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Urszula Szczepaniak, Robert Kolos, Marcin Gronowski, Michèle Chevalier, Jean-Claude Guillemin, et al.. Cryogenic Photochemical Synthesis and Electronic Spectroscopy of Cyanotetracetylene. *Journal of Physical Chemistry A*, 2017, 121 (39), pp.7374-7384. 10.1021/acs.jpca.7b07849 . hal-01617947

HAL Id: hal-01617947

<https://univ-rennes.hal.science/hal-01617947>

Submitted on 24 Oct 2017

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Cryogenic Photochemical Synthesis and Electronic Spectroscopy of Cyanotetracetylene

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1
2
3 ABSTRACT
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6 HC₉N is a molecule of astrochemical interest. In this study, it was produced in cryogenic Ar and
7
8 Kr matrices from UV-photolyzed diacetylene/cyanodiacetylene mixtures. Its strong
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10 phosphorescence was discovered and served for the identification of the compound.
11
12 Vibrationally-resolved phosphorescence excitation spectra gave insight into excited singlet
13
14 electronic states. Two electronic systems were observed: around 26 000 – 34 000 cm⁻¹ and
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16 35 000 – 50 000 cm⁻¹. Energies of the second excited singlet and the lowest triplet state were
17
18 derived from analysis of these systems. Vibrational and electronic spectroscopic features were
19
20 assigned with the assistance of density functional theory calculations. Some trends concerning
21
22 the electronic spectroscopy of HC_{2n+1}N family molecules are presented.
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INTRODUCTION

Monocyanopolyynes (HC_{2n+1}N) constitute the most prominent homologous series of astrochemically-relevant molecules. They have been detected via microwave rotational transitions in many extraterrestrial sources up to $n = 4$. Cyanoacetylene, HC_3N , the smallest neutral molecule possessing both $-\text{C}\equiv\text{C}-$ and $-\text{C}\equiv\text{N}$ structural motifs, was first observed in a star-forming region Sagittarius (Sgr B2(N))¹ and then in other Galactic²⁻⁴ and extragalactic⁵ radio sources. It has also been detected in the atmosphere of Titan^{6,7} and in Hale-Bopp comet⁸. Along with cyanoacetylene, longer members of the HC_{2n+1}N series ($n = 2, 3$) have been found in several molecular clouds.⁹ HC_9N (cyanotetraacetylene, 1-cyano-octa-1,3,5,7-tetrayne or nona-2,4,6,8-tetraynenitrile) was first observed in 1978 at millimeter wavelengths in the dense interstellar cloud HCl-2.¹⁰ It has also been found in expanding circumstellar envelopes (IRC +10216^{11,12} and CRL 2688¹²). As observations of the $n = 5$ species, HC_{11}N , in IRC +10216¹³ and in the Taurus Molecular Cloud¹⁴ have been challenged, first in IRC +10216¹⁴ and now in TMC-1,¹⁵ HC_9N is currently considered the longest member of the family to have been observed in space.

The astrochemical synthesis of monocyanopolyynes probably involves the reactions of CN^{\bullet} or $\text{C}_{2n+1}\text{N}^{\bullet}$ radicals with polyynic hydrocarbons HC_{2m}H . Cherchneff *et al.* proposed the following pathway for formation of monocyanopolyynes around IRC +10216: $\text{HC}_2\text{H} + \text{C}_{2n+1}\text{N}^{\bullet} \rightarrow \text{HC}_{2n+3}\text{N} + \text{H}^{\bullet}$ ^{16,17}. Loomis *et al.*¹⁵ suggested that cyclization reactions are responsible for non-detection of $n > 4$ cyanopolyynes.

The astronomical detections of HC_9N were based on microwave spectroscopy combined with quantum chemical studies of molecular structure.¹⁸⁻²¹ Density functional theory (B3LYP) investigations²² have suggested that HC_{2n+1}N compounds should be linear and polyynic (having alternating single and triple bonds) at least up to $n = 8$. Vichiatti and Haiduke predicted IR spectra of long cyano-²³ (HC_{2n}CN) and isocyanopolyynes²⁴ (HC_{2n}NC) and suggest that the central triple bond stretching mode is the one producing the strongest band.

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2 Gas-phase spectroscopic studies of HC₉N are limited to microwave measurements in which
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4 minute amounts of the substance are transiently formed in a discharge plasma using acetylene
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6 with acrylonitrile²⁵ or dicyanoacetylene with cyanoacetylene²⁶ as seed gases. These
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8 investigations allowed derivation of the molecular geometry. Independently, electronic
9
10 absorption and NMR spectra of HC₉N in organic solvents have been reported²⁷⁻³². In particular,
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12 Wakabayashi *et al.*³¹ obtained HC_{2n+1}N (*n* = 3-6) by laser ablation of isotope-enriched (99 %
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14 ¹³C) graphite in liquid acetonitrile followed by chromatographic purification. Very small
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16 amounts of the compound were then characterized by UV absorption and NMR spectroscopy.
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18 Isotopic experiments proved that the carbon atoms of HC₉N came both from graphite and
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20 solvent. The molecule has also appeared among the products of graphite bombardment with high
21
22 energy H₂ and N₂ beams.³³
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27 In order to extend the spectroscopic characterization of cyanotetraacetylene, we aimed at
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29 synthesizing the molecule in noble gas matrices. Cryogenic photochemical syntheses of
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31 cyanopolyacetylenes have already been demonstrated for cyanodiacetylene (HC₅N)^{34,35} and
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33 cyanotriacetylene (HC₇N)³⁶. Cyanodiacetylene appeared in solid Ar doped with HC₃N/C₂H₂
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35 mixtures³⁴ irradiated using a H₂ discharge lamp emitting in the far-UV. It was also seen in Ar,
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37 Kr, N₂, and pH₂ solids containing HC₃N alone and photolyzed at 193 nm using a laser.³⁵
38
39 Cyanotriacetylene was detected in solid Ar doped with a mixture of either HC₃N and C₄H₂
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41 (diacetylene) or HC₅N and C₂H₂,³⁶ and photolyzed either by excimer laser radiation or an H₂
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43 discharge lamp. The HC₇N molecule has also been produced by electric discharges in a mixture
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45 of HC₃N and Kr just prior to trapping on a cold window.³⁷ In all of these cryogenic approaches,
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47 the cyanopolyacetylenes generated were found to emit strong phosphorescence which has proved
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49 to be the most sensitive spectroscopic indicator of their presence. Here we verified that a mixture
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51 of C₄H₂ and HC₅N precursors could couple to produce HC₉N during UV-assisted, low-
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53 temperature synthesis. The spectroscopic identification has been supported using density
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55 functional theory calculations of electronic and vibrational energy levels.
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EXPERIMENT

The precursor molecules were prepared using the methods developed by Trolez & Guillemin³⁸ (HC₅N) and Khlifi *et al.*³⁹ (C₄H₂). HC₅N was alternately exposed to vacuum at T<200 K and then warmed to remove CO₂ and other volatile impurities. This cycle was repeated until the rate of pressure rise during warming was negligible. C₄H₂ was subjected to several freeze-pump-thaw cycles (T<200 K, with some loss of the product). Purification of both precursors was carried out directly before the experiments.

Noble gases (Kr 4.0 or Ar 6.0, Messer) were mixed with C₄H₂ and HC₅N at typical ratios of approx. 500:1:1 using standard manometric techniques. This mixture was subsequently trapped on a sapphire substrate window held at either 30 K (Kr) or at 22 K (Ar) as measured and regulated with a Scientific Instruments Inc. 9620-1 temperature controller. The closed-cycle helium refrigerator (Air Products *Displex* DE202FF) was equipped with external CaF₂ windows. The typical amount of deposited gas was 6-8 mmol. Composition of the samples was verified with a Nicolet *Nexus* 670/870 FTIR spectrometer with a maximal resolution of 0.125 cm⁻¹ and equipped with a liquid nitrogen-cooled MCT detector. Spectra consisted of 256 or 1024 averaged interferograms. To induce the photochemical transformations of precursor molecules, cryogenic matrices were irradiated with a 193 nm ArF excimer laser (Coherent *Compex Pro*), either during or after the sample deposition. The laser typically operated at a repetition rate of 10 Hz and the energy delivered to the sample surface did not exceed 5 mJ/cm² per pulse. While argon is the most commonly used rare gas in matrix experiments, krypton matrices were preferred here, as they have already been shown to supply strong and well resolved spectra of embedded cyanopolyacetylenes.^{35,37} Thermal processing, *i.e.* annealing, was accomplished by warming up to ~30-40 K and then re-cooling (only for Kr). The lowest temperature reached for the cryogenic samples was 7 K.

The identification of photolysis products relied on selectively excited electronic luminescence. Two modes of measurement were employed. The first mode involved excitation at a fixed

1 wavelength followed by recording the resulting dispersed phosphorescence spectrum. This
2 spectrum contains information on vibrational frequencies in the ground electronic state of light
3 emitting products. The second mode gave access to vibrations in an excited singlet state, and
4 relied on scanning the excitation wavelengths while recording the phosphorescence signal. A
5 Continuum Surelite II + OPO Horizon laser system operating in the 192-400 nm range was used
6 for the excitation. The pulse repetition rate of this laser system was 10 Hz. Phosphorescence was
7 dispersed with a 0.6 m Jobin-Yvon grating monochromator and detected with a gated CCD
8 camera (Andor *iStar* DH720) with a detection range of 380-800 nm and a resolution of approx.
9 0.04 nm. Time synchronization between laser pulses and detection of phosphorescence was
10 provided by a home-made triggering device.
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24 Phosphorescence decay time measurements were performed using a photomultiplier
25 (Hamamatsu H3177-50 PMT) with a detection range of 200 – 850 nm connected to the
26 monochromator. Parallel to the phosphorescence intensity measurements, the excitation laser
27 intensity was monitored with a photodiode.
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34 COMPUTATIONAL DETAILS

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36 All quantum chemical calculations were carried out using density functional theory (DFT).⁴⁰
37 Time-dependent methodologies⁴¹⁻⁴³ were applied together with the B3PW91 functional of
38 Perdew and Wang⁴⁴⁻⁴⁷ for all computations of singlet excited electronic states (B3PW91 differs
39 from the better known B3LYP⁴⁸ by the non-local correlation term). The B3LYP functional
40 modified with the Coulomb-attenuating method (CAM-B3LYP)⁴⁹ was applied in its
41 conventional form to predict the energetic separation between the ground and the lowest triplet
42 state. The Dunning-type basis set aug-cc-pVTZ^{50,51} was applied in all computations of this sort
43 and supplied geometries for different electronic states, corresponding harmonic vibrational
44 frequencies, and energies of transitions from the ground to excited electronic states.
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1 To take into account the anharmonicity and inaccuracies of the applied theory, vibrational
2 frequencies were scaled with the factor of 0.96,^{52,53} for ground state DFT as well as for excited
3 state TD-DFT computations. For the ground state, IR absorption intensities and Raman activities
4 were also predicted. Linearity of the structure in the excited singlet electronic states was verified
5 by optimizations starting from the bent geometry at the CIS/aug-cc-pVDZ^{50,51,54} level and
6 inspection of vibrational frequencies (checking for the degeneracy of bending modes and for the
7 possible occurrence of imaginary frequencies) at both CIS and DFT levels.

