Theoretical Characterization of C_3H and C_5H and Their Anions

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Abstract

Highly correlated ab initio calculations are employed for the structural and spectroscopic characterization of small odd chains of type $C_{2n+1}H$, considering neutral forms, cations, and giving special attention to the anions. This work confirms the stability of the linear carbon chains and carbon clusters containing three-body rings. The smallest species, C_3H , displays three stable structures, whereas C_5H possesses at least 8 neutral isomers and 11 and 10 isomers with a negative or a positive charge. The equilibrium geometries, which can be candidates for laboratory and astrophysical detection, are studied using the RCCSD(T)-F12 and MRCI/CASSCF levels of theory, specifying properties for various electronic states. Four different stable isomers are confirmed for the C_5H^- anion. They are two rings and two chains, all showing singlet ground electronic states. The viability of the triplet linear form of C_5H^- ($C_{\infty v}(X^3\Sigma^-)$) postulated in previous works, is not confirmed because it appears to be really dependent on the electron correlation energy denoting instability. A quasi-linear singlet ($C_s(X^1A')$) represents a secondary minimum. Electronic state crossing occurs close to the linear structure where spin-orbit effects are negligible. The most stable structure of C_5H^- is a three-carbon cycle in which rotational constants have been determined to be $A_0 = 35479.86$ MHz, $B_0 = 3618.29$ MHz, and $C_0 = 3280.10$ MHz. Its dipole moment is relatively large (6.4086 D).

Key words: astrochemistry – catalogs – ISM: abundances – ISM: molecules – molecular data

1. Introduction

Dense molecular clouds and carbon-rich circumstellar envelopes contain abundant carbon clusters and hydrogen-terminated clusters, with up to 13 atoms (Kaiser 2002). These unsaturated radicals are thought to be key intermediates in the synthesis of polycyclic aromatic hydrocarbons, carbonaceous grain particles, and fullerenes (Pascoli & Polleux 2000).

Although C_n and C_nH compounds are commonly observed in numerous gas sources, the dark Taurus molecular cloud TMC-1 and the evolved carbon star IRC+10216 had a leading role in the discoveries. The detections entail a previous laboratory characterization that can be extremely arduous in the case of unsaturated species. Experiments that are not always feasible as well as theoretical studies are crucial because the molecular properties determine the abundances, reactivity, and techniques applied for detection. Species with a zero permanent dipole moment, such as the linear carbon clusters, C_n , must be detected through infrared active rovibrational transitions or through electronic transitions. However, the presence of the hydrogen atom in the C_nH species assures a more or less strong permanent dipole moment and the observation using varied techniques. The carbon skeletal structure is a decisive issue. Small chains of type $C_{2n}H_m$ with an even number of carbon atoms appear to be more easily detectable than other compounds. Hence, the primary discoveries of the linear isomers $l-C_2H$ ($X^2\Sigma$) and $l-C_4H$ ($X^2\Sigma$) in the Orion Nebula and in IRC+10216 occur very early (Tucker et al. 1974; Guélin et al. 1978). First observations of large systems, such as C_6H ($X^2\Pi$) and C_8H ($X^2\Pi$), were delayed up to 1986 and 1996 (Suzuki et al. 1986; Guélin et al. 1987; Cernicharo & Guélin 1996). In general, neutral linear species with $^2\Sigma$ electronic ground states are considered more detectable than others with $^2\Pi$ ground states for which permanent dipole moments are usually relatively small. In general, the ground states of the

small even-species are nondegenerate whereas those of odd-carbon species and large clusters are degenerate (Jochnowitz & Maier 2008).

The discovery of even hydrogenated-terminated carbon clusters precedes the odd chains, although some small odd clusters, such as C_3H , are ever-present in interstellar sources that show high fractional abundances (Kaiser 2002). Abundances of the cyclic isomer, $c-C_3H$ (X^2B_1) in dense molecular clouds are relevant. Linear $l-C_3H$ ($X^2\Pi$) was first detected by Thaddeus et al. (1985) toward TMC-1 and the carbon star IRC+10216. Two years later, Yamamoto et al. (1987) identified rotational transitions of the cyclic isomer in TMC-1 prior to laboratory synthesis via radiofrequency discharge of He/CO/ C_2H_2 mixtures.

The C_5H radical was discovered in 1986 (Cernicharo et al. 1986a). Six line doublets were observed in IRC+10216 with the RAM telescope and were assigned to the $^2\Pi$ ground state of the linear form. Later on, Cernicharo et al. (1986b) detected four lines and assigned them to the $^2\Pi_{3/2}$ state. The hyperfine structure was first resolved in 1987 (Cernicharo et al. 1987). The detection of the C_7H radical is recent (Guélin et al. 1997).

Parity rules can be applied to the detectability of negative carbon chains (Senent & Hochlaf 2013). From the observation of the first interstellar anion, C_6H^- (McCarthy et al. 2006), the detection of only six anions, all of them revealing nondegenerate ground electronic states, is unquestionable. They are three hydrogen-terminated even carbon chains, C_6H^- , C_4H^- (Cernicharo et al. 2007), and C_8H^- (Brünken et al. 2007), and three nitrogen-terminated odd-carbon chains, CN^- (Agúndez et al. 2010), C_3N^- (Cernicharo et al. 2008), and C_5N^- (Agúndez et al. 2010). The present paper highlights the study of the undiscovered odd anions, C_3H^- and C_5H^- , for which searching is relevant. On the basis of ab initio calculations given the lack of experimental data, the quasi-linear form of C_3H^- was postulated

by Huang et al. (2013) and Fortenberry et al. (2013) as the source of the lines previously observed by Pety et al. (2012), who had assigned them to the cation. Lines observed toward SgrB2 (N), TMC-1, and IRC+10216 (McGuire et al. 2013) were also related to $\text{l-C}_3\text{H}^+$. Revisits of the assignments (McGuire et al. 2014a, 2014b) and new theoretical and experimental work of Botschwina et al. (2014) and Brünken et al. (2014), yield to the cation being responsible for the lines.

