Exotic isomers of dicyanoacetylene: A density functional theory and *ab initio* study

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Prospects for the existence and detection of yet unknown dicyanoacetylene (NCCCCN) isomers are discussed, based on quantum-chemical calculations for linear, hexagonal and branched C_4N_2 structural variants. It is concluded that apart from dicyanoacetylene itself and its two already discovered isomers, NCCCNC and CNCCNC, at least two other species are of importance: linear CCCNCN and Y-shaped CC(CN)CN (dicyanovinylidene). Combined CCSD(T) and MP4 calculations predict CC(CN)CN and CCCNCN to be 57 kcal/mol and 66 kcal/mol less stable than dicyanoacetylene, respectively. The height of the energy barrier for dicyanoacetylene ←dicyanovinylidene isomerization is about 5 kcal/mol. Density functional theory calculations indicate that CCCNCN should give rise to prominent IR absorption bands, two orders of magnitude stronger than those of dicyanoacetylene. © *2002 American Institute of Physics.*
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I. INTRODUCTION

Dicyanoacetylene (butynedinitrile; NCCCCN), first characterized in 1909 by Moureu and Bongrand,[1,2] was tentatively identified, eight decades later, in Titan's atmosphere.[3,4] Its detection in clouds of interstellar matter (along with strikingly abundant cyanoacetylene[5]) was not feasible due to the centrosymmetric structure of the molecule, resulting in the absence of rotational microwave spectra. However, interstellar dicyanoacetylene may eventually be discovered due to the rapid development of the astronomical infrared spectroscopy. The existence of such bare carbon–nitrogen chains in space was recently postulated,[6] and it seems important to explore, both theoretically and experimentally, the entire C_4N_2 potential energy hypersurface, including the ''exotic'' isomers, highly unstable at normal conditions. These studies, pioneered by Smith *et al.*[7,8] and backed with accurate *ab initio* calculations by Botschwina *et al.*,[9,10,11] so far resulted in the identification of NCCCNC (cyano-iso-cyanoacetylene) and CNCCNC (di-iso-cyanoacetylene), created through the *in situ* ultraviolet photolysis of NCCCCN in solid argon. Present work deals with a range of C_4N_2 molecules, supplying the theoretical predictions for their equilibrium structures, energies, electric dipole moments, and infrared transitions.

II. DETAILS OF CALCULATIONS

All calculations reported in this study were accomplished with GAUSSIAN 98 suite of programs.[12] Hartree–Fock (HF) method and the 6-31 G* basis set[13] were used for some preliminary geometry optimizations. Density functional theory[14,15,16] (DFT) calculations, aimed at the reproduction of molecular geometries and harmonic vibrational frequencies (normal modes of molecular vibrations being obtained through analytical second derivatives of the total energy, with respect to nuclear positions) were accomplished with the Becke's three parameter hybrid exchange functional method[17] and the correlation functional of Lee, Yang, and Parr[18] (B3LYP). The Dunning's correlation-consistent polarized valence triple-zeta basis set, augmented by *s*, *p*, *d*, and *f* functions (aug-cc-pVTZ) (Ref. 19) was used in final DFT calculations. Additionally, for selected species, the equilibrium geometries were found at the Møller–Plesset[20] fourth order perturbation theory level, MP4(SDTQ), involving single, double, triple, and quadruple excitations with frozen core electrons, and the Dunning's cc-pVTZ basis set.[21] The single, double, and perturbative triple excitation coupled-clusters[22] calculations, CCSD(T)/cc-pVTZ, served exclusively to obtain ''single point'' energies for fixed MP4-derived geometries. [This corresponds to CCSD(T)//MP4 according to the notation adopted throughout the article.] The search for the transition state geometry was carried out with the synchronous transit-guided quasi-Newton (STQN) method[23] in conjunction with B3LYP/aug-cc-pVTZ; the transition state nature was further verified by tracing the reaction paths in both directions from the saddle point with the method of Gonzalez and Schlegel.[24] The *ab initio* energies of the transition state and relevant stable structures were compared at the uniform CCSD(T)/cc-pVTZ//MP4(SDQ)/cc-pVTZ level. Post SCF *ab initio* dipole moment calculations were limited to the MP4(SDQ)/cc-pVTZ. Standard convergence criteria were applied in all computations.

