ISOCYANOGEN, CNCN: INFRARED AND MICROWAVE SPECTRA AND STRUCTURE

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The molecule CNCN, isocyanogen, has been identified on the basis of its vibrational and rotational spectra. Three of the five vibrational fundamentals have been recorded in the infrared with high resolution. The microwave spectra of the parent species and both ^{13}C-substituted species in natural abundance have been measured, and a preliminary structure determined.

1. Introduction

Because of its possible role in interstellar chemistry, the structure and dipole moment of CNCN were predicted from ab initio calculations in 1980 by Haese and Woods [1]. A year later the infrared spectrum of the molecule was predicted, also from ab initio calculations, by Sana and Leroy [2]. However, there has been until now no experimental evidence for the existence of the species CNCN. In August 1988, van der Does and Bickelhaupt [3] published a report of the synthesis and detection of the symmetric isomer of cyanogen, CNNC or diisocyanogen. We repeated their synthesis in our laboratory, and sublimed the thermolysis products into the absorption cells of a high-resolution infrared interferometer and a microwave spectrometer. The resulting infrared spectra indicate unambiguously the presence of CNCN and NCCN in the ratio 7:3 in the gaseous phase. The microwave spectrum confirmed the structure of the non-centrosymmetric species to be that of CNCN.

2. Experimental considerations

The chemical preparation of CNCN was carried out in close analogy to the synthesis of CNNC as described in ref. [3]. The precursor, norbornadienone azine, was held at 50–60°C and its vapor at 10^{-3} mbar was flash-pyrolyzed at a temperature of 500°C. The trapped products of the pyrolysis were redistilled at low temperature, and then allowed to sublime at -96°C into the absorption cells of the spectrometers.

Infrared spectra were recorded with a Bruker IFS 120 HR high-resolution vacuum interferometer [4]. For the measurement of the ν_1 and ν_2 bands above 2000 cm^{-1}, a 15 cm cell was filled to 1.0 mbar. The interferometer was equipped with a KBr beamsplitter, a globar source, a liquid-nitrogen-cooled MCT detector and a filter with a bandpass between 2130 and 2370 cm^{-1} for ν_1 and between 1740 and 2110 cm^{-1} for ν_2. The nominal resolution of 0.0033 cm^{-1} was chosen to match the slightly pressure-broadened lines. Residual CO_2 lines in the spectrum provided calibration. The far-infrared region was also recorded with the interferometer, which for this region was equipped with a 6 μm mylar beamsplitter, a liquid-helium-cooled silicon bolometer, and a low-pass filter with a cut-off at 375 cm^{-1}. The cell used for this measurement was 270 cm long, and was filled to only 0.25 mbar, in order to avoid pressure broadening. The nominal resolution could therefore be chosen to be 0.002 cm^{-1} for this measurement. Calibration was provided by residual water lines in the spectrum. The signal from the CNCN molecule showed no decay over 12 h.

The CNCN sample was not so stable in the metal

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cell of the microwave spectrometer. It exhibited a halflife of ≈6 min in the wavequide cell at 10^{-2} mbar. A slow flow was adjusted, with the sample held at −96°C, so that the rotational spectrum could be measured with a Hewlett–Packard 8460A MRR Stark spectrometer [5].

3. Infrared spectrum

The first indication that the observed spectrum could not belong to a centrosymmetric isomer of NCCN was the fact that two relatively strong stretching modes were observed in the CN stretching region of the spectrum, whereas only one infrared active mode would be allowed for CNCN. Furthermore, since we could completely resolve the rotational structure of both bands, as illustrated in figs. 1 and 2, it was immediately obvious that there is no spin-statistical alternation of intensity with J due to identical nitrogen nuclei. The analysis of the fundamental band of each band system confirmed that both bands come from the same molecule. This is shown in table 1, in which the most important parameters of the observed fundamentals, ν_1 and ν_2, are listed. The ν_2 (pseudo-asymmetric C≡N stretching) band is just twice as strong as the ν_1 (pseudo-symmetric C≡N stretching) band. A small amount of HCN was observed in a broad-band spectrum covering 1000–4000 cm^{-1}. No absorption was observed corresponding to the infrared-active stretching band of NCCN at 2157 cm^{-1}. Since we determined that the sample contained ≈30% NCCN, as shown below, the NCCN band must be considerably weaker than the bands shown in figs. 1 and 2.

In the far-infrared spectrum, both the ν_5 band of NCCN and a stronger new band system, the ν_5 of CNCN, could be observed. The Q-branch region of the new band system is shown in fig. 3. The parameters of this band, which again shows no spin statistics, are included in table 1. The extensive hot band systems associated with each of the bands so far observed will allow the determination of a significant number of energy levels of CNCN.

