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

Franco Cataldo

Soc. Lupi Chemical Research Institute, Via Casilina 1626/A, 00133 Rome, Italy
e-mail: cdcata@flashnet.it

Abstract: Monocyanopolyynes are formed by arcing graphite electrodes in ammonia. This work completes the parallelism existing between the polyynes formed by laser ablation experiments of graphite targets and those produced from the submerged electric arc. In both cases the same products are obtained. The products consist of hydrogen-terminated polyynes if water is present, monocyanopolyynes (mixed with hydrogen-terminated polyynes) if the carbon arc is sparked in acetonitrile or ammonia and dicyanopolyynes if the arc is struck in liquid nitrogen. The mechanism of formation of polyynes in the submerged carbon arc involves essentially neutral species; similar species and pathways may also occur in the circumstellar environment where polyynes have been detected by radioastronomy. It is shown that the relative abundances of the polyynes formed in the submerged carbon arc or in a carbon arc in vacuum decrease by a factor between three and five as the chain length increases by a C_2 unit. Exactly the same trend has been observed by radioastronomy both for polyynes and cyanopolyynes in the circumstellar environment around red giants and asymptotic giant branch (AGB) stars. This fact may be a simple coincidence or may suggest that the mechanism of formation of the polyynes in the carbon arc is the same as that occurring in the surroundings of carbon-rich stars.
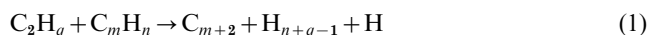
Introduction

Polyynes and cyanopolyynes from carbon-rich stars and in the interstellar medium

Polyynes H—$(C \equiv C)_n$—H, monocyanopolyynes H—$(C \equiv C)_n$—$C \equiv N$, dicyanopolyynes $N \equiv C$—$(C \equiv C)_n$—$C \equiv N$ and their radicals and ions are an exotic class of molecules that have been detected in many astrophysical objects in space together with other molecules (Bell *et al.* 1999). More precisely, they have been detected together with other molecular species in the circumstellar environment surrounding late-type carbon-rich stars such as, for instance, the star IRC + 10°216, but they have also been found in dense and dark interstellar molecular clouds such as TMC 1 and in hot molecular cores (in the latter case limited to HC_3N) (Millar 2004).

In the circumstellar environment it has been proposed that the formation of these long and unsaturated carbon chains takes place mainly by a radical mechanism involving neutral species. A general reaction path was proposed and modelled by Cherchneff & Glassgold (1993) and Cherchneff *et al.* (1993):

$$C_2H_q + C_mH_n \rightarrow C_{m+2} + H_{n+q-1} + H \tag{1}$$

with $q = 0,1$,

$$C_{2n+1}N + C_{2m}H_2 \rightarrow H—C_{2(n+m)+1}N + H. \tag{2}$$
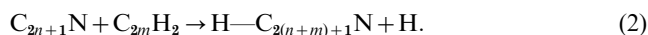
The classic ion–molecule mechanism has been demonstrated not to be operative in circumstellar shells because of kinetic and energetic reasons and the lack of ions (Kroto *et al.* 1987; Cherchneff & Glassgold 1993; Helling *et al.* 1996; Herbst 1998; Millar 2004). Only radiative association can supplement the above-mentioned reactions (Cherchneff & Glassgold 1993):

$$C_nH_m + C_{n'}H_{m'} \rightarrow C_{n+n'}H_{m+m'} + h\nu. \tag{3}$$
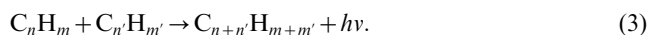
Another important point is the fact that the molecules produced in the circumstellar shell are thought to undergo complete destruction when released in space because they are

photolysed by the intense ultraviolet radiation field external to the carbon-rich star; this external field has an intensity several orders of magnitude higher than the ultraviolet field of the carbon star itself, which is considered negligible (Millar 2004). However, the polyynes reappear in cold dark clouds and hot molecular cores, and are then incorporated together with a plethora of other molecules and refractory materials in comets (Formenkova *et al.* 1994; Formenkova 1999; Ehrenfreund & Charnley 2000; Crovisier 2004; Markwick & Charnley 2004). As an alternative to the most common hypothesis that the polyynes form again by a series of low-temperature reactions in molecular clouds (Herbst 1998), it has also been proposed (Kroto *et al.* 1987; Kwok 2004) that the molecules produced in the circumstellar environment of carbon-rich stars are able to survive inside the carbon dust ejected into interstellar space. Furthermore, the carbon grains disrupted by shock waves in diffuse interstellar clouds release these protected molecules and produce additional polyynes by the vaporization of elemental carbon in vapour form (Duley & Williams 1984). In any case, the molecules formed in the circumstellar environment are the same as those incorporated in comets and later delivered to planets by bombardment. The idea that the molecules present in the solar nebula have been formed in the circumstellar environment is nowadays more than a simple hypothesis (Kwok 2004). In fact, the analysis of the interstellar grains with sophisticated techniques involving also the determination of the isotopic composition has given a further hint that the interstellar grains may come directly from circumstellar sources and are then incorporated into primitive bodies of the solar system such as comets and meteorites (Kwok 2004).

Recently, we have found that polyynes and cyanopolyynes are easily formed in the carbon arc between graphite electrodes and have proposed that the arc conditions mimic the conditions of temperature and chemical environment existing in the circumstellar medium (Cataldo 2003a; Cataldo 2004a–h; Cataldo 2005). Moreover, we have discovered that these molecules can be easily trapped in a solvent and can then be collected, separated and analysed.

Thus, the basic organic molecules that at a first glance appear highly unstable under laboratory conditions are instead abundant in certain astrophysical objects and are present in cometary bodies and in the atmosphere of planets (e.g. Jupiter) and satellites (e.g. Titan) of the Solar System. They are easily formed under certain unusual conditions and represent the first organic matter from which more complex organic, and may be biologically active, molecules are derived. For example, Miller (1998) has discussed the role of certain simple cyanopolyynes in pyrimidine base abiotic synthesis. Pyrimidines are essential constituents of DNA and RNA macromolecules.

