

Description

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

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

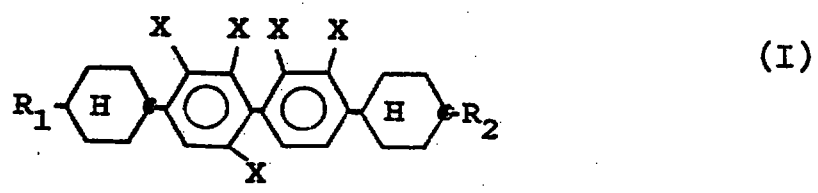
also required to have a liquid-crystalline mesophase in the temperature range from at least +10°C to +50°C, preferably from 0°C to 60°C, and the lowest possible viscosity at room temperature, which preferably should not
5 exceed 70×10^{-3} Pa.s. Finally, they must not have any characteristic absorption in the region of visible light, that is to say they must be colourless.

A number of liquid-crystalline compounds have already been disclosed, which fulfil the stability demands
10 made on dielectrics for electronic components, and which are also colourless. These include, in particular, the p,p'-disubstituted phenyl benzoates described in German Offenlegungsschrift 2,139,628 and the p,p'-disubstituted phenylcyclohexane derivatives described in German Offen-
15 legungsschrift 2,636,684. In both the classes of compounds mentioned, and also in other known series of compounds with a liquid-crystalline mesophase, there are no individual compounds which form a liquid-crystalline nematic mesophase in the required temperature range from
20 10°C to 60°C. As a rule, mixtures of two or more compounds are therefore prepared in order to obtain substances 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
25 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

arise again and again 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 mixtures. As a result, the switching 5 times of the electro-optical display elements produced with these mixtures are extended in an undesirable manner. Moreover, problems are frequently caused by the fact that the mutual solubility of the various components, in particular at room temperature or lower temperatures, is 10 only very limited.

It is the object of the invention to prepare liquid-crystalline dielectrics which have a nematic phase within the required temperature range and, in liquid crystal cells, make switching times possible which are 15 sufficiently short at room temperature.

It has now been found that the 4,4'-bis-(cyclohexyl)-biphenyl derivatives of the formula (I)



wherein R_1 and R_2 , which are identical or different, are 20 alkyl or alkoxy having up to 8 C atoms, and one or two of the substituents X are fluorine and the others are hydrogen, are outstandingly suitable for use as components of liquid-crystalline dielectrics. Additionally, these compounds have an extremely wide range of application:

25 Depending on the selection of the substituents, the compounds of the formula (I) can either be used as

base materials representing the predominant part of liquid-crystalline dielectrics, or compounds of the formula (I) can also be added in smaller proportions of, for example, 2 to 45 per cent by weight to liquid-crystalline base materials from other classes of compounds, in order thus to prepare dielectrics having a widened liquid-crystalline mesophase or to influence the magnitude of the dielectric anisotropy of such a dielectric.

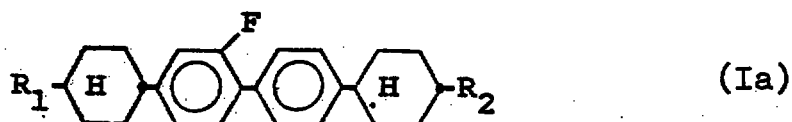
By a suitable selection of the substituents R_1 and R_2 , and the position or positions of the fluorine atoms, the compounds of the formula (I) can be used either for the preparation of dielectrics having a positive dielectric anisotropy, for use in display elements based on the twisted nematic cell or on the cholesteric-nematic phase transition, or it is also possible to prepare dielectrics having a dielectric anisotropy which only slightly differs 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).

In the pure state, the compounds of the formula (I) are colourless, and they form nematic mesophases of low viscosity in a temperature range which is astonishingly wide and is favourable for electro-optical application.

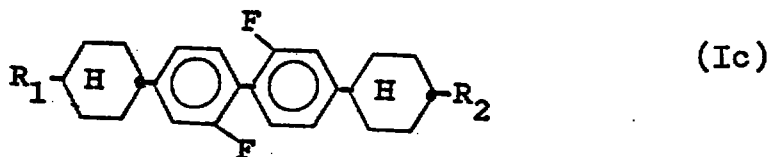
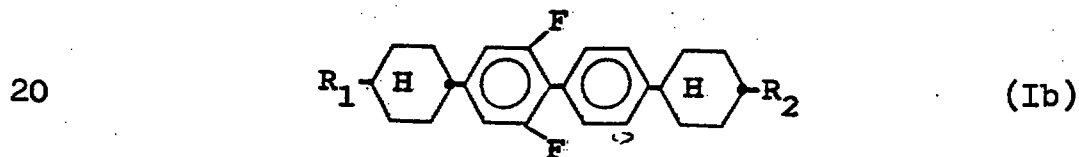
The invention thus relates to the 4,4'-bis-(cyclohexyl)-biphenyl derivatives of the formula (I) and to their use as components of liquid-crystalline dielectrics. Moreover, the invention relates to liquid-crystalline

dielectrics containing at least one 4,4'-bis-(cyclohexyl)-biphenyl derivative of the formula (I), and to electro-optical display elements based on a liquid crystal cell, which contain a liquid-crystalline dielectric of this
5 type.

