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PATENT SPECIFICATION

(11) 1 596 013

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

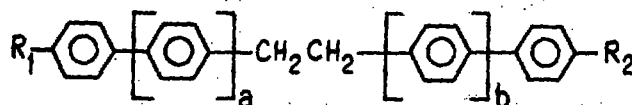
(71) I, SECRETARY OF STATE FOR DEFENCE, a British corporation sole of Whitehall, London, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

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 product mixtures with extended liquid crystal temperature ranges. If the resulting mixtures are optically active they may find use in electrical-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—e.g. surface thermography, temperature detection) or with the presence of an impurity (applications to detect unwanted particles, liquids or vapours, e.g. atmospheric pollutants).

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

In accordance with the present invention a thermochromic liquid crystal composition contains at least two optically active compounds at least one having a formula:



Formula (I)

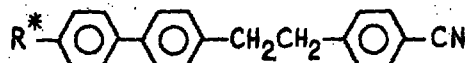
where a and b are 0 or 1 such that a + b = 1, where of the two groups R₁ and R₂ each contains up to 12 carbon atoms, one is an alkyl or alkoxy group and the other is an alkyl, alkoxy or cyano group, at least one of the groups R₁ and R₂ being or including a chiral alkyl group R*, with the proviso that when one of the groups R₁ and R₂ is cyano the other is alkyl.

Preferably the compound having Formula (I) has a positive optical rotation angle (+).

Certain of the compounds having Formula (I) fall within the scope of Claim 1 of U.K. Patent Specification No. 1,551,043.

Preferably, the optically active alkyl group in the compound of Formula (I) is CH₂CH₂CH(CH₃)(CH₂)_n where n is an integer in the inclusive range 1 to 3.

The compound having formula (I) may be one or more of the following:



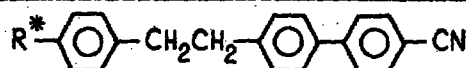
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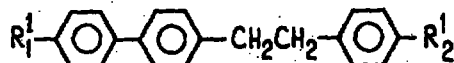
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ii



iii

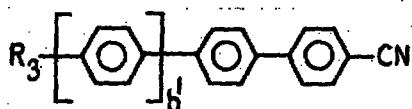


where R^* is a chiral alkyl group, preferably $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)(\text{CH}_2)_n$, n being equal to one, two or three, and where R_1^1 is alkyl and R_2^1 is alkyl or alkoxy, at least one of R_1^1 and R_2^1 being chiral.

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_1^1 , R_2^1 , R_3 , R_4 , R_5 , R , each contain up to 12 carbon atoms:

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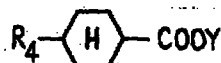
(a)



(Formula (II))

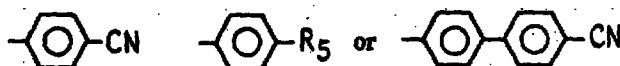
where R_3 is an alkyl and b^1 is 0 or 1, or R_3 is an alkoxy and b^1 is 0;

(b)



(Formula (III))

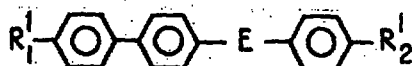
where R_4 is an alkyl group and Y is H ,



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where R_5 is an alkyl or alkoxy group.

(c)

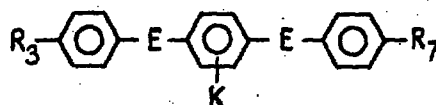


Formula (IV)

wherein E is an ester linkage group $-\text{O.CO}-$ or $-\text{CO.O}-$ wherein R_1 is alkyl or alkoxy when E is $-\text{CO.O}-$ and R_1^1 is cyano when E is $-\text{O.CO}-$ and wherein R_2^1 is an alkyl, alkoxy or cyano group when E is $-\text{CO.O}$ and R_2^1 is an alkyl or alkoxy group when E is $-\text{O.CO}-\text{O}$.

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(d)



(Formula (V))

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.

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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, e.g. 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. The compounds having Formulae (II) to (V) may accordingly be chiral or non-chiral. Preferably the mixtures are eutectics.

