

PATENT SPECIFICATION

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(54) BIPHENYL CARBOXYLIC ESTERS AND THEIR USE AS LIQUID CRYSTAL MATERIALS

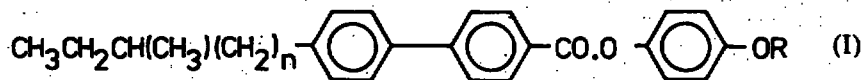
(71) I, SECRETARY OF STATE FOR DEFENCE, London do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with biphenyl carboxylic acid esters which exhibit liquid crystal -phases, and with electro-optic display devices incorporating such materials.

Liquid crystal phases are exhibited by certain organic compounds and constitute an intermediate state which exists between the crystalline solid and the fully disordered liquid phase and within which certain long range ordering of the molecules takes place.

There are two broad types of liquid crystal phase; the smectic mesophase in which the long range ordering is of a substantially lamellar type and the nematic mesophase in which the ordering is substantially linear, ie the molecules tend to line up with the long axes of the molecules parallel. Included sometimes as a subclass of the nematic mesophase and sometimes classified as a separate mesophase is the cholesteric mesophase. This last has a helical long range order imposed upon the linear order of the nematic mesophase. Compounds displaying a cholesteric mesophase are optically active (chiral) and the pitch of the helical twist is determined by the nature and extent of the optical activity. The pitch of the helical twist may be such that thin films of the cholesteric phase reflect visible light, resulting in the observation of bright colours, and the pitch may also be sharply temperature dependent resulting in the reflection of particular colours over particular temperature ranges so that the cholesteric mesophase in question can act as a "thermometer". This behaviour is known as thermochromism.

In accordance with the present invention a liquid crystal compound which is optically active is an ester which has the general formula:—



wherein n has the value 1, 2, or 3, when R is a normal or branched chain alkyl group containing up to ten carbon atoms which may also contain a chiral centre. The alkyl group R is preferably a normal chain alkyl group containing four to ten carbon atoms.

These compounds exhibit a cholesteric mesophase (hereinafter designated Ch) because of their molecular shape and optical activity and also a chiral smectic C mesophase (hereinafter designated S_c) underlying the cholesteric mesophase. They exhibit, either on their own or when mixed with one or more compounds capable of forming S_c liquid crystal phases, a chiral S_c liquid crystal phase in which the

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molecules lie tilted in the smectic layers which are themselves superimposed one upon the other to give a helical distribution of the tilt angles on passing through a stack of layers. A unique feature of the chiral S_c phases of the compounds of the present invention is that, in their planar S_c textures, these mesophases have a helical pitch which gives a selective reflection of coloured light of specific wavelengths which are dependent on temperature, ie, the compounds are thermochromic.

Also, above the S_c -Ch transition, the compounds of the present invention exhibit, either on their own or when mixed with one of more other liquid crystal compounds, a cholesteric liquid crystal phase in which the molecules are arranged in the helical formation of that phase such that a film of the phase in the Grandjean plane texture rotates the plane of polarisation of incident polarised light and reflects elliptically polarised light of specific wavelengths when illuminated by ordinary light, so that the mesophases are thermochromic.

The compounds of the present invention have properties such that they may be used in a liquid crystal electro-optic device such as a 'phase change' device in which the material is changed between a so-called 'focal-conic' cholesteric state, which scatters light, and a transparent nematic state by an applied electric field and in accordance with one aspect of the present invention an electro-optic device includes in its liquid crystalline material a compound as hereinbefore defined. It will of course be realised that there may be present, a mixture (solution) of compounds as hereinbefore defined and that other compounds exhibiting liquid crystalline behaviour may be included. Preferably the mixture of compounds used is a eutectic. The optical effect of the electro-optical device may be enhanced by the inclusion of pleochroic dyes. Suitable pleochroic dyes for this purpose are described in Copending UK patent applications numbered 25843/75 (now Specification No. 1,555,954) and 25859/75 (now Specification No. 1,555,955).

In accordance with a second aspect of the present invention an electro-optic display device includes as its liquid crystalline material a wide range chiral S_c phase composed of a mixture (solution) of the compounds hereinbefore defined such that the selectively light reflecting (ie coloured) chiral S_c phase is converted to a non-light reflecting, homeotropic (colourless) condition by an applied electric field. That is to say the pitch of the S_c planar structure is effectively unwound by an external electric field which changes the tilt orientation of molecules such that they finally adopt an orthogonal orientation with respect to the layers.

