

## Odd Carbon Long Linear Chains $\text{HC}_{2n+1}\text{H}$ ( $n = 4-11$ ): Properties of the Neutrals and Radical Anions

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**Abstract:** The optimized geometries, adiabatic electron affinities, vertical electron affinities, vertical electron detachment energies (for the anions), and IR-active vibrational frequencies have been predicted for the long linear carbon chains  $\text{HC}_{2n+1}\text{H}$  ( $n = 4-11$ ). The B3LYP density functional combined with DZP and TZ2P basis sets was used in this theoretical study. These methods have been extensively calibrated versus experiment for the prediction of electron affinities (*Chem. Rev.* **2002**, *102*, 231). The computed physical properties are discussed and compared with the even carbon chains  $\text{HC}_{2n}\text{H}$ . The predicted electron affinities form a remarkably regular sequence: 2.12 eV ( $\text{HC}_9\text{H}$ ), 2.42 eV ( $\text{HC}_{11}\text{H}$ ), 2.66 eV ( $\text{HC}_{13}\text{H}$ ), 2.85 eV ( $\text{HC}_{15}\text{H}$ ), 3.01 eV ( $\text{HC}_{17}\text{H}$ ), 3.14 eV ( $\text{HC}_{19}\text{H}$ ), 3.25 eV ( $\text{HC}_{21}\text{H}$ ), and 3.35 eV ( $\text{HC}_{23}\text{H}$ ). These electron affinities are as much as 0.4 eV higher than those for analogous even carbon chains. The predicted structures display an intermediate cumulene–polyacetylene type of bonding, with the inner carbons appearing cumulenic and the outer carbons polyacetylenic.

### I. Introduction

Increased attention has been given over the last two decades to the various carbon chains  $\text{C}_n$ ,  $\text{HC}_n\text{H}$ ,  $\text{C}_n\text{H}_2$ , their isomers and ions, related nitrogen and sulfur containing molecules, and polyaromatic hydrocarbons.<sup>1–7</sup> These are still considered leading contenders among larger molecules possibly existing in interstellar space, but also as possible carriers of diffuse interstellar bands (DIBs) or unidentified interstellar infrared (UIR) emission bands.<sup>8–10</sup> So far, the existence of 123 molecules<sup>11</sup> has been confirmed in interstellar space, but only a few of these have also been found in the DIBs' spectral region (400–900 nm). The largest molecule discovered in space,  $\text{HC}_{11}\text{N}$ , is one of the reasons why the family of long carbon chains  $\text{HC}_{2n+1}\text{H}$  is similarly expected to exist in the interstellar medium. Maier et al.<sup>12</sup> reported in 1998 that absorption bands of the carbon chain anion  $\text{C}_7^-$  match four of the DIBs exceedingly well. Despite critical comparisons of the laboratory data with new astrophysical observations<sup>13,14</sup> the assignment of  $\text{C}_7^-$  remains controversial.

Similarly controversial is the degree of contribution from long chain carbon molecules to both the DIB and UIR.

Another interesting question that has been raised concerns the size limit for the long carbon chains. Maier and co-workers<sup>15–17</sup> succeeded in observing the neutral clusters  $\text{C}_{2n}$  ( $n = 3-7$ ) and  $\text{C}_{2n+1}$  ( $n = 2-10$ ) and the anionic clusters  $\text{C}_{2n}^-$  ( $n = 2-11$ ) and  $\text{C}_{2n+1}^-$  ( $n = 2-10$ ) using laser ablation of graphite with trapping in neon matrixes. Recently, electronic absorption spectra of neutral  $\text{C}_{2n+1}$  ( $n = 5-14$ ) and anionic  $\text{C}_{2n}^-$  ( $n = 5-18$ ) in argon matrixes were presented by Szczepanski, Fuller, Ekern, and Vala,<sup>18</sup> thus further increasing the range of the carbon chains covered in the quest for the possible DIB/UIR bands' carriers. In the case of polyacetylenic chains, electronic absorption spectra of  $\text{HC}_{2n}\text{H}$  and  $\text{HC}_{2n}\text{H}^-$  ( $n = 6-12$ ) in neon matrices have been reported by Grutter, Wyss, Fulara, and Maier.<sup>19</sup> More importantly, electronic spectra of the chains  $\text{HC}_{2n}\text{H}$  ( $n = 8-13$ ) have been recorded using the resonant two-color two-photon ionization spectroscopy in the gas phase,<sup>20</sup> the latter essential for the proper comparison of the laboratory and astronomical data. Even though the detection of polyacetylenic chains  $\text{HC}_n\text{H}$  by radio astronomy is hindered by the absence of permanent dipole moments, they are expected to be abundant in interstellar space.

