. If we assume that the position of its maximum is at a weighted average value, $(2A + B)/3$, and that a, b, $(c + d)/2$, and e are represented by the corresponding shifts observed for (VIII) and (IX), then for solutions in MeOH eq. 1 yields $x = 0{\cdot}3$. However, the maximum possible error calculated from the component errors given by the data in Table I is $\pm 0{\cdot}2$, which is mostly dependent on the error in the shift $(2A + B)/3$. For 1,2,3-triazole (X) the situation is more favourable since two signals are observed in its ^{14}N NMR spectrum.

Comparison with the spectral data for XI and XII suggests that the symmetrical isomer is dominant in the equilibrium. From eq. 1 and a consideration of possible errors a range of 70 to 100 mole % of the symmetrical tautomer is calculated.

The tetrazole system (XIII) may include four tautomers:



which, at the limit of fast proton migration, should give two signals, one at $A = x(a + d) + \frac{1}{2}(1 - 2x)(f + g)$ and the other at $B = x(b + c) + \frac{1}{2}(1 - 2x)(e + h)$. The value of x is related to the observed shifts by eq. 2.

$$x = \frac{(A + B) - \frac{1}{2}(e + f + g + h)}{(a + b + c + d) - (e + f + g + h)} \tag{2}$$

Two resonances are discernible in the ^{14}N NMR spectrum of tetrazole XIII. If these are compared with the spectra of XIV and XV a close resemblance is observed with that of XV. No significant solution can be obtained by inserting the observed shifts into eq. 2. Therefore, it seems that the tautomer corresponding to XV is dominant and that there is no fast proton migration which could lead to signals at $A = (a + d)/2$ and $B = (b + c)/2$. This is supported by the fact that the high-field signal corresponds, within experimental error, to that of XV, and the low-field signal has a maximum at a weighted average of the lower-field shifts of XV. The assignments of the latter are based on the low-field shift effect of adjacent nitrogen atoms so that the value of +55 ppm is attributed to the nitrogen atom placed between NMe and CH, and the value of +10 ppm to the remaining pair of adjacent nitrogen atoms on the other side of NMe. In principle, if there were a proportionality between

the number of ^{14}N nuclei and the integral intensity of the corresponding ^{14}N NMR signal, then a fast proton migration would lead, in either case, to an intensity ratio of 1:1; otherwise, the ratio would be 3:1. However, there are considerable differences in the relaxation times (and signal widths) among the ^{14}N nuclei in tetrazoles so that large deviations from the proportionality should be expected, not to speak of the possible spin exchange effects on the intensities. In view of this, the observed $1:2{\cdot}0 \pm 0{\cdot}5$ ratio of integral intensities in the spectrum of XIII is not very helpful in the description of the tautomeric system of tetrazole.

These results are different from those reported[7] from proton resonance studies on acetone solutions of labile azoles where rather stable complexes of the solutes with the solvent were observed.

Correlation of ^{14}N chemical shifts with π-charge distributions

It has been shown that the ^{14}N chemical shifts in 6-membered heteroaromatic systems correlate reasonably well with the SCF–MO π-charge densities calculated by the Pariser-Parr-Pople approximation.[3] It has also been indicated[3] that the shifts may be satisfactorily explained in terms of the average excitation energy (AEE) approximation.[8] Similar methods have been used in the present work in an attempt

