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What Is the Nature of Polyacetylene Neutral and Anionic Chains $HC_{2n}H$ and $HC_{2n}H^-$ ($n = 6-12$) That Have Recently Been Observed?

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Abstract: The optimized geometries, adiabatic electron affinities, and IR-active vibrational frequencies have been predicted for the long linear carbon chains $HC_{2n}H$. The B3LYP density functional combined with the DZP basis set was used in this theoretical study. The computed physical properties are discussed. The predicted electron affinities form a remarkably regular sequence: 1.78 ($HC_{12}H$), 2.08 ($HC_{14}H$), 2.32 ($HC_{16}H$), 2.53 ($HC_{18}H$), 2.69 ($HC_{20}H$), 2.83 ($HC_{22}H$), and 2.95 eV ($HC_{24}H$). The predicted structures display an alternating triple and very short single bond pattern, with the degree of bond alternation significantly less for the radical anions.

I. Introduction

Diffuse interstellar bands (DIB) are observed in low-density interstellar clouds and in circumstellar shells of carbon-rich stars. These bands fall in the visible and infrared spectral regions (400−900 nm) and are positioned among the known spectral lines of atoms and simple molecules. Their positions measured with respect to the atomic lines are constant, irrespective of direction of observation, and exhibit almost constant half-widths. The well-known properties of the DIBs are the reasons why their origin remains one of the longest standing unsolved problems in spectroscopy.

The existence of 122 molecules[1−3] already has been confirmed in interstellar space,[4,5] but only a few of them have also been found in the DIBs spectral region. A great number of hypotheses[6−12] have been formulated about the origin of DIBs, with possible carriers ranging from dust grains to free gas-phase species. However, not one of the (recently 231) diffuse bands has yet been identified with confidence. One of the first hypotheses, put forth by Douglas[13] in 1977, suggested that linear carbon molecules C_n ($n = 5-15$) may be potential DIBs carriers. However, the spectral region in which these species absorbs was not known. The observation and assignment of numerous spectra for homologous series of several types of carbon chains and their anions has only been made possible in the past few years with the development of techniques for trapping mass selected species in neon matrices at low temperatures.[14] For a direct comparison with the astronomical data gas-phase spectra are required. Unfortunately, this information has been collected for only a few of the hypothesized DIBs carriers. The absorption bands for only one of these, the carbon chain anion C_7^- from the C_n-family, seem to match four of the DIBs.[15] These results are still under discussion.[16,17]

The work of Fulara et al.[18−21] and Freivogel et al.[22,23] led to the extension of potential DIBs carriers to the monohydride carbon molecules and their anions. The absence of a permanent dipole in polyacetylenic chains $HC_{2n}H$ hinders their detection by radio astronomy, although they are expected to be similarly abundant.[5,24] Carbon chains[6] C_n, HC_nH, and C_nH_2, their isomers and ions, related N- and O-containing molecules, and polyaromatic hydrocarbons are still among the leading contenders of the various molecules proposed as possible carriers of DIBs. It must also be emphasized that these molecules have to be large enough to be stable with respect to photodissociation in the

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(1) Lovas, F. J. *J. Chem. Phys. Ref. Data* **1992**, *21*, 181 (http://physics.nist.gov/PhysRefData/micro/html/contents.html).

(2) Pickett, H. M.; Poynter, R. L.; Cohen, E. A.; et al. *J. Quant. Spectrosc. Radiat. Transfer* **1998**, *60*, 883 (http://spec.jpl.nasa.gov/catalog/catdir.html).

(3) Müller, H. S. P.; Thorwirth, S.; Roth, D. A.; Winnerwisser, G. *Astron. Astrophys.* **2001**, *370*, L49 (http://www.cdms.de).

(4) Thaddeus, P.; McCarthy, M. C. *Spectrochim. Acta, Part A* **2001**, *57*, 757.

