

## Description

The present invention is concerned with novel optically active compounds and their use for electro-optical purposes as well as with liquid crystalline mixtures and liquid crystal cells which contain these compounds.

It is known that the optical characteristics of liquid crystal cells are temperature-dependent. For example, the threshold potential of twisted nematic liquid crystal displays (usually abbreviated to TN-LCDs) decreases with increasing temperature. This dependence is disadvantageous above all for multiplex applications.

On the other hand, liquid crystal materials for TN-LCDs are frequently treated with an optically active component in order to avoid the reversal of the twisting direction ("reverse twist"). The following equation approximates for the threshold potential  $V_{th}^p$  of TN-LCDs when such a material doped with an optically active component is used:

$$V_{th}^p \approx V_{th}^0 \cdot 1 + F \cdot d/|p|^{1/2} \quad (1)$$

in which  $V_{th}^0$  denotes the threshold potential when the undoped material is used,  $d$  signifies the plate separation (i.e. the layer thickness of the liquid crystal material),  $|p|$  denotes the absolute value of the natural pitch of the doped liquid crystal material and  $F$  is a function of the elastic constants and the twisting in the cell [Appl. Phys. Lett. 25, 12 (1974) and IEEE Trans. Electron Devices ED-10, 141 (1974)].

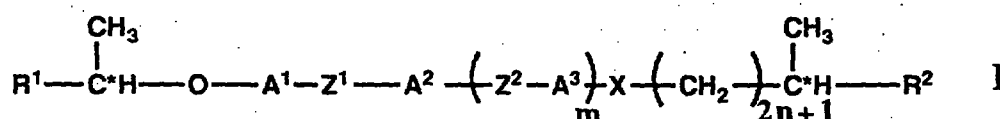
From equation (1) it follows that the decrease in the threshold potential can be compensated for wholly or partially by using optically active dopants which induce a decreasing absolute value of the pitch  $p$  with increasing temperature. Similar considerations also apply to liquid crystal cells such as STN-LCDs ("supertwisted nematic"), SBE-LCDs ("supertwisted birefringence effect"), OMI-LCDs ("optical mode interference") and the like.

From DE-A-2827471, Z. Naturforschung 34a, 594 (1979) and Phys. Lett. 78A, 285 (1980) it is known that a decreasing value of  $|p|$  with increasing temperature can be achieved by adding at least two suitable, optically active dopants in a fixed ratio insofar as one of the dopants in the nematic carrier substance produces a

right-handed twisting and the other produces a left-handed twisting. However, such a doping has the disadvantage that two or more optically active dopants are required and in general even small deviations in the ratio lead to large variations in the temperature pattern of the threshold potential and the pitch. Moreover, relatively high total concentrations of dopants are usually required.

However, only few individual compounds having the desired property are known and the decrease of  $|p|$  with increasing temperature is limited as a rule to a narrow or unfavourable temperature range, whereby the display quality or the utilizable temperature range is distinctly reduced. EP-A-0211646 discloses, for example, compounds having two similar centres of chirality, which have the desired temperature dependence above 0°C, but which lead to helix inversion between about -20°C and 0°C.

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



wherein  $R^1$  and  $R^2$  each independently denote alkyl with at least 2 carbon atoms;  $A^1$ ,  $A^2$  and  $A^3$  each individually represent unsubstituted or cyano-, halogen- and/or methyl-substituted 1,4-phenylene, in which optionally one or two CH groups is/are replaced by nitrogen, or unsubstituted or cyano- and/or methyl-substituted trans-1,4-cyclohexylene, in which optionally one or two  $CH_2$  groups is/are replaced by oxygen;  $Z^1$  and  $Z^2$  each independently signify a single covalent bond,  $-CH_2CH_2-$ ,  $-OCH_2-$ ,  $-CH_2O-$  or  $-C \equiv C-$ ;  $m$  stands for the number 0 or 1;  $n$  denotes a whole number of 0 to 4;  $X$  signifies oxygen or a methylene group; and each  $C^*$  represents a chiral carbon atom, whereby one of the chiral carbon atoms has the R-configuration and the other has the S-configuration.

