

PATENT SPECIFICATION

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(54) LIQUID CRYSTAL CYCLOHEXYLCYCLOHEXANES AND DIELECTRIC MATERIALS CONTAINING THEM

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Darmstadt, Federal Republic of Germany, a
Joint-Stock Company organised under the
laws of the Federal Republic of Germany, do
hereby declare the invention, for which we
pray that a patent may be granted to us, and
the method by which it is to be performed, to
be particularly described in and by the fol-
lowing statement:—

The present invention is concerned with
liquid crystalline cyclohexylcyclohexanes and
with dielectrics containing them.

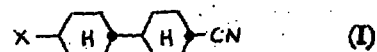
For electro-optical indicating elements,
there are utilised, to an increasing extent, the
properties of nematic or nematic-cholesteric
liquid crystalline materials significantly to
change their optical properties, such as light
scattering, birefringence, reflecting power or
colour, under the influence of electric fields.
The function of such indicator elements there-
by depends, for example, upon the phenomenon
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 materials are needed which must
satisfy a plurality of requirements. Especially
important are the chemical stability to
moisture, air and physical influences, such as
heat, radiation in the infra-red, visible and
ultra-violet range and direct and alternating
electric fields. Furthermore, there is required of
technically usable liquid crystalline materials
a liquid mesophase in the temperature range
of at least 10 to 60°C. and preferably of 0
to 60°C., and a low viscosity at ambient tem-
perature, which should preferably be not more
than 70 cP and preferably less than 50 cP.
Finally, in the range of visible light, they
must be colourless.

A number of liquid crystalline compounds
is already known which satisfy the stability
requirements demanded of dielectrics for elec-
tronic constructional elements and are also
colourless. These include, in particular, the
p,p - disubstituted benzoic acid phenyl esters
described in German Patent Specification No.
2,139,628 and the *p,p'* - disubstituted biphenyl
derivatives described in German Patent Speci-
fication No. 2,356,085. In both mentioned
classes of compounds, as well as in other
known compounds with liquid crystalline
mesophase, there are no individual compounds
which form a liquid crystalline mesophase in
the required temperature range of 10 to 60°C.
Therefore, as a rule, there are prepared mix-
tures of two or more compounds in order to
obtain substances which can be used as liquid
crystalline dielectrics. For this purpose, at
least one compound with low melting and
clear point is mixed with another compound
with a distinctly higher melting and clear
point. A mixture is thus usually obtained, the
melting point of which is below that of the
lowest melting component, whereas the clear
point is between the clear points of the com-
ponents. However, dielectrics with optimum
properties cannot be prepared in this way since
the components with high melting and clear
points almost always impart a high viscosity
to the mixture. The switch times of the elec-
tro-optical indicator elements produced there-
with are thus increased in an undesirable man-
ner.

It is an object of the present invention to
provide liquid crystalline dielectrics which
have a nematic phase in the required tempera-
ture range and permit sufficiently short switch
times in liquid crystal cells.

We have now found that cyclohexylcyclo-
hexanes of the general formula:—



wherein X is an —R, —OR or —O—CO—R radical and R is an alkyl radical containing up to 12 carbon atoms, are, surprisingly, outstandingly useful as base materials for the production of liquid crystalline dielectrics.

Hitherto, the presence of a long-extending molecule form with a rear portion of at least two conjugatively linked aromatic nuclei was regarded as an important pre-requisite for the appearance of a nematic liquid crystalline mesophase. Although the cyclohexylcyclohexanes of general formula (I) do not possess this structural characteristic, nevertheless they form liquid crystalline mesophases, the temperature range, especially with regard to the clear point, of which is, in many cases, even more favourable than that of the analogously substituted known liquid crystalline substances and especially of the corresponding biphenyl derivatives.

Like the known *p,p'*-disubstituted benzoic acid phenyl esters and the *p,p'*-disubstituted biphenyl derivatives, the compounds of general formula (I) are colourless and have a comparable chemical and photo-chemical stability.

The present invention also provides liquid crystalline dielectric containing at least two liquid crystalline components, at least one of which is a cyclohexylcyclohexane of general formula (I).

