

and β,α' -DCAN seems to demonstrate that the conformational structure of the exciplex fluorescent state is neither rigid nor stable.

Recently, the fluorescent state of the exciplex was proposed to be identical with that of the corresponding CT complex, although the Franck-Condon states are different from each other. According to this argument, two fluorescences may be observed in the same region. However, as summarized in Table I and shown in Figure 5, the two fluorescence spectra seem to have too large an energy difference to be assigned to the fluorescence from the identical excited state. It is likely that the exciplex and CT fluorescences are from the individual excited states. Further evidence was found by determination of the fluorescence lifetime at various temperatures, as shown in Figure 8. The fluorescence lifetimes of the exciplex in β,α' -DCAN and β,β' -DCAN are almost independent of temperature, respectively. The fluorescence lifetime of the CT complex determined at the same wavelength as that of the exciplex is also independent of temperature, and quite different from that of the corresponding

exciplex. These results demonstrate that there are two fluorescent states in the potential energy surface in DCAN.

The intramolecular electronic interaction leading to the differences in the excited fluorescent states of the exciplex and the CT complex can be understood by the following consideration. The electronic interaction and therefore the geometrical arrangement between the DCA and naphthalene moieties are different from each other in the Franck-Condon excited states of the exciplex and the CT complex, because the exciplex formation is the photochemical process but the formation of the latter is really the thermal process followed by the photoexcitation. The internal or geometrical conversion from their Franck-Condon states to the identical fluorescent state, if it is correct, is forbidden in our compounds by the steric factor concerned with the trimethylene chain.

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^{13}C and ^{15}N Nuclear Magnetic Resonance Spectroscopy of Nitrile Oxides and Related Reaction Products. Unexpected ^{13}C and ^{15}N Nuclear Magnetic Resonance Parameters of 2,4,6-Trimethylbenzonitrile Oxide^{1a}

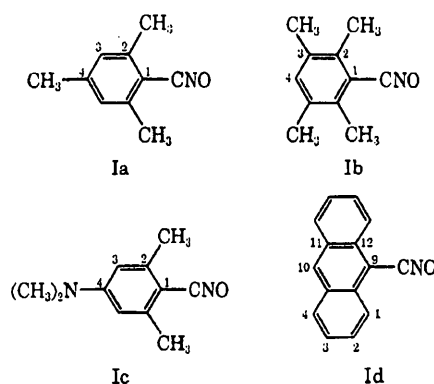
Manfred Christl,^{1b} John P. Warren, Bruce L. Hawkins, and John D. Roberts*

Contribution No. 4511 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109.

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Abstract: The ^{13}C nmr spectra of several aryl nitrile oxides have been taken. The magnitude of $^1J_{^{13}\text{C}-^{15}\text{N}}$ for 2,4,6-trimethylbenzonitrile- ^{15}N oxide has been found to be 77.5 Hz, by far the largest one-bond carbon-nitrogen spin-spin coupling constant yet reported. The ^{13}C resonance of the carbon atom bonded to the nitrogen atom in this nitrile oxide is considerably shifted upfield by comparison with the analogous ^{13}C resonances of nitriles; however, little change is seen in the paramagnetic shielding term for ^{15}N upon conversion of a nitrile to a nitrile oxide. The ^{13}C and ^{15}N spectra are reported for a precursor and some reaction products of 2,4,6-trimethylbenzonitrile- ^{15}N oxide. The low-field position of the ^{15}N resonances of isoxazole systems is discussed in relation to nitrogen chemical shifts for other five-membered heterocycles.

The cmr spectra of 2,4,6-trimethylbenzonitrile oxide (Ia) and three other stable nitrile oxides (Ib-d) have been investigated in an attempt to find a correlation between the chemical shifts of the carbon of the nitrile oxide group and the product ratios observed in the cycloaddition reactions of these nitrile oxides with methyl α,β -unsaturated carboxylates.² The cmr spectra were taken of concentrated solutions of the nitrile oxides in methylene chloride, with proton noise decoupling. After a few minutes of spectral accumulation, all the carbon resonances appeared except that



of the nitrile oxide carbon atom, and it did not show up even after several hours. There are three factors

(1) (a) Supported by the National Science Foundation and the Public Health Service, Research Grant No. GM-11072 from the Division of General Medical Sciences; (b) Max Kade Foundation, Inc., Fellow, 1970-1971.

(2) M. Christl and R. Huisgen, *Tetrahedron Lett.*, 5209 (1968); M. Christl and R. Huisgen, to be submitted for publication.

tending to produce difficulty in detecting this signal by comparison with the other carbon resonances: (i) no significant nuclear Overhauser enhancement is obtained because of the absence of directly bonded, or even closely bonded, protons; (ii) the spin-spin coupling with the ^{14}N nucleus splits the signal into three equally intense lines; and (iii) the ^{14}N nuclear quadrupole relaxation causes extensive line broadening.³ The second and third of these difficulties can be removed by replacement of ^{14}N by ^{15}N , which has no quadrupole moment and the spin-spin splitting from which would lead only to doublets for the carbon resonances. With the ^{15}N -labeled compound it was possible to detect the missing carbon resonance, as will be described below.

