



HCNCC – the possible isomer of cyanoacetylene

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Abstract

HCNCC, the exotic linear rearrangement of cyanoacetylene, is a probable interstellar molecule. The Letter compares CCSD(T)/aug-cc-pVTZ energies of five cyanoacetylene isomers, and predicts properties of the HCNCC ground singlet electronic state: geometry, equilibrium rotational constant, electric dipole moment and vibrational frequencies – based on the coupled-clusters and density functional theory (B3LYP/aug-cc-pVTZ) studies.

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1. Introduction

Even though cyanoacetylene (hereafter: **1**) is known since the beginning of the last century [1], its isomers are studied experimentally for but a decade. The rotational transitions of two carbene species: HCCNC (isocyanoacetylene; **2**) and CCCNH (imine isomer; **3**), were detected in interstellar gas clouds [2,3] and in the laboratory [4,5]. These discoveries were followed by the detection of vibrational spectra in the gas phase [6] (HCCNC) and in rare gas matrices [7,8] (HCCNC and CCCNH). Cyanovinylidene (CC(H)CN; henceforth: **5**), a *branched* rearrangement of cyanoacetylene, was thoroughly analysed theoretically by Hu and Schaefer [9], and, shortly afterwards, detected by mass spectrometry [10].

To our knowledge, the literature on HCNCC (**4**) – the missing fourth chain isomer of cyanoacetylene – is limited to the paper by Osamura et al. [11], who were interested in the gas phase chemistry following the reaction $\text{HCCCNH}^+ + e^-$, likely to occur in interstellar molecular clouds. One of Osamura's et al. findings was that HCNCC can indeed emerge from rearrangements triggered by this dissociative recombination, in addition to more stable species **1**, **2** and **3**. The energy difference between **4** and **1** was predicted as 67.9 kcal/mol (B3LYP/DZP) or 79.8 kcal/mol (CCSD(T)/cc-pVTZ//B3LYP/DZP).

In laboratories, despite being a highly energetic species, HCNCC is a conceivable product of electrical discharges through cyanoacetylene. It is particularly likely to be found among discharge products trapped and isolated in rare gas matrices.

The goal of this study was to improve the accuracy of HCNCC equilibrium geometry and

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dipole moment calculations, to shine some light on its peculiar electronic structure, and to supply predictions on the equilibrium rotational constant and vibrational frequencies.

2. Computational details

All calculations were carried out with GAUSSIAN 98 suite of programs [12]. The CCSD(T) method [13] (single, double and perturbative triple excitations coupled-clusters) with frozen core electrons was employed for geometry optimizations and to supply accurate predictions on energies. The electric charge distribution was derived with the theory variant CCD (coupled-clusters with double excitations). Independently, the equilibrium structures, energies and harmonic frequencies of molecular vibrations (the latter through analytical second derivatives of the total energy, with respect to nuclear positions) were predicted by the density functional theory (DFT) [14–16] using the B3LYP hybrid exchange-correlation functional [17,18]. The natural bond orbitals (NBO) [19,20] analysis (GAUSSIAN NBO Ver. 3.1) was accomplished at SCF and DFT levels. The

correlation-consistent polarized valence triple-zeta basis set augmented by s, p, d and f functions (aug-cc-pVTZ) [21] was employed in all computations. Standard convergence criteria were applied.

3. Results and discussion

Given the lack of a uniform (i.e., yielded by a single computational procedure) set of energy values for cyanoacetylene isomers, we find it useful to recalculate the structures of species **1–5** at the CCSD(T)/aug-cc-pVTZ level of theory (Table 1) – even though the variety of high-quality theoretical predictions already existed [9,22,23]. The difference between local minima of **4** and **1** is 79.2 kcal/mol, just 0.6 kcal/mol below the value predicted by Osamura et al. [11] at the lower level of theory (see Section 1). With the inclusion of the zero-point vibrational energy (as given by B3LYP/aug-cc-pVTZ) the **4–1** separation drops down to 77.6 kcal/mol. It is interesting to compare the energies of **3** and **5**; the elusive cyanovinylidene (**5**) molecule is predicted to be 2.3 kcal/mol more stable than the well-characterized imine **3** (zero-point energy included).

