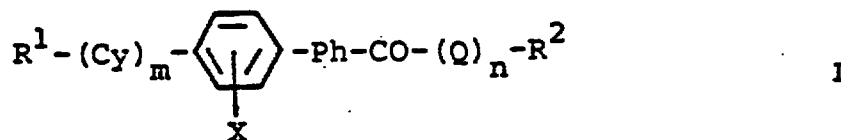


Description

The invention relates to new halogenobiphenyl derivatives of the formula I



wherein R^1 and R^2 are each alkyl or alkoxy with in each
 5 case 1 - 10 C atoms, Cy is 1,4-cyclohexylene, Ph is 1,4-phenylene, Q is -O-Cy- or -O-Ph-, m and n are each 0 or 1 and X is F, Cl, or Br.

Like similar compounds, for example those known from German Offenlegungsschrift 2,800,553, these substances can
 10 be used as components of liquid crystal dielectrics, in particular for displays which are based on the principle of the twisted cell.

The invention was based on the object of discover-
 ing new liquid crystal compounds which are suitable as com-
 15 ponents of liquid crystal dielectrics, in particular for nematic phases with a high optical anisotropy. This object was achieved by providing the compounds of the formula I.

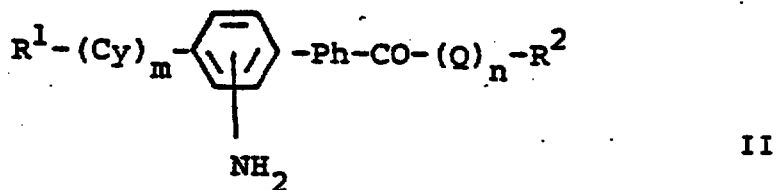
It has been found that the compounds of the formula I are outstandingly suitable as components of liquid crystal
 20 dielectrics. In particular, liquid crystal phases with a wide nematic range, a relatively high optical anisotropy and a positive dielectric anisotropy can be prepared with the aid of these compounds.

The compounds of the formula I are colourless in
 25 the pure state, and form liquid crystal mesophases in a temperature range which is advantageous for electrooptical

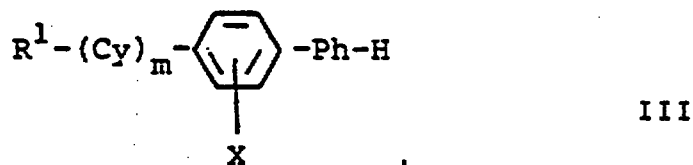
use.

Those compounds of the formula I which are optically active are suitable as chiral doping substances for the production of cholesteric phases such as can also be used for White-Taylor dyestuff cells. In low concentrations, these chiral compounds are capable of preventing interference with the optical phenomena in the twisted cell by "reverse twist" (compare Mol. Cryst. Liq. Cryst., Volume 34 (Letters), pages 211 - 217 [1977]).

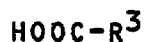
- 10 The invention thus relates to the compounds of the formula I, and to a process for their preparation, characterised in that an aminobiphenyl derivative of the formula II



- 15 wherein R^1 , R^2 , Cy, Ph, Q, m and n have the meaning given in the case of formula I, is diazotised and the diazonium group is then replaced by an X atom by known methods, or in that, for the preparation of a compound of the formula I (R^2 is alkyl, n is 0), a halogenobiphenyl derivative of
- 20 the formula III

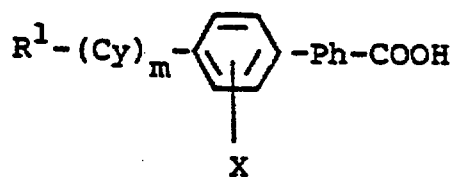


wherein R^1 , Cy, Ph, m and X have the meaning given in the case of formula I, is reacted with a carboxylic acid of the formula IV



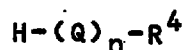
IV

wherein R^3 is alkyl with 1 - 10 C atoms, or with one of its reactive derivatives, in the presence of an acid or a Lewis acid, or in that, for the preparation of a compound of the formula I (R^2 is alkoxy and/or n is 1), a carboxylic acid of the formula V



V

wherein R^1 , Cy, Ph, m and X have the meaning given in the case of formula I, or one of its reactive derivatives, is reacted with a hydroxy compound of the formula VI



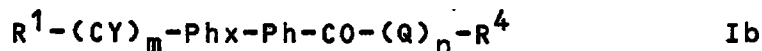
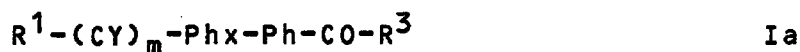
VI

wherein R^4 is alkoxy with 1 - 10 C atoms, or, if n is 1 can also be alkyl with 1 - 10 C atoms, and Q and n have the meaning given in the case of formula I, or one of its reactive derivatives.

The invention also relates to the use of the compounds of the formula I as components of liquid crystal dielectrics, liquid crystal dielectrics containing at least one compound of the formula I, and electrooptical display elements which contain such dielectrics.

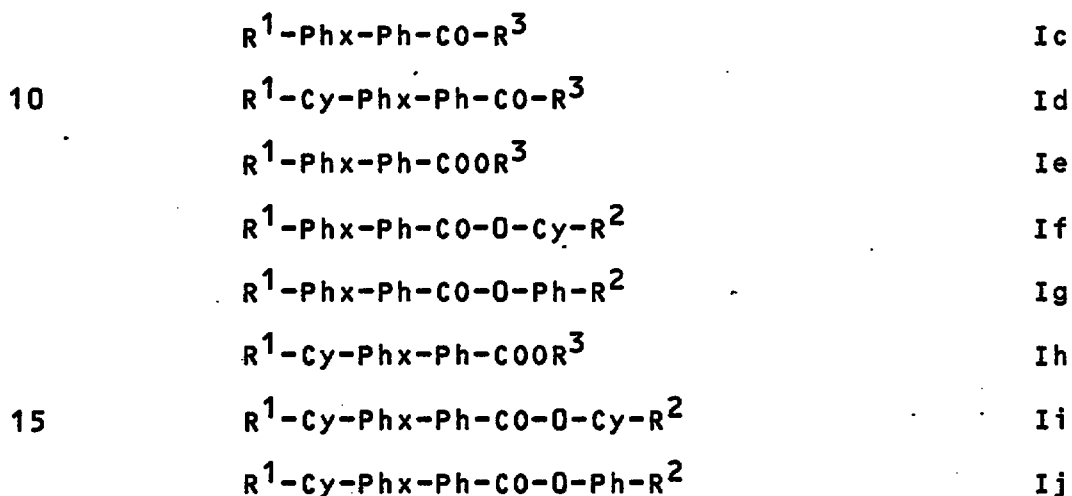
In the preceding and following text, R^1 , R^2 , Cy, Ph, Q, m, n, X, R^3 and R^4 have the meaning given, unless expressly indicated otherwise.

