

"Cyclohexylphenyl derivatives".

The present invention is concerned with cyclohexylphenyl derivatives, dielectrics containing them and electro-optical indicator elements.

For electro-optical indicator elements, the properties of nematic or nematic-cholesteric liquid crystalline materials of significantly changing their optical properties, such as light absorption, light scattering, birefringence, reflectivity or colour under the influence of electric fields, are widely utilised. The function of such indicator elements depends, for example, on the phenomena of dynamic scattering, the deformation of aligned phases, the Schadt-Helfrich effect in the twisted cell or the cholesteric-nematic phase transition.

For the technical use of these effects in electronic constructional elements, liquid crystalline dielectrics are needed which must satisfy a number of requirements, the chemical stability towards moisture, air and physical influences, such as heat, radiation in the infra-red, visible and ultra-violet range and electric direct and alternating fields being especially important. Furthermore, technically usable liquid crystalline dielectrics are to have a liquid crystalline mesophase in the temperature range of at least $+10^{\circ}\text{C.}$ to $+50^{\circ}\text{C.}$ and preferably of 0°C. to 60°C. , and the lowest possible viscosity at ambient temperature, which is preferably not more than 70×10^{-3} Pa.s. Finally,

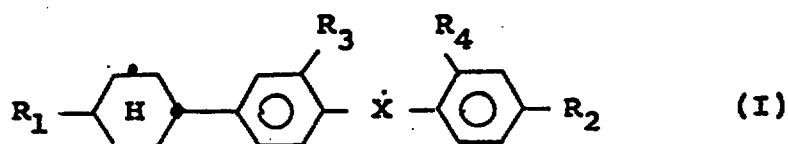
in the range of the visible light, they should not display any inherent absorption, i.e. they must be colourless.

A number of liquid crystalline compounds is already known which satisfy the stability requirements demanded of dielectrics for electronic constructional elements and are also colourless. These include, in particular, the *p,p'*-disubstituted benzoic acid phenyl esters described in Federal Republic of Germany Patent Specification No.2,139,628 and the *p,p'*-disubstituted phenylcyclohexane derivatives described in Federal Republic of Germany Patent Specification No.2,636,684. Both of the mentioned classes of compounds, as well as other known series of compounds with a liquid crystalline mesophase, do not contain individual compounds which, in the required temperature range of 10°C. to 60°C. form a liquid crystalline nematic mesophase. Therefore, as a rule, mixtures of two or more compounds are prepared in order to obtain materials which can be used as liquid crystalline dielectrics. For this purpose, at least one compound with a low melting or clear point is usually mixed with another compound with a distinctly higher melting and clear point, a mixture thereby normally being obtained, the melting point of which lies below that of the lower melting component, whereas the clear point lies between the clear points of the components. Nevertheless, the

preparation of dielectrics with optimum properties still causes difficulties since the components with the high melting and clear points frequently also impart a high viscosity to the mixtures, the operating
 5 times of the electro-optical indicator elements produced therewith thereby being undesirably prolonged. Furthermore, problems often arise due to the fact that the solubility of the various components in one another, especially at ambient temperature or at
 10 lower temperatures, is only very limited.

It is an object of the present invention to provide liquid crystalline dielectrics which have a nematic phase in the required temperature range and enable sufficiently short operating times in liquid
 15 crystal cells to be obtained at ambient temperature.

We have now found that the trans-cyclohexyl-phenyl derivatives of the general formula :-



wherein X is a $-\text{CH}_2-\text{CH}_2-$, $-\text{CH}_2-\text{O}-$, $-\text{CH}_2-\text{S}-$, $-\text{O}-\text{CH}_2-$ or $-\text{S}-\text{CH}_2-$ radical, R_1 is an alkyl radical containing
 20 up to 8 carbon atoms, R_2 is an alkyl or alkoxy radical containing up to 8 carbon atoms or a fluorine, chlorine or bromine atom or a cyano group and R_3 and R_4 are hydrogen atoms or one of these symbols also represents

a fluorine, chlorine or bromine atom or a cyano group, with the proviso that R_3 and R_4 both represent hydrogen atoms when X is a $-\text{CH}_2-\text{CH}_2-$ radical or R_2 is a fluorine, chlorine or bromine atom or a cyano group, are outstandingly useful as components of liquid crystalline dielectrics.

The compounds of general formula (I) have an extraordinarily wide range of usefulness: depending upon the selection of the substituents, the compounds of general formula (I) can be used not only as base materials of which liquid crystalline dielectrics are exclusively or preponderantly composed but compounds of general formula (I) can also be added in smaller proportions of, for example, 2 to 45 weight percent, to liquid crystalline base materials of other classes of compounds in order to obtain dielectrics with a wider liquid crystalline mesophase or to influence the degree of the dielectric anisotropy of such a dielectric.

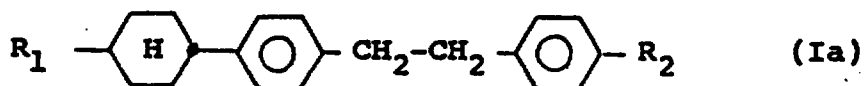
By appropriate selection of the substituents R_1 to R_4 , with the compounds of general formula (I) there can be produced not only dielectrics with an outstandingly positive dielectric anisotropy for use in indicator elements based on the twisted nematic cell or on the cholesteric-nematic phase transition but there can also be produced dielectrics with a dielectric anisotropy only very little different from zero or even

with a negative dielectric anisotropy which may be used in indicator elements based upon dynamic scattering or upon the deformation of aligned phases (DAP effect).

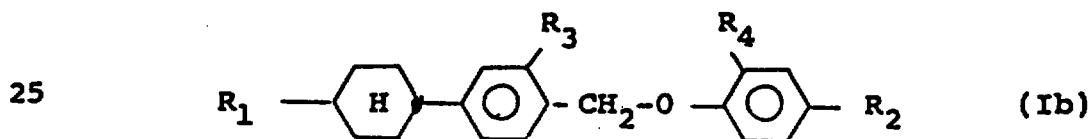
5 In a pure state, the compounds of general formula (I) are colourless and form nematic mesophases over an extremely broad temperature range which lies favourably for electro-optical use.

Thus, the present invention is concerned with
10 the trans-cyclohexylphenyl derivatives of general formula (I) and with the use thereof as components of liquid crystalline dielectrics. The present invention is also concerned with liquid crystalline dielectrics containing at least one trans-cyclohexyl-
15 phenyl derivative of general formula (I), as well as with electro-optical indicator elements based on a liquid crystal cell which contains such a liquid crystalline dielectric.

