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(71) Applicant *(for all designated States except US):* MERCK PATENT GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG[DE/DE]; Frankfurter Strasse 250, D-6100 Darmstadt (DE).

(72) Inventors; and
(75) Inventors/Applicants *(for US only) :* RIEGER, Bernhard [DE/JP]; Wacore, Tamagawagakuen, 2834, Ootadaira, Nara-machi, Midori-ku, Yokohama-shi, Kanagawa Pref. 227 (JP). YOSHITAKE, Hiroki [JP/JP]; 4-11-1, Miyanosato, Atsugi-shi, Kanagawa Pref. 243-02 (JP). JACOB, Thomas [DE/DE]; Im Wiesengrund 28, D-6105 Ober-Ramstadt (DE). PLACH, Herbert [DE/DE]; Wingertsbergstr. 5, D-6100 Darmstadt (DE). FINKENZELLER, Ulrich [DE/DE]; Waldpfad 74, D-6831 Plankstadt (DE). KURMEIER, Hans-Adolf [DE/DE]; Hinter der Schule 3a, D-6104 Seeheim-Jugenheim (DE).

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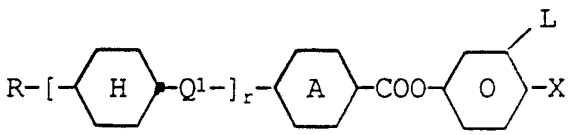

(I)

(57) Abstract

The invention relates to a liquid-crystalline medium based on a mixture of polar compounds having positive dielectric anisotropy, characterized in that it contains one or more compounds of general formula (I), in which r is 0 or 1, Q^1 is $-CH_2CH_2-$ or a single bond, A is 1,4-phenylene or trans-1,4-cyclohexylene, L is H or F, R is alkyl, alkoxy, oxaalkyl, fluoroalkyl or alkenyl, in each case having up to 7 carbon atoms and X is F, CF_3, or OCF_2H.

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Liquid crystalline medium

The present invention relates to a liquid-crystalline medium, to the use thereof for electrooptical purposes, and to displays containing this medium.

Liquid crystals are used, in particular, as dielectrics in display devices since the optical properties of such substances can be affected by an applied voltage. Electrooptical devices based on liquid crystals are extremely well known to those skilled in the art and may be based on various effects. Devices of this type are, for example, cells having dynamic scattering, DAP (deformation of aligned phases) cells, guest/host cells, TN cells having a twisted nematic structure, STN (super-twisted nematic cells, SBE (super-birefringence effect) cells and OMI (optical mode interference) cells. The most common display devices are based on the Schadt-Helfrich effect and have a twisted nematic structure.

The liquid-crystal materials must have good chemical and thermal stability and good stability toward electrical fields and electromagnetic radiation. Furthermore, the liquid-crystal materials should have low viscosity and give short addressing times, low threshold voltages and high contrast in the cells. Furthermore, they should have a suitable mesophase, for example, for the abovementioned cells, a nematic or cholesteric mesophase, at customary operating temperatures, i.e. in the broadest possible range above and below room temperature. Since liquid crystals are generally

used as mixtures of a plurality of components, it is important that the components are readily miscible with one another. Further properties, such as electrical conductivity, dielectric anisotropy and optical anisotropy, must meet various requirements depending on the cell type and the area of application. For example, materials for cells having a twisted nematic structure should have positive dielectric anisotropy and low electrical conductivity.

For example, the media desired for matrix liquid-crystal displays containing integrated nonlinear elements for switching individual image points (MLC displays) are those having high positive dielectric anisotropy, broad nematic phases, relatively low birefringence, very high specific resistance, good UV and temperature stability of the resistance and low vapor pressure.

Matrix liquid-crystal displays of this type are known. Examples of nonlinear elements which can be used to individually switch the individual image points are active elements (i.e. transistors). This is then referred to as an "active matrix", and a differentiation can be made between two types:

1. MOS (Metal Oxide Semiconductor) transistors on a silicon wafer as substrate.

2. Thin-film transistors (TFTs) on a glass plate as substrate.

The use of monocrystalline silicon as the substrate material limits the display size since even the modular assembly of various part displays results in problems at the joints.

In the case of the more promising type 2, which is preferred, the electrooptical effect used is usually the TN effect. A differentiation is made between two technologies: TFTs comprising compound semiconductors, such as, for example, CdSe, or TFTs based on polycrystalline or amorphous silicon. Intensive research efforts are being made worldwide in the latter technology.

The TFT matrix is applied to the inside of one glass plate of the display, while the inside of the other glass plate carries the transparent counterelectrode. Compared with the size of the image point electrode, the TFT is very small and hardly affects the image at all. This technology can also be extended to fully color-compatible image displays, where a mosaic of red, green and blue filters is arranged in such a manner that each filter element is located opposite a switchable image element.

The TFT displays usually operate as TN cells with crossed polarizers in transmission and are illuminated from the back.

The term MLC displays here covers any matrix display containing integrated nonlinear elements, i.e. in addition to the active matrix, also displays containing passive elements such as varistors or diodes (MIM = metal-insulator-metal).

MLC displays of this type are particularly suitable for TV application (for example pocket TV sets) or for high-information displays for computer applications (laptops) and in automobile or aircraft construction. In addition to problems with respect to the angle dependency of the contrast and the switching times, problems result in MLC displays due to inadequate specific resistance of the liquid-crystal mixtures TOGASHI, S., SEKIGUCHI, K., TANABE, H., YAMAMOTO, E., SORIMACHI, K., TAJIMA, E., WATANABE, H., SHIMIZU, H., Proc. Eurodisplay 84, Sept. 1984: A 210-288, Matrix LCD Controlled by Double Stage Diode Rings, p. 141 ff., Paris; STROMER, M:, Proc. Eurodisplay 84, Sept. 1984: Design of Thin Film Transistors for Matrix Adressing of Television Liquid Crystal Displays, p. 145 ff., Paris. As the resistance decreases, the contrast of an MLC display worsens and the problem of "after image elimination" may occur. Since the specific resistance of the liquid-crystal mixture generally decreases over the life of an MLC display due to interaction with the internal surfaces of the display, a high (initial) resistance is very important to give acceptable service lives. In particular, in the case of low-voltage mixtures, it was hitherto not possible to achieve very high specific resistances. It is furthermore important that the specific resistance increases as little as possible with increasing temperature and after heating and/or exposure to UV radiation. The MLC displays of the prior art do not satisfy current demands.

Thus, there continues to be a great demand for MLC displays of very high specific resistance and at the same time a broad operating temperature range, short switching times and low threshold voltage which do not have these disadvantages or only do so to a lesser extent.

For TN (Schadt-Helfrich) cells, media are desired which facilitate the following advantages in the cells:

- broadened nematic phase range (in particular down to low temperatures),
- switchability at extremely low temperatures (outdoor use, automobiles, avionics),
- increased stability to UV radiation (longer life).

The media available from the prior art do not make it possible to achieve these advantages whilst simultaneously retaining the other parameters.

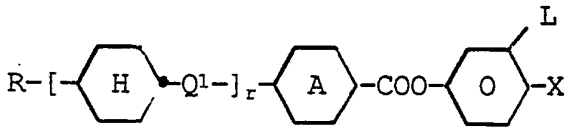
For supertwisted (STN) cells, media are desired which facilitate a greater multiplexing ability and/or lower threshold voltages and/or broader nematic phase ranges (in particular at low temperatures). To this end, a further extension of the parameter latitude available (clearing point, smectic-nematic transition or melting point, viscosity, dielectric values, elastic values) is urgently desired.

The invention has the object or providing media, in particular for MLC, TN or STN displays of this type, which do not

have the abovementioned disadvantages or only do so to a lesser extent, and preferably at the same time have very high specific resistance and low threshold voltages.

It has now been found that this object can be achieved if media according to the invention are used in displays.

The invention thus relates to a liquid-crystalline medium based on a mixture of polar compounds having positive dielectric anisotropy, characterized in that it contains one or more compounds of the general formula I

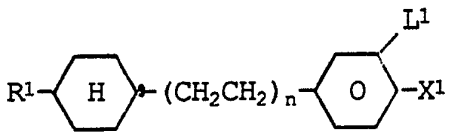


I

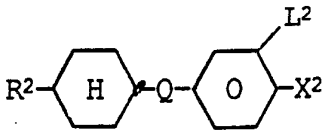
in which r is 0 or 1, Q^1 is $-CH_2CH_2-$ or a single bond, A is 1,4-phenylene or trans-1,4-cyclohexylene, L is H or F, R is alkyl, alkoxy, oxaalkyl, fluoroalkyl or alkenyl, in each case having up to 7 carbon atoms and X is F, CF_3, OCF_3 or OCF_2H.

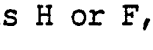
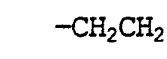
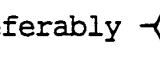
The invention also relates to electrooptical displays (in particular STN or MLC displays having two plane-parallel outer plates which, together with a frame, form a cell, integrated nonlinear elements for switching individual image points on the outer plates, and a nematic liquid-crystal mixture of positive dielectric anisotropy and high specific resistance located in the cell) which contain media of this type, and to the use of these media for electroptical purposes.

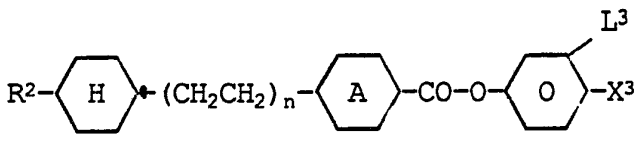
In particular the invention relates to a nematic liquid-crystal composition based on terminally and laterally fluorinated compounds, characterized in that it contains about 10 to 25 % by weight of one or more compounds from group 1:

group 1: 

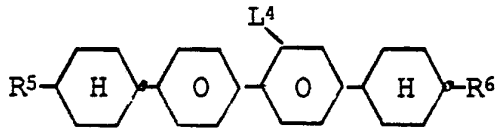
wherein R^1 denotes a straight-chain alkyl group of 1 to 12 carbon atoms, L^1 is H or F and X^1 is F, CF_3, OCF_3 or OCF_2H and n is 0 or 1, preferably 0, about 10 to 70 % by weight of one or more compounds from group 2:

group 2: 

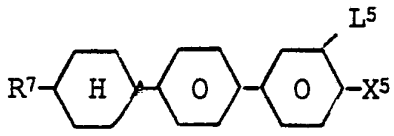
wherein R^2 denotes a straight-chain alkyl group of 1 to 12 carbon atoms L^2 is H or F, Q is  ,  or  , preferably  or  and X^2 is F, CF_3, OCF_3 or OCF_2H, about 5 to 40 %, in particular 5 to 25 % by weight of one or more compounds of the formula Ia.

