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Liquid crystal dielectrics containing halo-bicyclic compounds

This invention is concerned with certain novel liquid-crystalline halogen compounds, with processes for their preparation, with dielectrics containing such novel compounds, and with electro-optical display elements
5 comprising such dielectrics.

The property of nematic or nematic-cholesteric liquid-crystalline materials of significantly varying their optical properties, such as light absorption, light scattering, birefringence, reflectivity or colour, under
10 the influence of electric fields, is widely utilised for electro-optical display elements. The functioning of display elements of this kind is based, for example, on the phenomena of dynamic scattering, the deformation of aligned phases, the Schadt-Helfrich effect in the
15 twisted cell or the cholesteric-nematic phase transition.

For the industrial application of these effects in electronic components, liquid-crystalline dielectrics are required which must meet a large number of demands. The chemical resistance to moisture, air and physical
20 influences, such as heat, radiation in the infrared, visible and ultraviolet regions, and continuous and alternating electric fields, is of particular importance.

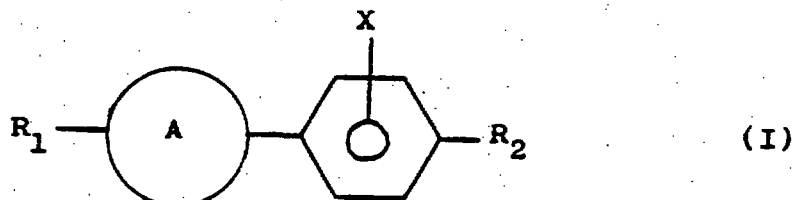
Industrially usable liquid-crystalline dielectrics are also required to have a liquid-crystalline
25 mesophase in the temperature range of at least 0°C to

+50°C, preferably from -10°C to 60°C, and the lowest possible viscosity at room temperature, which preferably should not exceed 70×10^{-3} Pa.s. Finally, they must not have any characteristic absorption in the region of visible light, that is to say they must be colourless.

A number of liquid-crystalline compounds have been described which fulfil such stability demands and which are also colourless. These include, in particular, the p,p'-disubstituted phenyl benzoates described in German OLS 2,139,628 and the p,p'-disubstituted phenylcyclohexane derivatives described in German OLS 2,636,684. In both the classes of compounds mentioned, and also in other series of compounds with a liquid-crystalline mesophase, no individual compounds have hitherto been disclosed which form a liquid-crystalline nematic mesophase in the required temperature range from 0°C to 60°C. As a rule, mixtures of two or more compounds are therefore prepared in order to obtain materials which can be used as liquid-crystalline dielectrics. For this purpose, at least one compound having a low melting point and clear point is usually mixed with another compound having a markedly higher melting point and clear point. This normally gives a mixture, the melting point of which is below that of the lower-melting component, whilst the clear point is between the clear points of the components. Nevertheless, difficulties repeatedly arise in the preparation of optimum dielectrics because the components having the high melting points and clear points frequently also impart a high viscosity to the mixture. As a result, the switching times of electro-optical display elements incorporating these mixtures are undesirably long.

Problems also frequently arise from the fact that the mutual solubility of the various components, in particular at room temperature or lower temperatures, is only very limited.

We have now found that halogen compounds of formula (I):



10 wherein the ring A is 1,4-phenylene or trans-1,4-cyclohexylene, R₁ is alkyl or alkoxy having 1 to 12 carbon atoms or, if A is 1,4-phenylene, is alkyl or alkoxy having 1 to 12 carbon atoms or cyano, R₂ is alkyl or alkoxy having 1 to 12 carbon atoms or, if A is 1,4-cyclohexylene, is chlorine or bromine, and X is fluorine, chlorine or hydrogen, with the proviso that at least one of the substituents R₂ and X is a halogen atom, are outstandingly suitable as components of liquid-crystalline dielectrics. In particular, these compounds have a
15
20 nematic phase within the required temperature range and, when used in liquid crystal cells, give switching times which are sufficiently short at room temperature.

The compounds of formula (I) are novel and constitute one aspect of the present invention.

25 Depending on the selection of the substituents, the compounds of formula (I) can either be used as base materials representing the major component of liquid, crystalline dielectrics, or they can be added in minor proportions of, for example, 2 to 45 % by weight to liquid-crystalline base materials constituted by other classes
30 of compounds so as to obtain dielectrics having a widened liquid-crystalline mesophase or a lower viscosity or to influence the magnitude of the dielectric anisotropy of the dielectric.

35 By suitable selection of the substituents R₁, R₂ and X, the compounds of formula (I) can be used either

for the preparation of dielectrics having a pronounced positive dielectric anisotropy for use in display elements based on the twisted nematic cell or on the cholesteric-nematic phase transition, or for the
5 preparation of dielectrics having a dielectric anisotropy which differs only slightly from zero or is even negative, the latter dielectrics being used in display elements based on dynamic scattering or on the deformation of aligned phases (DAP effect).

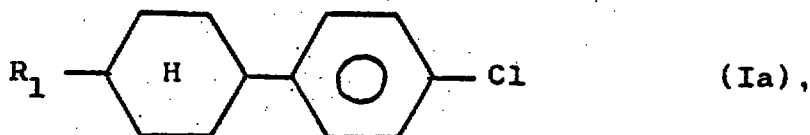
10 In the pure state, the compounds of formula (I) are colourless and they form liquid-crystalline mesophases in a temperature range which is surprisingly wide and is favourable for electro-optical applications.

According to a further aspect of the present
15 invention, therefore, there is provided a liquid-crystalline dielectric comprising at least two liquid-crystalline components, at least one of which is a liquid-crystalline halogen compound of formula (I).

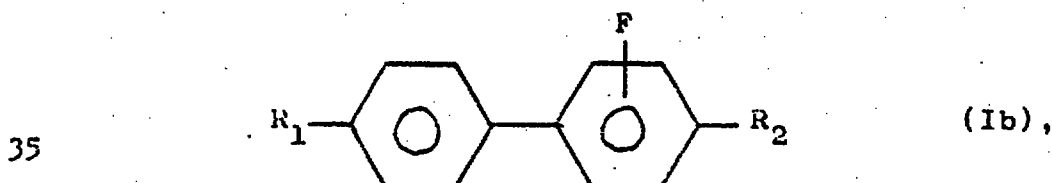
According to another aspect of the invention,
20 there is provided an electro-optical display element comprising a liquid crystal cell, in which the cell contains a dielectric according to the invention.

The liquid-crystalline halogen compounds of formula (I) comprise:

25 chlorophenylcyclohexanes of formula (Ia):

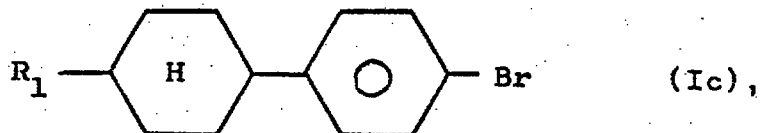


30 fluorinated biphenyl derivatives of formula (Ib):



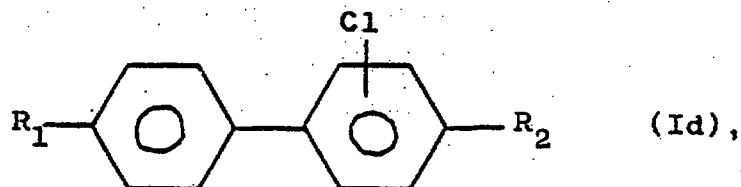
bromophenylcyclohexanes of formula (Ic):

5



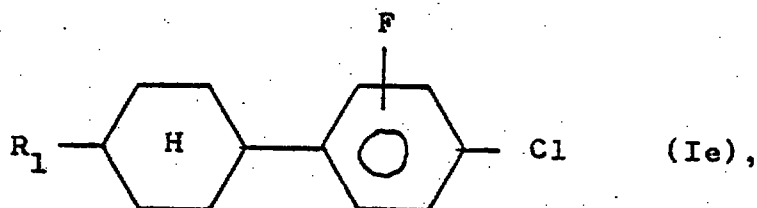
chlorinated biphenyl derivatives of formula (Id):

