

Description

The invention relates to liquid crystal phases (LC phases) with low optical anisotropy and wide nematic phases.

The properties of nematic or nematic-cholesteric liquid crystal materials are being increasingly utilised for liquid crystal display elements (LC display elements) to significantly modify their optical properties, such as light absorption, light scattering, birefringence, refractance or colour under the influence of electrical fields.

5 The function of such display elements here is based, for example, on the phenomena of dynamic scattering, the deformation of aligned phases, the guest-host effect, the Schadt-Helfrich effect in the twisted cell or the cholesteric-nematic phase transfer.

15 Liquid crystal phases which must fulfil a large number of requirements are required for industrial application of these effects in electronic components. Chemical stability towards moisture, air and physical influences, such as heat, infrared, visible and ultraviolet radiation

20 and constant and alternating electrical fields, are particularly important here. Furthermore, a liquid crystal mesophase in a suitable temperature range and the lowest possible viscosity at room temperature are required of industrially usable liquid crystal dielectrics. Finally,

25 they should not exhibit intrinsic absorption in the range of visible light, that is to say they must be colourless.

In none of the previously known series of compounds with liquid crystal mesophases is there an individual compound which meets all these requirements. Mix-

30 tures of two to twenty, preferably three to fifteen, compounds are therefore as a rule prepared in order to obtain substances which can be used as liquid crystal phases. At least one compound of low melting point and clear point is usually included in this mixture. A mixture is

35 usually obtained here with a melting point below that of the component of lower melting point, whilst the clear point is between the clear points of the components. However, optimum phases cannot easily be prepared in this

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manner, since the components of high melting point and clear points frequently also impart a high viscosity to the mixtures. The switching times in the electrooptical display elements produced with these mixtures are thereby
5 increased in an undesirable manner.

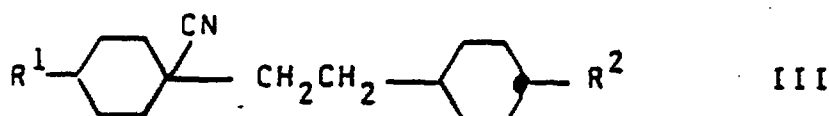
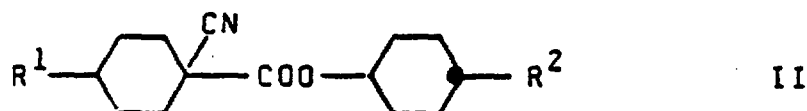
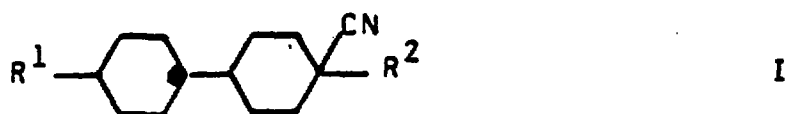
The invention is based on the object of preparing liquid crystal phases which have a nematic phase in the required temperature range and allow adequately short switching times in liquid crystal cells at room temperature.

10 A large number of liquid crystal phases based on a large number of compounds are already commercially available. However, there is still a great need for liquid crystal phases with high clear points, lower melting points, low viscosity (and hence short switching
15 times) and low optical anisotropy. Liquid crystal phases with a wide mesophase range, low viscosity, low optical anisotropy, steep characteristic transmission line and relatively highly negative dielectric anisotropy are particularly required for so-called guest-host displays with
20 positive contrast (the information appears in dark form on a light background) (T. J. Scheffer, Phil. Trans. R. Soc. Lond. A 309 (1983) 189; and F. Gharadjedazki and R. Voumasd, J. Appl. Phys. 53 (1982) 7306). Moreover, the liquid crystal phases must have a high stability to UV
25 and take up the dichroic dyestuffs to a sufficient degree. Such negative LC phases were not hitherto available. For wide-range mixtures, for example for external applications, the product of the layer thickness and optical anisotropy must have quite specific values, for example about 1.0 or
30 about 0.5, since otherwise the angle-dependency of the contrast becomes too great and interference colours arise, impairing the optical phenomenon. A coating thickness of about 6 - 7 micrometers and a liquid crystal phase with a positive dielectric anisotropy and an optical anisotropy are about + 0.07 to about + 0.08 are today generally
35 employed for such TN cells in order to achieve a particularly good angle-dependency of the contrast. It is particularly difficult to achieve sufficiently high clear points whilst at the same time avoiding the occurrence of

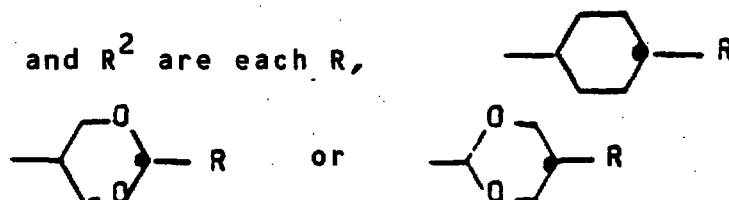
smectic phases and viscosity values which are too high at low temperatures. Such positive LC phases have not hitherto been available.

It has now been found that liquid crystal phases with particularly advantageous combinations of material properties, in particular wide mesophase ranges and low optical anisotropy, are obtained if they contain at least one component from Group A consisting of the compounds of the formulae I to IV

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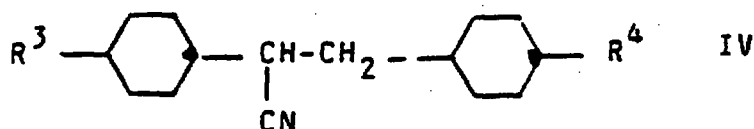


wherein R^1 and R^2 are each R,



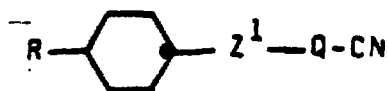
and R is alkyl with 1 to 12 C atoms, and wherein also one or two non-adjacent CH_2 groups can be replaced by $-\text{O}-$, $-\text{CO}-$, $-\text{O}-\text{CO}-$ or $-\text{CO}-\text{O}-$,

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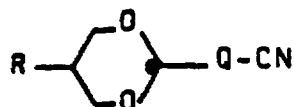


wherein R^3 and R^4 are each R or $\text{---} \text{C}_6\text{H}_4 \text{---} \text{R}$ and R has the abovementioned meaning, and/or at least one component selected from Group B consisting of the compounds of the formulae V and VI

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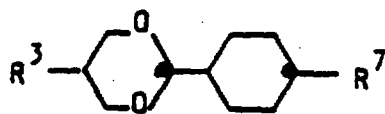
V



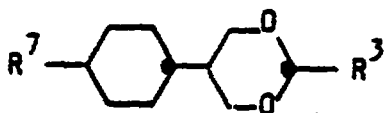
VI

wherein R has the abovementioned meaning, Q is C_6H_4 or C_6H_2 , and Z^1 is C_6H_4 , a single bond, $-\text{CH}_2\text{CH}_2-$, $-\text{CO}-\text{O}-$ or $-\text{O}-\text{CO}-$, and at least one component selected

5 from Group C consisting of the compounds of the formulae VII to X



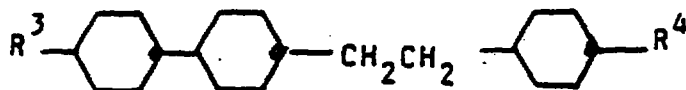
VII



VIII



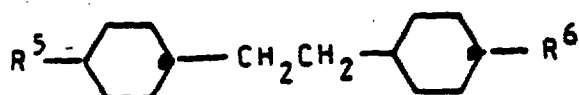
IX



X

wherein R^3 and R^4 have the abovementioned meaning and R^7 can assume the meaning of H or R^8 , wherein R is as defined above, and R^8 is alkyl with 1 to 12 C atoms, and wherein also one or two non-adjacent CH_2 groups can be replaced by $-\text{O}-$ or $-\text{CO}-$, and, if appropriate, one or more components selected from Group D consisting

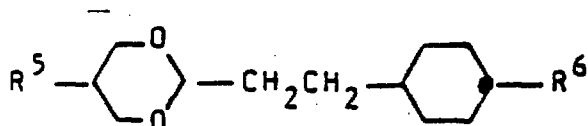
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XI

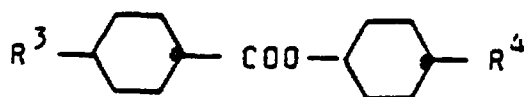


XII

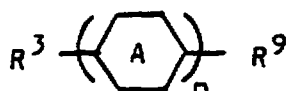


XIII

wherein R^5 and R^6 in each case independently of one another are alkyl with 1 to 12 C atoms, and wherein also one or two non-adjacent CH_2 groups can be replaced by
 5 -O-, -CO-, -O-CO- or -CO-O, and if appropriate, one or more components selected from Group E consisting of the compounds of the formulae XIV and XV



XIV



XV

wherein R^3 and R^4 is(sic) each R or $-\text{C}_6\text{H}_4-\text{R}$, R^9 is R,
 10 $-\text{C}_6\text{H}_4-\text{R}$, $-\text{C}_6\text{H}_3(\text{O})-\text{R}$ or, if n equals 2, also CN, n is 2 or, if R^3 equals $-\text{C}_6\text{H}_4-\text{R}$, also 1 and A is a 1,4-phenylene group which is optionally fluorinated in the 2- or 3-position, with the proviso that, if compounds of the formula V and/or VI wherein Q is 1,4-phenylene are
 15 present, the liquid crystal phase contains at least one component of the formula IX wherein R^3 is n-alkyl and R^4 is n-alkyl, n-alkoxy or n-alkanoyloxy with in each case 1 - 12 C atoms, and at least one component from Group E.

The invention thus relates to the liquid crystal
 20 phases described above, which can also contain, if appropriate, two or more pleochroic dyestuffs, and to the use of these phases in liquid crystal display elements.

The invention furthermore relates to liquid crystal display elements containing such phases.

25 Although display elements which are free from interference colours and which contain dielectrics with positive dielectric anisotropy and low optical anisotropy, preferably in the range from 0.05 to 0.10, are already known from German Offenlegungsschrift 3,022,818,
 30 the LC phases described therein do not allow an operating temperature range which permits external applications.



Surprisingly, it has now been found that a sufficiently wide operating temperature range, in particular also for external applications, is possible with the positive LC phases according to the invention, the occurrence of smectic phases and/or very high viscosity values at low temperatures being at the same time largely eliminated.

The negative liquid crystal guest-host systems according to the invention are particularly distinguished by a low optical anisotropy, excellent stability and high degrees of order of the dyestuffs. By providing the liquid crystal guest-host systems according to the invention, the applicability of such systems is also considerably increased from various technological viewpoints. The liquid crystal guest-host systems according to the invention and electrooptical display elements containing them can be provided for the most diverse applications, depending on the selection of the components of the host material and of the pleochroic dyestuffs.

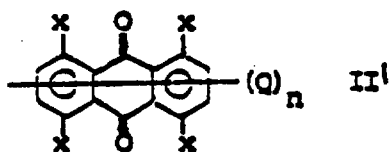
The negative LC guest-host systems according to the invention furthermore contain at least two, preferably 2 to 5, and in particular 3 or 4, pleochroic dyestuffs. In principle, all the pleochroic dyestuffs suitable for guest-host mixtures can be used as the dyestuffs. The most important of these dyestuffs belong to the classes of anthraquinone, naphthoquinone, azo, indigo, and/or perylene dyestuffs.

A rich variety of these dyestuffs are described in the literature. The expert can seek out the most suitable dyestuffs for the particular intended application without difficulty. Thus, for example, anthraquinone dyestuffs are described in European Patent 34,832, European Patent 44,893, European Patent 48,583, European Patent 54,217, European Patent 56,492, European Patent 59,036, British Patent 2,065,158, British Patent 2,065,695, British Patent 2,081,736, British Patent 2,082,196, British Patent 2,094,822, British Patent 2,094,825, Japanese Preliminary Published Application 55-123,673, Japanese Preliminary Published Application 56-112,967, Japanese Preliminary

Published Application 57-165,456, Japanese Preliminary
Published Application 59-020,355, German Patent 3,017,877,
German Patent 3,040,102, German Patent 3,048,552, German
Patent 3,100,533, German Patent 3,115,147, German Patent
5 3,115,762, German Patent 3,150,803, German Patent 3,201,120
and German Patent 3,309,045, naphthoquinone dyestuffs are
described in German Patents 3,126,108 and 3,202,761, azo
dyestuffs are described in European Patent 43,904, German
Patent 3,123,519, German Patent 3,238,702 (blue tetraazo
10 dyestuffs), German Patent 3,245,751, German Patent 3,309,
048, PCT WO 82/2054, British Patent 2,079,770, Japanese
Preliminary Published Application 56-57,850, Japanese
Preliminary Published Application 56-104,984, Japanese
Preliminary Published Application 55-052,375, Japanese
15 Preliminary Published Application 59-096-171, Japanese
Preliminary Published Application 59-093,776, U.S. Patent
4,308,161, U.S. Patent 4,308,162, U.S. Patent 4,340,973, T.
Uchida, C. Shishido, H. Seki and M. Wada: Mol. Cryst. Liq.
Cryst. 39, 39-52 (1977) and H. Seki, C. Shishido, S. Yasui
20 and T. Uchida: Jpn. J. Appl. Phys. 21, 191-192 (1982) and
perylene are described in European Patent 60,895, European
Patent 68,427 and PCT WO 82/1191.

