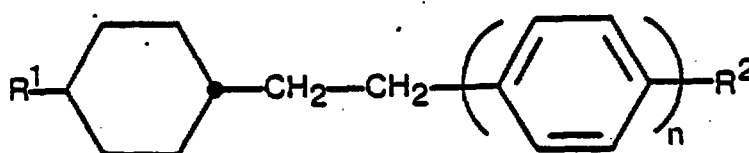


"1-CYCLOHEXYL-2-PHENYL-ETHANE DERIVATIVES FOR
USE IN LIQUID CRYSTAL MATERIALS"

The present invention is concerned with novel
(trans-4-alkylcyclohexyl)ethanes of the general formula



5

wherein R^2 represents one of the
groups $-R^3$, $-OR^3$, $-CO-R^3$, $-CO-OR^3$
or $-O-CO-R^3$, R^1 and R^3 signify
straight-chain alkyl groups con-
taining 1 to 12 carbon atoms and
n stands for one of the numbers 1 or 2.

10

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

15

The term "straight-chain alkyl group" used herein
embraces the groups methyl, ethyl, propyl, butyl, pentyl,
hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl.

The compounds in accordance with the invention are especially valuable as components of liquid crystalline mixtures and most of them themselves have liquid crystalline (nematic and/or smectic) properties.

5 The compounds in accordance with the invention are miscible with all known liquid crystals and can be used in all customary electro-optical devices, the choice of the mixture components generally depending on the special purpose of use. However, the compounds in accordance with
10 the invention are preferably used for the manufacture of nematic and cholesteric mixtures with positive anisotropy of the dielectric constants ($\epsilon_{||} > \epsilon_{\perp}$, $\epsilon_{||}$ signifying the dielectric constant along the molecular axis and $\epsilon_{\perp}$ signifying the dielectric constant perpendicular thereto).

15 Such mixtures orientate themselves in an electric field with the direction of their largest dielectric constants (i.e. with their longitudinal axes) parallel to the field direction. This effect is used, inter alia, in the interaction between embedded molecules and the liquid
20 crystalline molecules (guest-host interaction) described by J.H.Heilmeyer and L.A.Zanoni [Applied Physics Letters 13, 91 (1968)] or by D.L.White and G.N.Taylor [J. Appl. Phys. 45, 4718 (1974)]. A further interesting application of the dielectric field orientation exists in the rotation cell
25 discovered by M.Schadt and W.Helfrich [Applied Physics

Letters 18, 127 (1971)] as well as in the Kerr cell described in Molecular Crystals and Liquid Crystals 17, 355 (1972).

These electro-optical rotation cells comprise essentially a condenser with transparent electrodes, the dielectric of which is formed from a nematic crystal with $\epsilon_{||} > \epsilon_{\perp}$. The longitudinal molecular axes of the liquid crystals are arranged in twisted form between the condenser plates in the fieldless condition, the twisting structure being determined by the given wall orientation of the molecules. After the application of an electric potential to the condenser plates, the molecules adjust themselves with their longitudinal axes in the field direction (i.e. perpendicular to the surface of the plates), whereby linear polarized light is no longer rotated in the dielectric (the liquid crystal is uniaxially perpendicular to the surface of the plates). This effect is reversible and can be used to electrically control the optical transmissivity of the condenser.

Further, it is known that the addition of cholesteric substances (or, generally, of soluble, optically active substances as long as the total mixture remains liquid crystalline) to a matrix of nematic liquid crystals with positive anisotropy of the dielectric constants leads to a cholesteric mixture which undergoes a cholesteric-nematic

phase transition upon application of an electric field (phase change effect). By suitable choice of the concentration of cholesteric additives, such mixtures can also be used for improving the electro-optical properties of rotation cell indicators.

It has now surprisingly been found that the compounds in accordance with the invention are liquid crystalline compounds with low viscosities. The compounds of formula I in which n stands for 1 have especially low viscosities and relatively low melting points. Moreover, the melting points are often largely supercoolable. These compounds are accordingly suitable above all for lowering the viscosities and the melting points of liquid crystalline mixtures. On the other hand, the compounds of formula I in which n stands for 2 exhibit large mesophase ranges. These compounds are suitable above all for increasing the clearing point of low viscosity mixtures, whereby the viscosity is not increased or is increased only insignificantly.

The compounds in accordance with the invention are further distinguished by having a good chemical stability, by being colourless and by having a high UV-stability.

Of the compounds of formula I there are preferred those in which R^2 represents the group $-R^3$, $-OR^3$ or $-CO-OR^3$. Those compounds of formula I in which R^2 represents an alkyl group $-R^3$ or an alkoxy group $-OR^3$ are

especially preferred. Furthermore, those compounds of formula I in which n stands for 1 are preferred. The groups R^3 are preferably straight-chain alkyl groups containing 1 to 10 carbon atoms and especially straight-chain alkyl groups containing 1 to 7 carbon atoms. Further, the groups R^1 with 2 to 10 carbon atoms are preferred and those containing 3 to 7 carbon atoms are especially preferred.

The following can be named as examples of preferred compounds of formula I:

2-(Trans-4-propylcyclohexyl)-1-(p-propylphenyl)ethane,
2-(trans-4-propylcyclohexyl)-1-(p-pentylphenyl)ethane,
2-(trans-4-propylcyclohexyl)-1-(p-hexylphenyl)ethane,
2-(trans-4-butylcyclohexyl)-1-(p-propylphenyl)ethane,
15 2-(trans-4-butylcyclohexyl)-1-(p-pentylphenyl)ethane,
2-(trans-4-pentylcyclohexyl)-1-(p-propylphenyl)ethane,
2-(trans-4-pentylcyclohexyl)-1-(p-pentylphenyl)ethane,
2-(trans-4-pentylcyclohexyl)-1-(p-hexylphenyl)ethane,
2-(trans-4-heptylcyclohexyl)-1-(p-propylphenyl)ethane,
20 2-(trans-4-heptylcyclohexyl)-1-(p-butylphenyl)ethane,
2-(trans-4-heptylcyclohexyl)-1-(p-pentylphenyl)ethane,
2-(trans-4-ethylcyclohexyl)-1-(p-ethoxyphenyl)ethane,
2-(trans-4-ethylcyclohexyl)-1-(p-butyloxyphenyl)ethane,
2-(trans-4-ethylcyclohexyl)-1-(p-hexyloxyphenyl)ethane,
25 2-(trans-4-propylcyclohexyl)-1-(p-methoxyphenyl)ethane,
2-(trans-4-propylcyclohexyl)-1-(p-ethoxyphenyl)ethane,

2-(trans-4-propylcyclohexyl)-1-(p-propyloxyphenyl)-
ethane,

2-(trans-4-propylcyclohexyl)-1-(p-butyloxyphenyl)-
ethane,

5 2-(trans-4-butylcyclohexyl)-1-(p-methoxyphenyl) ethane,

2-(trans-4-butylcyclohexyl)-1-(p-ethoxyphenyl) ethane,

2-(trans-4-butylcyclohexyl)-1-(p-butyloxyphenyl) ethane,

2-(trans-4-pentylcyclohexyl)-1-(p-methoxyphenyl) ethane,

2-(trans-4-pentylcyclohexyl)-1-(p-ethoxyphenyl) ethane,

10 2-(trans-4-pentylcyclohexyl)-1-(p-propyloxyphenyl) ethane,

2-(trans-4-pentylcyclohexyl)-1-(p-butyloxyphenyl) ethane,

2-(trans-4-heptylcyclohexyl)-1-(p-methoxyphenyl) ethane,

2-(trans-4-heptylcyclohexyl)-1-(p-ethoxyphenyl) ethane,

2-(trans-4-heptylcyclohexyl)-1-(p-butyloxyphenyl) ethane,

15 p-[2-(trans-4-propylcyclohexyl)-1-ethyl]phenylacetate,

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

p-[2-(trans-4-butylcyclohexyl)-1-ethyl]phenylacetate,

p-[2-(trans-4-butylcyclohexyl)-1-ethyl]phenylbutyrate,

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

20 p-[2-(trans-4-pentylcyclohexyl)-1-ethyl]phenylbutyrate,

p-[2-(trans-4-heptylcyclohexyl)-1-ethyl]phenylacetate,

p-[2-(trans-4-ethylcyclohexyl)-1-ethyl]benzoic acid

methyl ester,

p-[2-(trans-4-ethylcyclohexyl)-1-ethyl]benzoic acid

25 ethyl ester,

p-[2-(trans-4-propylcyclohexyl)-1-ethyl]benzoic acid

methyl ester,

p-[2-(trans-4-propylcyclohexyl)-1-ethyl]benzoic acid

ethyl ester,

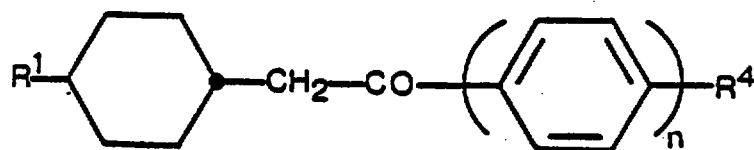
30 p-[2-(trans-4-propylcyclohexyl)-1-ethyl]benzoic acid

