

Description

This invention relates to liquid crystal mixtures and to compounds for use in them. The invention is particularly concerned with ferroelectric smectic liquid crystal mixtures and compounds. The invention also relates to electro-optical devices incorporating these mixtures.

Ferroelectric smectic liquid crystal materials utilise the ferroelectric properties of the chiral tilted smectic phase, ie the chiral smectic C, F, G, H, I, F and K phases (hereinafter designated to S_C^* etc, the asterisk * denoting chirality). The S_C^* phase is most commonly sought for use in electro-optical devices as it is the most fluid, and it is also desirable that the material shows an S_A phase at a temperature above the S_C^* phase, to assist in surface alignment.

Ferroelectric liquid crystal materials ideally have a low viscosity, a broad smectic liquid crystal temperature range, stability etc, and in particular should show a high spontaneous polarisation co-efficient (P_s , measured in $nCcm^{-2}$). Although some single component materials show these properties, it has become common practice to use a mixture which shows a smectic phase. At least one of the compounds in the mixture is optically active (chiral) so as to induce the smectic phase shown by the mixture to be chiral, especially S_C^* . Such optically active compounds are called "chiral dopants".

According to the present invention a novel compound suitable for inclusion in a ferroelectric smectic liquid crystal mixture has a formula I:



Formula I

wherein R_1 is C_3-10 straight chain or branched alkyl or alkoxy, and R_2 is C_1-12 alkyl, and the phenyl ring may carry one lateral halogen substituent.

Compounds of formula I are useful constituents of ferroelectric smectic liquid crystal mixtures. According to a second aspect of this invention there is provided a ferroelectric smectic liquid crystal mixture containing at least two compounds, at least one of which is a compound of formula I.

Suitability for use in such a mixture is among the factors determining the structural and other preferences discussed below.

The compound of formula I may be optically active, racemic, or non-optically active, but the mixture preferably contains at least one optically active compound of formula I.

In structure formula I R_2 is preferably 2-methyl heptyl.

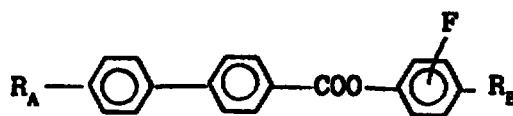
Preferably in formula I, R_1 is C_3 to C_{10} n-alkyl.

Japanese patent applications 56925/1984 (laid open No. 199856/1985) and 1984/161665 (laid open No. 199840/1985) disclose a series of nematic compounds. The former discloses compounds which are phenyl ester derivatives having a $-\text{CH}_2\text{CH}(\text{CH}_3)\text{COO}-$ link between a phenyl group and other cyclic components of the compounds. The latter patent application discloses substituted phenyl ethylene derivatives which have negative dielectric anisotropies. EP-A-168043 describes compounds suitable for providing a liquid crystal phase which has temperature-independent electro-optical parameters. In order to achieve such mixtures the specification describes addition of known chiral compounds to compounds of the invention, with all applications described being nematic. It is well known that the physics and chemistry of ferroelectric smectic liquid crystal mixtures is very different to that of nematic mixtures, particularly in terms of the requirement for miscibility and optical purity. Understanding of nematic systems thus provides very little guidance in formulating the far more idiosyncratic smectic mixtures.

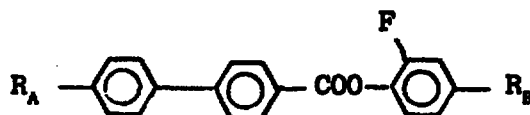
A ferroelectric smectic liquid crystal mixture of the invention will normally consist of a number of compounds, and will include one or more optically active compounds, preferably at least one of which is a compound of formula I. The other compounds in the mixture will normally include at least one compound which either alone or mixed with some or all of the other compounds in the mixture shows a smectic phase, preferably S_C , and at least one of these compounds may be a compound of formula I in a racemic form. These other compounds are often called 'smectic hosts'.