Some groups of these classes of dyestuffs are des-
cribed in still more detail below:

- 25 a) anthraquinone dyestuffs with S-alkyl, S-cyclo-
alkyl and/or S-aryl groups, for example of the formula II'

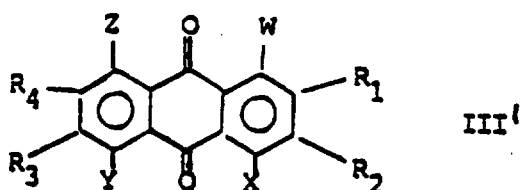


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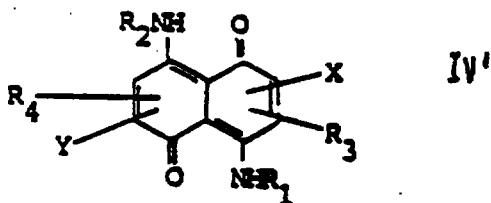
wherein Q is NH₂, OH, alkyl, aryl, NO₂ or halogen, n is
0, 1, 2, 3 or 4, X is in each case H, SR, NZ₁Z₂ or Q,
R is in each case alkyl, aryl or cycloalkyl and Z₁ and
35 Z₂ is(sic) in each case H, alkyl, aryl or cycloalkyl
dyestuffs are known, for example, from European Patent
0,059,036), and

- b) anthraquinone dyestuffs with substituted phenyl
and/or cyclohexyl groups, for example of the formula III'

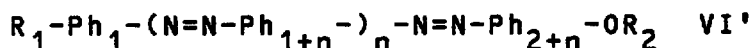
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- wherein W, X, Y and Z are hydrogen, NH₂, OH, NHCH₃ or NHC₂H₅ and one or two of the radicals R₁, R₂, R₃ and R₄ are a group of the part formulae
- 5 -Ph-R, -Ph-OR, -Cy-R, -Ph-Cy-R or -Cy-Cy-R
- and the others are hydrogen, wherein R is an alkyl group with 1 - 12 carbon atoms (such dyestuffs are known, for example, from German Patent 3,040,102), and
- c) naphthoquinone dyestuffs, for example of the
- 10 formula IV'



- wherein X and Y are identical or different and are hydrogen, chlorine or bromine, R₁, R₂, R₃ and R₄ are hydrogen, alkyl or alkoxyalkyl with up to 8 C atoms or a cyclic
- 15 group Z, Z is -Ph-R, -Ph-Ph-R, -Cy-R, -Cy-Cy-R, -Ph-Cy-R or -Cy-Ph-R and R is alkyl, alkoxy, alkoxyalkyl, alkoxy-alkoxy or alkanoyloxy with up to 8 C atoms (such dyestuffs are known, for example, from German Patent 3,126,108), and
- 20 d) azo dyestuffs, for example of the formula V'
- R₁-Ph₁-(N=N-Ph_{1+n}-)_n-N=N-Ph_{2+n}-R₂ V'
- wherein R₁ is alkyl or alkylsulfonyl, R₂ is dialkylamino, monoalkylamino or a 5-membered or 6-membered cycloalkyl-amino group and n is 1, 2 or 3, it being possible for a
- 25 second benzene ring to be fused onto the benzene ring to form naphthalene structures (such dyestuffs are known, for example, from U.S. Patent 4,340,973), and/or
- e) azo dyestuffs, for example of the formula VI'



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wherein R_1 is alkyl, R_2 is alkyl, alkylcarbonyl, aryl-
carbonyl or alkoxy carbonyl and n is 1, 2, 3 or 4, it being
possible for a second benzene ring to be fused onto the
benzene rings to form naphthalene structures (such dye-
5 stuffs are known, for example, from Japanese Preliminary
Published Application 56-104,984) used(sic).

The guest-host systems according to the invention
can be adapted to suit the most diverse fields of appli-
cation by appropriate choice of the dyestuff components
10 and of the relative dyestuff concentrations.

The guest-host systems according to the invention
as a rule contain 0.1 to 15, preferably 0.5 to 10 and in
particular 1 to 7, % by weight of pleochroic dyestuffs.

The pleochroic dyestuffs of the guest-host system
15 according to the invention are preferably chosen so that
they cover a suitable portion of the visible spectrum and
that the absorption in this range is more or less constant.

The guest-host systems according to the invention
are prepared in a manner which is customary per se. As
20 a rule, the desired amounts of the various pleochroic dye-
stuffs are dissolved in the host material, advantageously
at elevated temperature.

However, it is also possible to mix solutions of
the pleochroic dyestuff and the host material in a suit-
25 able organic solvent, for example acetone, chloroform or
methanol, and, after thorough mixing, to remove the sol-
vent again, for example by distillation under reduced
pressure. In this procedure, it must of course be ensured
that no impurities or undesirable doping substances are
30 included through the solvent.

The individual compounds of the formulae 1 - XV
of the liquid crystal phases according to the invention
are either known, or their methods of preparation can be
easily deduced from the prior art by the relevant expert
35 since they are based on standard processes described in
the literature.

Corresponding compounds are described, for ex-
ample, in German Offenlegungsschrift 3,231,707, German
Offenlegungsschrift 3,321,373, German Offenlegungsschrift

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2,702,598, German Offenlegungsschrift 2,948,836, U.S. Patent 4,323,473, U.S. Patent 4,325,830, U.S. Patent 4,322,354, German Offenlegungsschrift 3,320,024, German Offenlegungsschrift 3,332,691, German Offenlegungsschrift 3,328,638, German Offenlegungsschrift 3,100,142, German Offenlegungsschrift 2,429,093, German Offenlegungsschrift 2,944,905, German Offenlegungsschrift 3,227,916, German Offenlegungsschrift 3,206,269, German Offenlegungsschrift 3,933,611, German Offenlegungsschrift 2,800,553, German Offenlegungsschrift 2,636,684, German Offenlegungsschrift 2,927,277, German Offenlegungsschrift 3,117,152 and German Offenlegungsschrift 3,042,391.

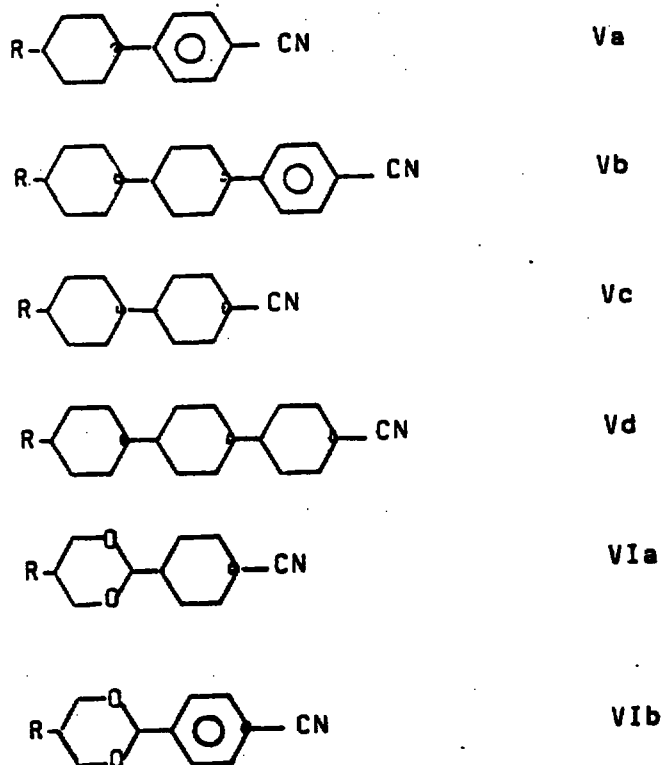
Surprisingly, it has been found that the compounds VII to X can particularly advantageously be used as components of positive and negative phases according to the invention which have wide nematic ranges and little or no interfering smectic phase ranges.

The negative LC phases according to the invention preferably contain 20 to 90%, in particular 55 to 85%, of compounds from Group A. They preferably contain at least two, in particular two to ten, and particularly preferably three to six, different compounds from Group A and no compounds from Group B.

The negative LC phases according to the invention with at least one, preferably two to four, compound(s) of the formula XIV are furthermore preferred.

The positive LC phases according to the invention preferably contain 15 to 60%, in particular 22 to 45%, of compounds from group B. They preferably contain only those compounds from Group B wherein Q is in each case 1,4-phenylene or 1,4-cyclohexylene. However, LC phases containing several compounds from group B where Q is in some cases 1,4-phenylene and in some cases 1,4-cyclohexylene are also of interest.

Preferred components selected from Group B are those of the formulae Va to Vd, VIa and VIb:



Of these, those of part formulae Va, Vb, Vd and VIa are particularly preferred.

Compounds of the formula V wherein Z^1 is $-CH_2CH_2-$ or a single bond and Q is trans-1,4-cyclohexylene are also preferred.

The positive LC phases according to the invention preferably contain at least two, in particular at least three, compounds from Group B. Positive LC phases according to the invention with at least one, preferably two to six and in particular four to six, compound(s) of the formula XIV and/or at least one, preferably two to four, compound(s) of the formula XV are furthermore preferred.

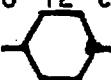
Of the positive or negative liquid crystal phases according to the invention, those which contain at least three components selected from group A or B and at least one component selected from Group C are particularly preferred. Those phases according to the invention which contain at least three components from group A or B and at least one component from Group D are furthermore preferred.

The phases according to the invention containing compounds from Group C, in particular those of the

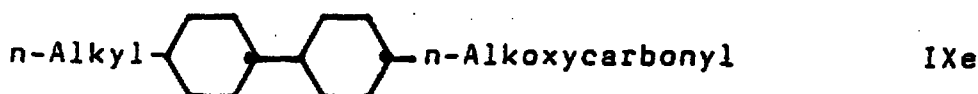
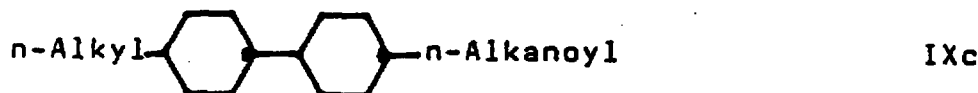
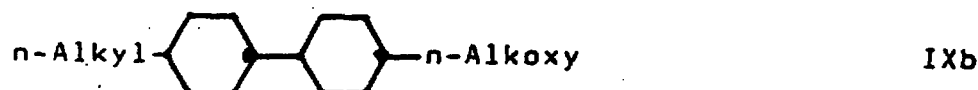
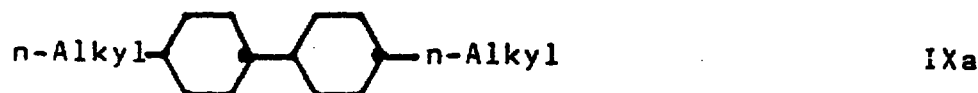
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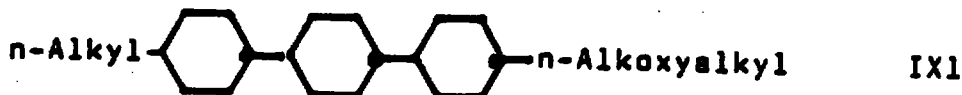
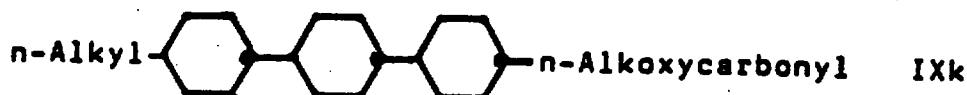
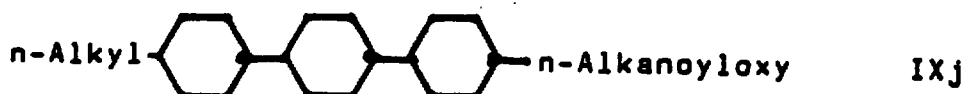
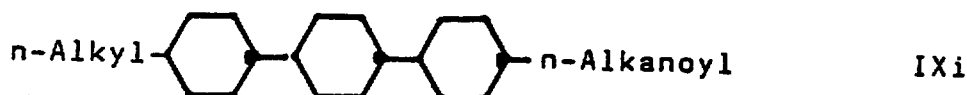
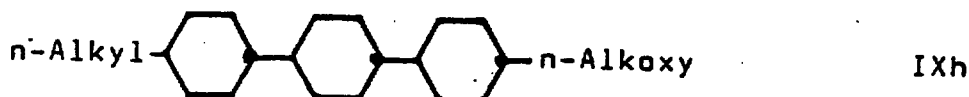
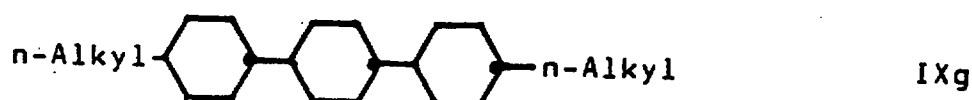
formula IXb, are distinguished by particularly short switching times, especially at low temperatures.

Preferred LC phases do not contain compounds of the formula VI and VII at the same time.

5 Preferred compounds from Group C are those of the formula ... (sic) VII and IX. Compounds of the formula IX wherein R^3 is straight-chain alkyl with 1 to 12 C atoms and wherein a CH_2 group can also be replaced by $-O-$, $-CO-$, $-O-CO-$ or $-CO-O-$, and R^4 is straight-chain alkyl with 1
10 to 12 C atoms, in particular n-propyl or n-pentyl, or  R, wherein R equals n-alkyl with 1 - 12 C atoms, in particular with 2 to 7 C atoms, are particularly preferred. In this case, R^3 is particularly preferably n-alkyl, n-alkoxyalkyl, n-alkoxy or n-alkanoyloxy with in each case
15 2 to 7 C atoms. Especially preferred meanings of R^3 here are, in particular, methoxy, ethoxy, n-butoxy, n-hexoxy, n-hexanoyloxy, n-butyryloxy and formyloxy.

Preferred LC phases according to the invention contain at least two, in particular at least three, components selected from the group of the formulae IXa to IXf:





Of the compounds of the formulae IXa to IXl, those of the formulae IXa, IXb, IXd, IXg, IXh and IXj are particularly preferred.

5 LC mixtures containing in each case at least one component of the formulae IXa, IXb and IXd at the same time are particularly preferred.

LC mixtures containing in each case at least one component of the formulae IXb and IXd and LC mix-
10 tures which contain only components of the formula IXb are furthermore preferred. LC mixtures which, besides at least one component selected from the formulae IXa to IXf, contain at least one other component selected from the formulae IXg to IXl, in particular IXg, IXh, IXi and/
15 or IXj, are also preferred.

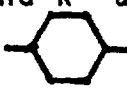
LC mixtures according to the invention containing at least one, preferably at least two, compounds of the formula X wherein R^3 and R^4 in each case independently of one another are preferably n-alkyl with 2 to 7 C atoms,
20 are furthermore preferred.

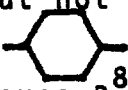
In the compounds of the formulae V and VI, R is

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preferably n-alkyl or n-alkoxyalkyl with in each case 2 to 9 C atoms. Z^1 in formula V is preferably trans-1,4-cyclohexylene or a single bond, in particular a single bond.

