Microwave Spectrum and Structure of Cyanogen Isocyanate

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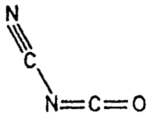
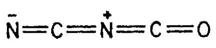
Summary The structure of cyanogen isocyanate has been determined from its microwave spectrum.

THE preparation of cyanogen isocyanate, NCNCO, has recently been reported.[1,2] Its structure is of considerable interest, for though on simple valence bond grounds the molecule is likely to be bent, it is isoelectronic with linear C_3O_2 and could reasonably be linear. Indeed, its i.r. spectrum has been interpreted as showing it to be linear in the gas phase but bent in the solid.[2] We have begun a study of its microwave spectrum to clarify the situation and to measure the bond lengths and angles.

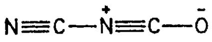


(I)



$\bar{N}=C=\overset{+}{N}=C=O$

(II)



$N\equiv C-\overset{+}{N}\equiv C-\bar{O}$

(III)

The rotational spectrum of the molecule in its ground vibrational state was assigned and measured at room temperature. The spectrum has been found to be that of a slightly asymmetric prolate rotor having components of its dipole moment along the *a*- and *b*- principal inertial axes. Though some of the transitions were found to be rather broad, probably because of nitrogen nuclear quadrupole coupling, we have not yet resolved any structure. To obtain accurate rotational constants it has been necessary to account for rather large centrifugal distortion; a preliminary analysis using the method previously described[3] has been carried out. Though we have thus far insufficient data to obtain accurate values for all the distortion constants this procedure has been shown to give good values for the rotational constants.[4] These are given in the Table along with the principal moments of inertia and the inertial defect.

We have also observed transitions of molecules in at least four excited vibrational states. From the relative intensities of the transitions in the ground and first excited vibrational states the vibration frequency was estimated to be 144 ± 40 cm^{-1}. This low vibration frequency is consistent with the large centrifugal distortion.

TABLE. *Rotational constants in* MHz *and principal moments of inertia and inertial defect in a.m.u.* Å^2 *of cyanogen isocyanate*

A	74358·7 ± 1·5
B	2699·04 ± 0·01
C	2597·87 ± 0·01
I^a	6·7967
I^b	187·249
I^c	194·541
Δ[a]	0·495

[a] $\Delta = I^c - I^b - I^a$.

Since the spectrum of cyanogen isocyanate is that of an asymmetric rotor we conclude that the molecule is not linear in the gas phase, in contrast to the previous report.[2] The small positive inertial defect suggests strongly that the molecule is planar. This deduction is consistent with the estimated vibration frequency, for if the vibration is assumed to be in the molecular plane its frequency can be calculated[5] using $\omega = 4K/\Delta$, with $K = 16{\cdot}863$ a.m.u. Å^2 cm^{-1}; the value obtained is 136 cm^{-1}, in agreement with that given earlier. We also deduce that the molecule is indeed the isocyanate, NCNCO; were it the cyanate, NCOCN, and planar, the molecule would have C_{2v} symmetry and either *a*- or *b*- type transitions, but not both, would have been observed.

If the N–C–N and N–C–O chains are assumed to be linear, with the cyanide and isocyanate bond lengths the same as in cyanogen azide[6] and chlorine isocyanate[7] respectively, the remaining C–N bond length is calculated to be 1·283 Å and the angle between the two chains 140·0°. These values are somewhat uncertain, since it is possible that bends of several degrees may occur in either or both parts of the molecule taken to be linear.[6,7] An accurate estimate must await study of further isotopic species. Nevertheless this length is much shorter than the sum of the single bond radii,[8] and the angle is considerably larger than that of an sp^2 hybridized atom. It seems likely that there are contributions from resonance forms (II) and (III) as well as form (I), which is probably the chief one. Though the molecule is bent, then, there is evidence of a considerable tendency towards linearity.

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