Alternation of Singlet and Triplet States in Carbon-Based Chain Molecules and Its Astrochemical Implications: Results of an Extensive Theoretical Study

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A variety of homologous carbon chains (HC\textsubscript{n}H, HC\textsubscript{n}N, C\textsubscript{n}S, C\textsubscript{n}O, and OC\textsubscript{n}O) are found to exhibit an appealing even–odd effect. Chains containing a number of carbon atoms of a certain parity possess singlet ground states, while members of opposite parity have triplet ground states. From a general perspective, it is important that this even–odd effect confounds straightforward chemical intuition. Whether the most stable form is a triplet or a singlet is neither simply related to the fact that the species in question is a “normal” (closed-shell, nonradical) molecule nor a (di)radical or to the (e.g., cumulene-type) C–C bond succession across the chain. From a computational perspective, the present results are important also because they demonstrate that electron correlations in carbon-based chains are extremely strong. Whether the “gold-standard” CCSD(T) (coupled-cluster expansions with single and double excitations and triple excitations corrections) framework suffices to describe such strongly correlated systems remains an open question that calls for further clarification. Most importantly for astrochemistry, the present results may explain why certain members are not astronomically observed although larger members of the same homologous series are detected; the missing species are exactly those for which the present calculations predict triplet ground states.

1. Introduction

Linear carbon chains represent a field of great current interest for fields ranging from (bio-)molecular electronics to astrochemistry. Until the advent of nanoelectronics,[1–3] such molecules were often of little interest for (terrestrial) laboratory studies and practical applications. Cyclic or combined ring-chain structures are usually more stable energetically than linear isomers.[4] This explains the scarcity of available information on carbon-based chains. For the vast majority of the molecular species to be considered in the present paper, the NIST database contains no entries. A number of molecules comprising carbon chains were observed in the past decades in cold interstellar and circumstellar clouds.[6–21] The identification of the type of ground state (which is the most stable isomer?) of the various molecular species of interest represents the most basic information, also needed to correctly understand a certain extraterrestrial environment and to simulate its astrochemical evolution. In the present paper, we addressed this issue by examining in detail representative homologous series of carbon-based linear chains (HC\textsubscript{n}H, HC\textsubscript{n}N, C\textsubscript{n}S, C\textsubscript{n}O, and OC\textsubscript{n}O). We found that, by successively adding atoms to the molecular backbone of all these astrochemically relevant families of carbon-based chains with an even number of electrons, the most stable form systematically switches back and forth between singlet and triplet isomers. Rephrasing, we will show below that the most stable state of members of a certain parity (even or odd) of a chain family is a singlet (ground) state, while members of opposite parity (odd or even, respectively) have a triplet ground state. One should note at this point that the present finding that triplet states of carbon-based chains can be surprisingly lower in energy and lie below singlet states contradicts some recent studies done in the astronomical/astrophysical community.[22,23] Those studies explicitly[24] or implicitly[22] claimed (see Section 3.8 and the Supporting Information) that all carbon chains of the type considered in the present paper possess a singlet ground state.

Noteworthily, the even–odd singlet–triplet alternation[25] extensively discussed in this paper is qualitatively different from all other even–odd effects (e.g., in multilayers,[26] self-assembled monolayers,[27] quantum dot arrays,[28–31] molecular electronic devices[2,3]) known since the early days of quantum mechanics.[32–35] In those cases, it is merely a certain property rather than the very nature of the ground state that exhibits alternation.
2. Experimental Section

All quantum chemical calculations done in conjunction with the present study were performed by running the GAUSSIAN 16 suite of programs[36] on the bwHPC platform.[37] Optimized geometries ($R_{T}$) of all singlet (S) and triplet (T) carbon-based chains considered in this paper were obtained from DFT calculations using the B3LYP hybrid exchange functional and, unless otherwise stated (cf. Tables S1–S4, Supporting Information) the largest Pople 6-311++g(3df, 3pd) basis sets. In all cases, we checked that all frequencies were real.

For the largest molecular species of each homologous series, we also performed state-of-the-art calculations based on coupled-cluster (CC) expansions with single and double excitations (CCSD) supplemented by perturbative treatment of triple excitations (CCSD(T)).[38] For triplet states, we employed the unrestricted and unrestricted open shell formalism for DFT calculations and CC-calculations, respectively. More technical details are presented in Section S1, Supporting Information.

Enthalpies of formations $\Delta_f H^0$ (Tables 1, 3, 5, 7, and 9) were computed using the standard methodology.[40] For comparison purposes (cf. Section 3.8), along with the values obtained within a DFT/B3LYP/6-311++g(3df, 3pd) approach, we also estimated enthalpies of formation using the CBS-QB3 protocol as implemented in GAUSSIAN 16, which are shown in Tables S1–S4, Supporting Information.

A thermochemical analysis may not be sufficient for molecules of interest for astrochemistry, where single-particle (kinetic) effects also deserve consideration. Therefore, in addition to enthalpies of formations for both the lowest singlet and triplet electronic ground states, we also report values estimates for the singlet–triplet separation energies $\Delta \equiv \mathcal{E}_T - \mathcal{E}_S$. They were obtained as differences of the corresponding total molecular energies $\mathcal{E}_{S, T}(R)$ at the pertaining molecular energies ($R = R_{S, T}$). For all the families of carbon chains considered (Tables 2, 4, 6, 8, and 10), we present values of both adiabatic and vertical singlet–triplet separation energies. The adiabatic value

$$\Delta_{\text{adiab}} \equiv \mathcal{E}_T(R_{\text{S}}) - \mathcal{E}_S(R_{\text{S}})$$  \hspace{1cm} (1)

| Molec. | Method | $\Delta_{\text{adiab}}$ | $\Delta_S$ | $\Delta_T$ |
|--------|--------|------------------------|------------|------------|
| HC$_5$H | B3LYP | 4.269 | 5.739 | 2.285 |
| HC$_6$H | B3LYP | 4.176 | 5.645 | 2.191 |
| HC$_7$H | B3LYP | -0.571 | -0.044 | -1.097 |
| HC$_8$H | B3LYP | -0.653 | -0.125 | -1.179 |
| HC$_9$H | B3LYP | 3.410 | 4.532 | 1.836 |
| HC$_10$H | B3LYP | 3.290 | 4.411 | 1.735 |
| HC$_11$H | B3LYP | -0.740 | -0.376 | -0.861 |
| HC$_12$H | B3LYP | -0.729 | -0.366 | -0.850 |
| HC$_13$H | B3LYP | 2.930 | 3.579 | 1.809 |
| HC$_14$H | B3LYP | 2.778 | 3.427 | 1.657 |

Table 1. Adiabatic ($\Delta_{\text{adiab}}$) and vertical ($\Delta_{S, T}$) values of the singlet-triplet energy separation (in eV) for HC$_n$H chains obtained within the methods indicated in the second column.

