

## DETECTION OF THE CARBON CHAIN NEGATIVE ION $C_8H^-$ IN TMC-1

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Received 2007 May 11; accepted 2007 May 25; published 2007 June 27

### ABSTRACT

The negative molecular ion  $C_8H^-$  has been detected in the Galactic molecular source TMC-1. Four rotational transitions have been observed in the centimeter-wave band with the NRAO 100 m Green Bank Telescope (GBT) at precisely the frequencies calculated from the recent laboratory spectroscopy of this large carbon chain anion.  $C_8H^-$  is about 5% as abundant as  $C_8H$ , or somewhat more than  $C_6H^-$  relative to  $C_6H$  (1.6%). Improved values of the column densities of  $C_6H^-$  and  $C_6H$ , and an upper limit for the abundance of the smaller carbon chain  $C_4H^-$  of 0.014% with respect to  $C_4H$ , have also been determined.

*Subject headings:* ISM: molecules — line: identification — molecular data — molecular processes — radio lines: ISM

The laboratory identification of the carbon chain negative ion  $C_8H^-$  as the carrier of the series of unidentified rotational lines observed by Kawaguchi et al. (1995) in the circumstellar envelope of the evolved carbon star IRC +10 216 and the detection of this anion in the dark molecular cloud TMC-1 have renewed interest in molecular anions with respect to laboratory, observational, and astrochemical studies (McCarthy et al. 2006). Three closely related carbon chain anions,  $CCH^-$ ,  $C_4H^-$ , and  $C_8H^-$  (Brünken et al. 2007; Gupta et al. 2007), and the first member of the isoelectronic  $C_{2n+1}N^-$  series,  $CN^-$  (Gottlieb et al. 2007), were subsequently detected by high-resolution rotational spectroscopy in this laboratory, allowing sensitive searches for these anions in space. Of these,  $C_4H^-$  has recently been detected in IRC +10 216 (Cernicharo et al. 2007) on the basis of the laboratory rest frequencies, which have been determined to better than  $0.1 \text{ km s}^{-1}$ .

Here we report detection of a still larger molecular anion in TMC-1: the carbon chain  $C_8H^-$ . The results of our observations are summarized in Figure 1, which is the main exhibit of this Letter. As shown, four rotational transitions have been detected in the centimeter-wave band at a modest signal-to-noise ratio (about 3). There are no anomalies in the identification: the velocities, widths, and relative intensities (see Table 1) of the lines are those expected for TMC-1, and they match well those of other molecules in this source (e.g.,  $HC_9N$ , shown at the bottom of Fig. 1). The confidence that can be placed on the identification of  $C_8H^-$  is considerably enhanced by the low density of lines in TMC-1 and by the apparent absence of blends and the ambiguities they introduce. From these observations, precise measurements of the abundance of  $C_8H^-$  relative to neutral  $C_8H$  and to the previously discovered  $C_6H^-$  have been obtained.

The observations were done with the NRAO 100 m Green Bank Telescope (GBT)<sup>3</sup> in 2007 April. Three successive transitions of  $C_8H^-$  that lie within the 12–15.4 GHz bandwidth of the Ku-band receiver and are close to the peak of the Boltzmann

distribution (for a source temperature of 5 K) were observed simultaneously. A fourth line at 18.7 GHz was found in GBT archival data taken between 2004 and 2006. The GBT spectrometer was configured for simultaneous observations of both polarizations in four frequency windows, each 50 MHz wide, at a frequency resolution of  $\delta\nu = 1.53 \text{ kHz}$ . The fourth frequency window was devoted to lines of  $C_6H$ ,  $C_8H$ , and  $C_6H^-$ . System temperatures were typically  $\sim 25 \text{ K}$  across the band. Additional measurements of  $C_8H^-$ ,  $C_6H$ ,  $C_6H^-$ ,  $C_4H$ , and  $C_4H^-$  were done at K band (18–22.4 GHz,  $T_{\text{sys}} = 40\text{--}50 \text{ K}$ ,  $\delta\nu = 6.1 \text{ kHz}$ ) and X band (8–10 GHz,  $T_{\text{sys}} = 30\text{--}40 \text{ K}$ ,  $\delta\nu = 1.53 \text{ kHz}$ ).

