

THIS SHEET HAS BEEN
REPLACED

RAN 6220/129

The present invention is concerned with novel liquid crystalline, optically active bis-methyldioxanes, liquid
5 crystalline mixtures which contain such compounds, the use of such compounds and mixtures for optical and electro-optical devices, and electro-optical devices containing one or more compounds of formula I.

10 Liquid crystals are used primarily as dielectrics in display devices, since the optical properties of such substances can be influenced by an applied voltage. Electro-optical devices based on liquid crystals will be well-known to a person skilled in the art and can be based on various effects. Such devices are, for
15 example, cells having dynamic scattering, DAP cells (deformation of aligned phases), guest/host cells, TN cells having a "twisted nematic" structure, STN cells ("super twisted nematic"), SBE cells ("super birefringence effect") and OMI cells ("optical mode interference"). For displays having a high content of information
20 actively controlled cells, e.g. TFT cells ("thin film transistor"), have in particular recently become important in addition to the passively controlled, multiplexed cells. In addition to the aforementioned cell types, which are based on the use of nematic or cholesteric liquid crystals, cell types which are based on the
25 principle of chiral tilted smectic phases have recently become known. Thereto there belong SSF cells (surface stabilized ferroelectric), SBF cells (short-pitch bistable ferroelectric) or DHF cells (deformed helix ferroelectric). For these cells types there are generally preferred as tilted smectic phases chiral
30 smectic C (Sc^*) phases, which permit especially large response speeds.

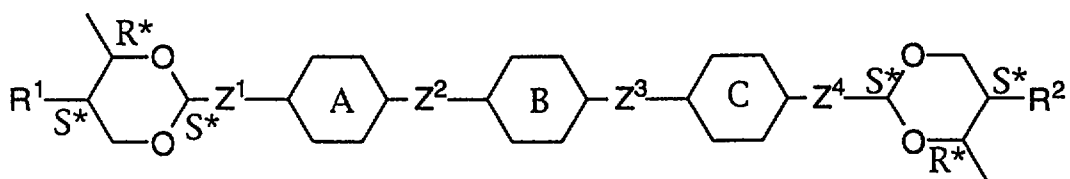
Materials for display devices based on chiral tilted smectic phases can preferably consist of a material having a tilted
35 smectic phase, usually a Sc phase, and one or more optically active dopants. The use of such chiral dopants in ferroelectric liquid crystals primarily serves to produce or alter a twisting of the tilted smectic phase and to induce a spontaneous polarization.

The chiral dopants should have an adequate thermal and photo-chemical stability, should have a good compatibility with the tilted smectic liquid crystals, should have a viscosity which is as low as possible and should not limit the mesophase range too severely. Further, a spontaneous polarization which is as high as possible and, depending on the cell type, a rather small twisting capacity (SSF cells) or a twisting capacity which is as high as possible (SBF, DHF cells) is desirable.

As chiral dopants there also come into consideration in principle compounds which themselves have no tilted phase or generally no mesophase. This is especially frequent in the case of dopants having a very high twisting capacity. However, such dopants usually have the disadvantage that they severely narrow the tilted phase range of host mixtures to which they are added. Accordingly, dopants have been sought which do not have this disadvantage or which have this disadvantage only to a small extent.

The compounds in accordance with the invention, which are distinguished by a high twisting capacity and a comparatively high spontaneous polarization, have mostly smectic mesophases, partially even Sc^* phases at comparatively high temperatures. In mixtures with Sc basic mixtures they give rise to no lowering or only to a relatively small lowering of the Sc^* phase. In spite of their basic structure comprising five rings they have a surprisingly good solubility in Sc basic mixtures. Having regard to these properties, they are outstandingly suitable as dopants for use in ferroelectric cells, especially in DHF cells. Moreover, they can also be used for cholesteric mixtures, especially in applications as cholesteric filters or as polarizers.

These compounds have the general formula



wherein

5	R ¹ and R ²	each independently signify alkyl or alkenyl in which optionally one methylene group or two non-adjacent methylene groups is/are replaced by -O-, -COO- and/or -OOC- and/or one or more hydrogen atoms is/are replaced by fluorine, chlorine or cyano; one
10	A, B and C	of rings signifies a 1,4-phenylene optionally substituted with 1 or 2 fluorine atoms, pyridine-2,5-diyl or pyrimidine-2,5-diyl and the other two rings each independently
15		signify 1,4-phenylene optionally substituted with 1 or 2 fluorine atoms or trans-1,4-cyclohexylene;
20	Z ¹ and Z ⁴	each independently signify a single bond, -CH ₂ CH ₂ -, -CH ₂ O-, -OCH ₂ -, -C≡C-, -(CH ₂) ₄ -, -(CH ₂) ₃ O-, -O(CH ₂) ₃ -, -CH=CH-CH ₂ O-, -OCH ₂ -CH=CH-, -CH=CH-(CH ₂) ₂ - or -(CH ₂) ₂ CH=CH-, with the proviso that the oxygen atom is not linked directly with the chiral dioxane
25		ring;
30	Z ² and Z ³	each independently signify a single bond, -CH ₂ -CH ₂ -, -O-CH ₂ -, -CH ₂ -O-, -COO-, -OOC-, -C≡C-, -(CH ₂) ₄ -, -O(CH ₂) ₃ -, -(CH ₂) ₃ O-, -CH=CH-CH ₂ O-, -OCH ₂ -CH=CH-, -(CH ₂) ₂ -CH=CH- or -CH=CH-(CH ₂) ₂ -; and
	R* and S*	signify the relative configurations of the chiral carbon atoms.

35 The terms used in the definitions will be explained hereinafter:

The term "alkyl or alkenyl in which optionally one methylene group or one or two non-adjacent methylene groups is/are replaced by -O-, -COO- and/or -OOC- and/or one or more hydrogen

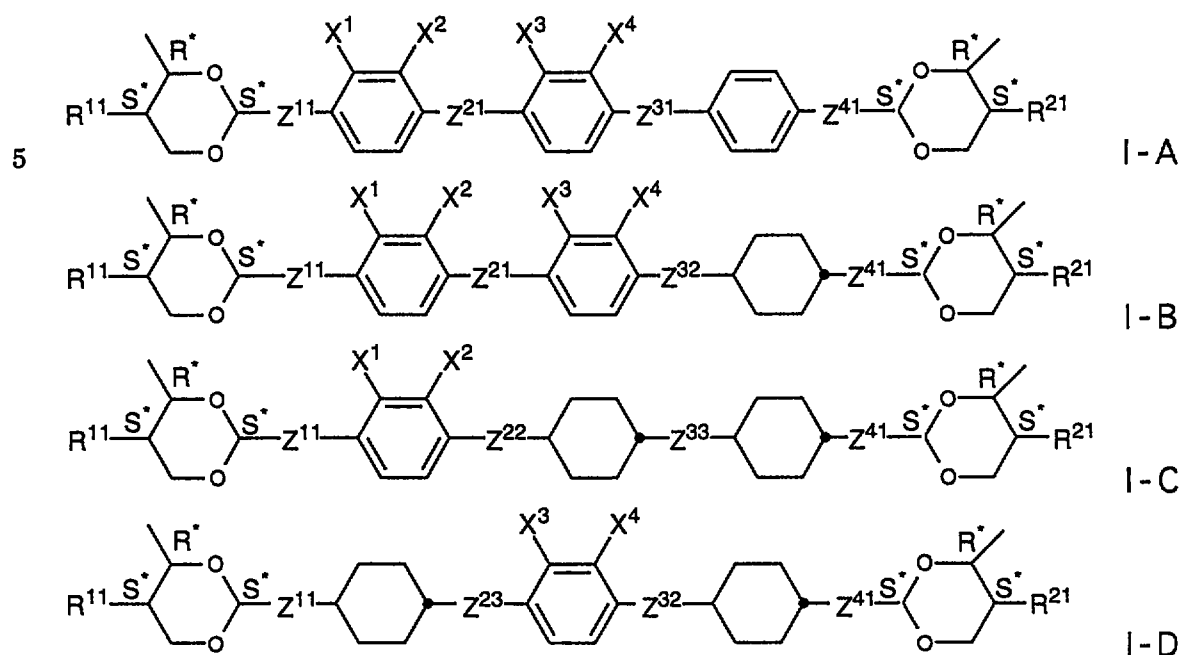
atoms is/are replaced by fluorine, chlorine or cyano" embraces straight-chain and branched (optionally chiral) groups such as alkyl, 2-alkenyl, 3-alkenyl, 4-alkenyl, alkenyl having a terminal double bond, alkoxyalkyl, alkenyloxyalkyl, alkylcarbonyloxyalkyl, alkoxycarbonylalkyl, fluoroalkyl, difluoroalkyl, trifluoroalkyl, chloroalkyl, cyanoalkyl, 1-methylalkyl, 2-methylalkyl and the like, in each case with a maximum of 16 carbon atoms, preferably a maximum of 12 carbon atoms. Examples of preferred groups are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, 1-methylpropyl, 1-methylheptyl, 2Z-pentenyl, 2Z-hexenyl, 2Z-heptenyl, 2Z-octenyl 3E-pentenyl, 3E-hexenyl, 3E-heptenyl, 3E-octenyl, 5E-octenyl, 3-butenyl, 4-pentenyl, 5-hexenyl, 6-heptenyl, 7-octenyl, methoxyethyl, methoxypropyl, methoxybutyl, ethoxyethyl, propyloxyethyl, 2-fluoropropyl, 2-fluoropentyl, 2-fluorooctyl, 2-chlorohexyl, 2-chlorooctyl and the like.

The term "1,4-phenylene optionally substituted with 1 or 2 fluorine atoms" signifies 1,4-phenylene, 2- or 3-fluoro-1,4-phenylene, 2,3-difluoro-1,4-phenylene, 2,6- or 3,5-difluoro-1,4-phenylene. Preferred fluorine-substituted rings are 2- or 3-fluoro-1,4-phenylene or 2,3-difluoro-1,4-phenylene.

