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Liquid crystal 4-fluorobiphenyl derivatives

This invention is concerned with certain novel 4-fluorobiphenyl derivatives, with a process for their preparation, with their use in liquid crystalline dielectrics, and with electro-optical display elements comprising such dielectrics.

We have found that 4-fluorobiphenyl derivatives of formula I:



in which X is -CO-O- or -O-CO-, Z is 1,4-phenylene or 1,4-cyclohexylene, and R is alkyl, alkoxy or alkanoyloxy, each having 1 to 8 C atoms, are useful as components of liquid crystalline dielectrics, in particular for electro-optical display elements which are based on the principle of the twisted cell.

Mixtures of compounds having a positive dielectric anisotropy are, in general, used in twisted cell displays. Suitable components of such mixtures are, for example, esters, most of which, however, have only a low positive dielectric anisotropy. p-Cyanophenyl esters have a high positive dielectric anisotropy, but it is combined with a relatively high viscosity which restricts their applicability. It is a particular advantage of the compound of formula I that they have a high positive dielectric anisotropy and a relatively

low viscosity. When used in mixtures with other suitable liquid crystal compounds, they provide liquid crystalline dielectrics which have short switching times at low temperatures.

5 The 4-fluorobiphenyl derivatives of formula I are novel and constitute an aspect of the present invention.

The compounds of formula I are colourless in the pure state and form liquid crystalline mesophases in a range of temperatures which is favourable for electro-
10 optical use.

Preferred compounds of formula I are 4'-fluorobiphenyl-4-yl benzoates and cyclohexane carboxylates of formula Ia and Ib:

	Fb-O-CO-Ph-R	Ia
15	Fb-O-CO-Cy-R	Ib

in which Fb is a 4'-fluorobiphenyl-4-yl radical; Cy is a 1,4-cyclohexylene radical, and Ph is a 1,4-phenylene radical.

Formula I also includes the phenyl 4'-fluorobiphenyl-
20 4-yl carboxylates of formula Ic and the cyclohexyl 4'-fluorobiphenyl-4-yl carboxylates of formula Id:

	Fb-CO-O-Ph-R	Ic
	Fb-CO-O-Cy-R	Id

in which R, Fb, Cy and Ph have the above-stated meanings.

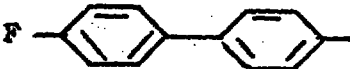
25 In the compounds of formulae I and Ib and Id, those stereoisomers are preferred in which the two 1,4-substituents are in the trans-position with respect to one another.

In the compounds of formula I, the R radical is
30 preferably straight chain and is thus preferably methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, methoxy, ethoxy, n-propyloxy, n-butyloxy, n-pentyloxy, n-heptyloxy, n-octyloxy, formyloxy, acetoxy, propionyloxy, butyryloxy, pentanoyloxy, hexanoyloxy,
35 heptanoyloxy or octanoyloxy.

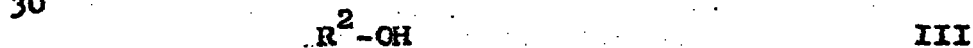
Compounds of formula I in which the R group is branched can sometimes be of importance in conventional liquid crystalline materials because of their better solubility, but they are of particular importance as chiral doping materials when they have optical activity due to the chain branching. In general, branched R groups should contain not more than one chain branching. Preferred branched R groups are isopropyl, 2-methylpropyl, 2-methylbutyl, 3-methylbutyl, 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 1-methylhexyl, 1-methylheptyl, isopropyloxy, 2-methylpropyloxy, 2-methylbutyloxy, 3-methylbutyloxy, 2-methylpentyloxy, 3-methylpentyloxy, 2-ethylhexyloxy, 1-methylhexyloxy, 1-methylheptyloxy, isobutyryloxy, 2-methylbutyryloxy, 3-methylbutyryloxy, 3-ethylbutyryloxy, 2-ethylbutyryloxy, 2-, 3- or 4-methylpentanoyloxy and 2- or 3-ethylpentanoyloxy. All R groups contain 1 - 8, and preferably 3 - 5, C atoms. Alkyl groups are, in general, preferred to alkoxy and alkanoyloxy groups.