The two vertical values shown here correspond to the optimized singlet ($\Delta_S$) and triplet ($\Delta_T$) geometries. Notice that the sign of $\Delta$ indicates that the most stable isomers are singlets for even members ($\Delta > 0$, HC$_{2n}$H) and triplets for odd members ($\Delta < 0$, HC$_{2n+1}$H). Corrections due to zero-point motion (label corr) were deduced within the DFT/B3LYP approach; see the last paragraph of Section 2. The almost equal values $\Delta_S \approx \Delta_T$ for larger odd-members (HC$_{2n+1}$H, $n = 7, 9, 13$) indicate that the singlet and triplet geometries are similar ($R_S \approx R_T$, cf. Equation (2)).

represents the difference between the triplet (T) and singlet (S) energies computed at the molecular geometries $R = R_{S, T}$ optimized for the singlet ($R_S$) and the triplet ($R_T$) isomers. The two distinct vertical values $\Delta_{S, T}$

$$\Delta_S \equiv \mathcal{E}_T(R_S) - \mathcal{E}_S(R_S)$$  \hspace{1cm} (2a)

$$\Delta_T \equiv \mathcal{E}_T(R_T) - \mathcal{E}_S(R_T)$$  \hspace{1cm} (2b)

represent differences between the triplet (T) and singlet (S) energies taken at the same molecular geometry (either singlet $R_S$ or triplet $R_T$).
According to Equation (2), positive $\Delta$-values imply that singlet isomers are more stable than triplet isomers; negative $\Delta$-values correspond to triplets more stable than singlets. The inspection of the various $\Delta$s presented in the next sections reveals that cases exist—for example, the even-member HC$_{2k}$H chains (cf. Table 2) and the odd-member HC$_{2k+1}$N chains (cf. Table 4), whose most stable isomers are singlets with polyyne structure—for which the values of $\Delta_S$ and $\Delta_T$ significantly differ from each other. By virtue of Equation (2), for such molecular species, the corresponding singlet and triplet isomers are characterized by significantly different geometries. In many other cases—like the longer odd-members HC$_{2k+1}$H chains whose most stable isomers are triplets possessing a cumulenic structure (cf. Table 2)—the values of $\Delta_S$ and $\Delta_T$ are almost equal.

Given the fact discussed in detail below that, depending on the parity of the number of atoms, singlet or triplet isomers are more stable, it makes sense to also consider vertical singlet–triplet splitting energies $\Delta_{m,i}$ at the geometry of the most stable (acronym $m.s.$) isomer, which are defined as

$$\Delta_{m,i} = \begin{cases} \Delta_S \equiv E_S(R_0) - E_T(R_0) > 0 & \text{if } E_S(R_0) < E_T(R_0) \\ \Delta_T \equiv E_T(R_0) - E_S(R_0) < 0 & \text{if } E_T(R_0) < E_S(R_0) \end{cases}$$

(singlet more stable that triplet)

(triplet more stable that singlet)

Values of $\Delta_{m,i}$ for the various families of chains considered are depicted in Figures 2c, 4c, 6c, 8c, and 10c.

In addition to DFT/B3LYP estimates of the singlet–triplet separations $\Delta$, we also report $\Delta$-values deduced by performing ab initio CCSD and state-of-the-art CCSD(T) calculations. To facilitate comparison with results of other elaborate ab initio electronic structure approaches that could (or should, cf. Section 3.9) be applied in subsequent studies, the CCSD and CCSD(T) $\Delta$-values reported here (cf. Tables 2, 4, 6, 8, and 10) do not include corrections due to zero-point motion. One should mention in this context that zero-point energy corrections within ab initio approaches like CCSD and CCSD(T) are very challenging; they require costly numerical frequency calculations. Currently, feasible studies of this kind are restricted to closed-shell (i.e., singlet but not triplet) species and smaller molecular sizes.\(^{[41]}\) As a trade-off between accuracy and computationally demanding ab initio frequency calculations, zero-point energy corrections can be applied within the DFT/B3LYP approach. Such estimates are indicated by label corr in Tables 2, 4, 6, 8, and 10. So, values labeled “B3LYP (corr)” in those tables refer to results of DFT/B3LYP calculations including corrections due to zero-point motion while values labeled “B3LYP” were obtained from DFT/B3LYP calculations without zero-point energy corrections. The rather minor differences between these two corrected and uncorrected values visible in Tables 2, 4, 6, 8, and 10 suggest that, in spite of the enormous computational effort, the benefit of CCSD(T) numerical frequency calculations, even if implemented, would be questionable.

3. Results and Discussion

In the sections that follow, we will extensively analyze the most representative families of carbon-based chains found in interstellar molecular clouds. For each family, we investigated molecular sizes exceeding the longest chain astronomically observed; the latter is indicated in the corresponding table caption. Depending on their chemical composition, the chains considered are either “normal” (i.e., closed-shell, nonradical) or diradical\(^{[42]}\) molecules characterized by polyyne- or cumulene-type structures.

3.1. HC$_n$H Homologous Series

The members with an even number ($n = 2k$) of carbon atoms of this family, HC$_{2k}$H ($k = 1, 2, \ldots$), which we first consider, are polyynes wherein single C--C and triple C=C--C carbon bonds alternate across the chain backbone H--C=C--\ldots C=C--H. This alternation is illustrated by the results shown in Figure 1a, which depicts the Wiberg bond order indices calculated for the singlet HC$_{12}$H chain. All valence electrons form pairs between adjacent atoms, and this typically renders the singlet state of the chain to be the most stable form.

Table 1, which collects our results for the enthalpies of formation $\Delta_f H^0 = \Delta_f H^0(T)$ at zero $\Delta_f H^0$ and room temperature $\Delta_f H^0(T) (T = 0 \text{ K and } T = 298.15 \text{ K})$, respectively, and the related Figure 2a confirm this picture. As visible there, for the even members HC$_{2k}$H, the values $\Delta_f H^0(T)$ for singlet (S) isomers are smaller than the values $\Delta_f H^0(T)$ for triplet (T) isomers.

The alternation between single and triple bonds is incompatible with the standard rules of valence for the odd members species HC$_{2k+1}$H. Forms that could come into question here are either of polyyne- (acetylenic)-type (e.g., H--C=C--\ldots C=C--H) or of cumulene type (e.g., H--C=C--\ldots C=C--H). As illustrated by a specific example, namely the HC$_{13}$H chain depicted in Figure 1b, calculations confirm the cumulene structure. By inspecting the enthalpies of formation (Table 1 and Figure 2a), one can see that the triplet state rather than the singlet state is the most stable form of the odd members of this family.

