Perfluoro Effects in ^{15}N Nuclear Magnetic Resonance Spectroscopy. Part 1. Aryl and *N*-Heteroaryl Azides

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^{15}N N.m.r. spectroscopic results are reported for a range of covalent azides $RN_\alpha N_\beta N_\gamma$ (where R is perfluoroaryl, perfluoro- or chlorofluoro-pyridyl or -pyrimidinyl, or trimethylsilyl), and compared with literature values for related azides. The N_α and N_γ chemical shifts vary over a range of 80—100 p.p.m., and correlate with weak long-wavelength bands in the electronic spectrum that arise from magnetically active transitions ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi'^*$), the $N_{\alpha,\gamma}$ lines moving downfield as the bands move to lower energies. The N_β chemical shift, however, varies rather little from its value in the azide anion. The $N_{\alpha,\gamma}$ chemical shifts are sensitive to the known inductive and conjugative influences of the R group. Perfluorination increases the shielding, by increasing the energy of the paramagnetic circulation; the perfluoro-effect diminishing with distance from the fluoro-substituent, and with the extent to which $n \rightarrow \pi^*$ circulations are important in the deshielding. Thus the patterns of chemical shifts are explained by the relationships of the frontier orbitals for rotation of charge in the magnetic field.

VARIOUS covalent azides (though none containing fluorine) have been studied by ^{14}N n.m.r. spectroscopy, but the quadrupolar broadening prevented the observation of spin–spin coupling constants, and precise determination of the chemical shifts.[1] The assignment of the β- and γ-nitrogen lines (in $RN_\alpha N_\beta N_\gamma$), which are often quite close together, was therefore insecure. Recently, however, Mueller has published ^{15}N chemical shifts and coupling constants for a variety of ^{15}N-enriched compounds in which the azido-function is attached to H or Cl,[2a] carbon,[2b] phosphorus,[2c] arsenic,[2d] *etc.* The coupling patterns allow the resonances to be assigned, and the nitrogen shielding commonly decreases in the sequence $N_\alpha > N_\gamma > N_\beta$, as was previously thought.[1] A crossover of the N_β and N_γ lines is observed, however, in several compounds in which the azido function is attached to an electronegative group [*e.g.* Cl,[2a] CN,[2b] 2,4,6-$(NO_2)_3C_6H_2$,[2b] 4-$MeC_6H_4SO_2$,[3] and PhCO [4]] and this prompted us to study a number of perhalogenated (fluoro or chlorofluoro) aryl and *N*-heteroaryl azides made available through work on these compounds as nitrene precursors,[5-7] the objective being to interpret the changes in the shielding of each of the three azide nitrogens in the light of changes in the electronic characteristics of the organic group R (in RN_3).

Our measurements are given in the Table with some literature values for comparison, and Figure 1 is a correlation diagram of the chemical shifts. Interestingly, the shielding of the γ-nitrogen is the most sensitive to the changes in the R group. The N_γ shift varies over a range of 100 p.p.m., compared with 80 for N_α and only 30 for N_β; indeed, the shielding of the central nitrogen varies rather little from its value in the azide anion.[2c] The most striking feature of Figure 1 is the tendency of the α and γ lines to move upfield or downfield together with changes in the R group.

The chemical shifts depend on virtual excitations in the magnetic field that involve a circulation of charge close to nitrogen.[8] The circulations are $a' \leftrightarrow a''$ in HN_3, and may be $\sigma \leftrightarrow \pi$ (which includes $n \longrightarrow \pi^*$, since the lone pair orbitals on nitrogen are part of the σ framework) or else $\pi \leftrightarrow \pi'$, where π′ describes an in-plane (a') π orbital. The deshielding is the greater the lower the energy ΔE of the excitation, the greater the imbalance of charge in the valence shell (which varies relatively little for a given group), and the closer the circulation is to nitrogen, as expressed by the radial factor $\langle r^{-3}\rangle_{2p}$.[8]

