

Description

The present invention is concerned with novel liquid crystalline esters, their manufacture, liquid crystalline mixtures which contain these esters as well as their use for electro-optical purposes.

Liquid crystals are used primarily as dielectrics in indicating devices, as the optical properties of such substances can be influenced by an applied voltage. Electro-optical devices based on liquid crystals are well-known to the person skilled in the art and can be based on various effects such as, for example, dynamic scattering, the deformation of aligned phases (DAP cells), the Schadt-Helfrich effect (TN cells [twisted-nematic] and STN cells [super twisted-nematic]), the guest/host effect (guest/host cells), a cholesteric-nematic phase transition (phase-change cells) or the SBE effect (super birefringence effect).

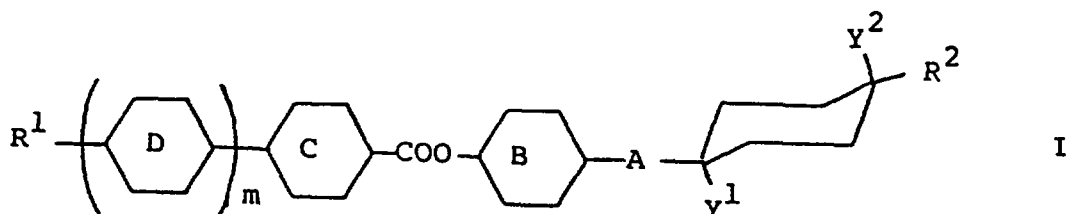
Cholesteric liquid crystals are used, for example, in the above-mentioned phase-change cells. Further, cholesteric additives or other chiral substances with suitable choice of the concentration can also be used to improve the electro-optical properties of liquid crystals for twisted nematic cell indicators. Nematic liquid crystal components can be used in all of the aforementioned applications.

The aforementioned indicating devices generally have response times in the order of several milliseconds or more. In order to improve in response times of indicating devices, liquid crystals with ferroelectric properties have recently also been used. In this application there are used chiral smectic phases, for example smectic C, F or I phases, mainly smectic C phases. Hitherto, however, relatively few of such liquid crystals have become known and their stability is often inadequate.

In order to be suitable for use in indicating devices liquid crystals should have a good chemical and thermal stability and a good stability towards electrical fields and electromagnetic radiation. Further, they should be colourless and have low viscosities and should give short response times and a high contrast in indicating devices. Furthermore, the liquid crystals should have a suitable mesophase, for example a cholesteric or a suitable chiral smectic phase, at the usual operating temperatures. As liquid crystals are usual used in mixtures, it is, moreover, important that the components have a good miscibility with one another. Other properties such as, for example, the threshold potential, the dielectric anisotropy and the optical anisotropy, must fulfil different

conditions depending on the type of cell which is used. Liquid crystals with ferroelectric properties preferably have a negative dielectric anisotropy or a small absolute value of the dielectric anisotropies.

The object of the present invention are the tricyclic and tetracyclic esters of the general formula



wherein m stands for the number 0 or 1; A signifies a single covalent bond, $-\text{CH}_2-\text{CH}_2-$, $-\text{OCH}_2-$, $-\text{COO}-$ or $-\text{OOC}-$; rings B, C and D denote 1,4-phenylene optionally substituted with cyano, halogen or lower alkyl; Y^1 and Y^2 signify hydrogen or one of the substituents Y^1 and Y^2 also signifies cyano; and R^1 and R^2 each individually represent optionally halogen-substituted C_1-C_{18} -alkyl or optionally halogen-substituted C_2-C_{18} -alkenyl in which optionally one CH_2 group or two non-adjacent CH_2 groups is/are replaced by oxygen; with the proviso that at least one of the residues R^1 and R^2 has a chiral carbon atom and/or a C-C double bond when A stands for $-\text{COO}-$ and that at least one of the residues R^1 and R^2 has a C-C double bond when A stands for a single covalent bond.

The compounds in accordance with the invention are suitable components for ferroelectric liquid crystals and themselves have for the most part a chiral smectic phase. They are, however, also basically suitable for cholesteric or nematic mixtures. They are optically active or optically inactive and have the requisite properties referred to above.

The above term "halogen" embraces fluorine, chlorine or bromine.

The term "lower alkyl" embraces alkyl groups with 1-5 carbon atoms such as methyl, ethyl, propyl and isopropyl, preferably methyl.

The term "1,4-phenylene optionally substituted with cyano, halogen or lower alkyl" embraces groups such as

1,4-phenylene, 2-cyano-1,4-phenylene, 2,3-dicyano-1,4-phenylene, 2-fluoro-1,4-phenylene, 2,3-difluoro-1,4-phenylene, 2-chloro-1,4-phenylene, 2-bromo-1,4-phenylene, 2-methyl-1,4-phenylene and the like. 1,4-Phenylene is generally preferred. However, the transition temperatures, the solubility, the dielectric anisotropy and the like can be modified and higher ordered phases can be suppressed by using substituted groups.

The term "alkyl or alkenyl in which optionally one CH₂ group or two non-adjacent CH₂ groups is/are replaced by oxygen" embraces straight-chain and branched groups such as alkyl, alkoxy, alkoxyalkyl, alkoxyalkoxy, alkenyl, alkenyloxy, alkoxyalkenyl, alkenyloxyalkyl, alkoxyalkenyloxy and the like. Corresponding halogen-substituted groups are, for example, halogenoalkyl, halogenoalkoxy, halogenoalkenyl, halogenoalkenyloxy and the like.

Compounds of formula I in which Y¹ or Y² signifies cyano have a negative anisotropy of the dielectric constants. In general, however, Y¹ and Y² preferably stand for hydrogen. In many instances, C-C double bonds in R¹ and/or R² lead to an improvement of the chiral smectic properties.

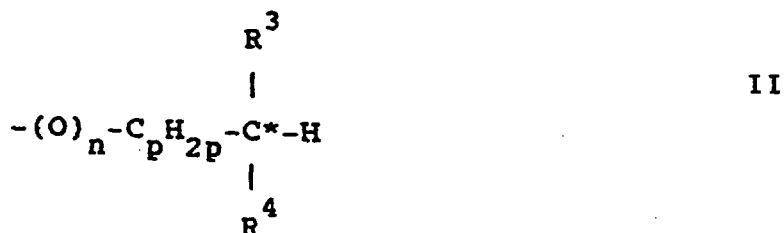
A preferred group of compounds in accordance with the invention comprises those in which Y¹ and Y² signify hydrogen and ring C and an optionally present ring D stand for 1,4-phenylene. Ring B preferably denotes 1,4-phenylene, 2-cyano-1,4-phenylene, 2,3-dicyano-1,4-phenylene, halogeno-1,4-phenylene or 2,3-dihalogeno-1,4-phenylene.

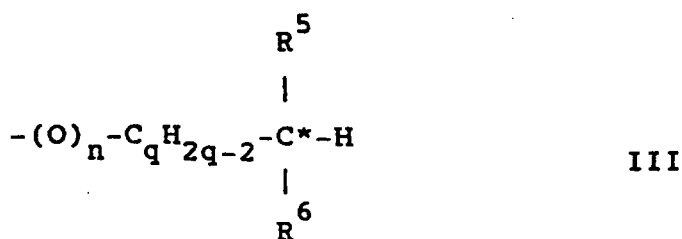
A further group of preferred compounds of formula I comprises those in which A signifies -CH₂CH₂-, -OCH₂- or -OOC-, especially -CH₂CH₂- or -OCH₂-.

In formula I above m preferably stands for the number 0.

A further preferred aspect is concerned with optically active compounds of formula I which have a chiral carbon atom in R¹ and/or R².

Preferred groups R¹ or R² having chiral carbon atoms are the groups of the general formulae





wherein n, p and q signify whole numbers and n stands for 0 or 1, p stands for 0-6 and q stands for 2-6; R³ signifies alkyl and R⁴ signifies halogen, alkoxy, alkenyl, alkenyloxy or alkyl different from R³; or R³ signifies alkenyl and R⁴ signifies alkoxy; R⁵ denotes alkyl and R⁶ denotes halogen, alkoxy or alkyl different from R⁵; and C* signifies the chiral carbon atom.

Groups of formula II in which R³ signifies methyl and R⁴ signifies alkyl different from methyl, preferably ethyl, are especially preferred.

In the case of optically active compounds of formula I, R¹ preferably has a chiral carbon atom. Those compounds of formula I in which R¹ stands for a group of formula II or III are therefore especially preferred.