Spectra were taken by position-switching with a period of 4 minutes, the OFF position lying 30' east in right ascension of TMC-1. The pointing and focusing of the telescope were checked approximately every 90 minutes by observing a strong nearby continuum source (0431+2037); the pointing was generally good to 10". Intensities at all frequencies were calibrated by observing the quasar 3C 147.

The column densities ( $N_T$ ) of the carbon chain anions and their corresponding neutrals studied here are summarized in Table 2, along with the dipole moments and partition functions ( $Z$ ) used in our calculations. The relevant line parameters are given in Tables 1 and 3. Because the observed transitions are few and come from levels that lie fairly close in energy, it was not feasible to extract a rotational temperature from the data; in our analysis, an excitation temperature of 5 K was assumed, the value obtained by Bell et al. (1999) from observations of  $C_6H$  with the NRAO 43 m telescope.

We find that  $C_8H^-$  is present in TMC-1 at an abundance of roughly 5% with respect to that of  $C_8H$ , a factor of 3 greater than our current estimate of 1.6% for  $C_6H^-$  relative to  $C_6H$  (Table 2). Our initial estimate of the  $C_6H^-/C_6H$  ratio (2.5%) was somewhat uncertain because it was derived from observations of  $C_6H$  with the NRAO 43 m telescope (Bell et al. 1999). To minimize uncertainties caused by different telescope beams, we reobserved with the GBT three transitions of  $C_6H$  and one of  $C_6H^-$ . In addition, a third transition of  $C_6H^-$  at 8.261 GHz ( $J = 3\text{--}2$ ) was detected (see Table 3).

Lines of  $C_8H^-$  are conspicuous in space owing to the smaller partition function and larger dipole moment relative to those of neutral  $C_8H$ . As shown in Figure 2, the  $C_8H^-$  lines are only about 3 times less intense than one of the hyperfine components of  $C_8H$ , although the neutral is 20 times more abundant. The large gain in line intensity of the anion is the result of “spectral com-

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<sup>3</sup> The National Radio Astronomy Observatory is a facility of the National Science Foundation operated under cooperative agreement by Associated Universities, Inc.