III. RESULTS AND DISCUSSION

Formally, dicyanodiacetylene has as many as 9 non-branched chain isomers, hereafter named **1–9** (see Fig. 1 for formulas). All were included in this study, together with dicyanovinylidene,

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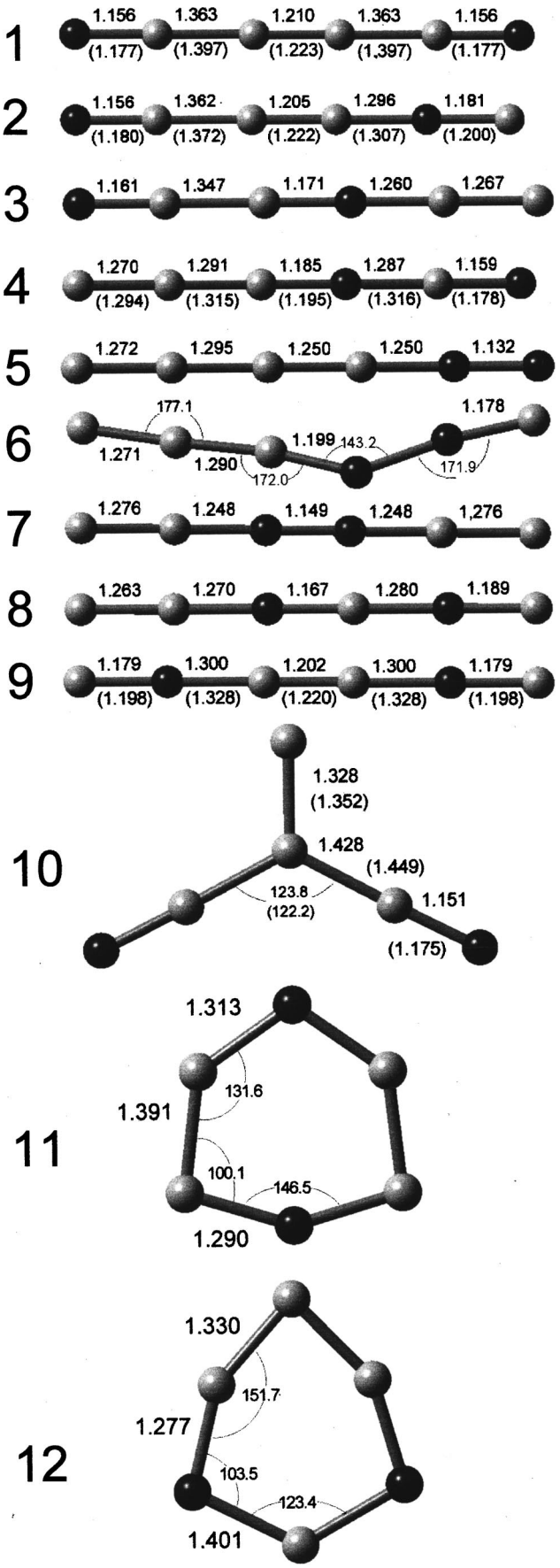
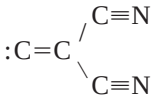


FIG. 1. Equilibrium geometries for selected isomers of C_4N_2, as derived by B3LYP/aug-cc-pVTZ calculations. Black balls represent nitrogen atoms. Bond lengths given in angstroms. Values in parentheses result from MP4(SDTQ)/cc-pVTZ geometry optimizations.



(**10**), presumably the most stable species among branched C_4N_2 structural variants. Additionally, the hexagonal arrangements with nitrogen atoms in para (**11**), meta (**12**), and ortho positions were considered.

The first stage of this project consisted in calculations of preliminary structures (in particular, in finding out what symmetries of chain species **1–9** are to be expected). Then, the geometries and IR spectra were obtained at the reliable DFT level. Finally, the geometry optimizations were repeated for selected species with *ab initio* methods, to improve the predictions on energies and dipole moments.