Alkyl, alkenyl, alkoxyalkenyl and alkenyloxyalkyl are preferred residues R². When R¹ has a chiral carbon atom, R² preferably stands for a straight-chain residue.

In general, there are particularly preferred those compounds of formula I in which R¹ stands for a chiral or achiral alkoxy or alkenyloxy group and R² stands for a chiral or achiral alkyl or alkenyl group. R² is preferably achiral.

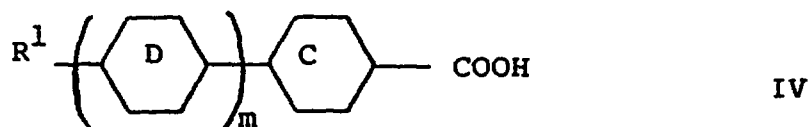
A double bond optionally present in R¹ and/or R² is preferably situated in position 1, 3 or 4 (excluding oxygen atoms which may be present) or in the terminal position of the side-chain R¹ or R², especially in position 4. Especially preferred unsaturated groups are therefore groups such as 1E-alkenyl, 3E-alkenyl, 4-alkenyl, 2E-alkenyloxy, 3-alkenyloxy, alkoxy-3E-alkenyl, alkoxy-4-alkenyl, alkoxy-3-alkenyloxy, 5-hexenyl, 4-pentenyl, 6-heptenyl, 5-hexenyloxy, 7-octenyl, 6-heptenyloxy, 8-nonenyl, 7-octenyloxy, 9-decenyl, 8-nonyloxy and the like.

The residues R¹ and R² conveniently have a maximum of 18 carbon atoms in each case. The group or groups with

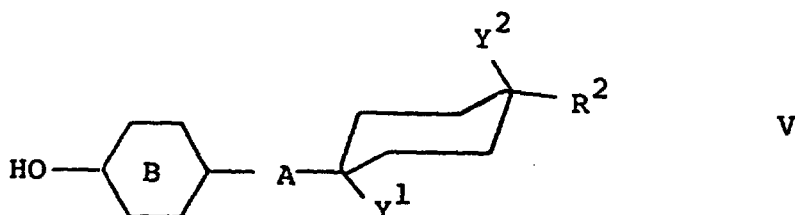
a chiral carbon atom preferably have 4-18, particularly 4-15, carbon atoms. An optionally present group R^1 or R^2 without a chiral carbon atom preferably has a maximum of 12, particularly a maximum of 7, carbon atoms. For chiral smectic applications there are, however, generally preferred compounds of formula I which have in R^1 and R^2 together have at least 7, especially at least 10, carbon atoms.

The compounds of formula I can be manufactured in accordance with the invention by

a) esterifying a compound of the general formula

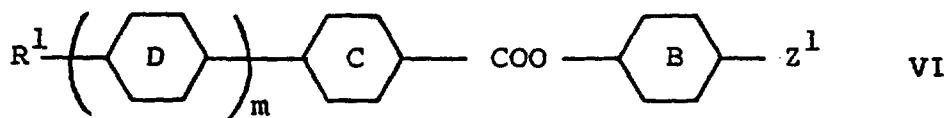


and a compound of the general formula

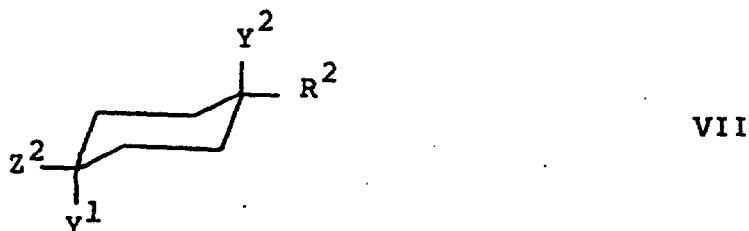


wherein A, R^1 , R^2 , Y^1 , Y^2 , m and rings B, C and D have the significances given above, or reactive derivatives of these compounds and, if desired, reacting a compound of formula I in which ring B, C or D signifies 1,4-phenylene substituted with chlorine or bromine with copper(I) cyanide, sodium cyanide or potassium cyanide, or

b) for the manufacture of compounds of formula I in which A signifies an ester group $-\text{COO}-$ or $-\text{OOC}-$, esterifying a compound of the general formula



and a compound of the general formula



wherein one of the groups Z^1 and Z^2 denotes the carboxyl group and the other denotes the hydroxy group and R^1 , R^2 , Y^1 , Y^2 , m and rings B, C and D have the significances given above, or reactive derivatives of these compounds and, if desired, reacting a compound of formula I obtained in which ring B, C or D signifies 1,4-phenylene substituted with chlorine or bromine with copper(I) cyanide, sodium cyanide or potassium cyanide.

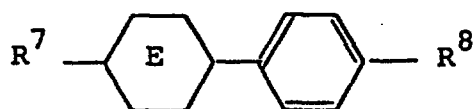
The reaction of the compounds of formulae IV and V or of the compounds of formulae VI and VII can be carried out in a manner known per se by esterifying the carboxylic acid or a reactive derivative thereof (e.g. acid chloride, bromide or anhydride) with the hydroxy compound or a suitable salt (e.g. the sodium salt). A preferred method comprises reacting the acid chloride (which is obtainable from the carboxylic acid e.g. by heating with thionyl chloride) with the hydroxy compound. This reaction is conveniently carried out in an inert organic solvent, for example diethyl ether, tetrahydrofuran, dimethylformamide, benzene, toluene, cyclohexane, carbon tetrachloride and the like. In order to bind the hydrogen chloride which is liberated during the reaction, an acid-binding agent, for example a tertiary amine, pyridine and the like, is conveniently used. The acid-binding agent can also simultaneously serve as the solvent. Further preferred methods comprise reacting the carboxylic acid with the hydroxy compound in the presence of 4-(dimethylamino)pyridine and N,N'-dicyclohexylcarbodiimide or in the presence of oxalyl chloride and dimethylformamide. The temperature and pressure at which the above esterification reactions are carried out are not critical and in general they are carried out at atmospheric pressure and a temperature between -30°C and the boiling temperature of the reaction mixture.

The reaction of a compound of formula I in which ring B, C or D signifies 1,4-phenylene substituted with chlorine or bromine to give the corresponding cyano-substituted compound is conveniently carried out with copper(I) cyanide, sodium cyanide or potassium cyanide in an inert organic solvent such as ethylene glycol, tetrahydrofuran, dimethylformamide, dimethyl sulphoxide, pyridine or acetonitrile. The temperature and pressure are not critical. Atmospheric pressure and a temperature between room temperature and the boiling temperature of the reaction mixture are conveniently used.

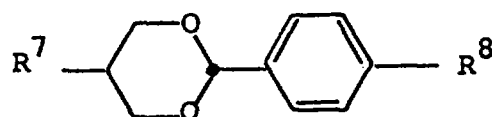
The starting materials of formulae IV-VII are known compounds or analogues of known compounds and can be prepared according to known methods.

The compounds in accordance with the invention can be used in the form of mixtures with one another and/or with other liquid crystals components. They are especially suitable for the manufacture of chiral smectic mixtures, primarily for mixtures with a smectic C phase. Compounds having ferroelectric properties, which may be suitable as components of mixtures, are, for example, the optically active 3- and 4-ring cyclohexylene derivatives which carry an axial methyl group, which are disclosed in Patent Abstracts of Japan C Section, volume 9, No. 7, page 148 C 262, as well as the optically inactive 4-ring compounds which are disclosed in Patent Abstracts of Japan, C Section, volumes 7, No. 252, page 146 C 193. However, the compounds in accordance with the invention can basically also be used as additives for nematic mixtures (in the case of optically inactive compounds) or cholesteric mixtures. The mixtures in accordance with the invention contain at least 2 components, of which at least one component is a compound of formula I. The amount of compounds of formula I in the mixtures in accordance with the invention can vary in a wide range depending of the purpose of use and, for example, can amount to about 1% to 100%. In general, the mixtures in accordance with the invention with a nematic, cholesteric or chiral smectic phase contain about 1-80 wt.%, preferably about 5-50 wt.%, of compounds of formula I. An especially preferred range for chiral smectic mixtures amounts to about 10-70 wt.%, particularly about 30-50 wt.%. When optically active compounds of formula I are used as additives in mixtures for twisted nematic cell applications the amount thereof can also be smaller and can, for example, amount to about 0.2-10 wt.% depending of the pitch and the cell thickness.

