

Optically active compounds

This invention relates to optically active materials and their use as doping agents for liquid crystals for a wide range of applications including solid state cholesteric filters for projection displays, circular polariser, optical filter, etc.

The addition of an optically-active compound to a non-optically-active liquid crystalline phase is one of procedures used for the conversion of non-optically-active into optically-active mesophases. The nematic phase, for example, is converted to the cholesteric one when being doped with a small amount of an optically-active substance. This conversion manifests itself by the occurrence of an intermolecular helix which is characterised by the so-called helical twisting power (HTP) given in Equation 1:

$$HTP = \left| \frac{dp^{-1}}{dx} \right|_{x=0} \cong \frac{P^{-1}}{x} = \sum_i x_i (HTP)_i \quad (1)$$

HTP (μm^{-1}) helical twisting power for small concentrations

p (μm) pitch of induced helix, + for (P)-, - for (M)-helix

x mole fraction of the dopant

$\sum_i$ sum over all optically-active conformers of the dopant

x_i mole fraction of conformer i

Said HTP is in fact a measure for the efficiency of a given dopant and is determined by the Cano method with solutions of the dopant in the host mesophase. Since the optically-active guest and the non-optically-active host compounds are not necessarily compatible at the molecular scale, their binary solution is frequently characterised by undesirable changes of the thermotropic sequence of the initial host liquid crystalline material,

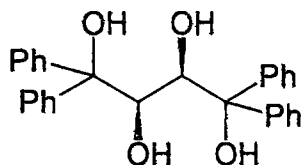
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like for example a depression of the clearing point. Those changes could in turn have negative effects on the phase properties of the host, such as a decrease of the birefringence etc. Therefore, an optically-active dopant is sought so that with
5 very small concentrations of this latter, large values of HTP could be induced.

As such efficient optically-active dopants there are the binaphthol derivatives described in GB-A-2 298 202. However optically-active binaphthol derivatives may undergo partial
10 racemisation when being heated. Besides, their preparation is expensive because it includes asymmetric resolution of binaphthol racemate as a crucial reaction step.

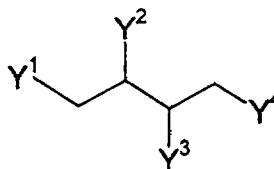
Another type of optically-active dopants are the TADDOLs derivatives ($\alpha,\alpha,\alpha',\alpha'$ -tetraaryl-1,3-dioxolane-4,5-dimethanols).
15 They have been known for 15 years in asymmetric syntheses (D. Seebach et al., *J. Org. Chem.* 60, 1788, (1995) and *Helv. Chim. Acta* 80, 2515, (1997)) and recently investigated as dopants in nematic host mesophases and found to induce large values of HTP (H. G. Kuball et al., *Helv. Chim. Acta* 80, 2507, (1997) and
20 International Patent Application WO-A-97/34886). This efficiency of TADDOLs compounds was essentially attributed to their conformational stability due to the presence of the dioxolane ring.

Tet. Lett. 36(11), 1995, 1827-1830 (Dubé et al.) discloses
25 the compound (2R,3R)-1,1,4,4-tetraphenylbutane-1,2,3,4-tetraol as an intermediate in asymmetric synthesis:



However, no activity is given for the compound.

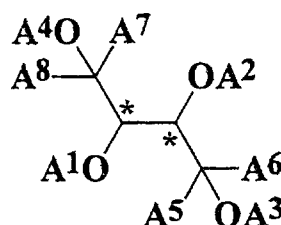
EP-A-0233602 (Hoechst AG) relates to chiral dopants for
30 liquid crystals. The compounds are all derivatives of butane-1,2,3,4-tetraol of general formula:



having no further substituents on the butane backbone.

It has been suggested that the large HTP observed with TADDOLs compounds is due to their conformational stability.
 5 However we have now discovered that further compounds that exhibit overcrowding of the chiral atoms and are sterically hindered at positions analogous to the α, α' positions in TADDOLs are equally effective at producing a large HTP.

Thus the invention provides optically active butane-1,2,3,4-
 10 -tetraol derivatives of formula I:



(I)

in which:

A^1, A^2, A^3, A^4 each independently represents hydrogen; or an optionally-substituted methyl group; or an
 15 optionally-substituted aliphatic group with 2 to 80 C-atoms, in which one or more C-atoms may be replaced by a heteroatom or a group $-SO-$, $-SO_2-$, $-SOO-$, $-OSO-$ or $-SOS-$; or an optionally-substituted aromatic or non-aromatic carbocyclic or heterocyclic ring system, with 1 to 80 C-atoms;
 20 and

A^5, A^6, A^7, A^8 each independently represents an optionally-substituted aliphatic group with 3 to 80 C-atoms, in which a C-atom, or two or more non-adjacent C-atoms, may be replaced by a heteroatom or a
 25

group -SO-, -SO₂-, -SOO-, -OSO- or -SOS-; or an optionally-substituted aromatic or non-aromatic carbocyclic or heterocyclic ring system, with 1 to 80 C-atoms; or

5 one, two or three of A⁵, A⁶, A⁷ and A⁸ independently represents hydrogen; or an optionally-substituted methyl group; or an optionally-substituted aliphatic group with 2 C-atoms, in which a C-atom may be replaced by a heteroatom; and the remainder of A⁵, A⁶, A⁷, A⁸ independently represent an optionally-substituted
10 aliphatic group with 3 to 80 C-atoms, in which a C-atom, or two or more non-adjacent C-atoms, may be replaced by a heteroatom, or a group -SO-, -SO₂-, -SOO-, -OSO- or -SOS-; or an optionally-substituted aromatic or non-aromatic carbocyclic or heterocyclic ring system, with 1 to 80 C-atoms;

15 with the provisos that:

- when one, two or three of A⁵, A⁶, A⁷ and A⁸ represents hydrogen, then A⁵, A⁶, A⁷ and A⁸ may not represent COOH; and
- when A⁵, A⁶, A⁷ and A⁸ are all phenyl, then at least one of A¹, A², A³, A⁴ does not represent hydrogen.

20 The term "aliphatic" includes straight-chain and branched alkyl, as well as saturated and unsaturated groups. Possible substituents include alkyl, aryl (thus giving an araliphatic group) and cycloalkyl, as well as amino, cyano, epoxy, halogen, hydroxy, nitro, oxo etc. Possible heteroatoms which may replace
25 carbon atoms include nitrogen, oxygen and sulphur. In the case of nitrogen further substitution is possible with groups such as alkyl, aryl and cycloalkyl.

In the case of the present invention, owing to the absence of the dioxolane ring, the new optically active butane-1,2,3,4-
30 -tetraol derivatives of formula I have obviously more conformational freedom than TADDOLs derivatives. However they were surprisingly found still to induce large values of HTP when

being used as dopants in nematic host systems, as will be demonstrated in the forthcoming sections.

The compounds of the invention may be used as doping agents for liquid crystals for a wide range of applications including
5 solid state cholesteric filters for projection displays, circular polarisers, optical filters, etc.

Although one or more of A⁵, A⁶, A⁷ and A⁸ may represent a small group such as hydrogen or an optionally-substituted methyl group, we prefer there to be two bulkier groups, A⁵ and A⁶,
10 attached to the same carbon atom. Thus preferably only A⁷ and A⁸ may represent hydrogen. More preferably only one of A⁵, A⁶, A⁷ and A⁸ may represent hydrogen. The best compounds are those which have four bulky groups. Thus, preferably A⁵, A⁶, A⁷ and A⁸ each independently represents an optionally-substituted aliphatic
15 group with 3 to 80 C-atoms, in which a C-atom, or two or more non-adjacent C-atoms, may be replaced by a heteroatom or a group -SO-, -SO₂-, -SOO-, -OSO- or -SOS-; or an optionally-substituted aromatic or non-aromatic carbocyclic or heterocyclic ring system, with 1 to 80 C-atoms. Carbocyclic or heterocyclic ring system
20 having two or more fused rings have been found to be particularly suitable.

The invention further relates to optically active butane-1,2,3,4-tetraol derivatives of formula I, in which:

A¹, A², A³, A⁴ each independently represents hydrogen; or an
25 optionally-substituted methyl group; or an optionally-substituted aliphatic group with 2 to 80 C-atoms, in which one or more C-atoms may be replaced by a heteroatom or a group -SO-, -SO₂-, -SOO-, -OSO- or -SOS-; or an optionally-
30 -substituted aromatic ring system, with 1 to 80 C-atoms; and

A⁵, A⁶, A⁷, A⁸ each independently represents an optionally-substituted aliphatic group with 3 to 80 C-atoms, in which a C-atom, or two or more non-adjacent

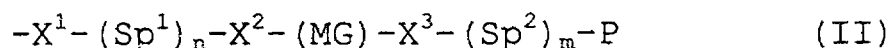
C-atoms, may be replaced by a heteroatom or a group -SO-, -SO₂-, -SOO-, -OSO- or -SOS-; or an optionally-substituted aromatic ring system, with 1 to 80 C-atoms;

- 5 with the proviso that, when A⁵, A⁶, A⁷ and A⁸ are all phenyl, then at least one of A¹, A², A³, A⁴ does not represent hydrogen.

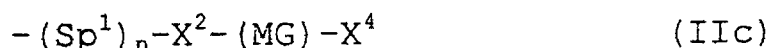
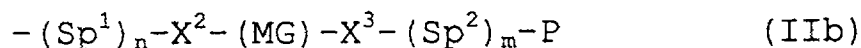
Particularly interesting applications are possible if at least one of the A¹ to A⁸ residues includes a polymerisable group.

