LONG CHAIN CARBON MOLECULES IN THE INTERSTELLAR MEDIUM

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1. INTRODUCTION

The long chain carbon molecules known as the cyanopolyynes (HC_nN, n=3,5,7,9) are becoming increasingly more important in astrophysics. At present, the smallest member of the family, cyanoacetylene (HC_3N), has been observed in at least 32 sources, and cyanodiacetylene (HC_5N) in at least ten. Some 29 transitions of these two molecules have been detected to date, and the number of new sources and new lines is increasing quickly. Although the larger members of the family have not yet been found in sufficient abundance to permit studies in more than a few sources, the fact that they exist at all in detectable amounts is of interest from the standpoint of astrochemistry.

As a family, these molecules share a number of properties that are unique or, at least, unusual among interstellar species. In the following section we shall review briefly some of these properties and how they contribute to the usefulness of the cyanopolyynes as astrophysical probes. Then we shall look at some specific studies in which these molecules have been utilized.

2. CYANOPOLYYNE NOMENCLATURE AND PROPERTIES

The cyanopolyyne molecules consist of a conjugated, unsaturated, carbon chain terminated at one end by an H atom and at the other by the cyano group, CN. So long as the carbon chain is relatively short, the structural resemblance to acetylene is sufficient to justify the commonly used names, cyanoacetylene (HC_3N) and cyanodiacetylene (HC_5N). However, for the larger molecules, it is perhaps better to adopt a more formal terminology as outlined, for example, in (1). The general formula for these molecules can be written $H(C{\equiv}C)_nCN$, n=1,2,3, ____, and the names deduced from the length of the carbon chains and the bonding. For example, if n=3, we have cyano-hexa-tri-yne. The prefix "cyano" obviously denotes the presence of CN, "hexa" indicates a 6-atom carbon chain, and "tri-yne" indicates there are three (tri) triple bonds (yne)

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in the chain. Similarly, for n=4, we have cyano-octa-tetra-yne, and the rationale for the generic term, cyanopolyynes is clear.

The cyanopolyynes can be described in terms of superlatives. Their long carbon chains make them the heaviest known interstellar molecules, and, to the writer's knowledge, they are the longest linear molecules known to exist anywhere. These properties, in turn, result in the largest moments of inertia and smallest rotational constants of the known interstellar species. In addition, they are characterized by very large dipole moments.

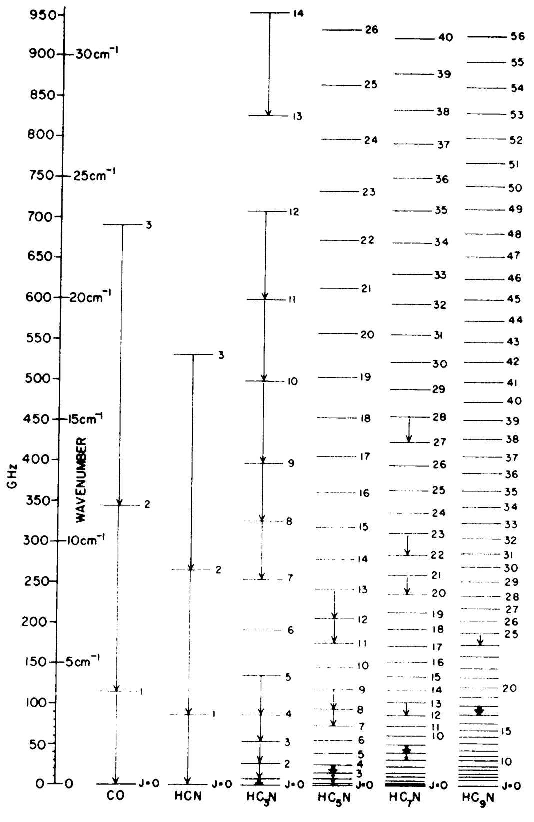

Figure 1: Ground state rotational energy levels for the known cyanopolyynes. The light arrows indicate the observed transitions and the dark arrows the discovery lines.

Figure 1 illustrates the large number of uniformly distributed, rotational spectral lines produced by the known cyanopolyynes. As a consequence of the large dipole moments and linear structure, their spectral lines are relatively strong, with frequencies that are easily and accurately computed. A summary of the spectroscopic constants of the cyanopolyynes, plus two closely related radicals, butadiynyl (C_4H) and cyanoethynyl (C_3N) is given in Table 1.

