1991ApJ...368L..43C

THE ASTROPHYSICAL JOURNAL, 368:L43–L45, 1991 February 20

ASTRONOMICAL DETECTION OF H_2CCCC

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Received 1990 October 17; accepted 1990 November 29

ABSTRACT

The carbon-chain carbene H_2CCCC, a highly polar isomer of diacetylene recently identified in the laboratory, has been detected in the circumstellar shell of IRC +10216 with the IRAM 30 m telescope. Eight transitions between 80 and 135 GHz have been assigned, all but two of the *ortho* symmetry species. The rotational temperature of H_2CCCC in IRC +10216 is 20 ± 3 K, and the column density averaged over the $\sim 25''$ beam of the 30 m telescope at 3 mm is $(1.6 \pm 0.4) \times 10^{13}$ cm^{-2}—6 times that of H_2CCC, the first member of this sequence of cumulene carbenes, also recently identified in TMC-1.

Subject headings: interstellar: molecules — line identifications — molecular processes — radio sources: lines — stars: circumstellar shells

Molecules discovered in interstellar space or in circumstellar shells form a remarkable mixture; although a slim majority are ordinary stable species, such as might be found in any chemical stockroom, the remainder are exotic molecules that fall into several less familiar categories: radicals, ions, unsaturated carbon chains, isomers, and carbenes. Here we describe the identification in space of the second interstellar molecule that has the distinction of belonging to three of these categories: H_2CCCC, butatrienylidene, an unsaturated carbon chain (Fig. 1) that is also an isomer of diacetylene (a nonpolar molecule not yet observed but almost certainly present in the interstellar gas since closely related molecules such as H_2C_2 and C_4H are found) and a carbene, the third known in space after the isomers cyclic-C_3H_2 (Thaddeus, Vrtilek, & Gottlieb 1985) and H_2CCC (Vrtilek et al. 1990). After H_2CCC, it is the second member of a new family of carbon-chain molecules, characterized by carbon-carbon double bonds and terminal nonbonded electrons, to be detected in space (Cernicharo et al. 1991).

As was the case for H_2CCC, H_2CCCC was detected first in the laboratory (Killian et al. 1990), where microwave observations of 45 lines in the frequency range 169–368 GHz have led to a determination of its lower rotational spectrum accurate to ~ 0.1 ppm or better, hence allowing an astronomical search with essentially no uncertainty as to frequencies (even though the lines observed in space are not the same ones observed in the laboratory). On the basis of what is known of H_2CCC and of the other carbon-chain molecules (e.g., Cernicharo et al. 1987), the best molecular sources toward which to search for H_2CCCC are IRC +10216 and TMC-1. With two equivalent off-axis H nuclei, the ground state of H_2CCCC is split into *ortho* (K_a odd) and *para* (K_a even) states, between which both radiative and collisional transitions are highly forbidden; as the statistical weight of the *ortho* levels is 3 times that of the corresponding *para* levels, the strongest astronomical transitions should generally belong to the *ortho* state, and in the cold interstellar gas preferentially to the lowest ($K_a = 1$) ladder of this state.

We accordingly first searched for H_2CCCC in the millimeter-wave spectral survey of IRC +10216 made with the IRAM 30 m telescope, a survey that covers, at high sensitivity, most of the 3 mm and 2 mm atmospheric windows and some of the window at 1.3 mm. Thirty-three 3 mm or 2 mm H_2CCCC $K_a = 0$ or $K_a = 1$ transitions fall in the range of this survey. Owing to the large density of weak astronomical lines, particularly in the 3 mm part of the survey which was predominantly done in the double-sideband mode, many lines of H_2CCCC are expected to be blended. A close inspection of the frequencies measured or calculated for the transitions of astrophysical molecules (e.g., Cernicharo 1988; Lovas 1986) revealed that about half of these 33 H_2CCCC transitions fall less than 10 MHz from low-lying transitions of known IRC +10216 molecules, and therefore should be partly or entirely blended. Eight *ortho* ($K_a = 1$) transitions and three *para* ($K_a = 0$) transitions are expected to be free of confusion. The five lowest *ortho* transitions (frequencies between 88 and 134 GHz) coincide in frequency with unidentified lines in the IRC +10216 survey (see Table 1 and Fig. 2). One of the low-frequency *para* transitions is also clearly detected. No higher (above 150 GHz) *ortho* or *para* lines, on the other hand, are detected; these have upper level energies in excess of 70 K and are difficult to excite at the low rotational temperature characteristic of IRC +10216. Two more lines, partly blended with known molecular lines, were also detected in our survey. Their rest frequencies, derived from the frequencies of the line edges, assuming a line width of 29 km s^{-1}, identical to that observed for all ground-state molecular lines, are also in excellent agreement with those calculated for H_2CCCC. Finally, one more *ortho* line at 133.4 GHz is marginally present (at the 3 σ level).

