Supporting Information for Long Carbon-Based Chains of Interstellar Medium Can Have a Triplet Ground State. Why Is This Important for Astrochemistry

Ioan Bâldea*,†,‡

Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany, and Institute of Space Sciences, National Institute of Lasers, Plasma and Radiation Physics, RO 077125, Bucharest-Măgurele, Romania

E-mail: ioan.baldea@pci.uni-heidelberg.de

S1 Additional Computational Details

For the reader's convenience, a comprehensive list of the various quantities discussed in this work is presented in Table S1.

*To whom correspondence should be addressed

†Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany

‡Institute of Space Sciences, National Institute of Lasers, Plasma and Radiation Physics, RO 077125, Bucharest-Măgurele, Romania

Table S1: Definition of the various quantities utilized in the present paper.

zero-point energies of the singlet, triplet, cation, anion	ε_S, ε_T, ε_c, ε_a
non-corrected adiabatic singlet-triplet separation	$\Delta_{ad} \equiv \mathcal{E}_T(\mathbf{R}_T) - \mathcal{E}_S(\mathbf{R}_S)$
non-corrected vertical singlet-triplet separation at singlet optimum	$\Delta_S \equiv \mathcal{E}_T(\mathbf{R}_S) - \mathcal{E}_S(\mathbf{R}_S)$
non-corrected vertical singlet-triplet separation at triplet optimum	$\Delta_T \equiv \mathcal{E}_T(\mathbf{R}_T) - \mathcal{E}_S(\mathbf{R}_T)$
corrected adiabatic singlet-triplet separation, *etc*	$\Delta_{ad}^{corr} \equiv \mathcal{E}_T(\mathbf{R}_T) + \varepsilon_T - [\mathcal{E}_S(\mathbf{R}_S) + \varepsilon_S]$, *etc* (S1)
non-corrected adiabatic ionization energy wrt singlet	$IP_S^{ad,non} \equiv \mathcal{E}_c(\mathbf{R}_c) - \mathcal{E}_S(\mathbf{R}_S)$
non-corrected vertical ionization energy at singlet optimum	$IP_S^{vert,non} \equiv \mathcal{E}_c(\mathbf{R}_S) - \mathcal{E}_S(\mathbf{R}_S)$
non-corrected adiabatic ionization energy wrt triplet	$IP_T^{ad,non} \equiv \mathcal{E}_c(\mathbf{R}_c) - \mathcal{E}_T(\mathbf{R}_T)$
non-corrected vertical ionization energy at triplet optimum	$IP_T^{vert,non} \equiv \mathcal{E}_c(\mathbf{R}_T) - \mathcal{E}_T(\mathbf{R}_T)$
corrected vertical ionization energy at singlet optimum, *etc*	$IP_S^{vert,corr} \equiv \mathcal{E}_c(\mathbf{R}_c) + \varepsilon_c - [\mathcal{E}_S(\mathbf{R}_S) + \varepsilon_S]$, *etc*
non-corrected adiabatic electroaffinity wrt singlet	$EA_S^{ad,non} \equiv \mathcal{E}_S(\mathbf{R}_S) - \mathcal{E}_a(\mathbf{R}_a)$
non-corrected vertical electroaffinity at singlet optimum	$EA_S^{vert,non} \equiv \mathcal{E}_S(\mathbf{R}_S) - \mathcal{E}_a(\mathbf{R}_S)$
non-corrected adiabatic electroaffinity wrt triplet	$EA_T^{ad,non} \equiv \mathcal{E}_T(\mathbf{R}_T) - \mathcal{E}_a(\mathbf{R}_a)$
non-corrected vertical electroaffinity at triplet optimum	$EA_T^{vert,non} \equiv \mathcal{E}_T(\mathbf{R}_T) - \mathcal{E}_a(\mathbf{R}_T)$
corrected vertical electroaffinity energy at triplet optimum, *etc*	$EA_T^{vert,corr} \equiv \mathcal{E}_T(\mathbf{R}_T) + \varepsilon_t - [\mathcal{E}_a(\mathbf{R}_T) + \varepsilon_T]$, *etc*
cation's reorganization energy wrt singlet	$\lambda_S^c \equiv \mathcal{E}_c(\mathbf{R}_S) - \mathcal{E}_c(\mathbf{R}_c)$
cation's reorganization energy wrt triplet	$\lambda_T^c \equiv \mathcal{E}_c(\mathbf{R}_T) - \mathcal{E}_c(\mathbf{R}_c)$
anion's reorganization energy wrt singlet	$\lambda_S^a \equiv \mathcal{E}_a(\mathbf{R}_S) - \mathcal{E}_a(\mathbf{R}_a)$
anion's reorganization energy wrt singlet	$\lambda_T^a \equiv \mathcal{E}_a(\mathbf{R}_T) - \mathcal{E}_a(\mathbf{R}_a)$
non-corrected chemical hardness of the singlet isomer	$\eta_S^{vert,non} \equiv IP_S^{vert,non} - EA_S^{vert,non}$
non-corrected chemical hardness of the triplet isomer	$\eta_S^{vert,non} \equiv IP_T^{vert,non} - EA_T^{vert,non}$
non-corrected "combined" hardness of the singlet isomer	$\eta_S^{ad,non} \equiv IP_S^{ad,non} - EA_S^{ad,non}$
non-corrected "combined" hardness of the triplet isomer	$\eta_T^{ad,non} \equiv IP_T^{ad,non} - EA_T^{ad,non}$
corrected chemical hardness of the singlet/triplet isomer	$\eta_{S/T}^{vert,corr} \equiv IP_{S/T}^{vert,corr} - EA_{S/T}^{vert,corr}$
corrected "combined" hardness of the singlet/triplet isomer	$\eta_{S/T}^{ad,corr} \equiv IP_{S/T}^{ad,corr} - EA_{S/T}^{ad,corr}$

