(12) UK Patent (19) GB (11) 2 107 733 B

(54) Title of invention

Phenylethanes

(51) INT CL[4]; C07C 13/28 1/26 5/03

(21) Application No
8229191

(22) Date of filing
13 Oct 1982

(30) Priority data

(31) 6572/81
1725/82
4172/82

(32) 14 Oct 1981
19 Mar 1982
8 Jul 1982

(33) Switzerland (CH)

(43) Application published
5 May 1983

(45) Patent published
2 Oct 1985

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(52) Domestic classification
C5E 237 284 342 391 CK

(56) Documents cited
GB A 2092146

(58) Field of search
C5E

Reprinted front page

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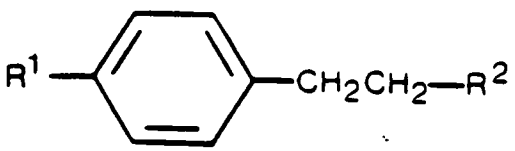
GB 2 107 733 B

"PHENYLETHANES"

The present invention is concerned with novel tri-, tetra- and pentacyclic phenylethanes of the general formula



I

wherein R^1 signifies trans-4-alkylcyclohexyl, 4'-alkyl-4-biphenylyl, p-(trans-4-alkylcyclohexyl)phenyl, 2-(trans-4-alkylcyclohexyl)ethyl or p-[2-(trans-4-alkylcyclohexyl)ethyl]phenyl and R^2 signifies trans-4-alkylcyclohexyl, or R^1 signifies trans-4-alkylcyclohexyl and R^2 signifies p-(trans-4-alkylcyclohexyl)phenyl, p-[2-(trans-4-alkylcyclohexyl)ethyl]phenyl or 4'-(trans-4-alkylcyclohexyl)-4-biphenylyl, or R^1 signifies p-alkylphenyl and R^2 signifies p-[2-(trans-4-alkylcyclohexyl)ethyl]phenyl, and the alkyl groups in the substituents R^1 and R^2 are straight-chain groups containing 1 to 7 carbon atoms.

The invention is also concerned with the manufacture of the compounds of formula I above, liquid crystalline mixtures which contain compounds of formula I above as well as their use for electro-optical purposes.

The compounds in accordance with the invention contain one or two terminal trans-4-alkylcyclohexyl groups as well as 1-3 p-phenylene groups and one or two ethylene groups. The term "alkyl" in the aforementioned substituents R^1 and R^2 embraces the groups methyl, ethyl, propyl, butyl, pentyl, hexyl and heptyl.

Liquid crystals have recently gained considerable importance primarily as dielectrics in indicating devices, since the optical properties of such substances can be influenced by an applied voltage. Electro-optical devices based on liquid crystals are well known to the person skilled in the art and can be based on various effects such as, for example, dynamic scattering, deformation of aligned phases (DAP type), the Schadt-Helfrich effect (rotation cell), the "guest-host effect" or a cholesteric--nematic phase transition.

The liquid crystals must satisfy a number of requirements in order to be suitable as dieletrics for electro-optical indicating devices. For example, they

must have a high chemical stability towards environmental factors (e.g. heat, air, moisture and the like), must be photochemically stable and colourless, must have short response times and not too high a viscosity, must have a nematic or cholesteric mesophase in all temperature ranges in which the liquid crystal cell is to be operated, and must give a good contrast. Other properties such as, for example, the threshold potential, the dielectric anisotropy and the electrical conductivity must fulfil different conditions depending on the type of cell which is used.

Since, in general, it is not possible to achieve all desired and to some extent contradictory properties with a single compound, attempts have mainly been made to optimize the properties for the particular applications by mixing several components. In this case it is, however, important that the components undergo no chemical reactions with one another and can be mixed well. Further, the mixtures formed should have no smectic mesophases.

The object of the present invention is therefore to provide novel compounds which permit the further improvement of the properties of liquid crystalline dielectrics.

It has now been found that the compounds provided

by the invention are very well suited as components of liquid crystalline mixtures, since they surprisingly at the same time have large mesophase ranges with high clearing points as well as low viscosities and accordingly short response times. Moreover, the melting points are often very considerably super-coolable. Further, the compounds provided by the invention have small absolute values of the dielectric anisotropies and generally a nematic and/or smectic mesophase. Furthermore, they have an excellent chemical and photochemical stability and are colourless. The compounds provided by the invention can be widely used, since they have a good miscibility with other liquid crystals and since liquid crystals having nematic or cholesteric mesophases can be manufactured readily by mixing the present compounds with other liquid crystalline and/or non-liquid crystalline compounds. On the basis of the aforementioned properties they are especially suitable for increasing the clearing points of mixtures having low viscosities, since in this case the viscosity is not increased or is increased only insignificantly.

Those compounds of formula I in which the sum of the carbon atoms in the two terminal alkyl groups of the substituents R^1 and R^2 is 5 to 10 are preferred. Those

compounds of formula I in which R^1 signifies trans-4-alkylcyclohexyl, 4'-alkyl-4-biphenylyl or p-(trans-4-alkylcyclohexyl)phenyl and R^2 signifies trans-4-alkylcyclohexyl, or R^1 signifies trans-4-alkylcyclohexyl and R^2 signifies 4'-(trans-4-alkylcyclohexyl)-4-biphenylyl are also preferred.

The following are examples of preferred compounds of formula I:

1-[2-(Trans-4-propylcyclohexyl)ethyl]-4-(trans-4--ethylcyclohexyl)benzene,

1-[2-(trans-4-propylcyclohexyl)ethyl]-4-(trans-4--propylcyclohexyl)benzene,

1-[2-(trans-4-propylcyclohexyl)ethyl]-4-(trans-4--pentylcyclohexyl)benzene,

1-[2-(trans-4-propylcyclohexyl)ethyl]-4-(trans-4--heptylcyclohexyl)benzene,

1-[2-(trans-4-butylcyclohexyl)ethyl]-4-(trans-4--pentylcyclohexyl)benzene,

1-[2-(trans-4-pentylcyclohexyl)ethyl]-4-(trans-4--propylcyclohexyl)benzene,

1-[2-(trans-4-pentylcyclohexyl)ethyl]-4-(trans-4--butylcyclohexyl)benzene,

1-[2-(trans-4-pentylcyclohexyl)ethyl]-4-(trans-4--pentylcyclohexyl)benzene,

4-(trans-4-ethylcyclohexyl)-4'-[2-(trans-4-propylcyclohexyl)ethyl]biphenyl,

4-(trans-4-propylcyclohexyl)-4'-[2-(trans-4-propyl-cyclohexyl)ethyl]biphenyl,

4-(trans-4-butylcyclohexyl)-4'-[2-(trans-4-pentyl-cyclohexyl)ethyl]biphenyl,

4-(trans-4-pentylcyclohexyl)-4'-[2-(trans-4-propyl-cyclohexyl)ethyl]biphenyl,

4-(trans-4-pentylcyclohexyl)-4'-[2-(trans-4-butyl-cyclohexyl)ethyl]biphenyl,

4-(trans-4-pentylcyclohexyl)-4'-[2-trans-4-pentyl-cyclohexyl)ethyl]biphenyl,

4-(trans-4-heptylcyclohexyl)-4'-[2-(trans-4-propyl-cyclohexyl)ethyl]biphenyl,

1-[2-(trans-4-ethylcyclohexyl)ethyl]-4-[2-(trans--4-propylcyclohexyl)ethyl]benzene,

1,4-bis[2-(trans-4-propylcyclohexyl)ethyl]benzene,

1-[2-(trans-4-butylcyclohexyl)ethyl]-4-[2-(trans-4--pentylcyclohexyl)ethyl]benzene,

1-[2-(trans-4-pentylcyclohexyl)ethyl]-4-[2-(trans-4--propylcyclohexyl)ethyl]benzene,

1,4-bis[2-(trans-4-pentylcyclohexyl)ethyl]benzene,

1-[2-(trans-4-heptylcyclohexyl)ethyl]-4-[2-(trans-4--propylcyclohexyl)ethyl]benzene,

4-[2-(trans-4-ethylcyclohexyl)ethyl]-4'-[2-(trans-4--propylcyclohexyl)ethyl]biphenyl,

4,4'-bis[2-(trans-4-propylcyclohexyl)ethyl]biphenyl,

4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-[2-(trans-4--pentylcyclohexyl)ethyl]biphenyl,

4-[2-(trans-4-pentylcyclohexyl)ethyl]-4'-[2-(trans-4--propylcyclohexyl)ethyl]biphenyl,

4,4'-bis[2-(trans-4-pentylcyclohexyl)ethyl]biphenyl,

4-[2-(trans-4-heptylcyclohexyl)ethyl]-4'-[2-(trans-4--propylcyclohexyl)ethyl]biphenyl,

4-(trans-4-ethylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-1,1'-ethylenedibenzene,

4,4'-bis(trans-4-propylcyclohexyl)-1,1'-ethylenedibenzene,

4-(trans-4-butylcyclohexyl)-4'-(trans-4-pentylcyclohexyl)-1,1'-ethylenebidenzene,