In this paper, we report the formation of cyanopolyynes by the reaction of carbon vapour with ammonia in an electric arc, and review and discuss our earlier results of polyyne and cyanopolyyne formation in the carbon arc. We compare our results with those of Kroto *et al.* (1987) concerning polyyne formation with laser ablation experiments of graphite targets.

Finally, we show that the relative abundance of any polyyne homologous series produced in a carbon arc matches the relative abundance of the same homologous series as detected by radioastronomy in the circumstellar shell of carbon-rich and asymptotic giant branch (AGB) stars.

Experimental details

The experimental set-up was as previously reported for the synthesis of other polyynes (Cataldo 2005) or dicyano-polyynes when liquid nitrogen was used (Cataldo 2004f, g). Liquid ammonia was obtained by liquefaction of gaseous ammonia produced according to standard laboratory procedures as recommended by Vogel (1966), by dissolving sodium hydroxide in 33% ammonia and drying the gaseous ammonia developed on a Fresenius cylinder filled with a soda-lime bed.

The electronic absorption spectra were recorded on a Shimadzu UV160A spectrophotometer, while the analysis of the products was performed on a high-performance liquid chromatograph (HPLC) from Agilent Technologies model 1100 equipped with a diode-array detector and a C-8 column Zorbax-XDC. As a mobile phase a mixture of 80/20 vol/vol acetonitrile/water was used. The products were recognized on the basis of the electronic absorption spectra reported in the literature (Eastmond *et al.* 1972) and recently detected spectra for both monocyanopolyynes and dicyanopolyynes (Cataldo 2005).

Carbon arc in 26% aqueous ammonia

A three-necked round-bottomed flask of 100 ml was filled with 15 ml of ethanol and 40 ml of 26% aqueous ammonia solution. The graphite electrodes were submerged into the aqueous liquid phase and the electric arc was struck at 10 A by placing in contact the two carbon electrodes. The flask was suspended over a large Dewar flask half-filled with a mixture of solid CO_2 and acetone at $-78\ ^{\circ}C$.

The arcing products were collected in a layer of heptane (20 ml) floating the aqueous-alcoholic solution of ammonia. After a few minutes of arcing the heptane layer was rich of products and the electronic absorption spectrum of the solution showed a series of absorption bands (in nanometres) as follows: 276 (m), 283 (sh), 298 (m), 317 (m), 325 (sh), 335 (m), 352 (broad), 369 (broad). The absorption bands at wavelengths shorter than 276 nm could not be visualized without the dilution of the solution. The additional bands in the ultraviolet (after dilution with pure heptane) were (in nanometres): 220 (m), 226 (m), 240 (m), 253 (m), 262 (m).

The HPLC analysis on the C8 column using a mobile phase of 80/20 vol/vol acetonitrile/water revealed the formation of the polyyne series from C_6H_2 to $C_{14}H_2$. The polyyne series is accompanied by a couple of monocyanopolyynes from HC_7N to HC_9N. $HC_{11}N$ was detected in trace amounts.

Carbon arc in 33% aqueous ammonia solution

In the same flask as for the above, a carbon arc between graphite electrodes was also struck at 10 A into a 33% aqueous solution of ammonia (35 ml) externally cooled at

Table 1. *Reaction products between carbon vapour and simple molecules*

| Reactants | Products | | | |
	Laser ablation of graphite (Kroto *et al.* 1987)	Kratschmer–Huffmann arc type (Grosser & Hirsch 1993)	Submerged carbon arc	Reference
Hydrogen	C_6H_2 to $C_{22}H_2$	PAHs	From C_6H_2 to $C_{18}H_2$	Cataldo (2004a–f, 2005)
Water	C_8H_2 to $C_{20}H_2$	n.a.	From C_6H_2 to $C_{14}H_2$	Cataldo (2004a–f, 2005)
Nitrogen	C_8N_2 to $C_{22}N_2$	n.a.	From C_8N_2 to $C_{12}N_2$	Cataldo (2004a–f, 2005)
Acetonitrile	HC_7N to HC_9N	n.a.	From HC_7N to $HC_{15}N$ and from C_6H_2 to $C_{18}H_2$	Cataldo (2004a–f, 2005)
Ammonia	HC_7N to HC_9N	n.a.	From HC_7N to $HC_{13}N$ and from C_6H_2 to $C_{14}H_2$	This work
Aqueous ammonia	n.a.	n.a.	From HC_7N to HC_9N and from C_6H_2 to $C_{14}H_2$	This work
Cyanogen	n.a.	C_8N_2 and some higher homologues	n.a.	
Helium 100 torr	n.a.	Fullerenes	n.a.	

n.a. = not applicable or not tested.
PAHs = Polycyclic aromatic hydrocarbons.

0 °C with water/ice. A layer of heptane of 20 ml was placed over the ammonia solution to collect the arcing products. Practically no soot was produced. After arcing the heptane solution was nitrogen flushed to remove the ammonia and then heptane was analysed by the HPLC. The complete polyyne series was found together with a couple of monocyanopolyynes as reported above.

Carbon arc in liquid ammonia

A three-necked round-bottomed flask filled with 30 ml of liquid ammonia was kept in a large Dewar flask filled with solid CO_2 and acetone. The electric arc was struck at 10 A between the two graphite electrodes submerged into the liquid phase. The heat generated by the arc gradually vaporized the ammonia together with the arcing products. A stream of ammonia gas generated by the action of the arc on liquid ammonia was forced to bubble into a Drechsell flask filled with acetonitrile cooled at 0 °C. The stream of gaseous ammonia that bubbled in the solvent caused the release of the arcing products, which were then analysed by liquid chromatography. The excess of ammonia dissolved in acetonitrile was removed by prolonged bubbling of dry nitrogen at 0 °C before HPLC analysis. The electronic absorption spectrum of the solution in acetonitrile showed the following absorption bands (in nanometres): 200 (m), 205 (sh), 215 (m), 225 (m), 238 (m), 250 (m), 259 (m), 273 (m), 295 (m), 314 (m). Again, a series of hydrogen-terminated polyynes from C_6H_2 to $C_{14}H_2$ was detected together with a series of monocyanopolyynes from HC_7N to $HC_{13}N$.

