

"Liquid crystalline dielectrics"

The present invention is concerned with liquid crystalline dielectrics for electro-optical indicator elements based on the guest-host effect having a content of at least one pleochroitic naphthoquinone
5 dyestuff.

In the case of electro-optical indicator elements with liquid crystalline dielectrics, it is known to produce the electro-optical effect of the indication by incorporation of dichroitic or pleochroitic dyestuffs as a so-called "guest phase" into
10 a liquid crystalline matrix as a so-called "host phase" (see G.H. Heilmeyer et al., Molecular Crystals and Liquid Crystals, Volume 8, pages 293-304/1969). The dyestuff molecules of the guest phase are hereby
15 oriented by the embedding host phase, in which they are dissolved or distributed, according to the applied electrical field and, because of their pleochroitic properties, show a differing light absorption depending upon the orientation. In contra-
20 distinction to normal monochroitic dyestuffs, the amount of light absorbed by pleochroitic dyestuffs depends upon the orientation of their molecules to the electric field vector of the incident light. By application of an electrical field to the di-
25 electric distributed in a cell as thin layer, the nematic liquid crystals of the host phase and, together with these, the pleochroitic dyestuffs incorporated as guest phase, are reoriented, which leads to a change of the light absorption. The
30 practical use of this technique, referred to in the

literature as the guest-host effect, is described, for example, in Federal Republic of Germany Patent Specification No. 1,928,003. As examples of pleochroitic or dichroitic dyestuffs, there are there mentioned indo-phenol blue, indigo derivatives, azo dyestuffs and the like. The contrasts which can thereby be achieved are only sufficient for a good readability when using a polarisation foil.

According to a more recent development, such as is described, for example in Federal Republic of Germany Patent Specification No. 2,410,557, the polariser can be omitted when to the dielectric composed of nematic liquid crystals with positive dielectric anisotropy (as host phase) and pleochroitic dyestuff incorporated therein (as guest phase) there is added a small amount, for example 0.1 to 15% by weight, of an optically-active material which brings about in the liquid crystal the formation of a helical structure (cholesteric structure). Examples of such compositions, as well as the physical bases of the light absorption therein, have been described by D.L. White and G.N. Taylor (see "New Absorptive Mode Reflective Liquid Crystal Display Device", J. Appl. Physics, 45, 4718-4723/1974). Examples of the construction and operation of electro-optical display elements based on this effect are described in Federal Republic of Germany Patent Specifications Nos. 2,639,675 and 2,658,568.

In the literature, the liquid crystal indicator elements with a cholesteric oriented host phase and a dyestuff embedded therein as guest phase are frequently referred to as cholesteric guest-host displays. These CGH indicator elements have proved to be advantageous because, without polarisation foils, they provide a good indication contrast and, in addition, display a greater brightness of the depicted image.

It has been shown that the selection of appropriate dyestuffs for CGH display elements is very difficult: in the first place, the dichroitic ratio values of such systems with host phase and dyestuff embedded therein as guest phase must be sufficiently large in order to impart to the indicator cell a sufficient brightness and a sufficient contrast ratio. The contrast which can thereby be achieved depends upon the degree of order S of the dyestuff in the liquid crystalline matrix. For the degree of order, there applies the relationship

$$S = \frac{1}{2} \cdot \langle 3 \cos^2 R - 1 \rangle = \frac{E_{II} - E_I}{E_{II} + 2E_I}$$

wherein R is the angle between the longitudinal axis of the dyestuff molecule and the optical axis of the liquid crystal; E_{II} and E_I are the values of the extinction of the indicator element when the measurements are carried out with parallel orientation (E_{II}) or vertical orientation (E_I), respectively, of the liquid crystal molecules.

A value which is easier to use in everyday practice and which permits a statement regarding the degree of order S and thus regarding the technical usefulness of a dyestuff-liquid crystal combination, is the so-called dichroitic ratio V , which represents the quotient of the above-defined extinction values:

$$V = \frac{E_{II}}{E_I}$$

In technically usable dyestuff-liquid crystal combinations, the value of V is 5 or above.

In practice, the degree of order of a dyestuff depends, in the first place, upon its chemical structure, as well as upon the nature of the liquid crystalline matrix. A number of examples heretofore has been described by R.I. Cox (see "Molecular Crystals and Liquid Crystals", 55, 1-33/1979).

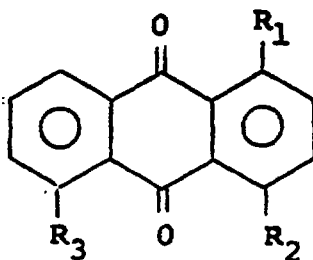
Apart from the degree of order or the dichroitic ratio, other parameters are, however, also important for the use of a dyestuff in CGH indicator elements: an absorption maximum of the dyestuff must lie in the range of the visible wavelengths, i.e. between 400 and 700 nm, and the dyestuff must be stable in the doped host phase up to a temperature of about 100°C. against alternating voltages of up to 20 V, against radiation in the infra-red, visible and ultra-violet range and against the components of the liquid-crystalline host

5

phase. Furthermore, a good solubility in the host phase and a high optical density are desirable.

However, the dyestuffs hitherto suggested for CGH indicator elements do not fulfil these requirements to a sufficient extent. In particular, the azo dyestuffs mostly suggested as being preferred for use in CGH indicator elements with regard to the dichroitic ratio and the absorption maximum have proved to be insufficiently stable towards light or ultra-violet radiation (too low a photochemical stability) and, in some cases, they are also chemically unstable. On the other hand, the photochemical and chemical stability of anthraquinone dyestuffs, which is generally higher in comparison with azo dyestuffs, is known and, indeed, proposals have been made in the literature for the use of anthraquinone dyestuffs for CGH indicator elements. However, most of the hitherto suggested anthraquinone dyestuffs have too small a dichroitic ratio V in order to make possible technically usable CGH indicator elements.

