SPECIAL TOPIC — The third carbon: Carbyne with one-dimensional sp-carbon

Chemical bonding in representative astrophysically relevant neutral, cation, and anion HC_nH chains

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Most existing studies assign a polyynic and cumulenic character of chemical bonding in carbon-based chains relying on values of the bond lengths. Building on our recent work, in this paper we add further evidence on the limitations of such an analysis and demonstrate the significant insight gained via natural bond analysis. Presently reported results include atomic charges, natural bond order and valence indices obtained from *ab initio* computations for representative members of the astrophysically relevant neutral and charged $HC_{2k/2k+1}H$ chain family. They unravel a series of counter-intuitive aspects and/or help naive intuition in properly understanding microscopic processes, *e.g.*, electron removal from or electron attachment to a neutral chain. Demonstrating that the Wiberg indices adequately quantify the chemical bonding structure of the $HC_{2k/2k+1}H$ chains — while the often heavily advertised Mayer indices do not — represents an important message conveyed by the present study.

Keywords: astrophysics, interstellar medium (ISM), carbon chains, Wiberg and Mayer bond order indices

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1. Introduction

With 46 members astronomically observed, linear carbon-based chains represent the most numerous class among the 204 molecular species reported in space.[1] They made the object of numerous experimental and theoretical investigations in the past.[2–35] For obvious topological reasons, the chains XC_nY wherein the terminal atoms X and Y are monovalent and/or trivalent (*e.g.*, HC_nH, HC_nN, and NC_nN) possess the following property: if even parity members ($n = 2k$) are "normal" closed shell molecules, then odd parity members ($n = 2k+1$) are open shell diradical species and *vice versa*. Closed shell species are spin singlets, and single and triple bonds alternate in their polyynic-type carbon backbone. By contrast, open shell diradcals are spin triplets exhibiting an intermediate structure switching from polyacetylenic bonding between outermost carbon atoms to cumulenic-like bonding between midmost carbon atoms.

In closed shell chains bond lengths between neighboring carbon-carbon pairs substantially vary. Lengths' difference amount to $\simeq 0.15$ Å (*cf.* Table 4). The alternation of single and triple bonds is fully consistent with chemical intuition. It is the direct consequence of the tetravalent carbon atom in the ideal Lewis picture. Still, assigning bonds' multiplicity merely based on bond length values is problematic. The longest single C–C bond ever reported (1.806 Å[36]) is much longer than "typical" single C–C bonds ($\sim$ 1.43–1.54 Å[37–39]). These are, in turn, substantially longer than the experimental value $d(C_2 - C_3) = 1.3633$ Å in triacetylene (*cf.* Table 4). The latter is in fact closer to the double bond length in ethene (1.3305 Å). Unless further microscopic details are known, reliable information on bond multiplicity cannot be derived merely from bond lengths. It is especially the nontrivial non-intuitive character of the structure of the open shell diradicals that makes the analysis of chemical bonding by merely inspecting the values of the bond lengths highly questionable.

Building on our recent work wherein bond order indices were introduced in studies on carbon chains of astrophysical interest,[34,35,40–44] we will present below a very detailed natural atomic orbital (NAO) and natural bond order (NBO) analysis,[45] with emphasis on HC_6H and HC_5H as representatives of the even-numbered and odd-numbered members of the HC_nH family. The results for the natural atomic charges are particularly interesting. They provide valuable information on the charge redistribution upon electron removal (ionization) and electron attachment.

Importantly, our results clearly demonstrate that Wiberg valence and bond order indices[46] represent an adequate basis for the quantitative understanding of chemical bonding in carbon chains. By contrast, Mayer index values [47] are completely at odds with chemical intuition.

2. Theoretical methods

The results reported below were obtained from quantum chemical calculations using the GAUSSIAN 16 (Ref. [48]) suite of programs. To ensure compatibility with our previous studies[35,41,42,49–53] single-point calculations for chemical bond and electronic properties were done at the CCSD(T)

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level of theory, wherein coupled-cluster expansions include single and double excitations along with perturbations due to triple excitations.[54] For these calculations, we used basis sets of triple-zeta quality augmented with diffuse functions (Dunning aug-cc-pVTZ[55–57]). Unless otherwise specified (see Tables S1, S2, and S13) the molecular geometries used for single point calculations were relaxed via the B3LYP three-parameter hybrid DFT/HF exchange correlation functional [58–61] and 6-311++G(3df,3pd) Pople's largest basis sets.[62,63]

For reasons explained elsewhere,[34] we employed unrestricted DFT (UB3LYP) methods and restricted open shell coupled-cluster (ROCCSD(T)) methods to handle open shell species. The cis-trans anion splitting and the electron attachment energies (Table S21) were estimated as zero-temperature limit of differences of the pertaining enthalpies of formation computed by compound model chemistries — G4,[64,65] W1BD,[66] and using complete basis set methods (CBS-QB3 and CBS-APNO)[63,67–69] — because they are more reliable than the computationally inexpensive Δ-DFT[49,70] values. For natural atomic orbital (NAO) and natural bond analysis (NBA),[45] we used the package NBO 6.0.[71] on top of GAUSSIAN 16 runs.

Figures 1 and 5 were generated with XCRSYDEN,[72] and figures 2 and 6 with GABEDIT.[73]

3. Results and discussion

3.1. Preliminary remarks

The numerous tables and figures presented below aim at providing the interested reader with a very detailed characterization of the electronic structure and chemical bonding of the specific molecular species considered. Comprehensively analyzing every data reported would make the paper disproportionately long. For this reason, in the discussion that follows we confine ourselves to emphasize the most relevant aspects which are "normally" not documented in existing literature studies.

Although not essential from the present perspective of gaining insight into the chemical bonding in carbon-based chains of astrophysical interest, to avoid misunderstandings, let us start with a technical remark. As previously demonstrated,[25,33,74–76] and also illustrated by our results presented in Table S13 geometry optimization for molecular sizes like those presently considered can be performed at the computationally demanding CCSD(T) level of theory with good basis sets. Nevertheless, most of the electronic and chemical bonding properties reported below were obtained at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G(3df,3pd) level of theory, *i.e.*, CCSD(T)/aug-cc-pVTZ single point calculations at geometries optimized via B3LYP/6-311++G(3df,3pd). This rationale is backed by calculations done by us [40–42] and others;[77] they revealed that bond metric and related rotational constants' data obtained via computationally inexpensive DFT-based optimization better agree with experiment than more sophisticated *ab initio* approaches.

In our study, special attention was paid to whether molecular vibrations (read Renner–Teller instability) lower the symmetric equilibrium geometry intuitively expected for HC_nH chains. Because too loose geometry relaxation may mask this possibility, we carried out calculations imposing very tight optimization conditions and various exchange-correlation functionals. Results like those presented in Tables S1 and S2 rule out this possibility for the HC_6H and HC_5H neutral chains and their cations. Giving in the various tables all Wiberg bond indices and natural charges obtained from quantum chemical computations better emphasizes whether the molecular species in question possess symmetric equilibrium structures or not. Molecules exist whose equilibrium geometry is asymmetric notwithstanding their symmetric stoichiometric formula; 4,4′-bipyridine is an example thereof (*cf.* Table 4 in Ref. [78]).

3.2. Wiberg indices *versus* Mayer indices

Except for the ideal cases wherein the electron charge transfer between atoms is complete (ideal ionic bond) or the neighboring atoms equally share an electron pair (ideal covalent bond), assigning numerical values to the bond multiplicity (= bond order), valence or charge of atoms forming a molecule from the wave function/density matrix obtained by quantum chemical calculations is a highly nontrivial task; the computed electron density is extended over the entire molecule rather than belonging to individual atoms.[79]

In our recent studies,[34,35,40–44] we demonstrated the utility of Wiberg's bond order indices[46] in quantitatively analyzing the chemical bonding in carbon-based chains of astrophysical interest. They are preferable to the more rudimentary Coulson bond order indices[80] introduced in conjunction with the Hückel theory or Mulliken's,[81] which do not properly describe the bond strength and formal bond multiplicity ("chemist's bond order", *i.e.*, half of the difference between the number of electrons occupying bonding and antibonding orbitals).