A. Preliminary structures

The rudimentary search for equilibrium geometries of chain molecules **1–9** was accomplished with simple HF/6-31G* optimizations. Planar starting geometries, with uniform bond lengths and all combinations of $+133°$ and $-133°$ angles between consecutive bonds were systematically tried. The nature of obtained stationary points on the potential energy surface was disclosed by the normal modes of molecular vibrations, saddle points being indicated by the appearance of imaginary frequencies. Energy minima corresponding to linear molecules were found for species **1–5** and **7–9**. The linear arrangement of molecule **6** was a second order saddle point; a bent structure was found as the local energy minimum. Some starting geometries led also to bent molecules **3**, **5**, and **7**. Bent **3** was 1.6 kcal/mol less stable than linear **3**, bent **5** had virtually the same energy as linear **5**, while bent **7** turned out to be a saddle point.

Preliminary calculations for the branched and hexagonal species consisted in geometry optimizations at the B3LYP/6-31G* level. The hexagon with adjacent nitrogen atoms (ortho structure) converged to dicyanoacetylene (**1**) and was rejected from further analysis.

It was checked that the ground states of all molecules under study were of singlet multiplicity. The UB3LYP/6-31G* scheme was used to find the geometries of triplet species for branched and cyclic isomers, while the combination of UHF/6-31G* and UB3LYP/6-31G* served to optimize diverse starting geometries of chain molecules. The potential energy minima of triplets (E_T) were compared to those of singlets (E_S) at the uniform DFT level. The $E_T - E_S$ differences were at least 19 kcal/mol, with the exception of isomer **11**, for which the triplet equilibrium structure was just 1.5 kcal/mol above the singlet.

B. Geometries and vibrational frequencies

In the second phase of the study, the B3LYP/aug-cc-pVTZ calculations were performed for singlet isomers **1–12**. This was aimed at producing the realistic predictions for geometries and corresponding harmonic vibrational frequencies, and at selecting the energetically favorable species. For molecules **1–5** and **7–9** the arbitrarily chosen zigzag starting geometries converged to linearity. Bent initial structures **3**, **5**, and **7** (yielded by HF calculations) were also subjected to

TABLE I. Former experimental and theoretical results for C_4N_2 isomers 1, 2, and 9.

	Species	Energy relative to species 1 (kcal/mol)	Electric dipole moment (D)	Rotational constant (GHz)			Main IR vibrational transitions			
							Frequency (cm^{-1})		Intensity	
				Expt. B_0	Theory B_e	Expt.+Theor. B_e[h]	Expt.[i]	Theory (anharmonic)	Expt.[l]	Theory (km/mol)
1	NCCCCN	0	0	1.336 68[d]	1.330 0[f]	1.3334[f]	471, 1154, 2241	466, 1134, 2272[j]	100, 8, 76	⋯
2	CNCCCN	25.3,[a] 25.7[b]	1.04[c]	1.409 98[e]	1.408 58[g]	1.408 92[e]	2053, 2210, 2296	2061, 2231, 2321[c]	100, 54, 54	186, 78, 57[c]
9	CNCCNC	52.5[a]	0				1288, 2115	1213, 2122[k]	13, 100	9, 553[k]

[a]CEPA-1 (Ref. 10).
[b]CCSD(T), (Ref. 11), zero-point energy included.
[c]CCSD(T) (Ref. 9).
[d]Reference 25.
[e]Reference 11.
[f]Reference 26.
[g]CCSD(T), geometry corrected for systematic errors (Ref. 11).
[h]$B_e = B_0(\text{expt.}) + \Delta B(\text{theor})$; see text.
[i]Gas phase data (Refs. 3, 11) for species 1 and 2; Ar matric data (Ref. 7) for 9.
[j]CEPA-1 (Ref. 26); frequency 466 cm^{-1} derived with the harmonic approximation.
[k]Unpublished *ab initio* results of Botschwina *et al.*, as cited in Ref. 7.
[l]Gas phase data (Ref. 3) for species 1; Ar matrix data (Ref. 7) for 2 and 9; intensity of the strongest band arbitrarily taken as 100 for each isomer.

B3LYP/aug-cc-pVTZ geometry optimizations; bent **3** was 1.2 kcal/mol higher in energy than linear **3**, whereas bent **5** and **7** ceased to be stationary points, at this level of theory, and evolved towards linear structures. For molecule **6**, similarly as in the HF study, the linear conformation was in fact a saddle point, and the energy minimum was found for a bent arrangement.