8 Special attention was paid to the formally forbidden $\tilde{B}^1\Delta - \tilde{X}^1\Sigma^+$ system, where vibronic bands
9 could be observed due to Herzberg–Teller coupling with a π -symmetry vibration. In order to
10 identify that promoting mode, we have carried out a series of transition intensity (oscillator
11 strength) calculations for the molecule distorted by each of the bendings. The vector representing
12 the change was always parallel to a given normal coordinate and had a length of 0.1 Å. (Of note,
13 when the movement along a bending normal coordinate of HC₉N is considered, shifts between
14 the equilibrium ground state (\tilde{X} , v=0) geometry and any of the two \tilde{B} -state vibrational
15 wavefunction $|\Psi_{v=1}|$ maxima are on the order of 0.1 Å.) The Herzberg-Teller effect was assumed
16 to be significant if the coupling to a given π -symmetry vibrational mode, simulated as outlined
17 above, produced the oscillator strength of at least 0.0001.

18 The GAUSSIAN 09 (Rev. B. 01) program was used for all computations⁵⁵ while Jmol,⁵⁶
19 Gabedit,⁵⁷ and Chemcraft⁵⁸ were used for preparation of inputs and visualization of outputs.
20 Additional computations were performed by DALTON 2.0⁵⁹ at the CC2/cc-pVDZ level^{60–62} in
21 order to predict the dominant character of the transitions.

22 RESULTS AND DISCUSSION

23 Theoretical predictions

24 Theoretical predictions for the excited electronic states of HC₉N are listed in Table 1. In Figure
25 1, the corresponding molecular geometries are compared to that of the ground state. The DFT-
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derived ground-state structure matches the experimental one reasonably well and suggests that the computational level used is sufficient for this application. The interatomic distances in states \tilde{A} , \tilde{B} and \tilde{a} , differ by less than 0.7 pm and, compared to \tilde{X} , the geometry in these excited states corresponds to an elongation of triple bonds and shortening of the CC single bonds. The electronic structures of \tilde{A} , \tilde{B} , and \tilde{a} , together with that of the \tilde{E} state, come mainly from the HOMO-LUMO excitation. The \tilde{E} state geometry, however, slightly differs from those of the three other HOMO-LUMO states, especially in the middle of the chain, where there is a less pronounced length alternation of consecutive carbon-carbon bonds. The lowest-energy fully allowed electronic excitation is $\tilde{E} \ ^1\Sigma^+ - \tilde{X} \ ^1\Sigma^+$. Orbitally forbidden $\tilde{B} \ ^1\Delta - \tilde{X} \ ^1\Sigma^+$ transitions may however also be quite important (as shown for $\text{HC}_3\text{N}^{63-65}$ and HC_5N^{66}), gaining sizable intensity *via* Herzberg–Teller vibronic coupling.

Table 1. Energy (eV) and Oscillator Strength for Transitions Involving the Ground ($X \ ^1\Sigma^+$) and Excited Electronic States of HC_9N Derived at the B3PW91/aug-cc-pVTZ Level of Theory. Wavelengths (nm) Corresponding to the Transitions are Given in Parentheses.

State ^a	Dominant orbital excitation	Vertical transition energy (λ)	f^b	0-0 transition energy (λ)
$\tilde{A} \ ^1\Sigma^-$	$5\pi \rightarrow 1\pi^*$	2.84 (437)	0	2.39 (519)
$\tilde{B} \ ^1\Delta$	$5\pi \rightarrow 1\pi^*$	2.93 (423)	0	2.52 (492)
$\tilde{C} \ ^1\Sigma^-$	$4\pi \rightarrow 1\pi^*$	4.38 (283)	0	4.10 (302)
$\tilde{D} \ ^1\Delta$	$4\pi \rightarrow 1\pi^*$	4.53 (274)	0	4.27 (290)
$\tilde{E} \ ^1\Sigma^+$	$5\pi \rightarrow 1\pi^*$	5.06 (245)	2.8	4.88 (254)
$\tilde{F} \ ^1\Sigma^-$	$5\pi \rightarrow 2\pi^*$	5.30 (234)	0	4.98 (249)
$\tilde{G} \ ^1\Delta$	$5\pi \rightarrow 2\pi^*$	5.32 (233)	0	5.00 (248)
$\tilde{H} \ ^1\Sigma^+$	$4\pi \rightarrow 1\pi^*$, $5\pi \rightarrow 2\pi^*$	5.40 (230)	1.7	5.11 (243)
$\tilde{a} \ ^3\Sigma^+$	$5\pi \rightarrow 1\pi^*$	-	-	2.16 (574)

^a Ground state electronic configuration: [core] $(1\sigma)^2 (2\sigma)^2 (3\sigma)^2 (4\sigma)^2 (5\sigma)^2 (6\sigma)^2 (7\sigma)^2 (8\sigma)^2 (9\sigma)^2 (10\sigma)^2 (1\pi)^4 (2\pi)^4 (11\sigma)^2 (3\pi)^4 (4\pi)^4 (5\pi)^4 (1\pi^*)^0 (2\pi^*)^0 (1\sigma^*)^0$.

^b Value of zero indicates $f < 5 \cdot 10^{-5}$.



$\tilde{X} \ ^1\Sigma^+$	115.9	135.6	121.7	134.0	122.2	133.8	122.0	134.9	120.8	106.4
CCSD(T)	116.20	136.95	121.53	135.71	121.87	135.64	121.78	136.37	121.04	106.27
Exp.	116.1(1)	136.6(1)	121.7(2)	134.9(4)	122.9(6)	135.0(4)	121.7(2)	136.0(1)	121.1(1)	105.7(1)
$\tilde{A} \ ^1\Sigma^-$	+1.3	-2.4	+3.7	-5.1	+5.4	-5.4	+4.4	-3.4	+1.9	0
$\tilde{B} \ ^1\Delta$	+1.2	-2.3	+3.6	-4.8	+5.1	-5.1	+4.2	-3.3	+1.9	0
$\tilde{C} \ ^1\Sigma^-$	+2.3	-3.2	+3.8	-1.9	+1.7	-0.3	+2.5	-2.7	+2.9	0
$\tilde{D} \ ^1\Delta$	+2.2	-3.0	+3.8	-2.0	+1.8	-0.3	+2.4	-2.4	+2.8	0
$\tilde{E} \ ^1\Sigma^+$	+1.8	-1.6	+2.5	-0.7	+1.5	+0.2	+1.8	-1.4	+2.1	+0.2
$\tilde{F} \ ^1\Sigma^-$	+2.3	-2.4	+3.0	-1.1	+1.9	-1.1	+3.4	-3.3	+3.3	0
$\tilde{G} \ ^1\Delta$	+2.3	-2.3	+2.9	-1.0	+1.7	-1.0	+3.4	-3.4	+3.3	0
$\tilde{H} \ ^1\Sigma^+$	+1.7	-2.2	+3.1	-2.3	+2.9	-2.1	+3.2	-2.7	+2.5	0
$\tilde{a} \ ^1\Sigma^+$	+1.3	-2.4	+4.0	-5.4	+5.7	-5.8	+4.7	-3.6	+2.1	0

Figure 1. HC₉N geometry in its ground and excited electronic states as derived at the B3PW91/aug-cc-pVTZ level of theory. Interatomic distances in pm. Values listed for the excited electronic states are relative, calculated with respect to \tilde{X} . Also given are the ground-state experimental distances²⁰ together with their respective CCSD(T) predictions¹⁹. The states \tilde{a} , \tilde{B} , and \tilde{E} were experimentally observed in this work (entries listed in bold).

Vibrational frequencies characterizing \tilde{X} , \tilde{B} , and \tilde{E} states are listed in Table 2, together with \tilde{X} -state IR absorption intensities and Raman scattering activities. Predictions obtained for the remaining singlet excited states of Tab. 1 and Fig. 1 can be found in Tab. S1 of the Supporting Information. Table 2 provides also a short description of vibrational modes (see Tab. S2 of the Supporting Information for the graphical representations). The corresponding modes closely resemble one another in these three electronic states with the exception of modes in the 2000-2200 cm⁻¹ range where the vibrations represent diverse mixtures of C≡C and C≡N stretches.

Table 2. Harmonic Vibrational Frequencies (in cm^{-1} ; Scaling Factor 0.96) for the Ground and Two Excited Electronic States of HC_9N , as Derived at the B3PW91/aug-cc-pVTZ Level of Theory. IR Intensity and Raman Activity Units are km/mol and $\text{\AA}^4/\text{amu}$, Respectively.

Mode	\tilde{X}		\tilde{B}	\tilde{E}	Short description ^a
	Freq.	IR intensity/ Raman activity	Freq.	Freq.	
	σ symmetry				
ν_1	3324	193/12	3318	3298	νCH
ν_2	2250	109/1922	2098	2150	Mixture of $\nu\text{C}\equiv\text{C}$ and $\nu\text{C}\equiv\text{N}$
ν_3	2201	1.5/473	2059	2059	Mixture of $\nu\text{C}\equiv\text{C}$ and $\nu\text{C}\equiv\text{N}$
ν_4	2146	291/32763	2000	2033	Mixture of $\nu\text{C}\equiv\text{C}$ and $\nu\text{C}\equiv\text{N}$
ν_5	2122	8.2/3523	1900	1956	Mixture of $\nu\text{C}\equiv\text{C}$ and $\nu\text{C}\equiv\text{N}$
ν_6	2037	0.1/1511	1848	1893	Mixture of $\nu\text{C}\equiv\text{C}$ and $\nu\text{C}\equiv\text{N}$
ν_7	1369	0.5/0.3	1479	1346	Adjacent $\nu\text{C}-\text{C}$ out of phase
ν_8	1074	0.5/38	1106	1071	$\nu\text{C}-\text{CH} + \nu\text{C}-\text{CN}$ in phase
ν_9	736	3.9/1.5	741	730	$\nu\text{C}-\text{CH} + \nu\text{C}-\text{CN}$ out of phase
ν_{10}	376	0.3/1.6	386	374	Chain stretch
	π symmetry				
ν_{11}	764	0.1/39	754	712	Chain bending (<i>zig-zag</i> ; 9 nodes)
ν_{12}	640	40/13	559	562	δCH
ν_{13}	578	0.5/0.0	547	519	Chain bending (8 nodes)
ν_{14}	511	4.2/12	486	458	Chain bending (7 nodes)
ν_{15}	451	0.1/0.9	432	419	Chain bending (6 nodes)
ν_{16}	301	4.0/0.0	309	253	Chain bending (5 nodes)
ν_{17}	198	0.1/1.1	191	147	Chain bending (4 nodes)
ν_{18}	107	4.4/1.2	105	88	Chain bending (3 nodes)
ν_{19}	40	0.1/0.9	39	35	Chain bending (2 nodes)

^a ν - stretching; δ - bending.