The stability of polyynes and monocyanopolyynes in acetonitrile in the presence of ammonia

Acetonitrile (40 ml) was arced between graphite electrodes at 10 A. As already reported (Cataldo 2004a), the HPLC analysis reveals the presence of the complete polyyne series from C_6H_2 to $C_{18}H_2$ accompanied by the monocyanopolyyne series from HC_7N to $HC_{15}N$ (see Table 1). If two drops of

33 % aqueous ammonia are added with a Pasteur pipette to 20 ml of the acetonitrile solution, a rapid disappearance of the monocyanopolyynes can be observed. Essentially, only HC_7N and HC_9N survive in reduced amounts in comparison to their original concentration before the ammonia addition.

Results and discussion

Products formed by arcing graphite electrodes in liquid and aqueous ammonia

In Fig. 1 the HPLC chromatograms of the products formed by arcing liquid ammonia and trapped in acetonitrile are reported. Two chromatograms are shown in Fig. 1. They were recorded at two selected wavelengths of the HPLC diode-array detector (namely at (a) 225 nm and (b) 250 nm) in order to detect the full range of compounds formed from the arc absorbing at different wavelengths.

Using data from the literature (Eastmond *et al.* 1972) and our earlier results (Cataldo 2004a, 2005), it was easy to identify a series of main products formed in the arc. The series consists of monocyanopolyynes from HC_7N to $HC_{13}N$ and normal polyynes from C_6H_2 to $C_{14}H_2$. The spectra of these two series of compounds are shown in Figs 2 and 3, respectively, and they correspond to the spectra we have already obtained in previous works by arcing acetonitrile (Cataldo 2004a, 2005). It is remarkable that by arcing liquid ammonia only three monocyanopolyynes were produced with $HC_{13}N$ in very small amounts, while arcing in acetonitrile produces not only $HC_{13}N$ in appreciable amounts but also $HC_{15}N$.

When ammonia is arced in aqueous solution only two monocyanopolyynes are found, HC_7N and HC_9N. Their concentrations are much lower than the concentrations of normal polyyne series, which in this case are in the range between C_6H_2 and $C_{14}H_2$ (see Table 1).

With the purpose of better understanding the reason for the lower yield of monocyanopolyynes, and especially explaining the fact that shorter chains are obtained by arcing
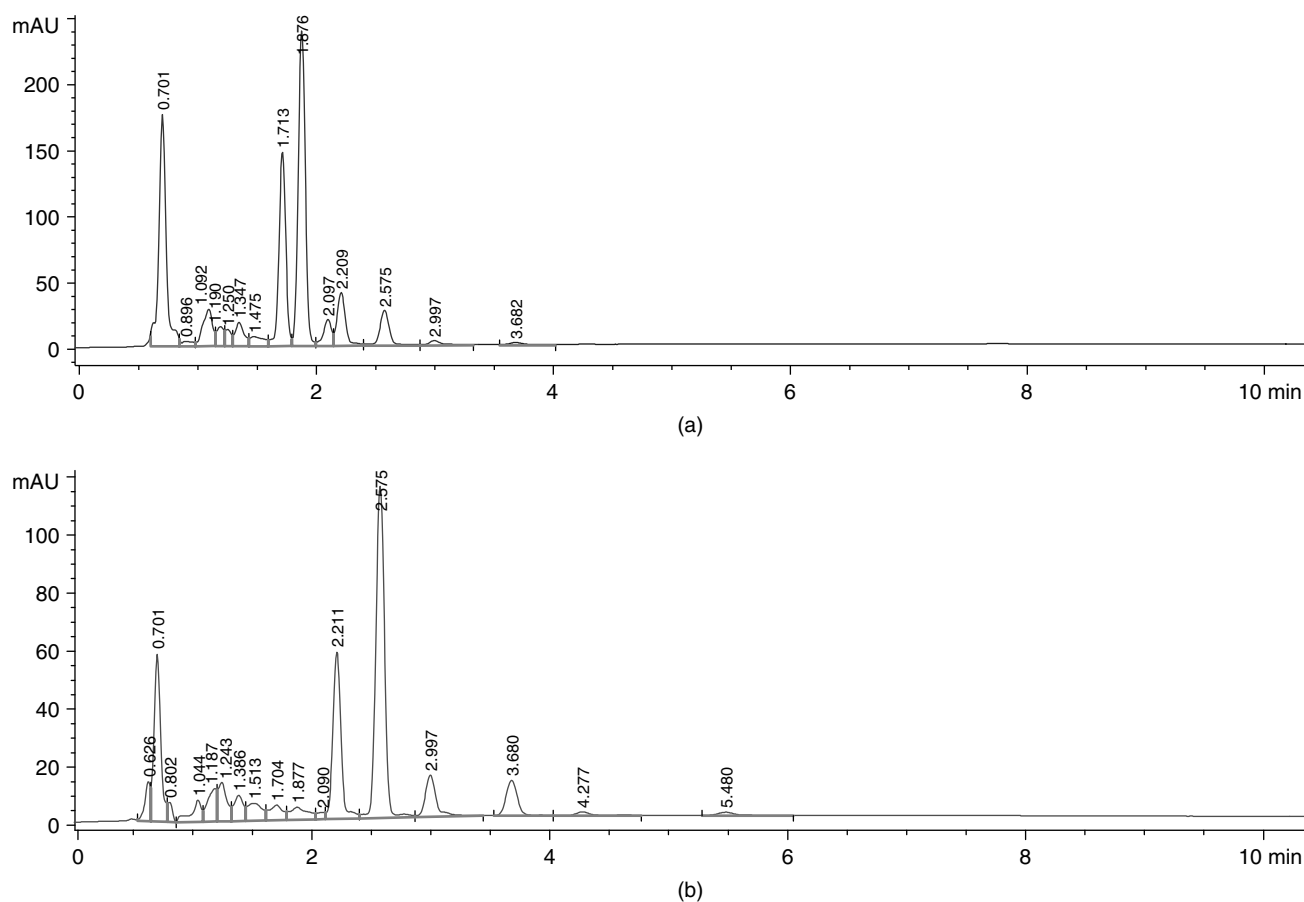
Fig. 1. HPLC chromatograms of the products produced by arcing graphite electrodes in liquid ammonia and collecting the products in acetonitrile. The chromatograms were recorded with the diode-array detector at two different wavelengths: (a) 225 nm; and (b) 250 nm. In (a) HC_7N and C_8H_2 at R_t (Retention time) equal to 1.713 and 1.876 min, respectively, can be easily distinguished. C_6H_2 is not easily distinguishable but elutes at 1.513 min and it is present. The two main peaks in (b) refer to HC_9N and $C_{10}H_2$ at R_t equal to 2.211 and 2.575 min, respectively. $HC_{11}N$ is detectable at R_t equal to 2.997 min followed by $C_{12}H_2$ at R_t equal to 3.680 min. The other two small peaks are assigned to $HC_{13}N$ and $C_{14}H_2$ at R_t equal to 4.277 and 5.480 min, respectively.

