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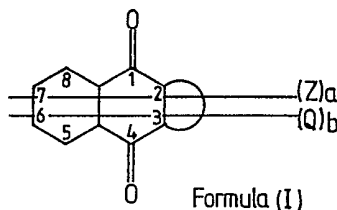
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None

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C4X

(54) Liquid crystal material incorporating a pleochroic dye

(57) A material suitable for a guest-host liquid crystal device comprises a solution of a liquid crystal material and a pleochroic dye wherein the pleochroic dye comprises at least one compound having a formula:



wherein:



represents a five membered heterocyclic ring which includes the carbon atoms in positions 2 and 3 of the naphthoquinone nucleus,

Z is a non-ionic substituent selected from SX, OX and NXX<sup>1</sup> where:

X is H or an optionally substituted alkyl, optionally substituted cycloalkyl or aryl radical;

X<sup>1</sup> is H or a lower alkyl or alkoxy group;

Q is a non-ionic substituent selected from halo, nitro, cyano, optionally substituted alkyl, optionally substituted cycloalkyl and optionally substituted aryl;

a is an integer from 1 to 4 inclusive and

b is an integer from 0 to 5 inclusive.

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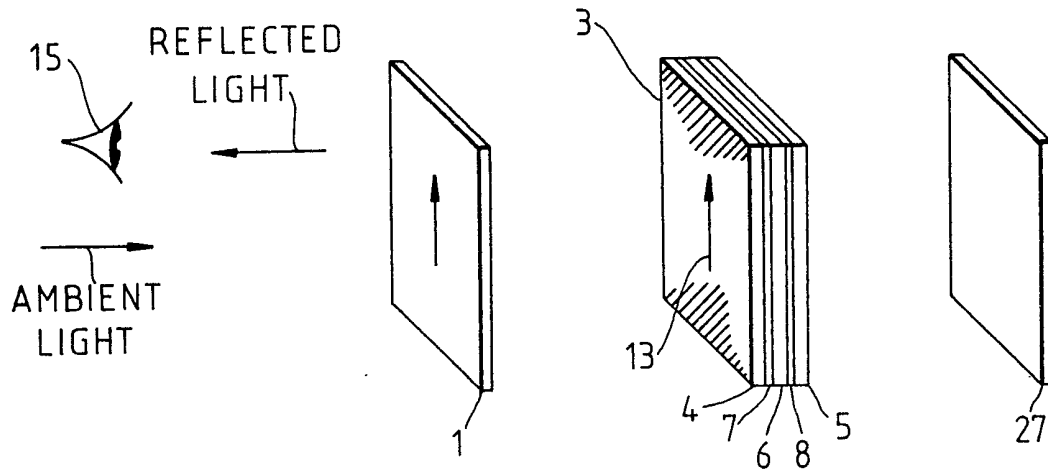


Fig. 1.

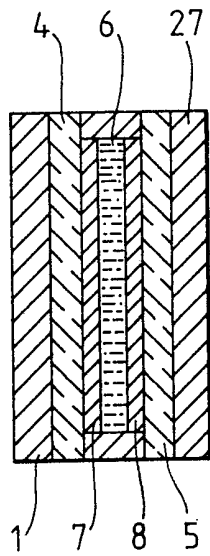


Fig. 2.

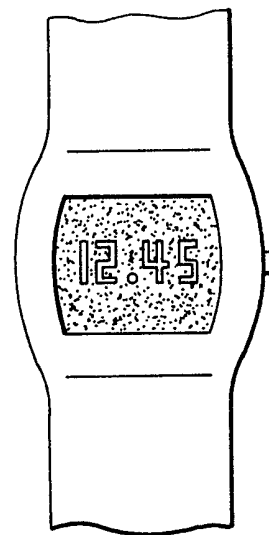


Fig. 3.

