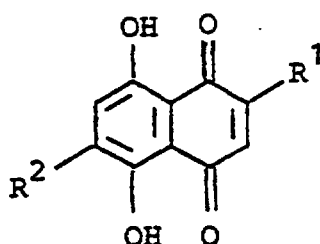


Description

The invention relates to a new liquid crystal dielectric containing one or more pleochroic dyestuffs for electrooptical display elements, characterised in that it contains at least one dyestuff of the formula I.



I

wherein R¹ and R² are identical or different and are alkyl or alkoxy with 3 to 8 C atoms or a group Z-Y-, and one of these radicals can also be hydrogen, methyl, ethyl, methoxy or ethoxy, Z is R-Ph-, R-Ph-Ph-, R-Cy-, R-Cy-Cy-, R-Cy-Ph- or R-Ph-Cy-, Ph is in each case a 1,4-phenylene radical, Cy is in each case a 1,4-cyclohexylene radical, Y is -CH₂-, -O-, -S-, -NH-, -CH₂CH₂-, -CH₂-O-, -CH₂-S-, -CH₂-NH- or a direct bond and R is hydrogen or alkyl or alkoxy with in each case 1 - 8 C atoms.

In electrooptical display elements containing liquid crystal dielectrics, the electrooptical effect of the display can be produced by embedding pleochroic dyestuffs ("guest phase") in a liquid crystal matrix ("host phase"). (In this context, compare the surveys by COX, Mol. Cryst. Liq. Cryst., Volume 55, pages 1 - 32 (1979); JONES and REEVE, ibid., Volume 60, pages 99 - 110 (1980); GRAY, Chimia, Volume 34, pages 47 - 58 (1980) and the literature quoted therein).

22

However, the dyestuffs which have hitherto been used for this, in particular the red dyestuffs hitherto used, fulfil the imposed requirements (for example high order parameter, satisfactory solubility in the host phase, and stability to UV rays and visible light and to up to voltages of about 20 V) only to an unsatisfactory extent.

The invention was based on the object of discovering pleochroic dyestuffs, in particular red dyestuffs, which do not have the disadvantages of the known dyestuffs, or display them only to a lesser extent, and are suitable as constituents of liquid crystal dielectrics. This object was achieved by providing the compounds of the formula I.

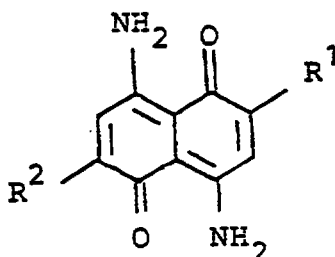
It has been found that these compounds of the formula I have a surprisingly high order parameter and are readily soluble in the liquid crystal matrix. They are also stable to UV rays and visible light and to voltages, and also have a good chemical stability.

Some of the compounds of the formula I are known, namely 2-anilino- (I, R^1 is anilino, R^2 is H; compare Helv. Chim. Acta, Volume 26, page 95 (1943)), 2-p-anisidino- (I, R^1 is p-anisidino, R^2 is H; ibid.), 2,6-bis-anilino- (I, R^1 and R^2 are anilino; ibid.), 2-p-tolylthio- (I, R^1 is p-tolylthio, R^2 is H; compare J. Chem. Soc. 1955, page 1095) and 2,6-bis-p-tolylthio-5,8-dihydroxy-1,4-naphthoquinone (I, R^1 and R^2 are p-tolylthio; ibid.). However, the use of these compounds as constituents of liquid crystal dielectrics has not yet been

described.

The invention relates to the liquid crystal dielectric mentioned, and furthermore to compounds of the general formula I, with the proviso that (a) R^1 and R^2 are not simultaneously p-tolylthio and not simultaneously anilino; (b) R^1 is only p-tolylthio, anilino or p-anisidino if R^2 is other than H; and moreover to a process for the preparation of the latter compounds, characterised in that a diaminonaphthoquinone of the formula II

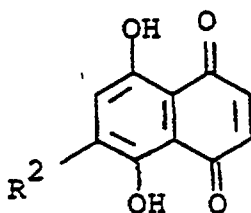
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II

wherein R^1 and R^2 have the meanings given, is hydrolysed, or in that, for the preparation of a compound of the formula I (R^1 is Z-S- or Z-NH-), a naphthazarine derivative of the formula III

15



III

wherein R^2 has the meanings given, is reacted with a compound of the formula IV



IV

20 wherein X is -S- or -NH- and Z has the meanings given.

The invention also relates to the use of a compound of the formula I according to Claim 1 as a constituent of a liquid crystal dielectric for electrooptical dis-

play elements, and to an electrooptical display element based on a guest/host liquid crystal cell, characterised in that it contains a liquid crystal dielectric according to Claim 1.

5 In the following text, R^1 , R^2 , Z, Ph, Cy, Y, R and X have the meanings given, unless expressly indicated otherwise.

