

Description

The present invention relates to novel chiral dopants for liquid crystals and to liquid crystalline mixtures which contain such dopants and to their use for optical and electro-optical purposes.

Liquid crystal materials for electro-optical display devices frequently contain one or more optically active additives for inducing a chiral structure. For example, a nematic liquid crystal is preferably doped with an optically active additive for use in display devices having a twisted nematic structure, e.g. in order to avoid reverse twist in TN (twisted nematic) cells or in order to achieve adequate twisting in cells having a highly twisted nematic structure, such as STN (supertwisted nematic) cells, SBE (super birefringence effect) cells or OMI (optical mode interference) cells. Furthermore, cholesteric liquid crystals for phase-change cells can preferably comprise a nematic base material and one or more optically active dopants and ferro-electric liquid crystals for display devices based on chiral tilted smectic phases can preferably comprise a material having a tilted smectic phase and one or more optically active dopants.

The electro-optical response curves of liquid crystal display devices are temperature dependent, which is particularly disadvantageous when operated in multiplex mode. However, it is known that this temperature dependence can be compensated, at least partially, by adding a chiral dopant which induces a pitch which decreases with increasing temperature. An inverse temperature dependence of this type has only been found for a few compounds. Such dopants are, for example, the tartaric acid derivatives described in EP-A-0 234 437. An inverse temperature dependence can, however, also be achieved by using at least two chiral dopants which have different relative temperature dependences and induce different twist directions (DE-A-2827471). However, this usually requires a relatively high proportion of chiral dopants.

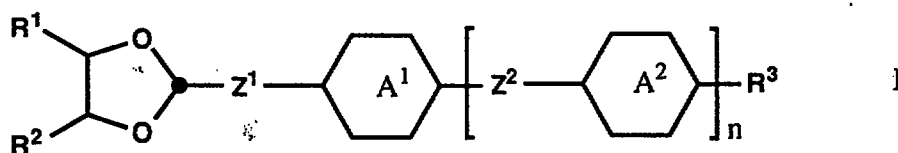
Cholesteric liquid crystals reflect light in a wavelength range for which the wavelength is approximately equal to the helix pitch. The spectral width of the reflected light can be varied by a suitable choice of the liquid crystal. The reflected light is fully circular-polarized. The direction of rotation of the reflected light depends on the direction of rotation of the cholesteric helical structure. The light circular-polarized in the opposite direction is transmitted without absorption. These

properties can be utilized to produce optical filters, polarizers, analyzers etc. Furthermore, cholesteric liquid crystals have also occasionally been used for thermochromic applications and in cosmetic preparations.

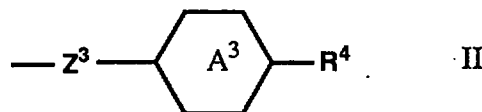
Cholesteric liquid crystals for the above applications can preferably comprise a nematic or cholesteric base material and one or more chiral dopants, which allows the desired helix pitch to be established.

In order to achieve cholesteric mixtures having a pitch in the range of the wavelength of visible light, the chiral dopants should have a high helical twisting power and be readily soluble in customary liquid crystal materials. In addition, the chiral dopants should have adequate stability, should be readily compatible with the mesophase type of liquid crystal material and should not restrict the mesophase range excessively. Such properties are also desirable for chiral dopants for achieving the twisted nematic structures mentioned at the outset, since their proportion could be kept so low that the properties of the liquid crystal material are affected only insignificantly.

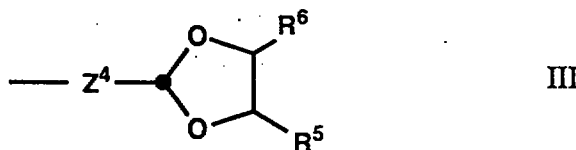
The invention relates to optically active compounds of the general formula



in which n represents the number 0 or 1; R^3 denotes a group of the general formula



or



rings A^1 , A^2 and A^3 each independently represent 1,4-phenylene, which is unsubstituted or substituted by halogen,

cyano and/or methyl and in which 1 or 2 CH groups may be replaced by nitrogen, trans-1,4-cyclohexylene, trans-1,3-dioxane-2,5-diyl or naphthalene-2,6-diyl, and ring A² additionally represents 1,4-biphenylene; Z¹ and Z⁴ each independently denote a single covalent bond or -CH₂CH₂-; Z² and Z³ each independently denote a single covalent bond, -CH₂CH₂-, -COO-, -OOC-, -CH₂O-, -OCH₂-, -C≡C-, -(CH₂)₄-, -(CH₂)₃O-, -O(CH₂)₃- or the trans form of -CH=CH-CH₂CH₂-, -CH₂CH₂-CH=CH-, -CH=CH-CH₂-O- or -O-CH₂-CH=CH-; with the proviso that, when R³ denotes a group of formula II, at least one of groups Z² and Z³ denotes -(CH₂)₄-, -(CH₂)₃-O-, -O-(CH₂)₃- or the trans form of -CH=CH-CH₂-CH₂-, -CH₂-CH₂-CH=CH-, -CH=CH-CH₂-O- or -O-CH₂-CH=CH-; R¹, R⁵ and R⁶ denote hydrogen, alkyl, phenyl or alkoxy carbonyl; R² denotes alkyl, phenyl or alkoxy carbonyl; R⁴ denotes halogen, cyano, trifluoromethyl, trifluoromethoxy or alkyl in which one -CH₂-CH₂- may be replaced by -CH=CH- and/or one or two non-adjacent methylene groups may be replaced by -O-, -COO- and/or -OOC- and/or one methylene group may be replaced by -CHX-; X denotes halogen, cyano or methyl; and the dioxolane ring shown in formula I is in optically active form.

The compounds of formula I are very readily soluble in customary liquid crystal materials and facilitate very high twisting of the liquid crystal structure. In contrast to known materials having a high helical twisting power, the clearing points of liquid crystals are, in addition, generally only decreased insignificantly, or not at all, when compounds of the formula I are added. Some of the compounds according to the invention even have liquid crystalline properties themselves. The compounds of formula I are easy to prepare, have relatively low viscosity and are adequately stable to electrical and magnetic fields. They therefore meet the above mentioned requirements in an optimum manner.

The properties of the compounds of formula I may be varied within broad ranges, depending on the number and meaning of the rings and substituents. For example, aromatic rings result in higher values of the optical anisotropy and saturated rings result in lower values. An increase in the clearing point can be achieved, for example, by introducing a further ring. Polar end groups, such as cyano, halogen, trifluoromethyl or trifluoromethoxy, and rings such as pyrimidine-2,5-diyl or trans-1,3-dioxane-2,5-diyl increase the dielectric anisotropy; rings such as 2,3-dicyano-1,4-phenylene reduce the dielectric anisotropy; and

lateral halogen and cyano substituents contribute towards the dielectric constant both parallel and perpendicular to the longitudinal molecular axis, which, depending on the substitution pattern, can be utilized to increase or reduce the dielectric anisotropy. Furthermore, lateral substituents on one or more rings can often be used to substantially suppress any tendency towards formation of highly ordered smectic phases and often also to improve the solubility. Moreover, a C=C double bond in the side chain can be used to further modify the elastic properties, the threshold voltages, the addressing times, the mesophases, etc.

The present invention therefore additionally facilitates, in addition to the induction of high twist, the optimization of liquid-crystalline and electro-optical properties in a broad range, depending on the application and the desired properties.

For the purposes of the present invention, the term "halogen" denotes fluorine, chlorine, bromine or iodine, in particular fluorine or chlorine.

The term "1,4-phenylene, which is unsubstituted or substituted by halogen, cyano and/or methyl and in which 1 or 2 CH groups may be replaced by nitrogen," covers 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. Preferred groups are 1,4-phenylene, 2-fluoro-1,4-phenylene, 2,3-difluoro-1,4-phenylene, pyridine-2,5-diyl and pyrimidine-2,5-diyl.

The term "alkyl" covers straight-chain and branched, optionally chiral, groups having 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), nonyl, decyl, undecyl, dodecyl and the like. Preferred alkyl residues in R¹, R², R⁵ and R⁶ are C₁-C₅-alkyl residues, in particular methyl.

