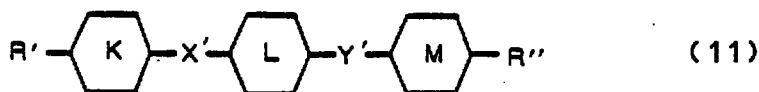
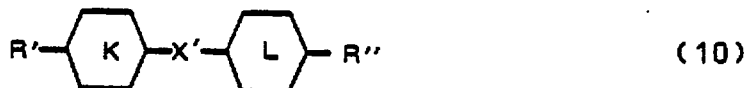


Description

The invention relates to anisotropic compounds and liquid crystal mixtures (LC mixtures) which contain these compounds and are used as a dielectric for liquid crystal displays. (52)

Most known LC compounds correspond to the formulae (10) or (11)



in which the rings K, L and, where appropriate, M are benzene, trans-cyclohexyl or heterocyclic rings, X' and, where appropriate, Y' are direct bonds or/and carboxyl groups or/and azomethine groups and R' and R'' are alkyl, alkoxy, alkylamino, alkylcarbonyloxy or nitrile groups.

German Offenlegungsschriften 2,306,738, 2,306,739, 2,545,121, 2,636,684 and 2,701,591 and the corresponding summaries in "Flüssige Kristalle in Tabellen" ("Liquid Crystals in Tables") by D. Demus et al, Leipzig 1974, may be mentioned as representative of this prior art.

For LC field effect twisted cells, it is generally known that a nematic LC mixture with a sufficiently high positive DC anisotropy is advantageous as the dielectric here, for which purpose substituents of high dipole moment are incorporated in the compounds (10) and (11) parallel to the longitudinal axis of the molecule. As is known, the DC anisotropy ($\Delta\epsilon$) is the difference in dipole moments normal (ϵ_I) and parallel (ϵ_{II}) to the molecular axis, that is to say

$$\Delta\epsilon = \epsilon_{II} - \epsilon_I$$





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Typically, R' is thus, for example, an alkyl or alkoxy group, whilst R'' denotes the nitrile, alkyl or alkoxy group. (53)

Due to this structure and the contributions of the substituents perpendicular to the molecular axis, this results in an $\epsilon_{\perp}$ of about 5, where $\epsilon_{\parallel}$ can, for example, be about 5 or can vary from 20 to 30. This has also been confirmed by various authors in the literature (see, for example, L. Pohl et al, Phys. Lett. 60 A, 421 (1977); A. Boller et al, Mol. Cryst. Liq. Cryst. 42, 215 (1977); and R.T. Klingbiel et al, J. Am. Soc. 96 (25), 7,651 (1974)).

The incorporation of cyclohexane rings into the structures (10) and (11) has the advantage, compared with benzene rings, of a reduced viscosity, but promotes the disadvantageous tendency to form smectic phases and reduces the so-called Δn value, which, analogously to $\Delta\epsilon$, is determined from the differences in refractive indices perpendicular and parallel to the molecular axis.

For commercial LC displays, LC mixtures with certain threshold voltages, which depend on the operation, or certain positive $\Delta\epsilon$ values, for example from 1 to 10 or more, are required. According to the prior art, this can at present be achieved only by mixing components which have high $\Delta\epsilon$ values and components which have very small $\Delta\epsilon$ values, which in turn promotes the tendency to form smectic phases, which has been confirmed by several authors (see G. Heppke et al, Z. Naturforsch. 33a, 185 (1978) and B. Engelen et al, Ann. Phys. (Paris) 3, 403 (1978)). It is desirable to increase the $\epsilon_{\perp}$ value whilst maintaining the $\Delta\epsilon$ value required for the threshold voltage value (see, for example, A.R. Kmetz, SJD Digest, Techn. Papers IX, 70 (1978)).

However, with the LC substances hitherto known (10), (11), this cannot be achieved because the only nematic LC substances with a positive $\Delta\epsilon$ value which are known are those with $\epsilon_{\perp}$ values of about 5. The problem has hitherto been overcome by mixing nematic LC substances

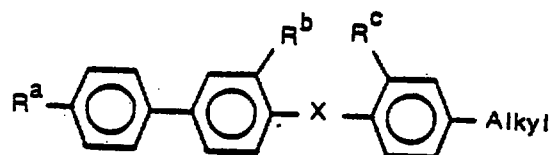


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which have positive $\Delta\epsilon$ values with components which have a negative $\Delta\epsilon$ value, which in turn leads to relatively high threshold voltage values and frequently also to the occurrence of smectic phases.