4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-1,1'-ethylenedibenzene,

4,4'-bis(trans-4-pentylcyclohexyl)-1,1'-ethylenedibenzene,

4-(trans-4-heptylcyclohexyl)-4'-trans-4-propylcyclohexyl)-1,1'-ethylenedibenzene,

4-[2-(trans-4-propylcyclohexyl)ethyl]-4'-(trans-4--ethylcyclohexyl)-1,1'-ethylenedibenzene,

4-[2-(trans-4-propylcyclohexyl)ethyl]-4'-(trans-4--propylcyclohexyl)-1,1'-ethylenedibenzene,

4-[2-(trans-4-propylcyclohexyl)ethyl]-4'-(trans-4--pentylcyclohexyl)-1,1'-ethylenedibenzene,

4-[2-(trans-4-propylcyclohexyl)ethyl]-4'-(trans-4--heptylcyclohexyl)-1,1'-ethylenedibenzene,

4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-(trans-4--propylcyclohexyl)-1,1'-ethylenedibenzene,

4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-(trans-4--pentylcyclohexyl)-1,1'-ethylenedibenzene,

4-[2-(trans-4-pentylcyclohexyl)ethyl]-4'-(trans-4--butylcyclohexyl)-1,1'-ethylenedibenzene,

4-[2-(trans-4-pentylcyclohexyl)ethyl]-4'-(trans-4--pentylcyclohexyl)-1,1'-ethylenedibenzene,

4-ethyl-4"-[2-(trans-4-propylcyclohexyl)ethyl]-p--terphenyl,

4-propyl-4"-[2-(trans-4-propylcyclohexyl)ethyl]-p--terphenyl,

4-butyl-4"-[2-(trans-4-pentylcyclohexyl)ethyl]-p--terphenyl,

4-pentyl-4"-[2-(trans-4-propylcyclohexyl)ethyl]-p--terphenyl,

4-pentyl-4"-[2-(trans-4-butylcyclohexyl)ethyl]-p--terphenyl,

4-pentyl-4"-[2-trans-4-pentylcyclohexyl)ethyl]-p--terphenyl,

4-heptyl-4"-[2-(trans-4-propylcyclohexyl)ethyl]-p--terphenyl,

4-(trans-4-ethylcyclohexyl)-4'-[2-(p-(trans-4-propyl-cyclohexyl)phenyl)ethyl]biphenyl,

4-(trans-4-propylcyclohexyl)-4'-[2-(p-(trans-4-propyl-cyclohexyl)phenyl)ethyl]biphenyl,

4-(trans-4-butylcyclohexyl)-4'-[2-(p-(trans-4-pentyl-cyclohexyl)phenyl)ethyl]biphenyl,

4-(trans-4-pentylcyclohexyl)-4'-[2-(p-(trans-4-propylcyclohexyl)phenyl)ethyl]biphenyl,

4-(trans-4-pentylcyclohexyl)-4'-[2-(p-(trans-4-butylcyclohexyl)phenyl)ethyl]biphenyl,

4-(trans-4-pentylcyclohexyl)-4'-[2-(p-(trans-4-pentylcyclohexyl)phenyl)ethyl]biphenyl,

4-(trans-4-heptylcyclohexyl)-4'-[2-(p-(trans-4-propylcyclohexyl)phenyl)ethyl]biphenyl,

4-[2-(trans-4-propylcyclohexyl)ethyl]-4'-(p-ethylphenyl)-1,1'-ethylenedibenzene,

4-[2-(trans-4-propylcyclohexyl)ethyl]-4'-(p-propylphenyl)-1,1'-ethylenedibenzene,

4-[2-(trans-4-propylcyclohexyl)ethyl]-4'-(p-pentylphenyl)-1,1'-ethylenedibenzene,

4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-(p-pentylphenyl)-1,1'-ethylenedibenzene,

4-[2-(trans-4-pentylcyclohexyl)ethyl]-4'-(p-butylphenyl)-1,1'-ethylenedibenzene and

4-[2-(trans-4-pentylcyclohexyl)ethyl]-4'-(p-pentylphenyl)-1,1'-ethylenedibenzene.

Especially preferred compounds of formula I are:

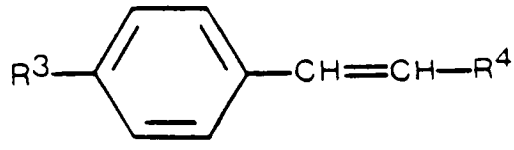
1-[2-(Trans-4-butylcyclohexyl)ethyl]-4-(trans-4-pentylcyclohexyl)benzene,

4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-(trans-4-pentylcyclohexyl)-1,1'-ethylenedibenzene and

4-(trans-4-pentylcyclohexyl)-4'-[2-(trans-4-butylcyclohexyl)ethyl]biphenyl.

The compounds of formula I can be manufactured in accordance with the invention by

(a) for the manufacture of the compounds of formula I in which R^1 signifies trans-4-alkylcyclohexyl, 4'-alkyl-4-biphenylyl, p-(trans-4-alkylcyclohexyl)phenyl or 2-(trans-4-alkylcyclohexyl)ethyl and R^2 signifies trans-4-alkylcyclohexyl, or R^1 signifies trans-4-alkylcyclohexyl and R^2 signifies p-(trans-4-alkylcyclohexyl)phenyl, p-[2-(trans-4-alkylcyclohexyl)ethyl]phenyl or 4'-(trans-4-alkylcyclohexyl)-4-biphenylyl, or R^1 signifies p-alkylphenyl and R^2 signifies p-[2-(trans-4-alkylcyclohexyl)ethyl]phenyl, catalytically hydrogenating a compound of the general formula



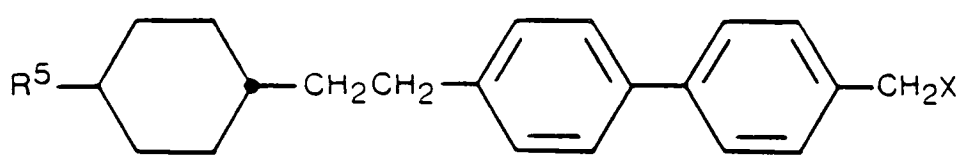
VII

wherein R^3 signifies trans-4-alkylcyclohexyl, 4'-alkyl-4-biphenylyl, p-(trans-4-alkylcyclohexyl)phenyl or 2-(trans-4-alkylcyclohexyl)-

ethyl and R^4 signifies trans-4-alkyl-cyclohexyl, or R^3 signifies trans-4--alkylcyclohexyl and R^4 signifies p--(trans-4-alkylcyclohexyl)phenyl, p-[2-(trans-4-alkylcyclohexyl)ethyl]-phenyl or 4'-(trans-4-alkylcyclohexyl)--4-biphenylyl, or R^3 signifies p-alkyl-phenyl and R^4 signifies p-[2-(trans-4--alkylcyclohexyl)ethyl]phenyl, and the alkyl groups in the substituents R^3 and R^4 are straight-chain groups containing 1 to 7 carbon atoms,

or

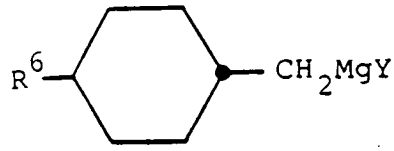
(b) for the manufacture of the compounds of formula I in which R^1 signifies p-[2-(trans-4-alkylcyclohexyl)ethyl]-phenyl and R^2 signifies trans-4-alkylcyclohexyl, reacting a compound of the general formula



XI

wherein R^5 signifies a straight-chain alkyl group containing 1 to 7 carbon atoms and X signifies a leaving group,

with a compound of the general formula



XX

wherein R^6 signifies a straight-chain alkyl group containing 1 to 7 carbon atoms and Y signifies chlorine or bromine,

in the presence of dilithium tetrachlorocuprate.