According to another aspect of the invention, there is provided a process for the preparation of a compound of formula I, which comprises reacting a carboxylic acid of formula II:

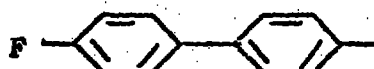


in which R^1 is (a)  or (b) R-Z-,

and R and Z have the above-stated meanings, or a reactive derivative thereof, with a hydroxy compound of formula III:



in which R^2 , in case (a), is R-Z-, or in case (b), is



, and R and Z have the above-stated meanings, or a reactive derivative thereof.

This esterification reaction can in principle, be carried out under conventional conditions as described in the literature (for example, in such standard works as Houben-Weyl, Methoden der Organischen Chemie (Methods of Organic Chemistry), Georg-Thieme-Verlag, Stuttgart). Use can also be made of process variants which are known per se, but which are not mentioned in more detail here.

The starting materials can, if desired, be formed in situ in such a manner that they are not isolated from the reaction mixture, but are immediately reacted further to give the compounds of formula I.

Particularly suitable reactive derivatives of the carboxylic acids of formula II are the acid halides, particularly the chlorides and bromides, and the anhydrides, including mixed anhydrides of the formula $R^1-CO-O-COCH_3$, azides, and esters, in particular alkyl esters having 1 - 4 C atoms in the alkyl group.

Particularly suitable reactive derivatives of the alcohols or phenols of formula III are the corresponding metal alcoholates or phenolates of the formula R^2-OM , in which M is one equivalent of a metal, preferably an alkali metal, such as Na or K.

The esterification is advantageously carried out in the presence of an inert solvent. Suitable solvents include, for example: ethers, such as diethyl ether, di-n-butyl ether, tetrahydrofuran, dioxan or anisole; ketones, such as acetone, butanone or cyclohexanone; amides, such as dimethylformamide or phosphoric hexamethyltri-*amide*; hydrocarbons, such as benzene, toluene or xylene; halogenated hydrocarbons, such as carbon tetrachloride or tetrachloroethylene; and sulfoxides, such as dimethyl sulphoxide or sulpholane. Solvents which are immiscible with water can advantageously be used at the same time for azeotropic removal of the water formed in the esterification. If appropriate, an

excess of an organic base, for example pyridine, quinoline or triethylamine, can be used as the solvent for the esterification. The esterification can also be carried out in the absence of a solvent, for example by simply heating the reactants in the presence of sodium acetate.

The reaction temperature is suitably from -50° to $+250^{\circ}\text{C}$, and preferably from -20° to $+80^{\circ}\text{C}$. At these temperatures, the esterification reaction is generally complete in from 15 minutes to 48 hours.

10 The specific preferred reaction conditions for the esterification largely depend on the nature of the starting materials used. Thus, it is generally preferred to react a free carboxylic acid of formula II with an alcohol or phenol of formula III in the presence of a strong acid, for example a mineral acid, such as hydrochloric or sulphuric acid.

A preferred embodiment of the process is to react an acid anhydride or, in particular, an acid chloride with an alcohol, preferably in a basic medium, which is preferably provided by an alkali metal hydroxide, such as sodium or potassium hydroxide, an alkali metal carbonate or bicarbonate, such as sodium carbonate, sodium bicarbonate, potassium carbonate or potassium bicarbonate, an alkali metal acetate, such as sodium or potassium acetate, or an alkaline earth metal hydroxide, such as calcium hydroxide, or an organic base, such as triethylamine, pyridine, lutidine, collidine or quinoline.

Another preferred embodiment of the process comprises initially converting the hydroxy compound of formula III, which is to be esterified, into the corresponding sodium or potassium alcoholate or phenolate, for example by treating with ethanolic sodium or potassium hydroxide solution, isolating the latter and suspending it, together with sodium bicarbonate or potassium

carbonate, with stirring, in acetone or diethyl ether and adding to this suspension a solution of the acid chloride or anhydride in diethyl ether, acetone or dimethylformamide, preferably at a temperature of from -25° to +20°C.

