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Acetylenic and diacetylenic liquid-crystalline monomers: towards ordered conjugated polymers

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Acetylenic and diacetylenic liquid-crystalline monomers: towards ordered conjugated polymers

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Acetylenic and diacetylenic mesomorphic monomers have been prepared in order to obtain long conjugated polymers able to give high non-linear optical hyperpolarizabilities. Here we report the synthesis of such monomers incorporating cholesteryl and methoxybiphenyl groups; their structural and thermal behaviour are described. The occurrence of mesophases in the acetylenic and diacetylenic derivatives is discussed as a function of the spacer length and of the size of the mesogen moiety. The diacetylenic derivatives containing the methoxybiphenyl groups do not exhibit any liquid-crystalline behaviour but are able to polymerize under U.V. radiation.

1. Introduction

In recent years, a major effort has been devoted to the synthesis of novel monomers to obtain polymers with a large conjugated electron delocalization in the main chain. π-electron delocalization in a long conjugated polymer chain gives rise to unusual non-linear optical properties under high light intensity. Large third-order non-linear responses have been obtained with insaturated polymers such as polyacetylenes [1] and polydiacetylenes [2].

Large third-order susceptibility (χ^3) values in polymeric materials are strongly dependent on two main factors: the molecular hyperpolarizability and the degree of macroscopic orientation. Large molecular hyperpolarizabilities are found in materials with high displaceable electron clouds e.g. in extended π-electron systems. Thus, single crystals of conjugated-chain polymers have been synthesized with symmetrical and unsymmetrical diacetylenic molecules. Macroscopic orientation can be obtained through the alignment of molecules in a liquid-crystalline state. In order to associate the properties of the conjugated backbone to those of polymers in the mesomorphic state, and more specifically of side chain liquid-crystalline polymers, several liquid-crystalline diacetylenic monomers have been synthesized and polymerized [3–8]. The concept of freezing the mesomorphic state by polymerization of a liquid-crystalline monomer has already been applied successfully in many cases [9].

In this paper, the synthesis and polymerization of new acetylenic and diacetylenic monomers incorporating cholesteryl and methoxybiphenyl mesogenic groups are reported, and their structural and thermal behaviour are described.

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2. Results and discussion

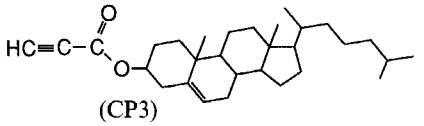
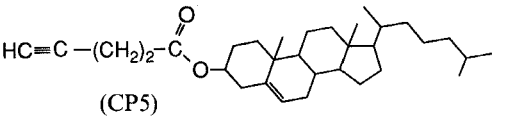
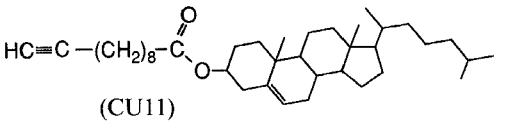
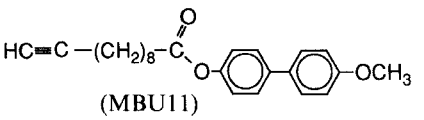
2.1. *Acetylenic monomers*

Acetylenic derivatives were used as precursors for the synthesis of diacetylenic compounds obtained by oxidative coupling and also as precursors for the synthesis of substituted polyacetylenes. The mesomorphic properties, which can be expected with the acetylenic derivatives of the present study, are very much dependent on the length and on the flexibility of the spacer located between the mesogenic group (cholesteryl or methoxybiphenyl) and the rigid triple bond. With the same cholesteryl group, three different spacers with zero, two and eight methylenes groups have been used.

2.1.1. *Thermodynamic results and polymorphism*

All of the experimental thermal parameters of the acetylenic derivatives are listed in table 1. Compounds CU11 and CP5 exhibit enantiotropic polymorphism. For each compound, DSC thermograms (see figures 1 and 2) show on heating two endothermic peaks, one of high intensity and another of low intensity at higher temperature. The reversibility of the low intensity peak (at 74°C for CU11 and 140°C for CP5) observed upon recooling may be considered as the signature of a transition between an isotropic phase and a mesomorphic phase. The supercooling effect observed for the high intensity peak is frequently encountered for a transition between a crystalline phase and a mesomorphic phase. The optical textures observed under the microscope for the mesophase of each compound are not the classical textures usually reported in the literature for liquid crystals [10, 11], but are nevertheless strongly birefringent and clearly suggest the existence of mesomorphic order. The X-ray diffraction pattern recorded at 38°C for CU11 is typical of a disordered smectic phase; it contains in the small angle region a sharp reflection corresponding to the layer stacking, and in the

Table 1. Acetylenic esters

 (CP3)	C —127°C→ I; I —105°C→ Ch —30°C→ C
 (CP5)	C —107°C, ±25·8 kJ/mol→ Ch —140°C, ±0·6 kJ/mol→ I
 (CU11)	C —51°C, ±18·9 kJ/mol→ S_A —74°C, ±0·8 kJ/mol→ I
 (MBU11)	C —65°C, 40·6 kJ/mol→ I; I —68°C→ ? —57°C→ C

