

NITROGEN-14 NUCLEAR MAGNETIC RESONANCE—V¹⁻⁴

NITRILES AND ISONITRILES

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Abstract—The N¹⁴ chemical shifts for R-CN are shown to move to lower fields on increasing the electronegativity of R, while an opposite effect is observed for R-NC. The relative chemical shifts between the resonances of nitriles, isonitriles and the cyanide ion are reasonably accounted for by the changes in the bond order and charge density matrix elements without necessity of making any assumptions on the value of the mean excitation energy. The effects of diamagnetic shielding do not seem to be important for the changes in the N¹⁴ chemical shifts.

INTRODUCTION

INVESTIGATIONS of the N¹⁴ chemical shifts of the nitro group^{1,2,4} by means of the internal reference technique using the shift for nitromethane as the origin of the scale³ showed a very regular dependence of the shifts on the electronegativity of the alkyl or aryl group attached to the NO₂ group. The direction of the effect (shifting the resonance signal to higher fields with increasing the electronegativity) and the lack of any appreciable influence of π -electron conjugation between the substituents in aromatic nitro compounds led to a conclusion⁴ that for a series of structurally related compounds the mobile bond orders are probably the most important factors in determining the magnitude of the paramagnetic term which should be dominant for the nitrogen NMR shifts. In further attempts to explain the N¹⁴ chemical shifts within a group of structurally similar molecules it seemed advisable to extend the investigations to simpler unsaturated nitrogen-containing groups and look for empirical correlations with molecular structure, that would lead to a reasonable explanation in terms of the electron distribution. The nitrile and isonitrile groups



are good models for this purpose because of their relatively simple electronic structure. By varying the electronegativity of R, and introducing various substituents, the π -bond polarity of the groups should be altered. While the direction of the effects should be opposite for the cyano and isocyano groups, the electron charge density at the nitrogen atom in RCN should increase as the electron-donating effect of R increases, while in RNC the increase should be partially cancelled by shifting the charge towards the carbon atom.

¹ M. Witanowski, T. Urbański and L. Stefaniak, *J. Am. Chem. Soc.* **86**, 2569 (1964).

² M. Witanowski and L. Stefaniak, *J. Chem. Soc.* in press.

³ M. Witanowski and H. Januszewski, *J. Chem. Soc.* in press.

⁴ M. Witanowski, L. Stefaniak and G. A. Webb, *J. Chem. Soc.* in press.

RESULTS AND DISCUSSION

The N^{14} chemical shifts for nitriles and isonitriles are given in Table 1. The measurements were carried out with nitromethane as an internal standard and expressed in terms of the recently proposed δ_N scale³ where $\delta_N(\text{CH}_3\text{NO}_2) = \delta_N(\text{NO}_3^-) = 0$, and positive values of δ_N indicate a shift to higher fields. The N^{14} shifts of some of the compounds in Table 1 have been measured,^{5,6} but the use of the external reference method gives less reliable results, particularly in the case of small differences in chemical shifts. The reliability of the values of the shifts obtained by the method of internal standards was thoroughly examined in an earlier work³ where the shift for acetonitrile ($\delta_N = +137 \pm 1$ ppm) was shown to be practically independent of the concentration, the polarity of the solvent and hydrogen bonding.