The starting materials of formulae II and III and their respective derivatives are for the most part known; insofar as they are not known they can be prepared without difficulty by standard processes in organic chemistry from known compounds.

According to a further aspect of the invention, there is provided a liquid crystalline dielectric for an electro-optical display element, which comprises at least one compound of formula I.

The dielectrics according to the invention may consist of 2 to 15, preferably 3 to 12, compounds, including at least one compound of formula I. The other constituents are nematic or nematogenic compounds from the classes of azoxybenzenes, benzylideneanilines, biphenyls, terphenyls, phenyl or cyclohexyl benzoates, phenyl or cyclohexyl cyclohexanecarboxylates, phenylcyclohexanes, cyclohexylbiphenyls, cyclohexylcyclohexanes, cyclohexylnaphthalenes, 1,4-biscyclohexylbenzenes, 4,4'-biscyclohexylbiphenyls, phenylpyrimidines or cyclohexylpyrimidines, phenyldioxanes or cyclohexyldioxanes, 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 are of the formula

IV:



IV

in which C and D are each a carbocyclic 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 and 1,3-dioxane rings, 2,6-disubstituted naphthalene, dihydronaphthalene and tetrahydronaphthalene, quinazoline and tetrahydroquinazoline, B is

5	-CH=CH-	-N(O)=N-
	-CH=CY-	-CH=N(O)-
	-C≡C-	-CH ₂ -CH ₂ -
	-CO-O-	-CH ₂ -O-
	-CO-S-	-CH ₂ -S-
10	-CH=N-	-COO-Ph-COO-

or a C-C single bond, Y is halogen, preferably chlorine, or -CN, and R¹ and R² are alkyl, alkoxy, alkanoyloxy or alkoxycarbonyloxy, having 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, R¹ and R² are different from one another, one of these radicals being an alkyl or alkoxy group in most cases. Substituents other than those mentioned are, however, also common. Many such substances, and mixtures thereof, are commercially available.

The dielectric according to the invention preferably contains from 0.1 to 30, in general at least 5, and more preferably 10 - 25, % of the compound(s) of formula I. However, the invention also comprises those liquid crystalline dielectrics which contain less than 5%, for example 0.1 to 3%, of one or more compounds of formula I, for example for doping purposes.

The preparation of the dielectric according to the invention is carried out in conventional manner. In general, the desired amount of the minor components is dissolved in the main constituent, preferably at an elevated temperature. If a temperature above the clear point of the main constituent is used for this procedure, the completion of dissolution can be observed with particular ease.

The liquid crystalline dielectrics according to the invention can be modified by the addition of suitable additives in such a way that they can be used in all known types of liquid crystal display elements.

5 Suitable additives for this purpose are known to those skilled in the art and are extensively described in the relevant literature. For example, it is possible to add dichroic dyes or compounds which are intended to modify the dielectric anisotropy, the viscosity, the
10 conductivity and/or the orientation of the nematic phases. Additives of these kinds are described, for example, in German OLS 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.

 In order that the invention may be more fully
15 understood, the following examples are given by way of illustration.

 In the examples, m.p. denotes the melting point, and c.p. denotes the clear point of a liquid crystalline compound. All parts or percentages are by weight; all
20 temperatures are given in degrees Celsius.

Example 1

 A solution of 18.8 g of trans-4-propylcyclohexane-carbonyl chloride in 20 ml of toluene is added dropwise to a solution of 18.8 g of 4'-fluoro-4-hydroxybiphenyl
25 and 8 g of pyridine in 25 ml of toluene and the mixture is heated, with stirring, at 80° for 20 hours. After cooling, water is added, the phases are separated, the organic phase is washed, evaporated and 4'-fluorobiphenyl-4-yl-(trans-4-propylcyclohexane)-carboxylate is
30 obtained, m.p. 96°, c.p. 174°.