Table 1. Molecular Constants of Cyanopolyynes and Related Molecules

	Rotational Constant B_o MHz	Centrifugal Constant D_o kHz	eqQ MHz	Dipole Moment Debyes
HC_3N	4549.0579(4) [2]	0.54311(45) [2]	-4.3187(29) [2]	3.724(30) [3]
HC_5N	1331.3323(5) [4]	0.02826(107) [4]	-4.242(30) [5] -4.275(15)	4.33(03) [6]
HC_7N	564.00074(16) [7]	0.003820(87) [7]	-	5.0 [8]
HC_9N	290.5184(2) [8]	0.00101 [8]	-	5.6 [8]
C_3N	4947.66(10) [9]	1.0(5) [9]	-	2.2 [10]
HC_4	4758.48(10) [9]	<1.0 [9]	-	0.9 [10]

One of the most important attributes of these molecules is the sensitivity with which they reflect density and temperature in molecular clouds. Because of its higher abundance HC_3N is likely to be the most useful for this purpose. As an example, Figure 2a shows how the ratio of brightness temperature for the J=4-3 line (36.4 GHz) and J=9-8 line (81.9 GHz) of HC_3N depends upon H_2 density and kinetic temperature for an optically thin cloud. The ratio varies by orders of magnitude over the range of $n(H_2)$ and T_k encountered in molecular clouds. Note, however, that it exceeds 10 for $n(H_2) \lesssim 10^4$ cm^{-3} which means that, in practice, the J=9-8 line may be too weak to observe easily. Under such conditions, one need not change molecules; only frequencies. Figure 2b shows the brightness temperature ratio of the J=1-0 (9.1 GHz) and J=3-2 (27.3 GHz) lines. For $n(H_2) \lesssim 10^4$ cm^{-3} the relative strength of these lines is clearly a useful density indicator.

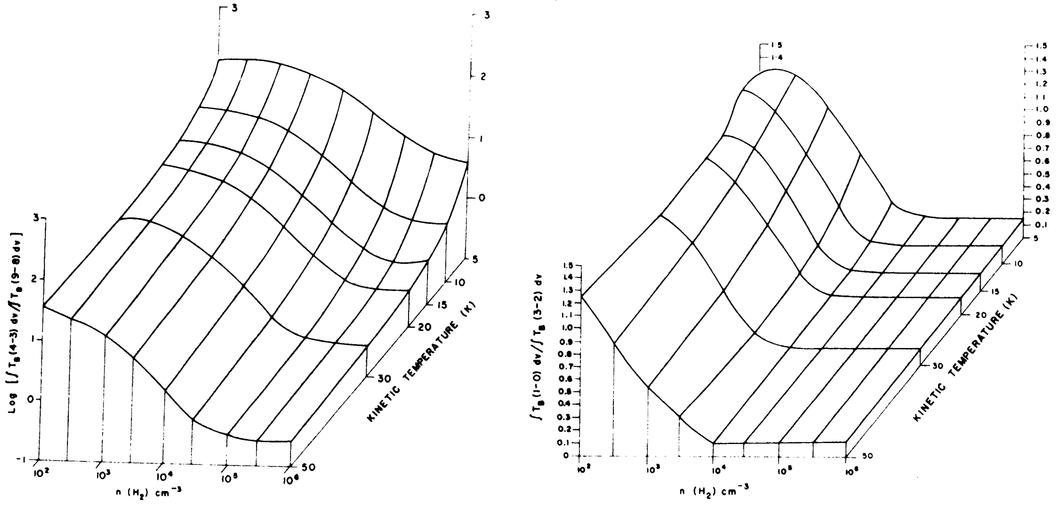

Figure 2. Ratios of integrated brightness temperature of HC_3N lines in in an optically thin cloud. (a) For J=4-3 and 9-8 lines. (b) For J=1-0 and 3-2 lines. Note difference in ordinate scale between (a) and (b).

