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Liquid Crystals

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Thermotropic diacetylenic liquid crystals

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Thermotropic diacetylenic liquid crystals

by G. H. W. MILBURN, C. CAMPBELL, A. J. SHAND
and A. R. WERNINCK

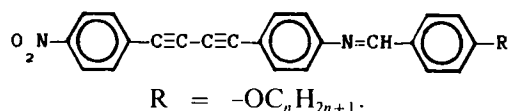
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Further studies are reported on polar diacetylenes with conjugated side chains which show liquid-crystalline behaviour. Results obtained using differential scanning calorimetry, thermogravimetry, and hot stage microscopy are reported. One group of materials forms a smectic liquid crystal phase and all polymerize from a nematic liquid crystal phase.

1. Introduction

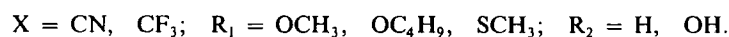
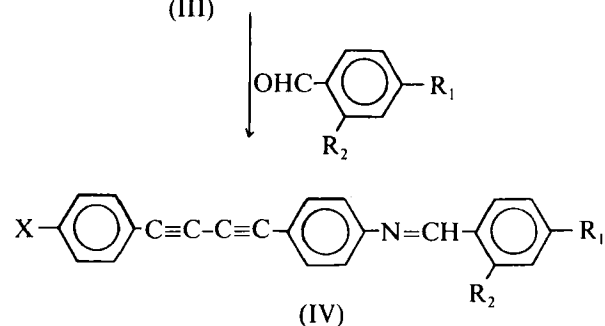
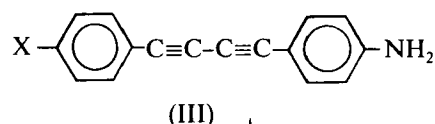
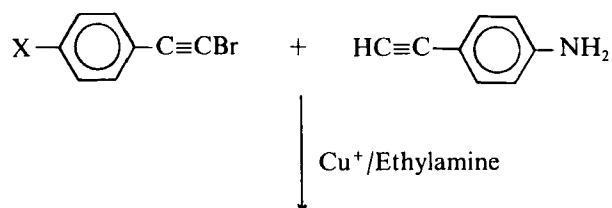
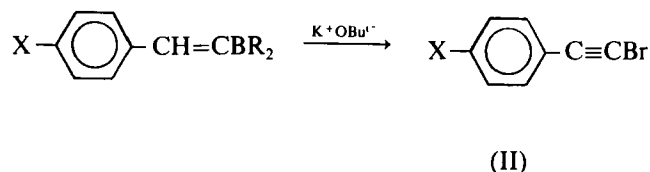
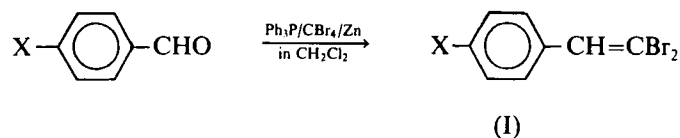
In recent years there has been extensive work reported on diacetylenes with liquid-crystalline properties [1-12]. We have reported [13, 14] the synthesis and evaluation of liquid-crystalline diacetylenes of the type:



The extensive conjugation and the polarity of these diacetylenes is associated with high non-linear optical coefficients and large values have been found for these [14]. This paper reports on similar materials where the electron withdrawing group is $-\text{CN}$ or $-\text{CF}_3$ in place of $-\text{NO}_2$. Such materials are expected to be both liquid-crystalline and to possess high values of the non-linear optical coefficients. This study is, therefore, an extension of our work on structure-property relationships of such diacetylenes. The central aim is the lowering of the temperature at which a mesophase appears and to obtain more ordered smectic rather than the less ordered nematic liquid-crystalline phases. A monomer of high smectic order may form a polymer of lesser liquid-crystalline order.

2. Experimental

The synthesis of the 1-bromoacetylene (II) is based on the procedure of Corey and Fuchs [15] and is outlined in Scheme 1. This synthesis is a general procedure based on the Wittig reaction for the preparation of aryl and alkylacetylenes from aldehydes. (II) ($X = \text{CN}$) has been reported by Grant *et al.* [10].