Examples 2 to 100

 The following compounds are obtained by esterification of the corresponding acids by the procedure of Example 1:

35 2. 4'-fluorobiphenyl-4-yl-(trans-4-methylcyclohexane)-

- carboxylate.
3. 4'-fluorobiphenyl-4-yl-(trans-4-ethylcyclohexane)-
carboxylate.
4. 4'-fluorobiphenyl-4-yl-(trans-4-butylcyclohexane)-
5 carboxylate.
5. 4'-fluorobiphenyl-4-yl-(trans-4-pentylcyclohexane)-
carboxylate.
6. 4'-fluorobiphenyl-4-yl-(trans-4-(2-methylbutyl)-
cyclohexane)-carboxylate.
- 10 7. 4'-fluorobiphenyl-4-yl-(trans-4-hexylcyclohexane)-

- carboxylate.
8. 4'-fluorobiphenyl-4-yl-(trans-4-heptylcyclohexane)-
carboxylate.
9. 4'-fluorobiphenyl-4-yl-(trans-4-octylcyclohexane)-
carboxylate.
- 5 10. 4'-fluorobiphenyl-4-yl-(trans-4-(1-methylheptyl)-
cyclohexane-carboxylate.
11. 4'-fluorobiphenyl-4-yl-(trans-4-methoxycyclohexane)-
carboxylate.
- 10 12. 4'-fluorobiphenyl-4-yl-(trans-4-ethoxycyclohexane)-
carboxylate.
13. 4'-fluorobiphenyl-4-yl-(trans-4-propoxycyclohexane)-
carboxylate.
14. 4'-fluorobiphenyl-4-yl-(trans-4-butoxycyclohexane)-
carboxylate.
- 15 15. 4'-fluorobiphenyl-4-yl-(trans-4-pentyloxycyclohexane)-
carboxylate.
16. 4'-fluorobiphenyl-4-yl-(trans-4-hexyloxycyclohexane)-
carboxylate.
- 20 17. 4'-fluorobiphenyl-4-yl-(trans-4-heptyloxycyclohexane)-
carboxylate.
18. 4'-fluorobiphenyl-4-yl-(trans-4-octyloxycyclohexane)-
carboxylate.
19. 4'-fluorobiphenyl-4-yl-(trans-4-formyloxycyclohexane)-
carboxylate.
- 25 20. 4'-fluorobiphenyl-4-yl-(trans-4-acetoxycyclohexane)-
carboxylate.
21. 4'-fluorobiphenyl-4-yl-(trans-4-propionyloxycyclohexane)-
carboxylate.

19

22. 4'-fluorobiphenyl-4-yl-(trans-4-butyryloxycyclohexane)-carboxylate.
23. 4'-fluorobiphenyl-4-yl-(trans-4-pentanoyloxycyclohexane)-carboxylate.
- 5 24. 4'-fluorobiphenyl-4-yl-(trans-4-hexanoyloxycyclohexane)-carboxylate.
25. 4'-fluorobiphenyl-4-yl-(trans-4-heptanoyloxycyclohexane)-carboxylate.
26. 4'-fluorobiphenyl-4-yl-(trans-4-octanoyloxycyclohexane)-carboxylate.
- 10
27. 4'-fluorobiphenyl-4-yl p-methylbenzoate.
28. 4'-fluorobiphenyl-4-yl p-ethylbenzoate.
29. 4'-fluorobiphenyl-4-yl p-propylbenzoate.
30. 4'-fluorobiphenyl-4-yl p-butylbenzoate.
- 15 31. 4'-fluorobiphenyl-4-yl p-pentylbenzoate.
32. 4'-fluorobiphenyl-4-yl p-(2-methylbutyl)benzoate.
33. 4'-fluorobiphenyl-4-yl p-hexylbenzoate.
34. 4'-fluorobiphenyl-4-yl p-heptylbenzoate.
35. 4'-fluorobiphenyl-4-yl p-octylbenzoate.
- 20 36. 4'-fluorobiphenyl-4-yl p-(1-methylheptyl)benzoate.
37. 4'-fluorobiphenyl-4-yl p-methoxybenzoate.
38. 4'-fluorobiphenyl-4-yl p-ethoxybenzoate.
39. 4'-fluorobiphenyl-4-yl p-propoxybenzoate.
40. 4'-fluorobiphenyl-4-yl p-butoxybenzoate.
- 25 41. 4'-fluorobiphenyl-4-yl p-pentyloxybenzoate.
42. 4'-fluorobiphenyl-4-yl p-hexyloxybenzoate.
43. 4'-fluorobiphenyl-4-yl p-heptyloxybenzoate.
44. 4'-fluorobiphenyl-4-yl p-octyloxybenzoate.
45. 4'-fluorobiphenyl-4-yl p-formyloxybenzoate.