(5) Thaddeus, P.; Travers, M. J.; McCarthy, M. C.; Gottlieb, C. A.; Chen, W. *Faraday Discuss.* **1998**, *109*, 121.

(6) Szcepanski, J.; Fuller, J.; Ekern, S.; Vala, M. *Spectrochim. Acta, Part A* **2001**, *57*, 775.

(7) Tielens, A. G. G. M.; Snow, T. P. The Diffuse Interstellar Bands. In *Astrophys. Space Libr.* **1995**, *202*, 325.

(8) Bromage, G. E. *Q. J. Royal Astronom. Soc.* **1987**, *28*, 294.

(9) Herbig, G. H. *Annu. Rev. Astron. Astrophys.* **1995**, *33*, 19.

(10) Herbig, G. H.; Leka, K. D. *Astrophys. J.* **1991**, *382*, 193.

(11) Smith, W. M.; Snow, T. P.; York, D. G. *Astrophys. J.* **1977**, *218*, 124.

(12) Krelowski, J. *Astron. Nachr.* **1989**, *310*, 255.

(13) Douglas, A. E. *Nature* **1977**, *269*, 130.

(14) Forney, D.; Jakobi, M.; Maier, J. P. *J. Chem. Phys.* **1989**, *90*, 600.

(15) Tulej, M.; Kirkwood, D. A.; Pachkov, M.; Maier, J. P. *Astrophys. J.* **1998**, *506*, L69.

(16) McCall, B. J.; Thorburn, J.; Hobbs, L. M.; Oka, T.; York, D. G. *Astrophys. J.* **2001**, *559*, L49.

(17) Galazutdinov, G.; Musaev, F.; Nirski, J. *Astron. Astrophys.* **2001**, *377*, 1063.

(18) Fulara, J.; Freivogel, P.; Forney, D.; Maier, J. P. *J. Chem. Phys.* **1995**, *103*, 8805.

(19) Fulara, J.; Jakobi, M.; Maier, J. P. *Chem. Phys. Lett.* **1993**, *206*, 203.

(20) Fulara, J.; Jakobi, M.; Maier, J. P. *Chem. Phys. Lett.* **1993**, *211*, 227.

(21) Fulara, J.; Lessen, D.; Freivogel, P.; Maier, J. P. *Nature* **1993**, *366*, 439.

(22) Freivogel, P.; Fulara, J.; Maier, J. P. *Astrophys. J.* **1994**, *431*, L151.

(23) Freivogel, P.; Fulara, J.; Forney, D.; Jakobi, M.; Maier, J. P. *J. Chem. Phys.* **1995**, *103*, 54.

(24) Cherchneff, I.; Glassgold, A. E. *Astrophys. J.* **1993**, *419*, L41.

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stellar radiation field. Estimates of the necessary size range from 10 to 50 atoms.[25]

In this study we focus on the linear $HC_{2n}H$ and $HC_{2n}H^-$ ($n = 6-12$) chains, for which electronic spectra in neon matrices have been observed by Maier and co-workers.[26,] Gas-phase electronic spectra for $HC_{2n}H$ ($n = 8-13$) also have been observed recently.[27] The longest wavelength transition, for $HC_{26}H$, appears to be at 340 nm, outside the range of the DIBs. However, anionic polyacetylenes are reported to have two strong electronic transitions with bands ranging from 780 to 1325 and 300−480 nm, respectively, well distributed about the DIB region (400−900 nm).