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Another excitation property shared by the cyanopolyynes is a tendency for the J=1-0 line to act as a weak maser. This phenomenon has been discussed by Morris et al. (11) for HC_3N and by Avery et al. (12) for HC_5N. The population inversion in the J=1 level occurs because of the dependence of the downward radiative rate coefficients upon J. For the transition $J \rightarrow J-1$, the radiative rate varies as $B_o{}^2\mu^2[J^3/(2J+1)]$ where μ is the dipole moment and B_o the rotational constant of the molecule. Thus, the downward rate from J=2 is about 5 times greater than that from J=1, resulting in an accumulation of population in J=1 relative to J=0, provided that the collisional rate coefficients, $C_{J,J-1}=n(H_2)\sigma_{J,J-1}V$, are approximately equal to the radiative rates. If the collisional rates significantly exceed the radiative rates, then the inversion is destroyed. This property of HC_5N is illustrated in Figure 3. For $n(H_2)<10^3 cm^{-3}$, T_{ex} (1-0)<0. Because of the requirement that $C_{J,J-1} \approx R_{J,J-1}$ for inversion, the density at which maximum inversion occurs for different cyanopolyynes is $\propto B_o{}^2$. Consequently, if maximum inversion occurs at $n(H_2) \approx 10^2 cm^{-3}$ for HC_5N, it will occur at $n(H_2) \approx 10^3 cm^{-3}$ for HC_3N.

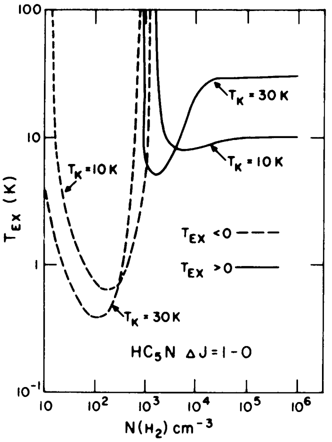

Figure 3. T_{ex} versus $n(H_2)$ for the J=1-0 line of HC_5N. The strongest maser effect occurs when T_{ex} is negative and closest to zero. The broken lines indicate negative T_{ex}.

Broten et al. (13) found evidence that the J=1-0 line of HC_5N in Sgr B_2 is enhanced relative to the J=4-3 and 8-7 lines. Following an analysis based on the principles discussed above, Avery et al. (12) interpreted these observations to indicate the presence of an extended, low density envelope in the Sgr B_2 molecular cloud.

3. SOME INTERESTING RESULTS OF OBSERVATIONS OF LONG CHAIN MOLECULES

Having considered some of the properties of these molecules, let us now turn to some specific studies based on them. It is not feasible to present a complete review of the observational status of the cyanopolyynes, so I shall single out three specific current topics of interest as representative.

3.1 Cyanoacetylene in OMC1

A number of authors have detected various transitions of HC_3N in OMC1 which have revealed some new properties of this well-studied cloud. Very recently, Loren et al. (14) have detected the J=31-30 and 30-29 lines at 282.0 GHz and 272.9 GHz. Morris et al. (15) have observed various lines up to J=16-15 which they interpret as arising in a new, very dense component ($n(H_2) \approx 10^6 cm^{-3}$) of the north-south ridge in OMC1. In the same source, Clark et al. (16) observed the ℓ-doublet, J=10-9 transitions of the ν_7 vibrationally excited state of HC_3N. This state lies 224 cm^{-1} above the ground state, and these lines are among the highest excitation, non-masering interstellar lines yet found. Deguchi et al. (17) undertook a statistical equilibrium study of these observations based on a new determination of the rate coefficients involving the excited state. Their results reveal the presence of a dense, compact cloud of vibrationally excited HC_3N, some 3" to 8" arc in diameter, with $n(H_2) > 3x10^7 cm^{-3}$ and a total mass of 10-100 $M_\odot$. It is probable that the recently detected J=31-30 and 30-29 ground state lines also arise from this cloud. The line widths and LSR velocities of these lines are $\approx$ 9.0 km. s^{-1} and $\approx$+6.5 km. s^{-1}, close to the values for the vibrational state lines. Typical values for the lower J lines observed by Morris et al. (15) are $\Delta V_{FWHM} \approx 4.0$ km s^{-1} and $V_{LSR} + \approx 9.0$ km s^{-1}.

