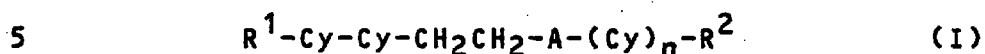


Description

The invention relates to new bicyclohexylethanes of the formula I

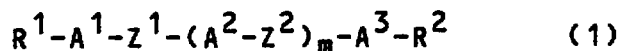


wherein R^1 is alkyl, R^2 is alkyl, in which one or two CH_2 groups can be replaced by O atoms, or is F, Cl, Br, CN, -COOalkyl or -O-CO-alkyl, and one of the radicals R^1 and
10 R^2 can also be H, A is Cy, or 1,4-phenylene which is unsubstituted or substituted by one or two F and/or Cl atoms and/or CH_3 groups or by a CN group, Cy is 1,4-cyclohexylene and n is 0 or 1, the alkyl groups in each case containing 1 - 10 C atoms, with the provisos that a) n is 1 if A
15 is Cy and R^2 is CN and b) the compounds 1-(4'-trans-pentyl-trans-bicyclohex-4-yl)-2-(2-methyl-4-pentylphenyl)-ethane, 1-(4'-trans-pentyl-trans-bicyclohex-4-yl)-2-(3-methyl-4-pentylphenyl)-ethane, 1-(4'-trans-pentyl-trans-bicyclohex-4-yl)-2-(4-butoxy-2-methylphenyl)-ethane, and 1-(4'-trans-
20 pentyl-trans-bicyclohex-4-yl)-2-(4-butoxy-3-methylphenyl)-ethane, are excluded.

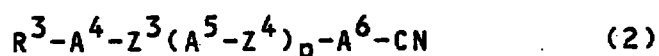
For simplicity, "Phe" in the following text is a 1,4-phenylene radical, it being possible for this radical to be unsubstituted or substituted by one or two fluorine
25 or chlorine atoms and/or CH_3 groups or by a CN group.

Although some laterally methylated bicyclohexylethanes (sic) have also already been reported, in addition to a large number of laterally substituted liquid crystal compounds, in EP-A-0,084,194, this document does not indicate the advantageous properties of the class of bicyclohexylethane substances according to the invention. As
30 compared with the structurally related cyclohexylcarbonitriles known from EP-A-0,056,113, the bicyclohexylethanes of the formula I show wider liquid-crystalline ranges and
35 lower viscosities.

German Offenlegungsschrift 3,148,148 and European Offenlegungsschrift 0,056,501 gives the general formula (1)



wherein R^1 can also be $CH_3(CH_2)_n-$, A^1 and A^2 can in each
 5 case also be Cy, Z^1 can also be a valency bond, Z^2 can
 also be $-CH_2CH_2-$, m can also be 1, A^3 can also be Cy or
 1,4-phenylene, R^2 can also be $CH_3(CH_2)_n$,
 $CH_3(CH_2)_n-2COO-$, $CH_3(CH_2)_n-2O-CO-$ or
 $CH_3(CH_2)_n-O-$ and n can be a number from zero to 11. These
 10 specifications also give the further general formula (2)



in which R^3 can also be $CH_3(CH_2)_n-$, A^4 and A^5 in each case
 15 can also be Cy, Z^3 can also be a valency bond, Z^4 can al-
 so be $-CH_2CH_2-$, p can also be 1, A^6 can also be Cy or 1,4-
 phenylene and n can be a number from zero to 11. However,
 neither part formulae nor individual compounds which con-
 20 tain the $-CH_2CH_2-$ group, as the bicyclohexylethanes of
 the present formula I, are mentioned therein. Compared
 with the two publications mentioned, these compounds are
 therefore still new, and they are not suggested by the
 prior art as stated by the two publications mentioned.

Like similar compounds, for example like the com-
 25 pounds known from German Offenlegungsschrift 3,225,290,
 the compounds of the formula I can be used as components
 of liquid crystal dielectrics, in particular for displays
 which are based on the principle of the twisted cell, the
 guest-host effect, the effect of deformation of orientated
 30 phases or the effect of dynamic scatter.

The invention was based on the object of discover-
 ing new stable liquid crystal or mesogenic compounds which
 are suitable as components of liquid crystal dielectrics.
 This object was achieved by providing the compounds of
 35 the formula I.

It has been found that the compounds of the for-
 mula I are outstandingly suitable as components of liquid
 crystal dielectrics. In particular, stable liquid crystal
 phases with a wide liquid crystal range and low viscosity,

- 3 -

in particular phases which are also liquid crystal and of low viscosity at low temperatures, can be prepared with the aid of these compounds.

Furthermore, by providing the compounds of the formula I, the range of liquid crystal substances which are suitable for the preparation of liquid crystal mixtures from various technological points of view is quite generally substantially increased.

The compounds of the formula I have a wide field of application. Depending on the choice of substituents, these compounds can be used as base materials, from which liquid crystal dielectrics are predominantly composed; however, it is also possible to add compounds of the formula I to liquid crystal base materials consisting of other classes of compounds, for example in order to reduce the viscosity or the birefringence of such a dielectric and/or to increase its clear point. The compounds of the formula I, especially those containing cyclohexane rings with substituents in cis-positions, and those wherein R^2 is H, Cl or Br, are furthermore suitable as intermediates for the preparation of other substances which can be used as constituents of liquid crystal dielectrics.

The compounds of the formula I are colourless in the pure state and form liquid crystal mesophases of low viscosity in a temperature range favourably located for electrooptical use. Chemically, they are very stable.

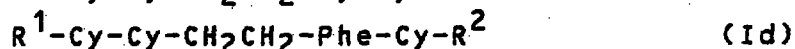
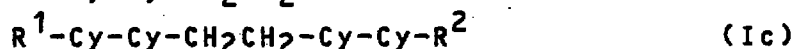
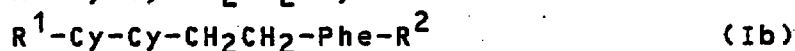
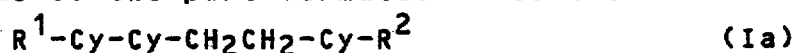
The invention thus relates to the compounds of the formula I and to a process for their preparation, characterised in that a compound which otherwise corresponds to the formula I but contains one or more reducible group(s) and/or C-C bond(s) instead of H atoms, is treated with a reducing agent, or in that, for the preparation of esters of the formula I (wherein R^2 is -COOalkyl or -O-COalkyl), a corresponding carboxylic acid or one of its reactive derivatives is reacted with a corresponding alcohol or phenol or one of its reactive derivatives, or in that, for the preparation of halogen derivatives of the formula I (wherein R^2 is F, Cl or Br and or A is 1,4-phenylene which is substituted by one or two F and/or

Cl atoms) with aromatically bonded halogen, a corresponding amino compound is diazotised and the diazonium group is then replaced by a fluorine, chlorine or bromine atom by methods which are known per se, or in that, for the preparation of nitriles of the formula I ($R^2 = CN$), a corresponding carboxylic acid amide is dehydrated or a corresponding carboxylic acid halide is reacted with sulfamide, or in that, for the preparation of ethers of the formula I (wherein R^2 is an alkyl group in which one or two CH_2 groups are replaced by O atoms), a corresponding hydroxy compound is etherified, and/or in that, if appropriate, a chlorine or bromine compound of the formula I (wherein R^2 is Cl or Br and/or wherein A denotes a 1,4-phenylene radical which is substituted by one or two Cl atoms) is reacted with a cyanide.

The invention also relates to the use of the compounds of the formula I as components of liquid crystal dielectrics. The invention furthermore relates to liquid crystal dielectrics containing at least one compound of the formula I, and electrooptical display elements containing such dielectrics.

R^1 , R^2 , A, Cy, Phe and n have, above and below, the meaning given, unless expressly indicated otherwise.

The compounds of the formula I accordingly include compounds of the part formulae Ia to Id:



Of these, those of the formulae Ia and Ib are preferred.

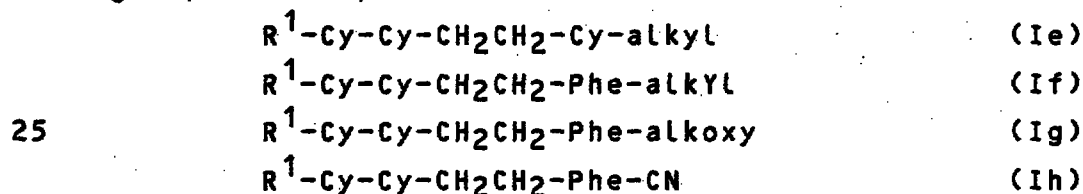
In the compounds of the formula I and Ia to Id, the alkyl radicals, wherein, in the case of R^2 , one or two CH_2 groups can also be replaced by O atoms, can be straight-chain or branched. Preferably, they are straight-chain and have 2, 3, 4, 5, 6 or 7 C atoms, and accordingly are preferably ethyl, propyl, butyl, pentyl, hexyl and heptyl, and in the case of R^2 also ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, methoxymethyl, ethoxymethyl, propoxymethyl,

- 5 -

methoxymethoxy and ethoxymethoxy, and furthermore methyl, octyl, nonyl, decyl, methoxy, octoxy, nonoxy or decoxy.

