Carbon chain extension processes in cryogenic environments: UV-assisted growth of polyynic nitriles in solidified rare gases

(Topical Review)

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As demonstrated in recent years, polyynic nitriles may photochemically arise from smaller unsaturated chain species in an apparently rigid environment of a cryogenic rare gas matrix. Here I summarize the highlights of respective research that has advanced the spectroscopic description of $R–(C{\equiv}C)_n–C{\equiv}N$ molecules (R = H, CN or CH_3).

Keywords: cyanopolyyne, cryogenic matrix isolation, phosphorescence, infrared spectroscopy.

Introduction

Chain molecules featuring multiply bonded carbon backbones have a prominent place among the known constituents of galactic gas clouds. Indeed, polyyne- or cumulene-type structures are relatively well protected against different forms of radiation in such otherwise hostile interstellar environments. Typical examples are offered by rod-like polyynic nitriles $H–(C{\equiv}C)_n–C{\equiv}N$ (cyanopolyynes, cyanoacetylenes); molecules with n number equal 0, 1, 2, 3, and 4 have thus far been identified in space [1,2] (and $n = 0$, 1, 2 for their methylated analogues, $CH_3–(C{\equiv}C)_n–C{\equiv}N$ [3,4]). Radio astronomical detection methods, relying on purely rotational spectroscopic transitions, are not useful for nonpolar species, *e.g.*, $NC_{2n}N$ dinitriles. However, infrared absorption measurements have already uncovered some extra-terrestrial centrosymmetric molecules including acetylene, diacetylene, triacetylene [5], and NC_4N, this latter one in the atmosphere of Titan, the Saturn's moon [6]. While gas-phase collisional processes (both ion-neutral and neutral-neutral) leading to interstellar polyynes have been proposed [7], important also seem the radiation-driven reactions taking place in frozen solids, *i.e.*, within icy mantles of interstellar dust grain particles [8].

Here I refer to some recent photochemical work concerning the growth of cyanopolyynic chains in solidified rare gases. Such inert environments, usually termed "rare gas matrices", cannot offer any realistic approximation of interstellar ices, but they nevertheless give insight to the poorly known or unknown spectroscopy of certain chain-elongation products, and they may also permit to obtain a crude estimate of the mobility of potential reaction partners embedded within the structure of a rigid solid. The majority of experimental results evoked in this short review were published by researchers from the Institut des Sciences Moléculaires d'Orsay, Physique des Interactions Ioniques et Moléculaires laboratory in Marseille, École Nationale Supérieure de Chimie de Rennes, as well as the Institute of Physical Chemistry in Warsaw.

The methods

Due to their inherent chemical inertness, rare gas cryogenic matrices are the perfect media for *in-situ* generation and spectroscopic studies of certain chemical compounds, in particular those that are unstable and/or hard to obtain at usual laboratory conditions. The corresponding molecular spectra are usually well resolved, as the rotational movements are suppressed. Frequency shifts with respect to the gas phase are typically small [9,10], tending to grow with the polarizability of the host medium. These general rules proved true also in the first spectroscopic and photochemical studies on matrix-isolated cyano- [11] and dicyanoacetylene [12].

In experiments devoted to the title topic, the inert gas, most often Ar or Kr, was first mixed (usually in a ratio of about 500 to 1) with either a single precursor or two precursor compounds of interest. The mixture, admitted through a nozzle to the vacuum chamber of a cryostat, was solidified therein onto an appropriately cold IR- and/or UV-Vis-transparent plate or a reflective metal surface. External windows of the cryostat allowed for the UV photolysis of the solid sample and for the measurement of resultant IR absorption, UV-Vis absorption or UV-Vis

luminescence spectra. In the latter case, crucial was the application of tuneable laser systems, as it gave the possibility to selectively excite certain luminescence emitters.

The rigidity of a cryogenic matrix is an obvious asset, minimizing the chances for intermolecular interactions of potentially reactive species once they are captured within a crystalline structure, confined to individual "cages" between noble gas atoms. However, one can intentionally warm up the sample to induce some mobility of the trapped molecules, *i.e.*, increase the respective diffusion coefficients. In the *annealing* procedure, temperature is gently raised, maintained at a properly chosen, elevated level for a fixed amount of time, and eventually lowered to an original value. Annealing often promoted the occurrence of select chemical processes (see, *e.g.*, Ref. [13]), reflected in evolution of the bands belonging to previously generated photoproducts and/or in the appearance of new spectral features.

