

The present invention is concerned with novel chiral dopants for liquid crystals as well as liquid crystalline mixtures which contain such dopants and their use for optical and electro-optical devices.

Liquid crystal materials for cholesteric filters frequently contain, in addition to nematic liquid crystals, one or more optically active additives for the induction of a chiral structure. For example, for the use of such liquid crystals in optical filters a nematic liquid crystal is doped with optically active additives such that on the one hand a fixed rotational direction of the helix results and on the other hand the desired helical pitch is induced. In addition to the chiral properties of dopants, certain dielectric and optical properties are also desirable for optimal application in cholesteric filters. In order to achieve a bandwidth of the selective filter reflection which is as great as possible, chiral dopants having a large optical anisotropy are, for example, required. Further, cholesteric filters can be built with dopants of negative dielectric anisotropy which give rise to a planar orientation without disinclinations in electric fields. A high optical quality of the filter can thus be realised [M. Schadt, Liquid Crystals 14, 73 (1993)].

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Cholesteric liquid crystals reflect selective light in a wavelength range for which the wavelength is about the same as the helical pitch. The spectral width of this reflection light can be varied by suitable choice of the liquid crystal. The reflected light is completely circularly polarized. The rotational direction of the reflected light depends on the direction of rotation of the cholesteric helical structure. The opposite circularly polarized light is transmitted unimpaired. These properties can be used for the production of optical filters, polarizers, analyzers etc.

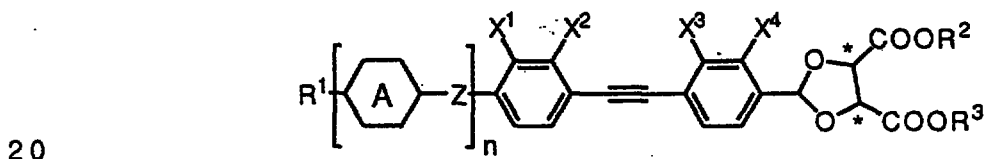
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Cholesteric liquid crystals for the above applications can preferably consist of a nematic or cholesteric basic material and

one or more chiral dopants, which permits a simple adjustment of the desired helical pitch.

In order to achieve cholesteric mixtures having a pitch in the range of the wavelength of visible light, the chiral dopants should have a twisting capacity which is as high as possible and should have a good solubility in usual liquid crystal materials. Furthermore, the chiral dopants should have an adequate stability, should have a good compatibility with the mesophase type of the liquid crystal material and should not restrict the mesophase range too severely. Such properties would also be desirable for chiral dopants in order to produce the highly twisted nematic structures referred to earlier, as their amount can be kept low in order that the properties of the liquid crystal material are influenced only immaterially.

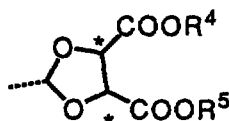
The invention is concerned with optically active compounds of the general formula



wherein

- ring A signifies 1,4-phenylene, which is unsubstituted or mono- or multiply-substituted and in which optionally one or two CH groups can be replaced by nitrogen, or trans-1,4-cyclohexylene;
- Z signifies a single covalent bond, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{O}-$ or $-\text{OCH}_2-$;
- $\text{X}^1, \text{X}^2, \text{X}^3, \text{X}^4$ each independently represent hydrogen or fluorine;
- R^1 signifies hydrogen, alkyl or alkenyl with 1 or, respectively, 2 to 12 carbon atoms, which is unsubstituted or mono- or multiply-substituted with fluorine or chlorine and in which one or two non-adjacent CH_2 groups can be replaced by $-\text{O}-$, or a group of the formula
- 35

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(a)

or - where R^1 is bonded to an aromatic ring -
also fluorine, chlorine, cyano, CF_3 , $OCHF_2$ or
 $-OCF_3$;

R^2, R^3, R^4, R^5 signify alkyl or alkenyl with 1 or, respectively,
2 to 8 carbon atoms;

n signifies 0 or 1; and

$*$ marks a centre of chirality.

The compounds of formula I accordingly have at least one
optically active dioxolane ring. The dioxolane set forth in
formula I has a chiral carbon atom in positions 4 and 5 (i.e.
adjacent to the residues $-COOR^2$ and $-COOR^3$). It will be evident
to a person skilled in the art that in order to achieve optical
activity the carbon atom in position 4 of the dioxolane ring must
be present wholly or predominantly in the R or S form and, where
 R^2 and R^3 are identical, the carbon atom in position 5 of the
dioxolane ring should have wholly or predominantly the same
configuration as the carbon atom in position 4 or basically can
also have a R/S ratio of 50:50. In order to achieve a twisting
capacity which is as high as possible, the carbon atom in position
4 of the dioxolane ring should preferably be present in the optically
most possible pure form in the R or S configuration and the
carbon atom in position 5 of the dioxolane ring should be present
in the optically most possible pure form in either configuration,
which intensifies the twisting capacity. The (4R,5R) isomers and
the (4S,5S) isomers of the compounds of formula I are preferred
optical isomers having a high twisting capacity.

The compounds of formula I have a very good solubility in
usual liquid crystal materials and permit a very high twisting of
the liquid crystal structure. In contrast to known materials
having a high twisting capacity, the clearing points of liquid
crystals are, moreover, as a rule not lowered or lowered only

insignificantly upon the addition of compounds of formula I. Many of the compounds in accordance with the invention even themselves have liquid crystalline properties. The compounds of formula I can be manufactured readily, have a relatively low viscosity and an adequate stability towards electric and magnetic fields. They therefore fulfil the requirements referred to above in an optimal manner.

The properties of the compounds of formula I can be varied depending on the choice and the significance of ring A and the substituents R^1 , R^2 , R^3 , X^1 , X^2 , X^3 and X^4 . For example, an additional aromatic ring leads to higher values of the optical anisotropy. Polar end groups R^1 , such as cyano, halogen, trifluoromethyl or trifluoromethoxy, or a ring, such as pyrimidine-2,5-diyl, increase e.g. the dielectric anisotropy. Lateral halogen substituents contribute to the dielectric constant not only parallel to, but also perpendicular to the longitudinal axis of the molecule, which can be used, depending on the substitution pattern, to increase or reduce the dielectric anisotropy or to produce a negative dielectric anisotropy. Further, a possible tendency to form highly ordered smectic phases can be largely suppressed for the most part and often the solubility can also be improved by lateral substituents on one or more rings. Furthermore, the elastic properties, the threshold potentials, the response times, the mesophases etc. can be modified by a C=C double bond in the side-chain.

The present invention therefore permits, in addition to the induction of a high twisting, additionally the optimization of liquid crystalline, optical and electro-optical properties in a wide range according to application and desired properties.

The term "1,4-phenylene, which is unsubstituted or mono- or multiply-substituted and in which optionally 1 or 2 CH groups is/are replaced by nitrogen," embraces groups such as 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-cyano-1,4-phenylene, 2,3-dicyano-1,4-phenylene, 2-methyl-1,4-phenylene,

pyridine-2,5-diyl, pyrazine-2,5-diyl, pyrimidine 2,5-diyl and the like. 1,4-Phenylene, 2-fluoro-1,4-phenylene, 2,3-difluoro-1,4-phenylene, pyridine-2,5-diyl, pyrimidine-2,5-diyl and the like are preferred groups.

