

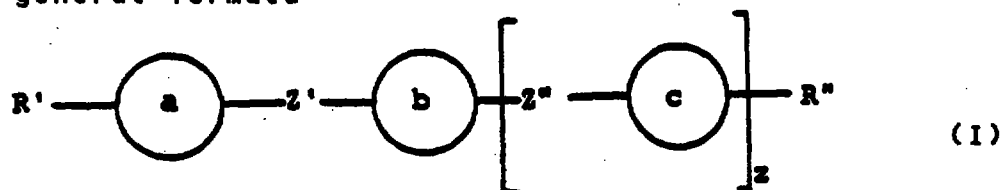
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Anisotropic compounds and liquid crystal mixturesDescription

The invention relates to new anisotropic compounds for use in liquid crystal mixtures (LC mixtures) for electrooptical displays. The invention also relates to LC mixtures containing the new anisotropic compounds.

As is known, anisotropic compounds, the molecules of which carry, for polarisation in the direction of the longitudinal axis of the molecule and/or at right angles thereto, certain substituents which effect this polarisation, are required for the operation of various types of electrooptical displays. The polarisation effect thereby caused is manifested by the positive or negative anisotropy of the dielectric constants ($\epsilon_{\parallel}$ or $\Delta\epsilon$) measured parallel ($\epsilon_{\parallel}$) and perpendicularly ($\epsilon_{\perp}$) to the molecular axis, where $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$.

Virtually all the known anisotropic compounds for liquid crystal mixtures contain two to four cyclic radicals which are linked with one another by bridge members (covalent bonds or particular divalent groups), and in most cases also carry so-called wing groups, according to the general formula

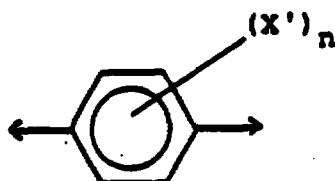


in which R' and R'' are the wing groups, a , b and c are the cyclic radicals and Z' and Z'' are the bridge members; z is 0, 1 or 2.

In a typical case, polarisation in the direction of the longitudinal axis of the molecule - called longitudinal polarisation for short below - and accordingly the contribution to $\epsilon_{\parallel}$ is effected by a highly polarising terminal group, such as the cyano group, on one end of the molecule (as R' or R'') and an alkyl or alkoxy group on the other end of the molecule (R'' or R').

The polarisation at right angles to the longitudinal axis of the molecule - called cross-polarisation for short below - is generally effected by polarising

substituents in the lateral position, and in particular hitherto virtually always by substituents on rings, such as cyano or halogen atoms, usually fluorine or chlorine, on the aromatic cyclic radicals, usually benzene rings, in accordance with the formula II



(II)

in which X' is the polarising group, n is 1 or 2 and the arrows approximately correspond to the longitudinal axis of the molecule.

Formula II shows unambiguously that this customary type of cross-polarisation with the aim of increasing ϵ_L for example for anisotropic substances with an overall negative DCA or for anisotropic substances with a positive DCA and at the same time by use of the smallest possible values of the ratio $\frac{\epsilon_L}{\epsilon_T}$, always unavoidably leads to a considerable widening of the molecule, which is a disadvantage because it leads to a reduction in the clear point, and may result in other disadvantages. The limitation of the cross-polarisation according to formula II to the presence of at least one aromatic ring in the molecule can also have an adverse effect.

The desirability of anisotropic compounds with a positive DCA and as small as possible values of $\frac{\epsilon_L}{\epsilon_T}$ is illustrated, for example, in EP-A-0,019,665, and is achieved there by combination of longitudinal polarisation and cross-polarisation with substituents on rings.

However, problems also result in longitudinal polarisation without cross-polarisation of the molecule if a highly polarising substituent must be attached to a cycloaliphatic radical. As is known, the replacement of the aromatic rings by cycloaliphatic radicals offers various advantages, such as lower viscosity and reduced optical anisotropy; however, it is found that substituents on the rings, such as cyano groups, on cycloaliphatic radicals, lead to a reduction in the clear point or can even effect

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disappearance of the mesophase, especially if O or N is at the same time bonded directly to the cycloaliphatic radical. Thus, for example, cyclohexyl derivatives with a terminal nitrile group, according to formula III

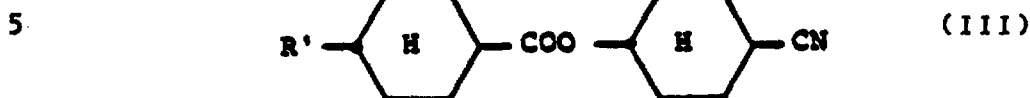
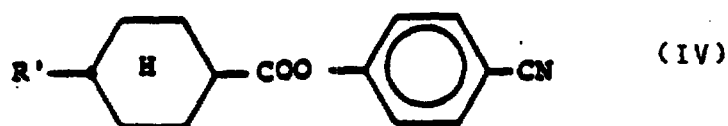


exhibit no mesophases, whilst the analogous phenylcyclohexyl derivatives of the formula IV



still have clear points between 70° and 80°C.

10 In the investigations leading to the present invention, it was found that the conformation energy of the groupings which form the anisotropic molecule, in particular the polarising substituents, and the difference between the free conformation energy $-\Delta G^\circ_x$ of the groupings
15 and substituents is of importance for their effect in reducing the clear point, and that it should be possible favourably to influence this effect by suitable choice of the substituents for longitudinal polarisation and/or cross-polarisation.

20 The object of the invention is to provide new anisotropic compounds for LC mixtures for the operation of electrooptical displays, which enable the longitudinal polarisation and/or cross-polarisation problems mentioned to be solved.

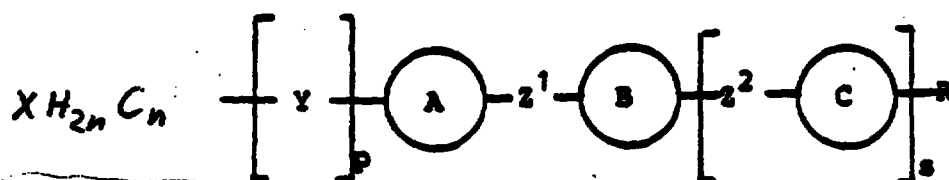
25 It has been found that this object can be achieved by introducing a highly polarising substituent chosen from the group comprising cyano and halogen, such as fluorine or chlorine, into the alkyl part of a wing group of particular anisotropic molecules.

30 Anisotropic compounds of the phenylbenzoate type which have a wing group of the formula $-(\text{CH}_2)_m - \text{CN}$ ($m = 0$ to 4) have already been described in Patent Specification CH-A5-619,485, but the advantages of the compounds

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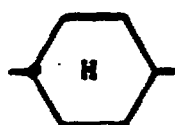
according to the invention, resulting from the conformation energy of the groupings forming the anisotropic molecule, is [sic] of virtually no importance in these compounds, which contain exclusively aromatic rings. Furthermore, 5 GB-2,111,993-A, discloses anisotropic acetonitriles having a wing group of the formula $-CH_2CN$, the mesoregions of which are drastically narrowed in comparison with the properties according to the invention (cf. Table 1). A comparison of 10 compound 10 from Table II with the structurally most similar compound from GB-2,111,993-A, that is to say with 4-(trans-4-pentylcyclohexyl)-phenyl-acetonitrile (Example 31) shows that compound 10 has a clear point which is higher by about $47^{\circ}C$.

The invention relates to new anisotropic compounds 15 of the formula (1)



(1)

which is defined as follows: the rings A, B and C are identical or different and are chosen from the cycloaliphatic 20 radicals of the formulae (1a) and (1b)



(1a)



(1b)

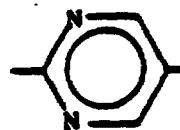
that is to say the trans-1,4-cyclohexyl or 1,4-bicyclo-(2,2,2)-octyl radicals, and aromatic radicals of the for- 25 mulae (1c), (1d) and (1e)



(1c)



(1d)



(1e)

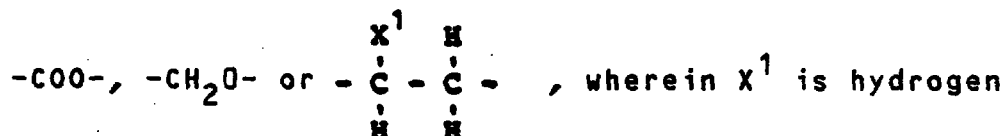
that is to say the 1,4-phenyl, 3,6-pyridazinyl or 2,5-pyrimidine radicals. The radical X, that is to say the

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highly polarising group present in the molecule, is the cyano group or a halogen atom, halogen atoms being fluorine and chlorine, in preference to bromine, and iodine being least preferred.

