Chemical bonding in representative astrophysically relevant neutral, cation, and anion HC\(_{n}\)H chains

Joan Băldea\(^\dagger\)

Theoretical Chemistry, Heidelberg University, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany

(Received 27 May 2022; revised manuscript received 26 September 2022; accepted manuscript online 18 October 2022)

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 \textit{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, \textit{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

PACS: 31.10.+z, 33.15.Fm, 36.40.–c

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_\(n\)Y wherein the terminal atoms X and Y are monovalent and/or trivalent (\textit{e.g.}, HC\(_n\)H, HC\(_n\)N, and NC\(_n\)N) 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 \textit{vice versa}. Closed shell species are spin singlets, and single and triple bonds alternate in their polyynic-type carbon backbone. By contrast, open shell diradicals 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 \(\sim 0.15\) Å (\textit{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 (\(~ 1.43–1.54\) Å\([37–39]\)). These are, in turn, substantially longer than the experimental value \(d(C_2–C_3) = 1.3633\) Å in triacetylene (\textit{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\(_n\)H and HC\(_{2k}\)H as representatives of the even-numbered and odd-numbered members of the HC\(_n\)H 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)
level of theory, wherein coupled-cluster expansions include single and double excitations along with perturbations due to triple excitations.\textsuperscript{[54]} For these calculations, we used basis sets of triple-zeta quality augmented with diffuse functions (Dunning aug-cc-pVTZ).\textsuperscript{[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\textsuperscript{[58–61]} and 6-311++G(3df,3pd) Pople’s largest basis sets.\textsuperscript{[62,63]}

For reasons explained elsewhere,\textsuperscript{[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 were obtained at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G(3df,3pd) Pople’s largest basis sets.\textsuperscript{[64,65]}

W1BD,\textsuperscript{[66]} and using complete basis set methods (CBS-QB3 and CBS-APNO)\textsuperscript{[67–69]} — because they are more reliable than the computationally inexpensive Δ-DFT\textsuperscript{[49,70]} values. For natural atomic orbital (NAO) and natural bond analysis (NBA),\textsuperscript{[45]} we used the package NBO 6.0.\textsuperscript{[71]} on top of GAUSSIAN 16 runs.

Figures 1 and 5 were generated with XCRSYDEN,\textsuperscript{[72]} and figures 2 and 6 with GABEDIT.\textsuperscript{[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,\textsuperscript{[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, \textit{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\textsuperscript{[40–42]} and others;\textsuperscript{[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 \textit{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 HCN 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 HCN and HCN 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 (\textit{cf.} Table 4 in Ref. [78]).

3.2. Wiberg indices \textit{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.\textsuperscript{[79]}

In our recent studies,\textsuperscript{[34,35,40–44]} we demonstrated the utility of Wiberg’s bond order indices\textsuperscript{[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\textsuperscript{[80]} introduced in conjunction with the Huckel theory or Mulliken’s,\textsuperscript{[81]} which do not properly describe the bond strength and formal bond multiplicity (“chemist’s bond order”, \textit{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).\textsuperscript{[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.\textsuperscript{[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 CND0.

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 \( \mathcal{N} \) computed for acetylene \( \text{H–C≡C–H} \). Atomic valencies \( \psi \) (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 \( \mathcal{N} \) - and \( \psi \)-values (extremely closed to three and four, respectively) are in excellent agreement with the Lewis representation. The very small deviation \( \approx 0.06 \) from the ideal Lewis value \( \psi^* = 4 \) is due to the weak polar character of the \( \text{H–C} \) bond tracing back to the different electronegativity of the \( \text{H} \) and \( \text{C} \) atoms (see numerical values below) also reflected in the natural atomic charges \( q_\text{H} \approx +0.22, q_\text{C} = -q_\text{H} \approx -0.22 \).

It is especially the independence of the basis sets of the Wiberg values exceeding 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 \( \text{C}_2\text{N}^- \) anion. 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 \( \text{HC}_6^+ \) molecule (Table 2), for the pentadiynylidene \( \text{HC}_5\text{H} \) diradical (Table 3) as well as the Mayer valencies included in other tables presented below convey the same message.