In this work, we use highly correlated ab initio methods to determine accurately significant physical properties of C_3H and C_5H , such as rotational and vibrational parameters, dipole moments, and the nature of the ground electronic states. In previous references, neutral and charged isomers of C_3H were investigated using different experimental and theoretical techniques (Huang et al. 2013; Fortenberry et al. 2013, 2014; Botschwina et al. 2014; Lakin et al. 2001; Stanton 1995; Woon 1995). This very small species presents very complex spectra where Renner–Teller (Ding et al. 2001), pseudo Jahn–Teller (Thaddeus et al. 1985; Stanton 1995), and spin–orbit effects (Yamamoto et al. 1990; Ding et al. 2001; Caris et al. 2009) can be identified. Previous ab initio calculations (Huang et al. 2013; Fortenberry et al. 2013; Botschwina et al. 2014) confirm the relevance of the electron correlation for the identification of the most stable isomeric forms. In Mintz & Crawford (2010) have explored the Jahn–Teller effect of the cyclic isomers comparing unrestricted and restricted coupled cluster calculations. Bassett & Fortenberry (2017) have determined theoretically rotational and vibrational parameters for both neutral and negative charged cycles. The experimental vibrational frequencies of the neutral form were measured in the gas phase and Ar matrix by Sheehan et al. (2008a), Huang & Graham (1990), and Jiang et al. (1993).

Few previous studies focused on the spectroscopy of C_5H . Crawford et al. (1999) determined the structure of the neutral cluster and their isomers using ab initio calculations. By using density functional theory (DFT), Sheehan et al. (2008a) reproduced the earlier calculations of Blanksby et al. (1999), who found one linear and various cyclic isomers for the negatively charged C_5H^- cluster. They determined a quasi-linear structure for the triplet chain, C_5H^- , consistent with the electron affinity measured using anion photoelectron spectroscopy. These authors focus on the effect of the electron correlation on the relative stabilities of the anions. Experimental rotational constants of C_5H were determined by Cernicharo et al. (1986a), McCarthy et al. (1999), and Apponi et al. (2001). The neutral form experimental vibrational frequencies were measured in gas phase and Ne matrix by Sheehan et al. (2008a) and Wu et al. (2009).

Structural isomerism is extensive in interstellar clouds (Lovas et al. 2010). In previous papers (Senent & Hochlaf 2010; Massó et al. 2007; Massó & Senent 2009; Hammoutène et al. 2012; Al-Mogren et al. 2013; Al-Mogren & Senent 2017), we focus on the large number of stable geometries of unsaturated chains containing a unique heteroatom; many of them are of very low stability. Frequently, linear forms and isomers with three-carbon cycles present noticeable stabilities.

2. Computational Details

The search for isomers and transitions states was carried out with the code GAUSSIAN 09, at the second-order Möller–Plesset level of theory in connection with the aug-cc-pVTZ basis set (AVTZ; Dunning 1989). The same level of theory was also employed to determine anharmonic force fields for the anions.

Although all the isomers can be intermediates of relevant chemical processes or can be building blocks of more complex species, the most stable ones are the best candidates for detection. For this reason, the most probable geometries and their spectroscopy parameters were reoptimized using explicitly correlated coupled cluster theory RCCSD(T)-F12 (Knizia et al. 2009; Werner et al. 2007) implemented in MOLPRO.⁴ For the later calculations, the default options were employed. The ensemble of three basis sets, the orbital AVTZ, the VTZ-MP2FIT (for the density fitting integral evaluation of the F12 integrals), and the VTZ/JKFIT (for the resolutions of the identity expansions), used in the explicitly correlated calculations is denoted in this paper by AVTZ-F12 (Weigend 2002; Weigend et al. 2002).

Vertical excitation energies to the excited electronic states were determined with the complete active space self-consistent field (CASSCF) method (Knowles & Werner 1985; Werner & Knowles 1985) followed by the internally contracted multi-reference configuration interaction (MRCI) approach (Werner & Knowles 1988; Knowles & Werner 1988). For C_3H , all the valence electrons and orbitals were considered to define the active space. For the linear C_5H forms, in the CASSCF calculations, the lowest ten σ molecular orbitals (MOs) and the lowest two π orbitals (MO) were kept doubly occupied, considering the upper five σ , and eight π MOs as active defining an active space of 13 active orbitals. For the nonlinear forms 13 MOs were employed to define the active space and 12 orbitals were kept doubly occupied.

For spin–orbit calculations, the CASSCF wave functions were used as the multi-electron basis for the two-step spin–orbit coupling calculation at the level of Breit–Pauli Hamiltonian (Berning et al. 2000). The T1 diagnostic (Lee & Taylor 1989; Lee 2003), as well as the coefficients of the most contributed configurations to the CASSCF wave functions were employed to evaluate the multiconfigurational character of the relevant isomers.

3. Equilibrium Geometries of the Neutral and Charged Species

The search for all the neutral and charged equilibrium structures obeying the C_3H and C_5H empirical formula was the first step of this work. Geometries were optimized at the MP2/AVTZ level of theory starting with all the possible atomic distributions shown in Figure 1. Table 1 displays the final structures, their relative energies and the corresponding symmetry and spin-multiplicity of the ground electronic states. The structures are labeled using the l and c symbols for the linear and cyclic chains, the ql symbol for the quasi-linear ones, and the t, s, and p symbols to distinguish the cyclic structures containing three, four, and five carbon rings. The harmonic frequencies were computed to assure the minimum energy character. In Figure 1, the ql clusters are omitted because they are considered slightly distorted linear chains.

The forms of prominent stabilities are emphasized in black (see Table 1). For C_3H , our work confirms the existence of three isomeric neutral forms, l- C_3H , 12- C_3H , and c- C_3H , three negative charged forms, c- C_3H^- , ql- C_3H^- , and 12- C_3H^- , and three isomers with a positive charge, l- C_3H^+ , c- C_3H^+ , and 12- C_3H^+ . The linear anion l- C_3H^- represents a transition state

⁴ H.-J. Werner & P. J. Knowles et al., MOLPRO version 2012.1, a package of ab initio programs, <http://www.molpro.net>.

Figure 1. Atomic distributions corresponding to the C_3H and C_5H empirical formula.