The compounds of the formula I include ketones of the formula Ia and esters of the formula Ib:



5 wherein Phx is a 1,4-phenylene radical substituted by an X atom.

Specifically, the formula I includes ketones of the formulae Ic and Id and esters of the formulae Ie to Ij:



wherein the alkyl and alkoxy groups in each case contain 1 - 10, preferably 1 - 6 and in particular 3, 4, 5 or 6, C atoms.

20 The compounds of the formulae Id and Ie are preferred.

The radicals R^1 and R^2 are preferably alkyl.

In the compounds of the formulae I and Ia, Ib, Id, If, Ih, Ii and Ij, those stereoisomers wherein the two substituents on the cyclohexylene radicals are in each case 25 in the trans-position relative to one another are preferred.

In the compounds of the formulae I and Ia to Ij, the alkyl and alkoxy groups are preferably straight-chain. Alkyl is preferably methyl, ethyl, n-propyl, n-butyl, n-pentyl or n-hexyl, and furthermore preferably n-heptyl,

n-octyl, n-nonyl or n-decyl; and alkoxy is preferably methoxy, ethoxy, n-propoxy, n-butoxy, pentyloxy or n-hexyloxy, and furthermore preferably n-heptyloxy, n-octyloxy, n-nonyloxy or n-decyloxy.

5 Compounds of the formula I and Ia to Ij with branched alkyl or alkoxy groups may occasionally be of importance because of their better solubility in the customary liquid crystal base materials, but especially as chiral doping substances, if they are optically active. Branched groups
10 of this type as a rule contain not more than one chain branching. Preferred branched alkyl radicals are isopropyl, 2-butyl (= 1-methylpropyl), isobutyl (= 2-methylpropyl), 2-methylbutyl, isopentyl (= 3-methylbutyl), 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-heptyl (= 1-methylhexyl),
15 or 2-octyl (= 1-methylheptyl); and preferred branched alkoxy radicals are isopropoxy, 2-methylpropoxy, 2-methylbutoxy, 3-methylbutoxy, 2-methylpentyloxy, 3-methylpentyloxy, 2-ethylhexyloxy, 1-methylhexyloxy and 1-methylheptyloxy.

20 The compounds of the formula I are otherwise prepared by methods which are known per se, such as are described in the literature (for example in the standard works, such as Houben-Weyl, Methoden der Organischen Chemie [Methods of Organic Chemistry], Georg-Thieme-Verlag, Stuttgart),
25 and in particular under reaction conditions which are known and suitable for the reactions mentioned. It is also possible to utilise variants which are known per se and are not mentioned here in more detail.

If desired, the starting substances can also be

formed in situ, in a manner such that they are not isolated from the reaction mixture but are immediately reacted further to give the compounds of the formula I.

The halogenobiphenyl derivatives of the formula
 5 I can be prepared from the amines of the formula II by the methods of the Schiemann reaction (compare, for example, The Merck Index, 9th Edition, Merck & Co., Inc., Rahway, N.J., U.S.A., 1976, page ONR - 80) or the Sandmeyer reaction (compare, for example, The Merck Index, loc.cit., page ONR-
 10 79).

Advantageously, the diazotisation is first carried out with a salt or ester of nitrous acid (such as NaNO_2 or butyl nitrite) in an aqueous acidic phase, it being possible to use as the acid, for example, HF, HCl, HBr, H_2SO_4 or
 15 HBF_4 , at temperatures between about -20° and $+10^\circ$. An additional inert solvent may be present, for example an ether, such as tetrahydrofuran or dioxane, or a hydrocarbon, such as toluene or xylene.

To prepare the chlorine compounds (I, X is F), the
 20 diazotisation is advantageously carried out in HBF_4 . The diazonium tetrafluoroborates are thereby formed, and can be decomposed at temperatures of only between about 10 and 100° . If the diazotisation is carried out with NaNO_2 in anhydrous HF, the desired fluorine compound is obtained
 25 directly by subsequent warming.

The diazonium group is preferably replaced by Cl or Br in aqueous solution in the presence of Cu_2Cl_2 or Cu_2Br_2 at temperatures between 30 and 100° .

The ketones of the formula Ia (= I, R_2 is alkyl, n is

0) can furthermore be obtained by acylation of the halogeno-
biphenyl derivatives of the formula III with carboxylic
acids of the formula IV or their reactive derivatives,
advantageously in the presence of an acid catalyst and an
5 inert solvent at temperatures between about 0° and about
120°. Suitable derivatives of the carboxylic acids of the
formula IV are, above all, their anhydrides and halides,
for example the corresponding acid chlorides and acid bro-
mides. Suitable catalysts are acids, such as HF, H₃PO₄ or
10 polyphosphoric acid, or, preferably, Lewis acids, such as
AlCl₃, AlBr₃, SnCl₄, ZnCl₂, FeCl₃, SbCl₅ or BF₃ or its
etherate, and examples of suitable solvents are CS₂, hydro-
carbons, such as hexane, nitrobenzene or tetramethylene-
sulfone.

15 The esters of the formula Ib can also be obtained
by esterification of the carboxylic acids of the formula V
with alcohols or phenols of the formula VI.

Particularly suitable reactive derivatives of these
carboxylic acids are the acid halides, above all the chlo-
20 rides and bromides, and furthermore the anhydrides, for
example also mixed anhydrides of the formula
 $R^1-(Cy)_m-Phx-Ph-CO-O-COCH_3$, azides and esters, in particular
alkyl esters with 1 - 4 C atoms in the alkyl group.