TABLE 1. N^{14} NMR SPECTRA OF NITRILES AND ISONITRILES

No.	Compound	Chemical shift ^a $\sigma_N(\text{ppm})$	Half-height width c/s
I	Me_3CCN	$+139 \pm 1$	190 ± 3
II	EtCN	$+137 \pm 1$	122 ± 3
III	MeCN	$+137 \pm 1^b$	88 ± 2
IV	CH_2ClCN	$+126 \pm 1$	175 ± 3
V	CCl_3CN	$+122 \pm 1$	220 ± 3
VI	BrCN	$+124 \pm 1$	165 ± 3
VII	$\text{NC}-\text{CH}_2-\text{CN}$	$+128 \pm 2$	280 ± 7
VIII	$\text{NC}-(\text{CH}_2)_2-\text{CN}$	$+134 \pm 2$	370 ± 10
IX	$\text{NC}-(\text{CH}_2)_3-\text{CN}$	$+136 \pm 2$	400 ± 10
X	$\text{EtCH}(\text{CN})_2$	$+132 \pm 2$	420 ± 10
XI	$\text{HO}-\text{CH}_2\text{CH}_2\text{CN}$	$+136 \pm 2$	370 ± 10
XII	$\text{MeOOC}-\text{CH}_2\text{CN}$	$+130 \pm 3$	460 ± 15
XIII	$\text{CH}_2=\text{CH}-\text{CH}_2\text{CN}$	$+133 \pm 1$	166 ± 3
XIV	$\text{CH}_2=\text{CH}-\text{CN}$	$+124 \pm 1$	110 ± 3
XV	PhCN	$+124 \pm 2$	390 ± 8
XIV	PhCH_2CN	$+133 \pm 3$	300 ± 15
XVII	$\text{CN}^-(\text{K}^+)$	$+99 \pm 1^c$	52 ± 3
XVIII	MeNC	$+218 \pm 0.5$	7.5 ± 0.5
XIX	EtNC	$+203 \pm 0.5$	8 ± 0.5

^a referred to nitromethane $\delta_N = 0$ as an internal standard; see Ref. 3.

^b from results of measurements in various solvents, referred to both nitromethane and the nitrate ion as internal standards.³

^c measured from the nitrate ion resonance ($\delta_N = 0$) as an internal standard in aqueous solution.

The N^{14} nuclei in the cyano group give fairly broad resonance signals within a rather narrow range of 20 ppm ($\delta_N = +120$ to $+140$ ppm). The general trend in the observed shifts is in the direction of a low field with increasing electronegativity of R in RCN. While the effect is only very slightly accentuated for the substitution of acetonitrile with Me groups (I, II, III), the substitution with chlorine atoms gives rise to an appreciable shift of -10 ppm for monochloroacetonitrile (IV) and -15

⁵ D. Herbison-Evans and R. E. Richards, *Mol. Phys.* **8**, 19 (1964).

⁶ J. D. Ray, L. H. Piette and D. P. Hollis, *J. Chem. Phys.* **29**, 1022 (1958).

ppm for trichloroacetonitrile (V). The same effect is observed for two cyano groups attached to the ends of an aliphatic chain

VII	VIII	IX	
$\text{NC}-\text{CH}_2-\text{CN}$	$\text{NC}-(\text{CH}_2)_2-\text{CN}$	$\text{NC}-(\text{CH}_2)_3-\text{CN}$	
+ 128	+ 132	+ 136	δ_{N} (ppm)

where at least three intervening methylene groups are necessary for the shift to attain the normal value of about +137 ppm. The introduction of an alkyl to the central carbon atom of VII, as in X, results in a shift of the signal to a higher field, as should be expected according to the observed scheme. The presence of the electro-negative carbomethoxyl group at the α carbon atom (XII) results in a shift of about 7 ppm to lower fields.

Comparing the δ_{N} values for the cyano group attached to an unsaturated system, as in vinyl cyanide (XIV) and benzonitrile (XV), with that for acetonitrile shows a downfield shift of the N^{14} resonance for the former. This may be considered as a result of either an increased electronegativity of the sp^2 -hybridized carbon atoms in such systems as compared with the sp^3 -hybridized ones in alkyl groups, or a conjugative effect due to π -electron delocalization. However, if the chemical shift for acetonitrile is compared with those of allyl and vinyl cyanide (XIII, XIV) or benzyl cyanide (XVI) and benzonitrile (XV), a gradual shift to lower fields is observed. This seems to indicate that at least a large part of the effect results from the electro-negativity of the phenyl and vinyl groups.

The general trend of the changes in the N^{14} chemical shifts for the cyano group in $\text{R}-\text{CN}$ is opposite to that observed for the nitro group^{1,2,4} in $\text{R}-\text{NO}_2$ if R is an alkyl as well as the phenyl group.