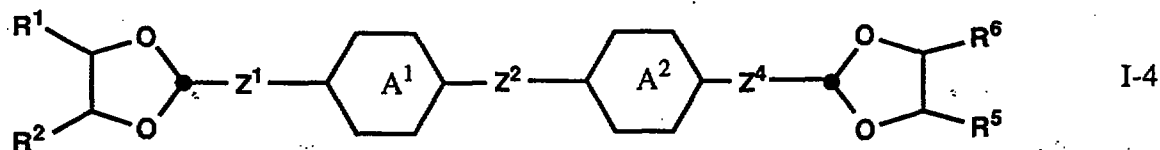
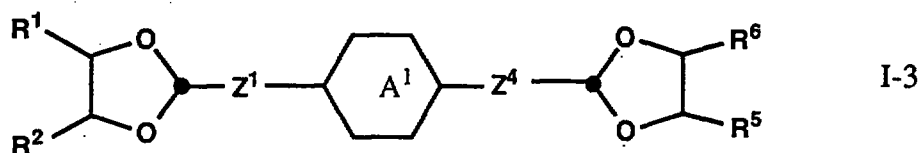
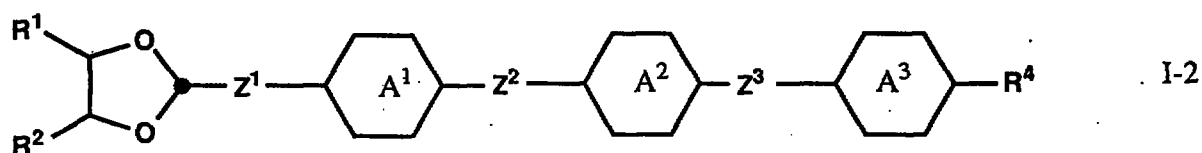
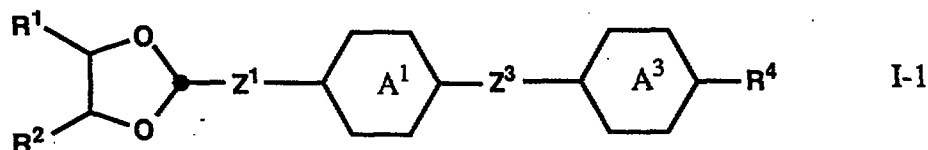
The term "alkoxycarbonyl" covers straight-chain and branched, optionally chiral, groups such as methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, isopropoxycarbonyl, butyloxycarbonyl, isobutyloxycarbonyl, (2-butyl)oxycarbonyl, (2-methylbutyl)oxycarbonyl, pentyloxycarbonyl, hexyloxycarbonyl and the like. Preferred alkoxycarbonyl residues in R¹, R², R⁵ and R⁶ are

the C₂-C₇-alkoxycarbonyl residues, in particular the C₂-C₅-alkoxycarbonyl residues.

The term "alkyl in which one -CH₂-CH₂- may be replaced by -CH=CH- and/or one or two non-adjacent methylene groups may be replaced by -O-, -COO- and/or -OOC- and/or one methylene group may be replaced by -CHX-" covers straight-chain and branched (optionally chiral) residues such as alkyl, 1E-alkenyl, 3E-alkenyl, 4-alkenyl, alkenyl containing a terminal double bond, alkoxy, 2E-alkenyloxy, 3-alkenyloxy, alkenyloxy containing a terminal double bond, alkoxyalkyl, alkenyloxyalkyl, alkoxycarbonyl, alkoxy-carbonylalkoxy (e.g. 1-(alkoxycarbonyl)-1-ethoxy), alkoxy-carbonylalkoxycarbonyl (e.g. (1-alkoxycarbonyl)-1-ethoxy-carbonyl), alkanoyloxy, 1-haloalkyl, 2-haloalkyl, 2-haloalkoxy, 2-haloalkoxycarbonyl, 1-cyanoalkyl, 2-cyanoalkyl, 2-cyanoalkoxy, 2-cyanoalkoxycarbonyl, 1-methylalkyl, 2-methylalkyl, 1-methyl-alkoxy, 2-methylalkoxy, 2-methylalkoxycarbonyl 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-hexenyl, 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, propoxy, butyloxy, pentyloxy, hexyloxy, heptyloxy, octyloxy, nonyloxy, decyloxy, undecyloxy, dodecyloxy, 1-methylpropoxy, 1-methylheptyloxy, 2-methylbutyloxy, 3-methylpentyloxy, allyloxy, 2E-butenyloxy, 2E-pentenlyoxy, 2E-hexenyloxy, 2E-heptenyloxy, 3-butenyloxy, 3Z-pentenlyoxy, 3Z-hexenyloxy, 3Z-heptenyloxy, 4-pentenlyoxy, 5-hexenyloxy, 6-heptenyloxy, 7-octenyloxy, 8-nonenlyoxy, 9-decenlyoxy, 10-undecenlyoxy, 11-dodecenlyoxy, methoxymethyl, ethoxymethyl, propoxymethyl, allyloxymethyl, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, 1-methylpropoxycarbonyl, 1-(methoxycarbonyl)ethoxy, 1-(ethoxycarbonyl)ethoxy, 1-(methoxycarbonyl)ethoxycarbonyl, 1-(ethoxycarbonyl)ethoxycarbonyl, 1-(isopropoxycarbonyl)ethoxycarbonyl, 1-(butyloxy-carbonyl)ethoxycarbonyl, acetoxymethyl, propionyl, butyryloxy, 1-fluoropropyl, 1-fluoropentyl, 1-chloropropyl, 2-fluoropropyl, 2-fluoropentyl, 2-chloropropyl, 2-fluoropropoxy, 2-fluorobutyloxy, 2-fluoropentyloxy, 2-fluorohexyloxy, 2-chloropropoxy, 2-chlorobutyloxy, 2-fluoropropoxycarbonyl, 2-fluorobutyloxy-carbonyl, 2-fluoropentyloxy-carbonyl, 2-fluoro-3-methylbutyloxy-carbonyl, 2-fluoro-4-methylpentyloxy-carbonyl, 2-chloropropoxy-carbonyl, 1-cyanopropyl, 1-cyanopentyl, 2-cyanopropyl, 2-cyanopentyl, 2-cyanopropoxy, 2-cyanobutyloxy, 2-cyanopentyloxy,

2-cyanohexyloxy, 2-cyanopropoxycarbonyl, 2-cyanobutyloxy-carbonyl, 2-cyano-3-methylbutyloxycarbonyl, 2-cyano-4-methyl-pentyloxycarbonyl and the like.

Formula I covers optically active compounds of the following general formulae



in which R^1 , R^2 , R^4 , R^5 , R^6 , A^1 , A^2 , A^3 , Z^1 , Z^2 , Z^3 and Z^4 each have the significances given above, with the proviso that in the compounds of the formulae I-1 and I-2 at least one of the groups Z^2 and Z^3 denotes $-(CH_2)_4-$, $-(CH_2)_3-O-$, $-O-(CH_2)_3-$ or the trans form of $-CH=CH-CH_2-CH_2-$, $-CH_2-CH_2-CH=CH-$, $-CH=CH-CH_2-O-$ or $-O-CH_2-CH=CH-$.

The compounds of formulae I-3 and I-4 are generally chiral dopants having a particularly high helical twisting power.

The compounds of formula I have at least one optically active dioxolane ring. The dioxolane ring shown in formula I has a chiral carbon atom in position 4 (i.e. adjacent to R^2) and, when R^1 is not hydrogen, a further chiral carbon atom in position 5 (i.e. adjacent to R^1). 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 completely or predominantly

be in R- or S-form and, when R^1 and R^2 are identical, that the carbon atom in position 5 of the dioxolane ring should completely or predominantly have the same configuration as the carbon atom in position 4 or in principle may also have a R/S ratio of 50:50. In order to achieve the highest possible helical twisting power, the carbon atom in position 4 of the dioxolane ring should preferably have a very high optical purity in the R- or S-configuration and, when R^1 is different from hydrogen, the carbon atom in position 5 of the dioxolane ring should preferably have a very high optical purity in that configuration which increases the helical twisting power. Preferred optical isomers having high helical twisting power are the (4R)-isomers and the (4S)-isomers of the compounds of formula I in which R^1 is hydrogen and the (4R,5R)-isomers and the (4S,5S)-isomers of the compounds of formula I in which R^1 denotes alkyl, phenyl or alkoxycarbonyl.

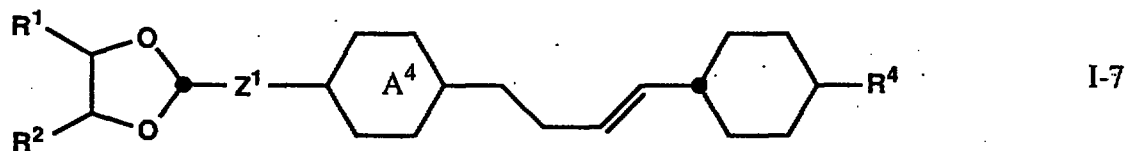
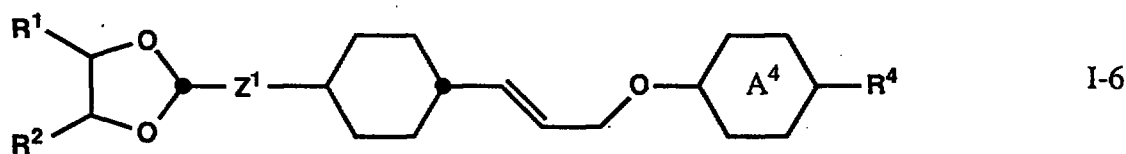
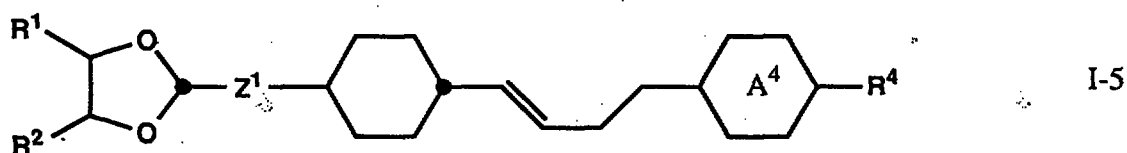
In general, particularly preferred compounds are those of formula I, I-1 and I-2 in which A^1 , A^2 and A^3 each independently represent 1,4-phenylene, which is unsubstituted or substituted by halogen, cyano and/or methyl (in particular 1,4-phenylene, 2-fluoro-1,4-phenylene or 2,3-difluoro-1,4-phenylene), or trans-1,4-cyclohexylene or one of groups A^1 , A^2 and A^3 also represents pyrimidine-2,5-diyl, and furthermore one of the groups Z^2 and Z^3 denotes $-(CH_2)_4-$, $-O-(CH_2)_3-$, $-(CH_2)_3-O-$ or the trans form of $-CH_2-CH_2-CH=CH-$, $-CH=CH-CH_2-CH_2-$, $-O-CH_2-CH=CH-$ or $-CH=CH-CH_2-O-$ and, when present, the other of the groups Z^2 and Z^3 denotes a single covalent bond. These compounds are very stable and in general particularly readily accessible from known precursors of liquid crystals.