Especially preferred compounds of formula I are those in which Z¹ and Z⁴ signify a single bond, -CH₂CH₂-, -CH₂O- or -OCH₂-; and Z² and Z³ signify a single bond, -CH₂CH₂-, -CH₂O-, -OCH₂-, -COO- or -OOC-, with an oxygen atom present in groups Z¹ to Z⁴ preferably being linked with an aromatic ring. In quite especially preferred compounds a maximum of two of groups Z¹ to Z⁴ are other than a single bond.

Particularly preferred are compounds of formula I in which rings A, B and C each independently signify 1,4-phenylene, 2- or 3-fluoro-1,4-phenylene or 2,3-difluoro-1,4-phenylene; or one of rings A, B and C signifies 1,4-phenylene, 2- or 3-fluoro-1,4-phenylene or 2,3-difluoro-1,4-phenylene and the other two rings each independently signify 1,4-trans-cyclohexylene, 1,4-phenylene, 2- or 3-fluoro-1,4-phenylene or 2,3-difluoro-1,4-phenylene.

Quite especially preferred compounds are those of the general formulae



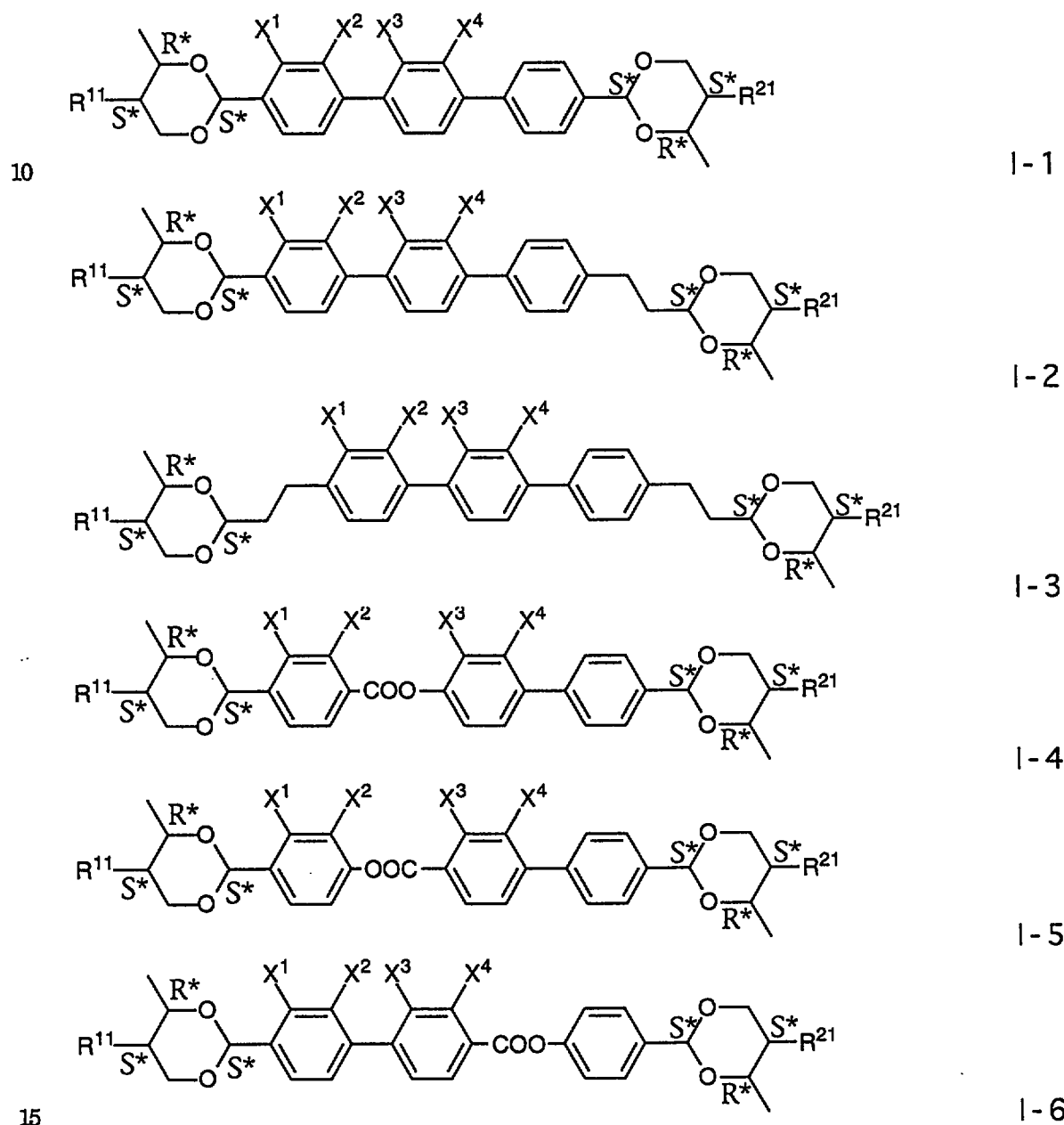
- 10 wherein
- R¹¹ and R²¹ each independently signify alkyl or alkenyl with a maximum of 12 carbon atoms in which optionally one methylene group is replaced by -O-, -COO- or -OOC-;
- 15 Z¹¹, Z³³ and Z⁴¹ each independently signify a single bond or -CH₂CH₂-;
- Z²¹ and Z³¹ each independently signify a single bond, -COO- or -OOC-;
- Z²² and Z³² each independently signify a single bond, -CH₂CH₂- or -OCH₂-;
- 20 Z²³ signifies a single bond, -CH₂CH₂- or -CH₂O-; and the substituents
- X¹ to X⁴ each independently signify hydrogen or fluorine.

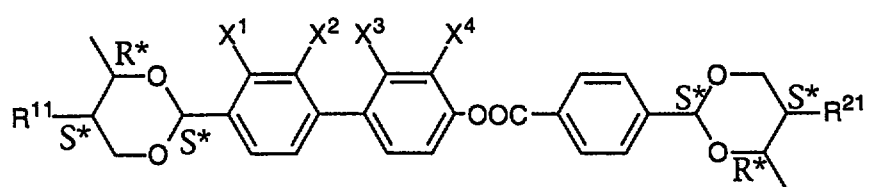
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The relative configurations of the chiral carbon atoms denoted by (S*) and (R*) in formula I and the subsequent formulae signify that the denoted carbon atoms as indicated have the (S) or (R) configuration or that all denoted carbon atoms have the mirror

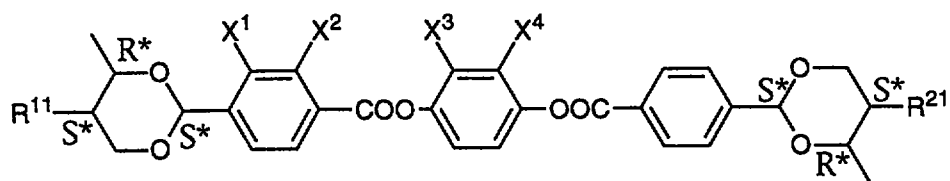
image configuration. The formulae accordingly embrace in each case the diastereoisomer in which (S^*) stands for the (S) configuration and (R^*) stands for the (R) configuration as well as its optical antipode in which (S^*) stands for the (R) configuration and (R^*) stands for the (S) configuration.

In particular, the compounds of the following general formulae are preferred:

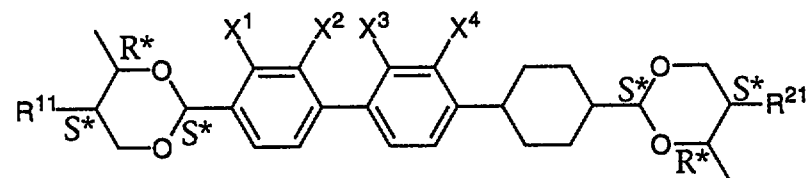




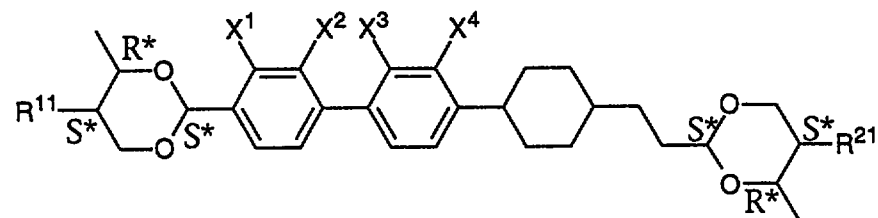
I-7



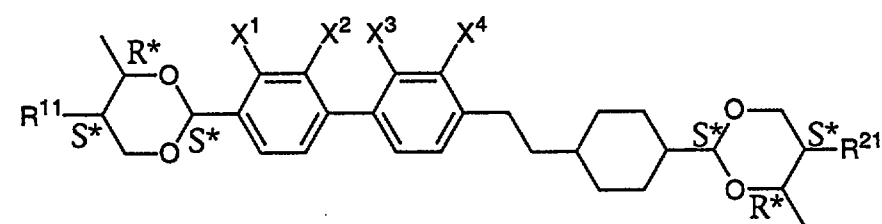
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I-9

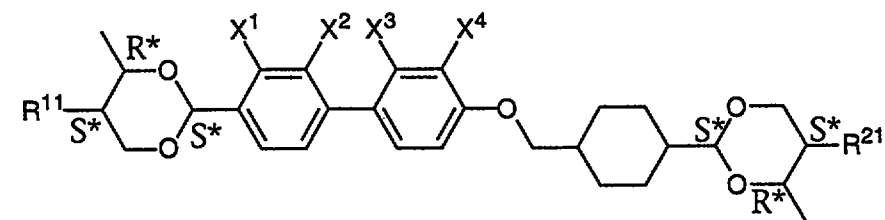


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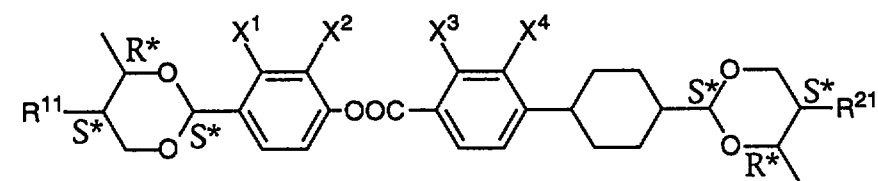


