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-coordinate Nitrogen in Planar Groupings (Azoxy, etc.)

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The $\delta - \lambda$ 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 $N-N-NO_2$, 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 $\delta - \lambda$ 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. $\sigma \rightarrow \pi^{\circ}$). 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 $n \longrightarrow$ π^* 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 $\delta - \lambda$ correlation can be extended to cover two-co-ordinate nitrogen in azoxy, oxime, nitrazine (Me₂NNNO₂), 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 correction ⁶ has not been applied.

The chemical shifts given in the Tables for nitrogen in $CF_3N(O)=NF$ were estimated from the frequencies required 7 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

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

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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.
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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 C. Fardert Par. Burgeneritscheft, D. L. Chem. 2010, 2010.

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

TABLE 1

¹⁴N Shifts of two-co-ordinate nitrogen relative to saturated aqueous NH_4^+ (positive downfield), compared with the reciprocal energy of the long wavelength ($n \rightarrow \pi^*$) band. Unless a solvent is given, the n.m.r. measurements refer to the neat liquid and the u.v. measurements to the gas

	δ(NH4+)	<i>i</i>			Ref.			Ref.
Compound	(p.p.m.)	w/Hz ª	tw/Hz °	S/N	(n.m.r.)	$\varepsilon_{max}/l mol^{-1} cm^{-1}$	λ _{max.} /nm	(u.v.)
$Me_{3}NNNO_{2}(H_{2}O)$	242(2) °		116					•
$CF_3N(O)=NF$	300				7	7.3	277	7
					(see text)			
$trans-Ph^{15}N(O)=^{15}NPh$ (ether)	304				11			
Me ₂ C=NOH (ether)	316(5)	930		15:1		$5\ 012$	190	d
							(EtOH)	
MeCH=NOH (CD_2Cl_2)	323(6)	1 200		8:1			$<\!220$	d
Ph ₂ C=NOH (ether)	327(17)	900		1:1			252	d
							(MeOH)	
MeCH=N-N=CHMe	338					inflection	295	е
	o / -						(C ₆ H ₁₂)	
PhCH=NOH (acetone)	347	1 000		2:1	0	4 000		,
Isoxazole (¹ ^o N)	358		400		3	4 000	211	Ĵ
2,3-Dimethylfurazan	379(5)		490		4	2 950		g
	007/5		4.00			9 400	(U_7H_{16})	,
Benzoturazan (CH_2CI_2)	381(5)		460		4	3 400	268	n
TIONO		000				100	(EtOH)	
ETUNU AD AIAD AINA	550	300		100.1		100	300	
CF_CICF_CINO	788	138		>100:1		25	080	
$C_{6}F_{5}NO$ (etner)	867(3)	510		3:1				
p-(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		0:1 10:1		00	ca. 070	
MegUNU	938			12:1		20	000	ı

Peak-peak width (±5-10%) of the derivative line, with modulation at 20-40 Hz.
Full line-width (±5-10%) at half-height measured by the side-band method, with modulation at 500 Hz.
The numbers in parentheses give uncertainties in units of the last digit.
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E. S. Stern and C. J. Timmons, 'Electronic Absorption Spectroscopy in Organic Chemistry,' Edward Arnold, London, 1970, p. 165.
D. Dal Monte and E. Sandri, Boll. sci. Fac. Chim. ind. Bologna, 1964, 22, 33.
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 NH_4^+ (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