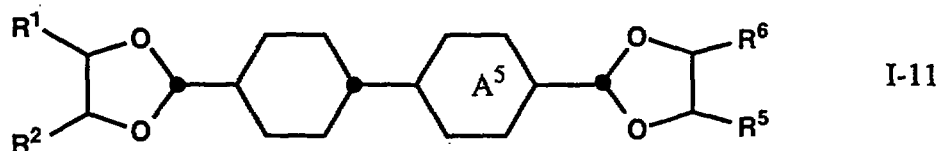
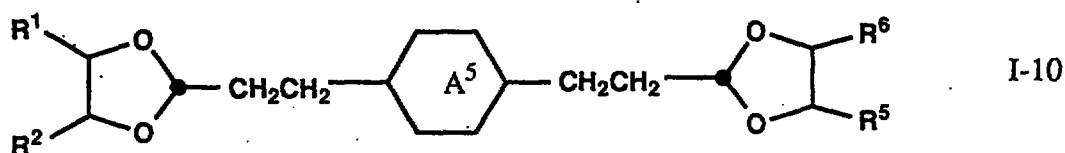
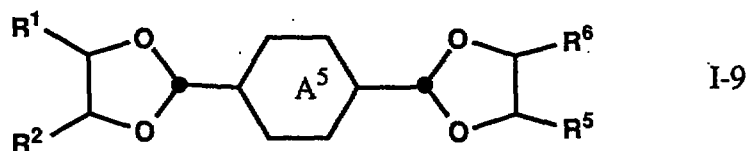
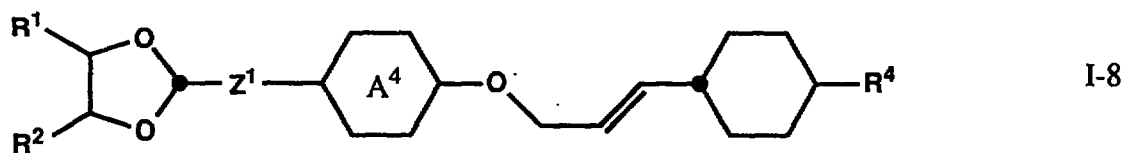
Very particularly preferred compounds are those of formulae I-3 and I-4 in which the rings A^1 and A^2 each independently represent 1,4-phenylene, which is unsubstituted or substituted by halogen, cyano and/or methyl (in particular 1,4-phenylene, 2-fluoro-1,4-phenylene or 2,3-difluoro-1,4-phenylene), or trans-1,4-cyclohexylene, or ring A^2 also represents pyrimidine-2,5-diyl or 4,4'-biphenylene and furthermore a group Z^2 , when present, denotes a single covalent bond, $-CH_2-CH_2-$, $-COO-$ or $-OOC-$ (in particular a single covalent bond).

However, since the helical twisting power of the compounds according to the invention is determined principally by the optically active dioxolane ring, it will be appreciated that one or more of these particularly preferred rings and bridging groups may be replaced by the other rings mentioned in formula I for A^1 , A^2 and A^3 and the bridging groups mentioned for Z^1 , Z^2 , Z^3 and Z^4 in order

to obtain a similar effect and likewise good compatibility with customary liquid crystals. However, preferred compounds of formulae I and I-1 to I-4 are those in which in each case one of rings A¹, A² and A³ represents 1,4-phenylene which is unsubstituted or substituted by halogen, cyano and/or methyl, or pyridine-2,5-diyl, pyrimidine-2,5-diyl, trans-1,4-cyclohexylene, trans-1,3-dioxane-2,5-diyl or naphthalene-2,6-diyl and ring A² additionally represents 4,4'-biphenylene, the others of rings A¹, A² and A³ (when present), each independently represent 1,4-phenylene, which is unsubstituted or substituted by halogen, cyano and/or methyl (in particular unsubstituted 1,4-phenylene), or trans-1,4-cyclohexylene, one of groups Z² and Z³ denotes a single covalent bond, -CH₂CH₂-, -COO-, -OOC-, -CH₂O-, -OCH₂-, -C≡C-, -(CH₂)₄-, -(CH₂)₃O-, -(CH₂)₃- or the trans form of -CH=CH-CH₂CH₂-, -CH₂CH₂-CH=CH-, -CH=CH-CH₂-O- or -O-CH₂-CH=CH-, and the other of the groups Z² and Z³ (when present) denotes a single covalent bond, with the proviso that, when R³ denotes a group of formula III, at least one of groups Z² and Z³ denotes -(CH₂)₄-, -(CH₂)₃-O-, -O-(CH₂)₃- or the trans form of -CH=CH-CH₂-CH₂-, -CH₂-CH₂-CH=CH-, -CH=CH-CH₂-O- or -O-CH₂-CH=CH-.

Examples of particularly preferred compounds of formula I are the optically active compounds of the following general formulae



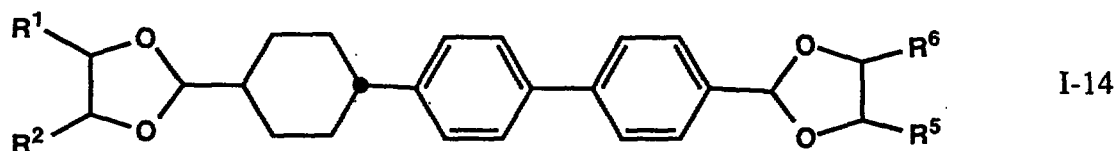
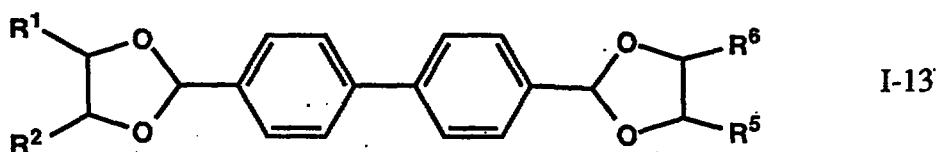
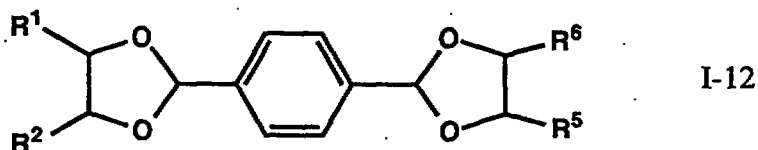


in which R^1 , R^2 , R^4 , R^5 and R^6 have the above significances and rings A^4 and A^5 represent 1,4-phenylene, which is unsubstituted or substituted by halogen, cyano and/or methyl (preferably 1,4-phenylene, 2-fluoro-1,4-phenylene or 2,3-difluoro-1,4-phenylene), or trans-1,4-cyclohexylene and ring A^5 additionally denotes 4,4'-biphenylene.

In the above formulae I, I-1, I-2 and I-5 to I-8, R^4 can in each case preferably denote halogen (in particular fluorine or chlorine), cyano, trifluoromethyl, trifluoromethoxy, alkyl, alkenyl, alkoxy or alkenyloxy. In an alkyl residue R^4 , however, one or two non-adjacent methylene groups may, if desired, be replaced by -O-, -COO- and/or -OOC-, and/or one methylene group may be replaced by -CHX- (in which X denotes halogen, cyano or methyl). This possibility can be utilized e.g. to increase the helical twisting power by introducing chiral groups starting from simple, optically active compounds. Preferred examples of such groups are the radicals derived from optically active lactic acid, such as 1-(alkoxycarbonyl)ethoxy and 1-(alkoxycarbonyl)-ethoxycarbonyl. In the above formulae, R^4 may therefore also preferably in each case denote one of these residues.

In general, R^4 has 1 to 18 carbon atoms. In general, R^4 residues having 1 to 12 carbon atoms, in particular those having 1 to 7 carbon atoms, are preferred.

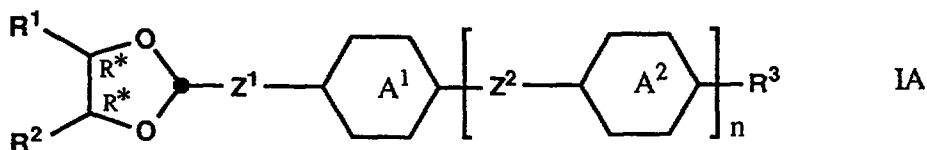
Very particularly preferred compounds of formula I in which R^3 is a group of formula III are the compounds of the general formulae



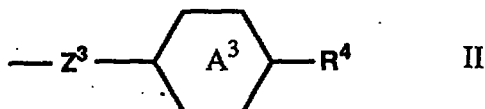
in which R^1 , R^2 , R^5 and R^6 have the significances given above.