10



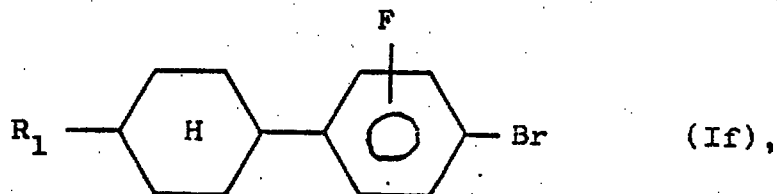
fluorochlorophenylcyclohexanes of formula (Ie):

15



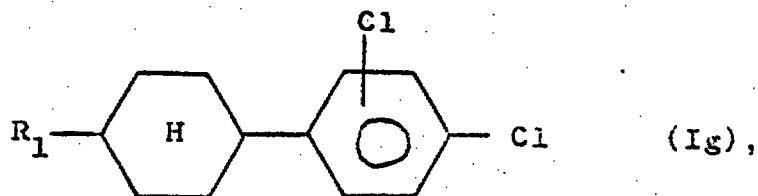
fluorobromophenylcyclohexanes of formula (If):

20



25

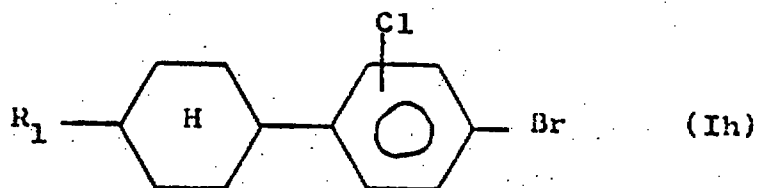
dichlorophenylcyclohexanes of formula (Ig):



30

and

chlorobromophenylcyclohexanes of formula (Ih):



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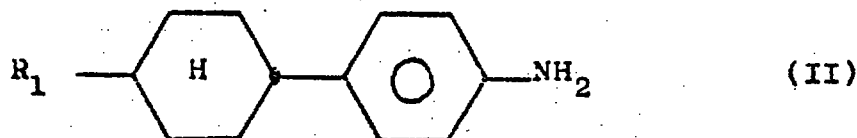
If the compounds of formula (I) contain a 1,4-disubstituted cyclohexane ring, the substituents in the 1- and 4-positions are in a trans-arrangement relative to one another; in the graphic formulae, this is indicated by an enlarged black dot on the right-hand side of the ring. The chloro- and bromo-phenylcyclohexanes of formulae (Ia) and (Ic) have a positive dielectric anisotropy and a nematic mesophase situated in a more favourable temperature range than that of the analogous fluorophenyl-cyclohexanes described in German OLS 2,907,332. The fluorinated and chlorinated biphenyl derivatives of formulae (Ib) and (Id) have a positive dielectric anisotropy if R_1 is a cyano group, and have a negative dielectric anisotropy if R_1 is alkyl or alkoxy. In these two sub-groups of the compounds according to the invention, the halogen substitution also causes a marked widening of the temperature range of the nematic mesophase and a displacement of this range to more favourable temperatures. Depending on the position and the nature of the lateral halogen substituent, the dihalogenocyclohexanes of formulae (Ie) to (Ih) have a moderate positive dielectric anisotropy (if the lateral substituent is vicinal to the terminal substituent), or the dielectric anisotropy has a value near zero (if the lateral substituent is vicinal to the bond between the two ring systems).

Among the compounds of formula (I), those of sub-formulae (Ia), (Ib), (Ic), (Id) and (Ig) are preferred because they can be prepared from more readily accessible starting materials. Of these, the compounds of the sub-formula (Ia) in which R_1 is alkyl having 2 - 12 C atoms, preferably 3 - 8 C, atoms, and those of sub-formula (Ib) have particularly advantageous properties for use in liquid crystal display elements.

In the compounds of formula (I), the alkyl or

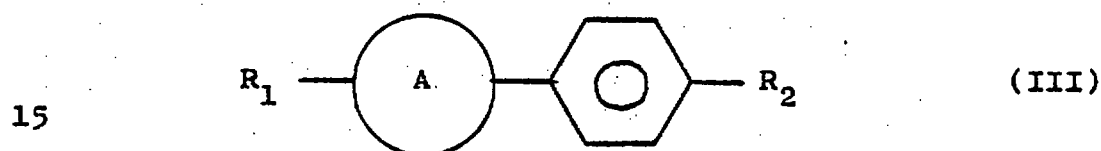
alkoxy radicals R_1 and R_2 can be straight-chain or branched. If they are straight-chain, that is to say they are methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, or n-dodecyl, or the corresponding alkoxy groups, then the compounds have, as a rule, higher clear points than the compounds with branched end groups R_1 and/or R_2 . For this reason, it is usually preferred that not more than one of the end groups R_1 and R_2 should contain a branched chain. The compounds of formula (I) with a branched end group R_1 or R_2 are occasionally important due to their having a higher solubility in conventional liquid-crystalline base materials and, in particular, they are important as chiral doping substances if they possess optical activity due to the chain branching. Such branched end groups should not, in general, contain more than one chain branching. Preferred branched R_1 and R_2 groups are those in which a methyl or ethyl group is present in the 1-position, 2-position or 3-position of a longer carbon chain, for example 2-methylpropyl, 2-methylbutyl, 3-methylbutyl, 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl or 1-methylhexyl. If R_1 and R_2 are alkyl or alkoxy, the end groups R_1 and R_2 together can contain up to 24 carbon atoms; compounds in which R_1 and R_2 together contain 3 to 16, more preferably 4 to 13, carbon atoms are preferred.

The compounds according to the invention can be prepared by methods which are conventional for compounds of the kind in question. Thus, for example, compounds of formulae (Ia) and (Ic) can be obtained by diazotising an aniline derivative of formula (II):

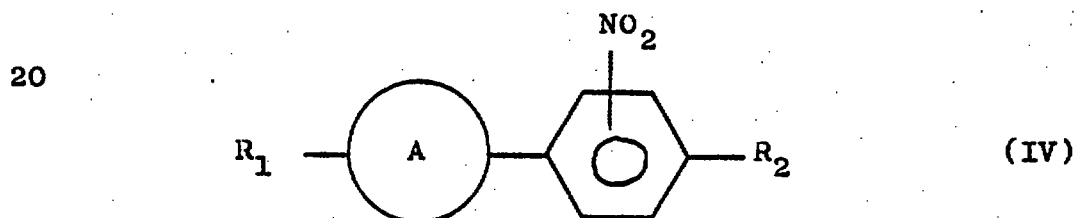


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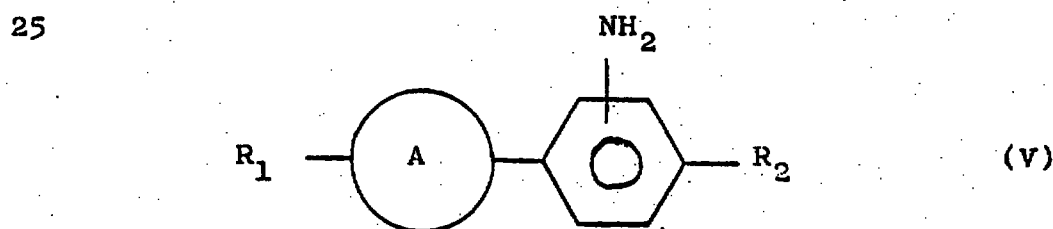
and reacting the product with copper (I) chloride or
bromide under the conditions of a Sandmeyer reaction.
The diazotisation and the Sandmeyer reaction may be
carried out in a manner known per se, as described, for
5 example, in Gattermann-Wieland, Die Praxis des
organischen Chemikers (Organic Chemistry in Practice),
40th edition (Walter de Gruyter & Co, Berlin 1961), pages
252 - 254. Compounds of formulae (Ib) and (Id) in which
 R_1 is alkyl or alkoxy, and also compounds of formulae
10 (Ie), (If), (Ig) and (Ih) are obtained by first nitrating
a corresponding laterally unsubstituted compound (III):



wherein A and R_2 have the above-stated meanings, to give
a compound of formula (IV):



reducing the nitro compound (IV) to an amino compound (V):