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According to the invention in another aspect a liquid crystal electro-optic device or thermochromic device includes as a liquid crystal material a mixture including

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at least one compound having Formula (I) with at least one having Formula (II), (III), (IV) or (V).

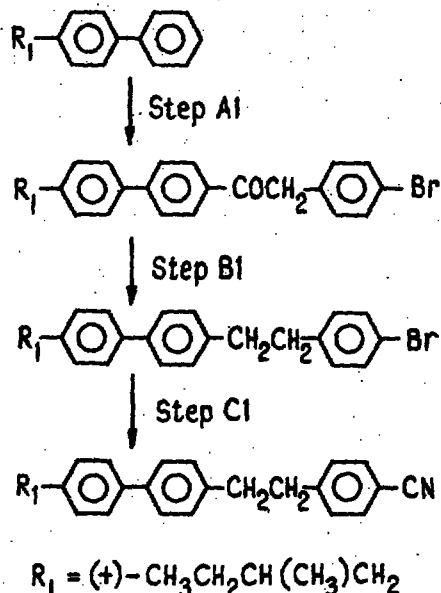
Compounds having the Formulae (II) and (V) are known and their methods of preparation are also known. Certain of the compounds having Formulae (III), (IV) and their preparations are described respectively in Application No. 8012466 (Serial No. 1590612) and No. 34063/76 (Serial No. 1590612), the latter being the parent Application from which this Application is divided and the former being another Application divided from that parent Application.

Examples of compounds having Formula (I) and methods of preparing them will now be given.

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 production of (+)-1,2-[4'-(2'''-methylbutyl)biphenyl]-4'''-cyano-phenyl] ethane by the following route:



Step A1: The production of (+)-4-[4'-(2'''-methylbutyl)biphenyl]-4'''-bromophenylmethyl ketone (by Friedel-Crafts Acylation).

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

A mixture of (+)-2-methylbutylbiphenyl (0.08 mole) (the preparation of which is known and described in United Kingdom Patent Application No. 36211/75 (Serial No. 1,556,994)) 4-bromophenyl acetyl chloride (0.1 mole—prepared by standard methods from commercially available 4-bromophenylacetic acid) and dry dichloromethane (140 ml) is added in drops to a mixture of dry dichloromethane (50 ml) and anhydrous aluminium trichloride (0.12 mole) cooled in an ice/salt bath to -7°C. The mixture is stirred at between -7°C and 0°C for 2 hr, and then at room temperature for 1 hr; it is then poured over ice, water and concentrated hydrochloric acid and the resultant mixture is stirred for 0.5 hr. The dichloromethane layer is separated, washed with water, dried, and evaporated to dryness; the residue is crystallised from ethanol/toluene. Its melting point is 154°C.

Step B1: The production of (+)-1,2-[4'-(2'''-methylbutyl)biphenyl]-4'''-bromophenyl] ethane.

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

To lithium aluminium hydride (0.063 mole) in sodium-dried ether (100 ml) are added:

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

(b) (+)-4-[4'-(2'''-methylbutyl)biphenyl]-4''-bromophenylmethyl ketone (0.0185 mole) prepared in step A14, 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 hr. 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 hr.

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 crystallised from ethanol/toluene; the melting point is 127°C .

Step C1: The production of 1-2[4'-(4''-(2'''-methylbutyl)biphenyl]cyanophenyl] ethane.

