

# Cyanopolyynes: carbon chains formation in a carbon arc mimicking the formation of carbon chains in the circumstellar medium

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**Abstract:** Monocyanopolyynes and dicyanopolyynes can be synthesized quite easily by the submerged electric arc. Monocyanopolyynes having the general formula  $\text{H}-(\text{C}\equiv\text{C})_n-\text{C}\equiv\text{N}$  can be synthesized together with ordinary polyynes series  $\text{H}-(\text{C}\equiv\text{C})_n-\text{H}$  by arcing graphite electrodes in acetonitrile. Dicyanopolyynes  $\text{N}\equiv\text{C}-(\text{C}\equiv\text{C})_n-\text{C}\equiv\text{N}$  are produced almost pure by arcing graphite electrodes directly into liquid nitrogen. These molecules are present in the envelope of post-AGB (asymptotic giant branch), carbon-rich giant stars and also in dark molecular clouds. They are incorporated into comets and also into other primitive materials and may play a role in the prebiotic synthesis of more complex organic molecules having a biological significance. Furthermore, the cyanopolyynes are involved in the atmospheric chemistry of some bodies of the solar system. The discovery of the easy formation of these molecules under laboratory conditions may explain why these molecules are so ubiquitous in space and may also stimulate new ideas about the mechanism of their formation.

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**Key words:** cyanopolyynes, dicyanopolyynes, polyynes, carbon arc, circumstellar medium, cosmochemistry.

## Introduction

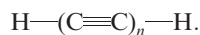
Polyynes and cyanopolyynes are very primitive organic molecules formed in the interstellar medium or around carbon-rich late-type stars (for a recent review see Marwick & Charnley 2004; Millar 2004). Cyanopolyynes are formed in dark molecular clouds at a temperature of 10 K essentially by neutral–neutral reactions mainly in the gas phase, while the ion–molecule reactions seem to play a minor role (Herbst 1998; Smith 2002). In this environment long polyyne chains as long as  $\text{HC}_{11}\text{N}$  have been detected by radioastronomy (Kroto 1992; Bell *et al.* 1999). Short-chain homologues of polyynes and cyanopolyynes have also been detected in hot molecular cores, i.e. in clumps of gas in the region of massive star formation (Millar 2004). Polyynes and cyanopolyynes are also formed in the stellar envelopes of the carbon-rich stars known as asymptotic giant branch (AGB) stars. When elemental carbon vapour is ejected from the star into the interstellar medium, it reacts with hydrogen to form polyynes and with nitrogen to form cyanopolyynes, as well as with other elements present (Marwick & Charnley 2004; Millar 2004). Today the amount of cyanopolyynes is taken as an indicator of late-time chemistry in stars (Ruffle *et al.* 1997). The carbon chains are considered the precursors of the formation of more complex molecular species in the circumstellar shell of the red giant stars (Millar 2004). For instance they are thought to be the precursors of polycyclic aromatic hydrocarbons and even of carbon grains, if it is assumed that

the mechanism of carbon dust formation around carbon-rich stars is analogous to that occurring in flames (Cataldo 2002; Cataldo & Pontier-Johnson 2002). Furthermore, the carbon grains may undergo degradation back to carbon chains under the action of shock waves of high-intensity UV radiation (Duley & Williams 1984). This primitive material ejected in the interstellar medium may survive and may be incorporated into clouds involved in the formation of protostars (Kwok 2004). At the end of the cycle and processing, it is incorporated into comets and meteorites. In fact, it is not a surprise to note that the organic chemical composition of comets for a certain instance reflects the organic molecules occurring in the circumstellar shells of carbon-rich stars or the interstellar medium (Crovisier 2004), although the organic composition of comets is also reflected in the ice chemistry of the interstellar medium of young stars. In this context, it is interesting to note that polyynes and cyanopolyynes have been found in the tails of comets (Fomenkova *et al.* 1994; Fomenkova 1999).

Polyynes and cyanopolyynes are of importance in the atmospheric chemistry of certain bodies of the solar system (Kaiser & Balucani 2001). They are objects of intense research efforts (Balucani *et al.* 2000; Fulara & Krelowski 2000; McCarthy & Thaddeus 2001; Thaddeus & McCarthy 2001; Maier *et al.* 2004). Much research has been dedicated to the modelling and understanding of the formation and evolution of cyanopolyynes and other acetylenic species in the atmosphere of Titan, Saturn's giant moon

(Coustenis & Taylor 1999). Furthermore, unsaturated polyynes are of paramount importance in the theories of the origin of life. For instance, one of the key components of nucleic acids, the pyrimidines, are thought to have been synthesized under prebiotic conditions from cyanoacetylene (Miller 2000). Surprisingly, cyanopolyynes are also produced by micro-organisms in the Earth. In fact, the molecule known under the trivial name diatreyne II, which is 7-cyano-2-heptene-4,6-dienoic acid, is produced by the basidiomycete *Tricholoma nudum* and by the fungus *Clitocybe diatreta* (Budavari 1996). It even has antibiotic properties.

In a series of papers (Cataldo 2003a, 2004a–g), we have shown that the polyynes can be synthesized on a laboratory scale under conditions mimicking those existing in the circumstellar medium. In fact, with the use of an electric arc between graphite electrodes it is possible to reach temperatures as high as 4500 °C causing the vaporization of elemental carbon. If the arc strikes organic solvents acting as hydrogen donors (hydrocarbons for instance), hydrogen end-capped polyynes are produced having the general formula



Since the arc strikes organic solvents or a particular atmosphere, the polyynes formed remain trapped in the solvent and can be easily detected by liquid chromatographic analysis (Cataldo 2003a, 2004a–f). The formation of polyynes occurs so easily that this fact justifies their abundance in the cosmos and around each carbon-rich star. The carbon vapour ejected into the circumstellar medium by the carbon-rich giant stars is made by polyynes chains. These chains may undergo end-capping reactions with hydrogen, nitrogen or even oxygen and sulphur, producing polyynes, cyanopolyynes and cumulenes, respectively (Cherchneff & Glassgold 1993). An alternative destiny of the carbon vapour is to react with and to crosslink into polycyclic aromatic hydrocarbons (PAHs) and into carbon grains.

The carbon arc which strikes the hydrocarbon solvents also causes the formation of PAHs together with polyynes, but it appears that the PAH molecules derive more from the pyrolysis/plasmalysis of the solvent rather than from the polyynes (Cataldo 2004f) although it is well known and widely accepted that in general the polyynes are considered the key precursors to PAH formation (Cherchneff *et al.* 1992). The formation of polyynes and PAHs from a carbon arc is also accompanied by the formation of carbon dust. Thus, it can be anticipated that such a process could be used as a very rough simulation of the phenomena occurring in AGB stars and protoplanetary nebulae. In the latter astrophysical objects, the presence of very complex mixtures of hydrocarbons (Cataldo *et al.* 2002, 2004; Cataldo 2003b; Cataldo & Keheyan 2003) as well as carbon dust is well documented.