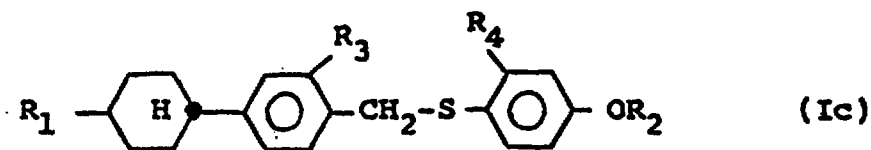
The trans-cyclohexylphenyl derivatives according to the present invention include the trans-1,2-diphenylethane derivatives of the general formula:-



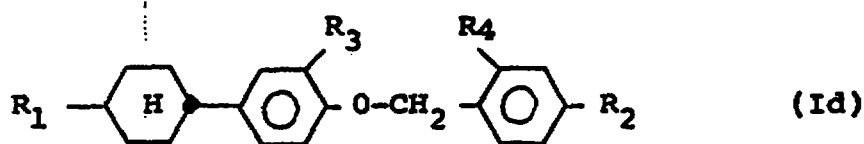
the 4-(trans-4-alkylcyclohexyl)-benzyl phenyl ethers of the general formula:-



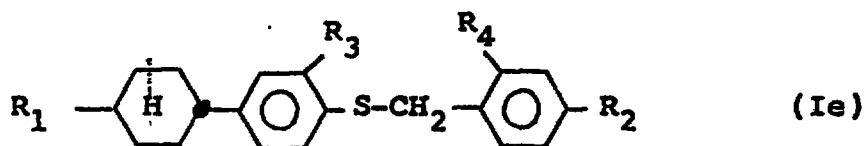
the 4-(trans-4-alkylcyclohexyl)-benzyl phenyl thioethers of the general formula:-



the benzyl-4-(trans-4-alkylcyclohexyl)-phenyl ethers of the general formula:-



and the benzyl-4-(trans-4-alkylcyclohexyl)-phenyl thioethers of the general formula:-



the substituents R_1 to R_4 having the same meanings as in general formula (I). The trans-position of the substituents in the 1- and 4-positions of the cyclohexane ring is indicated in the structural formulae by a black spot on the right side of the ring.

The 1,2-diphenylethane derivatives of general formula (Ia) have a dielectric anisotropy with a value of about zero when R_2 signifies an alkyl or alkoxy radical. If, on the other hand, R_2 signifies a fluorine, chlorine or bromine atom or a cyano group, the compounds of general formula (Ia) have a distinctly

positive dielectric anisotropy; these materials and especially those in which R_2 signifies a fluorine atom or a cyano group are mainly used for indicator elements based on the twisted cell.

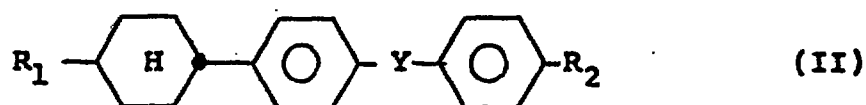
Insofar as R_3 and R_4 in the ether or thioether derivatives of general formulae (Ib) to (Ie) signify hydrogen atoms, the properties of these compounds with regard to the dielectric anisotropy are similar to those of the correspondingly substituted compounds of general formula (Ia). If, however, R_3 and R_4 in a compound of general formulae (Ib) to (Ie) signify fluorine, chlorine, bromine or cyano and R_2 is accordingly an alkyl or alkoxy radical, these compounds have, as a rule, a negative dielectric anisotropy; they are, therefore, preferably used in dielectrics for indicator elements based on dynamic scattering. In the benzyl ether or benzyl thioether derivatives of general formula (Ib) to (Ie), the substituent R_3 and R_4 which is in the ortho-position to the benzylic methylene group preferably always signifies a hydrogen atom.

In the compounds of general formula (I), the alkyl radical R_1 , as well as the alkyl or alkoxy radical R_2 , can be straight-chained or branched. When it is straight-chained, i.e. is a methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl or n-octyl radical, the compounds usually have higher clear points

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than those with branched radicals R_1 and/or R_2 . Consequently, usually at most one of the side chains R_1 and R_2 contains a branched carbon chain. Compounds of general formula (I) with a branched side chain R_1 or R_2 are sometimes of importance because of a better solubility in the usual liquid crystalline base materials but especially as chiral doping materials if, because of their chain branching, they possess optical activity. Such branched side chains contain not more than one chain branching. Preferred branched hydrocarbon radicals R are those in which, in a comparatively long carbon chain, a methyl or ethyl radical is present in the 1-, 2- or 3-position, for example 2-methylpropyl, 2-methylbutyl, 3-methylbutyl, 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl or 1-methylhexyl. When R_2 is an alkyl or alkoxy radical, the side chains R_1 and R_2 together contain up to 16 carbon atoms, preferred compounds according to the present invention including those in which R_1 and R_2 together contain 3 to 13 and especially 4 to 11 carbon atoms.

The compounds according to the present invention are prepared in the usual way for such compounds. Thus, for example, a 1-[4-(trans-4-alkylcyclohexyl)-phenyl]-2-(4- R_2 -phenyl)-ethane of general formula (Ia) is obtained by reducing a compound of general formula:-

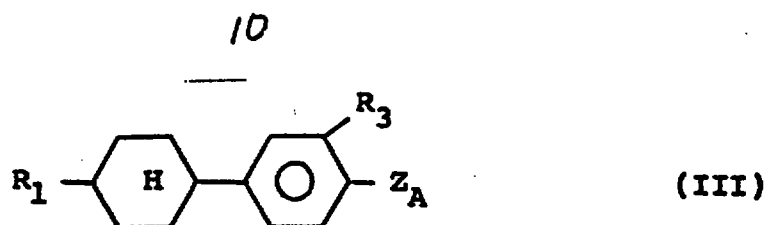


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wherein Y is a $-\text{CH}_2-\text{CO}-$, $-\text{CO}-\text{CH}_2-$ or $-\text{CH}=\text{CH}-$ radical and R_1 and R_2 have the same meanings as in general formula (I), in known manner, for example by catalytic hydrogenation. The catalyst used for this purpose is preferably a finely-divided platinum group metal, for example palladium precipitated on to active charcoal. The hydrogenation can be carried out by passing hydrogen into a solution of a compound of general formula (I) at ambient temperature and atmospheric pressure; as solvents, those are preferably used which, under the reaction conditions, do not themselves react, for example, lower alcohols, such as ethanol, or aromatic hydrocarbons, such as toluene. The starting compounds of general formula (II) can be prepared in known manner. Thus, the benzyl ketones (II, Y = $-\text{CO}-\text{CH}_2-$ or $-\text{CH}_2-\text{CO}-$) can be prepared by a Friedel-Crafts reaction from a 4-(trans-4-alkylcyclohexyl)-phenylacetic acid halide and an R_2 -benzene or from a 4- R_2 -phenylacetic acid halide and a (trans-4-alkylcyclohexyl)-benzene; and the stilbenes (II, Y = $-\text{CH}=\text{CH}-$) can be obtained by reacting a 4-(trans-4-alkylcyclohexyl)-benzyl magnesium halide with a 4- R_2 -benzaldehyde, followed by hydrolysis and splitting off water.