The N^{14} resonance signals of simple alkyl isocyanides (XVIII, XIX) have chemical shifts to much higher fields ($\delta_{\text{N}} > +200$ ppm) than those for alkyl cyanides ($\delta_{\text{N}} \cong +130$ ppm). The half-height widths (about 8 c/s) of the signals of isocyanides are among the smallest observed in N^{14} resonance and comparable with those for the nitrate ion³ and the ammonium ion³. There is a remarkable shift of the signal to a lower field (by 15 ppm) on going from methyl to ethyl isocyanide. The direction and the magnitude of the change is the same as those observed for the nitro group¹, i.e. moving the resonance to lower fields with decreasing the electronegativity of the alkyl, and opposite to that for the cyano group.

An explanation of the N^{14} shifts for nitriles and isonitriles may be sought for in terms of the theory^{7,8} that divides the shielding constant σ for atom A according to Eq (1).

$$\sigma^A = \sigma_d^{AA} + \sigma_p^{AA} + \sum_{B \neq A} \sigma^{AB} + \sigma^{\text{ring}} \quad (1)$$

The neighbour-anisotropy term, $\sum \sigma^{AB}$, and the ring-current term, σ^{ring} , are rather small in comparison with the observed range of nitrogen NMR chemical shifts and are probably very close to or just within the experimental error in N^{14} resonance measurements. The local diamagnetic term, σ_d^{AA} , may be expressed⁸ in terms of the

⁷ A. Saika and C. P. Slichter, *J. Chem. Phys.* **22**, 26 (1954).

⁸ J. A. Pople, *Discussions Faraday Soc.* **34**, 7 (1963).

MO theory as a function of orbital populations, P_{ii} , and mean inverse orbital radii, $(r^{-1})_{ii}$.

$$\sigma_d^{AA} = \frac{e^2}{3mc^2} \sum_i P_{ii}(r^{-1})_{ii} \quad (2)$$

This part of the shielding constant predicts a shift to higher fields with increasing the electron density at atom A, but the largest terms in the summation in Eq (2) are those from the inner-shell non-bonding orbitals and the expected changes in N^{14} shifts should be small in comparison with the observed ones. The changes in the N^{14} chemical shifts are in the direction of those expected from the diamagnetic term, but they are just opposite in the case of isonitriles. The appreciable high-field resonance shift for the nitrogen nuclei in isonitriles, where the nitrogen atom bears a formal positive charge, and a low-field shift for the cyanide ion (XVII) from the cyano group resonance are also just opposite to the changes in the diamagnetic term. It seems that the diamagnetic term may be neglected here and that the dominant factor is the paramagnetic term, σ_p^{AA} , which may be expressed^{8,9} in terms of the LCAO coefficients for the ground state,

$$\sigma_p^{AA} = -\frac{e^2\hbar^2}{2m^2c^2(\Delta E)} \langle r^{-3} \rangle_{2p} \sum_B Q_{AB} \quad (3)$$

where ΔE is the mean excitation energy and $\langle r^{-3} \rangle_{2p}$ is the mean value of r^{-3} for the $2p$ orbitals of A. The terms Q_{AB} contain the elements of the charge density and bond order matrix and are averaged over the x , y and z axes. For the z axis,

$$(Q_{AB})_{zz} = P_{xAxB}(2\delta_{AB} - P_{yAyB}) + P_{yAyB}(2\delta_{AB} - P_{xAxB}) + 2P_{xAyB}P_{xBVA} \quad (4)$$