To avoid confusion, a comment on the Wiberg indices used here and in our previous studies is in order. Historically, they were introduced within the semi-empirical framework of complete neglect of differential overlap (CNDO).[46] However, the values reported by us via GAUSSIAN+NBO combination are not obtained from the CNDO-based one-particle reduced density matrix (as initially done by Wiberg.[46]) They are "Wiberg" indices only in the sense that they are computed using Wiberg's expressions of these indices in terms of the

one-particle reduced density matrix. The latter is computed from the ab initio CCSD-based wave function, it is not based on CNDO.

Wiberg indices are not the only valence and bond order indices employed in the literature to quantify chemical bonding in molecules. In our earlier studies[34,35,40–44] we did not motivate our preference for Wiberg indices. To justify this preference, we also show below values of the heavily advertised *ab initio* Mayer bond order indices.[47] In Table 1 we compare Mayer and Wiberg bond order indices $\mathscr{N}$ computed for acetylene H–C≡C–H. Atomic valencies $\mathscr{V}$ (obtained by summing elements of the bond index matrix in the NAO basis) are also presented there. As visible in Table 1, the Wiberg values are completely satisfactory. The estimated $\mathscr{N}$- and $\mathscr{V}$-values (extremely closed to three and four, respectively) are in excellent agreement with the Lewis representation. The very small deviation (< 0.06) from the ideal Lewis value ($\mathscr{V}_C = 4$) is due to the weak polar character of the C–H bond tracing back to the different electronegativity of the H and C atoms (see numerical values below) also reflected in the natural atomic charges ($q_H \simeq +0.22, q_C = -q_H \simeq -0.22$).

It is especially the independence of the basis sets of the Wiberg values emerging Table 1 that makes the strongest contrast with the Mayer values. As seen there, the Mayer values computed with aug-cc-pVTZ basis sets are completely at odds with elementary chemistry. We chose aug-cc-pVTZ to illustrate the disastrous impact of employing basis sets augmented with diffuse functions on the Mayer values. Still, we showed[40] that employing augmented basis sets in studies on carbon chain anions of astrophysical interest is mandatory, *e.g.*, calculations without properly including diffuse functions fail to correctly predict both the structure and spin multiplicity of the C_4N^- anion.[82] Table 1 is just one example that Mayer valence and bond order indices are completely unacceptable for carbon chains. The Mayer bond order indices for the non-problematic triacetylene HC_6H molecule (Table 2), for the pentadiynylidene HC_5H diradical (Table 3) as well as the Mayer valencies included in other tables presented below convey the same message.

Table 1. The Wiberg and Mayer bond order $\mathscr{N}$ and valence $\mathscr{V}$ indices for the HC_2H^0 neutral singlet chain computed at the RCCSD(T)/BS//RB3LYP/6-311++G(3df,3pd) level of theory for the HC_2H^0 neutral singlet chain (H_1–C_1 ≡C_2–H_2). The basis sets (BS) employed are indicated below.

Type of index	Basis set	$\mathscr{N}(C_1C_2)$	$\mathscr{V}(C_1) = \mathscr{V}(C_2)$
Wiberg	cc-pVTZ	2.9956	3.9429
Wiberg	aug-cc-pVTZ	2.9950	3.9435
Mayer	cc-pVTZ	2.7851	3.7374
Mayer	aug-cc-pVTZ	1.6260	2.1109

Parenthetically, even if they are not so disastrous, the Mayer $\mathscr{N}$- and $\mathscr{V}$-values (2.79 and 3.74, respectively) computed with cc-pVTZ basis sets without diffuse functions inadequately describe the triple C≡C bond and the tetravalent carbon in the elementary textbook HCCH molecule.

Table 2. Wiberg and Mayer bond order indices $\mathscr{N}$ computed at the RCCSD(T)/BS//RB3LYP/6-311++G(3df,3pd) level of theory for the HC_6H^0 neutral chain (H_1–C_1–C_3 ≡C_4–C_5 ≡C_6–H_2). The basis sets (BS) are indicated below.

Type of bond index	Basis sets	H_1C_1	C_1C_2	C_3C_4	C_4C_5	C_4C_5	C_5C_6	C_6H_2
Wiberg	cc-pVTZ	0.9323	2.7715	1.1637	2.5967	1.1637	2.7715	0.9323
Wiberg	aug-cc-pVTZ	0.9319	2.7675	1.1646	2.5926	1.1645	2.7676	0.9319
Mayer	cc-pVTZ	0.9855	2.3864	1.2513	2.8632	1.2513	2.3864	0.9855
Mayer	aug-ccpVTZ	0.9522	-0.3728	0.4486	2.8862	0.4486	-0.3728	0.9522

Table 3. Wiberg and Mayer bond order indices $\mathscr{N}$ computed at the ROCCSD(T)/BS//UB3LYP/6-311++G(3df,3pd) level of theory for the HC_5H^0 neutral triplet chain ($H_1C_1C_2C_3C_4C_5H_2$). The basis sets (BS) are indicated below.

Type of bond index	Basis set	H_1C_1	C_1C_2	C_3C_4	C_4C_5	C_4C_5	C_5H_2
Wiberg	cc-pVTZ	0.9345	2.4965	1.4120	1.4120	2.4965	0.9345
Wiberg	aug-cc-pVTZ	0.9343	2.4939	1.4109	1.4109	2.4939	0.9343
Mayer	cc-pVTZ	1.0133	2.1123	1.4543	1.4543	2.1123	1.0133
Mayer	aug-cc-pVTZ	1.5979	0.2629	1.9935	1.9935	0.2629	1.5979

3.3. Chemical bonding in HC_6H chains

More to the main point, let us first consider the HC_6H chains. The Cartesian coordinates for equilibrium geometries of the neutral and charged species are presented in Tables S4, S5, S6, S7. Important insight into their ground state electronic structure can be gained at the MO picture level. The pertaining electronic configurations read as follows:

$$HC_6H^0\big|_{D_{\infty h}} : {}^1\Sigma_g^+ = \cdots 6\sigma_u^2 7\sigma_g^2 1\pi_u^4 1\pi_g^4 2\pi_u^4, \tag{1a}$$

$$HC_6H^+\big|_{D_{\infty h}} : {}^2\Pi_u = \cdots 6\sigma_u^2 7\sigma_g^2 1\pi_u^4 1\pi_g^4 2\pi_u^3, \tag{1b}$$

$$\text{unstable } HC_6H^-|_{D_{\infty h}}: \ ^2\Pi_g = \cdots 6\sigma_u^2 7\sigma_g^2 1\pi_u^4 1\pi_g^4 2\pi_u^4 2\pi_g^1 \rightsquigarrow$$
$$\begin{cases} \text{cis } HC_6H^-|_{C_{2v}}: & ^2B_2 = \cdots 6b_2^2 7a_1^2 8a_1^2 1b_1^2 7b_2^2 1a_2^2 9a_1^2 2b_1^2 8b_2^1, \\ \text{trans } HC_6H^-|_{C_{2h}}: & ^2A_g = \cdots 6b_u^2 7a_g^2 1a_u^2 7b_u^2 8a_g^2 1b_g^2 2a_u^2 8b_u^2 9a_g^1. \end{cases} \quad (1c)$$

The neutral HC_6H^0 molecule is a typical closed-shell linear polyyne (*cf.* Fig. 1) whose paired valence electrons in the completely filled highest occupied molecular orbital (HOMO) $2\pi_u^4$ (*cf.* Eq. (1a)) determines a singlet ground state. As depicted in Fig. 2, the calculated HOMO spatial density of the neutral linear HC_6H^0 chain is concentrated between atoms, or more precisely, on every second carbon–carbon bond starting from the molecular ends. This makes the HC_6H^0 a quantum chemistry textbook example wherein carbon–carbon bonds alternate between almost perfectly tetravalent carbon atoms.