### Table 2. Wiberg and Mayer bond order indices \( \mathcal{N} \) computed at the RCCSD(T)/BS//RB3LYP/6-311++G(3df,3pd) level of theory for the \( \text{HC}_2\text{H}^0 \) neutral singlet chain (\( \text{H}_1\text{C}_1\text{C}_2\text{C}_3\text{C}_1\text{C}_3 \equiv \text{C}_2\text{H}_3 \)). The basis sets (BS) employed are indicated below.

| Type of bond index | Basis set   | \( \mathcal{N} \) (\( \text{C}_1\text{C}_2 \)) | \( \psi \) (\( \text{C}_1 \)) = \( \psi \) (\( \text{C}_2 \)) |
|-------------------|-------------|---------------------------------|-----------------------------------|
| Wiberg            | cc-pVTZ     | 0.9323                          | 2.7715                            |
| Wiberg            | aug-cc-pVTZ | 0.9319                          | 2.7675                            |
| Mayer             | cc-pVTZ     | 0.9855                          | 2.3864                            |
| Mayer             | aug-cc-pVTZ | 0.9522                          | -0.3728                           |

### Table 3. Wiberg and Mayer bond order indices \( \mathcal{N} \) computed at the RCCSD(T)/BS//UB3LYP/6-311++G(3df,3pd) level of theory for the \( \text{HC}_2\text{H}^0 \) neutral triplet chain (\( \text{H}_1\text{C}_1\text{C}_2\text{C}_3\text{C}_4\text{C}_5 \)). The basis sets (BS) employed are indicated below.

| Type of bond index | Basis set   | \( \mathcal{N} \) (\( \text{C}_1\text{C}_2 \)) | \( \mathcal{N} \) (\( \text{C}_3\text{C}_4 \)) | \( \mathcal{N} \) (\( \text{C}_5\text{C}_6 \)) | \( \mathcal{N} \) (\( \text{C}_7\text{C}_8 \)) |
|-------------------|-------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Wiberg            | cc-pVTZ     | 0.9345                          | 2.4965                          | 1.4109                          | 2.4939                          |
| Wiberg            | aug-cc-pVTZ | 0.9343                          | 2.4939                          | 1.4109                          | 2.4939                          |
| Mayer             | cc-pVTZ     | 1.0133                          | 2.1123                          | 1.4543                          | 2.1123                          |
| Mayer             | aug-cc-pVTZ | 1.5979                          | 0.2629                          | 1.9935                          | 0.2629                          |

### 3.3. Chemical bonding in \( \text{HC}_n\text{H} \) chains

More to the main point, let us first consider the \( \text{HC}_n\text{H} \) 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:

\[
\text{HC}_6\text{H}^0|_{D_{\text{sh}}} : \quad ^1\Sigma_+^+ = \ldots 6\sigma_1^27\sigma_2^23\pi_1^24\pi_3^4, \tag{1a}
\]

\[
\text{HC}_6\text{H}^+|_{D_{\text{sh}}} : \quad ^2\Pi_u = \ldots 6\sigma_1^27\sigma_2^23\pi_1^24\pi_3^3, \tag{1b}
\]

123101-3
The neutral $\text{HC}_6\text{H}^0$ molecule is a typical closed-shell linear polyene (cf. Fig. 1) whose paired valence electrons in the completely filled highest occupied molecular orbital (HOMO) $2\pi_s^\dagger$ (cf. Eq. (1a)) determines a singlet ground state. As depicted in Fig. 2, the calculated HOMO spatial density of the neutral linear $\text{HC}_6\text{H}^0$ chain is concentrated between atoms, or more precisely, on every second carbon–carbon bond starting from the molecular ends. This makes the $\text{HC}_6\text{H}^0$ a quantum chemistry textbook example wherein carbon–carbon bonds alternate between almost perfectly tetravalent carbon atoms.

Mathematically, this is expressed by the numerical values of the atomic valences collected in Table 5 and Table S3.

![Fig. 1. Geometries of HC₆H chains investigated in the present paper. Like the HC₆H₀ neutral parent, the HC₆H⁺ cation is linear and therefore not shown here.](image)

In accord with the different electronegativity $\chi$ ($\chi_\text{H}^{\text{Pauling:Allen}} = 2.20;\ 2.300 < \chi_\text{C}^{\text{Pauling:Allen}} = 2.55;\ 2.544$), the hydrogen atoms are assigned a positive charge ($q_{\text{H}} = +0.23$). This value is roughly twice the negative charges of the nearest and next nearest carbon neighbors ($q_{\text{C}_1} = q_{\text{C}_6} \approx q_{\text{C}_2} = q_{\text{C}_5} \approx -0.1$), which are much larger than those of the inner, almost neutral carbon atoms ($q_{\text{C}_1} = q_{\text{C}_6} \approx -0.01$). This is visualized in Fig. 3(e). For comparison purposes, where appropriate, we will also refer to the case of the neutral benzene molecule C₆H₆. To make the paper self-contained, we computed and present all relevant data for C₆H₆ in supporting information. In benzene all carbon and hydrogen atoms (Wiberg valencies 3.9769 and 0.9666, respectively) have the same charge: $q_{\text{C}} = -0.19$, $q_{\text{H}} = +0.19$ (cf. Tables S20 and S2).

