

Nitrogen Nuclear Magnetic Resonance Spectroscopy. Part 7.¹ Extension of the Nuclear Magnetic Resonance-Ultraviolet Correlation in Nitroso-compounds to cover Two-co-ordinate Nitrogen in the Other Groupings with Oxygen and Carbon, and Comparison with Three-co-ordinate Nitrogen in Planar Groupings (Azoxy, etc.)

By Joan Mason,* The Open University, Milton Keynes MK7 6AA
William van Bronswijk and Jeremy G. Vinter, William Ramsay and Ralph Forster Laboratories, University College, London W.C.1

The δ - λ correlation [of the ¹⁴N chemical shift δ with the reciprocal energy of the ($n \rightarrow \pi^*$) long wavelength electronic absorption] previously demonstrated for nitroso-compounds (etc.) X-N=O (where X is alkyl, aryl, N, O, halogen, sulphur) is now extended to cover two co-ordinate nitrogen in $\overset{+}{N}-\overset{-}{N}-NO_2$, C=N-O, -N=N-O, -N=N-F, C=N-N=C, C=N-O, O-N=N-O, and C-N=N-C groupings. For the related planar groups with three-co-ordinate nitrogen the δ - λ correlation is less good but still evident, even though the long wavelength transitions are not magnetically active; perhaps their energies vary in parallel with those of the relevant excitations (e.g. $\sigma \rightarrow \pi^*$). Perfluorination of alkyl or aryl groups attached to unsaturated nitrogen shifts the resonance upfield by ca. 20 p.p.m. (or rather more, at very low field).

We report ¹⁴N chemical shifts for planar groupings of nitrogen with oxygen and carbon. In a study² of nitroso and nitrosyl compounds XN=O we found that the ¹⁴N chemical shift, corrected for variation in the local (atom + ligand) diamagnetic term σ_d^{AL} , was roughly proportional to the wavelength λ of the low lying $n \rightarrow \pi^*$ band, since λ represents the reciprocal of the energy ΔE of an excitation which plays a major part in the paramagnetic shielding in this group. Table 1 and Figure 1 show that this δ - λ correlation can be extended to cover two-co-ordinate nitrogen in azoxy, oxime, nitrazine (Me₃NNNO₂), and aldazine groupings, and in

related compounds which include isoxazole,³ furazans,⁴ azo-compounds,⁵ hyponitrites,⁵ etc. Since nitrogen of the same ligancy is being compared, and the ligands are confined to second row elements, the variation in σ_d^{AL} is not more than 20 p.p.m. and so the diamagnetic correction⁶ has not been applied.

The chemical shifts given in the Tables for nitrogen in CF₃N(O)=NF were estimated from the frequencies required⁷ to decouple ¹⁴N from ¹⁹F, together with McFarlane's ¹⁴N frequency for MeNC in the magnetic field at which tetramethylsilane protons resonate at 100 MHz,⁸ and the known chemical shift of MeNC.⁹ The

⁵ Part 4, J. Mason and W. v. Bronswijk, *J. Chem. Soc. (A)*, 1971, 791.

⁶ Part 3, R. Grinter and J. Mason, *J. Chem. Soc. (A)*, 1970, 2196.

⁷ J. W. Frazer, B. E. Holder, and E. F. Worden, *J. Inorg. Nuclear Chem.*, 1962, **24**, 45.

⁸ W. McFarlane, *J. Chem. Soc. (A)*, 1967, 1660.

⁹ W. B. Moniz and C. F. Poranski, *J. Phys. Chem.*, 1969, **73**, 4145.

¹ (a) Part 6, J. Mason, *J.C.S. Faraday II*, 1976, 2064.

(b) Part 5, J. Mason and J. G. Vinter, *J.C.S. Dalton*, 1975, 2522.

² Part 1, L.-O. Andersson, J. Mason, and W. v. Bronswijk, *J. Chem. Soc. (A)*, 1970, 296.

³ M. Christl, J. P. Warren, B. L. Hawkins, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1973, **95**, 4392.

