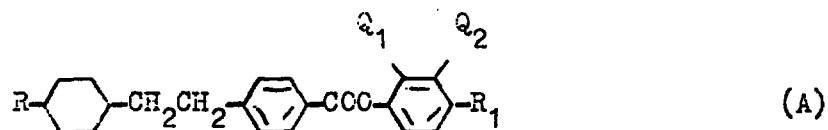


Phenyl Esters and their use in
Liquid Crystal Materials

This invention relates to phenyl esters and their use in liquid crystal materials.

Liquid crystal materials which show a nematic or chiral nematic (Cholesteric) phase at their working temperature, and their use in electro-optic display devices such as digital watches, calculators etc, are well known.

Many compounds which have liquid crystalline properties and which are suitable for use in liquid crystal materials are known. For example EPA 0126601 describes compounds of general formula (A):



- 10 where R is alkyl, R₁ is selected from H, alkyl, alkoxy, halogen or cyano, and each of Q₁ and Q₂ may independently be selected from H or halogen. The only examples of compounds actually prepared in EPA 0126601 are those in which R₁ is alkyl, alkoxy, cyano and fluoro, with Q₁ and Q₂ in all cases being hydrogen. GB 2132192A
- 15 describes compounds of formula (A) in which R₁ is cyano, Q₁ is hydrogen and Q₂ is fluorine, such as the R = propyl compound which shows a solid to nematic liquid crystal transition at 60°C.

Compounds of general formula (B):



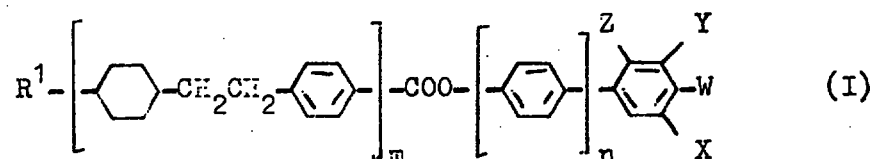
are described in US 4683078 and 4131618 but are not said to have any liquid crystalline properties.

Known liquid crystal materials are not ideal in all respects and there is a requirement for materials, and hence for compounds which can be used as constituents of such materials, which show improved properties such as lower melting point, higher clearing point, lower viscosity, higher dielectric anisotropy etc. In the field of liquid crystal chemistry it is well known that quite small modifications to the structure of a compound can have a drastic and unexpected effect on its liquid crystalline properties.

Additionally the field of organofluorine chemistry presents its own problems of synthesis and therefore the preparation of new organofluorine compounds has been impeded by difficulty.

It is an object of the present invention to provide novel phenyl esters which have improved usefulness as constituents of liquid crystal materials.

According to the invention novel phenyl esters of general formula I are provided:



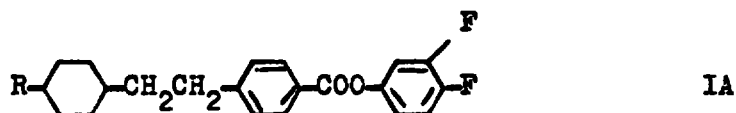
wherein R^1 is R, RO or ROCH_2 where R is C_{1-15} alkyl; the cyclohexyl ring is in its trans conformation, W is selected from fluorine and CN; X, Y and Z being selected from fluorine and hydrogen, no more than two of X, Y or Z being fluorine; m and n are 1 or 0 provided that when m is 1 then n is 0 and either W is F or two of X, Y or Z are F, and provided that when m is 0 then n is 1, W is CN and R^1 is not RO, and provided that all three of X, Y and Z are not hydrogen unless R^1 is ROCH_2 .

The invention also provides a liquid crystal material being a mixture of two or more compounds at least one being an ester of formula I. The structural preferences expressed below are inter alia on the basis of usefulness of the esters of formula I in such materials.

Preferably R contains 1-8 carbon atoms and is n-alkyl or contains an asymmetrically substituted carbon atom such as in a

2-methylbutyl group. Preferably Z is hydrogen.

In esters of formula I where m is 1 and n is 0, R¹ is preferably alkyl. In such compounds if W is fluorine then preferably Z is hydrogen and only one of X and Y is fluorine, ie esters of formula IA:

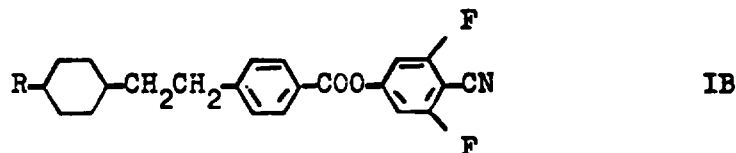


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Esters of formula IA are particularly preferred.