We have also taken the ^{13}C and ^{15}N nmr spectra of a ^{15}N -labeled precursor of Ia- ^{15}N , and of some reaction products derived from Ia- ^{15}N .

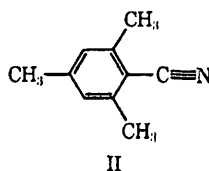
Results and Discussion

The cmr spectrum of Ia- ^{15}N revealed the resonance of the nitrile oxide carbon at 157.1 ppm (upfield from carbon disulfide) as a doublet, with a one-bond ^{13}C - ^{15}N coupling constant of 77.5 ± 0.5 Hz. This resonance is upfield by 81.8 ppm compared with that of the corresponding carbon of 2,4,6-trimethylbenzonitrile (II). In Table I, the chemical shifts of II and Ia- ^{15}N

Table I. Carbon-13 Chemical Shifts of 2,4,6-Trimethylbenzonitrile (II) and 2,4,6-Trimethylbenzonitrile Oxide (Ia- ^{15}N) and ^{13}C - ^{15}N Coupling Constants of the Latter Compound

Carbon	δ_{11} , ^a ppm	$\delta_{1a-^{15}\text{N}}$, ^a ppm	$ J_{^{13}\text{C}-^{15}\text{N}} $, Hz
CN, CNO	75.3 ^b	157.1	77.5 ± 0.5
C1	82.0 ^b	81.4	2.2 ± 0.1
C2	50.5	51.1	1.0 ± 0.1
C3	64.0	64.4	< 0.5
C4	49.4	51.6	0.8 ± 0.1
2-CH ₃	172.7	172.5	< 0.5
4-CH ₃	171.7	171.8	< 0.5

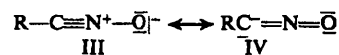
^a The chemical shifts are relative to internal methylene chloride and are corrected to carbon disulfide as external reference by the relation $\delta_0 = \delta_{\text{C}^{\text{CH}_2\text{Cl}_2}} + 138.9$ ppm. ^b The CN and C1 resonances were assigned according to the similar values in benzonitrile, given by F. W. Wehrli, J. W. de Haan, A. I. M. Keulemans, O. Exner, and W. Simon, *Helv. Chim. Acta*, **52**, 103 (1969).



are collected, together with some ^{13}C - ^{15}N coupling constants. It will be seen that the corresponding resonances of the mesityl moieties differ by a maximum of only 2.2 ppm, which shows that the electrical and steric interactions of the nitrile group and the nitrile oxide group with the rest of the molecule are similar. The difference in the chemical shifts of the nitrile and

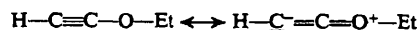
(3) (a) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Oxford, 1966, p 1037; (b) J. D. Memory, "The Analytical Chemistry of Nitrogen and Its Compounds," Part 1, C. A. Streuli and P. R. Averell, Ed., Wiley-Interscience, New York, N. Y., 1970, p 29.

nitrile oxide carbons must therefore arise from some special, very local difference between the electronic properties of the nitrile and nitrile oxide groups. The most likely difference is that, in the nitrile, there are two orthogonal, two-center, two-electron π -molecular orbitals associated with the triple bond, whereas in the nitrile oxide, there are two orthogonal two-electron, three-center π -type molecular orbitals. The most important valence-bond structures of nitrile oxides are expected to be III and IV. Evidence for a



considerable contribution of IV to the ground state of nitrile oxides has been deduced from infrared⁴ and microwave spectra⁵ of fulminic acid and from an X-ray structural analysis of 4-methoxy-2,6-dimethylbenzonitrile oxide.⁶ Chemical shift theory⁷ predicts a strong upfield shift of a carbon resonance with increasing charge. The effect can be large: approximately 160–200 ppm per unit of π -electron charge in substituted benzenes,⁸ nonalternant hydrocarbons,⁸ in the series C_6H_5^- , C_6H_6 , C_7H_7^+ ,⁹ and C_9H_9^- ,¹⁰ and in the mesitylenonium ion.¹¹ Molecular orbital calculations of benzonitrile and benzonitrile oxide¹² indicate that the π -electron density at the carbon of a nitrile oxide group has an average charge about 0.25 electron greater than that of a nitrile. This difference could account for roughly half of the observed shift of 81.8 ppm.

The ^{13}C resonance of the β -carbon atom of ethoxyethyne is 42.8 ppm upfield of the corresponding resonance in butylethyne.¹³ An explanation for this postulates charge transfer to the triple bond from the oxygen atom



which has an obvious parallel to the shielding of the sp-hybridized carbon in Ia- ^{15}N .