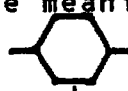
5 Those liquid crystal phases according to the invention in which the total amounts by weight of the component(s) of the formula XV and the component(s) of the formulae V and/or VI wherein Q is in each case 1,4-phenylene is $\leq 50\%$, in particular $\leq 40\%$, and/or is in the
10 range from 5 to 50%, in particular in the range from 13 to 35%, exhibit particularly advantageous properties.

Of the compounds of components I, II, III and IV from Group A, those in which R^1 and R^2 are at the same time R, R being alkyl with 1 - 12 C atoms, and wherein also
15 one or two non-adjacent CH_2 groups can be replaced by -O-, -CO-, -O-CO or -CO-O-, are preferred. Those compounds of components I to IV in which R^1 and R^2 are both optionally, but not at the same time, R or  R are furthermore preferred.

20 Of the preferred compounds VII and VIII from Group C, those in which R^3 is R and R^7 is R^8 (with the meanings given) or both optionally but not at the same time are R^3 or, respectively, R^8 or  R are also to be mentioned. Of the using groups R^8 , those in which
25 R^8 is alkyl with 1 to 12 C atoms are furthermore preferred.

Of the compounds of component IX, those in which R^3 always has the meaning defined for R and R^4 is optionally R, OR, -O-COR, -COOR or -CH₂OR are preferred.

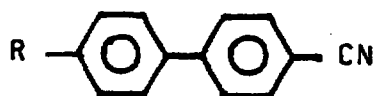
30 Preferred phases according to the invention contain 12 to 70%, in particular 18 to 55%, of compounds from Group C.

Of the compounds of component X, those in which R^3 and R^4 at the same time have the meaning of R or
35 R^3 has the meaning of R and R^4 is  R are preferably to be mentioned. Of the compounds of components XI, XII and XIII from Group D, all those in which R^5 and R^6 at the same time have the meaning given for R, in particular n-alkyl with 2 to 7 C atoms, are preferred. From

the optional Group E, those compounds of the formula XIV in which R^3 and R^4 either at the same time are R or both optionally, but not at the same time, can assume the meaning of R or -R and the symbols R in each case independently of one another are an n-alkyl group with 2 to 7 C atoms are preferred.

Of the numerous compounds of the formula XV, which always contain phenyl, those of the formulae XVa to XVI are particularly preferred:

10

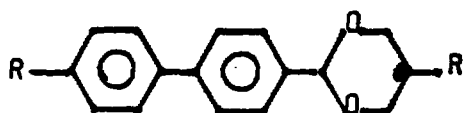


XVa

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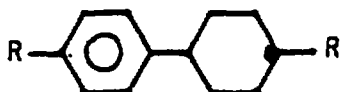


XVb



XVc

20

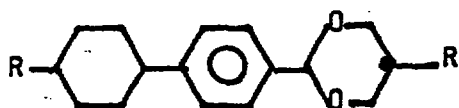


XVd



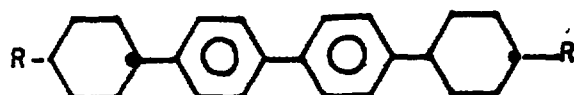
XVe

25

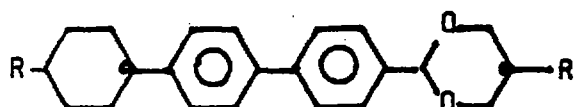


XVf

30

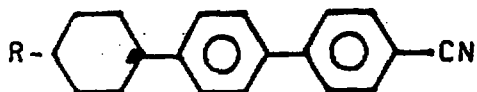


XVg

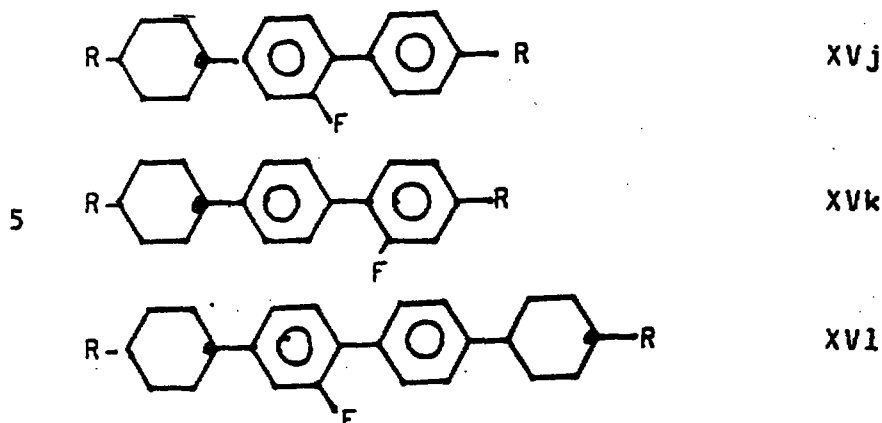


XVh

35



XVI



10 In these formulae the symbols R, which can in each case be identical or different, are preferably n-alkyl or n-alkoxy with in each case 2 to 7 C atoms. Compounds of the formulae XVb, XVd (especially those wherein the two symbols R are in each case n-alkyl or one R is n-alkyl
15 and the other is n-alkoxy), XVg, XVi and XVI are particularly preferred.

In all the compounds from Groups A to E, R is preferably alkyl, -O-alkyl, -O-CO-alkyl, -COO-alkyl or oxaalkyl, wherein alkyl contains 1 - 12 C atoms, preferably
20 2 - 10 and in particular 3 - 9 C atoms.

R⁸ in the compounds VII and VIII from Group C is alkyl, -O-alkyl or oxaalkyl, wherein alkyl contains 1 - 12 C atoms, preferably 2 - 10 and in particular 3 - 9 C atoms.

25 Compounds wherein the symbols R are alkyl, -O-alkyl and -O-CO-alkyl are particularly preferably used for the liquid crystal phases according to the invention.

Those compounds which contain two radicals R in which one radical R is alkyl and the other is alkyl, alkoxy
30 or alkanoyloxy are furthermore particularly preferred.

If the alkyl groups contain 3 or more carbon atoms, these can be arranged in a straight or branched chain. However, no components which contain more than one branched alkyl group are used in the phases according to the
35 invention. Such branched alkyl groups contain no more than one chain branching in the context of the present invention; this branching is preferably a methyl or ethyl group in the 1- or 2- position of the carbon skeleton, so that particularly possible branched alkyl groups are:

2-methylpropyl, 2-methylbutyl, 1-methylpentyl, 2-methylpentyl and 1-methylhexyl. The liquid crystal dielectrics according to the invention as a rule contain only one component with a branched alkyl radical, in order to induce optical activity, if desired. No more than 10% by weight, preferably 0.5 to 3% by weight, of a component with a branched alkyl radical is usually added for this purpose. Those compounds of the formulae (I) to (XV) in which the alkyl radicals are straight-chain, that is to say are methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl and n-dodecyl, are otherwise preferably used as components of the phase according to the invention.

The phases according to the invention are prepared in a manner which is customary per se. As a rule, the desired amount of the components used in smaller quantity is dissolved in the components which make up the main constituent, advantageously at elevated temperature. If a temperature above the clear point of the main constituent is chosen here, it is particularly easy to observe completion of the dissolving operation.

However, it is also possible to mix solutions of the components in a suitable organic solvent, for example acetone, chloroform or methanol and, after thorough mixing, to remove the solvent again, for example by distillation under reduced pressure. In this procedure, it must of course be ensured that no impurities or undesirable doping substances are included through the solvent.

The liquid crystal phases according to the invention can be modified by suitable additives so that they can be used in all the types of liquid crystal display elements which have hitherto been disclosed.

Such additives are known to the expert and are described in detail in the literature. For example, it is possible to add conductive salts, preferably ethyldimethyl-dodecyl-ammonium 4-hexyloxybenzoate, tetrabutylammonium tetraphenylboranate or complex salts of crown ethers (cf., for example, B. I. Haller et al., Mol. Cryst.Liq.Cryst. volume 24, pages 249-258 (1973) to

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improve the conductivity, or substances for modifying the dielectric anisotropy, the viscosity and/or the orientation of the nematic phases. Substances of this type are described, for example, in German Offenlegungsschriften
5 2,209,127, 2,240,864, 2,321,632, 2,338,281, 2,450,088, 2,637,430, 2,853,728 and 2,902,177.

The following examples are intended to illustrate the invention without limiting it. In the examples, the melting point and clear point of a liquid crystal substance are given in degrees Celsius. The percentage
10 figures relate to percentages by weight.

Example 1

A liquid crystal phase consisting of
34.0% of *r*-1-cyano-cis-4-(trans-4-butylcyclohexyl)-1-
15 heptylcyclohexane,
29.0% of *r*-1-cyano-cis-4-(trans-4-pentylcyclohexyl)-1-pentylcyclohexane,
10.8% of trans,trans-4-propyl-4'-methoxycyclohexylcyclohexane,
20 9.7% of trans,trans-4-propyl-4'-ethoxycyclohexylcyclohexane,
3.9% of trans-4-propylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate,
3.9% of trans-4-pentylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate,
25 4.8% of trans-4-propylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate and
3.9% of trans-4-pentylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate
30 has a melting point of -10° , a clear point of 70° and an optical anisotropy of +0.03.

Example 2

A liquid crystal phase consisting of
34.0% of *r*-1-cyano-cis-4-(trans-4-butylcyclohexyl)-1-
35 heptylcyclohexane,
29.0% of *r*-1-cyano-cis-4-(trans-4-pentylcyclohexyl)-1-pentylcyclohexane,
10.8% of trans,trans-4-propyl-4'-methoxycyclohexylcyclohexane,

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9.7% of trans,trans-4-propyl-4'-ethoxycyclohexylcyclohexane,
3.9% of trans-4-propylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate,
5 3.9% of trans-4-pentylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate,
4.8% of trans-4-propylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate, and
3.9% of r-1-cyano-cis-4-(trans-4-pentylcyclohexyl)-1-(trans-4-propylcyclohexyl)-cyclohexane
10 has a clear point of 72° and an optical anisotropy of +0.03.

Example 3

A liquid crystal phase consisting of
15 34.0% of r-1-cyano-cis-4-(trans-4-butylcyclohexyl)-1-heptylcyclohexane,
29.0% of r-1-cyano-cis-4-(trans-4-pentylcyclohexyl)-1-pentylcyclohexane,
10.8% of trans,trans-4-propyl-4'-methoxycyclohexylcyclohexane,
20 9.7% of trans,trans-4-propyl-4'-ethoxycyclohexylcyclohexane,
4.8% of r-1-cyano-cis-4-(trans-4-propylcyclohexyl)-1-(trans-4-propylcyclohexyl)-cyclohexane,
25 3.9% of r-1-cyano-cis-4-(trans-4-pentylcyclohexyl)-1-trans-4-propylcyclohexyl)-cyclohexane,
3.9% of r-1-cyano-cis-4-(trans-4-propylcyclohexyl)-1-(trans-4-butylcyclohexyl)-cyclohexane and
3.9% of r-1-cyano-cis-4-(trans-4-pentylcyclohexyl)-1-(trans-4-butylcyclohexyl)-cyclohexane
30 has a clear point of 75° and an optical anisotropy of +0.03.

Example 4

A liquid crystal phase consisting of
35 34% of r-1-cyano-cis-4-(trans-4-butylcyclohexyl)-1-heptylcyclohexane,
29% of r-1-cyano-cis-4-(trans-4-pentylcyclohexyl)-1-pentylcyclohexane,
7% of trans,trans-4'-methoxycyclohexyl-4-propylcyclo-

hexane,
 5% of trans,trans-4'-ethoxycyclohexyl-4-propylcyclo-
 hexane,
 5% of trans,trans-4'-propoxycyclohexyl-4-propylcyclo-
 5 hexane and
 20% of 1-(trans-4-propylcyclohexyl)-2-(trans-4-propyl-
 cyclohexyl)-ethane,
 has a melting point of -5.2° , a clear point of 60.3°
 and an optical anisotropy of +0.025.

10 Example 5

A liquid crystal phase consisting of
 19% of trans,trans-4-ethylcyclohexylcyclohexane-4'-
 carbonitrile,
 19% of trans,trans-4-butylcyclohexylcyclohexane-4'-
 15 carbonitrile,
 7% of trans,trans-4-propylcyclohexylcyclohexane-4'-
 carbonitrile,
 12% of trans,trans-4'-propoxycyclohexyl-4-propylcyclo-
 hexane,
 20 18% of trans,trans-4'-methoxycyclohexyl-4-propylcyclo-
 hexane,
 20% of trans,trans-4'-propylcyclohexyl-4-butyryloxy-
 cyclohexane and
 5% of trans,trans-4'-propylcyclohexyl-4-valeryloxy-
 25 cyclohexane
 has a melting point of -11.4° , a clear point of 57.5° ,
 and an optical anisotropy of +0.045.

Example 6

A liquid crystal phase consisting of
 30 19% of trans,trans-4-ethylcyclohexylcyclohexane-4'-
 carbonitrile,
 19% of trans,trans-4-butylcyclohexylcyclohexane-4'-
 carbonitrile,
 15% of trans,trans-4'-propoxycyclohexyl-4-propylcyclo-
 35 hexane,
 5% of trans,trans-4'-methoxycyclohexyl-4-propylcyclo-
 hexane,
 17% of trans,trans-4'-propylcyclohexyl-4-butyryloxy-
 cyclohexane,

20% of trans-4-propylcyclohexyl trans-4-pentylcyclohexanecarboxylate and

5% of 4-(trans-4-propylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-biphenyl

5 has a melting point of -14.3° , a clear point of 69.1° and an optical anisotropy of $+0.055$.