5 Y is an optional structural component (that is to say p is 0 or 1), and is the oxygen atom (-O-), the carboxyl group (-C(O)-O- or -O(O)C-) or the imino group (-N(H)-). If A is an aliphatic ring of the formulae [sic] (1a) or (1b), p is preferably 0.

10 The bridges Z^1 and Z^2 can be identical or different and are covalent bonds or groups of the formulae



15 or has the meaning given for X, and the groups can also be in the particular reverse sequence -OOC-, -OCH₂- and -CH₂C(X¹)(H)-, as long as these are not excluded by the provisos given below.

20 If X¹ has the meaning given for X, that is to say is cyano or halogen (F and Cl preferred as halogen), the corresponding bridge member contributes towards cross-polarisation of the molecule of the formula (1). However, X¹ can only be X if the wing group R or R¹ is also identical to halogen or cyano.

25 The index n is a number from 1 to 12.

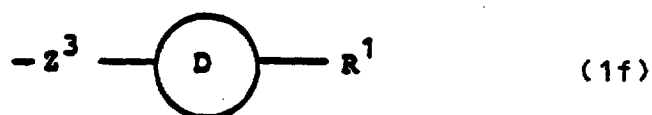
The ring C is an optional component of compounds according to the invention, that is to say s, like p, is 0 or 1.

30 R can have the meaning given for X¹ if the adjacent ring C (if s = 1) or B (if s = 0) is an aromatic radical of the formulae [sic] (1c), (1d) or (1e); alternatively, R is an alkyl (H_{2m+1}C_m-), alkoxy (H_{2m+1}C_m-O-), alkoxy-carbonyl (H_{2m+1}C_m-OC(O)-), alkylcarbonyloxy (H_{2m+1}C_m-C(O)-O-) or alkylamino (H_{2m+1}C_m-N(H)-) group, the alkyl part of
35 which contains 1 to 12 C atoms (m = 1-12) in a straight or branched, optionally chiral chain. Examples of the alkyl parts of the groups mentioned are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl groups, including the isomeric and

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chiral isomeric alkyls, such as 1-methylpropyl, 1-methylbutyl, 2-methylbutyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 1- or 2- or 3- or 4-methylhexyl and 1- or 2- or 3- or 4- or 5-methylheptyl, as well as the other alkyl-alkyl groups with an asymmetric C atom which are formed according to this principle.

The alkyl parts of R can carry one or more substituents, in particular halogen atoms or cyano groups, but at most in each case one such substituent is in each case attached to one C atom of the alkyl part. Furthermore, R can be a radical of the formula (1f)



in which the ring D has the meaning given for rings A, B and C, Z^3 has the meaning given for Z^1 and Z^2 and R^1 has the meaning given for R, with the exception of the radical of the formula (1f).

According to the invention, the formula (1) is subject to the following restrictive provisos (a), (b), (c), (d) and (e):

(a) no oxygen atom, on the one hand, and no oxygen or nitrogen atom or cyano or halogen radical, on the other hand, is on the same side [sic] bonded directly to any of the cycloaliphatic radicals of the formulae [sic] (1a) or (1b) present in the molecule of the formula (1); in other words, the molecule may not contain any rings of the formulae



and



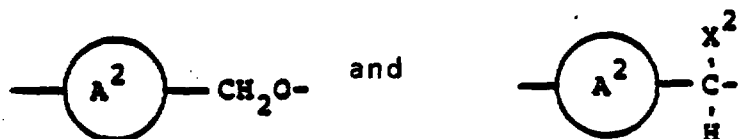
wherein A^1 is a radical of the formulae [sic] (1a) or (1b);

b) no groups of the formulae [sic] $-CH_2O-$ or $-C(X)(H)-$ are bonded directly, with the C atoms of these groups,

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to any of the aromatic radicals of the formulae [sic] (1c), (1d) or (1e) present in the molecule of the formula (1), except when X is the fluorine atom; in other words, the molecule may not contain any rings of the formulae

5



wherein A^2 is a radical of the formulae (1c) and (1e), and X^2 is cyano, chlorine, bromine or iodine, but not fluorine;

- 10 (c) the radical $\text{XH}_2\text{C}_n\text{---}$ is a group of the formula $\text{NC---CH}_2\text{CH}_2\text{---}$ if the substitution by X is terminal,
 (d) the molecule has the formula $\text{NCH---CH}_2\text{CH}_2\text{---}$ 

15 C_{1-12} -alkyl, if, in the molecule of the formula (1), the ring A is an aromatic radical bonded to a $\text{---CH}_2\text{CH}_2\text{CN---}$ group, and

- (e) X^1 can only be X if R and/or R^1 is halagen [sic] or cyano.

20 The provisos (a), (b) and (c) result from the fact that compounds of the formula (1) without these provisos do not have clear points or have clear points which are too low and/or do not have the required stability. The provisos (d) and (e) serve for the purpose of delimitation.

25 The knowledge, on which the invention is based, that the introduction of polarizing substituents into wing-located alkyl groups offers a large number of new anisotropic compounds with low μ values, and does so irrespective of whether the rings of the molecule are only cycloaliphatic radicals or only aromatic radicals, or whether cycloaliphatic radicals are present combined with aromatic radicals,
 30 is new and surprising. In this case, the molecule of the new compounds (1) according to the invention contains a combination of longitudinally polarising X and cross-polarising X, for example a terminal X at the end of a wing group
 35 or directly on an aromatic ring, together with at least one lateral X as part of a wing group.

The knowledge on which the invention is based furthermore offers a large number of new, highly longitudinally polarising anisotropic compounds, in which the longitudinally polarising cyano or halogen atom is terminal on an alkyl part of a wing group attached to a cycloaliphatic radical; longitudinally polarising compounds with high clear points are thereby obtainable.

This longitudinal polarisation by cyano or halogen in the wing group of a cycloaliphatic radical can optionally be combined with cross-polarising cyano or halogen in a wing group or/and a bridge member.

If the compound (1) according to the invention is to have a markedly positive DCA, it will in most cases carry a wing group which contains or consists of a terminal X - preferably cyano. Here is, as also in the ...[sic] to take into consideration, that a non-terminal X in the wing groups can also contribute towards longitudinal polarisation.

If the compound (1) is to have as small as possible a value of with a more or less markedly positive DCA, it carries a wing group which contains or consists of a terminal X, preferably cyano, combined with at least one non-terminal X in a wing group and/or an X on a bridge.

Compounds (1) with negative DCA are obtained if the sum of the lateral polarisation contributions of X in the wings and/or bridges exceeds the sum of the longitudinally polarising contributions, or if the longitudinally polarising groups are absent.

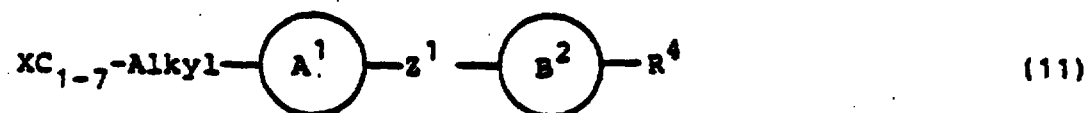
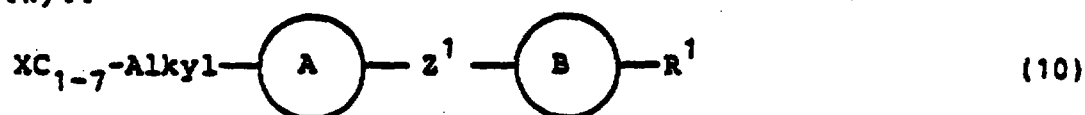
Preferred groups of compounds of the formula (1) according to the invention are defined in Claims 2-13 and have, in particular, the following features, individually or in combination:

- the molecule contains two or not more than three cyclic radicals and a total of 1 to not more than 4 cyano or halogen radicals;
- the ring A is preferably a cycloaliphatic radical, in particular one of the formula (1a);
- the ring A preferably carries an XC₁₋₇-alkyl group, in particular a cyano-C₁₋₇-alkyl group;