If W is CN then preferably Z is hydrogen and of X and Y are fluorine, ie esters of formula IB:

15



Esters of formula IB have lower solid to nematic liquid crystal transitions than their monofluorinated counterparts.

20

In esters of formula I where m is 0, n is 1 and R¹ is alkyl, W is CH, Z is preferably hydrogen and one or both of X and Y are fluorine, ie esters of formulae IC and ID:

25



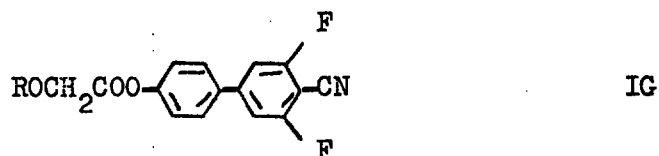
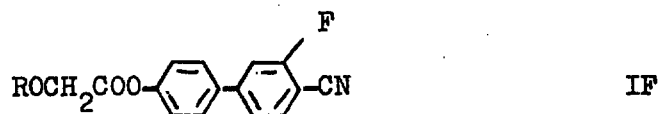
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In esters of formula I where m is 0, n is 1 and R¹ is ROCH₂, then W is CN and ^{preferably} all three of X, Y and Z are hydrogen, ie esters of formula IE:

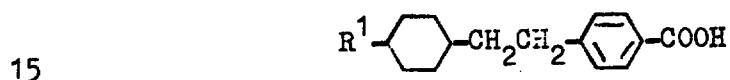
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Other useful esters in which R^1 is $ROCH_2$ are those of formulae IF and IG:



10 Esters of formula I may be prepared via esterification of a suitable carboxylic acid with a phenol. For example esters in which m is 1 (eg IA and IB) may be prepared using the acid:



which may be prepared using the methods described in EP 0126601. Esters in which m is 0 (eg IC-IG) may be prepared using known carboxylic acids $RCOOCH$ or $ROCH_2COOH$.

20 The phenols used may be known, eg 4-cyano phenol, 4-fluorophenol, 3, 4-difluorophenol (to make IA) see for example Chem Abs 87 (1977) 133305, 3-fluoro-4-cyano-phenol, 4-hydroxy-4¹-cyanobiphenyl (to make IE), or may be prepared by synthetic methods such as route A or route B shown in figures 1 and 2 respectively.

Route A may be used to prepare 4-hydroxy-3¹-fluoro-4¹-cyanobiphenyl (to make ID and IG) and 4-hydroxy-3¹,5¹-difluoro-4¹-cyanobiphenyl (to make IE and IH). The individual steps of route A are:

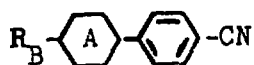
- 5 1A (i) Mg, THF (ii) (i-PrO)₃B, THF (iii) 10% HCl
 2A N-bromosuccinimide, CH₂Cl₂
 3A Br₂, Acetic acid
 4A (i) NaNO₂, H₂SO₄ (ii) CuSO₄·5H₂O, KCN, H₂O
 5A Pd(PPh₃)₄, Benzene, 2M Na₂CO₃
 6A BBr₃, CH₂Cl₂
 10 Route B may be used to prepare 3,5-difluoro-4-cyanophenol
 (to make IC). The individual steps of route B are:
 1D (i) nBuLi, THF (ii) solid CO₂, Et₂O
 2D Oxalyl chloride, DMF, benzene
 3D 35% ammonia
 15 4D Thionyl chloride, DMF
 5D AlCl₃, NaCl

Esterification reactions are among the best known in synthetic organic chemistry and suitable methods will be apparent to those skilled in the art.

- 20 Esters of formula I, in particular the preferred esters discussed above, in many cases show liquid crystal phases which are nematic if R is n-alkyl and cholesteric if R contains an asymmetrically substituted carbon atom. Esters in which W is fluorine, especially those of formula IA are useful for the further
 25 reason that they show a high $\Delta\epsilon$ and a low melting point. Esters of formula I are therefore useful constituents of liquid crystal mixtures.