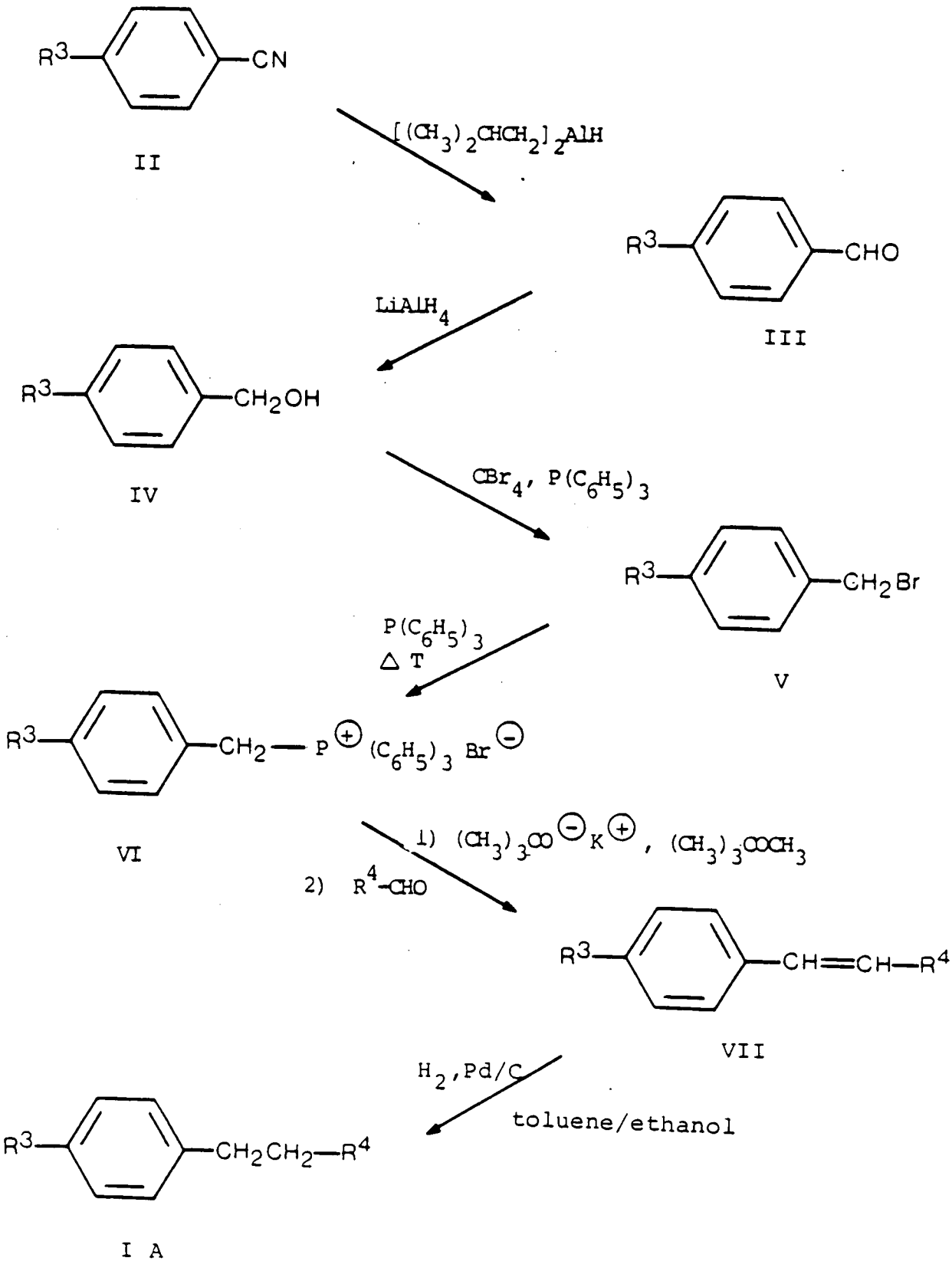
The catalytic hydrogenation of a compound of formula VII can be carried out according to methods known per se. Palladium is the preferred catalyst.

The reaction of a compound of formula XI with a compound of formula XX can be carried out according to methods known per se for the Fouquet-Schlosser coupling reaction. As leaving groups X there come into consideration all leaving groups which are usually used in such reactions. Preferred leaving groups are chlorine, bromine,

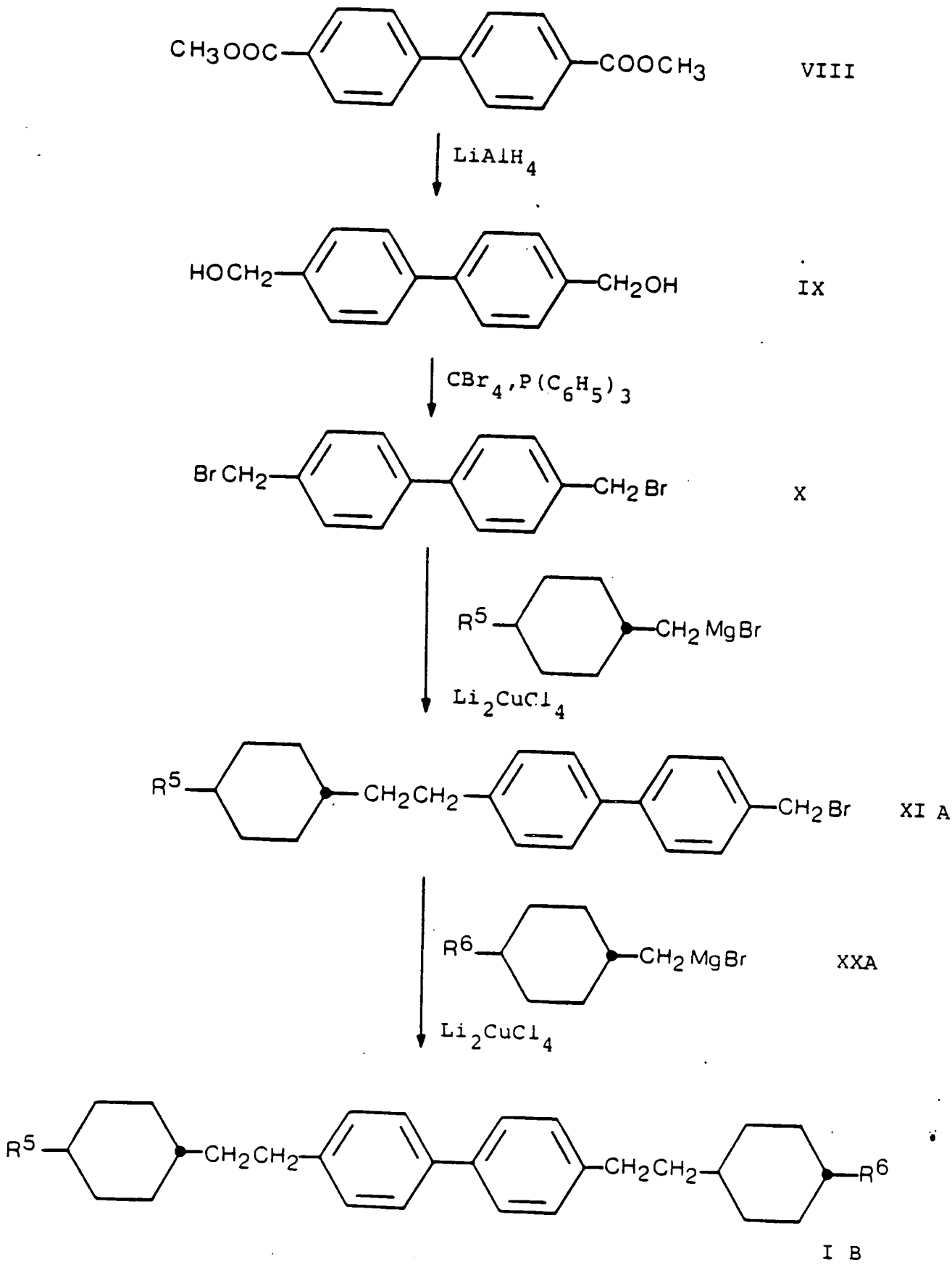
iodine and the p-tosyloxy group, especially bromine. Y preferably signifies bromine.

The preparation of the starting materials of formulae VII and XI and preferred methods for the manufacture of the compounds of formula I are illustrated hereinafter in Reaction Schemes 1 and 2 in which R^3, R^4, R^5 and R^6 have the significances given above.

Scheme 1


R3
CN
II
[(CH3)2CHCH2]2AlH
R3
CHO
III
LiAlH4
R3
CH2OH
IV
CBr4, P(C6H5)3
R3
CH2Br
V
P(C6H5)3
△ T
R3
CH2 — P ⊕ (C6H5)3 Br ⊖
VI
1) (CH3)3CO ⊖ K ⊕ , (CH3)3COCH3
2) R4-CHO
R3
CH=CH—R4
VII
H2, Pd/C
toluene/ethanol
R3
CH2CH2—R4
I A

Scheme 2


CH3OOC
COOCH3
VIII
LiAlH4
HOCH2
CH2OH
IX
CBr4, P(C6H5)3
Br CH2
CH2 Br
X
R5
CH2 MgBr
Li2CuCl4
R5
CH2CH2
CH2 Br
XI A
R6
CH2 MgBr
XXA
Li2CuCl4
R5
CH2CH2
CH2CH2
R6
I B

The compounds of the formula R^4-CHO in Scheme 1 can be obtained in a simple manner from known compounds; for example, the trans-4-alkylcyclohexanecarboxaldehydes can be obtained by Rosenmund reduction of the corresponding acid chlorides and the remaining compounds can be obtained by reduction of the corresponding cyano compounds (in an analogous manner to the preparation of the compounds of formula III).

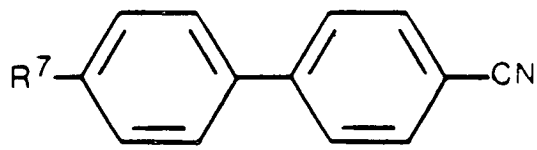
By reacting the compound of formula X with Grignard reagents in accordance with Scheme 2 there can be obtained compounds of formula XI or directly compounds of formula IB in which R^5 and R^6 have the same significance. When at least about 2 mol of Grignard reagent are used per mol of the compound of formula X a compound of formula IB is generally predominantly formed directly.