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Our previous study<sup>21</sup> focused on the description of the even-membered structures  $HC_{2n}H$  and  $HC_{2n}H^-$  ( $n = 6-12$ ). To complement this work, we turn our interest to the odd-membered structures  $HC_{2n+1}H$  and  $HC_{2n+1}H^-$  ( $n = 4-11$ ). Fulara, Freivogel, Forney, and Maier<sup>22</sup> pointed out in 1995 that the structures of these odd carbon species are linear and reported electronic transitions in the visible and near-infrared regions of the spectrum. Two years ago, the first gas-phase detection of linear  $HC_{11}H$  and  $HC_{13}H$  was provided by Ball, McCarthy, and Thaddeus using cavity ringdown spectroscopy.<sup>23</sup> Unfortunately, no satisfactory assignment to interstellar features has yet been made. To our knowledge, no experimental detection of long anionic carbon clusters  $HC_{2n+1}H^-$  has been yet reported.

Following controversy due to discussions of the self-interaction problem,<sup>24-35</sup> recent applications of density functional theory (DFT) methods to negatively charged molecules have shown several of these to be reliable methods for the prediction of adiabatic electron affinities. The self-interaction problem has been reputed to cause the DFT method to predict some anionic systems to be unbound relative to the analogous neutral systems.<sup>36,37</sup> This effect has been tested, and it has been shown that even though the HOMO energies obtained from pure DFT functionals may have positive eigenvalues, DFT nevertheless makes reasonable predictions of the anion physical properties.<sup>36</sup> Rösch and Trickey speculated<sup>37</sup> that for large molecules in which the electron population is delocalized over the molecule, the self-interaction problem is delocalized and therefore less significant. With these factors in mind, optimized geometries, adiabatic electron affinities, vertical electron affinities, vertical electron detachment energies, and harmonic vibrational frequencies of  $HC_{2n+1}H$  and  $HC_{2n+1}H^-$  ( $n = 4-11$ ) are presented in this work.

## II. Theoretical Method

Total energies, equilibrium geometries, and harmonic vibrational frequencies were determined for the neutral and anionic species for each of the eight molecules studied. The B3LYP density functional, which is a generalized gradient approximation and employs the dynamical correlation functional of Lee, Yang, and Parr<sup>38</sup> in conjunction with Becke's three-parameter HF/DFT hybrid exchange functional (B3),<sup>39</sup> was used. We employed the double- $\zeta$  plus polarization (DZP) [9s5p2d/4s2p1d] and triple- $\zeta$  plus polarization (TZ2P) [10s6p2d/5s3p2d]

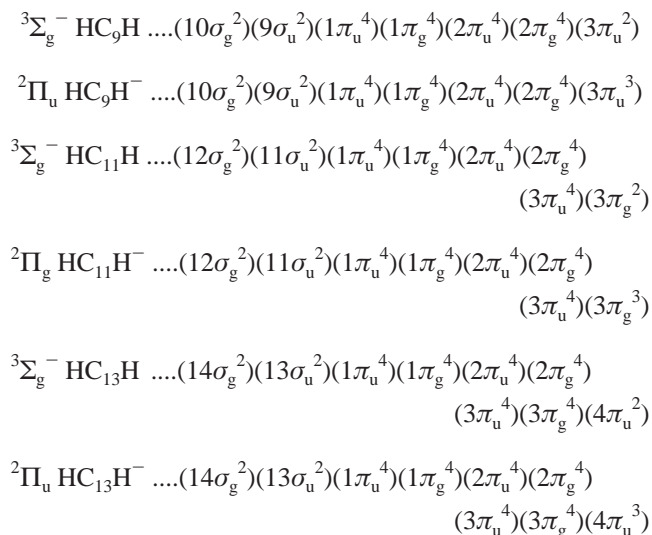
contracted Gaussian basis set due to Dunning.<sup>40</sup> Accordingly, for  $HC_{23}H$ , the DZP and TZ2P basis sets contain 355 and 570 contracted Gaussian functions, respectively. The specific choice of the B3LYP density functional was based on extensive previous calibrative studies of electron affinities.<sup>41</sup> It has been argued specifically that for the long carbon chains the B3LYP density functional should be used in order to predict the bond lengths properly.<sup>42,43</sup>