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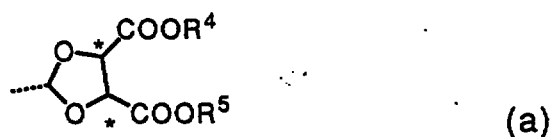
The term "alkyl or alkenyl with 1 or, respectively, 2 to 12 carbon atoms, which is unsubstituted or mono- or multiply-substituted by fluorine or chlorine and in which one or two non-adjacent CH₂ groups can be replaced by -O-," embraces in the scope of the present invention straight-chain and branched (optionally chiral) residues such as alkyl, 1E-alkenyl, 3E-alkenyl, 4-alkenyl, alkenyl having a terminal double bond, alkoxy, 2E-alkenyloxy, 3-alkenyloxy, alkenyloxy having a terminal double bond, alkoxyalkyl, alkenyloxyalkyl, 1-fluoroalkyl, 2-fluoroalkyl, 2-fluoroalkoxy, 1-chloroalkyl, 2-chloroalkyl, 2-chloroalkoxy, 1-methylalkyl, 2-methylalkyl, 1-methylalkoxy, 2-methylalkoxy and the like. Examples of preferred residues are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, 1-methylpropyl, 1-methylheptyl, 2-methylbutyl, 3-methylpentyl, vinyl, 1E-propenyl, 1E-butenyl, 1E-pentenyl, 1E-hexanyl, 1E-heptenyl, 3-butenyl, 3E-pentenyl, 3E-hexenyl, 3E-heptenyl, 4-pentenyl, 4Z-hexenyl, 4Z-heptenyl, 5-hexenyl, 6-heptenyl, 7-octenyl, 8-nonenyl, 9-decenyl, 10-undecenyl, 11-dodecenyl, methoxy, ethoxy, propyloxy, butyloxy, pentyloxy, hexyloxy, heptyloxy, octyloxy, nonyloxy, decyloxy, undecyloxy, dodecyloxy, 1-methylpropyloxy, 1-methylheptyloxy, 2-methylbutyloxy, 3-methylpentyloxy, allyloxy, 2E-butenyloxy, 2E-pentenyl, 2E-hexenyloxy, 2E-heptenyloxy, 3-butenyloxy, 3Z-pentenyl, 3Z-hexenyloxy, 3Z-heptenyloxy, 4-pentenyl, 5-hexenyloxy, 6-heptenyloxy, 7-octenyloxy, 8-nonenyl, 9-decenyl, 10-undecenyl, 11-dodecenyl, methoxymethyl, ethoxymethyl, propyloxymethyl, allyloxymethyl, 1-fluoropropyl, 1-fluoropentyl, 1-chloropropyl, 2-fluoropropyl, 2-fluoropentyl, 2-chloropropyl, 2-fluoropropyloxy, 2-fluorobutyloxy, 2-fluoropentyloxy, 2-fluorohexyloxy, 2-chloropropyloxy, chlorobutyloxy and the like.

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"Alkyl" in the residues R^2 , R^3 , R^4 and R^5 signifies straight-chain and branched, optionally chiral groups with 1 to 12 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, 2-butyl (= 1-methylpropyl), 2-methylbutyl, pentyl, hexyl, heptyl, octyl, 2-octyl (= 1-methylheptyl), and the like. Preferred alkyl residues in R^2 , R^3 , R^4 and R^5 are C_1 - C_5 -alkyl residues, especially methyl, ethyl, n-propyl, n-butyl and n-pentyl.

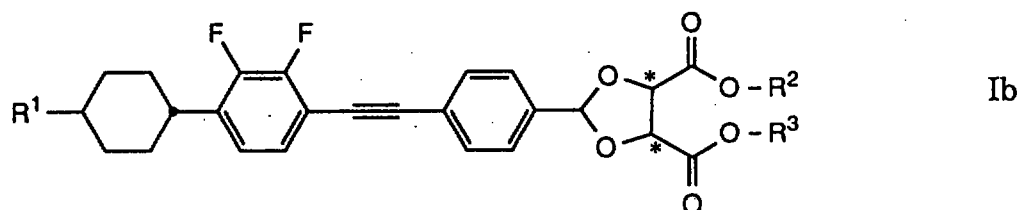
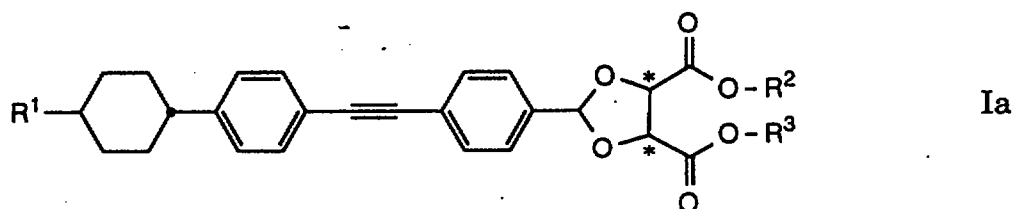
Preferred compounds of formula I are those in which $n = 1$. Further, those compounds of formula I in which X^1 and X^2 or X^3 and X^4 signify fluorine are preferred. In the case of particularly preferred compounds of formula I R^1 signifies alkyl, alkenyl, alkoxy, alkenyloxy, alkoxyalkyl or alkoxyalkenyl with 1 or, respectively, 2 to 6 carbon atoms.

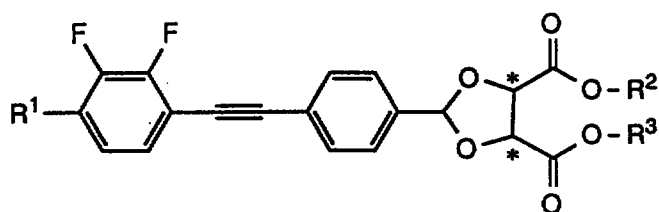
In particular, those compounds of formula I in which R^1 signifies a group of the formula



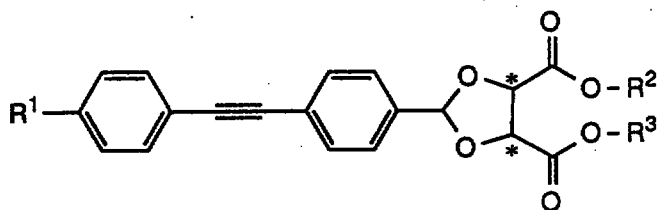
and $n = 0$ or 1 are preferred.

