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**Short communication**

# THE EXISTENCE OF GASEOUS CYANOFORM AS OBSERVED BY MICROWAVE SPECTRA

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The existence of $HC_4N_3$ in the gas phase either as cyanoform, $HC(CN)_3$ (I), or as di-cyanoketenimine, $(NC)_2C=C=NH$ (II), has recently been discussed and treated by an ab initio calculation [1]. It appeared that I is ca. 10 kcal mol$^{-1}$ more stable than II. The present communication reports experimental proof of the occurrence of I as a by-product in two different chemical procedures to be described. In both cases the small yields (< 1‰) of an unstable compound available over a limited period (ca. 2 h) made the use of microwave equipment appropriate since it is well adapted to the study of small quantities (< 1 mg) and in particular to highly polar species such as I and II.

## MICROWAVE OBSERVATIONS

Vapors from the contents of a vial evacuated at 20°C and placed close to (ca. 20 cm) the entrance of a conventional Stark-modulated microwave spectrometer (26—40 GHz) were pumped through a 3-m cell at an entrance pressure of 10—40 mtorr. Under these conditions spectra were obtained (Table 1). After 1 h, pumping could be disrupted for 10—15 min without serious loss of spectral quality. Keeping the sample vial at 20°C was necessary to maintain sublimation. However, at this temperature chemical changes of the sample (polymerisation?) produced yellow, presumably non-volatile compounds in the vial in considerable quantity as observed by Trofimenko at higher temperature [2]. Since the recorded spectra were satisfactory (recorded at a speed of 0.2 MHz s$^{-1}$) no cooling of the microwave cell has been attempted. Spectra were recorded at 100, 140, 200, 500 and 600 V cm$^{-1}$. The spectra (Table 1) showed all significant features of originating from a symmetric rotor. The experimental value of the rotational constant $B_0$ = 2865.08 MHz can be reproduced by a model of I with a C≡N distance of 1.158 Å, a C—C distance of 1.460 Å and a C—H distance of 1.100 Å, the angles $\alpha$ and $\beta$ (Fig. 1) having been taken as 106.59° and 177°, respectively. The choice of geometric parameters has been discussed in ref. 1 except in the case of $\alpha$ and $\beta$. $\beta$ = 177° was taken from experiments on $CH_2(CN)_2$, malononitrile [3], and $\alpha$ has been adjusted to reproduce our value of $B_0$. In ref. 1, $\alpha$ = 108° was applied.

TABLE 1

Observed transition frequencies (MHz) of a symmetric rotor with $B_0$ = 2865.08 ± 0.01 and $D_J$(kHz) = 2.26 ± 0.20

Calculated transition frequencies for $B_0$ = 2865.08 MHz and $D_J$ = 2.26 kHz. Numbers in parenthesis for vibrational satellite lines are peak-intensities taking the J = 6 ← 5 peak intensity as 100, all at 500 V cm$^{-1}$ Stark voltage

| Ground state | | | Vibrationally excited levels[a] (unassigned) | | |
|---|---|---|---|---|---|
| $J'' \leftarrow J'$ | $\nu_{\text{obs.}}$ | $\nu_{\text{calc.}}$ | | | |
| 5 ← 4 | 28 649.62 | 28 649.67 | 34 364.1 (16) | 34 452.0 (7) | 34 548.7[b] (10) |
| 6 ← 5 | 34 379.00 | 34 379.01 | 34 369.4[b] (10) | 34.471.9[b] (20) | 34 567.0 (9) |
| 7 ← 6 | 40 107.94 | 40 108.02 | 34 416.4 (13) | 34 477.5[b] (27) | 34 572.3[b] (7) |
| | | | 34 421.1[b] (9) | 34 481.1 (9) | 34 576.0 (9) |
| | | | 34 422.2[b] (9) | 34 487.2 (19) | 34 588.0[b] (9) |
| | | | 34 428.4 (29) | 34 499.3 (45) | 34 594.0 (15) |
| | | | 34 430.3 (23) | 34 521.6[b] (12) | 34 620.8 (22) |
| | | | 34 435.2 (11) | 34 546.7 (13) | |

[a] Transition frequencies reproducible at 100—500 V cm$^{-1}$ Stark voltage.
[b] Peak in non-resolved pattern.

