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NITROGEN-14 NUCLEAR MAGNETIC RESONANCE OF SOME SIX-MEMBERED AROMATIC HETEROCYCLES

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Abstract—The ^{14}N NMR chemical shifts of some aromatic heterocycles including pyridine, 1,2-diazine, 1,3-diazine, 1,4-diazine, and 1,3,5-triazine systems in mono-, bi-, and tricyclic structures (azabenzene, azanaphthalene, and azaphenanthrene type) are shown to depend almost linearly on the π-charge density at the N atom obtained from P–P–P calculations. This dependence is considered in terms of various approximations within the general theory of chemical shifts. A similar correlation is observed for the pyridine ring containing various electron-donating mono-substituents. The ^{14}N NMR shifts show that the three isomeric aminopyridines exist as such in acetone, whereas two of the corresponding hydroxy derivatives have essentially the pyridine-type structure. Careful re-examination of the δ_N scale of ^{14}N chemical shifts shows that the zero chemical shift difference between the two primary internal standards, nitromethane and the nitrate ion, is correct as previously indicated rather than the difference of 3 ppm reported by other authors.

INTRODUCTION

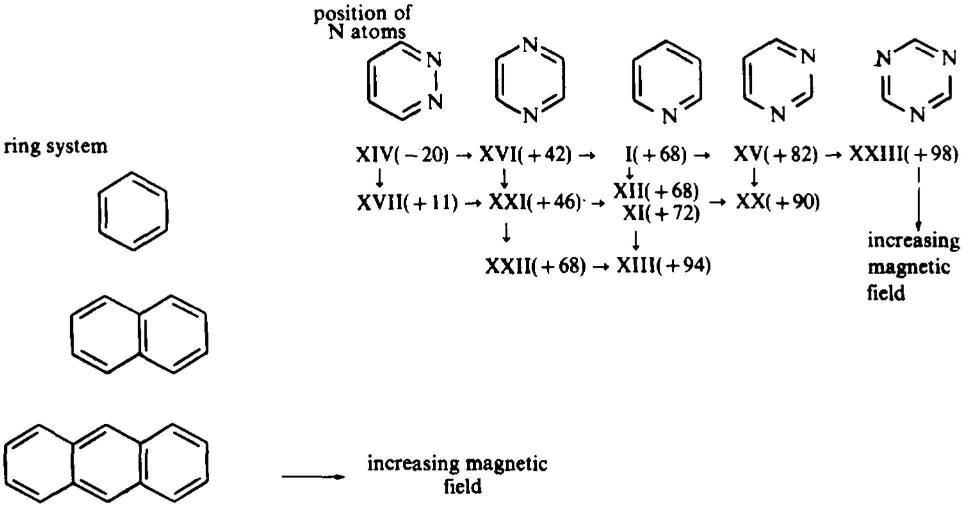
IN SPITE of growing interest in ^{14}N NMR studies there has so far been a paucity of experimental data on the ^{14}N chemical shifts of fundamental heteroaromatic systems. The reported data are limited to pyridine, the diazines, quinoline, isoquinoline, and certain derivatives thereof.[1–3]

Several attempts at a theoretical explanation of the ^{14}N chemical shifts of aromatic heterocycles have been made[2,4–6] in terms of various approximations within the general theory of chemical shifts. Since the approximations involve a few arbitrary assumptions and the adjustment of some parameters, there may be some doubt about their validity when applied to a larger set of experimental data which includes fused-ring systems. The problem is interesting because it is closely connected with the degree of complexity of the relationship between the ^{14}N chemical shifts and the electronic structure of conjugated systems containing N atoms. If the ^{14}N NMR data prove to be useful in understanding this relationship then either there must be a clear empirical correlation between the shifts and the electron distribution or the explanation offered should not contain any undetermined quantities which change from one case to another. So far there has been controversy as to which factors are dominant in the determination of the ^{14}N screening constant and which may be safely dismissed.[2–12] In this work, we have tried to obtain systematic experimental data using internal reference measurements for ^{14}N chemical shifts on a large number of aromatic heterocycles. The existing theories of nuclear screening are critically discussed in the interpretation of the observed ^{14}N shifts.

RESULTS AND DISCUSSION

The results of ^{14}N NMR measurements on heterocyclic compounds containing 6-membered aromatic rings and representing fundamental structural types are given in Table 1.

The data for pyridine, the diazines, quinoline and isoquinoline differ from those obtained using an external reference by up to 20 ppm. With the exception of methanol no important solvent or dilution shifts were observed. However, methanol introduced some changes in excess of experimental error, but without any apparent regularity. This seems to indicate that the effect of H-bonding on the ^{14}N resonance shifts is not straightforward, i.e. it does not simply move the signal to higher fields where the resonances of the corresponding protonated species generally occur. Some empirical correlations are evident from the spectra without resorting to a detailed consideration of the electronic structure of the aromatic rings. The sequence of shifts, from low to high fields, for some typical structures is 1,2-diazine, 1,4-diazine, pyridine, 1,3-diazine. 1,3,5-triazine, and is obeyed in each series of related structures (one, two, and three 6-membered rings, respectively).