5 It is known from DE-A-2,613,293, in compounds of the formula



wherein X is -CO-O-, O-CO-, -CO-S- or -S-CO-, to place a nitrile group into the position of the side group R^a or
10 into one of the two "lateral" positions R^b and R^c , whereby a positive DC anisotropy is obtained in the first case ($R^a = \text{CN}$) and a negative DC anisotropy of the molecule is obtained in the second case (R^b or $R^c = \text{CN}$). However,
15 this likewise does not solve the problem discussed above, because again mixtures of compounds with positive and negative DC anisotropies, that is to say with very different $\Delta\epsilon$ values, would have to be used and the above-mentioned disadvantages of such mixtures would have to be accepted.

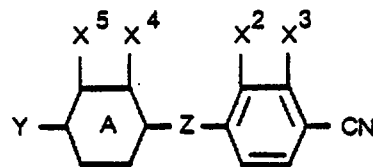
20 The object of the invention is to solve the above-mentioned problem without using substances with very different $\Delta\epsilon$ values, in particular in order to reduce or eliminate the tendency to form smectic phases. According to the invention, this problem is solved with compounds
25 of the formula (1) given below, which permit variation of the $\epsilon_{\parallel}$ values above the value of 5 and hence a substantially improved adaptation to the operating requirements by freer variation of the $\Delta\epsilon$ values, that is to say not just by variation of $\epsilon_{\parallel}$.

30 The object is achieved, according to the invention by anisotropic compounds of the formula (1)



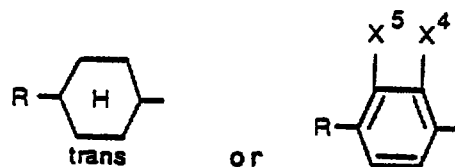
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(1)

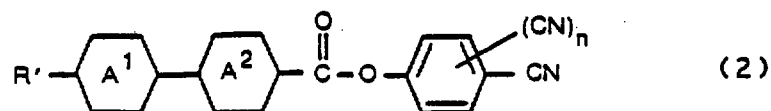
in which X^2 to X^5 are hydrogen atoms, halogen atoms or nitrile groups, with the proviso that at least one of these groups is a halogen atom or the nitrile group, Z is a covalent bond or the carboxyl group $-C(=O)O-$, the nucleus A is a benzene or trans-cyclohexane ring and Y is a group R,



wherein R is the hydrogen atom, an alkyl group with 1 to 12 C atoms or an alkoxy group with 1 to 12 C atoms and X_4 and X_5 are hydrogen atoms, halogen atoms or nitrile groups.

The designation "anisotropic" here means that a given compound is an enantiotropic liquid crystal compound or a potential liquid crystal compound; a compound is a potential liquid crystal compound if either (a) it can be supercooled in the melt and has liquid crystal properties in the supercooled state (monotropic liquid crystal compound), or (b) it shows a detectable mesophase, for example by extrapolation, in the determination of the T_c of a mixture of the potential liquid crystal compound and an enantiotropic liquid crystal compound.

A preferred group of compounds (1) according to the invention corresponds to the formula (2):



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(2)

in which R^1 is an alkyl or alkoxy group with 1 to 12 C atoms, the rings A^1 and A^2 are identical or different



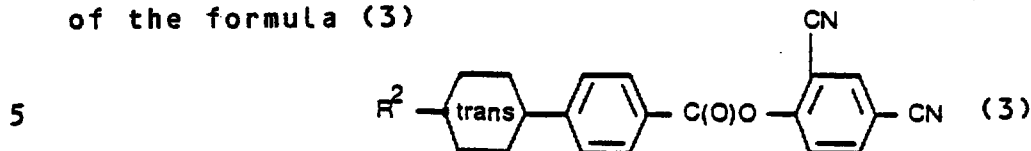
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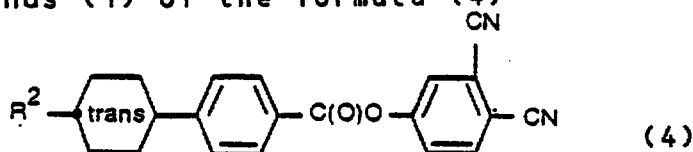
and denote benzene rings or trans-cyclohexane rings and n denotes 1 or 2.

