Nitrogen-14 Nuclear Magnetic Resonance. VI.[1-5] Trigonally Hybridized Nitrogen Atoms

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Abstract: Empirical correlations between molecular structure and N^{14} nuclear magnetic resonance shifts for sp^2-hybridized nitrogen atoms in nitro compounds, nitrates, pyridine-like aromatic bases, and the corresponding cations, alkyl azides, isocyanates, and isothiocyanates, have been explained in terms of ground-state molecular orbitals. The influence of the electronegativity of substituents at the nitrogen atoms may be accounted for without reference to the excited electronic states. Unambiguous assignments of the chemical shifts in the N^{14} spectra of alkyl azides have been made. Results of SCF molecular orbital calculations for the NO_3^- ion and the $CH_2NO_2^-$ ion are given. An experimental procedure for recording spectra containing several N^{14} resonance signals of very different widths is described.

Previous investigations[1,2,4] of N^{14} nuclear magnetic resonance in aliphatic and aromatic nitro compounds showed that the chemical shifts for the NO_2 group may be empirically correlated with the electronegativity of the attached alkyl or aryl group. The resonance of the nitro group moves to higher fields if the electronegativity increases. A similar effect was observed[5] for the sp-hybridized nitrogen atoms in isonitriles. The regular changes observed in the N^{14} spectra of nitro compounds seem to justify looking for more general correlations between the substituent effects and the N^{14} chemical shifts for molecules containing trigonally hybridized nitrogen atoms. Such correlations should be interesting from the point of view of the theory of nitrogen chemical shifts, particularly if one considers recent rather successful attempts[5,6] at theoretical explanation of the shifts for linear molecules and ions in terms of the LCAO molecular orbitals. Trigonally hybridized nitrogen atoms occur in many organic and inorganic molecules, such as those of nitrates, nitrites, aromatic heterocycles, alkyl isocyanates, isothiocyanates, azides, and, with a certain degree of approximation, amides. Three main structural types of such molecules involve delocalized π-orbital systems extending over one, two, or three atoms adjacent to the nitrogen atom, respectively. The purpose of this work was to find factors determining the changes in N^{14} chemical shifts within each of these structural types and, if possible, to draw conclusions concerning the general theory of nitrogen resonance shifts. The experimental data for theoretical considerations were obtained by the internal reference method, according to the recently proposed unified scale of N^{14} shifts.[3] The method gives reliable results even for small relative shifts in the spectra of structurally similar molecules.

Results and Discussion

The results of measurements of N^{14} chemical shifts for selected model molecules are given in Table I. The measured values of chemical shifts (δ_N) are referred, directly or indirectly, to either nitromethane or the nitrate ion (δ_N 0), using internal standards according to the method described elsewhere.[3] Positive values of δ_N are assigned to shifts to higher fields from the resonance of the primary standards. Some data are quoted from the author's previous papers.[1-4] The N^{14} chemical shifts for some of the molecules in Table I have already been reported by other investigators[6,7] who used external reference methods; their measurements, cited in the table for comparison purposes, show differences with respect to those carried out by the internal reference method. The differences range from a few to about 20 ppm.

The changes in the N^{14} chemical shifts for $R-NO_2$ systems, where R = alkyl or aryl, were discussed thoroughly elsewhere.[1,2,4] The resonance moves to higher fields on increasing the electronegativity of R, as was shown by substituting nitromethane with further nitro groups (a high-field shift from III to VI, Table I) or methyl groups (a low-field shift in the order III, IV, V in Table I), and by the substitution of nitrobenzene with nitro groups (*e.g.*, a shift to a higher field from VII to VIII). Replacing the carbon atom adjacent to the nitro group with a more electronegative nitrogen atom, as in nitramines, results in a shift of 30–40 ppm to higher fields.[1] Further examples of this are XIII and XIV. The N^{14} spectrum of the latter shows two separate signals at +22 and +34.5 ppm, respectively, with an approximate integral intensity ratio of 3:1 which indicates that the first signal corresponds to the NO_2 groups at the benzene ring, and the second represents the nitramine nitro group.

The results of measurements for the $R-ONO_2$ systems indicate that their N^{14} signals lie at appreciably higher fields (+40 to +60 ppm) from that of nitromethane, and slightly higher than those of nitramines. This is in good agreement with the changes expected from the electronegativity of the oxygen atom. Examining the shifts in the series

$R-ONO_2$	$R = NO_2$	$R = H$	$R = CH_2CH_3$
δ_N, ppm	+60	+47.5	+37

shows that a similar trend exists on varying the electronegativity of R. The half-height widths of the reso-

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

[2] M. Witanowski and L. Stefaniak, *J. Chem. Soc., B*, 1061 (1967).

[3] M. Witanowski and H. Januszewski, *ibid.*, 1062 (1967).

[4] M. Witanowski, L. Stefaniak, and G. A. Webb, *ibid.*, 1065 (1967).

[5] M. Witanowski, *Tetrahedron*, **23**, 4299 (1967).

[6] J. E. Kent and L. Wagner, *J. Chem. Phys.*, **44**, 3530 (1966).

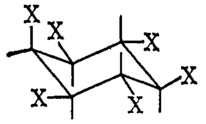
[7] D. Herbison-Evans and R. E. Richards, *Mol. Phys.*, **8**, 19 (1964), and references therein.