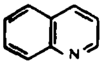
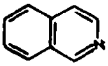
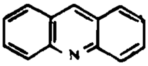
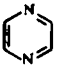
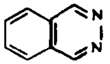
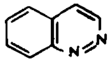
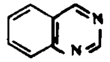
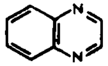
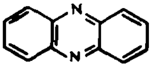


This indicates that the correlation is general, provided that similar structures are compared. Another rule, with the exception of the cinnoline ring system (XVIII, XIX), is that a shift to higher fields is observed upon enlarging the aromatic system, as can be seen from the vertical sequences in the scheme above.

In order to relate the observed regularity in ^{14}N shifts to the electronic structure of the heteroaromatic rings it is necessary to have uniform MO data on all types of rings.

We have performed SCF-MO calculations of the Pariser–Parr–Pople (P–P–P) type using the semi-empirical parameters reported by Nishimoto and Forster.[13] The two-center inter-electronic repulsion parameters, $\gamma_{\mu\nu}$, have been evaluated by means of the Nishimoto–Mataga formula,[14] as discussed previously,[15] from known molecular geometries. We have used the heteroatom model to describe the Me

TABLE 1. ^{14}N NUCLEAR MAGNETIC RESONANCE DATA FOR SOME SIX-MEMBERED AROMATIC HETEROCYCLES

No.	Compound		Solvent/Standard[a]	^{14}N Chemical shift[b] δ_N (ppm)	Half-height Width (Hz)
I	Pyridine		neat/NM	+ 68 ± 2	260 ± 8
			neat/DMF	+ 68 ± 2	260 ± 8
			CH_3OH/DMF	+ 73 ± 2	320 ± 8
II	2-Methylpyridine		neat/NM	+ 72 ± 2	350 ± 20
III	3-Methylpyridine		neat/NM	+ 68 ± 3	370 ± 25
IV	4-Methylpyridine		neat/NM	+ 74 ± 3	410 ± 30
V	2-Aminopyridine		acetone/NM	+128 ± 4[c]	650 ± 20
VI	3-Aminopyridine		acetone/NM	+ 88 ± 4[c]	680 ± 20
VII	4-Aminopyridine		acetone/NM	+105 ± 4[c]	680 ± 20
VIII	2-Hydroxypyridine (α-pyridone)		acetone/NM	+209 ± 2	90 ± 20
IX	3-Hydroxypyridine		acetone/NM	+ 85 ± 3	600 ± 30
X	4-Hydroxypyridine (γ-pyridone)		acetone/NM	+201 ± 2	390 ± 30
XI	Quinoline		neat/NM	+ 72 ± 3	650 ± 20
			neat/DMF		
XII	Isoquinoline		neat/NM	+ 68 ± 4	680 ± 20
			neat/DMF		
XIII	Acridine		CH_2Br_2/NM	+ 94 ± 8	820 ± 50
XIV	Pyridazine (1,2-Diazone)		DMF/DMF	− 20 ± 2	380 ± 10
			$CHCl_3$/DMF	− 20 ± 2	410 ± 20
			benzene/DMF	− 21 ± 3	320 ± 15
			CH_3OH/DMF	− 10 ± 2	410 ± 15
XV	Pyrimidine (1,3-Diazone)		DMF/DMF	+ 82 ± 2	205 ± 10
			CH_3OH/DMF	+ 86 ± 2	210 ± 10
XVI	Pyrazine (1,4-Diazone)		DMF/DMF	+ 42 ± 2	220 ± 10
			CH_3OH/DMF	+ 48 ± 3	470 ± 20
XVII	Phthalazine		dioxan/NM	+ 11 ± 4	800 ± 50
XVIII	Cinnoline		dioxan/NM	− 36 ± 5[d]	950 ± 50[d]
XIX	4-Methylcinnoline		acetone/NM	− 35 ± 4[d]	850 ± 50[d]
XX	Quinazoline		CH_2Br_2/NM	+ 90 ± 3[d]	950 ± 50[d]
XXI	Quinoxaline		dioxan/NM	+ 46 ± 3	950 ± 50
			CH_3OH/NM	+ 46 ± 3	950 ± 50
XXII	Phenazine		dioxan/NM	+ 68 ± 3	660 ± 50
			CH_2Br_2/NM	+ 67 ± 3	750 ± 50
XXIII	1,3,5-Triazine		dioxan/DMF	+ 98 ± 1	255 ± 5

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[a] internal; NM-nitromethane; DMF-dimethylformamide

[b] internal reference scale; $\delta_N(CH_3NO_2) = \delta_N(NO_3^-) = 0$; see ref. 27

[c] see ref. 3

[d] only one resonance signal was observed due to overlapping.

group with the parameters suggested by Roos[16] for the one-center repulsion integral $\gamma_{\mathrm{CH_3},\,\mathrm{CH_3}} = 10{\cdot}01$ eV and the two-center core integral $\beta_{\mathrm{C-CH_3}} = -1{\cdot}38$ eV. Since the Me group is considered as a two π electron contributor, the value of $-12{\cdot}02$ eV for the valence state ionization energy, $W_{\mathrm{CH_3}}$, reported by Roos appears to be rather low. Consequently we have calculated a value of $W_{\mathrm{CH_3}} = -22{\cdot}81$ eV from $\gamma_{\mathrm{CH_3},\,\mathrm{CH_3}}$ using the Nishimoto–Forster relationship.[13] This value has been used in a series of calculations on some Me substituted heterocycles which adequately account for their electronic spectra.[17] Although the value of $\beta_{\mathrm{C-CH_3}}$ is smaller than the Nishimoto–Forster values used for the other bonds in the calculations, it appears that β may be treated as a rather flexible parameter.[18] Consistent values of β have been used in our calculations. The calculated values of the π-charge density on the N atom, q_N^π, and the mobile bond orders p_{NB}^π, p_{NC}^π, for the bonds joining N to the neighbouring atoms B and C are reported in Table 2.

