POLYYNES and CYANOPOLYYNES: Their synthesis with the CARBON ARC gives the same abundances occurring in CARBON-RICH STARS

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Complex Molecules in Space: Physics and Chemistry

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SUMMARY

- Polyynes & Carbon Arc/Vapour
- Submerged carbon arc
- Hydrogen-terminated polyynes
- Monocyanopolyynes
- Dicyanopolyynes
- Parallelism laser ablation & carbon arc
- Polyynes & cyanopolyynes in AGB/carbon-rich stars
- Relative abundances in AGB
- Relative abundances in carbon arc
- Conclusions

RESEARCH ON POLYYNES

- 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 spectrometry of the carbon clusters generated (Heat et al. 1987).

- A further development on the study of cyanopolyyne formation on 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, the conditions which lead to fullerenes and carbon soot when He is used as buffer gas of 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

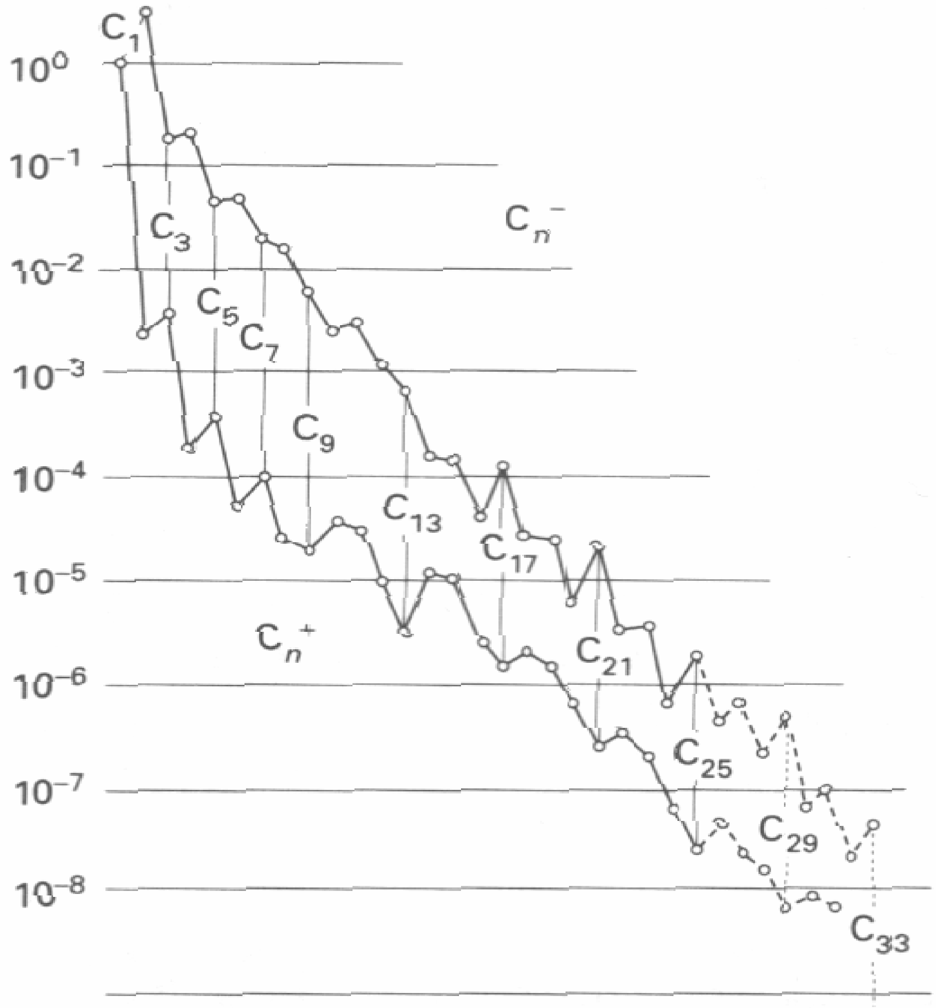
- Recently, it was reported that polyynes in solution can also be produced by the laser ablation of graphite (but also fullerene and diamond particles) suspended in an hydrocarbon solvent (**Tsuji et al**, 2002).

- We have shown that polyynes and cyanopolyynes are easily formed by arcing graphite in opportune liquid media (**Cataldo**, 2003).

THE KEY POINT: THE ROLE OF CARBON VAPOUR

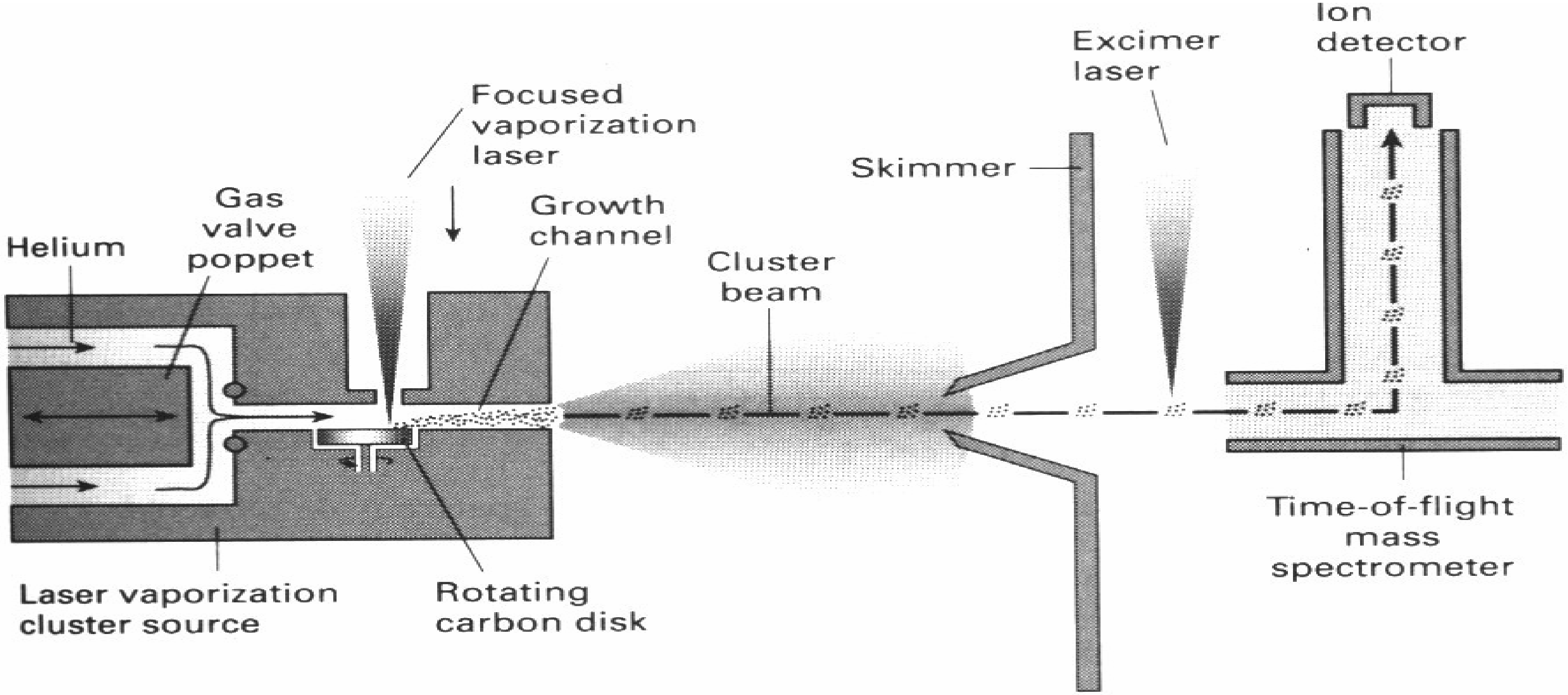
The unifying concept in these four different experimental approaches is the behavior of carbon vapor, which is able to form linear clusters, react with adventitious molecular or atomic species to form polyynes and cyanopolyynes.

POLYYNES DETECTION BY MASS SPECTROMETRY FROM ELECTRIC ARC IN VACUUM: 1963



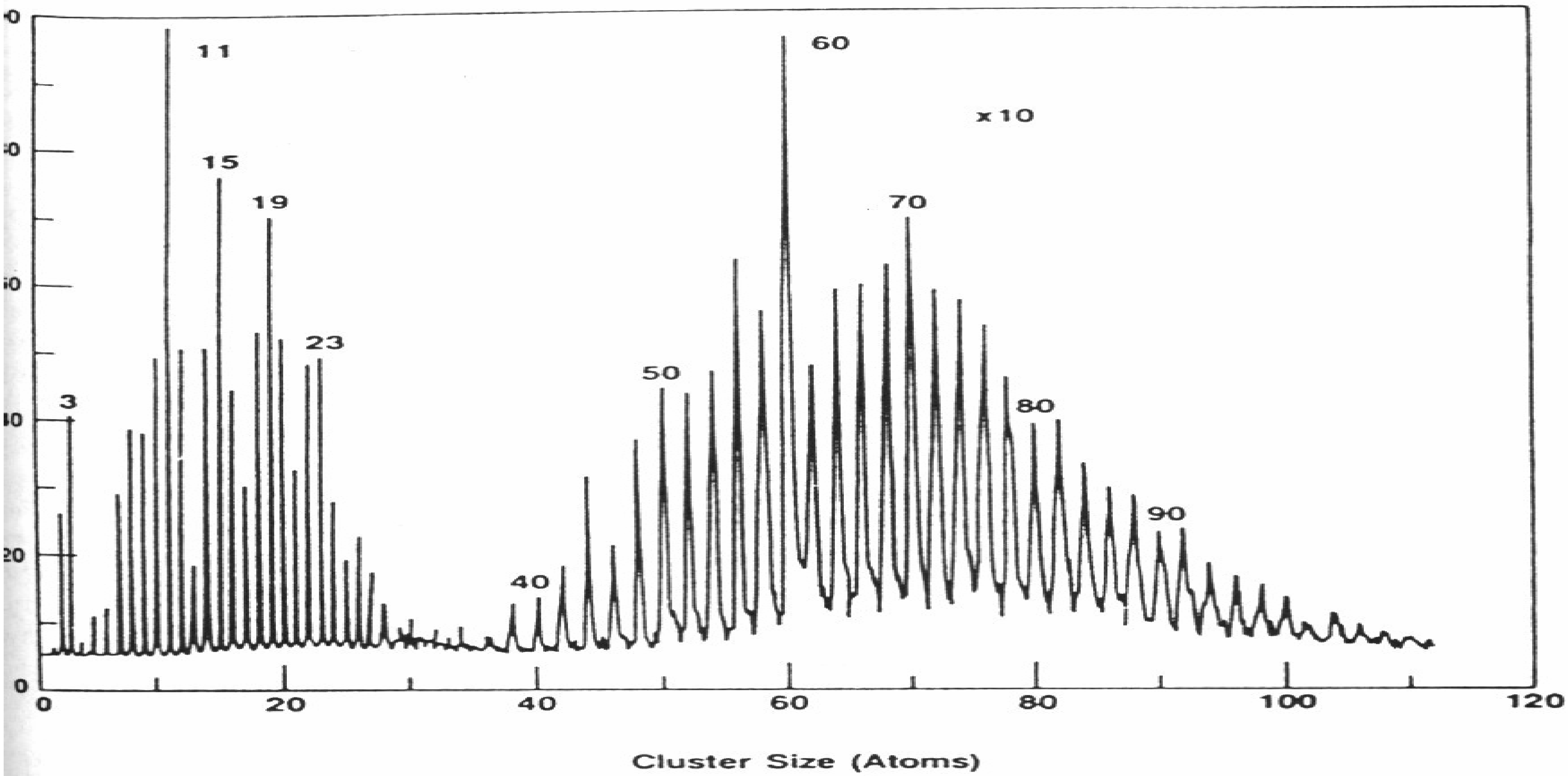
Distributions of positive and negative molecular ions formed in an arc discharge between two graphite electrodes. Adapted, with permission, from Hintenberger, H. von, Franzen, J., and Schuy, K. D. (1963). *Zeitschrift für Naturforschung A*, **18**, 1236.

Laser ablation of Graphite: 1985



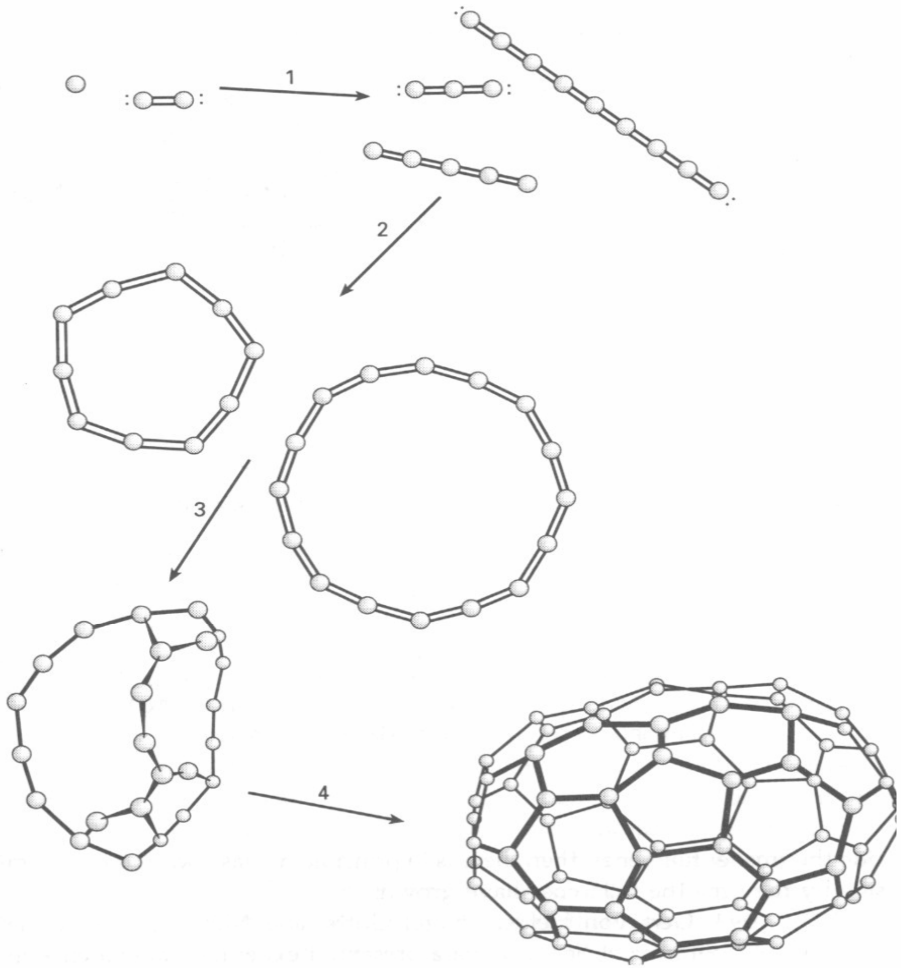
A schematic diagram of AP2. Pulses from the Nd:YAG laser are focused onto a rotating target. The laser is timed to fire just as a valve is opened, flooding the chamber with high-pressure helium gas. The plasma created by the laser is carried 'downstream', where the ions and electrons recombine and the atoms begin to form clusters before being expanded through a small nozzle to supersonic velocities. Further clustering occurs as the gas expands and cools. The middle of the expanding cone of gas is skimmed off and ionized using light from the excimer laser. The ions are deflected and accelerated down a 1.5-metre tube, where they spread out in order of mass with the lightest clusters reaching the ion detector first. By calibrating the 'time-of-flight' of the clusters (typically tens of microseconds), it is possible to deduce their relative masses and hence the cluster sizes (number of atoms per cluster). Adapted from 'Fullerenes' by Robert F. Curl and Richard E. Smalley. Copyright © 1991 by Scientific American Inc. All rights reserved.

Polyynes and Fullerenes simultaneously

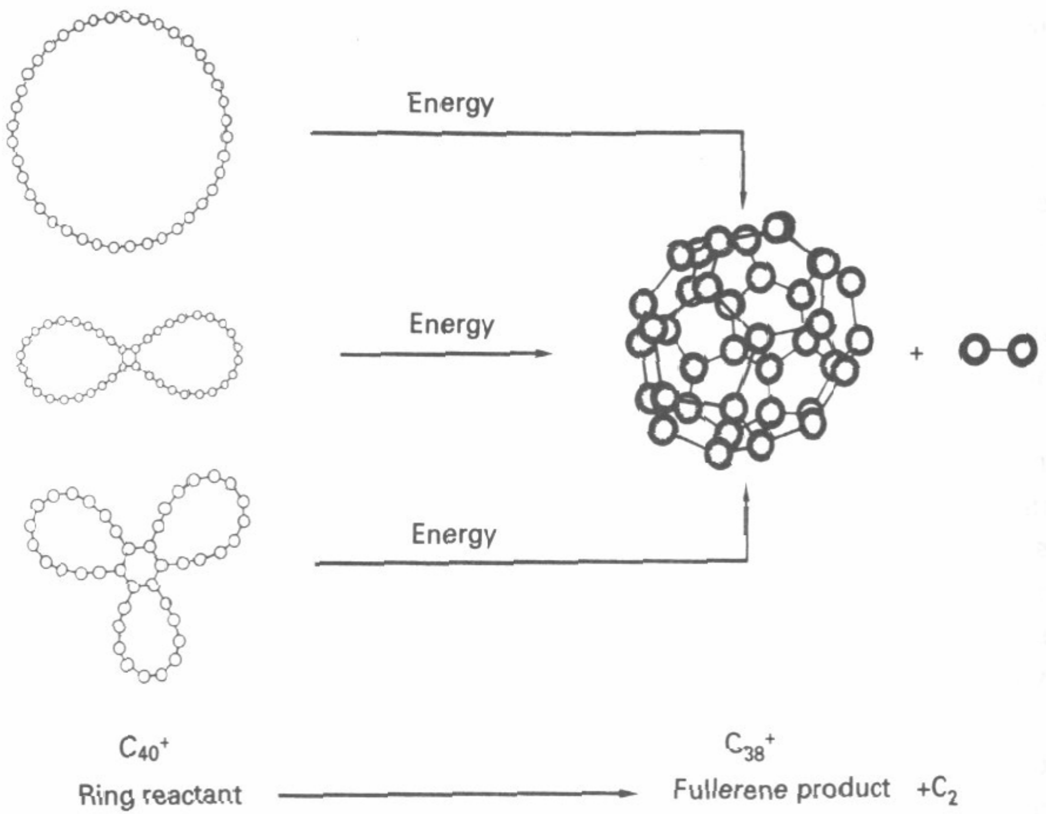


The cluster distribution reported by Rohlfing, Cox, and Kaldor. In this spectrum, the size of the positive ion signal is related to the number of ions detected (note the × 10 magnification for ions larger than C_{30}^{+}). The smaller clusters show a distribution not so dissimilar from that seen by von Hintenberger, Franzen, and Schuy in 1963. In contrast, the larger clusters show a distinctly different distribution, with no signals at all from clusters with an odd number of atoms. Adapted, with permission, from Rohlfing, E. A., Cox, D. M., and Kaldor, A. (1984). *Journal of Chemical Physics*. **81**, 3322.

