

PATENT SPECIFICATION

(11) 1 596 014

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(54) OPTICALLY ACTIVE LIQUID CRYSTAL MATERIALS
 AND LIQUID CRYSTAL DEVICES CONTAINING THEM

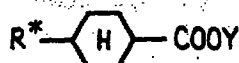
(71) I, SECRETARY OF STATE FOR DEFENCE, London, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to optically active liquid crystal materials and liquid crystal devices containing them.

It is known to mix together compounds having liquid crystal properties or tendencies to produce mixtures with extended liquid crystal temperature ranges. If the resulting mixtures are optically active they may find use in electro-optical devices of the cholesteric-to-nematic phase change kind, or in applications where the colour of the mixture can change with temperature (thermochromic applications — eg surface thermography, temperature detection) or with the presence of an impurity (applications to detect unwanted particles, liquids or vapours, eg atmospheric pollutants).

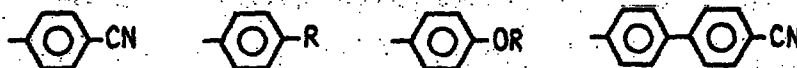
Copending United Kingdom Patent Application No 36211/75 (UK Patent Specification No 1,556,994) describes such mixtures formed by mixing 4'-alkyl-4-cyano-biphenyls with 4''-alkyl-4-cyano-p-terphenyls.

In accordance with the present invention an optically active thermochromic liquid crystal mixture includes at least one compound having a formula:



formula (I)

wherein R* is an asymmetric alkyl group containing not more than 12 carbon atoms and Y is selected from hydrogen,



where R is an alkyl group containing not more than 12 carbon atoms.

Copending Application 33858/76 (Serial No 1 592 147) claims compounds of the formula (I) where Y is



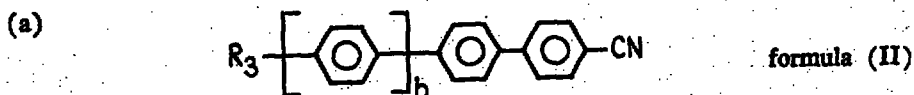
The group R may be n-alkyl or branched alkyl (including chiral alkyl).

Preferably the compound is optically active and has a positive optical rotation angle (+) (see below), but it could alternatively be racemic.

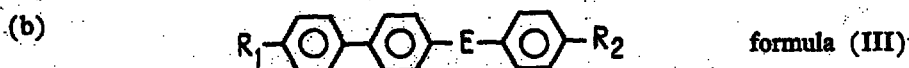
Preferably, the alkyl group R* in the compound of formula (I) is $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)(\text{CH}_2)_n$ where n is an integer in the inclusive range 1 to 3.

The compounds of formula (I) may be used to form thermochromic liquid crystal mixtures with one or more compounds in one or more of the categories characterised

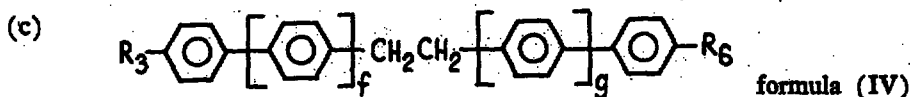
by the following formulae (I) to (V) in which the groups R_1 , R_2 , R_3 , R_6 and R_7 contain up to 12 carbon atoms:



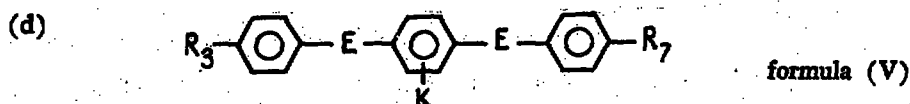
where R_3 is an alkyl and b is 0 or 1, or R_3 is an alkoxy and b is 0;



where E is an ester linkage group OCO or CO.O, where R_1 is alkyl or alkoxy or cyano and R_2 is alkyl or alkoxy or cyano (but R_1 and R_2 are not both cyano);



where R_3 is alkyl, R_6 is an alkyl, alkoxy or cyano group and f and g are 0 or 1 but $f+g=1$;



where R_3 is alkyl or alkoxy, R_7 is an alkyl, alkoxy or cyano group, E is an ester linkage group $-\text{COO}-$ or $-\text{OOC}-$ and K represents hydrogen or a lateral methyl or halogen substituent;

