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Liquid Crystals

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Thermotropic liquid crystals derived from benzopyranobenzopyran-dione. Preparation and physical characterization

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**Thermotropic liquid crystals derived from
benzopyranobenzopyran-dione
Preparation and physical characterization**

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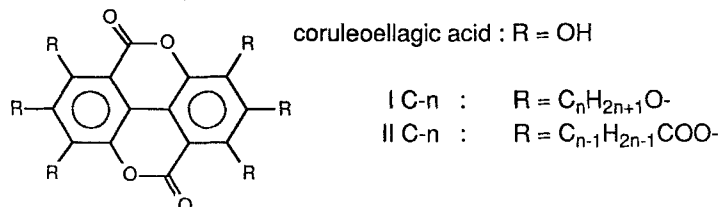
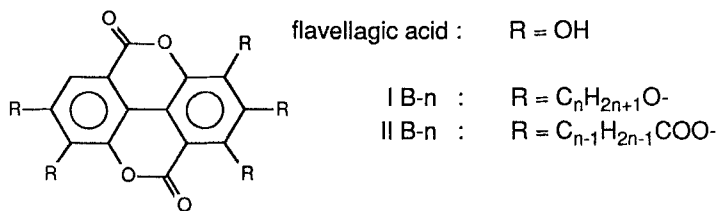
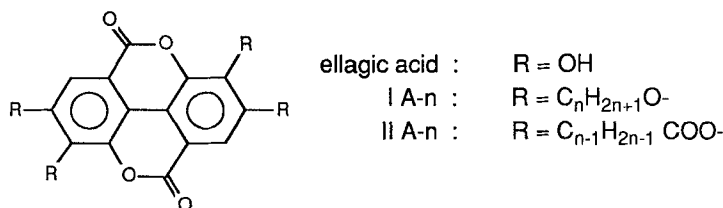
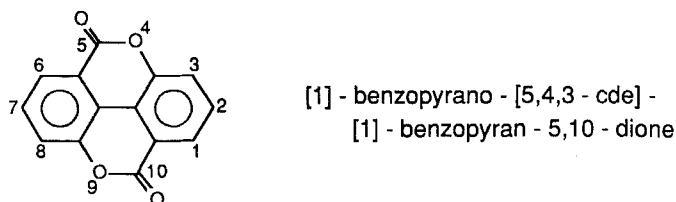
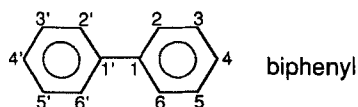
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Tetra-, penta- and hexasubstituted benzopyranobenzopyran-dione with side chains linked via ether or ester groups yield highly polymorphic compounds. The penta- and hexasubstituted ether and ester series include homologues which exhibit columnar discotic mesophases. Miscibility experiments on the ether series indicate that their mesophases are of the D_h (D_E) class. The tetrasubstituted ethers do not appear to be mesogenic, while the corresponding esters were previously shown to exhibit a highly ordered cubic phase. Differential scanning calorimetry, optical polarizing microscopy and X-ray measurements were used to characterize the mesophases and determine their structural parameters.

1. Introduction

Many calamitic liquid crystals are derived from the basic diphenylene moiety, particularly when disubstituted in the 4,4' positions by flexible alkyl chains [1]. It has been shown that the biphenyl moiety in isotropic and liquid-crystalline solutions is non-planar exhibiting a twist angle of about 45° between the planes of the two phenyl rings [2]. As part of a research project on the relation between mesomorphic properties and molecular structure [3-6] we have investigated several series of compounds derived from the [1]-benzopyrano [5,4,3-cde]-[1]-benzopyran-5,10-dione (see the structures), which consists essentially of biphenyl locked by two lactone groups into a planar structure. Six homologous series were studied in which this core was substituted by four, five and six alkyl chains via ether or ester linkages. All series were found to exhibit polymorphism with the high temperature phases of the penta- and hexasubstituted ether and ester series derivatives (IB-*n*, IIB-*n*, IC-*n*, IIC-*n*) being liquid-crystalline. The tetrasubstituted esters of ellagic acid (IIA-*n*) were studied by us earlier [6] and were found to exhibit more highly ordered intermediate phases [7]. Some of these homologues exhibit monotropic, optically isotropic phases which were identified as cubic. The corresponding tetrasubstituted ethers (IA-*n*) were also found to be polymorphic but our measurements indicate that they are probably not mesogenic. In the present work we report on the mesomorphic properties of the liquid-crystalline phases of these series as determined by differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction.

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Before describing the results, it is worth mentioning that the precursors of series A, B and C, better known by their common names ellagic acid, flavellagic acid and coruleoellagic acid occur in many natural products [8,9]. For example ellagic acid derivatives were isolated from eucalyptus wood, from Australian termites and from the castoreum of the Canadian beaver, where at least in part they serve as antioxidants and perhaps as metal ion binders.

2. Experimental

2.1. Materials

The preparation of the compounds studied in the present work are schematically summarized in figure 1. Ellagic acid, the precursor of series IA-*n* and IIA-*n* was obtained commercially (Aldrich) and dried for 24 h at 150°C before use. Flavellagic acid, the precursor of series IB-*n* and IIB-*n* was prepared from gallic acid by oxidation with potassium persulphate (K₂S₂O₈). To a suspension of gallic acid (20 g) in water

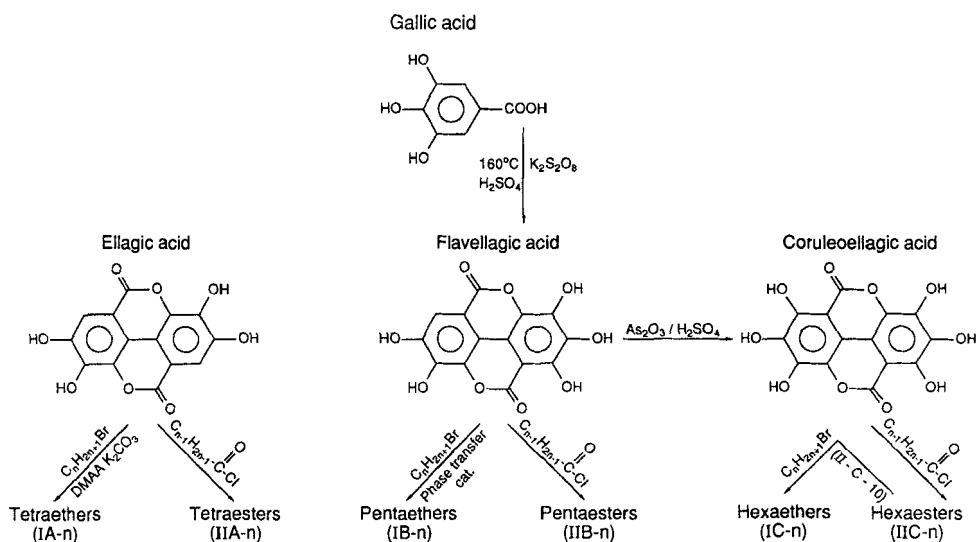


Figure 1. Schematic presentation of the synthetic routes used in the synthesis of the compounds studied in the present work. Ellagic acid and gallic acid were obtained commercially. Details of the synthetic procedures are given in the Experimental.