The large number of *U*-lines coinciding within 0.3 MHz with H_2CCCC transitions, and the fact that not a single confusion-free *ortho* line below $E/k \approx 70$ K was missed, leave little doubt that we have detected H_2CCCC. The number of remaining *U*-lines with intensities above 50 mK in the IRAM IRC +10216 survey is so small (fewer than two per GHz) that an

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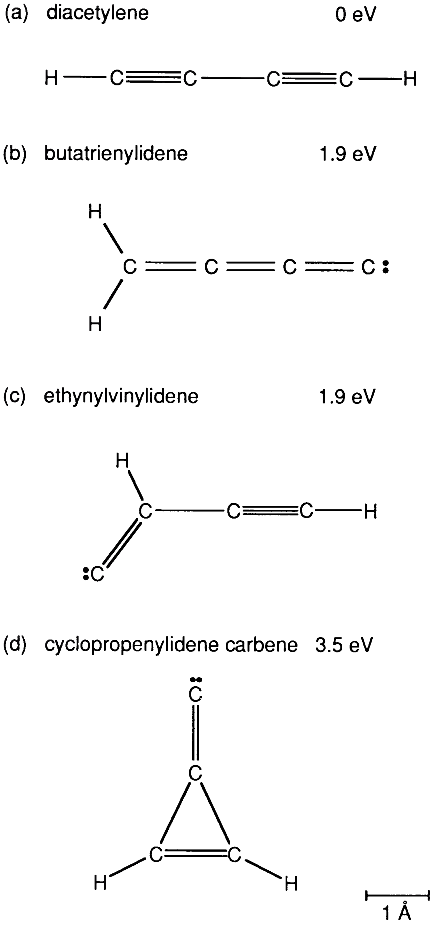

FIG. 1.—Molecular geometries of low-lying isomers of H_2CCCC. (*a*) Diacetylene, the ground configuration. (*b*) Butatrienylidene, H_2CCCC, 1.9 eV above diacetylene. (*c*) Ethynylvinylidene, computed to lie at nearly the same energy as butatrienylidene. Bond lengths, angles, and energies of (*b*) and (*c*) are from the *ab initio* calculations of Dykstra, Parsons, & Oates (1979). (*d*) The *ab initio* molecular geometry and energy of this isomer are from Andrade et al. (1981). Double dots in (*b*), (*c*), and (*d*) indicate the location of the two nonbonded electrons characteristic of carbenes. Isomers (*c*) and (*d*) are still unknown.

