

Description

This invention relates to cyanohydrin derivatives and also to liquid crystal materials containing them. In particular the invention relates to chiral derivatives and ferroelectric smectic liquid crystal compositions containing them.

Ferroelectric smectic liquid crystal materials are known, (eg N A Clark et al: Appl Phys Lett (1980) 36 899), and exploit the electro-optical properties of the ferroelectric chiral smectic phase. The chiral smectic $\bar{C}$ (abbreviated Sc^* the asterisk denoting chirality) is most used as it is the most fluid, but other chiral smectic phases eg I, F, J, K, G, H or X may also be used.

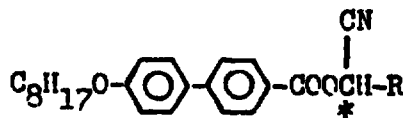
Although some ferroelectric smectic liquid crystal materials are single compounds it is more usual for such a material to be a composition. Generally such a composition contains one or more compounds which either singly or together show an Sc phase (termed a smectic "host"), together with one or more chiral (ie optically active) compounds which are generally added to induce the smectic material to show a high spontaneous polarisation. Ps . The composition may also contain additives. For example to broaden the Sc^* range, to suppress undesirable phases, or optically active compounds to modify the helical pitch of the Sc^* phase.

Among the features sought in a good ferroelectric smectic liquid crystal material are low viscosity, fast switching speeds, a broad Sc^* phase range, and a high spontaneous polarisation coefficient Ps and a long helical pitch. In view of the high cost of synthesis of optically pure compounds it is also desirable that the chiral compound is cheap.

Optically active compounds used in ferroelectric smectic liquid crystal compositions generally consist of a "core" consisting of a chain of linked cyclic groups, with an optically active group containing an asymmetric carbon atom at or near a terminal position of the chain. The core is selected from the reasonably well known combinations of cyclic groups which encourage the compound to be miscible with smectic liquid crystal phases. The goal of much research in ferroelectric smectic liquid crystal chemistry is to identify novel optically active groups which may be combined with such cores to form advantageous compounds.

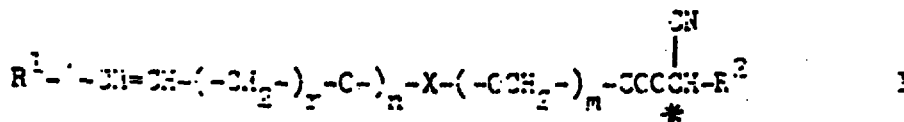
Many suitable optically active compounds are known.

PCT/GB 87/00441 (Agents Ref P0383) and JPA-61-243055 describe compounds of structure



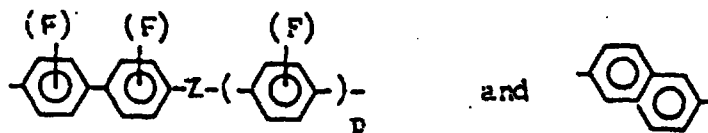
where R is alkyl. These compounds show a high Ps . PCT/GB87/00441 has a publication date later than the priority date of this application. It is an object of the present invention to provide novel compounds which are suitable optically active constituents of ferroelectric liquid crystal compositions, and which have advantageous properties relative to known compounds.

This invention provides compounds which are novel cyanohydrin derivatives having a general formula I:



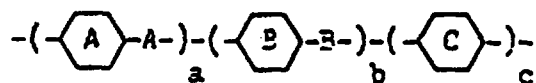
wherein R^1 is selected from hydrogen, $C_1 - C_{12}$ alkyl, alkoxy, perfluoroalkyl and perfluoroalkoxy and may be straight chain or branched chain; R^2 is alkyl, which may be $C_1 - C_8$ straight chain, $C_1 - C_{15}$ branched chain or cyclic; r is an integer 1 to 10, n and m are independently 0 or 1; with the provisos that:

if both n and m are 0 then X is selected from:



where the (F)'s indicate that X carries one or two fluorine substituents in any one or two of the available lateral substitution positions on the indicated phenyl rings, p is 0 or 1, Z is a single bond where p is 0 and COO when p is 1, and;

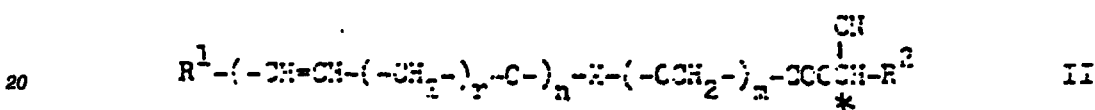
if one or both of n or m are 1 then X is a group of general formula:



where each ring A, B and C is independently selected from phenyl, fluoro or chloro substituted phenyl, cyclohexyl, pyrimidyl, pyridyl or dioxanyl, each link A and B is independently a single bond, COO, OOC, CH₂CH₂, CH=N, N=CH, CH₂O, OCH₂ or O, and each of a, b and c is 0 or 1 provided (a + b + c) is 2 or 3.

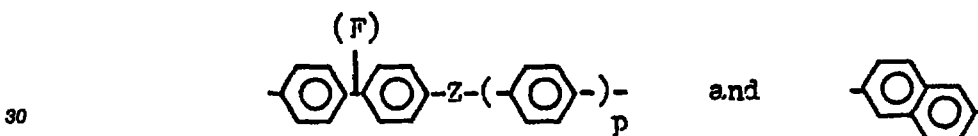
The structural preferences expressed below are on the basis of ease of preparation and/or advantage in liquid crystal compositions, particularly of the ferroelectric type.

Preferred compounds of formula I therefore have a formula II:



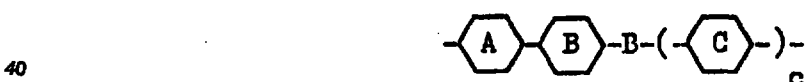
wherein R¹ is selected from C₁ - C₁₂ alkyl or alkoxy; R², r, n and m are as defined in formula I, with the provisos that:

if both n and m are 0 then X is selected from:



where p and Z and their relationship are as defined in formula I and (F) indicates that the biphenyl system carries one or two fluorine substituents on any one or two of the available substitutions positions of the biphenyl system, and

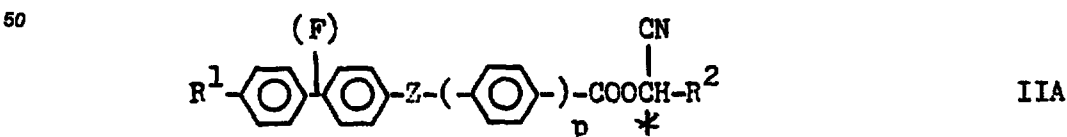
if one or both of n or m are 1 then X is a group of general formula:



where each ring A, B and C is independently selected from phenyl, fluoro or chloro substituted phenyl and trans-cyclohexane, c is 0 or 1, B is COO or a single bond, being a single bond if c is 0.

If n and m are not both 0, then preferably one rather than both of n or m is 1. In formula II, X is preferably biphenyl or laterally monofluorosubstituted biphenyl.

Particularly preferred compounds of formula II are those of formula IIA, ie a subclass of the case where n and m are both 0.



where R¹ (F), Z, p and R², and their relationship are as defined in formula II above. Preferably in formula IIA there is one substituent (F), or two in the 2,3 or 2',3' positions on the biphenyl.

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Some preferred structural types encompassed by formula 11A are those listed in table 1 below:

Table 1

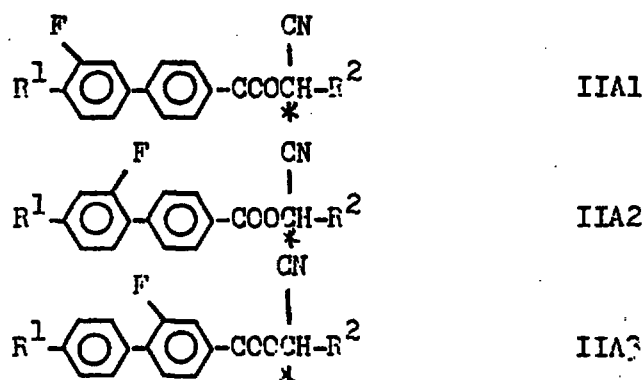
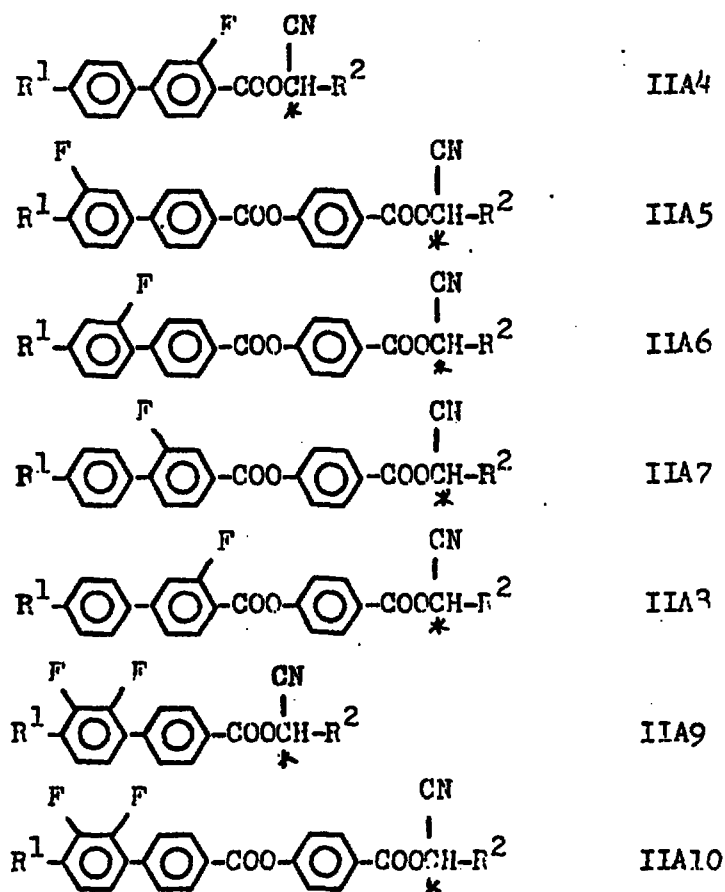
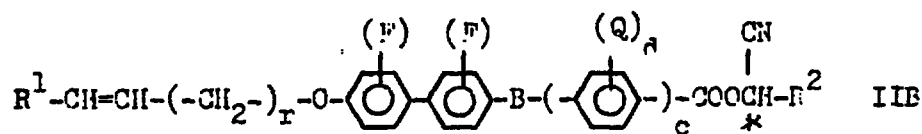


Table 1 (Cont)



of these, formulae IIA1, 2, 3, 4, 9 are particularly preferred.

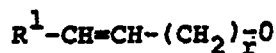
Another preferred class of compounds of formula II are those of formula IIB:



wherein R^1 , r , B , c and R^2 are as defined in formula II, (F) indicates that the relevant phenyl ring may carry a fluorine substituent, Q is fluorine or chlorine and d is 0 or 1.

Preferably r in formula IIB is 1 to 6, more preferably 1 to 4.

Some preferred structural types encompassed by formula IIB are those listed in Table 2 below where



is abbreviated to RB:

Table 2

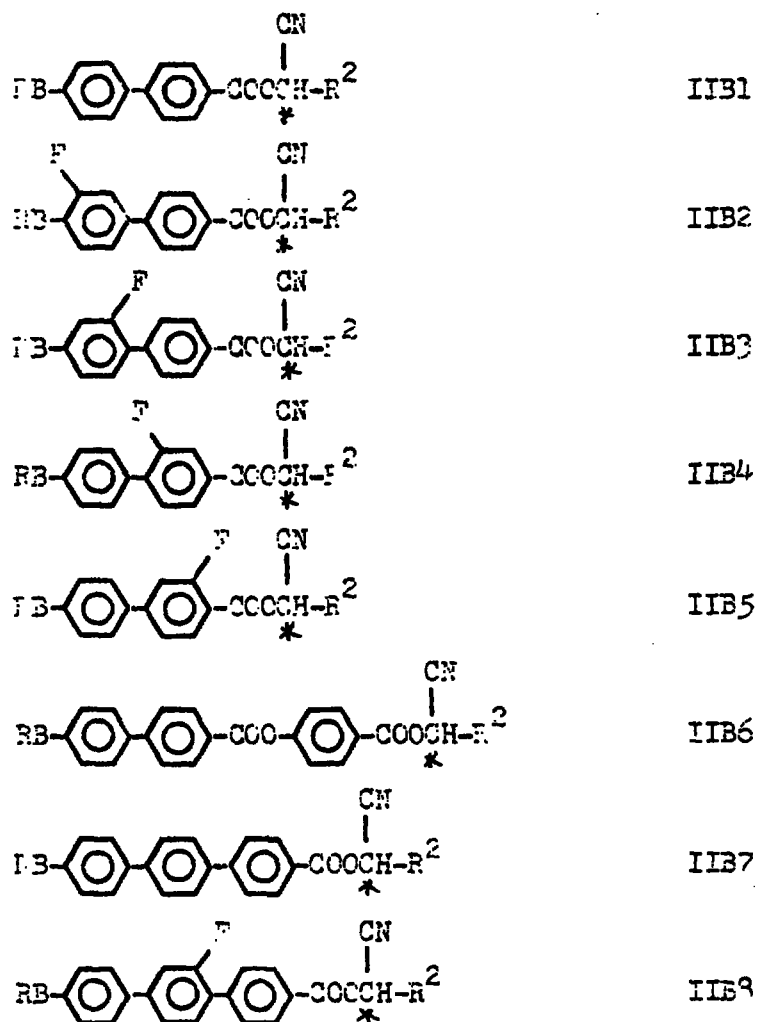
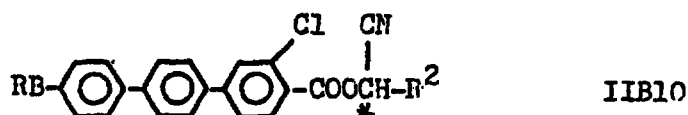
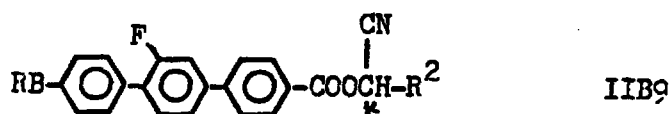
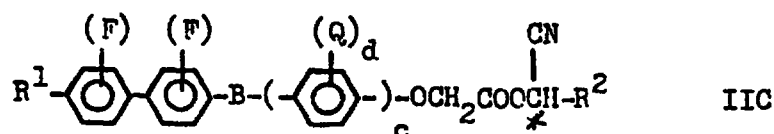


Table 2 (Contd)

Of these, formulae IIB 1, 2 3, 4 and 5 are particularly preferred.