Compounds (1) which are also preferred are those of the formula (3)



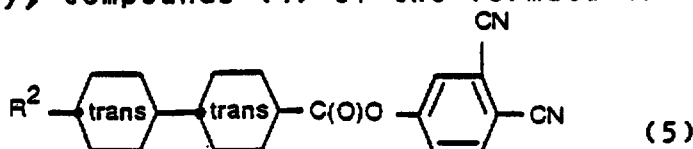
in which R^2 is an alkyl group with 1 to 12 C atoms.

Compounds (1) of the formula (4)



10 in which R^2 is an alkyl group with 1 to 12 C atoms, are also advantageous.

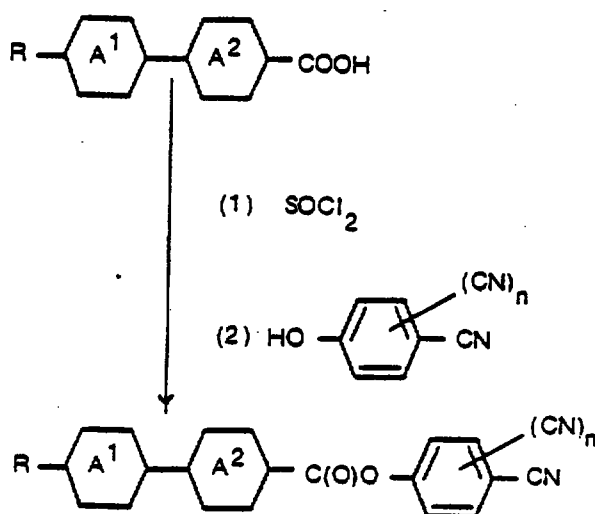
Finally, compounds (1) of the formula (5)



in which R^2 is an alkyl group with 1 to 12 C atoms, are also advantageous according to the invention.

15 Preferred examples which may be mentioned for the n-alkyl group R^2 in the formulae (3), (4) and (5) are those of medium chain length, for example from 3 to 7 C atoms, and n-pentyl is typical of these.

20 The preferred compounds of the formula (1) can be obtained, on particular, in accordance with the following synthesis equation:



wherein the symbols have the meaning given above for formula (2).

Compounds of the formula (1) in which Z denotes a direct bond (single bond) can be obtained in a manner analogous to that described in the abovementioned German Offenlegungsschriften 2,636,684 and 2,701,591, but using appropriately modified compounds for the nuclei substituted by X^2 to X^5 .

The compounds of the formula (1) in which Z is a covalent bond can be obtained in the customary manner by halogenation, for example bromination, of the corresponding hydrocarbon compounds (see, for example, G. Sundstrom et al, "The Science of Total Environment", Volume 6 (1976), pages 15-29), and can be converted into the corresponding nitrile compounds by reacting the halogen, or bromine, derivatives thus obtained with $CuCN$ in N-methylpyrrolidone in a manner which is known per se (G.W. Gray et al, J. Chem. Soc., Perkin Transactions, Volume 2 (1976), page 97).

The following Table I gives examples of compounds of the formula (2) according to the invention with the corresponding characteristic values. The preparation of the compounds are (sic) illustrated below.

Table I

Compound of the formula (2) according to the invention

No.	R ¹ *	A ¹	A ²	(CN) _n	T _m (°C)	T _c (°C)	ε _{II}	ε _I
1	nC ₅ H ₁₁	cyclohexyl	phenyl	2-CN	132.2	178.7	11.0	7.8
2	nC ₅ H ₁₁	cyclohexyl	phenyl	3-CN	85.2	143.9	28.2	7.5
3	nC ₅ H ₁₁	cyclohexyl	cyclohexyl	3-CN	96.8	165.5	16.4	5.5

Remarks: *The particular alkyl group R¹ can be varied between C₁ and C₁₂ or can be replaced by H without the characteristics of the compound being substantially altered; compound numbers 1-3 are thus preferred types of compounds according to the invention, which are in no way restricted to particular R¹ groups.

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Examples for the preparation of compounds according to the invention by processes which are known per se are given below.