The correctness of DFT-produced equilibrium structures can be evaluated making use of experimental ground-state rotational constants (B_0), available for isomers **1** (Ref. 25) and **2**.[11] These are related to equilibrium rotational constants, $B_e = B_0 + \Delta B$, where ΔB is half the sum of the vibration-rotation coupling coefficients multiplied by degeneracy factors. The ΔB values calculated with CEPA-1 for species **1** (Ref. 26) and with CCSD(T) for **2** (Ref. 11) gave, together with measured B_0, highly accurate equilibrium rotational constants (see Table I, and references therein). Present study leads to B_e higher by 1.2% (**1**) and 0.8% (**2**), which suggests that—also for other rod-shaped C_4N_2 isomers—our B3LYP/aug-cc-pVTZ-derived B_e constants should be scaled down with the factor 0.99. Mixed experimental-theoretical B_e values obtained for different isotopomers of **2** enabled Bartel *et al.*[11] to report the following equilibrium geometry (in Å, for N1–C1–C2–C3–N2–C4): $R_{N1-C1} = 1.1611$, $R_{C1-C2} = 1.3712$, $R_{C2-C3} = 1.2074$, $R_{C3-N2} = 1.3050$, $R_{N2-C4} = 1.1819$, with errors presumably smaller than 0.001 Å. Presently calculated values are shortened by 0.4%, 0.7%, 0.2%, 0.7%, and 0.1%, respectively.

Table II lists the energies and equilibrium electric dipole moments, together with harmonic frequencies and absolute intensities of IR vibrational transitions (strongest bands are given for each molecule). Values derived for species **1**, **2**,

TABLE II. Energies, dipole moments, and main IR vibrational transitions of C_4N_2 molecules, as predicted by the density functional theory (B3LYP/aug-cc-pVTZ).

C_4N_2 species		Symmetry	Total energy[a] (hartree)	Energy relative to species 1[a] (kcal/mol)	Equilibrium rotational constants[b] (GHz)	Electric dipole moment (D)	Main IR vibrational transitions[c]	
							Harmonic frequency[d] (cm^{-1})	Intensity (1000 km/mol)
1	NCCCCN	$D_{\infty h}$	−261.883 991	0	1.3494	0	109, 492, 1142, 2249	0.011, 0.008, 0.00008, 0.012
2	CNCCCN	$C_{\infty v}$	−261.846 202	23.7	1.4213	1.33	2029, 2205, 2285	0.23, 0.05, 0.11
3	CCNCCN	$C_{\infty v}$	−261.765 228	74.5	1.467	2.53	1939, 2173, 2262	0.71, 0.33, 0.62
4	CCCNCN	$C_{\infty v}$	−261.791 218	58.2	1.477	0.94	1918, 2216, 2278	0.25, 0.90, 1.68
5	CCCCNN	$C_{\infty v}$	−261.743 732	88.0	1.439	4.49	1876, 2134, 2207	0.47, 0.42, 3.04
6	CCCNNC	C_s	−261.712 545	107.6	103.8,1.619.1.594	1.60	2083, 2194	0.84, 1.47
7	CCNNCC	$D_{\infty h}$	−261.615 693	168.4	1.582	0	1963	2.46
8	CCNCNC	$C_{\infty v}$	−261.723 001	101.0	1.546	4.33	1914, 2017, 2296	0.13, 1.30, 0.35
9	CNCCNC	$D_{\infty h}$	−261.805 347	49.3	1.497	0	1230, 2092	0.004, 0.560
10	CC(CN)CN	C_{2v}	−261.785 274	61.9	8.860,2.742,2.094	1.28	215, 1554	0.02, 0.05
11	meta-cyclic	C_{2v}	−261.714 886	106.1	7.848,7.485,3.831	1.31	614, 1554, 1695	0.11, 0.16, 0.23
12	para-cyclic	C_{2v}	−261.659 069	141.1	8.105,7.236,3.823	0.59	347, 873, 897, 1413, 1533	0.12, 0.19, 0.16, 0.21, 0.19

[a]Zero-point correction included.
[b]B_e constants for linear species (B_e multiplied by 0.99 can serve as the prediction for B_0; see text); A_e, B_e, and C_e for nonlinear species.
[c]The most intense bands for each isomer are listed; transitions predicted as relatively weak are included for 1 and 9 to ease the comparison with available experimental and theoretical data (cf. Table I); complete listings of vibrational transitions for species 4 and 10 are given in Table III.
[d]Scaled down with the factor 0.96.