Another preferred class of compounds of formula II are those of general formula IIC, another subclass of formula II where both n and m are 0.



wherein R¹, B, C and R² are as defined in formula II, (F) indicates that the relevant phenyl ring may carry a fluorine substituent, Q is fluorine or chlorine and d is 0 or 1.

Some preferred structural types encompassed by formula IIC are those listed in Table 3 below:

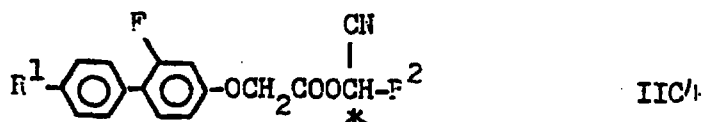
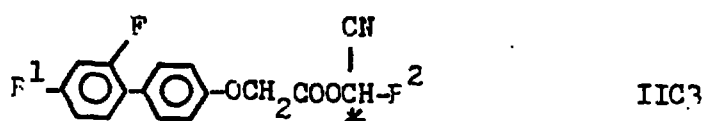
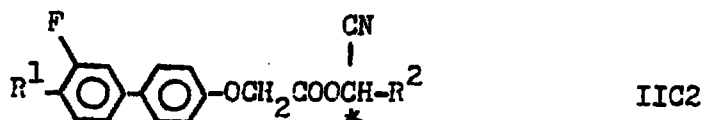
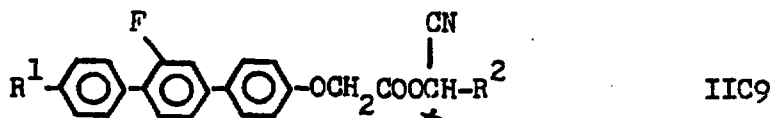
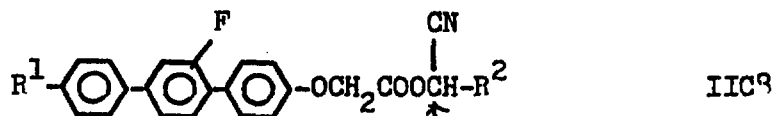
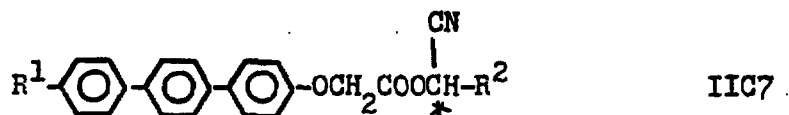
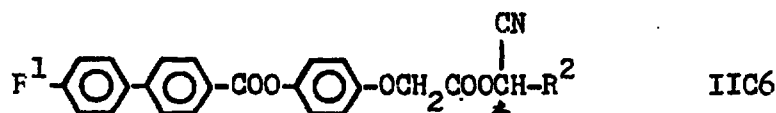
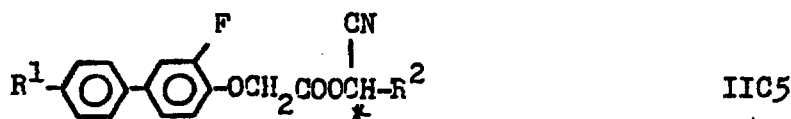
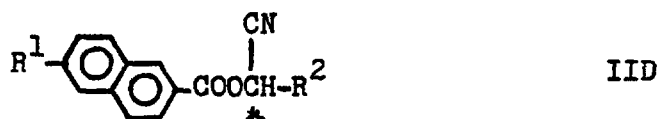
Table 3

Table 3 (Contd)



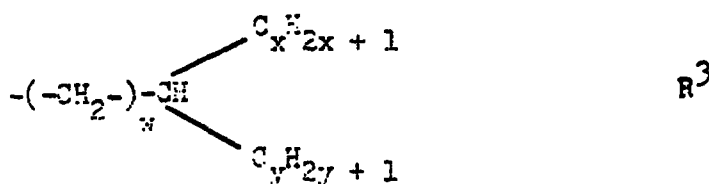
Of these, formulae II C1, 2, 3, 4 and 5 are particularly preferred.

A fourth class of preferred compounds of formula II are those of formula IID:-



35 where R¹ and R² are as defined in formula II above.

In all the formulae listed above the following preferences apply. R¹ is preferably n-alkyl or n-alkoxy containing 3 to 11 carbon atoms, especially 5 to 9 carbon atoms. R² is preferably C₁ - C₅ n-alkyl especially methyl, cyclohexyl, or in particular a branched or asymmetrically substituted alkyl group R³ of formula:



where w is 0 or an integer 1 to 5, and each of x and y are independently 1 to 6. Preferably w is 0, and preferably at least one of x and y is 1. R³ may be optically active or in a racemic mixture.

50 In the above formulae, the carbon atom indicated by an asterisk in formula I may be present in an optically active form or as a racemic mixture.

Preferred structures for R³ are listed below in table 4, the most preferred being underlined.

Table 4

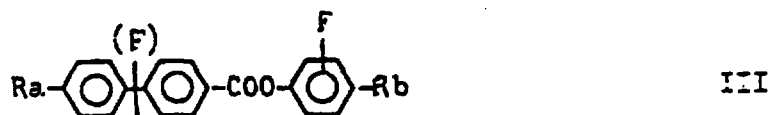
<u>CH₃</u>	<u>CH(CH₃)₂</u>	<u>CH₂CH(CH₃)₂</u>
C ₂ H ₅	<u>CH(CH₃)C₂H₅</u>	CH ₂ CH(CH ₃)C ₂ H ₅
C ₃ H ₇	CH(CH ₃)C ₃ H ₇	CH ₂ CH(CH ₃)C ₃ H ₇
C ₄ H ₉	CH(CH ₃)C ₄ H ₉	CH ₂ CH(CH ₃)C ₄ H ₉
<u>C₅H₁₁</u>	CH(CH ₃)C ₅ H ₁₁	CH ₂ CH(CH ₃)C ₅ H ₁₁
C ₆ H ₁₃	CH(CH ₃)C ₆ H ₁₃	CH ₂ CH(CH ₃)C ₆ H ₁₃
C ₇ H ₁₅	CH(CH ₃)C ₇ H ₁₅	CH ₂ CH(CH ₃)C ₇ H ₁₅
C ₈ H ₁₇	CH(CH ₃)C ₈ H ₁₇	CH ₂ CH(CH ₃)C ₈ H ₁₇
C ₉ H ₁₉	CH(CH ₃)C ₉ H ₁₉	CH ₂ CH(CH ₃)C ₉ H ₁₉
C ₁₀ H ₂₁	CH(CH ₃)C ₁₀ H ₂₁	

The invention also includes the use of compounds of formula I in liquid crystal compositions, and a liquid crystal composition which includes one or more compounds of formula I. The liquid crystal composition is preferably a smectic C (S_C) liquid crystal composition, especially a ferroelectric chiral S_C composition. Preferred compounds of formula I for use in such compositions are as discussed above.

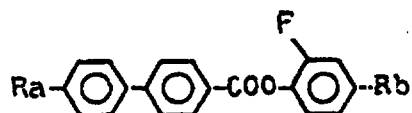
Compounds of formula IIA in an optically active form, preferably those of formulae IIA1, 2, 3 and 4, and especially those of formula IIA1 where R¹ is n-alkoxy are particularly useful components of ferroelectric smectic liquid crystal compositions. they generally have lower melting points, higher solubilities in S_C materials, and when included in such a composition generally lead to a higher spontaneous polarisation P_s, than their unfluorinated counterparts eg as described in the cited prior art. These are useful and unexpected advantages.

Compounds of formulae IIB, IIC and IID are also useful components of ferroelectric smectic liquid crystal compositions. One use to which they may be put is that of "pitch compensators" as defined below with compounds of formula IIA.

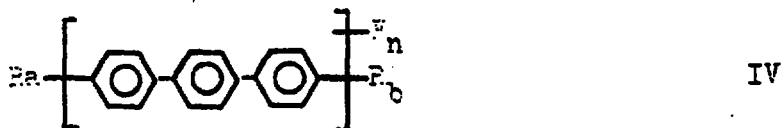
A ferroelectric smectic liquid crystal composition of this invention as well as one or more compounds of formula I also contains one or more "host" compounds which either separately or together show an S_C phase. Many such host compounds are known. Preferred host compounds are the known compounds of formula III:



where Ra and Rb are independently C₃ - C₁₂ alkyl or alkoxy and (F) indicates that the biphenyl system may carry a lateral fluorine substituent. Preferred compounds of formula III are those of formula IIIA below, ie those described in PCT/GB86/0040:



Other preferred host compounds are the known fluoro- and difluoroterphenyls of general formula IV



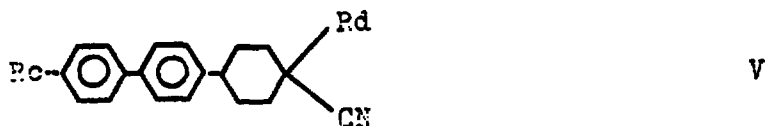
where n is 1 or 2 and Ra and Rb are independently C₃ - C₁₂ alkyl or alkoxy. Preferred terphenyls of formula IV are those described in EPA 8430494.3 of formula IV A:



and those described in GB-A-8806220 of formula IV B:



Preferably both Ra and Rb in formulae III and IV are n-alkyl or n-alkoxy. Other host compounds include cyanocyclohexanes of formula V:



and phenyl pyrimidines of formula VI:



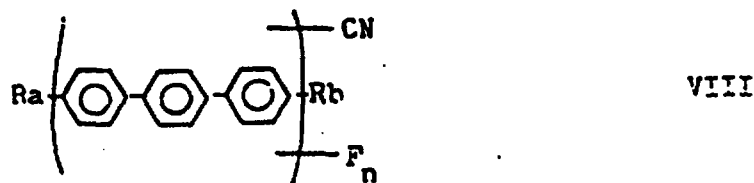
where Rc, Re and Rf are independently C₃ - C₁₂ alkyl or alkoxy and Rd is n-alkyl.

As well as containing one or more host compounds, the ferroelectric smectic liquid crystal composition of this invention may also contain additives. These may for example be additives which broaden the

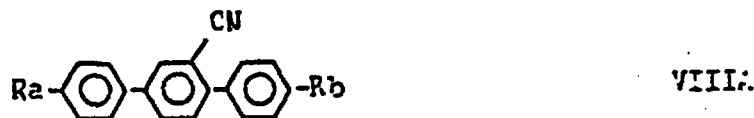
temperature range over which the S_C phase persists, eg known compounds of formula VII:



where R_a and R_b are independently C_1 to C_{12} alkyl or alkoxy and (F) indicates a fluorosubstituent may be present. Additives of formula VII are particularly useful when the host is or includes compounds of formula III or III A. Useful additives when the host is a terphenyl of formula IV, IVA, or IVB are the cyano-terphenyls of general formula VIII:

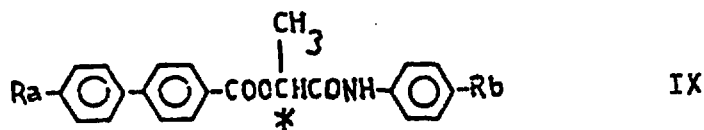


where n is 0 or 1 and R_a and R_b are independently C_3 - C_{12} n -alkyl or n -alkoxy. Compounds of formula VIII are described in PCT/GB88/00880 Preferred additives of formula VIII have a formula VIII A:



and are useful in suppressing S_B phases.

As well as containing these additives the ferroelectric smectic liquid crystal composition of this invention may also contain additives which are "pitch compensators" if the compound of formula I is in an optically active form. Pitch compensators are optically active compounds which have a twisting effect on the S_C phase which is of opposite handedness to that of the optically active compound of formula I. Some examples of pitch compensating additives are the compounds described in PCT/GB87/00223, eg IX:



where R_a and R_b are independently C_1 - C_{12} n -alkyl or n -alkoxy. If at least one of the optically active compounds of formula I is a compound of formula IIA, then pitch compensating additives may be compounds of formula IIB, IIC or IID.

In an alternative and preferred method of pitch compensation, two or more compounds each of any one of formulae IIA, IIB, IIC or IID, preferably of formula IIA, having twisting effects of opposite handedness may be used. For example two compounds of the same formula IIA but having the carbon atom indicated by * in formula I in mirror image configurations may be used.

By using pitch compensation the helical pitch of the ferroelectric smectic liquid crystal phase may be adjusted to provide a long pitch.

The ferroelectric liquid crystal composition of this invention typically but not exclusively has the following composition, expressed in weight percentages.

Host compound(s)	30-99	preferably 50 - 90
Additive(s)	0-30	preferably 0 - 20
Compound(s) of formula I	5-50	preferably 5 - 30
Total	100	

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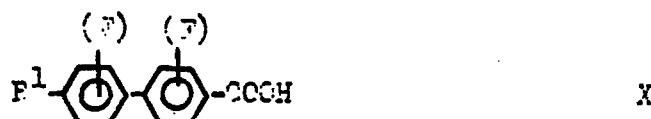
Such a ferroelectric smectic liquid crystal composition may be used in any of the known types of liquid crystal device suitable for such a composition, for example the "Clark-Lagerwall Device" described in Appl Phys Lett (1980), 36, 899. The physics of this device and methods of constructing and using one are well known.

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Methods for preparation of compounds of formula I will now be described.

Compounds of formula IIA may be prepared by a number of synthetic routes, but it is preferred to start from the acid X:

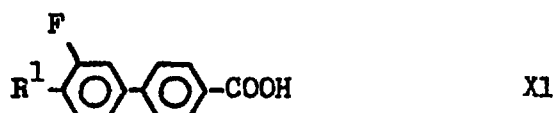
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Such acids may be commercially available, or else they may be prepared by for example routes A1 to A4 shown in Fig 1 starting from known compounds, yielding the acids X1, X2, X3 and X4:

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The steps in routes A1, A2, A3 and A4 are:

Steps A11, A22 THF solvent, Mg, triisopropyl borate

Steps A12, A23 A33 Ethanol solvent, palladium (triphenylphosphine): toluene, methyl 4-bromoacetate, 2M sodium carbonate.