S2 Restricted Open-Shell *vs.* Unrestricted Calculations

As noted in Sec. 2 of the main text, spin contamination may in principle affect properties obtained *via* unrestricted (U...) methods. To be on the safe side, calculations for open shell cases reported in the main text were carried out using restricted open-shell (RO...) methods.

In fact, as illustrated by the examples presented here, the impact of spin contamination is insignificant for the specific cases envisaged. For the triplet $HC_{10}N$, UB3LYP/6-311++g(3df, 3pd) calculations yielded $\langle \mathbf{S}^2 \rangle = 2.1457$ before annihilation of the first spin contaminant and $\langle \mathbf{S}^2 \rangle = 2.0136$ after annihilation. This corresponds to spin values $S = 1.0478$ and $S = 1.00045$, respectively. In view of the negligible deviation from the exact value $S = 1$, it is not surprising that ROB3LYP- and UB3LYP-based properties do not notably differ from each other, as shown by the values collected in Tables S2 and S3.

Table S2: Bond lengths (d) of a triplet $HC_{10}N$ linear chain obtained from restricted open shell and unrestricted DFT/B3LYP/6-311++g(3df, 3pd) calculations. The carbon atoms in the triplet $HC_{10}N$ chain are numbered consecutively (C_1, C_2, C_3, ...) starting from the H atom to the N atom.

	HC_1	C_1C_2	C_2C_3	C_3C_4	C_4C_5	C_5C_6	C_6C_7	C_7C_8	C_8C_9	C_9C_{10}	$C_{10}N$
ROB3LYP	1.0619	1.2143	1.3342	1.2418	1.2983	1.2734	1.2636	1.3081	1.2333	1.3470	1.1630
UB3LYP	1.0620	1.2166	1.3318	1.2459	1.2967	1.2748	1.2661	1.3057	1.2370	1.3452	1.1643

Table S3: Wiberg bond indices ($\mathcal{N}$) of a triplet $HC_{10}N$ linear chain obtained from restricted open shell and unrestricted DFT/B3LYP/6-311++g(3df, 3pd) calculations. The carbon atoms in the triplet $HC_{10}N$ chain are numbered consecutively (C_1, C_2, C_3, ...) starting from the H atom to the N atom.

	HC_1	C_1C_2	C_2C_3	C_3C_4	C_4C_5	C_5C_6	C_6C_7	C_7C_8	C_8C_9	C_9C_{10}	$C_{10}N$
UB3LYP	0.9287	2.5102	1.3648	2.0392	1.5793	1.7464	1.8290	1.5154	2.1374	1.2889	2.6138
ROB3LYP	0.9282	2.5411	1.3512	2.0812	1.5654	1.7562	1.8494	1.4985	2.1792	1.2801	2.6315

S3 Properties of the Triplet $HC_{11}N$

For completeness, bond lengths and bond orders of the triplet $HC_{11}N$ chain (*i.e.*, the metastable $HC_{11}N$ isomer) are depicted in Figs. S1 and S2. These results are particularly important because they suggest that a triplet state enforces a cumulenic structure even in cases where all electrons can form pairs according to the standard rules of valence.