In this paper we focus on monocyanopolyynes and dicyanopolyynes synthesis by a carbon arc under special conditions. We show that the synthesis with the carbon arc permits easy access to monocyanopolyynes and dicyanopolyynes, in contrast to the synthetic approaches currently used. In fact,

the bulk synthesis of cyanopolyynes (also called cyanoacetylenes and dicyanoacetylenes) is quite a complicated task. Hopf & Witulski (1995) have reviewed the organic synthesis of these molecules and proposed the best synthetic route. However, monocyanopolyynes and dicyanopolyynes can easily be produced in very small quantities by laser ablation of graphite targets in a He carrier gas in the presence of certain reactants (Heath *et al.* 1987; Kroto *et al.* 1987). For instance, when acetonitrile is added to the system, monocyanopolyynes are detected, but when N<sub>2</sub> is used as reagent, dicyanopolyynes form (Heath *et al.* 1987; Kroto *et al.* 1987). With an excess of H<sub>2</sub>, the exclusive products are instead hydrogen-terminated polyynes (Heath *et al.* 1987; Kroto *et al.* 1987; see also Kato *et al.* 2004). Polyyne synthesis with laser ablation is an approach that is sufficient to feed a mass spectrometer to identify the products, but is not useful for bulk synthesis. Cyanopolyynes are obtained in larger quantities when cyanogen gas at low pressure is admitted into the chamber confining the carbon arc working under Kratschmer–Huffman conditions (Grosser & Hirsch 1993; Gibtner *et al.* 2002). In the present work, the production of monocyanopolyynes and dicyanopolyynes produced with the submerged electric arc technique is reported. Thus, we present data concerning the formation of polyynes R–(C≡C)<sub>n</sub>–R' with R=H and R'=CN (monocyanopolyynes) and with R=R'=CN (dicyanopolyynes) in an electric arc under special conditions.

## Experimental

The experimental set-up was detailed in previous works (Cataldo 2003a, b, 2004a–g).

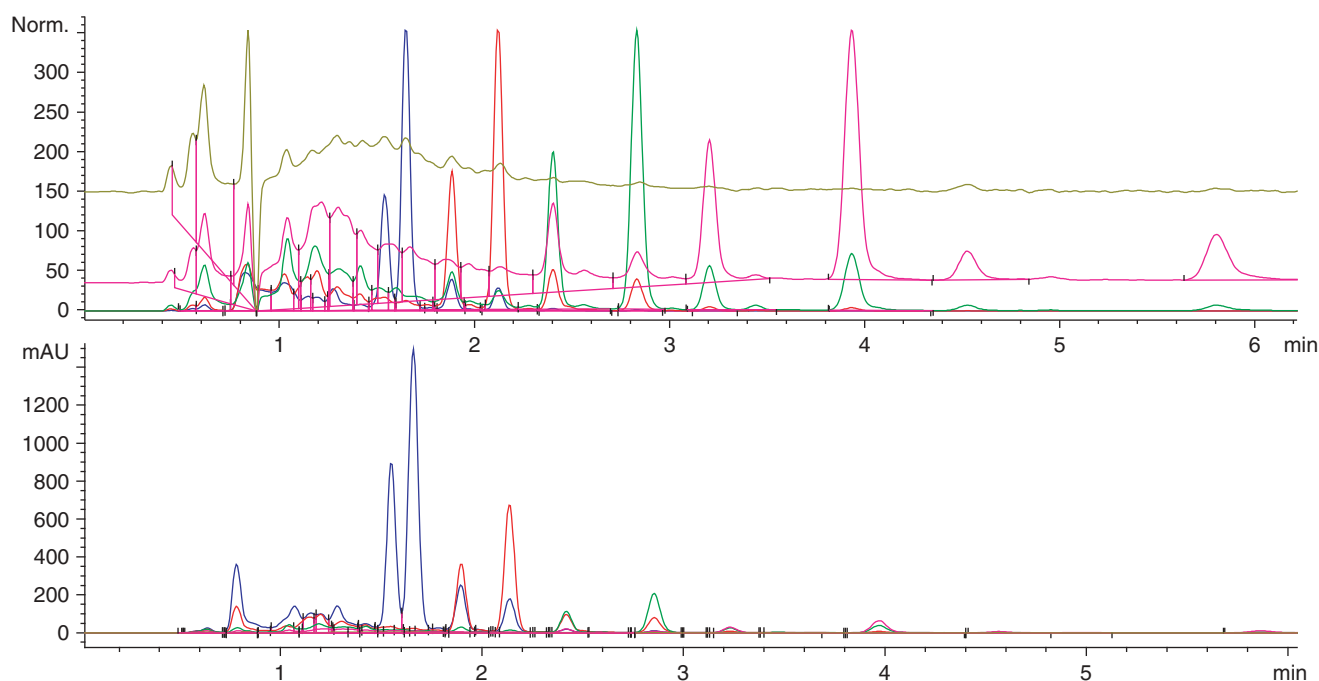
Graphite rods, 6 mm in diameter and 150 mm in length (99.999% purity), obtained from Springfield, Missouri, USA, were used as electrodes. All solvents used were analytical or high performance liquid chromatography grades from Buchs, Switzerland. Liquid nitrogen was supplied by SIAD gas tecnici (Milan, Italy).

The electric arc was conducted using a DC current set at 10 A. The electronic absorption spectra were recorded on a Shimadzu UV160A spectrophotometer on filtered solutions.

### *Synthesis of monocyanopolyynes by a submerged electric carbon arc in acetonitrile*

Two graphite electrodes were connected at the poles of the DC power supply and submerged in a Pyrex three-necked round-bottomed flask filled with 50 ml of acetonitrile. The two electrodes were arranged in a 'V' geometry (Cataldo 2003a, b, 2004a–f). The flask was immersed in a cooling bath. Under normal conditions (room temperature) the cooling bath was of tap water. In the experiment where acetonitrile was arced at –40 °C, the flask was suspended (not immersed) in a large Dewar flask half-filled with acetone/dry ice mixture.