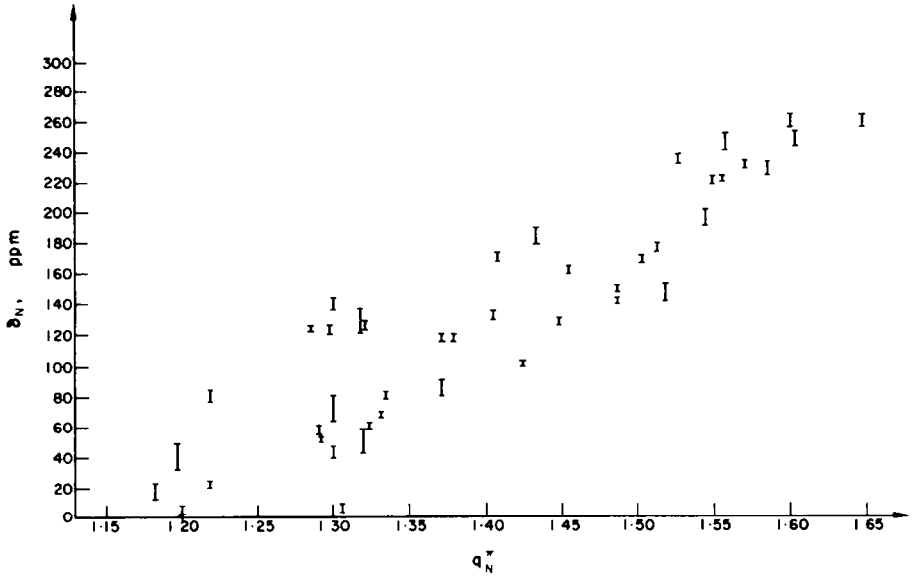


FIG 1.

to find possible relationships between the electron distribution in azole rings and their ^{14}N NMR spectra. Table II presents the π-charge densities and mobile bond orders calculated, as previously,[3] by the SCF–PPP–MO method. We have used parameters for the Me groups which consider them as heteroatoms providing additional π-electron centres in the σ-bond core. The most striking results of such calculations when compared with the experimental ^{14}N chemical shifts, is that a fairly linear correlation exists (Fig. 1) between the calculated π-charge densities, q_N^π, and

the observed shifts which include both the α- and β-types of nitrogen atom in azole rings. The charges were averaged for tautomeric systems. It should be pointed out that this correlation does not provide evidence of a significant contribution by the diamagnetic term to the shifts since the highest values of q_N^π correspond to the α-type nitrogen atoms which are likely to carry the smallest over-all electron density. This seems to indicate that the paramagnetic term provides the dominant contribution to changes in the chemical shifts of the ^{14}N nuclei in azoles.

In the AEE approximation, the magnitude of the paramagnetic term, σ_N^{para}, in the expression for the screening constant[8] is proportional to the mean reciprocal cube of the 2p-orbital radius, $\langle r^{-3}\rangle_{2p}$, and to the $\sum Q_{NX}$ term representing the distribution of 2*p*-electrons throughout the bonding system which includes the nitrogen atom. The $\langle r^{-3}\rangle_{2p}$ term, called the orbital expansion term, may be calculated from Slater-type atomic orbitals as[9]

$$\langle r^{-3}\rangle_{2p} = \tfrac{1}{3}\left(\frac{Z_{2p}}{na_0}\right)^3 \tag{3}$$

where Z_{2p} is the effective nuclear charge, n is the principal quantum number, and a_0 is the Bohr radius. The formulae for Z_{2p} are given in Table II following, as before,[3] Emsley[9] who used the rules of Burns[9a]. Another approach to the evaluation of the orbital expansion term is to use equation reported by Velenik and Lynden-Bell:[10]

$$\langle r^{-3}\rangle_{2p} = 3{\cdot}099 - 0{\cdot}732\ Q_N \tag{4}$$

where Q_N is the local charge at the nitrogen atom. In the case of the quantity $\sum Q_{NX}$ the formulae needed in this work[3] are given in Table II.

The plot of $(Z_{2p})^3\sum Q_{NX}$ versus the ^{14}N chemical shift (Fig. 2) contains two groups of points corresponding to the two types of nitrogen atoms present in azole ring systems. The character of the correlations with $(Z_{2p})^3$ and $\sum Q_{NX}$ taken separately (not shown on the figures) is much the same so that it seems that both of these factors act in the same direction for these molecules. The overall correlation (Fig. 2) for the α-type nitrogen atoms is very nearly linear. For the β-type nitrogen atoms, the spread of the experimental points on the plot is larger, nevertheless the general trend is evident. Thus, two different values of the average excitation energy would have to be assigned to the two types of nitrogen atoms; however, the AEE approximation appears to work well in either case, especially for the α-type. Essentially the same relationships are obtained if $\langle r^{-3}\rangle_{2p}$ is calculated from eq. 4. Thus, the two methods of evaluation of the orbital expansion term are practically equivalent in the approximation used in this work.