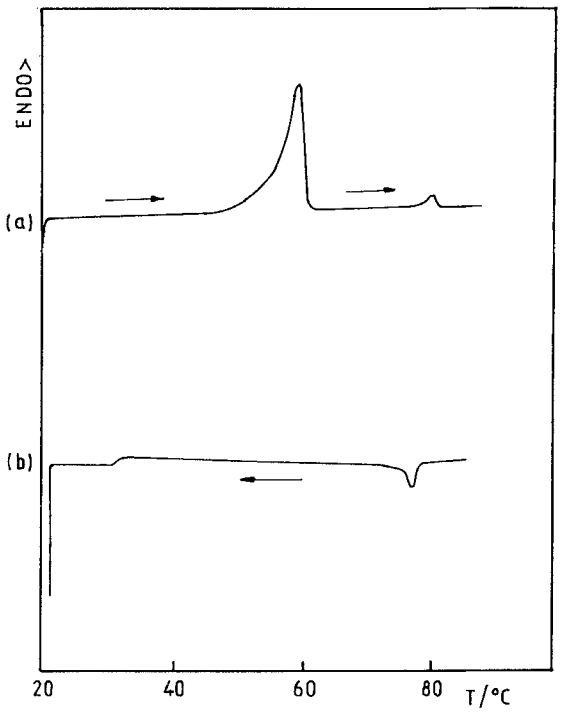


Figure 1. Heating (*a*) and cooling (*b*) D.S.C. thermograms of the cholesteryl acetylenic derivative CU11.

wide angle region a diffuse band related to the liquid-like order of the molecules within the smectic layers. The layer spacing found (28·5 Å) is in agreement with the length of the molecule determined from molecular models (30 Å) indicating that the mesophase is a smectic A phase. The X-ray diffraction patterns recorded for CP5 at several temperatures between 100° C and 140° C are typical of a nematic or a cholesteric phase since they contain only a diffuse band in both the small and wide angle regions. Due to the presence of a chiral cholesteric moiety in the molecule, we take the mesophase of CP5 to be cholesteric.

For compound CP3, only a monotropic cholesteric phase was detected below 105° C. The optical texture observed at 100° C is strongly birefringent and the X-ray pattern recorded at the same temperature is typical of a nematic or cholesteric phase. For the compound MBU11 containing a methoxybiphenyl moiety instead of a cholesteric one, no mesomorphic phase was clearly detected. The D.S.C. thermogram revealed the possible existence of a monotropic mesophase below 68° C, however it was impossible to correlate this phase with a corresponding X-ray diffraction pattern since the sample crystallized rapidly.

From these results it is clear that the rôle of the aliphatic chain is important in this series of monoacetylenic derivatives containing the cholesteric moiety. When there is no aliphatic chain, no stable mesophase can be observed. When the aliphatic chain is short, only a cholesteric phase appears, and when it is long, the compound exhibits a stable smectic A phase. It is also interesting to note the absence of a liquid-crystalline phase when the cholesteric moiety is replaced by methoxybiphenyl, the length of the aliphatic chain being kept the same.

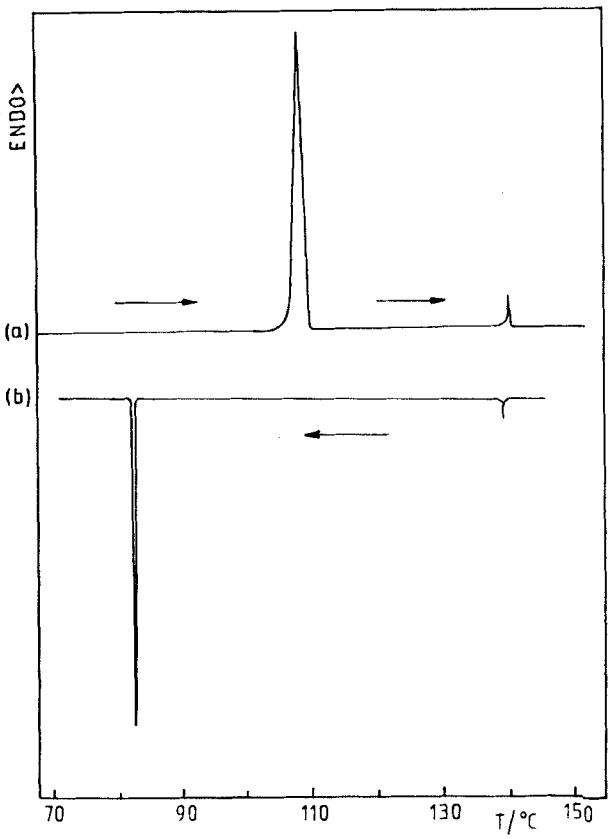


Figure 2. Heating (*a*) and cooling (*b*) D.S.C., thermograms of the cholesteryl acetylenic derivative CP5.

2.2. *Diacetylenic monomers*

2.2.1. *Thermodynamic results and polymorphism*

All of the experimental thermal parameters of the diacetylenic derivatives are summarized in table 2. Compounds CPD5-10 and CHD11-6 exhibit a monotropic mesophase, as shown by D.S.C. and optical microscopy. From the focal conic texture observed, the mesophase of CPD5-10 can be identified as smectic A; for the CHD11-6 monomer, no characteristic texture was obtained. In both cases, no X-ray patterns of the mesophases were recorded because of rapid sample crystallization.