To ignite the arc the two electrodes were placed so as to be touching each other under the solvent and then moved continuously up and down to produce an arc emitting bright



**Fig. 1.** A HPLC chromatogram of the polyynes and monocyanopolyynes produced by the carbon arc in acetonitrile at  $-40^{\circ}\text{C}$ . The chromatogram at the top of the figure has been normalized in order to show all the relevant peaks associated to the molecular species present in the mixture. The most intense peaks are hydrogen-capped polyynes, the others are monocyanopolyynes other than the peak with  $R_t = 5.86$  min. The peak due to  $\text{H}-(\text{C}\equiv\text{C})_9-\text{H}$  is not shown in the figure since it appears at  $R_t = 9.67$  min and is weak. The chromatogram at the bottom of the figure shows the relative intensity and hence the relative abundance of the various molecular species. The most abundant species is  $\text{H}-(\text{C}\equiv\text{C})_4-\text{H}$  with retention time  $R_t = 1.65$  min, followed by  $\text{H}-(\text{C}\equiv\text{C})_3-\text{CN}$ , then  $\text{H}-(\text{C}\equiv\text{C})_5-\text{H}$ , then  $\text{H}-(\text{C}\equiv\text{C})_4-\text{CN}$  and then  $\text{H}-(\text{C}\equiv\text{C})_6-\text{H}$  (see also Table 1).

white light. The best condition to ensure the formation of polyynes is to have the brightest light in the arc.

The solution containing the crude mixture of polyynes in acetonitrile was filtered with a syringe fitted with a polyvinylidene fluoride Acrodisc<sup>®</sup> membrane having a pore size of  $0.45\ \mu\text{m}$  to remove carbon particles suspended in the solvent.  $5\text{--}10\ \mu\text{L}$  per run of the filtered solution were injected into a  $4.6 \times 150\ \text{mm}^2$  column (Zorbax Eclipse XDB-C8) of an high performance liquid chromatography from Agilent Technologies model 1100. A mobile phase of  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  80/20 (v/v) was used under isocratic conditions at a flow rate of  $1.5\ \text{ml}\ \text{min}^{-1}$  and 151 bar. The polyynes eluted from the column were identified by a diode-array detectors through their typical spectra as previously detailed (Cataldo 2004a, b). The diode-array detectors were set at 225, 250, 274, 295 and 350 nm.

#### *Synthesis of dicyanopolyynes by the submerged electric carbon arc in liquid nitrogen*

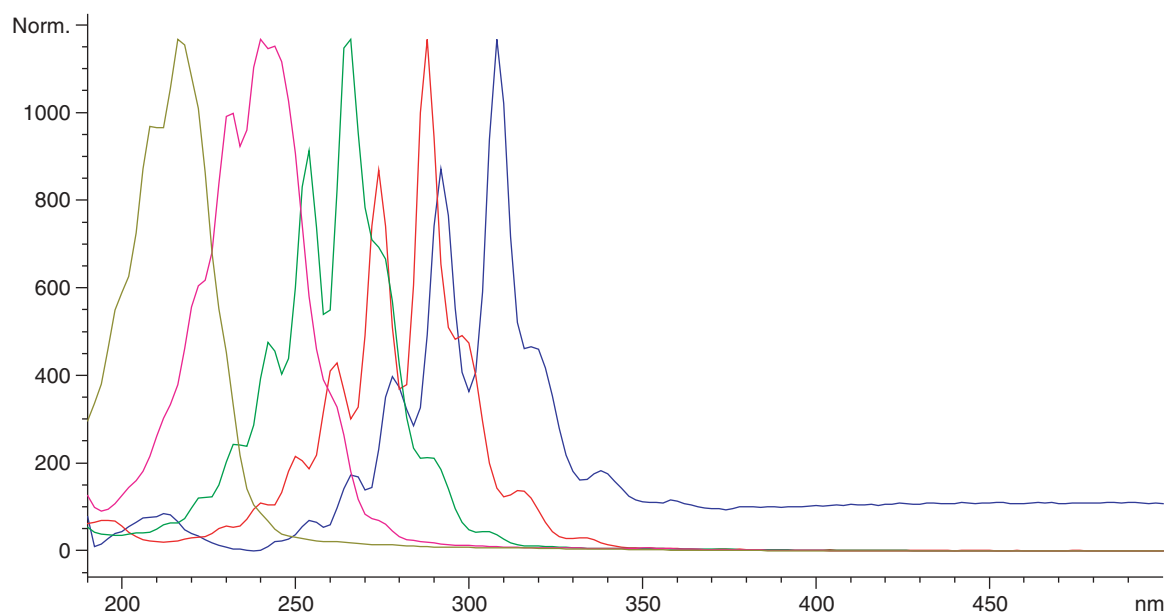
A three-necked round-bottomed Duran flask of 100 ml equipped with two graphite electrodes arranged in a 'V' geometry was filled with liquid nitrogen and immersed in liquid nitrogen contained in a Dewar flask. The third neck of the flask was fitted with a valve connected with a Drechsel tube (a gas washing bottle) of 250 ml filled with 100 ml of *n*-octane.

The electric arc was ignited and sustained at 10 A (DC current) by placing the two in-contact graphite electrodes

submerged in liquid nitrogen into the three-necked flask and slightly moving them up and down. The bright light of the arc was easily observed. The heat generated by the arc caused the partial vaporization of the liquid nitrogen, which was forced to bubble into the gas washing bottle attached to the reaction flask. The products formed in the electric arc were hence forced to pass together with nitrogen into the octane solvent outside the reactor, and they were then trapped into the solvent. Periodically, samples of the *n*-octane solution were collected and analysed by electronic absorption spectroscopy and by HPLC-DAD analysis, injecting up to  $20\ \mu\text{L}$  of the octane solution into the HPLC column and employing the usual mobile phase acetonitrile/water 80/20. The following polyynes were identified based on their retention time and electronic spectra:  $\text{C}_6\text{N}_2$ ,  $\text{C}_8\text{H}_2$ ,  $\text{C}_8\text{N}_2$ ,  $\text{C}_{10}\text{H}_2$ ,  $\text{C}_{10}\text{N}_2$ . Similar results were obtained by filling the Drechsel tube with ethanol and by suspending (but not immersing) the tube into a Dewar pot containing a small quantity of liquid nitrogen in the bottom.

#### *The electric arc between graphite electrodes submerged in *n*-octane*

To create a 'blank' or a reference to the products formed by the carbon arc in liquid nitrogen, we also arced graphite electrodes directly into *n*-octane at 10 A under the same conditions as described previously (Cataldo 2004c, d) for *n*-hexane. Indeed, the products were practically the same



**Fig. 2.** Overlapped electronic absorption spectra of monocyanopolynes  $\text{H}-(\text{C}\equiv\text{C})_n-\text{CN}$  produced by arcing graphite electrodes in an acetonitrile solution at  $-40^\circ\text{C}$  (see Table 1). The spectra of monocyanopolynes with 7, 9, 11, 13 and 15 carbon atoms are shown in their respective order.