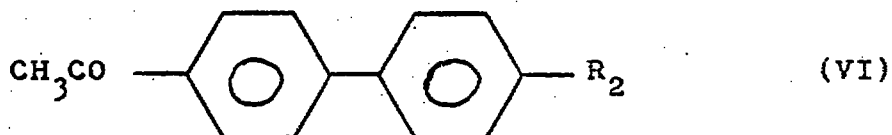


30 and reacting the latter, after diazotisation, with
copper (I) chloride under the conditions of a Sandmeyer
reaction, or with a tetrafluoroborate under the conditions
of a Schiemann-Balz reaction. The nitration of (III) to
give (IV) may be carried out in conventional manner for
35 compounds of this type. By suitable selection of the

(18)

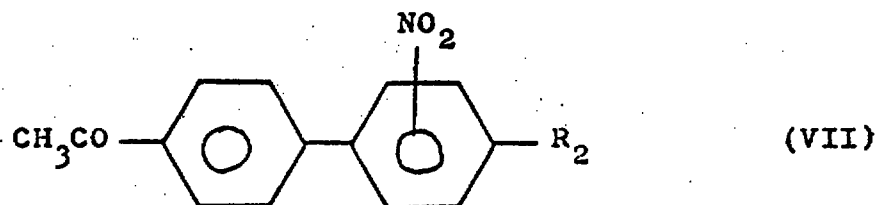
nitrating agent, the temperature, the reaction time and, if appropriate, a solvent or a catalyst, the formation of the possible isomeric nitro compounds, that is substituted in the ortho- or the meta-position relative to the R_2 group, can be directed towards a desired isomer. If desired, a resulting mixture of the isomeric nitro compounds is separated to give the individual components in a manner known per se, for example by fractional crystallisation or by chromatographic methods. The reduction of (IV) to (V) may also be carried out in a manner known from the literature, for example by catalytic hydrogenation with tin, zinc or iron and hydrochloric acid, with tin(II) chloride or with dithionite. The diazotisation of the amine and the Sandmeyer reaction to give the chloro compounds (Id), (Ig) and (Ih) is carried out in the same way as the above-described synthesis of the compounds (Ia) or (Ic); the Schiemann-Balz synthesis of the compounds (Ib), (Ic) and (If) from the corresponding amine (V) can be carried out according to one of the process variants described in "Organic Reactions", volume 5 (1949), pages 193 - 228.

The compounds of formula (I) in which A is 1,4-phenylene, R_1 is CN, X is fluorine or chlorine and R_2 is alkyl or alkoxy, are prepared by nitrating a compound of formula (VI):

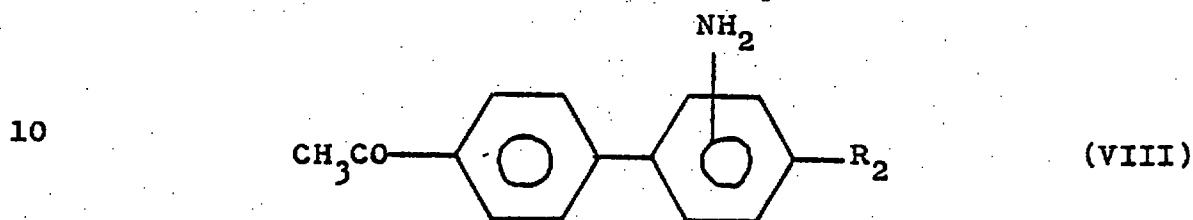


to give a nitro compound (VII):

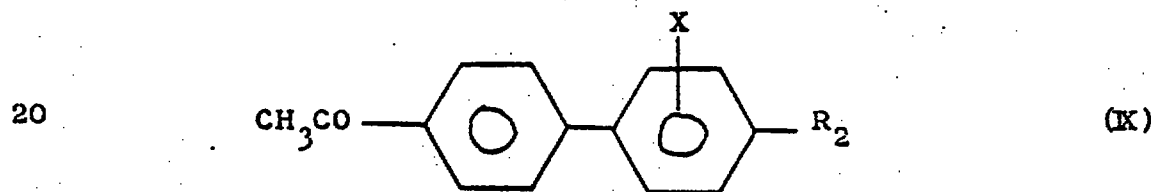
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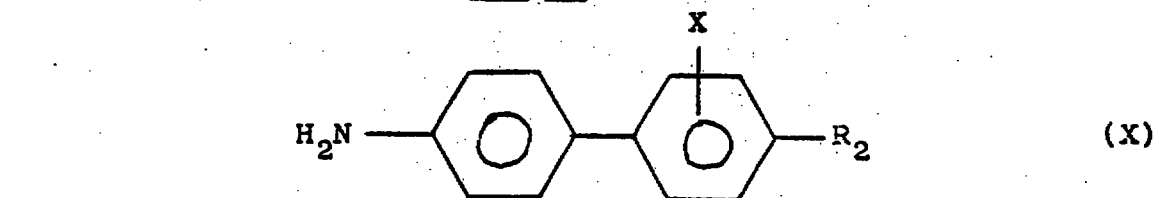
reducing the latter to an amino compound (VIII):



15 diazotising (VIII) and then reacting the product with copper(I) chloride under the conditions of a Sandmeyer reaction or with tetrafluoroborate under the conditions of a Schiemann-Balz reaction to give the halogen compound (IX),



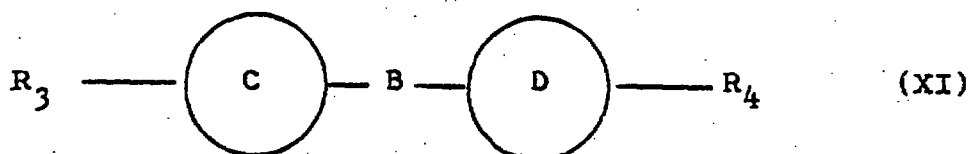
25 which is then reacted with hydroxylamine to give the oxime, from which an amine (X) is prepared by a Beckmann rearrangement known per se:



This amine (X) is then diazotised in conventional manner and the product is reacted with copper(I) cyanide to give the desired nitrile under the conditions of a Sandmeyer reaction.

35 Dielectrics according to the invention consist

of 2 to 15, preferably 3 to 12 components, of which at least one is a liquid-crystalline halogen compound of formula (I). The other constituents are selected from nematic or nematogenic compounds which are azoxybenzenes, benzylideneanilines, biphenyls, terphenyls, phenyl or cyclohexyl benzoates, phenyl or cyclohexyl cyclohexane-carboxylates, phenylcyclohexanes, cyclohexylbiphenyls, cyclohexylcyclohexanes, cyclohexylnaphthalenes, 1,4-bis-cyclohexylbenzenes, 4,4'-bis-cyclohexylbiphenyls, phenyl- or cyclohexyl-pyrimidines, phenyl- or cyclohexyldioxanes, stilbenes which may be halogenated, benzyl phenyl ethers, tolanes and substituted cinnamic acids. Preferred compounds for use as constituents of liquid-crystalline dielectrics of this type can be characterised by formula (XI):



wherein C and D are each a carboxyclic or heterocyclic ring system selected from 1,4-disubstituted benzene and cyclohexane rings, 4,4'-disubstituted biphenyl, phenylcyclohexane and cyclohexylcyclohexane systems, 2,5-disubstituted pyrimidine rings and 1,3-dioxane rings, 2,6-disubstituted naphthalene, dihydro- and tetrahydro-naphthalene, quinazoline and tetrahydroquinazoline, B is

-CH=CH-

-N(O)=N-

-CH=CY-

-CH=N(O)-

-C=C-

-CH₂-CH₂-

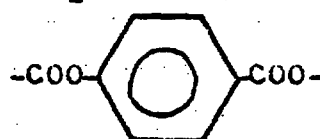
-CO-O-

-CH₂-O-

-CO-S-

-CH₂-S-

-CH=N-



or a C-C single bond, Y is halogen, preferably chlorine, or -CN, and R₃ and R₄ are alkyl, alkoxy, alkanoyloxy or alkoxy-carbonyloxy having up to 18, preferably up to 8, carbon atoms, or one of these radicals can also be -CN, -NC, -NO₂, -CF₃, F, Cl or Br. It is generally preferred that R₃ and R₄ should be different from one another, one of these radicals being an alkyl group or an alkoxy group in most cases. Many compounds of formula (XI), or mixtures thereof, are commercially available.