In the compounds of the formulae I to IV, the alkyl and alkoxy groups are preferably straight-chain; 10 they preferably contain 3 - 7 C atoms. Accordingly, alkyl is, in particular, propyl, butyl, pentyl, hexyl or heptyl, and also preferably octyl, nonyl, decyl, isopropyl, 2-methyl-propyl, 2-methyl-butyl, 3-methyl-butyl, 2-methyl-pentyl, 3-methyl-pentyl, 1-methyl-hexyl, 2-ethyl-hexyl or 15 1-methyl-heptyl; alkoxy is, in particular, propoxy, butoxy, pentyloxy, hexyloxy or heptyloxy, and furthermore preferably octyloxy, nonyloxy, decyloxy, isopropoxy, 2-methyl-propoxy, 2-methyl-butoxy, 3-methyl-butoxy, 2-methyl-pentyl-oxy, 3-methyl-pentyloxy, 1-methylhexyloxy, 2-ethylhexyl- 20 oxy or 1-methyl-heptyloxy. The radical R and one of the radicals R^1 or R^2 can moreover also be methyl, ethyl, methoxy or ethoxy.

The radical Z is preferably R-Ph-, and the radical Y is preferably -S-, -NH- or a direct bond.

25 Accordingly, the invention particularly relates to those compounds of the formula I in which at least one of the radicals mentioned has one of the abovementioned preferred meanings. Some preferred groups of compounds may be expressed by the following part formulae Ia to Id,

which correspond to the formula I and wherein the radicals not defined in more detail have the meanings given in the case of formula I, but wherein, in

- Ia R^1 is R-Ph-Y- and
5 Y is -S-, -NH- or a direct bond;
Ib R^1 is R-Ph-S- and
 R^2 is H or R-Ph-S,
wherein the radicals R in the groups R^1 and R^2
can be identical or different;
10 Ic R^1 is R-Ph-NH- and
 R^2 is H;
Id R^1 is R-Ph- and
 R^2 is H.

In the compounds of the formula I which contain
15 cyclohexylene radicals, those stereoisomers wherein the two 1,4-substituents are each in the trans-position relative to one another are preferred.

The compounds of the formula I are moreover prepared by methods which are known per se, such as those
20 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), and in particular under reaction conditions which are known and suitable for the reactions mentioned.
25 It is also possible to use 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 further

reacted to give the compounds of the formula I.

The compounds of the formula I can be obtained, in particular, by hydrolysis of the diaminonaphthoquinones of the formula II, advantageously by reaction with a mineral acid, such as sulfuric acid, in about 2 to 98%, preferably about 10 to 30%, aqueous solution, at temperatures between about 10 and about 150°, preferably between about 60 and 110°.

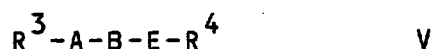
The starting substances of the formula II can be obtained, for example, by reacting the corresponding 1,5-dinitro-3-R¹-7-R²-naphthalenes with sulfur in oleum, and those of the formula II in which R¹ and/or R² are R-Ph- can also be obtained by arylation of 4,8-diamino-1,5-naphthoquinone with diazonium salts of the formula R-Ph-N₂⁺An⁻ (wherein An⁻ is an anion customary with aromatic diazonium salts, for example chloride, bromide or sulfate), or by an Ullmann reaction from 4,8-diamino-2,6-dibromo-1,5-naphthoquinone and iodobenzene derivatives of the formula R-Ph-I.

To prepare a compound of the formula I (R¹ is Z-S- or Z-NH-, in particular R-Ph-S- or R-Ph-NH-), it is furthermore possible to react a naphthazarine derivative of the formula III with a compound of the formula IV, in particular a mercaptan of the formula Z-SH or an amine of the formula Z-NH₂. This reaction is preferably carried out in the presence or absence of an additional inert solvent, at temperatures between about 0 and about 200°, preferably between 20 and 120°. Examples of suitable inert solvents are alcohols, such as methanol, ethanol and

isopropanol. An excess of the compound of the formula IV can also be used as the solvent. If naphthazarine (III, R^2 is H) itself is used, the reaction conditions can be controlled such that this compound reacts with one or two molecules of IV. If, for example, the mercaptan Z-SH is used in excess, the disubstituted product (I, R^1 and R^2 are Z-S-) is predominantly formed, and if III (R^2 is H) is used in excess, the monosubstituted product (I, R^1 is Z-S- and R^2 is H) is predominantly formed. In a similar manner, it is possible to obtain a disubstituted product (I, R^1 and R^2 are Z-NH-) by prolonged heating of III (R^2 is H) with excess amine Z-NH₂, while the monosubstituted product (I, R^1 is Z-NH-, R^2 is H) is predominantly formed at room temperature, even if the amine is used in excess.

