Microwave Spectrum and Structure of Nitrosyl Cyanide

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Summary The structure of nitrosyl cyanide, generated from silver cyanide and nitrosyl chloride, has been determined from its microwave spectrum.

NITROSYL chloride and silver cyanide react[1] at −30 to −20° to form a blue-green gas stable at room temperature in glass vessels for several hours. The structure ONCN, nitrosyl cyanide, was suggested for this gas on the basis of its colour (λ_{max} 738 nm),[2] typical of *C*-nitroso-compounds, and reaction with conjugated dienes to form *N*-cyano-3,6-dihydro-2*H*-1,2-oxazines. We now report a study of the microwave spectrum of nitrosyl cyanide and various isotopically labelled species.

TABLE

Rotational constants (MHz)

	B_0	C_0
NO·CN	5384·39	5040·63
^{15}NO·CN	5360·11	5005·99
NO·C^{15}N	5205·87	4882·49
NO·^{13}CN	5359·43	5018·62

μ_a, *R*-Branch transitions have been measured for the species NO·CN, ^{15}NO·CN, NO·C^{15}N, and NO·^{13}CN. The labelled substances were synthesised from suitably enriched starting materials and all measurements were made in a copper waveguide Stark cell cooled with solid CO_2. In this system a single sample could be studied for a period of about 30 min without renewal. The Table lists the B_0 and C_0 rotational constants which are directly obtained from the spectral analysis. With the assumption that the molecule is planar the structure given in the Figure was calculated from the data as follows. The *a*-co-ordinates of

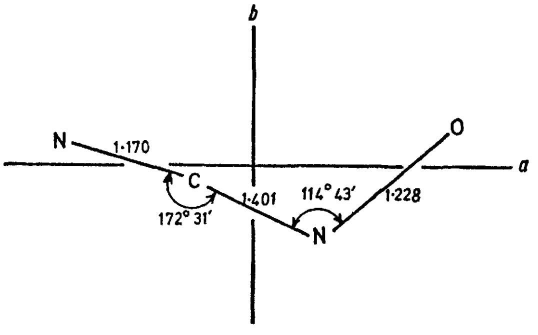

FIGURE. *Distances are in* Å.

the two nitrogen atoms and the carbon atom were determined by the direct substitution method and the *a*-co-ordinate of the oxygen fixed by the first moment condition. Only the *b*-co-ordinate of the nitrosyl nitrogen is reliably fixed by direct substitution so the remaining *b*-co-ordinates were determined by fitting the I_c value, the first moment condition, and the product of inertia relationship. The uncertainty in the bond distances is about ±0·005 Å while the ∠CNO is determined to ±1°. The ∠NCN is only precise to ±3° as its value is strongly dependent on the small *b*-co-ordinates of the nitrile group atoms.

Perhaps the most striking structural feature is the distinct bend at the carbon atom. A very similar distortion is found in NF_2CN.[3] The nitrile link is a little longer than is common; the NO distance is certainly longer than that found in NOCl (1·139 Å)[4] and is more like that bond in CH_3NO (1·213 Å).[5] The central CN distance is quite close to the corresponding parameter in NF_2CN(*ca.* 1·39 Å) and the ∠CNO to the structural angle of NOCl (113°20′).

These results clearly exclude a linear structure, $\overset{-}{N}=C=\overset{+}{N}=O$, for nitrosyl cyanide. Recently the related species, NC·NCO, cyanogen isocyanate, has also been shown to be bent (∠CNC = 140·0°).[6]

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