The quantum chemical computations of this study were conducted with the GAUSSIAN 94<sup>44</sup> system of DFT programs. To maintain consistency, spin unrestricted Kohn–Sham orbitals were used for all computations. Both the neutral and anion geometries were optimized via analytic gradients of the B3LYP density functional. Numerical integration of the functional was carried out using the GAUSSIAN 94 default grid consisting of 75 radial shells with 302 angular points per shell. The mass-weighted force constant matrix and, hence, the harmonic vibrational frequencies were determined analytically.

## III. Results and Discussion

One of the main goals of this study was to predict the fundamental properties of long odd-numbered carbon chains and compare them with the even-numbered chains. It has been shown before that properties of the smaller even- and odd-numbered structures can often differ extensively.<sup>45-48</sup>

In accordance with Hund's rules and experiment, we confirm that  $^3\Sigma_g^-$  is the electronic ground state for all neutral molecules. This is due to the partially occupied HOMOs,  $(\pi_g^2)$  for  $HC_{4n+1}H$  ( $n = 2-5$ ) and  $(\pi_u^2)$  for  $HC_{4n+3}H$ . An extra electron added to this molecular orbital leads to the  $^2\Pi_g$  or  $^2\Pi_u$  ground state of the anions  $HC_{2n+1}H^-$  ( $n = 4-11$ ). The electron configurations for the first few members of the series are as follows:

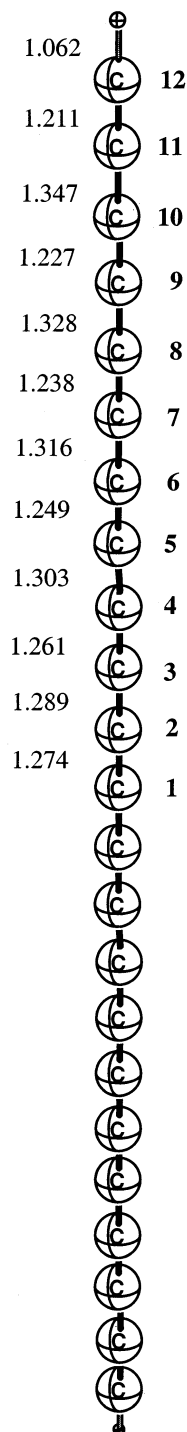


The remainder of the pattern through  $HC_{23}H$  and  $HC_{23}H^-$  should be reasonably clear. We note that in the case of even carbon series  $HC_{2n}H$  the HOMO  $\pi$ -orbital is fully occupied.<sup>21</sup>

The optimized equilibrium geometries ( $D_{\infty h}$ -symmetry) are all minima on their respective potential surfaces and are shown in Tables 1 and 2, where the  $C_1$  in our numbering scheme begins with the carbon atom in the center of the chain structure. The numbering scheme is further documented by the optimized structure of  $HC_{23}H$  in Figure 1. The geometry optimizations in

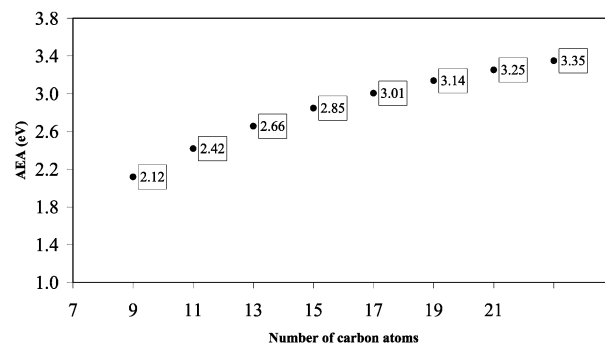
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**Figure 1.** An example of atom numbering in chain structures, with TZ2P B3LYP optimized bond distances in Å for  $\text{HC}_{23}\text{H}$ .

the present study began with equivalent bond lengths between the carbon atoms, thus imposing a strictly cumulenic structure. Ultimately, we found significant bond length alternation in the fully optimized structures, which may be rationalized as a strong