Compounds of the formula I and Ia to Id with branched end groups R^1 and/or R^2 may sometimes be of importance because of their better solubility in the usual liquid crystal base materials, but in particular as chiral doping substances, if they are optically active. Branched groups of this type as a rule contain not more than one chain branching. Preferred branched radicals R^1 and R^2 are isopropyl, 2-butyl (= 1-methylpropyl), isobutyl (= 2-methylpropyl), 2-methylbutyl, isopentyl (= 3-methylbutyl), 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl and 2-heptylpentyl, and for R^2 also isopropoxy, 2-methylpentoxy, 3-methylpentoxy, 2-ethylhexoxy, 1-methylhexoxy and 1-methylheptoxy.

Specifically, R^2 is preferably alkyl, alkoxy or CN, A is preferably Cy or unsubstituted 1,4-phenylene and n is preferably 0. Of the compounds of the formulae I and Ia to Id, those in which at least one of the radicals contained therein has one of the preferred meanings mentioned are preferred. Particularly preferred smaller groups of compounds are those of the formulae Ie to Ih:



In the compounds of the formulae I and Ia to Ih, those stereoisomers wherein the substituents on the cyclohexylene radicals are in each case in the trans-position relative to one another are preferred.

The compounds of the formula 1 are prepared by methods which are known per se, such as those described in the literature (for example in standard works such as Houben-Weyl, Methoden der Organischen Chemie [Methods of Organic Chemistry], Georg-Thieme Verlag, Stuttgart), and in particular under reaction conditions which are known and suitable for the reactions mentioned. Variants which are known per se and are not mentioned here in more detail can also be utilised.

If desired, the starting substances can also be formed in situ, such that they are not isolated from the reaction mixture but are immediately reacted further to give the compounds of the formula I.

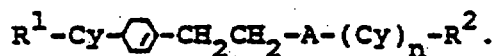
- 5 The compounds of the formula I are preferably prepared by reducing a compound which otherwise corresponds to the formula I but contains one or more reducible groups and/or C-C bonds instead of H atoms.

Preferred possible reducible groups are carbonyl groups, in particular keto groups, and furthermore, for example, free or esterified hydroxyl groups or aromatically bonded halogen atoms. Preferred starting substances for the reduction correspond to the formula I, but contain one of the groups -CO-CH₂-, -CH₂-CO- or -CH=CH- instead of the -CH₂CH₂- group and/or a cyclohexene ring instead of a cyclohexane ring.

Examples of preferred starting substances for the reduction are ketones of the formulae R¹-Cy-Cy-CH₂-CO-A-(Cy)_n-R² and R¹-Cy-Cy-CO-CH₂-A-(Cy)_n-R², but in particular R¹-Cy-Cy-CH₂-CO-Phe-(Cy)_n-R².

The ketones last mentioned can be obtained, for example, by a Friedel-Crafts reaction from the corresponding aromatics of the formula H-Phe-(Cy)_n-R² with the corresponding acid chlorides of the formula R¹-Cy-Cy-CH₂-CO-Cl.

25 Examples of starting substances with cyclohexene rings are those of the formula

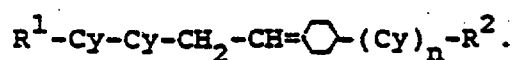


30

These can be obtained, for example, by reacting 4-R¹-Cy-cyclohexanones with organometallic compounds of the formula LiCH₂CH₂-A-(Cy)_n-R² or corresponding Grignard compounds and subsequently dehydrating the resulting carbinols.

35

Other preferred starting substances correspond to the formula



5 These can be obtained, for example, by a Wittig reaction from bromides of the formula $R^1-Cy-Cy-CH_2-CH_2-Br$ with triphenylphosphine, and then with 4- $R^2-(Cy)_n$ -cyclohexanones.

10 The reduction is preferably carried out by catalytic hydrogenation at temperatures between about 0° and about 200° under pressures between about 1 and about 200 bar in an inert solvent, for example an alcohol, such as methanol, ethanol or isopropanol, an ether, such as tetrahydrofuran (THF) or dioxane, an ester, such as ethyl acetate, a carboxylic acid, such as acetic acid, or a hydrocarbon, such as cyclohexane.

15 Preferred suitable catalysts are noble metals, such as Pt or Pd, which can be used in the form of oxides (for example PtO_2 or PdO), on a carrier (for example Pd-on-charcoal, -calcium carbonate or -strontium carbonate) or in finely divided form. The ketones mentioned can also be reduced by the methods of Clemmensen (with zinc, zinc amalgam or tin and hydrochloric acid, preferably in aqueous-alcoholic solution or in a heterogeneous phase system with water/benzene or water/toluene at temperatures between about 80 and 120°) or Wolff-Kishner (with hydrazine) preferably in the presence of alkali, such as KOH or NaOH, in a high-boiling solvent, such as diethyleneglycol or triethyleneglycol, at temperatures between about 100 and 200°).

25 Starting substances of the formula $R^1-Cy-Cy-CH=CH-Phe-(Cy)_n-R^2$, which can be obtained, for example, by a Wittig reaction from bromides of the formula $R^1-Cy-Cy-CH_2Br$ and aldehydes of the formula $O=CH-Phe-(Cy)_n-R^2$, can also be reduced with $NaBH_4$, preferably in an inert solvent, such as methanol, ethanol or diglyme, at temperatures between about 0 and 120°.

35 Esters of the formula I (wherein R^2 is -COOalkyl or -O-CO-alkyl) can also be obtained by esterification of

- 8 -

corresponding carboxylic acids of the formula $R^3\text{-COOH}$ [wherein R^3 is (a) $R^1\text{-Cy-Cy-CH}_2\text{CH}_2\text{-A-(Cy)}_n\text{-}$ or (b) alkyl] (or reactive derivatives thereof) with alcohols or phenols of the formula $R^4\text{-OH}$ [wherein R^4 in the case of (a) is alkyl and in the case of (b) is $R^1\text{-Cy-Cy-CH}_2\text{CH}_2\text{-A-(Cy)}_n\text{-}$] (or reactive derivatives thereof).

Particularly suitable reactive derivatives of the carboxylic acids mentioned are the acid halides, especially the chlorides and bromides, and furthermore the anhydrides, for example also mixed anhydrides of the formula $R^3\text{-CO-O-CO-CH}_3$, azides or esters, in particular alkyl esters with 1 - 4 C atoms in the alkyl group.

Possible reactive derivatives of the alcohols or phenols mentioned are, in particular, the corresponding metal alcoholates or phenolates of the formula $R^4\text{-OM}$, in which M is one equivalent of a metal, preferably an alkali metal, such as Na or K.

The esterification is advantageously carried out in the presence of an inert solvent. Particularly suitable solvents are ethers, such as diethyl ether, di-n-butyl ether, THF, dioxane or anisole, ketones, such as acetone, butanone or cyclohexanone, amides, such as dimethylformamide (DMF) or phosphoric acid hexamethyltriamide, hydrocarbons, such as carbon tetrachloride or tetrachloroethylene, and sulfoxides, such as dimethylsulfoxide or sulfolane. Water-immiscible solvents can at the same time advantageously be used for removal of the water formed during the esterification by azeotropic distillation. An excess of an organic base, for example pyridine, quinoline or triethylamine, can sometimes also be used as the solvent for the esterification.

The esterification can also be carried out in the absence of a solvent, for example by simply heating the components in the presence of sodium acetate. The reaction temperature is usually between -50° and $+250^\circ$, preferably between -20° and $+80^\circ$. At these temperatures, the esterification reactions have as a rule ended after 15 minutes to 48 hours.

Specifically, the reaction conditions for the

esterification largely depend on the nature of the starting substances used. Thus, a free carboxylic acid is as a rule reacted with a free alcohol or phenol in the presence of a strong acid, for example a mineral acid, such as hydrochloric acid or sulfuric acid. A preferred reaction procedure is the reaction of an acid anhydride or, in particular, an acid chloride with an alcohol, preferably in a basic medium, the important bases being, in particular, alkali metal hydroxides, such as sodium hydroxide or potassium hydroxide, alkali metal carbonates or bicarbonates, such as sodium carbonate, sodium bicarbonate, potassium carbonate or potassium bicarbonate, alkali metal acetates, such as sodium acetate or potassium acetate, alkaline earth metal hydroxides, such as calcium hydroxide, or organic bases, such as triethylamine, pyridine, lutidine, collidine or quinoline. A further preferred embodiment of the esterification consists in first converting the alcohol or the phenol into the sodium or potassium alcoholate or phenolate, for example by treatment with ethanolic sodium hydroxide solution or potassium hydroxide solution, isolating this alcoholate or phenolate and suspending it in acetone or diethyl ether, together with sodium bicarbonate or potassium carbonate, with stirring, and adding a solution of the acid chloride or anhydride in diethyl ether, acetone or DMF to this suspension, preferably at temperatures between about -25 and $+20^{\circ}$.

