

- 1 -

"Dichroitic anthraquinone dyestuffs"

The present invention is concerned with new dichroitic anthraquinone dyestuffs which are intended for use as components of liquid crystalline dielectrics for electro-optical indicator elements based upon the guest-host effect.

In the case of 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" in 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 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 their orientation. In contradistinction to normal monochroitic dyestuffs, the amount of light absorbed by pleochroitic dyestuffs depends upon the orientation of their molecules to the electrical field vector of the incident light. By application of an electric field to the dielectric distributed in a cell as a thin layer, the nematic liquid crystals of the host phase and, together with these, the pleochroitic dyestuffs embedded as guest phase, are reorientated, which leads to a change of

the light absorption. The 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, mention is there made of indophenol blue, indigo derivatives, azo dyestuffs and the like. However, 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 a small amount, for example 0.1 to 15% by weight of an optically-active material which brings about a helical structure (cholesteric structure) formation in the liquid crystal is incorporated into a dielectric composed of nematic liquid crystals with positive dielectric anisotropy (as host phase) and pleochroitic dyestuff (as guest phase). 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 indicator 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 comprising a cholesteric oriented host phase with 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 indicator contrast and, in addition, display a greater brightness of the depicted image.

It has been shown that the choice of appropriate dyestuffs for CGH indicator elements is very difficult: in the first place, the dichroitic comparative values of such systems with host phase and dyestuff embedded therein as guest phase must be sufficiently great 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

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

wherein Θ 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 more.

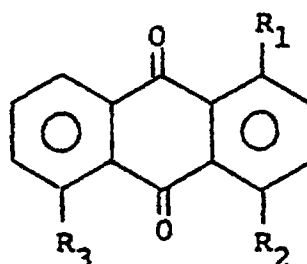
In practice, the degree of order of a dyestuff depends, in the first place, upon its chemical structure, as well as upon the nature of the liquid crystalline matrix. A number of examples of this has been described by R.I. Cox (see *Molecular Crystals and Liquid Crystals*, 55, 1-33/1979).

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 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 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 which are preferable with regard to the dichroitic ratio and the absorption maximum and have mostly been suggested for use in CGH indicator elements prove to be insufficiently stable against light or ultra-violet radiation (too low a photo-chemical 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 previously suggested anthraquinone dyestuffs have too small a dichroitic ratio V to make possible technically usable CGH indicator elements.

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



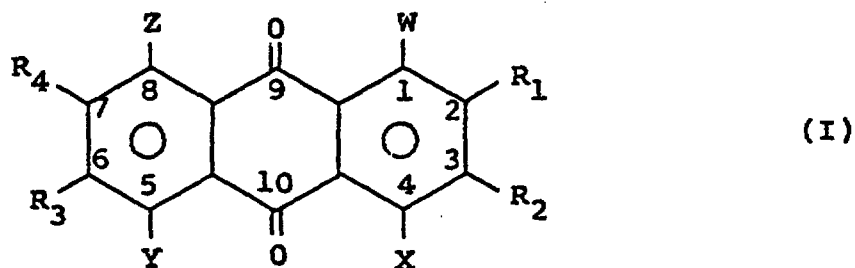
(A)

wherein R_1 is an optionally ring-substituted aniline group 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 by the aniline groups. In particular, in liquid crystalline base materials of the phenylcyclohexane class, used today to a wide extent, the solubility of these dyestuffs of the general formula (A) is too low for practical requirements.

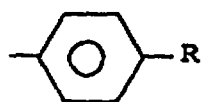
It is an object of the present invention to provide dichroitic dyestuffs which are sufficiently soluble in commercially available liquid crystalline base materials, for example to give a minimum concentration of 0.5% by weight. Furthermore, these dyestuffs

are to have a dichroitic ratio of at least V 5
and to be substantially chemically and photochemically
stable.

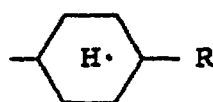
It has now been found that anthraquinone dye-
5 stuffs of the general formula:-



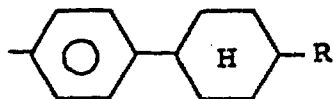
wherein W, X, Y and Z, which can be the same or
different, are hydrogen atoms, hydroxyl groups,
primary amino groups or methylamino or ethylamino
10 radicals, at most 3 of these symbols being the same,
and one or two of the symbols R₁, R₂, R₃ and R₄
represent radicals of the general formulae:-



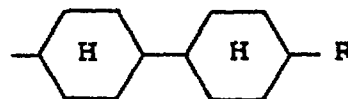
(IIa)



(IIb)



(IIc)



(IIId)

and the others represent hydrogen atoms, R being an alkyl radical containing up to 12 carbon atoms, are surprisingly well soluble in the conventional liquid crystalline base materials and display good dichroitic ratio values therein.