Especially preferred compounds of formula I are therefore optically active compounds of the following formulae



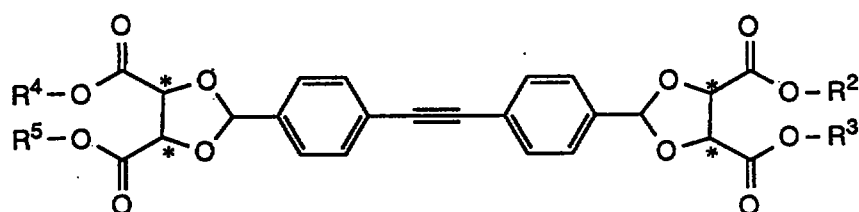


Ic

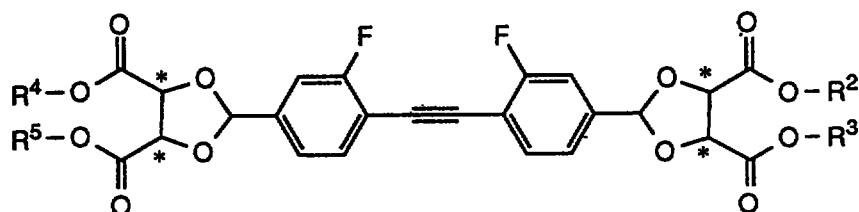


Ie

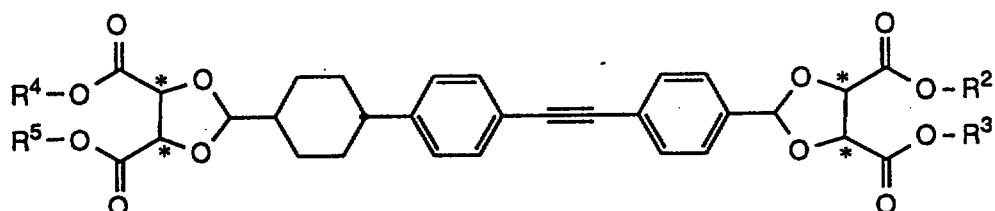
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If



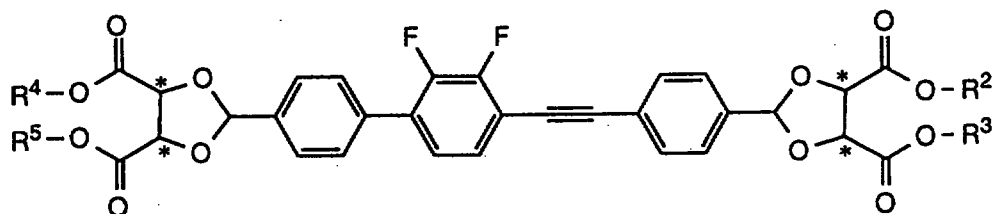
Ig



Ih

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and



Ii

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wherein R¹ signifies hydrogen, alkyl or alkenyl with 1 or, respectively, 2 to 12 carbon atoms, which is unsubstituted

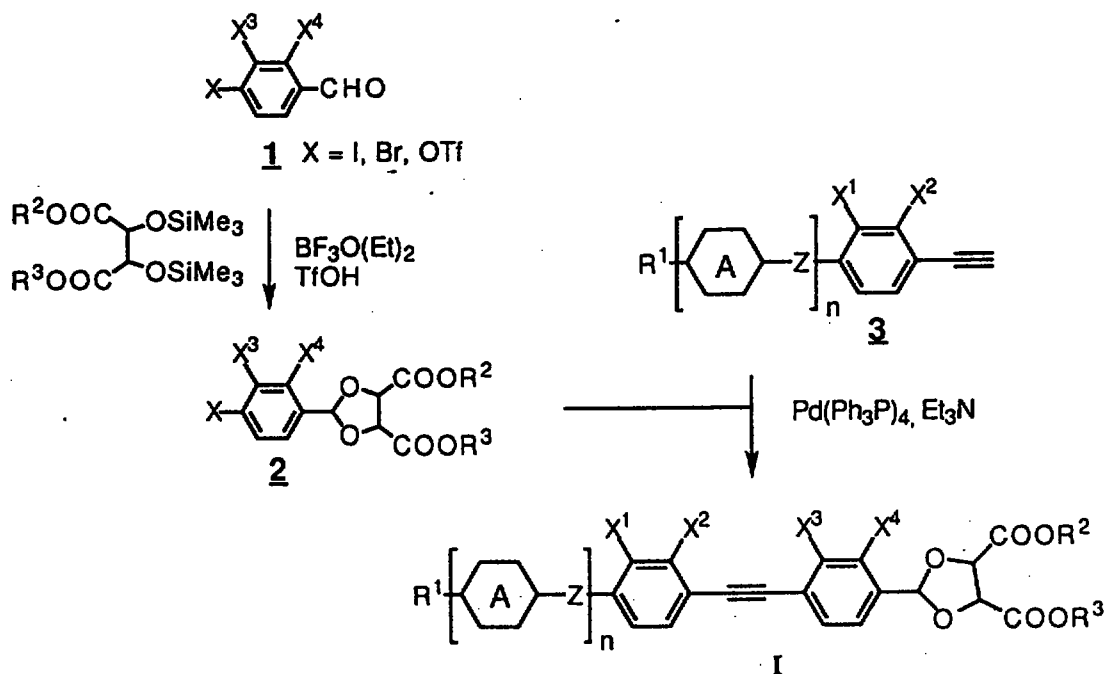
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or mono- or multiply-substituted by fluorine or chlorine and in which one $-\text{CH}_2$ -group can be replaced by $-\text{O}-$, or $-$ where R^1 is bonded to an aromatic ring - also fluorine, chlorine, cyano, $-\text{CF}_3$, $-\text{OCHF}_2$ or OCF_3 ; and R^2 , R^3 , R^4 and R^5 have the significances given above.

Of the compounds of formulae I f to I i there are preferred those in which R^2 is the same as R^4 and R^3 is the same as R^5 . Those compounds of formulae I f to I i in which R^2 and R^3 are the same as R^4 and R^5 are particularly preferred.

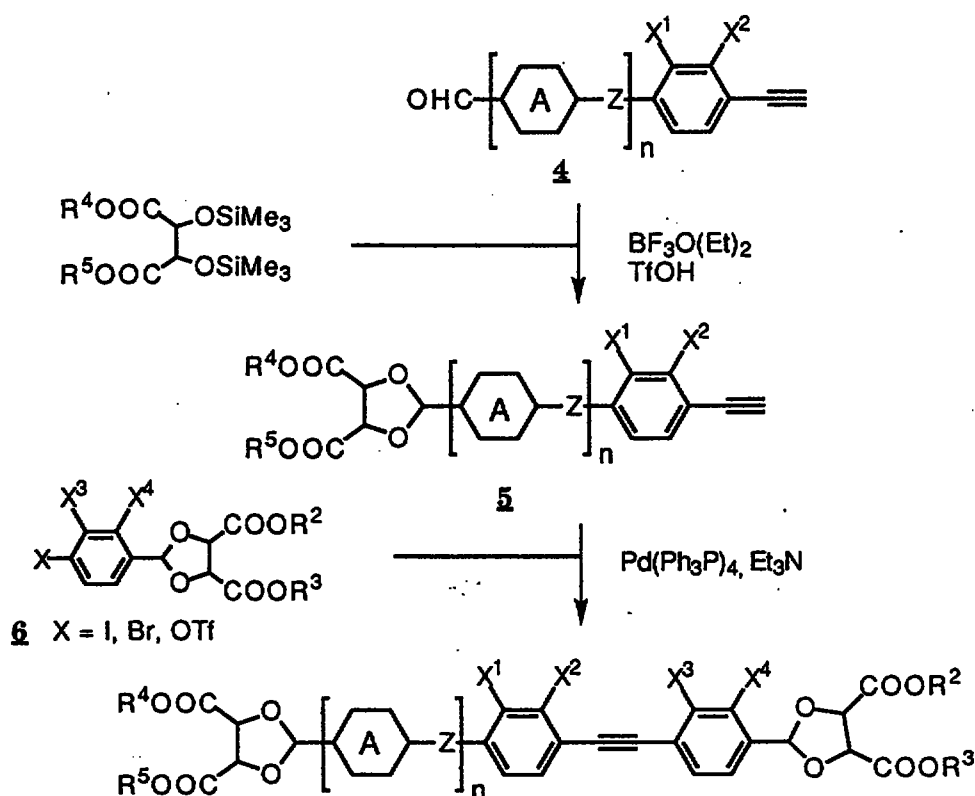
The compounds in accordance with the invention can be manufactured readily in a manner known per se. Acetylene couplings, as generally used for the manufacture of tolanses, are especially suitable. Thus, for example, a phenylacetylene derivative **3** can be coupled with an optically active phenyldioxolane **2**, which carries in the para-position a suitable substituent such as, for example, iodine, bromine or trifluoromethylsulphonate (OTf) as the leaving group, with the aid of a suitable palladium catalyst (Scheme 1).