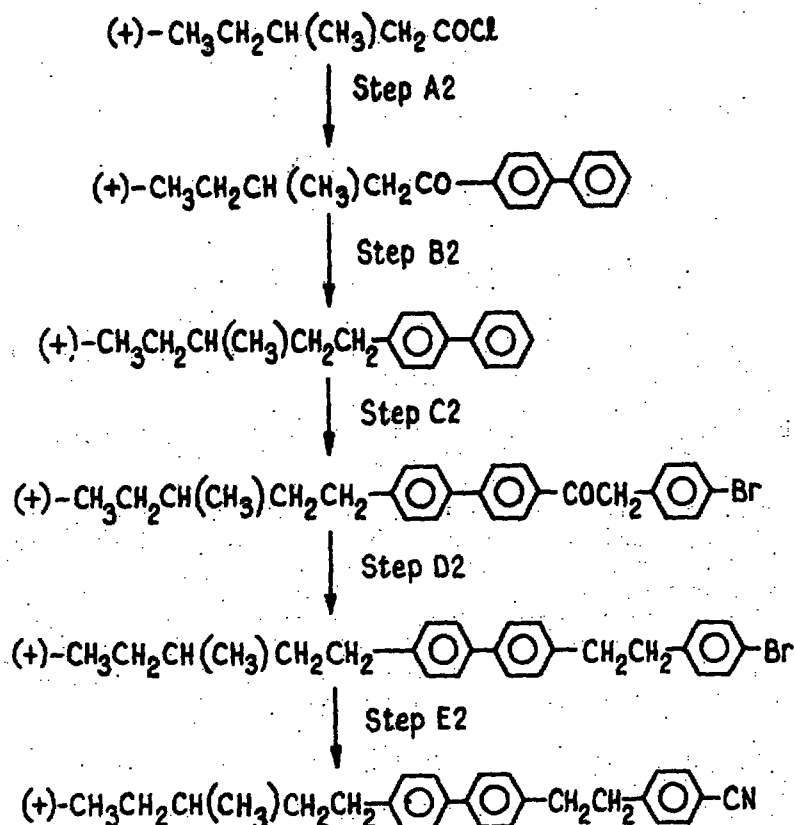
One example of a way of carrying out this step is as follows:

The product from Step B1 (1 g) is dissolved in dry, hot *N*-methyl-2-pyrrolidone (2 ml); copper(I) cyanide (0.5 g) is added and the mixture is vigorously stirred under reflux for 1.5 hr. On cooling, the mixture is poured into a solution of water (30 ml), iron(III) chloride (3 g) and concentrated hydrochloric acid (1 ml) and stirred for 0.5 hr at 60°C . After cooling, the mixture is shaken with chloroform. The chloroform layer is washed with water, dried over anhydrous sodium sulphate and evaporated to dryness. The residue is purified by column chromatography on silicic acid using chloroform as eluent, followed by crystallisation from ethanol.

Constants for this product are given in Table 1 below.

EXAMPLE 2.

The production of (+)-1,2-[4'-(4''-(3'''-methylpentyl)biphenyl]4'''-cyanophenyl] ethane by the following route:



Step A2: The production of (+)-4-(3'-methylpentanoyl)-bisphenyl.

To commercially available biphenyl (0.08 mole) and anhydrous aluminium trichloride (0.1 mole) dissolved in dry nitrobenzene (90 ml), (+)-3-methylpentanoyl-chloride (0.1 mole), the preparation of which is known and described in United Kingdom Patent Application No. 36211/75, is added in drops, the temperature being maintained at about -7°C during the addition. The mixture is then stirred for about 18 hr, with cooling in an ice bath. It is then poured onto a mixture of ice, water and concentrated hydrochloric acid and stirred for 0.5 hr, and the nitrobenzene layer is separated. The nitrobenzene is removed by steam distillation and the residue is crystallised from a small volume of ethanol to constant melting point.

Step B2: The production of (+)-4-(3'-methylpentyl)biphenyl by the following route:

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

The ketone produced in Step A2 is reduced in a manner analogous to Step B1 of Example 1. The product is purified by column chromatography and distillation.

Step C: The production of (+)-4-[4'-(3'''-methylpentyl)biphenyl]-4''-bromophenylmethyl ketone by (Friedel-Crafts Acylation).

One example of a way of carrying out this step is a Step analogous to Step A1 of Example 1. The melting point of the product is 148.5°C.

Step D2: The production of (+)-1,2-[4'-(4''-(3'''-methylpentyl)biphenyl)-4'''-bromophenyl] ethane.

One example of a way of carrying out this step is a step analogous to Step B1 of Example 1. The product is crystallised from ethanol and has a melting point of 136.3°C.