propyl ester,

- p-[2-(trans-4-butylcyclohexyl)-1-ethyl]benzoic acid
methyl ester,
p-[2-(trans-4-butylcyclohexyl)-1-ethyl]benzoic acid
ethyl ester,
5 p-[2-(trans-4-pentylcyclohexyl)-1-ethyl]benzoic acid
methyl ester,
p-[2-(trans-4-pentylcyclohexyl)-1-ethyl]benzoic acid
ethyl ester,
p-[2-(trans-4-hexylcyclohexyl)-1-ethyl]benzoic acid
10 methyl ester,
p-[2-(trans-4-hexylcyclohexyl)-1-ethyl]benzoic acid
ethyl ester,
p-[2-(trans-4-heptylcyclohexyl)-1-ethyl]benzoic acid
methyl ester,
15 p-[2-(trans-4-heptylcyclohexyl)-1-ethyl]benzoic acid
ethyl ester,
p-[2-(trans-4-propylcyclohexyl)-1-ethyl]propiophenone,
p-[2-(trans-4-propylcyclohexyl)-1-ethyl]valerophenone,
p-[2-(trans-4-pentylcyclohexyl)-1-ethyl]propiophenone,
20 p-[2-(trans-4-pentylcyclohexyl)-1-ethyl]valerophenone,
p-[2-(trans-4-pentylcyclohexyl)-1-ethyl]hexanophenone,
2-(trans-4-ethylcyclohexyl)-1-(4'-propyl-4-biphenyl)-
ethane,
2-(trans-4-propylcyclohexyl)-1-(4'-ethyl-4-biphenyl)-
25 ethane,
2-(trans-4-propylcyclohexyl)-1-(4'-propyl-4-biphenyl)-
ethane,
2-(trans-4-propylcyclohexyl)-1-(4'-pentyl-4-biphenyl)-
ethane,
30 2-(trans-4-pentylcyclohexyl)-1-(4'-ethyl-4-biphenyl)-
ethane,

- 2-(trans-4-pentylcyclohexyl)-1-(4'-propyl-4-biphenyl)-
ethane,
- 2-(trans-4-pentylcyclohexyl)-1-(4'-pentyl-4-biphenyl)-
ethane,
- 5 2-(trans-4-ethylcyclohexyl)-1-(4'-butyloxy-4-biphenyl)-
ethane,
- 2-(trans-4-propylcyclohexyl)-1-(4'-ethoxy-4-biphenyl)-
ethane,
- 2-(trans-4-propylcyclohexyl)-1-(4'-butyloxy-4-biphenyl)-
10 ethane,
- 2-(trans-4-pentylcyclohexyl)-1-(4'-ethoxy-4-biphenyl)-
ethane,
- 2-(trans-4-pentylcyclohexyl)-1-(4'-butyloxy-4-biphenyl)-
ethane,
- 15 4'-[2-(trans-4-propylcyclohexyl)-1-ethyl]-4-biphenyl-
acetate,
- 4'-[2-(trans-4-propylcyclohexyl)-1-ethyl]-4-biphenyl-
butyrate,
- 4'-[2-(trans-4-propylcyclohexyl)-1-ethyl]-4-biphenyl-
20 carboxylic acid methyl ester,
- 4'-[2-(trans-4-propylcyclohexyl)-1-ethyl]-4-biphenyl-
carboxylic acid ethyl ester,
- 4'-[2-(trans-4-propylcyclohexyl)-1-ethyl]-4-biphenyl-
carboxylic acid propyl ester,
- 25 4'-[2-(trans-4-pentylcyclohexyl)-1-ethyl]-4-biphenyl-
carboxylic acid methyl ester,
- 4'-[2-(trans-4-pentylcyclohexyl)-1-ethyl]-4-biphenyl-
carboxylic acid ethyl ester, and
- 2-(trans-4-propylcyclohexyl)-1-(4'-butyryl-4-biphenyl)-
30 ethane.

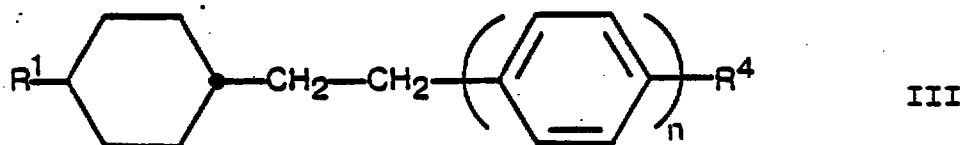
The compounds of formula I can be manufactured in accordance with the invention by reducing a compound of the general formula



II

5. wherein R⁴ represents hydrogen, hydroxy, halogen or the group -R³ or -OR³ and R¹, R³ and n have the significance given earlier,

and acylating the resulting compound of the general formula



wherein R^1 , R^4 and n have the
significance given earlier,
when R^4 signifies hydrogen, or, when R^4 signifies hydroxy,
5 esterifying the resulting compound of formula III with a
carboxylic acid of the formula $R^3\text{COOH}$ or a reactive
derivative thereof or, when R^4 signifies halogen, reacting
the resulting compound of formula III with magnesium and
subsequently with carbon dioxide, hydrolyzing the carboxylate
10 obtained and esterifying the resulting acid or a reactive
derivative thereof with an alcohol of the formula $R^3\text{OH}$.

The reduction of a compound of formula II can be
carried out according to methods known per se. Preferably,
a compound of formula II is reacted with hydrazine in the
15 presence of a base (e.g. potassium hydroxide, sodium
ethylete, potassium t-butyrate and the like) in an inert
organic solvent such as dimethyl sulphoxide or an alcohol
(e.g. ethanol, diethyleneglycol, triethyleneglycol and the
like) and subsequently the hydrazone formed is decomposed.
20 In general, the hydrazone formed is only decomposed at an
elevated temperature (e.g. at about 200°C). If, however,

dimethyl sulphoxide is used as the solvent, then the decomposition frequently occurs already at room temperature. In a preferred embodiment, the reduction is carried out according to the Huang-Minlon process, i.e. by heating
5 the ketone under reflux in a high-boiling solvent which is miscible with water (e.g. diethyleneglycol or triethylene-glycol) together with hydrazine hydrate and potassium hydroxide, subsequently distilling off the water until the hydrazone decomposes and continuing the boiling under
10 reflux until the reduction is complete.

A further preferred method for the reduction of a compound of formula II is the Clemmensen reduction. In accordance with this method, the ketone is warmed with amalgamated zinc and hydrochloric acid. If desired, an
15 organic solvent such as ethanol, acetic acid, dioxan, toluene and the like can be added.

Furthermore, a compound of formula II in which R^4 signifies hydrogen or an alkyl group can be reduced by catalytic hydrogenation. This hydrogenation can be
20 carried out with usual hydrogenation catalysts (e.g. palladium, platinum, Raney-nickel and the like), if desired supported on an inert carrier material (e.g. carbon). Palladium and platinum are the preferred catalysts. The solvent used can be any inert organic solvent such as a
25 saturated alcohol, an ether, an ester, a carboxylic

acid, a hydrocarbon and the like (e.g. ethanol, dioxan, ethyl acetate, glacial acetic acid or hexane). The temperature and pressure are not critical in this catalytic hydrogenation. A temperature between room temperature and the boiling point of the mixture and a pressure of about 1 to about 5 atmospheres are conveniently used.

The reduction of a compound of formula II in which R^4 signifies hydrogen or an alkyl group can also be carried out by reacting said compound with an alkanethiol or alkanedithiol (e.g. ethanethiol, 1,3-propanedithiol, ethanedithiol and the like) and subsequently cleaving the thioketal obtained by catalytic hydrogenation with Raney-nickel. Preferred thiols are 1,3-propanedithiol and especially ethanedithiol, which give cyclic thioketals. The formation of the thioketal can be catalyzed, for example, with boron trifluoride etherate. Conveniently, the preparation of the thioketal and the hydrogenation are carried out in an inert organic solvent such as, for example, diethyl ether, dioxan, methylene chloride, chloroform and the like; however, when the thiol used is a liquid, it can also simultaneously serve as the solvent. The pressure and temperature are not critical; atmospheric pressure and room temperature are conveniently used.

The compounds of formula II in which R^4 signifies the group $-R^3$ or $-OR^3$ are converted directly by the foregoing reduction into the corresponding compounds of formula I

(i.e. the compounds of formula III are in this case end products). Those compounds of formula II in which R^4 signifies hydrogen, hydroxy or halogen must, on the other hand, be reacted further after the reduction to compounds of formula III.

The acylation of a compound of formula III in which R^4 signifies hydrogen can be carried out by reaction with a carboxylic acid chloride, bromide or anhydride, preferably the corresponding carboxylic acid chloride, in the presence of a Lewis acid such as, for example, aluminium trichloride, tin tetrachloride, boron trifluoride and the like, preferably aluminium trichloride, according to methods which are known per se for the Friedel-Crafts acylation. The reaction is carried out in an inert organic solvent, for example carbon disulphide or a chlorinated hydrocarbon, preferably methylene chloride or chloroform. The reaction is conveniently carried out at a temperature between about 0°C and the reflux temperature of the reaction mixture. The pressure is not critical and the reaction is advantageously carried out at atmospheric pressure and room temperature.