**Table 1.** HPLC retention time of the dicyanopolynes versus other polyynes

$R_t = 1.55$ for $\text{C}_6\text{N}_2$ in comparison with $R_t = 1.547$ for $\text{HC}_7\text{N}$ (Cataldo 2004a, b)
$R_t = 1.64$ for $\text{C}_8\text{H}_2$ as already found in Cataldo (2004a, b)
$R_t = 1.87$ for $\text{C}_8\text{N}_2$ in comparison to $R_t = 1.89$ for $\text{HC}_9\text{N}$ (Cataldo 2004a, b)
$R_t = 2.11$ for $\text{C}_{10}\text{H}_2$ as already found in Cataldo (2004a, b)
$R_t = 2.39$ for $\text{C}_{10}\text{N}_2$ in comparison to $R_t = 2.41$ for $\text{HC}_{11}\text{N}$ (Cataldo 2004a, b)

as detected and reported for *n*-hexane. As usual, the polyne  $\text{C}_8\text{H}_2$  was the most abundant component in the polyne mixture consisting exclusively of hydrogen-terminated polyynes.

#### The electric arc between graphite electrodes submerged in water

The arc was conducted between graphite electrodes submerged in distilled water at 10 A. The electronic absorption spectrum of the crude aqueous solution of polyynes and other products showed the following absorption bands: 200, 215 and 226 nm as the most intense. Other weaker bands were observed at 238, 246, 250, 259, 274, 284, 300 and 323 nm.

The HPLC-DAD analysis revealed the presence of the following polyynes:  $\text{C}_4\text{H}_2$ ,  $\text{C}_6\text{H}_2$ ,  $\text{C}_8\text{H}_2$  and  $\text{C}_{10}\text{H}_2$ . Polyne  $\text{C}_8\text{H}_2$  was by far the most abundant product.

## Results and discussion

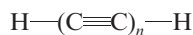
### Monocyanopolynes produced in acetonitrile

Arcing graphite electrodes in any hydrocarbon solvent or in any alcohol produces invariably a mixture of polyynes with

the molecular species  $\text{C}_8\text{H}_2$  as the dominant component in all cases. These results have been presented and discussed in several papers (Cataldo 2003a; Cataldo 2004a–f).

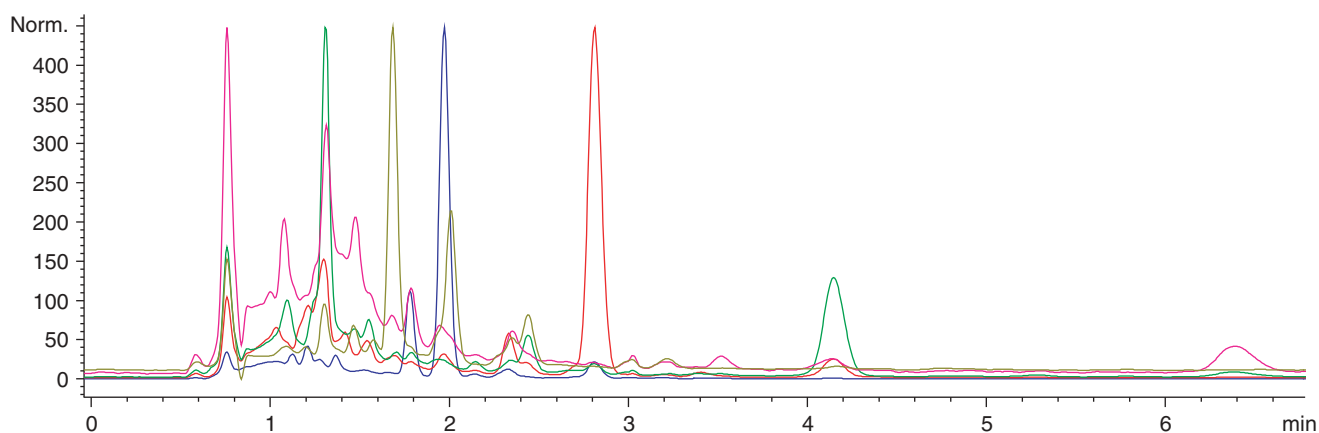
When acetonitrile is used as solvent for the arcing experiment, then a very peculiar liquid chromatogram is obtained as shown in Fig. 1. The chromatogram appears unusually rich in molecular species if compared with that obtained in hydrocarbons and in alcohols (see Cataldo 2004a–f).

The chromatogram at the top of Fig. 1 is normalized and puts in evidence the fact that, between each two consecutive intense peaks, it is possible to observe a series of less intense peaks having approximately one-third the intensity of the strong peaks. The analysis of the band pattern of the electronic absorption spectra of each individual strong peak of the chromatogram reveals that we are dealing with a series of hydrogen-capped polyynes  $\text{R}=\text{R}'=\text{H}$  having the general formula