 Ia

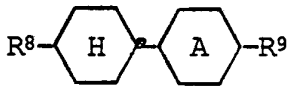
wherein L^3 is F or H, X^3 is F, CF_3, OCF_3 or OCF_2H, n is 0 or 1, preferably 0, and  is or , about 0 to 15 % by weight of one or more compounds from group 4:

group 4: 

wherein L^4 is H or F, about 0 to 25 % by weight of one or more compounds from group 5:

group 5: 

wherein R^3 to R^7 each independently denotes a straight-chain alkyl group of 1 to 12 carbon atoms, L^5 is H or F and X^5 is F, CF_3, OCF_3 or OCF_2H, and about 0 to 20 % by weight of one or more compounds from group 6:

group 6: 

wherein  has the meaning given for formula Ia, and R^8 and R^9 are each independently alkyl or alkoxy groups with one to 12 C atoms,

which is highly suited for AMD application. Very high RC time values can be obtained in such AMDs. These compositions also show a reduced viscosity, allow operation in AMDs in the first minimum of transmission and do not exhibit any crystallization over 1000 hrs at -30 °C.

Such compositions preferably contain at least two compounds of group 1 wherein R^1 is n-pently, n-hexyl and n-heptyl.

In a preferred embodiment the inventive nematic composition contains

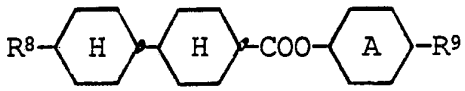
about 15 to 20 % by weight of two or more compounds from group 1, wherein L^1 is H and X^1 is F, CF_3 or OCF_3,

about 10 to 40 % by weight of two or more compounds from group 2, wherein L^2 is H, X^2 is OCF_3 and m is 0 and

about 10 to 40 % by weight of two or more compounds from group 2 wherein L^2 is H or F, X^2 is F or OCF_3 and m is 1,

about 5 to 15 % by weight of two or more compounds of formula Ia wherein L^3 is H and X^3 is F and/or about 5 to 15 % by weight of two or more compounds of formula Ia wherein L^3 is H and X^3 is OCF_3,

additionally the group 6 may contain 0-25 % by weight of one or more compounds of the formula



in which  , R^8 and R^9 have the meaning given for group 6.

The compounds from groups 1 to 6 are known from the German Patents 26 36 684 and 31 02 017, the European Patent 0 051 738 and 0 125 653, the International Patent Application WO 89/02884 and USP 4,302,352, USP 4,710,315 and USP 4,419,264 or can be prepared in analogy to known compounds.

The preparation of the compositions according to the invention is effected in the conventional manner. In general, the

desired amount of the components which is used in the smaller amount is dissolved in the components which constitutes the main constituent, preferably at elevated temperature. If this temperature is chosen to be above the clear point of the main constituent, the completeness of the process of dissolving can be observed particularly easily.

The liquid-crystal mixtures according to the invention facilitate a significant broadening of the parameter latitude available.

The achievable combinations of clearing point, viscosity at low temperature, thermal and UV stability and dielectric anisotropy are far superior to previous materials from the prior art.

The requirement for a high clearing point, a nematic phase at -40 °C and a high $\Delta\varepsilon$ was previously only achievable to an unsatisfactory extent. Although systems such as, for example, ZLI-3119 have a comparable clearing point and comparatively favorable viscosities, they have, however, a $\Delta\varepsilon$ of only +3.

Other mixture systems have comparable viscosities and values of $\Delta\varepsilon$, but only have clearing points in the region of 60 °C.

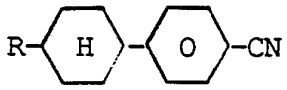
The liquid-crystal mixtures according to the invention make it possible to achieve, at low viscosities at low temperatures (at -30 °C $\leq$ 600, preferably $\leq$ 550 mPa·s; at -40 °C $\leq$ 1800, preferably $\leq$ 1700mPa·s), simultaneously dielectric anisotropy values $\Delta\varepsilon \geq 3.5$, preferably ≥ 4.0, clearing points above 65°, preferably above 70°, and a high value for the specific resistance, which means that excellent STN and MLC displays can be achieved.

It goes without saying that a suitable choice of the components of the mixtures according to the invention also allows higher clearing points (for example above 90°) to be achieved at higher threshold voltages or lower clearing points to be achieved at lower threshold voltages while retaining the other advantageous properties. The MLC displays according to the invention preferably operate in the first transmission minimum of Gooch and Tarry [C.H. Gooch and H.A. Tarry, Electron. Lett. 10, 2-4, 1974; C.H. Gooch and H.A. Tarry, Appl. Phys., Vol. 8, 1575-1584, 1975], in this case, a lower dielectric anisotropy in the second minimum is sufficient in addition to particularly favorable electrooptical properties, such as, for example, high gradient of the characteristic line and low angle dependency of the contrast (German Patent 30 22 818) at the same threshold voltage as in an analogous display. This allows significantly higher specific resistances to be achieved in the first minimum using the mixtures according to the invention than using mixtures containing cyano compounds. A person skilled in the art can use simple routine methods to produce the birefringence necessary for a prespecified cell thickness of the MLC display by a suitable choice of the individual components and their proportions by weight.

The viscosity at 20 °C is preferably ≤ 25mPa·s. The nematic phase range is preferably at least 70°, in particular at least 80°. This range preferably extends at least from -30° to +70° more preferred from -30° to 120°.

Measurements of the "voltage holding ratio" (HR) [S. Matsumoto et al., Liquid Crystals 5, 1320 (1989); K. Niwa et al., Proc. SID Conference, San Francisco, June 1984, p. 304 (1984); G. Weber et al., Liquid Crystals 5, 1381 (1989)] have

shown that mixtures according to the invention containing compounds of the formula I exhibit a considerably smaller decrease in the HR with increasing temperature than do analogous mixtures in which the compounds of the formula I are replaced by cyanophenylcyclohexanes of the formula



The UV stability of the mixtures according to the invention is also considerably better, i.e. they exhibit a significantly smaller decrease in the HR on exposure to UV radiation and/or high temperatures of e.g. 100°.

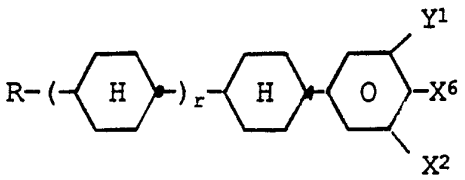
The media according to the invention are distinguished by favorable viscosity values in addition to an unusually broad nematic phase range, resulting, in particular when used in STN displays, in significant advantages over prior-art media.

The media according to the invention are preferably based on a plurality (preferably two or more) of compounds of the formula I, i.e. the proportion of these compounds is ≥ 25 %, preferably ≥ 40 %.

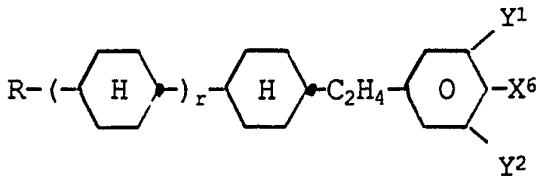
The individual compounds of the formulae I to XIV and their sub-formulae which can be used in the media according to the invention are either known or can be prepared analogously to the known compounds.

Preferred embodiments are indicated below:

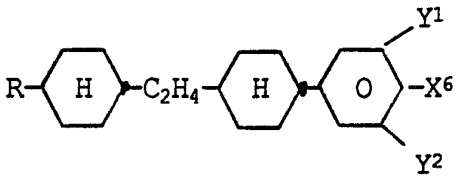
- a medium additionally contains one or more compounds selected from the group comprising the general formulae II, III and IV:



II



III



IV

in which the individual radicals are as defined below:

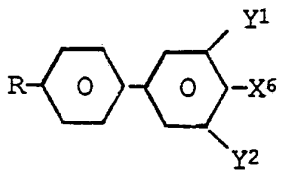
R: alkyl, oxaalkyl, fluoroalkyl or alkenyl, in each case having up to 7 carbon atoms

X^6: F, Cl, CF_3, OCF_3 or $OCHF_2$

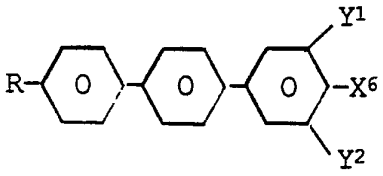
Y^1 and Y^2: in each case, independently of one another, H or F

r: 0 or 1.

- a medium additionally contains one or more compounds selected from the group comprising the general formulae V to VIII.



V



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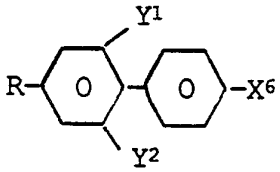
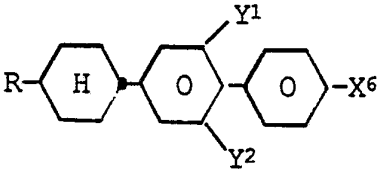


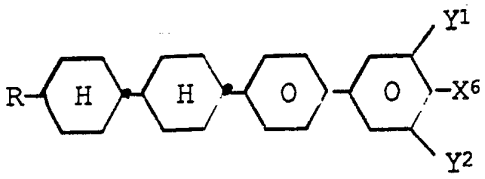
VII



VIII

in which R, X^6 and Y^1 and Y^2 are each, independently of one another, as defined in Claim 2.

- a medium additionally contains one or more compounds selected from the group comprising the general formulae IV to XV:



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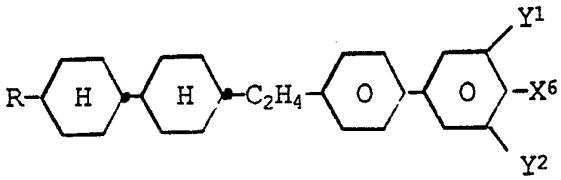
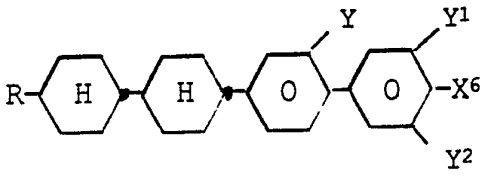
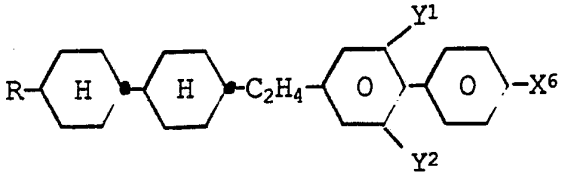


