Extensive Quantum Chemistry Study of Neutral and Charged C₄N Chains. An Attempt to Aid Astronomical Observations

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Abstract

Many molecular species can presumably still be observed in space if they are adequately characterized chemically. In this paper, we suggest that this could be the case of the neutral (C₄N⁰) and anion (C₄N⁻) cyanopropynylidene chains, which were not yet identified in space although both the neutral (C₃N⁰ and C₅N⁰) and anion (C₃N⁻ and C₅N⁻) neighboring members of the homologous series were observed. Extensive data obtained from quantum chemical calculations using density functional theory (DFT), coupled cluster (CC), and quadratic configuration interaction (QCI) methods for all charge and spin states of interest for space science (doublet and quartet neutrals, triplet and singlet anions, and singlet and triplet cations) are reported: e.g., bond metric and natural bond order data, enthalpies of formation, dissociation and reaction energies, spin gaps, rotational constants, vibrational properties, dipole and quadrupole momenta, electron attachment energies (EA) and ionization potentials (IP). The fact
that (not only for C\textsubscript{4}N but also for C\textsubscript{2}N and C\textsubscript{6}N) the quantum chemical methods utilized here are able to excellently reproduce the experimental \(EA\) value — which is often a challenge for theory — is particularly encouraging, since this indicates that theoretical estimates of chemical reactivity indices (which are key input parameters for modeling astrochemical evolution) can be trusted. The presently calculated enthalpies of formation and dissociation energies do not substantiate any reason to assume that C\textsubscript{4}N is absent in space. To further support this idea, we analyze potential chemical pathways of formation of both C\textsubscript{4}N\textsuperscript{0} and C\textsubscript{4}N\textsuperscript{−}, which include association and exchange reactions. In view of the substantially larger dipole moment (\(D_{\text{anion}} \gg D_{\text{neutral}}\)), we suggest that astronomical detection should first focus on C\textsubscript{4}N\textsuperscript{−} chains rather than on neutral C\textsubscript{4}N\textsuperscript{0} chains.

**Keywords:** astrochemistry; interstellar medium; carbon chains; cyanopropynylidenes C\textsubscript{4}N; ab initio calculations; singlet-triplet interplay; ionization and electron attachment energies; reaction and dissociation enthalpies; chemical reactivity indices; chemical pathways of C\textsubscript{4}N formation

**Introduction**

Carbon chains or obtained by adding heteroatoms at their ends represent a continuing important topic in space sciences\textsuperscript{1-10}. Thanks to intensive and extensive efforts numerous carbon-based chains could be detected in the last decades. Given the fact that many of these molecular species have a rather minor importance for terrestrial applications, information on many molecular species of this kind needed to properly interpret data acquired (or to be acquired) in astronomical observations is often very scarce. This state of affair may at least partially explain the puzzling fact that, across a given homologous series, certain members could not yet be observed although longer molecules were already detected.

The cyanopropynylidene (C\textsubscript{4}N) chains investigated theoretically in the present paper, which are expected to be relevant for interstellar chemistry\textsuperscript{3,11} belong to this category.
Although the presence in space of neutral C$_3$N$_0$ and C$_5$N$_0$ chains$^{4,12}$ was reported, C$_4$N$_0$ chains could not be detected so far. The situation of the corresponding anions is similar. C$_3$N$^-$ and C$_5$N$^-$ chains were astronomically observed$^{7,10}$ but C$_4$N$^-$ could not yet be reported.

Cyanopropynylidenes made the object of several publications. The neutral C$_4$N$_0$ radical has been previously investigated experimentally by microwave spectroscopy$^{13}$ and theoretically at Hartree-Fock (HF) level$^{14}$ and within density functional theory (DFT)$^{15,16}$. Previous theoretically studies to C$_4$N$^-$ anion reported results of second order Møller-Plesset (MP2)$^{17}$ and DFT$^{18-20}$ calculations. C$_4$N$^-$ anions produced by laser ablation$^{18,21}$ or sputtering$^{22}$ were studied experimentally via mass spectroscopy. The experimental study using slow photo-electron velocity-map imaging spectroscopy (SEVI)$^{20}$ is of particular interest in the context of the present paper. To anticipate, the very accurate experimental electron affinity (EA) reported there is very well reproduced by our theoretical calculations.

By reporting extensive data on doublet (spin $S = 1/2$) and quartet ($S = 3/2$) neutral (C$_4$N$_0$) chains, as well as on singlet ($S = 0$) and triplet ($S = 1$) anions (C$_4$N$^-$) and cations (C$_4$N$^+$) obtained within standard quantum chemical approaches the present paper aims at filling a gap in the literature and at assisting ongoing efforts in astronomical observation.

**Methods**

The results reported below were obtained by performing quantum chemical calculations on the bwHPC platform$^{23}$ using the GAUSSIAN$^{24,25}$ and CFOUR$^{26}$ packages. They are based both on the density functional theory (DFT) and on ab initio methods. The latter comprise coupled-cluster (CC)$^{27-30}$ and quadratic configuration interaction (QCI)$^{28,31,32}$ approaches including single and double excitations (CCSD, QCISD) also augmented with perturbative corrections due to triple excitations (CCSD(T), QCISD(T)).

All molecular geometries were optimized at the DFT level of theory using the B3LYP hybrid exchange-correlation functional$^{33-35}$ and the largest Pople 6-311++G(3df, 3pd) ba-
sis sets. For comparison purposes, the hybrid parameter free PBE0, M06-2X, and double-hybrid B2GP-PLYP functionals were also used for DFT geometry optimization. In all cases, we checked that all vibrational frequencies were real.

Similar to the spin gaps of all charge species ($\Delta^q; q = 0, \pm$) the lowest electronic attachment energies (EA) and ionization potentials (IP) can be and have been computed by using "$\Delta$" methods, i.e., by taking differences between the total energies $E_X(R)$ of the corresponding molecular species (neutral doublet ($D^0$) and quartet ($Q^0$), anion singlet ($S^-$) and triplet ($T^-$), and cation singlet ($S^+$) and triplet ($T^+$) at the appropriate geometries ($R = R_{S\pm}, R_{T\pm}, R_{D^0}, R_{Q^0}$) optimized as described above.

While not appearing to affect unrestricted DFT calculations, spin contamination becomes important and raises serious doubt on results obtained within ab initio approaches like CCSD/CCSD(T) applied on top of unrestricted Hartree-Fock (UHF) wave functions. For completeness and for comparison with previous studies employing unrestricted methods along with estimates obtained within more reliable restricted open shell (ROCCSD/ROCCD(T)) calculations, we also present properties obtained from unrestricted coupled-cluster (UCCSD/UCCSD(T)) calculations. The inspection of the various tables indicates that, without an adequate elimination of spin contamination (a task beyond the scope of the present paper), UCCSD/UCCSD(T)-based values cannot be trusted.

The quantities EA and IP were also computed by CC-based equation-of-motion (EOM) methods (EA-EOM-ROCCSD and IP-EOM-ROCCSD). To check whether long-range corrections improve the DFT-based estimates, EA and IP values were also computed by using the long-range corrected exchange-correlations LC-BLYP and LC-$\omega$PBE functionals.

Due to some numerical issues with the 6-311++G(3df, 3pd) basis sets, aug-cc-pVTZ basis sets were used in the EOM-ROCCSD calculations with CFOUR and the natural bond orbital (NBO) analysis carried out on top of RCCSD(T) and ROCCSD(T) calculations with GAUSSIAN 09.

Thermochemistry data presented in the main text were obtained in the standard way.
using the CBS-QB3 protocol as implemented in GAUSSIAN 16. Additional results based on the CBS-APNO and CBS-4M protocols are included in the SI.

To end this section, we note that at the small molecular size considered, geometry optimization and numerical frequency calculations at the more computationally demanding (RO)CCSD(T) level can and have also been done (cf. Table S8). However, we do not show single-point results for those geometries because the ROCCSD(T)-based values of the rotational constant of the neutral doublet species with cc-PVTZ and aug-cc-pVTZ basis sets ($B = 2.39187$ GHz and $B = 2.39093$ GHz, respectively) have larger deviation from experiment than the DFT-based values (cf. Table 5 and S15).

**Results and Discussion**

**Electronic Structure and Chemical Bonding**

In this section we present detailed results on properties of interest for all charge species and relevant spin states: neutral doublet ($\tilde{X}^2\Pi$) and quartet ($\tilde{a}^4\Sigma^-$), anion linear and bent ($1^1A'$) singlet, and anion triplet ($3^3\Sigma^-$) as well as cation singlet ($1^1\Sigma^+$) and triplet ($3^3\Sigma^-$).

Except for the anion singlet — whose most stable conformation ($1^1A'$) turned out to be bent (cf. Figure 1) —, geometry optimization (conducted without imposing symmetry constraints) yielded (within numerical accuracy) linear chains. To emphasize this aspect, in

![Figure 1](image-url)

Figure 1: Geometries of singlet ($1^1A'$) and triplet ($3^3\Sigma^-$) $C_4N^-$ anions (left and right panels, respectively) investigated in the present paper. Similar to the triplet $C_4N^-$ chain shown here, doublet and quartet $C_4N^0$ neutral chains as well as singlet and triplet cation $C_4N^+$ chains are also linear.
Table 1 we also included values of angles between adjacent atoms; within numerical noise inherent in optimization without symmetry constraints, they cannot be distinguished from the ideal value (180°) characterizing strictly linear chains.

Table 1: Bond lengths $l$ between atoms XY (in angstrom), angles $\alpha$ between atoms $\widehat{XYZ}$ (in degrees) and Wiberg bond order indices $N$. Results of B3LYP/6-311++G(3df, 3pd) geometry optimization without imposing symmetry constraints.

| Species                  | Property | $C_1C_2$ | $C_1C_2C_3$ | $C_2C_3$ | $C_2C_3C_4$ | $C_3C_4$ | $C_3C_4N$ | $C_4N$ |
|--------------------------|----------|----------|-------------|----------|-------------|----------|----------|-------|
| metastable linear anion  | $l, \alpha$ | 1.2892   | 179.97      | 1.2926   | 179.96      | 1.3178   | 179.98   | 1.1884 |
| singlet $1\Sigma^+$      | $N$      | 2.0579   | 1.7873      | 1.4279   |             |          |          |       |
| stable bent anion        | $l, \alpha$ | 1.2780   | 174.3       | 1.3295   | 125.7       | 1.3846   | 171.4    | 1.1702 |
| singlet $1\Lambda'$      | $N$      | 2.1785   | 1.6978      | 1.2309   |             |          |          |       |
| linear anion             | $l, \alpha$ | 1.2912   | 179.8       | 1.2917   | 178.7       | 1.3193   | 180.0    | 1.1874 |
| triplet $3\Sigma^-$      | $N$      | 1.8987   | 1.8251      | 1.3182   |             |          |          |       |
| neutral                  | $l, \alpha$ | 1.3165   | 179.8       | 1.2536   | 178.8       | 1.3371   | 180.0    | 1.1670 |
| doublet $2\Pi$           | $N$      | 1.4710   | 2.2142      | 1.2069   |             |          |          |       |
| neutral                  | $l, \alpha$ | 1.2585   | 179.9       | 1.2776   | 178.8       | 1.3257   | 179.9    | 1.1742 |
| quartet $4\Sigma^-$      | $N$      | 1.4896   | 2.2643      | 1.2001   |             |          |          |       |
| cation                   | $l, \alpha$ | 1.3343   | 178.8       | 1.2383   | 179.7       | 1.3413   | 179.6    | 1.1648 |
| singlet $1\Sigma^+$      | $N$      | 1.3932   | 2.3383      | 1.2060   |             |          |          |       |
| cation                   | $l, \alpha$ | 1.2531   | 179.8       | 1.2747   | 178.9       | 1.3204   | 179.7    | 1.1751 |
| triplet $3\Sigma^-$      | $N$      | 1.7742   | 1.9414      | 1.3077   |             |          |          |       |

For the pertaining optimized geometries, we present detailed molecular properties: Cartesian coordinates (adjusted to linearity where appropriate), atomic NBO valencies and charges (Tables S1 to S7), Results for bond lengths and Wiberg bond indices are collected in Table (Figures 2 and 6. Changes of these quantities with reference to the (most stable) neutral doublet are depicted in Figures S7 and S8.

In principle, chemical bonds of linear carbon species can be of cumulene type or of polyyn type. Our NBO calculations (see, e.g., Figures 2b and 6b) indicate that none of these structures (which are incompatible with standard rules of valence) is present in the $C_4N$ species investigated here. They do not support claims that neutral clusters favor a
cumulenic bonding while anionic species prefer polyyne-like bonding.\textsuperscript{18,21,55,56} The results presented in Figure S20 also reveal that — contrary to straightforward chemical intuition — there is no simple relationship between bond order indices and bond lengths.

Spatial distributions of the frontier molecular orbitals (highest occupied HOMO and lowest unoccupied LUMO) are depicted in Figures S17, S18, S16, S19. Because Kohn-Sham orbitals utilized in the DFT are mathematical rather than physical objects\textsuperscript{41,57} and ubiquitously utilized HF molecular orbitals rely on a very crude description, the MO spatial distributions depicted in the aforementioned figures have been obtained from the natural orbital expansion of the reduced density matrices at the EOM-CCSD level.\textsuperscript{41} For open-shell cases these results were obtained via restricted open-shell (ROHF-based) approaches. The inspection of the MOs is useful also because it provides insight into issues under debate in the past (see Section "Negatively Charged C\textsubscript{4}N\textsuperscript{−} Chains").

Neutral C\textsubscript{4}N\textsuperscript{0} Chains

Within an MO-based picture, having an unpaired \(\pi\) electron, the neutral ground state is a spin doublet with the electronic configuration

\[
\tilde{X}^2\Pi = [\text{core}] 6\sigma^2 7\sigma^2 8\sigma^2 9\sigma^2 1\pi^4 10\sigma^2 2\pi^4 11\sigma^2 3\pi^1
\]  

(1)

The lowest excited state of the neutral chain, obtained by promoting a \(\sigma\) electron into a \(\pi\) orbital, is a spin quartet possessing the following electronic configuration

\[
\tilde{a}^4\Sigma^- = [\text{core}] 6\sigma^2 7\sigma^2 8\sigma^2 9\sigma^2 1\pi^4 10\sigma^2 2\pi^4 11\sigma^1 3\pi^2
\]  

(2)

In agreement with these intuitive considerations, our calculations found that the quartet state lies higher in energy than the doublet state. By inspecting the values of the doublet-quartet splitting collected in Table\textsuperscript{2} a significant difference between the estimates obtained within the various quantum chemical methods utilized can be concluded. This behavior
confirms the fact noted recently\textsuperscript{42,58} that electron correlations (implying by definition that departures from the above MO-based picture are substantial) in carbon-based chains are strong, which represents a challenge for theory. Still, the large values ($\sim 1 \text{ eV}$) clearly demonstrate that the neutral quartet lies considerably higher in energy than the doublet.

The inspection of Table 1 and Figures 6 and S8 reveals that the strongest impact of the spin state on the neutral chain is on the moiety opposite to the N atoms. The $C_1C_2$ bond of the quartet is longer than that of the doublet, while $C_2C_3$ bond of the quartet is shorter than that of the doublet (cf. Table 1 and Figures 6). Electronic charge from the $C_3$ atom in the middle of the chain moves toward the end opposite to the N atom (cf. Tables S1 and S2, and Figure S7). This renders the dipole moment of the quartet substantially larger than that of the doublet (cf. Table 6 and S16).

Table 2: Vertical $\Delta^0_{DQ}(\mathbf{R}^0_D) \equiv \mathcal{E}^0_Q(\mathbf{R}^0_D,\mathbf{Q}) - \mathcal{E}^0_D(\mathbf{R}^0_D,\mathbf{Q})$ and adiabatic $\Delta^{0,ad}_{DQ} \equiv \mathcal{E}^0_Q(\mathbf{R}^0_Q) - \mathcal{E}^0_D(\mathbf{R}^0_D)$ of the doublet-quartet splitting computed by using the total energies $\mathcal{E}^0$ of the neutral ($C_4N^0$) chains taken at B3LYP/6-311++G(3df, 3pd) optimized geometries $\mathbf{R}^0_{D,Q}$ of the neutral doublet (label $D$) and quartet (label $Q$) without and with corrections due to zero point motion.

|                | B3LYP | UCCSD | UCCSD(T) | ROCCSD | ROCCSD(T) |
|----------------|-------|-------|----------|--------|-----------|
| $\Delta^0_{DQ}(\mathbf{R}^0_D)$ | uncorrected | 1.167 | 0.891 | 1.071 | 0.740 | 0.826 |
|                | corrected | 1.182 | 0.906 | 1.085 | 0.755 | 0.840 |
| $\Delta^0_{DQ}(\mathbf{R}^0_Q)$ | uncorrected | 1.062 | 0.714 | 0.898 | 0.557 | 0.679 |
|                | corrected | 1.076 | 0.729 | 0.914 | 0.571 | 0.693 |
| $\Delta^{0,ad}_{DQ}$ | uncorrected | 1.167 | 0.891 | 1.071 | 0.740 | 0.826 |
|                | corrected | 1.182 | 0.906 | 1.085 | 0.755 | 0.840 |

Negatively Charged C$_4$N$^-$ Chains

Whether the ground state of the C$_4$H$^-$ chain is a spin singlet or triplet was an issue of debate in the past. Based on earlier time-of-flight mass spectroscopy measurements, it was\textsuperscript{18} concluded that the anion possesses a linear triplet ground state. This conclusion was challenged by subsequent MP2-based calculations\textsuperscript{17} which suggested a bent singlet conformer. In con-
trast to them, DFT/B3LYP geometry optimization using aug-cc-pVTZ and 6-311G* basis sets\textsuperscript{19} yielded a linear triplet structure, a result supported by slow photoelectron velocity-map imaging spectroscopy (SEVI) data.\textsuperscript{20}

In view of the aforementioned, we paid particular attention to this aspect and conducted geometry optimization using several exchange-correlation functionals — B3LYP, PBE0 and M06-2X — which are among the most successful in correctly predicting the lowest energy conformers of a variety of molecules. In addition, we performed single-point calculations using CCSD, CCSD(T), QCISD and QCISD(T). Confirming the conclusion of ref. 19, all these results, which are collected in Table 3 and S12, indicate that the most stable conformer is a linear triplet with the electronic configuration

$$^3\Sigma^− = [\text{core}] 6\sigma^2 7\sigma^2 8\sigma^2 9\pi^4 10\sigma^2 2\pi^4 11\sigma^2 3\pi^2$$

At the linear triplet optimum geometry (cf. Figure 1b) of $R_{−T}$, the C$_4$N$^-$ anion singlet lies substantially higher than the triplet; the energy difference amounts to $\Delta_{−ST}(R_{−T}) \sim 0.7$ eV (cf. Table 3).