Compounds of the present invention exhibit both a chiral S_c phase and a Ch phase at higher temperatures and mixtures of such materials may exhibit thermochromism in both mesophases. This occurs, it is believed, because the helical pitch lengths of the molecular formations are such as to give strongly temperature dependent Bragg reflection of particular wavelengths of light in the visible spectral region. That is, the materials appear coloured with a colour which varies with the temperature of the material. The sequence of colours given with changing temperature in one direction by the cholesteric phase is the reverse of that given by the chiral S_c phase. The materials of the present invention and mixtures thereof may thus be used in surface thermography, eg for the detection of breast cancer. They may be applied in a thin film on the surface of interest. The colour of the film in reflection at right angles to the surface indicates the temperature of the surface.

This last mentioned property may be used to produce a temperature sensitive display device, eg a thermometer, giving a visual display resulting from the effect of changes of temperature upon the helical pitch of the material and consequently the reflected colour.

Compounds of general formula (I) given above have previously been disclosed and claimed amongst many other compounds in UK Patent Specification No 1,456,359. However the compounds of general formula (I) disclosed in that Specification are not optically active and so do not give the cholesteric, smectic C and thermochromic properties given by the compounds according to the present invention.

The present invention will now be described by way of example only with reference to following Examples which illustrate typical synthetic routes for the preparation of materials in accordance with the present invention.

In the following description of this specification the following symbols are used.

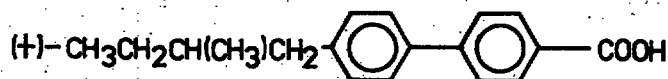
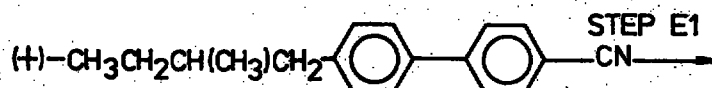
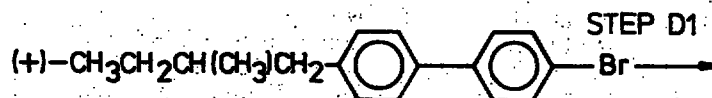
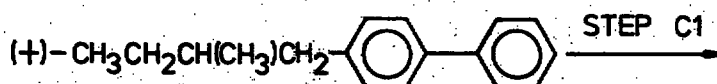
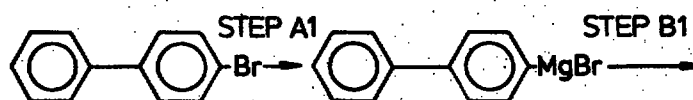
(+): which refers to an optically active material having a positive optical rotation angle.

(-): which refers to an optically active material having a negative optical rotation angle.

$[\alpha]_D^{20}$ which is an absolute measure of the rotatory power (specific rotation) of an optically active material when forming a 10% w/v solution in chloroform.

Example 1

This describes the production of (+) - 4 - (2" - methylbutyl)biphenyl - 4' - carboxylic acid by the following route:



Step A1: the production of biphenyl - 4 - magnesium bromide by the 'entrainment' method.

(+) - 2 - Methylbutyl bromide (0.07 mol), prepared as in Step A2 of Example 2, in dry tetrahydrofuran (20 ml), is added to magnesium turnings (0.2 g atom) in dry tetrahydrofuran (20 ml) and the mixture is stirred for 0.5 hours. The reaction is controlled by adding the alkyl bromide in drops.

4-Bromobiphenyl (0.13 mol) in dry tetrahydrofuran (20 ml) is then added in drops so as to maintain a steady refluxing of the solvent. When the addition is complete, the reaction mixture is stirred and heated under reflux for 4 hours and then left to stand overnight.

Step B1: The production of (+)-4-(2"-methylbutyl) biphenyl.