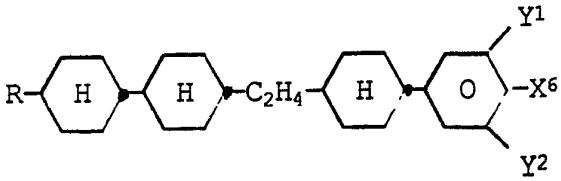
X



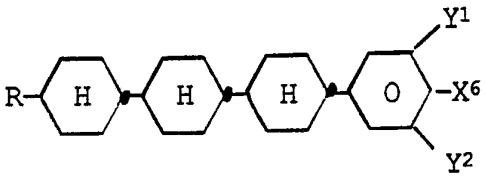
XI



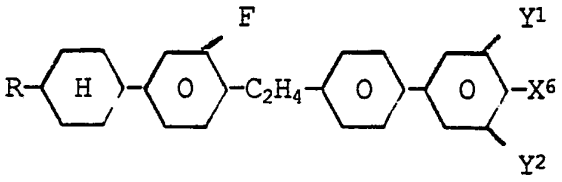
XII



XIII

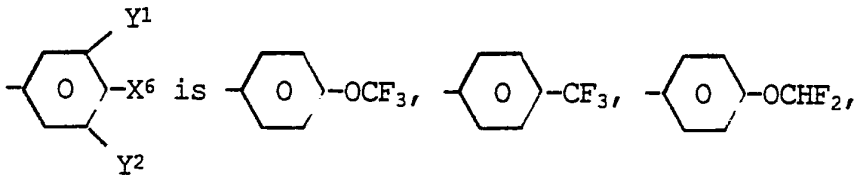


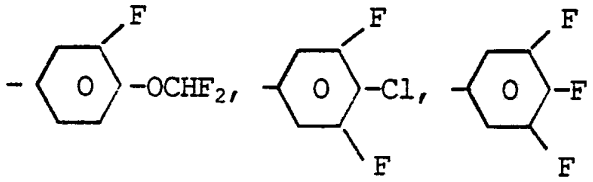
XIV

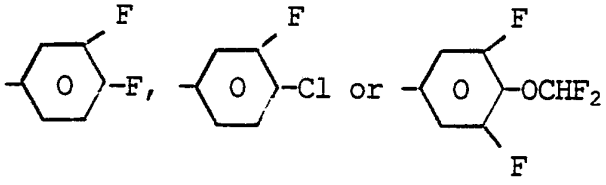


in which R, X^6 and Y^1 and Y^2 are each, independently of one another, as defined in Claim 2.

- The proportion of compounds of the formulae I to IV together is at least 50 % by weight in the total mixture
- the proportion of compounds of the formula I is from 10 to 50 % by weight in the total mixture
- the proportion of compounds of the formulae II to IV is from 30 to 70 % by weight in the total mixture





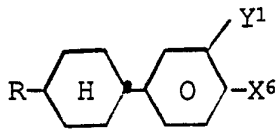


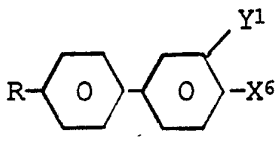
- the medium contains compounds of the formulae II and III or IV

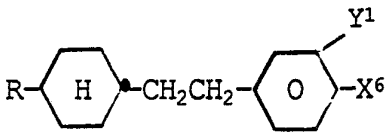
- R is straight-chain alkyl or alkenyl having 2 to 7 carbon atoms

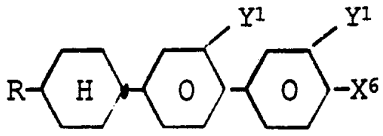
- the medium essentially comprises compounds of the formulae I to IV

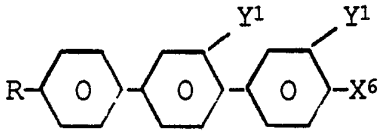
- the medium contains further compounds, preferably selected from the following group:

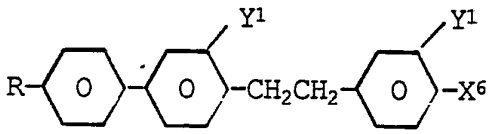


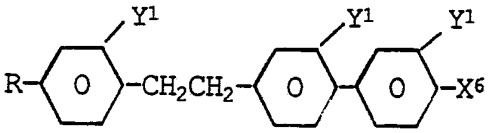












- The I: (II+ III+ IV) weight ratio is preferably from 1:4 to 1:1.

- The medium essentially comprises compounds selected from the group comprising the general formulae I to XIV.

It has been found that even a relatively small proportion of compounds of the formula I mixed with conventional liquid-crystal materials, but in particular containing one or more compounds of the formula II, III and/or IV, results in a significant improvement in the addressing times, in significantly lower values for the birefringence, and in low threshold voltages, and at the same time broad nematic phases with low smectic-nematic transition temperatures are observed. The compounds of the formulae I to IV are colorless, stable and readily miscible with one another and with other liquid-crystal materials.

The term "alkyl" covers straight-chain and branched alkyl groups having 1-7 carbon atoms, in particular the straight-chain groups methyl, ethyl, propyl, butyl, pentyl, hexyl and heptyl. Groups having 2-5 carbon atoms are generally preferred.

The term "alkenyl" covers straight-chain and branched alkenyl groups having 2-7 carbon atoms, in particular the straight-chain groups. Preferred alkenyl groups are C_2-C_7-1E-alkenyl, C_5-C_7-4-alkenyl, C_6-C_7-5-alkenyl and C_7-6-alkenyl, in particular C_2-C_7-1E-alkenyl, C_4-C_7-3E-alkenyl and C_5-C_7-4-alkenyl. Examples of preferred alkenyl groups are vinyl, 1E-propenyl, 1E-butenyl, 1E-pentenyl, 1E-hexenyl, 1E-heptenyl, 3-butenyl, 3E-pentenyl, 3E-hexenyl, 3E-heptenyl, 4-pentenyl, 4Z-hexenyl, 4E-hexenyl, 4Z-heptenyl, 5-hexenyl, 6-heptenyl and the like. Groups having up to 5 carbon atoms are generally preferred.

The term "fluoroalkyl" preferably covers straight-chain groups containing terminal fluorine, i.e. fluoromethyl, 2-fluoroethyl, 3-fluoropropyl, 4-fluorobutyl, 5-fluoropentyl, 6-fluorohexyl and 7-fluoroheptyl. However, other positions of the fluorine are not excluded.

The term alkoxy preferably covers straight-chain radicals of the formula C_nH_{2n+1}-O-, in which n is 1 to 6.

The term "oxaalkyl" preferably covers straight-chain radicals of the formula C_nH_{2n+1}-O-$(CH_2)_m$, in which n and m are each, independently of one another, from 1 to 6. n is preferably 1 and m is preferably from 1 to 6.

Through a suitable choice of the meanings of R, X and Y, the addressing times, the threshold voltage, the gradient of the transmission characteristic lines, etc., can be modified as desired. For example, 1E-alkenyl radicals, 3E-alkenyl radicals, 2E-alkenyloxy radicals and the like generally give shorter addressing times, improved nematic tendencies and a higher ratio between the elastic constants K_{33} (bend) and k_{11}

(splay) compared with alkyl and alkoxy radicals. 4-Alkenyl radicals, 3-alkenyl radicals and the like generally give lower threshold voltages and lover values of k_{33}/k_{11} compared with alkyl and alkoxy radicals. A $-CH_2CH_2-$ group in Z^1 or Z^2 generally results in higher values of k_{33}/k_{11} compared with a simple covalent bond. Higher values of k_{33}/k_{11} facilitate, for example, flatter transmission characteristic lines in TN cells with a 90° twist (for achieving gray tones) and steeper transmission characteristic lines in STN, SBE and OMI cells (greater multiplexing ability), and vice versa.

The optimum mixing ratios of the compounds of the formulae I and II + III + IV depends substantially on the desired properties, on the choice of the components of the formulae I, II, III and/or IV and on the choice of any other components which may be present. Suitable mixing ratios within the abovementioned range can easily be determined from case to case.

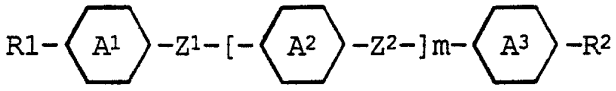
The total amount of compounds of the formulae I to XII in the mixtures according to the invention is not crucial. The mixtures may therefore contain one or more further components in order to optimize various properties. However, the effect observed on the addressing times and the threshold voltage is generally greater the higher the total concentration of compounds of the formulae I to XIV.

In a particularly preferred embodiment, the media according to the invention contain compounds of the formula II, III, V and/or VII (preferably II and/or III) in which X^6 is CF_3, OCF_3

or $OCHF_2$. A favorable synergistic effect with the compounds of the formula I results in particularly advantageous properties.

For STN applications, the media preferably contain compounds selected from the group comprising the formulae V to VIII in which X^6 is preferably $OCHF_2$.

The media according to the invention may furthermore contain a component A comprising one or more compounds of the general formula I' having a dielectric anisotropy of from -1.5 to +1.5.



I'

in which

R^1 and R^2 are each, independently of one another, n-alkyl, n-alkoxy, o-fluoroalkyl or n-alkenyl having up to 9 carbon atoms,

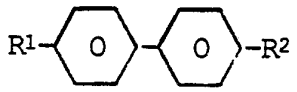
the rings A^1, A^2 and A^3 are each, independently of one another, 1,4-phenylene, 2- or 3-fluoro-1,4-phenylene, trans-1,4-cyclohexylene or 1,4-cyclohexenylene,

Z^1 and Z^2 are each, independently of one another, $-CH_2CH_2-$, $-C\equiv C-$, -CO-O-, -O-CO- or a single bond,

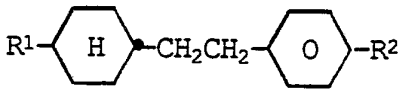
and

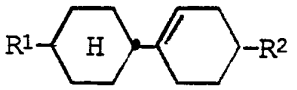
m is 0, 1 or 2.

Component A preferably contains one or more compounds selected from the group comprising II1 to II7:

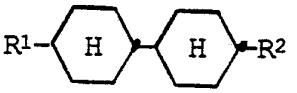

II1

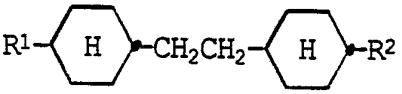

II2


II3


II4

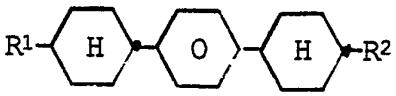

II5

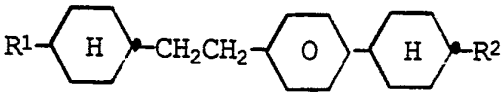

II6

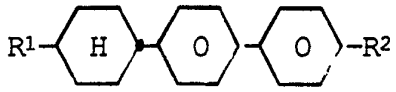

II7

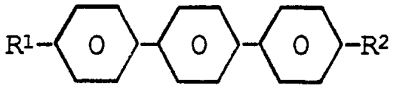
in which R^1 and R^2 are as defined under formula I'.