![Table 4. Results of B3LYP/6-311++G(3df,3pd) very tight geometry optimization for HC₆H chains without imposing symmetry constraints. Bond lengths $l$ between atoms XY (in unit Å), angles $\alpha$ between atoms $\angle$XYZ (in unit degrees) and Wiberg bond order indices $\alpha$.](table)

Albeit $\text{HC}_6\text{H}^+$ preserves both the linear $D_{\text{sh}}$ conformation of the neutral parent (Fig. 1) and the $2\pi_s$ 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 C₁≡C₆ 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 C₆H₆⁺ (Table S19 and Fig. S2(e)). In accord with intuitive expectation regarding the Coulomb repulsion minimization, our calculations found that the C₁ and C₆ 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 C₃ and C₄ atoms correlates with...
the increase in the C≡C bond length. Likewise, the shortening of the C2–C3 (or C4–C5) bond is compatible with the Coulomb attraction due to the extra charges of opposite sign on the C3 and C4 atoms (or C3 and C4 atoms). Nevertheless, our calculations reveal that variation of the bond lengths is not merely an electrostatic effect. The triple bonds C1≡C2 and C3≡C6 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 HC6H; 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 C2 and C3 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 HC6H+ singlet neutral chain.

| Atom | Natural charge | Core Rydberg | Wiberg | Mayer |
|------|----------------|--------------|--------|-------|
| H1   | 0.23347        | 0.00000      | 0.00269| 0.9487| 0.8490|
| C1   | -0.11511       | 1.99852      | 0.0784 | 3.9359| 1.0953|
| C2   | -0.10769       | 1.99860      | 0.02228| 3.9777| -0.1837|
| C3   | -0.01067       | 1.99837      | 0.02266| 3.9855| 3.6110|
| C4   | -0.00167       | 1.99837      | 0.02266| 3.9855| 3.6110|
| C5   | -0.10769       | 1.99860      | 0.02228| 3.9777| -0.1837|
| C6   | -0.11511       | 1.99852      | 0.0784 | 3.9359| 1.0952|
| H2   | 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 HC6H+ cation.

| Atom | Natural charge | Core Rydberg | Wiberg | Mayer |
|------|----------------|--------------|--------|-------|
| H1   | 0.27071        | 0.00000      | 0.00232| 0.9291| 0.7702|
| C1   | 0.27071        | 1.99863      | 0.00690| 3.6241| 1.0100|
| C2   | -0.20647       | 1.99876      | 0.02359| 3.8956| 0.0574|
| C3   | 0.21875        | 1.99859      | 0.02112| 3.6623| 3.1369|
| C4   | 0.21875        | 1.99859      | 0.02112| 3.6623| 3.1369|
| C5   | -0.20647       | 1.99876      | 0.02359| 3.8956| 0.0574|
| C6   | 0.21701        | 1.99863      | 0.00690| 3.6241| 1.0100|
| H2   | 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 HC6H. 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 C6H6. Notwithstanding the equivalent carbon–carbon bonds of the neutral molecule, ionization only shortens two opposite carbon–carbon bonds (C2C3 and C5C6 in Fig. S2(b)). Their bond order indices in C6H6+ are larger than in C6H6 (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 C6H6+ ends with nonequivalent carbon–carbon bonds in C6H6+. 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 HC6H+ cation.

| Atom | Natural charge | Core Rydberg | Wiberg | Mayer |
|------|----------------|--------------|--------|-------|
| H1   | -0.20424       | 0.00000      | 0.44961| 1.1812| -1.6284|
| C1   | -0.16160       | 1.99864      | 0.03167| 3.9158| 1.4547|
| C2   | -0.10529       | 1.99883      | 0.03230| 3.9765| -1.2703|
| C3   | -0.02888       | 1.99856      | 0.03819| 4.0027| -0.8041|
| C4   | -0.02888       | 1.99856      | 0.03819| 4.0027| -0.8041|
| C5   | -0.10529       | 1.99883      | 0.03230| 3.9765| -1.2703|
| C6   | -0.16160       | 1.99864      | 0.03167| 3.9158| 1.4547|
| H2   | -0.20424       | 0.00000      | 0.44961| 1.1812| -1.6284|

