

Description

The invention relates to a liquid-crystalline phase containing tolans of the formula I



5 in which

R^1 and R^2 are each, independently of one another, alkyl having up to 15 carbon atoms in which, in addition, one or two non-adjacent CH_2 groups may be replaced by $-O-$, and one of the radicals R^1 and R^2 is alternatively $-OCF_3$,
10 CF_3 , fluorine or chlorine,

A^1 is unsubstituted 1,4-phenylene or trans-1,4-cyclohexylene,

Z^1 is $-CH_2CH_2-$ or a single bond,

m is 0 or 1,

15 and

A^3 and A^4 are each, independently of one another, 1,4-phenylene which is unsubstituted or monosubstituted or polysubstituted by fluorine,

with the provisos that either

20 a) the tolans of the formula I contain a 2,3-difluoro-1,4-phenylene group, or

b) R^1 or R^2 is $-CF_3$, or OCF_3 ,

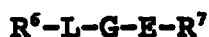
or that

c) in the case where $m = 0$ and A^3 and $A^4 =$ unsubstituted
25 1,4-phenylene, R^1 is ethoxy, propoxy, butoxy, pentoxy, hexoxy or heptoxy, and R^2 is fluorine, or one of the radicals R^1 and R^2 is an alkyl group in which at least two

d) compounds where $m = 0$ and A^3 and/or $A^4 =$ monosubstituted 1,4-phenylene are excluded,

e) in the case where A^3 and $A^4 =$ unsubstituted 1,4-phenylene, $m = 1$ and $Z^1 =$ a single bond, one of the radicals R^1 and R^2 is an alkoxy group and the other is then alkyl,

and contains, as the most important further constituents, compounds of the formula V



V

10 in which L and E are each a carbocyclic or heterocyclic ring system from the group formed by 1,4-disubstituted cyclohexane rings, 4,4-disubstituted phenylcyclohexane and cyclohexylcyclohexane systems, 2,5-disubstituted pyrimidine and 1,3-dioxane rings, 2,6-disubstituted
15 naphthalene, di- and tetrahydronaphthalene, quinazoline and tetrahydroquinazoline,

G is

-CH=CH-	-N(O)=N-
-CH=CY-	-CH=N(O)-
-C≡C	-CH ₂ -CH ₂ -
20 -CO-O-	-CH ₂ -O-
-CO-S-	-CH ₂ -S-
-CH=N-	-COO-Phe-COO-

or a C-C single bond,

Y is chlorine or -CN, and

25 R^6 and R^7 are alkyl, alkoxy, alkanoyloxy or alkoxy-carbonyloxy having up to 8 carbon atoms, or one of these radicals is alternatively CN, NC, NO₂, CF₃, F, Cl or Br, and also to preferred tolans of the formula I.

The invention also relates to the use of these
30 tolans as components of liquid-crystalline phases for electro-optical display elements based on the ECB effect.

For the sake of simplicity, in the following Phe is an unsubstituted 1,4-phenylene group, PheX is a mono-substituted or polysubstituted 1,4-phenylene group (X is halogen and/or nitrile), Cyc is a trans-1,4-cyclohexylene group, Dio is a 1,3-dioxane-2,5-diyl group, Pyd is a pyridine-2,5-diyl group, Pyr is a pyrimidine-2,5-diyl group, Dit is a 1,3-dithian-2,5-diyl group and Bco is a 1,4-bicyclo[2.2.2]-octylene group.

The compounds of the formula I can be used as components of liquid-crystalline phases, in particular for displays which are based on the principle of the twisted cell, the guest-host effect, the effect of the deformation of aligned phases or the effect of dynamic scattering.

Compounds of the formula I are preferably also suitable for use as components in liquid-crystalline phases for displays which are based on the ECB effect.

Similar compounds are disclosed for example in GB 2155 465 A or FR 2234 261, and in Mol. Cryst. and Liq. Cryst. 62, 127 (1980); Chem. Abs., 87, No. 166967 s (1977); EP-A-0 255 700; EP-A-0 276 067; DE-A-25 04 641 and WO-A-88/02130.

The object of the invention was to provide new stable liquid-crystalline or mesogenic compounds which are suitable as components of liquid-crystalline phases. This object has been achieved by the provision of the compounds of the formula I.

It has been found that the compounds of the formula I are highly suitable as components of liquid-crystalline phases. In particular, stable liquid-crystalline phases having relatively high optical anisotropy and pronounced negative dielectric anisotropy can be prepared with the help of these compounds. Accordingly, the substances of the formula I are preferably suitable for use in mixtures for ECB effects.

The ECB effect (electrically controlled birefringence) or also the DAP effect (deformation of aligned phases) was first described in 1971 (M.F. Schieckel and K. Fahrenschon, "Deformation of nematic liquid crystals

with vertical orientation in electrical fields", Appl. Phys. Lett. 19 (1971), 3912). This was followed by papers by J.F. Kahn (Appl. Phys. Lett. 20 (1972), 1193) and G. Labrunie and J. Robert (J. Appl. Phys. 44 (1973), 4869).

The papers by J. Robert and F. Clerc (SID 80 Digest Techn. Papers (1980), 30), J. Duchene (Displays 7 (1986), 3) and H. Schad (SID 82 Digest Techn. Papers (1982), 244) have shown that liquid-crystalline phases must have high values for the ratio of the elasticity constants K_2/K_1 , high values for the optical anisotropy A_n and negative values for the dielectric anisotropy $\Delta\epsilon$, so that they can be used for high information density display elements based on the ECB effect.

Electro-optical display elements based on the ECB effect exhibit a homeotropic edge orientation, that is to say the liquid-crystalline phase has a negative dielectric anisotropy.

For the industrial application of this effect in electro-optical display elements, LC phases are required which must satisfy numerous requirements. Of particular importance in this context are the chemical resistance to moisture, air and physical influences such as heat, radiation in the infrared, visible and ultraviolet range and electric direct fields and alternating fields. LC phases which can be used industrially must also have a liquid-crystalline mesophase in a suitable temperature range and a low viscosity.

There is not a single compound which fulfils all of these requirements in any of the hitherto known series of compounds having a liquid-crystalline mesophase. Thus mixtures of 2 to 25, preferably 3 to 18 compounds are generally prepared, in order to obtain substances which can be used as LC phases. However, optimum phases could not be prepared easily in this fashion, since no liquid-crystalline materials having clearly negative dielectric anisotropy and sufficient long-term stability were hitherto available.

There is therefore still a great need for liquid-

crystalline phases having favourable mesophase regions, high values for K_2/K_1 , high optical anisotropy A_n , negative dielectric anisotropy $\Delta\epsilon$ and high long-term stability.

Surprisingly, it has been found that the addition
5 of compounds of the formula I produces liquid-crystalline phases which fulfil all of the abovementioned criteria very well indeed.

In addition, by providing the compounds of the formula I, the whole range of liquid-crystalline sub-
10 stances which are suitable from a variety of technical viewpoints for the preparation of nematic mixtures, has been considerably broadened.

The compounds of the formula I have a wide area of application. Depending on the choice of substituents,
15 these compounds can serve as base materials from which the major part of liquid-crystalline phases are made up; liquid-crystalline base materials from other classes of compounds can however also be added to compounds of the formula I, for example to optimize the dielectric and/or
20 optical anisotropy of a dielectric of this type. The compounds of the formula I are also suitable as intermediates for the preparation of other substances which can be used as constituents of liquid-crystalline phases.

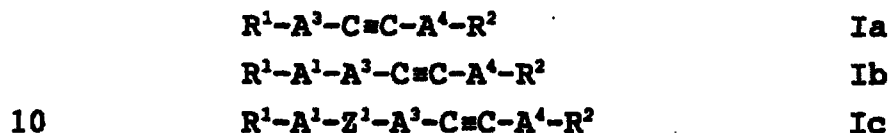
The compounds of the formula I are colourless in
25 their pure form and form liquid-crystalline mesophases in a temperature range which is favourable for electro-optical use. They are chemically and thermally very stable and are very stable to light.

The invention accordingly relates to liquid-
30 crystalline phases containing compounds of the formula I, preferred tolans of the formula I and the use of these compounds as components of liquid-crystalline phases and as components of liquid-crystalline phases for electro-optical display elements based on the ECB effect. The
35 invention furthermore relates to liquid-crystalline phases and liquid-crystalline phases for electro-optical display elements based on the ECB effect which contain at least one compound of the formula I, and also to liquid-crystal display elements, in particular electro-optical

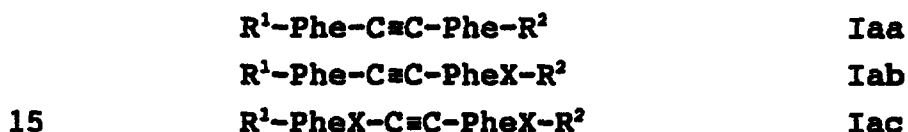
display elements, which contain phases of this type.

In the foregoing and in what follows R^1 , A^1 , Z^1 , m , A^3 , A^4 , A^2 , n and R^2 have the meaning indicated, unless specifically stated otherwise.

5 The compounds of the formula I accordingly include compounds of the sub-formulae Ia (having two rings), Ib and Ic (having three rings):

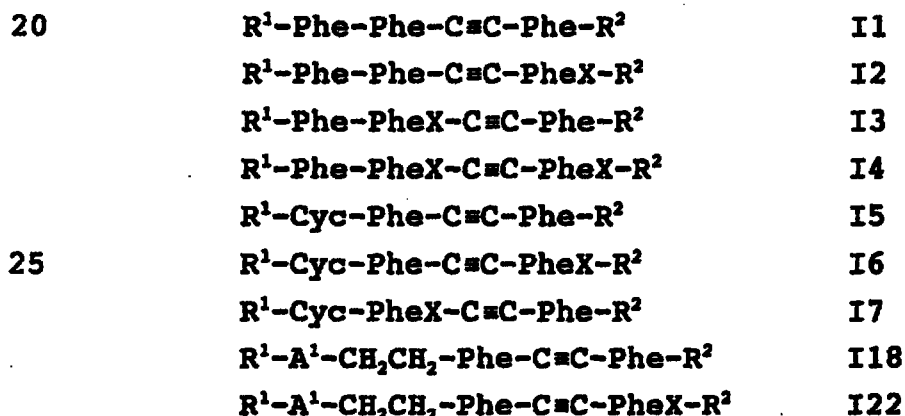


The preferred compounds of the sub-formula Ia include those of the sub-formulae Iaa to Iac:



Among these, those of the formulae Iaa and Iab are particularly preferred.

The preferred compounds of the sub-formulae Ib and Ic include those of the sub-formulae I1 to I22:



30 Among these, those of the formulae I1, I2, I5, I6, I18 and I22 are particularly preferred. The compounds of the sub-formula I5 are particularly preferred.

In the compounds of the formulae above and below, R^1 and R^2 are preferably alkyl, alkoxy or another oxaalkyl or dioxalkyl group. Furthermore compounds of the formula I are preferred in which one of the radicals R^1 and R^2 is halogen, -OCF, or -CF₃.

m is 0 or 1, m preferably being 0.

A^3 and A^4 are preferably unsubstituted 1,4-phenylene. If A^3 and A^4 are substituted 1,4-phenylene, then they

are substituted by fluorine. In the case of monosubstitution, the substituent is preferably in the o-position relative to R² or R¹. But the lateral substituent can also be in the o-position to the -C≡C- triple bond.

5 If R¹ and/or R² are alkyl radicals in which one ("alkoxy" or "oxaalkyl") or two ("alkoxyalkoxy" or "dioxalkyl") non-adjacent CH₂ groups can also be replaced by oxygen atoms, they can be straight-chain or branched. They are preferably straight-chain having 1, 2,
10 3, 4, 5, 6 or 7 carbon atoms and are accordingly preferably methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, 2-oxapropyl (= methoxymethyl), 2-
15 (= ethoxymethyl) or 3-oxabutyl (= 2-methoxyethyl), 2-, 3- or 4-oxapentyl, 2-, 3-, 4- or 5-oxahexyl, 2-, 3-, 4-, 5- or 6-oxaheptyl, furthermore octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, methoxy, octoxy, nonoxy, decoxy, undecoxy, dodecoxy, tridecoxy, tetradecoxy, pentadecoxy, 2-, 3-, 4-, 5-, 6- or 7-
20 oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl, 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl, 1,3-dioxabutyl (= methoxymethoxy), 1,3-, 1,4- or 2,4-dioxapentyl, 1,3-, 1,4-, 1,5-, 2,4-, 2,5- or 3,5-dioxahexyl, 1,3-, 1,4-, 1,5-, 1,6-, 2,4-, 2,5-, 2,6-, 3,5-, 3,6- or 4,6-dioxahep-
25 tyl.

Compounds of the formula I having branched wing groups R¹ or R² can occasionally be of significance because of their better solubility in the customary liquid-crystalline base materials, but in particular as
30 chiral dopes, if they are optically active.