The compounds of formula I may furthermore contain an end group of formula III, i.e. a further dioxolane ring. This group may in principle be optically inactive, but preferred groups of formula III are those which are present in an optically active form which increases the helical twisting power. Compounds having an increased helical twisting power which are particularly easy to prepare are those in which the two dioxolane rings have the same configuration and contain the same rings. In formula III, R^5 may therefore preferably have the same meaning and the same configuration at the adjacent carbon atom as R^1 and R^6 may preferably have the same meaning and the same configuration at the adjacent carbon atom as R^2 . This also applies analogously to the two dioxolane radicals in formulae I-3, I-4, I-12, I-13 and I-14.

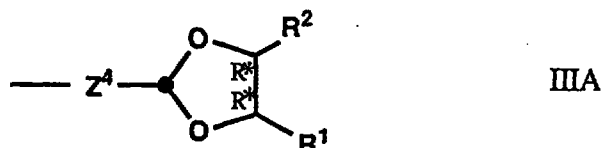
Preferred optical isomers are thus the compounds having the relative configuration indicated in the following general formula:



in which R^3 denotes a group of the general formula



or



n, A^1 , A^2 , A^3 , Z^1 , Z^2 , Z^3 , Z^4 , R^1 , R^2 and R^4 have the above significances, with the proviso that, when R^3 denotes a group of formula II, at least one of groups Z^2 and Z^3 denotes $-(CH_2)_4-$, $-(CH_2)_3-O-$, $-O-(CH_2)_3-$ or the trans form of $-CH=CH-CH_2-CH_2-$, $-CH_2-CH_2-CH=CH-$, $-CH=CH-CH_2-O-$ or $-O-CH_2-CH=CH-$; and the asymmetric carbon atoms labelled R^* are all in the R-configuration or are all in the S-configuration.

Formula IA covers the optical isomers indicated with R and the optical antipodes thereof which have the same helical twisting power, but the opposite twist direction.

Preferred optically active compounds of formula IA are those in which R^1 and R^2 are different or preferably have the same significance and denote C₂-C₇-alkoxycarbonyl, in particular C₂-C₅-alkoxycarbonyl. These compounds are readily accessible from the corresponding optically active tartaric acids or dialkyl tartrates. Particularly preferred compounds are those of formulae I-1 to I-14 in which in each case R^1 and R^2 are different or preferably have the same significance and denote C₂-C₇-alkoxycarbonyl (in particular C₂-C₅-alkoxycarbonyl), R^5 has the meaning of R^1 , R^6 has the meaning of R^2 and the asymmetric carbon atoms have the relative configuration indicated in formula IA.

Further preferred optically active compounds of formula IA are those in which R^2 denotes methyl or phenyl and R^1 has the meaning of R^2 or denotes hydrogen. These compounds are readily accessible from the corresponding optically active diols, namely 2,3-butanediol, 1,2-diphenyl-1,2-ethanediol, 1,2-propanediol or 1-phenyl-1,2-ethanediol. Particularly preferred compounds are

those of formulae I-1 to I-14 in which in each case R^2 denotes methyl or phenyl, R^1 has the meaning of R^2 or denotes hydrogen, R^5 has the meaning of R^1 , R^6 has the meaning of R^2 and the asymmetric carbon atoms have the relative configuration indicated in formula IA.

In formula IA above and in the subgroups of compounds of formula I referred to above as being preferred, rings A^1 , A^2 , A^3 , A^4 and A^5 , Z^1 , Z^2 , Z^3 and Z^4 may in each case in particular have the preferred meanings indicated in connection with formulae I and I-1 to I-14, with the proviso that, when R^3 denotes a group of formula II, at least one of groups Z^2 and Z^3 denotes $-(CH_2)_4-$, $-(CH_2)_3-O-$, $-O-(CH_2)_3-$ or the trans form of $-CH=CH-CH_2-CH_2-$, $-CH_2-CH_2-CH=CH-$, $-CH=CH-CH_2-O-$ or $-O-CH_2-CH=CH-$.

The compounds according to the invention may be prepared, for example, by reacting an aldehyde of the formula $OHC-Z^1-A^1-(Z^2-A^2)_n-R^3$ or an acetal thereof with an optically active diol of the formula $R^1-CH(OH)-CH(OH)-R^2$. The reaction of the aldehyde or of a suitable acetal (e.g. the dimethyl acetal) with the diol may be carried out in a manner known per se. The reaction is expediently carried out in an inert organic solvent (for example, an aromatic hydrocarbon, such as benzene, toluene or xylene) in the presence of a catalytic amount of an organic or inorganic acid, such as p-toluenesulphonic acid, sulphuric acid or dry hydrogen chloride. The temperature and pressure are not critical, but the reaction is preferably carried out at the reflux temperature (with separation of the water formed) and at atmospheric pressure.

When present, a second dioxolane ring (when R^3 denotes a group of the formula III) may be formed analogously, likewise from an aldehyde (or acetal) and a diol. If the two diols $[R^1-CH(OH)-CH(OH)-R^2$ and $R^5-CH(OH)-CH(OH)-R^6]$ are identical, the two dioxolane rings may, if desired, be formed in one step.

When the compound of formula I contains one or more ester groups in Z^2 , Z^3 and/or Z^4 , the esterification concerned may preferably also be delayed until after formation of the dioxolane ring. If desired, the introduction of ether groups and other functional groups may also be delayed until after formation of the dioxolane ring.

Methods of this type will be known in principle to those skilled in the art, e.g. from the preparation of liquid crystalline dioxanes. The diols required for the preparation are known or

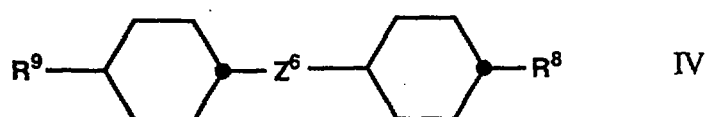
analogues of known compounds. The aldehydes required as starting materials are likewise known compounds or can be prepared by methods known per se. Such compounds and methods are known e.g. from EP-A-0115897, EP-A-0113459 and EP-A-0106991.

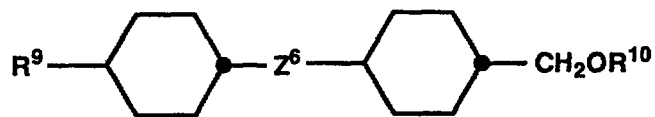
The invention also relates to a liquid crystalline mixture containing a liquid crystalline carrier material and one or more optically active compounds of formula I. Suitable carrier materials are in principle all liquid crystal materials which have a twistable liquid crystal phase with an adequate mesophase range. The compounds of formula I are particularly suitable as chiral dopants for nematic or cholesteric base materials. The liquid crystalline base material may be an individual compound or a mixture and preferably has a clearing point of at least about 60°C.

The proportion of chiral dopant of formula I is essentially determined by its helical twisting power and by the desired pitch. The proportion of chiral dopant can therefore vary within a broad range depending on the application and can be, for example, from about 0.1 to 30% by weight. For display devices based on liquid crystals having a twisted nematic structure, a pitch of from about 3 to 40 μm is usually necessary depending on the cell type and thickness and a correspondingly small proportion is therefore sufficient. By contrast, applications based on the reflection of visible light by cholesteric layers necessitate pitches of less than 2 μm , for example from about 0.4 to 0.6 μm , which requires a correspondingly higher proportion of chiral dopant.

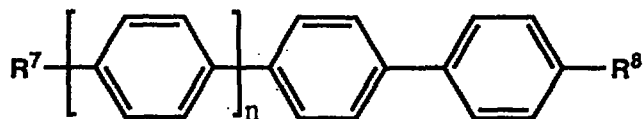
A large number of suitable liquid crystalline carrier materials are known and are commercially available. In general, liquid crystalline mixtures containing 2 or more components are preferred carrier materials. In principle, however, it is also possible to use one liquid crystalline compound as the base material if it has a sufficiently broad mesophase.