The dielectrics according to the invention consist of 2 to 15, preferably 3 to 12, constituents, at least one of which is a naphthoquinone dyestuff of the formula I. The other constituents are preferably chosen from the nematic or nematogenic substances, in particular the known substances from the classes of azoxybenzenes, benzylidene-anilines, biphenyls, terphenyls, phenyl or cyclohexylbenzoates, 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 com-

pounds which can be used as components of liquid crystal host materials can be characterised by the formula V



wherein A and E are each a carbocyclic or heterocyclic
5 ring system from the group formed by 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,
10 quinazoline and tetrahydroquinazoline, B is -CH=CH-, -CH=CG-, -C≡C-, -CO-O-, -CO-S-, -CH=N-, -N=N-, -N(O)=N-, -CH=N(O)-, -CH₂-CH₂-, -CH₂-O-, -CH₂-S-, -COO-Ph-COO- or a C-C single bond, G is halogen, preferably chlorine, or CN, and R³ and R⁴ are alkyl, alkoxy, alkanoyloxy or alkoxycar-
15 bonyloxy with up to 18, preferably up to 8, carbon atoms, or one of these radicals is CN, NC, NO₂, CF₃, F, Cl or Br. In most of these compounds, R³ and R⁴ differ from one another, one of these radicals usually being an alkyl or alkoxy group. However, other variants of the envisaged
20 substituents can also be used. Many such substances and mixtures thereof are commercially available.

The dielectrics according to the invention contain as a rule 0.1 to 15, preferably 0.5 to 10 and in particular 1 to 5, per cent by weight of one or more compounds of the
25 formula I. The dielectrics according to the invention are prepared in a manner which is customary per se. As a rule, the constituent used in the smaller amount is dissolved in the constituent which makes up the main constituent, preferably at elevated temperature. If a temperature

above the clear point of the main constituent is chosen, it is particularly easy to observe the completeness of the solution operation.

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 guest/host display elements which have hitherto been disclosed. Such additives are known to the expert and are described in detail in the literature. For example, substances for modifying the dielectric anisotropy, the viscosity, the conductivity and/or the orientation of the nematic phases may be added. Such substances are described in, for example, German Offenlegungsschriften 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 following examples 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 degrees centigrade. Percentages are by weight.

Example 1

A suspension of 1 g of 2,6-diphenyl-4,8-diamino-1,5-naphthoquinone in 200 ml of 20% H_2SO_4 is heated at 100° for 5 hours. The mixture is cooled and extracted with CH_2Cl_2 and the extract is evaporated to give 2,6-diphenyl-5,8-dihydroxy-1,4-naphthoquinone as red needles of m.p. 170 - 173°.

Examples 2 to 51

The following compounds are obtained analogously to Example 1, by hydrolysis of the corresponding 4,8-di-



amino-1,5-naphthoquinones:

2. 2-Phenyl-5,8-dihydroxy-1,4-naphthoquinone.
3. 2-p-Tolyl-5,8-dihydroxy-1,4-naphthoquinone.
4. 2-p-Ethylphenyl-5,8-dihydroxy-1,4-naphthoquinone.
- 5 5. 2-p-n-Propylphenyl-5,8-dihydroxy-1,4-naphthoquinone.
6. 2-p-n-Butylphenyl-5,8-dihydroxy-1,4-naphthoquinone.
7. 2-p-n-Pentylphenyl-5,8-dihydroxy-1,4-naphthoquinone.
8. 2-p-n-Hexylphenyl-5,8-dihydroxy-1,4-naphthoquinone.
9. 2-p-n-Heptylphenyl-5,8-dihydroxy-1,4-naphthoquinone.
- 10 10. 2-p-n-Octylphenyl-5,8-dihydroxy-1,4-naphthoquinone.
11. 2-p-Methoxyphenyl-5,8-dihydroxy-1,4-naphthoquinone.
12. 2-p-Ethoxyphenyl-5,8-dihydroxy-1,4-naphthoquinone.
13. 2-p-n-Propoxyphenyl-5,8-dihydroxy-1,4-naphthoquinone.
14. 2-p-n-Butoxy-5,8-dihydroxy-1,4-naphthoquinone.
- 15 15. 2-p-n-Pentyloxy-5,8-dihydroxy-1,4-naphthoquinone.
16. 2-p-n-Hexyloxy-5,8-dihydroxy-1,4-naphthoquinone.
17. 2-p-n-Heptyloxy-5,8-dihydroxy-1,4-naphthoquinone.
18. 2-p-n-Octyloxy-5,8-dihydroxy-1,4-naphthoquinone.
19. 2,6-Bis-p-tolyl-5,8-dihydroxy-1,4-naphthoquinone.
- 20 20. 2,6-Bis-p-ethylphenyl-5,8-dihydroxy-1,4-naphthoquinone.
21. 2,6-Bis-p-n-propylphenyl-5,8-dihydroxy-1,4-naphthoquinone.
22. 2,6-Bis-p-n-butylphenyl-5,8-dihydroxy-1,4-naphthoquinone.
- 25 23. 2,6-Bis-p-n-pentylphenyl-5,8-dihydroxy-1,4-naphthoquinone.
24. 2,6-Bis-p-n-hexylphenyl-5,8-dihydroxy-1,4-naphthoquinone.