10 In general, the dielectrics according to the invention contain at least 30, preferably 50 to 99, and more preferably 60 to 98, % by weight of compounds of formula (I) and (XI). Of this, preferably at least 5 % by weight, and in most cases 10 to 40 % by weight, 15 is accounted for one or more compounds of formula (I). However, the invention also comprises those liquid-crystalline dielectrics to which less than 5 % by weight, for example 0.1 to 3 % by weight, of one or more compounds of formula (I) have been added, for example for doping 20 purposes. On the other hand, compounds of formula (I) can account for up to 60% by weight of the dielectrics according to the invention. Preferably, the liquid-crystalline dielectrics according to the invention contain 10 to 30% by weight of one or more compounds of formula 25 (I).

The preparation of dielectrics according to the invention can be carried out in conventional manner. In general, the desired amount of the minor component(s) is dissolved in the major component, advantageously at an 30 elevated temperature. If a temperature above the clear point of the major constituent is chosen for this, the completeness of the dissolution can be very easily observed.

The liquid-crystalline dielectrics according to 35 the invention can be modified by suitable additives in

such a way that they can be used in all hitherto disclosed types of liquid crystal display elements. Additives for this purpose are known to those skilled in the art and are extensively described in the relevant literature.

5 for example, it is possible to add dichroic dyes or substances which are intended to modify the dielectric anisotropy, the viscosity, the conductivity and/or the orientation of the nematic phases. Substances of this type are described, for example, in German OLS 2,209,127,
10 2,240,864, 2,321,632, 2,338,281, 2,450,088, 2,637,430, 2,853,728 and 2,902,177.

In order that the invention may be more fully understood, the following examples are given by way of illustration only. In the examples, m.p. = melting point,
15 c.p. = clear point of a liquid crystalline substance, b.p. = boiling point; all temperatures are in °C. Unless otherwise stated, parts or percentages denote parts or percentages by weight.

Example 1

20 189 g of 4-(trans-4-n-propylcyclohexyl)-aniline hydrochloride were suspended in 500 ml of 15% aqueous hydrochloric acid and 300 ml of a 2.5 molar sodium nitrite solution were added thereto at -5° in the course of half an hour. This solution was added, at 2° in the
25 course of one hour, to a copper(I) salt solution prepared from 250 g of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, 88 g of NaCl, 63 g of Na_2SO_3 , 1,000 ml of water and 400 ml of 32% hydrochloric acid. After heating at 40°C for half an hour, the solution was cooled and extracted 3 times with 300
30 ml of dichloromethane.

The collected organic phases were washed with twice 300 ml of water.

After the solvent had been distilled off, the residue was subjected to a distillation in vacuo, using a spinning band column. The 4-(trans-4-n-propylcyclohexyl)-chlorobenzene distilling over between 105 and 120° under 0.01 mm Hg was recrystallised from ethanol; m.p. 36°, c.p. -17°.

The following were prepared analogously:

- 10 4-(trans-4-ethylcyclohexyl)-chlorobenzene,
- 4-(trans-4-n-butylcyclohexyl)-chlorobenzene,
- 4-(trans-4-n-pentylcyclohexyl)-chlorobenzene,
- 4-(trans-4-n-hexylcyclohexyl)-chlorobenzene,
- 4-(trans-4-n-heptylcyclohexyl)-chlorobenzene,
- 15 4-(trans-4-n-octylcyclohexyl)-chlorobenzene,
- 4-(trans-4-n-decylcyclohexyl)-chlorobenzene,
- 4-(trans-4-n-dodecylcyclohexyl)-chlorobenzene,
- 4-[trans-4-(2-methylbutyl)-cyclohexyl]-chlorobenzene,
- 4-[trans-4-(2-ethylhexyl)-cyclohexyl]-chlorobenzene,
- 20 4-(trans-4-ethylcyclohexyl)-bromobenzene,
- 4-(trans-4-n-propylcyclohexyl)-bromobenzene, m.p. 51°, c.p. 0°,
- 4-(trans-4-n-butylcyclohexyl)-bromobenzene,
- 4-(trans-4-n-pentylcyclohexyl)-bromobenzene,
- 4-(trans-4-n-hexylcyclohexyl)-bromobenzene,
- 25 4-(trans-4-n-heptylcyclohexyl)-bromobenzene,
- 4-(trans-4-n-octylcyclohexyl)-bromobenzene,
- 4-(trans-4-n-decylcyclohexyl)-bromobenzene,
- 4-(trans-4-n-dodecylcyclohexyl)-bromobenzene,

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4-[trans-4-(2-methylbutyl)-cyclohexyl]-bromobenzene and
4-[trans-4-(2-ethylhexyl)-cyclohexyl]-bromobenzene.

Example 2

a) 37 g of 4-n-hexyloxy-4'-n-pentyl-biphenyl were
5 dissolved in 100 ml of dichloromethane, and 14 ml of 65%
nitric acid were added to this solution at 5°C with intens-
ive stirring. After stirring for 1.5 hours, the mixture
was poured into 500 ml of water, and the organic phase was
separated off. After washing several times with water,
10 the dichloromethane was distilled off. The oily resi-
due was dissolved in 300 ml of methanol and, after the
addition of 10 g of Raney nickel, hydrogenated at room
temperature under normal pressure; the absorption of hydro-
gen ceased after 1 hour. After the catalyst had been
15 filtered off, the methanol was distilled off, the residue
was dissolved in 25 ml of toluene and the solution was
passed over a chromatography column (silica gel, toluene
as solvent). The main fraction was concentrated and
freed from the solvent by distillation. This gave 20 g
20 of 3-amino-4-n-hexyloxy-4'-n-pentyl-biphenyl, c.p. (smectic-
isotropic) 70°.

b) 16.5 g of 3-amino-4-n-hexyloxy-4'-n-pentyl-biphenyl
were stirred into 15 ml of 36% aqueous hydrochloric acid.
After 10 ml of dioxane had been added, the solution of 3.0 g
25 of sodium nitrite in 12 ml of water was added dropwise at
0° to the above solution. Immediately after this, and
likewise at 0°, a solution of 15 g of sodium tetrafluoro-
borate in 25 ml of water was added dropwise. The pre-
cipitate which formed was filtered off after 2 hours, washed

with ice water and dried under reduced pressure at room temperature. The dry powder of diazonium tetrafluoroborate was heated to 120°, until the evolution of gas ceased, and the remaining 3-fluoro-4-n-hexyloxy-4'-n-pentyl-
5 biphenyl was subjected to distillation in a bulb tube under the vacuum of a mercury diffusion pump; c.p. (smectic-isotropic) 84°.

