^{14}N Chemical Shifts of Isocyanates and Cyanates

By K. F. CHEW, W. DERBYSHIRE, and N. LOGAN*
(*Departments of Physics and Chemistry, University of Nottingham, Nottingham* NG7 2RD)
and A. H. NORBURY and A. I. P. SINHA
(*Department of Chemistry, Loughborough University of Technology, Loughborough* LE11 3TU)

Summary A ^{14}N n.m.r. study of the NCO group in a range of nitrogen-bonded compounds and in certain oxygen-bonded species demonstrates the value of ^{14}N chemical shifts in distinguishing these bonding modes.

THE NCO group shows a marked preference for *N*-bonding (isocyanate),[1] *O*-bonded (cyanate) species being comparatively rare.[1] Some rationalisation of this behaviour arises from the point-charge calculations of Wagner[2] which show a distinct accumulation of negative charge on the nitrogen atom of the cyanate ion and a correspondingly low negative charge on the oxygen atom. A more equitable distribution of negative charge between sulphur and nitrogen is calculated[2] for the thiocyanate ion, accounting for its versatility as an ambidentate ligand.[1]

At present, a small number of reasonably stable organic cyanates is known[3] but there is still no confirmed example of a metal cyanate or cyanato-complex. *O*-Bonding is suggested, although not definitively established, in the compounds $(Ph_4As)_2[Re(OCN)_6]$, $Cs[Re(OCN)_6]$, $(Ph_4As)_3[Mo(OCN)_6]$,[4] and $(\pi\text{-}C_5H_5)_2M(OCN)_2$ (M=Ti, Zr, or Hf),[5,6] on the basis of i.r.[4–6] and mass spectral[6] evidence.

We have now demonstrated that in general the bonding mode of the NCO system may be established by measurement of ^{14}N chemical shifts. Howarth, Richards, and Venanzi[7] demonstrated the applicability of this technique to the NCS ligand in soluble diamagnetic complexes. *S*-Bonded thiocyanato-complexes give rise to ^{14}N shifts to low field of the aqueous NCS^- ion resonance, whereas *N*-bonded systems resonate to high field of this position. In the present work, the ^{14}N n.m.r. spectra of a number of non-metallic and diamagnetic metallic isocyanate (*N*-bonded) species have been studied together with those of the *O*-bonded ethyl and phenyl cyanates. Chemical shifts [δ (NCO^-) Table] were measured by the substitution method and are quoted (p.p.m.) relative to aqueous K^+NCO^- (for which δ (NO_3^-) = 300 ± 1 p.p.m., line width 15 Hz). The spectra were recorded on a Varian H.A. 100 spectrometer operating at a frequency of 7·226 MHz using standard 5 mm sample tubes. All the isocyanates studied show chemical shifts to high field of the free ion and conversely, ethyl and phenyl cyanates give rise to large low-field shifts. Consequently, as in the case of the NCS group, ^{14}N n.m.r. provides a firm indication of the bonding mode adopted by the NCO group.

It is interesting that certain metal complexes containing co-ordinated fulminate, *i.e.* the isomeric –CNO system, exhibit ^{14}N resonances 10—20 p.p.m. to low field of fulminate ion, CNO^- which itself resonates at −124 p.p.m. relative to the NCO^- ion.[8]

TABLE

^{14}N *chemical shifts of isocyanates and cyanates*

Compound	Solvent	δ (NCO^-) (p.p.m.)	Line width (Hz)
$Ph_4As^+NCO^{-a}$	MeCN	−1±1	20
$Ag(NH_3)_2^+NCO^{-b}$	H_2O	0±1	7
$HNCO^c$	C_6H_{12}	+53±2	20
	Et_2O	+51±2	35
GeH_3NCO^d	C_6H_6	+64±1	45
	neat	+62±1	45
MeNCO	C_6H_6	+61±1	35
	neat	+61±1	35
Me_3SiNCO	neat	+53±1	38
Et_3GeNCO	neat	+52±1	65
$Pr^n{}_3GeNCO$	C_6H_6	+50±2	50
Pr^nNCO	neat	+46±1	70
EtNCO	neat	+43±1	37
PhNCO	neat	+30±3	50
$P(NCO)_3$	C_6H_6	+22±4	88
$Et_4N^+Ag(NCO)_2^-$	Me_2CO	+44±2	
$Me_4N^+Ag(NCO)_2^{-e}$	”	+42±2	50
$Ph_4As^+Ag(NCO)_2^-$	”	+42±2	51
$(Et_2NH_2^+)_2Zn(NCO)_4^{2-}$	”	+25±2	88
$(Et_3NH^+)_2Zn(NCO)_4^{2-}$	”	+22±4	
$(Me_4N^+)_2Hg(NCO)_4^{2-e}$	”	+17±2	73
$(Et_4N^+)_2Hg(NCO)_4^{2-}$	$MeNO_2$	+12±2	
$(Et_4N^+)_2Sn(NCO)_6^{2-f}$	Me_2CO	+ 8±1	58
EtOCN	Et_2O	−78±1	45
$PhOCN^g$	neat	−92	

[a] Line broadens due to hydrolysis.
[b] $Ag(NH_3)_2^+$ resonance at +82 p.p.m.
[c] Doublet, J_{NH} 69 ± 5 Hz, line width of each component = 20 ± 4 Hz, (K. M. Mackay and S. R. Stobart, submitted for publication in *Spectrochim. Acta*;) see also J. Nelson, R. Spratt, and S. M. Nelson, *J. Chem. Soc.* (*A*), **1970**, 583. (^1H resonance of HNCO, from which J_{NH} = 64 ± 1 Hz).
[d] See also K. M. Mackay and S. R. Stobart, *Spectrochim. Acta*, 1970, **26**, *A*, 373.
[e] Me_4N^+ resonance at +33 p.p.m.
[f] Et_4N^+ resonance at +12 p.p.m.
[g] Chemical shift value from ref. 8.

We thank the S.R.C. for the award of a studentship to K.F.C., Loughborough University of Technology for a Post-doctoral Fellowship to A.I.P.S., and Dr. K. M. Mackay and Dr. S. R. Stobart for supplying samples of the silicon and germanium compounds and isocyanic acid.

(*Received, August 25th,* 1970; *Com.* 1432.)

---

[1] A. H. Norbury and A. I. P. Sinha, *Quart. Rev.*, 1970, **24**, 69.
[2] E. L. Wagner, *J. Chem. Phys.*, **1965**, **43**, 2728.
[3] H. Hoyer, *Chem. Ber.*, 1961, **94**, 1042; D. Martin, *Angew. Chem. Internat. Edn.*, 1964, **3**, 311; K. A. Jensen, M. Due, and A. Holm, *Acta Chem. Scand.*, 1965, **19**, 438; N. Groving and A. Holm, *ibid.*, p. 443.
[4] R. A. Bailey and S. L. Kozak, *J. Inorg. Nuclear Chem.*, 1969, **31**, 689.
[5] J. L. Burmeister, E. A. Deardorff, and C. E. Van Dyke, *Inorg. Chem.*, 1969, **8**, 170.
[6] J. L. Burmeister, E. A. Deardorff, A. Jensen, and V. H. Christiansen, *Inorg. Chem.*, 1970, **9**, 58.
[7] O. W. Howarth, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.*, **1964**, 3335.
[8] W. Becker and W. Beck, *Z. Naturforsch.*, 1970, **25b**, 101.