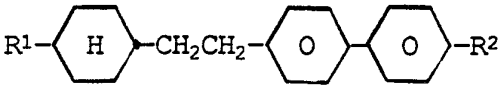
Component A preferably additionally contains one or more compounds selected from the group comprising II8 to II20:

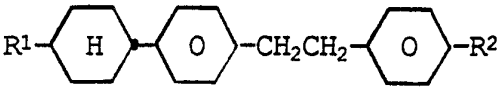

II8

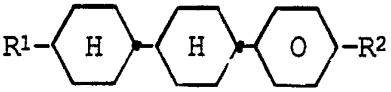

II9

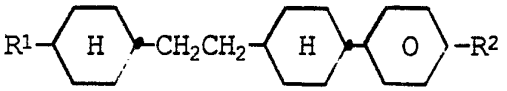

II10

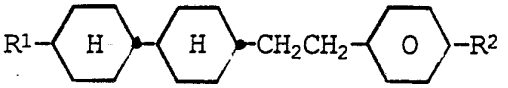

II11

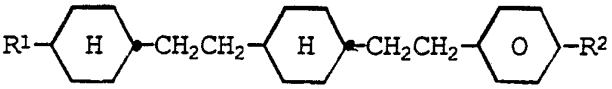

II12

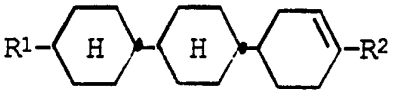

II13

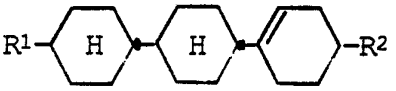

II14

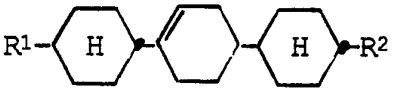

II15


II16


II17

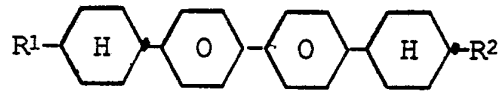

II18

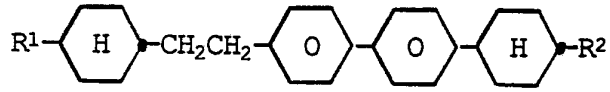

II19

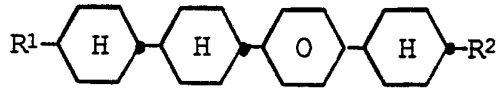

II20

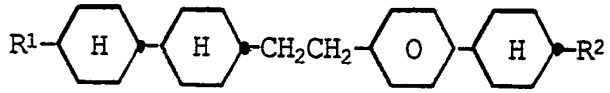
in which R^1 and R^2 are as defined under formula I', and the 1,4-phenylene groups in II8 to II17 may each, independently of one another, also be monosubstituted or polysubstistituted by fluorine.

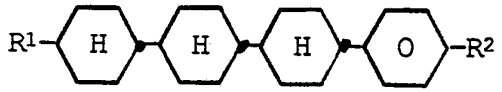
Furthermore, component A preferably additionally contains one or more compounds selected from the group comprising II21 to II25


II21


II22

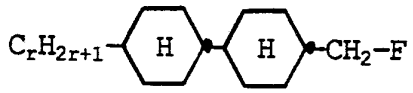

II23

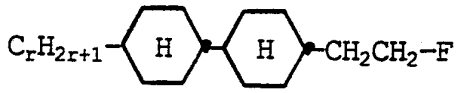

II24


II25

in which R1 and R2 are as defined under formula I', and the 1,4-phenylene groups in II21 ro II25 may also each, independently of one another, be monosubstituted or polysubstituted by fluorine.

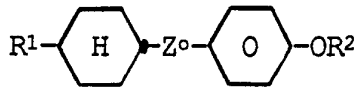
Finally, preferred mixtures of this type are those in which component A contains one or more compounds selected from the group comprising II26 and II27:


II26


II27

in which C_rH_{2r+1} is a straight-chain alkyl group having up to 7 carbon atoms.

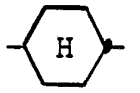
In some cases, the addition of compounds of the formula

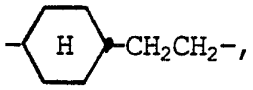


in which

R^1 and R^2 are as defined under formula I'

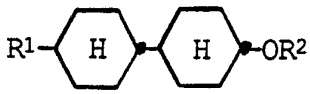
and

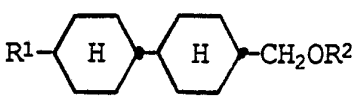
Z^o is a single bond, $-CH_2CH_2-$,  or



proves advantageous for suppressing smectic phases and improves the tilt angle, although this may reduce the specific resistance. In order to achieve parameter combinations which are ideal for the application, a person skilled in the art can easily determine whether and, if yes, in what amount these compounds may be added. Normally, less than 15 %, in particular 5-10 %, are used.

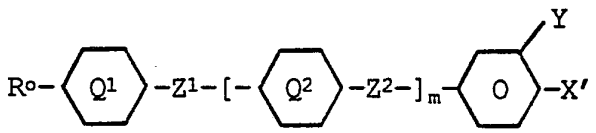
Preference is also given to liquid-crystal mixtures which contain one ore more compounds selected from the group comprising III' and VI':

 III'

 IV'

in which R^1 and R^2 are as defined under formula I'.

The type and amount of the polar compounds having positive dielectric anisotropy is not crucial per se. A person skilled in the art can use simple routine experiments to select suitable materials from a wide range of known and, in many cases, also commercially available components and base mixtures. The media according to the invention preferably contain one or more compounds of the formula I"



I"

in which Z^1, Z^2 and m are as defined under the formula I', Q^1 and Q^2 are each, independently of one another, 1,4-phenylene, trans-1,4-cyclohexylene or 3-fluoro-1,4-phenylene-, and one of the radicals Q^1 and Q^2 is alternatively trans-1,3-dioxane-2,5-diyl, pyrimidine-2,5-diyl, pyrimidine-2,5-diyl or 1,4-cyclohexenylene,

R^o is n-alkyl, n-alkenyl, n-alkoxy or n-oxaalkyl, in each case having up to 9 carbon atoms, Y is H or F and X' is CN, halogen, CF_3, OCF_3 or $OCHF_2$.

In a preferred embodiment, the media according to the invention for STN or TN applications are based on compounds of the formula I" in which X' is CN. It goes without saying that smaller or larger proportions of other compounds of the formula I" (X' ≠ CN) are also possible. For MLC applications, the media according to the invention preferably contain only

up to about 10 % of nitriles of the formula I" (but preferably no nitriles of the formula I", but instead compounds of the formula I' where X' = halogen, CF_3, OCF_3 or $OCHF_2$). These media are preferably based on the compounds of the formulae II to XII.

The construction of the STN and MLC displays according to the invention from polarizers, electrode base plates and electrodes with surface treatment corresponds to the construction which is conventional for displays of this type. The term conventional construction here is widely drawn and also covers all derivatives and modifications of the MLC display, in particular also matrix display elements based on poly-Si TFTs or MIMs.

An essential difference between the displays according to the invention and those customary hitherto based on the twisted nematic cell is, however, the choice of liquid-crystal parameters in the liquid-crystal layer.

The liquid-crystal mixtures which can be used according to the invention are prepared in a manner which is conventional per se. In general, the desired amount of the components used in the lesser amount is dissolved in the components making up the principal constituent, expediently at elevated temperature. It is also possible to mix solutions of the components in an organic solvent, for example in acetone, chloroform or methanol, and, after thorough mixing, to remove the solvent again, for example by distillation.

The dielectrics may also contain other additives known to those skilled in the art and described in the literature. For example, 0-15 % of pleochroic dyes or chiral dopes can be added.

C denotes a crystalline phase, S a smectic phase, S_B a smectic B phase, N a nematic phase and I the isotropic phase.

V_{10} denotes the voltage for 10 % transmission (view angle perpendicular to the plate surface). t_{on} denotes the switch-on time and t_{off} the switch-off time at an operating voltage corresponding to 2.5 times the value of V_{10}. Δn denotes the optical anisotropy and n_o the refractive index. $\Delta\varepsilon$ denotes the dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{||} - \varepsilon_{\perp}$, where $\varepsilon_{||}$ is the dielectric constant parallel to the longitudinal molecular axes and $\varepsilon_{\perp}$ is the dielectric constant perpendicular thereto. The electro-optical data were measured in a TN cell at the 1st minimum (i.e. at a d n value of 0.5) at 20 °C, unless expressly stated otherwise. The optical data were measured at 20 °C, unless expressly stated otherwise.

The examples below are intended to illustrate the invention without representing a limitation. Above and below all temperatures are given in °C. The percentages are percent by weight.

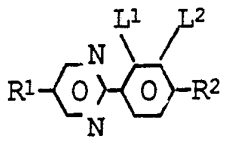
In the present application and in the examples below, the structures of the liquid-crystal compounds are indicated by

acronyms, with the transformation into chemical formulae taking place in accordance with Tables A and B below. All radicals C_nH_{2n+1} are straight-chain alkyl radicals containing n or m carbon atoms. The coding in Table B is self-evident. In Table A, only the acronym for the base structure is given. In individual cases, the acronym for the base structure is followed, separated by a hyphen, by a code for the substituents R^1, R^2, L^1, L^2 and L^3:

Code for R^1, R^2, L^1, L^2, L^3	R^1	R^2	L^1	L^2	L^3
nm	C_nH_{2n+1}	C_mH_{2m+1}	H	H	H
nOm	C_nH_{2n+1}	OC_mH_{2m+1}	H	H	H
nO.m	C_nH_{2n+1}	C_mH_{2m+1}	H	H	H
n	C_nH_{2n+1}	CN	H	H	H
nN.F	C_nH_{2n+1}	CN	H	H	H
nF	C_nH_{2n+1}	F	H	H	H
nOF	C_nH_{2n+1}	F	H	H	H
nCl	C_nH_{2n+1}	Cl	H	H	H
nF.F	C_nH_{2n+1}	F	H	F	H
nOmFF	C_nH_{2n+1}	OC_mH_{2m+1}	F	F	H
nmF	C_nH_{2n+1}	OC_mH_{2m+1}	F	H	H
nCF_3	C_nH_{2n+1}	CF_3	H	H	H
$nOCF_3$	C_nH_{2n+1}	OCF_3	H	H	H
$nOCF_2$	C_nH_{2n+1}	$OCHF_2$	H	H	H
nS	C_nH_{2n+1}	NCS	H	H	H
rVsN	C_nH_{2n+1}-CH-CH-C_sH_{2s}-	CN	H	H	H
rEsN	C_nH_{2n+1}-O-C_2H_{2s}-	CN	H	H	H
nNF	C_nH_{2n+1}	CN	F	H	H
nAm	C_nH_{2n+1}	$COOC_mH_{2m+1}$	H	H	H

Code for R^1, R^2, L^1, L^2, L^3	R^1	R^2	L^1	L^2	L^3
nF.F.F	C_nH_{2n+1}	F	H	F	F
nF.F.F.F.	C_nH_{2n+1}	F	F	F	F

Table A:



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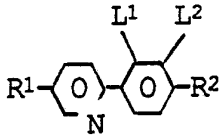
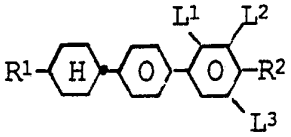