The compounds of formula I have the desired temperature dependence of the pitch in the entire temperature range which is usually required for commercial applications, especially in the range of about -30°C to +80°C. They frequently have liquid crystalline properties themselves and they are chemically stable and have a good miscibility with known liquid crystal materials.

The compounds of formula I are therefore suitable generally for modifying the temperature dependence of the pitch, but especially for compensating the temperature dependence of the threshold potential.

Formula I above embraces not only compounds in which  $R^1-C^*H(CH_3)-O-$  has the R-configuration and  $-X-(CH_2)_{2n+1}-C^*H(CH_3)-R^2$  has the S-configuration, but also their optical antipodes in which  $R^1-C^*H(CH_3)-O-$  has the S-configuration and  $-X-(CH_2)_{2n+1}-C^*H(CH_3)-R^2$  has the R-configuration. Both of the optical isomers have the same properties, but with opposite helix direction of rotation, opposite optical rotation signs etc.

The term "alkyl with at least 2 carbon atoms" embraces straight-chain and branched alkyl groups such as ethyl, propyl, isopropyl, butyl, isobutyl, 2-methylbutyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl and the like. Groups with 2 to 10 carbon atoms are generally preferred.

The term "halogen" embraces fluorine, chlorine, bromine and iodine, especially fluorine and chlorine.

The term "unsubstituted or cyano-, halogen- and/or methyl-substituted 1,4-phenylene, in which optionally one or two CH groups is/are replaced by nitrogen," embraces 1,4-phenylene, pyridine-2,5-diyl, pyrazine-2,5-diyl, pyrimidine-2,5-diyl and pyridazine-3,6-diyl as well as substituted rings derived therefrom such as 2-methyl-1,4-phenylene, 2-fluoro-1,4-phenylene, 2-cyano-1,4-phenylene, 2,3-dicyano-1,4-phenylene and the like.

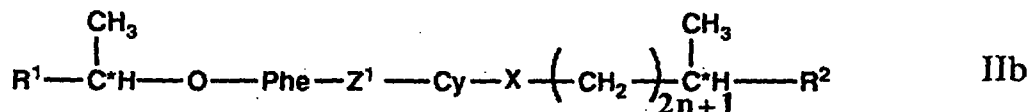
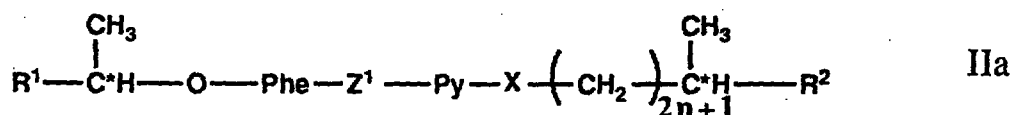
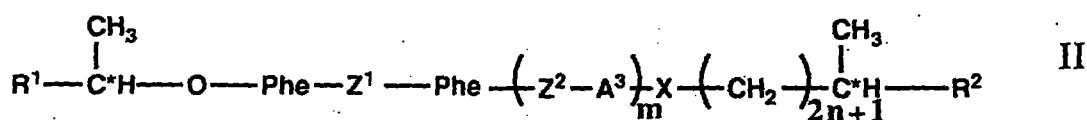
The term "unsubstituted or cyano- and/or methyl-substituted trans-1,4-cyclohexylene, in which optionally one or two  $CH_2$  groups is/are replaced by oxygen," embraces rings such as trans-1,4-cyclohexylene, trans-1,3-dioxane-2,5-diyl as well as substituted rings derived therefrom such as 2-methyl-trans-1,4-cyclohexylene, 1-cyano-trans-1,4-cyclohexylene and the like.

The decrease in the pitch  $|p|$  with increasing temperature is based principally on the terminal groups  $R^1-C^*H(CH_3)-O-$  and  $-X-(CH_2)_{2n+1}-C^*H(CH_3)-R^2$  present and especially on the relative configuration and on the position of the chiral carbon atoms. Variations in the central group have as a rule only a slight influence on the temperature dependence of the pitch. The central

group  $-A^1-Z^1-A^2-(Z^2-A^3)_m$  in formula I can therefore have the above-named rings and bridging groups which are usual in liquid crystals without essentially influencing the desired effect. On the other hand, depending on the choice of rings and bridging groups other properties such as the mesophase, dielectric anisotropy, viscosity, optical anisotropy and the like can be varied in a wide range. In particular, the central group can be selected, if desired, so that, independently of the temperature dependence of the pitch and the threshold potential, the remaining properties of a mixture are not altered or are altered only immaterially.