Possible reactive derivatives of the alcohols or
25 phenols of the formula VI are, in particular, the corres-
ponding metal alcoholates or phenolates of the formula
 $M-(Q)_n-R^4$, in which M is one equivalent of a metal, prefer-
ably an alkali metal, such as Na or K.

The esterification is advantageously carried out in

the presence of an inert solvent. Particularly suitable solvents are ethers, such as diethyl ether, di-n-butyl ether, tetrahydrofuran, dioxane or anisole, ketones, such as acetone, butanone or cyclohexanone, amides, such as dimethylformamide or phosphoric acid hexamethyltri-
5 methyltri- amide, hydrocarbons, such as benzene, toluene or xylene, halogeno- hydrocarbons, such as carbon tetrachloride or tetrachloro- ethylene, and sulfoxides, such as dimethylsulfoxide or sulfolane. Water-immiscible solvents may advantageously
10 be used at the same time for azeotropic distillation of the water formed during the esterification. An excess of an organic base, for example pyridine, quinoline or tri- ethylamine, may occasionally also be used as a solvent for the esterification. The esterification can also be carried
15 out in the absence of a solvent, for example by simple heating of the components in the presence of sodium acetate.

The reaction temperature is usually between -50° and $+250^{\circ}$, preferably between -20° and $+80^{\circ}$. At these temperatures, the esterification reaction has as a rule ended
20 after 15 minutes to 48 hours.

Specifically, the reaction conditions for the esterification largely depend on the nature of the starting substance used. Thus, a free carboxylic acid of the formula V is as a rule reacted with an alcohol or phenol of the
25 formula VI in the presence of a strong acid, for example a mineral acid, such as hydrochloric acid or sulfuric acid.

A preferred procedure is the reaction of an acid anhydride or, in particular, an acid chloride with an alcohol, preferably in a basic medium, bases which are of

particular importance being alkali metal hydroxides, such as sodium or potassium hydroxide, alkali metal carbonates or bicarbonates, such as sodium carbonate, sodium bicarbonate, potassium carbonate or potassium bicarbonate, alkali metal acetates, such as sodium or potassium acetate, alkaline earth metal hydroxides, such as calcium hydroxide, or organic bases, such as triethylamine, pyridine, lutidine, collidine or quinoline.

Another preferred embodiment of the process according to the invention comprises first converting the hydroxy compound of the formula VI to be esterified into the sodium alcoholate or phenolate or potassium alcoholate or phenolate, for example by treatment with ethanolic sodium hydroxide solution or potassium hydroxide solution, isolating this alcoholate or phenolate, suspending it in acetone or diethyl ether, together with sodium bicarbonate or potassium carbonate, while stirring, and adding a solution of the acid chloride or anhydride in diethyl ether, acetone or dimethylformamide to this suspension, advantageously at temperatures between about -25° and $+20^{\circ}$.

Some of the starting substances of the formulae II to VI and their reactive derivatives are known, and some of them can be prepared analogously to known compounds, from substances which are known from the literature.

Thus, the amines of the formula II can be obtained, for example, by nitration of biphenyl derivatives (corresponding to formula I, but X is H) and subsequent reduction, and the starting substances of the formulae III and V can be obtained analogously from the unsubstituted compounds

(corresponding to formulae III and V, but X is H), by nitration, reduction to give the amino compound, diazotisation and a Schiemann or Sandmeyer reaction.

The dielectrics 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 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 cyclohexyl-pyrimidines, phenyl- or cyclohexyl-dioxanes, optionally halogenated stilbenes, benzyl phenyl ethers, tolanes and substituted cinnamic acids. The most important compounds which can be used as constituents of such liquid crystal dielectrics can be characterised by the formula VII



wherein A and E are each a carbocyclic or heterocyclic ring system from the group comprising 1,4-disubstituted benzene and cyclohexane rings, 4,4'-disubstituted biphenyl, phenylcyclohexane and cyclohexylcyclohexane systems, 2,5-disubstituted pyrimidine and 1,3-dioxane rings, 2,6-disubstituted naphthalene, di- and tetra-hydronaphthalene, quinazoline and tetrahydroquinazoline, G is -CH=CH-, -CH=CL-,

-CH₃C-, -CO-O-, -CO-S-, -CH=N-, -N(O)=N-, -CH=N(O)-, CH₂-CH₂-, -CH₂-O-, -CH₂-S-, -COO-Ph-COO- or a C-C single bond, L is halogen, preferably chlorine, or CN, and R⁵ and R⁶ are alkyl, alkoxy, alkanoyloxy or alkoxycarbonyloxy with up to 18, preferably up to 8, carbon atoms, or one of these radicals is also CN, NC, NO₂, CF₃, F, Cl or Br. In most of these compounds, R⁵ and R⁶ differ, one of these radicals usually being an alkyl or alkoxy group. Many such substances or mixtures thereof are commercially available.

10 The dielectrics according to the invention contain about 0.1 to 30%, preferably 2 to 25%, of one or more compounds of the formula I.

 The dielectrics according to the invention are prepared in a manner which is customary per se. As a rule,
15 the components are dissolved in one another, advantageously at elevated temperature. If a temperature above the clear point of the main constituent is chosen, the completeness of the solution operation can be particularly easily observed.

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

 Such additives are familiar to the expert and are
25 described in detail in the literature. For example, dichroic dyestuffs or substances for modifying the dielectric anisotropy, the viscosity, the conductivity and/or the orientation of the nematic phases can be added. Such substances are described, for example, in German Offenlegungs-

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 illustrate the invention, without limiting it. In the examples, m.p. is the melting point and c.p. is the clear point of a liquid crystal substance. In the preceding and following text, percentages are by weight; all the temperatures are given in degrees Centigrade.

Example 1

10 180 ml of 35% aqueous tetrafluoboric acid solution are added dropwise to a suspension of 36.7 g of 4'-acetyl-2-amino-4-(trans-4-pentylcyclohexyl)-biphenyl (m.p. 118 - 123°; obtainable by nitration of 4'-acetyl-4-(trans-4-pentylcyclohexyl)-biphenyl and subsequent hydrogenation
15 of the resulting crude 2-nitro compound over Raney nickel in tetrahydrofuran) in 180 ml of dioxane at 15 - 20°, while stirring, and a solution of 7.2 g of NaNO₂ in 25 ml of water is then added dropwise at 0°. The mixture is subsequently stirred for 6 hours, the temperature being
20 allowed to rise to 15°. After customary working up (extraction with toluene, filtration over silica gel), 4'-acetyl-2-fluoro-4-(trans-4-pentylcyclohexyl)-biphenyl of m.p. 81° and c.p. 170° is obtained.