The compounds of formula I can be used in the form of mixtures with one or more other liquid crystalline and/or non-liquid crystalline substances such as, for example, with substances from the classes of the Schiff's bases, azobenzenes, azoxybenzenes, phenylbenzoates, cyclohexanecarboxylic acid phenyl esters, cyclohexanecarboxylic acid cyclohexyl esters, biphenyls, terphenyls, phenylcyclohexanes, cinnamic acid derivatives, phenylpyrimidines, diphenylpyrimidines, cyclohexylphenylpyrimidines, phenyldioxanes, 2-cyclohexyl--1-phenylethanes and the like. Such substances are known

to the person skilled in the art and many of them are, moreover, commercially available.

The liquid crystal mixtures in accordance with the invention contain, in addition to one or more compounds of formula I, preferably one or more of the following compounds:

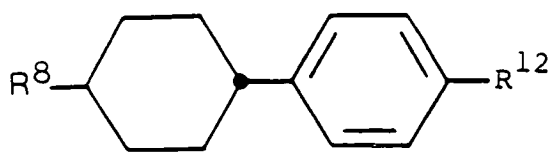
4-Cyanobiphenyls of the general formula



XII

wherein R^7 signifies a straight-chain alkyl or alkoxy group containing 2 to 7 carbon atoms,

p-(trans-4-alkylcyclohexyl)benzonitriles or p-(trans-4--alkylcyclohexyl)alkylbenzenes of the general formula

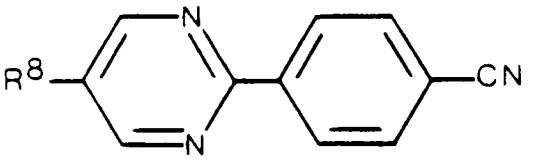


XIII

wherein R^8 signifies a straight-chain alkyl group containing 2 to 7 carbon

atoms and R^{12} signifies the cyano group or a straight-chain alkyl group containing 1 to 7 carbon atoms,

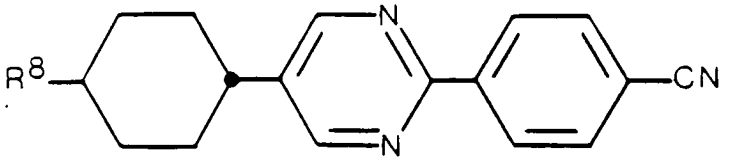
p-(5-alkyl-2-pyrimidinyl)benzonitriles of the general formula



XIV

wherein R^8 has the above significance,

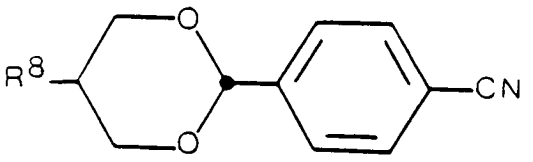
p-[5-(trans-4-alkylcyclohexyl)-2-pyrimidinyl]benzonitriles of the general formula



XV

wherein R^8 has the above significance,

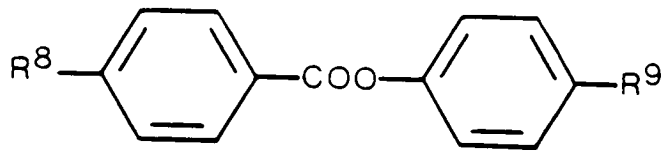
p-(trans-5-alkyl-m-dioxan-2-yl)benzonitriles of the general formula



XVI

wherein R^8 has the above significance,

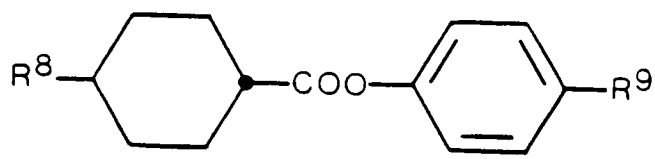
p-alkylbenzoic acid phenyl esters of the general formula



XVII

wherein R^9 signifies the cyano group or a straight-chain alkoxy group containing 1 to 6 carbon atoms and R^8 has the above significance,

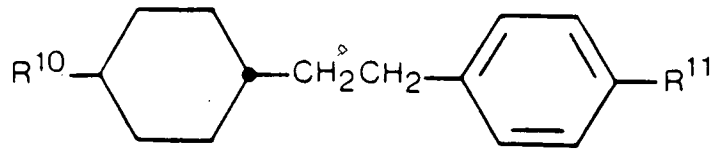
trans-4-alkylcyclohexanecarboxylic acid phenyl esters of the general formula



XVIII

wherein R^8 and R^9 have the above significances,

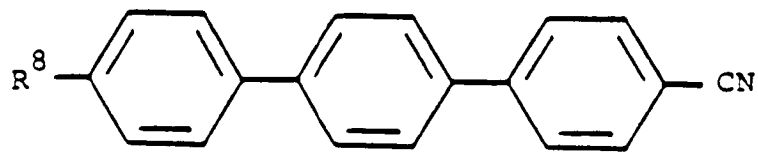
2-(trans-4-alkylcyclohexyl)-1-phenylethanes of the general formula



XIX

wherein R^{10} signifies a straight-chain alkyl group containing 3 to 7 carbon atoms and R^{11} signifies the cyano group or a straight-chain alkyl or alkoxy group containing 1 to 7 carbon atoms,

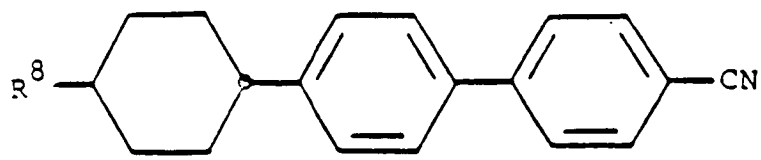
4"-alkyl-4-cyano-p-terphenyls of the general formula



XXI

wherein R^8 has the above significance,

or 4'-(trans-4-alkylcyclohexyl)-4-cyanobiphenyls of the general formula



XXII

wherein R^8 has the above significance.

The mixtures provided by the invention can contain one or more compounds of formula I. Mixtures which contain one or more compounds of formula I in an amount of about 1 weight % to about 50 weight % and one or more other suitable liquid crystalline and/or non-liquid crystalline substances are preferred. Mixtures which contain about 3 weight % to about 30 weight % of compounds of formula I are especially preferred.

The mixtures provided by the invention can contain other suitable optically active compounds (e.g. optically active biphenyls) and/or dichroic colouring substances (e.g. azo, azoxy and anthraquinone colouring substances). The amount of such compounds is determined by the solubility and the desired pitch, colour, extinction and the like. Preferably, the amount of optically active compounds is at most about 4 weight % and the amount of dichroic colouring substance is at most about 10 weight %.

The manufacture of the liquid crystalline mixtures and of the electro-optical devices can be carried out in a manner known per se and therefore need not be described herein in more detail.

The invention is also concerned with all novel

compounds, mixtures, processes, uses and devices as described herein.

The following Mixture Examples 1-11 are examples of preferred mixtures. The mixtures of Mixture Examples 5-8 are especially preferred. η signifies the viscosity (bulk viscosity), $\Delta\varepsilon$ signifies the dielectric anisotropy, Δn signifies the optical anisotropy, t_{on} signifies the switching-on time (0-50% transmission), t_{off} signifies the switching-off time (100-10% transmission), V_{10} and V_{50} signify the threshold potential for 10% or 50% transmission (tilt angle 0°), N_{max} signifies the maximum number of multiplexible lines. k_{11} (splay) and k_{33} (bend) are elastic constants.

Mixture Example 1

Basic mixture A:

5.2 weight % of p-(5-pentyl-2-pyrimidinyl)benzonitrile,

11.5 weight % of p-(5-heptyl-2-pyrimidinyl)benzonitrile,

5.8 weight % of p-butylbenzoic acid p'-cyanophenyl ester,

12.2 weight % of trans-4-propylcyclohexanecarboxylic acid p-cyanophenyl ester,

12.4 weight % of trans-4-pentylcyclohexanecarboxylic acid p-cyanophenyl ester,

22.0 weight % of trans-4-butylcyclohexanecarboxylic acid p-ethoxyphenyl ester,

19.9 weight % of trans-4-pentylcyclohexanecarboxylic acid p-methoxyphenyl ester,
11.0 weight % of p-[5-(trans-4-ethylcyclohexyl)-2-pyrimidinyl]benzonitrile,
cl.p. 72.5°C, η = 42 cp, nematic.

92 weight % of basic mixture A + 8 weight % of 4-(trans-4-pentylcyclohexyl)-4'-[2-(trans-4-pentylcyclohexyl)ethyl]biphenyl; cl.p. 91°C, η = 43 cp, nematic.

90 weight % of basic mixture A + 10 weight % of 4,4'-bis[2-(trans-4-pentylcyclohexyl)ethyl]biphenyl; cl.p. 90.2°C, η = 43 cp, nematic.