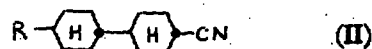
The cyclohexylcyclohexanes of general formula (I) comprise two *trans*-substituted cyclohexane rings which are joined together and are substituted in the 4- and 4'-position by an alkyl, alkoxy or alkanoyloxy radical or by a cyano group; in these alkyl, alkoxy and alkanoyloxy radicals, the moiety R contains up to 12, preferably up to 10 and especially up to 8 carbon atoms. They have a moderately positive dielectric anisotropy (DCA) with values between +3 to +12 and are, therefore, especially useful as components of dielectrics for indicator elements which operate on the basis of the Schadt-Helfrich effect in the twisted nematic cell or utilise the phenomenon of the cholesteric-nematic phase transition, especially when these indicator elements are operated in the multiplex process. Furthermore, the cyclohexylcyclohexanes of general formula (I) have a negative diamagnetic anisotropy (DMA), which means that the diamagnetic susceptibility of the nematic mesophase is smaller in the direction of the longitudinal axis of the molecule than the diamagnetic susceptibility measurable vertically to this direction. This property, which was previously only known for cholesterol derivatives forming cholesteric-liquid crystalline mesophases, but has never been observed in known nematic liquid crystalline substances, can, for example, be utilised to prevent the superimposition of liquid crystal indicator elements with electrode rasters or to shorten the switch-off times of liquid crystal indicator elements.

In the cyclohexylcyclohexanes according to

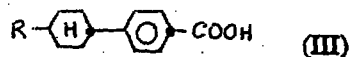
the present invention, the alkyl, alkoxy or alkanoyloxy radicals X can be straight-chained or branched. Amongst these, the compounds with unbranched side chains X, i.e. in which R signifies a methyl, ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *n*-heptyl, *n*-octyl, *n*-nonyl, *n*-decyl, *n*-undecyl or *n*-dodecyl radical, generally possesses higher melting and clear points than the corresponding isomers with branched side chains.

Branched-chained radicals in compounds of general formula (I) preferably contain not more than one chain branching, preferred branched side chains being those in which the carbon chain is branched on the binding carbon atom or one of the next two carbon atoms. Of importance amongst these are those branched radicals R in which, on a comparatively long carbon chain, a methyl or ethyl radical is present in the 1-, 2- or 3-position, for example, isopropyl, 1-methylpropyl, 2-methylpropyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 1-methylpentyl, 1-ethylpentyl, 2-methylpentyl, 1-methylhexyl, 2-ethylhexyl or 1-methylheptyl. Compounds of general formula (I) with a branched side chain X are frequently better soluble in other liquid crystal materials than the corresponding straight-chained isomers. When the branched chain contains an asymmetrical carbon atom, the compounds of general formula (I) can also be prepared or isolated in the form of their optical isomers. The compounds of general formula (I) are the first known compounds which possess a negative DMA and form cholesteric mesophases without being derived from the cholesterol or related cyclopentano-perhydrophenanthrenes.

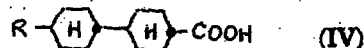
The cyclohexylcyclohexanes of general formula (I) can be prepared in the usual way for such compounds. For example, compounds of the general formula:—



in which R has the same meaning as in general formula (I), can be prepared by hydrogenation of the corresponding *trans*-R-cyclohexylbenzoic acids of the general formula:—



and subsequent successive reaction of the thereby obtained *trans-trans*-4-R-cyclohexylcyclohexane-4'-carboxylic acids of the general formula:—



with a chlorination agent, for example, thionyl chloride, ammonia and an agent splitting off water, for example, phosphorus oxychloride, via the *trans-trans*-4R-cyclohexylcyclo-

hexane - 4' - carboxylic acid chlorides and the *trans* - *trans* - 4R - cyclohexylcyclohexane - 4' - carboxylic acid amides.

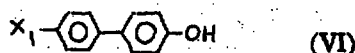
Compounds of general formula (I), in which X is —OR or —OCOR, can be prepared by first hydrogenating 4 - hydroxybiphenyl - 4' - carboxylic acid in the presence of a conventional hydrogenation catalyst, for example, Raney nickel, platinum oxide or palladium on active charcoal, possibly at an elevated temperature and/or an elevated pressure, to give a mixture of the *cis* - *cis* -, *cis* - *trans* -, *trans* - *cis* - and *trans* - *trans* - 4 - hydroxycyclohexyl - cyclohexane - 4' - carboxylic acids. From this mixture, there is separated the *trans* - *trans* - isomer in the usual way, for example chromatographically or by the formation of an inclusion compound with thiourea, which is then reacted with an alkanoyl chloride of the general formula R—CO—Cl to give the corresponding *trans* - *trans* - 4 - alkanoyl - cyclohexyl - cyclohexane - 4' - carboxylic acid. From this there is then prepared, in the above-described manner, *via* the corresponding acid chloride and acid amide, the *trans* - *trans* - 4 - alkanoyloxycyclohexyl - cyclohexane - 4' - carbonitrile. For the preparation of the analogous 4 - alkoxy compound, this 4 - alkanoyloxy compound is gently saponified, for example by gentle warming with alcoholic potassium hydroxide solution, to give the *trans* - *trans* - 4 - hydroxycyclohexyl - cyclohexane - 4' - carbonitrile which is subsequently converted into the *trans* - *trans* - 4 - alkoxy - cyclohexyl - cyclohexane - 4' - carbonitrile by a conventional etherification, for example with an alkyl halide in the presence of silver oxide.