Our DFT calculations (not only with the B3LYP exchange-correlation functional but also with the PBE0 and M06-2X functionals) yielded an energy minimum (all vibrational frequencies were real) of an anion singlet chain possessing a linear (at least within numerical accuracy) geometry $R_{−S} \approx R_{−T}$ very similar to that of the C$_4$N$^-$ triplet; compare the bond lengths (Table 1 and Figure 2) and the values of the corresponding reorganization energies (Table S26).

However, rather than a linear conformer, the most stable form of the anion singlet turned out to be a chain which is bent at the C$_3$ position by an angle of $\sim 54^\circ$ (Figure 1a). This stable bent singlet isomer lies significantly above the metastable linear singlet isomer; depending on the method utilized the energy separation amounts to $\Delta_{−S,bS} \sim 0.3 - 0.5$ eV (cf. Table 3).

To reiterate, the stable C$_4$N$^-$ triplet is a linear chain (Figure 1b). The bonds C$_1$C$_2$ and
Figure 2: (a) Bond lengths (in angstrom), (b) Wiberg bond indices, (c) Wiberg valencies and (d) atomic charges of C₄N chains considered in this paper.
Table 3: Values of the adiabatic (label $\text{ad}$) and vertical singlet-triplet splitting $\Delta_{bS,T}^{-} (\mathbf{R}_T^{-}) \equiv \mathcal{E}_{T}^{-} (\mathbf{R}_T^{-}) - \mathcal{E}_{bS}^{-} (\mathbf{R}_T^{-})$, $\Delta_{bS,T}^{-} (\mathbf{R}_{bS}^{-}) \equiv \mathcal{E}_{T}^{-} (\mathbf{R}_{bS}^{-}) - \mathcal{E}_{bS}^{-} (\mathbf{R}_{bS}^{-})$, $\Delta_{iS,T}^{-} (\mathbf{R}_i^{-}) \equiv \mathcal{E}_{T}^{-} (\mathbf{R}_i^{-}) - \mathcal{E}_{iS}^{-} (\mathbf{R}_i^{-})$ without or with corrections due to zero point motion. The geometries $\mathbf{R}_x^{-}$ of the triplet, bent singlet and linear singlet ($x = T, bS, lS$ were optimized at the B3LYP/6-311++G(3df, 3pd) level of theory.

|               | B3LYP       | UCCSD      | UCCSD(T)   | ROCCSD     | ROCCSD(T)  |
|---------------|-------------|------------|------------|------------|------------|
| $-\Delta_{bS,T}^{-} (\mathbf{R}_T^{-})$ | 0.785       | 0.815      | 0.646      | 0.743      | 0.711      |
|               | corrected   | 0.791      | 0.821      | 0.652      | 0.749      | 0.717      |
| $-\Delta_{bS}^{-} (\mathbf{R}_{bS}^{-})$ | 0.103       | 0.080      | -0.046     | 0.016      | -0.002     |
|               | corrected   | 0.109      | 0.086      | -0.040     | 0.022      | 0.005      |
| $-\Delta_{bS,T}^{-,\text{ad}} (\mathbf{R}_T^{-})$ | 0.527       | 0.361      | 0.228      | 0.289      | 0.292      |
|               | corrected   | 0.533      | 0.367      | 0.234      | 0.295      | 0.299      |
| $-\Delta_{iS}^{-} (\mathbf{R}_i^{-})$ | 0.785       | 0.816      | 0.647      | 0.744      | 0.712      |
|               | corrected   | 0.791      | 0.822      | 0.653      | 0.750      | 0.718      |
| $-\Delta_{iS,bS}^{-,\text{ad}}$ | 0.258       | 0.457      | 0.421      |            |            |
|               | corrected   | 0.264      | 0.463      | 0.427      |            |            |

C$_3$C$_4$ of the C$_4$N$^-$ anion triplet are shorter than in the neutral doublet while the bonds C$_2$C$_3$ and C$_4$N are longer (Table I and Figures 2a and S7a). As expected, bond order indices exhibit opposite changes: shorter bonds have larger bond indices and vice versa (Figures 2b and S7b). The calculated values of the atomic charges (Tables S1 and S5 and Figures 2d and S7d) reveal that the excess electron of the C$_4$N$^-$ anion triplet is democratically ($\approx 1/3$) shared by the C$_1$, C$_3$ and N atoms. Positively charged in the neutral chain, C$_1$ and C$_3$ atoms become negatively charged in the C$_4$N$^-$ anion triplet. By contrast, electron attachment has little impact on the charge of the atoms C$_2$ and C$_4$. Interestingly, changes in the valence state of the atoms do not follow changes in the atomic charges in a simple intuitive way. To exemplify, although both C$_1$ and C$_3$ atoms acquire negative charge, the (fractional) valence of the former increases while that of the latter decreases (Figures 2c and S7c).

Spin singlet appears to enhance delocalization of the excess electron. Even at the triplet geometry, the singlet state favors delocalization of the excess electronic charge, which also
involves the C$_2$ atom. The (most stable) bent singlet geometry (Figure 1a and Table 1) further enhances this delocalization; from their excess electronic charge in the triplet state, atoms C$_1$ and C$_3$ pour electrons into the C$_2$ atom, which becomes more negatively charged in the stable bent singlet state.

Returning to the controversial aspect noted in the beginning of this section — whether the most stable C$_4$N$^-$ anion is a singlet (as claimed in ref. 17) or a triplet (as emerged from subsequent work$^{19,20}$ and solidified by our results) —, it is worth emphasizing the overall strong delocalization revealed by our NBO results for structures investigated. This contrasts with the picture of ref. 17 claiming that the highest occupied molecular orbital of the C$_4$N$^-$ anion is mostly localized at the chain ends. The inspection of the HOMO spatial distributions of all anion species (Figures 1, S17 and S18) reveals that this is in reality not the case. This incorrect claim may be one reason why ref. 17 incorrectly ascribed the most stable anion conformer to be a bent spin singlet.

![Figure 3: HOMO and LUMO (left and right panel, respectively) of the C$_4$N$^0$ doublet ($\tilde{X}^2\Pi$).](image)

**Positively Charged C$_4$N$^+$ Chains**

Less surprising that in the case of anion, calculations indicate that the most stable cation C$_4$N$^+$ chain is a spin singlet possessing the following electronic configuration

$$^1\Sigma^+ = [\text{core}] 6\sigma^2 7\sigma^2 8\sigma^2 9\sigma^2 1\pi^4 10\sigma^2 2\pi^4 11\sigma^2 3\pi^0$$  \hspace{1cm} (4)
Figure 4: Degenerate HOMO and HOMO-1 (upper left and right panel, respectively) and LUMO (lower panel) of the C\textsubscript{4}N\textsuperscript{-} triplet (\textsuperscript{3}\Sigma\textsuperscript{−}).

Figure 5: Degenerate HOMO and HOMO-1 (upper left and right panel, respectively) and nearly degenerate LUMO and LUMO+1 (lower left and right panel, respectively) of the C\textsubscript{4}N\textsuperscript{+} singlet (\textsuperscript{1}\Sigma\textsuperscript{+}).
The lowest triplet state of the cation obtained by promoting a $\sigma$ electron into a $\pi$ orbital

$$^3\Sigma^- = [\text{core}] 6\sigma^2 7\sigma^2 8\sigma^2 9\sigma^2 1\pi^4 10\sigma^2 2\pi^4 11\sigma^1 3\pi^1$$  \hspace{1cm} (5)

lies above the cation singlet.

The cationic triplet state possesses a considerably higher energy (Table 4); the ROCCSD(T) approach predicts a value $\Delta_{ST}^{+}\text{ad} \approx 1.5$ eV for the adiabatic singlet-triplet splitting.

Whether in a triplet or a singlet state of the cation $\text{C}_4\text{N}^+$ chain, electron removal mainly affects (in decreasing order) the atomic charges of $\text{C}_1$ ($\sim 0.6$ e both for singlet and triplet), $\text{C}_3$ ($\sim 0.5$ e for singlet and $\sim 0.3$ e for triplet) and $\text{N}$ ($\sim 0.3$ e both for singlet and triplet); see Table S6, S7, and S1, and Figures 6d and S8d. Substantial electron removal at the $\text{C}_1$ site has a strong impact on the $\text{C}_1\text{C}_2$ bond, which becomes longer (Figures 6a and S8a). Noteworthily, the impact on the bond order index is different: the $\text{C}_1\text{C}_2$ bond order becomes significantly weaker in the cation triplet while remaining almost unaffected in the cation singlet (Figures 6b and S8b).

Charge redistribution upon ionization renders in both cases the $\text{C}_4$ atom more negative (electronic charge excess $\sim 0.15$ e for singlet and $\sim 0.12$ e for triplet). Interestingly, the charge of the $\text{C}_2$ atom remains unaffected in the cation triplet; this behavior is similar to that encountered above in the case of the anion triplet.

**Rotational Constants**

For the linear neutral doublet, the theoretical estimates of the rotational constant $B$ significantly differ from the experimental value $B_{\text{exp}} = 2.4226963 \text{GHz}$. Based on these values for the neutral doublet, a scaling factor of 0.991937 can be deduced to make more reliable B3LYP/6-311++G(3df, 3pd)-based estimates for the $\text{C}_4\text{N}$ species not investigated so far.

Table 5 collects values of the rotational constants $B$ computed at the B3LYP/6-311++G(3df, 3pd) level of theory along with the values scaled as indicated above.
Figure 6: (a) Bond lengths (in angstrom), (b) Wiberg bond indices, (c) Wiberg valencies and (d) atomic charges of C₄N chains considered in this paper.

Table 4: Values of the vertical $\Delta_{ST}^{+} \left( R_{S,T}^{\pm} \right)$ ≡ $\mathcal{E}_{T}^{+} \left( R_{S,T}^{\pm} \right) - \mathcal{E}_{S}^{+} \left( R_{S,T}^{\pm} \right)$ and adiabatic $\Delta_{ST}^{+}\text{ad} \equiv \mathcal{E}_{T}^{+} \left( R_{T}^{\pm} \right) - \mathcal{E}_{S}^{+} \left( R_{S}^{\pm} \right)$ singlet-triplet cation splitting computed without and with corrections due to zero point motion using the cation singlet (triplet) geometries $R_{S}^{\pm} \left( R_{T}^{\pm} \right)$ optimized at the B3LYP/6-311++G(3df, 3pd) level of theory.

|                   | B3LYP  | UCCSD  | UCCSD(T) | ROCCSD | ROCCSD(T) |
|-------------------|--------|--------|----------|--------|-----------|
| $\Delta_{ST}^{+} \left( R_{S}^{\pm} \right)$ uncorrected | 1.517  | 1.489  | 1.774    | 1.527  | 1.678     |
|                  | corrected | 1.489  | 1.461    | 1.746  | 1.499     | 1.650     |
| $\Delta_{ST}^{+} \left( R_{T}^{\pm} \right)$ uncorrected | 1.046  | 1.013  | 1.334    | 1.061  | 1.245     |
|                  | corrected | 1.018  | 0.985    | 1.306  | 1.033     | 1.217     |
| $\Delta_{ST}^{+}\text{ad}$ uncorrected | 1.311  | 1.350  | 1.626    | 1.398  | 1.538     |
|                  | corrected | 1.283  | 1.322    | 1.598  | 1.370     | 1.510     |
Excepting the non-linear anion singlet, the linear conformation is responsible for the fact that the rotational constants $B$ of all the other species have values close to each other. As Table 5: Rotational constants of the $C_4N$ chains investigated in this paper computed at the B3LYP/6-311++G(3df, 3pd) level of theory and scaled as described in the main text. The value given for the bent anion represents the average of the unscaled values $B = 2.82435$ GHz and $C = 2.69945$ GHz.

| Species                | $B$ (GHz)    |
|------------------------|--------------|
| neutral doublet        | 2.44239      |
|               scaled    | 2.42270      |
| neutral quartet        | 2.46635      |
|               scaled    | 2.44646      |
| anion triplet          | 2.42267      |
|               scaled    | 2.40313      |
| bent anion singlet     | 2.73467      |
|               scaled    | 2.80158      |
| linear anion singlet   | 2.42362      |
|               scaled    | 2.40408      |
| cation singlet         | 2.44330      |
|               scaled    | 2.42360      |
| cation triplet         | 2.47931      |
|               scaled    | 2.45932      |

known from studies on many other molecular species, differences in $B$-values computed using different theoretical approaches visible in Table S15 exceed the typical experimental accuracy ($\sim 10$ kHz). Nevertheless, the differences ($> 20$ MHz) between the various $C_4N$ chains are in all cases sufficiently larger than the measurement accuracy to not impede unambiguous assignment of a certain species from data (to be) acquired in experiment.

**Vibrational Properties**

The infrared and Raman spectra of the neutral and anionic species of $C_4N$ can be compared with each other by inspecting Figure 7. The comparison between the neutral and cationic species of $C_4N$ can be made based on Figure 8.

Let us start our discussion with the highest vibrational frequency $\nu_{CN}$, which corresponds
Figure 7: (a) Infrared and (b) Raman spectra of C₄N neutral (\( \tilde{X}^2\Pi \)) and anion (\( ^3\Sigma^- \) and \( ^1A' \)) chains investigated in the present paper.

Figure 8: (a) Infrared and (b) Raman spectra of C₄N neutral (\( \tilde{X}^2\Pi \) and (\( \tilde{a}^4\Sigma^- \)) and cation (\( ^3\Sigma^+ \) and \( ^1\Sigma^+ \)) chains investigated in the present paper.
to the nitrile radical C≡N stretching, a mode known to be significantly influenced by the adjacent atoms.42

For the various species investigated, the $\nu_{CN}$-values vary within a range $\Delta\nu_{CN} < 312\,\text{cm}^{-1}$ ($2013\,\text{cm}^{-1} < \nu_{CN} < 2325\,\text{cm}^{-1}$, cf. Table S18). For a more quantitative comparison with experiment, the aforementioned values should be corrected by means of appropriate scaling factors.59,60 We do not discuss these details at length here but still mention that the corresponding values are comparable to those estimated recently for HC$_n$N chains.42 Based on various experimental data,61-65 a scaling factor of 0.945 appears appropriate for the C≡N stretching mode.

Moving to lower frequencies, the vibration ($\nu_{C_1C_2}$) can be approximately described as a stretching mode of the C$_1$C$_2$ bond. Within the various C$_4$N species considered, this vibrational frequency lies within a range $\Delta\nu_{C_1C_2} < 445\,\text{cm}^{-1}$ ($1753\,\text{cm}^{-1} < \nu_{C_1C_2} < 2198\,\text{cm}^{-1}$) broader than that for $\nu_{CN}$.

The next mode can be approximately described as an out-of-phase combination of C$_1$C$_2$ and C$_4$N stretchings whose frequency varies within a more narrow range ($\Delta\nu < 258\,\text{cm}^{-1}$, $1321\,\text{cm}^{-1} < \nu < 1579\,\text{cm}^{-1}$). The next lower frequency corresponds to a symmetric stretching (“breathing”) mode ($\Delta\nu_{breath} < 75\,\text{cm}^{-1}$, $753\,\text{cm}^{-1} < \nu_{breath} < 827\,\text{cm}^{-1}$). The lowest frequency is associated to a C$_1$-C$_3$-N bending mode corresponding to oscillations of the angle whose vertex is the C$_3$ atom, its arms being determined by C$_1$C$_2$C$_3$ and C$_3$C$_4$N: $\Delta\nu_{bent} < 52\,\text{cm}^{-1}$, $107\,\text{cm}^{-1} < \nu_{bent} < 159\,\text{cm}^{-1}$.

Modes lying between the aforementioned bending mode and the breathing mode are C$_3$C$_4$N ($369\,\text{cm}^{-1} < \nu_{C_3C_4N} < 636\,\text{cm}^{-1}$) and C$_1$C$_2$C$_3$ bending modes ($171\,\text{cm}^{-1} < \nu_{C_1C_2C_3} < 417\,\text{cm}^{-1}$) Due to the bent shape, C$_3$C$_4$N and C$_1$C$_2$C$_3$ bending modes in the stable C$_4$N$^-$ singlet yield in-phase and out-of-phase normal mode combinations. Their frequencies are $\nu_{in-phase} \approx 591\,\text{cm}^{-1}$ $\nu_{out-of-phase} \approx 457\,\text{cm}^{-1}$, respectively.

Notwithstanding the differences in charge and spin of the various species investigated, the $\nu_{CN}$-values are reasonably well correlated with the length of the C≡N bond (Figure 9a).
in spite of the fact that the bond lengths and the bond indices are not so good correlated with each other (Figure S20a).

In contrast to this, the $\nu_{C_1C_2}$-values can be simply correlated neither with the length $l_{C_1C_2}$ nor with the index $N_{C_1C_2}$ of this bond (Figure S20b). In fact, even establishing a correlation between lengths $l_{XY}$ and bond order indices $N_{XY}$ across molecular species with different charge and/or spin appears to be problematic. This is visualized in Figure S20, where possible $N$-$l$ correlations are depicted by green lines.