The following were prepared analogously:

- 3-fluoro-4-methoxy-4'-n-propylbiphenyl,
- 10 3-fluoro-4-methoxy-4'-n-butylbiphenyl,
- 3-fluoro-4-methoxy-4'-n-pentylbiphenyl,
- 3-fluoro-4-methoxy-4'-n-hexylbiphenyl,
- 3-fluoro-4-methoxy-4'-n-heptylbiphenyl,
- 3-fluoro-4-methoxy-4'-n-octylbiphenyl,
- 15 3-fluoro-4-methoxy-4'-n-nonylbiphenyl,
- 3-fluoro-4-methoxy-4'-n-decylbiphenyl,
- 3-fluoro-4-methoxy-4'-n-undecylbiphenyl,
- 3-fluoro-4-methoxy-4'-n-dodecylbiphenyl,
- 3-fluoro-4-methoxy-4'-n-(2-methylbutyl)-biphenyl,
- 20 3-fluoro-4-ethoxy-4'-ethylbiphenyl,
- 3-fluoro-4-ethoxy-4'-n-propylbiphenyl,
- 3-fluoro-4-ethoxy-4'-n-butylbiphenyl,
- 3-fluoro-4-ethoxy-4'-n-pentylbiphenyl,
- 3-fluoro-4-ethoxy-4'-n-hexylbiphenyl,
- 25 3-fluoro-4-ethoxy-4'-n-heptylbiphenyl,
- 3-fluoro-4-ethoxy-4'-n-octylbiphenyl,
- 3-fluoro-4-ethoxy-4'-n-nonylbiphenyl,
- 3-fluoro-4-ethoxy-4'-n-decylbiphenyl,

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- 3-fluoro-4-ethoxy-4'-n-undecylbiphenyl,
3-fluoro-4-ethoxy-4'-n-dodecylbiphenyl,
3-fluoro-4-ethoxy-4'-(2-methylbutyl)-biphenyl,
- 3-fluoro-4-n-propoxy-4'-methylbiphenyl,
5 3-fluoro-4-n-propoxy-4'-ethylbiphenyl,
3-fluoro-4-n-propoxy-4'-n-propylbiphenyl,
3-fluoro-4-n-propoxy-4'-n-butylbiphenyl,
3-fluoro-4-n-propoxy-4'-n-pentylbiphenyl,
3-fluoro-4-n-propoxy-4'-n-hexylbiphenyl,
10 3-fluoro-4-n-propoxy-4'-n-heptylbiphenyl,
3-fluoro-4-n-propoxy-4'-n-octylbiphenyl,
3-fluoro-4-n-propoxy-4'-n-nonylbiphenyl,
3-fluoro-4-n-propoxy-4'-n-decylbiphenyl,
3-fluoro-4-n-propoxy-4'-n-undecylbiphenyl,
15 3-fluoro-4-n-propoxy-4'-n-dodecylbiphenyl,
3-fluoro-4-n-propoxy-4'-(2-methylbutyl)-biphenyl,
- 3-fluoro-4-n-butoxy-4'-methylbiphenyl,
3-fluoro-4-n-butoxy-4'-ethylbiphenyl,
3-fluoro-4-n-butoxy-4'-n-propylbiphenyl,
20 3-fluoro-4-n-butoxy-4'-n-butylbiphenyl,
3-fluoro-4-n-butoxy-4'-n-pentylbiphenyl,
3-fluoro-4-n-butoxy-4'-n-hexylbiphenyl,
3-fluoro-4-n-butoxy-4'-n-heptylbiphenyl,
3-fluoro-4-n-butoxy-4'-n-octylbiphenyl,
25 3-fluoro-4-n-butoxy-4'-n-nonylbiphenyl,
3-fluoro-4-n-butoxy-4'-n-decylbiphenyl,
3-fluoro-4-n-butoxy-4'-n-undecylbiphenyl,

- 3-fluoro-4-n-butoxy-4'-n-dodecylbiphenyl,
3-fluoro-4-n-butoxy-4'-(2-methylbutyl)-biphenyl,
3-fluoro-4-n-pentyloxy-4'-methylbiphenyl,
3-fluoro-4-n-pentyloxy-4'-ethylbiphenyl,
5 3-fluoro-4-n-pentyloxy-4'-n-propylbiphenyl,
3-fluoro-4-n-pentyloxy-4'-n-butylbiphenyl,
3-fluoro-4-n-pentyloxy-4'-n-pentylbiphenyl,
3-fluoro-4-n-pentyloxy-4'-n-hexylbiphenyl,
3-fluoro-4-n-pentyloxy-4'-n-heptylbiphenyl,
10 3-fluoro-4-n-pentyloxy-4'-n-octylbiphenyl,
3-fluoro-4-n-pentyloxy-4'-n-nonylbiphenyl,
3-fluoro-4-n-pentyloxy-4'-n-decylbiphenyl,
3-fluoro-4-n-pentyloxy-4'-n-undecylbiphenyl,
3-fluoro-4-n-pentyloxy-4'-(2-methylbutyl)-biphenyl,
15 3-fluoro-4-n-hexyloxy-4'-methylbiphenyl,
3-fluoro-4-n-hexyloxy-4'-ethylbiphenyl,
3-fluoro-4-n-hexyloxy-4'-n-propylbiphenyl,
3-fluoro-4-n-hexyloxy-4'-n-butylbiphenyl,
3-fluoro-4-n-hexyloxy-4'-n-hexylbiphenyl,
20 3-fluoro-4-n-hexyloxy-4'-n-heptylbiphenyl,
3-fluoro-4-n-hexyloxy-4'-n-octylbiphenyl,
3-fluoro-4-n-hexyloxy-4'-n-nonylbiphenyl,
3-fluoro-4-n-hexyloxy-4'-n-decylbiphenyl,
3-fluoro-4-n-hexyloxy-4'-(2-methylbutyl)-biphenyl,
25 3-fluoro-4-n-heptyloxy-4'-methylbiphenyl,
3-fluoro-4-n-heptyloxy-4'-ethylbiphenyl,

- 3-fluoro-4-n-heptyloxy-4'-n-propylbiphenyl,
3-fluoro-4-n-heptyloxy-4'-n-butylbiphenyl,
3-fluoro-4-n-heptyloxy-4'-n-pentylbiphenyl,
3-fluoro-4-n-heptyloxy-4'-n-hexylbiphenyl,
5 3-fluoro-4-n-heptyloxy-4'-n-heptylbiphenyl,
3-fluoro-4-n-heptyloxy-4'-n-octylbiphenyl,
3-fluoro-4-n-heptyloxy-4'-(2-methylbutyl)-biphenyl,

3-fluoro-4-n-octyloxy-4'-methylbiphenyl,
3-fluoro-4-n-octyloxy-4'-ethylbiphenyl,
10 3-fluoro-4-n-octyloxy-4'-n-propylbiphenyl,
3-fluoro-4-n-octyloxy-4'-n-butylbiphenyl,
3-fluoro-4-n-octyloxy-4'-n-pentylbiphenyl,
3-fluoro-4-n-octyloxy-4'-n-hexylbiphenyl,
3-fluoro-4-n-octyloxy-4'-n-heptylbiphenyl,
15 3-fluoro-4-n-octyloxy-4'-(2-methylbutyl)-biphenyl,

3-fluoro-4-(2-ethylhexyloxy)-4'-methylbiphenyl,
3-fluoro-4-(2-ethylhexyloxy)-4'-ethylbiphenyl,
3-fluoro-4-(2-ethylhexyloxy)-4'-n-propylbiphenyl,
3-fluoro-4-(2-ethylhexyloxy)-4'-n-butylbiphenyl,
20 3-fluoro-4-(2-ethylhexyloxy)-4'-n-pentylbiphenyl,
3-fluoro-4-(2-ethylhexyloxy)-4'-n-hexylbiphenyl,
3-fluoro-4-(2-ethylhexyloxy)-4'-n-heptylbiphenyl and
3-fluoro-4-(2-ethylhexyloxy)-4'-n-octylbiphenyl.