Scheme 1



This method is especially suitable for the manufacture of compounds of formulae Ia to Ie. Compounds of formula I in which R¹ signifies a dioxolane ring and in which R⁴ and R⁵ are different from R² and R³ can also be manufactured in this manner. The method is illustrated in more detail in Scheme 2.

Scheme 2



Compounds of general formulae Ia to Ie, or compounds of formulae If to Ii in which R² is the same as R⁴ and R³ is the same as R⁵, can conveniently be manufactured as shown in Scheme 3. In this, the dioxolane ring or both dioxolane rings are formed at the end of the synthesis by acetalization of a mono- or dialdehyde with the desired tartaric acid diester.



The acetylene derivatives set forth as starting materials in Schemes 1 and 2 are known or are analogues of known compounds. Their preparation has been described repeatedly in the literature, for example in EP-A 501268 or EP-A No. 0593997. Moreover, they can be prepared in accordance with Scheme 3 in a manner known per se by coupling with trimethylsilylacetylene and subsequent hydrolysis.

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The formation of the dioxolane ring takes place by acetalizing the aldehyde starting material with a suitable tartaric acid diester, preferably in silylated form. Analogous reactions are described, for example, in THL 21, 1357 (1980).

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In the case of aldehydes which have sufficient stability, the acetalization to the dioxolane can also be carried out using boron trifluoride etherate.

10

The invention is also concerned with liquid crystalline mixtures containing a liquid crystalline carrier material and one or more optically active compounds of formula I. Suitable carrier materials are basically all liquid crystal materials which have a twistable liquid crystal phase with an adequate mesophase range.

15

The compounds of formula I are especially suitable as chiral dopants for nematic or cholesteric carrier materials. 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.

20

The content of chiral dopant of formula I is determined essentially by its twisting capacity and the desired pitch. The content of chiral dopant can therefore vary in a wide range depending on the application and can be, for example, about 0.1-30 wt. %. For indicating devices based on liquid crystals having a twisted nematic structure a pitch of about 3-40 μm is mainly required depending on the type of cell and thickness of cell and therefore a correspondingly smaller amount is sufficient. On the other hand, for applications which are based on the reflection of visible light by cholesteric layers, pitches of less than 2 μm , for example about 0.4-0.6 μm , are necessary, which requires a correspondingly higher content of chiral dopant.

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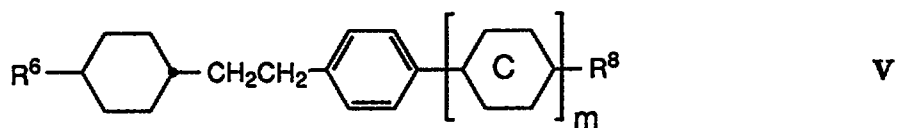
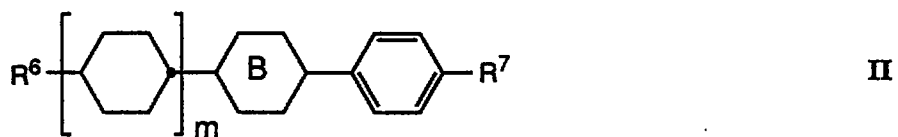
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Suitable liquid crystalline carrier materials are known in large numbers and are commercially available. As a rule, liquid crystalline mixtures containing 2 or more components as carrier materials are preferred. Basically, however, one liquid crystalline compound can also be used as the carrier material when it has a sufficiently broad mesophase.

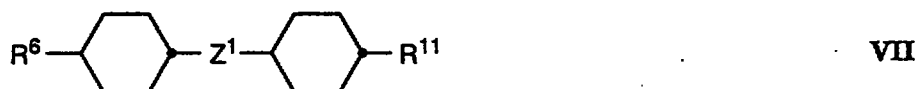
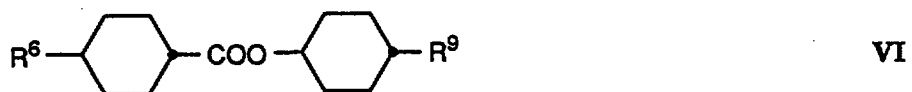
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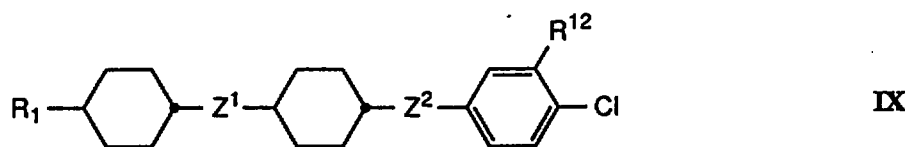
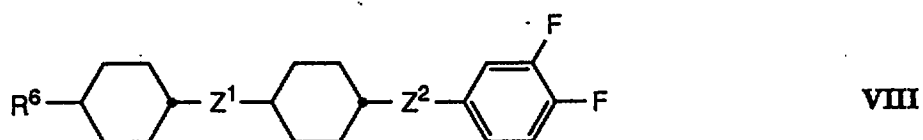
The mixtures in accordance with the invention preferably contain, in addition to one or more compounds of formula I, one or more compounds from the group of compounds of the general formulae



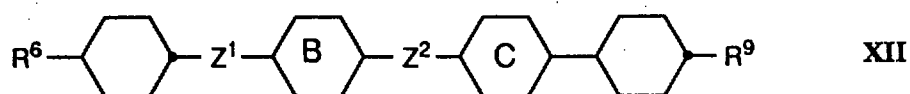
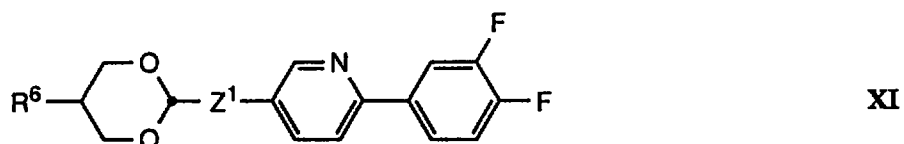
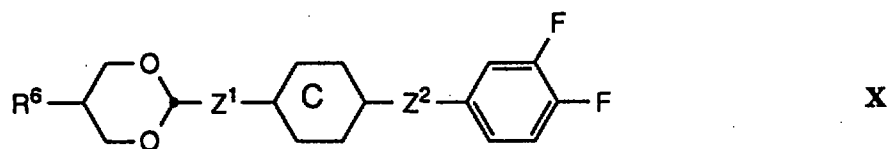
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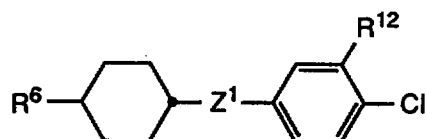
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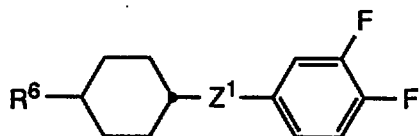
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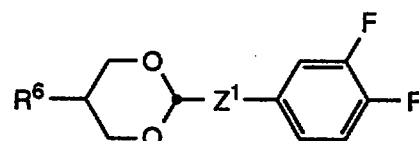
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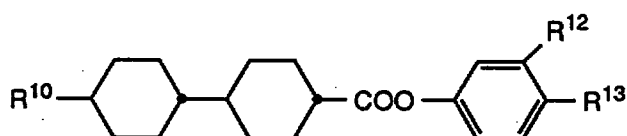
XIII