Switching to the HC6H− chain, we should first reiterate[43,44] that, contrary to what previously claimed[83] the anion is not linear. Calculations[43,44] yielded two non-linear 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-isenergetic 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 HC6H− cis isomer possesses a permanent dipole moment (cf. Table S21). This makes it a potential candidate for astronomical observation via rovibrational spectroscopy.[43] The HC6H− trans isomer does not have a permanent dipole (µ = 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...
HC₆H⁻ 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 these 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 C₂–C₃ and C₄–C₅ bonds are squeezed by virtually the same amount. Albeit more pronounced than for cation, the C–H and triple C₁≡C₂, C₃≡C₄, and C₅≡C₆ bonds of the anion are longer than in the neutral. Counternaturally, 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 C₂–C₃ and C₄–C₅ 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 C₁≡C₂, C₃≡C₄, and C₅≡C₆ 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 HC₆H⁻ 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 HC₆H⁻ chain and the HC₆H⁺ 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), C₆H₆⁻ 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 HC₆H⁺ the Coulomb repulsion is over-compensated by stabilization due to π-electron delocalization, a fact impossible in the C₆H₆⁻ anion whose shorter diameter makes repulsion too strong.

3.4. Chemical bonding in HC₆H chains

Let us now examine the HC₆H chains, whose Cartesian coordinates at energy minimum are presented in Tables S8–S12. The relevant ground state electronic configurations read as follows:

\[
\begin{align*}
\text{HC₆H}^0|_{D_{∞h}} & : 3\Sigma_g^+ = \cdots 6\sigma^2_x 5\sigma^2_y 4\pi^1 3\pi^1 2\pi^1, \\
\text{HC₆H}^+|_{D_{∞h}} & : 2\Pi_u = \cdots 6\sigma^2_x 5\sigma^2_y 4\pi^1 3\pi^1 2\pi^1, \\
\text{unstable HC₆H}^-|_{D_{∞h}} & : 3\Pi_u = \cdots 6\sigma^2_x 5\sigma^2_y 4\pi^1 3\pi^1 2\pi^1 \rightarrow \\
\text{cis HC₆H}^-|c_{2a} & : 2B_1 = \cdots 5\pi^2 2\sigma^1 6\pi^2 1\sigma^2 2\pi^2 2\sigma^2 2\pi^2 7\pi^2, \\
\text{trans HC₆H}^-|c_{2b} & : 2A_u = \cdots 6\pi^2 5\sigma^2 6\pi^2 1\sigma^2 2\pi^2 2\pi^2 7\pi^2 2\pi^2 2\pi^2.
\end{align*}
\]

In accord with earlier reports, the present quantum chemical study confirmed the D₂h symmetry of the HC₆H⁰. Our calculations comprise very tight geometry optimization with the widely employed B3LYP,[59–61] PBE0,[184] and M06-2X[85] functionals (cf. Tables S1 and S2). The triplet character of the ground state \(X^3\Sigma_g^-\) obtained from calculations confirms the physical intuition. According to Hund’s rule, the two electrons in the half-filled HOMO (2π^1, 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 HC₆H⁰ even member chain. “On atoms” and not “on bonds”; this is the reason why, in general, odd members HC₂k+₁H are less stable than even members HC₂kH.[444]

The comparison between the various panels of Fig. 3 reveals that the differences between the properties of the radical open shell HC₆H⁰ triplet and those of the non-radical closed shell HC₆H⁰ singlet are substantial. The most salient qualitative difference is, of course, the absence of bond alternation in HC₆H, but other differences are also notable. For instance, the fact that, unlike other C atoms, the central C₃ atom in the HC₆H⁰ neutral is positively charged (Fig. 3(f)).
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$_{6}$H and HC$_{5}$H 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$_6$H$^0$ and triplet HC$_5$H$^0$) 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$_6$H and HC$_5$H 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.
A significant role of the configuration with unpaired electrons on the peripheric C1 and C5 atoms

\[
\text{H}^+ + \text{C} = \text{C} = \text{C} = \text{C} = \text{H} \rightarrow \text{H}_{1} - \text{C}_{1} = \text{C}_{2} = \text{C}_{3} = \text{C}_{4} = \text{C}_{5} - \text{H}_{2}.
\]  

(3)

As visible in Fig. 3(h), the most substantial deviation from the Lewis valence value is exhibited by the C5 atom, which is nominally almost trivalent in the HC5H⁻ triplet. In fact, our NBO calculations for the triplet state found the lone pair residing on the central C3 atom according to the idealized Lewis structure

\[
\text{H} = \text{C} = \text{C} = \text{C} = \text{C} = \text{H} \rightarrow \text{H}_{1} - \text{C}_{1} = \text{C}_{2} = \text{C}_{3} = \text{C}_{4} = \text{C}_{5} - \text{H}_{2}.
\]  

(4)

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 HC₅H₃⁺ cation.