Preferably, the groups  $A^1$ ,  $A^2$  and  $A^3$  each independently signify unsubstituted or cyano-, halogen- and/or methyl-substituted 1,4-phenylene, unsubstituted or cyano- and/or methyl-substituted trans-1,4-cyclohexylene or one of the groups  $A^1$ ,  $A^2$  and  $A^3$  also signifies pyridine-2,5-diyl, pyrazine-2,5-diyl, pyrimidine-2,5-diyl, pyridazine-3,6-diyl or trans-1,3-dioxane-2,5-diyl.

A preferred group of compounds of formula I comprises the optically active compounds of the general formulae



wherein Phe denotes unsubstituted or cyano-, halogen- and/or methyl-substituted 1,4-phenylene, Py denotes pyridine-2,5-diyl, pyrazine-2,5-diyl, pyrimidine-2,5-diyl or pyridazine-3,6-diyl, Cy denotes unsubstituted or cyano- and/or methyl-substituted trans-1,4-cyclohexylene and  $R^1$ ,  $R^2$ ,  $Z^1$ ,  $Z^2$ ,  $A^3$ ,  $X$ ,  $m$ ,  $n$  and  $C^*$  have the above significances.

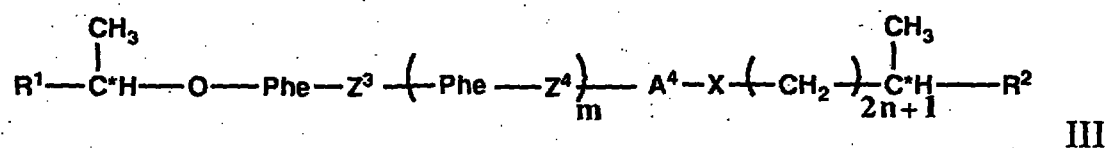
In formulae I and II above  $A^3$  preferably stands for 1,4-phenylene, trans-1,4-cyclohexylene, pyridine-2,5-diyl, pyrazine-2,5-diyl, pyrimidine-2,5-diyl, pyridazine-3,6-diyl or

trans-1,3-dioxane-2,5-diyl, especially for 1,4-phenylene, trans-1,4-cyclohexylene or pyrimidine-2,5-diyl.

Z<sup>1</sup> in formulae I and II above preferably signifies a single covalent bond. Z<sup>2</sup> in formulae I and II above preferably signifies a single covalent bond, -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>O- or -OCH<sub>2</sub>-, especially a single covalent bond.

Py in formula IIa preferably stands for pyrimidine-2,5diyl and Cy in formula IIb preferably stands for trans-1,4-cyclohexylene.

Especially preferred compounds are therefore the optically active compounds of the general formula