TABLE 2

Molecule	δ_N ppm	SCF-PPP		
		π-Charge density at N q_N^π	Mobile bond orders	
			p_{NB}^π	p_{NC}^π
Cinnoline	− 36	1·1240 1·1152	0·6130 0·5660	0·6992 0·6992
Pyridazine	− 20	1·1362	0·6936	0·6156
Phthalazine	+ 11	1·1598	0·7508	0·5448
Pyrazine	+ 42	1·1880	0·6620	0·6620
Quinoxaline	+ 46	1·1920	0·5442	0·7336
Phenazine	+ 68	1·1952	0·6114	0·6114
3-Methylpyridine	+ 68	1·2222	0·6522	0·6542
Isoquinoline	+ 68	1·2294	0·7252	0·6398
Pyridine	+ 68	1·2142	0·6614	0·6614
2-Methylpyridine	+ 72	1·2396	0·6500	0·6426
Quinoline	+ 72	1·2338	0·5338	0·7226
4-Methylpyridine	+ 74	1·2308	0·6502	0·6502
Pyrimidine	+ 82	1·2356	0·6502	0·6488
Quinazoline	+ 90	1·2352 1·2472	0·7060 0·7078	0·5922 0·5392
Acridine	+ 94	1·2516	0·5994	0·5994
s-Triazine	+ 98	1·2628	0·6454	0·6454
3-Aminopyridine	+ 88	1·2158	0·6680	0·6452
3-Hydroxypyridine	+ 85	1·2168	0·6486	0·6628
4-Aminopyridine	+105	1·2782	0·6314	0·6314
2-Aminopyridine	+128	1·3302	0·5566	0·6406

The comparison of the ^{14}N chemical shifts with the results of the P–P–P calculations (Fig 1) shows that there is almost a linear relationship between the shifts and the calculated π-charge densities at the N atoms.

For those systems with two-non-equivalent N atoms, where only one broad resonance signal was observed (XVIII, XIX, XX), mean values were used for the π-charge densities. The largest deviation from linearity is shown by a sub group of closely

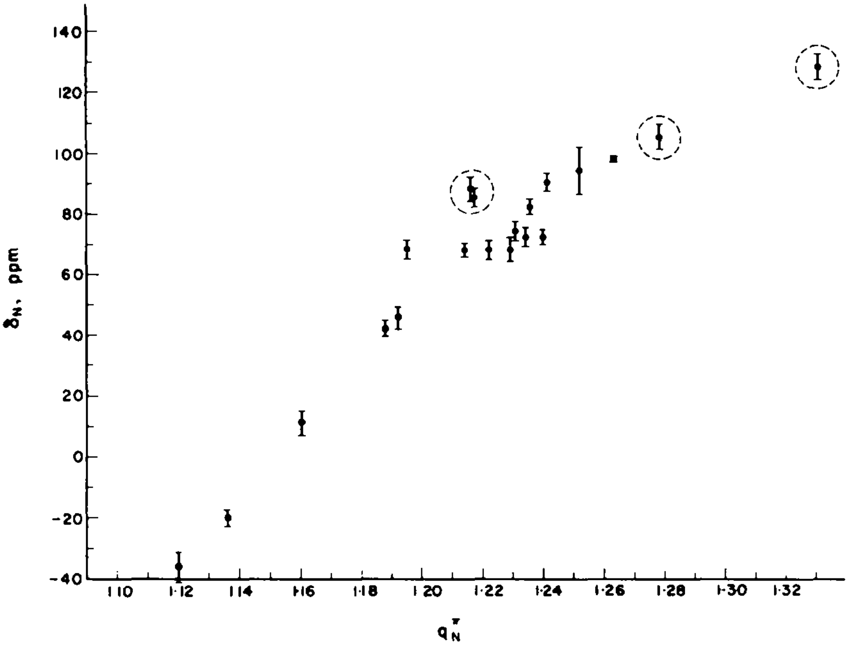


FIG 1. Plot of ^{14}N chemical shift δ_N in ppm against π charge density q_N^π calculated for the N atom by the P–P–P method.