Steps A13, A24, A34 Hydrolysis, ethanol sodium hydroxide: H_2SO_4 .

Step A21 1-bromoalkane, acetone, potassium carbonate.

Step A32 Diazotisation, KCN

Step A41 butyl lithium / -70°C / $\text{B}(\text{OCH}_3)_3$ reacted with the lithium Grignard reagent.

Step A42 Hydrogen Peroxide

Step A43 RBr / butanone / potassium carbonate / reflux

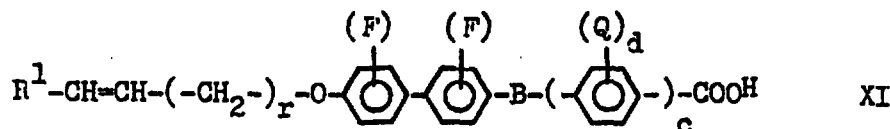
Step A44 as step A41.

Step A45 palladium (triphenylphosphine) / toluene / sodium carbonate / methyl-4-bromobenzoate.

Step A46 potassium hydroxide / IMS / reflux 2 hours.

Compounds of formula IIB may be prepared by a number of synthetic routes, but it is preferred to start from the acid XI:

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which may be prepared by route B shown in figure 2. This route is of general applicability for use with any appropriate hydroxy-ester.

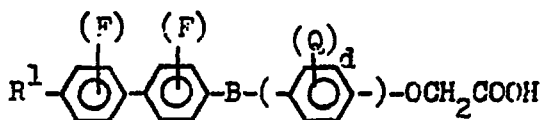
In route B the steps are as follows:-

B1 Bromoalkene, butanone solvent, K_2CO_3 .

5 B2 Potassium hydroxide, water/methylated spirit.

Compounds of formula IIC may be prepared by a number of synthetic routes, but it is preferred to start from the acid XII:

10



XII

15 which may be prepared by route C shown in figure 3. This route is of general applicability to any phenol or alcohol. In route C the steps are as follows:

Route C

20 C1 Ethylbromoacetate, potassium carbonate, butanone solvent.

C2 KOH, water, 2-methoxyethanol, ethanol.

Compounds of formula IID may be prepared using the known naphthoic acids.

These acids may then be esterified with an appropriately protected alpha-hydroxy acid, deprotected and converted into the nitrile.

25 Suitable routes are routes E, F and G in Figs 5, 6 and 7. Many alpha-hydroxy carboxylic acids $\text{HO}-\text{CH}-(R_2)\text{COOH}$ for use in these routes are commercially available, eg lactic acid and mandelic acid. Alternatively one may start from an alpha amino acid such as valine as shown in Fig 4 route D using the following steps:

D1 Sodium Nitrite, H_2SO_4 .

D2 (a) K_2CO_3 , methanol-water 9:1 pH7

30 (b) benzyl bromide, DMF

The individual steps of routes 5, 6 and 7 are as follows:

Route E

35 E1 As step D2

E2 N,N-dicyclohexyl carbodiimide (DCC), 4-(N-pyrrolidino)pyridine (N-PPy) CH_2Cl_2

E3 5% Pd/C, hydrogen, ethanol

E4 (a) oxalyl chloride, benzene, DMF

(b) aqueous ammonia, diglyme

40 E5 SOCl_2 , DMF

Route F

F1

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50 ethyl acetate, hydrogen chloride

F2 KOH, ethanol, water

F3 as step D2

Route F (Contd)

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F4 oxalic acid, 90% aqueous ethanol

F5 as step E2

F6 a series of steps analogous to steps E3 - E5

Route G

G1 hydrogen, 5% Rh/Al₂O₃, methanol (starting compound: mandelic acid)

G2 as step D2 using methanol solvent

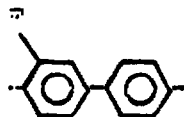
5 G3 DCC, N-PPy, CH₂Cl₂

G4 hydrogen, 5% Pd -C, ethanol

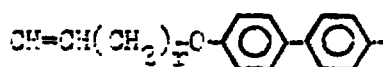
G5-G6 as steps E4 and E5

Related routes may be used to prepare other compounds of formula IIA.

10 In routes E, F and G, Y represents the particular group between R¹ and COO in formula I, for example Y may be:



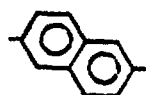
YA



YB



YC



YD

in the preferred formula II compounds discussed above.

The invention will now be described by way of example only, with reference to Figs 1 - 7 which show preparative routes for compounds of formula I, and Fig 8 which shows a cross sectional view through a liquid crystal display device.

Abbreviations

C = solid crystal

N = nematic liquid crystal

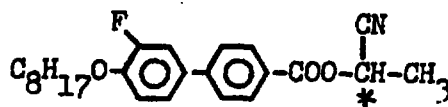
40 S_C = smectic C

S_A = smectic A

I = isotropic liquid

All temperatures (melting point, boiling point, liquid crystal transitions, eg C-I, are in degrees centi-grade).

45 Example 1: Routes A1 and E to prepare:

Steps A11 - A13

55 3'-fluoro-4'-octoxybiphenyl-4-carboxylic acid was first prepared by the following method:

4-Bromo-2-fluorooctoxybenzene (95g) (made by standard bromination of 2-fluorooctoxybenzene) was dissolved in dry tetrahydrofuran (250ml) and slowly added to a mixture of magnesium turnings (8.5g) and

tetrahydrofuran (50ml) containing a crystal of iodine. The Gagnard reaction was initiated by heating the solution. After the addition of bromide solution the mixture was stirred and refluxed under nitrogen for one hour. this solution was then transferred via a flexi-needle into a solution of triisopropylborate (123g) in tetrahydrofuran (10ml) at -70 °C in a nitrogen atmosphere over 30 minutes. The mixture was then allowed to warm up to room temperature over 3 hrs. 10% HCL was added to the mixture and the organic layer separated, washed with brine, dried and solvent removed. The crude solid was dried in vacuo at 20 °C. Yield 80.4g.

The product (32.2g) in methylated spirits (50ml) was added to a mixture of palladium tetra (triphenylphosphine) (0.6g), toluene (200ml), methyl 4-bromobenzoate (21.5g) and a 2M solution of sodium carbonate (100ml). The mixture was heated under reflux and stirred vigorously for 16 hrs. After cooling, the reaction mixture was poured into water and the organic layer separated. The aqueous layer was extracted twice with toluene and the combined organic layers washed once with water. The solvent was removed, and the dark brown solid chromatographed on alumina (100g) using a mixture of dichloromethane and petroleum ether. Yield 46.9g. After crystallisation from methylated spirits the yield was 24.4g : mp 90 °C. HPLC 99.9%.

Step E1

S-(+)- lactic acid (200g) was dissolved in 90% aqueous methanol (2000 ml) and treated with 20% aqueous sodium carbonate until the pH was 7. The solvent was removed at 50 °C under vacuum and then azeotropically removed using dichloromethane (600 ml). The lactic acid potassium salt was dissolved in dry dimethyl formamide (12 ml) and benzyl bromide (278 ml) added over 30 minutes. This solution was stirred for 16 hours. Solvent was removed under vacuum at 40-50 °C, water (600 ml) was added and the product was extracted into ether. After drying over sodium sulphate the ether layer was distilled to yield a colourless oil bp 88-90 °C at 0.5 mm Hg/Yield 279g, 70%, glc 99.2%.

Step E2

The product from Step A13 (10g) was stirred for 16 hrs with dry toluene (120 ml), oxalyl chloride (12.4g) and ten drops of dry DMF. The toluene was distilled off and the acid chloride and redissolved in toluene (40 mls) and added to the product from Step E1 (4.41g) a pyridine (20 mls). The mixture was stirred for 30 minutes at 20 °C then heated under reflux for 3 hours. After cooling the solution was carefully neutralized with dilute hydrochloric acid, the organic layer was removed and washed with sodium bicarbonate solution, then water. After drying, the organic layer was chromatographed on aluminium. Yield 65% after crystallization from IMS.

Step E3

The product from Step E2 (8.2g) was dissolved in ethyl acetate (65 mls). 5% Pd on carbon (1g) was added and the mixture stirred under a hydrogen atmosphere overnight. The catalyst was filtered off and the solution evaporated and the white solid dried under vacuum. Yield 98%.

Step E4

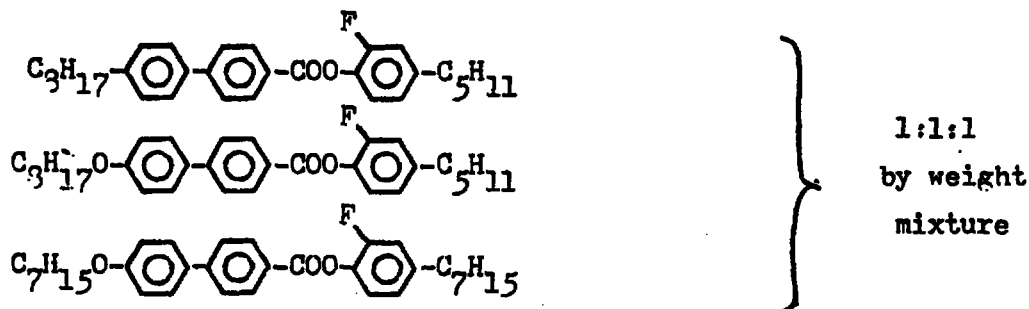
The product from Step E3 (5g) was stirred at 20 °C with toluene (100 ml), DMF (10 drops) and oxalyl chloride (2.87g) for 3hrs. The solvents were removed and the acid chloride dissolved in dry dichloromethane (100 mls). To this solution was added a mixture of dichloromethane (100 ml) and cone ammonia solution (1.5 ml) over about 10 minutes. After a further 10 minutes stirring at 20 °C, water (200 mls) was added and the solution separated. The organic layer yielded 4g of a white solid. This was dried at 40 °C under vacuum and used in the next step.

Step E5

DMF (8 ml) was added to thionyl chloride (10.7g), and the product from Step E4 (4g), dissolved in dimethylformamide (40 ml), was added to the cooled thionyl chloride solution. This mixture was stirred at 10.75 °C for 2 hours and then ice/water (200 g) was added. The product was isolated by extraction into ether followed by chromatography on silica gel. After crystallation from heptane a white solid was obtained. Yield 2.8g . The product showed C-I transition at 56°C

Mixture Example 1

A ferroelectric smectic liquid crystal mixture was prepared which consisted of a 10 weight % solution of the product of Step E5 in:



This composition had the following properties:

(1) Liquid crystal transitions:

Sc at room temperature and below

Sc-S_A 83 °C

S_A-N 109.6 °C

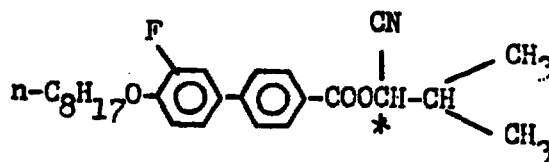
N-I 137.140 °C

(2) Ferroelectric properties:

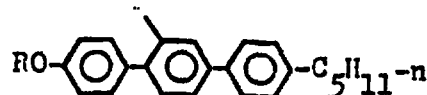
Temp (°C)	Ps(nC cm ⁻²)	Tilt (°)
80	3.39	
75	9.67	21.5
70	14.11	
65	17.78	
60	20.67	
55	23.56	22.0
50	26.67	
40	33.33	

The extrapolated Ps of the cyanohydrin compound, deduced from this composition, 20°C below the S_C - S_A transition was 190 nCcm⁻¹

Example 2



was prepared using the acid prepared in steps A11 - A13 of Example 1 above, and route D. The experimental conditions for route D were the same as used for steps 4(1) and 4(2) of Example 5 on page 31 of WO 87/07890. C-I = 50 °C. The extrapolated Ps value of a 10 wt % solution in the same liquid crystal host as used in mixture Example 1 was 250 nCcm⁻¹ 20 °C below the S_C-S_A transition temperature. In a host mixture consisting of a 1:1:1:1 ratio of terphenyls of formula



where R was C_6H_{13} , C_8H_{17} , C_7H_{15} and $C_{10}H_{21}$ (all n-) the extrapolated Ps was 236 nCcm^{-1} .

Using analogous methods, compounds of analogous structure but where R^3 was $CH_2CH(CH_3)_2$, $CH(CH_2)C_3H_5$ and $(CH_2)_3CH$, starting from L-leucine, L-isoleucine, and L-norleucine were prepared.

The following results compare the solubility of the compounds of examples 1 and 2 in the host mixture used in mixture example 1, their melting points, and their extrapolated Ps values at 20°C below $S_C - S_A$, with the corresponding values for their unfluorinated analogues.

Compound	<u>soly.</u>	<u>mpt.</u>	<u>ext. Ps</u>
$n-C_8H_{17}O-\text{C}_6\text{H}_4(\text{F})-\text{C}_6\text{H}_4-\text{COOCH}(\text{CN})\text{CH}_3$	10%	56	190
$n-C_8H_{17}O-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{COOCH}(\text{CN})\text{CH}_3$		126	
$n-C_9H_{19}O-\text{C}_6\text{H}_4(\text{F})-\text{C}_6\text{H}_4-\text{COOCH}(\text{CN})\text{CH}_3$	10%	98	170
$n-C_8H_{17}O-\text{C}_6\text{H}_4(\text{F})-\text{C}_6\text{H}_4-\text{COOCH}(\text{CN})\text{CH}(\text{CH}_3)_2$	15%	50	250
$n-C_8H_{17}O-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{COOCH}(\text{CN})\text{CH}(\text{CH}_3)_2$		67	164
$n-C_9H_{19}O-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{COOCH}(\text{CN})\text{CH}(\text{CH}_3)_2$	10%	67	170

Two more mixture examples are given below. using compounds of examples 1 and 2, and taking advantage of their high solubility:

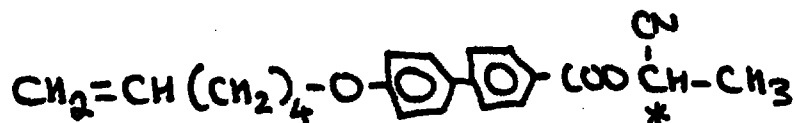
$n-C_8H_{17}O-\text{C}_6\text{H}_4(\text{F})-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4(\text{F})-\text{C}_7H_{15}-n$	20	33 wt %	
$n-C_8H_{17}O-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4(\text{F})-\text{C}_5H_{11}-n$	20.33	wt %	
$n-C_7H_{15}O-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4(\text{F})-\text{C}_7H_{15}-n$	20.33	wt %	
$n-C_7H_{17}O-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4(\text{F})-\text{C}_5H_{11}-n$	16	wt %	
$n-C_8H_{17}O-\text{C}_6\text{H}_4(\text{F})-\text{C}_6\text{H}_4-\text{COOCH}(\text{CN})\text{CH}(\text{CH}_3)_2$	16	wt %	asymmetric centres (*) in these two were of opposite configurations.
$n-C_8H_{17}O-\text{C}_6\text{H}_4(\text{F})-\text{C}_6\text{H}_4-\text{COOCH}(\text{CN})\text{CH}_3$	7	wt %	

This mixture showed: S_C-S_A 28°C , S_A-N 73°C , $N-I$ 88.6°C
 Ps at 18°C = 46 nCcm^{-1}
 .. 8°C = 66 ..

