^{14}N Nuclear Magnetic Resonance of Covalent Azides

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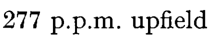
^{14}N Chemical shifts are reported for hydrazoic acid, certain organic and organoarsenic azides, and a number of metal azido-complexes. The shifts are related where possible to the electronic characteristics of the atom or group to which the azide is covalently attached and to the mode of attachment.

No spin–spin coupling effects are observed but the shifts provide some evidence for molecular association or azide exchange in the compounds Me_2AsN_3 and Et_2AsN_3. The covalent character of the metal–azide bond is demonstrated by the appearance of three distinct ^{14}N n.m.r. signals for each of the azido-complexes studied.

THE linear azide ion, N_3^-, in aqueous solution gives rise to two ^{14}N resonances with integrated intensities of 1 : 2 at 128 and 277 p.p.m. upfield from aqueous nitrate ion as standard.[1,2] These resonances are attributable to the differing electronic arrangements at the central atom and the two outer equivalent atoms respectively. Spin–spin splitting is not observed, presumably as a result of the large quadrupole moment of ^{14}N. It has been estimated, however, that the ^{14}N–^{14}N coupling constant in the azide ion must be less than 30 Hz.[3] Correspondingly, covalent *e.g.* organic azides, RN_3, are expected to furnish a distinct ^{14}N signal from each of the non-equivalent nitrogen sites in the structure (I)


(I)

and three well-resolved resonances are indeed found for methyl[4] and ethyl[1,4] azides (Table). Again, however, no spin–spin splitting was observed. In the work reported here the ^{14}N n.m.r. study of covalent azides has been extended to include hydrazoic acid and a further group of organic azides as well as certain organoarsenic azides and metal azido-complexes. Chemical shifts for these compounds are recorded in the Table and assignment of the individual resonances to N_a, N_b, and N_c is made on the basis of the arguments given by Witanowski.[4] These will be summarised briefly here. The signal at *ca.* 130—140 p.p.m. is assigned to the central nitrogen atom (N_b) since the shift is closely similar to that of the central atom of the azide ion. One of the other two signals is at higher field (*ca.* 300 p.p.m.) and shows a downfield shift from methyl to ethyl azide. Organic isocyanates[4,5] and isothiocyanates[4] show a corresponding value with the same dependence on R, indicating that it is the resonance of the nitrogen atom adjacent to the alkyl group (N_a). The remaining signal at *ca.* 170 p.p.m. is thus assigned to the terminal nitrogen atom (N_c).

Hydrazoic Acid, HN_3.—A dilute solution of hydrazoic acid in diethyl ether gave the expected three-line ^{14}N spectrum, the resonance positions corresponding closely to those in methyl and ethyl azides (Table). In contrast to the situation in HNCO,[5] no splitting of the N_a signal into a doublet as a result of ^{14}N–^{1}H coupling was observed for HN_3. A solution of HN_3 in diethyl ether containing some water shows two resonances only, the high-field signal being of relative intensity 2 positioned at the mean value of the bonded and terminal shifts of the acid in anhydrous ether. The evident equivalence of the outer nitrogens of the azide group in this case is presumably achieved *via* proton exchange with water molecules. An acidified aqueous sample of the sodium salt also shows only two resonances. The positions of the resonances obtained from increasingly acidified (H_2SO_4) aqueous solutions of sodium azide indicate that here, the line of intensity 2 to high field of the practically immobile central atom resonance is an exchange peak intermediate between the positions of the terminal azide ion resonance and the mean of the terminal and bonded resonances of the hydrazoic acid molecule. When an excess of strong acid is present, no azide ion remains in the solution and the final resonance position again corresponds to the mean of the two outer nitrogen shifts in the acid.

Organic Azides.—Predictably, in the organic species RN_3, the N_a chemical shift is most markedly affected by the nature of R. As found for RNCO and RNCS, there is a correlation between the chemical shift and the electronegativity of the substituent R, *i.e.* a shift to lower field is observed with decreasing electronegativity of R^4. Of the aryl azides studied, PhN_3 shows the lowest field N_a resonance. Higher field N_a shifts in the other three aryl azides examined are attributable to the electron-withdrawing effects of –CO–, $-SO_2-$ and $-NO_2$ groups respectively. The signals arising from N_b and N_c in organic azides show no similar dependence on the nature of the attached organic group which is separated from these atoms by two or three bonds.