In spite of all the assumptions and approximations involved in the calculation of the electron distribution and its transmission to the ^{14}N NMR spect.a, the correlations found here may provide a basis for understanding the relative nitrogen chemical shifts within the azole group of molecules. A comparison with the data[3] for 6-membered hetero-aromatic rings suggests that similar relationships between the ^{14}N chemical shifts and the electronic structure are observed for the entire group of five- and six-membered hetero-aromatic rings.

TABLE 2. PARAMETERS FOR CORRELATION WITH ^{14}N RESONANCE SHIFTS IN AZOLES

No.	Structure	Nitrogen atom	SCF-PPP calculations π-charge density	mobile bond orders[a]			$\sum_{A,B,C} Q_{NX}$[b]	$(Z_{2p})^3 c$	$(Z_{2p})^3 \sum Q_{NX}$	$\langle r^{-3} \rangle_{2p}$[d]	$\langle r^{-3} \rangle_{2p} \sum Q_{NX}$
			q_N^π	p_{NA}^π	p_{NB}^π	p_{NC}^π					
I	pyrrole	1 (NH)	1·5258	0·5500 (1, 2)	0·5500 (1, 5)	—	2·489	47·28	117·7	3·446	8·577
II	N-methylpyrrole	1 (NMe)	1·5702	0·5244 (1, 2)	0·5244 (1, 5)	0·0648 (NMe)	2·495	46·67	116·4	3·414	8·517
III	pyrazole	1 (NH)	1·4824	0·5060 (1, 2)	0·6040 (1, 5)	—	2·493	47·88	119·4	3·478	8·671
		2	1·3270	0·5060 (1, 2)	0·6776 (2, 3)	—	2·381	35·47	84·44	2·860	6·808
IV	N-methylpyrazole	1 (NMe)	1·5126	0·4922 (1, 2)	0·5796 (1, 5)	0·0766 (NMe)	2·510	47·46	119·1	3·456	8·675
		2	1·3306	0·4922 (1, 2)	0·6880 (2, 3)	—	2·378	35·43	84·23	2·857	6·793
V	imidazole	1 (NH)	1·5166	0·5912 (1, 2)	0·5318 (1, 5)	—	2·499	47·41	118·5	3·453	8·629
		3	1·3010	0·6734 (2, 3)	0·6152 (3, 4)	—	2·439	35·76	87·22	2·879	7·021
VI	N-methylimidazole	1 (NMe)	1·5546	0·5728 (1, 2)	0·5042 (1, 5)	0·0676 (NMe)	2·509	46·89	117·6	3·425	8·592
		3	1·2974	0·6908 (2, 3)	0·5964 (3, 4)	—	2·440	35·80	87·36	2·881	7·030
VIIa	1,2,4-triazole (1-H)	1 (NH)	1·4764	0·4876 (1, 2)	0·6410 (1, 5)	—	2·501	47·96	120·0	3·482	8·711
		2	1·3266	0·4876 (1, 2)	0·7048 (2, 3)	—	2·385	35·47	84·59	2·860	6·820
		4	1·3068	0·6346 (3, 4)	0·6546 (4, 5)	—	2·437	35·70	86·98	2·874	7·004
VIIb	1,2,4-triazole (4-H)	1	1·2290	0·5818 (1, 2)	0·7182 (1, 5)	—	2·476	36·59	90·60	2·931	7·258
		2	1·2290	0·5818 (1, 2)	0·7182 (2, 3)	—	2·476	36·59	90·60	2·931	7·258
		4 (NH)	1·5152	0·5668 (3, 4)	0·5668 (4, 5)	—	2·504	47·43	118·7	3·454	8·648
VIII	1-methyl-1,2,4-triazole	1 (NMe)	1·5034	0·4712 (1, 2)	0·6250 (1, 5)	0·0788 (NMe)	2·522	47·59	120·0	3·462	8·733
		2	1·3386	0·4712 (1, 2)	0·7090 (2, 3)	—	2·374	35·34	83·89	2·851	6·768
		4	1·3030	0·6256 (3, 4)	0·6650 (4, 5)	—	2·439	35·74	87·17	2·877	7·017
IX	4-methyl-1,2,4-triazole	1	1·2186	0·5750 (1, 2)	0·7286 (1, 5)	—	2·482	36·71	91·12	2·939	7·295
		2	1·2186	0·5750 (1, 2)	0·7286 (2, 3)	—	2·482	36·71	91·12	2·939	7·295
		4 (NMe)	1·5490	0·5478 (3, 4)	0·5478 (4, 5)	0·0692 (NMe)	2·518	46·96	118·2	3·429	8·633

