HC$_n$H$^-$ Anion Chains with $n \leq 8$ Are Nonlinear and Their Permanent Dipole Makes Them Potential Candidates for Astronomical Observation

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Abstract: To be detectable in space via radio astronomy, molecules should have a permanent dipole moment. This is the plausible reason why HC$_n$H chains are underproportionally represented in the interstellar medium in comparison with the isoelectronically equivalent HC$_n$N chain family, which is the most numerous homologous series astronomically observed so far. In this communication, we present results of quantum chemical calculations for the HC$_n$H family at several levels of theory: density functional theory (DFT/B3LYP), coupled-cluster expansions (ROCCSD(T)), and G4 composite model. Contradicting previous studies, we report here that linear HC$_n$H$^-$ anion chains with sizes of astrochemical interest are unstable (i.e., not all calculated frequencies are real). Nonlinear cis and trans HC$_n$H$^-$ anion chains turn out to be stable both against molecular vibrations (i.e., all vibrational frequencies are real) and against electron detachment (i.e., positive electroaffinity). The fact that the cis anion conformers possess permanent dipole is the main encouraging message that this study is aiming at conveying to the astrochemical community, as this makes them observable by means of radio astronomy.

Keywords: astrochemistry; astrophysics; interstellar medium; carbon chains; polyynes; anions; quantum chemistry; radio astronomy; rovibrational spectroscopy; cis and trans isomers

1. Introduction

Although only representing a small fraction of the extraterrestrial matter, astronomical molecules are very interesting for space sciences because they provide valuable information on the physical and chemical conditions as well as the time evolution of the environments where they are detected. Searching for and confirming the presence of new molecular species plays a role of paramount importance in deepening understanding of astrochemical evolution in the interstellar and circumstellar medium [1].

According to the 2018 census [2], 204 molecules were astronomically detected. Out of them, carbon-based chains represent an important class. With seven members astronomically observed (HCN [3], HC$_2$N [4], HC$_3$N [5], HC$_4$N [6], HC$_5$N [7], HC$_7$N [8], HC$_9$N [9]), the HC$_n$N chains form the most numerous homologous series detected so far. This is in contrast to the case of the isoelectronically equivalent HC$_n$H chains [10–16], out of which only three members ($n = 2, 4, 6$) were astronomically detected: acetylene H−C≡C−H [17,18], diacetylene H−C≡C−C≡C−H [19], and triacetylene H−C≡C−C≡C−C≡C−H [19].

However, based on chemical intuition and substantiated below (see discussion related to Figure 1), it would be completely implausible to claim that members of the HC$_n$N family are more numerous in nonterrestrial environments than members of the HC$_n$H family. Rather, this underproportional representation of the HC$_n$H chains found so far in space relative to the HC$_n$N chains should be related to the complete different difficulty facing HC$_n$H detection versus HC$_n$N detection in space.

Possessing permanent dipole, linear HC$_n$N chains can be detected by radio astronomy, which is *par excellence* the method to observe extraterrestrial molecules that marked the

boom in reporting new molecules in space since the early 1960s [2]. According to existing studies—comprising not only neutral HC_nH^0 [10,20] but also cation HC_nH^+ [21,22] and anion HC_nH^- species [23–25]—HC_nH chains are linear. If they are linear (more precisely, centrosymmetric), they have zero dipole moments. Such chains cannot be detected via radio astronomy.

Still, are all HC_nH^- chains with molecular sizes of astrochemical interest really linear and centrosymmetric? This was the fundamental question that triggered the investigation whose results will be presented below, and emphasizing anions is part of our recent [26–30] and ongoing effort to understand their role in astrochemistry, which is claimed to even compete with that of the parent neutrals [29,31–33].