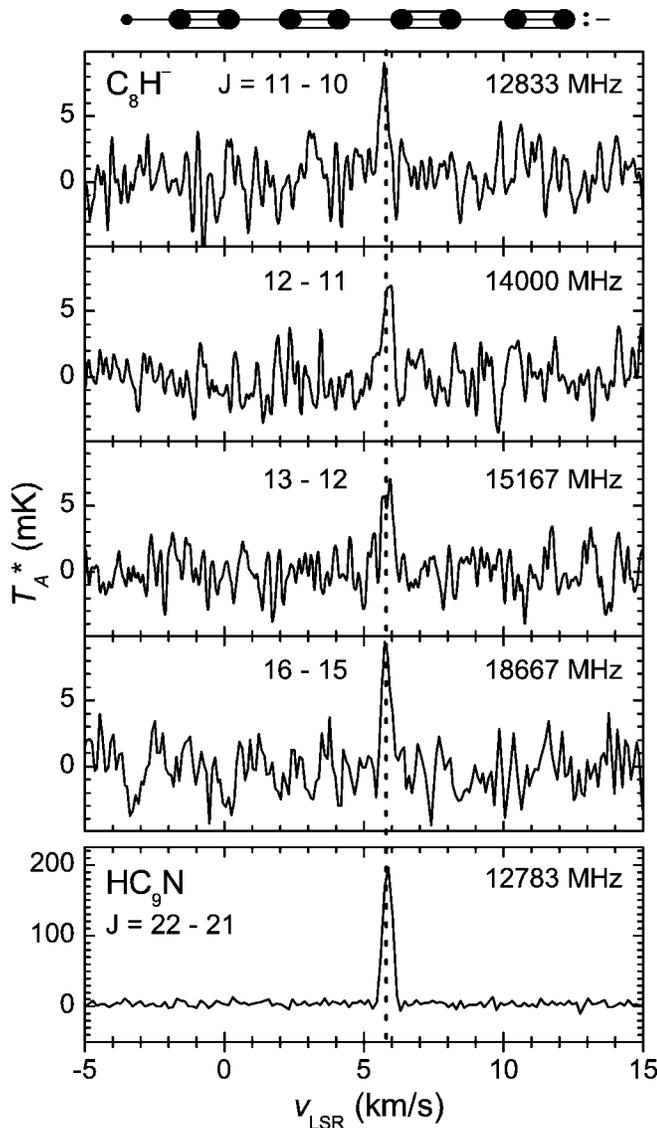


FIG. 1.—Observed lines of  $C_8H^-$  in TMC-1 and one  $HC_9N$  for comparison (bottom). The dashed line is at  $v_{LSR} = 5.8 \text{ km s}^{-1}$ , the assumed source velocity. The spectra have been smoothed to a resolution of 6.1 kHz. Data from several observing sessions and from both polarizations were averaged to enhance the signal-to-noise ratio. The total integration time for the  $C_8H^-$  lines was  $\sim 37$  hr in the Ku band and  $\sim 27$  hr in the K band.

pression”: the intensity that is spread over several lines in the open-shell radical because of fine and hyperfine interactions and  $\Lambda$ -doubling collapses into a single line for the closed-shell anion. Line intensities are further enhanced by a factor of nearly 4, owing to the greater polarity of the anion—to the obvious benefit of astronomical detection. It is worth noting that  $C_8H^-$  has a larger dipole moment (11.9 D) than any other molecule yet found in space.

We were unable to detect the shorter chain  $C_4H^-$  with the GBT in a fairly short observation time ( $\sim 3$  hr). However, even with this modest level of integration, a very low upper limit for the  $C_4H^-/C_4H$  ratio of  $<0.014\%$  is derived. Such a low ratio can be obtained because the enhancement in line intensity due to spectral compression and increased polarity for  $C_4H^-$  relative to  $C_4H$  is nearly 2 orders of magnitude, and because neutral  $C_4H$  is abundant in TMC-1. The derived anion-to-neutral ratio is at least 2 orders of magnitude smaller than that determined for the two longer chains in TMC-1, but it is comparable to

TABLE 1  
LINES OF  $C_8H^-$  IN TMC-1

Transition $J'-J$	Frequency <sup>a</sup> (MHz)	$T_A^*$ (mK)	$v_{LSR}$ ( $\text{km s}^{-1}$ )	$\Delta v$ ( $\text{km s}^{-1}$ )
11–10	12833.460	8(1)	5.71(5)	0.36(4)
12–11	14000.134	7(1)	5.86(5)	0.37(4)
13–12	15166.806	6(1)	5.84(6)	0.45(4)
16–15	18666.814	10(2)	5.80(7)	0.34(5)

NOTES.—The  $1 \sigma$  uncertainties in parentheses are in the units of the last significant digit. Line parameters are derived from a least-squares fit of a Gaussian profile to the spectra shown in Fig. 1;  $\alpha(1950) = 04^{\text{h}}38^{\text{m}}38.6^{\text{s}}$ ,  $\delta(1950) = +25^{\circ}35'45.0''$ .

<sup>a</sup> From Gupta et al. (2007).

the value of  $\sim 0.02\%$  found for  $C_4H^-/C_4H$  in IRC +10 216 (Cernicharo et al. 2007).

