LONG CARBON CHAIN MOLECULES IN THE LABORATORY AND IN SPACE

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The unsaturated long carbon chain molecules of the type $HC_{2n+1}N$ (with n=1,2..) have the remarkable property of being very stable under a wide variety of different laboratory and interstellar conditions. In fact, they can be synthesized in the laboratory under the action of a radio frequency discharge in a mixture of acetylene, HCCH, and hydrogen cyanide, HCN (Creswell et al. 1977 , Winnewisser et al. 1978). Once they are formed they are for example very stable towards temperature changes as well as saturation of the carbon bonds due to hydrogen addition. In the laboratory their chief cause of destruction is polymerization. These experiments were triggered by our observation that in the course of producing hydrogen isocyanide, HNC, (Creswell et al. 1976) by reacting CH_3I with N_2 in a gas discharge, also small amounts of HC_3N were present which clearly requires the joining together of four heavy atoms from different starting molecules.

Over the last couple of years we have carried out more detailed experiments of the acetylene/hydrogen cyanide discharges to elucidate the reaction mechanism and its suspected relevance to the formation of interstellar cyanopolyynes by using ^{13}C isotopic tracers and different functional groups, such as CH_3, ... The present state of our laboratory experiments can be summarized by:

$$HCCH + HCN + discharge \longrightarrow HC_3N + H_2; \quad HC_5N + H_2; \quad (HC_7N + H_2?);$$
$$+ \text{ unidentified lines.}$$
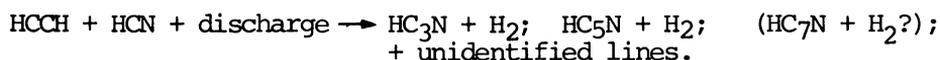
If the experiment is repeated with CH_3CCH the appropriate methyl-cyanopolyynes are obtained. A sample spectrum is shown in Fig.1. If the experiment is performed with carbon-13 enriched hydrogen cyanide the ^{13}C remains entirely with the cyanide group:

$$HCCH + H^{13}CN + discharge \longrightarrow HCC^{13}CN + \quad H_2$$
$$\longrightarrow HCCCC^{13}CN + H_2$$
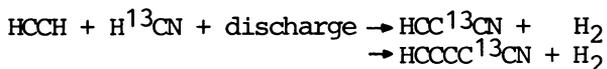
suggesting that the long carbon chain is essentially being formed from the acetylene. In this connection it is interesting to mention that we

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succeeded in detecting the $J = 1 \to 0$; $F = 2 \to 1$ transition of $HCC^{13}CN$ in TMC1, yielding an $^{12}C/^{13}C$ ratio of approximately 60. The appropriate transitions of $H^{13}CCCN$ and $HC^{13}CCN$ were not detected to similar limits, suggesting ^{13}C fractionation which could be caused by the formation mechanism. The $HCC^{13}CN$ emission signal was detected from the peak of the HC_3N cloud in TMC1. This position lies within 1 arc min of the HC_5N emission peaks. Typical medium velocity resolution (0.1 kms $^{-1}$) spectra of TMC1 are displayed in Fig. 2, indicating that the intrinsic linewidths in dark clouds can be as low as 0.2 kms $^{-1}$ which is close to the thermal limit. Cool dark dust clouds offer a great potential for studying precisely the physical conditions with high spectral and spatial resolution.

We have used the high angular resolution of the 100 m radiotelescope to conduct a detailed survey of selected dark dust clouds by employing the cyanopolyyne molecules HC_3N, HC_5N, HC_7N and ammonia NH_3 as molecular probes (see table I). The indication from our surveys of the core regions of dark dust clouds is that the Taurus region is one of many dark dust cloud complexes which contain a sizeable number of small (L < 1 pc) dense ($n(H_2) \sim 10^4 cm^{-3}$) but cool ($T_{kin} \sim 10K$) and low mass (M < 5M$_\odot$) fragments. As judged either from the temperature estimates or from the line widths the studied core regions in TMC1, TMC2, L1544 and L183 (L134N) all have in common being temporarily in a very quiescent stage, with no evidence of embedded protostellar objects. Of the four studied clouds TMC1 shows the highest line intensities in the cyanopolyyne molecules and encompasses the largest projected area. In both the cyanopolyyne and ammonia molecular cloud TMC1 exhibits a conspicous elongated structure forming a common major axis and essentially two minor axes.