The prediction of nonlinear HC_nH^- anion chains stable against both molecular vibrations (i.e., computed vibrational frequencies are all real) and (excepting $n = 4$) electron detachment (i.e., positive electroaffinity EA > 0) and possessing permanent dipole moments ($\mu \neq 0$) is the main finding reported here. This is the encouraging new message that we aim at conveying to the astrochemical community. To better emphasize it, a series of technical details will be skipped here and deferred to a longer write-up that follows.
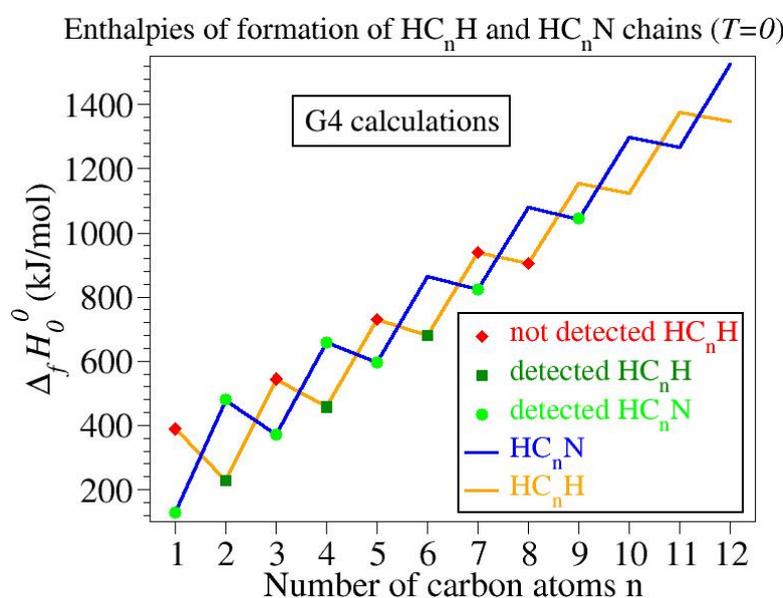
Figure 1. Enthalpies of formation $\Delta_f H_0^0$ of some astronomically observed HC_nN chains are larger than enthalpies of formation of shorter HC_nH chains not yet detected in space. On this basis, there is no reason to assume that HC_nH species are less numerous in space than HC_nN species, although, as visible in this figure, HC_nN molecules already astronomically observed are much more numerous than HC_nH molecules.

2. Methods

All quantum chemical calculations in conjunction with this study were done using the GAUSSIAN 16 [34] suite of programs on the bwHPC platform [35].

The enthalpies of formation $\Delta_f H_0^0$ and cis-trans splitting (see Section 3.3) were computed by means of the G4 composite model [36,37]. Recall that in contrast to "simple" models wherein the total electronic energy at frozen geometry—often obtained from optimization at another/lower level of theory (e.g., DFT with smaller basis sets)—is computed by means of a given method (e.g., CCSD(T) and larger basis sets), to achieve high ("chemical") accuracy, "composite" models (also referred to as compound model chemistries [38]) combine several results obtained via ab initio high-level methods with smaller basis sets with lower-level (DFT) theories using larger basis sets. Within G4, optimization and vibrational frequency calculations are done at the DFT/B3LYP/GTBas3 [34] level. The pertaining zero point energy corrected using an adequate scaling factor as well as thermal correc-

tions to enthalpy and Gibbs free energy are added to the electronic energy estimated at frozen geometry by combining various ab initio methods and basis sets (GAUSSIAN keywords [34] CCSD(T), E4T, FrzG4)/GTBas1, MP4 = FrzG4/GTBas2, MP4 = FrzG4/GTBas3, MP2 = Full/GTLargeXP, HF/GFHFB1, HF/GFHFB2) to obtain values of the total energy, enthalpy, and Gibbs free energy. These estimates turn out to be more accurate than the most elaborate and computationally demanding "simple" ab initio methods (including coupled-cluster (CC) and quadratic configuration interaction (QCI) expansions with singles, doubles and triples corrections (CCSD(T) and QCISD(T), respectively) [36,37].

The values of the adiabatic electron attachment energy EA including corrections due to zero point energy (ZPE) adjusted by means of adequate scaling factors, as standard in compound model chemistries [34,38], were estimated as energies of reaction $HC_nH^0 + e^- \rightarrow HC_nH^-$ at zero temperature, which obviates issues related to the so-called "ion convention" or "electron convention" for the charged species [39,40].

For consistency with previous and ongoing work on related systems [20,27,29,41–46] and in order to handle shorter and longer molecules on the same footing, all single-point quantum chemical calculations were carried out at the ROCCSD(T) level of theory, wherein restricted open-shell coupled-cluster expansions include single and double excitations as well as perturbative corrections due to triple excitations [47]. All molecular geometries utilized in these single-point calculations were optimized by means of the three parameter B3LYP hybrid DFT/HF exchange correlation functional [48–51] and 6-311++G(3df,3pd) basis sets [52,53]; more precisely, restricted RB3LYP for closed shell and unrestricted UB3LYP for open shell species. See Appendix B for further details.