The benzyl ethers or benzyl thioethers of general formulae (Ib) to (Ie) are prepared by reacting a compound of the general formula:-



wherein R_1 and R_3 have the same meanings as above and Z_A is OH, OMe, SH, SMe or $-\text{CH}_2\text{-Hal}$, Me being one equivalent of a metal cation and Hal being a halogen atom, preferably a chlorine or bromine atom, in the presence of a base with a compound of the general formula:-



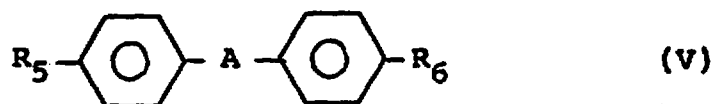
wherein R_2 and R_4 have the same meanings as above and Z_B is $-\text{CH}_2\text{-Hal}$ when Z_A is OH, OMe, SH or SMe or Z_B is OH, OMe, SH or SMe when Z_A is $-\text{CH}_2\text{-Hal}$. The reaction conditions for preparing these ethers or thioethers from compounds of general formulae (III) and (IV) are those conventionally used for such reactions. As solvents there are used polar, aprotic ones, for example dimethyl sulphoxide, N,N-dimethylformamide or N-methylpyrrolidone and as bases there are preferably used alkali metal salts of weak acids, for example sodium acetate, potassium carbonate or sodium carbonate. The reactions can be carried out at temperatures of from 0°C . to the boiling point of the lowest boiling component of the reaction mixture, it having proved to be especially advantageous to use temperatures of

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from 60 to 120°C. Some of the starting materials of general formulae (III) and (IV) are known and the others can be prepared analogously to known compounds by standard processes of synthetic organic chemistry. Thus, the phenols of general formulae (III) or (IV) ($Z_A, Z_B = OH$) are known when R_3 and R_4 are hydrogen atoms and the corresponding o-chloro- and o-bromophenols are prepared by simple nuclear halogenation of these phenols. The o-cyanophenols can be prepared by reacting the o-bromophenols with copper(I) cyanide in pyridine. Finally, the o-fluorophenols are obtained by nitrating a phenol protected on the hydroxyl group, for example an acetylphenol, and subsequently reducing to give the o-aminoacetylphenol in which the amino group is then exchanged for a fluorine atom by diazotisation in the presence of a tetrafluoroborate and thermal decomposition of the diazonium tetrafluoroborate. The benzyl halides, preferably benzyl chlorides of general formula (III) or (IV) ($Z_A, Z_B = CH_2Cl$), are prepared in an equally conventional manner by reacting the corresponding benzene derivative with paraformaldehyde and hydrogen chloride in the presence of hydrochloric acid. Finally, the thiophenols of general formulae (III) or (IV) are obtained either by reducing the corresponding sulphochlorides or by converting the corresponding phenols into the thiophenols by esterification with dimethylthionocarbamoyl chloride, isomer-

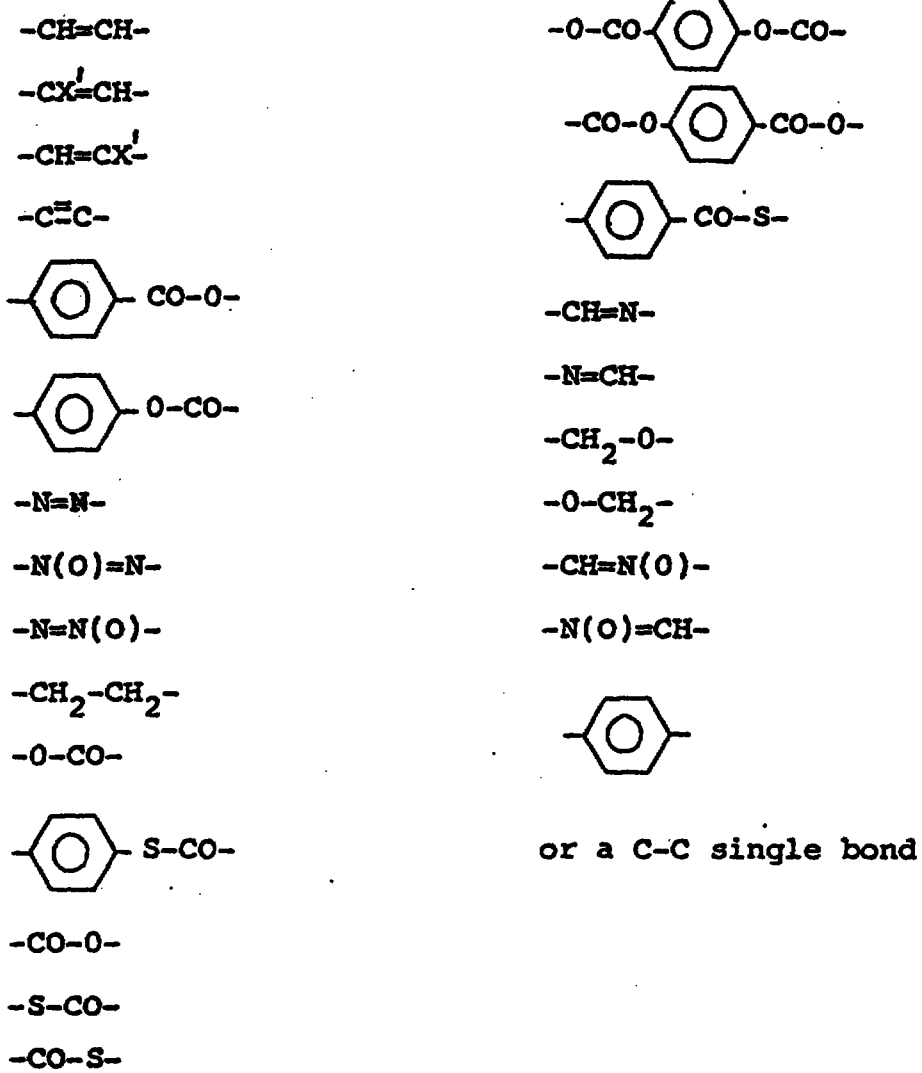
ising to give the dimethylthiocarbamic acid S-phenyl esters and subsequently splitting hydrolytically.

The liquid crystalline dielectrics according to the present invention comprise two or more components, including at least one of general formula (I); however, dielectrics according to the present invention can consist exclusively of compounds of general formula (I), apart from possibly additionally present doping or additive materials, which themselves need not necessarily be liquid crystalline materials. Further components possibly employed are preferably nematic or nematogenic compounds selected from the azobenzenes, azoxybenzenes, biphenyls, optionally partly hydrogenated terphenyls and quaterphenyls, Schiff bases, especially benzylidene derivatives, phenyl benzoates, phenylpyrimidines, phenylcyclohexanes, optionally halogenated stilbenes, diphenylacetylene derivatives, diphenyl nitrones, phenyl- and cyclohexylnaphthalenes, which can also be partly hydrogenated in the naphthalene moiety or contain nitrogen atoms, as well as substituted cinnamic acids. The most important compounds which can be considered as such further components can be characterised by the general formula:-



wherein A is

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and X' is a halogen atom, preferably a chlorine atom, or a cyano group and R₅ and R₆, which can be the same or different, signify alkyl, alkoxy, alkanoyl, alkanoyloxy or alkoxy carbonyloxy radicals containing up to 18 and preferably up to 8 carbon atoms or one of these symbols can also signify a trans-4-alkylcyclohexyl radical or -CN, -NC, NO₂, CF₃ or halogen.