(64 ml) concentrated H_2SO_4 (160 ml) was slowly added while keeping the temperature below $60^\circ C$. Potassium persulphate (Aldrich, 40 g) was added and the mixture was stirred for 10 min, then transferred to a preheated oil-bath at $160^\circ C$ and stirring continued for 15 min. The dark coloured solution was cooled to room temperature and poured on to 2 l of ice. It was kept overnight, filtered and washed with water to $pH \approx 5$. The brownish flavellagic acid so obtained was dried and purified by recrystallization from boiling pyridine. The salt was subsequently decomposed by heating to $160^\circ C$ for 2 h while removing the liberated pyridine by continuous pumping. The resulting flavellagic acid ($C_{14}H_6O_9$, 8 g, $m/z = 318$) was used for alkylation and esterification without further treatment.

Coruleoellagic acid, the precursor of series IC-n and IIC-n was obtained from flavellagic acid by further oxidation with As_2O_3 . Concentrated sulphuric acid (64 g) was mixed under stirring at room temperature with arsenic acid 85 per cent (Merck, 12 g). Flavellagic acid (3.6 g) was then added and the mixture kept at $120^\circ C$ for 48 h. The cooled reaction product was poured into an ice-water mixture (1 l) which was stirred overnight, filtered, washed with water and dried (yield 2 g). The mass spectrum of the product showed $m/z = 334$ for coruleoellagic acid ($C_{14}H_6O_{16}$) and in various quantities (10 to 20 per cent) also flavellagic acid ($m/z = 318$, $C_{14}H_6O_9$). This product was used for the preparations of the hexaesters (and subsequently hexaethers) of the coruleoellagic acid and the derivatives of the flavellagic acid impurity were removed by column chromatography.

The pentaesters of the flavellagic acid and the hexaesters of the coruleoellagic acid were prepared by esterification of the corresponding precursors with alkanoylchlorides and purified by recrystallization and column chromatography. As an example the preparation of IIB-9 is described. Flavellagic acid (1 g, pyridine free) was heated with *n*-decanoylchloride while stirring at $160^\circ C$ for 20 h. The excess of the acid chloride was

removed by vacuum distillation and the residue was repeatedly recrystallized from $\text{CH}_2\text{Cl}_2/\text{EtOH}$. The pentaester was then purified by column chromatography (silica eluent $\text{CH}_2\text{Cl}_2/n\text{-hexane}$) and the final product recrystallized again. The ^1H NMR spectrum (500 MHz, CDCl_3/TMS) consists of three triplets at 2.69 ppm; 2 triplets at 2.60 ppm ($-\text{C}(\text{O})-\text{CH}_2-$)₅; multiplet 1.76–1.78 ppm ($-\text{C}(\text{O})-\text{CH}_2-\text{CH}_2-$)₅; multiplet 1.29–1.43 ppm; triplet 0.89 ppm ($-\text{CH}_3$)₅. Elemental analysis of $\text{C}_{59}\text{H}_{86}\text{O}_{14}$ gave, C = 68.96 per cent, H = 8.84 per cent (calculated: C = 69.51 per cent, H = 8.50 per cent).

The tetraethers of ellagic acid and the pentaethers of flavellagic acid were prepared by alkylation of the precursors with the corresponding alkylbromide. Two examples follow:

- (i) IA-13. Tridecylbromide (7 g) and K_2CO_3 (2.5 g, pulverized) were added to a solution of ellagic acid (0.5 g) in *N,N*-dimethylacetamide (DMAA), (30 ml, Aldrich). The reaction mixture was stirred for 3 days at 90°C. After cooling the mixture was diluted with CHCl_3 , filtered hot and the solvent as well as the excess tridecylbromide removed by vacuum distillation and the residue recrystallized twice from CHCl_3 . TLC (Silica, $\text{CH}_2\text{Cl}_2/n\text{-hexane}$ 9 : 1, one spot). 500 MHz ^1H NMR (CDCl_3/TMS): singlet 7.68 ppm 2 H arom., 4.38 ppm triplet ($-\text{O}-\text{CH}_2-$)₂, 4.14 ppm triplet ($-\text{O}-\text{CH}_2-$)₂, 1.80–1.94 ppm multiplet ($-\text{O}-\text{CH}_2-\text{CH}_2-$)₄, 1.46–1.54 ppm multiplet, 1.26–1.34 ppm broad multiplet, 0.86–0.89 ppm triplet ($-\text{CH}_3$)₄. Elemental analysis of $\text{C}_{66}\text{H}_{110}\text{O}_8$ gave: C = 76.80 per cent, H = 10.93 per cent (calculated: C = 76.84 per cent, H = 10.75 per cent).
- (ii) IB-8. Flavellagic acid (1.27 g) was mixed under stirring with *n*-octylbromide (10 g) and 4 drops of the phase transfer catalyst Aliquat 336 (tricaprylmethylammoniumchloride, Aldrich) and was kept at 60°C for 30 min. Pulverized KOH (1.23 g) was then added and the mixture left for four hours at 130°C. After cooling, the mixture was diluted with CH_2Cl_2 (300 ml), separated from the KBr and evaporated. The residue was purified by column chromatography (silica, eluent $\text{CH}_2\text{Cl}_2/n\text{-hexane}$ 3 : 2) followed by recrystallization from EtOH. TLC (silica, $\text{CH}_2\text{Cl}_2/n\text{-hexane}$ 3 : 2, one spot). 500 MHz ^1H NMR (CDCl_3/TMS): singlet 7.65 ppm arom. H₁, singlet 4.44 ppm ($-\text{O}-\text{CH}_2-$)₁, triplet 4.34 ppm ($-\text{O}-\text{CH}_2-$)₁, multiplet 4.10–4.18 ppm ($-\text{O}-\text{CH}_2$)₃, multiplet 1.78–1.95 ppm ($-\text{O}-\text{CH}_2-\text{CH}_2-$)₅, multiplet 1.45–1.56 ppm, broad line 1.24–1.42 ppm, 2 triplets 0.85–0.92 ppm. Elemental analysis of $\text{C}_{54}\text{H}_{86}\text{O}_9$ gave: C = 73.94 per cent, H = 10.4 per cent (calculated: C = 73.76 per cent, H = 9.85 per cent).

Hexaethers of the coruleoellagic acid were prepared by alkylation of the hexadecanylester of the coruleoellagic acid. This procedure was found to be superior to direct alkylation of the coruleoellagic acid. As an example the preparation of IC-7 is described. Hexadecanoyloxy-coruleoellagic-ester (1 g) was dissolved in *N,N*-dimethylacetamide (100 ml). *n*-Heptylbromide (15 g) and K_2CO_3 (6 g, pulverized) were added and the mixture stirred at 70°C for 4 days. After cooling the mixture was filtered and the solvent and the excess of the *n*-heptylbromide were removed by vacuum distillation. The residue was recrystallized from acetone followed by column chromatography (silica, $\text{CH}_2\text{Cl}_2/n\text{-hexane}$). TLC (silica, $\text{CH}_2\text{Cl}_2/n\text{-hexane}$ 8.5 : 1.5) gave a single spot. 500 MHz ^1H NMR (CDCl_3/TMS): triplet 4.41 ppm ($-\text{O}-\text{CH}_2$)₂, multiplet 4.03–4.07 ppm ($-\text{O}-\text{CH}_2-\text{CH}_2-$)₄, multiplet 1.78–1.95 ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-$)₆, multiplet 1.14–1.28 ppm and broad line, 2 triplets 0.95 ppm ($-\text{CH}_3$)₆.