Scheme 1.

2.1. Preparation of compound (II)

Triphenylphosphine (26.1 g, 0.1 mol) was added, in portions, to a stirred mixture of carbon tetrabromide (33.2 g, 0.1 mol) and zinc powder (6.5 g, 0.1 mol) in sodium dried dichloromethane (340 cm³). The suspension was stirred for *c.* 48 hours until a pale purple colour developed. 4-cyanobenzaldehyde (6.5 g, 0.05 mol) or 4-trifluoromethylbenzaldehyde (8.70 g, 0.05 mol) was then added to this mixture and stirring was continued for *c.* 2 hours. A deep purple colour developed as the reaction proceeded. The solutions were filtered and the solvent removed under reduced pressure. Pentane in 2 dm³ portions was added to extract the β,β' -dibromostyrenes (I). After filtration, the solvent was removed under reduced pressure.

(i) *Isolation of 4-cyano- β,β' -dibromostyrene*

The dirty white solid obtained on removal of pentane was dissolved in *c.* 50 cm³ of dichloromethane. After filtration, pentane was added to the solution until permanent turbidity existed. The mixture was cooled to -10°C and filtered. Solvent was removed under reduced pressure to yield a slurry which was allowed to dry in air to give a solid; m.p. $82\text{--}84^{\circ}\text{C}$.

(ii) *Isolation of 4-trifluoromethyl- β,β' -dibromostyrene*

The pale yellow liquid obtained after removal of pentane was vacuum distilled to give a colourless liquid b.p. $84\text{--}86^{\circ}/1\text{ mm Hg}$. The corresponding 1-bromoacetylenes were produced by refluxing equimolar proportions of the β,β' -dibromostyrenes with potassium *t*-butoxide in toluene for *c.* 5 hours. The 4-cyanophenyl-1-bromoacetylene was isolated by filtration and cooling to *c.* -78°C and collection of the precipitated product; m.p. $136\text{--}138^{\circ}\text{C}$. The 4-trifluoromethylphenyl-1-bromoacetylene was obtained by removing the solvent after cooling and filtering. The residual oil was vacuum distilled to yield the product; b.p. $54\text{--}55^{\circ}\text{C}/3\text{ mm Hg}$.

2.2. Preparation of diacetylenes (III) and (IV)

The diacetylenes (III) were prepared by Cadiot–Chodkiewicz coupling of product (II) with 4-aminophenylacetylene by the method previously reported [16]. The imines (IV) were synthesized by stirring the diacetylenes (III) with an excess of the appropriate aldehyde in ethanol for *c.* 2 hours, followed by filtration and recrystallization in ethanol.

2.3. Instrumental

The structures of the diacetylenes synthesized were confirmed by elemental analysis using a Carlo–Erba 1106 elemental analyser equipped with a Spectra Physics SP4100 computing integrator and by UV, IR, and NMR spectroscopy, using, respectively a Perkin–Elmer $\lambda 7$ spectrophotometer, a Perkin–Elmer 598 or 275 spectrophotometer and a Jeol GX 270 MHz spectrometer.

The thermal behaviour and liquid crystal studies reported herein were carried out, using:

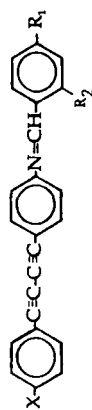
- (a) a Mettler DSC 30 low temperature cell with data processed by a Mettler TC10A automated data processor for differential scanning calorimetry (DSC);
- (b) a Stanton–Redcroft STA 780 thermal analyser for thermogravimetry (TG);
- (c) a Nikon Optiphot-Pol polarizing microscope fitted with a Linkam TH 600 hot stage and Nikon camera for optical microscopy.

3. Results and discussions

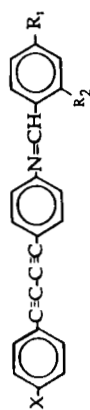
The compounds synthesized and representative analytical data are shown in tables 1 and 1(a); the data are in agreement with the structures shown.