An estimate of the relative abundance of NCCN and CNCN in the sample was obtained by comparing the intensities of the ν_5 bending mode of NCCN in the newly synthesized sample and in a pure sample of NCCN. This comparison indicated that the sample we prepared contained in the gas phase 30% NCCN. The NCCN band shows clear spin statistics, in contrast to the band of CNCN. There was no sign between 50 and 350 cm^{-1} of a further band which could be the corresponding bending mode of CNNC.

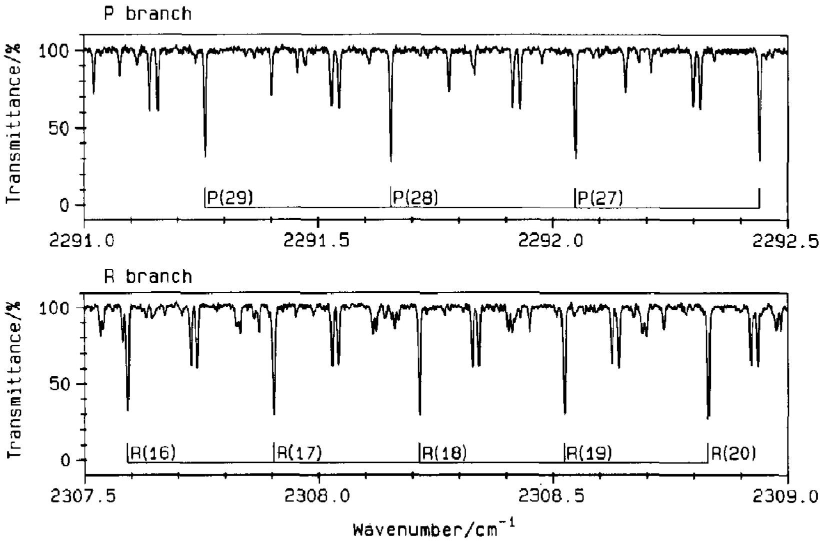

Fig. 1. Excerpts from the P and R branches of the ν_1 fundamental vibrational band of CNCN.

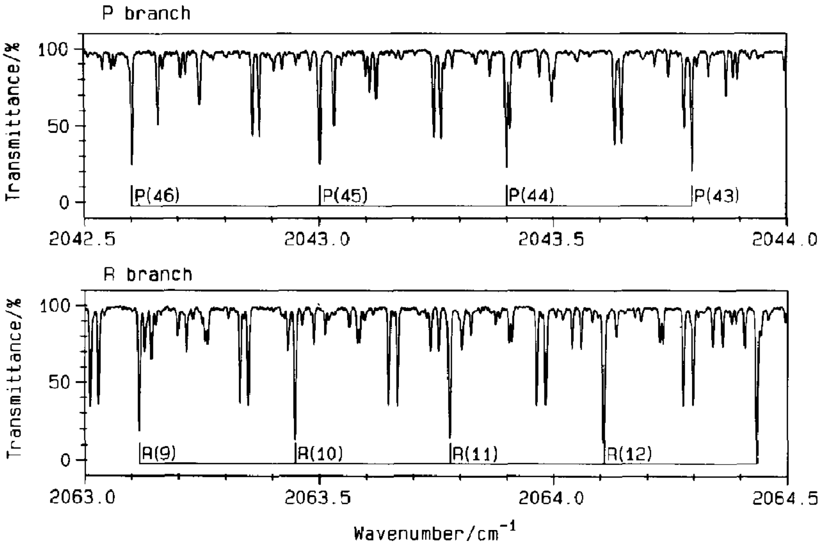

Fig. 2. Excerpts from the P and R branches of the ν_2 fundamental vibrational band of CNCN.

Table 1
Spectroscopic constants of observed infrared fundamental bands of CNCN

	ν_1	ν_2	ν_5
ν_0 (cm^{-1})	2302.001	2059.731	194.753
B'' (cm^{-1})	0.17259	0.17259	0.17259
$10^4(B'-B'')$ (cm^{-1})	−9.044	−6.079	4.954
$10^8 D_0$ (cm^{-1})	2.4	2.4	2.5

We therefore conclude that the remaining 70% of our sample consisted of the new species CNCN plus an undetermined amount of HCN.