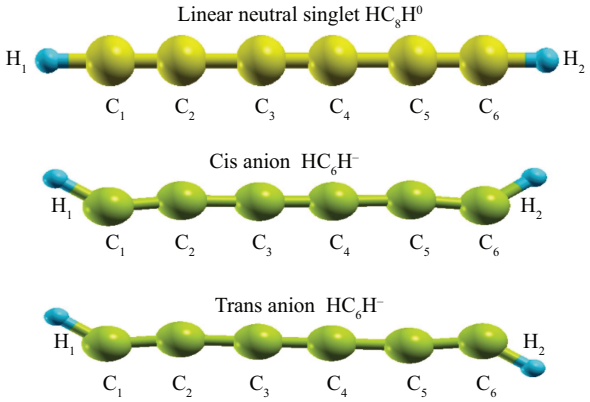


Fig. 1. Geometries of HC_6H chains investigated in the present paper. Like the HC_6H^0 neutral parent, the HC_6H^+ cation is linear and therefore not shown here.

Mathematically, this is expressed by the numerical values of the atomic valencies collected in Table 5 and Table S3 and the bond order indices included in Table 6. For all carbon atoms, the computed values for the Wiberg valence depicted in Table S3 and Table 5 are only very slightly different from the value of four in the idealized Lewis representation H–C≡C–C≡C–C≡C–H. Similar to the aforementioned HC_2H, the small differences from the Lewis value (< 0.07), which are comparable with that for the hydrogen atoms, reveal a very weak polar character of the bonds. These slight departures from the localized Lewis picture arise from the small values of the Rydberg natural bond orbitals and the small differences from the core electrons of the isolated atoms presented in Table 5 and Table S3.

In accord with the different electronegativity χ ($\chi_H^{\text{Pauling;Allen}} = 2.20$; $2.300 < \chi_C^{\text{Pauling;Allen}} = 2.55$; 2.544), the hydrogen atoms are assigned a positive charge ($q_{H_{1,2}} \gtrsim +0.23$). This value is roughly twice the negative charges of the nearest and next nearest carbon neighbors ($q_{C_1} = q_{C_6} \approx q_{C_2} = q_{C_5} \approx -0.1$), which are much larger than those of the inner, almost neutral carbon atoms ($q_{C_3} = q_{C_4} \approx -0.01$). This is visualized in Fig. 3(e). For comparison purposes, where appropriate, we will also refer to the case of the neutral benzene molecule C_6H_6. To make the paper self-contained, we computed and present all relevant data for C_6H_6 in supporting information. In benzene all carbon and hydrogen atoms (Wiberg valencies 3.9769 and 0.9666, respectively) have the same charge: $q_C \simeq -0.19$, $q_H = +0.19$ (*cf.* Tables S20 and S2).

Table 4. Results of B3LYP/6-311++G(3df,3pd) very tight geometry optimization for HC_6H chains without imposing symmetry constraints. Bond lengths l between atoms XY (in unit Å), angles α between atoms ∠XYZ (in unit degrees) and Wiberg bond order indices $\mathcal{N}$.

Species	Property	H_1C_1	$\angle H_1C_1C_2$	C_1C_2	$\angle C_1C_2C_3$	C_2C_3	$\angle C_2C_3C_4$	C_3C_4	$\angle C_3C_4C_5$	C_4C_5	$\angle C_4C_5C_6$	C_5C_6	$\angle C_5C_6H_2$	C_6H_2
Singlet	l, α	1.0614	180.0	1.2068	180.0	1.3539	180.0	1.2147	180.0	1.3539	180.0	1.2068	180.0	1.0614
	Expt.[a]	1.0639	180.0	1.2092	180.0	1.3633	180.0	1.2179	180.0	1.3633	180.0	1.2092	180.0	1.0639
	$\mathcal{N}$	0.9319		2.7675		1.1646		2.5925		1.1646		2.7675		0.9319
Cis anion	l, α	1.0764	138.1	1.2560	172.9	1.3212	178.9	1.2543	178.9	1.3212	172.9	1.2560	138.1	1.0764
	$\mathcal{N}$	0.9223		2.6780		1.2365		2.4755		1.2365		2.6780		0.9223
Trans anion	l, α	1.0764	138.1	1.2560	172.9	1.3212	179.1	1.2543	179.1	1.3212	172.9	1.2560	138.1	1.0764
	$\mathcal{N}$	0.9228		2.6779		1.2366		2.4756		1.2366		2.6779		0.9228
Cation	l, α	1.0693	180.0	1.2222	180.0	1.3213	180.0	1.2393	180.0	1.3213	180.0	1.2222	180.0	1.0693
	$\mathcal{N}$	0.9182		2.4990		1.3461		2.1096		1.3461		2.4990		0.9182

[a] Cited after Ref. [33]

Albeit HC_6H^+ preserves both the linear $D_{\infty h}$ conformation of the neutral parent (Fig. 1) and the $2\pi_u$ character of its HOMO (*cf.* Eq. (1b)), the bond lengths are not similarly affected by electron removal. The single bonds of the cation become shorter while the triple bonds become longer (Table 4 and Fig. 4(a). Most affected is the central C_3≡C_4 bond whose Wiberg bond order index decreases by almost 0.5 (Fig. 3(c)); this is more than two times larger than in the case of $C_6H_6^+$ (Table S19 and Fig. S2(e). In accord with intuitive expectation regarding the Coulomb repulsion minimization, our calculations found that the C_1 and C_6 atoms, which are most distant of each other, acquire the largest positive charge (Fig. 3(e)). In the same vein, the Coulomb repulsion due to the additional positive charge on the C_3 and C_4 atoms correlates with

the increase in the $C_3{\equiv}C_4$ bond length. Likewise, the shortening of the C_2–C_3 (or C_4–C_5) bond is compatible with the Coulomb attraction due to the extra charges of opposite sign on the C_3 and C_4 atoms (or C_3 and C_4 atoms). Nevertheless, our calculations reveal that variation of the bond lengths is not merely an electrostatic effect. The triple bonds $C_1{\equiv}C_2$ and $C_5{\equiv}C_6$ become longer although the atoms involved acquire extra charges of opposite sign which would imply an additional bond squeezing. Calculations also show that chemical intuition may be problematic even in a closed shell molecule like HC_6H; inspection of Figs. 3(e) and 3(g) reveals a decreasing in the valence state of all carbon atoms although the extra negative charge of C_2 and C_5 has opposite sign to the extra (positive) charge of the other C atoms.

Table 5. Natural atomic charges, numbers of core and Rydberg electrons, and Wiberg and Mayer valencies computed via RCCSD(T)/aug-cc-pvtz//RB3LYP/6-311++G(3df,3pd) for the HC_6H singlet neutral chain.

Atom	Natural charge	Core	Rydberg	Wiberg	Mayer
H_1	0.23347	0.00000	0.00269	0.9487	0.8490
C_1	-0.11511	1.99852	0.00784	3.9359	1.0953
C_2	–0.10769	1.99860	0.02228	3.9777	–0.1837
C_3	–0.01067	1.99837	0.02266	3.9855	3.6110
C_4	–0.01067	1.99837	0.02266	3.9855	3.6110
C_5	–0.10769	1.99860	0.02228	3.9777	–0.1837
C_6	–0.11511	1.99852	0.00784	3.9359	1.0952
H_2	0.23347	0.00000	0.00269	0.9487	0.8490

Table 6. Natural atomic charges, numbers of core and Rydberg electrons, and Wiberg and Mayer valencies computed via ROCCSD(T)/aug-cc-pvtz//UB3LYP/6-311++G(3df,3pd) for the HC_6H^+ cation.