THE MECHANISM OF FULLERENE FORMATION INVOLVES POLYYNES CYCLIZATION AND CROSSLINKING: 1992-1993

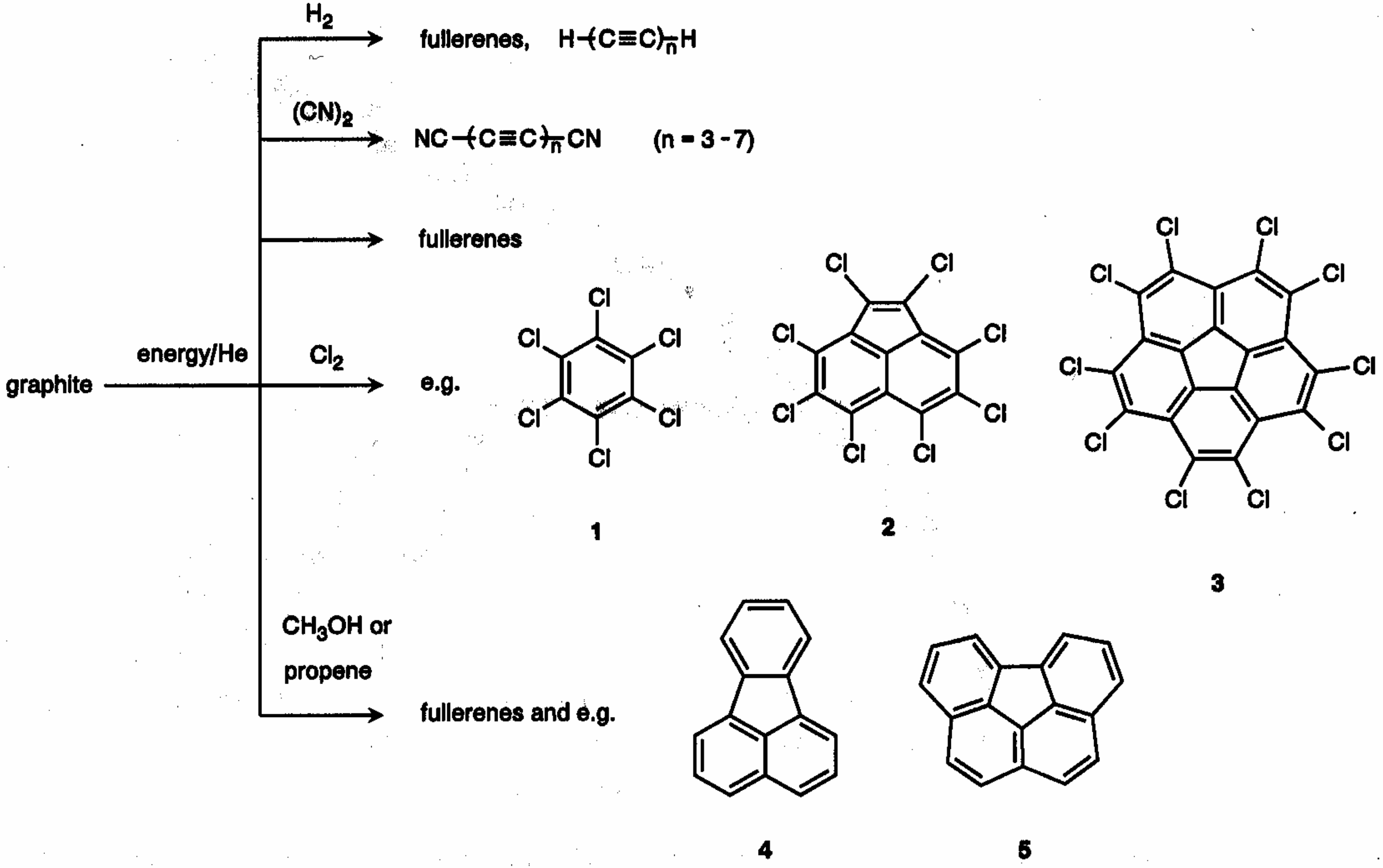


Heath's alternative mechanism involves the transition from linear carbon chains (C_n, where n is less than 10) to monocyclic rings (C_n, n between 9 and 21). Fullerenes are then formed by the further growth of these rings through unstable intermediates, which rearrange to give closed-cage structures. Adapted, with permission from Heath, James R. (1992). *Fullerenes*. (Hammond, George S. and Kuck, Valerie J. eds.). American Chemical Society, Washington D.C. Copyright (1992) American Chemical Society.

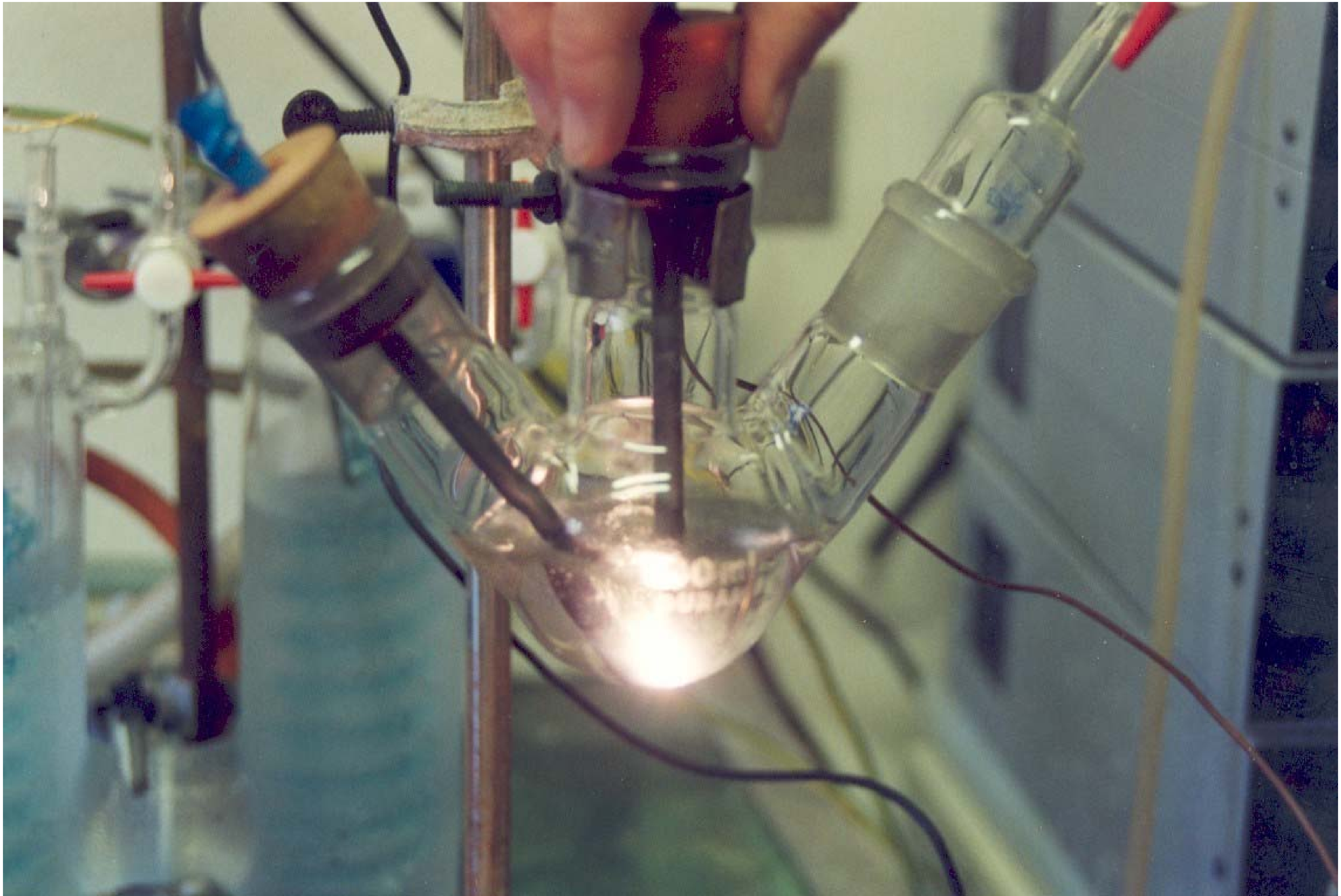


The mechanism proposed by von Helden, Gotts, and Bowers begins with linear chains which transform to monocyclic, bicyclic, and tricyclic planar rings. Through the annealing process, these rings then collapse into closed cages with the ejection of C_2 radicals or C atoms and C_3 radicals. This diagram shows the collapse of three different C_{40}^+ rings into a C_{38}^+ fullerene ion plus a C_2 radical. Adapted, with permission, from von Helden, Gert, Gotts, Nigel G., and Bowers, Michael T. (1993). *Nature*, **363**, 60. Copyright (1993) Macmillan Magazines Limited.

The intermediate species to fullerenes are polyynes

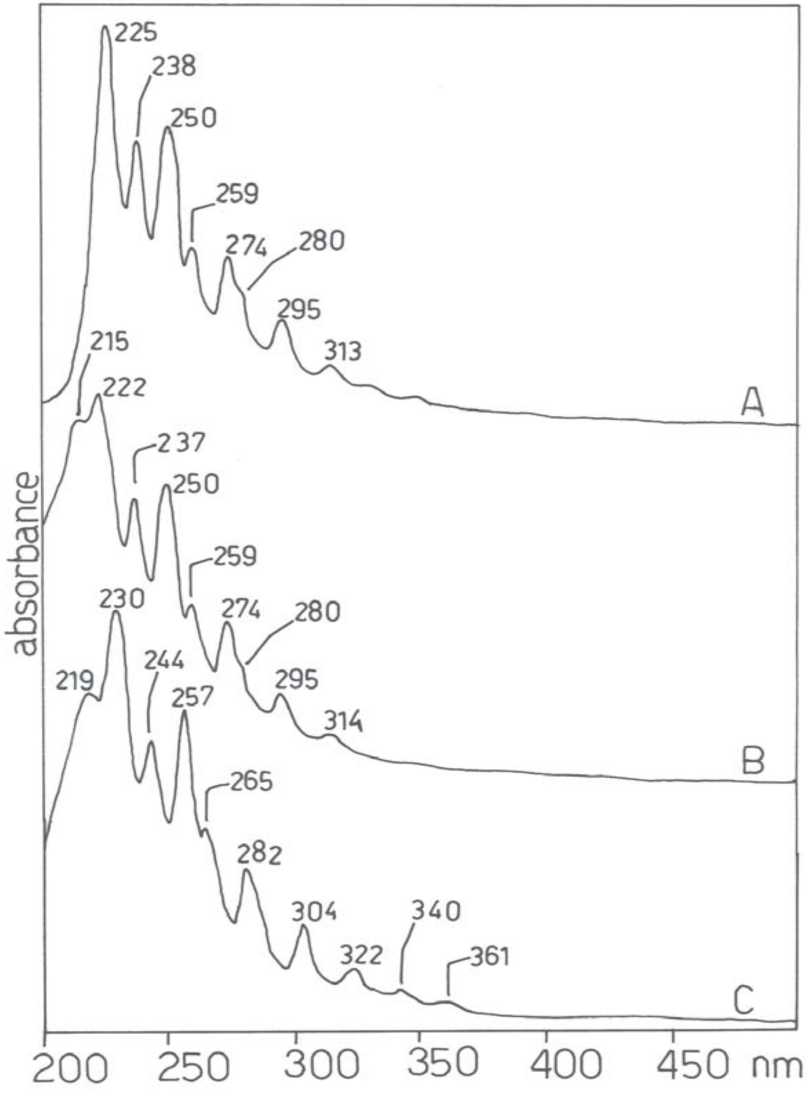


SUBMERGED ELECTRIC ARC. CATALDO’S LAB, JULY 2003



Polyynes spectra were recorded in 1997-1998 in our lab. during the attempted synthesis of carbyne and carbynoid structures

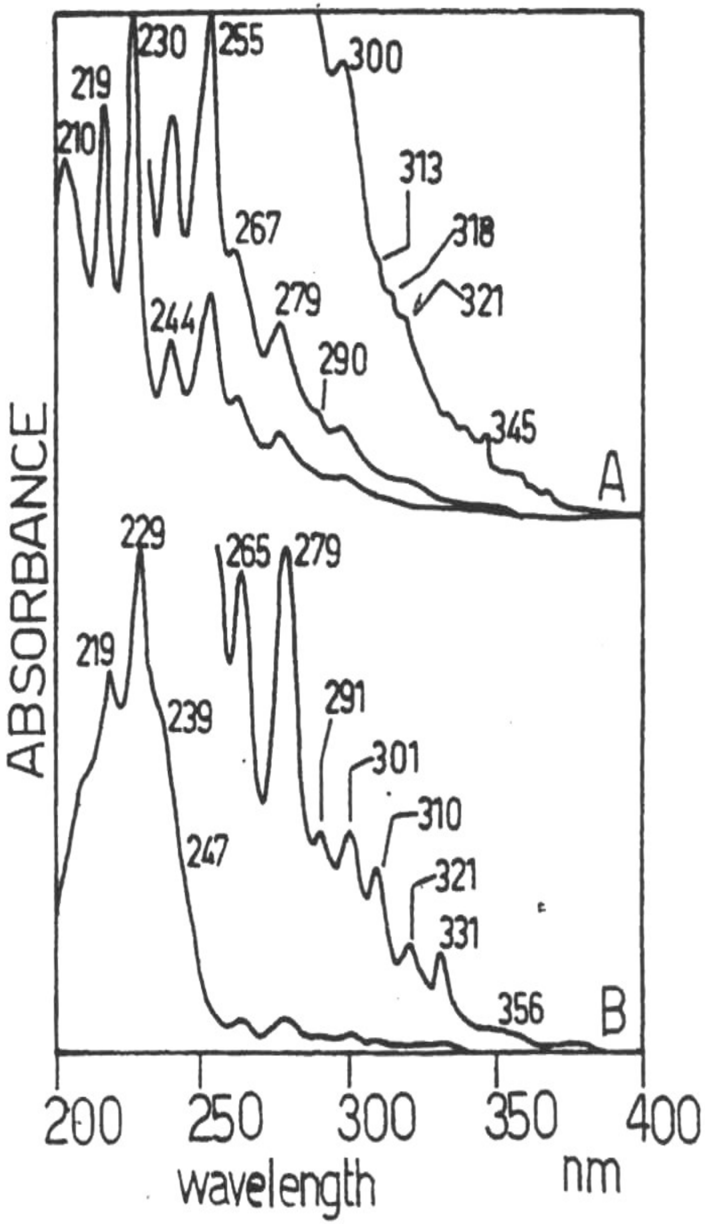
It was easy for us to recognize the polyynes as products of the submerged electric arc based simply on the electronic spectra.



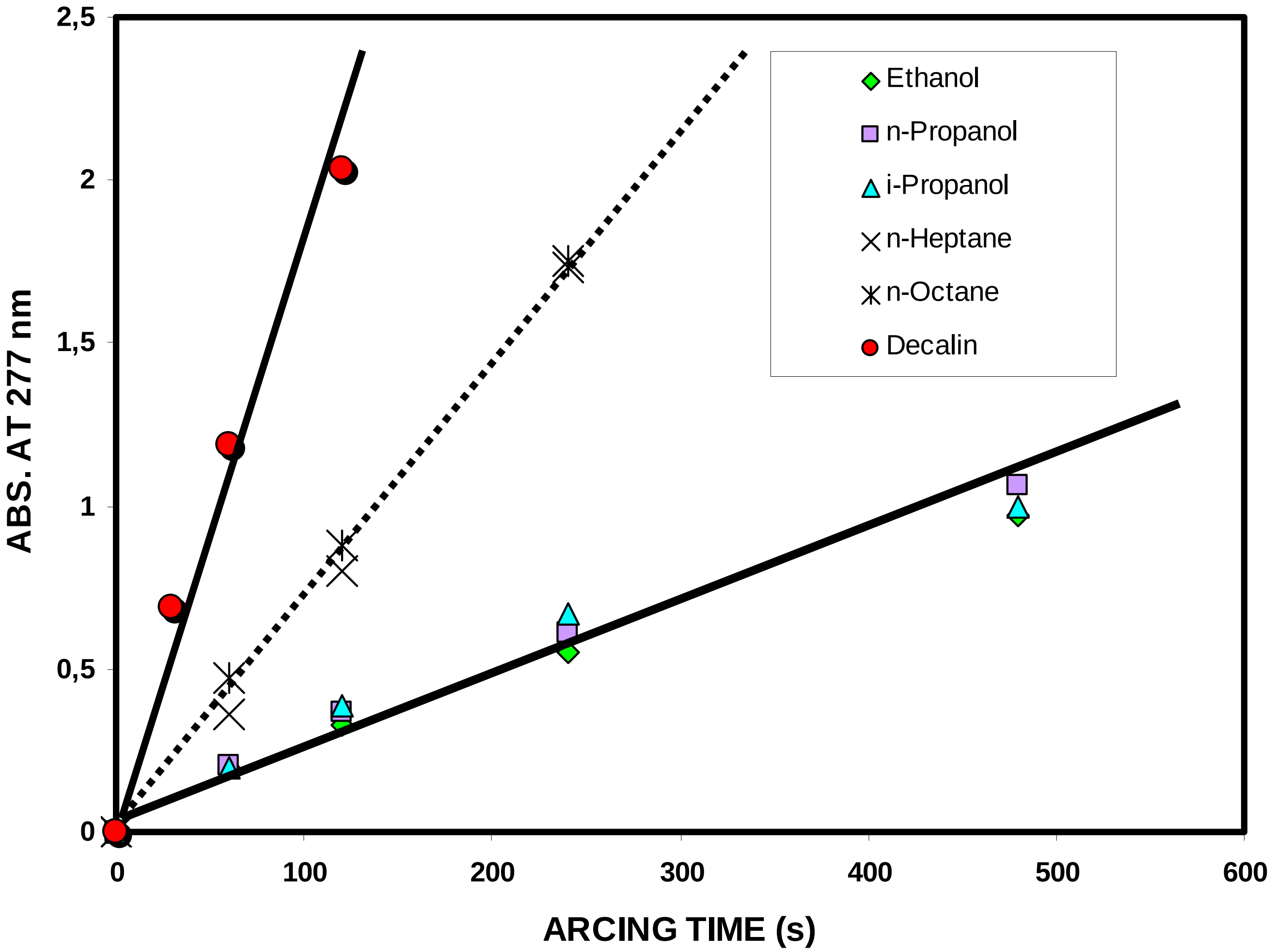
Electronic absorption spectra of polyynes generated by submerged electric arc between graphite electrodes in CH_3CN (curves A and B) and decalin (curve C) as solvents.

FIGURE 1

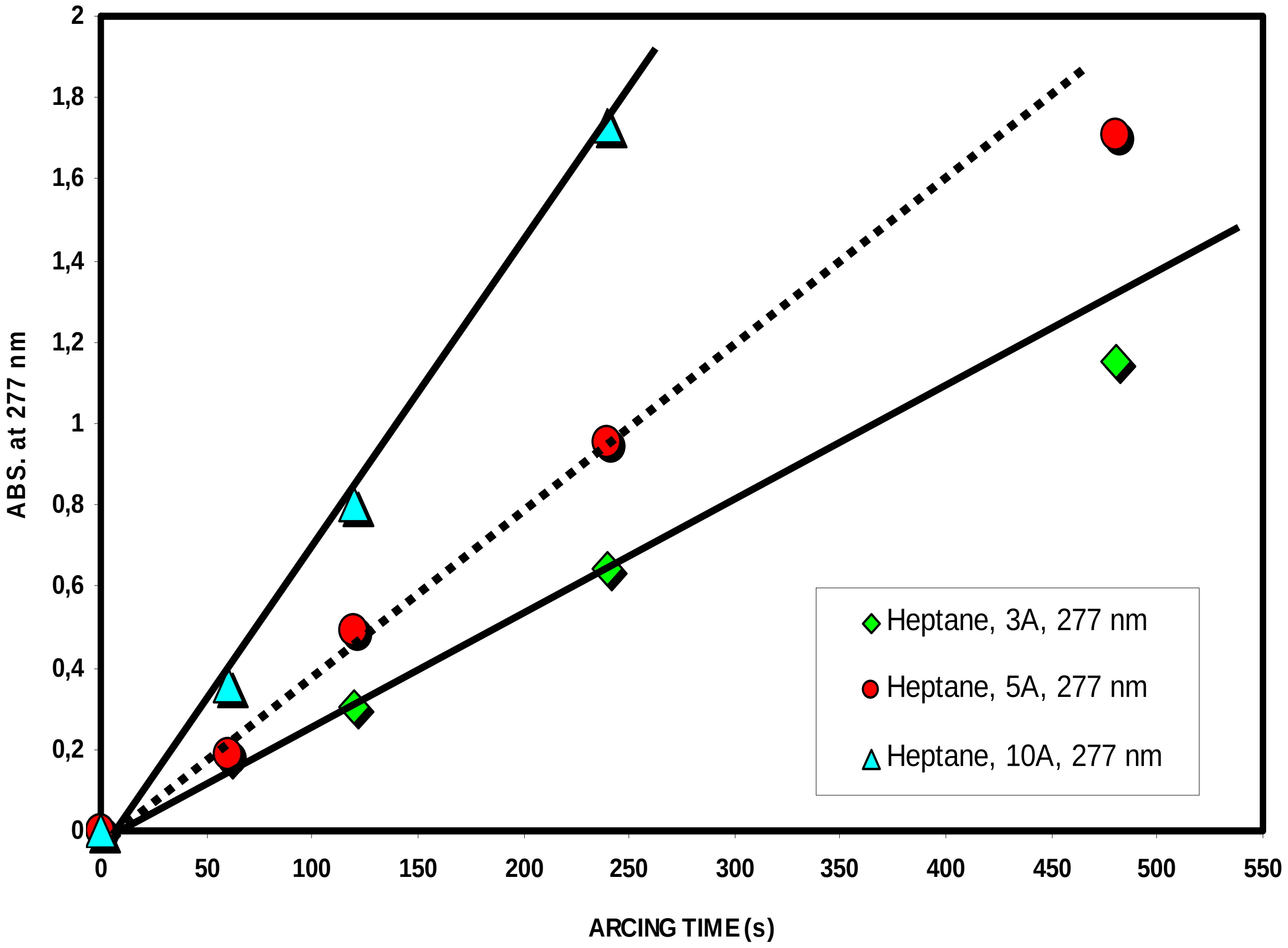
Electronic spectra of cyclohexane extracts: (1A) polyynes evolved during dicopper acetylide Cu-C≡C-Cu hydrolysis in HCl (1-day aged sample); **(1B)** polyynes evolved during dicopper diacetylide Cu-C≡C-C≡C-Cu hydrolysis in HCl (6-days aged sample).