## SPECIFICATION

**Liquid crystal materials incorporating pleochroic dyes**

- 5 The present invention is concerned with organic materials, in particular with pleochroic dyes in solution with liquid crystal materials e.g. for electro-optic display applications. 5
- Liquid crystal materials are well known organic materials which display phases, known as liquid crystal phases or mesophases, having a degree of molecular ordering intermediate between that of the fully ordered crystalline solid state and the fully disordered isotropic liquid state.
- 10 Electro-optical devices incorporating liquid crystal materials are well known and widely used as digital displays in such applications as watches, calculators and digital voltmeters. These devices utilise the optical contrast when an electric field is applied across a thin insulating film of suitable liquid crystal material. The molecules of the material (in a liquid crystal phase at the temperature of operation) are re-orientated by the field causing a change in an optical property of the part of the film where the field is applied, e.g. a change in ambient light scattering or transmissivity. 10 15
- Liquid crystal materials have the property that their molecules can impose their ordering upon the molecules of other suitable dopant materials incorporated within them. This property is the basis of so-called "guest-host" devices e.g. display devices in which the host liquid crystal material and its guest material have one molecular configuration in the absence of an applied electric field and another molecular configuration when an electric field is applied across the material. The guest material is usually a pleochroic dye, which is a dye whose molecular absorption properties vary with the orientation of the electric vector of light incident upon its molecules. 20
- The presence of such a dye can be used to enhance the contrast between the off state (with no electric field applied) and the on state (with electric field applied) of a liquid crystal display because the orientation of the dye molecules is in effect switchable by the effect of the applied electric field on the liquid crystal molecules and by the consequent re-orientation of the dye molecules by the guest-host effect. 25
- As discussed further below there are several kinds of liquid crystal effects which can make use of the guest-host effect in electro-optical displays. These vary according to the kind of liquid crystal material used and the configuration of its molecules in the off state (e.g. as determined by the surface treatments of the substrates employed to contain the film of liquid crystal material). 30
- In order to provide maximum contrast between the on and off states of a guest-host liquid crystal display it is important that the guest molecules adopt as closely as possible the time averaged orientation of the host molecules. However this is achieved only to a limited degree because of random thermal fluctuations. The degree to which the orientation varies from the ideal is measured by a quantity known as the order parameter S which is given by the following equation: 35
- $$S = \frac{1}{2} (3 \cos^2 \theta - 1) \quad \text{Equation (1)}$$
- where  $\cos^2 \theta$  is a time averaged term and  $\theta$  is the instantaneous angular orientation of the molecules with respect to the time averaged orientation of the host molecules. The determination of the value of the order parameter S is well understood in the art; see for example the paper "A new absorptive mode reflective liquid crystal display device" by D.L.White and G.N.Taylor in the Journal of Applied Physics, 1974, 45 pages 4718 to 4723. 40
- For perfect orientation the order parameter S is unity (that is  $\theta$  is zero). Thus, pleochroic dyes for use in guest-host devices should have an order parameter in the liquid crystal host as high as possible (i.e. less than one but as near to one as possible). However they must also have adequate chemical, photochemical and electrochemical stability, e.g. stability when exposed to atmospheric contaminants, electric fields (as in device operation) and to ultra-violet radiation. They should not be ionic or have any ionisable character (otherwise the liquid crystal material will lose its insulating nature and conduct making the device useless). 45
- 50 They must also have sufficient solubility in the host materials; although the concentration of guest pleochroic dye required for the desired effect is generally quite small (e.g. not more than a few per cent of dye) nevertheless many pleochroic dyes are unsuitable because they are essentially insoluble in liquid crystal materials.
- The use in liquid crystal materials of a small number of dyes which are naphthoquinone derivatives has previously been investigated but the order parameters obtained were generally low (mostly less than 0.5). 55

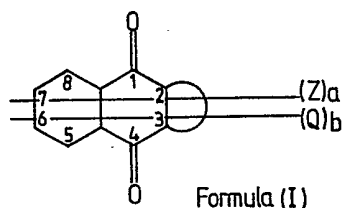
According to the present invention in a first aspect a material suitable for a guest-host liquid crystal device comprises a solution of a liquid crystal material and a pleochroic dye wherein the pleochroic dye comprises at least one compound which is a heterocyclic derivative of 1,4 naphthoquinone having a formula:

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15 wherein:

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represents a five membered heterocyclic ring which includes the carbon atoms in positions 2 and 3 of the naphthoquinone nucleus;

Z is a non-ionic substituent selected from SX, OX and NXX' where:

X is H or an optionally substituted alkyl, optionally substituted cycloalkyl or aryl radical;

25 X' is H or a lower alkyl or alkoxy group;

25

Q is a non-ionic substituent selected from halo, nitro, cyano, optionally substituted alkyl, optionally substituted cycloalkyl and optionally substituted aryl;

a is an integer from 1 to 4 inclusive

b is an integer from 0 to 5 inclusive.

30 The substituents Z and Q may be contained either in the main naphthoquinone nucleus and/or in the five membered heterocyclic ring.

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Where the structure contains more than one substituent Z these may be the same or different groups. Likewise, where the structure contains more than one substituent Q these may be the same or different groups.

35 Preferably, where Z is NXX', X' is H and X is aryl, especially phenyl or substituted phenyl, or optionally substituted alkyl containing from 1 to 12 carbon atoms. Preferred optional substituents where X in NXX' is substituted alkyl are lower alkoxy, OH and monocyclic aryl.

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Preferably, where Z is SX, X is monocyclic aryl, especially phenyl or substituted phenyl.

Preferably, where Z is OX, X is H.

40 Where X is SX is optionally substituted.

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Where X in SX or Q is alkyl it preferably contains up to 10 carbon atoms in a straight or branched chain and more preferably contains from 3 to 10 carbon atoms. As optional substituents there are preferred lower alkoxy, OH and monocyclic aryl.

45 Where X or Q is substituted phenyl it is preferably substituted by a lower alkyl, lower alkoxy, halo, NO<sub>2</sub>, OH or NXX' group (where NXX' is as defined above) - which may be the same as or different from the aforementioned group(s) NXX'.

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The five membered heterocyclic ring preferably has one of the following groups in one of its ring positions: N, NH, O, NX'' or S, where X'' is lower alkyl or lower alkoxy. It may contain two such groups in its ring positions provided that at least one is N.

50 Preferably, a substituent Z is attached to the naphthoquinone nucleus at position 5 or position 8, as indicated in Formula (I).

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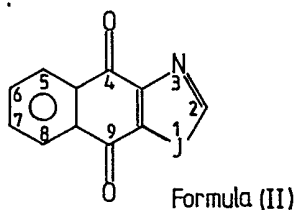
As an example, dyes of Formula (I) may have the following structure:

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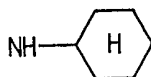
where J is O or NR<sub>A</sub> where R<sub>A</sub> is hydrogen or simple alkyl or alkoxy.

65 For dyes of Formula (II) it is preferred that there is a substituent Z in position 5, as indicated in Formula (II)

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on the naphthoquinone nucleus. The substituents Q, if any, are preferably in one or more of positions 2, 6 or 7 as indicated in Formula (II). Z may for example be

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or NHA<sub>r</sub> where Ar is an aryl group in this case.