The DFT level of quantum chemical calculations was usually sufficient to assist in identification of photolysis products and in the analysis of their IR absorption spectra or of vibrationally resolved electronic transitions.

HC$_5$N, the simplest cyanopolyyne

The first attempt to photochemically elongate a cyanoacetylenic chain in a noble-gas matrix was carried out by Coupeaud *et al.* [13] (it was preceded by their theoretical study of hydrogen-bonded bimolecular cyanoacetylene-acetylene and dicyanoacetylene-acetylene complexes [14]). Far-UV radiation emitted by a low power electrodeless hydrogen lamp photolyzed the mixtures of two dopants isolated in an argon matrix: cyanoacetylene/acetylene or dicyanoacetylene/acetylene. Infrared absorption spectroscopy was the photoproduct identification method. Similarity of processes observed for the both said precursor pairs (studied also with the application of ^{13}C- or ^{2}H-isotopic versions of acetylene or with ^{15}N-labelled nitriles) led the authors to propose the recombination of short-living free radicals C$_2$H and C$_3$N as the most likely route toward HC$_5$N; no chemical kinetics studies have however been presented. Infrared absorption bands of the product, even though weak, could be identified with no ambiguity. It was of interest to note certain differences upon comparison to the spectrum measured for pure matrix-isolated HC$_5$N (the compound being independently obtained by preparative organic synthesis [15]). Indeed, the molecule was presumably subject to strain or even slight deviation from linearity once it emerged from smaller precursors in a hardly adaptable microenvironment.

NC$_6$N, the simplest dicyanopolyyne

Cyanoacetylene-doped cryogenic matrices were found to emit white, long-lived, vibrationally-resolved luminescence upon prolonged irradiation with an ArF excimer laser beam (193 nm). A tentative conjecture, attributing the phenomenon to C$_3$N radical [16], proved false in the course of further studies; the emission carrier was dicyanodiacetylene, NC$_6$N [17]. Its $\tilde{a}\,^3\Sigma_u^+ - \tilde{X}\,^1\Sigma_g^+$ phosphorescence was very efficiently excited with the same ultraviolet radiation that induced HC$_3$N photolysis. However, with the adequate selection of luminescence excitation wavelengths provided by a tuneable laser, Crépin *et al.* [17] managed to find the additional chain-elongation products in a photolyzed, HC$_3$N-doped Kr matrix, namely dicyanoacetylene (NC$_4$N) and HC$_5$N. Electronic luminescence was indeed the preferred detection method, given that all these products appeared in too low a quantity to exhibit any measurable IR absorption signature. NC$_6$N ability to phosphoresce came as no surprise; the analogous property was previously discovered for NC$_2$N (cyanogen) [18] and NC$_4$N [12]*.

In contrast to unimolecular photochemical reactions, in particular the isomerizations reported for matrix-isolated HC$_3$N [11,21–24], chain growth processes obviously require an interaction of separate objects. For NC$_6$N, these seemed to be two C$_3$N radicals. Plotted against irradiation time (Fig. 1), the intensity of phosphorescence indicated that the NC$_6$N production rate, originally low, was increasing in the crucial stage of photolysis, in parallel to the growing number of C$_3$N radicals susceptible to recombination. Vanishing production rate, *i.e.*, a plateau in the curve of growth, was approached at long irradiation times (much longer than those included in Fig. 1), reflecting the disappearance of properly spaced and mutually oriented radicals. On the whole, two UV photons seemed necessary to yield a single NC$_6$N molecule.

For the syntheses of NC$_4$N and HC$_5$N, Crépin *et al.* [17] envisaged another scheme, requiring just one UV photon, with a key role played by [HC$_3$N⋯HC$_3$N] intermolecular complexes. The process was pictured as starting with the photochemical fission of a single CC bond: [HCC CN⋯HCCCN]. This, followed by the CN radical advance towards the nearby HC$_3$N molecule, could give rise to NC$_4$N. The required turnover of CN and expulsion of the hydrogen atom seemed feasible. It should be more difficult, given the steric reasons, to create HC$_5$N from the considered hydrogen-bonded complex, once the two potential reaction partners, HC$_2$ radical and HC$_3$N, are separated by the CN fragment. HC$_5$N emission was indeed weaker