The high abundances of  $C_6H^-$  and  $C_8H^-$  with respect to their parent radicals suggest that the anions are formed by a simple and efficient mechanism. A likely process is electron radiative attachment:  $X + e^- \rightarrow X^- + h\nu$ , which is favored by a large electron affinity (EA) of the parent neutral, and a high density of vibronic states, which allows rapid relaxation to the anionic ground state (Terzieva & Herbst 2000). Both  $C_6H$  and  $C_8H$  possess unusually high electron affinities (3.8 and 4.0 eV, respectively; Rienstra-Kiracofe et al. 2002) and are large by the standards of astronomical molecules. The threefold greater ratio of  $C_8H^-$  to  $C_8H$  compared to the ratio of  $C_6H^-$  to  $C_6H$  is plausibly the result of size. The abundances of the  $C_{2n}H^-$  anions recently predicted by Millar et al. (2007) are in good agreement with our observed values, suggesting that electron radiative attachment may indeed be the main route to anion formation.

$C_4H$  also has a large electron affinity (3.6 eV; Rienstra-Kiracofe et al. 2002) and is only somewhat smaller than  $C_6H$ , so the surprisingly low abundance limit for  $C_4H^-/C_4H$  in TMC-1 suggests that other factors may be important in anion formation. A conspicuous difference between  $C_4H$  and the two larger radicals is its polarity: only 0.9 D for  $C_4H$  versus 5.5 and 6.3 D for  $C_6H$  and  $C_8H$ , respectively. As discussed in the literature (e.g., Lykke et al. 1984; Güthe et al. 2001), cross sections for electron attachment are considerably enhanced for highly polar molecules, particularly those with dipole moments in excess of 2–2.5 D owing to the existence of long-lived dipole-bound states (DBSs) that may facilitate anion formation. Because of its small dipole moment and the absence of a DBS supported by its electronic ground state (Pino et al. 2002), electron capture and the formation of the temporary negative ion, the first steps in electron radiative attachment (Desfrancois et al. 1996), may be very inefficient for  $C_4H$ . The high  $C_4H^-/C_4H$  ratio of 1% predicted by Millar et al. (2007) might therefore only provide an upper limit

TABLE 2  
ABUNDANCES OF  $C_{2n}H^-$  ANIONS AND RADICALS IN TMC-1

Molecule	Dipole Moment <sup>a</sup> (D)	$Z(5 \text{ K})$	$N_T$ ( $10^{10} \text{ cm}^{-2}$ )	Anion-to-Neutral Ratio (%)
$C_4H^-$	6.2	23	$<8.5$	$<0.014(1)$
$C_4H$	0.9	89	6100(500)	...
$C_6H^-$	8.2	76	12(2)	1.6(3)
$C_6H$	5.5	312	750(80)	...
$C_8H^-$	11.9	179	2.1(4)	5(1)
$C_8H$	6.3	720	46(4)	...

NOTE.—The  $1 \sigma$  uncertainties in parentheses are in the units of the last significant digit.

<sup>a</sup> Values for  $C_4H^-$  and  $C_6H^-$  are from Blanksby et al. (2001), for  $C_4H$  and  $C_6H$  from Woon (1995), for  $C_8H^-$  from Gupta et al. (2007), and for  $C_8H$  from McCarthy et al. (1996).