The solution of the Grignard reagent, produced in Step A1, is cooled in an ice bath and, with vigorous stirring, a solution of ferric chloride (0.005 mol) in dry tetrahydrofuran (1.5 ml) is added in drops followed by a solution of (+)-2-methylbutyl bromide (0.2 mol) in dry tetrahydrofuran (20 ml). The mixture is stirred for 12 hours, then stirred and heated under reflux for 12 hours. After

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cooling, the mixture is poured into a beaker containing ice (200 g), water (400 ml) and concentrated hydrochloric acid (40 ml), and stirred for 0.5 hours.

The aqueous mixture is shaken with ether (4×200 ml) and the combined extracts are washed with water (3×100 ml) before drying over anhydrous sodium sulphate. The solvent is evaporated off and the crude oily product is purified using a silica gel column, eluting this with petroleum ether, b.p. 40–60°. The purified product is then distilled at 0.1 mm Hg pressure.

Step C1: The production of (+)-4-(2"-methylbutyl)-4'-bromobiphenyl.

Under anhydrous conditions, a solution of bromine (0.5 ml) in dry chloroform (5 ml) is added to (+)-4-(2'-methylbutyl) biphenyl (0.04 mol), produced in step B1, dissolved in dry chloroform (10 ml). The reaction mixture is kept at 0°C throughout the reaction time and light is excluded from the reaction vessel.

After 18 hours and 36 hours two further additions (2×4 ml) of the chloroform solution of bromine (10% v/v) are added.

18 hours after the second addition, the mixture is poured into a sodium metabisulphite solution (150 ml). The aqueous solution is shaken with ether (3×80 ml). The combined extracts are washed with water (3×50 ml), dried over anhydrous sodium sulphate and the solvent evaporated off. The crude solid is recrystallised from ethanol to a constant melting point.

Step D1: The production of (+)-4-(2"-methylbutyl)-4'-cyanobiphenyl.

This reaction, which is a conventional synthetic organic chemical reaction, is carried out in a manner analogous to step F2 in Example 2 below.

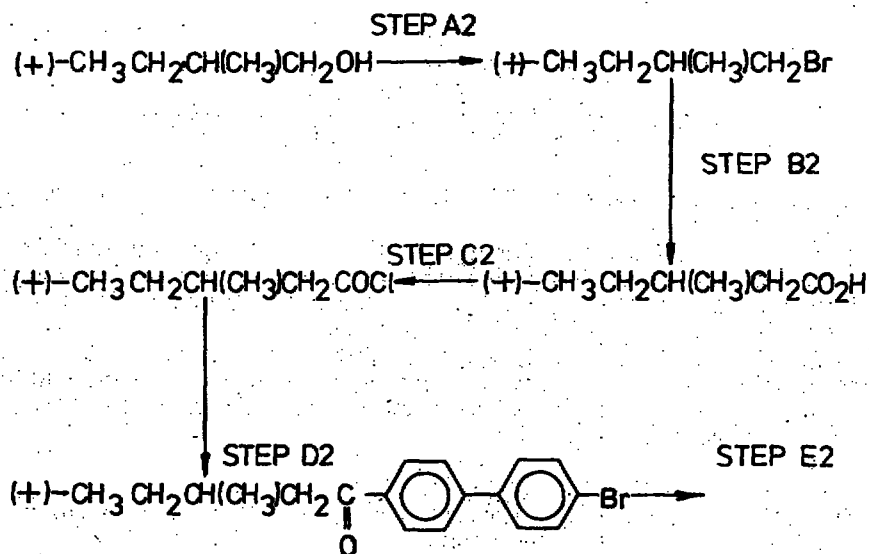
Step E1: The production of (+)-4-(2"-methylbutyl) biphenyl-4'-carboxylic acid from the corresponding nitrile.

This step may be carried out as follows:—

(+)-4-(2"-Methylbutyl)-4'-cyanobiphenyl (0.015 mole), prepared in Step D1, is dissolved in methanol (50 ml) and is added to a mixture of potassium hydroxide (0.54 mole) and sodium hydroxide (0.75 mole) in methanol (40 ml) and water (20 ml). The solution is heated under reflux until evolution of ammonia ceases (ca 72 hr). The mixture is diluted with water (1000 ml) and acidified with concentrated hydrochloric acid. The precipitated product is filtered off and crystallised twice from ethanol: crystal—cholesteric liquid crystal, 224°C, cholesteric liquid crystal—isotropic liquid, 247.4°C.