Above, we described the stability of the two subclasses (HC$_{2k+1}$H and HC$_{2k}$H) in a picture based on thermochemistry, which may not be the most adequate for systems of interest for astrochemistry, where single-molecule kinetic effects may prevail. Therefore, as a counterpart of this thermochemical analysis, in Table 2 and Figure 2b,c, we also report results for the singlet–triplet separation energies $\Delta$ computed as differences between the corresponding total electronic energies of a molecule (cf. Section 2). The negative values ($\Delta < 0$) for odd members indicate that the triplet state rather than the singlet state is preferentially energetically for the odd members of this family, while the opposite ($\Delta > 0$) holds for even members, for which the singlet isomers are the most stable.

3.2. HC$_n$N Homologous Series

Let us next consider the related HC$_n$N family.
Out of the various carbon-based homologous series, this is probably the most numerous family investigated in different contexts in the past.\cite{9,11,12,18,43–45} In this case, it is the odd-member (n = 2k + 1) subclass HC_{2k+1}N (k = 1, 2, \ldots) H\text{\longrightarrow}C\equiv\ldots\equiv\text{C\equivN} wherein the standard valence rules allow a singlet–triplet alternation of the carbon–carbon bonds along the chain. This is illustrated by the case of the HC_{9}N chain in Figure 3a. Calculations confirm that the electronic ground state of this HC_{2k+1}N cyanopolyne structure is of “normal” type, that is, a singlet state. Indeed, the corresponding enthalpies of formation for singlet are lower than for triplet (\Delta_f H_0^0|_S < \Delta_f H_0^0|_T), and the values of the singlet–triplet energy separation are positive (\Delta > 0); see Tables 3 and 4, and Figure 4.

Calculations for even members HC_{2k}N show that, out of the two possible forms—namely, of polyyne type, for example, 

H\text{\longrightarrow}C\equiv\ldots\equiv\text{C\equivC\equivN} or of cumulene type, for example,
not surprising; it can be expected based on chemical intuition. Cumulene-like series possess two electrons that cannot be involved in covalent bonds. Linear carbon chains terminated with a sulfur atom, C_{n}S (S=O· · ·=O), which we next consider and were also reported in astronomical observations (e.g., refs. [13, 47]), belong to this category.

As exemplified with the aid of the cases of the C_{6}S and C_{3}S chains depicted in Figure 5, calculations confirm the cumulene-type structure both for even and odd members. This result is not surprising; it can be expected based on chemical intuition. However, what is nontrivial is the fact that the state corresponding to the lowest electronic energy is found to be a singlet state for odd members C_{2k+1}S, while for even members C_{2k}S the lowest state is a triplet. Indeed, the results of our calculations presented in Table 5 and Figure 6a show that the lower enthalpies of formation correspond to singlet isomers for odd members (ΔS > 0, H_{C_{2k+1}S}) and to triplet isomers for even members C_{2k}S. Alternatively rephrased, the negative values of the singlet–triplet energy splitting Δ indicate that the singlet state is the most stable for even members (C_{2k}S), in contrast to the odd members (C_{2k+1}S) for which the most stable is a singlet, as expressed by the positive Δ-values (cf. Table 6 and Figure 6b,c).

### Table 3. Enthalpies of formation of linear H_{C_{2k}}N chains at zero and room temperature (subscript 0 and RT, respectively).

| Molec.   | Δ_{0} H_{0}^0 | Δ_{0} H_{0}^0_{th} | Δ_{RT} H_{RT}^0 | Δ_{RT} H_{RT}^0_{th} |
|----------|---------------|--------------------|-----------------|-----------------------|
| HCN      | 30.479        | 30.369             | 135.813         | 135.906               |
| HC_{2}N  | 122.292       | 122.567            | 106.606         | 107.014               |
| HC_{3}N  | 88.613        | 88.933             | 174.805         | 175.320               |
| HC_{4}N  | 164.202       | 165.109            | 146.902         | 147.704               |
| HC_{5}N  | 141.802       | 142.735            | 205.424         | 206.859               |
| HC_{6}N  | 209.099       | 210.827            | 191.840         | 193.150               |
| HC_{7}N  | 193.670       | 195.288            | 246.645         | 248.688               |
| HC_{8}N  | 254.993       | 257.248            | 238.960         | 241.102               |
| HC_{9}N  | 245.201       | 247.476            | 290.266         | 292.834               |
| HC_{10}N | 301.872       | 304.711            | 287.203         | 289.986               |
| HC_{11}N | 296.620       | 299.539            | 336.070         | 339.228               |
| HC_{12}N| 349.399       | 353.385            | 336.219         | 339.636               |

HC_{2k}N and HC_{2k+1}N are presented in Tables 3 and 4, and Figure 4a. They demonstrate an "anomalous" behavior; the triplet state is more stable than the singlet state. The enthalpies of formation (Table 3 and Figure 4a) for triplet are lower than for singlet, the singlet–triplet separation energies (Table 4 and Figure 4b,c) are negative.

To sum up, the electronic ground state for even members H_{C_{2k}}N is a triplet state, which is in contrast with the singlet electronic ground state of the odd members H_{C_{2k+1}}N.

### Table 4. Adiabatic (Δ_{ad,ab}) and vertical (Δ_{ST}) values of the singlet–triplet energy separation (in eV) for H_{C_{2k}}N chains obtained within the methods indicated in the second column.

| Molec.   | Method | Δ_{ad,ab} | Δ_{S} | Δ_{T} |
|----------|--------|-----------|-------|-------|
| HCN      | B3LYP  | 4.670     | 7.438 | 3.141 |
| HCN      | B3LYP (corr) | 4.568 | 7.336 | 3.019 |
| HC_{2}N  | B3LYP  | -0.658    | -0.223 | -1.116 |
| HC_{2}N  | B3LYP (corr) | -0.680 | -0.245 | -1.138 |
| HC_{3}N  | B3LYP  | 3.845     | 4.961 | 2.318 |
| HC_{3}N  | B3LYP (corr) | 3.738 | 4.854 | 2.210 |
| HC_{4}N  | B3LYP  | -0.731    | -0.326 | -0.925 |
| HC_{4}N  | B3LYP (corr) | -0.750 | -0.345 | -0.944 |
| HC_{5}N  | B3LYP  | 2.898     | 3.456 | 2.120 |
| HC_{6}N  | B3LYP (corr) | 2.759 | 3.137 | 1.981 |
| HC_{6}N  | B3LYP | -0.753    | -0.601 | -0.766 |
| HC_{6}N  | B3LYP (corr) | -0.748 | -0.597 | -0.762 |
| HC_{7}N  | B3LYP  | 2.407     | 2.865 | 1.960 |
| HC_{7}N  | B3LYP (corr) | 2.297 | 2.755 | 1.849 |
| HC_{8}N  | B3LYP  | -0.670    | -0.669 | -0.670 |
| HC_{8}N  | B3LYP (corr) | -0.695 | -0.695 | -0.696 |
| HC_{9}N  | B3LYP  | -0.837    | -0.812 | -0.833 |
| HC_{9}N  | B3LYP (corr) | -0.774 | -0.766 | -0.768 |
| HC_{10}N | B3LYP  | 2.058     | 2.703 | 1.640 |
| HC_{10}N | B3LYP (corr) | 1.954 | 2.599 | 1.536 |
| HC_{11}N | B3LYP  | 3.194     | 3.514 | 2.433 |
| HC_{11}N | B3LYP (corr) | 2.999 | 3.430 | 2.494 |
| HC_{12}N | B3LYP  | -0.607    | -0.606 | -0.607 |
| HC_{12}N | B3LYP (corr) | -0.636 | -0.636 | -0.637 |
| HC_{13}N | B3LYP  | -0.807    | -0.787 | -0.789 |
| HC_{13}N | B3LYP (corr) | -0.728 | -0.722 | -0.723 |
| HC_{14}N | B3LYP  | 1.815     | 2.413 | 1.411 |
| HC_{14}N | B3LYP (corr) | 1.711 | 2.309 | 1.307 |
| HC_{15}N | B3LYP  | 2.551     | 2.839 | 1.721 |
| HC_{15}N | B3LYP (corr) | 2.350 | 2.742 | 1.813 |
| HC_{16}N | B3LYP  | -0.563    | -0.562 | -0.563 |
| HC_{16}N | B3LYP (corr) | -0.595 | -0.594 | -0.595 |