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, despite controversy due to the self-interaction problem.[28−39] 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.[40,41] 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.[40] Roesch and Trickey speculated[41] that for large molecules in which the electron population is delocalized over the molecule, the self-interaction problem is delocalized and therefore less significant.[37] With these factors in mind, optimized geometries, adiabatic electron affinities, and harmonic vibrational frequencies of $HC_{2n}H$ and $HC_{2n}H^-$ ($n = 6-12$) 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 seven molecules studied. The B3LYP density functional, which is a generalized gradient approximation and employs the dynamical correlation functional of Lee, Yang, and Parr[42] in conjunction with the Becke's 3-parameter HF/DFT hybrid exchange functional (B3),[43] was used. We employed the double-ζ plus polarization (DZP) [9s5p2d/4s2p1d] contracted Gaussian basis set due to Dunning.[44] The specific choice of the B3LYP density functional and DZP basis set was based on extensive previous studies of electron affinities.[45] 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.[46,47]

Table 1. Ground-State Total Energies (in hartrees) for $HC_{2n}H$ [$^1\Sigma_g^+$] and $HC_{4n}H^-$ [$^2\Pi_u$] ($n = 3-6$) and $HC_{4n+2}H^-$ [$^2\Pi_g$] ($n = 3-5$) with Adiabatic Electron Affinities (in eV)

molecule	neutral	anion	AEA
$HC_{12}H$	−458.13886	−458.20416	1.78
$HC_{14}H$	−534.30116	−534.37763	2.08
$HC_{16}H$	−610.46353	−610.54893	2.32
$HC_{18}H$	−686.62594	−686.71864	2.53
$HC_{20}H$	−762.78836	−762.88715	2.69
$HC_{22}H$	−838.950 79	−839.054 72	2.83
$HC_{24}H$	−915.11323	−915.22156	2.95

The quantum chemical computations of this study were conducted with the GAUSSIAN 94[48] 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 Hessian matrix, and hence the harmonic vibrational frequencies, were determined analytically. The adiabatic electron affinities (AEAs) for the molecules were evaluated as differences between the total energies of the optimized neutral and the corresponding optimized anion.

III. Results and Discussion

The main goal of this study was to determine the adiabatic electron affinities (AEA) of $HC_{2n}H$ ($n = 6-12$). As was shown in previous work on linear carbon chains,[49−51] the properties of the even- and odd-numbered structures differ extensively. Because none of the odd-numbered chains has yet been ($n > 15$) observed experimentally, we focus on chains with an even number of carbons.

We confirm $^1\Sigma_g^+$ to be the electronic ground state for all neutral molecules. This is due to the fact that the HOMOs, π_g for $HC_{4n}H$ ($n = 3-6$) and π_u for $HC_{4n+2}H$ ($n = 3-5$), are fully occupied. The ground-state configurations follow from the corresponding C_n electronic configurations, with the two last electrons appended for the two hydrogen atoms, resulting in the completely filled π HOMO's of the chain. An extra electron added to the LUMO orbital (π_u) leads to the $^2\Pi_u$ ground state of the anions $HC_{4n}H^-$ ($n = 3-6$). The addition of this last electron to the LUMO (π_g) of the anions $HC_{4n+2}H^-$ ($n = 3-5$) gives the $^2\Pi_g$ ground state.

The ground-state energies and corresponding AEAs for all molecules studied are listed in Table 1. The trend of increasing