Consequently, the present invention provides new anthraquinone dyestuffs of general formula (I) and is also concerned with their use as components of liquid crystalline dielectrics. Furthermore, the present invention provides a liquid crystalline dielectric comprising at least one dichroitic dyestuff for electro-optical indicator elements based on the guest-host effect, which contains at least one anthraquinone dyestuff of general formula (I); furthermore, the present invention provides an electro-optical indicator element based on a guest-host liquid crystal cell in which the liquid crystalline dielectric contains an anthraquinone dyestuff of general formula (I).

In the compounds of general formula (I), the symbols W, X, Y and Z signify hydrogen atoms, hydroxyl or amino groups or methylamino or ethylamino radicals, not more than three of these substituents being the same. Amongst these, compounds of general formula (I) are preferred which contain not more than two and preferably only one of the strongly polar hydroxyl or amino groups since these are better soluble in the usual liquid crystalline base materials and especially

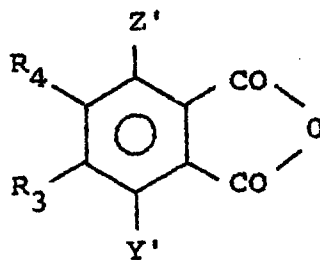
in those with the phenylcyclohexane structure. Two
of the symbols W, X, Y and Z preferably signify
hydrogen atoms and at least one of them methylamino
or ethylamino radicals; amongst these, those compounds
5 of general formula (I) are especially preferred in
which either W and X or Y and Z signify hydrogen atoms.

With regard to the symbols R_1 , R_2 , R_3 and R_4 ,
those compounds of general formula (I) are preferred
in which one of these symbols represents a cyclohexyl-
10 phenyl radical of general formula (IIc) or a cyclohexyl-
cyclohexyl radical of general formula (IId) and the
other three symbols represent hydrogen atoms. Also
preferred as guest dyestuffs in the scope of the
present invention are those in which one of the symbols
15 R_1 , R_2 , R_3 and R_4 represents a radical of general
formulae (IIc) or (IId) and a second one represents a
4-alkylphenyl (IIa) or 4-alkylcyclohexyl (IIb) radical.
This second cyclic radical is preferably in the peri-
position to the first one, i.e. the two cyclic
20 radicals are present in the 2- and 6- or 3- and 7-
positions of the anthraquinone base structure. The
same arrangement is also preferred when two of the
symbols R_1 , R_2 , R_3 and R_4 each signify a radical of
the general formulae (IIa) or (IIb).

25 The alkyl radicals R in the radicals of general
formulae (IIa), (IIb), (IIc) and (IId) contain up
to 12 and preferably up to 7 carbon atoms. When

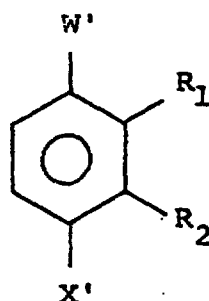
the alkyl radicals R contain 3 or more carbon atoms, they can be straight or branched chained. However, those dyestuffs of general formula (I) in which R is a straight-chained alkyl radical are easier to synthesise and are, therefore, preferred. If, however, a branched alkyl radical is present in the compounds of general formula (I), for example for the alteration of the solubility or for the production of optical activity, then such an alkyl radical is, as a rule, not branched more than once; preferred branched radicals of this kind are those in which a methyl or ethyl group is present in the 1- or 2-position of a longer carbon chain, for example 1-methylpropyl, 2-methylbutyl, 2-methylpentyl, 2-ethylhexyl, 1-methylheptyl or 2-methyloctyl. If two alkyl radicals R are present in a compound of general formula (I), preferably at most one of them is branched.