The two vertical values shown here correspond to the optimized singlet (ΔS) and triplet (ΔT) geometries. Notice that the sign of Δ indicates that the most stable isomers are singlets for odd members (Δ > 0, H_{C_{2k+1}N}) and triplets for even members (Δ < 0, H_{C_{2k}N}). Corrections due to zero-point motion (label corr) were deduced within the DFT/B3LYP approach; see the last paragraph of Section 2. The almost equal optical values Δs ≈ ΔT for larger even members (H_{C_{2n}}, n = 8, 10, 12) indicate that the singlet and triplet geometries are similar (R_{s} ≈ R_{T}, cf. Equation (2)).
Figure 4. Results for HC\(_n\)N chains. a) Enthalpies of formation for singlet and triplet chain isomers. b) Adiabatic singlet–triplet separation energy \(\Delta_{\text{adiab}}\). c) Vertical singlet–triplet separation at the geometry of the most stable state \(\Delta_{m1}\). Lines are guide to the eye. The numerical values underlying this figure are presented in Tables 3 and 4.

Figure 5. Wiberg bond order indices for C\(_n\)S chains: a) triplet C\(_6\)S and b) singlet C\(_7\)S. The coordinates of these molecules at the corresponding energy minima as well as the HOMO spatial distributions are presented in Tables S14 and S15 and Figures S5 and S6, Supporting Information, respectively.

Table 5. Enthalpies of formation of linear C\(_n\)S chains at zero and room temperature (subscript 0 and RT, respectively).

| Molec. | \(\Delta_f H^0_0\) | \(\Delta_f H^0_{0\text{RT}}\) | \(\Delta_f H^0_{T}\) | \(\Delta_f H^0_{T\text{RT}}\) |
|--------|------------------|------------------|------------------|------------------|
| CS     | 70.934           | 69.634           | 146.830          | 147.617          |
| C\(_2\)S | 162.418          | 163.565          | 145.630          | 146.834          |
| C\(_3\)S | 135.505          | 136.805          | 190.378          | 191.944          |
| C\(_4\)S | 196.846          | 198.489          | 182.693          | 184.308          |
| C\(_5\)S\(^a\) | 191.231          | 193.097          | 232.108          | 234.229          |
| C\(_6\)S | 243.319          | 245.553          | 232.214          | 234.417          |

\(^a\)Longest chain of this family astronomically observed.\(^{47,48}\) Notice that for the odd members C\(_{2k+1}\)S the values for singlet (label S) are smaller than those for triplet (label T), while for the even members C\(_{2k}\)S the values for triplet are smaller than those for singlet.

3.4. C\(_3\)O Homologous Series

Let us next consider linear carbon chains terminated with an oxygen atom (C\(_3\)O). Similar to C\(_n\)S, C\(_3\)O chains also possess two electrons that cannot be involved in covalent bonds. Such chains were also reported in astronomical observations.\(^{113}\)

Calculations confirm again the cumulene-type structure of the ground state O\(=\text{C}==\ldots\text{C}^*\) irrespective whether the number of carbon atoms is even or odd. Figure 7 illustrates this fact for the specific case of C\(_3\)O and C\(_4\)O chains. Inspection reveals only slight differences between this figure and Figure 5, which refers to the isoelectronic C\(_3\)S and C\(_4\)S chains. The slightly broader range of the bond order index variation in Figure 7 as compared to Figure 5 can be attributed to the oxygen electronegativity (\(\chi_{\text{Pauling}}^{\text{O}} = 3.44, \chi_{\text{Allen}}^{\text{O}} = 3.610\)), which is larger than the sulfur electronegativity (\(\chi_{\text{Pauling}}^{\text{S}} = 2.58, \chi_{\text{Allen}}^{\text{S}} = 2.589\)).

Calculations also confirm the alternation of the singlet and triplet states of the C\(_n\)O chains with increasing number of carbon atoms found for the isoelectronic C\(_n\)S chains reported in Section 3.3. The values of the enthalpies of formations (Table 7 and Figure 8a) and the singlet–triplet separations (Table 8 and Figure 8b,c) demonstrate that, for even members (C\(_{2k}\)O), the triplet state is more stable than the singlet state while the opposite holds true for the odd members (C\(_{2k+1}\)O).

3.5. OC\(_n\)O Homologous Series

Out of the chains investigated in Sections 3.1 and 3.2, all diradical species HC\(_{2k+1}\)H and HC\(_{2k}\)N turned out to possess triplet ground states. The results of Sections 3.3 and 3.4 indicated that the diradical character of a carbon chain does not automatically imply that the most stable state is a triplet. Although all C\(_n\)S and C\(_n\)O chains are diradical species, only the C\(_{2k}\)S and C\(_{2k}\)O chains considered have triplet ground states; the C\(_{2k+1}\)S and C\(_{2k+1}\)O chains possess singlet ground states.

Conversely, because the most stable isomers of the “normal” (nonradical) chains HC\(_n\)H and HC\(_{2k+1}\)N examined in Sections 3.1 and 3.2 were found to be a singlet state, one may next
ask whether all nonradical carbon-based chains possess singlet ground states. In order to inquire this possibility, we will next consider carbon chains having oxygen atoms attached at the both ends (OC\textsubscript{2k+1}O).

Irrespective of whether the number of carbon atoms is even or odd, the cumulene-type structure O═C○⋅⋅⋅○C═O characterized by successive double bonds along the chain ensures that all valence electrons are involved in chemical (double) bonds. Results of calculations confirming this behavior are depicted in Figure 9.