3. Results and Discussion

3.1. Enthalpies of Formation: HC_nH versus HC_nN

In vein with those noted in the Introduction, let us start by comparing the values of the enthalpies of formation of the HC_nH chains with those of the HC_nN chains. Numerical results obtained using the G4 composite model are collected in Table 1 and depicted in Figure 1. As visible in Figure 1, by and large, neutral HC_nN and HC_nH chains possess comparable enthalpies of formation $\Delta_f H_0^0$. Importantly, some astronomically detected members of the HC_nN family have values of $\Delta_f H_0^0$ larger than values for shorter members of the HC_nH family not yet detected in space. With the grain of salt that formation mechanisms and kinetics are more important for the interstellar synthesis than in laboratory synthesis, the trend seen in Figure 1—corroborated with the important fact that, after all, the HC_nN synthesis requires the presence of extra nitrogen atoms—does by no means substantiate any claim on HC_nN members more numerous in space than HC_nH members. HC_nH's unfavorable balance in space should not be sought in the production mechanism but rather in the lack of a dipole moment.

Table 1. Enthalpies of formation of the HC_nH and HC_nN chain families computed using the G4 composite model. All values are in kJ/mol.

Number of Carbon Atoms	HC_nH	HC_nN
1	128.668	389.195
2	479.383	228.807
3	370.720	544.779
4	659.255	457.818
5	597.481	729.829
6	863.361	679.914
7	822.640	938.613
8	1080.580	905.162
9	1043.330	1153.130
10	1298.220	1124.610
11	1266.560	1375.680
12	1525.320	1347.420

3.2. Stable HC_nH^- Anion Chains with Astrochemically Interesting Sizes Are Nonlinear

Insight gained in conjunction with our recent investigations of astrochemically relevant carbon chain anions [26–29] made us skeptical that shorter HC_nH^- anion chains possess a stable linear geometry, as claimed earlier [23]. Our extensive attempts to optimize HC_nH^- anions imposing strict linear conformation confirmed previous results reported for sizes $n \geq 9$ [24,25]; we also found that irrespective whether n is odd or even, such sufficiently long HC_nH^- anions, linear and invariant under spatial inversion, are stable against molecular vibrations, i.e., all calculated frequencies were real.

However, our calculations disagreed with previous work [23] claiming that HC_4H^-, HC_6H^-, and HC_8H^- are linear and possess a $^2\Pi_u$, $^2\Pi_g$, and $^2\Pi_u$ ground state, respectively. Whether even ($n = 4k$, $n = 4k + 2$) or odd ($n = 2k + 1$), we found that strictly linear structures at $n \leq 8$ are unstable. Optimization of these anions constrained to be linear invariably ended with molecular conformations having exactly two imaginary frequencies. These two imaginary frequencies correspond to the in-phase and out-of-phase superposition of two vibrational modes, namely the two H−C−C bending modes of the chain ends. In view of this state of affairs, it was not at all surprising to find out that genuine anions' local energy minima (i.e., all vibrational frequencies real) correspond to cis and trans conformers wherein the two chain ends are bent, as visualized in Figure 2. Full information on the optimized cis and trans anions is presented in Tables A2–A6 of Appendix B.
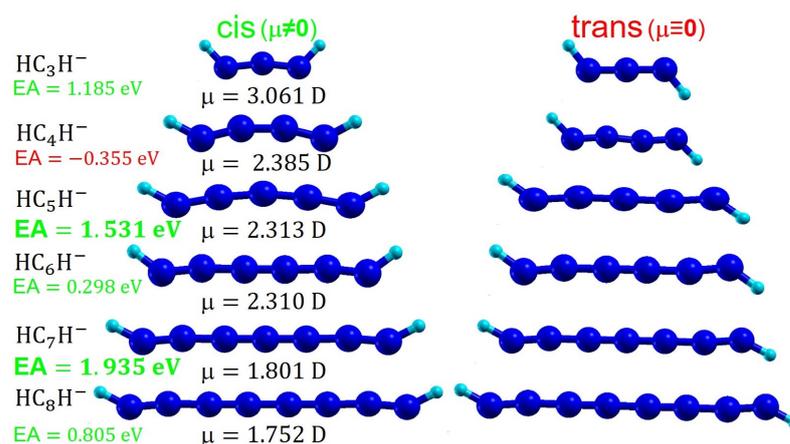
Figure 2. In contrast to the linear conformers, which are unstable against H−C−C bending vibrations at the two molecular ends, cis and trans HC_nH^- anion isomers with $n \leq 8$ correspond to local energy minima.