**Figure 2.** Odd carbon adiabatic electron affinities (AEA) vs the number of carbon atoms in the chain. The TZ2P B3LYP method was used.

competition between two resonance structures, cumulenic and polyacetylenic. Polyacetylenic type bond distance alternation begins to prevail as one moves outward along the chain. It is very interesting that the bond length alternation for the outermost carbons is equal to if not more pronounced than that in the even-numbered  $\text{HC}_{2n}\text{H}$  ( $n = 6-12$ ) species of our previous study.<sup>21</sup>

The fact that these chains have an odd number of carbons implies that, if one starts with triple/single bond alternation from the ends, there will occur a mismatch in the center of the chain. This mismatch is reminiscent of soliton formation in odd polyenes.<sup>49,50</sup> In other words, the mismatch forces the switch from the acetylenic to the cumulenic structure. Note that the mismatch is of a different nature for the  $\text{HC}_{(4n+1)}\text{H}$  and  $\text{HC}_{(4n+3)}\text{H}$  chains, which explains the oscillation in the optimized central bonds, found in Tables 1 and 2, a feature not previously discussed. The fact that the less stable cumulenic structure is forced by the mismatch also likely explains the higher electron affinity of the odd carbon compounds with respect to the even structures.

It is commonly agreed that because of overlap and repulsion within the ( $\pi$ ) HOMOs, the addition of hydrogen at the ends of the chain leads to changes in the bonding and structure.<sup>46</sup> In their work on the linear carbon cluster anions  $\text{C}_n^-$  ( $n = 2-10$ ), Watts and Bartlett observed<sup>47</sup> continuous shifts from cumulenic to acetylenic structures after the addition of an electron to the  $\text{C}_n$  chain. This trend was recently also confirmed in the extensive DFT (B3LYP/6-31G\*) study for  $\text{C}_n$  and  $\text{C}_n^-$  ( $n = 2-20$ ).<sup>48</sup> The addition of the second electron in the dianions  $\text{C}_n^{2-}$  increased the degree of bond length alternation substantially. We have, however, pointed out<sup>21</sup> that the addition of an electron to the neutral  $\text{HC}_{2n}\text{H}$  ( $n = 6-12$ ) structures, which are isoelectronic with  $\text{C}_n^{2-}$ , leads to a slight shift away from acetylenic character as the triple bonds lengthen and the single bond shortens with respect to those of neutral  $\text{HC}_{2n}\text{H}$ . In the present study, the addition of an electron appears to have a negligible effect on the bond length alternation when the structures of neutral molecules are compared with the anions  $\text{HC}_{2n+1}\text{H}^-$ . Rotational constants calculated from the equilibrium structures (TZ2P basis set) are also reported in Table 1.

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**Table 1.** Optimized Geometries (Bond Distances in Å) and Rotational Constants (MHz) for the <sup>3</sup>Σ<sub>g</sub><sup>-</sup> Ground States of Neutral HC<sub>2n+1</sub>H (B3LYP, DZP/TZ2P basis sets, n = 4–11)

	HC <sub>9</sub> H	HC <sub>11</sub> H	HC <sub>13</sub> H	HC <sub>15</sub> H	HC <sub>17</sub> H	HC <sub>19</sub> H	HC <sub>21</sub> H	HC <sub>23</sub> H
C <sub>1</sub> C <sub>2</sub>	1.302/1.290	1.285/1.273	1.297/1.285	1.286/1.274	1.295/1.283	1.287/1.274	1.294/1.282	1.287/1.274
C <sub>2</sub> C <sub>3</sub>	1.268/1.254	1.314/1.302	1.275/1.261	1.306/1.295	1.278/1.265	1.302/1.291	1.280/1.267	1.300/1.289
C <sub>3</sub> C <sub>4</sub>	1.342/1.331	1.259/1.245	1.321/1.311	1.267/1.254	1.313/1.302	1.272/1.258	1.308/1.297	1.274/1.261
C <sub>4</sub> C <sub>5</sub>	1.236/1.220	1.347/1.336	1.253/1.239	1.327/1.317	1.262/1.248	1.318/1.308	1.267/1.253	1.313/1.303
C <sub>5</sub> C <sub>6</sub>		1.233/1.217	1.351/1.334	1.249/1.235	1.331/1.321	1.258/1.244	1.322/1.312	1.263/1.249
C <sub>6</sub> C <sub>7</sub>			1.231/1.215	1.353/1.342	1.246/1.232	1.334/1.324	1.255/1.241	1.326/1.316
C <sub>7</sub> C <sub>8</sub>				1.299/1.213	1.355/1.344	1.244/1.230	1.337/1.327	1.253/1.238
C <sub>8</sub> C <sub>9</sub>					1.228/1.213	1.356/1.346	1.243/1.222	1.338/1.329
C <sub>9</sub> C <sub>10</sub>						1.226/1.212	1.357/1.347	1.242/1.227
C <sub>10</sub> C <sub>11</sub>							1.227/1.212	1.358/1.347
C <sub>11</sub> C <sub>12</sub>								1.227/1.211
C <sub>(n+1)2</sub> H	1.070/1.062	1.070/1.062	1.070/1.062	1.070/1.062	1.070/1.062	1.071/1.062	1.071/1.062	1.071/1.062
A	402.7	222.4	135.6	88.7	61.1	43.9	32.6	24.9