PYRP



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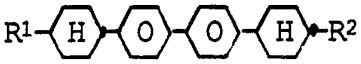
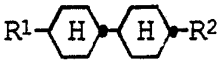


CBC



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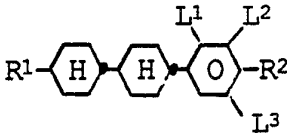

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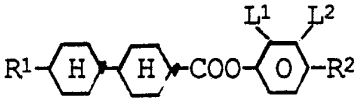

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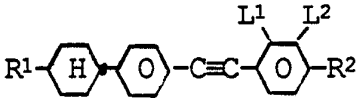

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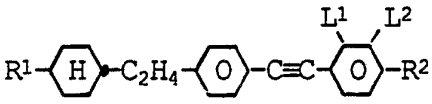

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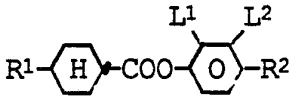

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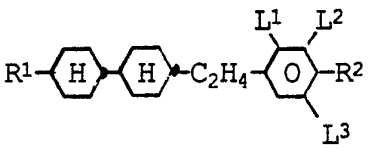
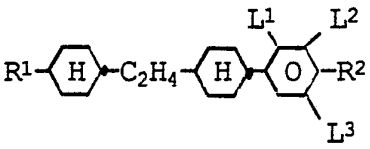


ECCP



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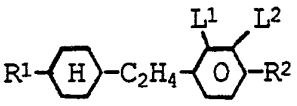

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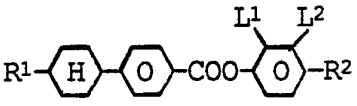

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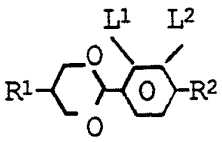

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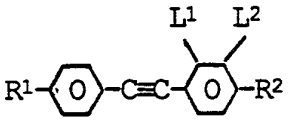

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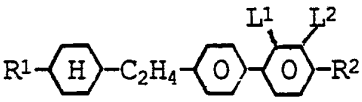

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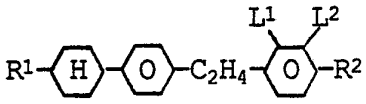

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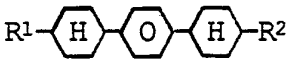

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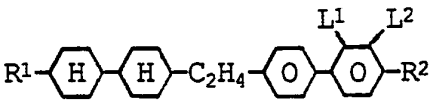

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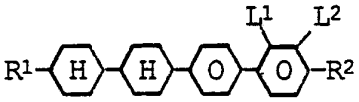

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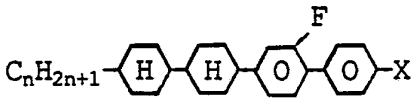

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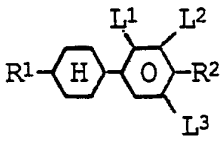

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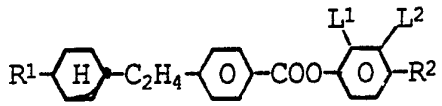

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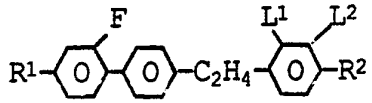

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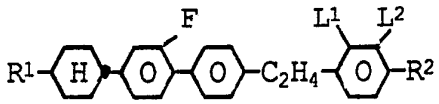

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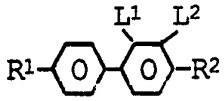

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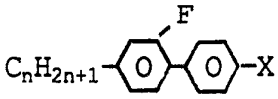

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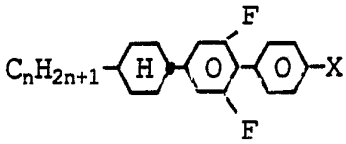

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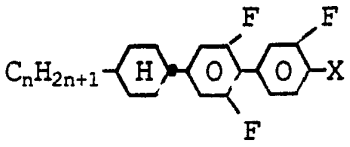

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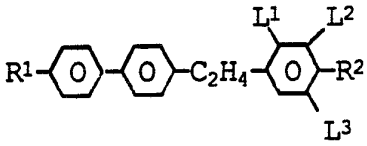

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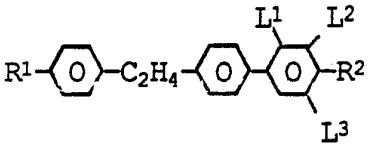

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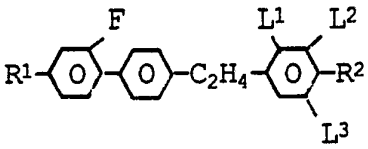

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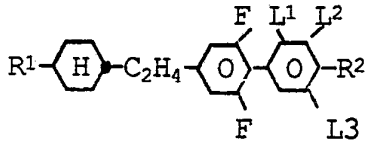

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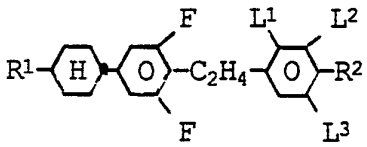

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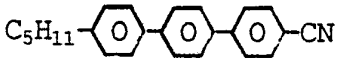

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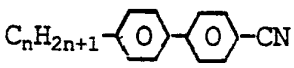
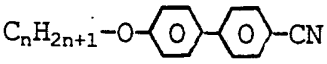
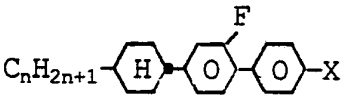


K3n



M3n



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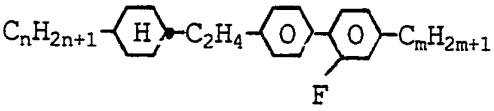
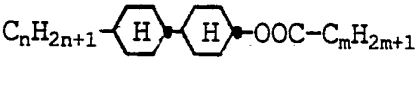
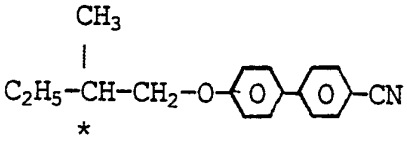


Inm



C-nm



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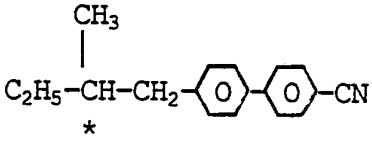

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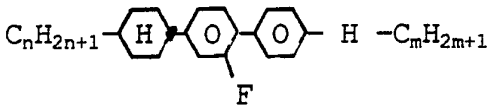
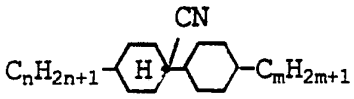


CBC-nmF



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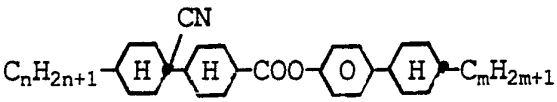
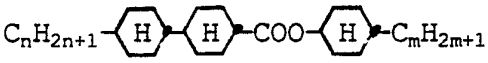
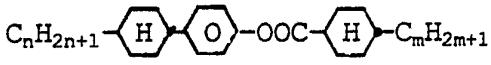


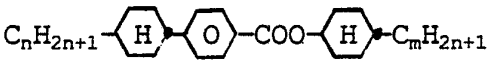
CCPC-nm



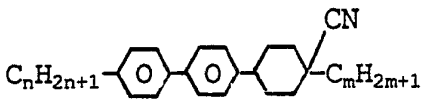
CH-nm



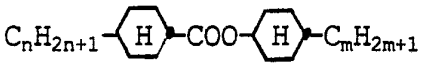
HD-nm



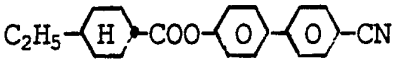
HH-nm



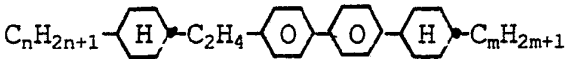
NCB-nm



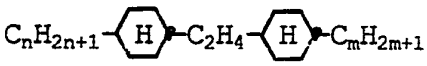
OS-nm



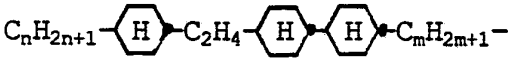
CHE



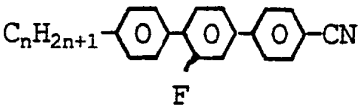
ECBC-nm



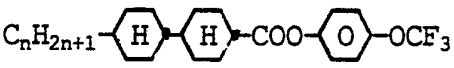
ECCH-nm



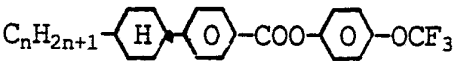
CCH-n1Em



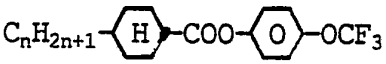
T-nFn



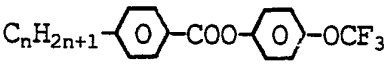
CP-nOCF$_3$



HP-nOCF$_3$



D-nOCF$_3$



ME-nOCF$_3$

Example 1

PCH-6F	13.0
PCH-7F	7.0
CCP-20CF3	10.0
CCP-30CF3	11.0
CCP-40CF3	10.0
CCP-50CF3	12.0
BCH-3F.F	12.0
BCH-5F.F	12.0
CP-30CF3	6.0
CP-50CF3	7.0

Example 2

PCH-6F	13.0
PCH-7F	7.0
CCP-20CF3	10.0
CCP-30CF3	11.0
CCP-40CF3	10.0
CCP-50CF3	12.0
BCH-3F.F	12.0
BCH-5F.F	12.0
HP-30CF3	6.0
HP-50CF3	7.0

Example 3

ME30CF3	5.0
PCH-6F	8.0
PCH-7F	7.0
CCP-20CF3	10.0
CCP-30CF3	11.0
CCP-40CF3	10.0
CCP-50CF3	12.0
BCH-3F.F	12.0
BCH-5F.F	12.0
CP-30CF3	6.0
CP-50CF3	7.0

Example 4

PCH-5F	5.0
PCH-6F	13.0
PCH-7F	7.0
CCP-20CF3	10.0
CCP-30CF3	11.0
CCP-40CF3	10.0
CCP-50CF3	12.0
BCH-3F.F	12.0
BCH-5F.F	12.0
HP-30CF3	4.0
HP-50CF3	4.0

Example 5

PCH-5F	13.0
PCH-7F	7.0
CCP-20CF3	8.0
CCP-30CF3	10.0
CCP-40CF3	8.0
CCP-50CF3	10.0
BCH-3F.F	12.0
BCH-5F.F	12.0
HP-30CF3	5.0
HP-50CF3	5.0
CP-30CF3	5.0
CP-50CF3	5.0

Example 6

PCH-5F	5.0
PCH-6F	13.0
PCH-7F	7.0
CCP-20CF3	10.0
CCP-30CF3	11.0
CCP-40CF3	10.0
CCP-50CF3	12.0
BCH-3F.F	12.0
BCH-5F.F	12.0
CP-30CF3	4.0
CP-50CF3	4.0