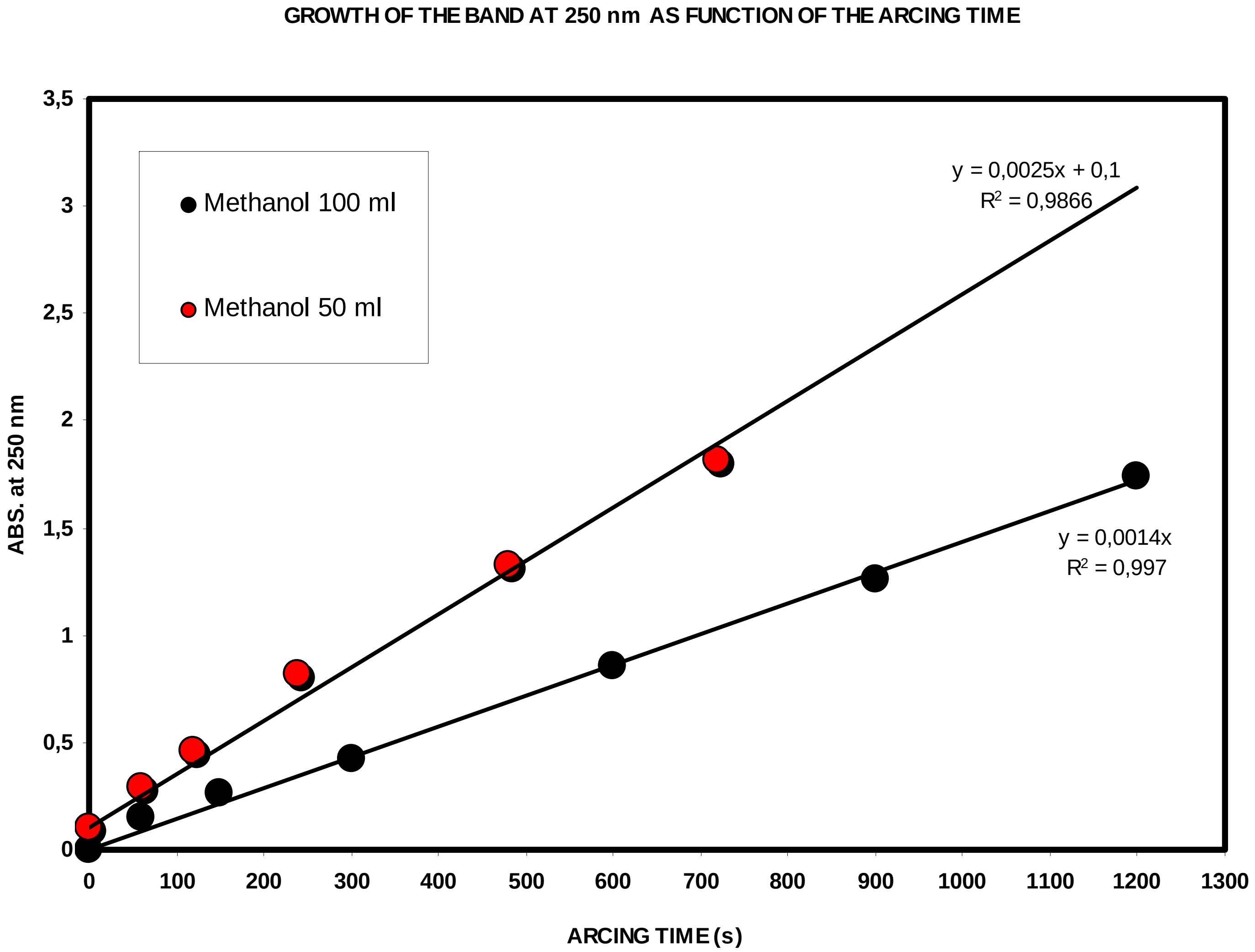
Kinetics of polyynes formation during graphite arcing in selected solvents.
Solvent volume 55 ml; current 10 A.



Polyynes formation in n-heptane (55 ml vol) at different electric current intensity



Polyyne formation by arcing graphite at 10A in methanol at different solvent volumes.



Effect of the nature of the electrodes on polyynes formation

- When Ti electrodes are used in methanol/ethanol, no polyynes are formed
- When Ti electrodes are struck in hydrocarbons, PAHs are formed and even polyynes but in trace amounts.
- When C electrodes are arced either in methanol/ethanol or in hydrocarbons, polyynes are the main or exclusive product.
- Even arcing C electrodes in water or $HCONH_2$ produces exclusively polyynes.

TABLE 1 - SYNOPSIS OF PRODUCTS FORMED BY ARCING GRAPHITE OR TITANIUM IN SELECTED SOLVENTS

SOLVENT	Hexane	Hexane	Benzene	Benzene	Methanol	Methanol	Ethanol	Ethanol
ELECTRODES	Graphite % mol	Titanium % mol	Graphite % mol	Titanium % mol	Graphite % mol	Titanium % mol	Graphite % mol	Titanium % mol
POLYYNE C6	**20.3**	**23.9**	**13.8**	**detected**	**7.2**	n.d.	**8.9**	n.d.
POLYYNE C8	**61.2**	**72.7**	**68.3**	**83**	**77.8**	n.d.	**73.5**	n.d.
POLYYNE C10	**14.8**	**3.4**	**12.6**	**17**	**12.8**	n.d.	**12.3**	n.d.
POLYYNE C12	**2.9**	n.d.	**3.2**	**traces**	**2.2**	n.d.	**3.7**	n.d.
POLYYNE C14	**0.63**	n.d.	**2.1**	**traces**	**detected**	n.d.	**1.5**	n.d.
POLYYNE C16	**0.17**	n.d.	**traces**	n.d.	n.d.	n.d.	**0.1**	n.d.
POLYYNE C18	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benzene	n.d.	**traces ?**			n.d.	**traces**	n.d.	**traces**
Indene	n.d.	**traces**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d
Naphthalene	**traces**	**traces**	**detected**	**detected**	**traces**	**traces**	**traces**	**traces**
Acenaphthene	**traces**	n.d.	**detected**	n.d.	n.d.	**traces**	n.d.	**traces**
Acenaphtylene	**traces**	**traces**	**detected**	**detected**	n.d.	n.d.	n.d.	n.d.
Biphenyl	n.d.	n.d.	**detected**	**detected**	n.d.	**traces**	n.d.	n.d.
Phenanthrene	n.d.	n.d.	**detected**	**detected**	n.d.	**traces**	n.d.	n.d.
Anthracene	n.d.	n.d.	**detected**	**detected**	n.d.	**traces**	n.d.	n.d.
Perylene	n.d.	n.d.	**detected**	**detected**	**traces**	**traces**	n.d.	n.d.
Pyrene	**traces**	n.d.	**detected**	n.d.	n.d.	n.d.	n.d.	n.d.
Crysene	**traces**	n.d.	**detected**	n.d.	n.d.	n.d.	n.d.	n.d.
Fluoranthene	n.d.	n.d.	**detected**	**detected**	n.d.	**traces**	n.d.	n.d.
Benzo[b]fluoranthene	**traces**	**traces ?**	**detected**	**detected**	**traces**	n.d.	n.d.	n.d.
Benzo[b]naphto[2,1-cd]thiophene	n.d.	n.d.	**traces**	**traces**	n.d.	n.d.	n.d.	n.d.
Total Polyyne conc. Mol/l	4×10^{-4}	2×10^{-6}	5×10^{-4}	2×10^{-5}	5×10^{-4}	none	3×10^{-4}	none
Carbon Black formation	Yes	Yes	Abundant			Small	Small	Small

Hydrogen-terminated polyynes: when carbon vapour reacts with atomic hydrogen

- The temperature of the carbon arc is so high 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, >60% of molecular hydrogen is dissociated into atomic hydrogen (MacKay, 1973).
- Because of energetic reasons involving hydrogen recombination 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 Heat et al. (1987) has shown that the carbon radicals are able to get the hydrogen also from H_2 molecules.

Hydrogen-terminated polyynes: when carbon vapour reacts with atomic hydrogen

$\text{Graphite} \rightarrow C$

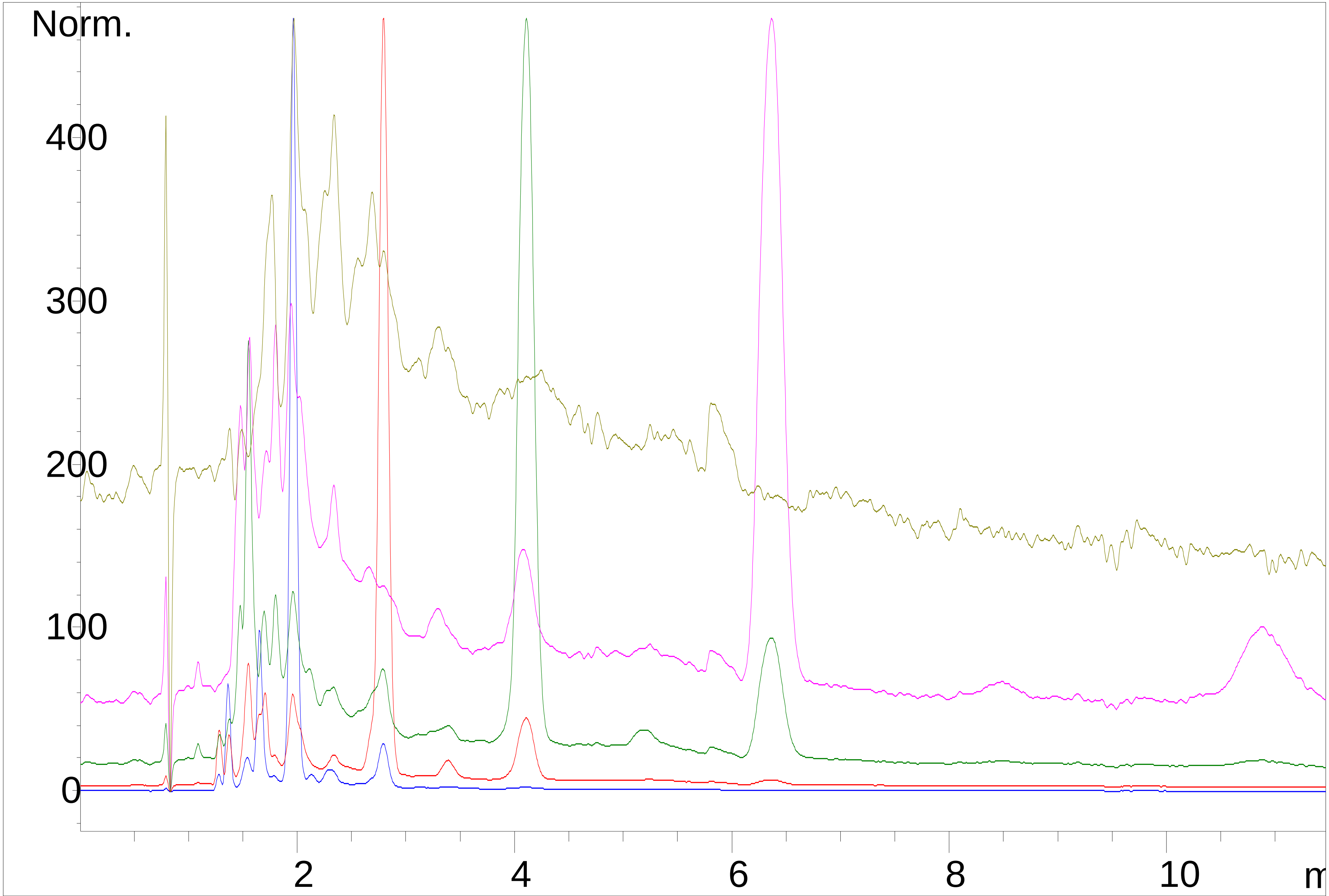
$C_{2n+2}H_n \rightarrow m\,H + s\,H_2 + \text{PAHs} + C_{soot}$

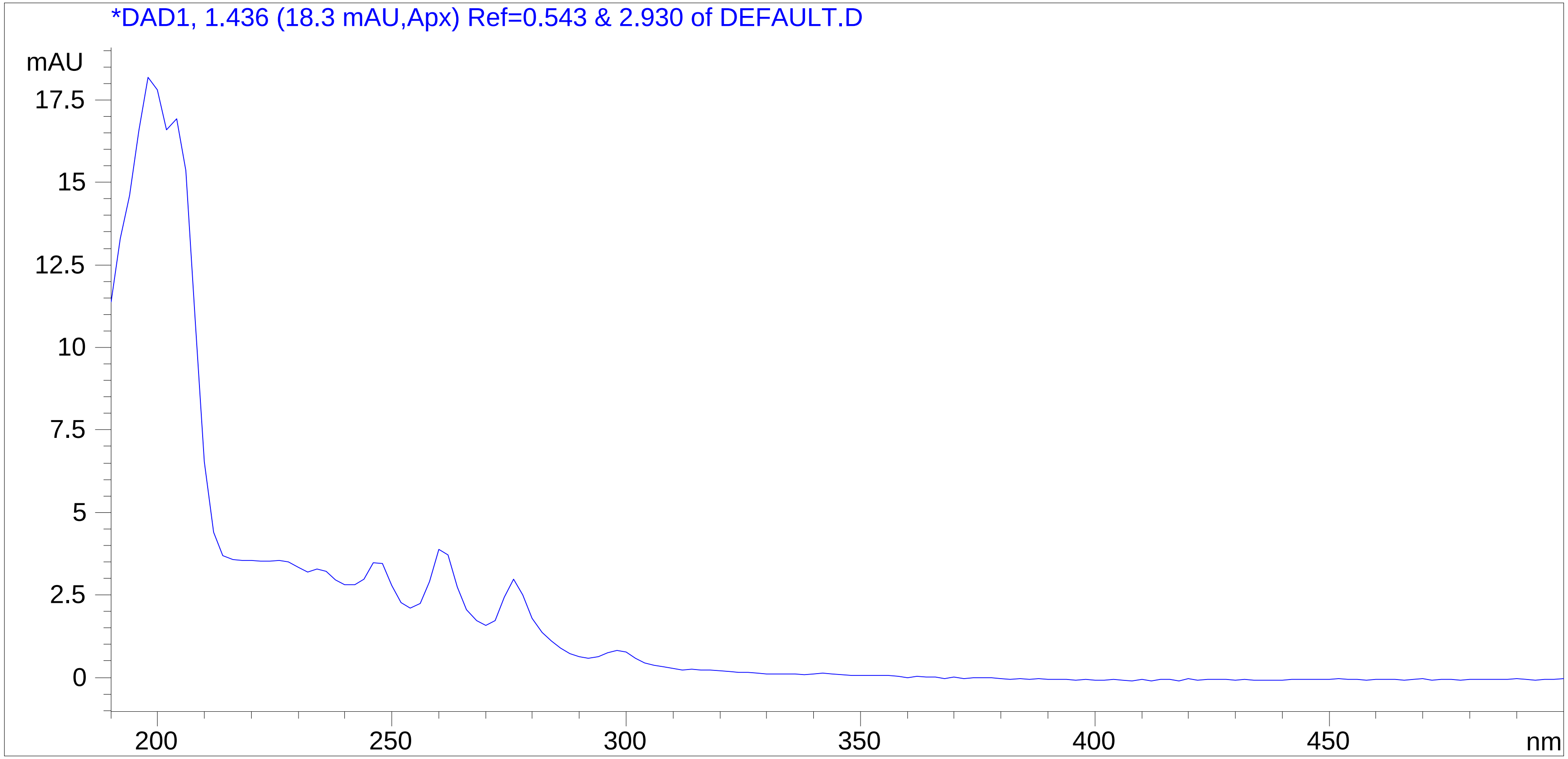
$2\,C \rightarrow C_2$

$n\,C_2 + 2\,H \rightarrow H\text{-}(C{\equiv}C)_n\text{-}H$

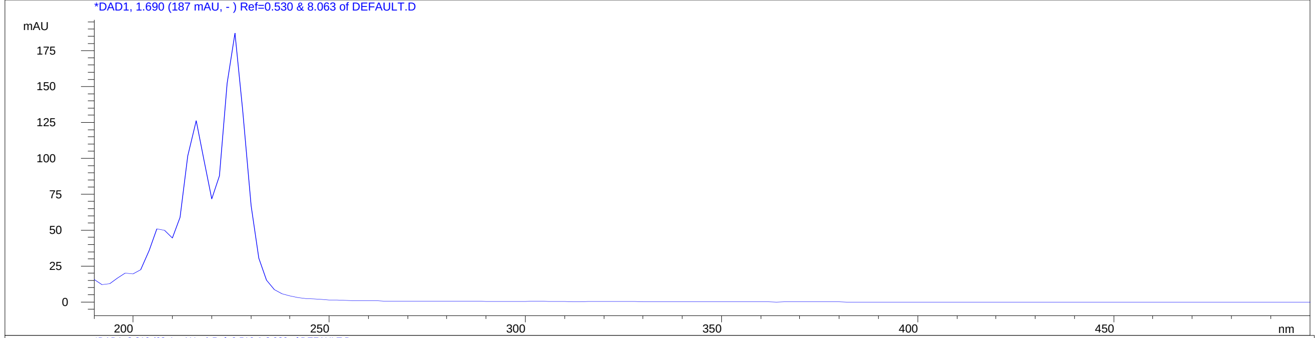
$C_{2n} + 2H_2O \rightarrow H\text{-}(C{\equiv}C)n\text{-}H + H_2O_2$

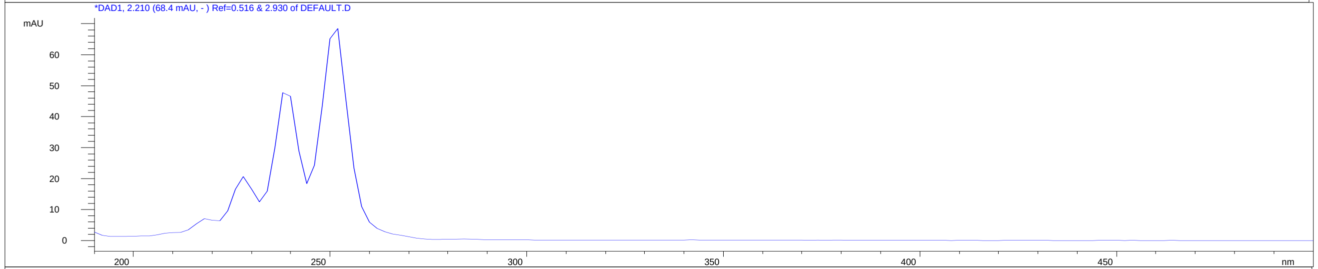
HPLC analysis of polyynes prepared by arcing graphite in n-hexane @ -80°C. The peak above 10 MIN is m=8, thus a chain with 16 carbon atoms.