⁴ G. Englert, *Ber. Bunsengesellschaft Phys. Chem.*, 1961, **65**, 854.

TABLE 1

¹⁴N Shifts of two-co-ordinate nitrogen relative to saturated aqueous NH₄⁺ (positive downfield), compared with the reciprocal energy of the long wavelength (*n* → π*) band. Unless a solvent is given, the n.m.r. measurements refer to the neat liquid and the u.v. measurements to the gas

Compound	δ(NH ₄ ⁺) (p.p.m.)	<i>w</i> /Hz ^a	<i>tw</i> /Hz ^b	<i>S</i> / <i>N</i>	Ref. (n.m.r.)	ε _{max.} /l mol ⁻¹ cm ⁻¹	λ _{max.} /nm	Ref. (u.v.)
Me ₃ NNO ₂ (H ₂ O)	242(2) ^c		116					
CF ₃ N(O)=NF	300				7 (see text)	7.3	277	7
<i>trans</i> -Ph ¹⁵ N(O)= ¹⁵ NPh (ether)	304				11			
Me ₂ C=NOH (ether)	316(5)	930		15 : 1		5 012	190 (EtOH)	<i>d</i>
MeCH=NOH (CD ₂ Cl ₂)	323(6)	1 200		8 : 1			< 220	<i>d</i>
Ph ₂ C=NOH (ether)	327(17)	900		1 : 1			252 (MeOH)	<i>d</i>
MeCH=N-N=CHMe	338					inflection	295 (C ₆ H ₁₂)	<i>e</i>
PhCH=NOH (acetone)	347	1 000		2 : 1				
Isoxazole (¹⁵ N)	358				3	4 000	211	<i>f</i>
2,3-Dimethylfuran	379(5)		490		4	2 950	211 (C ₇ H ₁₀)	<i>g</i>
Benzofurazan (CH ₂ Cl ₂)	381(5)		460		4	3 400	268 (EtOH)	<i>h</i>
EtONO	550	300				100	356	
CF ₃ CICF ₂ CINO	788	138		> 100 : 1		25	685	
C ₆ F ₅ NO (ether)	867(3)	510		3 : 1				
<i>p</i> -(CO ₂ CMe ₂ CMe ₂ NO) ₂ C ₆ H ₄ (ether)	923	850		2 : 1			ca. 670	
PhCO ₂ CMe ₂ CMe ₂ NO (ether)	928	780		5 : 1			ca. 670	
Me ₃ CNO	938			12 : 1		20	665	<i>i</i>

^a Peak-peak width (±5—10%) of the derivative line, with modulation at 20—40 Hz. ^b Full line-width (±5—10%) at half-height measured by the side-band method, with modulation at 500 Hz. ^c The numbers in parentheses give uncertainties in units of the last digit. ^d 'Atlas of Spectral Data and Physical Constants for Organic Compounds,' ed. J. G. Grasselli, C.R.C. Press, Ohio, 1973. ^e P. Grammaticakis, *Bull. Soc. chim. France*, 1948, **15**, 987. ^f D. S. Noyce, E. Ryder, and B. H. Walker, *J. Org. Chem.*, 1955, **20**, 1681. ^g E. S. Stern and C. J. Timmons, 'Electronic Absorption Spectroscopy in Organic Chemistry,' Edward Arnold, London, 1970, p. 165. ^h D. Dal Monte and E. Sandri, *Boll. sci. Fac. Chim. ind. Bologna*, 1964, **22**, 33. ⁱ E. C. C. Baly and C. H. Desch, *J. Chem. Soc.*, 1908, **93**, 1747.