Example 7

D-30CF3	5.0
PCH-6F	8.0
PCH-7F	7.0
CCP-20CF3	10.0
CCP-30CF3	11.0
CCP-40CF3	10.0
CCP-50CF3	12.0
BCH-3F.F	12.0
BCH-5F.F	12.0
CP-30CF3	6.0
CP-50CF3	7.0

Example 8

PCH-5F	7.0
PCH-6F	7.0
PCH-7F	6.0
CP-30CF3	10.0
CP-50CF3	10.0
CCP-20CF3	10.0
CCP-30CF3	10.0
CCP-40CF3	9.0
CCP-50CF3	10.0
ECCP-3F.F	11.0
ECCP-5F.F	10.0

Example 9

PCH-5F	10.0
PCH-6F	8.0
PCH-7F	6.0
CCP-20CF3	8.0
CCP-30CF3	12.0
CCP-40CF3	7.0
CCP-50CF3	11.0
BCH-3F.F	12.0
BCH-5F.F	10.0
CP-30CF3	5.0
CP-50CF3	5.0
CBC-33F	2.0
CBC-53F	2.0
CBC-55F	2.0

Example 10

PCH-5F	3.0
PCH-6F	3.0
PCH-7F	3.0
CCP-20CF3	7.0
CCP-30CF3	8.0
CCP-40CF3	7.0
CCP-50CF3	8.0
CP-30CF3	6.0
CP-50CF3	6.0
ECCP-30CF3	6.0
ECCP-50CF3	6.0
ECCP-3F.F	8.0
ECCP-5F.F	8.0
CCH-301	11.0
CCH-303	10.0

Example 11

PCH-5F	7.0
PCH-6F	7.0
PCH-7F	6.0
CP-3F	10.0
CP-5F	10.0
CCP-20CF3	10.0
CCP-30CF3	10.0
CCP-40CF3	9.0
CCP-50CF3	10.0
CP-30CF3	11.0
CP-50CF3	10.0

Example 12

PCH-5F	4.0
PCH-6F	4.0
CCH-301	10.0
CCH-303	10.0
CP-30CF3	10.0
CP-50CF3	10.0
CCP-20CF3	11.0
CCP-30CF3	11.0
CCP-40CF3	9.0
CCP-50CF3	10.0
EHP-3F.F	6.0
EHP-3F.F	6.0

Example 13

PCH-6F	9.0
PCH-6F	7.0
PCH-7F	6.0
CP-3F	7.0
CP-5F	7.0
CCP-20CF3	9.0
CCP-30CF3	9.0
CCP-40CF3	8.0
CCP-50CF3	9.0
CP-30CF3	10.0
CP-50CP3	9.0
CCH-301	10.0

The properties of the Examples 1-13 are given in the following table:

Example	1	2	3	4	5	6	7	8	9	10	11	12	13
S --> N [° C]	-	<-20	<+20	-	<-20	<0	<-20	-	-	-	-	-	-
Clearing point [° C]	+95	+92	+98	+81	+96	+83	99	101	79	76	118	101	95
Viscosity [mm^2s^{-1}] 20° C	15	16	-	14	16	14	15	-	14	13	-	-	-
Viscosity [mm^2s^{-1}] 0° C	41	cryst.	-	37	42	37	42	-	-	-			
Viscosity [mm^2s^{-1}] -20° C	180	-	-	147	0.5<kr<1h	153	-	-	-	-	-	-	-
Viscosity [mm^2s^{-1}] -30° C	cryst.	-	-	smekt.	-	cryst.	cryst.	-	-	-	-	-	-
Δn (589nm, 20° C)	+0.0940	+0.0986	+0.0991	+0.0943	+0.0911	0.0911	0.0968	0.0768	0.097	0.078	0.0786	0.0773	0.0732
ne (589nm, 20° C)	1.5706	1.5775	1.5749	1.5734	1.5768	1.5687	-	1.5483	-	-	1.5504	1.5468	1.5449
no (589nm, 20° C)	1.4765	1.4789	1.4758	1.4791	1.4777	1.4776	-	1.4715	-	-	-	-	-
$V_{(10,0,20)}$ d.Δn=0,4µm	1.73	1.59	1.72	1.58	1.68	1.67	1.78	2.28	-	-	2.26	2.22	2.12
$V_{(50,0,20)}$	2.20	2.02	2.19	2.00	2.13	2.11	2.28	2.70	-	-	2.68	2.62	2.55
$V_{(90,0,20)}$	2.87	2.62	2.87	2.59	2.81	2.74	2.99	3.30	-	-	3.27	3.21	3.13
HR (100° C)/%	95.0	96.9	94.0	95.5	90.0	95.5	90.2						
HR (20° C)/%	98.3	98.6	98.3	98.5	98.0	98.5	98.2	-	-	-	-	-	-
HR (20° C)/%	-	-	-	-	-	-	97.4	-	-	-	-	-	-

Example 14

A liquid-crystal composition consisting of

PCH-5F	8.0 %
PCH-6F	8.0 %
CP-3F	5.0 %
CP-5F	5.0 %
BCH-3F.F	7.0 %
BCH-5F.F	7.0 %
CCP-2OCF_3	8.0 %
CCP-3OCF_3	7.0 %
CCP-4OCF_3	7.0 %
CCP-5OCF_3	7.0 %
ECCP-3F.F	9.0 %
ECCP-5F.F	8.0 %
ECCP-3OCF_3	7.0 %
ECCP-5OCF_3	7.0 %

shows the following properties:

Clearing point	+102 °C
Viscosity (+20 °C)	16 mm^2 s^{-1}
Optical anisotropy (20 °C, 589 nm)	Δn +0.0876
V(10,0,20)	2.10 (1st) V

Example 15

PCH-5F	7.6	S < -10 N 82 I
PCH-6F	7.6	V_{10} 2.25 Volt
PCH-7F	7.6	Δn 0.1210
FET-3F	5.7	
FET-5F	3.8	
CFET-3F.F	7.6	
CFET-5F	8.5	
BCH-3F.F.F	13.3	
BCH-5F.F.F	12.3	
BCH-52F	7.6	
ECCP-30CF3	6.7	
CBC-33F	1.9	
CBC-53F	2.9	
CBC-55F	1.9	
CP-4F	5.0	

Example 16

PCH-5F	17.0	S < -30 N 111 I
CCP-20CF3	15.0	Δn 0.0894
CCP-30CF3	12.0	Viscosity (20 °C): 15 $mm^2 s^{-1}$
CCP-40CF3	12.0	V_{10} 2.26 Volt
CCP-50CF3	12.0	
CP-3F	10.0	
CP-5F	10.0	
PCH-301	7.0	
CPTP-301	5.0	

Example 17

A liquid crystalline composition consisting of

PCH-5F	9.0
PCH-6F	6.0
PCH-7F	6.0
CCP-20CF3	12.0
CCP-30CF3	12.0
CCP-40CF3	10.0
CCP-50CF3	12.0
BCH-3F.F	12.0
BCH-3F.F	10.0
CP-3F	6.0
CP-5F	5.0

exhibits a broad nematic phase range.

Example 18

A liquid crystalline composition consisting of

PCH-5F	7.0
PCH-7F	7.0
CCP-20CF3	6.0
CCP-30CF3	6.0
CCP-40CF3	6.0
CCP-50CF3	6.0
CP-20CF3	5.0
CP-30CF3	5.0
CP-40CF3	5.0

CP-50CF3	5.0
ECCP-3F.F	9.0
ECCP-5F.F	9.0
CCH-303	12.0
CCH-501	12.0

shows the following properties:

Clearing point:	+86 °C
Optical anisotropy: (20 °C, 589 nm)	Δn +0.0666
$V_{10,0,20}$	2.10 (1st) V

All compositions (Examples 1 to 18) shown above show $HR_{20}/HRo \geq 98$ % and are thus highly valuable as mixtures for active matrix displays.

HR_{20}: Voltage eholding ratio after 20 hours exposure to UV-light (280-400 nm, 12 mW cm^{-2})

HRo: Voltage holding ratio before exposure to UV-light

Example 19

A liquid crystalline composition consisting of

PCH-3	8.0
PCH-4	9.0
PCH-5	5.0
PCH-302	19.0
PCH-304	13.0
CP-30CF3	5.0
CP-50CF3	5.0
ECCP-3F	6.0
CP-33	7.0
CP-35	8.0
CP-43	8.0
CP-45	7.0

shows the following properties:

Clearing point:	+ 92 °C
Optical anisotropy:	Δn 0.0951
$V_{10,0,20}$:	2.22 V

Example 20

PCH-5F	3.0
PCH-6F	3.0
PCH-7F	3.0
CCP-20CF3	6.0
CCP-30CF3	6.0
CCP-40CF3	6.0
CCP-50CF3	6.0
ECCP-30CF3	3.0
ECCP-50CF3	3.0
ECCP-3F.F	8.0
ECCP-5F.F	8.0
CH-33	4.0
CH-35	4.0
CCH-301	11.0
CCH-303	11.0
CCH-501	10.0
CP-30CF3	3.0
CP-50CF3	3.0

Clearing point:	88 °C
Δn:	0.0651
$V_{10,0,20}$:	2.75 V (1st Min.)

Example 21

PCH-5F	7.0
PCH-7F	7.0
CCP-20CF3	6.0
CCP-30CF3	6.0
CCP-40CF3	6.0
CCP-50CF3	6.0
CP-20CF3	5.0
CP-30CF3	5.0
CP-40CF3	5.0
CP-50CF3	5.0
ECCP-3F.F	9.0
ECCP-5F.F	9.0
CCH-303	12.0
CCH-501	12.0

Clearing point:	86 °C
Δn:	0.0666
$V_{10,0,20}$:	2.14 V (1st Min.)

Example 22

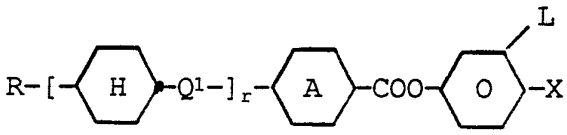
A liquid crystal medium is prepared consisting of:

K6	6.0
K9	7.0
K15	8.0
PCH-3	23.0
PCH-302	7.0
CP-30CF_3	6.0
CP-50CF_3	6.0
PTP-102	5.0
PTP-201	5.0
ECCP-3	6.0
ECCP-31	6.0
ECCP-32	5.0
ECCP-33	5.0
BCH-32	5.0

and exhibits a broad nematic phase range and a short switching time in a STN display.