Such thermochromic mixtures may be used in known applications for optically active liquid crystal materials, the actual application depending on the specific properties of the mixture, eg the helical pitch of its molecular arrangement. As is well understood in the liquid crystal art the thermochromic effect is dependent upon the pitch of the helical structure adopted by the liquid crystal material being of the order of the wavelength of visible light and also being temperature dependent. As is also well understood, on admixture of a non-chiral liquid crystal material with a chiral liquid crystal material the pitch tends to increase and accordingly the pitch of chiral liquid crystal material may be adjusted by admixture with non-chiral materials in appropriate proportions, which may be determined by trial and error. Preferably the mixtures are eutectics.

According to the invention in another aspect a liquid crystal electro-optic device or thermochromic device includes as a liquid crystal material a mixture as defined above, preferably one also containing one or more compounds having the formulae (II) to (V) above.

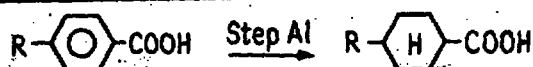
Compounds having the formulae (II) and (V) above are known and their methods of preparation are also known. Certain of the compounds having formulae (III) and (IV) and their preparations are respectively described in Application No 34063/76 (Serial No 1 596 012) (from which the present Application is divided) and Application No 80105/94 (Serial No 1 596 013) divided therefrom.

Examples of the preparation and properties of compounds having formula (I) will now be given. Those compounds which are esters may be produced by conventional esterification procedures, eg as in Example 6 below. Examples of obtaining the appropriate acids and phenols for use in the esterification are given in Examples 1 to 5.

The optically active compounds produced as products in the following description have a positive optical rotation angle denoted by the symbol (+). Analogous compounds with negative optical rotation angles (-) or racemic compounds ($\pm$) may be prepared by analogous routes using the appropriate 'negative' or racemic reactants in the preparation routes.

EXAMPLE 1.

The preparation of (+)-trans-4-alkylcyclohexane-1-carboxylic acids by the following route:



Step A1: The production of (+)-trans-4-alkylcyclohexane-1-carboxylic acids.

Ways of carrying out this step are exemplified by the preparation of (+)-trans-4-(2'-methylbutyl)cyclohexane-1-carboxylic acid as follows:

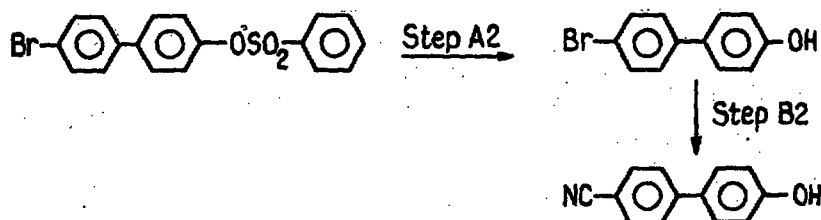
A solution of (+)-4-(2'-methylbutyl)benzoic acid (0.2 mole) in sodium hydroxide (6.205 mole) dissolved in water (160 ml) is hydrogenated in the presence of Raney Nickel catalyst (10 g) in an autoclave (1 litre) at 195°C and a pressure of 170 atm of hydrogen for 30 hr.