Organoarsenic(III) *Azides.*—Each of the disubstituted azidoarsines listed in the Table gave rise to the clearly defined and relatively sharp resonance line at *ca.* 130 p.p.m. (attributable to N_b) which is characteristic of all ^{14}N n.m.r. spectra of azides, examined to date. The resonances arising from N_a and N_c are almost

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[1] T. Kanda, Y. Saito, and K. Kawamura, *Bull. Chem. Soc. Japan*, 1962, **35**, 172.

[2] R. A. Forman, *J. Chem. Phys.*, 1963, **39**, 2393.

[3] D. Herbison-Evans and R. E. Richards, *Mol. Phys.*, 1964, **7**, 515.

[4] M. Witanowski, *J. Amer. Chem. Soc.*, 1968, **90**, 5683.

[5] K. F. Chew, W. Derbyshire, N. Logan, A. H. Norbury, and A. I. P. Sinha, *Chem. Comm.*, 1970, 1708.

invariably broader, particularly that due to N_a, and neither could be observed for certain of the azidoarsines, *e.g.* $Ph(Et)AsN_3$, either in the pure liquid form or when diluted with carbon tetrachloride. In the diphenyl, chlorophenyl, and bromophenyl derivatives, resonances assignable to N_b and N_c were observed, but the N_a resonance was presumed to be so broad as to be indistinguishable from the noise level. The failure to observe the three possible resonances in the above compounds may be attributed to viscosity broadening of signals from the pure liquids and insufficient intensity from solutions in carbon tetrachloride. In the case of the dimethyl and diethyl compounds however a different phenomenon was encountered. When run as pure liquids, two resonances were again observed, but the high-field signal had twice the intensity of the N_b line and was situated [$\delta(NO_3^-)$ *ca.* 250 p.p.m.] approximately at the mean position of the N_a and N_c resonances observed in RN_3 compounds (see Table). This implies that environmental equivalence of bonded and terminal nitrogen atoms in Me_2AsN_3 and Et_2AsN_3 is achieved in some fashion. This could conceivably arise from association of molecules by azide bridging of arsenic atoms as shown in (II).

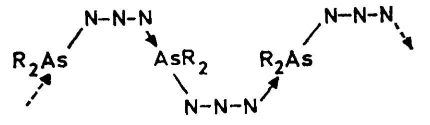
^{14}N Chemical shifts of covalent azides *