3.2 Studies of the $^{12}C/^{13}C$ ratio and isotope fractionation

The cyanopolyyne molecules, especially HC_3N because of its relatively strong lines, offer unique opportunities to study ^{13}C fractionation and abundances. The opacity in the ^{12}C species is generally small so that radiative trapping is not a problem as it is in the case of isotope studies based on ^{12}CO or ^{12}CS. Churchwell et al. (18) have observed the J=1-0 transition of the three ^{13}C-substituted isotopic species of HC_3N in Sgr B_2. They concluded there was strong evidence for ^{13}C fractionation in that $H^{13}CCCN$ was twice as abundant as each of the other two ^{13}C species. However, Wannier and Linke (19) have observed the various J=9-8 transitions in Sgr B_2 and OMC1, and find no evidence for isotope fractionation. They deduced a $^{12}C/^{13}C$ ratio of 22 in Sgr B_2 and 50 in OMC1.

The situation regarding ^{13}C fractionation has been further confused following a theoretical study by Wolfsberg et al (20). These theoretical findings are at odds with both of the above observational results! They predict that $H^{13}CCCN$ should be 30% less abundant than $HC^{13}CCN$ and 50% less abundant than $HCC^{13}CN$.

Clearly, this is an area where more work is required, for the question of whether ^{13}C fractionation occurs and if so to what degree has an important bearing on determinations of the $^{12}C/^{13}C$ abundance ratio.

3.3 Cyanopolyynes in the Taurus Dark Cloud Complex

In recent years, the collection of dark clouds in the constellation Taurus has been revealed as a most remarkable location for cyanopolyyne studies. The premier source within the complex is TMC1, a small, condensation buried within Heiles' Cloud 2. The first indication of the potential of TMC1 as a cyanopolyyne source was provided by Morris et al. (11) who detected relatively strong emission in the J=5-4 line of HC_3N. Subsequently, HC_5N was detected and studied there (21,22,23), and both HC_7N and HC_9N were first discovered in TMC1 (7,8). Indeed, HC_9N has not, to date, been detected in any other source. Table 2 shows the estimated column densities of the various cyanopolyynes at the peak position in TMC1. Other studies (24,25,26) have revealed HC_5N in three more locations in the Taurus complex, TMC2 (L1529), L1544 and L1521 B. In the following, it will not be possible to review all the work relevant to our topic. I shall restrict the discussion to some of the more recent developments and implications of the Taurus observations.

Table 2. Cyanopolyyne Column Density in TMC1

Molecule	$NL(10^{13} cm^{-3})$
HC_3N	13.0 †
HC_5N	5.0 *
HC_7N	1.2 *
HC_9N	0.3 *

† This paper. * Reference (8).

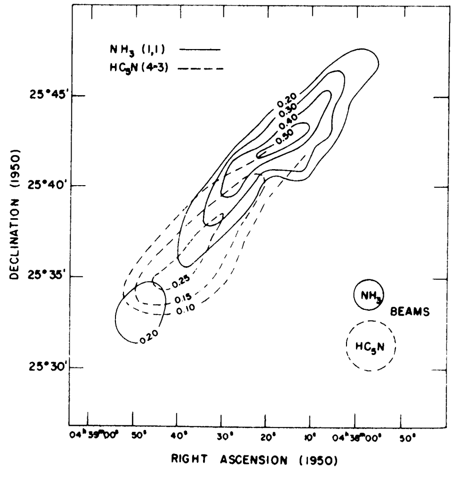

Figure 4. Distributions of HC_5N, J=4-3 and $NH_3(1,1)$ emission in TMC1. Contour scale for NH_3 is T_A of strongest hyperfine component, and $\int T_A dV$ for HC_5N.

The HC_5N distribution in TMC1 is in the form of a narrow ellipse of dimensions > 10' x 2' which corresponds to a physical size of >0.4x0.08 pc. The ridge of emission is not distinguished optically within the much larger area of Heiles' Cloud 2, and represents only 1% of the Cloud 2 area. Its total mass is 1 $M_\odot$. Figure 4 shows a superposition of the HC_5N J=4-3 and NH_3 (1,1) line emission observed at ARO[1] (21,27). Although emission from both molecules overlaps along the same ridge, the peak of the NH_3 distribution lies some 10' arc northwest of the HC_5N peak. This has also been observed by Ungerechts et al (28) and Little et al. (29). Little et al. attribute this effect to an abundance difference, not an excitation phenomenon. Wootten (30) has mapped TMC1 in C_2H and finds the C_2H contours also form an emission ridge, with two separate, equal maxima - one at the HC_5N peak, and the other at the NH_3

peak. Apparently, the physical conditions at the southeast end of TMC1 differ in a way not yet understood from those at the northwest end. Conditions at the SE end favour production of the cyanopolyynes; conditions to the NW favour NH_3, and both sets of conditions are kindly disposed to C_2H.