	$n\text{-C}_8\text{H}_{17}\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_3(\text{F})-\text{C}_5\text{H}_{11}-n$	20.33 wt%
5	$n\text{-C}_8\text{H}_{17}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_3(\text{F})-\text{C}_5\text{H}_{11}-n$	20.33 wt%
10	$n\text{-C}_7\text{H}_{15}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_3(\text{F})-\text{C}_7\text{H}_{15}-n$	20.33 wt%
	$n\text{-C}_8\text{H}_{17}\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_3(\text{F})-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	14 wt%
15	$n\text{-C}_{12}\text{H}_{25}\text{O}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_3(\text{F})-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ (+)	5 wt%
	$n\text{-C}_8\text{H}_{17}\text{O}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_3(\text{F})-\text{C}_5\text{H}_{11}-n$	15 wt%
20	$n\text{-C}_8\text{H}_{17}\text{O}-\text{C}_6\text{H}_3(\text{F})-\text{C}_6\text{H}_4-\text{COO}-\text{CH}(\text{CN})\text{CH}_2$	5 wt%

This mixture showed: $S_C-S_A = 62.4^\circ\text{C}$, $S_A-N = 84.0^\circ\text{C}$, $N-I = 117.6^\circ\text{C}$ Ps at $30^\circ\text{C} = 16.46 \text{ nC cm}^{-1}$

Example 3 Routes B and E Preparation of:



Step B1

Methyl 4-hydroxybiphenyl-4-carboxylate (17g), bromopentene (12.7g) butanone (200ml) and anhydrous potassium carbonate (22g) were stirred and heated under reflux for 16 hrs. The cooled solution was filtered, and the solid washed with acetone (1000 l). The combined filtrates were evaporated to dryness, taken up in dichloromethane (200 ml), washed with water (2 x 50 l), dried over sodium sulphate and evaporated to dryness. The solid was crystallized from methylated spirits. Yield 20g.

Step B2

The product from Step B1 (19.5g) was stirred and heated under reflux for 2 hours with potassium hydroxide (8.4g), water (30 ml) and methylated spirits (100 ml). The solution was poured into water (100 mls) and acidified with cone HCl. The solid was filtered off, washed with water and dried in vacuo. After crystallization from acetic acid a yield of 15g was found. HPLC 99.6%.

Step E1

S-(+)- lactic acid (200g) was dissolved in 90% aqueous methanol (2000 ml) and treated with 20% aqueous sodium carbonate until the pH was 7. The solvent was removed at 50°C under vacuum and then azeotropically removed using dichloromethane (600 ml). The lactic acid potassium salt was dissolved in dry dimethyl formamide (12 ml) and benzyl bromide (278 ml) added over 30 minutes. This solution was stirred for 16 hours. Solvent was removed under vacuum at $40-50^\circ\text{C}$, water (600 ml) was added and the product was extracted into ether. After drying over sodium sulphate the ether layer was distilled to yield a colourless oil bp $88-90^\circ\text{C}$ at 0.5 mm Hg/Yield 279g, 70%, glc 99.2%.

Step E2

The product from Step B2 (10g) was stirred for 16 hrs with dry toluene (120 ml), oxalyl chloride (12.4g) and ten drops of dry DMF. The toluene was distilled off and the acid chloride and redissolved in toluene (40 mls) and added to the product from Step E1 (4.41g) a pyridine (20 mls). The mixture was stirred for 30 minutes at 20°C then heated under reflux for 3 hours. After cooling the solution was carefully neutralised with dilute hydrochloric acid, the organic layer was removed and washed with sodium bicarbonate solution, then water. After drying, the organic layer was chromatographed on aluminium. Yield 65% after crystallisation from IMS.

Step E3

The product from Step E2 (8.2g) was dissolved in ethyl acetate (65 mls). 5% Pd on carbon (1g) was added and the mixture stirred under a hydrogen atmosphere overnight. The catalyst was filtered off and the solution evaporated and the white solid dried under vacuum. Yield 98%.

Step E4

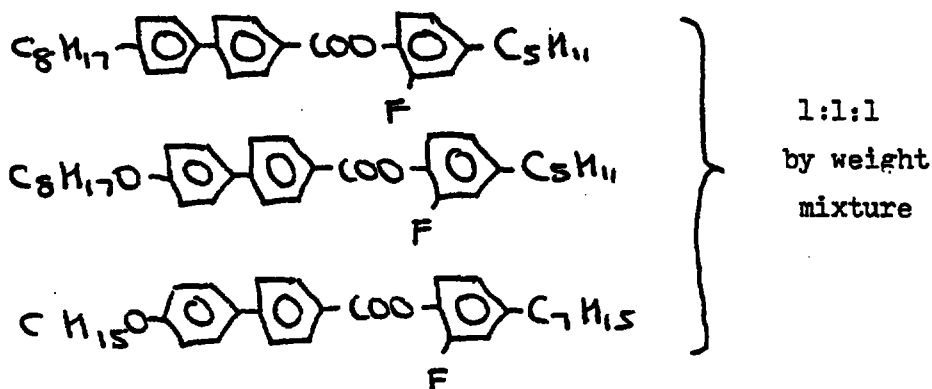
The product from Step E3 (5g) was stirred at 20°C with toluene (100 ml), DMF (10 drops) and oxalyl chloride (2.87g) for 3hrs. The solvents were removed and the acid chloride dissolved in dry dichloromethane (100 mls). To this solution was added a mixture of dichloromethane (100 ml) and cone ammonia solution (1.5 ml) over about 10 minutes. After a further 10 minutes stirring at 20°C, water (200 mls) was added and the solution separated. The organic layer yielded 4g of a white solid. This was dried at 40°C under vacuum and used in the next step.

Step E5

DMF (8 ml) was added to thionyl chloride (10.7g), and the product from Step E4 (4g), dissolved in dimethylformamide (40 ml), was added to the cooled thionyl chloride solution. This mixture was stirred at 10.75°C for 2 hours and then ice/water (200 g) was added. The product was isolated by extraction into ether followed by chromatography on silica gel. After crystallation from heptane a white solid was obtained. Yield 2.8g.

Mixture Example 3

A ferroelectric smectic liquid crystal mixture was prepared which consisted of a 10 weight % solution of the product of Step in:



This composition had the following properties:

(1) Liquid crystal transitions:

Sc at room temperature and below

Sc-S_A 83°C

S_A-N 109.6°C

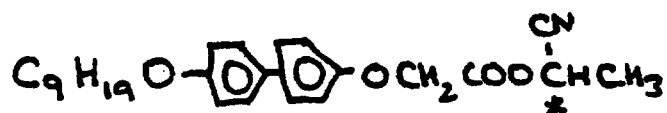
N-I 137.140°C

(2) Ferroelectric properties:

Temp (°C)	Ps(nC cm ⁻²)	Tilt (°)
80	3.39	21.5
75	9.67	
70	14.11	
65	17.78	
60	20.67	22.0
55	23.56	
50	26.67	
40	33.33	

Example 4

Preparation of



Using Routes C and E

Step C1

4-nonyloxy-4-biphenol (59.4g), ethyl bromoacetate (26ml), potassium carbonate (40g) and butanone (960ml) were stirred and heated under reflux for 28 hrs. The hot solution was filtered and allowed to cool with stirring. The product was filtered off under vacuum and dried. Yield 53.7g; 71.6%. Hplc 99.3%.

Step C2

The product from Step C1 (53.7g) was heated on a steam bath for 5 hrs with potassium hydroxide (20g), water (60ml) and 2-methoxyethanol (800ml). About 400ml of industrial methylated spirits was added to reduce foaming. After cooling, conc.HCL was added to adjust the mixture to pH1. The mixture was then stirred and heated for 1 hour. After cooling the solid was filtered and dried at 40°C under vacuum. Yield 43g.

Step E1

S-(+)-Lactic acid (200g) was dissolved in 90% aq. methanol (2000 ml) and treated with 20%aq. potassium carbonate until the pH was 7. The solvent was removed at 50°C under vacuum and then azeotropically removed using dichloromethane (600ml). The lactic acid potassium salt was dissolved in dry dimethylformamide (1200ml) and benzyl bromide (278ml) added over 30 minutes, this solution was stirred for 16 hrs. Solvent was removed under vacuum at 40-50°C, water (600ml) was added and the product extracted into ether. After drying over sodium sulphate the ether layer was distilled to yield a colourless oil bp 88-90°C at 0.5 mmHg. Yield 279g; 70%, glc 99.2% $[\alpha]_D^{24} = -12.9^\circ$

Step E3

The product from Step C2 (10g) was stirred for 16 hrs with dry toluene (120ml), oxalyl chloride (12.4g) and ten drops of dry dimethylformamide. The toluene was distilled off and the acid chloride redissolved in toluene (40mls) and added to the product from Step E1 (4.41g) on pyridine (20mls). The mixture was stirred for 30 minutes at 20°C then heated under reflux for 3 hours. After cooling the solution was carefully neutralized with dilute hydrochloric acid, the organic layer was removed and washed with sodium bicar-

bonate solution, then water. After drying, the organic layer was chromatographed on alumina. Yield 8.5g; 65%, after crystallization from IMS.

Step E3

The product from Step E2 (8.2g) was dissolved in ethyl acetate (65mls). 5% Pd on carbon (1g) was added and the mixture stirred under a hydrogen atmosphere overnight. The catalyst was filtered off and the solution evaporated and the white solid dried under vacuum. Yield 6.7g; 98% mpt 150 °C.

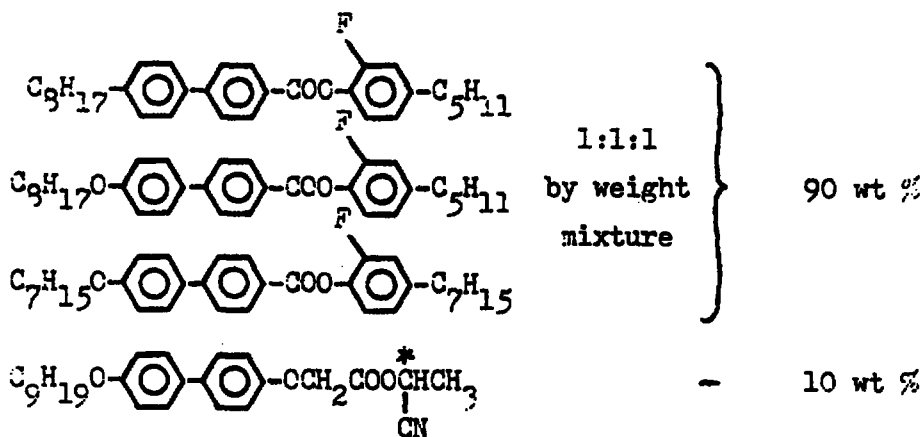
Step E4

The product from Step E3 (5g) was stirred at 20 °C with Toluene (100ml), dimethylformamide (10 drops) and oxalyl chloride (2.87g) for 3 hrs. The solvents were removed and the acid chloride dissolved dry dichloromethane (100 ml). To this solution was added a mixture of dichloromethane (100ml) and conc ammonia solution (1.5ml) over about 10 minutes. After a further 10 minutes stirring at 20 °C, water (200 mls) was added and the solution separated. The organic layer yielded 4g of a white solid. This was dried at 40 °C under vacuum and used in the next step.

Step E5

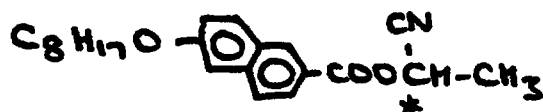
Dimethylformamide (8mls) was added to thionyl chloride (10.7g), and the product from Step D 4, dissolved in dimethylformamide (40ml), was added to the cooled thionyl chloride solution. This mixture was stirred at 10-75 °C for 2 hours and then ice/water (200g) was added. The product was isolated by extraction into ether followed by chromatography on silica gel. After crystallization from heptane a white solid was obtained. Yield 2.8g, Mpt 108-110 °C.

Mixture Example 4



This material had the following properties:
 Room temperature and below S_C , 91°C S_C-S_A , 110°C S_A-N , 134°C $N-I$

Temp. (°C)	Ps (nCcm ⁻²)
80	7.3
70	12.2
60	16.4
50	22.2
40	31.1

Example 5Preparation of:

10 using route E

Step E1

15 S-(+)-Lactic acid (200g) was dissolved in 90% aqueous methanol (2 L) and treated with 20% aqueous potassium carbonate until the pH was 7. The solvent was removed at 50°C under vacuum and then azeotropically removed using dichloromethane (600 ml). The lactic acid potassium salt was dissolved in dry dimethylformamide (1200 ml) and benzyl bromide (278 ml) added over 30 minutes. This solution was stirred for 16 hours. Solvent was removed under vacuum at 40-50°C, water (600 ml) was added and the product
20 extracted with ether. After drying over sodium sulphate the ether layer was distilled to yield a colourless oil bp 88-90°C at 0.5 mm Hg. Yield 279g, 70%. glc 99.2, $[\alpha]_D^{24} = -12.9^\circ$.

Step E2

25 6-Octyloxy-2-Naphthoic acid (15g) [prepared by standard methods] was condensed with the product from Step E1 (8.33g) by dissolving both compounds in dichloromethane (300 ml) and adding trifluoroacetic anhydride (10.7g). The mixture was stirred at 20°C for 3 hrs, poured into water and the organic layer washed with dilute sodium bicarbonate solution until neutral. The organic layer was dried on sodium sulphate and purified by column chromatography on alumina. After crystallisation from petroleum spirit (bp
30 40-60°C) a white solid was obtained. Yield 8.5g; 38%.