With regard to the specific cases considered in ref. [23], let us mention that at the UB3LYP/6-311++G(3df,3pd) level of theory, we found that the (unstable) linear HC_4H^-, HC_6H^-, and HC_8H^- conformers lie at 520 meV, 229 meV, and 60 meV above the stable nonlinear conformers. These values are much larger that the cis-trans energy splittings $\Delta_{cis-trans}$ presented in Table 3.

The foregoing analysis made it clear that nonlinear cis and trans anions are "stable" in the sense that they correspond to local energy minima. Equally important for the anions's "stability" is whether they are also stable against electron detachment, i.e., whether their electroaffinity EA (difference between the total energy of the neutral and the total energy of the anion) is positive. Inspection of Table 2 reveals that with one exception, all computed values of EA computed by us are positive. The exception in question is HC_4H; this is not surprisingly for small closed-shell molecular species whose anions are rarely stable. Still, given the fact that diacetylene (HC_4H) was already detected in space [19], HC_4H^-'s instability against electron detachment is not so "dramatic" from an astrochemical perspective.

Table 2. Adiabatic electron attachment energies EA computed using the G4 composite model and via ROCCSD(T) at the B3LYP/6-311++G(3df,3pd) minima. Values in eV. Notice that except for HC_4H^-, all the other HC_nH^- listed possess positive EAs and are therefore stable against electron detachment.

Molecule	G4	ROCCSD(T)
HC_3H	1.185	1.047
HC_4H	-0.355	-0.736
HC_5H [1]	1.531	1.420
HC_6H	0.298	0.195
HC_7H [2]	1.935	2.029
HC_8H	0.805	0.667

[1] Ref. [54] reported EA = 1.51 eV at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G level of theory. [2] Ref. [55] reported EA = 1.86 eV at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G level of theory.

3.3. Relevant Properties of Cis and Trans Anions

To obtain the cis-trans energy splitting, we estimated $\Delta_{cis-trans} \equiv \Delta_f H^0_{0,cis}\left(HC_nH^-\right) - \Delta_f H^0_{0,trans}\left(HC_nH^-\right)$ via the G4 composite model. Inspection of the values thus obtained, which are presented in Table 3 and Figure 3, reveals that pragmatically speaking, none of the cis-trans energy splitting significantly differs from zero; all values listed in Table 3 are definitely smaller than the "chemical accuracy" of ∼1 kcal/mol. Consequently, it is reasonable to assume that if present, cis and trans conformers of HC_nH^- anion chains coexist in extraterrestrial environments.
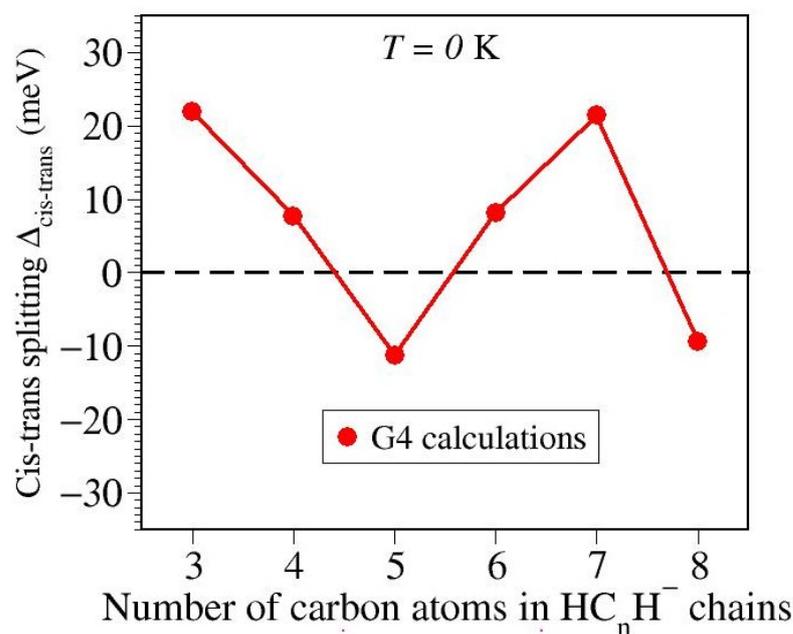
Figure 3. Because the cis-trans energy splitting $\Delta_{cis-trans} \equiv \Delta_f H^0_{cis}\left(HC_nH^-\right) - \Delta_f H^0_{trans}\left(HC_nH^-\right)$ computed via G4 as enthalpy of isomerization at zero temperature is very small, cis and trans anion conformers are expected to coexist in the interstellar medium.