The absolute value of the one-bond ^{13}C - ^{15}N coupling constant in Ia- ^{15}N is, as far as we are aware, larger by a factor of 4.4 than the absolute value of any published ^{13}C - ^{15}N coupling constant.^{14,15} The Fermi contact interaction has usually been considered to be the dominant spin-spin coupling mechanism. In an earlier study, it was found that the magnitudes of a number of one-bond ^{13}C - ^{15}N couplings could be correlated reasonably well with the products of the s characters

(4) W. Beck, P. Swoboda, K. Feldl, and R. S. Tobias, *Chem. Ber.*, **104**, 533 (1971).

(5) M. Winnewisser and H. K. Bodenseh, *Z. Naturforsch. A*, **22**, 1724 (1967); H. K. Bodenseh and M. Winnewisser, *ibid.*, **24**, 1966, 1973 (1969).

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(15) G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 5564 (1964).

of the atoms under consideration¹⁵

$$S_0 S_n = 80^1 J_{13C-15N} \quad (1)$$

but benzalmethylamine (both $^1J_{13C-15N}$ values) and acetonitrile deviated from the correlation with the hybridizations that were assumed.¹⁵ According to eq 1, and taking the simplest possible formulation of the hybridizations involved, Ia is predicted to have $^1J_{13C-15N}$ of about 30 Hz. The observed coupling of 77.5 Hz is clearly indicative of another example for which eq 1 is inadequate. The assumptions made in setting up eq 1 have been criticized,¹⁶ and it appears that theoretical calculations which assume the Fermi contact term to be dominant (this also is the basis for eq 1) do not satisfactorily reproduce C-N coupling constants¹⁶ in contrast to the situation with C-C or C-H couplings,^{16,17} where equations such as eq 1 work quite well. Recent calculations suggest that orbital and dipole-dipole terms can make quite substantial contributions to the coupling between first-row nuclei.^{18,19}

The magnitude of $^1J_{13C-15N}$ in Ia-¹⁵N can only really be compared with coupling constants between other directly bonded nuclei on the basis of the reduced coupling constants,²⁰ $^1K_{AB} = (J_{AB}/h)(4\pi^2/\gamma_A\gamma_B)$. Some $^1K_{AB}$ values are given in Table II, calculated

Table II. Some Reduced Coupling Constants for Directly Bonded Nuclei

Nuclei	Compd	$ J_{AB} $, Hz	$ ^1K_{AB} $, 10^{20} N A ³ m ⁻³
¹ H, ¹ H	H-H	278 ^a	2.3
¹ H, ¹³ C	[H-C≡N-H] ⁺ SbF ₆ ⁻	320 ^b	10.6
¹ H, ¹⁵ N	[CH ₃ C≡N-H] ⁺ SbF ₆ ⁻	136 ^b	11.2
¹¹ B, ¹³ C	Ph ₄ B ⁻	49.5 ^c	5.1
¹³ C, ¹³ C	PhC≡CH	175.9 ^d	23.2
¹³ C, ¹⁵ N	2,4,6-(CH ₃) ₂ PhCNO	77.5 ^e	25.3
¹⁶ N, ¹⁵ N	Ph-N=N ⁺ (O ⁻)Ph	13.7 ^f	11.1
¹³ C, ¹⁹ F	H-CO-F	369 ^g	13.0
¹⁴ N, ¹⁹ F	[F-N=N] ⁺ AsF ₆ ⁻	328 ^h	40.2
¹³ C, ²⁹ Si	(CH ₃) ₄ Si	51 ⁱ	8.5
¹³ C, ³¹ P	Ph ₃ MeP ⁺ Br ⁻	88.4 ^c	7.2
³¹ P, ³¹ P	P ₂ H ₄	108 ⁱ	5.5
¹⁴ N, ¹⁹⁵ Pt	cis-[Pt(NCS) ₂ (Bu ₃ P) ₂]	430 ^h	230.5
¹¹⁷ Sn, ¹¹⁹ Sn	Sn ₂ Me ₆	4264 ⁱ	267.4

^a T. F. Wilmott, *Phys. Rev.*, **91**, 476 (1953); M. Barfield and D. M. Grant, *Advan. Magn. Resonance*, **1**, 149 (1965). ^b G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **90**, 4666 (1968). ^c F. J. Weigert and J. D. Roberts, *ibid.*, **91**, 4940 (1969). ^d K. Frei and H. J. Bernstein, *J. Chem. Phys.*, **38**, 1216 (1963). ^e Present investigation. ^f Reference 15. ^g N. Muller and D. T. Carr, *J. Phys. Chem.*, **67**, 112 (1963). ^h D. Moy and A. R. Young II, *J. Amer. Chem. Soc.*, **87**, 1889 (1965). ⁱ F. J. Weigert, M. Winokur, and J. D. Roberts, *ibid.*, **90**, 1566 (1968). ^j Reference 20, p 107. ^k O. W. Howarth, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.*, 3335 (1964).

from the largest J_{AB} values available from the sources consulted. Reduced coupling constants generally increase in magnitude as the atomic numbers of the

(16) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 11 (1970).