The *cis* - *cis* -, *cis* - *trans* - and *trans* - *cis* - 4 - hydroxycyclohexyl - cyclohexane - carboxylic acids separated off after the hydrogenation can also be wholly or partly rearranged to give the desired, thermodynamically more stable *trans* - *trans* - isomer by equilibration in the presence of a conventional catalyst for this purpose, for example, potassium *tert* - butylate in ethanolic solution.

Furthermore, compounds of general formula:



in which X₁ is —R or —OR and R has the same meaning as given in formula (I), can be prepared by hydrogenating a compound of the general formula:—



under conditions analogous to those described above for 4 - hydroxybiphenyl - 4' - carboxylic acid, to give a mixture of *cis* - *cis* -, *cis* - *trans* -, *trans* - *cis* - and *trans* - *trans* - 4 - X₁ - cyclohexylcyclohexane - (4) - ols from which the *trans* - *trans* - isomer is separated.

This is converted, by reaction with a chlorination agent, for example thionyl chloride or phosgene, with reversal of configuration, into the *trans* - *cis* - 4 - X₁ - cyclohexyl - cyclohexyl - 4 - chloride and from this, by reaction with a cyanide, for example potassium cyanide, with renewed reversal of configuration, the *trans* - *trans* - 4 - X₁ - cyclohexyl - cyclohexane - (4) - carbonitrile is prepared.

The starting materials used for the preparation of the compounds according to the present invention in the above-described manner are known or can be prepared analogously to known compounds according to standard processes described in the literature. Thus, for example, compounds of general formula (III) can be obtained in the manner described in German Patent Specification No. 2,636,684 by reacting a 4 - R - cyclohexanone with phenyl magnesium bromide and hydrogenating the *cis* - *trans* - isomeric 4 - R - 1 - phenylcyclohexanols obtained after hydrolysis, with inversion or retention of the configuration, after isomer separation, to give the *trans* - 4 - R - 1 - phenylcyclohexane, which is reacted, in the presence of aluminium chloride, with acetyl chloride to give the 4 - (*trans* - 4 - R - cyclohexyl)acetophenone, followed by oxidation of this acetophenone with a hypohalite to give the benzoic acid derivative (III).

The compounds of general formula (I) are valuable components of liquid crystalline dielectrics which are used for the production of electro - optical indicator elements.

Furthermore, the compounds of general formula (I) are valuable solvents for nuclear resonance spectrometry. They enable the recording of nuclear resonance spectra with a high degree of sensitivity, i.e. a large signal/noise level ratio, as well as with good resolution. The half life breadth of the absorption signals in nuclear resonance spectra of a sample dissolved in a compound of general formula (I) is 1—2 Hertz (cpc) and thus achieves the same magnitude as the half life breadth of signals isotropic system-registered spectra.

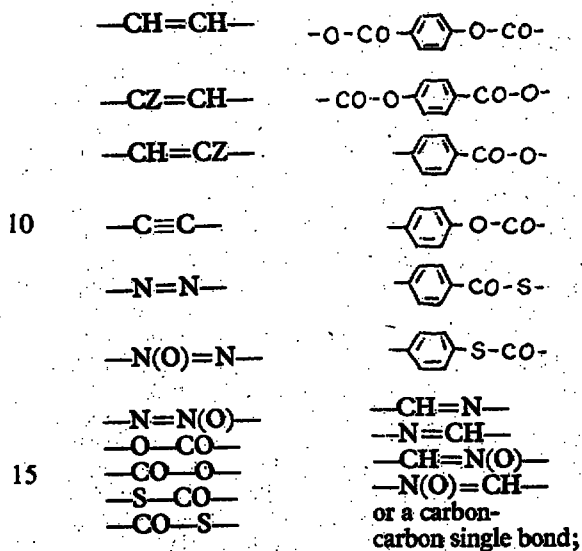
The compounds of general formula (I) are also excellent solvents for absorption spectroscopy in anisotropic systems in the ultraviolet and visible ranges. An especial advantage of the compounds according to the present invention with regard to this particular use is that their spectra are free of absorption signals in the wavelength range above 200 nm.