In the 4,4'-bis-(cyclohexyl)-biphenyl derivatives of the formula (I) according to the invention, the biphenyl part is substituted by one or two Fluorine atoms. If the molecule contains only one fluorine atom, those
10 compounds of the formula (Ia) are preferred in which the fluorine atom is in an ortho-position relative to the bond between the two phenyl rings.



If the compounds of the formula (I) contain two
15 fluorine atoms, those are again preferred amongst these in which the fluorine atoms are arranged in ortho-positions relative to the bond between the two phenyl rings, that is to say the compounds of the formulae (Ib) and (Ic):



In these part formulae, R_1 and R_2 have the same meanings as in the formula (I). The substituents in the 1- and 4-positions of the cyclohexane rings are always in the trans-arrangement; this is marked in the formula illustrations by the thickened black dot on the right-hand side of the cyclohexane rings.

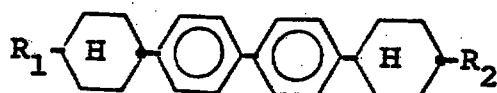
Those compounds of the formula (I) which are not covered by the part formulae (Ia) to (Ic) admittedly have the same advantageous properties as those of the groups singled out, but they are more difficult to prepare and therefore less economical; the compounds of the part formulae (Ia) to (Ic) are therefore preferred.

In the compounds of the 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 or n-octyl, or the corresponding alkoxy groups, the compounds characterised in this way have, as a rule, higher clear points than the compounds with branched wing groups R_1 and/or R_2 . For this reason, usually at most one of the wing groups R_1 and R_2 contains a branched carbon chain. The compounds of the formula (I) with a branched wing group R_1 or R_2 are occasionally important due to a higher solubility in the conventional liquid-crystalline base materials, and in particular they are important as chiral doping substances, if they possess optical activity because of the chain branching. Such branched wing groups do not contain more than one chain branching. Those branched hydrocarbon radicals

are preferred 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-ethyl-
5 hexyl or 1-methylhexyl. The wing groups R_1 and R_2 together can contain up to 16 carbon atoms. Within the scope of the present invention, those are preferred amongst these in which R_1 and R_2 together contain 3 to 14, in particular 4 up to 12, carbon atoms. Preferably, at
10 least one of the wing groups is an alkyl group.

The compounds according to the invention are prepared by a method which is conventional for substances of this type. In a preferred process, compounds of the formula (II)

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(II)

wherein R_1 and R_2 have the meanings indicated under formula (I), are treated with a nitrating agent, the mono-nitro- and dinitro-4,4'-bis-(cyclohexyl)-biphenyls thus formed are, in a manner conventional per se, separated
20 off and reduced to the corresponding monoamino and diamino compounds; these amino compounds are then diazotised, converted by reaction with a fluoborate into the corresponding diazonium fluoborates and, from the latter, fluorine-containing 4,4'-bis-(cyclohexyl)-biphenyls of
25 the formula (I) are prepared by thermal decomposition.

Any mixtures of monofluoro and difluoro compounds or isomers thus obtained are then separated in a manner conventional per se, for example by fractional crystallisation, extraction or by a chromatographic method. Of course, 5 such a separation can also already be carried out at one of the preceding synthesis steps, for example after the nitration or subsequent to the reduction or the preparation of the diazonium tetrafluoroborates.

The nitration of the starting materials of the 10 formula (II) is carried out in a manner known per se, for example with a mixture of sulfuric acid and nitric acid, with acetic acid/nitric acid, or with an acyl nitrate, such as benzoyl nitrate or acetyl nitrate. The distribution of isomers in the resulting mixture of nitration products can be influenced in the direction of the 15 main desired products by a suitable selection of the nitration conditions which are known per se from the literature, for example the nature and concentration of the nitrating agent, the solvent, the temperature, the duration of the reaction and/or the catalyst. The reduction 20 of the nitro compounds to the amino compounds is carried out by standard methods, for example by catalytic hydrogenation or by treatment with sodium sulfide, with aqueous dithionite or with tin(II) chloride and hydrochloric acid. 25

The diazotisation, conversion to the diazonium tetrafluoroborate and thermal decomposition (Schiemann-Balz synthesis) are likewise carried out in a manner known per se, for example according to one of the process

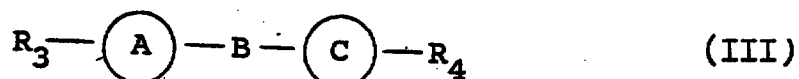
variants described in "Organic Reactions", volume 5 (1949), pages 193 - 228.