Particularly suitable components for liquid crystalline carrier materials are compounds of the following general formulae

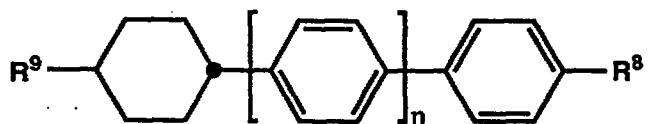




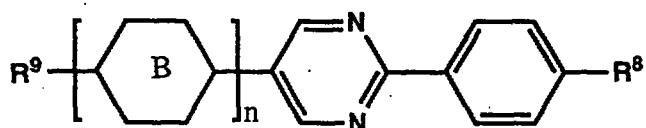
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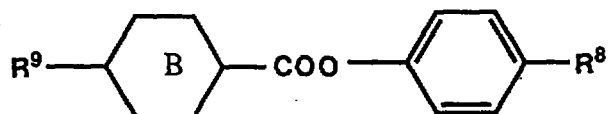
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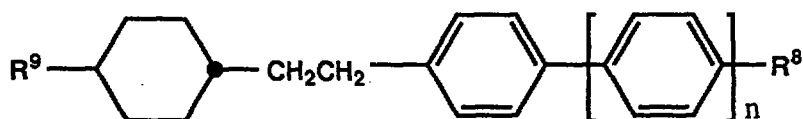
VII



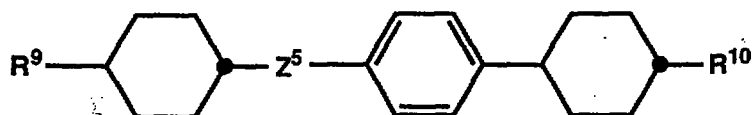
VIII



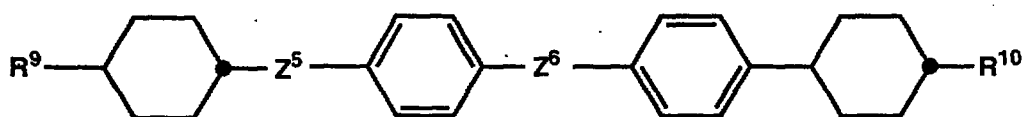
IX



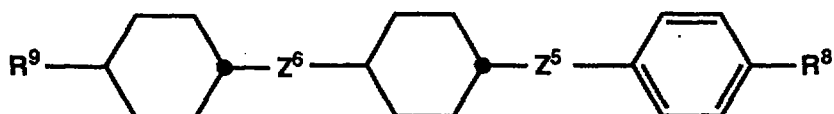
X



XI



XII



XIII

in which n represents the number 0 or 1; R^7 denotes alkyl, alkoxy, alkenyl or alkenyloxy; R^8 denotes cyano, alkyl, alkoxy, alkenyl or alkenyloxy; R^9 and R^{10} each independently denote alkyl or alkenyl; ring B represents 1,4-phenylene or trans-1,4-cyclohexylene; Z^5 denotes a single covalent bond, -COO- or -CH₂CH₂-; and Z^6 denotes a single covalent bond or -CH₂CH₂-.

R⁷, R⁸, R⁹ and R¹⁰ preferably each contain a maximum of 12 carbon atoms, particularly a maximum of 7 carbon atoms. Preferred alkenyl groups are 1E-alkenyl, 3E-alkenyl and 4Z-alkenyl. Preferred alkenyloxy groups are 2E-alkenyloxy and 3Z-alkenyloxy.

The invention is illustrated in greater detail by the following Examples. In connection with liquid crystal phases and phase transitions, C denotes a crystalline phase, S_B denotes a smectic B phase, N denotes a nematic phase, N* denotes a cholesteric phase and I denotes the isotropic phase. p denotes the helix pitch, and $\lambda_{\max}$ denotes the wavelength of the selectively reflected, circular-polarized light. Optical antipodes have in each case "mirror-image properties", i.e. the same melting points, etc., but result in an opposite direction of rotation of the helix and the opposite circular-polarization of reflected light.

Example 1

A solution of 0.8 g of 4-[(E)-3-(trans-4-pentylcyclohexyl)allyloxy]benzaldehyde and 1.0 g of dimethyl L(+)-tartrate in 50 ml of toluene was treated with 2 drops of 10% (vol.) sulphuric acid. The mixture was boiled for 2.5 hours, the water formed being simultaneously removed by distillation. Then, 4 drops of triethylamine were added to the reaction mixture. After cooling, the mixture was washed with 20 ml of 1N sodium bicarbonate solution and twice with 20 ml of water each time, dried over sodium sulphate, filtered and evaporated. Chromatography of the residue on silica gel using toluene/ethyl acetate (vol. 1:1) and recrystallization from ethanol gave pure dimethyl (4R,5R)-2-(4-[(E)-3-(trans-4-pentylcyclohexyl)allyloxy]phenyl)-1,3-dioxolane-4,5-dicarboxylate.

The following compounds can be prepared in an analogous manner:

diethyl (4R,5R)-2-(4-[(E)-3-(trans-4-pentylcyclohexyl)allyloxy]phenyl)-1,3-dioxolane-4,5-dicarboxylate;

diisopropyl (4R,5R)-2-(4-[(E)-3-(trans-4-pentylcyclohexyl)allyloxy]phenyl)-1,3-dioxolane-4,5-dicarboxylate;

diisobutyl (4R,5R)-2-(4-[(E)-3-(trans-4-pentylcyclohexyl)allyloxy]phenyl)-1,3-dioxolane-4,5-dicarboxylate;

dimethyl (4R,5R)-2-(4-[3-(trans-4-pentylcyclohexyl)-1-propoxy]phenyl)-1,3-dioxolane-4,5-dicarboxylate;

diethyl (4R,5R)-2-(4-[3-(trans-4-pentylcyclohexyl)-1-propoxy]phenyl)-1,3-dioxolane-4,5-dicarboxylate;

diisopropyl (4R,5R)-2-(4-[3-(trans-4-pentylcyclohexyl)-1-propoxy]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 dibutyl (4R,5R)-2-(4-[3-(trans-4-pentylcyclohexyl)-1-propoxy]phenyl)-1,3-dioxolane-4,5-dicarboxylate, m.p. 42°C;
 dimethyl (4R,5R)-2-(4-[4-(trans-4-pentylcyclohexyl)-1-butyl]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 diethyl (4R,5R)-2-(4-[4-(trans-4-pentylcyclohexyl)-1-butyl]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 diisopropyl (4R,5R)-2-(4-[4-(trans-4-pentylcyclohexyl)-1-butyl]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 dibutyl (4R,5R)-2-(4-[4-(trans-4-pentylcyclohexyl)-1-butyl]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 dimethyl (4R,5R)-2-(4-[(E)-(trans-4-pentylcyclohexyl)-3-butenyl]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 diethyl (4R,5R)-2-(4-[(E)-(trans-4-pentylcyclohexyl)-3-butenyl]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 diisopropyl (4R,5R)-2-(4-[(E)-(trans-4-pentylcyclohexyl)-3-butenyl]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 dibutyl (4R,5R)-2-(4-[(E)-(trans-4-pentylcyclohexyl)-3-butenyl]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 dimethyl (4R,5R)-2-(4-[(E)-3-(trans-4-propylcyclohexyl)-allyloxy]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 diethyl (4R,5R)-2-(4-[(E)-3-(trans-4-propylcyclohexyl)-allyloxy]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 diisopropyl (4R,5R)-2-(4-[(E)-3-(trans-4-propylcyclohexyl)-allyloxy]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 diisobutyl (4R,5R)-2-(4-[(E)-3-(trans-4-propylcyclohexyl)-allyloxy]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 dimethyl (4R,5R)-2-(4-[3-(trans-4-propylcyclohexyl)-1-propoxy]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 diethyl (4R,5R)-2-(4-[3-(trans-4-propylcyclohexyl)-1-propoxy]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 diisopropyl (4R,5R)-2-(4-[3-(trans-4-propylcyclohexyl)-1-propoxy]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 dibutyl (4R,5R)-2-(4-[3-(trans-4-propylcyclohexyl)-1-propoxy]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 dimethyl (4R,5R)-2-(4-[4-(trans-4-propylcyclohexyl)-1-butyl]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 diethyl (4R,5R)-2-(4-[4-(trans-4-propylcyclohexyl)-1-butyl]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 diisopropyl (4R,5R)-2-(4-[4-(trans-4-propylcyclohexyl)-1-butyl]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 dibutyl (4R,5R)-2-(4-[4-(trans-4-propylcyclohexyl)-1-butyl]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 dimethyl (4R,5R)-2-(4-[(E)-(trans-4-propylcyclohexyl)-3-butenyl]phenyl)-1,3-dioxolane-4,5-dicarboxylate;