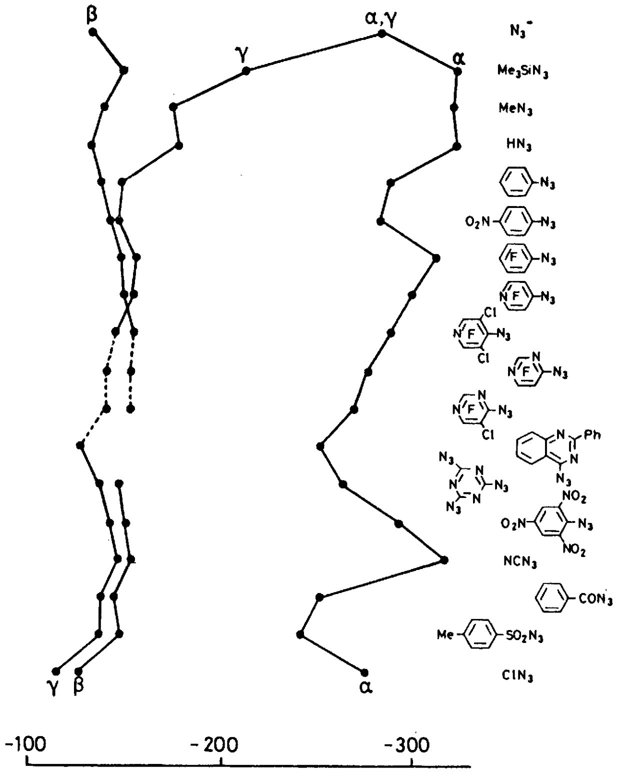
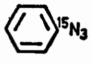
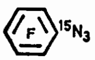
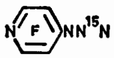
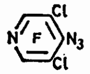
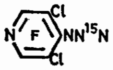
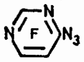
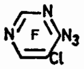
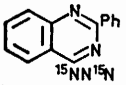
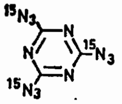
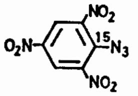
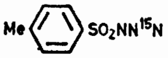


FIGURE 1 Correlation of the N_α, N_β, and N_γ chemical shifts in azides $RN_\alpha N_\beta N_\gamma$

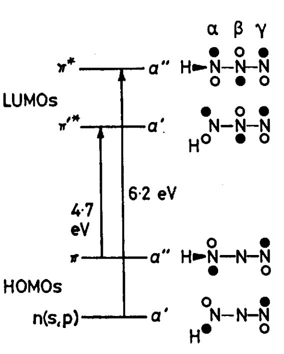
Figure 2 shows the two HOMOs (highest occupied

^{15}N Chemical shifts and coupling constants of azides

Azide	Solvent	δ (p.p.m.)[a]					$^1J_{NN}$/Hz[b]		$^2J_{NF}$/Hz[b]	Ref.
		N$_\alpha$	N$_\beta$	N$_\gamma$	N-1	N-2	αβ	βγ		
$^{15}N_3^-$	D_2O	−281.4	−130.9	−281.4			11.3			2*c*
Me_3SiN_3	$CDCl_3$	−324.3	−149.7	−213.0						
$CH_3{}^{15}N_3$	C_6D_6	−321.7	−130.2	−171.5			14.4	8.2		2*b*
$H_3{}^{15}N_3$	Et_2O	−324.5	−134.1	−178.6			13.95	7.2		2*a*
	$(CD_3)_2CO$	−288.5	−136.7	−147.4			13.4	7.8		2*b*
	$(CD_3)_2SO$	−282.0	−140.0	−144.1			13.8	7.4		2*b*
	$CDCl_3$	−307.6	−145.4	−150.3						
	$CDCl_3$	−308.2	−145.4	−150.3						
	$CDCl_3$	−307.0	−144.7	−149.8			14.3 (0.3)	7.3 (0.2)		
	$CDCl_3$	−296.2	−144.4	−147.9	−147.8				50	
	$CDCl_3$			−147.9	−147.8			8.8 (1)		
	$CDCl_3$	−285.1	−150.3	−142.1	−146.4				52(2)	
	$CDCl_3$			−142.6						
	$CDCl_3$	−272.9	−136.9 [c]	−148.8 [c]	−158.9	−149.9			50.6 59.5	
	$CDCl_3$	−266.2	−135.6 [c]	−148.5 [c]	−161.1	−152.7			52.1 (1.5) 53.6	
	CF_3COOH $(CD_3)_2CO$	−250.8		−128.8						27
	CD_2Cl_2	−261.1	−145.6	−134.8			16.1	6.1		2*b*
	$(CD_3)_2SO$	−289.3	−151.1	−142.7			14.0	6.3		2*b*
$N{\equiv}C{-}^{15}N_3$	CD_3CN (−20 °C)	−315.3	−149.7	−147.5			16.0	6.0		2*b*
$PhCO^{15}N_3$	Et_2O (−30 °C)	−251.2	−141.8	−136.9						4
	$(CH_3)_2SO$	−240.4	−148.2	−138.3						3
$Cl^{15}N_3$	CD_2Cl_2	−273.1	−123.7	−114.1			24.0	7.8		2*a*