Table 1

Relative Energies (in eV)^a of the Equilibrium Structures Calculated at the MP2/AVTZ Level of Theory (TS = Transition State)^b

	Neutral	Anion	Cation
C_3H			
l- C_3H	0.75 $C_{\infty v}(X^2\Pi)$	-1.60 (TS) $C_{\infty v}(X^3\Sigma^-)$	9.19 $C_{\infty v}(X^1\Sigma^+)$
ql- C_3H		-1.51 $C_s(X^1A')$	
c- C_3H	0.0 $C_{2v}(X^2B_2)$	-2.01 $C_{2v}(X^1A_1)$	9.84 $C_{2v}(X^1A_1)$
l2- C_3H	3.26 $C_{2v}(X^2A_2)$	-1.09 $C_{2v}(X^3B_1)$	12.14 $C_{2v}(X^1A_1)$
C_5H			
l1- C_5H	0.94 $C_{\infty v}(X^2\Pi)$	-1.64 $C_{\infty v}(X^3\Sigma^-)$	7.9 $C_{\infty v}(X^1\Sigma^+)$
ql- C_5H		-1.84 $C_s(X^1A')$	
l2- C_5H			10.92 $C_s(X^1A')$
l3- C_5H	2.52 $C_{2v}(X^2A_1)$	-2.70 $C_{2v}(X^1A_1)$	12.98 $C_{2v}(X^3B_2)$
t1- C_5H	3.69 $C_s(X^4A'')$	-2.87 $C_s(X^1A')$	10.81 $C_s(X^3A')$
t2- C_5H	0.0 $C_{2v}(X^2B_2)$	-2.64 $C_{2v}(X^1A_1)$	9.65 $C_{2v}(X^3B_2)$
t3- C_5H	4.29 $C_s(X^4A')$	0.80 $C_s(X^3A'')$	
t4- C_5H			12.24 $C_s(X^1A')$
t5- C_5H	4.84 $C_s(X^4A'')$	-1.32 $C_s(X^1A')$	11.73 $C_s(X^1A')$
s1- C_5H		-0.22 $C_s(X^1A')$	...
s2- C_5H	1.81 $C_{2v}(X^2B_2)$	-0.45 $C_1(X^1A)$	10.14 $C_{2v}(X^1A_1)$
s3- C_5H	1.57 $C_s(X^2A')$	-1.39 $C_s(X^1A')$	11.09 $C_{2v}(X^3B_2)$
p1- C_5H		-0.70 $C_1(X^1A)$	10.33 $C_s(X^1A')$

Note.

^a The reference for the relative energies are the most stable neutral forms (a) c- C_3H ($E = -114.427308$ au) and (b) t2- C_5H form ($E = -190.415892$ au).

^b The energies of the most stable forms are in bold.

of a triplet potential energy surface. Our results support previous ab initio calculations (Fortenberry et al. 2013, 2014).

The search yielded to 8, 11, and 10 isomers of C_3H , C_5H^- , and C_5H^+ , respectively. Eight very stable geometries of Table 1 are emphasized in black: the two isomeric neutral forms l1- C_5H and t2- C_5H , the four negative charged forms ql- C_5H^- , l3- C_5H^- , t1- C_5H^- , and t2- C_5H^- , and two isomers with a positive charge, l1- C_5H^+ and t2- C_5H^+ . At the MP2 level of theory, the l1- C_5H^- triplet behaves as an isomer with real harmonic frequencies, a behavior that is not confirmed when highly correlated methods are employed. For this reason, the viability of this triplet is the object of discussion in the next sections. Discrepancies due to electron correlation effects were anticipated by Sheehan et al. (2008a).

With the exception of the neutral three-body cycle t2- C_5H (Apponi et al. 2001), the rotational spectra of the nonlinear C_5H clusters have not received prior attention, failing the comparison of our results with previous works and experimental data. The main part of our calculated properties must be understood as theoretical predictions. We highlight the unusual behaviors of C_3H^- and C_5H^- in comparison with other carbon clusters. Generally, as occurs for even chains of type $C_{2n}H^-$, the stability of the negative charged linear carbon chains is prominent with respect to other isomers. Commonly, as we already pointed out (Senent & Hochlaf 2010; Hammoutène et al. 2012; Al-Mogren et al. 2013; Al-Mogren & Senent 2017),

Figure 2. Relative energies, ionization potential, and electron affinity of the most stable neutral and charged forms of C_3H .

the stability of both linear chains and the clusters containing three-carbon cycles is noticeable.

4. Neutral and Positive Charged Forms of C_3H and C_5H

Explicitly correlated coupled cluster theory CCSD(T)-F12 was employed to reoptimize the preferred geometries, in order to obtain accurate relative energies and reliable spectroscopic properties, such as equilibrium rotational constants and harmonic frequencies. The resulting structures and energies are summarized in the Schemes of Figures 2 and 3. Table 2 collects the most relevant outcomes for the neutral and positive charged forms.

For C_3H , the RCCSD(T)-F12 method delivers a qualitative description of the minimum energy geometries similar to that obtained with MP2. The relative order of stabilities coincides in Tables 1 and 2. The cyclic $c\text{-}C_3H$ represents the most stable neutral isomer and the reference for the relative energies. However, for C_5H , both levels of theory provide divergent orders of stabilities. With the most accurate procedure RCCSD(T)-F12, $11\text{-}C_5H$ lies below $t2\text{-}C_5H$, and both isomers are almost isoenergetic ($E_r = 0.14$ eV). Fourier transform microwave spectroscopy reveals a structure of the cyclic $t2\text{-}C_5H$ isomer that is apparently unsymmetrical, which is plausibly the result of pseudo-Jahn–Teller deformation (Apponi et al. 2001).

Computed electron affinities of $l\text{-}C_3H$ (−1.76 eV), $c\text{-}C_3H$ (−2.05 eV), $l\text{-}C_5H$ (−2.41 eV), and $t2\text{-}C_5H$ (−2.46 eV) are in good agreement with previous experimental data obtained via

anion photoelectron spectroscopy (Sheehan et al. 2008b, 2008a). In the next sections of the present paper, which are devoted to the anions, we reconsider the detachment energy of $l\text{-}C_5H$, which depends on the stability of the negative charged forms. The dipole moments of Table 2 were computed with MRCI/AVTZ. In the case of charged species, they were computed from the center of masses.

The comparison of the RCCSD(T)-F12 equilibrium rotational constants B_e with the B_0 experimental values measured in the vibrational ground state, is satisfactory. At this level of theory, $B_e(l\text{-}C_3H)$ and $B_e(l\text{-}C_5H)$ were computed to be 11096.13 MHz and 2378.85 MHz, respectively (see Table 2). The corresponding C_3H experimental parameters ($B_0 = 11189.052(48)$ MHz and $B_0 = 11189.1033(84)$ MHz) were fitted from observed microwave and submillimeter lines (Yamamoto et al. 1990; Caris et al. 2009; Yamamoto & Saito 1994). In the case of C_5H , the experimental rotational constants of the linear form ($B_0 = 2387.01 \pm 0.02$ MHz and $B_0 = 2395.12650(12)$ MHz) resulting from the works of Cernicharo et al. (1986a, 1986b) and McCarthy et al. (1999) and those of the cyclic isomer were measured by Apponi et al. (2001).