Example 2

The preparation of (+)-4-(3"-methylpentyl)-4' carboxylic acid by the following route:—

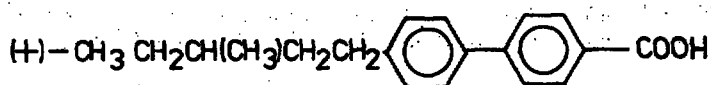
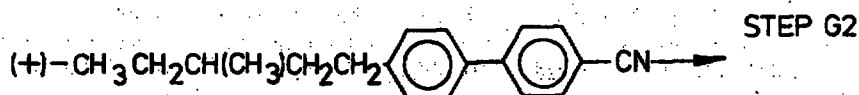
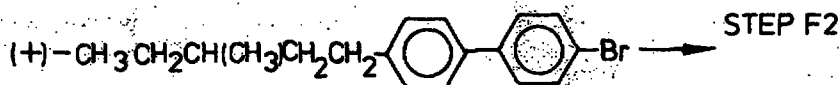


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Step A2: The production of (+)-2-methylbutyl bromide.

To a stirred solution of commercially available (–)-2-methylbutanol (0.34 mol) in dry 'Analar' (Trade Mark) pyridine (0.12 mol) is added in drops phosphorus tribromide (0.135 mol). The temperature during the addition is maintained below 15°C by cooling the mixture in an ice bath. The white emulsion which forms is stirred at room temperature for 2 hours. After this time the crude bromide is distilled from the emulsion under reduced pressure (300 mm Hg) until the mixture turns orange and 'seeths'.

The crude distillate is taken up in petroleum ether (b.p. 40/60°C; 100 ml) and is washed with:

- (a) 5% sodium hydroxide solution (3×50 ml);
- (b) water (3×50 ml);
- (c) 10% sulphuric acid (2×50 ml);
- (d) concentrated sulphuric acid (100 ml);
- (e) water (2×100 ml).

The solution is dried over anhydrous sodium sulphate and the solvent is then evaporated off. The residue is distilled and the fraction boiling at 121°C collected (96.5% pure by g.l.c.). The product has $[\alpha]_D^{20}$ 3.9°.

Step B2: The production of (+)-3-methylpentanoic acid.

Under anhydrous reaction conditions, the Grignard reagent from (+)-2-methylbutyl bromide (0.38 mol), produced by Step A2, is prepared by conventional methods. The freshly made reagent is poured onto crushed solid carbon dioxide (450 g) in ether and the mixture is left stirring until a paste forms. The paste is acidified with 50% aqueous hydrochloric acid (240 ml). The combined ether layer and ether extracts of the aqueous layer are extracted with 25% sodium hydroxide solution (3+60 ml). The sodium hydroxide extracts are acidified with concentrated hydrochloric acid and then shaken with ether (4×100 ml). The ether extracts are washed with water (2×50 ml), dried over anhydrous sodium sulphate and the solvent is evaporated off. The residue is distilled under slight vacuum (450 mm Hg) and the fraction boiling at 136°C is collected $[\alpha]_D^{20}$ 6.4°.

Step C2: The production of (+)-3-methylpentanoyl chloride.

The acid from step B2 is converted to its acid chloride using thionyl chloride according to a standard method. After removal of the excess of thionyl chloride, the residual acid chloride is used in step D2 without further purification.

Step D2: The production of (+)-4-(3'-methylpentanoyl)-4'-bromobiphenyl.

To a mixture of anhydrous aluminium trichloride (0.1 mol) in dry dichloromethane (40 ml) is added in drops a mixture of 4-bromobiphenyl (0.086 mol) and (+)-3-methylpentanoyl chloride (0.1 mol) in dichloromethane (80 ml). The mixture is left stirring for 18 hours. After this time, the mixture is poured into a beaker containing, ice (100 g), water (30 ml) and concentrated hydrochloric acid (50 ml) and left stirring for 0.5 hour. The organic layer is separated off, washed with water (2×40 ml), dried over anhydrous sodium sulphate and the solvent evaporated off. The crude product is then crystallised to constant melting point (97°C) from ethanol.