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* However, while HC$_5$N was shown to phosphoresce intensely [19], matrix-isolated HC$_3$N emits only weak, structureless emission, most likely corresponding to fluorescence that was previously reported for gaseous HC$_3$N [20].
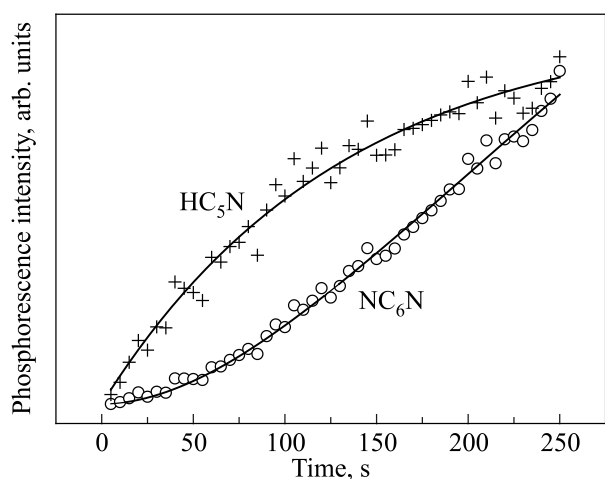
Fig. 1. Curves of growth for the phosphorescence of HC_5N and NC_6N nitriles, as observed by Crépin *et al.* [17] in the course of the 193 nm laser photolysis of HC_3N isolated in solid krypton. Solid lines represent least squares fitting to a simple kinetic model proposed by the authors.

than that from NC_4N, giving some grounds for that reasoning. As can be seen in Fig. 1, the kinetics of HC_5N formation qualitatively differed from what was observed for NC_6N. The rate at which HC_5N appeared, initially very high, steadily dropped down throughout the photolysis, possibly due to the decreasing availability of hydrogen-bonded dimers.

If started from [$HC_3N\cdots HC_3N$] dimers, NC_6N synthesis would require a bulky, photochemically created C_3N radical to turn by 180 degrees in a rigid environment. Worthy of note, NC_6N was also detected in UV-irradiated *para*-H_2 solids, at a fairly low concentration of the HC_3N dopant, prohibiting any significant formation of dimers [17].
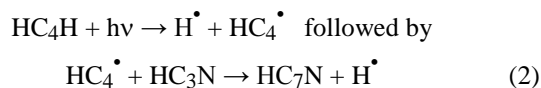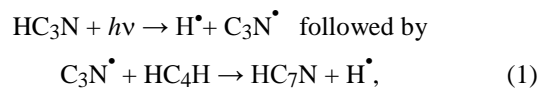
HC$_7$N

It was natural to continue this line of research trying to obtain and characterize larger cyanopolyynic chains, starting with $H–(C{\equiv}C)_3–C{\equiv}N$. Matrix-isolated precursor mixtures, either cyanodiacetylene/acetylene or cyanoacetylene/diacetylene were applied. Linear intermolecular complexes (similar to the ones previously found for the cyanoacetylene-acetylene pair) were shown to form and were identified in both cases [25,26]. In a series of experimental approaches that followed, collectively reported by Couturier-Tamburelli *et al.* [27], far-UV (H_2 lamp) or 193 nm ArF laser radiation served for the photolysis of precursors isolated in solid argon, while detection of the reaction products was accomplished with infrared absorption spectroscopy, mass spectrometry, and electronic phosphorescence measurements.

Vibrational spectroscopy of HC_7N was not explored, prior to those studies. IR absorption of photolyzed samples revealed the presence of two spectral features located reasonably close to the positions predicted for the strongest HC_7N bands (at the CCSD(T) level of theory, with DFT-derived anharmonic corrections). The best results were obtained with the cyanodiacetylene/acetylene pair of precursors; cyanoacetylene/diacetylene mixture led to weaker product bands. IR identification of HC_7N, while supported with the use of ^{2}D-, ^{13}C-, and ^{15}N-labelled precursor molecules, was rather ambiguous due to a low signal-to-noise ratio and to the occasional presence of neighbouring weak, unidentified bands. Additional credence to the assignment came from mass spectrometry. Temperature of a thoroughly irradiated sample was raised up to the sublimation point of argon, and further on, slowly, to induce gradual evaporation of the frozen reactants and products. Composition of the released gas was continuously monitored with a quadrupole mass spectrometer. A peak corresponding to the HC_7N stoichiometry was detected.
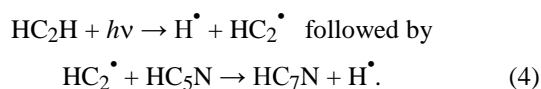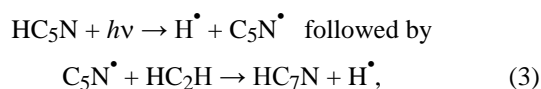
The ensuing spectrofluorimetric study of the photolyzed (193 nm) solid argon matrix doped with the HC_5N/HC_2H pair provided the final proof for the identification of HC_7N and led to the first description of the electronic luminescence of this compound. The main vibronic progression of the long-lived emission ($\tilde{a}^3\Sigma^+ – \tilde{X}^1\Sigma^+$ phosphorescence) featured a spacing that corresponded, within the experimental accuracy, to the frequency of a pseudosymmetric $C{\equiv}C$ stretching vibration of HC_7N, in harmony with IR absorption measurements. The observed location of phosphorescence origin was in good agreement with the DFT-predicted singlet-triplet energy gap.