Further possible components of the dielectrics according to the present invention are those compounds of general formula (V) in which one or more phenyl

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rings are replaced by a corresponding number of trans-cyclohexyl rings; furthermore, one of these rings can also be a 2,5-disubstituted pyrimidine ring, an optionally partly hydrogenated 2,6-disubstituted naphthalene radical or a quinazoline system.

In the case of most of these compounds, R_5 and R_6 are preferably different, one of the symbols usually signifying an alkyl or alkoxy radical. However, a large number of other variants of the substituents is also possible. Many such substances are commercially available.

As a rule, the dielectrics according to the present invention contain at least 30, preferably 50 to 99, especially 60 to 98 parts by weight of the compounds of general formula (I) and possibly (V). Of this, preferably at least 5 parts by weight, but usually 10 or more parts by weight are one or more compounds of general formula (I). The present invention also includes those liquid crystalline dielectrics to which have been added, for example for doping purposes, only less than 5 parts by weight, for example 0.1 to 3 parts by weight, of one or more compounds of general formula (I).

The dielectrics according to the present invention are prepared in the usual manner. As a rule, the desired amount of the components used in lesser amount is dissolved in the components making up the main

component, preferably at an elevated temperature. When a temperature above the clear point of the main component is used, the completeness of the dissolving can be observed especially easily.

However, it is also possible to mix solutions of the components of general formula (I) and possibly of general formula (V) in an appropriate organic solvent, for example acetone, chloroform or methanol, and again to remove the solvent after thorough mixing, for example by distillation under reduced pressure. Of course, in the case of this method, care must be taken that no impurities or undesired doping materials are entrained by the solvent.

By means of appropriate additives, the liquid crystalline dielectrics according to the present invention can be modified in such a manner that they can be employed in all previously known kinds of liquid crystal indicator elements. Such additives are well known and are described in detail in the appropriate literature. For example, substances can be added for changing the dielectric anisotropy, the optical anisotropy, the viscosity, the conductivity and/or the orientation of the nematic phases. Such substances are described, for example, in Federal Republic of Germany Patent Specifications Nos. 2,209,127; 2,240,864; 2,321,632; 2,338,281; 2,535,046; 2,637,430; 2,702,598; 2,900,312 and 3,000,375.

The following Examples are given for the purpose of illustrating the present invention. In the Examples, m.p. means the melting point and K the clear point of a liquid crystalline substance in degrees Celsius; boiling temperatures are indicated by b.p. If nothing is stated to the contrary, the parts and percentages are by weight.

Example 1.

(a) A solution of 61 g. 4-(trans-4-n-propyl-cyclohexyl)-acetophenone in 350 ml. ethanol is mixed with a solution of 28 g. hydroxylammonium chloride in 460 ml. of water and the mixture, after the addition of a solution of 39 g. potassium hydroxide in 39 ml. water, is boiled under reflux for 2 hours. After cooling, the reaction mixture is diluted with 2 litres of cold water and the precipitated 4-(trans-4-n-propyl-cyclohexyl)-acetophenone oxime is filtered off, washed with water and dried in a vacuum for 24 hours at 90°C.; yield 67 g.

(b) 130 g. 4-(trans-4-n-Propylcyclohexyl)-acetophenone oxime are introduced portionwise into a suspension of 125 g. phosphorus pentachloride in 500 ml. dichloromethane, with stirring and cooling to 20 to 25°C. After subsequently stirring for 2 hours, the reaction mixture is mixed with 1000 ml. of water and the dichloromethane is distilled off azeotropically. Subsequently, the reaction mixture is mixed with

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250 ml. of 37% aqueous hydrochloric acid and boiled for 1 hour. After cooling to 20°C., the precipitated 4-(trans-4-n-propylcyclohexyl)-aniline hydrochloride is filtered off, washed with water and dried; yield 120 g.

(c) 76 g. 4-(trans-4-n-Propylcyclohexyl)-aniline hydrochloride are suspended in a mixture of 350 ml. of water and 60 g. concentrated sulphuric acid. A solution of 21 g. sodium nitrite in 120 ml. of water is slowly added dropwise, with stirring, in the temperature range of 0 to 5°C. and the reaction mixture then subsequently stirred for 1 hour. It is subsequently mixed with 450 ml. methanol and slowly heated to 70°C. After gas evolution has ended, the reaction mixture is again cooled to 0°C. and the precipitated 4-(trans-4-n-propylcyclohexyl)-phenol is filtered off, dried and recrystallised from methanol; yield 35 g.

(d) A mixture of 11 g. 4-(trans-4-n-propylcyclohexyl)-phenol, 9.8 g. 4-cyanobenzyl bromide, 7.6 g. potassium carbonate and 50 ml. dimethylformamide is heated to 85°C. for 8 hours. After cooling, the reaction mixture is diluted with 100 ml. of water and extracted three times with a total of 200 ml. dichloromethane. The combined extracts are washed with water, dried over anhydrous sodium sulphate and evaporated. The 4-(trans-4-n-propylcyclohexyl)-phenyl-(4-cyano-

benzyl)-ether remaining behind is recrystallised from ethanol; m.p. $93^{\circ}\text{C}.$; K $138^{\circ}\text{C}.$, dielectric anisotropy $\Delta\epsilon = +16.8$.

The following compounds are prepared analogously:-

4-(trans-4-ethylcyclohexyl)-phenyl-(4-cyanobenzyl) ether,

4-(trans-4-n-hexylcyclohexyl)-phenyl-(4-cyanobenzyl)
ether,

4-(trans-4-n-propylcyclohexyl)-phenyl-(4-fluorobenzyl)
ether,

4-(trans-4-n-pentylcyclohexyl)-phenyl-(4-fluorobenzyl)
ether,

4-(trans-4-methylcyclohexyl)-phenyl-(4-n-pentyloxy-
benzyl) ether,

4-(trans-4-n-butylcyclohexyl)-phenyl-(4-ethoxybenzyl)
ether,

4-(trans-4-n-heptylcyclohexyl)-phenyl-(4-ethylbenzyl)
ether,

4-(trans-4-ethylcyclohexyl)-phenyl-(4-n-hexylbenzyl)
ether.

Example 2.

(a) 33 g. 4-(trans-4-n-Propylcyclohexyl)-benzene-sulphochloride are added portionwise to a suspension of 36 g. zinc dust in 100 ml. of water at $50^{\circ}\text{C}.$, with stirring, in such a manner that the temperature of the reaction mixture does not exceed $60^{\circ}\text{C}.$ After completion of the addition of the sulphochloride, a further 5 g. of zinc dust are added thereto and the reaction mixture is

heated for 10 minutes to 70°C. After cooling to 15°C., a solution of 250 g. of 37% aqueous hydrochloric acid in 100 ml. of water is added dropwise and the reaction mixture is stirred overnight at ambient temperature. Subsequently, a further 25 g. of zinc dust are added thereto and the mixture is boiled for 4 hours. After cooling, the 4-(trans-4-n-propylcyclohexyl)-thiophenol formed is extracted with diethyl ether. The extracts are washed with water, dried over anhydrous sodium sulphate and evaporated, the thiophenol remaining behind being distilled in a vacuum; b.p. 196°C./0.05 mbar.