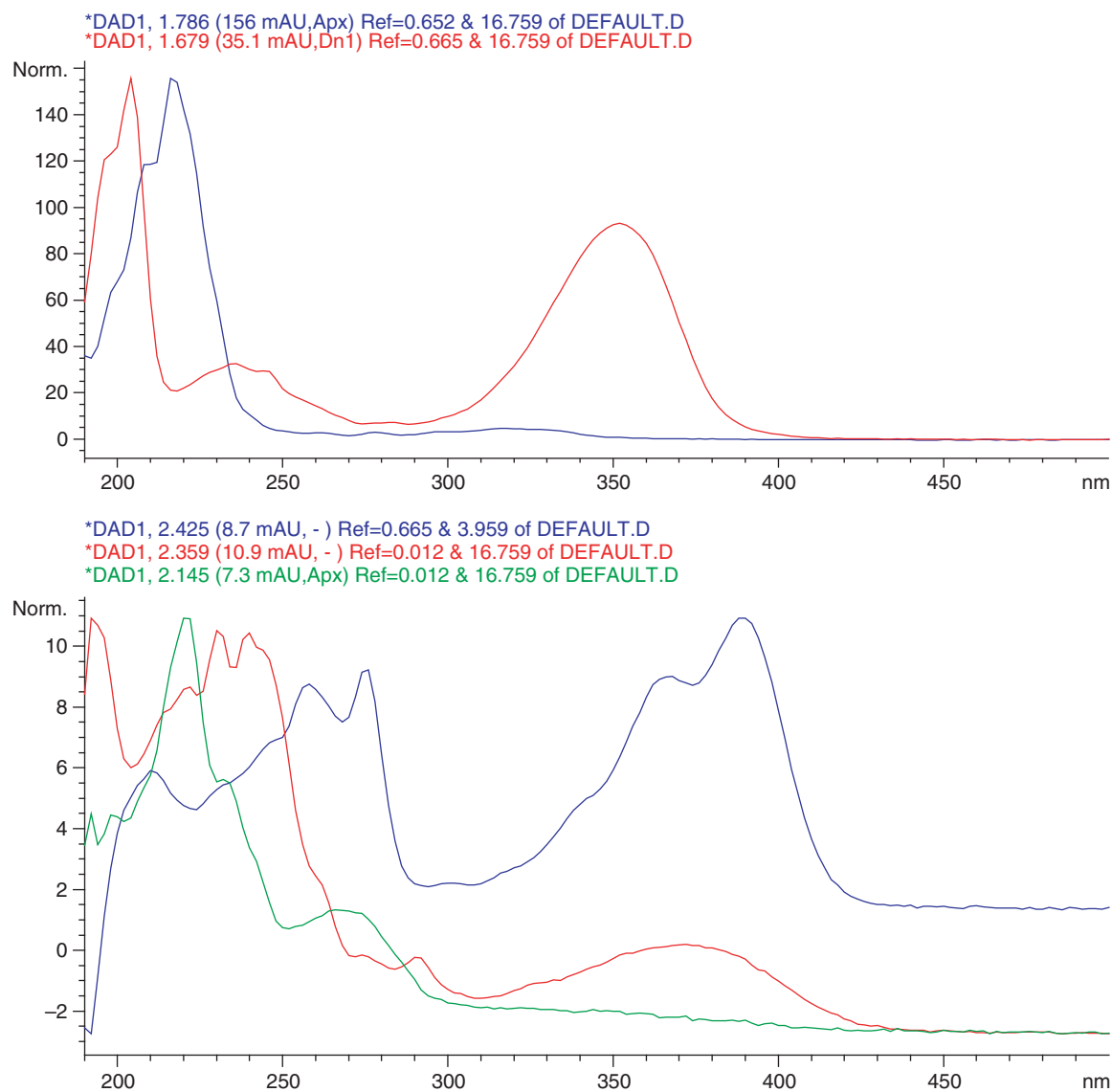


already reported elsewhere (Cataldo 2004a–f). The assignment is also confirmed by comparing the retention times as discussed in previous works (Cataldo 2003a, 2004a, b).

However, the other series of molecules eluted between the ‘ordinary’ polyne series shows another set of homologous spectra systematically red-shifted (see Fig. 2) and with a different band pattern in comparison with the normal hydrogen-capped polyynes as clearly illustrated in Table 1. Based on the regular red shift of the most intense absorption band observed in these polyne series, based on the fact that this series was observed exclusively in acetonitrile solvent and based finally on the intermediate retention time in the HPLC column between two ‘ordinary’ hydrogen-capped polyynes, we reached the conclusion (Cataldo 2004a) that we were dealing



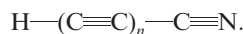
**Fig. 3.** A HPLC chromatogram of the polyynes and monocyanopolyne solutions prepared by arcing graphite at  $-40\text{ }^{\circ}\text{C}$ , after 5 days storage at room temperature. The monocyanopolyynes have disappeared completely while the hydrogen-capped polyynes are still present.



**Fig. 4.** Electronic absorption spectra of unknown products derived from the decomposition or rearrangement of monocyanopolyynes.



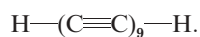
with a series of monocyanopolyynes with  $R=H$  and  $R=CN$ , i.e. with molecules having the general formula



This conclusion is in perfect agreement with the work of Kroto and colleagues, who detected the formation of monocyanopolyynes when they added acetonitrile to their carbon cluster generator employing the laser ablation technique (Heath *et al.* 1987; Kroto *et al.* 1987).

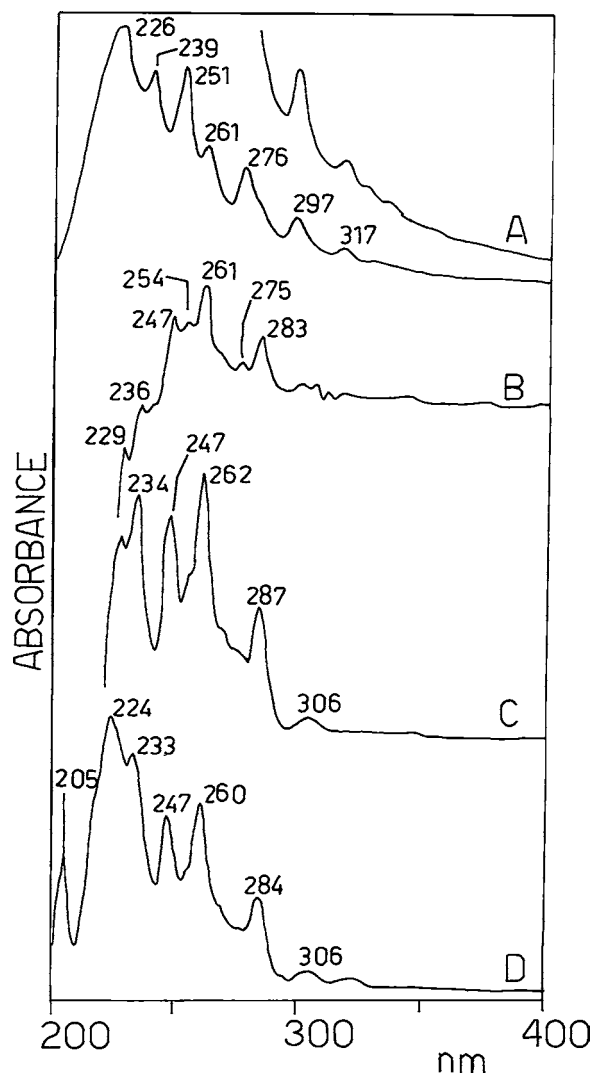
The chromatogram at the bottom of Fig. 1 shows the relative intensity and hence the relative abundance of the various molecular species. The most abundant species detected is, as usual,  $H-(C\equiv C)_4-H$  with retention time  $R_t=1.65$  min, followed by  $H-(C\equiv C)_3-CN$  which in its turn is followed by  $H-(C\equiv C)_5-H$ , then  $H-(C\equiv C)_4-CN$  and then  $H-(C\equiv C)_6-H$  (see also Table 1).

It is worth reporting here that arcing at  $-40^\circ\text{C}$  also leads us to detect hydrogen-capped polyynes having 18 carbon atoms, the longest polyyne chain we have yet detected (Cataldo 2004a, b):



The polyyne  $C_{18}H_2$  was not detected in the acetonitrile solution arced at room temperature and was also not found in the methanol or hexane solutions arced at room and low temperatures. In these cases, the longest polyyne chain only had 16 carbon atoms.

