ASTRONOMICAL DETECTION OF H₂CCC

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ABSTRACT

 H_2CCC , an isomer of the widely distributed interstellar ring C_3H_2 , has been detected in TMC-1 and possibly IRC + 10216 with the IRAM 30 m telescope, following a recent laboratory determination of the rotational spectrum of this new type of highly polar carbon chain. The rotational temperature of H_2CCC in TMC-1, like that of other highly polar molecules in this source, is very low: 4–6 K; the column density is also fairly low: $(2.5 \pm 0.5) \times 10^{12}$ cm⁻², slightly more than 1% that of the cyclic isomer.

Subject headings: interstellar: molecules — line identifications — molecular processes —

radio sources: lines - stars: circumstellar shells

Propadienylidene (Fig. 1) is the first stable member of a new family of cumulene carbon chains characterized by carboncarbon double bonds and terminal nonbonded electrons. As an isomer of the ubiquitous interstellar ring C_3H_2 , it is a good candidate for astronomical detection, especially favorable for radio observation because of the large dipole moment (4.1 D: DeFrees & McLean 1986) and hence intense rotational spectrum produced by the nonbonded electrons. Very recently H_2CCC has been produced in a laboratory discharge and its rotational spectrum determined to high precision (Vrtilek et al. 1990). Here we report its identification in TMC-1, one of the best astronomical sources of carbon chains, and tentative detection in the molecular envelope of IRC + 10216.

Owing to the linear carbon backbone and low mass of the off-axis hydrogens, H₂CCC is very nearly a symmetric top (asymmetry parameter $\kappa = -0.997$ versus -1 for a prolate symmetric top), and its rotational spectrum is characterized by nearly harmonically related transitions separated by about B + C = 20.8 GHz. Its radio spectrum is therefore somewhat simpler than that of the cyclic isomer, an oblate rotor far from the symmetric limit ($\kappa = 0.686$), for which the geometrical symmetry is not immediately apparent from the rotational spectrum. As with $c-C_3H_2$, however, the equivalent off-axis H nuclei of H₂CCC impose additional symmetry, segregating the rotational levels into ortho and para species with relative statistical weights of 3:1, between which both radiative and collisional transitions are highly forbidden. Presumably the ratio of ortho to para molecules in space is also 3-although this assumption is subject to some doubt at the very low temperature of TMC-1 (Ohishi et al. 1990); ortho lines are therefore generally expected to be stronger than para.

In TMC-1 we have definitely identified three lines and marginally detected a fourth; Table 1 summarizes the observa-

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⁶ Postal address: Division of Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, MA 02138. Also Harvard-Smithsonian Center for Astrophysics. tions. The three higher frequency lines, one of which is shown in Figure 2, are all of the ortho species. They were observed in 1990 September during a deliberate search for H_2CCC with the IRAM 30 m telescope at the position of maximum 23964 MHz (J = 9-8) HC₅N emission (Churchwell, Winnewisser, & Walmsley 1978)—a secondary maximum in the distribution of C₃H₂ (Guélin & Cernicharo 1988). Spectra were obtained by position switching against a location 10' E and 10' N, chosen because the visual extinction there is low and ¹³CO emission is very weak. The lowest frequency line in Table 1, also shown in Figure 2, is the lowest lying transition of the para species; it is a previously unidentified line in a spectrum of C_6H obtained at the same source position several years ago with the Effelsberg 100 m telescope (Cernicharo et al. 1987). Because the radial velocities of the four lines assigned in TMC-1 agree to within 0.1 km s^{-1} and agree well with the velocities of other molecules in this source, which generally fall in the narrow range 5.75 ± 0.15 km s⁻¹ (Tölle et al. 1981), the identification of H_2CCC is extremely secure. Aside from the para H_2CCC line in Figure 2, only one unidentified line was observed in a 24 MHz band adjacent to the C₆H doublet, so we estimate the density of unidentified lines at less than one per velocity interval of 100 km s⁻¹; therefore, even if the least certain line is ignored, the probability that we are observing unrelated lines is very small, i.e., $< 10^{-8}$.

The rotational temperature of most molecules is extremely low in TMC-1—typically only 5–10 K, and we derive from the three ortho transitions in Table 1 a value in this range: $T_{rot} = 6.0 \pm 1.0$ K. However, a rotational temperature of only about 4 K is derived from the relative intensity of the single para line to the three ortho lines if an ortho/para ratio of three is assumed. To estimate the amount of H₂CCC in TMC-1 we compromised and assumed an ortho/para ratio of two, rotational equilibrium at 5 K within the lowest para (K = 0) and the lowest ortho (K = 1) ladder, and negligible population in higher ladders (plausible since no lines with K > 1 have yet been detected). The total (ortho plus para) column density obtained under these assumptions, after making a small correction for absorption by the 2.7 K microwave background, is

$$N(H_2CCC) = (2.5 \pm 0.5) \times 10^{12} \text{ cm}^{-2}$$
,

an average over the 25" beam of the 30 m telescope at $\lambda = 3$ mm. The uncertainty is an estimate, and largely derives from

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FIG. 1.—Molecular geometry of H_2CCC . Double dots denote the two nonbonded electrons characteristic of carbenes; bond lengths and the HCH angle are from an *ab initio* calculation by DeFrees & McLean (1986).

uncertainty in the *ortho/para* ratio and the rotational partition function. For comparison, the column density of CCCH at the position we observed is $\sim 50\%$ larger, and that of $c-C_3H_2$ about 70 times larger (Madden et al. 1989).