Step E2: The production of (+)-1,2-[4'-(4''-(3'''-methylpentyl)biphenyl)-4'''-cyanophenyl] ethane.

One example of a way of carrying out this step is a step analogous to Step C1 of Example 1. Constants for the product are given in Table 1 below.

EXAMPLE 3.

The product of (+)-1,2-[4'-(4''-(4'''-methylhexyl)-biphenyl)-4'''-cyanophenyl] ethane.

This is prepared in an analogous manner to that described in Example 2, but starting with (+)-4-methylhexanoyl chloride, the preparation of which is known and described in United Kingdom Patent Application No. 36211/75.

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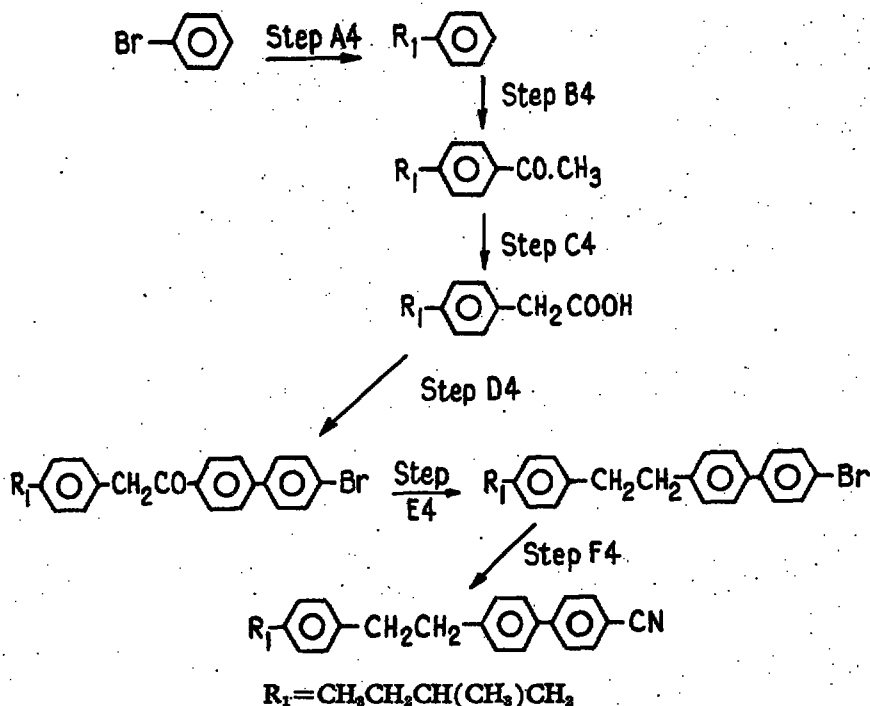
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EXAMPLE 4.

The preparation of 1,2-[4'-(2'''-methylbutyl)phenyl-4''-(4'''-cyano-biphenyl)] ethane by the following route:



5 Step A4, the production of (+)-2-methylbutylbenzene, and Step B17, the production of 4-(+)-2'-methylbutylacetophenone, may be carried out as described in Steps A4 and B4 of Example 4 respectively in U.K. Patent Application No. 34063/76 (Serial No. 1596012), the parent Application.

10 Step C4: The production of (+)-4-(2'-methylbutyl)phenylacetic acid. One example of a way of carrying out this step is as follows:

A mixture of the acetophenone (0.2 mole), prepared in the previous step B4, sulphur (10.5 g) and morpholine (65 ml) is heated under reflux for 6 hr. The hot mixture is poured into methanol (250 ml) and, after cooling, the solid is filtered off and washed with methanol.

15 The crude thioacetomorpholide (0.2 mole), 70% aqueous ethanol (380 ml) and 50% aqueous sodium hydroxide solution (75 ml) are refluxed for 8 hr. A volume of liquid equal to the ethanol present is removed by distillation and the residue is acidified with dilute hydrochloric acid. The crude acid is extracted into ether, the extract is dried (Na₂SO₄) and the ether evaporated off, leaving the acid residue which is crystallised from ethanol/water.