On cooling, the catalyst is filtered off and the filtrate washed with ether. The aqueous layer is acidified and the precipitated acids are extracted into ether, washed with water and dried (Na_2SO_4). The ether is distilled off and the acids are taken up in methanol (200 ml); the solution is treated successively with 40 g and 30 g of thiourea. After each treatment with thiourea, the crystallisate is filtered from the methanol. The combined crystallisates are dissolved in a 5% potassium hydroxide solution (800 ml) which is then acidified and the (+)-trans-4-(2'-methylbutyl)cyclohexane-1-carboxylic acid precipitated is extracted into ether; the extract is washed with water and dried (Na_2SO_4).

The ether is evaporated off and the acid recrystallised from acetone. The melting point of the product is 50.3°C.

EXAMPLE 2.

Preparation of 4'-cyano-4-hydroxybiphenyl by the following route:



Step A2: The production of 4'-bromo-4-hydroxybiphenyl.

One example of a way of carrying out this Step is by a standard method using sodium hydroxide to hydrolyse commercially available 4'-bromo-4-benzene-sulphonyloxybiphenyl in a mixture of water and dioxan as solvent. The colourless crystals obtained by crystallisation of the product from ethanol having a melting point of 166°C.

Step B2: The production of 4'-cyano-4-hydroxybiphenyl.

One example of a way of carrying out this step is as follows:

A mixture of 4'-bromo-4-hydroxybiphenyl (6 g), N-methyl-2-pyrrolidone (23 ml) and copper (I) cyanide (2.5 g) is heated under reflux and vigorously stirred for 2 hr. The mixture is protected from atmospheric moisture using CaCl_2 guard tubes. After cooling, the mixture is poured into a warm (60°C) solution of iron (III) chloride in water (200 ml) and concentrated hydrochloric acid (8 ml) and stirred (20 min). The cooled mixture is shaken twice with ether (2 x 100 ml) and the combined organic extracts are water washed. Rotary evaporation of the solvent gives a pale brown solid which is crystallised from a mixture of water and ethanol. This yields pale tan needles of melting point 198°C.

EXAMPLE 3.

The preparation of 4-alkylphenols — where the alkyl group may or may not be chiral.

These are prepared by standard methods such as those described by Van der Veen, de Jeu, Grobben and Boven (*Mol. Cryst. Liq. Cryst.*, 1972, 17, 291) for the preparation of 4-alkylanilines, followed by diazotisation of the amines and hydrolysis of the diazonium sulphates.

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EXAMPLE 4.

Preparation of 4-alkoxyphenols — where the alkyl chain may or may not be chiral.

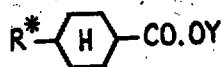
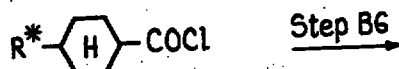
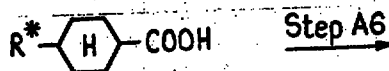
These are prepared by the mono-alkylation of *p*-quinol using the method of Neubert, Carlino, D'Sidocky and Fishel (Liquid Crystals and Ordered Fluids, Vol 2 (Edited by J F Johnson and R S Porter). Plenum Press, N.Y., 1973 p. 303). The colourless products are purified by column chromatography and crystallisation.

EXAMPLE 5.

4-cyanophenol is a commercially available material.

EXAMPLE 6.

The preparation of ester compounds having formula (I) defined above by the following route:



where R* and Y are as defined above.

Step A6: The production of the optically active acid chloride.

The carboxylic acid (0.002 mole) prepared in Step A1 of Example 1, is heated with thionyl chloride (20 ml) under anhydrous conditions for 1.5 hr. 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.

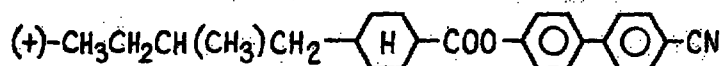
Step B6: The production of the ester.

The carboxylic acid chloride (0.002 mole), prepared in Step A6, is dissolved in dry 'AnalaR' (Trade Mark) pyridine (10 ml) and cooled in an ice bath. The appropriate phenol (0.002 mole) (see Examples 2 to 5 above) is added to the stirred solution and the mixture is left, with stirring, for 18 hr 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.