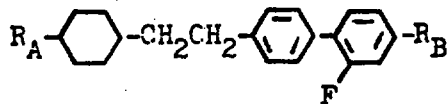
- When used in a liquid crystal mixture the mixture is preferably a nematic or cholesteric mixture particularly the former. Esters of
 30 formula I may be mixed with known liquid crystalline compounds. For example they may be mixed with compounds having a high positive dielectric anisotropy, such as those of formulae IIIa to IIIi on page 5 of EPA 0126601, especially compounds of formula:

35



where R_B is C₁-8 n-alkyl or n-alkoxy and ring A is phenyl or cyclohexyl.

The mixture may also for example include compounds having a low positive dielectric anisotropy, such as those of formula IVa to IVp on page 6-7 of EPA 0126601, especially of formula:



where R is C₁₋₉n-alkyl or n-alkoxy and R is n-alkyl.

The mixture may also for example include compounds having a high clearing point, such as those of formula Va to Vj on page 7-8 of
10 EPA 0126601 especially of formula:



where R is C₁₋₉ n-alkyl or n-alkoxy.

15 Typically but not exclusively a nematic liquid crystal material of this invention will contain 0-100 wt % of esters of formula I, 0-95 wt % of high positive dielectric anisotropy compounds, 0-95 wt % of low positive dielectric anisotropy compounds, and 0-30 wt % of high clearing point compounds. The mixture may additionally contain
20 optically active additives such as (+)-4-(2-methylbutyl)-4¹-cyanobiphenyl or one or more pleochroic dyes.

The liquid crystal materials of the invention may be used in any of the known types of electro-optical display device which use a nematic liquid crystal material.

25 The invention will now be illustrated by way of example only with reference to figures 1 and 2 which show Routes A and B for preparation of phenols for use in synthesis of esters of formula I, and figure 3 which shows a sectional view of a liquid crystal electro optic display device.

30 In the following examples all temperatures are in °C, N-I = nematic liquid crystal to isotropic liquid transition, C-N = solid crystal to nematic liquid crystal transition, C-I = solid crystal to isotropic liquid transition. Examples 1, 2 and 3 are examples of preparation of compounds which are useful as precursors
35 of the compounds of the invention.

Example 1: Route A.4-Methoxyphenylboronic acid (1). (Step 1A)

A solution of the Grignard reagent, prepared from
4-bromoanisole (80.0 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 (58.5 g) which was recrystallised from water to
give colourless crystals.

Yield 27.7 g, 43%.

mp 201-202 °C.

Note: A cream-coloured oil was separated during the above
recrystallisation which solidified on cooling to give a cream-coloured
solid.

Yield 17.5 g.

4-Bromo-2-fluoroaniline (2). (Step 2A)

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 (MgSO_4). The solvent was removed in vacuo to yield a red solid (180 g) which was steam distilled to give a colourless solid.

Yield	120.0 g, 70%.
mp	41-42 °C.

4-Bromo-2-fluorobenzonitrile (3). (Step 4A)

Concentrated sulphuric acid (60 ml) was added dropwise to a stirred mixture of compound 2 (75.0 g, 0.39 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, 1.98 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 °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 (78.0 g) which was steam distilled to give an off-white solid.

Yield 59.2 g, 76%.

5 mp 69-70 °C.

4-Cyano-3-fluoro-4'-methoxybiphenyl (4). (Step 5A)

A solution of compound 1 (10.64 g, 0.07 mol) in ethanol (90 ml) was added dropwise to a stirred mixture of compound 3 (12.0 g, 0.06 mol) and tetrakis(triphenylphosphine)palladium(0) (2.10 g, 1.82 mmol) in benzene (125 ml) and 2M-sodium carbonate (100 ml) at room temperature under dry nitrogen. The stirred mixture was heated under reflux (90-95 °C) for 2.5 h (i.e., 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 cooled further to 2 °C, the product was filtered off and washed with water. The product was dried (CaCl₂) in vacuo to give a yellow powder.

Yield 11.9 g, 88%.

mp 153-154 °C.