- 10 Preferred embodiments of the invention relates to optically active butane-1,2,3,4-tetraol derivatives of formula I, wherein:

A⁵ to A⁸ have each independently one of the meanings of formula II:



- 15 A¹ to A⁴ are hydrogen atoms or have each independently one of the meanings of formula IIb or one of the meanings of formula IIc:



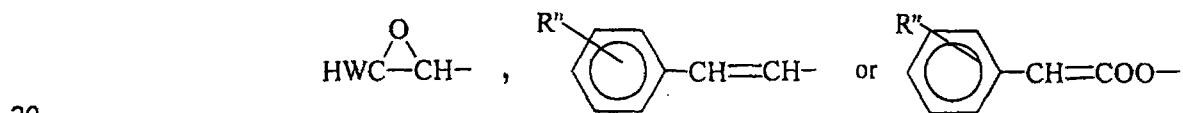
in which:

- 20 X¹ to X³ each independently denote -O-, -S-, -NH-, -N(CH₃)-, -CH(OH)-, -CO-, -CH₂(CO)-, -SO-, -CH₂(SO)-, -SO₂-, -CH₂(SO₂)-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -SOO-, -OSO-, -SOS-, -CH₂-CH₂-, -OCH₂-, -CH₂O-, -CH=CH-, -C≡C- or a single bond, in such a manner that oxygen atoms are not linked directly to one another;
- 25

X⁴ is a halogen;

Sp¹ and Sp² are each independently straight or branched spacer groups having 1 to 20 C-atoms which may be unsubstituted, or mono- or polysubstituted by halogen or CN, it being also possible for one or more non-adjacent CH₂ groups to be replaced, in each case independently from one another, by -O-, -S-, -NH-, -N(CH₃)-, -CH(OH)-, -CO-, -CH₂(CO)-, -CH₂(SO)-, -CH₂(SO₂)-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -C≡C-, -(CF₂)_r-, -(CD₂)_s- or -C(W¹)=C(W²)-, r and s ranging between 1 and 15, and W¹ and W² each independently denoting H, H-(CH₂)_q- or Cl with q ranging between 1 and 15;

P is hydrogen or preferably a polymerisable group selected from the formulae CH₂=CW-, CH₂=CW-COO-, CH₂=C(Ph)-COO-, CH₂=CH-COO-Ph-, CH₂=CW-CO-NH-, CH₂=C(Ph)-CONH-, CH₂=C(COOR')-CH₂-COO-, CH₂=CH-O-, CH₂=CH-OOC-, Ph-CH=CH-, CH₃-C=N-(CH₂)_{m3}, HO-, HS-, HO-(CH₂)_{m3}-, HS-(CH₂)_{m3}-, HO(CH₂)_{m3}COO-, HS(CH₂)_{m3}COO-, HWN-, HOC(O)-, CH₂=CH-Ph-(O)_{m4},

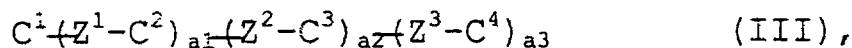


with W being H, Cl or alkyl with 1-5 C atoms, m₃ being 1-9, m₄ being 0 or 1, Ph being phenyl, R' being alkyl with 1-5 C atoms, and R'' having the meaning of R' or being methoxy, cyano or a halogen;

25 n and m are each independently 0 or 1; and

MG denotes a mesogenic group comprising 1 to 4 aromatic or non-aromatic carbocyclic or heterocyclic ring systems and optionally up to 3 bridging groups, and preferred are those selected from the meanings of formula III:

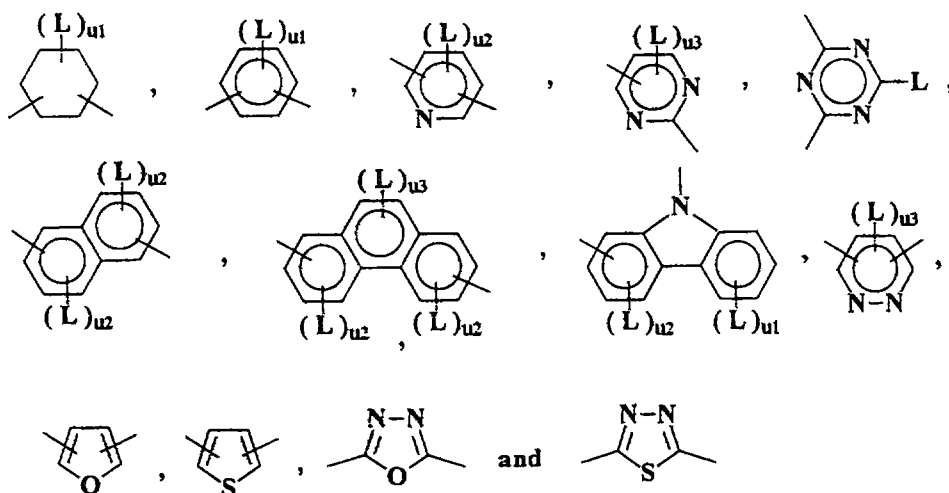
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in which:

- 5 C^1 to C^4 are in each case independently optionally-substituted non-aromatic, aromatic, carbocyclic or heterocyclic groups;
- Z^1 to Z^3 are independently from each other $-COO-$, $-OCO-$, $-CH_2-CH_2-$, $-OCH_2-$, $-CH_2O-$, $-CH=CH-$, $-C\equiv C-$, $-CH=CH-COO-$, $-OCO-CH=CH-$ or a single bond; and
- 10 a_1 , a_2 and a_3 are independently integers 0 to 3, such that $a_1 + a_2 + a_3 \leq 4$.

Especially preferred are those in which C^1 to C^4 are selected from:



with:

- 15 L being $-CH_3$, $-COCH_3$, $-NO_2$, CN , or halogen,
- u_1 being 0, 1, 2, 3, or 4,
- u_2 being 0, 1, 2, or 3, and
- u_3 being 0, 1, or 2.

We have discovered that, to attain high values of HTP for a given guest-host liquid crystalline system, it is desirable to increase the size and the conformational stability of the substituents around the chiral centre(s) of the optically active host molecule(s). It is possible to realise such a strategy in the present invention with optically active butane-1,2,3,4-tetraol derivatives of formula I where the two 1 and 4 positions could be derivatised with bulky A⁵ to A⁸ substituents starting, for example, from the Grignard analogues of A⁵ to A⁸ of appropriate structure, selected from the formula II and tartaric acid, commercially available in both (R,R) and (S,S) enantiomeric forms. The four generated hydroxy groups could be then derivatised, using classical synthetic methods, with A¹ to A⁴ appropriately selected from the formula IIb as organic residues permitting the increase of solubility and/or the increase of compatibility of I with the guest liquid crystalline systems.

More preferred embodiments of the present invention are:

a) for ease of synthesis, optically active butane-1,2,3,4-tetraol derivatives of formula I wherein:

A¹ and A² are identical, and

A³ and A⁴ are identical, and

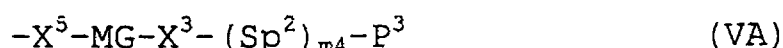
A⁵ to A⁸ are identical; and

b) optically active butane-1,2,3,4-tetraol derivatives of formula I wherein:

A³ and A⁴ have one of the meanings of formula IV:

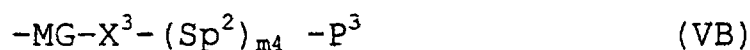


A¹ and A² have one of the meanings of formula VA:



and

A⁵ to A⁸ have one of the meanings of formula VB:



in which:

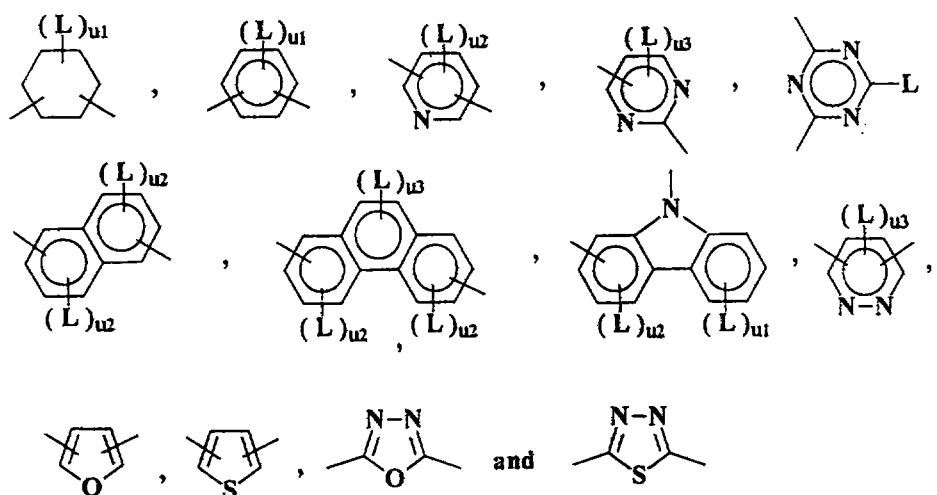
Sp² is alkylene with 0 to 20 C-atoms,

5 p² is H, CH₂=CW⁵- or CH₂=CW⁵-CO-,

p³ is H, CH₂=CW⁵-, CH₂=CW⁵-COO-, W⁵CH=CH-O- or
CH₂=CW⁵-O-, with W⁵ being H, CH₃, or Cl,

m⁴ and m⁵ are each independently 0 or 1 in such a manner that
oxygen atoms are not linked directly to one
10 another,

MG is selected from:



x³ is -O-, -CO-, -COO-, -OCO-, -CH₂-CH₂-, -OCH₂-,
-CH₂O-, -CH=CH-, -C≡C-, -CH=CH-COO-, -OCO-CH=CH- or
15 a single bond, and

x⁵ is -CO- or -CH₂-.

Preferred compounds of formula I are those for which A³ and
A⁴ have one of the meanings of formula IV, A¹ and A² have one of

the meanings of formula VA and A⁵ to A⁸ have one of the meanings of formula VB, in which:

- MG is cyclohexylene, phenylene, biphenylene, naphthylene or phenanthrylene,
- 5 X³ denotes -O-, -CO-, -COO-, -OCO-, -C≡C-, or a single bond, in particular -O- or a single bond,
- Sp² is straight-chain of formula -(CH₂)_v-, with v being an integer between 0 and 20, especially preferred being ethylene, propylene, butylene, pentylene, 10 hexylene, heptylene, octylene, nonylene, decylene, undecylene, or dodecylene,
- P² is H, CH₂=CW⁵- or CH₂=CW⁵-CO-,
- P³ is H, CH₂=CW⁵-, CH₂=CW⁵-COO-, W⁵CH=CH-O- or CH₂=CW⁵-O-, with W⁵ being H, CH₃, or Cl, and
- 15 m⁴ and m⁵ are each independently 0 or 1 in such a manner that oxygen atoms are not linked directly to one another.