The symmetrical diacetylenic monomer BCED11-11 exhibits several interesting properties. Upon cooling the DSC diagram (see figure 3) shows a small exothermic peak ($-3{\cdot}2$ kJ/mol) at 114°C and the optical texture observed at 110°C is highly birefringent but without any specific feature (see figure 4). The X-ray diffraction pattern recorded at 110°C indicates clearly that the monotropic mesophase obtained below 114°C is a smectic phase (cf. the presence of a sharp reflection in the small angle region and a diffuse band in the wide angle region). The spacing corresponding to the sharp reflection is 28 Å, which is exactly half the molecular length, as determined by molecular models (see figure 5). When trying to model the molecular arrangement within the layers, we are immediately confronted with the question as to whether the disordered smectic phase observed is A or C in nature. Indeed, the unsuccessful

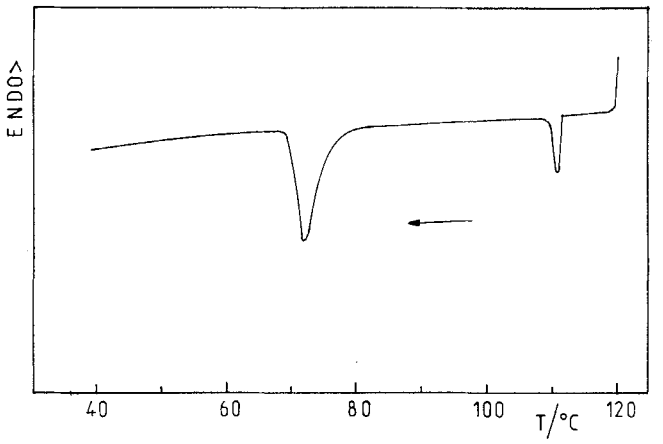


Figure 3. Cooling D.S.C. thermogram of the symmetrical cholesteryl diacetylenic derivative BCED11-11.

Table 2. Diacetylenic esters.

$CH_3(CH_2)_7-C\equiv C-C\equiv C-(CH_2)_2-C(=O)-O$-Chol. (CPD5-10)	(np)	C ⟶ I: 80°C, 19·6 kJ/mol; I ⟶ S_A: 69°C; S_A ⟶ I: 82°C, −1·8 kJ/mol
$CH_3(CH_2)_3-C\equiv C-C\equiv C-(CH_2)_8-C(=O)-O$-Chol. (CHD11-6)	(np)	C ⟶ I: 53°C, 38.4 kJ/mol; I ⟶ ?: 53°C; ? ⟶ C: 39°C, −1.3 kJ/mol
Chol.-O-C(=O)-$(CH_2)_8-C\equiv C-C\equiv C-(CH_2)_8$-C(=O)-O-Chol. (BCED11-11)	(np)	C ⟶ I: 114°C, 37·1 kJ/mol; I ⟶ S_A: 76°C; S_A ⟶ C: 114°C, −3·2 kJ/mol
$CH_3(CH_2)_9-C\equiv C-C\equiv C-C(=O)-O-C_6H_4-OCH_3$ (MBPD3-12)	(p ?)	C ⟶ N: 54°C, 28.3 kJ/mol; N ⟶ I: 86°C, ±0.8 kJ/mol; N ⟶ C: 28°C, −16.2 kJ/mol
$CH_3(CH_2)_3-C\equiv C-C\equiv C-(CH_2)_8-C(=O)-O-C_6H_4-OCH_3$ (MBHD11-6)	(p +)	C ⟶ C′: 33°C; C′ ⟶ I: 72°C
$CH_3(CH_2)_3-C\equiv C-C\equiv C-(CH_2)_8-C(=O)-O-(CH_2)_2-C_6H_4-OCH_3$ (MEBHD11-6)	(p +)	C ⟶ C′: 79°C; C′ ⟶ I: 86°C
$CH_3(CH_2)_3-C\equiv C-C\equiv C-(CH_2)_8-C(=O)-O-C_6H_4-CN$ (CBHD11-6)	(np)	C ⟶ I: 59°C

(np) non-polymerizable monomer, (p +) polymerizable monomer under U.V., 254 nm, Chol: cholesteryl group