**Dipole and Quadrupole Moments**

Values of electric dipole momentum $\mathbf{D}$ are collected in Tables 6 and S16. Quadrupole moments $\mathbf{Q}$ are also presented (Table S17). Attention should be paid in such calculations to the fact that, for charged species, these quantities depend on the coordinate system employed. By default, GAUSSIAN rotates/translates the molecule to the so-called “Standard Orientation”, which puts the center of nuclear charge (for the most abundant isotopes $^{12}_6C$ and $^{14}_7N$ this coincides with the center of mass) at the origin of the Cartesian axes. Reported values refer to this “Standard Orientation”. For dipole calculations, the GAUSSIAN keyword “NoSymm” (used for geometry optimizations in order to unbiasedly search for absolute minima, cf. Section ”Electronic Structure and Chemical Bonding”) should not be given in the section route; otherwise the geometry utilized is that of the input file, wherein the center of charge is not necessarily at the origin of the Cartesian axes.

From computational perspective, the inspection of Table 6 and S16 reveals that spin contamination is an important challenge for unrestricted calculations to open-shell chains; the UHF-based values substantially differ from the ROHF-based values. Noteworthily, the UHF-based estimates are not uniformly affected. For the neutral C$_4$N doublet, values computed within UHF — like those reported earlier$^{14}$ (cf. Table S16) — or on top of UHF are drastically underestimated with respect to the DFT-based values, which are not notably affected by spin contamination. Albeit less pronounced, this is also the case of the cation.
Table 6: Values of the dipole momentum $\mathbf{D}$ (field independent basis, debye) of the C$_4$N chains investigated in this paper at various levels of theory using B3LYP/6-311++G(3df, 3pd) optimized geometries.

| Species           | Method                      | $D_X$ | $D_Y$ | $D_Z$ | $D_{total}$ |
|-------------------|-----------------------------|-------|-------|-------|-------------|
| neutral doublet   | B3LYP/6-311++G(3df, 3pd)    | 0.0000| 0.0000| 0.3347| 0.3347      |
|                   | UCCSD(T)/6-311++G(3df, 3pd) | 0.0000| 0.0000| 0.0907| 0.0907      |
|                   | ROCCSD(T)/6-311++G(3df, 3pd)| 0.0000| 0.0000| 0.4512| 0.4512      |
| neutral quartet   | B3LYP/6-311++G(3df, 3pd)    | 0.0000| 0.0000| 3.4628| 3.4628      |
|                   | UCCSD(T)/6-311++G(3df, 3pd) | 0.0000| 0.0000| 3.2558| 3.2558      |
|                   | ROCCSD(T)/6-311++G(3df, 3pd)| 0.0000| 0.0000| 4.5003| 4.5003      |
| anion triplet     | B3LYP/6-311++G(3df, 3pd)    | 0.0000| 0.0000| 2.9398| 2.9398      |
|                   | UCCSD(T)/6-311++G(3df, 3pd) | 0.0000| 0.0000| 4.4930| 4.4930      |
|                   | ROCCSD(T)/6-311++G(3df, 3pd)| 0.0000| 0.0000| 2.2379| 2.2379      |
| bent anion singlet| B3LYP/6-311++G(3df, 3pd)    | 0.0000| 0.5970| -2.6678| 2.7338     |
|                   | RCCSD(T)/6-311++G(3df, 3pd) | 0.0000| 0.4227| -2.5695| 2.6040     |
| linear anion singlet| B3LYP/6-311++G(3df, 3pd)   | 0.0000| 0.0000| 2.5344| 2.5344      |
|                   | RCCSD(T)/6-311++G(3df, 3pd) | 0.0000| 0.0000| 2.4302| 2.4302      |
| cation singlet    | B3LYP/6-311++G(3df, 3pd)    | 0.0000| 0.0000| 2.1890| 2.1890      |
|                   | RCCSD(T)/6-311++G(3df, 3pd) | 0.0000| 0.0000| 2.1898| 2.1898      |
| cation triplet    | B3LYP/6-311++G(3df, 3pd)    | 0.0000| 0.0000| 4.8254| 4.8254      |
|                   | UCCSD(T)/6-311++G(3df, 3pd) | 0.0000| 0.0000| 4.1447| 4.1447      |
|                   | ROCCSD(T)/6-311++G(3df, 3pd)| 0.0000| 0.0000| 6.0065| 6.0065      |
C$_4$N$^+$ triplet. By contrast, UHF-based estimates of $D$ for the neutral quartet and anion triplet are smaller than those based on ROHF, although on the other side they are closer to the DFT-based values.

The fact that all C$_4$N species possess a non-vanishing dipole momentum $D$ is particularly appealing for astronomical detection because the intensities of rotational lines scales as $D^2$. According to Table 6, the most stable anion C$_4$H$^-$ triplet chain possesses a dipole momentum roughly ten times larger than the most stable natural C$_4$H doublet. For this reason, at comparable abundances, spectral lines of C$_4$H$^-$ anion chains should be about hundred times stronger than those of their neutral counterparts. Moreover, in view of the fact that anions have an enthalpy of formation lower than neutral chains (cf. Table 13) the aforementioned factor ($\sim 100$) is likely underestimated. By and large, based on these arguments we expect that the astronomical detection of anion C$_4$N$^-$ chains will be easier than that of neutral C$_4$N$^0$ chains.

**Chemical Reactivity Indices**

Anionic $^{66,67}$ and cationic $^{68,69}$ species are important constituents of extraterrestrial environment. Therefore, the lowest electron attachment energies $EA$ (Tables 7, S19, S20, and S21) and ionization potentials $IP$ (Tables 8, S22, S23, and S24) examined in this section are quantities of central interest in astrochemistry.

Table 7 and 8 include values pertaining both to vertical and to adiabatic processes. Vertical quantities correspond to electron addition (or removal) at a given geometry, e.g. $EA_{vert}^{T_D}$ ($R_D^0$) $\equiv \mathcal{E}_D^0 (R_D^0) - \mathcal{E}_T^- (R_D^0)$ at the energy minimum ($R_D^0$) of the (most stable) neutral doublet. Adiabatic values correspond to molecular energy differences of anionic (or cationic) and neutral species computed at their own optimum geometries, e.g. $EA_{adi}^{T_D} \equiv \mathcal{E}_D^0 (R_D^0) - \mathcal{E}_T^- (R_T^-)$. The inspection of Table 7 and 8 reveals that differences between the vertical and adiabatic $EA$ and $IP$ values are very small. Accordingly, most reorganization energies $\lambda$ are small (cf. Tables S26 and S27). This is the consequence of the fact that most molecular isomers are
linear. The only notable exception is the (most stable) bent (non-linear) anion singlet ($bS$) (Figure 1).

Importantly, our CC-based estimate for the adiabatic electron affinity $E_{\text{A}}^{\text{ad}} \simeq 3.1 \text{ eV}$ (Table 7) excellently agrees with the experimental value $E_{\text{A}}^{\text{ad}}_{\text{exp}} = 3.1113 \pm 0.0010 \text{ eV}$ deduced by means of high-resolution SEVI spectroscopy. One could note in this context that inaccuracies of up to $\sim 50 \text{ meV}$ of CC-based $E_{\text{A}}$-estimates are unavoidable for present state-of-the-art of theory.

Such inaccuracies result because various single-point ab initio calculations ($\Delta$-UCCSD, $\Delta$-UCCSD(T), $\Delta$-ROCCSD, $\Delta$-ROCCSD(T), $\Delta$-QCISD, $\Delta$-QCISD(T) and $E_{\text{A}}$-EOM-CCSD) at a certain (optimum) geometry yield values slightly differ from each other (cf. Table 7). Another source of inaccuracy is the geometry utilized in single-point calculations, which is also slightly affected by the optimization procedure (B3LYP/6-311++G(3df, 3pd), PBE0/6-311++G(3df, 3pd), or M06-2X/6-311++G(3df, 3pd), cf. Tables S19, S20, and S21).

Confirming previous report, the DFT/B3LYP-based estimate (Table 7) departs from the experimental value by about 0.2 eV. This DFT-based inaccuracy — which is comparable to that found for other molecular species — may not be sufficient to derive accurate chemical reactivity indices (see below) needed for reliable astrochemical modeling.

In addition to electron affinities, ionization energies $I_{\text{P}}$ are also needed for modeling extraterrestrial environments. $I_{\text{P}}$-values of vertical and adiabatic ionization energies with and without corrections due to zero-point motion were also computed by means of the same methods utilized for $E_{\text{A}}$’s. They are reported in Tables 8, S22, S23, and S24.

Once the $I_{\text{P}}$ and $E_{\text{A}}$ values are known, other basic chemical reactivity indices can be estimated, which are important because they serve as input information for modeling astrochemical evolution of a given environment. As an example, results for the chemical hardness $\eta \equiv I_{\text{P}} - E_{\text{A}}$ are reported in Table 9 and 10. These tables include values of both “global” ($\eta_{\text{vert}}$) and “combined” hardness ($\eta_{\text{ad}}$); the former are computed using the vertical $I_{\text{Pvert}}$ and $E_{\text{Avert}}$ values, the latter are obtained from the adiabatic $I_{\text{Pad}}$ and $E_{\text{Aad}}$ values.
We chose to show this quantity (η) also because it reveals that, along with the recently examined HC$_{10}$N chain, C$_4$N is another carbon-based chain of astrochemical interest agreeing with Pearson’s conjecture. Being more stable than the neutral quartet (cf. Table 13 and Figure 10), the neutral doublet is chemically harder (η$_D$ > η$_Q$, cf. Table 9 and 10).

Table 7: Values of the vertical and adiabatic doublet-triplet electron attachment ($EA^{vert}_{TD}$ (R) ≡ $\mathcal{E}_D^0$ (R)− $\mathcal{E}_T^-$ (R) and $EA^{ad}_{TD}$ ≡ $\mathcal{E}_D^0$ (R$_D^0$)− $\mathcal{E}_T^-$ (R$_T^-$), respectively) computed using the neutral doublet R$_D^0$ and anion triplet R$_T^-$ B3LYP/6-311++G(3df, 3pd) optimum geometries without or with corrections due to zero point motion. The present B3LYP/6-311++G(3df, 3pd)-based adiabatic value ($EA^{ad}_{TD}$ = 3.274 eV) agrees with the B3LYP/aug-cc-pVTZ estimate (3.29 eV$^{20}$). The vertical uncorrected value $EA^{vert}_{TD}$ (R$_T^-$) = 1.91 eV deduced via Koopmans theorem at RHF/3-21G level$^{18}$ is drastically underestimated.

|                  | B3LYP | UCCSD | UCCSD(T) | ROCCSD | ROCCSD(T) | EOM-ROCCSD |
|------------------|-------|-------|----------|--------|-----------|------------|
| $EA^{vert}_{TD}$ (R$_D^0$) |       |       |          |        |           |            |
| uncorrected      | 3.217 | 3.077 | 3.038    | 3.003  | 2.983     | 3.027      |
| corrected        | 3.207 | 3.066 | 3.029    | 2.993  | 2.973     | 3.017      |
| $EA^{vert}_{TD}$ (R$_T^-$) |       |       |          |        |           |            |
| uncorrected      | 3.360 | 3.262 | 3.218    | 3.182  | 3.135     | 3.199      |
| corrected        | 3.350 | 3.252 | 3.208    | 3.172  | 3.124     | 3.189      |
| $EA^{ad}_{TD}$   |       |       |          |        |           |            |
| uncorrected      | 3.285 | 3.121 | 3.100    | 3.034  | 3.059     | 3.109      |
| corrected        | 3.274 | 3.111 | 3.090    | 3.024  | 3.048     | 3.099      |

Table 8: Values of the vertical and adiabatic doublet-singlet ionization energy ($IP^{vert}_{SD}$ (R) ≡ $\mathcal{E}_S^+$ (R)− $\mathcal{E}_D^0$ (R) and $IP^{ad}_{SD}$ ≡ $\mathcal{E}_S^+$ (R$_S^+$)− $\mathcal{E}_D^0$ (R$_D^0$), respectively) computed using the neutral doublet R$_D^0$ and cation singlet R$_S^+$ B3LYP/6-311++G(3df, 3pd) optimum geometries without and with corrections due to zero point motion.

|                  | B3LYP | UCCSD | UCCSD(T) | ROCCSD | ROCCSD(T) | EOM-ROCCSD |
|------------------|-------|-------|----------|--------|-----------|------------|
| $IP^{vert}_{SD}$ (R$_D^0$) |       |       |          |        |           |            |
| uncorrected      | 9.812 | 9.666 | 9.408    | 9.681  | 9.514     | 9.802      |
| corrected        | 9.852 | 9.705 | 9.448    | 9.721  | 9.554     | 9.842      |
| $IP^{vert}_{SD}$ (R$_S^+$) |       |       |          |        |           |            |
| uncorrected      | 9.780 | 9.639 | 9.396    | 9.663  | 9.493     | 9.797      |
| corrected        | 9.819 | 9.678 | 9.436    | 9.703  | 9.533     | 9.836      |
| $IP^{ad}_{SD}$   |       |       |          |        |           |            |
| uncorrected      | 9.794 | 9.631 | 9.392    | 9.646  | 9.497     | 9.783      |
| corrected        | 9.833 | 9.670 | 9.431    | 9.686  | 9.537     | 9.823      |

We do not want to end this section without making two technical remarks.

First, to improve the agreement with experiment, DFT approaches to estimate $EA$ and $IP$ often use long-range corrected functionals. To check whether this is the case of C$_4$N
Table 9: Values of the “global” (vertical) $\eta_D^{\text{vert}}$ and “combined” (adiabatic) $\eta_D^{\text{ad}}$ chemical hardness of the neutral doublet without and with corrections due to zero point motion. All geometries were optimized at the B3LYP/6-311++G(3df, 3pd) level of theory.

|         | B3LYP | UCCSD | UCCSD(T) | ROCCSD | ROCCSD(T) | EOM-ROCCSD |
|---------|-------|-------|----------|--------|-----------|------------|
| $\eta_D^{\text{vert}}$ uncorrected | 6.595 | 6.589 | 6.370 | 6.678 | 6.531 | 6.775 |
|         | corrected | 6.645 | 6.639 | 6.420 | 6.728 | 6.581 | 6.825 |
| $\eta_D^{\text{ad}}$ uncorrected | 6.509 | 6.509 | 6.292 | 6.612 | 6.438 | 6.675 |
|         | corrected | 6.559 | 6.559 | 6.342 | 6.662 | 6.489 | 6.724 |

Table 10: Values of the “global” (vertical) $\eta_Q^{\text{vert}}$ and “combined” (adiabatic) $\eta_Q^{\text{ad}}$ chemical hardness of the neutral quartet without and with corrections due to zero point motion. All geometries were optimized at the B3LYP/6-311++G(3df, 3pd) level of theory.

|         | B3LYP | UCCSD | UCCSD(T) | ROCCSD | ROCCSD(T) |
|---------|-------|-------|----------|--------|-----------|
| $\eta_Q^{\text{vert}}$ uncorrected | 4.467 | 5.093 | 4.491 | 4.952 | 4.558 |
|         | corrected | 4.488 | 5.113 | 4.512 | 4.973 | 4.579 |
| $\eta_Q^{\text{ad}}$ uncorrected | 4.175 | 4.725 | 4.148 | 4.590 | 4.208 |
|         | corrected | 4.195 | 4.746 | 4.169 | 4.611 | 4.229 |

chains, we also conducted DFT calculations using two such functionals (LC-BLYP and LC-ωPBE) embodying long-range corrections. The results presented in Tables S19 and S22 do not substantiate this expectation. The long-range corrected (lrc) LC-BLYP and LC-ωPBE functionals estimates ($EA_{lrc}^{\text{ad}} \sim 3.5$ eV) for $EA$ yield larger deviations from the experimental value ($EA_{\text{exp}}^{\text{ad}} \sim 3.1113 \pm 0.001$ eV)\textsuperscript{20} than the values ($EA_{\text{wo-lrc}}^{\text{ad}} \sim 3.3$ eV) based on the non-corrected B3LYP and PBE0 functionals. Double-hybrid functionals do not perform better; with zero-point energy corrections DSD-PBEP86/6-311++G(3df, 3pd) gives $EA^{\text{ad}} = 3.423$ eV.

Second, we noted above that spin-splitting ($\Delta_{DQ}^0$, $\Delta_{ST}^\pm$) values estimated within unrestricted CC-based approaches substantially differ from those based on restricted open shell approaches. By contrast, similar to other cases,\textsuperscript{41,71} spin contamination does not appear to be an issue for $IP$ and $EA$; UCC-based values do not notably differ from those obtained within ROCC approaches.
**C₄N⁻ versus HC₄N⁰**

The C₄N⁻ and HC₄N chains are isoelectronic. For this reason, it may be not surprising that they both have spin triplet ground states. Likewise, their most stable singlet state is a bent conformer (Figures 1 and S9).

Surprisingly, notwithstanding these qualitative similarities, quantitative differences between their properties are significant. This holds for all properties: structural (Table 11), electronic (Tables S25, S9, and S10) and vibrational (Figures S14 and S15).

Let us refer to a few specific aspects. As visible in Figures S10a, S11a, S12a, and S13a, bond lengths differences can amount up to 0.05 Å, as the case of the C₁C₂ bond at the molecular end opposite to the N atom. This is associated with a substantial change in the (fractional) valence state of the C₁ atom (Figures S10c, S11c, S12c, and S13c). Noteworthily, the other molecular end is also affected; see, for example, the charge of the N atom both in singlet (Figures S10d and S12d) and triplet (Figures S11d and S13d) states. Again, in spite of their isoelectronicity, both infrared and Raman spectra of HC₄N⁰ are significantly different from those of C₄N⁻; compare Figures S14a and S14b and Figures S15a and S15b, respectively.