In another synthesis process, the starting material used is a 4-bromobiphenyl which is monosubstituted or disubstituted by fluorine. This starting material is reacted successively with magnesium, a 4-alkylcyclohexanone or 4-alkoxycyclohexanone and an acid, and the 4-[4-alkyl- or -alkoxycyclohexen-1-yl]-mono- or -di-fluorobiphenyl thus obtained is then hydrogenated to the 4-(4-alkyl- or -alkoxycyclohexyl)-mono- or -di-fluorobiphenyl. This intermediate is brominated and the bromine atom in the resulting 4'-bromo-4-(4-alkyl- or -alkoxycyclohexyl)-mono- or -di-fluorobiphenyl is exchanged for a 4-alkyl- or -alkoxy-cyclohexyl group in the manner described above.

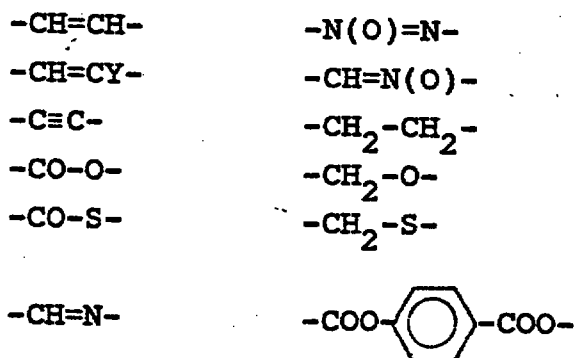
In place of the reaction with magnesium to form the intermediate Grignard compound, the bromine atoms in the intermediates can also be exchanged for the cyclohexyl groups by treatment with a metal-organic compound, for example butyllithium, and subsequent reaction with the cyclohexanone derivatives. If mixtures of cis-cyclohexyl and trans-cyclohexyl derivatives are obtained in this step, these can be converted in a manner conventional per se, for example by treatment with potassium tert.-butylate in dimethylformamide, into the trans-compounds which are thermodynamically more stable.

Fractions of the undesired cis-isomers which may still be contained in the equilibrium mixture can then be separated off by fractional crystallisation or by chromatographic methods.

The dielectrics according to the invention consist of 2 to 15, preferably 3 to 12, components of which at least one is a fluorine-containing 4,4'-bis-(cyclohexyl)-biphenyl derivative of the formula (I). The other constituents are selected from amongst nematic or nematogenic substances from the group comprising the classes of azoxybenzenes, benzylideneanilines, biphenyls, terphenyls, phenyl or cyclohexyl benzoates, phenyl or cyclohexyl cyclohexanecarboxylates, phenylcyclohexanes, cyclohexylbiphenyls, cyclohexylcyclohexanes, cyclohexylnaphthalenes, 1,4-bis-cyclohexylbenzenes, 4,4'-bis-cyclohexylbiphenyls, phenyl- or cyclohexylpyrimidines, phenyl- or cyclohexyl-dioxanes, stilbenes which may be halogenated, benzyl phenyl ethers, tolanes and substituted cinnamic acids. The most important compounds which can be used as constituents of liquid-crystalline dielectrics of this type can be characterised by the formula (III)



wherein A and C are each a carbocyclic or heterocyclic ring system selected from the group comprising 1,4-disubstituted benzene rings 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



or a C-C single bond, Y is halogen, preferably chlorine, or -CN, and R₃ and R₄ are alkyl, alkoxy, alkanoyloxy or alkoxycarbonyloxy 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. In most of these compounds, R₃ and R₄ are different from one another, one of these radicals being an alkyl group or an alkoxy group in most cases. Other variants of the envisaged substituents, however, are also common. Many such substances, or mixtures thereof, are commercially available.

The dielectrics according to the invention contain, as a rule, at least 30, preferably 50 - 99, in particular 60 - 98, parts by weight of the compounds of the formulae (I) and (III). Of this, preferably at least 5 parts by weight, and in most cases even 10 or more parts by weight, account for one or more compounds of the formula (I). However, the invention also comprises those liquid-crystalline dielectrics to which only less than 5 parts by weight, for example 0.1 to 3 parts by weight, of one or more compounds of the formula (I) have been added, for example for doping purposes. On the other hand, the compounds of the formula (I) can account for up to 60 per cent by weight of the dielectrics

according to the invention. Preferably, the liquid-crystalline dielectrics according to the invention contain 10 to 30 per cent by weight of one or more compounds of the formula (I).

5 The preparation of the dielectrics according to the invention is carried out in a manner conventional per se. As a rule, the desired amount of the components used in a smaller quantity is dissolved in the component representing the main constituent, advantageously at an
10 elevated temperature. If a temperature above the clear point of the main constituent is chosen for this, the completeness of the solution process can be observed with particular ease.

 The liquid-crystalline dielectrics according to
15 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 of this type are known to those skilled in the art and are extensively described in the relevant literature.
20 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 Offenlegungs-
25 schriften 2,209,127, 2,240,864, 2,321,632, 2,338,281, 2,450,088, 2,637,430, 2,853,728 and 2,902,177.

 The examples which follow are intended to explain the invention without restricting it. In the examples, m.p. denotes the melting point, and c.p. denotes the

clear point of a liquid-crystalline substance in degrees centigrade; boiling points are marked b.p. Unless otherwise stated, parts or percentage data denote parts by weight or per cent by weight.