Still, in spite of the fact that both even and odd members of this family are “normal” molecules with a similar (cumulene-type) structure, their most stable form is not necessarily a singlet state. As seen in Table 9 and Figure 10a, only odd members (OC\textsubscript{2k+1}O) have enthalpies of formation for singlet lower than for triplet. However, for even members (OC\textsubscript{2k}O), triplet isomers possess enthalpies of formation lower than for singlets. The fact that the most stable form is a singlet state for odd members but a triplet for even members can alternatively be seen by inspecting the single–triplet energy separations \( \Delta \) (cf. Table 10, and Figure 10b and c), which are positive for OC\textsubscript{2k+1}O but negative for OC\textsubscript{2k}O.

To conclude this subsection, carbon-based chains can have a triplet ground state notwithstanding the fact that the corresponding species have always “normal” (nonradical) character. Parenthetically, one can still note that, in carbon chains, a triplet state yields an overall enforcement of the cumulenic character even in species (e.g., HC\textsubscript{12}H, Figure S11, Supporting Information) where the most stable isomer is of singlet polynye type compatible with the standard rules of valence.

### 3.6. Infrared and UV–Visible Absorption of Carbon Chains in Singlet and Triplet States

One of the main aims of this paper is to emphasize that the lowest electronic state of carbon-based chains of interest for astrochemistry systematically switches back and forth between singlet and triplet as the carbon chain length increases. A detailed analysis of the differences between properties of the lowest singlet and triplet states for each carbon-based chain of astrochemical interest is certainly important, for example, for adequately processing data acquired (or to be acquired) in astronomical observations. This analysis is out of the scope of the present paper and will be deferred to a forthcoming publication.

Certainly, the nature of the ground state (i.e., singlet vs triplet) can have a pronounced impact on various observable molecular properties. While important differences between properties of singlet and triplet states of various molecular species would not be surprising in general, the specific example presented below reveals that the impact can be significant even in situations less expected.

For illustration, let us consider HC\textsubscript{11}H chains. By inspection, the HOMO spatial distributions of HC\textsubscript{11}H chains...
Figure 7. Wiberg bond order indices for C_nO chains: a) triplet C_6O and b) singlet C_7O. The coordinates of these molecules at the corresponding energy minima as well as the HOMO spatial distributions are presented in Tables S18 and S19 and Figures S7 and S8, Supporting Information, respectively.

Table 7. Enthalpies of formation of linear C_nO chains at zero and room temperature (subscript 0 and RT, respectively).

| Molec. | \( \Delta_f H_0^0 \) | \( \Delta_f H_0^{\text{RT}} \) | \( \Delta_f H_T^0 \) | \( \Delta_f H_T^{\text{RT}} \) |
|--------|----------------|----------------|----------------|----------------|
| CO     | −24.140        | 110.602        | 111.387        | 111.387        |
| C_2O   | 110.227        | 111.332        | 85.497         | 86.550         |
| C_3O \( a) \) | 76.170  | 143.236        | 133.039        | 134.532        |
| C_4O   | 149.118        | 133.039        | 134.532        | 134.532        |
| C_5O   | 135.765        | 186.814        | 188.994        | 188.994        |
| C_6O   | 193.343        | 182.161        | 183.327        | 183.327        |
| C_7O   | 190.940        | 228.914        | 231.450        | 231.450        |

\( a) \) Longest chain of this family astronomically observed\[13\] Notice that for the odd members C_{2k+1}O the values for singlet (label S) are smaller than those for triplet (label T), while for the even members C_{2k}O the values for triplet are smaller than those for singlet.

(cf. Figure S1, Supporting Information) one can conclude that the differences between the singlet and triplet states are rather minor. Nevertheless, the infrared spectra presented in Figure 11 (calculated within the harmonic approximation) reveal significant differences between the singlet and triplet HC_11H isomers.

Less surprisingly, calculations showed that the spin multiplicity has little impact on the high frequency strong peak depicted in Figure 11 due to the stretching mode of the C–H bonds with pronounced s-character; the corresponding frequency values \( \nu_{C–H}^S = 3462.46 \text{ cm}^{-1} \) and \( \nu_{C–H}^T = 3461.93 \text{ cm}^{-1} \) are identical.

Table 8. Adiabatic (\( \Delta_{\text{adiab}} \)) and vertical (\( \Delta_S, \Delta_T \)) values of the singlet-triplet energy separation (in eV) for C_nO chains obtained within the methods indicated in the second column.

| Molec. | Method       | \( \Delta_{\text{adiab}} \) | \( \Delta_S \) | \( \Delta_T \) |
|--------|--------------|----------------|----------------|----------------|
| CO     | B3LYP        | 5.869          | 6.148          | 5.572          |
| CO     | B3LYP (corr) | 5.843          | 6.122          | 5.545          |
| C_2O   | B3LYP        | −1.078         | −1.063         | −1.072         |
| C_2O   | B3LYP (corr) | −1.072         | −1.058         | −1.067         |
| C_3O   | B3LYP        | 2.988          | 3.104          | 2.143          |
| C_3O   | B3LYP (corr) | 3.080          | 3.124          | 2.063          |
| C_4O   | B3LYP        | −0.698         | −0.698         | −0.699         |
| C_4O   | B3LYP (corr) | −0.697         | −0.697         | −0.698         |
| C_5O   | B3LYP        | 2.314          | 2.626          | 2.221          |
| C_5O   | B3LYP (corr) | 2.214          | 2.525          | 2.121          |
| C_6O   | B3LYP        | −0.523         | −0.523         | −0.524         |
| C_6O   | B3LYP (corr) | −0.524         | −0.523         | −0.524         |
| C_7O   | CCSD         | −0.194         | −0.193         | −0.194         |
| C_7O   | CCSD (T)     | −0.217         | −0.219         | −0.220         |
| C_7O   | B3LYP        | 1.725          | 1.761          | 1.684          |
| C_7O   | B3LYP (corr) | 1.647          | 1.683          | 1.606          |
| C_7O   | CCSD         | 1.645          | 1.681          | 1.595          |
| C_7O   | CCSD (T)     | 1.956          | 2.025          | 1.962          |

The two vertical values shown here correspond to the optimized singlet (\( \Delta_S \)) and triplet (\( \Delta_T \)) geometries. Notice that the sign of \( \Delta \) indicates that the most stable isomers are singlets for odd members (\( \Delta > 0, \text{C}_{2k+1}O \)) and triplets for even members (\( \Delta < 0, \text{C}_{2k}O \)). Corrections due to zero-point motion (label corr) were deduced within the DFT/B3LYP approach; see the last paragraph of Section 2.