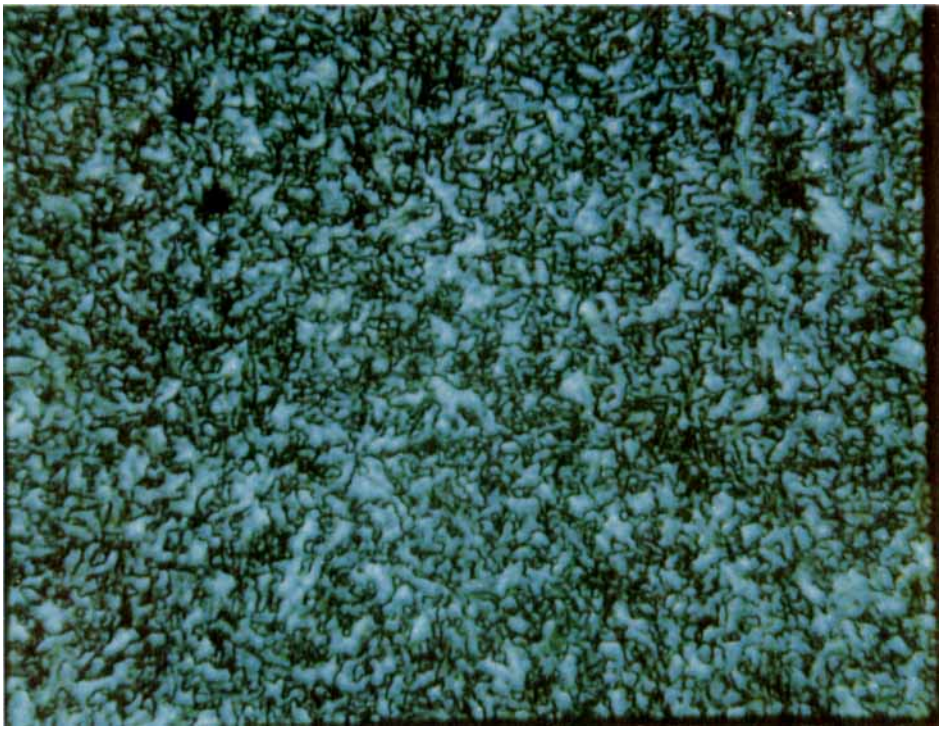


Figure 4. Optical texture observed with a polarizing microscope at 110°C for the symmetrical cholesteryl diacetylenic derivative BCED11-11.

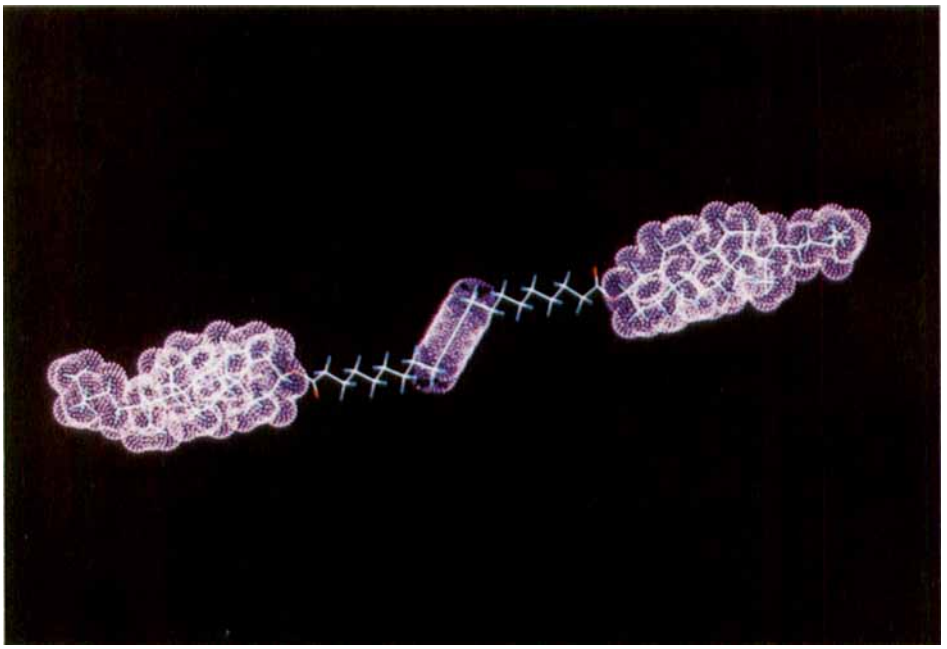


Figure 5. Molecular model of the symmetrical cholesteryl diacetylenic derivative BCED11-11.

attempts to develop typical optical textures and X-ray diffraction patterns from well oriented samples do not help us distinguish between the two possible structures. We are therefore, reduced to considering the two structures separately.

A classical smectic C arrangement with the molecules in a straight conformation, tilted with respect to the layer normal, seems highly improbable for at least two reasons. First, the tilt angle, $\cos^{-1}(d/l) = 60°$, would be intolerably high; it would be much larger than the highest tilt angles ever reported in the literature. Second, the layer thickness being exactly half the molecular length appears to be a suspicious coincidence. As for the smectic A possible arrangements of the molecules, were are led to propose the following two models. The first corresponds to the molecules set side by side as represented in figure 6 (*a*). The intermolecular van der Waals interactions would obviously be satisfied in such an arrangement as the cholesteric moiety on one hand and the diacetylenic segment on the other, are in good lateral register. However, this type of structure is not satisfactory, since it cannot explain the absence of the Bragg reflection at 56 Å, that is at a spacing corresponding to the molecular length. The second model is represented in figure 6 (*b*). Instead of being all located in a single sublayer such as in the model illustrated in figure 6 (*a*), the triple bonds are statistically located in two sublayers separated by a distance equal to half of the molecular length.