Some examples of smectic hosts include:

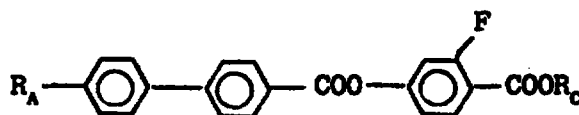
(a) The compounds, and mixtures thereof, disclosed in PCT/GB86/0040, eg of formula:



where R_A and R_B are independently selected from alkyl (preferably n-alkyl), alkoxy (preferably n-alkoxy), alkanoyloxy or alkoxycarbonyl (preferably n-alkoxycarbonyl) and contain 1 - 12 carbon atoms, preferably 3 to 10 carbon atoms. Preferred compounds of this type have structures:

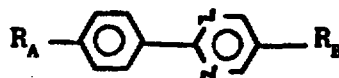


or



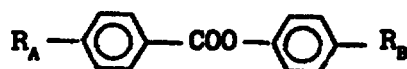
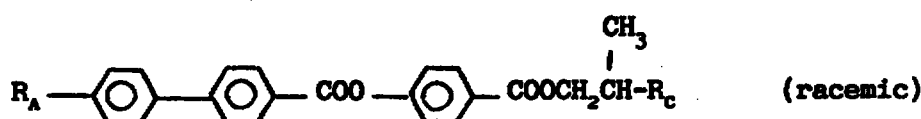
where R_C is alkyl.

(b) The compounds, and mixtures thereof, of formula:



where R_A and R_B are independently alkyl (preferably n-alkyl) or alkoxy (preferably n-alkoxy) and contain up to 12 carbon atoms.

(c) Other examples of known smectic host compounds include those of the following general formulae:

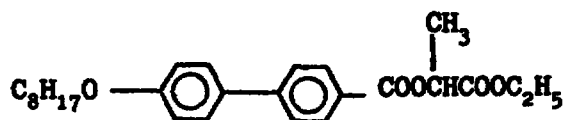


where R_A and R_B are independently selected from n-alkyl and n-alkoxy and R_C is n-alkyl, preferably ethyl.

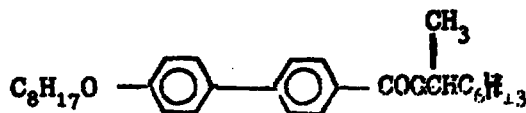
(d) r-l-cyano cis - 4 -(4'-alkyl or alkoxy-biphenyl-4-yl)-l-alkyl or alkoxy cyclohexanes.

r-l-cyano cis - 4 -(trans-4-alkyl or alkoxy cyclohexyl)-l-l-(trans-4-alkyl or alkoxy cyclohexyl)-cyclohexanes.

The mixture may also contain other optically active compounds which are miscible with smectic materials, for example the lactic acid derivatives disclosed in PCT GB/85/00512, eg



or the compounds disclosed in EPA 0110299, eg:

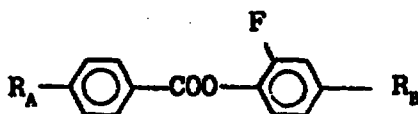


or the terpenoid derivatives disclosed in PCT/GB86/0046.

If the mixture includes more than one optically active compound, eg a compound of formula I and one of the other optically active compounds mentioned above, then the helical twist senses of the S^* phase induced by these compounds may be the same or opposite, eg by the use of both (+) and (-) optically active compounds. It is often desirable to include compounds which induce opposite twist senses of the S^* phase in order to increase the helical pitch length.

It is desirable that each optically active compound in the mixture induces the same sense of Ps in the mixture.

The mixture may also contain other known additives to improve the properties, eg Ps, Sc phase breadth, viscosity etc or to induce the appearance of an S_A phase of a temperature above the S^*_C to assist alignment. An example of a class of compounds which may be used to broaden the Sc phase is:



where R_A and R_B are independently C_1 - C_{12} n-alkyl or n-alkoxy.

The mixture may also contain pleochroic dyes.

Typically but not exclusively a ferroelectric smectic liquid crystal mixture of the invention will have the following composition:

One or more smectic host compounds	30 - 99 weight %
Optically active compound(s) of formula I	1 - 50 weight %
Other optically active compounds(s)	0 - 20 weight %
Additives and pleochroic dye if present	0 - 20 weight %
Racemic compounds(s) of formula I	0 - 20 weight %

The total being 100 weight %. The nature and relative proportions of the various components of a liquid crystal material of the invention will depend upon the use for which the material is intended, and some experimentation may be necessary to suit a particular requirement, but the basic principles of mixing and assessment of such materials is well known in the field.

Compounds of formula I may be prepared by generally applicable routes as exemplified below.