Example 3

- 25 a) 59 g of 4,4'-di-n-pentyl-biphenyl in the solid form
were introduced into a warm mixture, at 40°, of 40 ml of
65% nitric acid and 48 ml of 96% sulphuric acid. After

the end of the addition, the mixture was stirred for 1 further hour at 60° and poured onto 600 g of ice. The 4,4'-di-n-pentyl-2-nitro-biphenyl which had crystallised out was filtered off and recrystallised from ethanol.

5 b) 34 g of 4,4'-di-n-pentyl-2-nitro-biphenyl were dissolved in 200 ml of tetrahydrofuran. After the addition of 3 g of palladium-on-carbon (10% of Pd), hydrogen was passed into the mixture for 1 hour under normal pressure and at room temperature. The catalyst was then
10 filtered off and the filtrate was evaporated. The remaining 2-amino-4,4'-di-n-pentyl-biphenyl was recrystallised from petroleum ether (boiling range 40 - 60°).

 c) 15.5 g of 2-amino-4,4'-di-n-pentyl-biphenyl were converted, analogously to Example 2, by reaction with nitrous
15 acid, sodium tetrafluoborate, heating and by high-vacuum distillation and recrystallisation from ethanol into 2-fluoro-4,4'-di-n-pentyl-biphenyl; m.p. -3°, c.p. -35°.

The following were prepared analogously:

- 2-fluoro-4-methyl-4'-n-propylbiphenyl,
- 20 2-fluoro-4-methyl-4'-n-butylbiphenyl,
- 2-fluoro-4-methyl-4'-n-pentylbiphenyl,
- 2-fluoro-4-methyl-4'-n-hexylbiphenyl,
- 2-fluoro-4-methyl-4'-n-heptylbiphenyl,
- 2-fluoro-4-methyl-4'-n-octylbiphenyl,
- 25 2-fluoro-4-methyl-4'-n-nonylbiphenyl,
- 2-fluoro-4-methyl-4'-n-decylbiphenyl,
- 2-fluoro-4-methyl-4'-n-undecylbiphenyl,
- 2-fluoro-4-methyl-4'-n-dodecylbiphenyl,
- 2-fluoro-4-methyl-4'-(2-methylbutyl)-biphenyl,

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- 2-fluoro-4-ethyl-4'-methylbiphenyl,
2-fluoro-4-ethyl-4'-ethylbiphenyl,
2-fluoro-4-ethyl-4'-n-propylbiphenyl,
2-fluoro-4-ethyl-4'-n-butylbiphenyl,
5 2-fluoro-4-ethyl-4'-n-pentylbiphenyl,
2-fluoro-4-ethyl-4'-n-hexylbiphenyl,
2-fluoro-4-ethyl-4'-n-heptylbiphenyl,
2-fluoro-4-ethyl-4'-n-octylbiphenyl,
2-fluoro-4-ethyl-4'-n-nonylbiphenyl,
10 2-fluoro-4-ethyl-4'-n-decylbiphenyl,
2-fluoro-4-ethyl-4'-n-undecylbiphenyl,
2-fluoro-4-ethyl-4'-n-dodecylbiphenyl,
2-fluoro-4-ethyl-4'-(2-methylbutyl)-biphenyl,

15 2-fluoro-4-n-propyl-4'-methylbiphenyl,
2-fluoro-4-n-propyl-4'-ethylbiphenyl,
2-fluoro-4-n-propyl-4'-n-propylbiphenyl,
2-fluoro-4-n-propyl-4'-n-butylbiphenyl,
2-fluoro-4-n-propyl-4'-n-pentylbiphenyl,
20 2-fluoro-4-n-propyl-4'-n-hexylbiphenyl,
2-fluoro-4-n-propyl-4'-n-heptylbiphenyl,
2-fluoro-4-n-propyl-4'-n-octylbiphenyl,
2-fluoro-4-n-propyl-4'-n-nonylbiphenyl,
2-fluoro-4-n-propyl-4'-n-decylbiphenyl,
25 2-fluoro-4-n-propyl-4'-n-undecylbiphenyl,
2-fluoro-4-n-propyl-4'-n-dodecylbiphenyl,
2-fluoro-4-n-propyl-4'-(2-methylbutyl)-biphenyl,

2-fluoro-4-n-butyl-4'-methylbiphenyl,

- 2-fluoro-4-n-butyl-4'-ethylbiphenyl,
2-fluoro-4-n-butyl-4'-n-propylbiphenyl,
2-fluoro-4-n-butyl-4'-n-butylbiphenyl,
2-fluoro-4-n-butyl-4'-n-pentylbiphenyl,
5 2-fluoro-4-n-butyl-4'-n-hexylbiphenyl,
2-fluoro-4-n-butyl-4'-n-heptylbiphenyl,
2-fluoro-4-n-butyl-4'-n-octylbiphenyl,
2-fluoro-4-n-butyl-4'-n-nonylbiphenyl,
2-fluoro-4-n-butyl-4'-n-decylbiphenyl,
10 2-fluoro-4-n-butyl-4'-n-undecylbiphenyl,
2-fluoro-4-n-butyl-4'-n-dodecylbiphenyl,
2-fluoro-4-n-butyl-4'-(2-methylbutyl)-biphenyl,

2-fluoro-4-n-pentyl-4'-methylbiphenyl,
2-fluoro-4-n-pentyl-4'-ethylbiphenyl,
15 2-fluoro-4-n-pentyl-4'-n-propylbiphenyl,
2-fluoro-4-n-pentyl-4'-n-butylbiphenyl,
2-fluoro-4-n-pentyl-4'-n-hexylbiphenyl,
2-fluoro-4-n-pentyl-4'-n-heptylbiphenyl,
2-fluoro-4-n-pentyl-4'-n-octylbiphenyl,
20 2-fluoro-4-n-pentyl-4'-n-nonylbiphenyl,
2-fluoro-4-n-pentyl-4'-n-decylbiphenyl,
2-fluoro-4-n-pentyl-4'-n-undecylbiphenyl,
2-fluoro-4-n-pentyl-4'-(2-methylbutyl)-biphenyl,

2-fluoro-4-n-hexyl-4'-methylbiphenyl,
25 2-fluoro-4-n-hexyl-4'-ethylbiphenyl,
2-fluoro-4-n-hexyl-4'-n-propylbiphenyl,
2-fluoro-4-n-hexyl-4'-n-butylbiphenyl,

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- 2-fluoro-4-n-hexyl-4'-n-pentylbiphenyl,
2-fluoro-4-n-hexyl-4'-n-hexylbiphenyl,
2-fluoro-4-n-hexyl-4'-n-heptylbiphenyl,
2-fluoro-4-n-hexyl-4'-n-octylbiphenyl,
5 2-fluoro-4-n-hexyl-4'-n-nonylbiphenyl,
2-fluoro-4-n-hexyl-4'-n-decylbiphenyl,
2-fluoro-4-n-hexyl-4'-(2-methylbutyl)-biphenyl,

2-fluoro-4-n-heptyl-4'-methylbiphenyl,
2-fluoro-4-n-heptyl-4'-ethylbiphenyl,
10 2-fluoro-4-n-heptyl-4'-n-propylbiphenyl,
2-fluoro-4-n-heptyl-4'-n-butylbiphenyl,
2-fluoro-4-n-heptyl-4'-n-pentylbiphenyl,
2-fluoro-4-n-heptyl-4'-n-hexylbiphenyl,
2-fluoro-4-n-heptyl-4'-n-heptylbiphenyl,
15 2-fluoro-4-n-heptyl-4'-n-octylbiphenyl,
2-fluoro-4-n-heptyl-4'-(2-methylbutyl)-biphenyl,

2-fluoro-4-n-octyl-4'-methylbiphenyl,
2-fluoro-4-n-octyl-4'-ethylbiphenyl,
2-fluoro-4-n-octyl-4'-n-propylbiphenyl,
20 2-fluoro-4-n-octyl-4'-n-butylbiphenyl,
2-fluoro-4-n-octyl-4'-n-pentylbiphenyl,
2-fluoro-4-n-octyl-4'-n-hexylbiphenyl,
2-fluoro-4-n-octyl-4'-n-heptylbiphenyl and
2-fluoro-4-n-octyl-4'-(2-methylbutyl)-biphenyl.