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(25) Maier, J. P. *J. Phys. Chem. A* **1998**, *102*, 3462.
(26) Grutter, M.; Wyss, M.; Fulara, J.; Maier, J. P. *J. Phys. Chem. A* **1998**, *102*, 9785.
(27) Pino, T.; Ding, H.; Guethe, F.; Maier, J. P. *J. Chem. Phys.* **2000**, *114*, 2208.
(28) Tschumper, G. S.; Fermann, J. T.; Schaefer, H. F. *J. Chem. Phys.* **1995**, *104*, 3676.
(29) Zeigler, T.; Gutsev, G. L. *J. Comput. Chem.* **1991**, *13*, 70.
(30) King, R. A.; Mastryukov, V. S.; Tschumper, G. S. *J. Chem. Phys.* **1996**, *105*, 6880.
(31) Van Huis, T. J.; Galbraith, J. M.; Schaefer, H. F. *Mol. Phys.* **1996**, *89*, 607.
(32) Chong, D. P.; Ng, C. Y. *J. Chem. Phys.* **1993**, *98*, 759.
(33) King, R. A.; Galbraith, J. M.; Schaefer, H. F. *J. Phys. Chem.* **1996**, *100*, 6061.
(34) Cole, L. A.; Perdew, J. P. *Phys. Rev. A* **1982**, *25*, 1265.
(35) Grafton, A. K.; Wheeler, R. A. *J. Phys. Chem.* **1997**, *101*, 7154.
(36) Boesch, S. E.; Grafton, A. K.; Wheeler, R. A. *J. Phys. Chem.* **1996**, *100*, 10083.
(37) Rienstra-Kiracofe, J. C.; Graham, D. E.; Schaefer, H. F. *Mol. Phys.* **1998**, *94*, 767.
(38) Tschumper, G. S.; Schaefer, H. F. *J. Chem. Phys.* **1997**, *107*, 2529.
(39) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 42.
(40) Galbraith, J. M.; Schaefer, H. F. *J. Chem. Phys.* **1996**, *105*, 862.
(41) Roesch, T.; Trickey, S. B. *J. Chem. Phys.* **1997**, *106*, 8941.
(42) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(43) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(44) Dunning, T. H., Jr. *J. Chem. Phys.* **1971**, *55*, 3958.
(45) Rienstra-Kiracofe, J. C.; Tschumper, G. S.; Schaefer, H. F.; Nandi, S.; Ellison, G. B. *Chem. Rev.* In press.
(46) Choi, C. H.; Kertesz, M. *J. Chem. Phys.* **1997**, *107*, 6712.
(47) Martin, J. M. L.; El-Yazal, J.; Francois, J.-P. *Chem. Phys. Lett.* **1995**, *242*, 570.
(48) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresmen, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A.; *GAUSSIAN 94*, Revision C.3; Gaussian,Inc.: Pittsburgh, PA,1995.
(49) Brown, S. T.; Rienstra-Kiracofe, J. C.; Schaefer, H. F. *J. Phys. Chem. A* **1999**, *103*, 4065.
(50) Fan, Q.; Pfeiffer, G. V. *Chem. Phys. Lett.* **1989**, *162*, 472.
(51) Watts, J. D.; Bartlett, R. D. *J. Chem. Phys.* **1992**, *97*, 3445.

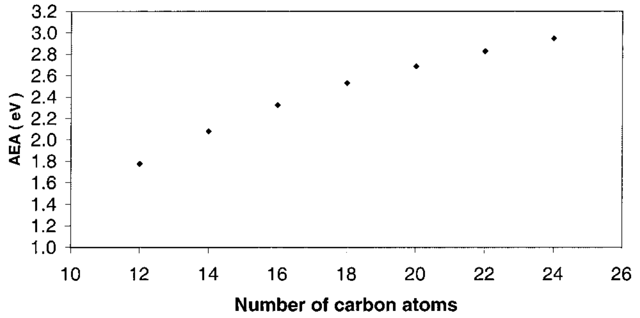

Figure 1. Adiabatic electron affinities (AEA) vs the number of carbon atoms in the chain.

Table 2. Optimized Geometries (bond distances in Å) for Ground States of Neutral $HC_{2n}H$ [$^1\Sigma_g{}^+$]

	$HC_{12}H$	$HC_{14}H$	$HC_{16}H$	$HC_{18}H$	$HC_{20}H$	$HC_{22}H$	$HC_{24}H$
HC_1	1.0704	1.0704	1.0704	1.0704	1.0705	1.0705	1.0705
C_1C_2	1.2245	1.2246	1.2246	1.2246	1.2247	1.2247	1.2247
C_2C_3	1.3621	1.3618	1.3616	1.3614	1.3613	1.3613	1.3613
C_3C_4	1.2353	1.2357	1.2359	1.2360	1.2361	1.2361	1.2361
C_4C_5	1.3495	1.3486	1.3481	1.3478	1.3476	1.3475	1.3475
C_5C_6	1.2392	1.2402	1.2407	1.2409	1.2411	1.2412	1.2412
C_6C_7	1.3469	1.3449	1.3438	1.3432	1.3423	1.3427	1.3425
C_7C_8		1.2413	1.2423	1.2429	1.2432	1.2434	1.2435
C_8C_9			1.3427	1.3415	1.3409	1.3405	1.3402
C_9C_{10}				1.2435	1.2441	1.2444	1.2446
$C_{10}C_{11}$					1.3403	1.3396	1.3392
$C_{11}C_{12}$						1.2447	1.2451
$C_{12}C_{13}$							1.3389