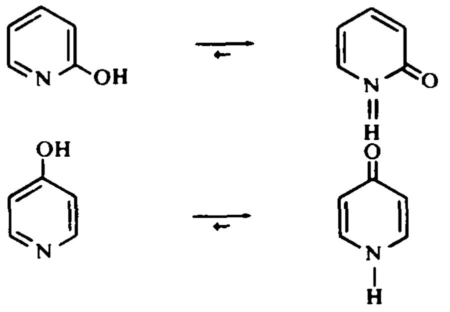
related molecules (aminopyridines V–VII, and 3-hydroxypyridine IX); this results in a slightly different slope in the linear correlation rather than a random distribution of the experimental points. This is an important conclusion since the results indicate that the ^{14}N chemical shifts of heteroaromatic rings may serve as a reasonably accurate measure of the π-charge density at the N atoms. For unsubstituted or Me substituted systems the relationship is:

$$q_N^\pi = (1{\cdot}153 + 0{\cdot}001014\,\delta_N) \pm 0{\cdot}006 \qquad (1)$$

Whereas for 3-hydroxypyridine and the aminopyridines a different linear relationship is obtained:

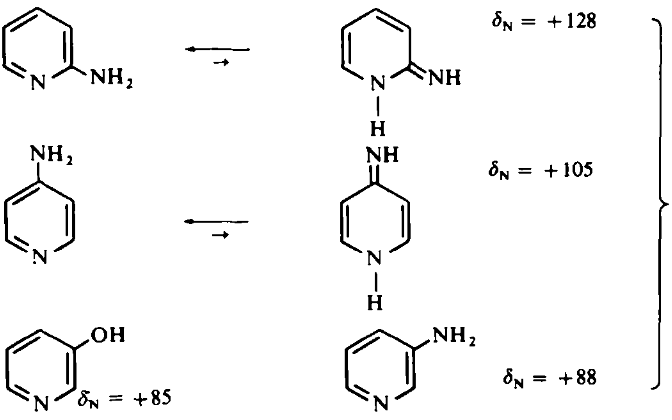
$$q_N^\pi(\mathrm{PyNH_2, PyOH}) = (0{\cdot}9678 + 0{\cdot}002875\,\delta_N) \pm 0{\cdot}006 \qquad (2)$$

While the high-field shifts of the ^{14}N resonances for 2-hydroxypyridine (VIII) and 4-hydroxypyridine (X) show that they exist essentially as the corresponding pyridones.



observed δ_N	calculated δ_N for the OH form from Eq. 2
+209	+120 ppm
+201	+104 ppm

the linearity of the shifts for V, VI, VII and IX with the charge density shows that the corresponding aminopyridines exist as such rather than in the tautomeric imino form.



The values given for δ_N are observed ones.

linear dependence on π-charge density calculated for the hydroxy-and amino-forms

It should be noted that the linearity observed here in the relationship between the ^{14}N chemical shifts and π-electron density in aromatic heterocycles, is contrary to the earlier findings[4] for diazines.

In the general expression for the nuclear screening constant σ, given by Eq. 3,[19]

$$\sigma_A = \sigma_A^{dia} + \sigma_A^{para} + \sigma_{AB}(\text{long-range}) \qquad (3)$$

only the first two terms are considered to be important for nitrogen nuclei. The local diamagnetic term, σ_A^{dia}, may be expressed[20] in terms of mean inverse orbital radii, $\langle r^{-1}\rangle$, and orbital populations, $P_{\mu\mu}$:

$$\sigma_A^{dia} = \frac{e^2}{3mc^2}\sum_{\mu} P_{\mu\mu}\langle r^{-1}_{\mu}\rangle \qquad (4)$$

where the summation is over all of the atomic orbitals μ, on atom A. The values of $\langle r_\mu^{-1}\rangle$ may be calculated[8] from the electron charge density terms, P, and effective nuclear charge, Z, for the nitrogen nucleus.

However it is rather difficult to obtain a reliable estimate of the individual charge density terms. The use of π-charge density alone may be warranted only if there is no appreciable difference in the polarization of the sigma-bonds between the structures compared. Since the largest contributions to Eq. (4) arise from the inner-shell electrons, it appears that changes in the diamagnetic term are rather insignificant in accounting for the observed ^{14}N chemical shifts. Calculations of σ_N^{dia} involving both the σ and π-electrons[6] suggest that the contribution is of the order of 0·5 ppm, well within the experimental error of our measurements. However, in principle, the observed correlation of the ^{14}N shifts versus π-charge density is consistent with the expected changes in the σ_N^{dia} term.

The paramagnetic term, σ_A^{para}, may be expressed in terms of the linear combination of gauge invariant atomic orbitals--MO approximation (LCGI--MO) as,[21]

$$\sigma_{\mathrm{A}}^{\mathrm{para}} = -\tfrac{2}{3}\frac{e^2\hbar^2}{m^2c^2}\langle r^{-3}\rangle_{2p}\sum_{i}^{\mathrm{occ.}}\sum_{j}^{\mathrm{unocc.}}(\Delta\mathrm{E}_{i\to j})^{-1}\Big[(c_{i,x_{\mathrm{A}}}c_{j,y_{\mathrm{A}}} - c_{i,y_{\mathrm{A}}}c_{j,x_{\mathrm{A}}})\sum_{\mathrm{B}}(c_{i,x_{\mathrm{B}}}c_{j,y_{\mathrm{B}}} - c_{i,y_{\mathrm{B}}}c_{j,x_{\mathrm{B}}}) + (c_{i,y_{\mathrm{A}}}c_{j,z_{\mathrm{A}}} - c_{i,z_{\mathrm{A}}}c_{j,y_{\mathrm{A}}})\sum_{\mathrm{B}}(c_{i,y_{\mathrm{B}}}c_{j,z_{\mathrm{B}}} - c_{i,z_{\mathrm{B}}}c_{j,y_{\mathrm{B}}}) + (c_{i,z_{\mathrm{A}}}c_{j,x_{\mathrm{A}}} - c_{i,x_{\mathrm{A}}}c_{j,z_{\mathrm{A}}})\sum_{\mathrm{B}}(c_{i,z_{\mathrm{B}}}c_{j,x_{\mathrm{B}}} - c_{i,x_{\mathrm{B}}}c_{j,z_{\mathrm{B}}})\Big] \tag{5}$$