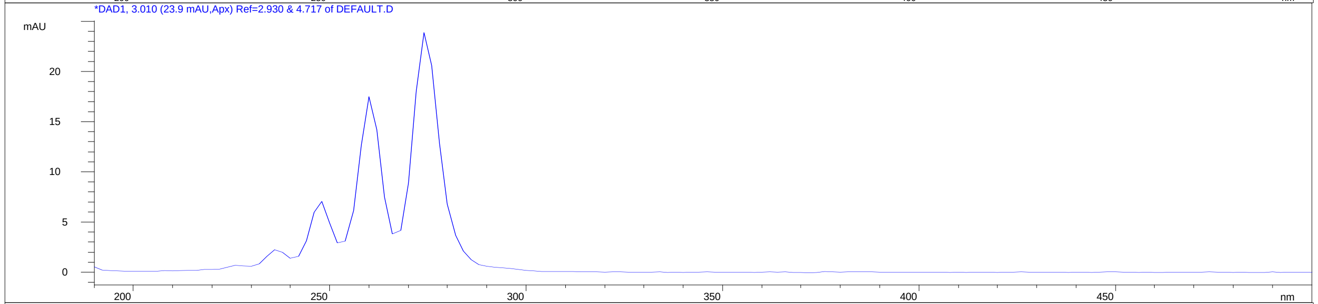


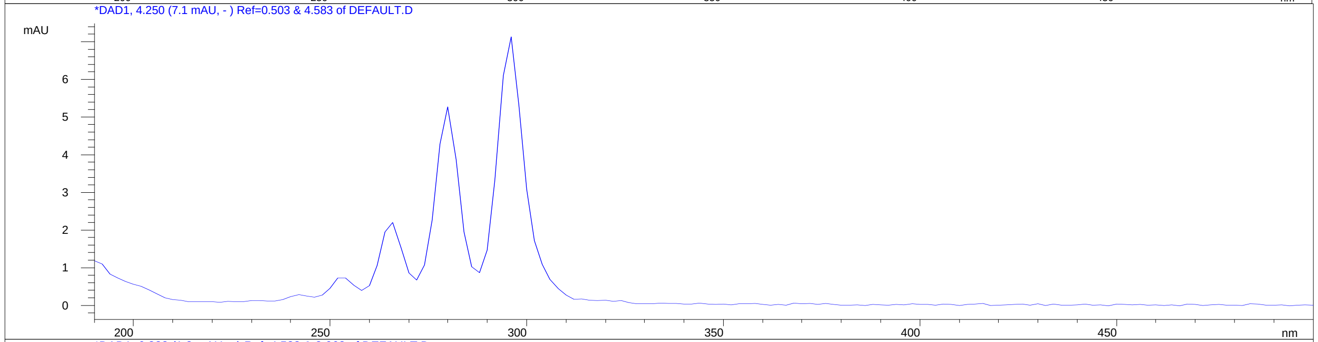


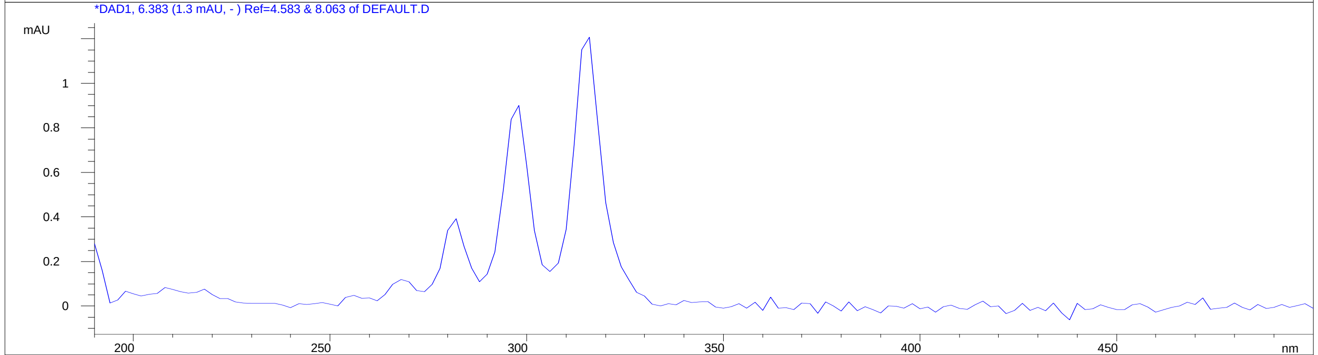
Electronic absorption spectra recorded by the diode-array detector of the HPLC system. **This spectrum was assigned to the polyyne having m=3**



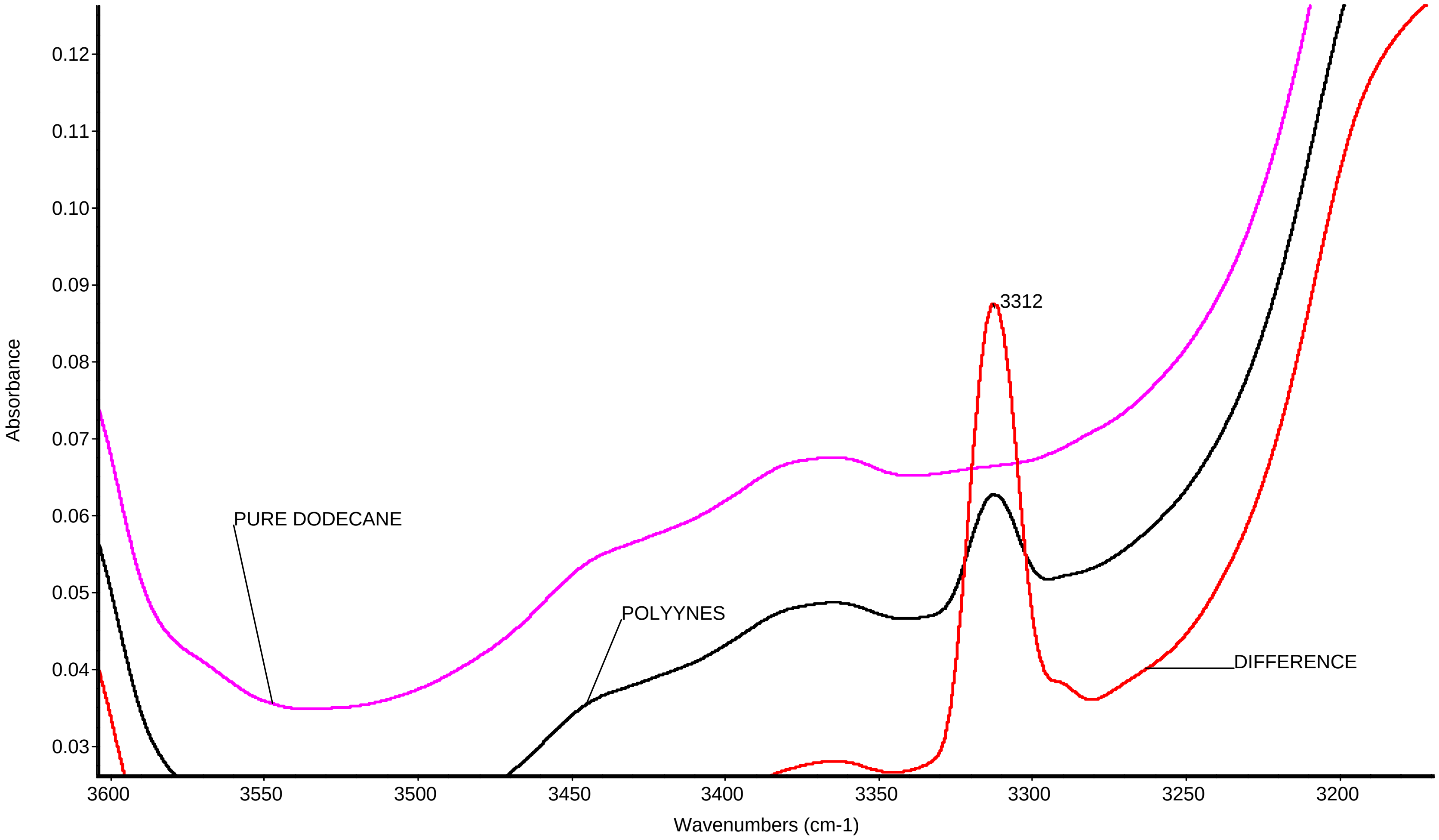






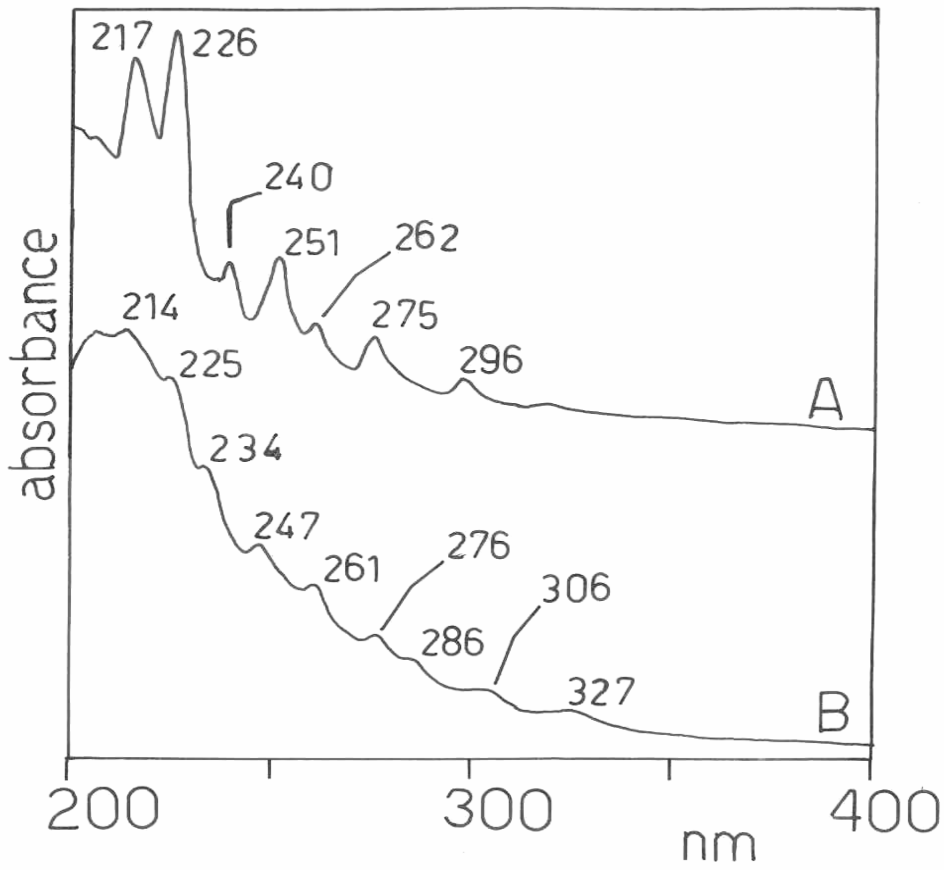


From top to bottom are reported the electronic absorption spectra of polyynes prepared in acetonitrile at room temperature with m = 4, 5, 6, 7 and 8, **hence having carbon chains from 8 to 16 carbon atoms**. Each of these spectra were recorded by the diode-array detector of the HPLC system on each individual chemical specie eluted by the C-8 HPLC column.

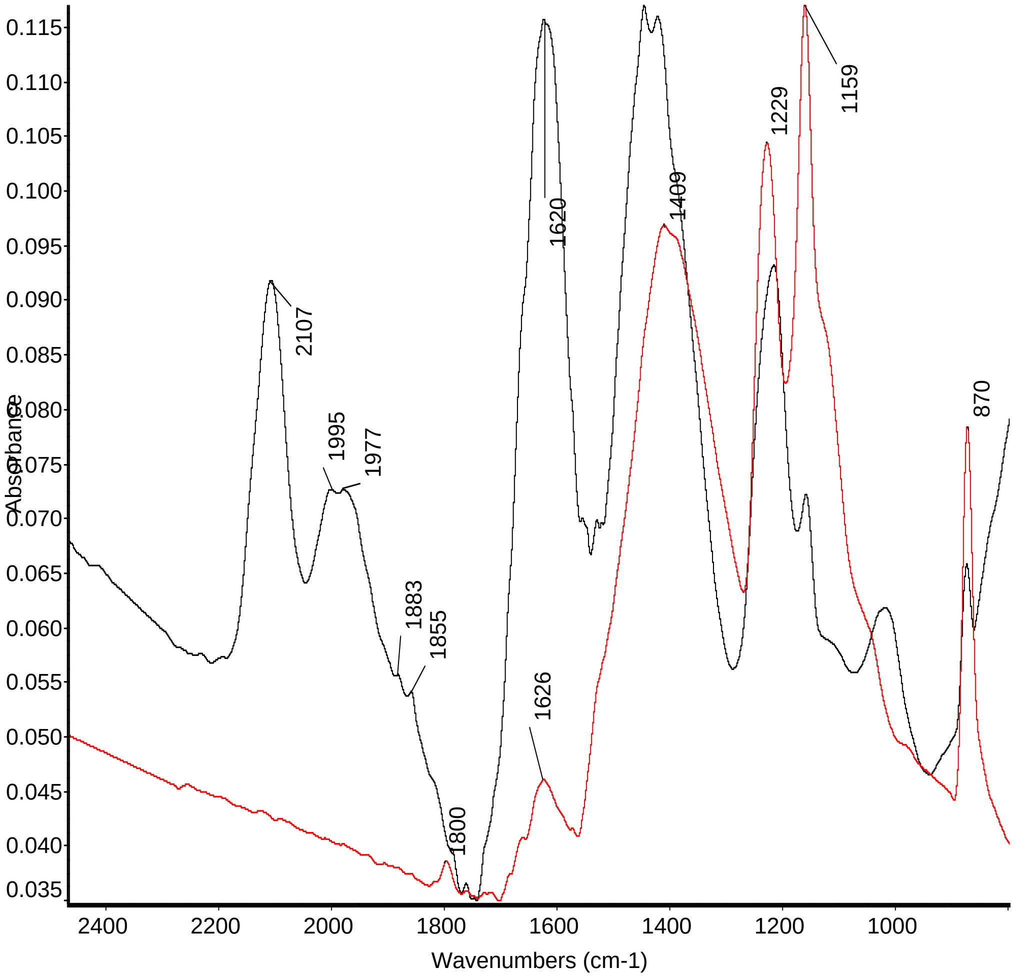


FT-IR spectra (recorded in a IR cell for liquids) of pure dodecane (blank) and polyynes dissolved in dodecane after arcing of graphite electrodes submerged in dodecane. The polyyne solution shows the peak at 3312 cm-1 which is due to the stretching of the -C≡C-H group[19]. This absorption band is enhanced by the subtraction of the blank. The -C≡C-H stretching demonstrates that the polyynes are hydrogen-capped.

A) Electronic absorption spectrum of polyynes obtained in n-hexane after arcing with graphite electrodes.
B) Spectrum after polyyne precipitation from solution as acetylides. The residual absorption bands are due to PAHs formed as secondary products during arcing.



Copper polyynides were isolated



- FT-IR spectra. copper polyynides prepared from the carbon arc.
- Before and after annealing at 300°C; all the triple bonds stretching bands disappeared.

Monocyanopolyynes by arcing graphite in ammonia or in acetonitrile

$NH_3 \rightarrow N + 3H$

$\text{Graphite} \rightarrow C$

$2\,C \rightarrow C_2$

$H + nC_2 + CN \rightarrow H\text{-}(C{\equiv}C)_n\text{-}CN$

$H + nC_2 + H \rightarrow H\text{-}(C{\equiv}C)_n\text{-}H$

$CH_3\text{-}CN \rightarrow CH_3 + CN$

$CH_3 \rightarrow CH + {}_2H$

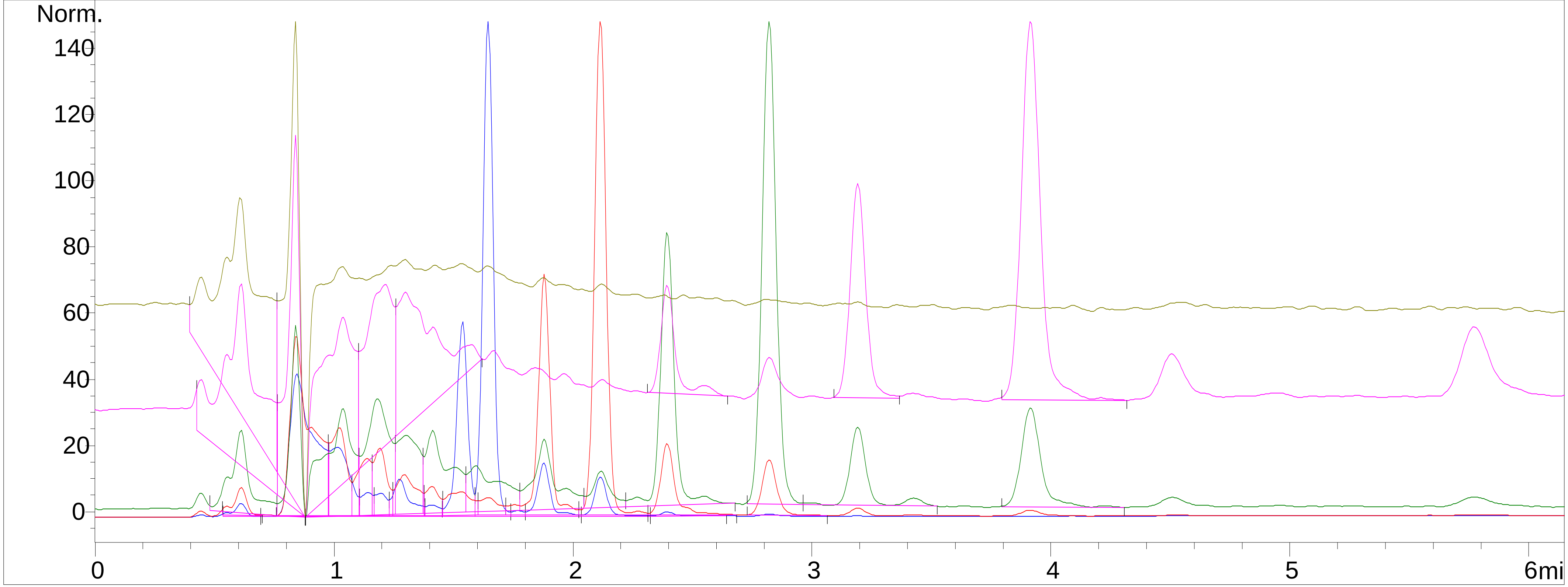
$\text{Graphite} \rightarrow C$

$2\,C \rightarrow C_2$

$H + nC_2 + CN \rightarrow H\text{-}(C{\equiv}C)_n\text{-}CN$

Monocyanopolyynes by arcing graphite in ammonia or in acetonitrile

- Ammonia is easily cracked into the 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. So the carbon vapor released by the graphite electrodes is in a mixed environment where hydrogen is prevailing over nitrogen.
- 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.