ammonia in comparison to the monocyanopolyyne yield and chain length produced by arcing acetonitrile, we have performed a simple experiment (see section 'The stability of polyynes and monocyanopolyynes in acetonitrile in the presence of ammonia') where aqueous ammonia was added to a monocyanopolyyne series prepared by arcing acetonitrile. The result of this addition was the relatively rapid disappearance of the polyynes from $HC_{15}N$ to $HC_{11}N$. Only HC_9N and HC_7N survived the ammonia addition but their concentration was dramatically reduced. Thus, aqueous ammonia reacts with monocyanopolyynes or causes their rearrangement; this explains very clearly why we have observed only HC_7N and HC_9N in our arcing experiments in aqueous and liquid ammonia (see Table 1). The details of the effects of aqueous ammonia on monocyanopolyynes will be reported in detail elsewhere. In contrast with the behaviour of monocyanopolyynes, we have found that the hydrogen-terminated polyynes are completely insensitive to the addition of aqueous ammonia to the acetonitrile solution, and in fact they form abundantly and without problems by arcing liquid and aqueous ammonia (see Table 1).

There are other products in the chromatograms that are formed during ammonia arcing that have not been identified owing to the lack of reference spectra and standard compounds. However, the other products formed by arcing ammonia represent only a minor fraction in comparison to the main products obtained and identified.

It is also remarkable that no polycyclic aromatic hydrocarbons (PAHs) were detected by arcing liquid and aqueous ammonia, whereas these products are always formed (as secondary products and in much lower concentration than the polyyne concentration) when a carbon arc is struck in hydrocarbon solvents and even in alcohols. Thus, it is confirmed that the PAHs in our system derive from the pyrolysis of the hydrocarbon solvent caused by the high temperatures of the electric arc and they are not formed directly from the polyynes. The absence of PAH formation was also observed in our earlier experiments involving the carbon arc in liquid water and in liquid nitrogen (Cataldo 2004f, g). The absence of PAH formation is also accompanied by the absence of soot formation.
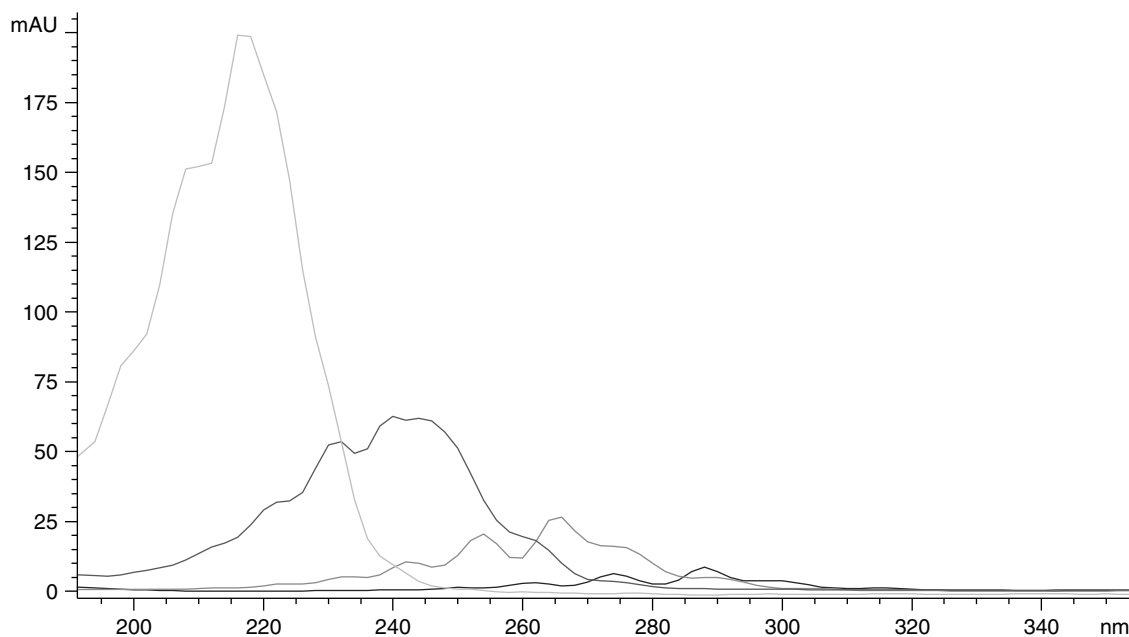
Fig. 2. Electronic absorption spectra of monocyanopolyynes as recorded by the diode-array detector. The first spectrum on the left is due to HC_7N followed by HC_9N, $HC_{11}N$ and $HC_{13}N$. It is clear that the concentration of the monocyanopolyynes decreases with increasing chain length.
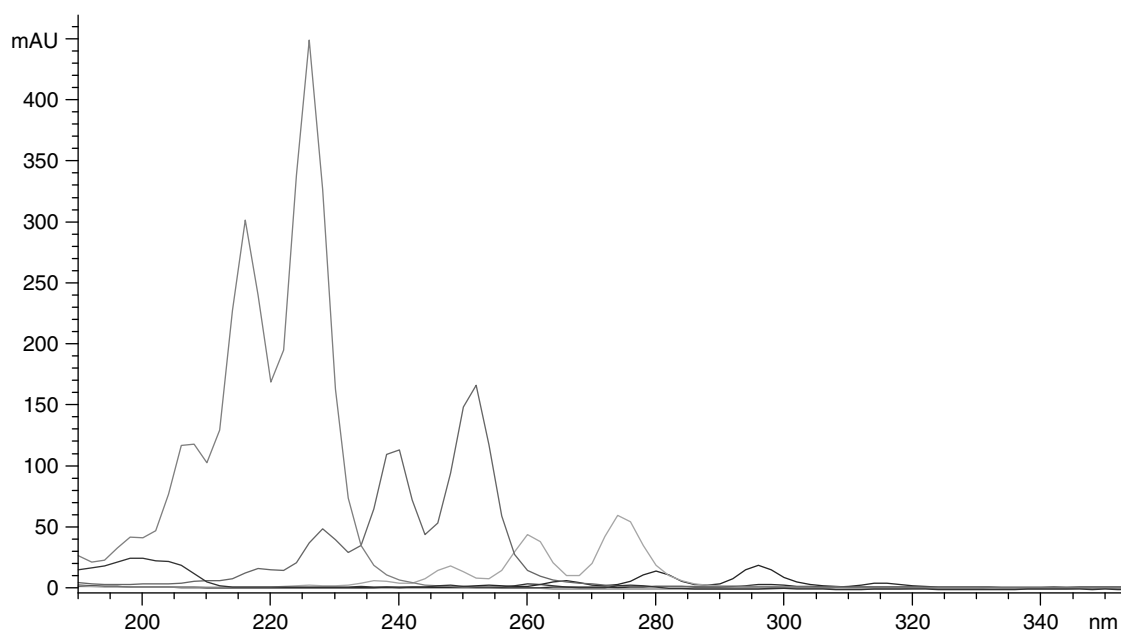