Halogen derivatives of the formula I (wherein R^2 is F, Cl or Br and/or A is 1,4-phenylene which is substituted by one or two F and/or Cl atoms) with aromatically bonded halogen can be prepared from the corresponding amines by the methods of the Schiemann reaction (compare, for example, The Merck Index, 9th Edition, Merck & Co., Inc., Rahway, N.J., USA, 1976, page ONR-80) or the Sandmeyer reaction (compare, for example, The Merck Index, Loc.cit., page ONR-79).

The diazotisation is preferably effected first with a salt or an ester of nitrous acid (such as NaNO_2 or butyl nitrite), in an aqueous-acid phase, it being possible to use, for example, HF, HCl, HBr, H_2SO_4 or HBF_4 as the

- 10 -

acid, at temperatures between about -20° and $+10^{\circ}$. An additional inert solvent may be present, for example an ether, such as THF or dioxane, or a hydrocarbon, such as toluene or xylene.

5 To prepare the fluorine compounds of the formula I (wherein R^2 is F and/or A is 1,4-phenylene which is substituted by one or two F atoms), the diazotisation is preferably carried out in HBF_4 . The diazonium tetrafluoroborates are thereby formed, and these can already be decomposed at temperatures between about 10 and 100° . If
10 the diazotisation is carried out with NaNO_2 in anhydrous HF, the desired fluorine compound is obtained directly by subsequent warming.

A replacement of the diazonium group by Cl or Br
15 is preferably carried out in aqueous solution in the presence of Cu_2Cl_2 or Cu_2Br_2 at temperatures between 30 and 100° .

To prepare nitriles of the formula I ($R^2 = \text{CN}$ and or A = 1,4-phenylene which is substituted by a CN group),
20 in particular those of the formula I_h, corresponding acid amides, for example those of the formula $R^1\text{-Cy-Cy-CH}_2\text{CH}_2\text{-A-(Cy)}_n\text{-CONH}_2$, can be dehydrated. The amides can be obtained, for example, from corresponding esters or acid halides by reaction with ammonia. Examples of suitable agents which
25 split off water are inorganic acid chlorides, such as SOCl_2 , PCl_3 , PCl_5 , POCl_3 , SO_2Cl_2 and COCl_2 , and furthermore P_2O_5 , P_2S_5 , AlCl_3 (for example as a double compound with NaCl), aromatic sulfonic acids and sulfonic acid halides. This reaction can be carried out in the presence
30 or absence of an inert solvent at temperatures between about 0 and 150° ; examples of possible solvents are bases, such as pyridine or triethylamine, aromatic hydrocarbons, such as benzene, toluene or xylene, or amides, such as DMF.

35 Alkoxy compounds of the formula I ($R^2 = \text{alkoxy}$) can be obtained by alkylation of corresponding hydroxy compounds, preferably corresponding phenols, the hydroxy compound preferably first being converted into a corresponding metal derivative, for example into the correspond-

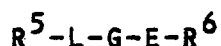
ing alkali metal alcoholate or alkali metal phenolate by treatment with NaOH, KOH, Na₂CO₃ or K₂CO₃. This can then be reacted with the corresponding alkyl halide or sulfonate or dialkyl sulfate, preferably in an inert solvent, such as acetone, DMF or dimethylsulfoxide, or an excess of aqueous or aqueous-alcoholic NaOH or KOH at temperatures between about 20 and 100°.

To prepare the nitriles, it is also possible to react corresponding chlorine or bromine compounds with a cyanide, preferably with a metal cyanide, such as NaCN, KCN or Cu₂(CN)₂, for example in the presence of pyridine in an inert solvent, such as DMF or N-methylpyrrolidone, at temperatures between 20 and 200°.

To prepare the abovementioned nitriles, it is also possible to react corresponding acid halides, preferably the chlorides, with sulfamide, preferably in an inert solvent, such as tetramethylene sulfone, at temperatures between about 80 and 150°, preferably at about 120°. After customary working up, the nitriles can be isolated directly.

The dielectrics according to the invention consist of 2 to 15, preferably 3 to 12, components, at least one of which is a compound of the formula I. The other constituents are preferably chosen from the nematic or nematogenic substances, in particular the known substances from the classes of azoxybenzenes, benzylideneanilines, biphenyls, terphenyls, phenyl or cyclohexyl benzoates, phenyl or cyclohexyl cyclohexanecarboxylates, phenylcyclohexanes, cyclohexylbiphenyls, cyclohexylcyclohexanes, cyclohexylnaphthalenes, 1,4-bis-cyclohexylbenzenes, 4,4'-bis-cyclohexylbiphenyls, phenyl- or cyclohexyl-pyrimidines, phenyl- or cyclohexyl-dioxanes, optionally halogenated stilbenes, benzyl phenyl ethers, tolanes and substituted cinnamic acids.

The most important compounds which can be used as constituents of such liquid crystal dielectrics can be characterised by the formula III



(III)

- 12 -

wherein L and E are each a carbocyclic or heterocyclic ring system from the group comprising 1,4-disubstituted benzene and cyclohexane rings, 4,4'-disubstituted biphenyl, phenylcyclohexane and cyclohexylcyclohexane systems, 2,5-
 5 disubstituted pyrimidine and 1,3-dioxane rings, 2,6-disubstituted naphthalene, di- and tetra-hydronaphthalene, quinazoline and tetrahydroquinazoline, G is

	-CH=CH-	-N(O)=N-
	-CH=CY-	-CH=N(O)-
10	-C≡C-	-CH ₂ -CH ₂ -
	-CO-O-	-CH ₂ -O-
	-CO-S-	-CH ₂ -S-
	-CH=N-	-COO-Phe-COO-

or a C-C single bond, Y is halogen, preferably chlorine,
 15 or -CN, and R⁵ and R⁶ are alkyl, alkoxy, alkanoyloxy or alkoxycarbonyloxy with up to 18, preferably up to 8, carbon atoms, or one of these radicals is also CN, NC, NO₂, CF₃, F, Cl or Br.

In most of these compounds, R⁵ and R⁶ differ from
 20 one another, one of these radicals usually being an alkyl or alkoxy group. However, other variants of the envisaged substituents are also usual. Many such substances or mixtures thereof are commercially available.

The dielectrics according to the invention contain
 25 about 1 to 60%, preferably 5 to 40%, of one or more compounds of the formula I.

The dielectrics according to the invention are prepared in a manner which is customary per se. As a rule, the components are dissolved in one another, preferably at
 30 elevated temperature.

The liquid crystal dielectrics according to the invention can be modified by suitable additives such that they can be used in all the types of liquid crystal display elements as yet disclosed.

35 Such additives are known to the expert and are described in detail in the literature. For example, conductive salts, preferably ethyl-dimethyl-dodecyl-ammonium 4-hexyloxybenzoate, tetrabutylammonium tetraphenylboronate or complex salts of crown ethers (compare, for example,

I. Haller et al., Mol. Cryst. Liq. Cryst. Volume 24, pages 249 - 258 (1973)) can be added to improve the conductivity, dichroic dyestuffs can be added to produce coloured guest-host systems or substances can be added to modify the dielectric anisotropy, the viscosity and/or the orientation of the nematic phases. Such substances are described, for example, in German Offenlegungsschriften 2,209,127, 2,240,864, 2,321,632, 2,338,281, 2,450,088, 2,637,430, 2,853,728 and 2,902,177.

The examples which follow are intended to illustrate the invention, without limiting it. M.p. = melting point, c.p. = clear point. The percentages given above and below are percentages by weight; all the temperatures are given in degrees Celsius. "Customary working up" means: water is added, the mixture is extracted with methylene chloride, the organic phase is separated off, dried and evaporated and the resulting product is purified, if necessary, by chromatography on silica gel.

Example 1

A mixture of 36.8 g of trans/trans-4-p-propylbenzoylmethyl-4'-propyl-bicyclohexyl (obtainable by reduction of trans/trans-4'-propyl-bicyclohexyl-4-carboxylic acid to trans/trans-4-hydroxymethyl-4'-propyl-bicyclohexyl with LiAlH_4 , conversion of the product into the tosylate, reaction with KCN to give trans/trans-4-cyanomethyl-4'-propyl-bicyclohexyl, hydrolysis to the carboxylic acid, reaction with SOCl_2 to give the acid chloride and reaction with propylbenzene in the presence of AlCl_3), 30 g of KOH, 50 ml of 85% hydrazine and 500 ml of triethylene glycol is warmed at 120° for 1 hour. The temperature is slowly increased until the hydrazone formed decomposes, and the mixture is boiled for a further 4 hours, cooled and worked up in the customary manner to give trans/trans-4-(2-p-propylphenyl-ethyl)-4'-propyl-bicyclohexyl, m.p. 34° , c.p. 158° .