Examples 2 to 49

25 The following compounds are obtained analogously to Example 1 from the corresponding amino compounds:

2. 4'-Acetyl-2-fluoro-4-methylbiphenyl.
3. 4'-Acetyl-2-fluoro-4-ethylbiphenyl.
4. 4'-Acetyl-2-fluoro-4-propylbiphenyl.

5. 4'-Acetyl-2-fluoro-4-butylbiphenyl.
6. 4'-Acetyl-2-fluoro-4-pentylbiphenyl.
7. 4'-Acetyl-2-fluoro-4-hexylbiphenyl.
8. 4'-Acetyl-2-fluoro-4-heptylbiphenyl.
- 5 9. 4'-Acetyl-2-fluoro-4-octylbiphenyl.
10. 4'-Acetyl-2-fluoro-4-nonylbiphenyl.
11. 4'-Acetyl-2-fluoro-4-decylbiphenyl.
12. 4'-Acetyl-2-fluoro-4-methoxybiphenyl.
13. 4'-Acetyl-2-fluoro-4-ethoxybiphenyl.
- 10 14. 4'-Acetyl-2-fluoro-4-propoxybiphenyl.
15. 4'-Acetyl-2-fluoro-4-butoxybiphenyl.
16. 4'-Acetyl-2-fluoro-4-pentyloxybiphenyl.
17. 4'-Acetyl-2-fluoro-4-hexyloxybiphenyl.
18. 4'-Acetyl-2-fluoro-4-heptyloxybiphenyl.
- 15 19. 4'-Acetyl-2-fluoro-4-octyloxybiphenyl.
20. 4'-Acetyl-2-fluoro-4-nonyloxybiphenyl.
21. 4'-Acetyl-2-fluoro-4-decyloxybiphenyl.
22. 4'-Acetyl-2-fluoro-4-(trans-4-methylcyclohexyl)-
biphenyl.
- 20 23. 4'-Acetyl-2-fluoro-4-(trans-4-ethylcyclohexyl)-
biphenyl.
24. 4'-Acetyl-2-fluoro-4-(trans-4-propylcyclohexyl)-
biphenyl.
25. 4'-Acetyl-2-fluoro-4-(trans-4-butylcyclohexyl)-
25 biphenyl.
26. 4'-Acetyl-2-fluoro-4-(trans-4-hexylcyclohexyl)-
biphenyl.
27. 4'-Acetyl-2-fluoro-4-(trans-4-heptylcyclohexyl)-
biphenyl.

28. 4'-Acetyl-2-fluoro-4-(trans-4-octylcyclohexyl)-biphenyl.
29. 4'-Acetyl-2-fluoro-4-(trans-4-nonylcyclohexyl)-biphenyl.
- 5 30. 4'-Acetyl-2-fluoro-4-(trans-4-decylcyclohexyl)-biphenyl.
31. 4'-Acetyl-2-fluoro-4-(trans-4-methoxycyclohexyl)-biphenyl.
32. 4'-Acetyl-2-fluoro-4-(trans-4-ethoxycyclohexyl)-
- 10 biphenyl.
33. 4'-Acetyl-2-fluoro-4-(trans-4-propoxycyclohexyl)-biphenyl.
34. 4'-Acetyl-2-fluoro-4-(trans-4-butoxycyclohexyl)-biphenyl.
- 15 35. 4'-Acetyl-2-fluoro-4-(trans-4-pentyloxycyclohexyl)-biphenyl.
36. 4'-Acetyl-2-fluoro-4-(trans-4-hexyloxycyclohexyl)-biphenyl.
37. 4'-Acetyl-2-fluoro-4-(trans-4-heptyloxycyclohexyl)-
- 20 biphenyl.
38. 4'-Acetyl-2-fluoro-4-(trans-4-octyloxycyclohexyl)-biphenyl.
39. 4'-Acetyl-2-fluoro-4-(trans-4-nonyloxycyclohexyl)-biphenyl.
- 25 40. 4'-Acetyl-2-fluoro-4-(trans-4-decyloxycyclohexyl)-biphenyl.
41. 2-Fluoro-4'-propionyl-4-propylbiphenyl.
42. 2-Fluoro-4'-propionyl-4-butylbiphenyl.
43. 2-Fluoro-4'-propionyl-4-pentylbiphenyl.

44. 2-Fluoro-4'-propionyl-4-methoxybiphenyl.
45. 2-Fluoro-4'-propionyl-(trans-4-propylcyclohexyl)-biphenyl.
46. 2-Fluoro-4'-propionyl-(trans-4-pentylcyclohexyl)-biphenyl.
- 5 47. 4'-Butyryl-2-fluoro-4-(trans-4-propylcyclohexyl)-biphenyl.
48. 4'-Decanoyl-2-fluoro-4-(trans-4-pentylcyclohexyl)-biphenyl.
- 10 49. 4'-Acetyl-3-fluoro-4-(trans-4-pentylcyclohexyl)-biphenyl.

Example 50

A solution of 7.2 g of NaNO_2 in 25 ml of water is added to a suspension of 36.7 g of 4'-acetyl-2-amino-4-(trans-4-pentylcyclohexyl)-biphenyl in 150 ml of 15% aqueous hydrochloric acid at -5° in the course of 0.5 hours. The solution thus obtained is added dropwise, at $0-5^\circ$ in the course of 1 hour, to a Cu(I) salt solution which has been prepared from 25 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 8.8 g of NaCl, 6.3 g of Na_2SO_3 , 100 ml of water and 40 ml of 32% hydrochloric acid. After the mixture has been heated to 40° for half an hour, it is cooled and extracted with CH_2Cl_2 and the product is worked up in the customary manner. 4'-Acetyl-2-chloro-4-(trans-4-pentylcyclohexyl)-biphenyl is obtained.