The thermal behaviour of the diacetylenes (IV), is shown in a series of DSC thermograms (figures 1–6) and a set of thermogravimetry traces (figures 7 and 8) recorded with heating/cooling rates of 10 K min^{-1} under a nitrogen atmosphere. Figures 1 and 2 illustrate the effect of keeping the same electron withdrawing group while changing the electron donating groups. Figure 1 shows that an increase in the

Table 1. Diacetylenes



Compound	χ	R ₁	R ₂	Elemental analysis; found (calculated)				$\bar{\nu}(\text{N}=\text{C})/\text{cm}^{-1}$
				C/%	H/%	N/%	$\bar{\nu}(\text{C}\equiv\text{C})/\text{cm}^{-1}$	
IV (a)	CN	OCH ₃	H	80.35(83.31)	3.80(4.47)	8.54(7.77)	2200	1565
IV (b)	CN	OCH ₃	OH	79.04(79.79)	3.83(4.26)	8.61(8.51)	2200	1600
IV (c)	CN	OC ₄ H ₉	H	81.42(83.56)	4.49(5.51)	8.44(6.96)	2200	1565
IV (d)	CN	SCH ₃	H	79.89(79.79)	3.86(4.26)	8.28(8.51)	2200	1600
IV (e)	CF ₃	OCH ₃	H	73.93(74.07)	4.02(3.95)	3.69(3.46)	2210	1590
IV (f)	CF ₃	OCH ₃	OH	70.08(71.60)	3.78(3.85)	3.37(3.34)	2210	1595
IV (g)	CF ₃	OC ₄ H ₉	H	74.44(75.49)	4.85(4.98)	3.14(3.14)	2210	1595
IV (h)	CF ₃	SCH ₃	H	70.88(71.26)	3.73(3.80)	3.29(3.33)	2210	1590

Table 1 (a). Diacetylenes: ^1H NMR

Compound	χ	R_1	R_2	δ (Mult.)								
				-N=CH-	Arom. H	-OCH ₃	-OH	-OCH ₂	-CH ₂	-CH ₃		
IV (b)	CN	OCH ₃	OH	8.87(1)	7.2(m)	3.81(1)	13.21(1)					
IV (c)	CN	OC ₄ H ₉	H	8.70(1)	7.5(m)			4.07(3)	1.74(5)	1.45(6)	0.92(3)	
IV (f)	CF ₃	OCH ₃	OH	8.88(1)	7.0(m)	3.82(1)	13.25(1)					
IV (g)	CF ₃	OC ₄ H ₉	H	8.70(1)	7.5(m)			4.07(3)	1.74(5)	1.45(5)	0.92(3)	

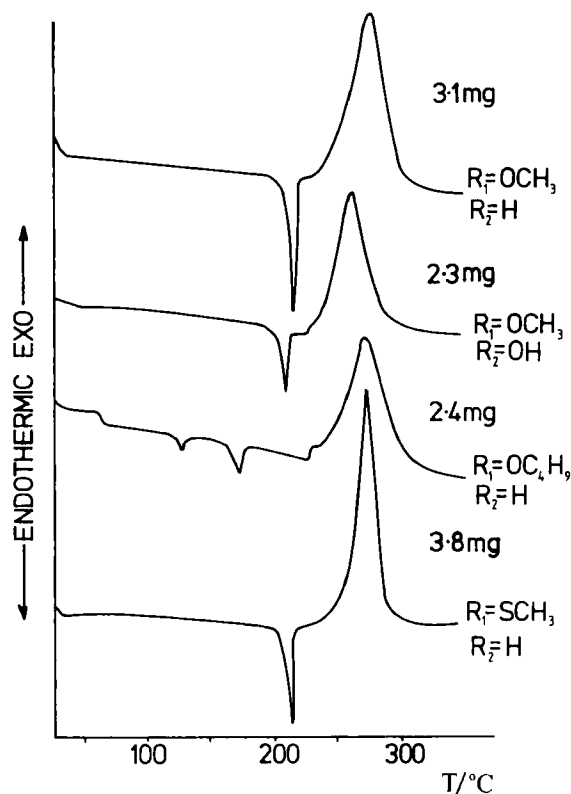
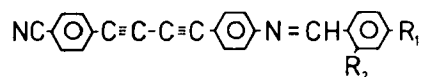