Table I. Nitrogen-14 Nuclear Magnetic Resonance Spectra

No.	Molecule	Internal[a] standard	Chem shift,[a] ppm	Half-height signal width, cps	Ext ref chem shift (lit. data), ppm
I	NO_3^-	. . .	0[a]	12 ± 1	0[f,g]
II	$(CH_2NO_2)^-Na^+$	KNO_3	+79 ± 3	450 ± 15	+60[f]
III	CH_3NO_2	. . .	0[a,b]	24 ± 2	−5[f]
IV	$CH_3CH_2NO_2$	NM	−12 ± 0.5[b]	30 ± 2	
V	$(CH_3)_3CNO_2$	NM	−30 ± 0.5[b]	43 ± 2	
VI	$C(NO_2)_4$	NM	+48 ± 0.5[b]	10 ± 2	+46[f]
VII	Nitrobenzene	DMF, NM	+8 ± 1[c]	60 ± 4	+5[f]
VIII	*sym*-Trinitrobenzene	DMF	+18.5 ± 1[c]	63 ± 4	
IX	N_2O_5	NM	−60 ± 1	80 ± 4	
X	$HONO_2$ (97%)	NM	+47.5 ± 0.5	17 ± 2	
XI	$CH_3CH_2ONO_2$	NM	+37 ± 0.5	17 ± 2	
XII	Myoinositol hexanitrate	NM	+60 ± 4	370 ± 20	
XIII	$NH_2CONHNO_2$	NM	+40 ± 1[h]	30 ± 4	
XIV	N,2,4,6-Tetranitroaniline	NM	+34.5 ± 1[i] (NNO_2)	32 ± 4	
			+22 ± 1[i] (CNO_2)	85 ± 4	
XV	NO_2^-	KNO_3	−237 ± 4	520 ± 20	−247[f]
XVI	Pyridine	DMF, NM	+68 ± 2	260 ± 8	+57[f]
XVII	Pyridinium ion (concn HCl)	NM	+181 ± 1	20 ± 3[d]	+176[f]
XVIII	Quinoline	DMF	+71 ± 3	650 ± 15	+72[f]
XIX	Quinolinium ion HCl	NM	+185 ± 2	50 ± 6[d]	
XX	Isoquinoline	DMF	+68 ± 4	680 ± 20	+64[f]
XXI	Isoquinolinium ion (HCl)	NM	+188 ± 2	55 ± 6[d]	
XXII	CH_3CH_2NCO	NM	+346 ± 1	72 ± 4	
XXIII	CH_3NCO	NM	+363 ± 0.5	50 ± 2	
XXIV	$(NCO)^-K^+$	$NaNO_3$	+300 ± 0.5	13 ± 2	+288[g]
XXV	$CH_3CH_2N_3$	NM	+129.5 ± 0.5 (central)	22 ± 2	
			+167.5 ± 0.5 (terminal)	28 ± 2	
			+305 ± 1 (R–*N*)	122 ± 4	
XXVI	CH_3N_3	NM	+128 ± 0.5 (central)	17 ± 2	
			+170.5 ± 0.5 (terminal)	19 ± 2	
			+320 ± 1 (R–*N*)	101 ± 4	
XXVII	$(N_3)^-Na^+$	KNO_3	+128 ± 0.5 (central)	20 ± 2	+129[g]
			+277 ± 1 (terminal)	60 ± 4	+277[g]
XXVIII	CH_3CH_2NCS	NM	+273 ± 1	55 ± 3	+271[f]
XXIX	CH_3NCS	NM	+291 ± 1	40 ± 3	
XXX	$(NCS)^-K^+$	$NaNO_3$	+168 ± 1	147 ± 4	+165[g]
XXXI	CH_3CH_2SCN	NM	+103 ± 2	140 ± 8	+99[f]
XXXII	$HCON(CH_3)_2$	NM	+276 ± 1	135 ± 3	+271[f]
XXXIII	$(NH_2)_2CO$	KNO_3	+304 ± 3	340 ± 10	+298[f]
XXXIV	CH_3CONH_2	NM	+260 ± 5	540 ± 20	+267[f]
XXXV	$N(C_2H_5)_3$	NM	+327 ± 3	320 ± 15	+329[f]
XXXVI	$NH_3(H_2O)$	KNO_3	+375 ± 1	110 ± 4	
XXXVII	$NH_4^+ (NO_3^-)(HCl)$	. . .	+354.5 ± 0.5	5 ± 0.5[e]	+353[f]

[a] Measured from primary internal standards, nitromethane or the nitrate ion, ref 3; NM = nitromethane, DMF = dimethylformamide. [b] Data from ref 1. [c] Data from ref 4. [d] A doublet, $J_{NH} = 68 \pm 1$ cps. [e] A quintet, $J_{NH} = 50 \pm 1$ cps. [f] See ref 7. [g] See ref 6. [h] The NH and NH_2 resonances appear as a broad signal at 250–300 ppm. [i] The NH resonance is a broad signal at about +250 ppm.

nance signals of $RONO_2$ molecules are rather small for the systems where the internal rotation is not seriously hindered (IX–XI). However, a rather broad N^{14} signal is observed for myoinositol hexanitrate (XII)



XII, X = ONO_2

which should have a rigid structure of the chair form of a six-membered ring with one axial and five equatorial substituents, as suggested by the infrared spectra[8] of the melt and the solid phase. In this case direct through-space interactions would not be averaged out, resulting in a substantial decrease in the transverse relaxation time and an increase in signal width.