Figure 8. Results for C_nO chains. a) Enthalpies of formation for singlet and triplet chain isomers. b) Adiabatic singlet-triplet separation energy \( \Delta_{\text{adiab}} \). c) Vertical singlet-triplet separation at the geometry of the most stable state \( \Delta_{\text{m}} \) (namely, singlet for odd members and triplet for even members, cf. Equation (3)). Lines are guide to the eye. The numerical values underlying this figure are presented in Tables 7 and 8.
Figure 9. Wiberg bond order indices for OCₐO chains: a) triplet OC₆O and b) singlet OC₇O. The coordinates of these molecules at the corresponding energy minima as well as the HOMO spatial distributions are presented in Tables S22 and S23 and Figures S9 and S10, Supporting Information, respectively.

Table 9. Enthalpies of formation of linear OCₙO chains at zero and room temperature (subscript 0 and RT, respectively).

| Molec. | Δf H₀ | Δf H₀ | Δf H₀ | Δf H₀ |
|--------|-------|-------|-------|-------|
| OCO    | −94.430 | −94.529 | 16.393 | 16.655 |
| OC₂O   | −29.465 | −26.888 | 43.260 | 44.194 |
| OC₃O   | 44.030  | 45.323  | 31.070 | 32.001 |
| OC₄O   | 29.782  | 30.933  | 84.659 | 86.351 |
| OC₅O   | 88.330  | 90.169  | 78.024 | 79.532 |
| OC₆O   | 85.409  | 87.231  | 126.150| 128.203 |

Notice that for the odd members OC₂k+1O the values for singlet (label S) are smaller than those for triplet (label T), while for the even members OC₂kO the values for triplet are smaller than those for singlet. (Values for singlet OC₂O are missing; calculations for geometry optimization invariably yielded two spatially separated CO dimers.)

within the numerical accuracy. However, as visible in Figure 11, differences between the singlet and triplet HC₁₁H infrared spectra significant especially in the spectral range ≈400 – 800 cm⁻¹ characteristic for CCH bending modes. We referred above to vibrational properties because infrared (vibrational) spectroscopy is an important tool for detecting symmetric molecules like HC₁₁H; given the fact that their dipole moment vanishes, rotational spectroscopy cannot be utilized in such cases. Another example revealing the impact of the nature of the ground state on the infrared spectra is presented in Figure S12a,b, Supporting Information.

In addition to the significant impact on the vibrational transitions underlying the differences between the singlet and triplet infrared spectra of Figure 11a,b, we can also mention a similar effect on the UV–visible absorption. To exemplify, our TD-DFT/CAM-B3LYP/6-311++g(3df, 3pd) calculations yielded a value ε_T = 2.614 eV (474 nm) for the lowest A' Σ⁻⁻ → X' Σ⁻⁻ electronic transition. Similar calculations done for the lowest electronic transition of the singlet HC₁₁H found a significantly different value of ε_S = 2.303 eV (538 nm).

One should still note here that estimates based on the methods utilized above may not be sufficiently accurate to be directly compared with measured data.

Unfortunately, ab initio (e.g., CC-)methods to compute vibrational properties for such large and open-shell molecular species, which can be employed to smaller closed-shell chains,[41] are currently prohibitive. Still, we believe that the significant differences between Figure 11a,b (and between Figure S12a,b, Supporting Information) represent a convincing argument that experiments—which the present theoretical study hopes to motivate—can discriminate between the singlet and triplet HC₁₁H (and HC₁₂H) chains.

Figure 10. Results for OCₙO chains. a) Enthalpies of formation for singlet and triplet chain isomers. b) Adiabatic singlet–triplet separation energy Δₜₐₘₚ.(c) Vertical singlet–triplet separation at the geometry of the most stable state Δₚₑₚₚₚ. (namely, singlet for odd members and triplet for even members, cf. Equation (3)). Lines are guide to the eye. The numerical values underlying this figure are presented in Tables 9 and 10. (Values for singlet OC₂O are missing; calculations for geometry optimization invariably yielded two spatially separated CO dimers.)
straightforward chemical intuition. We first considered (Sections 3.1 and 3.2) carbon chain systems, wherein the nature of the terminal heteroatom(s), the chain possesses a singlet ground state for a certain parity (i.e., even or odd) of the number of carbon atoms, which switches to a triplet ground state for the other parity (odd or even, respectively) of this number. It is worth emphasizing that the singlet–triplet alternation discussed above is a subtle effect that confounds straightforward intuition. We first considered (Sections 3.1 and 3.2) carbon chain families, wherein members of a certain parity are normal (closed-shell, nonradical) molecules having all valence electrons paired in chemical bonds between adjacent atoms while members of the opposite parity are diradicals. Chains of HCN and HCN, (as well as NCN, a case not explicitly discussed because of its similarity with the first two) belonging to this category seemed to fit an intuitive rule of thumb (ground state of normal chains is a singlet; diradical chains have triplet ground states). In disagreement to that, subsequent examples examined revealed that not all diradical chains (C,S, Section 3.3 and C,O, Section 3.4) have a triplet ground state, while not all normal (nonradical) chains (OC.O, Section 3.5) possess singlet ground states.

3.8. Remarks on Some Recent Studies on Carbon Chains Done in the Astrophysics/Astronomical Community

Without any intention to target the entire astrophysical/astrochemical community, we have to emphasize that our present findings disagree with some recent studies claiming that for all carbon-based chains with an even number of switching back and forth in a manner similar to that depicted in our Figures 2, 4, 6, 8, and 10. Examples of this kind include, for example, the case of aromatic 4n + 2 (Hückel) and 4n (anti-Hückel) cyclic polyenes (annulenes) dating back to the early days of quantum mechanics or their more recent counterpart in mesoscopic and quantum dot rings as well as a variety of even–odd effects in multilayers self-assembled monolayers, molecular electronic devices, or atomic nuclei.

Compared to those and all other cases of which we are aware, the even–odd effect reported previously and extensively analyzed in this paper for carbon-based chains of astrochemical interest is unique. This even–odd effect does not merely consist of an alternation of a certain (ground state) property upon size increasing. Rather, it is the very nature of the electronic ground state that switches back and forth between a singlet and triplet state. Specifically, we showed here that, depending on the chemical nature of the terminal heteroatom(s), the chain possesses a singlet ground state for a certain parity (i.e., even or odd) of the number of carbon atoms, which switches to a triplet ground state for the other parity (odd or even, respectively) of this number.

It is worth emphasizing that the singlet–triplet alternation discussed above is a subtle effect that confounds straightforward intuition. We first considered (Sections 3.1 and 3.2) carbon chain families, wherein members of a certain parity are normal (closed-shell, nonradical) molecules having all valence electrons paired in chemical bonds between adjacent atoms while members of the opposite parity are diradicals. Chains of HCN and HCN, (as well as NCN, a case not explicitly discussed because of its similarity with the first two) belonging to this category seemed to fit an intuitive rule of thumb (ground state of normal chains is a singlet; diradical chains have triplet ground states). In disagreement to that, subsequent examples examined revealed that not all diradical chains (C,S, Section 3.3 and C,O, Section 3.4) have a triplet ground state, while not all normal (nonradical) chains (OC.O, Section 3.5) possess singlet ground states.