Detection of HC₉N

Since both C₄H₂ and HC₅N precursors are strong phosphorescence emitters^{66,67} with long vibronic progressions in the UV-visible range, it was important to have reliable predictions concerning the electronic spectroscopy of HC₉N, in order to unambiguously distinguish the product from its precursors.

In the homologous series of polyynes, UV absorption wavelengths have been shown to change almost linearly with the size of the chain.^{68,69} This can be simplistically rationalized by considering a classical particle-in-a-box model, where a valence electron (a 'particle') is delocalized in a system ('box') of conjugated bonds.⁶⁸ Prior to the present study, phosphorescence of HC₇N,³⁶ HC₅N,³⁵ and C₃N⁻ anion⁷⁰ has been observed (HC₃N, isoelectronic with C₃N⁻, does not phosphoresce), and the wavelengths of the corresponding vibrationless $\tilde{a} - \tilde{X}$ emission origins were found to be linearly correlated with the length of the carbon-nitrogen chain.³⁶ Extrapolation of this empirical trend places the origin of HC₉N phosphorescence near 588 nm or 2.11 eV. CAM-B3LYP calculations (Table 1) predict a value of 574 nm or 2.16 eV (Figure 2).

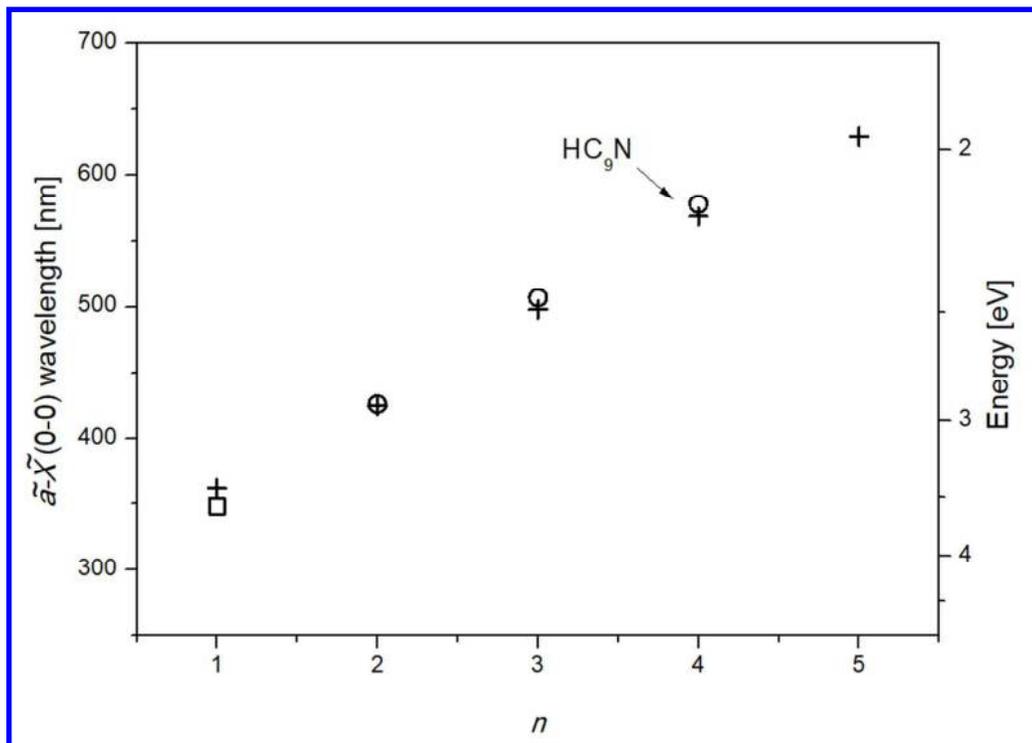
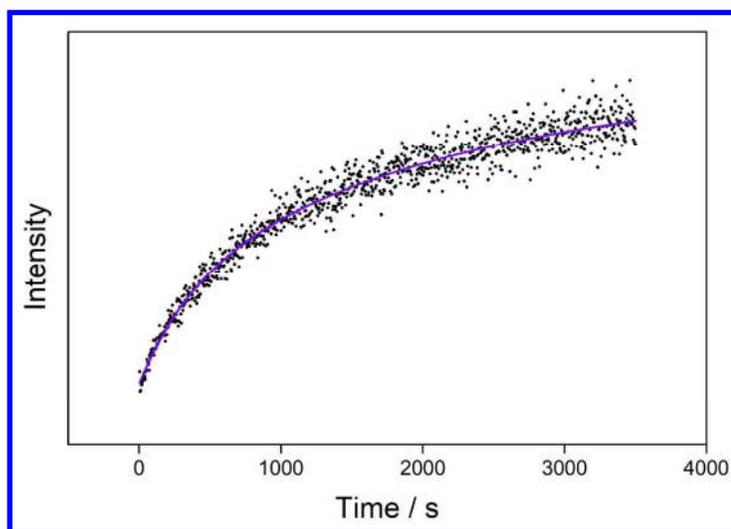


Figure 2. Phosphorescence origin wavelength as a function of carbon chain length for HC_{2n+1}N molecules. Circles mark the experimental values for Kr matrices (HC_3N does not phosphoresce; value observed for the isoelectronic C_3N^- anion⁷⁰ is entered for $n=1$ as an open square). Crosses correspond to CAM-B3LYP/aug-cc-pVTZ predictions. Experimental data for HC_5N and HC_7N come from Refs. 37,66.

While our CCD camera and spectrograph were well suited to record the anticipated HC_9N phosphorescence, we did not rely on exciting this emission with the ArF excimer laser (193 nm) employed for the photolysis. Instead, selective excitation of a sample previously subjected to extensive 193 nm irradiation was performed using a less powerful, tunable OPO operating in the expected region of $\tilde{E} - \tilde{X}$ transitions (around 250 nm). The corresponding dispersed phosphorescence spectra showed a 578 nm band which was the origin of a vibronic progression and whose excitation spectrum exhibited strong bands between 240 and 260 nm (as shown later). Once the emission and excitation wavelengths of HC_9N phosphorescence were determined, it was possible to follow the photochemical reaction kinetics in a fresh Kr/ C_4H_2 / HC_5N sample. For these measurements, the intensity of the 578 nm emission induced *via* OPO excitation (273.7 nm) was monitored over the course of 193 nm excimer laser irradiation. Time delays on the

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2 order of a few to tens of ms between the OPO, excimer laser, and signal acquisition were fixed to
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4 avoid, as much as possible, any perturbation of the collected spectrum by the phosphorescence of
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6 precursors excited at 193 nm. The time evolution of the resulting signal is depicted in Figure 3.
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8 No signal could be seen for an unphotolyzed sample showing that the emission certainly came
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10 from a photoproduct. The growth rate of this species decreased with irradiation time.
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32 **Figure 3. Time evolution of HC₉N formation, as monitored by intensity of phosphorescence (excited at 273.7**
33 **nm and measured at 578 nm) emitted from an irradiated (193 nm) Kr/C₄H₂/HC₅N (1000/1/1) matrix. Solid**
34 **line added for better visibility of the trend.**
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36 Phosphorescence and vibrational modes of the ground state

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40 The luminescence presented in Figure 4 was emitted from UV-photolyzed Kr/C₄H₂/HC₅N
41
42 matrices. The first intense band at 17 300 cm⁻¹ (578 nm, 2.14 eV) is the origin of the $\tilde{a} - \tilde{X}$
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44 transition of HC₉N and almost matches the theoretical prediction. This band is clearly correlated
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46 to those around 15 150 and 13 000 cm⁻¹; all three groups of spectral features share a common
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48 phosphorescence excitation spectrum. Two vibronic bands, separated from the 0-0 transition by
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50 2143 cm⁻¹ and 2170 cm⁻¹, can be distinguished in the spectrum and are indicative of excitation of
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52 triple bond stretching vibrations. The former can be assigned to mode ν_4 of HC₉N (*cf.* predicted
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54 \tilde{X} -state frequencies listed in Table 2). This mode corresponds to the in-phase stretching of the
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1
2 three central C≡C bonds (see Table S2). Mode ν_4 is likely to play the key role in
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4 phosphorescence transitions, as it deforms the molecule (alternately shrinking and elongating the
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6 consecutive bonds along the chain) in a similar fashion as predicted for electronic transitions
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8 between states \tilde{X} and \tilde{a} (Fig. 1). Stretching modes having similar characteristics also shaped the
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10 main vibronic progressions in low-temperature phosphorescence of HC₅N,^{35,66} and HC₇N.^{36,37}
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12 These modes also had the highest Raman activity in ground electronic states of the said
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14 cyanopolyynes. This is also true for the Raman activity of ν_4 in the ground electronic state of
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16 HC₉N (Table 2). The spacing of 2170 cm⁻¹ is unlikely to be associated with ν_3 . There is a poor
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18 match with the predicted ν_3 value of 2201 cm⁻¹ and atomic displacements involved in the
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20 vibration (Table 2 and Table S2) are qualitatively different from those of ν_4 . We propose
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22 assignment of this spacing to $2\nu_8$ (harmonic prediction: 2·1074 cm⁻¹). Mode ν_8 is C-C stretching,
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24 resembling *gerade* symmetry. A similar vibronic spacing, produced by a C-C stretching overtone
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26 ($2\nu_5$), was observed for HC₅N.⁶⁶ Assignments of several vibronic bands of HC₉N in Kr and in Ar
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28 hosts are proposed in Table 3. A π -symmetry mode, possibly ν_{14} , was observed only in Ar
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30 (497 cm⁻¹ with respect to the vibrationless origin); an alike bending-mode vibronic band of
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32 HC₅N phosphorescence was intense in Ar and weak in Kr.⁶⁶
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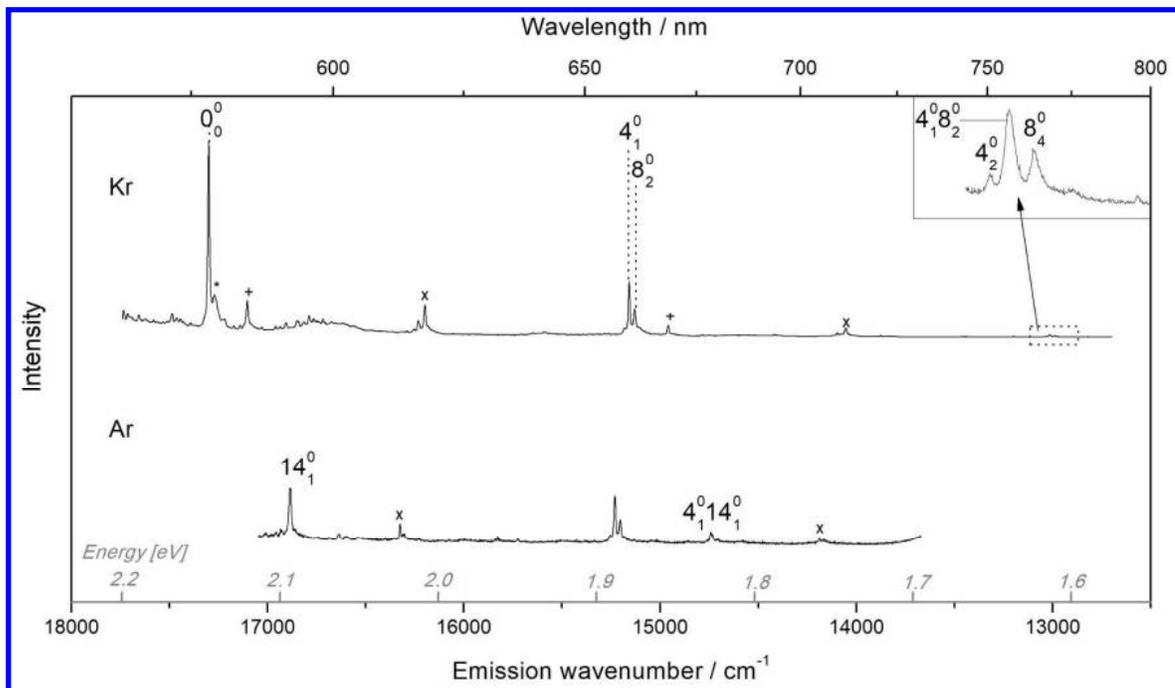