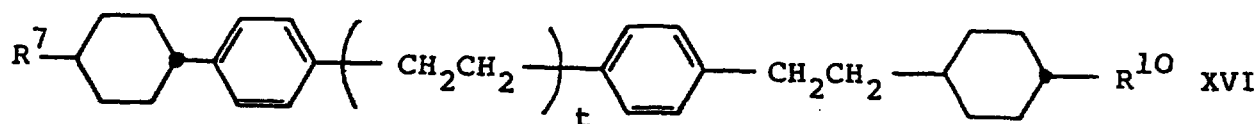
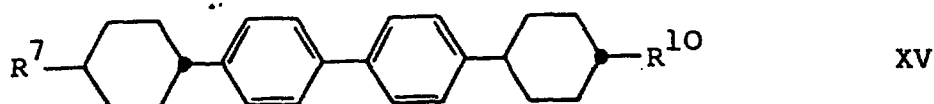
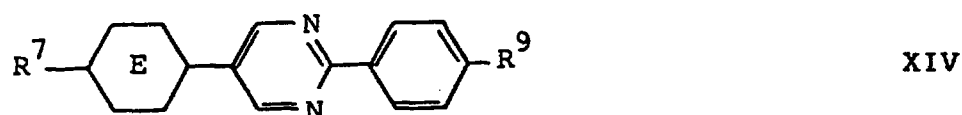
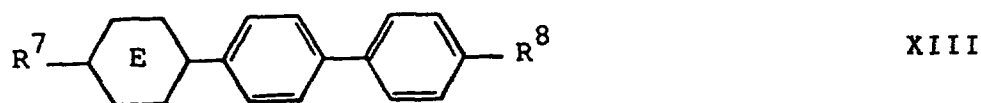
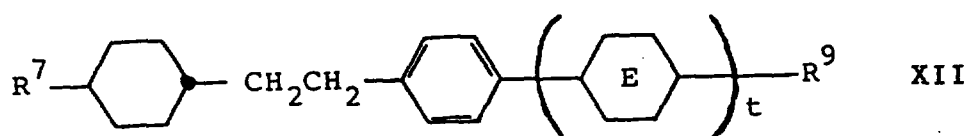
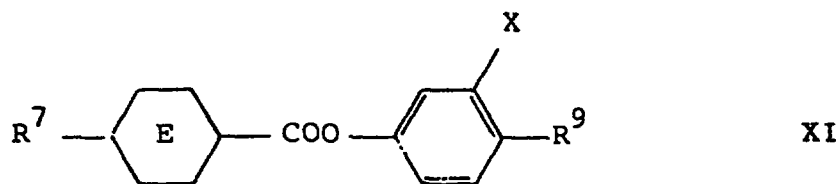
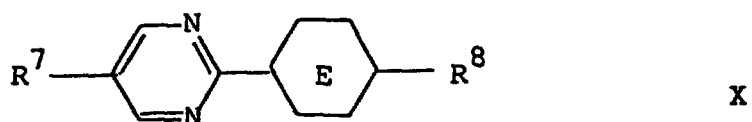
The liquid crystal mixtures in accordance with the invention with nematic or cholesteric properties and the mixtures for twisted nematic cell indicators preferably contain, in addition to one or more compounds of formula I, one or more of the compounds of the following general formulae



VIII



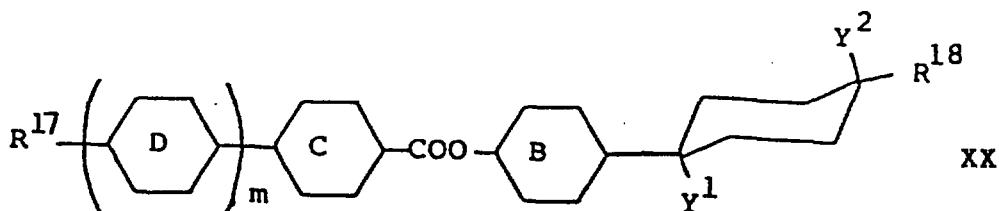
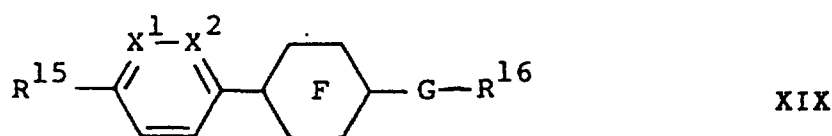
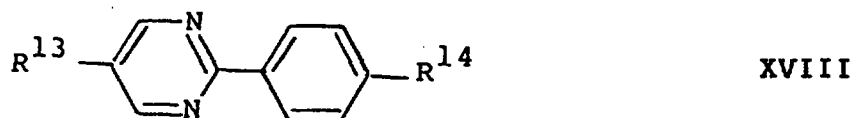
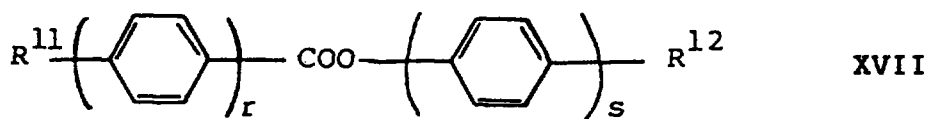
IX



wherein R^7 , R^8 , R^9 and R^{10} each independently signify alkyl, alkoxy, alkenyl or alkenyloxy with a maximum of 7 carbon atoms in each case or R^8 on a benzene ring also signifies cyano or $-\text{NCS}$ or R^9 on a benzene ring also signifies cyano; ring E represents trans-1,4-cyclohexylene or 1,4-phenylene; X denotes hydrogen or fluorine; and t stands for the number 0 or 1.

The liquid crystal mixtures in accordance with the invention with chiral smectic phases can contain, in

addition to one or more compounds of formula I, usual components for chiral smectic mixtures. They preferably contain one or more compounds of the general formulae



wherein R^{11} and R^{12} signify alkyl, alkoxy, alkanoyl, alkanoyloxy, alkoxy carbonyl or alkoxy carbonyloxy with up to 18 carbon atoms; r and s denote the numbers 1 or 2; R^{13} and R^{14} represent alkyl or alkoxy with 1-18 carbon atoms; X^1 stands for CH and X^2 stands for N or X^1 stands for N and X^2 stands for CH; G signifies a single covalent bond, trans-1,4-cyclohexylene, cis-4-cyano-trans-1,4-cyclohexylene or 1,4-phenylene optionally substituted with halogen or methyl; ring F represents trans-1,4-cyclohexylene, 1,4-phenylene optionally substituted with halogen or methyl or, when G signifies a single covalent bond, also cis-4-cyano-trans-1,4-cyclohexylene; R^{15} and R^{16} each denote an optionally halogen-substituted alkyl or alkenyl group in which optionally one CH_2 group or two non-adjacent CH_2 groups is/are replaced by -O-, -COO- and/or -OOC-; m , Y^1 , Y^2 and rings B, C and D have the significances given in formula I; and R^{17} and R^{18} represent $\text{C}_1\text{-C}_{18}$ -alkyl in which optionally one CH_2 group or two non-adjacent CH_2 groups is/are replaced by oxygen.

The chiral smectic mixtures in accordance with the invention can basically consist of optically inactive compounds. However, they preferably contain one or more optically active compounds in order to produce a spontaneous polarization, i.e. they preferably contain at least one optically active compound of formula I with a chiral carbon atom in R^1 and/or R^2 and/or at least one optically active additive. Preferred chiral smectic mixtures with at least 2 components are accordingly those in which at least one component is an optically active compound of formula I and a second component can be optically active or optically inactive, as well as those in which at least one component is an optically inactive, preferably achiral, compound of formula I and a second component is optically active. The second component is preferably a further compound of formula I or a compound of formulae XVII-XX.

The optically active compounds of formula XX which are laterally-substituted on B, C and/or D and/or which are axially-substituted on the cyclohexane ring are novel. They can be manufactured in an analogous manner to the compounds of formula I.

The mixtures in accordance with the invention can also contain dichroic colouring substances, for example azo, azoxy or anthraquinone colouring substances. The amount of colouring substance is determined by the solubility and the desired colour, extinction and the like and generally amounts to a maximum of about 10 wt.% in the total mixture.

The manufacture of the mixtures in accordance with the invention and of the electro-optical devices can be effected in a manner known per se.

The manufacture of the compounds in accordance with the invention, of the novel compounds of formula XX and of the starting materials as well as mixtures in accordance with the invention are illustrated in more detail by the following Examples. The phases are denoted by the following symbols: C stands for crystalline, S stands for smectic, S_A stands for smectic A, S_B stands for smectic B, S_C stands for smectic C, S^*_C stands for chiral smectic C, Ch stands for cholesteric, N stands for nematic and I stands for isotropic.