Mixture Example 2

Basic mixture B:
4.1 weight % of p-(5-pentyl-2-pyrimidinyl)benzonitrile,
7.3 weight % of p-(5-heptyl-2-pyrimidinyl)benzonitrile,
14.0 weight % of trans-4-pentylcyclohexanecarboxylic acid p-methoxyphenyl ester,
22.9 weight % of trans-4-pentylcyclohexanecarboxylic acid p-propyloxyphenyl ester,
8.6 weight % of p-[5-(trans-4-ethylcyclohexyl)-2-pyrimidinyl benzonitrile,

6.5 weight % of p-[5-(trans-4-pentylcyclohexyl)-2-pyrimidinyl]benzonitrile,
36.6 weight % of 2-(trans-4-pentylcyclohexyl)-1-(p-ethoxyphenyl)ethane; cl.p. 69.9°C, η = 26.3 cp, nematic.

90 weight % of basic mixture B + 10 weight % of 4-(trans-4-pentylcyclohexyl)-4'-[2-(trans-4-pentylcyclohexyl)ethyl]biphenyl; cl.p. 87°C, η = 27 cp, nematic.

Mixture Example 3

Basic mixture C:
6.3 weight % of p-(5-pentyl-2-pyrimidinyl)benzonitrile,
12.3 weight % of p-(5-heptyl-2-pyrimidinyl)benzonitrile,
22.0 weight % of trans-4-pentylcyclohexanecarboxylic acid p-methoxyphenyl ester,
30.2 weight % of trans-4-pentylcyclohexanecarboxylic acid p-propyloxyphenyl ester,
15.5 weight % of 2-(trans-4-heptylcyclohexyl)-1-(p-ethoxyphenyl)ethane,
13.7 weight % of trans-4-(p-pentylphenyl)cyclohexanecarboxylic acid trans-4-propylcyclohexyl ester; cl.p. 60.3°C, η = 30.0 cp, nematic.

90 weight % of basic mixture C + 10 weight % of 4-(trans-4-pentylcyclohexyl)-4'-[2-(trans-4-pentylcyclohexyl)ethyl]biphenyl; cl.p. 79°C, η = 30.6 cp, nematic.

Mixture Example 4

Basic mixture D:

4.1 weight % of p-(5-pentyl-2-pyrimidinyl)benzonitrile,

8.2 weight % of p-(5-heptyl-2-pyrimidinyl)benzonitrile,

15.9 weight % of trans-4-pentylcyclohexanecarboxylic acid p-methoxyphenyl ester,

27.1 weight % of trans-4-pentylcyclohexanecarboxylic acid p-propyloxyphenyl ester,

24.7 weight % of 2-(trans-4-pentylcyclohexyl)-1-(p-ethoxyphenyl)ethane,

6.5 weight % of p-[5-(trans-4-pentylcyclohexyl)-2-pyrimidinyl]benzonitrile,

7.4 weight % of p-[(4aαH,8aβH)-decahydro-6β-propyl-2α--naphthyl]benzonitrile (racemate),

6.1 weight % of p-[(4aαH,8aβH)-decahydro-6β-pentyl-2α--napthyl]benzonitrile (racemate); cl.p. 68.9°C, η = 28.2 cp, nematic.

90 weight % of basic mixture D + 10 weight % of 4--(trans-4-pentylcyclohexyl)-4'-[2-(trans-4-pentylcyclohexyl)ethyl]biphenyl; cl.p. 87°C, η = 29 cp, nematic.

Mixture Example 5

3.89 weight % of 4'-propyl-4-cyanobiphenyl,

19.00 weight % of 4'-pentyl-4-cyanobiphenyl,

16.08 weight % of 2-(trans-4-propylcyclohexyl)-1-(p-ethoxyphenyl)ethane,

22.16 weight % of 2-(trans-4-pentylcyclohexyl)-1-(p-ethoxyphenyl)ethane,

5.72 weight % of 4"-pentyl-4-cyano-p-terphenyl,

5.83 weight % of 4'-(trans-4-pentylcyclohexyl)-4-cyanobiphenyl,

12.79 weight % of 1-[2-(trans-4-butylcyclohexyl)ethyl]-4--(trans-4-pentylcyclohexyl)benzene,

8.55 weight % of 4-[2-(trans-4-butylcyclohexyl)ethyl]-4'--(trans-4-pentylcyclohexyl)-1,1'-ethylenedibenzene,

5.98 weight % of 4-(trans-4-pentylcyclohexyl)-4'-[2-(trans--4-butylcyclohexyl)ethyl]biphenyl; m.p. < -30°C, cl.p. 91.2°C, nematic; η = 24.8 cp; $\Delta\varepsilon$ = 6.19; Δn = 0.142; t_{on} = 25 ms, t_{off} = 40 ms; V_{10} = 2.76V, V_{50} = 3.10V; N_{max} = 76; k_{33}/k_{11} = 1.17.

Mixture Example 6

3.70 weight % of 4'-propyl-4-cyanobiphenyl,

18.09 weight % of 4'-pentyl-4-cyanobiphenyl,

15.32 weight % of 2-(trans-4-propylcyclohexyl)-1-(p-ethoxyphenyl)ethane,

21.10 weight % of 2-(trans-4-pentylcyclohexyl)-1-(p-ethoxyphenyl)ethane,

5.45 weight % of 4"-pentyl-4-cyano-p-terphenyl,

5.55 weight % of 4'-(trans-4-pentylcyclohexyl)-4-cyanobiphenyl,

12.18 weight % of 1-[2-(trans-4-butylcyclohexyl)ethyl]-4-(trans-4-pentylcyclohexyl)benzene,

8.14 weight % of 4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-(trans-4-pentylcyclohexyl)-1,1'-ethylenedibenzene,

5.70 weight % of 4-(trans-4-pentylcyclohexyl)-4'-[2-(trans-4-butylcyclohexyl)ethyl]biphenyl,

4.77 weight % of 1-propyl-4-(trans-4-pentylcyclohexyl)benzene; m.p. <-30°C, cl.p. 88.2°C, nematic; η = 21.0 cp; $\Delta\varepsilon$ = 5.84, Δn = 0.140; t_{on} = 24 ms, t_{off} = 38 ms; V_{10} = 2.75V, V_{50} = 3.08V; N_{max} = 78; k_{33}/k_{11} = 1.05.

Mixture Example 7

3.23 weight % of 4'-propyl-4-cyanobiphenyl,

16.75 weight % of 4'-pentyl-4-cyanobiphenyl,

16.03 weight % of 2-(trans-4-propylcyclohexyl)-1-(p-ethoxyphenyl)ethane,

9.72 weight % of 2-(trans-4-propylcyclohexyl)-1-(p-butyloxyphenyl)ethane,

18.56 weight % of 2-(trans-4-pentylcyclohexyl)-1-(p-ethoxyphenyl)ethane,

4.75 weight % of 4"-pentyl-4-cyano-p-terphenyl,

4.84 weight % of 4'-(trans-4-pentylcyclohexyl)-4-cyanobiphenyl,

11.59 weight % of 1-[2-(trans-4-butylcyclohexyl)ethyl]-4-
-(trans-4-pentylcyclohexyl)benzene,

8.55 weight % of 4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-
-(trans-4-pentylcyclohexyl)-1,1'-ethylenedibenzene,

5.98 weight % of 4-(trans-4-pentylcyclohexyl)-4'-[2-(trans-
-4-butylcyclohexyl)ethyl]biphenyl; m.p. <-30°C, cl.p. 85.7,
nematic; η = 21.5 cp; $\Delta\varepsilon$ = 5.40; Δn = 0.133; t_{on} = 23 ms,
t_{off} = 37 ms; V_{10} = 2.84V, V_{50} = 3.20V; N_{max} = 73; k_{33}/k_{11}=
1.07.

Mixture Example 8

4.36 weight % of 4'-ethyl-4-cyanobiphenyl,

3.33 weight % of 4'-propyl-4-cyanobiphenyl,

16.49 weight % of 4'-pentyl-4-cyanobiphenyl,

15.67 weight % of 2-(trans-4-propylcyclohexyl)-1-(p-ethoxy-
phenyl)ethane.

6.36 weight % of 2-(trans-4-propylcyclohexyl)-1-(p-butyl-
oxyphenyl)ethane,

18.19 weight % of 2-(trans-4-pentylcyclohexyl)-1-(p-ethoxy-
phenyl)ethane,

4.90 weight % of 4"-pentyl-4-cyano-p-terphenyl,

4.98 weight % of 4'-(trans-4-pentylcyclohexyl)-4-cyano-
biphenyl,

11.92 weight % of 1-[2-(trans-4-butylcyclohexyl)ethyl]-4-
-(trans-4-pentylcyclohexyl)benzene,

6.90 weight % of 4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-

-(trans-4-pentylcyclohexyl)-1,1'-ethylenedibenzene,

6.90 weight % of 4-(trans-4-pentylcyclohexyl)-4'-[2-(trans--4-butylcyclohexyl)ethyl]biphenyl; m.p. <-30°C, cl.p. 87.0°C, nematic; η = 24.0 cp; $\Delta\varepsilon$ = 6.10; Δn = 0.143; t_{on} = 26 ms, t_{off} = 43 ms; V_{10} = 2.63V, V_{50} = 2.94 V; N_{max} = 78; k_{33}/k_{11} = 1.10.