Other aspects of the present invention are:

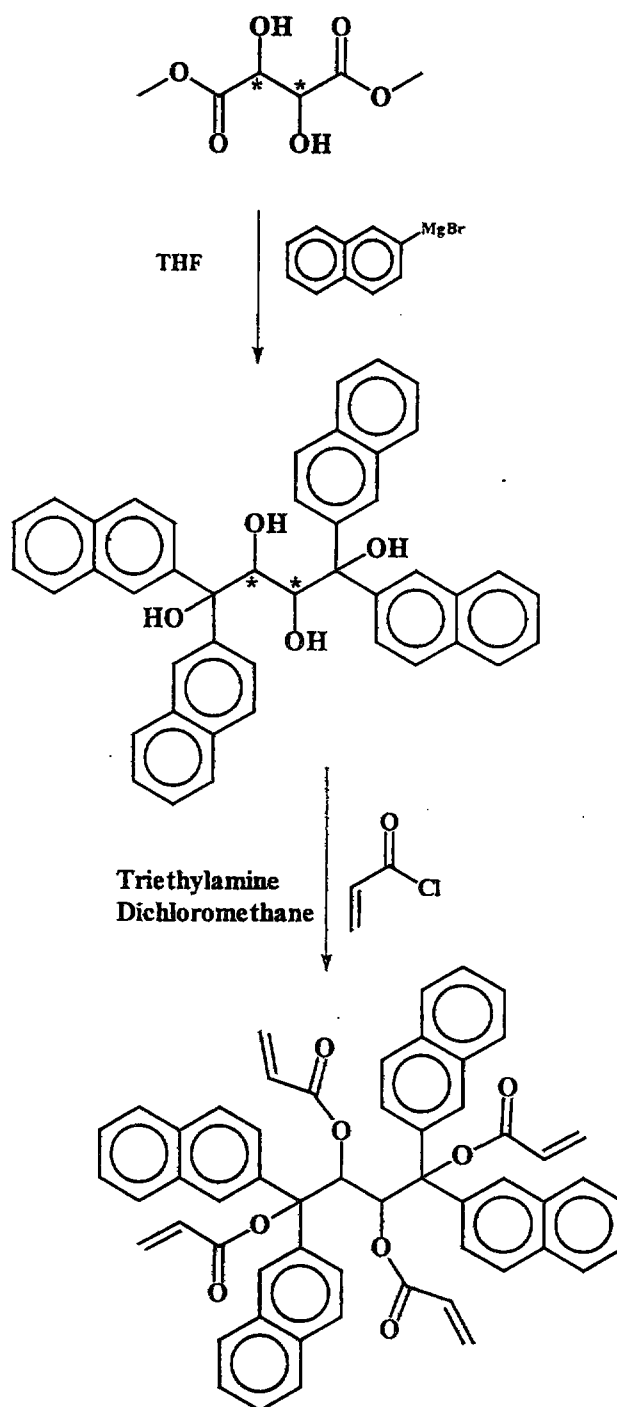
- a) a liquid crystalline material, especially in the form of a liquid crystalline mixture, (co)polymer, elastomer, polymer 20 gel or polymer network, comprising at least two components, at least one of which is an optically active compound, characterised in that the optically active compound is a butane-1,2,3,4-tetraol derivative of formula I;
- b) a liquid crystalline material, especially in the form of a cholesteric mixture, or cholesteric polymer network, 25 comprising at least two components, at least one of which is an optically active compound, characterised in that the optically active compound is a butane-1,2,3,4-tetraol derivative of formula I;

- c) a cholesteric polymer network obtainable by copolymerisation of an optically active polymerisable mesogenic mixture comprising:
- 5 i) at least one optically-active or/and non-optically-active nematic polymerisable compound which can be chosen from the already reported broad range of optically-active and non-optically-active nematic materials, for example in *Adv. Mater.* 5, 107 (1993), *Mol. Cryst. Liq. Cryst.* 307, 111 (1997), *J. Mat. Chem.* 5, 2047 (1995) or in patent applications US-A-5,593,617; US-A-5,567,349; GB-A-2 297 556; 10 GB-A-2 299 333; DE-A-19 504 224; EP-A-0 606 940; EP-A-0 643 121 and EP-A-0 606 939; optionally selected from EP-A-0 606 940, EP-A-0 643 121 and EP-A-0 606 939,
 - ii) at least one optically active dopant of formula I,
 - 15 iii) an initiator,
 - iv) optionally a non-mesogenic compound having at least one polymerisable functional group, more optionally a diacrylate compound, and
 - v) optionally a stabiliser;
- 20 d) optically-active polymerisable cholesteric mixtures, essentially consisting of:
- i) 70 to 99 %, preferably 85 to 95 % by weight of at least one non-optically-active polymerisable liquid crystal,
 - 25 ii) 0.1 to 30 %, preferably 1 to 15 % by weight of an optically active compound of formula I,
 - iii) 0.1 to 5 %, preferably 0.2 to 2 % by weight of a photoinitiator,
 - iv) 0 to 5 %, preferably 0.1 to 1 % of a stabiliser, and

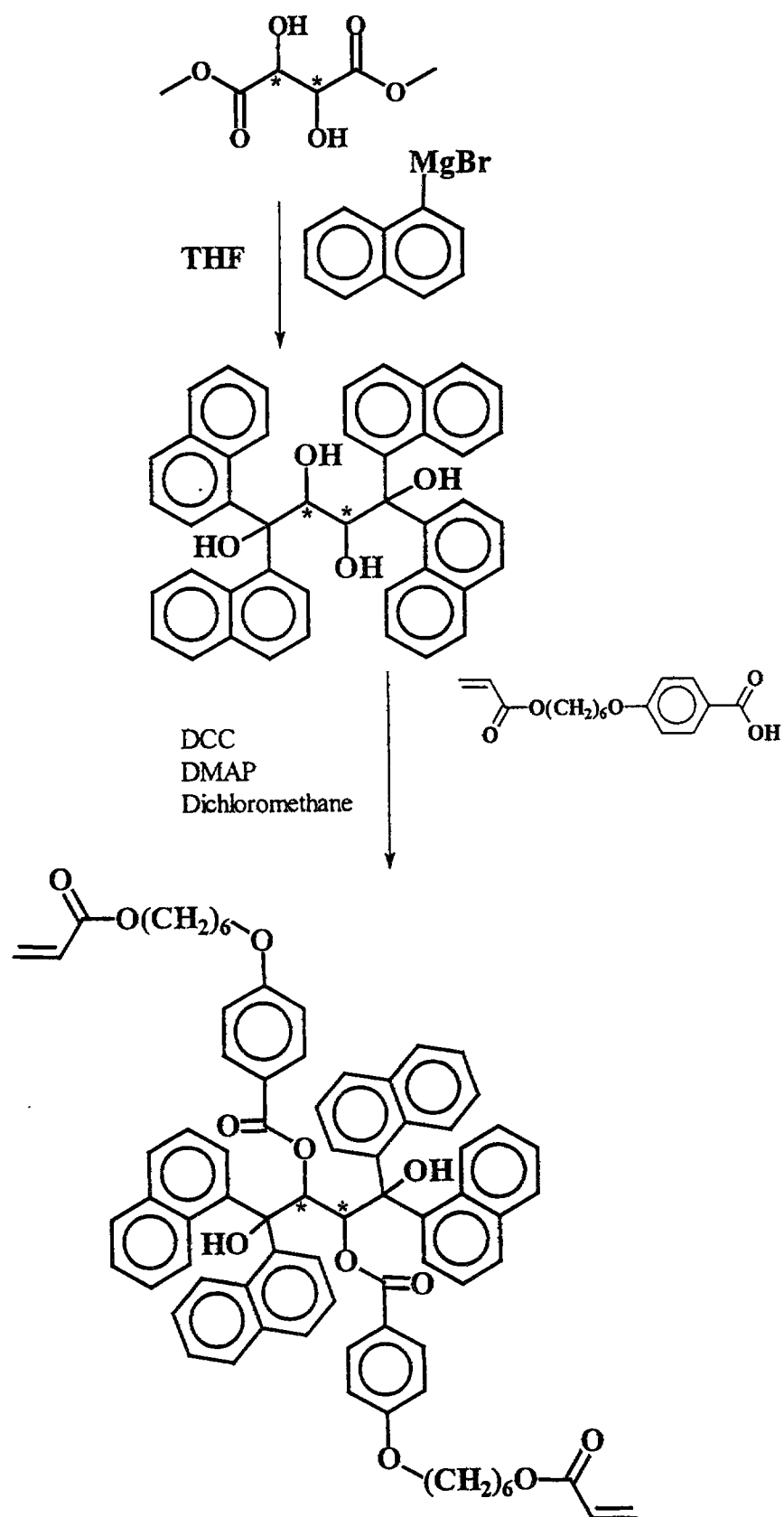
- e) a cholesteric film obtainable by the steps comprising ordering the above mixture in the monomeric state and *in situ* UV polymerisation of the resulting ordered mixture.