Figure 4. HC₉N-dominated phosphorescence of photolyzed (193 nm) Kr/C₄H₂/HC₅N (1000/1/1) (upper) and Ar/C₄H₂/HC₅N (1000/1/1) (lower) matrices excited at 36 540 cm⁻¹ (273.7 nm) and 41 440 cm⁻¹ (241.3 nm), respectively. Bands marked with '+' belong to additional photolysis products (as determined with the analysis of phosphorescence excitation spectra). The asterisked band is interpreted as being due to a secondary matrix site. Bands marked with 'x' are assigned to C₁₀N₂ phosphorescence (to be reported separately).

Table 3. Wavenumbers (in cm⁻¹) of Electronic Emission Bands Assigned to HC₉N Phosphorescence in Solid Ar and Kr.

Ar		Kr		Assignment
Absolute	Relative ^a	Absolute	Relative ^a	
17379	0	17300	0	0 ₀ ⁰
16881	497			14 ₁ ⁰
15231	2148	15157	2143	4 ₁ ⁰
15205	2174	15130	2170	8 ₂ ⁰
14740	2639			4 ₁ ⁰ 14 ₁ ⁰
		13038	4262	4 ₂ ⁰
		13018	4282	4 ₁ ⁰ 8 ₂ ⁰

		12992	4308	8_4^0
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^a Relative values give distances from the vibrationless origin.

No IR absorption attributable to HC₉N could be measured. This is not surprising, considering that earlier, analogous experiments aimed at synthesizing longer chains from HC₃N + C₂H₂ or from HC₅N + C₂H₂ led to fairly weak IR bands for HC₅N,³⁴ and bands near the limit of HC₇N detection,³⁶ respectively. Furthermore, the yield of (poly)acetylene+cyano(poly)acetylene reactions in rigid matrices is likely decreasing with the increasing size of a cyanopolyacetylenic product.

The phosphorescence decay time in solid krypton, 3.9 ± 0.1 ms (*0-0* band), was for HC₉N smaller than for other members of the HC_{2n+1}N homologous series including HC₅N (40 ms)⁶⁶ and HC₇N (8.2 ms)⁷¹. The increased number of internal degrees of freedom presumably promotes non-radiative relaxation channels, decreasing the triplet state lifetime. As chains get longer, the phosphorescence lifetime can be expected to decrease further.

Singlet excited electronic states

The excitation spectrum of HC₉N phosphorescence revealed two distinct electronic systems, in 26 000 – 34 000 cm⁻¹ and 35 000 – 50 000 cm⁻¹ regions.

The first (Figure 5), characterized by a series of bands spaced by ~2100 cm⁻¹, was assigned to $\tilde{B}^1\Delta - \tilde{X}^1\Sigma^+$ transitions, based on very similar patterns already observed in UV absorption and/or phosphorescence excitation spectra for the smaller molecules of the series: HC₃N,⁶³⁻⁶⁵ HC₅N,⁶⁶ and HC₇N.⁷² Geometry changes implied by $\tilde{B} - \tilde{X}$ and $\tilde{a} - \tilde{X}$ excitations are mutually similar (see Figure 1), therefore both systems are expected to feature alike vibronic patterns. One of possible choices for the mode responsible for the vibronic $\tilde{B} - \tilde{X}$ progression is ν_3 , because the corresponding vibrational motions of atoms in the \tilde{B} state (see Table S2 for visualization) resemble those of ν_4 in the ground electronic state (ν_4 already mentioned as prominently appearing in $\tilde{a}-\tilde{X}$ phosphorescence). While we cannot exclude the above possibility, we prefer to

assign the $\tilde{B} - \tilde{X}$ progression to the stretching mode ν_2 , for which the predicted \tilde{B} -state frequency better matches the observed vibronic spacing (see Table 2).

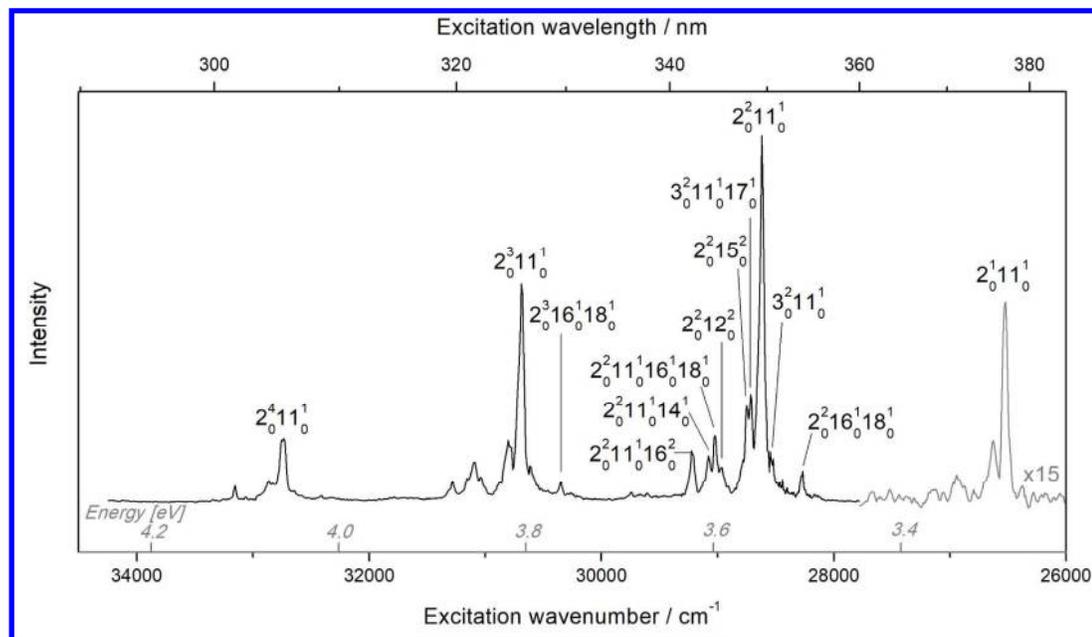


Figure 5. $\tilde{B} \ ^1\Delta - \tilde{X} \ ^1\Sigma^+$ system detected in the phosphorescence excitation spectrum of HC_9N , coming from a previously photolyzed (193 nm) $\text{Kr}/\text{C}_4\text{H}_2/\text{HC}_5\text{N}$ (1000/1/1) matrix. Detection centered at the most intense phosphorescence band ($17\ 300\ \text{cm}^{-1}$, 2.14 eV). Wavelength-dependent laser intensity variations might distort the phosphorescence intensity pattern.

No band corresponding to the $\tilde{B} - \tilde{X}$ origin is expected to appear in the spectrum, since the transitions of this orbital symmetry-forbidden system require coupling to a π -symmetry vibrational mode. In the analysis of respective analogous $\tilde{B} - \tilde{X}$ transitions, such π -symmetry modes were identified as ν_5 for HC_3N ,^{63–65} ν_8 for HC_5N ,⁶⁶ and ν_{10} and/or ν_{12} for HC_7N .⁷² Looking at the common features of the above vibrations, one can find that: (i) these are the chain bendings of the highest energy, sharing specific, qualitatively similar molecular distortion patterns, and (ii) their ground and excited state frequencies are very different. Moreover, in the case of Ar matrix-isolated HC_5N , the ν_8 mode stands out in the phosphorescence spectrum.⁶⁶ For HC_9N , it was in principle possible to assign the observed vibronic features assuming the participation of either ν_{11} , ν_{12} , or ν_{14} (predicted \tilde{B} -state wavenumbers: $754\ \text{cm}^{-1}$, $559\ \text{cm}^{-1}$ and

486 cm⁻¹, respectively). To further narrow down which of the three modes is involved, $\tilde{B} - \tilde{X}$ oscillator strength values were derived for \tilde{B} -state molecular geometry slightly distorted along respective normal bending coordinates (see Computational Details). A noticeable oscillator strength has appeared only for the geometry distorted along the coordinate of mode ν_{11} . This coarse computational simulation of the Herzberg-Teller coupling suggests that the $\tilde{B} \leftarrow \tilde{X}$ absorption may gain probability *via* excitation of the ν_{11} mode in the upper electronic state. The corresponding assignment is given in Figure 5 and Table 4 using the theoretical values of Table 2 for vibrational frequencies. Assuming that ν_{11} is the promoting mode, the origin of $\tilde{B} - \tilde{X}$ can be expected approximately 750 cm⁻¹ below the first detectable band of the ν_2 progression (26 530 cm⁻¹), namely at $\sim 25\,780$ cm⁻¹ (388 nm). However, DFT calculations (Table 1) locate the vibrationless $\tilde{B} - \tilde{X}$ origin much lower, at 492 nm (20 330 cm⁻¹). As taken into account in Figure 5 and Table 4, this implies the presence of at least one additional, less energetic element of the ν_2 progression and a possible placement of the system origin around 23 700 cm⁻¹ (corresponding to 422 nm, which is out of the detection range limited here to $\lambda < 400$ nm).

Table 4. Vibronic Bands in the $\tilde{B} \ ^1\Delta - \tilde{X} \ ^1\Sigma^+$ Electronic System of HC₉N in Solid Krypton, Revealed by the Phosphorescence Excitation Spectrum.