British Patent Specification No. 2,011,940 describes substituted anthraquinone dyestuffs of the general formula:-

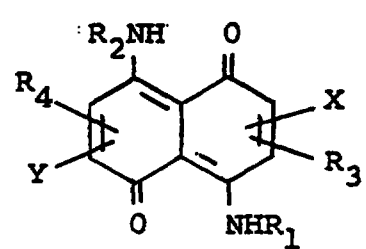


(A)

wherein R_1 is an optionally ring-substituted aniline attached via the nitrogen atom, R_2 is a hydrogen atom or a hydroxyl group and R_3 is a hydrogen atom or, when R_2 is a hydrogen atom, can also signify an optionally substituted aniline group. The dichroitic ratio of these anthraquinone dyestuffs, measured in commercially available cyanobiphenyl/cyanoterphenyl liquid crystal mixtures, is from 3.8 to 8.4, most values being from 5 to 6. However, the solubility of the dyestuffs in most conventional liquid crystalline host phases is reduced due to the aniline group. In particular, in the liquid crystalline base materials of the phenyl-cyclohexane class, which are today used to a large extent, the solubility of these dyestuffs of general formula (A) is too low for practical requirements.

It is an object of the present invention to provide liquid crystalline dielectrics containing dichroitic dyestuffs which are sufficiently well soluble in commercially available liquid crystalline base materials, for example to a minimum concentration of 0.5 wt.%. Furthermore, these dyestuffs are to have a dichroitic ratio of at least $V \gg 5$ and to be substantially chemically and photochemically stable.

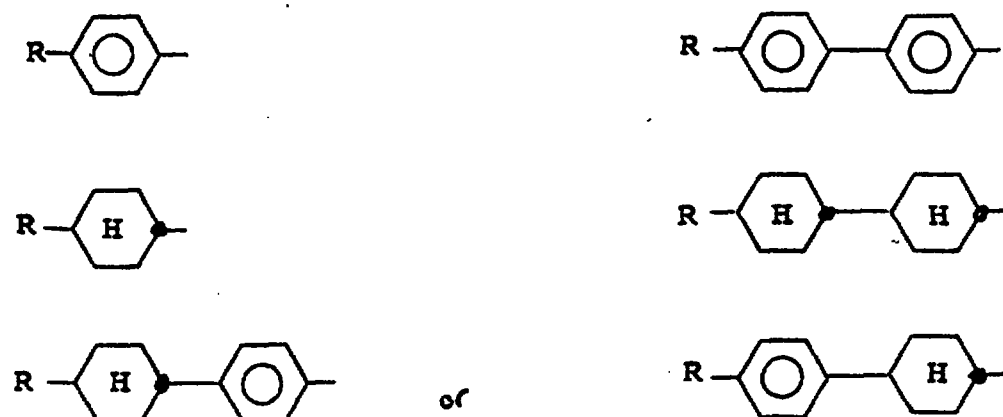
We have now found that naphthoquinone dyestuffs of the general formula:-



(I)

7

wherein X and Y, which are the same or different, are hydrogen, chlorine or bromine atoms, R_1 , R_2 , R_3 and R_4 , which are the same or different, are hydrogen atoms or alkyl or alkoxyalkyl radicals containing up to 8 carbon atoms or a cyclic group Z, Z is



and R is an alkyl, alkoxy, alkoxyalkyl, alkoxyalkoxy or alkanoyloxy radical containing up to 8 carbon atoms, with the proviso that at least one and at most two of the symbols R_1 , R_2 , R_3 and R_4 represent a cyclic group Z and when two cyclic groups Z are present, these stand either for R_1 and R_2 or for R_3 and R_4 and when the residues R_3 and R_4 are cyclic groups Z, these are in the 2- and 6- or 3- and 7-positions of the naphthalene structure, are surprisingly well soluble in conventional liquid crystalline base materials and display good dichroitic ratio values (degrees of order) therein.

The naphthoquinone dyestuffs of the general formula (I) essentially display green, blue-green, blue and violet base colours and are, therefore, a valuable

supplement to the anthraquinone dyestuffs used for the same purpose, for example according to Federal Republic of Germany Patent Specification No. 30 28 593, which preponderantly display red, orange or yellow colour shades.

Therefore, the present invention provides a liquid crystalline dielectric for electro-optical indicator elements containing at least one pleochroitic dyestuff, wherein it contains at least one naphthoquinone dyestuff of general formula (I), as well as an electro-optical indicator element based on the guest-host liquid crystal cell which contains such a dielectric.

Some of the naphthoquinone dyestuffs of general formula (I) are new compounds and these are described and claimed in our copending Patent Application No. 8418701.

In the compounds of general formula (I), the symbols X and Y signify hydrogen, chlorine or bromine atoms, compounds in which X and Y are both hydrogen atoms being preferred. Furthermore, those compounds of general formula (I) are especially preferred in which one of these substituents is a chlorine or bromine atom when the adjacent group (R_3 to X or R_4 to Y) is a hydrogen atom. When both substituents X and Y signify chlorine or bromine atoms, they are preferably the same; in this case, R_3 and R_4 are

preferably a hydrogen atom or a short-chained, unbranched alkyl radical, for example a methyl, ethyl, n-propyl or n-butyl radical.

Of the residues R_1 , R_2 , R_3 and R_4 , one or two
5 signify a cyclic group Z. When two of these residues signify a cyclic group Z, these are either the two residues R_1 and R_2 or the two radicals R_3 and R_4 . Cyclic groups Z in the meaning of the present invention are Z_{AR} signifying phenyl and Z_{cy} signifying
10 cyclohexyl rings substituted in the 4-position, all the cyclohexane rings present in the compounds of general formula (I) used according to the present invention thereby having the trans configuration; in the formulae drawings, this is indicated in each case by a black
15 spot on the right side of the cyclohexane ring. The substituents in the 4-position of the phenyl or cyclo-

hexyl rings can be alkyl radicals, alkoxy radicals, alkanoyloxy radicals, alkoxyalkyl radicals or alkoxy-alkoxy radicals with, in each case, up to 8 carbon atoms and preferably with 2 to 6 carbon atoms or can be phenyl or cyclohexyl rings substituted in the 4-position by one of these groups. Thus, examples of cyclic groups Z include the following: 4-(R)-phenyl, trans-4-(R)-cyclohexyl, 4'-(R)-biphenyl-(4)-yl, 4-[trans-4-(R)-cyclohexyl]-phenyl, trans-4-[4-(R)-phenyl]-cyclohexyl and trans-trans-4-[4-(R)-cyclohexyl]-cyclohexyl. Amongst these, because of the comparative ease of their preparation, the following are especially preferred:

4-alkylphenyl, 4-alkoxyphenyl, 4-alkanoyloxyphenyl,

4-alkoxyalkylphenyl, 4-alkoxyalkoxyphenyl;

4-alkylcyclohexyl;

4'-alkylbiphenyl-(4)-yl, 4'-alkoxybiphenyl-(4)-yl,

4'-alkanoyloxybiphenyl-(4)-yl, 4'-alkoxyalkylbiphenyl-(4)-yl;

4-(trans-4-alkylcyclohexyl)-phenyl, 4-(trans-4-alkoxy-alkylcyclohexyl)-phenyl;

trans-4-(4-alkylphenyl)-cyclohexyl, trans-4-(4-alkoxyphenyl)-cyclohexyl, trans-4-(4-alkanoyloxyphenyl)-cyclohexyl;

trans-trans-4-(4-alkylcyclohexyl)-cyclohexyl.