Branched groups of this type do not, as a rule, contain more than one chain branch. Preferred branched radical [sic] are isopropyl, 2-butyl (= 1-methylpropyl), isobutyl (= 2-methylpropyl), 2-methylbutyl, isopentyl
35 (= 3-methylbutyl), 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-propylpentyl, 2-octyl, isopropoxy, 2-methylpropoxy, 2-methylbutoxy, 3-methylbutoxy, 2-methylpentoxy, 3-methylpentoxy, 2-ethylhexoxy, 1-methylhexoxy, 1-methylheptoxy (= 2-octyloxy), 2-oxa-3-

methylbutyl, 3-oxa-4-methylpentyl, 4-methylhexyl, 2-nonyl, 2-decyl, 2-dodecyl, 6-methyloctoxy, 6-methyloctanoyloxy, 5-methylheptyloxycarbonyl, 2-methylbutyryloxy, 3-methylvaleryloxy, 4-methylhexanoyloxy, 2-methyl-3-oxapentyl and 2-methyl-3-oxahexyl.

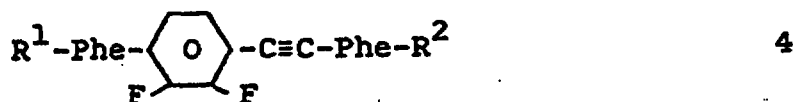
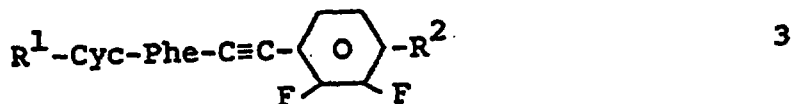
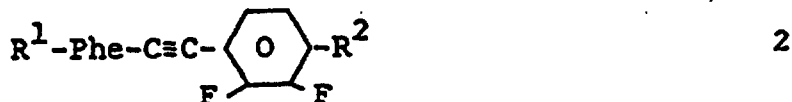
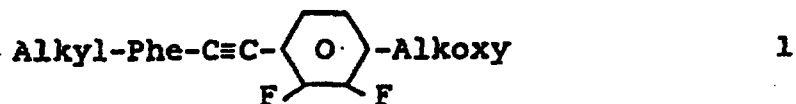
For compounds having branched wing groups, formula I encompasses both the optical antipodes and racemates and also mixtures thereof.

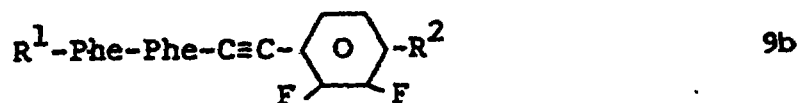
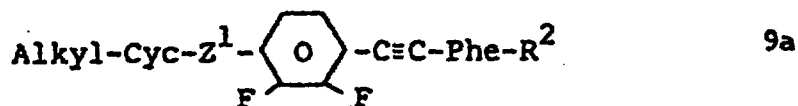
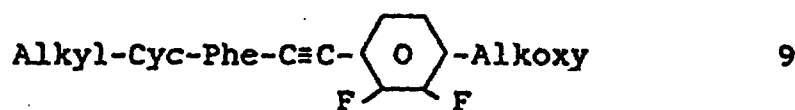
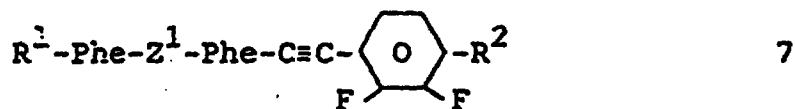
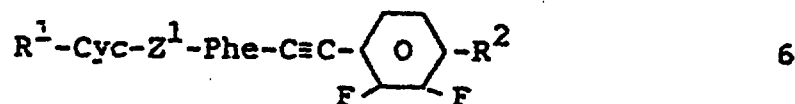
Preferred compounds of the formula I and their subformulae are those in which at least one of the radicals contained therein has one of the indicated preferred meanings.

Particularly preferred compounds of the formula I are those in which at least one of the groups A³ and A⁴ is a 2,3-difluoro-1,4-phenylene group.

Examples of preferred representatives of compounds of the formula I having a 2,3-difluoro-1,4-phenylene group are illustrated in the following (subformulae 1-9b):

20





Where $m = 0$, the following substances of the sub-formulae 10-14 are particularly preferred among the compounds of the formula I:

	alkoxy-Phe-C $\equiv$ C-Phe-F	10
5	alkoxyalkoxy-Phe-C $\equiv$ C-Phe-alkyl	13
	alkoxyalkoxy-Phe-C $\equiv$ C-Phe-halogen	14

A smaller group of particularly preferred compounds of the formula I where $m \neq 0$ are those of the sub-formulae 21-28:

10	alkyl-Cyc-Phe-C $\equiv$ C-Phe-alkoxy	21
	alkyl-Cyc-CH ₂ CH ₂ -Phe-C $\equiv$ C-Phe-alkyl	22

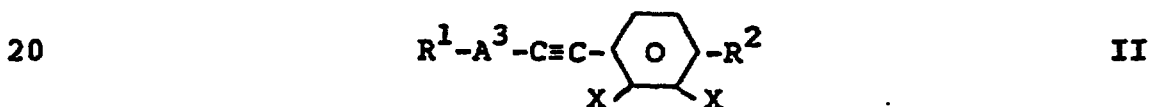
	alkyl-Cyc-CH ₂ CH ₂ -Phe-C≡C-Phe-alkoxy	23
	alkyl-Phe-Phe-C≡C-PheF-halogen	24
	alkyl-Cyc-Phe-C≡C-PheF-alkoxy	26
	alkyl-Phe-CH ₂ CH ₂ -Phe-C≡C-Phe-alkyl	27
5	alkyl-Phe-PheX-C≡C-Phe-alkoxy	28

Also particularly preferred are compounds of the formula I wherein one of the radicals R¹ and R² is an -OCF₃ or trifluoromethyl. Especially preferred compounds in this case are, for example, those of the sub-formulae

10 Iga to Igk:

	alkyl-Cyc-Phe-C≡C-Phe-CF ₃ ,	Iga
	alkyl-Phe-Phe-C≡C-Phe-CF ₃ ,	Igc
	alkyl-Phe-  -C≡C-Phe-CF ₃	Ige
	R ¹ -Phe-C≡C-Phe-CF ₃ ,	Igg
15	R ¹ -PheX-C≡C-Phe-CF ₃ ,	Igi
	R ¹ -Phe-C≡C-Phe-OCF ₃ ,	Igj
	R ¹ -Cyc-Phe-C≡C-Phe-OCF ₃ ,	Igk

Preferred compounds of the formula I are those of the sub-formula II



wherein

X is F,

R¹ and R² have the meaning given in formula I,

25 A³ is 1,4-phenylene which is unsubstituted or monosubstituted or polysubstituted by fluorine,

where R¹ is preferably an alkyl group and R² is an alkoxy group.

Also preferred are compounds of the sub-formula



wherein

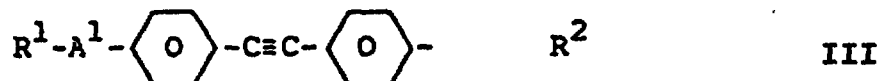
A³ and A⁴ are each unsubstituted 1,4-phenylene,

R¹ is alkoxy having up to 14 carbon atoms in the alkyl group,

R² is fluorine or

- 5 one of the radicals R¹ and R² is an alkyl group, wherein at least two non-adjacent CH₂ groups are replaced by -O-.

Preferred compounds of the formula I are also those of the sub-formula III



- 10 wherein

one of the radicals R¹ and R² is an alkoxy group having up to 14 carbon atoms in the alkyl group,

the other of the radicals R¹ and R² is halogen or alkyl having up to 15 carbon atoms,

- 15 and

A¹ is 1,4-phenylene.

- The compounds of the formula I are prepared by methods known per se, as are described in the literature (for example, in the standard reference works such as
- 20 Houben-Weyl, Methoden der Organischen Chemie, Georg-Thieme-Verlag, Stuttgart), specifically under reaction conditions which are known and suitable for the reactions mentioned. Variants may also be used which are known per se but are not mentioned in more detail here.

- 25 If desired, the starting substances can also be formed in situ, in such a manner that they are not isolated from the reaction mixture, but are immediately reacted further to the compounds of the formula I.

- The compounds of the formula I can thus be
- 30 prepared by brominating the corresponding stilbenes and

subsequently subjecting them to a dehydrohalogenation. Variants of this reaction can be used which are known per se but are not mentioned in detail here.

The stilbenes can be prepared by reacting a
5 4-substituted benzaldehyde with a corresponding phosphorus ylide according to Wittig or by reacting a 4-substituted phenylethylene with a corresponding bromobenzene derivative according to Heck.

A further possibility of forming the C-C triple
10 bond consists in reacting a compound which corresponds to the formula I except that it contains a $\text{-CH}_2\text{-CO-}$ group in place of the $\text{-C}\equiv\text{C-}$ bond, either with an inorganic acid chloride and dehydrohalogenating the $\text{-CH}_2\text{-CCl}_2\text{-}$ group then formed in the presence of a base, or reacting the com-
15 pound with semicarbazide and selenium dioxide and subsequently converting it into the triple bond by heating in the presence of methyllithium.

It is also possible to convert a corresponding benzyl derivative into the tolan using hydrazine and
20 subsequently HgO .

Compounds of the formula I can also be prepared by coupling alkynyl-zinc compounds with arylhalides analogously to the process described by A.O. King, E. Negishi, F.J. Villani and A. Silveira in J. Org. Chem.
25 43 (1978) 358.

Compounds of the formula I can also be prepared by the Fritsch-Buttenberg-Wiechell rearrangement (Ann. 279, 319, 327, 332, 1894) in which 1,1-diaryl-2-halogenoethylenes are rearranged in the presence of strong bases
30 to form diarylacetylenes.

Compounds of the formula I can furthermore be prepared from 4-substituted phenylacetylenes and aryl halides in the presence of a palladium catalyst, for example bis(triphenylphosphine)palladium(II) chloride and
35 copper(I) iodide (described in Synthesis (1980) 627 or Tetrahedron Letters 27 (1986) 1171).

The liquid-crystalline phases according to the invention consist of 2 to 15, preferably 3 to 12 components, at least one of which is a compound of the formula

I. The other constituents are preferably selected from the nematic or nematogenic substances, in particular the known substances from the classes of the azoxybenzenes, benzylideneanilines, biphenyls, terphenyls, phenyl
 5 benzoates or cyclohexyl benzoates, phenyl cyclohexane-carboxylates or cyclohexyl cyclohexanecarboxylates, phenylcyclohexanes, cyclohexylbiphenyls, cyclohexyl-cyclohexanes, cyclohexylnaphthalenes, 1,4-biscyclohexyl-benzenes, 4,4-biscyclohexylbiphenyls, phenylpyrimidines
 10 or cyclohexylpyrimidines, phenyldioxanes or cyclohexyl-dioxanes, phenyl-1,3-dithianes or cyclohexyl-1,3-dithianes, 1,2-diphenylethanes, 1,2-dicyclohexylethanes, 1-phenyl-2-cyclohexylethanes, optionally halogenated stilbenes, benzyl phenyl ethers and substituted cinnamic
 15 acids.

The most important compounds which are suitable as constituents of liquid-crystalline phases of this type can be characterized by the formula V



V

20 in which L and E are each a carbocyclic or heterocyclic ring system from the group formed by 1,4-disubstituted cyclohexane rings, 4,4-disubstituted phenylcyclohexane and cyclohexylcyclohexane systems, 2,5-disubstituted pyrimidine and 1,3-dioxane rings, 2,6-disubstituted
 25 naphthalene, di- and tetrahydronaphthalene, quinazoline and tetrahydroquinazoline,

30	G is	-CH=CH-	-N(O)=N-
		-CH=CY-	-CH=N(O)-
		-C≡C-	-CH ₂ -CH ₂ -
		-CO-O-	-CH ₂ -O-
		-CO-S-	-CH ₂ -S-
		-CH=N-	-COO-Phe-COO-

or a C-C single bond,

Y is chlorine or -CN, and

R' and R' are alkyl, alkoxy, alkanoyloxy or alkoxy-carbonyloxy having up to 8 carbon atoms, or one of these radicals is alternatively CN, NC, NO₂, CF₃, F, Cl or Br.

In most of these compounds R' and R' are different
5 from one another, where one of these radicals is usually an alkyl or alkoxy group. Other variants of the intended substituents are also useful. Many substances of this type or also mixtures thereof are commercially available. All these substances can be obtained by methods which are
10 known from the literature.

The phases according to the invention contain about 0.1 to 99, preferably 10 to 95% of one or more compounds of the formula I. Liquid-crystalline phases according to the invention which are further preferred
15 are those which contain 0.1 to 40, preferably 0.5 to 30% of one or more compounds of the formula I.

The compounds of the formula I can also be used as components of smectic or chirally tilted smectic liquid-crystalline phases. These phases are preferably
20 chirally tilted smectic liquid-crystalline phases, the achiral base mixture of which contains, in addition to compounds of the formula I, at least one other component having negative or relatively low positive dielectric anisotropy. This/these further component(s) of the
25 achiral base mixture can comprise up to 1 to 50%, preferably 10 to 25%, of the base mixture.

The preparation of the phases according to the invention is carried out by a method known per se. As a rule, the components are dissolved in one another,
30 preferably at an elevated temperature.

By means of suitable additives, the liquid-crystalline phases according to the invention can be modified in such a way that they can be used in all types of liquid crystal display elements which are hitherto
35 known.