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Step E2: The production of (+) - 4 - (3" - methylpentyl) - 4' - bromobiphenyl.
To lithium aluminium hydride (0.063 mol) in sodium dried ether (100 ml) are added:

(a) anhydrous aluminium trichloride (0.135 mol) in sodium dried ether (100 ml) and

(b) (+) - 4 - (3" - methylpentanoyl) - 4' - bromobiphenyl (0.0185 mol) in dry chloroform (200 ml) at such a rate that the mixture gently boils.

The reaction mixture is then left stirring and boiling for 18 hours. The excess of lithium aluminium hydride is then destroyed by cautiously adding water to the mixture.

The mixture is then poured into a solution of ice (200 g), water (60 ml) and concentrated hydrochloric acid (100 ml) and left stirring for 0.5 hours.

The organic layer is separated off, washed with water (3×100 ml), dried over anhydrous sodium sulphate and the ether is then evaporated off. The solid product is recrystallised from ethanol to constant melting point (101—102°C).

Step F2: The production of (+)-4-(3"-methylpentyl)-4'-cyanobiphenyl.

A mixture of (+ - 4 - (3" - methylpentyl) - 4' - bromobiphenyl (0.03 mol), (the product of step E2), cuprous cyanide (0.03 mol) and *N*-methylpyrrolidone (38 ml) is heated under reflux and stirred for 2 hours. The cooled reaction mixture is poured into a solution of ferric chloride (12 g) concentrated hydrochloric acid, (5 ml) and water (150 ml), and stirred at 60°C for 0.5 hour.

The organic material is then taken up in ether; the extract is washed with dilute hydrochloric acid (2×100 ml) and water (3×100 ml), dried over anhydrous sodium sulphate, and the solvent is then evaporated off.

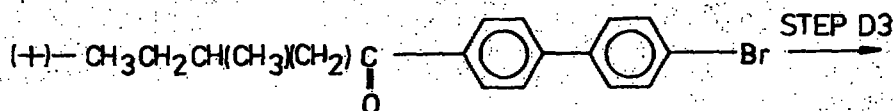
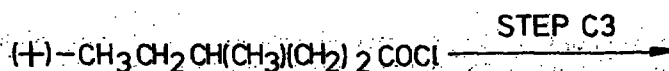
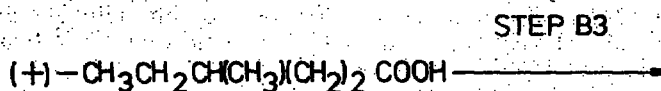
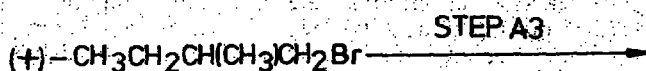
The crude oily product is purified by column chromatography using a silica gel column and eluting with chloroform. The purified product is then distilled at 0.1 mm Hg, at an oil bath temperature of 180°C.

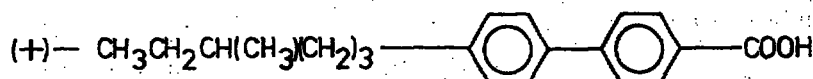
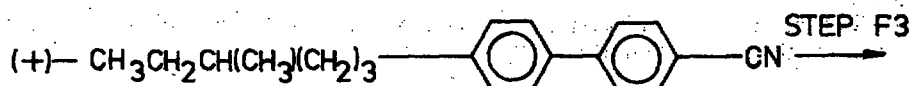
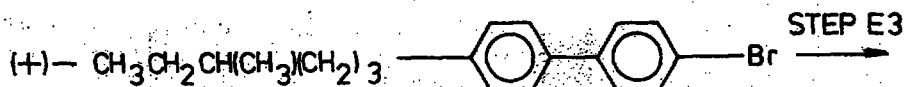
Step G2: The production of (+) - 4 - (3" - methylpentyl)biphenyl - 4' - carboxylic acid from the corresponding nitrile.

The acid may be prepared and purified by a method analogous to that in Step E1 of Example 1. The colourless crystals have crystal-cholesteric liquid crystal, 219°C, cholesteric liquid crystal—isotropic liquid, 242.2°C.

Example 3

The preparation of (+) - 4 - (4" - methylhexyl)biphenyl - 4' - carboxylic acid by the following route:—





Step A3: The production of (+)-4-methylhexanoic acid.