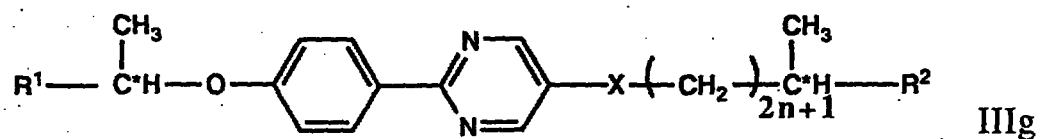
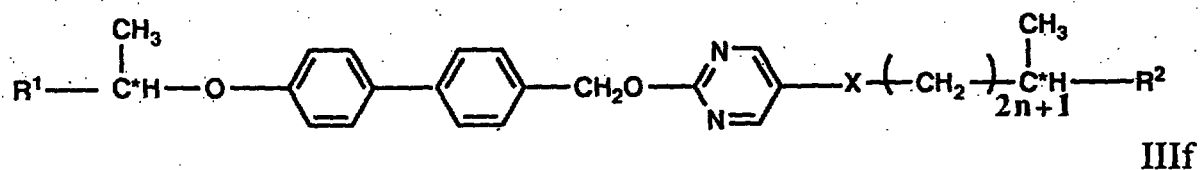
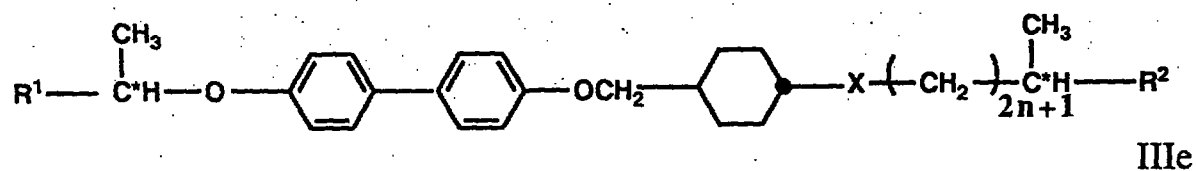
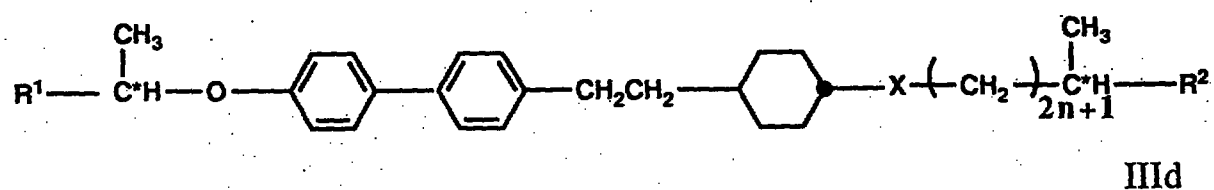
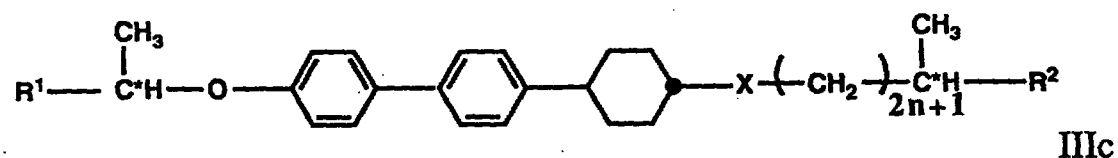
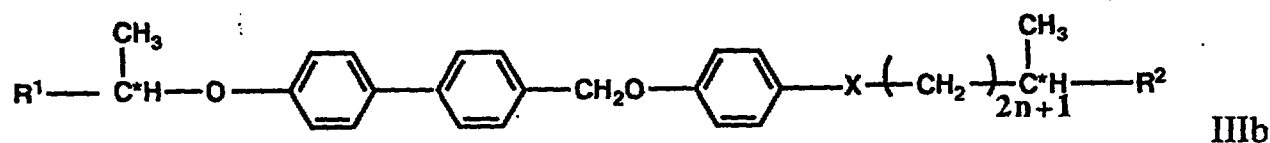
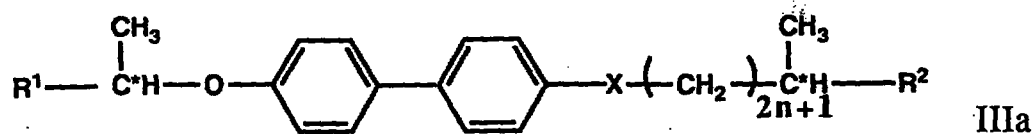


wherein Z<sup>3</sup> signifies a single covalent bond, -COO- or -OOC-, Z<sup>4</sup> denotes a single covalent bond, -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>O- or -OCH<sub>2</sub>- (especially a single covalent bond), A<sup>4</sup> represents 1,4-phenylene, trans-1,4-cyclohexylene or pyrimidine-2,5-diyl and Phe, R<sup>1</sup>, R<sup>2</sup>, X, m, n and C\* have the above significances.

Preferably, Z<sup>1</sup> and/or Z<sup>2</sup> in formulae I and II and, respectively, Z<sup>3</sup> and/or Z<sup>4</sup> in formula III stand for a single covalent bond.

In general, there are preferred compounds of formulae I, II, IIa, IIb and III with unsubstituted rings (i.e. Phe preferably stands for 1,4-phenylene and Cy preferably stands for trans-1,4-cyclohexylene). However, if desired, the dielectric anisotropy, the mesophase, the solubility and the like can be modified by using rings having cyano, halogen and/or methyl substituents.