25

The examples which follow relate to dielectrics
according to the invention, containing at least one compound

of the formula (I):

Example 4

A liquid-crystalline dielectric composed of
20% of 4-ethoxyphenyl trans-4-propylcyclohexanecarboxylate,
5 20% of 4-ethoxyphenyl trans-4-n-butylcyclohexanecarboxylate,
20% of 4-methoxyphenyl trans-4-n-pentylcyclohexanecarboxylate,
30% of 4-(trans-4-n-propylcyclohexyl)-chlorobenzene and
10% of 4-(trans-4-n-propylcyclohexyl)-phenyl trans-4-n-
butylcyclohexanecarboxylate
10 has a nematic phase in the temperature range from -3 to
+ 55°, a dielectric anisotropy of $\Delta\epsilon = + 0.9$ and an
astonishingly low viscosity of only 12×10^{-3} Pa.s at 20°.

Example 5

A liquid-crystalline dielectric composed of
15 40% of 4-n-pentyl-4'-cyanobiphenyl,
30% of 4-(trans-4-n-pentylcyclohexyl)-chlorobenzene,
15% of 4-(trans-4-n-pentylcyclohexyl)-4'-ethylbiphenyl and
15% of 4-(trans-4-n-propylcyclohexyl)-4'-ethylbiphenyl
has a nematic phase in the temperature range from -7° to
20 +54°, a dielectric anisotropy of $\Delta\epsilon = +6.7$, an optical
anisotropy of $\Delta n = 0.18$ and a viscosity of only $14 \times$
 10^{-3} Pa.s at 20°. By virtue of this low viscosity and
the comparatively high optical and dielectric anisotropies,
this dielectric is very suitable for liquid crystal display
25 elements based on the twisted nematic cell.

Example 6

A liquid-crystalline dielectric composed of
27% of 4-(trans-4-n-propylcyclohexyl)-chlorobenzene,
18% of 4-ethoxyphenyl trans-4-n-propylcyclohexanecarboxylate,

18% of 4-ethoxyphenyl trans-4-n-butylcyclohexanecarboxylate,
17% of 4-(trans-4-n-propylcyclohexyl)-phenyl trans-4-n-
butylcyclohexanecarboxylate,
10% of 2-(4-cyanophenyl)-5-n-propyl-1,3-dioxane and
5 10% of 2-(4-cyanophenyl)-5-n-butyl-1,3-dioxane
has a nematic phase in the temperature range from -6° to
+57°, a dielectric anisotropy of $\Delta\epsilon = +7$ and a viscosity
of only 16×10^{-3} Pa.s. In liquid crystal display ele-
ments based on the twisted nematic cell, this dielectric
10 has a steep characteristic and is therefore very suitable
for displays driven in multiplex operation.

Example 7

A liquid-crystalline dielectric composed of
30% of 4-n-pentyl-4'-cyanobiphenyl,
15 25% of 4-(trans-4-n-butylcyclohexyl)-chlorobenzene,
18% of 4-(trans-4-n-propylcyclohexyl)-benzonitrile,
10% of 4-(trans-4-n-pentylcyclohexyl)-4'-(trans-4-n-propyl-
cyclohexyl)-biphenyl,
9% of 4-(trans-4-n-pentylcyclohexyl)-4'-cyanobiphenyl and
20 8% of 4-n-pentyl-4''-cyanoterphenyl
has a nematic phase in the temperature range from -9° to
+75°, a dielectric anisotropy of $\Delta\epsilon = +9.4$, an optical
anisotropy of $\Delta n = +0.18$ and a viscosity of only $21 \times$
 10^{-3} Pa.s at 20°. It is very suitable for large-area,
25 fast-switching display elements based on the twisted nematic
cell.

Example 8

A liquid-crystalline dielectric composed of
27% of 4-(trans-4-n-heptylcyclohexyl)-chlorobenzene,

23% of 4-(trans-4-n-pentylcyclohexyl)-2'-fluoro-4'-ethylbiphenyl,

22% of 4-(trans-4-n-pentylcyclohexyl)-4'-ethylbiphenyl,

18% of 4-(trans-4-n-propylcyclohexyl)-benzonitrile and

5 10% of 4-(trans-4-n-pentylcyclohexyl)-4'-(trans-4-n-propylcyclohexyl)-biphenyl

has a nematic phase in the temperature range from -9° to +95°, a dielectric anisotropy of $\Delta\epsilon = +3.8$ and a viscosity of 19×10^{-3} Pa.s at 20°, which even at 0° does not
10 rise to more than 55×10^{-3} . This dielectric is very suitable for liquid crystal display elements which are operated under extreme temperature conditions.

Example 9

A liquid-crystalline dielectric composed of
15 15% of 4-(trans-4-n-propylcyclohexyl)-benzonitrile,
11% of 4-(trans-4-n-butylcyclohexyl)-benzonitrile,
21% of 4-(trans-4-n-pentylcyclohexyl)-benzonitrile,
21% of 4-(trans-4-n-pentylcyclohexyl)-4'-ethylbiphenyl,
4% of 4-(trans-4-n-pentylcyclohexyl)-4'-cyanobiphenyl,
20 12% of 4-(trans-4-n-pentylcyclohexyl)-4'-(trans-4-n-propylcyclohexyl)-biphenyl and
16% of 4,4'-bis-n-pentyl-2-fluorobiphenyl

has a nematic phase in the temperature range from -20° to +90°, a dielectric anisotropy of $\Delta\epsilon = 10.5$ and a viscosity
25 of only 20×10^{-3} Pa.s. It is especially suitable for use in display elements based on the twisted nematic cell under extreme temperature conditions.

Example 10

A liquid-crystalline dielectric composed of

- 25% of 4-(trans-4-ethylcyclohexyl)-chlorobenzene,
20% of 4-(trans-4-n-propylcyclohexyl)-phenetole,
15% of 4-(trans-4-n-propylcyclohexyl)-ethylbenzene,
15% of 4-(trans-4-n-propylcyclohexyl)-4'-ethylbiphenyl,
5 15% of 4-(trans-4-n-pentylcyclohexyl)-4'-ethylbiphenyl and
10% of 4-(trans-4-n-pentylcyclohexyl)-4'-(trans-4-n-propyl-
cyclohexyl)-biphenyl

has a nematic phase in the temperature range from -13 to
+62° and a viscosity of only 9×10^{-3} Pa.s at 20°.

10 Example 11

- A liquid-crystalline dielectric composed of
27% of 4-(trans-4-n-propylcyclohexyl)-chlorobenzene,
18% of 4-(trans-4-n-propylcyclohexyl)-benzonitrile,
16% of 4-(trans-4-n-propylcyclohexyl)-phenetole,
15 22% of 4-(trans-4-n-pentylcyclohexyl)-4'-ethylbiphenyl,
7% of 4-(trans-4-n-pentylcyclohexyl)-4'-cyanobiphenyl and
10% of 4-(trans-4-n-pentylcyclohexyl)-biphenyl

- has a nematic phase in the temperature range from -15° to
+86° and a viscosity of only 15×10^{-3} Pa.s at 20°; even
20 at 0°, the viscosity rises only to 48×10^{-3} .



