Detection of the Millimeter Wave Spectrum of Hydrogen Isocyanide, HNC[1,2]

R. A. Creswell, E. F. Pearson, M. Winnewisser, and G. Winnewisser

Physikalisch-Chemisches Institut, Justus Liebig-Universität, Giessen
and Max Planck-Institut für Radioastronomie, Bonn

(Z. Naturforsch. **31 a**, 221–224 [1976]; received March 11, 1976)

The rotational spectra of three isotopic species of HNC have been observed in the millimeter wave region. In the case of the parent species, $H^{14}N^{12}C$, our measurement of the $J=1\leftarrow 0$ transition unequivocally confirms the assignment of the U90.7 interstellar line to HNC. For the parent species the molecular constants obtained are $B_0 = 45332.005\,(40)$ MHz and $D_0 = 0.1019\,(50)$ MHz. Structural parameters derived from the ground state rotational constants of this linear molecule are $r\,(H-N) = 0.987\,(3)$ Å and $r\,(N-C) = 1.171\,(4)$ Å.

I. Introduction

Many compounds of general formula R – N – C have been well characterised and they constitute an important branch of organic chemistry [1]. Among the simpler compounds of this type are CH_3NC, C_2H_5NC, C_2H_3NC and C_6H_5NC all of which have been studied in the gas phase by rotational spectroscopy [2–5]. However the parent molecule HNC, hydrogen isocyanide, has hitherto proved to be somewhat elusive. Evidence for its existence was first obtained in 1963 by Milligan and Jacox [6] who observed its infrared absorption spectrum following the photolysis of methylazide in an argon matrix at 4 °K. The authors later reported that similar absorption bands were produced by the photolysis of HCN in both argon and nitrogen matrices at 14 °K [7].

In 1971 Snyder and Buhl [8, 9] reported the observation of a new interstellar emission line known as U90.7 at 90665 ± 1 MHz from the radio sources W51 and DR21. Following a suggestion by Herzberg [9] concerning the interstellar X-ogen line U89.2, now known [10] to be due to HCO^+, it was found that assigning the U90.7 line as the $J=1\leftarrow 0$ transition of HNC implied a not unreasonable range of structural parameters for this species. Observations by Zuckerman et al. [11] of the emission from the very young cluster NGC 2264 led to an improved value of 90663.9 ± 0.5 MHz for its rest frequency. Even though the emission lines from this source are narrow, no hyperfine structure could be resolved for U90.7 which is consistent with the small ^{14}N quadrupole splitting observed in other isocyanides [2–5].

Ab initio calculations on HNC have been performed by Barsuhn [12], Pearson et al. [13] and Kramer et al. [20] yielding a structure and hence a rotational constant consistent with the assignment of the observed interstellar line to HNC. Calculations on the HCN – HNC isomerisation have been made by Booth and Murrell [14] and more elaborately by Pearson et al. [15], this latter work indicating that HNC is higher in energy than HCN by 5100 cm^{-1}. An attempt to observe a line at 90665 MHz in HCN by Blackman et al. [16] was unsuccessful and was interpreted to give a lower limit of 3790 ± 160 cm^{-1} for the energy difference between HCN and HNC.

Recently Arrington and Ogryzlo [17] observed an IR emission feature at 2.74 μ when active nitrogen produced in a 2450 MHz discharge was reacted with HCN, C_2H_2, C_2H_4, CH_3CN, CH_3Br or CH_3I. This feature is close to the 2.76 μ observed for the N – H stretch in the matrix study of Milligan and Jacox [6, 7]. Furthermore the emission was sufficiently strong in the case of the CH_3Br reaction to permit resolution of the rotational structure and B_0 was thus found to be 45270 ± 60 MHz, again supporting but not definitely proving the assignment of the interstellar line to HNC.

This paper reports the observation of the laboratory rotational spectrum of HNC and the unequivocal assignment of the U90.7 interstellar line to HNC.

II. Experimental Procedures

The millimeter wave spectrometer, which has previously been described in detail [18, 19], consisted of an harmonic generator radiation source with video detection and a dedicated PDP 8/1 computer system

Reprint requests and correspondence to Dr. Robert A. Creswell, Physikalisch-Chemisches Institut, Justus Liebig-Universität, Heinrich-Buff-Ring 58, *D-6300 Giessen*.