Examples of preferred compounds of formula III are the optically active compounds of the general formulae



In the above formulae I, II, III and IIIa-IIIg R<sup>1</sup> preferably stands for C<sub>3</sub>-C<sub>10</sub>-alkyl, especially for straight-chain alkyl such as propyl, butyl, pentyl, hexyl or heptyl, and R<sup>2</sup> preferably stands for C<sub>2</sub>-C<sub>6</sub>-alkyl, especially for straight-chain alkyl such as ethyl, propyl or butyl. Those compounds in which R<sup>1</sup> signifies hexyl and R<sup>2</sup> signifies ethyl are in general especially preferred. Further, n in formulae I-III and IIIa-IIIg preferably stands for the number 0, 1 or 2.

The compounds in accordance with the invention can be manufactured according to methods known per se. Suitable methods are well-known to a person skilled in the art, especially from the corresponding achiral compounds as well as from corresponding compounds having a chiral carbon atom. Suitable reagents for introducing the chiral end-group are also known from the preparation of the latter.

The compounds in accordance with the invention are especially suitable as components of liquid crystalline mixtures. The invention is therefore also concerned with a liquid crystalline mixture having at least 2 components, which is characterized in that at least one component is an optically active compound of formula I, especially one of the compounds referred to as being preferred.

The compounds in accordance with the invention have a pitch decreasing with increasing temperature in a wide temperature range. They can be used in nematic, cholesteric or smectic liquid crystal materials for influencing the temperature dependence of the pitch, especially for producing a pitch decreasing with increasing temperature or, for example, in combination with other chiral materials or chiral dopants for producing an essentially temperature-constant pitch. The compounds in accordance with the invention can be used in principle in all known liquid crystal materials.

The amount of compounds of formula I in the mixtures in accordance with the invention can vary in wide limits depending on the range of application, the nature of the other components, the desired pitch or the desired temperature dependence of the pitch etc and can amount to, for example, about 0.1-50 wt.%.

Mixtures which contain one or more compounds of formula I and a nematic carrier material are especially preferred. Such mixtures are especially suitable for the temperature compensation of the threshold potential of indicating devices having a twisted nematic liquid crystal layer. The amount of compounds of formula I in these mixtures depends mainly on the desired pitch (typically about 5-500  $\mu\text{m}$ ) and on the desired temperature pattern of the pitch and in general amounts to about 0.1-10 wt.%, for example about 1-5 wt.%. If desired, the mixture can contain one or more additional chiral dopants. The mixture conveniently has a positive dielectric anisotropy when used in TN-LCDs, STN-LCDs, SBE-LCDs or OMI-LCDs.

The invention is also concerned with an indicating cell having this mixture, namely a liquid crystal cell comprising a twisted nematic liquid crystal layer arranged between two plates, provided with electrodes and surface orientations, and polarizers, wherein the liquid crystal contains one or more compounds of formula I. The liquid crystal preferably has a positive dielectric anisotropy.

The mixtures and liquid crystal cells in accordance with the invention can be manufactured in a manner known per se.

The invention is illustrated in more detail by the following Examples. The phases are denoted by the following symbols: C stands for crystalline,  $SC^*$  stands for chiral smectic C, Ch stands for cholesteric and I stands for isotropic.

#### Example 1

0.8 g of sodium hydroxide is dissolved in a solution of 5.09 g of 4'-[(S)-3-methylpentyl]-4-biphenylol (EP-A-131373) in 40 ml of ethanol. The solution is treated with 6.26 g of (S)-2-octyl-p-toluenesulphonate and heated to boiling for 6 hours. Subsequently, the solvent is distilled off and the residue is taken up in 100 ml of diethyl ether and 50 ml of 0.5N hydrochloric acid. The aqueous phase is separated and back-extracted with 50 ml of diethyl ether. The combined organic phase is washed in succession with 50 ml of water, with 30 ml of 3N sodium hydroxide solution and three times with 50 ml of water each time, then dried over sodium sulphate and concentrated. Crystallization of the residue from ethanol gives 4-[(R)-1-methylheptyloxy]-4'-[(S)-3-methylpentyl]-biphenyl, m.p. (C-I) 12°C.