The inventive optically active compounds disclosed in the foregoing and the following can be prepared by methods which are known *per se* and which are described in standard works of organic chemistry such as, for example, Houben-Weyl, *Methoden der Organischen Chemie*, Thieme-Verlag, Stuttgart. In the present case of compounds I the commercially available (R,R)- and (S,S)-dimethyl tartrate are used as starting materials, for example according to the following reaction schemes:

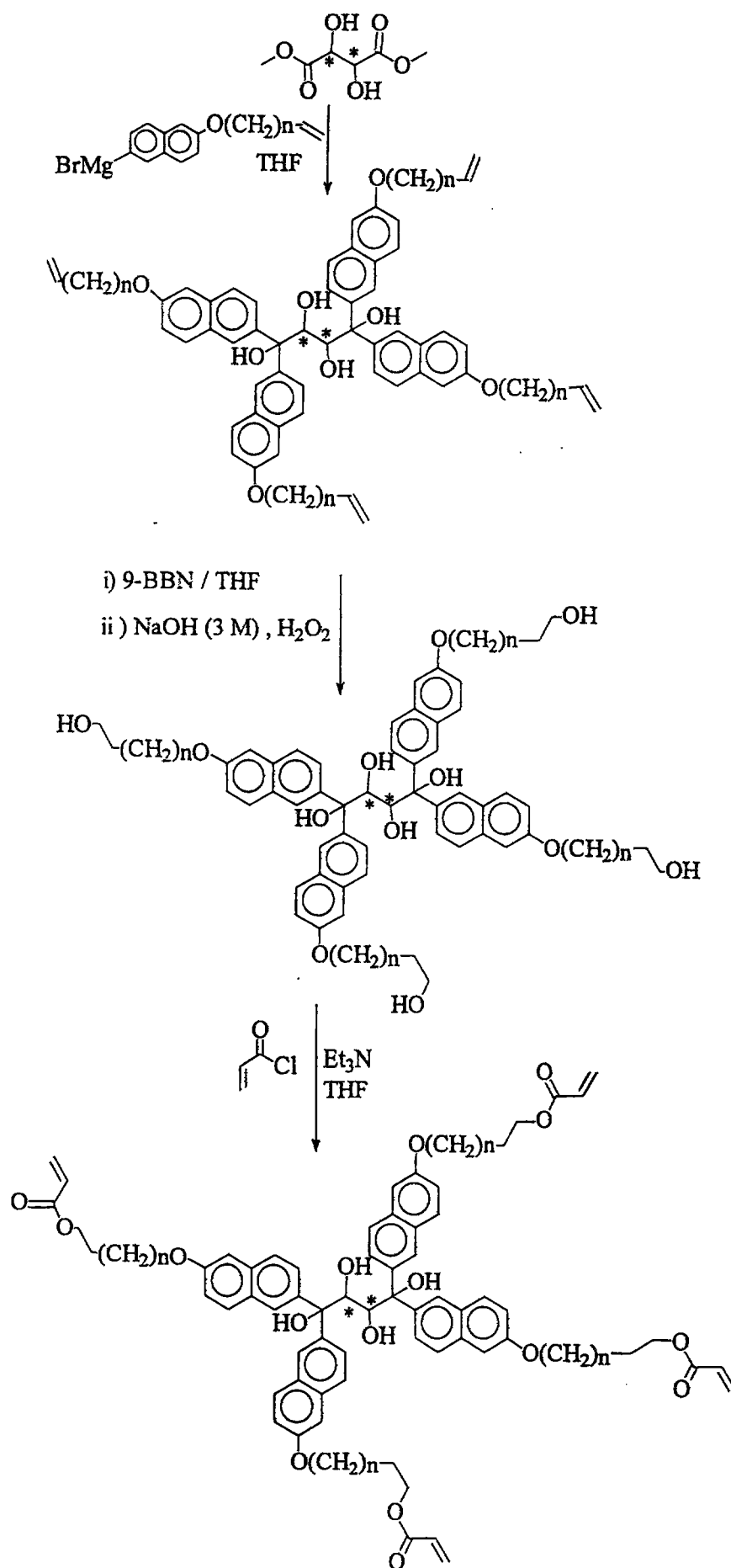
(Scheme 1)



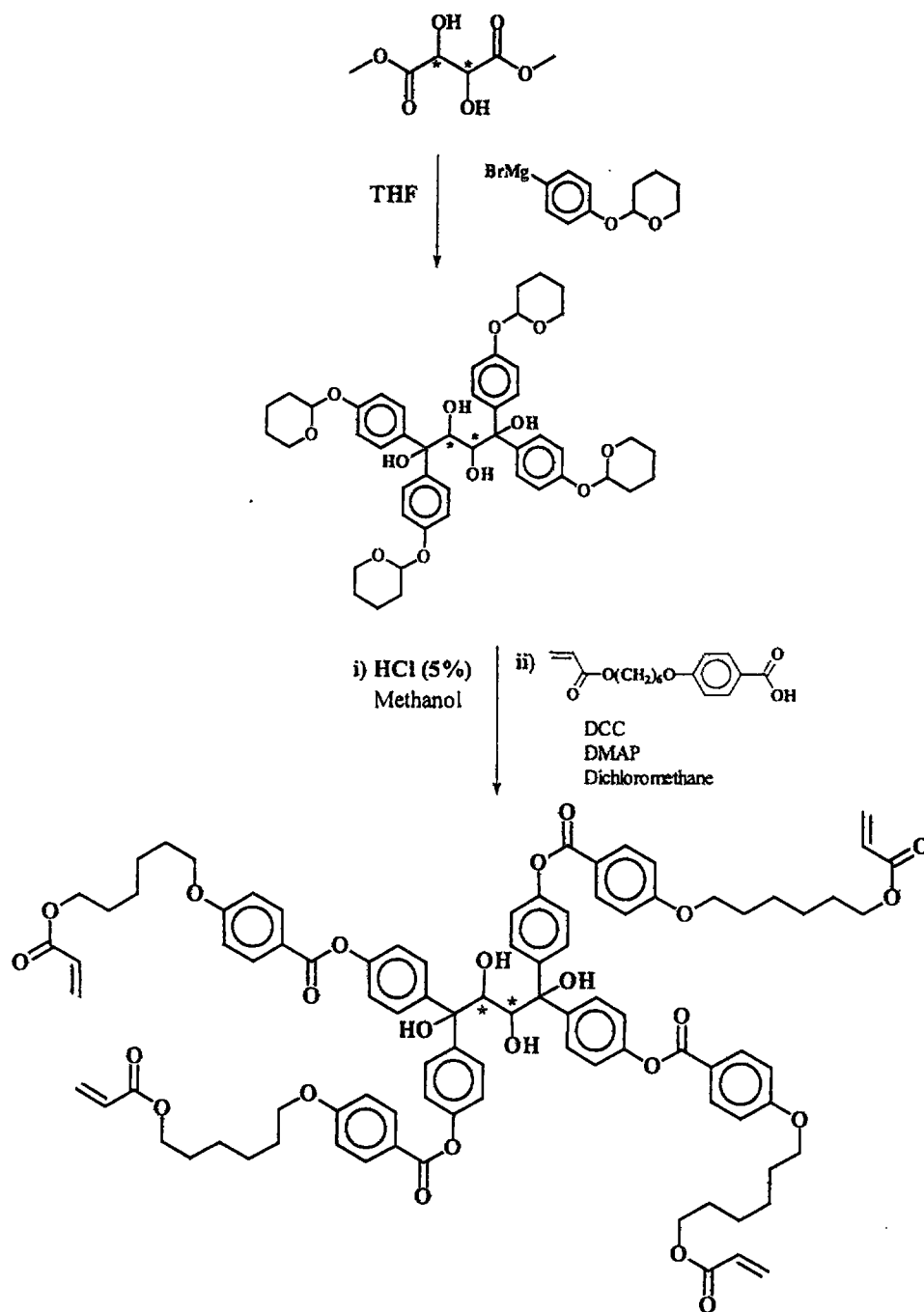
(Scheme 2)



(Scheme 3)



(Scheme 4)



Different methods can be used for the formation of the sought cholesteric network, starting from the polymerisable coloured
 5 cholesteric mixture manufactured as described above. Preferably, transparent substrates, optionally coated with ITO (indium tin oxide), and more preferably glass or plastic substrates, were used. Said substrates carried a layer of rubbed polyimide or

polyamide or a layer of coated photopolymer. Said layers are used to orient the molecular helix which forms spontaneously in the cholesteric mixture. To preclude the formation of disclinations, the polymerisable cholesteric mixture was:

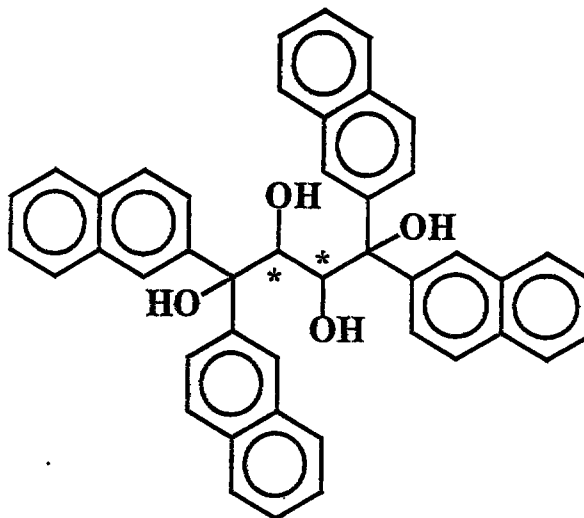
- 5 • coated into a thin film, or
- provided between two of the said substrates which were sheared over a small distance until a planar order was obtained, or
- capillary filled between two of the said substrates,

10 then subsequently cured, for example, by UV light, preferably in the presence of a photoinitiator, for example an IRGACURE™. Owing to the strength of the three-dimensional polymer network thus formed, the film may be peeled off and used, for example, as a self-supporting cholesteric polariser.

15 The reflected colour from the formed cholesteric layer is dependent on the pitch length of the cholesteric helix, said pitch length being itself dependent on the concentration of the optically-active dopant in, for example, a nematic host. For small and high concentrations of the optically-active dopant, the cholesteric network reflects red and blue colours respectively.

20 The novel optically active butane-1,2,3,4-tetraol derivatives of formula I are highly suitable for producing cholesteric films which can be used in different optical and electro-optical applications.

Example 1: Preparation of (2*R*,3*R*)-1,1,4,4-tetranaphthalen-2-ylbutane-1,2,3,4-tetraol



Under argon, 20.71 g of 2-bromonaphthalene are added to a
 5 suspension of magnesium (2.43 g) in 60 ml of dry THF. The
 obtained mixture is stirred for 2 h at room temperature (with
 occasional cooling within a ice bath, the reaction being
 exothermic). Then a solution of L-(+)-dimethyl tartrate (2.23 g)
 in 20 ml of dry THF is added dropwise to the cooled reaction
 10 mixture at 0°C. After complete addition (20 min), the reaction
 mixture is stirred for a further 4 h at room temperature, poured
 into saturated NH₄Cl solution (150 ml) and extracted with ether
 (3 x 250 ml). The combined ether extracts are washed with
 saturated NaCl solution, dried over magnesium sulphate and
 15 evaporated to dryness. The obtained yellow-brown residue is
 chromatographed on silica gel (CH₂Cl₂, CH₂Cl₂/Et₂O : 9/1). This
 affords (2*R*,3*R*)-1,1,4,4-tetranaphthalen-2-ylbutane-1,2,3,4-
 -tetraol as white crystalline material.