(b) Hydrogen chloride gas is passed into a mixture of 9.6 g. paraformaldehyde and 40 ml. of 37% aqueous hydrochloric acid until a clear solution is formed. Subsequently, a solution of 30 g. n-butyloxybenzene in 20 ml. benzene is added dropwise at 15 - 20°C. and the reaction mixture is stirred for 4 hours at this temperature. The organic phase is separated off, washed twice with 30 ml. amounts of water, dried and distilled. After distilling off of the benzene, there are obtained 27 g. 4-n-butyloxybenzyl chloride; b.p. 102°C./1 mbar.

(c) Analogously to Example 1(d), from 23 g. 4-(trans-4-n-propylcyclohexyl)-thiophenol and 20 g. 4-n-butyloxybenzyl chloride, there are obtained 31 g. 4-(trans-4-n-propylcyclohexyl)-phenyl-4-n-butyloxybenzyl) thioether.

The following compounds are prepared analogously:-

4-(trans-4-n-propylcyclohexyl)-phenyl-(4-ethoxybenzyl)

thioether,

4-(trans-4-ethylcyclohexyl)-phenyl-(4-n-butyloxybenzyl)

thioether,

4-(trans-4-methylcyclohexyl)-phenyl-(4-n-hexyloxybenzyl)

thioether,

4-(trans-4-n-butylcyclohexyl)-phenyl-(4-n-butylbenzyl)

thioether,

4-(trans-4-n-hexylcyclohexyl)-phenyl-(4-methylbenzyl)

thioether,

4-(trans-4-n-pentylcyclohexyl)-phenyl-(4-fluorobenzyl)

thioether,

4-(trans-4-n-propylcyclohexyl)-phenyl-(4-fluorobenzyl)

thioether,

4-(trans-4-n-butylcyclohexyl)-phenyl-(4-chlorobenzyl)

thioether,

4-(trans-4-ethylcyclohexyl)-phenyl-(4-bromobenzyl)

thioether,

4-(trans-4-n-propylcyclohexyl)-phenyl-(4-cyanobenzyl)

thioether,

4-(trans-4-n-pentylcyclohexyl)-phenyl-(4-cyanobenzyl)

thioether.

Example 3.

A suspension of 11 g. 4-(trans-4-n-propylcyclohexyl)-phenol in 80 ml. dichloromethane is mixed dropwise at 0°C. with a solution of 8 g. bromine in 20 ml.

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dichloromethane, subsequently stirred for 1 hour and then mixed with 200 ml. of water. The organic phase is separated off, washed with dilute sodium bisulphite solution, dried over anhydrous sodium sulphate and evaporated in a vacuum. The 4-(trans-4-n-propylcyclohexyl)-2-bromophenol remaining behind is heated for 3 hours at 95°C. with 4-methoxybenzyl chloride, 7.6 g. potassium carbonate and 50 ml. dimethylformamide. After cooling, the reaction mixture is diluted with 100 ml. of water and extracted with 150 ml. dichloromethane. The combined dichloromethane extracts are washed with water and evaporated in a vacuum. The 4-(trans-4-n-propylcyclohexyl)-2-bromophenyl-(4-methoxybenzyl) ether remaining behind is recrystallised from ethanol; m.p. 65°C.; K 74.5°C.; $\Delta\epsilon = -2.3$.

The following compounds are prepared analogously:-

4-(trans-4-n-butylcyclohexyl)-2-bromophenyl-(4-n-butylbenzyl) ether,

4-(trans-4-n-butylcyclohexyl)-2-chlorophenyl-(4-n-hexyloxybenzyl) ether,

4-(trans-4-ethylcyclohexyl)-2-chlorophenyl-(4-n-hexylbenzyl) ether.

Example 4.

(a) 61 g. 4-(trans-4-n-Propylcyclohexyl)-2-bromophenol are dissolved in 200 ml. toluene and the solution is boiled for 2 hours with 25 g. acetic anhydride, with the addition of 1 ml. concentrated

sulphuric acid. The reaction mixture is washed neutral with aqueous sodium hydrogen carbonate solution, dried over anhydrous sodium sulphate and evaporated. The 4-(trans-4-n-propylcyclohexyl)-2-bromophenyl acetate remaining behind is recrystallised from ethanol; yield 65.9 g.

(b) 65 g. 4-(trans-4-n-Propylcyclohexyl)-2-bromophenyl acetate and 18 g. cuprous cyanide are heated to 160°C. for 2 hours in 360 ml. of a mixture of pyridine and N-methylpyrrolidone (2:1 v/v). After cooling, a solution of 250 g. ferric trichloride hexahydrate in 1.2 litres of 20% hydrochloric acid is added thereto and the mixture is heated, with stirring, to 70°C. After cooling, it is extracted 5 times with 400 ml. amounts of diethyl ether. The extracts are washed with aqueous sodium hydrogen carbonate solution and water, dried over anhydrous sodium sulphate and evaporated. The 4-(trans-4-n-propylcyclohexyl)-2-cyanophenyl acetate remaining behind is recrystallised from ethanol; yield: 34 g.

(c) 34 g. 4-(trans-4-n-Propylcyclohexyl)-2-cyanophenyl acetate are boiled for 30 minutes with 150 ml. 10% aqueous potassium hydroxide solution. The mixture is then acidified with dilute hydrochloric acid and the precipitated 4-(trans-4-n-propylcyclohexyl)-2-cyanophenol is filtered off and recrystallised from methanol; yield: 28.5 g.

(d) 28 g. 4-(trans-4-n-Propylcyclohexyl)-2-cyanophenol are etherified, analogously to Example 1(d), with 26.4 g. 4-n-propyloxybenzyl bromide, 39 g. 4-(trans-4-n-propylcyclohexyl)-2-cyanophenyl-(4-n-propyloxybenzyl) ether being obtained.

The following compounds are prepared analogously:-
4-(trans-4-ethylcyclohexyl)-2-cyanophenyl-(4-n-heptylbenzyl) ether,
4-(trans-4-n-pentylcyclohexyl)-2-cyanophenyl-(4-ethylbenzyl) ether.

Example 5.

31.5 g. 4-(trans-4-n-Propylcyclohexyl)-2-bromothiophenol [prepared from 4-(trans-4-n-propylcyclohexyl)-2-bromophenol, obtained according to Example 3, by reaction with dimethylthiocarbamoyl chloride, thermal rearrangement and hydrolysis analogously to the procedure described in Organic Syntheses, 51, 139-142/1972] are etherified with 21.5 g. 4-ethoxybenzyl bromide analogously to Example 1(d) to give 40.2 g. 4-(trans-4-n-propylcyclohexyl)-2-bromophenyl-(4-ethoxybenzyl) thioether.