The esterification of a compound of formula III in which R^4 signifies hydroxy with an alkanecarboxylic acid of the formula R^3COOH or a reactive derivative thereof (e.g. an anhydride or acid halide) can be carried out in a manner known per se. The esterification of an alcohol with a carboxylic

acid is conveniently carried out in the presence of a catalytic amount of a strong acid (e.g. sulphuric acid or a hydrohalic acid), in the presence or absence of an inert organic solvent. It can, however, also be carried out in the presence of N,N'-dicyclohexylcarbodiimide and 4-(dimethylamino)-pyridine. The preferred method is, however, the esterification of the alcohol with an acid chloride. This esterification is conveniently carried out in an inert organic solvent, for example an ether such as diethyl ether or tetrahydrofuran, dimethylformamide, benzene, toluene, cyclohexane, carbon tetrachloride and the like. In order to bind the hydrogen chloride which is liberated during the esterification, an acid-binding agent (e.g. tertiary amines, pyridines and the like) is conveniently used. The acid-binding agent is preferably used in large excess, so that it can simultaneously serve as the solvent. The temperature and pressure are not critical and this esterification is generally carried out at atmospheric pressure and a temperature between room temperature and the boiling point of the mixture. The compounds of formula III in which R⁴ signifies hydroxy can be obtained, instead of from corresponding compounds of formula II, also from compounds of formula III in which R⁴ signifies alkoxy according to ether cleavage methods which are known per se.

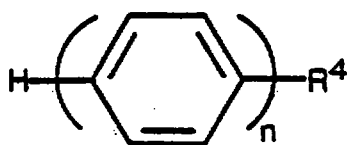
The compounds of formula III in which R^4 signifies halogen can be converted in a manner known per se with magnesium into the corresponding Grignard compounds. The solvent used is conveniently an ether, preferably diethyl ether or tetrahydrofuran. The pressure and temperature at which this reaction is carried out are not critical. This reaction is generally carried out at atmospheric pressure and a temperature between about 0°C and the reflux temperature of the reaction mixture, preferably at approximately room temperature. The term "halogen" used herein signifies chlorine, bromine or iodine, especially bromine.

The Grignard compounds obtained can be converted with carbon dioxide into corresponding carboxylates and these can be subsequently hydrolyzed to carboxylic acids. The reaction with carbon dioxide is conveniently carried out by conducting carbon dioxide gas into the solution of the Grignard compound obtained as described earlier at about 0°C or by pouring said solution on to dry-ice. The hydrolysis of the carboxylate can be carried out using a strong acid, preferably a dilute inorganic acid such as as hydrohalic acid, sulphuric acid and the like.

The esterification of the resulting acids or the corresponding acid halides or anhydrides with an alkanol of the formula $R^3\text{OH}$ can be carried out in an analogous manner to the esterification described earlier. The acid

halides and anhydrides can be prepared in a manner known per se; for example, acid chlorides are obtained by reacting the acid with phosphorus trichloride, phosphorus pentachloride, thionyl chloride and the like and anhydrides are obtained by reacting the acid with acetic anhydride, acetyl chloride, ethyl chloroformate and the like. Methyl esters can also be obtained by reacting the corresponding carboxylic acid with diazomethane in an inert organic solvent, preferably diethyl ether.

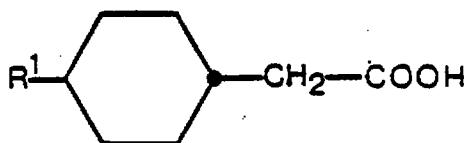
The compounds of formula II used as the starting materials can be prepared by acylating a compound of the general formula



IV

wherein R^4 and n have the significance given earlier,

with the acid chloride derived from a compound of the general formula



V

wherein R^1 has the significance
given earlier.

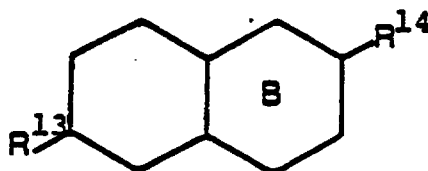
This reaction can be carried out according to methods
known per se for the Friedel-Crafts acylation (and es-
5 pecially in an analogous manner to the Friedel-Crafts acy-
lation described earlier). The acid chlorides can be
prepared, for example, by heating the corresponding acids
of formula V with thionyl chloride.

The compounds of formulae IV and V are known or are
10 analogues of known compounds.

The compounds of formula I can be used in the form
of their mixtures with other liquid crystalline or non-
liquid crystalline substances such as, for example, with
substances from the classes of Schiff's bases, azobenzenes,
15 azoxybenzenes, phenyl benzoates, cyclohexanecarboxylic
acid phenyl esters, biphenyls, terphenyls, phenylcyclo-
hexanes, cinnamic acid derivatives, phenylpyrimidines,
diphenylpyrimidines, phenyldioxanes, cyclohexylphenyl-
pyrimidines, cyclohexylethanes and the like. Such
20 compounds are familiar and known to the person skilled
in the art; for example, from German Offenlegungsschriften
2 306 738, 2 306 739, 2 429 093, 2 356 085, 2 636 684,
2 459 374, 2 547 737, 2 641 724, 2 708 276, 2 811 001,
2 922 236, from East German Patent Specifications 139 852,
25 139 867 and from the European Patent Application published

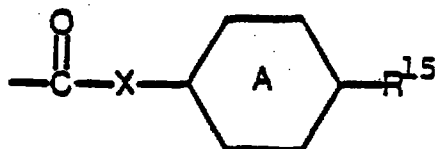
under Number 0014885. Many of such substances are, moreover, commercially available.

The mixtures in accordance with the invention can contain, in addition, hydrogenated naphthalenes of the
5 general formula



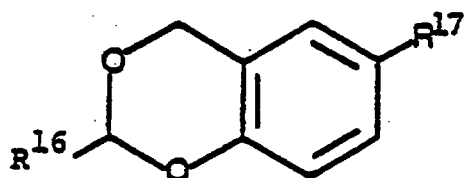
XXI

wherein ring B is saturated or aromatic and a saturated ring B which may be present is trans-
10 -linked with the second ring;
 R^{13} denotes a straight-chain alkyl or alkoxy group containing 1 to 11 carbon atoms; R^{14} signifies cyano, a straight-chain
15 alkyl group containing 1 to 11 carbon atoms, an ester group of the general formula



XXII

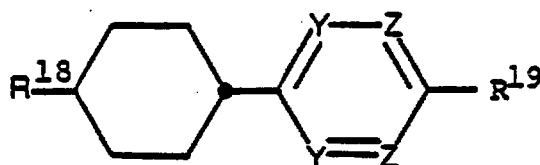
or, when ring B is saturated,
additionally a straight-chain
alkoxy group containing 1 to 11
carbon atoms; in the ester
group of formula XXII ring A is
either aromatic and X represents
oxygen or sulphur and R¹⁵ re-
presents cyano or a straight-
chain alkyl or alkoxy group
containing 1 to 10 carbon atoms,
or ring A signifies a trans-1,4-
disubstituted cyclohexane ring
and X signifies oxygen and R¹⁵
signifies cyano or a straight-
chain alkyl group containing
1 to 10 carbon atoms; and the
total number of carbon atoms
in the alkyl and/or alkoxy groups
present amounts to at most 12,
and/or benzodioxanes of the general formula



XXIII

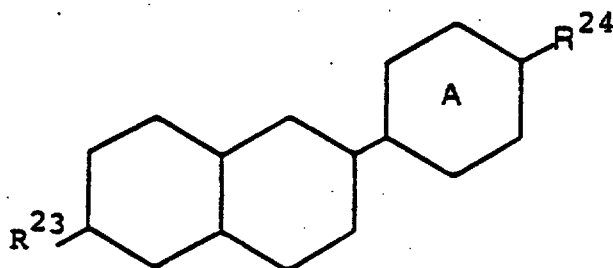
wherein R^{16} denotes a straight-chain alkyl group containing 1 to 11 carbon atoms; R^{17} represents cyano, a straight-chain alkyl group containing 1 to 11 carbon atoms or an ester group of formula XXII hereinbefore in which X, A and R^{15} have the significance given earlier; and the total number of carbon atoms in the alkyl and alkoxy groups present amounts to at most 12,

and/or trans-(4-alkylcyclohexyl)pyrimidines of the general formula



XXIV

wherein the symbols Y stand for
 nitrogen and the symbols Z stand
 for =CH- or the symbols Z stand
 for nitrogen and the symbols Y
 stand for =CH-, R^{18} represents
 alkyl and R^{19} represents cyano,
 alkyl, p-alkylphenyl or trans-4-
 -alkylcyclohexyl, the term alkyl
 signifies straight-chain alkyl
 containing 1 to 12 carbon atoms
 or in one of the residues R^{18} or
 R^{19} also signifies a branched alkyl
 group $C_2H_5-CH(CH_3)-(CH_2)_m-$, m is
 an integer of 1 to 3 and the sum
 of the carbon atoms in the alkyl
 groups present amounts to at most
 14,
 and/or equatorially substituted trans-decalins of the
 general formula



XXXVIII

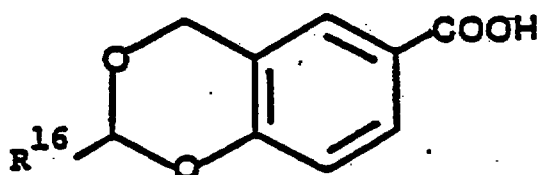
wherein ring A is aromatic or represents
a trans-1,4-disubstituted cyclohexane
ring; R^{24} denotes methyl or one of the
groups $-CH_2R'$, $-OR'$, $-CO-R'$, $-CN$, $-COOH$,
5 $-CO-OR'$, $-CO-SR'$ or $-O-CO-R'$; R^{23}
signifies hydrogen, methyl or one of the
groups $-CH_2R$, $-OR$, $-CH_2OR$ or, when R^{24}
denotes methyl or one of the groups
10 $-CH_2R'$, $-OR'$ or $-CO-R'$, R^{23} also signi-
fies $-CN$, $-COOH$, $-CO-OR$, $-CO-SR$ or
 $-O-CO-R$; R and R' stand for straight-
chain or branched-chain alkyl groups;
and the number of carbon atoms in R^{23}
or R^{24} amounts to up to 12 and in R^{23}
15 and R^{24} together amounts to at most 14.