The constants measured for some Examples of the esters having formula (I) are given in the Tables 1 and 2 below, in which the following symbols have the stated meaning: C = crystal; S_A = Smectic A; Ch = cholesteric; I = isotropic liquid; → = transition temperature; ΔH = enthalpy of fusion in K cal mol⁻¹ and the temperatures are in °C; for monotropic transitions, the temperatures are in parenthesis.

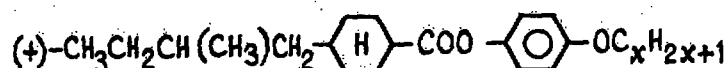
It should be noted that the chiral S_C and Ch phases of any single compound always have the same sense (right or left-handed) of pitch. However, compounds having the value of n odd in the grouping CH₃CH₂CH(CH₃)(CH₂)_n— with an absolute configuration which is S, have right-handed helical pitch senses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

TABLE 1



$\text{C} \rightarrow \text{S}_\text{A}$ °C	$\text{S}_\text{A} \rightarrow \text{Ch}$ °C	$\text{Ch} \rightarrow \text{I}$ °C	ΔH k cal mol ⁻¹
77.6	138	190.4	4.63

TABLE 2



x	$\text{C} - \text{I}$ °C	$\text{S}_\text{A} - \text{Ch}$ °C	$\text{Ch} - \text{I}$ °C	Pitch m
6	50.0	—	(29.5)	0.46
10	49.1	(41.8)	(45.4)	0.46

Examples of mixtures embodying the invention are as follows.

Mixture I

- 5 42.5% by weight $(+)\text{-CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{-}\langle\text{H}\rangle\text{-COO-}\langle\bigcirc\rangle\text{-OC}_6\text{H}_{13}$ 5
- 28.0% by weight $(+)\text{-CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{-}\langle\text{H}\rangle\text{-COO-}\langle\bigcirc\rangle\text{-OC}_{10}\text{H}_{21}$
- 29.5% by weight $(+)\text{-CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{-}\langle\bigcirc\rangle\text{-}\langle\bigcirc\rangle\text{-COO-}\langle\bigcirc\rangle\text{-C}_6\text{H}_{13}$
- $\text{S}_\text{C}\text{-Ch}; 20^\circ\text{C}$ $\text{Ch-I } 57.4^\circ\text{C}$

Selective ReflectionTemperature (°C)

10	Infra-red	20	10
	Red	28	
	Yellow	34	
	Green	36	
15	Turquoise	45	15
	Blue	47	
	Isotropic liquid	57.4	

Mixture II

- 37.5% by weight $(+)\text{-CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{-}\langle\text{H}\rangle\text{-COO-}\langle\bigcirc\rangle\text{-OC}_6\text{H}_{13}$
- 62.5% by weight $(+)\text{-CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{-}\langle\bigcirc\rangle\text{-}\langle\bigcirc\rangle\text{-COO-}\langle\bigcirc\rangle\text{-C}_6\text{H}_{13}$

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 S_o —Ch, 27°C; Ch—I, 86°C.

	Selective Reflection	Temperature (°C)	
5	Red	27.0	5
	Yellow	29.5	
	Green	31.0	
	Turquoise	37.0	
	Blue	39.0	
	Isotropic	86.0	

Mixture III

10	14% by weight	$n-C_5H_{11}-\text{H}-COOH$	10
	17% by weight	$n-C_7H_{15}-\text{H}-COOH$	
	63% by weight	$(+)-CH_3CH_2CH(CH_3)CH_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-COO-\text{C}_6\text{H}_4-C_6H_{13}-n$	
	6% by weight	$(+)-CH_3CH_2CH(CH_3)CH_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-COO-\text{C}_6\text{H}_4-C_7H_{15}-n$	
	S_A —Ch, 22°C; Ch—I, 107.8°C.		