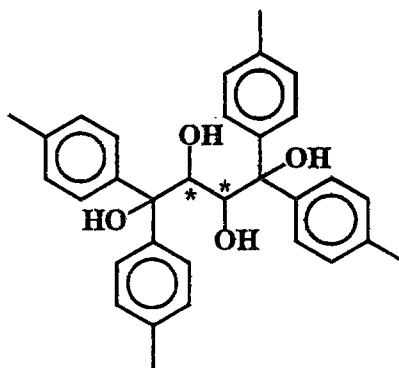
Yield: 6.2 g.

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According to the procedure of Example 1, the following chiral
 1,1,4,4-tetraarylbutane-1,2,3,4-tetraol derivatives are prepared:

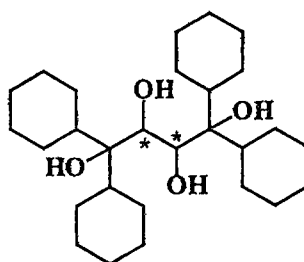
(2*R*,3*R*)-1,1,4,4-Tetra-*p*-tolylbutane-1,2,3,4-tetraol

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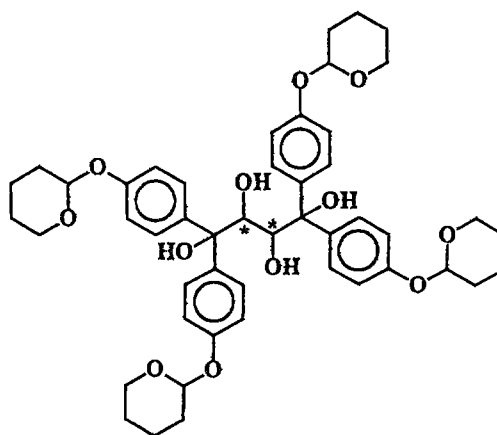


(2*R*,3*R*)-1,1,4,4-Tetracyclohexylbutane-1,2,3,4-tetraol

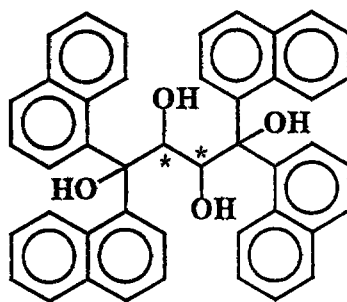
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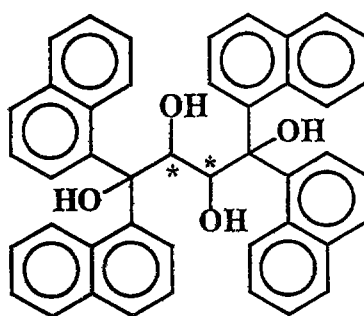
(2*R*,3*R*)-1,1,4,4-Tetrakis-[4-(tetrahydropyran-2-yloxy)phenyl]-
butane-1,2,3,4-tetraol



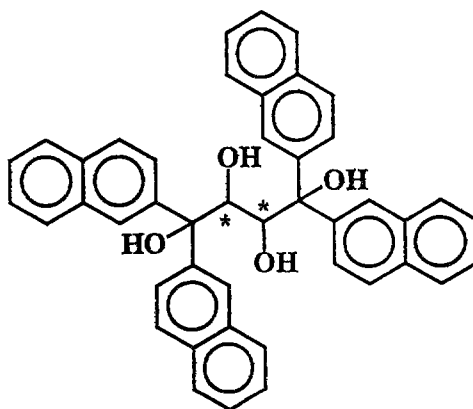
(2R,3R) -1,1,4,4-Tetranaphthalen-1-ylbutane-1,2,3,4-tetraol



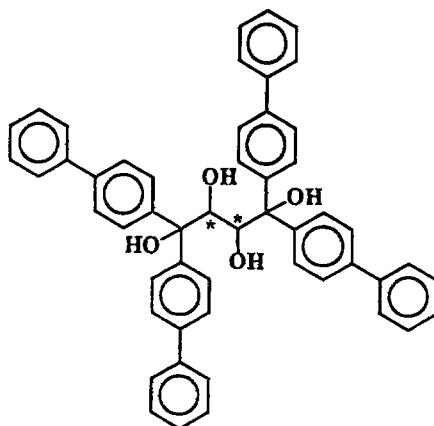
(2S,3S) -1,1,4,4-Tetranaphthalen-1-ylbutane-1,2,3,4-tetraol



5 (2S,3S) -1,1,4,4-Tetranaphthalen-2-ylbutane-1,2,3,4-tetraol

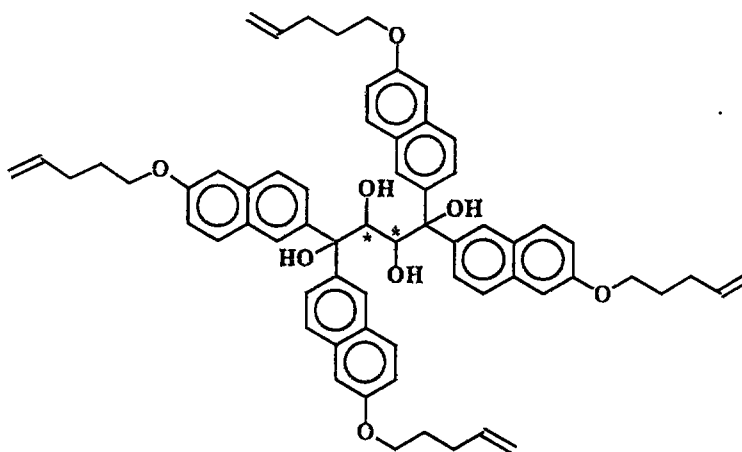


(2*R*,3*R*)-1,1,4,4-Tetrakisbiphenyl-4-ylbutane-1,2,3,4-tetraol



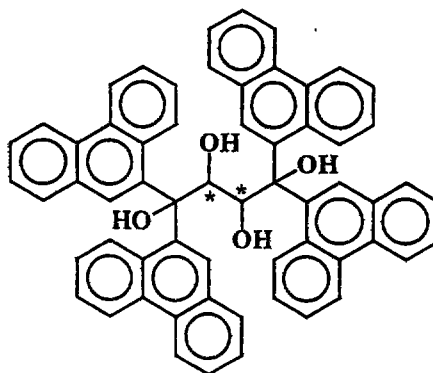
(2*R*,3*R*)-1,1,4,4-Tetrakis-(6-pent-4-enyloxynaphthalen-2-yl)-butane-1,2,3,4-tetraol

5

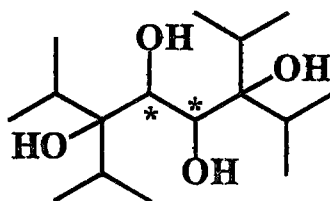


10

(2*R*,3*R*)-1,1,4,4-Tetraphenanthren-9-ylbutane-1,2,3,4-tetraol

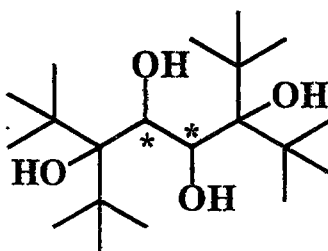


(4*R*,5*R*)-3,6-Diisopropyl-2,7-dimethyloctane-3,4,5,6-tetraol



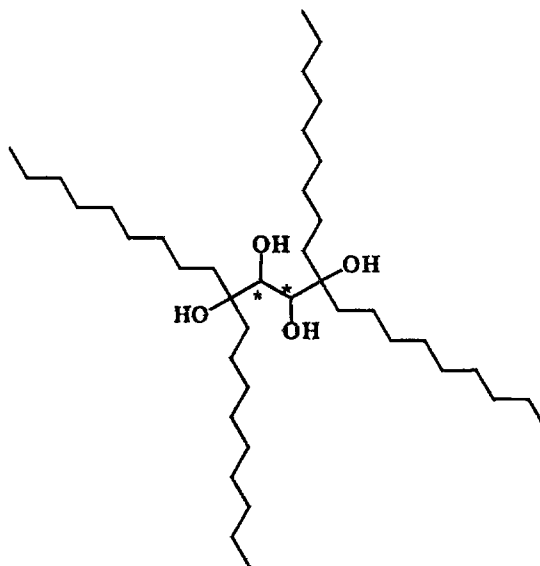
(4*R*,5*R*)-3,6-Di-*tert*-butyl-2,2,7,7-tetramethyloctane-3,4,5,6-tetraol

5



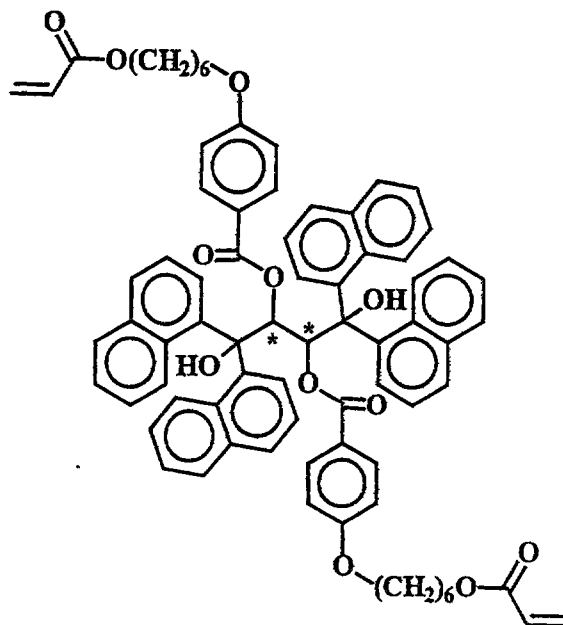
(11*R*,12*R*)-10,13-Dinonyldocosane-10,11,12,13-tetraol