Xa	1,2,3-triazole (1-H)	1 (NH)	1·4606	0·5648 (1, 2)	0·5854 (1, 5)	—	2·511	48·18	121·0	3·494	8·773
		2	1·2304	0·5648 (1, 2)	0·6504 (2, 3)	—	2·438	36·57	89·16	2·930	7·143
		3	1·2138	0·6504 (2, 3)	0·6566 (3, 4)	—	2·486	36·77	91·39	2·942	7·314
Xb	1,2,3,-triazole (2-H)	1	1·2624	0·5366 (1, 2)	0·7136 (1, 5)	—	2·439	36·21	88·30	2·907	7·090
		2 (NH)	1·4570	0·5366 (1, 2)	0·5366 (2, 3)	—	2·477	48·23	119·5	3·496	8·660
		3	1·2624	0·5366 (2, 3)	0·7136 (3, 4)	—	2·439	36·21	88·30	2·907	7·090
XI	1-methyl-1,2,3-triazole	1 (NMe)	1·4874	0·5508 (1, 2)	0·5672 (1, 5)	0·0858 (NMe)	2·535	47·81	121·2	3·474	8·807
		2	1·2306	0·5508 (1, 2)	0·6614 (2, 3)	—	2·436	36·57	89·10	2.932	7·139
		3	1·2060	0·6614 (2, 3)	0·6442 (3, 4)	—	2·489	36·86	91·72	2·948	7·337
XII	2-methyl-1,2,3-triazole	1	1·2916	0·5482 (1, 2)	0·6758 (1, 5)	—	2·414	35·87	86·61	2·885	6·967
		2 (NMe)	1·4488	0·5482 (1, 2)	0·5482 (2, 3)	0·0914 (NMe)	2·528	48·35	122·2	3·502	8·854
		3	1·2916	0·5482 (2, 3)	0·6758 (3, 4)	—	2·414	35·87	86·61	2·885	6·967
XIIIa	tetrazole (1-H)	1 (NH)	1·4586	0·5420 (1, 2)	0·6208 (1, 5)	—	2·517	48·21	121·3	3·495	8·797
		2	1·2204	0·5420 (1, 2)	0·6942 (2, 3)	—	2·451	36·69	89·94	2·938	7·201
		3	1·1228	0·6942 (2, 3)	0·6334 (3, 4)	—	2·535	37·83	95·92	3·009	7·629
		4	1·2172	0·6334 (3, 4)	0·6818 (4, 5)	—	2·488	36·73	91·38	2·940	7·315
XIIIb	tetrazole (2-H)	1	1·2872	0·5506 (1, 2)	0·6762 (1, 5)	—	2·418	35·92	86·84	2·889	6·984
		2 (NH)	1·4034	0·5506 (1, 2)	0·6194 (2, 3)	—	2·520	48·98	123·4	3·536	8·910
		3	1·1892	0·6194 (2, 3)	0·6370 (3, 4)	—	2·474	37·05	91·68	2·960	7·325
		4	1·2188	0·6370 (3, 4)	0·6700 (4, 5)	—	2·484	36·72	91·17	2·939	7·299
XIV	1-methyltetrazole	1 (NMe)	1·4860	0·5282 (1, 2)	0·6026 (1, 5)	0·0834 (NMe)	2·540	47·83	121·5	3·475	8·826
		2	1·2230	0·5282 (1, 2)	0·7028 (2, 3)	—	2·448	36·66	89·74	2·936	7·187
		3	1·1138	0·7028 (2, 3)	0·6236 (3, 4)	—	2·539	37·94	96·33	3·016	7·657
		4	1·2118	0·6236 (3, 4)	0·6948 (4, 5)	—	2·492	36·79	91·67	2·944	7·336
XV	2-methyltetrazole	1	1·3002	0·5342 (1, 2)	0·6838 (1, 5)	—	2·408	35·77	86·13	2·879	6·933
		2 (NMe)	1·4246	0·5342 (1, 2)	0·6066 (2, 3)	0·0976 (NMe)	2·550	48·68	124·2	3·520	8·978
		3	1·1920	0·6066 (2, 3)	0·6478 (3, 4)	—	2·472	37·02	91·52	2·959	7·314
		4	1·2116	0·6478 (3, 4)	0·6578 (4, 5)	—	2·486	36·79	91·47	2·944	7·320