Step E3

35 The product of step E2 (8.2g) was dissolved in ethyl acetate (85ml) 5% Pd on carbon (1g) was added and the mixture stirred under a hydrogen atmosphere overnight. The catalyst was filtered off and the solution evaporated and the white solid product dried under vacuum. Yield 95% after recrystallisation from petroleum spirit (bp 80-100°C)

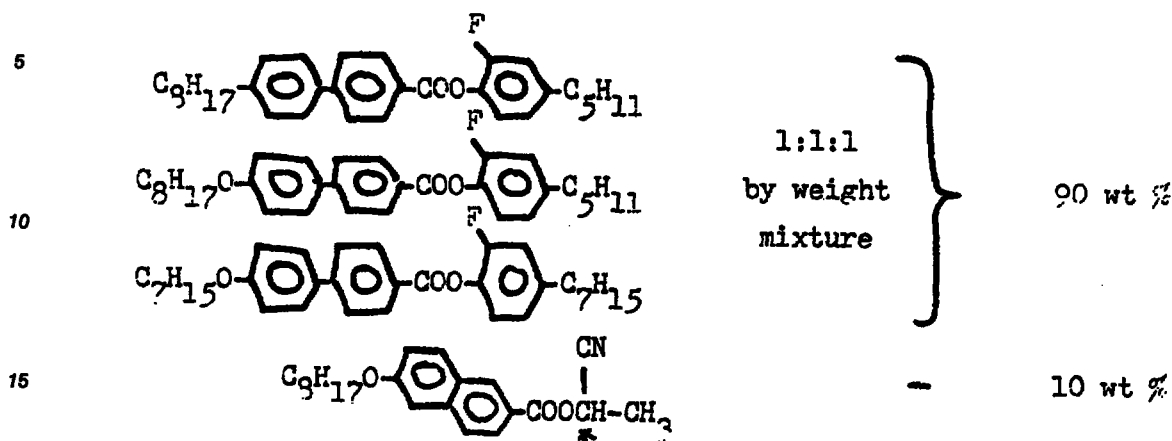
Step E4

40 The product from Step E3 (6g) was dissolved in toluene (80ml), oxalyl chloride (3.85g) and dimethylformamide (6 drops) by stirring the mixture at 20°C for 3 hrs. the excess oxalyl chloride and toluene were removed under reduced pressure and the solid was dissolved in diglyme (45ml) and added dropwise to a stirred solution of 0.880 ammonia (50ml). After 30 min the mixture was diluted with water (180ml) and
45 filtered. The solid was washed with water and dried at 40°C under vacuum.

Yield 5.9g; 98%.

Step E5

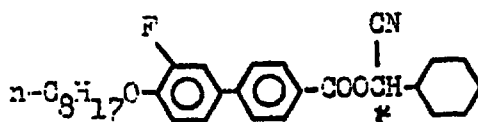
50 The product from Step E4 (5.8g) was dissolved in dimethylformamide (20ml) and added dropwise to a vigorously stirred solution of thionyl chloride (17.5g) [previously redistilled] and dimethylformamide (60ml). After 2 hrs the mixture was poured into white/ice (200ml) and extracted with ether (2 x 150 ml). The combined ether extracts were washed with sodium bicarbonate, water and then dried over sodium sulphate. After removal of solvents the product was chromatographed on silica gel and recrystallised from heptane.
55 Yield 3.0g; 55%. Mp 47°C.

Mixture Example 5

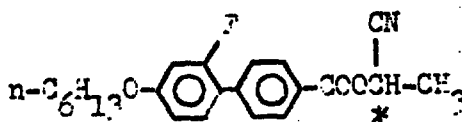
The properties of this mixture were:

20 Room temp. and below S_C , 51.8°C S_C-S_A , 100.7 S_A-N , 130.7°C $N-I$

Temp (°C)	Ps(nC/cm ²)
56	0.02
50	3.11
40	11.8
30	16.4
20	20.4
10	24.0

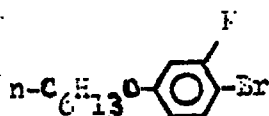
Example 6

40 was prepared using the acid prepared in steps A11-A13 of Example 1 above, and route G. The experimental conditions for route G were the same as used for steps 3(1) - 3(6) of Example 3 on pages 23-25 of WO 87/07890.

Example 7

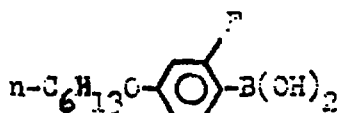
was prepared as follows:

Step A21



A solution of 1-bromohexane (9.33g) in acetone (20 ml) was added dropwise to a stirred mixture of 4-bromo-3-fluorophenol (9.00g) and potassium carbonate (13.5g) in acetone (75 ml) at room temperature. The stirred mixture was heated under reflux for 21 hr (ie until glc analysis revealed a complete reaction). The product was extracted into ether twice, and the combined ether extracts were washed with water, 10% sodium hydroxide, water and dried (Mg SO₄). The solvent was removed under vacuo and the residue was distilled (bp 100-105 °C at 0.1mm Hg) to yield a colourless liquid (12.7g, 98%).

Step A22



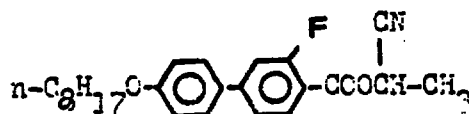
A solution of n-butyllithium (10.0M in hexane, 3.30 ml) was added dropwise to a stirred cooled (-78 °C) solution of A21(9.0g) in dry THF (70 ml) under dry N₂. The stirred mixture was maintained under these conditions for 2.5 hr and then a cooled solution of triisopropyl borate (11.28g) in dry THF (50 ml) was added dropwise at -78 °C. The stirred mixture was allowed to warm to room temperature overnight and then stirred for 1 hr at room temperature with 10% HCL (50 ml). The product was extracted into ether twice and the combined ethereal extracts were washed with water and dried (Mg SO₄). The solvent was removed in vacuo to afford an off-white solid (7.3g, 99%).

Steps A23 and A24

These were performed using reaction conditions identical to those of Steps A12 and A13 of Example 1. The product was obtained as white crystals in a similar yield to that obtained in Example 1.

Using the acid produced in this way, and route E following the procedure as outlined in Example 1, the product cyanohydrin was obtained.

Example 8



Step A31

N-Bromosuccinimide (160.4 g, 0.90 mol) was added in small portions to a stirred, cooled solution of 2-fluoroaniline (100.0 g, 0.90 mol) in dry dichloromethane (400 ml). The stirred mixture was allowed to warm to 0 °C over 45 min, washed with water and dried (MgSO₄). The solvent was removed in vacuo to yield a red solid (180 g) which was steam distilled to give a colourless solid.

Step A32

Concentrated sulphuric acid (60 ml) was added dropwise to a stirred mixture of the product of Step A31 (75.0 g, 0.90 mol), water (150 ml) and glacial acetic acid (185 ml). The clear solution was cooled to -5 °C

(an emulsion formed) and a solution of sodium nitrite (30.0 g, 0.44 mol) in water (100 ml) was added dropwise; the stirred mixture was maintained at -5°C for 15 min.

A solution of potassium cyanide (128.3 g, 1.90 mol) in water (300 ml) was added dropwise to a stirred solution of copper (II) sulphate pentahydrate (118.1 g, 0.48 mol) in water (300 ml) and ice (300 g) at $10-20^{\circ}\text{C}$. Sodium hydrogen carbonate (265.1 g, 3.16 mol) and cyclohexane (450 ml) were added, the temperature was raised to 50°C and the cold diazonium salt mixture was added in portions with rapid stirring. The mixture was cooled, the organic layer was separated and the aqueous layer was washed with ether (twice). The combined organic phases were washed with water, 10% sodium hydroxide, water and dried (MgSO_4). The solvent was removed in vacuo to afford a dark brown solid (78.0g) which was steam distilled to give an off-white solid.

Step A33

A solution of the Grignard reagent, prepared from 4-bromooctylphenyl ether (122.6 g, 0.43 mol) and magnesium (11.96 g, 0.49 mol) in dry THF (300 ml) was added dropwise to a stirred, cooled (-78°C) solution of tri-isopropyl borate (161.7 g, 0.86 mol) in dry THF (50 ml) under dry nitrogen. The stirred mixture was allowed to warm to room temperature overnight and was then stirred at room temperature for 1h with 10% hydrochloric acid (300 ml). The product was extracted into ether (twice), the combined ethereal extracts were washed with water and dried (MgSO_4). The solvent was removed in vacuo to yield a cream-coloured solid which was recrystallised from water to give colourless crystals.

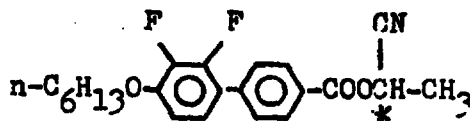
A solution of the above (0.076 mol) in ethanol (90 ml) was added dropwise to a stirred mixture of the product of Step A32 (15.0 g, 0.069 mol) and tetrakis(triphenylphosphine)palladium(0) (2.38 g, 2.06 mmol) in benzene (130 ml) and 2M-sodium carbonate (100 ml) at room temperature under dry nitrogen. The stirred mixture was heated under reflux ($90-95^{\circ}\text{C}$) for 4.5h (ie, until glc analysis revealed absence of starting material). The mixture was cooled and stirred for 1 h at room temperature with 30% hydrogen peroxide (2 ml). The mixture was further cooled to 2°C , and the product was filtered off and washed with water. The product was dried (CaCl_2) in vacuo to give fawn-coloured needles.

Step A34

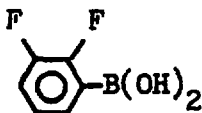
The product of Step A33 was hydrolysed to the acid by conventional reflux with 50% hydrochloric acid and to one, until glc analysis revealed absence of the nitrile starting compound. At the end of this time the acid liquid was cooled to room temperature. The organic layer was separated and further purification was as Step A13.

The carboxylic acid product of Step A34 was made into the product via route E, using a procedure analogous to example 1 above.

Example 9



Steps A41

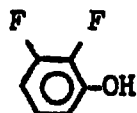


A solution of n-butyllithium (6.60 ml, 10.0M in hexane) was added dropwise to a stirred, cooled (-78°C) solution of 1,2-difluorobenzene (7.50 g) in dry THF (70 ml) under dry H_2 . The stirred mixture was maintained under these conditions for $2\frac{1}{2}$ hours and then a cooled solution of tri-isopropyl borate (24.82 g) in dry THF (50 ml) was added dropwise at -78°C . The stirred mixture was allowed to warm to room temperature

overnight and then stirred for 1 hour at room temperature with 10 % HCl (50 ml) The product was extracted twice into ether and the combined extracts were washed with water twice and dried (MgSO₄). Solvent was removed in vacuo to yield an off-white solid yield = 99%.

5 Step A42

10



The method used was that of M F Hawthorne, J Org. Chem. (1957), 22, 1001

15 Quantities:

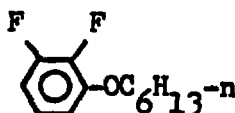
A41 product	4.40 g
10 % hydrogen peroxide	30 ml

20

Yield: 2.01 g, (80 %), off-white solid, mp 34-36°C

Step A43

25



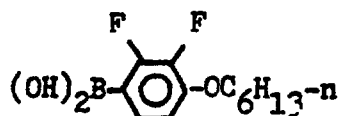
30

A solution of 1-bromohexane (9.33 g) in acetone (20 ml) was added dropwise to a stirred solution of A42 product (6.12 g) and potassium carbonate (13.5 g) in acetone (75 ml) at room temperature. The stirred mixture was refluxed for 21 hours (complete reaction by TLC). The product was extracted twice into ether and the combined extracts were washed with water, 10% sodium hydroxide, water, and dried (MgSO₄).

35 Solvent was removed in vacuo and the residue was distilled (0.1 mm Hg) to yield a colourless liquid (93 %).

Step A44

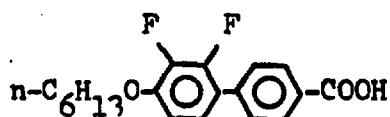
40



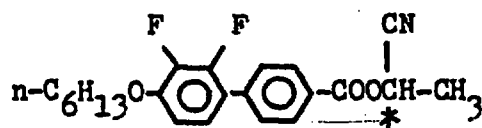
45 The experimental conditions for this step were the same as step A41 above.

Steps A45 and A46

50



55 The method used was that of steps A12 and A13 described above.



By a similar procedure the $n\text{-C}_8\text{H}_{17}\text{O-}$ analogue was prepared.

In Figure 8 a liquid crystal cell comprises a layer 1 of liquid crystal material exhibiting a chiral smectic phase sandwiched between a glass slide 2 having a transparent conducting layer 3 on its surface, eg of tin oxide or indium oxide, and a glass slide 4 having a transparent conducting layer 5 on its surface. The slides 2,4 bearing the layers 3,5 are respectively coated by films 6,7 of a polyimide polymer. Prior to construction of the cell the films 6 and 7 are rubbed with a soft tissue in a given direction the rubbing directions being arranged parallel upon construction of the cell. A spacer 8 eg of polymethyl methacrylate, separates the slides 2, 4 to the required distance, eg 5 microns.

The liquid crystal material 1 is introduced between the slides 2,4 by filling the space between the slides 2, 4 and spacer 8 and sealing the spacer 8 in a vacuum in a known way. Preferably the liquid crystal material is in the smectic A, nematic or isotropic liquid phase (obtained by heating the material) when it is introduced between the slides 2,4 to facilitate alignment of the liquid crystal molecules with the rubbing directions on the slides 2,4.

A polarizer 9 is arranged with its polarization axis parallel to the rubbing direction on the films 6,7 and an analyzer (crossed polarizer) 10 is arranged with its polarization axis perpendicular to that rubbing direction.

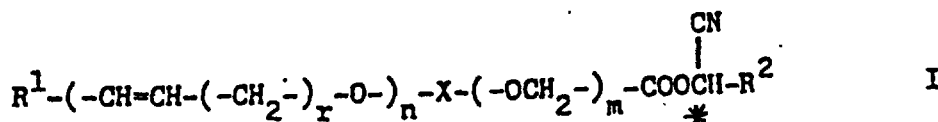
When a square wave voltage (from a conventional source not shown) varying between about +10 volts and -10 volts is applied across the cell by making contact with the layers 3 and 5 the cell is rapidly switched upon the change in sign of the voltage between a dark state and a light state as explained above.