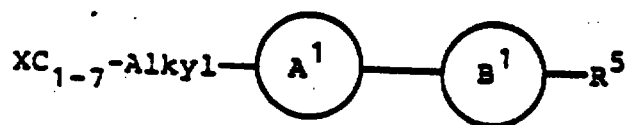


- if X is halogen, fluorine and chlorine are preferred;
- if R and/or R¹ contain a substituted alkyl part, this preferably carries one or two substituents, preferred halogen atoms being fluorine and chlorine;
- 5 - the molecule of the formula (1) preferably contains a total of at most one carboxyl group -COO- or -OOC-;
- the molecule of the formula (1) preferably contains at most one aromatic ring of the formulae [sic] (1c), (1d) or (1e);
- 10 - the molecule of the formula (1) contains at least one bridge member Z in the form of a covalent bond;
- the molecule of the formula (1) contains two or three cycloaliphatic radicals of the formulae (1a), (1b);
- if R and/or R¹ has an alkyl part, this preferably contains 3 to 9 C atoms;
- 15 - if R and/or R¹ is hydrogen or X, the adjacent ring is an aromatic radical of the formulae [sic] (1c), (1d) or (1e);
- the radical X in the left wing group and the substituent optionally present on the alkyl part of R and/or R¹ is [sic] preferably attached to a C atom of the alkyl chain which is separated from the associated ring by not more than 2 C atoms.
- 20

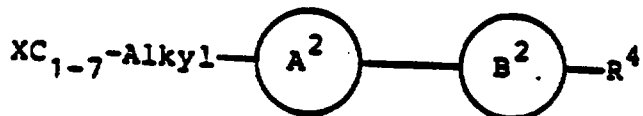
The following formulae illustrate the structure of specific groups of compounds according to the invention, A¹, B¹ and C¹ in each case being the cycloaliphatic radicals (1a) and (1b), A², B² and C² in each case being the aromatic radicals (1c), (1d) and (1e), R⁴ being C₁₋₁₂-alkyl, C₁₋₁₂-alkoxy, XC₁₋₇-alkyl, cyano, F or Cl and R⁵ being C₁₋₁₂-alkyl, C₁₋₁₂-alkoxy, C₁₋₁₂-alkoxycarbonyl, or C₁₋₁₂-alkyl-carbonyloxy; the symbols A, B, C, Z¹, Z² and R¹ have the abovementioned meaning. R⁴ and R⁵ are preferably C₁₋₁₂-alkyl.



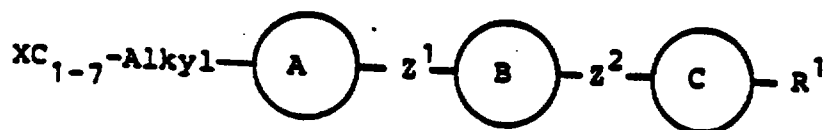
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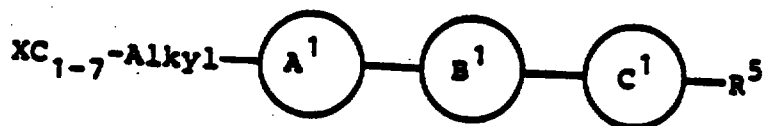
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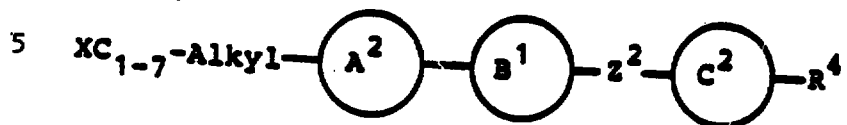
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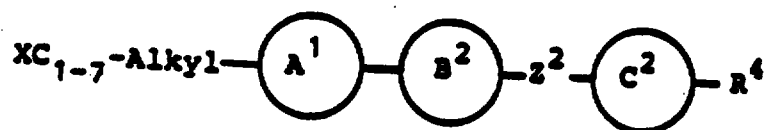
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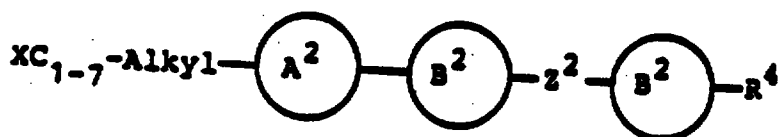
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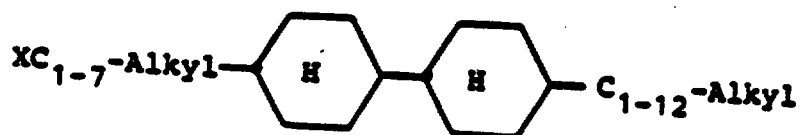
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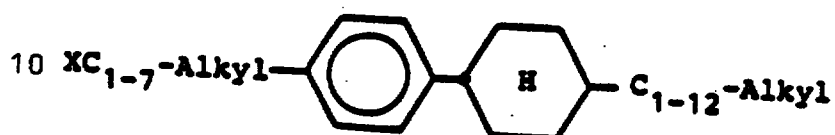
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(18)



(19)



(20)



$\text{XC}_{1-7}\text{-Alkyl}$ is an n-alkyl group with 1-7 C atoms substituted by X. The substitution is preferably terminal in the ω -position. $\text{XC}_{1-7}\text{-Alkyl}$ is especially preferably $\text{NC-CH}_2\text{CH}_2\text{-}$.

5 The invention also relates to liquid crystal mixtures which contain at least one compound of the formula (1), for example in amounts of 1-30 mol %, it being possible for the mixture also to contain several different compounds of the formula (1), for example in an amount of
10 up to 90 mol % in total. As further components, the LC mixtures according to the invention can contain known anisotropic compounds and the additives corresponding to the intended use, such as dyestuffs, in particular pleochroic dyestuffs, optically active or cholesteric components and
15 the like.

 The new compounds of the formula (1) can be obtained by various methods which are known per se; a first general method is based, for example, on modifying a precursor corresponding to the molecule (1), without an X
20 radical or without X-alkyl, by introduction of X or X-alkyl, for example by halogenation, such as bromination, if appropriate transhalogenation and if appropriate nitration, or by Friedel-Crafts reaction and reduction in a manner which is known per se.

25 A second general method is based, for example, on forming the molecule (1) by combining corresponding molecular fragments, for example by condensation, esterification or etherification on a bridge member.

 Corresponding precursors or molecular fragments
30 are either known as such or can be obtained analogously to the known compounds.

 A general example for the first method is illustrated in the equation which follows; the chain length of the X-carrying wing group can be further increased by repeating the steps: bromination/carboxylation/reduction/
35 bromination, the radical X in each case being terminal; the formation of an alkyl-wing group with a non-terminal X, for example cyano, is illustrated in equation Va, in which case a "compound (1)", that is to say a compound of