Compound	$\delta(NO_3^-)$			Solvent	Ref. to prepn.
	N_a	N_b	N_c		
$Na^+N_3^-$	277 † (55)	128 (22)	277 †	H_2O	
$Na^+N_3^-$	277 †	129 (23)	277 †	H_2SO_4	*a*
	$\rightarrow$ 245		$\rightarrow$ 245		
HN_3	240 † (100)	129 (30)	240 †	Et_2O-H_2O	*b*
HN_3	300 (100)	129 (24)	165 (100)	Et_2O	*b*
MeN_3 ‡	320 (101)	128 (17)	170 (19)	$MeNO_2$	*c*
EtN_3 ‡	305 (122)	129 (22)	167 (28)	$MeNO_2$	*c*
PhN_3	286 (1200)	135 (180)	194 (55)	C_6H_6	*c*
$PhCON_3$	322 (430)	140 (300)	237 (73)	C_6H_6	*c*
p-$MeC_6H_4SO_2N_3$	304 (410)	152 (250)	209 (120)	Liquid	*c*
p-$NO_2C_6H_4N_3$	310 (270)	139 (75)	211 (45)	C_6H_6	*c*
Me_2AsN_3	253 † (80)	132 (37)	253 †	Liquid	*d*
Et_2AsN_3	251 † (85)	133 (40)	251 †	Liquid	*d*
Et_2AsN_3		130 (23)		CCl_4	
Ph_2AsN_3		134 (94)		Liquid	*d*
Ph_2AsN_3		132 (37)	188 (75)	CCl_4	
$Ph(Et)AsN_3$		134 (100)		Liquid	*d*
$Ph(Et)AsN_3$		131 (30)		CCl_4	
$Ph(Cl)AsN_3$		134 (43)	170 (86)	Liquid	*d*
$Ph(Br)AsN_3$		134 (87)	170 (200)	Liquid	*d*
$(Ph_4As)_2Sn(N_3)_6$	293 (800)	143 (90)	225 (90)	CH_2Cl_2	*e*
$(Ph_4As)_2Pb(N_3)_6$	280 (328)	143 (185)	200 (185)	CH_2Cl_2	*e*
$(Ph_4As)Au(N_3)_4$	310 (410)	140 (55)	183 (127)	CH_2Cl_2	*e*
$(Ph_4As)Au(N_3)_2$	336 (180)	140 (75)	248 (75)	CH_2Cl_2	*e*
$(Ph_4As)_2Pd(N_3)_4$	334 (245)	143 (110)	225 (125)	CH_2Cl_2	*e*
$(Ph_4As)_2Pt(N_3)_4$	345 (180)	130 (110)	237 (250)	CH_2Cl_2	*e*
$(Ph_4As)_2Pd_2(N_3)_6$	355 (218)	135 (145)	230 (324)	CH_2Cl_2	*e*
Ph_3PAuN_3	315 (330)	132 (110)	229 (290)	CH_2Cl_2	*f*
cis-$(Bu_3P)_2Pt(N_3)_2$	326 (220)	135 (145)	226 (110)	CH_2Cl_2	*g*
cis-$(PhBu_2P)_2Pt(N_3)_2$	344 (180)	130 (290)	230 (360)	CH_2Cl_2	*g*
cis-$(Ph_2BuP)_2Pt(N_3)_2$	365 (73)	135 (220)	230 (220)	CH_2Cl_2	*g*
cis-$(Ph_3P)_2Pt(N_3)_2$	351 (110)	131 (180)	225 (250)	CH_2Cl_2	*e*
$(Ph_3P)_2Pd(N_3)_2$	363 (145)	140 (110)	230 (75)	CH_2Cl_2	*e*
$(Ph_3P)_2Pd_2(N_3)_4$	374 (218)	134 (145)	255 (320)	CH_2Cl_2	*f*
$(Ph_3P)_4Pd_2(N_3)_2(BF_4)_2$	365 (110)	129 (40)	192 (92)	CH_2Cl_2	*f*

* Line widths (Hz) at half peak height in parentheses. † Resonance of intensity 2 relative to the N_b signal. ‡ Data from ref. 4.

[a] Solution prepared by careful addition of conc. H_2SO_4 to a cooled aqueous solution of NaN_3. [b] G. Brauer, 'Handbook of Preparative Inorganic Chemistry,' vol. I, 1963, p. 472. [c] C. Grundmann in Houben-Weyl: Methoden der organischen Chemie, Bd. X/3, p. 777, Thieme, Stuttgart, 1965. [d] Ref. 6. [e] Ref. 8. [f] W. P. Fehlhammer, W. Beck, and P. Pollmann, *Chem. Ber.*, 1969, **102**, 3903; W. Beck, P. Kreutzer, and K. v. Werner, *Chem. Ber.*, 1971, **104**, 528; W. Beck, W. P. Fehlhammer, P. Pöllmann, and R. S. Tobias, *Inorg. Chim. Acta*, 1968, **2**, 467. [g] P. Kreutzer, Dissertation, München, 1971.

However, in order to explain the occurrence of a single resonance for N_a and N_c it would be necessary to assume either that all As–N bonds in such a system are equally strong, or that easy exchange of N_3 groups between R_2As moieties can occur. Two related observations may be cited in support of these proposals. First, the significantly higher boiling point of Me_2AsN_3 (82—84 °C at 125 mmHg) compared to Me_2AsCl (57—59 °C at 125 mmHg) may be a reflection of association in the liquid state. Secondly, the organoarsenic azides studied here were prepared as possible precursors of As–N ring compounds *via* thermal decomposition,[6]



(II)

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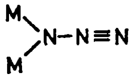
[6] D. M. Revitt and D. B. Sowerby, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 459.