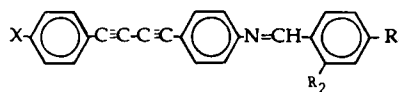
Figure 1. DSC Thermograms of



size of the R_1 group moves the endothermic transition to a lower temperature. Replacement of the oxygen atom by a sulphur atom causes little change; the large exotherm commences at 220–230°C. In figure 2, the same trends are observed with trifluoromethyl as the electron withdrawing group. However, replacement of a cyano group by a trifluoromethyl group lowers the temperature of the endothermic transition while slightly elevating the temperature of the exothermic transition. This is illustrated in figures 3 to 6. Quantitative data are displayed in table 2. The percentage weight loss between 50°C and 300°C was determined by thermogravimetry; the results of which are shown in figures 7 and 8.

The endothermic changes observed by polarizing optical microscopy are the result of a crystal to liquid crystal transition. Wu *et al.* [1] have shown, using DSC and optical microscopy that symmetrical dialkyldiphenyldiacetylenes are liquid crystalline, in agreement with the observations of Grant [11] who, in addition, examined the thermal behaviour of symmetrical dialkoxydiphenyldiacetylenes using only optical microscopy. The behaviour of the diacetylenes in this study is similar to those reported by Wu and Grant, namely, that an increase in the size of the alkoxy side chains lowers the crystal to liquid crystal transition temperature. Work on similar compounds giving parallel results has also been performed by Ozcayir *et al.* [12].

Table 2. Diacetylenes



Compound	X	R ₁	R ₂	Onset temperature/°C	Phase change	$\Delta H/\text{kJ mol}^{-1}$	% wt. loss
IV (a)	CN	OCH ₃	H	195 230	C-N	33 - 220	
IV (b)	CN	OCH ₃	OH	190 220	C-N	18 - 215	3
IV (c)	CN	OC ₄ H ₉	H	120 160 225	CI-III CII-N	4.4 14 (Double peak) 260	3
IV (d)	CN	SCH ₃	H	193 230	C-N	31 - 220	
IV (e)	F ₃ C	OCH ₃	H	157 229	C-S	20 - 150	
IV (f)	F ₃ C	OCH ₃	OH	135 145 250	CI-CII CII-S	4.5 18 - 230	2
IV (g)	F ₃ C	OC ₄ H ₉	H	140 160 250	C-S S-S	11 1.9 - 160	3.5
IV (h)	F ₃ C	SCH ₃	H	120 180 250	CI-III CII-S	3.5 15 - 140	

C, crystal; N, nematic; S, smectic.

The magnitudes of the endothermic phase transitions, with one exception, are below 20 kJ mol^{-1} . This is less than the solid to liquid phase transition enthalpy of 34.5 kJ mol^{-1} obtained by Barrall *et al.* [17] for the toluenesulphonate ester of 1,6-hexa-2,4-diindiol and is of a similar order to the enthalpies obtained by Wu *et al.* [1] and by Ozcayir *et al.* [12] for the crystal to nematic phase change for dialkyldiphenyldiacetylenes.

For the diacetylenes containing cyano groups (IV (a-d)), it is believed that the endothermic transitions denote changes from crystal to nematic liquid crystal and a photomicrograph showing threads characteristic of such phases is given in figure 9. However, for diacetylenes containing a trifluoromethyl substituent (IV (e-h)), a smectic liquid-crystalline phase is formed. All of these diacetylenes melt to a transparent homeotropic phase from which a smectic phase develops on continued heating. This is illustrated in figure 10 which shows a typical focal conic texture [18], in this case for compound (IV) (e). Table 2 shows that the enthalpy change associated with the endotherms of diacetylenes with trifluoromethyl groups is less than those for diacetylenes with cyano groups. This is in agreement with relative values expected for a crystal \rightarrow smectic phase transition as compared to a crystal \rightarrow nematic phase transition since smectic liquid crystals are intermediate in order between crystals and nematic liquid crystals.