The dyestuffs of general formula (I) may be prepared in the usual way for anthraquinone dyestuffs. A preferred synthesis consists in reacting a substituted phthalic anhydride derivative of the general formula:-



(III)

with a benzene derivative of the general formula:-



(IV)

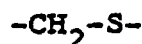
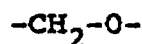
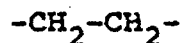
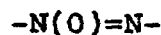
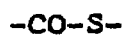
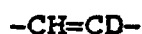
in the manner of a Friedel-Crafts reaction in the presence of an acid catalyst. In general formulae (III) and (IV), R_1 , R_2 , R_3 and R_4 have the meanings given in general formula (I) and W' , X' , Y' and Z' have the same meanings as W , X , Y and Z or represent substituents convertible into these groups by simple reaction steps. The reaction conditions for the Friedel-Crafts reaction (solvent, catalyst, temperature and time) are selected in analogy to the processes used for preparing constitutionally similar anthraquinone dyestuffs known from the literature, depending upon the structure and reactivity of the starting materials. The starting materials are, as a rule, known or can be prepared without difficulty analogously to known compounds by standard processes of synthetic organic chemistry, such as are described, for example, in Houben-Weyl-Müller, Methoden der Organischen Chemie, 4th edition, 1960.

The dielectrics according to the present invention contain 2 to 15 and preferably 3 to 12

components, including at least one anthraquinone dye-stuff of general formula (I). The other components are selected from the nematic or nematogenic azoxybenzenes, benzylideneanilines, biphenyls, terphenyls, phenyl or cyclohexyl benzoates, cyclohexanecarboxylic acid phenyl or cyclohexyl esters, phenylcyclohexanes, cyclohexylbiphenyls, cyclohexylcyclohexanes, cyclohexylnaphthalenes, 1,4-bis-cyclohexylbenzenes, 4,4'-bis-cyclohexylbiphenyls, phenyl- or cyclohexylpyrimidines, phenyl and cyclohexyldioxanes, optionally halogenated stilbenes, benzyl phenyl ethers, tolanes and substituted cinnamic acids. The most important compounds which can be considered as components of liquid crystalline host materials may 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 naphthalenes and di- and tetrahydronaphthalenes, quinazoline and tetrahydroquinazoline, B is



or a C-C- single bond,

D is a halogen atom and preferably a chlorine atom or a cyano group and R_5 and R_6 , 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 can also signify a cyano, isocyano, nitro or trifluoromethyl group or a fluorine, chlorine or bromine atom. In the case of most of these compounds, R_5 and R_6 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 can be prepared in the usual manner. As a rule, the desired amount of the components

employed in lesser amount is dissolved in the component making up the main constituent, preferably at an elevated temperature. If a temperature above the clear point of the main component is used, the completeness of the dissolving can be observed especially easily.

However, it is also possible to mix solutions of the components of general formulae (I) and (V) in an appropriate organic solvent, for example, acetone, chloroform or methanol, and, after thorough mixing up, the solvent is again removed, for example by distilling under reduced pressure. Of course, in the case of this method, care must be taken that no impurities or undesired doping materials are entrained by the solvent.

By means of appropriate additives, the liquid crystalline dielectrics according to the present invention may be so modified that they can be used in all previously known kinds of guest-host indicator elements. Such additives are well known and are described in detail in the appropriate literature. Thus, for example, substances can be added for altering 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. 2,209,127; 2,240,364; 2,321,632; 2,338,281 and 2,450,088.

The following Examples are given for the purpose of illustrating the present invention. In the Examples, m.p. means the melting point and K the clear point of a liquid crystalline substance in degrees Celsius and boiling points are indicated by b.p. If nothing is stated to the contrary, statements of parts or percentages are by weight.

Example 1.

a) To a solution of 32.1 g. 4-amino-4'-(trans-4-n-pentylcyclohexyl)-biphenyl in 300 ml. glacial acetic acid are added at 50°C., with stirring, 50 g. of 65% aqueous nitric acid. After subsequently stirring for 2 hours, the reaction mixture is poured on to 1 kg. of ice and the precipitated 4-acetamino-3-nitro-4'-(trans-4-n-pentylcyclohexyl)-biphenyl is filtered off, washed with water and transferred to a solution of 12 g. potassium hydroxide in 100 ml. ethanol. The reaction mixture is boiled for 2 hours, poured into 500 ml. of water and the 4-amino-3-nitro-4'-(trans-4-n-pentylcyclohexyl)-biphenyl formed is extracted therefrom with toluene. After distilling off the toluene, the residue is slurried in 40 ml. of 50% aqueous sulphuric acid. After adding 20 ml. dioxan, a solution of 4.8 g. sodium nitrite in 25 ml. water is added dropwise at 0°C. The resultant suspension is introduced into a solution of sodium tetracyanocuprate-(I) kept at 0°C. and prepared from

cupric sulphate, sodium sulphite and sodium cyanide, whereafter the reaction mixture is further heated for 1 hour on a boiling waterbath. The cooled suspension is extracted several times with dichloromethane and the organic phase is washed with 2N aqueous sodium hydroxide solution and water and dried over anhydrous sodium sulphate. After the distilling off of the solvent, the 3-nitro-4-cyano-4'-(trans-4-n-pentyl-cyclohexyl)-biphenyl remaining behind is recrystallised from ethanol; m.p. 118°C.