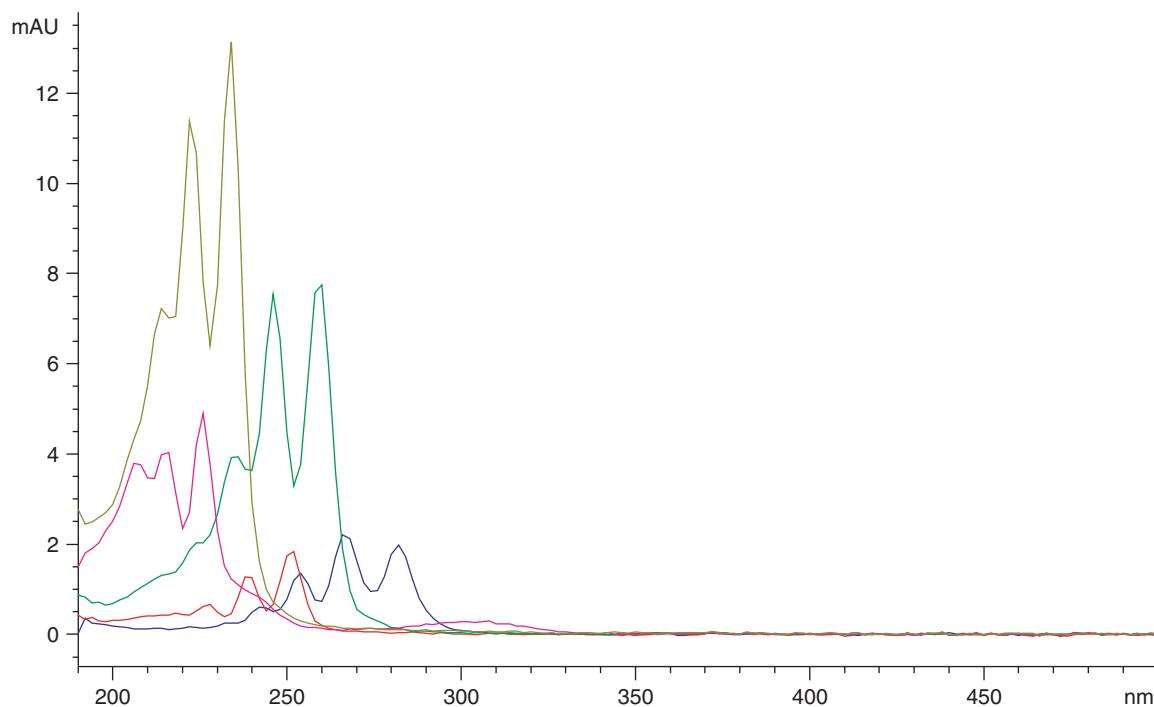
The filtered polyyne and monocyanopolyyne solution prepared in acetonitrile at  $-40^\circ\text{C}$  is not stable if stored at room temperature for 5 days in a closed flask. In fact, on standing the solution becomes deep yellow. The HPLC analysis of the aged solution produces the chromatogram shown in Fig. 3, where it is possible to observe that the ordinary hydrogen-terminated polyynes survive unchanged while the monocyanopolyynes disappear completely. In their place it is possible to record some unusual spectra of unknown molecules. Some of these spectra are shown in Fig. 4. These spectra are characterized by absorption bands at  $\lambda \geq 350$  nm, which justify the yellow colour of the solution. The long-term stability of the hydrogen-terminated polyynes in diluted solutions is well known since we have previously reported this property (Cataldo 2004c, e); however, the rather high instability of monocyanopolyynes in the same solution is quite unexpected. At present we do not know what kind of rearrangement takes place on these molecules. Whatever the case, the knowledge that the hydrogen-terminated polyynes are much more stable than the monocyanopolyynes may have astrochemical implications. In fact, the latter are easily detected by radioastronomy because they possess a dipole moment; however, the ordinary polyynes are not because they do not have a permanent dipole moment (McCarthy & Thaddeus 2001; Thaddeus & McCarthy 2001). It is reasonable to propose that the ordinary polyynes may be as abundant or even more abundant than the monocyanopolyynes due to their higher stability and to the large abundance of hydrogen in the interstellar medium.



**Fig. 5.** Electronic absorption spectra of the polyyne mixture. A, polyynes obtained by arcing graphite directly into *n*-octane (the top curve of A is an expansion of the spectrum above 280 nm to show finer details). B, initial spectrum of the polyyne mixture produced from the graphite arc in liquid nitrogen and trapped in *n*-octane at the beginning of the experiment. C, the same as B but after prolonged arcing in liquid nitrogen. D, the same as C at the end of the experiment; the final total concentration of polyynes was estimated to be about  $8 \times 10^{-6}$  M.

#### *Formation of polyynes from an electric arc in liquid nitrogen between graphite electrodes*

When the graphite electrodes are arced in liquid nitrogen the polyynes formed in the arc are quenched into the very cold reservoir of the liquid nitrogen surrounding the plasma ball. During arcing, part of the liquid nitrogen vaporizes to dissipate the heat generated by the electric arc. When liquid nitrogen vaporizes, a continuous stream of gaseous nitrogen drags the polyynes outside the reactor (see the Experimental section) into the gas washing bottle connected to the reactor, which is filled with a solvent (*n*-octane). When nitrogen bubbles into the bottle, it releases the polyynes into the *n*-octane solvent, which acts as a trap. In fact, in Fig. 5 it is



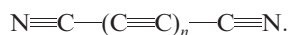
**Fig. 6.** Electronic absorption spectra of the polyynes formed from graphite arcing in liquid nitrogen. The liquid chromatographic analysis (HPLC) was able to separate the mixture into its components. The electronic spectrum of each component eluted was recorded by the diode-array detector (DAD). The three main components are easily and definitively identified from their electronic absorption spectra and are respectively  $C_6N_2$ ,  $C_8N_2$  and  $C_{10}N_2$ . The spectra of these three dicyanopolyynes in the figure are easily identifiable from their longest wavelength absorption bands lying at 233, 260 and 283 nm, respectively. There are also two other minor components in the figure: the hydrogen-terminated polyynes  $C_8H_2$  and  $C_{10}H_2$ . Furthermore,  $C_{12}H_2$  has also been identified although at very low concentration (not shown in the figure).

possible to observe the typical polyyne spectrum from the octane solution used as a trap for these molecules.