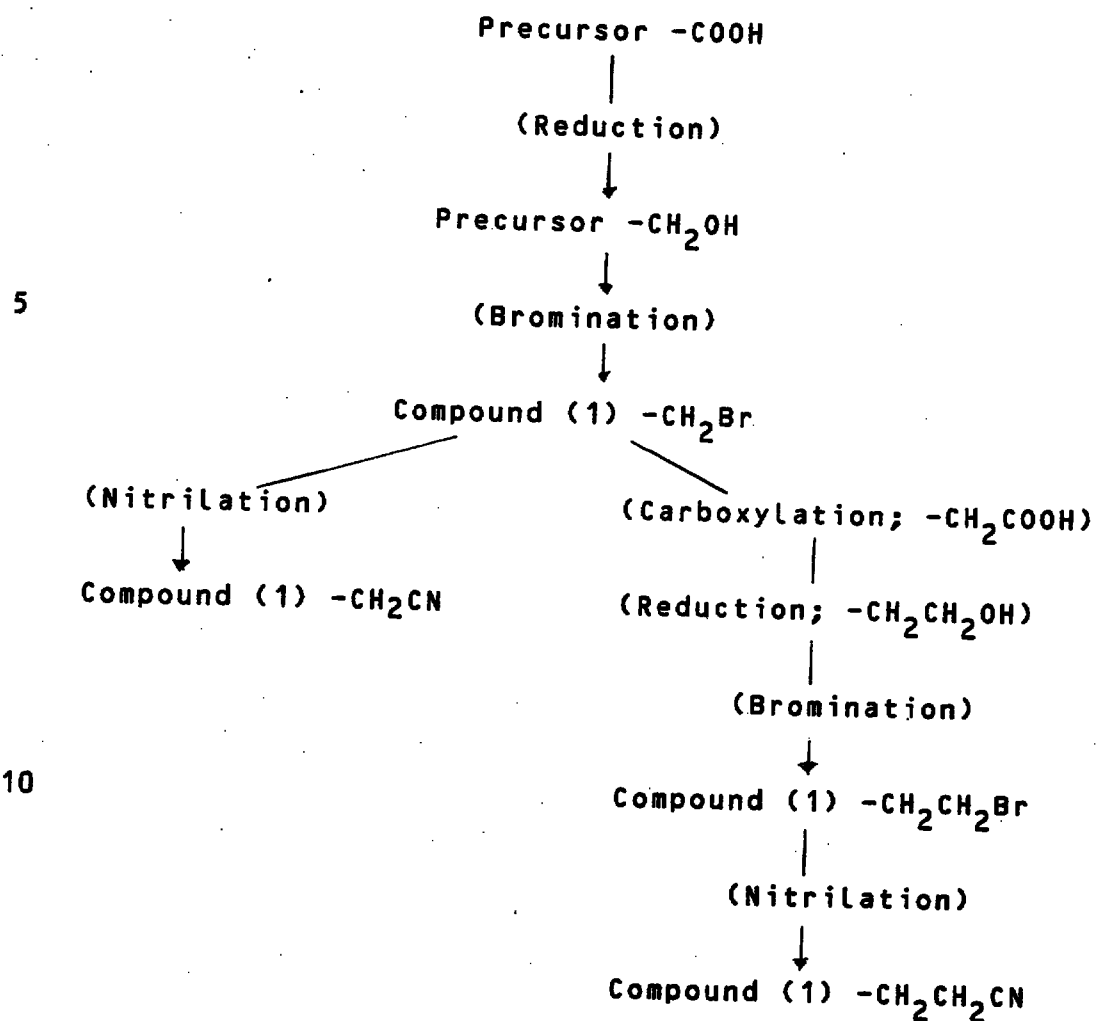


the formula (1), or a corresponding "precursor" can in each case be used as the starting substance.

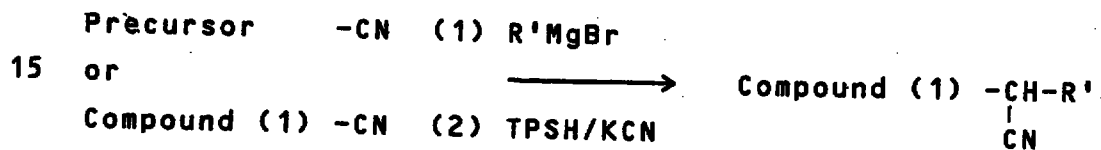
Equation Vb illustrates a specific example for the preparation of suitable "precursors-COOH", that is to say
5 of corresponding carboxylic acids for the synthesis according to equation V or for the preparation of compounds of the formula (1) with terminal cyano on a ring by modification of the carboxyl group by known methods, for example directly or via the corresponding amide. "X-alkyl" in
10 equation Vb here is a group of the formula $XH_{2n'}C_{n'-1}-$, in which n' is in each case one smaller than that desired in formula (1).



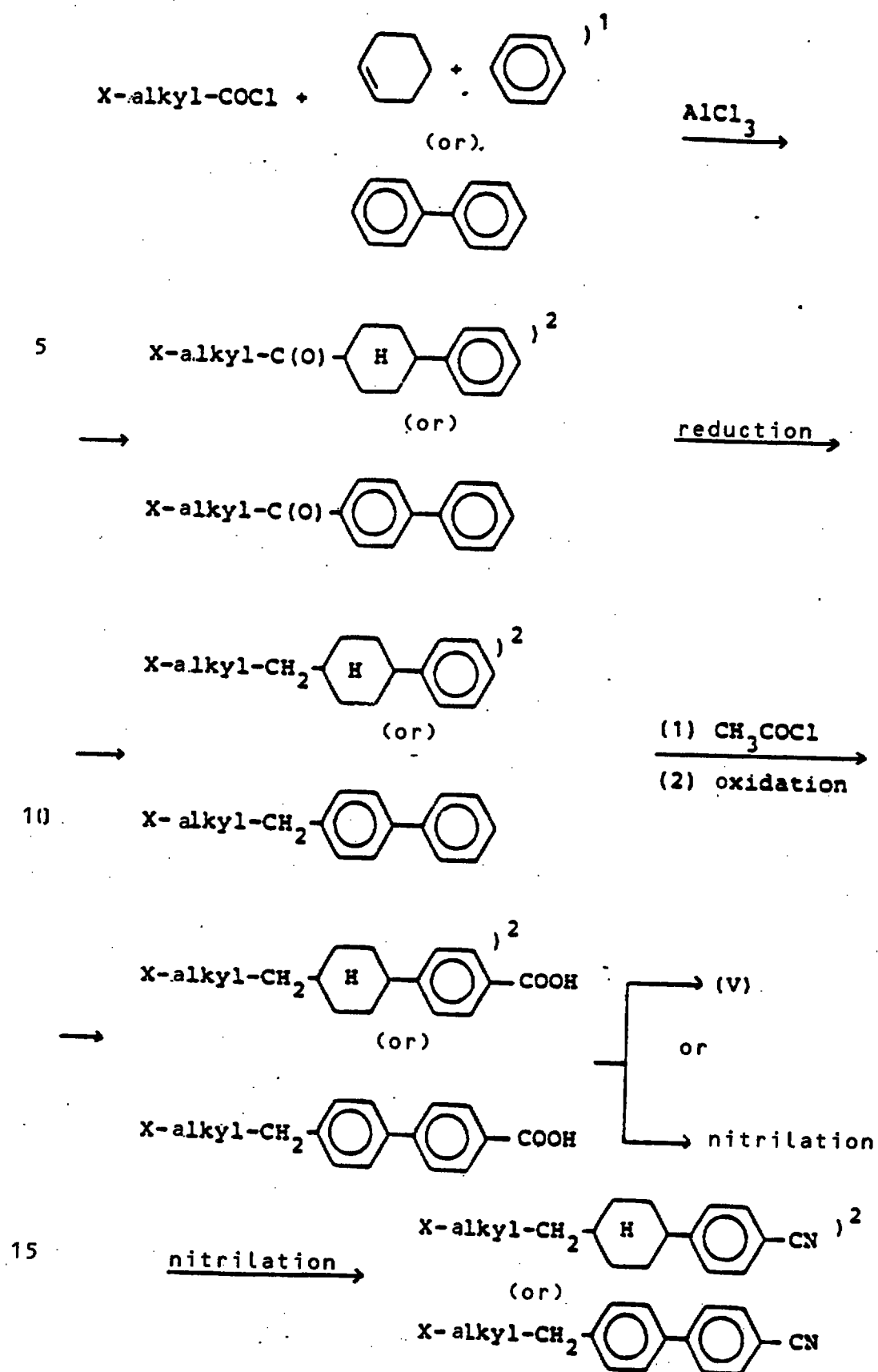
Equation V



Equation Va



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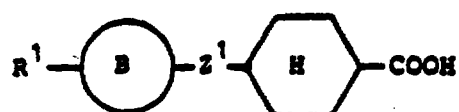


¹ See J.A.C.S. 67 (1945) 1045

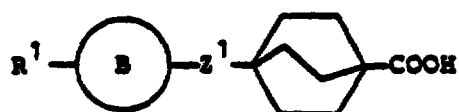
² if appropriate subsequent separation and isolation of the trans-isomer

The reduction of the carboxyl compounds can be carried out with, for example, lithium aluminium hydride; the bromination is in most cases advantageously carried out with elemental bromine in the presence of triphenylphosphine, and the nitrilation is carried out, for example, with copper(I) cyanide or KCN; the Grignard method or, in certain circumstances, nitrile group hydrolysis, is suitable for the carboxylation.