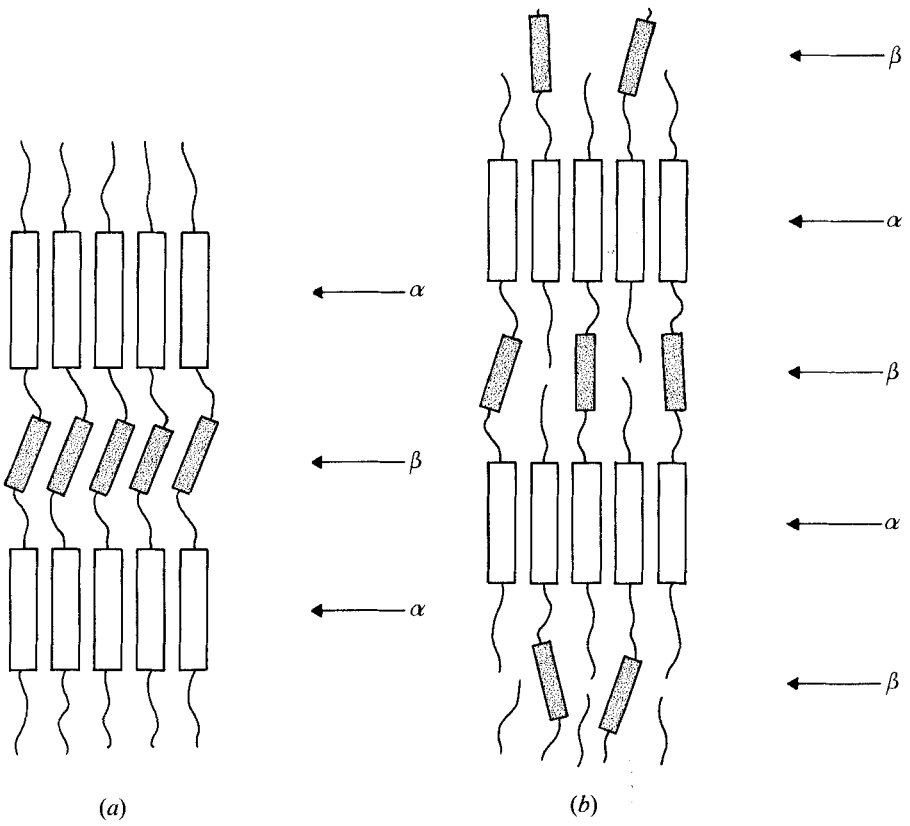


Figure 6. Schematic of the possible arrangement of the symmetrical diacetylenic molecules within the smectic A layers. Large rectangles represent the cholesteryl moiety, and dotted rectangles the rigid diacetylene part. (*a*) All of the triple bonds are located in the same sublayer; (*b*) the triple bonds are statistically located in two distinct sublayers.

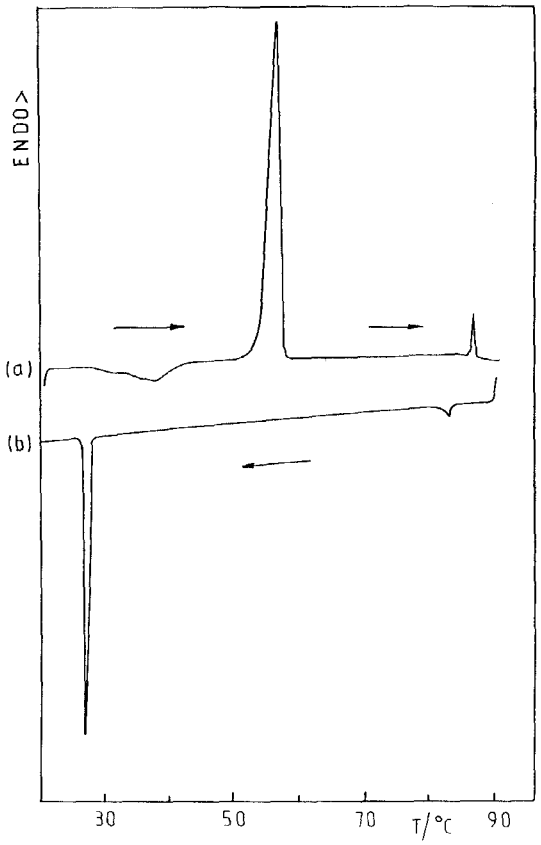


Figure 7. Heating (*a*) and cooling (*b*) D.S.C. thermograms of the methoxybiphenyl diacetylenic ester MBPD3-12.

This molecular arrangement ensures a good lateral register of the cholesteric moieties, and also provides a fair understanding of the absence of the first order Bragg reflection in the X-ray diffraction patterns.

The compound MBPD3-12, containing the methoxybiphenyl moiety, exhibits an enantiotropic nematic phase easily detected by D.S.C. (see figure 7) and optical microscopy (see figure 8). Unfortunately, the sample decomposes too rapidly in its nematic phase and unreproducible X-ray diffraction patterns were recorded. Finally, the MBHD11-6, MEBHD11-6, and CBHD11-6 compounds, in which the rigid triple bonds are located far from the mesogenic part (methoxy-or cyanobiphenyl) do not exhibit any liquid-crystalline behaviour.

In this series of diacetylenic derivatives, it is clear that monotropic mesophases are observed when the mesogenic part is a cholesteryl group. Only one enantiotropic nematic phase has been detected when the mesogenic part is a methoxybiphenyl group, directly linked to the diacetylene rod through a carboxylic group.

2.3. *Polymerization of acetylenic and diacetylenic derivatives*

The polymerization of acetylenic derivatives is usually performed in solution by using of transition metal catalysts. Work on the polymers obtained from the acetylenic derivatives reported in the present study are in progress.