The compounds of formula XXIII are novel. Those
of formulae XXI, XXIV and XXXVIII are described in
GB. 2082179A, 2085877A and 2090593A respectively, and
attention is directed to those Specifications. Those
20 compounds of formula XXI in which R^{14} signifies cyano,
straight-chain alkyl or straight-chain alkoxy and the
compounds of formula XXIII in which R^{17} signifies
cyano or straight-chain alkyl are above all suitable
as doping agents in liquid crystal mixtures and in
25 general are not liquid crystalline

themselves. In the case of mixtures which contain such doping agents, care must accordingly be taken that they contain in addition at least one compound with liquid crystalline properties in sufficient amount so that the
5 total mixture also has liquid crystalline properties. The remaining compounds of formulae XXI and XXIII as well as the compounds of formulae XXIV and XXXVIII are, on the other hand, to a large extent themselves liquid crystalline.

The compounds of formula XXIII can be manufactured by

- (a) for the manufacture of the compounds of formula XXIII in which R^{17} signifies an ester group of formula XXII, esterifying a compound of the general formula



XXX

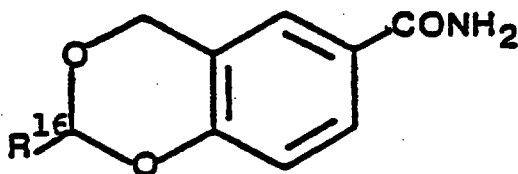
wherein R^{16} has the significance given earlier
with a compound of the general formula



XXV

wherein X, A and R^{15} have the significance given earlier,

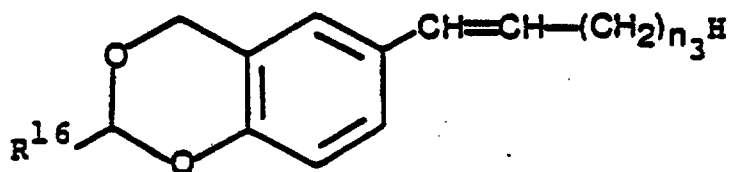
- (b) for the manufacture of the compounds of formula XXIII in which R^{17} signifies cyano, dehydrating a compound of the general formula



XXXI

wherein R^{16} has the significance
given earlier,

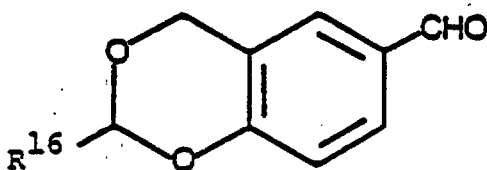
- (c) for the manufacture of the compounds of formula
XXIII in which R^{17} signifies a straight-chain alkyl group
5 containing 2 to 11 carbon atoms, catalytically hydrogenat-
ing a compound of the general formula



XXXII

wherein n_3 denotes an integer
of 0 to 9 and R^{16} has the
10 significance given earlier,

- (d) for the manufacture of the compounds of formula
XXIII in which R^{17} signifies methyl, reacting a compound
of the general formula



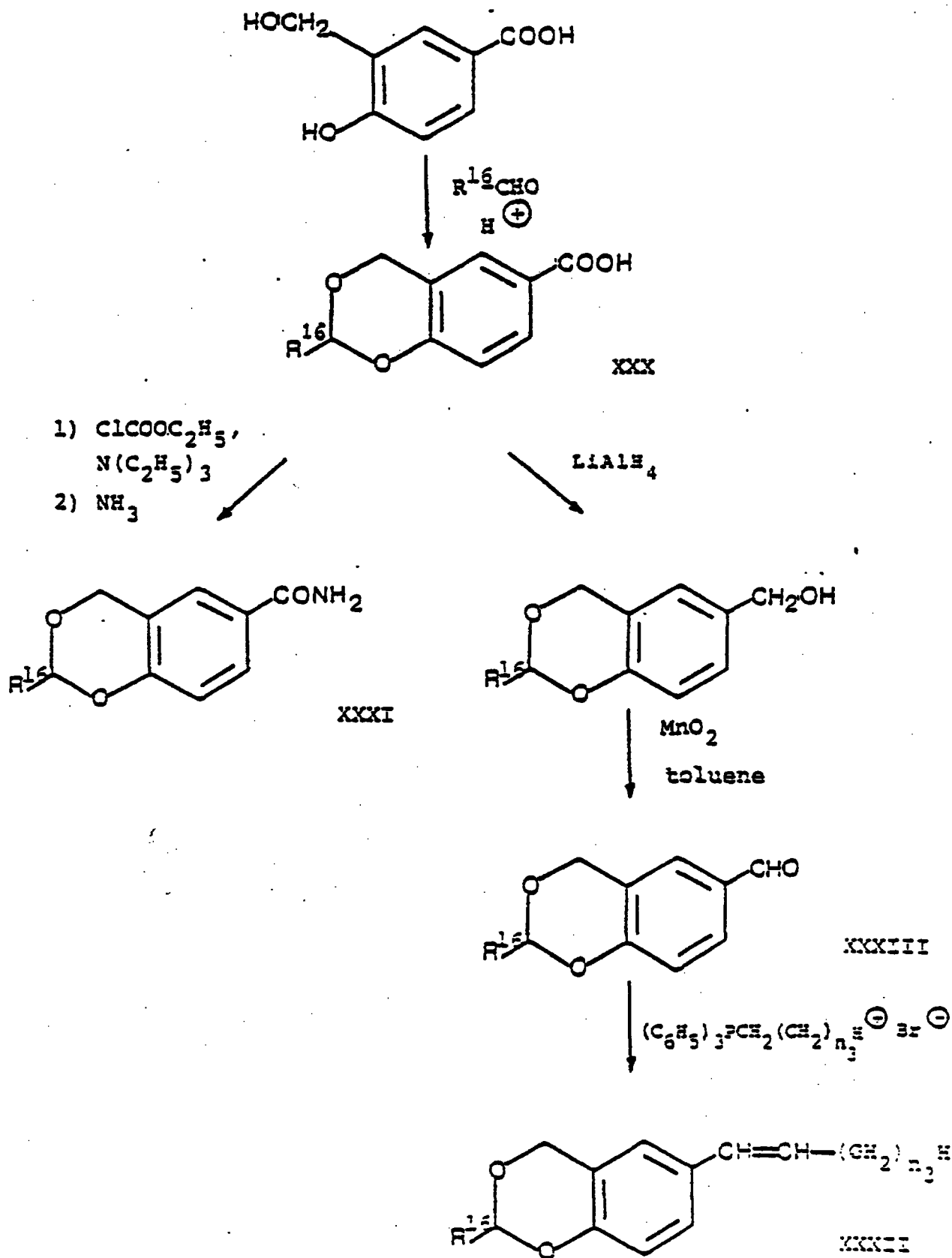
XXXIII

38

wherein R^{16} has the significance
given earlier,
with hydrazine in the presence of a base.

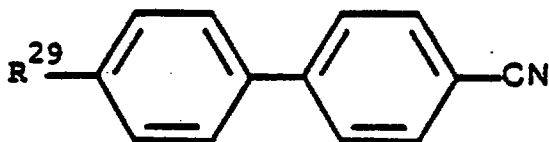
5 The compounds of formula XXX-XXXIII used as the
starting materials can be prepared according to the
following Scheme D in which R^{16} and n_3 have the signifi-
cance given earlier.