The dielectrics according to the present invention comprise two or more components, including at least one of general formula (I). Other components possibly present are preferably nematic or nematogenic substances selected from the azobenzenes, azoxybenzenes, biphenyls, Schiff bases, especially benzylidene derivatives, phenyl benzoates, phenylcyclohexanes, optionally halogenated stilbenes, diphenylacetylene derivatives, diphenyl nitrones

and substituted cinnamic acids. The most important compounds which can be used as such further components can be represented by the general formula:—



wherein A is



when A is —CO—O—, —O—CO— or a carbon-carbon single bond, one of the two phenyl rings can also be replaced by a *trans*-cyclohexyl ring; Z is a halogen atom and preferably a chlorine atom, R₁ and R₂, which can be the same or different, are alkyl, alkoxy, alkanoyl, alkanoyloxy or alkoxy-carbonyloxy radicals containing up to 18 and preferably up to 8 carbon atoms; furthermore, one of these symbols can also represent a cyano, nitro or isonitrile group. In most of these compounds, R₁ and R₂ 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 conventional, many such nematic substances being commercially available.

Furthermore, the dielectrics according to the present invention can also contain cholesteric-liquid crystalline compounds, for example cholesterol esters.

The dielectrics according to the present invention generally contain at least 40, preferably 50—99 and especially 60—98 parts by weight of compounds of general formula (I) and possibly of general formula (VII). Of this, preferably at least 15 parts by weight and usually 20 or more parts by weight are one or more compounds of general formula (I). However, dielectrics according to the present invention can also be prepared which consist exclusively of two or more compounds of general formula (I).

By means of appropriate additives, the liquid crystalline dielectrics according to the

present invention can be so modified that they can be employed in all previously known types of indicator elements which use liquid crystals with positive dielectric anisotropy. Such additives are known and are described in detail in the appropriate literature. For example, substances can be added for changing the dielectric anisotropy and/or of the orientation of the nematic phases, such substances being described, for example, in German Patent Specifications Nos. 2,209,127; 2,321,632 and 2,611,453.

The following Examples are given for the purpose of illustrating the present invention. In the Examples, m.p. indicates the melting point and c.p. the clear point of a liquid crystalline substance; boiling temperatures are indicated with b.p. Unless stated to the contrary, parts and percentages are by weight.

Example 1

(a) 36.4 g. 4 - (*trans* - 4 - *n* - pentylcyclohexyl) - benzoic acid (prepared according to Example 1 of German Patent Specification No. 2,636,684 by reaction of phenyl magnesium bromide with 4 - *n* - pentylcyclohexanone, hydrolysis, hydrogenation, acetylation and oxidation) are hydrogenated in 500 ml. glacial acetic acid in the presence of 5 g. platinum oxide at ambient temperature and at a pressure of 3 bar. The hydrogen take up is ended after 8 hours. After filtering off the solvent and evaporating, the residue obtained is boiled with 120 g. thionyl chloride for 16 hours. Subsequently, excess thionyl chloride is distilled off and the residue is poured into 500 ml. water. The aqueous mixture is stirred for 1 hour at 50°C. and then extracted twice with 200 ml. amounts of diethyl ether. The extracts are dried over anhydrous sodium sulphate and evaporated. The *trans* - *trans* - 4 - *n* - pentylcyclohexyl - cyclohexane - 4' - carboxylic acid remaining behind is recrystallised from petroleum ether (b.p. 50—70°C.); m.p. 220°C.; c.p. 245°C.

(b) 15 g. *trans* - *trans* - 4 - *n* - pentylcyclohexyl - cyclohexane - 4' - carboxylic acid are boiled for 20 minutes with 36 g. thionyl chloride; subsequently, excess thionyl chloride is distilled off, finally under reduced pressure. The *trans* - *trans* - 4 - *n* - pentylcyclohexyl - cyclohexane - 4' - carboxylic acid chloride obtained is dissolved in 450 ml. dioxan and mixed, while cooling with ice, with 180 ml. 25% aqueous ammonia solution. After stirring for one hour, the reaction mixture is poured on to 2000 g. of ice and the precipitated *trans* - *trans* - 4 - *n* - pentylcyclohexyl - cyclohexane - 4' - carboxylic acid amide is filtered off and recrystallised from ethanol; m.p. 215—218°C.

(c) To a solution of 10 g. *trans* - *trans* - 4 - *n* - pentylcyclohexyl - cyclohexane - 4' - carboxylic acid amide in 180 ml. N,N - di-

methylformamide there are added dropwise at 40°C., 50 g. phosphorus oxychloride. The reaction mixture is further stirred for 30 minutes at 50°C. and, after cooling to ambient temperature, poured on to 300 g. of ice. The aqueous reaction mixture is extracted three times with 100 ml. amounts of diethyl ether and the extract is dried over anhydrous sodium sulphate and evaporated. The *trans-trans*-4-*n*-pentylcyclohexyl - cyclohexane - 4' - carbonitrile remaining behind is recrystallised from ethanol; m.p. 62°C.; c.p. 85°C.