In an alternative device (not shown) based on the cell construction shown in Figure 8 the layers 3 and 5 may be selectively shaped in a known way, eg by photoetching or deposition through a mask, eg to provide one or more display symbols, eg letters, numerals, words or graphics and the like as conventionally seen on displays. The electrode portions formed thereby may be addressed in a variety of ways which include multiplexed operation.

The liquid crystal mixtures described in examples 1 to 6 above were found to be suitable for use as the layer 1.

Claims

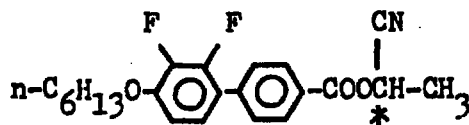
- 1. A cyanohydrin derivative of general formula I:**



wherein R¹ is selected from hydrogen, C₁ - C₁₂ alkyl, alkoxy, perfluoroalkyl and perfluoroalkoxy and may be straight chain or branched chain; R² is alkyl, which may be C₁ - C₈ straight chain, C₁ - C₁₅ branched chain or cyclic; r is an integer 1 to 10, n and m are independently 0 or 1; with the provisos that:

if both n and m are 0 then X is selected from:

Steps E1-E5



The procedure followed was analogous to that described above.

By a similar procedure the $n\text{-C}_8\text{H}_{17}\text{O}$ - analogue was prepared.

An example of the use of a compound of Formula I in a liquid crystal material and device embodying the present invention will now be described with reference to Figure 8

In Figure 8 a liquid crystal cell comprises a layer 1 of liquid crystal material exhibiting a chiral smectic phase sandwiched between a glass slide 2 having a transparent conducting layer 3 on its surface, eg of tin oxide or indium oxide, and a glass slide 4 having a transparent conducting layer 5 on its surface. The slides 2,4 bearing the layers 3,5 are respectively coated by films 6,7 of a polyimide polymer. Prior to construction of the cell the films 6 and 7 are rubbed with a soft tissue in a given direction the rubbing directions being arranged parallel upon construction of the cell. A spacer 8 eg of polymethyl methacrylate, separates the slides 2, 4 to the required distance, eg 5 microns.

The liquid crystal material 1 is introduced between the slides 2,4 by filling the space between the slides 2, 4 and spacer 8 and sealing the spacer 8 in a vacuum in a known way. Preferably the liquid crystal material is in the smectic A, nematic or isotropic liquid phase (obtained by heating the material) when it is introduced between the slides 2,4 to facilitate alignment of the liquid crystal molecules with the rubbing directions on the slides 2,4.

A polarizer 9 is arranged with its polarization axis parallel to the rubbing direction on the films 6,7 and an analyzer (crossed polarizer) 10 is arranged with its polarization axis perpendicular to that rubbing direction.

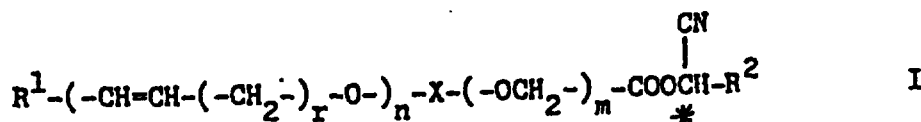
When a square wave voltage (from a conventional source not shown) varying between about +10 volts and -10 volts is applied across the cell by making contact with the layers 3 and 5 the cell is rapidly switched upon the change in sign of the voltage between a dark state and a light state as explained above.

In an alternative device (not shown) based on the cell construction shown in Figure 8 the layers 3 and 5 may be selectively shaped in a known way, eg by photoetching or deposition through a mask, eg to provide one or more display symbols, eg letters, numerals, words or graphics and the like as conventionally seen on displays. The electrode portions formed thereby may be addressed in a variety of ways which include multiplexed operation.

The liquid crystal mixtures described in examples 1 to 6 above were found to be suitable for use as the layer 1.

Claims

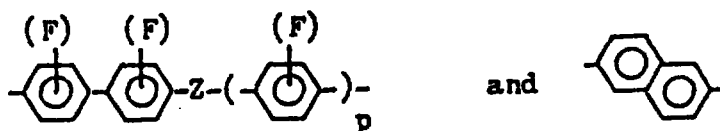
1. A cyanohydrin derivative of general formula I:



wherein R^1 is selected from hydrogen, C_1 - C_{12} alkyl, alkoxy, perfluoroalkyl and perfluoroalkoxy and may be straight chain or branched chain; R^2 is alkyl, which may be C_1 - C_8 straight chain, C_1 - C_{15} branched chain or cyclic; r is an integer 1 to 10, n and m are independently 0 or 1; with the provisos that:

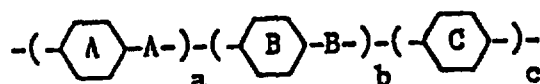
if both n and m are 0 then X is selected from:





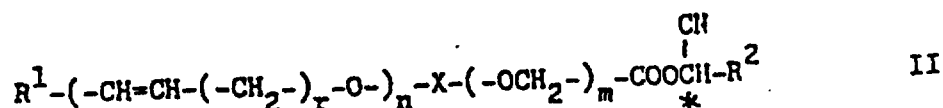
where the (F)'s indicate that X carries one or two fluorine substituents in any one or two of the available lateral substitution positions on the indicated phenyl rings, p is 0 or 1, Z is a single bond where p is 0 and COO when p is 1, and;

if one or both of n or m are 1 then X is a group of general formula:



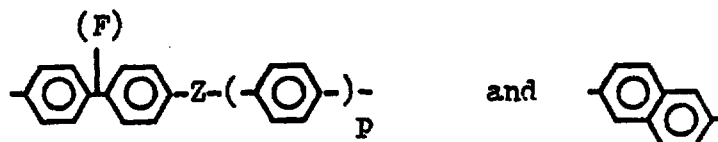
where each ring A, B and C is independently selected from phenyl, fluoro or chloro substituted phenyl, cyclohexyl, pyrimidyl, pyridyl or dioxanyl, each link A and B is independently a single bond, COO, OOC, CH₂CH₂, CH=N, N=CH, CH₂O, OCH₂ or O, and each of a, b and c is 0 or 1 provided (a + b + c) is 2 or 3.

2. A cyanohydrin derivative according to claim 1, characterised by a general formula II:



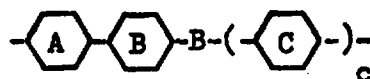
wherein R¹ is selected from C₁ - C₁₂ alkyl or alkoxy; R², r, n and m are as defined in formula I, with the provisos that:

if both n and m are 0 then X is selected from:



where p and Z and their relationship are as defined in formula I, and (F) indicates that the biphenyl system carries one or two fluorine substituents on any one or two of the available substitution positions of the biphenyl system, and;

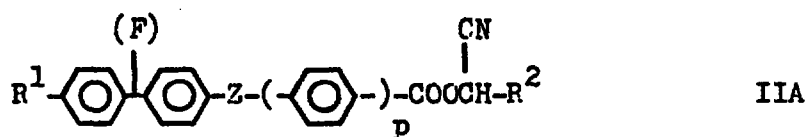
if one or both of n or m are 1 the X is a group of general formula



where each ring A, B and C is independently selected from phenyl, fluoro or chloro substituted phenyl and trans-cyclohexane, c is 0 or 1, B is COO or a single bond, being a single bond if c is 0.



3. A cyanohydrin derivative according to claim 2, characterised by a general formula IIA:

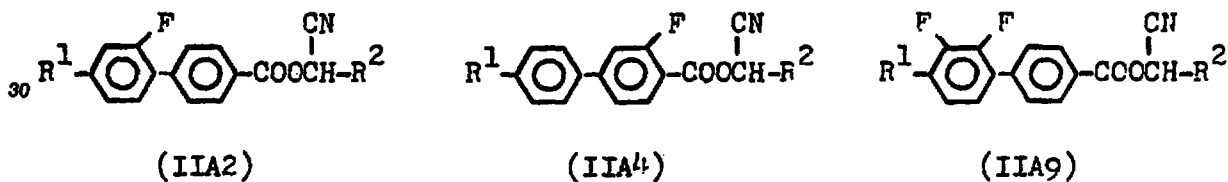


where R¹, (F), Z, p and R² and their relationship are as defined in formula II.

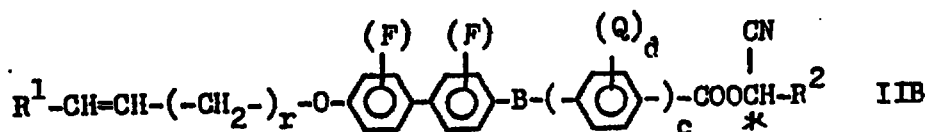
4. A cyanohydrin derivative according to claim 3, characterised by having one substituent (F), or two in 2, 3 or 2', 3' positions.
5. A cyanohydrin derivative according to claim 4, characterised in that in formula IIA p is 0 and Z is a single bond.
6. A cyanohydrin derivative according to claim 5, characterised by a formula IIA1:



7. A cyanohydrin derivative according to claim 5, characterised by a formula IIA2, IIA4 or IIA9:

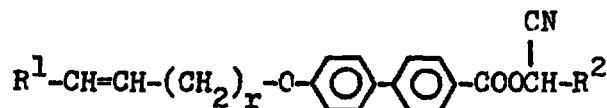


8. A cyanohydrin derivative according to claim 2, characterised by a general formula IIB:



wherein R¹, r, B, c and R² are as defined in formula II, (F) indicates that the relevant phenyl ring may carry a fluorine substituent, Q is fluorine or chlorine and d is 0 or 1.

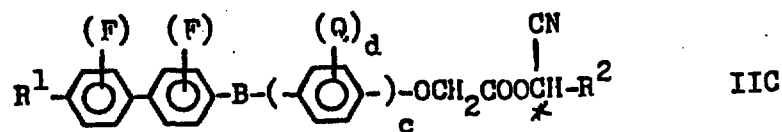
9. A cyanohydrin derivative according to claim 8, characterised by a formula:



where r is 1 to 6.

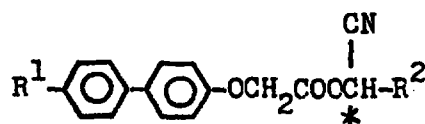


10. A cyanohydrin derivative according to claim 2, characterised by a general formula IIC:

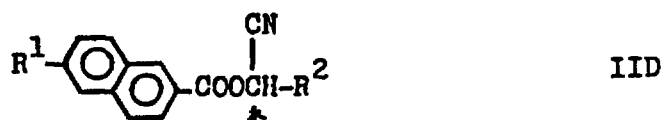


wherein R^1 , B, C and R^2 are as defined in formula II, (F) indicates that the relevant phenyl ring may carry a fluorine substituent, Q is fluorine or chlorine and d is 0 or 1.

11. A cyanohydrin derivative according to claim 10, characterised by a formula:



12. A cyanohydrin derivative according to claim 2, characterised by a formula IID:



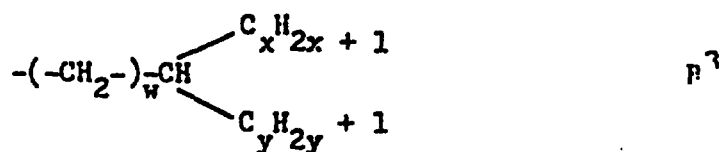
where R^1 and R^2 are as defined in formula II

13. A cyanohydrin derivative according to any one of the preceding claims characterised in that R^1 is C_3 - C_{11} n-alkyl.

14. A cyanohydrin derivative according to claim 13, characterised in that R^2 is C_1 - C_5 n-alkyl.

15. A cyanohydrin derivative according to claim 14, characterised in that R^2 is methyl.

16. A cyanohydrin derivative according to claim 13, characterised in that R^2 is an alkyl group of formula R^3 :



where w is 0 or an integer 1 to 5, and each of x and y are independently 1 to 6.

17. A cyanohydrin derivative according to claim 16, characterised in that w is 0 and at least one of x and y is 1.

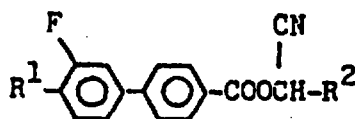
18. A cyanohydrin derivative according to claim 17, characterised in that R^2 is $-\text{CH}(\text{CH}_3)_2$.

19. A cyanohydrin derivative according to claim 13, characterised in that R^2 is cyclohexyl.

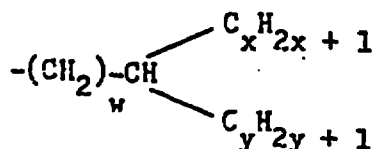
20. A liquid crystal material being a mixture of compounds, characterised in that at least one is a derivative as claimed in claim 1.



21. A liquid crystal material according to claim 20, characterised in that at least one of the derivatives of formula I has a formula:

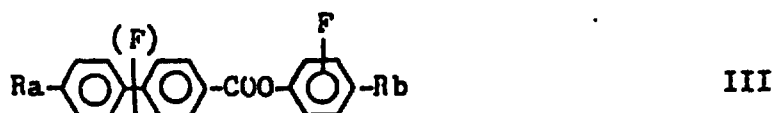


wherein R^1 is $\text{C}_3 - \text{C}_{11}$ n-alkyl or n-alkoxy, and R^2 is $\text{C}_1 - \text{C}_5$ n-alkyl or an alkyl group of formula:



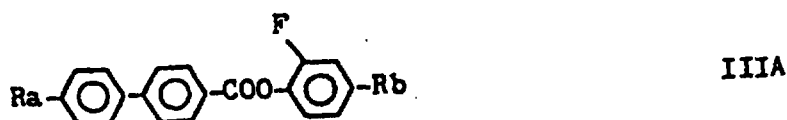
where w is 0 or an integer 1 to 5 and each of x and y are independently 1 to 6.

22. A liquid crystal material according to claim 20 or 21, characterised in that the mixture additionally contains at least one compound of formula III:

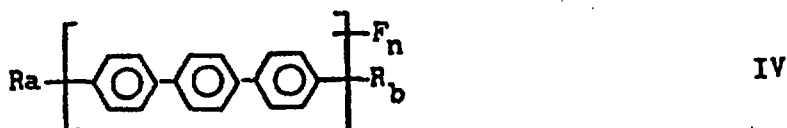


where Ra and Rb are independently $\text{C}_3 - \text{C}_{12}$ alkyl or alkoxy and (F) indicates that the biphenyl system may carry a lateral fluorine substituent.