Table 3. Optimized Geometries (bond distances in Å) for Ground States of the Anions $HC_{4n}H^-$ [^2P_u] ($n = 3-6$) and $HC_{4n+2}H^-$ [^2P_g] ($n = 3-5$)

	$HC_{12}H^-$	$HC_{14}H^-$	$HC_{16}H^-$	$HC_{18}H^-$	$HC_{20}H^-$	$HC_{22}H^-$	$HC_{24}H^-$
HC_1	1.0672	1.0675	1.0678	1.0680	1.0682	1.0684	1.0686
C_1C_2	1.2375	1.2351	1.2333	1.2319	1.2309	1.2300	1.2293
C_2C_3	1.3507	1.3528	1.3545	1.3558	1.3567	1.3576	1.3582
C_3C_4	1.2577	1.2540	1.2511	1.2489	1.2470	1.2455	1.2443
C_4C_5	1.3278	1.3301	1.3325	1.3345	1.3363	1.3378	1.3391
C_5C_6	1.2681	1.2653	1.2624	1.2599	1.2575	1.2556	1.2539
C_6C_7	1.3212	1.3207	1.3218	1.3235	1.3253	1.3271	1.3287
C_7C_8		1.2690	1.2680	1.2662	1.2642	1.2623	1.2605
C_8C_9			1.3183	1.3181	1.3190	1.3203	1.3217
C_9C_{10}				1.2684	1.2677	1.2664	1.2649
$C_{10}C_{11}$					1.3189	1.3169	1.3176
$C_{11}C_{12}$						1.2678	1.2672
$C_{12}C_{13}$							1.3162

AEA as the $HC_{2n}H$ series lengthens is documented in Figure 1. Under the conditions of strong UV radiation occurring in the interstellar media, even longer $HC_{2n}H$ chains may exist and might be DIB carriers. As seen from Figure 4 of ref 26, the wavelengths of electronic transitions (origin bands) of polyacetylenic chains increase linearly with size, covering parts of the DIB spectral region. Further we note from the logarithmic-like character of the EA vs chain length curve (Figure 1) that a possible limit (~5.5 eV) for the EA exists. The results are not surprising because it is well-known that linear carbon chains C_n with an even number of atoms have some relatively higher EAs. For example, the electron affinity of C_8 is 4.38 eV (Zhao et al.).[52]

The optimized equilibrium geometries are shown in Tables 2 and 3. The numbering scheme of atoms and typical bond distances (in Å) are documented by Figure 2 using the $HC_{24}H$ molecule as an example. Extensive studies[46,47,53−57] (and references therein) on carbon clusters have shown that the ground electronic states of clusters smaller than C_{10} possess a linear structure with cumulenic bonding. However, there is a tendency of larger clusters to adopt bond alternating, acetylenic structures. It is agreed that the tendency for bond alternation is greater in

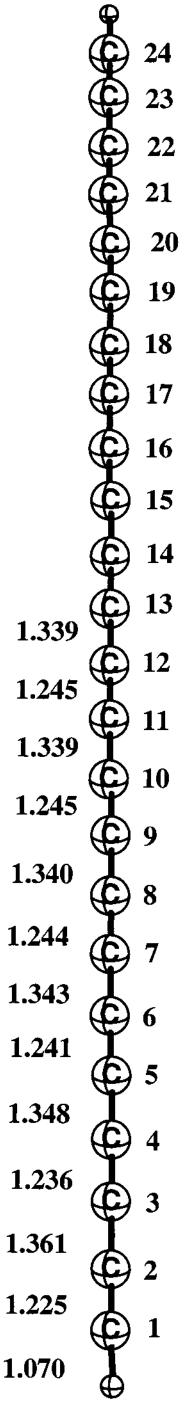

Figure 2. An example of atom numbering in chain structures, with bond distances (in Å) for $HC_{24}H$.