It has been found unexpectedly that by using dyes of Formula (I), particularly of Formula (II), in liquid crystal material it is possible to achieve an order parameter greater than that obtained with naphthoquinone dyes investigated in the prior art in liquid crystal materials.

The liquid crystal material (host material) in which the dye of Formula (I) is dissolved in the first aspect above is not critical since a dye which shows reasonable solubility in one liquid crystal material is likely to show reasonable solubility in other liquid crystal materials and also a dye which gives an improved order parameter in one liquid crystal material is likely to give an improved order parameter in other liquid crystal materials, as most popular liquid crystal materials have a similar rod-like molecular shape; however the order parameter if any dye will vary to a limited extent from host-to-host.

Suitable host materials include:

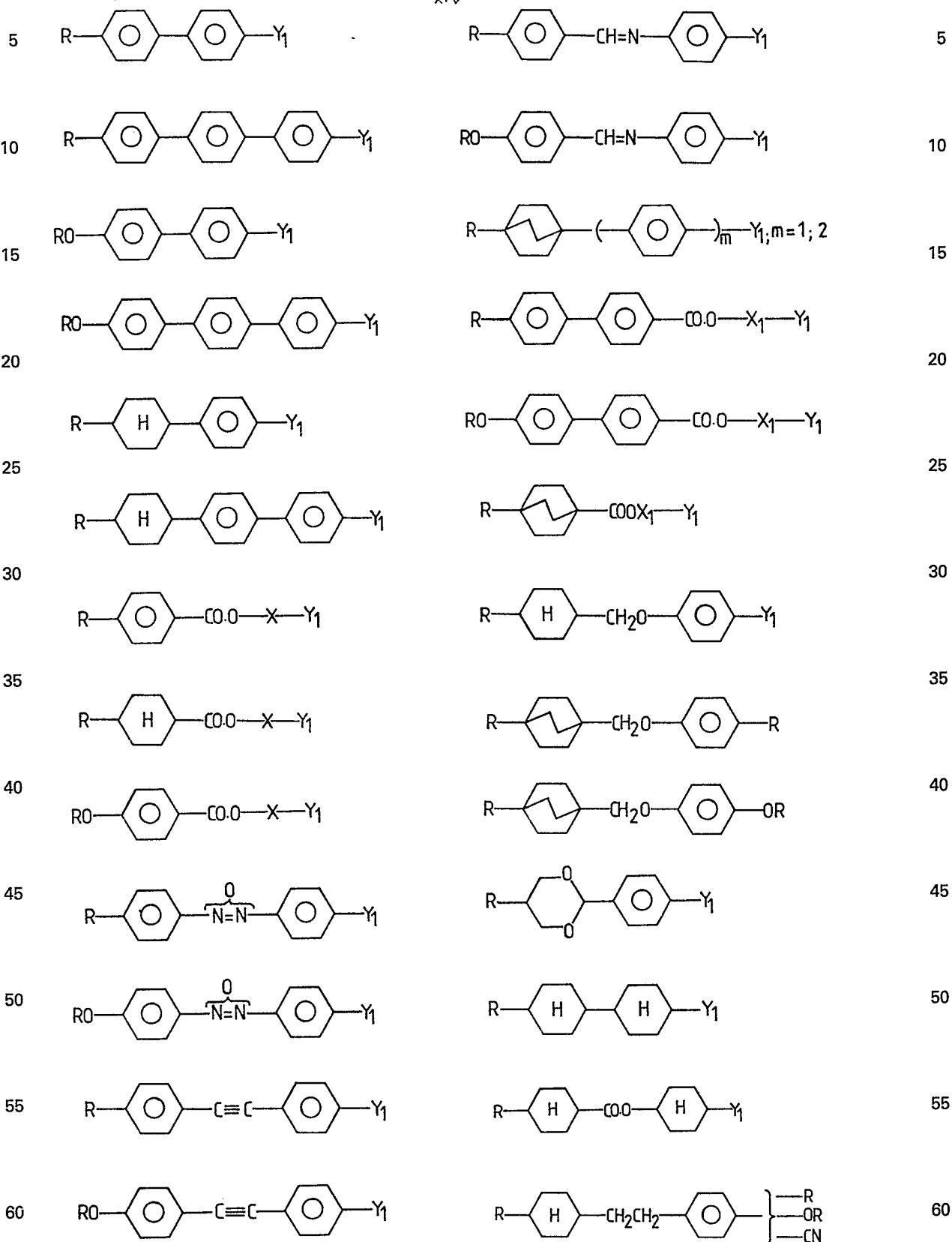
a. mixtures having a positive dielectric anisotropy incorporating cyanobiphenyls preferably together with a few per cent of a compound having a clearing point (liquid crystal to isotropic liquid transition) above 150°C (eg a cyano-p-terphenyl) such as the material E7, marketed by BHD Chemicals Ltd, of Broom Road, Poole, Dorset, England; (composition given below.)

b. mixtures having a positive dielectric anisotropy incorporating 1-(4'-cyanophenyl) 4-alkylcyclohexane compounds preferably together also with a few per cent of a high clearing point compound such as a 1-(4'-cyanobiphenyl)-4-alkylcyclohexane compound; eg the material ZLI 1132;