The following corresponding ketones [sic] are obtained analogously by reduction:

trans/trans-4-(2-p-phenyl-ethyl)-4'-propyl-bicyclohexyl
trans/trans-4-(2-p-tolyl-ethyl)-4'-propyl-bicyclohexyl

- trans/trans-4-(2-p-ethylphenyl-ethyl)-4'-ethyl-bicyclohexyl
- trans/trans-4-(2-p-ethylphenyl-ethyl)-4'-propyl-bicyclohexyl
- 5 trans/trans-4-(2-p-ethylphenyl-ethyl)-4'-butyl-bicyclohexyl
- trans/trans-4-(2-p-ethylphenyl-ethyl)-4'-pentyl-bicyclohexyl
- trans/trans-4-(2-p-ethylphenyl-ethyl)-4'-hexyl-bicyclohexyl
- 10 trans/trans-4-(2-p-ethylphenyl-ethyl)-4'-heptyl-bicyclohexyl
- trans/trans-4-(2-p-propylphenyl-ethyl)-4'-ethyl-bicyclohexyl
- 15 trans/trans-4-(2-p-propylphenyl-ethyl)-4'-butyl-bicyclohexyl
- trans/trans-4-(2-p-propylphenyl-ethyl)-4'-pentyl-bicyclohexyl
- trans/trans-4-(2-p-propylphenyl-ethyl)-4'-hexyl-bicyclohexyl
- 20 trans/trans-4-(2-p-propylphenyl-ethyl)-4'-heptyl-bicyclohexyl
- trans/trans-4-(2-p-butylphenyl-ethyl)-4'-ethyl-bicyclohexyl
- 25 trans/trans-4-(2-p-butylphenyl-ethyl)-4'-propyl-bicyclohexyl
- trans/trans-4-(2-p-butylphenyl-ethyl)-4'-butyl-bicyclohexyl
- trans/trans-4-(2-p-butylphenyl-ethyl)-4'-pentyl-bicyclohexyl
- 30 trans/trans-4-(2-p-butylphenyl-ethyl)-4'-hexyl-bicyclohexyl
- trans/trans-4-(2-p-butylphenyl-ethyl)-4'-heptyl-bicyclohexyl
- 35 trans/trans-4-(2-p-pentylphenyl-ethyl)-4'-ethyl-bicyclohexyl
- trans/trans-4-(2-p-pentylphenyl-ethyl)-4'-propyl-bicyclohexyl
- trans/trans-4-(2-p-pentylphenyl-ethyl)-4'-butyl-bicyclohexyl

- hexyl
trans/trans-4-(2-p-pentylphenyl-ethyl)-4'-pentyl-bicyclo-
hexyl
trans/trans-4-(2-p-pentylphenyl-ethyl)-4'-hexyl-bicyclo-
5 hexyl
trans/trans-4-(2-p-pentylphenyl-ethyl)-4'-heptyl-bicyclo-
hexyl
trans/trans-4-(2-p-hexylphenyl-ethyl)-4'-ethyl-bicyclo-
hexyl
10 trans/trans-4-(2-p-hexylphenyl-ethyl)-4'-propyl-bicyclo-
hexyl
trans/trans-4-(2-p-hexylphenyl-ethyl)-4'-butyl-bicyclo-
hexyl
trans/trans-4-(2-p-hexylphenyl-ethyl)-4'-pentyl-bicyclo-
15 hexyl
trans/trans-4-(2-p-hexylphenyl-ethyl)-4'-hexyl-bicyclo-
hexyl
trans/trans-4-(2-p-hexylphenyl-ethyl)-4'-heptyl-bicyclo-
hexyl
20 trans/trans-4-(2-p-heptylphenyl-ethyl)-4'-ethyl-bicyclo-
hexyl
trans/trans-4-(2-p-heptylphenyl-ethyl)-4'-propyl-bicyclo-
hexyl
trans/trans-4-(2-p-heptylphenyl-ethyl)-4'-butyl-bicyclo-
25 hexyl
trans/trans-4-(2-p-heptylphenyl-ethyl)-4'-pentyl-bicyclo-
hexyl
trans/trans-4-(2-p-heptylphenyl-ethyl)-4'-hexyl-bicyclo-
hexyl
30 trans/trans-4-(2-p-heptylphenyl-ethyl)-4'-heptyl-bicyclo-
hexyl
trans/trans-4-(2-p-methoxymethylphenyl-ethyl)-4'-ethyl-
bicyclohexyl
trans/trans-4-(2-p-methoxymethylphenyl-ethyl)-4'-propyl-
35 bicyclohexyl
trans/trans-4-(2-p-methoxymethylphenyl-ethyl)-4'-butyl-
bicyclohexyl
trans/trans-4-(2-p-methoxymethylphenyl-ethyl)-4'-pentyl-
bicyclohexyl

- trans/trans-4-(2-p-methoxymethylphenyl-ethyl)-4'-hexyl-bicyclohexyl
trans/trans-4-(2-p-methoxymethylphenyl-ethyl)-4'-heptyl-bicyclohexyl
- 5 trans/trans-4-(2-p-methoxyphenyl-ethyl)-4'-ethyl-bicyclohexyl
trans/trans-4-(2-p-methoxyphenyl-ethyl)-4'-propyl-bicyclohexyl
trans/trans-4-(2-p-methoxyphenyl-ethyl)-4'-butyl-bicyclohexyl
- 10 trans/trans-4-(2-p-methoxyphenyl-ethyl)-4'-pentyl-bicyclohexyl
trans/trans-4-(2-p-methoxyphenyl-ethyl)-4'-hexyl-bicyclohexyl
- 15 trans/trans-4-(2-p-methoxyphenyl-ethyl)-4'-heptyl-bicyclohexyl
trans/trans-4-(2-p-ethoxyphenyl-ethyl)-4'-ethyl-bicyclohexyl
trans/trans-4-(2-p-ethoxyphenyl-ethyl)-4'-propyl-bicyclohexyl
- 20 trans/trans-4-(2-p-ethoxyphenyl-ethyl)-4'-butyl-bicyclohexyl
trans/trans-4-(2-p-ethoxyphenyl-ethyl)-4'-pentyl-bicyclohexyl
- 25 trans/trans-4-(2-p-ethoxyphenyl-ethyl)-4'-hexyl-bicyclohexyl
trans/trans-4-(2-p-ethoxyphenyl-ethyl)-4'-heptyl-bicyclohexyl
trans/trans-4-(2-p-propoxyphenyl-ethyl)-4'-ethyl-bicyclohexyl
- 30 trans/trans-4-(2-p-propoxyphenyl-ethyl)-4'-propyl-bicyclohexyl
trans/trans-4-(2-p-propoxyphenyl-ethyl)-4'-butyl-bicyclohexyl
- 35 trans/trans-4-(2-p-propoxyphenyl-ethyl)-4'-pentyl-bicyclohexyl
trans/trans-4-(2-p-propoxyphenyl-ethyl)-4'-hexyl-bicyclohexyl
trans/trans-4-(2-p-propoxyphenyl-ethyl)-4'-heptyl-bicyclohexyl

- hexyl
trans/trans-4-(2-p-butoxyphenyl-ethyl)-4'-ethyl-bicyclo-
hexyl
trans/trans-4-(2-p-butoxyphenyl-ethyl)-4'-propyl-bicyclo-
5 hexyl
trans/trans-4-(2-p-butoxyphenyl-ethyl)-4'-butyl-bicyclo-
hexyl
trans/trans-4-(2-p-butoxyphenyl-ethyl)-4'-pentyl-bicyclo-
hexyl
10 trans/trans-4-(2-p-butoxyphenyl-ethyl)-4'-hexyl-bicyclo-
hexyl
trans/trans-4-(2-p-butoxyphenyl-ethyl)-4'-heptyl-bicyclo-
hexyl
trans/trans-4-(2-p-methoxymethoxyphenyl-ethyl)-4'-ethyl-
15 bicyclohexyl
trans/trans-4-(2-p-methoxymethoxyphenyl-ethyl)-4'-propyl-
bicyclohexyl
trans/trans-4-(2-p-methoxymethoxyphenyl-ethyl)-4'-butyl-
bicyclohexyl
20 trans/trans-4-(2-p-methoxymethoxyphenyl-ethyl)-4'-pentyl-
bicyclohexyl
trans/trans-4-(2-p-methoxymethoxyphenyl-ethyl)-4'-hexyl-
bicyclohexyl
trans/trans-4-(2-p-methoxymethoxyphenyl-ethyl)-4'-heptyl-
25 bicyclohexyl
trans/trans-4-[2-p-(trans-4-ethylcyclohexyl)-phenylethyl]-
4'-ethyl-bicyclohexyl
trans/trans-4-[2-p-(trans-4-ethylcyclohexyl)-phenylethyl]-
4'-propyl-bicyclohexyl
30 trans/trans-4-[2-p-(trans-4-ethylcyclohexyl)-phenylethyl]-
4'-butyl-bicyclohexyl
trans/trans-4-[2-p-(trans-4-ethylcyclohexyl)-phenylethyl]-
4'-pentyl-bicyclohexyl
trans/trans-4-[2-p-(trans-4-ethylcyclohexyl)-phenylethyl]-
35 4'-hexyl-bicyclohexyl
trans/trans-4-[2-p-(trans-4-ethylcyclohexyl)-phenylethyl]-
4'-heptyl-bicyclohexyl
trans/trans-4-[2-p-(trans-4-propylcyclohexyl)-phenylethyl]-
4'-ethyl-bicyclohexyl