Additives of this type are known to the skilled worker and are described in detail in the literature. For example, conductive salts, preferably ethyl-dimethyldodecyl-ammonium-4-hexyloxybenzoate, tetrabutylammonium-

tetraphenylboranate or complex salts of crown ethers (compare, for example, I. Haller et al., Mol. Cryst. Liq. Cryst. Vol. 24, pages 249-258 (1973)) can be added to improve the conductivity, dichroic dyes can be added to
5 produce coloured guest-host systems or substances can be added to change the dielectric anisotropy, the viscosity and/or the orientation of the nematic phases. Substances of this type are described for example in DE-A 22 09 127, 22 40 864, 23 21 632, 23 38 281, 24 50 088, 26 37 430,
10 28 53 728 and 29 02 177.

The phases according to the invention for electro-optical display elements based on the ECB effect contain preferably at least 7% of compounds of the formula I, particularly preferably 7 to 30% of compounds
15 of the formula I.

The following examples are intended to illustrate the invention without limiting it. Above and below, percentages are per cent by weight; all temperatures are stated in degrees centigrade.

20 "Customary working up" means: water is added, the mixture is extracted with methylene chloride, the organic phase is separated off, dried and concentrated by evaporation, and the product is purified by crystallization and/or chromatography.

25 m.p. means melting point and c.p. means clear point.

Example 1

0.2 mmol of bis(triphenylphosphine)palladium(II) chloride and 0.1 mmol of copper(I) iodide are added to a
30 mixture of 0.01 mol of 4-ethoxyiodobenzene, 0.01 mol of 4-(trans-4-propylcyclohexyl)phenylacetylene (which can be prepared, for example, according to Smith, Hoehn, Am. Soc. 63 (1941) 1175) and 40 ml of triethylamine at room temperature and stirred for 12 hours. The course of the
35 reaction can be followed with the aid of thin-layer chromatography. After completion of the reaction, the suspension is filtered, and the filtrate is concentrated by evaporation. Purification by chromatography and/or

crystallization gives 4-ethoxy-4'-(trans-propylcyclohexyl)tolan having m.p. = 110° and c.p. = 253°.

The following are prepared analogously:

- 4-methoxy-4'-(trans-4-propylcyclohexyl)tolan, m.p. 99°,
5 c.p. 245°
- 4-propyloxy-4'-(trans-4-propylcyclohexyl)tolan, m.p. 97°,
c.p. 236°
- 4-butyloxy-4'-(trans-4-propylcyclohexyl)tolan
4-pentyloxy-4'-(trans-4-propylcyclohexyl)tolan
- 10 4-methoxy-4'-(trans-4-methylcyclohexyl)tolan
4-ethoxy-4'-(trans-4-methylcyclohexyl)tolan
4-propyloxy-4'-(trans-4-methylcyclohexyl)tolan
4-butyloxy-4'-(trans-4-methylcyclohexyl)tolan
4-pentyloxy-4'-(trans-4-methylcyclohexyl)tolan
- 15 4-methoxy-4'-(trans-4-ethylcyclohexyl)tolan
4-ethoxy-4'-(trans-4-ethylcyclohexyl)tolan
4-propyloxy-4'-(trans-4-ethylcyclohexyl)tolan
4-butyloxy-4'-(trans-4-ethylcyclohexyl)tolan
4-pentyloxy-4'-(trans-4-ethylcyclohexyl)tolan
- 20 4-methoxy-4'-(trans-4-butylcyclohexyl)tolan
4-ethoxy-4'-(trans-4-butylcyclohexyl)tolan
4-propyloxy-4'-(trans-4-butylcyclohexyl)tolan
4-butyloxy-4'-(trans-4-butylcyclohexyl)tolan
4-pentyloxy-4'-(trans-4-butylcyclohexyl)tolan
- 25 4-methoxy-4'-(trans-4-pentylcyclohexyl)tolan
4-ethoxy-4'-(trans-4-pentylcyclohexyl)tolan
4-propyloxy-4'-(trans-4-pentylcyclohexyl)tolan
4-butyloxy-4'-(trans-4-pentylcyclohexyl)tolan
4-pentyloxy-4'-(trans-4-pentylcyclohexyl)tolan
- 30 4-methoxy-4'-(trans-4-heptylcyclohexyl)tolan
4-ethoxy-4'-(trans-4-heptylcyclohexyl)tolan

4-propyloxy-4'-(trans-4-heptylcyclohexylethyl)tolan
4-butyloxy-4'-(trans-4-heptylcyclohexylethyl)tolan
4-pentyloxy-4'-(trans-4-heptylcyclohexylethyl)tolan

4-methoxy-4'-(trans-4-methylcyclohexylethyl)tolan
5 4-ethoxy-4'-(trans-4-methylcyclohexylethyl)tolan
4-propyloxy-4'-(trans-4-methylcyclohexylethyl)tolan
4-butyloxy-4'-(trans-4-methylcyclohexylethyl)tolan
4-pentyloxy-4'-(trans-4-methylcyclohexylethyl)tolan

4-methoxy-4'-(trans-4-ethylcyclohexylethyl)tolan
10 4-ethoxy-4'-(trans-4-ethylcyclohexylethyl)tolan
4-propyloxy-4'-(trans-4-ethylcyclohexylethyl)tolan
4-butyloxy-4'-(trans-4-ethylcyclohexylethyl)tolan
4-pentyloxy-4'-(trans-4-ethylcyclohexylethyl)tolan

4-methoxy-4'-(trans-4-propylcyclohexylethyl)tolan
15 4-ethoxy-4'-(trans-4-propylcyclohexylethyl)tolan
4-propyloxy-4'-(trans-4-propylcyclohexylethyl)tolan
4-butyloxy-4'-(trans-4-propylcyclohexylethyl)tolan
4-pentyloxy-4'-(trans-4-propylcyclohexylethyl)tolan

4-methoxy-4'-(trans-4-pentylcyclohexylethyl)tolan
20 4-ethoxy-4'-(trans-4-pentylcyclohexylethyl)tolan
4-propyloxy-4'-(trans-4-pentylcyclohexylethyl)tolan
4-butyloxy-4'-(trans-4-pentylcyclohexylethyl)tolan
4-pentyloxy-4'-(trans-4-pentylcyclohexylethyl)tolan

4-methyl-4'-(trans-4-propylcyclohexylethyl)tolan
25 4-ethyl-4'-(trans-4-propylcyclohexylethyl)tolan
4-propyl-4'-(trans-4-propylcyclohexylethyl)tolan
4-butyl-4'-(trans-4-propylcyclohexylethyl)tolan
4-pentyl-4'-(trans-4-propylcyclohexylethyl)tolan

4-methyl-4'-(trans-4-pentylcyclohexylethyl)tolan
30 4-ethyl-4'-(trans-4-pentylcyclohexylethyl)tolan
4-propyl-4'-(trans-4-pentylcyclohexylethyl)tolan
4-butyl-4'-(trans-4-pentylcyclohexylethyl)tolan
4-pentyl-4'-(trans-4-pentylcyclohexylethyl)tolan

- 3,4-difluoro-4'-(-4-methylphenyl)tolan
3,4-difluoro-4'-(4-ethylphenyl)tolan
3,4-difluoro-4'-(4-propylphenyl)tolan
3,4-difluoro-4'-(4-butylphenyl)tolan
5 3,4-difluoro-4'-(4-pentylphenyl)tolan
- 3-fluoro-4-methoxy-4'-(trans-4-propylcyclohexyl)tolan,
m.p. 107°, c.p. 208°
3-fluoro-4-ethoxy-4'-(trans-4-propylcyclohexyl)tolan
3-fluoro-4-propyloxy-4'-(trans-4-propylcyclohexyl)tolan
10 3-fluoro-4-butyloxy-4'-(trans-4-propylcyclohexyl)tolan
3-fluoro-4-pentyloxy-4'-(trans-4-propylcyclohexyl)tolan
- 3-fluoro-4-methoxy-4'-(trans-4-pentylcyclohexyl)tolan
3-fluoro-4-ethoxy-4'-(trans-4-pentylcyclohexyl)tolan
3-fluoro-4-propyloxy-4'-(trans-4-pentylcyclohexyl)tolan
15 3-fluoro-4-butyloxy-4'-(trans-4-pentylcyclohexyl)tolan
3-fluoro-4-pentyloxy-4'-(trans-4-pentylcyclohexyl)tolan
- 4-methyl-4'-(4-propylphenylethyl)tolan
4-ethyl-4'-(4-propylphenylethyl)tolan
4-propyl-4'-(4-propylphenylethyl)tolan
20 4-butyl-4'-(4-propylphenylethyl)tolan
4-pentyl-4'-(4-propylphenylethyl)tolan
- 4-methyl-4'-(4-butylphenylethyl)tolan
4-ethyl-4'-(4-butylphenylethyl)tolan
4-propyl-4'-(4-butylphenylethyl)tolan
25 4-butyl-4'-(4-butylphenylethyl)tolan
4-pentyl-4'-(4-butylphenylethyl)tolan
- 4-methyl-4'-(4-ethylphenylethyl)tolan
4-ethyl-4'-(4-ethylphenylethyl)tolan
4-propyl-4'-(4-ethylphenylethyl)tolan
30 4-butyl-4'-(4-ethylphenylethyl)tolan
4-pentyl-4'-(4-ethylphenylethyl)tolan
- 4-methyl-4'-(4-pentylphenylethyl)tolan
4-ethyl-4'-(4-pentylphenylethyl)tolan

- 4-propyl-4'-(4-pentylphenylethyl)tolan
4-butyl-4'-(4-pentylphenylethyl)tolan
4-pentyl-4'-(4-pentylphenylethyl)tolan
- 4-fluoro-4'-(4-ethoxyphenyl)tolan
5 4-fluoro-4'-(4-propyloxyphenyl)tolan
4-fluoro-4'-(4-butyloxyphenyl)tolan
4-fluoro-4'-(4-pentyloxyphenyl)tolan
- 4-chloro-4'-(4-methoxyphenyl)tolan
4-chloro-4'-(4-ethoxyphenyl)tolan
10 4-chloro-4'-(4-propyloxyphenyl)tolan
4-chloro-4'-(4-butyloxyphenyl)tolan
4-chloro-4'-(4-pentyloxyphenyl)tolan
- 4-methoxy-3'-fluoro-4'-(4-ethylphenyl)tolan
4-methoxy-3'-fluoro-4'-(4-propylphenyl)tolan
15 4-methoxy-3'-fluoro-4'-(4-butylphenyl)tolan
4-methoxy-3'-fluoro-4'-(4-pentylphenyl)tolan
4-methoxy-3'-fluoro-4'-(4-hexylphenyl)tolan
4-methoxy-3'-fluoro-4'-(4-heptylphenyl)tolan
- 4-ethoxy-3'-fluoro-4'-(4-ethylphenyl)tolan
20 4-ethoxy-3'-fluoro-4'-(4-propylphenyl)tolan
4-ethoxy-3'-fluoro-4'-(4-butylphenyl)tolan, m.p. = 88°,
c.p. = 208°
4-ethoxy-3'-fluoro-4'-(4-pentylphenyl)tolan
4-ethoxy-3'-fluoro-4'-(4-hexylphenyl)tolan
25 4-ethoxy-3'-fluoro-4'-(4-heptylphenyl)tolan
- 4-propoxy-3'-fluoro-4'-(4-ethylphenyl)tolan
4-propoxy-3'-fluoro-4'-(4-propylphenyl)tolan
4-propoxy-3'-fluoro-4'-(4-butylphenyl)tolan
4-propoxy-3'-fluoro-4'-(4-pentylphenyl)tolan
30 4-propoxy-3'-fluoro-4'-(4-hexylphenyl)tolan
4-propoxy-3'-fluoro-4'-(4-heptylphenyl)tolan
- 4-butoxy-3'-fluoro-4'-(4-ethylphenyl)tolan
4-butoxy-3'-fluoro-4'-(4-propylphenyl)tolan

- 4-butoxy-3'-fluoro-4'-(4-butylphenyl)tolan
4-butoxy-3'-fluoro-4'-(4-pentylphenyl)tolan
4-butoxy-3'-fluoro-4'-(4-hexylphenyl)tolan
4-butoxy-3'-fluoro-4'-(4-heptylphenyl)tolan
- 5 4-pentyloxy-3'-fluoro-4'-(4-ethylphenyl)tolan
4-pentyloxy-3'-fluoro-4'-(4-propylphenyl)tolan
4-pentyloxy-3'-fluoro-4'-(4-butylphenyl)tolan
4-pentyloxy-3'-fluoro-4'-(4-pentylphenyl)tolan
4-pentyloxy-3'-fluoro-4'-(4-hexylphenyl)tolan
10 4-pentyloxy-3'-fluoro-4'-(4-heptylphenyl)tolan
- 4-(4-methoxyphenyl)-4'-(trans-4-methylcyclohexyl)tolan
4-(4-ethoxyphenyl)-4'-(trans-4-methylcyclohexyl)tolan
4-(4-propyloxyphenyl)-4'-(trans-4-methylcyclohexyl)tolan
4-(4-butyloxyphenyl)-4'-(trans-4-methylcyclohexyl)tolan
15 4-(4-pentyloxyphenyl)-4'-(trans-4-methylcyclohexyl)tolan
- 4-(4-methoxyphenyl)-4'-(trans-4-ethylcyclohexyl)tolan
4-(4-ethoxyphenyl)-4'-(trans-4-ethylcyclohexyl)tolan
4-(4-propyloxyphenyl)-4'-(trans-4-ethylcyclohexyl)tolan
4-(4-butyloxyphenyl)-4'-(trans-4-ethylcyclohexyl)tolan
20 4-(4-pentyloxyphenyl)-4'-(trans-4-ethylcyclohexyl)tolan
- 4-(4-methoxyphenyl)-4'-(trans-4-propylcyclohexyl)tolan
4-(4-ethoxyphenyl)-4'-(trans-4-propylcyclohexyl)tolan
4-(4-propyloxyphenyl)-4'-(trans-4-propylcyclohexyl)tolan
4-(4-butyloxyphenyl)-4'-(trans-4-propylcyclohexyl)tolan
25 4-(4-pentyloxyphenyl)-4'-(trans-4-propylcyclohexyl)tolan
- 4-(4-methoxyphenyl)-4'-(trans-4-butylcyclohexyl)tolan
4-(4-ethoxyphenyl)-4'-(trans-4-butylcyclohexyl)tolan
4-(4-propyloxyphenyl)-4'-(trans-4-butylcyclohexyl)tolan
4-(4-butyloxyphenyl)-4'-(trans-4-butylcyclohexyl)tolan
30 4-(4-pentyloxyphenyl)-4'-(trans-4-butylcyclohexyl)tolan

Example 2

The corresponding 4-fluoro-4'-heptyloxytolan having m.p. 63° and c.p. 52.3° is obtained, analogously

to Example 1, from 4-heptyloxyphenylacetylene and 4-fluoro-iodobenzene.