e.g. the first example of a simple arsenic(v)–nitrogen ring compound $(Ph_2AsN)_4$ had been previously obtained from the thermal decomposition of Ph_2AsN_3.[7] However the thermal decomposition of Me_2AsN_3 and Et_2AsN_3 gave only nitrogen-free products, indicating that cleavage of the As–N bond occurs more readily in these molecules as would be necessary to facilitate N_3 exchange between R_2As groups. The observation of the N_c resonance at *ca.* 170 p.p.m. in Ph_2AsN_3, $Ph(Cl)AsN_3$, and $Ph(Br)AsN_3$ can be rationalised in terms of the greater steric hindrance of arsenic atoms by phenyl or substituted phenyl groups, resulting in a diminished tendency towards molecular association or exchange of N_3 groups.

In an attempt to ascertain whether association or exchange was still indicated in the presence of a solvent, spectra of Et_2AsN_3 were also recorded in CCl_4 solution. Unfortunately, the attendant dilution resulted in the observance of only the single, sharp N_b resonance.

Azido-complexes of Metals.—Each of the metal azido-complexes displays the three ^{14}N resonances expected for co-ordinated azide ligands (see Table). The observed chemical shifts indicate that the bonding is very similar to that in the organic azides. The covalent character of metal azide bonds in such complexes has also been established by vibrational and electronic spectroscopy,[8] and *X*-ray structural determinations of a number of azido-complexes [9-12] revealed significantly different N–N bond distances within each azide ligand. In common with the organic azides and other complexes which have been studied by ^{14}N n.m.r.[5,13-15] each of the azide complexes listed in the Table shows a chemical shift for the bonded nitrogen (N_a) atom to high field of that observed for the free ligand. These 'co-ordination shifts' for the N_a atom increase for the anionic azide complexes in the following order of the metal oxidation state involved: $\mathrm{Pb^{IV}} < \mathrm{Sn^{IV}} < \mathrm{Au^{III}} < \mathrm{Au^{I}} \sim \mathrm{Pd^{II}} < \mathrm{Pt^{II}}$. This order corresponds closely to increasing 'class (b)' behaviour [16] ('softness' [17]) along this series.

In the complexes $Pd_2(N_3)_6{}^{2-}$ and $(Ph_3P)_2Pd_2(N_3)_4$ which contain both terminal and bridging azide ligands only one N_a signal could be observed. Also the N_a co-ordination shift of $(Ph_3P)_4Pd(N_3)_2{}^{2+}$ which possesses only azide bridges is close to that of the terminal azide groups in $(Ph_3P)_2Pd(N_3)_2$. Actually a recent *X*-ray structural determination [12] of $(N_3)_2Pd(N_3)_2Pd(N_3)_2{}^{2-}$ showed a surprising similarity of the N–N distances and Pd–N_3 angles in both terminal and bridging N_3 ligands. The azide bridges in these complexes proved to be of N-diazonium type (III) [12,18]; obviously attachment of a second metal to the lone pair of the N_a atom does not significantly alter the bonding within the azide group.



(III)

The N_b resonances change very little from the value in the free azide ion and are remarkably constant in all covalent azides, indicating high electronic mobility in the π-bonded structure of the azide group. Electron withdrawal *via* the bonded atom is compensated by a movement of electrons from the terminal atom region towards the central nitrogen. The terminal N_c shows a downfield shift from the value in free azide ion as is usually observed for linear triatomic nitrogen-containing ligands which are not directly bonded *via* the nitrogen to an organic group or a metal, *e.g.* in ROCN [5,15] and MSCN.[13]

EXPERIMENTAL

Reference to preparative methods for the compounds studied here is made in the Table. Spectra were recorded at *ca.* 30 °C on a Varian HA 100 n.m.r. spectrometer operating at 7·226 MHz using standard 5 mm sample tubes (8 mm sample tubes for the metal azido-complexes) and concentrated (preferably saturated) solutions or pure liquid samples due to the low sensitivity of ^{14}N to n.m.r. detection. Chemical shifts were measured by the sample-substitution method relative to $NO_3{}^-$ ion in a saturated aqueous solution of $NaNO_3$ or NH_4NO_3.

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