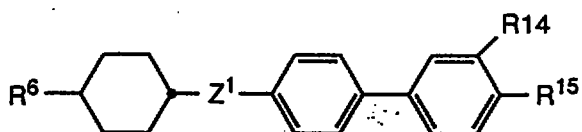
XIV



XV



XVII



XVIII

wherein

R^6, R^9 signify alkyl, alkoxyalkyl, 3E-alkenyl, 4-alkenyl or on saturated rings also 1E-alkenyl;

m signifies 0 or 1;

ring B signifies 1,4-phenylene, pyridine-2,5-diyl, pyrimidine-2,5-diyl, trans-1,4-cyclohexylene or trans-1,3-dioxane-2,5-diyl;

R^7 represents cyano, isothiocyanato, fluorine, alkyl, 3E-alkenyl, 4-alkenyl, alkoxy, 2E-alkenyloxy, 3-alkenyloxy or 1-alkynyl;

ring C signifies 1,4-phenylene or trans-1,4-cyclohexylene;

R^8 represents alkyl, 3E-alkenyl, 4-alkenyl or on trans-1,4-cyclohexylene also 1E-alkenyl or on 1,4-phenylene also cyano, isothiocyanato, alkoxy, 2E-alkenyloxy or 3-alkenyloxy;

R^{10} signifies alkyl, 1E-alkenyl, 3E-alkenyl or 4-

		alkenyl;
	R ¹¹	represents cyano, alkyl, 1E-alkenyl, 3E-alkenyl, 4-alkenyl, alkoxy, 2E-alkenyloxy, 3-alkenyloxy, alkoxymethyl or (2E-alkenyl)oxymethyl;
5	Z ¹ , Z ²	each independently signify a single covalent bond or -CH ₂ CH ₂ -, with two aromatic rings always being linked by a single covalent bond;
	R ¹²	signifies hydrogen, fluorine or chlorine;
	R ¹³	represents cyano, fluorine or chlorine;
10	R ¹⁴	represents hydrogen or fluorine; and
	R ¹⁵	represents fluorine or chlorine.

The above term "saturated ring" embraces trans-1,4-cyclohexylene and trans-1,3-dioxane-2,5-diyl. Each of the
 15 residues R⁶ to R¹¹ preferably has 1 or, respectively, 2 to 12 carbon atoms, especially 1 or, respectively, 2 to 7 carbon atoms. Straight-chain residues are generally preferred.

The term "alkyl" preferably signifies in this connection
 20 straight-chain residues with 1 to 12 carbon atoms, preferably with 1 to 7 carbon atoms, such as, for example, methyl, ethyl, propyl, butyl, pentyl, hexyl or heptyl.

The term "alkoxyalkyl" preferably signifies in this
 25 connection straight-chain residues with 1 to 12 carbon atoms, especially with 1 to 7 carbon atoms, such as, for example, methoxymethyl, ethoxymethyl, propyloxymethyl, butyloxymethyl, methoxypropyl and the like.

30 The term "alkoxy" preferably signifies in this connection straight-chain residues with 1 to 12 carbon atoms, especially with 1 to 7 carbon atoms, such as, for example, methoxy, ethoxy, propyloxy, butyloxy, pentyloxy, hexyloxy, heptyloxy and the like.

35 The term "1E-alkenyl" preferably signifies in this connection straight-chain alkenyl residues with 2 to 12, especially with 2 to 7, carbon atoms in which the double bond is situated in the

1-position, such as, for example, vinyl, 1E-propenyl, 1E-butenyl, 1E-pentyl, 1E-hexenyl, 1E-heptenyl and the like.

5 The term "3E-alkenyl" preferably signifies in this connection straight-chain alkenyl residues with 4 to 12, especially with 4 to 7, carbon atoms in which the double bond is situated in the 3-position, such as, for example, 3-butenyl, 3E-pentenyl, 3E-hexenyl, 3E-heptenyl and the like.

10 The term "4-alkenyl" preferably signifies in this connection straight-chain alkenyl residues with 5 to 12 carbon atoms in which the double bond is situated in the 4-position, such as, for example, 4-pentenyl, 4-hexenyl, 4-heptenyl and the like.

15 The term "2E- or 3Z-alkenyloxy" preferably signifies in this connection straight-chain alkenyloxy residues with 3 or 4 to 12 carbon atoms, especially with 3 or 4 to 7 carbon atoms, in which the double bond is situated in the 2- or 3-position and E or Z indicates the preferred configuration, such as, for example, allyloxy,
20 2E-butenyloxy, 2E-pentenylöxy, 2E-hexenyloxy, 2E-heptenyloxy, 3-butenyloxy, 3Z-pentenylöxy, 3Z-hexenyloxy, 3Z-heptenyloxy, 4-pentenylöxy, 5-hexenyloxy, 6-heptenyloxy and the like.

25 The term "1-alkynyl" preferably signifies in this connection straight-chain alkynyl residues with 2 to 12, especially with 2 to 7, carbon atoms in which the triple bond is situated in the 1-position, such as, for example, ethynyl, 1-propynyl, 1-butylnyl, 1-pentylnyl and the like.

30 The manufacture of the liquid crystalline mixtures and of the electro-optical devices can be effected in a manner known per se.

35 The invention is illustrated in more detail by the following Examples. In connection with liquid crystal phases and phase transitions C signifies a crystalline phase, S_B signifies a smectic B phase, N signifies a nematic phase, N* signifies a cholesteric phase and I signifies the isotropic phase. The helical pitch is

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denoted by p and the wavelength of the selectively reflected, circular polarized light is denoted by $\lambda_{\max}$. Optical antipodes have in each case "mirror image properties", i.e. the same melting points etc., but lead to opposite helical direction of rotation and opposite circular polarization of the reflected light.