Example 1

5 p-(4-trans-n-Pentylcyclohexyl)-benzoic acid (10 g, 36.5 mmol) was boiled under reflux with thionyl chloride (50 ml) for 1 hour. The acid chloride formed was freed from excess thionyl chloride. The acid chloride was added dropwise to a solution of 5.3 g (36.5 mmol) of 2,4-
10 dicyanophenol (melting point 230°C, decomposition) 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 was obtained from the organic phase
15 by evaporation of the solvent. For purification, the crude product was distilled in vacuo (250°C/0.02 mm Hg) and then recrystallized from benzene/hexane, melting point 132.2°C, T_c 178.7°C (clear point).

The resulting compound is compound No. 1 from the
20 above Table I; the compound has nematic liquid crystal properties.

Example 2

p-(4-trans-n-Pentylcyclohexyl)-benzoic acid (10 g, 36.5 mmol) was boiled under reflux with thionyl chloride
25 (50 ml) for 1 hour. The excess thionyl chloride was distilled. The acid chloride formed was added dropwise to a solution of 5.3 g (36.5 mmol) of 3,4-dicyanophenol (melting point 158°C) in 100 ml of pyridine. The reaction mixture was stirred overnight and then poured onto dilute
30 hydrochloric acid. The product was extracted with methylene chloride. For purification, the product was recrystallized from hexane (melting point 85.2°C; T_c 143.9°C). The resulting compound is compound No. 2 from Table I. It gives an enantiotropic nematic phase.

35 Example 3

4-trans-(4'-trans-n-Pentylcyclohexyl)-cyclohexanecarboxylic acid (7 g, 25 mmol) was warmed at the reflux temperature with thionyl chloride (40 ml) for 30 minutes.



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The acid chloride formed was freed from excess thionyl chloride. The acid chloride thus obtained was now added dropwise to a solution of 3,4-dicyanophenol (3.5 g; 25 mmol) in 100 ml of pyridine at 0°C. When the reaction has ended, the reaction mixture was worked up as in Example 2. The product was recrystallized from hexane (melting point 96.8°C, T_c 165.5°C), and is compound No. 3 from Table I; the compound has nematic-enantiotropic properties.

10 Examples 4-6

The homologs corresponding to compound No. 1 from Table I ($R^1 = H$; $R^1 = CH_3$; and $R^1 = nC_{12}H_{25}$) were prepared by the procedure of Example 1.

Examples 7-10

15 The homologs corresponding to compound No. 2 from Table I ($R^1 = H$; $R^1 = CH_3$; and $R^1 = nC_{12}H_{25}$) were prepared by the procedure of Example 2.

Examples 11-13

20 The homologs corresponding to compound No. 3 from Table I ($R^1 = H$; $R^1 = CH_3$; and $R^1 = nC_{12}H_{25}$) were prepared by the procedure of Example 3.

All the compounds according to the invention prepared as described in Examples 1-13 proved to be anisotropic (liquid crystal or potentially liquid crystal) in the context of the definition given above. The values of ϵ_{II} and of ϵ_I of the compounds of Examples 4-13 were similar to the values of the particular compounds of Examples 1-3 which correspond structurally, the absolute values differing slightly with the length of the alkyl chain (that is to say somewhat higher absolute values as the length of the alkyl chain decreases); however, the ratios ϵ_{II}/ϵ_I in each structural group which corresponded to one of the compounds Nos. 1-3 of Table I with different R^1 groups were virtually identical.

35 Example 14

Compound No. 1 from Table I was also prepared by the following method:

10 g (36.5 mmol) of p-(4-trans-n-pentylcyclohexyl)-



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benzoic acid, 5.3 g (36.5 mmol) of 2,4-dicyanophenol, 0.25 g of concentrated sulfuric acid and 0.15 g of boric acid are added to 350 ccm of toluene. The solution is kept under reflux for 120 hours, the water formed during the reaction being stripped off. The toluene is then distilled off. A crude product is obtained, and is purified by chromatography on a silica column. 10 g of pure substance are thereby obtained, that is to say a yield of 67% is achieved.

10 The homologs corresponding to compound No. 1 ($R^1 = H$ or $R^1 = C_1-C_{12}$ -alkyl) can also be obtained by this procedure, using the corresponding benzoic acid derivatives.