(17) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 1 (1970).

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(20) Cf. R. M. Lynden-Bell and R. K. Harris, "Nuclear Magnetic Resonance Spectroscopy," Appleton-Century-Crofts, New York, N. Y., 1969.

coupled nuclei increase.²⁰ Thus the most pertinent comparisons of $^1K_{13C-15N}$ in Ia-¹⁵N are those with reduced coupling constants between other first-row nuclei. It can be seen that for coupling between first-row nuclei only the $^1K_{15N-19F}$ value for [N₂F]⁺ AsF₆⁻ exceeds $^1K_{13C-15N}$ for Ia-¹⁵N.

The long-range $^{13}C-^{15}N$ coupling constants in Ia-¹⁵N (see Table I) are small and comparable to those found for pyridine^{14,21} and quinoline.²² The five-bond coupling constant of 0.8 Hz with C4, however, seems noteworthy. In the proton spectrum of Ia-¹⁵N, no splittings due to couplings involving ¹⁵N have been observed.

Knowing the resonance positions of all the carbon atoms in Ia-¹⁵N, we looked again at the ¹³C spectrum of Ia-¹⁴N. After 7 hr of spectral accumulation, a triplet with somewhat broadened lines appeared at 156.9 ppm for the nitrile oxide carbon atom. The one-bond ¹³C-¹⁴N coupling constant was determined to be 52 ± 2 Hz. Division of $^1J_{13C-15N}$ (77.5 Hz) by $\gamma_{15N}/\gamma_{14N}$ (-1.402) gives a comparison value for $^1J_{13C-14N}$ of 55.3 ± 0.4 Hz.

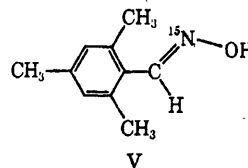
Table III shows the cmr data for the nitrile oxides

Table III. Carbon-13 Chemical Shifts of Some Nitrile Oxides^a (in ppm) Relative to Carbon Disulfide

Compd	CNO	C1	C2	C3	C4	
Ia	157.1	81.4	51.1	64.4	51.6	2-CH ₃ , 172.5; 4-CH ₃ , 171.8
Ib	<i>b</i>	77.9	<i>c</i>	<i>c</i>	59.0	2-CH ₃ ; ^d 3-CH ₃ ^d
Ic	<i>b</i>	92.7	50.0	82.1	41.4	2-CH ₃ , 171.8; NCH ₃ , 153.1
Id	<i>b</i>	<i>e</i>	<i>e</i>	<i>e</i>	<i>e</i>	C9, 86.1; C10, 62.5; C11; C12 ^f

^a See footnote a of Table I. ^b Not observed. ^c 55.3 or 58.2 ppm. ^d 173.5 or 175.3 ppm. ^e 63.8 or 64.5 or 66.8 or 68.0 ppm. ^f 59.4 or 62.0 ppm.

Ib-d. The resonance of the nitrile oxide carbon atom could not be observed in any of these compounds. 2,4,6-Trimethylbenzaloxime-¹⁵N (V) was used as pre-



cursor for Ia-¹⁵N, and the proton spectrum shows a 2.3-Hz coupling between the aldehyde proton and ¹⁵N. This value²³ suggests a syn configuration for the oxime group.

The heterocyclic compounds VI and VII were obtained from Ia-¹⁵N and ethylene and acetylene, respectively. The protons in the 4 and 5 positions of VI appear as the AA'BB' portion of the expected AA'-BB'X spin system. Because of the adjacent electronegative oxygen atom, the protons in the 5 position

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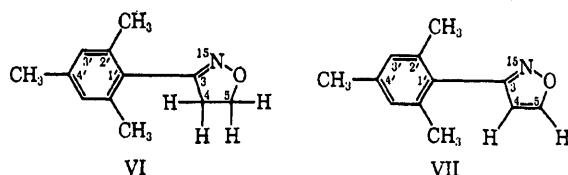
(22) P. S. Pregosin, E. W. Randall, and A. I. White, *J. Chem. Soc., Perkin Trans. 2*, 1 (1972).

(23) (a) D. Crepau and J. M. Lehn, *Mol. Phys.*, **14**, 547 (1968); (b) D. Crepau, J. M. Lehn, and R. R. Dean, *ibid.*, **16**, 225 (1969).