The substituents R in the 4-position of the cyclic groups can be straight-chained, for example, methyl,

101

11

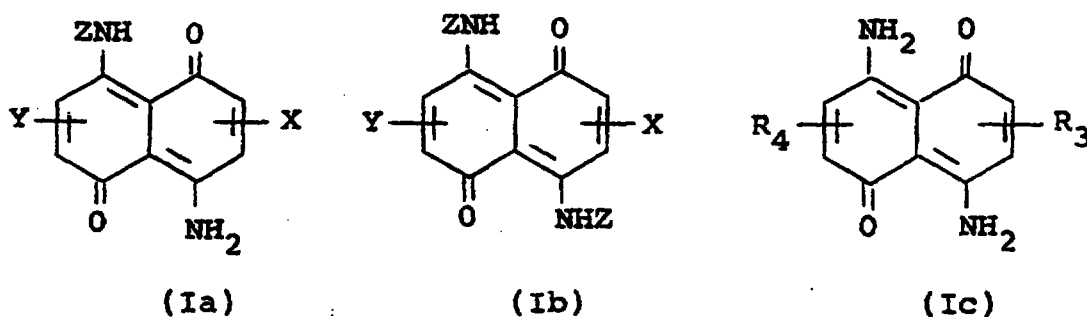
ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, methoxy, ethoxy, n-propyloxy, n-butyloxy, n-pentyloxy, n-hexyloxy, n-heptyloxy, n-octyloxy, acetoxy, propionyloxy, n-butyryloxy, n-pentanoyloxy, n-hexanoyloxy, n-heptanoyloxy, n-octanoyloxy, 2-oxa-n-propyl, 2- or 3-oxa-n-butyl, 2-, 3- or 4-oxa-n-pentyl, 2-, 3-, 4- or 5-oxa-n-hexyl, 2-, 3-, 4-, 5- or 6-oxa-n-heptyl, 2-, 3-, 4-, 5-, 6- or 7-oxa-n-octyl, 2-oxa-n-propyloxy, 2- or 3-oxa-n-butyloxy, 2-, 3- or 4-oxa-n-pentyloxy, 2-, 3-, 4- or 5-oxa-n-hexyloxy, 2-, 3-, 4-, 5- or 6-oxa-n-heptyloxy or 2-, 3-, 4-, 5-, 6- or 7-oxa-n-octyloxy; when they contain 3 or more carbon atoms or, in the case of alkanoyloxy radicals, 4 or more carbon atoms, these can also have a branched chain.

As a rule, however, in a dyestuff used according to the present invention, not more than one radical R and also, insofar as one or more of the radicals R₁, R₂, R₃ and R₄ are alkyl or alkoxyalkyl radicals, has a branched carbon chain which, in this case, is usually only branched once. Preferred alkyl radicals are those in which, on a comparatively long carbon chain, a methyl or ethyl radical is present in the 2- or 3-position, for example 2-methylpropyl, 2-methylbutyl, 3-methylbutyl, 2-methylpentyl or 2-ethylhexyl. When an alkoxy or alkanoyloxy radical is branched, these criteria also apply to the alkyl moiety of these radicals; in addition, however, alkyl moieties branched in the 1-position are

also of interest so that, as alkoxy radicals, apart from those derived from the above-mentioned alkyl radicals, there are also of importance, for example, 1-methylpropyloxy, 1-methylbutyloxy, 1-methylpentyloxy, 1-methylhexyloxy and 1-methylheptyloxy; as branched alkanoyloxy radicals, isobutyryloxy and isovaleryloxy are of special interest.

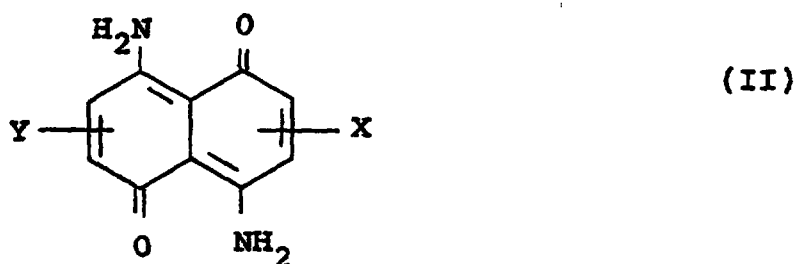
The naphthoquinone dyestuffs of general formula (I) in which all such carbon chains are unbranched are, in practical use, preferred because they usually display a higher degree of order; dyestuffs with branched-chain substituents are sometimes better soluble in some liquid crystal base mixtures; otherwise, as a rule, they are only used where, because of the chain branching, they simultaneously impart optical activity to the liquid crystalline dielectric or strengthen this.

Preferred liquid crystalline dielectrics according to the present invention are those which, as naphthoquinone dyestuffs, contain those of the general formulae:-



wherein X, Y, Z, R₃ and R₄ have the meanings given in general formula (I).

The compounds of general formula (I) are prepared in the usual way for this class of substances. Thus, compounds of general formula (Ia) are obtained by reacting an optionally halogenated 4,8-diamino-1,5-naphthoquinone of the general formula:-



with an amine $Z-NH_2$ in a mole ratio of about 1:1 under conditions known for such transaminations. The transamination reaction with an aromatic amine $Z_{AR}-NH_2$ is thereby preferably carried out by heating the reaction components in a polar solvent, for example acetic acid, methanol, ethanol, *N,N*-dimethylformamide or dimethyl sulphoxide, optionally in the presence of small amounts of up to 25% of water.