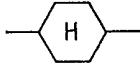
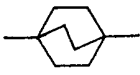
c. mixtures having a positive dielectric anisotropy incorporating at least one cyanobiphenyl and at least one cyanophenylpyrimidine, preferably together also with a few per cent of a high clearing point compound, eg a cyanophenylpyrimidinephenyl compound, eg the material ROTN 30;


d. mixtures incorporating esters, eg containing bicyclo (2,2,2) octane and benzene rings; these generally have a weakly positive or negative dielectric anisotropy but the magnitude of the dielectric anisotropy may be enhanced by the addition of a dopant liquid crystal material having a strongly positive or strongly negative dielectric anisotropy as appropriate; suitable negative dopants are the dicyano compounds which are specified in claim 2 of UK Patent Application No. 2,061,256A;

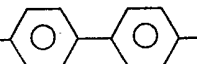
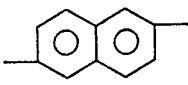
e. any other liquid crystal material incorporating one or more compounds selected from the following known families (where R = alkyl):



or derivatives of any of these containing benzene rings wherein the benzene rings contain one or more substituents, eg fluoro;

where  is a trans -1,4 substituted cyclohexane ring,  is a 1,4

5 substituted bicyclo (2.2.2) octane ring,  $X_1$  is a 1,4 phenylene group , or a 4,4' biphenyl

10 group  or a 2,6 naphthyl group ; and Y is CN, or  $R^1$ , or  $OR^1$  or CO. 10

15  $O-X_1-Y^1$  where  $Y^1$  is CN, or  $R^1$  or  $OR^1$ ; the definition of  $R^1$  being the same as that of R. 15

Preferably, the dye/liquid crystal solution contains at least 0.5% by weight of the dye and preferably between about 0.75% and 5% by weight of the dye or more (possibly up to 10% by weight).

Solutions of dye and liquid crystal material may be made in a conventional way simply by mixing the dye and the liquid crystal material together and then heating the mixture at about 80°C with stirring for about 10 20 minutes and then allowing the mixture to cool. 20

Pleochroic dyes of Formula (I) above may be mixed together with other dyes (which may or may not also be of Formula (I)) to extend their spectral absorption properties (when dissolved in liquid crystal material). For example, where a dye of Formula (I) is a yellow or red dye it may be mixed with a red or yellow dye respectively and a blue dye. Alternatively, where a dye of Formula (I) is orange it may be mixed together with 25 a blue dye, optionally together with a yellow and/or red dye. The relative proportions of the dyes mixed together are determined by the desired spectral response as determined by the extinction coefficients of the constituent dye compounds. The dye mixture is then used with liquid crystal material as above or as follows. 25

According to the present invention in a second aspect a liquid crystal electro-optical display includes two electrically insulating substrates at least one of which is optically transparent, electrodes on the inner 30 surfaces of the substrates and a film of dielectric material contained between the electrodes and substrates, wherein the dielectric material is material according to the first aspect of the invention as defined above. 30

The liquid crystal/dye solution which is the material according to the first aspect of the invention may be used in any known electro-optical display as defined in the second aspect. Examples, which will be familiar to those skilled in the liquid crystal art, are the known devices operating by the following effects: 35

35 a. *The twisted nematic effect*

In this case a film of nematic liquid crystal material of positive dielectric anisotropy has an off state in which (the long axes of) its molecules lie in the plane of the device substrate inner surfaces (which are normally parallel to one another), or at a small angle thereto, and undergo roughly a  $\pi/2$  helical twist in 40 orientation from one substrate to the other by virtue of the orientations at the surfaces caused by treatment, eg unidirectional rubbing, of those surfaces prior to assembly. This is the twisted "homogeneous texture". Application of an electric field between the electrodes on the respective substrate inner surfaces to give the on state causes re-arrangement of the liquid crystal molecules to lie (with their long axes) effectively 45 perpendicular to the substrate inner surfaces in the "homeotropic texture". A change in optical activity (rotary power) of the film occurs between the on and off states by virtue of the molecular re-arrangement and the optical effect observed can be enhanced by the use of a linear polariser adjacent to one of the substrates and pleochroic dye dissolved in the liquid crystal material. The polariser has its polarisation axis parallel to the direction of the liquid crystal molecules at the adjacent substrate inner surface (or, more strictly, parallel to the average axis of projection of the molecules on that surface). By the guest-host effect 50 the dye causes the off state to appear relatively dark or strongly coloured whereas the on state appears clear or weakly coloured. 50

b. *The Fréedericksz effect in negative nematics*

In this case a film of nematic liquid crystal material of negative dielectric anisotropy has an off state in 55 which its molecules lie perpendicular (ie in the homeotropic texture) to the substrate inner surfaces (which are parallel) by virtue of surface treatments to these inner surfaces prior to assembly. A single polariser is placed adjacent to one substrate with its transmission axis perpendicular to the normal to the inner surfaces. Application of an electric field between the electrodes on the respective substrate inner surfaces to give the on state causes re-arrangement of the liquid crystal molecules to lie parallel to the substrate inner surfaces 60 (ie in the homogeneous texture). Incorporation of pleochroic dye in the liquid crystal ensures that the off state appears relatively clear or weakly coloured whereas the on state appears dark or strongly coloured. The effect observed is enhanced by the presence of the polariser. 60

c. *The Fréedericksz effect in positive nematics*

In this case a nematic liquid crystal material of positive dielectric anisotropy has an off state in which the molecules lie roughly parallel and in the plane of the substrate inner surfaces (which are parallel) by virtue of treatment of those surfaces prior to assembly (ie the homogeneous texture). A single polariser is placed adjacent to one substrate with its transmission axis parallel to the substrate inner surfaces.