No lines attributable to other molecular species such as II (with an estimated asymmetry parameter $\kappa \sim$ 0.62—0.73) were observed but it needs emphasizing that our search necessarily was limited to rather narrow regions around 28650 and 40000 MHz while wider scans of the 34210—34700 MHz range (Table 1) were produced. The suggested interpretation of the weaker lines in this latter region as originating from vibrationally excited levels is in harmony with what one would expect from a symmetric rotor with some low-lying vibrational levels as exemplified by Careless and Kroto [4] for $SiH_3CN$. Spectral lines from $H^{13}C(CN)_3$ and from $HC(CN)_2(^{13}CN)$ are expected at lower

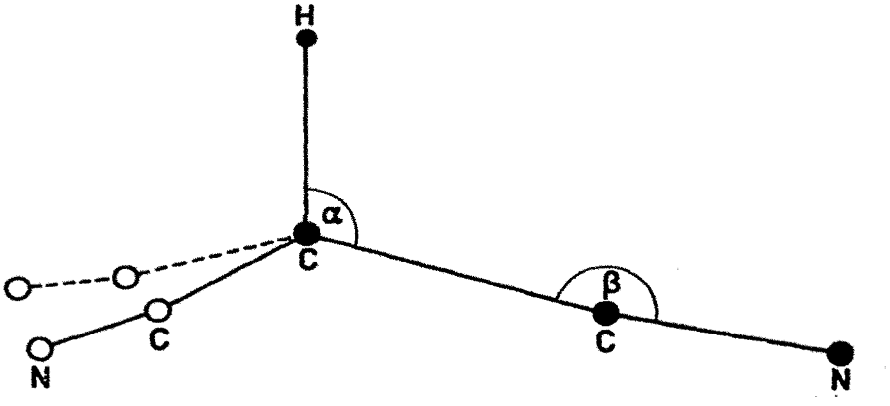

Fig. 1. Cyanoform model (point group $C_{3v}$) showing definition of angles α and β. Atoms in- and outside plane of paper represented by ● and ○, respectively.

frequencies for a $J = 6 \leftarrow 5$ transition (at ca. 34330 and a group at ca. 34180 MHz). They were searched for briefly but not identified.

## CHEMICAL WORK

Our reasons for proposing that the microwave spectrum of Table 1 can be assigned to I and to no other symmetric rotor rests also upon the fact that the species was produced by two different chemical procedures.

In one case the aquo-ethereal solution of $HC_4N_3$ which has been most frequently applied and referred to [2], was evaporated in vacuo at 0°C where decomposition is slight. At a final "equilibrium" pressure of ca. 40 mtorr slowly rising due to decomposition, fractions collected in a vial later to be placed on the spectrometer were solid, even when heated briefly to 20°C. The combined fractions collected overnight represented a very low yield. Initially, 3.22 g of $KC(CN)_3$ (0.025 moles) [5] had been dissolved in water, acidified, extracted with ether a.s.o. The stoichiometric yield of $HC_4N_3$ would be 2.2 g. The vial contained an estimated 5—10 mg of substance (not weighed). As mentioned sublimation at 20°C from the vial through the spectrometer allowed us to work for ca. 2 h. According to our experience as to what quantity of compound is transported per hour through the particular spectrometer at 10—40 mtorr of entrance pressure we must conclude that less than 1 mg gaseous product ever passed the microwave cell.

The microwave spectra obtained were, however, identical with spectra from a second preparation also starting with 3.22 g of $KC(CN)_3$ which was first converted to $AgC(CN)_3$ [5] in a 90% yield. While stirring $AgC(CN)_3$ in vacuo at $-50$°C pure dry $H_2S$ was admitted at an initial pressure of 370 torr, decreasing to 230 torr in 90 min. This corresponded to consumption of 0.0089 moles of $H_2S$ or 80% of the quantity necessary for the process $AgC(CN)_3 + \frac{1}{2} H_2S \rightarrow \frac{1}{2} Ag_2S + HC_4N_3$. The reaction mixture was left in contact with $H_2S$ at 230 torr overnight with the temperature gradually raising to 0°C. At this temperature $HC_4N_3$ was distilled from $Ag_2S$ into a vial overnight together with $H_2S$. It was finally separated from $H_2S$ at 0°C in the vial until the pressure was ca. 40 mtorr. The yield appeared lower than above, but was still large enough to permit recording of spectra for ca. 2 h, the quantity passing the spectrometer again being less than 1 mg. Again, chemical change of the substance in the vial was a limiting factor.

Since the elements common to the two preparations are H, C and N no alternative interpretation of the observed spectra involving O and/or S containing species is possible. Also, prodution of hypothetical symmetric top species such as $N(CN)_3$, $HC(NC)_3$ etc. by *both* methods is impossible. Continued attention to $HC(CN)_3$ should primarily be directed towards producing larger quantities, probably not in a bulb but in a "flow" system. Here, the data of Table 1 should help. It may be of interest that simply flowing $H_2S$ over $AgC(CN)_3$ at room temperature, as tried by us, produced no spectral lines in the 34370—34385 MHz region in which the strong line at 34379.0 MHz should occur.

At the present stage it would be far-fetched to associate $HC(CN)_3$ with laboratory practice. However, its existence might interest astrophysicists. Related compounds such as cyano-acetylene, $HC{\equiv}C{-}C{\equiv}N$, exist in interstellar space [6] where $HC(CN)_3$ now must be expected to be stable as far as temperature is concerned.

## ACKNOWLEGEMENTS

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