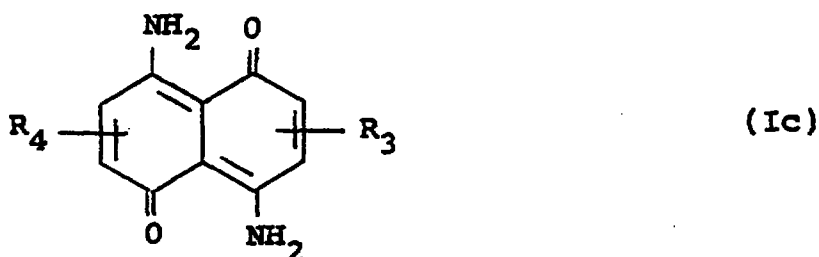
When a 4,8-diamino-1,5-naphthoquinone of general formula (II) is reacted with a cycloaliphatic amine $Z_{cy}-NH_2$, it has proved to be desirable first to convert the naphthoquinone derivative (II) into a leuco compound, for example by reduction with a stannous salt, a sulphite or a dithionite. The leuco compound is then reacted in the above-described manner with the amine $Z_{cy}-NH_2$ and the reaction product subsequently oxidised to give a compound of general formula (Ia); as

oxidation agents, there can be used all those usually employed for such reactions; advantageously, air is passed through the reaction mixture, optionally at an elevated temperature.

The compounds of general formula (Ib) are prepared in an analogous manner either by reacting a compound of general formula (Ia) in the above-described manner with an amine $Z-NH_2$ or reacting a compound of general formula (II) with about the double molar amount of such an amine. In the case of the first route, the radical Z of the amine used in the second step can be the same as or different from that of the amine used in the first step. Usually, this two-step process is only used when those compounds of general formula (Ib) are to be prepared in which the two residues Z are different. In an analogous manner, from the compounds of general formula (Ia), there can also be prepared those compounds of general formula (I) in which R_1 is an alkyl or alkoxyalkyl radical: for this purpose, in the above-described manner, the compound (Ia) is reduced to the leuco compound, this then reacted with an alkyl or alkoxyalkylamine and the reaction product again oxidised. For the preparation of those compounds (Ib) in which the two residues Z are the same, the 4,8-diamino-1,5-naphthoquinone of the formula (II) is preferably reacted with about the two fold molar amount of the amine $Z-NH_2$.

In the same way as the compounds of general formulae (Ia) and (Ib), there also are prepared those compounds of general formula (I) which otherwise correspond to the compounds (Ia) or (Ib) but are additionally substituted on the naphthoquinone ring system by one or two alkyl or alkoxyalkyl radicals; for the preparation of these compounds, appropriately substituted analogues of the compounds of general formula (II) are used as starting material.

The compounds of the general formula :-



wherein R_3 and/or R_4 signify a group Z_{AR} attached via an aromatic ring to the naphthoquinone structure, can be prepared by arylation of those compounds of general formula (II), in which X and Y signify hydrogen atoms, with aromatic diazonium compounds $Z_{AR}-N \equiv N^+A^-$, wherein A^- is an anion conventionally used in the case of aromatic diazonium salts (e.g. Cl^- , Br^- , SO_4^{2-} , BF_4^-). The diazonium compounds $Z_{AR}-N \equiv N^+A^-$ are, as a rule, prepared in the form of their aqueous solutions by conventional processes from the corresponding aromatic amines $Z_{AR}-NH_2$ and, as such, reacted with compounds of

general formula (II) at a temperature of from -5 to 40°C., molecular nitrogen thereby being split off and the cyclic group Z_{AR} entering into the free β -position of the naphthalene structure. By appropriate selection of the amount ratio of the reaction components (mole ratio of 1:1 or 1:2), compounds of general formula (Ic) can thereby be obtained in which one or both groups R_3 or R_4 signifies cyclic residues Z_{AR} . The preparation of compounds of general formula (Ic) with two residues Z_{AR} different from one another takes place in two successive arylation reactions with appropriate, different diazonium compounds $Z_{AR}-N \equiv N^+A^-$.

The compounds of general formula (Ic) can also be prepared by reacting those compounds of general formula (II), in which X or Y are chlorine or bromine atoms, with iodobenzene derivatives $Z_{AR}-I$ under the conditions of an Ullmann reaction, for example heating the reaction components in a high boiling, polar solvent, such as nitrobenzene or N,N-dimethylformamide, or in the melt, in the presence of copper powder or nickel-triphenylphosphine complexes. By appropriate choice of the amount ratio of the reaction components (mole ratio 1:1 or 1:2), the compounds of general formula (Ic) are thereby obtained in which one or both symbols R_3 or R_4 signify cyclic residues Z_{AR} . The synthesis of compounds of general formula (Ic) with two residues Z_{AR} differing from one another takes place in two successive Ullmann

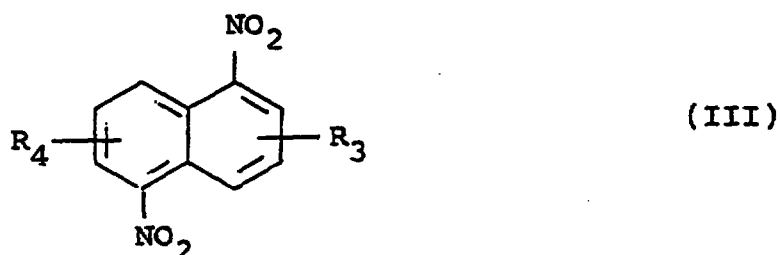
17

(25)

reactions with appropriate, different iodobenzene derivatives $Z_{AR}-I$.

Instead of a compound of general formula (II), as starting material for the Ullmann reaction there can also be used 1,5-dinitro-2,6- (or 3,7-)-dichloro-

5 naphthalene. An intermediate of the general formula:-

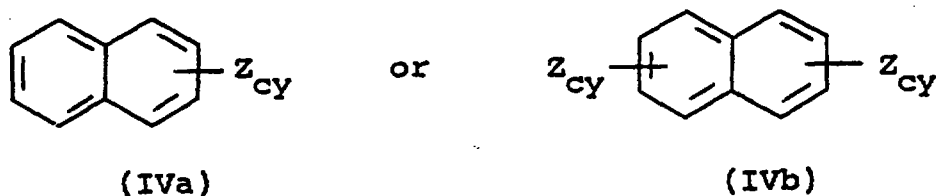


is thereby first isolated, which is then converted into a compound of general formula (Ic) in a manner

10 known for such compounds, for example by treatment with sulphur sesquioxide (see U.S. Patent Specification No. 2,238,959).