- trans/trans-4-[2-p-(trans-4-propylcyclohexyl)-phenylethyl]-
4'-propyl-bicyclohexyl
- trans/trans-4-[2-p-(trans-4-propylcyclohexyl)-phenylethyl]-
4'-butyl-bicyclohexyl
- 5 trans/trans-4-[2-p-(trans-4-propylcyclohexyl)-phenylethyl]-
4'-pentyl-bicyclohexyl
- trans/trans-4-[2-p-(trans-4-propylcyclohexyl)-phenylethyl]-
4'-hexyl-bicyclohexyl
- trans/trans-4-[2-p-(trans-4-propylcyclohexyl)-phenylethyl]-
10 4'-heptyl-bicyclohexyl
- trans/trans-4-[2-p-(trans-4-butylcyclohexyl)-phenylethyl]-
4'-ethyl-bicyclohexyl
- trans/trans-4-[2-p-(trans-4-butylcyclohexyl)-phenylethyl]-
4'-propyl-bicyclohexyl
- 15 trans/trans-4-[2-p-(trans-4-butylcyclohexyl)-phenylethyl]-
4'-butyl-bicyclohexyl
- trans/trans-4-[2-p-(trans-4-butylcyclohexyl)-phenylethyl]-
4'-pentyl-bicyclohexyl
- trans/trans-4-[2-p-(trans-4-butylcyclohexyl)-phenylethyl]-
20 4'-hexyl-bicyclohexyl
- trans/trans-4-[2-p-(trans-4-butylcyclohexyl)-phenylethyl]-
4'-heptyl-bicyclohexyl
- trans/trans-4-[2-p-(trans-4-pentylcyclohexyl)-phenylethyl]-
4'-ethyl-bicyclohexyl
- 25 trans/trans-4-[2-p-(trans-4-pentylcyclohexyl)-phenylethyl]-
4'-propyl-bicyclohexyl
- trans/trans-4-[2-p-(trans-4-pentylcyclohexyl)-phenylethyl]-
4'-butyl-bicyclohexyl
- trans/trans-4-[2-p-(trans-4-pentylcyclohexyl)-phenylethyl]-
30 4'-pentyl-bicyclohexyl
- trans/trans-4-[2-p-(trans-4-pentylcyclohexyl)-phenylethyl]-
4'-hexyl-bicyclohexyl
- trans/trans-4-[2-p-(trans-4-pentylcyclohexyl)-phenylethyl]-
4'-heptyl-bicyclohexyl
- 35 trans/trans-4-[2-p-(trans-4-hexylcyclohexyl)-phenylethyl]-
4'-ethyl-bicyclohexyl
- trans/trans-4-[2-p-(trans-4-hexylcyclohexyl)-phenylethyl]-
4'-propyl-bicyclohexyl
- trans/trans-4-[2-p-(trans-4-hexylcyclohexyl)-phenylethyl]-

- 4'-butyl-bicyclohexyl
 trans/trans-4-[2-p-(trans-4-hexylcyclohexyl)-phenylethyl]-
 4'-pentyl-bicyclohexyl
 trans/trans-4-[2-p-(trans-4-hexylcyclohexyl)-phenylethyl]-
 5 4'-hexyl-bicyclohexyl
 trans/trans-4-[2-p-(trans-4-hexylcyclohexyl)-phenylethyl]-
 4'-heptyl-bicyclohexyl
 trans/trans-4-[2-p-(trans-4-heptylcyclohexyl)-phenylethyl]-
 4'-ethyl-bicyclohexyl
 10 trans/trans-4-[2-p-(trans-4-heptylcyclohexyl)-phenylethyl]-
 4'-propyl-bicyclohexyl
 trans/trans-4-[2-p-(trans-4-heptylcyclohexyl)-phenylethyl]-
 4'-butyl-bicyclohexyl
 trans/trans-4-[2-p-(trans-4-heptylcyclohexyl)-phenylethyl]-
 15 4'-pentyl-bicyclohexyl
 trans/trans-4-[2-p-(trans-4-heptylcyclohexyl)-phenylethyl]-
 4'-hexyl-bicyclohexyl and
 trans/trans-4-[2-p-(trans-4-heptylcyclohexyl)-phenylethyl]-
 4'-heptyl-bicyclohexyl.

20 Example 2

A solution of 39.6 g of trans/trans-4-p-propyl-
 benzoylmethyl-4'-pentyl-bicyclohexyl (obtainable from trans/
 trans-4'-pentyl-bicyclohexyl-4-acetyl chloride and propyl-
 benzene/ AlCl_3) in 500 ml of ethyl acetate is hydrogenated
 25 on 5 g of 10% Pd-on-charcoal at 20° under 5 bar. The mix-
 ture is filtered and the filtrate is evaporated to give
 trans/trans-4-(2-p-propylphenyl-ethyl)-4'-pentyl-bicyclo-
 hexyl.

The other compounds mentioned in Example 1 are also
 30 obtainable analogously.

Example 3

A solution of 34 g of 1-(2-p-methoxyphenyl-ethyl)-
 4-(trans-4-propylcyclohexyl)-cyclohexene [obtainable by
 reaction of 2-p-methoxyphenyl-ethyl-magnesium bromide with
 35 4-(trans-4-propylcyclohexyl)-cyclohexanone and subsequent
 hydrolysis to 1-(2-p-methoxyphenyl-ethyl)-4-(trans-4-propyl-
 cyclohexyl)-cyclohexanol and dehydration with p-toluene-
 sulfonic acid in boiling toluene] in 600 ml of THF is hy-
 drogenated on 5 g of PdO at 40° under 1 bar until the

- 20 -

reaction stops. The mixture is filtered, the filtrate is evaporated, the residue is taken up in 200 ml of boiling methanol and the resulting hot solution is poured into a boiling solution of 70 g of thiourea in 300 ml of methanol. The mixture is cooled to 0° and the thiourea inclusion compound precipitated is filtered off and boiled up with 350 ml of petroleum ether (boiling point 40-60°). The undissolved residue is warmed at 50° with 350 ml of 2 N aqueous potassium hydroxide solution for 30 minutes. The resulting solution is acidified with 10% H₂SO₄ and the trans/trans-4-(2-p-methoxyphenyl-ethyl)-4'-propylbicyclohexyl which has precipitated is filtered off.

The other compounds mentioned in Example 1 are also obtainable analogously.

15 Example 4

A mixture of 36.3 g of trans/trans-4-(2-p-cyanophenyl-vinyl)-4'-pentyl-bicyclohexyl (obtainable by a Wittig reaction from 4-bromomethyl-4'-pentyl-bicyclohexyl and p-cyanobenzaldehyde), 3.7 g of NaBH₄ and 350 ml of methanol is boiled for 4 hours. After customary working up, trans/trans-4-(2-p-cyanophenyl-ethyl)-4'-pentyl-bicyclohexyl is obtained.

The following compounds are obtained analogously, by reduction of the corresponding vinyl compounds:

25 trans/trans-4-(2-p-cyanophenyl-ethyl)-4'-ethyl-bicyclohexyl

trans/trans-4-(2-p-cyanophenyl-ethyl)-4'-propyl-bicyclohexyl

30 trans/trans-4-(2-p-cyanophenyl-ethyl)-4'-butyl-bicyclohexyl

trans/trans-4-(2-p-cyanophenyl-ethyl)-4'-hexyl-bicyclohexyl and

trans/trans-4-(2-p-cyanophenyl-ethyl)-4'-heptyl-bicyclohexyl.

35 Example 5

35.6 g of p-[2-(trans/trans-4'-propyl-bicyclohexyl-4-yl)-ethyl]-benzoic acid (obtainable by a Wittig reaction from trans/trans-4-bromomethyl-4'-propyl-bicyclohexyl and terephthalaldehydic acid to give p-[2-(trans/trans-4'-propyl-

- 21 -

bicyclohexyl-4-yl)-vinyl]-benzoic acid and hydrogenation) are boiled with 24 g of SOCl_2 for 1 hour, the mixture is evaporated, the resulting crude acid chloride is dissolved in 300 ml of toluene, 8 ml of pyridine and 13 g of (-)-2-octanol are added and the mixture is boiled for 2 hours. After cooling and customary working up, (-)-2-octyl p-[2-(trans/trans-4'-propyl-bicyclohexyl-4-yl)-ethyl]-benzoate is obtained.