25. 2,6-Bis-p-n-heptylphenyl-5,8-dihydroxy-1,4-naphthoquinone.
26. 2,6-Bis-p-n-octylphenyl-5,8-dihydroxy-1,4-naphthoquinone.
- 5 27. 2,6-Bis-p-methoxyphenyl-5,8-dihydroxy-1,4-naphthoquinone.
28. 2,6-Bis-p-ethoxyphenyl-5,8-dihydroxy-1,4-naphthoquinone.
29. 2,6-Bis-p-n-propoxyphenyl-5,8-dihydroxy-1,4-naphthoquinone.
- 10 30. 2,6-Bis-p-n-butoxyphenyl-5,8-dihydroxy-1,4-naphthoquinone.
31. 2,6-Bis-p-n-pentyloxyphenyl-5,8-dihydroxy-1,4-naphthoquinone.
- 15 32. 2,6-Bis-p-n-hexyloxyphenyl-5,8-dihydroxy-1,4-naphthoquinone.
33. 2,6-Bis-p-n-heptyloxyphenyl-5,8-dihydroxy-1,4-naphthoquinone.
34. 2,6-Bis-p-n-octyloxyphenyl-5,8-dihydroxy-1,4-naphthoquinone.
- 20 35. 2,6-Dipropyl-5,8-dihydroxy-1,4-naphthoquinone.
36. 2,6-Dioctyl-5,8-dihydroxy-1,4-naphthoquinone.
37. 2,6-Dipropoxy-5,8-dihydroxy-1,4-naphthoquinone.
38. 2,6-Dioctyloxy-5,8-dihydroxy-1,4-naphthoquinone.
- 25 39. 2-Methyl-6-p-propoxyphenyl-5,8-dihydroxy-1,4-naphthoquinone.
40. 2-Ethyl-6-p-butoxyphenyl-5,8-dihydroxy-1,4-naphthoquinone.
41. 2-Methoxy-6-p-pentyloxyphenyl-5,8-dihydroxy-1,4-

- naphthoquinone.
42. 2-Ethoxy-6-p-hexyloxyphenyl-5,8-dihydroxy-1,4-naphthoquinone.
43. 2-(4'-Pentyloxy-4-biphenyl)-5,8-dihydroxy-1,4-naphthoquinone.
- 5 44. 2-(trans-4-Pentyl-cyclohexyl)-5,8-dihydroxy-1,4-naphthoquinone.
45. 2-(trans-4-(trans-4-Pentylcyclohexyl)-cyclohexyl)-5,8-dihydroxy-1,4-naphthoquinone.
- 10 46. 2-(p-trans-4-Pentylcyclohexyl-phenyl)-5,8-dihydroxy-1,4-naphthoquinone.
47. 2-(trans-4-p-Pentyloxyphenyl-cyclohexyl)-5,8-dihydroxy-1,4-naphthoquinone.
48. 2-p-Hexyloxybenzyl-5,8-dihydroxy-1,4-naphthoquinone.
- 15 49. 2-p-Hexyloxyphenoxy-5,8-dihydroxy-1,4-naphthoquinone.
50. 2-(2-p-Hexyloxyphenylethyl)-5,8-dihydroxy-1,4-naphthoquinone.
51. 2-p-Hexyloxybenzyloxy-5,8-dihydroxy-1,4-naphthoquinone.

20 Example 52

A solution of 5 g of 5,8-dihydroxy-1,4-naphthoquinone and 1.1 g of thiophenol in 500 ml of ethanol is boiled for 10 minutes and cooled. The mixture is filtered, the filtrate is concentrated to about 200 ml and the 2-phenylthio-5,8-dihydroxy-1,4-naphthoquinone which has precipitated is filtered off. m.p. 133 - 134°.

Examples 53 to 68

The following compounds are obtained analogously to Example 52, with the corresponding phenylmercaptans:

- 53. 2-p-Ethylphenylthio-5,8-dihydroxy-1,4-naphthoquinone.
- 54. 2-p-Propylphenylthio-5,8-dihydroxy-1,4-naphthoquinone.
- 55. 2-p-Butylphenylthio-5,8-dihydroxy-1,4-naphthoquinone.
- 56. 2-p-Pentylphenylthio-5,8-dihydroxy-1,4-naphthoquinone.
- 5 57. 2-p-Hexylphenylthio-5,8-dihydroxy-1,4-naphthoquinone.
- 58. 2-p-Heptylphenylthio-5,8-dihydroxy-1,4-naphthoquinone.
- 59. 2-p-Octylphenylthio-5,8-dihydroxy-1,4-naphthoquinone.
- 60. 2-p-Methoxyphenylthio-5,8-dihydroxy-1,4-naphthoquinone.
- 10 61. 2-p-Ethoxyphenylthio-5,8-dihydroxy-1,4-naphthoquinone.
- 62. 2-p-Propoxyphenylthio-5,8-dihydroxy-1,4-naphthoquinone.
- 63. 2-p-Butoxyphenylthio-5,8-dihydroxy-1,4-naphthoquinone.
- 15 64. 2-p-Pentyloxyphenylthio-5,8-dihydroxy-1,4-naphthoquinone.
- 65. 2-p-Hexyloxyphenylthio-5,8-dihydroxy-1,4-naphthoquinone.
- 20 66. 2-p-Heptyloxyphenylthio-5,8-dihydroxy-1,4-naphthoquinone.
- 67. 2-p-Octyloxyphenylthio-5,8-dihydroxy-1,4-naphthoquinone.
- 68. 2-p-Hexyloxybenzylthio-5,8-dihydroxy-1,4-naphthoquinone.
- 25

Example 69

A solution of 7 g of thiophenol in 30 ml of ethanol is added to a solution of 1.9 g of 5,8-dihydroxy-1,4-naphthoquinone in 130 ml of ethanol at 20°. The mix-

ture is boiled for 15 minutes and cooled. The 2,6-bis-phenylthio-5,8-dihydroxy-1,4-naphthoquinone is filtered off. m.p. 206 - 207°.

Examples 70 to 85

5 The following compounds are obtained analogously to Example 69, with excesses of the corresponding phenylmercaptans:

70. 2,6-Bis-(p-ethylphenylthio)-5,8-dihydroxy-1,4-naphthoquinone.
- 10 71. 2,6-Bis-(p-propylphenylthio)-5,8-dihydroxy-1,4-naphthoquinone.
72. 2,6-Bis-(p-butylphenylthio)-5,8-dihydroxy-1,4-naphthoquinone.
73. 2,6-Bis-(p-pentylphenylthio)-5,8-dihydroxy-1,4-naphthoquinone.
- 15 74. 2,6-Bis-(p-hexylphenylthio)-5,8-dihydroxy-1,4-naphthoquinone.
75. 2,6-Bis-(p-heptylphenylthio)-5,8-dihydroxy-1,4-naphthoquinone, m.p. 161 - 162°.
- 20 76. 2,6-Bis-(p-octylphenylthio)-5,8-dihydroxy-1,4-naphthoquinone.
77. 2,6-Bis-(p-methoxyphenylthio)-5,8-dihydroxy-1,4-naphthoquinone.
78. 2,6-Bis-(p-ethoxyphenylthio)-5,8-dihydroxy-1,4-naphthoquinone.
- 25 79. 2,6-Bis-(p-propoxyphenylthio)-5,8-dihydroxy-1,4-naphthoquinone.
80. 2,6-Bis-(p-butoxyphenylthio)-5,8-dihydroxy-1,4-naphthoquinone.

81. 2,6-Bis-(p-pentyloxyphenylthio)-5,8-dihydroxy-1,4-naphthoquinone.
82. 2,6-Bis-(p-hexyloxyphenylthio)-5,8-dihydroxy-1,4-naphthoquinone.
- 5 83. 2,6-Bis-(p-heptyloxyphenylthio)-5,8-dihydroxy-1,4-naphthoquinone.
84. 2,6-Bis-(p-octyloxyphenylthio)-5,8-dihydroxy-1,4-naphthoquinone.
85. 2,6-Bis-(p-hexyloxybenzylthio)-5,8-dihydroxy-1,4-naphthoquinone.
- 10

Example 86

1.9 g of 5,8-dihydroxy-1,4-naphthoquinone are introduced into 30 ml of p-toluidine and the mixture is stirred at 20° for 10 hours. After 80 ml of ethanol have been added dropwise, 2-p-toluidino-5,8-dihydroxy-1,4-naphthoquinone precipitates.

15

Examples 87 to 102

The following compounds are obtained analogously to Example 86, with the corresponding aniline derivatives:

- 20 87. 2-p-Ethylanilino-5,8-dihydroxy-1,4-naphthoquinone.
88. 2-p-Propylanilino-5,8-dihydroxy-1,4-naphthoquinone.
89. 2-p-Butylanilino-5,8-dihydroxy-1,4-naphthoquinone.
90. 2-p-Pentylanilino-5,8-dihydroxy-1,4-naphthoquinone.
91. 2-p-Hexylanilino-5,8-dihydroxy-1,4-naphthoquinone.
- 25 92. 2-p-Heptylanilino-5,8-dihydroxy-1,4-naphthoquinone.
93. 2-p-Octylanilino-5,8-dihydroxy-1,4-naphthoquinone.
94. 2-p-Methoxyanilino-5,8-dihydroxy-1,4-naphthoquinone.
95. 2-p-Ethoxyanilino-5,8-dihydroxy-1,4-naphthoquinone.
96. 2-p-Propoxyanilino-5,8-dihydroxy-1,4-naphthoquinone.