10



15

Example 2: (2*R*,3*R*)-2,3-Bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-
-1,1,4,4-tetranaphthalen-1-ylbutane-1,4-diol



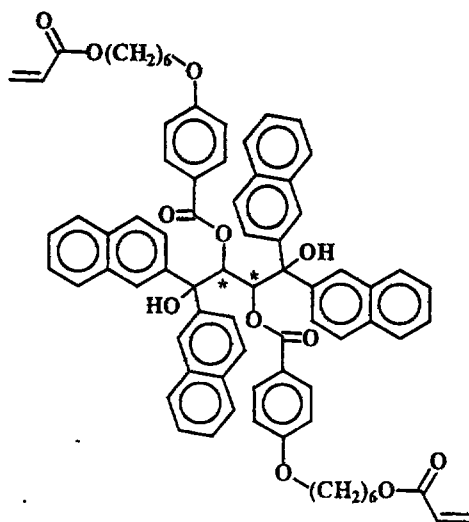
To a stirred solution of (2*R*,3*R*)-1,1,4,4-tetranaphthalen-
5 -1-ylbutane-1,2,3,4-tetraol (0.78 g), 4-(6-acryloyloxyhexyloxy)-
benzoic acid (1.46 g) and 4-dimethylaminopyridine (DMAP) (0.61 g)
in dichloromethane (20 ml), a solution of *N,N'*-dicyclohexylcarbo-
diimide (DCC) (1.03 g) in dichloromethane (10 ml) was added drop-
wise. After complete addition (15 min), the reaction mixture was
10 further stirred for 48 h at room temperature. It was then fil-
tered and the filtrate was concentrated under reduced pressure.
The obtained oily residue was chromatographed on silica gel
(CH₂Cl₂, CH₂Cl₂/Et₂O : 9/1) affording (2*R*,3*R*)-2,3-bis-[4-(6-acryl-
oyloxyhexyloxy)benzoyloxy]-1,1,4,4-tetranaphthalen-1-ylbutane-
15 -1,4-diol as white crystalline material.

Yield: 0.56 g.

According to the procedure of Example 2, the following chiral
polymerisable 1,1,4,4-tetraarylbutane-1,2,3,4-tetraol derivatives
20 are prepared:

(2*R*,3*R*)-2,3-Bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-1,1,4,4-tetranaphthalen-2-ylbutane-1,4-diol

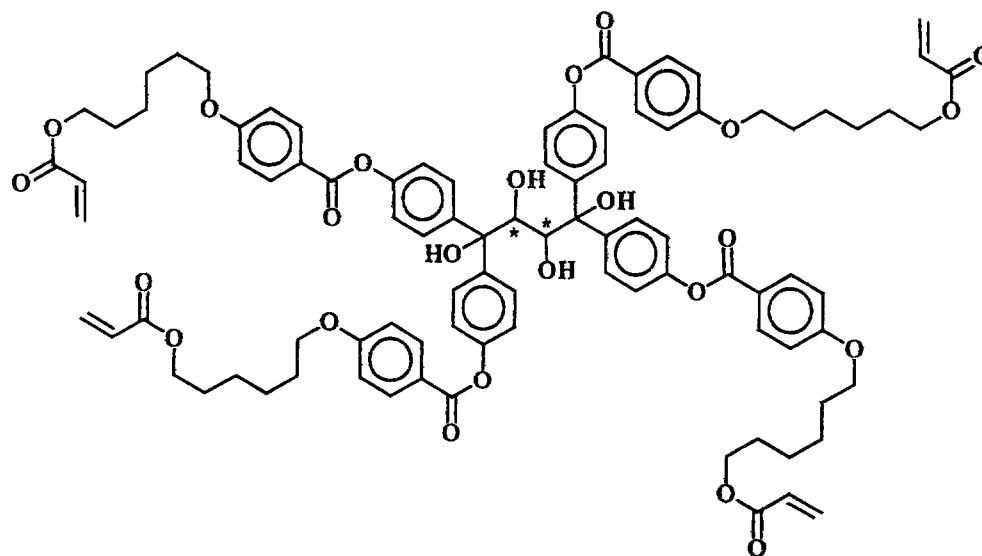
5



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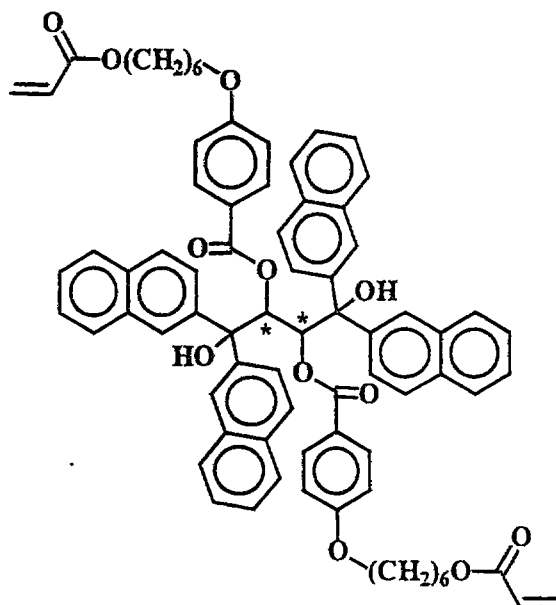
(2*R*,3*R*)-1,1,4,4-Tetrakis-[4-(6-acryloyloxyhexyloxy)benzoyloxy-phenyl]butane-1,2,3,4-tetraol

15

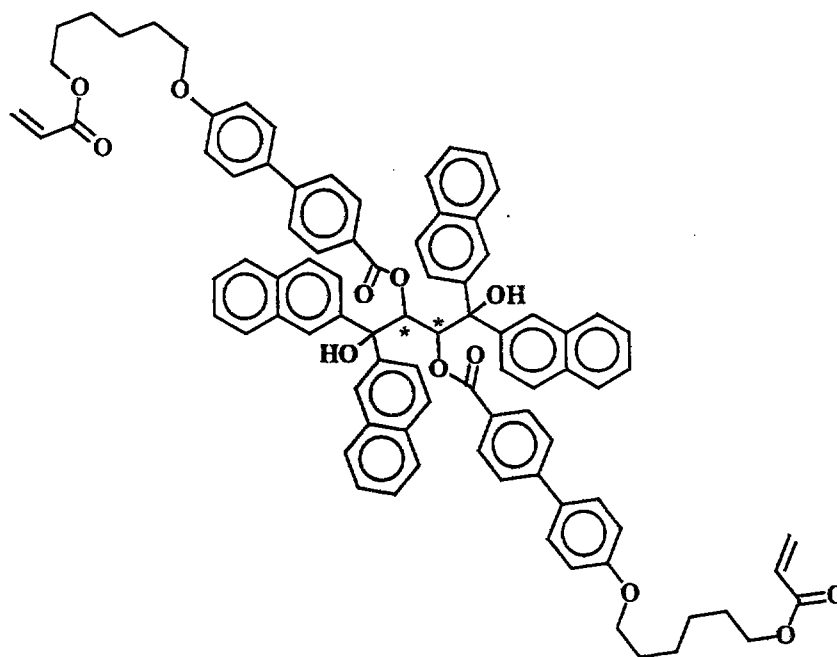


20

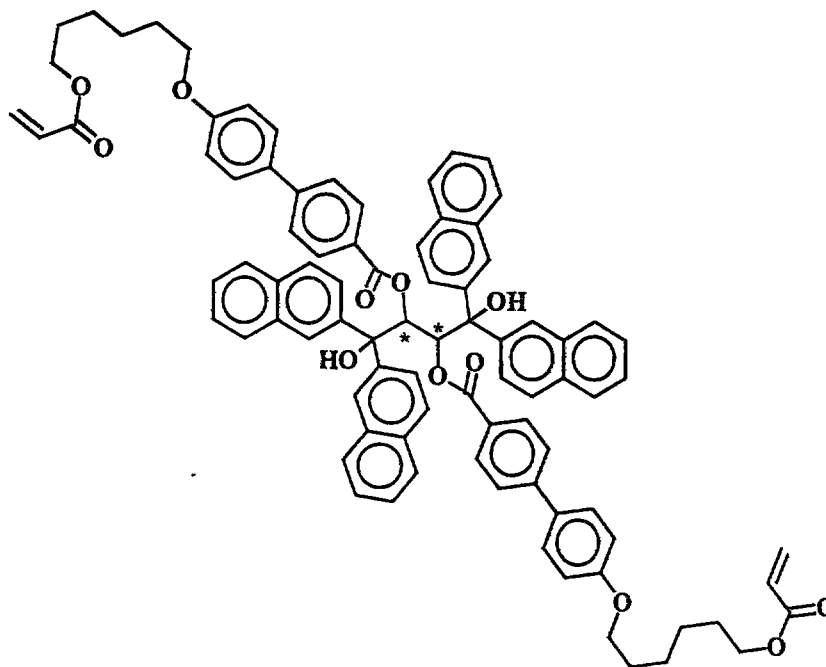
(2*S*,3*S*)-2,3-Bis-[4-(6-acryloyloxyhexyloxy)-benzoyloxy]-1,1,4,4-tetranaphthalen-2-ylbutane-1,4-diol