The following compounds can be manufactured in an analogous manner:

- 4-[(R)-1-Methylheptyloxy]-4'-[(S)-2-methylbutyloxy]-biphenyl, m.p. (C-I) 42°C;
- 4-[(R)-1-methylheptyloxy]-4'-[(S)-4-methylhexyloxy]-biphenyl;
- 4-[(R)-1-methylheptyloxy]-4'-[(S)-6-methyloctyloxy]-biphenyl;
- 4-[(R)-1-methylheptyloxy]-4'-[(S)-8-methyldecyloxy]-biphenyl;
- 4-[(R)-1-methylheptyloxy]-4'-[(S)-10-methyldodecyl-oxy]biphenyl;
- 4-[(R)-1-methylheptyloxy]-4'-[(S)-5-methylheptyl]-

-biphenyl;  
     4-[(R)-1-methylheptyloxy]-4'-[(S)-7-methylnonyl]-  
 -biphenyl;  
     4-[(R)-1-methylheptyloxy]-4'-[(S)-9-methylundecyl]-  
 -biphenyl;  
     5-[(S)-2-methylbutyloxy]-2-(4-[(R)-1-methylheptyloxy]-  
 phenyl)pyrimidine;  
     5-[(S)-4-methylhexyloxy]-2-(4-[(R)-1-methylheptyloxy]-  
 phenyl)pyrimidine;  
     5-[(S)-6-methyloctyloxy]-2-(4-[(R)-1-methylheptyloxy]-  
 phenyl)pyrimidine;  
     5-[(S)-8-methyldecyloxy]-2-(4-[(R)-1-methylheptyloxy]-  
 phenyl)pyrimidine;  
     5-[(S)-10-methyldodecyloxy]-2-(4-[(R)-1-methylheptyl-  
 oxy]phenyl)pyrimidine;  
     5-[(S)-3-methylpentyl]-2-(4-[(R)-1-methylheptyloxy]-  
 phenyl)pyrimidine;  
     5-[(S)-5-methylheptyl]-2-(4-[(R)-1-methylheptyloxy]-  
 phenyl)pyrimidine,  $[\alpha]_D^{22} = +0.060^\circ$ ;  
     5-[(S)-7-methylnonyl]-2-(4-[(R)-1-methylheptyloxy]-  
 phenyl)pyrimidine;  
     5-[(S)-9-methylundecyl]-2-(4-[(R)-1-methylheptyloxy]-  
 phenyl)pyrimidine;

as well as the optical antipodes of the named compounds, i.e. those optical isomers in which in each case (R) is replaced by (S) and (S) is replaced by (R).

### Example 2

A nematic liquid crystal mixture (mixture A) was doped with a compound of formula I and the temperature pattern of the natural pitch  $p$  of the cholesteric mixture was investigated. The results are compiled in Table 1. Negative values of the pitch denote a left-handed twisting and positive values denote a right-handed twisting.

#### Mixture A:

|              |                                                             |
|--------------|-------------------------------------------------------------|
| 7.10 wt.% of | 4'-ethyl-4-biphenylcarbonitrile,                            |
| 3.95 "       | '-propyl-4-biphenylcarbonitrile,                            |
| 7.10 "       | 4'-butyl-4-biphenylcarbonitrile,                            |
| 7.89 "       | 4-(trans-4-propylcyclohexyl)benzonitrile,                   |
| 15.78 "      | 4-(trans-4-pentylcyclohexyl)benzonitrile,                   |
| 16.57 "      | 4-ethoxy-1-[2-(trans-4-propylcyclohexyl)-<br>ethyl]benzene, |

|       |   |                                                  |
|-------|---|--------------------------------------------------|
| 4.73  | " | 4-cyano-4"-pentyl-p-terphenyl,                   |
| 4.73  | " | 4'-(trans-4-pentylcyclohexyl)-4-biphenyl-        |
|       |   | carbonitrile,                                    |
| 11.05 | " | 4-(trans-4-pentylcyclohexyl)-1-[2-(trans-4-      |
|       |   | -butylcyclohexyl)ethyl]benzene,                  |
| 6.42  | " | 4-ethyl-1-(trans-4-propylcyclohexyl)benzene,     |
| 4.59  | " | 4'-(trans-4-pentylcyclohexyl)-4-[2-(trans-4-     |
|       |   | -butylcyclohexyl)ethyl]biphenyl,                 |
| 7.34  | " | 4'-(trans-4-pentylcyclohexyl)-4-[2-(trans-4-     |
|       |   | -butylcyclohexyl)ethyl]-1,1-ethylene- dibenzene, |
| 2.75  | " | trans-4-[2-(trans-4-propylcyclohexyl)ethyl]-     |
|       |   | cyclohexanecarboxylic acid 4-cyanophenyl ester.  |