Example 1

A solution of 2.6 g of boron tribromide in 50 ml of absolute dichloromethane was treated dropwise at 0°C with a solution of 2.0 g of 2-(trans-4-pentylcyclohexyl)-1-(4-methoxyphenyl)ethane in 50 ml of absolute dichloromethane. The mixture was stirred for 1 hour and then

poured into ice-water. The organic phase was separated and the aqueous phase was back-extracted three times with 50 ml of dichloromethane each time. The combined organic phases were washed with 50 ml of 2N sodium carbonate solution and several times with water, dried over magnesium sulphate and concentrated. Recrystallization of the resulting crude product from hexane at 0°C gave 1.8 g of 4-[2-(trans-4-pentylcyclohexyl)ethyl]phenol of m.p. 102°C.

Example 2

A mixture of 5.0 g of (trans-4-heptylcyclohexyl)methyl bromide, 10.0 g of hydroquinone, 10.0 g of anhydrous potassium carbonate and 100 ml of absolute dimethylformamide was heated under reflux overnight. The cooled reaction mixture was subsequently poured into ice-water and extracted three times with 50 ml of diethyl ether each time. The organic phases were washed with 500 ml of water, dried over magnesium sulphate and concentrated. Chromatography of the residue on silica gel with toluene/ethyl acetate (vol. 4:1) gave 1.8 g of 4-[(trans-4-heptylcyclohexyl)methoxy]phenol; m.p. 107-108°C.

Example 3

A finely powdered mixture was prepared from 2.2 g of 2-(trans-4-pentylcyclohexyl)-1-(2,3-dicyano-4-butyloxyphenyl)ethane, 1.4 g of anhydrous aluminium chloride and 0.3 g of sodium chloride and this mixture was heated to 150°C on an oil-bath for 40 minutes under anhydrous conditions. The cooled mixture was treated with 250 ml of water and extracted three times with 50 ml of dichloromethane each time. The combined organic phases were washed with 250 ml of water, dried over magnesium sulphate and concentrated. Chromatography of the residue on silica gel with toluene/ethyl acetate (vol. 4:1) gave 0.6 g of 2,3-dicyano-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenol; m.p. 100-102°C.

Example 4

A solution of 2.7 g of 4-[2-(trans-4-pentylcyclohexyl)ethyl]phenol in absolute dichloromethane was treated dropwise at 0°C with a solution of 1.6 g of bromine in 20 ml of absolute dichloromethane. The mixture was stirred for 1 hour and then poured into ice-water. The organic phase was separated and the aqueous phase was back-extracted three times with 50 ml of dichloromethane each time. The combined organic phases were washed with 50 ml of 2N sodium carbonate solution and several times with water, dried over magnesium sulphate and concentrated. Recrystallization of the resulting crude product from

hexane at 0°C gave 3.4 g of 2-bromo-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenol.

Example 5

A mixture of 0.25 g of (S)-4-(6-methyloctyloxy)benzoic acid, 5 ml of thionyl chloride (excess) and 20 ml of toluene was heated to boiling for 1 hour. The solvent and excess thionyl chloride were subsequently distilled off and the residue was taken up twice in 25 ml of toluene each time and concentrated each time.

The crude (S)-4-(6-methyloctyloxy)benzoyl chloride obtained was dissolved in 20 ml of toluene and then added dropwise to a solution of 0.26 g of 4-[2-(trans-4-pentylcyclohexyl)ethyl]phenol in 2 ml of pyridine. The reaction mixture was stirred at room temperature overnight, then poured into ice-water and extracted with diethyl ether. The extract was washed four times with 25 ml of 3N hydrochloric acid each time, then washed with 25 ml of 2N sodium carbonate solution and several times with water, dried over magnesium sulphate and concentrated. Chromatography of the residual oil on silica gel with toluene gave 0.2 g of (S)-4-(6-methyloctyloxy)benzoic acid 4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester. The product was recrystallized several times from ethanol until the phase transition temperatures were constant. M.p. (C-S) 58°, transition S-S*_C 58.5°C, transition S*_C-Ch 93°C, cl.p. (Ch-I) 140°C.

The following compounds can be manufactured in an analogous manner: ..

(S)-4-(2-Methylbutyloxy)benzoic acid 4-[2-(trans-4-propylcyclohexyl)ethyl]phenyl ester, m.p. (C-Ch) 81°C, cl.p. (Ch-I) 146°C;

(S)-4-(3-methylpentyloxy)benzoic acid 4-[2-(trans-4-propylcyclohexyl)ethyl]phenyl ester,

(S)-4-(4-methylhexyloxy)benzoic acid 4-[2-(trans-4-propylcyclohexyl)ethyl]phenyl ester m.p. (C-Ch) 82°C, cl.p. (Ch-I) 149°C;

(S)-4-(5-methylheptyloxy)benzoic acid 4-[2-(trans-4-propylcyclohexyl)ethyl]phenyl ester,

(S)-4-(6-methyloctyloxy)benzoic acid 4-[2-(trans-4-propylcyclohexyl)ethyl]phenyl ester, m.p. (C-S*_C) 73°C, transition S-S*_C 60.5°C, transition S*_C-Ch 77°C, cl.p. (Ch-I) 144°C;

(S)-4-(2-methylbutyloxy)benzoic acid 4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester, m.p. (C-Ch) 74°C, cl.p. (Ch-I) 130°C;

(S)-4-(3-methylpentyloxy)benzoic acid 4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,

(S)-4-(4-methylhexyloxy)benzoic acid 4-[2-(trans-4-

-pentylcyclohexyl)ethyl]phenyl ester, m.p. (C-Ch) 66°C, cl.p. (Ch-I) 137°C;
(S)-4-(5-methylheptyloxy)benzoic acid 4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,
(S)-4-(2-methylbutyloxy)benzoic acid 4-[2-(trans-4-heptylcyclohexyl)ethyl]phenyl ester, m.p. (C-Ch) 66°C, cl.p. (Ch-I) 131°C;
(S)-4-(4-methylhexyloxy)benzoic acid 4-[2-(trans-4-heptylcyclohexyl)ethyl]phenyl ester, m.p. (C-S) -6°C, transition S-S 61.5°C, transition S-S*_C 69.5°C, transition S*_C-Ch 75°C, cl.p. (Ch-I) 135.5°C;
(S)-4-(6-methyloctyloxy)benzoic acid 4-[2-(trans-4-heptylcyclohexyl)ethyl]phenyl ester, m.p. (C-S) 42°C, transition S-S 44°C, transition S-S*_C 68.5°C, transition S*_C-Ch 102.5°C, cl.p. (Ch-I) 135.5°C;
(S)-4'-(2-methylbutyl)-4-biphenylcarboxylic acid 4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester, m.p. (C-S_B) 96°C, transition S_B-S*_C 102°C, transition S*_C-Ch 104°C, cl.p. (Ch-I) 238.5°C;
(S)-4'-(4-methylhexyl)-4-biphenylcarboxylic acid 4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,
(S)-4'-(2-methylbutyloxy)-4-biphenylcarboxylic acid 4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester, m.p. (C-S*_C) 128°C, transition S*_C-Ch 130°C, cl.p. (Ch-I) 247°C;
(S)-4'-(4-methylhexyloxy)-4-biphenylcarboxylic acid 4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,
(S)-4-(2-methylbutyloxy)benzoic acid 4-[(trans-4-propylcyclohexyl)methoxy]phenyl ester, m.p. (C-Ch) 91.5°C, cl.p. (Ch-I) 143.5°C;
(S)-4-(4-methylhexyloxy)benzoic acid 4-[(trans-4-propylcyclohexyl)methoxy]phenyl ester, m.p. (C-Ch) 74°C, cl.p. (Ch-I) 148°C;
(S)-4-(6-methyloctyloxy)benzoic acid 4-[(trans-4-propylcyclohexyl)methoxy]phenyl ester, m.p. (C-S*_C) 83°C, transition S-S*_C 68°C, transition S*_C-Ch 94°C, cl.p. (Ch-I) 144.5°C;
(S)-4-(2-methylbutyloxy)benzoic acid 4-[(trans-4-pentylcyclohexyl)methoxy]phenyl ester, m.p. (C-Ch) 87.5°C, cl.p. (Ch-I) 140.5°C;
(S)-4-(4-methylhexyloxy)benzoic acid 4-[(trans-4-pentylcyclohexyl)methoxy]phenyl ester, m.p. (C-Ch) 85.5°C, transition S-S*_C 44°C, transition S*_C-Ch 85°C, cl.p. (Ch-I) 147.5°C;
(S)-4-(6-methyloctyloxy)benzoic acid 4-[(trans-4-pentylcyclohexyl)methoxy]phenyl ester, m.p. (C-S*_C) 72.5°C, transition S-S*_C 65°C, transition S*_C-Ch 107.5°C, cl.p. (Ch-I) 145.5°C;
(S)-4-(2-methylbutyloxy)benzoic acid 4-[(trans-4-heptylcyclohexyl)methoxy]phenyl ester, m.p. (C-Ch) 66.5°C, transition S-S*_C 63°C, transition S*_C-Ch 65°C, cl.p. (Ch-I) 135.5°C;
(S)-4-(3-methylpentyloxy)benzoic acid 4-[(trans-4-