I-11

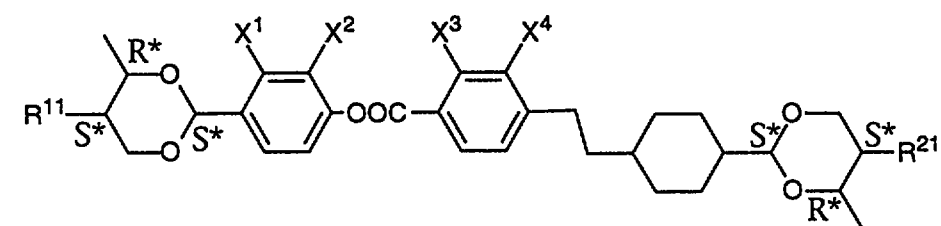
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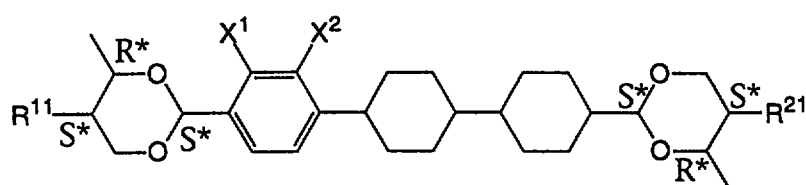
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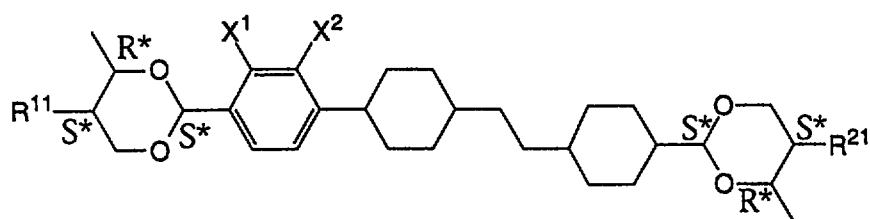
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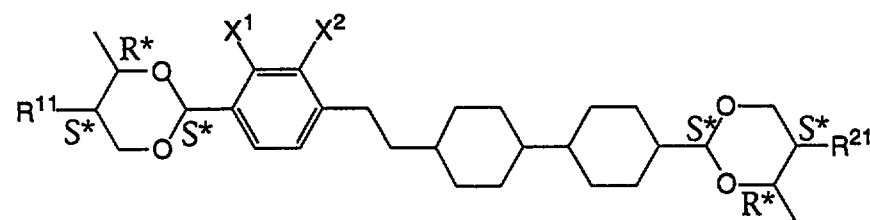
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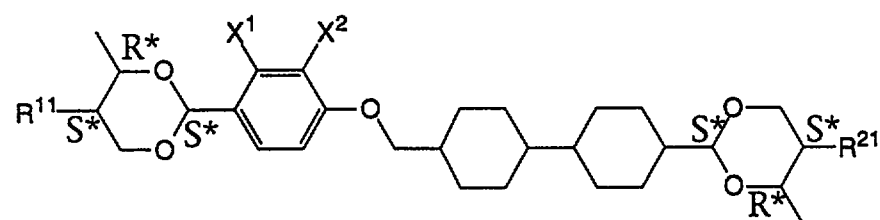
I-15



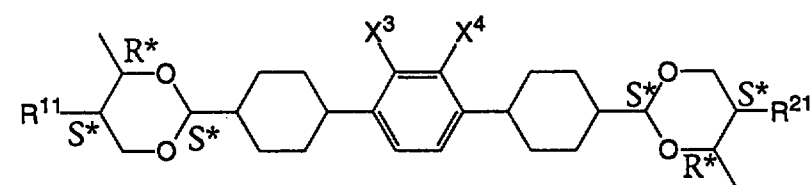
I-16



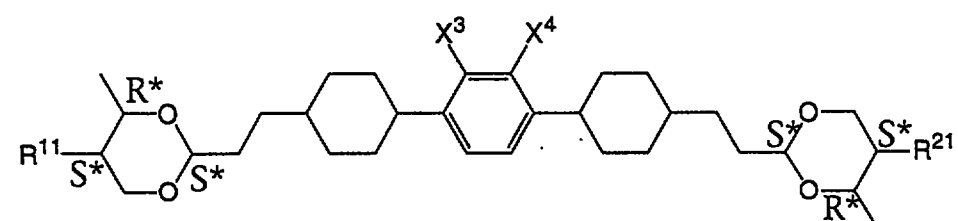
I-17



I-18



I-19



I-20

wherein

R¹¹ and R²¹

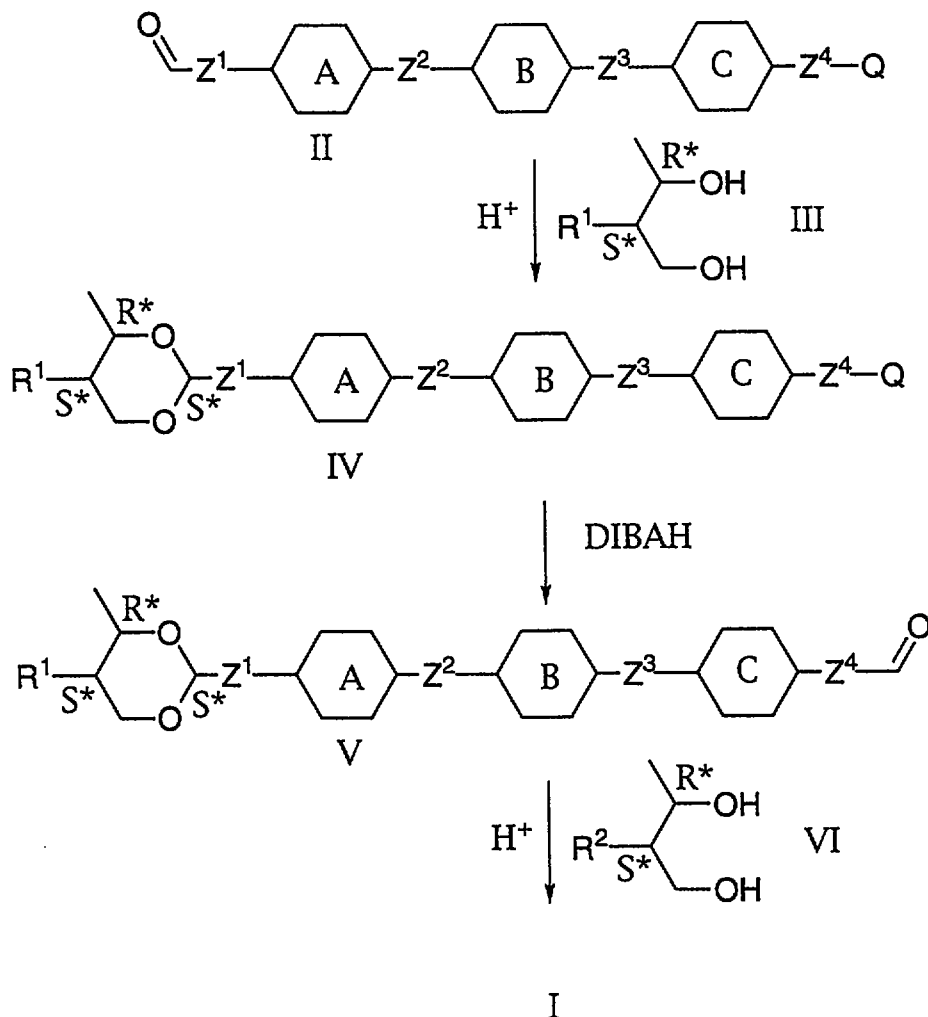
have the significances given above; and the substituents

X¹ to X⁴signify hydrogen or fluorine; preferably in each case a maximum of one or two of the substituents X¹ to X⁴ is/are different from hydrogen.

The compounds of general formula I can be produced in a manner known per se, for example in accordance with Scheme 1.

Scheme 1

5



wherein

Q

signifies -CN or -COOR;

10

R

signifies lower alkyl such as methyl, ethyl, propyl, i-propyl, butyl, 2-butyl or tert.-butyl;

and the remaining symbols have the above significance.

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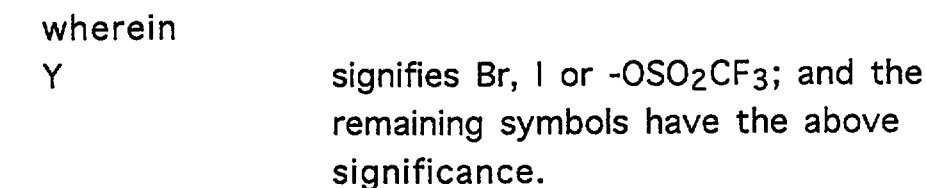
Thus, an aldehyde of general formula II, which contains a second group Q readily convertible into an aldehyde, is firstly reacted with a diol of general formula III to give a monoacetal of

general formula IV. Thereafter, the nitrile or the ester of general formula IV is converted by reduction, for example with diisobutylaluminium hydride (DIBAH), into an aldehyde of formula V which, by a second acetalization with a diol of general formula VI, gives the diacetal of general formula I.

When ester groups are present in R^1 and/or R^2 , the esterification is preferably not carried out until the dioxane rings have been formed. Further, when R^1 and/or R^2 contain ether groups, the etherification can also be effected, if desired, after formation of the dioxane rings.

Compounds of formula I in which Z^2 and/or Z^3 signify an ester group are preferably produced by esterifying corresponding partial structures having pre-formed dioxane rings.

Furthermore, those compounds of general formula I which contain two adjacent directly linked phenyl rings can be produced by palladium-catalyzed coupling, for example, of an appropriately substituted aromatic halide or sulphonate of general formula VII with an appropriately substituted arylboric ester of general formula VIII (see Scheme 2). Such couplings have been described many times, thus, for example, in Tetrahedron Letters 35, 3277 (1994)



5 wherein
Y signifies Br, I or -OSO₂CF₃; and the
remaining symbols have the above
significance.