Frequency (cm ⁻¹)		Assignment
Absolute	Relative ^a	
26533	0	$2_0^1 11_0^1$
26925	392	$2_0^1 11_0^1 16_0^1 18_0^1$
27150	617	$2_0^1 11_0^1 16_0^2$
28165	1632	$2_0^2 17_0^1 18_0^1$
28274	1741	$2_0^2 16_0^1 18_0^1$
28546	2013	$3_0^2 11_0^1 / 2_0^2 14_0^1 17_0^1$
28623	2090	$2_0^2 11_0^1$
28719	96	$3_0^2 11_0^1 17_0^1 / 2_0^2 11_0^1 18_0^1$

28753	130	$2_0^2 15_0^2$
28970	347	$2_0^2 12_0^2$
29027	404	$2_0^2 11_0^1 16_0^1 18_0^1$
29083	460	$2_0^2 11_0^1 14_0^1$
29225	602	$2_0^2 11_0^1 16_0^2$
29606	983	$2_0^2 11_0^1 12_0^1 15_0^1$
29743	1120	$2_0^2 11_0^1 12_0^2$
30267	1644	$2_0^3 17_0^1 18_0^1$
30349	1726	$2_0^3 16_0^1 18_0^1$
30613	1990	$3_0^3 11_0^1 / 2_0^3 14_0^1 17_0^1$
30691	2068	$2_0^3 11_0^1$
30780	89	$3_0^3 11_0^1 17_0^1 / 2_0^3 11_0^1 18_0^1$
30807	116	$2_0^3 15_0^2$
31040	349	$2_0^3 12_0^2$
31098	407	$2_0^3 11_0^1 16_0^1 18_0^1$
31155	464	$2_0^3 11_0^1 14_0^1$
31281	590	$2_0^3 11_0^1 16_0^2$
32324	1633	$2_0^4 17_0^1 18_0^1$
32408	1717	$2_0^4 16_0^1 18_0^1$
32639	1948	$3_0^4 11_0^1 / 2_0^4 14_0^1 17_0^1$
32734	2043	$2_0^4 11_0^1$
32828	94	$3_0^4 11_0^1 17_0^1 / 2_0^4 11_0^1 18_0^1$
32862	128	$2_0^4 15_0^2$
33152	418	$2_0^4 11_0^1 16_0^1 18_0^1$

^a Relative values give distances from the previous member of the $2_0^n 11_0^1$ progression (bold).

The systematic bathochromic shift of $\tilde{B} - \tilde{X}$ spectra with increasing the HC_{2n+1}N chain length is shown in Figure 6. While singlet-triplet energy splittings are well predicted by DFT (Figure 2), $\tilde{B} - \tilde{X}$ excitation energies are sizably underestimated (note that the ordinate axis in Figure 6 corresponds to wavelength). It is still true after accounting for a gas-to-matrix shift on the order

of 5 nm. Accidentally, our DFT-derived *vertical* transition energies match the experimental $\tilde{B} - \tilde{X}$ origin values. As exemplified e.g. by a recent study⁷³ for atoms, TD-B3PW91/aug-cc-pVTZ excitation energies tend, on average, to be underestimated by a few percent. For the series of molecules investigated here, this TD-DFT error happens to have a similar size as the difference between vertical and vibrationless transitions. The plot adds credibility to the analysis of the HC₉N phosphorescence excitation spectrum presented above, and in particular to the ensuing derivation of the $\tilde{B} - \tilde{X}$ origin (at ~422 nm, represented by a black dot for $n=4$). Indeed, had our assignment of $2_0^1 11_0^1$ been incorrect, the first band of the progression would have had to be assigned to $2_0^2 11_0^1$, placing the system origin at ~465 nm. The red dot, depicting that latter possibility in Figure 6, spoils a trend set by lower n values.

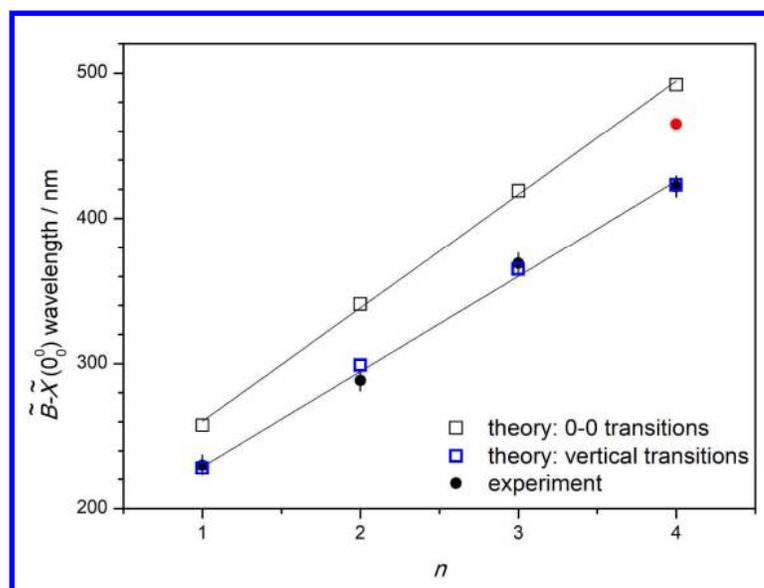


Figure 6. Dependence of the $\tilde{B}-\tilde{X}$ system origin wavelength on the carbon chain size (n), for HC_{2 n +1}N molecules. Data based on Kr-matrix measurements, with the exception of $n = 1$ measured in solid Ar (expected Kr-to-Ar wavelength shift is on the order of 0.5 nm). Theoretical predictions carried out at the TD-B3PW91/aug-cc-pVTZ level of theory. Red dot assumes misassignment of the first element of the progression (see text).

The second series consists of intense bands in the 35 000 – 50 000 cm⁻¹ range of the HC₉N phosphorescence excitation spectrum and coincides with the spectral region of fully allowed \tilde{E}

${}^1\Sigma^+ - \tilde{X} {}^1\Sigma^+$ and $\tilde{H} {}^1\Sigma^+ - \tilde{X} {}^1\Sigma^+$ systems. These features can be compared (see Figure 7) to those of HC_9N observed in UV absorption spectra following the laser ablation of graphite in acetonitrile³¹ or to the ones found in a similar, though less detailed, UV absorption spectrum (not presented here) of a solution produced after immersion of a carbon arc in liquid ammonia.³⁰ The DFT-computed $\tilde{E} - \tilde{X}$ vertical excitation energy of 5.06 eV (40 820 cm^{-1}) reasonably corresponds to the maximal signal in Figure 7. The theoretically predicted vertical transitions of several electronic systems marked in Figure 7 point to a high density of states in the spectral window. This impedes reliable identification of individual bands. The complexity of the spectrum is presumably due to a mixing of vibronic transitions involving various electronic states. The lowest-energy band in this region, at 34 600 cm^{-1} (4.29 eV), is weak and strongly red-shifted with respect to the predicted $\tilde{E} - \tilde{X}$ origin (4.88 eV). Noteworthy, a substantial *blue* shift was observed between experimental and theoretical $\tilde{B} - \tilde{X}$ transitions (Figure 5). The 34 600 cm^{-1} band may therefore belong to the $\tilde{D} {}^1\Delta - \tilde{X} {}^1\Sigma^+$ system, similar in nature to $\tilde{B} {}^1\Delta - \tilde{X} {}^1\Sigma^+$ transitions, partly allowed owing to Herzberg–Teller vibronic coupling. Band progressions starting at 34 600 cm^{-1} can be followed up to around 42 000 cm^{-1} . The vibronic spacings of approx. 1950 cm^{-1} could correspond to \tilde{D} -state $\text{C}\equiv\text{C}$ stretchings. Two examples of such progressions are marked in Figure 7 (lower energy part). A very narrow band observed at 39 610 cm^{-1} (4.91 eV) is possibly the origin of $\tilde{E} {}^1\Sigma^+ - \tilde{X} {}^1\Sigma^+$ system (which would make a good agreement with the theoretical prediction of Table 1). There are no evident candidates for other $\tilde{E} - \tilde{X}$ transitions. However, the pattern of intense bands in Figure 7 resembles the one obtained in the excitation spectrum of HC_7N ³⁷ around the first fully allowed electronic transition. Figure S1 of the Supporting Information provides a direct comparison of HC_7N and HC_9N observed in our experiments. It suggests that other bands of $\tilde{E} - \tilde{X}$ are present in this spectrum, contributing to the most intense features. Apart from the excitations to \tilde{D} and \tilde{E} , the states \tilde{G} or \tilde{H} may also be considered. The proposed assignment of progressions in Figure 7 points to 41 970 cm^{-1} (5.20 eV) as the origin of the allowed $\tilde{H} {}^1\Sigma^+ - \tilde{X} {}^1\Sigma^+$ system (implying a

slight blue shift from the theoretical value of Table 1). Just as in the case of $\tilde{D} - \tilde{X}$ or $\tilde{B} - \tilde{X}$, the vibronic progressions of $\tilde{G} - \tilde{X}$ and $\tilde{H} - \tilde{X}$ should involve a specific triple bond stretching mode of the upper electronic state. A very tentative interpretation of the main bands discussed here is presented in Table 5.

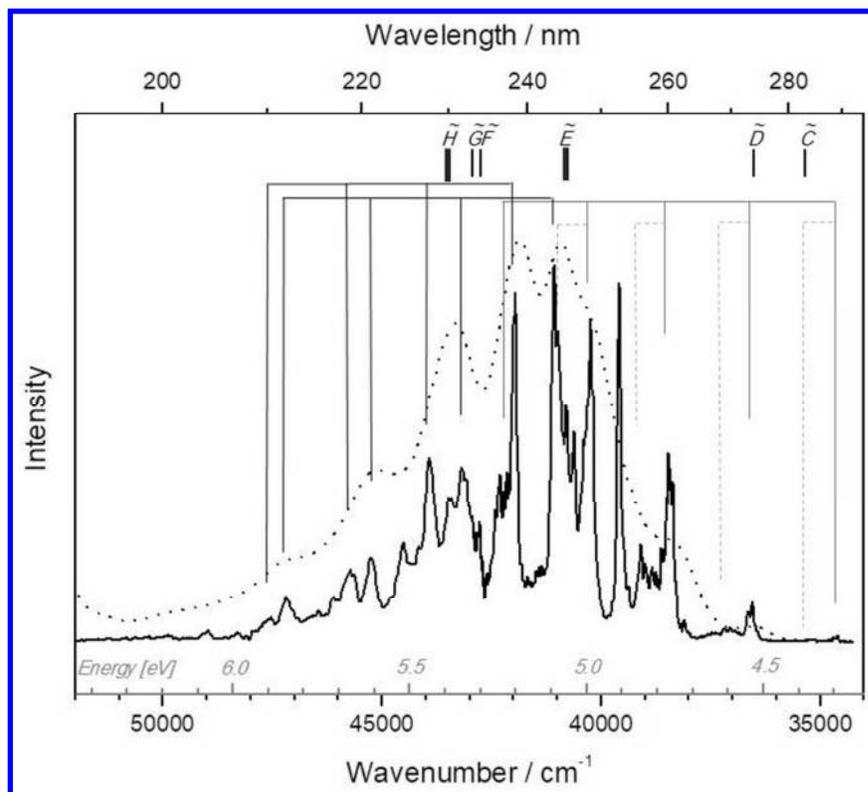


Figure 7. A fragment of the HC₉N phosphorescence excitation spectrum (detection centered at 17 300 cm⁻¹), measured for a previously photolyzed (193 nm) Kr/C₄H₂/HC₅N (1000/1/1) sample, compared to the room-temperature absorption spectrum of HC₉N in acetonitrile (dotted; Wakabayashi *et al.*³¹). Wavelength-dependent laser intensity variations might distort the phosphorescence intensity pattern. Theoretically predicted energies of \tilde{X} -originating vertical electronic excitations (data of Table 1) are indicated by top bars (bold ones for the fully allowed transitions). Also marked are the tentatively discerned vibronic progressions (see Table 5).