	δ(NH₄+)				Ref.			
Compound	(p.p.m.)	w/Hz ª	tw/Hz ^b	S N	(n.m.r.)	ε _{max.} /l mol⁻¹ cm⁻¹	λ_{max}/nm	(u.v.)
$CF_N(O) = NF$	235				7	4 500	212.5	7
$MeCH = \dot{N}(O)C_{6}H_{11}$ (acetone)	247					9 500	232	30
							(MeOH)	
$trans-C_{6}H_{11}N(O)=N(O)C_{6}H_{11}$	287	174		4:1		6 700	294	d
[(CH ₂ OMe) ₂]				FO 1		F 000	$(C_{6}H_{12})$	
trans-PhN(O)=NPh (ether)	297	138		50:1		5 000	282	e
						atc	(EUH)	
trana Dh15 N(O)-15 NDh (othor)	200				11	<i>ciu</i> .		
C(NO) (CH C1)	314 5		8		23			
$C_{6}(1, O_{2})_{6}$ (C11 ₂ C1 ₂) $C_{1}N_{1}O_{2}$ (acetone)	328(2)		600	30:1	20	7 600	293	f
Certe Ce (acctone)	020(2)					(inflection)	(CHCl ₃)	,
Furazan N-oxide	330(5)		490		4	`7775 ´	`258 ´´	g
							(EtOH)	
Benzofurazan N-oxide (CH ₂ Cl ₂)	332(5)		460		4	7 300	355	f
	• ·						(CHCl ₃)	·.
N ₂ O ₄	340				25	175	340	h
$Me_{3}NNNO_{3}(H_{2}O)$	343(2)		14			0.000	940	10
-O ₂ N=NO-(0.1м-NaOH)	368		2040			8 300	248 (H_O)	12
(0 5 N-OII)	910		1 100		i		$(\Pi_2 O)$	
(U.OM-NAUH)	310		1 1 1 1 1		τ			

^{a-c} As Table 1. ⁴ 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. ^e 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. ^c N. Logan and W. L. Jolly, unpublished results.

upfield shift for $CF_3N(O)=NF$, 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 $n \rightarrow \pi^*$ energy, as

discussed in Part 4; ⁵ the radius term $\langle r^{-3} \rangle$ and constitutive term (ΣQ) are likely to be similar in FN=NF and in CF₃N(O)=NF.

The close similarity of the chemical shifts of benzo- and

dimethyl-furazan accords with the results of a microwave study ¹⁰ which supports double-bond fixation in benzofurazan. Thus the longer wavelength absorption in the



FIGURE 1 Correlation of the 14N chemical shift of two-coordinate nitrogen in various groups with λ_{max} of the *n* band. The data for Me₂NNO are in ref. 2 and for the azo and hyponitrite compounds in ref. 5

u.v. spectrum of benzofurazan is probably not relevant to the magnetically active excitations around nitrogen, and Figure 1 has been restricted to non-aromatic compounds to avoid this problem.

In Figure 1 the lines move to higher field (lower δ) and the absorption to shorter wavelengths, in the order XN=O > XN=NX > XN=CX₂, as the decreasing electronegativity of the atom doubly bonded to nitrogen raises the π^* orbital relative to the n_N orbital: and there are



FIGURE 2 Correlation of the 14N chemical shift for three-coordinate nitrogen in planar groups with λ_{max} , of the long wavelength band thought to be associated with the group. The data for the nitro-compounds are in ref. 25

conjugative effects acting in the same sense when the atoms attached to nitrogen have lone pair electrons.

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¹² C. C. Addison, G. A. Gamlen, and R. Thompson, J. Chem. Soc., 1952, 338. ¹³ R. D. Feltham, Inorg. Chem., 1964, **3**, 900.

Thus the ΔE term overcomes the effect of the radius term, for the constitutive terms are much the same.

Table 2 and Figure 2 contain corresponding information for three-co-ordinate nitrogen in azoxy (1), nitrone (2), nitroso dimer (3), and furazan N-oxide (4) groupings, and in nitrohydroxamate ion (5), with nitramine and nitrocompounds for comparison. Again the shift between aliphatic and aromatic compounds is small for the same chromophore. Figure 2 shows that there is some $\delta - \lambda$ correlation (and this is improved by the diamagnetic correction,⁶ which brings the nitro-group lines upfield by ca. 25 p.p.m. relative to azoxy- or N-oxy-resonances). However there are complications both with the chemical shift and with the choice of relevant absorption for many of the compounds listed in Table 2. As to the azoxycompounds, two resonance frequencies for the two kinds of nitrogen have been observed for CF₃N(O)=NF in ¹⁴N resonance ⁷ and for azoxybenzene in ¹⁵N resonance,¹¹



but the long wavelength $n \longrightarrow \pi^*$ band in azoxybenzene is hidden by stronger bands.