The following compounds are prepared analogously:

- 15 *trans-trans*-4-methylcyclohexyl - cyclohexane - 4' - carbonitrile,
- trans-trans*-4-ethylcyclohexyl - cyclohexane - 4' - carbonitrile,
- 20 *trans-trans*-4-*n*-propylcyclohexyl - cyclohexane - 4' - carbonitrile,
- trans-trans*-4-*n*-butylcyclohexyl - cyclohexane - 4' - carbonitrile,
- trans-trans*-4-*n*-hexylcyclohexyl - cyclohexane - 4' - carbonitrile,
- 25 *trans-trans*-4-*n*-heptylcyclohexyl - cyclohexane - 4' - carbonitrile,
- trans-trans*-4-*n*-octylcyclohexyl - cyclohexane - 4' - carbonitrile,
- trans-trans*-4-*n*-nonylcyclohexyl - cyclohexane - 4' - carbonitrile,
- 30 *trans-trans*-4-*n*-decylcyclohexyl - cyclohexane - 4' - carbonitrile,
- trans-trans*-4-*n*-undecylcyclohexyl - cyclohexane - 4' - carbonitrile,
- 35 *trans-trans*-4-*n*-dodecylcyclohexyl - cyclohexane - 4' - carbonitrile,
- trans-trans*-4-isopropylcyclohexyl - cyclohexane - 4' - carbonitrile,
- 40 *trans-trans*-4-(1-methylpropyl) - cyclohexyl - cyclohexane - 4' - carbonitrile,
- trans-trans*-4-(2-methylpropyl) - cyclohexyl - cyclohexane - 4' - carbonitrile,
- 45 *trans-trans*-4-(1-methylbutyl) - cyclohexyl - cyclohexane - 4' - carbonitrile,
- trans-trans*-4-(2-methylbutyl) - cyclohexyl - cyclohexane - 4' - carbonitrile,
- trans-trans*-4-(3-methylbutyl) - cyclohexyl - cyclohexane - 4' - carbonitrile,
- 50 *trans-trans*-4-(1-methylpentyl) - cyclohexyl - cyclohexane - 4' - carbonitrile,
- trans-trans*-4-(2-methylpentyl) - cyclohexyl - cyclohexane - 4' - carbonitrile,
- 55 *trans-trans*-4-(1-methylhexyl) - cyclohexyl - cyclohexane - 4' - carbonitrile,
- trans-trans*-4-(2-ethylpentyl) - cyclohexyl - cyclohexane - 4' - carbonitrile,
- trans-trans*-4-(1-methylheptyl) - cyclohexyl - cyclohexane - 4' - carbonitrile,
- 60 *trans-trans*-4-(2-ethylhexyl) - cyclohexyl - cyclohexane - 4' - carbonitrile.

Example 2

(a) A solution of 100 g. 4-hydroxy-biphenyl-4'-carboxylic acid in 1000 ml. acetic acid is hydrogenated in the presence of 10 g. platinum oxide at ambient temperature and atmospheric pressure for 16 hours. Subsequently, the catalyst is filtered off, the filtrate is evaporated and the residue is boiled in 500 ml. *tert.*-butanol in the presence of 150 g. potassium *tert.*-butoxide. After cooling to ambient temperature, the reaction mixture is poured on to 1000 g. of ice, neutralised with 10% sulphuric acid and extracted twice with 500 ml. amounts of diethyl ether. The ether extract is dried over anhydrous sodium sulphate, evaporated and the residue taken up in 500 ml. boiling methanol. The hot solution obtained is poured into a boiling solution of 200 g. thiourea in 800 ml. methanol. After 30 minutes, the mixture is cooled to 0°C. and the thiourea inclusion compound which crystallises out is filtered off and boiled with 1000 ml. petroleum ether (b.p. 40–60°C.). The undissolved residue is heated to 50°C. for 30 minutes with 1000 ml. aqueous 2N aqueous potassium hydroxide solution. The solution obtained is, after cooling, acidified with 10% sulphuric acid and the precipitated *trans-trans*-4-hydroxycyclohexyl - cyclohexane - 4' - carboxylic acid filtered off and recrystallised from petroleum ether (b.p. 50–70°C.).