Couplings between nearly isoenergetic vibronic levels of adjacent electronic states can occur. These may have a sensitive dependence on the chemical environment. Interaction with solvent can lead to the broadening of spectral lines as can differences in temperature at which the spectrum was taken. Although not pictured here, the excitation spectrum of HC₉N in solid Ar

exhibited, when compared to that registered for solid Kr, non-uniform, matrix-related spectral shifts, as might be expected for a mixture of bands originating in various electronic systems. Low S/N ratio in measurement of the Ar matrices did not allow for any vibronic patterns to be reliably discerned. Further studies in varied cryogenic matrices will help in proposing further spectral assignments and in verifying those of Table 5.

Table 5. Vibronic Bands Tentatively Attributed to Excited Singlet States in the HC₉N Phosphorescence Excitation Spectrum of Figure 7.

$\tilde{\nu}$ (cm ⁻¹)	Provisional assignment
34 598	\tilde{D} (main progression)
34 706	\tilde{D}
35 288	\tilde{D} (secondary progression)
36 554	\tilde{D} (main progression)
36 647	\tilde{D}
37 201	\tilde{D} (secondary progression)
38 358	\tilde{D} (main progression)
38 449	\tilde{D}
39 085	\tilde{D} (secondary progression)
39 605	\tilde{E}
40 252	\tilde{D} (main progression)
40 986	\tilde{D} (secondary progression)
41 070	\tilde{G} / \tilde{E}
41 973	\tilde{H} / \tilde{E}
42 148	\tilde{D} (main progression)
43 189	\tilde{G}
43 921	\tilde{H}
45 247	\tilde{G}
45 729	\tilde{H}
47 201	\tilde{G}

47 534	\tilde{H}
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Chain growth mechanism

For a bimolecular photochemical reaction between C_4H_2 and HC_5N (or between any other closed-shell precursors) to occur in a cryogenic matrix, at least one of these molecules must first undergo dissociation or electronic excitation. Following such an event, the excited molecule(s) or radical(s) may come into contact with a reaction partner. As mobility of large molecules is greatly hindered in cryogenic matrices, the reactants should be in the same or adjacent matrix sites for the process to proceed with any probability. Having reactants in the same matrix site may imply the existence of an intermolecular complex prior to excitation/dissociation. If reaction partners are in neighboring sites, some small fraction may already be appropriately oriented for reaction while others must undergo reorientation such that appropriate contact with a partner can be made. Reorientation energy may come from exothermicity of the preceding reactions or from local heating supplied by the photolysing radiation. This leaves a number of possible reaction mechanisms to be explored, some of which can be ruled out.

Dissociation of the cyanide containing species was previously suggested as being responsible for the formation of HC_7N in cryogenic matrices³⁶ (reactions 1-3). This mechanism is consistent with that proposed by Cherchneff *et al.* for the formation of long chains in the ISM.^{16,17}



Dissociation of acetylene or diacetylene to form C_2H^{\bullet} or C_4H^{\bullet} radicals was deemed less significant on the basis of the higher acidity of HC_5N or cyanide containing polyynes in general. Abstraction of the acetylene proton by the cyanide containing radical was ruled out on the basis

1 of isotopic substitution experiments, although this process would not lead to formation of a
2 longer chain.³⁶

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7 It is reasonable to expect that formation of HC₉N proceeds in a similar fashion starting with (1)
8 and followed by (4) below:



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14 The same products may arise following the formation of [•]C₄H:

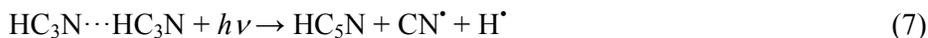


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20 Each of these mechanisms entails the absorption of a single photon by a C₄H₂/HC₅N pair. The
21 two precursors should be in close contact or, possibly, occupy neighboring matrix cages.

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25 Just to be complete, one should also consider several other possibilities. The first is a mechanism
26 involving the recombination of radicals:



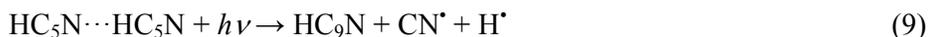
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33 Another might be reactions within existing intermolecular complexes where the reactants are
34 hydrogen bonded in a linear arrangement. Such complexes have been used to explain formation
35 of HC₅N from matrix-isolated cyanoacetylene:³⁵



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44 A scheme similar to (7) involving the intermolecular complex HC₃N^{•••}HC₂H and leading to
45 HC₅N has also been suggested for the UV-irradiated acetylene/cyanoacetylene mixture in a
46 cryogenic matrix.³⁴



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54 The equivalent of reactions (7) or (8) can also be envisioned to lead to formation of HC₉N:





The importance of precursors bound in a complex is rather unlikely for syntheses of chains longer than HC_5N . Experiments leading to formation of HC_7N showed no IR spectroscopic traces of such complexes, regardless of whether $\text{HC}_3\text{N}+\text{C}_4\text{H}_2$ or $\text{HC}_5\text{N}+\text{C}_2\text{H}_2$ mixtures were used.³⁶ The same is true for the present experiment using HC_5N and C_4H_2 . In addition, experiments using HC_5N as a sole precursor did not result in the appearance of HC_9N (this argument, however, should be treated with caution, given that conditions were not optimized for the detection of HC_9N).

Reaction (6) would conclude an overall two-photon process (one photon for each radical to form). The generated radicals need to be in close physical proximity to one another for chain elongation to occur. Such a process was observed in the case of NC_6N (dicyanodiacetylene) formation from HC_3N , where the production rate increased with irradiation time during the initial stages of the photolysis. This increase demonstrates that $\text{C}_3\text{N}^{\bullet}$ radicals first needed to be created in sufficient concentration (*i.e.* sufficiently close to one another) before they could begin to recombine.³⁵ Our measurements (Figure 2) show that the HC_9N production rate decreases with irradiation time suggesting that the radical recombination mechanism (6) does not occur to any great extent.

One last processes that has not yet been discussed involves precursor molecules excited to a high electronic level, rather than dissociating into a free radical. If such excitation is occurring, it could not be distinguished from a radical path with the presently reported experiments.

CONCLUSIONS

UV-driven synthesis of HC_9N in a solid rare gas matrix, *via* coupling of HC_5N and C_4H_2 , does occur. The targeted molecule, obtained here in amounts too small for producing measurable IR absorption signals, could be detected due to its strong phosphorescence, observed here for the first time. Experimentally derived spectroscopic characteristics are in a good accordance with

1 theoretical predictions. Phosphorescence excitation spectra gave insight to excited singlet
2 electronic states, unattainable with standard UV absorption measurements. The forbidden $\tilde{B}^1\Delta -$
3 $\tilde{X}^1\Sigma^+$ system (rendered detectable due to coupling with a π -symmetry vibration) is well
4 understood, while the analysis of fully allowed $\tilde{E}^1\Sigma^+ - \tilde{X}^1\Sigma^+$ and $\tilde{H}^1\Sigma^+ - \tilde{X}^1\Sigma^+$ transitions,
5 entangled with forbidden transitions, requires further studies.
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13 The described results are in agreement with previous reports on photochemical generation of
14 similar but smaller molecules³⁴⁻³⁶ in inert cryogenic matrices and suggest the validity of the
15 adopted approach for the synthesis and spectral studies of even longer unsaturated carbon-
16 nitrogen chains. In particular, the spectral origin of phosphorescence of a linear HC₁₁N can be
17 safely predicted. The cryogenic environment proved soft enough to adapt its structure during the
18 synthesis of an approximately 1.2 nm long HC₉N molecule from precursors themselves too large
19 to occupy single trapping sites (approx. 0.4 nm wide) of the *fcc*-type krypton lattice. It would be
20 interesting to go a step further and find out whether it is possible to synthesize HC₁₁N within a
21 similar scheme.
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34 Apart from HC₉N, we have observed other luminescing products in the described experiments,
35 such as C₁₀N₂ (to be described separately), some of which remain unassigned. Further
36 spectroscopic work on matrix isolated HC_{2n+1}N species may lead to the detection of their isomers
37 (in particular: isonitriles) and, as pointed out by the referee of this paper, possibly also to new
38 insertion compounds HRgC_{2n+1}N, where Rg stands for Kr or Xe atoms.⁷⁴⁻⁷⁵
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46 SUPPORTING INFORMATION

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49 Calculated IR frequencies and intensities in accessible electronic states; visualization of
50 vibrational modes in selected electronic states; phosphorescence excitation spectra of HC₇N and
51 HC₉N.
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55 ACKNOWLEDGMENT

1 This work was financially supported by the Polish National Science Centre, project no.
2
3 2011/03/B/ST4/02763, French-Polish scientific cooperation programs *Partenariat Hubert-*
4
5 *Curien Polonium* (2012-2013) and *PICS* (2014-2016). U.S. is a beneficiary of the French
6
7 Government scholarship *Bourse Eiffel*, managed by Campus France, and of the project
8
9 “Scholarships for PhD students of Podlaskie Voivodeship”. The project is co-financed by
10
11 European Social Fund, Polish Government and Podlaskie Voivodeship. J.-C.G. thanks the Centre
12
13 National d’Etudes Spatiales (CNES) and the French program Physique et Chimie du Milieu
14
15 Interstellaire (PCMI) funded by the Conseil National de la Recherche Scientifique (CNRS) and
16
17 CNES for financial support. Thanks are also due to Prof. Tomonari Wakabayashi for sharing his
18
19 data on electronic absorption of HC₉N.
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24 REFERENCE LIST