2.2. Physical measurements

The differential scanning calorimetry and optical microscopy measurements were performed as described in several earlier reports from our laboratories [3–6, 10]. X-ray measurements were made using a Searle low angle camera operating with Ni-filtered Cu-K α radiation (average wavelength 1.54 Å) which was further monochromated and collimated by double Franks mirrors. The X-rays were generated by an Elliot GX6 rotating anode generator operating at 35 kV and 35 mA with a 200 μ m focus. Samples were held in 1.5 mm glass X-ray capillaries which were sometimes flame sealed, to prevent oxidative degradation at high temperatures. The samples were placed in a homemade furnace which consisted of a copper and teflon cavity equipped with a triac temperature control. The temperature was monitored with an iron-constantan thermocouple. The diffraction pattern was recorded on direct exposure film (Kodak). The distance from the sample to the film was varied from 34 to 42 mm and was calibrated with powdered calcite ($d = 3.029$ Å) which coated the outside of the capillary wall. Exposure times were of the order of 16 h. The X-ray films were analysed using a Joyce Loebel MK IIIB densitometer.

3. Results and discussion

3.1. Alkyloxy substituted ellagic, flavellagic and coruleoellagic acids

Plots of the phase sequences of the IA- n , IB- n and IC- n homologues as determined by differential scanning calorimetry are summarized in figure 2 and tables 1 (a), (b) and (c). It should be noted that the thermograms obtained on first heating of the compounds were sometimes different from those recorded upon subsequent heating-cooling cycles. This may be due to the fact that the crystals prepared by crystallization from a solvent were not identical to those formed by cooling the melt, or due to supercooling effects. The results in table 1 (and table 3) include data obtained both on first as well as subsequent heating after cooling the melt to well below room temperature. Cooling often resulted in very significant supercooling of the isotropic liquids as well as of the mesophases, sometimes yielding new monotropic phases.

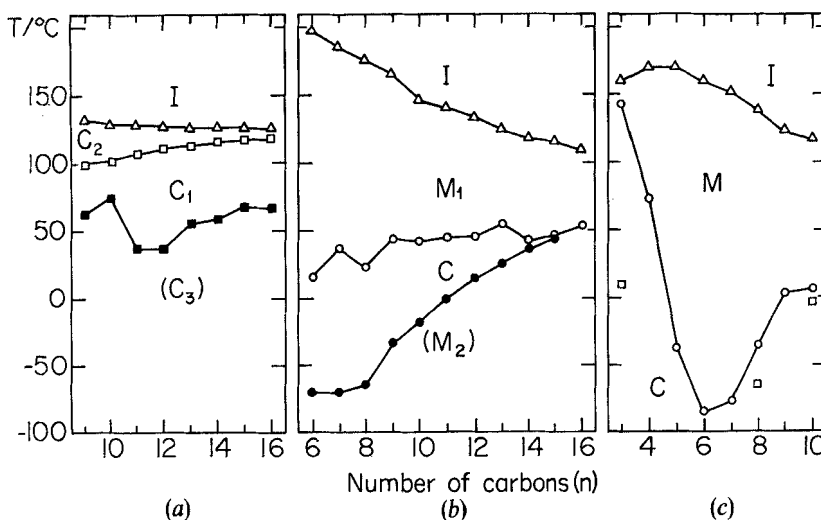


Figure 2. Phase transition temperatures observed upon heating of the compounds of series (a) IA- n , (b) IB- n and (c) IC- n . I, M and C correspond respectively to isotropic liquid, mesophase and crystalline states. Brackets indicate monotropic phases and n is the total number of carbons in each of the side chains.

Table 1(a). Transition temperatures (in °C) and (in brackets) transition enthalpies (in kJ mol⁻¹) obtained by DSC upon heating the compounds of series IA-*n*. The letters I, M and C correspond respectively to isotropic liquid, mesophase and crystalline phases. Monotropic phases are shown in brackets.

<i>n</i>	C ₁	C ₃	C ₂	I
9	● 99.7 (67.6)	(● 62.5 (16.8))	● 131.2 (79.7)	●
10†	● 102.2 (46.1)	(● 74.4 (18.5))	● 128.0 (87.4)	●
11	● 107.0 (77.8)	(● 36.8 (6.6))	● 128.0 (94.7)	●
12	● 111.2 (90.0)	(● 36.3 (14.1))	● 126.8 (101.9)	●
13	● 112.8 (97.3)	(● 56.0 (9.0))	● 126.5 (113.3)	●
14	● 115.4 (98.3)	(● 58.4 (10.0))	● 125.4 (125.0)	●
15	● 117.0 (114.4)	(● 67.8 (7.7))	● 126.0 (127.1)	●
16	● 118.0 (118.8)	(● 66.8 (10.1))	● 125.0 (130.1)	●

† A solid–solid transition at 85°C is not indicated in the table.

Table 1(b). Transition temperatures (in °C) and (in brackets) transition enthalpies (in kJ mol⁻¹) obtained by DSC upon heating the compounds of series IB-*n*.

<i>n</i>	C	M ₂	M ₁	I
6	● 15.8 (—)†	(● ~ -70 (—)‡)	● 197.6 (9.3)	●
7	● 36.8 (—)†	(● ~ -70 (7.8))	● 186.0 (8.7)	●
8	● 23.3 (—)†	(● -64.6 (14.9))	● 175.5 (8.6)	●
9	● 44.6 (93.8)	(● -33.3 (17.0))	● 165.6 (8.4)	●
10	● 42.2 (103.2)	(● -17.8 (21.8))	● 145.8 (7.2)	●
11	● 44.7 (110.7)	(● 0.1 (41.7))	● 140.6 (4.4)	●
12	● 45.5 (124.7)	(● 14.1 (59.2))	● 133.6 (4.3)	●
13	● 55.0 (112.8)	(● 26.1 (71.6))	● 125.2 (4.6)	●
14	● 42.4 (97.5)	(● 36.5 (86.8))	● 118.2 (4.2)	●
15	● 44.5 (106.0)	(● 46.0 (88.9))	● 116.3 (4.3)	●
16	● 53.0 (100.0)		● 108.9 (4.6)	●

† Sample partially crystallized after immersion in liquid nitrogen.

‡ Broad transition.

Table 1(c). Transition temperatures (in °C) and (in brackets) transition enthalpies (in kJ mol⁻¹) obtained by DSC upon heating the compounds of series IC-*n*.

<i>n</i>	C ₁	C ₂	M	I
3	● 9.8 (3.0)	● 142.7	● 159.9 (22.4)†	●
4		● 72.9 (2.2)	● 170.3 (7.5)	●
5		● -3.7 (—)	● 169.7 (5.8)	●
6		● -85.0 (5.9)	● 158.9 (7.2)	●
7		● -77.0 (11.0)	● 151.8 (8.6)	●
8	● -64 (—)	● -34.7 (—)	● 138.0 (8.3)	●
9		● 3.8 (34.8)	● 123.0 (7.5)	●
10	● -3.7 (—)	● 6.1 (52.3)†	● 117.0 (5.5)	●

† Enthalpy is the sum of two transitions.