where the summation over B includes all atoms (also A), the c terms are the coefficients of the corresponding $2p$ orbitals, in the MO's i and j while $\langle r^{-3}\rangle_{2p}$ is the mean value of the reciprocal cube of the $2p$ orbital radius or, as it is sometimes called, the orbital expansion term. The latter is usually calculated from Eq. 6,

$$\langle r^{-3}\rangle_{2p} = \tfrac{1}{3}\left(\frac{Z_{2p}}{2a_0}\right)^3 \tag{6}$$

where Z_{2p} is the effective nuclear charge for the $2p$ orbitals. An increase in the electron density at the atom results in a decrease in $\langle r^{-3}\rangle_{2p}$ so that changes in this term affect the screening constant in a similar manner to changes in the diamagnetic term. shifting the ^{14}N resonance to higher fields with the increasing electron charge density at the N atom. It should be noted that both the σ and π-electrons effect the orbital expansion term, and an approximation which includes only variation in the π-charge density may not be valid. However, it is difficult to estimate actual contributions to the term from both the σ and π-electrons. The general trend in the ^{14}N resonance shifts for aromatic heterocycles observed in this work is in agreement with that expected from the changes in the $\langle r^{-3}\rangle_{2p}$ term. One should be cautious, however, when assigning the dominant role to this term, since the relationship observed is almost linear with the π-charge density, whereas that from Eq. (6) is not. Inclusion of the $\langle r^{-3}\rangle_{2p}$ term reduces the calculated chemical shift between pyridine and the pyridinium ion to zero, whilst the actual shift is as large as about 120 ppm.[2,8]

It is also difficult to obtain a significant value of the summation term in Eq. 5. since all excited electronic states would have to be known. The $\pi \to \pi^*$ transitions do not contribute to this term, since they involve only one component (e.g., $2p_z$) of the $2p$-orbital system. A simplified approach called the different excitation energy, DEE, approximation has been proposed,[6] where the matrix elements between the occupied and unoccupied MO's divided by the corresponding energy interval are summed for the lower excitation energies and the average energy of 10 eV, is used for the remaining transitions. This method has reproduced the ^{13}C shifts rather accurately, but was much less satisfactory for the ^{14}N shifts in diazines. However, the DEE approximation appears to fail, even qualitatively, for the ^{14}N resonance shifts presented here. It tends to predict a low-field shift with an increase in the number of fused aromatic rings which is contrary to the experimental results.

If the excitation energies, ΔE, in Eq. 5 are replaced by a mean value, $\Delta\mathrm{E}_{\mathrm{av}}$, the so-called average excitation energy, AEE, approximation is obtained. The expression for the paramagnetic term using the AEE approximation has been derived by Pople,[21]

$$\sigma_{\mathrm{A}}^{\mathrm{para}}(\mathrm{AEE}) = -\frac{e^2\hbar^2}{2m^2c^2}\langle r^{-3}\rangle_{2p}(\Delta\mathrm{E}_{\mathrm{av}})^{-1}\sum_{\mathrm{B}} Q_{\mathrm{AB}} \tag{7}$$

where the summation over B includes A, and

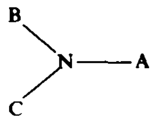
$$Q_{AB} = \tfrac{4}{3}\delta_{AB}(P_{x_Ax_B} + P_{y_Ay_B} + P_{z_Az_B}) - \tfrac{2}{3}(P_{x_Ax_B}P_{y_Ay_B} + P_{x_Ax_B}P_{z_Az_B} + P_{y_Ay_B}P_{z_Az_B})$$
$$+ \tfrac{2}{3}(P_{x_Ay_A}P_{x_By_A} + P_{x_Az_B}P_{x_Bz_A} + P_{y_Az_B}P_{y_Bz_A}) \qquad (8)$$

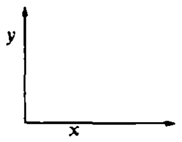
where the P's are the charge-density and bond-order matrix elements for the unperturbed wave functions and δ_{AB} is the Kroenecker delta. If Eq. 6 is used for the $\langle r^{-3}\rangle_{2p}$ term then it may become dominant. However, the same caution should be exercised here as in the discussion of Eq. 6. The mean excitation energy, ΔE_{av}, is usually an undetermined quantity which is useful to the extent that it may be assumed constant throughout a group of related molecules. There have been attempts[1, 11] at explaining the ^{14}N shifts for various molecules mainly in terms of changes in ΔE_{av}, represented in a crude approximation by the lowest-energy electronic transitions. Comparison of the $n \rightarrow \pi^*$ transition energies for the molecules examined here with their ^{14}N spectra does not indicate any correlation (Table 3); there is even a general discrepancy between the lower excitation energies for polynuclear aromatic systems and the high-field shift of the ^{14}N resonances as compared with the monocyclic structures (e.g. phthalazine versus pyridazine, quinazoline versus pyrimidine, etc.)