10 The starting materials required for the synthesis of the
compounds of formula I are known or are analogues of known
compounds. Thus, for example, numerous nitriles or esters of
formula II have been described as intermediates in the synthesis
of liquid crystals, for example in EP-A-0 122 389. The prepar-
15 ation of the diols of formula III is also known from the literature,
for example from Mol Cryst. Liq. Cryst 213, 159 (1992)

The analogues of the starting materials of formulae VII or VIII, for example compounds having an achiral dioxane or dioxo-
20 lane ring, which usually serves as a protecting group, are also known from the literature. Linkage reactions of rings by ester formation, ether formation or by direct aromatic couplings via boric acids, as described, for example, in Tetrahedron Letters, 35, 3277 (1994), will be known to a person skilled in the art.
25 These reactions belong to standard methods in the synthesis of

liquid crystals and will therefore be very familiar to a person skilled in the art.

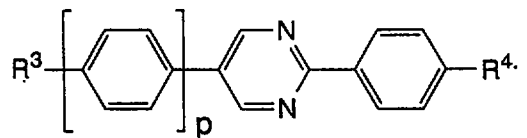
The compounds in accordance with the invention are
5 suitable as chiral dopants for liquid crystalline mixtures. The invention is therefore also concerned with liquid crystalline mixtures having at least two components, with at least one of the components being an optically active compound of formula I.

10 Preferably, the mixtures in accordance with the invention contain a single liquid crystalline compound or a liquid crystalline mixture as the carrier material and one or more optically active compounds of formula I. Suitable carrier materials are in principle all liquid crystal materials which have
15 a twistable liquid crystal phase with an adequate mesophase range. As mentioned, the liquid crystalline carrier material can be a single compound or a mixture and preferably has a clearing point of at least about 60°C. The compounds of formula I are especially suitable as chiral dopants for carrier materials having
20 a nematic, cholesteric or tilted smectic phase, especially for carrier materials having an achiral or chiral smectic C phase. Suitable liquid crystal components will be known to a person skilled in the art in large numbers, e.g. from D. Demus et al., Flüssige Kristalle in Tabellen, VEB Deutscher Verlag für
25 Grundstoffindustrie, Leipzig, volumes I and II, or from Landolt-Börnstein, Liquid Crystals, volume IV 7a-d, many of them are, moreover, commercially available.

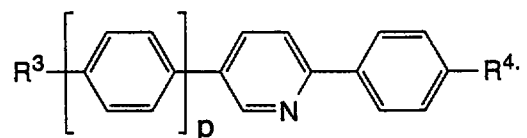
The content of chiral dopant of formula I is determined
30 largely by the twisting capacity, the spontaneous polarization and the desired pitch. The content of chiral dopant can accordingly vary in a wide range according to use and can be, for example, about 0.1-40 wt.%. In general, a content of about 1-30 wt.% especially of about 3-25 wt.%, of optically active dopants of
35 formula I is preferred for display devices based on liquid crystals having tilted smectic phases.

Preferably, the mixtures in accordance with the invention contain, in addition to one or more compounds of formula I, one or more compounds from the group of compounds of the general formulae

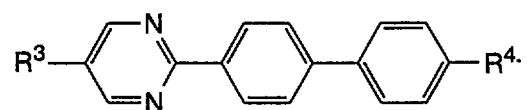
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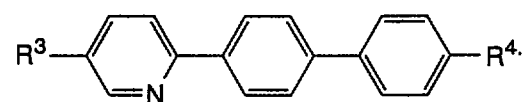
IX



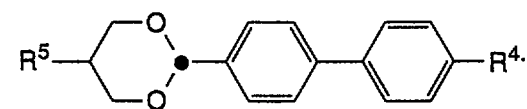
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XI

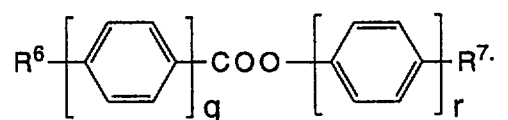


XII

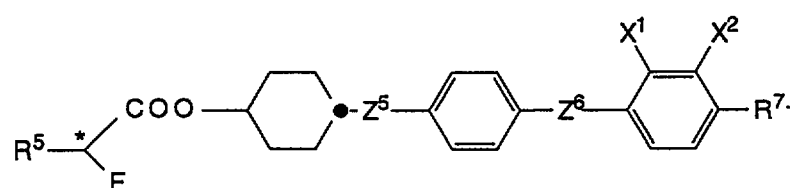


XIII

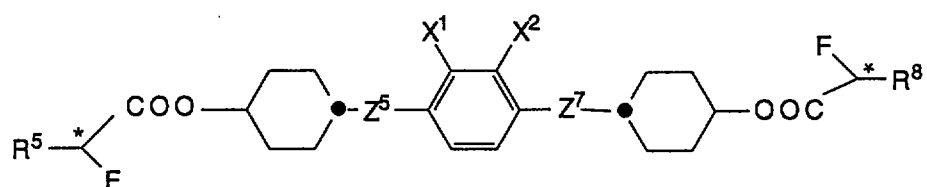
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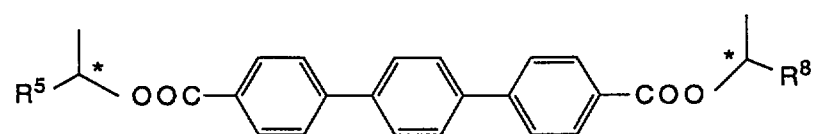
XIV



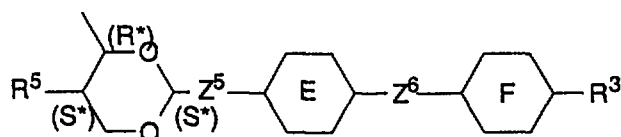
XV



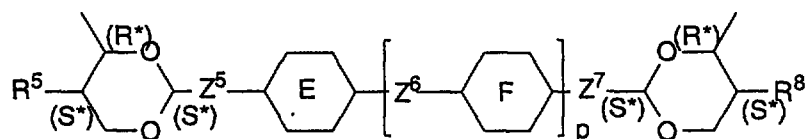
XVI



XVII



XVIII



XIX

wherein

- 5 p signifies 0 or 1;
 q and r each independently signify 1 or 2, whereby
 q + r = 2 or 3;
 R³ and R⁴ each independently signify alkyl, alkenyl,
 alkoxy, alkenyloxy, alkoxyalkyl, alkoxy-
 10 alkoxy, alkanoyloxy, alkenoyloxy, alkoxy-
 carbonyl, alkenyloxycarbonyl;
 R⁵ and R⁸ each independently signify alkyl or
 alkenyl,
 R⁶ and R⁷ each independently signify alkyl, alkenyl,
 15 alkoxy and/or alkenyloxy;
 Z⁵, Z⁶ and Z⁷ each independently signify a single bond,
 -CH₂CH₂- or -CH₂O-, and Z⁶ also signifies
 -OCH₂-, -COO- or -OOC-;
 E and F each independently signify phenylene-1,4-
 20 diyl or cyclohexylene-1,4-diyl;
 X¹ and X² each independently signify hydrogen or
 fluorine; and
 (R^{*}) and (S^{*}) signify the relative configurations.

25 The compounds of formulae XV to XIX are optically active
 dopants which, depending on the desired effect, can be present in
 the mixture in one of the two enantiomeric forms in addition to
 one or more compounds of formula I.

30 The substituents R³ to R⁸ have a maximum of in each case
 18 carbon atoms, preferably 5-12 carbon atoms. They can be
 straight-chain or branched, but are preferably straight-chain.

Electro-optical devices containing one or more compounds of formula I are also an object of the present invention. The production of the liquid crystalline mixtures and of the electro-optical devices can be effected in a known manner.

The production of the compounds of formula I and of liquid crystalline mixtures containing these compounds are illustrated in more detail by the following Examples. Optical antipodes of the compounds of formula I have in each case the same phase transition temperatures and induce the same absolute values of the spontaneous polarization and of the twisting, but with opposite signs. The abbreviations used for the characterization of the phase transitions have the following significances:

15	C	crystalline,
	S	smectic,
	S _A , S _B , S _C etc.	smectic A, B, C etc.,
	S _A [*] , S _F [*] etc.	chiral smectic C, F etc.
20	N	nematic,
	N [*]	cholesteric, and
	I	isotropic.

Example 1

25 a) A mixture of 0.80 g of 4-cyano-4'-(trans-4-formyl-cyclohexyl)biphenyl (preparation see. Mol Cryst. Liq. Cryst. Vol. 131, 327 (1985)), 0.587 g of (2R,3S)-2-octyl-1,3-butanediol (preparation see EP-0 457 105) 40 ml of toluene and 8 drops of 30 2N sulphuric acid was heated under reflux in a round flask having a magnetic stirrer, water separator and condenser under nitrogen for 15 hrs. Then, the mixture was cooled to room temperature, 30 drops of triethylamine were added and the mixture was partitioned between diethyl ether and sat. sodium bicarbonate 35 solution. The organic phases were separated thereupon dried over magnesium sulphate, filtered and the filtrate was evaporated. This gave 1.4 g of crude 4'-{trans-4-[(2R,3S,5R)-5-octyl-4-

methyl-1,3-dioxan-2-yl]cyclohexyl}-4-cyanobiphenyl as a light yellowish solid.

b) 1.4 g of 4'-{trans-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]cyclohexyl}-4-cyanobiphenyl were dissolved in 30 ml of toluene, cooled to 0°C and treated dropwise with 3.2 ml of DIBAH solution (20% in toluene) within 3 min. The reaction mixture was warmed to room temperature and stirred at this temperature for 15 hrs. Thereafter, the mixture was partitioned between diethyl ether and water, the ether phases were poured into 80 ml of water, the mixture was cooled to 0°C and treated dropwise with 1N hydrochloric acid while stirring vigorously until the pH was 2. The mixture was transferred to a separating funnel, the aqueous phase was separated and the organic phase was washed immediately with sat. sodium bicarbonate solution. The ether phase was dried over magnesium sulphate, filtered and the filtrate was evaporated. This gave 1.37 g of crude 4'-{trans-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]cyclohexyl}biphenyl-4-carboxaldehyde as a yellow solid.