20 Step D4: The production of (+)-4-(2''-methylbutyl)phenylacetyl-4'-bromobiphenyl (by Friedel-Crafts acylation).

25 This Step is carried out in a manner analogous to Step A1 of Example 1, the acid chloride being prepared from (+)-4-(2'-methylbutyl)phenylacetic acid by a conventional method using thionyl chloride.

Step E4: The production of 1,2-[4'-(2'''-methylbutyl)phenyl-4''-(4'''-bromobiphenyl)] ethane.

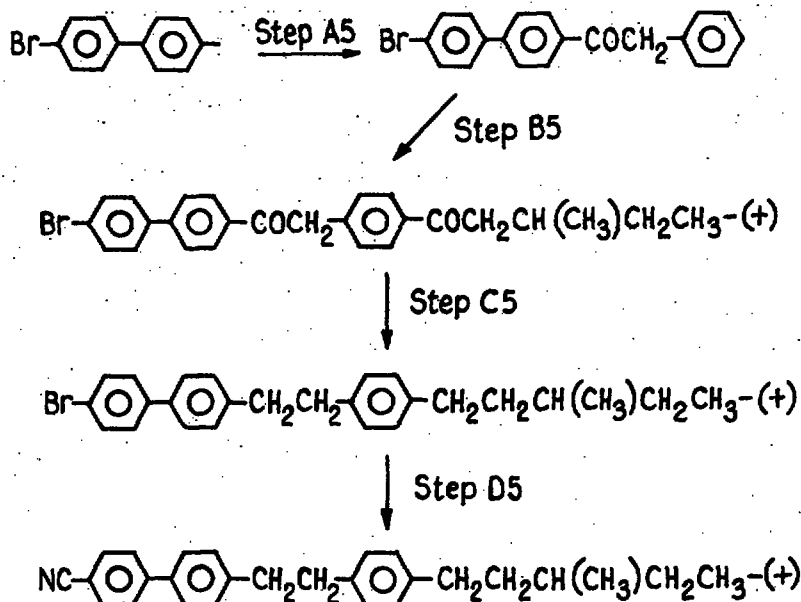
This Step is carried out in a manner analogous to Step B1 of Example 1.

30 Step F4: The production of 1,2-[4'-(2'''-methylbutyl)phenyl-4''-(4'''-cyano-biphenyl)] ethane.

This Step is carried out in a manner analogous to Step C1 of Example 1.

EXAMPLE 5.

The preparation of 1,2-[4'-(3'''-methylpentyl)phenyl-4''-(4'''-cyanobiphenyl)] ethane by the following route:



5 Steps A5—D5: The production of 1,2-[4'-(3'''-methylpentyl)phenyl-4''-(4'''-cyanobiphenyl)] ethane. 5

This preparative route is known and is carried out in the manner described in United Kingdom Patent Application No. 16643/75 (Specification No. 1,551,043) using (+)-3-methylpentanoyl chloride, the preparation of which is described in United Kingdom Patent Specification No. 1,433,130, as a starting material. 10

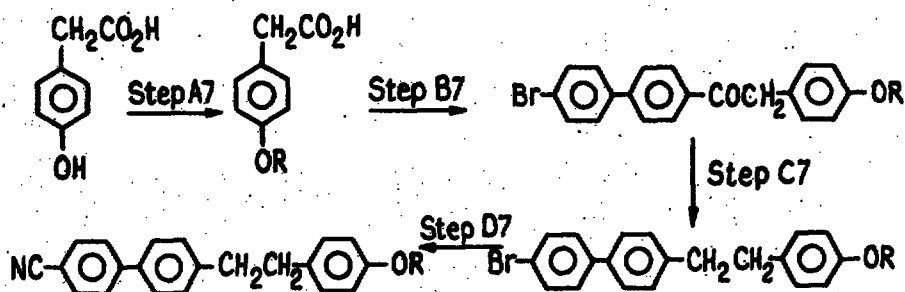
EXAMPLE 6.

The preparation of 1,2-[4'-(4'''-methylhexyl)phenyl-4''-(4'''-cyanobiphenyl)] ethane.