Putting it better, one can rephrase as follows: cis HC_nH^- anion conformers can be present in the interstellar medium even if they are slightly higher in energy than their trans counterparts. We said "better" because from the present standpoint, cis anions have a paramount advantage. While the (nearly) centrosymmetric trans anions have (nearly) zero dipole moments, dipole moments of cis HC_nH^- anions are substantial; see Table 4 and Figure 4. Above, we wrote "nearly" because the (inherently finite) numerical accuracy prevents us to say whether—in contrast with the well-resolved C_{2v} symmetry of the cis anions—the trans anions are strictly C_{2h} symmetric or only approximately.

Table 3. Cis-trans anion energy splitting $\Delta_{cis-trans}$ estimated within the G4 composite model. Because all these values are smaller than the "chemical accuracy" of $\sim$1 kcal/mol, one can expect that cis and trans HC$_n$H anions coexist in space.

Anion	kcal/mol	meV
HC$_3$H$^-$	0.505	21.9
HC$_4$H$^-$	0.178	7.7
HC$_5$H$^-$	$-$0.260	$-$11.3
HC$_6$H$^-$	0.188	8.2
HC$_7$H$^-$	0.494	21.4
HC$_8$H$^-$	$-$0.217	$-$9.4
HC$_9$H$^-$	$-$0.668	29.0

Table 4. Dipole moment μ of anion's cis isomers computed via single-point ROCCSD(T) calculations at the geometry optimized via UB3LYP/6-311++G(3df,3pd).

Cis Anion	Dipole Moment (Debye)
HC$_3$H$^-$	3.061
HC$_4$H$^-$	2.385
HC$_5$H$^-$	2.313
HC$_6$H$^-$	2.310
HC$_7$H$^-$	1.801 [1]
HC$_8$H$^-$	1.752

[1] Ref. [55] reported $\mu = 1.63$ D at the B3LYP/aug-cc-pVDZ//B3LYP/6-31G level of theory.
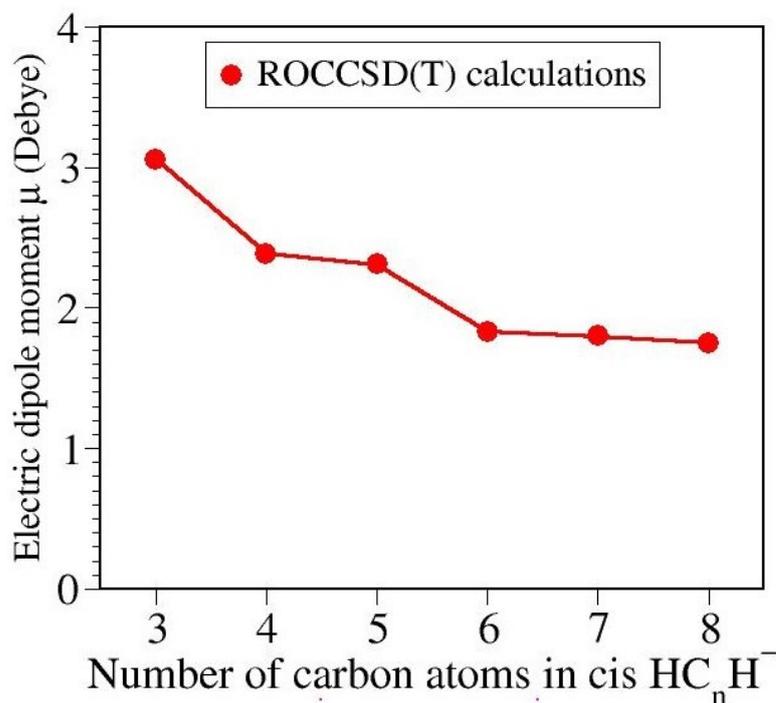
Figure 4. Cis HC$_n$H$^-$ anions with $n \leq 8$ possess reasonably large permanent dipole moments, and this can make them observable via rovibrational spectroscopy.

We do not want to end this section before mentioning that although not very well separated in energy, cis and trans anion isomers have properties sufficiently different from each other enabling experiments to distinguish between them. As illustration, infrared spectra of cis isomers are depicted along with those of trans isomers in Figure A2 of Appendix C. To understand that choosing above infrared spectra as a specific example was

not coincidental, let us note that the detection of HC$_4$H in ISO observations of CRL 618 [19] relied on laboratory information on the bending mode $\nu_8 = 627.89423(10)\,\mathrm{cm}^{-1}$ [56].