Among the transitions used in this survey (Table 1) the three hyperfine components of the $J = 1 \to 0$ transition of HC_3N can best be used for high velocity resolution studies of dark clouds, since spectroscopically no additional splitting is expected to be observable. We have, therefore, used these transitions to study with high spectral resolution (0.027 kms^{-1} = 760 Hz) the dynamics of TMC1. All three hyperfine
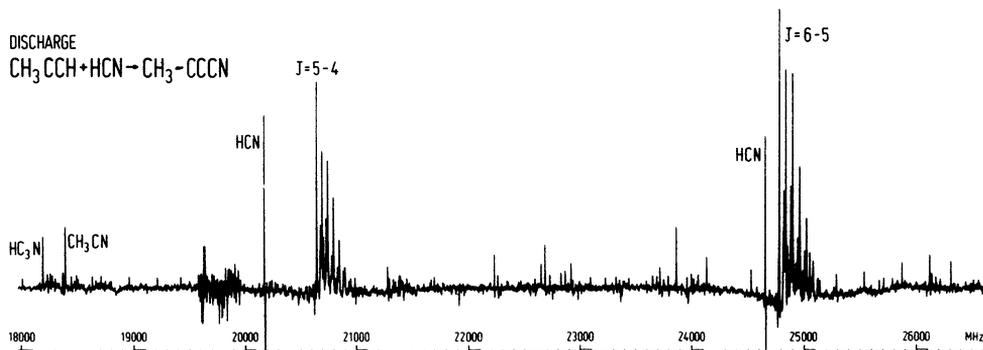

Figure 1. Laboratory Spectrum of CH_3CCCN obtained by discharge. (from Winnewisser and Ziurys, unpublished results).

components exhibit additional structure. The almost identical line profiles of the $F = 1 \rightarrow 1$ and $F = 2 \rightarrow 1$ hyperfine components and their relative intensities which are close to the LTE ratio of 3 to 5 resp., show that the lines are optically thin. The line profiles indicate that two or more separate velocity components are present with a velocity spread of ~ 0.3 kms^{-1} and an intrinsic linewidth ~ 0.2 kms^{-1}. This might be caused by a blend of emission from several filaments aligned with the TMC1 main axis and which are rotating slowly (~ 0.1 kms^{-1}) around the minor and major axis. Although the abundances of the cyanopolyyne and ammonia molecules coincide with the predominant molecular ridge (major axis) in TMC1 their distribution is strikingly different. The maximum of the NH$_3$ emission is conspicuously displaced from the cyanopolyyne maxima by more than 400 arc sec to the northwest, (Fig. 4). Simultaneous observation of the NH$_3$(1,1) and (2,2) transitions at three positions have been used to derive a kinetic temperature of (9 ± 1)K along the main ridge. A sample of the NH$_3$ spectra is given in Fig. 5. From statistical equilibrium calculations on HC$_3$N and NH$_3$ we estimate that the gas density is $\sim 4 \times 10^4$ cm^{-3} and nearly constant along the main ridge but declines sharply along the minor axis. A detailed account of the HC$_{2n+1}$N (n = 1,2,3) and NH$_3$ results will be published elsewhere (Toelle, Ungerechts, Walmsley, Winnewisser and Churchwell). We have, therefore, the curious fact that regions of similar physical parameters such as density, and temperature and age show different chemical composition. The laboratory and interstellar data seem to suggest that the formation of cyanopolyynes
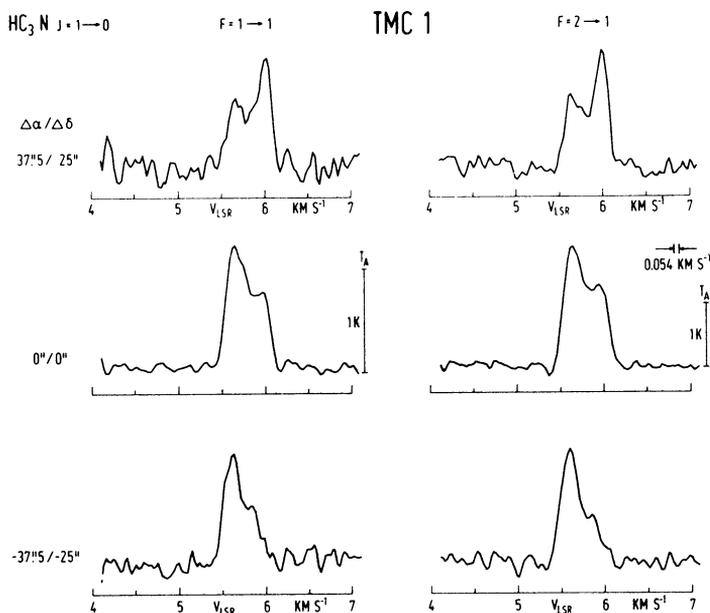