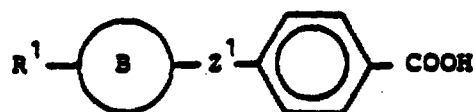
The following are general examples of known carboxyl-precursors or carboxyl-precursors which are obtainable in a known manner, R¹, B, C, Z and Z having the abovementioned meaning:



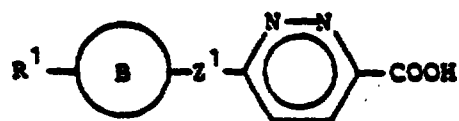
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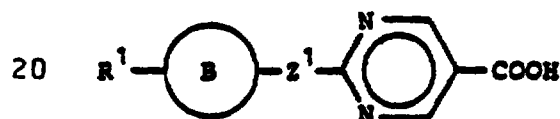
(V-2)



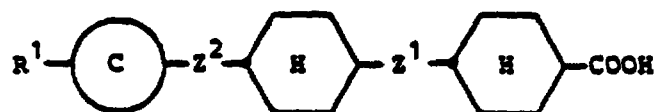
(V-3)



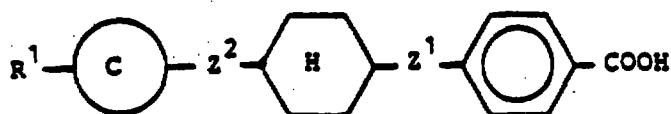
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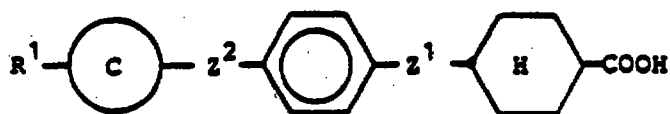
(V-5)



(V-6)



(V-7)



(V-8)

A general example of the second method for the preparation of compounds (1) according to the invention is illustrated in Equation VI below, in which the compound (1) to be prepared consists of two fragments, for example fragment^a and fragment^b, which are bonded to one another by a bridge member Z, for example a carboxyl or methoxy group. Depending on the nature of the bridge group, the reaction is, for example, esterification, etherification or the like, and the fragment can carry a part (Z^a, Z^b) of the bridge to be formed; L¹ and L² are corresponding leaving groups.

Equation VI



15. Suitable compounds for the synthesis according to Equation VI are also either known or can be obtained in a manner which is known per se.

The following examples serve to further illustrate the invention:

Example 1Preparation of 4-trans-cyanoethyl-cyclohexyl trans-propyl-cyclohexyl-1-carboxylate

4-trans-propyl-cyclohexane-1-carboxylic acid (25 mmol) was warmed with thionyl chloride (40 ml) at the reflux temperature for 30 minutes. The acid chloride formed was freed from excess thionyl chloride. The acid chloride thus obtained was now added dropwise to a solution of 4-trans-cyanoethyl-cyclohexanol (melting point 52°C, 25 mmol obtainable in the following manner: 2-(4-hydroxyphenyl)-propionamide is catalytically hydrogenated in 95% strength acetic acid (Nishimura catalyst). The 1:1 cis/trans mixture obtained is brought into equilibrium with aluminiumpropylate. The trans-alcohol obtained is acetylated, converted into the nitrile using SO₂ and the acetyl group is subsequently hydrolysed with NaOH) in 100 ml of pyridine. When the reaction had ended, the mixture was poured into excess dilute hydrochloric acid and extracted with methylene chloride. The product obtained from the extract by evaporation was recrystallised. The target compound of this example thus obtained is monotropically liquid crystal and has a melting point of 73.0°C and a clear point of 14.6°C.

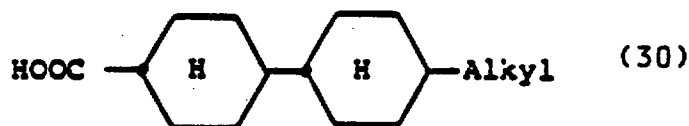
Example 2Preparation of 4-trans-cyanoethyl-cyclohexyl 4-trans-pentyl-cyclohexyl-1-carboxylate

4-trans-pentyl-cyclohexane-1-carboxylic acid (36.5 mmol) was boiled under reflux with thionyl chloride (50 ml) for 1 hour. The excess thionyl chloride was distilled. The resulting acid chloride was added dropwise to a solution of 36.5 mmol of 4-trans-cyanoethyl-cyclohexanol in 100 ml of pyridine. The reaction mixture was stirred until the reaction had ended and then poured onto dilute hydrochloric acid. The product was extracted with methylene chloride. For purification, the product was recrystallised. It has a monotropic liquid crystal phase and a melting point of 61.5°C and a clear point of 39.3°C.

Examples 3-7

By the process described in Equation V or Va and

from the corresponding carboxylic acids of the formula (30)



the compounds of the formula (31) according to the invention



are prepared and their transition temperatures are determined.

The results are summarized in the following Table I

TABLE I

10	Example	X-alkyl	alkyl	melting point	clear point (°C)
	3	Br-CH ₂ -CH ₂ -	n-pentyl	46.0	67.9
	4	NC-CH ₂ -CH ₂ -	n-pentyl	9	108.8
	5	H ₃ C(CH ₂) ₃ C(H)(CN)-	n-pentyl	35	80.0

15 Example 6

The preparation of 4-trans-cyanoethyl-4'-trans-propyl-bicyclohexane according to equation V;

Step 1: a solution of 4'-propyl-trans,trans-bicyclohexane-4-carboxylic acid (0.1 mol) [R. Eidenschink, D, Erdmann, J. Krause and L. Pohl, Angew. Chem. Int. Ed. 17, 133 (1978)]
 20 in dry THF was added dropwise to a suspension of LiAlH₄ (10 g) in 100 ml of dry THF at 0°C. The reaction mixture was boiled under reflux for one hour and poured into cold dilute hydrochloric acid, and the product was extracted with
 25 ether.

Step 2: bromine (0.12 mol) was added dropwise to a suspension of P(Ph)₃ (0.12 mol) in dry CH₃CN at 0°C. A solution in dry CH₃CN of the alcohol prepared above was added dropwise to this suspension, and the mixture was stirred at
 30 this temperature for 15 mins. The solvent was then distilled off and the residue was heated at 130°C for 30 mins. After customary working-up of the reaction mixture, the crude product was extracted with CH₂Cl₂ and the solution was added to hexane to precipitate out the triphenylphosphine



oxide. The product was purified by chromatography (silica gel/toluene).

Step 3: a solution in dry ether of the bromide prepared above was added dropwise to a suspension of magnesium (4 g) in dry ether, and the mixture was stirred for 1 hour at room temperature. CO₂ gas was subsequently passed through the reaction mixture for 30 minutes, which was then worked up as usual. The crude product was recrystallised from toluene or hexane. Steps 1 and 2 were then repeated using this product as the starting material.

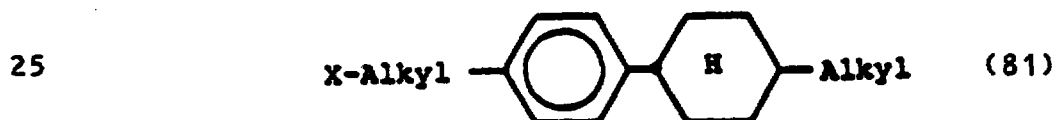
Step 4: a mixture with solid KCN of 4-trans-bromoethyl-4'-trans-propylbicyclohexane thus obtained was heated in DMSO for 2 hours at 100°C, and was then poured into water. The reaction product was extracted with ether and filtered through a short silica gel column using toluene as eluent. The reaction product was recrystallised from EtOH and had a melting point of 13°C and a clear point of 99°C.

Examples 7-8

By the process according to Reaction Equation V or Va from the corresponding carboxylic acids of the formula (80)



the corresponding compounds of the formula (81) according to the invention



were prepared. The resulting anisotropic compounds are summarized in the following Table II.

TABLE II

Example	X-alkyl	alkyl	melting point	clear point (°C)
7	NC-CH ₂ -CH ₂ -	n-pentyl	44.8	(28.3)
8	H ₃ C(CH ₂) ₃ C(H)(CN)-	n-pentyl	34	

Example 9Preparation of 4-cyanoethylphenyl 4-trans-pentyl-cyclohexyl-1-carboxylate

A solution of trans-4-pentylcyclohexanecarbonyl chloride (0.1 mol) in pyridine was added dropwise to a solution of 4-trans-cyanoethyl-cyclohexanol (0.1 mol) in pyridine at 0 - 5°C, and the mixture was stirred at this temperature for 2 hours. The reaction mixture was then worked up as usual, and the product was recrystallised twice from methanol, melting point 75°, clear point 51°.