Atom	Natural charge	Core	Rydberg	Wiberg	Mayer
H_1	0.27071	0.00000	0.00232	0.9291	0.7702
C_1	0.21701	1.99863	0.00690	3.6241	1.0100
C_2	–0.20647	1.99876	0.02359	3.8956	0.0574
C_3	0.21875	1.99859	0.02112	3.6623	3.1369
C_4	0.21875	1.99859	0.02112	3.6623	3.1369
C_5	–0.20647	1.99876	0.02359	3.8956	0.0574
C_6	0.21701	1.99863	0.00690	3.6241	1.0100
H_2	0.27071	0.00000	0.00232	0.9291	0.7702

It might be tempting to relate the opposite change of the Wiberg indices of the adjacent carbon-carbon bonds driven by ionization to the alternation of the single and triple bonds in HC_6H. If this held true, one could expect a more democratic impact of electron removal in molecules with similar carbon-carbon bonds. To demonstrate that this is not the case, let us refer again to C_6H_6. Notwithstanding the equivalent carbon–carbon bonds of the neutral molecule, ionization only shortens two opposite carbon–carbon bonds (C_2C_3 and C_5C_6 in Fig. S2(b)). Their bond order indices in $C_6H_6{}^+$ are larger than in $C_6H_6{}^0$ (Fig. S2(d)). The other four carbon–carbon bonds are stretched and the corresponding bond order indices are reduced. That is, the process starting with equivalent (aromatic) carbon–carbon bonds in $C_6H_6{}^0$ ends with nonequivalent carbon–carbon bonds in $C_6H_6{}^+$. Two carbon–carbon bonds acquire partial double bond character and four carbon–carbon bonds acquire partial single bond character.

Table 7. Natural atomic charges, numbers of core and Rydberg electrons, and Wiberg and Mayer valencies computed via ROCCSD(T)/aug-cc-pvtz//UB3LYP/6-311++G(3df,3pd) for the HC_6H^- cis anion.

Atom	Natural charge	Core	Rydberg	Wiberg	Mayer
H_1	–0.20424	0.00000	0.44961	1.1812	–1.6284
C_1	–0.16160	1.99864	0.03167	3.9158	1.4547
C_2	–0.10529	1.99883	0.03230	3.9765	–1.2703
C_3	–0.02888	1.99856	0.03819	4.0027	–0.8041
C_4	–0.02888	1.99856	0.03819	4.0027	–0.8041
C_5	–0.10529	1.99883	0.03230	3.9765	–1.2703
C_6	–0.16160	1.99864	0.03167	3.9158	1.4547
H_2	–0.20424	0.00000	0.44961	1.1812	–1.6284

Table 8. Natural atomic charges, numbers of core and Rydberg electrons, and Wiberg and Mayer valencies computed via ROCCSD(T)/aug-cc-pvtz//UB3LYP/6-311++G(3df,3pd) for the HC_6H^- trans anion.

Atom	Natural charge	Core	Rydberg	Wiberg	Mayer
H1	–0.20318	0.00000	0.44886	1.1819	–1.7028
C1	–0.16077	1.99864	0.03078	3.9160	1.9272
C2	–0.10689	1.99883	0.03444	3.9788	–0.1883
C3	–0.02916	1.99856	0.03889	4.0040	–2.2379
C4	–0.02916	1.99856	0.03889	4.0040	–2.2379
C5	–0.10689	1.99883	0.03444	3.9788	–0.1883
C6	–0.16077	1.99864	0.03078	3.9160	1.9272
H2	–0.20318	0.00000	0.44886	1.1819	–1.7028

Switching to the HC_6H^- chain, we should first reiterate[43,44] that, contrary to what previously claimed,[83] the anion is not linear. Calculations[43,44] yielded two nonlinear conformers — more precisely, a cis and a trans isomer (*cf.* Eq. (1c) and Fig. 5) — stable both against molecular vibrations (*i.e.*, all computed vibrational frequencies are real) and against electron detachment (*i.e.*, positive electron attachment energy EA>0). The cis-trans energy separation is smaller than the "chemical" accuracy (~ 1 kcal/mol) expected for the various compound model chemistries used in our calculations (*cf.* Table S21). Therefore, it is reasonable to assume that in fact they are quasi-isoenergetic and coexist. This should be the more so especially in extraterrestrial environments where dedicated paths of synthesis to generate a given (preferably, cis) conformer are unlikely. We said "preferably" because only the HC_6H^- cis isomer possesses a permanent dipole moment (*cf.* Table S21). This makes it a potential candidate for astronomical observation via rovibrational spectroscopy.[43] The HC_6H^- trans isomer does not have a permanent dipole ($\mu = 0$) and cannot be detected by radio astronomy. Inspection of Tables 4, 7, and 8 reveals that, apart from the different atom location with respect to the molecular axis, the cis and trans

HC_6H^- isomers possess properties that do not notably differ from each other. They could be hardly distinguished from each other within the drawing accuracy in Figs. 3 and 4. For this reason, only results for the cis anions are depicted in those figures.

While agreeing with the intuitive expectation that electron addition makes the anion longer than the neutral parent, inspection of the bond metric data (Table 4, and Figs. 3(a) and 4(a) reveals that electron addition does not stretch all chemical bonds. Interestingly and unexpectedly at the same, electron addition and electron removal have similar bond squeezing and bond stretching effects. That is, the same bonds that are, *e.g.*, elongated upon electron removal are also elongated upon electron attachment. As depicted in Fig. 4(a), the single C_2–C_3 and C_4–C_5 bonds are squeezed by virtually the same amount. Albeit more pronounced than for cation, the C–H and triple $C_1{\equiv}C_2$, $C_3{\equiv}C_4$, and $C_5{\equiv}C_6$ bonds of the anion are longer than in the neutral. Counterintuitively, the quantitative changes in the Wiberg bond order indices do not follow the changes in the bond lengths. Notwithstanding the virtually identical squeezing of the single C_2–C_3 and C_4–C_5 bonds, the increase in anion's bond order indices only amounts one third from that in cation. Moreover, although the stretching of the C–H and triple $C_1{\equiv}C_2$, $C_3{\equiv}C_4$, and $C_5{\equiv}C_6$ bonds is more pronounced in anion than in cation, the reduction in the corresponding bond order indices in anions is substantially smaller than in cation (*cf.* Fig. 4(c)).

As intuitively expected, the extra electron migrate towards the HC_6H^- chain ends (*cf.* Fig. 4(e)). This increases the fractional valence of the H atoms in the anion while leaving the valence of the C atoms unchanged from the ideal Lewis value of four (*cf.* Fig. 4(g)).

The comparison between the HC_6H^- chain the $C_6H_6{}^-$ ring is also interesting. In the latter, the excess electron also migrates towards the outermost H atoms (*cf.* Fig. S2(g)) reducing thereby the Coulomb repulsion. Still, while being stable against molecular vibrations (*i.e.*, all computed vibrational frequencies are real), $C_6H_6{}^-$ is not stable against electron detachment; *i.e.*, its electron attachment energy is negative (EA < 0). This behavior can be rationalized in terms of electrostatic repulsion. In the longer HC_6H^- the Coulomb repulsion is overcompensated by stabilization due to π-electron delocalization, a fact impossible in the $C_6H_6{}^-$ anion whose shorter diameter makes repulsion too strong.

3.4. Chemical bonding in HC_5H chains

Let us now examine the HC_5H chains, whose Cartesian coordinates at energy minimum are presented in Tables S8–S12. The relevant ground state electronic configurations read as follows:

$$HC_5H^0\big|_{D_{\infty h}}:\ {}^3\Sigma_g^- = \cdots 6\sigma_g^2\,5\sigma_u^2\,1\pi_u^4\,1\pi_g^4\,2\pi_u^2, \tag{2a}$$

$$HC_5H^+\big|_{D_{\infty h}}:\ {}^2\Pi_u = \cdots 6\sigma_g^2\,5\sigma_u^2\,1\pi_u^4\,1\pi_g^4\,2\pi_u^1, \tag{2b}$$

$$\begin{aligned}&\text{unstable } HC_5H^-\big|_{D_{\infty h}}:\ {}^2\Pi_u = \cdots 6\sigma_g^2\,5\sigma_u^2\,1\pi_u^4\,1\pi_g^4\,2\,\pi_u^3 \rightsquigarrow\\ &\begin{cases}\text{cis } HC_5H^-|_{C_{2v}}: {}^2B_1 = \cdots 5a_1^2\,5b_2^2\,6a_1^2\,1b_1^2\,1a_2^2\,6b_2^2\,2b_1^1\,7a_1^2,\\ \text{trans } HC_5H^-|_{C_{2h}}: {}^2A_u = \cdots 6a_g^2\,5b_u^2\,1a_u^2\,6b_u^2\,1b_g^2\,7a_g^2\,2a_u^1\,2b_u^2.\end{cases}\end{aligned} \tag{2c}$$