The liquid crystal materials of the invention may be used in any of the known types of ferroelectric smectic liquid crystal display device, eg the "Clark-Lagerwall Device" described in Appl. Phys Lett (1980), 36 899 and in Recent Developments in Condensed Matter Physics (1981), 4,309. The physics of this type of device and the method of constructing it are well known, and are described for example in PCT/GB85/00512, and PCT/GB86/0040.

In practice such a device usually consists of two substrates, at least one of which is optically transparent, electrodes on the inner surfaces of the substrates by which a voltage may be applied and a

layer of the liquid crystal materials sandwiched between the substrates. It is desirable that the helical pitch length of the S_C^* phase is comparable to the thickness of the material, which is why long pitch mixtures are useful. The material of the invention may be used in both the birefringence type display mode and the guest-host type display mode of the Clark-Lagerwall device. The device may for example be in the form of a clock, calculator or video screen display, and method of making the device in this form will be well known to those skilled in the art.

The invention will now be described by way of example only, with reference to: Fig. 1 which shows a cross section through a liquid crystal device.

10 Example 1

Preparation of:



20 (S-1-methyl heptyl 4-n-decylbiphenyl-4'-oxyacetate)

Stage I (ethyl 4-n-decylbiphenyl-4'-oxyacetate)

25 A 500 ml round bottomed flask was charged with 4-n-decyl-4'-hydroxybiphenyl (10g), ethylbromo acetate (6.5g), anhydrous potassium carbonate (6.6g), and butanone (160 mls). The resulting mixture was stirred and boiled under reflux for 20 hours. The reaction mixture was filtered hot through a Whatman 541 filter paper, and the butanone removed on a rotary evaporator to yield the crude product as a light yellow solid (12g). The material was purified by recrystallisation from 24 mls of industrial methylated spirit to yield a white crystalline product (8.9g).

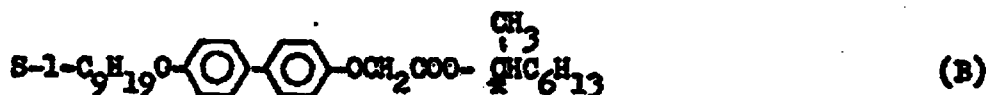
30 Stage II (4-n-decylbiphenyl-4'-oxyacetic acid)

A mixture of ethyl 4-n-decylbiphenyl-4'-oxyacetate (9.8g), potassium hydroxide (3.5g), water (11 mls), and industrial methylated spirit (400 mls) was stirred and heated under reflux overnight. The reaction mixture was cooled, added to 2 litres of cold water and acidified to pH 1 by the addition of concentrated hydrochloric acid. The resulting precipitated solid was filtered off, dried, and used in the following stage of the synthesis without further purification. The yield was 8.3 grams.

40 Stage III (S-1-methylheptyl 4-n-decylbiphenyl-4'-oxyacetate)

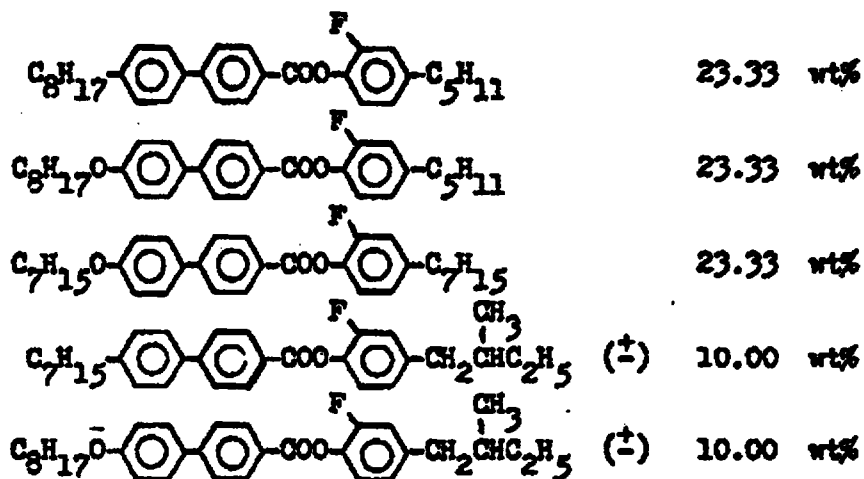
A mixture of 4-n-decylbiphenyl-4'-oxyacetic acid (4g), S-2-octanol (1.56g), dicyclohexyl carbodiimide (2.47g), 4-dimethylamino pyridine (0.2g) and dichloromethane (50 mls) was stirred overnight at room temperature. The reaction mixture was filtered, the solid residue washed with dichloromethane (25 mls) and the combined liquid extracts evaporated to dryness on a rotary evaporator. The product was an off white solid (5.2g). The product was purified by chromatography on 52g neutral alumina, eluted with petroleum ether, followed by recrystallisation from 10 mls of industrial methylated spirit. The yield of pure white product, purity 99.9% by hplc was 1.15g. Melting point was recorded as 42 - 42.5 °C.