The following are prepared analogously:

- 4-fluoro-4'-ethoxytolan
- 5 4-fluoro-4'-propyloxytolan
- 4-fluoro-4'-butyloxytolan
- 4-fluoro-4'-pentyloxytolan

- 4-methyl-4'-methoxymethoxytolan
- 4-ethyl-4'-methoxymethoxytolan
- 10 4-propyl-4'-methoxymethoxytolan
- 4-butyl-4'-methoxymethoxytolan
- 4-pentyl-4'-methoxymethoxytolan
- 4-hexyl-4'-methoxymethoxytolan
- 4-heptyl-4'-methoxymethoxytolan

- 15 4-methyl-4'-(2-methoxyethoxy)tolan
- 4-ethyl-4'-(2-methoxyethoxy)tolan
- 4-propyl-4'-(2-methoxyethoxy)tolan
- 4-butyl-4'-(2-methoxyethoxy)tolan
- 4-pentyl-4'-(2-methoxyethoxy)tolan
- 20 4-hexyl-4'-(2-methoxyethoxy)tolan
- 4-heptyl-4'-(2-methoxyethoxy)tolan

- 4-methyl-4'-ethoxymethoxytolan
- 4-ethyl-4'-ethoxymethoxytolan
- 4-propyl-4'-ethoxymethoxytolan
- 25 4-butyl-4'-ethoxymethoxytolan
- 4-pentyl-4'-ethoxymethoxytolan
- 4-hexyl-4'-ethoxymethoxytolan
- 4-heptyl-4'-ethoxymethoxytolan

- 4-methyl-4'-(2-ethoxyethoxy)tolan
- 30 4-ethyl-4'-(2-ethoxyethoxy)tolan
- 4-propyl-4'-(2-ethoxyethoxy)tolan
- 4-butyl-4'-(2-ethoxyethoxy)tolan
- 4-pentyl-4'-(2-ethoxyethoxy)tolan
- 4-hexyl-4'-(2-ethoxyethoxy)tolan

4-heptyl-4'-(2-ethoxyethoxy)tolan

4-methyl-4'-propyloxymethoxytolan

4-ethyl-4'-propyloxymethoxytolan

4-propyl-4'-propyloxymethoxytolan

5 4-butyl-4'-propyloxymethoxytolan

4-pentyl-4'-propyloxymethoxytolan

4-hexyl-4'-propyloxymethoxytolan

4-heptyl-4'-propyloxymethoxytolan

4-methyl-4'-(2-propyloxyethoxy)tolan

10 4-ethyl-4'-(2-propyloxyethoxy)tolan

4-propyl-4'-(2-propyloxyethoxy)tolan

4-butyl-4'-(2-propyloxyethoxy)tolan

4-pentyl-4'-(2-propyloxyethoxy)tolan

4-hexyl-4'-(2-propyloxyethoxy)tolan

15 4-heptyl-4'-(2-propyloxyethoxy)tolan

4-fluoro-4'-methoxymethoxytolan

4-fluoro-4'-(2-methoxyethoxy)tolan

4-chloro-4'-propyloxymethoxytolan

4-chloro-4'-(2-methoxyethoxy)tolan

20 4-fluoro-4'-(2-ethoxyethoxy)tolan

4-fluoro-4'-(2-propyloxyethoxy)tolan

Example 3

- a) n-Butyllithium (0.105 mol) is added to a mixture of 0.1 mol of 2,3-difluoroethoxybenzene, 0.1 mol of
- 25 tetramethylethylenediamine (TMEDA) and 200 ml of THF at -70° to -60°, and the mixture is stirred for about 4 hours at -70°. 0.1 mol of 4-(trans-4-propylcyclohexyl)-acetophenone is then added to the reaction mixture at this temperature. The mixture is then allowed to come to
- 30 room temperature and is hydrolysed with saturated NH₄Cl solution. The organic phase is separated off and worked up. The residue is heated with 2 g of p-toluenesulfonic acid and 200 ml of toluene on a water separator. Working up and recrystallization give 1-(2,3-difluoro-4-ethoxy-

phenyl)-1-[4-(trans-4-propylcyclohexyl)phenyl]ethylene.

b) 0.065 mol of bromine is added at 0° to a solution of 0.065 mol of the ethylene derivative prepared in a) in 100 ml of CH₂Cl₂ and 50 ml of acetonitrile. 10 g of
5 triethylamine are then added and the mixture is worked up in the customary manner.

The residue is taken up in about 50 ml of THF and added at -50° to a solution, prepared at -30°, of lithium diisopropylamide in THF (120 ml THF, 0.13 mol of diisopropylamine and 0.13 mol of n-butyllithium). The reaction
10 mixture is stirred overnight, slowly rising to room temperature. It is then hydrolysed with H₂O, and the organic phase is worked up and recrystallized from acetone/ethanol to give 2,3-difluoro-4-ethoxy-4'-(trans-
15 4-propylcyclohexyl)tolan having m.p. = 87° and c.p. = 231°.

The following are prepared analogously:

2,3-difluoro-4-ethoxy-4'-(trans-4-methylcyclohexyl)tolan
2,3-difluoro-4-ethoxy-4'-(trans-4-ethylcyclohexyl)tolan
20 2,3-difluoro-4-ethoxy-4'-(trans-4-butylcyclohexyl)tolan
2,3-difluoro-4-ethoxy-4'-(trans-4-pentylcyclohexyl)tolan
2,3-difluoro-4-ethoxy-4'-(trans-4-hexylcyclohexyl)tolan
2,3-difluoro-4-ethoxy-4'-(trans-4-heptylcyclohexyl)tolan

2,3-difluoro-4-methoxy-4'-(trans-4-methylcyclohexyl)tolan
25 2,3-difluoro-4-methoxy-4'-(trans-4-ethylcyclohexyl)tolan
2,3-difluoro-4-methoxy-4'-(trans-4-propylcyclohexyl)tolan
2,3-difluoro-4-methoxy-4'-(trans-4-butylcyclohexyl)tolan
2,3-difluoro-4-methoxy-4'-(trans-4-pentylcyclohexyl)tolan
2,3-difluoro-4-methoxy-4'-(trans-4-hexylcyclohexyl)tolan
30 2,3-difluoro-4-methoxy-4'-(trans-4-heptylcyclohexyl)tolan

2,3-difluoro-4-propoxy-4'-(trans-4-methylcyclohexyl)tolan
2,3-difluoro-4-propoxy-4'-(trans-4-ethylcyclohexyl)tolan
2,3-difluoro-4-propoxy-4'-(trans-4-propylcyclohexyl)tolan
2,3-difluoro-4-propoxy-4'-(trans-4-butylcyclohexyl)tolan
35 2,3-difluoro-4-propoxy-4'-(trans-4-pentylcyclohexyl)tolan
2,3-difluoro-4-propoxy-4'-(trans-4-hexylcyclohexyl)tolan

- 2,3-difluoro-4-propoxy-4'-(trans-4-heptylcyclohexyl)tolan
- 2,3-difluoro-4-butoxy-4'-(trans-4-methylcyclohexyl)tolan
2,3-difluoro-4-butoxy-4'-(trans-4-ethylcyclohexyl)tolan
2,3-difluoro-4-butoxy-4'-(trans-4-propylcyclohexyl)tolan
5 2,3-difluoro-4-butoxy-4'-(trans-4-butylcyclohexyl)tolan
2,3-difluoro-4-butoxy-4'-(trans-4-pentylcyclohexyl)tolan
2,3-difluoro-4-butoxy-4'-(trans-4-hexylcyclohexyl)tolan
2,3-difluoro-4-butoxy-4'-(trans-4-heptylcyclohexyl)tolan
- 2,3-difluoro-4-pentyloxy-4'-(trans-4-methylcyclohexyl)-
10 tolan
2,3-difluoro-4-pentyloxy-4'-(trans-4-ethylcyclohexyl)-
tolan
2,3-difluoro-4-pentyloxy-4'-(trans-4-propylcyclohexyl)-
tolan
15 2,3-difluoro-4-pentyloxy-4'-(trans-4-butylcyclohexyl)-
tolan
2,3-difluoro-4-pentyloxy-4'-(trans-4-pentylcyclohexyl)-
tolan
2,3-difluoro-4-pentyloxy-4'-(trans-4-hexylcyclohexyl)-
20 tolan
2,3-difluoro-4-pentyloxy-4'-(trans-4-heptylcyclohexyl)-
tolan
- 2,3-difluoro-4-pentyloxy-4'-(4-methylphenyl)tolan
2,3-difluoro-4-pentyloxy-4'-(4-ethylphenyl)tolan
25 2,3-difluoro-4-pentyloxy-4'-(4-propylphenyl)tolan
2,3-difluoro-4-pentyloxy-4'-(4-butylphenyl)tolan
2,3-difluoro-4-pentyloxy-4'-(4-pentylphenyl)tolan
2,3-difluoro-4-pentyloxy-4'-(4-hexylphenyl)tolan
2,3-difluoro-4-pentyloxy-4'-(4-heptylphenyl)tolan
- 30 2,3-difluoro-4-butoxy-4'-(4-methylphenyl)tolan
2,3-difluoro-4-butoxy-4'-(4-ethylphenyl)tolan
2,3-difluoro-4-butoxy-4'-(4-propylphenyl)tolan
2,3-difluoro-4-butoxy-4'-(4-butylphenyl)tolan
2,3-difluoro-4-butoxy-4'-(4-pentylphenyl)tolan
35 2,3-difluoro-4-butoxy-4'-(4-hexylphenyl)tolan

- 2,3-difluoro-4-butoxy-4'-(4-heptylphenyl)tolan
- 2,3-difluoro-4-propoxy-4'-(4-methylphenyl)tolan
2,3-difluoro-4-propoxy-4'-(4-ethylphenyl)tolan
2,3-difluoro-4-propoxy-4'-(4-propylphenyl)tolan
5 2,3-difluoro-4-propoxy-4'-(4-butylphenyl)tolan
2,3-difluoro-4-propoxy-4'-(4-pentylphenyl)tolan
2,3-difluoro-4-propoxy-4'-(4-hexylphenyl)tolan
2,3-difluoro-4-propoxy-4'-(4-heptylphenyl)tolan
- 2,3-difluoro-4-ethoxy-4'-(4-methylphenyl)tolan
10 2,3-difluoro-4-ethoxy-4'-(4-ethylphenyl)tolan
2,3-difluoro-4-ethoxy-4'-(4-propylphenyl)tolan
2,3-difluoro-4-ethoxy-4'-(4-butylphenyl)tolan
2,3-difluoro-4-ethoxy-4'-(4-pentylphenyl)tolan
2,3-difluoro-4-ethoxy-4'-(4-hexylphenyl)tolan
15 2,3-difluoro-4-ethoxy-4'-(4-heptylphenyl)tolan
- 2,3-difluoro-4-methoxy-4'-(4-methylphenyl)tolan
2,3-difluoro-4-methoxy-4'-(4-ethylphenyl)tolan
2,3-difluoro-4-methoxy-4'-(4-propylphenyl)tolan
2,3-difluoro-4-methoxy-4'-(4-butylphenyl)tolan
20 2,3-difluoro-4-methoxy-4'-(4-pentylphenyl)tolan
2,3-difluoro-4-methoxy-4'-(4-hexylphenyl)tolan
2,3-difluoro-4-methoxy-4'-(4-heptylphenyl)tolan
- 2,3-difluoro-4-(4-methylphenyl)-4'-methyltolan
2,3-difluoro-4-(4-ethylphenyl)-4'-methyltolan
25 2,3-difluoro-4-(4-propylphenyl)-4'-methyltolan
2,3-difluoro-4-(4-butylphenyl)-4'-methyltolan
2,3-difluoro-4-(4-pentylphenyl)-4'-methyltolan
- 2,3-difluoro-4-(4-methylphenyl)-4'-ethyltolan
2,3-difluoro-4-(4-ethylphenyl)-4'-ethyltolan
30 2,3-difluoro-4-(4-propylphenyl)-4'-ethyltolan
2,3-difluoro-4-(4-butylphenyl)-4'-ethyltolan
2,3-difluoro-4-(4-pentylphenyl)-4'-ethyltolan
- 2,3-difluoro-4-(4-methylphenyl)-4'-propyltolan