b) A solution of 16 g. 3-nitro-4-cyano-4'-(trans-4-n-pentylcyclohexyl)-biphenyl in 100 ml. dioxan is carefully introduced into a solution of 29.0 g. stannous chloride in 25 ml. of 37% hydrochloric acid, taking care that the temperature does not exceed 45°C. After stirring for 2 hours, the reaction mixture is slowly introduced into 200 ml. ice-cooled 30% aqueous sodium hydroxide solution. The 3-amino-4-cyano-4'-(trans-4-n-pentylcyclohexyl)-biphenyl which thereby crystallises out is filtered off, washed with water and recrystallised from ethanol. The material purified in this manner is slurried in 40 ml. of 50% sulphuric acid. After the addition of 20 ml. of dioxan, a solution of 4.8 g. sodium nitrite in 25 ml. of water is added dropwise at 0°C. The resultant suspension is introduced into a solution of sodium tetracyanocuprate (I) kept at 0°C. and prepared from cupric sulphate,

sodium sulphite and sodium cyanide, whereafter the reaction mixture is further heated for 1 hour on a boiling waterbath. The cooled suspension is extracted several times with dichloromethane and the organic phase is washed with 2N aqueous sodium hydroxide solution and water and dried over anhydrous sodium sulphate. After distilling off the solvent, the 4'-(trans-4-n-pentylcyclohexyl)-biphenyl-3,4-dicarbonitrile remaining behind is recrystallised from ethanol; m.p. 134°C.

c) 2 g. 4'-(trans-4-n-Pentylcyclohexyl)-biphenyl-3,4-dicarbonitrile are boiled for 16 hours in a solution of 1.5 g. potassium hydroxide in 15 ml. amyl alcohol. Subsequently, the reaction mixture is poured into 25 ml. of 5% aqueous hydrochloric acid and the 4'-(trans-4-n-pentylcyclohexyl)-biphenyl-3,4-dicarboxylic acid which crystallises out is filtered off and boiled with 2.5 ml. acetic anhydride and 0.5 g. zinc chloride for 1 hour. After cooling, the 4'-(trans-4-n-pentylcyclohexyl)-biphenyl-3,4-dicarboxylic anhydride which has crystallised out is filtered off, washed with a little cold water and dried under reduced pressure; yield 1.5 g.

d) 1.2 g. 4'-(trans-4-n-Pentylcyclohexyl)-biphenyl-3,4-dicarboxylic anhydride, 2.0 g. hydroquinone and 10 g. oxalic acid are heated for 2 hours to 220°C. After cooling, the 1,4-dihydroxy-6-[4-

(trans-4-n-pentylcyclohexyl)-phenyl]-anthraquinone obtained is purified by recrystallisation from ethanol.

The following compounds are prepared analogously:

- 1,4-dihydroxy-6-(4-n-butylphenyl)-anthraquinone,
5 1,4-dihydroxy-6-(trans-4-n-propylcyclohexyl)-anthraquinone,
1,4-dihydroxy-6-[4-(trans-4-ethylcyclohexyl)-cyclohexyl]-anthraquinone.

Example 2.

- 10 0.7 g. 1,4-Dihydroxy-6-[4-(trans-4-n-pentylcyclohexyl)-phenyl]-anthraquinone is dissolved in 5 ml. pyridine and 50 ml. of gaseous methylamine are passed into the solution. The resultant solution is heated for 16 hours to 90°C. and then poured into
15 50 ml. of water. The mixture of the violet dyestuffs 1-N-methylamino-4-hydroxy-6-[4-(trans-4-n-pentylcyclohexyl)-phenyl]-anthraquinone and 1-hydroxy-4-N-methylamino-6-[4-(trans-4-n-pentylcyclohexyl)-phenyl]-anthraquinone which crystallises out is separated by
20 column chromatography on silica gel (eluent: toluene).