The CCSD(T)-F12 harmonic frequencies of the neutral species $l\text{-}C_3H$ and $11\text{-}C_5H$ and for $t2\text{-}C_5H$ denote the presence of Renner–Teller and Jahn–Teller deformations. The bending fundamentals of the linear forms, both showing $^2\Pi$ degenerate ground electronic states, split as a consequence of the Renner–Teller effect. For $t2\text{-}C_5H$, some unrealistic fundamentals derive from an evident Jahn–Teller deformation. Because of the inevitable numerical derivatives used for the computation of the CCSD(T)-F12 vibrational force fields, the distortion can be overestimated.

5. The Negative Charged Isomers C_3H^- and C_5H^- : Nature of the Ground Electronic State of the Negative Chains

To our knowledge, despite the electron affinities derived from anion photoelectron spectroscopy (Sheehan et al. 2008a, 2008b) and high-resolution photoelectron spectroscopy (Garand et al. 2010), experimental rovibrational data are not available for the negative forms. The available characterizations of the ground electronic states are mainly theoretical studies. The electronic spectrum analysis revealed vibrational features (Pachkov et al. 2001) (Pino et al. 2004; Tulej et al. 2011). For both species, C_3H^- and C_5H^- , the RCCSD(T)-F12 structural and spectroscopic data and the MRCI dipole moments of the most stable isomers, are summarized in Table 3.

From the qualitative point of view, the RCCSD(T)-F12 results of C_3H^- coincide with those obtained using MP2. The most stable isomer $c\text{-}C_3H^-$ is a three-carbon cycle of C_{2v} symmetry with a ground electronic state of singlet spin-multiplicity (X^1A_1). A secondary minimum laying at 0.33 eV, presents a quasi-linear geometry with a singlet ground electronic state (X^1A'), confirming the previous calculations of Fortenberry et al. (2013, 2014). The hydrogen-terminated linear structure $l\text{-}C_3H^-$ ($X^3\Sigma^-$) represents a transition state of the low triplet state potential energy surface.

More challenging is C_5H^- , for which the present work carries out novelties and emphasize uncertain aspects for their clarification on the basis of very accurate methodology (CCSD(T)-F12). In 1999, Blanksby et al. predicted the existence of

Figure 3. Relative energies, ionization potential, and electron affinity of the most stable neutral and charged forms of C_5H .

four C_5H^- isomers of low energy using DFT and the AVTZ basis set. Three of them, a chain and two rings, showed ground electronic state of spin-multiplicity. The remaining isomer was a triplet quasi-linear chain of C_1 symmetry neighboring the linear form. Later on, Sheehan et al. (2008a), using the same functional (B3LYP) and the basis set (VDZ), confirmed the stability of the four structures. They added new CCSD(T) computations, but unfortunately, without providing the corresponding vibrational frequencies. This structure was considered for the interpretation of detachment experiments (Sheehan et al. 2008a) and electronic transitions (Tulej et al. 2010) on the basis of the experimental value of the electron affinity (-2.421 ± 0.019 eV) which coincides with the triplet chain relative energy.

CCSD(T)-F12/AVTZ calculations evidence the existence of four very stable and close-in energy isomers. Two of them are chains, l3- C_5H^- (C_{2v} (X^1A_1)) and ql- C_5H^- (C_s (X^1A')) and two contain three-body rings, t1- C_5H^- (C_s (X^1A')) and t2- C_5H^- (C_{2v} (X^1A_1)). From the qualitative point of view, the present calculations confirm the statements of Sheehan et al. (2008a) for the l3-, t1-, and t2- isomers derived from CCSD(T) theory. The t1- C_5H^- cycle represents the absolute minimum. The secondary minima l3- C_5H^- and t2- C_5H^- lie at 0.08 eV and 0.26 eV above t1- C_5H^- , respectively.

The quasi-linear triplet ql- C_5H^- (X^3A), predicted by Blanksby et al. (1999) and Sheehan et al. (2008a) using B3LYP, appears to be really dependent on the correlation

energy. At the MP2 level of theory, the most stable triplet structure is linear l1- C_5H^- ($C_{\infty v}$ ($X^3\Sigma^-$)) and all its frequencies are real. This triplet isomer appears to be less stable than the ql- C_5H^- (C_s (X^1A')) singlet geometry (see Table 1). However, using CCSD(T)-F12 or multiconfigurational CASSCF theories, the most stable triplet is linear but behaves as a transition state presenting an imaginary bending fundamental. With CCSD(T)-F12, the triplet geometry is more stable than the singlet, and its relative energy with respect to the neutral linear form (-2.41 eV) coincides exactly with the experimental electron affinity.

Then, whereas the singlet ql- C_5H^- (C_s (X^1A')) is a confirmed isomer, we cannot establish if the triplet l1- C_5H^- ($C_{\infty v}$ ($X^3\Sigma^-$)) is a real isomer. We must ponder that the theoretical procedure can introduce inaccuracies due to the inevitable use of numerical derivatives in a region where the potential energy surface is very flat when CCSD(T)-F12 is applied. With MP2 theory, we can employ analytical derivatives and find real frequencies. Previous works are unhelpful because, to our knowledge, a unique experimental vibrational frequency assigned to a skeletal bending mode is available (169 ± 5 , Tulej et al. 2010). It does not have anything to do with our bending frequencies.

The T1 diagnostic was determined for the stable anions obtaining the values of 0.017 (t1- C_5H^-), 0.017 (t2- C_5H^-), 0.021 (l3- C_5H^-), and 0.023 (ql- C_5H^-), for the singlets, and 0.020 (l1- C_5H^-) for the triplet. $T1 > 0.02$, as it is obtained for the