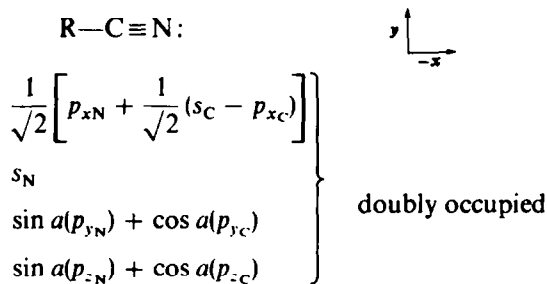
where δ_{AB} is the Kronecker delta (zero for $A \neq B$, one for $A = B$), B denotes any atom bonded to A or atom A itself, the P terms are the matrix elements. Similar equations may be written for the x and y axes. The $\langle r^{-3} \rangle_{2p}$ term should be affected by the screening constant¹⁰ for the nucleus so that it should increase with decreasing electron charge density at the nucleus, thus giving a downfield shift of the resonance signal. The effect operates in the same direction as that of the changes in the diamagnetic term, so it seems that the $\langle r^{-3} \rangle_{2p}$ term is not important for the relative N^{14} shifts for nitriles and isonitriles since the same arguments apply as those against the diamagnetic term as the dominant factor. The mean excitation energy, ΔE , is hard to evaluate without a knowledge of all excited states.¹¹ The usefulness of Eq (3) lies in the possibility of an assumption that ΔE does not change appreciably for structurally related molecules, except for eventual allowances for known low-lying excited states. We shall neglect the possible changes in ΔE as well as those in $\langle r^{-3} \rangle_{2p}$ and try to interpret the observed shifts for nitriles and isonitriles in terms of changes in $\sum Q_{AB}$.

Assuming the axis of the C—N bond to coincide with the x axis, the following molecular orbitals centered at the nitrogen atom may be written:

⁹ J. A. Pople, *Mol. Phys.* **7**, 301 (1963-4).

¹⁰ M. Karplus and J. A. Pople, *J. Chem. Phys.* **38**, 2803 (1963).

¹¹ J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution Resonance Spectroscopy* Vol. I; p. 71. Pergamon Press, Oxford (1965).



The nonzero elements appearing in $\sum Q_{AB}$ are:

$$\begin{array}{l}
 P_{xNxN} = 1; \quad P_{yNyN} = P_{zNzN} = 2 \sin a \sin a = \frac{1}{2} q_N^\pi; \\
 P_{xNxC} = -\frac{1}{\sqrt{2}}; \quad P_{yNyC} = P_{zNzC} = 2 \sin a \cos a = \frac{1}{2} p_{NC}^\pi
 \end{array}$$

where p^π and q^π are the corresponding π -bond orders and π -electron charge densities, respectively. The calculated values of the Q_{AB} terms are:

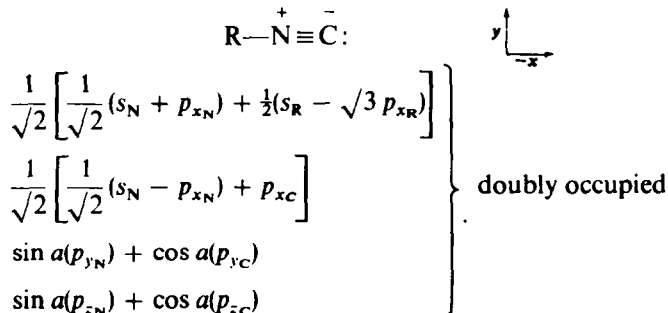
$$\begin{array}{ll}
 (Q_{NN})_{xx} = 2q_N^\pi - \frac{1}{2}(q_N^\pi)^2 & (Q_{NC})_{xx} = -\frac{1}{2}(p_{NC}^\pi)^2 \\
 (Q_{NN})_{yy} = 2 & (Q_{NC})_{yy} = \frac{1}{\sqrt{2}} p_{NC}^\pi \\
 (Q_{NN})_{zz} = 2 & (Q_{NC})_{zz} = \frac{1}{\sqrt{2}} p_{NC}^\pi \\
 \hline
 Q_{NN} = \frac{1}{3} [2q_N^\pi - \frac{1}{2}(q_N^\pi)^2 + 4] & Q_{NC} = \frac{1}{3} [\sqrt{2} p_{NC}^\pi - \frac{1}{2}(p_{NC}^\pi)^2]
 \end{array}$$

Considering the fact that the structure $\text{R}-\text{C}\equiv\text{N}:$ should have an excess of negative charge on the nitrogen atom (the degree of the polarization depending on the inductive effect of R), but the excess should be rather small because of interelectronic repulsion¹², the following limits for the values of q_N^π , p_N^π and, hence, $\sum Q_{AB}$ may be assumed for the cyano group:

$$\text{R}-\text{CN} \begin{cases} q_N^\pi = 2; & p_N^\pi = 2 \text{ (no charge splitting)} \quad \sum Q_{AB} = 2.28 \\ q_N^\pi = 2.5; & p_N^\pi = 1.956 \text{ (-}\frac{1}{2}\text{ charge on nitrogen)} \quad \sum Q_{AB} = 2.24 \end{cases}$$

The calculated values of $\sum Q_{AB}$ predict a downfield shift of the N^{14} resonance of the cyano group with increasing the electron-attracting effect of R. This is in agreement with the observed changes in the shifts for nitriles.