To accurately determine the density and temperature of the cyanopolyyne TMC1 ridge, we have undertaken observations at Kitt Peak[2] of the J=4-3, 5-4, 9-8, 10-9, and 11-10 HC_3N lines at the peak position. The details will be published elsewhere, but preliminary results indicate the observations require a two-component, core-halo model. The model parameters computed for a cylindrical cloud are shown in Table 3. The density and temperature of the core are somewhat higher than earlier estimates, but not exceptional for dark clouds. It thus appears that the enhanced abundance of long chain carbon molecules cannot be attributed to obviously unusual physical conditions. Figure 5 shows the relative contributions of the core and halo regions to the perceived brightness temperatures of different HC_3N transitions at the cloud centre. The cool halo is optically thick over the middle range of J, which accounts for the shape of the core contribution.

Table 3. Model of TMC1 Based on HC_3N Observations

	Dimensions FWHM	T_k K	NL HC_3N	$n(H_2)$	$\frac{n(HC_3N)}{n(H_2)}$
Core	1'x3'	20	$2\times10^{13}cm^{-2}$	$6\times10^{4}cm^{-3}$	3×10^{-9}
Halo	2.5'x10'	10	$1.1\times10^{14}cm^{-2}$	$9\times10^{3}cm^{-3}$	4×10^{-8}

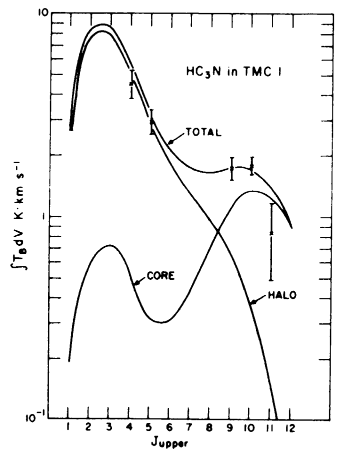

Figure 5. Calculated integrated brightness temperature of HC_3N lines in TMC1 for the model of Table 3. For comparison the observations on which the model is based are also shown. The J=1-0 observation is from G. Winnewisser, private communication.

If we cannot attribute the enhanced abundance of cyanopolyynes in Taurus to unusual densities, temperatures, or grain properties [cf. Elias, (31)], what other factors could be invoked? Myers et al. (26) have put forth a suggestion based on their study of TMC2. TMC2 appears similar to TMC1, except it is round, and the column density of HC_5N is smaller by a factor of three. Myers et al. find $n(H_2)\approx4\times10^4$ cm^{-3}, $T_K\approx20K$, and the total mass is $1M_\odot$ as for TMC1.

The observed HC_5N line width in TMC2 is less than that expected for a cloud in free-fall contraction, and Myers et al. conclude that TMC2 is a small, dense condensation that is in hydrostatic equilibrium inside a larger, less dense cloud. For a self-gravitating, isothermal spherical cloud surrounded by a medium of $n(H_2)=3x10^3 cm^{-3}$ and $T_K=10K$, the critical mass above which the cloud collapses is $\simeq 6M_\odot$ [see, for example Jura (32)]. This is consistent with the idea that TMC2 is in hydrostatic equilibrium. Myers et al. argue that TMC2 and the other HC_5N clouds in Taurus are potential star forming regions which are temporarily stable [see also (23)]. As such they may have been at high density - i.e. $n(H_2)>10^4 cm^{-3}$ - for a sufficiently long time that chemical evolution has proceeded to an unusual degree, thereby explaining the high cyanopolyyne abundances.