4. Microwave spectrum

The rotational constant B_0 calculated from the infrared bands allowed the rotational spectrum of CNCN to be found immediately at the expected frequency. It is shown in fig. 4, which displays the observed spectrum of the parent isotopic species for the $J=2\leftarrow1$ rotational transition. An increase in amplification after the ground state line allows the details of the vibrational satellites to be seen. Each line is split into a complex nuclear quadrupole hyperfine pattern by two distinctly non-equivalent nitrogen atoms. The l-type doubling is identical to that exhibited in the infared bands. The relative intensity of the l-type doublets for 0001^10^0 and 0000^01^1 and the l-type doubling constant q_4 may be used to estimate the wavenumber of the as yet unobserved bending mode ν_4, which is thus expected to lie in the range 420–470 cm^{-1}.

The microwave spectrum of each of the ^{13}C-substituted species of CNCN was observed in natural abundance, and the frequencies of the ground state lines are listed in table 2 together with the frequencies so far determined for the parent species. All the frequencies listed are preliminary and are only accurate to ±0.5 MHz, since the quadrupole hyperfine structure has not yet been analyzed. For the same reason, we can give only an approximate value, 0.68 D, for the electric dipole moment of CNCN.

As the flow rate was first being adjusted in the microwave cell, the presence of a more volatile substance, showing no microwave spectrum in the range 18–26 GHz, contributed to the vapor pressure. Later, at the same total pressure, the CNCN signal increased, after most of the more volatile compound had sublimed. In view of the infrared results, this more volatile component is presumed to be NCCN.

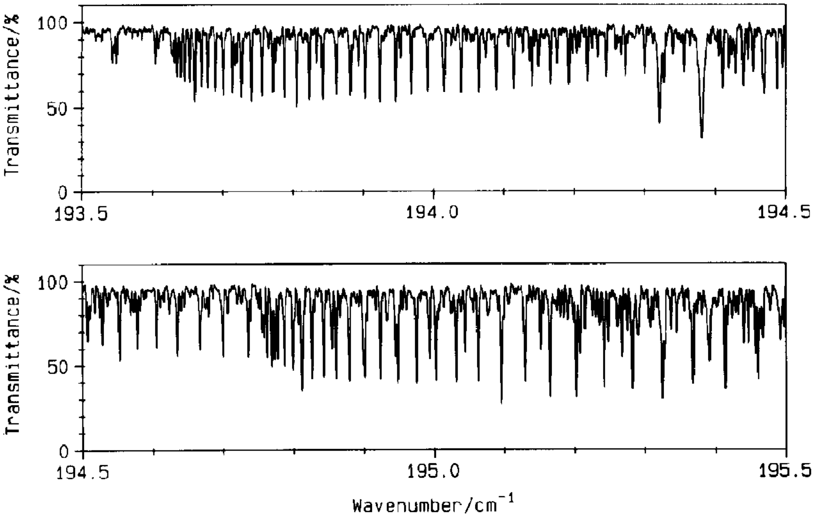

Fig. 3. The Q-branch region of the ν_5 fundamental band of CNCN.

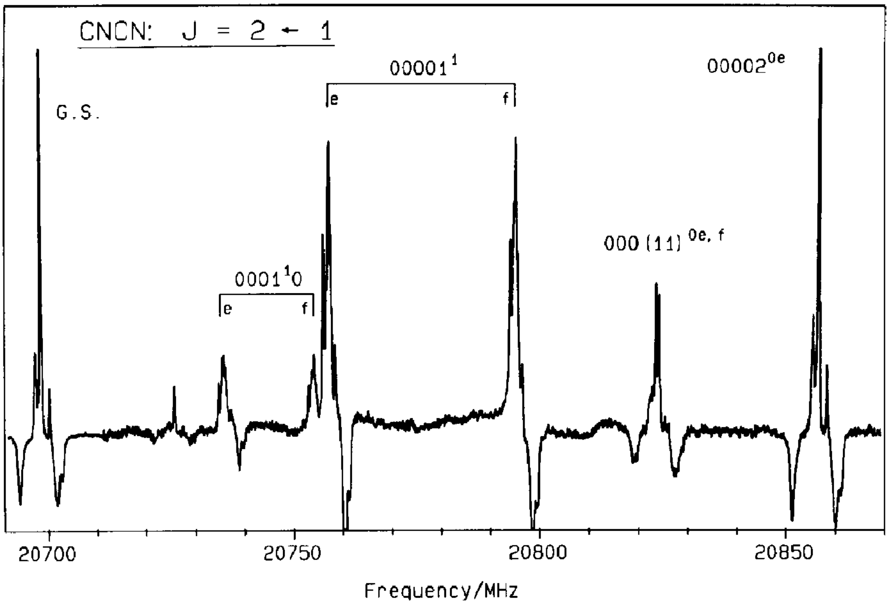

Fig. 4. Microwave spectrum of CNCN recorded with 2000 V/cm Stark modulation. The amplification was increased by 20 dBm at 20710 MHz.