Example 7

A liquid crystal phase consisting of

- 10 13% of trans,trans-4-ethylcyclohexylcyclohexane-4'-carbo-
nitrile,
- 13% of trans,trans-4-butylcyclohexylcyclohexane-4'-carbo-
nitrile,
- 5% of trans,trans-4-pentylcyclohexylcyclohexane-4'-carbo-
nitrile,
- 15 15% of 4-propylcyclohexyl trans-4-pentylcyclohexane-
carboxylate,
- 13% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propyl-
cyclohexyl)-biphenyl,
- 25% of trans,trans-4'-propoxycyclohexyl-4-propylcyclo-
hexane,
- 20 7% of trans,trans-4'-methoxycyclohexyl-4-propylcyclo-
hexane and
- 9% of trans,trans-4'-propylcyclohexyl-4-butyryloxy-
cyclohexane

25 has a melting point of -10.4° , a clear point of 81° and an optical anisotropy of $+0.065$.

Example 8

A liquid crystal phase consisting of

- 6% of 2-p-cyanophenyl-5-propyl-1,3-dioxane,
- 30 6% of 2-p-cyanophenyl-5-butyl-1,3-dioxane,
- 15% of p-trans-4-propylcyclohexyl-benzonitrile,
- 9% of trans-4-propylcyclohexyl trans-4-propylcyclo-
hexanecarboxylate,
- 10% of trans-4-propylcyclohexyl trans-4-pentylcyclohexane-
carboxylate,
- 35 9% of trans,trans-4'-propylcyclohexyl-4-butyryloxycyclo-
hexane,
- 9% of trans,trans-4'-propylcyclohexyl-4-hexanoyloxy-
cyclohexane,

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- 6% of trans-4-propylcyclohexyl trans,trans-4-propyl-
cyclohexyl-cyclohexane-4'-carboxylate,
6% of trans-4-pentylcyclohexyl trans,trans-4-propylcyclo-
hexyl-cyclohexane-4'-carboxylate,
5 6% of trans-4-propylcyclohexyl trans,trans-4-butylcyclo-
hexyl-cyclohexane-4'-carboxylate,
5% of trans-4-pentylcyclohexyl trans,trans-4-butylcyclo-
hexyl-cyclohexane-4'-carboxylate,
5% of 4-(trans-4-propylcyclohexyl)-2'-fluoro-4'-(trans-
10 4-propylcyclohexyl)-biphenyl,
4% of 4-(trans-4-pentylcyclohexyl)-2'-fluoro-4'-(trans-
4-propylcyclohexyl)-biphenyl and
4% of 4-(trans-4-pentylcyclohexyl)-2'-fluoro-4'-(trans-
4-pentylcyclohexyl)-biphenyl
15 has a melting point of -16.5° and a clear point of $+96^{\circ}$.

Example 9

- A liquid crystal phase consisting of
6% of 2-p-cyanophenyl-5-propyl-1,3-dioxane,
6% of 2-p-cyanophenyl-5-butyl-1,3-dioxane,
20 10% of p-trans-4-propylcyclohexyl-benzonitrile
9% of trans-4-propylcyclohexyl trans-4-propylcyclohexane-
carboxylate,
10% of trans-4-propylcyclohexyl trans-4-pentylcyclohexane-
carboxylate,
25 12% of trans,trans-4'-propylcyclohexyl-4-butyryloxy-
cyclohexane,
11% of trans,trans-4'-propylcyclohexyl-4-hexanoyloxycyclo-
hexane,
6% of trans-4-propylcyclohexyl trans,trans-4-propyl-
30 cyclohexyl-cyclohexane-4'-carboxylate,
6% of trans-4-pentylcyclohexyl trans,trans-4-propyl-
cyclohexyl-cyclohexane-4'-carboxylate,
6% of trans-4-propylcyclohexyl trans,trans-4-butylcyclo-
hexyl-cyclohexane-4'-carboxylate,
35 5% of trans-4-pentylcyclohexyl trans,trans-4-butylcyclo-
hexyl-cyclohexane-4'-carboxylate,
5% of 4-(trans-4-propylcyclohexyl)-2'-fluoro-4'-(trans-
4-propylcyclohexyl)-biphenyl,
4% of 4-(trans-4-pentylcyclohexyl)-2'-fluoro-4'-(trans-

— 4-propylcyclohexyl)-biphenyl and
4% of 4-(trans-4-pentylcyclohexyl)-2'-fluoro-4'-(trans-4-pentylcyclohexyl)-biphenyl

has a melting point of -15.9° and a clear point of $+98^{\circ}$.

5 Example 10

A liquid crystal phase consisting of

- 6% of 2-p-cyanophenyl-5-propyl-1,3-dioxane,
- 6% of 2-p-cyanophenyl-5-butyl-1,3-dioxane,
- 15% of p-trans-4-propylcyclohexyl-benzonitrile,
- 10 19% of trans,trans-4'-propylcyclohexyl-4-butyryloxy-cyclohexane,
- 18% of trans,trans-4'-propylcyclohexyl-4-hexanoyloxy-cyclohexane,
- 6% of trans-4-propylcyclohexyl trans,trans-4-propyl-
- 15 cyclohexyl-cyclohexane-4'-carboxylate,
- 6% of trans-4-pentylcyclohexyl trans,trans-4-propylcyclo-
- hexyl-cyclohexane-4'-carboxylate,
- 6% of trans-4-propylcyclohexyl trans,trans-4-butylcyclo-
- hexyl-cyclohexane-4'-carboxylate,
- 20 5% of trans-4-pentylcyclohexyl trans,trans-4-butyl-
- cyclohexyl-cyclohexane-4'-carboxylate,
- 5% of 4-(trans-4-propylcyclohexyl)-2'-fluoro-4'-(trans-4-propylcyclohexyl)-biphenyl,
- 4% of 4-(trans-4-pentylcyclohexyl)-2'-fluoro-4'-(trans-
- 25 4-propylcyclohexyl)-biphenyl and
- 4% of 4-(trans-4-pentylcyclohexyl)-2'-fluoro-4'-(trans-4-pentylcyclohexyl)-biphenyl

has a melting point of -7.6° and a clear point of $+102^{\circ}$.

Example 11

- 30 A liquid crystal phase consisting of
- 6% of 2-p-cyanophenyl-5-propyl-1,3-dioxane,
- 6% of 2-p-cyanophenyl-5-butyl-1,3-dioxane,
- 15% of p-trans-4-propylcyclohexyl-benzonitrile,
- 15% of trans,trans-4'-methoxycyclohexyl-4-propylcyclohexane,
- 35 9% of trans,trans-4'-propylcyclohexyl-4-butyryloxy-cyclo-
- hexane,
- 9% of trans,trans-4'-propylcyclohexyl-4-hexanoyloxy-
- cyclohexane,
- 6% of trans-4-propylcyclohexyl trans,trans-4-propylcyclo-

(67)

- hexyl-cyclohexane-4'-carboxylate,
- 6% of trans-4-pentylcyclohexyl trans,trans-4-propyl-
cyclohexylcyclohexane-4'-carboxylate,
- 6% of trans-4-propylcyclohexyl trans,trans-4-butyl-
cyclohexyl-cyclohexane-4'-carboxylate,
- 5 5% of trans-4-pentylcyclohexyl trans,trans-4-butylcyclo-
hexyl-cyclohexane-4'-carboxylate,
- 5% of 4-(trans-4-propylcyclohexyl)-2'-fluoro-4'-(trans-
4-propylcyclohexyl)-biphenyl,
- 10 5% of 4-(trans-4-pentylcyclohexyl)-2'-fluoro-4'-(trans-
4-propylcyclohexyl)-biphenyl,
- 5% of 4-(trans-4-pentylcyclohexyl)-2'-fluoro-4'-(trans-
4-pentylcyclohexyl)-biphenyl and
- 2% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propyl-
cyclohexyl)-biphenyl
- 15

has a melting point of -17.4° and a clear point of $+102^{\circ}$.

Example 12

- A liquid crystal phase consisting of
- 6% of 2-p-cyanophenyl-5-propyl-1,3-dioxane,
- 20 6% of 2-p-cyanophenyl-5-butyl-1,3-dioxane,
- 10% of p-trans-4-propylcyclohexyl-benzonitrile,
- 17% of trans,trans-4'-methoxycyclohexyl-4-propylcyclo-
hexane,
- 11% of trans,trans-4'-propylcyclohexyl-4-butyryloxy-
cyclohexane,
- 25 10% of trans,trans-4'-propylcyclohexyl-4-hexanoyloxy-
cyclohexane,
- 6% of trans-4-propylcyclohexyl trans,trans-4-propyl-
cyclohexylcyclohexane-4'-carboxylate,
- 30 6% of trans-4-pentylcyclohexyl trans,trans-4-propyl-
cyclohexylcyclohexane-4'-carboxylate,
- 6% of trans-4-propylcyclohexyl trans,trans-4-butyl-
cyclohexyl-cyclohexane-4'-carboxylate,
- 5% of trans-4-pentylcyclohexyl trans,trans-4-butyl-
cyclohexyl-cyclohexane-4'-carboxylate,
- 35 5% of 4-(trans-4-propylcyclohexyl)-2'-fluoro-4'-(trans-
4-propylcyclohexyl)-biphenyl,
- 5% of 4-(trans-4-pentylcyclohexyl)-2'-fluoro-4'-(trans-
4-propylcyclohexyl)-biphenyl,

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- 25 -

5% of 4-(trans-4-pentylcyclohexyl)-2'-fluoro-4'-(trans-4-pentylcyclohexyl)-biphenyl and

2% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-biphenyl

5 has a melting point of -17.2° and a clear point of $+103^{\circ}$.

Example 13

A liquid crystal phase consisting of

34% of r-1-cyano-cis-4-(trans-4-butylcyclohexyl)-1-heptylcyclohexane,

10 29% of r-1-cyano-cis-4-(trans-4-pentylcyclohexyl)-1-pentylcyclohexane,

11% of trans,trans-4'-methoxycyclohexyl-4-propylcyclohexane,

10% of trans,trans-4'-ethoxycyclohexyl-4-propylcyclohexane,

4% of 1-(trans-4'-pentylcyclohexyl-4-cyclohexyl)-2-cyano-2-(trans-4-pentylcyclohexyl)-ethane,

15 4% of 1-(trans-4'-pentylcyclohexyl)-4-cyclohexyl)-2-cyano-2-(trans-4-propylcyclohexyl)-ethane(sic),

4% of trans-4-propylcyclohexyl trans,trans-4-propylcyclohexyl-cyclohexane-4'-carboxylate and

20 4% of trans-4-pentylcyclohexyl trans,trans-4-propylcyclohexyl-cyclohexane-4'-carboxylate

has a melting point of -8° , a clear point of $+68^{\circ}$ and an optical anisotropy of $+0.028$.

Example 14

25 A liquid crystal phase consisting of

10% of trans-1-p-methoxyphenyl-4-propylcyclohexane,

10% of trans-1-p-ethoxyphenyl-4-propylcyclohexane,

33% of trans,trans-4'-methoxycyclohexyl-4-propylcyclohexane,

30 11% of r-1-cyano-cis-4-(trans-4-butylcyclohexyl)-1-heptylcyclohexane,

10% of r-1-cyano-cis-4-(trans-4-pentylcyclohexyl)-1-pentylcyclohexane,

5% of 4,4'-bis-(trans-4-propylcyclohexyl)-2-fluoro-biphenyl,

35 5% of 4,4'-bis-(trans-4-pentylcyclohexyl)-2-fluoro-biphenyl,

5% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-2-fluoro-biphenyl,

5% of 4,4'-bis-(trans-4-propylcyclohexyl)-biphenyl and
6% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propyl-
cyclohexyl)-biphenyl

has a melting point of -19° , a clear point of 82° , an
5 optical anisotropy of 0.074 and a dielectric anisotropy
of -1.5.

Example 15

A liquid crystal phase consisting of the following
compounds is prepared:

- 10 6% of trans,trans-4-ethylcyclohexylcyclohexane-4'-
carbonitrile,
- 6% of 2-p-cyanophenyl-5-butyl-1,3-dioxane,
- 3% of p-trans-4-propylcyclohexyl-benzonitrile,
- 17% of trans,trans-4'-methoxycyclohexyl-4-propylcyclo-
15 hexane,
- 11% of trans,trans-4-methoxycyclohexyl-4-pentylcyclo-
hexane,
- 10% of trans,trans-4-ethoxycyclohexyl-4-pentylcyclo-
hexane,
- 20 10% of trans,trans-4-butoxycyclohexyl-4-propylcyclo-
hexane,
- 8% of 4-(trans-4-propylcyclohexyl)-2'-fluoro-4'-(trans-
4-propylcyclohexyl)-biphenyl,
- 7% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propyl-
25 cyclohexyl)-biphenyl,
- 6% of trans-4-pentylcyclohexyl trans,trans-4-propyl-
cyclohexylcyclohexane-4'-carboxylate,
- 6% of trans-4-propylcyclohexyl trans,trans-4-butyl-
cyclohexylcyclohexane-4'-carboxylate,
- 30 5% of trans-4-propylcyclohexyl trans,trans-4-butylcyclo-
hexylcyclohexane-4'-carboxylate and
- 5% of trans-4-pentylcyclohexyl trans,trans-4-butylcyclo-
hexylcyclohexane-4'-carboxylate.

Example 16

- 35 A liquid crystal phase consisting of
- 10% of p-trans-4-propylcyclohexylbenzonitrile,
- 6% of 2-p-cyanophenyl-5-propyl-1,3-dioxane,
- 6% of 2-p-cyanophenyl-5-butyl-1,3-dioxane,
- 32% of trans,trans-4'-methoxycyclohexyl-4-propylcyclo-

- hexane,
- 7% of trans,trans-4'-ethoxycyclohexyl-4-propylcyclohexane,
- 5 6% of trans-4-propylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate,
- 6% of trans-4-pentylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate,
- 6% of trans-4-propylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate,
- 10 6% of trans-4-pentylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate,
- 5% of 4,4'-bis-(trans-4-propylcyclohexyl)-2-fluorobiphenyl,
- 4% of 4,4'-bis-(trans-4-pentylcyclohexyl)-2-fluorobiphenyl and
- 15 6% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-2-fluoro-biphenyl
- has a melting point of -13° , a clear point of 90° , an optical anisotropy of 0.077 and a viscosity of 19 (800; 20 $3,050) \times 10^{-3}$ Pa . s at 20° (-30° ; -40°).