25 Examples 51 to 55

The following compounds are obtained analogously to Example 50 from the corresponding amino compounds:

51. 2-Chloro-4'-acetyl-4-propylbiphenyl.
52. 2-Chloro-4'-acetyl-4-butylbiphenyl.

53. 2-Chloro-4'-acetyl-4-pentylbiphenyl.

54. 2-Chloro-4'-acetyl-4-(trans-4-propylcyclohexyl)-biphenyl.

55. 2-Chloro-4'-acetyl-4-(trans-4-pentylcyclohexyl)-
5 biphenyl.

Example 56

The procedure followed is analogous to Example 50, but HBr is used instead of HCl and NaBr is used instead of NaCl, and 4'-acetyl-2-bromo-4-(trans-4-pentylcyclohexyl)-
10 biphenyl is obtained.

Example 57

27 g of $AlCl_3$ are added to a mixture of 32.4 g of 2-fluoro-4-(trans-4-pentylcyclohexyl)-biphenyl and 200 ml of CS_2 at 20° , while stirring, 10 g of acetic anhydride
15 are then added dropwise, while stirring and boiling, and the mixture is boiled for another hour. The mixture is cooled, filtered and decomposed by being discharged into hydrochloric acid/ice, and 4'-acetyl-2-fluoro-4-(trans-4-pentylcyclohexyl)-biphenyl of m.p. 81° and c.p. 170° is
20 obtained.

The compounds mentioned in Examples 2 to 56 can be obtained analogously.

Example 58

28.6 g of 2'-fluoro-4'-pentylbiphenyl-4-carboxylic
25 acid (obtainable by nitration of 4'-pentylbiphenyl-4-carboxylic acid to give the 2'-nitro derivative, reduction to give the 2'-amino compound and a Schiemann reaction) are boiled with 24 g of $SOCl_2$ for one hour, the mixture is evaporated, the resulting crude acid chloride is

dissolved in 150 ml of toluene, 7.9 g of pyridine and 6 g. of propanol are added and the mixture is boiled for 2 hours. The mixture is cooled and washed with water and the organic phase is dried over Na_2SO_4 and evaporated. Propyl 2'-

- 5 fluoro-4'-pentylbiphenyl-4-carboxylate is obtained.
59. Methyl 2'-fluoro-4'-propylbiphenyl-4-carboxylate.
60. Ethyl 2'-fluoro-4'-propylbiphenyl-4-carboxylate.
61. Propyl 2'-fluoro-4'-propylbiphenyl-4-carboxylate.
62. Butyl 2'-fluoro-4'-propylbiphenyl-4-carboxylate.
- 10 63. Pentyl 2'-fluoro-4'-propylbiphenyl-4-carboxylate.
64. Hexyl 2'-fluoro-4'-propylbiphenyl-4-carboxylate.
65. Heptyl 2'-fluoro-4'-propylbiphenyl-4-carboxylate.
66. Octyl 2'-fluoro-4'-propylbiphenyl-4-carboxylate.
67. 1-Methylheptyl 2'-fluoro-4'-propylbiphenyl-4-
- 15 carboxylate.
68. Nonyl 2'-fluoro-4'-propylbiphenyl-4-carboxylate.
69. Decyl 2'-fluoro-4'-propylbiphenyl-4-carboxylate.
70. Trans-4-propylcyclohexyl 2'-fluoro-4'-propyl-
- biphenyl-4-carboxylate.
- 20 71. Trans-4-butylcyclohexyl 2'-fluoro-4'-propyl-
- biphenyl-4-carboxylate.
72. Trans-4-pentylcyclohexyl 2'-fluoro-4'-propyl-
- biphenyl-4-carboxylate.
73. p-Propylphenyl 2'-fluoro-4'-propylbiphenyl-4-
- 25 carboxylate.
74. p-Butylphenyl 2'-fluoro-4'-propylbiphenyl-4-
- carboxylate.
75. p-Pentylphenyl 2'-fluoro-4'-propylbiphenyl-4-
- carboxylate.

76. p-Methoxyphenyl 2'-fluoro-4'-propylbiphenyl-4-carboxylate.
77. p-Ethoxyphenyl 2'-fluoro-4'-propylbiphenyl-4-carboxylate.
- 5 78. Ethyl 4'-butyl-2'-fluorobiphenyl-4-carboxylate.
79. Propyl 4'-butyl-2'-fluorobiphenyl-4-carboxylate.
80. Butyl 4'-butyl-2'-fluorobiphenyl-4-carboxylate.
81. Pentyl 4'-butyl-2'-fluorobiphenyl-4-carboxylate.
82. Hexyl 4'-butyl-2'-fluorobiphenyl-4-carboxylate.
- 10 83. 1-Methylheptyl 4'-butyl-2'-fluorobiphenyl-4-carboxylate.
84. Trans-4-propylcyclohexyl 4'-butyl-2'-fluorobiphenyl-4-carboxylate.
85. Trans-4-pentylcyclohexyl 4'-butyl-2'-fluorobiphenyl-4-carboxylate.
- 15 86. p-Propylphenyl 4'-butyl-2'-fluorobiphenyl-4-carboxylate.
87. p-Pentylphenyl 4'-butyl-2'-fluorobiphenyl-4-carboxylate.
- 20 88. p-Methoxyphenyl 4'-butyl-2'-fluorobiphenyl-4-carboxylate.
89. p-Ethoxyphenyl 4'-butyl-2'-fluorobiphenyl-4-carboxylate.
90. Ethyl 2'-fluoro-4'-pentylbiphenyl-4-carboxylate.
- 25 91. Butyl 2'-fluoro-4'-pentylbiphenyl-4-carboxylate.
92. Pentyl 2'-fluoro-4'-pentylbiphenyl-4-carboxylate.
93. Hexyl 2'-fluoro-4'-pentylbiphenyl-4-carboxylate.
94. 1-Methylheptyl 2'-fluoro-4'-pentylbiphenyl-4-carboxylate.