TABLE 3

Molecule	δ^N (ppm)	$n \rightarrow \pi^*$ Transition[22] (nm)
s-Triazine	+98	2720
Quinazoline	+90 (mean)	3300
Pyrimidine	+82	2980
Pyridine	+68	2700
Quinoxaline	+46	3390
Pyrazine	+42	3280
Phthalazine	+11	3570
Pyridazine	−20	3400
Cinnoline	−36 (mean)	3890

For a trigonally hybridized nitrogen atom N, in a delocalised π-electron system with polarized sigma-bonds, NA, NB and NC the sigma-bond wavefunctions may be written as:





$$\psi_{NA} = \frac{1}{\sqrt{2}}\left[\sqrt{1+a}\,\frac{1}{\sqrt{3}}(s_N - \sqrt{2}\,p_{x_N}) + \sqrt{1-a}\,\frac{1}{\sqrt{3}}(s_A + \sqrt{2}\,p_{x_A})\right];$$
$$\psi_{NB} = \frac{1}{\sqrt{2}}\left[\sqrt{1+b}\,\frac{1}{\sqrt{3}}(s_N + \frac{1}{\sqrt{2}}p_{x_N} + \frac{\sqrt{6}}{2}p_{y_N})\right.$$

$$+\sqrt{1-\mathrm{b}}\frac{1}{\sqrt{3}}\left(s_{\mathrm{B}}-\frac{1}{\sqrt{2}}p_{x_{\mathrm{B}}}-\frac{\sqrt{6}}{2}p_{y_{\mathrm{B}}}\right)\Bigg];$$

$$\psi_{\mathrm{NC}}=\frac{1}{\sqrt{2}}\left[\sqrt{1+\mathrm{c}}\frac{1}{\sqrt{3}}\left(s_{\mathrm{N}}+\frac{1}{\sqrt{2}}p_{x_{\mathrm{N}}}-\frac{\sqrt{6}}{2}p_{y_{\mathrm{N}}}\right)\right.$$

$$\left.+\sqrt{1-\mathrm{c}}\frac{1}{\sqrt{3}}\left(s_{\mathrm{C}}-\frac{1}{\sqrt{2}}p_{x_{\mathrm{C}}}+\frac{\sqrt{6}}{2}p_{y_{\mathrm{C}}}\right)\right];$$

where a, b and c are the sigma-bond polarization coefficients ($\leqslant 1$), with the π-charge density, q_{N}^{π}, and the corresponding mobile bond orders P_{NA}^{π}, P_{NB}^{π}, and P_{NC}^{π}, the summation according to Eq. 8 yields

$$\sum_{\mathrm{N,A,B,C}} Q_{\mathrm{NB}} = 2 - \tfrac{4}{9}(a+b+c)(q_{\mathrm{N}}^{\pi}-1) - \tfrac{2}{9}(ab+bc+ac) + \tfrac{4}{9}\left(\sqrt{1-a^2}\,p_{\mathrm{NA}}^{\pi}+\sqrt{1-b^2}\,p_{\mathrm{NB}}^{\pi}+\sqrt{1-c^2}\,p_{\mathrm{NC}}^{\pi}\right) \quad (9)$$

If A is a lone electron pair, n, then $a = 1$, and Eq. 9 becomes

$$\sum_{\mathrm{N,n,B,C}} Q_{\mathrm{NB}} = \tfrac{22}{9} + \tfrac{2}{9}(b+c-bc) - \tfrac{4}{9}(1+b+c)\,q_{\mathrm{N}}^{\pi} + \tfrac{4}{9}\left(\sqrt{1-b^2}\,P_{\mathrm{NB}}^{\pi}+\sqrt{1-c^2}\,P_{\mathrm{NC}}^{\pi}\right) \quad (10)$$