Table 11: Results for the isoelectronic molecular pair (C₄N⁻, HC₄N) geometries optimized at the B3LYP/6-311++G(3df, 3pd) level of theory without imposing symmetry constraints. Bond lengths \( l \) between atoms XY (in angstrom), angles \( \alpha \) between atoms \( \overline{XYZ} \) (in degrees) and Wiberg bond order indices \( \mathcal{N} \).

| Species              | Property | C₁C₂ | C₁C₂C₃ | C₂C₃ | C₂C₃C₄ | C₃C₄ | C₃C₄N | C₄N |
|----------------------|----------|------|--------|------|--------|------|-------|-----|
| stable bent C₄N⁻ singlet | \( l, \alpha \) | 1.2780 | 174.3 | 1.3295 | 125.7 | 1.3846 | 171.4 | 1.1702 |
|                      | \( \mathcal{N} \) | 2.1785 | 1.6978 | 1.2309 |       |       |       | 2.6995 |
| HC₄N singlet         | \( l, \alpha \) | 1.2267 | 172.5 | 1.3353 | 127.5 | 1.3645 | 173.2 | 1.1682 |
|                      | \( \mathcal{N} \) | 2.4495 | 1.4297 | 1.2551 |       |       |       | 2.6754 |
| linear C₄N⁻ triplet  | \( l, \alpha \) | 1.2912 | 179.8 | 1.2917 | 178.7 | 1.3193 | 180.0 | 1.1874 |
|                      | \( \mathcal{N} \) | 1.8987 | 1.8251 | 1.3182 |       |       |       | 2.5775 |
| HC₄N triplet         | \( l, \alpha \) | 1.2406 | 179.8 | 1.2920 | 178.8 | 1.3181 | 179.9 | 1.1790 |
|                      | \( \mathcal{N} \) | 2.4537 | 1.4572 | 1.2929 |       |       |       | 2.6509 |

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Table 12: Values of the dipole momentum $\mathbf{D}$ (field independent basis, debye) of the isoelectronic $\text{C}_4\text{N}^-$ and $\text{HC}_4\text{N}$ chains at various levels of theory.

| Species       | Method                  | $D_X$  | $D_Y$  | $D_Z$  | $D_{total}$ |
|---------------|-------------------------|--------|--------|--------|-------------|
| $\text{C}_4\text{N}^-$ triplet | B3LYP/6-311++G(3df, 3pd) | 0.0000 | 0.0000 | 2.9398 | 2.9398      |
|               | B3LYP/aug-cc-pVTZ       | 0.0000 | 0.0000 | 2.9400 | 2.9400      |
|               | UCCSD(T)/6-311++G(3df, 3pd) | 0.0000 | 0.0000 | 4.5215 | 4.5215      |
|               | UCCSD(T)/aug-cc-pVTZ    | 0.0000 | 0.0000 | 4.5002 | 4.5002      |
|               | ROCCSD(T)/6-311++G(3df, 3pd) | 0.0000 | 0.0000 | 2.2379 | 2.2379      |
|               | ROCCSD(T)/aug-cc-pVTZ   | 0.0000 | 0.0000 | 2.2447 | 2.2447      |
| $\text{HC}_4\text{N}$ triplet   | B3LYP/6-311++G(3df, 3pd) | 0.0000 | 0.0000 | 4.3495 | 4.3495      |
|               | B3LYP/aug-cc-pVTZ       | 0.0000 | 0.0000 | 4.3460 | 4.3460      |
|               | UCCSD(T)/6-311++G(3df, 3pd) | 0.0000 | 0.0000 | 4.0705 | 4.0705      |
|               | UCCSD(T)/aug-cc-pVTZ    | 0.0000 | 0.0000 | 4.0656 | 4.0656      |
|               | ROCCSD(T)/6-311++G(3df, 3pd) | 0.0000 | 0.0000 | 4.6327 | 6.6327      |
|               | ROCCSD(T)/aug-cc-pVTZ   | 0.0000 | 0.0000 | 4.6267 | 4.6267      |
| bent $\text{C}_4\text{N}^-$ singlet | B3LYP/6-311++G(3df, 3pd) | 0.0000 | 0.5970 | -2.6678 | 2.7338      |
|               | B3LYP/aug-cc-pVTZ       | 0.0000 | 0.5970 | -2.6678 | 2.7338      |
|               | RCCSD(T)/6-311++G(3df, 3pd) | 0.0000 | 0.4227 | -2.5695 | 2.6040      |
|               | RCCSD(T)/aug-cc-pVTZ    | 0.0000 | 0.4233 | -2.5714 | 2.6061      |
| $\text{HC}_4\text{N}$ singlet     | B3LYP/6-311++G(3df, 3pd) | 0.0000 | -1.0005 | 4.1944 | 4.3121      |
|               | B3LYP/aug-cc-pVTZ       | 0.0000 | -1.0020 | 4.1968 | 4.3148      |
|               | RCCSD(T)/6-311++G(3df, 3pd) | 0.0000 | -1.1285 | 4.4508 | 4.5916      |
|               | RCCSD(T)/aug-cc-pVTZ    | 0.0000 | -1.1300 | 4.4518 | 4.5929      |

Figure 9: Correlation between the vibrational frequency of the nitrile group CN stretching mode and the CN and $\text{C}_1\text{C}_2$ bond lengths (panels a and b, respectively).
Chemical Stability and Potential Chemical Pathways of Formation

To address the problem of chemical stability, we first calculated relevant enthalpies of formation $\Delta_f^0 H_x$'s. Values at zero ($x = 0$) and at room ($x = RT$) temperature are presented in Table 13 and Figure 10. According to Figure 10a, the enthalpies of formation for spin doublets — which are the most stable states of the neutral chains — linearly increase with the chain size ($n$).

Table 13: Enthalpies of Formation of Carbon Chains Discussed in This Paper at zero (Subscript 0) and Room Temperature (Subscript RT) Computed by Using CBS-QB3 Protocol. All values in kcal/mol. Values at RT for Anions Computed Using the ion convention (see, e.g., https://webbook.nist.gov/chemistry/ion/#A.) Notice that the values in this table are those corrected in ref. 72 which are somewhat different from those of ref. 73.

| Species      | $\Delta_f^0 H^0$ | $\Delta_f^0 H^{RT}$ |
|--------------|------------------|---------------------|
| $C_3N^0$ doublet | 175.502          | 178.540             |
| $C_4N^0$ doublet | 206.071          | 209.938             |
| $C_5N^0$ doublet | 231.981          | 235.726             |
| $C_3N^-$ singlet  | 72.856           | 75.820              |
| $C_4N^-$ triplet  | 133.775          | 137.288             |
| $C_5N^-$ singlet  | 123.892          | 127.992             |

Figure 10: Enthalpies of formation of neutral $C_nN^0$ and anion $C_nN^-$ chains (panel a and b, respectively).

A similar conclusion emerges from the inspection of the lower part of Table 13 where the values for the most stable anionic species are presented. Because the values for the $C_4N^-$ (triplet) chains are smaller than those for the longer (singlet) $C_5N^-$ chains — which were
already reported in space\textsuperscript{10} — one can still hope that they are observable. The results for enthalpies of formation (Table 13 and Figure 10b) indicate again that C\textsubscript{4}N\textsuperscript{−} triplet chains are more stable than C\textsubscript{4}N\textsuperscript{−} singlet chains, in contrast to C\textsubscript{3}N\textsuperscript{−} and C\textsubscript{5}N\textsuperscript{−}, for which singlets are more stable than triplets, in agreement with the odd-even singlet-triplet alternation reported earlier for the C\textsubscript{n}N\textsuperscript{−} homologous series\textsuperscript{10} as well as for its HC\textsubscript{n}N isoelectronic counterpart.\textsuperscript{42,58}

So, the above results suggest that neutral C\textsubscript{4}N\textsuperscript{0} chains can still be observed in space; the values for C\textsubscript{4}N chains are smaller than for the longer C\textsubscript{5}N chains already astronomically detected.\textsuperscript{4} This result is supported by the fact that in laboratory molecular beam C\textsubscript{4}N was indeed produced more abundantly than C\textsubscript{5}N.\textsuperscript{42} We next checked that neutral C\textsubscript{4}N chains are stable against dissociation. Our calculations indicated that all possible dissociation processes (reactions 1 to 4 in Tables 14 and S28) are endoenergetic. The same holds true for anion’s dissociation; reactions 5 to 8 in the same Tables 14 and S28 are also endoenergetic. In particular, this rules out a (n a priori conceivable) fragmentation of the not yet detected C\textsubscript{4}N\textsuperscript{0} and C\textsubscript{4}N\textsuperscript{−} into already astronomically observed C\textsubscript{3}N\textsuperscript{0} and C\textsubscript{3}N\textsuperscript{−} or C\textsubscript{2}N\textsuperscript{0}.
Table 14: Dissociation of neutral and anion C$_4$N chains. Enthalpies of reaction at zero (subscript 0) and room temperature (subscript RT) computed by using CBS-QB3 protocol. All values (in kcal/mol) refer to the electronic ground states.

| No. | Species | Reaction     | $\Delta_r H^0_0$ | $\Delta_r H^0_{RT}$ |
|-----|---------|--------------|------------------|---------------------|
| 1   | C$_4$N  | C$_4$N $\rightarrow$ C + C$_3$N | 139.4            | 140.1               |
| 2   | C$_4$N  | C$_4$N $\rightarrow$ C$_2$ + C$_2$N | 152.0            | 152.8               |
| 3   | C$_4$N  | C$_4$N $\rightarrow$ C$_3$ + CN | 95.3             | 96.4                |
| 4   | C$_4$N  | C$_4$N $\rightarrow$ C$_4$ + N | 159.6            | 160.5               |
| 5a  | C$_4$N$^-$ | C$_4$N$^-$ $\rightarrow$ C + C$_3$N$^-$ | 109.1            | 109.4               |
| 5b  | C$_4$N$^-$ | C$_4$N$^-$ $\rightarrow$ C$^-$ + C$_3$N | 184.4            | 185.4               |
| 6a  | C$_4$N$^-$ | C$_4$N$^-$ $\rightarrow$ C$_2$ + C$_2$N$^-$ | 160.6            | 161.6               |
| 6b  | C$_4$N$^-$ | C$_4$N$^-$ $\rightarrow$ C$_2$ + C$_2$N$^-$ | 151.0            | 152.1               |
| 7a  | C$_4$N$^-$ | C$_4$N$^-$ $\rightarrow$ C$_3$ + CN$^-$ | 77.6             | 79.0                |
| 7b  | C$_4$N$^-$ | C$_4$N$^-$ $\rightarrow$ C$_3$ + CN$^-$ | 122.0            | 123.3               |
| 8a  | C$_4$N$^-$ | C$_4$N$^-$ $\rightarrow$ C$_4$ + N$^-$ | 238.1            | 239.4               |
| 8b  | C$_4$N$^-$ | C$_4$N$^-$ $\rightarrow$ C$_4$ + N$^-$ | 141.8            | 142.8               |

Furthermore, our values for bond dissociation enthalpies do not support claims that C$_4$N is less stable than the already detected C$_2$N, C$_3$N and C$_5$N. For illustration, let us consider the bond breaking at molecular ends. The values presented in Tables 14, S28, 15, and S29 reveal that breaking the end C≡N bond in C$_4$N requires a significantly larger energy than in all (C$_2$N, C$_3$N and C$_5$N) already astronomically detected members of the homologous series C$_n$N.$^{4,12,74}$ Switching to the opposite molecular end, removing the terminal C atom of C$_4$N$^0$ requires an energy larger than for C$_2$N$^0$ and comparable to that for C$_5$N$^0$ (cf. reactions 9a and 12a in Tables 15 and S29), respectively. The same conclusion emerges from the direct comparison of the structural and chemical properties of C$_3$N, C$_4$N, and C$_5$N presented in detail in Figures S1, S2, S3, and S4.

To sum up, the foregoing analysis indicates that C$_4$N nonobservability in space cannot be due to molecule’s fragmentation; none of the above processes involves an unusually low dissociation energy.

Putting differently, the stability against dissociation says that all converse (association) reactions depicted in Tables 14 and S28 are exoenergetic. That is, they represent poten-
Table 15: Dissociation of neutral C$_2$N, C$_3$N, and C$_5$N chains already detected in space. Enthalpies of reaction at zero (subscript 0) and room temperature (subscript RT) computed by using CBS-QB3 protocol. All values (in kcal/mol) refer to the electronic ground states.

| No. | Species | Reaction | $\Delta_r H_0^0$ | $\Delta_r H_0^{RT}$ |
|-----|---------|----------|------------------|---------------------|
| 9a  | C$_2$N  | C$_2$N $\rightarrow$ C + CN | 113.4 | 114.4 |
| 9b  | C$_2$N  | $\rightarrow$ C$_2$ + N | 145.8 | 146.8 |
| 10a | C$_3$N  | C$_3$N $\rightarrow$ C + C$_2$N | 156.8 | 157.9 |
| 10b | C$_3$N  | $\rightarrow$ C$_2$ + CN | 126.0 | 127.1 |
| 10c | C$_3$N  | $\rightarrow$ C$_3$ + N | 132.6 | 134.0 |
| 12a | C$_5$N  | C$_5$N $\rightarrow$ C + C$_4$N | 144.1 | 145.7 |
| 12b | C$_5$N  | $\rightarrow$ C$_2$ + C$_3$N | 139.2 | 140.6 |
| 12c | C$_5$N  | $\rightarrow$ C$_3$ + C$_2$N | 126.0 | 127.8 |
| 12d | C$_5$N  | $\rightarrow$ C$_4$ + CN | 126.9 | 128.6 |
| 12e | C$_5$N  | $\rightarrow$ C$_5$ + N | 135.8 | 137.3 |

Tentative chemical pathways of C$_4$N$^0$/C$_4$N$^-$ formation from precursors already reported in space (CN, C$_2$N, C$_3$N, C$_2$H, C$_3$H, C$_4$H, and C$_4$H$^-$ were also astronomically observed) presented in Tables 16, S30, S31, and S32 are chemical pathways of production that come into question. Along with exoenergetic exchange reactions (which may also be problematic without third party energy removal), we also included there several endoenergetic processes (e.g., reactions 13, 14a, 15e, 17d, and 17e) corresponding to small or moderate (positive) reaction energies; they are significant for reactants in electronic excited states.

Technical Remark on the Complete Basis Set (CBS) Approaches

To compute enthalpies of formation and reaction energies (cf. Section “Chemical Stability and Potential Chemical Pathways of Formation”), GAUSSIAN 16 allows choosing between several complete basis set protocols: CBS-4M, CBS-APNO, and CBS-QB3. The first is recommended for new studies. In some cases, the second attains a root mean square deviation $RMSD_{CBS-APNO} = 1.16$ kcal/mol, which is better than $RMSD_{CBS-QB3} = 2.27$ kcal/mol. One may therefore wonder why we have presented in the main text numer-
Table 16: Relevant exchange reactions. Enthalpies of reaction at zero (subscript 0) and room temperature (subscript RT) computed by using CBS-QB3 protocol. All values (in kcal/mol) refer to the electronic ground states.

| No. | Reaction | $\Delta_r H_0$ | $\Delta_r H_{RT}$ |
|-----|----------|----------------|------------------|
| 13  | $C_5 + N \rightarrow C + C_{4N}$ | 8.3 | 8.4 |
| 14a | $N + C_{4H}^- \rightarrow C_{4N} + H^-$ | 23.9 | 24.3 |
| 14b | $N^- + C_{4H} \rightarrow C_{4N}^- + H$ | -36.0 | -35.9 |
| 14c | $N^- + C_{4H} \rightarrow C_{4N}^- + H$ | -125.0 | -124.8 |
| 14d | $N^- + C_{4H} \rightarrow C_{4N} + H^-$ | -65.1 | -64.6 |
| 15a | $CN + C_3H \rightarrow H + C_{4N}$ | -20.5 | -20.4 |
| 15b | $CN^- + C_3H \rightarrow H + C_{4N}^-$ | -2.8 | -3.0 |
| 15c | $CN^- + C_3H \rightarrow H^- + C_{4N}$ | 57.1 | 57.2 |
| 15d | $CN + C_3H^- \rightarrow H + C_{4N}^-$ | -50.9 | -50.8 |
| 15e | $CN + C_3H^- \rightarrow H^- + C_{4N}$ | 9.0 | 9.4 |
| 16a | $CH + C_3N \rightarrow H + C_{4N}$ | -59.4 | -59.2 |
| 16b | $CH^- + C_3N \rightarrow H^- + C_{4N}^-$ | -105.6 | -105.8 |
| 16c | $CH^- + C_3N \rightarrow H^+ + C_{4N}$ | -45.8 | -45.5 |
| 16d | $CH + C_3N^- \rightarrow H + C_{4N}^-$ | -29.1 | -29.1 |
| 17a | $CH + C_3N^- \rightarrow H^- + C_{4N}$ | 30.8 | 31.1 |
| 17b | $C_2H + C_2N \rightarrow H + C_{4N}$ | -40.5 | -40.3 |
| 17c | $C_2H^- + C_2N \rightarrow H + C_{4N}^-$ | -44.6 | -44.5 |
| 17d | $C_2H^- + C_2N \rightarrow H^- + C_{4N}$ | 15.3 | 15.7 |
| 17e | $C_2H + C_2N^- \rightarrow H^- + C_{4N}$ | 10.8 | 11.2 |
| 17f | $C_2H + C_2N^- \rightarrow H + C_{4N}^-$ | -49.1 | -49.0 |
| 18  | $NC_2N + C_2 \rightarrow N + C_{4N}$ | 48.6 | 49.0 |
| 19  | $NC_2N + C_2N \rightarrow N_2 + C_{4N}$ | -29.8 | -29.3 |
| 20  | $NC_2N + C_2H \rightarrow NH + C_{4N}$ | 82.3 | 82.7 |
ical values obtained via the “less” performant CBS-QB3 protocol, and put CBS-4M- and CBS-APNO-based estimates in the SI.

To justify this preference, CBS-based values of the adiabatic electron affinity $E_{A_{CBS}}$ for all even-members ($C_2N$, $C_4N$, and $C_6N$) of astrophysical interest are shown in Table 17. In these calculations, $E_{A_{CBS}}$ was estimated as an energy of reaction ($C_n N^− \xrightarrow{E_A = \Delta_e H_0^0} C_n N^0 + e^−$). For completeness, adiabatic ionization potentials $I_{P_{CBS}}$ estimated in a similar manner ($C_n N^0 \xrightarrow{I_P = \Delta_e H_0^0} C_n N^+ + e^−$) are also shown (cf. Table S33).