(+)-2-Methylbutyl bromide, prepared as in step A2 of Example 2 above is converted into (+)-4-methylhexanoic acid by interaction with diethyl malonate followed by hydrolysis of the ester according to a literature method. The product (96% pure by g.l.c.) has an $[\alpha]_D^{20}$ 9.4° and boiled at 134°C at 25 mm Hg.

Step B4: The production of (+)-4-methylhexanoyl chloride.

The acid from step A3 is converted into the acid chloride by interaction with thionyl chloride according to a standard method. After removal of the excess of thionyl chloride, the residual acid chloride is used in step C3 without further purification.

Step C3: The production of (+)-4-(4''-methylhexanoyl)-4'-bromobiphenyl.

The acid chloride from step B3 is interacted with 4-bromobiphenyl by the method described in step D2 of Example 2. The product is crystallised to constant melting point (56°C) from ethanol.

The product gives a monotropic smectic phase on cooling the isotropic liquid below the melting point to 28°C.

Step D3: The production of (+)-4-(4''-methylhexyl)-4'-bromobiphenyl.

This compound is prepared by a reduction method analogous to Step E2 of Example 2. The solid product is crystallised to constant melting point (86—89°C) from ethanol.

Step E3: The production of (+)-4-(4''-methylhexyl)-4'-cyanobiphenyl.

This is prepared and purified by the a method analogous to step F2 of Example 2.

Step F3: The production of (+)-4-(4''-methylhexyl)biphenyl-4'-carboxylic acid from the corresponding nitrile.

This step may be carried out and the product purified by a method analogous to that of Step E1 of Example 1 to yield a material having the physical constants C—Sc, 175.4°C, Sc—CH, 219.1°C, Ch—I, 235.8°C.

Example 4

The preparation of 4-alkoxyphenols by the following route:—



where R is an alkyl group, for example a n-alkyl group.

Step A4: The production of 4-alkoxyphenols illustrated by the preparation of 4-n-octyloxyphenol.

A solution of potassium hydroxide (2.13 mole) in water (238 ml) is added over 30 min to a refluxing mixture of p-quinol (2 moles) and 1-bromo-octane (2.3 moles) in ethanol (640 ml). After heating for an additional 4 hr, the cooled, diluted mixture is shaken with ether (500 ml); the aqueous phase is then acidified. When cold, this is

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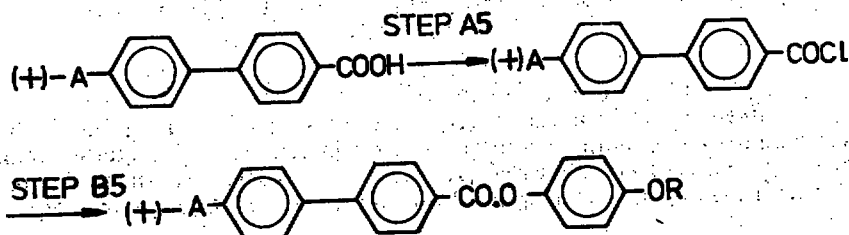
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then shaken with chloroform (4×500 ml) and the combined extracts are washed with water (3×200 ml). After drying (Na₂SO₄), the chloroform solution is evaporated, and the residue chromatographed on silica gel using chloroform as eluent. The combined monoether fractions are crystallised from hexane (m.p. 63°C).

The remaining 4-alkoxyphenols may be prepared by analogous reactions, starting with the appropriate 1-bromo-alkane.

Example 5

The production of the biphenyl-4'-carboxylate esters of the present invention by the following route:



where A and R are as specified above.

Step A5: The production of (+) - 4 - alkylbiphenyl - 4' - carboxylic acid chlorides exemplified by the preparation of (+) - 4 - (2" - methylbutyl)biphenyl - 4' - carboxylic acid chloride.

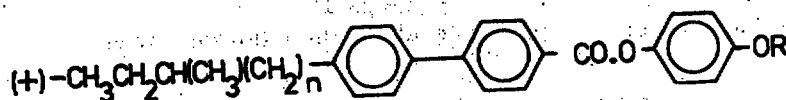
(+) - 4 - (2" - methylbutyl)biphenyl - 4' - carboxylic acid (0.002 mole), prepared as in Step E1 of Example 1, is heated with thionyl chloride (20 ml) under anhydrous conditions for 1.5 hrs. The excess of thionyl chloride is removed by distillation under reduced pressure. The acid chloride residue is used in the next step without further purification.