20

c) A solution of 1.37 g of 4'-{trans-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]cyclohexyl}biphenyl-4-carboxaldehyde and 0.61 g of (2R,3S)-2-octyl-1,3-butanediol in 40 ml of toluene was treated with 8 drops of 2N sulphuric acid in a round flask having a magnetic stirrer, water separator and condenser under nitrogen and stirred under reflux for 2.5 hrs. Then, the mixture was cooled to room temperature, 30 drops of triethylamine were added and the reaction mixture was partitioned between diethyl ether and sat. sodium carbonate solution. The organic phases were dried over magnesium sulphate, filtered, the filtrate was evaporated and the residue was chromatographed on 140 g of silica gel with toluene/ethyl acetate (50:1). Three-fold crystallization from hexane gave 0.95 g of pure 4'-{trans-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]cyclohexyl}-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]biphenyl as colourless crystals m.p. (C/S_B): 73.5°C, S_B/S_A: 75.5°C, S_A/N*: 106°C, cl.p. (N*/I): 219°C, [α]_D (CHCl₃): -23.9°.

35

The following compounds can be produced in an analogous manner:

5 4'-{trans-4-[(2R,3S,5R)-5-Heptyl-4-methyl-1,3-dioxan-2-yl]cyclohexyl}-4-[(2R,3S,5R)-5-heptyl-4-methyl-1,3-dioxan-2-yl]biphenyl,

 4'-{trans-4-[(2R,3S,5R)-5-hexyl-4-methyl-1,3-dioxan-2-yl]cyclohexyl}-4-[(2R,3S,5R)-5-hexyl-4-methyl-1,3-dioxan-2-yl]biphenyl,

10 4'-{trans-4-[(2R,3S,5R)-5-nonyl-4-methyl-1,3-dioxan-2-yl]cyclohexyl}-4-[(2R,3S,5R)-5-nonyl-4-methyl-1,3-dioxan-2-yl]biphenyl,

 2',3'-difluoro-4'-{trans-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]cyclohexyl}-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]biphenyl,

 2,3-difluoro-4'-{trans-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]cyclohexyl}-4-[(2R,3S,5R)-5-heptyl-4-methyl-1,3-dioxan-2-yl]biphenyl,

20 4'-{2-{trans-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]cyclohexyl}ethyl}-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]biphenyl,

 4'-{trans-4-{2-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]ethyl}cyclohexyl}-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]biphenyl, m.p. (C/S_A): 88°C, (S_A/N^{*}): 98°C, cl.p. (N/I): 184.6°C,

 4'-{{trans-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]cyclohexyl}methoxy}-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]biphenyl,

30 4'-{2-{trans-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]cyclohexyl}ethyl}-4-{2-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]ethyl}biphenyl,

 1,4-bis-{trans-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]cyclohexyl}benzene, m.p. (C/N^{*}): 106.1°C, cl.p. (N^{*}-I): 222°C,

35 1,4-bis-{2-{trans-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]cyclohexyl}ethyl}benzene and

1,4-bis-{trans-4-{2-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]ethyl}cyclohexyl}benzene.

Example 2

5

a) A mixture of 0.871 g of 4-bromobenzaldehyde, 0.587 g of (2R,3S)-2-octyl-1,3-butanediol (preparation see EP-A-0 457 105) 40 ml of toluene and 8 drops of 2N sulphuric acid was heated under reflux and under nitrogen in a round flask having
10 a magnetic stirrer, water separator and condenser for 15 hrs. Then, the mixture was cooled to room temperature, 30 drops of triethylamine were added and the mixture was partitioned between diethyl ether and sat. sodium bicarbonate solution. The organic phases were combined dried over magnesium sulphate,
15 filtered and the filtrate was evaporated. Chromatography of the residue on 140 g of silica gel with 3% ethyl acetate in hexane gave 0.69 g of 1-bromo-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]benzene as a brownish oil.

20 b) A mixture of 1.33 g of 1-bromo-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]benzene, 0.3 g of phenyl-1,4-bis-boric acid, 0.077 g of 10% palladium on charcoal, 0.477 g of finely ground sodium carbonate and 20 ml of ethanol was stirred at 90°C for 100 hrs. Then, a further 0.050 g of phenyl-1,4-bis-
25 boric acid, 0.02 g of catalyst and 0.2 g of sodium carbonate were added and the mixture was stirred at 90°C for a further 15 hrs. The reaction mixture was then cooled, filtered over Celite/silica gel and the filtrate was partitioned between diethyl ether and 1N ammonium chloride solution. Thereupon, the organic phases were
30 combined dried over magnesium sulphate, filtered and the filtrate was evaporated. Chromatography of the residue on 200 g of silica gel with 3% ethyl acetate in hexane and subsequent crystallization from hexane gave 0.1 g of 1,4-bis-{4-
[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]phenyl}benzene as
35 colourless crystals, m.p.: < 25°C, S_G/S_C*: 129.8°C, S_C*/N*: 193°C, cl.p. (N*/I): 246.3°C.

The following compounds can be produced in an analogous manner:

- 1,4-Bis-{4-[(2R,3S,5R)-5-heptyl-4-methyl-1,3-dioxan-2-yl]phenyl}benzene,
 5 1,4-bis-{4-[(2R,3S,5R)-5-hexyl-4-methyl-1,3-dioxan-2-yl]phenyl}benzene,
 1,4-bis-{4-[(2R,3S,5R)-5-pentyl-4-methyl-1,3-dioxan-2-yl]phenyl}benzene,
 10 1,4-bis-{4-[(2R,3S,5R)-5-nonyl-4-methyl-1,3-dioxan-2-yl]phenyl}benzene,
 1,4-bis-{4-[(2R,3S,5R)-5-decyl-4-methyl-1,3-dioxan-2-yl]phenyl}benzene,
 1-{4-[(2R,3S,5R)-5-heptyl-4-methyl-1,3-dioxan-2-yl]phenyl}-4-{4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]phenyl}benzene,
 15 1,4-bis-{4-[(2R,3S,5R)-5-(7-octenyl)-4-methyl-1,3-dioxan-2-yl]phenyl}benzene,
 1,4-bis-{4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]phenyl}-2,3-difluorobenzene,
 20 1,4-bis-{3-fluoro-4-[(2R,3S,5R)-5-(7-octenyl)-4-methyl-1,3-dioxan-2-yl]phenyl}benzene,
 1,4-bis-{2-fluoro-4-[(2R,3S,5R)-5-(7-octenyl)-4-methyl-1,3-dioxan-2-yl]phenyl}benzene,
 25 1-{2,3difluoro-4-[(2R,3S,5R)-5-(7-octenyl)-4-methyl-1,3-dioxan-2-yl]phenyl}-4-{4-[(2R,3S,5R)-5-(7-octenyl)-4-methyl-1,3-dioxan-2-yl]phenyl}benzene and
 1,4-bis-{4-{2-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]ethyl}phenyl}benzene, m.p. (S/A_A): 140.2°C, (S_A/N^{*}): 175°C, cl.p. (N^{*}/I): 181.8°C.
 30

Example 3

- 1.2 g of N,N'-dicyclohexylcarbodiimide are added portion-
 35 wise within 10 min. while stirring to a solution of 2.05 g of 4-{4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]phenyl}-benzoic acid, 1.4 g of 4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]phenol and 0.1 g of 4-(dimethylamino)pyridine in

250 ml of dichloromethane. The mixture is stirred at room temperature overnight and then filtered. The filtrate is diluted with dichloromethane, washed twice with 50 ml of saturated sodium carbonate solution each time and then with water, dried
 5 over magnesium sulphate, filtered and the filtrate is concentrated. Chromatography of the residue on silica gel with toluene and recrystallization from hexane gives 4'-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]biphenylcarboxylic acid 4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]phenyl ester:
 10 m.p. (C/S_A): 95.6°C, (S_A/N^{*}): 106.6°C, cl.p. (N^{*}/I) 234°C.

The following compounds can be produced in an analogous manner:

15 4'-[(2R,3S,5R)-5-Octyl-4-methyl-1,3-dioxan-2-yl]-biphenylcarboxylic acid 4-[(2R,3S,5R)-5-nonyl-4-methyl-1,3-dioxan-2-yl]phenyl ester,
 4'-[(2R,3S,5R)-5-nonyl-4-methyl-1,3-dioxan-2-yl]-biphenylcarboxylic acid 4-[(2R,3S,5R)-5-hyptyl-4-methyl-1,3-
 20 dioxan-2-yl]phenyl ester,
 4'-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]-biphenylcarboxylic acid 4-[(2R,3S,5R)-5-(7-octenyl)-4-methyl-1,3-dioxan-2-yl]phenyl ester,
 4'-[(2R,3S,5R)-5-(7-octenyl)-4-methyl-1,3-dioxan-2-
 25 yl]biphenylcarboxylic acid 4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]phenyl ester,
 2,3-difluoro-4'-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]biphenylcarboxylic acid 4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]phenyl ester,
 30 2',3'-difluoro-4'-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]biphenylcarboxylic acid 4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]phenyl ester,
 4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]benzoic acid 4'-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]biphenyl
 35 ester, m.p. (C/S_A): 114.1°C, (S_A/N^{*}): 128.5°C, cl.p. (N^{*}/I): 230.6°C,
 4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]benzoic acid 4-{trans-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]cyclohexyl}phenyl ester and

4-{trans-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]cyclohexyl}benzoic acid 4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]phenyl ester.

5

Example 4

Test mixtures each with the two basic mixtures BM-I and BM-II were prepared in order to investigate the properties of the compounds of formula I in mixtures. GM-I is an achiral (non-doped) mixture and serves to determine the phase sequence, especially the extent of the S_C^* phase transition, as well as the spontaneous polarization (P_s). GM-II is a chiral doped mixture and serves to measure the wavelength of the selective reflection (λ_{sel}). This is a measurement for the helical pitch, i.e. the smaller the measured value for λ_{sel} is, then the smaller is the pitch and the stronger is the twisting capacity of the dopant. Moreover, two comparative mixtures were prepared for comparison purposes. For this purpose, the two basic mixtures GM-I and GM-II were each doped with a tetranuclear chiral bis-methyldioxane.

The measurements were carried out under the following conditions: P_s measurements at about 8 m μ cell thickness and a delta voltage of 10 Hz and 5 V/ μ . Measurements of λ_{sel} with homeotropic orientation. A temperature of 25°C was observed for all measurements.