(b) A solution of 30 g. *trans-trans*-4-hydroxycyclohexyl - cyclohexane - 4' - carboxylic acid in a mixture of 300 ml. toluene and 30 ml. pyridine is mixed at ambient temperature with 13.6 g. *n*-butyryl chloride and the reaction mixture stirred for 2 hours at 50°C. The reaction mixture is then poured on to 500 g. of ice and the organic phase separated off, washed with water, dried over anhydrous sodium sulphate and evaporated. The *trans-trans*-4-*n*-butyryloxycyclohexyl - cyclohexane - 4' - carboxylic acid remaining behind is recrystallised from ethanol.

(c) Analogously to Example 1(b) and 1(c), from 20 g. *trans-trans*-4-*n*-butyryloxycyclohexyl - cyclohexane - 4' - carboxylic acid there are prepared 9.8 g. *trans-trans*-4-*n*-butyryloxycyclohexyl - cyclohexane - 4' - carbonitrile.

The following compounds are prepared analogously:

- trans-trans*-4-acetoxycyclohexyl - cyclohexane - 4' - carbonitrile,
- trans-trans*-4-propionyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
- 120 *trans-trans*-4-isobutyryloxycyclohexyl - cyclohexane - 4' - carbonitrile,
- trans-trans*-4-*n*-pentanoyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
- trans-trans*-4- α -methylpropionyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
- 125 *trans-trans*-4-*n*-hexanoyloxycyclohexyl - cyclohexane - 4' - carbonitrile,

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- 5 *trans* - *trans* - 4 - *n* - heptanoyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - octanoyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - nonanoyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - decanoyloxycyclohexyl - cyclohexane - 4' - carbonitrile.

Example 3

- 10 10 g. *trans* - *trans* - 4 - *n* - Butyryloxy-cyclohexyl - cyclohexane - 4' - carbonitrile are warmed with 250 ml. ethanolic 2N potassium hydroxide solution for 30 minutes at 40°C., while stirring; the reaction mixture is then
 15 diluted with 500 ml. water and neutralised with 10% sulphuric acid. The neutral solution is extracted four times with 250 ml. amounts of diethyl ether and the extracts are dried over
 20 anhydrous sodium sulphate and evaporated. The *trans* - *trans* - 4 - hydroxycyclohexyl - cyclohexane - 4' - carbonitrile remaining behind is dissolved in 100 ml. *n* - butyl iodide and the solution boiled for 24 hours after the
 25 addition of 10 g. silver (I) oxide. Subsequently, the reaction mixture is filtered and excess butyl iodide is distilled from the filtrate. The residue is taken up in 30 ml. toluene and purified on a silica gel column (20×2 cm.). After
 30 evaporation of the toluene, the *trans* - *trans* - 4 - *n* - butyloxycyclohexyl - cyclohexane - 4' - carbonitrile remaining behind is recrystallised from ethanol.

The following compounds are obtained analogously:

- 35 *trans* - *trans* - 4 - methoxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - ethoxycyclohexyl - cyclohexane - 4' - carbonitrile,
 40 *trans* - *trans* - 4 - *n* - propyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - pentyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - hexyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
 45 *trans* - *trans* - 4 - *n* - heptyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - octyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - nonyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
 50 *trans* - *trans* - 4 - *n* - decyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - undecyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
 55 *trans* - *trans* - 4 - *n* - dodecyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - isopropyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - (1 - methylpropyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,
 60 *trans* - *trans* - 4 - (1 - methylbutyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,

- trans* - *trans* - 4 - (2 - methylbutyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - (1 - methylpentyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - (2 - methylpentyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - (3 - methylpentyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - (1 - methylhexyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - (2 - ethylpentyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - (1 - methylheptyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - (2 - ethylhexyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,

The following Examples describe liquid crystalline dielectrics according to the present invention:

Example 4

A mixture of 33% *trans* - *trans* - 4 - *n* - pentyloxycyclohexyl - cyclohexane - 4' - carbonitrile and 67% *trans* - 4 - *n* - propyl - 1 - (4' - cyanophenyl) - cyclohexane has a nematic liquid crystalline phase in the temperature range of 25—57°C. and a DCA of +8.2.

Example 5

A mixture of 40% *trans* - *trans* - 4 - *n* - pentyloxycyclohexyl - cyclohexane - 4' - carbonitrile and 60% 4 - *n* - octyloxy - 4' - cyano-biphenyl has a nematic liquid crystalline phase in the temperature range of 34—75°C. and a DCA of +9.

Example 6

A mixture of 10% *trans* - *trans* - 4 - *n* - pentyloxycyclohexyl - cyclohexane - 4' - carbonitrile, 60% 4 - *n* - butyl - 4' - methoxyazoxybenzene and 30% 4 - ethyl - 4' - methoxyazoxybenzene has a nematic liquid crystalline phase in the temperature range of 5—74°C. and a DCA of +1.3.