By analogous methods the following compounds were prepared:



55 obtained as white solid, purity by hplc 99.5 % mpt, 53.5 - 54 °C

Ferroelectric smectic liquid crystal compositions were prepared containing compounds (A) and (B) above. Each composition contained 10 wt% of the compound in a host consisting of:



totalling 100 wt% with the compound (A) or (B). The mixtures are designated mixture (A) and (B) as appropriate below:

LC Transitions ($^{\circ}\text{C}$)

Mixture $\rightarrow$	(A)	(B)
$S_C - S_A$	71.3	80.1
$S_A - N^+$	88.1	93.0
$N^+ - I$	127.4	130.9

Ps (nC cm^{-2})

Temp. ($^{\circ}\text{C}$)	(A)	(B)
20	8.9	11.3
30	6.6	8.2
40	5.5	6.6
50	4.1	5.4
60	2.7	4.2
70	0.2	2.7

An example of the use of a compound of Formula I in a liquid crystal material and device embodying the present invention will now be described with reference to Figure 1.

In Figure 1 a liquid crystal cell comprises a layer 1 of liquid crystal material exhibiting a chiral smectic phase sandwiched between a glass slide 2 having a transparent conducting layer 3 on its surface, eg of tin oxide or indium tin oxide, and a glass slide 4 having a transparent conducting layer 5 on its surface. The slides 2, 4 bearing the layers 3, 5 are respectively coated by films 6, 7 of a polyimide polymer. Prior to construction of the cell the films 6 and 7 are rubbed with a soft tissue in a given direction, the rubbing directions being arranged parallel upon construction of the cell. A spacer 8 eg of polymethylmethacrylate, separates the slides 2, 4 to the required distance, eg 5 microns. The liquid crystal material 1 is introduced between the slides 2, 4 by filling the space between the slides 2, 4 and spacer 8 and sealing the spacer 8 in a vacuum in a known way. Preferably, the liquid crystal material is in the smectic A or isotropic liquid phase (obtained by heating the material) when it is introduced between the slides 2, 4 to facilitate alignment of the liquid crystal molecules with the rubbing directions on the slides 2, 4.

A polariser 9 is arranged with its polarisation axis parallel to the rubbing direction on the films 6, 7 and an analyzer (crossed polariser) 10 is arranged with its polarisation axis perpendicular to that rubbing direction.

When a square wave voltage (from a conventional source not shown) varying between about +10 volts and -10 volts is applied across the cell by making contact with the layers 3 and 5 the cell is rapidly switched upon the change in sign of the voltage between the dark state and a light state as explained above.

In an alternative device (not shown) based on the cell construction shown in Figure 1 the layers 3 and 5 may be selectively shaped in a known way, eg by photoetching or deposition through a mask, eg to provide one or more display symbols, eg letters, numerals, words or graphics and the like as seen on displays. The

electrode portions formed thereby may be addresses in a variety of ways which include multiplexed operation.

The ferroelectric smectic liquid crystal compositions described above, which show room temperature S_C phases may be used as the liquid crystal material 1.

Claims

1. A compound suitable for inclusion in a ferroelectric smectic liquid crystal mixture, having a formula I:



wherein R_1 is C_3-10 straight chain or branched alkyl or alkoxy, and R_2 is C_1-12 alkyl, and the phenyl ring may carry one lateral halogen substituent.