| Atom | Natural charge | Core | Rydberg | Wiberg | Mayer |
|------|---------------|------|---------|--------|-------|
| H₁   | 0.23331       | 0.00000 | 0.00293 | 0.9486 | 1.1108 |
| C₁   | -0.12417      | 1.99870 | 0.01046 | 3.5024 | 0.8651 |
| C₂   | -0.16472      | 1.99879 | 0.02153 | 3.9666 | 1.5530 |
| C₃   | 0.11118       | 1.99867 | 0.02815 | 2.8980 | -1.7531 |
| C₄   | -0.16472      | 1.99879 | 0.02153 | 3.9666 | 1.5530 |
| C₅   | -0.12417      | 1.99870 | 0.01046 | 3.5024 | 0.8651 |
| H₂   | 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 ROCCSD(T)/aug-cc-pvtz//RB3LYP/6-311++G(3df,3pd) for the HC₅H₃⁻ cis anion.

| Atom | Natural charge | Core | Rydberg | Wiberg | Mayer |
|------|---------------|------|---------|--------|-------|
| H₁   | 0.18012       | 0.00000 | 0.00386 | 0.9727 | 0.9097 |
| C₁   | -0.09139      | 1.99899 | 0.03055 | 3.0827 | 1.2855 |
| C₂   | -0.16042      | 1.99892 | 0.02314 | 3.8824 | 2.5210 |
| C₃   | 0.06271       | 1.99858 | 0.02771 | 3.6583 | 1.0890 |
| C₄   | -0.14690      | 1.99871 | 0.02263 | 3.9427 | 1.9299 |
| C₅   | -0.07936      | 1.99861 | 0.00944 | 3.7977 | 2.3121 |
| H₂   | 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)/aug-cc-pvtz//UB3LYP/6-311++G(3df,3pd) for the HC₅H⁻ trans anion.

| Atom | Natural charge | Core | Rydberg | Wiberg | Mayer |
|------|---------------|------|---------|--------|-------|
| H₁   | 0.17941       | 0.00000 | 0.00898 | 0.9791 | 0.9378 |
| C₁   | -0.51439      | 1.99883 | 0.03490 | 3.4528 | 1.8919 |
| C₂   | -0.00713      | 1.99888 | 0.02443 | 3.9458 | 2.6770 |
| C₃   | -0.31578      | 1.99858 | 0.03811 | 3.4170 | 1.5040 |
| C₄   | -0.00713      | 1.99888 | 0.02443 | 3.9458 | 2.6770 |
| C₅   | -0.51439      | 1.99883 | 0.03490 | 3.4528 | 1.8919 |
| H₂   | 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 HC₅H⁺ neutral triplet.

| Atom | Natural charge | Core | Rydberg | Wiberg | Mayer |
|------|---------------|------|---------|--------|-------|
| H₁   | 0.17996       | 0.00000 | 0.00850 | 0.9782 | 1.0234 |
| C₁   | -0.51330      | 1.99884 | 0.03299 | 3.4508 | 2.3621 |
| C₂   | -0.00700      | 1.99888 | 0.02529 | 3.9475 | 2.9195 |
| C₃   | -0.31932      | 1.99857 | 0.04100 | 3.4196 | 1.0419 |
| C₄   | -0.00700      | 1.99888 | 0.02529 | 3.9475 | 2.9195 |
| C₅   | -0.51330      | 1.99884 | 0.03299 | 3.4508 | 2.3621 |
| H₂   | 0.17996       | 0.00000 | 0.00850 | 0.9782 | 1.0234 |

Fig. 5. Geometries of HC₅H chains investigated in the present paper. Like the HC₅H⁺ neutral triplet parent, the HC₅H⁻ cation is linear and therefore not shown here.

Neutral triplet HC₅H HOMO

Neutral triplet HC₅H LUMO

Neutral cation HC₅H⁺

Cis anion HC₅H⁻

Neutral singlet HC₅H HOMO

Cation HC₅H⁺ HOMO

Trans anion HC₅H⁻

Fig. 6. MO spatial distributions of the HC₅H chains investigated in the present paper: neutral triplet, neutral singlet, cation, cis anion, trans anion.
was previously claimed. Our NBO analysis does not substantiate this claim. In the same vein, we also examined a potential contribution to the HC$_5$H triplet from asymmetric Lewis structures that can a priori come into question

\[
\text{H–C≡C–C≡C} \rightarrow \text{H}_1–\text{C}_1–\text{C}_2–\text{C}_3–\text{C}_4–\text{C}_5–\text{H}_2, \tag{5a}
\]

or

\[
\text{H–C}≡\text{C}–\text{C}≡\text{C}–\text{C}≡\text{C}–\text{C}_5–\text{H}_2. \tag{5b}
\]

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$_5$H 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 (a$^1A'$, C$_2$ 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$_1$C$_1$C$_2$ z 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$_2$C$_1$ and the C$_1$C$_3$ bonds. In the bent HC$_5$H singlet, the corresponding bond lengths become significantly longer than in the linear HC$_5$H triplet (cf. Fig. 4(b)). The reduction with respect to the triplet of the C$_1$C$_3$ bond order is considerable; it amounts to about 0.7 (cf. Fig. 4(d)).