Example 1

- 5 a) 45.8 g of 4,4'-bis-(trans-4-n-pentylcyclohexyl)-biphenyl are introduced into a warm mixture, at 40°, of 20 ml of 65% nitric acid and 24 ml of 96% sulfuric acid. After the end of the addition, the reaction mixture is stirred for 1 further hour at 60° and is poured onto 300 g
10 of ice. The 4,4'-bis-(trans-4-n-pentylcyclohexyl)-2-nitrobiphenyl which has crystallised out is filtered off and recrystallised from ethanol.
- b) 20 g of 4,4'-bis-(trans-4-n-pentylcyclohexyl)-2-nitrobiphenyl are dissolved in 150 ml of tetrahydrofuran.
15 After 3 g of palladium-on-carbon (10% of Pd) have been added, hydrogen is passed into the mixture for 1 hour under normal pressure and at room temperature. The catalyst is then filtered off and the filtrate is evaporated. The remaining 4,4'-bis-(trans-4-n-pentylcyclohexyl)-2-
20 aminobiphenyl is recrystallised from petroleum ether (boiling range 40-60°).
- c) 15.0 g of 4,4'-bis-(trans-4-n-pentylcyclohexyl)-2-aminobiphenyl are suspended in 10 ml of 36% aqueous hydrochloric acid. After 10 ml dioxane have been added,
25 a solution of 3.8 g of sodium nitrate in 15 ml of water is added dropwise at 0°C. Immediately afterwards, and likewise at 0°C, a solution of 12 g of sodium tetrafluoroborate in 20 ml of water is added dropwise. The

precipitate which forms is filtered off after 30 minutes, washed with ice water and dried in vacuo at room temperature; the dried powder of diazonium tetrafluoborate is heated to 120° until the evolution of gas ceases, and the
5 remaining 4,4'-bis-(trans-4-n-pentylcyclohexyl)-2-fluorobiphenyl is recrystallised from ethanol.

The following are prepared analogously:

- 4,4'-bis-(trans-4-n-propylcyclohexyl)-2-fluorobiphenyl,
4-(trans-4-methylcyclohexyl)-4'-(trans-4-n-butylcyclo-
10 hexyl)-2-fluorobiphenyl,
4-(trans-4-ethylcyclohexyl)-4'-(trans-4-n-propylcyclohexyl)-2-fluorobiphenyl,
4-(trans-4-n-propylcyclohexyl)-4'-(trans-4-n-pentylcyclohexyl)-2-fluorobiphenyl,
15 4-(trans-4-n-pentylcyclohexyl)-4'-(trans-4-n-propylcyclohexyl)-2-fluorobiphenyl,
4-(trans-4-ethoxycyclohexyl)-4'-(trans-4-n-propylcyclohexyl)-2-fluorobiphenyl,
4-(trans-4-n-hexylcyclohexyl)-4'-(trans-4-n-butoxycyclo-
20 hexyl)-2-fluorobiphenyl,
4-(trans-4-n-heptylcyclohexyl)-4'-(trans-methylcyclohexyl)-2-fluorobiphenyl,
4-(trans-4-methoxycyclohexyl)-4'-[trans-4-(2-methylbutyl)cyclohexyl]-2-fluorobiphenyl,
25 4,4'-bis-(trans-4-n-butylcyclohexyl)-2-fluorobiphenyl,
4,4'-bis-(trans-4-ethylcyclohexyl)-2-fluorobiphenyl and
4,4'-bis-(trans-4-n-propylcyclohexyl)-2,5-difluorobiphenyl.

Example 2

- a) A solution of 24.5 g of 4-(trans-4-n-pentylcyclohexyl)-aniline in 100 ml of toluene is treated successively with 35 ml of pyridine and then dropwise with a solution of 12 g of acetyl chloride in 25 ml of toluene. Subsequently, the reaction mixture is extracted by shaking with 100 ml of water, and the organic phase is separated off, dried over sodium sulfate and evaporated. 20 g of the acetyl-N-4-(trans-4-n-pentylcyclohexyl)-anilide which remains are introduced in portions of 1 - 2 g into a mixture of 118 ml of nitric acid ($d = 1.40$) and 47 ml of sulfuric acid ($d = 1.84$) in such a way that the temperature remains between 30°C and 40° . After the end of the addition, the mixture is stirred for a further 15 minutes and is then poured into 700 ml of cold water. The two-phase system is extracted with methylene chloride, after which the organic phase is freed from solvent by distillation. The residue is dissolved in 100 ml of boiling ethanol, a solution of 15 g of potassium hydroxide in 20 ml of water is then added and the mixture is heated under reflux for a further 20 minutes. After it has been poured into 500 ml of water, the mixture is again extracted with methylene chloride, the solvent is distilled off and the 4-(trans-4-n-pentylcyclohexyl)-2-nitroaniline which remains is purified by distillation under reduced pressure; b.p. 0.3 mbar $139 - 143^{\circ}$.
- b) 12.0 g of 4-(trans-4-n-pentylcyclohexyl)-2-nitroaniline are suspended in 10 ml of 36% hydrochloric acid. After 10 ml of dioxane have been added, a solution of