Parenthetically, the difference between the aforementioned value of ν_8 with so many digits after the comma and its counterpart at the B3LYP/6-311++G(3df,3pd) level of theory computed by us is $\nu_8 = 624.650\,\mathrm{cm}^{-1}$, which may give a (non-astro-)chemist who is not up with astrophysical ways a flavor that only a perfect match between laboratory spectra and observed lines can give a reliable astronomical identification.

4. Conclusions

Contrary to previous literature reports [23], we demonstrated that stable HC$_n$H$^-$ anion chains with astrochemically sizes ($n \leq 8$) not too large to be accessible via chemical synthesis in extraterrestrial environments are nonlinear. They can be astronomically observed via radio astronomy because they possess sufficiently large permanent dipoles (cf. Table 4) and electron detachment energies (cf. Table 2).

We do hope that this finding will stimulate laboratory experiments aiming at the accurate characterization of HC$_n$H$^-$ anions as a necessary prerequisite for the proper assignment of extraterrestrial signals associated with rovibrational lines. Because any calculation, even obtained with the most sophisticated quantum chemical methods, is unable to give a rovibrational spectrum precise enough to generate a detection in space, it can only help (though it is a lot!) with the laboratory interpretation of an experimental spectrum, which, then, can be used for astronomical observations.

Data Availability Statement: The data that support the findings of this study are available from the author upon reasonable request.

Conflicts of Interest: No conflict of interest to declare.

Appendix A
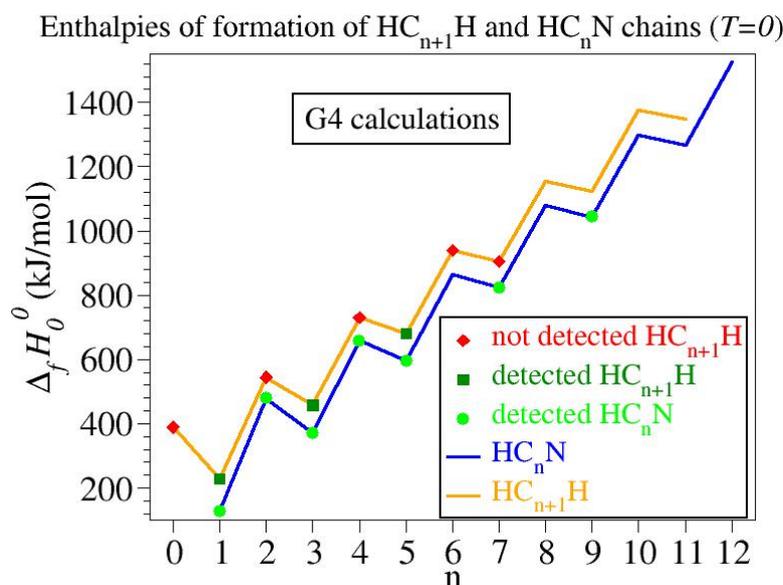
Figure A1. Enthalpies of formation $\Delta_f H_0^0$ presented in Figure 1 are redrawn here to allow direct comparison between the isoelectronic chains HC$_{n+1}$H and HC$_n$N.

Table A1. Enthalpies of formation of the isoelectronic $HC_{n+}H$ and HC_nN chain species computed using the G4 composite model. All values are in kJ/mol.

n	$HC_{n+1}H$	HC_nN
0	128.668	
1	479.383	389.195
2	370.720	228.807
3	659.255	544.779
4	597.481	457.818
5	863.361	729.829
6	822.640	679.914
7	1080.580	938.613
8	1043.330	905.162
9	1298.220	1153.130
10	1266.560	1124.610
11	1525.320	1375.680
12		1347.420

Appendix B

Except for HC_4H^-—which is less interesting in view of its instability against electron detachment (EA < 0, cf. Table 2)—we report below the Cartesian coordinates of the presently considered cis and trans anions; see Tables A2–A6.

For open shell optimization, we carried out unrestricted calculations UB3LYP because, according to our experience [26], spin contamination has a negligible impact on the DFT estimates. This obviates the need for restricted open shell ROB3LYP calculations. This sharply contrasts the coupled-cluster (CC) estimates, for which we employed restricted open shell ROCCSD(T) methods; similar to previous studies of related species [26], the impact of spin contamination turned out again to be important, which is a fact that makes less computationally demanding unrestricted UCCSD(T) methods inadequate.