Example 1

a) 18.8 ml of butyllithium in hexane were added dropwise under nitrogen at -50°C to 4 ml of ethynyltrimethylsilane in 50 ml of anhydrous tetrahydrofuran and after 30 min. 57 ml of 1M ethereal zinc chloride solution were added dropwise. Thereupon, the cooling was removed and the mixture was left to react for 1 hr. Then, the reaction solution was cooled to 0°C and 5 g of 4-(trans-4-propylcyclohexyl)phenyl trifluoromethylsulphonate in 50 ml of dimethylformamide, 0.824 g of tetrakis(triphenylphosphine) palladium(0) and 1.2 g of lithium chloride were added in succession. The reaction mixture was heated to 85°C and left to react at this temperature overnight. In order to complete the reaction an equal amount of the zinc ethynyltrimethylsilane solution, prepared as above, was thereupon added and the mixture was left to react at 85°C . After one hour it was cooled, treated with 20 ml of water, partitioned between 1N sulphuric acid and pentane and the separated organic phase was washed with water. The organic phase was dried over magnesium sulphate, filtered over Celite and evaporated completely. This gave 3.82 g of 1[-4-(trans-4-propylcyclohexyl)phenyl]-2-trimethylsilylacetylene as a solid mass (GC purity 97%), which was used directly in the next step.

b) A mixture of 3.8 g of 1[-4-(trans-4-propylcyclohexyl)phenyl]-2-trimethylsilylacetylene, 0.4 g of potassium carbonate and 50 ml of methanol/ether (2:1) was stirred at room temperature for 1 hr. Then, the mixture was partitioned between water and ether and the organic phase was washed in succession with saturated sodium chloride solution and water, dried over magnesium sulphate, filtered over Celite and evaporated. After chromatography of the residue over 150 silica gel with cyclo-

hexane 1.95 g of 4-(trans-4-propylcyclohexyl)phenylacetylene were obtained as a colourless solid.

c) 0.54 ml of boron trifluoride etherate was added dropwise at 0°C to a solution of 5 g of 4-bromobenzaldehyde and 13.2 g of dibutyl (2R,3R)-2,3-bis-trimethylsilyloxy-glutarate and then the mixture was left to react for 30 min. Thereafter, 0.24 ml of trifluoromethanesulphonic acid was added at 0°C and the mixture was left to react for 30 min. Then, the cooling bath was removed and the reaction mixture was stirred at room temperature for 4 hrs. Subsequently, the reaction solution was poured into a saturated aqueous sodium bicarbonate solution, partitioned between water and methylene chloride and the organic phase was separated, dried over magnesium sulphate, filtered over Celite and evaporated. Chromatography of the residue on 250 g of silica gel with ethyl acetate/cyclohexane (1:9) gave 9.3 g of dibutyl (4R,5R)-2-(4-bromophenyl)-1,3-dioxolane-4,5-dicarboxylate (GC purity 98%).

d) 1.45 ml of an about 1.6M butyllithium solution in hexane were added dropwise at -50°C to a solution of 0.5 g of 4-(trans-4-propylcyclohexyl)phenylacetylene in 5 ml of dry tetrahydrofuran and the mixture was left to react at this temperature for 30 min. Then, 4.4 ml of a 1M zinc chloride solution in ether were added dropwise, the cooling bath was removed and the mixture was left to react for 30 min. Thereupon, the mixture was cooled to 0°C and at this temperature a solution of 0.95 g of dibutyl (4R,5R)-2-(4-bromophenyl)-1,3-dioxolane-4,5-dicarboxylate in 5 ml of dry tetrahydrofuran was added dropwise and thereafter 0.128 g of tetrakis(triphenylphosphine) palladium(0) was added. The reaction mixture was then heated to 60°C for 15 hrs., then cooled, partitioned between water and ether and the organic phase was separated and dried over magnesium sulphate. Thereupon, it was filtered over Celite, the solvent was evaporated and the residue was chromatographed on 100 g of silica gel with 5% ethyl acetate in cyclohexane. Further purification with active charcoal in isopropanol and two-fold crystallization from isopropanol gave 0.23 g of dibutyl



(4R,5R)-2-{4-[4-(trans-4-propylcyclohexyl)phenylethynyl]-phenyl}-1,3-dioxolane-4,5-dicarboxylate, m.p. (K-N*) 74.9°C, cl.p. (N*-I) 78.3°C

5 The following compounds can be prepared in an analogous manner:

- Diethyl (4R,5R)-2-{4-[4-(trans-4-propylcyclohexyl)phenylethynyl]phenyl}-1,3-dioxolane-4,5-dicarboxylate;
- 10 dibutyl (4R,5R)-2-{4-[4-(trans-4-pentylcyclohexyl)phenylethynyl]phenyl}-1,3-dioxolane-4,5-dicarboxylate;
- dibutyl (4R,5R)-2-{4-[2,3-difluoro-4-(trans-4-propylcyclohexyl)phenylethynyl]phenyl}-1,3-dioxolane-4,5-dicarboxylate;
- 15 dibutyl (4R,5R)-2-{2,3-difluoro-4-[4-(trans-4-propylcyclohexyl)phenylethynyl]phenyl}-1,3-dioxolane-4,5-dicarboxylate; m.p. (K-I) 73.4°C, cl.p. (N*-I) 68.2°C;
- dibutyl (4R,5R)-2-{3-fluoro-4-[2-fluoro-4-(trans-4-propylcyclohexyl)phenylethynyl]phenyl}-1,3-dioxolane-4,5-dicarboxylate;
- 20 dibutyl (4R,5R)-2-[4-(4-propyl-phenylethynyl)phenyl]-1,3-dioxolane-4,5-dicarboxylate;
- dibutyl (4R,5R)-2-{4-[4-(2,3-difluoro-4-propylphenyl)phenylethynyl]phenyl}-1,3-dioxolane-4,5-dicarboxylate;
- 25 dibutyl (4R,5R)-2-{4-[4-(2,3-difluoro-4-pentylphenyl)phenylethynyl]phenyl}-1,3-dioxolane-4,5-dicarboxylate;
- dibutyl (4R,5R)-2-{4-[2,3-difluoro-4-(4-propylphenyl)phenylethynyl]phenyl}-1,3-dioxolane-4,5-dicarboxylate;
- 30 dibutyl (4R,5R)-2-{4-[4-(2,3-difluoro-4-propyloxyphenyl)phenylethynyl]phenyl}-1,3-dioxolane-4,5-dicarboxylate;
- dibutyl (4R,5R)-2-[4-(2,3-difluoro-4-propyl-phenylethynyl)phenyl]-1,3-dioxolane-4,5-dicarboxylate m.p. (K-I) 35°C;
- dibutyl (4R,5R)-2-[2,3-difluoro-4-(4-propyl-phenylethynyl)phenyl]-1,3-dioxolane-4,5-dicarboxylate m.p. (K-I)
- 35 75.3°C;
- dibutyl (4R,5R)-2-[3-fluoro-4-(2-fluoro-4-propyl-phenylethynyl)phenyl]-1,3-dioxolane-4,5-dicarboxylate;

dibutyl (4R,5R)-2-[4-(2,3-difluoro-4-pentyl-phenyl-ethynyl)phenyl]-1,3-dioxolane-4,5-dicarboxylate;

diethyl (4R,5R)-2-[4-(2,3-difluoro-4-pentyl-phenyl-ethynyl)phenyl]-1,3-dioxolane-4,5-dicarboxylate;

5 dibutyl (4R,5R)-2-[4-[4-(2-(trans-4-propylcyclohexyl)-ethyl)phenylethynyl]phenyl]-1,3-dioxolane-4,5-dicarboxylate;

dibutyl (4R,5R)-2-[4-[2,3-difluoro-4-(2-(trans-4-propylcyclohexyl)ethyl)phenylethynyl]phenyl]-1,3-dioxolane-4,5-dicarboxylate;

10

Example 2

a) A mixture of 1 g of 4-ethynyl-benzaldehyde, 1.56 g of 4-bromobenzaldehyde, 0.22 g of tetrakis(triphenylphosphine)-
15 palladium(0) and 10 ml of triethylamine was stirred at 80°C for 16 hrs. Then, the reaction mixture was partitioned between water and methylene chloride and the organic phase was separated, dried over magnesium sulphate, filtered and evaporated. This gave 1.54 g of tolane-4,4'-dicarboxaldehyde as
20 a solid brownish residue (GC purity 98.8%), which was used without further purification for the following step.