3.1.1. Ethers of the ellagic acid

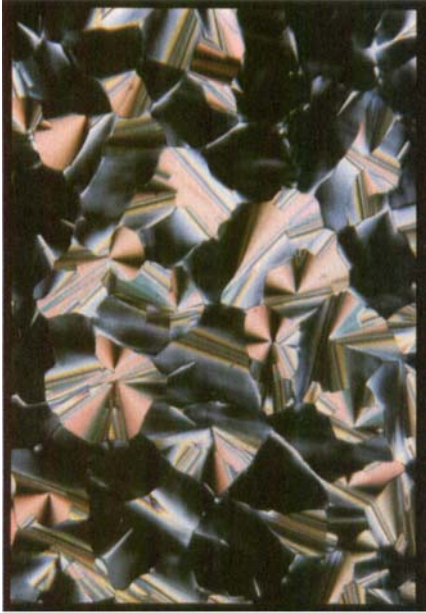
On cooling the compounds of the IA-*n* series from the isotropic liquid very slow growing of birefringent needles (see figure 3(a)) with occasional rectilinear defects is observed. Upon pressing, the needles transform to a very viscous paste which exhibits a positive optical sign. A contact preparation between IA-9 and IA-11 shows a miscibility gap for this high temperature phase with an eutectic temperature of $\sim 120^\circ\text{C}$. This fact and the high enthalpy of melting (see table 1(a)) suggests that this phase (C_2) is not liquid-crystalline but rather a (soft) solid. This conclusion is supported by X-ray measurements as exemplified by the diffraction pattern for IA-11 in the supercooled (80°C) C_2 phase in the left diffractogram of figure 4. It reveals a series of sharp low angle peaks with a d spacing ratio of approximately $1:\frac{1}{2}:\frac{1}{3}:\frac{1}{4}$. This sequence could correspond to a solid layered structure, but other structures cannot be excluded. The conspicuous peak at 4.3 \AA falls in a region often associated with reflections from aliphatic groups [11]; its sharpness is consistent with a rigid state of the aliphatic chains. The origins of the weaker diffuse peak at 7.6 \AA was not clarified.

Cooling C_2 to below the melting temperature does not usually result in the original crystalline phase, C_1 . Instead after considerable supercooling a monotropic solid (C_3) is obtained which exhibits a different X-ray pattern and optical microscope picture from C_1 . The monotropic (C_3) solid transforms to C_2 at a lower temperature than C_1 , as indicated in table 1 and by the full squares in figure 2(a).

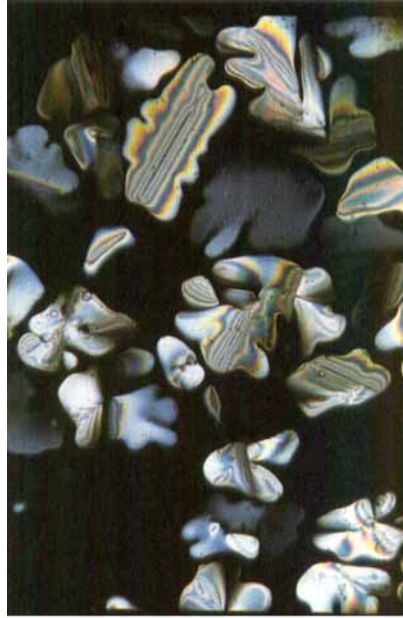
3.1.2. Ethers of the flavellagic acid

All compounds of this series which were investigated by us ($6 \leq n \leq 16$) exhibit an enantiotropic phase, M_1 , and except for $n = 15$ and 16 also a monotropic phase (M_2) (see figure 2(b) and table 1(b)). Compounds IB-6 to IB-9 apparently do not crystallize so that the transition C to M_1 is not observed. However, after long cooling (approximately 1 hour) in liquid nitrogen we observed in the DSC thermogram both the (M_2)– M_1 and C– M_1 transitions, indicating that only part of the material crystallizes under these extreme conditions. For compounds $n = 10$ to 14 on first heating we observed the C– M_1 transition while in subsequent heating only the (M_2)– M_1 transition is detected. Optical microscopy examination of IB-15 shows the sequence C– M_2 – M_1 , i.e. in this case M_2 is enantiotropic. IB-16, on the other hand, melts directly to M_1 and no M_2 is observed even upon cooling. In general the melting temperature of the solids gradually increases with the side chain length, while the clearing temperature decreases. Consequently the stability range of the mesophase M_1 decreases with the number of atoms in the side chains.

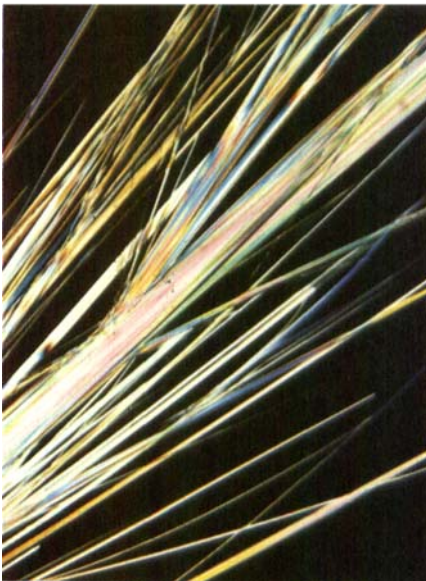
When M_1 is formed by slow cooling of the liquid phase, large domains may be observed under the optical microscope with normal or nearly normal orientation (see figure 3(b)), suggesting that the phase is uniaxial. Optical microscopy examination showed it to have a negative optical sign. The domains often exhibit six finger-like contours and sometimes rectilinear defects similar to those observed in conventional uniaxial hexagonal discotic mesophases. The X-ray patterns of this mesophase usually exhibit three sharp peaks with d values in a ratio of $1:1/\sqrt{3}:\frac{1}{2}$ as expected for a two dimensional hexagonal array. This is shown for IB-14 in figure 4(b) and in table 2. In addition there are diffuse peaks at around 4.6 \AA and 3.4 \AA and often also at 7.4 \AA . The 4.6 \AA peak is characteristic of disordered aliphatic chains while the 3.4 \AA diffraction is typical of the stacking distances in discotic columnar phases [11]. All of these observations are consistent with M_1 being a columnar hexagonal phase in which the molecules are stacked parallel to each other in the columns.



(b)



(d)



(a)



(c)