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26
27 (1) Turner, B. E. Detection of Interstellar Cyanoacetylene. *Astrophys. J. Lett.* **1971**, *163*, L35.
28
29 (2) Dickinson, D. F. Detection of Cyanoacetylene at 18 GHz. *Astrophys. Lett.* **1972**, *12*, 235–
30
31 236.
32
33 (3) McGee, R. X.; Balister, M.; Newton, L. M. Interstellar Cyanoacetylene – J=2→1, J=4→3
34
35 Transitions. *Mon. Not. R. Astron. Soc.* **1977**, *180* (4), 585–592.
36
37 (4) Gardner, F. F.; Winnewisser, G. Observations of the J = 1→0 Transitions of the ¹³C Isotopic
38
39 Species of Cyanoacetylene (HCCCN) in the Direction of Sagittarius B2. *Astrophys. J.* **1975**,
40
41 *197*, L73.
42
43 (5) Mauersberger, R.; Henkel, C.; Sage, L. J. Dense Gas in Nearby Galaxies. III - HC₃N as an
44
45 Extragalactic Density Probe. *Astron. Astrophys.* **1990**, *236*, 63–68.
46
47 (6) Kunde, V. G.; Aikin, A. C.; Hanel, R. A.; Jennings, D. E.; Maguire, W. C.; Samuelson, R. E.
48
49 C₄H₂, HC₃N and C₂N₂ in Titan’s Atmosphere. *Nature* **1981**, *292* (5825), 686–688.
50
51 (7) Coustenis, A. The Atmospheric Structure of Titan from Voyager to Cassini. *AGU Spring*
52
53 *Meet. Abstr.* **2007**, *44*.
54
55
56
57
58
59
60

- 1
2
3
4
5
6
7
8
9
10
11
12
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41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- (8) Bockelée-Morvan, D.; Lis, D. C.; Wink, J. E.; Despois, D.; Crovisier, J.; Bachiller, R.; Benford, D. J.; Biver, N.; Colom, P.; Davies, J. K.; et al. New Molecules Found in Comet C/1995 O1 (Hale-Bopp). Investigating the Link between Cometary and Interstellar Material. *Astron. Astrophys.* **2000**, *353*, 1101–1114.
- (9) Snell, R. L.; Schloerb, F. P.; Young, J. S.; Hjalmarsen, A.; Friberg, P. Observations of HC₃N, HC₅N, and HC₇N in Molecular Clouds. *Astrophys. J.* **1981**, *244*, 45–53.
- (10) Broten, N. W.; Oka, T.; Avery, L. W.; MacLeod, J. M.; Kroto, H. W. The Detection of HC₉N in Interstellar Space. *Astrophys. J.* **1978**, *223*, L105.
- (11) Bell, M. B.; Avery, L. W.; MacLeod, J. M.; Matthews, H. E. The Excitation Temperature of HC₉N in the Circumstellar Envelope of IRC + 10216. *Astrophys. J.* **1992**, *400*, 551–555.
- (12) Truong-Bach; Graham, D.; Nguyen-Q-Rieu. HC₉N from the Envelopes of IRC+10216 and CRL:2688. *Astron. Astrophys.* **1993**, *277*, 133.
- (13) Bell, M. B.; Feldman, P. A.; Kwok, S.; Matthews, H. E. Detection of HC₁₁N in IRC + 10^o216. *Nature* **1982**, *295* (5848), 389–391.
- (14) Bell, M. B.; Feldman, P. A.; Travers, M. J.; McCarthy, M. C.; Gottlieb, C. A.; Thaddeus, P. Detection of HC₁₁N in the Cold Dust Cloud TMC-1. *Astrophys. J. Lett.* **1997**, *483* (1), L61.
- (15) Loomis, R. A.; Shingledecker, C. N.; Langston, G.; McGuire, B. A.; Dollhopf, N. M.; Burkhardt, A. M.; Corby, J.; Booth, S. T.; Carroll, P. B.; Turner, B.; et al. Non-Detection of HC₁₁N towards TMC-1: Constraining the Chemistry of Large Carbon-Chain Molecules. *Mon. Not. R. Astron. Soc.* **2016**, *463* (4), 4175–4183.
- (16) Cherchneff, I.; Glassgold, A. E. The Formation of Carbon Chain Molecules in IRC +10216. *Astrophys. J. Lett.* **1993**, *419*, L41.
- (17) Cherchneff, I.; Glassgold, A. E.; Mamon, G. A. The Formation of Cyanopolyynes Molecules in IRC + 10216. *Astrophys. J.* **1993**, *410*, 188–201.

- 1
2
3
4
5
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52
53
54
55
56
57
58
59
60
- (18) Woon, D. E.; Herbst, E. Quantum Chemical Predictions of the Properties of Known and Postulated Neutral Interstellar Molecules. *Astrophys. J. Suppl. Ser.* **2009**, *185* (2), 273.
- (19) Botschwina, P.; Horn, M. Accurate Equilibrium Structure and Electric Dipole Moment of HC₉N: Predictions on the Basis of Large-Scale Coupled Cluster Calculations. *J. Mol. Spectrosc.* **1997**, *185* (1), 191–193.
- (20) Thaddeus, P.; McCarthy, M. C. Carbon Chains and Rings in the Laboratory and in Space. *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* **2001**, *57* (4), 757–774.
- (21) Boyd, R. J.; Jones, W. E.; Ling, K. W. Geometries, Energies and Polarities of Cyanopolyynes. *Chem. Phys.* **1981**, *58* (2), 203–210.
- (22) Qi, J. Y.; Chen, M. D.; Wu, W.; Zhang, Q. E.; Au, C. T. Parity Alternation of Interstellar Molecules Cyanopolyynes HC_{*n*}N (*n* = 1–17). *Chem. Phys.* **2009**, *364* (1–3), 31–38.
- (23) Vichiatti, R. M.; Haiduke, R. L. A. The Infrared Fundamental Intensities of Some Cyanopolyynes. *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* **2012**, *90*, 1–11.
- (24) Vichiatti, R. M.; Haiduke, R. L. A Theoretical Systematic Study of a Series of Isocyanopolyynes. *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* **2013**, *114*, 197–204.
- (25) Iida, M.; Ohshima, Y.; Endo, Y. Laboratory Detection of HC₉N Using a Fourier Transform Microwave Spectrometer. *Astrophys. J.* **1991**, *371*, L45.
- (26) McCarthy, M. C.; Levine, E. S.; Apponi, A. J.; Thaddeus, P. Experimental Structures of the Carbon Chains HC₇N, HC₉N, and HC₁₁N by Isotopic Substitution. *J. Mol. Spectrosc.* **2000**, *203* (1), 75–81.
- (27) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. Long Carbon Chain Molecules in Circumstellar Shells. *Astrophys. J.* **1987**, *314*, 352–355.
- (28) Schermann, G.; Grösser, T.; Hampel, F.; Hirsch, A. Dicyanopolyynes: A Homologous Series of End-Capped Linear Sp Carbon. *Chem. – Eur. J.* **1997**, *3* (7), 1105–1112.

- 1
2
3
4
5
6
7
8
9
10
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14
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43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- (29) Cataldo, F. Polyynes and Cyanopolyynes: Their Synthesis with the Carbon Arc Gives the Same Abundances Occurring in Carbon-Rich Stars. *Orig. Life Evol. Biospheres* **2006**, *36* (5–6), 467–475.
- (30) Cataldo, F. Monocyanopolyynes from a Carbon Arc in Ammonia: About the Relative Abundance of Polyynes Series Formed in a Carbon Arc and Those Detected in the Circumstellar Shells of AGB Stars. *Int. J. Astrobiol.* **2006**, *5* (01), 37–45.
- (31) Wakabayashi, T.; Saikawa, M.; Wada, Y.; Minematsu, T. Isotope Scrambling in the Formation of Cyanopolyynes by Laser Ablation of Carbon Particles in Liquid Acetonitrile. *Carbon* **2012**, *50* (1), 47–56.
- (32) Forte, G.; D’Urso, L.; Fazio, E.; Patanè, S.; Neri, F.; Puglisi, O.; Compagnini, G. The Effects of Liquid Environments on the Optical Properties of Linear Carbon Chains Prepared by Laser Ablation Generated Plasmas. *Appl. Surf. Sci.* **2013**, *272*, 76–81.
- (33) Devienne, F. M.; Barnabé, C.; Ourisson, G. Synthesis of Further Biological Compounds in Interstellar-like Conditions. *Comptes Rendus Chim.* **2002**, *5* (10), 651–653.
- (34) Coupeaud, A.; Kołos, R.; Couturier-Tamburelli, I.; Aycard, J. P.; Piétri, N. Photochemical Synthesis of the Cyanodiacetylene HC₅N: A Cryogenic Matrix Experiment. *J. Phys. Chem. A* **2006**, *110* (7), 2371–2377.
- (35) Crépin, C.; Turowski, M.; Cefonkus, J.; Douin, S.; Boyé-Péronne, S.; Gronowski, M.; Kołos, R. UV-Induced Growth of Cyanopolyne Chains in Cryogenic Solids. *Phys. Chem. Chem. Phys. PCCP* **2011**, *13* (37), 16780–16785.
- (36) Couturier-Tamburelli, I.; Piétri, N.; Crépin, C.; Turowski, M.; Guillemin, J.-C.; Kołos, R. Synthesis and Spectroscopy of Cyanotriacetylene (HC₇N) in Solid Argon. *J. Chem. Phys.* **2014**, *140* (4), 044329.
- (37) Turowski, M.; Crépin, C.; Douin, S.; Kołos, R. Formation and Spectroscopy of Dicyanotriacetylene (NC₈N) in Solid Kr. *J. Phys. Chem. A* **2014**.

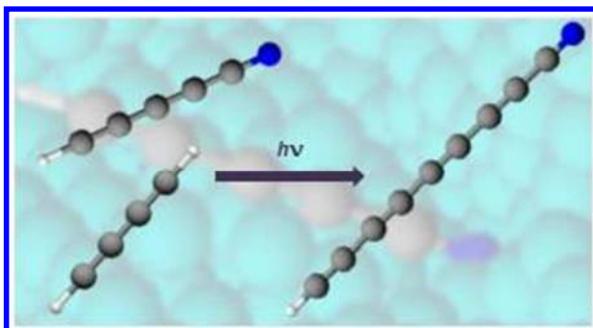
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41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- (38) Trolez, Y.; Guillemin, J.-C. Synthesis and Characterization of 2,4-Pentadiynenitrile—A Key Compound in Space Science. *Angew. Chem. Int. Ed.* **2005**, *44* (44), 7224–7226.
- (39) Khlifi, M.; Paillous, P.; Delpech, C.; Nishio, M.; Bruston, P.; Raulin, F. Absolute IR Band Intensities of Diacetylene in the 250 - 4300 cm^{-1} Region: Implications for Titan's Atmosphere. *J. Mol. Spectrosc.* **1995**, *174*, 116–122.
- (40) Parr, R. G.; Weitao, Y. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press, 1989.
- (41) Bauernschmitt, R.; Ahlrichs, R. Treatment of Electronic Excitations within the Adiabatic Approximation of Time Dependent Density Functional Theory. *Chem. Phys. Lett.* **1996**, *256* (4), 454–464.
- (42) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. Molecular Excitation Energies to High-Lying Bound States from Time-Dependent Density-Functional Response Theory: Characterization and Correction of the Time-Dependent Local Density Approximation Ionization Threshold. *J. Chem. Phys.* **1998**, *108* (11), 4439–4449.
- (43) Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. An Efficient Implementation of Time-Dependent Density-Functional Theory for the Calculation of Excitation Energies of Large Molecules. *J. Chem. Phys.* **1998**, *109* (19), 8218–8224.
- (44) Perdew, J. P.; Ziesche, P.; Eschrig, H. *Electronic Structure of Solids' 91*; Akademie Verlag, Berlin, 1991; Vol. 11.
- (45) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. Atoms, Molecules, Solids, and Surfaces: Applications of the Generalized Gradient Approximation for Exchange and Correlation. *Phys. Rev. B* **1992**, *46* (11), 6671–6687.
- (46) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. Erratum: Atoms, Molecules, Solids, and Surfaces: Applications of the