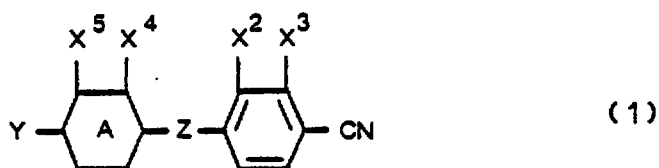
15 Advantageous LC mixtures for the known field effect twisted cells can be formed with the compounds according to the invention. Such LC mixtures preferably contain up to 25% by weight of at least one compound of the formula (1), preferably 10 to 20% by weight. However, the LC mixtures can advantageously contain several
20 compounds of the formula (1), for example in a total amount of up to half of the weight of the LC mixture.



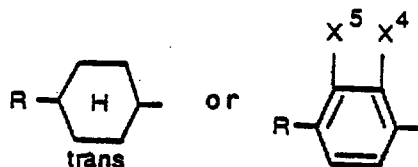
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Patent Claims

1. Anisotropic compounds of the formula (1)

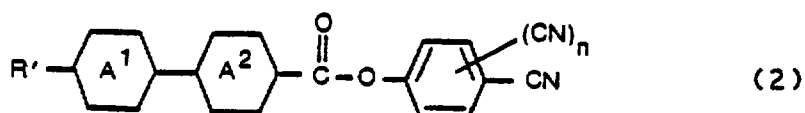


in which X^2 to X^5 are hydrogen atoms, halogen atoms or nitrile groups with the proviso that at least one of these groups is a halogen atom or the nitrile group, Z is a covalent bond or the carboxyl group $-C(O)O-$, the nucleus A is a benzene or trans-cyclohexane ring and Y is a group R,



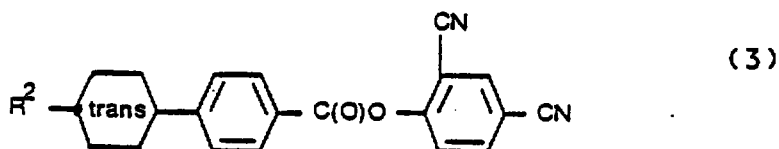
wherein R is the hydrogen atom, an alkyl group with 1 to 12 C atoms or an alkoxy group with 1 to 12 C atoms and X_4 and X_5 are hydrogen atoms, halogen atoms or nitrile groups.

2. Compound according to Patent Claim 1, characterized by the formula (2)



in which R' is an alkyl or alkoxy group with 1 to 12 C atoms, the rings A^1 and A^2 are identical or different and denote benzene rings or trans-cyclohexane rings and n denotes 1 or 2.

3. Compound according to Patent Claim 1, characterized by the formula (3)



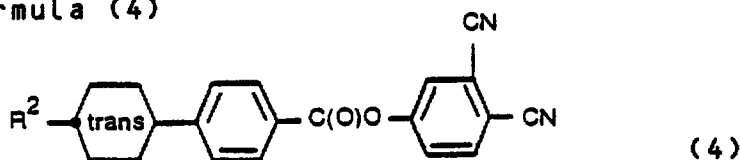


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in which R^2 is an alkyl group with 1 to 12 C atoms.

4. Compound according to Patent Claim 3, characterized in that R^2 denotes the n-pentyl group.

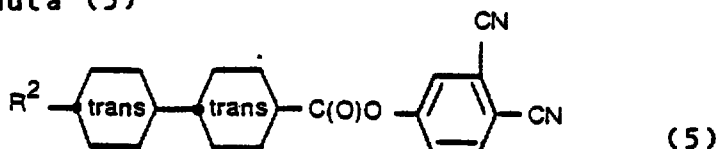
5. Compound according to Patent Claim 1, characterized by the formula (4)



in which R^2 is an alkyl group with 1 to 12 C atoms.

6. Compound according to Patent Claim 5, characterized in that R^2 denotes the n-pentyl group.

7. Compound according to Patent Claim 1, characterized by the formula (5)



in which R^2 is an alkyl group with 1 to 12 C atoms.

8. Compound according to Patent Claim 7, characterized in that R^2 denotes the n-pentyl group.

9. Liquid crystal mixture, characterized in that it contains at least one compound according to one of Patent Claims 1-8.

10. Mixture according to Patent Claim 9, characterized in that it contains at least one compound in an amount of 10 to 20% of the weight of the mixture.

11. Mixture according to Patent Claim 10, characterized in that it contains several compounds according to one of the Patent Claims 1-8 in a total amount of up to 50% of the weight of the mixture.