-heptylcyclohexyl)methoxy]phenyl ester,
(S)-4-(4-methylhexyloxy)benzoic acid 4-[(trans-4-heptylcyclohexyl)methoxy]phenyl ester, m.p. (C-S*) 77°C, transition S*-Ch 92.5°C, cl.p. (Ch-I) 142°C;
(S)-4-(5-methylheptyloxy)benzoic acid 4-[(trans-4-heptylcyclohexyl)methoxy]phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-[(trans-4-heptylcyclohexyl)methoxy]phenyl ester, m.p. (C-S) 72°C, transition S-S* 74°C, transition S*-Ch 114.5°C, cl.p. (Ch-I) 142°C;
(S)-4-(4-methylhexyloxy)benzoic acid 2,3-dicyano-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 2,3-dicyano-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester, m.p. (C-I) 123°C, transition S*-Ch 113°C, cl.p. (Ch-I) 116°C;
(S)-4-(6-methyloctyloxy)benzoic acid 2-bromo-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester m.p. (C-Ch) 57°C, cl.p. (Ch-I) 97°C;
(S)-4-(2-methylbutoxy)benzoic acid 4-[2-(trans-4-[2-propenyl]cyclohexyl)ethyl]phenyl ester,
(S)-4-(4-methylhexyloxy)benzoic acid 4-[2-(trans-4-[2-propenyl]cyclohexyl)ethyl]phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-[2-(trans-4-[2-propenyl]cyclohexyl)ethyl]phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-[2-(trans-4-[1E-pentenyl]cyclohexyl)ethyl]phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-[2-(trans-4-[2Z-pentenyl]cyclohexyl)ethyl]phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-[2-(trans-4-[3E-pentenyl]cyclohexyl)ethyl]phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-[2-(trans-4-[4-pentenyl]cyclohexyl)ethyl]phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-[2-(trans-4-[1E-heptenyl]cyclohexyl)ethyl]phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-[2-(trans-4-[2Z-heptenyl]cyclohexyl)ethyl]phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-[2-(trans-4-[3E-heptenyl]cyclohexyl)ethyl]phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-[2-(trans-4-[4Z-heptenyl]cyclohexyl)ethyl]phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-[2-(trans-4-[5E-heptenyl]cyclohexyl)ethyl]phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-[2-(trans-4-[6-heptenyl]cyclohexyl)ethyl]phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-[2-(trans-4-[1E-pentenyl]cyclohexyl)methoxy]phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-[2-(trans-4-[2Z-pentenyl]cyclohexyl)methoxy]phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-[2-(trans-4-[3E-pentenyl]cyclohexyl)methoxy]phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-[2-(trans-4-[4-pentenyl]cyclohexyl)methoxy]phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-(trans-4-[1E-

-pentenyl]cyclohexyl)phenyl ester,
 (S)-4-(6-methyloctyloxy)benzoic acid 4-(trans-4-[2Z-
-pentenyl]cyclohexyl)phenyl ester,
 (S)-4-(6-methyloctyloxy)benzoic acid 4-(trans-4-[3E-
-pentenyl]cyclohexyl)phenyl ester,
 (S)-4-(6-methyloctyloxy)benzoic acid 4-(trans-4-[4-
-pentenyl]cyclohexyl)phenyl ester,
 4-hexyloxybenzoic acid 4-[2-(trans-4-propylcyclo-
hexyl)ethyl]phenyl ester,
 4-heptyloxybenzoic acid 4-[2-(trans-4-propylcyclo-
hexyl)ethyl]phenyl ester,
 4-octyloxybenzoic acid 4-[2-(trans-4-propylcyclo-
hexyl)ethyl]phenyl ester,
 4-nonyloxybenzoic acid 4-[2-(trans-4-propylcyclo-
hexyl)ethyl]phenyl ester,
 4-decyloxybenzoic acid 4-[2-(trans-4-propylcyclo-
hexyl)ethyl]phenyl ester,
 4-undecyloxybenzoic acid 4-[2-(trans-4-propylcyclo-
hexyl)ethyl]phenyl ester,
 4-dodecyloxybenzoic acid 4-[2-(trans-4-propylcyclo-
hexyl)ethyl]phenyl ester,
 4-hexyloxybenzoic acid 4-[2-(trans-4-pentylcyclo-
hexyl)ethyl]phenyl ester,
 4-heptyloxybenzoic acid 4-[2-(trans-4-pentylcyclo-
hexyl)ethyl]phenyl ester, m.p. (C-S_C) 67°C, transition
S-S_C 51°C, transition S_C-N 67.5°C, cl.p. (N-I) 160°C;
 4-octyloxybenzoic acid 4-[2-(trans-4-pentylcyclo-
hexyl)ethyl]phenyl ester, m.p. (C-S_C) 68°C, transition
S-S_C 57°C, transition S_C-N 86.5°C, cl.p. (N-I) 157.5°C;
 4-nonyloxybenzoic acid 4-[2-(trans-4-pentylcyclo-
hexyl)ethyl]phenyl ester, m.p. (C-S_C) 61°C, transition
S-S_C 57°C, transition S_C-N 101°C, cl.p. (N-I) 153.5°C;
 4-decyloxybenzoic acid 4-[2-(trans-4-pentylcyclo-
hexyl)ethyl]phenyl ester, m.p. (C-S_C) 60°C, transition
S-S_C 57.5°C, transition S_C-N 106.5°C, cl.p. (N-I)
152.5°C;
 4-undecyloxybenzoic acid 4-[2-(trans-4-pentylcyclo-
hexyl)ethyl]phenyl ester,
 4-dodecyloxybenzoic acid 4-[2-(trans-4-pentylcyclo-
hexyl)ethyl]phenyl ester, m.p. (C-S) 58°C, transition
S-S_C 78°C, transition S_C-S_A 118°C, transition S_A-N
131.5°C, cl.p. (N-I) 147°C;
 4-heptyloxybenzoic acid 4-[2-(trans-4-heptylcyclo-
hexyl)ethyl]phenyl ester,
 4-octyloxybenzoic acid 4-[2-(trans-4-heptylcyclo-
hexyl)ethyl]phenyl ester,
 4-nonyloxybenzoic acid 4-[2-(trans-4-heptylcyclo-
hexyl)ethyl]phenyl ester,
 4-decyloxybenzoic acid 4-[2-(trans-4-heptylcyclo-
hexyl)ethyl]phenyl ester,
 4-undecyloxybenzoic acid 4-[2-(trans-4-heptylcyclo-
hexyl)ethyl]phenyl ester,
 4-dodecyloxybenzoic acid 4-[2-(trans-4-heptylcyclo-

hexyl)ethyl]phenyl ester,

4-(5-hexenyloxy)benzoic acid 4-[2-(trans-4-propyl-cyclohexyl)ethyl]phenyl ester,

4-(6-heptenyloxy)benzoic acid 4-[2-(trans-4-propyl-cyclohexyl)ethyl]phenyl ester,

4-(7-octenyloxy)benzoic acid 4-[2-(trans-4-propyl-cyclohexyl)ethyl]phenyl ester,

4-(8-nonyloxy)benzoic acid 4-[2-(trans-4-propyl-cyclohexyl)ethyl]phenyl ester,

4-(9-decenyloxy)benzoic acid 4-[2-(trans-4-propyl-cyclohexyl)ethyl]phenyl ester,

4-(10-undecenyloxy)benzoic acid 4-[2-(trans-4-propyl-cyclohexyl)ethyl]phenyl ester,