Table IV. ^{13}C Chemical Shifts and ^{13}C - ^{15}N Coupling Constants in 2,4,6-Trimethylbenzaloxime- ^{15}N (V), 3-Mesityl- Δ^2 -isoxazoline- ^{15}N (VI), and 3-Mesitylisoxazole- ^{15}N (VII)^a

Compd	CHNOH		C1	C2	C3	C4	2-CH ₃	4-CH ₃	
V ^b	47.7 2.8 ± 0.1		67.5 6.2 ± 0.1	58.2 1.2 ± 0.1	65.9	57.5	173.8	174.0	
	C3	C4	C5	C1'	C2'	C3'	C4'	2'-CH ₃	4'-CH ₃
VI ^c	36.5	153.5	124.3	65.2 7 ± 1	56.0	64.1	54.2	173.3	172.0
VII ^c	32.2 4.0 ± 0.5	87.1	34.1	66.4 7.0 ± 0.5	55.9	64.5	54.4	173.2	172.4

^a The upper line of figures for compounds gives the chemical shifts in ppm upfield from carbon disulfide; the lower line gives the absolute values of the ^{13}C - ^{15}N coupling constants in hertz. The chemical shifts have been measured relative to the solvent peak and are corrected to carbon disulfide as external reference. ^b In dimethyl sulfoxide, $\delta_{\text{C}}^{\text{CS}_2} = \delta_{\text{C}}^{\text{dimethyl sulfoxide}} + 154.4$ ppm. ^c In dioxane, $\delta_{\text{C}}^{\text{CS}_2} = \delta_{\text{C}}^{\text{dioxane}} + 126.0$ ppm.



come at lower field (δ 4.33) than the ones in the 4 position (δ 3.04). Only the C4 protons of VI show spin-spin coupling to ^{15}N ; the coupling constant is 2.2 Hz, the same order of magnitude as for other three-bond ^{15}N - ^1H couplings.^{14,15} The same situation was found for VII. Only the signal of H4 (δ 6.20) which, in the unlabeled compound, appears as a doublet (because of the coupling ($J = 1.6$ Hz) with H5 (δ 8.44)) is split further due to the coupling with ^{15}N ; the ^{15}N - ^1H coupling constant is 1.0 Hz. A similar value for a three-bond coupling has been found in pyridine- ^{15}N .^{14,21} In VI and VII, the protons in the 5 position are separated from the nitrogen atom by the same number of bonds as the ones in the 4 position. Obviously, the oxygen atom does not propagate the coupling as well as the carbon atom in the 3 position.

Table IV shows the ^{13}C chemical shifts and the ^{13}C - ^{15}N coupling constants of V-VII. All assignments are consistent with the off-resonance proton-decoupled spectra. In contrast to the nitrile oxide (Ia- ^{15}N), no unexpected parameters are observed. The mesityl moieties in VI and VII have comparable chemical shifts, indicating that they interact with the heterocyclic rings in similar ways. This is not surprising because steric strain presumably prevents attainment of coplanarity of the two rings in both compounds. This assumption is supported by the corresponding ^{13}C chemical shifts in mesitylene (C1, 56.4; C2, 66.1; CH₃, 172.2 ppm)⁸ which do not differ much from the corresponding values for VI and VII. In the oxime (V) a coplanar arrangement of the ring and oxime groups is also expected to lead to serious steric repulsions. The somewhat higher chemical shifts of the mesityl moiety may arise here from a solvent effect, because the spectrum of V was run in dimethyl sulfoxide while dioxane was used as the solvent for VI and VII.

The carbon atom of V bonded to nitrogen comes into resonance approximately 7 ppm upfield from analogous carbon atoms in comparable α,β -ethylenic oximes.²⁴ On going from V to VI, the signal of this

carbon atom moves downfield by 12.1 ppm as the expected result of the replacement of the hydrogen atom in V by C4 in VI (α effect). The corresponding resonance in VII is at still lower field by 3.4 ppm, which is probably the result of electronic changes in the isoxazole ring of VII, which is potentially "aromatic," compared to VI, which is not. C4 and C5 in VI show typical ^{13}C chemical shifts for saturated carbon atoms. The higher chemical shift of C4 and the lower one of C5 in VII, compared to the corresponding carbon atoms in furan (C2, C5, 49.8; C3, C4, 82.9 ppm),²⁵ might indicate that isoxazoles are less aromatic than furans.

The magnitudes of the ^{13}C - ^{15}N coupling constants in V-VII are not surprising on the basis of other data.¹⁴ The two-bond coupling to C1 of the mesityl moieties is practically the same in all three compounds, thereby emphasizing the similar electronic interactions in these systems, but is larger by a factor of about 3 than for Ia- ^{15}N . The one-bond coupling shows some variation; it could not be resolved in VI.