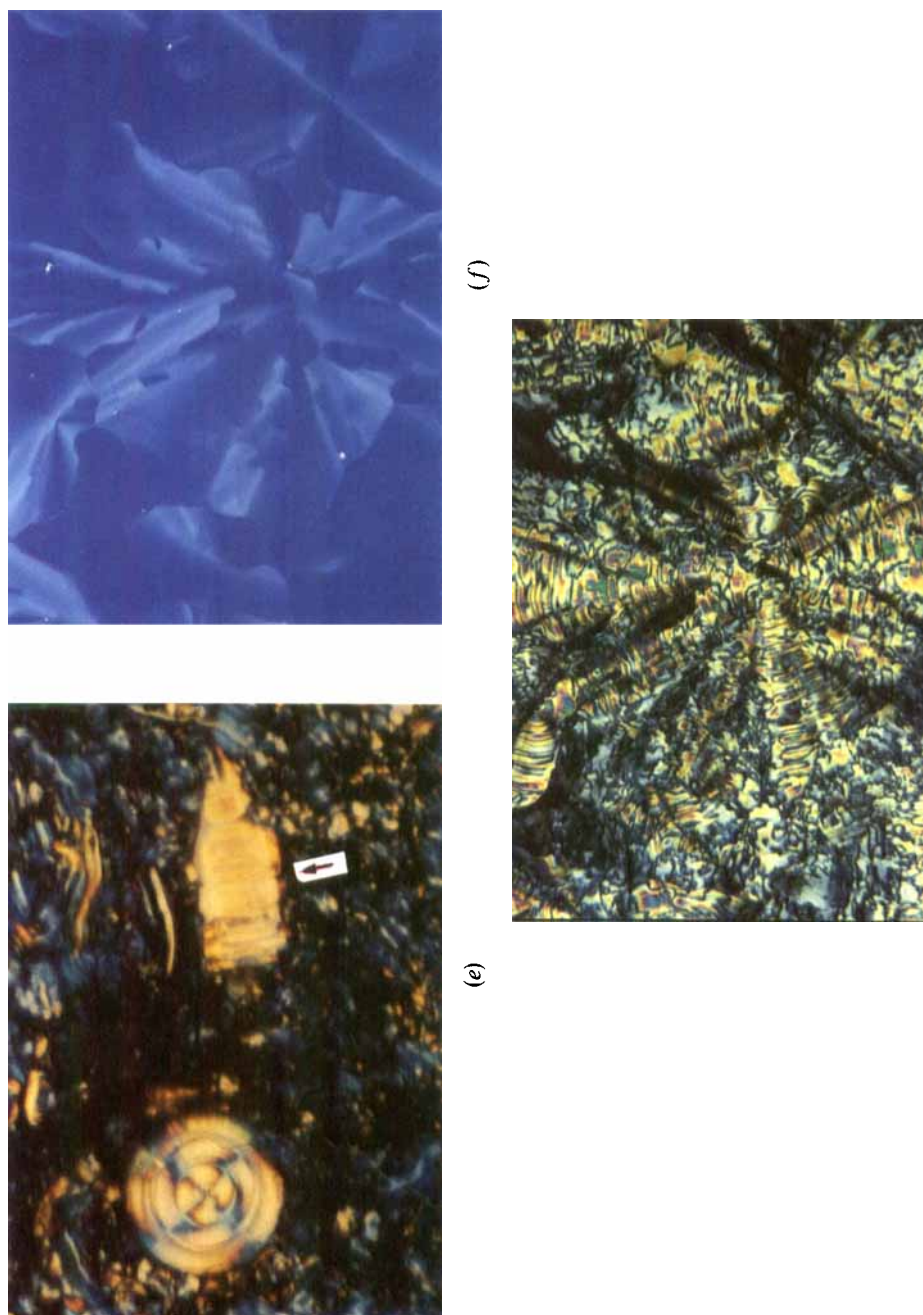


Figure 3. Polarizing optical microscopy pictures of mesophases from representative homologues of compounds studied in the present work. (a) Needle structure of the C_2 phase of 1A-11 at 125°C. (b) Domain texture in the M_1 mesophase of IB-12 supercooled to 40°C. (c) The same sample as in plate (b) after cooling to the M_2 mesophase at 6°C. (d) Domain structure of the mesophase of IC-7 at 151°C. (e) Pattern observed for the mesophase of IIB-12 just below the clearing point. Note the defects with myelinic helical tubes (arrow). (f) Pattern observed in the M_b form of the mesophase in IIC-12 at 168°C. (g) Same sample as in (f) but for the M_a form at 157°C.

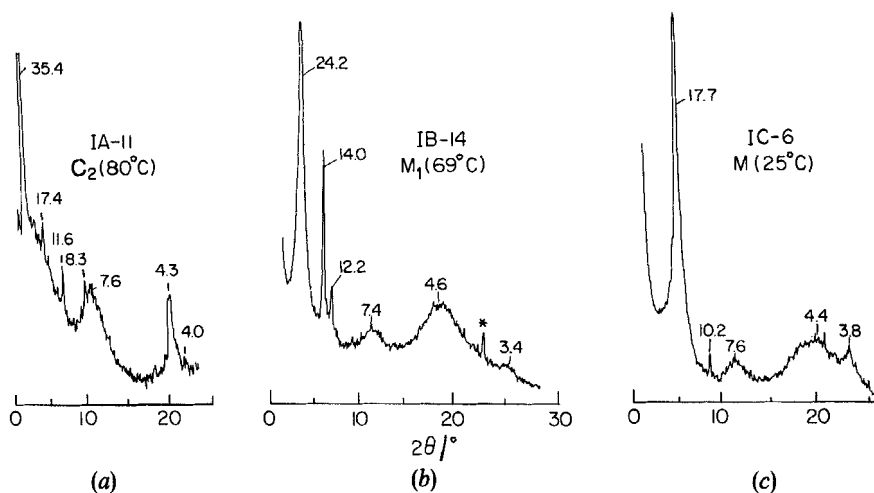


Figure 4. X-ray diffraction patterns from the mesophases of representative compounds from the ether substituted ellagic, flavellagic, and coruleoellagic acids (a) IA-11, (b) IB-14, (c) IC-6. The peak positions are indicated by their corresponding d spacings in Å. In (b) the asterisk refers to a spurious peak in the densitometer tracing.

Table 2. d spacings (in Å) of X-ray diffraction peaks obtained in the mesophase of representative compounds of the series IB- n and IC- n .

	IB-8	IB-14	IC-6
	M ₁ (110°C)	M ₁ (69°C)	M (25°C)
{10}	19.5	24.2	17.7
{11}	11.2	14.0	10.2
{20}	9.7	12.2	
		7.4†	7.6†
	4.6†	4.6†	4.4†
	3.5†	3.4†	3.8†
a Å‡	22.4	28.3	20.4

† Diffuse scattering.

‡ Hexagonal lattice parameter.

The assignment is supported by the observation made from the M₁ phase of IB-14 which was partially aligned by slow cooling from the isotropic liquid within a magnetic field of 0.75 T. The X-ray patterns show intensity maxima of the 3.4 Å reflections along the meridian (perpendicular to the field direction) while no anisotropy in the intensity of the 4.6 Å peak was observed. These results also indicate that the M₁ phase orients perpendicular to the magnetic field as is usually the case for columnar discotics with aromatic cores [12]. The unit cell parameters for the M₁ mesophase of the IB- n series were determined from the low angle reflection peaks for a number of homologues. They were found to increase with the length of the side chains, for example from 22.4 Å for $n=8$ to 28.3 Å for $n=14$ (cf. table 2), but they are essentially independent of temperature.

The optical microscopy domain pattern of the monotropic M_2 phase is identical to that of M_1 from which it is formed by cooling, but the surface becomes grainy and formation of arcs is also observed (see figure 3(c)). Upon reheating, the texture of M_1 is completely recovered. We were unable to identify definitely the structure of the M_2 mesophase by X-ray diffraction: the pattern observed in this region always contained reflections characteristic of the solid phase. If M_2 is a mesophase, however, a significant difference from M_1 is the fact that a sharp (rather than diffuse) 4.2 \AA peak is observed, suggesting that in M_2 the aliphatic chains are more rigid than in M_1 .

Binary phase diagram measurements on neighbouring homologues of the IB- n series show complete miscibility of both the M_1 and (M_2) mesophases; an example is shown in figure 5. A binary mixture of IB-6 with hexahexyloxytriphenylene exhibits complete miscibility of M_1 with the D_{h0} (D_E) mesophase of the latter compound [13, 14].