Application of an electric field between the electrodes on the respective substrate inner surfaces to give the on state causes re-arrangement of the liquid crystal molecules to lie perpendicular to the substrate inner surfaces, ie the homeotropic texture. Incorporation of pleochroic dye in the liquid crystal material ensures that the off state appears relatively dark or strongly coloured whereas the on state appears colourless or weakly coloured as in the twisted nematic effect above. The effect observed by the presence of the polariser.

d. *The phase change effect (negative contrast type)*

In this case a cholesteric liquid crystal material of positive dielectric anisotropy and long molecular helical pitch, typically  $3\ \mu\text{m}$ , has an off state in which its molecules lie in random helices, ie the "focal conic texture". Application of an electric field between the electrodes on the respective substrate inner surfaces to give the on state causes re-arrangement of the liquid crystal molecules to lie perpendicular to the substrate inner surfaces (ie the homeotropic texture as for positive nematics in the Fréedericksz effect). Incorporation of pleochroic dye in the liquid crystal material gives an off state which appears relatively dark or strongly coloured and an on state which appears colourless or weakly coloured.

e. *The phase change effect (positive contrast type)*

In this case a cholesteric liquid crystal material of negative dielectric anisotropy and long molecular helical pitch has an off state in which its molecules lie perpendicular to the substrate inner surfaces, ie in the homeotropic texture. Application of an electric field between electrodes on the respective substrate inner surfaces causes re-orientation of the molecules to lie in the plane of the substrate inner surfaces in a helical arrangement ie the twisted homogeneous texture. Incorporation of pleochroic dye in the liquid crystal material gives an off state which is relatively colourless or weakly coloured and an on state which is relatively dark or strongly coloured.

f. *The Fréedericksz effect in smectics*

In this case a smectic A liquid crystal material of positive dielectric anisotropy having a dielectric relaxation frequency  $f_c$  less than about 10 kHz (ie the material has a negative dielectric anisotropy above this frequency) has an off state in which its molecules lie roughly parallel to the substrate inner surfaces with the molecules at the two inner surfaces parallel as in the Fréedericksz effect (c). Application of an electric field with a frequency less than  $f_c$  to give the on state causes re-orientation of the liquid crystal molecules to lie perpendicular to the substrate inner surfaces, ie in the homeotropic texture. The on state is preserved when the field is removed. Clearing of the on state may be achieved by the application of a high frequency electric field, ie with a frequency  $> f_c$ . A single polariser is used, as with the Fréedericksz effect (c) above, when the molecular alignment at the two substrate inner surfaces in the off state is parallel. Incorporation of pleochroic dye in the liquid crystal material gives an off state which is relatively dark or strongly coloured and an on state which is clear or weakly coloured.

Use of the material defined in the first aspect of the invention above is not limited to electro-optical displays (as defined in the second aspect). The material may, in fact, be used in any known application of a dyed liquid crystal material. An example of such a 'non electro-optical' application is a thermally addressed display in which a symbol or character is provided in a smectic or cholesteric material by selective heating of the material eg by a laser (eg He/Ne) beam, to produce a localised change in the molecular texture of the material. The dye enhances the contrast between the different regions of the display, ie between those which are selectively heated and those which are not heated.

Dyes of Formula (I) above may be prepared by known methods.

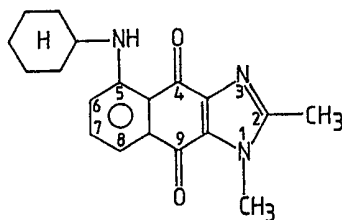
Example of the preparation, properties and uses of dyes of Formula (I) will now be given.



**Example 1**

Preparation of Compound No 1 of the Formula:

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15 This compound was prepared as described by G G-Buckley and J. Griffiths in "Naphthoquinone colouring matters; Part 4: Amino-substituted 1,2-dimethylnaphth (2,3-*d*)imidazole-4,9-diones", J. Chem. Soc. Perkin I (1979) pages 702 et seq., Reference 1, as follows.

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*Step 1a* Compound No 1 was made from 1,2-dimethylnaphth(2,3-*d*)imidazole-4,9-dione, Compound No 1a, which was prepared as follows.

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Sodium hydroxide solution (25 ml 2M) was added dropwise to a boiling solution of 2-acetylamino-3-methylamino-1,4-naphthoquinone (5 g) in ethanol (200 ml) and refluxed for 1 h. The crystalline deposit that formed on cooling was [2,3-*d*] imidazole-4,9-dione (4) as pale yellow needles (3.6 g, 78%) m.p. 250-252°C.

25 *Step 1b* A mixture of 5- and 8-nitro-1,2 dimethylnaphth [2,3-*d*] imidazole 4,9-diones (Mixture 1b) was then prepared from Compound No 1a as follows.

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A solution of Compound No 1a (4.5 g) in concentrated sulphuric acid (23 ml) and fuming nitric acid (d 1.5, 1.5 ml) was heated at 100°C for 1 h and the cooled solution poured over crushed ice (450 g). The yellow suspension was extracted thoroughly with dichloromethane, and the extracts washed with 5% sodium carbonate solution until the washings were no longer red. The dichloromethane solution was washed with water and dried (MgSO<sub>4</sub>). The yellow solid obtained after evaporation of the solvent was recrystallised from benzene-petroleum (b.p. 60-80°C), giving Mixture 1b as golden yellow needles (4.95 g, 89%) m.p. 262-264°C.