95. Trans-4-propylcyclohexyl 2'-fluoro-4'-pentylbiphenyl-4-carboxylate.
96. Trans-4-pentylcyclohexyl 2'-fluoro-4'-pentylbiphenyl-4-carboxylate.
- 5 97. p-Propylphenyl 2'-fluoro-4'-pentylbiphenyl-4-carboxylate.
98. p-Pentylphenyl 2'-fluoro-4'-pentylbiphenyl-4-carboxylate.
99. p-Methoxyphenyl 2'-fluoro-4'-pentylbiphenyl-4-
- 10 carboxylate.
100. p-Ethoxyphenyl 2'-fluoro-4'-pentylbiphenyl-4-carboxylate.
101. Ethyl 2'-fluoro-4'-(trans-4-propylcyclohexyl)-biphenyl-4-carboxylate.
- 15 102. Propyl 2'-fluoro-4'-(trans-4-propylcyclohexyl)-biphenyl-4-carboxylate.
103. Butyl 2'-fluoro-4'-(trans-4-propylcyclohexyl)-biphenyl-4-carboxylate.
104. Pentyl 2'-fluoro-4'-(trans-4-propylcyclohexyl)-
- 20 biphenyl-4-carboxylate.
105. Hexyl 2'-fluoro-4'-(trans-4-propylcyclohexyl)-biphenyl-4-carboxylate.
106. 1-Methylheptyl 2'-fluoro-4'-(trans-4-propylcyclohexyl)-biphenyl-4-carboxylate.
- 25 107. Trans-4-propylcyclohexyl 2'-fluoro-4'-(trans-4-propylcyclohexyl)-biphenyl-4-carboxylate.
108. Trans-4-pentylcyclohexyl 2'-fluoro-4'-(trans-4-propylcyclohexyl)-biphenyl-4-carboxylate.
109. p-Propylphenyl 2'-fluoro-4'-(trans-4-propylcyclo-

- hexyl)-biphenyl-4-carboxylate.
110. p-Pentylphenyl 2'-fluoro-4'-(trans-4-propylcyclohexyl)-biphenyl-4-carboxylate.
111. p-Methoxyphenyl 2'-fluoro-4'-(trans-4-propylcyclohexyl)-biphenyl-4-carboxylate.
112. p-Ethoxyphenyl 2'-fluoro-4'-(trans-4-propylcyclohexyl)-biphenyl-4-carboxylate.
113. Ethyl 4'-(trans-4-butylcyclohexyl)-2'-fluorobiphenyl-4-carboxylate.
- 10 114. Propyl 4'-(trans-4-butylcyclohexyl)-2'-fluorobiphenyl-4-carboxylate.
115. Butyl 4'-(trans-4-butylcyclohexyl)-2'-fluorobiphenyl-4-carboxylate.
116. Pentyl 4'-(trans-4-butylcyclohexyl)-2'-fluorobiphenyl-4-carboxylate.
- 15 117. Hexyl 4'-(trans-4-butylcyclohexyl)-2'-fluorobiphenyl-4-carboxylate.
118. 1-Methylheptyl 4'-(trans-4-butylcyclohexyl)-2'-fluorobiphenyl-4-carboxylate.
- 20 119. Trans-4-propylcyclohexyl 4'-(trans-4-butylcyclohexyl)-2'-fluorobiphenyl-4-carboxylate.
120. Trans-4-pentylcyclohexyl 4'-(trans-4-butylcyclohexyl)-2'-fluorobiphenyl-4-carboxylate.
121. p-Propylphenyl 4'-(trans-4-butylcyclohexyl)-2'-fluorobiphenyl-4-carboxylate.
- 25 122. p-Pentylphenyl 4'-(trans-4-butylcyclohexyl)-2'-fluorobiphenyl-4-carboxylate.
123. p-Methoxyphenyl 4'-(trans-4-butylcyclohexyl)-2'-fluorobiphenyl-4-carboxylate.

124. p-Ethoxyphenyl 4'-(trans-4-butylcyclohexyl)-2'-fluorobiphenyl-4-carboxylate.
125. Ethyl 2'-fluoro-4'-(trans-4-pentylcyclohexyl)-biphenyl-4-carboxylate, m.p. 53.5°, c.p. 153.4°.
- 5 126. Propyl 2'-fluoro-4'-(trans-4-pentylcyclohexyl)-biphenyl-4-carboxylate.
127. Butyl 2'-fluoro-4'-(trans-4-pentylcyclohexyl)-biphenyl-4-carboxylate, m.p. 52°, c.p. 120.3°.
128. Pentyl 2'-fluoro-4'-(trans-4-pentylcyclohexyl)-
10 biphenyl-4-carboxylate.
129. Hexyl 2'-fluoro-4'-(trans-4-pentylcyclohexyl)-biphenyl-4-carboxylate.
130. 1-Methylheptyl 2'-fluoro-4'-(trans-4-pentylcyclohexyl)-biphenyl-4-carboxylate.
- 15 131. Trans-4-propylcyclohexyl 2'-fluoro-4'-(trans-4-pentylcyclohexyl)-biphenyl-4-carboxylate.
132. Trans-4-pentylcyclohexyl 2'-fluoro-4'-(trans-4-pentylcyclohexyl)-biphenyl-4-carboxylate.
133. p-Propylphenyl 2'-fluoro-4'-(trans-4-pentylcyclohexyl)-biphenyl-4-carboxylate.
20
134. p-Pentylphenyl 2'-fluoro-4'-(trans-4-pentylcyclohexyl)-biphenyl-4-carboxylate.
135. p-Methoxyphenyl 2'-fluoro-4'-(trans-4-pentylcyclohexyl)-biphenyl-4-carboxylate.
- 25 136. p-Ethoxyphenyl 2'-fluoro-4'-(trans-4-pentylcyclohexyl)-biphenyl-4-carboxylate.

Examples of dielectrics containing at least one compound of the formula I follow:

Example A

A mixture of 28% of p-(trans-4-pentylcyclohexyl)-benzonitrile, 11% of 2-p-cyanophenyl-5-pentyl-1,3-dioxane, 32% of 4-pentyl-4'-cyanobiphenyl, 9% of 4-(trans-4-pentyl-5-cyclohexyl)-4'-cyanobiphenyl and 20% of 4'-acetyl-2-fluoro-4-(trans-4-pentylcyclohexyl)-biphenyl has an m.p. of -11° and a c.p. of 80° .