The following compounds are obtainable by esterification:

- 10 Ethyl p-[2-(trans/trans-4'-ethyl-bicyclohexyl-4-yl)-ethyl]-benzoate
- Propyl p-[2-(trans/trans-4'-ethyl-bicyclohexyl-4-yl)-ethyl]-benzoate
- 15 Butyl p-[2-(trans/trans-4'-ethyl-bicyclohexyl-4-yl)-ethyl]-benzoate
- Ethyl p-[2-(trans/trans-4'-propyl-bicyclohexyl-4-yl)-ethyl]-benzoate
- Propyl p-[2-(trans/trans-4'-propyl-bicyclohexyl-4-yl)-ethyl]-benzoate
- 20 Butyl p-[2-(trans/trans-4'-propyl-bicyclohexyl-4-yl)-ethyl]-benzoate
- Ethyl p-[2-(trans/trans-4'-propyl-bicyclohexyl-4-yl)-ethyl]-benzoate
- 25 Propyl p-[2-(trans/trans-4'-propyl-bicyclohexyl-4-yl)-ethyl]-benzoate
- Butyl p-[2-(trans/trans-4'-propyl-bicyclohexyl-4-yl)-ethyl]-benzoate
- Ethyl p-[2-(trans/trans-4'-butyl-bicyclohexyl-4-yl)-ethyl]-benzoate
- 30 Propyl p-[2-(trans/trans-4'-butyl-bicyclohexyl-4-yl)-ethyl]-benzoate
- Butyl p-[2-(trans/trans-4'-butyl-bicyclohexyl-4-yl)-ethyl]-benzoate
- 35 Ethyl p-[2-(trans/trans-4'-pentyl-bicyclohexyl-4-yl)-ethyl]-benzoate
- Propyl p-[2-(trans/trans-4'-pentyl-bicyclohexyl-4-yl)-ethyl]-benzoate
- Butyl p-[2-(trans/trans-4'-pentyl-bicyclohexyl-4-yl)-ethyl]-benzoate

ethyl]-benzoate

Ethyl p-[2-(trans/trans-4'-hexyl-bicyclohexyl-4-yl)-ethyl]-benzoate

5 Propyl p-[2-(trans/trans-4'-hexyl-bicyclohexyl-4-yl)-ethyl]-benzoate

Butyl p-[2-(trans/trans-4'-hexyl-bicyclohexyl-4-yl)-ethyl]-benzoate

Ethyl p-[2-(trans/trans-4'-heptyl-bicyclohexyl-4-yl)-ethyl]-benzoate

10 Propyl p-[2-(trans/trans-4'-heptyl-bicyclohexyl-4-yl)-ethyl]-benzoate and

Butyl p-[2-(trans/trans-4'-heptyl-bicyclohexyl-4-yl)-ethyl]-benzoate.

Example 6

15 32.8 g of trans/trans-4-(2-p-hydroxyphenylethyl)-4'-propyl-bicyclohexyl and 30 g of CH_3COONa in 100 ml of acetic anhydride are heated at 80° for 1 hour and the mixture is cooled and worked up in the customary manner to give trans/trans-4-(2-p-acetoxyphenylethyl)-4'-propyl-

20 bicyclohexyl.

The following compounds are obtained analogously by esterification:

trans/trans-4-(2-p-acetoxyphenylethyl)-4'-ethyl-bicyclohexyl

25 trans/trans-4-(2-p-acetoxyphenylethyl)-4'-butyl-bicyclohexyl

trans/trans-4-(2-p-acetoxyphenylethyl)-4'-pentyl-bicyclohexyl

30 trans/trans-4-(2-p-acetoxyphenylethyl)-4'-hexyl-bicyclohexyl

trans/trans-4-(2-p-acetoxyphenylethyl)-4'-heptyl-bicyclohexyl

trans/trans-4-(2-p-propionyloxyphenylethyl)-4'-ethyl-bicyclohexyl

35 trans/trans-4-(2-p-propionyloxyphenylethyl)-4'-propyl-bicyclohexyl

trans/trans-4-(2-p-propionyloxyphenylethyl)-4'-butyl-bicyclohexyl

trans/trans-4-(2-p-propionyloxyphenylethyl)-4'-pentyl-

bicyclohexyl

trans/trans-4-(2-p-propionyloxyphenylethyl)-4'-hexyl-

bicyclohexyl

trans/trans-4-(2-p-propionyloxyphenylethyl)-4'-heptyl-

5 bicyclohexyl

trans/trans-4-(2-p-butyryloxyphenylethyl)-4'-ethyl-

bicyclohexyl

trans/trans-4-(2-p-butyryloxyphenylethyl)-4'-propyl-

bicyclohexyl

10 trans/trans-4-(2-p-butyryloxyphenylethyl)-4'-butyl-

bicyclohexyl

trans/trans-4-(2-p-butyryloxyphenylethyl)-4'-pentyl-

bicyclohexyl

trans/trans-4-(2-p-butyryloxyphenylethyl)-4'-hexyl-

15 bicyclohexyl and

trans/trans-4-(2-p-butyryloxyphenylethyl)-4'-heptyl-

bicyclohexyl.

Example 7

180 ml of 35% aqueous tetrafluoboric acid solution
 20 are added to a suspension of 39.7 g of trans/trans-4-[2-(3-amino-4-propylphenyl)-ethyl]-4'-pentyl-bicyclohexyl
 (obtainable by nitration of trans/trans-4-p-propylbenzoyl-methyl-4'-pentyl-bicyclohexyl and subsequent hydrogenation
 of the resulting crude 3-nitro compound on Pd in THF) in
 25 180 ml of dioxane at 15 - 20°, with stirring, and a solution of 7.2 g of NaNO₂ in 25 ml of water is then added dropwise at 0°. The mixture is subsequently stirred for 6
 hours, during which the temperature is allowed to rise to 15°. After customary working up (extraction with toluene,
 30 filtration over silica gel), trans/trans-4-[2-(3-fluoro-4-propylphenyl)-ethyl]-4'-pentyl-bicyclohexyl is obtained.

The following compounds can be obtained analogously from the corresponding amino compounds:

trans/trans-4-(2-o-fluorophenyl-ethyl)-4'-propyl-bicyclo-
 35 hexyl

trans/trans-4-(2-p-fluorophenyl-ethyl)-4'-ethyl-bicyclo-
 hexyl

trans/trans-4-(2-p-fluorophenyl-ethyl)-4'-propyl-bicyclo-
 hexyl

trans/trans-4-(2-p-fluorophenyl-ethyl)-4'-butyl-bicyclohexyl

trans/trans-4-(2-p-fluorophenyl-ethyl)-4'-pentyl-bicyclohexyl

5 trans/trans-4-(2-p-fluorophenyl-ethyl)-4'-hexyl-bicyclohexyl and

trans/trans-4-(2-p-fluorophenyl-ethyl)-4'-heptyl-bicyclohexyl.

Example 8

10 A solution of 7.2 g of NaNO_2 in 25 ml of water is added to a suspension of 35.5 g of trans/trans-4-(2-p-aminophenyl-ethyl)-4'-pentyl-bicyclohexyl [obtainable by nitration of trans/trans-4-(2-phenylethyl)-4'-pentyl-bicyclohexyl to 4-(2-p-nitrophenyl-ethyl)-4'-pentyl-bicyclohexyl and hydrogenation on Pd] in 150 ml of 15% aqueous hydrobromic acid at -5° in the course of 0.5 hour. The solution thus obtained is added dropwise, at $0 - 5^\circ$ in the course of 1 hour, to a Cu(I) salt solution which has been prepared from 25 g of copper sulfate, 15.4 g of NaBr, 6.3 g of Na_2SO_3 , 100 ml of water and 40 ml of 32% hydrobromic acid. After the mixture has been heated to 40° for half an hour, it is extracted with CH_2Cl_2 and the extract is worked up in the customary manner. Trans/trans-4-(2-p-bromophenyl-ethyl)-4'-pentyl-bicyclohexyl is obtained.

25 The following compounds are obtainable analogously from the corresponding amino compounds by a Sandmeyer reaction:

trans/trans-4-(2-p-chlorophenyl-ethyl)-4'-ethyl-bicyclohexyl

30 trans/trans-4-(2-p-chlorophenyl-ethyl)-4'-propyl-bicyclohexyl

trans/trans-4-(2-p-chlorophenyl-ethyl)-4'-butyl-bicyclohexyl

35 trans/trans-4-(2-p-chlorophenyl-ethyl)-4'-pentyl-bicyclohexyl

trans/trans-4-(2-p-chlorophenyl-ethyl)-4'-hexyl-bicyclohexyl

trans/trans-4-(2-p-chlorophenyl-ethyl)-4'-heptyl-bicyclohexyl

- 25 -

trans/trans-4-(2-p-bromophenyl-ethyl)-4'-ethyl-bicyclohexyl

trans/trans-4-(2-p-bromophenyl-ethyl)-4'-propyl-bicyclohexyl

5 trans/trans-4-(2-p-bromophenyl-ethyl)-4'-butyl-bicyclohexyl

trans/trans-4-(2-p-bromophenyl-ethyl)-4'-hexyl-bicyclohexyl and

10 trans/trans-4-(2-p-bromophenyl-ethyl)-4'-heptyl-bicyclohexyl.

Example 9

A solution of 45.7 g of trans/trans-4-[2-p-(trans-4-chlorocarbonylcyclohexyl)-phenyl-ethyl]-4'-propyl-bicyclohexyl and 8 g of sulfamide in 500 ml of tetramethylene sulfone is heated at 120° for 4 hours and evaporated and the residue is worked up in the customary manner. Trans/trans-4-[2-p-(trans-4-cyanocyclohexyl)-phenyl-ethyl]-4'-propyl-bicyclohexyl is obtained.