3.7. A Sui Generis Even–Odd Effect that Confounds Straightforward Chemical Intuition

It is known that successive addition of repeat units to homologous classes of systems may result in properties periodically
electronics like those examined above singlet isomers are the most stable. Refuting that claim and drawing attention on the fact that triplet states deserve consideration in astrochemical context (cf. Section 3.10 below) was an important aim of conducting the extensive theoretical investigation presented in this paper.

To demonstrate that, even if not explicitly stated, ref. [22] tacitly admitted singlet electronic ground states; in Tables S1–S4, Supporting Information, we present results reported in that work along with $\Delta_f$ $H^0$-estimates for both singlets and triplets based on the DFT/B3LYP/6-311+g(3df, 3pd) approach underlying Tables 1, 3, 7, 5, and 9. As visible from the inspection of Tables S1–S4, Supporting Information, the $\Delta_f$ $H^0$-values of ref. [22] agree with our $\Delta_f$ $H^0$ values obtained for the lowest singlet states. So, although not explicitly stated in ref. [22], the results presented there do refer to the singlet states. The small differences between $\Delta_f$ $H^0$-values of Tables 1, 3, 7, 5, and 9 and those of ref. [22] may reflect the slightly different methods utilized. These differences due to the different approaches are comparable to those between the B3LYP/6-311+g(3df, 3pd)-based values and the $\Delta_f$ $H^0$-estimates obtained by using the CBS-QB3 protocol as implemented in GAUSSIAN 16, which are also shown in Tables S1–S4, Supporting Information for comparison purposes.

3.9. Computational Issues

Important insight from a computational perspective can be gained from the comparison between the various estimates presented in Tables 2, 4, 6, 8, and 10.

First, the results presented there emphasize limitations of popular Delta-SCF[50] or Delta-DFT[51–53] methods to estimate the singlet–triplet energy separation. Properties like the singlet–triplet separation $\Delta$ examined above as well as other quantities, for example, ionization or electron attachment energies can be expressed as differences between pertaining total molecular energies. Similar to other cases[54–56] the comparison with state-of-the-art approaches based on coupled-cluster expansions (cf. Tables 2, 4, 6, 8, and 10) reveals differences of several tenth of electronvolt. Such differences are significantly larger than the accuracy needed for reliable astrochemical modeling or achieved in experiments.[57]

More importantly, the differences between CCSD and CCSD(T) estimates appear to be unusually large. In “normal” cases, where electron correlations are “moderately” strong, quantities obtained within the CCSD(T) approach do not substantially differ from those based on the CCSD approach. The reason is that, within the CCSD(T) approach, triple excitation are only perturbatively treated on top of the single and double excitations embodied within the CCSD approach. Such a perturbative approach can be hardly justified in cases like those shown above for longer chains, where the differences between CCSD(T) and CCSD estimates amount to $\approx 0.3–0.4$ eV (cf. Tables 6, 8, and 10). This state of affairs calls for further clarification. Possible further developments in this direction include other theoretical treatments (e.g., SAC-Cl[58]), CC approaches including higher-order electron correlations (e.g., CCSDT or CC3[59]), or based on the (particularly suited for 1D systems) density matrix renormalization group (DMRG).[60–62]

3.10. Relevance for Astronomical Detectability

From an astrochemical perspective, the inspection of the results presented above unravels a striking correlation. Across the various families of linear carbon-chains presently considered, the members that were not identified in astronomical data are preponderantly those for which our present calculations predict a triplet ground state. Examples will be presented below in support of this assertion.

$C_4S$ is the longest chain detected in space[47] from the $C_nS$ family. However, the shorter $C_4S$ chain was not reported so far. Still, the enthalpy of formation for the most stable $C_4S$ chain (which is a triplet) is lower than that for the most stable (singlet) $C_5S$ chain observed (cf. Table 5). On the contrary, the less stable singlet $C_5S$ isomer has an enthalpy of formation higher than that of the singlet $C_5S$ chain. So, it is not unexpected that it is more difficult to detect $C_4S$ chains implicitly assuming that they are singlets than to detect (singlet) $C_5S$ chains.

A similar situation is encountered in the $HC_nH$ series. Out of the $HC_nH$ family, $HC_6H$ is the longest chain observed.[59] Nevertheless, the shorter $HC_6H$ chain was not detected in space so far. Its most stable (triplet) isomer is more stable than the most stable (singlet) $HC_6H$ chain (cf. Table 1) although the singlet $HC_6H$ chain is thermodynamically less stable than the singlet $HC_6H$ chain.

Most notorious is the case of the $HC_nN$ family. The even members $HC_6N$, $HC_8N$, and $HC_{10}N$ were not observed in space; nevertheless, the next larger odd members $HC_7N$[11] $HC_9N$[12] and $HC_{11}N$[18] were detected in astronomical data. The inspection of Table 3 reveals that, again, it is the most stable (triplet) isomer of the even members that is more stable than the most stable (singlet) isomer of the odd members. A triplet $HC_nN$ chain is more stable thermodynamically than a singlet $HC_nN$ chain, a triplet $HC_6N$ chain is more stable than a singlet $HC_6N$ chain, and a triplet $HC_6N$ chain is more stable than a singlet $HC_6N$ chain.[45,63] Although a singlet $HC_nN$ chain is less stable thermodynamically than a singlet $HC_nN$ chain, a singlet $HC_nN$ chain is less stable than a singlet $HC_nN$ chain, and a singlet $HC_{10}N$ chain is less stable than a singlet $HC_{11}N$ chain.

In all cases of the aforementioned type, ref. [22] arrived at an opposite conclusion on the thermodynamical instability/stability across various chain families because of the incorrect (implicit[23]) assumption that the most stable chains of species with an even number of electrons are always singlets.