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(52) Zhao, Y.; de Beer, E.; Xu, C.; Travis, T.; Neumark, D. M. *J. Chem. Phys.* **1996**, *105*, 4905.

(53) van Orden, A.; Saykally, R. J. *Chem. Rev.* **1998**, *98*, 2313.

(54) Li, X.; Paldus, J. *Int. J. Quantum Chem.* **1996**, *60*, 513.

(55) Martin, J. M. L.; Taylor, P. R. *J. Phys. Chem.* **1996**, *100*, 6047.

(56) Hutter, J.; Lüthi, H. P.; Diederich, F. *J. Am. Chem. Soc.* **1994**, *116*, 750.

(57) Ohno, M.; Zakrzewski, V. G.; Ortiz, J. V.; von Niessen, W. J. *Chem. Phys.* **1997**, *106*, 3258.

Table 4. Theoretically Predicted IR-Active Harmonic Vibrational Frequencies (in cm^{-1}) for $X^1\Sigma_g^+$ $HC_{2n}H$[a]

vibrational mode	$HC_{12}H$	$HC_{14}H$	$HC_{16}H$	$HC_{18}H$	$HC_{20}H$	$HC_{22}H$	$HC_{24}H$
π_u (bend)	149	113	197	161	134	113	96
π_u (bend)					226	194	168
π_u (bend)	297	243	304	265	308	278	246
σ_u (CC stretch)		556*	489*	437*	394*	359*	330*
π_u (bend)	631*	631*	631*	631*	632*	632*	632*
σ_u (CC stretch)	644*				777*	710*	653*
σ_u (CC stretch)		1076*	955*	857*		1042	963
σ_u (CC stretch)	1230	1504	1366	1242	1134	1340	1248
σ_u (CC stretch)					1441	1569	1488
σ_u (CC stretch)	2076*		2069*	2096*	2062	2088	2058
σ_u (CC stretch)		2113*				2127*	2100*
σ_u (CC stretch)			2162	2179*	2156*	2177*	2121*
σ_u (CC stretch)	2208*	2236	2211*	2212*			2208
σ_u (CC stretch)		2253*			2240	2256	2245
σ_u (CH stretch)	3468	3468	3467	3467	3468	3467	3467

[a] An asterisk (*) denotes the most intense harmonic vibrational frequencies.

Table 5. Theoretically Predicted IR-Active Harmonic Vibrational Frequencies (in cm^{-1}) for $X^2\Pi$ $HC_{2n}H^-$ [a]

vibrational mode	$HC_{12}H^-$	$HC_{14}H^-$	$HC_{16}H^-$	$HC_{18}H^-$	$HC_{20}H^-$	$HC_{22}H^-$	$HC_{24}H^-$
π_u (bend)	126	104	179	153	130	186	164
σ_u (CC stretch)		560	494	440	398	363	333
π_u (bend)	239	246	381	340	406	413	418
π_u (bend)	367	332	391	406	426	437	444
π_u (bend)	438	384	397	411	489		479
π_u (bend)	468	450	464	440	496	489	490
π_u (bend)		479	484	481	499	495	494
π_u (bend)	501	500	499	487		514	528
π_u (bend)	571	575	579	582	585	588	590
σ_u (CC stretch)	649		964	864	783	715	659
σ_u (CC stretch)		1087			1146	1051	971
σ_u (CC stretch)	1248		1390	1257		1359	1262
σ_u (CC stretch)		1565		1610	1470	1635	1520
σ_u (CC stretch)	1956*				1938*	1905*	1873*
σ_u (CC stretch)		2023*	1965*	1971*	1972*		1971
σ_u (CC stretch)	2068*	2069*	2010*	2045*	2088		2076
σ_u (CC stretch)	2129		2107	2153		2128	2159*
σ_u (CC stretch)		2170			2186	2185*	2176*
σ_u (CC stretch)			2192*	2196*	2195*	2207*	2218*
σ_u (CH stretch)	3486	3484	3483	3482	3481	3480	3479