- 2,3-difluoro-4-(4-ethylphenyl)-4'-propyltolan
2,3-difluoro-4-(4-propylphenyl)-4'-propyltolan
2,3-difluoro-4-(4-butylphenyl)-4'-propyltolan
2,3-difluoro-4-(4-pentylphenyl)-4'-propyltolan
- 5 2,3-difluoro-4-(4-methylphenyl)-4'-butyltolan
2,3-difluoro-4-(4-ethylphenyl)-4'-butyltolan
2,3-difluoro-4-(4-propylphenyl)-4'-butyltolan
2,3-difluoro-4-(4-butylphenyl)-4'-butyltolan
2,3-difluoro-4-(4-pentylphenyl)-4'-butyltolan
- 10 2,3-difluoro-4-(4-methylphenyl)-4'-pentyltolan
2,3-difluoro-4-(4-ethylphenyl)-4'-pentyltolan
2,3-difluoro-4-(4-propylphenyl)-4'-pentyltolan
2,3-difluoro-4-(4-butylphenyl)-4'-pentyltolan
2,3-difluoro-4-(4-pentylphenyl)-4'-pentyltolan
- 15 2,3-difluoro-4-(4-methylphenyl)-4'-fluorotolan
2,3-difluoro-4-(4-ethylphenyl)-4'-fluorotolan
2,3-difluoro-4-(4-propylphenyl)-4'-fluorotolan
2,3-difluoro-4-(4-butylphenyl)-4'-fluorotolan
2,3-difluoro-4-(4-pentylphenyl)-4'-fluorotolan
- 20 Example 4
a) 1-(4-Pentylphenyl)-1-(2,3-difluoro-4-ethoxyphenyl)-ethylene is obtained, analogously to Example 3a, from 0.1 mol of 2,3-difluoroethoxybenzene and 0.1 mol of 4-pentylacetophenone.
- 25 b) 2,3-Difluoro-4-ethoxy-4'-pentyltolan having m.p. = 57° and c.p. = 61° is obtained, analogously to Example 3b, from 1-(4-pentylphenyl)-1-(2,3-difluoro-4-ethoxyphenyl)ethylene after recrystallization from methanol/ethanol.
- 30 The following are prepared analogously:
- 2,3-difluoro-4-ethoxy-4'-methyltolan
2,3-difluoro-4-ethoxy-4'-ethyltolan
2,3-difluoro-4-ethoxy-4'-propyltolan
2,3-difluoro-4-ethoxy-4'-butyltolan

2,3-difluoro-4-ethoxy-4'-hexyltolan
2,3-difluoro-4-ethoxy-4'-heptyltolan

2,3-difluoro-4-methoxy-4'-methyltolan
2,3-difluoro-4-methoxy-4'-ethyltolan
5 2,3-difluoro-4-methoxy-4'-propyltolan
2,3-difluoro-4-methoxy-4'-butyltolan
2,3-difluoro-4-methoxy-4'-pentyltolan
2,3-difluoro-4-methoxy-4'-hexyltolan
2,3-difluoro-4-methoxy-4'-heptyltolan

10 2,3-difluoro-4-propoxy-4'-methyltolan
2,3-difluoro-4-propoxy-4'-ethyltolan
2,3-difluoro-4-propoxy-4'-propyltolan
2,3-difluoro-4-propoxy-4'-butyltolan
2,3-difluoro-4-propoxy-4'-pentyltolan
15 2,3-difluoro-4-propoxy-4'-hexyltolan
2,3-difluoro-4-propoxy-4'-heptyltolan

2,3-difluoro-4-butoxy-4'-methyltolan
2,3-difluoro-4-butoxy-4'-ethyltolan
2,3-difluoro-4-butoxy-4'-propyltolan
20 2,3-difluoro-4-butoxy-4'-butyltolan
2,3-difluoro-4-butoxy-4'-pentyltolan
2,3-difluoro-4-butoxy-4'-hexyltolan
2,3-difluoro-4-butoxy-4'-heptyltolan

2,3-difluoro-4-pentyloxy-4'-methyltolan
25 2,3-difluoro-4-pentyloxy-4'-ethyltolan
2,3-difluoro-4-pentyloxy-4'-propyltolan
2,3-difluoro-4-pentyloxy-4'-butyltolan
2,3-difluoro-4-pentyloxy-4'-pentyltolan
2,3-difluoro-4-pentyloxy-4'-hexyltolan
30 2,3-difluoro-4-pentyloxy-4'-heptyltolan

2,3-difluoro-4-hexyloxy-4'-methyltolan
2,3-difluoro-4-hexyloxy-4'-ethyltolan
2,3-difluoro-4-hexyloxy-4'-propyltolan
2,3-difluoro-4-hexyloxy-4'-butyltolan

2,3-difluoro-4-hexyloxy-4'-pentyltolan
2,3-difluoro-4-hexyloxy-4'-hexyltolan
2,3-difluoro-4-hexyloxy-4'-heptyltolan

2,3-difluoro-4-ethyl-4'-methoxytolan
5 2,3-difluoro-4-propyl-4'-methoxytolan
2,3-difluoro-4-butyl-4'-methoxytolan
2,3-difluoro-4-pentyl-4'-methoxytolan

2,3-difluoro-4-ethyl-4'-ethoxytolan
2,3-difluoro-4-propyl-4'-ethoxytolan
10 2,3-difluoro-4-butyl-4'-ethoxytolan
2,3-difluoro-4-pentyl-4'-ethoxytolan

2,3-difluoro-4-ethyl-4'-propoxytolan
2,3-difluoro-4-propyl-4'-propoxytolan
2,3-difluoro-4-butyl-4'-propoxytolan
15 2,3-difluoro-4-pentyl-4'-propoxytolan

2,3-difluoro-4-ethyl-4'-butoxytolan
2,3-difluoro-4-propyl-4'-butoxytolan
2,3-difluoro-4-butyl-4'-butoxytolan
2,3-difluoro-4-pentyl-4'-butoxytolan

20 2,3-difluoro-4-ethyl-4'-pentoxytolan
2,3-difluoro-4-propyl-4'-pentoxytolan
2,3-difluoro-4-butyl-4'-penthoxytolan [sic]
2,3-difluoro-4-pentyl-4'-pentoxytolan

2,3-difluoro-4-(trans-4-ethylcyclohexylethylene)-4'-
25 ethyltolan
2,3-difluoro-4-(trans-4-propylcyclohexylethylene)-4'-
ethyltolan
2,3-difluoro-4-(trans-4-butylcyclohexylethylene)-4'-
ethyltolan
30 2,3-difluoro-4-(trans-4-pentylcyclohexylethylene)-4'-
ethyltolan

- 2,3-difluoro-4-(trans-4-ethylcyclohexylethylene)-4'-propyltolan
2,3-difluoro-4-(trans-4-propylcyclohexylethylene)-4'-propyltolan
5 2,3-difluoro-4-(trans-4-butylcyclohexylethylene)-4'-propyltolan
2,3-difluoro-4-(trans-4-pentylcyclohexylethylene)-4'-propyltolan

2,3-difluoro-4-(trans-4-ethylcyclohexylethylene)-4'-butyltolan
10 2,3-difluoro-4-(trans-4-propylcyclohexylethylene)-4'-butyltolan
2,3-difluoro-4-(trans-4-butylcyclohexylethylene)-4'-butyltolan
15 2,3-difluoro-4-(trans-4-pentylcyclohexylethylene)-4'-butyltolan

2,3-difluoro-4-(trans-4-ethylcyclohexylethylene)-4'-pentyltolan
2,3-difluoro-4-(trans-4-propylcyclohexylethylene)-4'-pentyltolan
20 2,3-difluoro-4-(trans-4-butylcyclohexylethylene)-4'-pentyltolan
2,3-difluoro-4-(trans-4-pentylcyclohexylethylene)-4'-pentyltolan

25 2,3-difluoro-4-(trans-4-ethylcyclohexylethylene)-4'-fluorotolan
2,3-difluoro-4-(trans-4-propylcyclohexylethylene)-4'-fluorotolan
2,3-difluoro-4-(trans-4-butylcyclohexylethylene)-4'-fluorotolan
30 2,3-difluoro-4-(trans-4-pentylcyclohexylethylene)-4'-fluorotolan

2,3-difluoro-4-(trans-4-ethylcyclohexylethylene)-4'-trifluoromethyltolan

- 2,3-difluoro-4-(trans-4-propylcyclohexylethylene)-4'-trifluoromethyltolan
2,3-difluoro-4-(trans-4-butylcyclohexylethylene)-4'-trifluoromethyltolan
5 2,3-difluoro-4-(trans-4-pentylcyclohexylethylene)-4'-trifluoromethyltolan

Example 5

A mixture of 0.02 mol of 4-(trans-4-propylcyclohexyl)phenylacetylene, 0.02 mol of 4-trifluoromethoxy-
10 iodobenzene and 50 ml of triethylamine is admixed at room temperature with 0.4 mmol of bis(triphenylphosphine)-palladium(II) chloride and 0.2 mmol of CuI. The reaction mixture is stirred for 2 hours at room temperature and then diluted with 100 ml of methyl tert-butyl ether,
15 filtration is carried out with suction and the solution is concentrated by evaporation. Purification by chromatography and/or crystallization gives 4-trifluoromethoxy-4'-(trans-4-propylcyclohexyl)tolan having a c.p. of 88°; S_b 126° S_a 163° N 198° I.

20 The following are prepared analogously:

- 4-trifluoromethoxy-4'-(trans-4-ethylcyclohexyl)tolan
4-trifluoromethoxy-4'-(trans-4-butylcyclohexyl)tolan
4-trifluoromethoxy-4'-(trans-4-pentylcyclohexyl)tolan
4-trifluoromethoxy-4'-(trans-4-hexylcyclohexyl)tolan
25 4-trifluoromethoxy-4'-(trans-4-heptylcyclohexyl)tolan
4-trifluoromethoxy-4'-(trans-4-octylcyclohexyl)tolan

- 4-trifluoromethoxy-4'-ethyltolan
4-trifluoromethoxy-4'-propyltolan
4-trifluoromethoxy-4'-butyltolan
30 4-trifluoromethoxy-4'-pentyltolan
4-trifluoromethoxy-4'-hexyltolan
4-trifluoromethoxy-4'-heptyltolan
4-trifluoromethoxy-4'-octyltolan
4-trifluoromethoxy-4'-ethoxytolan
35 4-trifluoromethoxy-4'-propoxytolan
4-trifluoromethoxy-4'-butoxytolan

- 4-trifluoromethoxy-4'-(trans-4-propylcyclohexylethyl)-tolan
 4-trifluoromethoxy-4'-(trans-4-butylcyclohexylethyl)tolan
 4-trifluoromethoxy-4'-(trans-4-pentylcyclohexylethyl)-
 5 tolan
 4-trifluoromethoxy-4'-(trans-4-hexylcyclohexylethyl)tolan
 4-trifluoromethoxy-4'-(trans-4-heptylcyclohexylethyl)-tolan
 4-trifluoromethoxy-4'-(trans-4-octylcyclohexylethyl)tolan
- 10 1-(4-trifluoromethoxyphenyl)-2-[2,3-difluoro-4-(4-ethyl-phenyl)phenyl]ethyne
 1-(4-trifluoromethoxyphenyl)-2-[2,3-difluoro-4-(4-propyl-phenyl)phenyl]ethyne
 1-(4-trifluoromethoxyphenyl)-2-[2,3-difluoro-4-(4-butyl-phenyl)phenyl]ethyne
 15 1-(4-trifluoromethoxyphenyl)-2-[2,3-difluoro-4-(4-pentyl-phenyl)phenyl]ethyne
 1-(4-trifluoromethoxyphenyl)-2-[2,3-difluoro-4-(4-hexyl-phenyl)phenyl]ethyne
 20 1-(4-trifluoromethoxyphenyl)-2-[2,3-difluoro-4-(4-ethoxy-phenyl)phenyl]ethyne
 1-(4-trifluoromethoxyphenyl)-2-[2,3-difluoro-4-(4-propoxyphenyl)phenyl]ethyne
 1-(4-trifluoromethoxyphenyl)-2-[2,3-difluoro-4-(4-butoxy-phenyl)phenyl]ethyne
 25 1-(4-trifluoromethoxyphenyl)-2-[2,3-difluoro-4-(4-pentyl-oxyphenyl)phenyl]ethyne.

