Synthesis and properties of some novel unsymmetrically substituted diacetylenes

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A variety of diacetylenes have been prepared and characterized. Both symmetrically and unsymmetrically substituted types are discussed with regard to their polymerization and to their potential as liquid crystalline or optoelectronic materials.

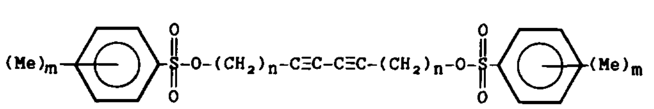
(Keywords: diacetylenes; polydiacetylenes; liquid crystals; optoelectronics)

INTRODUCTION

The current extensive interest in diacetylenes and polydiacetylenes began with the work of Wegner[1] who found that the polymerization of certain diacetylenes occurred in the solid state. The first diacetylenes to polymerize were those of the symmetrical type R—C≡C—C≡C—R, but in order to achieve polymerization the monomer had to crystallize in a suitable form[2,3].

SYMMETRICAL DIACETYLENES

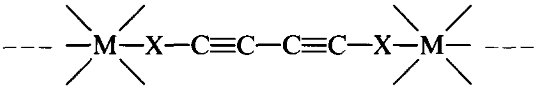
Studies first conducted at Napier Polytechnic involved the synthesis and X-ray crystallographic determination of a series of diacetylenes of the form[4–8]:



$1 < n < 4$ and $1 < m < 5$

Diacetylenes and polydiacetylenes which are highly conjugated and of rigid molecular structure can be readily made, and in recent years much effort has been channelled into the investigation of the electrical conduction[9], optoelectronic behaviour[10] and the liquid crystallinity of these compounds.

Metal complex polymers of the form:



$$---\ -M-X-C\equiv C-C\equiv C-X-M-\ ---$$

have been made where M = Fe, Co, Cu and Zn, and X = 4-pyridyl, 4-aminocyclohexyl and 1-amino-1-methylethyl.

Metal complexes of symmetrical diacetylenes. Experimental

(**1**) *1,4-Bis(4-aminocyclohexyl)butadiyne.* (a) This ligand was prepared by the addition of an aqueous solution of copper(I) chloride and ammonium chloride to a solution of 4-ethynylcyclohexylamine in 2 M hydrochloric acid. Addition of concentrated ammonium hydroxide and extraction with ether yielded a yellow/brown product which on recrystallization from ethanol/water gave white crystals.

(b) Reaction of the product from (a) with the appropriate metal halide or thiocyanate in warm ethanol gave the copper(II), cobalt(II) and nickel(II) complexes.

(**2**) *1,4-Bis(4-pyridyl)butadiyne.* The method of Ciana and Haim[11] was used to synthesize the ligand from 1-ethynylpyridine. The ligand was then refluxed with salts of copper(II), nickel(II) and cobalt(II) in ethanol to yield the resultant complexes.

(**3**) *1,6-Diamino-1,1,6,6-tetramethyl-2,4-hexadiyne.* The diacetylene 1,6-diamino-1,1,6,6-tetramethyl-2,4-hexadiyne was prepared from 1,1-dimethylpropargylamine. The corresponding metal complexes were then prepared by reaction of this ligand with solutions of cobalt(II), nickel(II) and copper(II) chlorides and thiocyanates in ethanol.

The crystal structures of the ligands **1**, **2**, and **3** were solved using the SHELX 86 programmes after collection of X-ray diffraction data on a ENRAF-NONIUS CAD-4 diffractometer. These results are reported elsewhere[12–14].

The metal ion content of the prepared complexes was determined by atomic absorption spectroscopy on a Perkin-Elmer 373 atomic absorptiometer; the CHN analyses were carried out on a Carlo-Erba Elemental Analyser. Electronic spectra were obtained on a Beckman ACTA MIV spectrophotometer, and magnetic moments were obtained using the Gouy method. Infra-red (i.r.) absorption spectra were obtained from KBr and polyethylene discs on a Perkin-Elmer 598 spectrophotometer.