Example 7

A mixture of 55% *trans* - *trans* - 4 - *n* - pentyloxycyclohexyl - cyclohexane - 4' - carbonitrile and 45% *trans* - *trans* - 4 - *n* - propyloxycyclohexyl - cyclohexane - 4' - carbonitrile has a clear point of 81°C., a DCA of about +4 and a negative DMA.

WHAT WE CLAIM IS:—

1. Cyclohexylcyclohexanes of the general formula:—



trans - *trans* - 4 - *n* - heptanoyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - octanoyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - nonanoyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - decanoyloxycyclohexyl - cyclohexane - 4' - carbonitrile.

Example 3

10 g. *trans* - *trans* - 4 - *n* - Butyryloxy-cyclohexyl - cyclohexane - 4' - carbonitrile are warmed with 250 ml. ethanolic 2N potassium hydroxide solution for 30 minutes at 40°C., while stirring; the reaction mixture is then diluted with 500 ml. water and neutralised with 10% sulphuric acid. The neutral solution is extracted four times with 250 ml. amounts of diethyl ether and the extracts are dried over anhydrous sodium sulphate and evaporated. The *trans* - *trans* - 4 - hydroxycyclohexyl - cyclohexane - 4' - carbonitrile remaining behind is dissolved in 100 ml. *n* - butyl iodide and the solution boiled for 24 hours after the addition of 10 g. silver (I) oxide. Subsequently, the reaction mixture is filtered and excess butyl iodide is distilled from the filtrate. The residue is taken up in 30 ml. toluene and purified on a silica gel column (20×2 cm.). After evaporation of the toluene, the *trans* - *trans* - 4 - *n* - butyloxycyclohexyl - cyclohexane - 4' - carbonitrile remaining behind is recrystallised from ethanol.

The following compounds are obtained analogously:

trans - *trans* - 4 - methoxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - ethoxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - propyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - pentyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - hexyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - heptyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - octyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - nonyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - decyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - undecyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - dodecyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - *n* - isopropyloxycyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - (1 - methylpropyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - (1 - methylbutyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - (2 - methylbutyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - (1 - methylpentyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - (2 - methylpentyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - (3 - methylpentyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - (1 - methylhexyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - (2 - ethylpentyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - (1 - methylheptyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,
trans - *trans* - 4 - (2 - ethylhexyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,

The following Examples describe liquid crystalline dielectrics according to the present invention:

Example 4

A mixture of 33% *trans* - *trans* - 4 - *n* - pentylcyclohexyl - cyclohexane - 4' - carbonitrile and 67% *trans* - 4 - *n* - propyl - 1 - (4' - cyanophenyl) - cyclohexane has a nematic liquid crystalline phase in the temperature range of 25—57°C. and a DCA of +8.2.

Example 5

A mixture of 40% *trans* - *trans* - 4 - *n* - pentylcyclohexyl - cyclohexane - 4' - carbonitrile and 60% 4 - *n* - octyloxy - 4' - cyano - biphenyl has a nematic liquid crystalline phase in the temperature range of 34—75°C. and a DCA of +9.

Example 6

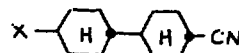
A mixture of 10% *trans* - *trans* - 4 - *n* - pentylcyclohexyl - cyclohexane - 4' - carbonitrile, 60% 4 - *n* - butyl - 4' - methoxyazoxybenzene and 30% 4 - ethyl - 4' - methoxyazoxybenzene has a nematic liquid crystalline phase in the temperature range of 5—74°C. and a DCA of +1.3.

Example 7

A mixture of 55% *trans* - *trans* - 4 - *n* - pentylcyclohexyl - cyclohexane - 4' - carbonitrile and 45% *trans* - *trans* - 4 - *n* - propylcyclohexyl - cyclohexane - 4' - carbonitrile has a clear point of 81°C., a DCA of about +4 and a negative DMA.

WHAT WE CLAIM IS:—

1. Cyclohexylcyclohexanes of the general formula:—



wherein X is —R, —OR or —O—CO—R and R is an alkyl radical containing up to 12 carbon atoms.

5 2. Cyclohexylcyclohexanes according to claim 1, wherein R is a straight-chained alkyl radical.

3. Cyclohexylcyclohexanes according to claim 1, wherein R is a branched-chained alkyl radical with one chain branching.

10 4. Cyclohexylcyclohexanes according to any of the preceding claims, wherein R is an alkyl radical containing up to 10 carbon atoms.

5. Cyclohexylcyclohexanes according to claim 4, wherein R is an alkyl radical containing up to 8 carbon atoms.

15 6. Cyclohexylcyclohexanes according to claim 1, which are hereinbefore specifically exemplified.