[a] Chemical shifts (downfield positive) relative to liquid CD_3NO_2. [b] Uncertainty 3 Hz, unless otherwise recorded. [c] Tentative assignment (see text).

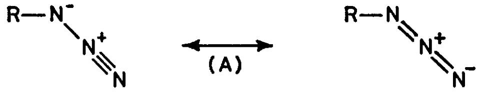
molecular orbitals) and LUMOs (lowest unoccupied molecular orbitals) for HN_3, with ionisation energies determined by p.e.s.,[9,10] and orbital energies calculated by *ab initio*[11] or Wolfsberg–Helmholtz[12] methods. The low-energy excitations which are magnetically active ($a' \longleftrightarrow a''$) are indicated. These are expected to dominate the nitrogen shielding, since there is a sizeable interval between the HOMOs and the lower bonding orbitals.[9-12] The weak (ε *ca.* 20) absorption at 264 nm in the u.v. spectrum of HN_3 has been assigned[9,13] as $\pi \longrightarrow \pi'^*$ [*cf.* 253 for Me_3SiN_3,[9] 288 for MeN_3,[9] and 330 nm for PhN_3,[14] but the absorption for $C_6F_5N_3$ is masked by strong bands at shorter wavelengths (244.5, 241 nm); shoulders are observed at 268 for 4-$N_3C_5F_4N$ and 326 nm for 4-$N_3C_5Cl_2F_2N$]. This $\pi \longrightarrow \pi'^*$ excitation is from a non-bonding π orbital located mainly on N_α, partly on N_γ. The next lowest excitation, at 200 nm (ε 450) for HN_3 (*cf.* 214 for Me_3SiN_3, 218 for MeN_3, 280 nm for PhN_3) is thought [9,13] to be $n \longrightarrow \pi^*$, from the lone pair (n) orbital which is located largely on N_α, but with some component on N_γ. (The slightly higher intensity is due to the s component in the lone pair orbital, the $s \longrightarrow \pi^*$ excitation being electric dipole allowed; but it is the forbidden $p \longrightarrow \pi^*$ component of the excitation that is magnetically active, since charge rotates.)



I.E./eV	Calculated orbital energies (eV)		
HN_3 (p.e.s.)[a]	HN_3 *ab initio*[b]	HN_3 MWH[c]	ClN_3 *ab initio*[d]
		-7·02	
		-7·75	
10·72	-11·09	-11·84	-10·83
12·24	-12·60	-12·76	-12·57
15·47	-18·50	-14·49	-14·02
etc.	*etc.*	*etc.*	*etc.*

FIGURE 2 Low energy $a' \longleftrightarrow a''$ excitations in HN_3. [a] Refs. 9 and 10. [b] Ref. 11. [c] Mulliken–Wolfsberg–Helmholtz, ref. 12. [d] Ref. 25

A δ–λ correlation is evident for the N_α and N_γ (but not the N_β) lines, for these move to lower field (δ increases) as the $a' \longleftrightarrow a''$ bands move to longer wavelengths [$(\Delta E)^{-1}$ increases]. The parallelism of the α and γ lines and the small variation in the N_β shielding are well interpreted by the orbital picture, since both of the two HOMOs are located largely on the α- and γ-nitrogens, and charge tends to move from end to middle of the azide group in both excitations. This accords also with the valence bond formulation (A), in which N_β is positively charged and N_α and N_γ negatively charged.


(A)

The $\widehat{RNN}$ angle varies from 108.7° for ClN_3 [15] to 120° for cyanogen azide NCN_3,[16] so that N_α varies from sp^3 to sp^2 in character. The bond lengths and force constants, which vary rather little, give a bond order of *ca.* 1.5 for $N_\alpha N_\beta$ and 2.5 for $N_\beta N_\gamma$.[17] In ClN_3 there may be some $\overset{+}{Cl}{=}N{-}N{=}N^-$ contribution, for the molecule is slightly *trans*-bent.[15] Clearly the azido-group is electronically labile, and this lability is reflected in the range of the nitrogen shifts and coupling constants; but there is no obvious correlation of the shifts or coupling constants with the geometry of the azido group.