The nitrogen chemical shifts of V, Ia, VI, VII, and isoxazole (VIII) are given in Table V, as are nitro-

Table V. ^{15}N Chemical Shifts

Compd	δ_{N} , ppm ^a	J , Hz
syn-2,4,6-Trimethylbenzaloxime- ^{15}N (V)	331.0	$^2J_{^{15}\text{N}-\text{C}-^1\text{H}}$, 2.4 ± 0.2
2,4,6-Trimethylbenzoxonitrile- ^{15}N oxide (Ia- ^{15}N)	166.3	
3-Mesityl- Δ^2 -isoxazoline- ^{15}N (VI)	326.7	$^3J_{^{15}\text{N}-\text{CC}-^1\text{H}}$, 2.3 ± 0.2
3-Mesitylisoxazole- ^{15}N (VII)	335.9	
Isoxazole	339.6	

^a Downfield from approximately 12 M aqueous tetramethylammonium chloride solution.



gen-proton spin-spin coupling constants where these could be measured from proton-coupled ^{15}N spectra (although the values will be less reliable than those measured from the proton spectra). The nitrogen chemical shifts are referred to tetramethylammonium chloride, unless otherwise indicated, with downfield shifts being positive.

(25) T. F. Page, Jr., T. Alger, and D. M. Grant, *J. Amer. Chem. Soc.*, 87, 5333 (1965).

(24) (a) Z. W. Wolkowski, E. Vauthier, B. Gonbeau, H. Sauvairat, and J. A. Musso, *Tetrahedron Lett.*, 565 (1972); (b) Z. W. Wolkowski, D. ès-Sc. Thesis, University of Paris, 1971.

Few nitrogen chemical shifts have been reported for oximes. The ^{14}N resonance of 2-butanone oxime was found at 251 ± 60 ppm.²⁶ The ^{15}N chemical shift of formaldoxime was measured by means of indor experiments; data are given from which a shift for formaldoxime of 49 ppm (with respect to quinoline in carbon tetrachloride solution) can be calculated.^{23b} Referring this shift to one of the usual nitrogen chemical shift reference compounds²⁷ is somewhat uncertain. However, with a value of 288.5 ppm (with respect to ammonium chloride) for the nitrogen shift of quinoline in carbon tetrachloride,²² the shift of formaldoxime relative to tetramethylammonium chloride is approximately 319 ppm. It has been reported that α,β -ethylenic oximes give ^{14}N nmr resonances at 281 ± 15 ppm;^{24b} however, the chemical-shift variations between different oximes are smaller than the experimental error in measuring the ^{14}N chemical shifts because of line broadening due to ^{14}N quadrupolar relaxation.

The ^{15}N chemical shift that we have measured for Ia agrees with the ^{14}N shift of 166 ppm.²⁸ Benzonitrile has a nitrogen shift of 212 ppm,²⁶ and the upfield shift of about 46 ppm (neglecting possible methyl substituent shifts) in going from the nitrile to the nitrile oxide is large in relation to either the downfield shift on protonation of an aliphatic amine (about 25 ppm¹⁴) or the upfield shift associated with the change from 2-methylpyridine to the *N*-oxide (about 32 ppm²⁶). However, the shift is small by comparison with the upfield ^{15}N shift of 96 ppm when methanolic pyridine is protonated to form the pyridinium ion.²¹ The downfield shift on protonation of amines has been ascribed to removal of diamagnetic screening of the nitrogen nucleus by the nitrogen lone pair, while the upfield shifts on protonation or *N*-oxide formation of pyridines must involve a larger change in the paramagnetic screening.¹⁴ On protonation of aniline, the two effects are almost equal.²⁹

The sort of qualitative argument used here can be expressed more precisely as the sum of three terms^{14, 20, 30, 31}

$$\sigma^A = \sigma_d^A + \sigma_p^A + \sum_{B \neq A} \sigma^{AB}$$

where σ^A is the shielding constant of the nucleus concerned, σ_d^A is the diamagnetic term (which is a function of the ground state only), σ_p^A is the paramagnetic term (involving matrix elements between the ground state and all excited states of appropriate symmetry), and the $\sum_{B \neq A} \sigma^{AB}$ term (normally considered to be small and therefore neglected) arises from the shielding effects of other atoms in the molecule and from medium effects. The normal approach to calculating σ_p^A is by means of an LCAO-MO treatment.³² For carbon and nitrogen, the following relation (in SI

units) may be used

$$\sigma_p^A = \frac{e^2 \hbar^2}{2m^2} \frac{1}{\Delta E} \langle r^{-3} \rangle_{2p} \sum_B Q_{AB}$$

where ΔE is the average excitation energy, $\langle r^{-3} \rangle_{2p}$ is the mean value of the inverse cube of the 2p orbital radius, and the Q_{AB} terms (where B is the neighbor of A) contain the elements of the charge-density/bond-order matrix. Recently, a rather simple method has been published for calculating the diamagnetic contribution to chemical shifts³³ (in SI units)

$$\sigma_d^{(k)} = \sigma_d^{(\text{free atom})} - \frac{e^2}{3m} \sum_{\alpha} (Z_{\alpha}/r_{\alpha}) \quad (2)$$

where $\sigma_d^{(k)}$ is the diamagnetic contribution to the shielding of the *k*th nucleus in a molecule, $\sigma_d^{(\text{free atom})}$ is the diamagnetic shielding of the appropriate free atom, Z_{α} is the atomic number of nucleus α , r_{α} is the distance between nuclei *k* and α , and the summation runs over all atoms directly bound to nucleus *k*.