The compounds of general formula (Ic), wherein R_3 and/or R_4 signify a group Z_{cy} attached via the

15 cyclohexane ring to the naphthoquinone system, are prepared, for example, by nitration of naphthalene derivatives of the general formula:-



to give the corresponding 1,5-dinitronaphthalene

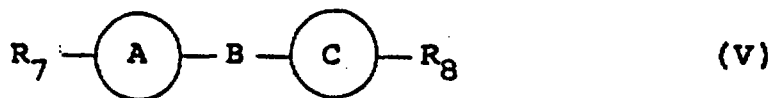
derivatives, which are then converted in the above-described manner into the desired compounds of general formula (Ic). Starting materials of general formula (IVa) are known from Federal Republic of Germany Patent Specification No. 29 29 080 and those of general formula (IVb) can be prepared in a manner analogous to the processes described therein.

For the preparation of those compounds of general formula (Ic), in which one of the symbols R_3 and R_4 signifies a group Z_{cy} and the other a group Z_{AR} , a compound of general formula (IVa) is preferably first subjected to an Ullmann reaction with an iodobenzene derivative $Z_{AR}-I$ and the reaction product thereby obtained converted via the 1,5-dinitro compound into the desired compound of general formula (Ic).

Compounds of general formula (I), wherein R_5 and/or R_6 are alkyl or alkoxyalkyl radicals, are obtained from the corresponding compounds of general formula (Ic) ($R_5 = R_6 = H$) by conversion into the leuco compound, reaction with an amine(s) R_5-NH_2 and/or R_6-NH_2 and subsequent oxidation. For the preparation of the compounds of general formula (I), in which X and/or Y are chlorine or bromine atoms, a compound of

general formula (III) is preferably halogenated in known manner and the reaction product obtained is then converted, as described above, into the naphthoquinone derivative or a compound of general formula (II), in which X and/or Y are chlorine or bromine atoms, is arylated in the above-described manner with an aromatic diazonium compound.

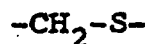
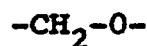
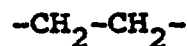
The dielectrics according to the present invention consist of 2 to 15 and preferably of 3 to 12 components, including at least one naphthoquinone dyestuff of general formula (I). The other components are selected from the nematic or nematogenic substances of the following classes: azoxybenzenes, benzylideneanilines, biphenyls, terphenyls, phenyl and cyclohexyl benzoates, cyclohexanecarboxylic acid phenyl and cyclohexyl esters, phenylcyclohexanes, cyclohexylbiphenyls, cyclohexyl-cyclohexanes, cyclohexylnaphthalenes, 1,4-bis-cyclohexyl-benzenes, 4,4'-bis-cyclohexylbiphenyls, phenyl- and cyclohexyl-pyrimidines, phenyl- and cyclohexyldioxans, optionally halogenated stilbenes, benzyl phenyl ethers, tolanes and substituted cinnamic acids. The most important compounds to be considered as components of liquid crystalline host materials can be represented by the general formula:-



wherein A and C each represent a carbo- 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-dioxan rings, 2,6-disubstituted naphthalene, di- and tetrahydro-naphthalene, quinazoline and tetrahydroquinazoline,

B is:



or a C-C single bond,

D is a halogen atom, preferably a chlorine atom, or a cyano group, and R_7 and R_8 , which can be the same or different, are alkyl, alkoxy, alkanoyloxy or alkoxy-carbonyloxy radicals containing up to 18 and preferably up to 8 carbon atoms, or one of these symbols also signifies $-\text{CN}$, $-\text{NC}$, $-\text{NO}_2$, CF_3 , F, Cl or Br. In the case of most of these compounds, R_7 and R_8 differ from one another, one of these symbols usually representing an alkyl or alkoxy radical. However, other variants of the above-mentioned substituents are also conventional. Many such substances or also mixtures thereof are commercially available. .

The dielectrics according to the present invention usually contain 0.1 to 15, preferably 0.5 to 10 and especially 1 to 5% by weight of one or more compounds of general formula (I). The dielectrics according to the present invention are prepared in the usual way. As a rule, the desired amount of the components used in lesser amount are dissolved in the components constituting the main part, preferably at an elevated temperature. If a temperature above the clear point of the main component is thereby chosen, the completeness of the dissolving process can be observed especially easily.

By means of appropriate additives, the liquid crystalline dielectrics according to the present invention can be so modified that they can be used in all previously known types of guest-host indicator elements. Such additives are well known and are described in detail in the appropriate literature. For example, substances can be added for changing the dielectric anisotropy, the viscosity, the conductivity and/or the orientation of the nematic phases. Such substances are described, for example, in Federal Republic of Germany Patent Specifications Nos. 22 09 127; 22 30 864; 23 21 632; 23 38 281 and 24 50 088.

The following Examples are given for the purpose of illustrating the present invention. If nothing is stated to the contrary, statements of percentages are percentages by weight.

Example 1.

A suspension of 25 g. 4-(trans-4-n-propylcyclohexyl)-aniline hydrochloride in 250 ml. 5% aqueous sodium hydroxide solution and 420 ml. toluene is vigorously stirred for 30 minutes at 90°C. After cooling to 20°C., the organic phase is separated off, evaporated and the residue added dropwise to a boiling solution of 9.4 g. 4,8-diamino-1,5-naphthoquinone in 100 ml. acetic acid. The reaction mixture is boiled for 6 hours, thereafter poured into 1000 ml. of water and the precipitated 4,8-bis-[4-(trans-4-n-propylcyclohexyl)-anilino]-1,5-naphthoquinone is filtered off and recrystallised from dichloromethane; m.p. 261°C.