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*Step 1c* Reduction of the mixed nitro-isomers to the corresponding amino-isomers (Mixture 1c) was effected by heating a solution of the mixture (2 mmol) together with acetic acid (7ml) and concentrated hydrochloric acid (4 ml) containing tin (II) chloride dihydrate (1.8 g) at 80°C for 20 min, and oxidising the product with iron (III) chloride. The red-brown solid was recrystallised from benzene-petroleum (b.p. 60-80°C) to give the corresponding mixed 5- and 8-amino-isomers (6) (45%), m.p. 244-248°C (Mixture 1c).

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40 *Step 1d* Mixture 1c (2 g) was then heated in benzene (200 ml) under reflux and cyclohexylamine (10 ml) was added to the boiling solution over 30 min. Heating was continued for 24 h and the solution cooled and diluted by the addition of dichloromethane (200 ml). The solution was washed thoroughly with dilute hydrochloric acid and water, and dried (MgSO<sub>4</sub>). The residue obtained after removal of the solvent was chromatographed over neutral alumina, using benzene-dichloromethane as eluant. The 5- and 8-

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45 cyclohexylamino isomers separated as deep purple bands, the 5-isomer Compound No 1, being eluted first. Compound No 1 formed bright red plates (0.75 g yield: 31%) m.p. 192-194°C.

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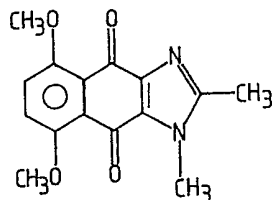
**Example 2**

Preparation of the Compound No 2 of Formula:

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This compound was prepared by the method described in Reference 1 as follows.

*Step 2a* A solution of 2,3-dichlo-5,8-dimethoxy-1,4-naphthoquinone (7.5 g) in the minimum volume of di-chloromethane was added to ethanol (1.6) and ammonia was bubbled through for 20 min. The solution was sealed in a stoppered flask and maintained at room temperature in the dark for 15 h. Concentration of

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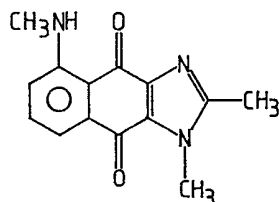
the solution under reduced pressure to a volume of ca. 250 ml gave orange-brown plates of 2-amino-3-chloro-5,8-dimethoxy-1,4-naphthoquinone (5.1 g 72%) m.p. 247-249°C.

*Step 2b* The solid obtained in Step 2a was heated under reflux in a mixture of acetic acid (100 ml) and acetic anhydride (100 ml) for 4 hr. The residue, obtained after evaporation of the solvent under reduced pressure, was chromatographed over neutral alumina in dichloromethane to give the N-acetyl-derivative (3.75 g, 63%) as orange plates, m.p. 225-227°C. The product was heated under reflux in toluene (400 ml) and methyl-amine was bubbled through the solution for 2 h. The solvent was removed under reduced pressure, and the residue recrystallised from benzene-petroleum (b.p. 60-80°C) to give 2-acetamido-5,8-dimethoxy-3-methylamino-1,4-naphthoquinone as brown needles (3.1 g, 85%) m.p. 24-217°C.

*Step 2c* The product of Step 2b was dissolved in absolute ethanol(650 ml) containing 6 drops of 2M-sodium hydroxide solution, and the solution heated under reflux. After 10 min a similar quantity of sodium hydroxide solution was added, and heating continued for 1.5 h. The solvent was removed under reduced pressure, and the residue dissolved in di-chloromethane. The solution was extracted with dilute hydrochloric acid until no more colour was removed, and the washings neutralised and extracted with dichloro-methane. The residue obtained after evaporation of the dichloromethane extracts was recrystallised from benzene-petroleum (b.p. 60-80°C) giving 5,8-dimethoxy-1,2-dimethylnaphth[2,3-d]imidazole-4,9-dione Compound No 2, as lustrous orange needles (2.2 g. 75%) m.p. 210°C.

### Example 3

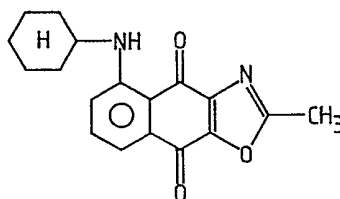
Compound No 3 having the formula:



was prepared by the method of Example 1 except that methylanine, as a 33% solution in ethanol [40 ml], was used in place of cyclohexylamine in Step 1d.

### Example 4

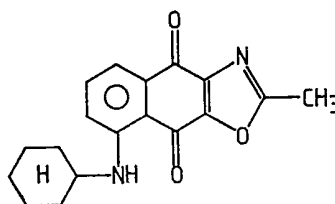
Compound No 4 having the formula:



was prepared by the method described in the PhD thesis by G.G-Buckley (University of Leeds, 1979) entitled: "Some heterocyclic derivatives of anthraquinone dyes", page 253, herein referred to as Reference 2.

### Example 5

Compound No 5 having the formula:



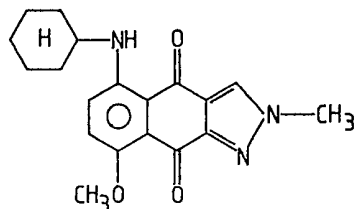
was prepared as the 5-isomer of compound 4 by separation from the reaction mixture as given by the method described in Reference 2 specified above.