23. A liquid crystal material according to claim 22 characterised in that the compound of formula III has a formula IIIA:



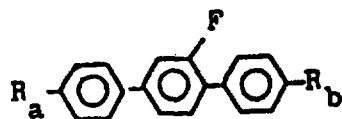
24. A liquid crystal material according to claim 20 or 21, characterized in that the mixture additionally contains at least one compound of formula IV:



where n is 1 or 2 and Ra and Rb are independently $\text{C}_3 - \text{C}_{12}$ alkyl or alkoxy.

25. A liquid crystal material according to claim 24, characterized in that the compound of formula IV has a formula IVA:



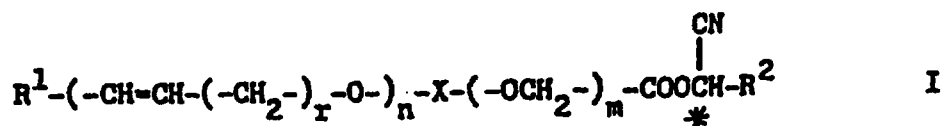


IV A

26. A liquid crystal material according to claim 20 or 21, characterised by containing two derivatives of formula I which have twisting effects of opposite handedness in the smectic C phase.
27. A liquid crystal electrooptic display device, characterised in that it uses a liquid crystal material as claimed in claim 20 or 21.

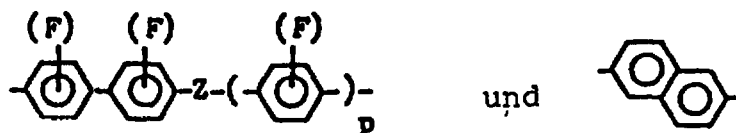
Patentansprüche

1. Cyanhydrinderivat der allgemeinen Formel I:



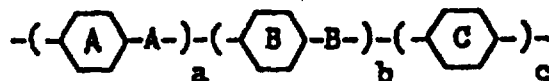
worin R^1 ausgewählt ist aus Wasserstoff, C_1 - C_{12} -Alkyl, -Alkoxy, -Perfluoralkyl und Perfluoralkoxy und geradkettig oder verzweigt sein kann; R^2 Alkyl ist, das C_1 - C_8 geradkettig, C_1 - C_{15} verzweigt oder zyklisch sein kann; r eine ganze Zahl von 1 bis 10 ist, n und m unabhängig voneinander 0 oder 1 sind; mit den Maßgaben, daß:

falls sowohl n als auch m 0 sind X ausgewählt ist aus



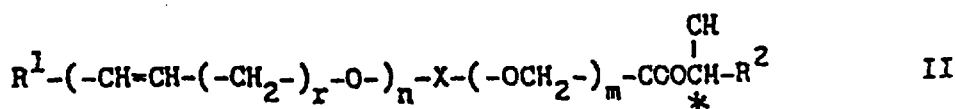
worin die (F) anzeigen, daß X einen oder zwei Fluorsubstituenten in irgend einer oder zwei der verfügbaren seitlichen Substitutionsstellen an den angegebenen Phenylringen trägt, p 0 oder 1 ist, Z eine einfache Bindung ist, wobei p 0 und COO ist, wenn p 1 ist, und:

falls n oder m oder beide 1 sind, bedeutet X eine Gruppe der allgemeinen Formel:



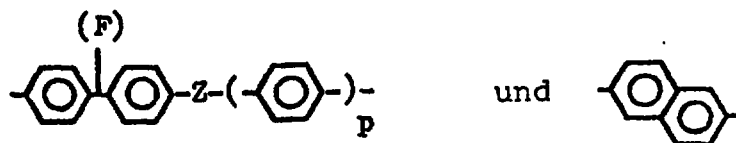
wobei jeder Ring A, B und C unabhängig ausgewählt ist aus phenyl-, fluor- oder chloresubstituiertem Phenyl, Cyclohexyl, Pyrimidyl, Pyridyl oder Dioxanyl, wobei jedes Glied A und B unabhängig eine einfache Bindung, COO, OOC, CH_2CH_2 , $CH=N$, $N=CH$, CH_2O , OCH_2 oder O bedeutet, und a, b und c jeweils 0 oder 1 bedeuten, vorausgesetzt $(a+b+c)$ ist 2 oder 3.

2. Cyanhydrinderivat nach Anspruch 1, gekennzeichnet durch die allgemeine Formel II:



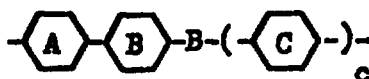
wobei R^1 ausgewählt ist aus $C_1 - C_{12}$ -Alkyl oder -Alkoxy; R^2 , r , n und m wie in Formel I definiert sind, mit den Maßgaben, daß:

falls sowohl n als auch m 0 sind, X ausgewählt ist aus



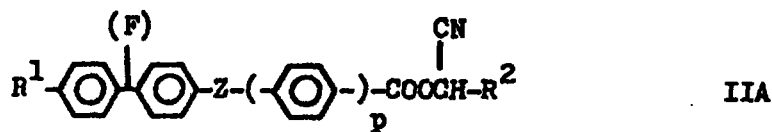
10 wobei p und z und ihre Beziehung wie in Formel I definiert sind und (F) anzeigt, daß das Biphenylsystem ein oder zwei Fluorsubstituenten an irgendeiner oder zwei der verfügbaren Substitutionspositionen des Biphenylsystems trägt, und:

falls n oder m oder beide 1 sind, X eine Gruppe der allgemeinen Formel ist:



20 wobei jeder Ring A, B und C unabhängig ausgewählt ist aus phenyl, fluor- oder chloresubstituiertem Phenyl und Trans-Cyclohexan, wobei c 0 oder 1 ist, B COO oder eine einfache Bindung ist, und eine einfache Bindung ist, wenn c 0 ist.

25 3. Cyanhydrinderivat nach Anspruch 2, gekennzeichnet durch die allgemeine Formel IIA:



worin R^1 , (F), Z, p und R^2 und ihre Beziehung wie in Formel II definiert sind.

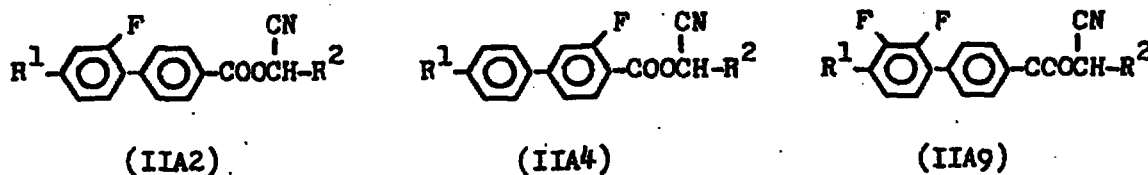
35 4. cyanhydrinderivat nach Anspruch 3, gekennzeichnet durch einen oder zwei Substituenten (F) in den Positionen 2, 3 oder 2', 3'.

5. cyanhydrinderivat nach Anspruch 4, dadurch gekennzeichnet, daß in Formel IIA p 0 und Z eine einfache Bindung sind.

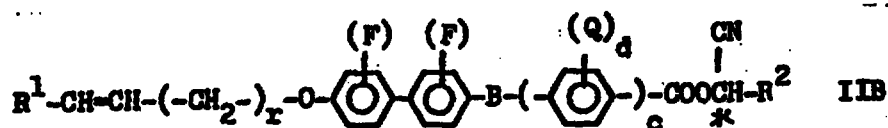
40 6. Cyanhydrinderivat, gekennzeichnet durch eine Formel IIA1:



7. cyanhydrinderivat nach Anspruch 5, gekennzeichnet durch eine Formel IIA2, IIA4 oder IIA9:

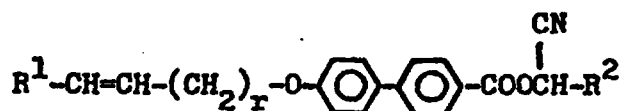


8. Cyanhydrinderivat nach Anspruch 2, gekennzeichnet durch eine allgemeine Formel IIB:



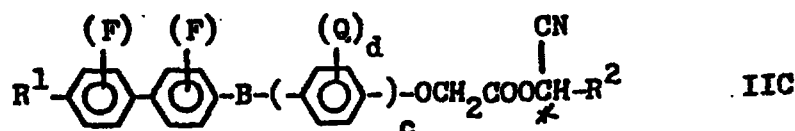
worin R^1 , r , B , c und R^2 wie in Formel II definiert sind, (F) anzeigt, daß der relevante Phenylring einen Fluorsubstituenten tragen kann, Q Fluor oder Chlor ist und d 0 oder 1 ist.

9. Cyanhydrinderivat nach Anspruch 8, gekennzeichnet durch eine Formel:



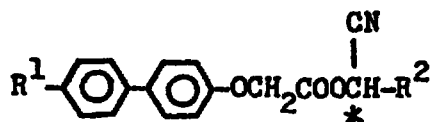
worin r 1 bis 6 ist.

10. Cyanhydrinderivat nach Anspruch 2, gekennzeichnet durch eine allgemeine Formel IIC:

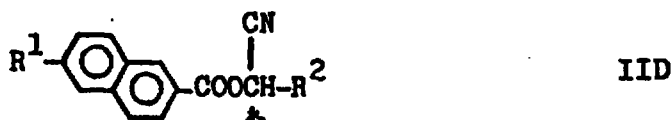


worin R^1 , B , c und R^2 wie in Formel II definiert sind, (F) angibt, daß der relevante Phenylring einen Fluorsubstituenten tragen kann, Q Fluor oder Chlor ist und d 0 oder 1 ist.

11. Cyanhydrinderivat nach Anspruch 10, gekennzeichnet durch eine Formel:



12. Cyanhydrinderivat nach Anspruch 2, gekennzeichnet durch eine Formel IID:



worin R^1 und R^2 wie in Formel II definiert sind.

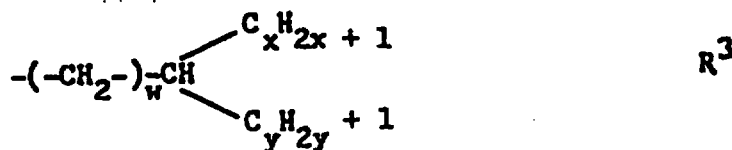
13. Cyanhydrinderivat nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß R^1 C_3 - C_{11} n-Alkyl ist.

14. Cyanhydrinderivat nach Anspruch 13, dadurch gekennzeichnet, daß R^2 C_1 - C_5 n-Alkyl ist.

15. Cyanhydrinderivat nach Anspruch 14, dadurch gekennzeichnet, daß R^2 Methyl ist.



16. Cyanhydrinderivat nach Anspruch 13, dadurch gekennzeichnet, daß R^2 eine Alkylgruppe der Formel R^3 ist:



worin w 0 oder eine ganze Zahl von 1 bis 5 und x und y jeweils unabhängig 1 bis 6 sind.

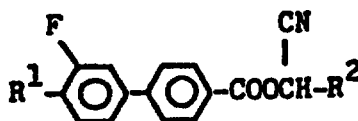
17. Cyanhydrinderivat nach Anspruch 16, dadurch gekennzeichnet, daß w 0 und wenigstens eines von x und y 1 sind.

18. Cyanhydrinderivat nach Anspruch 17, dadurch gekennzeichnet, daß R^2 $-\text{CH}(\text{CH}_3)_2$ ist.

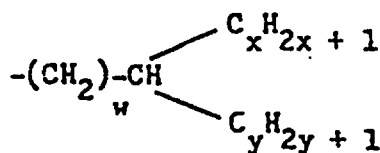
19. Cyanhydrinderivat nach Anspruch 13, dadurch gekennzeichnet, daß R^3 Cyclohexyl ist.

20. Flüssigkristall-Material bestehend aus einer Mischung von Verbindungen, dadurch gekennzeichnet, daß wenigstens eine ein Derivat nach Anspruch 1 ist.

21. Flüssigkristall-Material nach Anspruch 20, dadurch gekennzeichnet, daß wenigstens eines der Derivate der Formel I eine Formel hat:

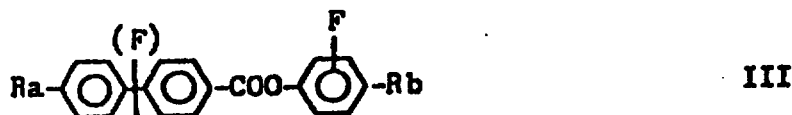


worin R^1 C_3 - C_{11} n-Alkyl oder n-Alkoxy und R^2 C_1 - C_5 n-Alkyl oder eine Alkylgruppe der folgenden Formel sind:



worin w 0 oder eine ganze Zahl von 1 bis 5 und x und y jeweils unabhängig 1 bis 6 sind.

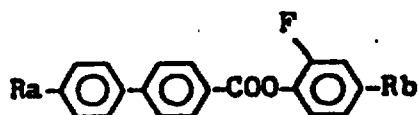
22. Flüssigkristall-Material nach Anspruch 20 oder 21, dadurch gekennzeichnet, daß das Gemisch zusätzlich wenigstens eine Verbindung der Formel III enthält:



worin Ra und Rb unabhängig C_3 - C_{12} Alkyl oder Alkoxy sind und (F) angibt, daß das Biphenylsystem einen seitlichen Fluorsubstituenten tragen kann.

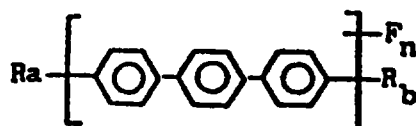
23. Flüssigkristall-Material nach Anspruch 22, dadurch gekennzeichnet, daß die Verbindung der Formel III eine Formel IIIA hat:





IIIA

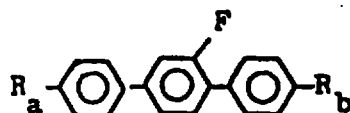
24. Flüssigkristall-Material nach Anspruch 20 oder 12, dadurch gekennzeichnet, daß das Gemisch zusätzlich wenigstens eine Verbindung der Formel IV hat:



IV

worin n 1 oder 2 und Ra und Rb unabhängig C₃ - C₁₂ Alkyl oder Alkoxy sind.