Typical HPLC chromatogram of a polyyne mixture prepared by electric arc between graphite electrodes submerged in acetonitrile at –40°C. Each peak above 1.5 min retention time represents a **polyyne** member of the homologous series

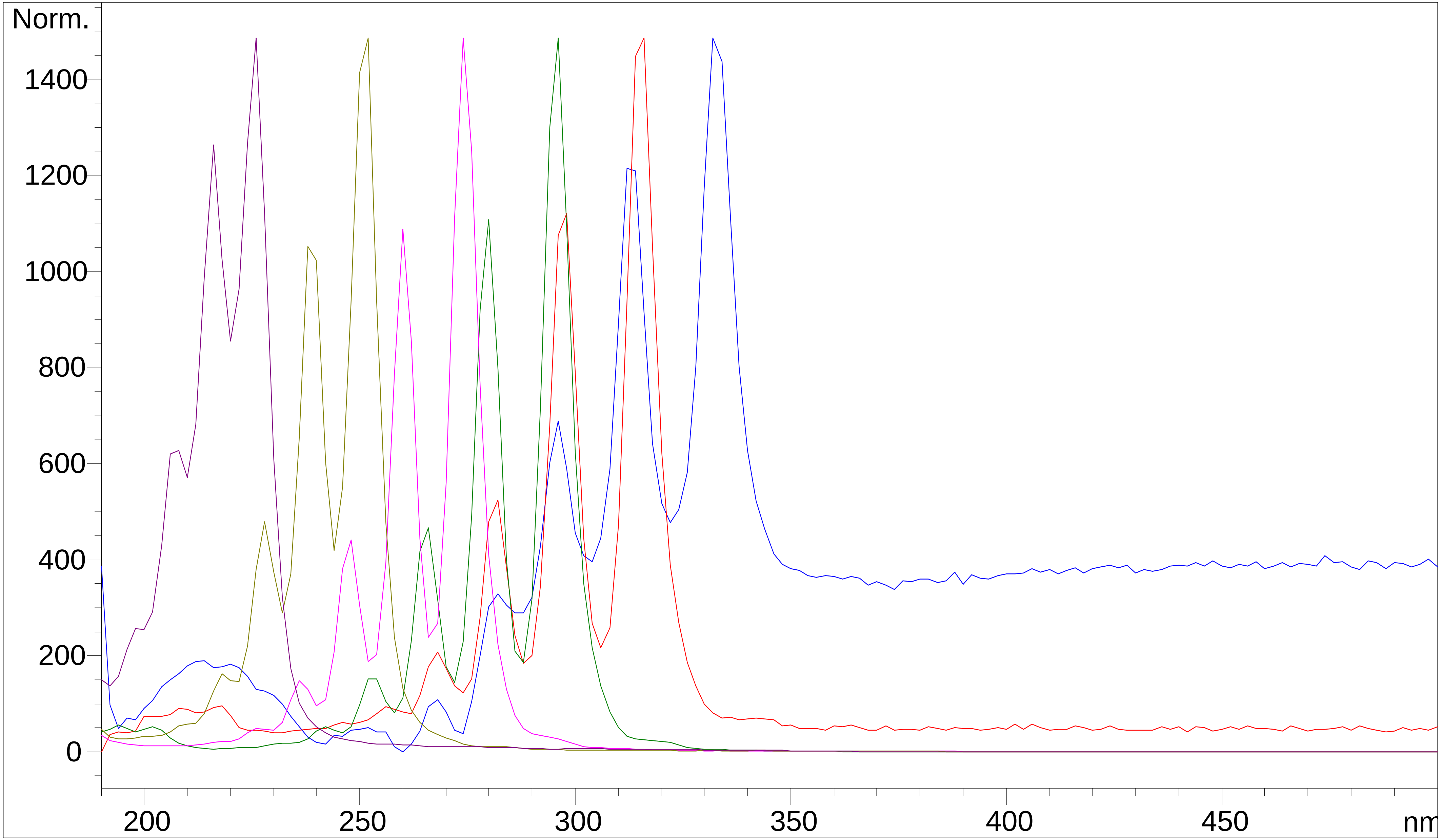
$H(C{\equiv}C)_mH$ (with m an integer).

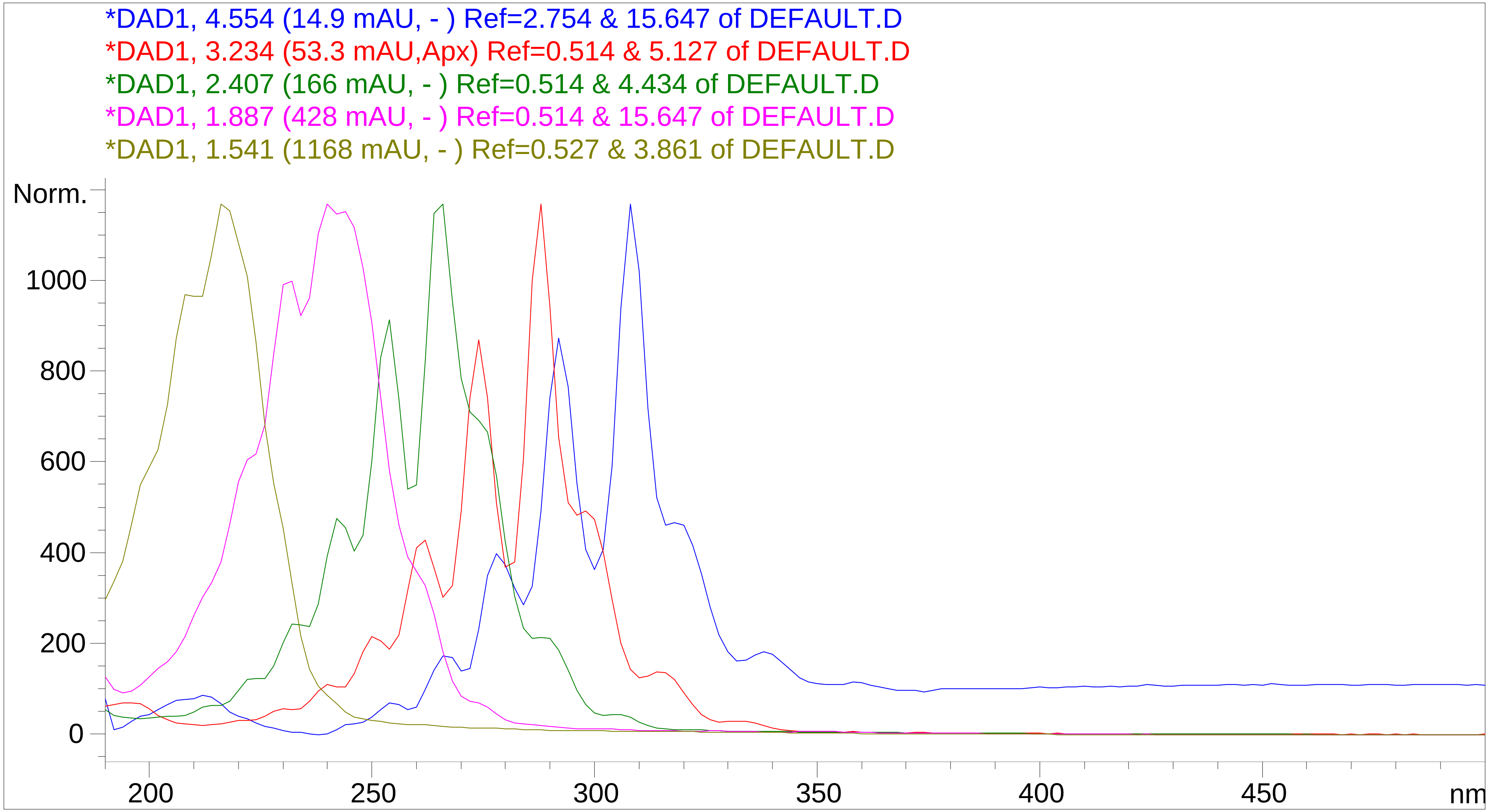
The mentioned series is accompanied by the **monocyanopolyyne series** (the small peaks between the the tallest peaks):

$H(C{\equiv}C)_m\text{-}CN$

The peak at 5.8 MIN is the polyyne with m=8, hence an acetylenic carbon chain of **16 carbon atoms.**

Detection of polyyne with m=9: a chain with 18 carbon atoms





Overlapped electronic absorption spectra of **monocyanopolyynes** produced by arcing graphite electrodes in an acetonitrile solution at –40°C.

Monocyanopolyynes with 7, 9, 11, 13, 15 carbon atoms separated and identified.

Dicyanopolyynes by arcing graphite in liquid nitrogen

$N_2 \rightarrow 2\ N$

Graphite → C

$C + N \rightarrow CN$

$2\ C \rightarrow C_2$

$n\ C_2 + 2\ CN \rightarrow NC\text{-}(C\equiv C)n\text{-}CN$

Graphite → C_{2n}

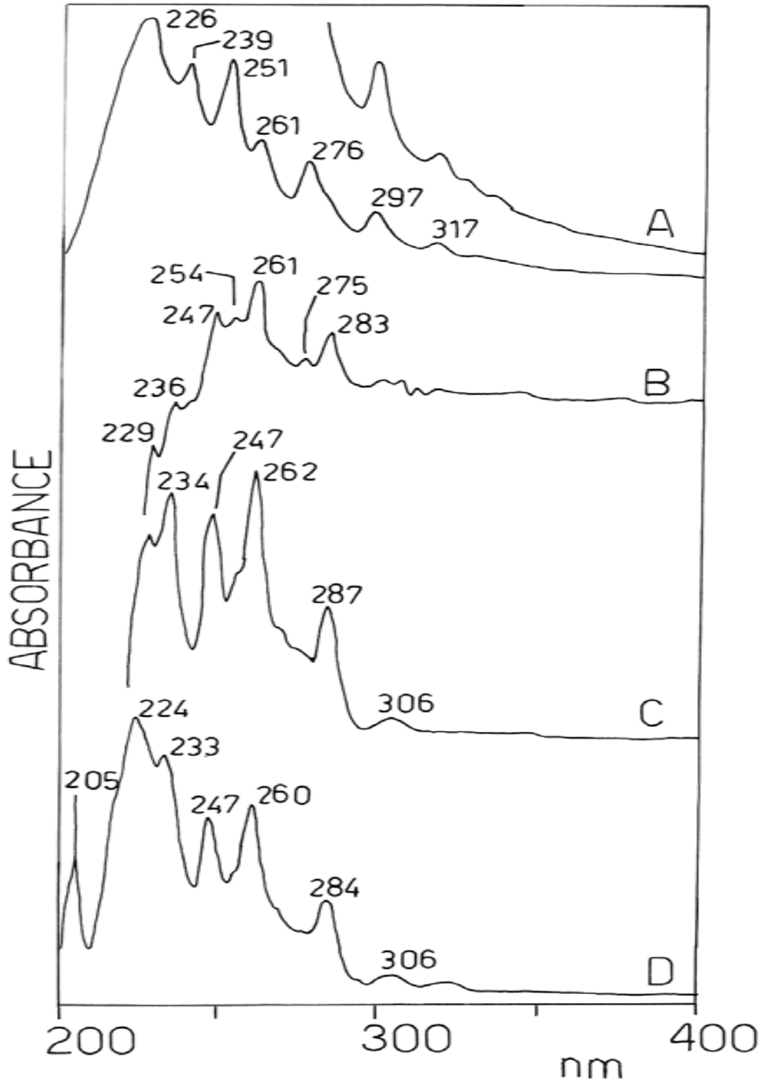
$C_2N_2 \rightarrow 2\ CN$

$C_{2n} + 2\ CN \rightarrow NC\text{-}(C\equiv C)n\text{-}CN$

Dicyanopolyynes by arcing graphite in liquid nitrogen

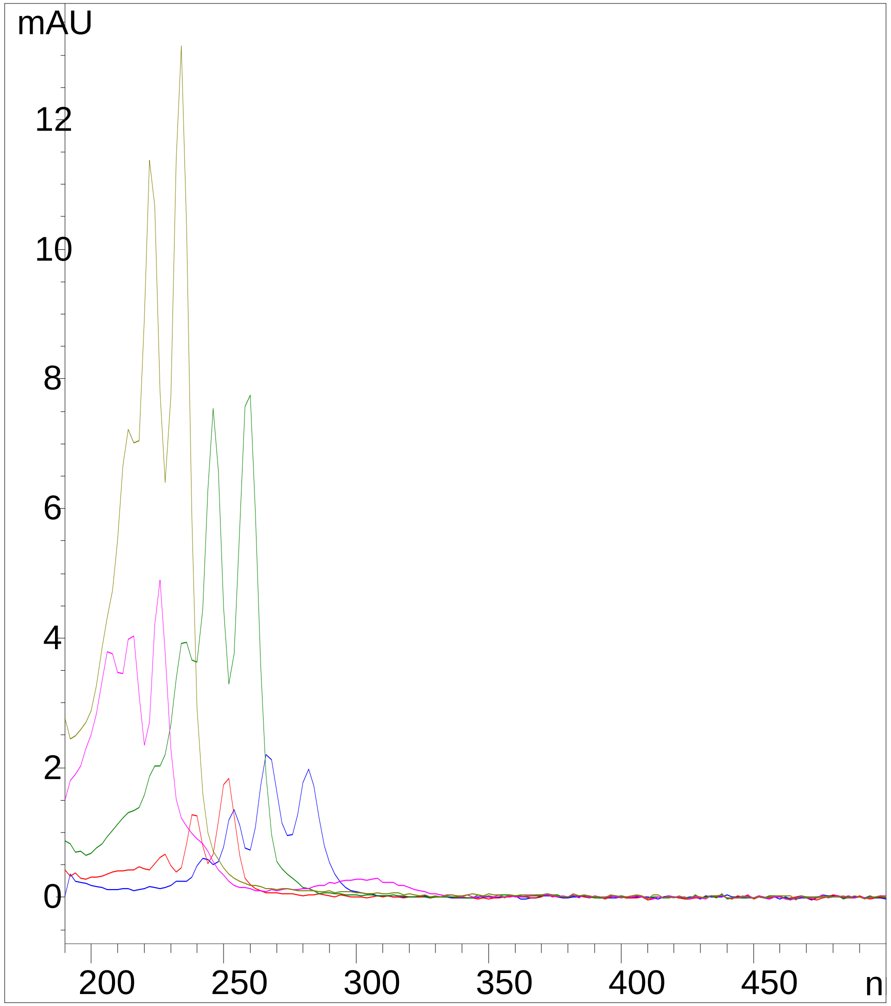
- Since no hydrogen is available all the polyynes chains are nitrogen-terminated.
- The formation of atomic nitrogen from molecular nitrogen in an electric arc or discharge is a well known phenomenon (Jones, 1973).
- As for atomic hydrogen, the lifetime of atomic nitrogen in its ground state is relatively long and sufficient to permit the reaction with carbon vapour.

Dicyanopolyynes spectra



- Electronic absorption spectra of polyynes mixture. 5A –Polyynes obtained by arcing graphite directly into n-octane
- B - Initial spectrum of the polyynes mixtures produced from the graphite arc in liquid nitrogen and trapped in n-octane at the beginning of the experiment.
- C – Same as 5B but after prolonged arcing in liquid nitrogen.
- D – Same as 5C at the end of the experiment; a final total concentration of polyynes estimated at about 8 x 10-6 M was achieved.

HPLC detection of dicyanopolyynes



- The three main components are easily and definitively identified from their electronic absorption spectra and are respectively C_6N_2, C_8N_2 and $C_{10}N_2$.
- There are also other two minor components the hydrogen-terminated polyynes C_8H_2, $C_{10}H_2$.

SUMMARY: PARALLELISM BETWEEN THE PRODUCTS OBTAINED BY LASER ABLATION AND BY ARCING

TABLE 1 - REACTION PRODUCTS BETWEEN CARBON VAPOR AND SIMPLE MOLECULES

REACTANTS	PRODUCTS **Laser Ablation of Graphite** (Ref. Kroto et al. 1987)	PRODUCTS from **Kratschmer-Hufmann Arc Type** (Ref. Grosser and Hirsch, 1993)	PRODUCTS **Submerged Carbon Arc** (Ref. Cataldo 2003-2006)
Hydrogen	C_6H_2 - $C_{22}H_2$	PAHs	from C_6H_2 to $C_{18}H_2$
Water	C_8H_2 - $C_{20}H_2$	n.a.	from C_6H_2 to $C_{14}H_2$
Nitrogen	C_8N_2 - $C_{22}N_2$	n.a.	from C_8N_2 to $C_{12}N_2$
Acetonitrile	HC_7N - HC_9N	n.a.	from HC_7N to $HC_{15}N$ and from C_6H_2 to $C_{18}H_2$
Ammonia	HC_7N - HC_9N	n.a.	from HC_7N to $HC_{13}N$ and from C_6H_2 to $C_{14}H_2$
Aqueous ammonia	n.a.	n.a.	from HC_7N to HC_9N and from C_6H_2 to $C_{14}H_2$
Cyanogen	n.a.	C_8N_2 and some higher homologues	n.a.
Helium 100 torr	n.a.	Fullerenes	n.a.

The largest molecule detected in the interstellar/circumstellar medium so far:

$$\mathbf{H\text{-}(C{\equiv}C)_5\text{-}C{\equiv}N}$$

The largest polyyne produced in lab scale by step-synthesis using silyl-protected acetylene chemistry (Walton, 1972):

$$\mathbf{H\text{-}(C{\equiv}C)_{12}\text{-}H}$$

Polyynes in the circumstellar medium (late-type carbon rich stars)

Polyynes $H\text{-}(C{\equiv}C)_n\text{-}H$,

Monocyanopolyynes $H\text{-}(C{\equiv}C)_n\text{-}C{\equiv}N$,

Dicyanopolyynes $N{\equiv}C\text{-}(C{\equiv}C)_n\text{-}C{\equiv}N$

and their radicals and ions have been detected

- in exceptional abundance in the **circumstellar environment surrounding late-type carbon-rich stars like for instance the star IRC + 10°216**
- in **dense and dark interstellar molecular clouds** like TMC 1
- in **hot molecular cores**

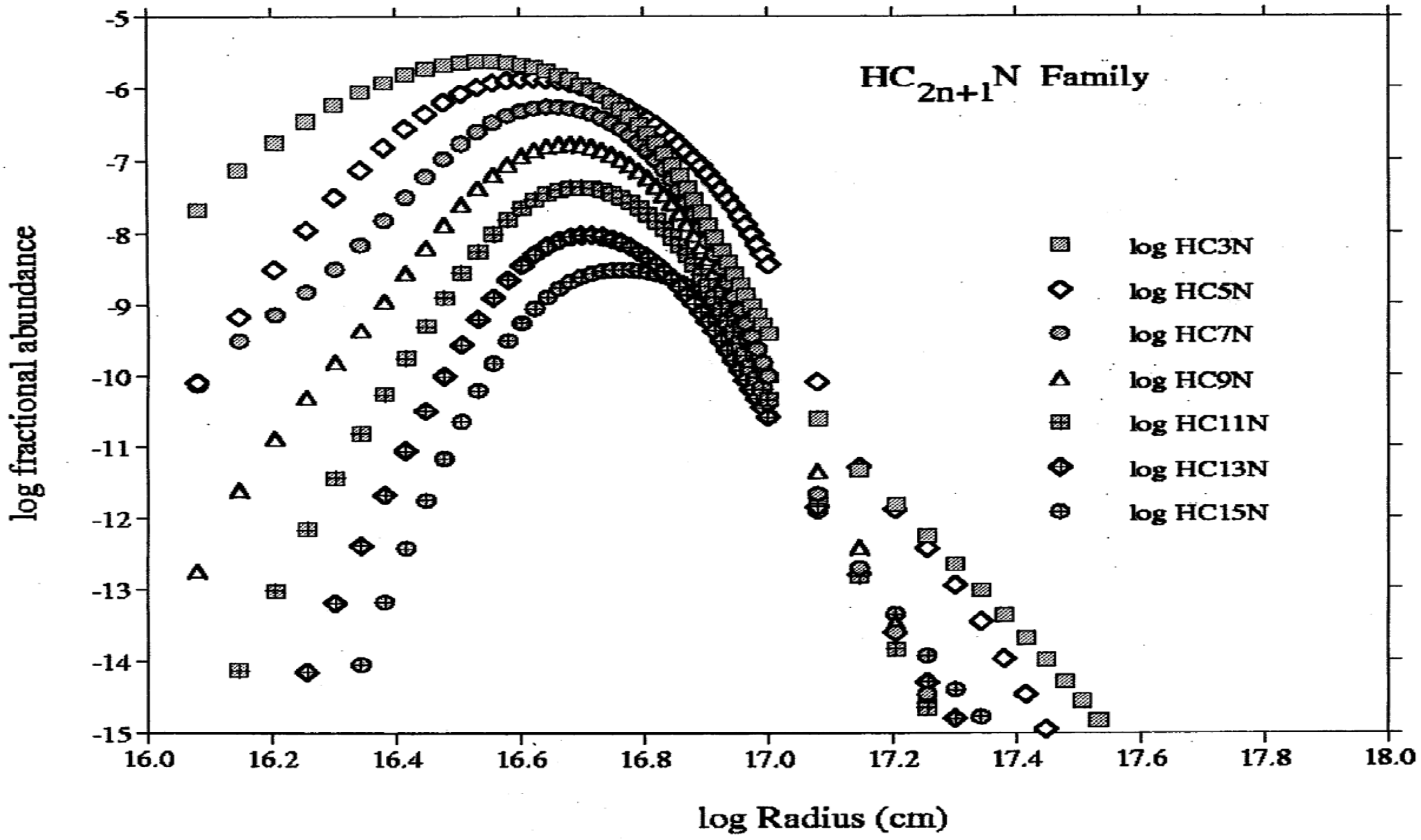
AGB Stars

- Late stages of stellar evolution of normal stars
- High mass loss rate - evolving in to WD + PN stage
- Cool - effective temperatures $\sim$ 2000-3000 K
- Carbon rich ($C/O > 1$) or Oxygen rich ($C/O < 1$)
- Major formations sites of dust grains
- C-rich stars contain many organic species
- More than 50 molecules detected