As the case of longer carbon-based chains, a terminal C–H function confers the adjacent carbon–carbon bond (C$_1$≡C$_2$ and C$_4$≡C$_5$ in the HC$_5$H$^0$ 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$_5$H$^0$ polyenic 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$_5$H$^0$. 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$_7$H$^0$ (cf. Fig. 7(b)). We said “some cumulenic” because not even the longer HC$_{2l}$H$^0$ triplet chain exhibits a true cumulenic bonding (cf. Fig. 7(c)).

As expected on the basis of Eq. (2(a)), calculations confirmed that the cation HC$_3$H$^+$ possesses a $^4\Pi_u$ 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$_3$H$^+$ 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$_3$H (cf. Figs. 4(a) and 4(b), the changes in the bond index orders are larger than for HC$_5$H (cf. Figs. 4(c) and 4(d)). Figure 4(f) depicts that, similar to HC$_4$H$^+$, the hole created by ionization is also delocalized over the HC$_5$H$^+$ chain.

Overall, changes in the atomic charges upon electron removal are larger in HC$_5$H than in HC$_6$H (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$_5$H$^0$ triplet chain (Fig. 3(f)).

The anions of the HC$_4$H chain are interesting for several reasons. Prior to our recent work, the existence of a cis HC$_3$H$^-$ anion chain was also claimed. In addition, we reported that a trans HC$_3$H$^-$ anion chain also exists (cf. Fig. 5). Like the cis isomer, the trans HC$_3$H$^-$ chain is also stable both against molecular vibrations (all calculated vibrational frequencies are real) and against electron.
Similar to the case of HC5H−, apart from the different position of the H atoms relative to the carbon backbone, the structural and bond metric data of the HC5H− 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 HC5H− chains are, like the cis and trans HC6H− chains discussed above, also almost isoelectronic. 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 HC5H− chain are significantly smaller than in the HC5H0 triplet chain: 

\[
d(C_{2}C_{3}) - d(C_{1}C_{2}) \approx 0.03 \text{ Å versus} \approx 0.07 \text{ Å.}
\]

Based on this similarity between adjacent anion’s bond lengths markedly contrasting with the neutral triplet, reference [16] claimed that HC5H− 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 (\(\mathcal{N}(C_{1}C_{2}) \approx 2.25\), \(\mathcal{N}(C_{2}C_{3}) \approx 1.57\), 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 HC5H and HC6H chains. As already noted, the carbon–carbon bonds of HC6H elongated/compressed upon electron removal are also elongated/compressed upon electron attachment (Fig. 4(a)). This is no longer the case in HC5H. Removing an electron from HC5H0 squeezes all carbon–carbon bonds. Adding an electron merely squeezes the midstid C2C3 and C3C4 bonds; the farthest C1C2 and C4C5 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 HC5H chain (Fig. 4(f)). That is, if ionization yields a variation \(\delta q_l\) 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 HC5H− and HC6H− anion chains. Confirming straightforward intuition, we found in Subsection 3.3 that the spatial distribution of the excess electron in HC5H− 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 C1, C3, and C5 atoms, a process that is furthermore accompanied by electron depletion on the C2 and C4 atoms.

**Table 14.** Results of B3LYP/6-311++G(3df,3pd) very tight geometry optimization for HC5H chains without imposing symmetry constraints. Bond lengths \(l\) between atoms \(XY\) (in unit Å), angles \(\alpha\) between atoms \(XZY\) (in unit degrees) and Wiberg bond order indices \(\mathcal{N}\).