Quite apart from any conjecture as to <u>why</u> the cyanopolyyne cloudlets exist in Taurus, an important fact is that they <u>do</u> exist. As we have seen, typical parameters are $n(H_2)\sim10^4 cm^{-3}$, $T_K=15-20K$, $M\sim1M_\odot$ and scale sizes $\lesssim$ 0.1 pc. It is tempting to identify these clouds as the manifestation of the fragmentation process that has long been discussed by theoreticians. Silk (33) states that detection of clumpiness in large clouds on scales of $\sim$ 0.1 pc, involving $1M_\odot$ or less, at densities $\sim10^4 cm^{-3}$, would provide support for existing theories of fragmentation, and "could provide a vital link between molecular clouds and the star-formation process". It seems that the compact clouds detected in Taurus are exactly what the theoreticians ordered!

1. The Algonquin Radio Observatory is operated by the National Research Council of Canada as a national radio astronomy facility.
2. The National Radio Astronomy Observatory is operated by Associated Universities, Inc., under contract with the National Science Foundation.

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DISCUSSION FOLLOWING AVERY

Bok: This was one of the most beautiful papers I have heard, and it was beautifully presented. My congratulations to my Ottawa friends on a marvellous piece of research. Now I have a couple of questions. My first question: how did you arrive at the temperatures and densities shown in your slide?

Avery: We used a multilevel statistical equilibrium programme to compute the excitation temperatures for each of the observed lines, and then used the transfer equation, with appropriate allowance for beam dilution effects, to give calculated antenna temperatures. The kinetic temperature and H_2 density are parameters in the statistical equilibrium programme which are varied until the best agreement between the calculated and observed quantities is obtained. The values quoted in this paper are preliminary as we have not yet allowed for the effects of radiative trapping on T_{ex}. These effects could be important, especially for the J=4-3 and 5-4 lines, which are optically thick in our model.

Bok: Is the search for these molecules being extended to other dark clouds or molecular clouds? Specifically, have you in mind studies of several choice dark clouds of the southern hemisphere?

Avery: A number of investigators, including ourselves, have looked for HC_5N in many dark clouds, but to date it has been found only in four parts of the Taurus complex, and in B 335. However, the search for new cyanopolyyne sources is continuing at a number of observatories. I agree that observations of southern dark clouds would be very interesting, but I am not aware that any systematic searches are under way at present.

Elmegreen: We have made an optical survey of dark filaments, like those in Taurus, that show dark globular condensations along their length. They all show a similar pattern of nearly equally spaced primary condensations, which is typical of the mechanism of self-gravitational fragmentation in magnetic filaments. The catalogue contains some 100 condensations similar to those in Taurus, and it covers both the northern and southern hemispheres. It might be a good sample of objects for your cyanopolyynes search.

Avery: I have seen a preprint of your catalogue, and I believe that it will be a very useful guide for future searches for new carbon chain molecules. Systematic searches in regions other than Taurus will be important to establish the degree to which Taurus is unique with regard to the cyanopolyynes.

Greenberg: Do you have an estimate of the age of the Taurus cloud TMC 2, whose size and density you stated were 0.1 pc and $\sim 10^4 cm^{-3}$ respectively? If it is 10^6 years or more then photolysis of the grains could be substantial, and *if* grains could collide at $\sim$0.1 km/sec (is there turbulence supporting this cloud from collapse?) then we have a potential molecule source.

Myers: The cloud age is probably considerably greater than 10^6 years if it is in stable equilibrium.

Feldman: It might not be necessary for TMC 1 and 2 to be very old objects in hydrostatic equilibrium in order to form abundant cyanopolyyne chains. After all, relatively large quantities of HC_5N and HC_7N have been found in the circumstellar envelope of the carbon star IRC+10216.

Avery: The idea of Myers *et al.* is that these clouds may be older than average so that the relatively high abundances of cyanopolyynes can be attributed to advanced chemical evolution. The idea is a speculative one, and it is true that these molecules have also been found in the dynamic envelope of IRC+10216. However the chemistry of the two environments is very probably different in view of the different physical conditions, so I do not think the presence of cyanopolyynes in IRC+10216 necessarily argues against the suggestion of Myers *et al.*

Biermann: Theoretical work done in Munich recently has shown that long-lived stable fragments may be due to an approximate equilibrium between rotations and gravity. Are there any observational indications that rotation plays a role in the clouds you discussed?