Table 2

RCCSD(T)-F12/AVTZ Relative Energies (E_r , in eV)^a of the Neutral and Positive Charged Forms, Ionization Potential (IP, in eV), Electron Affinity (EA, in eV), Equilibrium Spin–Orbit Constant ($|A_{SO,e}|$, in cm^{-1}), Structural Parameters (Distances in Å; Angles in Degrees), Rotational Constants (in MHz), and Harmonic Frequencies (ω , in cm^{-1}). MRCI Dipole Moments (μ , D)

l-C ₃ H C _{∞v} (X ² Π)		l-C ₃ H ⁺ C _{∞v} (X ¹ Σ ⁺)		c-C ₃ H C _{2v} (X ² B ₂)		c-C ₃ H ⁺ C _{2v} (X ¹ A ₁)	
	Calc.	Exp.	Calc.		Calc.	Exp.	Calc.
E_r	0.16		9.17	E_r	0.00		9.84
IP	9.01			IP	9.84		
EA	−1.76	−1.844 ± 0.003 ^b		EA	−2.05	−1.999 ± 0.003 ^b	
$ A_{SO,e} $	27.86						
C1C2	1.3429		1.3439	C1C2	1.3761		1.3779
C2C3	1.2439		1.2387	C1H	1.0791		1.0875
C3H	1.0654		1.0807	C2C1C3	59.9		56.3
μ_C	3.5192		2.9902	μ_A	2.901		1.3998
B_e	11096.13	11189.052(48) ^c 11189.1033(84) ^d	11112.69	A_e	44643.18	44536.821(67) ^e	49865.7975
$\omega(\sigma)$	3428 1870 1136	3238 ^f 1839 ± 10 ^b 1167 ^g , 1159.8 ^h	3300 2131 1181	$B_e C_e$	34103.62 19334.04	34016.3412(88) ^c 19188.8530(55) ^e	32943.2382 19837.7005
$\omega(\pi)$	788-371 230 32	376 ± 10 ^b 20.35 ^c	805 131	$\omega_1(a_1)$	3246, 1578, 1214	1613 ± 25 ^b	3211, 1715, 1391
				$\omega_4(b_1)$	858	508 ± 25 ^b	1391
				$\omega_5(b_2)$	2639, 900		1002, 874
ll-C ₅ H C _{∞v} (X ² Π)		ll-C ₅ H ⁺ C _{∞v} (X ¹ Σ ⁺)		t2-C ₅ H C _{2v} (X ² B ₂)		t2-C ₅ H ⁺ C _{2v} (X ³ B ₂)	
	Calc.	Exp.	Calc.		Calc.	Exp.	Calc.
E_r	0.0		8.40	E_r	0.14	1.136 ^b	9.93
IP	8.40			IP	9.79		
EA	−2.41	−2.421 ± 0019 ^b		EA	−2.46	−2.857 ± 0028 ^b	
$ A_{SO,e} $	27.51						
C1C2	1.3167		1.3277	C1C2	1.3894		1.4108
C2C3	1.2641		1.2564	C4C1	1.3895		1.3623
C3C4	1.3405		1.3266	C5C4	1.2116		1.2155
C4C5	1.2224		1.2253	C5H	1.0647		1.0716
C5H	1.0647		1.0742	C2C1C3	59.0		57.7
μ_C	4.4872		3.1839	μ_A	3.5352		0.0761
B_e	2378.85	2387.01 ± 002 ^f 2395.12650(12) ^g	2391.66	A_e	45003.53	45018(20) ^h	45467.33
$\omega(\sigma)$	3439, 2057, 1866, 1388, 741	$\nu_1 = 3319.3^j$ $\nu_3 = 1912.40^b$	3360, 2224, 2071, 1435, 764	$B_e C_e$	3493.66 3241.98	3504.0621(3) ^h 3246.9414(4) ^h	3493.92 3244.59
$\omega(\pi)$	696-360 526-483 316-250 100-82		750, 514, 218, 92	$\omega(a_1)$	3446, 2138, 1636, 1314, 717		3386, 2141, 1630, 1345, 749
				$\omega(b_1)$	711, 537, 203		789, 538, 181
				$\omega(b_2)$	..., ..., 646, 380		1067, 717, 489, 178

Notes.

^a The reference for the relative energies of the most stable neutral forms c-C₃H (−114.502973 au) and ll-C₅H form (−190.544737 au).

^b Sheehan et al. (2008a, 2008b).

^c Yamamoto et al. (1990).

^d Caris et al. (2009).

^e Yamamoto & Saito (1994).

^f Cernicharo et al. (1986a, 1986b).

^g McCarthy et al. (1999).

^h Apponi et al. (2001).

ⁱ Measured in Ar matrix; Huang & Graham (1990), (Jiang et al. 1993).

^j Measured in Ne matrix, Wu et al. (2009).

chains of singlet multiplicity denotes a multiconfigurational character (Lee & Taylor 1989). The triplet geometry (ll-C₅H[−]) presents a low T1 diagnostic, which can be interpreted as

monoconfigurational character. The contribution of the Hartree–Fock determinant to the CASSCF wave function denotes that ll-C₅H[−] is less dependent on the static correlation than ql-C₅H[−].

Table 3

RCCSD(T)-F12/AVTZ Relative Energies (E_r , in eV)^a of the Negative Charged Forms, Structural Parameters (Distances in Å; Angles in Degrees), Rotational Constants and Quartic Centrifugal Distortion Constants (in MHz) and Anharmonic Frequencies (ν , in cm^{-1}); MRCI Dipole Moments (μ , D)