97. 2-p-Butoxyanilino-5,8-dihydroxy-1,4-naphthoquinone.
98. 2-p-Pentyloxyanilino-5,8-dihydroxy-1,4-naphthoquinone.
99. 2-p-Hexyloxyanilino-5,8-dihydroxy-1,4-naphthoquinone.
- 5 100. 2-p-Heptyloxyanilino-5,8-dihydroxy-1,4-naphthoquinone.
101. 2-p-Octyloxyanilino-5,8-dihydroxy-1,4-naphthoquinone.
102. 2-p-Hexyloxybenzylamino-5,8-dihydroxy-1,4-naphthoquinone.

10 Example 103

A mixture of 1.9 g of 5,8-dihydroxy-1,4-naphthoquinone and 40 ml of aniline is heated at 100° for 8 hours. After the mixture has been cooled and diluted with ethanol, 2,6-bis-anilino-5,8-dihydroxy-1,4-naphthoquinone is

15 obtained.

Examples 104 to 120

The following compounds are obtained analogously to Example 103, with the corresponding aniline derivatives:

104. 2,6-Bis-p-toluidino-5,8-dihydroxy-1,4-naphthoquinone.
- 20 105. 2,6-Bis-p-ethylanilino-5,8-dihydroxy-1,4-naphthoquinone.
106. 2,6-Bis-p-propylanilino-5,8-dihydroxy-1,4-naphthoquinone.
107. 2,6-Bis-p-buty lanilino-5,8-dihydroxy-1,4-naphthoquinone.
- 25 108. 2,6-Bis-p-pentylanilino-5,8-dihydroxy-1,4-naphthoquinone.
109. 2,6-Bis-p-hexylanilino-5,8-dihydroxy-1,4-naphthoquinone.

- 110. 2,6-Bis-p-heptylanilino-5,8-dihydroxy-1,4-naphtho-quinone.
- 111. 2,6-Bis-p-octylanilino-5,8-dihydroxy-1,4-naphtho-quinone.
- 5 112. 2,6-Bis-p-methoxyanilino-5,8-dihydroxy-1,4-naphtho-quinone.
- 113. 2,6-Bis-p-ethoxyanilino-5,8-dihydroxy-1,4-naphtho-quinone.
- 114. 2,6-Bis-p-propoxyanilino-5,8-dihydroxy-1,4-naphtho-10 quinone.
- 115. 2,6-Bis-p-butoxyanilino-5,8-dihydroxy-1,4-naphtho-quinone.
- 116. 2,6-Bis-p-pentyloxyanilino-5,8-dihydroxy-1,4-naphtho-quinone.
- 15 117. 2,6-Bis-p-hexyloxyanilino-5,8-dihydroxy-1,4-naphtho-quinone.
- 118. 2,6-Bis-p-heptyloxyanilino-5,8-dihydroxy-1,4-naphtho-quinone.
- 119. 2,6-Bis-p-octyloxyanilino-5,8-dihydroxy-1,4-naphtho-20 quinone.
- 120. 2,6-Bis-p-hexyloxybenzylamino-5,8-dihydroxy-1,4-naphthoquinone.

The following examples are examples of dielectrics according to the invention:

25 Example A

1% of 2-phenylthio-5,8-dihydroxy-1,4-naphthoquinone is added to a liquid crystal dielectric consisting of 18% of 4-(trans-4-propylcyclohexyl)-benzonitrile, 14% of 4-(trans-4-butylcyclohexyl)-benzonitrile, 25% of 4-(trans-

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4-pentylcyclohexyl)-benzonitrile, 15% of 4-(trans-4-heptyl-cyclohexyl)-benzonitrile, 7% of 4-(trans-4-pentylcyclohexyl)-4'-cyanobiphenyl, 7% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-biphenyl, 6% of 4-pentyl-4'-cyano-p-terphenyl and 8% of p-trans-4-propylcyclohexylphenyl trans-4-butylcyclohexanecarboxylate. The resulting dielectric exhibits a red colour with an absorption maximum at 523 nm.

Example B

10 0.8% of 2,6-bis-(p-propylphenylthio)-5,8-dihydroxy-1,4-naphthoquinone is dissolved in a liquid crystal dielectric consisting of 22% of 4-(trans-4-propylcyclohexyl)-benzonitrile, 19% of 4-(trans-4-butylcyclohexyl)-benzonitrile, 30% of 4-(trans-4-pentylcyclohexyl)-benzonitrile, 15 15% of 4-(trans-4-pentylcyclohexyl)-4'-cyanobiphenyl and 14% of 4-pentyl-4'-cyano-p-terphenyl; $\lambda_{\max}$ 538 nm.