[1] This work was supported in part by funds from the Deutsche Forschungsgemeinschaft.

[2] Presented in part at the Astronomische Gesellschaft, Wissenschaftliche Tagung, Oberkochen, March 10–12, 1976.

for signal averaging and frequency measurement. The free space absorption cell was built with sections of 10 cm diameter glass pipe to give a total length of 2.5 m. At one end of this cell an inlet port was constructed to enable the reactant gas to be mixed with the products of a radio frequency discharge. The discharge tube passed through the inductive section of a tank circuit tuned to about 4.5 MHz, and in this way up to 300 Watts of continuous R.F power could be coupled in.

Methyl bromide or iodide was reacted with the active nitrogen produced by the discharge and absorption due to HNC was readily detected in the products which were continuously flowed through the cell. HCN and BrCN or ICN, depending upon the methyl halide used, were also identified as reaction products by their millimeter wave absorptions. A golden brown deposit appeared on the cell wall during the course of the experiments. Total gas pressures employed were typically 30 mtorr with a nitrogen partial pressure of about 20 mtorr. The DNC and $HN^{13}C$ isotopic species were observed using CD_3I (99.5% D) and $^{13}CH_3I$ (90% ^{13}C).

III. Spectra, Assignment and Analysis

Weak lines close to the expected frequencies of the $1 \leftarrow 0$ and $2 \leftarrow 1$ HNC transitions were observed and are illustrated in Figure 1. The corresponding transitions in the isotopic species DNC and $HN^{13}C$ were found close to the positions predicted using the calculations of Kraemer, Hennig and Dierckxsen[20]. The measured frequencies are listed in Table I. Ground state rotational constants, B_0, and centrifugal distortion constants, D_0, were calculated from the observed frequencies using the relationship

$$\nu = 2B_0(J+1) - 4D_0(J+1)^3$$

and the derived constants are listed in Table II.

Table I. Observed transition frequencies[a] of HNC.

Transition $J+1 \leftarrow J$	HNC	DNC	$HN^{13}C$
$1 \leftarrow 0$	90663.602	76305.727	87090.851
$2 \leftarrow 1$	181324.758	152609.774	174179.411

[a] Frequencies are in MHz with an estimated experimental uncertainty of ±50 kHz corresponding to three times the standard deviations.

Proof that the observed transitions do in fact arise from HNC comes from several sources. Shown in Fig. 1 is the absence of absorption which results when the discharge and gas flows are stopped thus trapping the reaction products in the cell. This null test indicates that the absorption is arising from a transient species, and it was repeated for all of the lines assigned to HNC in this paper. It also indicates that the life-time of the species, under the conditions of the present experiment, is appreciably less than one second. The second piece of evidence comes