Scheme D



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:

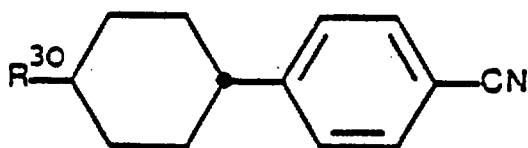
4-Cyanobiphenyls of the general formula



XXXXIV

wherein R^{29} signifies a straight-chain alkyl or alkoxy group containing 2 to 7 carbon atoms,

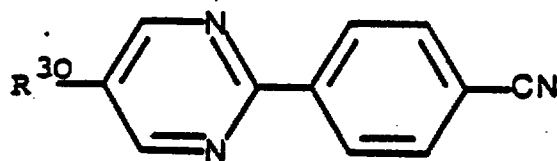
trans-p-(4-alkylcyclohexyl)benzonitriles of the general formula



VL

wherein R^{30} signifies a straight-
-chain alkyl group containing 3 to
7 carbon atoms,

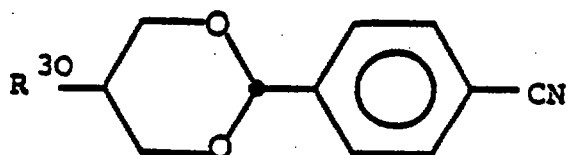
p-(5-alkyl-2-pyrimidinyl)benzonitriles of the general
5 formula



VLI

wherein R^{30} has the significance
given earlier,

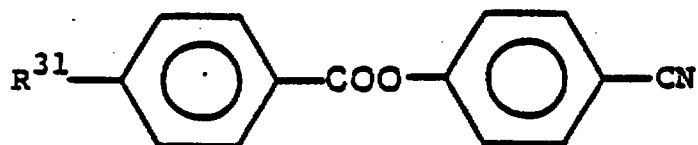
p-(trans-5-alkyl-m-dioxan-2-yl)benzonitriles of the
10 general formula



VLII

wherein R^{30} has the significance
given earlier,

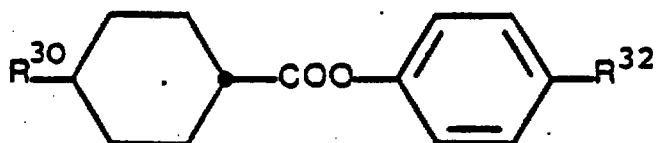
p-alkylbenzoic acid p'-cyanophenyl esters of the general
15 formula



VLI

wherein R^{31} signifies a straight-chain alkyl group containing 2 to 7 carbon atoms,

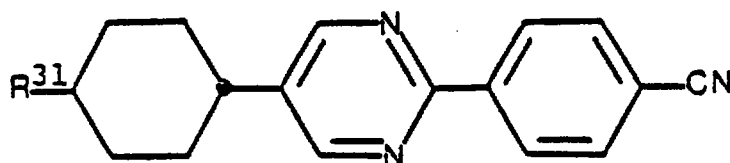
trans-4-alkylcyclohexanecarboxylic acid phenyl esters of the general formula



II

wherein R^{30} has the significance given earlier and R^{32} signifies cyano or a straight-chain alkoxy group containing 1 to 3 carbon atoms,

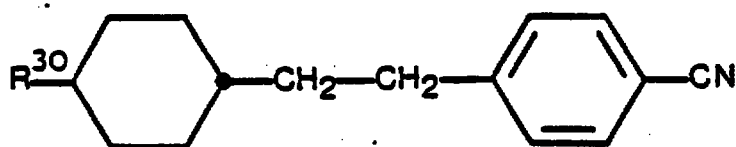
trans-p-[5-(4-alkylcyclohexyl)-2-pyrimidinyl]benzonitriles of the general formula



L

wherein R^{31} has the significance
given earlier,
and 2-(trans-4-alkylcyclohexyl)-1-(p-cyanophenyl)-ethanes
of the general formula

5



LI

wherein R^{30} has the significance
given earlier.

The weight ratio of the components of the mixture preferably corresponds to the eutectic composition. The
10 amount of the compounds of formula I in the liquid crystal mixtures in accordance with the invention is, however, generally about 1 to about 90 mol percent, preferably about 10 to about 85 mol percent. The mixtures must, however, contain at least one liquid crystal compound in sufficient
15 amount so that the total mixture also has liquid crystal-line properties.

Further, the mixtures in accordance with the invention can contain optically active compounds, for example optically active biphenyls, and/or dichroic colouring substances,
20 for example azo, azoxy and anthraquinone colouring sub-

stances. The amount of such compounds is determined by the desired pitch, colour, extinction, solubility and the like.

5 The manufacture of the liquid crystalline mixtures in accordance with the invention can be carried out in a manner known per se; for example, by heating a mixture of the components to a temperature barely above the clearing point and subsequently cooling down.

10 The manufacture of an electro-optical device containing one or more compounds of formula I can also be carried out in a manner known per se; for example, by evacuating a suitable cell and introducing the corresponding compound or mixture into the evacuated cell.

15 The invention is also concerned with all novel compounds, mixtures, processes, uses and devices as herein described.

Examples of preferred mixtures are the following
Mixture Examples 1 - 12 in which η denotes the viscosity (bulk viscosity) and $\Delta\epsilon$ denotes the dielectric anisotropy.
20 The compounds of formulae XXI and XXXVIII were in each case used as the racemate of the two equatorial 2,6-disubstituted isomers.

Mixture Example 1

- 5 mol % of p-(5-pentyl-2-pyrimidinyl)benzonitrile,
9 mol % of p-(5-heptyl-2-pyrimidinyl)benzonitrile,
16 mol % of trans-4-pentylcyclohexanecarboxylic acid p-
5 -methoxyphenyl ester,
25 mol % of trans-4-pentylcyclohexanecarboxylic acid p-
-propyloxyphenyl ester,
6 mol % of p-[5-(trans-4-pentylcyclohexyl)-2-pyrimidinyl]-
benzonitrile,
10 8 mol % of p-[(4 α H,8 α H)-decahydro-6 β -propyl-2 α -naphthyl]-
benzonitrile,
6 mol % of p-[(4 α H,8 α H)-decahydro-6 β -pentyl-2 α -naphthyl]-
benzonitrile,
25 mol % of 2-[trans-4-pentylcyclohexyl)-1-(p-ethoxyphenyl)-
15 ethane;
m.p. <0°C, cl.p. 69°C, η (22°C) = 28.2 cp, nematic.

Mixture Example 2

- 6 mol % of p-(5-pentyl-2-pyrimidinyl)benzonitrile,
12 mol % of p-(5-heptyl-2-pyrimidinyl)benzonitrile,
20 20 mol % of trans-4-pentylcyclohexanecarboxylic acid p-
-methoxyphenyl ester,
26 mol % of trans-4-pentylcyclohexanecarboxylic acid p-
-propyloxyphenyl ester,
8 mol % of p-[(4 α H,8 α H)-decahydro-6 β -ethyl-2 α -naphthyl]-
25 benzonitrile,

- 8 mol % of p-[(4acH,8aSH)-decahydro-6 β -propyl-2 α -naphthyl]-benzonitrile,
8 mol % of p-[(4acH,8aSH)-decahydro-6 β -pentyl-2 α -naphthyl]-benzonitrile,
5 12 mol % of 2-(trans-4-heptylcyclohexyl)-1-(p-ethoxyphenyl)-ethane;
m.p. <0°C, cl.p. 63.5°C, n (22°C) = 32.5 cp, nematic.

Mixture Example 3

- 7 mol % of p-(5-pentyl-2-pyrimidinyl)benzonitrile,
10 13 mol % of p-(5-heptyl-2-pyrimidinyl)benzonitrile,
21 mol % of trans-4-pentylcyclohexanecarboxylic acid p-methoxyphenyl ester,
27 mol % of trans-4-pentylcyclohexanecarboxylic acid p-propyloxyphenyl ester,
15 11 mol % of p-[5-(trans-4-ethylcyclohexyl)-2-pyrimidinyl]-benzonitrile,
8 mol % of p-[5-(trans-4-pentylcyclohexyl)-2-pyrimidinyl]-benzonitrile,
13 mol % of 2-(trans-4-heptylcyclohexyl)-1-(p-ethoxyphenyl)-
20 ethane;
m.p. <0°C, cl. p. 80°C, nematic.

Mixture Example 4

- 5 mol % of p-(5-pentyl-2-pyrimidinyl)benzonitrile,
8 mol % of p-(5-heptyl-2-pyrimidinyl)benzonitrile,

- 14 mol % of trans-4-pentylcyclohexanecarboxylic acid p-methoxyphenyl ester,
- 21 mol % of trans-4-pentylcyclohexanecarboxylic acid p-propyloxyphenyl ester,
- 5 9 mol % of p-[5-(trans-4-ethylcyclohexyl)-2-pyrimidinyl]-benzonitrile,
- 6 mol % of p-[5-(trans-4-pentylcyclohexyl)-2-pyrimidinyl]-benzonitrile,
- 37 mol % of 2-(trans-4-pentylcyclohexyl)-1-(p-ethoxyphenyl)-ethane;
- 10 m.p. $< 0^{\circ}\text{C}$, cl.p. 70°C , n (22°C) = 26.3 cp, nematic.

Mixture Example 5

- 17 mol % of trans-4-butylcyclohexanecarboxylic acid p-ethoxyphenyl ester,
- 15 19 mol % of trans-4-butylcyclohexanecarboxylic acid p-pentyloxyphenyl ester,
- 16 mol % of trans-4-pentylcyclohexanecarboxylic acid p-methoxyphenyl ester,
- 22 mol % of trans-4-pentylcyclohexanecarboxylic acid p-propyloxyphenyl ester,
- 20 26 mol % of 2-(trans-4-pentylcyclohexyl)-1-(p-ethoxyphenyl)-ethane;
- m.p. $< 0^{\circ}\text{C}$, cl.p. 62.2°C , n (22°C) = 21.0 cp, $\Delta\varepsilon = -1.09$, nematic.

Mixture Example 6

- 6 mol % of p-(5-pentyl-2-pyrimidinyl)benzonitrile,
 12 mol % of p-(5-heptyl-2-pyrimidinyl)benzonitrile,
 19 mol % of trans-4-pentylcyclohexanecarboxylic acid p-
 5 -methoxyphenyl ester,
 12 mol % of p-[5-(trans-4-ethylcyclohexyl)-2-pyrimidinyl]-
 benzonitrile,
 7 mol % of p-[5-(trans-4-pentylcyclohexyl)-2-pyrimidinyl]-
 benzonitrile,
 10 12 mol % of p-[2-(trans-4-heptylcyclohexyl)ethyl]benzonitrile,
 32 mol % of 2-(trans-4-propylcyclohexyl)-1-(p-butyloxyphenyl)-
 ethane;
 m.p. <0°C, cl.p. 69°C, η (22°C) = 28.5 cp, nematic.