As mentioned above, the lone pair orbital on N_α is part of the manifold of σ orbitals. The upfield shift of all three nitrogen lines with perfluorination of phenyl azide resembles the 'perfluoro effect' that is used diagnostically in photoelectron and electronic spectroscopy,[18] and has been remarked also in the ^{13}C nuclear magnetic shielding of alkenes and other π-bonded groups.[19] If all hydrogen in a planar group is replaced by fluorine, the strong inductive effect stabilizes the σ and π orbitals, but the π stabilization is offset by the conjugation of fluorine lone pair electrons ($+I_\pi$ effect). The net result is the stabilisation of the σ manifold relative to the π, frequently by 2—3 eV, and bands in the electronic spectrum due to excitations of $\sigma \longrightarrow \pi$ type, including $n \longrightarrow \pi^*$ from nitrogen, may be blue-shifted in this way. We may therefore expect a corresponding upfield shift in the nitrogen resonance lines. Pyridine is a prime example of nitrogen deshielded by $n \longrightarrow \pi^*$ circulations,[20] and the perfluoro effect is nearly 90 p.p.m.; the effect of chlorine substituents is similar but much smaller in magnitude.[21] As expected the perfluoro effect diminishes with distance from the fluorine substituents. In azidobenzene it is 20 p.p.m. for the α-nitrogen, and 10 and 5, respectively, for N_β and N_γ. The small effect on the γ-nitrogen shielding also reflects a smaller contribution to the shielding from $\sigma \longrightarrow \pi^*$ than from $\pi' \longrightarrow \pi^*$ circulations. The π' bonding orbital, which is not shown in Figure 2, is located largely on N_β and N_γ; and the 'lone pair' electrons on N_γ are rather strongly bound (sp) compared with those on N_α.

Figure 1 demonstrates various inductive and conjugative (π-inductive) effects on the chemical shifts which correlate satisfactorily with the evidence from other substituent effects, on reactivity, dipole moment, or ionisation constants, or in other forms of spectroscopy. The azido-group itself has a negative σ-inductive effect and positive π-inductive effect comparable to that of fluorine.[22] The electronegativity of the C_6F_5 group is comparable to that of chlorine or bromine, and is enhanced by aza-substitution in the ring.[23] Figure 1 shows the deshielding of α- or γ-nitrogen in PhN_3 relative to HN_3 or MeN_3, with extension of π-delocalisation, and the further deshielding by aza-substitution in the ring, bringing down the π- relative to the σ-manifold at azido-nitrogen. Relatively high shielding of N_γ and N_α seems to be associated with the more electropositive R groups such as Me_3Si or H (Table), or Me_2As (δ — 199).[2d]

Relatively high shielding of N_α coupled with deshielding of N_γ, against the general trend, is found in ClN_3 and NCN_3, in which there is a negative σ-inductive and positive π-inductive effect of the R group. Chlorine azide is unusual in having a slightly bent azide chain, with $\widehat{NNN}$ equal to 172°.[15] (For cyanogen azide the NNN chain was assumed linear, with the HN_3 dimensions, and the $\widehat{NCN}$ angle found to be 176°.[21]) Bending at nitrogen in a conjugated group is associated with deshielding. In a diazenido group which is 125° bent at N_α this nitrogen is deshielded by 350 p.p.m. compared with a corresponding linear group;[24] and in the ditosyltriazene anion $(TsNNNTs)^-$ the central nitrogen resonates 285 p.p.m. downfield and the outer nitrogen 250 p.p.m. downfield of the corresponding nitrogen in azide ion.[3] In ClN_3 both N_β and N_γ are somewhat deshielded, compared with other azides. This molecule is unusual also in having the largest $^1J_{NN}$ coupling constant yet recorded, 24 Hz for $N_\alpha N_\beta$,[2a] compared with 13—16 Hz for the other azides. This coupling constant seems to increase (numerically) with electronegativity of the R group.