Fig. 3. Electronic absorption spectra of polyynes as recorded by the diode-array detector. The first spectrum in the left is due to C_6H_2 (weak) followed by the strongest spectrum due to C_8H_2, then $C_{10}H_2$, $C_{12}H_2$ and $C_{14}H_2$ follow in sequence. $C_{16}H_2$ is present in trace amounts. The concentration of the polyynes decreases with increasing chain length.

Parallelism between the products formed from the carbon arc and from laser ablation of graphite and other carbon sources

A couple of decades ago, Kroto and colleagues (1987) performed a series of very interesting experiments using the laser ablation of a graphite target into a helium entraining gas to feed a time-of-flight mass spectrometer with the carbon clusters generated (Heath *et al.* 1987). The breakthrough of the work of Kroto and colleagues (1987) was not only the demonstration that carbon clusters up to 30 carbon atoms where essentially made by linear carbon chains whereas the clusters having more that 40 carbon atoms were essentially constituted by fullerene cages, but it also involved the

demonstration that the carbon chains were extremely reactive with selected adventitious molecules that are present in interstellar and even circumstellar environments.
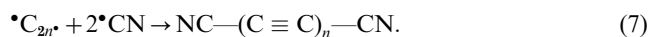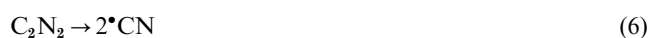
In fact, it was found that the addition of hydrogen to the carbon clusters generated very easily a series of hydrogen-terminated polyynes in the range C_6H_2 to $C_{22}H_2$. Also astrochemical important radicals such as $^\bullet C_6H$ to $^\bullet C_{10}H$ were detected (Heath *et al.* 1987; Kroto *et al.* 1987).

The addition of water also permitted the detection of the formation of hydrogen-terminated polyynes from C_8H_2 to $C_{20}H_2$, and it was suggested that the carbon radicals were able to abstract hydrogen from water:

$$^\bullet C_{2n}{}^\bullet + 2H_2O \rightarrow H—(C \equiv C)_n—H + H_2O_2. \tag{4}$$
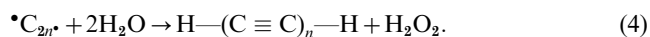
Really astonishing was the formation of monocyanopolyynes from HC_7N to HC_9N when the carbon vapour was reacted with acetonitrile or ammonia, and dicyanopolyynes from C_8N_2 to $C_{22}N_2$ when N_2 was added to the He entraining gas (see Table 1). These results demonstrated for the first time the easy formation of cyanopolyynes from carbon vapours and atomic nitrogen. The exclusive presence of nitrogen led to the formation of dicyanopolyynes; when nitrogen was present together with hydrogen, as in the case of ammonia, then monocyanopolyynes were obtained.

A further development in the study of cyanopolyyne formation on a laboratory scale derived from the work of Grosser and Hirsch (1993), when it was shown that dicyanopolyynes can be easily produced under Kratschmer–Huffmann conditions; these are the conditions that lead to fullerenes and carbon soot when He is used as a buffer gas for the carbon arc. By replacing helium with cyanogen, Grosser and Hirsch (1993) were able to show that the reaction products were essentially soot and a mixture of dicyanopolyynes (which were solvents extracted from the soot), demonstrating that reactions involving radical species and the high temperatures of a carbon arc (more than 4000 K) are able to lead to chemical species abundant in circumstellar and interstellar media but considered extremely exotic and unstable under terrestrial conditions. The reactions occurring in the experiment of Grosser and Hirsch may be represented schematically as follows:

$$\text{Graphite} \rightarrow {}^\bullet C_{2n}{}^\bullet \tag{5}$$

$$C_2N_2 \rightarrow 2{}^\bullet CN \tag{6}$$

$${}^\bullet C_{2n}{}^\bullet + 2{}^\bullet CN \rightarrow NC—(C \equiv C)_n—CN. \tag{7}$$
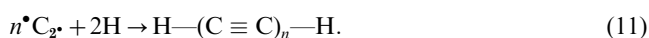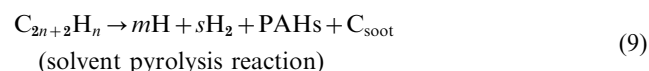
Recently, it was reported that polyynes in solution can also be produced by the laser ablation of graphite (but also fullerene and diamond particles) suspended in an hydrocarbon solvent (Tsuji *et al.* 2002).

The unifying concept in these three different experimental approaches is the behaviour of carbon vapour, which is able to form linear clusters to react with adventitious molecular or atomic species to form polyynes and cyanopolyynes.