The following compounds are prepared analogously:

- 1-N-methylamino-4-hydroxy-6-(4-n-butylphenyl)-anthraquinone and 1-hydroxy-4-N-methylamino-6-(4-n-butylphenyl)-anthraquinone;
25 1-amino-4-hydroxy-6-(trans-4-n-propylcyclohexyl)-anthraquinone and 1-hydroxy-4-amino-6-(trans-4-n-propylcyclohexyl)-anthraquinone.

Example 3.

By the reaction of 1.5 g. phthalic anhydride with 2 g. (4-methylphenyl)-hydroquinone (prepared from p-toluidine and p-benzoquinone as described in J.A.C.S., 56, 2478/1934) analogously to Example 1 d), there is prepared 1,4-dihydroxy-2-(4-methylphenyl)-anthraquinone.

The following compounds are obtained analogously:

1,4-dihydroxy-2-[4-(trans-4-n-propylcyclohexyl)-phenyl]-anthraquinone,
1,4-dihydroxy-2-(4-n-pentylcyclohexyl)-anthraquinone.

Example 4.

Analogously to Example 2, from the dyestuffs prepared according to Example 3, there are obtained:

1-amino-4-hydroxy-2-(4-methylphenyl)-anthraquinone and 1-amino-4-hydroxy-3-(4-methylphenyl)-anthraquinone;

1-N-ethylamino-4-hydroxy-2-[4-(trans-4-n-propylcyclohexyl)-phenyl]-anthraquinone and 1-N-ethylamino-4-hydroxy-3-[4-(trans-4-n-propylcyclohexyl)-phenyl]-anthraquinone.

The following Examples illustrate the preparation of liquid crystalline dielectrics according to the present invention:

Example 5.

In the liquid crystal mixture 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)-biphenyl-4'-
carbonitrile and
14% 4-n-pentyl-4"-cyanoterphenyl
there are dissolved 3 parts by weight of the right-handed helix-inducing 4-(2-methylbutyl)-biphenyl-4'-carbonitrile and 1 part by weight of 1-hydroxy-4-N-methylamino-6-[4-(trans-4-n-pentylcyclohexyl)-phenyl]-anthraquinone. With this dielectric, there can be achieved in CGH indicator elements with a layer thickness of 12 μ m., very good contrasts between violet (cholesteric phase, planar, without electric field) and colourless (nematic phase, homeotropic, with electric field).

Similar results are obtained when, as dyestuff, there is used, for example, 1,5-diamino-4,8-dihydroxy-2-[trans-(4-n-pentylcyclohexyl)-phenyl]-anthraquinone or 1,5-bis-N-methylamino-2,6-bis-(4-n-pentylphenyl)-anthraquinone.

Example 6.

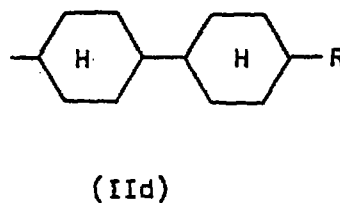
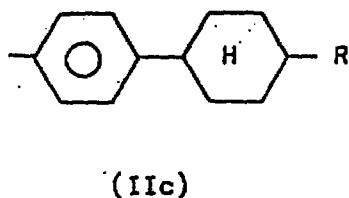
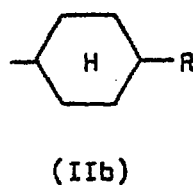
To the liquid crystal mixture of Example 5 is added 0.5% of the dichroitic dyestuff 1-N-methylamino-4-hydroxy-6-[4-(trans-4-n-pentylcyclohexyl)-phenyl]-anthraquinone of Example 2. In this solution, the dichroitic dyestuff displays a dichroitic ratio of 11.1 and a degree of order S of 0.77.

3

- 1



1



and the others represent hydrogen atoms, R being an alkyl radical containing up to 12 carbon atoms.

34



2. Dichroitic dyestuffs according to claim 1 which are hereinbefore specifically exemplified.

3. A liquid crystalline dielectric containing at least one dichroitic dyestuff for electro-optical indicator elements based on the guest-host effect, wherein it contains at least one dichroitic dyestuff according to claim 1.

4. Liquid crystalline dielectric according to claim 3, substantially as hereinbefore described and exemplified.

5. An electro-optical indicator element based on a guest-host liquid crystal cell, wherein the liquid crystal cell contains a liquid crystalline dielectric according to claim 3.