46. 4'-fluorobiphenyl-4-yl p-acetoxybenzoate.
47. 4'-fluorobiphenyl-4-yl p-propionyloxybenzoate.
48. 4'-fluorobiphenyl-4-yl p-butyryloxybenzoate.
49. 4'-fluorobiphenyl-4-yl p-pentanoyloxybenzoate.
- 5 50. 4'-fluorobiphenyl-4-yl p-hexanoyloxybenzoate,
m.p. 124°, c.p. 199°.
51. 4'-fluorobiphenyl-4-yl p-heptanoyloxybenzoate.
52. 4'-fluorobiphenyl-4-yl p-octanoyloxybenzoate.
53. p-methylphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
- 10 54. p-ethylphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
55. p-propylphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
56. p-butylphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
57. p-pentylphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
58. p-hexylphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
- 15 59. p-heptylphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
60. p-octylphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
61. p-methoxyphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
62. p-ethoxyphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
63. p-propoxyphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
- 20 64. p-butoxyphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
65. p-pentyloxyphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
66. p-hexyloxyphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
67. p-heptyloxyphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
68. p-octyloxyphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
- 25 69. p-formyloxyphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
70. p-acetoxyphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
71. p-propionyloxyphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
72. p-butyryloxyphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
73. p-pentanoyloxyphenyl 4'-fluorobiphenyl-4-ylcarboxylate.

74. p-hexanoyloxyphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
75. p-heptanoyloxyphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
76. p-octanoyloxyphenyl 4'-fluorobiphenyl-4-ylcarboxylate.
77. (trans-4-methylcyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
- 5 78. (trans-4-ethylcyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
79. (trans-4-propylcyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
- 10 80. (trans-4-butylcyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
81. (trans-4-pentylcyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
82. (trans-4-hexylcyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
- 15 83. (trans-4-heptylcyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
84. (trans-4-octylcyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
- 20 85. (trans-4-methoxycyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
86. (trans-4-ethoxycyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
87. (trans-4-propoxycyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
- 25 88. (trans-4-butoxycyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
89. (trans-4-pentyloxycyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.

90. (trans-4-hexyloxycyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
91. (trans-4-heptyloxycyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
- 5 92. (trans-4-octyloxycyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
93. (trans-4-formyloxycyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
94. (trans-4-acetoxycyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
- 10 95. (trans-4-propionyloxycyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
96. (trans-4-butyryloxycyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
- 15 97. (trans-4-pentanoyloxycyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
98. (trans-4-hexanoyloxycyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
99. (trans-4-heptanoyloxycyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.
- 20 100. (trans-4-octanoyloxycyclohexyl)-4'-fluorobiphenyl-4-yl-carboxylate.

The following examples of liquid crystalline dielectrics containing compounds of formula I are given by way of illustration.

Example A

A dielectric consisting of:

25% of p-(trans-4-propylcyclohexyl)benzonitrile,

37% of p-(trans-4-pentylcyclohexyl)benzonitrile,

30 25% of p-(trans-4-heptylcyclohexyl)benzonitrile,

and

13% of 4'-fluorobiphenyl-4-yl-(trans-4-propylcyclohexane)-carboxylate

has the following properties: m.p. -6° ; c.p. $+65^{\circ}$.