*Example 6*

5 Compound No 6 having the formula:

5

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was prepared by the method described in Reference 2 above pp279-281 by u.v. irradiation of a solution of 5,8-dimethoxy-2-methyl benz[f]indazole-4,9-dione in the presence of cyclohexylamine and subsequent chromatographic separation of the 5-cyclohexylamine isomer.

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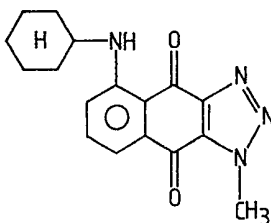
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*Example 7*

Compound No 7 having the formula:

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35 was prepared by the method given in Reference 2 p250 from a mixture of the 5- and 8-nitro isomers of 1-methyl naphth[2,3-d]triazole-4,9-dione by heating under reflux in benzene with cyclohexylamine (Reference 2, p262) the 5-cyclohexylamine derivative, (Compound 7), being separated by chromatographic means.

35

40 *Properties of compound nos 1 to 7*

40

Properties which have been measured for Compound Nos 1-7 are as given in Table 1 below.

In relation to Table 1 the following symbols are used:

45

$\lambda_{max}$  = wavelength(s) of maximum absorption (nm)

in the following

45

S = order parameter (measured at 20°C)

host material:

the commercially available material E43 (having a positive dielectric anisotropy) supplied by BDH Chemicals Ltd., this consists of a mixture of cyanobiphenyls, a cyano-p-terphenyl and a cyanobiphenylcyclohexane compound.

50

50

TABLE 1

*Properties of compound nos 1 to 7*

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55

Compound No	$\lambda_{max}$	S
1	530	0.67
2	437	0.4
3	520	0.53
4	552	0.50
5	552	0.51
6	528	0.55
7	560	0.55

60

60

Examples of liquid crystal devices embodying the second aspect of the present invention will now be described with reference to the accompanying drawings in which:

*Figure 1* is an exploded view of a Fréedericksz effect display device embodying the present invention,

*Figure 2* is a sectional view of the device shown in *Figure 1*; and

5 *Figure 3* is a front view of a watch having a liquid crystal display constructed as shown in *Figures 1* and *2*. 5

As shown in *Figure 1* a liquid crystal display of the Fréedericksz effect (positive nematic) type includes a liquid crystal cell 3 comprising two glass slides 4, 5 containing a layer of liquid crystal material 6 which is basically a positive nematic material together with a pleochroic dye. Electrodes 7, 8 eg of tin oxide are arranged on the inner faces of the slides 4, 5. A brushed aluminium reflector 27 may be located behind the  
10 slide 5. 10

Prior to assembling the cell 3 the slides 4, 5 (already bearing the electrodes 7, 8) are coated on their inner faces with silicon monoxide or magnesium fluoride. This coating is formed by evaporating a stream of eg silicon monoxide onto the slide at an angle of about 5° to the surface as for example described in UK Patent Specification No 1,454,296. On assembly the slides are arranged with the evaporation direction on the two  
15 slides 4,5 parallel to one another. With such coatings applied liquid crystal molecules at the coated surfaces lie in a single direction (parallel) to the evaporation direction) and at an angle of about 25° to 35° typically about 30° to the adjacent slide surface. As a result the liquid crystal molecules lie in a parallel homogeneous texture as indicated by arrow 13 (*Figure 1*). The dye molecules in guest-host relationship with the liquid  
20 crystal molecules are also roughly in this texture giving a relatively strongly coloured appearance to the cell 3 (which is black or grey if the dye absorbs uniformly throughout the visible spectrum). 20

A single polariser 1 placed in front of, or behind, the cell 3 (shown in front in *Figure 1*) with its transmission axis parallel to the alignment direction of the liquid crystal material 6, will enhance the colour of the display in this state, the "off" state.

By this arrangement the electric vector of the incident or reflected light is confined roughly parallel to the  
25 transition of the dye molecules. 25

When a suitable voltage, eg a few volts, (greater than the threshold to give the effect) is applied between the electrodes 7 and 8, ie to give the "on" state, the molecules of the liquid crystal material are switched to the homeotropic mixture, ie to lie parallel to the electric field along an axis perpendicular to the slides 4, 5. The dye molecules are also switched to this texture by the guest-host effect and have their long axes  
30 essentially parallel (ie they are essentially "end-on") to light incident on the cell 3 in a direction perpendicular to the slides 4, 5, effectively reducing their absorption of ambient light. This gives the cell 3 a relatively clear or weakly coloured appearance. 30

If the electrodes 7 and 8 cover only part of the inner surface of the slides 4 and 5 respectively the entire cell 3 will appear strongly coloured (ie strongly reflects) in the "off" state whereas in the "on" state only the  
35 region of the liquid crystal material 6 between the electrodes 7, 8 will appear clear or weakly coloured in the "on" state the remainder of the cell 3 appearing strongly coloured, ie remaining in the "off" state. (If the pleochroic dye absorbs uniformly throughout the visible spectrum the strong colouration will appear black or grey.) 35

Thus, by shaping the electrodes 7, 8 into discrete facing parts, eg bars of a digit separately connectable to a  
40 voltage source (not shown), symbols or letters may be displayed. This may be achieved by photoetching (in a known way) the layers, eg SnO<sub>2</sub>, used to form the electrodes 7, 8 prior to assembly. 40

For example, in the watch display of *Figure 3* the electrodes 7, 8 are shaped to provide four seven bar numeric digits to display time; eg the digits are displaying 12,45 as shown in *Figure 3*. A pulsed period dot P is also included, as in conventional watch displays, to indicate operation of the display.