Table 1
Total energies for five C₃HN isomers and relative energies against cyanoacetylene

C ₃ HN species	Total energy (hartree)	Zero-point vibrational energy (kcal/mol)	Relative energy (kcal/mol)	Reference
HCCCN (1)	–169.223358 ^a	16.17 ^b	–	[9]
	–169.265277 ^c		–	[23]
	–169.289101	16.42	–	This work
HCCNC (2)	–169.193112 ^c		26.2	[22]
			27.2 ^d	[11]
	–169.245868	15.85	26.6 [*]	This work
CCCNH (3)			53.8 ^c	[22]
			52.5 ^d	[11]
	–169.206662	15.56	50.9 [*]	This work
HCNCC (4)			79.8 ^d	[11]
	–169.162940	14.87	77.6 [*]	This work
CC(H)CN (5)	–169.145887 ^a	14.74 ^b	47.2 [*]	[9]
	–169.209774	15.23	48.6 [*]	This work

^aThis work' refers to total energies for structures optimized with CCSD(T)/aug-cc-pVTZ and to zero-point vibrational energies given by B3LYP/aug-cc-pVTZ. Other methods: (a) CCSD(T)/TZ2P; (b) CCSD(T)/DZP; (c) coupled-electron-pair approximation (CEPA-1) with 118 contracted Gaussian-type orbitals; (d) CCSD(T)/cc-pVTZ for B3LYP/DZP geometry.

^{*}Corrected for zero-point vibrational energies.

We found that the lowest triplet state of **4** is much higher in energy (30 kcal/mol at the UB3LYP/aug-cc-pVTZ theory level) than the singlet, and corresponds to a nonlinear chain. Fig. 1 presents the geometries of HCNCC ground state given by our ab initio and DFT calculations. The molecule is linear, similarly to other chain isomers of cyanoacetylene, with the exception of the quasi-linear imine **3** [22]. The substantial separation of charges along this rod-like species results in a very high equilibrium dipole moment, $\mu_e = 8.10$ D; such high a value was also predicted by Osamura et al.

HCNCC is a bizarre molecule, with an unusual electronic organization. The NBO analysis (Table 2) points to the Lewis formula with eight bonding electron pairs, and a lone pair on the terminal carbon atom: $\text{H}-\text{C}\equiv\text{N}^+-\text{C}\equiv\text{C}^-$. This picture gives some rationale to the predicted charge distribution but is certainly oversimplified; calculated $r_{\text{C2-C3}}$ is too long for a true triple bond; in fact it is only slightly shorter than $r_{\text{N-C2}}$ (numbering convention: H-C1-N-C2-C3). This elongation of $r_{\text{C2-C3}}$ stems from the sizeable electronic delocal-

ization, most clearly seen in the decreased occupancy of relevant π -type NBOs, and in the corresponding population of antibonding $\pi_{\text{C1-N}}^*$ orbitals. (Within the framework of the idealized Lewis structure, $\pi_{\text{C2-C3}}$ and $\pi_{\text{C1-N}}^*$ would be highest occupied and lowest unoccupied orbitals, respectively.)

The highly precise bond lengths were already given for species **1** and **2** by a mixed experimental–theoretical approach [22,23] based on the measurements of ground state rotational constants for different isotopomers, and on ab initio vibration-rotation coupling constants. These can serve to estimate the accuracy of present calculations. As evidenced by Table 3, our equilibrium geometries of **1** and **2** advocate for a simple scaling recipe: take the B3LYP value of C–H distance as exact, and multiply CCSD(T) values for all remaining bonds by 0.995. Applying this procedure to species **4** we obtained the corrected internuclear distances (Å): $r_{\text{H-C1}} = 1.063$, $r_{\text{C1-N}} = 1.163$, $r_{\text{N-C2}} = 1.278$, $r_{\text{C2-C3}} = 1.266$. The ensuing value of the equilibrium rotational constant is $B_e = 4992$ MHz.

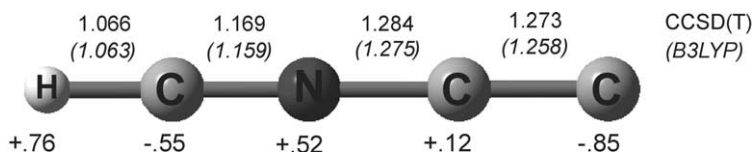


Fig. 1. Bond lengths (Å) and the partition of charges for the $X^1\Sigma$ state of HCNCC. See text for the final geometry prediction based on the appropriate scaling of calculated distances. Atomic charges produced by the Mulliken population analysis (CCD/aug-cc-pVTZ).