In calculating σ_d values for compounds in which the nitrogen atom does not bear a formal charge, we have taken the shielding of a free nitrogen atom (with respect to the bare nitrogen nucleus) to be -325.47 ppm.³⁴ In the case of 2,4,6-trimethylbenzonitrile oxide and tetramethylammonium chloride, however, where the nitrogen atoms bear formal positive charges, a value of -314.30 ppm^{34a} for the shielding of a free N^+ ion has been used in eq 2 when calculating σ_d values, rather than the value for a free nitrogen atom. The σ_d^{N} value calculated for nitrile oxides can be expected to depend on which canonical form is taken to predominate. We have considered the effective atomic numbers of carbon and oxygen to be one greater when negatively charged, and one less when positively charged. The variation so introduced is about 4 ppm. Equation 2 is applicable only when the electronegativity differences between atoms directly bonded to the atom in question are not too great.^{33d}

Conversion of a nitrile to a nitrile oxide provides an interesting case for application of diamagnetic shielding corrections calculated in this way. The σ_d^{N} values of benzonitrile and benzonitrile oxide (average of the several canonical forms) can be calculated to be -374 and about -430 ppm (with respect to the bare nitrogen nucleus), respectively. The bond lengths used were those given elsewhere¹² except for the nitrogen-oxygen bond length in benzonitrile oxide, which was taken to be 1.25 Å.^{6, 35} Thus, there is an upfield diamagnetic correction of about 56 ppm on going from nitrile to nitrile oxide. The actual change in the nitrogen chemical shift on going from II to Ia is -46 ppm, so that the diamagnetic shielding term can account for most of the difference.

Electronic spectra of Ia and II³⁶ show that there

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is a shift to longer wavelength of the long-wavelength absorption band of only about 6 nm on going from II to Ia. There is a moderate correlation between the position of the long-wavelength band in electronic spectra and the paramagnetic shielding contribution, σ_p^N , to nitrogen chemical shifts,^{14,26,38f} so that little change in σ_p^N upon conversion of II to Ia is to be expected.

The nitrogen chemical shifts of VII and isoxazole seem quite unusual by comparison with nitrogen shifts of other azoles (see Table VI). Extended Hückel

Table VI. Nitrogen Chemical Shifts of Some Azoles

Compd	δ_N , ppm ^a	Solvent
Isoxazole	339.6 ^b	Neat
3-Mesitylisoxazole (VII)	339.5 ^b	CH ₂ Cl ₂
Isothiazole	251 ^c	Neat
2-Methyltetraazole (N1)	287 ^c	CCl ₄
2-Methylbenzo-1,2,3-triazole (N1, N3)	281 ^c	Neat
2-Methyl-1,2,3-triazole (N1, N3)	278 ^c	MeOH
Thiazole	279.4 ^d	Neat
Benzothiazole	271.0 ^e	Acetone
1-Methylpyrazole (N2)	263 ^c	CCl ₄
2-Methylbenzothiazole	268 ^c	Neat
1-Methylbenzopyrazole (N2)	260 ^c	Acetone
Benzisothiazole	212 ^c	Neat
4-Hydroxybenzothiazole	265 ^c	Acetone
6-Nitrobenzothiazole (N3)	264 ^c	Acetone
4-Methyl-1,2,4-triazole (N1, N2)	251 ^c	MeOH
2-Methylbenzopyrazole (N1)	246 ^c	Acetone
1-Methylimidazole (N3)	215 ^f	CCl ₄
Oxazole	207 ^c	CCl ₄
2,5-Diphenyloxazole	206 ^g	Et ₂ O
1-Methylbenzimidazole (N3)	201 ^c	Acetone
Benzoxazole	191 ^c	Neat

^a Downfield from tetramethylammonium chloride. ^b Present investigation. ^c Reference 38e. ^d J. P. Warren, unpublished result. ^e Reference 38a. ^f Reference 38c. ^g Reference 26.

calculations on azoles indicate that the σ charges on the "pyrrole-type" nitrogen atoms are consistently higher than those on the "pyridine-type" nitrogen atoms.³⁷ The nitrogen chemical shifts of azoles reflect the difference between these two types of nitrogen atoms;^{14,26,38} except in the case of heterocycles that have another heteroatom adjacent to nitrogen, "pyridine-like" nitrogen atoms give nitrogen chemical shifts in the region of 215–280 ppm, while "pyrrole-like" nitrogen atoms show nitrogen resonances at about 70–125 ppm. The nitrogen resonances of systems such as pyrazoles, triazoles, and tetraazoles lie at somewhat lower fields.^{38a}

Experimental Section

2,4,6-Trimethylbenzaloxime-¹⁵N (V) was obtained according to

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Beckmann's procedure³⁹ from commercial 2,4,6-trimethylbenzaldehyde and hydroxylamine-¹⁵N hydrochloride (95% ¹⁵N) and purified by recrystallization from methanol.