Step B5: Production of the ester exemplified by the production of n-heptyloxyphenyl (+) - 4 - (2" - methylbutyl)biphenyl - 4' - carboxylate.

(+) - 4 - (2" - methylbutyl)biphenyl - 4' - carboxylic acid chloride (0.002 mole), prepared in Step A5 above is dissolved in dry 'Analar' pyridine (10 ml) and cooled in an ice bath. 4-n-heptyloxyphenol (0.002 mole), prepared as in Step A4 of Example 4, is added to the stirred solution and the mixture is left, with stirring, for 18 hrs to rise to room temperature. It is then heated at 100°C for 1 hr. The pyridine is removed by rotary evaporation and the residue column chromatographed on silica gel, eluting with chloroform. The combined fractions of ester are crystallised from hexane.

Analogous esters may be prepared by analogous reactions employing the appropriate starting carboxylic acids and phenols. Physical constants for a series of esters prepared in this way are given in Table 1 below:—

TABLE 1
Constants for some compounds of general structure:



R	C—Sc or Ch	Sc—Ch	Ch—I	ΔH
n=1	°C	°C	°C	kcal mol ⁻¹
n—C ₄ H ₉	81.7	—	169.3	5.3
n—C ₅ H ₁₁	79.8	(70)	164.5	6.9
n—C ₆ H ₁₃	68.8	80.2	163.5	5.3
n—C ₇ H ₁₅	80.4	87.3	157.5	7.2
n—C ₈ H ₁₇	76.6	88.6	155.4	10.7
n—C ₉ H ₁₉	79.3	89.5	147.6	10.2
n—C ₁₀ H ₂₁	73.5	90.5	146.4	10.5
n=3				
n—C ₈ H ₁₃	81.0	120.3	120.3	—

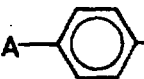
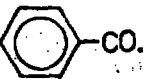
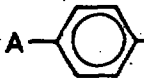
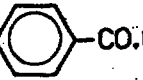
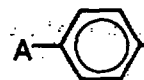
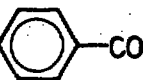
The symbols in Table 1 above have the following meanings:—

	C—S _c or Ch	is the crystal to chiral smectic C or cholesteric transition temperature;	
	S _c —Ch	is the chiral smectic C to cholesteric transition temperature;	
5	Ch—I	is the cholesteric to isotropic liquid transition temperature;	5
	ΔH	is the total enthalpy of fusion for the change stable crystal (C) to S _c or Ch liquid crystal phase.	
10	()	brackets around a temperature indicate a monotropic transition which is not observed during a heating cycle but may be observed on cooling, ie, the transition is monotropic.	10

The data in Table 1 show that none of the pure materials listed exhibits a liquid crystal phase at a low enough temperature to be of direct interest for applications, eg, at room temperature. However, the compounds are of interest and use in this connection when used as eutectic mixtures with one or with other compatible liquid crystal forming materials, because the mixtures (solutions) then exhibit a cholesteric and/or a chiral S_c phase at much lower temperatures.

In this connection it should be noted that the chiral S_c and Ch phases of any single compound always have the same sense (right or left-handed) of pitch. However, compounds having n odd in the group CH₃CH₂CH(CH₃)(CH₂)_n— with an absolute configuration which is S have right-handed helical pitch senses, whereas those with even values of n have left-handed helical pitch senses for the S_c and Ch phases.

The following two mixtures are exemplary and the temperatures of the colour changes seen are also recorded.

25	Mixture 1		25
	Component	Mole fraction	
	A—  —CO.O—  —OC ₄ H _{9-n}	0.40	
	A—  —CO.O—  —OC ₅ H _{11-n}	0.31	
	A—  —CO.O—  —OC ₇ H _{15-n}	0.29	
30	where A is (+)CH ₃ CH ₂ CH(CH ₃)CH ₂ —		30