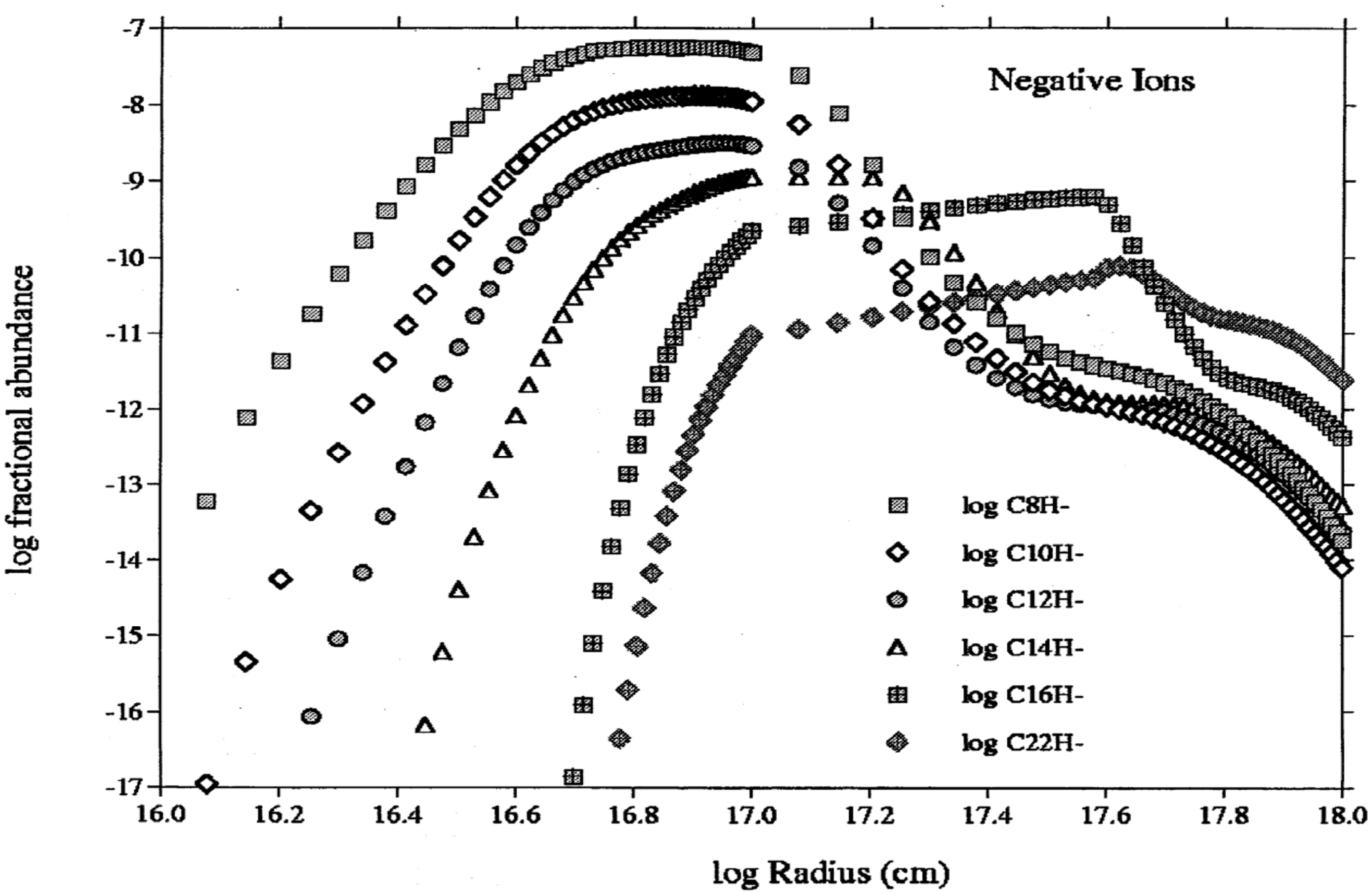
How polyynes are formed in circumstellar shell?

- In the circumstellar environment it has been demonstrated that the formation of polyynes takes place mainly by a radical mechanism involving neutral species Cherchneff and Glassgold (1993) and Cherchneff, Glassgold and Mamon (1993).
- The classic ion-molecule mechanism has been demonstrated to be not operative in circumstellar shells because of kinetic and energetic reasons and the lack of ions (Millar, 2004; Herbst, 1998; Helling et al. 1996; Cherchneff and Glassgold, 1993; Kroto et al. 1987)

POLYYNES FORMATION & DESTRUCTION



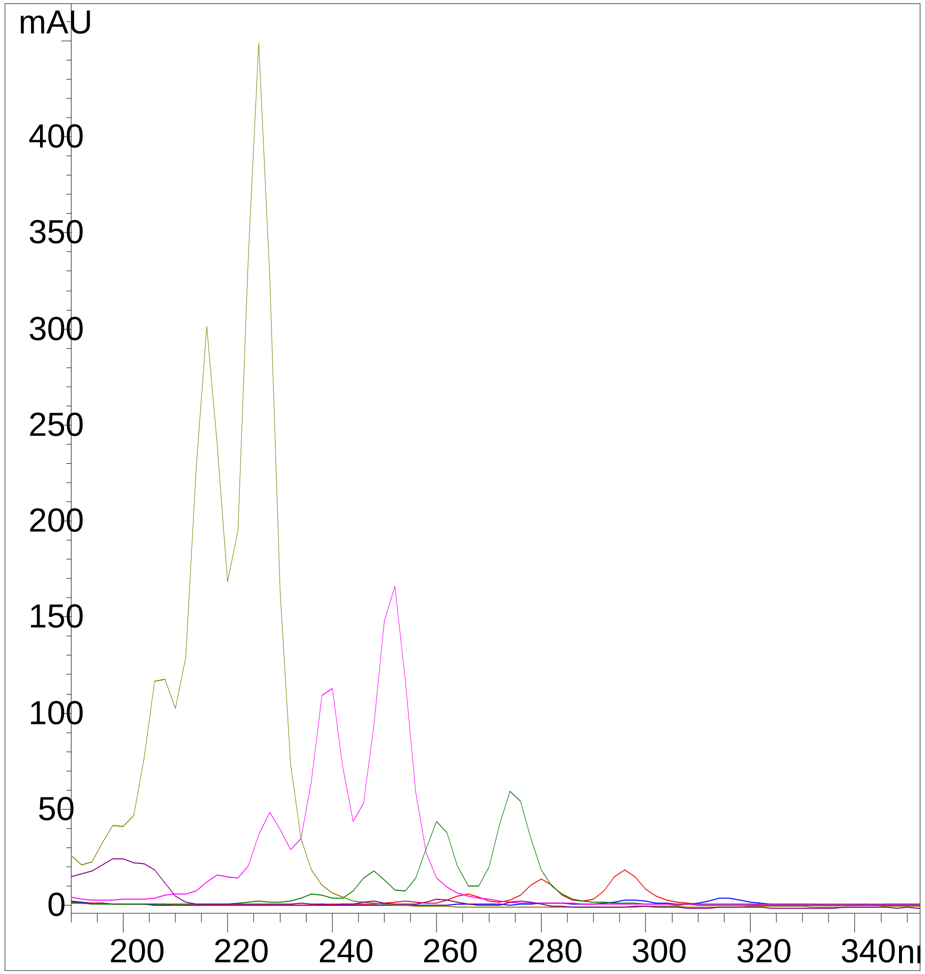
FORMATION/DESTRUCTION OF OTHER SPECIES



RELATIVE ABUNDANCE OF POLYYNES FROM ARC: A COMPARISON WITH CIRCUMSTELLAR ENVIRONMENT

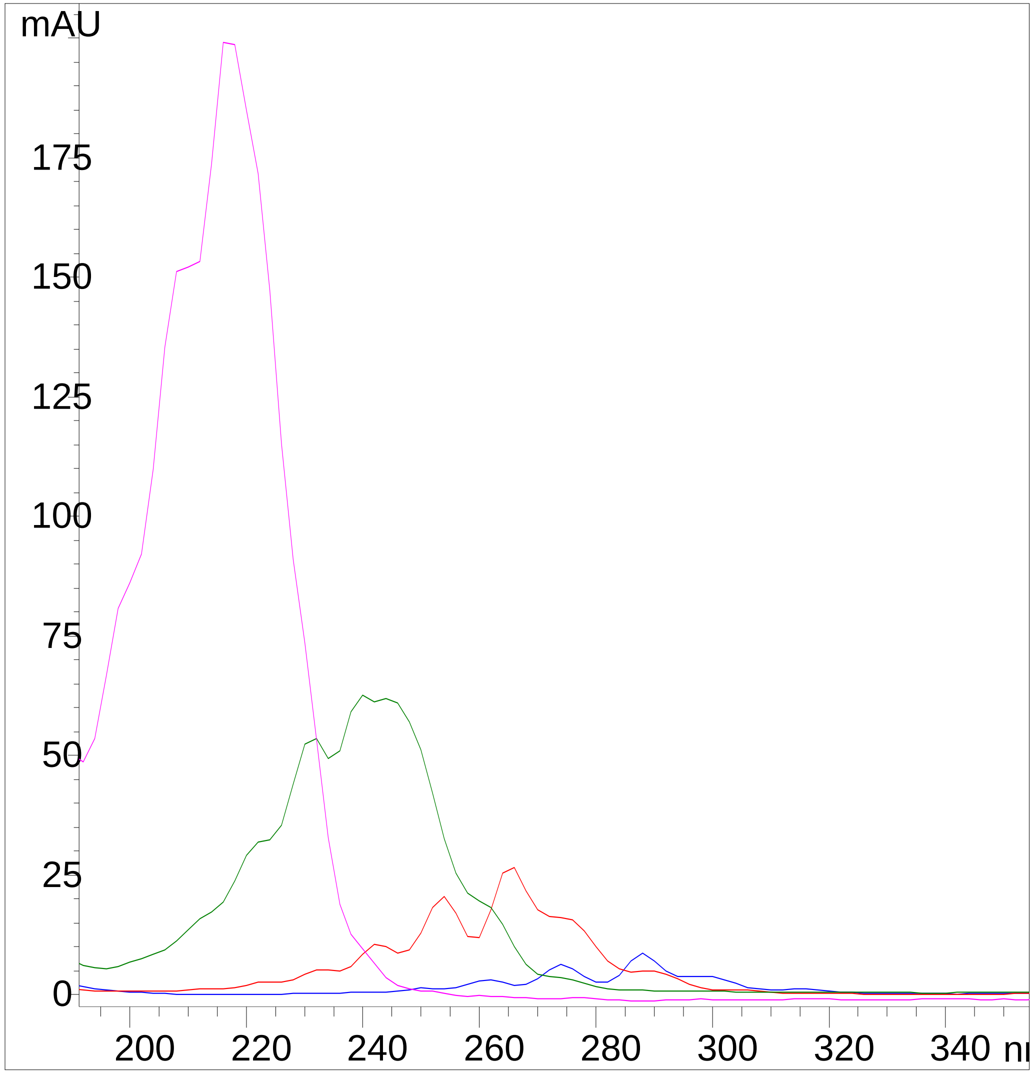
- Radioastronomy has measured the relative abundace of polyynes around late-type carbon-rich stars (Cherchneff et al. 2004).
- If the temperature and the mechanism of polyynes formation is the same as in our arc conditions, we should get the same distribution of products i.e. The same relative abundance.
- The temperature of late-type carbon rich stars is at 3000-4000K. The molecules are formed essentially by radical reaction paths (there are a negligible fraction of ions). These are the same conditions existing in our arc.

Relative abundance of H-terminated polyynes from carbon arc



- 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 by increasing the chain length.

Relative abundance of monocyanopolyynes



- Electronic absorption spectra of monocyanopolyynes as recorded by the diode array detector. The first spectrum in the left is due to HC_7N followed by HC_9N, $HC_{11}N$ and $HC_{13}N$ (traces).
- It is clear that the concentration of the monocyanopolyynes decreases by increasing the chain length.

TABLE 2 - RELATIVE ABUNDANCE OF POLYYNES FROM CARBON ARC
A COMPARISON WITH THE ABUNDANCE IN CIRCUMSTELLAR MEDIUM

Polyynes species	Arc in Hexane (*)	Arc in Acetonitrile (*)	Arc in Nitrogen (**)	Arc in Vacuum (***)	Carbon clusters	In Circumstellar Enviromnent (****)
				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				3 - 5
$HC_9N/HC_{11}N$		3.0				3 - 5
$HC_{11}N/HC_{13}N$		2.8				3 - 5
$HC_{13}N/HC_{15}N$		2.9				3 - 5
C_6N_2/C_8N_2			2.7			
$C_8N_2/C_{10}N_2$			4.9			

(*) Cataldo, 2004a-f
(**) Cataldo, 2004g-h
(***) Hintenberger et al., 1963
(****) Cernicharo, 2004; Chernicharo et al., 2004

CONCLUSIONS

- In the carbon arc the C vapour is released by the electrodes.
- The C vapour aggregates to form polyyne chains.
- The chains are terminated by reacting with molecules present in the environment: H, N, CN which will act as end group of the chains.
- The mechanism of formation of polyynes in the arc involves non-ionic but rather radical species.
- **Since the distribution of products in the arc are mimicking those present in circumstellar environment it is suggested that the chemistry in the carbon arc is able to reproduce that occurring in the carbon-rich stars.**

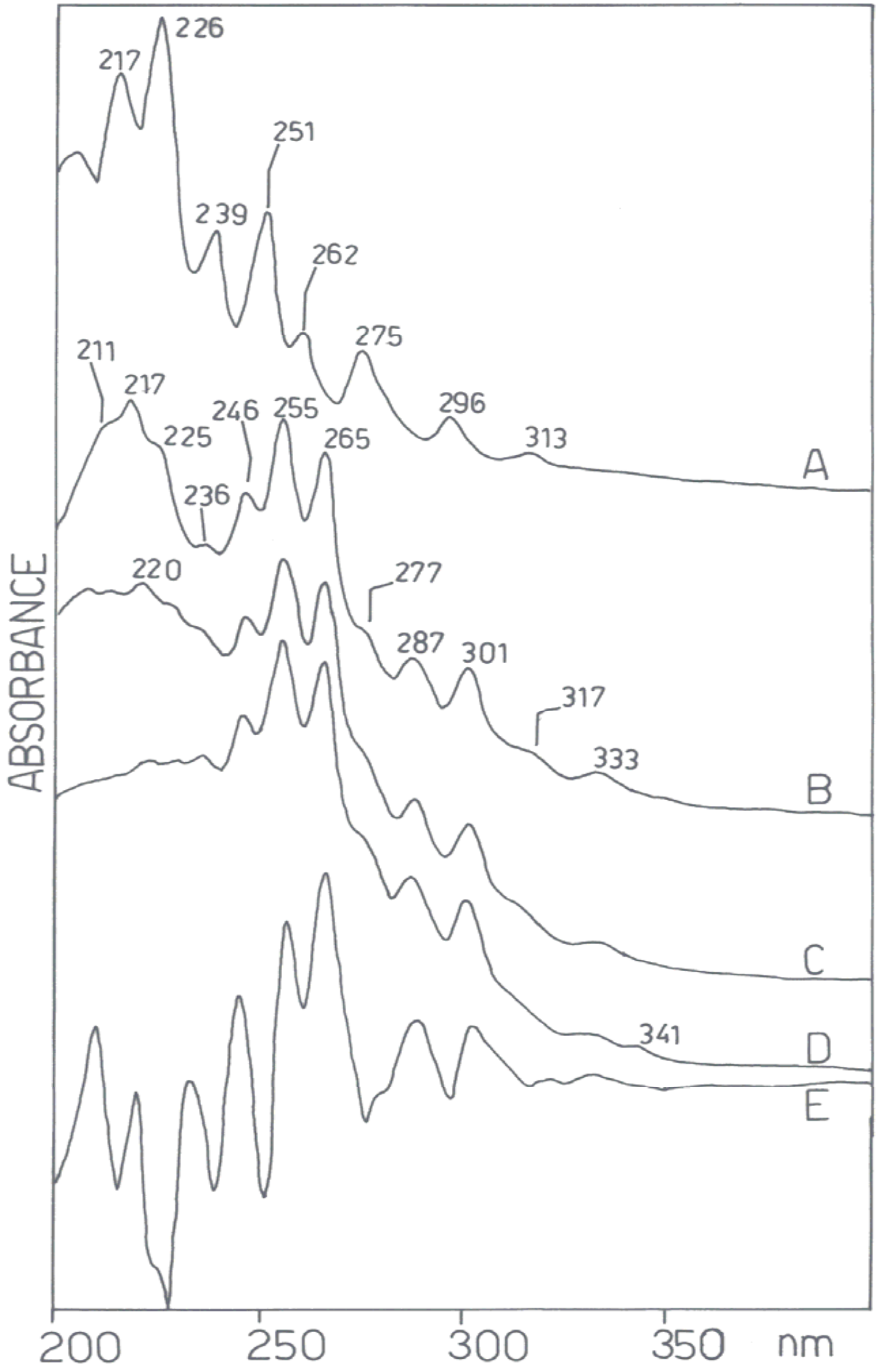
APPENDIX

- The polyyne chemistry has been started to be explored.
- Hydrogenation

SYNTHESIS OF ENE-YNES FROM POLYYNES

$H-C\equiv C-C\equiv C-C\equiv C-C\equiv C-H$ + Zn/HCl →

- $H_2C=CH-(C\equiv C)_2-CH=CH_2$ (1,2 addition)
- $H_2C=C=C=CH-(C\equiv C)-CH=CH_2$ (1,4 addition)
- $H_2C=C=C=C=C=CH-CH=CH_2$ (1,6 addition)
- $H_2C=C=C=C=C=C=C=CH_2$ (1,8 addition)
- $H_2C=C-CH=CH-C\equiv C-CH=CH_2$ (3,4 addition)
- $H_2C=HC-CH=C=C=CH-CH=CH_2$ (3,6 addition)