35 Example B

A dielectric consisting of:

- 16% of p-(trans-4-ethylcyclohexyl)benzonitrile,
- 27% of p-(trans-4-butylcyclohexyl)benzonitrile,
- 13% of 4-ethyl-4'-cyanobiphenyl,
- 5 18% of 4-butyl-4'-cyanobiphenyl,
- 15% of 4'-fluorobiphenyl-4-yl-(trans-4-propylcyclohexane)-carboxylate, and
- 11% of 4'-fluorobiphenyl-4-yl p-hexanoyloxybenzoate

10 has the following properties: m.p. -5° ; c.p. $+60^{\circ}$.

Example C

A dielectric consisting of:

- 34% of p-(trans-4-propylcyclohexyl)benzonitrile,
- 30% of p-(trans-4-butylcyclohexyl)benzonitrile,
- 15 10% of p-cyanophenyl p-ethylbenzoate,
- 6% of p-cyanophenyl p-propylbenzoate,
- 12% of 4'-fluorobiphenyl-4-yl-(trans-4-propylcyclohexane)-carboxylate, and
- 8% of 4'-fluorobiphenyl-4-yl p-hexanoyloxybenzoate

20 has the following properties: m.p. -3° ; c.p. $+67^{\circ}$.

Example D

A dielectric consisting of:

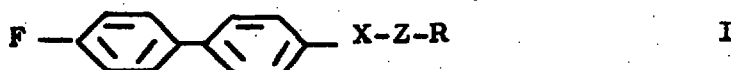
- 14% of 2-p-cyanophenyl-5-propyl-1,3-dioxane,
- 20% of 2-p-cyanophenyl-5-butyl-1,3-dioxane,
- 25 15% of 2-p-cyanophenyl-5-pentyl-1,3-dioxane,
- 21% of p-ethoxyphenyl trans-4-propylcyclohexane-carboxylate,
- 20% of p-ethoxyphenyl trans-4-butylcyclohexane-carboxylate, and
- 30 10% of 4'-fluorobiphenyl-4-yl-(trans-4-propylcyclohexane)-carboxylate

has the following properties: m.p. -4° ; c.p. $+67^{\circ}$.



CLAIMS:

1. 4-Fluorobiphenyl derivatives of formula I:

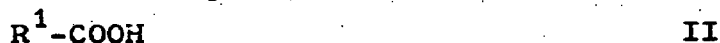


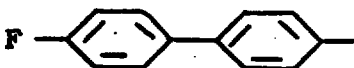
5 in which X is -CO-O- or -O-CO-, Z is 1,4-phenylene or 1,4-cyclohexylene, and R is alkyl, alkoxy or alkanoyloxy, each having 1 to 8 C atoms.

2. 4'-Fluorobiphenyl-4-yl-(trans-4-propylcyclohexane)-carboxylate.

3. 4'-Fluorobiphenyl-4-yl p-hexanoyloxybenzoate.

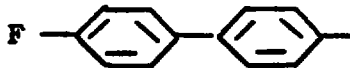
4. A process for the preparation of a 4-fluorobiphenyl derivative of formula I specified in claim 1, which comprises reacting a carboxylic acid of formula II:



- 5 in which R^1 is (a)  or (b), R-Z-, and R and Z have the meanings specified in claim 1, or a reactive derivative thereof, with a hydroxy compound of formula III:



in which R^2 , in case (a), is R-Z-, or, in case (b), is

, and R and Z have the meanings specified in claim 1, or a reactive derivative thereof.

5. A process for the preparation of a 4-fluorobiphenyl derivative of formula I specified in claim 1, substantially as herein described in any of Examples 1 to 100.



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6. A liquid crystalline dielectric for electro-optical display elements, which comprises at least one compound of formula I specified in claim 1.

7. A liquid crystalline dielectric substantially as herein described in any of Examples A to D.

8. An electro-optical display element comprising a liquid crystal cell which contains a dielectric according to claim 6 or 7.