4-Cyano-3-fluoro-4'-hydroxybiphenyl (5). (Step 6A)

A solution of boron tribromide (12.0 ml, 31.8 g, 0.13 mol) in dry dichloromethane (100 ml) was added dropwise to a stirred, cooled (-78 °C) solution of compound 4 (14.0 g, 0.06 mol) in dry dichloromethane (250 ml) under dry nitrogen. The stirred mixture was allowed to warm

to room temperature over 20 h (i.e., until glc analysis revealed absence of starting material). Water was added and a yellow precipitate was produced. The product was extracted into ether (twice), and the combined ethereal extracts were washed with water and dried (MgSO_4). The solvent was removed in vacuo to afford a pale-yellow powder.

Yield 13.1 g, 100%.
mp 201-202 °C.

10 4-Bromo-2,6-difluoroaniline (6). (Step 3A)

A solution of bromine (127.0 g, 0.79 mol) in glacial acetic acid (200 ml) was added slowly, dropwise to a stirred solution of 2,6-difluoroaniline (101.5 g, 0.79 mol) in glacial acetic acid (550 ml) keeping the temperature below 25 °C. The mixture was stirred at room temperature for 2 h, and then sodium thiosulphate (50 g), sodium acetate (125 g) and water (700 ml) were added and the mixture was cooled in a refrigerator overnight. The product was filtered off, dissolved in ether, and the ether phase was washed with water, 10% sodium hydroxide, water and dried (MgSO_4). The solvent was removed in vacuo to yield a pale yellow solid (134 g) which was steam distilled to give a colourless solid.

Yield 117.9 g, 72%.
mp 67-68 °C.

4-Bromo-2,6-difluorobenzonitrile (7). (Step 4A)

A stirred mixture of compound 6 (56.0 g, 0.27 mol) and concentrated sulphuric acid-water (1:1, 250 ml) was heated until a solution was obtained. The mixture was cooled to -10°C and a
5 solution of sodium nitrite (30.9 g, 0.45 mol) in water (70 ml) was added dropwise. The mixture was stirred at -5°C for 2.5 h.

A solution of potassium cyanide (97.5 g, 1.50 mol) in water was added dropwise to a stirred solution of copper(II) sulphate pentahydrate (86.5 g, 0.35 mol) in water (200 ml) and ice (130 g).
10 Sodium hydrogen carbonate (300 g), cyclohexane (1200 ml) and glacial acetic acid (130 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
15 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 (58.5 g) which was steam distilled to give a light-orange solid.

20 Yield 31.7 g, 54%.
mp 79-80 $^{\circ}\text{C}$.

4-Cyano-3,5-difluoro-4'-methoxybiphenyl (8). (Step 5A)

A solution of compound 1 (11.50 g, 0.076 mol) in ethanol (90 ml) was added dropwise to a stirred mixture of compound 7 (15.0 g, 0.069 mol) and tetrakis(triphenylphosphine)palladium(0)
25 (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 °C) for 4.5 h (i.e., 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 (CaCl₂) in vacuo to give fawn-coloured needles.

Yield	14.1 g, 84%.
mp	205-207 °C.

10 4-Cyano-3,5-difluoro-4'-hydroxybiphenyl (9). (Step 6A)

A solution of boron tribromide (25.0 ml, 61.5 g, 0.25 mol) in dry dichloromethane (140 ml) was added dropwise to a stirred, cooled (-78 °C) solution of compound 8 (12.22 g, 0.05 mol) in dry dichloromethane (250 ml) under dry nitrogen. The stirred mixture was allowed to warm to room temperature over 9 h (i.e., until glc analysis revealed absence of starting material). The mixture was cooled to -10 °C, water was added slowly (exothermic) and cooled to 2 °C. The product was filtered off, washed with water and dried (CaCl₂) in vacuo to give a pale-yellow powder.

20	Yield	13.3 g, 100%.
	mp	230-231 °C.

Example 2; Route B.2,6-Difluoro-4-methoxybenzoic acid (24). (Step 1B)

A solution of n-butyllithium (10.0 M in hexane; 25.0 ml, 0.25 mol) was added dropwise to a stirred, cooled (-78°C) solution of 3,5-difluoroanisole (35.9 g, 0.25 mol) in dry THF (200 ml) under dry nitrogen. The stirred mixture was maintained under these conditions for 2.5 h and then poured into a slurry of solid carbon dioxide and dry ether. The product was extracted into 10% sodium hydroxide (twice), the combined basic extracts were acidified with 36% hydrochloric acid, and 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 give a colourless solid.

Yield 46.5 g, 99%.
mp 184-185 $^{\circ}\text{C}$.