Electronic absorption spectra in n-hexane

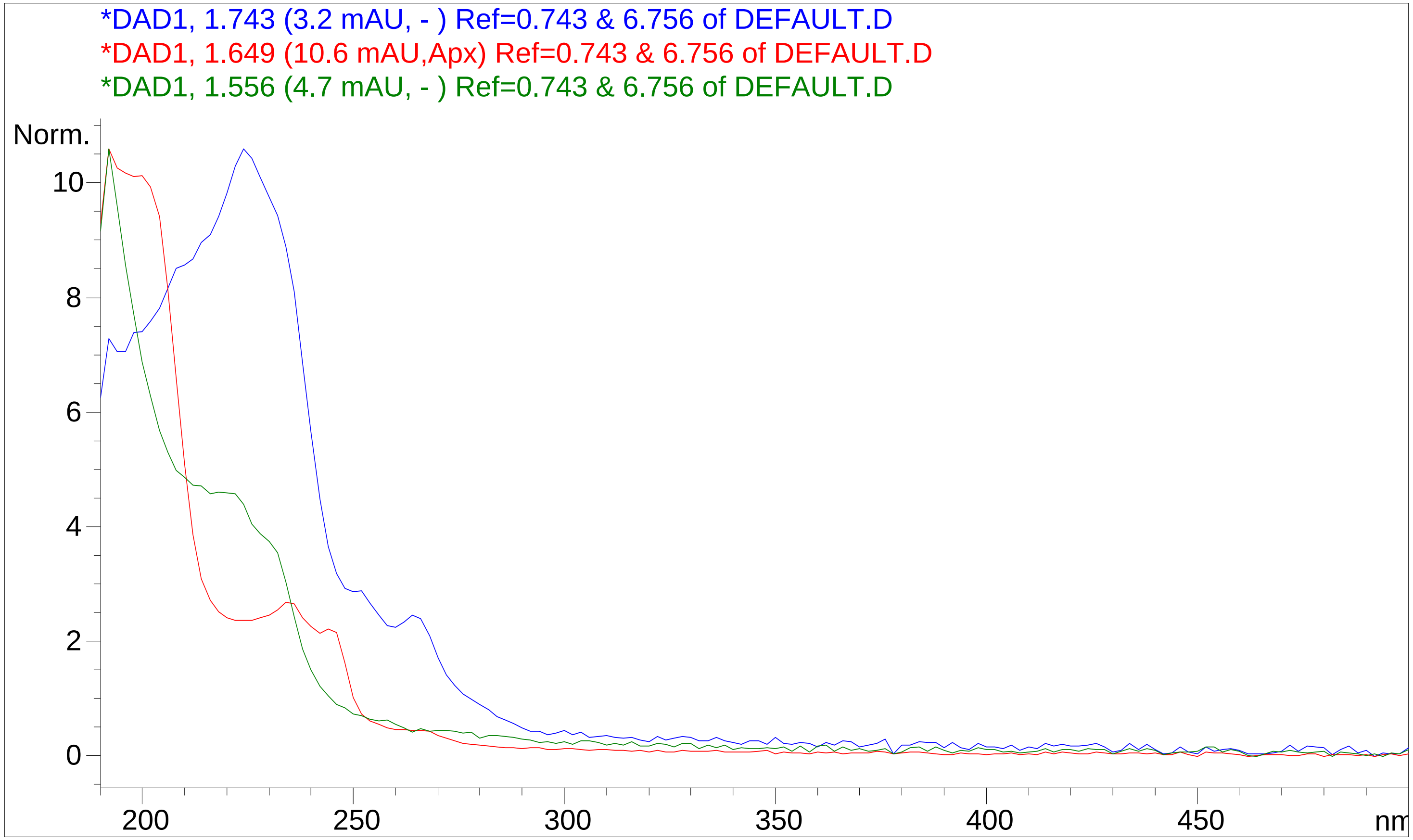
A- polyynes solution as prepared;

B- Ene-ynes solution after 5 min reduction of polyynes with Zn/HCl;

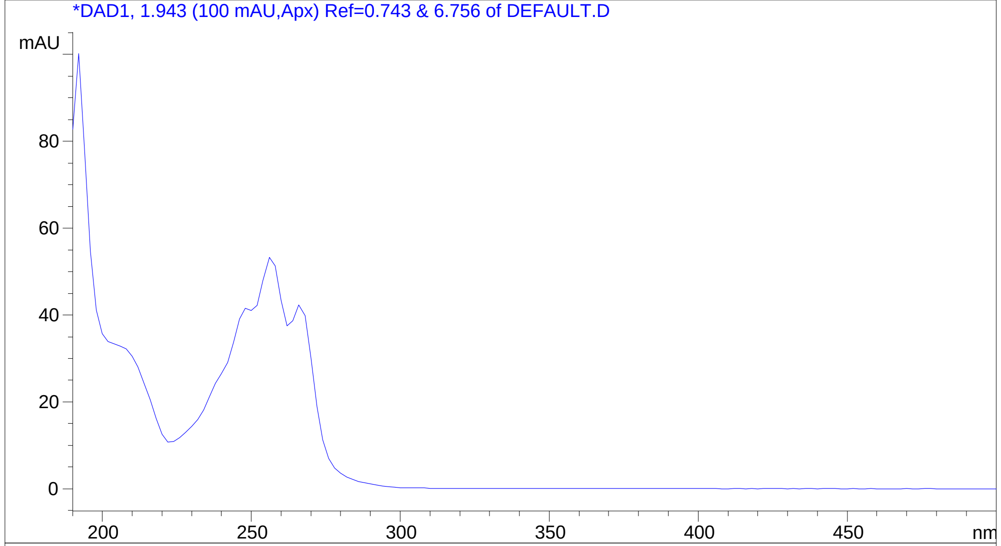
C- Ene-ynes solution after prolonged treatment with Zn/HCl;

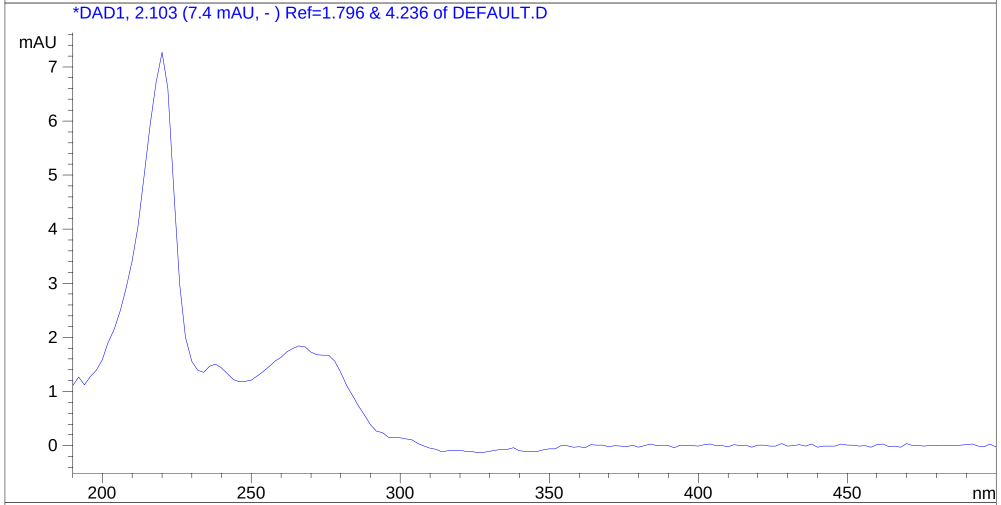
D- Ene-ynes solution left overnight in contact with Zn/HCl solution;

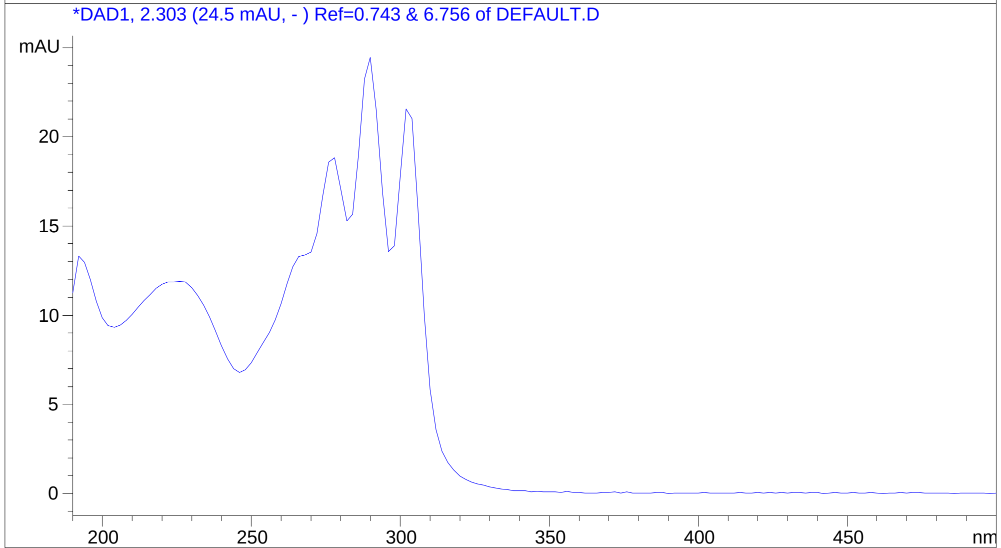
E- Difference spectrum between ene-ynes solution and original polyynes solution.



Electronic absorption spectra recorded by the diode-array detector of the HPLC showing of two dienes and a triene (Rt = 1.743 min) present in the reduced mixture







Electronic absorption spectra recorded by the diode-array detector of the HPLC.

top - C_8 →

R–(C≡C)-(CH=CH)- (C≡C)-CH_2-CH_2-R’

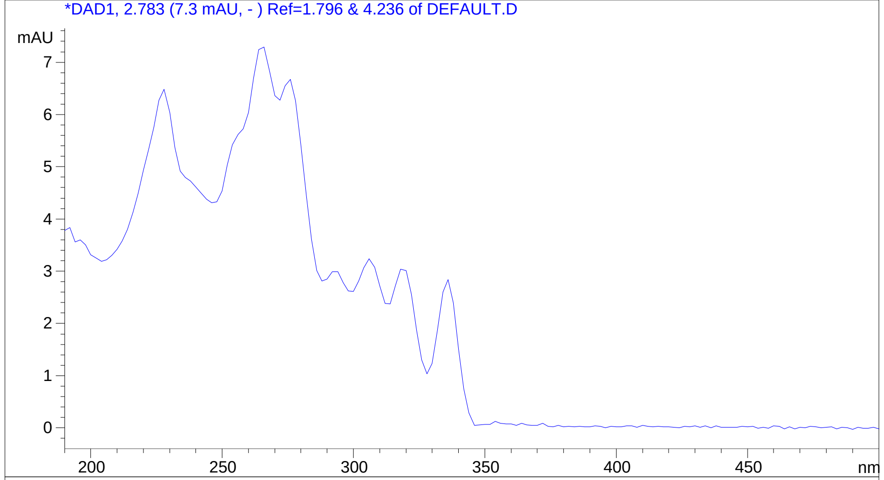
middle - C_8 →

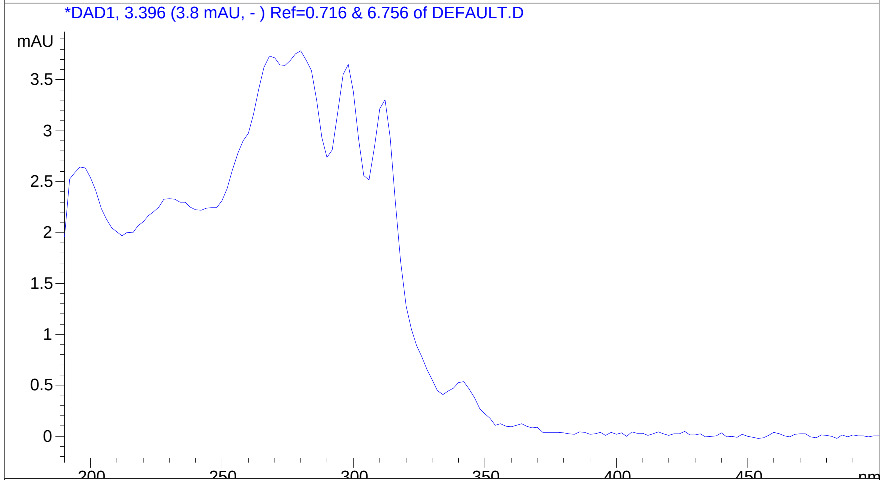
ene-yne not assigned or naphtalene?

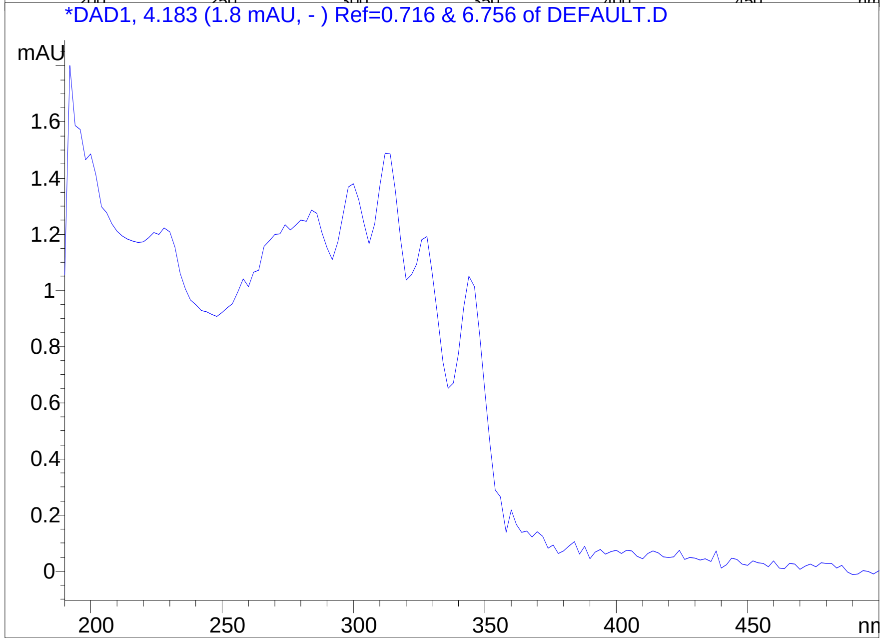
bottom - C_8 →

R-CH=CH-C≡C-C≡C-CH=CH-R’

(allene moiety possibly present



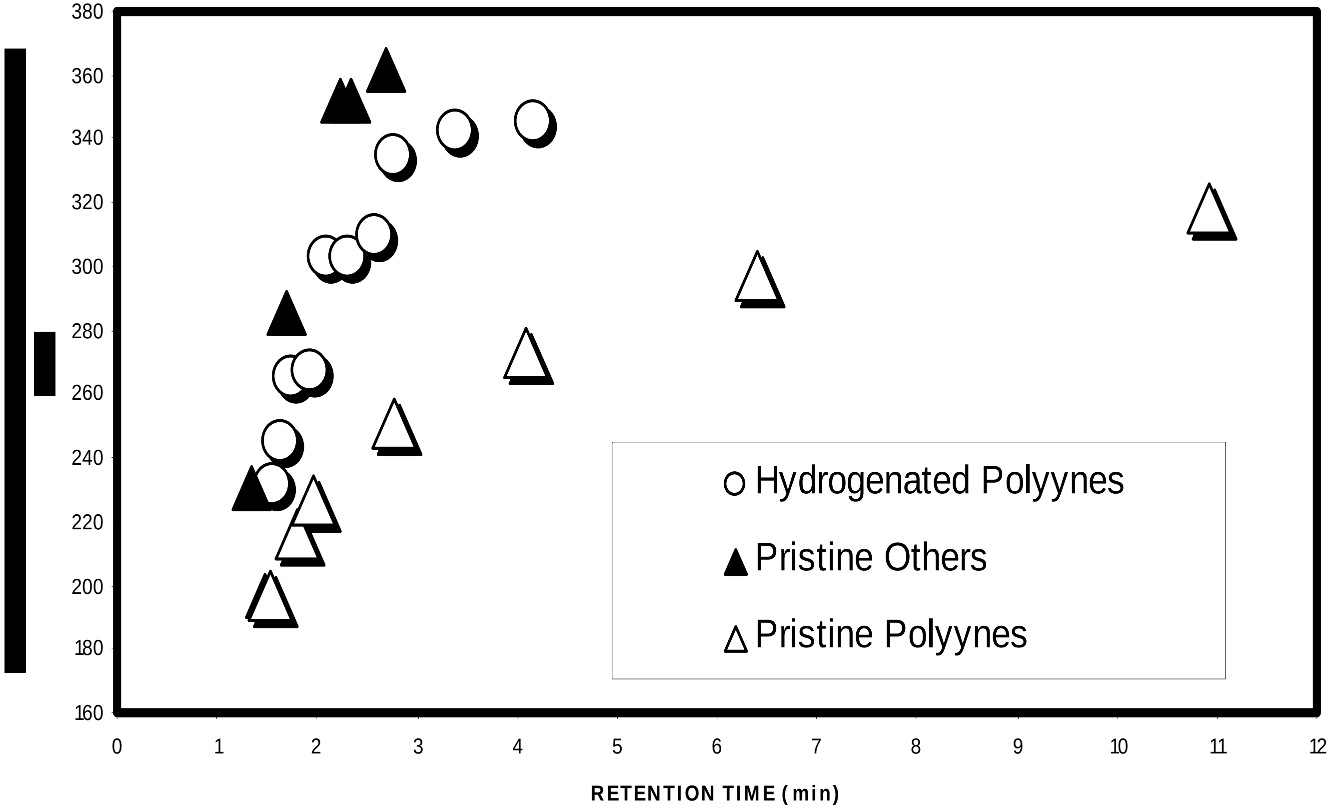




Electronic absorption spectra recorded by the diode-array detector of the HPLC

top C_{10} →
$R\text{-}CH{=}CH\text{-}(C{\equiv}C)_3\text{-}CH{=}CH\text{-}R'$ or
$R\text{-}(CH{=}CH)_2\text{-}(C{\equiv}C)_3\text{-}R'$
middle C_{10} →
$R\text{-}(CH{=}CH)_2\text{-}(C{\equiv}C)_2\text{-}(CH{=}CH)\text{-}R'$
bottom C_{12} →
$R\text{-}(CH{=}CH)_3\text{-}(C{\equiv}C)_3\text{-}R'$ or
$R\text{-}(CH{=}CH)_2\text{-}(C{\equiv}C)_2(CH{=}CH)_2\text{-}R'$

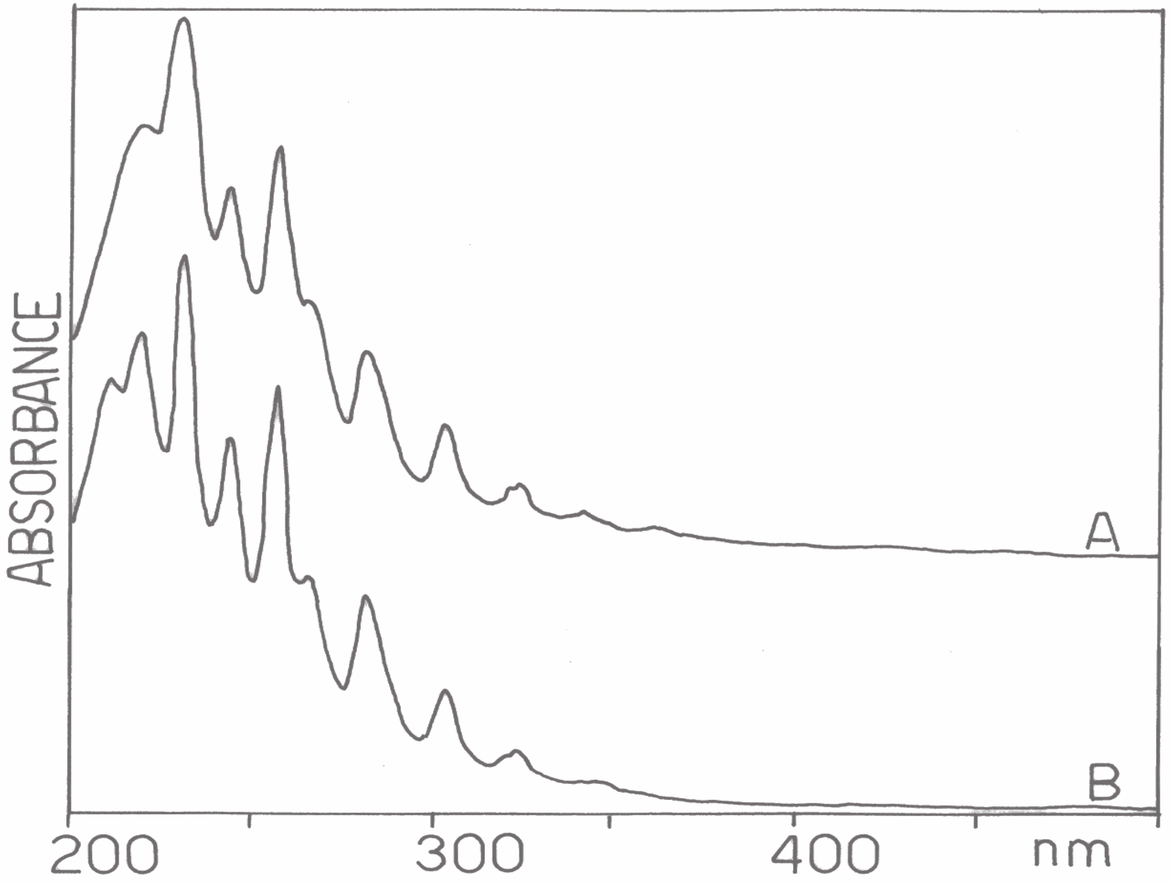
FIG.8 - RETENTION TIME OF POLYYNES AND HYDROGENATED POLYYNES IN HEXANE



Graph showing the longest wavelength peak in the electronic spectra of polyynes series produced in hexane (with the by-products) in comparison with the partially hydrogenated polyynes (ene-ynes) as function of the retention time in a C-8 column. This graph suggests that the by-products formed in hexane together with the polyynes are similar for certain instances to the partially hydrogenated polyynes.