We have not yet attempted to map H_2CCC in TMC-1, but we did observe the 5_{15} - 4_{14} transition at one other location: the NH₃ and c- C_3H_2 peak, 7'15" N and 4'15" W of our main position near the HC₅N peak. There this transition decreases in intensity by about 40% ($T_{mb} = 0.14 \pm 0.03$ K), similar to the decline in intensity observed in C₄H and HC₅N and other cyanopolyynes. Since there is evidence that the density is higher in this NW condensation than at the HC₅N peak, but the kinetic temperature is about the same, this decrease is probably indicative of an actual decline in abundance of H₂CCC.

We attempted using old and new data from the 30 m telescope to find all the *ortho* lines in Table 1 in IRC +10216, with partial success. There is a distinct 3 σ line ($T_{\rm mb} = 0.015$ K) at 83933 MHz which is probably the 4_{13} - 3_{12} transition, and a second of similar intensity (0.020 K) at 102992 MHz which is probably the 5_{15} - 4_{14} transition; for the others only upper limits (3σ) to the line intensity of about 0.06 K could be set. There is evidence in this source, however, of the $11_{1,10}$ - $10_{1,9}$ transition at 230778.0 MHz: a weak 0.03 K line, on the wing of the 7-6 line of AIF, at precisely the right velocity. Analysis of all the data on the assumption that the source is resolved with the 30 m telescope (the lines have the characteristic U shape of a resolved expanding shell) yields a rotational temperature for H₂CCC in IRC +10216 of 25 K—a plausible value close to that of other molecules—and a column density of 2.6×10^{12} cm^{-2} —comparable to that in TMC-1.

We also attempted to observe the ortho lines in Table 1 in



FIG. 2.—*Top*: The 5_{15} - 4_{14} transition of H₂CCC in TMC-1, observed with the IRAM 30 m telescope at a spectral resolution of 0.23 km s⁻¹. *Bottom*: The lowest lying *para* transition: published data from the Effelsberg 100 m telescope at a spectral resolution of 0.08 km s⁻¹.

Sgr B2(OH) and toward the rich source of radicals 3' N of Ori A, but generally we were only able to set upper limits to the line intensities of ~ 0.2 K. There is an 0.3 K line in Ori A at the expected frequency of the 5_{15} - 4_{14} transition, but there are so many weak molecular lines in this source that without confirming evidence there is little reason to suppose that this is H₂CCC.

A general survey of H_2CCC in molecular sources has yet to be undertaken. M. Bell informs us that the lowest lying *para* transition in Figure 2 is apparently present in a spectrum he has obtained of W51 with the NRAO 43 m telescope at about 1/30 the intensity of the intense 18343 MHz ortho line of $c-C_3H_2$ in this source; we hope to survey this *para* transition of H_2CCC in other sources with the same instrument in the near future. As mentioned in the laboratory paper (Vrtilek et al. 1990), no evidence for H_2CCC has been found in published molecular line surveys or compendia of observed lines.

No one to our knowledge has yet attempted to predict

TABLE 1 H,CCC in TMC-1

Transition	Symmetry	Rest Frequency (MHz)	E/k (K)	S	T_{mb} (K)	v _{LSR} (km s ^{−1})	$\frac{\Delta v}{(\mathrm{km \ s}^{-1})}$
101-000	Р	20792.59	1.0	1.00	0.233 (20)	5.8 (1)	0.49 (10)
5,5-4,4,	0	102992.38	13.9	4.80	0.210 (40)	5.8 (1)	0.50 (10)
514-413	0	104915.58	14.2	4.80	0.257 (86)	5.7 (1)	0.35 (10)
7 ₁₆ -6 ₁₅	0	146876.06	27.2	6.86	0.050 (20)	5.8 (1)	0.60 (10)

Note.—Symmetry species, ortho (O) or para (P); rest frequencies are from Vrtilek et al. 1990; E is the energy of the upper level of the transition above the O or P ground state; S is the asymmetric rotor line strength; T_{mb} is the peak line intensity, corrected for atmospheric absorption and beam efficiency; Δv is the full line width at half-intensity. Source position (1950): $\alpha = 4^{h}38^{m}36^{s}9$, $\delta = 25^{\circ}36'00''$.