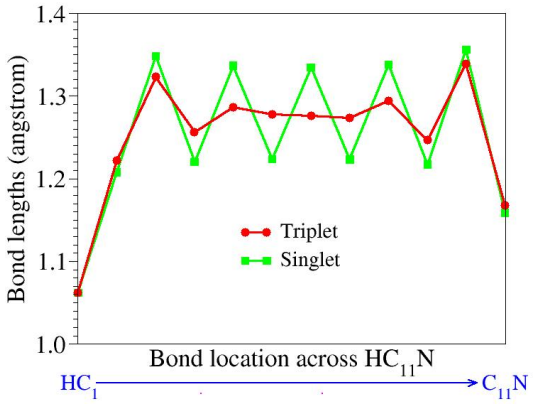

Figure S1: Bond lengths of triplet and singlet $HC_{11}N$ chains. The carbon atoms in chains are numbered consecutively (C_1, C_2, C_3, ...) starting from the H atom to the N atom. Notice that the triplet $HC_{11}N$ chain is characterized by a cumulenic structure, in contrast to the polyyne character of the singlet $HC_{11}N$ chain (*cf.* Fig. S2 and Fig. 2 in the main text).

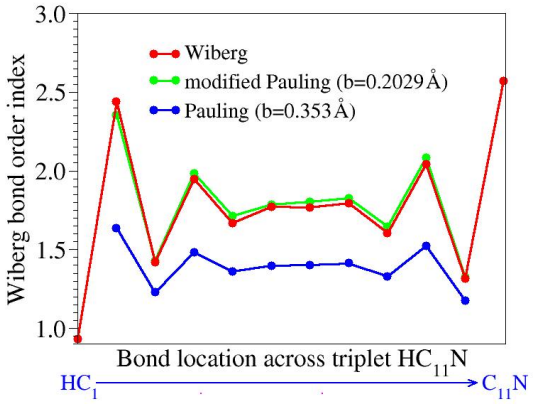

Figure S2: Wiberg bond indices ($\mathcal{N}$) of a triplet $HC_{11}N$ linear chain. The carbon atoms in chains are numbered consecutively (C_1, C_2, C_3, ...) starting from the H atom to the N atom. Notice that the triplet $HC_{11}N$ chain is characterized by a cumulenic structure, in contrast to the polyyne character of the singlet $HC_{11}N$ chain (*cf.* Fig. S1 and Fig. 2 in the main text).

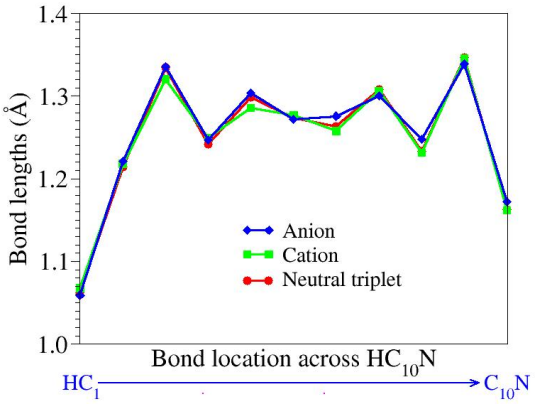

Figure S3: Bond lengths of various $HC_{10}N$ linear chains: neutral triplet, cation, and anion (labels T, +, and - in the main text). The carbon atoms in chains are numbered consecutively (C_1, C_2, C_3, ...) starting from the H atom to the N atom. The small differences in the geometries of these charge species (chain lengths $L_{n.t.} = 13.7390\,\text{Å}$, $L_+ = 13.7217\,\text{Å}$, $L_- = 13.7745\,\text{Å}$) reflect themselves in the very small reorganization energies λ indicated in Tables 7 and 8 of the main text.

S4 Additional Data for Electric Dipole and Quadrupole Momentum of $HC_{10}N$ Chains

To demonstrate the robustness of the estimates for electric dipole D and quadrupole momentum $\mathbf{Q}$ presented in Table 5 of the main text, values obtained by using various basis sets are collected in Table S4

S5 Additional Vibrational Spectra of $HC_{10}N$ Chains

Fig. S4 depicts additional infrared spectra. All numerical data underlying this figure and the related Fig. 5 of the main text are collected in Tables S5 and S6 where the $C_{\infty v}$-symmetries ($a_1 = \sigma_+$, $a_2 = \sigma_-$, $e_1 = \pi$) are indicated as obtained from GAUSSIAN 16[1] calculations.

Table S4: Electric dipoles **D** (debye) and quadrupole moments **Q** (debye-angstrom) of singlet ($S = 0$) and triplet ($S = 1$) $HC_{10}N$ chains in field-independent basis ($D_x = D_y = Q_{i\neq j} = 0$, molecular z-axis from H (positively charged) to N (negatively charged). Results obtained *via* DFT/B3LYP and CCSD(T) using the basis sets indicated in the second column. (Dipole oriented from H (positive) N (negative).