[a] An asterisk (*) denotes the most intense harmonic vibrational frequencies.

the C_n than in the C_nH_m systems. In the present study geometry optimizations began with equivalent bond lengths between the carbon atoms. Ultimately, we found significant bond length alternation and acetylenic-type bonding as a consequence of localized π orbitals. It is commonly agreed that the addition of two hydrogen atoms to the n-even C_n clusters[50] leads to the changes in bonding structure which are due to overlap and repulsion within the $HC_{2n}H$ π HOMO's. This results in a continuous shift from the cumulenic to acetylenic structure of the chain. Watts and Bartlett[51] earlier observed the same effect in the linear carbon cluster anions C_n^- ($n = 2-10$), as the addition of an electron to the C_n chain changed the bond length substantially. The bond length alternation was increased further[51] in the dianions, which are isoelectronic to $HC_{2n}H$ (the electronic ground states are also the same, $^1\Sigma_g^+$). On the other hand, in the anions $HC_{2n}H^-$ we observe a slight shift in structure away from the acetylenic structure as the triple bonds lengthen and the single bonds shorten with respect to $HC_{2n}H$. This indicates that the singly occupied molecular orbitals π_u and π_g are more delocalized than the doubly occupied HOMOs and tend to preserve cumulenic type of bonding. To summarize, the addition of an electron to neutral $HC_{2n}H$ leads, unlike the C_n systems, to less pronounced bond length alternation. Finally, we note that in all molecules studied, the observed effect of bond length alternation increases for the outermost bonds. The optimized equilibrium geometries for neutral $HC_{4n+2}H$ ($n = 3-5$) are consistent with 6-31G* B3LYP bond lengths reported previously.[27]

Theoretical IR-active harmonic frequencies are presented in Tables 4 and 5. Those predicted to be the most intense are marked by an asterisk. No exact comparison with experiment can be made, as the frequencies reported by Maier and co-workers[26,27] correspond to the excited state ($^1\Sigma_u^+$) of the $^1\Sigma_u^+ \leftarrow X\ ^1\Sigma_g^+$ electronic transition of $HC_{2n}H$ and the excited state ($^2\Pi$) of the $^2\Pi \leftarrow X\ ^2\Pi$ electronic transition of the anions $HC_{2n}H^-$. The general feature of the number of active CC stretches in region 1900−2200 cm^{-1} is however preserved.

IV. Conclusions

This study of linear carbon clusters $HC_{2n}H$, $HC_{2n}H^-$ ($n = 6-12$) confirms their acetylenic-type bonding structure (bond length alternation) for both neutral and anion radical species. We demonstrate that the electronic ground states are $^1\Sigma_g^+$ for the neutral molecules and $^2\Pi_u$ or $^2\Pi_g$ for the radical anions. In the anion radical we observe a slight delocalization of π-bonds when both triple bonds lengthen and single bonds shorten from 0.005 Å up to 0.03 Å in comparison to the neutral species. The high predicted adiabatic electron affinities, which are increasing with the number of carbon atoms in the chain, indicate that $HC_{2n}H^-$ may exist under conditions of strong UV-radiation in the interstellar media. The vibrational frequencies of these molecules, presented for the first time, may help in the future to confirm or reject the hypothesis of $HC_{2n}H$ and $HC_{2n}H^-$ as possible carriers of the DIBs.

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