2,6-Difluoro-4-methoxybenzoyl chloride (25). (Step 2B)

A solution of oxalyl chloride (36.5 g, 0.29 mol) in dry benzene (50 ml) was added dropwise to a stirred solution of compound 24 (25.5 g, 0.14 mol) and dry DMF (40 drops) in dry benzene (500 ml) at room temperature. The mixture was stirred at room temperature overnight and the excess of oxalyl chloride and benzene were removed in vacuo.

2,6-Difluoro-4-methoxybenzamide (26). (Step 3B)

The crude acid chloride (25) was dissolved in dry diglyme (60 ml) and added dropwise at room temperature with gentle stirring to 35% ammonia (750 ml). The resulting colourless precipitate was
5 filtered off and dried (CaCl_2) in vacuo to give a colourless solid.

Yield 21.2 g, 81%.

mp 158-159 °C.

2,6-Difluoro-4-methoxybenzonitrile (27). (Step 4B)

10 A solution of thionyl chloride (139.0 g, 1.17 mol) in dry DMF (150 ml) was added to a stirred solution of compound 26 (20.0 g, 0.11 mol) in dry DMF (250 ml) at room temperature. The mixture was stirred at room temperature overnight and then poured onto ice-water. The
15 product was extracted into ether (twice), and the combined ethereal extracts were washed with water, saturated sodium hydrogen carbonate, water and dried (MgSO_4). The solvent was removed in vacuo to give off-white crystals.

Yield 17.7 g, 95%.

20 mp 59-60 °C.

2,6-Difluoro-4-hydroxybenzonitrile (28). (Step 5B)

A stirred, homogeneous mixture of finely powdered, compound 27 (17.0 g, 0.10 mol), aluminium chloride (29.4 g, 0.22 mol) and sodium chloride (7.1 g, 0.12 mol) was heated to 180 °C over 25 min
25 and then at 180 °C for 1h (glc and tlc analyses both revealed a complete reaction). Ice-water was added, and the product was extracted

into ether (twice). The combined ethereal extracts were washed with water, and the product was extracted into 10% sodium hydroxide (twice) and the combined basic extracts were acidified with 36% hydrochloric acid. The product was extracted into ether (twice), and the combined
5 ethereal extracts were washed with water and dried (MgSO_4). The solvent was removed in vacuo to give a fawn solid.

Yield 14.6 g, 94%.

mp 119-120 °C.

Example 3 Preparation of 4-(2-(trans-4-pentylcyclohexyl)ethyl) benzoic acid.

A mixture of 1-(trans 4-pentylcyclohexyl)-2-(4'-cyanophenyl) ethane (known from EPA 0126601) (25g), acetic acid (325ml), conc. sulphuric acid (84 ml) and water (163 ml) was gently stirred and heated under reflux for 36 hours. After cooling, the reaction mixture was poured into water, the solid was filtered off, washed well with water and dried. The crude product was then crystallised from acetic acid. Yield 26g. The propyl analogue of this acid was also prepared.

Example 4 Esterification Reaction

The acid from Example 3 (12.3g), was mixed with dichloromethane (60 ml) and trifluoroacetic anhydride (6.23 ml) was added. After 15 minutes, 3,4-difluorophenol (5.3g) was added and the mixture stirred at 20°C for 16 hours. The reaction mixture was washed with water and evaporated to dryness. The crude product was chromatographed on silica gel and crystallised from industrial methylated spirit. Yield 10.1g HPLC 99.6%.

The use of trifluoroacetic anhydride is a generally applicable esterification method. Using this method and the appropriate acid and phenols the esters listed and characterised in table 1 below were prepared. In each case R was n-alkyl.