Mixture Example 9

14.62 weight % of 4'-pentyl-4-cyanobiphenyl,

12.35 weight % of 4-hexyl-4-cyanobiphenyl,

14.48 weight % of 2-(trans-4-propylcyclohexyl)-1-(p-ethoxyphenyl)ethane,

7.98 weight % of 2-(trans-4-propylcyclohexyl)-1-(p-butyloxyphenyl)ethane,

15.96 weight % of 2-(trans-4-pentylcyclohexyl)-1-(p-ethoxyphenyl)ethane,

4.77 weight % of 4"-pentyl-4-cyano-p-terphenyl,

4.85 weight % of 4'-(trans-4-pentylcyclohexyl)-4-cyanobiphenyl,

10.46 weight % of 1-[2-(trans-4-butylcyclohexyl)ethyl]-4--(trans-4-pentylcyclohexyl)benzene,

8.55 weight % of 4-[2-(trans-4-butylcyclohexyl)ethyl]-4'--(trans-4-pentylcyclohexyl)-1,1'-ethylenedibenzene;

5.98 weight % of 4-(trans-4-pentylcyclohexyl)-4'-[2-(trans--4-butylcyclohexyl)ethyl]biphenyl; cl.p. 86.1°C, nematic.

Mixture Example 10

14.02 weight % of 4'-pentyl-4-cyanobiphenyl,
11.84 weight % of 4'-hexyl-4-cyanobiphenyl,
13.89 weight % of 2-(trans-4-propylcyclohexyl)-1-(p-ethoxyphenyl)ethane,
7.66 weight % of 2-(trans-4-propylcyclohexyl)-1-(p-butyloxyphenyl)ethane,
15.30 weight % of 2-(trans-4-pentylcyclohexyl)-1-(p-ethoxyphenyl)ethane,
4.57 weight % of 4"-pentyl-4-cyano-p-terphenyl,
4.66 weight % of 4'-(trans-4-pentylcyclohexyl)-4-cyanobiphenyl,
10.03 weight % of 1-[2-(trans-4-butylcyclohexyl)ethyl]-4--(trans-4-pentylcyclohexyl)benzene,
9.83 weight % of 4-[2-(trans-4-butylcyclohexyl)ethyl]-4'--(trans-4-pentylcyclohexyl)-1,1'-ethylenedibenzene,
8.20 weight % of 4-[2-(trans-4-butylcyclohexyl)ethyl]-4'--(trans-4-propylcyclohexyl)-1,1'-ethylenedibenzene; nematic.

Mixture Example 11

4.29 weight % of 4'-ethyl-4-cyanobiphenyl,
3.27 weight % of 4'-propyl-4-cyanobiphenyl,
16.21 weight % of 4'-pentyl-4-cyanobiphenyl,
15.41 weight % of 2-(trans-4-propylcyclohexyl)-1-(p-ethoxyphenyl)ethane,

6.26 weight % of 2-(trans-4-propylcyclohexyl)-1-(p-butyloxyphenyl)ethane,

17.88 weight % of 2-(trans-4-pentylcyclohexyl)-1-(p-ethoxyphenyl)ethane,

4.81 weight % of 4"-pentyl-4-cyano-p-terphenyl,

4.90 weight % of 4'-(trans-4-pentylcyclohexyl)-4-cyanobiphenyl,

11.72 weight % of 1-[2-(trans-4-butylcyclohexyl)ethyl]-4--(trans-4-pentylcyclohexyl)benzene,

8.47 weight % of 4-[2-(trans-4-butylcyclohexyl)ethyl]--4'-(trans-4-pentylcyclohexyl)-1,1'-ethylenedibenzene,

6.78 weight % of 4-[2-(trans-4-butylcyclohexyl)ethyl]-4'--(trans-4-propylcyclohexyl)-1,1'-ethylenedibenzene; nematic.

The following Examples illustrate in more detail the manufacture of the compounds provided by the invention. C denotes a crystalline phase, S denotes a smectic phase, N denotes a nematic phase and I denotes the isotropic phase.

Example 1

2.20 g of 4-(trans-4-pentylcyclohexyl)-4'-[2-(trans--4-pentylcyclohexyl)vinyl]biphenyl were suspended in a toluene/ethanol mixture (3:2) in a sulphonation flask, treated with 200 mg of palladium/carbon (10%) and hydrogenated at normal pressure and 50°C until the hydrogen uptake came to a standstill. Filtration of the mixture and concentration of the filtrate gave a white, semi--crystalline residue which, after recrystallization from 100 ml of hexane, yielded 1.55 g of 4-(trans-4-pentylcyclohexyl)-4'-[2-(trans-4-pentylcyclohexyl)ethyl]biphenyl as colourless needles; transition (presumably S-S) 219.5°C, transition S-N 243.2°C, cl.p. (N-I) 256.1°C. This substance showed itself to be very considerably super-coolable; it did not crystallize upon cooling to room temperature. Rf value (hexane): 0.32.

The 4-(trans-4-pentylcyclohexyl)-4'-[2-(trans-4--pentylcyclohexyl)vinyl]biphenyl used as the starting material was prepared as follows:

(a) A solution of 10.0 g of 4'-(trans-4-pentylcyclohexyl)--4-biphenylcarbonitrile in 150 ml of methylene chloride was placed at -35°C in a sulphonation flast while gassing with argon and treated within 8 minutes with 40 ml of an about 1.5N solution of diisobutylaluminium hydride in toluene. After completion of the addition, the mixture was stirred for 2 hours at -35°C and then for a further 1.5 hours with gradual warming to 0°C, before it was treated cautiously with 100 ml of 1N sulphuric acid and extracted three times with 150 ml of diethyl ether each time. The organic phases were washed with 100 ml of 1N sulphuric acid, twice with 100 ml of water each time and once with 100 ml of saturated sodium chloride solution, dried over magnesium sulphate and concentrated. There were obtained 9.5 g (95%) of 4'-(trans--4-pentylcyclohexyl)-4-biphenylcarboxaldehyde as a colourless, crystalline mass (m.p. 115-116°C) which was used in the following step without further purification. Rf value [toluene/ethyl acetate (19:1)]: educt 0.65, product 0.52.

(b) A mixture of 930 mg of lithium aluminium hydride in 100 ml of absolute tetrahydrofuran was placed at 0°C in a sulphonation flask and treated within 20 minutes with a solution of 8.2 g of 4'-(trans-4-pentylcyclohexyl)-4--biphenylcarboxaldehyde in 100 ml of absolute tetrahydrofuran. After completion of the addition, the mixture

was stirred for a further 2 hours while warming to room temperature, subsequently cautiously quenched with 100 ml of 1N sulphuric acid and extracted three times with 200 ml of methylene chloride each time. The organic phases were washed twice with 100 ml of water each time, dried over magnesium sulphate and concentrated. There were obtained 7.90 g (96%) of 4'-(trans-4-pentylcyclohexyl)-4-biphenylmethanol as a colourless, crystalline mass (purity 99.4% in accordance with gas chromatography) which was used in the following step without further purification. M.p. 180.4°C; Rf value [petroleum ether/ethyl acetate (9:1)]: educt 0.70, product 0.30.

(c) A mixture of 3.5 g of 4'-(trans-4-pentylcyclohexyl)--4-biphenylmethanol and 2.9 g of triphenylphosphine in 150 ml of absolute methylene chloride was placed at -20°C in a sulphonation flask while gassing with argon and treated portionwise within 10 minutes with 3.8 g of solid tetrabromomethane. Partially undissolved educt thereby dissolved slowly. The mixture was stirred for a further 2 hours while warming to room temperature. The mixture was subsequently concentrated on a rotary evaporator and the crystalline residue was suspended in 300 ml of warm hexane, freed by filtration from precipitated triphenylphosphine oxide (rinsing with hexane) and the filtrate was

concentrated. Low-pressure chromatography (0.7 bar) of the residue on silica gel with toluene as the eluant gave 3.39 g (82%) of 4-(bromomethyl)-4'-(trans-4-pentylcyclohexyl)biphenyl as colourless crystals. This material was used in the following step without further purification. Rf value of the product [petroleum ether/ethyl acetate (97:3)]: 0.47.

(d) A mixture of 2.63 g of 4-(bromomethyl)-4'-(trans-4--pentylcyclohexyl)biphenyl and 2.2 g of triphenylphosphine in 150 ml of o-xylene was heated to reflux (bath temperature 160°C) for 15 hours in a sulphonation flask while gassing with argon. After cooling, the white precipitate formed was filtered off, washed several times with benzene and dried in a high vacuum (0.1 mmHg) at 80°C for 1 hour. There were obtained 3.48 g (80%) of [[4'-(trans-4-pentylcyclohexyl)--4-biphenylyl]methyl]triphenylphosphonium bromide as a white powder (m.p. 263-265°C) which was used in the following Wittig reaction without further purification.