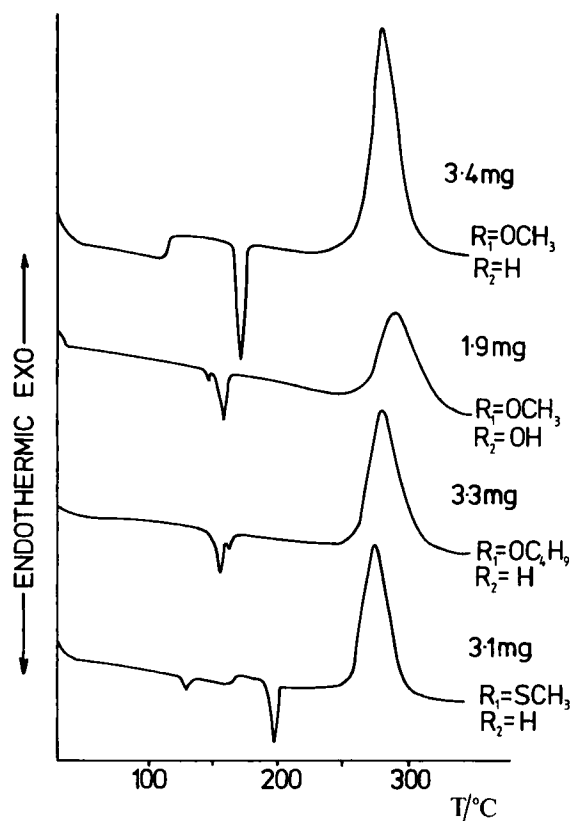
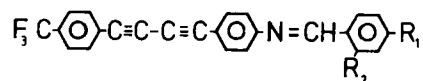


Figure 2. DSC thermograms of



Exothermic changes begin near 225°C for molecules with cyano groups and near 250°C for molecules with trifluoromethyl groups. The enthalpy changes measured by DSC for these exotherms vary in the range -170 kJ mol^{-1} to -220 kJ mol^{-1} . With diacetylenes, such high temperature exotherms may be due to polymerization and/or degradation. Diacetylenes polymerize thermally by 1:4 addition process [19] between neighbouring molecules when these have reactive points within about 4 \AA of each other [20, 21]. This is only realized in the solid state for a few diacetylenes, in the liquid state and in regular films such as Langmuir Blodgett films [19, 22]. It conceivable therefore that polymerization could occur in smectic layers, particularly if the orientation of the molecules is suitable and thermal motion is considerable as would be expected at the high temperatures of these exotherms. Random thermal polymerization is also possible with nematics and the results of our microscopy studies tend to show this as we describe later.

The magnitudes reported for the enthalpy of polymerization, ΔH_p of diacetylenes in the solid state are less than those found in this study. Chance *et al.* [23] report a value of -152 kJ mol^{-1} and Garito [24] a value of -162 kJ mol^{-1} using symmetrical diacetylenes while Bertault *et al.* [25] report similar values for unsymmetrical diacetylenes. However, Garito [26] does state that ΔH_p for a series of diphenyldivinyldiacetylenes of the symmetrical conjugated structure $\text{ArCH}=\text{CH}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CH}=\text{CHAr}$ is greater than the magnitude of ΔH_p commonly found.

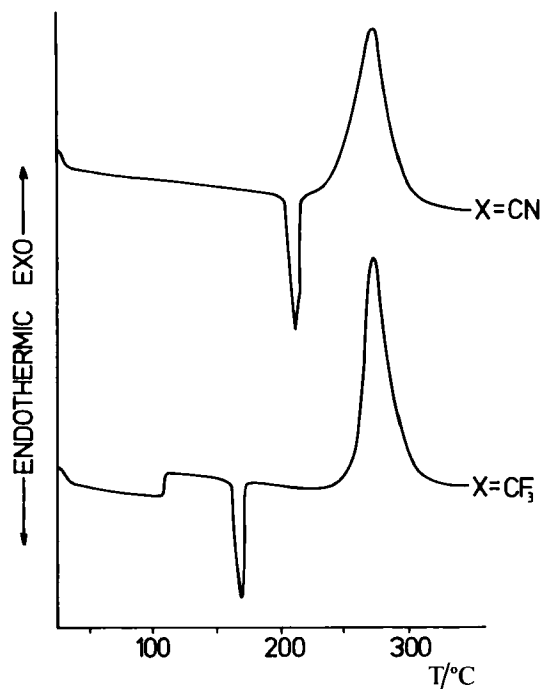


Figure 3. DSC thermograms of
 $X-\text{C}_6\text{H}_4-\text{C}=\text{C}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{N}=\text{CH}-\text{C}_6\text{H}_4-\text{OCH}_3$