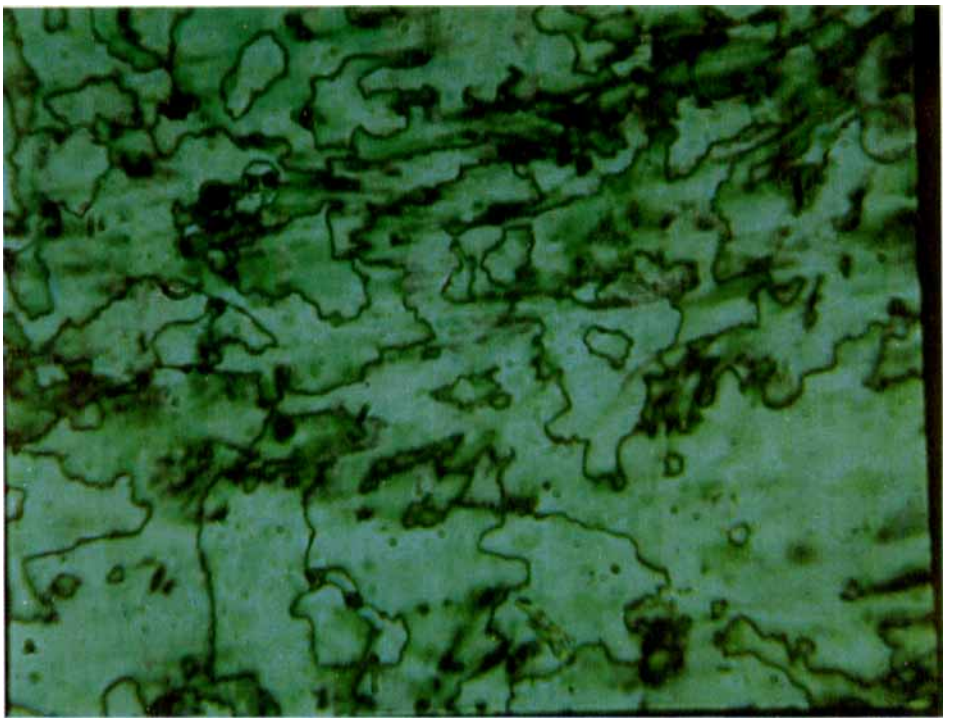


Figure 8. Optical texture observed with a polarizing microscope (×300) at 80°C for the methoxybiphenyl diacetylenic ester MBPD3-12.

The polymerization of diacetylenic derivatives occurs in the solid state by a 1-4 addition reaction, following a topochemical mechanism described previously [12]. The maximum reactivity of the diacetylene monomers is obtained for a packing distance of 5 Å (corresponding to a lateral distance of 3·8 Å) and an angle Φ between the diacetylene rod and the stacking axis of about 45° [13]. Thus, the solid state reactivity of disubstituted diacetylenes is, in general, better satisfied with monomers containing large end-groups than with monomers containing small end-groups [14].

The polymerization reactivity of the diacetylenic esters synthesized is presented in table 2. The diacetylenic acids with long aliphatic chains are well known to polymerize in Langmuir–Blodgett films or in a monocrystalline form under U.V. or γ-irradiation. In the present work, the diacetylenic monomers were able to polymerize depending on their ability to form liquid-crystalline phases. The diacetylenic monomers without thermotropic phase (MBHD11-6 and MEBHD11-6) were successfully polymerized under U.V. radiation. The resulting red or red-orange colour was characteristic of the polymerization of a diacetylenic moiety into conjugated chains. For the other monomers (CHD11-6, CPD5-10, BCED11-11, CBHD11-6 and MBPD3-12), the polymerization failed in the solid state, in the thermotropic phase, as well as under U.V. or γ-irradiation.

When comparing the results of the present study with others already reported in the literature with similar compounds [5, 7], it is clear that subtle variations in the monomer architecture can introduce large differences in the liquid-crystalline phase behaviour and in the polymerization reactivities. In fact, two types of monomeric architecture can be distinguished: type I in which the diacetylene rod is integrated into

the mesogenic group, and type II in which the diacetylene rigid rod is separated from the mesogenic group by a flexible spacer.

In type I, liquid-crystalline phase behaviour may occur with the monomers, generally at high temperature, and polymerization of some of them have been recently reported [8 (*b*)].

In type II, mesophases are observed with a large mesogenic block such as the cholesteryl group attached to a rather long flexible spacer (CHD11-6 and BCED11-11). Mesophases can also be observed with other mesogenic blocks (methoxy-or cyanobiphenyl) attached to a short spacer (one or two methylene groups) which ensures a relatively rigid architecture of the monomer (MBPD3-12 and reported 1-OBOA [7]).

In the present work, the polymerization reactivity of mesogenic esters of type II is small compared to that of the corresponding acids; it depends on both the spacer length and the size of the mesogen part. Molecules with a cholesteryl group do not exhibit polymerization reactivity at all, the solid state polymerization being prevented by the molecular packing and by the lateral bulkiness of the cholesteryl part (BCED11-11). X-ray diffraction has shown that the average lateral distance between molecules in the smectic A phase of BCED11-11 is 5·4 Å, compared to the optimal lateral distance of 3·8 Å for maximum polymerization reactivity. Molecules with other mesogenic groups can easily polymerize, but do not present mesomorphic phases (MBHD11-6, MEBHD11-6, CBHD11-6, reported 4-COB, 4-OBAO [7] and diacetylenic ester I in [5]).

3. Experimental section

X-ray diffraction: The X-ray powder diffraction patterns were recorded photographically as a function of temperature, using either a Guinier focusing camera equipped with a bent quartz monochromator (copper $K\alpha_1$ radiation from a Philips PW-1009 generator) and an electrical oven, or a Searle camera with toroïdal optics (Ni-filtered copper radiation from an Elliot GX20 rotating anode generator) and an electronically controlled oven.

Optical microscopy: Optical observations (transition temperatures and textures) were obtained with a Leitz Orthoplan polarizing microscope equipped with a Mettler FP52 hot stage.

Differential scanning calorimetry: D.S.C. studies were carried out with a Perkin Elmer DSC4 or Mettler FP84 instrument, in aluminium pans or saphire cells. Measurements were made systematically with a heating or cooling rate of $2{\cdot}5\,K\,min^{-1}$.