7. A compound selected from the group consisting of:

trans - *trans* - 4 - methylcyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - ethylcyclohexyl - cyclohexane - 4' - carbonitrile,

25 *trans* - *trans* - 4 - *n* - propylcyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - *n* - butylcyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - *n* - hexylcyclohexyl - cyclohexane - 4' - carbonitrile,

30 *trans* - *trans* - 4 - *n* - pentylcyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - *n* - heptylcyclohexyl - cyclohexane - 4' - carbonitrile,

35 *trans* - *trans* - 4 - *n* - octylcyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - *n* - nonylcyclohexyl - cyclohexane - 4' - carbonitrile, and

40 *trans* - *trans* - 4 - *n* - decylcyclohexyl - cyclohexane - 4' - carbonitrile,

8. A compound selected from the group consisting of:

trans - *trans* - 4 - isopropylcyclohexyl - cyclohexane - 4' - carbonitrile,

45 *trans* - *trans* - 4 - (1 - methylpropyl) - cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - (2 - methylpropyl) - cyclohexyl - cyclohexane - 4' - carbonitrile,

50 *trans* - *trans* - 4 - (1 - methylbutyl) - cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - (2 - methylbutyl) - cyclohexyl - cyclohexane - 4' - carbonitrile,

55 *trans* - *trans* - 4 - (3 - methylbutyl) - cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - (1 - methylpentyl) - cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - (2 - methylpentyl) - cyclohexyl - cyclohexane - 4' - carbonitrile,

60 *trans* - *trans* - 4 - (1 - methylhexyl) - cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - (2 - ethylpentyl) - cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - (1 - methylheptyl) - cyclohexyl - cyclohexane - 4' - carbonitrile, and

trans - *trans* - 4 - (2 - ethylhexyl) - cyclohexyl - cyclohexane - 4' - carbonitrile. 70

9. A compound selected from the group consisting of:

trans - *trans* - 4 - methoxycyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - ethoxycyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - *n* - propyloxycyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - *n* - butyloxycyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - *n* - pentyloxycyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - *n* - hexyloxycyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - *n* - heptyloxycyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - *n* - octyloxycyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - *n* - nonyloxycyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - *n* - decyloxycyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - *n* - undecyloxycyclohexyl - cyclohexane - 4' - carbonitrile, and

trans - *trans* - 4 - *n* - dodecyloxycyclohexyl - cyclohexane - 4' - carbonitrile, 95

10. A compound selected from the group consisting of:—

trans - *trans* - 4 - isopropoxy - cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - (1 - methylpropoxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - (1 - methylbutyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - (2 - methylbutyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - (1 - methylpentyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - (2 - methylpentyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - (3 - methylpentyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - (1 - methylheptyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - (2 - ethylpentyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - (1 - methylhexyloxy) - cyclohexyl - cyclohexane - 4' - carbonitrile and

trans - *trans* - 4 - (2 - ethylhexyloxy) -



cyclohexyl - cyclohexane - 4' - carbonitrile,

11. A compound selected from the group consisting of:

5 *trans* - *trans* - 4 - acetoxy cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - propionyloxy cyclohexyl - cyclohexane - 4' - carbonitrile,

10 *trans* - *trans* - 4 - *n* - butyryloxy cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - isobutyryloxy cyclohexyl - cyclohexane - 4' - carbonitrile,

15 *trans* - *trans* - 4 - *n* - pentanoyloxy cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - α - methylpropionyloxy cyclohexyl - cyclohexane - 4' - carbonitrile,

20 *trans* - *trans* - 4 - *n* - hexanoyloxy cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - *n* - heptanoyloxy cyclohexyl - cyclohexane - 4' - carbonitrile,

trans - *trans* - 4 - *n* - octanoyloxy cyclohexyl - cyclohexane - 4' - carbonitrile,

25 *trans* - *trans* - 4 - *n* - nonanoyloxy cyclohexyl - cyclohexane - 4' - carbonitrile, and

trans - *trans* - 4 - *n* - decanoyloxy cyclohexyl - cyclohexane - 4' - carbonitrile.

12. Process for the preparation of cyclohexylcyclohexanes according to claim 1, substantially as hereinbefore described and exemplified. 30

13. Cyclohexylcyclohexanes according to claim 1, whenever prepared by the process according to claim 12.

14. A liquid crystalline dielectric comprising at least 2 liquid crystalline components, at least one of which is a compound of the general formula given in claim 1. 35

15. Liquid crystalline dielectrics according to claim 14, substantially as hereinbefore described and exemplified. 40

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