q1-C ₃ H ⁻ C _s (X ¹ A')				c-C ₃ H ⁻ C _{2v} (X ¹ A ₁)			
E_r	-1.72	A_e	525807.22	E_r	-2.05	A_e	37822.48
C1C2	1.2862	B_e	11277.98	C1C2	1.3791	B_e	35704.09
C2C3	1.3547	C_e	11041.16	C1H	1.0871	C_e	18366.38
C3H	1.1096	A_0	535588.53	C2C1C3	65.5	A_0	37859.09
C1C2C3	174.4	B_0	11316.76	μ	3.4333	B_0	35611.05
C2C3H	109.3	C_0	11055.54	$\nu(a_1)$	2950, 1464,	C_0	18284.08
$\nu(a')$	2714, 1791, 1101,	ΔJ	0.004836		874	ΔJ	0.184126
	1007, 417	ΔK	430.797156	$\nu(b_1)$	821	ΔK	0.211474
$\nu(a'')$	296	ΔJK	1.414456	$\nu(b_2)$	1259, 839	ΔJK	-0.382717
μ_A	1.3870	δ_J	0.000061			δ_J	0.027861
μ_B	1.4702	δ_K	0.534850			δ_K	-0.506906
q1-C ₅ H ⁻ C _s (1A')				l3-C ₅ H ⁻ C _{2v} (1A ₁)			
E_r	-1.88		-2.50		-2.58		-2.32
	C1C2 = 1.2764		C1C2 = 1.2668		C1C2 = 1.3536		C1C2 = 1.3917
	C2C3 = 1.3256		C2C3 = 1.3768		C1C3 = 1.4558		C4C1 = 1.3985
	C3C4 = 1.2754		C3H = 1.0934		C4C1 = 1.3791		C5C4 = 1.2200
	C4C5 = 1.3250		C2C3C4 = 128.3		C5C4 = 1.2577		C5H = 1.0618
	C5H = 1.0998		C1C2C3 = 174.2		C2H = 1.0811		C2C1C3 = 63.7
	C1C2C3 = 179.8				C2C1C3 = 59.4		
	C2C3C4 = 176.5				C1C2H = 148.7		
	C3C4C5 = 171.3				C1C2C4 = 150.7		
	HC5C4 = 113.6				C1C4C5 = 179.2		
	μ_A = 3.3776	μ_B = 3.2784			μ_A = 5.7390	μ_A = 6.4403	
	μ_B = 1.4747				μ_B = 2.8520		
A_e	571580.07		43259.67		35526.54		39069.02
B_e	2381.62		2831.01		3608.51		3512.70
C_e	2371.74		2657.13		3275.78		3222.93
A_0	793138.84		44207.12		35479.86		39184.91
B_0	2410.34		2838.34		3618.29		3519.65
C_0	2379.99		2662.72		3280.10		3225.69
$\nu(a')$	2852, 1896, 1850, 1364, 841, 746, 390, 377, 150	$\nu(a_1)$	2912, 1973, 946, 561, 142; $\nu(a_2)$ = 252	$\nu(a')$	3050, 1984, 1606, 1269, 1070, 904, 697, 490, 194	$\nu(a_1)$	3330, 2043, 1549, 959, 676
$\omega(a'')$	575, 284, 145	$\nu(b_1)$	888, 283, 225	$\nu(a'')$	818, 512, 183	$\nu(b_1)$	618, 560, 228
ΔJ	0.000094	$\nu(b_2)$	1918, 1363, 1145			$\nu(b_2)$	1173, 532, 440, 204
ΔK	7471.576362		0.000927		0.000333		0.000311
ΔJK	2.899106		9.809857		0.120691		0.210593
δ_J	-0.000006		-0.156557		0.028341		0.035698
δ_K	0.709861		0.000215		0.000035		0.000029
			0.005479		0.015839		0.019612
l1-C ₅ H ⁻ C _{∞v} (X ³ Σ ⁻)				C1—C2—C3—C4—C5—H			
E_r	-2.41		C1C2 = 1.2931		C2C3 = 1.3084		C3C4 = 1.3180
	C4C5 = 1.2481		C5H = 1.0613				
$B_0 \sim B_e$	2361.85	$\omega(\sigma)$	3459, 2144, 1844, 1463, 742				
	μ_C = 6.6638	$\omega(\pi)$	417, 366, 113, 47i				

Note.

^a The reference for the relative energies of the most stable neutral forms c-C₃H (-114.502973 au) and l1-C₅H form (-190.544737 au).

The molecular properties of the four confirmed singlet isomers and of the unconfirmed triplet are summarized in Table 3. The high values of the three-body cycle dipole moments must be emphasized (μ_A = 5.7390 D and μ_B = 2.8520 D (t1-C₅H⁻); μ = 6.4403 D (t2-C₅H⁻)). For the anions,

as our main objective is their characterization, the anharmonic effect computed using second-order perturbation and a MP2 force field was considered in the computation of the spectroscopic properties. The anharmonic fundamentals were

Table 4
MRCI Vertical Excitation Energies (ΔE , in eV) to the Low Excited Electronic States of C_3H

Sym.	ΔE	Configuration	Sym	ΔE	Configuration	Sym	ΔE	Configuration
l- C_3H			ql- C_3H^-			l- C_3H^+		
$X^2\Pi$	0.0 ^a	$(7\sigma)^2(1\pi)^4(2\pi)^1$	X^1A'	0.0 ^b	$(9a')^2(1a'')^2$	$X^1\Sigma^+$	0.0 ^c	$(7\sigma)^2(1\pi)^4$
$a^4\Sigma^-$	1.3	$(7\sigma)^1(1\pi)^4(2\pi)^2$	a^3A''	0.39	$(9a')^1(1a'')^2(2a'')^1$	$a^3\Pi$	1.8	$(7\sigma)^1(1\pi)^4(2\pi)^1$
$A^2\Delta$	2.9	$(7\sigma)^1(1\pi)^4(2\pi)^2$	A^1A''	1.15	$(9a')^1(1a'')^2(2a'')^1$	$A^1\Pi$	3.20	$(7\sigma)^1(1\pi)^4(2\pi)^1$
$b^4\pi$	3.4	$(7\sigma)^2(1\pi)^4(2\pi)^2$				$b^3\Sigma^+$	3.18	$(7\sigma)^1(1\pi)^3(2\pi)^1$
$B^2\Sigma^+$	3.6	$(7\sigma)^1(1\pi)^4(2\pi)^2$				$c^3\Delta$	3.7	$(7\sigma)^2(1\pi)^3(2\pi)^2$
$C^2\Pi$	3.8	$(7\sigma)^2(1\pi)^3(2\pi)^2$						
c- C_3H			c- C_3H^-			c- C_3H^+		
X^2B_2	0.0 ^d	$(6a_1)^2(1b_1)^2(2b_2)^2(3b)^1(1a_2)^0$	X^1A_1	0.0 ^e	$(6a_1)^2(1b_1)^2(2b_2)^2(3b_2)^2$	X^1A_1	0.0 ^f	$(6a_1)^2(1b_1)^2(2b_2)^2$
A^2A_1	1.2	$(6a_1)^1(1b_1)^2(2b_2)^2(3b)^2$	A^1B_2	2.5	$(6a_1)^2(7a_1)^1(1b_1)^2(2b_2)^2(3b_2)^1$	a^3B_2	0.4	$(6a_1)^1(1b_1)^2(2b_2)^2(3b_2)^1$
B^2B_1	3.3	$(6a_1)^2(1b_1)^2(2b_2)^2$				A^1B_1	2.4	$(6a_1)^1(1b_1)^2(2b_2)^2(3b_2)^1$
a^4B_1	3.7	$(6a_1)^1(1b_1)^2(2b_2)^2(3b)^1$						
b^4A_2	3.7	$(6a_1)^1(1b_1)^2(2b_1)^1(2b_2)^2(3b_2)^1$						
C^2A_2	3.9	$(6a_1)^2(1b_1)^2(2b_2)^2(1a_2)^1$						

Notes.

^a $E = -114.443429$ au.

^b $E = -114.498728$ au.

^c $E = -114.120848$ au.