Spin	Method	D_z	Q_{xx}	Q_{yy}	Q_{zz}
$S = 0$	B3LYP, 6-311++g(3df, 3pd)	-7.0103	-59.7616	-63.1138	-67.7443
	B3LYP, cc-pvTZ	-6.9045	-59.5597	-62.8507	-65.8263
	B3LYP, aug-cc-pvTZ	-6.9985	-63.0100	-59.7976	-67.6938
	CCSD(T), 6-311++g(3df, 3pd)	-7.0202	-64.4555	-61.1693	-67.0326
	CCSD(T), cc-pVTZ	-6.9619	-64.2501	-61.0084	-65.8328
	CCSD(T), aug-cc-pVTZ	-7.0078	-64.3279	-61.1934	-66.9847
$S = 1$	RO-B3LYP, 6-311++g(3df, 3pd)	-6.8902	-61.3902	-61.3902	-67.9786
	RO-B3LYP, cc-pvTZ	-6.7830	-61.1659	-61.1659	-66.1385
	RO-B3LYP, aug-cc-pVTZ	-6.8777	-61.3555	-61.3555	-67.9323
	RO-CCSD(T), 6-311++g(3df, 3pd)	-6.9117	-62.8235	-62.8235	-67.9001
	RO-CCSD(T), cc-pVTZ	-6.8525	-62.6438	-62.6438	-66.7272
	RO-CCSD(T), aug-cc-pVTZ	-6.8976	-62.7706	-62.7706	-67.8580

Table S5: Unscaled phonon frequencies of the molecular vibrations with significant infrared (IR) intensities obtained *via* DFT/ROB3LYP/6-311++g(3df, 3pd) calculations for the triplet $HC_{10}N$ chain.

$\nu\,\mathrm{cm}^{-1}$	IR intensity (km/mol)	Symmetry
91.02	3.5134	π
91.02	3.5134	π
254.14	3.2010	π
254.14	3.2010	π
478.38	5.6058	π
478.38	5.6058	π
585.81	6.5847	π
585.81	6.5847	π
637.66	17.8412	π
637.66	17.8412	π
663.25	19.3101	π
663.25	19.3101	π
709.80	8.3849	σ_+
2075.25	22.2267	σ_+
2105.85	122.2943	σ_+
2258.32	169.4757	σ_+
3460.05	257.9971	σ_+

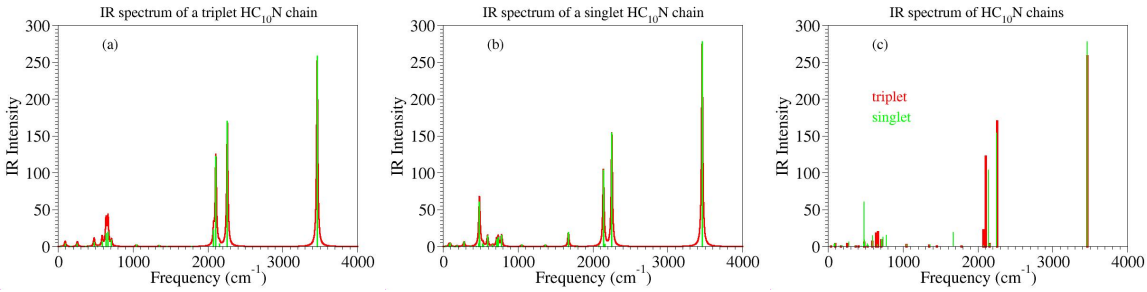

Figure S4: Additional infrared spectra of the triplet and singlet $HC_{10}N$ isomers. The spectra depicted here were convoluted by using obtained by using Lorentzian convolutions of the spectral lines (green spikes) calculated *via* DFT/B3LYP/6-311++g(3df, 3pd) (halfwidth $hw = 10\,\mathrm{cm}^{-1}$).

References

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, Gaussian 16, Revision B.01, 2016.

Table S6: Unscaled phonon frequencies of the molecular vibrations with significant infrared (IR) intensities obtained *via* DFT/RB3LYP/6-311++g(3df, 3pd) calculations for the singlet $HC_{10}N$ chain.

$\nu\,\mathrm{cm}^{-1}$	IR intensity (km/mol)	Symmetry
77.71	2.8889	?a
91.04	3.7212	?a
277.56	6.2471	?a
470.59	3.5720	?a
481.68	60.1046	?a
488.98	8.5384	?a
523.90	3.3852	?a
591.51	14.5577	?a
712.92	9.4541	σ_+
733.86	12.5985	?a
779.22	15.2197	?a
1671.86	18.7659	σ_+
2139.68	103.0968	σ_+
2252.12	153.6603	σ_+
3459.40	277.1618	σ_+