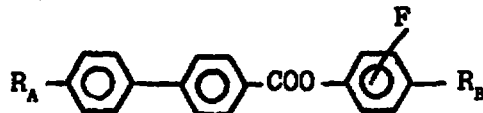
2. A compound according to claim 1 wherein R_2 is a chiral alkyl group.
3. A compound according to claim 2 wherein R_2 is 1-methylheptyl.
4. A compound according to claim 1, 2 or 3 wherein R_1 is C_3-10 n-alkyl.
5. A compound according to claim 2 and 3 wherein R_2 is optically active 1-methylheptyl and R_1 is selected from the group consisting of n-decyl and n-nonyloxy.
6. A ferroelectric smectic liquid crystal material, being a mixture of compounds, wherein at least one of the compounds is a compound of formula:



wherein R_1 is C_3-10 straight chain or branched alkyl or alkoxy, and R_2 is C_1-12 alkyl, and the phenyl ring may carry one lateral halogen substituent, and at least one of the compounds is a compound which shows a smectic phase, and the mixture having a composition:

compound(s) of Formula I	1-50 wt%
compound(s) showing a smectic phase	50-99 wt %

7. A material according to claim 6 wherein at least one of the compounds which shows a smectic phase has a formula:



where R_A and R_B are independently C_1-12 alkyl or alkoxy.

8. A material according to claim 7 wherein R_A is n-alkyl or n-alkoxy, R_B is alkyl and the fluorine substituent is positioned adjacent to the -COO- link.



electrode portions formed thereby may be addresses in a variety of ways which include multiplexed operation.

The ferroelectric smectic liquid crystal compositions described above, which show room temperature S_C phases may be used as the liquid crystal material 1.

Claims

1. A compound suitable for inclusion in a ferroelectric smectic liquid crystal mixture, having a formula I:



Formula I

wherein R_1 is C_3-10 straight chain or branched alkyl or alkoxy, and R_2 is C_1-12 alkyl, and the phenyl ring may carry one lateral halogen substituent.

2. A compound according to claim 1 wherein R_2 is a chiral alkyl group.

3. A compound according to claim 2 wherein R_2 is 1-methylheptyl.

4. A compound according to claim 1, 2 or 3 wherein R_1 is C_3-10 n-alkyl.

5. A compound according to claim 2 and 3 wherein R_2 is optically active 1-methylheptyl and R_1 is selected from the group consisting of n-decyl and n-nonyloxy.

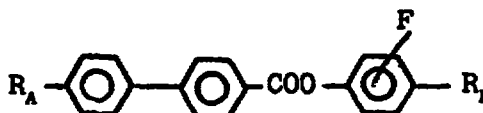
6. A ferroelectric smectic liquid crystal material, being a mixture of compounds, wherein at least one of the compounds is a compound of formula:



wherein R_1 is C_3-10 straight chain or branched alkyl or alkoxy, and R_2 is C_1-12 alkyl, and the phenyl ring may carry one lateral halogen substituent, and at least one of the compounds is a compound which shows a smectic phase, and the mixture having a composition:

compound(s) of Formula I	1-50 wt%
compound(s) showing a smectic phase	50-99 wt %

7. A material according to claim 6 wherein at least one of the compounds which shows a smectic phase has a formula:



where R_A and R_B are independently C_1-12 alkyl or alkoxy.

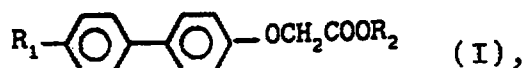
8. A material according to claim 7 wherein R_A is n-alkyl or n-alkoxy, R_B is alkyl and the fluorine substituent is positioned adjacent to the -COO- link.



9. A liquid crystal electro-optic display device which uses a liquid crystal material as claimed in any of claims 6, 7 or 8.

Patentansprüche

1. Verbindung, die geeignet ist zur Verwendung in einem ferroelektrischen smektischen Flüssigkristallgemisch und die Formel I besitzt



worin R_1 eine geradkettige oder verzweigte Alkyl- oder Alkoxygruppe mit 3-10 Kohlenstoffatomen, R_2 eine Alkylgruppe mit 1-12 Kohlenstoffatomen sind und der Phenylring einen seitlichen Halogensubstituenten enthalten kann.