3.1.3. Ethers of the coruleoellagic acid

The phase sequence of the IC- n homologues studied ($3 \leq n \leq 10$) are summarized in figure 2(c) and in table 1(c). Cooling the isotropic liquid under the microscope stage yields, after appreciable supercooling, a birefringent phase with normally oriented domains characteristic of uniaxial mesophases. The domain boundaries often exhibit finger-like contours, and defects with rectilinear axes are usually observed (see figure 3(d)). The range of stability has a maximum at around $n = 6-7$ where it spans an overall

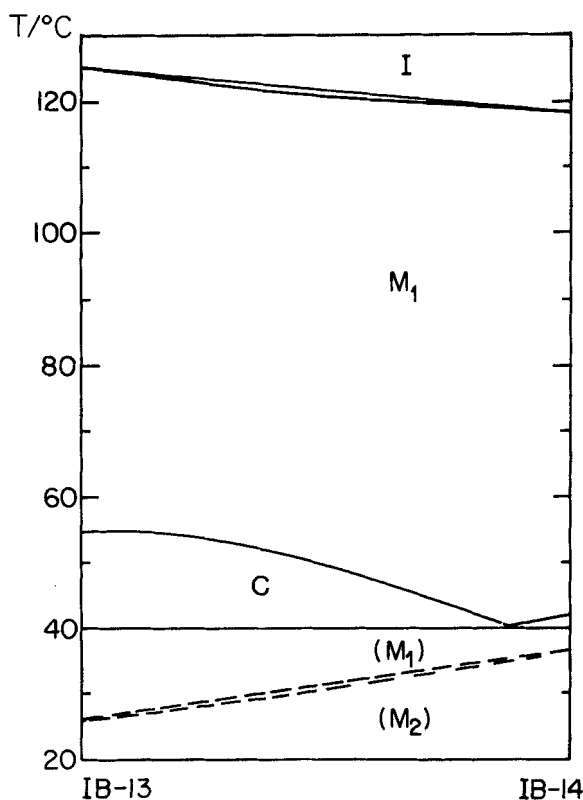


Figure 5. Binary phase diagram between the neighbouring homologues IB-13 and IB-14. Note that both M_1 and M_2 are completely miscible.

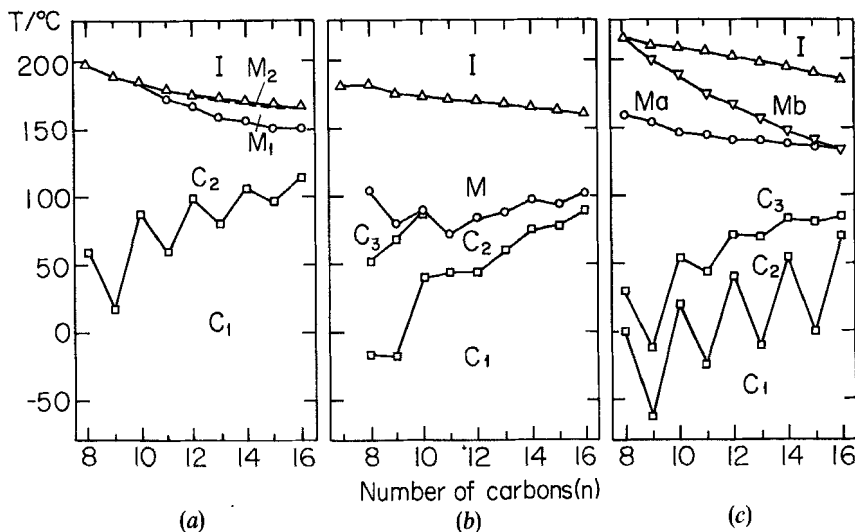


Figure 6. Phase transition temperatures observed upon heating of the compounds of series (a) IIA-*n*, (b) IIB-*n* and (c) IIC-*n*. The results for IIA-*n* are from [6]. The inverted triangles in (c) correspond to transitions that are observed by optical microscopy but not by DSC.

Table 3(a). Transition temperatures (in °C) and (in brackets) transition enthalpies (in kJ mol⁻¹) obtained on heating compounds of series IIA-*n*.

<i>n</i>	C ₁	C ₂	M ₁	M ₂	I
8	● 60.5 (23.5)	● 198.5 (77.4)			●
9	● 17.6 (13.0)	● 189.4 (84.3)			●
10	● 87.5 (24.2)	● 183 (—)	● 184.5 (85.7)†		●
11	● 58.8 (23.3)	● 173.0 (10.0)	● 179.2 (83.2)		●
12	● 98.8 (29.6)	● 166.4 (10.7)	● 176.1 (80.4)	(● 175.2 (74.2))	●
13	● 80.0 (22.8)	● 158.1 (17.6)	● 173.1 (83.3)	(● 172.4 (79.2))	●
14	● 107.2 (37.9)	● 155.8 (21.9)	● 170.8 (87.0)	(● 169.0 (72.9))	●
15	● 96.5 (24.1)	● 151.5 (25.1)	● 168.2 (80.4)	(● 166.9 (70.9))	●
16	● 114.6 (44.0)	● 151.0 (36.8)	● 166.2 (91.4)	(● 165.5 (75.5))	●

† Sum of melting and clearing enthalpies.

Table 3(b). Transition temperatures (in °C) and (in brackets) transition enthalpies (in kJ mol⁻¹) obtained by DSC upon heating compounds of series IIB-*n*.

<i>n</i>	C ₁	C ₂	C ₃	M	I
7	●			180.8 (49.3)	●
8	● -16.5 (4.4)	● 52.3 (2.7)	● 103.9 (4.9)	● 182.5 (51.4)	●
9	● -17.8 (6.0)	● ~68‡	● 79.3 (14.3)†	● 175.3 (50.5)	●
10	● ~40‡	● ~89‡	● 89.8 (13.7)†	● 173.9 (49.4)	●
11	● ~44‡		● 71.7 (46.8)†	● 170.9 (48.6)	●
12	● ~44‡		● 83.1 (62.9)†	● 169.7 (46.4)	●
13	● ~60‡		● 88.1 (75.9)†	● 167.8 (47.4)	●
14	● ~75‡		● 97.3 (92.5)†	● 164.8 (47.0)	●
15	● ~78‡		● 93.4 (124.0)†	● 163.5 (49.4)	●
16	● ~90‡		● 102.3 (117.0)†	● 161.5 (49.3)	●

† Enthalpies are the sum of two transitions.

‡ Very broad peak, partially overlapping with a nearby sharper signal.

range of 230 to 240°C. For shorter and longer side chains the stability range is considerably narrower. The physical properties of the mesophase are very similar to those of M_1 of the flavellagic acid ethers. The mesophase is highly viscous at room temperature but it becomes more fluid upon heating.

X-ray diffraction measurements on one homologue of the series (IC-6), reveal only two sharp reflections (see figure 4(c)) at 17.7 and 10.2 Å. The ratio of $\sqrt{3}:1$ suggests that M is a columnar hexagonal phase with a lattice parameter $a = 20.4$ Å. As usual there are also diffuse bands at 7.6, 4.4 and 3.8 Å and we interpret the latter two as arising from the hydrocarbon methylenes and the intracolumnar stacking distances, respectively. A contact preparation of IC-10 with the corresponding homologue of the flavellagic series (IB-10) showed complete miscibility of M with M_1 indicating that M also belongs to the D_h (D_E) class [14].