Example A

- A liquid-crystalline phase, consisting of
- 30 20 % of p-trans-4-pentylcyclohexylbenzonitrile,
 18 % of p-trans-4-propylcyclohexylbenzonitrile,
 20 % of trans-1-p-ethoxyphenyl-4-propylcyclohexane,
 18 % of trans-1-p-butoxyphenyl-4-propylcyclohexane,
 8 % of 4-methoxy-4'-(trans-4-propylcyclohexyl)tolan,
 35 8 % of 4-ethoxy-4'-(trans-4-propylcyclohexyl)tolan and
 8 % of 4-propyloxy-4-(trans-4-propylcyclohexyl)tolan
 has a clear point of +85° and $\Delta n = +0.154$.

Example B

A liquid-crystalline phase, consisting of
10 % of 4-ethyl-4'-cyanobiphenyl,
10 % of 4-propyl-4'-cyanobiphenyl,
5 10 % of 4-butyl-4'-cyanobiphenyl,
15 % of 4-pentyl-4'-cyanobiphenyl,
15 % of 4-hexyl-4'-cyanobiphenyl,
16 % of trans-1-p-methoxyphenyl-4-propylcyclohexane,
8 % of 4-methoxy-4'-(trans-4-propylcyclohexyl)tolan,
10 8 % of 4-ethoxy-4'-(trans-4-propylcyclohexyl)tolan, and
8 % of 4-propyloxy-4'-(trans-4-propylcyclohexyl)tolan
has a clear point of +72° and $\Delta n = +0.212$.

Example C

A liquid-crystalline phase, consisting of
15 10 % of p-trans-4-propylcyclohexylbenzonitrile,
18 % of trans-1-p-methoxyphenyl-4-propylcyclohexane,
15 % of trans-1-p-ethoxyphenyl-4-propylcyclohexane,
8 % of 4-fluoro-4'-heptyloxytolan,
4 % of 4-methoxy-4'-(trans-4-propylcyclohexyl)tolan,
20 3 % of 4-ethoxy-4'-(trans-4-propylcyclohexyl)tolan,
5 % of 4-propyloxy-4'-(trans-4-propylcyclohexyl)tolan,
12 % of 4-ethyl-4'-(trans-4-propylcyclohexyl)biphenyl,
12 % of 4-ethyl-4'-(trans-4-pentylcyclohexyl)biphenyl,
4 % of 4,4'-bis(trans-4-propylcyclohexyl)biphenyl,
25 5 % of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propyl-
cyclohexyl)biphenyl and
4 % of 4,4'-bis(trans-4-pentylcyclohexyl)biphenyl
has a clear point of +110° and $\Delta n = +0.160$.

Example D

30 A liquid-crystalline phase consisting of
13 % of r-1-cyano-cis-4-(trans-4-propylcyclohexyl)-1-
propylcyclohexane,
21 % of trans-1-p-methoxyphenyl-4-propylcyclohexane,
24 % of 1-(trans-4-propylcyclohexyl)-2-(4'-ethyl-2'-
35 fluorobiphenyl-4-yl)ethane,
4 % of 4,4'-bis(trans-4-propylcyclohexyl)-2-fluorobi-
phenyl,

- 4 % of 4,4'-bis(trans-4-pentylcyclohexyl)-2-fluorobiphenyl,
4 % of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-2-fluorobiphenyl,
5 12 % of 4-pentyl-4-propyltolan,
6 % of 4-(trans-4-propylcyclohexyl)4'-methoxytolan [sic],
5 % of 4-(trans-4-propylcyclohexyl)4'-ethoxytolan [sic] and
10 7 % of 4-(trans-4-propylcyclohexyl)4'-propoxytolan [sic] has a clear point of 101°, an optical anisotropy of 0.15 and a viscosity of 24 mPa.s at 20°.

Example E

- A liquid-crystalline phase consisting of
15 13 % of r-1-cyano-cis-4-(trans-4-propylcyclohexyl)-1-propylcyclohexane,
19 % of 1-(trans-4-propylcyclohexyl)-2-(4'-ethyl-2'-fluorobiphenyl-4-yl)ethane,
19 % of 1-(trans-4-propylcyclohexyl)-2-(4'-pentyl-2'-fluorobiphenyl-4-yl)ethane,
20 16 % of 1-(trans-4-pentylcyclohexyl)-2-(4'-ethyl-2'-fluorobiphenyl-4-yl)ethane,
5 % of 4,4'-bis(trans-4-propylcyclohexyl)-2-fluorobiphenyl,
25 7 % of 4-butyl-4'-ethoxytolan,
7 % of 4-pentyl-4'-methoxytolan,
7 % of 4-pentyl-4'-ethoxytolan and
7 % of 4-(trans-4-propylcyclohexyl)-4'-methoxytolan has a clear point of 99°, an optical anisotropy of 0.17
30 and a viscosity of 29 mPa.s at 20°.

Example F

- A liquid-crystalline phase consisting of
12 % of r-1-cyano-cis-4-(trans-4-propylcyclohexyl)-1-propylcyclohexane,
35 21 % of trans-1-p-methoxyphenyl-4-propylcyclohexane,

- 21 % of 1-(trans-4-propylcyclohexyl)-2-(4'-ethyl-2'-fluorobiphenyl-4-yl)ethane,
6 % of 4,4'-bis(trans-4-propylcyclohexyl)-2-fluorobiphenyl,
5 6 % of 4,4'-bis(trans-4-pentylcyclohexyl)-2-fluorobiphenyl,
6 % of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-2-fluorobiphenyl,
7 % of 4-butyl-4'-ethoxytolan,
10 7 % of 4-pentyl-4'-methoxytolan,
7 % of 4-pentyl-4'-ethoxytolan and
7 % of 4-(trans-4-propylcyclohexyl)-4'-methoxytolan
has a clear point of 98°, an optical anisotropy of 0.16
and a viscosity of 24 mPa.s at 20°.

15 Example G

- A liquid-crystalline phase consisting of
13 % of r-1-cyano-cis-4-(trans-4-propylcyclohexyl)-1-propylcyclohexane,
22 % of trans-1-p-methoxyphenyl-4-propylcyclohexane,
20 26 % of 1-(trans-4-propylcyclohexyl)-2-(4'-ethyl-2'-fluorobiphenyl-4-yl)ethane,
6 % of 4,4'-bis(trans-4-propylcyclohexyl)-2-fluorobiphenyl,
6 % of 4,4'-bis(trans-4-pentylcyclohexyl)-2-fluorobiphenyl,
25 6 % of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-2-fluorobiphenyl,
5 % of 4-butyl-4'-ethoxytolan,
5 % of 4-pentyl-4'-methoxytolan,
30 4 % of 4-pentyl-4'-ethoxytolan and
7 % of 4-(trans-4'-propylcyclohexyl)-4-methoxytolan
has a clear point of 99°, an optical anisotropy of 0.15
and a viscosity of 24 mPa.s at 20°.

Example H

- 35 A liquid-crystalline phase consisting of
3 % of r-1-cyano-cis-4-(trans-4-propylcyclohexyl)-1-propylcyclohexane,

- 20 % of trans-1-p-methoxyphenyl-4-propylcyclohexane,
8 % of trans-1-p-ethoxyphenyl-4-propylcyclohexane,
3% of 2-fluoro-4,4'-bis(trans-4-propylcyclohexyl)-
biphenyl,
5 5 % of 2-fluoro-4-(trans-4-pentylcyclohexyl)-4'-(trans-
4-propylcyclohexyl)biphenyl,
16 % of 4-propyl-4'-butyltolan,
15 % of 4-propyl-4'-pentyltolan,
4 % of 4-methyl-4'-ethoxytolan,
10 5 % of 4-ethyl-4'-methoxytolan,
3 % of 4-(trans-4-propylcyclohexyl)-4'-ethoxytolan and
18 % of 2,3-difluoro-4-ethoxy-4'-(trans-4-propylcyclo-
hexyl)tolan
has a melting point of $< -40^{\circ}$, a clear point of $+80^{\circ}$,
15 $\Delta\epsilon = -0.9$ and $\Delta n = 0.2006$.

Example I

- A liquid-crystalline phase consisting of
20 % of 2,3-difluoro-4-ethoxy-4'-pentyltolan,
20 % of trans-1-p-methoxyphenyl-4-propylcyclohexane,
20 10 % of trans-1-p-ethoxyphenyl-4-propylcyclohexane,
5 % of trans-1-p-butoxyphenyl-4-propylcyclohexane,
4% of 2-fluoro-4,4'-bis(trans-4-propylcyclohexyl)-
biphenyl,
4 % of 2-fluoro-4-(trans-4-pentylcyclohexyl)-4'-
25 (trans-4-propylcyclohexyl)biphenyl,
5 % of 4-propyl-4'-butyltolan,
5 % of 4-propyl-4'-pentyltolan,
5 % of 4-methyl-4'-ethoxytolan,
4 % of 4-ethyl-4'-methoxytolan,
30 6 % of 4-(trans-4-propylcyclohexyl)-4'-methoxytolan,
5 % of 4-(trans-4-propylcyclohexyl)-4'-ethoxytolan and
7 % of 4-(trans-4-propylcyclohexyl)-4'-propoxytolan
has a melting point of $< -40^{\circ}$, a clear point of 85° , $\Delta\epsilon =$
 -1.1 and $\Delta n = 0.2040$.



* C L M S *

Patent Claims

1. Liquid-crystalline phase, characterized in that it contains at least one tolan of the formula I



5 in which

R^1 and R^2 are each, independently of one another, alkyl having up to 15 carbon atoms in which, in addition, one or two non-adjacent CH_2 groups may be replaced by $-O-$, and one of the radicals R^1 and R^2 is alternatively $-OCF_3$,
10 CF_3 , fluorine or chlorine,

A^1 is unsubstituted 1,4-phenylene or trans-1,4-cyclohexylene,

Z^1 is $-CH_2CH_2-$ or a single bond,

m is 0 or 1,

15 and

A^3 and A^4 are each, independently of one another, 1,4-phenylene which is unsubstituted or monosubstituted or polysubstituted by fluorine,

with the provisos that either

20 a) the tolan of the formula I contain a 2,3-difluoro-1,4-phenylene group, or

b) R^1 or R^2 is $-CF_3$ or OCF_3 ,

or that

c) in the case where $m = 0$ and A^3 and $A^4 =$ unsubstituted
25 1,4-phenylene, R^1 is ethoxy, propoxy, butoxy, pentoxy, hexoxy or heptoxy, and R^2 is fluorine, or one of the radicals R^1 and R^2 is an alkyl group in which at least two



CH₂ groups have been replaced by -O-,

d) compounds where $m = 0$ and A³ and/or A⁴ = mono-substituted 1,4-phenylene are excluded,

e) in the case where A³ and A⁴ = unsubstituted 1,4-phenylene, $m = 1$ and Z¹ = a single bond, one of the radicals R¹ and R² is an alkoxy group and the other is then alkyl,

and contains, as the most important further constituents, compounds of the formula V

10 R⁶-L-G-E-R⁷

V

in which L and E are each a carbocyclic or heterocyclic ring system from the group formed by 1,4-disubstituted cyclohexane rings, 4,4-disubstituted phenylcyclohexane and cyclohexylcyclohexane systems, 2,5-disubstituted pyrimidine and 1,3-dioxane rings, 2,6-disubstituted naphthalene, di- and tetrahydronaphthalene, quinazoline and tetrahydroquinazoline,

20	G is	-CH=CH-	-N(O)=N-
		-CH=CY-	-CH=N(O)-
		-C≡C	-CH ₂ -CH ₂ -
		-CO-O-	-CH ₂ -O-
		-CO-S-	-CH ₂ -S-
		-CH=N-	-COO-Phe-COO-

or a C-C single bond,

25 Y is chlorine or -CN, and

R⁶ and R⁷ are alkyl, alkoxy, alkanoyloxy or alkoxy-carbonyloxy having up to 8 carbon atoms, or one of these radicals is alternatively CN, NC, NO₂, CF₃, F, Cl or Br.

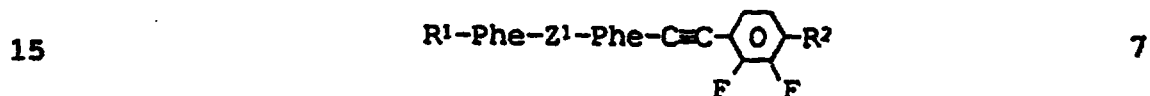
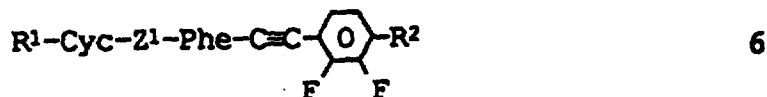


2. Liquid-crystalline phase according to Claim 1, characterized in that it contains compounds selected from the sub-formulae I5, I6, I18 and I22:

	$R^1\text{-Cyc-Phe-C}\equiv\text{C-Phe-R}^2$	I5
5	$R^1\text{-Cyc-Phe-C}\equiv\text{C-PheX-R}^2$	I6
	$R^1\text{-A}^1\text{-CH}_2\text{CH}_2\text{-Phe-C}\equiv\text{C-Phe-R}^2$	I18
	$R^1\text{-A}^1\text{-CH}_2\text{CH}_2\text{-Phe-C}\equiv\text{C-PheX-R}^2$	I22

in which Cyc is trans-1,4-cyclohexylene, Phe is unsubstituted 1,4-phenylene and PheX is 1,4-phenylene
10 which is monosubstituted or polysubstituted by fluorine.