b) A suspension of 0.5 g of tolane-4,4'-dicarboxaldehyde in 5 ml of methylene chloride was added to a mixture of 2.6 g of
25 dibutyl (2R,3R)-2,3-bis-trimethylsilyloxy-glutarate, 0.039 ml of trimethylsilyl trifluoromethanesulphonate and 10 ml of methylene chloride and the reaction mixture was stirred at room temperature for 4 hrs. Thereupon, a further 0.04 ml of trimethylsilyl trifluoromethanesulphonate was added and the
30 mixture was stirred at room temperature for a further 64 hrs. After adding 0.5 ml of pyridine the reaction mixture was partitioned between sodium bicarbonate and methylene chloride and the organic phase was separated, dried over magnesium sulphate, filtered over a mixture of Celite/Alox (neutral, act. III)
35 and evaporated. Chromatography of the residue on 100 g of silica gel with 5% ethyl acetate in toluene and subsequent crystallization from hexane and then from isopropanol gave

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0.88 g of 4,4'-bis-[(4R,5R)-4,5-dibutyloxycarbonyl-1,3-dioxolan-2-yl]tolane as white crystals, m.p. 54°C.

The following compounds can be prepared in an analogous manner:

4,4'-Bis-[(4R,5R)-4,5-diethoxycarbonyl-1,3-dioxolan-2-yl]tolane;

4,4'-bis-[(4R,5R)-4,5-dimethoxycarbonyl-1,3-dioxolan-2-yl]tolane;

2,3-difluoro-4,4'-bis-[(4R,5R)-4,5-dibutyloxycarbonyl-1,3-dioxolan-2-yl]tolane;

2,2'-difluoro-4,4'-bis-[(4R,5R)-4,5-dibutyloxycarbonyl-1,3-dioxolan-2-yl]tolane, m.p. (K-I) 70°C, cl.p. monotropic (S*-I) 59.8°C;

4-{4-[(4R,5R)-4,5-diethoxycarbonyl-1,3-dioxolan-2-yl]phenyl}-4'-[(4R,5R)-4,5-dibutyloxycarbonyl-1,3-dioxolan-2-yl]tolane;

4-{2,3-difluoro-4-[(4R,5R)-4,5-diethoxycarbonyl-1,3-dioxolan-2-yl]phenyl}-4'-[(4R,5R)-4,5-dibutyloxycarbonyl-1,3-dioxolan-2-yl]tolane;

2,3-difluoro-4-{4-[(4R,5R)-4,5-dibutyloxycarbonyl-1,3-dioxolan-2-yl]phenyl}-4'-[(4R,5R)-4,5-dibutyloxycarbonyl-1,3-dioxolan-2-yl]tolane, m.p. (K-I) 73.1°C

4-{4-[(4R,5R)-4,5-diethoxycarbonyl-1,3-dioxolan-2-yl]phenyl}-2',3'-difluoro-4'-[(4R,5R)-4,5-dibutyloxycarbonyl-1,3-dioxolan-2-yl]tolane;

Example 3

30

The following liquid crystal basic mixture BM-1 was used to measure the induced pitch and its temperature dependence in liquid crystal materials:

35	5.36 wt.% of	4'-ethyl-4-cyanobiphenyl,
	3.8 "	4'-propyl-4-cyanobiphenyl,
	6.08 "	4'-butyl-4-cyanobiphenyl,
	6.53 "	4-(trans-4-propylcyclohexyl)benzonitrile,

	14.64	"	4-(trans-4-pentylcyclohexyl)benzonitrile,
	5.21	"	4-ethyl-1-(trans-4-propylcyclohexyl)benzene,
	16.54	"	4-ethoxy-1-[2-(trans-e-propylcyclohexyl)-ethyl]benzene,
5	5.60	"	4"-pentyl-4-cyano-p-terphenyl,
	5.71	"	4'-(trans-4-pentylcyclohexyl)-4-cyanobiphenyl,
	15.59	"	1-[2-trans-4-butylcyclohexyl)ethyl]-4-(trans-4-pentylcyclohexyl)benzene,
	4.74	"	1-[2-trans-4-butylcyclohexyl)ethyl]-4'-(trans-4-pentylcyclohexyl)biphenyl,
10	7.59	"	1-[2-trans-4-butylcyclohexyl)ethyl]-4'-(trans-4-pentylcyclohexyl)-1,1'-ethylenedibenzene,
	2.84	"	1-[2-trans-4-propylcyclohexyl)ethyl]-cyclohexanecarboxylic acid 4-cyanophenyl ester.

15

Liquid crystal basic mixture BM-1 was treated with 1.0 wt.% of each of the following optically active dopants:

20	D-1	=	dibutyl 4R,5R)-2-{4-[4-(trans-4-propylcyclohexyl)-phenylethynyl]phenyl}-1,3-dioxolane-4,5-dicarboxylate,
	D-2	=	dibutyl (4R,5R)-2-{2,3-difluoro-4-[4-(trans-4-propylcyclohexyl)phenylethynyl]phenyl}-1,3-dioxolane-4,5-dicarboxylate,
25	D-3	=	dibutyl (4R,5R)-2-[4-(2,3-difluoro-4-propylphenylethynyl)phenyl]-1,3-dioxolane-4,5-dicarboxylate,
	D-4	=	dibutyl (4R,5R)-2-[2,3-difluoro-4-(4-propylphenylethynyl)phenyl]-1,3-dioxolane-4,5-dicarboxylate,
	D-5	=	4,4'-bis-[(4R,5R)-4,5-dibutyloxycarbonyl-1,3-dioxolan-2-yl]tolane,
30	D-6	=	4,4'-bis-[(4S,5S)-4,5-dibutyloxycarbonyl-1,3-dioxolan-2-yl]tolane,
	D-7	=	2,2'-difluoro-4,4'-bis-[(4R,5R)-4,5-dibutyloxycarbonyl-1,3-dioxolan-2-yl]tolane,
35	D-8	=	2,3-difluoro-4-{4-[(4R,5R)-4,5-dibutyloxycarbonyl-1,3-dioxolan-2-yl]-phenyl}-4'-[(4R,5R)-4,5-dibutyloxycarbonyl-1,3-dioxolan-2-yl]tolane.

The results compiled in Table 1 were obtained for the chiral doped mixtures, with A, B and C denoting the parameters of the equation

$$\frac{1}{pc} = A + BT_1 + CT_1^2$$

and p, c and T_1 having the following significances:

- T_1 = T-22°C
 T = temperature in °C
 p = pitch in mm (a positive value signifies dextrorotating helical structure and a negative value signifies levorotating helical structure)
 C = concentration of the optically active dopant in wt.%.