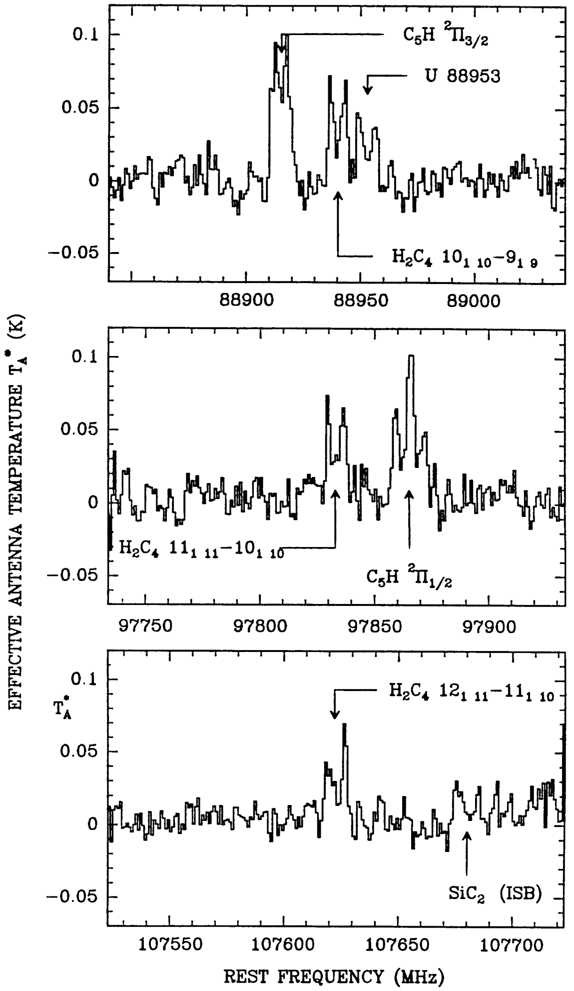

FIG. 2.—Lines of H_2CCCC observed toward IRC +10216 with the IRAM 30 m telescope at a spectral resolution of 1 MHz; integration times are 1–3 hr. The frequency scale is computed for an LSR source velocity of −26.5 km s^{-1}. Line widths are normal for IRC +10216: 29 km s^{-1}. T_A^* (corrected for atmospheric absorption) is related to T_{mb} (see Cernicharo et al. 1991) by $T_A^* = \eta T_{mb}$, where $\eta = 0.65$ at 3 mm and 0.60 at 2 mm.

TABLE 1

H_2CCCC IN IRC +10216

Transition J_{K_a,K_c}	Symmetry	Rest Frequency (MHz)	E/k (K)	S	W (K km s^{-1})	v_{LSR} (km s^{-1})
$9_{0,9}-8_{0,8}$	P	80383.96	19.3	9.00	1.2 ± 0.3[a]	−23 ± 7
$10_{1,10}-9_{1,9}$	O	88940.21	23.0	9.90	1.8 ± 0.2	−25.5 ± 1.3
$11_{1,11}-10_{1,10}$	O	97833.60	27.7	10.91	2.0 ± 0.2	−27.1 ± 1.2
$11_{0,11}-10_{0,10}$	P	98245.01	28.3	11.00	0.7 ± 0.2	−26.8 ± 4.6
$11_{1,10}-10_{1,9}$	O	98655.07	27.9	10.91	1.5 ± 0.3[b]	−26.6 ± 3.0
$12_{0,12}-11_{0,11}$	P	107175.10	33.4	12.00	<1.0	...
$12_{1,11}-11_{1,10}$	O	107622.92	33.1	11.92	2.0 ± 0.2	−26.4 ± 1.1
$15_{1,15}-14_{1,14}$	O	133405.23	50.8	14.93	1.1 ± 0.4	−26.0 ± 2.2
$15_{1,14}-14_{1,13}$	O	134525.20	51.2	14.93	1.1 ± 0.3	−26.0 ± 2.2
$16_{1,16}-15_{1,15}$	O	142297.56	57.6	15.94	<0.9	...

NOTE.—Symmetry species, *ortho* (O) or *para* (P); 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; W is the velocity-integrated line intensity, corrected for beam efficiency (with 1 σ errors that include calibration uncertainties). Line widths are 29 km s^{-1}. Source position (1950): $\alpha = 09^h45^m14^s.8$; $\delta = +13°30'40''$.

[a] Partially blended with C_3H.

[b] Partially blended with HC_3N.

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accidental configuration of unrelated lines can be ruled out. The relative intensities of the lines, all consistent with a single rotational temperature and an *ortho/para* ratio of 3, provide additional confirmation for the identification.

The shape of the 3 mm lines of H_2CCCC indicates a source partly resolved by the 25″ telescope beam: all lines observed with good signal-to-noise ratio are U-shaped, which is uncommon for lines at that intensity level. The horn-to-center ratio of these U-shaped lines, ~3, is about equal to that of the 3 mm C_4H and C_3N lines observed with the 30 m telescope. This line shape indicates that the H_2CCCC source, like that of C_4H and C_3N, is a partially resolved expanding shell. If we assume a uniformly bright source of 25″ diameter, we can derive the brightness temperatures of *ortho* and *para* lines as a function of the energies of their upper levels relative to the lowest *ortho* and *para* states. Figure 3 shows the rotational temperature diagram; all lines in Table 1 can be fitted by a single rotational temperature: 20 ± 3 K. Using the calculated dipole moment of 4.5 debye (Dykstra, Parsons, & Oates 1979), 10% larger than that of H_2CCC, and an *ortho/para* ratio of 3:1, we obtain the total (*ortho* + *para*) H_2CCCC column density averaged over a 25″ source: $(1.6 \pm 0.4) \times 10^{13}$ cm^{-2}, 6 times that of H_2CCC, but some 300 times smaller than the column density of C_4H (Cernicharo et al. 1987).