3. Tolans, characterized by the sub-formulae 2, 6 and 7:



in which Cyc is trans-1,4-cyclohexylene and Phe is unsubstituted 1,4-phenylene, R^1 and R^2 are each, independently of one another, alkyl having up to 15
20 adjacent CH_2 groups may be replaced by $-\text{O}-$, and one of the radicals R^1 and R^2 is alternatively $-\text{OCF}_3$, CF_3 , fluorine or chlorine, and Z^1 is $-\text{CH}_2\text{CH}_2-$ or a single bond.

4. Tolans, characterized by the sub-formula 21:



25 in which Cyc is trans-1,4-cyclohexylene, and Phe is



unsubstituted 1,4-phenylene and alkyl and alkoxy each have up to 15 carbon atoms.

5. Tolans, characterized by the sub-formulae Igj and Igk:



in which Cyc is trans-1,4-cyclohexylene, Phe is unsubstituted 1,4-phenylene, and R^1 is alkyl having up to 15 carbon atoms in which, in addition, one or two non-adjacent CH_2 groups may be replaced by $-\text{O}-$.

6. 4-Methoxy-4'-(trans-4-propylcyclohexyl)tolan
4-Ethoxy-4'-(trans-4-propylcyclohexyl)tolan
4-Propyloxy-4'-(trans-4-propylcyclohexyl)tolan

7. 4-Fluoro-4'-ethoxytolan
15 4-Fluoro-4'-propyloxytolan
4-Fluoro-4'-butyloxytolan
4-Fluoro-4'-pentyloxytolan
4-Fluoro-4'-heptyloxytolan

8. 4-Methyl-4'-(2-methoxyethoxy)tolan
20 4-Ethyl-4'-(2-methoxyethoxy)tolan
4-Propyl-4'-(2-methoxyethoxy)tolan
4-Butyl-4'-(2-methoxyethoxy)tolan
4-Pentyl-4'-(2-methoxyethoxy)tolan
4-Hexyl-4'-(2-methoxyethoxy)tolan
25 4-Heptyl-4'-(2-methoxyethoxy)tolan

9. 4-Fluoro-4'-methoxymethoxytolan
4-Fluoro-4'-(2-methoxyethoxy)tolan

10. 2,3-Difluoro-4-ethoxy-4'-(trans-4-methylcyclohexyl)tolan
30 2,3-Difluoro-4-ethoxy-4'-(trans-4-ethylcyclohexyl)tolan
2,3-Difluoro-4-ethoxy-4'-(trans-4-propylcyclohexyl)tolan



2,3-Difluoro-4-ethoxy-4'-(trans-4-butylcyclohexyl)tolan
2,3-Difluoro-4-ethoxy-4'-(trans-4-pentylcyclohexyl)tolan
2,3-Difluoro-4-ethoxy-4'-(trans-4-hexylcyclohexyl)tolan
2,3-Difluoro-4-ethoxy-4'-(trans-4-heptylcyclohexyl)tolan

- 5 11. 2,3-Difluoro-4-ethoxy-4'-methyltolan
2,3-Difluoro-4-ethoxy-4'-ethyltolan
2,3-Difluoro-4-ethoxy-4'-propyltolan
2,3-Difluoro-4-ethoxy-4'-butyltolan
2,3-Difluoro-4-ethoxy-4'-pentyltolan
10 2,3-Difluoro-4-ethoxy-4'-hexyltolan
2,3-Difluoro-4-ethoxy-4'-heptyltolan
12. 4-Trifluoromethoxy-4'-(trans-4-ethylcyclohexyl)tolan
4-Trifluoromethoxy-4'-(trans-4-propylcyclohexyl)tolan
15 4-Trifluoromethoxy-4'-(trans-4-butylcyclohexyl)tolan
4-Trifluoromethoxy-4'-(trans-4-pentylcyclohexyl)tolan
4-Trifluoromethoxy-4'-(trans-4-hexylcyclohexyl)tolan
4-Trifluoromethoxy-4'-(trans-4-heptylcyclohexyl)tolan
4-Trifluoromethoxy-4'-(trans-4-octylcyclohexyl)tolan
- 20 4-Trifluoromethoxy-4'-ethyltolan
4-Trifluoromethoxy-4'-propyltolan
4-Trifluoromethoxy-4'-butyltolan
4-Trifluoromethoxy-4'-pentyltolan
4-Trifluoromethoxy-4'-hexyltolan
25 4-Trifluoromethoxy-4'-heptyltolan
4-Trifluoromethoxy-4'-octyltolan
4-Trifluoromethoxy-4'-ethoxytolan
4-Trifluoromethoxy-4'-propoxytolan
4-Trifluoromethoxy-4'-butoxytolan
30 4-Trifluoromethoxy-4'-pentyloxytolan
4-Trifluoromethoxy-4'-hexyloxytolan
4-Trifluoromethoxy-4'-heptyloxytolan
4-Trifluoromethoxy-4'-octyloxytolan

13. Liquid-crystalline phase having at least two
35 liquid-crystalline components, characterized in that it



contains at least one compound according to one of Claims 3 to 12.

14. Use of the compounds according to one of Claims 3 to 12 as components of liquid-crystalline phases.

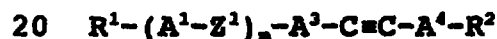
5 15. Use of compounds according to one of Claims 3 to 12 as components of liquid-crystalline phases for electro-optical display elements based on the ECB effect.

10 16. Liquid-crystalline phase for electro-optical display elements based on the ECB effect, having at least two liquid-crystalline components, characterized in that it contains at least one compound according to one of Claims 3 to 12.

15 17. Electro-optical display element, characterized in that it contains, as liquid-crystalline dielectric, a liquid-crystalline phase according to Claim 1, 2 or 13.

18. Electro-optical display element based on the ECB effect, characterized in that it contains, as dielectric, a phase according to Claim 16.

19. Tolans of the formula I



I

in which

R^1 is alkyl having up to 15 carbon atoms,

R^2 is $-OCF_3$,

A^1 is trans-1,4-cyclohexylene,

25 Z^1 is a single bond,

m is 1



and

A³ and A⁴ are each, independently of one another, 1,4-phenylene which is unsubstituted or monosubstituted or polysubstituted by fluorine.

- 5 20. Tolans of the formula I according to Claim 19, in which R¹ is a straight-chain alkyl group having 1-7 carbon atoms.



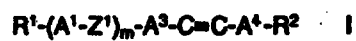
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[As printed]

Claims

1. Liquid-crystalline phase, characterised in that it contains at least one tolan of the formula I



in which

R^1 and R^2 are each, independently of one another, alkyl having up to 15 carbon atoms in which, in addition, one or two non-adjacent CH_2 groups may be replaced by $-O-$, and one of



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- the radicals R^1 and R^2 is alternatively $-OCF_3$, CF_3 , fluorine or chlorine,
 A^1 is unsubstituted 1,4-phenylene or trans-1,4-cyclohexylene,
 Z^1 is $-CH_2CH_2-$ or a single bond,
 m is 0 or 1,
 and
 A^3 and A^4 are each, independently of one another, 1,4-phenylene which is unsubstituted or monosubstituted or polysubstituted by fluorine,
 with the provisos that either
 a) the tolans of the formula I contain a 2,3-difluoro-1,4-phenylene group, or
 b) R^1 or R^2 is $-CF_3$ or OCF_3 ,
 or that
 c) in the case where $m = 0$ and A^3 and $A^4 =$ unsubstituted 1,4-phenylene, R^1 is ethoxy, propoxy, butoxy, pentoxy, hexoxy or heptoxy, and R^2 is fluorine, or one of the radicals R^1 and R^2 is an alkyl group in which at least two CH_2 groups have been replaced by $-O-$,
 d) compounds where $m = 0$ and A^3 and/or $A^4 =$ monosubstituted 1,4-phenylene are excluded,
 e) in the case where A^3 and $A^4 =$ unsubstituted 1,4-phenylene, $m = 1$ and $Z^1 =$ a single bond, one of the radicals R^1 and R^2 is an alkoxy group and the other is then alkyl,
 and contains, as the most important further constituents, compounds of the formula V



in which L and E are each a carbocyclic or heterocyclic ring system from the group formed by 1,4-disubstituted cyclohexane rings, 4,4-disubstituted phenylcyclohexane and cyclohexylcyclohexane systems, 2,5-disubstituted pyrimidine and 1,3-dioxane rings, 2,6-disubstituted naphthalene, di- and tetrahydronaphthalene, quinazoline and tetrahydroquinazoline,

G is	$-CH=CH-$	$-N(O)=N-$
	$-CH=CY-$	$-CH=N(O)-$
	$-C=C$	$-CH_2-CH_2-$
	$-CO-O-$	$-CH_2-O-$
	$-CO-S-$	$-CH_2-S-$
	$-CH=N-$	$-COO-Phe-COO-$

or a C-C single bond,

Y is chlorine or $-CN$, and

R^6 and R^7 are alkyl, alkoxy, alkanoyloxy or alkoxy-carbonyloxy having up to 8 carbon atoms, or one of these radicals is alternatively CN , NC , NO_2 , CF_3 , F , Cl or Br .

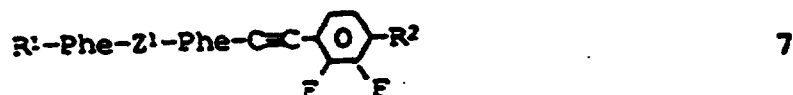
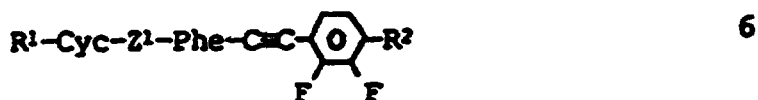
2. Liquid-crystalline phase according to Claim 1, characterised in that it contains compounds selected from the sub-formulae I5, I6, I18 and I22:



in which Cyc is trans-1,4-cyclohexylene, Phe is unsubstituted 1,4-phenylene and PheX is 1,4-phenylene which is monosubstituted or polysubstituted by fluorine.



3. Tolans, characterised by the sub-formulae 2, 6 and 7:



in which Cyc is trans-1,4-cyclohexylene and Phe is unsubstituted 1,4-phenylene, R¹ and R² are each, independently of one another, alkyl having up to 15 carbon atoms in which, in addition, one or two non-adjacent CH₂ groups may be replaced by -O-, and one of the radicals R¹ and R² is alternatively -OCF₃, CF₃, fluorine or chlorine, and Z¹ is -CH₂CH₂- or a single bond.

4. Tolans, characterised by the sub-formula 21:



in which Cyc is trans-1,4-cyclohexylene, and Phe is unsubstituted 1,4-phenylene and alkyl and alkoxy each have up to 15 carbon atoms.

5. Tolans, characterised by the sub-formulae lgj and lgk:



in which Cyc is 1,4-cyclohexylene, Phe is unsubstituted 1,4-phenylene, and R¹ is alkyl having up to 15 carbon atoms in which, in addition, one or two non-adjacent CH₂ groups may be replaced by -O-.

6. 4-Methoxy-4'-(trans-4-propylcyclohexyl)tolan
4-Ethoxy-4'-(trans-4-propylcyclohexyl)tolan
4-Propyloxy-4'-(trans-4-propylcyclohexyl)tolan
7. 4-Fluoro-4'-ethoxytolan
4-Fluoro-4'-propyloxytolan
4-Fluoro-4'-butyloxytolan
4-Fluoro-4'-pentyloxytolan
4-Fluoro-4'-heptyloxytolan
8. 4-Methyl-4'-(2-methoxyethoxy)tolan
4-Ethyl-4'-(2-methoxyethoxy)tolan
4-Propyl-4'-(2-methoxyethoxy)tolan
4-Butyl-4'-(2-methoxyethoxy)tolan
4-Pentyl-4'-(2-methoxyethoxy)tolan
4-Hexyl-4'-(2-methoxyethoxy)tolan
4-Heptyl-4'-(2-methoxyethoxy)tolan