**Table 2.** Optimized Geometries (Bond Distances in Å) for the <sup>2</sup>Π Ground States of the Anions HC<sub>2n+1</sub>H<sup>-</sup> (B3LYP, DZP/TZ2P basis sets, n = 4–11)

	HC <sub>9</sub> H <sup>-</sup>	HC <sub>11</sub> H <sup>-</sup>	HC <sub>13</sub> H <sup>-</sup>	HC <sub>15</sub> H <sup>-</sup>	HC <sub>17</sub> H <sup>-</sup>	HC <sub>19</sub> H <sup>-</sup>	HC <sub>21</sub> H <sup>-</sup>	HC <sub>23</sub> H <sup>-</sup>
C <sub>1</sub> C <sub>2</sub>	1.305/1.293	1.289/1.277	1.300/1.288	1.289/1.277	1.297/1.285	1.289/1.276	1.295/1.283	1.289/1.276
C <sub>2</sub> C <sub>3</sub>	1.274/1.261	1.315/1.304	1.279/1.266	1.307/1.296	1.281/1.268	1.303/1.291	1.282/1.270	1.301/1.289
C <sub>3</sub> C <sub>4</sub>	1.343/1.331	1.265/1.251	1.322/1.311	1.271/1.258	1.313/1.302	1.250/1.262	1.308/1.297	1.277/1.264
C <sub>4</sub> C <sub>5</sub>	1.244/1.229	1.345/1.336	1.258/1.245	1.327/1.316	1.266/1.253	1.318/1.307	1.270/1.257	1.312/1.302
C <sub>5</sub> C <sub>6</sub>		1.239/1.224	1.351/1.340	1.254/1.241	1.331/1.320	1.262/1.249	1.322/1.311	1.266/1.253
C <sub>6</sub> C <sub>7</sub>			1.236/1.221	1.353/1.342	1.251/1.237	1.334/1.323	1.259/1.245	1.325/1.314
C <sub>7</sub> C <sub>8</sub>				1.234/1.219	1.355/1.344	1.248/1.235	1.336/1.326	1.256/1.243
C <sub>8</sub> C <sub>9</sub>					1.232/1.218	1.356/1.345	1.247/1.233	1.338/1.327
C <sub>9</sub> C <sub>10</sub>						1.232/1.216	1.357/1.346	1.245/1.231
C <sub>10</sub> C <sub>11</sub>							1.230/1.215	1.358/1.347
C <sub>11</sub> C <sub>12</sub>								1.223/1.215
C <sub>(n+1)2</sub> H	1.067/1.059	1.067/1.059	1.067/1.059	1.068/1.059	1.068/1.060	1.068/1.060	1.068/1.060	1.069/1.060