TABLE 2

¹⁴N Shifts of three-co-ordinate nitrogen relative to saturated aqueous NH₄⁺ (positive downfield), compared with the reciprocal energy of the long wavelength electronic absorption. Unless a solvent is given, the n.m.r. measurements refer to the neat liquid and the u.v. measurements to the gas

Compound	δ(NH ₄ ⁺) (p.p.m.)	<i>w</i> /Hz ^a	<i>tw</i> /Hz ^b	<i>S</i> / <i>N</i>	Ref. (n.m.r.)	ε _{max.} /l mol ⁻¹ cm ⁻¹	λ _{max.} /nm	Ref. (u.v.)
CF ₃ N(O)=NF	235				7	4 500	212.5	7
MeCH=N(O)C ₆ H ₁₁ (acetone)	247					9 500	232 (MeOH)	30
<i>trans</i> -C ₆ H ₁₁ N(O)=N(O)C ₆ H ₁₁ [(CH ₂ OMe) ₂]	287	174		4 : 1		6 700	294 (C ₆ H ₁₂)	<i>d</i>
<i>trans</i> -PhN(O)=NPh (ether)	297	138		50 : 1		5 000	282 (EtOH)	<i>e</i>
							<i>etc.</i>	
<i>trans</i> -Ph ¹⁵ N(O)= ¹⁵ NPh (ether)	300				11			
C ₆ (NO) ₆ (CH ₂ Cl ₂)	314.5		8		23			
C ₆ N ₆ O ₆ (acetone)	328(2)	600		30 : 1		7 600 (inflection)	293 (CHCl ₃)	<i>f</i>
Furazan <i>N</i> -oxide	330(5)		490		4	7 775	258 (EtOH)	<i>g</i>
Benzofurazan <i>N</i> -oxide (CH ₂ Cl ₂)	332(5)		460		4	7 300	355 (CHCl ₃)	<i>f</i>
N ₂ O ₄	340				25	175	340	<i>h</i>
Me ₃ NNNO ₂ (H ₂ O)	343(2)		14					
-O ₂ N=NO-(0.1M-NaOH)	368		2 040			8 300	248 (H ₂ O)	12
(0.5M-NaOH)	310		1 100		<i>i</i>			

^{a-c} As Table 1. ^d B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 1956, 1670. ^e H. H. Jaffé and M. Orchin, 'Theory and Applications of Ultraviolet Spectroscopy,' Wiley, New York, 1962, pp. 282 and 432 (assignments p. 284). ^f A. S. Bailey and J. R. Case, *Tetrahedron*, 1958, **3**, 113. ^g J. H. Boyer and V. Toggweiler, *J. Amer. Chem. Soc.*, 1957, **79**, 895. ^h T. C. Hall and F. E. Blacet, *J. Chem. Phys.*, 1952, **20**, 1745. ⁱ N. Logan and W. L. Jolly, unpublished results.

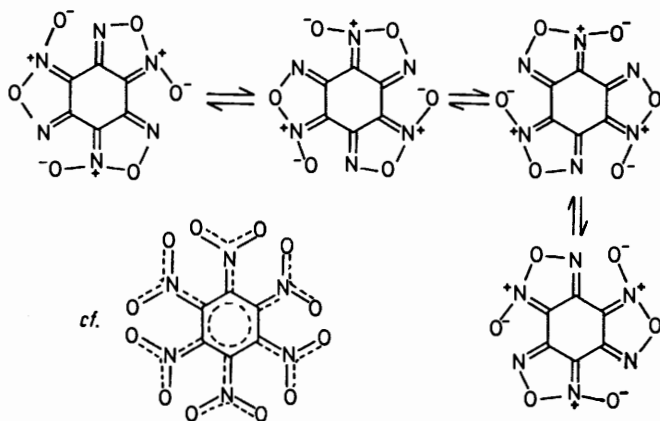
upfield shift for CF₃N(O)=NF, compared with *cis*- or *trans*-FN=NF,⁵ provides evidence for the overlap and splitting of the two nitrogen lone-pair orbitals in azo-compounds, which lowers the *n* → π* energy, as

discussed in Part 4;⁵ the radius term ⟨*r*⁻³⟩ and constitutive term (Σ*Q*) are likely to be similar in FN=NF and in CF₃N(O)=NF.

The close similarity of the chemical shifts of benzo- and

nitroso-dimer, favouring the mainly N=N doubly bonded structure.