The research in this field can be dated back to the 1950s and 1960s (Hintenberger *et al.* 1963), when the composition of the carbon vapour was explored both by mass spectrometric analysis and by theoretical calculations. The mass spectrometric analysis of the carbon vapour generated by a carbon arc in vacuum revealed a series of carbon clusters describable by the general formula C_n, which were essentially interpreted in terms of acetylenic or oligoyne chains, and eventually rings. Naturally, the experimental set-up used at that time did not permit the isolation of the carbon radicals, which were produced just in sufficient quantities to feed a mass spectrometer.

Thus, we had the idea to perform an experiment with the electric carbon arc submerged in a solvent in order to trap and eventually accumulate the species formed into a solvent. The idea proved to be successful (Cataldo 2003a). In detail, it was found that the polyynes were produced only when graphite electrodes were struck when submerged in a solvent. When the graphite electrodes were replaced with titanium electrodes no polyynes were obtained. Thus, elemental carbon was released from the electrodes during arcing. Instead, PAHs derived from the plasmalysis of the solvent were obtained (Cataldo 2004f, g, 2005). The plasma caused by the arc was able to vaporize the elemental carbon from the electrodes and this, in its turn, reacted invariably with hydrogen atoms necessarily derived from the plasmalysis of the hydrocarbon solvent. The reaction may be shown very schematically as follows:

$$\text{Graphite} \rightarrow C \tag{8}$$

$$C_{2n+2}H_n \rightarrow mH + sH_2 + PAHs + C_{soot} \tag{9}$$
$$\text{(solvent pyrolysis reaction)}$$

$$2C \rightarrow {}^\bullet C_2{}^\bullet \tag{10}$$

$$n{}^\bullet C_2{}^\bullet + 2H \rightarrow H—(C \equiv C)_n—H. \tag{11}$$

The temperature of the carbon arc is so high as to cause the pyrolysis, or better, the plasmalysis of the hydrocarbon into a mixture of PAHs and soot, generating abundant free atomic hydrogen. At 4000 K, the temperature of the arc, more than 60% of molecular hydrogen is dissociated into atomic hydrogen (MacKay 1973). Because of energetic reasons involving hydrogen recombination (Cataldo 2003b), the lifetime of free atomic hydrogen is extremely long under these conditions, up to 0.5 s. Therefore, hydrogen is available in atomic form to react with carbon radicals to generate the polyynes, although the work of Heath *et al.* (1987) has shown that the carbon radicals are able to access the hydrogen also from H_2 molecules.
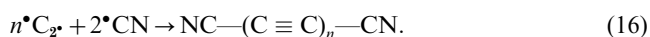
The formation of polyynes also occurs when the carbon arc is struck in alcohols. In this case, H is also supplied by the high-temperature decomposition of the solvent, but the polyyne yield is much lower than in hydrocarbon solvents and also the PAH and soot formation are much lower.

It appears that the lower availability of hydrogen affects negatively the yield of stable polyynes.

In any case, the polyynes produced by arcing graphite electrodes in a solvent usually reach a concentration that is two to three orders of magnitude higher than the concentration of PAHs. The mixture of polyynes is always dominated by the molecule C_8H_2, which can represent up to the 70% of the polyyne mixture. Also C_6H_2 was found but at concentrations comparable to that of $C_{10}H_2$, whereas the higher homologues $C_{12}H_2$, $C_{14}H_2$, $C_{16}H_2$ and even $C_{18}H_2$ were found in decreasing amounts so that the latter was only found in trace amounts. The reason why C_8H_2 is dominant in all submerged arcing experiments but also in laser ablation of graphite particles suspended in a solvent (Tsuji *et al.* 2002) remains obscure.

A striking correspondence between the results of Kroto *et al.* (1987) concerning the reactivity of carbon vapour with various molecules and our experiments with a carbon arc is reported in Table 1. We have obtained hydrogen-terminated polyynes by arcing graphite electrodes directly in water or in hydrocarbons, and Kroto has obtained the same species in his apparatus involving laser ablation of graphite targets.
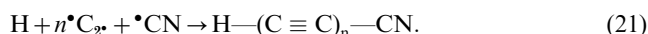
Dicyanopolyynes were produced by glowing the carbon arc in liquid nitrogen. In this case it appears obvious to think that the high temperature of the arc is able to split the molecular nitrogen into atomic nitrogen, which in its turn reacts promptly with the carbon vapour. This can be shown schematically as follows:

$$N_2 \rightarrow 2N \tag{12}$$

$$\text{Graphite} \rightarrow C \tag{13}$$

$$C + N \rightarrow {}^\bullet CN \tag{14}$$

$$2C \rightarrow {}^\bullet C_2{}^\bullet \tag{15}$$

$$n\,{}^\bullet C_2{}^\bullet + 2\,{}^\bullet CN \rightarrow NC—(C \equiv C)_n—CN. \tag{16}$$

Since no hydrogen is available all the polyynes chains are nitrogen-terminated. The formation of atomic nitrogen from molecular nitrogen in an electric arc or discharge is a well-known phenomenon (Jones 1973). As for atomic hydrogen, the lifetime of atomic nitrogen in its ground state is relatively long and sufficient to permit the reaction with carbon vapour. As outlined in Table 1, analogous results were obtained by Kroto *et al.* (1987) in the laser ablation experiment. It should be noticed that in general longer carbon chains either hydrogen- or nitrogen-terminated were detected by Kroto *et al.* (1987) when compared to our results with the submerged arc. This may be simply due to the higher sensitivity of the mass spectrometric analysis in comparison to the HPLC analysis.
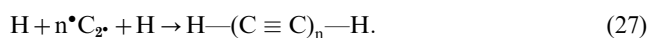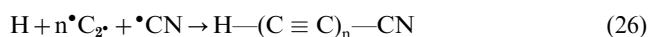
Again in line with Kroto results from graphite laser ablation, we have also obtained monocyanopolyynes by

arcing graphite electrodes in CH_3CN (Table 1). In our case both monocyanopolyynes and hydrogen-terminated polyynes were obtained. Under these conditions the ${}^\bullet CN$ radical originates from the scission of the acetonitrile molecule, while hydrogen may be derived from the plasmalysis of the methyl radical or from adventitious water:

$$CH_3\text{-}CN \rightarrow {}^\bullet CH_3 + {}^\bullet CN \tag{17}$$

$$CH_3 \rightarrow CH + 2H \tag{18}$$

$$\text{Graphite} \rightarrow C \tag{19}$$

$$2C \rightarrow {}^\bullet C_2{}^\bullet \tag{20}$$

$$H + n\,{}^\bullet C_2{}^\bullet + {}^\bullet CN \rightarrow H—(C \equiv C)_n—CN. \tag{21}$$

Another way to produce monocyanopolyynes according to Kroto *et al.* (1987) is the reaction of carbon vapour with ammonia. In the present paper we have demonstrated again the analogy of products between laser ablation and the submerged electric arc. In fact, monocyanopolyynes were produced by arcing liquid ammonia with carbon and even by arcing aqueous ammonia, although in the latter case the monocyanopolyynes were present in very limited amounts and the main products were the normal hydrogen terminated polyynes (see Table 1).