We focused on the adiabatic electron affinity because it is the only quantity that can be compared with high accuracy SEVI experimental data. The comparison reveals that for this quantity — which is notoriously problematic even for small normal (nonradical) carbon-based chains — the CBS-QB3 protocol attains the best agreement with experiment.

One should still aid that values of the energy of reactions computed by means of CBS-APNO and CBS-4M (cf. Tables S28, S29, S30, S31, and S32) do not notably differ from those based on CBS-QB3. Most importantly, they do by no means change the above conclusions on $C_4N$’s stability and formation pathways.

Table 17: Adiabatic electron affinities of $C_2N$, $C_4N$ and $C_6N$ radicals measured in high-resolution SEVI experiments and computed using several CBS protocols. All values are in eV. Notice that the CBS-QB3 estimates are the closest to experiment. The root mean square deviations are $\text{RMSD}_{CBS-QB3} = 0.862$ kcal/mol, $\text{RMSD}_{CBS-APNO} = 1.841$ kcal/mol, and $\text{RMSD}_{CBS-4M} = 4.538$ kcal/mol.

| Method   | $C_2N$         | $C_4N$         | $C_6N$         |
|----------|----------------|----------------|----------------|
| Experiment | $E_A$ (eV) | $E_A$ (eV) | $E_A$ (eV) |
| CBS-QB3 | 2.7489 ± 0.0010 | 3.1113 ± 0.0010 | 3.3715 ± 0.0010 |
| CBS-APNO | 2.7615 | 3.1351 | 3.4804 |
| PBS-4M | 2.921 | 0.549 | 2.511 |
| CBS-APNO | 2.7728 | 3.2506 | 3.5648 |
| CBS-4M | 0.551 | 3.212 | 4.458 |
| CBS-APNO | 3.0115 | 3.4596 | 3.7693 |
| CBS-4M | 6.056 | 8.032 | 9.173 |
Conclusions

In closing, our results for electronic structure, chemical bonding, and chemical stability do not substantiate claims (made explicitly or implicitly in previous literature on similar molecular species) that even $C_nN$ chains are less stable than odd members to justify why the former were not detected in space; Figure 10 shows that the point for the neutral $C_4N$ chain lies exactly on the line joining the points for neutral $C_3N$ and neutral $C_5N$ chains which were already astronomically observed.

The present investigation demonstrates that whether neutral or charged, all $C_4N$ chains possess strongly delocalized structures. In particular, in spite of the significantly different atomic ionization energies ($IP_C = 11.26\,eV$ versus $IP_N = 14.53\,eV$) electron removal also affects the charge of the nitrogen atom (Figures 2d and S7d). Furthermore, the excess electron attached to a neutral chain does not preponderantly go to the N atom (Figures 3d and S8d), although this element is more electronegative than the C atoms ($\chi_{Pauling}^N = 3.04$ versus $\chi_{Pauling}^C = 2.55$). Interestingly, it is the same group of atoms ($C_1$, $C_3$, and N) that shares more or less democratically both the hole created by ionization and the excess electron attached to the neutral chain.

The fact that, for all even-members ($C_2N$, $C_4N$, $C_6N$) of astrophysical interest, the present theoretical estimate for electron affinity $EA$ excellently agrees with experiment is another significant report. $EA$-data for molecular species of astrochemical interest are very scarce; even values for small “normal” (i.e., nonradical) cyanopolyynes continue to be missing. Even for small(er) carbon chains, accurate $EA$-estimates are very challenging for theory.

Last but not least, our results suggest that astronomical detection should first focus on anion $C_4N^-$ chains rather than on neutral $C_4N^0$ chains. Letting alone their substantially lower enthalpy of formation (cf. Table 13 and Figure 10), at comparable abundances, $C_4N^-$ anions should be much easier detectable than neutrals via rotational transition spectroscopy. More quantitatively, in view of the different dipole momenta presently estimated (Table 6), $C_4N^-$ anions transition intensities should be about hundred times stronger than for neutral
chains. Distinguishing between neutral and anion C₄N chains also appears to be feasible; the difference between the estimated rotational constants (Table 5) exceeds by far the experimental resolution currently achieved. More specific astrophysical details are presented separately.⁸⁷

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Appendix

This appendix presents additional theoretical and computational details, additional tables and figures.

Figure S1: Bond lengths (in angstrom) of neutral C\textsubscript{4}N, C\textsubscript{4}N, and C\textsubscript{5}N chains in their electronic ground state.

Figure S2: Wiberg bond indices of neutral C\textsubscript{4}N, C\textsubscript{4}N, and C\textsubscript{5}N chains in their electronic ground state.

Table S1: Cartesian coordinates (in angstrom), natural charges and Wiberg valencies of the atoms of the (most stable) C\textsubscript{4}N\textsuperscript{0} neutral doublet (\( \tilde{X}^2\Pi \)).

| Atom | X       | Y       | Z       | charge  | valence |
|------|---------|---------|---------|---------|---------|
| C\textsubscript{1} | 0.000000 | 0.000000 | 2.65410363 | 0.27537 | 1.6424  |
| C\textsubscript{2} | 0.000000 | 0.000000 | 1.33769693 | -0.34620 | 3.8239  |
| C\textsubscript{3} | 0.000000 | 0.000000 | 0.08416284 | 0.09058 | 3.6263  |
| C\textsubscript{4} | 0.000000 | 0.000000 | -1.25284849 | 0.17730 | 3.9745  |
| N     | 0.000000 | 0.000000 | -2.41981278 | -0.19705 | 2.9459  |
Figure S3: Wiberg valencies of neutral C\textsubscript{4}N, C\textsubscript{4}N, and C\textsubscript{5}N chains in their electronic ground state.

Figure S4: Atomic charges of neutral C\textsubscript{4}N, C\textsubscript{4}N, and C\textsubscript{5}N chains in their electronic ground state.

Figure S5: HOMO of neutral doublet C\textsubscript{3}N\textsuperscript{0}, C\textsubscript{4}N\textsuperscript{0}, and C\textsubscript{5}N\textsuperscript{0} chains.

Figure S6: LUMO of neutral doublet C\textsubscript{3}N\textsuperscript{0}, C\textsubscript{4}N\textsuperscript{0}, and C\textsubscript{5}N\textsuperscript{0} chains.
Figure S7: Changes with respect to the neutral doublet C$_4$N$^0$ of several molecular properties: (a) bond lengths (in angstrom), (b) Wiberg bond order indices, (c) Wiberg valencies and (d) atomic charges.

Table S2: Cartesian coordinates (in angstrom), natural charges and Wiberg valencies of the atoms of the (metastable) C$_4$N$^0$ neutral quartet ($\tilde{\alpha}^4\Sigma^-$).

| Atom | X    | Y    | Z         | charge | valence |
|------|------|------|-----------|--------|---------|
| C$_1$| 0.000000 | 0.000000 | -2.61882889 | 0.38999 | 1.5361  |
| C$_2$| 0.000000 | 0.000000 | -1.36043777 | -0.25338 | 3.9155  |
| C$_3$| 0.000000 | 0.000000 | -0.08294868 | -0.08296 | 3.3536  |
| C$_4$| 0.000000 | 0.000000 | 1.24266035  | 0.21504 | 3.9845  |
| N    | 0.000000 | 0.000000 | 2.41676142  | -0.26869 | 2.9311  |

Table S3: Cartesian coordinates (in angstrom), natural charges and Wiberg valencies of the atoms of the (most stable) bent C$_4$N$^-$ singlet ($^1A'$).

| Atom | X    | Y    | Z         | charge | valence |
|------|------|------|-----------|--------|---------|
| C$_1$| 2.452143 | -0.396162 | 0.0000000  | -0.12258 | 2.4933  |
| C$_2$| 1.261801 | 0.069056 | 0.0000000  | -0.46722 | 3.9608  |
| C$_3$| 0.078147 | 0.674522 | 0.0000000  | -0.20040 | 3.3211  |
| C$_4$| -1.153197 | 0.041285 | 0.0000000  | 0.26342 | 3.9784  |
| N    | -2.261910 | -0.333173 | 0.0000000  | -0.47322 | 2.9340  |
Figure S8: Changes with respect to the neutral doublet $C_4N^0$ of several molecular properties: (a) bond lengths (in angstrom), (b) Wiberg bond order indices, (c) Wiberg valencies and (d) atomic charges.

Table S4: Cartesian coordinates (in angstrom), natural charges and Wiberg valencies of the atoms of the (metastable, nearly) linear $C_4N^-\text{singlet (}^1\Sigma^-\text{)}$.

| Atom | X       | Y       | Z       | charge   | valence |
|------|---------|---------|---------|----------|---------|
| C_1  | 5.057640| 0.060822| 0.000000| -0.16047 | 2.4257  |
| C_2  | 3.768464| 0.050142| 0.000000| -0.39695 | 3.9445  |
| C_3  | 2.475903| 0.039685| 0.000000| -0.15945 | 3.6447  |
| C_4  | 1.158166| 0.029423| 0.000000| 0.20914  | 3.9811  |
| N    | -0.030173| 0.019929| 0.000000| -0.49227 | 2.8156  |

Table S5: Cartesian coordinates (in angstrom), natural charges and Wiberg valencies of the atoms of the most stable linear $C_4N^-\text{triplet (}^3\Sigma^-\text{)}$.

| Atom | X        | Y        | Z        | charge   | valence |
|------|----------|----------|----------|----------|---------|
| C_1  | 0.000000 | 0.000000 | -2.65415168| -0.17449 | 1.9735  |
| C_2  | 0.000000 | 0.000000 | -1.36306952| -0.32969 | 3.8275  |
| C_3  | 0.000000 | 0.000000 | -0.07146272| -0.24430 | 3.2586  |
| C_4  | 0.000000 | 0.000000 | 1.24775715 | 0.27001  | 3.9430  |
| N    | 0.000000 | 0.000000 | 2.43504970 | -0.52154 | 2.7338  |
Table S6: Cartesian coordinates (in angstrom), natural charges and Wiberg valencies of the atoms of the linear singlet C\(_{4}N^+\) cation \((^1\Sigma^+)\).

| Atom | X     | Y     | Z            | charge   | valence |
|------|-------|-------|--------------|----------|---------|
| C\(_1\) | 0.000000 | 0.000000 | 2.66019710 | 0.85764  | 1.6873  |
| C\(_2\) | 0.000000 | 0.000000 | 1.32621289 | -0.58628 | 3.8834  |
| C\(_3\) | 0.000000 | 0.000000 | 0.08794830 | 0.57113  | 3.8399  |
| C\(_4\) | 0.000000 | 0.000000 | -1.25330642| 0.03453  | 3.9900  |
| N     | 0.000000 | 0.000000 | -2.41804446| 0.12297  | 3.0149  |

Table S7: Cartesian coordinates (in angstrom), natural charges and Wiberg valencies of the atoms of the (metastable) linear triplet C\(_{4}N^+\) cation \((^3\Sigma^+)\).

| Atom | X     | Y     | Z            | charge   | valence |
|------|-------|-------|--------------|----------|---------|
| C\(_1\) | 0.000000 | 0.000000 | 2.61065996 | 0.81831  | 1.9491  |
| C\(_2\) | 0.000000 | 0.000000 | 1.35771105 | -0.37213 | 3.8271  |
| C\(_3\) | 0.000000 | 0.000000 | 0.08308407 | 0.39549  | 3.4954  |
| C\(_4\) | 0.000000 | 0.000000 | -1.23722188| 0.06271  | 3.9643  |
| N     | 0.000000 | 0.000000 | -2.41219988| 0.09561  | 2.8723  |

Table S8: Bond metric data for C\(_{4}N\) chains at geometries optimized using several exchange-correlation functionals and basis sets. Bond lengths \(l\) between atoms XY (in angstrom), angles \(\alpha\) between atoms \(\hat{X}YZ\) (in degrees). Whenever angles between adjacent bonds are indicated, the geometries were optimized without imposing symmetry constraints.

| Species      | Method            | Property  | \(C_1C_2\) | \(C_2C_3\) | \(C_3C_4\) | \(C_4N^0\) | \(C_4N^+\) |
|--------------|-------------------|-----------|-------------|-------------|-------------|-------------|-------------|
| bent C\(_4N^0\) singlet | RB3LYP/6-311++G(3df, 3pd) | \(l, \alpha\) | 1.2780 | 174.3 | 1.3295 | 125.7 | 1.3846 | 171.4 | 1.1702 |
| C\(_4N^0\) triplet | RB3LYP/6-311++G(3df, 3pd) | \(l, \alpha\) | 1.2792 | 174.3 | 1.3287 | 125.0 | 1.3847 | 171.6 | 1.1688 |
| C\(_4N^0\) doublet | UB3LYP/6-311++G(3df, 3pd) | \(l, \alpha\) | 1.2924 | 178.8 | 1.3262 | 127.8 | 1.3393 | 172.0 | 1.1929 |
| C\(_4N^0\) quartet | UB3LYP/6-311++G(3df, 3pd) | \(l, \alpha\) | 1.3165 | 179.8 | 1.2536 | 178.8 | 1.3371 | 180.0 | 1.1670 |
| C\(_4N^0\) singlet | UB3LYP/6-311++G(3df, 3pd) | \(l, \alpha\) | 1.3169 | 179.8 | 1.2537 | 178.8 | 1.3377 | 180.0 | 1.1671 |
| C\(_4N^+\) cation | UB3LYP/6-311++G(3df, 3pd) | \(l, \alpha\) | 1.3193 | 179.8 | 1.2522 | 178.8 | 1.3386 | 180.0 | 1.1653 |
| C\(_4N^+\) triplet | UB3LYP/6-311++G(3df, 3pd) | \(l, \alpha\) | 1.3258 | 179.8 | 1.2530 | 178.8 | 1.3394 | 180.0 | 1.1539 |
| C\(_4N^+\) singlet | UB3LYP/6-311++G(3df, 3pd) | \(l, \alpha\) | 1.3343 | 178.8 | 1.2383 | 179.7 | 1.3413 | 179.6 | 1.1648 |
| C\(_4N^+\) triplet | UB3LYP/6-311++G(3df, 3pd) | \(l, \alpha\) | 1.3345 | 179.8 | 1.2741 | 179.6 | 1.3421 | 179.7 | 1.1638 |

S6
Figure S9: Geometries of singlet and triplet HC$_4$N chains (left and right panels, respectively) investigated in the present paper.

Table S9: Natural charges and Wiberg valencies of the atoms of the bent stable HC$_4$N (second and third columns) and C$_4$N$^-$ (fourth and fifth columns) singlets.

| Atom | charge | valence | charge | valence |
|------|--------|---------|--------|---------|
| H    | 0.23992| 0.9448  | —      | —       |
| C$_1$| -0.02018| 3.6818  | -0.12258| 2.4933  |
| C$_2$| -0.19260| 3.9373  | -0.46722| 3.9608  |
| C$_3$| 0.06473 | 3.0972  | -0.20040| 3.3211  |
| C$_4$| 0.15035 | 3.9731  | 0.26342 | 3.9784  |
| N    | -0.24222| 2.9193  | -0.47322| 2.9340  |

Table S10: Natural charges and Wiberg valencies of the atoms of the stable HC$_4$N (second and third columns) and C$_4$N$^-$ (fourth and fifth columns) triplets.

| Atom | charge | valence | charge | valence |
|------|--------|---------|--------|---------|
| H    | 0.24010| 0.9448  | —      | —       |
| C$_1$| -0.06097| 3.4399  | -0.17449| 1.9735  |
| C$_2$| -0.21113| 3.9731  | -0.32969| 3.8275  |
| C$_3$| 0.16184 | 2.8127  | -0.24430| 3.2586  |
| C$_4$| 0.14022| 3.9897  | 0.27001 | 3.9430  |
| N    | -0.27006| 2.7173  | -0.52154| 2.7338  |
Figure S10: (a) Bond lengths (in angstrom), (b) Wiberg bond indices, (c) Wiberg valencies and (d) atomic charges of the isoelectronic HC\textsubscript{4}N and C\textsubscript{4}N\textsuperscript{−} singlet bent chains considered in this paper.

Table S11: Values of the vertical and adiabatic doublet-quartet splitting ($\Delta_{DQ}^0 (R_{D,Q}) = \mathcal{E}_Q^0 (R_{D,Q}^0) - \mathcal{E}_{DQ}^0 (R_{D,Q}^0)$) and $\Delta_{DQ}^{0,ad} \equiv \mathcal{E}_Q^0 (R_{Q}^0) - \mathcal{E}_D^0 (R_{D}^0)$, respectively) computed without and with corrections due to zero point motion at geometries ($R_{x}^0, x = D, Q$) optimized using the largest Pople basis sets 6-311++G(3df, 3pd) and several exchange-correlation functionals.

|                  | B3LYP | PBE0 | M06-2X |
|------------------|-------|------|--------|
| $\Delta_{DQ}^0 (R_D^0)$ |       |      |        |
| uncorrected      | 1.167 | 0.921| 0.979  |
| corrected        | 1.182 | 0.946| 0.971  |
| $\Delta_{DQ}^0 (R_Q^0)$ |       |      |        |
| uncorrected      | 1.062 | 0.742| 0.777  |
| corrected        | 1.076 | 0.766| 0.770  |
| $\Delta_{DQ}^{0,ad}$ |       |      |        |
| uncorrected      | 1.167 | 0.839| 0.889  |
| corrected        | 1.182 | 0.864| 0.881  |
Figure S11: (a) Bond lengths (in angstrom), (b) Wiberg bond indices, (c) Wiberg valencies and (d) atomic charges of HC$_4$N and C$_4$N$^-$ triplet chains considered in this paper.