Materials: Chemical products were purchased from Aldrich (Cholesterol $\alpha = -40°$, 4-4′biphenol) or Fluka (pentynoic acid, propiolic acid, undecenoic acid), they were used without further purification.

Characterization: ^1H N.M.R. spectra were taken with 60, 90, 200, 400 MHz Brücker spectrometers. Infra-red spectra were obtained with a Perkin–Elmer 983.

3.1. *Synthesis*

Undecynoic acid was prepared from undecenoic acid as described in the literature [15].

4-methoxy-4′-hydroxybiphenyl was synthesized from 4,4′-biphenol and dimethylsulphate according to the procedure described in the literature [16].

Esterification was performed by dehydrating condensation of the diacetylenic acid with the corresponding alcohol using DCC [17].

Esterification typical procedure: 17 mmol (6.7 g) of cholesterol in 40 ml of methylene chloride with 100 mg of DMAP was added to a stirred solution of 20 mmol (1·98 g) pentynoic acid in 20 ml of anhydrous CH_2Cl_2. DCC was slowly added to the mixture at 0°C and urea precipitates. The mixture was then stirred at 20°C for 3 h and the precipitated urea filtered off. The filtrate was evaporated under vacuum and the residue was taken up in methylene chloride in order to filter the insoluble urea. The organic solution was successively washed with aqueous solutions of HCl, $NAHCO_3$ and pure water, and finally dried. The solvent was removed and the chromatography of the residue was performed on a SiO_2 column with $CHCl_3$ as eluent. Crystallization in ether/methanol gave 4·60 g of white platelets, of cholesteryl-5-pentynoate (CP5), yield 57 per cent: C: 82·60 (82·35), H: 10·77 (10·80), O: 7·05 (6·85); I.R., 3292 cm^{-1} ≡C–H, 2120 cm^{-1} –C≡C–, 1724 cm^{-1} C=O;

Cholesteryl-11-undecynoate (CU11) was obtained from undecynoic acid and cholesterol. Purification was made by chromatography SiO_2 with $CHCl_3$ as eluent and crystallization in ether/ethanol 1/1 gave white crystals, yield 44 per cent: C: 82·30, (82·85), H: 11·19 (11·34), O: 5·85 (5·81); I.R., 3310 cm^{-1} ≡C–H, 2118 cm^{-1} –C≡C–, 1734 cm^{-1} C=O; ^{1}H N.M.R. ($CDCl_3$, δ 5·39 (*d*, 1 H, alkenyl), 4·83–4·80 (m, 1 H, oxycyclohexyl), 2·29 (m, 2 H, α carbonyl), 2·19–2·18 (*d* of *t*, 2H, ≡C–CH_2), 1·944 (*t*, 2·6 Hz, 1 H, H–C≡), 1·7–0·68 (m + s, 53 H, methylene and cholesteryl)

Cholesteryl-3-propynoate (CP3) was obtained from propynoic acid and cholesterol. Purification: chromatography SiO_2/toluene, recrystallized from ether/ethanol to give white crystals, yield 14 per cent: C: 82·04 (82·14), H: 10·49 (10·57), O: 7·61 (7·29); I.R., 3302 cm^{-1} ≡C–H, 2117 cm^{-1} –C≡C–, 1708 cm^{-1} C=O;

4-methoxy biphenyl-4′(11-undecynoate) (MBU11) was obtained from 11-undecynoic acid and 4-methoxy 4′-hydroxy biphenyl. Purification: chromatography SiO_2/$CHCl_3$, recrystallization from ether/ethanol gave white crystals. C: 79·41 (79·09), H: 7·80 (7·73), O: 13·06 (13·17); I.R., 3384 cm^{-1} ≡C–H, 2120 cm^{-1} –C≡C–, 1757 cm^{-1} C=O; ^{1}H N.M.R. ($CDCl_3$), δ 7·5–7·4 (m, 4H), 7·1–6·8 (m, 4H), 3·8 (s, 3H), 2·54 (*t*, 2H), 2·15 (m, 2H), 1·913 (*t*, 1H), 1·75–1·36 (12 H).

Synthesis of cholesteryl heptadeca-10,12-diynoate (CHD11-6) was carried out by first preparing heptadeca-10,12-diynoic acid from 1-hexyne and 11-undecynoic acid according to the oxidative unsymmetrical coupling method described in the literature (yield 28 per cent; Mp = 41·3°C) [18].

Esterification with cholesterol yielded cholesteryl-10,12-diynoate as white leaflets (yield 25 per cent). C: 83·52 (83·75), H: 11·07 (11·18), O: 5·26 (5·07); I.R., 1732 cm^{-1} C=O; ^{1}H N.M.R. ($CDCl_3$) δ 5·3 (*d*, 1H, alkenyl), 4·7 (*m*, 1 H, oxycyclohexyl), 2·2 (*t*, 2H, α carbonyl)

Synthesis of cholesteryl pentadeca-4,6-diynoate (CPD5-10) was carried out from cholesteryl-5-pentynoate and 1-decyne by oxidative coupling [19]. The catalyst solution was prepared with 10 g of $CuCl_2$ and 30 ml of pyridine and 30 ml of ethanol. After complete dissolution, the two monomers were added: 2·15 mmol of cholesteryl monomer and 4·27 mmol of 1-decyne. The resulting mixture was stirred and heated up to 75°C for 4 h with low oxygen bubbling. The cold mixture was then poured onto ice in a HCl solution. The product was extracted with chloroform, purified on a silica column with toluene as eluent and recrystallized from pentane. Yield 9·5 per cent: C: 83·84 (83·66), H: 11·23 (11·03), O: 5·51 (5·31); I.R., 2120 cm^{-1} –C≡C–, 1721 cm^{-1} C=O;