In accord with earlier reports,[3,35] the present quantum chemical study confirmed the $D_{\infty h}$ symmetry of the HC_5H^0. Our calculations comprise very tight geometry optimization with the widely employed B3LYP,[59–61] PBE0,[84] and M06-2X[85] functionals (*cf.* Tables S1 and S2). The triplet character of the ground state $\tilde{X}\,{}^3\Sigma_g^-$ obtained from calculations confirms the physical intuition. According to Hund's rule, the two electrons in the half-filled HOMO ($2\pi_u^2$, *cf.* Eq. (2a)) should have parallel spin. Inspection of the HOMO depicted in Fig. 2 reveals that its highest density is concentrated on every second carbon atom starting from the chain ends and not between the carbon atoms, as the case of the HC_6H^0 even member chain. "On atoms" and not "on bonds"; this is the reason why, in general, odd members $HC_{2k+1}H$ are less stable than even members $HC_{2k}H$.[44]

The comparison between the various panels of Fig. 3 reveals that the differences between the properties of the diradical open shell HC_5H^0 triplet and those of the non-radical closed shell HC_6H^0 singlet are substantial. The most salient qualitative difference is, of course, the absence of bond alternation in HC_5H, but other differences are also notable. For instance, the fact that, unlike other C atoms, the central C_3 atom in the HC_5H^0 neutral is positively charged (Fig. 3(f).

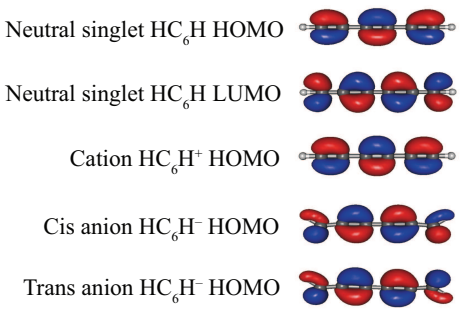


Fig. 2. MO spatial distributions of the HC_6H chains investigated in the present paper: neutral singlet, cation, cis anion, trans anion.

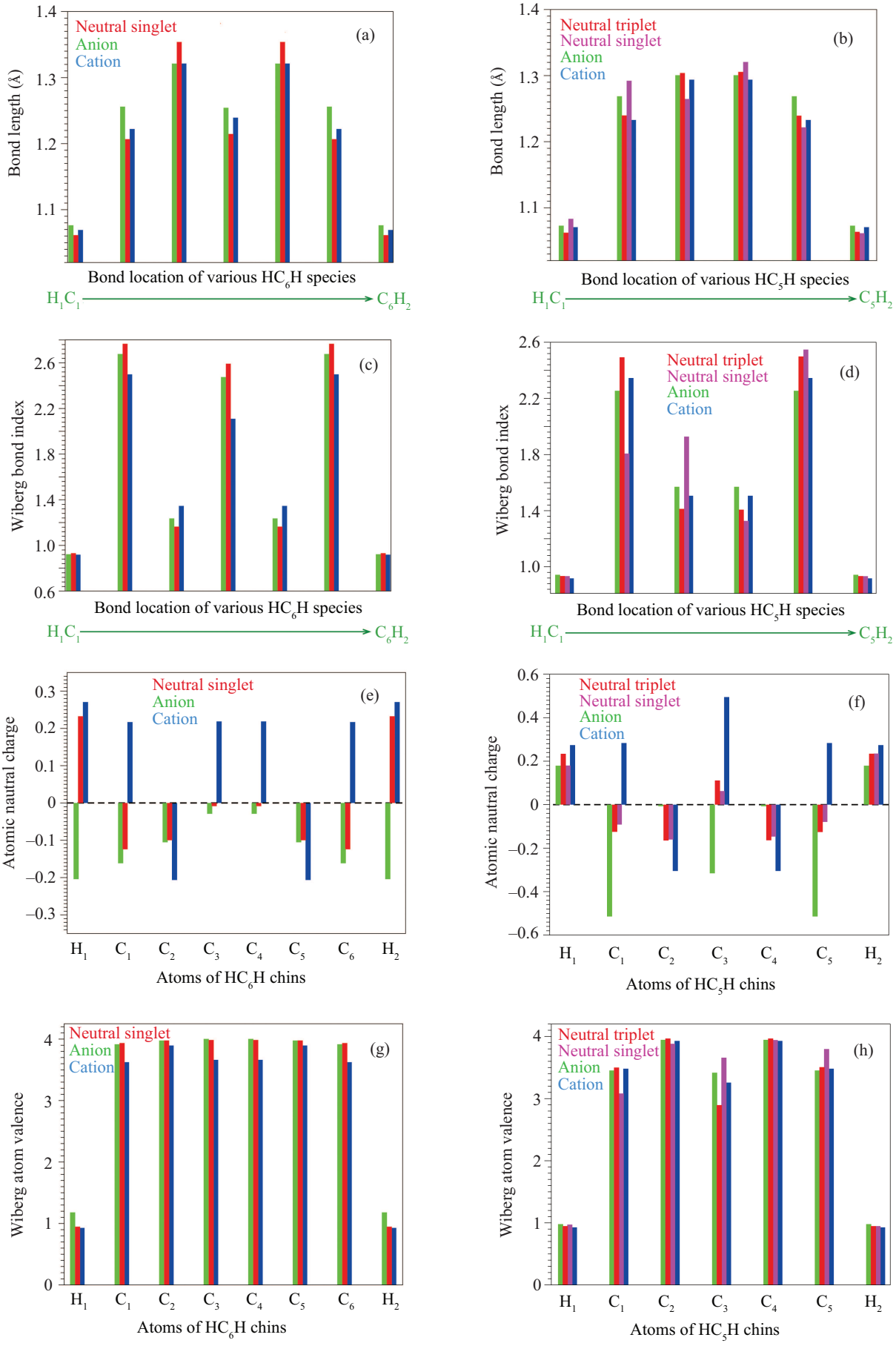


Fig. 3. (a)–(b) Bond lengths, (c)–(d) Wiberg bond order indices, (e)–(f) natural atomic charges, and (g)–(h) Wiberg valencies of neutral and charged HC_6H and HC_5H chains investigated in the present paper. Because differences between cis and trans anion isomers would be indistinguishable within the drawing accuracy, only properties of the cis isomers are depicted here.