Table S12: Values of the vertical ($\Delta_{bS,T}^{-} (R_T)$) $\equiv \mathcal{E}_T^{-} (R_T) - \mathcal{E}_{bS}^{-} (R_{bS})$ $\Delta_{bS,T}^{-} (R_{bS}) \equiv \mathcal{E}_T^{-} (R_{bS}) - \mathcal{E}_{bS}^{-} (R_{bS})$ $\Delta_{ls,T}^{-} (R_{ls}) \equiv \mathcal{E}_T^{-} (R_{ls}) - \mathcal{E}_{ls}^{-} (R_{ls})$ and adiabatic singlet-triplet splitting computed without and with corrections due to zero point motion using geometries ($R_x$, $x = T, bS, ls$) optimized using the largest Pople basis sets 6-311++G(3df, 3pd) and several exchange-correlation functionals.

|                        | B3LYP | PBE0 | M06-2X |
|------------------------|-------|------|--------|
| $-\Delta_{bS,T}^{-} (R_T)$ uncorrected | 0.785 | 0.917 | 0.615  |
|                        | corrected | 0.791 | 0.923 | 0.615  |
| $-\Delta_{bS,T}^{-} (R_{bS})$ uncorrected | 0.103 | 0.224 | -0.013 |
|                        | corrected | 0.109 | 0.230 | -0.013 |
| $-\Delta_{ls,T}^{-,ad} (R_{ls})$ uncorrected | 0.527 | 0.661 | 0.503  |
|                        | corrected | 0.533 | 0.667 | 0.503  |
Figure S12: Differences between several molecular properties of the isoelectronic HC\(_4\)N and C\(_4\)N\(^-\) singlet bent chains considered in this paper: (a) bond lengths (in angstrom), (b) Wiberg bond indices, (c) Wiberg valencies and (d) atomic charges.

Table S13: Values of adiabatic anion singlet-triplet splittings obtained within unrestricted ab initio methods with zero-point motion corrections. Values in italics are deduced from Pascoli and Lavendy\textsuperscript{19}.

| Method      | Basis set                  | \(\Delta_{T,BS}^{-,ad}\) | \(\Delta_{T,1S}^{-,ad}\) |
|-------------|----------------------------|--------------------------|--------------------------|
| B3LYP       | 6-311G\(^*\)              | 0.57                     | 0.81                     |
| B3LYP       | aug-cc-pVTZ                | 0.53                     | 0.78                     |
| B3LYP       | 6-311++G(3df, 3pd)         | 0.533                    | 0.791                    |
| QCISD       | 6-311G\(^*\)              | 0.40                     | 0.87                     |
| QCISD       | 6-311++G(3df, 3pd)         | 0.374                    | 0.824                    |
| QCISD(T)    | 6-311G\(^*\)              | 0.27                     | 0.72                     |
| QCISD(T)    | 6-311++G(3df, 3pd)         | 0.243                    | 0.671                    |
| CCSD        | 6-311G\(^*\)              | 0.39                     | 0.87                     |
| CCSD        | 6-311++G(3df, 3pd)         | 0.367                    | 0.822                    |
| CCSD(T)     | 6-311G\(^*\)              | 0.25                     | 0.71                     |
| CCSD(T)     | 6-311++G(3df, 3pd)         | 0.234                    | 0.653                    |
Figure S13: Differences between several molecular properties of the isoelectronic HC$_4$N and C$_4$N$^-$ linear triplet chains considered in this paper: (a) bond lengths (in angstrom), (b) Wiberg bond indices, (c) Wiberg valencies and (d) atomic charges.

Figure S14: (a) Infrared and (b) Raman spectra of HC$_4$N and C$_4$N$^-$ bent singlet chains considered in this paper.
Figure S15: (a) Infrared and (b) Raman spectra of HC₄N and C₄N⁻ triplet chains considered in this paper.

Figure S16: Degenerate HOMO and HOMO-1 (upper left and right panel, respectively) and LUMO (lower panel) of the neutral C₄N⁰ quartet (a⁴Σ⁻).
Figure S17: HOMO and LUMO (upper and lower panel, respectively) of the bent C$_4$N$^-$ singlet (1$^A'$).

Figure S18: HOMO (upper panel) and nearly degenerate LUMO and LUMO+1 (lower left and right panel, respectively) of the linear C$_4$N$^-$ singlet (1$^\Sigma^-$).
Figure S19: HOMO and LUMO (left and right panel, respectively) of the C₄N⁺ triplet (²Σ⁺).

Table S14: Values of vertical and adiabatic cation singlet-triplet splitting (Δ⁺₁ ST (R⁺ S,T) ≡ E⁺₁ (R⁺ S,T) – E⁺₁ (R⁺ S,T)) and Δ⁺₁ ad ST (R⁺ T) ≡ E⁺₁ (R⁺ T) – E⁺₁ (R⁺ T), respectively) computed without and with corrections due to zero point motion with geometries R⁺ S,T optimized using several exchange-correlation functionals and 6-311++G(3df, 3pd) basis sets.

|                  | B3LYP  | PBE0  | M06-2X |
|------------------|--------|-------|--------|
| Δ⁺₁ ST (R⁺ S)    |        |       |        |
| uncorrected      | 1.517  | 1.250 | 1.451  |
| corrected        | 1.489  | 1.251 | 1.441  |
| Δ⁺₁ ST (R⁺ T)    |        |       |        |
| uncorrected      | 1.046  | 0.796 | 0.965  |
| corrected        | 1.018  | 0.797 | 0.955  |
| Δ⁺₁ ad ST        |        |       |        |
| uncorrected      | 1.311  | 1.052 | 1.247  |
| corrected        | 1.283  | 1.054 | 1.236  |
Table S15: Longitudinal (nonvanishing $A$ only for bent anion singlet) and perpendicular ($B = C$ except for the bent anion singlet) rotational constants of the C$_4$N chains investigated in this paper computed by using methods indicated in the second column.

| Species                | Method                        | $A$ (GHz) | $B$ (GHz) | $C$ (GHz) |
|------------------------|-------------------------------|-----------|-----------|-----------|
| neutral doublet        | UB3LYP/6-311++G(3df, 3pd)     | 2.44239   |           |           |
|                        | UPBE0/6-311++G(3df, 3pd)      | 2.44128   |           |           |
|                        | UM06-2X/6-311++G(3df, 3pd)    | 2.43646   |           |           |
|                        | UB2GP-PLYP/6-311++G(3df, 3pd)| 2.44310   |           |           |
|                        | UHF/3-21G$^{14}$              | 2.4075    |           |           |
|                        | UHF/svp$^{14}$                | 2.3963    |           |           |
| neutral quartet        | UB3LYP/6-311++G(3df, 3pd)     | 2.46635   |           |           |
|                        | UPBE0/6-311++G(3df, 3pd)      | 2.46586   |           |           |
|                        | UM06-2X/6-311++G(3df, 3pd)    | 2.46171   |           |           |
| anion triplet          | UB3LYP/6-311++G(3df, 3pd)     | 2.42267   |           |           |
|                        | UPBE0/6-311++G(3df, 3pd)      | 2.42220   |           |           |
|                        | UM06-2X/6-311++G(3df, 3pd)    | 2.42084   |           |           |
|                        | UB2GP-PLYP/6-311++G(3df, 3pd)| 2.42361   |           |           |
| bent anion singlet     | RB3LYP/6-311++G(3df, 3pd)     | 56.30860  | 2.82435   | 2.68945   |
|                        | RPBE0/6-311++G(3df, 3pd)      | 54.50451  | 2.84356   | 2.70256   |
|                        | RM06-2X/6-311++G(3df, 3pd)    | 46.19743  | 2.92536   | 2.75115   |
| cation singlet         | RB3LYP/6-311++G(3df, 3pd)     | 2.44330   |           |           |
|                        | RPBE0/6-311++G(3df, 3pd)      | 2.44262   |           |           |
|                        | RM06-2X/6-311++G(3df, 3pd)    | 2.44031   |           |           |
|                        | RB2GP-PLYP/6-311++G(3df, 3pd)| 2.42933   |           |           |
| cation triplet         | UB3LYP/6-311++G               | 2.47931   |           |           |
|                        | UPBE0/6-311++G                | 2.47907   |           |           |
|                        | UM06-2X/6-311++G(3df, 3pd)    | 2.47802   |           |           |
Table S16: Values of the dipole momentum $D$ (field independent basis, debye) at various levels of theory indicated in the second column. Notice that the value in italics obtained by Pauzat et al.\textsuperscript{14} within the UHF/svp approach is somewhat different from that of our calculations at the same level of theory.

| Species               | Method                        | $D_X$  | $D_Y$  | $D_Z$  | $D_{\text{total}}$ |
|-----------------------|-------------------------------|--------|--------|--------|-------------------|
| neutral doublet       | B3LYP/6-311++G(3df, 3pd)      | 0.0000 | 0.0000 | 0.3347 | 0.3347            |
|                       | B3LYP/aug-cc-pVTZ             | 0.0000 | 0.0000 | 0.3393 | 0.3393            |
|                       | UCCSD(T)/6-311++G(3df, 3pd)   | 0.0000 | 0.0000 | 0.0907 | 0.0907            |
|                       | UCCSD(T)/aug-cc-pvtz          | 0.0000 | 0.0000 | 0.0990 | 0.0990            |
|                       | ROCCSD(T)/6-311++G(3df, 3pd)  | 0.0000 | 0.0000 | 0.4512 | 0.4512            |
|                       | ROCCSD(T)/aug-cc-pVTZ         | 0.0000 | 0.0000 | 0.4436 | 0.4436            |
|                       | UHF/3-21g                     | 0.0000 | 0.0000 | 0.0544 | 0.0544            |
|                       | UHF/svp                       | 0.0000 | 0.0000 | 0.1119 | 0.1119            |
|                       | UHF/svp\textsuperscript{14}   | 0.0000 | 0.0000 | 0.14   | 0.14              |
|                       | UHF/6-311++G(3df, 3pd)        | 0.0000 | 0.0000 | 0.0587 | 0.0587            |
|                       | UHF/aug-cc-pvtz               | 0.0000 | 0.0000 | 0.0654 | 0.0654            |
|                       | ROHF/3-21g                    | 0.0000 | 0.0000 | 0.5486 | 0.5486            |
|                       | ROHF/svp                      | 0.0000 | 0.0000 | 0.6216 | 0.6216            |
|                       | ROHF/6-311++G(3df, 3pd)       | 0.0000 | 0.0000 | 0.7821 | 0.7821            |
|                       | ROHF/aug-cc-pVTZ              | 0.0000 | 0.0000 | 0.7781 | 0.7781            |
| neutral quartet       | B3LYP/6-311++G(3df, 3pd)      | 0.0000 | 0.0000 | 3.4628 | 3.4628            |
|                       | B3LYP/aug-cc-pVTZ             | 0.0000 | 0.0000 | 3.4586 | 3.4586            |
|                       | UCCSD(T)/6-311++G(3df, 3pd)   | 0.0000 | 0.0000 | 3.2558 | 3.2558            |
|                       | ROCCSD(T)/6-311++G(3df, 3pd)  | 0.0000 | 0.0000 | 4.5003 | 4.5003            |
|                       | ROCCSD(T)/aug-cc-pVTZ         | 0.0000 | 0.0000 | 4.4940 | 4.4940            |
|                       | UHF/3-21G                     | 0.0000 | 0.0000 | 2.9749 | 2.9749            |
|                       | UHF/svp                       | 0.0000 | 0.0000 | 3.1581 | 3.1581            |
|                       | UHF/aug-cc-pVTZ               | 0.0000 | 0.0000 | 3.2558 | 3.2558            |
|                       | ROHF/3-21G                    | 0.0000 | 0.0000 | 4.2865 | 4.2865            |
|                       | ROHF/svp                      | 0.0000 | 0.0000 | 4.5003 | 4.5003            |
|                       | ROHF/aug-cc-pVTZ              | 0.0000 | 0.0000 | 4.4940 | 4.4940            |
| anion triplet         | B3LYP/6-311++G(3df, 3pd)      | 0.0000 | 0.0000 | 2.9398 | 2.9398            |
|                       | B3LYP/aug-cc-pVTZ             | 0.0000 | 0.0000 | 2.9340 | 2.9400            |
|                       | UCCSD(T)/6-311++G(3df, 3pd)   | 0.0000 | 0.0000 | 3.2479 | 3.2479            |
|                       | ROCCSD(T)/6-311++G(3df, 3pd)  | 0.0000 | 0.0000 | 3.2479 | 3.2479            |
|                       | ROCCSD(T)/aug-cc-pVTZ         | 0.0000 | 0.0000 | 3.8729 | 3.8729            |
|                       | UHF/3-21G                     | 0.0000 | 0.0000 | 4.5640 | 4.5640            |
|                       | UHF/svp                       | 0.0000 | 0.0000 | 4.8990 | 4.8990            |
|                       | UHF/aug-cc-pVTZ               | 0.0000 | 0.0000 | 4.8682 | 4.8682            |
|                       | ROHF/3-21G                    | 0.0000 | 0.0000 | 5.9571 | 5.9571            |
|                       | ROHF/svp                      | 0.0000 | 0.0000 | 6.0789 | 6.0789            |
|                       | ROHF/aug-cc-pVTZ              | 0.0000 | 0.0000 | 6.0065 | 6.0065            |

\textsuperscript{14} Notice that the value in italics obtained by Pauzat et al. within the UHF/svp approach is somewhat different from that of our calculations at the same level of theory.
Table S17: Values of the quadrupole momentum $Q$ (field independent basis, debye-angstrom) of the C$_4$N chains investigated in this paper obtained using geometries optimized as indicated in the second column.

| Species                  | Method                      | $Q_{xx}$ | $Q_{yy}$ | $Q_{zz}$ | $Q_{xy}$ | $Q_{xz}$ | $Q_{yz}$ |
|--------------------------|-----------------------------|----------|----------|----------|----------|----------|----------|
| neutral doublet          | B3LYP/6-311++G(3df, 3pd)    | -26.3541 | -27.9983 | -42.2421 | 0.0000   | 0.0000   | 0.0000   |
|                          | B3LYP/aug-cc-pVTZ           | -26.3443 | -27.9421 | -42.2635 | 0.0000   | 0.0000   | 0.0000   |
|                          | UCCSD(T)/6-311++G(3df, 3pd)| -26.4146 | -28.2057 | -42.2981 | 0.0000   | 0.0000   | 0.0000   |
|                          | UCCSD(T)/aug-cc-pvtz        | -26.3955 | -28.1379 | -42.3180 | 0.0000   | 0.0000   | 0.0000   |
|                          | ROCCSD(T)/6-311++G(3df, 3pd)| -28.4353 | -26.8169 | -41.6984 | 0.0000   | 0.0000   | 0.0000   |
|                          | ROCCSD(T)/aug-cc-pVTZ      | -26.8005 | -28.3699 | -41.7230 | 0.0000   | 0.0000   | 0.0000   |
|                          | UHF/3-21g                  | -28.2685 | -26.4478 | -41.7598 | 0.0000   | 0.0000   | 0.0000   |
|                          | UHF/svp                    | -26.5232 | -28.3367 | -42.6564 | 0.0000   | 0.0000   | 0.0000   |
|                          | UHF/6-311++G(3df, 3pd)     | -26.4489 | -28.2494 | -42.2687 | 0.0000   | 0.0000   | 0.0000   |
|                          | UHF/aug-cc-pvtz            | -28.1845 | -26.4327 | -42.2852 | 0.0000   | 0.0000   | 0.0000   |
| neutral quartet          | B3LYP/6-311++G(3df, 3pd)    | -27.5520 | -27.5520 | -30.7287 | 0.0000   | 0.0000   | 0.0000   |
|                          | B3LYP/aug-cc-pVTZ           | -27.5250 | -27.5250 | -30.7352 | 0.0000   | 0.0000   | 0.0000   |
|                          | UCCSD(T)/6-311++G(3df, 3pd)| -27.6065 | -27.6065 | -30.5244 | 0.0000   | 0.0000   | 0.0000   |
|                          | ROCCSD(T)/6-311++G(3df, 3pd)| -28.0387 | -28.0387 | -29.5375 | 0.0000   | 0.0000   | 0.0000   |
|                          | ROCCSD(T)/aug-cc-pVTZ      | -27.9995 | -27.9995 | -29.5470 | 0.0000   | 0.0000   | 0.0000   |
| anion triplet            | B3LYP/6-311++G(3df, 3pd)    | -31.7023 | -31.7023 | -71.4631 | 0.0000   | 0.0000   | 0.0000   |
|                          | B3LYP/aug-cc-pVTZ           | -31.6879 | -31.6879 | -71.5144 | 0.0000   | 0.0000   | 0.0000   |
|                          | UCCSD(T)/6-311++G(3df, 3pd)| -31.8018 | -31.8018 | -71.7508 | 0.0000   | 0.0000   | 0.0000   |
|                          | ROCCSD(T)/6-311++G(3df, 3pd)| -32.1142 | -32.1142 | -70.2281 | 0.0000   | 0.0000   | 0.0000   |
|                          | ROCCSD(T)/aug-cc-pVTZ      | -32.0834 | -32.0834 | -70.2791 | 0.0000   | 0.0000   | 0.0000   |
| bent anion singlet       | B3LYP/6-311++G(3df, 3pd)    | -63.8640 | -36.8339 | -30.3058 | 1.4754   | 0.0000   | 0.0000   |
|                          | B3LYP/aug-cc-pVTZ           | -63.8640 | -36.8339 | -30.3058 | 1.4754   | 0.0000   | 0.0000   |
|                          | RCCSD(T)/6-311++G(3df, 3pd)| -62.9911 | -37.1863 | -30.6481 | 1.1594   | 0.0000   | 0.0000   |
|                          | RCCSD(T)/aug-cc-pVTZ       | -63.0000 | -37.1600 | -30.6336 | 1.1690   | 0.0000   | 0.0000   |
| linear anion singlet     | B3LYP/6-311++G(3df, 3pd)    | -29.8650 | -33.8601 | -71.3765 | 0.0000   | 0.0000   | 0.0000   |
|                          | B3LYP/aug-cc-pVTZ           | -29.9174 | -33.8018 | -71.4570 | 0.0000   | 0.0000   | 0.0000   |
|                          | RCCSD(T)/6-311++G(3df, 3pd)| -30.2092 | -34.2094 | -70.3492 | 0.0000   | 0.0000   | 0.0000   |
|                          | RCCSD(T)/aug-cc-pVTZ       | -34.1124 | -30.2533 | -70.4022 | 0.0000   | 0.0000   | 0.0000   |
| cation singlet           | B3LYP/6-311++G(3df, 3pd)    | -23.7770 | -23.7770 | -15.6956 | 0.0000   | 0.0000   | 0.0000   |
|                          | B3LYP/aug-cc-pVTZ           | -23.7770 | -23.7770 | -15.6957 | 0.0000   | 0.0000   | 0.0000   |
|                          | RCCSD(T)/6-311++G(3df, 3pd)| -23.7366 | -23.7366 | -15.7048 | 0.0000   | 0.0000   | 0.0000   |
|                          | RCCSD(T)/aug-cc-pVTZ       | -24.3542 | -24.3542 | -14.1423 | 0.0000   | 0.0000   | 0.0000   |
| cation triplet           | B3LYP/6-311++G(3df, 3pd)    | -23.4092 | -24.8186 | -6.0974  | 0.0000   | 0.0000   | 0.0000   |
|                          | B3LYP/aug-cc-pVTZ           | -24.7575 | -23.3930 | -6.1030  | 0.0000   | 0.0000   | 0.0000   |
|                          | UCCSD(T)/6-311++G(3df, 3pd)| -25.0731 | -23.7379 | -7.4195  | 0.0000   | 0.0000   | 0.0000   |
|                          | ROCCSD(T)/6-311++G(3df, 3pd)| -24.0058 | -25.3116 | -5.2179  | 0.0000   | 0.0000   | 0.0000   |
|                          | ROCCSD(T)/aug-cc-pVTZ      | -25.2346 | -23.9786 | -5.2274  | 0.0000   | 0.0000   | 0.0000   |
Table S18: Values of the higher vibrational frequencies (in cm$^{-1}$) of the presently investigated molecular species obtained via B3LYP/6-311++G(3df, 3pd) calculations.