Example 17

- A liquid crystal phase consisting of
- 10% of p-trans-4-propylcyclohexylbenzonitrile,
- 6% of 2-p-cyanophenyl-5-propyl-1,3-dioxane,
- 25 6% of 2-p-cyanophenyl-5-butyl-1,3-dioxane,
- 11% of trans,trans-4'-methoxycyclohexyl-4-propylcyclohexane,
- 10% of trans,trans-4'-ethoxycyclohexyl-4-propylcyclohexane (sic),
- 30 11% of trans,trans-4'-methoxycyclohexyl-4-butylcyclohexane (sic),
- 11% of trans-1-p-ethoxyphenyl-4-propylcyclohexane,
- 4% of trans-4-propylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate,
- 35 4% of trans-4-pentylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate,
- 4% of trans-4-propylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate,
- 4% of trans-4-pentylcyclohexyl trans,trans-4-butylcyclo-

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hexylcyclohexane-4'-carboxylate,
4% of 4,4'-bis-(trans-4-propylcyclohexyl)-2-fluorobiphenyl,
4% of 4,4'-bis-(trans-4-pentylcyclohexyl)-2-fluorobiphenyl,
4% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propyl-
5 cyclohexyl)-2-fluoro-biphenyl,
3% of 4,4'-bis-(trans-4-propylcyclohexyl)-biphenyl and
4% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propyl-
cyclohexyl)-biphenyl
has a melting point of -6° , a clear point of 90° , an
10 optical anisotropy of 0.084 and a viscosity of 18 (780;
2,900) $\times 10^{-3}$ Pa.s at 20° (-30° ; -40°).

Example 18

A liquid crystal phase consisting of
10% of p-trans-4-propylcyclohexylbenzonitrile,
15 6% of 2-p-cyanophenyl-5-propyl-1,3-dioxane,
6% of 2-p-cyanophenyl-5-butyl-1,3-dioxane,
32% of trans,trans-4'-methoxycyclohexyl-4-propylcyclo-
hexane,
7% of trans-1-p-ethoxyphenyl-4-propylcyclohexane,
20 6% of trans-4-propylcyclohexyl trans,trans-4-propyl-
cyclohexylcyclohexane-4'-carboxylate,
5% of trans-4-pentylcyclohexyl trans,trans-4-propylcyclo-
hexylcyclohexane-4'-carboxylate,
6% of trans-4-propylcyclohexyl trans,trans-4-butylcyclo-
25 hexylcyclohexane-4'-carboxylate,
6% of trans-4-pentylcyclohexyl trans,trans-4-butylcyclo-
hexylcyclohexane-4'-carboxylate,
5% of 4,4'-bis-(trans-4-propylcyclohexyl)-2-fluorobi-
phenyl,
30 6% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propyl-
cyclohexyl)-2-fluorobiphenyl and
5% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propyl-
cyclohexyl)-biphenyl
has a melting point of -20° , a clear point of 90° , an
35 optical anisotropy of 0.082 and a viscosity of 19.6 (283;
842) $\times 10^{-3}$ Pa.s at 20° (-20° ; -30°).

Example 19

A liquid crystal phase consisting of
10% of p-trans-4-propylcyclohexylbenzonitrile,

- 6% of 2-p-cyanophenyl-5-propyl-1,3-dioxane,
6% of 2-p-cyanophenyl-5-butyl-1,3-dioxane,
32% of trans,trans-4'-methoxycyclohexyl-4-propylcyclohexane,
5 7% of trans-1-p-ethoxyphenyl-4-propylcyclohexane,
6% of trans-4-propylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate,
6% of trans-4-pentylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate,
10 6% of trans-4-propylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate,
6% of trans-4-pentylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate,
5% of 4,4'-bis-(trans-4-propylcyclohexyl)-2-fluorobiphenyl,
15 6% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-2-fluorobiphenyl and
4% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-biphenyl
20 has a melting point of -20° , a clear point of 80° , an optical anisotropy of 0.082 and a viscosity of 20×10^{-3} Pa.s at 20° .
Example 20
A liquid crystal phase consisting of
25 10% of p-trans-4-propylcyclohexylbenzonitrile,
6% of 2-p-cyanophenyl-5-propyl-1,3-dioxane,
6% of 2-p-cyanophenyl-5-butyl-1,3-dioxane,
20% of trans,trans-4'-methoxycyclohexyl-4-propylcyclohexane,
30 6% of trans,trans-4'-ethoxycyclohexyl-4-propylcyclohexane,
7% of trans,trans-4'-methoxycyclohexyl-4-butylcyclohexane,
5% of trans-1-p-ethoxyphenyl-4-propylcyclohexane,
35 6% of trans-4-propylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate,
6% of trans-4-pentylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate,
6% of trans-4-propylcyclohexyl trans,trans-4-butyl-

- cyclohexylcyclohexane-4'-carboxylate,
 6% of trans-4-pentylcyclohexyl trans,trans-4-butyl-
 cyclohexylcyclohexane-4'-carboxylate,
 5% of 4,4'-bis-(trans-4-propylcyclohexyl)-2-fluorobi-
 5 phenyl,
 6% of 4,4'-bis-(trans-4-pentylcyclohexyl)-2-fluorobi-
 phenyl and
 5% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propyl-
 cyclohexyl)-2-fluoro-biphenyl
- 10 has a melting point of -16° , a clear point of 93° , an
 optical anisotropy of 0.079 and a viscosity of 22 (970;
 4,000) $\times 10^{-3}$ Pa.s at 20°C (-30° ; -40°).

Example 21

- A liquid crystal phase consisting of
- 15 10% of p-trans-4-propylcyclohexylbenzonitrile,
 6% of 2-p-cyanophenyl-5-propyl-1,3-dioxane,
 6% of 2-p-cyanophenyl-5-butyl-1,3-dioxane,
 7% of trans,trans-4'-methoxycyclohexyl-4-propylcyclo-
 hexane,
- 20 7% of trans,trans-4'-ethoxycyclohexyl-4-propylcyclo-
 hexane,
 7% of trans,trans-4'-methoxycyclohexyl-4-butylcyclo-
 hexane,
- 17% of trans-1-p-ethoxyphenyl-4-propylcyclohexane,
- 25 6% of trans-4-propylcyclohexyl trans,trans-4-propyl-
 cyclohexylcyclohexane-4'-carboxylate,
 6% of trans-4-pentylcyclohexyl trans,trans-4-propyl-
 cyclohexylcyclohexane-4'-carboxylate,
 6% of trans-4-propylcyclohexyl trans,trans-4-butyl-
 30 cyclohexylcyclohexane-4'-carboxylate,
 6% of trans-4-pentylcyclohexyl trans,trans-4-butyl-
 cyclohexylcyclohexane-4'-carboxylate,
 5% of 4,4'-bis-(trans-4-propylcyclohexyl)-2-fluoro-
 biphenyl,
- 35 6% of 4,4'-bis-(trans-4-pentylcyclohexyl)-2-fluoro-
 biphenyl and
 5% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propyl-
 cyclohexyl)-2-fluoro-biphenyl

has a melting point of -13° , a clear point of 95° , an

optical anisotropy of 0.084 and a viscosity of 21 (900; 3,800) $\times 10^{-3}$ Pa.s at 20° (-30°; -40°).

Example 22

- 1.0% of azo dyestuff (λ max = 460 nm, formula VI', R_1 = 2-nonylmercapto-1,3,4-thiadiazol-5-yl, R_2 = p-(4-butylcyclohexyl)-benzyl, n = 1, Ph_2 = 1,4-naphthylene and Ph_3 = 2,5-tolylene) and
- 1.3% of azo dyestuff (λ max = 615 nm, formula V', R_1-Ph_1 = 3-octylmercapto-1,2,4-thiadiazol-5-yl, R_2 = p-(4-butylcyclohexyl)-benzylamino, n = 1, Ph_2 = 2,5-xylylene and Ph_3 = 1,4-naphthylene)
- were dissolved in a liquid crystal phase consisting of
- 21% of r-1-cyano-cis-4-(trans-4-butylcyclohexyl)-1-heptylcyclohexane,
- 22% of r-1-cyano-cis-4-(trans-4-pentylcyclohexyl)-1-pentylcyclohexane,
- 12% of trans,trans-4-propyl-4'-methoxycyclohexylcyclohexane,
- 9% of trans,trans-4-propyl-4'-ethoxycyclohexylcyclohexane,
- 4% of trans-4-propylcyclohexyl trans,trans-4-propylcyclohexylchlorohexane-4'-carboxylate,
- 4% of trans-4-pentylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate,
- 4% of trans-4-propylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate,
- 4% of trans-4-pentylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate(sic) and
- 20% of r-1-cyano-cis-4-(trans-4-pentylcyclohexyl)-1-(trans-4-pentylcyclohexyl)-cyclohexane
- (c.p. 100°C).

In an electrooptical display element at a layer thickness of 1 μ m, this guest-host system exhibits a colour interval ΔE up to the point of achromatism of 0.3 in artificial light (CIU-A) and a colour interval ΔE of 1.0 in daylight (CIU-D 65).

Example 23

0.12% of azo dyestuff (λ max = 430 nm, formula V', R_1 = R_2 = p-(4-propylcyclohexyl)-benzyloxy and n = 2), 0.88%



of azo-dyestuff (λ max = 460 ... (sic), formula VI', R_1 = 2-nonylmercapto-1,3,4-thiadiazol-5-yl, R_2 = p-(4-butylcyclohexyl)-benzyl, n = 1, Ph_2 = 1,4-naphthylene and Ph_3 = 2,5-tolylene) and

- 5 1.30% of azo dyestuff (λ max = 615 nm, formula V', R_1 - Ph_1 = 3-octylmercapto-1,2,4-thiadiazol-5-yl, R_2 = p-(4-butylcyclohexyl)-benzylamino, n = 1, Ph_2 = 2,5-xylylene and Ph_3 = 1,4-naphthylene) were dissolved in a liquid crystal phase consisting of
- 10 34% of r-1-cyano-cis-4-(trans-4-butylcyclohexyl)-1-heptylcyclohexane,
30% of r-1-cyano-cis-4-(trans-4-pentylcyclohexyl)-1-pentylcyclohexane,
11% of trans,trans-4-propyl-4'-methoxycyclohexylcyclohexane,
15 9% of trans,trans-4-propyl-4'-ethoxycyclohexylcyclohexane,
4% of trans-4-propylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate,
20 4% of trans-4-pentylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate,
4% of trans-4-propylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate and
4% of trans-4-pentylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate
25 (c.p. 72°).

In an electrooptical display element at a layer thickness of 5 μ m (10 μ m), this guest-host system exhibits a colour interval ΔE up to the point of achromatism

30 of 0.62 (0.81) in artificial light (CIU-A) and a colour interval ΔE of 0.22 (0.43) in daylight (CIU-D 65).

Example 24

0.45% of azo dyestuff (λ max = 393 nm, formula VI', R_1 C_4H_9 , R_2 = C_3H_7 and n = 1),

- 35 1.55% of azo dyestuff (λ max = 460 nm, formula VI', R_1 = 2-nonylmercapto-1,3,4-thiadiazol-5-yl, R_2 = p-(4-butylcyclohexyl)-benzyl, n = 1, Ph_2 = 1,4-naphthylene, and Ph_3 = 2,5-tolylene) and
2.22% of azo dyestuff (λ max = 615 nm, formula V', R_1 - Ph_1

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= 3-octylmercapto-1,2,4-thiadiazol-5-yl, R_2 = p-(4-butylcyclohexyl)-benzylamino, $n = 1$, Ph_2 = 2,5-xylylene and Ph_3 = 1,4-naphthylene)

were dissolved in the liquid crystal phase from Example 22 (c.p. 101°).

In an electrooptical display element at a layer thickness of $4 \mu m$ ($10 \mu m$), this guest-host system exhibits a colour interval ΔE up to the point of achromatism of 0.99 (0.81) in artificial light (CIU-A) and a colour interval ΔE of 2.27 (0.38) in daylight (CIU-D 65).

Example 25

0.39% of azo dyestuff G 232 ($\lambda_{max} = 443 \text{ nm}$, formula V', $R_1 = R_2 = NHC_4H_9$, $n = 2$ and Ph_3 = 1,4-naphthylene),

0.50% of azo dyestuff G 241 ($\lambda_{max} = 558 \text{ nm}$, formula V', $R_1 = C_4H_9$, $R_2 = N(C_2H_5)_2$, $n = 2$ and Ph_3 = 1,4-naphthylene) and

1.30% of a mixture of naphthoquinone dyestuffs of the formula IV' (obtainable by reacting 4,8-diamino-1,5-naphthoquinone with equimolar amounts of 4-n-butoxyaniline, 4-n-pentoxyaniline and 4-n-hexyloxyaniline and 4-n-heptyloxyaniline, $\lambda_{max} = 685 \dots$ (sic))

are dissolved in the liquid crystal phase from Example 22 (c.p. 99°).

In an electrooptical display element at a layer thickness of $1 \mu m$ ($2 \mu m$), this guest-host system exhibits a colour interval ΔE up to the point of achromatism of 0.40 (0.79) in artificial light (CIU-A) and a colour interval ΔE of 0.54 (0.96) in daylight (CIU-D 65).

Example 26

0.29% of azo dyestuff G 232 ($\lambda_{max} = 443 \text{ nm}$, formula V', $R_1 = R_2 = -NHC_4H_9$, $n = 2$ and Ph_3 = 1,4-naphthylene),

0.09% of azo dyestuff G 239 ($\lambda_{max} = 512 \text{ nm}$, formula V', $R_1 = C_4H_9$, $R_2 = N(CH_3)_2$, $n = 1$ and Ph_2 = 1,4-naphthylene),

0.33% of azo dyestuff G 241 ($\lambda_{max} = 558 \text{ nm}$, formula V', $R_1 = C_4H_9$, $R_2 = N(C_2H_5)_2$, $n = 2$ and Ph_3 = 1,4-naphthylene) and

1.32% of a mixture of naphthoquinone dyestuffs of the formula IV' (obtainable by reacting 4,8-diamino-1,4-naphthoquinone with equimolar amounts of 4-n-butoxyaniline, 4-n-pentoxylaniline, 4-n-hexyloxylaniline and 4-n-heptyloxyaniline, $\lambda_{\max} = 685 \text{ nm}$) are dissolved in the liquid crystal phase from Example 23 (c.p. 70°).