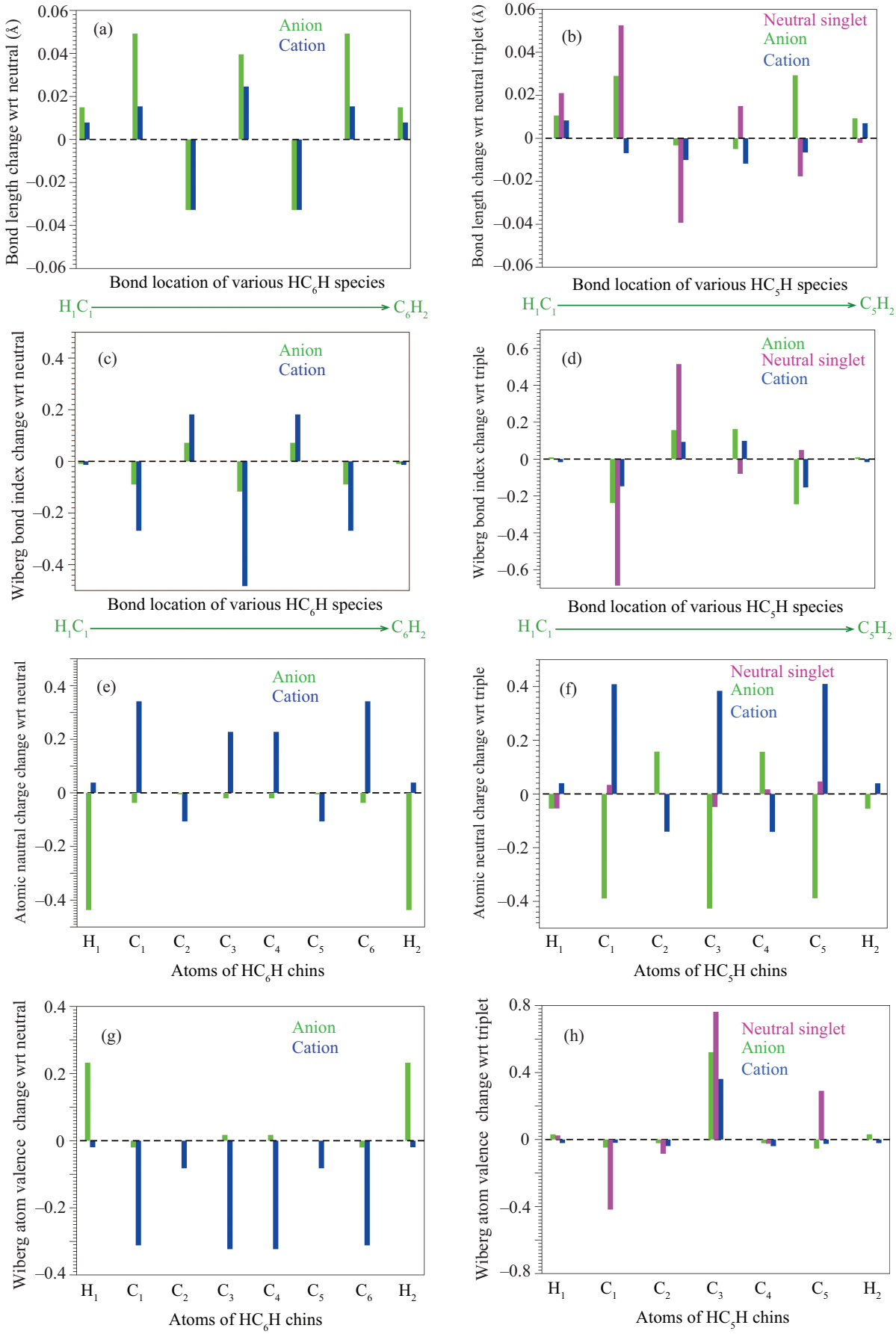


Fig. 4. Changes relative to the most stable neutral isomer (singlet HC_6H^0 and triplet HC_5H^0) of the properties depicted in Fig. 3: (a)–(b) bond lengths, (c)–(d) Wiberg bond order indices, (e)–(f) natural atomic charges, and (g)–(h) Wiberg valencies of neutral and charged HC_6H and HC_5H chains investigated in the present paper. Because differences between cis and trans anion isomers would be indistinguishable within the drawing accuracy, only properties of the cis isomers are depicted here.

Table 9. Natural atomic charges, numbers of core and Rydberg electrons, and Wiberg and Mayer valencies computed via ROCCSD(T)/aug-cc-pvtz//UB3LYP/6-311++G(3df,3pd) for the HC_5H triplet.

Atom	Natural charge	Core	Rydberg	Wiberg	Mayer
H_1	0.23331	0.00000	0.00293	0.9486	1.1108
C_1	–0.12417	1.99870	0.01046	3.5024	0.8651
C_2	–0.16472	1.99879	0.02153	3.9666	1.5530
C_3	0.11118	1.99867	0.02815	2.8980	–1.7531
C_4	–0.16472	1.99879	0.02153	3.9666	1.5530
C_5	–0.12417	1.99870	0.01046	3.5024	0.8651
H_2	0.23331	0.00000	0.00293	0.9486	1.1108

Table 10. Natural atomic charges, numbers of core and Rydberg electrons, and Wiberg and Mayer valencies computed via RCCSD(T)/aug-cc-pvtz//RB3LYP/6-311++G(3df,3pd) for the HC_5H singlet.

Atom	Natural charge	Core	Rydberg	Wiberg	Mayer
H_1	0.18012	0.00000	0.00386	0.9727	0.9097
C_1	–0.09139	1.99899	0.03055	3.0827	1.2855
C_2	–0.16042	1.99892	0.02314	3.8824	2.5210
C_3	0.06271	1.99858	0.02771	3.6583	1.0890
C_4	–0.14690	1.99871	0.02283	3.9427	1.9299
C_5	–0.07936	1.99861	0.00944	3.7977	2.3121
H_2	0.23524	0.00000	0.00289	0.9482	1.0012

Table 11. Natural atomic charges, numbers of core and Rydberg electrons, and Wiberg and Mayer valencies computed via ROCCSD(T)/augcc-pvtz//UB3LYP/6-311++G(3df,3pd) for the cis HC_5H^- anion.

Atom	Natural charge	Core	Rydberg	Wiberg	Mayer
H_1	0.17941	0.00000	0.00898	0.9791	0.9378
C_1	–0.51439	1.99883	0.03490	3.4528	1.8919
C_2	–0.00713	1.99888	0.02443	3.9458	2.6770
C_3	–0.31578	1.99858	0.03811	3.4170	1.5040
C_4	–0.00713	1.99888	0.02443	3.9458	2.6770
C_5	–0.51439	1.99883	0.03490	3.4528	1.8919
H_2	0.17941	0.00000	0.00898	0.9791	0.9378

Table 12. Natural atomic charges, numbers of core and Rydberg electrons, and Wiberg and Mayer valencies computed via ROCCSD(T)/aug-cc-pvtz//UB3LYP/6-311++G(3df,3pd) for the trans HC_5H^- anion.

Atom	Natural charge	Core	Rydberg	Wiberg	Mayer
H_1	0.17996	0.00000	0.00850	0.9782	1.0234
C_1	-0.51330	1.99884	0.03299	3.4508	2.3621
C_2	-0.00700	1.99888	0.02529	3.9475	2.9195
C_3	-0.31932	1.99857	0.04100	3.4196	1.0419
C_4	-0.00700	1.99888	0.02529	3.9475	2.9195
C_5	-0.51330	1.99884	0.03299	3.4508	2.3621
H_2	0.17996	0.00000	0.00850	0.9782	1.0234

Table 13. Natural atomic charges, numbers of core and Rydberg electrons, and Wiberg and Mayer valencies computed via ROCCSD(T)/aug-cc-pvtz//UB3LYP/6-311++G(3df,3pd) for the HC_5H+ cation.

Atom	Natural charge	Core	Rydberg	Wiberg	Mayer
H_1	0.27408	0.00000	0.00231	0.9272	1.0069
C_1	0.28358	1.99868	0.00766	3.4812	0.6909
C_2	-0.30517	1.99882	0.02342	3.9285	1.7308
C_3	0.49503	1.99867	0.02187	3.2572	-1.1691
C_4	-0.30517	1.99882	0.02342	3.9285	1.7308
C_5	0.28358	1.99868	0.00766	3.4812	0.6909
H_2	0.27408	0.00000	0.00231	0.9272	1.0069

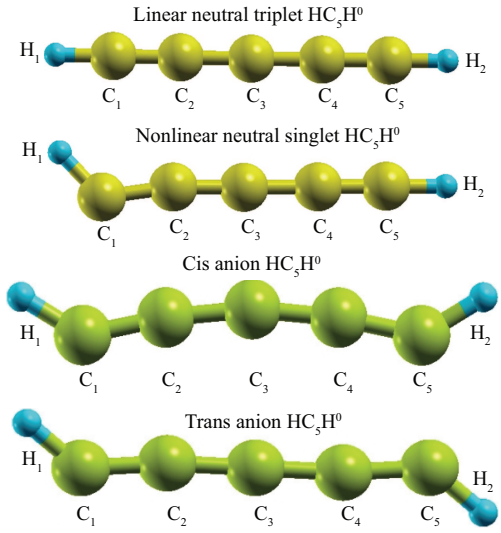


Fig. 5. Geometries of HC_5H chains investigated in the present paper. Like the HC_5H^0 neutral triplet parent, the HC_5H^+ cation is linear and therefore not shown here.

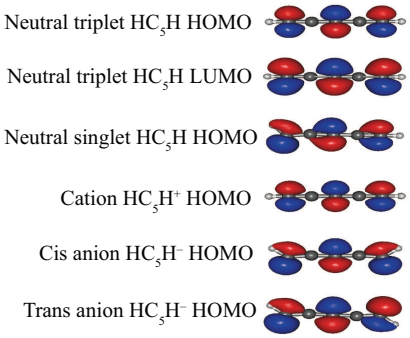


Fig. 6. MO spatial distributions of the HC_5H chains investigated in the present paper: neutral triplet, neutral singlet, cation, cis anion, trans anion.