Example C

2% of 2-p-propylphenylthio-5,8-dihydroxy-1,4-naphthoquinone is dissolved in the base dielectric mentioned in Example B; $\lambda_{\max}$ 522 nm.

Example D

1.8% of 2,6-bis-(p-heptylphenylthio)-5,8-dihydroxy-1,4-naphthoquinone is dissolved in the base dielectric mentioned in Example A; $\lambda_{\max}$ 539 nm.

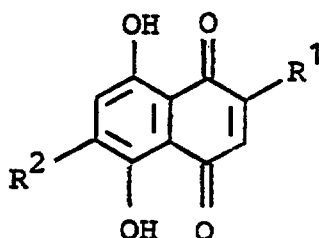
25 Example E

2.5% of 2-p-heptylphenylthio-5,8-dihydroxy-1,4-naphthoquinone is dissolved in the base dielectric mentioned in Example A; $\lambda_{\max}$ 522 nm.



Patent Claims

1. Liquid crystal dielectric containing one or more pleochroic dyestuffs for electrooptical display elements, characterised in that it contains at least one dyestuff of the formula I



I

wherein R^1 and R^2 are identical or different and are alkyl or alkoxy with 3 to 8 C atoms or a group Z-Y-, and one of these radicals can also be hydrogen, methyl, ethyl, methoxy or ethoxy, Z is R-Ph-, R-Ph-Ph-, R-Cy-, R-Cy-Cy-, R-Cy-Ph- or R-Ph-Cy-, Ph is in each case a 1,4-phenylene radical, Cy is in each case a 1,4-cyclohexylene radical, Y is $-CH_2-$, $-O-$, $-S-$, $-NH-$, $-CH_2CH_2-$, $-CH_2O-$, $-CH_2S-$, $-CH_2NH-$ or a direct bond and R is hydrogen or alkyl or alkoxy with in each case 1 - 8 C atoms.

2. Compounds of the formula I according to Claim 1, with the proviso that (a) R^1 and R^2 are not simultaneously p-tolylthio and not simultaneously anilino; (b) R^1 is only p-tolylthio, anilino or p-anisidino if R^2 is other than H.

3. Process for the preparation of compounds of the formula I according to Claim 1, with the proviso that (a) R^1 and R^2 are not simultaneously p-tolylthio and not

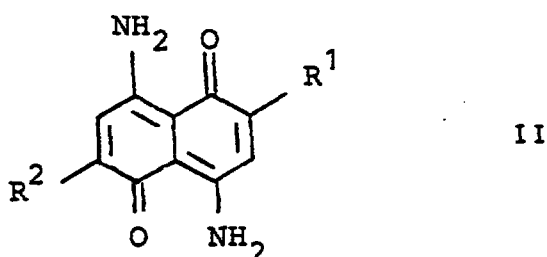


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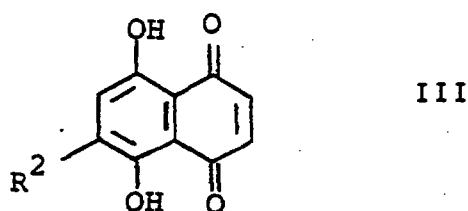
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0,085,335

simultaneously anilino; (b) R^1 is only p-tolylthio, anilino or p-anisidino if R^2 is other than H, characterised in that a diaminonaphthoquinone of the formula II



wherein R^1 and R^2 have the meanings given, is hydrolysed, or in that, for the preparation of a compound of the formula I (R^1 is Z-S- or Z-NH-), a naphthazarine derivative of the formula III



wherein R^2 has the meanings given, is reacted with a compound of the formula IV

Z-XH

IV

wherein X is -S- or -NH- and Z has the meanings given.

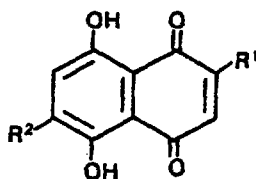
4. Use of a compound of the formula I according to Claim 1 as a constituent of a liquid crystal dielectric for electrooptical display elements.

5. Electrooptical display element, characterised in that it contains a liquid crystal dielectric according to Claim 1.

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Claims (as printed)

1. Liquid crystal dielectric containing one or more pleochroic dyestuffs for electrooptical display elements, characterised in that it contains at least one dyestuff of the formula I



wherein

R¹ and R² are identical or different and are alkyl or alkoxy with 3 to 8 C atoms or a group Z-Y, and one of these radicals can also be hydrogen, methyl, ethyl, methoxy or ethoxy,

Z is R-Ph-, R-Ph-Ph-, R-Cy-, R-Cy-Cy-, R-Cy-Ph- or R-Ph-Cy-,

Ph is in each case a 1,4-phenylene radical,

Cy is in each case a 1,4-cyclohexylene radical,

Y is -CH₂-, -O-, -S-, -NH-, -CH₂CH₂-, -CH₂-O-, -CH₂-S-, -CH₂-NH- or a direct band and

R is hydrogen or alkyl or alkoxy with in each case 1 - 8 C atoms.