4-(11-dodecenyloxy)benzoic acid 4-[2-(trans-4-propyl-cyclohexyl)ethyl]phenyl ester,

4-(5-hexenyloxy)benzoic acid 4-[2-(trans-4-pentyl-cyclohexyl)ethyl]phenyl ester,

4-(6-heptenyloxy)benzoic acid 4-[2-(trans-4-pentyl-cyclohexyl)ethyl]phenyl ester,

4-(7-octenyloxy)benzoic acid 4-[2-(trans-4-pentyl-cyclohexyl)ethyl]phenyl ester, m.p. (C-S_C) 62°C, transition S-S_C 43.5°C, transition S_C-N 73°C, cl.p. (N-I) 152.5°C;

4-(8-nonyloxy)benzoic acid 4-[2-(trans-4-pentyl-cyclohexyl)ethyl]phenyl ester, m.p. (C-S_C) 55°C, transition S-S_C 44°C, transition S_C-N 91.5°C, cl.p. (N-I) 153°C;

4-(9-decenyloxy)benzoic acid 4-[2-(trans-4-pentyl-cyclohexyl)ethyl]phenyl ester, m.p. (C-S_C) 69°C, transition S-S_C 57°C, transition S_C-S_A 104°C, transition S_A-N 110°C, cl.p. (N-I) 148°C;

4-(10-undecenyloxy)benzoic acid 4-[2-(trans-4-pentyl-cyclohexyl)ethyl]phenyl ester, m.p. (C-S) 51°C, transition S-S_C 69°C, transition S_C-S_A 100.5°C, transition S_A-N 124°C, cl.p. (N-I) 147.5°C;

4-(11-dodecenyloxy)benzoic acid 4-[2-(trans-4-pentyl-cyclohexyl)ethyl]phenyl ester,

4-(5-hexenyloxy)benzoic acid 4-[2-(trans-4-heptyl-cyclohexyl)ethyl]phenyl ester,

4-(6-heptenyloxy)benzoic acid 4-[2-(trans-4-heptyl-cyclohexyl)ethyl]phenyl ester,

4-(7-octenyloxy)benzoic acid 4-[2-(trans-4-heptyl-cyclohexyl)ethyl]phenyl ester,

4-(8-nonyloxy)benzoic acid 4-[2-(trans-4-heptyl-cyclohexyl)ethyl]phenyl ester,

4-(9-decenyloxy)benzoic acid 4-[2-(trans-4-heptyl-cyclohexyl)ethyl]phenyl ester,

4-(10-undecenyloxy)benzoic acid 4-[2-(trans-4-heptyl-cyclohexyl)ethyl]phenyl ester,

4-(11-dodecenyloxy)benzoic acid 4-[2-(trans-4-heptyl-cyclohexyl)ethyl]phenyl ester,

4-hexyloxybenzoic acid 2-cyano-4-[2-(trans-4-pentyl-cyclohexyl)ethyl]phenyl ester,

4-heptyloxybenzoic acid 2-cyano-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,

4-octyloxybenzoic acid 2-cyano-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,

4-nonyloxybenzoic acid 2-cyano-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,

4-decyloxybenzoic acid 2-cyano-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,

4-undecyloxybenzoic acid 2-cyano-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,

4-dodecyloxybenzoic acid 2-cyano-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester, m.p. (C-S_C) 62°C, transition S_C-N 66°C, cl.p. (N-I) 120.5°C;

4-hexyloxybenzoic acid 2-cyano-4-[2-(trans-4-heptylcyclohexyl)ethyl]phenyl ester,

4-heptyloxybenzoic acid 2-cyano-4-[2-(trans-4-heptylcyclohexyl)ethyl]phenyl ester,

4-octyloxybenzoic acid 2-cyano-4-[2-(trans-4-heptylcyclohexyl)ethyl]phenyl ester,

4-nonyloxybenzoic acid 2-cyano-4-[2-(trans-4-heptylcyclohexyl)ethyl]phenyl ester,

4-decyloxybenzoic acid 2-cyano-4-[2-(trans-4-heptylcyclohexyl)ethyl]phenyl ester,

4-undecyloxybenzoic acid 2-cyano-4-[2-(trans-4-heptylcyclohexyl)ethyl]phenyl ester,

4-dodecyloxybenzoic acid 2-cyano-4-[2-(trans-4-heptylcyclohexyl)ethyl]phenyl ester,

4-octyloxybenzoic acid 4-[(trans-4-pentylcyclohexyl)-methoxy]phenyl ester,

4-octyloxybenzoic acid 4-[(trans-4-(1E-pentenyl)-cyclohexyl)methoxy]phenyl ester,

4-octyloxybenzoic acid 4-[(trans-4-(4-pentenyl)cyclohexyl)methoxy]phenyl ester,

4-(7-octenyloxy)benzoic acid 4-[(trans-4-pentylcyclohexyl)methoxy]phenyl ester,

4-(8-nonenyloxy)benzoic acid 4-[(trans-4-pentylcyclohexyl)methoxy]phenyl ester,

4-(9-decenyloxy)benzoic acid 4-[(trans-4-pentylcyclohexyl)methoxy]phenyl ester,

(S)-4-(6-methyloctyloxy)benzoic acid 4-[trans-4-(1E-pentenyl)cyclohexyl]phenyl ester,

(S)-4-(6-methyloctyloxy)benzoic acid 4-[trans-4-(4-pentenyl)cyclohexyl]phenyl ester,

4-octyloxybenzoic acid 4-[trans-4-(1E-pentenyl)cyclohexyl]phenyl ester,

4-octyloxybenzoic acid 4-[trans-4-(4E-pentenyl)cyclohexyl]phenyl ester,

4-(7-octenyloxy)benzoic acid 4-[trans-4-pentylcyclohexyl]phenyl ester,

4-(8-nonenyloxy)benzoic acid 4-[trans-4-pentylcyclohexyl]phenyl ester,

4-(9-decenyloxy)benzoic acid 4-[trans-4-pentylcyclohexyl]phenyl ester,

4-(5-hexenyloxy)benzoic acid 2-cyano-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,

4-(6-heptenyloxy)benzoic acid 2-cyano-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,

4-(7-octenyloxy)benzoic acid 2-cyano-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,

4-(8-nonyloxy)benzoic acid 2-cyano-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,

4-(9-decenyloxy)benzoic acid 2-cyano-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,

4-(10-undecenyloxy)benzoic acid 2-cyano-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,

4-(11-dodecenyloxy)benzoic acid 2-cyano-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,

Example 6

A mixture of 2 g of (S)-4-(6-methyloctyloxy)benzoic acid 2-bromo-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester, 0.5 g of anhydrous copper(I) cyanide and 50 ml of absolute 1-methyl-2-pyrrolidone was heated to 185°C on a oil-bath for 2 hours. The cooled mixture was subsequently treated with 50 ml of 15% ammonia solution and stirred for 30 minutes. Thereafter, the reaction mixture was extracted three times with 50 ml of diethyl ether each time. The combined organic phases were washed twice with 250 ml of water each time, dried over magnesium sulphate and concentrated. Chromatography of the residue on silica gel with toluene/hexane (vol. 1:1) gave 0.1 g of (S)-4-(6-methyloctyloxy)benzoic acid 2-cyano-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester; m.p. (C-Ch) 80°C, transition S*_C-Ch 50°C (monotropic), cl.p. (Ch-I) 120°C.

Example 7

2.5 g of (S)-4-(6-methyloctyloxy)benzoic acid were heated to 80°C for 1 hour with 25 ml of thionyl chloride in toluene. The solution obtained was evaporated under reduced pressure, the residue was treated with 20 ml of absolute toluene and the solution was again evaporated under reduced pressure. The acid chloride obtained was taken up in 50 ml of absolute toluene and treated with a solution of 1.1 g of hydroquinone in 10 ml of absolute pyridine. The reaction mixture was heated to reflux for 1 hour, then cooled, treated with dilute hydrochloric acid and extracted three times with 50 ml of dichloromethane each time. The combined organic phases were washed twice with 250 ml of water each time, dried over magnesium sulphate and concentrated. The crude product obtained was purified by column chromatography on silica gel with toluene/ethyl acetate (vol. 4:1). Recrystallization of the resulting product from ethanol gave 2.0 g of (S)-4-(6-methyloctyloxy)benzoic acid 4-hydroxyphenyl ester of m.p. 75°C.