TABLE 2—*Continued*

No.	Structure	Nitrogen atom	π-charge density	SCF-PPP calculations mobile bond orders[a]			$\sum_{A,B,C} Q_{NX}$[b]	$(Z_{2p})^{3c}$	$(Z_{2p})^3 \sum Q_{NX}$	$\langle r^{-3}\rangle_{2p}$[d]	$\langle r^{-3}\rangle_{2p} \sum Q_{NX}$
			q_N^π	p_{NA}^π	p_{NB}^π	p_{NC}^π					
XVI	oxazole	3	1·2848	0·7138 (2, 3)	0·5884 (3, 4)	—	2·452	35·95	88·15	2·890	7·088
XVII	isoxazole	2	1·3058	0·4396 (1, 2)	0·7274 (2, 3)	—	2·383	35·71	85·09	2·872	6·851
XVIII	thiazole	3	1·2906	0·6964 (2, 3)	0·5944 (3, 4)	—	2·444	35·88	87·71	2·886	7·056
XIX	isothiazole	2	1·3342	0·4744 (1, 2)	0·7068 (2, 3)	—	2·376	35·39	84·09	2·854	6·783
XX	indole	1 (NH)	1·5568	0·5308 (1, 2)	0·4976 (1, 1a)	—	2·457	46·86	115·1	3·423	8·411
XXI	N-methylindole	1 (NMe)	1·6024	0·5016 (1, 2)	0·4660 (1, 1a)	0·0608 (NMe)	2·457	46·24	113·6	3·390	8·329
XXIIa	benzopyrazole (1-H)	1 (NH)	1·5138	0·4940 (1, 2)	0·5420 (1, 1a)	—	2·460	47·44	116·7	3·455	8·500
		2	1·2932	0·4940 (1, 2)	0·7246 (2, 3)	—	2·411	35·85	86·45	2·884	6·955
XXIIb	benzopyrazole (2-H)	1	1·3660	0·5282 (1, 2)	0·5664 (1, 1a)	—	2·324	35·03	81·39	2·831	6·579
		2 (NH)	1·4276	0·5282 (1, 2)	0·6466 (2, 3)	—	2·522	48·64	122·7	3·518	8·873
XXIII	1-methylbenzopyrazole	1 (NMe)	1·5464	0·4790 (1, 2)	0·5096 (1, 1a)	0·0724 (NMe)	2·471	47·00	116·2	3·431	8·480
		2	1·2996	0·4790 (1, 2)	0·7342 (2, 3)	—	2·406	35·78	86·08	2·880	6·929
XXIV	2-methylbenzopyrazole	1	1·3714	0·5152 (1, 2)	0·5742 (1, 1a)	—	2·319	34·97	81·09	2·827	6·556
		2 (NMe)	1·4544	0·5151 (1, 2)	0·6258 (2, 3)	0·0928 (NMe)	2·548	48·27	123·0	3·498	8·915
XXV	benzimidazole	1 (NH)	1·5434	0·5846 (1, 2)	0·4756 (1, 1a)	—	2·471	47·04	116·2	3·433	8·484
		3	1·3238	0·7056 (2, 3)	0·5232 (3, 4)	—	2·402	35·50	85·29	2·862	6·875
XXVI	N-methylbenzimidazole	1 (NMe)	1·5848	0·5630 (1, 2)	0·4424 (1, 1a)	0·0648 (NMe)	2·476	46·48	115·0	3·403	8·424
		3	1·3178	0·7268 (2, 3)	0·4996 (3, 4)	—	2·404	35·57	85·51	2·866	6·890