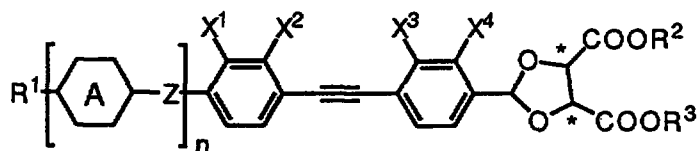
Table 1: Measured parameter of 1 wt.% of the respective dopant in the basic mixture BM-1 at 22°C

Dopant	A [10 ⁻² ·mm ⁻¹ ·wt.% ⁻¹]	B [10 ⁻⁴ ·mm ⁻¹ ·wt.% ⁻¹]	C [10 ⁻⁶ ·mm ⁻¹ ·wt.% ⁻¹]	p.c (22°C) [mm·wt.%]
D-1	-16.9	4.99	-1.84	-5.90
D-2	-10.5	-0.77	-0.61	-9.50
D-3	-17.2	7.40	-3.30	-5.81
D-4	-11.9	-0.34	-1.51	-8.38
D-5	-26.1	8.39	-4.52	-3.83
D-6	25.7	-7.93	2.77	3.89
D-7	-18.0	2.0	-0.76	-5.57
D-8	-22.1	2.70	-0.70	-4.53



Claims

1. Optically active compounds of the general formula:



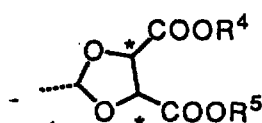
wherein

ring A signifies 1,4-phenylene, which is unsubstituted or mono- or multiply-substituted and in which optionally one or two CH groups can be replaced by nitrogen, or trans-1,4-cyclohexylene;

Z signifies a single covalent bond, -CH₂CH₂-, -CH₂O- or -OCH₂-;

X¹, X², X³, X⁴ each independently represent hydrogen or fluorine;

R¹ signifies hydrogen, alkyl or alkenyl with 1 or, respectively, 2 to 12 carbon atoms, which is unsubstituted or mono- or multiply-substituted with fluorine or chlorine and in which one or two non-adjacent CH₂ groups can be replaced by -O-, or a group of the formula



(a)

or - where R¹ is bonded to an aromatic ring - also fluorine, chlorine, cyano, CF₃, OCHF₂ or -OCF₃;

R², R³, R⁴, R⁵ signify alkyl or alkenyl with 1 or, respectively, 2 to 8 carbon atoms;

n signifies 0 or 1; and

* marks a centre of chirality.

2. Optically active compounds according to claim 1, wherein the centres of chirality in the 4-position and 5-position

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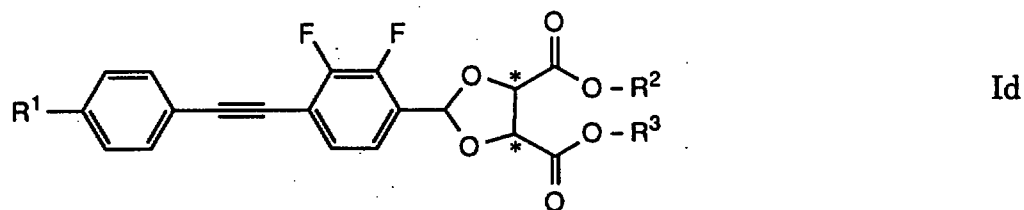
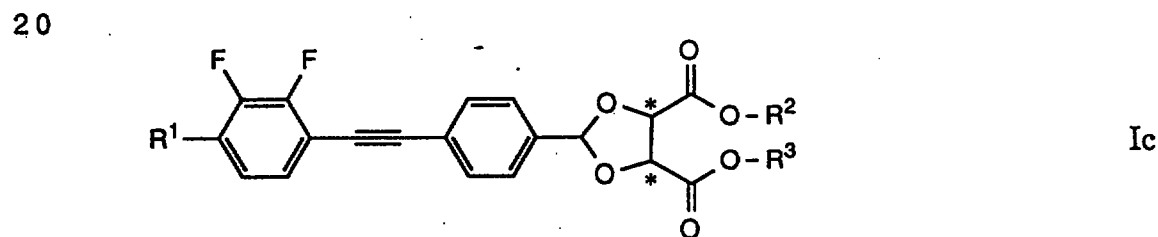
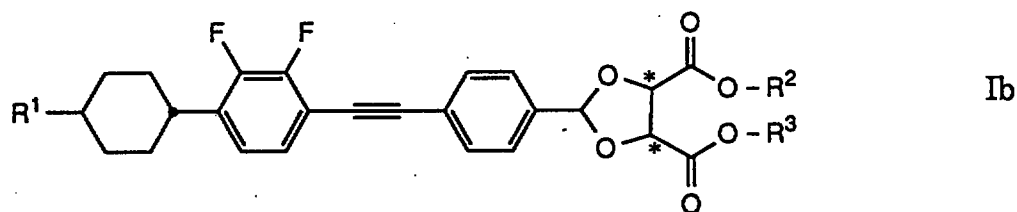
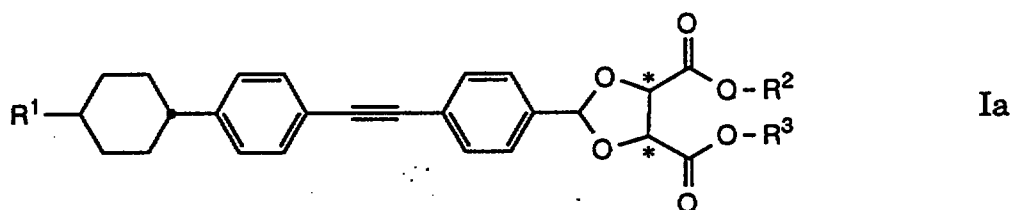
of the dioxolane ring both have the [R] configuration or both have the [S] configuration.

3. Optically active compounds according to claim 1 or 2,
5 wherein $n = 1$.

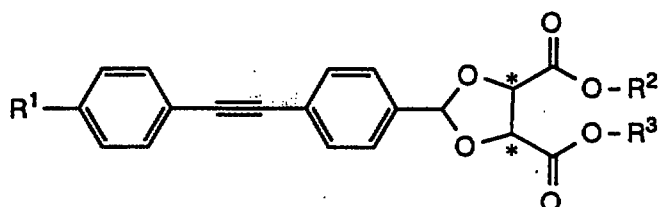
4. Optically active compounds according to any one of
claims 1 to 3, wherein X^1 and X^2 or X^3 and X^4 signify fluorine.

10 5. Optically active compounds according to any one of
claims 1 to 4, wherein R^1 signifies alkyl, alkenyl, alkoxy,
alkenyloxy, alkoxyalkyl or alkoxyalkenyl with 1 or, respectively,
2 to 6 carbon atoms.

15 6. Optically active compounds of the formulae



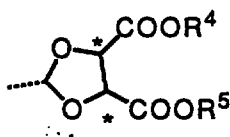
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wherein R¹ signifies hydrogen, alkyl or alkenyl with 1 or, respectively, 2 to 12 carbon atoms, which is unsubstituted or mono- or multiply-substituted with fluorine or chlorine and in which one -CH₂- group can be replaced by -O-, or - where R¹ is bonded to an aromatic ring - also fluorine, chlorine, cyano, CF₃, -OCHF₂ or -OCF₃, and R² and R³ have the significances given in claim 1.

7. Optically active compounds according to claim 1, wherein R¹ signifies a group of the formula



(a)

and n = 0 or 1.

8. A liquid crystalline mixture containing at least one compound in accordance with any one of claims 1 to 7 as a chiral dopant.

9. The use of optically active compounds of general formula I defined in claim 1 for optical and electro-optical devices.

10. The use of liquid crystalline mixtures according to claim 8 for optical and electro-optical devices.

11. A process for the manufacture of compounds of formula I defined in claim 1, which process comprises coupling an optically active dioxolane derivative 2 with an acetylene derivative 3 (both from Scheme 1), with the aid of a palladium catalyst.

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