One should note that considering the values of the N^{14} shifts obtained in this work for the $RONO_2$ systems, as well as those reported by Ogg and Ray,[9] the value of +46 ppm (NO_3^- external standard) for the NO_2^+ ion from Kent and Wagner's work[6] seems to represent the $HONO_2$ species rather than the nitronium ion. The single resonance signal in the N^{14} spectrum of N_2O_5 (IX) may correspond to the structure of a true anhydride of nitric acid, $O_2N–O–NO_2$; it may also represent a fast equilibrium

$$O_2N—O—NO_2 \rightleftarrows NO_2^+ + NO_3^-$$

with an appreciable amount of nitronium nitrate provided that the shift for the NO_2^+ ion is much higher than +46 ppm (probably about +120 ppm, as can be read from the spectra published by Ogg and Ray[9]).

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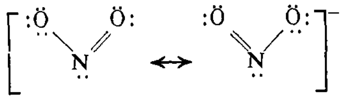
(8) T. Urbański and M. Witanowski, *Trans. Faraday Soc.*, **59**, 1046 (1963).

(9) R. A. Ogg and J. D. Ray, *J. Chem. Phys.*, **25**, 1285 (1956).

The nitrite ion



may be considered as the limiting case of R–NO_2 where a strongly electron-repelling group R has brought about a complete charge splitting in the R–N bond. The position of the NO_2^- nitrogen resonance (XV) at a very low field (δ_N −237 ppm) is in qualitative agreement with the observed trend in the N^{14} shifts for nitro groups. In the absence of nonaveraged long-range effects, such as may exist in XII, the width of the N^{14} resonance peaks for nitro groups seems to increase with increasing electron density at the nitrogen atom; this may be seen in the series tetranitromethane (VI), ethyl nitrate (XI), nitromethane (III), nitroethane (IV), 1,1-dimethylnitroethane (V), and the nitrite ion (XV).

The N^{14} spectra of pyridine (XVI), quinoline (XVIII), isoquinoline (XX), and the corresponding cations (XVII, XIX, XXI) show an appreciable shift to higher fields occurring on the protonation of the base (this shift has already been reported for pyridine, with slightly different numerical values, by other authors[10,11]). The spectra of the cations, as may be seen in Figure 1, contain rather sharp doublets ($J_{NH} \cong$ 67 cps), leaving no doubt about the identity of the species. This may be important for investigations concerning the equilibrium between the protonated and nonprotonated species by means of nitrogen chemical shifts; in a recent article,[11] only rather broad resonance signals were reported. The structural change occurring on the protonation of the base may be thought of as that due to replacing a strongly electron-donating "substituent," *i.e.*, the lone electron pair, with a more electronegative hydrogen atom, as in changing from the nitrite ion to the nitro group. The resulting N^{14} shift is in the same direction and roughly of the same magnitude as that from the nitrite ion to nitro compounds. One should expect from this that hydrogen bonding of the nitrogen atom in pyridine should give a resonance shift to higher fields. Such a shift (9 ± 3 ppm) was reported in the literature[12] for the 1:1 molar solution of pyridine and methanol. The N^{14} chemical shifts for pyridine in organic solvents capable of hydrogen bonding, measured in this work by means of the internal reference technique (see Table II), are rather within the experimental error of the shift for pyridine itself. The shift of the reference signal of dimethylformamide (δ_N +276 ppm), measured directly from nitromethane internal standard, is independent, within the ±1-ppm error, of hydrogen-bonding effects. It seems that hydrogen bonding has no significant effect on the N^{14} shift of pyridine, even if one considers the possibility of such bonding to the molecules of the standard used in the experiments. However, the width of the pyridine resonance signal is much more affected by the formation of hydrogen bonds.

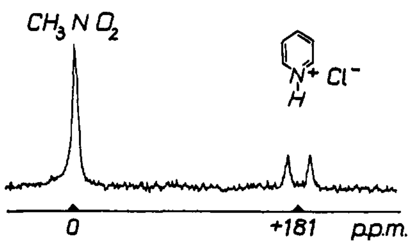
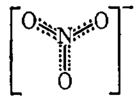
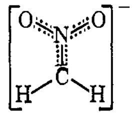


Figure 1. The N^{14} spectrum at 4.33 Mc/sec of the pyridinium ion in concentrated HCl. The spacing of the doublet is 68 ± 1 cps.

The N^{14} resonance spectra for systems containing trigonally hybridized nitrogen atoms with the π-orbital system extending over three adjacent atoms, as in



I
δ_N 0



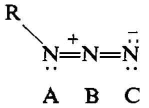
II
δ_N +79 ppm

indicate a shift to higher fields on replacing one oxygen atom in the NO_3^- ion with a less electronegative carbon atom in the σ-bond core. This is opposite to the changes observed for the molecules where only two adjacent atoms participate in the π-orbital system. There is a remarkable increase of signal width from I to II, probably because of the decreased symmetry of the latter. The half-height width of the resonance signal of the nitromethane anion (II) approaches that for the nitrite ion (XV), belonging to the same symmetry group.