XXVIIa	benzotriazole (1-H)	1 (NH)	1·4836	0·5622 (1, 2)	0·5252 (1, 1a)	—	2·483	47·86	118·8	3·477	8·634
		2	1·1870	0·5622 (1, 2)	0·6894 (2, 3)	—	2·473	37·08	91·70	2·962	7·326
		3	1·2206	0·6894 (2, 3)	0·5622 (3, 3a)	—	2·458	36·69	90·18	2·937	7·221
XXVIIb	benzotriazole (2-H)	1	1·3072	0·5976 (1, 2)	0·5536 (1, 1a)	—	2·375	35·69	84·77	2·874	6·826
		2 (NH)	1·3650	0·5976 (1, 2)	0·5976 (2, 3)	—	2·531	49·52	125·3	3·564	9·020
		3	1·3072	0·5976 (2, 3)	0·5536 (3, 3a)	—	2·375	35·69	84·77	2·874	6·826
XXVIII	1-methylbenzotriazole	1 (NMe)	1·5182	0·5482 (1, 2)	0·4892 (1, 1a)	0·0790 (NMe)	2·496	47·38	118·3	3·452	8·616
		2	1·1830	0·5482 (1, 2)	0·7088 (2, 3)	—	2·477	37·12	91·97	2·965	7·345
		3	1·2120	0·7088 (2, 3)	0·5352 (3, 3a)	—	2·459	36·79	90·44	2·944	7·238
XXIX	2-methylbenzotriazole	1	1·3194	0·5856 (1, 2)	0·5556 (1, 1a)	—	2·365	35·55	84·09	2·865	6·777
		2 (NMe)	1·3788	0·5856 (1, 2)	0·5856 (2, 3)	0·1108 (NMe)	2·570	49·33	126·8	3·554	9·132
		3	1·3194	0·5856 (2, 3)	0·5556 (3, 3a)	—	2·365	35·55	84·09	2·865	6·777
XXX	benzoxazole	3	1·3002	0·7554 (2, 3)	0·4904 (3, 3a)	—	2·420	35·77	86·57	2·879	6·968
XXXI	benzothiazole	3	1·3130	0·7348 (2, 3)	0·4976 (3, 3a)	—	2·409	35·62	85·81	2·870	6·912
XXXIII	benzisothiazole	1	1·3708	0·5076 (1, 2)	0·5944 (1, 1a)	—	2·325	34·97	81·31	2·828	6·574
XXXIV	carbazole	9 (NH)	1·5998	0·4772 (1a,9)	0·4772 (8a, 9)	—	2·424	46·27	112·2	3·392	8·222
XXXV	N-methylcarbazole	9 (NMe)	1·6470	0·4444 (1a,9)	0·4444 (8a, 9)	0·0530 (NMe)	2·418	45·63	110·4	3·357	8·120

[a] atoms involved in the bonds are numbered in parentheses; π-bond orders for the N-Me result from the assumed model of the Me group as a π-electron centre in the calculations

[b] calculated as $2 + \frac{4}{9}(p^{\pi}_{NA} + p^{\pi}_{NB} + p^{\pi}_{NC})$ for pyrrole-type nitrogen atom, and $\frac{2}{9}^2 + \frac{4}{9}(p^{\pi}_{NA} + p^{\pi}_{NB} + q^{\pi}_{N})$ otherwise