(e) A mixture of 3.31 g of [[4'-(trans-4-pentylcyclohexyl)-4-biphenylyl]methyl]triphenylphosphonium bromide in 50 ml of t-butyl methyl ether was placed at 0°C in a sulphonation flask while gassing with argon and treated with 617 mg of solid potassium 5-butylate. After completion of the addition, the mixture was stirred at 0°C for a

further 15 minutes (a deep orange coluration resulting) and then treated within 10 minutes at 0°C with a solution of 912 mg of trans-4-pentylcyclohexanecarboxaldehyde in 20 ml of t-butyl methyl ether. The mixture was subsequently stirred at 0°C for a further 30 minutes and at room temperature for 90 minutes and then the yellow mixture was poured into 150 ml of water and extracted three times with 150 ml of diethyl ether each time. The organic phases were washed twice with 100 ml of water each time, dried over magnesium sulphate and concentrated. Low-pressure chromatography (0.7 bar) of the residue on silica gel with toluene as the eluant gave 2.43 g (100%) of 4-(trans-4-pentylcyclohexyl)-4'-[2-(trans-4-pentylcyclohexyl)vinyl]biphenyl as a colourless, crystalline mass. This material was used without further purification in the hydrogenation described in the first paragraph of this Example. Rf values of the product (hexane): 0.20 and 0.32 (cis/trans mixture).

The following compounds can be manufactured in an analogous manner:

4-(Trans-4-pentylcyclohexyl)-4'-[2-(trans-4-propylcyclohexyl)ethyl]biphenyl; transition S-S 208.1°C, transition S-N 234.0°C, cl.p. (N-I) 263.5°C;

4-(trans-4-pentylcyclohexyl)-4'-[2-(trans-4-butylcyclohexyl)ethyl]biphenyl; transition S-S 215.9°C,

transition S-N 240°C, cl.p. (N-I) 259°C;

4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-(trans-4--propylcyclohexyl)-1,1'-ethylenedibenzene; m.p. (C-S) 68.9°C, transition S-S 117.5°C, transition S-N 171.5°C, cl.p. (N-I) 187.3°C;

4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-(trans-4--pentylcyclohexyl)-1,1'-ethylenedibenzene; m.p. (C-S) 48.0°C, cl.p. (S-I) 188.0°C;

4-(trans-4-pentylcyclohexyl)-4'-[2-(p-(trans-4-butylcyclohexyl)phenyl)ethyl]biphenyl; m.p. 65°C, cl.p. 331.6°C;

4-(trans-4-pentylcyclohexyl)-4'-[2-(p-(trans-4-pentylcyclohexyl)phenyl)ethyl]biphenyl; cl.p. 323.5°C;

4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propylcyclohexyl)-1,1'-ethylenedibenzene; m.p. (C-S) 116.8°C, transition S-N 198.5°C, cl.p. (N-I) 221.9°C;

4-pentyl-4"-[2-(trans-4-butylcyclohexyl)ethyl]-p--terphenyl; m.p. (C-S) 149.8°C, transition S-S 215.5°C, transition S-N 263°C, cl.p. (N-I) 267°C;

4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-(p-pentylphenyl)-1,1'-ethylenedibenzene; m.p. (C-S) 0°C, transition S-S 76.5°C, cl.p. (S-I) 194°C;

1-[2-(trans-4-butylcyclohexyl)ethyl]-4-(trans-4--pentylcyclohexyl)benzene; m.p. (C-S) 28.1°C, cl.p. (S-I) 138.4°C;

1-[2-(trans-4-pentylcyclohexyl)ethyl]-4-(trans-4--propylcyclohexyl)benzene; m.p. (C-S) 40.2°C, transition S-N 126°C, cl.p. (N-I) 132.7°C; and

1-[2-(trans-4-butylcyclohexyl)ethyl]-4-[2-(trans-4--pentylcyclohexyl)ethyl]benzene; m.p. (C-S) 10.4 or 21.6°C (2 modifications), cl.p. (S-I) 125.8°C.

Example 2

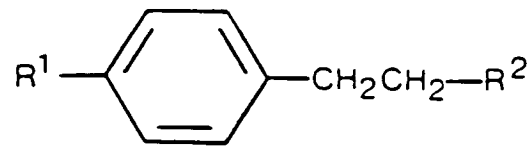
(a) A suspension of 2.14 g of 4,4'-bis(hydroxymethyl)biphenyl (prepared by reducing dimethyl biphenyl-4,4'-dicarboxylate with lithium aluminium hydride) and 5.5 g of triphenylphosphine in 60 ml of methylene chloride was placed at -10°C in a sulphonation flask while gassing with argon and treated within 3 minutes with 7.3 g of tetrabromoethane. After completion of the addition, the mixture was stirred for a further 16 hours with gradual warming to +10°C and then, after concentration on a rotary evaporator, triturated with hot benzene. Filtration and concentration gave 12.67 g of crude product which, after low-pressure chromatography (0.5 bar) with toluene on silica gel, yielded 2.60 g (76%) of 4,4'-bis(bromomethyl)biphenyl. A recrystallization from 50 ml of acetone gave 1.78 g of the dibromide as colourless crystals of melting point 172.8°C. Rf value [hexane/toluene (2:1)]: 0.41.

(b) 122 mg of magnesium shavings were covered with 3 ml of absolute tetrahydrofuran in a sulphonation flask while gassing with argon and, after the addition of a crystal of iodine, treated with a solution of 1.24 g of trans-1--(bromomethyl)-4-pentylcyclohexane in 7 ml of absolute tetrahydrofuran. After completion of the addition the mixture was heated to reflux for a further 30 minutes and then the mixture, cooled to -78°C, was treated in sequence with 0.7 ml of a 0.1N solution of dilithium tetrachlorocuprate in tetrahydrofuran and with a solution of 670 mg of 4,4'-bis(bromomethyl)biphenyl in 10 ml of absolute tetrahydrofuran. The yellow colouration which initially appeared disappeared again after a few minutes. The mixture, warmed to -15°C, was subsequently stirred for a further 17 hours, then treated with 25 ml of 2N hydrochloric acid and extracted three times with 50 ml of diethyl ether each time. The organic phases were washed with 50 ml of saturated sodium chloride solution, dried over magnesium sulphate and concentrated. Low-pressure chromatography (0.5 bar) of the residue (1.06 g) on silica gel with hexane and subsequently hexane/diethyl ether (19:1) as the eluant gave in succession 1,1'-ethylene-bis(trans--4-pentylcyclohexane), 228 mg (22%) of 4,4'-bis[2-(trans--4-pentylcyclohexyl)ethyl]biphenyl, 78 mg (9%) of 4-(bromomethyl)-4'-[2-(trans-4-pentylcyclohexyl)ethyl]biphenyl and 4,4'-bis(bromomethyl)biphenyl. A single crystallization of the 228 mg of 4,4'-bis[2-(trans-4-pentylcyclohexyl)ethyl]-

biphenyl from hexane yielded 194 mg of colourless needles of clearing point >300°C (further phase transitions at 68°C, 84°C, 161°C, 203°C,221°C and 224°C). Rf values (hexane): 4,4,-bis(bromomethyl)biphenyl 0.14; 4-(bromomethyl)-4'--[2-(trans-4-pentylcyclohexyl)ethyl]biphenyl 0.24; 4,4'--bis[2-(trans-4-pentylcyclohexyl)ethyl]biphenyl 0.40.

CLAIMS:

1. Compounds of the general formula



I

wherein R^1 signifies trans-4-alkylcyclohexyl, 4'-alkyl-4-biphenylyl, p-(trans-4-alkylcyclohexyl)phenyl, 2-(trans-4-alkylcyclohexyl)ethyl or p-[2-(trans-4-alkylcyclohexyl)ethyl]phenyl and R^2 signifies trans-4-alkylcyclohexyl, or R^1 signifies trans-4-alkylcyclohexyl and R^2 signifies p-(trans-4-alkylcyclohexyl)phenyl, p-[2-(trans-4-alkylcyclohexyl)ethyl]phenyl or 4'-(trans-4-alkylcyclohexyl)-4-biphenylyl, or R^1 signifies p-alkylphenyl and R^2 signifies p-[2-(trans-4-alkylcyclohexyl)ethyl]phenyl, and the alkyl groups in the substituents R^1 and R^2 are straight-chain groups containing 1 to 7 carbon atoms.

2. Compounds according to claim 1,

wherein the sum of the carbon atoms in the alkyl groups of the substituents R^1 and R^2 is 5 to 10.

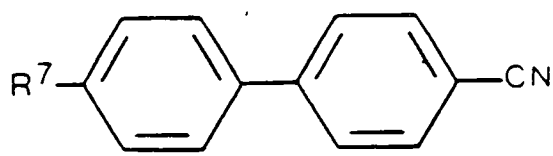
3. 1-[2-(Trans-4-butylcyclohexyl)ethyl]-4-(trans-4--pentylcyclohexyl)benzene.

4. 4-[2-(Trans-4-butylcyclohexyl)ethyl]-4'-(trans-4-pentylcyclohexyl)-1,1'-ethylenedibenzene.

5. 4-(Trans-4-pentylcyclohexyl)-4'-[2-(trans-4-butylcyclohexyl)ethyl]biphenyl.

6. A liquid crystalline mixture containing one or more compounds of formula I defined in claim 1 and one or more other suitable liquid crystalline and/or non-liquid crystalline substances.