diethyl (4R,5R)-2-(4-[(E)-(trans-4-propylcyclohexyl)-3-butenyl]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 diisopropyl (4R,5R)-2-(4-[(E)-(trans-4-propylcyclohexyl)-3-butenyl]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 dibutyl (4R,5R)-2-(4-[(E)-(trans-4-propylcyclohexyl)-3-butenyl]phenyl)-1,3-dioxolane-4,5-dicarboxylate;
 4-[(4R,5R)-4,5-dimethoxycarbonyl-1,3-dioxolan-2-yl]-4'-[(E)-3-(trans-4-pentylcyclohexyl)allyloxy]biphenyl;
 4-[(4R,5R)-4,5-diethoxycarbonyl-1,3-dioxolan-2-yl]-4'-[(E)-3-(trans-4-pentylcyclohexyl)allyloxy]biphenyl;
 4-[(4R,5R)-4,5-diisopropoxycarbonyl-1,3-dioxolan-2-yl]-4'-[(E)-3-(trans-4-pentylcyclohexyl)allyloxy]biphenyl;
 4-[(4R,5R)-4,5-diisobutyloxycarbonyl-1,3-dioxolan-2-yl]-4'-[(E)-3-(trans-4-pentylcyclohexyl)allyloxy]biphenyl;
 4-[(4R,5R)-4,5-dimethoxycarbonyl-1,3-dioxolan-2-yl]-4'-[4-(trans-4-pentylcyclohexyl)-1-propoxy]diphenyl;
 4-[(4R,5R)-4,5-diethoxycarbonyl-1,3-dioxolan-2-yl]-4'-[4-(trans-4-pentylcyclohexyl)-1-propoxy]diphenyl;
 4-[(4R,5R)-4,5-diisopropoxycarbonyl-1,3-dioxolan-2-yl]-4'-[4-(trans-4-pentylcyclohexyl)-1-propoxy]diphenyl;
 4-[(4R,5R)-4,5-dibutyloxycarbonyl-1,3-dioxolan-2-yl]-4'-[4-(trans-4-pentylcyclohexyl)-1-propoxy]diphenyl;
 4-[(4R,5R)-4,5-dimethoxycarbonyl-1,3-dioxolan-2-yl]-4'-[4-(trans-4-pentylcyclohexyl)-1-butyl]biphenyl;
 4-[(4R,5R)-4,5-diethoxycarbonyl-1,3-dioxolan-2-yl]-4'-[4-(trans-4-pentylcyclohexyl)-1-butyl]biphenyl;
 4-[(4R,5R)-4,5-diisopropoxycarbonyl-1,3-dioxolan-2-yl]-4'-[4-(trans-4-pentylcyclohexyl)-1-butyl]biphenyl;
 4-[(4R,5R)-4,5-dibutyloxycarbonyl-1,3-dioxolan-2-yl]-4'-[4-(trans-4-pentylcyclohexyl)-1-butyl]biphenyl;
 4-[(4R,5R)-4,5-dimethoxycarbonyl-1,3-dioxolan-2-yl]-4'-[(E)-3-(trans-4-pentylcyclohexyl)butenyl]diphenyl;
 4-[(4R,5R)-4,5-diethoxycarbonyl-1,3-dioxolan-2-yl]-4'-[(E)-3-(trans-4-pentylcyclohexyl)butenyl]diphenyl;
 4-[(4R,5R)-4,5-diisopropoxycarbonyl-1,3-dioxolan-2-yl]-4'-[(E)-3-(trans-4-pentylcyclohexyl)butenyl]diphenyl;
 4-[(4R,5R)-4,5-dibutyloxycarbonyl-1,3-dioxolan-2-yl]-4'-[(E)-3-(trans-4-pentylcyclohexyl)butenyl]diphenyl;
 4-[(4R,5R)-4,5-dimethoxycarbonyl-1,3-dioxolan-2-yl]-4'-[(E)-3-(trans-4-propylcyclohexyl)allyloxy]biphenyl;
 4-[(4R,5R)-4,5-diethoxycarbonyl-1,3-dioxolan-2-yl]-4'-[(E)-3-(trans-4-propylcyclohexyl)allyloxy]biphenyl;
 4-[(4R,5R)-4,5-diisopropoxycarbonyl-1,3-dioxolan-2-yl]-4'-[(E)-3-(trans-4-propylcyclohexyl)allyloxy]biphenyl;
 4-[(4R,5R)-4,5-diisobutyloxycarbonyl-1,3-dioxolan-2-yl]-4'-[(E)-3-(trans-4-propylcyclohexyl)allyloxy]biphenyl;

4-[(4R,5R)-4,5-dimethoxycarbonyl-1,3-dioxolan-2-yl]-4'-
 [4-(trans-4-propylcyclohexyl)-1-propoxy]diphenyl;
 4-[(4R,5R)-4,5-diethoxycarbonyl-1,3-dioxolan-2-yl]-4'-[4-
 (trans-4-propylcyclohexyl)-1-propoxy]diphenyl;
 4-[(4R,5R)-4,5-diisopropoxycarbonyl-1,3-dioxolan-2-yl]-
 4'-[4-(trans-4-propylcyclohexyl)-1-propoxy]diphenyl;
 4-[(4R,5R)-4,5-dibutyloxycarbonyl-1,3-dioxolan-2-yl]-4'-
 [4-(trans-4-propylcyclohexyl)-1-propoxy]diphenyl;
 4-[(4R,5R)-4,5-dimethoxycarbonyl-1,3-dioxolan-2-yl]-4'-
 [4-(trans-4-propylcyclohexyl)-1-butyl]biphenyl;
 4-[(4R,5R)-4,5-diethoxycarbonyl-1,3-dioxolan-2-yl]-4'-[4-
 (trans-4-propylcyclohexyl)-1-butyl]biphenyl;
 4-[(4R,5R)-4,5-diisopropoxycarbonyl-1,3-dioxolan-2-yl]-
 4'-[4-(trans-4-propylcyclohexyl)-1-butyl]biphenyl;
 4-[(4R,5R)-4,5-dibutyloxycarbonyl-1,3-dioxolan-2-yl]-4'-
 [4-(trans-4-propylcyclohexyl)-1-butyl]biphenyl;
 4-[(4R,5R)-4,5-dimethoxycarbonyl-1,3-dioxolan-2-yl]-4'-
 [(E)-3-(trans-4-propylcyclohexyl)butenyl]diphenyl;
 4-[(4R,5R)-4,5-diethoxycarbonyl-1,3-dioxolan-2-yl]-4'-
 [(E)-3-(trans-4-propylcyclohexyl)butenyl]diphenyl;
 4-[(4R,5R)-4,5-diisopropoxycarbonyl-1,3-dioxolan-2-yl]-
 4'-[(E)-3-(trans-4-propylcyclohexyl)butenyl]diphenyl;
 4-[(4R,5R)-4,5-dibutyloxycarbonyl-1,3-dioxolan-2-yl]-4'-
 [(E)-3-(trans-4-propylcyclohexyl)butenyl]diphenyl;

Example 2

A solution of 1.0 g of terephthaldehyde, 5.8 g of dimethyl
 (R,R)-2,3-bis(trimethylsiloxy)succinate in 25 ml of ethylene
 chloride was treated at 0°C and while gassing with nitrogen with
 0.14 ml of boron trifluoride ethyl etherate, stirred for 15
 minutes, treated with 0.06 ml of trifluoromethanesulphonic acid,
 stirred at 0°C for a further 30 minutes, then at room
 temperature overnight. The mixture was cooled to 0°C, treated
 dropwise with 25 ml of concentrated sodium carbonate solution
 and stirred at room temperature for a further 15 minutes. The
 organic phase was separated and the aqueous phase was back-
 extracted twice with 25 ml of dichloromethane each time. The
 combined organic phases were washed twice with 100 ml of
 water each time, dried over magnesium sulphate, filtered and
 subsequently concentrated. The residue was purified by
 chromatography on silica gel using hexane/ethyl acetate (vol.
 1:1). Recrystallization from a hexane/ethyl acetate mixture (vol.
 1:1) gave pure dimethyl 2,2'-(4-phenylene)-bis-(4R,5R)-1,3-
 dioxolane-4,5-dicarboxylate of m.p. (C-I) 88°C.

The dimethyl (R,R)-2,3-bis(trimethylsiloxy)succinate used as starting material was prepared as follows:

A solution of 20 g of dimethyl L(+)-tartaric acid and 35 ml of triethylamine in 200 ml of toluene was treated dropwise at -5°C and while gassing with nitrogen with 32 g of trimethylchlorosilane. A white reaction mixture formed, which was stirred at room temperature for a further 90 minutes. The mixture was treated with 100 ml of saturated sodium bicarbonate solution and then extracted three times with 50 ml of ethyl acetate each time. The combined organic phases were washed twice with 100 ml of saturated sodium bicarbonate solution each time, dried over magnesium sulphate, filtered and then concentrated. Distillation of the residue gave 36 g of dimethyl (R,R)-2,3-bis-(trimethylsiloxy)succinate, b.p. 123-125°C/0.07 mm Hg.

The following compounds can be prepared in an analogous manner:

diethyl 2,2'-(4-phenylene)-bis(4R,5R)-1,3-dioxolane-4,5-dicarboxylate, m.p. 75°C;

diisopropyl 2,2'-(4-phenylene)-bis(4R,5R)-1,3-dioxolane-4,5-dicarboxylate, m.p. 78°C;

dibutyl 2,2'-(4-phenylene)-bis(4R,5R)-1,3-dioxolane-4,5-dicarboxylate, m.p. 41°C;

dimethyl 2,2'-(4,4'-biphenylyl)-bis[(4R,5R)-1,3-dioxolane]-4,5-dicarboxylate, m.p. 133°C;

diethyl 2,2'-(4,4'-biphenylyl)-bis[(4R,5R)-1,3-dioxolane]-4,5-dicarboxylate, m.p. 79°C;

diisopropyl 2,2'-(4,4'-biphenylyl)-bis[(4R,5R)-1,3-dioxolane]-4,5-dicarboxylate, m.p. 97°C;

dibutyl 2,2'-(4,4'-biphenylyl)-bis[(4R,5R)-1,3-dioxolane]-4,5-dicarboxylate, m.p. 67°C;

Example 3

In order to measure the induced pitch and the temperature dependence thereof in liquid crystal materials, the following liquid crystal base mixture BM-1 was used:

5.36	wt.%	of 4'-ethyl-4-cyanobiphenyl,
3.18	"	4'-propyl-4-cyanobiphenyl,
6.08	"	4'-butyl-4-cyanobiphenyl,
6.53	"	4-(trans-4-propylcyclohexyl)benzonitrile,
14.67	"	4-(trans-4-pentylcyclohexyl)benzonitrile,

5.21	"	4-ethyl-1-(trans-4-propylcyclohexyl)benzene,
16.54	"	4-ethoxy-1-[2-(trans-4-propylcyclohexyl)ethyl] benzene,
5.60	"	4"-pentyl-4-cyano-p-terphenyl,
5.71	"	4'-(trans-4-pentylcyclohexyl)-4-cyanobiphenyl,
15.95	"	1-[2-(trans-4-butylcyclohexyl)ethyl]-4-(trans-4- pentylcyclohexyl)benzene,
4.74	"	4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-(trans-4- pentylcyclohexyl)biphenyl,
7.59	"	4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-(trans-4- pentylcyclohexyl)-1,1'-ethylenedibenzene,
2.84	"	4-cyanophenyl trans-4-[2-(trans-4-propylcyclo- hexyl)ethyl]cyclohexanecarboxylate;

m.p. <-30°C, c.p. (N-I) 90°C; $\Delta\epsilon = 8.5$, $\Delta n = 0.139$ and $\eta = 22 \text{ mPa}\cdot\text{s}$,
measured at 22°C.