The energy term $(\Delta E)^{-1}$ is usually the dominant factor in the approximate expression for the local paramagnetic shielding term, but the radial factor $\langle r^{-3}\rangle_{2p}$ varies significantly if there are sizeable changes in atomic charge.[8] With electronegative substituents, the increase in (positive) atomic charge shrinks the $2p$ orbitals of the resonating atom, increasing the radial factor, and tending to decrease the shielding. In the perfluoro effect in planar systems (such as the alkenes[19]) the increase in radial factor is outweighed by the larger increase in ΔE, described above. The perfluoro effect observed in nuclear magnetic shielding is therefore diminished, compared with the perfluoro effect in electronic or electron spectroscopy. Within the azido group, *ab initio* calculations indicate that the N_α charge varies from *ca.* -0.5 e in HN_3 (in which hydrogen bears an opposite and almost equal charge)[8] to -0.2 e in ClN_3, in which chlorine bears very little charge.[25] The consequent increase in the radial factor contributes *ca.* $+15$ p.p.m. to the N_α chemical shift (relative to HN_3) in ClN_3, and also apparently in NCN_3, in which N_α bears a similar negative charge.[26] These radial effects are clearly subsidiary, and tend to be smaller for N_β and N_γ than for N_α.

The crossover of the β and γ lines reflects a balance of factors and so is difficult to predict as the lines approach closely. The dotted correlations in Figure 1 for the pyrimidinyl compounds in which the azido-group was not ^{15}N-enriched (because of experimental constraints) have been drawn, tentatively, on the expectation of the variation in N_γ shift following that for N_α, and on the evidence of the low-field shifts observed for N_γ in a 4-azido-quinazoline derivative,[27] and in triazido-*sym*-triazine,[5] as shown in the Table and Figure 1.

EXPERIMENTAL

Synthesis of Azides.—4-Azido-2,3,5,6-tetrafluoro- and 4-azido-3,5-dichloro-2,6-difluoro-pyridine were prepared by treating pentafluoropyridine and 3,5-dichlorotrifluoropyridine respectively with sodium azide, as described in the literature.[5] 4-Azido-2,5,6-trifluoro- and 4-azido-5-chloro-2,6-difluoro-pyrimidine were obtained by nucleophilic azidation (with NaN_3 in MeCN) of tetrafluoropyrimidine and 5-chlorotrifluoropyrimidine,[6] respectively, and azidopentafluorobenzene by nitrosation of pentafluorophenylhydrazine.[28] ^{15}N-Labelled specimens of azidopentafluorobenzene were synthesised by nitrosation ($Na^{15}NO_2$–aqueous HCl) of $C_6F_5NHNH_2$ and $C_6F_5{}^{15}NH^{15}NH_2$, the latter being obtained through treatment of hexafluorobenzene with $^{15}N_2H_4\cdot H_2O$ in ethanol (*cf.* ref. 28). Partial labelling of 4-azidotetrafluoropyridine and 4-azido-3,5-dichloro-2,6-difluoropyridine was achieved by nitrosation[5] of 4-hydrazinotetrafluoropyridine[29] and 4-hydrazino-3,5-dichloro-2,6-difluoropyridine[30] respectively with aqueous $Na^{15}NO_2$–HCl. The latter hydrazinopyridine is a new compound (Found: C, 28.2; H, 1.1; N, 19.7. $C_5H_3Cl_2F_2N_3$ requires C, 28.0; H, 1.4; N, 19.6%), m.p. 138—140 °C after purification by vacuum sublimation. It was made by treatment of 3,5-dichloro-2,4,6-trifluoropyridine with ethanolic hydrazine hydrate,[30] as described previously for the conversion of pentafluoropyridine into 4-hydrazinotetrafluoropyridine.[29]

N.m.r. Measurements.—^{15}N.m.r. spectra were recorded on a Bruker WH180 spectrometer at 293—295 K. The ^{15}N was in natural abundance unless enrichment was necessary for a particular assignment, as recorded in the Table. N.m.r. tubes of 10 mm or 25 mm OD were used, with a concentric 5 mm OD tube of neat CD_3NO_2 as both reference standard and deuterium lock. $[Cr(CH_3COCHCOCH_3)_3]$ was added to the reference (30 mg dm^{-3}) and to the samples to facilitate relaxation; no effects on the chemical shifts were observed.

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