| Description | C$_4$N doublet | C$_4$N quartet | bent C$_4$N | singlet C$_4$N | triplet C$_4$N$^+$ | singlet C$_4$N$^+$ triplet | HC$_4$N singlet | HC$_4$N triplet |
|-------------|----------------|----------------|-------------|-----------------|---------------------|--------------------------|----------------|----------------|
| symmetric stretch (breath.) | 752.62 | 765.66 | 827.08 | 753.17 | 756.09 | 775.07 | 847.97 | 754.26 |
| out-of-phase C$_1$C$_2$—C$_4$N stretch | 1421.85 | 1559.49 | 1320.77 | 1475.77 | 1418.37 | 1906.48 | 1997.43 | 1762.66 |
| in-phase C$_1$C$_2$—C$_4$N stretch | 1989.43 | 1753.86 | 1835.45 | 1906.48 | 1997.43 | 1579.14 | 1577.41 |
| CN stretch | 2181.87 | 2071.92 | 2149.62 | 2156.55 | 2029.44 | 2138.33 | 2156.55 | 2029.44 |
| CH stretch | — | — | — | — | — | 3449.65 | — | — |

Table S19: Values of the vertical and adiabatic doublet-triplet electron attachment energies ($E_{AD}^{vert}(R) \equiv E_{D}^{0}(R) - E_{T}^{0}(R)$ and $E_{AD}^{ad}(R) \equiv E_{D}^{0}(R_{D}) - E_{T}^{0}(R_{T})$, respectively) computed without and with corrections due to zero point motion using the neutral doublet ($R = R_{D}$) and anion triplet ($R = R_{T}$) B3LYP/6-311++G(3df, 3pd) optimum geometries.

| Method | EOM-ROCCSD | B3LYP | LC-BLYP | LC-ωPBE |
|--------|------------|-------|---------|---------|
| $E_{AD}^{vert}(R_{D})$ | 3.027 | 3.217 | 3.479 | 3.514 |
| $E_{AD}^{vert}(R_{T})$ | 3.199 | 3.360 | 3.670 | 3.690 |
| $E_{AD}^{ad}(R)$ | 3.109 | 3.285 | 3.497 | 3.545 |

Table S20: Values of the vertical and adiabatic doublet-triplet electron attachment energies ($E_{AD}^{vert}(R) \equiv E_{D}^{0}(R) - E_{T}^{0}(R)$ and $E_{AD}^{ad}(R) \equiv E_{D}^{0}(R_{D}) - E_{T}^{0}(R_{T})$, respectively) computed without and with corrections due to zero point motion using the neutral doublet $R_{D}$ and anion triplet $R_{T}$ geometries optimized within B3LYP/6-311++G(3df, 3pd) and PBE0/6-311++G(3df, 3pd).

| Method | B3LYP | PBE0 | EOM-ROCCSD@B3LYP | EOM-ROCCSD@PBE0 |
|--------|-------|------|------------------|------------------|
| $E_{AD}^{vert}(R_{D})$ | 3.217 | 3.288 | 3.027 | 3.006 |
| $E_{AD}^{vert}(R_{T})$ | 3.360 | 3.431 | 3.199 | 3.175 |
| $E_{AD}^{ad}(R)$ | 3.285 | 3.355 | 3.109 | 3.086 |

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Table S21: Values of the vertical and adiabatic doublet-triplet electron attachment $E_A$ computed without and with corrections due to zero point motion using the neutral doublet $\mathbf{R}_D^0$ and anion triplet $\mathbf{R}_T^-$ geometries optimized by means of several functionals and 6-311++G(3df, 3pd) basis sets.

|                | B3LYP  | PBE0   | M06-2X |
|----------------|--------|--------|--------|
| $E_A^{vert} (\mathbf{R}_D^0)$ |
| uncorrected   | 3.217  | 3.288  | 3.304  |
| corrected     | 3.207  | 3.275  | 3.317  |
| $E_A^{vert} (\mathbf{R}_T^-)$ |
| uncorrected   | 3.360  | 3.431  | 3.273  |
| corrected     | 3.350  | 3.418  | 3.285  |
| $E_A^{ad}$    |
| uncorrected   | 3.285  | 3.355  | 3.386  |
| corrected     | 3.274  | 3.342  | 3.398  |

Table S22: Values of the vertical and adiabatic doublet-singlet ionization energy ($I_P^{vert} (\mathbf{R}) = \mathcal{E}_S^+ (\mathbf{R}) - \mathcal{E}_D^0 (\mathbf{R})$ and $I_P^{ad} = \mathcal{E}_S^+ (\mathbf{R}_S^+) - \mathcal{E}_D^0 (\mathbf{R}_D^0)$, respectively) computed without and with corrections due to zero point motion using the neutral doublet ($\mathbf{R} = \mathbf{R}_D^0$) and cation singlet ($\mathbf{R} = \mathbf{R}_S^+$) B3LYP/6-311++G(3df, 3pd) optimum geometries.

|                | EOM-ROCCSD | B3LYP | LC-BLYP | LC-ω-PBE |
|----------------|------------|-------|---------|---------|
| $I_P^{vert} (\mathbf{R}_D^0)$ |
| uncorrected   | 9.802      | 9.812 | 10.258  | 10.226  |
| corrected     | 9.842      | 9.852 | 10.297  | 10.265  |
| $I_P^{vert} (\mathbf{R}_S^+)$ |
| uncorrected   | 9.797      | 9.780 | 10.225  | 10.194  |
| corrected     | 9.836      | 9.819 | 10.265  | 10.233  |
| $I_P^{ad}$    |
| uncorrected   | 9.783      | 9.794 | 10.215  | 10.187  |
| corrected     | 9.823      | 9.833 | 10.254  | 10.227  |
Table S23: Values of the vertical and adiabatic doublet-singlet ionization energy $(IP_{SD}^{\text{vert}}(\mathbf{R}) \equiv \mathcal{E}_S^+(\mathbf{R}) - \mathcal{E}_D^0(\mathbf{R})$ and $IP_{SD}^{\text{ad}} \equiv \mathcal{E}_S^+(\mathbf{R}_S^+) - \mathcal{E}_D^0(\mathbf{R}_D^0)$, respectively) computed without and with corrections due to zero point motion using 6-311++G(3df, 3pd) basis sets and the neutral doublet ($\mathbf{R} = \mathbf{R}_D^0$) and cation singlet ($\mathbf{R} = \mathbf{R}_S^+$) geometries optimized within B3LYP/6-311++G(3df, 3pd) and PBE0/6-311++G(3df, 3pd).

|                | B3LYP | PBE0 | EOM-ROCCSD@B3LYP | EOM-ROCCSD@PBE0 |
|----------------|-------|------|------------------|-----------------|
| $IP_{SD}^{\text{vert}}(\mathbf{R}_D^0)$ |       |      |                  |                 |
| uncorrected    | 9.812 | 9.874| 9.802            | 9.805           |
| corrected      | 9.852 | 9.915| 9.842            | 9.845           |
| $IP_{SD}^{\text{vert}}(\mathbf{R}_S^+)$ |       |      |                  |                 |
| uncorrected    | 9.780 | 9.844| 9.797            | 9.801           |
| corrected      | 9.819 | 9.884| 9.836            | 9.841           |
| $IP_{SD}^{\text{ad}}$ |       |      |                  |                 |
| uncorrected    | 9.794 | 9.857| 9.783            | 9.800           |
| corrected      | 9.833 | 9.897| 9.823            | 9.840           |

Table S24: Values of the vertical and adiabatic doublet-singlet ionization energy $IP$ computed without and with corrections due to zero point motion using the neutral doublet $\mathbf{R}_D^0$ and cation singlet $\mathbf{R}_S^+$ geometries optimized by means of several functionals and 6-311++G(3df, 3pd) basis sets.

|                | B3LYP | PBE0 | M06-2X |
|----------------|-------|------|--------|
| $IP_{SD}^{\text{vert}}(\mathbf{R}_D^0)$ |       |      |        |
| uncorrected    | 9.812 | 9.874| 9.835  |
| corrected      | 9.852 | 9.915| 9.946  |
| $IP_{SD}^{\text{vert}}(\mathbf{R}_S^+)$ |       |      |        |
| uncorrected    | 9.780 | 9.844| 9.812  |
| corrected      | 9.819 | 9.884| 9.822  |
| $IP_{SD}^{\text{ad}}$ |       |      |        |
| uncorrected    | 9.794 | 9.857| 9.822  |
| corrected      | 9.833 | 9.897| 9.832  |
Table S25: Quadrupole moment $Q$ (field independent basis, debye-angstrom) of the isoelectronic $\text{C}_4\text{N}^-$ and $\text{HC}_4\text{N}$ chains computed as indicated in the second column.

| Species      | Method          | $Q_{xx}$  | $Q_{yy}$  | $Q_{zz}$  | $Q_{xy}$ | $Q_{xz}$ | $Q_{yz}$ |
|--------------|-----------------|-----------|-----------|-----------|----------|----------|----------|
| $\text{C}_4\text{N}^-$ triplet | B3LYP/6-311++G(3df, 3pd) | -34.2070  | -68.9571  | -31.7034  | -9.6536  | 0.0000   | 0.0000   |
|              | B3LYP/aug-cc-pVTZ | -34.1971  | -69.0040  | -31.6890  | -9.6702  | 0.0000   | 0.0000   |
|              | UCCSD(T)/6-311++G(3df, 3pd) | -34.3255  | -69.2273  | -31.8029  | -9.7128  | 0.0000   | 0.0000   |
|              | ROCCSD(T)/6-311++G(3df, 3pd) | -34.5067  | -67.8437  | -32.1155  | -9.2375  | 0.0000   | 0.0000   |
|              | ROCCSD(T)/aug-cc-pVTZ | -34.4814  | -67.8801  | -32.0848  | -9.2581  | 0.0000   | 0.0000   |
| $\text{HC}_4\text{N}$ triplet | B3LYP/6-311++G(3df, 3pd) | -28.4399  | -27.7588  | -28.4371  | -0.1693  | 0.0000   | 0.0000   |
|              | B3LYP/aug-cc-pVTZ | -28.4196  | -27.7593  | -28.4116  | -0.1574  | 0.0000   | 0.0000   |
|              | UCCSD(T)/6-311++G(3df, 3pd) | -28.4547  | -27.4563  | -28.5638  | -0.3883  | 0.0000   | 0.0000   |
|              | ROCCSD(T)/6-311++G(3df, 3pd) | -29.0226  | -28.2790  | -29.0194  | -0.1844  | 0.0000   | 0.0000   |
|              | ROCCSD(T)/aug-cc-pVTZ | -28.9932  | -28.2743  | -28.9830  | -0.1694  | 0.0000   | 0.0000   |
| bent $\text{C}_4\text{N}^-$ singlet | B3LYP/6-311++G(3df, 3pd) | -63.8640  | -30.8339  | -30.3058  | 1.4754   | 0.0001   | 0.0001   |
|              | B3LYP/aug-cc-pVTZ | -63.8640  | -30.8339  | -30.3058  | 1.4754   | 0.0001   | 0.0001   |
|              | RCCSD(T)/6-311++G(3df, 3pd) | -62.9911  | -37.1863  | -30.6481  | 1.1594   | 0.0000   | 0.0001   |
|              | RCCSD(T)/aug-cc-pVTZ | -63.0000  | -37.1600  | -30.6336  | 1.1690   | 0.0001   | 0.0001   |
| $\text{HC}_4\text{N}$ singlet | B3LYP/6-311++G(3df, 3pd) | -27.3591  | -30.3776  | -27.1872  | -4.3257  | 0.0000   | 0.0000   |
|              | B3LYP/aug-cc-pVTZ | -27.3407  | -30.3437  | -27.1738  | -4.3184  | 0.0000   | 0.0000   |
|              | RCCSD(T)/6-311++G(3df, 3pd) | -27.1081  | -30.8650  | -27.7089  | -4.6705  | 0.0000   | 0.0000   |
|              | RCCSD(T)/aug-cc-pVTZ | -27.0845  | -30.8217  | -27.6860  | -4.6599  | 0.0000   | 0.0000   |
Figure S20: Bond order indices versus bond lengths of the C₄N chains investigated in the present paper. The linear fitting line suggests possible correlations.

Table S26: Reorganization energies $\lambda_a^b \equiv \mathcal{E}_a (R_b) - \mathcal{E}_a (R_a)$ of the C₄N anions — triplet ($T^-$), bent singlet ($bS^-$) and (metastable) linear singlet ($lS^-$) — with respect to the neutral doublet ($D$).

| Functional | $\lambda_D^D$ | $\lambda_T^D$ | $\lambda_{bS}^D$ | $\lambda_{lS}^D$ | $\lambda_D^{T-}$ | $\lambda_T^{T-}$ | $\lambda_{bS}^{T-}$ | $\lambda_{lS}^{T-}$ | $\lambda_D^{bS-}$ | $\lambda_T^{bS-}$ | $\lambda_{bS}^{bS-}$ | $\lambda_{lS}^{bS-}$ | $\lambda_D^{lS-}$ | $\lambda_T^{lS-}$ | $\lambda_{bS}^{lS-}$ | $\lambda_{lS}^{lS-}$ |
|------------|----------------|---------------|-----------------|-----------------|----------------|----------------|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| B3LYP      | 0.067          | 0.076         | 0.338           | 0.488           | 0.082         | 0.082         | 0.338           | 0.488           | 0.082         | 0.082         | 0.338           | 0.488           | 0.082         | 0.082         | 0.338           | 0.488           |
| PBE0       | 0.067          | 0.076         | 0.342           | 0.509           | 0.087         | 0.087         | 0.342           | 0.509           | 0.087         | 0.087         | 0.342           | 0.509           | 0.087         | 0.087         | 0.342           | 0.509           |
| M06-2X     | 0.081          | -0.113        | 0.446           | 0.600           | 0.111         | 0.111         | 0.446           | 0.600           | 0.111         | 0.111         | 0.446           | 0.600           | 0.111         | 0.111         | 0.446           | 0.600           |
Table S27: Reorganization energies $\lambda_b^a \equiv \mathcal{E}_a (R_b) - \mathcal{E}_a (R_a)$ of the C$_4$N singlet ($S^+$) and triplet ($T^+$) cations with respect to the neutral doublet ($D$).

| Functional | $\lambda_{S^+}^D$ | $\lambda_{D^+}^S$ | $\lambda_{T^+}^D$ | $\lambda_{D^+}^T$ |
|------------|----------------|----------------|----------------|----------------|
| B3LYP      | 0.019          | 0.014          | 0.124          | 0.124          |
| PBE0       | 0.018          | 0.013          | 0.121          | 0.121          |
| M06-2X     | 0.014          | 0.010          | 0.138          | 0.138          |
Table S28: Dissociation of neutral and anion C₄N chains. Enthalpies of reaction at zero (subscript 0) and room temperature (subscript RT) computed by several CBS protocols. All values (in kcal/mol) refer to the electronic ground states.