The following set of molecular orbitals may be written for the isocyano group:



¹² See, for example, the results of VESCF calculations, R. D. Brown and M. L. Heffernan, *Trans Faraday Soc.* **54**, 757 (1958).

The expressions for Q_{NN} and Q_{NC} , calculated from these orbitals, are the same as those for the cyano group, while $Q_{NR} = 0$ so that the expression for $\sum Q_{AB}$ is also identical. However, the structure of the isocyano group should be characterized by an opposite polarization and contained within the following limits:

$$\text{R-NC} \begin{cases} q_N^\pi = 2; & p_{NC}^\pi = 2 \text{ (+1 charge on nitrogen)} \sum Q_{AB} = 2.28 \\ q_N^\pi = 3; & p_{NC}^\pi = 1.74 \text{ (zero charge on nitrogen)} \sum Q_{AB} = 2.15 \end{cases}$$

The interelectronic repulsions probably make the structure closer to that with no charge splitting ($\sum Q_{AB} = 2.15$). Electron-donating substituents R should affect the structure by changing it in the direction of charge splitting in the π -orbitals. Thus, the calculated values of $\sum Q_{AB}$ predict generally a shift of the N^{14} resonance of the isocyano group to higher fields from that for the cyano group, and a downfield shift of the N^{14} resonance within isonitriles themselves with increasing positive inductive effect of substituent R. This is in agreement with the observed values of chemical shifts for the cyano and isocyano groups.

The calculations were made with an assumption that the lone electron pairs in the cyano and isocyano groups are in the $2s$ orbitals. The assumption seems to be warranted by low nucleophilicity of the molecules as well as by the fact that the promotion of a $2s$ electron to a $2p$ orbital would not result in formation of additional bonds. However, if one uses sp -hybrids for the nitrogen atom in R-CN and the carbon atom in R-NC, the result is only a proportional decrease in $\sum Q_{AB}$ to about 2.00 for nitriles and about 1.90 for isonitriles, without affecting the postulated explanation of their relative N^{14} chemical shifts. No attempt was made, either, to include σ -bond polarization in the calculations, but this is justified by the results obtained for C-O and C-N multiple bonds by advanced MO theory.^{12, 13}

In the cyanide ion, $(:C \equiv N:)^-$, in view of the higher nucleophilicity of the carbon atom, its lone electron pair may have more p character than that at the nitrogen atom. Assuming sp -hybrids for the carbon atom, the expression for $\sum Q_{AB}$ will be the same as for R-CN, and the calculated values will be 2.28 for zero charge at the nitrogen atom and 2.24 for $-\frac{1}{2}$ unit charge. On the other side, if the lone pair has the $2s$ character, the following calculation may be made:

$$\begin{array}{l} \left. \begin{array}{l} \frac{1}{\sqrt{2}}(p_{xN} - p_{xC}) \\ s_N \\ \sin a(p_{yN}) + \cos a(p_{yC}) \\ \sin a(p_{zN}) + \cos a(p_{zC}) \end{array} \right\} \text{doubly occupied orbitals} \\ P_{xNxN} = 1; \quad P_{yNyN} = P_{zNzN} = 2 \sin a \sin a = \frac{1}{2}q_N^\pi \\ P_{xNxC} = -1; \quad P_{yNyC} = P_{zNzC} = 2 \sin a \cos a = \frac{1}{2}p_{NC}^\pi \\ \frac{(Q_{NN})_{xx} = 2q_N^\pi - \frac{1}{2}(q_N^\pi)^2}{(Q_{NN})_{yy} = (Q_{NN})_{zz} = 2} \\ \frac{Q_{NN} = \frac{1}{3}[2q_N^\pi - \frac{1}{2}(q_N^\pi)^2 + 4]}{Q_{NC} = \frac{1}{3}[2p_{NC}^\pi - \frac{1}{2}(p_{NC}^\pi)^2]} \end{array}$$

¹³ R. D. Brown and A. Penfold, *Trans Faraday Soc.* 53, 397 (1957).