Liquid crystal base mixture BM-1 was treated with one of the following optically active dopants:

- D-1 = dimethyl 2,2'-(4-phenyl)-bis-(4R,5R)-1,3-dioxolane-4,5-dicarboxylate,
D-2 = diisopropyl 2,2'-(4,4'-biphenyl)-bis-(4R,5R)-1,3-dioxolane-4,5-dicarboxylate.

The results shown in Table 1 were obtained for the mixtures containing chiral dopants, with A, B and C denoting the parameters of the expansion into a series

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

and p, c and T_1 have the following meanings:

- T_1 = $T - 22^\circ\text{C}$
T = temperature in $^\circ\text{C}$
p = pitch in μm (a positive value denotes a right-hand helical structure and a negative value denotes a left-hand helical structure)
c = concentration of the optically active dopant in wt.%.

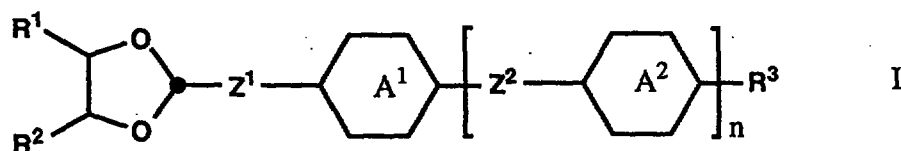
Table 1

Mixture	Dopant	A [10 ⁻² •μm ⁻¹ • wt.% ⁻¹	B [10 ⁻⁴ •μm ⁻¹ • wt.% ⁻¹ •°C]	C [10 ⁻⁶ •μm ⁻¹ • wt.% ⁻¹ •°C]	P.C (at 22°C) [μm•wt.%]
M-1	1.0 wt.% D-1	-25.50	-15.92	0.77	-3.92
M-2	1.0 wt.% D-2	-26.86	8.82	-2.00	-3.72

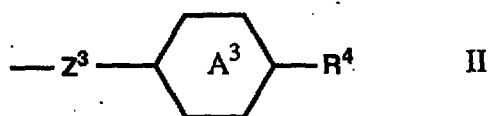


Claims

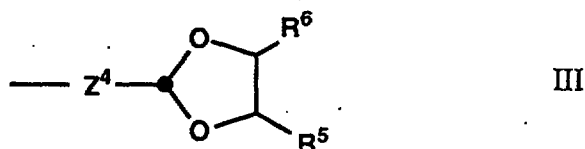
1. Optically active compounds of the general formula



in which n represents the number 0 or 1; R^3 denotes a group of the general formula



or

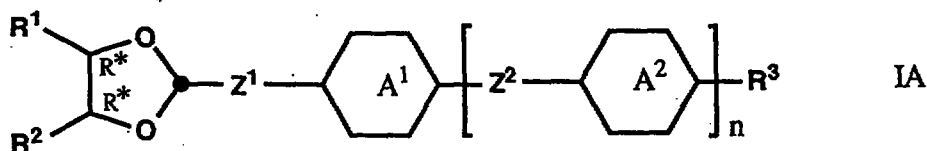


rings A^1 , A^2 and A^3 each independently represent 1,4-phenylene, which is unsubstituted or substituted by halogen, cyano and/or methyl and in which 1 or 2 CH groups may be replaced by nitrogen, trans-1,4-cyclohexylene, trans-1,3-dioxane-2,5-diyl or naphthalene-2,6-diyl, and ring A^2 additionally represents 1,4-biphenylene; Z^1 and Z^4 each independently denote a single covalent bond or $-\text{CH}_2\text{CH}_2-$; Z^2 and Z^3 each independently denote a single covalent bond, $-\text{CH}_2\text{CH}_2-$, $-\text{COO}-$, $-\text{OOC}-$, $-\text{CH}_2\text{O}-$, $-\text{OCH}_2-$, $-\text{C}\equiv\text{C}-$, $-(\text{CH}_2)_4-$, $-(\text{CH}_2)_3\text{O}-$, $-\text{O}(\text{CH}_2)_3-$ or the trans form of $-\text{CH}=\text{CH}-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2-\text{CH}=\text{CH}-$, $-\text{CH}=\text{CH}-\text{CH}_2-\text{O}-$ or $-\text{O}-\text{CH}_2-\text{CH}=\text{CH}-$; with the proviso that, when R^3 denotes a group of formula II, at least one of groups Z^2 and Z^3 denotes $-(\text{CH}_2)_4-$, $-(\text{CH}_2)_3\text{O}-$, $-\text{O}-(\text{CH}_2)_3-$ or the trans form of $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-$, $-\text{CH}=\text{CH}-\text{CH}_2-\text{O}-$ or $-\text{O}-\text{CH}_2-\text{CH}=\text{CH}-$; R^1 , R^5 and R^6 denote hydrogen, alkyl, phenyl or alkoxy carbonyl; R^2 denotes alkyl, phenyl or alkoxy carbonyl; R^4 denotes halogen, cyano, trifluoromethyl, trifluoromethoxy or alkyl in which one $-\text{CH}_2-\text{CH}_2-$ may be replaced by $-\text{CH}=\text{CH}-$ and/or one or two non-adjacent methylene groups may be replaced by $-\text{O}-$, $-\text{COO}-$ and/or $-\text{OOC}-$ and/or one methylene group may be replaced by $-\text{CHX}-$; X denotes halogen, cyano or methyl;

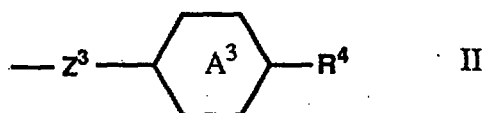


and the dioxolane ring shown in formula I is in optically active form.

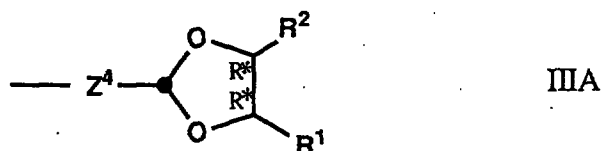
2. Optically active compounds according to claim 1, having the relative configuration of the general formula



in which R³ denotes a group of the general formula

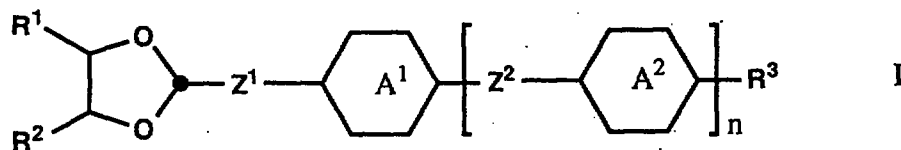


or

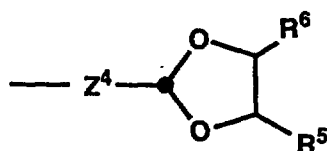


n , A^1 , A^2 , A^3 , Z^1 , Z^2 , Z^3 , Z^4 , R^1 , R^2 and R^4 have the significances given in claim 1, with the proviso that, when R^3 denotes a group of formula II, at least one of groups Z^2 and Z^3 denotes $-(CH_2)_4-$, $-(CH_2)_3-O-$, $-O-(CH_2)_3-$ or the trans form of $-CH=CH-CH_2-CH_2-$, $-CH_2-CH_2-CH=CH-$, $-CH=CH-CH_2-O-$ or $-O-CH_2-CH=CH-$; and the asymmetric carbon atoms labelled R^* are all in the R-configuration or are all in the S-configuration.