15 This compound is prepared by a route analogous to that in Example 4, but using (+)-4-methylhexanoylchloride as a starting material. 15

EXAMPLE 7.

Preparation of (+)-1,2-[4'-alkoxyphenyl-4''-(4'''-cyanobiphenyl)] ethanes by the following route:



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Step A7: The production of (+)-4-alkoxyphenylacetic acids. 20

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

This alkylation is carried out by standard techniques starting with commercially 4-hydroxyphenylacetic acid which is heated with the chiral alkyl bromide and sodium hydroxide in aqueous ethanol (See, Gray and Jones, *J. Chem. Soc.*, 1954, 678).

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Step B7: The production of (+)-4-alkoxyphenylmethyl-4'-(4'''-bromobiphenyl) ketones (by Friedel-Crafts Acylation).

This Step is carried out in a manner similar to Step A14, but the reaction mixture is heated for 4 hr. under reflux (instead of being cooled in ice for 2 hr.). The acid chloride used in the reaction is prepared from the product of Step A7 by a conventional method using thionyl chloride.

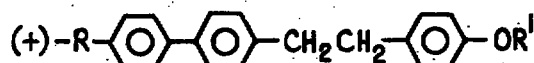
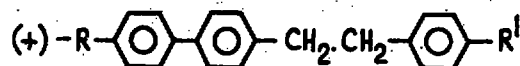
Steps C7 and D7: These Steps are achieved by methods analogous to Steps B1 and C1, respectively.

EXAMPLE 8.

The preparation of (+)-1,2-[4'-(4''-alkyl/alkoxy-biphenyl)-4'''-alkyl/alkoxyphenyl] ethanes.

These compounds whose formulae are given in List 1 below are prepared by the Friedel-Crafts acylation reactions described in above Examples using either 4-alkyl or 4-alkoxyphenylacetyl chlorides and reacting them with either 4-alkylbiphenyls or 4-alkoxybiphenyls. The ketones are reduced to give the desired products in the same way as described in above Examples.

List 1



where R is an alkyl or alkoxy group and R' is an alkyl group which may be the same or different and at least one of the alkyl groups is chiral.

Physical constants for Examples of the compounds embodying the invention in the following table, the compounds being of the form

TABLE 1.



n	C → Ch °C	Ch → I °C	Pitch (μm) 10% in 5CB	$[\alpha]_D^{20}$
1	91.7	103.4	1.5	7.6
2	91.6	110.8	4.5	9.6
3	95.0	105.8	4.3	—

Further Key to Table 1.

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

Pitch is the molecular helical pitch of the compound (10%) when forming a mixture with 90% of 4-n-pentyl-4'-cyanobiphenyl (hereafter designated 5CB).

The following is an example of a mixture which exhibits a cholesteric liquid crystal phase at or near room temperature. The mixture incorporates compounds of Formula (I) defined above and also a member of the series of chiral 4-alkyl-4'-cyanobiphenyls (Formula II).

Mixture I

20% by weight $(+)-\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_4-\text{CN}$
and

80% by weight $(+)-\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$

This mixture has a Smectic A-to-cholesteric transition at -3°C and a cholesteric-to-isotropic liquid transition at 15°C .

Mixture I is thermochromic and the selective colour reflected by the mixture when in the Grandjean plane texture as follows:

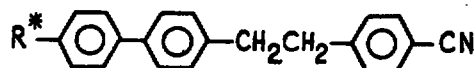
Selective Reflection	Temperature ($^\circ\text{C}$)
Red	-3.0
Yellow	-2.5
Green	-2.0
Turquoise	-1.5
Blue	-1.0

Examples of the use of mixtures as hereinbefore defined, e.g. 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 (Serial No. 1,556,994).

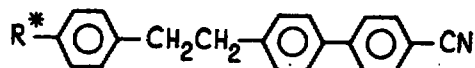
WHAT I CLAIM IS:—

1. A thermochromic liquid crystal composition containing at least two optically active compounds, at least one having Formula (I) is defined hereinbefore.