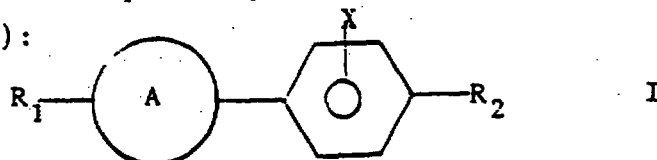
* C L M S *

(37)

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Claims:

1. A liquid-crystalline dielectric comprising at least two liquid-crystalline components, at least one of which is a liquid-crystalline halogen compound of formula (I):

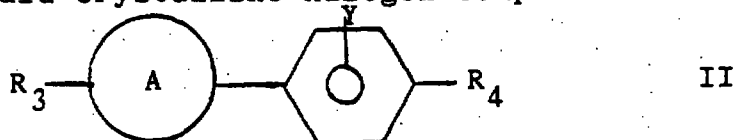


in which the ring A is 1,4-phenylene or trans-1,4-cyclohexylene, R_1 is alkyl or alkoxy having 1 to 12 carbon atoms or, when A is 1,4-phenylene, is alkyl or alkoxy having 1 to 12 carbon atoms or cyano, R_2 is alkyl or alkoxy having 1 to 12 carbon atoms when A is 1,4-phenylene or is chlorine or bromine when A is 1,4-cyclohexylene, and X is fluorine, chlorine or hydrogen, with the proviso that at least one of the substituents R_2 and X is a halogen atom.

2. A liquid-crystalline dielectric according to claim 1, which contains from 5 to 40% by weight of at least one compound of formula (I).

3. An electro-optical display element comprising a liquid crystal cell, in which the liquid crystal cell contains a dielectric according to claim 1 or 2.

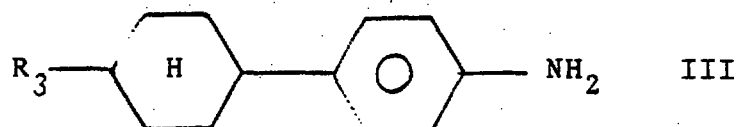
4. Liquid-crystalline halogen compounds of formula (II):



in which the ring A is 1,4 phenylene or trans-1,4-cyclohexylene, R_3 is alkyl or alkoxy having 1 to 12 carbon atoms or, when A is 1,4-phenylene, is alkyl or alkoxy having 1 to 12 carbon atoms or cyano, and R_4 is alkyl or alkoxy having 1 to 12 carbon atoms and Y is fluorine when A is 1,4-phenylene, and R_4 is chlorine or bromine and Y is fluorine, chlorine or hydrogen when A is 1,4-cyclohexylene.

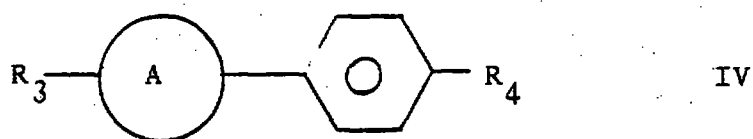
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5. A process for the preparation of a liquid-crystalline halogen compound of formula II specified in claim 4, in which the ring A is trans-1,4-cyclohexylene and Y is hydrogen, which comprises diazotising an aniline derivative of formula III:

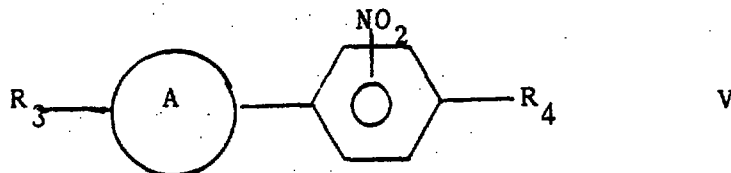


in which R_3 has the meaning stated in claim 4, and reacting the resulting diazonium compound with copper (I) chloride or bromide under the conditions of a Sandmeyer reaction.

6. A process for the preparation of a liquid-crystalline halogen compound of formula II specified in claim 4, in which the ring A is 1,4-phenylene, R_3 is alkyl or akoxyl and Y is fluorine or the ring A is 1,4-cyclohexylene and Y is fluorine or chlorine, which comprises nitrating a compound of formula (IV):

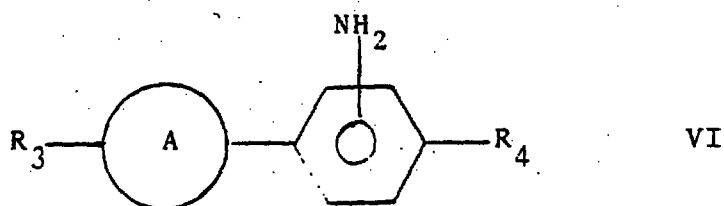


in which R_4 has the meaning specified in claim 4, reducing the resulting nitro compound of formula (V):



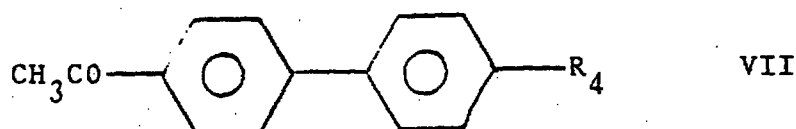
to form an amino compound of formula (VI):



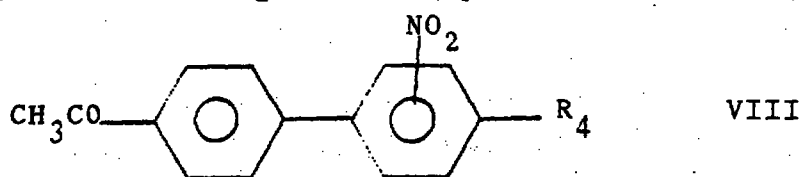


diazotising the amino compound of formula (VI), and reacting the resulting diazonium compound with copper (I) chloride under the conditions of a Sandmeyer reaction (for the A = cyclohexylene, Y = Cl compounds) or with tetrafluoborate under the conditions of a Schiemann-Balz reaction (for the Y = F compounds).

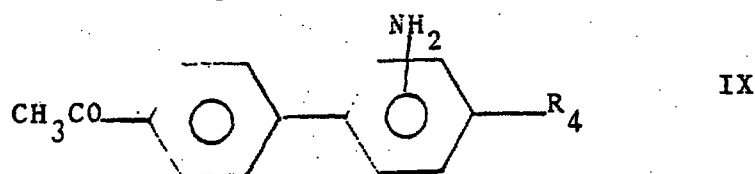
7. A process for the preparation of a liquid-crystalline halogen compound of formula II specified in claim 4, in which A is 1,4-phenylene, R₃ is -CN, and Y is fluorine, which comprises nitrating a compound of formula (VII):



in which R₄ has the meaning specified in claim 4, reducing the resulting nitro compound of formula (VIII):



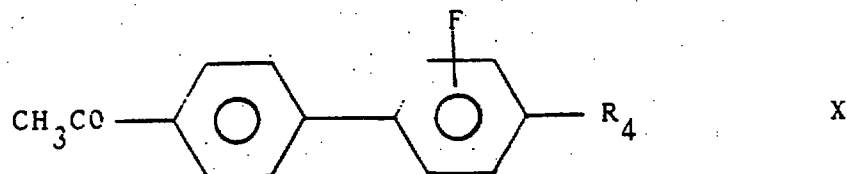
to form an amino compound of formula (IX):



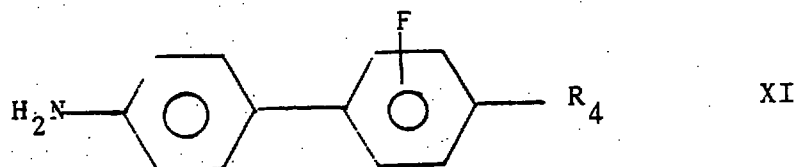
diazotising the amino compound of formula (IX), reacting the resulting diazonium compound with tetrafluoborate



under the conditions of a Schiemann-Balz reaction to give a fluorine compound of formula (X):



reacting the fluorine compound of formula (X) with hydroxylamine and effecting a Beckmann rearrangement to give an amine of formula (XI):



diazotising the amine of formula (XI), and reacting the resulting diazonium compound with copper (I) cyanide under the conditions of a Sandmeyer reaction.

8. A process for the preparation of a liquid-crystalline halogen compound of formula (II) specified in claim 4, substantially as herein described in any of Examples 1 to 3.

9. A liquid-crystalline dielectric substantially as herein described in any of Examples 4 to 11.