The following compounds are prepared analogously:-
4-(trans-4-n-pentylcyclohexyl)-2-bromophenyl-(4-ethylbenzyl) thioether,
4-(trans-4-n-hexylcyclohexyl)-2-chlorophenyl-(4-n-propylbenzyl) thioether,

- 4-(trans-4-methylcyclohexyl)-2-chlorophenyl-(4-n-hexyloxybenzyl) thioether,
4-(trans-4-ethylcyclohexyl)-2-fluorophenyl-(4-n-pentylbenzyl) thioether,
4-(trans-4-n-propylcyclohexyl)-2-fluorophenyl-(4-n-butyloxybenzyl) thioether,
4-(trans-4-n-propylcyclohexyl)-2-cyanophenyl-(4-n-butyloxybenzyl) thioether,
4-(trans-4-n-butylcyclohexyl)-2-cyanophenyl-(4-n-pentylbenzyl) thioether,
4-(trans-4-n-heptylcyclohexyl)-2-cyanophenyl-(4-ethylbenzyl) thioether.

Example 6.

(a) A solution of 23.2 g. 4-(trans-4-n-propylcyclohexyl)-phenol in 300 ml. chloroform is mixed portionwise, with stirring, with 30 ml. of 65% aqueous nitric acid in such a manner that the temperature does not increase above 15°C. Subsequently, 200 ml. of water are added thereto and the organic phase is separated off and evaporated under reduced pressure. The 4-(trans-4-n-propylcyclohexyl)-2-nitrophenol remaining behind is suspended in 250 ml. of 5% aqueous ammonia solution and slowly added to a solution of 75 g. sodium dithionite in 250 ml. of water. The reaction mixture is stirred for 2 hours at ambient temperature and then extracted three times with 150 ml. amounts of toluene. The extract is evaporated and the 4-(trans-4-n-propyl-

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cyclohexyl)-2-aminophenol remaining behind is recrystallised from methanol; yield 7.2 g.

(b) 116.5 g. 4-(trans-4-n-Propylcyclohexyl)-2-aminophenol, 80 g. potassium carbonate and 110 g. benzyl bromide are heated to 100°C. for 10 seconds in 500 ml. N,N-dimethylformamide. Subsequently, the reaction mixture is poured into 1 litre of water. From the mixture obtained, the 4-(trans-4-n-propylcyclohexyl)-2-aminophenyl benzyl ether formed is extracted with dichloromethane and, after distilling off the extraction agent, is recrystallised from isopropanol; yield 120 g.

(c) 81 g. 4-(trans-4-n-Propylcyclohexyl)-2-aminophenylbenzyl ether are dissolved in a mixture of 100 ml. of 42% aqueous tetrafluoroboric acid and 100 ml. of water and the solution mixed, with cooling to 5 - 10°C., with a solution of 17.3 g. sodium nitrite in 35 ml. of water. After subsequent stirring for 1 hour, the reaction mixture is cooled to 0°C. and the 4-(trans-4-n-propylcyclohexyl)-1-benzyloxy-2-diazonium fluoroborate which crystallises out is filtered off, washed with 40 ml. of cold 5% aqueous tetrafluoroboric acid, 50 ml. cold methanol and 200 ml. diethyl ether and dried at ambient temperature under reduced pressure; yield 135 g.

(d) To a suspension of 9.9 g. sodium fluoride in 200 ml. 1,2,4-trichlorobenzene there is added, with

stirring at 145 - 150°C., a suspension of 211 g. 4-(trans-4-n-propylcyclohexyl)-1-benzyloxy-2-diazonium tetrafluoroborate and 39.6 g. sodium fluoride in 600 ml. 1,2,4-trichlorobenzene in the course of 50 minutes. After subsequent stirring for 15 minutes, the reaction mixture is cooled to 40°C., filtered and the filtered off salts washed with toluene. The filtrate is extracted with toluene, the extracts are combined with the wash liquid and the combined toluene phases are washed with water, dried and evaporated; as residue there are obtained 82 g. 4-(trans-4-n-propylcyclohexyl)-2-fluorophenyl benzyl ether.

(e) 40 g. 4-(trans-4-n-Propylcyclohexyl)-2-fluorophenyl benzyl ether and 35 g. pyridine hydrochloride are heated for 1 hour at 200 - 220°C. After cooling, the comminuted reaction mass is taken up in 200 ml. of water and this mixture is extracted with toluene. The extracts are dried over sodium sulphate and evaporated; the 4-(trans-4-n-propylcyclohexyl)-2-fluorophenol remaining behind is recrystallised from methanol; yield 21 g.

(f) 11.8 g. 4-(trans-4-n-Propylcyclohexyl)-2-fluorophenol are etherified with 11 g. 4-n-propylbenzyl bromide analogously to Example 1(d). There are obtained 14.1 g. 4-(trans-4-n-propylcyclohexyl)-2-fluorophenyl-(4-n-propylbenzyl) ether; m.p. 38°C.; K 84°C.

The following compounds are prepared analogously:-

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4-(trans-4-n-butylcyclohexyl)-2-fluorophenyl-(4-ethylbenzyl) ether,

4-(trans-4-n-pentylcyclohexyl)-2-fluorophenyl-(4-n-propylbenzyl) ether,

4-(trans-4-ethylcyclohexyl)-2-fluorophenyl-(4-n-pentylbenzyl) ether,

4-(trans-4-methylcyclohexyl)-2-fluorophenyl-(4-n-butyloxybenzyl) ether.

Example 7.

(a) While cooling with ice, gaseous hydrogen chloride is passed into a mixture of 20 g. of 85% phosphoric acid, 40 ml. of 36.5% aqueous hydrochloric acid and 9 g. paraformaldehyde. To this is added dropwise at 0°C., while stirring, a solution of 40 g. trans-4-n-butylphenylcyclohexane in 50 ml. glacial acetic acid and the reaction mixture is subsequently stirred for 5 hours at ambient temperature. The reaction mixture is subsequently boiled under reflux for 20 hours and, after cooling, poured on to 200 g. of ice. The mixture obtained is extracted three times with 150 ml. amounts of diethyl ether and the ether extracts are washed neutral with 5% aqueous sodium hydrogen carbonate solution, dried over anhydrous potassium carbonate and evaporated. The 4-(trans-4-n-butylcyclohexyl)-benzyl chloride remaining behind is purified by distilling under reduced pressure; b.p. 164°C./1 mb.; yield: 28.5 g.

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(b) From 26.4 g. 4-(trans-4-n-butylcyclohexyl)-benzyl chloride and 15 g. 4-n-butylphenol are obtained, analogously to Example 1(d), 31.9 g. 4-(trans-4-n-butylcyclohexyl)-benzyl-(4-n-butylphenyl) ether; m.p. 47°C.; K 102°C.