25. Flüssigkristall-Material nach Anspruch 24, dadurch gekennzeichnet, daß die Verbindung der Formel IV eine Formel IVA hat:

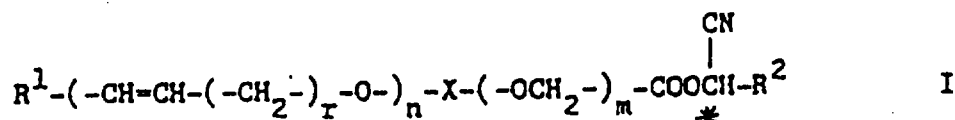


IVA

26. Flüssigkristall-Material nach Anspruch 20 oder 21, gekennzeichnet durch einen Gehalt an zwei Derivaten der Formel I, die in der smektischen C-Phase entgegengesetzte Drehwirkungen haben.
27. Elektrooptische Flüssigkristall-Anzeigevorrichtung, dadurch gekennzeichnet, daß sie ein Flüssigkristall-Material nach Anspruch 20 oder 21 verwendet.

Revendications

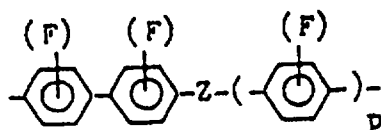
1. Dérivé de cyanhydrine, de formule générale I



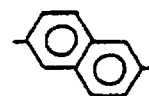
I

dans laquelle R¹ est choisi parmi un atome d'hydrogène, un groupe alkyle, alcoxy, Perfluoroalkyle et perfluoroalcoxy ayant 1 à 12 atomes de carbone et qui peut être linéaire ou ramifié ; R² représente un groupe alkyle, qui peut être linéaire en C₁ à C₈, ramifié en C₁ à C₁₅ ou cyclique ; r est un nombre entier valant 1 à 10 ; n et m valent chacun, indépendamment, 0 ou 1 ; à la condition que :

si n et m sont tous deux nuls, X est choisi parmi



et

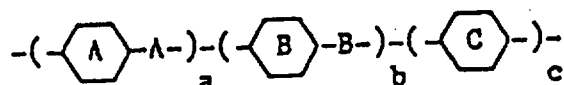


formules dans lesquelles les (F) indiquent que X porte un ou deux atomes de fluor comme substituant dans l'une quelconque ou dans les deux positions latérales disponibles pour une substitution sur les



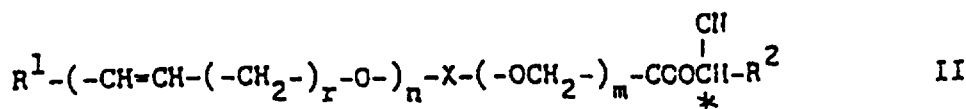
noyaux phényles indiqués ; p vaut 0 ou 1 ; Z est une liaison simple lorsque p est nul et représente COO lorsque p vaut 1 ; et

si l'un des indices n ou m, ou les deux, vaut ou valent 1, le symbole X représente un groupe de formule générale



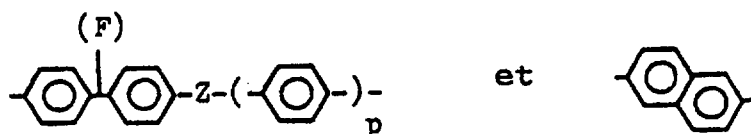
dans laquelle chaque noyau A, B et C est choisi, indépendamment, parmi un noyau phényle, un noyau phényle à substituant(s) fluoro ou chloro, un noyau cyclohexyle, pyrimidyle, pyridyle ou dioxannyle, chaque chaînon A et B représente, indépendamment, une liaison simple, COO, OOC, CH₂CH₂, CH=N, N=CH, CH₂O, OCH₂O ou O, et chacun des indices a, b et c vaut 0 ou 1, à la condition que la somme (a + b + c) vale 2 ou 3.

2. Dérivé de cyanhydrine selon la revendication 1, caractérisé par une formule générale II



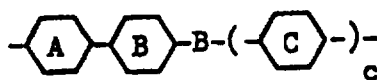
dans laquelle R¹ est choisi parmi un groupe alkyle ou alcoxy en C₁ à C₁₂ ; R², r, n et m sont tels que définis à la revendication 1, à la condition que :

si n et m valent tous deux 0, X est alors choisi parmi



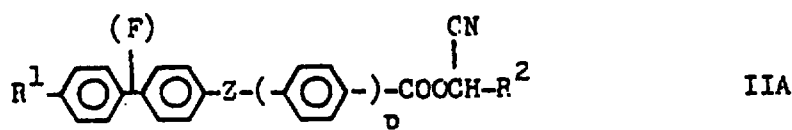
formules dans lesquelles p et Z et leur relation sont comme défini pour la formule I ; et (F) indique que le système biphenylique porte un ou deux atomes de fluor comme substituant(s) sur l'une quelconque ou sur les deux positions disponibles pour une substitution du système biphenylique, et

si l'un des indices n ou m, ou les deux, vaut ou valent 1, le symbole X représente un groupe de formule générale



dans laquelle chaque noyau A, B et C est choisi, indépendamment, parmi un noyau phényle, un noyau phényle à substituant(s) fluoro ou chloro et un noyau trans- cyclohexane ; c est nul ou vaut 1 ; B représente COO ou une liaison simple, et est une liaison simple si c est nul.

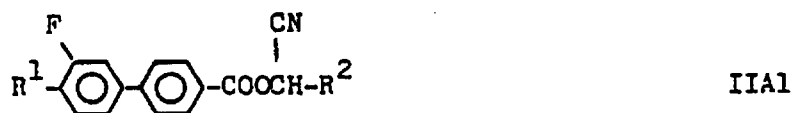
3. Dérivé de cyanhydrine selon la revendication 2, caractérisé par une formule générale IIA



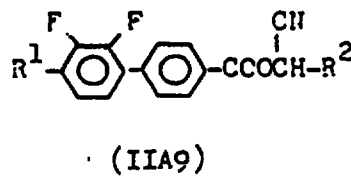
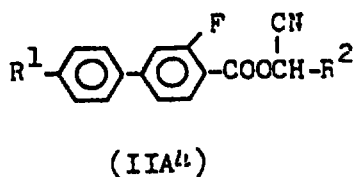
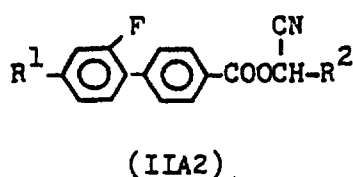
dans laquelle R¹, (F), Z, p et R² et leur relation sont comme défini dans le cas de la formule II.



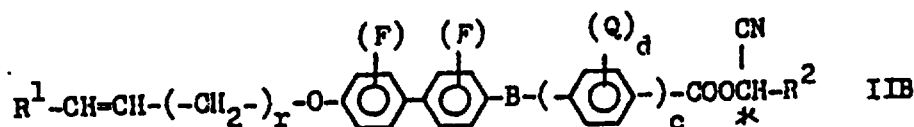
4. Dérivé de cyanhydrine selon la revendication 3, caractérisé en ce qu'il comporte un substituant (F) ou deux substituants (F) sur les positions 2, 3 ou 2', 3'.
5. Dérivé de cyanhydrine selon la revendication 4, caractérisé en ce que, dans la formule IIA, p est nul et Z représente une liaison simple.
6. Dérivé de cyanhydrine selon la revendication 5, caractérisé par une formule IIA1 :



7. Dérivé de cyanhydrine selon la revendication 5, caractérisé par une formule IIA2, IIA4 ou IIA9

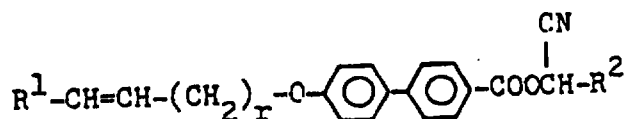


8. Dérivé de cyanhydrine selon la revendication 2, caractérisé par une formule générale IIB



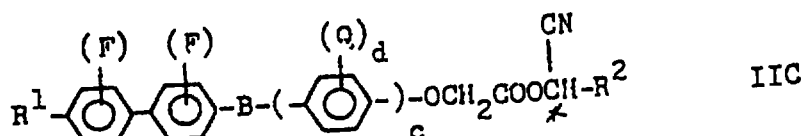
dans laquelle R¹, r, B, c et R² sont comme défini dans le cas de la formule II, (F) indique que le noyau phényle en cause peut porter un atome de fluor comme substituant ; Q représente un atome de fluor ou de chlore, et d vaut 0 ou 1.

9. Dérivé de cyanhydrine selon la revendication 8, caractérisé par une formule



dans laquelle r vaut 1 à 6.

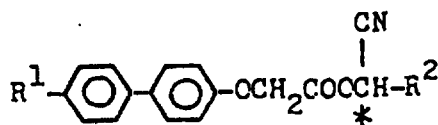
10. Dérivé de cyanhydrine selon la revendication 2, caractérisé par une formule générale IIC :



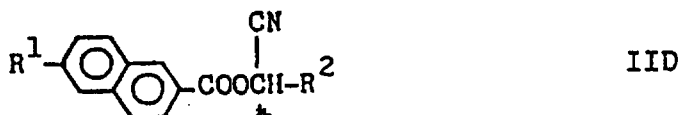
dans laquelle R¹, B, C et R² sont comme défini pour la formule II ; (F) indique que le noyau phényle en cause peut porter un atome de fluor comme substituant ; Q représente un atome de fluor ou de chlore et d vaut 0 ou 1.



11. Dérivé de cyanhydrine selon la revendication 10, caractérisé par une formule :



12. Dérivé de cyanhydrine selon la revendication 2, caractérisé par une formule IID



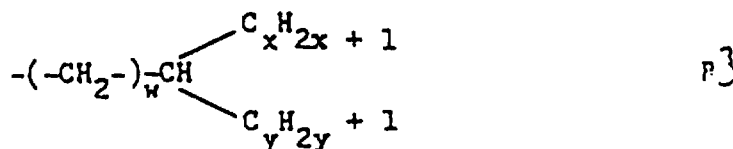
dans laquelle R^1 et R^2 sont tels que défini dans le cas de la formule II.

13. Dérivé de cyanhydrine selon l'une quelconque des revendications précédentes, caractérisé en ce que R^1 représente un groupe n-alkyle en C_3 à C_{11} .

14. Dérivé de cyanhydrine selon la revendication 13, caractérisé en ce que R^2 représente un groupe n-alkyle en C_1 à C_5 .

15. Dérivé de cyanhydrine selon la revendication 14, caractérisé en ce que R^2 représente un groupe méthyle.

16. Dérivé de cyanhydrine selon la revendication 13, caractérisé en ce que R^2 représente un groupe alkyle de formule R^3



dans laquelle w est nul ou représente un nombre entier valant 1 à 5, et chacun des indices x et y vaut, indépendamment, 1 à 6.

17. Dérivé de cyanhydrine selon la revendication 16, caractérisé en ce que w est nul et au moins l'un des indices x et y vaut 1.

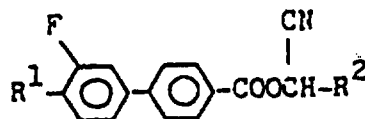
18. Dérivé de cyanhydrine selon la revendication 17, caractérisé en ce que R^2 représente $-\text{CH}(\text{CH}_3)_2$.

19. Dérivé de cyanhydrine selon la revendication 13, caractérisé en ce que R^2 représente un groupe cyclohexyle.

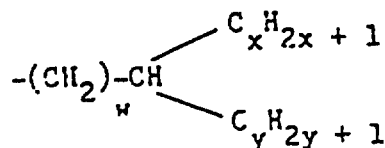
20. Matière à propriétés de cristaux liquides, qui est un mélange de composés, matière caractérisée en ce qu'au moins l'un des composés est un dérivé tel que revendiqué à la revendication 1.

21. Matière à propriétés de cristaux liquides selon la revendication 20, caractérisée en ce qu'au moins l'un des dérivés de formule I a pour formule



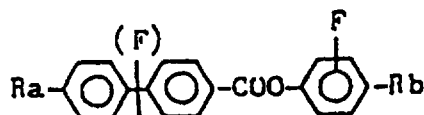


dans laquelle R¹ représente un groupe n-alkyle ou n-alcoxy en C₃ à C₁₁, et R² représente un groupe n-alkyle en C₁ à C₅ ou un groupe alkyle de formule



dans laquelle w est nul ou représente un nombre entier valant 1 à 5, et chacun des indices x et y vaut indépendamment 1 à 6.

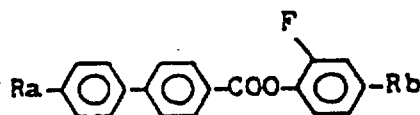
22. Matière à propriétés de cristaux liquides selon la revendication 20 ou 21, caractérisée en ce que le mélange contient en outre au moins un composé de formule III



III

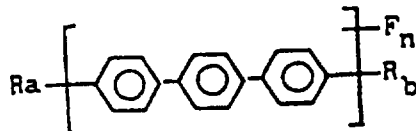
dans laquelle Ra et Rb représentent chacun, indépendamment, un groupe alkyle ou alcoxy en C₃ à C₁₂, et (F) indique que le système biphénylique peut porter un atome de fluor comme substituant latéral.

23. Matière à propriétés de cristaux liquides selon la revendication 22, caractérisée en ce que le composé de formule III a pour formule IIIA :



IIIA

24. Matière à propriétés de cristaux liquides selon la revendication 20 ou 21, caractérisée en ce que le mélange contient en outre au moins un composé de formule IV

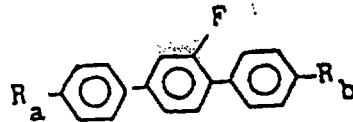


IV

dans laquelle n vaut 1 ou 2, et Ra et Rb représentent chacun, indépendamment, un groupe alkyle ou alcoxy en C₃ à C₁₂.

25. Matière à propriétés de cristaux liquides selon la revendication 24, caractérisée en ce que le composé de formule IV a pour formule IVA :





IV A

26. Matière à propriétés de cristaux liquides selon la revendication 20 ou 21, caractérisée en ce qu'elle contient deux dérivés de formule I, qui ont des effets de torsadage de sens opposé dans la phase smectique C.

27. Dispositif électro-optique d'affichage à cristaux liquides, caractérisé en ce qu'il utilise une matière à propriétés de cristaux liquides telle que revendiquée dans la revendication 20 ou 21.