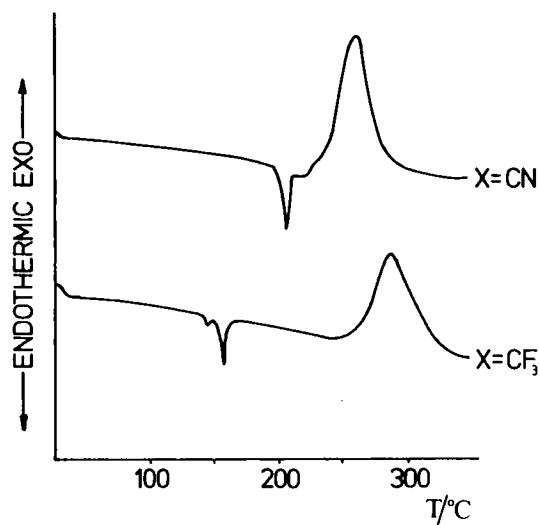


Figure 4. DSC thermograms of
 $X-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{OCH}_3$
 HO

Examination of the materials formed by heating these diacetylenes to temperatures beyond that of the exotherm shows them to be red, transparent and generally glassy. They do not have the characteristic appearance of pTS but as they are insoluble in common organic solvents, colligative properties or viscosity methods

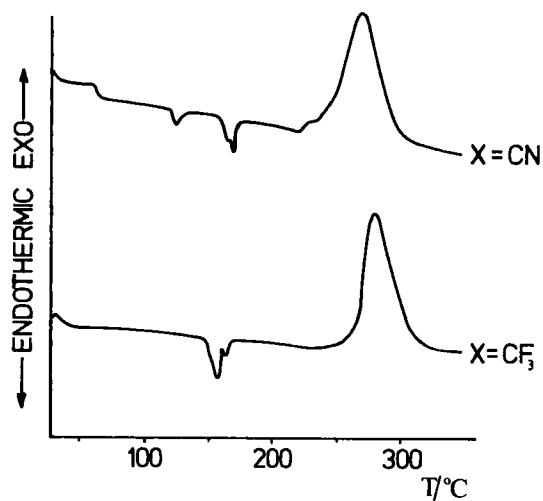


Figure 5. DSC thermograms of

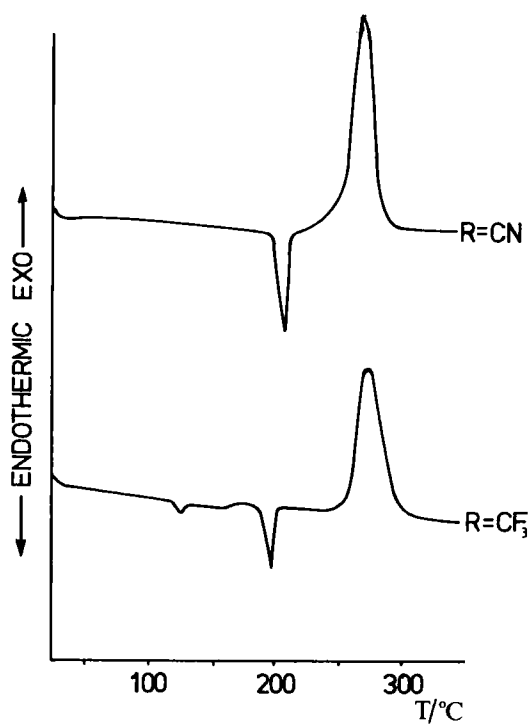
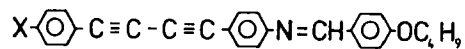
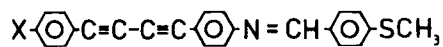