Table II

	δ_N, ppm	Half-height width, cps
Pyridine + DMF (internal standard)	+68 ± 2	260 ± 5
Pyridine + DMF + $CHCl_3$ (2:1:2 molar ratio)	+68 ± 2	275 ± 5
Pyridine + DMF + CH_3OH (2:1:2)	+73 ± 2	320 ± 7
Pyridine + DMF + CH_3COOH (2:1:2)	+70 ± 4	550 ± 20

The molecules with trigonally hybridized nitrogen atoms and delocalized π-orbital systems extending over only one adjacent atom are represented by alkyl isocyanates, isothiocyanates, and azides. The N^{14} spectra of the latter (XXV, XXVI) require special consideration since they contain three well-resolved signals corresponding to the three nonequivalent nitrogen atoms in



as shown in Figure 2. Japanese investigators[13] made a tentative assignment B, C, A in the order of increasing magnetic field, but it could not be considered as conclusive. Comparing the chemical shifts obtained in the present work for the azide ion (XXVII), methyl

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[10] J. D. Baldeschwieler and E. W. Randall, *Proc. Chem. Soc.*, 303 (1961).

[11] M. Bose, N. Das, and N. Chatterjee, *J. Mol. Spectry.*, **18**, 32 (1965).

[12] H. Saito, K. Wukada, H. Kato, T. Yonezawa, and K. Fukui, *Tetrahedron Letters*, 111 (1965).

[13] T. Kanada, Y. Saito, and K. Kawamura, *Bull. Chem. Soc. Japan*, **35**, 172 (1962).

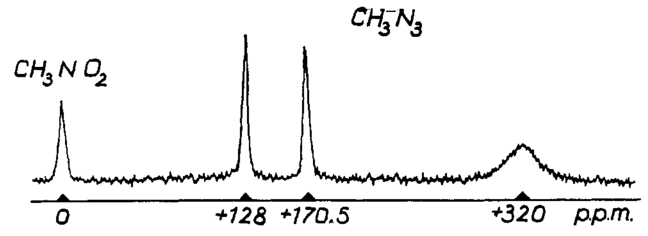
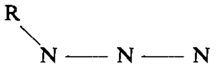


Figure 2. The N^{14} spectrum at 4.33 Mc/sec of methyl azide.

and ethyl azides (XXV, XXVI), isocyanates (XXII, XXIII), and isothiocyanates (XXVIII, XXIX), an unambiguous assignment may be made. There is no doubt about the +277-ppm signal representing the terminal atoms and the +128-ppm signal representing the central atom of the azide ion, as indicated by the 2:1 integral intensity ratio. The resonance at +128 ppm is also found in the spectra of both methyl and ethyl azides and is also assigned to the central nitrogen atom (B). One of the two remaining signals lies at a rather high field, about +300 ppm, and shows a down-field shift of 15 ppm from methyl to ethyl azide. This corresponds to the position and relative shifts of the resonance signals for alkyl cyanates and isothiocyanates and indicates that it is the resonance of the nitrogen atom adjacent to the alkyl group. The remaining signal at about +170 ppm should, therefore, represent the terminal nitrogen atom (C). The final assignment of the N^{14} chemical shifts of azides is shown below, with only the σ bonds shown. If we compare

N —— N —— N
+277 +128 +277 ppm



R = CH_3 +320 +128 +170.5 ppm
R = C_2H_5 +305 +129 +167.5 ppm

the N^{14} resonance shifts for methyl and ethyl isocyanates, isothiocyanates, and azides (the signal at the highest field for the latter), we observe that the direction and the magnitude of the shift on replacing the methyl with the ethyl group is the same as in the case of nitroalkanes, that is, about 15 ppm to lower magnetic fields. If the corresponding anions (XXIV, XXVII, XXX) are included in the considerations as "alkyl" derivatives with the least electron-attracting substituents at the nitrogen atom (*i.e.*, the lone electron pairs), then the shift of the N^{14} resonance in the series

$$\text{anion} \rightarrow \text{ethyl derivative} \longrightarrow \text{methyl derivative}$$

is analogous to that for the nitrite ion, nitroethane, and nitromethane. The direction of the shift is to lower magnetic fields with the decreasing electronegativity of the substituent.

The amide nitrogen atom may be considered as nearly sp^2-hybridized, since there are positive indications of a partly double-bond character of the C–N bond in amides.[14–16] Its position in the N^{14} chemical shift scale is about +300 ppm which is just in the range of occurrence of other sp^2-hybridized nitrogen atoms with only one of the neighboring atoms participating in the π-orbital system; it is about 50 ppm lower than the range of the shifts for sp^3-hybridized nitrogen atoms (XXXV–XXXVII).

For nucleus A in a polyatomic molecule, the nuclear magnetic screening constant, σ, is usually divided[17–19] into the local diamagnetic term $\sigma_A{}^d$, the local paramagnetic term $\sigma_A{}^p$, and terms representing long-range effects of other atoms. The latter are rather unimportant for nitrogen chemical shifts which extend over a range of hundreds of parts per million. The diagmagnetic term contributes to a resonance shift to lower magnetic fields with increasing electron density at atom A. For trigonally hybridized nitrogen atoms, this term does not seem to have an important contribution to the shift, as indicated by the high-field direction of the changes observed for the resonance signals when increasing the electronegativity of R in RNO_2, RNCO, RN_3, RNCS, as well as by a remarkable down-field shift for the corresponding anions and a high-field shift observed for the protonation of pyridine or similar bases. The paramagnetic term may be expressed[18,19] in terms of excited electronic states of the molecule (2p electrons only) for the *z* direction as

$$(\sigma_A{}^p)_{zz} = -2\frac{e^2\hbar^2}{m^2c^2}\langle r^{-3}\rangle_{2p}\sum_i^{\text{occ}}\sum_j^{\text{unocc}}(\Delta E_{i\rightarrow j})^{-1}(c_{i,x_A}c_{j,y_A} - c_{i,y_A}c_{j,x_A})\sum_B(c_{i,x_B}c_{j,y_B} - c_{i,y_B}c_{j,x_B}) \quad (1)$$