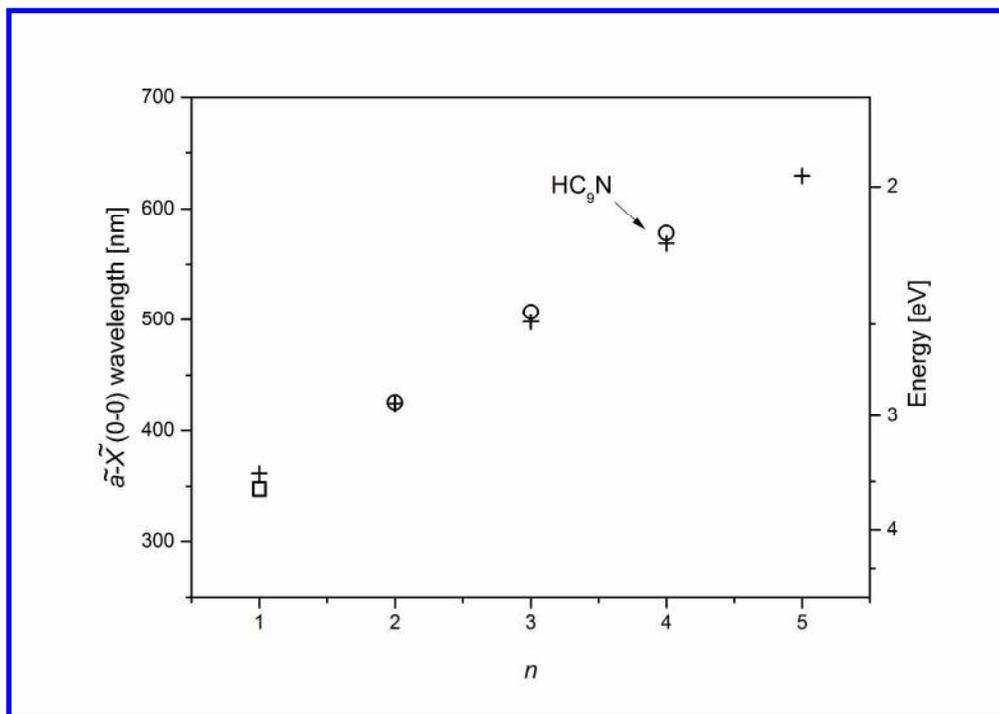
- 1
2 Generalized Gradient Approximation for Exchange and Correlation. *Phys. Rev. B* **1993**, *48*
3
4 (7), 4978–4978.
5
6 (47) Perdew, J. P.; Burke, K.; Wang, Y. Generalized Gradient Approximation for the
7
8 Exchange-Correlation Hole of a Many-Electron System. *Phys. Rev. B* **1996**, *54* (23), 16533–
9
10 16539.
11
12 (48) Becke, A. D. Density-functional Thermochemistry. III. The Role of Exact Exchange. *J.*
13
14 *Chem. Phys.* **1993**, *98* (7), 5648–5652.
15
16 (49) Yanai, T.; Tew, D. P.; Handy, N. C. A New Hybrid Exchange–Correlation Functional
17
18 Using the Coulomb-Attenuating Method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393* (1–3),
19
20 51–57.
21
22
23 (50) Dunning, T. H. J. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I.
24
25 The Atoms Boron through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90* (2), 1007–1023.
26
27 (51) Kendall, R. A.; Jr, T. H. D.; Harrison, R. J. Electron Affinities of the First-row Atoms
28
29 Revisited. Systematic Basis Sets and Wave Functions. *J. Chem. Phys.* **1992**, *96* (9), 6796–
30
31 6806.
32
33 (52) Andersson, M. P.; Uvdal, P. New Scale Factors for Harmonic Vibrational Frequencies
34
35 Using the B3LYP Density Functional Method with the Triple- ζ Basis Set 6-311+G(d,p). *J.*
36
37 *Phys. Chem. A* **2005**, *109* (12), 2937–2941.
38
39 (53) Merrick, J. P.; Moran, D.; Radom, L. An Evaluation of Harmonic Vibrational Frequency
40
41 Scale Factors. *J. Phys. Chem. A* **2007**, *111* (45), 11683–11700.
42
43 (54) Foresman, J. B.; Head-Gordon, M.; Pople, J. A.; Frisch, M. J. Toward a Systematic
44
45 Molecular Orbital Theory for Excited States. *J. Phys. Chem.* **1992**, *96* (1), 135–149.
46
47 (55) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman,
48
49 J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*;
50
51 Gaussian, Inc.: Wallingford, CT, USA, 2009.
52
53 (56) *Jmol: An Open-Source Java Viewer for Chemical Structures in 3D*. <http://www.jmol.org/>
54
55
56
57
58
59
60

- 1
2
3
4
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9
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41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- (57) *GABEDIT 2.4.8*, Allouche, A.-R. Gabedit--a Graphical User Interface for Computational Chemistry Softwares. *J. Comput. Chem.* **2011**, 32 (1), 174–182.
- (58) *Chemcraft - Graphical Program for Visualization of Quantum Chemistry Computations*, <http://chemcraftprog.com/>; Andrienko G.A.; *Chemcraft 1.8 (build 180)*.
- (59) *Dalton, a Molecular Electronic Structure Program*, Release 2.0 (2005), See <http://www.kjemi.uio.no/software/dalton/dalton.html>; C. Angeli, K. L. Bak, V. Bakken, O. Christiansen, R. Cimiraglia, S. Coriani, P. Dahle, E. K. Dalskov, T. Enevoldsen, B. Fernandez, et al..
- (60) Christiansen, O.; Koch, H.; Jørgensen, P. The Second-Order Approximate Coupled Cluster Singles and Doubles Model CC2. *Chem. Phys. Lett.* **1995**, 243 (5), 409–418.
- (61) Christiansen, O.; Koch, H.; Halkier, A.; Jørgensen, P.; Helgaker, T.; Merás, A. S. de. Large-scale Calculations of Excitation Energies in Coupled Cluster Theory: The Singlet Excited States of Benzene. *J. Chem. Phys.* **1996**, 105 (16), 6921–6939.
- (62) Hald, K.; Hättig, C.; Jørgensen, P. Triplet Excitation Energies in the Coupled Cluster Singles and Doubles Model Using an Explicit Triplet Spin Coupled Excitation Space. *J. Chem. Phys.* **2000**, 113 (18), 7765–7772.
- (63) Job, V. A.; King, G. W. The Electronic Spectrum of Cyanoacetylene: Part II. Analysis of the 2300-Å System. *J. Mol. Spectrosc.* **1966**, 19 (1–4), 178–184.
- (64) Bruston, P.; Poncet, H.; Raulin, F.; Cossart-Magos, C.; Courtin, R. UV Spectroscopy of Titan's Atmosphere, Planetary Organic Chemistry, and Prebiological Synthesis: I. Absorption Spectra of Gaseous Propynenitrile and 2-Butynenitrile in the 185- to 250-nm Region. *Icarus* **1989**, 78 (1), 38–53.
- (65) Kołos, R. *Carbon-Nitrogen Chain Molecules in the Laboratory and in Interstellar Medium*; Institute of Physical Chemistry of the Polish Academy of Sciences: Warsaw, 2003.

- 1
2
3
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5
6
7
8
9
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11
12
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15
16
17
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20
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41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- (66) Turowski, M.; Crépin, C.; Gronowski, M.; Guillemain, J.-C.; Coupeaud, A.; Couturier-Tamburelli, I.; Piétri, N.; Kołos, R. Electronic Absorption and Phosphorescence of Cyanodiacetylene. *J. Chem. Phys.* **2010**, *133* (7), 074310.
- (67) Vuitton, V.; Gée, C.; Raulin, F.; Bénilan, Y.; Crépin, C.; Gazeau, M.-C. Intrinsic Lifetime of Metastable Excited C₄H₂: Implications for the Photochemistry of C₄H₂ in Titan's Atmosphere. *Planet. Space Sci.* **2003**, *51* (13), 847–852.
- (68) Anderson, B. D.; Gordon, C. M. The Laser Synthesis of Linear Polyynes: The Particle in a Box Revisited. *J. Chem. Educ.* **2008**, *85* (9), 1279.
- (69) Maier, J. P. Electronic Spectroscopy of Carbon Chains. *J. Phys. Chem. A* **1998**, *102* (20), 3462–3469.
- (70) Turowski, M.; Gronowski, M.; Boyé-Péronne, S.; Douin, S.; Monéron, L.; Crépin, C.; Kołos, R. The C₃N⁻ Anion: First Detection of Its Electronic Luminescence in Rare Gas Solids. *J. Chem. Phys.* **2008**, *128* (16), 164304.
- (71) Turowski, M. Niskotemperaturowe Badania Fotochemii I Spektroskopii Cyjanoacetylenów O Znaczeniu Astrofizycznym. PhD Dissertation, Institute of Physical Chemistry, Polish Academy of Sciences: Warsaw, 2012.
- (72) Szczepaniak, U. Spectroscopy and Photochemistry of Astrophysically Relevant Molecules of the Cyanoacetylene Family. PhD Dissertation, Institute of Physical Chemistry, Polish Academy of Sciences; Université Paris-Sud, Université Paris-Saclay: Warsaw, 2017.
- (73) Gronowski, M. TD-DFT Benchmark: Excited States of Atoms and Atomic Ions. *Comput. Theor. Chem.* **2017**, *1108*, 50–56.
- (74) Khriachtchev, L.; Lignell, A.; Tanskanen, H.; Lundell, J.; Kiljunen, H.; Räsänen, M. Insertion of Noble Gas Atoms into Cyanoacetylene: An ab Initio and Matrix Isolation Study. *J. Phys. Chem. A* **2006**, *110*, 11876–11885.
- (75) Turowski, M.; Gronowski, M.; Guillemain, J.-C.; Kołos, R. Generation of H-Kr-C₅N and H-Xe-C₅N molecules. *J. Mol. Struct.* **2012**, *1025*, 140–146.

TOC Graphic





Phosphorescence origin wavelength as a function of carbon chain length for HC_{2n+1}N molecules. Circles mark the experimental values for Kr matrices (HC_3N does not phosphoresce; value observed for the isoelectronic C_3N^- anion⁷⁰ is entered for $n=1$ as an open square). Crosses correspond to CAM-B3LYP/aug-cc-pVTZ predictions. Experimental data for HC_5N and HC_7N come from Refs. 37,66.

289x203mm (300 x 300 DPI)