**Table 3.** Theoretically Predicted IR-Active Harmonic Vibrational Frequencies (cm<sup>-1</sup>) and Intensities (km/mol) for the X <sup>3</sup>Σ<sub>g</sub><sup>-</sup> Ground States of HC<sub>2n+1</sub>H (n = 4–11)<sup>a</sup>

vibrational mode	HC <sub>9</sub> H	HC <sub>11</sub> H	HC <sub>13</sub> H	HC <sub>15</sub> H	HC <sub>17</sub> H	HC <sub>19</sub> H	HC <sub>21</sub> H	HC <sub>23</sub> H
π <sub>u</sub>	223 (3)	166 (3)	124 (2)	96 (~2)	76 (~1)	61 (~1)	50 (~1)	42 (~1)
π <sub>u</sub>	44 (~2)	37 (~2)	26 (~2)	216 (2)	17 (~2)	14 (~2)	12 (~1)	10 (~1)
π <sub>u</sub>		47 (~1)	42 (~1)	37 (~1)	28 (~1)	24 (~2)	20 (~2)	17 (~2)
π <sub>u</sub>				45 (~1)	41 (~1)	36 (~1)	29 (~1)	26 (~2)
π <sub>u</sub>					47 (~1)	44 (~1)	40 (~1)	43 (~1)
π <sub>u</sub>							46 (~1)	48 (~1)
π <sub>u</sub>	56 (96)	59 (95)	64 (94)	61 (93)	62 (93)	62 (92)	62 (92)	63 (92)
σ <sub>u</sub>	85 (11)	71 (14)	60 (16)	53 (18)	47 (19)	42 (20)	38 (21)	34 (22)
σ <sub>u</sub>	1536 (12)	13 (~2)	116 (5)	102 (8)	918 (9)	82 (10)	75 (11)	69 (11)
σ <sub>u</sub>	1735 (6)	1440 (25)	1342 (34)	1251 (45)	1166 (55)	1087 (66)	1013 (76)	944 (86)
σ <sub>u</sub>	2085 (9)	2028 (10)	1779 (3)	1468 (4)	1323 (7)	1204 (9)	1102 (11)	1016 (12)
σ <sub>u</sub>	3462 (409)	2123 (6)	2092 (16)	2022 (7)	1797 (~2)	1530 (2)	1413 (5)	1312 (6)
σ <sub>u</sub>		3463 (506)	2134 (4)	2118 (31)	2069 (6)	2016 (5)	1805 (~1)	1586 (~2)
σ <sub>u</sub>			3464 (602)	2144 (13)	2110 (15)	2062 (~1)	2036 (4)	2004 (2)
σ <sub>u</sub>				3465 (696)	2173 (10)	2128 (27)	2072 (17)	2012 (15)
σ <sub>u</sub>					3465 (788)	2191 (7)	2153 (23)	2103 (21)
σ <sub>u</sub>						3466 (877)	2201 (6)	2168 (19)
σ <sub>u</sub>							3466 (~1000)	2208 (6)
σ <sub>u</sub>								3466 (~1000)

<sup>a</sup> The TZ2P B3LYP method was used.

Theoretically predicted IR-active harmonic vibrational frequencies together with infrared intensities for the TZ2P basis set are presented in Tables 3 and 4. No scale factors were used to correct the predicted vibrational frequencies. These should serve as a guide for identifying the basic features in infrared spectra that might be attributed to the molecules under study. The strongest modes for the neutral species are predicted to be the highest (π<sub>u</sub>) bending vibration and antisymmetric CH stretch (σ<sub>u</sub>). While the CH stretch exhibits a constant frequency (3464 ± 2 cm<sup>-1</sup> for the neutrals; 3481 ± 3 cm<sup>-1</sup> for the anions) for all molecules, the wavelength of the (π<sub>u</sub>) bending vibration

features a continuous shift from 568 cm<sup>-1</sup> for HC<sub>9</sub>H up to 632 cm<sup>-1</sup> for HC<sub>23</sub>H. This is a very real trend, confirmed for smaller systems by earlier results of Seburg, McMahon, Stanton, and Gauss,<sup>51</sup> in which the corresponding mode for the HC<sub>5</sub>H molecule predicted at the CCSD/DZP level was 440 cm<sup>-1</sup>. Fulara et al.<sup>22</sup> reported earlier electronic absorption spectra for linear carbon chains HC<sub>2n+1</sub>H (n = 2–7) in neon matrixes with characteristic vibronic progressions in the CC stretching mode (1961–1973 cm<sup>-1</sup>). However, an assignment of several of the

(51) Seburg, R. A.; McMahon, R. J.; Stanton, J. F.; Gauss, J. *J. Am. Chem. Soc.* **1997**, *119*, 10838.