explicitly the abundance of interstellar H₂CCC relative to $c-C_3H_2$ and other molecules, but in attempting to explain the formation of the cyclic isomer, Adams & Smith (1987) discuss an ion-molecule mechanism which they suggest should yield an appreciable amount of H₂CCC. Following previous workers, they find that interstellar $c-C_3H_2$ is mainly made via dissociative recombination of the cyclopropenium ion $c-C_3H_3^+$, which in turn is produced from the radiative association of C_3H^+ and H_2 . They provide arguments and evidence, however, that this latter reaction is likely to yield roughly equal amounts of $c-C_3H_3^+$ and the isomeric propargyl ion H_2CCCH^+ , a molecule with the same symmetry as H_2CCC . Dissociative recombination of this latter ion is presumably fast and is plausibly the source of the H₂CCC we observe, since dissociative recombination of the cyclic isomer would require

the improbable transfer of both H atoms to a single carbon. By analogy with the production of HCN and HNC from HCNH⁺, a consequence of production via dissociative recombination may be the formation of yet a third isomer of C_3H_2 , the quasi-linear carbene propargylene, HCCCH. Both in the laboratory and in space, this isomer-calculated to be less

- Adams, N. G., & Smith, D. 1987, ApJ, 317, L25
- Cernicharo, J., Guélin, M., Menten, K. M., & Walmsley, C. M. 1987, A&A, 181, L1
- Cernicharo, J., Gottlieb, C. A., Guélin, M., Killian, T. C., Thaddeus, P., & Vrtilek, J. M. 1991, ApJ, 368, L43
- Churchwell, E., Winnewisser, G., & Walmsley, C. M. 1978, A&A, 67, 139
- Cooper, D. L., & Murphy, S. C. 1988, ApJ, 333, 482 DeFrees, D. J., & McLean, A. D. 1986, ApJ, 308, L31
- Dykstra, C. E., Parsons, C. A., & Oates, C. L. 1979, J. Am. Chem. Soc., 101, 1962
- Guélin, M., & Cernicharo, J. 1988, in Molecular Clouds in the Milky Way and External Galaxies, ed. R. L. Dickman, R. L. Snell, & J. S. Young (New York: Springer-Verlag), p. 81
- Irvine, W. M., et al. 1988, ApJ, 334, L107

stable than H₂CCC by 0.53 eV (DeFrees & McLean 1986)has proved to be extremely elusive. Although Merer (1967) many years ago attributed laboratory optical lines to a possibly linear isomer of C_3H_2 , no trace of the rotational spectrum of such a molecule has been identified in the millimeter-wave band in laboratory discharges where $c-C_3H_2$ and now H_2CCC are readily observed. Astronomical lines tentatively attributed at one time to HCCCH (Thaddeus, Vrtilek, & Gottlieb 1985) turned out instead to be the cyanomethyl radical CH₂CN (Irvine et al. 1988).

Longer cumulene chains than H₂CCC are calculated to be still more polar (Dykstra, Parsons, & Oates 1979; Cooper & Murphy 1988) and are therefore also of potential astronomical interest. The next member of the sequence, H₂C₄, an isomer of the fairly stable, nonpolar molecule diacetylene, has recently been found in the laboratory (Killian et al. 1990), and its rotational spectrum is now known to high accuracy. Just as this Letter was finished, we identified at least seven lines of H_2CCCC between 88 and 108 GHz in IRC +10216; an account of this work appears in a companion Letter (Cernicharo et al. 1991).

REFERENCES

- Killian, T. C., Vrtilek, J. M., Gottlieb, C. A., Gottlieb, E. W., & Thaddeus, P.
- Mann, I. C., VILLER, J. M., GOLLIED, C. A., GOLLIED, E. W., & Thaddeus, P. 1990, ApJ, 365, L89
 Madden, S. C., Irvine, W. M., Matthews, H. E., Friberg, P., & Swade, D. A. 1989, AJ, 97, 1403
- Merer, A. J. 1967, Canadian J. Phys., 45, 4103 Ohishi, M., Irvine, W. M., Minh, Y., & Kaifu, N. 1990, in Proc. of the Third Haystack Conference on Atoms, Ions, and Molecules, ed. A. D. Haschick & P. T. P. Ho (Provo, UT: ASP), in press
- Thaddeus, P., Vrtilek, J. M., & Gottlieb, C. A. 1985, ApJ, 299, L63
- Tölle, F., Ungerechts, H., Walmsley, C. M., Winnewisser, G., & Churchwell, E. 1981, A&A, 95, 143
- Vrtilek, J. M., Gottlieb, C. A., Gottlieb, E. W., Killian, T. C., & Thaddeus, P. 1990, ApJ, 364, L53