3. Optically active compounds according to claim 1 of the general formula



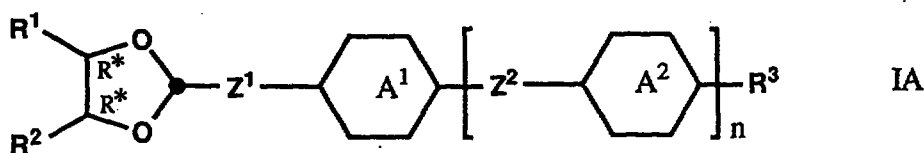
in which R³ denotes a group of the general formula



III

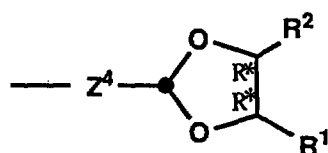
n, R¹, R², R⁵, R⁶, Z¹, Z², Z⁴, rings A¹ and A² have the significances given in claim 1.

4. Optically active compounds according to any one of claims 1 to 3 of the general formula



IA

in which R³ denotes a group of the general formula



IIIA

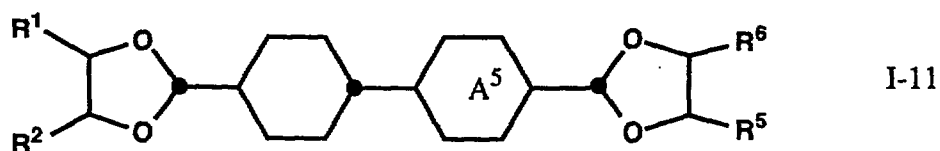
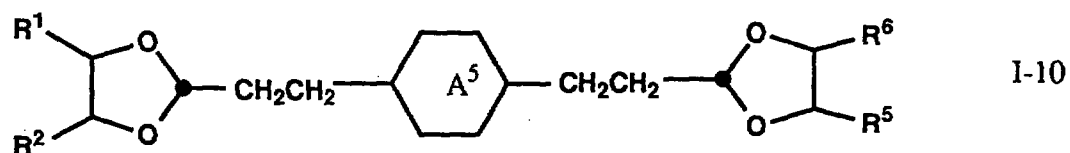
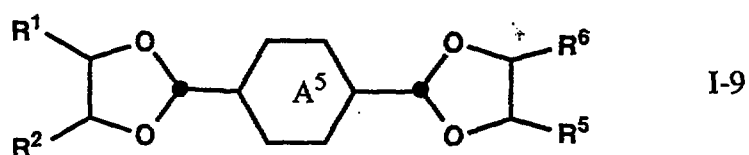
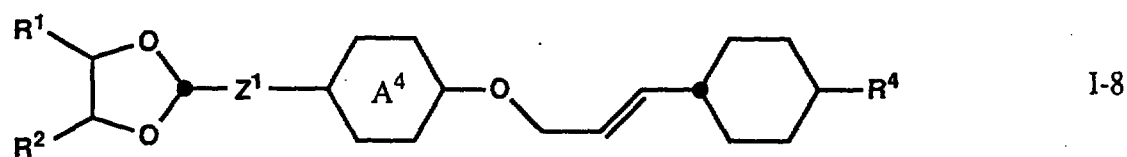
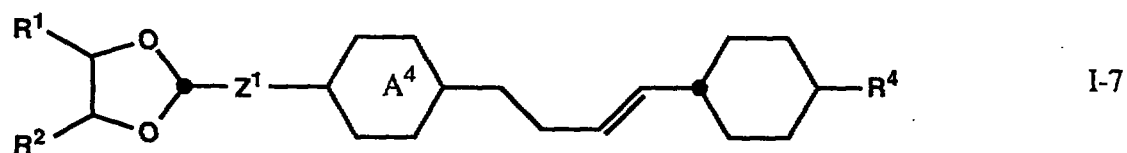
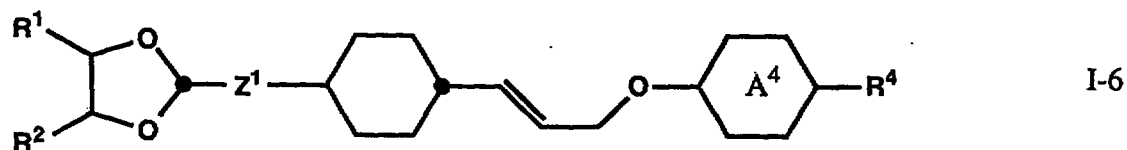
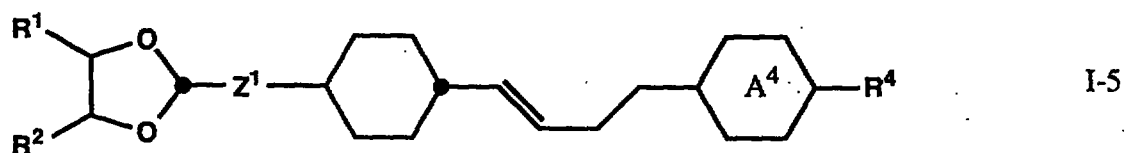
R¹, R², Z¹, Z², Z⁴, rings A¹ and A² have the significances given in claim 2.

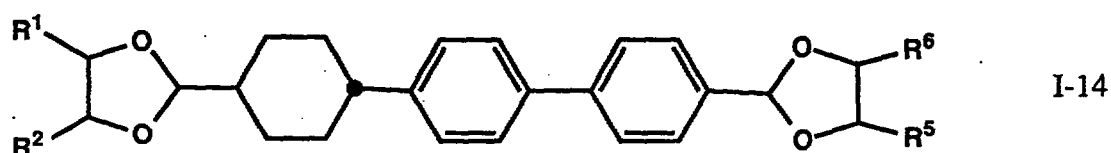
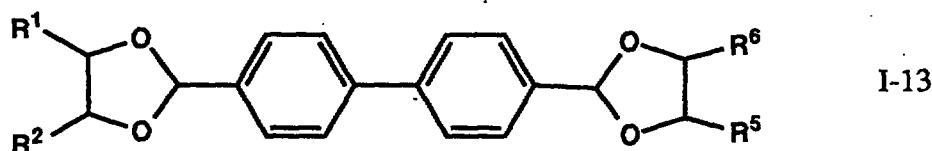
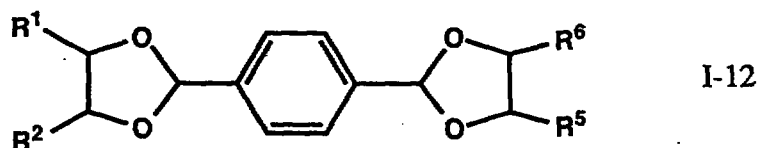
5. Optically active compounds according to claim 1 or 2, characterized in that rings A¹, A² and A³ denotes 1,4-phenylene, which is unsubstituted or substituted by halogen, cyano and/or methyl, pyridine-2,5-diyl, pyrimidine-2,5-diyl, trans-1,4-cyclohexylene, trans-1,3-dioxane-2,5-diyl or naphthalene-2,6-diyl and A² additionally denotes 4,4'-biphenylene, and the others of rings A¹, A² and A³ each independently represent 1,4-phenylene, which is unsubstituted or substituted by halogen, cyano and/or methyl, or trans-1,4-cyclohexylene.

6. Optically active compounds according to claim 5, characterized in that rings A¹, A² and A³ each independently represent 1,4-phenylene, which is unsubstituted or substituted by halogen, cyano and/or methyl, or trans-1,4-cyclohexylene or one of groups A¹, A² and A³ also represents pyrimidine-2,5-diyl, one of groups Z² and Z³ denotes -(CH₂)₄-, -(CH₂)₃-O-, -O(CH₂)₃- or the transform of -CH=CH-CH₂-CH₂-, -CH₂-CH₂-CH=CH-, -CH=CH-CH₂-O- or -O-CH₂-CH=CH- and the other of groups Z² and Z³ denotes a single covalent bond.



7. Optically active compounds according to any one of claims 1 to 6, characterized by the general formulae





in which R¹, R² and R⁴ have the significances given in claim 1; R⁵ and R⁶ have the significances given in claim 1, with R⁵ preferably having the same meaning and the same configuration at the adjacent C atom as R¹ and R⁶ preferably having the same meaning and the same configuration at the adjacent C atom as R²; rings A⁴ and A⁵ represent 1,4-phenylene, which is unsubstituted or substituted by halogen, cyano and/or methyl, or trans-1,4-cyclohexylene and A⁵ additionally denotes 4,4'-biphenylene.

8. Optically active compounds according to any one of claims 1, 2 and 5 to 7, characterized in that R⁴ denotes halogen, cyano, trifluoromethyl, trifluoromethoxy, alkyl, alkenyl, alkoxy, alkenyloxy, 1-(alkoxycarbonyl)ethoxy or 1-(alkoxycarbonyl)-ethoxycarbonyl.

9. Optically active compounds according to any one of claims 1, 2 and 5 to 8, characterized in that R⁴ has 1 to 12, preferably 1 to 7, carbon atoms.

10. Optically active compounds according to any one of claims 1 to 9, characterized in that R¹ and R² denote C₂-C₇-alkoxycarbonyl or R¹ and R² denote methyl or R¹ and R² denote phenyl or R¹ denotes hydrogen and R² denotes methyl or phenyl, R⁵ has the meaning of R¹, R⁶ has the meaning of R² and the asymmetric carbon atoms have the relative configuration indicated in claim 2.



11. Liquid crystalline mixture containing a liquid crystalline carrier material and one or more optically active compounds according to claims 1 to 10.

12. Use of liquid crystalline mixtures according to claim 11 for optical and electro-optical purposes.