In an electrooptical display element at a layer thickness of $2 \mu\text{m}$ ($7 \mu\text{m}$), this guest-host system exhibits a colour interval ΔE up to the point of achromatism of 0.13 (0.32) in artificial light (CIU-A) and a colour interval ΔE of 0.27 (0.57) in daylight (CIU-D 65).

Example 27

0.20% of azo dyestuff ($\lambda_{\max} = 430 \text{ nm}$, formula V', $R_1 = R_2 = p\text{-(4-propylcyclohexyl)-benzyloxy}$ and $n = 2$), 0.50% of azo dyestuff ($\lambda_{\max} = 460 \dots(\text{sic})$, formula VI', $R_1 = 2\text{-nonylmercapto-1,3,4-thiadiazol-5-yl}$, $R_2 = p\text{-(4-butylcyclohexyl)-benzyl}$, $n = 1$, $\text{Ph}_2 = 1,4\text{-naphthylene}$ and $\text{Ph}_3 = 2,5\text{-tolylene}$), 0.36% of azo dyestuff ($\lambda_{\max} = 548 \dots(\text{sic})$, formula V', $R_1 = 2\text{-nonylmercapto-1,3,4-thiadiazol-5-yl}$, $R_2 = \text{butyl-methyl-amino}$, $n = 1$, and $\text{Ph}_2 = 1,4\text{-naphthylene}$), 0.70% of anthraquinone dyestuff ($\lambda_{\max} = 638 \text{ nm}$, formula III', $R_2 = R_3 = R_4 = Z = Y = \text{H}$, $W = X = \text{NH}_2$, and $R_1 = 2\text{-[p-(4-butylcyclohexyl)-benzylmercapto-1,3,4-oxadiazol-5-yl]}$ (sic) and 1.10% of a mixture of naphthoquinone dyestuffs of the formula IV' (obtainable by reacting 4,8-diamino-1,5-naphthoquinone with equimolar amounts of 4-n-butoxyaniline, 4-n-pentoxylaniline, 4-n-hexyloxylaniline and 4-n-heptyloxyaniline, $\lambda_{\max} = 685 \text{ nm}$) are dissolved in the liquid crystal phase from Example 23 (c.p. 71°).

In an electrooptical display element at a layer thickness of $2 \mu\text{m}$ ($9 \mu\text{m}$), this guest-host system exhibits a colour interval ΔE up to the point of achromatism of 0.18 (0.57) in artificial light (CIU-A) and a colour interval of 0.19 (0.01) in daylight (CIU-D 65).

Example 28

- 0.85% of azo dyestuff ($\lambda_{\text{max}} = 460 \text{ nm}$, formula VI', $R_1 =$
2-nonylmercapto-1,3,4-thiadiazol-5-yl, $R_2 = p$ -(4-butyl-
cyclohexyl)-benzyl, $n = 1$, $\text{Ph}_2 = 1,4$ -naphthylene and
 $\text{Ph}_3 = 2,5$ -tolylene),
5 0.90% of azo dyestuff ($\lambda_{\text{max}} = 615 \text{ nm}$, formula V', $R_1\text{-Ph}_1 =$
3-octylmercapto-1,2,4-thiadiazol-5-yl, $R_2 = p$ -(4-
butylcyclohexyl)-benzyl-amino, $n = 1$, $\text{Ph}_2 = 2,5$ -xylylene
and $\text{Ph}_3 = 1,4$ -naphthylene),
0.20% of azo dyestuff ($\lambda_{\text{max}} = 430 \text{ nm}$, formula V', $R_1 =$
10 $R_2 = p$ -(4-propylcyclohexyl)-benzyloxy and $n = 2$),
0.28% of azo dyestuff ($\lambda_{\text{max}} = 548 \text{ nm}$, formula V', $R_1 =$
2-nonylmercapto-1,3,4-thiadiazol-5-yl, $R_2 =$ butyl-methyl-
amino, $n = 1$ and $\text{Ph}_2 = 1,4$ -naphthylene) and
1.10% of a mixture of naphthoquinone dyestuffs of the
15 formula IV' (obtainable by reacting 4,8-diamino-1,5-
naphthoquinone with equimolar amounts of 4-n-butoxyaniline,
4-n-pentoxyaniline, 4-n-hexyloxyaniline and 4-n-heptyloxy-
aniline, $\lambda_{\text{max}} = 685 \text{ nm}$)
are dissolved in the liquid crystal phase from Example
20 22 (c.p. 101°).

In an electrooptical display element at a layer
thickness of $2 \mu\text{m}$ ($10 \mu\text{m}$), this guest-host system exhibits
a colour interval ΔE up to the point of achromatism
of 0.64 (0.33) in artificial light (CIU-A) and a colour
25 interval ΔE of 0.35 (0.29) in daylight (CIU-D 65).

The guest-host systems described in Examples 22
to 28 are very stable and are outstandingly suitable for
positive representation and exhibit steep characteristic
transmission lines. The corresponding electrooptical
30 display elements which can be used can have a simple cell
technology, that is to say no polariser and no pretilt
are necessary.

Unless otherwise indicated, Ph in the azo dye-
stuffs of the formulae V' and VI' in Examples 22 to 28 is
35 in each case 1,4-phenylene.

Example 29

A liquid crystal phase consisting of
8% of 2-(trans-4-cyanocyclohexyl)-5-propyl-1,3-dioxane,
10% of 2-(trans-4-cyanocyclohexyl)-5-butyl-1,3-dioxane,

- 8% of 2-(trans-4-cyanocyclohexyl)-5-pentyl-1,3-dioxane,
 10% of p-trans-4-propylcyclohexyl-benzonitrile,
 8% of trans,trans-4'-methoxycyclohexyl-4-propylcyclohexane,
 5 5% of trans,trans-4'-ethoxycyclohexyl-4-propylcyclohexane,
 13% of trans,trans-4'-methoxycyclohexyl-4-butylcyclohexane,
 11% of trans,trans-4'-methoxycyclohexyl-4-pentylcyclohexane,
 10 6% of trans,trans-4'-ethoxycyclohexyl-4-pentylcyclohexane,
 7% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-2-fluorobiphenyl,
 15 7% of 4,4'-bis-(trans-4-propylcyclohexyl)-2-fluorobiphenyl and
 7% of 4,4'-bis-(trans-4-pentylcyclohexyl)-2-fluorobiphenyl
 has a melting point of -14° , a clear point of 72° , a
 20 viscosity of 23×10^{-3} Pa.s at 20° , an optical anisotropy of 0.08 and threshold voltage of 1.8 volts. This phase is distinguished by a positive dielectric anisotropy and a low optical anisotropy.

Example 30

- 25 A liquid crystal phase consisting of
 20% of r-1-cyano-cis-4-(trans-4-butylcyclohexyl)-1-heptylcyclohexane,
 20% of r-1-cyano-cis-4-(trans-4-pentylcyclohexyl)-1-pentylcyclohexane,
 30 12% of trans,trans-4'-methoxycyclohexyl-4-butylcyclohexane,
 10% of trans,trans-4'-methoxycyclohexyl-4-pentylcyclohexane,
 8% of trans,trans-4'-ethoxycyclohexyl-4-pentylcyclohexane,
 35 11% of 1-(trans-4-propylcyclohexyl)-2-(trans,trans-4'-propylbicyclohexyl-4-yl)-ethane,
 11% of 1-(trans-4-pentylcyclohexyl)-2-(trans,trans-4'-pentylbicyclohex-4-yl)-ethane and

8% of 4,4'-bis-(trans-4-propylcyclohexyl)-2-fluorobiphenyl

has a melting point of -10° , a clear point of 85° , a viscosity of 32×10^{-3} Pa.s at 20° , an optical anisotropy of 0.045 and a dielectric anisotropy of -3.2. This phase is distinguished by a negative dielectric anisotropy and a very low optical anisotropy.

Example 31

- 10 A liquid crystal phase consisting of
- 6% of 2-p-cyanophenyl-5-propyl-1,3-dioxane,
 - 6% of 2-p-cyanophenyl-5-butyl-1,3-dioxane,
 - 10% of p-trans-4-propylcyclohexyl-benzonitrile,
 - 6% of trans,trans-4'-ethoxycyclohexyl-4-propylcyclohexane,
 - 15 18% of trans,trans-4'-methoxycyclohexyl-4-pentylcyclohexane,
 - 12% of trans,trans-4'-ethoxycyclohexyl-4-pentylcyclohexane,
 - 20 12% of trans,trans-4'-butyryloxycyclohexyl-4-propylcyclohexane,
 - 3% of trans-4-propylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate,
 - 3% of trans-4-pentylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate,
 - 25 3% of trans-4-propylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate,
 - 3% of trans-4-pentylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate,
 - 30 3% of 1-(trans-4-propylcyclohexyl-2-(trans,trans-4'-propylbicyclohex-4-yl)-ethane,
 - 4% of 1-(trans-4-pentylcyclohexyl-2-(trans,trans-4'-pentylbicyclohex-4-yl)-ethane,
 - 3% of 4,4'-bis-(trans-4-propylcyclohexyl)-2-fluorobiphenyl,
 - 35 4% of 4,4'-bis-(trans-4-pentylcyclohexyl)-2-fluorobiphenyl and
 - 4% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-2-fluorobiphenyl

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has a melting point of -17° , a clear point of 85° , no smectic/nematic phase transition up to -40° , a viscosity of 19×10^{-3} (780×10^{-3}) Pa.s at 20° (-30°), an optical anisotropy of 0.084 and a threshold voltage of 2.7 volts. This phase is distinguished by a positive dielectric anisotropy, a high clear point and a wide nematic range.

Example 32

A liquid crystal phase consisting of

10 11% of p-trans-4-propylcyclohexyl-benzonitrile,
10% of p-trans-4-butylcyclohexyl-benzonitrile,
18% of 2-(trans-4-pentylcyclohexyl)-5-ethyl-1,3-dioxane,
15% of 2-(trans-4-ethoxycyclohexyl)-5-propyl-1,3-dioxane,
5% of p-(trans,trans-4-propylcyclohexylcyclohex-4'-yl)-
15 benzonitrile,
4% of 4-cyano-4'-(trans-4-pentylcyclohexyl)-biphenyl,
25% of trans-4-propylcyclohexyl trans-4-propylcyclohexane-
carboxylate,
6% of trans-4-propylcyclohexyl trans,trans-4-propyl-
20 cyclohexylcyclohexane-4'-carboxylate and
6% of 4,4'-bis-(trans-4-propylcyclohexyl)-2-fluorobiphenyl
has a melting point of -16° , a clear point of 61° ,
a viscosity of 17×10^{-3} Pa.s at 20° , an optical aniso-
tropy of 0.09 and a threshold voltage of 2.7 volts. This
25 phase is distinguished by a positive dielectric aniso-
tropy, a low optical anisotropy, a particularly low vis-
cosity and a good steepness of the characteristic electro-
optical lines.

Example 33

A liquid crystal phase consisting of

30 8% of 2-p-cyanophenyl-5-propyl-1,3-dioxane,
7% of 2-p-cyanophenyl-5-butyl-1,3-dioxane,
7% of 2-p-cyanophenyl-5-pentyl-1,3-dioxane,
6% of trans,trans-4'-ethoxycyclohexyl-4-propylcyclo-
35 hexane,
9% of trans,trans-4'-methoxycyclohexyl-4-butylcyclo-
hexane,
14% of trans,trans-4'-methoxycyclohexyl-4-pentylcyclo-
hexane,

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- 10% of trans,trans-4'-ethoxycyclohexyl-4-pentylcyclohexane,
12% of trans,trans-4'-butyryloxycyclohexyl-4-propylcyclohexane,
5 3% of trans,trans,trans-4-propylcyclohexylcyclohexylcyclohexane-4''-carbonitrile,
3% of trans,trans,trans-4-butylcyclohexylcyclohexylcyclohexane-4''-carbonitrile,
3% of trans,trans,trans-4-pentylcyclohexylcyclohexylcyclohexane-4''-carbonitrile,
10 3% of p-(trans,trans-4-propylcyclohexylcyclohex-4'-yl)-benzonitrile,
3% of 4,4'-bis-(trans-4-propylcyclohexyl)-2-fluorobiphenyl,
15 4% of 4,4'-bis-(trans-4-pentylcyclohexyl)-2-fluorobiphenyl,
4% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-2-fluorobiphenyl and
4% of 4,4'-bis-(trans-4-propylcyclohexyl)-biphenyl
20 has a melting point of -16° , a clear point of 93° , a viscosity of 24×10^{-3} (850×10^{-3}) Pa.s at 20° (-30°), an optical anisotropy of 0.082 and a threshold voltage of 2.5 volts. This phase is distinguished by a low viscosity, a low optical anisotropy and a wide nematic
25 range.

Example 34

- A liquid crystal phase consisting of
16% of p-trans-4-propylcyclohexylbenzonitrile,
9% of p-trans-4-butylcyclohexylbenzonitrile,
30 12% of trans,trans-4'-propoxycyclohexyl-4-propylcyclohexane,
12% of trans,trans-4'-methoxycyclohexyl-4-pentylcyclohexane,
12% of trans,trans-4'-ethoxycyclohexyl-4-pentylcyclohexane,
35 9% of trans,trans-4'-propylcyclohexyl-4-butyryloxycyclohexane,
12% of 1-(trans-4-propylcyclohexyl)-2-[trans-4-(trans-4-pentylcyclohexyl)-cyclohexyl]-ethane,

- 3% of 4,4'-bis-(trans-4-pentylcyclohexyl)-2-fluorobiphenyl,
3% of 4,4'-bis-(trans-4-pentylcyclohexyl)-2-fluorobiphenyl,
5 5% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-2-fluorobiphenyl,
3% of 4,4'-bis-(trans-4-propylcyclohexyl)-biphenyl and
4% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-biphenyl
10 has a clear point of 95°, a viscosity of 20×10^{-3} Pa.s at 20°, an optical anisotropy of 0.084 and a threshold voltage of 2.5 volts.