| Species          | Property | \(l\)  | \(\alpha\) | \(\angle H_{1}C_{1}C_{2}\) | \(\angle C_{1}C_{2}C_{3}\) | \(\angle C_{2}C_{3}C_{4}\) | \(\angle C_{3}C_{4}C_{5}\) | \(\angle C_{4}C_{5}C_{6}\) | \(\angle C_{5}C_{6}H_{2}\) | \(\angle C_{6}H_{2}\) |
|------------------|----------|-------|--------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| Linear triplet   | \(l\)    | 1.0612| 180.0  | 1.2362                   | 1.3017                   | 1.3017                   | 1.3017                   | 1.3262                   | 180.0                    | 1.0612                   |
| \(\mathcal{N}\)  | \(\mathcal{N}\) | 0.9343| 2.4939 | 1.4109                   | 1.4109                   | 2.4939                   | 1.4109                   | 2.4939                   | 0.9343                   |
| Singlet@triplet  | \(l\)    | 1.0833| 125.2  | 1.2922                   | 1.2646                   | 1.3206                   | 1.3206                   | 1.2217                   | 179.4                    | 1.0615                   |
| \(\mathcal{N}\)  | \(\mathcal{N}\) | 0.9335| 2.3281 | 1.5090                   | 1.5090                   | 2.3280                   | 1.5090                   | 2.3280                   | 0.9355                   |
| Bent singlet     | \(l\)    | 1.0872| 125.2  | 1.2922                   | 1.2646                   | 1.3206                   | 1.3206                   | 1.2217                   | 179.4                    | 1.0615                   |
| \(\mathcal{N}\)  | \(\mathcal{N}\) | 0.9335| 1.9600 | 1.4395                   | 1.4395                   | 1.4395                   | 1.4395                   | 1.4395                   | 0.9290                   |
| Anion cis        | \(l\)    | 1.0729| 138.1  | 1.2687                   | 1.3006                   | 1.3006                   | 1.3006                   | 1.2687                   | 138.1                    | 1.0729                   |
| \(\mathcal{N}\)  | \(\mathcal{N}\) | 0.9433| 2.2545 | 1.5701                   | 1.5701                   | 1.5701                   | 1.5701                   | 1.5701                   | 0.9433                   |
| Anion trans      | \(l\)    | 1.0747| 135.3  | 1.2716                   | 1.2981                   | 1.2981                   | 1.2981                   | 1.2716                   | 135.3                    | 1.0747                   |
| \(\mathcal{N}\)  | \(\mathcal{N}\) | 0.9426| 2.2547 | 1.5711                   | 1.5711                   | 1.5711                   | 1.5711                   | 1.5711                   | 0.9426                   |
| Cation           | \(l\)    | 1.0706| 180.0  | 1.2328                   | 1.2938                   | 1.2938                   | 1.2938                   | 1.2328                   | 180.0                    | 1.0706                   |
| \(\mathcal{N}\)  | \(\mathcal{N}\) | 0.9176| 2.3455 | 1.5062                   | 1.5062                   | 1.5062                   | 1.5062                   | 1.5062                   | 0.9176                   |

**4. Conclusion**

We believe that this investigation on the chemical bonding in HC5H 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 different context.\(^{[60]}\)

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 HC5H chain (that is, a chain whose length is comparable with the longest chain HC\(_{5}\)H 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\(_{5}\)H chains that definitely deserves further consideration. As of now, monitoring the natural atomic charges in anion chains turned out to

123101-11
be particularly useful:

(i) Inspection of the natural atomic charges unraveled that electron attachment to the HC$_6$H$_4^-$ chain has an impact on charge redistribution that qualitatively differ from that on the HC$_6$H$_6^-$ chain.

(ii) Based on naive intuition, one may expect that the excess electron attached to a neutral chain migrates towards the HC chain ends. Sometimes NAO calculations do not confirm this expectation; this happens in HC$_6$H$_2$ (Fig. 4(f)). Sometimes NAO calculations support the intuitive expectation. C$_6$H$_6$ belongs 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$_6$H also substantiate the aforementioned intuitive expectation; see Fig. 4(c). However, the LUMO shape of HC$_6$H (Fig. 2) can hardly be taken as confirmation of the intuitive expectation in spite of the fact that, after all, HC$_6$H is a “normal” (i.e., non-radical) closed shell molecule.

(iii) Noteworthy, electron removal and electron addition have a virtually perfectly symmetric impact on the individual atomic charges of the HC$_6$H 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$_6$H$^-$ chain is a valence anion$^{[90]}$ created by putting an extra electron into a higher unoccupied valence ($2\pi_u$, cf. Eq. (1c)) orbital of a molecule whose highest shell ($2\pi^d_u$, 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 parent.$^{[90]}$ Therefore, although contradicting previous work$^{[83]}$ claiming that HC$_6$H$^-$ chains preserve the linear shape of the neutral parent, our finding that stable HC$_6$H$^-$ chains are nonlinear while linear HC$_6$H$^-$ chains are unstable should not be too surprising. On the contrary, a HC$_6$H$^-$ chain amounts to put an extra electron into a partially occupied valence orbital ($2\pi^d_u$, 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.