45 Examples of suitable dyed liquid crystal material for use as the material 6 above are Dye Mixture No 1 (about 1% by weight) defined below dissolved in the host liquid crystal material E43 mentioned above (the thickness of the material 6 layer being 12µm). 45

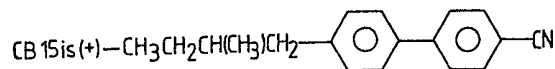
In an alternative device embodying the second aspect of the present invention a cholesteric to nematic phase change effect is made in a known way. The method of construction is the same as that described  
50 above with reference to *Figures 1* to *3* except that no MgF<sub>2</sub> or SiO coating is applied to the inner surfaces of the electrode bearing slides 4, 5, no polariser 1 is required and the liquid crystal material 6 in this case is essentially a long pitch cholesteric material (having a molecular helical pitch of the order of about 2 m containing a pleochroic dye. A suitable material is the host material E43 specified above modified by the inclusion of 5% by weight of CB15 as defined below and also containing the Dye Mixture No 1 defined below  
55 (about 1% by weight) (the thickness of the material 6 layer again being 12 m). 55

In the "off" state (with no voltage applied) the cell 3 again appears strongly coloured in this case (as in the Fréedericksz effect device). The liquid crystal material 6 in this state is in the focal conic texture which comprises an arrangement of random molecular helices. The dye molecules take up the same arrangement by the guest-host effect. The strong colouration (which may be black or dark grey) is because ambient white  
60 light incident on the material 6 via the slide 4 is partially absorbed by the dye molecules which are perpendicular or oblique to the light propagation direction. 60

In the "on" state a voltage (typically 10-15 volts) is applied between the electrodes 7, 8 sufficient to give the homeotropic texture, ie with the liquid crystal molecules between the electrodes 7, 8 essentially re-orientated to lie perpendicular to the slides 4,5. The dye molecules between the electrodes 7, 8 are  
65 re-orientated to this arrangement by the guest-host effect. The region between the electrodes 7, 8 appears 65

clear or weakly coloured in this state (as with Freedericksz effect device) because the dye molecules are essentially "end-on" to ambient light propagating in a direction perpendicular to the cell 3, ie perpendicular to the slides 4, 5 (via the slide 4).

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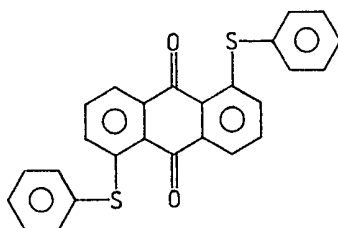
Dye Mixture 1 as referred to above:

- 15 Compound No 1 (red) 2 parts by weight  
Compound No 8 (yellow) 2½ parts by weight  
Compound No 9 (blue) 1 part by weight

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Compound No 8 is a known dye, having the following formula:

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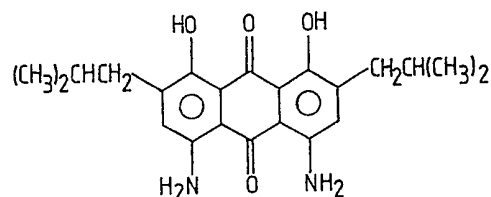
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Compound No 9 is a known dye having the following formula:

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## CLAIMS

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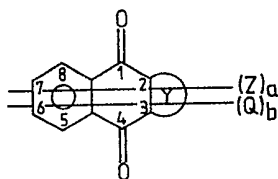
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1. A material suitable for guest-host liquid crystal device comprising a solution of a liquid crystal material and a pleochroic dye wherein the pleochroic dye comprises at least one compound having a formula:

FORMULA (I)

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wherein:

Y represents a five membered heterocyclic ring which includes the carbon atoms in positions 2 and 3 of the naphthoquinone nucleus;

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Z is a non-ionic substituent selected from SX OX and NXX<sup>1</sup> where:

X is H or an optionally substituted alkyl, optionally substituted cycloalkyl or aryl radical;

X<sup>1</sup> is H or a lower alkyl or alkoxy group;

Q is a non-ionic substituent selected from halo, nitro, cyano, optionally substituted alkyl, optionally substituted cycloalkyl and optionally substituted aryl;

65

a is an integer from 1 to 4 inclusive  
 b is an integer from 0 to 5 inclusive.

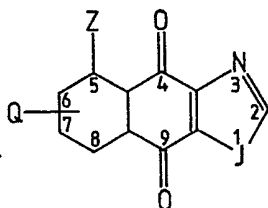
2. A material as claimed in claim 1 and wherein the said compound has at least one of the following groups in one of its ring positions: N, NH, O, NX<sup>a</sup> or S where X<sup>a</sup> is lower alkyl or lower alkoxy having from 1 to 5 carbon atoms. 5

3. A material as claimed in claim 1 and wherein the said compound carries a substituent in the 5 and/or 8 position of the naphthoquinone nucleus.

4. A material as claimed in claim 1 and wherein the said compound has a formula:

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20 wherein J is O or NR<sub>A</sub> where R<sub>A</sub> is hydrogen or simple alkyl or alkoxy having from 1 to 5 carbon atoms. 20

5. A material as claimed in claim 5 and wherein the substituent Z is TAKE IN HERE 26 or NHAr where

25 Ar is an aryl group and is in position 5 of the naphthoquinone nucleus. 25

6. A material as claimed in claim 1 and wherein the compound of formula 1 is any one of the specific compounds mentioned in the Examples hereinbefore.