Example 35

- A liquid crystal phase consisting of
15 12% of trans,trans-4'-propoxycyclohexyl-4-propylcyclohexane,
12% of trans,trans-4'-methoxycyclohexyl-4-propylcyclohexane,
12% of trans,trans-4'-ethoxycyclohexyl-4-pentylcyclohexane,
20 9% of trans,trans-4'-propylcyclohexyl-4-butyryloxy-cyclohexane,
3% of trans-4-propylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate,
25 3% of trans-4-pentylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate,
3% of trans-4-propylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate,
3% of trans-pentylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate (sic),
30 3% of 4,4'-bis-(trans-4-propylcyclohexyl)-2-fluorobiphenyl,
3% of 4,4'-bis-(trans-4-pentylcyclohexyl)-2-fluorobiphenyl,
35 3% of 4,4'-bis-(trans-4-propylcyclohexyl)-biphenyl,
4% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-biphenyl,
5% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-2-fluorobiphenyl,

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16% of p-trans-4-propylcyclohexylbenzonitrile and
9% of p-trans-4-butylcyclohexylbenzonitrile
has a melting point of -16° , a clear point of 95° , no
smectic/nematic phase transition down to -40° , a
5 viscosity of $20 (300; 3100) \times 10^{-3}$ Pa.s at 20° (-20° ;
 -40°), a dielectric anisotropy of + 4.6, an optical
anisotropy of 0.0868 and a threshold voltage of 2.5 volts.

Example 36

A liquid crystal phase consisting of

10 12% of trans,trans-4'-propoxycyclohexyl-4-propylcyclo-
hexane,
16% of trans,trans-4'-methoxycyclohexyl-4-pentylcyclo-
hexane,
10% of trans,trans-4'-ethoxycyclohexyl-4-pentylcyclo-
15 hexane,
10% of trans,trans-4'-propylcyclohexyl-4-butyryloxy-
cyclohexane,
3% of trans-4-propylcyclohexyl trans,trans-4-
propylcyclohexylcyclohexane-4'-carboxylate
20 3% of trans-4-pentylcyclohexyl trans,trans-4-propyl-
cyclohexylcyclohexane-4'-carboxylate,
3% of trans-4-propylcyclohexyl trans,trans-4-butyl-
cyclohexylcyclohexane-4'-carboxylate,
3% of trans-4-pentylcyclohexyl trans,trans-4-butyl-
25 cyclohexylcyclohexyne-4'- carboxylate (sic),
3% of 4,4'-bis-(trans-4-propylcyclohexyl)-2-fluoro-
biphenyl,
3% of 4,4'-bis-(trans-4-pentylcyclohexyl)-2-fluoro-
biphenyl,
30 3% of 4,4'-bis-(trans-4-propylcyclohexyl)-biphenyl,
5% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propyl-
cyclohexyl)-biphenyl,
4% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propyl-
cyclohexyl)-2-fluorobiphenyl,
15% of p-trans-4-propylcyclohexylbenzonitrile and
7% of trans-1-p-ethoxyphenyl-4-propylcyclohexane
35 has a melting point of -18° , a clear point of 95° , no
smectic/nematic phase transition down to -40° , a
viscosity of $19 (235; 2270) \times 10^{-3}$ Pa.s at 20° (-20° ;



-40°), a dielectric anisotropy of +2.8, an optical anisotropy of 0.0830 and a threshold voltage of 3.1 volts.

Example 37

A liquid crystal phase consisting of

- 5 20% of r-1-cyano-cis-4-(trans-4-butylcyclohexyl)-1-heptylcyclohexane,
- 21% of r-1-cyano-cis-4-(trans-4-pentylcyclohexyl)-1-pentylcyclohexane,
- 11% of trans,trans-4'-methoxycyclohexyl-4-propylcyclohexane,
- 10 10% of trans,trans-4'-ethoxycyclohexyl-4-propylcyclohexane,
- 4% of trans-4-propylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate,
- 15 4% of trans-4-pentylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate,
- 4% of trans-4-propylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate,
- 4% of trans-4-pentylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate (sic) and
- 20 22% of r-1-cyano-1-propyl-cis-4-[trans-4-(trans-4-pentylcyclohexyl)-cyclohexyl]-cyclohexane.

Example 38

A liquid crystal phase consisting of

- 25 20% of r-1-cyano-cis-4-(trans-4-butylcyclohexyl)-1-heptylcyclohexane,
- 21% of r-1-cyano-cis-4-(trans-4-pentylcyclohexyl)-1-pentylcyclohexane,
- 11% of trans,trans-4'-methoxycyclohexyl-4-propylcyclohexane,
- 30 10% of trans,trans-4'-ethoxycyclohexyl-4-propylcyclohexane,
- 4% of trans-4-propylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate
- 35 4% of trans-4-pentylcyclohexyl trans,trans-4-propylcyclohexylcyclohexane-4'-carboxylate
- 4% of trans-4-propylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate,
- 4% of trans-4-pentylcyclohexyl trans,trans-4-butyl-

— cycloheptylcyclohexane-4'-carboxylate (sic) and 22% of r-1-cyano-1-(5-propyl-1,3-dioxan-2-yl)-cis-4-(trans-4-pentylcyclohexyl)-cyclohexane is prepared.

5 Example 39

A liquid crystal phase consisting of
20% of r-1-cyano-cis-4-(trans-4-butylcyclohexyl)-1-heptylcyclohexane,
21% of r-1-cyano-cis-4-(trans-4-pentylcyclohexyl)-1-
10 pentylcyclohexane,
11% of trans,trans-4'-methoxycyclohexyl-4-propyl-cyclohexane,
10% of trans,trans-4'-ethoxycyclohexyl-4-propyl-cyclohexane,
15 4% of trans-4-propylcyclohexyl trans,trans-4-propyl-cyclohexylcyclohexane-4'-carboxylate,
4% of trans-4-pentylcyclohexyl trans,trans-4-propyl-cyclohexylcyclohexane-4'-carboxylate,
4% of trans-4-propylcyclohexyl trans,trans-4-butyl-
20 cyclohexylcyclohexane-4'-carboxylate,
4% of trans-4-pentylcyclohexyl trans,trans-4-butyl-cycloheptylcyclohexane-4'-carboxylate (sic) and
22% of r-1-cyano-cis-4-(trans-4-pentylcyclohexyl)-1-(trans-4-pentylcyclohexyl)-cyclohexane
25 has a melting point of -3° , a clear point of 100° and an optical anisotropy of 0.0437.

The phase is an excellent host for pleochroic dye-stuffs, in particular for azo dyestuffs. The guest-host mixtures are outstandingly suitable for GH displays with
30 positive contrast.

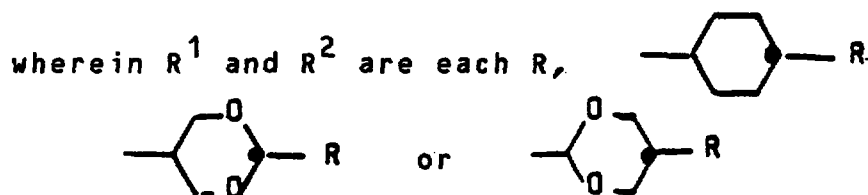
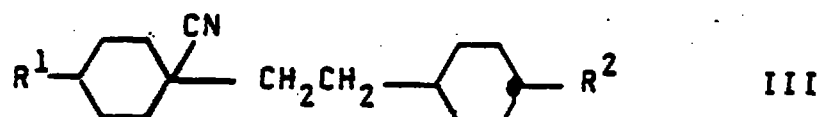
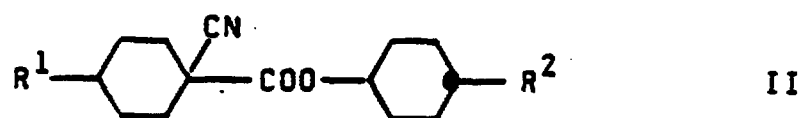
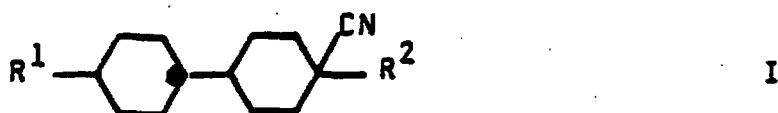
The LC phases described in Examples 5 to 12, 15 to 21, 29 and 31 to 36 are particularly suitable as wide-range mixtures, whilst the LC phases described in Examples 1 to 4, 13, 14 and 30 are particularly suitable
35 for guest-host displays with positive contrast.



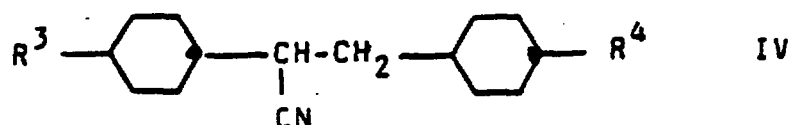
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Patent claims:

1. Liquid crystal phase, characterised in that it contains at least one component selected from Group A consisting of the compounds of the formulae I to IV



and R is alkyl with 1 to 12 C atoms, and wherein also one or two non-adjacent CH_2 groups can be replaced by $-O-$, $-CO-$, $-O-CO-$ or $-CO-O$,

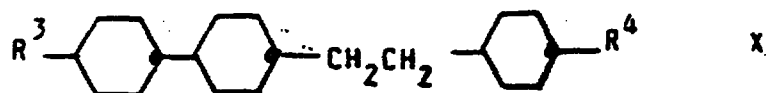
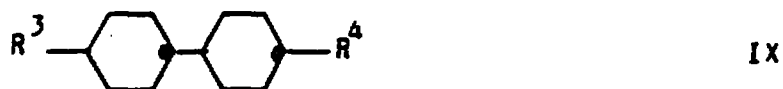
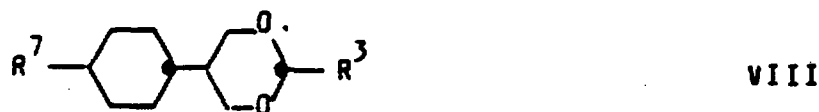
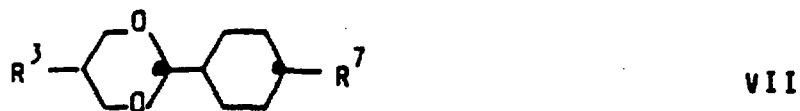


wherein R^3 and R^4 are each R or 
and R has the abovementioned meaning, and/or at least one component selected from Group B consisting of the compounds of the formulae V and VI



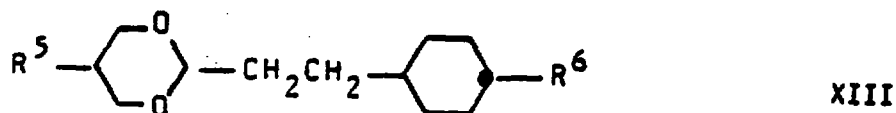
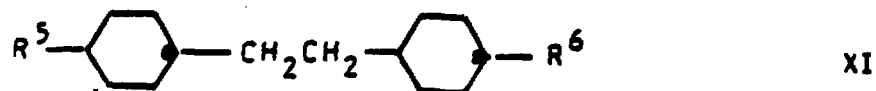


wherein R has the abovementioned meaning, Q is  or  and Z¹ is , a single bond, -CH₂CH₂-, -CO-O or -O-CO-, and at least one component selected from Group C consisting of the compounds of the formulae VII to X



wherein R³ and R⁴ have the abovementioned meaning and R⁷ can assume the meaning of -R or R⁸, wherein R

is as defined above, and R⁸ is alkyl with 1 to 12 C atoms, and wherein also one or two non-adjacent CH₂ groups can be replaced by -O- or -CO-, and, if appropriate, one or more components selected from Group D consisting of the compounds of the formulae XI to XIII

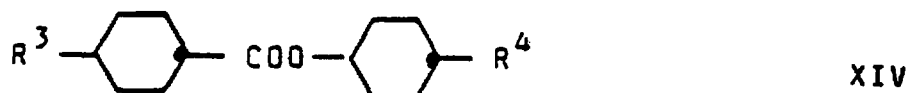




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wherein R^5 and R^6 in each case independently of one another are alkyl with 1 to 12 C atoms, and wherein also one or two non-adjacent CH_2 groups can be replaced by $-O-$, $-CO-$, $-O-CO-$ or $-CO-O-$, and, if appropriate, one or more components selected from Group E consisting of the compounds of the formulae XIV and XV



wherein R^3 and R^4 are each R or $-\text{C}_6\text{H}_4-R$, R^9 is R,

$-\text{C}_6\text{H}_4-R$, $-\text{C}_6\text{H}_3\text{O}_2-R$ or, if n equals 2, also CN, n is 2 or, if R^3 equals $-\text{C}_6\text{H}_4-R$, also 1 and A is a 1,4-phenylene group which is optionally fluorinated in the 2- or 3-position, with the proviso that, if compounds of the formula V and/or VI wherein Q is 1,4-phenylene are present, the liquid crystal phase contains at least one component of the formula IX wherein R^3 is n-alkyl and R^4 is n-alkyl, n-alkoxy or n-alkanoyloxy with in each case 1 - 12 C atoms, and at least one component from Group E.

2. Liquid crystal phase according to Claim 1, characterised in that it contains at least two components selected from Group A.

3. Liquid crystal phase according to Claim 1, characterised in that it contains at least two components selected from Group B.

4. Liquid crystal phase according to Claim 1, characterised in that it contains at least two components selected from Group A or B and at least one component selected from Group D.

5. Liquid crystal phase according to one of Claims 1, 2, 3 or 4, characterised in that the weight content of the components of the formula XV from Group E is less than 30%.

6. Liquid crystal phase with negative dielectric



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anisotropy containing at least two pleochroic dyestuffs, characterised in that the host material is a liquid crystal phase according to Claim 1.

7. Liquid crystal phase according to Claim 6, characterised in that the host material contains at least two components from Group A and one component from Group D.

8. Liquid crystal phase according to one of Claims 6 and 7, characterised in that at least one dyestuff belongs to the class of azo dyestuffs.

9. Liquid crystal phase according to one of Claims 6 to 8, characterised in that at least one dyestuff is an azo dyestuff with a wavelength of maximum absorption of greater than 580 nm.

10. Liquid crystal phase according to one of Claims 6 to 9, characterised in that an electrooptical display element containing the liquid crystal phase has a colour interval, measured by CIU (1964), up to the point of achromatism of less than 5 units.