[c] calculated as $(4{\cdot}15 - 0{\cdot}35q^{\pi}_{N})^3$ for pyrrole-type nitrogen atom, and $(3{\cdot}75 - 0{\cdot}35q^{\pi}_{N})^3$ otherwise

[d] calculated as $3{\cdot}099 - 0{\cdot}732(q^{\pi}_{N} - 2)$ for pyrrole-type nitrogen atom, and $3{\cdot}099 - 0{\cdot}732(q^{\pi}_{N} - 1)$ otherwise; eq. 4.[10]

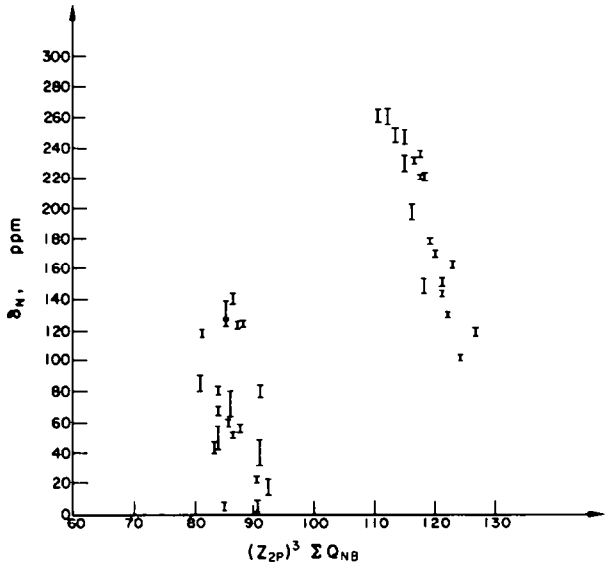


FIG 2.

EXPERIMENTAL

Some of the substances used in the ^{14}N NMR measurements are available commercially (I, III, V, XVIII, XX, XXV, XXVII, XXXI, XXXIII). They were purified by conventional methods before the NMR measurements were taken. Others were prepared by published procedures (II,[11] IV,[12] VI,[13] VIII,[14] IX,[15] X,[16] XI,[16] XII,[16] XIII,[17] XIV,[18] XV,[18] XVI,[19] XVII,[20] XIX,[21] XXI,[22] XXII,[23] XXIII,[24] XXIV,[24] XXVI,[24] XXVIII,[25] XXIX,[25] XXX,[26] XXXII,[27] XXXIV[28]).

The ^{14}N NMR spectra were measured at 4·33 MHz. The technique was the same as before.[3] The approximate probe temperature was 32°. $MeNO_2$ was used as an internal standard. The direction of increasing magnetic field was assumed to be positive in the denomination of the chemical shifts.

The calculation of the chemical shifts and half-height signal widths from the spectra containing two or more overlapping ^{14}N resonances was carried out by a line-shape analysis which involved the least-squares fitting of a curve represented by a combination of Lorentzian lines. The latter included both the 2 kHz modulation sidebands in the inverted absorption mode[29] and the central band in the upright absorption mode superimposed on to the background line (eq. 5),

$$F(\nu) = A + B\nu + \sum_n C_n b_n^2 \left(\frac{1}{b_n^2 + (\nu_n - \nu)^2} + \frac{-k}{b_n^2 + (\nu_n + M - \nu)^2} + \frac{-k}{b_n^2 + (\nu_n - M - \nu)^2} \right) \qquad (5)$$

where ν is the frequency, $A + B\nu$ is the equation of slanting background, C_n is the maximum height of a separated signal relative to the true background line, $2b_n$ is the half-height width, ν_n is the chemical shift of nucleus n, M is the modulation frequency (2014 Hz in our case), and k is a proportionality factor of the sideband-to-centreband intensity (0·7 in our measurements). The zeroth order approximation for the iterative fitting of the curve was found by inspection of the spectra at high RF power settings where broad resonances were clearly visible in the central band and narrow resonance signals were far from saturated in the sidebands. The errors quoted in Table 1 for such systems are standard deviations of the least-squares fit.

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