Basic mixture I (BM-I)

7.0 wt.% of	5-(5-heptyl-1,3-dioxan-2-yl)-2-(4-octyloxy-phenyl)pyridine;
7.0 wt.% of	5-(5-octyl-1,3-dioxan-2-yl)-2-(4-octyloxy-phenyl)pyridine;
6.0 wt.% of	5-(5-decyl-1,3-dioxan-2-yl)-2-(4-octyl-phenyl)pyridine;
15.9 wt.% of	4-decyloxybenzoic acid 4-[2-(trans-4-pentyl-cyclohexyl)ethyl]phenyl ester;
7.1 wt.% of	4-dodecyloxybenzoic acid 4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester;

- 7.0 wt.% of 2,3-difluoro-4-undecyloxybenzoic acid 4-[2-(trans-4-pentylcyclohexyl)ethyl]phenyl ester;
 14.9 wt.% of 2-(4-hexyloxyphenyl)-5-nonylpyrimidine;
 19.9 wt.% of 2-(4-nonyloxyphenyl)-5-nonylpyrimidine;
 5 5.0 wt.% of 2-(4-octyloxyphenyl)-5-heptylpyrimidine;
 10.1 wt.% of 2-(4-hexyloxyphenyl)-5-octylpyrimidine;
 Phase sequence: I - 103°C - N - 80°C - S_A - 76.5°C - S_C - -17.5°C
 C

10. Comparative mixture I

- 7.0 wt.% of 1,4-bis-{4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]}benzene
 93.0 wt.% of BM-I
 sequence: I - 104.0°C - N* - 67.4°C - S_C* - ;
 15 Ps: 10.1 nC/cm²

Test mixture I-1

- 7.0 wt.% of 1,4-bis-{4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]phenyl}benzene
 20 93.0 wt.% of BM-I
 sequence: I - 109.4°C - N* - 80°C - S_A - 72.9°C - S_C* - ;
 Ps: 13.1 nC/cm²

Test mixture I-2

- 25 7.0 wt.% of 4'-{trans-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]cyclohexyl}-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]biphenyl
 93.0 wt.% of BM-I
 sequence: I - 110.1°C - N* - 72.0°C - S_C* - ;
 30 Ps: 11.5 nC/cm²

Basic mixture II (BM-II)

- 27.0 wt.% of 1,4-bis-{4-[(S)-2-octyloxy]phenyl}benzene
 15.7 wt.% of 2-(4-octyloxyphenyl)-5-[(4E)-4-octenoyloxy]-
 35 pyrimidine;
 5.2 wt.% of 2-(4-octanoyloxyphenyl)-5-octylpyridine;
 5.2 wt.% of 2-{4-[(2E)-2-octenoyloxy]phenyl}-5-heptylpyridine;

	5.2 wt.% of	2-{4-[(2E)-2-octenoyloxy]phenyl}-5-octylpyridine;
	10.4 wt.% of	2-(4-heptylphenyl)-5-[(2E)-2-octenyloxy]pyrimidine;
5	15.6 wt.% of	2-(4-hexyloxyphenyl)-5-nonylpyrimidine;
	15.6 wt.% of	2-(4-nonyloxyphenyl)-5-nonylpyrimidine;
	λ_{sel} :	508 nm

Comparative mixture II

10	3.0 wt.% of	1,4-bis-{4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]}benzene
	93.0 wt.% of	BM-I
	λ_{sel} :	437 nm

Test mixture II-1

15	3.0 wt.% of	1,4-bis-{4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]phenyl}benzene
	97.0 wt.% of	BM-II
	λ_{sel} :	404 nm

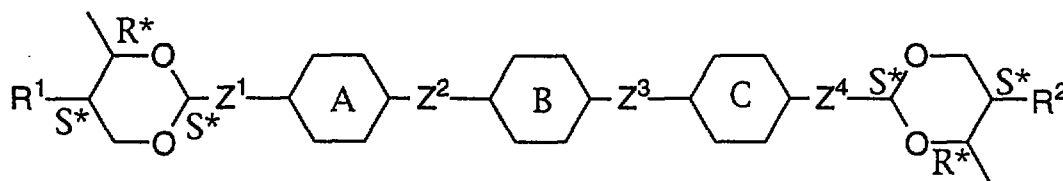
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Test mixture II-2

	3.0 wt.% of	4'-{trans-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]cyclohexyl}-4-[(2R,3S,5R)-5-octyl-4-methyl-1,3-dioxan-2-yl]biphenyl
25	97.0 wt.% of	BM-II
	λ_{sel} :	414 nm

Claims

1. Compounds of the general formula



wherein

R¹ and R²

each independently signify alkyl or alkenyl in which optionally one methylene group or two non-adjacent methylene groups is/are replaced by -O-, -COO- and/or -OOC- and/or one or more hydrogen atoms is/are replaced by fluorine, chlorine or cyano; one of rings

A, B and C

signifies a 1,4-phenylene optionally substituted with 1 or 2 fluorine atoms, pyridine-2,5-diyl or pyrimidine-2,5-diyl and the other two rings each independently signify 1,4-phenylene optionally substituted with 1 or 2 fluorine atoms or trans-1,4-cyclohexylene;

Z¹ and Z⁴

each independently signify a single bond, -CH₂CH₂-, -CH₂O-, -OCH₂-, -C≡C-, -(CH₂)₄-, -(CH₂)₃O-, -O(CH₂)₃-, -CH=CH-CH₂O-, -OCH₂-CH=CH-, -CH=CH-(CH₂)₂- or -(CH₂)₂CH=CH-, with the proviso that the oxygen atom is not linked directly with the chiral dioxane ring;

Z² and Z³

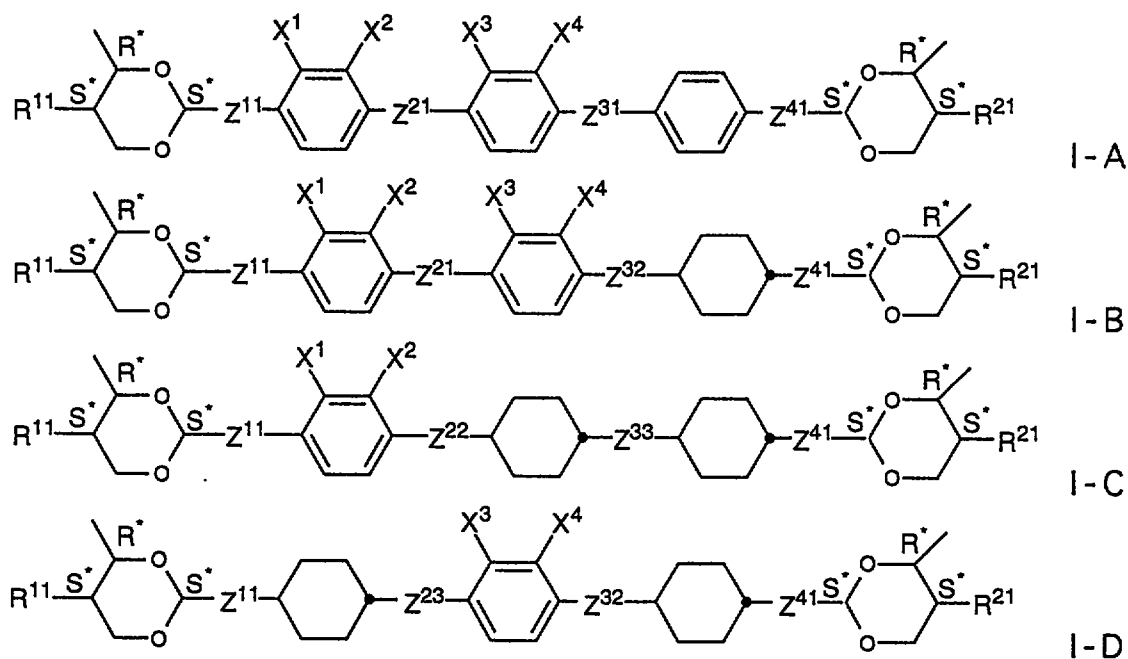
each independently signify a single bond, -CH₂-CH₂-, -O-CH₂-, -CH₂-O-, -COO-, -OOC-, -C≡C-, -(CH₂)₄-, -O(CH₂)₃-, -(CH₂)₃O-, -CH=CH-CH₂O-, -OCH₂-CH=CH-, -(CH₂)₂-CH=CH- or -CH=CH-(CH₂)₂-; and

R^* and S^* signify the relative configurations of the chiral carbon atoms.

2. Compounds according to claim 1, wherein Z^1 and Z^4 signify a single bond, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{O}-$ or $-\text{OCH}_2-$; and Z^2 and Z^3 signify a single bond, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{O}-$, $-\text{OCH}_2-$, $-\text{COO}-$ or $-\text{OOC}-$, with an oxygen atom present in groups Z^1 to Z^4 preferably being linked with an aromatic ring.

3. Compounds according to claim 1 or claim 2, wherein a maximum of two of groups Z^1 to Z^4 are other than a single bond.