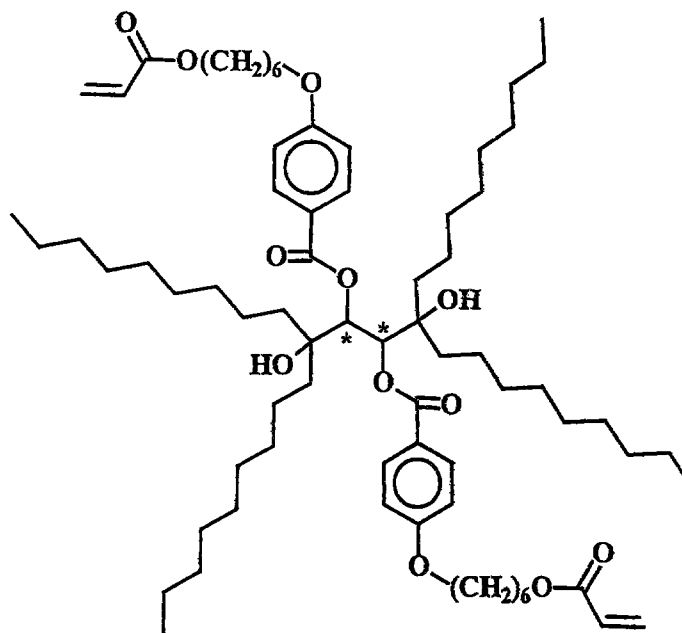
(2*R*,3*R*)-2,3-Bis-[4'-(6-acryloyloxyhexyloxy)biphenyl-4-carbonyl-
5 oxy]-1,1,4,4-tetranaphthalen-2-ylbutane-1,4-diol



(2*S*,3*S*)-2,3-Bis-[4'-(6-acryloyloxyhexyloxy)biphenyl-4-carbonyloxy]-1,1,4,4-tetranaphthalen-2-ylbutane-1,4-diol

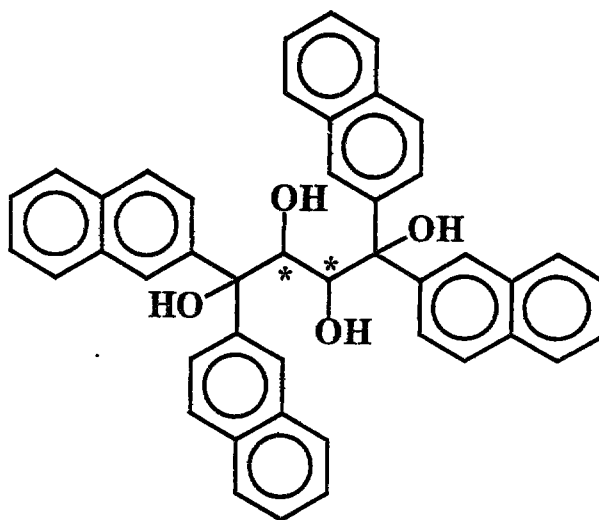


(11*R*,12*R*)-11,12-Bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-10,13-dinonyldocosane-10,13-diol



Example 3

A mixture is formulated consisting of:



1 % by weight

5 and

ROTN 3010

99 % by weight.

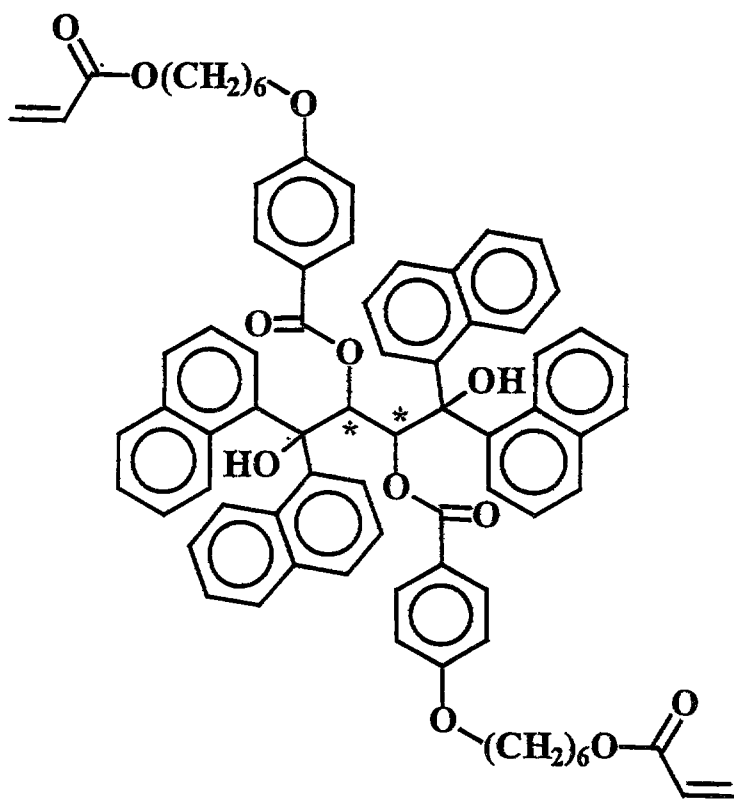
The liquid crystal mixture ROTN 3010 is available from Rolic Research Ltd., Switzerland.

Forms a cholesteric phase with a pitch of $p = 2.25 \mu\text{m}$.

10

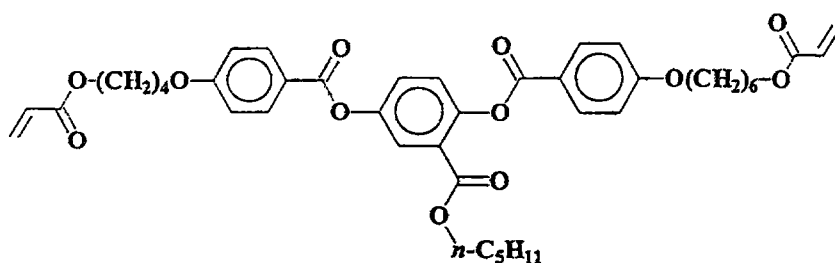
Example 4

A mixture is formulated consisting of:



15 % by weight

and

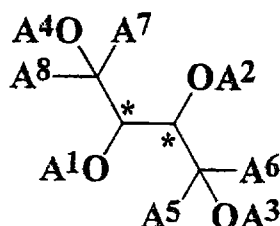


85 % by weight

Forms a cholesteric phase with a pitch of $p = 370$ nm.

CLAIMS

1. An optically active butane-1,2,3,4-tetraol derivative of formula I:



(I)

5 in which:

10 A¹, A², A³, A⁴ each independently represents hydrogen; or an optionally-substituted methyl group; or an optionally-substituted aliphatic group with 2 to 80 C-atoms, in which one or more C-atoms may be replaced by a heteroatom or a group -SO-, -SO₂-, -SOO-, -OSO- or -SOS-; or an optionally-substituted aromatic or non-aromatic carbocyclic or heterocyclic ring system, with 1 to 80 C-atoms; and

15 A⁵, A⁶, A⁷, A⁸ each independently represents an optionally-substituted aliphatic group with 3 to 80 C-atoms, in which a C-atom, or two or more non-adjacent C-atoms, may be replaced by a heteroatom or a group -SO-, -SO₂-, -SOO-, -OSO- or -SOS-; or an optionally-substituted aromatic or non-aromatic carbocyclic or heterocyclic ring system, with 1 to 80 C-atoms; or

20 one, two or three of A⁵, A⁶, A⁷ and A⁸ independently represents hydrogen; or an optionally-substituted methyl group; or an optionally-substituted aliphatic group with 2 C-atoms, in which a C-atom may be replaced by a heteroatom or a group -SO-, -SO₂-, -SOO-, -OSO- or -SOS-; and the remainder of A⁵, A⁶, A⁷, A⁸ independently represent an optionally-substituted aliphatic group

with 3 to 80 C-atoms, in which a C-atom, or two or more non-adjacent C-atoms, may be replaced by a heteroatom or a group -SO-, -SO₂-, -SOO-, -OSO- or -SOS-; or an optionally-substituted aromatic or non-aromatic carbocyclic or heterocyclic ring system,
 5 with 1 to 80 C-atoms;

with the provisos that:



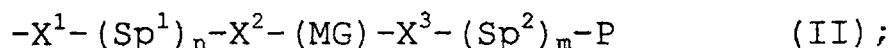
- when one, two or three of A⁵, A⁶, A⁷ and A⁸ represents hydrogen, then A⁵, A⁶, A⁷ and A⁸ may not represent COOH; and
- when A⁵, A⁶, A⁷ and A⁸ are all phenyl, then at least one of A¹,
 10 A², A³, A⁴ does not represent hydrogen.

2. An optically active butane-1,2,3,4-tetraol derivative as claimed in claim 1, wherein A⁵, A⁶, A⁷ and A⁸ each independently represents an optionally-substituted aliphatic group with 3 to 80 C-atoms, in which a C-atom, or two or more non-adjacent C-atoms,
 15 may be replaced by a heteroatom or a group -SO-, -SO₂-, -SOO-, -OSO- or -SOS-; or an optionally-substituted aromatic or non-aromatic carbocyclic or heterocyclic ring system, with 1 to 80 C-atoms.

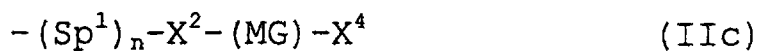
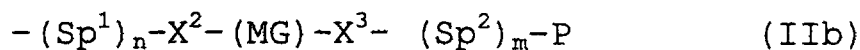
3. An optically active butane-1,2,3,4-tetraol derivative as claimed in claim 1 or 2, wherein at least one of the A¹ to A⁸ residues includes a polymerisable group.
 20

4. An optically active butane-1,2,3,4-tetraol derivative as claimed in any preceding claim, wherein:

A⁵ to A⁸ have each independently one of the meanings of
 25 formula II:

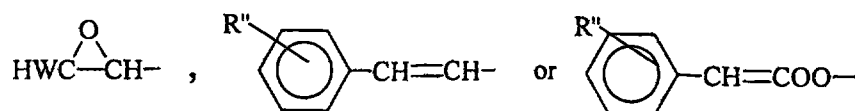


A¹ to A⁴ are hydrogen atoms or have each independently one of the meanings of formula IIb or one of the meanings of formula IIc:



in which:

- 5 X^1 to X^3 each independently denote -O-, -S-, -NH-, -N(CH₃)-, -CH(OH)-, -CO-, -CH₂(CO)-, -SO-, -CH₂(SO)-, -SO₂-, -CH₂(SO₂)-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -SOO-, -OSO-, -SOS-, -CH₂-CH₂-, -OCH₂-, -CH₂O-, -CH=CH-, -C≡C- or a single bond, in such a manner that oxygen atoms are not linked directly to one another;
- 10 X^4 is a halogen;
- 15 Sp^1 and Sp^2 are each independently straight or branched spacer groups having 1 to 20 C-atoms which may be unsubstituted, or mono- or polysubstituted by halogen or CN, it being also possible for one or more non-adjacent CH₂ groups to be replaced, in each case independently from one another, by -O-, -S-, -NH-, -N(CH₃)-, -CH(OH)-, -CO-, -CH₂(CO)-, -CH₂(SO)-, -CH₂(SO₂)-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -C≡C-, -(CF₂)_r-, -(CD₂)_s- or -C(W¹)=C(W²)-, r and s ranging between 1 and 15, and W¹ and W² each independently denoting H, H-(CH₂)_q- or Cl with q ranging between 1 and 15;
- 20 P is hydrogen or a polymerisable group selected from the formulae CH₂=CW-, CH₂=CW-COO-, CH₂=C(Ph)-COO-, CH₂=CH-COO-Ph-, CH₂=CW-CO-NH-, CH₂=C(Ph)-CONH-, CH₂=C(COOR¹)-CH₂-COO-, CH₂=CH-O-, CH₂=CH-OOC-, Ph-CH=CH-, CH₃-C=N-(CH₂)_{m3}, HO-, HS-, HO-(CH₂)_{m3}-, HS-(CH₂)_{m3}-, HO(CH₂)_{m3}COO-, HS(CH₂)_{m3}COO-, HWN-, HOC(O)-, CH₂=CH-Ph-(O)_{m4},
- 25 P
- 30



- 5 with W being H, Cl or alkyl with 1-5 C atoms, m3 being 1-9, m4 being 0 or 1, Ph being phenyl, R' being alkyl with 1-5 C atoms, and R'' having the meaning of R' or being methoxy, cyano or a halogen;

n and m are each independently 0 or 1; and

MG is a mesogenic group comprising 1 to 4 aromatic or non-aromatic carbocyclic or heterocyclic ring systems and optionally up to 3 bridging groups.

- 10 5. An optically active butane-1,2,3,4-tetraol derivative as claimed in claim 4, in which P is a polymerisable group.

6. An optically active butane-1,2,3,4-tetraol derivative as claimed in claim 4 or 5, in which MG is a group selected from the meanings of formula III:

- 15
$$\text{C}^1-(\text{Z}^1-\text{C}^2)_{a1}-(\text{Z}^2-\text{C}^3)_{a2}-(\text{Z}^3-\text{C}^4)_{a3} \quad (\text{III}),$$

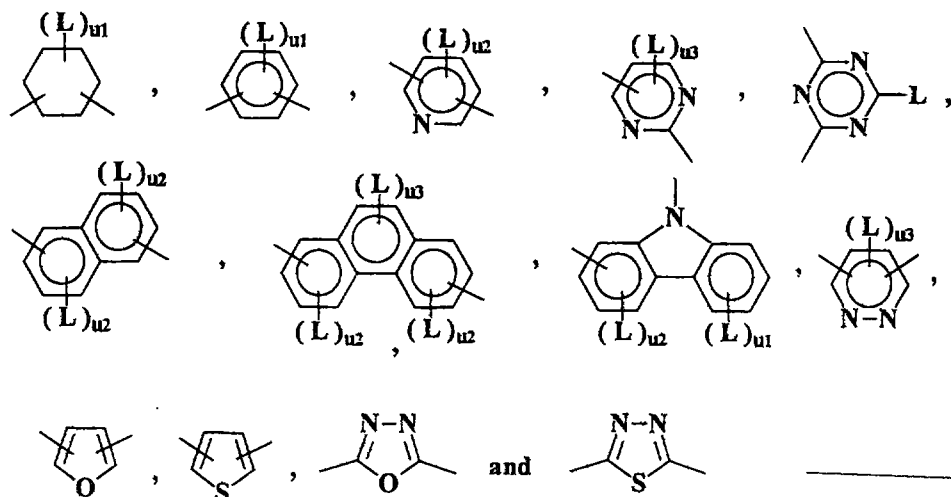
in which:

C¹ to C⁴ are in each case independently optionally-substituted non-aromatic, aromatic, carbocyclic or heterocyclic groups;

- 20 Z¹ to Z³ are independently from each other -COO-, -OCO-, -CH₂-CH₂-, -OCH₂-, -CH₂O-, -CH=CH-, -C≡C-, -CH=CH-COO-, -OCO-CH=CH- or a single bond; and

a₁, a₂ and a₃ are independently integers 0 to 3, such that a₁ + a₂ + a₃ ≤ 4.

- 25 7. An optically active butane-1,2,3,4-tetraol derivative as claimed in claim 6, in which C¹ to C⁴ are selected from:



with:



L being $-\text{CH}_3$, $-\text{COCH}_3$, $-\text{NO}_2$, CN, or halogen,

u_1 being 0, 1, 2, 3, or 4,

5 u_2 being 0, 1, 2, or 3, and

u_3 being 0, 1, or 2.

8. An optically active butane-1,2,3,4-tetraol derivative as claimed in any of the preceding claims, wherein:

A^1 and A^2 are identical, and

10 A^3 and A^4 are identical, and

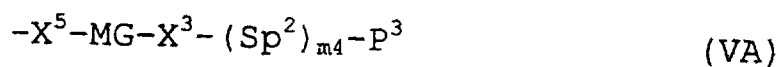
A^5 and A^8 are identical.

9. An optically active butane-1,2,3,4-tetraol derivative as claimed in claim 8, wherein:

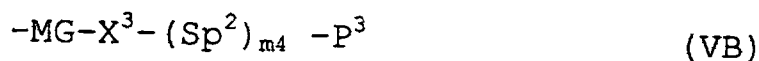
A^3 and A^4 have one of the meanings of formula IV:

15 $(\text{Sp}^2)_{m4} - (\text{O})_{m5} - \text{P}^2$ (IV),

A^1 and A^2 have one of the meanings of formula VA:



and A^5 to A^8 have one of the meanings of formula VB:



in which:

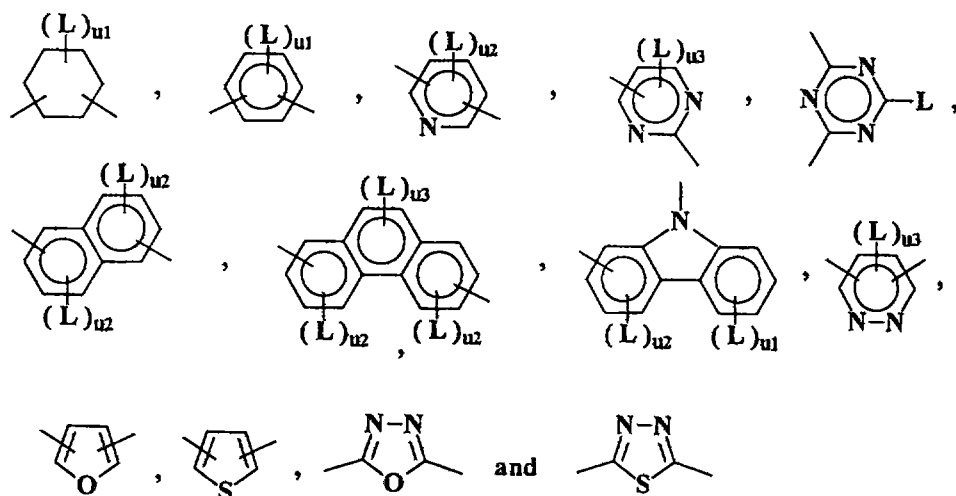
5 Sp^2 is alkylene with 0 to 20 C-atoms;

P^2 is H, $CH_2=CW^5-$ or $CH_2=CW^5-CO-$;

P^3 is H, $CH_2=CW^5-$, $CH_2=CW^5-COO-$, $W^5CH=CH-O-$ or $CH_2=CW^5-O-$, with W^5 being H, CH_3 , or Cl;

10 m^4 and m^5 are each independently 0 or 1 in such a manner that oxygen atoms are not linked directly to one another;

MG is selected from:



15 X^3 is $-O-$, $-CO-$, $-COO-$, $-OCO-$, $-CH_2-CH_2-$, $-OCH_2-$, $-CH_2O-$, $-CH=CH-$, $-C\equiv C-$, $-CH=CH-COO-$, $-OCO-CH=CH-$ or a single bond; and

X^5 is $-CO-$ or $-CH_2-$.

10. An optically active butane-1,2,3,4-tetraol derivative as claimed in claim 9, in which:



- MG is cyclohexylene, phenylene, biphenylene, naphthylene or phenanthrylene;
- x³ denotes -O-, -CO-, -COO-, -OCO-, -C≡C-, or a single bond, in particular, -O-, or single bond;
- 5 Sp² is a straight-chain of formula -(CH₂)_v-, with v being an integer between 0 and 20;
- p² is H, CH₂=CW⁵- or CH₂=CW⁵-CO-;
- p³ is H, CH₂=CW⁵-, CH₂=CW⁵-COO-, W⁵CH=CH-O- or CH₂=CW⁵-O-, with W⁵ being H, CH₃, or Cl; and
- 10 m⁴ and m⁵ are each independently 0 or 1 in such a manner that oxygen atoms are not linked directly to one another.
11. An optically active butane-1,2,3,4-tetraol derivatives as claimed in claim 10, in which Sp² is ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, 15 decylene, undecylene, or dodecylene.
12. Use of an optically active butane-1,2,3,4-tetraol derivative as claimed in any of the preceding claims as a dopant for liquid crystals.
13. A liquid crystalline mixture comprising at least one 20 optically active butane-1,2,3,4-tetraol derivative of formula I according to claims 1 to 11.
14. A liquid crystalline mixture as claimed in claim 13, essentially consisting of:
- 25 i) at least one polymerisable non-optically-active liquid crystal,
- ii) an optically active compound of formula I,
- iii) a photoinitiator, and
- iv) a stabiliser.



15. An optically-active liquid crystalline film obtainable by the steps comprising ordering the mixture claimed in claim 14 in the monomeric state and *in situ* UV polymerisation on the resulting ordered mixture.
- 5 16. Polymer film according to claim 15 being capable of selectively reflecting light of visible wavelengths.
17. Use of a polymer film according to claim 15 or 16 as a broad-band polariser.