HC_7N phosphorescence was further studied by Szczepaniak *et al.* [28] in photochemical experiments involving a matrix-isolated mixture of propyne (CH_3C_2H) and HC_5N. Phosphorescence excitation spectra gave access to the analysis of formally forbidden $\tilde{B}^1\Delta – \tilde{X}^1\Sigma^+$ transitions and uncovered a fully permitted $\tilde{E}^1\Sigma^+ – \tilde{X}^1\Sigma^+$ system.

Couturier-Tamburelli *et al.* [27] considered the following *a priori* possible reaction paths for the HC_3N/HC_4H pair of reactants:[*]

$$HC_3N + h\nu \rightarrow H^{\bullet} + C_3N^{\bullet} \text{ followed by}$$

$$C_3N^{\bullet} + HC_4H \rightarrow HC_7N + H^{\bullet}, \tag{1}$$

$$HC_4H + h\nu \rightarrow H^{\bullet} + HC_4^{\bullet} \text{ followed by}$$

$$HC_4^{\bullet} + HC_3N \rightarrow HC_7N + H^{\bullet} \tag{2}$$

and, for the HC_5N/HC_2H pair:

$$HC_5N + h\nu \rightarrow H^{\bullet} + C_5N^{\bullet} \text{ followed by}$$

$$C_5N^{\bullet} + HC_2H \rightarrow HC_7N + H^{\bullet}, \tag{3}$$

$$HC_2H + h\nu \rightarrow H^{\bullet} + HC_2^{\bullet} \text{ followed by}$$

$$HC_2^{\bullet} + HC_5N \rightarrow HC_7N + H^{\bullet}. \tag{4}$$

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[*] Noteworthy, similar reactions of acetylenic and cyanoacetylenic radicals were postulated by Cherchneff *et al.* [8] for monocyanopolyyne formation in the UV-irradiated circumstellar shell of an evolved star.

Some prevalence for the production of $C_3N^\bullet$ or $C_5N^\bullet$ over the production of $^\bullet C_4H$ or $^\bullet C_2H$ radicals was expected, given that the involved parent nitriles HC_3N and HC_5N feature higher acidity than diacetylene or acetylene.

Mass spectrometry revealed no $^2HC_7N$ during sublimation of a previously photolyzed $Ar/^2HC_3N/HC_4H$ sample; cyanotriacetylene appeared there only as the natural isotopologue. Cyanoacetylenic hydrogen is indeed lost in all above-listed paths. This is consistent also with the observation, reported by Couturier-Tamburelli *et al.*, that an irradiated $Ar/HC_5N/^2HC_2{}^2H$ sample led to $^2HC_7N$ but to no natural HC_7N. Worthy of note, $^2HC_5N$ could not be detected in that latter experiment, *i.e.*, no evidence was found for the reaction

$$C_5N^\bullet + {}^2HC_2{}^2H \rightarrow {}^2HC_5N + {}^2HC_2 \qquad (5)$$

suggesting that $C_5N^\bullet$ would rather tend, in this environment, to enlarge its carbon skeleton than recreate the parent nitrile with an acetylene-originating hydrogen atom.*

It should be remarked that a process consisting in (i) hydrogen abstraction from one of the precursor molecules and (ii) reaction of a resultant free radical with a neighbouring precursor species could be difficult to distinguish, in the discussed experiments, from a scenario involving (i) sufficiently high electronic excitation of a precursor followed by (ii) the reaction between that excited and an intact precursor molecule. The issue may deserve an advanced theoretical approach (see, *e.g.*, Ref. 29).