9. 4-Fluoro-4'-methoxymethoxytolan
4-Fluoro-4'-(2-methoxyethoxy)tolan
10. 2,3-Difluoro-4-ethoxy-4'-(trans-4-methylcyclohexyl)tolan
2,3-Difluoro-4-ethoxy-4'-(trans-4-ethylcyclohexyl)tolan
2,3-Difluoro-4-ethoxy-4'-(trans-4-propylcyclohexyl)tolan
2,3-Difluoro-4-ethoxy-4'-(trans-4-butylcyclohexyl)tolan
2,3-Difluoro-4-ethoxy-4'-(trans-4-pentylcyclohexyl)tolan
2,3-Difluoro-4-ethoxy-4'-(trans-4-hexylcyclohexyl)tolan
2,3-Difluoro-4-ethoxy-4'-(trans-4-heptylcyclohexyl)tolan
11. 2,3-Difluoro-4-ethoxy-4'-methyltolan
2,3-Difluoro-4-ethoxy-4'-ethyltolan
2,3-Difluoro-4-ethoxy-4'-propyltolan
2,3-Difluoro-4-ethoxy-4'-butyltolan
2,3-Difluoro-4-ethoxy-4'-pentyltolan
2,3-Difluoro-4-ethoxy-4'-hexyltolan
2,3-Difluoro-4-ethoxy-4'-heptyltolan
12. 4-Trifluoromethoxy-4'-(trans-4-ethylcyclohexyl)tolan
4-Trifluoromethoxy-4'-(trans-4-propylcyclohexyl)tolan
4-Trifluoromethoxy-4'-(trans-4-butylcyclohexyl)tolan
4-Trifluoromethoxy-4'-(trans-4-pentylcyclohexyl)tolan
4-Trifluoromethoxy-4'-(trans-4-hexylcyclohexyl)tolan
4-Trifluoromethoxy-4'-(trans-4-heptylcyclohexyl)tolan
4-Trifluoromethoxy-4'-(trans-4-octylcyclohexyl)tolan
4-Trifluoromethoxy-4'-ethyltolan
4-Trifluoromethoxy-4'-propyltolan
4-Trifluoromethoxy-4'-butyltolan
4-Trifluoromethoxy-4'-pentyltolan
4-Trifluoromethoxy-4'-hexyltolan
4-Trifluoromethoxy-4'-heptyltolan
4-Trifluoromethoxy-4'-octyltolan
4-Trifluoromethoxy-4'-ethoxytolan
4-Trifluoromethoxy-4'-propoxytolan
4-Trifluoromethoxy-4'-butoxytolan
4-Trifluoromethoxy-4'-pentyloxytolan
4-Trifluoromethoxy-4'-hexyloxytolan
4-Trifluoromethoxy-4'-heptyloxytolan
4-Trifluoromethoxy-4'-octyloxytolan
13. Liquid-crystalline phase having at least two liquid-crystalline components, characterised in that it contains at least one compound according to one of Claims 3 to 12.
14. Use of the compounds according to one of Claims 3 to 12 as components of liquid-crystalline phases.
15. Use of compounds according to one of Claims 3 to 12 as components of liquid-crystalline phases for electro-optical display elements based on the ECB effect.
16. Liquid-crystalline phase for electro-optical display elements based on the ECB effect, having at least two liquid-crystalline components, characterised in that it contains at least one compound according to one of Claims 3 to 12.
17. Electro-optical display element, characterised in that it contains, as liquid-crystalline dielectric, a liquid-crystalline phase according to Claim 1, 2 or 13.
18. Electro-optical display element based on the ECB effect, characterised in that it contains, as dielectric, a phase according to Claim 16.



19. Tolans of the formula I



in which

R^1 is alkyl having up to 15 carbon atoms,

R^2 is $-OCF_3$,

A^1 is trans-1,4-cyclohexylene,

Z^1 is a single bond,

m is 1

and

A^3 and A^4 are each, independently of one another, 1,4-phenylene which is unsubstituted or monosubstituted or polysubstituted by fluorine.

20. Tolans of the formula I according to Claim 19, in which R^1 is a straight-chain alkyl group having 1-7 carbon atoms.

[As printed]

Revendications

1. Phase cristalline liquide, caractérisée en ce qu'elle contient au moins un tolane de formule I



dans laquelle

R^1 et R^2 représentent chacun indépendamment l'un de l'autre un alcoyle en C_1 à C_{15} , où également un ou deux groupes CH_2 non voisins peuvent être remplacés par $-O-$, l'un des radicaux R^1 et R^2 représente également $-OCF_3$, CF_3 , fluor ou chlore,

A^1 représente un 1,4-phénylène ou trans-1,4-cyclohexylène non substitué,

Z^1 représente $-CH_2CH_2$ ou une liaison simple,

m vaut 0 ou 1

et

A^3 et A^4 représentent chacun indépendamment l'un de l'autre un 1,4-phénylène non substitué ou mono- ou polysubstitué par un fluor,

avec ces précisions que

ou bien

a) les tolans de formule I contiennent un groupe 2,3-difluoro-1,4-phénylène, ou

b) R^1 ou R^2 représente $-CF_3$ ou OCF_3 ,

ou bien

c) dans le cas où $m = 0$ et A^3 et $A^4 = 1,4$ -phénylène non substitué, R^1 représente un éthoxy, propoxy, butoxy, pentoxy, hexoxy ou heptoxy et R^2 représente un fluor ou l'un des radicaux R^1 et R^2 est un groupe alcoyle, où au moins deux groupes CH_2 sont remplacés par $-O-$,

d) les composés où $m = 0$ et A^3 et/ou A^4 1,4-phénylène monosubstitué sont exclus,

e) dans le cas où A^3 et $A^4 = 1,4$ -phénylène non substitué, $m = 1$ et $Z^1 =$ une liaison simple, l'un des radicaux R^1 et R^2 représente un groupe alcoxy et l'autre est un alcoyle,

et comme autres composants très importants des composés de formule V



où L et E représentent chacun un système cyclique carbo- ou hétérocyclique parmi les suivants: noyaux cyclohexane 1,4-disubstitués, systèmes phényl-cyclohexane et cyclohexyl-cyclohexane 4,4-disubstitués, noyaux pyrimidine et 1,3-dioxane 2,5-disubstitués, naphthalène 2,8-disubstitué, di- et tétrahydronaphthalène, quinazoline et tétrahydroquinazoline,



G	-CH=CH-	-N(O)=N-
	-CH=CY-	-CH=N(O)-
	-C=C	-CH ₂ -CH ₂ -
	-CO-O-	-CH ₂ -O-
	-CO-S-	-CH ₂ -S-
	-CH=N-	-COO-Phe-COO-

ou une liaison simple C-C,

Y un chlore au -CN, et

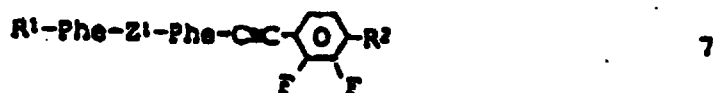
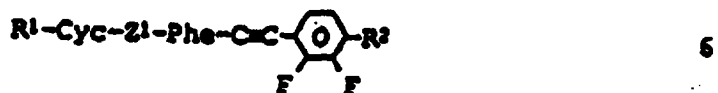
R⁶ et R⁷ représentent un alcoyle, alcoxy, alcanoyloxy ou alcoxycarbonyloxy avec jusqu'à 8 atomes de carbone, ou un de ces radicaux représente également CN, NC, NO₂, CF₃, F, Cl ou Br.

2. Phase cristalline liquide selon la revendication 1, caractérisée en ce qu'elle contient des composés de formules partielles 15, 16, 118 et 122:



où Cyc représente un trans-1,4-cyclohexylène, Phe un 1,4-phénylène non substitué et PheX est un 1,4-phénylène mono- ou polysubstitué par un fluor.

3. Tolanes caractérisés par les formules partielles 2, 6 et 7:



où Cyc représente un trans-1,4-cyclohexylène et Phe un 1,4-phénylène non substitué, R¹ et R² représentent à chaque fois indépendamment l'un de l'autre un alcoyle ayant jusqu'à 15 atomes de carbone, où également un ou deux groupes CH₂ non voisins peuvent être remplacés par -O-, l'un des radicaux R¹ et R² représente par -O-, l'un des radicaux R¹ et R² représente également -OCF₃, CF₃, un fluor ou un chlore, et Z¹ représente -CH₂CH₂- ou une liaison simple.

4. Tolanes caractérisés par la formule partielle 21:



où Cyc représente un trans-1,4-cyclohexylène et Phe un 1,4-phénylène non substitué et alcoyle et alcoxy présentent à chaque fois jusqu'à 15 atomes de carbone.



5. Tolanes caractérisés par les formules partielles Igi et Igk:



où Cyc représente un trans-1,4-cyclohexylène, Phe un 1,4-phénylène non substitué et R¹ un alcoyle ayant jusqu'à 15 atomes de carbone, où également un ou deux groupes CH₂ non voisins peuvent être remplacés par -O-.

6. 4-Méthoxy-4'-(trans-4-propylcyclohexyl)-tolane
4-Ethoxy-4'-(trans-4-propylcyclohexyl)-tolane
4-Propyloxy-4'-(trans-4-propylcyclohexyl)-tolane
7. 4-Fluoro-4'-éthoxy-tolane
4-Fluoro-4'-propyloxy-tolane
4-Fluoro-4'-butyloxy-tolane
4-Fluoro-4'-pentyloxy-tolane
4-Fluoro-4'-heptyloxy-tolane
8. 4-Méthyl-4'-(2-méthoxyéthoxy)-tolane
4-Ethyl-4'-(2-méthoxyéthoxy)-tolane
4-Propyl-4'-(2-méthoxyéthoxy)-tolane
4-Butyl-4'-(2-méthoxyéthoxy)-tolane
4-Pentyl-4'-(2-méthoxyéthoxy)-tolane
4-Hexyl-4'-(2-méthoxyéthoxy)-tolane
4-Heptyl-4'-(2-méthoxyéthoxy)-tolane
9. 4-Fluoro-4'-méthoxyméthoxy-tolane
4-Fluoro-4'-(2-méthoxyéthoxy)-tolane
10. 2,3-Difluoro-4-éthoxy-4'-(trans-4-méthylcyclohexyl)-tolane
2,3-Difluoro-4-éthoxy-4'-(trans-4-éthylcyclohexyl)-tolane
2,3-Difluoro-4-éthoxy-4'-(trans-4-propylcyclohexyl)-tolane
2,3-Difluoro-4-éthoxy-4'-(trans-4-butylcyclohexyl)-tolane
2,3-Difluoro-4-éthoxy-4'-(trans-4-pentylcyclohexyl)-tolane
2,3-Difluoro-4-éthoxy-4'-(trans-4-hexylcyclohexyl)-tolane
2,3-Difluoro-4-éthoxy-4'-(trans-4-heptylcyclohexyl)-tolane
11. 2,3-Difluoro-4-éthoxy-4'-méthyltolane
2,3-Difluoro-4-éthoxy-4'-éthyltolane
2,3-Difluoro-4-éthoxy-4'-propyltolane
2,3-Difluoro-4-éthoxy-4'-butyltolane
2,3-Difluoro-4-éthoxy-4'-pentytolane
2,3-Difluoro-4-éthoxy-4'-hexyltolane
2,3-Difluoro-4-éthoxy-4'-heptytolane
12. 4-Trifluorométhoxy-4'-(trans-4-éthylcyclohexyl)-tolane
4-Trifluorométhoxy-4'-(trans-4-propylcyclohexyl)-tolane
4-Trifluorométhoxy-4'-(trans-4-butylcyclohexyl)-tolane
4-Trifluorométhoxy-4'-(trans-4-pentylcyclohexyl)-tolane
4-Trifluorométhoxy-4'-(trans-4-hexylcyclohexyl)-tolane
4-Trifluorométhoxy-4'-(trans-4-heptylcyclohexyl)-tolane
4-Trifluorométhoxy-4'-(trans-4-octylcyclohexyl)-tolane
4-Trifluorométhoxy-4'-éthyltolane
4-Trifluorométhoxy-4'-propyltolane
4-Trifluorométhoxy-4'-butyltolane
4-Trifluorométhoxy-4'-pentytolane



4-Trifluorométhoxy-4'-hexyitolane
4-Trifluorométhoxy-4'-heptytolane
4-Trifluorométhoxy-4'-octyitolane
4-Trifluorométhoxy-4'-éthoxytolane
4-Trifluorométhoxy-4'-propoxytolane
4-Trifluorométhoxy-4'-butoxytolane
4-Trifluorométhoxy-4'-pentyloxytolane
4-Trifluorométhoxy-4'-hexyloxytolane
4-Trifluorométhoxy-4'-heptyloxytolane
4-Trifluorométhoxy-4'-octyloxytolane

13. Phase cristalline liquide avec au moins deux composants cristallins liquides, caractérisée en ce qu'elle contient au moins un composé selon l'une des revendications 3 à 12.
14. Application des composés selon l'une des revendications 3 à 12 comme composants de phases cristallines liquides.
15. Application des composés selon l'une des revendications 3 à 12 comme composants de phases cristallines liquides pour éléments d'affichage électro-optiques à base d'effet ECB.
16. Phase cristalline liquide pour éléments d'affichage électro-optiques à base d'effet ECB avec au moins deux composants cristallins liquides, caractérisée en ce qu'elle contient au moins un composé selon l'une des revendications 3 à 12.
17. Élément d'affichage électro-optique caractérisé en ce qu'il contient comme diélectrique cristallin liquide une phase cristalline liquide selon la revendication 1, 2 ou 13.
18. Élément d'affichage électro-optique à base d'effet ECB, caractérisé en ce qu'il contient comme diélectrique une phase selon la revendication 16.
19. Tolanes de formule I



dans laquelle

R¹ représente un alcoyle ayant jusqu'à 15 atomes de carbone,

R² représente -OCF₃,

A¹ un trans-1,4-cyclohexylène,

Z¹ une liaison simple,

m vaut 1

et

A³ et A⁴ représentent chacun indépendamment l'un de l'autre un 1,4-phénylène non substitué ou mono- ou polysubstitué par un fluor.

20. Tolanes de formule I selon la revendication 19, où R¹ représente un groupe alcoyle en C₁ à C₇.