- 15 The following compounds are prepared analogously:
- 4,8-bis-[4-(trans-4-ethylcyclohexyl)-anilino]-1,5-naphthoquinone,
- 4,8-bis-[4-(trans-4-n-butylcyclohexyl)-anilino]-1,5-naphthoquinone,
- 20 4,8-bis-[4-(trans-4-n-pentylcyclohexyl)-anilino]-1,5-naphthoquinone,
- 4,8-bis-(4-ethylanilino)-1,5-naphthoquinone, m.p. 232°C.,
- 4,8-bis-(4-n-propylanilino)-1,5-naphthoquinone,
- 4,8-bis-(4-n-butylanilino)-1,5-naphthoquinone, m.p.
- 25 164°C.,

4,8-bis-(4-n-pentylanilino)-1,5-naphthoquinone,
4,8-bis-(4-n-hexylanilino)-1,5-naphthoquinone, m.p. 151°C.,
4,8-bis-(4-methoxyanilino)-1,5-naphthoquinone,
4,8-bis-(4-ethoxyanilino)-1,5-naphthoquinone, m.p. 260°C.,
4,8-bis-(4-n-propyloxyanilino)-1,5-naphthoquinone,
4,8-bis-(4-n-butyloxyanilino)-1,5-naphthoquinone,
4,8-bis-(4-n-pentyloxyanilino)-1,5-naphthoquinone,
4,8-bis-(4-n-hexyloxyanilino)-1,5-naphthoquinone,
m.p. 166°C.,
4,8-bis-(4-n-heptyloxyanilino)-1,5-naphthoquinone,
m.p. 163°C.,
4,8-bis-(4-n-octyloxyanilino)-1,5-naphthoquinone,
m.p. 164°C.,
4,8-bis-[4-(3-oxabutyloxy)-anilino]-1,5-naphthoquinone,
m.p. 191°C.,
4,8-bis-[4-(3-oxapentyloxy)-anilino]-1,5-naphthoquinone,
4,8-bis-(trans-4-ethylcyclohexylamino)-1,5-naphthoquinone,
4,8-bis-(trans-4-n-propylcyclohexylamino)-1,5-naphtho-
quinone,
4,8-bis-(trans-4-n-butylcyclohexylamino)-1,5-naphtho-
quinone,
4,8-bis-(trans-4-n-pentylcyclohexylamino)-1,5-naphtho-
quinone,
4,8-bis-(trans-4-n-hexylcyclohexylamino)-1,5-naphtho-
quinone,
4,8-bis-(trans-4-n-heptylcyclohexylamino)-1,5-naphtho-
quinone.

Example 2.

To a solution of 9.4 g. 4,8-diamino-1,5-naphthoquinone in 100 ml. 90% acetic acid are added dropwise at 90°C., 10.8 g. 4-(trans-4-n-propylcyclohexyl)-aniline and the reaction mixture is stirred for 6 hours at this temperature. Subsequently, after cooling to ambient temperature, the reaction mixture is poured into 1000 ml. of water and the precipitated 4-(trans-4-n-propylcyclohexyl)-anilino-8-amino-1,5-naphthoquinone is filtered off and recrystallised from glacial acetic acid; m.p. 199°C.

The following compounds are prepared analogously:

- 4-(trans-4-ethylcyclohexyl)-anilino-8-amino-1,5-naphthoquinone,
- 4-(trans-4-n-butylcyclohexyl)-anilino-8-amino-1,5-naphthoquinone,
- 4-(trans-4-n-pentylcyclohexyl)-anilino-8-amino-1,5-naphthoquinone,
- 4-(4-ethylanilino)-8-amino-1,5-naphthoquinone,
- 4-(4-n-propylanilino)-8-amino-1,5-naphthoquinone,
- 4-(4-n-butylanilino)-8-amino-1,5-naphthoquinone,
- 4-(4-n-pentylanilino)-8-amino-1,5-naphthoquinone,
- 4-(4-n-hexylanilino)-8-amino-1,5-naphthoquinone,
- 4-(4-methoxyanilino)-8-amino-1,5-naphthoquinone,
- 4-(4-ethoxyanilino)-8-amino-1,5-naphthoquinone,
- 4-(4-n-propyloxyanilino)-8-amino-1,5-naphthoquinone,
- 4-(4-n-butyloxyanilino)-8-amino-1,5-naphthoquinone,

4-(4-n-pentyloxyanilino)-8-amino-1,5-naphthoquinone,
4-(4-n-hexyloxyanilino)-8-amino-1,5-naphthoquinone,
4-(4-n-heptyloxyanilino)-8-amino-1,5-naphthoquinone,
4-(4-n-octyloxyanilino)-8-amino-1,5-naphthoquinone,
4-[4-(3-oxabutyloxy)-anilino]-8-amino-1,5-naphthoquinone,
4-[4-(3-oxapentyloxy)-anilino]-8-amino-1,5-naphthoquinone,
4-(trans-4-ethylcyclohexylamino)-8-amino-1,5-naphtho-
quinone,
4-(trans-4-n-propylcyclohexylamino)-8-amino-1,5-
naphthoquinone,
4-(trans-4-n-butylcyclohexylamino)-8-amino-1,5-naphtho-
quinone,
4-(trans-4-n-pentylcyclohexylamino)-8-amino-1,5-naphtho-
quinone,
4-(trans-4-n-hexylcyclohexylamino)-8-amino-1,5-naphtho-
quinone,
4-(trans-4-n-heptylcyclohexylamino)-8-amino-1,5-naphtho-
quinone,
4-(4'-ethylbiphenyl-4-ylamino)-8-amino-1,5-naphthoquinone,
4-(4'-n-butylbiphenyl-4-ylamino)-8-amino-1,5-naphtho-
quinone,
4-(4'-n-pentylbiphenyl-4-ylamino)-8-amino-1,5-naphtho-
quinone,
4-(4'-n-hexylbiphenyl-4-ylamino)-8-amino-1,5-naphtho-
quinone,
4-(4'-n-heptylbiphenyl-4-ylamino)-8-amino-1,5-naphtho-
quinone,

4-(4'-ethoxybiphenyl-4-ylamino)-8-amino-1,5-naphthoquinone,

4-(4'-n-propyloxybiphenyl-4-ylamino)-8-amino-1,5-naphthoquinone,

4-(4'-n-pentyloxybiphenyl-4-ylamino)-8-amino-1,5-naphthoquinone,

4-(4'-n-octyloxybiphenyl-4-ylamino)-8-amino-1,5-naphthoquinone.

Example 3.