NC₈N

Turowski *et al.* [30] reported on dicyanotriacetylene formation during a gentle warm-up of cyanoacetylene/Kr matrices that were previously solidified in presence of high-voltage electric discharges through the respective gaseous mixture (CWRD technique [31]). The discovered $\tilde{a}^3\Sigma_u^+ - \tilde{X}^1\Sigma_g^+$ phosphorescence, assignable to NC_8N, appeared along with the emission from other nitriles (HC_5N, HC_7N), dinitriles (NC_2N, NC_4N, NC_6N), anions (C_3N^- and CN^-), and small neutrals (CN, CH, C_2H, C_2). This wealth of products reflected the diversity of processes initiated by a gas-phase electric discharge and continued, in the solid, due to some thermally induced mobility of reaction partners. Analysis of vibrationally resolved NC_8N emission was assisted with DFT calculations. Phosphorescence excitation spectra revealed a band pattern attributable to fully permitted $C^{1+}_u - \tilde{X}^1\Sigma_g^+$ system, resembling that reported by Grosser and Hirsch [32], Schermann *et al.* [33] or Cataldo [34] for UV absorption of NC_8N in, respectively, *n*-hexane, acetonitrile, and *n*-octane solutions.

While ionic species may be important for NC_8N synthesis in HC_3N/Kr mixtures subjected to electric discharges, it should be noticed that phosphorescence of that product was also emitted from an HC_5N-doped Kr matrix photolysed at 193 nm [35].

HC₉N

Adopting the same experimental scheme as for the UV-assisted cryosyntheses of HC_5N and HC_7N, it was possible to obtain cyanotetraacetylene, the next species of the homologous series. Szczepaniak *et al.* [36] discovered and analyzed the vibrationally-resolved $\tilde{a}^3\Sigma^+ - \tilde{X}^1\Sigma^+$ emission of HC_9N molecules formed by UV-photolysis of a HC_5N/HC_4H mixture isolated in solid krypton. Figure 2 illustrates the selectivity of the adopted detection method. Appropriately chosen phosphorescence excitation led preferentially to HC_9N emission, with a small admixture of that due to $NC_{10}N$ (see the next section). Phosphorescence excitation spectra disclosed the near-UV $\tilde{B}^1\Delta - \tilde{X}^1\Sigma^+$ system (featuring a well-resolved vibronic structure, in analogy to what was seen for shorter molecules of the series) and sharp, strong, congested bands in the region of the predicted fully permitted transitions. These latter were a good match to broad features observed by Wakabayashi *et al.* [37] in absorption of an acetonitrile solution.

Just as proposed for HC_7N formation [27], the main reaction path may, in principle, involve the attack of a photogenerated radical on the other molecule of the pair of precursors. Reaction (6) seems, *a priori*, more likely than (7), given the above discussed experiments with isotopically labelled HC_7N precursors:
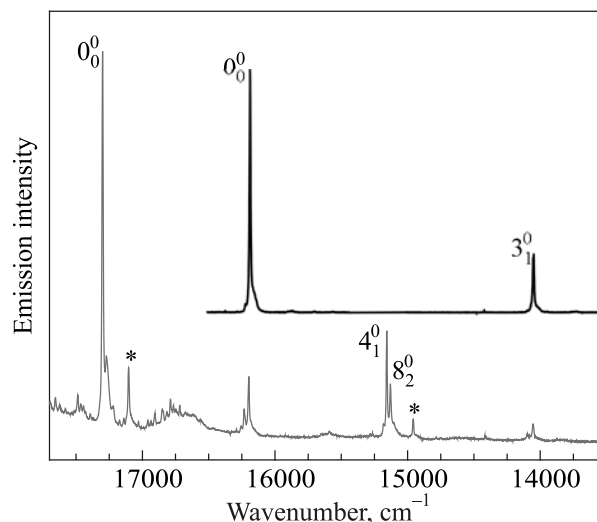

Fig. 2. Dispersed phosphorescence spectra of photoproducts generated upon 193 nm irradiations, solid krypton environment. Lower trace: mixture of $HC_5N + HC_4H$ parent species; emission excited at the wavenumber of a HC_9N vibronic band (36 540 cm^{-1}); $\tilde{a}^3\Sigma^+ - \tilde{X}^1\Sigma^+$ bands recognised as due to this nitrile are marked with their vibronic assignments; asterisks point to unspecified photolysis products. Upper (bold) trace: $\tilde{a}^3\Sigma_u^+ - \tilde{X}^1\Sigma_g^+$ emission due to $NC_{10}N$, excited at the location of $\tilde{H}^3\Sigma_u^+ - \tilde{X}^1\Sigma_g^+$ system origin (38 390 cm^{-1}); the same two bands are visible in the lower spectrum. Data come from Refs. 36 and 38.