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2.8 g of sodium nitrite in 6 ml of water is added dropwise at 0°C. With vigorous stirring, a solution of 4.5 g of copper(I) chloride in 17 ml of 36% hydrochloric acid is then allowed to run in. After stirring for 1 hour, the reaction mixture is warmed to room temperature, poured into 200 ml of water and extracted with methylene chloride. The organic phase is dried over calcium chloride and evaporated, and the 4,4'-bis-(trans-4-n-pentylcyclohexyl)-2,2'-dinitrobiphenyl which remains is recrystallised from ethanol.

c) 2 g of palladium-on-carbon (10% of Pd) are added to a solution of 7.5 g of 4,4'-bis-(trans-4-n-pentylcyclohexyl)-2,2'-dinitrobiphenyl in 100 ml of tetrahydrofuran, and hydrogen is passed into this suspension for 1 hour at room temperature. The catalyst is then filtered off and the filtrate is evaporated. 4.0 g of the 4,4'-bis-(trans-4-n-pentylcyclohexyl)-2,2'-diaminobiphenyl which remains are suspended in 15 ml of 26% aqueous tetrafluoboric acid. After 5 ml of dioxane have been added, a solution of 1.2 g of sodium nitrite in 6 ml of water is added dropwise at 0°C. The precipitate which forms is filtered off after 1 - 2 hours, washed with ice water and dried in vacuo at room temperature. The dried powder is heated to 120°. After the evolution of BF₃ has ceased, the 4,4'-bis-(trans-4-n-pentylcyclohexyl)-2,2'-difluorobiphenyl which remains is recrystallised.

The following are prepared analogously:

4,4'-bis-(trans-4-ethylcyclohexyl)-2,2'-difluorobiphenyl,

4,4'-bis-(trans-4-n-propylcyclohexyl)-2,2'-difluorobiphenyl,

4,4'-bis-(trans-4-n-butylcyclohexyl)-2,2'-difluorobiphenyl,

5 4,4'-bis-(trans-4-n-hexylcyclohexyl)-2,2'-difluorobiphenyl and

4,4'-bis-(trans-4-ethoxycyclohexyl)-2,2'-difluorobiphenyl.

Example 3

10 A liquid-crystalline mixture of
23.9% of 4-(trans-4-n-propylhexyl)-benzonitrile,
36.1% of 4-(trans-4-n-pentylcyclohexyl)-benzonitrile,
25.0% of 4-(trans-4-n-heptylcyclohexyl)-benzonitrile and
15.0% of 4-(trans-4-n-pentylcyclohexyl)-4'-cyanobiphenyl
15 has a melting point of -6° , a clear point of $+70^{\circ}$ and a
viscosity of 29×10^{-3} Pa.s at 20° .

A liquid-crystalline dielectric consisting of
90% of this mixture and 10% of 4,4'-bis-(trans-4-n-pentyl-
cyclohexyl)-2-fluorobiphenyl has a melting point of -15° ,
20 a clear point of 86° and a viscosity of 27×10^{-3} Pa.s
at 20° .

Example 4

A liquid-crystalline mixture of
21.1% of 4-(trans-4-ethylcyclohexyl)-benzonitrile,
25 22.2% of 4-(trans-4-n-butylcyclohexyl)-benzonitrile,
13.9% of 4-ethyl-4'-cyanobiphenyl,
17.8% of 4-n-butyl-4'-cyanobiphenyl,
16.1% of 4-(trans-4-n-pentylcyclohexyl)-4'-cyanobiphenyl
and

8.9% of 4-n-pentyl-4"-cyano-p-terphenyl
has a nematic phase in the temperature range from -6° to $+64^{\circ}$ and a viscosity of 32×10^{-3} Pa.s at 20° .

A liquid-crystalline dielectric consisting of
5 90% of this mixture and 10% of 4,4'-bis-(trans-4-n-pentyl-cyclohexyl)-2-fluorobiphenyl has a nematic phase in the widened temperature range from -12° to $+80^{\circ}$ and a viscosity of 33×10^{-3} Pa.s at 20° .

Example 5

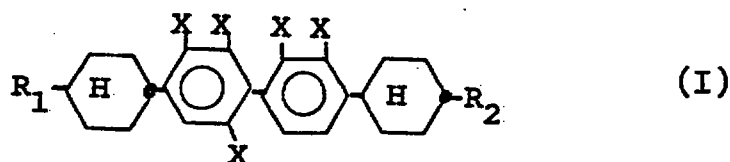
10 The liquid-crystalline mixture of
38.2% of 4-(trans-4-n-pentylcyclohexyl)-benzonitrile,
15.3% of 4-(trans-5-n-propyl-1,3-dioxan-2-yl)-benzonitrile,
15.9% of 4-(trans-5-n-pentyl-1,5-dioxan-2-yl)-benzonitrile,
18.8% of 4-(trans-5-n-hexyl-1,3-dioxan-2-yl)-benzonitrile
15 and
11.8% of 4-(trans-4-n-pentylcyclohexyl)-4'-cyanobiphenyl
has a nematic mesophase in the temperature range from -5°
to $+62^{\circ}$ and a viscosity of 35×10^{-3} Pa.s at 20° .