Figure 3. Cyanoacetylene emission in two hyperfine components from three positions along the minor axis of TMC1 taken with high velocity resolution. Crosses (x) in Figure 4 mark the corresponding positions.
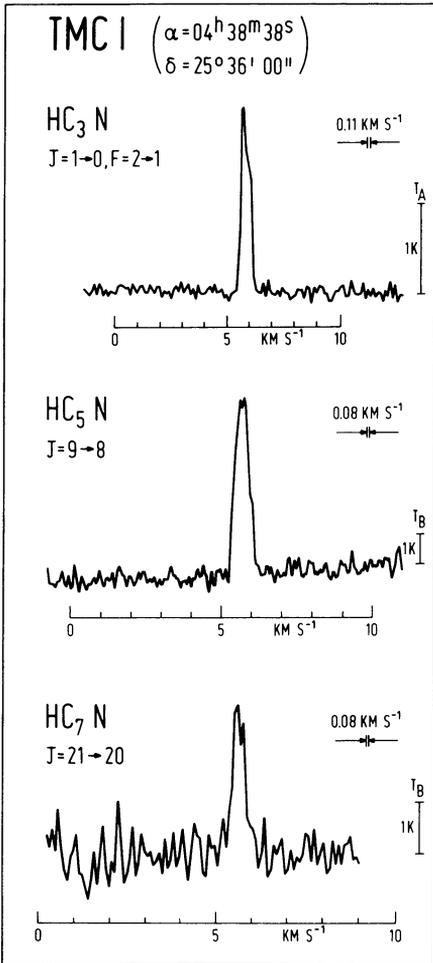
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TMC 1 $\left(\begin{array}{l}\alpha=04^h38^m38^s \\ \delta=25°36'00''\end{array}\right)$

HC$_3$N
$J=1\to0, F=2\to1$
0.11 KM S^{-1}
T_A
1K

HC$_5$N
$J=9\to8$
0.08 KM S^{-1}
T_B
1K

HC$_7$N
$J=21\to20$
0.08 KM S^{-1}
T_B
1K

Figure 2. Medium velocity resolution spectra of cyanopolyynes from TMC1.

Figure 5. NH$_3$ (1,1) and (2,2) emission spectra from TMC1. ⟶

T_B (NH$_3$(1,1)) IN TMC 1

OFFSET IN DEC. (ARC SEC.)

NH$_3$ HPBW

HC$_3$N

HC$_3$N
$J=1\to0$
$F=2\to1$

0.05 pc

OFFSET IN R.A.(ARC SEC.)
Figure 4

TMC 1 $(\alpha_o=04^h38^m38^s,\delta_o=25°36'00'')$ NH$_3$ (2,2)
$\Delta\alpha=-125''$
$\Delta\delta=187''$
0.08 KM S^{-1}
$V_{LSR}=5.87$ KM S^{-1}

NH$_3$ (1,1)
0.08 KM S^{-1}
$V_{LSR}=5.87$ KM S^{-1}

MAIN BEAM BRIGHTNESS TEMPERATURE (K)

V_{LSR} (KM S^{-1})
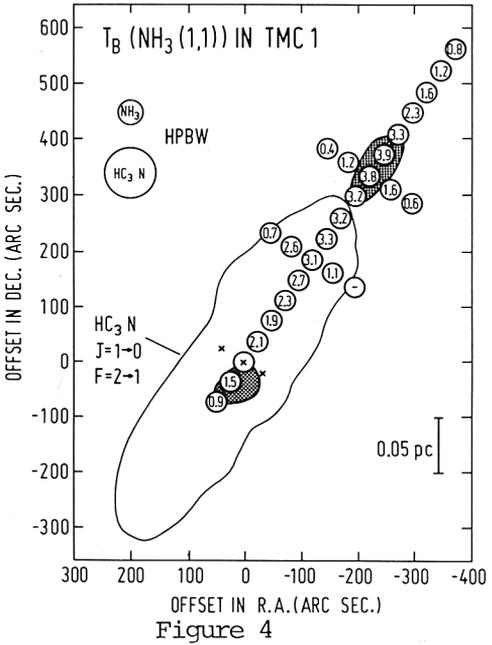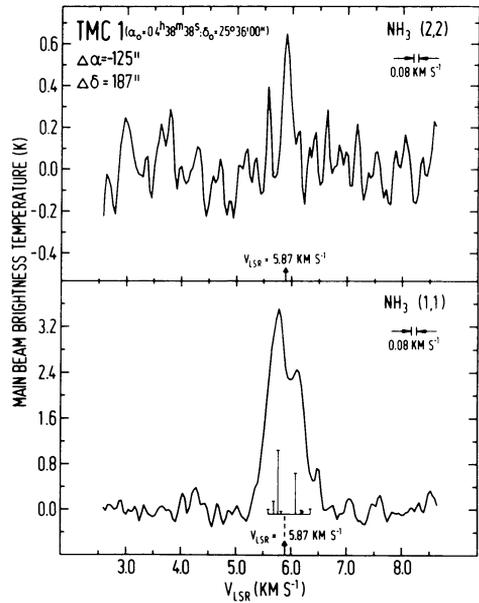
Figure 4. Map of the cyanopolyyne and ammonia clouds in TMC1. The hatched areas indicate the position of the cyanopolyyne (south-east) and ammonia (north-west) emission peaks.