TABLE 4

Molecule	$(Z_{2p})^3$		ΣQ_{NB}		$(Z_{2p})^3\,\Sigma Q_{\mathrm{NB}}$	
	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2
Cinnoline	37·8181	36·4918	2·5280	2·4985	95·4143	90·9690
	37·9229	36·5844	2·5110	2·4820		
Pyradazine	37·6728	36·3402	2·5212	2·4913	94·9807	90·5343
Phtalazine	37·3971	36·0712	2·5047	2·4737	93·6685	89·2293
Pyrazine	37·0660	35·7480	2·5048	2·4725	92·8429	88·3869
Quinoxaline	37·0194	35·7022	2·4825	2·4501	91·9007	87·4740
Phenazine	36·9825	35·6666	2·4566	2·4241	90·8512	86·4594
3-Methylpyridine	36·6671	35·3585	2·4818	2·4480	91·0004	86·5576
Isoquinoline	36·5844	35·2778	2·5046	2·4705	91·6293	87·1538
Pyridine	36·7599	35·4491	2·4926	2·4591	91·6277	87·1729
2-Methylpyridine	36·4655	35·1617	2·4679	2·4333	89·9932	85·5590
Quinoline	36·5350	35·2295	2·4544	2·4201	89·6715	85·2589
4-Methylpyridine	36·5680	35·2619	2·4753	2·4411	90·5168	86·0778
Pyrimidine	36·5117	35·2069	2·4725	2·4382	90·2752	85·8415
Quinazoline	36·5183	35·2133	2·4724	2·4380	89·6074	85·1837
	36·3799	35·0782	2·4444	2·4094		
Acridine	36·3272	35·0267	2·4210	2·3858	87·9482	83·5667
s-Triazine	36·1991	34·9016	2·4568	2·4212	88·9339	84·5038
3-Aminopyridine	36·7434	35·4329	2·4877	2·4542	91·4066	86·9594
3-Hydroxypyridine	36·7300	35·4200	2·4864	2·4529	91·3255	86·8817
4-Aminopyridine	36·0221	34·7291	2·4376	2·4012	87·8075	83·3915
2-Aminopyridine	35·4298	34·1509	2·3853	2·3467	84·5107	80·1419

Case 1: $a = 1$, $b = c = 0$; Case 2: $a = 1$, $b = c = 0{\cdot}05$

while

$$Z_{2p} = 3{\cdot}75 - 0{\cdot}4\,(b + c) - 0{\cdot}35\, q_N^{\pi} \tag{11}$$

It should be noted that analogous equations reported in the literature[4] are not correct because of an error in sign in Eq. 8.

It is rather difficult to obtain reliable estimates of the sigma-bond polarization coefficients, but it is evident from Eq. 10 that as b and c become larger the effect on ΣQ_{NB} of changes in q_N^{π} increases whilst the effect of changes in the mobile bond orders decreases. Table 4 shows the results of calculations based on Eqs 10 and 11 compared with the ^{14}N resonance shifts and MO parameters obtained in this work. Case 1 involves no sigma-bond polarization; in case 2 the polarization was assumed to give a net sigma-charge of 0·1 at the N atom. This value is based on some CNDO-type calculations reported in the literature[6]. The plots (Figs 2 and 3) of the ^{14}N chemical shift δ_N versus the product $(Z_{2p})^3\, \Sigma Q_{NB}$ show an improved correlation when compared with that in Fig 1. The relationship is not quite linear but follows a reasonably smooth curve. The effect of including uniform sigma-bond polarization is negligible as far as the correlation is concerned. Larger differences in the sigma-bond polarization coefficients might effect the value of the product to a considerable extent. However, from the correlations observed it seems that this is not the case; a linear relationship may be obtained if one assumes a small regular decrease in the polarization coefficients with an increase in q_N^{π} which may reasonably be explained in terms of electron-repulsion.

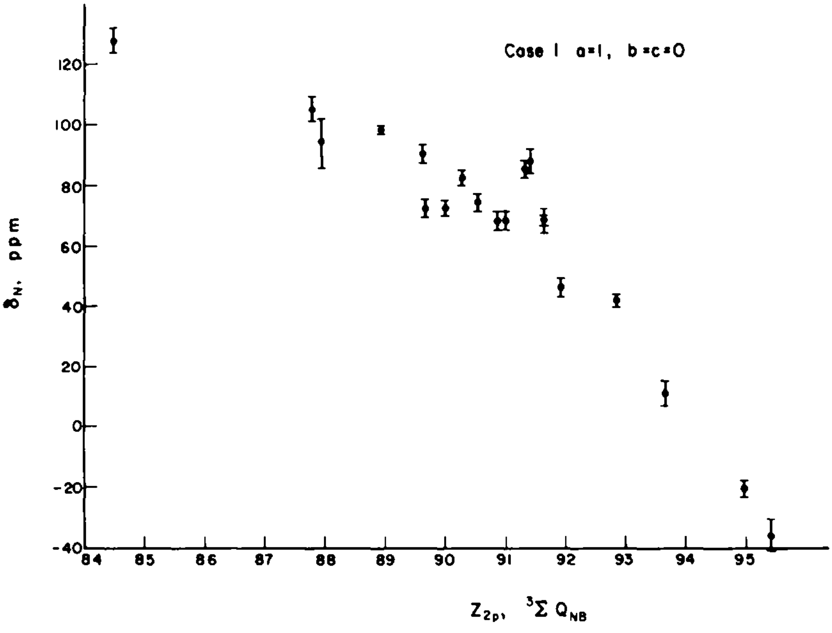


FIG 2. Plot of ^{14}N chemical shift δ_N in ppm against $(Z_{2p})^3\, \Sigma Q_{NB}$ for case 1 ($a = 1$, $b = c = 0$).