A liquid-crystalline dielectric consisting of
20 85% of this mixture and 15% of 4,4'-bis-(trans-4-n-pentyl-cyclohexyl)-2-fluorobiphenyl has a nematic phase in the widened temperature range from -15° to $+86^{\circ}$ and a viscosity of 26×10^{-3} Pa.s at 20° .



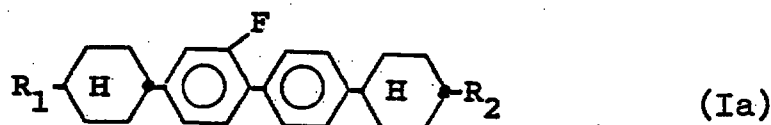
Patent Claims

1. Compounds of the formula (I)



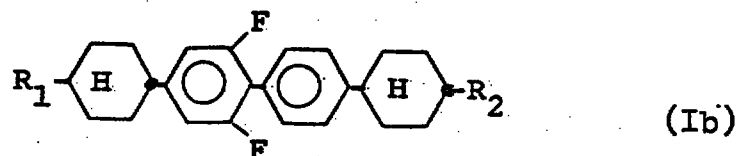
wherein R_1 and R_2 , which are identical or different, are alkyl or alkoxy having up to 8 C atoms, and one or two of the substituents X are fluorine and the others are hydrogen.

2. Compounds according to Claim 1, of the formula (Ia)



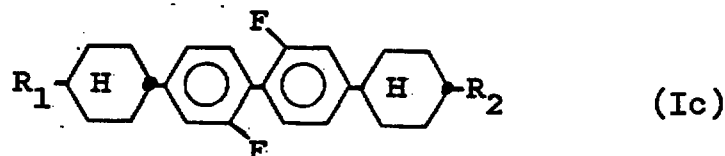
wherein R_1 and R_2 , which are identical or different, are alkyl or alkoxy having up to 8 C atoms.

3. Compounds according to Claim 1, of the formula (Ib)



wherein R_1 and R_2 , which are identical or different, are alkyl or alkoxy having up to 8 C atoms.

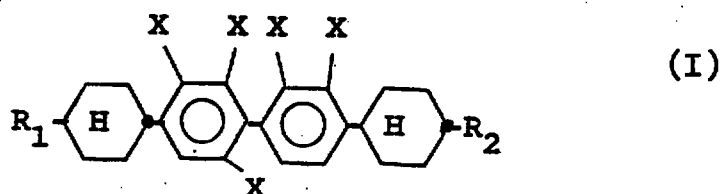
4. Compounds according to Claim 1, of the formula (Ic)





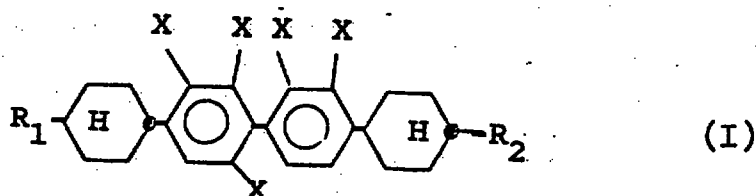
wherein R_1 and R_2 , which are identical or different, are alkyl or alkoxy having up to 8 C atoms.

5. Use of the compounds of the formula (I)



wherein R_1 and R_2 , which are identical or different, are alkyl or alkoxy having up to 8 C atoms, and one or two of the substituents X are fluorine and the others are hydrogen, as components of liquid-crystalline dielectrics.

6. Liquid-crystalline dielectric for electro-optical display elements, having at least two liquid-crystalline components, characterised in that at least one of these liquid-crystalline components is a compound of the formula (I)



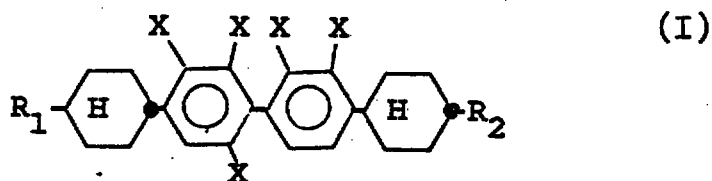
wherein R_1 and R_2 , which are identical or different, are alkyl or alkoxy having up to 8 C atoms, and one or two of the substituents X are fluorine and the others are hydrogen.

7. Electro-optical display element based on a liquid crystal cell, characterised in that the liquid crystal cell contains a dielectric according to Claim 6.