Table 1

Molecular Transitions surveyed and mapped in selected sources
(TMC1, TMC2, Ll544, Ll83)

Molecule	Transition	Frequency MHz	Angular Resolution arc sec
HC_3N	$J = 1 \rightarrow 0$		90
	$F = 1 \rightarrow 1$	9 097.0346	
	$2 \rightarrow 1$	9 098.3321	
	$0 \rightarrow 1$	9 100.2727	
HC_5N	$J = 9 \rightarrow 8$	23 963.897	40
HC_7N	$J = 8 \rightarrow 7$	9 024.014	90
	$21 \rightarrow 20$	23 687.890	40
NH_3	$J,K = 1, 1$	23 694.495	40
	$2, 2$	23 722.633	40

is linked with the existence of acetylene. A summary on the distri-
bution of carbon chain molecules has been given (Winnewisser and
Walmsley, 1979). We suggest that the longer cyanopolyyne molecules
are formed via the acetylene "backbone" reaction

$$C_2H_x^+ + C_2H_2 \rightarrow C_4H_y^+ + C_2H_2 \rightarrow C_6H_z^+ + C_2H_2 \rightarrow \ldots$$
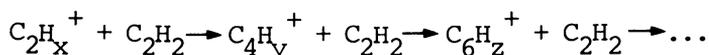
the appropriate species will then react with CN, HCN or HCN^+ to form
intermediates of the form $H_2C_3N^+,\ldots$ which by dissociative recombina-
tion form the cyanopolyynes $HC_3N,\ldots$ .We conclude, therefore, that
(1) the abundance of the cyanopolyyne molecules will decrease with
increasing length of the carbon chain, (2) that long chain molecules
with other functional groups such as CH_3, NH_2 should be observable,
(3) that molecules with no permanent dipole moment such as acetylene,
diacetylene,... have to be abundant in space and (4) that unstable
species such as HCCN, H_2CCN may be abundant in interstellar clouds.
Some of the unidentified lines may be caused by them.

Thus our high spectral and spatial resolution data indicate that
TMC1 is presently in a quiescent phase of temporary gravitational equi-
librium. This equilibrium might be ended either by slowly accreting
material which eventually causes gravitational collapse or by external
influences such as shock waves which can trigger collapse. The spatial
proximity of low-mass stars seems to support the speculation that its
evolutionary path will lead from its present "pre-protostellar" stage
to the formation of a low-mass star (or stars) in a time scale which is
longer than the free-fall time ($\sim 10^5$ years).

REFERENCES

Creswell, R.A., Pearson, E.F., Winnewisser, M., and Winnewisser, G.,
     (1976), Z. Naturforsch. 31a, 222.
Creswell, R.A., Winnewisser, G., and Gerry, M.C.L. (1977),
     J. Mol. Spectrosc. 65, 420.
Winnewisser, G., Creswell, R.A., and Winnewisser, M. (1978).
     Z. Naturforsch. 33a, 1169.
Winnewisser, G., and Walmsley, C.M., (1979)
     Astrophys. Space Sci. 65, 83.