3.2. Alkanoyloxy substituted ellagic, flavellagic and coruleoellagic acids

The phase sequences of the homologues of the series IIB- n and IIC- n studied in the present work are summarized in figures 6(b) and (c) and in tables 3(b) and (c). For completeness we also show in figure 6(a) and table 3(a) the phase diagrams of the series IIA- n compounds which were studied earlier [6].

3.2.1. Esters of the ellagic acid

The phase diagrams of compounds belonging to this series with $n = 10$ to 16 show an enantiotropic mesophase M_1 and for $n = 12$ to 16 also a monotropic mesophase M_2 . The latter was tentatively identified as a cubic mesophase because no birefringence was observed on optical microscopy examination of this phase [6]. We have now performed X-ray measurements on both the M_1 and M_2 phases of some representative members of the IIA- n series. Both phases exhibit a large number of sharp diffraction peaks indicating a high degree of order but we have so far been unable to interpret these peak arrays and thus to confirm the previous assignments by optical microscopy.

3.2.2. Esters of the flavellagic acid

The compounds of this series show two or three crystalline phases and an enantiotropic mesophase (see figure 6(b) and table 3(b)). The solid–solid transitions are usually quite broad, ranging over $\sim 20^\circ\text{C}$ while the melting and the clearing transitions are much sharper. The viscosity of the mesophases of these compounds is quite high but decreases somewhat upon heating. Under the polarizing microscope they exhibit irregular textures with very low birefringence and occasional textures with myelinic helical tubes (see figure 3(e)). The birefringence could clearly be verified using a wave retarding plate, but the effect was too weak to allow the determination of the optical sign. Contact preparations on several neighbouring homologues confirm the identity of the phase structure in the series.

The X-ray patterns obtained from the mesophases of the IIB- n compounds are straightforward to interpret. An example is shown in figure 7(a) for IIB-16 where as many as seven sharp diffraction peaks and a broad diffuse band are observed. The sharp peaks in this compound can readily be indexed on a two dimensional hexagonal lattice (see table 4) and so we conclude that the M phases of the IIB- n series are columnar hexagonal. As for the compounds in the corresponding IB- n series the lattice parameters are almost independent of temperature but they increase with the number of carbon atoms in the side chains (see table 4). A strong diffuse peak at around 4.8 Å due to reflections from the aliphatic chains is also observed in these compounds but

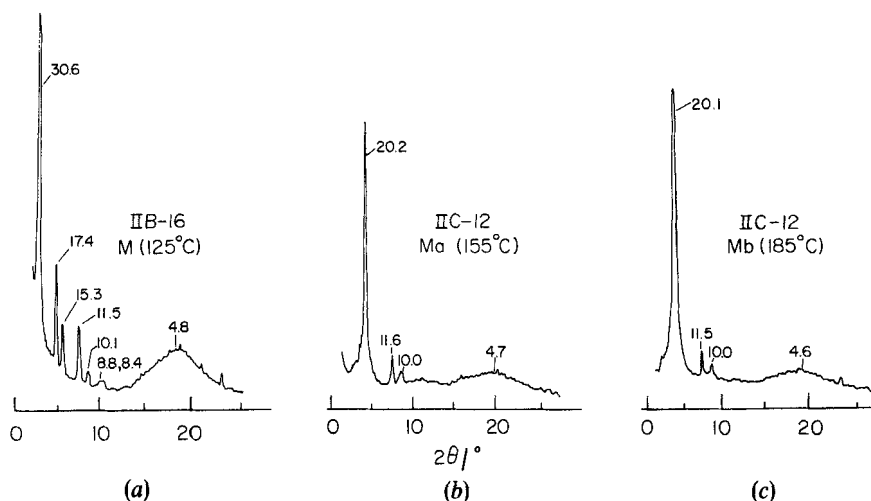


Figure 7. X-ray diffraction patterns from the mesophases of representative compounds from the ester substituted flavellagic and coruleoellagic acids. (a) IIB-16, (b) and (c) IIC-12 at 155 and 185°C.

Table 4. d spacings (in Å) of the X-ray diffraction peaks obtained in the mesophases of representative compounds of the series IIB- n and IIC- n .

$\{hk\}$	IIB-12		IIB-16		IIC-10		IIC-12		IIC-16
	M (125°C)	M (154°C)	M (125°C)	M _a (158°C)	M _b (189°C)	M _a (155°C)	M _b (185°C)	M _b (141°C)	
{10}	25.0	24.5	30.6	18.2	18.0	20.2	20.1	23.4	
{11}	14.4	14.4	17.4	10.9	10.8	11.6	11.5	13.3	
{20}	12.4	12.7	15.3	9.6	9.5	10.0	10.0	11.6	
{21}	9.4	9.5	11.5						
{30}	8.4	8.6	10.1						
{22}			8.8						
{31}			8.4						
	7.7†	7.7†		7.9†	7.4†	7.9†	7.4†	8.2†	
	4.3†		4.8†	4.7†	4.7†	5.5†	5.6†	5.6†	
						4.7†	4.6†	4.7†	
$a/\text{Å}^\ddagger$	28.8	29.0	35.1	21.7	21.4	23.2	23.0	26.8	

† Diffuse scattering.

‡ Hexagonal lattice parameter.

none is detected at around 3.5 Å due to the intracolumnar repeat distances. There appears, however, to be some additional intensity at approximately 5.6 Å which might correspond to the intracolumnar spacing. Such a reflection was also observed in the coruleoellagic esters and will be further discussed later.

3.2.3. Esters of the coruleoellagic acid

The phase sequences of the homologues of this series are summarized in figure 6(c) and table 3(c). Here too the compounds possess several solid phases and apparently two forms of mesophases. The solid-solid transitions exhibit even-odd alternation

both with regard to the transition temperatures, and for the C_1 to C_2 transitions also in the width of the transitions; the odd members (i.e. with odd n 's) consistently exhibit a narrower DSC peak than the even ones. Differential scanning calorimetry does not reveal any phase transition within the mesophase region; however under the polarizing optical microscope very clear and (for fresh samples) reproducible transformations between two textures are observed. They are indicated by the inverted triangles in the diagram of figure 6(c) and the mesophases above and below the dividing line are referred to as M_b and M_a , respectively. These transitions as well as the clearing and melting temperatures decrease during the course of the examinations, apparently due to thermal decomposition of the samples. A binary phase diagram of the neighbouring compounds IIC-14 and IIC-15 show complete miscibility of both the M_b and M_a forms (see figure 8).

Cooling the isotropic liquid under the optical microscope into the M_b region yields domains with digitized contours and sometimes with rectilinear defects, but very weak birefringence. Further cooling into the M_a region results in a sudden increase in the birefringence while preserving the texture of the domains; the optical sign was found to be negative. The transition between M_a and M_b is reversible upon heating and cooling (but as indicated previously, it decreases with time). Textures of the M_a and M_b forms for the homologue IIC-12 are shown in figures 3(f) and (g), respectively. Note that the homologue IIC-16 exhibits only the high temperature M_b form of the mesophase while IIC-8 only the low temperature M_a form.