The following compounds are obtained analogously from the corresponding acid chlorides:

20 trans/trans-4-[2-p-(trans-4-cyanocyclohexyl)-phenyl-ethyl]-4'-ethyl-bicyclohexyl

trans/trans-4-[2-p-(trans-4-cyanocyclohexyl)-phenyl-ethyl]-4'-butyl-bicyclohexyl

25 trans/trans-4-[2-p-(trans-4-cyanocyclohexyl)-phenyl-ethyl]-4'-pentyl-bicyclohexyl

trans/trans-4-[2-p-(trans-4-cyanocyclohexyl)-phenyl-ethyl]-4'-hexyl-bicyclohexyl

trans/trans-4-[2-p-(trans-4-cyanocyclohexyl)-phenyl-ethyl]-4'-heptyl-bicyclohexyl

30 trans/trans-4-[2-(trans/trans-4'-cyanobicyclohexyl-4-yl)-ethyl]-4'-ethyl-bicyclohexyl

trans/trans-4-[2-(trans/trans-4'-cyanobicyclohexyl-4-yl)-ethyl]-4'-propyl-bicyclohexyl

35 trans/trans-4-[2-(trans/trans-4'-cyanobicyclohexyl-4-yl)-ethyl]-4'-butyl-bicyclohexyl

trans/trans-4-[2-(trans/trans-4'-cyanobicyclohexyl-4-yl)-ethyl]-4'-pentyl-bicyclohexyl

trans/trans-4-[2-(trans/trans-4'-cyanobicyclohexyl-4-yl)-

ethyl]-4'-hexyl-bicyclohexyl and
trans/trans-4-[2-(trans/trans-4'-cyanobicyclohexyl-4-yl)-
ethyl]-4'-heptyl-bicyclohexyl.

Example 10

- 5 A mixture of 41.9 g of trans/trans-4-(2-p-bromo-
phenyl-ethyl)-4'-pentyl-bicyclohexyl, 10 g of $\text{Cu}_2(\text{CN})_2$,
120 ml of pyridine and 60 ml of N-methylpyrrolidone is
heated at 150° for 2 hours. The mixture is cooled, a solu-
10 tion of 120 g of iron(III) chloride hexahydrate in 600 ml
of 20% hydrochloric acid is added and the mixture is warmed
at 70° for 1.5 hours, with stirring, and worked up in the
customary manner to give trans/trans-4-(2-p-cyanophenyl-
ethyl)-4'-pentyl-bicyclohexyl.

- The nitriles mentioned in Examples 4, 9 and 10 (sic)
15 are obtainable analogously, as well as
trans/trans-4-[2-(2-cyano-4-propylphenyl)-ethyl]-4'-propyl-
bicyclohexyl
trans/trans-4-[2-(2-3-difluoro-4-cyanophenyl)-ethyl]-4'-
propyl-bicyclohexyl and
20 trans/trans-4-[2-(2-methyl-4-cyanophenyl)-ethyl]-4'-propyl-
bicyclohexyl.

Example 11

- A mixture of 35.6 g of trans/trans-4-(2-p-hydroxy-
phenyl-ethyl)-4'-pentyl-bicyclohexyl (obtainable by a
25 Wittig reaction from trans/trans-4-bromomethyl-4'-pentyl-
bicyclohexyl and p-hydroxybenzaldehyde to give trans/trans-
4-(2-p-hydroxyphenyl-vinyl)-4'-pentyl-bicyclohexyl and
hydrogenation), 6.9 g of K_2CO_3 , 25 g of hexyl iodide and
250 ml of DMF is heated at 80° for 16 hours, with stirring,
30 and the mixture is then cooled and worked up in the custom-
ary manner. Trans/trans-4-(2-p-hexoxyphenyl-ethyl)-4'-
pentyl-bicyclohexyl is obtained.

- The ethers mentioned in Example 1 are obtained
analogously by etherification, as well as the following
35 compounds:
trans/trans-4-(2-p-pentoxyphenyl-ethyl)-4'-propyl-bicyclo-
hexyl
trans/trans-4-(2-p-pentoxyphenyl-ethyl)-4'-butyl-bicyclo-
hexyl

- trans/trans-4-(2-p-pentoxyphenyl-ethyl)-4'-pentyl-bicyclohexyl
- trans/trans-4-(2-p-hexoxyphenyl-ethyl)-4'-propyl-bicyclohexyl
- 5 trans/trans-4-(2-p-hexoxyphenyl-ethyl)-4'-butyl-bicyclohexyl
- trans/trans-4-(2-p-hexoxyphenyl-ethyl)-4'-pentyl-bicyclohexyl
- trans/trans-4-(2-p-heptoxyphenyl-ethyl)-4'-propyl-bicyclohexyl
- 10 trans/trans-4-(2-p-heptoxyphenyl-ethyl)-4'-butyl-bicyclohexyl
- trans/trans-4-(2-p-heptoxyphenyl-ethyl)-4'-pentyl-bicyclohexyl
- 15 trans/trans-4-(2-p-octoxyphenyl-ethyl)-4'-propyl-bicyclohexyl
- trans/trans-4-(2-p-octoxyphenyl-ethyl)-4'-butyl-bicyclohexyl
- trans/trans-4-(2-p-octoxyphenyl-ethyl)-4'-pentyl-bicyclohexyl
- 20 trans/trans-4-(2-p-nonoxyphehyl-ethyl)-4'-propyl-bicyclohexyl
- trans/trans-4-(2-p-nonoxyphehyl-ethyl)-4'-butyl-bicyclohexyl
- 25 trans/trans-4-(2-p-nonoxyphehyl-ethyl)-4'-pentyl-bicyclohexyl
- trans/trans-4-(2-p-decoxyphenyl-ethyl)-4'-propyl-bicyclohexyl
- trans/trans-4-(2-p-decoxyphenyl-ethyl)-4'-butyl-bicyclohexyl and
- 30 trans/trans-4-(2-p-decoxyphenyl-ethyl)-4'-pentyl-bicyclohexyl.

The following examples relate to dielectrics according to the invention containing at least one compound of the formula I:

35

Example A

Addition of trans/trans-4-(2-p-propylphenyl-ethyl)-4'-propyl-bicyclohexyl ("A") increases the clear point of a mixture ("M") of 29% of p-trans-4-propylcyclohexyl-

benzonitrile, 41% of p-trans-4-pentylcyclohexyl-benzonitrile and 30% of p-trans-4-heptylcyclohexyl-benzonitrile as follows:

	100% "M"	c.p.	52°
5	90% "M" + 10% "A"	c.p.	61°
	80% "M" + 20% "A"	c.p.	70°
	70% "M" + 30% "A"	c.p.	79°

Example B

10 Addition of "A" increases the clear point of a mixture ("N") of 24% of p-trans-4-propylcyclohexyl-benzonitrile, 36% of p-trans-4-pentylcyclohexyl-benzonitrile, 25% of p-trans-4-heptylcyclohexyl-benzonitrile and 15% of 4-cyano-4'-(trans-4-pentylcyclohexyl)-biphenyl as follows:

	100% "N"	c.p.	71°
15	90% "N" + 10% "A"	c.p.	78°
	80% "N" + 20% "A"	c.p.	85°
	70% "N" + 30% "A"	c.p.	93°

Example C

A mixture of

20 17% of "A"

15% of p-trans-4-propylcyclohexyl-benzonitrile

27% of trans-1-p-ethylphenyl-4-propylcyclohexane

10% of trans-2-p-ethoxyphenyl-4-propylcyclohexane

7% of 4-cyano-4'-(trans-4-pentylcyclohexyl)-biphenyl

25 10% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propyl-
cyclohexyl)-biphenyl

8% of p-propylphenyl p-trans-4-propylcyclohexyl-benzoate
and

6% of p-propylphenyl p-trans-4-pentylcyclohexyl-benzoate

30 has a c.p. of 85°.

Example D

A mixture of

19% of "A"

15% of p-trans-4-propylcyclohexyl-benzonitrile

35 12% of p-trans-4-butylcyclohexyl-benzonitrile

14% of trans-1-p-ethylphenyl-4-propylcyclohexane

10% of trans-1-p-ethoxyphenyl-4-propylcyclohexane

6% of 4-cyano-4'-(trans-4-pentylcyclohexyl)-biphenyl

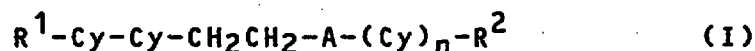
4% of 4,4'-bis-(trans-4-propylcyclohexyl)-biphenyl

- 29 -

- 6% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-propyl-cyclohexyl)-biphenyl
- 8% of p-propylphenyl p-trans-4-propylcyclohexyl-benzoate
and
- 5 6% of p-propylphenyl p-trans-4-pentylcyclohexyl-benzoate
has a c.p. of 100°.