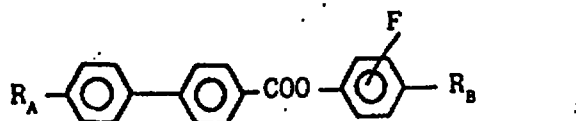
2. Verbindung nach Anspruch 1, worin R_2 eine chirale Alkylgruppe ist.
3. Verbindung nach Anspruch 2, worin R_2 1-Methylheptyl ist.
4. Verbindung nach Anspruch 1, 2 oder 3, worin R_1 eine n-Alkylgruppe mit 3-10 Kohlenstoffatomen ist.
5. Verbindung nach Anspruch 2 und 3, worin R_2 optisch aktives 1-Methylheptyl ist und R_1 ausgewählt wird unter n-Decyl und n-Nonyloxy.
6. Ferroelektrisches smektisches Flüssigkristallmaterial, das ein Gemisch von Verbindungen ist, worin mindestens eine der Verbindungen eine Verbindung der folgenden Formel ist



worin R_1 eine geradkettige oder verzweigte Alkyl- oder Alkoxygruppe mit 3-10 Kohlenstoffatomen und R_2 eine Alkylgruppe mit 1-12 Kohlenstoffatomen ist, der Phenylring einen seitlichen Halogensubstituenten enthalten kann und mindestens eine der Verbindungen eine Verbindung ist, die eine smektische Phase aufweist und wobei das Gemisch die folgende Zusammensetzung besitzt:

Verbindung(en) der Formel I	1 - 50 Masse-%
Verbindung(en), die eine smektische Phase aufweist (aufweisen)	50 - 99 Masse-%.

7. Material nach Anspruch 6, worin mindestens eine der eine smektische Phase aufweisenden Verbindungen folgende Formel besitzt:



worin R_A und R_B unabhängig voneinander eine Alkyl- oder Alkoxygruppe mit 1-12 Kohlenstoffatomen sind.



8. Material nach Anspruch 7, worin R_A n-Alkyl oder n-Alkoxy, R_B eine Alkylgruppe sind und der Fluorsubstituent der -COO- -Brücke benachbart ist.

9. Elektrooptische Flüssigkristall-Anzeigevorrichtung, bei der ein Flüssigkristallmaterial nach einem der Ansprüche 6, 7 oder 8 verwendet wird.

Revendications

1. Composé convenant pour son inclusion dans un mélange ferroélectrique smectique à propriétés de cristaux liquides, ce composé ayant une formule I



Formule I

dans laquelle R_1 représente un groupe alkyle ou alcoxy linéaire ou ramifié, en C_3 à C_{10} , et R_2 représente un groupe alkyle en C_1 à C_{12} , et le noyau phényle peut porter un halogène comme substituant latéral.

2. Composé selon la revendication 1, dans lequel R_2 est un groupe alkyle chirale.

3. Composé selon la revendication 2, dans lequel R_2 représente le groupe 1-méthylheptyle.

4. Composé selon la revendication 1, 2 ou 3, dans lequel R_1 représente un groupe n-alkyle en C_3 à C_{10} .

5. Composé selon la revendication 2 et la revendication 3, dans lequel R_2 représente un groupe 1-méthylheptyle optiquement actif, et R_1 est choisi dans l'ensemble consistant en un groupe n-décyle et un groupe n-nonyloxy.

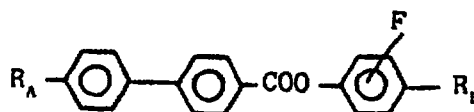
6. Matière smectique ferroélectrique à propriétés de cristaux liquides, qui est un mélange de composés dans lequel l'un au moins des composés est un composé de formule



(dans laquelle R_1 représente un groupe alkyle ou alcoxy, linéaire ou ramifié en C_3 à C_{10} , et R_2 représente un groupe alkyle en C_1 à C_{12} , et le noyau phényle peut porter un atome d'halogène comme substituant latéral, et au moins l'un des composés est un composé présentant une phase smectique, le mélange ayant pour composition :

composé(s) de formule I	1 à 50 % en poids
composé(s) présentant une phase smectique	50 à 99 % en poids

7. Matière selon la revendication 6, dans laquelle au moins l'un des composés présentant une phase smectique a pour formule



dans laquelle R_1 et R_B représentent chacun, indépendamment, un groupe alkyle ou alcoxy en C_1 à C_{12} .



8. Matière selon la revendication 7, dans laquelle R_A représente un groupe n-alkyle ou n-alcoxy, R_B représente un groupe alkyle et le fluor, fixé comme substituant, est placé près du chaînon de liaison -COO-.
- 5 9. Dispositif d'affichage électro-optique à cristaux liquides, qui utilise une matière à propriétés de cristaux liquides, telle que revendiquée dans l'une quelconque des revendications 6, 7 ou 8.

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