OTHER POLYYNES DERIVATIVES

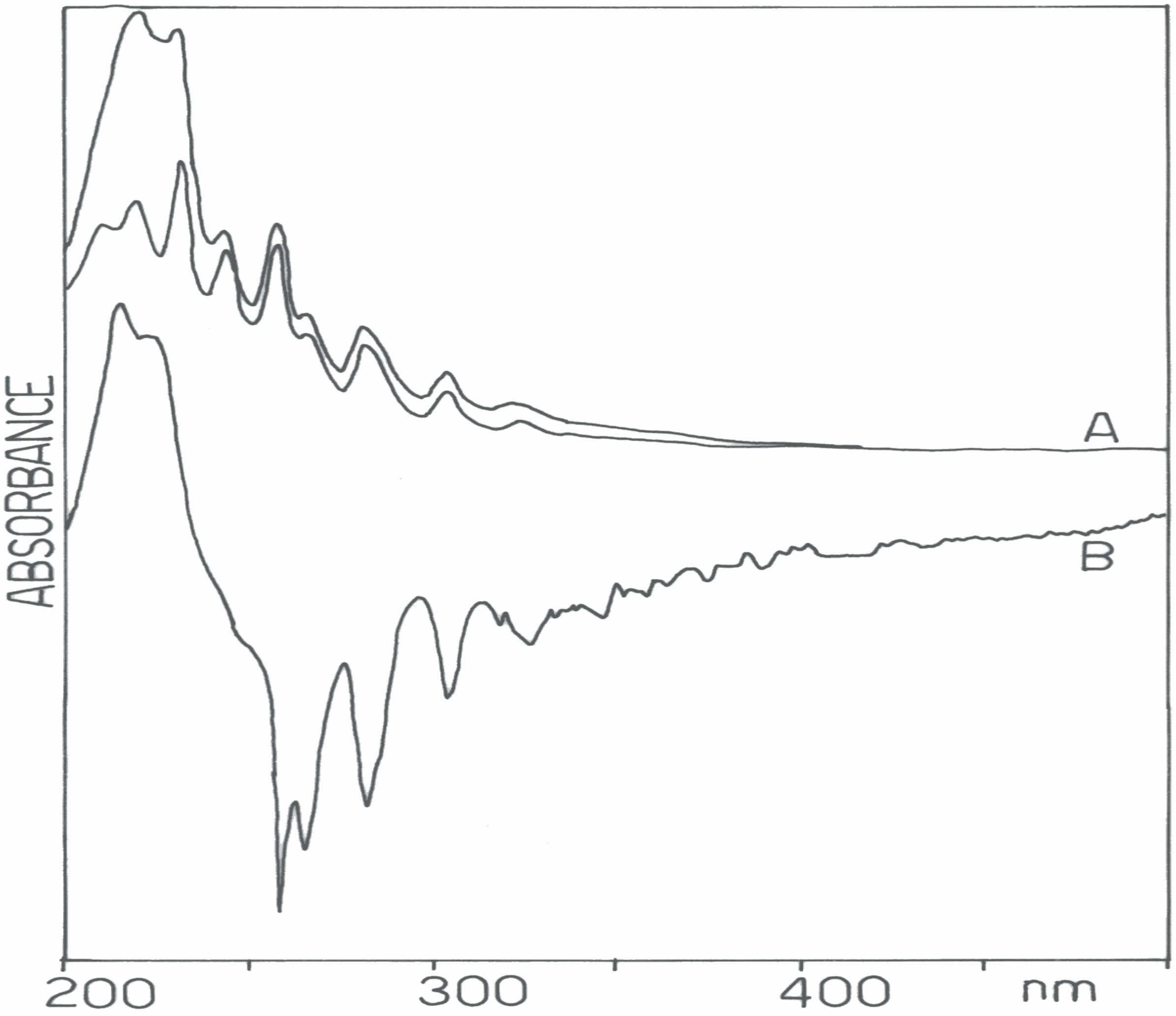
- Polyynes stability in air
- Reaction of polyynes with ozone
- Addition of Bromine to polyynes
- Photolysis of polyynes under the action of UV light.



Electronic absorption spectra in DHNP: study of the <u>stability in air</u>

A Freshly prepared solution of polyynes

B Same solution as 1A after 1week exposure to air in the dark

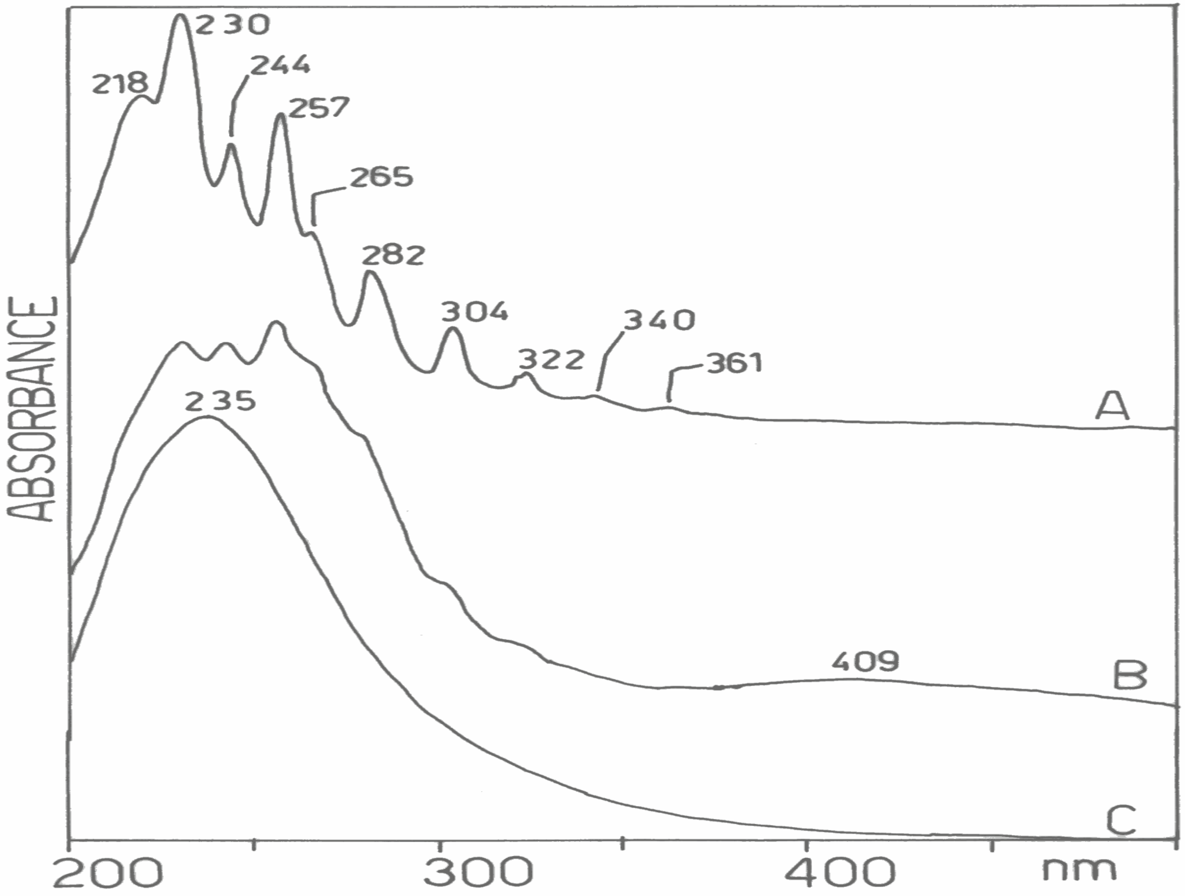


Electronic absorption spectra in DHNP: study of the O_3 oxidation

A – Bottom curve. Pristine solution of polyynes

A –Top curve. Solution of polyynes after the addition of ozone

B – Difference spectrum.



Electronic absorption spectra in DHNP: study of the Br$_2$ addition

A Pristine solution of polyynes

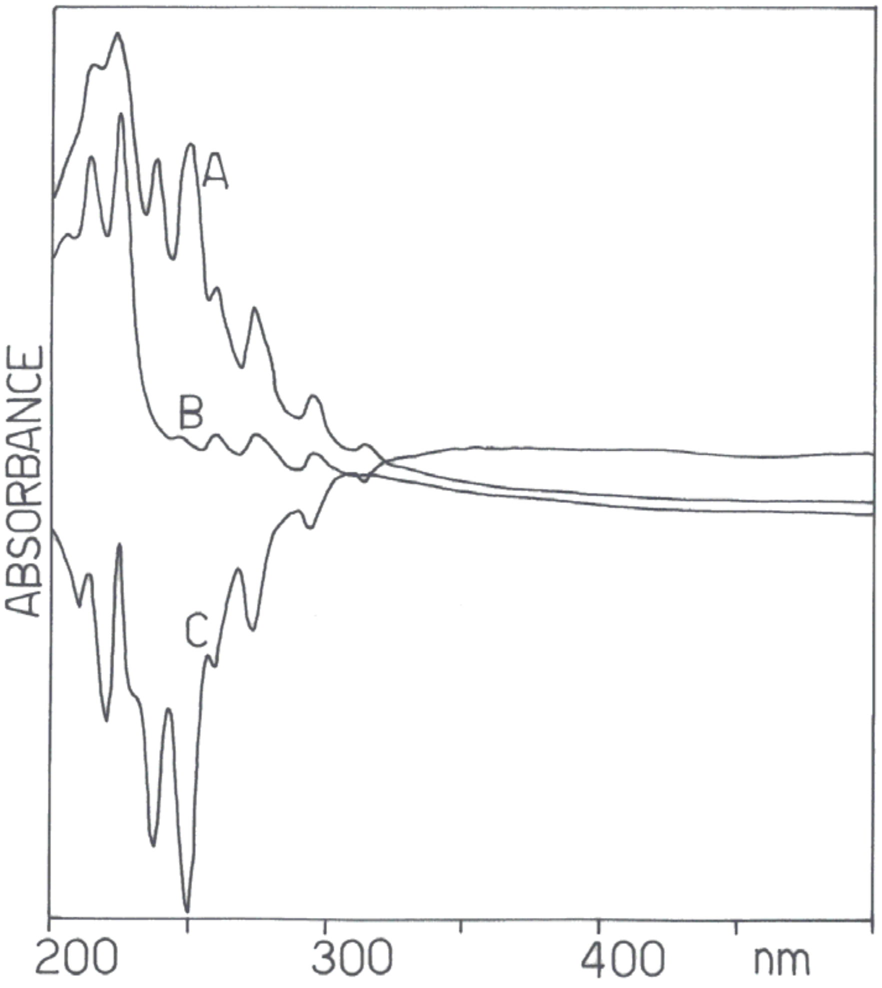
B Polyyne solution few minutes after the addition of bromine

C Polyyne solution after the complete addition of bromine (left overnight)

Electronic absorption spectra in CH3CN / H2O of polyynes photolyzed with a low pressure Hg lamp in air. Main emission 254 nm.

A- Top curve. Pristine solution of polyynes

A –Bottom curve. Solution of polyynes after 90 min photolysis



Electronic absorption spectra in n-hexane of polyynes photolyzed with a low pressure Hg lamp in air. Main emission 254 nm.

A – From top to bottom absorption spectra taken before and after 21, 27 and 83 min photolysis.

B-D Difference spectra (with respect to the pristine solution spectrum) after 21, 27 and 83 min photolysis.

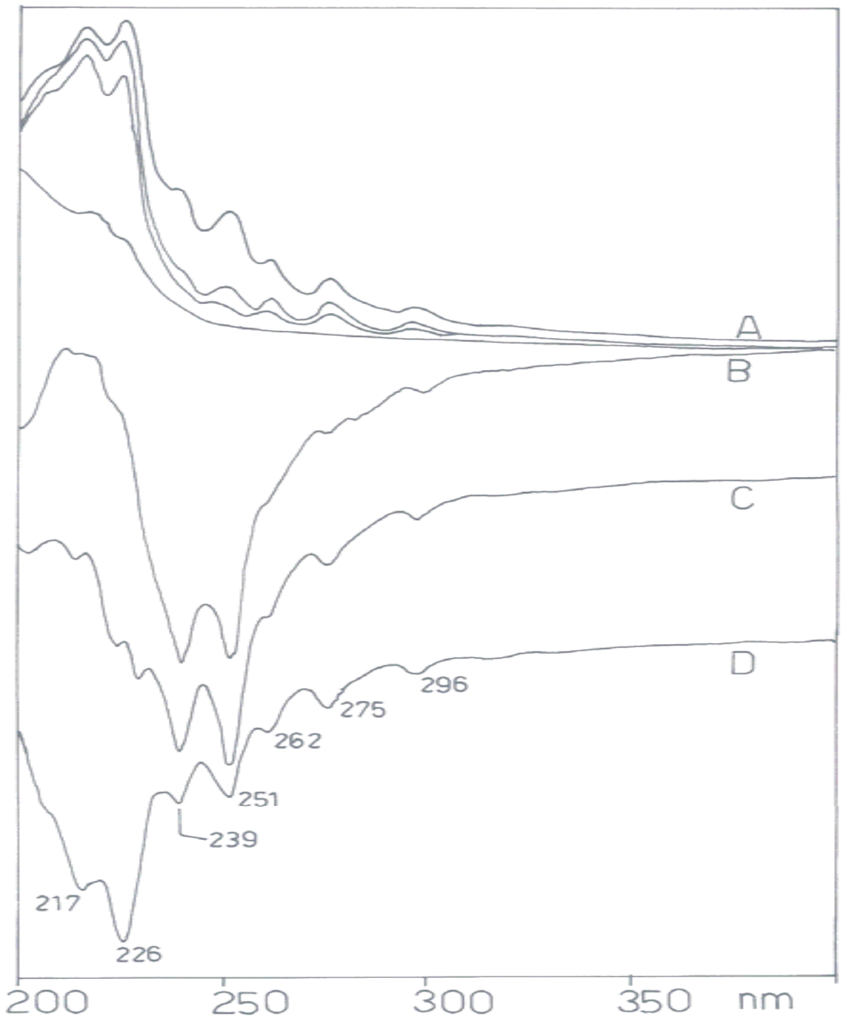
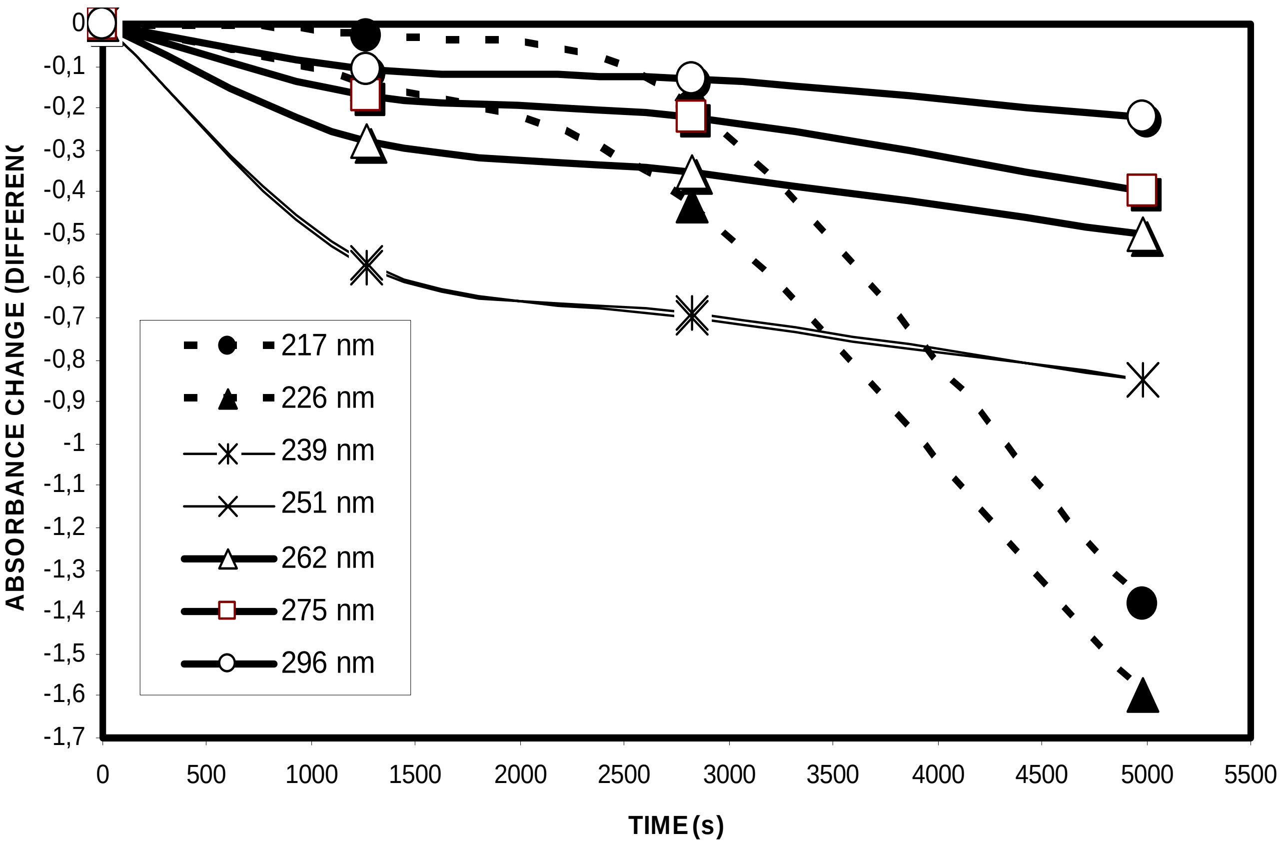


FIGURE 6 - POLYYNES PHOTOLYSIS IN HEXANE (LOW P LAMP)



Graph reporting the data of polyynes photolysis in n-hexane under the action of a low pressure Hg lamp (254 nm). The decay of the absorption bands of the pristine spectrum as function of the photolysis time.

Electronic absorption spectra in n-hexane of polyynes photolyzed with a high pressure Hg lamp in N_2.

A – From top to bottom absorption spectra taken before and after 26, 50, 75 and 160 min photolysis.

B-E Difference spectra (with respect to the pristine solution spectrum) after 26, 50, 75 and 160 min photolysis.

The decay of the absorption bands of the pristine spectrum as function of the photolysis time. Main lamp emission at 365, 297-313, 265 nm.