DISCUSSION FOLLOWING WINNEWISSER

Kutner: How would these chains be destroyed, once they are formed?
Winnewisser: Good question. I don't know.
Thaddeus: For several years now Guelin and I have been trying to
identify a doublet at 85.3 GHz. In TMC 1 the strongest line is remarkably
strong - about 3 K. The best candidate we now have is the triplet
molecule H_2CCN, so we are very interested in any laboratory data that you
have on this radical.
Winnewisser: We have no data on HCCN or H_2CCN. However we do have
some unidentified lines in our HCCH+HCN discharge. Maybe we should
exchange diaries.
Langer: I would like to play the role of archaeologist for a moment
by talking about CO amidst all these modern studies of long chain
molecules. An extensive $C^{18}O$ survey of the Taurus region by Frerking and
myself at Bell Labs. reveals at least five fragments where you see about
two. Clearly there is a great deal of material and fragmentary structure
which is not revealed by the long chain molecules with their large dipole
moments, so one should be careful about interpretations of density and
physical conditions.
Winnewisser: I feel you are correct, but it is very worthwhile try-
ing to check the cyanopolyyne molecules in the positions you have found
$C^{18}O$ emission.
Langer: Is there any evidence for self-absorption effects in the
HC_3N data as is the case with HCO^+ and HNC?
Winnewisser: There is no evidence for self-absorption in HC_3N.
Among other reasons we reach this conclusion from the similarity of the
hyperfine components of HC_3N in the J=1-0 transition. They just look
completely alike.
Clark: We have previously reported an apparent minor axis rotation
in an adjacent region in Taurus, B213 NW. It is superimposed on small
motions about the major axis. Thus your apparent minor axis rotation is
not without precedent, although it is difficult to understand why it
occurs.
Winnewisser: The rotation observed in TMC 1 is only detected by
means of the three hyperfine components of the J=1-0 transition of HC_3N.
Vital to this detection is the high velocity resolution which we have
used ($\Delta V=0.027$ km s^{-1}). At lower velocity resolutions the spatial
difference between the two observed velocity components could have easily

been interpreted as a much larger rotation of TMC 1 than actually is present. I would like to emphasise that very high velocity resolution is necessary to obtain the proper dynamics of these quiescent clouds.

Glassgold: Have deuterated molecules been observed in TMC 1, especially DCO^+, which might give information on the electron abundance, and its possible correlation with long chain molecules?

Winnewisser: We ourselves have made no observations of DCO^+. However, Guélin, R. Wilson et al. have made those measurements. From the data one concludes that the electron abundance is low in TMC 1. But Guélin can comment better on his data than I can. We have not yet made measurements of DC_3N etc.

Guélin: In answer to Dr. Glassgold's question about the DCO^+ abundance, Langer, R. Wilson and myself have completed a survey of HCO^+ isotopic species in TMC 1. The HCO^+ source is exactly like the NH_3 source. It peaks $\sim 10'$ to the north-west of the HC_7N maximum. We *do* find DCO^+ everywhere. In other words, there is widespread deuterium enhancement in all the dense regions, which implies that the electron density is very low everywhere the heavy cyanopolyynes (HC_5N, HC_7N....) are observed.

T. Wilson: Henkel, Pankonin and myself have mapped $^{12}C^{16}O$ and $^{13}C^{16}O$ toward TMC 1, and find no variation in the intensities. In H_2CO, the 2_{11}-2_{12} line at 14.5 GHz peaks within 1.3' of the center of TMC 1. The 1_{10}-1_{11} line of H_2CO, at 4.8 GHz, varies more slowly with distance from the center of TMC 1.

Winnewisser: We have defined the center of TMC 1 by the position of the peak of the HC_5N emission. However the NH_3 position of maximum emission in TMC 1 is displaced by ~ 7 arc min to the north-west of the HC_3N peak. Our data also show that the HC_5N maximum emission is displaced from the HC_3N position by ~ 1 arc min.

Greenberg: What is the visual extinction in these clouds, and what is the photodissociation rate for the chain molecules? The reason for this question is that I would like to know the required production rate.

Winnewisser: The extinction in TMC 1 is $A_V \sim 6$. T. Wilson et al. have made star counts and obtained a more precise number. There is nothing known about photodissociation to my knowledge.

T. Wilson: From star counts of POSS red prints, the *minimum* A_V toward TMC 1 is 5 magnitudes.

Irvine: In order to compare different molecular species in regions as quiescent as TMC 1 or TMC 2, it is necessary to know rest frequencies very accurately. How well are these known for the long carbon chains?

Winnewisser: We can supply rest frequencies to a calculated standard deviation of $\lesssim 5$ KHz. In the case of HC_5N we have measured the rotational spectrum as high as ~ 300 GHz. We will publish these laboratory data soon.