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* The kinetic isotope effect, due to $^1H - {}^2H$ mass difference, could not be quantified there.

$$C_5N^\bullet + HC_4H \rightarrow HC_9N + H^\bullet, \qquad (6)$$

$$HC_5N + {}^\bullet C_4H \rightarrow HC_9N + H^\bullet. \qquad (7)$$

As for any successful chain-growth process, reaction partners should be sufficiently close to one another. Nevertheless, photoreactions invoked in the archetypic case of HC$_3$N, requiring complicated rearrangements within hydrogen-bonded complexes, were not supposed to play a significant role here, given the large size of potentially involved molecular fragments.

Szczepaniak *et al*. [36] could also exclude the formation of HC$_9$N via the direct encounter of two radicals:

$$HC_4^\bullet + C_5N^\bullet \rightarrow HC_9N \qquad (8)$$

based on the shape of the HC$_9$N curve of growth; it did not resemble the one observed for the NC$_6$N formation (where C$_3$N$^\bullet$ + C$_3$N$^\bullet$ recombination was evoked; *cf.* Fig. 1). Rather than that, the rate of HC$_9$N production decreased steadily from the very onset of UV irradiations, in qualitative similarity to what Fig. 1 depicts for HC$_5$N.

NC$_{10}$N

Given that NC$_6$N was shown to form out of matrix-isolated, UV-photolyzed HC$_3$N, one could anticipate an analogous coupling in the case of HC$_5$N acting as the sole precursor. However, chain-growth efficiency could be expected to decline with the increasing size and decreasing mobility of involved reactants.

As very recently reported by Szczepaniak *et al*. [38], strong phosphorescence, unambiguously attributed to the $\tilde{a}^3\Sigma_u^+ - \tilde{X}^1\Sigma_g^+$ system of NC$_{10}$N, has in fact appeared in UV-photolyzed, HC$_5$N-doped solid krypton (Fig. 2, top). The vibronic structure of dispersed emission and phosphorescence excitation spectra was analyzed. Dicyanotetraacetylene is thus far the largest photoproduct derived in the course of such cryosynthetic approaches.

Considering possible mechanisms, the authors gave preference to

$$HC_5N + C_5N^\bullet \rightarrow H^\bullet + NC_{10}N, \qquad (9)$$
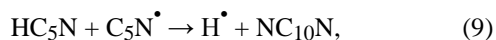
as the radical recombination process

$$C_5N^\bullet + C_5N^\bullet \rightarrow NC_{10}N \qquad (10)$$
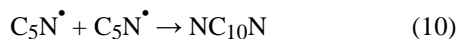
was not evidenced (just as in the case of the HC$_9$N formation; see above) by the shape of the relevant curve of growth.

Methyl derivatives

The growth of methylated cyanopolyynic chains was shown to proceed within a scheme similar to those observed for the hydrogen-capped ones. Szczepaniak *et al*. [28] reported on the successful detection of CH$_3$C$_7$N phosphorescence in the UV-irradiated mixture of propyne (CH$_3$C$_2$H) and HC$_5$N isolated in solid krypton (likewise, CH$_3$C$_5$N was formed by pairing CH$_3$C$_2$H with HC$_3$N). Vibrationless origins of CH$_3$C$_7$N and CH$_3$C$_5$N emissions

were located at wavelengths almost identical to those found for HC$_7$N and HC$_5$N, respectively.

Photochemical syntheses of HC$_7$N and HC$_9$N in cryogenic matrices suggested, as the dominant paths, either the reaction of a cyanoacetylenic radical with an intact acetylenic molecule or the reaction of a cyanoacetylenic molecule with an acetylenic radical (*viz.* reactions (1)–(4), (6), (7)). *A priori* then, the following scheme may be at work once C$_{2n+1}$N$^\bullet$ or CH$_3$C$_2^\bullet$ radicals become available:

$$C_{2n+1}N^\bullet + CH_3C_2H \rightarrow CH_3C_{2n+3}N + H^\bullet, \qquad (11)$$

$$CH_3C_2^\bullet + HC_{2n+1}N \rightarrow CH_3C_{2n+3}N + H^\bullet, \qquad (12)$$

Neither CH$_3$C$_5$N nor CH$_3$C$_3$N were leading, when combined with HC$_2$H, to the respective longer polyynic nitriles, CH$_3$C$_7$N and CH$_3$C$_5$N [28]. Indeed, HC$_2^\bullet$ was supposedly the only efficiently produced radical there. Any chain-growth mechanism following the encounters of that latter with CH$_3$C$_{2n+1}$N would require the separation of bulky molecular fragments.