Mixture Example 7

- 15 5 mol % of p-(5-pentyl-2-pyrimidinyl)benzonitrile,
 9 mol % of p-(5-heptyl-2-pyrimidinyl)benzonitrile,
 16 mol % of trans-4-butylcyclohexanecarboxylic acid p-
 -ethoxyphenyl ester,
 15 mol % of trans-4-pentylcyclohexanecarboxylic acid p-methoxy-
 20 phenyl ester,
 11 mol % of p-[5-(trans-4-ethylcyclohexyl)-2-pyrimidinyl]-
 benzonitrile,
 7 mol % of p-[5-(trans-4-pentylcyclohexyl)-2-pyrimidinyl]-
 benzonitrile,
 25 37 mol % of 2-(trans-4-propylcyclohexyl)-1-(p-ethoxyphenyl)-

ethane;

m.p. $<0^{\circ}\text{C}$, cl.p. 71°C , η (22°C) = 28.2 cp, nematic.

Mixture Example 8

- 5 mol % of p-butylbenzoic acid p'-cyanophenyl ester,
- 5 mol % of p-(5-pentyl-2-pyrimidinyl)benzonitrile,
- 9 mol % of p-(5-heptyl-2-pyrimidinyl)benzonitrile,
- 10 mol % of p-[5-(trans-4-ethylcyclohexyl)-2-pyrimidinyl]-benzonitrile,
- 34 mol % of p-[2-trans-4-pentylcyclohexyl)ethyl]benzonitrile,
- 10 37 mol % of 2-(trans-4-propylcyclohexyl)-1-(p-ethoxyphenyl)-ethane;

m.p. $<-10^{\circ}\text{C}$, cl.p. 54°C , η (22°C) = 27.0 cp, nematic.

Mixture Example 9

- 4 mol % of p-(5-pentyl-2-pyrimidinyl)benzonitrile,
- 15 7 mol % of p-(5-heptyl-2-pyrimidinyl)benzonitrile,
- 12 mol % of trans-4-butylcyclohexanecarboxylic acid p-ethoxyphenyl ester,
- 11 mol % of trans-4-pentylcyclohexanecarboxylic acid p-methoxyphenyl ester,
- 20 9 mol % of p-[5-(trans-4-ethylcyclohexyl)-2-pyrimidinyl]-benzonitrile,
- 5 mol % of 6-pentyl-trans-decalin-2-carboxylic acid p-ethylphenyl ester,
- 7 mol % of 6-butyl-trans-decalin-2-carboxylic acid trans-

-4-pentyl-1-cyclohexyl ester,

27 mol % of p-[2-(trans-4-pentylcyclohexyl)ethyl]benzo-
nitrile,

18 mol % of 2-(trans-4-propylcyclohexyl)-1-(p-butyloxy-
5 phenyl)ethane;

m.p. <-10°C, cl.p. 63°C, η (22°C) = 27.0 cp, nematic.

Mixture Example 10

3 mol % of p-(5-pentyl-2-pyrimidinyl)benzonitrile,

8 mol % of p-(5-heptyl-2-pyrimidinyl)benzonitrile,

10 10 mol % of trans-4-butylcyclohexanecarboxylic acid p-
-ethoxyphenyl ester,

9 mol % of trans-4-pentylcyclohexanecarboxylic acid p-
-methoxyphenyl ester,

15 15 mol % of trans-4-pentylcyclohexanecarboxylic acid p-
-propyloxyphenyl ester

7 mol % of p-[5-(trans-4-ethylcyclohexyl)-2-pyrimidinyl]-
benzonitrile,

9 mol % of p-[5-(trans-4-heptylcyclohexyl)-2-pyrimidinyl]-
benzonitrile,

20 24 mol % of 2-(trans-4-propylcyclohexyl)-1-(p-ethoxyphenyl)-
ethane;

15 mol % of 2-(trans-4-propylcyclohexyl)-1-(p-butyloxyphenyl)-
ethane;

m.p. <-10°C, cl.p. 69°C, η (22°C) = 25.8 cp, nematic.

Mixture Example 11

4 mol % of p-(5-pentyl-2-pyrimidinyl)benzonitrile,
6 mol % of p-(5-heptyl-2-pyrimidinyl)benzonitrile,
13 mol % of trans-4-butylcyclohexanecarboxylic acid p-
5 -ethoxyphenyl ester,
12 mol % of trans-4-pentylcyclohexanecarboxylic acid p-
-methoxyphenyl ester,
8 mol % of p-[5-(trans-4-ethylcyclohexyl)-2-pyrimidinyl]-
benzonitrile,
10 10 mol % of p-[5-(trans-4-heptylcyclohexyl)-2-pyrimidinyl]-
benzonitrile,
29 mol % of p-[2-(trans-4-pentylcyclohexyl)ethyl]-benzo-
nitrile,
18 mol % of 2-(trans-4-propylcyclohexyl)-1-(p-butyloxy-
15 phenyl)-ethane;
m.p. <-10°C, cl.p. 74°C, η (22°C) = 28.3 cp, nematic.

Mixture Example 12

8 mol % of p-(5-pentyl-2-pyrimidinyl)benzonitrile,
14 mol % of p-(5-heptyl-2-pyrimidinyl)benzonitrile,
20 23 mol % of trans-4-pentylcyclohexanecarboxylic acid p-
-methoxyphenyl ester,
29 mol % of trans-4-pentylcyclohexanecarboxylic acid p-pro-
pyloxyphenyl ester,
11 mol % of trans-4-(p-pentylphenyl)cyclohexanecarboxylic
25 acid trans-4-propylcyclohexyl ester,

15 mol % of 2-(trans-4-heptylcyclohexyl)-1-(p-ethoxyphenyl)-
ethane;

m.p. $< 0^{\circ}\text{C}$, cl.p. 60.3°C , η (22°C) = 30.0 cp, nematic.

The manufacture of the compounds of formula I in accordance with the invention is illustrated on the basis of the following Examples. The abbreviations used for phase transitions have the following significances: C

- 5 stands for crystalline, S_A stands for smectic A, S_B stands for smectic B, N stands for nematic and I stands for isotropic phase (accordingly, for example, S_B -N denotes a phase transition smectic B-nematic).

Example 1

- 10 A mixture of 9.7 g of 4-ethoxy- α -(trans-4-pentylcyclohexyl)acetophenone, 125 ml of diethyleneglycol, 50 ml of ethanol, 6.2 g of hydrazine hydrate and 8.2 g of potassium hydroxide is heated to boiling for 4 hours at a bath temperature of 110°C. Thereafter, the bath temperature is
- 15 increased to 220°C and the ethanol and the excess hydrazine hydrate are allowed to distil off. Subsequently, the mixture is heated to an internal temperature of 180°C for a further 4.5 hours, left to stand overnight, the mixture is poured into ice-water and the product is taken up in
- 20 three 150 ml portions of ether. The combined organic phase is washed neutral with water, dried over sodium sulphate, evaporated and distilled in a bulb-tube at 180°C/about 1 Torr. The resulting 7.4 g of 2-(trans-4-pentylcyclohexyl)-1-(p-ethoxyphenyl)ethane (purity about 98.5%) are re-
- 25 crystallized once from isopropanol and once from diisopropyl

ether at about -20°C ; m.p. (C-N) 18°C or 27°C (2 modifications), transition S_B -N 8°C (monotropic), cl.p. (N-I) 47°C .

The 4-ethoxy- α -(trans-4-pentylcyclohexyl)acetophenone
5 used as the starting material can be prepared as follows:

A mixture of 8.7 g of trans-4-pentylcyclohexylacetic
acid chloride (prepared by boiling 8.0 g of trans-4-pentyl-
cyclohexylacetic acid with 4.1 ml of thionyl chloride in 75
ml of benzene for 2 hours and subsequently evaporating the
10 product) and 4.6 g of phenetole in 120 ml of dichloromethane
is treated portionwise in an inert gas atmosphere with 5.5 g
of aluminium chloride. The mixture is stirred at room
temperature for 5 hours and then poured into ice-water which
contains 50 ml of concentrated hydrochloric acid. The
15 organic phase is separated and the aqueous phase is back-
-extracted with 300 ml of dichloromethane. The combined
organic phase is washed in sequence with water, 3N sodium
hydroxide, water and saturated sodium chloride solution,
dried over sodium sulphate, filtered and evaporated. There
20 are obtained 9.7 g of crude, oily 4-ethoxy- α -(trans-4-pentyl-
cyclohexyl)acetophenone.