We have so far searched for H_2CCCC in only one other source: TMC-1; there, we set an upper limit of 0.2 K (3 σ) for the $10_{1,9}$–$9_{1,8}$ line. The position observed is the one where we discovered H_2CCC and where long chain molecules generally peak: $\alpha(1950) = 4^h38^m36^s.9$, $\delta(1950) = 25°36'0''$. Since the $10_{1,9}$ level lies 23.2 K above the *ortho* ground state, the implied limit on H_2CCCC column density depends sensitively on the excitation conditions; it is $\sim 4 \times 10^{12}$ cm^{-2} if $T_{\rm rot} \approx 6$ K, as it is for H_2CCC. Further observations of this source are in progress.

The detection of H_2CCCC in the circumstellar envelope of IRC +10216 yields interesting clues on some of the chemical processes at work there. The "freeze-out" model of molecule formation in IRC +10216 (McCabe, Smith, & Clegg 1979) cannot explain the observed column density of H_2CCCC; owing to the 1.9 eV (22,000 K) energy difference between diacetylene and H_2CCCC, that model would predict, for a freeze-out temperature of 1000–1400 K, diacetylene abundances far in excess of those observed for CO or acetylene, a result incompatible with thermochemical equilibrium. A freeze-out temperature sufficient to explain our results would exceed the surface temperature of the central star, CW Leo.

Ion-molecule processes, on the other hand, seem able to account for the observed H_2CCCC. As pointed out in the laboratory discovery paper (Killian et al. 1990), both H_2CCCC and diacetylene are plausibly formed through dissociative recombination of the $C_4H_3^+$ ion, the most stable isomer of which is thought to be the quasi-linear configuration H_2CCCCH^+, with the same symmetry as H_2CCCC. In cold interstellar clouds, the well-known fast reaction $C_2H_2^+ + C_2H_2 \rightarrow C_4H_3^+ + H$ produces this ion in fairly high concentration, and the same reaction presumably occurs also in the envelope of IRC +10216: the photoionization models of Glassgold et al. (1987) predict high abundances of the acetylene ion at a distance from CW Leo of a few times 10^{16} cm, where outflowing gas is first exposed to the interstellar UV field, which is of the order of the size of the H_2CCCC shell implied by the observed line profile. Glassgold et al. calculate a concentration of diacetylene that is large, comparable to that of C_4H and HC_3N. Therefore even a small branching ratio in the dissociative recombination of $C_4H_3^+$ is adequate to produce the observed concentration of H_2CCCC.

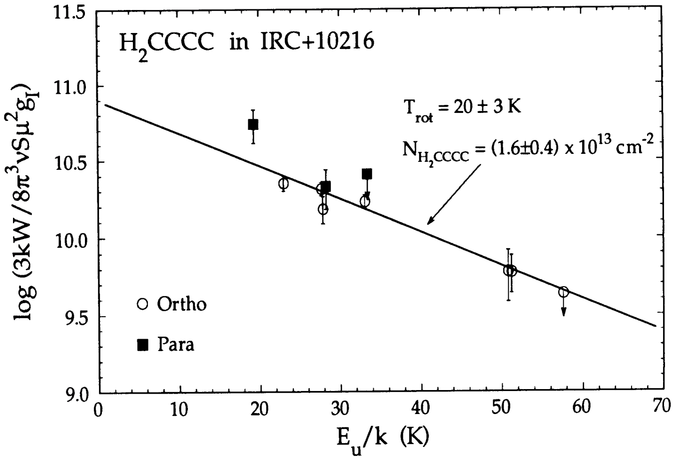

FIG. 3.—Rotational temperature diagram of H_2CCCC in IRC +10216

The formation of both H_2CCC and H_2CCCC in space is apparently a natural consequence of the formation via dissociative recombination of the more familiar acetylenic chains, and this conclusion can probably be generalized to still larger members of this series. Because acetylenic chains with up to 11 carbon atoms have been detected in at least one astronomical source, there is strong motivation to search for still larger cumulene carbene chains both in the laboratory and in space.

We are indebted to N. Adams, C. Dykstra, and E. Herbst for useful discussions.

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