**Table 4.** Theoretically Predicted IR-Active Harmonic Vibrational Frequencies ( $\text{cm}^{-1}$ ) and Intensities ( $\text{km/mol}$ ) for the X  $^2\Pi$  Ground States of  $\text{HC}_{2n+1}\text{H}^-$  ( $n = 4-11$ )<sup>a</sup>

vibrational mode	$\text{HC}_9\text{H}^-$	$\text{HC}_{11}\text{H}^-$	$\text{HC}_{13}\text{H}^-$	$\text{HC}_{15}\text{H}^-$	$\text{HC}_{17}\text{H}^-$	$\text{HC}_{19}\text{H}^-$	$\text{HC}_{21}\text{H}^-$	$\text{HC}_{23}\text{H}^-$
$\pi_u$	115 (200)	151 (~2)	118 (~1)	93 (~1)	74 (~1)	60 (~1)	119 (~1)	99 (~1)
$\pi_u$	144 (9)	294 (181)	210 (~1)	205 (~1)	170 (~1)	141 (~1)	197 (~1)	176 (~1)
$\pi_u$	233 (~1)	420 (~2)	272 (~1)	424 (40)	292 (~1)	236 (~1)	212 (~1)	245 (~1)
$\pi_u$	445 (12)	455 (13)	379 (155)	430 (97)	462 (97)	475 (7)	483 (~2)	268 (~1)
$\pi_u$	508 (116)	531 (91)	445 (5)	457 (9)	471 (5)	485 (4)	491 (~2)	489 (2)
$\pi_u$	536 (3)	541 (26)	466 (14)	473 (16)	481 (30)	491 (110)	504 (62)	496 (3)
$\pi_u$		711 (14)	540 (17)	494 (~1)	503 (6)	511 (26)	524 (73)	512 (29)
$\pi_u$					543 (3)	544 (2)	546 (2)	536 (99)
$\pi_u$			553 (95)	563 (105)	572 (105)	580 (105)	585 (104)	590 (104)
$\sigma_u$	855 (19)	1349 (59)	607 (11)	1027 (52)	470 (5)	423 (2)	754 (61)	692 (67)
$\sigma_u$	1706 (>1000)	1680 (>1000)	1166 (53)	1469 (53)	917 (53)	827 (56)	1102 (66)	1015 (62)
$\sigma_u$	1763 (>1000)	2009 (51)	1606 (>1000)	1536 (>1000)	1323 (89)	1203 (72)	1344 (>1000)	1286 (>1000)
$\sigma_u$	2078 (389)	2129 (711)	2079 (205)	2008 (123)	1469 (>1000)	1404 (>1000)	1415 (22)	1312 (458)
$\sigma_u$	3484 (450)	3483 (600)	2148 (~1000)	2129 (142)	1794 (4)	2005 (102)	1804 (4)	1574 (2)
$\sigma_u$			3482 (~1000)	2148 (>1000)	2065 (504)	2094 (>1000)	2057 (>1000)	1999 (113)
$\sigma_u$				3482 (~1000)	2135 (>1000)	2128 (535)	2086 (>1000)	2058 (>1000)
$\sigma_u$					2167 (772)	2189 (756)	2152 (2)	2174 (17)
$\sigma_u$					3481 (>1000)	3479 (>1000)	2199 (862)	2204 (~1000)
$\sigma_u$							3479 (>1000)	3478 (>1000)

<sup>a</sup> The TZ2P B3LYP method was used.**Table 5.** Adiabatic Electron Affinities (AEA), Vertical Electron Affinities (VEA), and Anion Vertical Detachment Energies (VDE) in eV for  $\text{HC}_{2n+1}\text{H}$  [ $^3\Sigma_g^-$ ],  $\text{HC}_{2n+1}\text{H}^-$  [ $^2\Pi$ ] ( $n = 4-11$ )<sup>a</sup>

molecule	AEA (DZP)	AEA (TZ2P)	VEA (DZP)	VEA (TZ2P)	VDE (DZP)	VDE (TZ2P)
$\text{HC}_9\text{H}$	2.03	2.12	2.02	2.11	2.04	2.13
$\text{HC}_{11}\text{H}$	2.35	2.42	2.34	2.41	2.36	2.42
$\text{HC}_{13}\text{H}$	2.60	2.66	2.59	2.65	2.60	2.67
$\text{HC}_{15}\text{H}$	2.80	2.85	2.79	2.84	2.80	2.85
$\text{HC}_{17}\text{H}$	2.96	3.01	2.95	3.00	2.96	3.01
$\text{HC}_{19}\text{H}$	3.10	3.14	3.09	3.13	3.10	3.14
$\text{HC}_{21}\text{H}$	3.21	3.25	3.21	3.24	3.22	3.29
$\text{HC}_{23}\text{H}$	3.31	3.35	3.31	3.34	3.32	3.37