TABLE III. Harmonic vibrational frequencies and IR intensities of CCCNCN (4) and CC(CN)CN (dicyanovinylidene, 10), as predicted with B3LYP/aug-cc-pVTZ.

Mode	Symmetry	Frequency[a] (cm^{-1})	Intensity (km/mol)
		CCCNCN	
ν_1	σ	2279	1679
ν_2	σ	2216	898
ν_3	σ	1918	249
ν_4	σ	1210	8.6
ν_5	σ	660	0.7
ν_6	π	497	4.9
ν_7	π	439	14
ν_8	π	161	3.4
ν_9	π	52	8.9
		CC(CN)CN	
ν_1	a_1	2252	2.1
ν_2	b_2	2247	0.4
ν_3	a_1	1554	53
ν_4	b_2	1107	2.5
ν_5	a_1	707	1.9
ν_6	b_1	578	0.8
ν_7	a_1	540	0.0
ν_8	a_2	384	0.0
ν_9	b_2	368	0.2
ν_{10}	b_1	215	20
ν_{11}	b_2	130	4.9
ν_{12}	a_1	127	9.6

[a]Scaled down with the factor 0.96.

and **9** generally agree well with former experimental and theoretical data collected in Table I. As expected, however, when compared with advanced *ab initio* treatment of anharmonic vibrations, DFT is much worse in reproducing IR intensities.

The most important predictions of the DFT study concern species **10**, CC(CN)CN, and **4**, CCCNCN. It appears that the energy of **4**, corrected for the zero-point energy (ZPE), is just several kcal/mol above that of the known centrosymmetric isomer **9**. Isomer **4** is remarkable due to the outstanding strength of its infrared bands, approaching 1700 and 900 km/mol—which may facilitate their detection in forthcoming laboratory experiments and astronomical searches. Isomer **10**, of the similar energy, is expected to have medium intensity IR bands. The complete listings of predicted fundamental modes for species **4** and **10**, given in Table III, can serve as guidelines in the spectroscopic work. Frequency values were scaled down with a uniform factor to account for the anharmonicity, incomplete inclusion of electron correlation, and deficiencies in the basis set. The factor 0.96 was chosen after comparing the calculated values with available experimental frequencies for species **1**, **2**, and **9**. Similar scaling factors were shown to work well for B3LYP calculations with basis sets 6-31G* (0.9613; huge selection of arbitrarily chosen molecules[27]) and 6-311+G* (0.956; recent work on cyanoacetylene isomers[28]).

C. *Ab initio* calculations

In the final stage of the study, geometry optimizations for most important isomers were repeated at the higher level of theory—to refine the energetics. The *ab initio* calculations were performed on molecules with frozen symmetries (either $D_{\infty h}$, $C_{\infty v}$ or C_{2v}, as predicted with DFT). MP4(SDTQ)-derived bond lengths and angles for **1**, **2**, **4**, **9**, and **10** are listed in Fig. 1. Calculated lengths are expected to be too large by not more than 2%, as exemplified by molecule **2**, for which the experimental data are available;[11] the main share of this elongation presumably stems from the neglect of the core electrons correlation. B3LYP/aug-cc-pVTZ geometries seem more accurate.

TABLE IV. *Ab initio* potential energy minima, relative energies, and equilibrium electric dipole moments for selected C_4N_2 isomers.

	Species	CCSD(T)/cc-pVTZ energy (hartree)[a]	Zero-point energy[b] (kcal/mol)	Energy[c] relative to species 1 (kcal/mol)	Electric dipole moment[d] (D)
1	NCCCCN	−261.364 808	16.7		0
2	CNCCCN	−261.323 774	16.3	25.3	1.10
4	CCCNCN	−261.257 982	15.8	66.1	1.58
9	CNCCNC	−261.279 672	15.9	52.6	0
10	CC(CN)CN	−261.270 927	15.2	57.4	1.88

[a]Single point calculation for fixed MP4(SDTQ)/cc-pVTZ geometry.
[b]B3LYP/aug-ccpVTZ.
[c]Including the zero-point vibrational energy.
[d]MP4(SDQ)/cc-pVTZ//MP4(SDQ)/cc-pVTZ.