Example B

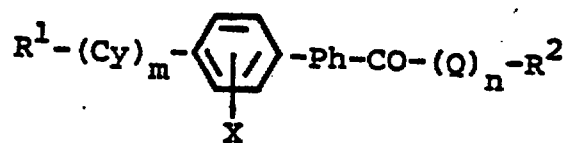
A mixture of 18% of p-(trans-4-propylcyclohexyl)-benzonitrile, 26% of p-(trans-4-pentylcyclohexyl)-benzonitrile, 13% p-ethoxyphenyl trans-4-propylcyclohexanecarboxylate, 12% of p-ethoxyphenyl trans-4-butylcyclohexanecarboxylate, 14% of p-methoxyphenyl trans-4-pentylcyclohexanecarboxylate and 17% of 4'-acetyl-2-fluoro-4-(trans-4-pentylcyclohexyl)-biphenyl has an m.p. of -14° and a c.p. of 77° .

Example C

A mixture of 13% of p-(trans-4-ethylcyclohexyl)-benzonitrile, 18% of p-(trans-4-propylcyclohexyl)-benzonitrile, 13% of p-(trans-4-butylcyclohexyl)-benzonitrile, 25% of p-(trans-4-pentylcyclohexyl)-benzonitrile, 15% of p-(trans-4-heptylcyclohexyl)-benzonitrile and 16% of 4'-acetyl-2-fluoro-4-(trans-4-pentylcyclohexyl)-biphenyl has an m.p. of -17° and a c.p. of 58° .

Patent claims

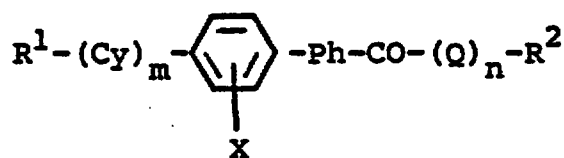
1. Halogenobiphenyl derivatives of the formula I



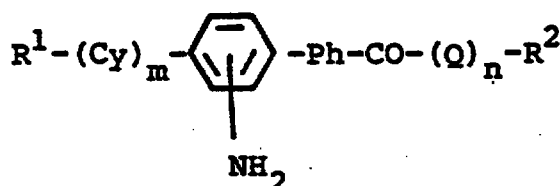
wherein R^1 and R^2 are each alkyl or alkoxy with in each case 1 - 10 C atoms, Cy is 1,4-cyclohexylene, Ph is 1,4-phenylene, Q is -O-Cy- or -O-Ph-, m and n are each 0 or 1 and X is F, Cl or Br.

2. 4'-Acetyl-2-fluoro-4-(4-trans-n-pentylcyclohexyl)-biphenyl.

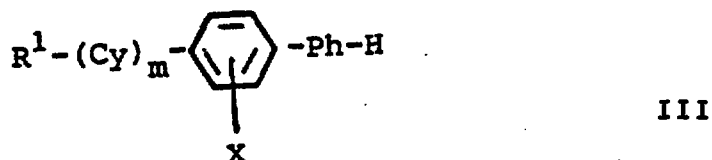
3. Process for the preparation of halogenobiphenyl derivatives of the formula I



wherein R^1 and R^2 are each alkyl or alkoxy with in each case 1 - 10 C atoms, Cy is 1,4-cyclohexylene, Ph is 1,4-phenylene, Q is -O-Cy- or -O-Ph-, m and n are each 0 or 1 and X is F, Cl or Br, characterised in that an aminobiphenyl derivative of the formula II



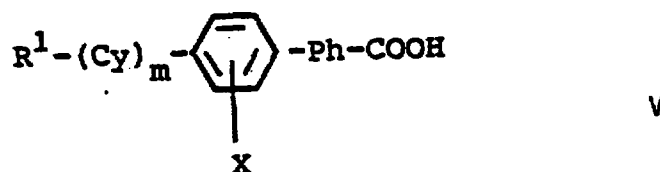
wherein R^1 , R^2 , Cy, Ph, Q, m and n have the meaning given in the case of formula I, is diazotised and the diazonium group is then replaced by an X atom by known methods, or in that, for the preparation of a compound of the formula I (R^2 is alkyl, n is 0), a halogenobiphenyl derivative of the formula III



wherein R^1 , Cy, Ph, m and X have the meaning given in the case of formula I, is reacted with a carboxylic acid of the formula IV



wherein R^3 is alkyl with 1 - 10 C atoms, or with one of its reactive derivatives, in the presence of an acid or a Lewis acid, or in that, for the preparation of a compound of the formula I (R^2 is alkoxy and/or n is 1), a carboxylic acid of the formula V



wherein R^1 , Cy, Ph, m and X have the meaning given in the case of formula I, or one of its reactive derivatives, is reacted with a hydroxy compound of the formula VI



wherein R^4 is alkoxy with 1 - 10 C atoms, or, if n is 1, can also be alkyl with 1 - 10 C atoms, and Q and n have the meaning given in the case of formula I, or one of its reactive derivatives.

4. Use of the compounds of the formula I according to Claim 1 as components of liquid crystal dielectrics for electrooptical display elements.

5. Liquid crystal dielectric for electrooptical display elements with at least two liquid crystal components, characterised in that at least one component is a compound of the formula I according to Claim 1.

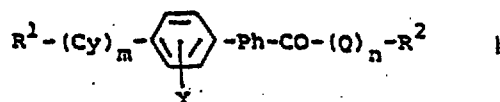
6. Electrooptical display element based on a liquid crystal cell, characterised in that the liquid crystal cell contains a dielectric according to Claim 5.



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Claims (as printed)

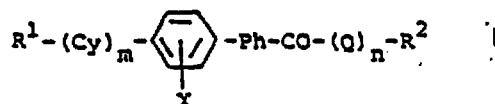
1. Halogenobiphenyl derivatives of the formula I



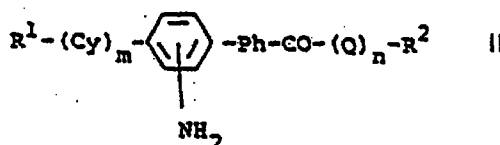
wherein R^1 and R^2 are each alkyl or alkoxy with in each case 1-10 C atoms, Cy is 1,4-cyclohexylene, Ph is 1,4-phenylene, Q is $-\text{O}-\text{Cy}-$ or $-\text{O}-\text{Ph}-$, m and n are each 0 or 1 and X is F, Cl or Br.