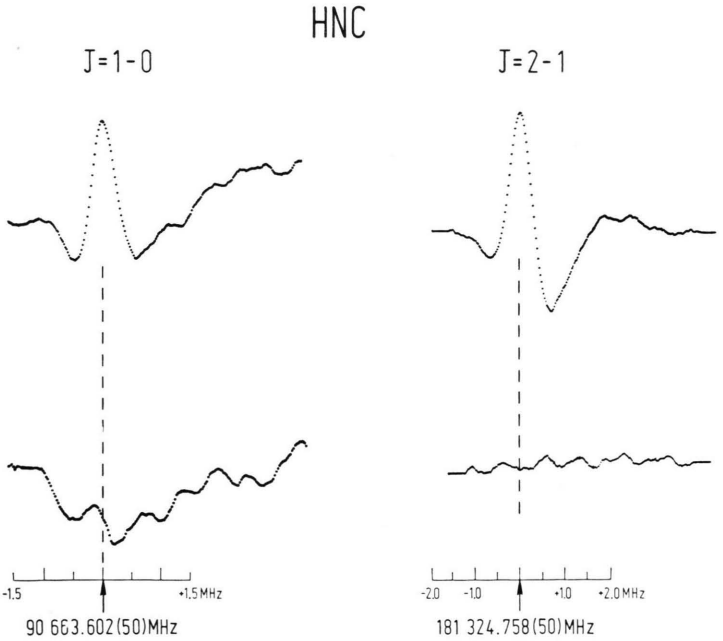

Fig. 1. The $J=1 \leftarrow 0$ and $2 \leftarrow 1$ transitions of HNC observed in the products of the reaction of CH_3I with excited N_2. The upper traces show the absorption lines with the discharge and flow system running, the lower show the absence of absorption found when the reaction products are trapped in the cell and the discharge is turned off. The lower trace for the $1 \leftarrow 0$ transition is expanded by a factor of two relative to the upper $1 \leftarrow 0$ trace. Each trace shown consists of 250 data points averaged over 2000 sweeps each of 15 ms duration followed by 25 point smoothing. The total time needed to acquire one of the traces was approximately 2 minutes.

Table II. Spectroscopic constants of HNC.

Species	B_0/MHz (obs)	D_0/MHz (obs)	D_0/MHz (calc) [a]
HNC	45332.005 (40)	0.1019 (50)	0.0977
DNC	38153.004 (40)	0.0700 (50)	0.0657
$HN^{13}C$	43545.616 (40)	0.0955 (50)	0.0905

[a] For harmonic force field see Reference [6].

from the sharpness of the observed lines. These line widths imply an absolute value of eqQ less than 1 MHz whereas eqQ in HCN is -4.708 MHz. This situation is consistent both with observations on other cyanide isocyanide pairs [2–5] and the calculated value [13] of 0.93 MHz for eqQ in HNC. All other observed lines in the frequency region of the $J = 1 \leftarrow 0$ transitions of the various HNC isotopic species displayed resolvable hyperfine structure.

The third piece of evidence comes from the chemistry of the production; the same absorptions are found for both methyl bromide and methyl iodide thus indicating that the molecule does not contain a halogen atom. Also the IR emission found in Ref. [17] from a similar reaction was assigned as coming from HNC. Comparison of the absorption intensity of HNC with that of HCN indicates an HNC partial pressure of less than 1 mtorr in the reaction mixture. Further support for the observed species being HNC comes from the close agreement between values of D_0 calculated from the harmonic force field [6] with the experimentally determined D_0 constants. These values are compared in Table II.

The final piece of evidence that the species observed is in fact HNC, and the most conclusive of all, is the effect of isotopic substitution upon the rotational constants and the structure which is deduced from this. Since no ^{15}N isotopic species have so far been studied it is not possible to calculate a complete r_s structure. However, a close approximation to such a structure is obtained using the substitution coordinates of the H and C atoms and applying the first moment condition to locate the nitrogen atom. Such a procedure gives $r_{NH} = 0.987094(23)$ Å and $r_{NC} = 1.170947(30)$ Å, where these uncertainties reflect only the experimental uncertainties in the parameters. Estimation of error limits for r_s structures is a difficult problem since they have no clear physical significance but merely a convenient operational definition. Perhaps the most useful rule for estimating uncertainties is that due to Costain [21] which gives $r_{NH} = 0.9871(33)$ Å and $r_{NC} = 1.1709(38)$ Å. Again the meaning of these uncertainties is not wholly clear but they are useful if the parameters are to be compared with those of other molecules. The extensive C I calculation reported in Ref. [13] gives 0.995 Å and 1.169 Å for the NH and NC bond lengths respectively, but these are equilibrium distances. Table III presents a comparison of the structure of HNC with parameters from similar molecules, and it is evident from this that the HNC structure shows no special peculiarities.

Table III. Internuclear distances of HNC and some related Molecules in units of Å.

Molecule	H−N or C−N	H−C or C−C	C≡N	N=C	Reference
HNC	0.987			1.171	This work [a]
HCN		1.063	1.155		22
CH_3NC	1.424			1.166	23
CH_3CN		1.458	1.157		23
HNCO	0.986			1.209	24
HCNO		1.060	1.161		25

[a] The moments of inertia I_b were calculated using BXI = 505379 MHz uÅ².