The following compounds can be manufactured in an
analogous manner:

2-(Trans-4-ethylcyclohexyl)-1-(p-ethoxyphenyl)ethane;
m.p. (C-I) 20.5°C, cl.p. (S_B -I) 3°C (monotropic);

2-(trans-4-ethylcyclohexyl)-1-(p-butyloxyphenyl)-
ethane; m.p. (C-N) 4°C, transition S_B -N 0°C (monotropic),
5 cl.p. (N-I) 6.5°C;

2-(trans-4-ethylcyclohexyl)-1-(p-hexyloxyphenyl)-
ethane; m.p. (C-N) 10°C, transition S_B -N 1°C (monotropic),
cl.p. (N-I) 13°C;

2-(trans-4-propylcyclohexyl)-1-(p-ethoxyphenyl)ethane;
10 m.p. (C-N) 21°C, cl.p. (N-I) 34°C;

2-(trans-4-propylcyclohexyl)-1-(p-propyloxyphenyl)-
ethane; m.p. (C-I) 20.5°C, transition S_B -N 13.5°C (mono-
tropic), cl.p. (N-I) 19.5°C (monotropic);

2-(trans-4-propylcyclohexyl)-1-(p-butyloxyphenyl)-
15 ethane; m.p. (C-N) 20.5°C, transition S_B -N 20°C (monotropic),
cl.p. (N-I) 33°C;

2-(trans-4-butylcyclohexyl)-1-(p-methoxyphenyl)ethane;
m.p. (C-I) 28°C, cl.p. (N-I) 16.5°C (monotropic);

2-(trans-4-butylcyclohexyl)-1-(p-ethoxyphenyl)ethane;
20 m.p. (C- S_B) 10°C, transition S_B -N 11°C, cl.p. (N-I) 32°C;

2-(trans-4-butylcyclohexyl)-1-(p-butyloxyphenyl)-
ethane; m.p. (C- S_B) 11°C, cl.p. (S_B -I) 37°C;

2-(trans-4-pentylcyclohexyl)-1-(p-methoxyphenyl)-
ethane; m.p. (C-N) 31°C, cl.p. (N-I) 33°C;

25 2-(trans-4-pentylcyclohexyl)-1-(p-propyloxyphenyl)-
ethane; m.p. (C- S_B) 24.5°C, transition S_B -N 32.5°C, cl.p.
(N-I) 33.5°C;

2-(trans-4-pentylcyclohexyl)-1-(p-butyloxyphenyl)-ethane; m.p. (C-S_B) 25.5°C, transition S_B-N 44°C, cl.p. (N-I) 45°C;

2-(trans-4-heptylcyclohexyl)-1-(p-methoxyphenyl)ethane;
5 m.p. (C-N) 28.5°C, transition S_B-N 17°C (monotropic), cl.p. (N-I) 40°C;

2-(trans-4-heptylcyclohexyl)-1-(p-ethoxyphenyl)ethane;
m.p. (C-N) 36°C, transition S_B-N 30°C (monotropic), cl.p. (N-I) 51°C;

10 2-(trans-4-propylcyclohexyl)-1-(p-pentylphenyl)ethane;
m.p. (C-S_B) 3°C, cl.p. (S_B-I) 6°C;

2-(trans-4-pentylcyclohexyl)-1-(p-propylphenyl)ethane;
m.p. (C-S_B) 4.5°C, cl.p. (S_B-I) 18°C;

2-(trans-4-pentylcyclohexyl)-1-(p-pentylphenyl)ethane;
15 m.p. (C-S_B) 9.5°C, cl.p. (S_B-I) 30°C;

2-(trans-4-pentylcyclohexyl)-1-(p-hexylphenyl)ethane;
m.p. (C-S_B) 11°C, cl.p. (S_B-I) 34°C;

2-(trans-4-heptylcyclohexyl)-1-(p-butylphenyl)ethane;
m.p. (C-S_B) 3.5°C, cl.p. (S_B-I) 30.5°C; crystallization
20 from the S_B-phase could not be achieved even upon cooling to -24°C.

Example 2

A mixture of 4.3 g of 4-(4'-pentylphenyl)- α -(trans-4-propylcyclohexyl)acetophenone, 75 ml of diethyleneglycol,
25 25 ml of ethanol, 2.2 g of hydrazine hydrate and 7.0 g of potassium hydroxide is heated to boiling for 4 hours at

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a bath temperature of 110°C. Thereafter, the bath temperature is increased to 220°C and the ethanol and the excess hydrazine hydrate are allowed to distil off. Subsequently, the mixture is heated to an internal temperature of 180°C for a further 5 hours, left to cool, diluted with water and extracted with diethyl ether. The organic phase is washed neutral with water, dried over sodium sulphate and evaporated. The yellow foam obtained (3.9 g) is "recrystallized" once from isopropanol and once from ethanol. There are obtained 2.7 g of 2-(trans-4-propylcyclohexyl)-1-(4'-pentyl-4-biphenyl)ethane which is presumably smectic at room temperature; phase transitions at 43.5°C and 130°C, transition S_A-N 132.5°C, cl.p. (N-I) 141.5°C.

The 4-(4'-pentylphenyl)- α -(trans-4-propylcyclohexyl)-acetophenone used as the starting material can be prepared as follows:

A mixture of 3.5 g of trans-4-propylcyclohexylacetic acid chloride and 4.0 g of 4-pentylbiphenyl in 125 ml of dichloromethane is treated portionwise within 15 minutes with 2.6 g of aluminium chloride. The mixture is stirred at room temperature for 5 hours and then poured into 250 ml of 2N hydrochloric acid. The organic phase is separated and the aqueous phase is back-extracted with two 150 ml portions of dichloromethane. The combined organic phase

is washed in sequence with water, 1N sodium hydroxide and water, dried over sodium sulphate and evaporated. The crude product is dissolved in boiling acetone and filtered while hot with a small amount of active carbon. 4-(4'-
 5 -Pentylphenyl)- α -(trans-4-propylcyclohexyl)acetophenone crystallizes out upon cooling. Yield 4.3 g; m.p. (C-S_A) 100°C, cl.p. (S_A-I) 143°C.

The following compounds can be manufactured in an analogous manner:

- 10 2-(Trans-4-ethylcyclohexyl)-1-(4'-propyl-4-biphenyl)-ethane; m.p. about 55°C, transition S-S_B 51.5°C, transition S_B-N 98.5°C, cl.p. (N-I) 121.5°C;
- 2-(trans-4-propylcyclohexyl)-1-(4'-butyloxy-4-biphenyl)-
 15 yl)ethane; m.p. (C-S) 84.5°C, transition S-S_A 139.5°C, transition S_A-N 152.5°C, cl.p. (N-I) 172.5°C.

Example 3

- a) In an analogous manner to Example 1 there is manufactured p-[2-(trans-4-butylcyclohexyl)ethyl]phenol (solvent in the Friedel-Crafts acylation of the phenol: nitro-
 20 benzene or nitromethane); m.p. 101.5-102.5°C.

b) A solution of 0.68 g of butyric acid chloride in 3 ml of benzene is added dropwise while stirring to a solution of 1.6 g of p-[2-(trans-4-butylcyclohexyl)ethyl]phenol in 5 ml of dry pyridine. The mixture is left to stand overnight, then poured into ice/water and extracted with diethyl ether. The organic phase is washed several times with 3N hydrochloric acid, washed neutral with water, dried over sodium sulphate and evaporated. The smectic crude product (2.05 g) is purified by chromatography on silica gel with hexane/diethyl ether (19:1). The fractions which are pure according to thin-layer chromatography (1.9 g) are recrystallized once from isopropanol and once from ethanol at -20°C. There is obtained 0.8 g of analytically pure p-[2-(trans-4-butylcyclohexyl)-1-ethyl]phenylbutyrate; m.p. -13°C or +4°C (2 modifications), cl.p. (S_B-I) 45°C.

p-[2-(Trans-4-butylcyclohexyl)ethyl]phenol can also be obtained in the following manner:

A solution of 4.7 g of 2-(trans-4-butylcyclohexyl)-1-(p-methoxyphenyl)ethane (manufactured according to Example 1) in 50 ml of dichloromethane is added dropwise to a solution of 6.9 g of aluminium chloride in 100 ml of dichloromethane and 10 ml of ethyl mercaptan, the mixture is stirred at room temperature for 4 hours, then poured into ice/water,

the organic phase is separated and the aqueous phase is extracted twice with 100 ml of dichloromethane each time. The combined organic phase is washed neutral with saturated sodium chloride solution, dried over sodium sulphate and evaporated. The resulting crude p-[2-(trans-4-butyl-cyclohexyl)ethyl]phenol (4.4 g) is recrystallized from hexane. Yield 3.8 g; m.p. 101.5-102.5°C.

The following compounds can be manufactured in an analogous manner:

- 10 p-[2-(Trans-4-butylcyclohexyl)-1-ethyl]phenylacetate;
m.p. (C-I) 32.5°C, cl.p. (N-I) 23°C (monotropic);
p-[2-(trans-4-pentylcyclohexyl)-1-ethyl]phenylacetate;
m.p. (C-I) 41.5°C, cl.p. (N-I) 40.5°C (monotropic);
p-[2-(trans-4-pentylcyclohexyl)-1-ethyl]phenylbutyrate;
15 m.p. (C-S_B) 31°C, cl.p. (S_B-I) 52°C.