with analogous expressions for the *xx* and *yy* components of the shielding tensor. For rapid molecular motions the term is averaged over the three axes. The term $\langle r^{-3}\rangle_{2p}$ is the mean value of the reciprocal cube of the 2p-orbital radius and should generally decrease with increasing electron density at atom A, thus contributing to changes in the same direction as the diamagnetic term. Since the changes observed for sp^2-hybridized nitrogen atoms are in the opposite direction, it seems that the $\langle r^{-3}\rangle_{2p}$ term does not participate in them to any significant extent. The expression[6] based on Slater orbitals seems to give an exaggerated contribution to the changes in the screening constants. The term was neglected in considerations of the N^{14} shifts for pyridine,[19] nitriles, and isonitriles.[5] The summation in eq 1 is over all excited states. Only in rare instances is there sufficient knowledge of even a few low-lying excited states to apply the equation directly. Using the average excitation energy[20] approximation, this may be put in terms of the ground-state bond-order and charge-density matrix elements *P* as shown in eq 2 and 3,[17–19]

$$(\sigma_A{}^p)_{zz} = -\frac{e^2\hbar^2}{2m^2c^2}\langle r^{-3}\rangle_{2p}(\Delta E)^{-1}\sum_B(Q_{AB})_{zz} \quad (2)$$

$$(Q_{AB})_{zz} = P_{x_Ax_B}(2\delta_{AB} - P_{y_Ay_B}) + P_{y_Ay_B}(2\delta_{AB} - P_{x_Ax_B}) - 2P_{x_Ax_B}P_{y_Ay_B} \quad (3)$$

where ΔE is the mean excitation energy and the summation over B involves all atoms directly bonded to A and

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[14] L. H. Piette, J. D. Ray, and R. A. Ogg, *J. Mol. Spectry.*, **2**, 66 (1958).

[15] C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960).

[16] M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).

[17] J. A. Pople, *Discussions Faraday Soc.*, **34**, 7 (1963).

[18] J. A. Pople, *J. Chem. Phys.*, **37**, 53, 60 (1962).

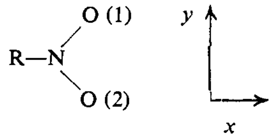
[19] V. M. S. Gil and J. N. Murrell, *Trans. Faraday Soc.*, **60**, 248 (1964).

[20] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance," Vol. I, Pergamon Press, Oxford, 1965, p 71.

atom A itself. Similar expressions may be written for the xx and yy components.

We shall assume that the changes in ΔE are negligible for structurally related molecules and try to find relationships between the N^{14} chemical shifts and the ΣQ terms. So far there have been attempts to correlate nitrogen resonance shifts with the mean excitation energy through the long-wavelength transitions in electronic spectra,[7,21] but, apart from the error made by neglecting the rest of transitions, in many cases the electronic spectra are obscured by the absorption due to lone electron pairs at neighboring atoms, *e.g.*, the oxygen atoms in the nitro group or the nitrate ion. The simple cases where the n → π^* transitions for the nitrogen atom are well defined involve aliphatic amines, simple aromatic heterocycles,[7] and some other molecules[21] with lone pairs only at the nitrogen atom. For most of nitrogen-containing molecules, however, it is very difficult to explain the N^{14} shifts without making arbitrary assumptions of the value of ΔE, particularly if the shifts are small and occur in a group of similar molecules. Finding an explanation of such shifts in terms of the ground-state molecular orbitals would provide a simple means of predicting changes in nitrogen resonance shifts which result from various structural modifications of the molecule, and *vice versa.*

Considering the structure of the nitro group as that with sp^2-hybridized nitrogen and oxygen atoms, the following molecular orbitals may be written.



$$\psi_{\mathrm{RN}} = \frac{1}{\sqrt{2}}\left[\frac{1}{2}\,(s_{\mathrm{R}} + \sqrt{3}p_{x_{\mathrm{R}}}) + \frac{1}{\sqrt{3}}\,(s_{\mathrm{N}} - \sqrt{2}p_{x_{\mathrm{N}}})\right]$$

$$\psi_{\mathrm{NO}(1,2)} = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{3}}\left(s_{\mathrm{N}} + \frac{1}{\sqrt{2}}\,p_{x_{\mathrm{N}}} \pm \frac{\sqrt{6}}{2}p_{y_{\mathrm{N}}}\right) + \frac{1}{\sqrt{3}}\left(s_{\mathrm{O}} - \frac{1}{\sqrt{2}}p_{x_{\mathrm{O}}} \mp \frac{\sqrt{6}}{2}p_{y_{\mathrm{O}}}\right)\right]$$

$$\psi_1{}^{\pi} = (\sin a)(p_{z_{\mathrm{N}}}) + \frac{1}{\sqrt{2}}\,(\cos a)(p_{z_{\mathrm{O}(1)}} + p_{z_{\mathrm{O}(2)}})$$

$$\psi_2{}^{\pi} = \frac{1}{\sqrt{2}}(p_{z_{\mathrm{O}(1)}} - p_{z_{\mathrm{O}(2)}})$$