UNSYMMETRICAL DIACETYLENES

Liquid crystallinity of a series of symmetrically substituted diacetylenes and the corresponding polymers in which the substituted group is either cholesteric or of similar form has been investigated[15]. More interestingly it was found that some unsymmetrically substituted diacetylenes displayed liquid crystalline behaviour.

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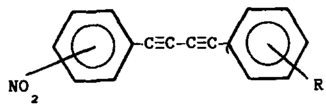
Unsymmetrical diacetylenes of the form:

$$R{-}C{\equiv}C{-}C{\equiv}C{-}R'$$

have been prepared using the method developed by Cadiot and Chodkiewicz[16]. The series investigated was:

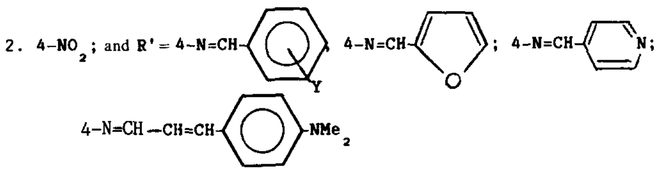


(I)

with substituents:

1. 4-NO_2; and R' = 4-NH_2; 2-,4-OMe; 4-Br; 2-OH.

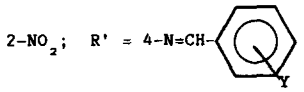
2-NO_2; and R' = 2-,4-NH_2; 2-,4-OMe; 2-OH.



2. 4-NO_2; and R' = 4-N=CH-, 4-N=CH-; 4-N=CH-N;

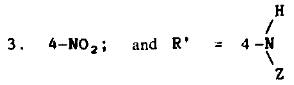
4-N=CH—CH=CH-NMe_2

with Y = 4-OMe; 2-,4-OH; 3-OMe-4-OH; 3,4-OCH_2O-; 4-CHO.

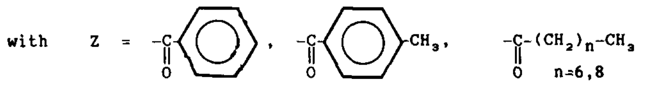


2-NO_2; R' = 4-N=CH-

with Y = 4-OMe; 2-OH.



3. 4-NO_2; and R' = 4-N(H)(Z)



with Z = $-\underset{\|}{C}(O)-C_6H_5$, $-\underset{\|}{C}(O)-C_6H_4-CH_3$, $-\underset{\|}{C}(O)-(CH_2)_n-CH_3$ n=6,8

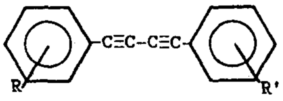
The compounds in *Table 1* showed solid-state polymerization. The imines (type 2) and the amides (type 3) were synthesized from the diacetylene I, 4—NO_2, R'=4—NH_2 (ref. 17).

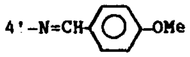
Almost all of the compounds of types 2 and 3 polymerized in the liquid crystal state; the onset of liquid crystal state polymerization is exemplified by the results shown in *Figure 1* (ref. 17) for imine **2**, Y=4—OMe where peak A represents the formation of the smectic mesophase and peak B the polymerization of the nematic mesophase.

A photomicrograph between crossed polars of this compound is shown in *Figure 2*. Nematic polymer phase (A) is growing from smectic monomer phase B at 225°C.

Further studies have been carried out in which the —NO_2 moiety of the diacetylene has been replaced by —CN. Similar results were obtained.