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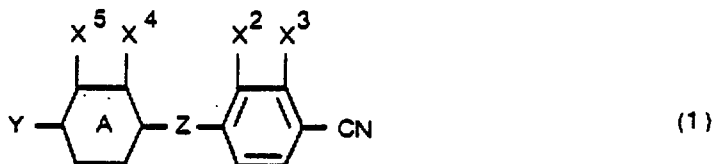




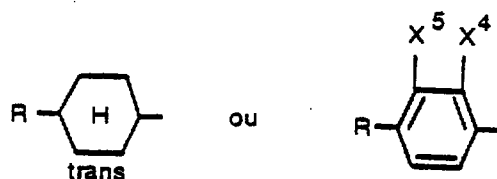
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Revendications (as printed)

1. Combinaisons anisotropes de la formule (1)

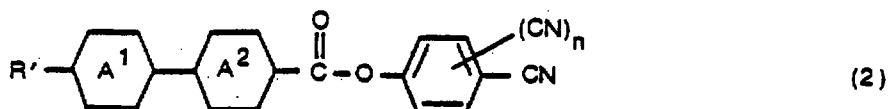


dans laquelle X^2 à X^5 sont des atomes d'hydrogène, des atomes d'halogène ou des groupes nitrile, un de ces groupes au moins étant un atome d'halogène ou le groupe nitrile, Z une liaison de covalence ou le groupe carboxyle $—C(O)O—$, le noyau A un cycle benzène ou transcyclohexane et Y un groupe R.



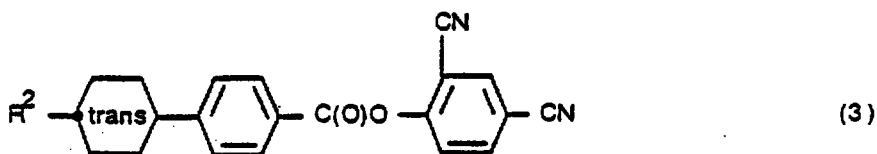
dans lequel R représente l'atome d'hydrogène, un groupe alkyle avec 1 à 12 atomes de C ou un groupe alcoxy avec 1 à 12 atomes de C, et X_4 et X_5 sont des atomes d'hydrogène, des atomes d'halogène ou des groupes nitrile.

2. Combinaison selon la revendication 1, caractérisée par la formule (2)



dans laquelle R' est un groupe alkyle ou alcoxy avec 1 à 12 atomes de C, les noyaux A^1 et A^2 étant identiques ou différents et représentant des noyaux benzène ou des noyaux trans-cyclohexane et n signifie 1 ou 2.

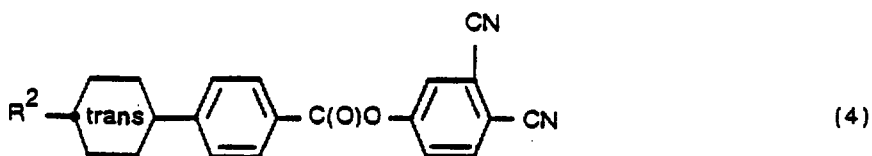
3. Combinaison selon la revendication 1, caractérisée par la formule (3)



dans laquelle R^2 est un groupe alkyle avec 1 à 12 atomes de C.

4. Combinaison selon la revendication 3, caractérisée par le fait que R^2 représente le groupe n-pentyle.

5. Combinaison selon la revendication 1, caractérisée par la formule (4).



dans laquelle R^2 est un groupe alkyle avec 1 à 12 atomes de C.

6. Combinaison selon la revendication 5, caractérisée par le fait que R^2 représente le groupe n-pentyle.

7. Combinaison selon la revendication 1, caractérisée par la formule (5)

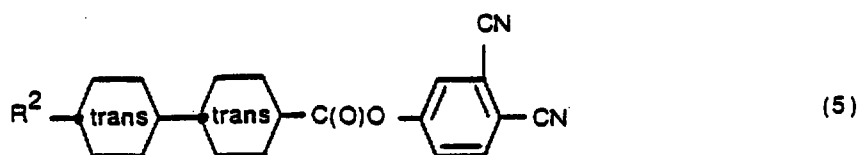
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dans laquelle R² est un groupe alkyle avec 1 à 12 atomes de C.

8. Combinaison selon la revendication 7, caractérisée par le fait que R² représente le groupe n-pentyle.

9. Mélange de cristaux liquides, caractérisés par le fait qu'il renferme au moins une combinaison selon une des revendications 1 à 8.