2. 4'-Acetyl-2-fluoro-4-(4-trans-n-pentylcyclohexyl)biphenyl.

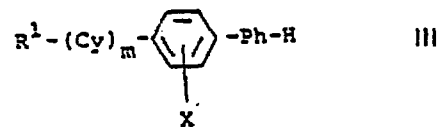
3. Process for the preparation of halogenobiphenyl derivatives of the formula I



wherein R^1 and R^2 are each alkyl or alkoxy with in each case 1-10 C atoms, Cy is 1,4-cyclohexylene, Ph is 1,4-phenylene, Q is $-\text{O}-\text{Cy}-$ or $-\text{O}-\text{Ph}-$, m and n are each 0 or 1 and X is F, Cl or Br, characterised in that an aminobiphenyl derivative of the formula II



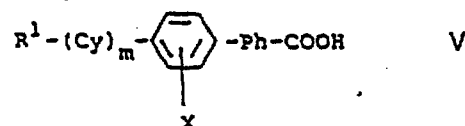
wherein R^1 , R^2 , Cy, Ph, Q, m and n have the meaning given in the case of formula I, is diazotised and the diazonium group is then replaced by an X atom by known methods, or in that, for the preparation of a compound of the formula I (R^2 is alkyl, n is 0), a halogenobiphenyl derivative of the formula III



wherein R^1 , Cy, Ph, m and X have the meaning given in the case of formula I, is reacted with a carboxylic acid of the formula IV



wherein R^3 is alkyl with 1-10 C atoms, or with one of its reactive derivatives, in the presence of an acid or a Lewis acid, or in that, for the preparation of a compound for the formula I (R^2 is alkoxy and/or n is 1), a carboxylic acid of the formula V



wherein R^1 , Cy, Ph, m and X have the meaning given in the case of formula I, or one of its reactive derivatives, is reacted with a hydroxy compound of the formula VI



wherein R^4 is alkoxy with 1-10 C atoms, or, if n is 1, can also be alkyl with 1-10 C atoms, and Q and n have the meaning given in the case of formula I, or one of its reactive derivatives.

4. Use of the compounds of the formula I according to Claim 1 as components of liquid crystal dielectrics for electrooptical display elements.

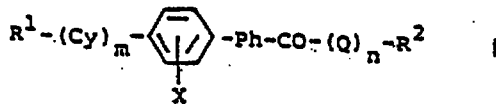
5. Liquid crystal dielectric for electrooptical display elements with at least two crystal components, characterised in that at least one component is a compound of the formula I according to Claim 1.

6. Electrooptical display element based on a liquid crystal cell, characterised in that the liquid crystal cell contains a dielectric according to Claim 5.



Revendications (as printed)

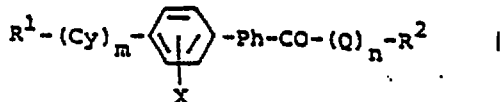
1. Dérivés d'halogènebiphényle de formule I



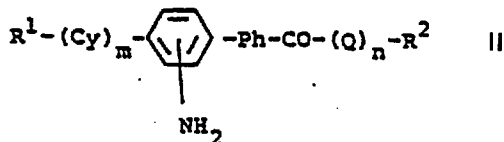
où
R¹ et R² représentent chacun un alcoyle avec à chaque fois de 1 à 10 atomes de carbone,
Cy représente un 1,4-cyclohexylène,
Ph représente un 1,4-phénylène,
Q représente -O-Cy- ou -O-Ph-
m et n valent l'un et l'autre 0 ou 1 et
X représente F, Cl ou Br.

2. 4'-Acétyl-2-fluoro-4-(4-trans-n-pentylcyclohexyl)biphényle.

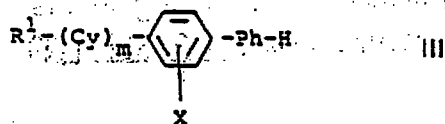
3. Procédé de préparation de dérivés d'halogènebiphényle de formule I



où
R¹ et R² représentent chacun un alcoyle ou un alcoyle avec à chaque fois de 1 à 10 atomes de carbone,
Cy représente un 1,4-cyclohexylène,
Ph représente un 1,4-phénylène,
Q représente -O-Cy- ou -O-Ph-
m et n valent l'un et l'autre 0 ou 1 et
X représente F, Cl ou Br,
caractérisé en ce qu'on diazote un dérivé d'aminobiphényle de formule II



où
R¹, R², Cy, Ph, Q, m et n ont la signification donnée pour la formule I, puis en ce qu'on remplace le groupe diazonium selon des procédés connus par un atome de X ou en ce que pour préparer un composé de formule I (R² = alcoyle, n = 0) on fait réagir un dérivé d'halogènebiphényle de formule III

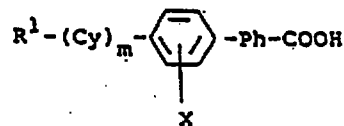


où
R¹, Cy, Ph, m et X ont la signification donnée pour la formule I avec un acide carboxylique de formule IV



IV

où
R³ représente un alcoyle en C1 à C10, ou avec un de ses dérivés réactifs en présence d'un acide ou d'un acide de Lewis, ou en ce que pour préparer un composé de formule I (R² = alcoyle et/ou n = 1) on fait réagir un acide carboxylique de formule V



où
R¹, Cy, Ph, m et X ont la signification donnée pour la formule I, ou un de ses dérivés réactifs, avec un composé hydroxy de formule VI



VI

où
R⁴ représente un alcoyle en C1 à C10 et peut également, si n = 1, représenter un alcoyle en C1 à C10 et
Q et n ont la signification donnée pour la formule I, ou avec un de ses dérivés réactifs.

4. Application des composés de formule I selon la revendication 1 comme composants de diélectriques à cristaux liquides pour éléments d'affichage électro-optiques.

5. Diélectrique à cristaux liquides pour éléments d'affichage électro-optiques avec au moins deux composants à cristaux liquides, caractérisé en ce qu'au moins un composant est un composé de formule I selon la revendication 1.

6. 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 5.