Table 1 Solid-state polymerization of:



		Solid state polymerization		
R	R'	Heat	Ultraviolet	Visible
4—NO_2	2'—OMe		✓	✓
2—NO_2	2'—OMe		✓	✓
4—NO_2	2'—OH	✓		
2—NO_2	 4'-N=CH-⟨ ⟩-OMe		✓	✓

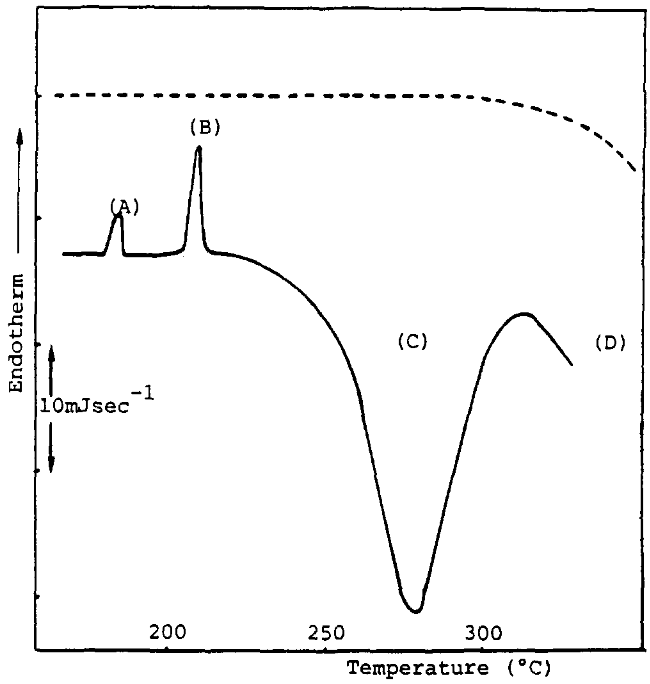
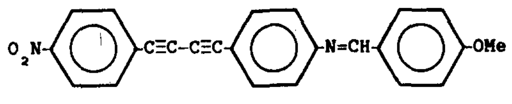


Figure 1 Thermogram (---) and d.s.c. of (—) of:



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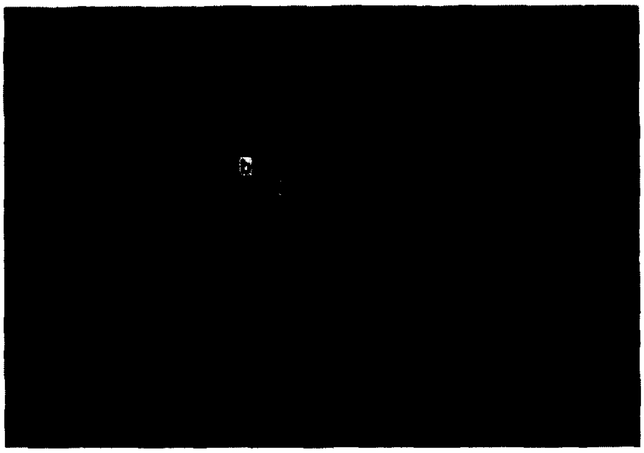
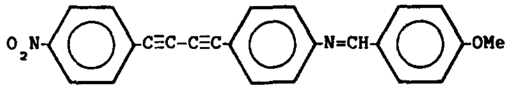


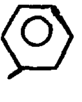
Figure 2 Photomicrograph (×67) of:



between crossed polars at 225°C. a, nematic polymer phase; b, smectic monomer phase

The results of optoelectronic studies are shown in *Table 2*.

These results have been obtained by rapid scan $\chi^{(2)}$ measurements on powder samples in a KCl disc matrix and show that to date, only the diacetylene with 4—NO_2,

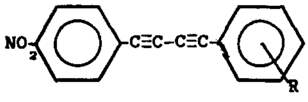


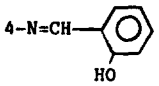
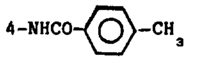
R'=4—N=CH— is comparable to standard nitroanilines.