| No. | Species | Method | Reaction | $\Delta_r H^0_{0}$ | $\Delta_r H^0_{RT}$ |
|-----|---------|--------|----------|-------------------|-------------------|
| 1   | C₄N    | CBS-QB3| C₄N → C + C₃N | 139.4             | 140.1             |
|     |         | CBS-APNO| C₄N → C + C₃N | 137.3             | 138.0             |
|     |         | CBS-4M | C₄N → C + C₃N | 138.6             | 139.6             |
| 2   | C₄N    | CBS-QB3| C₂ + C₃N     | 152.0             | 152.8             |
|     |         | CBS-APNO| C₂ + C₃N     | 152.0             | 155.9             |
|     |         | CBS-4M | C₂ + C₃N     | 155.2             | 156.3             |
| 3   | C₄N    | CBS-QB3| C₃ + CN      | 95.3              | 96.4              |
|     |         | CBS-APNO| C₃ + CN      | 94.2              | 95.3              |
|     |         | CBS-4M | C₃ + CN      | 103.0             | 104.3             |
| 4   | C₄N    | CBS-QB3| C₄ + N       | 159.6             | 160.5             |
|     |         | CBS-APNO| C₄ + N       | 157.8             | 158.5             |
|     |         | CBS-4M | C₄ + N       | 156.6             | 157.7             |
| 5a  | C₄N⁻   | CBS-QB3| C₄N⁻ → C + C₃N⁻ | 109.1             | 109.4             |
|     |         | CBS-APNO| C₄N⁻ → C + C₃N⁻ | 110.8             | 111.6             |
|     |         | CBS-4M | C₄N⁻ → C + C₃N⁻ | 116.6             | 117.5             |
| 5b  | C₄N⁻   | CBS-QB3| C⁻ + C₃N⁻   | 184.4             | 185.4             |
|     |         | CBS-APNO| C⁻ + C₃N⁻   | 183.9             | 184.8             |
|     |         | CBS-4M | C⁻ + C₃N⁻   | 190.9             | 191.8             |
| 6a  | C₄N⁻   | CBS-QB3| C₂ + C₂N⁻   | 160.6             | 161.6             |
|     |         | CBS-APNO| C₂ + C₂N⁻   | 166.2             | 170.0             |
|     |         | CBS-4M | C₂ + C₂N⁻   | 165.5             | 166.6             |
| 6b  | C₄N⁻   | CBS-QB3| C₂⁻ + C₂N⁻ | 151.0             | 152.1             |
|     |         | CBS-APNO| C₂⁻ + C₂N⁻ | 152.6             | 153.5             |
|     |         | CBS-4M | C₂⁻ + C₂N⁻ | 156.9             | 158.0             |
| 7a  | C₄N⁻   | CBS-QB3| C₃ + CN⁻   | 77.6              | 79.0              |
|     |         | CBS-APNO| C₃ + CN⁻   | 79.7              | 81.0              |
|     |         | CBS-4M | C₃ + CN⁻   | 88.4              | 89.7              |
| 7b  | C₄N⁻   | CBS-QB3| C₃⁻ + CN   | 122.0             | 123.3             |
|     |         | CBS-APNO| C₃⁻ + CN   | 122.4             | 123.4             |
|     |         | CBS-4M | C₃⁻ + CN   | 130.2             | 131.5             |
| 8a  | C₄N⁻   | CBS-QB3| C₄ + N⁻    | 238.1             | 239.4             |
|     |         | CBS-APNO| C₄ + N⁻    | 241.8             | 243.0             |
|     |         | CBS-4M | C₄ + N⁻    | 241.8             | 243.0             |
| 8b  | C₄N⁻   | CBS-QB3| C₄⁻ + N    | 141.8             | 142.8             |
|     |         | CBS-APNO| C₄⁻ + N    | 142.5             | 143.3             |
|     |         | CBS-4M | C₄⁻ + N    | 144.6             | 145.8             |
Table S29: Dissociation of neutral C$_2$N, C$_3$N, and C$_5$N chains already detected in space. Enthalpies of reaction at zero (subscript 0) and room temperature (subscript RT) computed by several CBS protocols. All values (in kcal/mol) refer to the electronic ground states.

| No. | Species | Reaction | Method   | $\Delta_r H^0_0$ | $\Delta_r H^0_{RT}$ |
|-----|---------|----------|----------|-----------------|---------------------|
| 9a  | C$_2$N  | C$_2$N $\rightarrow$ C + CN | CBS-QB3 | 113.4           | 114.4               |
|     |         |          | CBS-APNO | 113.1           | 114.1               |
|     |         |          | CBS-4M   | 116.6           | 117.7               |
| 9b  |         | C$_2$N $\rightarrow$ C$_2$ + N | CBS-QB3 | 145.8           | 146.8               |
|     |         |          | CBS-APNO | 149.3           | 148.7               |
|     |         |          | CBS-4M   | 147.5           | 148.7               |
| 10a | C$_3$N  | C$_3$N $\rightarrow$ C + C$_2$N | CBS-QB3 | 156.8           | 157.9               |
|     |         |          | CBS-APNO | 158.8           | 159.7               |
|     |         |          | CBS-4M   | 158.0           | 159.0               |
| 10b |         | C$_3$N $\rightarrow$ C$_2$ + CN | CBS-QB3 | 126.0           | 127.1               |
|     |         |          | CBS-APNO | 131.0           | 132.0               |
|     |         |          | CBS-4M   | 133.2           | 134.4               |
| 10c |         | C$_3$N $\rightarrow$ C$_3$ + N | CBS-QB3 | 132.6           | 134.0               |
|     |         |          | CBS-APNO | 133.9           | 135.2               |
|     |         |          | CBS-4M   | 136.7           | 138.0               |
| 12a | C$_5$N  | C$_5$N $\rightarrow$ C + C$_4$N | CBS-QB3 | 144.1           | 145.7               |
|     |         |          | CBS-APNO | 147.2           | 148.1               |
|     |         |          | CBS-4M   | 147.3           | 148.2               |
| 12b |         | C$_5$N $\rightarrow$ C$_2$ + C$_3$N | CBS-QB3 | 139.2           | 140.6               |
|     |         |          | CBS-APNO | 143.7           | 144.3               |
|     |         |          | CBS-4M   | 144.6           | 145.5               |
| 12c |         | C$_5$N $\rightarrow$ C$_3$ + C$_2$N | CBS-QB3 | 126.0           | 127.8               |
|     |         |          | CBS-APNO | 128.3           | 129.3               |
|     |         |          | CBS-4M   | 133.7           | 134.8               |
| 12d |         | C$_5$N $\rightarrow$ C$_4$ + CN | CBS-QB3 | 126.9           | 128.6               |
|     |         |          | CBS-APNO | 128.0           | 128.7               |
|     |         |          | CBS-4M   | 131.6           | 132.7               |
| 12e |         | C$_5$N $\rightarrow$ C$_5$ + N | CBS-QB3 | 135.8           | 137.3               |
|     |         |          | CBS-APNO | 136.0           | 136.8               |
|     |         |          | CBS-4M   | 142.9           | 143.8               |
Table S30: Relevant exchange reactions. Enthalpies of reaction at zero (subscript 0) and room temperature (subscript RT) computed by several CBS protocols. All values (in kcal/mol) refer to the electronic ground states.

| No. | Reaction | Method  | $\Delta_r H^0_0$ | $\Delta_r H^0_{RT}$ |
|-----|----------|---------|------------------|-------------------|
| 13  | $C_5 + N \rightarrow C + C_4N$ | CBS-QB3 | 8.3              | 8.4               |
|     | $C_5 + N \rightarrow C + C_4N$ | CBS-APNO | 11.2             | 11.3              |
|     | $C_5 + N \rightarrow C + C_4N$ | CBS-4M   | 4.5              | 4.3               |
| 14a | $N + C_4H^- \rightarrow C_4N + H^-$ | CBS-QB3 | 23.9             | 24.3              |
|     | $N + C_4H^- \rightarrow C_4N + H^-$ | CBS-APNO | 32.2             | 32.9              |
|     | $N + C_4H^- \rightarrow C_4N + H^-$ | CBS-4M   | 24.3             | 24.6              |
| 14b | $N + C_4H^- \rightarrow C_4N^- + H$ | CBS-QB3 | -36.0            | -35.9             |
|     | $N + C_4H^- \rightarrow C_4N^- + H$ | CBS-APNO | -36.6            | -36.1             |
|     | $N + C_4H^- \rightarrow C_4N^- + H$ | CBS-4M   | -41.6            | -41.3             |
| 14c | $N^- + C_4H \rightarrow C_4N^- + H$ | CBS-QB3 | -125.0           | -124.8            |
|     | $N^- + C_4H \rightarrow C_4N^- + H$ | CBS-APNO | -137.1           | -136.9            |
|     | $N^- + C_4H \rightarrow C_4N^- + H$ | CBS-4M   | -129.2           | -129.2            |
| 14d | $N^- + C_4H \rightarrow C_4N + H^-$ | CBS-QB3 | -65.1            | -64.6             |
|     | $N^- + C_4H \rightarrow C_4N + H^-$ | CBS-APNO | -68.3            | -67.9             |
|     | $N^- + C_4H \rightarrow C_4N + H^-$ | CBS-4M   | -63.3            | -63.3             |
| 15a | $CN + C_3H \rightarrow H + C_4N$ | CBS-QB3 | -20.5            | -20.4             |
|     | $CN + C_3H \rightarrow H + C_4N$ | CBS-APNO | -18.9            | -18.9             |
|     | $CN + C_3H \rightarrow H + C_4N$ | CBS-4M   | -24.8            | -24.8             |
| 15b | $CN^- + C_3H \rightarrow H + C_4N^-$ | CBS-QB3 | -2.8             | -3.0              |
|     | $CN^- + C_3H \rightarrow H + C_4N^-$ | CBS-APNO | -4.5             | -4.6              |
|     | $CN^- + C_3H \rightarrow H + C_4N^-$ | CBS-4M   | -10.2            | -10.2             |
| 15c | $CN^- + C_3H \rightarrow H^- + C_4N$ | CBS-QB3 | 57.1             | 57.2              |
|     | $CN^- + C_3H \rightarrow H^- + C_4N$ | CBS-APNO | 64.4             | 64.4              |
|     | $CN^- + C_3H \rightarrow H^- + C_4N$ | CBS-4M   | 55.7             | 55.8              |
| 15d | $CN + C_3H^- \rightarrow H + C_4N^-$ | CBS-QB3 | -50.9            | -50.8             |
|     | $CN + C_3H^- \rightarrow H + C_4N^-$ | CBS-APNO | -51.9            | -51.6             |
|     | $CN + C_3H^- \rightarrow H + C_4N^-$ | CBS-4M   | -56.7            | -56.8             |
| 15e | $CN + C_3H^- \rightarrow H^- + C_4N$ | CBS-QB3 | 9.0              | 9.4               |
|     | $CN + C_3H^- \rightarrow H^- + C_4N$ | CBS-APNO | 16.9             | 17.4              |
|     | $CN + C_3H^- \rightarrow H^- + C_4N$ | CBS-4M   | 9.2              | 9.2               |
Table S31: Relevant exchange reactions. Enthalpies of reaction at zero (subscript 0) and room temperature (subscript RT) computed by several CBS protocols. All values (in kcal/mol) refer to the electronic ground states.

| No. | Reaction | Method   | $\Delta_r H^0_0$ | $\Delta_r H^0_{RT}$ |
|-----|----------|----------|------------------|---------------------|
| 16a | CH + C$_3$N $\rightarrow$ H + C$_4$N | CBS-QB3 | -59.4            | -59.2              |
|     | CH + C$_3$N $\rightarrow$ H + C$_4$N | CBS-APNO | -57.4            | -57.2              |
|     | CH + C$_3$N $\rightarrow$ H + C$_4$N | CBS-4M    | -58.9            | -58.9              |
| 16b | CH$^-$ + C$_3$N $\rightarrow$ H$^-$ + C$_4$N$^-$ | CBS-QB3 | -105.6           | -105.8             |
|     | CH$^-$ + C$_3$N $\rightarrow$ H$^-$ + C$_4$N$^-$ | CBS-APNO | -105.0           | -105.0             |
|     | CH$^-$ + C$_3$N $\rightarrow$ H$^-$ + C$_4$N$^-$ | CBS-4M    | -111.0           | -111.1             |
| 16c | CH$^-$ + C$_3$N $\rightarrow$ H$^-$ + C$_4$N | CBS-QB3 | -45.8            | -45.5              |
|     | CH$^-$ + C$_3$N $\rightarrow$ H$^-$ + C$_4$N | CBS-APNO | -36.2            | -36.0              |
|     | CH$^-$ + C$_3$N $\rightarrow$ H$^-$ + C$_4$N | CBS-4M    | -45.1            | -45.2              |
| 16d | CH + C$_3$N$^-$ $\rightarrow$ H + C$_4$N$^-$ | CBS-QB3 | -29.1            | -29.1              |
|     | CH + C$_3$N$^-$ $\rightarrow$ H + C$_4$N$^-$ | CBS-APNO | -31.0            | -30.8              |
|     | CH + C$_3$N$^-$ $\rightarrow$ H + C$_4$N$^-$ | CBS-4M    | -36.8            | -36.9              |
| 17a | CH + C$_3$N$^-$ $\rightarrow$ H$^-$ + C$_4$N | CBS-QB3 | 30.8             | 31.1                |
|     | CH + C$_3$N$^-$ $\rightarrow$ H$^-$ + C$_4$N | CBS-APNO | 37.9             | 38.2                |
|     | CH + C$_3$N$^-$ $\rightarrow$ H$^-$ + C$_4$N | CBS-4M    | 29.1             | 29.1                |
| 17b | C$_2$H + C$_2$N $\rightarrow$ H + C$_4$N | CBS-QB3 | -40.4            | -40.3              |
|     | C$_2$H + C$_2$N $\rightarrow$ H + C$_4$N | CBS-APNO | -41.0            | -40.5              |
|     | C$_2$H + C$_2$N $\rightarrow$ H + C$_4$N | CBS-4M    | -40.4            | -40.3              |
| 17c | C$_2$H$^-$ + C$_2$N $\rightarrow$ H$^-$ + C$_4$N$^-$ | CBS-QB3 | -44.6            | -44.5              |
|     | C$_2$H$^-$ + C$_2$N $\rightarrow$ H$^-$ + C$_4$N$^-$ | CBS-APNO | -46.6            | -46.2              |
|     | C$_2$H$^-$ + C$_2$N $\rightarrow$ H$^-$ + C$_4$N$^-$ | CBS-4M    | -51.7            | -51.5              |
| 17d | C$_2$H$^-$ + C$_2$N $\rightarrow$ H$^-$ + C$_4$N | CBS-QB3 | 15.3             | 15.7                |
|     | C$_2$H$^-$ + C$_2$N $\rightarrow$ H$^-$ + C$_4$N | CBS-APNO | 22.2             | 22.8                |
|     | C$_2$H$^-$ + C$_2$N $\rightarrow$ H$^-$ + C$_4$N | CBS-4M    | 14.2             | 14.5                |
| 17e | C$_2$H + C$_2$N$^-$ $\rightarrow$ H$^-$ + C$_4$N | CBS-QB3 | 10.8             | 11.2                |
|     | C$_2$H + C$_2$N$^-$ $\rightarrow$ H$^-$ + C$_4$N | CBS-APNO | 16.8             | 17.5                |
|     | C$_2$H + C$_2$N$^-$ $\rightarrow$ H$^-$ + C$_4$N | CBS-4M    | 15.1             | 15.3                |
| 17f | C$_2$H + C$_2$N$^-$ $\rightarrow$ H + C$_4$N$^-$ | CBS-QB3 | -49.1            | -49.0              |
|     | C$_2$H + C$_2$N$^-$ $\rightarrow$ H + C$_4$N$^-$ | CBS-APNO | -52.0            | -51.5              |
|     | C$_2$H + C$_2$N$^-$ $\rightarrow$ H + C$_4$N$^-$ | CBS-4M    | -50.8            | -50.6              |
Table S32: Relevant exchange reactions. Enthalpies of reaction at zero (subscript 0) and room temperature (subscript RT) computed by several CBS protocols. All values (in kcal/mol) refer to the electronic ground states.

| No. | Reaction | Method   | $\Delta_r H^0_0$ | $\Delta_r H^0_{RT}$ |
|-----|----------|----------|-------------------|---------------------|
| 18  | NC$_2$N + C$_2$ $\rightarrow$ N + C$_4$N | CBS-QB3  | 48.6              | 49.0                |
|     | NC$_2$N + C$_2$ $\rightarrow$ N + C$_4$N | CBS-APNO | 45.2              | 45.6                |
|     | NC$_2$N + C$_2$ $\rightarrow$ N + C$_4$N | CBS-4M   | 41.4              | 41.5                |
| 19  | NC$_2$N + C$_2$N $\rightarrow$ N$_2$ + C$_4$N | CBS-QB3  | -29.8             | -29.3               |
|     | NC$_2$N + C$_2$N $\rightarrow$ N$_2$ + C$_4$N | CBS-APNO | -29.4             | -28.9               |
|     | NC$_2$N + C$_2$N $\rightarrow$ N$_2$ + C$_4$N | CBS-4M   | -31.7             | -31.4               |
| 20  | NC$_2$N + C$_2$H $\rightarrow$ NH + C$_4$N | CBS-QB3  | 82.3              | 82.7                |
|     | NC$_2$N + C$_2$H $\rightarrow$ NH + C$_4$N | CBS-APNO | 81.4              | 82.2                |
|     | NC$_2$N + C$_2$H $\rightarrow$ NH + C$_4$N | CBS-4M   | 78.0              | 78.4                |

Table S33: Adiabatic electron affinities and ionization potentials (in eV) of C$_4$N and C$_6$N computed with various CBS protocols. Notice that, out of these protocols, the CBS-QB3 $EA$-estimates are the closest to the experimental values $EA_{C_2N} = 2.74890 \pm 0.00010$ eV, $EA_{C_4N} = 3.1113 \pm 0.00010$ eV and $EA_{C_6N} = 3.3715 \pm 0.00010$ eV.

| Method    | $EA_{C_2N}$ | $IP_{C_2N}$ | $EA_{C_4N}$ | $IP_{C_4N}$ | $EA_{C_6N}$ | $IP_{C_6N}$ |
|-----------|-------------|-------------|-------------|-------------|-------------|-------------|
| CBS-QB3   | 2.7615      | 10.8166     | 3.1351      | 9.6913      | 3.4804      | 8.9994      |
| CBS-APNO  | 2.7728      | 10.8178     | 3.2506      | 9.6332      | 3.5648      | 8.9491      |
| CBS-4M    | 3.0115      | 11.1315     | 3.4596      | 10.0462     | 3.7693      | 9.5614      |
Atomic charges

-0.6 -0.4 -0.2 0.0 0.2 0.4 0.6

Neutral doublet
Anion singlet

Atoms of C₃N chains

C₂ C₃
astronomically observed may yet be observable