IV. Astrophysical Implications

It has been demonstrated by Buhl and Snyder [26] and more recently by Morris et al. [27] that the interstellar distribution of HNC and HCO^+ follows that of HCN more closely than that of any other common interstellar molecule. Buhl and Snyder deduced that the upper levels of these transitions of each of these molecules must have similar life-times. In Table IV we have summarized the characteristics of the observed interstellar features attributed to HNC, HCN and HCO^+. For the interstellar sources DR21 (OH) and W51 we have corrected the velocity of the local standard of rest quoted by Snyder and Buhl using the new laboratory rest frequency. In the case of DR21 (OH) two distinct velocity components are observed for HCO^+, one at -1.2 kms^{-1} and a stronger one at -5.2 kms^{-1}, the latter of which is correlated with the HNC feature. Thus for both molecular sources the results are in good agreement with the known velocities of HCN and HCO^+.

Further strong support for the assignment of HNC as the carrier of U90.7 comes from a recent study of the newly discovered molecular cloud in

Table IV. Interstellar emission features of HNC, HCN and HCO^+.

Source	Molecules observed	T_A/K	Δv/km s^{-1}	LSR Radial velocity/km s^{-1}	Ref.
SgrA (NH_3)	HNC	(values not reported)			i
	HCN	8	40	+26	d
	HCO^+	1.6	38	+23.8	a
ORi A	HNC	(values not reported)			i
	HCN	12.9/18.0	3.67	+9.43	h, c
	HCO^+	12.4	3.8	**+8.8**	a
OMC 2	HNC	6.5	1.62(17)	(+11.14)†	b
	HCN	8	1.70(17)	+11.14(10)	b
	HCO^+	8.5	1.81(17)	(+11.14)†	b
NGC 2024	HNC	(values not reported)			i
	HCN	4.22	2.0	+11.0	e, k
	HCO^+	2.4	3.5	+8.8	a
W3 (OH)	HNC	(values not reported)			i
	HCN	3	14	−49	d
	HCO^+	2.5	5.0	−48.2	a
W51	HNC	1.6	∼15	+55.4 *	f
	HCN	5	16	+55	d
	HCO^+	5.0	11.0	+58.3	a
DR21 (OH)	HNC	—	—	−5.5 *	f
	HCN	1.94/5	2.5/12	−4.9/−1.0	k, d
	HCO^+	3.9/2.1	3.7/3.7	−5.2/−1.2	a
NGC 2264	HNC	2.5	∼2.5	+7.6	g
	HCN	5/2.08(6)	∼3/5.81(9)	+7.0/4.7(1)	g, h
	HCO^+	4.0	5.0	+7.3	a

† These velocities have been used to derive the rest frequencies for the $J=1\leftarrow 0$ transitions of $\nu_0(HNC) = 90663.59(15)$ MHz and $\nu_0(HCO^+) = 89188.51(15)$ MHz.

* Corrected V_{LSR} shift to laboratory rest frequency.

a J. M. Hollis, L. E. Snyder, D. Buhl, and P. T. Giguere, Astrophys. J. **200**, 584 [1975].

b M. Morris, B. Zuckerman, B. E. Turner, and P. Palmer, Astrophys. J. **192**, L 27 [1974].

c F. O. Clark, Astrophys. J. **200**, L 115 [1975].

d L. E. Snyder and D. Buhl, Highlights of Astronomy **1971**, p. 407 (De Jager, ed.).

e D. Buhl and L. E. Snyder, Astrophys. J. **180**, 791 [1973].

f L. E. Snyder and D. Buhl, Ann. N. Y. Acad. Science **194**, 17 [1972].

g B. Zuckerman, M. Morris, P. Palmer, and B. E. Turner, Astrophys. J. **173**, L 125 [1972].

h C. A. Gottlieb, C. J. Lada, E. W. Gottlieb, A. E. Lilley, and M. M. Litvak, Astrophys. J. **202**, 655 [1975].

i L. E. Snyder and D. Buhl, Bull. Amer. Astr. Soc. **4**, 227 [1972].

k M. Morris, P. Palmer, B. E. Turner, and B. Zuckerman, Astrophys. J. **191**, 349 [1974].