Mixture B:

99 wt.% of mixture A,

1 " 4-[(R)-1-methylheptyloxy]-4'-[(S)-3-methyl-  
pentyl]biphenyl;

m.p. &lt; -40°C.

Mixture C:

99 wt.% of mixture A,

1 " 4-[(R)-1-methylheptyloxy]-4'-[(S)-2-methyl-  
butyloxy]biphenyl;

m.p. &lt; -40°C.

Mixture D:

99 wt.% of mixture A,

1 " 5-[(S)-5-methylheptyl]-2-(4-[(R)-1-methyl-  
heptyloxy]phenyl)pyrimidine;

m.p. &lt; -40°C.

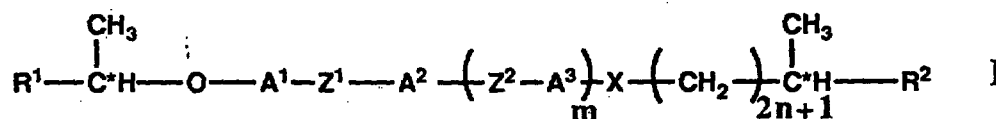
Table 1

| Temperature | Pitch p ( $\mu\text{m}$ ) |           |           |
|-------------|---------------------------|-----------|-----------|
|             | Mixture B                 | Mixture C | Mixture D |
| -40         | -60.6                     | -63.5     | -111.8    |
| -30         | -50.2                     | -59.5     | -82.1     |
| -20         | -43.3                     | -55.7     | -65.9     |
| -10         | -38.5                     | -52.0     | -55.7     |
| 0           | -35.0                     | -48.5     | -48.9     |
| 10          | -32.3                     | -45.2     | -43.9     |
| 20          | -30.3                     | -42.1     | -40.3     |
| 30          | -28.7                     | -39.2     | -37.5     |
| 40          | -27.5                     | -36.6     | -35.4     |
| 50          | -26.6                     | -34.1     | -33.8     |
| 60          | -25.9                     | -31.9     | -32.6     |



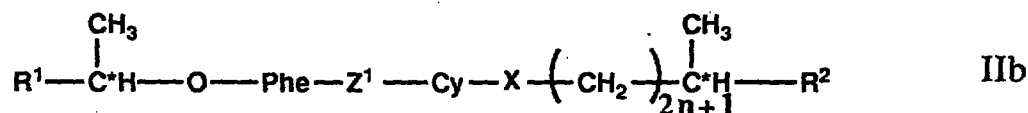
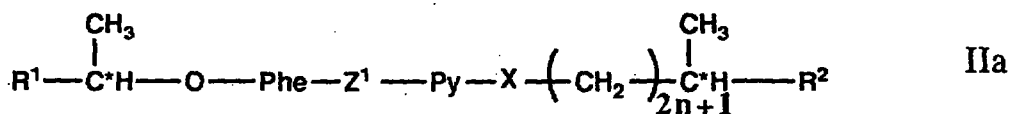
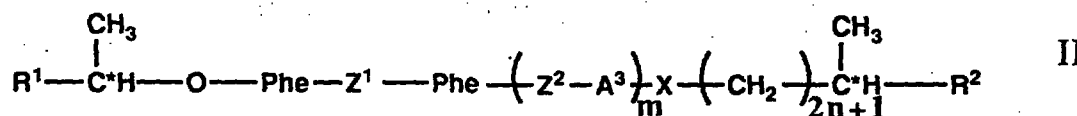
### Claims