11. Use of the liquid crystal phase according to one of Claims 1 to 10, in liquid crystal display elements.

12. Liquid crystal display element, characterised in that it contains a liquid crystal phase according to one of Claims 1 to 10.

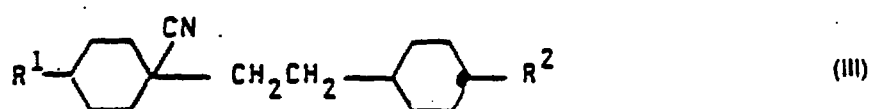
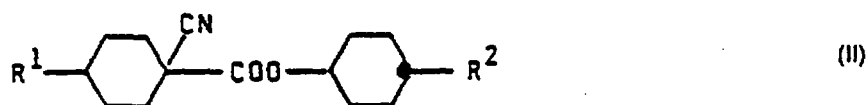
13. Electrooptical display element, characterised in that it contains, as the dielectric, a liquid crystal phase according to one of Claims 1 to 10.



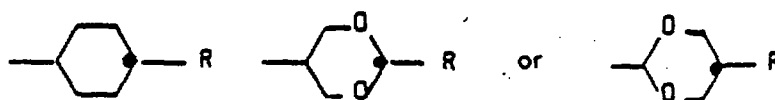
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Claims As printed.

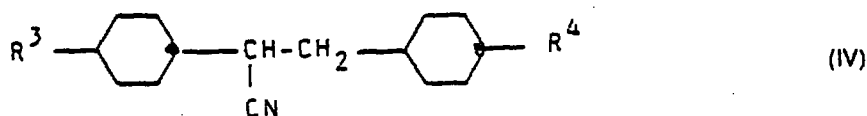
1. Liquid crystal phase, characterised in that it contains at least one component selected from Group A consisting of the compounds of the formulae I to IV



wherein R¹ and R² are each R,



and R is alkyl with 1 to 12 C atoms, and wherein also one or two non-adjacent CH₂ groups can be replaced by -O-, -CO-, -O-CO- or -CO-O-,



wherein R³ and R⁴ are each R or



and R has the abovementioned meaning,

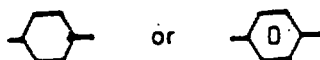
and/or at least one component selected from Group B consisting of the compounds of the formulae V and VI





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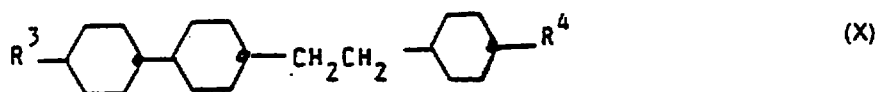
wherein R has the abovementioned meaning, Q is



and Z, is



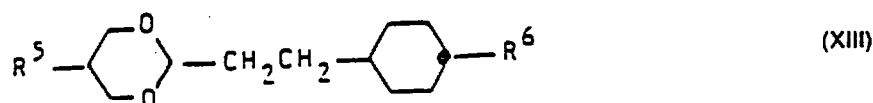
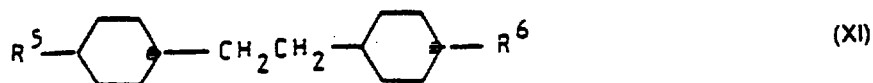
a single bond, $-\text{CH}_2\text{CH}_2-$, $-\text{CO}-\text{O}-$ or $-\text{O}-\text{CO}-$,
and at least one component selected from Group C consisting of the compounds of the formulae VII to X



wherein R³ and R⁴ have the abovementioned meaning and R⁷ can assume the meaning of



or R⁶, wherein R is as defined above, and R⁶ is alkyl with 1 to 12 C atoms, and wherein also one or two non-adjacent CH₂ groups can be replaced by $-\text{O}-$ or $-\text{CO}-$,
and, if appropriate, one or more components selected from Group D consisting of the compounds of the formulae XI to XIII

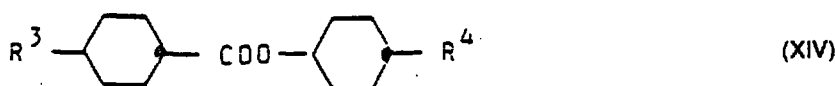


wherein R⁵ and R⁶ in each case independently of one another are alkyl with 1 to 12 C atoms, and wherein also one or two non-adjacent CH₂ groups can be replaced by $-\text{O}-$, $-\text{CO}-$, $-\text{O}-\text{CO}-$ or $-\text{CO}-\text{O}-$,
and, if appropriate, one or more components selected from Group E consisting of the compounds of the formulae XIV and XV



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wherein R^3 and R^4 are each R or



R^9 is R,



or, if n equals 2, also CN,
n is 2 or, if R^3 equals



also 1 and

A is a 1,4-phenylene group which is optionally fluorinated in the 2- or 3-position, with the proviso that, if compounds of the formula V and/or VI wherein Q is 1,4-phenylene are present, the liquid crystal phase contains at least one component of the formula IX wherein R^3 is n-alkyl and R^4 is n-alkyl, n-alkoxy or n-alkanoyloxy with in each case 1-12 C atoms, and at least one component from Group E.

2. Liquid crystal phase according to Claim 1, characterised in that it contains at least two components selected from Group A.

3. Liquid crystal phase according to Claim 1, characterised in that it contains at least two components selected from Group B.

4. Liquid crystal phase according to Claim 1, characterised in that it contains at least two components selected from Group A or B and at least one component selected from Group D.

5. Liquid crystal phase according to one of Claims 1, 2, 3 or 4, characterised in that the weight content of the components of the formula XV from Group E is less than 30 %.

6. Liquid crystal phase with negative dielectric anisotropy containing at least two pleochroic dyestuffs, characterised in that the host material is a liquid crystal phase according to Claim 1.

7. Liquid crystal phase according to Claim 6, characterised in that the host material contains at least two components from Group A and one component from Group D.

8. Liquid crystal phase according to one of Claims 6 and 7, characterised in that at least one dyestuff belongs to the class of azo dyestuffs.

9. Liquid crystal phase according to one of Claims 6 to 8, characterised in that at least one dyestuff is an azo dyestuff with a wavelength of maximum absorption of greater than 580 nm.

10. Liquid crystal phase according to one of Claims 6 to 9, characterised in that an electrooptical display element containing the liquid crystal phase has a colour interval, measured by CIU (1964), up to the point of achromatism of less than 5 units.

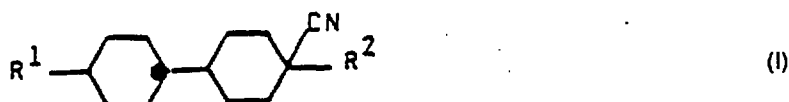
11. Use of the liquid crystal phase according to one of Claims 1 to 10, in liquid crystal display elements.

12. Liquid crystal display element, characterised in that it contains a liquid crystal phase according to one of Claims 1 to 10.

13. Electrooptical display element, characterised in that it contains, as the dielectric, a liquid crystal phase according to one of Claims 1 to 10.

Revendications

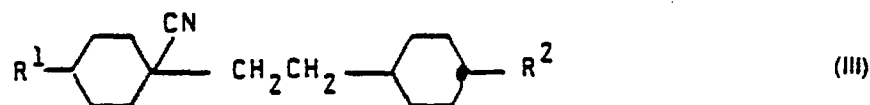
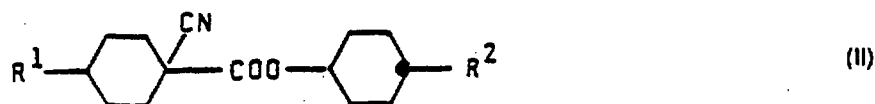
1. Phase à cristaux liquides caractérisée en ce qu'elle contient au moins un composant choisi dans le groupe A consistant en les composés de formules I à IV



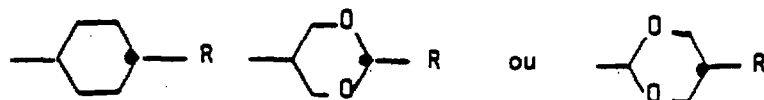


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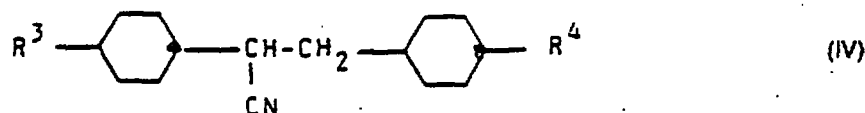
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dans lesquelles R^1 et R^2 représentent chacun R,



et R représente un groupe alkyle en C 1-C 12 dans lequel un ou deux groupes CH_2 non voisins peuvent encore être remplacés par ---O--- , ---CO--- , ---O---CO--- ou ---CO---O--- ,



dans laquelle R^3 et R^4 représentent chacun R ou

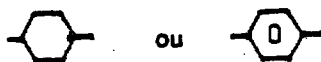


et R a les significations indiquées ci-dessus,

et/ou au moins un composant choisi dans le groupe B consistant en les composés de formules V et VI



dans lesquelles R a les significations indiquées ci-dessus, Q représente



et Z^1 représente



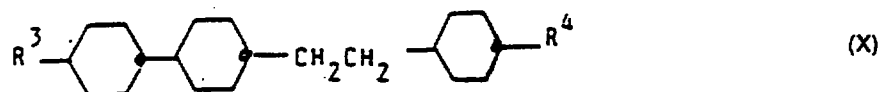
une liaison simple, $\text{---CH}_2\text{CH}_2\text{---}$, ---CO---O--- ou ---O---CO--- ,

et au moins un composant choisi dans le groupe C consistant en les composés de formules VII à X





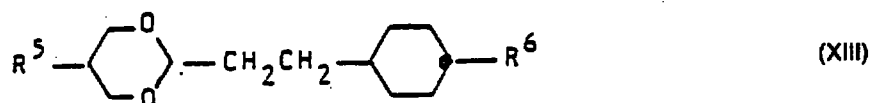
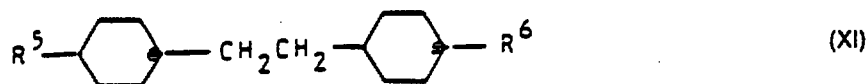
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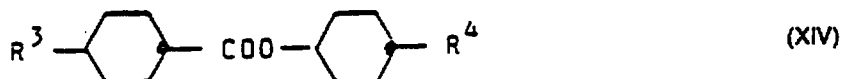
dans lesquelles R^3 et R^4 ont les significations indiquées ci-dessus et R^7 peut représenter



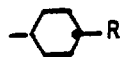
ou R^8 , R ayant les significations indiquées ci-dessus et R^8 représentant un groupe alkyle en C 1-C 12 dans lequel un ou deux groupes CH_2 non voisins peuvent également être remplacés par $-O-$ ou $-CO-$, et le cas échéant, un ou plusieurs composants choisis dans le groupe D consistant en les composés de formules XI à XIII



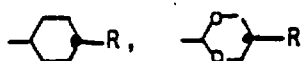
dans lesquelles R^5 et R^6 représentent chacun, indépendamment l'un de l'autre, un groupe alkyle en C 1-C 12 dans lequel un ou deux groupes CH_2 non voisins peuvent également être remplacés par $-O-$, $-CO-$, $-O-CO-$ ou $-CO-O-$, et le cas échéant, un ou plusieurs composants choisis dans le groupe E consistant en les composés de formules XIV et XV



dans lesquelles R^3 et R^4 représentent chacun R ou



R^9 représente R ,



ou bien encore, lorsque $n = 2$, un groupe CN ,
 n est égal à 2, ou bien encore, lorsque R^3 représente



à 1,

A représente un groupe 1.4-phénylène éventuellement fluoré en position 2 ou 3.



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sous réserve que la phase à cristaux liquides, dans le cas de la présence de composés de formules V et/ou VI dans lesquelles Q représente un groupe 1,4-phénylène, contient au moins un composant de formule IX dans laquelle R³ représente un groupe n-alkyle et R⁴ un groupe n-alkyle, n-alcoxy ou n-alcanoyloxy contenant chacun 1 à 12 atomes de carbone, et au moins un composant du groupe E.

2. Phase à cristaux liquides selon la revendication 1, caractérisée en ce qu'elle contient au moins deux composants choisis dans le groupe A.

3. Phase à cristaux liquides selon la revendication 1, caractérisée en ce qu'elle contient au moins deux composants choisis dans le groupe B.

4. Phase à cristaux liquides selon la revendication 1, caractérisée en ce qu'elle contient au moins deux composants choisis dans le groupe A ou le groupe B et au moins un composant choisi dans le groupe D.

5. Phase à cristaux liquides selon l'une des revendications 1, 2, 3 ou 4, caractérisée en ce que la proportion relative en poids des composants de formule XV du groupe E est inférieure à 30 %.

6. Phase à cristaux liquides à anisotropie diélectrique négative contenant au moins deux colorants pléochroïques, caractérisée en ce que la matière Host est une phase à cristaux liquides selon la revendication 1.

7. Phase à cristaux liquides selon la revendication 6, caractérisée en ce que la matière Host contient au moins deux composants du groupe A et un composant du groupe D.

8. Phase à cristaux liquides selon l'une des revendications 6 et 7, caractérisée en ce qu'un colorant au moins appartient à la classe des colorants azoïques.

9. Phase à cristaux liquides selon l'une des revendications 6 à 8, caractérisée en ce qu'un colorant au moins est un colorant azoïque présentant une longueur d'ondes d'absorption maximale supérieure à 580 nm.

10. Phase à cristaux liquides selon l'une des revendications 6 à 9, caractérisée en ce qu'un élément d'affichage électro-optique contenant la phase à cristaux liquides présente un intervalle de couleur jusqu'au point d'achromasie, mesuré selon CIE (1964) inférieur à 5 unités.

11. Utilisation de la phase à cristaux liquides selon l'une des revendications 1 à 10, dans des éléments d'affichage à cristaux liquides.

12. Élément d'affichage à cristaux liquides caractérisé en ce qu'il contient une phase à cristaux liquides selon l'une des revendications 1 à 10.

13. Élément d'affichage électro-optique caractérisé en ce qu'il contient en tant que diélectrique une phase à cristaux liquides selon l'une des revendications 1 à 10.