Fig. 5(B) shows the initial spectrum of the polyyne mixtures produced from the graphite arc in liquid nitrogen at the beginning of the experiment. Under these conditions, the initial polyyne concentration was estimated to be around  $10^{-7}$  M in the *n*-octane trap from the optical density in the spectrum. Furthermore, the spectrum of the polyynes in Fig. 5(B) produced from the arc in liquid nitrogen shows a different band pattern than does the mixture of polyynes produced by arcing graphite electrodes directly into *n*-octane (compare Fig. 5(B) with Fig. 5(A)). In particular, in Fig. 5(B) we can observe two main bands at 261 and 283 nm while the most intense bands in Fig. 5(A) are located at 226, 239 and 251 nm. Since the end groups of polyyne chains are affected by the nature of the solvent where the graphite arc is struck, and since we know that usually the polyynes are hydrogen-terminated when the arc is made in hydrocarbon solvents like *n*-hexane or *n*-octane and they are also cyano-terminated when the arc is made in acetonitrile, these spectral differences can be taken as a first hint that the polyynes formed in liquid nitrogen are nitrogen- and hence cyano-terminated.

From the previous subsection, we know the electronic absorption spectra of a series of monocyanopolyynes and from the literature (Grosser & Hirsch 1993) we know the spectrum of the dicyanopolyyne  $C_8N_2$  whose maximum wavelength

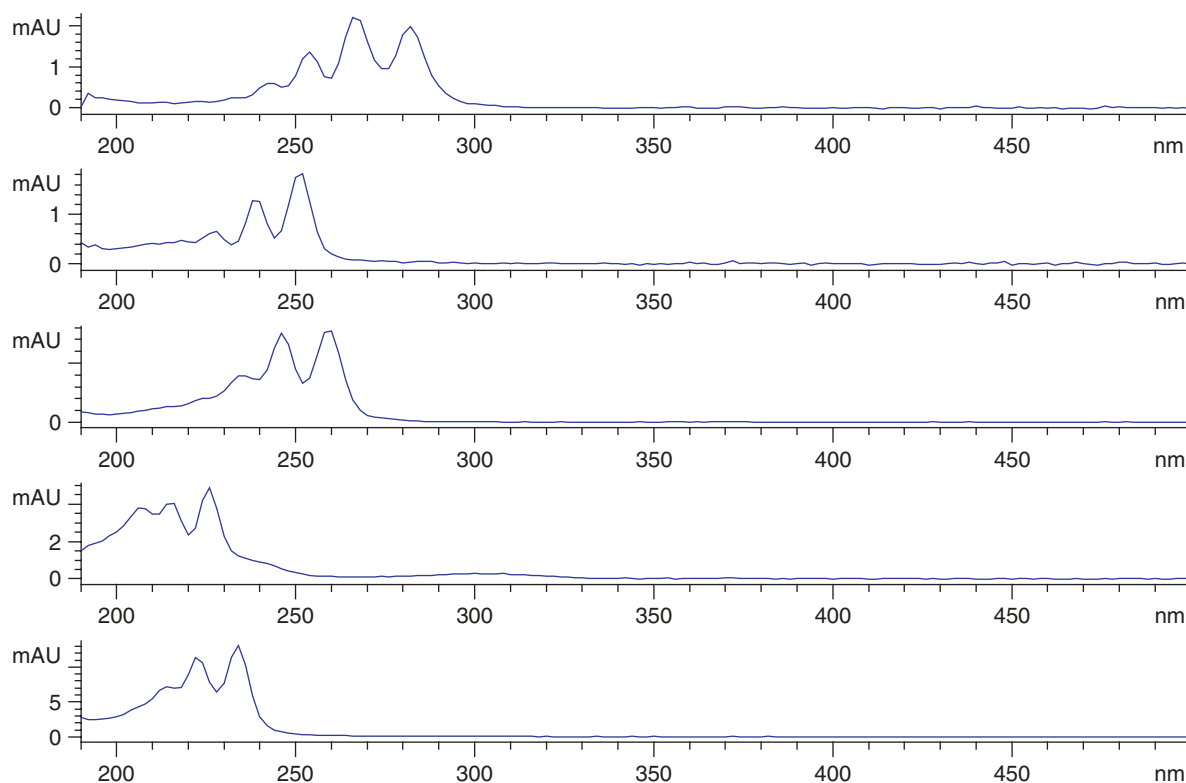
absorption band lies just at 261 nm. In principle, it is quite obvious to expect to produce nitrogen-terminated polyynes by arcing graphite in liquid nitrogen; the high temperatures of the electric arc may cause plasmalysis of molecular nitrogen into atomic nitrogen, which in its turn can easily form cyano-groups with carbon vapour and hence terminate the polyyne chains into dicyanopolyynes:



It is fascinating to think that similar synthetic processes leading to these or similar molecules are known to occur in the outflow of certain carbon-rich giant stars in space (Herbst 1998; Smith 2002).

By continuing arcing in liquid nitrogen with graphite electrodes, it is possible to accumulate the reaction products into the octane trap. This is illustrated in Fig. 5(C) where the bands become more intense and better defined as the arcing time elapses. In particular, in Fig. 5(C) the concentration of polyynes can be estimated to be about  $2.5 \times 10^{-6}$  M. Arcing was stopped when all liquid nitrogen in the reaction flask was consumed, i.e. disappeared by vaporization. The final spectrum of the products collected is shown in Fig. 5(D) with the final total concentration of polyynes estimated to be about  $8 \times 10^{-6}$  M.

The crude *n*-octane solution, after filtration, was chromatographed in the HPLC apparatus (see the Experimental



**Fig. 7.** Individual spectra of each molecular species separated by liquid chromatographic analysis. From the bottom to the top it is possible to distinguish the spectrum of  $C_6N_2$  with  $R_t=1.55$ , then  $C_8H_2$  with  $R_t=1.64$ , followed by  $C_8N_2$  ( $R_t=1.87$ ),  $C_{10}H_2$  ( $R_t=2.11$ ) and  $C_{10}N_2$  ( $R_t=2.39$ ).

section). The complex polyne mixture formed by arcing graphite directly into liquid nitrogen was resolved into six main components whose electronic absorption spectra are shown together in Fig. 6. The three main components are easily and definitively identified from their electronic absorption spectra and are respectively  $C_6N_2$ ,  $C_8N_2$  and  $C_{10}N_2$  (see below for further details). The former is the most abundant, followed by the other two in respectively lower concentrations. Other minor components detected were hydrogen-terminated polyynes  $C_8H_2$ ,  $C_{10}H_2$  and  $C_{12}H_2$  in decreasing concentration and in general at much lower concentrations than the corresponding dicyanopolyynes ( $C_{12}H_2$  is not shown in Fig. 6).