Other examples of compounds of the formula (1) are the following:

- 4-(2-fluorobutyl)-4'-cyano-biphenyl
- 4-(1-fluoropentyl)-4'-cyano-biphenyl
- 15 4-(2-fluoropentyl)-4'-cyano-biphenyl
- 4-(3-fluoropentyl)-4'-cyano-biphenyl
- 4-(2-chloroethyl)-4''-(2-fluoropropyl)-p-terphenyl [sic]
- 4-(1-fluoropentyl)-4''-cyano-p-terphenyl
- 4-(2-fluoropropyl)-4''-cyano-p-terphenyl
- 20 1-(4-trans-(1-fluoropentyl)-cyclohexyl)-4-cyano-benzene
- 1-(4-trans-(2-cyanoethyl)-cyclohexyl)-4-butoxy-benzene
- 1-(4-trans-(2-fluoropentyl)-cyclohexyl)-4-cyano-benzene
- 1-(4-trans-(3-fluoropentyl)-cyclohexyl)-4-cyano-benzene
- 1-(4-trans-(2-cyanoethyl)-cyclohexyl)-2-(4-cyanophenyl)-
- 25 ethane
- 3-(4-(3-fluoropentyl)-phenyl)-6-(4-cyanophenyl)-pyridazine
- 3-(4-trans-(2-cyanoethyl)-cyclohexyl)-6-(4-pentylphenyl)-pyridazine
- 3-(4-trans-(2-cyanoethyl)-cyclohexyl)-6-butoxy-pyridazine
- 30 1-(4-trans-(2-cyanoethyl)-cyclohexyl)-2-(4-(5-(2-chloroethyl)-2-pyrimidine)-phenyl)-ethane
- 1-(4-trans-(2-cyanoethyl)-cyclohexyl)-2-(4-(5-(3-fluoropropyl)-2-pyrimidine)-phenyl)-ethane
- 4-trans-(2-bromoethyl)-4'-trans-propyl-bicyclohexane
- 35 4-trans-(2-cyanoethyl)-4'-trans-propyl-bicyclohexane
- 4-trans-(2-cyanoethyl)-4'-trans-pentyl-bicyclohexane
- 4-trans-(2-cyanoethyl)-4''-trans-(4-pentyl-1-bicyclo-(2,2,2)-octyl)-bicyclohexane
- 4-trans-(2-cyanoethyl)-cyclohexyl 4-cyano-benzoate



- 4-trans-(2-cyanoethyl)-cyclohexyl 4-pentyl-benzoate
 1-(4-trans-(2-cyanoethyl)-cyclohexyl)-methoxy-4-butoxy-
 benzene
 4-trans-(2-cyanoethyl)-cyclohexyl 4-trans-(4-butoxyphenyl)-
 5 cyclohexane-1-carboxylate
 4-trans-(2-cyanoethyl)-cyclohexyl 4-(4-trans-(2-cyano-
 ethyl)-cyclohexyl)-benzoate
 4-trans-(2-cyanoethyl)-cyclohexyl 4-(4-trans-pentyl-cyclo-
 hexyl)-benzoate
 10 1-(4-trans-(2-cyanoethyl)-cyclohexyl)-4-(4-trans-(3-fluoro-
 propyl)-cyclohexyl)-methoxy-benzene
 4-trans-(fluoromethyl)-cyclohexyl-4'-(2-cyanoethyl)-bi-
 cyclohexane-4-carboxylate
 4-trans-(2-cyanoethyl)-cyclohexyl-4'-(3-fluoropropyl)-
 15 bicyclohexane-4-carboxylate
 1-(4'-(2-cyanoethyl)-bicyclohex-4-yl)-methoxy-4-trans-
 (2-cyanoethyl)-cyclohexane
 4-trans-(2-cyanoethyl)-cyclohexyl-4-(2-cyanoethyl)-bi-
 cyclo-(2,2,2)-octane-1-carboxylate
 20 1-(4-(2-cyanoethyl)-1-bicyclo-(2,2,2)-octyl)-methoxy-4-
 trans-(2-cyanoethyl)-cyclohexane

Examples follow for liquid crystal mixtures accord-
 ing to the invention:

Example A

- 25 A liquid crystal mixture is prepared which consists of
 9% of 2-p-cyanophenyl-5-propyl-1,3-dioxane
 12% of 2-p-cyanophenyl-5-butyl-1,3-dioxane
 9% of 2-p-cyanophenyl-5-pentyl-1,3-dioxane
 6% of 2-p-octoxyphenyl-5-pentyl-pyrimidine
 30 5% of 2-p-nonoxyphenyl-5-pentyl-pyrimidine
 5% of 2-p-heptoxyphenyl-5-hexyl-pyrimidine
 4% of 2-p-nonoxyphenyl-5-hexyl-pyrimidine
 6% of 4,4'-bis(trans-4-propylcyclohexyl)-biphenyl
 9% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcy-
 35 clohexyl)-biphenyl
 17% of r-1-cyano-1-pentyl-cis-4-(trans-4-propylcyclohexyl)-
 cyclohexane
 and
 18% of 4-trans-cyanoethyl-4'-trans-propyl-bicyclohexane.

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Example B

A liquid crystal mixture is prepared which consists of
27% of trans,trans-4-pentylcyclohexylcyclohexane-4'-
carbonitrile

- 5 17% of trans,trans-4-propylcyclohexylcyclohexane-4'-
carbonitrile

30% of 4-trans-cyanoethyl-4'-trans-pentyl-bicyclohexane

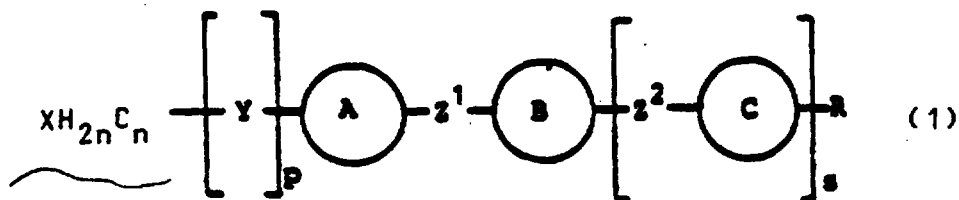
16% of p-ethoxyphenyl trans-4-propylcyclohexanecarboxylate
and

- 10 10% of trans,trans-4-pentyl-4'-butyryloxybicyclohexane.



Patent claims

1. New anisotropic compounds for use in liquid crystal mixtures for electrooptical displays, characterised by the formula (1)



in which the rings A, B and C are identical or different and are chosen from cycloaliphatic radicals of the formulae (1a) and (1b)

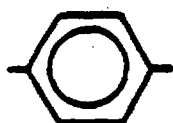


(1a)



(1b)

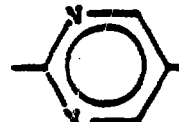
and aromatic radicals of the formulae (1c), (1d) and (1e)



(1c)



(1d)



(1e)

X is cyano or

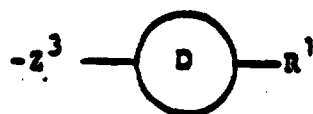
halogen, Y is oxygen, carboxyl or imino, Z^1 and Z^2 are identical or different and are covalent bonds or groups

of the formulae $-\text{COO}-$, $-\text{CH}_2\text{O}-$ or $-\text{C}^{\text{X}^1}(\text{H})-\text{C}^{\text{H}}(\text{H})-$, wherein X^1

is the hydrogen atom or has the meaning given for X, n is a number from 1 to 12, p and s are in each case identical or different and are 0 or 1 and R has the meaning given for X^1 or is an alkyl, alkoxy, alkoxycarbonyl, alkylcarbonyloxy or alkylamino group, the alkyl part of which in each case contains 1 to 12 C atoms in a straight or branched, optionally chiral [sic] carbon chain, which chain optionally carries one or more substituents chosen from halogen and cyano, at most one of the substituents mentioned in each case being attached to one atom of the chain, or is a

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radical of the formula (1f)



(1f)

in which the ring D has the meaning given for rings A, B and C, Z^3 has the meaning given for Z^1 and Z^2 and R^1 has the meaning given for R, with the exception of the radical of the formula (1f), with the provisos that

- (a) no oxygen atom, on the one hand, and no oxygen or nitrogen atom or cyano or halogen radical, on the other hand, is at the same time bonded directly to any of the cycloaliphatic radical [sic] of the formulae (1a) and (1b) present in the molecule,
- (b) no groups of the formulae [sic] $-CH_2O-$ or $-C(X)(H)-$ are bonded directly with the C atoms of this group, to any of the aromatic radical [sic] of the formula (1c), (1d) or (1e) present in the molecule, except when X is Flour [sic],
- (c) the radical XH_2nC_n- is a group of the formula $NC-CH_2CH_2-$, if the substitution by X is terminal,
- (d) the molecule has the formula $NC-CH_2CH_2-$ 

C_{1-12} -alkyl, if, in the molecule of the formula (1), the ring A is an aromatic radical bonded to a $-CH_2CH_2CN$ group, and

- (e) X^1 can only be X if R and/or R^1 is halogen or cyano.
2. Compound according to Claim 1, characterised in that the ring A in formula (1) is a cycloaliphatic radical of the formulae [sic] (1a) or (1b).
3. Compound according to Claim 1 or 2, characterised in that p and s are 0.
4. Compound according to one of Claims 1 or 2, characterised in that R and/or R^1 contains an alkyl part which is at most disubstituted.
5. Compound according to one of Claims 1-3, characterised in that R is only cyano, fluorine or chlorine if the ring bonded directly to R is an aromatic radical of

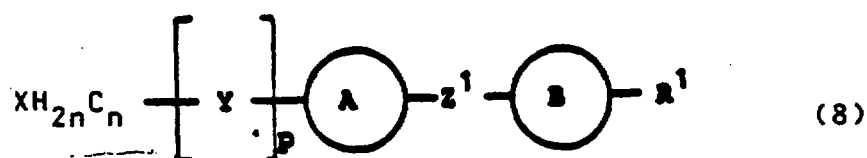
(26)

the formulae [sic] (1c), (1d) or (1e).