Transition temperatures: C—S_c — 49°C

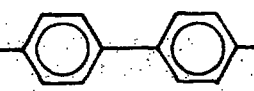
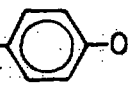
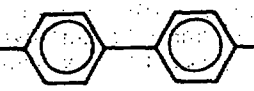
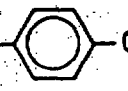
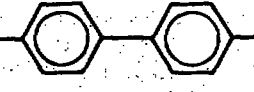
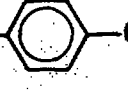
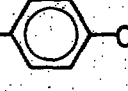
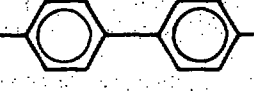
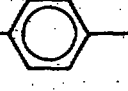
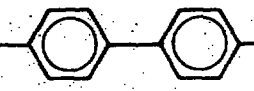
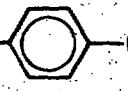
S_c—Ch — 72°C

Ch—I — 163.3°

The colours seen on viewing a thin film of the planar texture of this mixture in a direction at right angles to the film and in reflection are:

35	Selective Reflection	Temperature (°C)	35
	Blue	50.0	
	Turquoise	57.0	
	Green	59.0	
40	Yellow	66.5	40
	Orange	67.2	
	Red	68.5	
	Transition to cholesteric (S _c —Ch)	72.0	
	Red	72.5	
45	Yellow	72.8	45
	Green	74.0	
	Turquoise	83.0	
	Blue	84.5	
	Blue/violet	92.0	
50	Transition to isotropic liquid	163.3	50

18

10		1,592,161	10
	Component	Mixture 2	Mole fraction
	A- 		0.24
	A- 		0.16
5	A- 		0.32
	A- 		0.15
	A- 		0.07
	A- 		0.06
	Transition temperatures: C—S _c — 39.4°C		
10		S _c —Ch — 74.3°C	10
		Ch—I — 162.2°C	

The colours seen on viewing a thin film of the planar texture of this mixture is a direction at right angles to the film and in reflection are:—

	Selective Reflection	Temperature (°C)	
15	Red	39.0	15
	Yellow	41.0	
	Green	43.0	
	Turquoise	43.4	
20	Blue	43.7	20
	Turquoise	58.7	
	Green	60.0	
	Yellow	67.0	
	Red	69.0	
25	Transition to cholesteric (S _c —Ch)	74.3	25
	Red	74.5	
	Yellow	74.8	
	Green	77	
	Turquoise	85	
	Blue	90	
30	Blue/violet	97	30
	Transition to isotropic liquid	162.2	

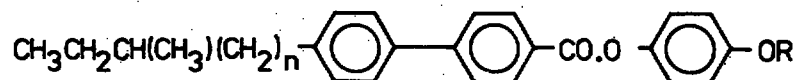
The colour changes within the temperature range 39—43.7°C constitute a fairly narrow rainbow.

The racemic analogues of the optically active esters disclosed above may also be used as components of eutectic mixtures and this provides a valuable facility for altering the pitch of the chiral phase and therefore the colour which it exhibits without altering the mixture composition.

35

**WHAT I CLAIM IS**

1. A liquid crystal compound which is optically active and is an ester having the general formula:—



- 5 wherein n has the value 1, 2, or 3 and R is a normal or branched chain alkyl group containing up to ten carbon atoms and which may also include a chiral centre. 5
2. A liquid crystal compound as claimed in claim 1 and wherein R is a normal alkyl group containing four to ten carbon atoms.
- 10 3. A liquid crystal compound as claimed in claim 1 or claim 2 and wherein n has the value 1. 10
4. A liquid crystal compound which is one of the compounds listed in Table 1 of the specific description.
- 15 5. A liquid crystal electro-optic device of the phase-change type in which the liquid crystal material is an ester as claimed in any one preceding claim or a mixture of solution of such esters or of one or more of such esters with other liquid crystal materials. 15
6. A device as claimed in claim 5 and wherein the mixture of liquid crystal materials is a eutectic.
- 20 7. A device as claimed in claim 5 or claim 6 and wherein the liquid crystal material also includes a pleochroic dye. 20
8. A device as claimed in any one of claims 5 to 7 and wherein the liquid crystal material is an ester as hereinbefore described with particular reference to Table 1 of the specific description.
- 25 9. A method of surface thermography which includes the step of applying a thin film of an ester, or of a mixture of esters as claimed in any one of claims 1 to 4 to a surface and observing the colour of the film in reflection at right angles to the surface. 25
10. A method as claimed in claim 9 substantially as hereinbefore described and with particular reference to mixtures 1 and 2 of the specific description.

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