The synthesis of bis(cholesteryl)-10,12-eicosadiynedioate (BCED11-11) was carried out from symmetrical oxidative coupling of cholesteryl 11-undecynoate: 1·9 g of

cholesteryl undecynoate (3·5 mmol), 12 g of cupric acetate were dissolved in a mixture of methanol (450 ml), pyridine (200 ml), and ether (500 ml). The solution was heated to 30–33°C for 71 h with oxygen bubbling. The ether was then removed from the solution by rotoevaporation and 450 ml of pyridine was added. The solution was heated at 40–42°C for 70 h. A part of the solvent was removed by evaporation and the residue was poured on to ice in HCl solution. The product was extracted with ether, purified on a silica column with chloroform and crystallized from ether/ethanol. Yield 37 per cent C: 83·08 (83·00), H: 11·15 (11·18), O: 5·77 (5·82); I.R., 1730 cm^{-1} C=O, ^{1}H N.M.R., (C_6D_6), δ 5·45 (d, 2 H, alkenyl), 5·1–5·0 (*m*, 2 H, oxycyclohexyl), 2·7–2·5 (2*d*, 2 H, chl CH_2, 4), 2·29 (*t*, 4 H α carbonyl), 2·04 (*t*, 4 H, $\equiv C-CH_2$) 1·8–0·73 (*m* + *s*, 1O6H, methylene and cholesteryl)

4-methoxybiphenyl (heptadeca-10,12-diynoate) (MBHD11-6) was obtained by esterification of heptadeca-10,12-diynoic acid with 4-methoxy-4′-hydroxy biphenyl under standard conditions. Recrystallization in EtOH/Ether gave fine needles. Yield 53 per cent, C: 81·44 (81·04), H: 8·21 (8·16), O: 10·73 (10·80); I.R. 1746 cm^{-1} C=O, 1606 cm^{-1} C–C arom., 852 cm^{-1} C–H; N.M.R., ($CDCl_3$), δ 7·5–6·87 (2*q*, 8H, arom.), 3·8 (*s*, 3H, CH_3–O), 2·2 (*t*, 2 H, CH_2 α carbonyl)

4-methoxy-4′-ethoxybiphenyl (heptadeca-10,12-diynoate) (MEBHD11-6): methoxy-4′ (2-hydroxy-ethoxy)-biphenyl was likely given by Dr. Ph. Gramain [20]. Esterification made in the standard conditions gave a white crystalline powder after recrystallization from toluene. Yield 51 per cent, C: 78·52 (78·65), H: 8·26 (8·25), O: 13·36 (13·10); ^{1}H N.M.R., δ 7·53, 7·42 (*d*, 4 H, Ar), 7·00, 6·91 (*d*, 4 H, Ar), 4·46–4·15 (2*t*, 4 H, O–CH_2), 3·85 (*s*, 3 H, O–CH_3), 2·4–2·2 (*m*, 6 H, CH_2–C=O, CH_2–C$\equiv$), 1·59–0·90 (*m*, 19 H, CH_2, Me)

4-cyano-biphenyl-4′(heptadeca-10,12-diynoate) (CBHD11-6) was prepared from 4-hydroxy-4′-cyanobiphenyl (0·54 g, 3·1 mmol) (Tokyo Kaesi Organic Chemicals) and heptadeca-10,12-diynoate (0·79 g, 3·0 mmol). Yield 78 per cent, C: 81·96 (81·97), H: 7·57 (7·57), O: 7·46 (7·30), N: 3·09 (3·19); I.R. 2226 cm^{-1} Ar–C$\equiv$N, 1754 cm^{-1} C=O; ^{1}H N.M.R. ($CDCl_3$), δ 7·8–7·0 (*m*, 8 H, Ar), 2·6 (*t*, 2H, α carbonyl), 2·2 (*t*, 4 H, $\equiv C-CH_2$), 2·0–1·0 (*m*, 16 H, methylene), 0·9 (*t*, 3 H, Me)

4-methoxybiphenyl-4′(pentadeca-2,4-diynoate) (MBPD3-12) was prepared by, first, synthesizing pentadeca-2,4-diynoic acid using the Cadiot–Chodkiewicz coupling method [21]. Esterification was carried out by the thionyl chloride method. The diacetylenic acid (0.70 g) was treated with $SOCl_2$ (30 ml) for 2 h. After evaporation of the excess, the residue (0·81 g) of reagent was esterified with methoxy-hydroxybiphenyl (0·66 g, 3·3 mmol) in THF (90 ml) with 2 ml (15 mmol) of triethylamine for 3 h at room temperature. After evaporation, the residue was washed and extracted in the etheral phase. The product was purified on SiO_2/toluene and recrystallized in ether/ethanol mixture. Light yellow crystals, yield 31 per cent, C: 80·62 (80·73), H: 7·72 (7·74), O: 11·62 (11·52); I.R., 2236 cm^{-1} and 2151 cm^{-1} –C$\equiv$C–, 1718 cm^{-1} C=O.

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