6. Compound according to one of Claims 1-5, characterised in that the compound of the formula (1) contains at most one carboxyl group.

7. Compound according to one of Claims 1-5, characterised in that in formula (1) at least one of the bridge members z^1, z^2, z^3 is a covalent bond.

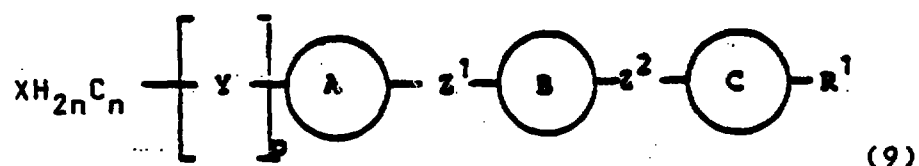
8. Compound according to Claim 1, characterised by the formula (8)



in which X, Y, A, B, z^1 , R^1 , n and p have the meaning given in Claim 1.

9. Compound according to Claim 8, characterised in that the rings A and B are radicals of the formulae (1a), (1b) or/and (1c).

10. Compound according to Claim 1, characterised by the formula (9)



in which X, Y, A, B, C, z^1, z^2, R^1 , n and p have the meaning given in Claim 1.

11. Compound according to Claim 10, characterised in that the rings A, B and C are radicals of the formulae (1a), (1b) or/and (1c).

12. Compound according to one of Claims 1-11, characterised in that the C atom of the wing group of the formula $XH_{2n}C_n[Y]_p$, which carries the radical X, is separated from the ring A by not more than two atoms of the wing group chain.

13. Compound according to one of Claims 1-12, in which R or R^1 contains a substituted alkyl part, characterised in that none of the substituents is attached to a C atom of the alkyl part which is separated from the ring C



or D by more than two chain atoms of the wing group chain.

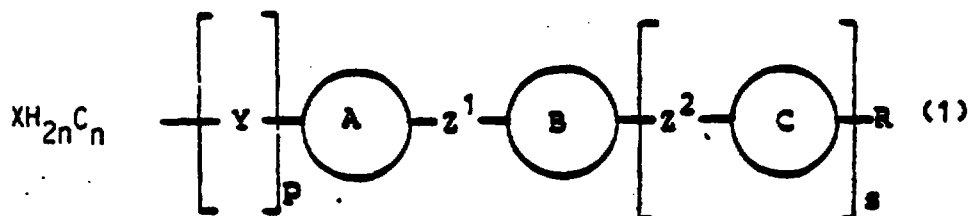
14. Liquid crystal mixture, characterised in that it contains at least one compound according to one of Claims 1-13.

15. Electrooptical display element characterised in that it contains a liquid crystal mixture according to Claim 14.

16 Use of a compound according to one of Claims 1-13 as components in liquid crystal mixtures.

**Claims**

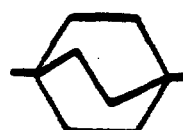
1. New anisotropic compounds for use in liquid crystal mixtures for electrooptical displays, characterised by the formula (1)



in which the rings A, B and C are identical or different and are chosen from cycloaliphatic radicals of the formulae (1a) and (1b)



(1a)



(1b)

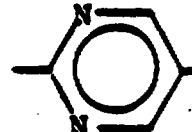
and aromatic radicals of the formulae (1c), (1d) and (1e)



(1c)



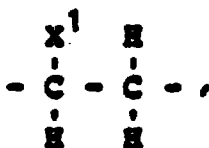
(1d)



(1e)

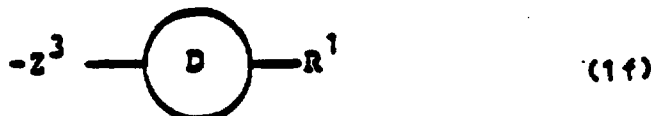
X is cyano or halogen

Y is oxygen carboxyl or imino, Z¹ and Z² are identical or different and are covalent bonds or groups of the formula -COO-, -CH₂C- or



wherein X¹ is the hydrogen atom or has the meaning given for X, n is a number from 1 to 12,

p and s are in each case identical or different and are 0 or 1 and R has the meaning given for X¹ or is an alkyl, alkoxy, alkoxycarbonyl, alkylcarbonyloxy or alkylamino group, the alkyl part of which in each case contains 1 to 12 C atoms in a straight or branched, optionally chiral carbon chain, which chain optionally carries one or more substituents chosen from halogen and cyano, at most one of the substituents mentioned in each case being attached to one atom of the chain, or is a radical of the formula (1f)



in which the ring D has the meaning given for rings A, B and C, Z³ has the meaning given for Z¹ and Z² and R¹ has the meaning given for R, with the exception of the radical of the formula (1f), with the provisos that

(a) no oxygen atom, on the one hand, and no oxygen or nitrogen atom or radical cyano or halogen, on the other hand, are at the same time bonded directly to any of the cycloaliphatic radicals of the formulae (1a) and (1b) present in the molecule,

(b) no groups of the formulae -CH₂O- and -C(X)(H)- are bonded directly, with the C atoms of this group, to any of the aromatic radicals of the formulae (1c), (1d) and (1e) present in the molecule, except when X is the fluorine atom,

(c) the radical XH_{2n}C_n- is a group of formula NC-CH₂CH₂- if the substituent X is in terminal position,

0,139,996



(d) the molecule has the formula $\text{NC-CH}_2\text{CH}_2$ 

C_{1-12} -alkyl if the ring A in the molecule of the formula (1) is a aromatic radical linked to a group $-\text{CH}_2\text{CH}_2\text{CN}$, and

(e) X^1 can only be X if R and/or R^1 is halogen or cyano.

2. Compound according to Claim 1, characterised in that the ring A in formula (1) is a cycloaliphatic radical of the formula (1a) or (1b).

3. Compound according to Claim 1 or 2, characterised in that p and s are 0.

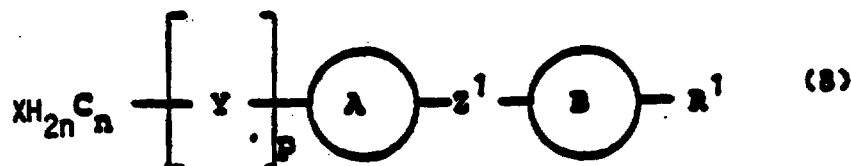
4. Compound according to one of Claims 1 or 2, characterised in that R and/or R^1 contains an alkyl part which is at most disubstituted.

5. Compound according to one of Claims 1-3, characterised in that R only denotes cyano, fluorine or chlorine if the ring bonded directly to R is an aromatic radical of the formula (1c), (1d) or (1e).

6. Compound according to one of Claims 1-5, characterised in that the compound of the formula (1) contains at most one carboxyl group.

7. Compound according to one of Claims 1-5, characterised in that in formula (1) at least one of the bridge members Z^1 , Z^2 or Z^3 is a covalent bond.

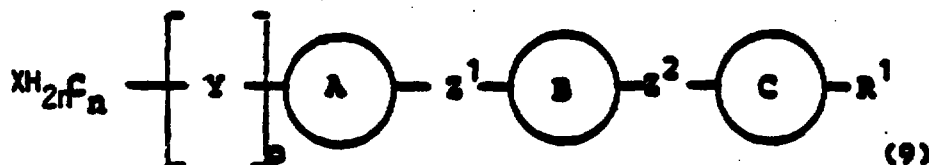
8. Compound according to Claim 1, characterised by the formula (8)



in which X, Y, A, B, Z^1 , R^1 , n and p have the meaning given in Claim 1.

9. Compound according to Claim 8, characterised in that the rings A and B are radicals of the formulae (1a), (1b) or/and (1c)

10. Compound according to Claim 1, characterised by the formula (9)



in which X, Y, A, B, C, Z^1 , Z^2 , R^1 , n and p have the meaning given in Claim 1.