7. A liquid crystalline mixture according to claim 6 containing one or more compounds of formula I and one or more compounds of the general formulae



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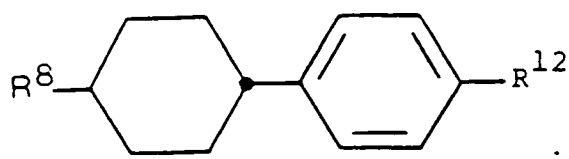

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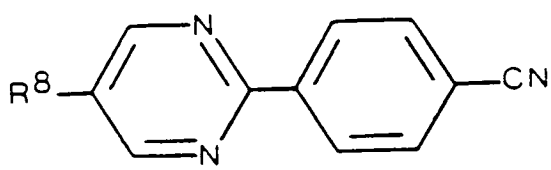

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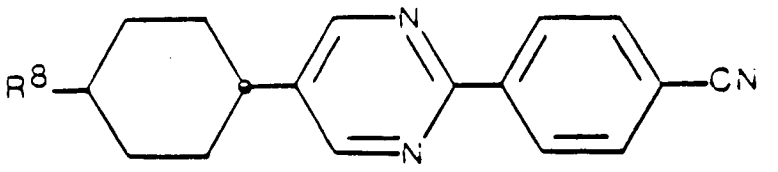

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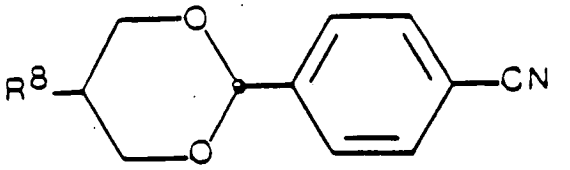

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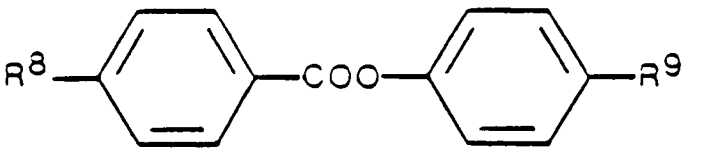

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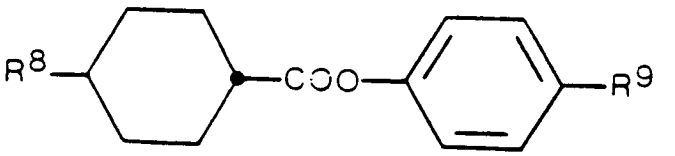

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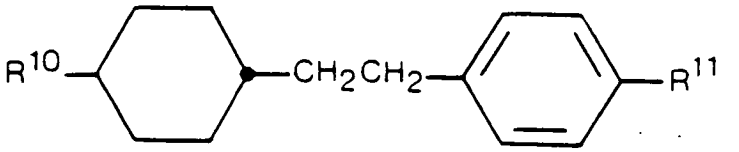

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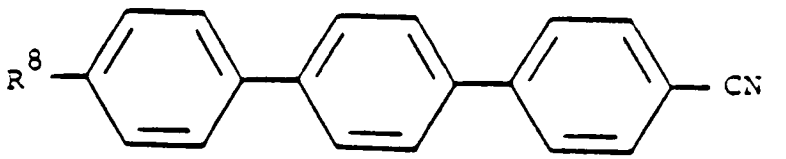
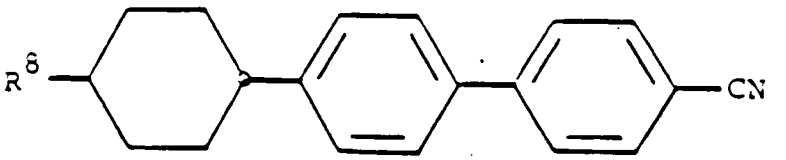


XXI



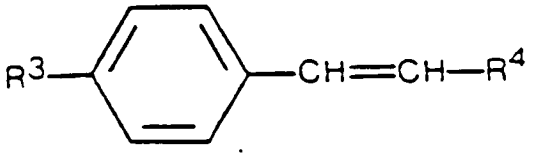
XXII

wherein R^7 signifies a straight-chain alkyl or alkoxy group containing 2 to 7 carbon atoms, R^8 signifies a straight-chain alkyl group containing 2 to 7 carbon atoms, R^9 signifies the cyano group or a straight-chain alkoxy group containing 1 to 6 carbon atoms, R^{10} signifies a straight-chain alkyl group containing 3 to 7 carbon atoms, R^{11} signifies the cyano group or a straight-chain alkyl or alkoxy group containing 1 to 7 carbon atoms and R^{12} signifies the cyano group or a straight-chain alkyl group containing 1 to 7 carbon atoms.

8. A liquid crystalline mixture according to claim 6 or 7 containing 4'-propyl-4-cyanobiphenyl, 4'-pentyl-4-cyanobiphenyl, 2-(trans-4-propylcyclohexyl)-1-(p-ethoxyphenyl)ethane, 2-(trans-4-pentylcyclohexyl)-1-(p-ethoxyphenyl)ethane, 4"-pentyl-4-cyano-p-terphenyl, 4'-(trans-4-pentylcyclohexyl)-4-cyanobiphenyl, 1-[2-(trans-4-butylcyclohexyl)ethyl]-4-(trans-4-pentylcyclohexyl)benzene, 4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-(trans-4-pentylcyclohexyl)-1,1'-ethylenedibenzene and 4-(trans-4-pentylcyclohexyl)-4'-[2-(trans-4-butylcyclohexyl)ethyl]biphen .

9. A process for the manufacture of the compounds of formula I defined in claim 1, which process comprises

(a) for the manufacture of the compounds of formula I in which R^1 signifies trans-4-alkylcyclohexyl, 4'-alkyl-4-biphenylyl, p-(trans-4-alkylcyclohexyl)phenyl or 2-(trans-4-alkylcyclohexyl)ethyl and R^2 signifies trans-4-alkylcyclohexyl, or R^1 signifies trans-4-alkylcyclohexyl and R^2 signifies p-(trans-4-alkylcyclohexyl)phenyl, p-[2-(trans-4-alkycyclohexyl)ethyl]phenyl or 4'-(trans-4-alkylcyclohexyl)-4-biphenylyl, or R^1 signifies p-alkylphenyl and R^2 signifies p-[2-(trans-4-alkylcyclohexyl)ethyl]-phenyl, catalytically hydrogenating a compound of the general formula



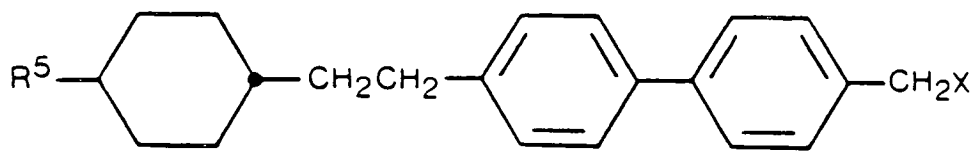
VII

wherein R^3 signifies trans-4-alkylcyclohexyl, 4'-alkyl-4-biphenylyl, p-(trans-4-alkylcyclohexyl)phenyl or 2-(trans-4-alkylcyclohexyl)ethyl and R^4 signifies trans-4-alkylcyclohexyl, or R^3 signifies trans-4-alkylcyclohexyl and R^4 signifies p-(trans-4-

-alkylcyclohexyl)phenyl, p-[2-(trans-
-4-alkylcyclohexyl)ethyl]phenyl or
4'-(trans-4-alkylcyclohexyl)-4-biphenylyl,
or R^3 signifies p-alkylphenyl and R^4 signifies p-[2-(trans-4-alkylcyclohexyl)ethyl]-phenyl, and the alkyl groups in the substituents R^3 and R^4 are straight-chain groups containing 1 to 7 carbon atoms,

or

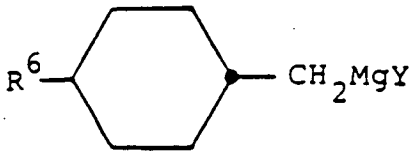
(b) for the manufacture of the compounds of formula I in which R^1 signifies p-[2-(trans-4-alkylcyclohexyl)ethyl]-phenyl and R^2 signifies trans-4-alkylcyclohexyl, reacting a compound of the general formula



XI

wherein R^5 signifies a straight-chain alkyl group containing 1 to 7 carbon atoms and X signifies a leaving group,

with a compound of the general formula



XX

wherein R^6 signifies a straight-chain alkyl group containing 1 to 7 carbon atoms and Y signifies chlorine or bromine,

in the presence of dilithium tetrachlorocuprate.

10. Compounds of formula I according to any one of claims 1 to 5 when manufactured by the process claimed in claim 9 ~~or by an obvious chemical equivalent thereof~~.

11. The use of the compounds of formula I defined in claim 1 for electro-optical purposes.

Publication No.
2107733 A dated 5 May 1963

Patent Granted:
WITH EFFECT FROM SECTION 25(1) 2 OCT 1985

Application No.
8229191 filed on 13 October 1982

Priorities claimed:
14 October 1981 in Switzerland doc: 6572/81
19 March 1982 in Switzerland doc: 1725/82
8 July 1982 in Switzerland doc: 4172/82

Title:
Phenylethanes

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Classified to:
C5E

EXAMINATION REQUESTED 2 3 NOV 1983

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Printed by the Patent Office at St. Mary Cray, 09 MAR 83