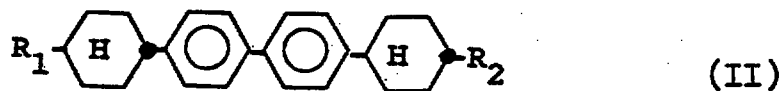
8. Process for the preparation of compounds of the formula (I)



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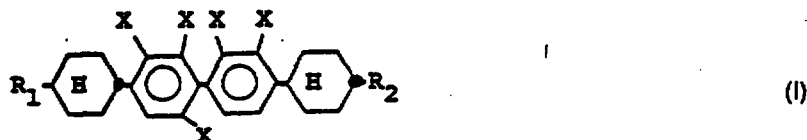
wherein R_1 and R_2 , which are identical or different, are alkyl or alkoxy having up to 8 C atoms, and one or two of the substituents X are fluorine and the others are hydrogen, characterised in that compounds of the formula (II)



wherein R_1 and R_2 have the meanings indicated above, are treated with a nitrating agent, the mononitro and dinitro derivatives thus formed are, in a manner known per se, separated off and reduced to monoamino and diamino compounds, the latter are, in a manner conventional per se, diazotised and converted, by adding tetrafluoborate, into the monodiazonium and didiazonium tetrafluoborates, these are thermally decomposed and the resulting mixture of mono-fluoro and difluoro compounds of the formula (I) is separated into its components in a manner known per se.

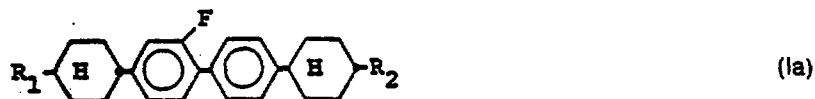


1. Compounds of the formula (I)



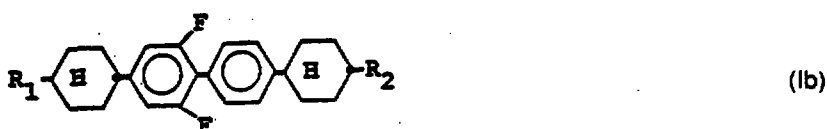
wherein R₁ and R₂, which are identical or different, are alkyl or alkoxy having up to 8 C atoms, and one or two of the substituents X are fluorine and the other are hydrogen.

2. Compounds according to Claim 1, of the formula (Ia)



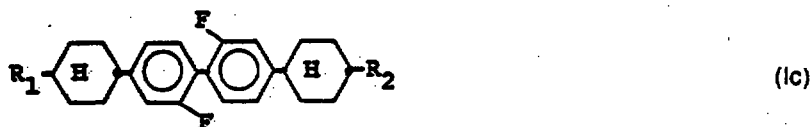
wherein R₁ and R₂, which are identical or different, are alkyl or alkoxy having up to 8 C atoms.

3. Compounds according to Claim 1, of the formula (Ib)



wherein R₁ and R₂, which are identical or different, are alkyl or alkoxy having up to 8 C atoms.

4. Compounds according to Claim 1, of the formula (Ic)



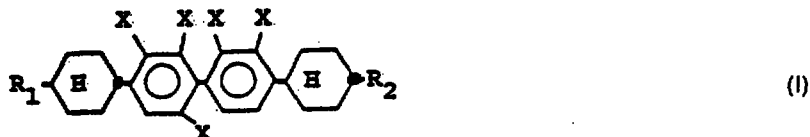
wherein R₁ and R₂, which are identical or different, are alkyl or alkoxy having up to 8 C atoms.

5. Use of the compounds of the formula (I)



wherein R₁ and R₂, which are identical or different, are alkyl or alkoxy having up to 8 C atoms, and one or two of the substituents X are fluorine and the others are hydrogen, as components of liquid-crystalline dielectrics.

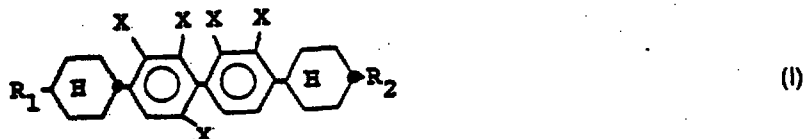
6. Liquid-crystalline dielectric for electro-optical display elements, having at least two liquid-crystalline components, characterised in that at least one of these liquid-crystalline components is a compound of the formula (I)



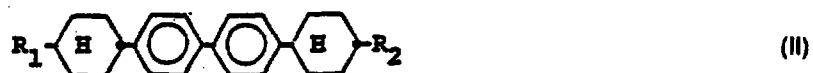
wherein R₁ and R₂, which are identical or different, are alkyl or alkoxy having up to 8 C atoms, and one or two of the substituents X are fluorine and the others are hydrogen.

7. Electro-optical display element based on a liquid crystal cell, characterised in that the liquid crystal cell contains a dielectric according to Claim 6.

8. Process for the preparation of compounds of the formula (I)



wherein R_1 and R_2 , which are identical or different, are alkyl or alkoxy having up to 8 C atoms, and one or two of the substituents X are fluorine and the others are hydrogen, characterised in that compounds of the formula (II)



wherein R_1 and R_2 have the meanings indicated above, are treated with a nitrating agent, the mononitro and dinitro derivatives thus formed are, in a manner known per se, separated off and reduced to monoamino and diamino compounds, the latter are, in a manner conventional per se, diazotised and converted, by adding tetrafluoborate, into the monodiazonium and didiazonium tetrafluoborates, these are thermally decomposed and the resulting mixture of monofluoro and difluoro compounds of the formula (I) is separated into its components in a manner known per se.