2,4,6-Trimethylbenzonitrile-¹⁵N oxide (Ia-¹⁵N) was prepared by hypobromite oxidation of 2,4,6-trimethylbenzaloxime-¹⁵N according to the method of Grundmann and Dean.⁴⁰ The substance was recrystallized from methanol-methylene chloride.

2,4,6-Trimethylbenzonitrile (II) was a commercial product.
 3-Mesityl- Δ^3 -isoxazoline-¹⁵N (VI). Ethylene was bubbled through a solution of 2,4,6-trimethylbenzonitrile-¹⁵N oxide in diethyl ether-methylene chloride until a small aliquot removed from the reaction mixture showed no sign of the characteristic infrared absorption of nitrile oxides at about 2300 cm⁻¹. After completion of the reaction, the solvents were evaporated and the spectra of the residue taken without purification. The identity of VI was checked by comparison of the nmr spectrum with that of the unlabeled compound which, after recrystallization from methanol, had mp 108–109° (lit.⁴¹ 109°); nmr (CCl₄) δ 6.83 (s, H-3'), 4.33 (m, H-5), 3.04 (m, H-4), 2.26 (s, 4'-CH₃), 2.19 (s, 2'-CH₃).

Anal. Calcd for C₁₅H₁₅NO: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.34; H, 8.08; N, 7.28.

3-Mesitylisoxazole-¹⁵N (VII) was obtained from 2,4,6-trimethylbenzonitrile-¹⁵N oxide and acetylene by the same procedure described for VI and was also used without purification. Its identity was checked by nmr comparison with the unlabeled compound which, after recrystallization from methanol, had mp 106–107°; nmr (CCl₄) δ 8.44 (d, $J = 1.6$ Hz, H-5), 6.87 (s, H-3'), 6.20 (d, $J = 1.6$ Hz, H-4), 2.29 (s, 4'-CH₃), 2.08 (s, 2'-CH₃).

Anal. Calcd for C₁₅H₁₃NO: C, 76.97; H, 7.00; N, 7.48. Found: C, 76.74; H, 6.97; N, 7.74.

Isoxazole was a commercial sample and was distilled before use.

The ¹³C nmr spectra of compounds Ia–d, II, and V were obtained on concentrated methylene chloride solutions, using the continuous-wave mode of operation (with noise decoupling of the protons) of the DFS-60 spectrometer described earlier.⁴² When measuring the smaller coupling constants, a sweep rate of 1 Hz/sec was used. The ¹³C nmr spectra of VI and VII were taken on dioxane solutions on the DFS-60 spectrometer equipped with a Fourier transform accessory.

The ¹⁵N nmr spectra were taken using the continuous-wave mode of operation (with proton noise decoupling) of the DFS-60 spectrometer;⁴³ methylene chloride was the solvent for Ia, VI, and VII, dimethyl sulfoxide for V, and isoxazole was run neat.

The ¹⁵N nmr spectra were referenced to external standards by means of a thin-wall, 5-mm tube containing the reference coaxially centered in a 10-mm tube containing the sample. An approximately 12 M aqueous solution of ¹⁵N-labeled tetramethylammonium chloride was used as the external reference for all the nitrogen chemical shifts except that for Ia, where an approximately 10 M aqueous ¹⁵N-labeled nitric acid solution was used. The chemical shift referenced with nitric acid was converted to the tetramethylammonium chloride chemical-shift scale by adding 330.64 ppm. All downfield nitrogen chemical shifts have been taken to be positive. Becker has proposed the use of tetramethylammonium iodide as a primary chemical-shift standard for nitrogen chemical shifts;⁴⁴ we find this salt to be too insoluble to be used routinely as a chemical-shift reference for directly observed continuous-wave ¹⁵N nmr spectra, and for this reason we prefer to use the more soluble tetramethylammonium chloride. We have determined the nitrogen chemical shift of our nitric acid reference sample to be +331.7 ppm with respect to a saturated aqueous solution (≈ 0.3 M) of ¹⁵N-labeled tetramethylammonium iodide. Thus, the 12 M aqueous tetramethylammonium chloride solution gives a nitrogen resonance 1.1 ppm downfield from that of a 0.3 M aqueous tetramethylammonium iodide solution.

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