'Hexanitrosobenzene' $C_6N_6O_6$ is known to have a tris-furazan *N*-oxide structure (C_{3h}) from the evidence of *X*-ray diffraction¹⁸ and *X*-ray photoelectron spectroscopy,¹⁹ and of vibrational spectroscopy.^{20,21} Only a single ^{14}N resonance was observed, and the shift value agrees with those found by Englert⁴ for benzo- and dimethyl-furazan *N*-oxide (Table 2). This single resonance is explained by oxygen switching between the nitrogens at a rate that is fast on the n.m.r. timescale^{4,22} (*cf.* also the closeness of the resonances of 'hexanitroso'- and hexanitro-benzene²³). Localised furazan *N*-oxide structures have now been observed at 'lower' temperatures (depending on the n.m.r. timescale for the various nuclei) in 1H ,^{4,22} ^{17}O ,^{22b,24} and ^{13}C resonances,⁴ and averaged structures at the appropriate 'higher' temperatures in proton^{4,22} and ^{17}O resonance^{22b} as well as for ^{14}N .



The resonances for three-co-ordinate (planar) nitrogen tend to be upfield of those for the two-co-ordinate nitrogen, and this must be due to a larger energy term ΔE , since the radius term $\langle r^{-3} \rangle$ is increased by co-ordination of an electronegative atom, and the constitutive term ΣQ (as discussed earlier)^{2,25,26} increases also, *e.g.* from *ca.* 2.44 for azo-nitrogen (as for ethylenic carbon) to *ca.* 2.6 for azoxy-nitrogen (as for RNO_2). An increase of say 10% in the paramagnetic term in this range amounts to *ca.* 50 p.p.m., and such increase must be outweighed by increase in ΔE . Figure 2 shows however that the long wavelength absorption has not undergone a blue shift compared with those in Figure 1, although interestingly the slopes of the lines in the two Figures are much the same. Since there is no $n_N \rightarrow \pi^*$ absorption for the three-co-ordinate nitrogen, the choice of relevant (magnetically active) excitation is difficult. Some of the compounds show weak $n_O \rightarrow \pi^*$ absorption, *e.g.* the

¹⁸ H. H. Cady, A. C. Larson, and D. T. Cromer, *Acta Cryst.*, 1966, **20**, 336.

¹⁹ J. Bus, *Rec. Trav. chim.*, 1972, **91**, 552.

²⁰ A. S. Bailey and J. R. Case, *Tetrahedron*, 1958, **3**, 113.

²¹ N. Bacon, A. J. Boulton, and A. R. Katritzky, *Trans. Faraday Soc.*, 1966, **63**, 833.

²² (a) G. Englert, *Z. Naturforsch.*, 1961, **16b**, 413; (b) P. Diehl, H. A. Christ, and F. B. Mallory, *Helv. Chim. Acta*, 1962, **45**, 504.

²³ M. Y. Mägi, *Eesti NSV Tead. Akad. Toim., Keem.-Geol.*, 1971, **20**, 364.

nitroalkanes at 275 nm. This circulation deshields nitrogen as well as oxygen since they share the π^* orbital and there is some mixing of n_O and σ electrons, but the $\sigma \rightarrow \pi^*$ circulations around nitrogen deshield it more closely. In comparing the ^{14}N shifts in XNO_2 compounds for a variety of X substituents (halogen, O, N, alkyl *etc.*) we found²⁵ that the lines tended to move upfield with increase in electronegativity of X (against the effect of the radius and constitutive terms) which implicates $\sigma \rightarrow \pi^*$ rather than $\pi \rightarrow \sigma^*$ excitations, since the inductive effect stabilises the bonding and raises the anti-bonding orbitals. (The $\pi \rightarrow \sigma^*$ energy decreases with increase in the conjugative effect of X and this order is not followed.)²⁵