Orion, OMC 2, which produces unusually narrow line widths. Morris et al.[27] derived a rest frequency for U90.7 in this cloud of 90663.59(15) MHz which is in excellent agreement with our laboratory rest frequency of the $J=1\leftarrow 0$ transition of HNC.

Recently Thaddeus and Turner[28] observed in this same source the emission spectrum of the molecular ion HN_2^+ and were able to resolve the nuclear hyperfine structure of both the outer and inner ^{14}N nuclei. From their data and the line width of HNC in this source we derive an upper limit for $|eqQ| = 1.0$ MHz, in agreement with the reported laboratory measurements.

Acknowledgements

R.A.C. and E.F.P. are grateful to the Alexander von Humboldt Stiftung for fellowships. We thank Professor D. Seebach for providing the initial sample of CD_3I. Drs. Kraemer, Hennig and Diercksen kindly furnished us with their calculations on HNC before publication.

1 I. Ugi (Ed.), Isonitrile Chemistry, Academic Press, New York 1971.

2 S. N. Ghosh, R. Trambarulo, and W. Gordy, J. Chem. Phys. **21**, 308 [1953].

3 K. Bolton, N. L. Owen, and J. Sheridan, Spectrochim. Acta, **25 A**, 1 [1969].

4 K. Yamada and M. Winnewisser, Z. Naturforsch. **30 a**, 672 [1975].

5 B. Bak, B. P. Van Eijck, and C. Kierkegaard, J. Mol. Struct. **18**, 429 [1973].

6 D. E. Milligan and M. E. Jacox, J. Chem. Phys. **39**, 712 [1963].

7 D. E. Milligan and M. E. Jacox, J. Chem. Phys. **47**, 278 [1967].

8 L. E. Snyder and D. Buhl, Bull. Amer. Astr. Soc. **3**, 388 [1971].

9 L. E. Snyder and D. Buhl, Ann. N. Y. Acad. Sci. **194**, 17 [1972].

10 R. C. Woods, T. A. Dixon, R. J. Saykally, and P. G. Szanto, Phys. Rev. Lett. **35**, 1269 [1975].

11 B. Zuckerman, M. Morris, P. Palmer, and B. E. Turner, Astrophys. J. **173**, L125 [1972].

12 J. Barsuhn, Astrophys. Letters **12**, 169 [1972].

13 P. K. Pearson, G. L. Blackman, H. F. Schaefer, B. Ross, and U. Wahlgren, Astrophys. J. Lett. **184**, L19 [1973].

14 D. Booth and J. N. Murrell, Mol. Phys. **24**, 1117 [1972].

15 P. K. Pearson, H. F. Schaefer, and U. Wahlgren, J. Chem. Phys. **62**, 350 [1975].

16 G. L. Blackman, R. D. Brown, P. D. Godfrey, and H. I. Gunn, Chem. Phys. Lett. **34**, 241 [1975].

17 C. A. Arrington and E. A. Ogryzlo, J. Chem. Phys. **63**, 3670 [1975].

18 M. Winnewisser, Z. Angew. Phys. **30**, 359 [1971].

19 M. Winnewisser and B. P. Winnewisser, Z. Naturforsch. **29 a**, 633 [1974].

20 W. P. Kraemer, P. Henning, and G. H. F. Diercksen, to be published.

21 C. C. Costain, Trans. Amer. Cryst. Assoc. **2**, 157 [1966].

22 G. Winnewisser, A. G. Maki, and D. R. Johnson, J. Mol. Spectroscop. **39**, 149 [1971].

23 C. C. Costain, J. Chem. Phys. **29**, 864 [1958].

24 W. H. Hocking, M. C. L. Gerry, and G. Winnewisser, Can. J. Phys. **53**, 1869 [1975].

25 J. A. Duckett, A. G. Robiette, and I. M. Mills, to be published.

26 D. Buhl and L. E. Snyder, Astrophys. J. **180**, 791 [1973].

27 M. Morris, B. Zuckerman, B. E. Turner, and P. Palmer, Astrophys. J. **192**, L27 [1974].

28 P. Thaddeus and B. E. Turner, Astrophys. J. **201**, L25 [1975].