The following compounds are prepared analogously:-

4-(trans-4-n-heptylcyclohexyl)-benzyl-(4-methylphenyl) ether,

4-(trans-4-ethylcyclohexyl)-benzyl-(4-n-pentylphenyl) ether,

4-(trans-4-n-pentylcyclohexyl)-benzyl-(4-n-hexyloxyphenyl) ether,

4-(trans-4-n-pentylcyclohexyl)-benzyl-(4-n-butyloxyphenyl) ether,

4-(trans-4-n-hexylcyclohexyl)-benzyl-(4-bromophenyl) ether,

4-(trans-4-n-butylcyclohexyl)-benzyl-(4-chlorophenyl) ether,

4-(trans-4-n-propylcyclohexyl)-benzyl-(4-fluorophenyl) ether,

4-(trans-4-n-pentylcyclohexyl)-benzyl-(4-fluorophenyl) ether,

4-(trans-4-ethylcyclohexyl)-benzyl-(4-cyanophenyl) ether,

4-(trans-4-n-hexylcyclohexyl)-benzyl-(4-cyanophenyl) ether,

4-(trans-4-n-heptylcyclohexyl)-benzyl-(2-bromo-4-methoxyphenyl) ether,

- 4-(trans-4-ethylcyclohexyl)-benzyl-(2-bromo-4-n-heptyl-phenyl) ether,
- 4-(trans-4-n-propylcyclohexyl)-benzyl-(2-chloro-4-n-butyloxyphenyl) ether,
- 4-(trans-4-n-butylcyclohexyl)-benzyl-(2-fluoro-4-n-propylphenyl) ether,
- 4-(trans-4-ethylcyclohexyl)-benzyl-(2-fluoro-4-n-butylphenyl) ether,
- 4-(trans-4-n-pentylcyclohexyl)-benzyl-(2-fluoro-4-ethoxyphenyl) ether,
- 4-(trans-4-ethylcyclohexyl)-benzyl-(2-fluoro-4-n-pentyloxyphenyl) ether,
- 4-(trans-4-n-butylcyclohexyl)-benzyl-(2-cyano-4-n-butylphenyl) ether,
- 4-(trans-4-n-butylcyclohexyl)-benzyl-(2-cyano-4-ethylphenyl) ether,
- 4-(trans-4-n-hexylcyclohexyl)-benzyl-(2-cyano-4-n-propyloxyphenyl) ether,
- 4-(trans-4-n-heptylcyclohexyl)-benzyl-(4-ethoxyphenyl) thioether,
- 4-(trans-4-n-butylcyclohexyl)-benzyl-(4-n-pentyloxyphenyl) thioether,
- 4-(trans-4-n-pentylcyclohexyl)-benzyl-(4-n-butylphenyl) thioether,
- 4-(trans-4-methylcyclohexyl)-benzyl-(4-n-hexylphenyl) thioether,
- 4-(trans-4-n-butylcyclohexyl)-benzyl-(4-fluorophenyl) thioether,

4-(trans-4-n-pentylcyclohexyl)-benzyl-(4-chlorophenyl)
thioether,

4-(trans-4-ethylcyclohexyl)-benzyl-(4-bromophenyl)
thioether,

4-(trans-4-n-butylcyclohexyl)-benzyl-(4-cyanophenyl)
thioether,

4-(trans-4-n-propylcyclohexyl)-benzyl-(4-cyanophenyl)
thioether,

4-(trans-4-ethylcyclohexyl)-benzyl-(4-cyanophenyl)
thioether,

4-(trans-4-ethylcyclohexyl)-benzyl-(2-fluoro-4-n-
butyloxyphenyl) thioether,

4-(trans-4-n-heptylcyclohexyl)-benzyl-(2-fluoro-4-
ethylphenyl) thioether,

4-(trans-4-methylcyclohexyl)-benzyl-(2-fluoro-4-n-
pentylphenyl) thioether,

4-(trans-4-n-propylcyclohexyl)-benzyl-(2-chloro-4-n-
propylphenyl) thioether,

4-(trans-4-n-butylcyclohexyl)-benzyl-(2-chloro-4-n-
propyloxyphenyl) thioether,

4-(trans-4-n-hexylcyclohexyl)-benzyl-(2-bromo-4-methyl-
phenyl) thioether,

4-(trans-4-ethylcyclohexyl)-benzyl-(2-bromo-4-n-
hexyloxyphenyl) thioether,

4-(trans-4-n-butylcyclohexyl)-benzyl-(2-cyano-4-n-
propylphenyl) thioether,

4-(trans-4-n-butylcyclohexyl)-benzyl-(2-cyano-4-n-butyloxyphenyl) thioether,

4-(trans-4-n-pentylcyclohexyl)-benzyl-(2-cyano-4-methoxyphenyl) thioether.

Example 8.

(a) To a Grignard solution prepared from 23.6 g. 4-(trans-4-ethylcyclohexyl)-benzyl chloride and 2.5 g. magnesium in 35 ml. diethyl ether there is added dropwise, with stirring, a solution of 21 g. 4-n-hexyloxybenzaldehyde in 35 ml. diethyl ether. The reaction mixture is further boiled for 2 hours and, after cooling, hydrolysed by the addition of 20 g. ice. The precipitate thereby formed is dissolved by the dropwise addition of aqueous 10% hydrochloric acid and the organic phase is then separated off, washed with water and evaporated. The residue is boiled in 200 ml. toluene with 0.5 g. p-toluene-sulphonic acid on a water separator until no more water separates. After cooling, the toluene solution is washed with 5% aqueous sodium hydrogen carbonate solution and water, dried over anhydrous sodium sulphate and evaporated. The 4-(trans-4-ethylcyclohexyl)-4'-n-hexyloxystilbene remaining behind is recrystallised from ethanol; yield 31.5 g.

(b) Hydrogen is passed at ambient temperature into a suspension of 1 g. palladium-charcoal (5% Pd) in a solution of 20 g. 4-(trans-4-ethylcyclohexyl)-4'-

n-hexyloxystilbene in 200 ml. toluene until cessation of the hydrogen uptake. Subsequently, the catalyst is filtered off, the filtrate is evaporated and the 1-[4-(trans-4-ethylcyclohexyl)-phenyl]-2-(4-n-hexyloxyphenyl)-ethane remaining behind is recrystallised from ethanol; yield: 19.6 g.

The following compounds are prepared analogously:-

- 1-[4-(trans-4-n-butylcyclohexyl)-phenyl]-2-(4-n-heptyloxyphenyl)-ethane,
1-[4-(trans-4-n-butylcyclohexyl)-phenyl]-2-(4-n-pentyloxyphenyl)-ethane,
1-[4-(trans-4-n-propylcyclohexyl)-phenyl]-2-(4-n-butyloxyphenyl)-ethane,
1-[4-(trans-4-n-butylcyclohexyl)-phenyl]-2-(4-n-propyloxyphenyl)-ethane,
1-[4-(trans-4-n-hexylcyclohexyl)-phenyl]-2-(4-ethoxyphenyl)-ethane,
1-[4-(trans-4-n-hexylcyclohexyl)-phenyl]-2-(4-methoxyphenyl)-ethane,
1-[4-(trans-4-n-pentylcyclohexyl)-phenyl]-2-(4-ethoxyphenyl)-ethane,
1-[4-(trans-4-ethylcyclohexyl)-phenyl]-2-(4-n-butyloxyphenyl)-ethane,
1-[4-(trans-4-methylcyclohexyl)-phenyl]-2-(4-n-hexyloxyphenyl)-ethane.

Example 9.