Example 4

A mixture of 4.6 g of 2-(trans-4-propylcyclohexyl)-1-phenylethane (manufactured analogously to Example 1 by Friedel-Crafts acylation of benzene and reduction of the ketone obtained) and 1.94 g of propionic acid chloride in 100 ml of dichloromethane is treated portionwise under an inert gas atmosphere with 3.2 g of aluminium chloride. The

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mixture is stirred at room temperature for 5 hours and poured into ice/water with which are admixed 25 ml of concentrated hydrochloric acid. The organic phase is separated and the aqueous phase is back-extracted twice with 100 ml of dichloromethane each time. The combined organic phase is washed with 1N sodium hydroxide, washed neutral with water, dried over sodium sulphate and evaporated. The resulting p-[2-(trans-4-propylcyclohexyl)-1-ethyl]-propiophenone (5.5 g) is recrystallized twice from ethanol; m.p. (C-N) 40°C, cl.p. (N-I) 56°C.

The following compounds can be manufactured in an analogous manner:

p-[2-(Trans-4-propylcyclohexyl)-1-ethyl]valerophenone; m.p. (C-I) 47.5°C, transition S_B-N 30°C (monotropic), cl.p. (N-I) 46°C (monotropic);

p-[2-(trans-4-pentylcyclohexyl)-1-ethyl]valerophenone; m.p. (C-N) 48.5°C, transition S_B-S_A 33°C (monotropic), transition S_A-N 39°C (monotropic), cl.p. (N-I) 57°C.

Example 5

a) A mixture of 182.3 g of trans-4-pentylcyclohexane-carboxaldehyde, 2 l of methylene chloride and 589.6 g of

(p-methoxycarbonylphenyl)methyl-triphenylphosphonium bromide is cooled to 0-5°C and, thereafter, the cold solution is treated at 0-5°C within ca. 1 hour with a solution of 27.6 g sodium in 276 ml of methanol (1.2 moles of sodium methylate). The obtained brown-red solution is stirred at 0-5°C for a further 15 minutes and, then, the temperature is left to rise to room temperature. The solution is stirred at room temperature for 1 hour, then poured into a stirring vessel and washed with 1 litre of 5% sodium bicarbonate solution. The upper colourless phase is back-extracted with 250 ml of methylene chloride. The combined methylene chloride phases are dried over sodium sulphate, filtered and partly evaporated, while a total amount of 5 l of methanol is added continuously through a dropping funnel. When a reaction volume of 4 l and a distillation temperature of 63°C is reached, the reaction mixture is cooled to -20°C and treated at this temperature with 400 ml of water within 30 minutes while stirring. The p-[2-(trans-4-pentylcyclohexyl)ethenyl]benzoic acid methyl ester, which crystallizes, is suction filtered, washed with 1 litre of 90% methanol at -20°C and the solvent is pressed well from the crystalline mass.

b) The obtained crystalline mass is dissolved in 1.5 l of methylene chloride and washed with 750 ml of water. The aqueous phase is back-extracted with 250 ml methylene

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chloride and then the combined methylene chloride phases are dried over sodium sulphate, filtered and concentrated to a volume of 1.5 l. 5 ml of triethylamine and 5 g of palladium/carbon (5%) are added and the mixture is

5 hydrogenated after gassing the hydrogenation flask twice with hydrogen, while shaking at room temperature. After 2 hours the hydrogen uptake comes to a standstill and the catalyst is filtered off and washed with 250 ml of methylene chloride. The filtrate is treated with 30 g of

10 activated carbon, stirred and filtered. The filter residue is back-washed with 250 ml of methylene chloride and the filtrate is evaporated on a rotary evaporator. The colourless oily residue is treated with 1 litre of methanol and heated at reflux on a steam bath while stirring, whereby

15 the oil is dissolved almost completely. The mixture is cooled while stirring and the product left to crystallize at -25°C . The crystalline product is filtered off and washed with 250 ml of methanol at -25°C and the solvent is pressed well from the crystalline mass. After drying at

20 room temperature in a stream of nitrogen under reduced pressure, there are obtained 252 g of crystalline p-[2-(trans-4-pentylcyclohexyl)-1-ethyl]benzoic acid methyl ester, which can be further purified by chromatography on silica gel with toluene and recrystallization from pentane;

25 m.p. (C-N) 36.7°C , cl.p. (N-I) 48.7°C .

The following compounds can be manufactured in an analogous manner:

p-[2-(trans-4-ethylcyclohexyl)-1-ethyl]benzoic acid
methyl ester; m.p. (C-I) 34.2°C.

5 p-[2-(trans-4-propylcyclohexyl)-1-ethyl]benzoic acid
methyl ester; m.p. (C-I) 38.3°C, cl.p. (N-I) 37.7°C

p-[2-(trans-4-butylcyclohexyl)-1-ethyl]benzoic acid
methyl ester; m.p. (C-I) 39.6°C, cl.p. (N-I) 32°C

10 p-[2-(trans-4-heptylcyclohexyl)-1-ethyl]benzoic acid
methyl ester; m.p. (C-N) 33.5°C, cl.p. (N-I) 53°C

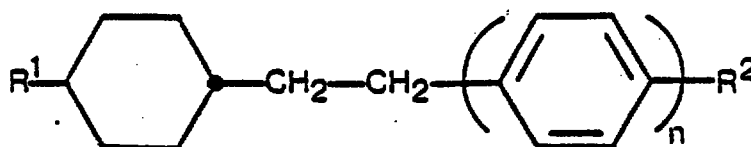


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CLAIMS:

1. Compounds of the general formula:



wherein R^2 represents one of the groups
- R^3 , - OR^3 , - $CO-R^3$, - $CO-OR^3$ or $O-CO-R^3$,
 R^1 and R^3 signify straight-chain alkyl
groups containing 1 to 12 carbon atoms
and n stands for one of the numbers 1
or 2.

2. Compounds according to claim 1, wherein R^2 represents
one of the groups - R^3 , - OR^3 or - $CO-OR^3$.
3. Compounds according to claim 2, wherein R^2 represents
one of the groups - R^3 or - OR^3 .
4. Compounds according to any one of claims 1 to 3,
wherein n stands for the number 1.
5. Compounds according to any one of claims 1 to 4,

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wherein R^3 signifies a straight-chain alkyl group containing 1 to 10 carbon atoms.

6. Compounds according to claim 5 wherein R^3 contains 1 to 7 carbon atoms.

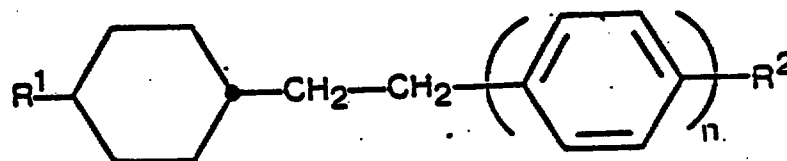
5 7. Compounds according to any one of claims 1 to 6, wherein R^1 signifies a straight-chain alkyl group containing 2 to 10 carbon atoms.

8. Compounds according to claim 7 wherein R^1 contains 3 to 7 carbon atoms.

10 9. Compounds of formula I given in claim 1 for use as liquid crystalline substances.

10. A liquid crystalline mixture with at least two components, wherein at least one component is a compound of formula I defined in claim 1.

15 11. A process for the manufacture of compounds of the general formula



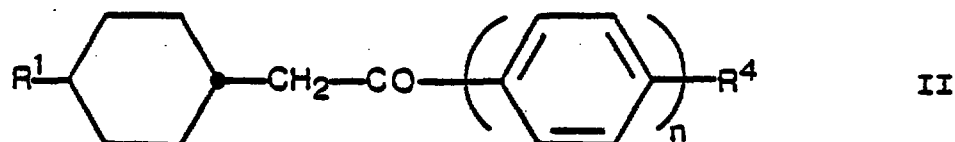
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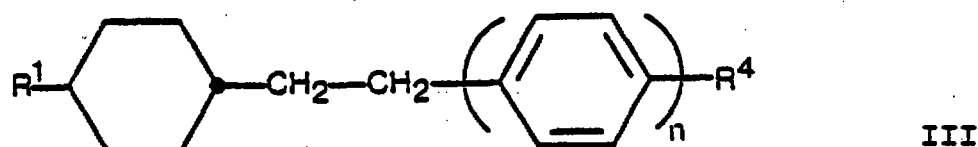
wherein R^2 represents one of the groups $-R^3$, $-OR^3$, $-CO-R^3$ or $-O-CO-R^3$, R^1 and R^3 signifies straight-chain alkyl groups containing 1 to 12 carbon atoms and n stands for one of the numbers 1 or 2,



which process comprises reducing a compound of the general formula



wherein R^4 represents hydrogen, hydroxy,
 5 halogen or one of the groups $-\text{R}^3$ or $-\text{OR}^3$
 and R^1 , R^3 and n have the significance
 given earlier in this claim,
 and acylating the resulting compound of the general formula



10 wherein R^1 , R^4 and n have the signi-
 ficance given earlier in this claim,
 when R^4 signifies hydrogen, or, when R^4 signifies hydroxy,
 esterifying the resulting compound of formula III with a
 carboxylic acid of the formula R^3COOH or a reactive deriva-
 15 tive thereof or, when R^4 signifies halogen, reacting the
 resulting compound of formula III with magnesium and

subsequently with carbon dioxide, hydrolyzing the carboxylate obtained and esterifying the resulting acid or a reactive derivative thereof with an alcohol of the formula R^3OH .

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

13. 2-(Trans-4-propylcyclohexyl)-1-(p-ethoxyphenyl) ethane.

14. 2-(Trans-4-propylcyclohexyl)-1-(p-butyloxyphenyl) ethane.
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15. 2-(Trans-4-pentylcyclohexyl)-1-(p-ethoxyphenyl) ethane.