In Section 1, we mentioned that information on the presently considered carbon-based chains are very scarce. Given this data scarcity, it may be tempting to resort to empirical interpolation/extrapolation schemes[20]; namely, to utilize available properties of molecular species of a certain homologous family to deduce unavailable properties of other molecular species, and use the latter in attempting to reveal their presence by processing the astronomical data. However, such a procedure will inherently fail. Properties of, for example, triplet $HC_nN$, $HGnN$, or $HC_{10}N$ chains can by no means be obtained by interpolating/extrapolating properties of singlet $HC_nN$, $HC_nN$, and $HC_{11}N$ chains. The reason for this failure should be clear; we have seen that differences between the singlet and triplet isomers of a given carbon chain may be important even in situations where one can expect that they are less significant (cf. Section 3.6).
4. Conclusion

In this paper, we demonstrated that, in families of carbon-based chains, most stable members of one parity (even or odd) are singlets while most stable members of the opposite parity (odd or even) are triplets. This is a sui generis effect qualitatively different from other even–odd effects known from studies over decades in other areas.[2,3,26–35]

From a more general perspective, the present paper aimed at bridging astronomy/astrophysics and physical/computational chemistry. The results reported here are most significant in the context of the observability in space. As elaborated in Section 3.10, we strongly believe that it is not coincidental that absent in the list of various homologous series detected in space is just carbon-based chains for which our calculations predict a triplet ground state. Emphasizing that most stable isomers of carbon-based chains of the type considered in our paper are not invariably singlets is important because this was incorrectly claimed in some recent studies done in the astronomical/astrophysical community.[22,24] Prior to the present extensive study, a series of authors drew attention on the fact that triplet isomers of carbon-based chains are more stable than singlet isomers: HC_{25}H[25,64] C_{2x}[25,65] HC_{2x}N[26–69] NC_{2x}N[70] C_{2x}O[71] C_{2x}S[72] and HC_{2x}N[73].

Last but not least, from a computational perspective, the present results are important because they emphasize that electron correlations in carbon-based chains are unusually strong. The analysis of Section 3.9 indicated that the “standard gold” CCSD(T) quantum chemical approach may not be sufficiently accurate to quantify these strong electron correlations. This is an important challenge for the community of theoretical chemistry that deserves further consideration.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The author declares no conflict of interest.

Keywords

ab initio methods, carbon chains, interstellar matter, molecular electronic structure, singlet-triplet interplay

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[1] S. Datta, *Quantum Transport: Atom to Transistor*, Cambridge University Press, Cambridge 2005.
[2] J. C. Cuevas, E. Scheer, *Molecular Electronics: An Introduction to Theory and Experiment*, 2nd ed., World Scientific Series in Nanoscience and Nanotechnology, Vol. 15, World Scientific, Singapore 2017.
[3] *Molecular Electronics: An Experimental and Theoretical Approach* (Ed.: I. Bádeia), Pan Stanford, Singapore 2015.
[4] D. Fazzi, C. Vozzi, in *Carbon Nanomaterials Sourcebook: Nanofibers, Nanoporous Structures, and Nanocomposites* (Ed. K. D. Sattler), Vol. 2, Linear Carbon Chains, CRC Press, Boca Raton, FL 2016, Ch. 2.
[5] F. Goulay, A. J. Trevitt, G. Meloni, T. M. Selby, C. A. Tautjes, L. Vereecken, S. R. Leone, *J. Am. Chem. Soc.* 2009, 131, 993.
[6] A. M. Smith, T. P. Stecher, *Astrophys. J. Lett.* 1971, 164, L43.
[7] L. E. Snyder, D. Buhl, *Astrophys. J. Lett.* 1971, 163, L47.
[8] B. E. Turner, *Astrophys. J. Lett.* 1971, 163, L35.
[9] L. W. Avery, N. W. Broten, J. M. MacLeod, T. Oka, H. W. Kroto, *Astrophys. J. Lett.* 1976, 205, L173.
[10] S. P. Souza, B. L. Lutz, *Astrophys. J. Lett.* 1977, 216, L49.
[11] H. W. Kroto, C. Kirby, D. R. M. Walton, L. W. Avery, N. W. Broten, J. M. MacLeod, T. Oka, *Astrophys. J. Lett.* 1978, 194, L133.
[12] N. W. Broten, T. Oka, L. W. Avery, J. M. MacLeod, H. W. Kroto, *Astrophys. J. Lett.* 1978, 223, L105.
[13] H. E. Matthews, W. M. Irvine, P. Friberg, R. D. Brown, P. D. Godfrey, *Nature* 1984, 310, 125.
[14] K. W. Hinkle, J. J. Keedy, P. F. Bernath, *Science* 1988, 241, 1319.
[15] P. F. Bernath, K. H. Hinkle, J. J. Keedy, *Science* 1989, 244, 562.
[16] M. Ohishi, H. Suzuki, S.-I. Ishikawa, C. Yamada, H. Kamonari, W. M. Irvine, R. D. Brown, P. D. Godfrey, N. Kaifu, *Astrophys. J. Lett.* 1991, 380, L39.
[17] M. Guélin, J. Cernicharo, *Astron. Astrophys.* 1991, 244, L21.
[18] M. B. Bell, P. A. Feldman, M. J. Travers, M. C. McCarthy, C. A. Gottlieb, P. Thaddeus, *Astrophys. J. Lett.* 1997, 483, L61, see also ref. [73].
[19] J. Cernicharo, J. R. Goicoechea, E. Caux, *Astrophys. J. Lett.* 2000, 534, L199.
[20] J. Cernicharo, M. Guélin, J. R. Pardo, *Astrophys. J. Lett.* 2004, 615, L145.
[21] K. Graupner, T. A. Field, G. C. Saunders, *Astrophys. J. Lett.* 2008, 685, L95.
[22] E. E. Etim, P. Gorai, A. Das, S. K. Chakrabarti, E. Arunan, *Astrophys. J.* 2016, 832, 144.
[23] Ref. [24] contains an explicit (and incorrect) assertion on the type of ground state (namely, singlet, cf. Table 1 of ref. [24]). Ref. [22], a work done by the same group, does not explicitly state what is the spin multiplicity of the state of the molecules considered but tacitly admitted singlet ground states of all cases where our results indicate triplet ground states. For more details the reader is referred to the Supporting Information.
[24] E. E. Etim, E. Arunan, *Astrophys. Space Sci.* 2016, 362, 4.
[25] Q. Fan, G. V. Pfeiffer, *Chem. Phys. Lett.* 1989, 162, 472, see also Section S1, Supporting Information.
[26] Z. Wu, S. Xu, X. Xu, M. Khamoshi, Q.-B. Liu, T. Han, Y. Wu, J. Lin, G. Long, Y. He, Y. Cai, Y. Yao, F. Zhang, N. Wang, *Nat. Commun.* 2016, 7, 12955.
[27] F. Tao, S. L. Bernasek, *Chem. Rev.* 2007, 107, 1408.
[28] I. Bádeia, H. Köppel, L. S. Cederbaum, *Phys. Rev. B* 1999, 60, 6646.
[29] I. Bádeia, H. Köppel, L. S. Cederbaum, *J. Phys. Soc. Jpn.* 1999, 68, 1954.
[30] I. Bádeia, H. Köppel, L. S. Cederbaum, *Eur. Phys. J. B* 2001, 20, 289.
[31] I. Bádeia, L. S. Cederbaum, *Phys. Rev. Lett.* 2002, 89, 133003.
[32] E. Hückel, *Z. Phys.* 1931, 70, 204.
[33] E. Hückel, *Z. Phys.* 1931, 72, 370.
[34] E. Hückel, *Z. Phys.* 1932, 76, 628.
[35] F. London, *J. Phys. Radium* 1937, 8, 397.