X-ray measurements were performed on both the high and low temperature forms of the mesophase for several homologues of this series. Diffraction patterns for IIC-12

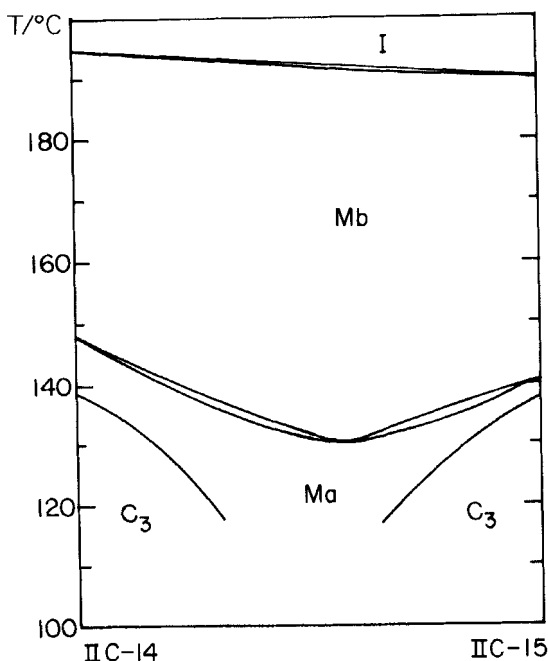


Figure 8. A binary phase diagram of the two neighbouring homologues IIC-14 and IIC-15 showing complete miscibility of both forms of the mesophases.

are shown in figures 7(b) and (c), and results for this and several other members are summarized in table 4. In all cases three sharp diffraction peaks were observed which could be indexed on a two dimensional hexagonal lattice. The corresponding lattice parameters were found to increase with the chain length, however within each compound, essentially the same values were found in M_a and M_b . A diffuse peak at 4.6–4.7 Å from the aliphatic chains is also clearly observed but again no reflections are detected at around 3.5 Å. In this case, however, close examination of the X-ray exposed photographic films, clearly reveals an additional diffuse ring at around 5.5–5.7 Å that could be related to the intracolumnar stacking distance. The ring is very weak and, therefore, not readily observable in the densitometric tracings in figures 7(b) and (c). It is likely that in the ester derivatives of the coruleoellagic acid as well as in the flavellagic acid discussed previously the cores are less closely packed and less ordered compared with the corresponding ether derivatives, due to steric hindrance effects of the bulkier carboxylic groups. A similar stacking distance (5.6 Å) was observed within the columnar phase of an ester substituted anthraquinone (hexaoctanoyloxyanthraquinone) [15].

We thus conclude that the mesophases observed for the IIC-*n* compounds are also columnar hexagonal. Whether the transformation from the weakly birefringent to the strongly birefringent form is a phase transition or not is not yet clear. If it is a phase transition it must be second order or at least very weakly first order. The transition could then perhaps be associated with very little distortions of the hexagonal structure, or very small changes in the correlation length within the columns which are too small to be observed in our X-ray diffraction patterns.

4. Summary and conclusions

We have shown that homologous series derived from benzopyranobenzopyran-dione with four, five and six side chains per molecule linked via ether or ester groups are highly polymorphic with the high temperature phases usually being mesomorphic. The only exceptions are the ethers of ellagic acid which are apparently not mesogenic. The four series consisting of the ethers and esters of flavellagic and coruleoellagic acids exhibit at least one columnar hexagonal mesophase. These compounds must therefore be added to the ever increasing list of discotic liquid crystals [15]. The X-ray and optical microscopy measurements on these phases are consistent with a columnar structure in which the molecules are stacked parallel to each other as in the conventional discotics such as the derivatives of triphenylene and truxene. They seem however to be considerably more highly ordered and less mobile than the latter. It would therefore be interesting to study the dynamic properties of the new series using NMR spectroscopy and similar methods. It should also be interesting to extend this study to 2,7-disubstituted benzopyranobenzopyran-dione. This molecule has the general structure of the conventional calamitic liquid crystals but with the two phenyl rings locked in a common plane by the lactone groups. If these compounds were found to be mesomorphic, we could learn more about the role played by the side chains in determining the nature (discotic or calamitic) of the resulting mesophases.

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References

- [1] KELKER, H., and HATZ, R., 1980, *Handbook of Liquid Crystals* (Verlag Chemie). DEMUS, D., and ZASCHKE, H., 1984, *Flüssige Kristalle in Tabellen*, Vol. II (VEB).
- [2] D'ANNIBADE, A., LUNAZZI, L., BOICELLI, A. C., and MACCIANTELLI, D., 1973, *J. chem. Soc., Perkin II*, p. 1396. NIEDERBERGER, W., DIEHL, P., and LUNAZZI, L., 1973, *Molec. Phys.*, **26**, 571.
- [3] ZIMMERMANN, H., POUPKO, R., LUZ, Z., and BILLARD, J., 1985, *Z. Naturf. (a)*, **40**, 149; 1986, *Ibid.*, **41**, 1137.
- [4] POUPKO, R., LUZ, Z., SPIELBERG, N., and ZIMMERMANN, H., 1989, *J. Am. chem. Soc.*, **111**, 6094.
- [5] ZIMMERMANN, H., POUPKO, R., LUZ, Z., and BILLARD, J., 1988, *Liq. Crystals*, **3**, 759; 1989, *Ibid.*, **6**, 151.
- [6] BILLARD, J., ZIMMERMANN, H., POUPKO, R., and LUZ, Z., 1989, *J. Phys., Paris*, **50**, 539.
- [7] BILLARD, J., 1987, *C.r. hebd. Séance Acad. Sci., Paris*, **305**, serie II, 843.
- [8] DEAN, F. M., 1949, *Progress in Chemistry of Organic Natural Products*, Vol. IX, (Springer-Verlag), p. 283. JURD, L., 1956, *J. Am. chem. Soc.*, **78**, 3445.
- [9] MATHIESON, MCL., and POPPLETON, B. J., 1968, *Acta crystallogr. B*, **24**, 1456. GEEVANANDA, Y. A., GUNAWARDANA, P., KUMAR, N. S., and SULTANBAWA, M. U. S., 1979, *Phytochemistry*, **18**, 1017. BLEULER, H., and PERKIN, A. G., 1916, *J. chem. Soc.*, **109**, 529.
- [10] GUTMAN, H., LUZ, Z., WACHTEL, E. J., POUPKO, R., and CHARVOLIN, J., 1990, *Liq. Crystals*, **7**, 335.
- [11] LEVELUT, A. M., 1983, *J. Chim. phys.*, **80**, 149.
- [12] GOLDFARB, D., LUZ, Z., and ZIMMERMANN, H., 1981, *J. Phys., Paris*, **42**, 1303.
- [13] DUBOIS, J. C., and BILLARD, J., 1984, *Liquid Crystals and Ordered Fluids*, Vol. 4, edited by A. C. Griffin and J. F. Johnson (Plenum), p. 1043.
- [14] The miscibility diagrams only indicate the equivalence of the symmetry of the mesophases with those of the reference samples, i.e. that they are hexagonal columnar (D_h). Whether the mesophases are ordered or disordered within the columns cannot readily be determined from miscibility experiments. From the diffuseness of the 3.4 Å peak in the X-ray diffraction pattern of IB-14 we may conclude that in this compound the mesophase is intermediate between D_{ho} and D_{hd} .
- [15] NGUYEN, H. T., DESTRADE, C., and MALTHETE, J., 1990, *Liq. Crystals*, **8**, 797.