For Angeli's salt Na2N2O3, formerly (and contradictorily) called an oxyhyponitrite, an asymmetric nitrohydroxamate structure $(O_2NNO)^{2-}$ has been demonstrated by spectroscopy,^{12,13} by calorimetry,¹⁴ by asymmetric labelling and decomposition,^{15a} by X-ray photoelectron spectroscopy,¹⁵⁶ and by X-ray diffraction.¹⁶ Some authors have favoured a structure with an NN double bond,¹² some an NN single bond.^{15a, b} The i.r. stretching frequencies 13 compared with those of azoxymethane¹⁷ suggest some contribution from N-N singly bonded structures. The bond lengths and angles ¹⁶ correspond most closely to the N=N doubly bonded structure, but suggest that the others are also significant. Only one



broad n.m.r. line is observed (Table 2); the lineshape suggests the presence of two unresolved lines, and the position is between those of hyponitrite ion and the

¹⁷ B. W. Langley, B. Lythgoe, and L. S. Rayner, J. Chem. Soc., 1952, 4191.

¹⁴ H. R. Hunt, J. R. Cox, and J. D. Ray, Inorg. Chem., 1962,

^{1, 938.} ¹⁶ (a) D. N. Hendricksen and W. L. Jolly, *Inorg. Chem.*, 1969, 8, 693; (b) D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, ibid., p. 2642. ¹⁶ H. Hope and M. R. Sequeira, *Inorg. Chem.*, 1973, **12**, 286.

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 diffraction 18 and X-ray photoelectron spectroscopy,¹⁹ and of vibrational spectroscopy.^{20,21} Only a single ¹⁴N 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} ¹⁷O,^{22b,24} and ¹³C resonances,⁴ and averaged structures at the appropriate ' higher ' temperatures in proton ^{4,22} and ¹⁷O resonance ^{22b} as well as for ¹⁴N.



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 RNO₂). 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 $n_N \longrightarrow \pi^*$ absorption for the three-co-ordinate nitrogen, the choice of relevant (magnetically active) excitation is difficult. Some of the compounds show weak $n_0 \rightarrow \pi^*$ absorption, e.g. the 18 H. H. Cady, A. C. Larson, and D. T. Cromer, Acta Cryst.,

1966, 20, 336.

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 ²⁰ A. S. Bailey and J. R. Case, Tetrahedron, 1958, 8, 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_0 and σ electrons, but the $\sigma \longrightarrow \pi^*$ circulations around nitrogen deshield it more closely. In comparing the ¹⁴N shifts in XNO₂ compounds for a variety of X substituents (halogen, O, N, alkyl etc.) we found 25 that the lines tended to move upfield with increase in electronegativity of X (against the effect of the radius and constitutive terms) which implicates $\sigma \longrightarrow \pi^*$ rather than $\pi \longrightarrow \sigma^*$ excitations, since the inductive effect stabilises the bonding and raises the anti-bonding orbitals. (The $\pi \longrightarrow \sigma^*$ 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 $\pi \longrightarrow \pi^*$ excitations which are not magnetically active since there is no rotation of charge. $\pi \rightarrow$ σ^* and $\sigma \longrightarrow \pi^*$ 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 $\sigma \longrightarrow \pi^*$ transition at 310 nm with zero intensity,²⁷ and it is likely that other magnetically active $\sigma \leftrightarrow \pi$ (and $\sigma_x \longrightarrow \sigma_y^*$) excitations at shorter wavelengths are hidden by stronger bands. Thus the $\delta - \lambda$ 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 C₆F₅NO line is 23 p.p.m. upfield of that for PhNO,²⁸ just as the C₆F₅NO₂ line is 22 p.p.m. upfield of that for PhNO₂.²⁹ This follows the pattern of the alkyl azo- ⁵ and nitro-compounds,²⁵ together with CF₃N(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 CF₃NO₂ and Me₃CNO₂ lines are separated by 53 p.p.m., the CF₃NO and Me₃CNO lines are separated by three times as much, and the CH₃NO resonance is perhaps in the $\delta(850-900)$ region.

EXPERIMENTAL

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

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 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.

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87, 4087. ²⁹ E. F. Mooney, M. A. Qaseem, and P. H. Winson, J. Chem.

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.

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