Ammonia is easily cracked into its elements at the temperature of the carbon arc (Jones 1973) and the formation of each nitrogen atom is accompanied by the formation of three hydrogen atoms. Therefore, the carbon vapour released by the graphite electrodes is in a mixed environment where hydrogen is prevailing over nitrogen:

$$NH_3 \rightarrow N + 3H \tag{22}$$

$$\text{Graphite} \rightarrow C \tag{23}$$

$$C + N \rightarrow {}^\bullet CN \tag{24}$$

$$2C \rightarrow {}^\bullet C_2{}^\bullet \tag{25}$$

$$H + n\,{}^\bullet C_2{}^\bullet + {}^\bullet CN \rightarrow H—(C \equiv C)_n—CN \tag{26}$$

$$H + n\,{}^\bullet C_2{}^\bullet + H \rightarrow H—(C \equiv C)_n—H. \tag{27}$$

Therefore, only monocyanopolyynes are formed together with the hydrogen-terminated polyynes, which seem to be quite ubiquitous since they are formed so easily in any arcing conditions.

Relative concentration of the polyynes formed in the carbon arc: comparison with radioastronomy data pertaining to AGB stars and similar astrophysical objects

Table 2 shows the relative molar abundance of the polyynes, the monocyanopolyynes and the dicyanopolyynes

Table 2. *The relative abundance of polyynes from a carbon arc. A comparison with the abundance in the circumstellar medium*

| Polyynes species | Polyynes molar ratio | | | | | In circumstellar environment (Cernicharo 2004; Cernicharo et al. 2004) |
	Arc in hexane (Cataldo 2004a–f)	Arc in acetonitrile (Cataldo 2004a–f)	Arc in nitrogen (Cataldo 2004g, h)	Arc in vacuum (Hintenberger et al. 1963)	Carbon clusters	
				5.0–3.7	C_4/C_6	4–5
C_6H_2/C_8H_2		2.2		4.2–2.1	C_6/C_8	4–5
$C_8H_2/C_{10}H_2$	4.1	3.8		3.9–1.0	C_8/C_{10}	4–5
$C_{10}H_2/C_{12}H_2$	5.1	3.3		5.0	C_{10}/C_{12}	4–5
$C_{12}H_2/C_{14}H_2$	4.5	3.1		3.3–1.5	C_{12}/C_{14}	4–5
$C_{14}H_2/C_{16}H_2$	5.1	3.0		5.0–2.5	C_{14}/C_{16}	4–5
HC_7N/HC_9N		3.3				4–5
$HC_9N/HC_{11}N$		3.0				4–5
$HC_{11}N/HC_{13}N$		2.8				4–5
$HC_{13}N/HC_{15}N$		2.9				4–5
C_6N_2/C_8N_2			2.7			
$C_8N_2/C_{10}N_2$			4.9			

produced in the submerged electric arc in different liquid media. A gradual but regular decrease in the abundance of the molecular species as a function of the chain length can be observed in all cases. The calculations of the relative concentration of the polyynes and cyanopolyynes produced in the arc were made by using the absorbance from the electronic absorption spectra of the polyynes and cyanopolyynes separated by HPLC and the molar extinction coefficient reported in the literature (Eastmond et al. 1972).

More precisely, in the case of hydrogen-terminated polyynes the increase of the chain length of a C_2 unit drops the abundance by a factor of between three and five depending on whether the polyynes are produced in acetonitrile or in hexane, respectively. This trend follows the trend of the abundance of the carbon clusters produced by arcing graphite electrodes in vacuum (Hintenberger et al. 1963). Thus, there is a clear correspondence between the composition of the carbon vapour in vacuum and the polyynes formed in a solvent. However, the most striking aspect regards the fact that in space, for instance in the molecular shell around IRC +10216 and in the dark cloud TMC1, the hydrogen-terminated polyynes with even carbon atoms follow exactly the same trend that we have measured in the carbon arc in Table 2 with $C_nH/C_{n+2}H = 4-5$ (Cernicharo 2004; Cernicharo et al. 2004; Pardo et al. 2005).

The same trend is applicable for monocyanopolyynes where the ratio $HC_{2n+1}N/HC_{2n+3}N$ is between three and five. If we compare these values with those in Table 2, we will find that all the monocyanopolyyne series produced with the carbon arc decrease regularly by a factor of three as the chain growths by a C_2 unit and by a factor between three and five in the case of the dicyanopolyynes.

This astonishing correspondence between the astrophysical data and the laboratory data may be a simple coincidence but may also stimulate the idea that the synthesis of polyynes and cyanopolyynes with the carbon arc represents a formidable laboratory simulation of the processes occurring in the surroundings of carbon-rich stars.

Conclusions

Arcing graphite electrodes in liquid ammonia produces a series of monocyanopolyynes. Since ammonia is cracked into the elements, a lot of atomic hydrogen is available in the system so that together with the monocyanopolyyne series a complete series of hydrogen-terminated polyynes is also obtained. The mechanism of formation necessarily involves the reaction of carbon vapour released from the graphite electrodes with the atomic species available, i.e. nitrogen and hydrogen.