The nonzero elements of the bond-order and charge-density matrix are

$$P_{x_{\mathrm{N}}x_{\mathrm{N}}} = P_{y_{\mathrm{N}}y_{\mathrm{N}}} = 1; \quad P_{x_{\mathrm{N}}x_{\mathrm{O}}} = -\frac{1}{6}; \quad P_{y_{\mathrm{N}}y_{\mathrm{O}}} = -\frac{1}{2}$$

$$P_{z_{\mathrm{N}}z_{\mathrm{N}}} = 2(\sin a)(\sin a) = q_{\mathrm{N}}{}^{\pi}$$

$$P_{z_{\mathrm{N}}z_{\mathrm{O}}} = \frac{2}{\sqrt{2}}(\sin a)(\cos a) = p_{\mathrm{NO}}{}^{\pi}$$

$$P_{x_{\mathrm{N}}y_{\mathrm{O}(1)}} = P_{y_{\mathrm{N}}x_{\mathrm{O}(1)}} = -P_{x_{\mathrm{N}}y_{\mathrm{O}(2)}} = -P_{y_{\mathrm{N}}x_{\mathrm{O}(2)}} = -\frac{1}{2\sqrt{3}}$$

The ΣQ term may be calculated as follows.

$$(Q_{\mathrm{NN}})_{xx} = (Q_{\mathrm{NN}})_{yy} = (Q_{\mathrm{NN}})_{zz} = 2; \quad Q_{\mathrm{NN}} = 2$$

$$(Q_{\mathrm{NO}})_{xx} = p_{\mathrm{NO}}{}^{\pi}; \quad (Q_{\mathrm{NO}})_{yy} = \frac{1}{3}p_{\mathrm{NO}}{}^{\pi}$$

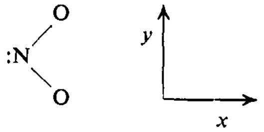
$$(Q_{\mathrm{NO}})_{zz} = 0; \quad Q_{\mathrm{NO}} = \frac{4}{9}p_{\mathrm{NO}}{}^{\pi}$$

$$\sum Q_{\mathrm{RNO_2}} = 2 + \frac{8}{9}p_{\mathrm{NO}}{}^{\pi}$$

$$\psi_{\mathrm{NN}} = \frac{1}{\sqrt{3}}(s_{\mathrm{N}} + \sqrt{2}p_{x_{\mathrm{N}}})$$

For the nitrite ion, NO_2^-, assuming the lone pair as a sp^2 hybrid, the change involves only the Q_{NN} term, since only ψ_{RN} is changed to

$$\psi_{\mathrm{NN}} = (1/\sqrt{3})(s_{\mathrm{N}} + \sqrt{2}p_{x_{\mathrm{N}}})$$



$$P_{x_{\mathrm{N}}x_{\mathrm{N}}} = \frac{5}{3}; \quad P_{y_{\mathrm{N}}y_{\mathrm{N}}} = 1; \quad P_{z_{\mathrm{N}}z_{\mathrm{N}}} = q_{\mathrm{N}}{}^{\pi}$$

and the rest remains unchanged.

$$(Q_{\mathrm{NN}})_{xx} = 2; \quad (Q_{\mathrm{NN}})_{yy} = \frac{10}{3} - \frac{4}{3}q_{\mathrm{N}}{}^{\pi}; \quad (Q_{\mathrm{NN}})_{zz} = 2$$

$$\sum Q_{\mathrm{NO_2^-}} = \frac{22}{9} - \frac{4}{9}q_{\mathrm{N}}{}^{\pi} + \frac{8}{9}p_{\mathrm{NO}}{}^{\pi}$$

where $q_{\mathrm{N}}{}^{\pi}$ is the π charge density at the nitrogen atom rather than the net charge. The changes in ΣQ shown in Table III may be considered for a few structures with various values of $p_{\mathrm{NO}}{}^{\pi}$ and $q_{\mathrm{N}}{}^{\pi}$. In the range of structures $1 < q_{\mathrm{N}}{}^{\pi} < 2$, where the actual structure of the NO_2 group should occur, the total mobile bond order at the nitrogen atom decreases with increasing $q_{\mathrm{N}}{}^{\pi}$, and so does ΣQ, thus predicting a resonance shift to higher fields with increasing electronegativity of R. This is just what was observed for nitro compounds, nitramines, and covalent nitrates. The value of ΣQ for the nitro group should be about 2.5–2.6, explaining the low magnetic field of its nitrogen resonance signal, as compared with $\Sigma Q \cong 2.3$ for nitriles[5] and about 2.2 for isonitriles,[5] while $\Sigma Q \cong 2$ for molecules with no π bonds at the nitrogen atom. The structure of the nitrite ion should be close to that with $q_{\mathrm{N}}{}^{\pi} = 1$, because of a decrease in the effective electronegativity of the nitrogen atom due to the presence of the lone electron pair. This would correspond to $\Sigma Q \cong 2.7$, explaining, at least partly, the large downfield shift of the nitrite resonance from that of the nitro group. Another explanation, not ex-

Table III

		R–NO₂		NO₂⁻	
$q_{\mathrm{N}}{}^{\pi}$	$p_{\mathrm{NO}}{}^{\pi}$	Net charge at N	ΣQ	Net charge at N	ΣQ
2	0	0	2.00	1	1.56
1.50	0.612	+1/2	2.54	−1/2	2.32
1.33	0.667	+2/3	2.59	−1/3	2.48
1	0.707	+1	2.63	0	2.67
0.75	0.684	+5/4	2.61	+1/4	2.72

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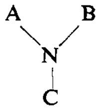
(21) J. B. Lambert and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 4087 (1965).

cluding the former, may be a decrease in the excitation energy due to the low-energy n → π^* transition from the lone pair of electrons at the nitrogen atom.