Acknowledgment

The author thanks Jochen Schirmer for valuable discussions. The author gratefully acknowledges financial support from the German Research Foundation (DFG Grant No. BA 1799/3-2) in the initial stage of this work and computational support by the state of Baden–Württemberg through bwHPC and the German Research Foundation through Grant No. INST 40/575-1 FUGG (bwUniCluster 2.0, bwForCluster/MLS&WISO 2.0/HELIX, and JUSTUS 2.0 cluster).

References

[1] McGuire B A 2018 The Astrophysical Journal Supplement Series 239 17
[2] Thaddeus P, Vrtilek J M and Gottlieb C A 1985 Astrophys. J. Lett. 299 L63
[3] Fan Q and Pfeiffer G V 1989 Chem. Phys. Lett. 162 472
[4] Maier G, Reisenauer H P, Schwab W, Carsky P, Sprko V, Hess B A and Schaad L J 1989 J. Chem. Phys. 91 4763
[5] Cornicharo J, Gottlieb C A, Guelin M, Killian T C, Paulbert G, Thaddeus P and Vrtilek J M 1991 Astrophys. J. Lett. 368 L39
[6] Cornicharo J, Gottlieb C A, Guelin M, Killian T C, Thaddeus P and Vrtilek J M 1991 Astrophys. J. Lett. 368 L43
[7] Gottlieb C A, Killian T C, Thaddeus P, Botschwina P, Glüge J and Oswald M 1993 J. Chem. Phys. 98 4478
[8] Haas S, Wnimewisser G, Yamada K, Matsumura K and Kagawuchi K 1994 Journal of Molecular Spectroscopy 167 176
[9] Natterer J, Koch W, Schröder D, Goldberg N and Schwarz H 1994 Chem. Phys. Lett. 229 429
[10] Fulara J, Freivogel P, Forney D and Maier J P 1995 J. Chem. Phys. 103 8805
[11] McCarthy M C, Gottlieb C A, Thaddeus P, Horn M and Botschwina P 1995 J. Chem. Phys. 103 7820
[12] Seburg R A, DePinto J T, Patterson E V and McMahon R J 1995 J. Am. Chem. Soc. 117 835
[13] Botschwina P 1996 Chem. Phys. Lett. 259 627
[14] Seburg R A, Patterson E V, Stanion J F and McMahon R J 1997 J. Am. Chem. Soc. 119 5847
[15] Seburg R A, McMahon R J, Stanion J F and Gaus S 1997 J. Am. Chem. Soc. 119 10838
[16] Blanksby S J, Dua S, Bowle J H, Schröder D and Schwarz H 1998 J. Phys. Chem. A 102 9949
[17] Stanton J F and Byun K 1999 J. Mol. Phys. 96 505
[18] Dua S, Blanksby S J and Bowle J H 2000 J. Phys. Chem. A 104 77
[19] Ball C D, McCarthy M C and Thaddeus P 2000 J. Chem. Phys. 112 10149
[20] Pino T, Ding H, Gutiêre F and Maier J P 2001 J. Chem. Phys. 114 2208
[21] Horný L, Petraco N D K, Pak C and Schaefer H F 2002 J. Am. Chem. Soc. 124 5861
[22] Horný L, Petraco N D K and Schaefer H F 2002 J. Am. Chem. Soc. 124 14716
[23] Ding H, Schmidt T W, Pino T, Boguslavskiy A E, Gutiêre F and Maier J P 2003 J. Chem. Phys. 119 814
[24] Achkasova E, Araki M, Denisov A and Maier J P 2006 J. Phys. Chem. A 110 447
[25] Botschwina P, Oswald R and Knizia G E A 2009 J. Phys. Chem. A 113 12447
[26] Vázquez J, Harding M E, Gauss S and Stanion J F 2009 J. Phys. Chem. A 113 10147
[27] Kaiser R I, Sun B J, Lin H M, Chang A H H, Mebel A M, Kostko O and Ahmad M 2010 Astrophys. J. 719 1584
[28] Steinbauer M, Lang M, Fischer L, de Miranda B K C, Romanzin C and Alcaraz C 2011 Phys. Chem. Chem. Phys. 13 17956
[29] Neiss C, Trushin E and Görling A 2013 Phys. Chem. Chem. Phys. 15 2497
[30] Osborn D L, Vogelhuber K M, Wren S W, Miller E M, Lu Y J, Case A S, Sheps L, McMahon R J, Stanion J F, Harding L B, Ruscic B and Lineberger W C 2014 J. Am. Chem. Soc. 136 10361
[31] Stegelich M, Fulara J, Maity S, Nagy A and Maier J P 2015 J. Chem. Phys. 142 244511