As visible in Fig. 3(h), the most substantial deviation from the Lewis valence value is exhibited by the C_3 atom, which is nominally almost trivalent in the HC_5H^0 triplet. In fact, our NBO calculations for the triplet state found the lone pair residing on the central C_3 atom according to the idealized Lewis structure

$$\mathrm{H–C{\equiv}C–\ddot{C}–C{\equiv}C–H} \rightarrow \mathrm{H_1–C_1{\equiv}C_2–\ddot{C}_3–C_4{\equiv}C_5–H_2}. \quad (3)$$

A significant role of the configuration with unpaired electrons on the peripheric C_1 and C_5 atoms

$$\mathrm{H–\dot{C}=C=C=C=\dot{C}–H} \rightarrow \mathrm{H_1–\dot{C}_1=C_2=C_3=C_4=\dot{C}_5–H_2} \quad (4)$$

was previously claimed.[16] Our NBO analysis does not substantiate this claim. In the same vein, we also examined a potential contribution to the HC_5H triplet from asymmetric Lewis structures that can a priori come into question

$$H–C{\equiv}C–C{\equiv}\ddot{C}–H \rightarrow H_1–C_1{\equiv}C_2–C_3{\equiv}C_4–\ddot{C}_5–H_2, \tag{5a}$$

or

$$H–\ddot{C}–C{\equiv}C–C{\equiv}C–H \rightarrow H_1–\ddot{C}_1–C_2{\equiv}C_3–C_4{\equiv}C_5–H_2. \tag{5b}$$

This possibility was also ruled out by our NBO analysis.

By contrast, equations (5a) and (5b) appeared to contribute to the electronic configuration of the singlet HC_5H chain computed at the triplet optimum geometry. However, that configuration, which is an admixture of Eqs. (3) and (5), renders the linear singlet chain unstable. It eventually evolves into the nonlinear conformer ($\tilde{a}^1A'$, C_s symmetry) depicted in Fig. 5(b), which is stable against molecular vibrations (*i.e.*, vibrational frequencies are all real). The bent chain end ($\angle H_1C_1C_2 \simeq 125°$, *cf.* Table 14) appears to stabilize the antiparticle spins in the lone pair residing on the terminal C_1 atom. It is then understandable that this asymmetric lone pair significantly weakens the H_1C_1 and the C_1C_3 bonds. In the bent HC_5H singlet, the corresponding bond lengths become significantly longer than in the linear HC_5H triplet (*cf.* Fig. 4(b). The reduction with respect to the triplet of the C_1C_2 bond order is considerable; it amounts to about 0.7 (*cf.* Fig. 4(d).

As the case of longer carbon-based chains,[34,35,44,76] a terminal C–H function confers the adjacent carbon–carbon bond ($C_1{\equiv}C_2$ and $C_4{\equiv}C_5$ in the HC_5H^0 triplet) a triple bond character. In their turn, triple C≡C bonds enforce single bonds in their vicinity. This is visible in Fig. 3(c). C_2–C_3 and C_3–C_4 are basically single bonds. The values of the bond order indices of these C_2–C_3 and C_3–C_4 bonds are very similar to those of the C_2–C_3 and C_4–C_5 single bonds of the HC_6H^0 polyynic chain (Fig. 3(c)). In this way, all carbon–carbon bonds are exhausted, and there is no room for double carbon–carbon bonds in HC_5H^0. A cumulenic character can only set in sufficiently deep inside sufficiently long $HC_{2k+1}H^0$ triplet chains. The shortest $HC_{2k+1}H^0$ triplet chain exhibiting some cumulenic character onset is therefore HC_7H^0 (*cf.* Fig. 7(b)). We said "some cumulenic" because not even the longer HC_9H^0 triplet chain exhibits a true cumulenic bonding (*cf.* Fig. 7(c)).

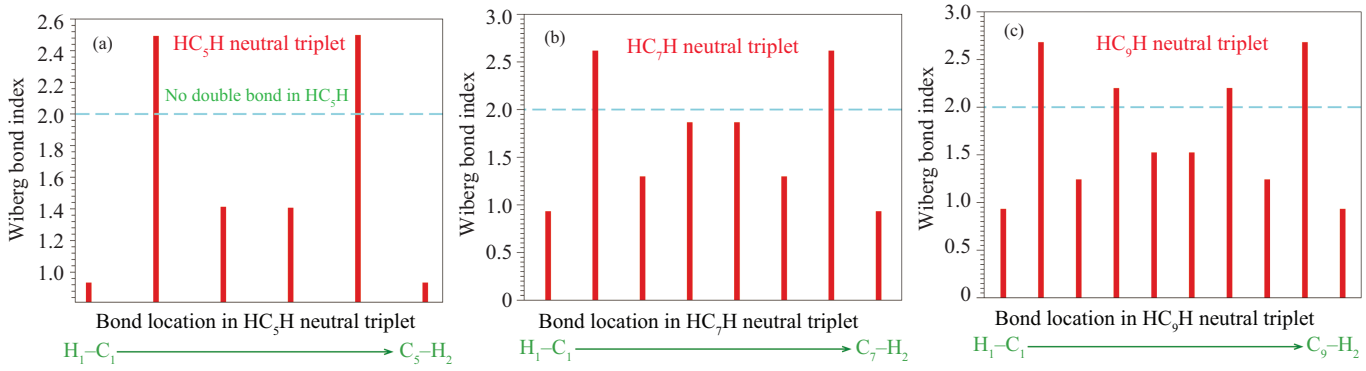


Fig. 7. Wiberg bond order indices of (a) HC_5H^0, (b) HC_7H^0, and (c) HC_9H triplet chains illustrating that the carbon backbone can acquire a cumulenic character only in sufficiently long odd-numbered members, too long to be among the candidates to be searched for is space in the next future.

As expected on the basis of Eq. (2(a)), calculations confirmed that the cation HC_5H^+ possesses a $^2\Pi_u$ ground state whose electronic configuration expressed by Eq. (2(b)). Electron removal does not have much impact on the geometry. Unlike the terminal C–H bonds, which become slightly longer, the carbon–carbon bonds are altogether slightly shorter in the HC_5H^+ cation, which preserves the linear geometry of the neutral parent (Fig. 5(c)). Still, counterintuitively, in spite of the bond length changes with respect to the neutral smaller than those of HC_6H (*cf.* Figs. 4(a) and 4(b), the changes in the bond index orders are larger than for HC_6H (*cf.* Figs. 4(c) and 4(d)). Figure 4(f) depicts that, similar to HC_6H^+, the hole created by ionization is also delocalized over the HC_5H^+ chain. Overall, changes in the atomic charges upon electron removal are larger in HC_5H than in HC_6H (*cf.* Figs. 4(e) and 4(f)). Regarding the valence of the carbon atoms, nontrivially, ionization merely impact on the valence of the central C_3 atom which effectively behaves as trivalent in the neutral HC_5H^0 triplet chain (Fig. 3(f)).

The anions of the HC_5H chain are interesting for several reasons. Prior to our recent work,[43,44] the existence of a cis HC_5H^- anion chain was also claimed.[16] In addition, we reported that a trans HC_5H^- anion chain also exists (*cf.* Fig. 5).[43,44] Like the cis isomer, the trans HC_5H^- chain is also stable both against molecular vibrations (all calculated vibrational frequencies are real) and against electron

detachment.[43,44] Similar to the case of HC_6H^-, apart from the different position of the H atoms relative to the carbon backbone, the structural and bond metric data of the HC_5H^- cis and trans isomers are very close to each other (*cf.* Table 14).

As evident from the data for the cis-trans isomerization obtained by several composite models (Table S21), the cis and trans HC_5H^- chains are, like the cis and trans HC_6H^- chains discussed above, also almost isoenergetic. So, one can also expect that they coexist.