To a solution of 5 g. 2,6-dibromo-4,8-diamino-1,5-naphthoquinone in 100 ml. N,N-dimethylformamide are added at ambient temperature 13.7 g. 4-n-hexyloxyiodobenzene and 2.9 g. copper powder. The reaction mixture is heated, with stirring, to 100°C. for 50 minutes under an atmosphere of nitrogen, thereafter cooled to ambient temperature and stirred into 1000 ml. of water. The resulting precipitate is filtered off, dried and extracted with 200 ml. acetone. The extract is evaporated and the 2,6-bis-(4-n-hexyloxyphenyl)-4,8-diamino-1,5-naphthoquinone remaining behind is purified by chromatography on silica gel (eluent: dichloromethane); m.p. 168°C.

The following compounds are prepared analogously:

2,6-bis-(4-methylphenyl)-4,8-diamino-1,5-naphthoquinone,

2,6-bis-(4-ethylphenyl)-4,8-diamino-1,5-naphthoquinone,

2,6-bis-(4-n-propylphenyl)-4,8-diamino-1,5-naphthoquinone,

2,6-bis-(4-n-butylphenyl)-4,8-diamino-1,5-naphthoquinone,

2,6-bis-(4-n-pentylphenyl)-4,8-diamino-1,5-naphthoquinone,
2,6-bis-(4-n-hexylphenyl)-4,8-diamino-1,5-naphthoquinone,
2,6-bis-(4-methoxyphenyl)-4,8-diamino-1,5-naphthoquinone,
2,6-bis-(4-ethoxyphenyl)-4,8-diamino-1,5-naphthoquinone,
2,6-bis-(4-n-propyloxyphenyl)-4,8-diamino-1,5-naphtho-
quinone,
2,6-bis-(4-n-butyloxyphenyl)-4,8-diamino-1,5-naphtho-
quinone,
2,6-bis-(4-n-pentyloxyphenyl)-4,8-diamino-1,5-naphtho-
quinone.

Example 4.

A suspension of 14.9 g. 4-n-butylaniline in 55 ml. of 17% aqueous hydrochloric acid is diazotised at 5°C. with a solution of 7.3 g. sodium nitrite in 75 ml. of water and excess sodium nitrite is removed by the addition of amidosulphonic acid. The clear diazonium salt solution so obtained is added dropwise at 5 - 10°C. to a solution of 18.1 g. 4,8-diamino-1,5-naphthoquinone in 300 ml. N,N-dimethylformamide and the reaction mixture subsequently stirred for 5 days at 15°C. Thereafter, the reaction mixture is poured into 2000 ml. of water and the precipitated 2-(4-n-butylphenyl)-4,8-diamino-1,5-naphthoquinone is filtered off and recrystallised from acetone; m.p. 201°C.

The following compounds are prepared analogously:

2-(4-methylphenyl)-4,8-diamino-1,5-naphthoquinone,
2-(4-ethylphenyl)-4,8-diamino-1,5-naphthoquinone,

2-(4-n-propylphenyl)-4,8-diamino-1,5-naphthoquinone,
2-(4-n-pentylphenyl)-4,8-diamino-1,5-naphthoquinone,
2-(4-n-hexylphenyl)-4,8-diamino-1,5-naphthoquinone,
2-(4-n-heptylphenyl)-4,8-diamino-1,5-naphthoquinone,
2-(4-methoxyphenyl)-4,8-diamino-1,5-naphthoquinone,
2-(4-ethoxyphenyl)-4,8-diamino-1,5-naphthoquinone,
2-(4-n-propyloxyphenyl)-4,8-diamino-1,5-naphthoquinone,
2-(4-n-butyloxyphenyl)-4,8-diamino-1,5-naphthoquinone,
2-(4-n-pentyloxyphenyl)-4,8-diamino-1,5-naphthoquinone,
2-(4-n-hexyloxyphenyl)-4,8-diamino-1,5-naphthoquinone,
2-[4-(trans-4-ethylcyclohexyl)-phenyl]-4,8-diamino-1,5-naphthoquinone,
2-[4-(trans-4-n-propylcyclohexyl)-phenyl]-4,8-diamino-1,5-naphthoquinone, m.p. 300°C.,
2-[4-(trans-4-n-butylcyclohexyl)-phenyl]-4,8-diamino-1,5-naphthoquinone,
2-[4-(trans-4-n-pentylcyclohexyl)-phenyl]-4,8-diamino-1,5-naphthoquinone,
2-[4-(trans-4-n-hexylcyclohexyl)-phenyl]-4,8-diamino-1,5-naphthoquinone.

Example 5.

A liquid crystalline dielectric of
24% 4-(trans-4-n-propylcyclohexyl)-benzonitrile,
36% 4-(trans-4-n-pentylcyclohexyl)-benzonitrile,
25% 4-(trans-4-n-heptylcyclohexyl)-benzonitrile and
15% 4-(trans-4-n-pentylcyclohexyl)-4'-cyanobiphenyl
is mixed with 1.0% 4,8-bis-(4-methoxyanilino)-1,5-

naphthoquinone. The dielectric obtained has a green colour with an extinction maximum at 670 nm. The degree of order of the dyestuff is 0.701.

Example 6.

In a liquid crystalline dielectric of 22% 4-(trans-4-n-propylcyclohexyl)-benzonitrile, 19% 4-(trans-4-n-butylcyclohexyl)-benzonitrile, 30% 4-(trans-4-n-pentylcyclohexyl)-benzonitrile, 15% 4-(trans-4-n-pentylcyclohexyl)-4'-cyanobiphenyl and 14% 4-n-pentyl-4'-cyano-p-terphenyl, the dyestuff 4,8-bis-(4-ethoxyanilino)-1,5-naphthoquinone is soluble at 0°C. in an amount of 0.1%. The dielectric obtained has a green colour with an extinction maximum at 675 nm. The degree of order of the dyestuff is 0.73.

Example 7.

In the base dielectric described in Example 6, the dyestuff 4,8-bis-(4-n-butylanilino)-1,5-naphthoquinone is soluble at 0°C. in an amount of up to 0.8%. The dielectric obtained has a green colour with an extinction maximum at 670 nm. The degree of order of the dyestuff is 0.69.

Example 8.

In the base dielectric described in Example 6, the dyestuff 4-(trans-4-n-propylcyclohexyl)-anilino-8-amino-1,5-naphthoquinone is soluble at 20°C. in an amount of up to 1.8%. The dielectric obtained has a

30

blue colour with an extinction maximum at 635 nm. The degree of order of the dyestuff is 0.67.

Example 9.