Avery: Ungerrechts, Walmsley and Winnewisser at Bonn have made maps of TMC 1 with high angular and velocity resolution. They find that the cloud is very quiescent, and shows little evidence of any systematic rotation.

Ho: A velocity gradient of $\sim$1 km s^{-1}pc^{-1} is observed in the TMC 2 region (Ho *et al.* 1977). The problem in dark clouds is that typically size scales are small, $\sim$0.1 pc, so that velocity shifts are difficult to detect. Because of the small sizes, the contribution of rotational energy to the dynamical stability is small, despite substantial velocity gradients.

Sherwood: From our study of the visual extinction in Heiles Cloud 2 T. Wilson and I find suggestions of fragmentation; we note some seven fragments with *minimum* extinction in the range 7-8 magnitudes. The age may be crudely estimated in two ways: (i) T Tauri and Hα emission stars in the vicinity imply $\sim 10^7$ years, and (ii) if the gradient in the radial velocity of H_2CO is matched by a transverse velocity, then the separation of components also implies $\sim 10^7$ years. We estimate $n(H_2) > 10^3 cm^{-3}$, and hence a free-fall time of only $\sim 10^5$ years.

Avery: I am interested to learn of these results. I think it would be important to continue these kinds of studies in the infrared, where the fragments might be more sharply defined.

Guelin: Observations of HC_3N, HC_5N, HC_7N and HC_9N with the 36 ft. and 140 ft. NRAO telescopes (Bujarrabal, Guelin, Morris and Thaddeus) also show that TMC 1 is clumpy. LVG statistical equilibrium computations imply densities of $\sim 10^5$ for the clumps and 10^3-10^4 in between. This result has some bearing on the HC_3N/HC_5N, HC_5N/HC_7N and HC_9N/HC_7N abundance ratios, derivations of which depend on the clump model. The 'decrement' of four in the abundances derived by previous studies has to be considered with caution.

Macdonald: Since TMC 1 is elongated along a sharp velocity discontinuity in HI, it is tempting to suggest, as several authors have, that fragmentation in this object has been triggered by a collision between two molecular clouds. Would you care to comment on this idea?

Avery: I think this suggestion was first made by Little et al.; it is an interesting possibility in view of the HI velocity ridge. It would be an unlikely coincidence, given the narrowness of TMC 1 and the velocity discontinuity, if the two features which align so well were unrelated. However, it is unlikely that similar collisions could be invoked to account for the other HC_nN condensations observed, such as TMC 2 or L1544, so fragmentation in this region can apparently proceed without cloud collisions. If TMC 1 is coincident with a collision interface, it may well be flattened in such a way that our line of sight is along a diameter of a disc, resulting in a longer column length of molecules than in the other observed condensations. Thus the enhancement of the carbon chain molecules in TMC 1 relative to TMC 2 and L1544 may be a geometrical effect.

Wootten: The comment that the HC_5N emission region in TMC 1 is not distinguishable in H_2CO maps is, I think, somewhat misleading. It is true if one considers only the 6 cm maps; a 2 cm map we have recently made follows the contours of the C_2H and HC_5N emission very well, with local absorption maxima coinciding with C_2H emission maxima. We attribut this behavior to the fact that the 2 cm line, arising in a more excited level than the 6 cm line, samples a denser region of the cloud.

Avery: I was not aware that a 2 cm H_2CO map of this region existed. My statement, that TMC 1 is not evident in H_2CO observations, referred to the 6 cm map. It may be that the cloud does not appear in the 6 cm line because of the large beamwidth used in the observations.

Gilmore: There exist faint radio continuum sources in the direction of both TMC 1 and TMC 2. The source toward TMC 1 is nonthermal, the one toward TMC 2 has three components, one with a flat spectrum. Both sources may be extragalactic background objects; I mention them because of the unusual chemistry in Taurus.

Thaddeus: I just wanted to make the obvious point that we see the cyanopolyynes only because of their large dipole moments and simple partition functions. Almost the entire table of molecules, certainly all the big ones, would not be visible at the same distances and same column densities as HC_7N or HC_9N. It is therefore almost impossible to prove that the cyanopolyyne clouds are chemically unique - it is possible that all the other substances are there and we just cannot see them, nor are we likely to in the foreseeable future.