Patent Claims

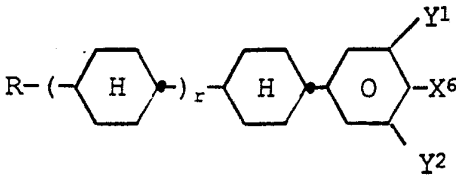
1. Liquid-crystalline medium based on a mixture of polar compounds having positive dielectric anisotropy, characterized in that it contains one or more compounds of the general formula I



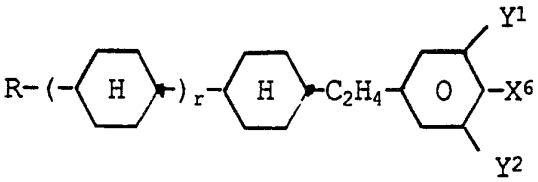
I

in which r is o or 1, Q^1 is $-CH_2CH_2-$ or a single bond, A is 1,4-phenylene or trans-1,4-cyclohexylene, L is H or F, R is alkyl, alkoxy, oxaalkyl, fluoroalkyl or alkenyl, in each case having up to 7 carbon atoms and X is F, CF_3, or OCF_2H.

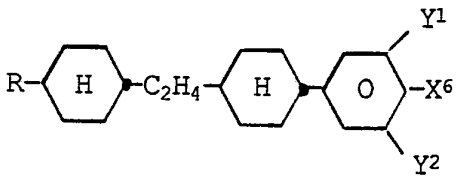
2. Medium according to Claim 1, characterized in that it additionally contains one or more compounds selected from the group comprising the general formulae II, III and IV:



II



III



II

in which the individual radicals are as defined below:

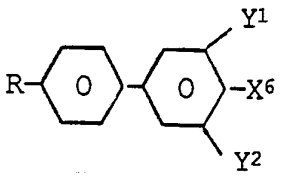
R: alkyl, oxaalkyl, fluoroalkyl or alkenyl, in each case having up to 7 carbon atoms

X^6: F, Cl, CF_3, OCF_3 or $OCHF_2$

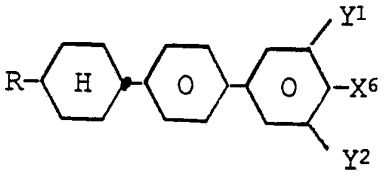
Y^1 and Y^2: in each case, independently of one another, H or F

r: 0 or 1.

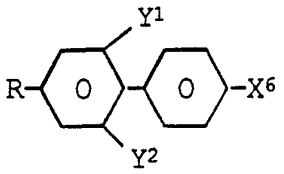
3. Medium according to Claim 1 or 2, characterized in that it additionally contains one or more compounds selected from the group comprising the general formulae V to VIII:



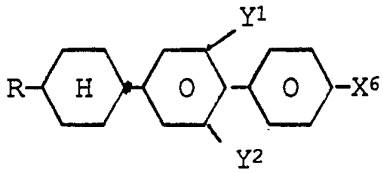
V



VI



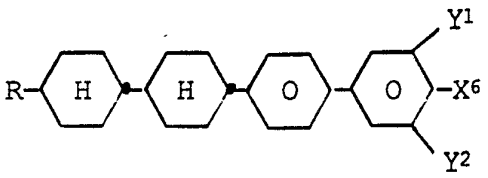
VII



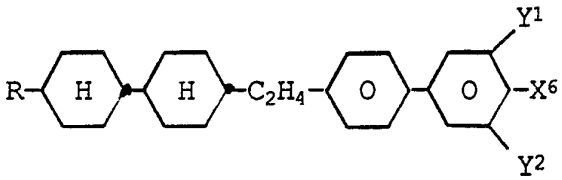
VIII

in which R, X^6, Y^1 and Y^2 are each, independently of one another, as defined in Claim 2.

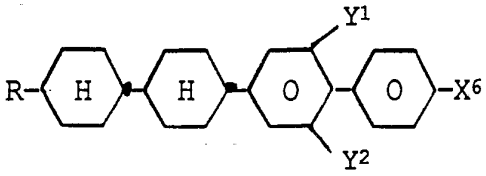
4. Medium according to at least one of Claims 1 to 3, characterized in that it additionally contains one or more compounds selected from the group comprising the general formulae IX to XIV:



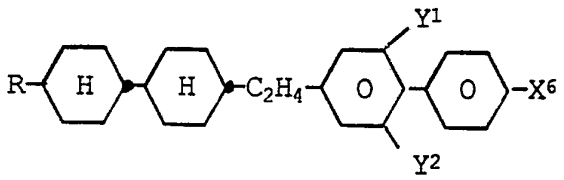
IX



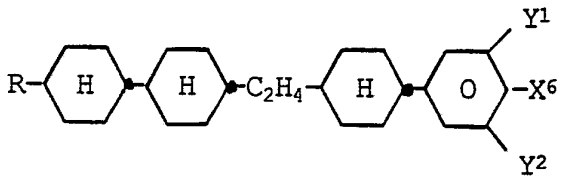
X



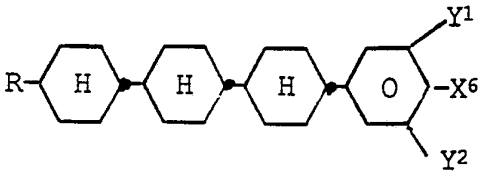
XI



XII



XIII



XIV

in which R, X^6, Y^1 and Y^2 are each, independently of one another, as defined in Claim 2.

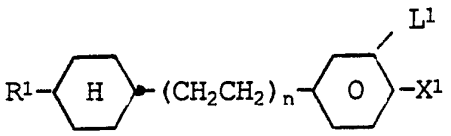
5. Medium according to Claim 2, characterized in that the proportion of compounds of the formulae I to IV together is at least 50 % by weight in the total mixture.

6. Medium according to Claim 1 or 2, characterized in that the proportion of compounds of formula I is from 10 to 50 % by weight in the total mixture.

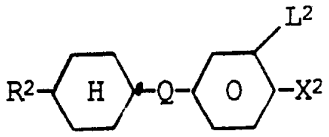
7. Medium according to at least one of Claims 2 to 4, characterized in that the proportion of compounds of the formulae II to IV is from 30 to 70 % by weight in the total mixture.

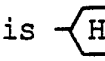
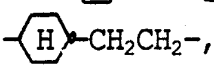
8. Medium according to at least one of Claims 1 to 4, characterized in that it essentially comprises compounds selected from the group comprising the general formulae I to XIV.

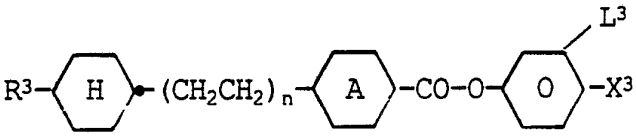
9. Medium according to at least one of Claims 1 to 8 based on terminally and laterally fluorinated compounds, characterized in that it contains about 10 to 25 % by weight of one or more compounds from group 1:

group 1: 

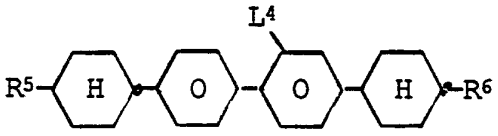
wherein R^1 denotes a straight-chain alkyl group of 5 or more carbon atoms, L^1 is H or F, X^1 is F, CF_3, OCF_3 or OCF_2H and n is 0 or 1, preferably 0, about 10 to 70 %, preferably 15 to 25 %, by weight of one or more compounds from group 2:

group 2: 

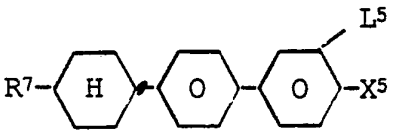
wherein R^2 denotes a straight-chain alkyl group of 3 to 5 carbon atoms, L^2 is H or F, X^2 is F, CF_3, OCF_3 or OCF_2H, Q is  , or , preferably or  , about 5 to 40 %, in particular 5 to 25 % by weight of one or more compounds of the formula Ia:

 Ia

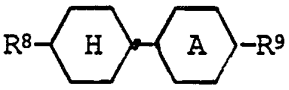
wherein L^3 is H or F, X^3 is F, CF_3, OCF_3 or OCF_2H, n is 0 or 1, preferably 0, and -(A)- is -(H)- or -(O)-, about 0 to 15 % by weight of one or more compounds from group 4.

group 4: 

wherein L^4 is H or F about 0 to 25 %, preferably 1 to 5 %, by weight of one or more compounds from group 5:

group 5: 

wherein R^3 to R^7 each independently denotes a straight-chain alkyl group of 1 to 12 carbon atoms, L^5 is H or F, L^5 is H or F, X^5 is F, CF_3, OCF_3 or OCF_2H, and about 0 to 20 % by weight of one or more compounds from group 6:

group 6: 

wherein -(A)- has the meaning given for formula Ia, and R^8 and R^9 are each independently alkyl or alkoxy groups with one to 12 carbon atoms.

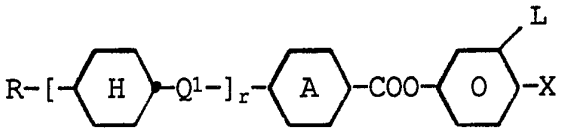
10. Use of the liquid-crystalline medium according to Claim 1 for electrooptical purposes.

11. Electrooptical liquid-crystal display containing a liquid-crystalline medium according to Claim 1.

AMENDED CLAIMS

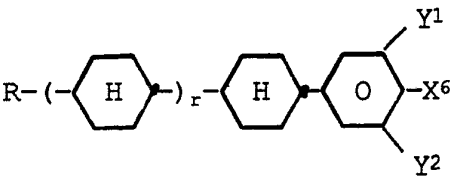
[received by the International Bureau on 23 January 1992 (23.01.92); original claims 1-11 replaced by amended claims 1-10 (6 pages)]

1. Liquid-crystalline medium based on a mixture of polar compounds having positive dielectric anisotropy, characterized in that it contains one or more compounds of the general formula I

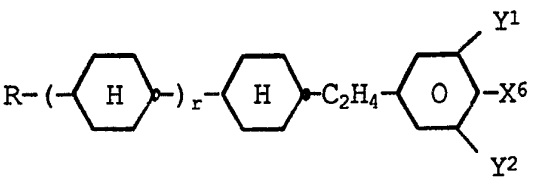


I

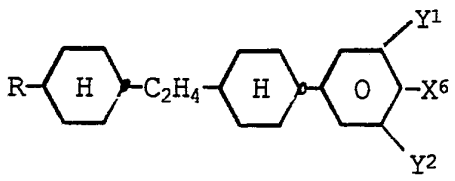
in which r is o or 1, Q^1 is $-CH_2CH_2-$ or a single bond, A is 1,4-phenylene or trans-1,4-cyclohexylene, L is H or F, R is alkyl, alkoxy, oxaalkyl, fluoroalkyl or alkenyl, in each case having up to 7 carbon atoms and X is F, CF_3, OCF_3 or OCF_2H and additionally one or more compounds selected from the group comprising the general formulae II, III and IV:



II



III



II

in which the individual radicals are as defined below:

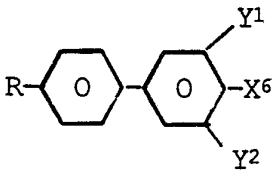
R: alkyl, oxaalkyl, fluoroalkyl or alkenyl, in each case having up to 7 carbon atoms

X^6: F, Cl, CF_3, OCF_3 or $OCHF_2$

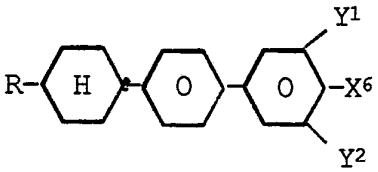
Y^1 and Y^2: in each case, independently of one another, H or F

r: 0 or 1.