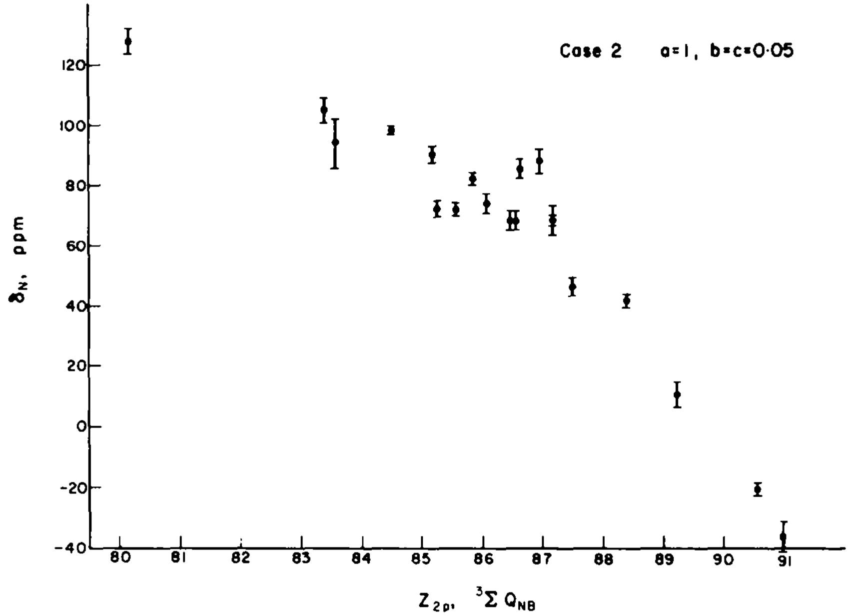


FIG 3. Plot of ^{14}N chemical shift δ_N in ppm against $(Z_{2p})^3 \Sigma Q_{NB}$ for case 2 ($a = 1, b = c = 0{\cdot}05$).

CONCLUSIONS

The results reported in this work indicate that the average excitation energy approximation is valid for the heterocycles examined and that ΔE_{av} may be assumed to be approximately constant. There seems to be no simple correlation between ΔE_{av} and the longest-wavelength electronic transitions in this case and any attempt at including changes in ΔE_{av} on the basis of the $n \rightarrow \pi^*$ transitions would result in an obvious deterioration of the correlation given in Figs 2 and 3. The importance of high-energy transitions in the average excitation energy has already been suggested for the ^{14}N resonance shifts of amines.[3]

It can be seen from Table 4 that both the orbital expansion term (expressed here in terms of $Z_{2p}{}^3$) and the ΣQ_{NB} term make significant contributions to the changes in the paramagnetic term. The variation calculated for either is of the order of a few per cent. The observed relationship between the π-charge density and the ^{14}N resonance shifts may be explained on the basis that either term depends to a considerable extent on q_N^*. However this does not apply to ΣQ_{NB} if there is no lone electron pair at the N atom in which case the polarization coefficients (*a*, *b* and *c*) are small (Eq. 8). This may at least partially explain the dependence of the ^{14}N shifts of the nitro group and similar systems on the π-mobile bond orders rather than the π-charge density[2, 23] which is in contrast to the dependence observed for the aromatic heterocycles.

EXPERIMENTAL

Most of the substances examined were available commercially, and were used as such or after purification by conventional methods. Cinnoline and 4-methylcinnoline were obtained in a multi-step synthesis starting from anthranilic acid[24]. Quinazoline was prepared from *o*-nitrobenzaldehyde[25, 26]; the authors are indebted to Mr. Z. Grabowski for the preparations.

The ^{14}N NMR spectra were measured with a Varian HA-60 spectrometer operating at 4·33 MHz and 14,100 Gauss using 15 mm o.d. sample tubes. The technique employed was described elsewhere[2]. The chemical shifts were measured from internal standards according to the δ_N scale[27] where $\delta_N(CH_3NO_2) = 0$; dimethylformamide was used occasionally as a secondary standard ($\delta_N = +276$ ppm). The positive sign was used for shifts to higher fields. Several runs in either direction of the field sweep were made. The results given in Table 1 were calculated as the averages after two extreme values had been discarded. The uniform scale of ^{14}N chemical shifts (δ_N) for non-aqueous and aqueous solutions, based on two primary internal standards, CH_3NO_2 and NO_3^-, has already been proposed by some of us[27]; it was shown that the relative shift between these two standards is within the experimental error of ± 1 ppm and may be assumed to be zero. Since then other authors[26] have reported a difference of 3 ppm for the two reference substances but no experimental details were given. In order to clarify the situation we have re-examined the shift using acetonitrile and dimethylformamide as intermediate reference points. The results obtained were as follows:

Solution	Relative ^{14}N NMR shift (ppm)
$CH_3CN + CH_3NO_2$ (3:1 v/v)	137 ± 1
(5:1 v/v)	136 ± 1
(10:1 v/v)	136 ± 1
$CH_3CN + H_2O$ (1:1 v/v) satd with KNO_3	139 ± 1
(2:1 v/v) satd with KNO_3	138 ± 1
DMF + H_2O (2:1 v/v) + trace CH_3NO_2	271 ± 1
DMF + H_2O (2:1 v/v) satd with KNO_3	270 ± 1

While the results for the acetonitrile solns show some solvent and dilution effects which may sometimes reach the upper limit of 3 ppm, the results for DMF where either standard was dissolved in the same medium show that the CH_3NO_2—NO_3^- shift is actually within the experimental error of ± 1 ppm, and may be assumed to be zero for all practical purposes, as was done originally[27]. All the results quoted here were obtained with a very careful absorption mode adjustment of the signals with power appreciably below the saturation level.

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