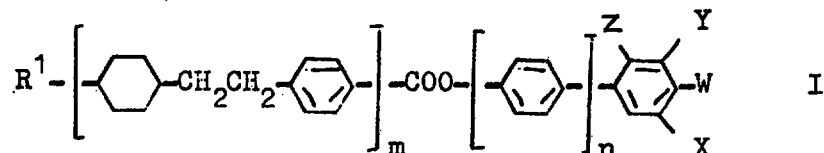
Table 1

<u>Formula</u>	<u>R</u>	<u>C-N/I (°C)</u>	<u>N-I (°C)</u>	<u>$\Delta\epsilon$</u>	<u>η (20°C_{st})</u>	<u>Δn</u>
IA	C ₂ H ₅	58.3 (C-N)	85.0			
IA	C ₃ H ₇	59.3 (C-N)	108.9	20.8	50.5	0.120
IA	C ₄ H ₉	56.7 (C-N)	106.4			
IA	C ₅ H ₁₁	57.3 (C-N)	112.7	20.0	53.4	0.120
IB	C ₃ H ₇	55 (C-N)	134.5			
IC	C ₅ H ₁₁	35 (C-I)	(25)			
ID	C ₅ H ₁₁	58 (C-I)	-			
IE	C ₅ H ₁₁	51 (C-I)	(41)			

Referring to Fig 3, a liquid crystal electro optical display device comprises a layer of a liquid crystal material 31 between a front glass support plate 32 and a back glass support plate 33. The front glass plate 32 is coated on the inner surface thereof with a transparent conducting layer 34 eg tin oxide, to form an electrode. The back glass plate 33 is also coated on the inside surface thereof with a conductive layer 35. If light is to be transmitted through the device the back electrode 15 and the back plate 33 are also transparent and made of the same materials as the front plate and electrode 32 and 34. If the device is to reflect light the back electrode 35 may be made reflective, eg of aluminium. The front and back electrodes 34, 35 are coated with a transparent aligning layer 36, 37 eg of poly-vinyl alcohol which have each been rubbed prior to assembly of the device in a single rubbing direction. On assembly the rubbing directions of the layers 36, 37 are arranged orthogonal to each other. In operation the electrodes 34, 35 are connected to a source of voltage (not shown).

CLAIMS

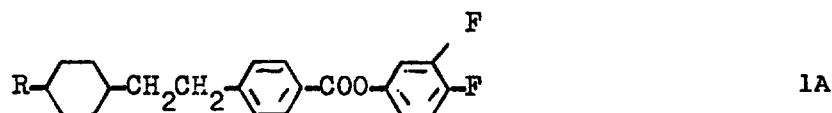
1. A phenyl ester of Formula 1:



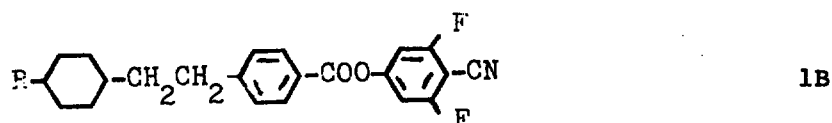
wherein R^1 is R, RO or ROCH_2 where R is C_{1-15} alkyl, the cyclohexyl ring is in its trans conformation, W is selected from fluorine and CN, X, Y and Z being selected from fluorine and hydrogen, no more than two of X, Y or Z being fluorine, m and n are 1 or 0 provided that when m is 1 then n is 0, and either W is F or two of X, Y or Z are F, and provided that when m is 0 then n is 1, W is CN and R^1 is not RO, and provided that all three of X, Y and Z are not hydrogen unless R^1 is ROCH_2 .

2. A phenyl ester according to Claim 1 wherein R is C_{1-8} n-alkyl or contains an asymmetrically substituted carbon atom, and Z is hydrogen.

3. A phenyl ester according to Claim 1 or 2 having a Formula 1A:



4. A phenyl ester according to Claim 1 or 2 having a Formula 1B:



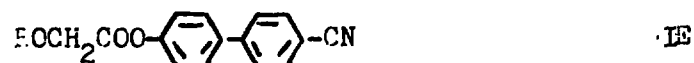
5. A phenyl ester according to Claim 1 or 2 having a Formula 1C:



6. A phenyl ester according to Claim 1 or 2 having a Formula 1D:

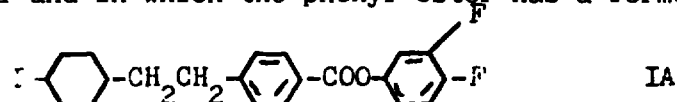


7. A phenyl ester according to claim 1 or 2 having a formula IE:



8. A liquid crystal material being a mixture of two or more compounds at least one of which is a phenyl ester of formula I as claimed in claim 1.

9. A liquid crystal material according to claim 8 which is a nematic material and in which the phenyl ester has a formula IA



where R is C_{1-8} n-alkyl or is an alkyl group containing an asymmetrically substituted carbon atom.