The long wavelength absorption observed for most of the groups in Table 2 is relatively intense and probably represents $\pi \rightarrow \pi^*$ excitations which are not magnetically active since there is no rotation of charge. $\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ transitions are magnetic dipole allowed but electric dipole forbidden, and so are difficult to locate in electronic spectra. Evidence from magnetic circular dichroism studies of the nitroalkanes suggests that there is a $\sigma \rightarrow \pi^*$ transition at 310 nm with zero intensity,²⁷ and it is likely that other magnetically active $\sigma \leftrightarrow \pi$ (and $\sigma_x \rightarrow \sigma_y^*$) excitations at shorter wavelengths are hidden by stronger bands. Thus the δ - λ correlation that is evident in Figure 2 may arise because the long wavelength absorptions that we can see, although they represent the wrong excitations, vary among our compounds in roughly the same fashion as the right ones do.

Tables 1 and 2 contain information on the effect of perfluorination of alkyl or aryl groups on nitrogen shifts. The C_6F_5NO line is 23 p.p.m. upfield of that for $PhNO$,²⁸ just as the $C_6F_5NO_2$ line is 22 p.p.m. upfield of that for $PhNO_2$.²⁹ This follows the pattern of the alkyl azo-⁵ and nitro-compounds,²⁵ together with $CF_3N(O)=NF$, that perfluorination of an organic group shifts the resonance of attached nitrogen upfield by *ca.* 20 p.p.m. [Here again the ΔE term outweighs the effect of the $\langle r^{-3} \rangle$ and Q_{AA} (charge density) terms.] At low fields however the resonances tend to spread out, and whereas the CF_3NO_2 and Me_3CNO_2 lines are separated by 53 p.p.m., the CF_3NO and Me_3CNO lines are separated by three times as much, and the CH_3NO resonance is perhaps in the $\delta(850-900)$ region.

EXPERIMENTAL

The ^{14}N measurements were made as described previously.^{1b} Sodium nitrohydroxamate was made by an

²⁴ H. A. Christ, P. Diehl, H. R. Schneider, and H. Dahn, *Helv. Chim. Acta*, 1961, **44**, 865.

²⁵ Part 2, J. Mason and W. v. Bronswijk, *J. Chem. Soc. (A)*, 1970, 1763.

²⁶ J. Mason, *J. Chem. Soc. (A)*, 1971, 1038.

²⁷ G. Barth, N. Waespe-Sercevic, R. E. Linder, E. Bunnenberg, C. Djerassi, L. Seamans, and A. Moscowitz, *J.C.S. Chem. Comm.*, 1975, 672.

²⁸ J. B. Lambert and J. D. Roberts, *J. Amer. Chem. Soc.*, 1965, **87**, 4087.

²⁹ E. F. Mooney, M. A. Qaseem, and P. H. Winson, *J. Chem. Soc. (B)*, 1968, 224.

adaptation of Angeli's method,¹² measured in alkaline solution with exclusion of oxygen, and shown to be pure by the u.v. spectrum.¹² The free acid was too unstable to be measured. Acetaldehyde azine was made from acetaldehyde and hydrazine, and the nitrone, *N*-ethylidenecyclohexylamine *N*-oxide, from acetaldehyde and *N*-cyclohexylhydroxylamine.³⁰ The remaining compounds were bought, or made by well known methods, or given to us.

We thank Dr. Epstajn for Me₃NNNO₂, Dr. R. K. Harris for CF₂ClCFCINO, Dr. T. R. Sharpe for the nitroso-esters

ArCOOCMe₂CMe₂NO, Professors B. G. Gowenlock and A. G. Davies for Me₃CNO, and Professor Th. J. de Boer for the cyclohexyl nitroso-dimer.³¹ We also thank J. Cobb for measuring C₈F₅NO and 'hexanitrosobenzene', Dr. N. Logan for preliminary measurements on Me₃NNNO₂, and S.R.C. for support while this work was being done.

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³⁰ M. Yamakawa, T. Kubota, and H. Akazawa, *Theor. Chim. Acta*, 1969, **15**, 244.

³¹ A. Mackor, Th. A. J. Wajer, and Th. J. de Boer, *Tetrahedron Letters*, 1967, 2757.