Table 2
Most populated valence shell Natural Bond Orbitals (NBO) for HCNCC

Orbitals ^a	Occupancy (electrons)		Relative energy (hartree)	
	HF/aug-cc-pVTZ	B3LYP/aug-cc-pVTZ	HF/aug-cc-pVTZ	B3LYP/aug-cc-pVTZ
σ (H-C1)	2.00	1.99	-0.86	-0.69
σ (C1-N)	2.00	1.99	-1.38	-1.13
π (C1-N)	1.98	1.97	-0.58	-0.46
π (C1-N)	1.98	1.97	-0.58	-0.46
σ (N-C2)	2.00	1.99	-1.12	-1.01
σ (C2-C3)	2.00	1.99	-0.87	-0.81
π (C2-C3)	1.82	1.74	-0.25	-0.27
π (C2-C3)	1.82	1.74	-0.25	-0.27
Lone pair C3	1.99	1.97	-0.46	-0.40
π^* (C1-N)	0.18	0.26	0.21	-0.03
π^* (C1-N)	0.18	0.26	0.21	-0.03

^a Atom numbering: H-C1-N-C2-C3.

Table 3

CCSD(T)/aug-cc-pVTZ and B3LYP/aug-cc-pVTZ bond lengths (Å) for HCCCN and HCCNC, together with their percentage deviations from best known experimental/theoretical values

	H–C–C–N				H–C–C–N–C			
	R(H–C)	R(C–C)	R(C–C)	R(C–N)	R(H–C)	R(C–C)	R(C–N)	R(N–C)
CCSD(T)	1.065 0.28%	1.212 0.49%	1.383 0.51%	1.167 0.52%	1.064 0.28%	1.210 0.58%	1.320 0.46%	1.186 0.59%
B3LYP	1.062 0%	1.201 –0.41%	1.368 –0.58%	1.155 –0.52%	1.061 0%	1.199 –0.33%	1.306 –0.61%	1.177 –0.17%
Exp./theor. (Botschwina et al. [22,23])	1.062	1.206	1.376	1.161	1.061	1.203	1.314	1.179

Table 4

Harmonic frequencies (downscaled^a by 0.96) and absolute intensities for three isotopomers of HCNCC, as derived with B3LYP/aug-cc-pVTZ

Mode/symmetry	¹ H ¹² C ¹⁴ N ¹² C ¹² C		¹ H ¹² C ¹⁵ N ¹² C ¹² C		² H ¹² C ¹⁴ N ¹² C ¹² C	
	(cm ⁻¹)	(km/mol)	(cm ⁻¹)	(km/mol)	(cm ⁻¹)	(km/mol)
ν_1/σ	3325	415	3324	407	2599	517
ν_2/σ	2159	772	2121	797	2071	727
ν_3/σ	1934	272	1931	227	1872	100
ν_4/σ	948	6.6	943	7.1	933	7.2
ν_5/π	501	0.7	492	1.0	493	0.6
ν_6/π	395	34	388	34	401	15
ν_7/π	359	49	359	49	282	22
ν_8/π	184	0.04	184	0.06	190	1.0
ν_9/π	182	0.07	181	0.07	174	0.17

^a To account for the anharmonicity, incomplete inclusion of electron correlation and basis set deficiencies [8].

Table 4 presents the vibrational transitions of HCNCC calculated with B3LYP. The predicted infrared spectrum is dominated by the C–H stretch band and two highly delocalized modes in the triple bond stretching region. Data for deuterated and ¹⁵N-substituted species are included to help in the interpretation of possible IR features generated from isotopically modified precursors.

4. Conclusions

Chances for the discovery of HCNCC, the fourth formally possible chain isomer of cyanoacetylene, albeit reduced by the molecule high energy, may still be significant due to its prominent dipole moment and strong infrared transitions.

The predicted IR spectrum and the recommended value of the equilibrium rotational constant should assist in ongoing¹ and planned spectroscopic experiments.

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