A parallelism has been outlined between the polyyne chains and their end-groups formed in the submerged carbon arc and the same molecular species formed with the laser ablation technique in the presence of certain simple interstellar or circumstellar gases such as hydrogen, nitrogen, water ammonia and acetonitrile (see Table 1). The products are the same although the mechanism of formation may be different in some specific cases, since in the case of laser ablation of graphite is has been proposed that the carbon chains are able to abstract hydrogen radicals for instance from the substrate (e.g. water), while most probably in the submerged carbon arc the radicals are produced by the pyrolysis of the solvent substrate.

Concerning the length of the carbon chains obtained, in general longer chains were detected with the laser ablation technique than with the submerged electric arc. This may be due to the different sensitivity of the analytical technique used.

The distribution of polyyne products found in the submerged electric arc was compared with the relative abundance of these species found in certain astrophysical objects and with the relative abundance of the linear carbon clusters produced by the carbon arc in vacuum. A surprisingly good

correspondence was found in all cases. Both on the laboratory scale and in astrophysical objects rich in polyynes and cyanopolyynes, a decrease in abundance was found to follow a factor between three and five by increasing the chain length by a C_2 unit.

Acknowledgements

References

Bell, M.B., Feldman P.A., Watson, J.K.G., McCarthy, M.C., Travers, M.J., Gottlieb, C.A. & Thaddeus, P. (1999). *Astrophys. J.* **518**, 740–747.

Cataldo, F. (2003). *Carbon* **41**, 2671–2674.

Cataldo, F. (2003b). *Fullerenes, Nanotubes Carbon Nanostruct.* **11**, 317–331.

Cataldo, F. (2004a). *Carbon* **42**, 129–142.

Cataldo, F. (2004b). *Tetrahedron Lett.* **45**, 141–144.

Cataldo, F. (2004c). *Fullerenes Nanotubes Carbon Nanostruct.* **12**, 603–617.

Cataldo, F. (2004d). *Fullerenes Nanotubes Carbon Nanostruct.* **12**, 619–631.

Cataldo, F. (2004e). *Fullerenes Nanotubes Carbon Nanostruct.* **12**, 633–646.

Cataldo, F. (2004f). *Tetrahedron* **60**, 4265–4274.

Cataldo, F. (2004g). *Polyhedron* **23**, 1889–1896.

Cataldo, F. (2004h). *Int. J. Astrobiol.* **3**, 237–246.

Cataldo, F. (ed.) (2005). *Polyynes: Synthesis, Properties and Applications.* CRC Press.

Cernicharo, J. (2004). *Astrophys. J.* **608**, L41–L44.

Cernicharo, J., Guelin, M. & Pardo, J.R. (2004). *Astrophys. J.* **615**, L145–L148.

Cherchneff, I. & Glassgold, A.E. (1993). *Astrophys. J.* **419**, L41–L44.

Cherchneff, I., Glassgold, A.E. & Mamon, G.A. (1993). *Astrophys. J.* **410**, L188–L201.

Crovisier, J. (2004). The molecular complexity of comets. In *Astrobiology: Future Perspectives*, ed. Ehrenfreund, P. and the ISSI Team, ch. 8. Springer/Kluwer.

Duley, W.W. & Williams, D.A. (1984). *Mon. Not. R. Astron. Soc.* **211**, 97–103.

Eastmond, R., Johnson. T.R. & Walton, D.R.M. (1972). *Tetrahedron* **28**, 4601–4616.

Ehrenfreund, P. & Charnley, S.B. (2000). *Annual Rev. Astron, Astrophys* **38**, 427–483.

Formenkova, M.N., Chang, S. & Mukhin, L.M. (1994). *Geochim. Cosmochim. Acta* **58**, 4503–4512.

Formenkova, M.N. (1999). *Space Sci. Rev.* **90**, 109–114.

Grosser, T. & Hirsch, A. (1993). *Angew. Chem. Int. Ed. Engl.* **32**, 1340–1343.

Heath, J.R., Zhang, Q., O'Brien, S.C., Curl, R.F., Kroto, H.W. & Smalley, R.E. (1987). *J. Amer. Chem. Soc.* **109**, 359–363.

Helling, C., Jorgensen, U.G., Plez, B. & Johnson, H.R. (1996). *Astron. Astrophys.* **315**, 194–203.

Herbst, E. (1998). *Adv. Gas-Phase Ion Chem.* **3**, 1–47.

Hintenberger, Von, H., Franzen, J. & Schuy, K.D. (1963). *Z. Naturf.* a **18**, 1236–1240.

Jones, K. (1973). Nitrogen. In *Comprehensive Inorganic Chemistry*, eds Bailar, J.C., Emeleus, H.J., Nyholm, R. & Trotman-Dickenson, A.F., ch. 19. Pergamon Press, Oxford.

Kroto, H.W., Heat, J.R., O'Brien, S.C., Curl, R.F. & Smalley, R.E. (1987). *Astrophys. J.* **314**, 352–355.

Kwok, S. (2004). *Nature* **430**, 985–991.

Mackay, K.M. (1973). The element hydrogen. In *Comprehensive Inorganic Chemistry*, eds Bailar, J.C., Emeleus, H.J., Nyholm, R. & Trotman-Dickenson, A.F., ch. 1. Pergamon Press, Oxford.

Marwick, A.J. & Charnley, S.B. (2004). Chemistry of protoplanetary disks. In *Astrobiology: Future Perspectives*, eds Ehrenfreund, P. & the ISSI Team, ch. 3. Springer/Kluwer.

Millar, T.J. (2004). Organic molecules in the interstellar medium. In *Astrobiology: Future Perspectives*, eds Ehrenfreund, P. & the ISSI Team, ch. 2. Springer/Kluwer.

Miller, S.L. (1998). The endogenous synthesis of organic compounds. *The Molecular Origin of Life. Assembling Pieces of the Puzzle*, ed. Brack, A. ch. 3. Cambridge University Press.

Pardo, J.R., Cernicharo, J. & Goicoechea, J.R. (2005). *Astrophys. J.* **628**, 275–282.

Tsuji, M., Tsuji, T., Kuboyama, S., Yoon, S.H., Korai, Y., Tsujimoto, T., Kubo, K., Mori, A. & Mochida, I. (2002). *Chem. Phys. Lett.* **355**, 101–108.

Vogel, A.I. (1966). *Practical Organic Chemistry*. Longmans and Green Co. Ltd.