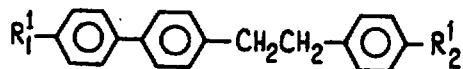
2. A composition as claimed in Claim 1 and in which Formula I is:



3. A composition as claimed in Claim 1 and in which Formula (I) is:



4. A composition as claimed in Claim 1 and in which Formula (I) is:



R_1^1 being an alkyl group and R_2^1 being an alkyl or alkoxy group as defined.

5. A composition as claimed in Claim 2 and wherein the one compound has a positive optical rotation angle (+), R^* being (+)-2 methylbutyl.

6. A composition as claimed in Claim 2 and wherein the one compound has a positive optical rotation angle (+), R^* being (+)-3 methylpentyl.

7. A composition as claimed in Claim 2 and wherein the one compound has a positive optical rotation angle (+), R^* being (+)-3 methylhexyl.

8. A liquid crystal composition as claimed in any one of the preceding claims and wherein the one compound is made by a method substantially as hereinbefore described.

9. A thermochromic mixture as claimed in any one of the preceding claims and comprising a compound having one of formulae (II), (III) or (V) as defined hereinbefore.

10. Mixture I as hereinbefore defined.

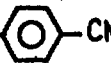
11. A liquid crystal electro-optic device or a thermochromic device including as its liquid crystal material a mixture as claimed in any one of the preceding claims.



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Mixture I

20% by weight $(+)\text{-CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{-}$  $\text{-CH}_2\text{CH}_2\text{-}$ 

and

80% by weight $(+)\text{-CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{-}$  -CN

5 This mixture has a Smectic A-to-cholesteric transition at -3°C and a cholesteric-to-isotropic liquid transition at 15°C . 5

Mixture I is thermochromic and the selective colour reflected by the mixture when in the Grandjean plane texture as follows:

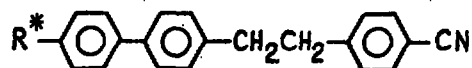
	Selective Reflection	Temperature ($^\circ\text{C}$)	
10	Red	-3.0	10
	Yellow	-2.5	
	Green	-2.0	
	Turquoise	-1.5	
	Blue	-1.0	

15 Examples of the use of mixtures as hereinbefore defined, e.g. 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 (Serial No. 1,556,994). 15

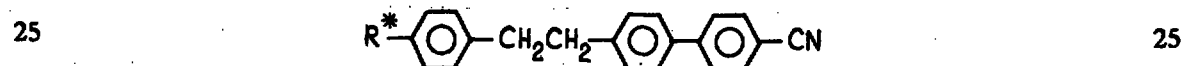
WHAT I CLAIM IS:—

20 1. A thermochromic liquid crystal composition containing at least two optically active compounds, at least one having Formula (I) is defined hereinbefore. 20

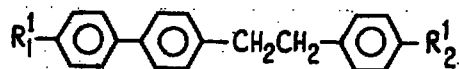
2. A composition as claimed in Claim 1 and in which Formula I is:



3. A composition as claimed in Claim 1 and in which Formula (I) is:



4. A composition as claimed in Claim 1 and in which Formula (I) is:



R_1^1 being an alkyl group and R_2^1 being an alkyl or alkoxy group as defined.

5. A composition as claimed in Claim 2 and wherein the one compound has a positive optical rotation angle (+), R^* being (+)-2 methylbutyl. 30

6. A composition as claimed in Claim 2 and wherein the one compound has a positive optical rotation angle (+), R^* being (+)-3 methylpentyl.

7. A composition as claimed in Claim 2 and wherein the one compound has a positive optical rotation angle (+), R^* being (+)-3 methylhexyl.

8. A liquid crystal composition as claimed in any one of the preceding claims and wherein the one compound is made by a method substantially as hereinbefore described. 35

9. A thermochromic mixture as claimed in any one of the preceding claims and comprising a compound having one of formulae (II), (III) or (V) as defined hereinbefore. 40

10. Mixture I as hereinbefore defined.

11. A liquid crystal electro-optic device or a thermochromic device including as its liquid crystal material a mixture as claimed in any one of the preceding claims.

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