10. Mélange selon la revendication 9, caractérisé par le fait qu'il renferme au moins une combinaison dans une proportion de 10 à 20% du poids du mélange.

11. Mélange selon la revendication 10, caractérisé par le fait qu'il renferme plusieurs combinaisons selon une des revendications 1 à 8, dans une proportion totale allant jusqu'à 50% du poids du mélange.

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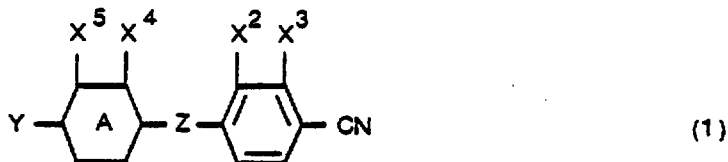




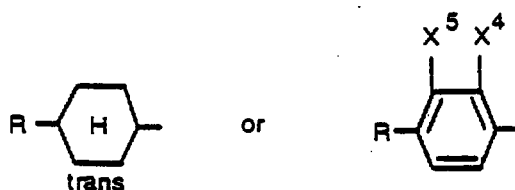
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Claims (as printed)

1. Anisotropic compounds of the formula (1)

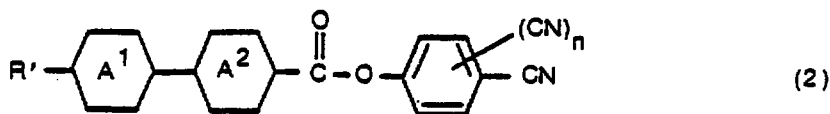


in which X^2 to X^5 are hydrogen atoms, halogen atoms or nitrile groups, wherein at least one of these groups is a halogen atom or the nitrile group, Z is a covalent bond or the carboxyl group —C(O)O— , the ring A is a benzene or trans-cyclohexane ring and Y is a group R,



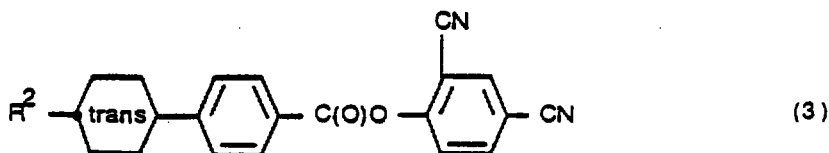
wherein R is hydrogen, alkyl having 1 to 12 carbon atoms or alkoxy having 1 to 12 carbon atoms, and X^4 and X^5 are hydrogen, halogen atoms or nitrile groups.

2. The compounds of claim 1, having the formula (2)



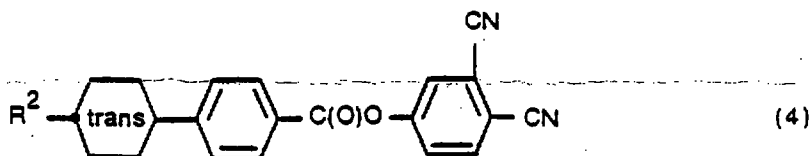
wherein R' is a alkyl or alkoxy group having 1 to 12 carbon atoms, the rings A^1 and A^2 are identical or different and are benzene or trans-cyclohexane rings, and n is 1 or 2.

3. The compounds of claim 1, having the formula (3)



wherein R^2 is a alkyl group having 1 to 12 carbon atoms.

4. The compound of claim 3, wherein R^2 is the n-pentyl group.
5. The compounds of claim 1, having the formula (4)



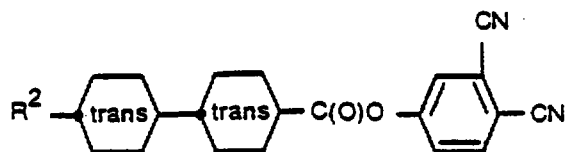
wherein R^2 is a alkyl group having 1 to 12 carbon atoms.

6. The compound of claim 5, wherein R^2 is the n-pentyl group.
7. The compounds of claim 1, having the formula (5)

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(5)

wherein R² is a alkyl group having 1 to 12 carbon atoms.

8. The compound of claim 7, wherein R² is the n-pentyl group.

9. A liquid crystal composition which comprises as components at least one compound of claims 1—8.

10. The composition of claim 9 which comprises as components at least one compound in a portion of 10 to 20% by weight of the composition.

11. The composition of claim 10 which comprises several compounds of claims 1—8 in a total portion of up to 50% by weight of the composition.

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