<sup>a</sup> The B3LYP method was used throughout; adiabatic EAs are not corrected for zero-point vibrational energies.

modes was not made. On the basis of the present results, we speculate that the vibration denoted  $\nu_{(a)}$  at  $619\text{ cm}^{-1}$  for  $\text{HC}_{13}\text{H}^{22}$  can be assigned to the C–H bending mode. In addition to the two above-discussed strong IR-active harmonic vibrational frequencies, a number of weaker CC stretching modes ( $\sigma_u$  symmetry) and bending modes is listed. The vibronic band, which corresponds to the excitation of the triple bond stretch, has been reported by Ball, McCarthy, and Thaddeus<sup>23</sup> to lie at about  $1950\text{ cm}^{-1}$  for  $\text{HC}_7\text{H}$ ,  $\text{HC}_9\text{H}$ , and  $\text{HC}_{11}\text{H}$ . Harmonic vibrational frequencies obtained for the anions  $\text{HC}_{2n+1}\text{H}^-$  (Table 4) suggest that the infrared spectrum should be dominated mostly by CH stretching over  $3000\text{ cm}^{-1}$ , as in a case of the neutral molecules, and by a number of strong CC stretching modes above  $2000\text{ cm}^{-1}$ . The last strong CC stretching mode predicted here progresses from  $\sim 1700\text{ cm}^{-1}$  for  $\text{HC}_9\text{H}^-$  to  $\sim 1300\text{ cm}^{-1}$  for  $\text{HC}_{23}\text{H}^-$ .

Table 5 summarizes the predicted adiabatic electron affinities (AEAs) and vertical electron affinities (VEAs) for all molecules studied, and the vertical electron detachment energies (VDEs) for the corresponding anions. The trend of increasing AEA as

the number of carbon atoms in the chain increases is further documented in Figure 2. The relatively high odd carbon AEAs exceed those predicted for the even-numbered  $\text{HC}_{2n}\text{H}$  series by  $\sim 0.4\text{ eV}$  (the value obtained<sup>21</sup> for  $\text{HC}_{24}\text{H}$  was  $2.95\text{ eV}$ ). This supports the hypothesis that even  $\text{HC}_{2n+1}\text{H}^-$  can possibly exist in the interstellar medium. Finally, for comparison, we note that, for the linear  $C_n$  family, even-numbered structures have been reported to have higher AEAs than odd-numbered ones.<sup>47,48</sup> Thus, the trend with alternating carbons for  $\text{HC}_n\text{H}$  is the opposite of that for  $C_n$ .

#### IV. Conclusions

For both neutral and anion radical species  $\text{HC}_{2n+1}\text{H}$  and  $\text{HC}_{2n+1}\text{H}^-$  ( $n = 4-11$ ), we observe intermediate cumulene–polyacetylene type bonding with pronounced bond length alternation as the length of the carbon chain increases. The shorter carbon–carbon bonds at the chain ends take on triple bond character as their length decreases from  $\sim 1.29$  to  $\sim 1.21\text{ \AA}$ . We demonstrate that the electronic ground states are  $^3\Sigma_g^-$  for the neutral molecules and  $^2\Pi$  for the radical anions. Substantially higher adiabatic electron affinities, when compared with the even-numbered carbon chains  $\text{HC}_{2n}\text{H}$ , are another example of the differences between odd- and even-membered structures. These conclusions support the hypothesis that  $\text{HC}_n\text{H}^-$  (even or odd carbon) may exist in interstellar media. The IR-active vibrational frequencies and the patterns of the IR spectra, presented for the first time for these molecules, may help to identify  $\text{HC}_{2n+1}\text{H}$  and  $\text{HC}_{2n+1}\text{H}^-$  in the laboratory in future gas-phase experiments and possibly lead to their confirmation or rejection as DIB carriers.

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