4. Compounds according to any one of claims 1 to 3 of the general formulae



wherein

R^{11} and R^{21} each independently signify alkyl or alkenyl with a maximum of 12 carbon atoms in which optionally one methylene group is replaced by $-\text{O}-$, $-\text{COO}-$ or $-\text{OOC}-$;

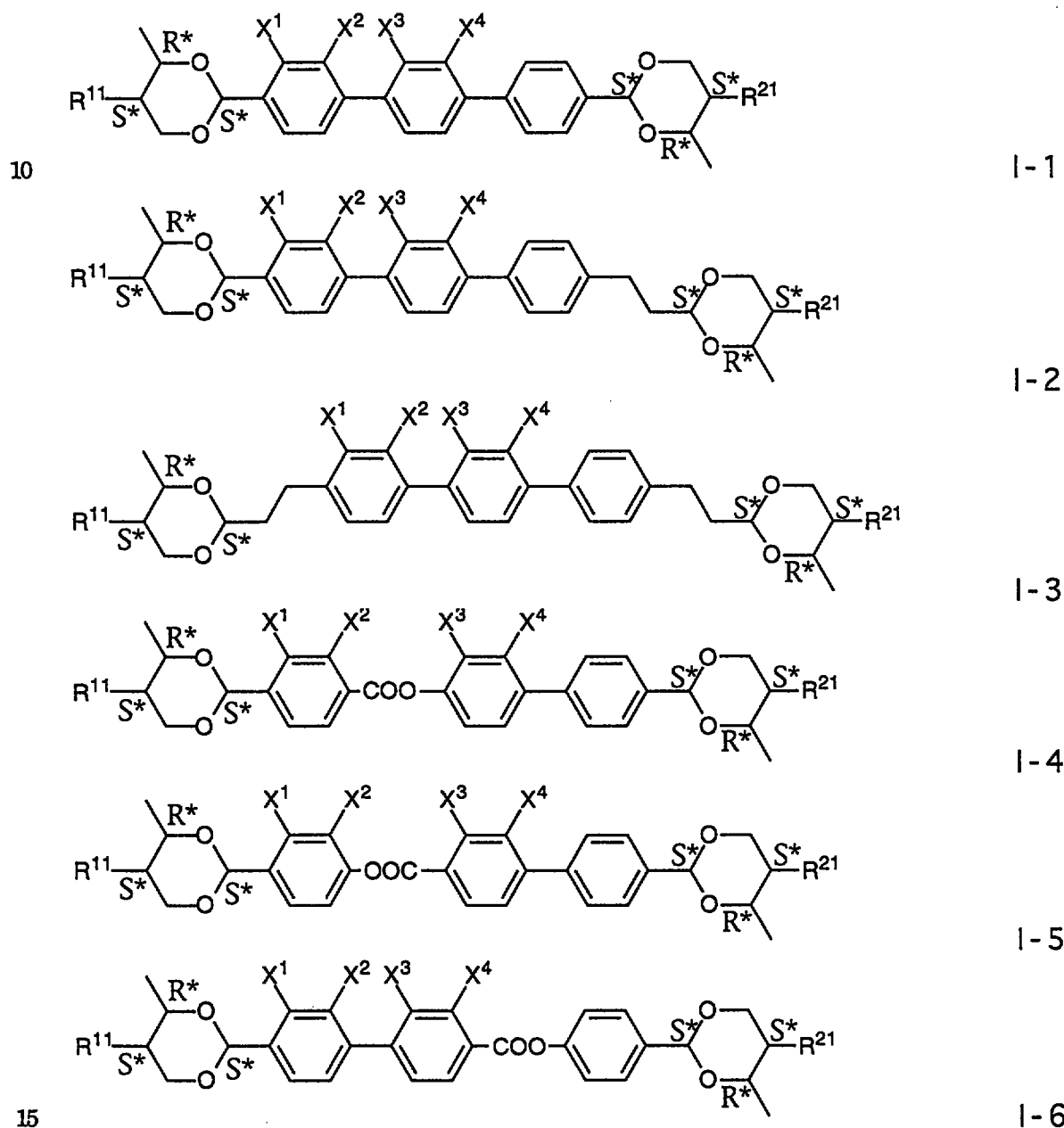
25 Z^{11} , Z^{33} and Z^{41} each independently signify a single bond, or $-\text{CH}_2\text{CH}_2-$;

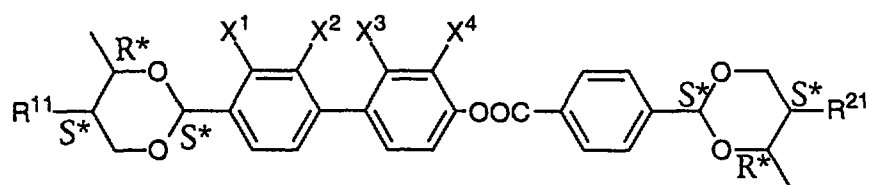
Z^{21} and Z^{31} each independently signify a single bond, $-\text{COO}-$ or $-\text{OOC}-$;



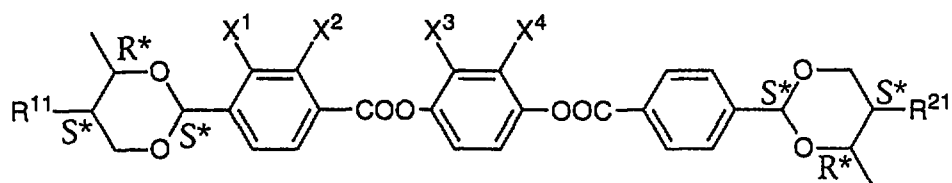
- Z²² and Z³² each independently signify a single bond,
 -CH₂CH₂- or -OCH₂-;
 Z²³ signifies a single bond, -CH₂CH₂- or
 -CH₂O-; and the substituents
 5 X¹ to X⁴ each independently signify hydrogen or
 fluorine.

5. Compounds according to claim 4 of the formulae





I-7

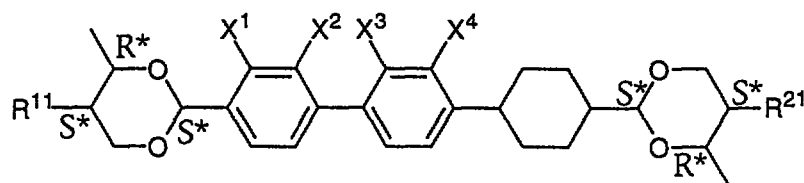


I-8

wherein

- 5 R^{11} and R^{21} each independently signify alkyl or
 or alkenyl with a maximum of 12 carbon
 atoms in which optionally one methylene
 group is replaced by -O-, -COO- or -OOC-;
 and the substituents
 10 X^1 to X^4 each independently signify hydrogen or
 fluorine.

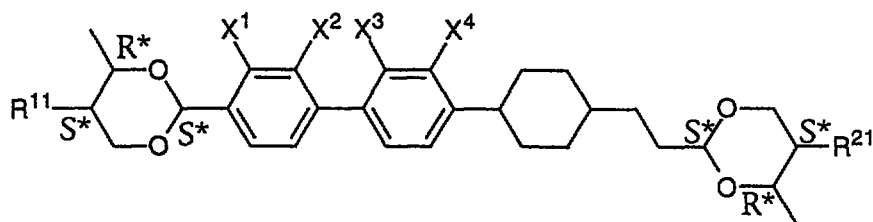
6. Compounds according to claim 4 of the formulae



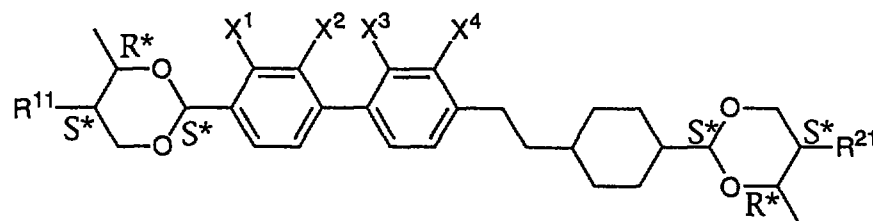
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I-9

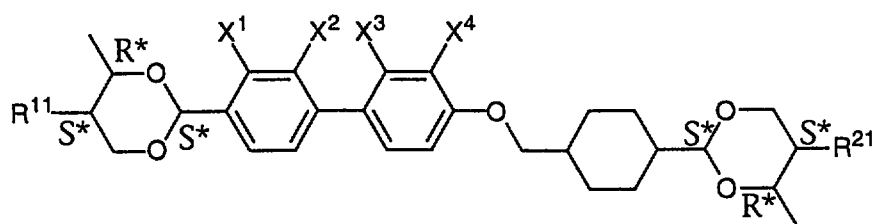


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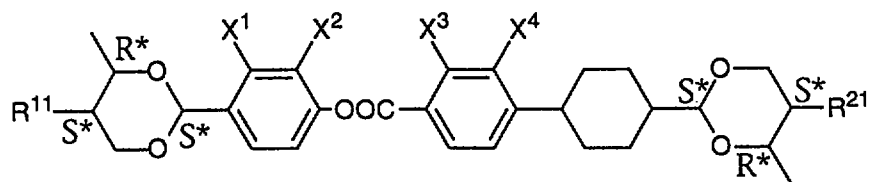


I-11

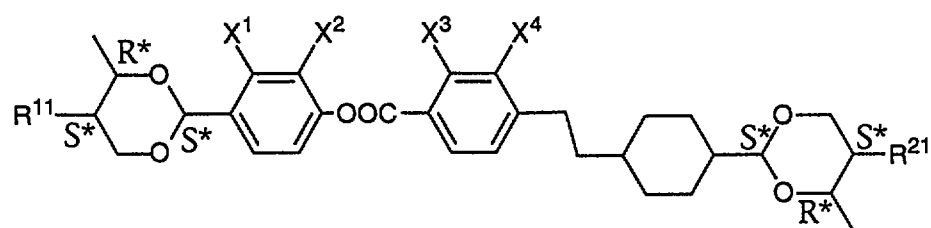
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I-12



I-13



I-14

5

wherein

R¹¹ and R²¹

each independently signify alkyl or alkenyl with a maximum of 12 carbon atoms in which optionally one methylene group is replaced by -O-, -COO- or -OOC-; and the substituents

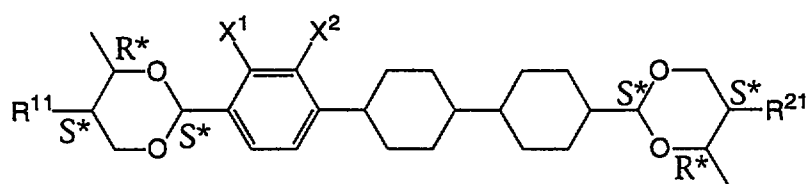
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X¹ to X⁴

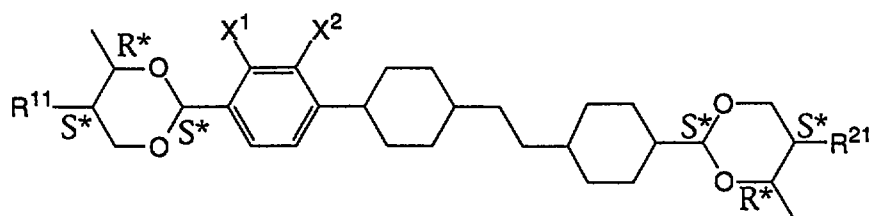
each independently signify hydrogen or fluorine.