1. Optically active compounds of the general formula



wherein  $R^1$  and  $R^2$  each independently denote alkyl with at least 2 carbon atoms;  $A^1$ ,  $A^2$  and  $A^3$  each individually represent unsubstituted or cyano-, halogen- and/or methyl-substituted 1,4-phenylene, in which optionally one or two CH groups is/are replaced by nitrogen, or unsubstituted or cyano- and/or methyl-substituted trans-1,4-cyclohexylene, in which optionally one or two  $CH_2$  groups is/are replaced by oxygen;  $Z^1$  and  $Z^2$  each independently signify a single covalent bond,  $-CH_2CH_2-$ ,  $-OCH_2-$ ,  $-CH_2O-$  or  $-C \equiv C-$ ;  $m$  stands for the number 0 or 1;  $n$  denotes a whole number of 0 to 4;  $X$  signifies oxygen or a methylene group; and each  $C^*$  represents a chiral carbon atom, whereby one of the chiral carbon atoms has the R-configuration and the other has the S-configuration.

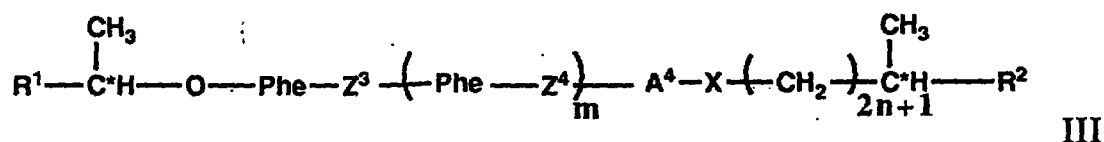
2. Optically active compounds according to claim 1, characterized by the general formulae



wherein Phe denotes unsubstituted or cyano-, halogen- and/or methyl-substituted 1,4-phenylene, Py denotes pyridine-2,5-diyl, pyrazine-2,5-diyl, pyrimidine-2,5-diyl or pyridazine-3,6-diyl, Cy denotes unsubstituted or cyano- and/or methyl-substituted trans-1,4-cyclohexylene and  $R^1$ ,  $R^2$ ,  $Z^1$ ,  $Z^2$ ,  $A^3$ ,  $X$ ,  $m$ ,  $n$  and  $C^*$  have the significances given in claim 1.



3. Optically active compounds according to claim 1 or 2, characterized by the general formula



wherein Phe denotes unsubstituted or cyano-, halogen- and/or methyl-substituted 1,4-phenylene,  $Z^3$  signifies a single covalent bond,  $Z^4$  denotes a single covalent bond,  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{O}-$  or  $-\text{OCH}_2-$ ,  $A^4$  represents 1,4-phenylene, trans-1,4-cyclohexylene or pyrimidine-2,5-diyl and  $R^1$ ,  $R^2$ ,  $X$ ,  $m$ ,  $n$  and  $C^*$  have the significances given in claim 1.

4. Optically active compounds according to any one of claims 1 to 3, characterized in that  $Z^1$  and/or  $Z^2$  or  $Z^3$  and/or  $Z^4$  signify a single covalent bond.

5. Optically active compounds according to any one of claims 1 to 4, characterized in that  $R^1$  denotes  $\text{C}_3$ - $\text{C}_{10}$ -alkyl, preferably propyl, butyl, pentyl, hexyl or heptyl.

6. Optically active compounds according to any one of claims 1 to 5, characterized in that  $R^2$  denotes  $\text{C}_2$ - $\text{C}_6$ -alkyl, preferably ethyl, propyl or butyl.

7. Optically active compounds according to any one of claims 1 to 6, characterized in that  $n$  stands for the number 0, 1 or 2.

8. A liquid crystalline mixture having at least 2 components, characterized in that at least one component is an optically active compound in accordance with claims 1 to 7.

9. A liquid crystalline mixture according to claim 8, characterized in that it contains one or more optically active compounds in accordance with claims 1 to 7 and a nematic carrier material.

10. A liquid crystal cell comprising a twisted nematic liquid crystal layer arranged between two plates, provided with electrodes and surface orientations, and polarizers, characterized



in that the liquid crystal contains one or more compounds in accordance with claims 1 to 7.

11. The use of the compounds in accordance with claims 1 to 7 for electro-optical purposes.

12. The use of the compounds in accordance with claims 1 to 7 for compensating the temperature dependence of the threshold potential of liquid crystal cells.