Figure 6. DSC thermograms of



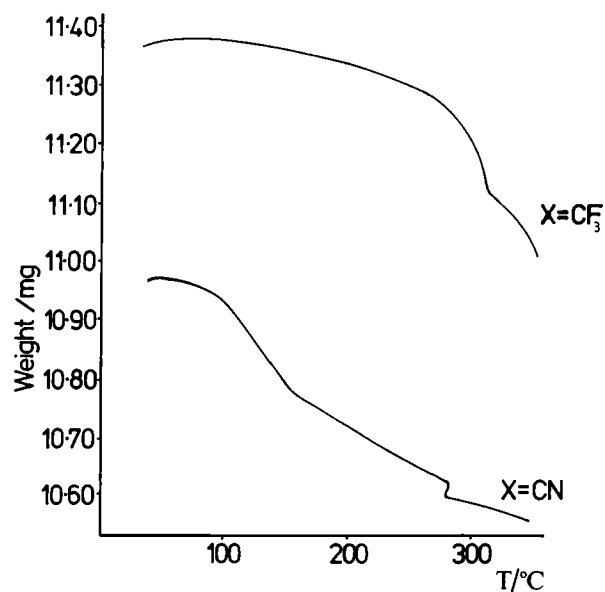


Figure 7. Thermogravimetry results for

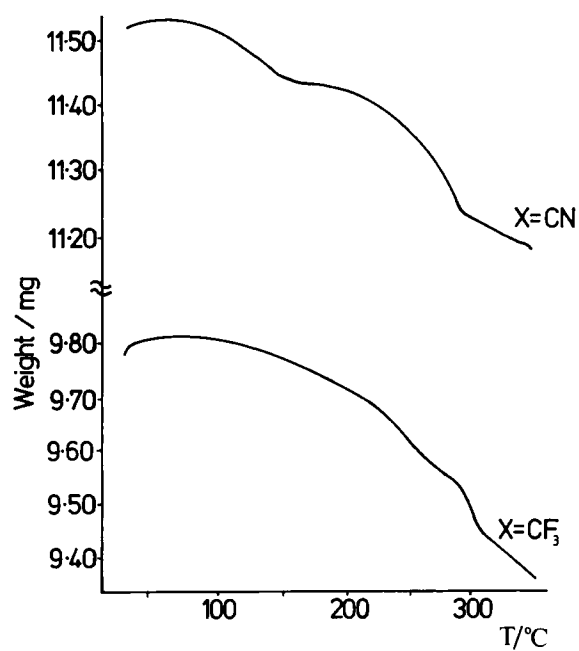
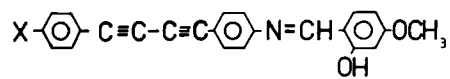


Figure 8. Thermogravimetry results for

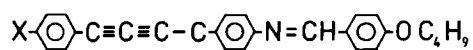




Figure 9. Photomicrograph of:
 $\text{NC}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{N}=\text{CH}-\text{C}_6\text{H}_4-\text{OC}_2\text{H}_5$
 showing the appearance of a nematic texture at *c.* 200°C.