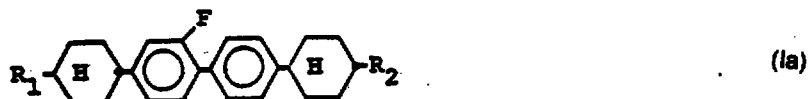


1. Composés de formule (I)



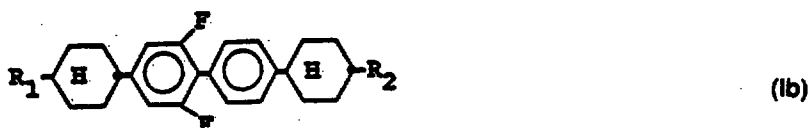
dans laquelle R_1 et R_2 , identiques ou différents, représentent des groupes alkyle ou alcoxy contenant jusqu'à 8 atomes de carbone, un ou deux des symboles X représentent le fluor et les autres l'hydrogène.

2. Composés selon la revendication 1 de formule (Ia)



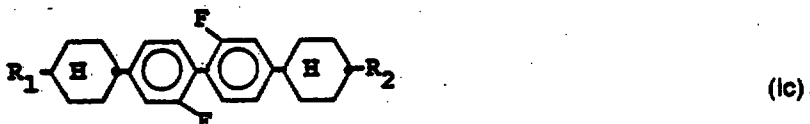
dans laquelle R_1 et R_2 , identiques ou différents, représentent des groupes alkyle ou alcoxy contenant jusqu'à 8 atomes de carbone.

3. Composés selon la revendication 1 de formule (Ib)



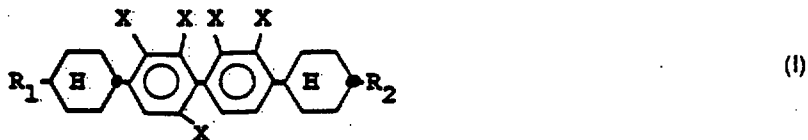
dans laquelle R_1 et R_2 , identiques ou différents, représentent des groupes alkyle ou alcoxy contenant jusqu'à 8 atomes de carbone.

4. Composés selon la revendication 1 de formule (Ic)



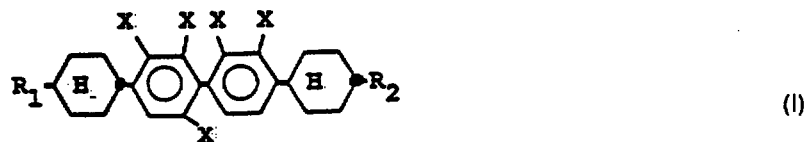
dans laquelle R_1 et R_2 , identiques ou différents, représentent des groupes alkyle ou alcoxy contenant jusqu'à 8 atomes de carbone.

5. Utilisation des composés de formule (I)



dans laquelle R_1 et R_2 , identiques ou différents, représentent des groupes alkyle ou alcoxy contenant jusqu'à 8 atomes de carbone, un ou deux symboles X représentent le fluor, les autres l'hydrogène, en tant que composants de diélectriques à cristaux liquides.

6. Diélectrique à cristaux liquides pour éléments d'affichage électro-optiques à au moins deux composants à cristaux liquides, caractérisé en ce que l'un au moins de ces composants à cristaux liquides est un composé de formule (I)

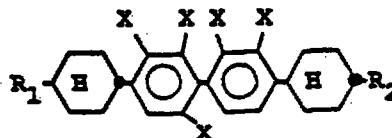




dans laquelle R_1 et R_2 , identiques ou différents, représentent des groupes alkyle ou alcoxy contenant jusqu'à 8 atomes de carbone, un ou deux des symboles X représentent le fluor et les autres l'hydrogène.

7. Élément d'affichage électro-optique à base d'une cellule à cristaux liquides, caractérisé en ce que la cellule à cristaux liquides contient un diélectrique selon la revendication 6.

8. Procédé de préparation des composés de formule (I)



(I)

dans laquelle R_1 et R_2 , identiques ou différents, représentent des groupes alkyle ou alcoxy contenant jusqu'à 8 atomes de carbone, un ou deux des symboles X représentent le fluor et les autres l'hydrogène, caractérisé en ce que l'on traite les composés de formule (II)



(II)

dans laquelle R_1 et R_2 , ont les significations indiquées ci-dessus, par un agent nitrant, on sépare les dérivés mono- et di-nitrés formés de manière connue en soi, on les réduit respectivement en composés mono- et di-aminés, on diazote ces composés de la manière habituelle et on convertit, par addition d'un tétrafluoborate, en les tétrafluoborates de mono- et di-diazonium respectivement, on décompose ces composés à la chaleur et on sépare le mélange de composés mono- et di-fluorés de formule I ainsi obtenu en ses composants de manière connue en soi.