Setting the limiting structures as that with a full negative charge on the carbon atom and that with an even charge splitting, we obtain:

$$\text{CN}^- \quad q_{\text{N}}^{\pi} = 2; \quad p_{\text{NC}}^{\pi} = 2 \text{ (zero charge on nitrogen)} \quad \sum Q_{AB} = 2.67$$

$$q_{\text{N}}^{\pi} = 2.5; \quad p_{\text{NC}}^{\pi} = 1.936 \text{ } (-\frac{1}{2} \text{ charge on nitrogen)} \quad \sum Q_{AB} = 2.62$$

The results of the calculations indicate that the N^{14} resonance shifts in the series CN^- , R-CN , R-NC as well as the shifts among nitriles and isonitriles, respectively, may be explained in terms of changes in $\sum Q_{AB}$, without having to resort to more or less arbitrary estimates of changes in the mean excitation energy.

Structure	$\sum Q_{AB}$	Observed N^{14} shifts δ_{N} (ppm)
$q = \text{R}-\underset{0}{\text{N}}\equiv\underset{0}{\text{C}} : \leftrightarrow \text{R}-\overset{+1}{\text{N}}\equiv\underset{-1}{\text{C}} :$	2.15 \leftrightarrow 2.28	+218–+203
$q = \text{R}-\underset{0}{\text{C}}\equiv\underset{0}{\text{N}} : \leftrightarrow \text{R}-\overset{+1}{\text{C}}\equiv\underset{-1}{\text{N}} :$	2.28 \leftrightarrow 2.24	+120–+140
$(:\text{C}\equiv\text{N}:)^-$	2.6 \leftrightarrow 2.3	+99

One should note that a quite wide range of π -bond polarization was allowed for in the calculations. It is very probable that the actual net charges, q , are of the order of only 0.01 electron charge, as it was calculated for the carbonyl group,¹² and that the values of $\sum Q_{AB}$ for the non-polar structures are more proper.

EXPERIMENTAL

Most of the substances investigated in this work were commercial c.p. grade products. Some (I,¹⁴ V,¹⁵ XVIII,¹⁶ XIX¹⁶) were prepared by methods described in the literature. The N^{14} spectra were measured at 4.33 Mc/s (14,100 Gauss) with a Varian HR-60 spectrometer; 15 mm o.d. sample tubes were used. The chemical shifts were expressed in the δ_{N} scale,³ using nitromethane ($\delta_{\text{N}} = 0$) as an internal standard. No effects on the shifts, at least beyond the experimental error, were observed on diluting the samples with carbon tetrachloride or acetone. The calibration of the spectra was carried out by the audio-sideband method. The very narrow resonance signals of isonitriles were recorded at the 2 kc/s modulation sidebands from the base-line stabilizing system in order to minimize saturation effects and obtain a better signal-to-noise ratio, as suggested before.³ Using this technique it is rather easy to detect spectrally both the cyano and isocyano groups, as, for example, in the mixture after reacting an alkyl halide with AgCN .¹⁶ Dimethylformamide ($\delta_{\text{N}} = +276$ ppm) may be used as a secondary internal standard for the nitriles that give broad N^{14} resonance signals, as discussed elsewhere.³ The shifts obtained in this way are within the experimental error of those measured directly from nitromethane, as it was checked for I–III, V, VII, XII, and XV.

¹⁴ C. Clemett and M. Davies, *Trans. Faraday Soc.* **58**, 1707 (1962).

¹⁵ G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, p. 505. F. Enge Verlag, Stuttgart (1954).

¹⁶ H. L. Jackson and B. M. McKusick, *Org. Syntheses* **35**, 62 (1955).