^d $E = -114.444216$ au.

^e $E = -114.499917$ au.

^f $E = -114.095517$ au.

determined using the equation:

$$E = \sum_i \omega_i^{\text{CCSD(T)-F12}} \left(\nu_i + \frac{1}{2} \right) + \sum_{i \geq j} x_{ij}^{\text{MP2}} \times \left(\nu_i + \frac{1}{2} \right) \left(\nu_j + \frac{1}{2} \right), \quad (1)$$

where ω_i represents the harmonic fundamentals, ν_i and ν_j represent vibrational quanta, and x_{ij} represents the anharmonic constants. The anharmonic fundamentals are shown in Table 3. The quasi-linearity of t1- C_5H^- introduces errors in the computations of the anharmonic force field calculated using numerical derivatives as is implemented in the Gaussian package. For this reason, only harmonic fundamentals are provided for the large amplitude motions. Inaccuracies can affect the A rotational constant.

The rotational constants at the ground electronic state were computed with the expression:

$$B_0 = B_e(\text{CCSD(T)} - \text{F12}) + \Delta B_e^{\text{core}}(\text{CCSD(T)}) + \Delta B^{\text{vib}}(\text{MP2}), \quad (2)$$

where ΔB^{vib} represents the vibrational contribution to the rotational constants derived from the VPT2 α_r^{vib} vibration-rotation interaction parameters determined using the MP2 cubic force fields, and ΔB_e^{core} contains the effect of the core-electron correlation. This equation was employed for predicting rotational constants of many molecules always giving very accurate parameters with differences of a few megahertz to the experimental data (Motiyenko et al. 2018). Final parameters are collected in Table 3. The c- C_3H^- rotational parameters compare well with those computed by Bassett & Fortenberry (2017), using a CCSD(T)/AV5Z anharmonic force field. Such a result was expected due to the high efficiency of the CCSD

(T)-F12/AVTZ level of theory that produces similar results to those obtained by CCSD(T)/AV5Z, using a smaller basis set.

6. Excited Electronic States

Tables 4 and 5 display vertical excitation energies to the low electronic states of C_3H and C_5H , respectively, and the most probable configurations. Calculations have been performed at the MRCI level of theory using the RCCSD(T)-F12 optimized geometries of the ground electronic states. For the anions, few states that can be assumed to be valence states considering the electron affinity values are provided.

For the linear neutral forms with doublet degenerate ground electronic states, the spin-orbit constants are provided. Spin-orbit effects are expected to be similar in both chains, l- C_3H and l1- C_5H (see Table 2). The two first excited electronic states of l- C_3H , a quartet $a^4\Sigma^-$ and a doublet $A^2\Delta$, were computed to be at 1.3 and 2.9 eV over the ground state. By considering that the computed values are vertical energies, they compare well with the experimental observations of Sheehan et al. (2008b) using anion photoelectron spectroscopy that observed transitions at 1.326 ± 0.018 eV ($^2\Pi \rightarrow ^4\Sigma^-$), 2.271 ± 0.023 eV and 2.546 ($^2\Pi \rightarrow ^2\Delta$). The same authors observed the $^2B_2 \rightarrow ^2A_1$ transition of the cyclic isomer at 1.003 ± 0.012 eV with the same technique, whereas our computed value is 1.2 eV. Computations of the excitation energies were performed by Ding et al. (2001).

Transitions of l- C_5H , observed by Garand et al. (2010) and Ding et al. (2002) at 1.31, 2.32, and 2.55 eV were assigned to the first quartet ($a^4\Sigma^-$) and to the doublets $A^2\Delta$ and $B^2\Sigma^-$, respectively. Sheehan et al. (2008b) placed the first $a^4\Sigma^-$ at 1.38 eV on the basis of the experimental detachment energies. The MRCI vertical excitations computed in this paper (1.33, 2.79, and 2.95 eV) are in good agreement with the experimental data and with the previous calculations of Haubrich et al. (2002) who determined vertical excitations for the doublet. The

Table 5
MRCI Vertical Excitation Energies (ΔE , in eV) to the Low Excited Electronic States of C_5H

Sym.	ΔE	Configuration	Sym	ΔE	Configuration	Sym	ΔE	Configuration
11- C_5H			ql- C_5H^-			11- C_5H^+		
$X^2\Pi$	0.0 ^a	$(11\sigma)^2(2\pi)^4(3\pi)^1$	X^1A'	0.0 ^b	$(13a')^2(14a')^2(2a'')^2$	$X^1\Sigma^+$	0.0 ^c	$(11\sigma)^2(2\pi)^4$
$a^4\Sigma^-$	1.33	$(11\sigma)^1(2\pi)^4(3\pi)^2$	a^3A''	0.30	$(13a')^2(14a')^1(2a'')^2(3a'')^1$	$a^3\Pi$	1.82	$(11\sigma)^1(2\pi)^4(3\pi)^1$
$A^2\Delta$	2.79	$(11\sigma)^1(2\pi)^4(3\pi)^2$	B^1A''	0.77	$(13a')^2(14a')^1(2a'')^2(3a'')^1$	$b^3\Sigma^+$	2.62	$(11\sigma)^2(2\pi)^3(3\pi)^1$
$b^4\Pi$	2.90	$(11\sigma)^2(2\pi)^3(3\pi)^2$	C^1A'	1.90	$(13a')^2(2a'')^2(3a'')^2$	$A^1\Pi$	2.92	$(11\sigma)^1(2\pi)^4(3\pi)^1$
$B^2\Sigma^-$	2.95	$(11\sigma)^1(2\pi)^4(3\pi)^2$	b^3A''	2.28	$(13a')^1(14a')^2(2a'')^2(3a'')^1$	$c^3\Delta$	3.04	$(11\sigma)^2(2\pi)^3(3\pi)^1$
$C^2\Sigma^+$	3.39	$(11\sigma)^1(2\pi)^4(3\pi)^2$	c^3A'	2.36	$(13a')^2(14a')^2(2a'')^1(3a'')^1$	$B^1\Sigma^-$	3.19	$(11\sigma)^2(2\pi)^3(3\pi)^1$
						$C^1\Delta$	3.54	$(11\sigma)^2(2\pi)^3(3\pi)^1$
t2- C_5H			t2- C_5H^-			t2- C_5H^+		
X^2B_2	0.0 ^d	$(10a_1)^2(2b_1)^2(3b_2)^2(4b_2)^1$	X^1A_1	0.0 ^e	$(10a_1)^2(2b_1)^2(3b_2)^2(4b_2)^2$	X^1A_1	0.0 ^f	$(10a_1)^2(2b_1)^2(3b_2)^2$
A^2A_1	1.22	$(10a_1)^1(2b_1)^2(3b_2)^2(4b_2)^2$	a^3A_2	2.53	$(10a_1)^2(2b_1)^2(3b_1)^1(3b_2)^2(4b_2)^1$	a^3B_2	0.34	$(10a_1)^1(2b_1)^2(3b_2)^2(4b_2)^1$
B^2B_1	2.82	$(10a_1)^2(2b_1)^2(3b_2)^1(4b_2)^2$				c^3A_2	2.60	$(10a_1)^2(2b_1)^1(3b_2)^2(4b_2)^1$
a^4A_2	3.25	$(10a_1)^1(2b_1)^2(3b_1)^1(3b_2)^2(4b_2)^1$				b^3A_1	2.81	$(10a_1)^2(2b_1)^2(3b_2)^1(4b_2)^1$
C^2A_2	3.68	$(10a_1)^2(2b_1)^2(3b_1)^1(3b_2)^2(4b_2)^1$						
D^2B_1	3.84	$(10a_1)^2(2b_1)^1(3b_2)^2(4b_2)^2$						
b^4B_1	3.84	$(10a_1)^1(2b_1)^2(3b_2)^2(4b_2)^1$						
E^2B_2	4.14	$(10a_1)^2(2b_1)^2(3b_2)^1(4b_2)^2$						
c^4B_2	4.58	$(10a_1)^2(2b_1)^1(3b_1)^1(3b_2)^2(4b_2)^1$						
13- C_5H^-			t1- C_5H^-					
X^1A_1	0.0 ^g	$(8a_1)^2(1b_1)^1(6b_2)^2(1a_2)^2$	X^1A_1	0.0 ^h	$(14a')^2(2a'')^2$			
a^3B_2	2.0	$(8a_1)^2(1b_1)^1(6b_2)^2(1a_2)^1$						