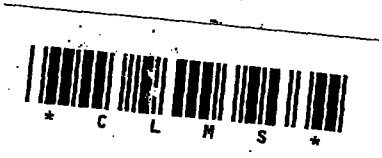
In the base dielectric described in Example 6, the dyestuff 4,8-bis-(4-n-heptyloxyanilino)-1,5-naphthoquinone is soluble at 0°C. in an amount of up to 1.1%. The dielectric obtained has a green colour with an extinction maximum at 675 nm. The degree of order of the dyestuff is 0.74.

Example 10.

In the base dielectric described in Example 6, the dyestuff 4,8-bis-(4-n-hexyloxyanilino)-1,5-naphthoquinone is soluble at 0°C. in an amount of up to 0.8%. The dielectric obtained has a green colour with an extinction maximum at 675 nm. The degree of order of the dyestuff is 0.74.

Example 11.

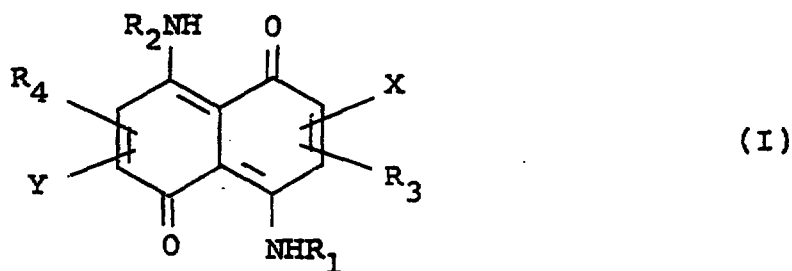
In the base dielectric described in Example 5, the dyestuff 4,8-diamino-2,6-bis-(4-n-hexyloxyphenyl)-1,5-naphthoquinone is soluble at 20°C. in an amount of up to 2.5%. The dielectric obtained has a green colour with an extinction maximum at 675 nm. The degree of order of the dyestuff is 0.77.



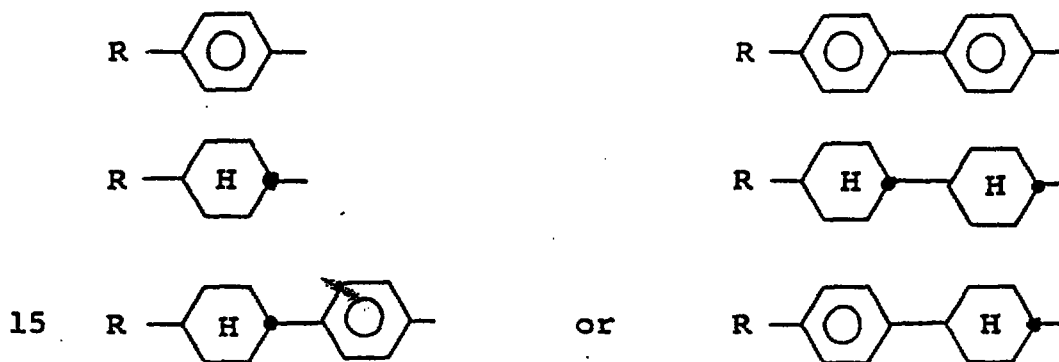
31

Claims

1. Liquid crystalline dielectric based on the guest-host effect containing at least one pleochroitic dye-stuff for electro-optical indicator elements, wherein
5 it contains at least one dyestuff of the general formula:-



- in which X and Y, which are the same or different, are hydrogen, chlorine or bromine atoms, R_1 , R_2 , R_3 and
10 R_4 , which are the same or different, are hydrogen atoms or alkyl or alkoxyalkyl radicals containing up to 8 carbon atoms or a cyclic group Z, Z is



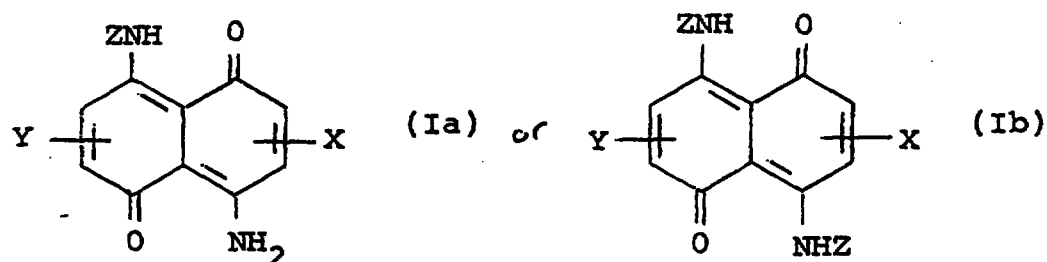
and R is an alkyl, alkoxy, alkoxyalkyl, alkoxyalkoxy or alkanoyloxy radical containing up to 8 carbon atoms, with the proviso that at least one and at most



32

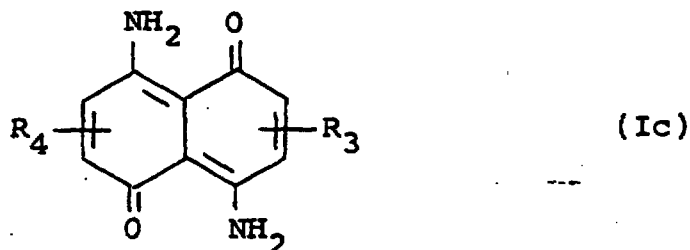
two of the symbols R_1 , R_2 , R_3 and R_4 represent a cyclic group Z and, when two cyclic groups Z are present, these stand either for R_1 and R_2 or for R_3 and R_4 and, when the residues R_3 and R_4 are cyclic groups Z, these are in the 2- and 6- or 3- and 7- positions of the naphthalene structure, said dyestuff (I) being dissolved in the liquid crystalline base material.

2. Liquid crystalline dielectric according to claim 1, wherein the dyestuff is a naphthoquinone derivative of the general formula:-



in which X, Y and Z have the same meanings as in claim 1.

3. Liquid crystalline dielectric according to claim 1, wherein the dyestuff is a naphthoquinone derivative of the general formula:-



in which R_3 and R_4 have the same meanings as in claim 1.



41

33

4. Liquid crystalline dielectrics according to claim 1, substantially as hereinbefore described and exemplified.
 5. An electro-optical indicator element based upon a guest-host liquid crystal cell, wherein it contains a liquid crystalline dielectric according to claim 1.
-