Table A2. Cartesian coordinates in Å of the cis and trans HC_3H^- anion conformers optimized at the UB3LYP/6-311++G(3df,3pd) level of theory. Subscripts "before" and "after" label the values of the total spin before and after annihilation of the first spin contaminant.

HC_3H^-		cis			Trans	
$\langle S^2 \rangle_{before}$		0.7692			0.7692	
$\langle S^2 \rangle_{after}$		0.7502			0.7502	
Atom	**X**	**Y**	**Z**	**X**	**Y**	**Z**
H	0.000000	0.566638	−2.029360	0.000000	−0.431664	−2.096631
C	0.000000	−0.226564	−1.293825	0.000000	0.267660	−1.271822
C	0.000000	−0.080148	−0.000000	0.000000	−0.000000	0.000000
C	0.000000	−0.226564	1.293825	0.000000	−0.267660	1.271822
H	0.000000	0.566638	2.029360	0.000000	0.431664	2.096631

Table A3. Cartesian coordinates in Å of the cis and trans HC_5H^- anion conformers optimized at the UB3LYP/6-311++G(3df,3pd) level of theory. Subscripts "before" and "after" label the values of the total spin before and after annihilation of the first spin contaminant.

HC_5H^-		cis			Trans	
$\langle S^2 \rangle_{before}$		0.7791			0.7794	
$\langle S^2 \rangle_{after}$		0.7505			0.7505	
Atom	**X**	**Y**	**Z**	**X**	**Y**	**Z**
H	0.000000	0.325138	−3.463683	0.000000	−0.389640	−3.424168
C	0.000000	−0.217856	−2.538309	0.000000	0.241108	−2.553977
C	0.000000	0.034756	−1.295056	0.000000	0.047397	−1.297268
C	0.000000	0.154378	0.000000	0.000000	−0.000000	−0.000000
C	0.000000	0.034756	1.295056	0.000000	−0.047397	1.297268
C	0.000000	−0.217856	2.538309	0.000000	−0.241108	2.553977
H	0.000000	0.325138	3.463683	0.000000	0.389640	3.424168

Table A4. Cartesian coordinates in Å of the cis and trans HC_6H^- anion conformers optimized at the UB3LYP/6-311++G(3df,3pd) level of theory. Subscripts "before" and "after" label the values of the total spin before and after annihilation of the first spin contaminant.

HC_6H^-		cis			Trans	
$\langle S^2 \rangle_{before}$		0.7660			0.7660	
$\langle S^2 \rangle_{after}$		0.7502			0.7501	
Atom	**X**	**Y**	**Z**	**X**	**Y**	**Z**
H	0.000000	0.509362	−4.068471	0.000000	−0.429635	−4.080898
C	0.000000	−0.122855	−3.197356	0.000000	0.179751	−3.193660
C	0.000000	0.007350	−1.948075	0.000000	0.017416	−1.948151
C	0.000000	−0.019817	−0.627139	0.000000	0.011855	−0.626980
C	0.000000	−0.019817	0.627139	0.000000	−0.011855	0.626980
C	0.000000	0.007350	1.948075	0.000000	−0.017416	1.948151
C	0.000000	−0.122855	3.197356	0.000000	−0.179751	3.193660
H	0.000000	0.509362	4.068471	0.000000	0.429635	4.080898

Table A5. Cartesian coordinates in Å of the cis and trans HC_7H^- anion conformers optimized at the UB3LYP/6-311++G(3df,3pd) level of theory. Subscripts "before" and "after" label the values of the total spin before and after annihilation of the first spin contaminant.

HC_7H^-		cis			Trans	
$\langle S^2 \rangle_{before}$		0.7870			0.7871	
$\langle S^2 \rangle_{after}$		0.7509			0.7509	
Atom	**X**	**Y**	**Z**	**X**	**Y**	**Z**
H	0.431660	0.000000	−0.921860	0.000000	−0.330843	−4.787382
C	−0.017204	0.000000	0.047244	0.000000	0.144397	−3.832244
C	0.160726	0.000000	1.283517	0.000000	0.020735	−2.589456
C	0.226367	0.000000	2.596912	0.000000	0.016697	−1.275568
C	0.291294	0.000000	3.870346	0.000000	−0.000000	−0.000000
C	0.367671	0.000000	5.146221	0.000000	−0.016697	1.275568
C	0.445956	0.000000	6.455698	0.000000	−0.020735	2.589456
C	0.395178	0.000000	7.708239	0.000000	−0.144397	3.832244
H	0.997605	0.000000	8.593355	0.000000	0.330843	4.787382

Table A6. Cartesian coordinates in Å of the cis and trans HC_8H^- anion conformers optimized at the UB3LYP/6-311++G(3df,3pd) level of theory. Subscripts "before" and "after" label the values of the total spin before and after annihilation of the first spin contaminant.