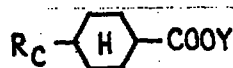
15	Selective Reflection	Temperature (°C)	15
20	Red	27	20
	Yellow	45	
	Green	54	
	Turquoise	97	
	Blue	105	
	Isotropic	107.8	

Examples of the use of mixtures as hereinbefore defined, eg in electro-optic phase change devices (when mixed with nematic materials) and in thermochromic devices, are described in copending United Kingdom Patent Application No 36211/75. (UK Patent Specification No 1,556,994).

WHAT I CLAIM IS:—

1. An optically active thermochromic liquid crystal mixture including at least one compound having formula (I) as defined hereinbefore.

2. A mixture as claimed in claim 1 and wherein the compound having formula (I) is of the form

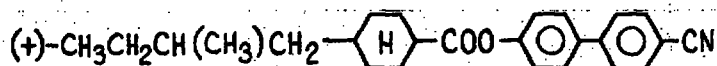


where R_C is $CH_3CH_2CH(CH_3)(CH_2)_n$ where n is an integer in the inclusive range 1 to 3 and Y is as defined as for formula (I) hereinbefore.

3. A mixture as claimed in claim 1 or 2 and wherein the compound having formula (I) is itself optically active.

4. A mixture as claimed in claim 3 and wherein the compound having formula (I) has a positive optical rotation angle.

5. A mixture as claimed in claim 1 and wherein the compound having formula (I) is



(14)

S₀-Ch, 27°C; Ch-I, 86°C.

	Selective Reflection	Temperature (°C)	
5	Red	27.0	5
	Yellow	29.5	
	Green	31.0	
	Turquoise	37.0	
	Blue	39.0	
	Isotropic	86.0	

Mixture III

10	14% by weight	$n\text{-C}_5\text{H}_{11}-\text{H}-\text{COOH}$	10
	17% by weight	$n\text{-C}_7\text{H}_{15}-\text{H}-\text{COOH}$	
	63% by weight	$(+)\text{-CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_{13}-n$	
	6% by weight	$(+)\text{-CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{C}_7\text{H}_{15}-n$	

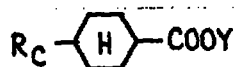
S_A-Ch, 22°C; Ch-I, 107.8°C.

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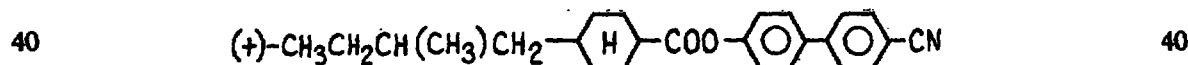
WHAT I CLAIM IS:—

- 30 1. An optically active thermochromic liquid crystal mixture including at least one compound having formula (I) as defined hereinbefore. 30
2. A mixture as claimed in claim 1 and wherein the compound having formula (I) is of the form



where R_c is CH₃CH₂CH(CH₃)(CH₂)_n where n is an integer in the inclusive range 1 to 3 and Y is as defined as for formula (I) hereinbefore.

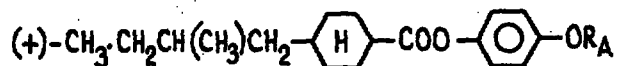
- 35 3. A mixture as claimed in claim 1 or 2 and wherein the compound having formula (I) is itself optically active. 35
4. A mixture as claimed in claim 3 and wherein the compound having formula (I) has a positive optical rotation angle.
5. A mixture as claimed in claim 1 and wherein the compound having formula (I) is



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6. A mixture as claimed in claim 1 and wherein the compound having formula (I) is



where R_A is an n-alkyl group.

7. A mixture as claimed in claim 6 and wherein the alkyl group R_A is hexyl.
8. A mixture as claimed in claim 6 and wherein the alkyl group R_A is decyl.
9. A liquid crystal electro-optic or thermochromic device including as its liquid crystal material a mixture as claimed in any one of the preceding claims.

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