Regularities

Ability to emit strong phosphorescence turned out to be a characteristic spectroscopic trait of H–(C≡C)$_n$–C≡N ($n \geq 2$), CH$_3$–(C≡C)$_n$–C≡N ($n \geq 2$) and N≡C–(C≡C)$_n$–C≡N ($n \geq 0$) species. Spectrofluorimetry was therefore the perfect tool indicating the presence of these cryogenically isolated nitriles. Phosphorescence origin wavelengths closely followed the Lewis–Calvin relation [39], *i.e.*, $\lambda_{\text{origin}}^2$ depended linearly on n [28,38].

As suggested by Fig. 3, extrapolation towards higher, as yet unexplored chain lengths seems reliable. Phosphorescence exhibited well-resolved spectral structure, the main
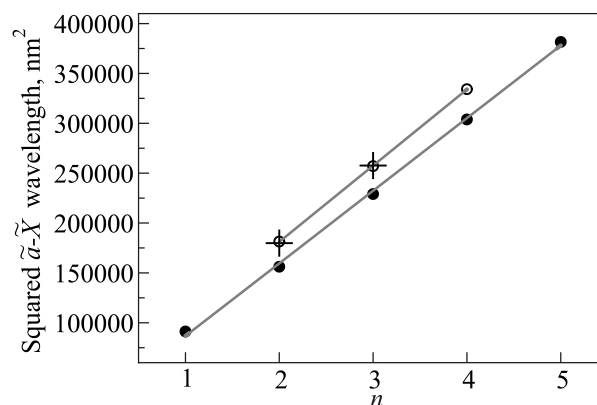

Fig. 3. Dependence of the (squared) $\tilde{a} - \tilde{X}$ phosphorescence origin wavelength on molecular size, as experimentally found for the nitrile series HC$_{2n+1}$N (open circles), NC$_{2n}$N (full circles), and CH$_3$C$_{2n+1}$N (crosses) photochemically formed in solid Kr. Data come from Refs. 17–19, 27, 28, 30, 36, 38, 40. Note that no phosphorescence has been reported for $n = 1$ mononitriles (HC$_3$N and CH$_3$C$_3$N).
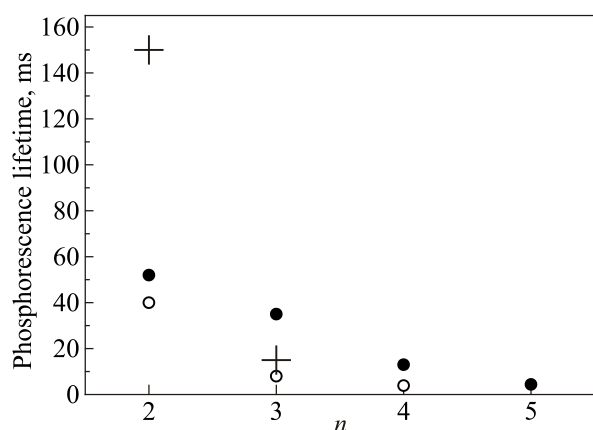
Fig. 4. Dependence of $\tilde{a} - \tilde{X}$ phosphorescence lifetime on molecular size, as experimentally found for the nitrile series $HC_{2n+1}N$ (open circles), $NC_{2n}N$ (full circles), and $CH_3C_{2n+1}N$ (crosses) photochemically formed in solid Kr. Data come from Refs. 19, 28, 36, 38, 40.

vibronic progression coming from a specific symmetric (for dinitriles) or pseudosymmetric (for mononitriles) stretching mode, namely the one characterized by the highest DFT-predicted Raman activity. Phosphorescence lifetime is expected to shorten with the increasing host atom size; respective values of 200 ms, 40 ms, and 4 ms were measured for HC_5N in Ar, Kr, and Xe matrices, respectively [19].