Table 14 and figure 3(b) reveal that the differences between the lengths of adjacent bonds in the HC_5H^- chain are significantly smaller than in the HC_5H^0 triplet chain: $d(C_2C_3) - d(C_1C_2) \simeq 0.03$ Å *versus* $\simeq 0.07$ Å. Based on this similarity between adjacent anion's bond lengths markedly contrasting with the neutral triplet, reference [16] claimed that HC_5H^- exhibits cumulenic character. Nevertheless, the inspection of Fig. 3(d) along with the underlying values from Table 14 conveys a different message. The differences in the Wiberg bond order indices of the anion's adjacent carbon-carbon bonds are substantial ($\mathscr{N}(C_1C_2) \simeq 2.25$, $\mathscr{N}(C_2C_3) \simeq 1.57$, *cf.* Table 14) and do not substantiate a homogeneous cumulenic picture, contrary to what the small differences between adjacent bond lengths may suggest.

The comparison between Figs. 4(a) and 4(b) unravels an interesting difference between the HC_5H and HC_6H chains. As already noted, the carbon–carbon bonds of HC_6H elongated/compressed upon electron removal are also elongated/compressed upon electron attachment (Fig. 4(a)). This is no longer the case in HC_5H. Removing an electron from HC_5H^0 squeezes all carbon–carbon bonds. Adding an electron merely squeezes the midmost C_2C_3 and C_3C_4 bonds; the farthest C_1C_2 and C_4C_5 bonds get longer (Fig. 4(b)). And still: amazingly, electron removal and electron addition have a virtually perfect (anti)symmetric impact on the individual charges of the HC_5H chain (Fig. 4(f)). That is, if ionization yields a variation δq_l of the charge of atom X_l ($X = C, H$), electron attachment gives to a variation $-\delta q_l$ of the same atom.

The inspection of Fig. 3(f) reveals what is perhaps the most striking difference between the HC_5H^- and HC_6H^- anion chains. Confirming straightforward intuition, we found in Subsection 3.3 that the spatial distribution of the excess electron in HC_6H^- is concentrated on the two terminal H atoms (Fig. 3(e)). By contrast, figure 3(f) shows that the extra electron preferentially goes to the C_1, C_3, and C_5 atoms, a process that is furthermore accompanied by electron depletion on the C_2 and C_4 atoms.

Table 14. Results of B3LYP/6-311++G(3df,3pd) very tight geometry optimization for HC_5H chains without imposing symmetry constraints. Bond lengths l between atoms XY (in unit Å), angles α between atoms $\angle XYZ$ (in unit degrees) and Wiberg bond order indices $\mathscr{N}$.

Species	Property	H_1C_1	$\angle H_1C_1C_2$	C_1C_2	$\angle C_1C_2C_3$	C_3C_4	$\angle C_2C_3C_4$	C_4C_5	$\angle C_3C_4C_5$	C_4C_5	$\angle C_4C_5H_2$	C_5H_2
Linear triplet	l, α	1.0612	180.0	1.2362	180.0	1.3017	180.4	1.3017	180.0	1.2362	180.0	1.0612
	$\mathscr{N}$	0.9343		2.4939		1.4109		1.4109		2.4939		0.9343
Singlet@triplet	$\mathscr{N}$	0.9355		2.3281		1.5090		1.5090		2.3280		0.9355
Bent singlet	l, α	1.0833	125.2	1.2922	171.8	1.2646	179.3	1.3206	179.9	1.2217	179.4	1.0615
	$\mathscr{N}$	0.9335		1.8070		1.9279		1.3272		2.5482		0.9330
Anion cis	l, α	1.0729	138.1	1.2687	173.8	1.3006	169.4	1.3006	173.8	1.2687	138.1	1.0729
	$\mathscr{N}$	0.9433		2.2545		1.5701		1.5701		2.2545		0.9433
Anion trans	l, α	1.0747	135.3	1.2716	173.3	1.2981	180.0	1.2981	173.3	1.2716	135.3	1.0747
	$\mathscr{N}$	0.9426		2.2547		1.5711		1.5711		2.2547		0.9426
Cation	l, α	1.0706	180.0	1.2328	180.0	1.2938	180.0	1.2938	180.0	1.2328	180.0	1.0706
	$\mathscr{N}$	0.9176		2.3455		1.5062		1.5062		2.3455		0.9176

4. Conclusion

We believe that this investigation on the chemical bonding in HC_nH chains was rewarding for several reasons.

The present results reiterated and added further support to the fact that monitoring bond lengths alone does not suffice to adequately characterize chemical bonding in carbon chains. Changes in bond order indices upon electron removal or electron addition do not simply (not even monotonically) follow changes in bond lengths. This is an aspect was also emphasized recently in a a different context.[86]

Our NBO analysis does not substantiate general and undifferentiated claims often made previously in the literature that odd-numbered chains $HC_{2k+1}H$ are cumulenes. Figure 7(c) depicts that not even the HC_9H chain (that is, a chain whose length is comparable with the longest chain HC_9H ever observed astronomically[87]) possesses a genuine cumulenic character.

Overall, the present results for charge redistribution upon ionization and electron attachment clearly discredit simplistic views of ionization as electron removal from one atom (let it be an H atom or a C atom) or electron attachment as electron addition to one atom; the electron is removed from the neutral's HOMO, which is delocalized, and the electron is added to the neutral's LUMO, which is also delocalized (Figs. 2 and 6). Our results unraveled a subtle interplay between electrostatic interaction and π-delocalization in HC_nH chains that definitely deserves further consideration. As of now, monitoring the natural atomic charges in anion chains turned out to

be particularly useful:

(i) Inspection of the natural atomic charges unraveled that electron attachment to the HC_6H^0 chain has an impact on charge redistribution that qualitatively differ from that on the HC_5H^0 chain.

(ii) Based on naive intuition, one may expect that the excess electron attached to a neutral chain migrates towards the chain ends. Sometimes NAO calculations do not confirm this expectation; this happens in HC_5H (Fig. 4(f)). Sometimes NAO calculations support the intuitive expectation. C_6H_6 belong to this category. This behavior is depicted by the changes in natural atomic charges (Fig. S2(g)); it is also understandable by inspecting the benzene's LUMO shape (Fig. S1(c)). The changes in natural atomic charges calculated for HC_6H also substantiate the aforementioned intuitive expectation; see Fig. 4(c). However, the LUMO shape of HC_6H (Fig. 2) can hardly be taken as confirmation of the intuitive expectation in spite of the fact that, after all, HC_6H is a "normal" (*i.e.*, nonradical) closed shell molecule.

(iii) Noteworthily, electron removal and electron addition have a virtually perfectly symmetric impact on the individual atomic charges of the HC_5H chain: (Fig. 3(f)). This points towards an unexpected charge conjugation invariance. Invariance properties under particle-hole transformation were previously reported in other one-dimensional systems with strong electron correlations (*e.g.*, Refs. [88,89] and citations therein) but not in carbon-based chains. This is an important point to be addressed in detail in a separate publication.

With regards to anions, we still want to make the following remark. Basically, a HC_6H^- chain is a valence anion[90] created by putting an extra electron into a higher unoccupied valence ($2\pi_g$, *cf.* Eq. (1c)) orbital of a molecule whose highest shell ($2\pi_u^4$, *cf.* Eq. (1a)) is fully occupied. Such an orbital possesses an anti-bonding character, and in most cases the equilibrium geometry of the valence anions strongly departs from that of the neutral parents.[90] Therefore, although contradicting previous work[83] claiming that HC_6H^- chains preserve the linear shape of the neutral parent, our finding that stable HC_6H^- chains are nonlinear while linear HC_6H^- chains are unstable should not be too surprising. On the contrary, a HC_5H^- chain amounts to put an extra electron into a partially occupied valence orbital ($2\pi_u^2$, *cf.* Eq. (2a)). It would not be too surprising if this anion inherited the (linear) conformation of the neutral molecule. However, calculations showed that the contrary is true.

Finally, by and large the results presented in this paper unambiguously demonstrated that the appropriate framework to deal with chemical bonding in carbon chains is Wiberg's; Mayer's valence and bond order indices turned out to be totally inappropriate.

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