TABLE 3  
OTHER LINES OF  $C_{2n}H$  ANIONS AND RADICALS OBSERVED IN TMC-1

MOLECULE	TRANSITION			FREQUENCY (MHz)	$T_A^*$ (mK)	$\Delta v$ (km s <sup>-1</sup> )	$\int T_A^* \Delta v$ (K km s <sup>-1</sup> )
	$J'-J$	$F'-F$	Parity				
$C_8H^a$ .....	12.5–11.5	...	<i>e</i>	14666.686	...	...	0.0108(5)
			<i>f</i>	14666.771	...	...	0.0115(5)
$C_6H^{-b}$ .....	3–2	...	...	8261.174	13(1)	0.41(5)	0.0058(8)
	5–4	...	...	13768.612	41(2)	0.33(2)	0.0153(1)
$C_6H^c$ .....	3.5–2.5	4–3	<i>e</i>	9703.498	71(3)	0.40(2)	0.031(2)
		3–2	<i>e</i>	9703.609	61(4)	0.30(2)	0.020(2)
		4–3	<i>f</i>	9703.834	66(3)	0.45(3)	0.033(2)
		3–2	<i>f</i>	9703.945	45(3)	0.60(4)	0.030(2)
	5.5–4.5	6–5	<i>e</i>	15248.247	214(4)	0.39(1)	0.096(2)
		5–4	<i>e</i>	15248.322	169(4)	0.39(12)	0.076(2)
		6–5	<i>f</i>	15249.084	206(4)	0.36(1)	0.086(2)
		5–4	<i>f</i>	15249.158	189(4)	0.37(1)	0.081(2)
	6.5–5.5	7–6	<i>e</i>	18020.574	278(13)	0.34(3)	0.112(8)
		6–5	<i>e</i>	18020.644	231(13)	0.30(3)	0.083(7)
		7–6	<i>f</i>	18021.752	267(13)	0.33(2)	0.105(7)
		6–5	<i>f</i>	18020.818	241(14)	0.29(2)	0.082(7)
	7.5–6.5	8–7	<i>e</i>	20792.872	187(8)	0.37(2)	0.085(5)
		7–6	<i>e</i>	20792.945	170(7)	0.37(2)	0.076(5)
		8–7	<i>f</i>	20794.444	194(7)	0.38(2)	0.090(5)
		7–6	<i>f</i>	20794.512	176(8)	0.34(2)	0.073(4)
$C_4H^{-d}$ .....	1–0	...	...	9309.887	<8	...	...
	2–1	...	...	18619.758	<26	...	...
$C_4H^e$ .....	1.5–0.5	1–0	...	9493.060	186(7)	0.33(2)	0.070(4)
		2–1	...	9497.615	605(11)	0.31(7)	0.208(5)
		1–1	...	9508.005	162(7)	0.33(2)	0.606(4)

NOTES.—The  $1\sigma$  uncertainties in parentheses are in the units of the last significant digits;  $\alpha(1950) = 04^h38^m38.6^s$ ,  $\delta(1950) = +25^\circ35'45.0''$ .

<sup>a</sup> The frequencies are from McCarthy et al. (1999); *ef* is the  $\Lambda$ -doublet parity; and the hyperfine structure has not been fully resolved. The integrated area was obtained from the spectrum shown in Fig. 2.

<sup>b</sup> Frequencies from McCarthy et al. (1999); *ef* is the  $\Lambda$ -doublet parity.

<sup>c</sup> Frequencies from McCarthy et al. (2006).

<sup>d</sup> Frequencies from Gupta et al. (2007);  $T_A^*$  is the peak noise.

<sup>e</sup> Frequencies from Chen et al. (1995) and Gottlieb et al. (1983).

of the anion abundance, since their model assumes that the temporary negative ion is formed upon each collision with an electron.

The observation of isovalent  $C_3N^-$  in the laboratory and in space may clarify the role of the dipole moment in electron

attachment and of DBSs in anion formation. Like  $C_4H$ ,  $C_3N$  also has a large electron affinity (EA = 4.6 eV; Graupner et al. 2006) and is similar in size, but its dipole moment is far larger—large enough to support a DBS (2.85 D; McCarthy et al. 1995)—implying that electron attachment and anion formation may be much more efficient and that the abundance ratio of  $C_3N^-$  to  $C_3N$  may be much higher than that of  $C_4H^-$  to  $C_4H$ . The detection of more exotic species, like the asymmetric rotor  $CH_2CN^-$ , may also clarify the role of electron affinity in anion formation, because the parent neutral, which is abundant in a variety of astronomical sources (e.g., Irvine et al. 1988), has a large dipole moment (3.5 D) but a fairly low electron affinity (1.5 eV; Rienstra-Kiracofe et al. 2002). Autodetachment studies (Lykke et al. 1987) established the existence of a DBS for  $CH_2CN^-$  and provided precise rotational constants for an astronomical search.