(a) To a suspension of 16 g. aluminium chloride

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in 13 ml. dichloromethane is added at -5°C ., with stirring, a solution of 21.4 g. 4-n-butylphenylacetyl chloride in 8 ml. dichloromethane. After 30 minutes, a solution of 20.2 g. 4-(trans-4-n-propylcyclohexyl)-benzene in 46.5 ml. dichloromethane is added dropwise to this reaction mixture in such a manner that the temperature of the reaction mixture does not increase above 0°C . Subsequently, the reaction mixture is further stirred for one hour at 0°C . and then poured into a mixture of 250 g. of ice and 75 ml. of 35% aqueous hydrochloric acid. The organic phase is separated off, washed neutral with water, dried over anhydrous sodium sulphate and evaporated. The 2-(4-n-butylphenyl)-4'-(trans-4-n-propylcyclohexyl)-acetophenone remaining behind is recrystallised from ethanol; yield: 23.7 g.

(b) Hydrogen is passed into a suspension of 0.5 g. palladium-charcoal (5% Pd) in a solution of 7 g. 2-(4-n-butylphenyl)-4'-(trans-4-n-propylcyclohexyl)-acetophenone in 200 ml. ethanol at 35°C . until cessation of the take up of hydrogen. Subsequently, the catalyst is filtered off, the filtrate is evaporated and the residue is recrystallised from petroleum ether (boiling range $40 - 60^{\circ}\text{C}$.); yield 6.2 g. 1-[4-(trans-4-n-propylcyclohexyl)-phenyl]-2-(4-n-butylphenyl)-ethane.

The following compounds are prepared analogously:-

- 1-[4-(trans-4-n-hexylcyclohexyl)-phenyl]-2-(4-methyl-phenyl)-ethane,
- 1-[4-(trans-4-n-pentylcyclohexyl)-phenyl]-2-(4-ethyl-phenyl)-ethane,
- 1-[4-(trans-4-n-pentylcyclohexyl)-phenyl]-2-(4-n-propyl-phenyl)-ethane,
- 1-[4-(trans-4-n-butylcyclohexyl)-phenyl]-2-(4-ethyl-phenyl)-ethane,
- 1-[4-(trans-4-n-butylcyclohexyl)-phenyl]-2-(4-n-butyl-phenyl)-ethane,
- 1-[4-(trans-4-n-butylcyclohexyl)-phenyl]-2-(4-n-pentyl-phenyl)-ethane,
- 1-[4-(trans-4-n-propylcyclohexyl)-phenyl]-2-(4-n-butyl-phenyl)-ethane,
- 1-[4-(trans-4-ethylcyclohexyl)-phenyl]-2-(4-n-heptyl-phenyl)-ethane,
- 1-[4-(trans-4-methylcyclohexyl)-phenyl]-2-(4-n-hexyl-phenyl)-ethane,
- 1-[4-(trans-4-n-propylcyclohexyl)-phenyl]-2-(4-bromo-phenyl)-ethane,
- 1-[4-(trans-4-n-hexylcyclohexyl)-phenyl]-2-(4-chloro-phenyl)-ethane,
- 1-[4-(trans-4-ethylcyclohexyl)-phenyl]-2-(4-fluoro-phenyl)-ethane,
- 1-[4-(trans-4-n-butylcyclohexyl)-phenyl]-2-(4-fluoro-phenyl)-ethane,
- 1-[4-(trans-4-n-pentylcyclohexyl)-phenyl]-2-(4-fluoro-phenyl)-ethane.

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Example 10.

Analogously to Example 4(b), 1-[4-(trans-4-n-propylcyclohexyl)-phenyl]-2-(4-bromophenyl)-ethane is reacted with cuprous cyanide in pyridine/N-methylpyrrolidone to give 1-[4-(trans-4-n-propylcyclohexyl)-phenyl]-2-(4-cyanophenyl)-ethane; m.p. 36°C.

The following compounds are prepared analogously:-
1-[4-(trans-4-n-heptylcyclohexyl)-phenyl]-2-(4-cyanophenyl)-ethane,
1-[4-(trans-4-n-butylcyclohexyl)-phenyl]-2-(4-cyanophenyl)-ethane.

The following Examples describe the use, according to the present invention, of compounds of general formula (I) as components of liquid crystalline dielectrics:

Example 11.

A dielectric of
19% 4-(trans-4-n-propylcyclohexyl)-benzonitrile,
29% 4-(trans-4-n-pentylcyclohexyl)-benzonitrile,
20% 4-(trans-4-n-heptylcyclohexyl)-benzonitrile,
12% trans-4-n-pentyl-(4'-cyanobiphenyl-4)-cyclohexane,
20% 1-[4-(trans-4-n-propylcyclohexyl)-phenyl]-2-(4-n-butylphenyl)-ethane
has a clear point of 76°C., a threshold voltage in the twisted nematic cell of 1.8 V (20°C.) and a viscosity of 24 cSt at 20°C.

Example 12.

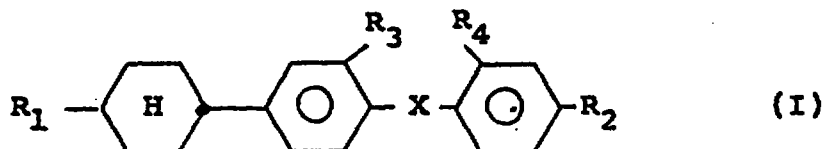
A dielectric of

- 19% 4-(trans-4-n-propylcyclohexyl)-benzonitrile,
28% 4-(trans-4-n-pentylcyclohexyl)-benzonitrile,
11% trans-4-n-pentyl-(4'-cyanobiphenyl-4)-cyclohexane,
10% 4-(trans-4-n-propylcyclohexyl)-benzoic acid (4-propylphenyl) ester
12% 4-(trans-4-n-propylcyclohexyl)-benzoic acid (trans-4-n-propylcyclohexyl ester
20% 1-[4-(trans-4-n-propylcyclohexyl)-phenyl]-2-(4-n-butylphenyl)-ethane.

has a clear point of 91°C., a threshold voltage of 2.0 v (at 20°C.) and a viscosity of 32 cSt at 20°C.

Claims

1. Liquid crystalline trans-cyclohexylphenyl derivatives of the general formula:-



5 wherein X is a $-\text{CH}_2-\text{CH}_2-$, $-\text{CH}_2-\text{O}-$, $-\text{CH}_2-\text{S}-$, $-\text{O}-\text{CH}_2-$ or $-\text{S}-\text{CH}_2-$ radical, R_1 is an alkyl radical containing up to 8 carbon atoms, R_2 is an alkyl or alkoxy radical containing up to 8 carbon atoms or a fluorine, chlorine or bromine atom or a cyano group and R_3 and R_4 are
 10 hydrogen atoms or one of these symbols also represents a fluorine, chlorine or bromine atom or a cyano group, with the proviso that R_3 and R_4 both represent hydrogen atoms when X is a $-\text{CH}_2-\text{CH}_2-$ radical or R_2 is a fluorine, chlorine or bromine atom or a cyano
 15 group.

2. trans-Cyclohexylphenyl derivatives according to claim 1 which are hereinbefore specifically exemplified.

3. A liquid crystalline dielectric for electro-optical indicator elements, wherein it contains at
 20 least one trans-cyclohexylphenyl derivative according to claim 1.

4. Liquid crystalline dielectrics for electro-optical indicator elements according to claim 3, substantially as hereinbefore described and exemplified.

25 5. An electro-optical indicator element based on a



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liquid crystal cell, wherein it contains a liquid
crystalline dielectric according to claim 3.



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