Example 8

2.0 g of (S)-4-(6-methyloctyloxy)benzoic acid 4-hydroxyphenyl ester, 1.1 g of trans-4-pentylcyclohexanecarboxylic acid and 0.1 g of 4-(dimethylamino)pyridine were dissolved in 50 ml of dichloromethane and the solution was treated portionwise in 10 minutes while stirring with 1.4 g of N,N'-dicyclohexylcarbodiimide. The mixture was stirred at room temperature overnight and then filtered. The filtrate was diluted with dichloromethane, washed twice with 50 ml of saturated sodium bicarbonate solution each time and then washed with water, dried over sodium sulphate and concentrated. The crude product obtained was purified by chromatography on silica gel with toluene. The resulting (S)-4-(6-methyloctyloxy)benzoic acid 4-(trans-4-pentylcyclohexylcarbonyloxy)phenyl ester was recrystallized from methanol and ethanol; m.p. (C-S) 66°C, transition S-S*_C 80°C, transition S*_C-Ch 112°C, cl.p. (Ch-I) 186°C.

The following compounds can be manufactured in an analogous manner:

(S)-4-(2-Methylbutyloxy)benzoic acid 4-(trans-4-pentylcyclohexylcarbonyloxy)phenyl ester,

(S)-4-(4-methylhexyloxy)benzoic acid 4-(trans-4-pentylcyclohexylcarbonyloxy)phenyl ester,

(S)-4-(2-methylbutyl)benzoic acid 4-(trans-4-pentylcyclohexylcarbonyloxy)phenyl ester,

(S)-4-(4-methylhexyl)benzoic acid 4-(trans-4-pentylcyclohexylcarbonyloxy)phenyl ester,

(S)-4-(6-methyloctyl)benzoic acid 4-(trans-4-pentylcyclohexylcarbonyloxy)phenyl ester,

(S)-4-(6-methyloctyloxy)benzoic acid 4-[trans-4-(1E-pentenyl)cyclohexylcarbonyloxy]phenyl ester,

(S)-4-(6-methyloctyloxy)benzoic acid 4-[trans-4-(4-pentenyl)cyclohexylcarbonyloxy]phenyl ester,

(S)-4-(6-methyloctyloxy)benzoic acid 4-[trans-4-(5-hexenyl)cyclohexylcarbonyloxy]phenyl ester,

(S)-4-(6-methyloctyloxy)benzoic acid 4-[trans-4-(6-heptenyl)cyclohexylcarbonyloxy]phenyl ester,

4-(5-hexenyloxy)benzoic acid 4-(trans-4-pentenylcyclohexylcarbonyloxy)phenyl ester,

4-(6-heptenyloxy)benzoic acid 4-(trans-4-pentenylcyclohexylcarbonyloxy)phenyl ester,

4-(7-octenyloxy)benzoic acid 4-(trans-4-pentenylcyclohexylcarbonyloxy)phenyl ester,

4-(8-nonyloxy)benzoic acid 4-(trans-4-pentenylcyclohexylcarbonyloxy)phenyl ester,

4-(9-decenyloxy)benzoic acid 4-(trans-4-pentenylcyclohexylcarbonyloxy)phenyl ester,

4-octyloxybenzoic acid 4-[trans-4-(1E-pentenyl)cyclohexylcarbonyloxy]phenyl ester,

4-octyloxybenzoic acid 4-[trans-4-(4-pentenyl)cyclohexylcarbonyloxy]phenyl ester,
4-octyloxybenzoic acid 4-[trans-4-(5-hexenyl)cyclohexylcarbonyloxy]phenyl ester,
4-octyloxybenzoic acid 4-[trans-4-(6-heptenyl)cyclohexylcarbonyloxy]phenyl ester,
(S)-4-(4-methylhexyloxy)benzoic acid 4-(trans-4-pentylcyclohexyloxy)carbonyl)phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-(trans-4-pentylcyclohexyloxy)carbonyl)phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-[trans-4-(1E-pentenyl)cyclohexyloxy)carbonyl)phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-[trans-4-(4-pentenyl)cyclohexyloxy)carbonyl)phenyl ester,
(S)-4-(6-methyloctyloxy)benzoic acid 4-[trans-4-(5-hexenyl)cyclohexyloxy)carbonyl)phenyl ester,
4-(7-octenyloxy)benzoic acid 4-(trans-4-pentylcyclohexyloxy)carbonyl)phenyl ester,
4-(8-nonyloxy)benzoic acid 4-(trans-4-pentylcyclohexyloxy)carbonyl)phenyl ester,
4-(9-decenyloxy)benzoic acid 4-(trans-4-pentylcyclohexyloxy)carbonyl)phenyl ester,
4-octyloxybenzoic acid 4-[trans-4-(1E-pentenyl)cyclohexyloxy)carbonyl)phenyl ester,
4-octyloxybenzoic acid 4-[trans-4-(4-pentenyl)cyclohexyloxy)carbonyl)phenyl ester,
4-octyloxybenzoic acid 4-[trans-4-(5-hexenyl)cyclohexyloxy)carbonyl)phenyl ester.

Mixture Example A

27.2 wt.% of 4-dodecyloxybenzoic acid 4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,
23.6 wt.% of 4-(10-undecenyloxy)benzoic acid 4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,
17.0 wt.% of 5-decyl-2-(4-hexyloxyphenyl)pyrimidine,
17.0 wt.% of 5-decyl-2-(4-octyloxyphenyl)pyrimidine,
15.2 wt.% of 5-decyl-2-(4-decyloxyphenyl)pyrimidine,
cl.p. (N-I) 100°C, transition N-S_A 80°C, transition S_A-S_C 69°C. The S_C phase did not crystallize upon cooling to -2°C.

Mixture Example B

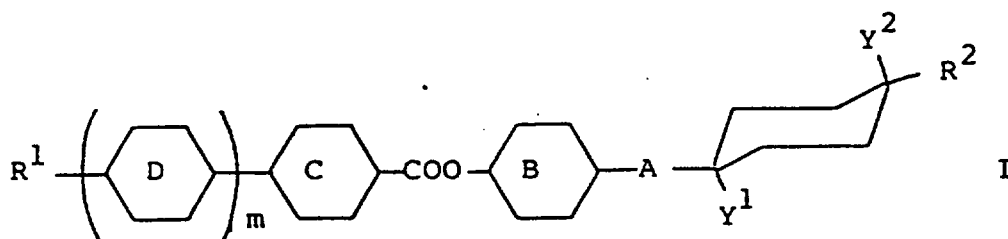
55 wt.% of (S)-4-(6-methyloctyloxy)benzoic acid 4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester,
45 wt.% of (S)-4-decyloxybenzoic acid 4-(2-methylbutyloxy)phenyl ester.
cl.p. (Ch-I) 96.5°C, transition Ch-S*_C 64°C, transition S*_C-S 27°C.

Mixture Example C

50 wt.% of 4-nonyloxybenzoic acid 4-[2-(trans-4-pentyl-cyclohexyl)ethyl]phenyl ester,
 50 wt.% of 4-dodecyloxybenzoic acid 2-cyano-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester.
 cl.p. (N-I) 134°C, transition N-S_C 68°C, m.p. (C-S_C) 46°C.

Claims

1. Compounds of the general formula



wherein m stands for the number 0 or 1; A signifies a single covalent bond, -CH₂-CH₂-, -OCH₂-, -COO- or -OOC-; rings B, C and D denote 1,4-phenylene optionally substituted with cyano, halogen or lower alkyl; Y¹ and Y² signify hydrogen or one of the substituents Y¹ and Y² also signifies cyano; and R¹ and R² each individually represent optionally halogen-substituted C₁-C₁₈-alkyl or optionally halogen-substituted C₂-C₁₈-alkenyl in which optionally one CH₂ group or two non-adjacent CH₂ groups is/are replaced by oxygen; with the proviso that at least one of the residues R¹ and R² has a chiral carbon atom and/or a C-C double bond when A stands for -COO- and that at least one of the residues R¹ and R² has a C-C double bond when A stands for a single covalent bond.

2. Compounds according to claim 1, characterized in that R¹ and R² each independently represent C₁-C₁₈-alkyl or C₂-C₁₈-alkenyl in which optionally one CH₂ group or two non-adjacent CH₂ groups is/are replaced by oxygen.

3. Optically active compounds according to claim 1 or 2, characterized in that at least one of the residues R¹ and R² has a chiral carbon atom.