The resonance shift occurring on the protonation of pyridine has already been discussed[19] in the literature using directly eq 1, since sufficient data on the lower excited states of pyridine were available.

Before making an attempt to explain the relative nitrogen chemical shift for the NO_3^- ion and the $(CH_2NO_2)^-$ ion (I, II), we shall consider a general structure NABC where the σ-bond core consists of sp^2-hybridized



atomic orbitals and the π-orbital system extends over all four atoms and is characterized by $q_N{}^\pi$, $p_{NA}{}^\pi$, $p_{NB}{}^\pi$, and $p_{NC}{}^\pi$. The σ orbitals at the nitrogen atom are

$$\psi_{NA} = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{3}}(s_N - \sqrt{2}p_{x_N}) + \frac{1}{\sqrt{3}}(s_A + \sqrt{2}p_{x_A})\right]$$

$$\psi_{NB} = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{3}}\left(s_N + \frac{1}{\sqrt{2}}p_{x_N} + \frac{\sqrt{6}}{2}p_{y_N}\right) + \frac{1}{\sqrt{3}}\left(s_B - \frac{1}{\sqrt{2}}p_{x_B} - \frac{\sqrt{6}}{2}p_{y_B}\right)\right]$$

$$\psi_{NC} = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{3}}\left(s_N + \frac{1}{\sqrt{2}}p_{x_N} - \frac{\sqrt{6}}{2}p_{y_N}\right) + \frac{1}{\sqrt{3}}\left(s_C - \frac{1}{\sqrt{2}}p_{x_C} + \frac{\sqrt{6}}{2}p_{y_C}\right)\right]$$

$$P_{x_N x_N} = P_{y_N y_N} = 1; \quad P_{z_N z_N} = q_N{}^\pi$$

$$P_{x_N x_A} = -{}^2/_3; \quad P_{z_N z_A} = p_{NA}{}^\pi$$

$$P_{x_N x_B} = P_{x_N x_C} = -{}^1/_6; \quad P_{y_N y_B} = P_{y_N y_C} = -{}^1/_2$$

$$P_{z_N z_B} = p_{NB}{}^\pi; \quad P_{z_N z_C} - p_{NC}{}^\pi$$

$$P_{x_N y_B} = P_{y_N x_B} = -P_{x_N y_C} = -P_{y_N x_C} = -\sqrt{3}/6$$

From these elements the ΣQ term is calculated to be

$$\sum Q_{NABC} = 2 + \frac{4}{9}(p_{NA}{}^\pi + p_{NB}{}^\pi + p_{NC}{}^\pi)$$

which means that a resonance shift to lower fields is predicted with the increasing mobile bond order at the nitrogen atom. Calculations of the π-orbital system for the NO_3^- ion and the $(CH_2NO_2)^-$ ion were carried out employing the self-consistent field molecular orbital method neglecting overlap and penetration integrals (the Pariser–Parr–Pople method[22–24]). The method must be considered here as an approximate one and useful only for a direct comparison of two similar structures, because the net charges at the atoms in the ions involved are quite large. However, the lack of reliable data on spectral fitting of the integrals in the SCF matrix of the ions makes the application of more advanced methods, like the VESCF one,[25] rather pointless. The following geometry of the ions was assumed[26] in the calculations

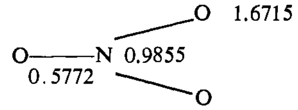
$$NO_3^- \begin{cases} \text{N–O} = 1.22 \text{ Å} \\ \text{ONO} = 120° \end{cases} \qquad CH_2NO_2^- \begin{cases} \text{N–O} = 1.39 \text{ Å} \\ \text{C–N} = 1.39 \text{ Å} \\ \text{CNO} = 120° \end{cases}$$

The values for the nitromethane anion were based on preliminary Hückel MO calculations suggesting an "aromatic" CN bond and almost single NO bonds. The ionization potentials W and the one-center $(\mu\mu|\mu\mu)$ and two-center $(\mu\mu|\nu\nu)$ integrals were calculated according to a recently proposed[27] method for heterocyclic systems (Table IV). The resonance integrals were calculated from the Allinger[28] formula as $\beta_{1.22 Å} = -4.15$ eV, $\beta_{1.39 Å} = -2.64$ eV, and zero otherwise. The iterative SCF calculations gave the following π-electron densities and mobile bond orders.

Table IV

	$W\mu$, eV	$\mu\mu\|\mu\mu$, eV
C^+	11.16	11.13
O^+	17.70	15.23
N^{2+}	26.70	17.44
$N^+N^+/OO_{1.22 Å} = 7.04$ eV	$N^+N^+/OO_{1.39 Å} = N^+N^+/CC_{1.39 Å} = 6.50$ eV	
$OO/OO_{2.11 Å} = 4.71$ eV	$CC/OO_{2.32 Å} = OO/OO_{2.32 Å} = 4.41$ eV	