The fact that the triplet state lifetime, in a given homologous series, decreases with the growing chain length (*cf.* Fig. 4) reflects, most likely, the increasing number of nonradiative relaxation channels (that latter changes with the number of internal degrees of freedom). Well resolved, vibronically allowed $\tilde{B}^1\Delta - \tilde{X}^1\Sigma^+$ transitions, detected via phosphorescence excitation spectra, appeared for all considered (*viz.* $n = 1$ to 4) monocyanoacetylenes. With growing n, just as in the case of phosphorescence, the vibrationless origin of that system shifted regularly to the red (see Fig. 5).
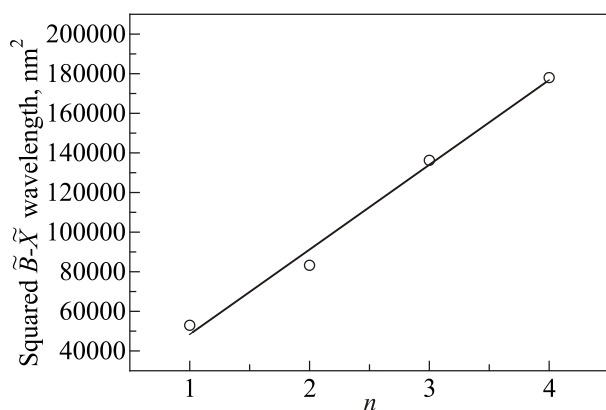

Fig. 5. Dependence of the (squared) $\tilde{B}^1\Delta - \tilde{X}^1\Sigma^+$ vibrationless origin wavelength on the size of $HC_{2n+1}N$ chains. Based on the data compiled by Szczepaniak *et al.* [38] for matrix-isolated compounds.

Conclusions

With their tendency to evolve towards longer, unsaturated linear chain species, cryogenically isolated polyynic nitriles follow the photochemical comportment of gaseous cyanoacetylene [41] or solid matrix-isolated acetylene [42]. It is also reminiscent of approach that led to gas-phase NC_nN (n up to 18) by combining cyanogen with graphite vapours [33] or of the experiments with electrical discharges between graphite rods immersed in liquid nitrogen or ammonia, reportedly yielding both NC_nN (up to $n = 10$) and HC_nN (up to $n = 15$) [34,43,44].

In the studies covered by this review, relatively short chain-growth products, in particular NC_6N, were shown to arise via recombination of two photogenerated free radicals. For larger products, however, it was postulated that a radical (or electronically excited) species attacks another, intact, suitably placed, ground-state precursor molecule. This difference seems to stem from the mobility of the involved precursors — obviously decreasing with their growing lengths.

Considering that a single trapping site in krypton is *ca.* 0.4 nm wide, it was an important finding of these works that an otherwise quite rigid cryogenic rare-gas matrix becomes soft enough (apparently due to exothermicity of the involved photoreactions) to accommodate even a 1.4 nm long product, in the extreme case of $NC_{10}N$ formed from HC_5N. The applied experimental approach has a potential to be extended towards larger linear chain molecules, of as yet unexplored electronic and vibrational spectroscopy.

Acknowledgment

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Процеси подовження вуглецевого ланцюга в кріогенних середовищах: УФ-стимульоване вирощування поліалкінових нітрилів у затверділих інертних газах
(Огляд)

Robert Kołos

Як продемонстровано в останні роки, поліалкінові нітрили можуть фотохімічно створюватись з більш дрібних ненасичених фрагментів у жорсткому середовищі замороженої матриці інертного газу. У роботі підсумовано основні моменти досліджень, які сприяли прогресу спектроскопічного опису молекул виду R–(C≡C)n–C≡N (R = H, CN або CH$_3$).

Ключові слова: ціаноалкін, кріогенна матрична ізоляція, фосфоресценція, інфрачервона спектроскопія.

Процессы удлинения углеродной цепи в криогенных средах: УФ-стимулированное выращивание полиалкиновых нитрилов в отвердевших инертных газах
(Обзор)

Robert Kołos

Как продемонстрировано в последние годы, полиалкиновые нитрилы могут фотохимически образовываться из более мелких ненасыщенных фрагментов в жесткой среде замороженной матрицы инертного газа. В работе просуммированы основные моменты исследований, которые способствовали прогрессу спектроскопического описания молекул вида R-(C≡C)n-C≡N (R = H, CN или CH$_3$).

Ключевые слова: цианоалкин, криогенная матричная изоляция, фосфоресценция, инфракрасная спектроскопия.