Patent claims:

1. Bicyclohexylethanes of the formula I



wherein R^1 is alkyl, R^2 is alkyl, in which one or two CH_2 groups can be replaced by O atoms, or is F, Cl, Br, CN, $-COOalkyl$ or $-O-CO-alkyl$, and one of the radicals R^1 and R^2 can also be H, A is Cy, or 1,4-phenylene which is unsubstituted or substituted by one or two F and/or Cl atoms and/or CH_3 groups or by a CN group, Cy is 1,4-cyclohexylene and n is 0 or 1, the alkyl groups in each case containing 1 - 10 C atoms, with the provisos that a) n is 1 if A is Cy and R^2 is CN and b) the compounds 1-(4'-trans-pentyl-trans-bicyclohex-4-yl)-2-(2-methyl-4-pentyphenyl)-ethane, 1-(4'-trans-pentyl-trans-bicyclohex-4-yl)-2-(3-methyl-4-pentyphenyl)-ethane, 1-(4'-trans-pentyl-trans-bicyclohex-4-yl)-2-(4-butoxy-2-methylphenyl)-ethane, and 1-(4'-trans-pentyl-trans-bicyclohex-4-yl)-2-(4-butoxy-3-methylphenyl)-ethane, are excluded.

2. Process for the preparation of bicyclohexylethanes of the formula I according to Claim 1, characterised in that a compound which otherwise corresponds to the formula I but contains one or more reducible group(s) and/or additional C-C bond(s) instead of H atoms, is treated with a reducing agent, or in that, for the preparation of esters of the formula I (wherein R^2 is $-COOalkyl$ or $-O-COalkyl$), a corresponding carboxylic acid or one of its reactive derivatives is reacted with a corresponding alcohol or phenol or one of its reactive derivatives, or in that, for the preparation of halogen derivatives of the formula I (wherein R^2 is F, Cl or Br and/or A is 1,4-phenylene which is substituted by one or two F and/or Cl atoms) with aromatically bonded halogen, a corresponding amino compound is diazotised and the diazonium group is then replaced by a fluorine, chlorine or bromine atom by methods which are known per se, or in that, for the preparation of nitriles of the formula I ($R^2 = CN$), a corresponding carboxylic



acid amide is dehydrated or a corresponding carboxylic acid halide is reacted with sulfamide, or in that, for the preparation of ethers of the formula I (wherein R^2 is an alkyl group in which one or two CH_2 groups are replaced by O atoms), a corresponding hydroxy compound is etherified, and/or in that, if appropriate, a chlorine or bromine compound of the formula I (wherein R^2 is Cl or Br and/or wherein A denotes a 1,4-phenylene radical which is substituted by one or two Cl atoms) is reacted with a cyanide.

3. Use of the compounds of the formula I according to Claim 1 as components of liquid crystal dielectrics.

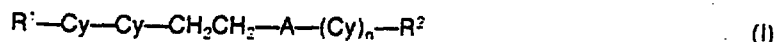
4. Liquid crystal dielectric containing at least one compound of the formula I according to Claim 1.

5. Electrooptical display element, characterised in that it contains a dielectric according to Claim 4.



Claims (as printed)

1. Bicyclohexylethanes of the formula I



wherein

R¹ is alkyl.

R² is alkyl, in which one or two CH₂

groups can be replaced by O atoms, or is F, Cl, Br, CN, —COOalkyl or O—CO-alkyl,

and one of the radicals R¹ and R² can also be H.

A is Cy, or 1,4-phenylene which is unsubstituted or substituted by one or two F and/or Cl atoms and/or CH₂ groups or by a CN group.

Cy is 1,4-cyclohexylene and

n is 0 or 1.

the alkyl groups in each case containing 1-10 C atoms, with the proviso that

a) n is 1 if A is Cy and R² is CN and

b) the compounds

1-(4'-trans-pentyl-trans-bicyclohex-4-yl)-2-(2-methyl-4-pentylphenyl)-ethane

1-(4'-trans-pentyl-trans-bicyclohex-4-yl)-2-(3-methyl-4-pentylphenyl)-ethane

1-(4'-trans-pentyl-trans-bicyclohex-4-yl)-2-(4-butoxy-2-methylphenyl)-ethane

1-(4'-trans-pentyl-trans-bicyclohex-4-yl)-2-(4-butoxy-3-methylphenyl)-ethane

are excluded.

2. Process for the preparation of bicyclohexylethanes of the formula I according to Claim 1, characterised in that a compound which otherwise corresponds to the formula I but contains one or more reducible group(s) and/or additional C—C bond(s) instead of H atoms, is treated with a reducing agent, or in that, for the preparation of esters of the formula I (wherein R² is —COOalkyl or —O—COalkyl), a corresponding carboxylic acid or one of its reactive derivatives is reacted with a corresponding alcohol or phenol or one of its reactive derivatives, or in that, for the preparation of halogen derivatives of the formula I (wherein R² is F, Cl or Br and/or A is 1,4-phenylene which is substituted by one or two F and/or Cl atoms) with aromatically bonded halogen, a corresponding amino compound is diazotised and the diazonium group is then replaced by a fluorine, chlorine or bromine atom by methods which are known per se, or in that, for the preparation of nitriles of the formula I (R²=CN), a corresponding carboxylic acid amide is dehydrated or a corresponding carboxylic acid halide is reacted with sulfamide, or in that, for the preparation of ethers of the formula I (wherein R² is an alkyl group in which one or two CH₂ groups are replaced by O atoms), a corresponding hydroxy compound is etherified, and/or in that, if appropriate, a chlorine or bromine compound of the formula I (wherein R² is Cl or Br and/or wherein A denotes a 1,4-phenylene radical which is substituted by one or two Cl atoms) is reacted with a cyanide.

3. Use of the compounds of the formula I according to Claim 1 as components of liquid crystal dielectrics.

4. Liquid crystal dielectric containing at least one compound of the formula I according to Claim 1.

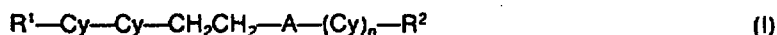
5. Electrooptical display element, characterised in that it contains a dielectric according to Claim 4.



Revendications (as printed)

0,125,563

1. Bicyclohexyléthanes de formule I



dans laquelle

R^1 représente un groupe alkyle.

R^2 représente un groupe alkyle dans lequel un ou deux groupes CH_2 peuvent être remplacés par des atomes d'oxygène, F, Cl, Br, CN, un groupe $-COO$ -alkyle ou $-O-CO$ -alkyle.

l'un des symboles R^1 et R^2 pouvant également représenter l'hydrogène.

A représente le groupe Cy ou un groupe 1,4-phénylène non substitué ou substitué par 1 ou 2 atomes de F et/ou Cl et/ou groupes CH_3 ou par un groupe CN.

Cy représente le groupe 1,4-cyclohexylène, et

n est égal à 0 ou 1.

les groupes alkyle contenant chacun 1 à 10 atomes de carbone, avec les restrictions suivantes :

a) n est égal à 1 lorsque A représente Cy et R^2 représente CN, et

b) les composés :

1-(4'-trans-pentyl-trans-bicyclohexa-4-yl)-2-(2-méthyl-4-pentylphényl)-éthane.

1-(4'-trans-pentyl-trans-bicyclohexa-4-yl)-2-(3-méthyl-4-pentylphényl)-éthane.

1-(4'-trans-pentyl-trans-bicyclohexa-4-yl)-2-(4-butoxy-2-méthylphényl)-éthane.

1-(4'-trans-pentyl-trans-bicyclohexa-4-yl)-2-(4-butoxy-3-méthylphényl)-éthane

sont exclus.

2. Procédé de préparation des bicyclohexyléthanes de formule I selon la revendication 1, caractérisé en ce que l'on traite un composé répondant par ailleurs à la formule I, mais contenant un ou plusieurs groupes réductibles et/ou une ou plusieurs liaisons C—C supplémentaires à la place d'atomes d'hydrogène, par un agent réducteur, ou bien, pour préparer les esters de formule I (dans laquelle R^2 représente un groupe $-COO$ -alkyle ou $-O-CO$ -alkyle) on fait réagir un acide carboxylique correspondant ou l'un de ses dérivés réactifs avec un alcool ou phénol correspondant ou l'un de leurs dérivés réactifs, ou bien, pour préparer les dérivés halogénés de formule I (dans laquelle R^2 représente F, Cl ou Br et/ou A représente un groupe 1,4-phénylène substitué par 1 ou 2 atomes de F et/ou Cl) portant des halogènes à liaisons aromatiques, on diazote un composé aminé correspondant puis on remplace le groupe diazonium, selon des procédés connus en soi, par un atome de fluor, de chlore ou de brome, ou bien, pour préparer les nitriles de formule I ($R^2=CN$), on déshydrate un carboxamide correspondant ou on fait réagir un halogénure d'acide carboxylique correspondant avec le sulfonamide, ou bien, pour préparer les éthers de formule I (dans laquelle R^2 représente un groupe alkyle dans lequel 1 ou 2 groupes CH_2 sont remplacés par des atomes d'oxygène), on éthérifie un composé hydroxylé correspondant, et/ou le cas échéant, on fait réagir un composé chloré ou bromé de formule I (dans laquelle R^2 représente Cl ou Br et/ou dans laquelle A représente un groupe 1,4-phénylène substitué par 1 ou 2 atomes de chlore) avec un cyanure.

3. Utilisation des composés de formule I selon la revendication 1, en tant que composants de diélectriques à cristaux liquides.

4. Diélectrique à cristaux liquides contenant au moins un composé de formule I selon la revendication 1.

5. Élément d'affichage électro-optique, caractérisé en ce qu'il contient un diélectrique selon la revendication 4.