Notes.

- ^a $E = -190.363309$ au.
^b $E = -190.429663$ au.
^c $E = -190.062043$ au.
^d $E = -190.354301$ au.
^e $E = -190.437521$ au.
^f $E = -190.019234$ au.
^g $E = -190.446473$ au.
^h $E = -190.454405$ au.

first excited state of the cyclic isomer ($\Delta E = 1.22$ eV), was observed at 0.86 eV by Sheehan et al. (2008b).

For the neutral isomers, the excitation energy to the first excited electronic state ($\Delta E > 1.0$ eV) is larger in the case of the neutral even chains C_2H , C_4H , or C_6H where the first excited state was found at 0.69 eV, <0.25 eV, and 0.46 eV, respectively (Senent & Hochlaf 2013).

For anions, the ground electronic states of all the stable structures show singlet multiplicity, although ql- C_5H^- presents a triplet excited state (a^3A'') that is very close in energy ($\Delta E = 0.39$ eV). Spin–spin effects are negligible. In the case of the C_5H^- chains, the low energy corresponds to the triplet form whose stability is not confirmed (see the previous section). The quasi-linear form appears at 0.53 eV above the triplet. The most stable anion form t1- C_5H^- shows a single bond state of singlet multiplicity.

For a better understanding of the stability and ground electronic state nature of the C_5H^- hydrogen-terminated chain, the low states of the linear and the quasi-linear isomers were correlated (Figure 4). In the ql- C_5H^- region, the singlet state represents the ground electronic state, whereas in the 11- C_5H^- region, the lowest potential energy surface corresponds to a triplet state containing the absolute minimum. The existence of this minimum is not supported by the vibrational study described in the last section. The isomerization process ql- $C_5H^- \rightarrow$ 11- C_5H^- seems to be forbidden. Electronic state crossing occurs close to the linear structure whereas the

calculation of spin–spin coupling constants performed including the $^3\Sigma^-$, $^2\Delta$, and $^3\Sigma^+$ states reveals an almost negligible splitting of the triplet state components (~ 0.07 cm $^{-1}$).

7. Conclusions

The three negatively charged hydrogen-terminated carbon chains detected in circumstellar sources contain an even number of carbon atoms. Observations of the negative odd chains failed, although it can be anticipated that they can play important roles in the gas phase chemistry and chemical evolution. This paper provides new, very accurate molecular data that are useful for the identification of C_3H^- and C_5H^- , revealing that the linear structures are not always the most probable or detectable. For their computations, the CCSD(T)-F12 method that usually provides rotational parameters with a usual accuracy of about 10 MHz, has been employed. Renner–Teller and pseudo Jahn–Teller effects are predicted. Excited electronic states are provided. We expect that the new parameters make spectrum assignments easier for future investigations.

Neutral and charged structures have been described, although special attention is given to the linear and to the cyclic stable forms of the anions. For C_3H , our work confirms the existence of three isomeric neutral forms l- C_3H , l2- C_3H , and c- C_3H , three negatively charged forms c- C_3H^- , ql- C_3H^- , and l2- C_3H^- , and three isomers with a positive charge, l- C_3H^+ ,

Figure 4. Correlation between the low electronic states of ql-C₅H and 1l-C₅H⁻.

c-C₃H⁺, and 12-C₃H⁺. The search yielded to 8, 11, and 10 isomers of C₅H, C₅H⁻, and C₅H⁺, respectively.

For C₅H⁻, the present work carries out novelties and emphasizes uncertain aspects. The calculations evidence the existence of four very stable isomers very close in energy. Two of them are chains, 13-C₅H⁻ (C_{2v} (X¹A₁)) and ql-C₅H⁻ (C_s (X¹A')) and two contain three-body rings, t1-C₅H⁻ (C_s (X¹A')) and t2-C₅H⁻ (C_{2v} (X¹A₁)). We cannot establish if the triplet linear form 1l-C₅H⁻ (C_{∞v} (X³Σ⁻)) postulated in previous works is a real isomer, because it appears to be really dependent on the electron correlation energy, denoting instability. However, the singlet ql-C₅H⁻ (C_s (X¹A')) represents a secondary minimum. Electronic state crossing occurs close to the linear structure where spin-orbit effects are negligible. The most stable geometry is the cycle t1-C₅H⁻ (C_s (X¹A')) that presents a relatively high dipole moment (6.4085D). The corresponding ground vibrational rotational constants have been computed to be A₀ = 35479.86 MHz, B₀ = 3618.29 MHz, and C₀ = 3280.10 MHz.

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