The individual spectra of the molecular species separated by the liquid chromatographic analysis are shown in Fig. 7, following their retention times ( $R_t$ ) from the bottom to the top of the figure. The first molecular species eluted with  $R_t=1.55$  min was identified as  $C_6N_2$  from its absorption spectrum ( $\lambda_m=$ **235**, 222, 213 and 205 nm) (the most intense band is written in bold), in comparison with the well-known (Cataldo 2004a, b, d) spectrum of  $C_8H_2$  which eluted immediately after that species with  $R_t=1.64$  min ( $\lambda_m=$ **227**, 218 and 208 nm). It can be observed that both  $C_6N_2$  and  $C_8H_2$  have similar molecular weight (about 100 Da versus 98 Da, respectively), but from our previous study on polyynes and cyanopolyynes (Cataldo 2004a, b) we know that at more or less equal molecular weight the nitrogen-capped polyynes

have shorter retention time than the hydrogen-capped polyynes on our HPLC column. Thus, the assignment appears correct. The next compound eluted with  $R_t=1.87$  min is  $C_8N_2$ , which has been recognized from the band pattern of its spectrum which matches that reported in the literature for this compound (Grosser & Hirsch 1993) ( $\lambda_m$  (found))=**260**, 247, 233, 223 and 214 nm;  $\lambda_m$  (Grosser & Hirsch 1993)=261, 248, 236, 225 and 215 nm). After  $C_8N_2$  with a molecular weight of about 124 Da, the hydrogen-capped polyne  $C_{10}H_2$  was eluted with a molecular weight of 122 Da and  $R_t=2.11$  min. Its spectrum matches completely the known (Cataldo 2004a, b) band pattern of this compound ( $\lambda_m=$ **251**, 239, 227 and 218 nm). Finally, the detection of  $C_{10}N_2$  occurs at  $R_t=2.39$  min and the spectrum is characterized by  $\lambda_m=$ 303, 283, **268**, 253, 243 and 232 nm. It is important to underline that in the assignments reported here we have also been guided by the typical retention times measured in earlier works for hydrogen-capped polyynes of monocyano-polyynes as reported in Table 1.

The formation of polyynes in the electric arc in liquid nitrogen represents a clear indication that the elemental carbon for the polyne chains is supplied essentially from the graphite electrodes and not from the solvent. This result is quite expected since we know that the electric arc in vacuum conditions between graphite electrodes produces polyne radicals. Furthermore, Hirsch and colleagues (Grosser & Hirsch 1993) have shown that the electric arc between



graphite electrodes under Kratschmer–Huffman conditions in a reduced pressure of cyanogen ( $C_2N_2$ ) produces a mixture of dicyanopolynes whose main components are  $C_8N_2$  and  $C_{10}N_2$  (55 and 35%, respectively).  $C_{12}N_2$ ,  $C_{14}N_2$  and  $C_{16}N_2$  were also detected (Grosser & Hirsch 1993).

In the products of the electric arc in liquid nitrogen (Fig. 6), we can estimate, from the chromatographic analysis, that  $C_6N_2$  represents approximately 50% (by mol.) of the mixture, followed by  $C_8N_2$  with about 25% and  $C_{10}N_2$  with about 5%. The remaining products are essentially  $C_8H_2$ ,  $C_{10}H_2$  and  $C_{12}H_2$ .

The hydrogen-terminated polyynes formed in minor quantities in our synthesis derive their hydrogen end-groups from the plasmalysis of the humidity present in the reactor and in the liquid nitrogen. Therefore, they must be regarded merely as secondary products. In the next section, we demonstrate experimentally that the hydrogen-terminated polyynes are formed from water plasmalysis. In fact, in our electric arc in liquid nitrogen we have excluded the presence of any organic solvent but not the presence of humidity. Therefore, the arc between graphite electrodes in liquid nitrogen also involves necessarily the plasmalysis of small amounts of water, which supplies the hydrogen necessary for end-capping the polyyne chain.

#### *Polyynes from an electric arc from graphite electrodes in water*

In the previous subsection, the electric arc in liquid nitrogen produces cyanopolynes as expected but also hydrogen-terminated polyynes, which are rather unexpected unless we admit that traces of water supply hydrogen atoms during the plasmalysis caused by the electric arc. In the Experimental section, we have clearly demonstrated that when the submerged electric arc between graphite electrodes strikes under distilled water, it is possible to observe a typical electronic spectrum of a mixture of polyynes in water. Furthermore, the liquid chromatographic analysis permits one to separate and identify all the hydrogen-terminated polyyne series normally observed in organic solvents like methanol and *n*-hexane. Thus, it is demonstrated that the hydrogen atoms in a system of graphite electrodes and water are supplied by the plasmalysis of the water molecules. Consequently, it is now clear that the hydrogen-terminated polyynes observed as secondary products in the arcing experiment in liquid nitrogen derive from the humidity and the traces of water present in the liquid nitrogen itself and in the reactor.

## Conclusions

Arcing graphite electrodes in acetonitrile produces two series of polyynes simultaneously: the ‘ordinary’ hydrogen-terminated polyynes and a series of monocyanopolynes. Thus acetonitrile is a solvent able to supply both H and CN radicals, which attach to the growing carbon chains. In our earlier works (Cataldo 2003a, b, 2004a–e) we found that all the other solvents tested, whether hydrocarbons or alcohols, invariably were able to supply hydrogen atoms as end-capping and

stabilizing moieties of the carbon chains. This approach may open the door for easier access to monocyanopolynes.

In acetonitrile solution the monocyanopolynes are unstable and disappear completely after several days if stored at room temperature. The hydrogen-terminated polyynes present in the same solution appear much more stable and remain unchanged for a much longer time period in comparison with monocyanopolynes.

The dicyanopolyyne series can be easily produced by arcing graphite electrodes into liquid nitrogen.

$C_6N_2$ ,  $C_8N_2$  and  $C_{10}N_2$  have been easily trapped into solvents where the vaporized liquid nitrogen is bubbled and detected by liquid chromatography. This approach shows the very easy access to dicyanopolynes. Although not easily detectable by radioastronomy, dicyanopolynes must be as abundant as monocyanopolynes and polyynes.

In our experimental system the synthesis of dicyanopolynes is accompanied by the formation of small amounts of hydrogen-terminated polyynes, whose formation is due to the presence of water humidity in the experimental system adopted.

The easy access to these molecules will permit deeper laboratory studies into the chemistry of these molecules, which until now has largely been unexplored, and will permit the elucidation of the role played by these molecules in the prebiotic synthesis of complex organic molecules.

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