HC_8H^-		cis			trans	
$\langle S^2 \rangle_{\text{before}}$		0.7695			0.7695	
$\langle S^2 \rangle_{\text{after}}$		0.7502			0.7502	
Atom	**X**	**Y**	**Z**	**X**	**Y**	**Z**
H	0.000000	0.395448	−5.421548	−0.570041	0.000000	−0.903775
C	0.000000	−0.095135	−4.472275	0.000000	0.000000	0.000000
C	0.000000	0.012485	−3.233941	0.000000	0.000000	1.242922
C	0.000000	−0.007051	−1.908770	0.134072	0.000000	2.561466
C	0.000000	−0.010887	−0.656694	0.247551	0.000000	3.808382
C	0.000000	−0.010887	0.656694	0.364166	0.000000	5.116584
C	0.000000	−0.007051	1.908770	0.477517	0.000000	6.363543
C	0.000000	0.012485	3.233941	0.611671	0.000000	7.681980
C	0.000000	−0.095135	4.472275	0.611324	0.000000	8.925066
H	0.000000	0.395448	5.421548	1.183595	0.000000	9.827551

Appendix C
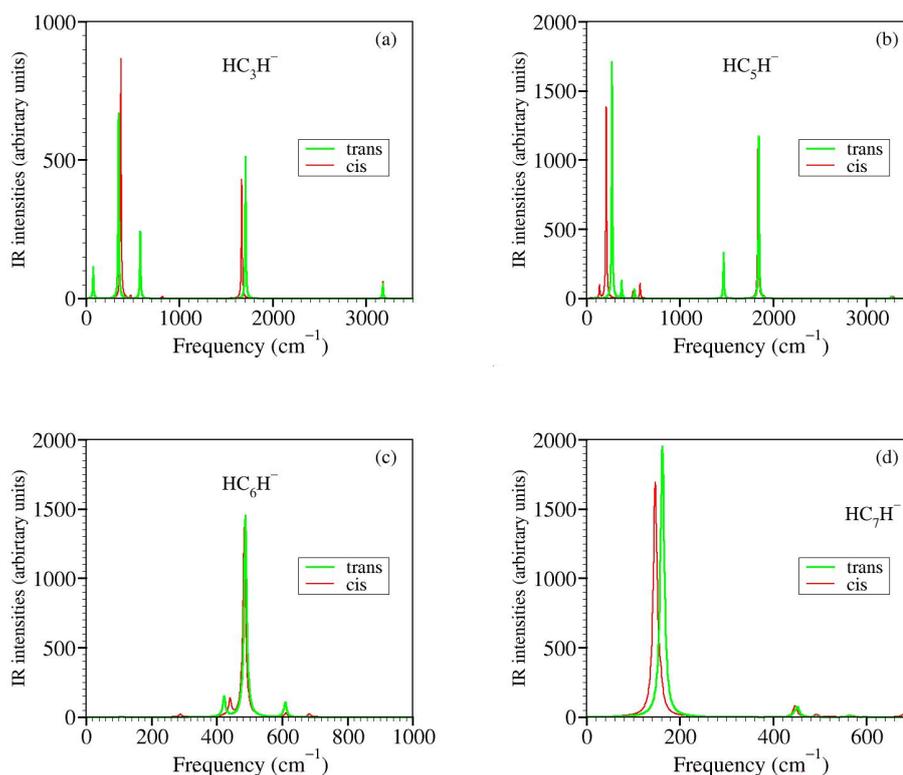
Figure A2. Differences between infrared spectra of cis and trans HC_nH^- anion conformers visible here make it possible to experimentally differentiate between them. Curves obtained by using a Lorentzian convolution of halfwidth of $5 \, \text{cm}^{-1}$. (**a**) HC_3H^-; (**b**) HC_5H^-; (**c**) HC_6H^-; (**d**) HC_7H^-.

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