2. Compounds of the formula I according to claim 1, with the proviso that

(a) R¹ and R² are not simultaneously p-tolythio and not simultaneously anilino;

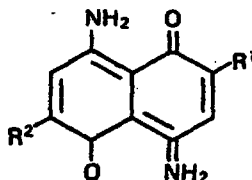
(b) R¹ is only p-tolythio, anilino or p-anisidino if R² is other than H.

3. Process for the preparation of compounds of the formula I according to claim 1, with the proviso that

(a) R¹ and R² are not simultaneously p-tolythio and not simultaneously anilino;

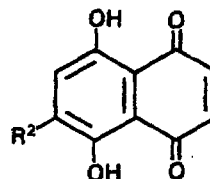
(b) R¹ is only p-tolythio, anilino or p-anisidino if R² is other than H,

characterised in that a diaminonaphthoquinone of the formula II



wherein R¹ and R² have the meanings given, is hydrolysed,

or in that, for the preparation of a compound of the formula I (R¹ is Z-S- or Z-NH-), a naphthazarine derivative of the formula III



wherein R² has the meanings given, is reacted with a compound of the formula IV



IV

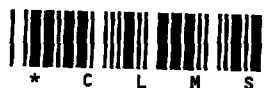
wherein

X is -S- or -NH-and

Z has the meanings given.

4. Use of a compound of the formula I according to claim 1 as a constituent of a liquid crystal dielectric for electrooptical display elements.

5. Electrooptical display element, characterised in that it contains a liquid crystal dielectric according to claim 1.

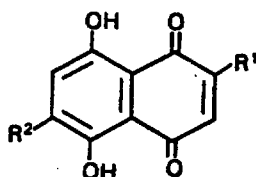


* C L M S



Revendications (as printed)

1. Diélectrique à cristaux liquides pour éléments d'affichage électro-optiques contenant un ou plusieurs colorants pléochroïques, caractérisé en ce qu'il renferme au moins un colorant de formule I



dans laquelle

R¹ et R² sont identiques ou différents et représentent un alkyle ou un alcoxy avec 3 à 8 atomes de C ou un groupe Z-Y-, l'un de ces restes représentant également l'hydrogène, un méthyle, un éthyle, un méthoxy ou un éthoxy,

Z représente R-Ph-, R-Ph-Ph-, R-Cy-, R-Cy-Cy-, R-Cy-Ph- ou R-Ph-Cy-.

Ph représente chaque fois un reste phénylène-1,4, Cy représente chaque fois un reste cyclohexylène-1,4,

Y représente -CH₂-, -O-, -S-, -NH-, -CH₂CH₂-, -CH₂-O-, -CH₂-S-, -CH₂-NH- ou une liaison directe et

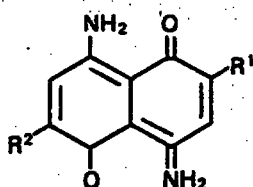
R représente l'hydrogène, un alkyle ou un alcoxy avec chaque fois 1 à 8 atomes de C.

2. Composés de formule I selon la revendication 1, dans la mesure où

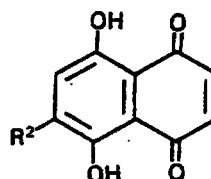
- (a) R¹ et R² ne représentent pas simultanément un p-tolylthio et pas simultanément un anilino;
- (b) R¹ ne représente un p-tolylthio, un anilino ou un p-anisidino que lorsque R² est différent de H.

3. Procédé pour la préparation de composés de formule I selon la revendication 1, dans la mesure où

- (a) R¹ et R² ne représentent pas simultanément un p-tolylthio et pas simultanément un anilino;
- (b) R¹ ne représente un p-tolylthio, un anilino ou un p-anisidino que lorsque R² est différent de H, caractérisé en ce qu'on hydrolyse un diaminonaphtoquinone de formule II



dans laquelle R¹ et R² ont la signification indiquée ou que, pour la préparation d'un composé de formule I (R¹ = Z-S- ou Z-NH-), on fait réagir un dérivé de naphazarine de formule III



dans laquelle R² a la signification indiquée, avec un composé de formule IV

Z-XH

où

X représente -S- ou -NH- et Z a la signification indiquée.

4. Utilisation d'un composé de formule I selon la revendication 1 en tant que constituant d'un diélectrique à cristaux liquides pour des éléments d'affichage électro-optiques.

5. Élément d'affichage électro-optique, caractérisé en ce qu'il contient un diélectrique à cristaux liquides selon la revendication 1.