Conversely, the energies yielded by CCSD(T)//MP4(SDTQ) (Table IV) are more reliable than corresponding DFT values. The relative numbers for species **2** and **9** practically match those found by Botschwina *et al.* (cf. Table I); the latter have to be regarded as highly precise. The energies of **4** and **10** suggest, just as precedent DFT results, that these two molecules are potentially detectable C_4N_2 isomers. It has to be noticed that the reverse—when compared to DFT—energy order for compounds **4** and **10** was obtained. Namely, the ZPE-corrected dicyanovinylidene (**10**) potential energy is 5 kcal/mol above that of known species **9**, while the energy of **4** is higher by an additional 9 kcal/mol (ZPEs calculated with B3LYP/aug-cc-pVTZ).

The MP4(SDQ)-derived electric dipole moment of **2** (Table IV) is very close to the more refined CCSD(T) value reported by Horn *et al.*[9] (cf. Table I), which enables us to draw reliable conclusions from two other μ_e values delivered by present *ab initio* calculations. Specifically, rather low (though higher than predicted by DFT) dipole moments of **4** and **10** mean that the detection of corresponding interstellar rotational microwave spectra would be difficult, if possible.

The barrier height for dicyanoacetylene←dicyanovinylidene (**1**←**10**) isomerization, calculated at the CCSD(T)//MP4(SDQ) level, amounts to 5.8 kcal/mol classically, and diminishes to 5.1 kcal/mol after the inclusion of ZPE corrections. [The ZPE of the transition state (**TS**) is 14.5 kcal/mol, as predicted by B3LYP/aug-cc-pVTZ.] At the B3LYP/aug-cc-pVTZ level the ZPE-corrected barrier is 3.5 kcal/mol. The imaginary vibrational mode of **TS** (Fig. 2) moves the terminal carbon atom towards one of cyano groups, thus distorting the structure in the direction of **1**. The vibrational mode of **10**, which promotes the **1**←**10** isomerization, is ν_9 (Table III) with corresponding harmonic vibra-

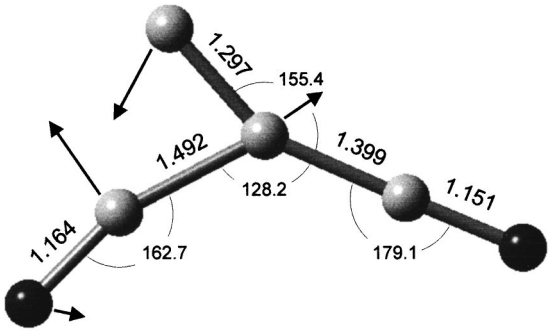


FIG. 2. Geometry of the transition state (saddle point) between dicyanoacetylene and dicyanovinylidene potential energy minima, as derived by B3LYP/aug-cc-pVTZ. Bond lengths given in angstroms, black balls are nitrogen atoms, arrows represent displacement vectors for the imaginary normal mode.

tional quantum of $\approx$1 kcal/mol. Calculations indicate that it takes several such quanta to climb the barrier towards **1**. These qualitative considerations suggest dicyanovinylidene to be a well bound species.

It is of interest at this point to recall the results of Hu and Schaefer,[29] who did extensive *ab initio* calculations on cyanovinylidene, CC(H)CN. Their CCSD(T)/TZ2P study yielded 47 kcal/mol as the ZPE-corrected energy difference between cyanoacetylene (the global minimum on the PES of HC_3N) and cyanovinylidene. The barrier for reverse isomerization (towards cyanoacetylene) was 2.2 kcal/mol with ZPE (roughly two quanta of the cyanovinylidene mode that leads to the transition state). These predictions were very quickly followed by the experimental (mass-spectrometric) evidence for the existence of cyanovinylidene.[30]

IV. CONCLUSIONS

Despite relatively high potential energy, the linear species CCCNCN is—considering the strength of its infrared spectrum—the candidate for detection in laboratory samples and in interstellar molecular clouds. It can probably be trapped and isolated, together with its Y-shaped isomer dicyanovinylidene, CC(CN)CN, in cryogenic rare gas matrices, after the suitable decomposition and rearrangement of gaseous dicyanoacetylene. The entire C_4N_2 hypersurface, with transition states linking numerous minima, deserves further exploration in order to adequately evaluate the stabilities of different isomers, including the highly energetic ones. Likewise, the availability of synthetic routes, which could possibly lead to the interstellar formation of polycarbon–dinitrogen molecules, remains an open issue.

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