NO_3^-



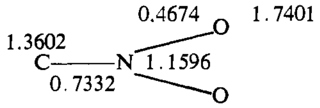
$$\psi_1{}^\pi = 0.7019\varphi_N + 0.4112(\varphi_{O_1} + \varphi_{O_2} + \varphi_{O_3})$$

$$\psi_2{}^\pi = \frac{1}{\sqrt{2}}(\varphi_{O_2} - \varphi_{O_3})$$

$$\psi_3 = \frac{1}{\sqrt{6}}(2\varphi_{O_1} - \varphi_{O_2} - \varphi_{O_3})$$

$$\sum p_N{}^\pi = 1.7316$$

$CH_2NO_2^-$



$$\psi_1{}^\pi = 0.3423\varphi_C + 0.7470\varphi_N + 0.4030(\varphi_{O_1} + \varphi_{O_2})$$

$$\psi_2{}^\pi = \frac{1}{\sqrt{2}}(\varphi_{O_1} - \varphi_{O_2})$$

$$\psi_3{}^\pi = 0.7503\varphi_C + 0.1478\varphi_N - 0.4557(\varphi_{O_1} + \varphi_{O_2})$$

$$\sum p_N{}^\pi = 1.6680$$

According to the results of the calculations, the total mobile bond order at the nitrogen atom is higher in the NO_3^- ion than in the $CH_2NO_2^-$ ion. Hence, a shift to a lower magnetic field is predicted for the nitrogen reso-

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(22) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(23) J. A. Pople, *J. Phys. Chem.*, **61**, 6 (1957).

(24) R. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, Inc., New York, N. Y., 1963.

(25) R. D. Brown and M. L. Heffernan, *Trans. Faraday Soc.*, **54**, 757 (1958).

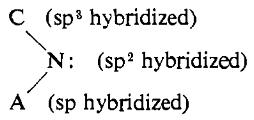
(26) "Tables of Interatomic Distances and Configurations," L. Sutton, Ed., Methuen & Co., London, 1958.

(27) K. Nashimoto and L. S. Forster, *Theoret. Chim. Acta*, **4**, 155 (1966).

(28) N. Allinger, *J. Org. Chem.*, 27, 433 (1962).

nance of the former, in agreement with the observed values (I, II).

A general expression for the ΣQ term for the system



characterizing alkyl isocyanates, isothiocyanates, and azides, may be derived according to the method described before

$$\sum Q_{\mathrm{CNA}} = \frac{22}{9} - \frac{4}{9} q_{\mathrm{N}}^{\pi} + \frac{2}{3\sqrt{3}} p_{\mathrm{NA}}^{\pi}$$

which, as can be easily checked, increases with decreasing q_{N}^{π} and suggests a downfield resonance shift with decreasing electronegativity of the alkyl substituent at the nitrogen atom. This also is in agreement with the experimentally found shifts for the methyl and ethyl derivatives.

For amides, where delocalization of the lone electron pair at the nitrogen atom is postulated, $\Sigma Q = 2 + {}^{4}/_{9} p_{\mathrm{NC}}^{\pi}$, while for a sp^3-hybridized nitrogen atom, as in NH_4^+, $\Sigma Q = 2$, if we neglect σ-bond polarization effects. Since the CN bond in amides has a partly double-bond character[14–16] ($p_{\mathrm{NC}}^{\pi} > 0$), the values of ΣQ suggest a lower magnetic field for their nitrogen resonances than for ammonium ions and amines. This is actually observed (XXXII–XXXVII, and data of other authors[7,29]).

The comparison of the experimentally found correlations between the N^{14} chemical shifts for sp^2-hybridized nitrogen atoms and structural changes within a group of similar molecules with the calculations of the ΣQ terms shows that the changes in the shifts may be explained without reference to the excited states. Considering the previously reported[5,6] successful applications, the method seems to be generally useful, particularly in the cases where it is difficult to obtain estimates of the excitation energy. One should note, however, that the changing electronegativity of the substituents at the nitrogen atom is not likely to be the sole criterion for N^{14} shifts for very different structures.

Experimental Section

The substances used in the measurements of the N^{14} resonance spectra were commercially available CP grade products or were prepared according to the literature (IX,[30] XI,[31] XII,[8] XXII,[32] XXIII,[32] XXV,[33] XXVI,[34] XXVIII,[35] XXIX,[35] XXXI[36]). The N^{14} resonance spectra were measured using a Varian HR-60 nmr spectrometer operating at 4.33 Mc/sec (14,100 G) with the audiomodulation base-line stabilizing system from the integrator unit and slow sweep from the flux stabilizer. The resonance shifts were measured employing the internal reference method, described elsewhere,[3] using nitromethane or the nitrate ion as the primary standards (δ_{N} 0) and dimethylformamide as a secondary standard (δ_{N} +276 ppm). The calibration was carried out by the sideband method. The half-height widths of the resonance signals were measured under conditions eliminating saturation effects. Caution was necessary there since the relaxation times differ appreciably among N^{14} nuclei in various molecular environments.

A useful procedure for recording in one run N^{14} spectra containing signals of various widths is to sweep the central band at a high radiofrequency power level in order to obtain a good signal-to-noise ratio for broad resonances, and then to sweep through either of the 2-kc/sec side bands at the same radiofrequency power level with an adjustment of the phase-reference system to inverted absorption mode, looking for narrow resonance signals that might have been saturated in the central band. The procedure may be conveniently applied when measuring an unknown N^{14} spectrum, particularly if the concentration of the nitrogen nuclei is low. The selection of the pure absorption mode was important for accurate calibration of the shifts and was carried out on the narrowest signals in the spectrum, usually those of the standards.

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(32) (a) G. Schröter, *Ber.*, 42, 3356 (1909); (b) see also, C. F. H. Allen and A. Bell, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 846.

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(36) P. Walden, *Ber.*, **40**, 3215 (1907).