Experimental

Infra-red spectra were recorded and CHN analyses carried out as described previously. Thermal studies used a Mettler DSC30 low temperature cell and a Mettler

Table 2 Results of optoelectronic studies with:



Compound	SHG	Standard	SHG
R = 2—OMe	0.01	mNa[a]	0.59
4—OMe	0.03		
4—Br	0.10	BNB[b]	0.02
	0.33		
4—NH_2	0.10		
	0.01		
4—$NHCO(CH_2)_6CH_3$	0.07		

[a] mNa = 3-nitroaniline
[b] BNB = 1-bromo-3-nitrobenzene

TC10A automated data processor and results were confirmed by dynamic thermal analysis and thermogravimetric analysis, carried out on a Stanton Redcroft STA-780 thermal analyser. Optical studies were carried out on a Nikon Optiphot-Pol polarizing microscope equipped with a Linkam TH600 hot-stage at various magnifications.

Molecular weights were determined by gel phase chromatography in tetrahydrofuran solution. Details of the synthesis and analysis are reported elsewhere[17,18].

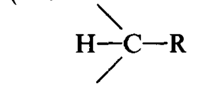
CHIRAL DIACETYLENES

The polarization *P* induced in bulk media by an external field *E* can be expressed as:

$$P = \chi^{(1)}E + \chi^{(2)}E.E + \chi^{(3)}E.E.E + \cdots$$

with high values of $\chi^{(2)}$ suggesting that the media may be applicable in devices such as modulators, second harmonic generators and parametric amplifiers[10].

In order to obtain high values of $\chi^{(2)}$ it is necessary for materials to crystallize in a non-centrosymmetric space group and one way to achieve this is to incorporate chiral centres within molecules. With this objective, a series of chiral diacetylenes of the form:



$$\left(\begin{array}{l} R'CONH \\ \quad\diagdown \\ \quad H—C—R \\ \quad\diagup \\ CO_2CH_2C{\equiv}C \end{array}\right)_2$$

have been prepared where R and R′ are alkyl and aryl units and several of these polymerize under ultraviolet radiation[19]. The optoelectronic properties of these compounds are currently under investigation.

Experimental

The synthesis of novel polydiacetylenes derived from the L-α-aminoacids valine, alanine and phenylalanine proceeded via the initial formation of propargyl amino acid 4-toluenesulphonate which was then reacted with acyl chlorides before carrying out oxidative coupling to the diacetylenes using copper(I) chloride and tetramethylenediamine in acetone.

Optical activity of the diacetylenes was measured on a Perkin-Elmer 141 automatic polarimeter and CHN analyses were carried out as described earlier. Infra-red spectra were recorded as KBr discs on a Perkin-Elmer 598 i.r. spectrometer. Solid state Raman spectra were recorded on a Cary-81 Raman spectrometer with a Spectrophysics argon laser ($\lambda = 174$ nm). Proton nuclear magnetic resonance (n.m.r.) spectra were recorded on Perkin-Elmer R128 or Bruker WP20057 spectrometers. Solid-state ^{13}C n.m.r. spectra were recorded on the SERC solid-state n.m.r. spectrometer at Durham University. Differential scanning calorimetry was performed as described earlier. Full details of the preparation and analysis of these materials are given elsewhere[19].

DISCUSSION

The metal complexes of diacetylene ligands are readily prepared but yield intractable coloured products. The crystal structures of the ligands show that they do not conform to the chain spacing requirements for solid-state polymerization[2,3].

Unsymmetrically substituted diacetylenes often exist in smectic and nematic mesophases which polymerize in the liquid state whereas the incorporation of diacetylenes into potentially liquid crystalline material does not always lead to liquid crystalline polymers. The monomers of these materials are sometimes $\chi^{(2)}$ active but the polymers are not. It is suspected that the polymerization in the liquid crystalline state may proceed by an alternative route to that observed in the solid state.

Using chirally controlled synthetic methods, diacetylenes with L-α-amino acid units may be prepared which polymerize readily under ultraviolet light and because of their essential asymmetric crystal structures should be $\chi^{(2)}$ active. Further studies on these materials are being carried out.

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