11. Compound according to Claim 10, characterised in that the rings A, B and C denote radicals of the formulae (1a), (1b) or/and (1c).

12. Compound according to one of Claims 1-11, characterised in that the C atom of the end group of the formula $\text{XH}_{2n}\text{C}_n[\text{Y}]_p$ which carries the radical X, is separated from the ring A by not more than two atoms of the end group chain.

13. Compound according to one of Claims 1-12, in which R or R^1 contains a substituted alkyl part, characterised in that none of the substituents is attached to a C atom of the alkyl part which is separated from the ring C or D by more than two chain atoms of the end group chain.

14. Liquid crystal mixture, characterised in that it contains at least one compound according to one of Claims 1-13.

15. Electrooptical display element, characterised in that it contains a liquid crystal mixture according to Claim 14.

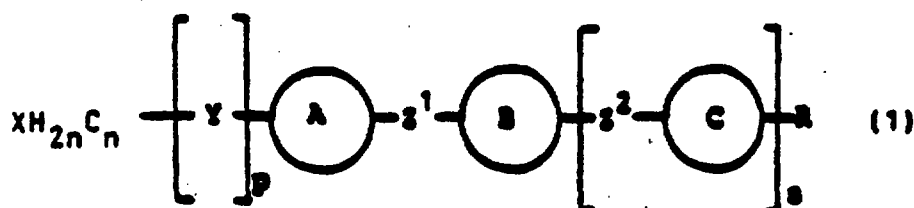
16. Use of a compound according to one of Claims 1 - 13 as components of liquid crystal mixtures.

Revendications

1. Nouveaux composés anisotropes pour l'utilisation dans des mélanges à cristaux liquides servant dans des affichages électro-optiques, caractérisés par la formule 1



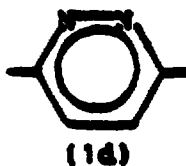
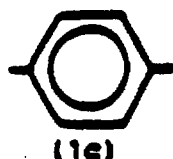
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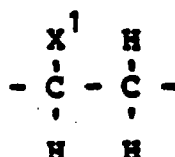
dans laquelle les cycles A, B et C, identiques ou différents, sont choisis parmi les groupes cycloaliphatiques de formules 1a, 1b



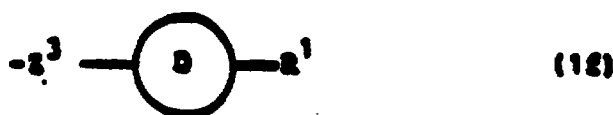
et les groupes aromatiques de formules 1c, 1d, 1e



X représente un groupe cyano ou un halogène et Y représente l'oxygène, un groupe carboxyle ou imino, Z¹ et Z², ayant des significations identiques ou différentes, représentent des liaisons covalentes ou des groupes de formules -COO-, -CH₂O- ou



dans lequel X¹ représente l'atome d'hydrogène ou a les significations indiquées pour X, n est un nombre de 1 à 12, et p et s, ayant des significations identiques ou différentes, sont chacun égaux à 0 ou 1 et R a les significations indiquées pour X¹ ou représente un groupe alkyle, alcoxy, alcoxycarbonyle, alkylcarbonyloxy ou alkylamino dont la partie alkyle contient dans chaque cas 1 à 12 atomes de carbone en chaîne droite ou ramifiée et le cas échéant chirale, ladite chaîne portant le cas échéant un ou plusieurs substituants choisis parmi les halogènes et les groupes cyano, étant spécifié qu'un atome de la chaîne porte au maximum un des substituants mentionnés, ou un groupe de formule 1f



dans laquelle le cycle D a les significations indiquées pour les cycles A, B et C, Z³ a les significations indiquées pour Z¹ et Z² et R¹ les significations indiquées pour R à l'exception du groupe de formule 1f, avec les restrictions suivantes:

(a) sur aucun des groupes cycloaliphatiques de formule 1a ou 1b existant dans la molécule, il ne peut y avoir simultanément liaison directe d'un atome d'oxygène d'une part et liaison directe d'un atome d'oxygène ou d'un atome d'azote ou du groupe cyano ou d'un halogène d'autre part,

(b) sur aucun des groupes aromatiques de formule 1c, 1d ou 1e existant dans la molécule, il ne peut y avoir liaison directe de groupes de formule -CH₂O- ou -C(X)(H)- par l'intermédiaire des atomes de carbone de ce groupe, sauf lorsque X représente le fluor,



(c) le groupe $XH_{2n}C_n$ est un groupe de formule $NC-CH_2CH_2-$ lorsque la substitution par X est en position terminale,

(d) la molécule répond à la formule $NC-CH_2CH_2-$ 

C_{1-12} -Alkyl lorsque, dans la molécule de formule 1, le cycle A est un groupe aromatique relié à un groupe $-CH_2CH_2CN$, et

(e) X^1 ne peut représenter que X lorsque R ou R^1 représente un halogène ou le groupe cyano.

2. Composé selon la revendication 1, caractérisé en ce que le cycle A de la formule 1 est un groupe cycloaliphatique de formule 1a ou 1b.

3. Composé selon la revendication 1 ou 2, caractérisé en ce que p et s sont égaux à 0.

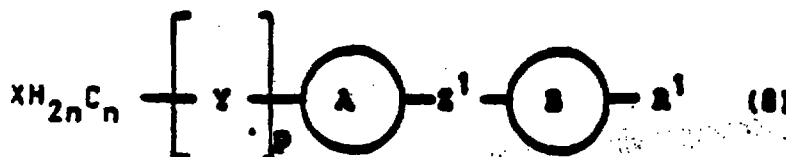
4. Composé selon l'une des revendications 1 ou 2, caractérisé en ce que R et R^1 contiennent une partie alkyle substituée deux fois au maximum.

5. Composé selon l'une des revendications 1 à 3, caractérisé en ce que R ne peut représenter qu'un groupe cyano, le fluor ou le chlore lorsque le cycle relié directement à R est un groupe aromatique de formule 1c, 1d ou 1e.

6. Composé selon l'une des revendications 1 à 5, caractérisé en ce que le composé de formule 1 contient au maximum un groupe carboxyle.

7. Composé selon l'une des revendications 1 à 5, caractérisé en ce que, dans la formule 1, au moins un des ponts Z^1 , Z^2 , Z^3 est une liaison covalente.

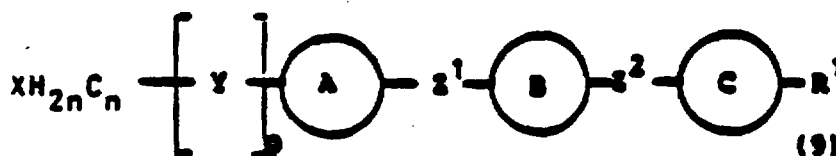
8. Composé selon la revendication 1, caractérisé par la formule 8



dans laquelle X, Y, A, B, Z^1 , R^1 , n et p ont les significations indiquées dans la revendication 1.

9. Composé selon la revendication 8, caractérisé en ce que les cycles A et B sont des groupes de formule 1a, 1b et/ou 1c.

10. Composé selon la revendication 1, caractérisé par la formule 9



dans laquelle X, Y, A, B, C, Z^1 , Z^2 , R^1 , n et p ont les significations indiquées dans la revendication 1.

11. Composé selon la revendication 10, caractérisé en ce que les cycles A, B et C sont des groupes de formules 1a, 1b et/ou 1c.

12. Composé selon l'une des revendications 1 à 11, caractérisé en ce que l'atome de carbone du groupe d'extrémité de formule $XH_{2n}C_n[Y]_p$, qui porte le reste X, est séparé du cycle A par deux atomes au maximum de la chaîne du groupe d'extrémité.

13. Composé selon l'une des revendications 1 à 12, dans lequel R ou R^1 contient une partie alkyle substituée, caractérisé en ce qu'aucun des substituants n'est placé sur un atome de carbone de la partie alkyle qui est séparée du cycle C ou D respectivement par plus de deux atomes de chaîne de la chaîne du groupe d'extrémité.

14. Mélange à cristaux liquides, caractérisé en ce qu'il contient au moins un composé selon l'une des revendications 1 à 13.

15. Élément d'affichage électro-optique, caractérisé en ce qu'il contient un mélange à cristaux liquides selon la revendication 14.

16. Utilisation d'un composé selon l'une des revendications 1 à 13 en tant que composant de mélanges à cristaux liquides.