5. Discussion

A full analysis of all of the observed microwave, millimeter wave and infrared spectra, including an analysis of the nitrogen nuclear quadrupole hyperfine splitting in the microwave spectrum and a full rotational analysis of the infrared bands, will be published separately. A precise determination of the permanent electric dipole moment depends on a completed hyperfine analysis. The two remaining infrared fundamental bands ν_3 and ν_4 will be recorded and analyzed.

Table 2
Observed $J=2\leftarrow1$ rotational transitions of CNCN and derived parameters

	v_1	v_2	v_3	v_4	v_5	ν (MHz)	B_{eff} [a] (MHz)
CNCN	0	0	0	0	0	20696.4	5174.1 [b]
	0	0	0	0	1^{1e}	20757.0	5189.3
	0	0	0	0	1^{1f}	20794.3	5198.6
	0	0	0	1^{1e}	0	20735.0	5183.8
	0	0	0	1^{1f}	0	20753.5	5188.4
	0	0	0	(1	$1)^{0e,f}$	20823.0	5205.8
	0	0	0	0	2^{0e}	20854.5	5213.6
^{13}CNCN	0	0	0	0	0	19989.0	4997.3
CN^{13}CN	0	0	0	0	0	20617.8	5154.4
	$q_5=9.33$ MHz						
	$q_4=4.63$ MHz						

[a] $B_{\mathrm{eff}}=\nu/(2J''+2)$.

[b] $B_0=5216$ MHz was calculated by Haese and Woods [1].

The spectra shown here clearly are all due to one linear, polar molecule. The ground state B value from all three infrared bands and from the rotational spectrum agree within the present experimental error. The ΔB value obtained from the ν_5 band agrees with the difference in B values between the ground state and the 0000^01^{1e} state in the microwave spectrum. The pattern of vibrational satellites in the rotational spectrum can only be due to a linear molecule. Finally, the rotational transitions due to the ^{13}C-substituted species allow no carrier of the spectra to be considered other than CNCN.

From the data presently available, we can make a comparison of the structure and infared spectrum of CNCN with ab initio predictions for these parameters. This information is summarized in table 3.

It appears that van der Does and Bickelhaupt [3] may indeed have measured the NMR spectrum of CNNC in solution at −30°C, but that if the trapped sample is allowed to vaporize, an isomerization takes place between liquid-nitrogen temperature and the temperature of sublimation leading to the approximate abundances of NCCN and CNCN indicated above. There is no indication in our infrared spectra of the other symmetric isomer, CNNC. The degree of isomerization may depend on the conditions of thermolysis of the azine precursor and on the subsequent sublimation conditions.

CNCN is very stable in the gas phase in a glass absorption cell at low pressure, but decays slowly in a metal cell. It is a polar molecule for which a directed search in the interstellar medium can now be attempted.

Since HCN and HNC [6–9] are prominent constituents of interstellar clouds with equal abundances [10], the following reaction might occur:

$$HCNH^+ + HCN \rightarrow H_2CNCNH^+ + h\nu\,,$$

Table 3
Vibrational fundamentals and structure of CNCN compared with predicted values

	Theoretical		Experimental this work
	ref. [2]	ref. [2], corr. [a]	
$\tilde{\nu}_1$ (cm^{-1})	2642	2261	2302.00
$\tilde{\nu}_2$ (cm^{-1})	2309	2004	2059.73
$\tilde{\nu}_3$ (cm^{-1})	1035	944	– [b]
$\tilde{\nu}_4$ (cm^{-1})	590	492	420–480 [b]
$\tilde{\nu}_5$ (cm^{-1})	262	239	194.753
	r_e (pm)		r_0 (pm) this work
	ref. [1]	ref. [2]	
r(C≡N–)	117.5	117.3	117.5
r(N–C)	131.0	130.5	131.4
r(–C≡N)	115.0	114.6	116.0

[a] Values from ref. [2], corrected for each mode by the difference $\tilde{\nu}_i$(theor) − $\tilde{\nu}_i$(exp) determined for cyanogen.

[b] Spectral range not yet recorded.

$H_2CNCNH^+ + e \rightarrow CNCN + H_2 + H$.

The production of cyanoacetylene by the reaction

$HCCH + HCN \rightarrow H_2 + HCCCN$

in electric discharges is very efficient [1,11]. A corresponding reaction between HCN and HNC mediated by ion–molecule reaction steps could also lead to CNCN.

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