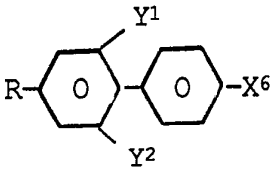
2. Medium according to Claim 1, characterized in that it additionally contains one or more compounds selected from the group comprising the general formulae V to VIII:



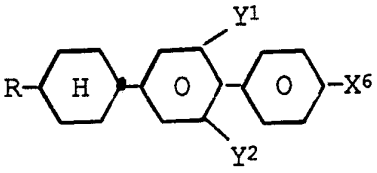
V



VI



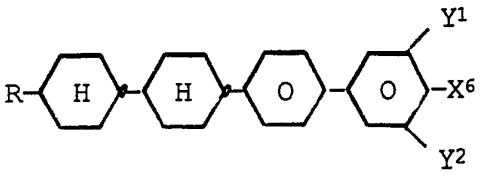
VII



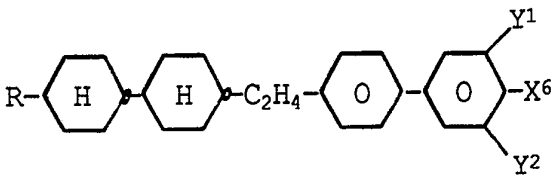
VIII

in which R, X^6, Y^1 and Y^2 are each, independently of one another, as defined in Claim 1.

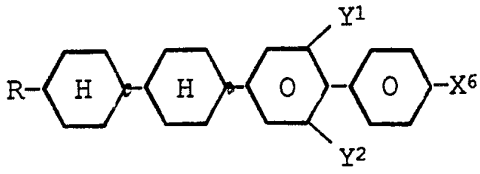
3. Medium according to at least one of Claims 1 to 2, characterized in that it additionally contains one or more compounds selected from the group comprising the general formulae IX to XIV:



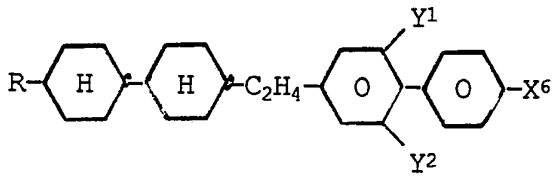
IX



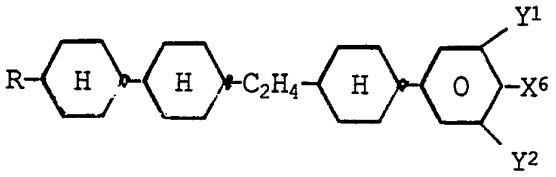
X



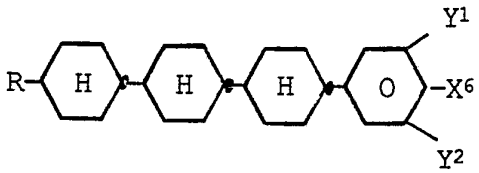
XI



XII



XIII



XIV

in which R, X^6, Y^1 and Y^2 are each, independently of one another, as defined in Claim 1.

4. Medium according to Claim 1, characterized in that the proportion of compounds of the formulae I to IV together is at least 50 % by weight in the total mixture.

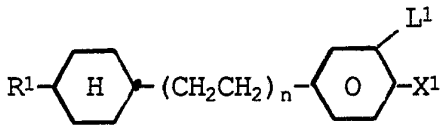
5. Medium according to Claim 1, characterized in that the proportion of compounds of formula I is from 10 to 50 % by weight in the total mixture.

6. Medium according to at least one of Claims 1 to 3, characterized in that the proportion of compounds of the formulae II to IV is from 30 to 70 % by weight in the total mixture.

7. Medium according to at least one of Claims 1 to 3, characterized in that it essentially comprises compounds selected from the group comprising the general formulae I to XIV.

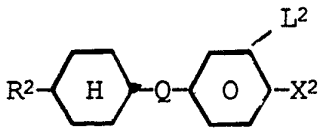
8. Medium according to at least one of Claims 1 to 7 based on terminally and laterally fluorinated compounds, characterized in that it contains about 10 to 25 % by weight of one or more compounds from group 1:

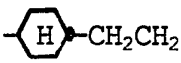
group 1:

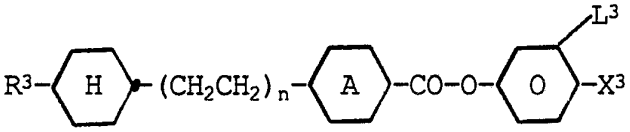


wherein R^1 denotes a straight-chain alkyl group of 5 or more carbon atoms, L^1 is H or F, X^1 is F, CF_3, OCF_3 or OCF_2H and n is 0 or 1, preferably 0, about 10 to 70 %, preferably 15 to 25 %, by weight of one or more compounds from group 2:

group 2:

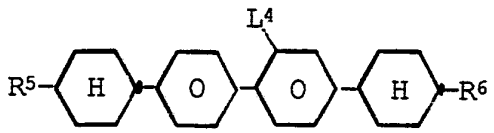


wherein R^2 denotes a straight-chain alkyl group of 3 to 5 carbon atoms, L^2 is H or F, X^2 is F, CF_3, OCF_3 or OCF_2H, Q is  , or , preferably or  , about 5 to 40 %, in particular 5 to 25 % by weight of one or more compounds of the formula Ia:

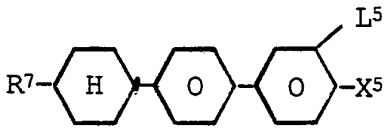


Ia

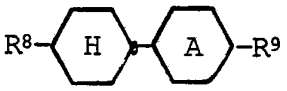
wherein L^3 is H or F, X^3 is F, CF_3, OCF_3 or OCF_2H, n is 0 or 1, preferably 0, and - A - is - H - or - O -, about 0 to 15 % by weight of one or more compounds from group 4.

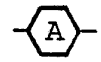
group 4: 

wherein L^4 is H or F about 0 to 25 %, preferably 1 to 5 %, by weight of one or more compounds from group 5:

group 5: 

wherein R^3 to R^7 each independently denotes a straight-chain alkyl group of 1 to 12 carbon atoms, L^5 is H or F, L^5 is H or F, X^5 is F, CF_3, OCF_3 or OCF_2H, and about 0 to 20 % by weight of one or more compounds from group 6:

group 6: 

wherein  has the meaning given for formula Ia, and R^8 and R^9 are each independently alkyl or alkoxy groups with one to 12 carbon atoms.

9. Use of the liquid-crystalline medium according to Claim 1 for electrooptical purposes.

10. Electrooptical liquid-crystal display containing a liquid-crystalline medium according to Claim 1.

STATEMENT UNDER ARTICLE 19

The new main claim relates to a liquid crystalline medium containing at least one ester compound of the general formula I, in which one terminal group X is F, CF_3, OCF_3 or OCF_2H, **and**

at least one compound without an ester group selected from the compounds of the general formulae II, III and IV, in which one terminal group X^6 is Cl, F, CF_3, OCF_3 or OCF_2H.

Such media are not anticipated by any of the documents cited by the International Searching Authority, therefore, the subject matter of the present main claim is novel under Article 33(2) and Rule 64.

Furthermore, there is no motivation in any of these documents to combine the compounds of the formula I with any of the compounds of the formulae II to IV, nor is there any hint that a synergystic effect can be achieved by combining those compounds, i.e. that the resulting media exhibit improved properties, in particular higher clearing points, compared with those known from the prior art. Therefore, the subject matter of the present main claim is inventive under Article 33(3) and Rule 65.

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 91/01785

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C09K19/30; C09K19/20

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C09K

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
P,X Y	EP,A,0 431 402 (MERCK) 12 June 1991 see page 1, line 1 - page 2, line 36 see claims 1-5; examples 1,A,B,C,D	1,10,11 2-9
P,X Y	GB,A,2 232 156 (SECRETARY OF STATE FOR DEFENCE) 5 December 1990 see page 2, line 12 - page 3, line 10; claims 1-3,8,9	1,10,11 1-9
X Y	MOLECULAR CRYSTALS AND LIQUID CRYSTALS. vol. 112, no. 3/4, 1984, MONTREUX CH pages 165 - 180; H.TAKATSU: 'synthesis and some properties of 3,4-difluorophenyl trans-4'-substituted cyclohexane-1'-carboxylates' see page 166, line 17 - line 25; table III see page 173 - page 179	1,10,11 2-9

-/--

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
09 DECEMBER 1991	27. 12. 91
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	BOULON A.F.J.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X Y	JP,A,59 193 850 (DAINIPPON) 2 November 1984 & WPIL (DERWENT PUBL.)AN 84-309707 see the whole document	1,10,11 2-9
X Y	JP,A,59 170 042 (DAINIPPON) 26 September 1984 & WPIL (DERWENT PUBL.) AN 84-278314 see the whole document	1,10-11 2-9
Y	WO,A,9 009 419 (CHISSO) 23 August 1990 &EP 416117(13-9-91) see page 3, line 25 - page 4, line 55; claims 1-7; example 15	2-9
X Y	WO,A,8 706 602 (MERCK) 5 November 1987 see page 1, line 1 - line 28 see page 8, line 15 - page 9, line 20; claims 1-5; example 15	1,10-11 2-9
Y	EP,A,0 387 032 (CHISSO) 12 September 1990 see page 5, line 10 - line 25 see page 32, line 25 - page 33, line 22	1,2-9
P,Y	WO,A,9 103 445 (MERCK) 21 March 1991 see example B	2-9

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. EP 9101785 SA 51173

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 09/12/91

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0431402	12-06-91	DE-A- 4037154	06-06-91
GB-A-2232156	05-12-90	None	
JP-A-59193850	02-11-84	JP-B- 2056343	29-11-90
JP-A-59170042	26-09-84	JP-C- 1357147	13-01-87
		JP-B- 61021937	29-05-86
WO-A-9009419	23-08-90	JP-A- 2289682	29-11-90
		EP-A- 0416117	13-03-91
WO-A-8706602	05-11-87	DE-A- 3614778	05-11-87
		EP-A- 0264435	27-04-88
		JP-T- 63503226	24-11-88
		US-A- 4871469	03-10-89
EP-A-0387032	12-09-90	JP-A- 2233626	17-09-90
		US-A- 5032313	16-07-91
WO-A-9103445	21-03-91	GB-A- 2240101	24-07-91
		DE-A- 4027315	07-03-91
		EP-A- 0441951	21-08-91