Because the lines of  $C_8H^-$  were only detected after long integration, the prospect of finding still larger anions would seem to be bleak, but that may be an overly pessimistic conclusion. The longer chain  $C_{10}H^-$  is expected to form even more efficiently owing to its still larger size and a higher electron affinity of neutral  $C_{10}H$  (Blanksby et al. 2001). We estimate by extrapolation from the smaller  $C_{2n}H^-$  chains a rotational constant of  $B = 299.88(3)$  MHz for  $C_{10}H^-$  (e.g., see McCarthy et al. 2000) and an exceptionally large dipole moment of  $\geq 14$  D (compared to 7.5 D for the neutral). Because of high polarity and spectral compression, lines of the anion are expected to be stronger than those of neutral  $C_{10}H$  if the anion-to-neutral ratio is in excess of 30%.

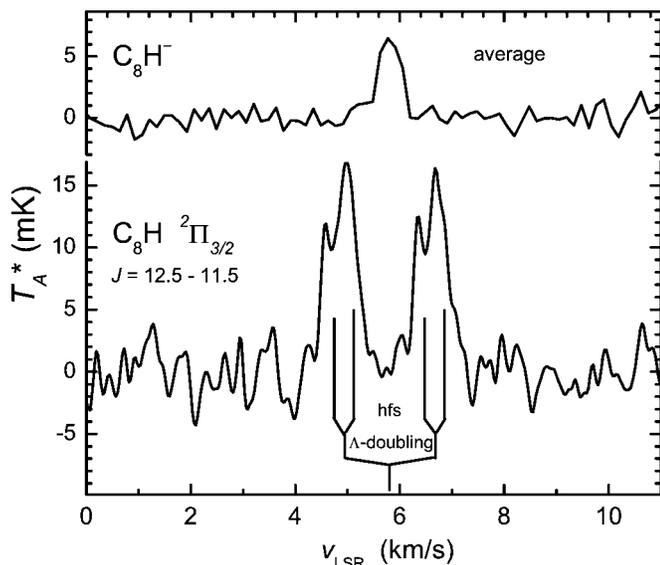


FIG. 2.—Average of the four lines of the  $C_8H^-$  anion in TMC-1 is shown at the top. The indicated transition of neutral  $C_8H$  in TMC-1 is shown at the bottom, with well-resolved  $\Lambda$ -doubling and partially resolved hyperfine structure. The spectra have been smoothed to a resolution of 6.1 kHz.

The astronomical detection of yet a third molecular anion suggests that negative ions are more widely distributed and easier to observe than previously assumed. Many other anions probably exist in space, and their rotational spectra may be detectable with sensitive radio telescopes such as the GBT. There is very little high-resolution spectroscopic data on molecular anions, so laboratory detection is an important prerequisite for astronomical discovery. Large anions with high binding energies, large dipole moments, and simple rotational spectra remain the prime targets for these studies.

Anions have been detected so far in two well-known sources, which are both rich in carbon chains but are otherwise very distinct physically and chemically: the cold dark cloud TMC-1 and the metal-rich, warm molecular envelope around IRC +10 216. There may well be better sources, which remain to be identified by a Galactic survey of molecular anions toward a

variety of interstellar and circumstellar environments, the starting point obviously being the most abundant anion,  $C_6H^-$ . The results of such a survey and further investigations of the anionic inventory may serve to improve our understanding of the formation processes and sites of negative ions in space. Such a study may also result in the detection of still larger anions, e.g.,  $C_{10}H^-$ .

We thank the NRAO staff for assistance with the GBT observations, data reduction, and archive search. We are especially grateful to R. J. Maddalena for his continuing support. This work is supported by the National Science Foundation grant CHE-0353693; support for H. G. is provided by the Robert A. Welch Foundation through a grant to J. F. Stanton at the University of Texas, and by the NSF through award GSSP07A-0010 from the NRAO.

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