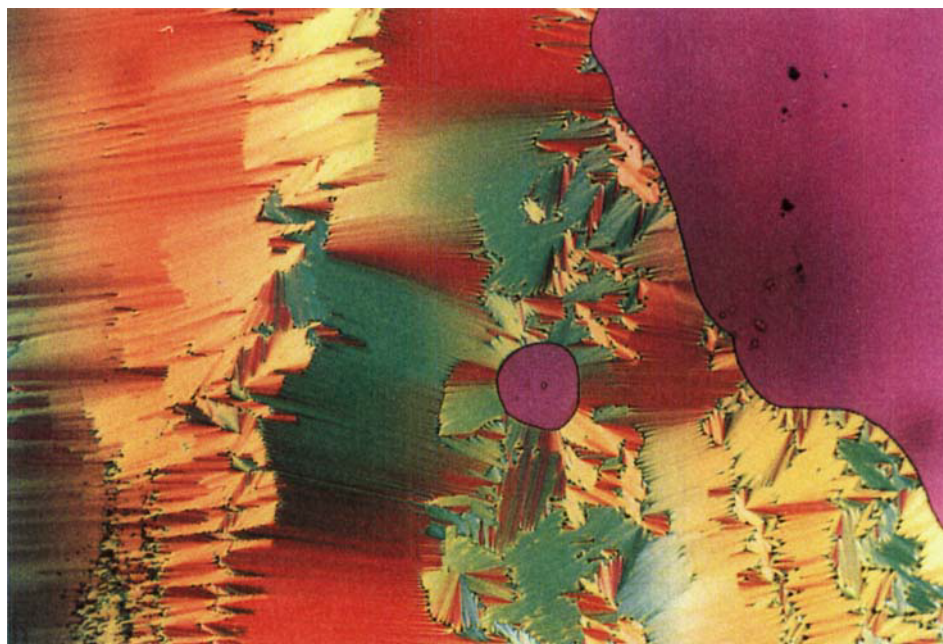


Figure 10. Photomicrograph of:
 $\text{F}_3\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{N}=\text{CH}-\text{C}_6\text{H}_4-\text{OCH}_3$
 showing the appearance of a smectic texture at *c.* 226°C.

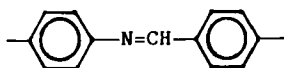


Figure 11. Photomicrogram of:

$$\text{F}_3\text{C}-\text{C}_6\text{H}_4-\text{C}=\text{C}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{N}=\text{CH}-\text{C}_6\text{H}_4-\text{SCH}_3$$

showing a schlieren texture at 257°C in the non-polymerized area which is a homeotropic nematic phase (by shearing).

cannot, as yet, be employed to determine average molar masses. The results of the thermogravimetry studies show small percentage weight losses implying some degree of degradation has occurred. The nature of the degradation is not clear and further investigations into the effects of heating these compounds to 280°C are in progress. Compounds with the structural fragment:



seem to be very stable to thermal degradation. Recent work on polyazomethines confirm the thermal stability in a nitrogen atmosphere to beyond 300°C [27–29].

The optical microscopy studies of diacetylenes containing the CF_3 group show an interesting pattern of phase changes on heating. Figure 10 exemplifies the appearance of a focal conic liquid-crystalline texture. This phase formed from a homeotropic phase at relatively elevated temperatures, around 210°C in this case. The formation of this homeotropic phase corresponds to the sample melting endotherms observed in the DSC studies.

When the samples were further heated, the smectic phase texture was observed to collapse to a birefringent fluid with no obvious texture. Some transparent regions were also observed. On shearing the cover slips, a schlieren texture could be observed, indicative of the formation of a nematic phase. An example of this is shown in figure 11 (IV (h)) at 257°C. The brown area to the right of the nematic region is material which has already changed. This material shows no birefringence and does not flash on shearing the sample between coverslips so it is clearly not liquid-crystalline.

The endotherm expected for the liquid crystal change from smectic to nematic phases is absent from the DSC results but is believed to be hidden within the large exothermic change. Further, when the materials were maintained at the temperatures at which the nematic phases were observed, all of the sample changed to the red, transparent amorphous material described previously. Cooling the sample from these high temperatures revealed no recurrence of liquid crystal phases and little or no birefringence was observed in the solidified product at ambient temperatures.

For DSC studies involving heating and cooling cycles between ambient temperature and 170°C for diacetylenes with CF₃ groups, reversible behaviour is observed with the transitional enthalpies all below those found for the melting of TS and similar diacetylenes. Isothermal DSC studies at 170°C on these compounds over a period of 15 hours showed no change in the samples.

The diacetylenes containing cyano groups exhibit thermal behaviour similar to the diacetylenes containing nitro groups previously reported [13]. Replacement of cyano or nitro groups by trifluoromethyl produces a more interesting range of compounds in which a smectic phase forms at a lower temperature. The presence of flexible alkoxy groups at the electron donating end of the molecule tends to lower the temperature at which liquid-crystallinity occurs and long flexible alkoxy groups may promote the formation of smectic liquid crystals as reported by Grant [11]. As the smectic phase reverts to a nematic phase, an irreversible exothermic reaction to amorphous polymer with some degradation occurs. This polymer is not liquid-crystalline, unlike those reported by Garito [9, 26] and work continues with these compounds to achieve the formation of a liquid crystal polymer retaining a polar highly conjugated molecular structure suitable for non-linear optical materials from a liquid crystal monomer.

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