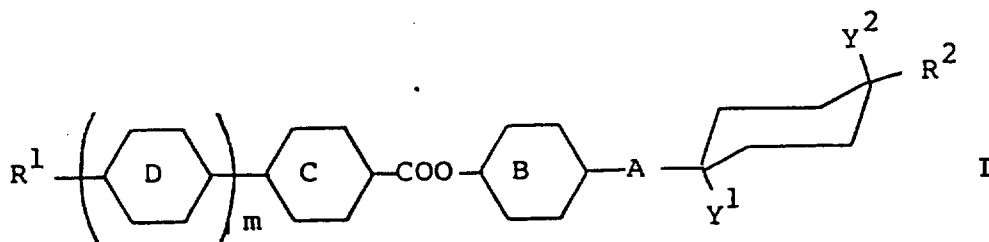


Mixture Example C

50 wt.% of 4-nonyloxybenzoic acid 4-[2-(trans-4-pentyl-cyclohexyl)ethyl]phenyl ester,
 50 wt.% of 4-dodecyloxybenzoic acid 2-cyano-4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester.
 cl.p. (N-I) 134°C, transition N-S_C 68°C, m.p. (C-S_C) 46°C.

Claims

1. Compounds of the general formula



wherein m stands for the number 0 or 1; A signifies a single covalent bond, -CH₂-CH₂-, -OCH₂-, -COO- or -OOC-; rings B, C and D denote 1,4-phenylene optionally substituted with cyano, halogen or lower alkyl; Y¹ and Y² signify hydrogen or one of the substituents Y¹ and Y² also signifies cyano; and R¹ and R² each individually represent optionally halogen-substituted C₁-C₁₈-alkyl or optionally halogen-substituted C₂-C₁₈-alkenyl in which optionally one CH₂ group or two non-adjacent CH₂ groups is/are replaced by oxygen; with the proviso that at least one of the residues R¹ and R² has a chiral carbon atom and/or a C-C double bond when A stands for -COO- and that at least one of the residues R¹ and R² has a C-C double bond when A stands for a single covalent bond.

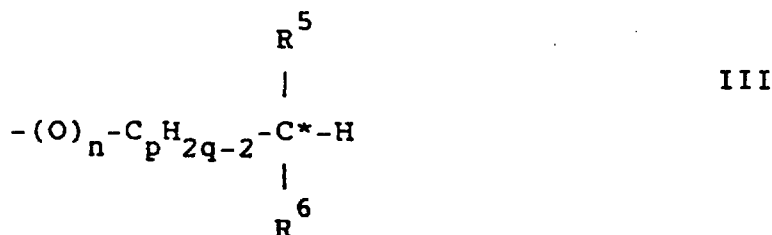
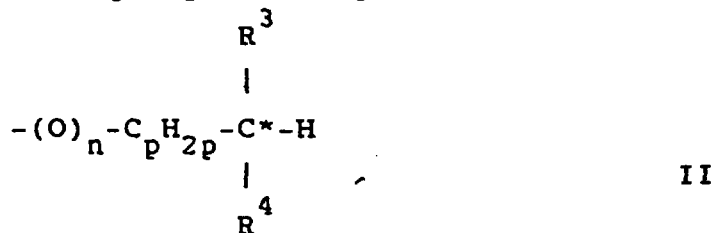
2. Compounds according to claim 1, characterized in that R¹ and R² each independently represent C₁-C₁₈-alkyl or C₂-C₁₈-alkenyl in which optionally one CH₂ group or two non-adjacent CH₂ groups is/are replaced by oxygen.

3. Optically active compounds according to claim 1 or 2, characterized in that at least one of the residues R¹ and R² has a chiral carbon atom.



4. Optically active compounds according to claim 3, characterized in that R¹ has a chiral carbon atom.

5. Optically active compounds according to claim 3 or 4, characterized in that the residue with a chiral carbon atom signifies a group of the general formula



wherein n, p and q signify whole numbers and n stands for 0 or 1, p stands for 0-6 and q stands for 2-6; R³ signifies alkyl and R⁴ signifies halogen, alkoxy, alkenyl, alkenyloxy or alkyl different from R³; or R³ signifies alkenyl and R⁴ signifies alkoxy; R⁵ denotes alkyl and R⁶ denotes halogen, alkoxy or alkyl different from R⁵; and C* signifies the chiral carbon atom.

6. Optically active compounds according to claim 5, characterized in that the residue with a chiral carbon atom signifies a group of formula II in which R³ denotes methyl and R⁴ denotes alkyl different from methyl.

7. Compounds according to any one of claims 1 to 6, characterized in that A signifies -CH₂CH₂-, -OCH₂- or -OOC-, preferably -CH₂CH₂- or -OCH₂-.

8. Compounds according to any one of claims 1 to 7, characterized in that Y¹ and Y² signify hydrogen and rings C and D denote 1,4-phenylene.

9. Compounds according to any one of claims 1 to 8, characterized in that ring B denotes 1,4-phenylene, 2-cyano-1,4-phenylene, 2,3-dicyano-1,4-phenylene, 2-halogeno-1,4-phenylene or 2,3-dihalogeno-1,4-phenylene.

10. Compounds according to any one of claims 1 to 9, characterized in that m stands for the number 0.



11. Compounds according to any one of claims 1 to 10, characterized in that R^1 represents alkoxy or alkenyloxy and R^2 represents alkyl or alkenyl.

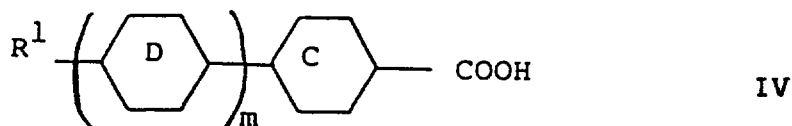
12. Compounds according to any one of claims 1 to 11, characterized in that R^1 and R^2 together have at least 7, preferably at least 10, carbon atoms.

13. A liquid crystalline mixture with at least 2 components, characterized in that at least one component is a compound of formula I defined in claim 1.

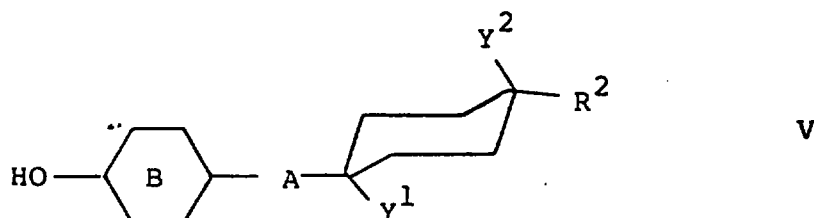
14. A chiral smectic mixture according to claim 13, characterized in that it contains an optically active compound of formula I and/or an optically active additive.

15. A process for the manufacture of the compounds of formula I defined in claim 1, characterized by

a) esterifying a compound of the general formula

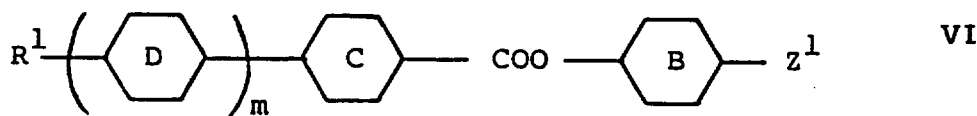


and a compound of the general formula



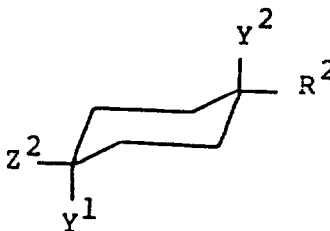
wherein A, R^1 , R^2 , Y^1 , Y^2 , m and rings B, C and D have the significances given in claim 1, or reactive derivatives of these compounds and, if desired, reacting a compound of formula I in which ring B, C or D signifies 1,4-phenylene substituted with chlorine or bromine with copper(I) cyanide, sodium cyanide or potassium cyanide, or

b) for the manufacture of compounds of formula I in which A signifies an ester group $-COO-$ or $-OOC-$, esterifying a compound of the general formula





and a compound of the general formula



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wherein one of the groups Z^1 and Z^2 denotes the carboxyl group and the other denotes the hydroxy group and R^1 , R^2 , Y^1 , Y^2 , m and rings B, C and D have the significances given in claim 1, or reactive derivatives of these compounds and, if desired, reacting a compound of formula I obtained in which ring B, C or D signifies 1,4-phenylene substituted with chlorine or bromine with copper(I) cyanide, sodium cyanide or potassium cyanide.

16. The use of the compounds of formula I defined in claim 1 for electro-optical purposes.