7. Compounds according to claim 4 of the formulae

15

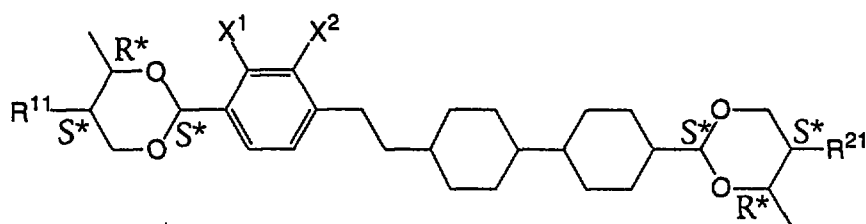


I-15

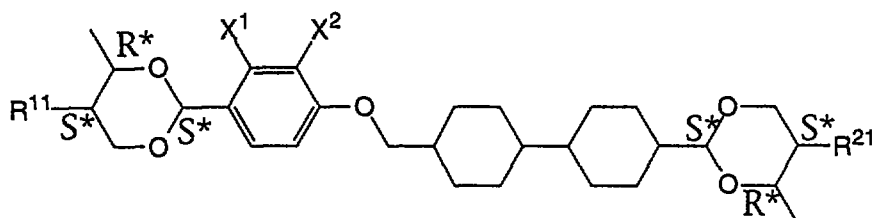


I-16





I-17

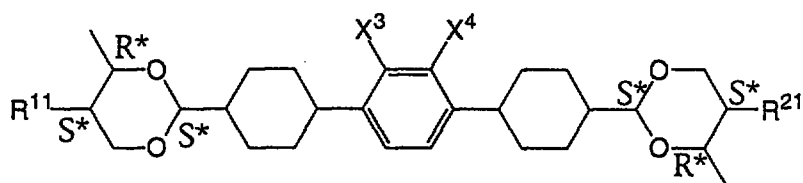


I-18

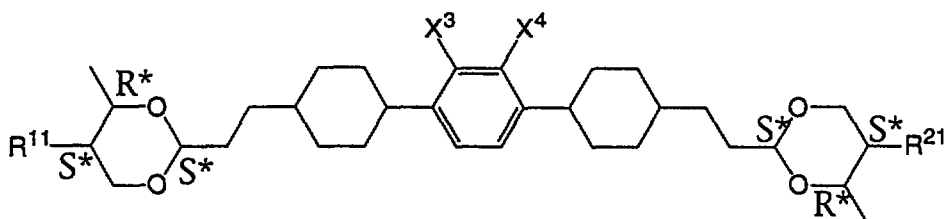
wherein

- 5 R^{11} and R^{21} each independently signify alkyl or alkenyl with a maximum of 12 carbon atoms in which optionally one methylene group is replaced by -O-, -COO- or -OOC-; and the substituents
- 10 X^1 to X^4 each independently signify hydrogen or fluorine.

8. Compounds according to claim 4 of the formulae



I-19



I-20

wherein

- 20 R^{11} and R^{21} each independently signify alkyl or alkenyl with a maximum of 12 carbon atoms in which optionally one methylene group is replaced by -O-, -COO- or -OOC-; and the substituents

X¹ to X⁴ each independently signify hydrogen or fluorine.

9. Compounds according to any one of claims 4 to 8,
5 wherein a maximum of two of groups X¹ to X⁴ signify fluorine.

10. Liquid crystalline mixtures containing at least two components, wherein at least one component is an optically active compound of formula I defined in claim 1.

10

11. Liquid crystalline mixtures in accordance with claim 10, wherein the content of optically active compounds of formula I defined in claim 1 is 1-30 wt.%.

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

13. The use of liquid crystalline mixtures in accordance with any one of claims 10 to 12 for electro-optical purposes.

20

14. An electro-optical device containing a compound according to any one of claims 1 to 9.

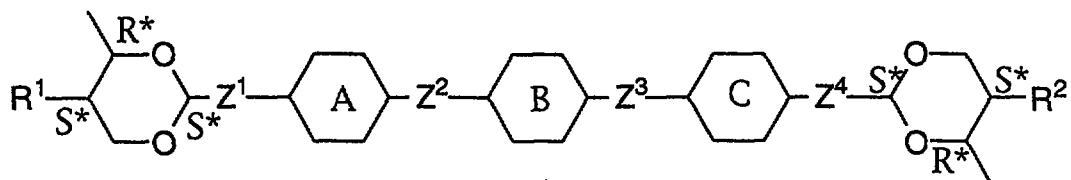
15. An electro-optical device containing a mixture
25 according to claim 10 or claim 11.

* * *



Abstract

5 Compounds of the general formula



wherein

10

R¹ and R²

each independently signify alkyl or alkenyl in which optionally one methylene group or two non-adjacent methylene groups is/are replaced by -O-, -COO- and/or -OOC- and/or one or more hydrogen atoms is/are replaced by fluorine, chlorine or cyano; one of rings

15

A, B and C

signifies a 1,4-phenylene optionally substituted with 1 or 2 fluorine atoms, pyridine-2,5-diyl or pyrimidine-2,5-diyl and the other two rings each independently signify 1,4-phenylene optionally substituted with 1 or 2 fluorine atoms or trans-1,4-cyclohexylene;

20

Z¹ and Z⁴

each independently signify a single bond, -CH₂CH₂-, -CH₂O-, -OCH₂-, -C≡C-, -(CH₂)₄-, -(CH₂)₃O-, -O(CH₂)₃-, -CH=CH-CH₂O-, -OCH₂-CH=CH-, -CH=CH-(CH₂)₂- or -(CH₂)₂CH=CH-, with the proviso that the oxygen atom is not linked directly with the chiral dioxane ring;

30

Z² and Z³

each independently signify a single bond, -CH₂-CH₂-, -O-CH₂-, -CH₂-O-, -COO-, -OOC-, -C≡C-, -(CH₂)₄-, -O(CH₂)₃-,



R* and S*

$-(\text{CH}_2)_3\text{O}-$, $-\text{CH}=\text{CH}-\text{CH}_2\text{O}-$, $-\text{OCH}_2-\text{CH}=\text{CH}-$,
 $-(\text{CH}_2)_2-\text{CH}=\text{CH}-$ or $-\text{CH}=\text{CH}-(\text{CH}_2)_2-$; and
signify the relative configurations of the
chiral carbon atoms;

- 5 as well as liquid crystalline mixtures which contain such
compounds and the use of such compounds and mixtures for
optical and electro-optical purposes.

03 APR 1997

OPTICALLY ACTIVE BIS-METHYLDIOXANE DERIVATIVES

The present invention is concerned with novel liquid crystalline, optically active bis-methyldioxanes, liquid
5 crystalline mixtures which contain such compounds, the use of such compounds and mixtures for optical and electro-optical devices, and electro-optical devices containing one or more compounds of formula I.

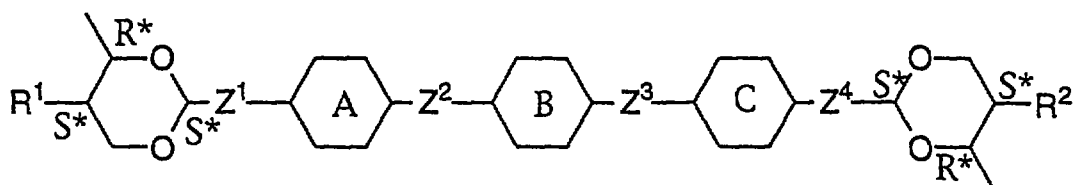
10 Liquid crystals are used primarily as dielectrics in display devices, since the optical properties of such substances can be influenced by an applied voltage. Electro-optical devices based on liquid crystals will be well-known to a person skilled in the art and can be based on various effects. Such devices are, for
15 example, cells having dynamic scattering, DAP cells (deformation of aligned phases), guest/host cells, TN cells having a "twisted nematic" structure, STN cells ("super twisted nematic"), SBE cells ("super birefringence effect") and OMI cells ("optical mode interference"). For displays having a high content of information
20 actively controlled cells, e.g. TFT cells ("thin film transistor"), have in particular recently become important in addition to the passively controlled, multiplexed cells. In addition to the aforementioned cell types, which are based on the use of nematic or cholesteric liquid crystals, cell types which are based on the
25 principle of chiral tilted smectic phases have recently become known. Thereto there belong SSF cells (surface stabilized ferroelectric), SBF cells (short-pitch bistable ferroelectric) or DHF cells (deformed helix ferroelectric). For these cells types there are generally preferred as tilted smectic phases chiral
30 smectic C (Sc^*) phases, which permit especially large response speeds.

Materials for display devices based on chiral tilted smectic phases can preferably consist of a material having a tilted
35 smectic phase, usually a Sc phase, and one or more optically active dopants. The use of such chiral dopants in ferroelectric liquid crystals primarily serves to produce or alter a twisting of the tilted smectic phase and to induce a spontaneous polarization.

03 APR 1997

OPTICALLY ACTIVE BIS-METHYLDIOXANE DERIVATIVESAbstract

5 Compounds of the general formula



wherein

10

R¹ and R²

each independently signify alkyl or alkenyl in which optionally one methylene group or two non-adjacent methylene groups is/are replaced by -O-, -COO- and/or -OOC- and/or one or more hydrogen atoms is/are replaced by fluorine, chlorine or cyano; one of rings

15

A, B and C

signifies a 1,4-phenylene optionally substituted with 1 or 2 fluorine atoms, pyridine-2,5-diyl or pyrimidine-2,5-diyl and the other two rings each independently signify 1,4-phenylene optionally substituted with 1 or 2 fluorine atoms or trans-1,4-cyclohexylene;

20

Z¹ and Z⁴

each independently signify a single bond, -CH₂CH₂-, -CH₂O-, -OCH₂-, -C≡C-, -(CH₂)₄-, -(CH₂)₃O-, -O(CH₂)₃-, -CH=CH-CH₂O-, -OCH₂-CH=CH-, -CH=CH-(CH₂)₂- or -(CH₂)₂CH=CH-, with the proviso that the oxygen atom is not linked directly with the chiral dioxane ring;

30

Z² and Z³

each independently signify a single bond, -CH₂-CH₂-, -O-CH₂-, -CH₂-O-, -COO-, -OOC-, -C≡C-, -(CH₂)₄-, -O(CH₂)₃-,