

Ferroelectric liquid crystals

This invention relates to ferroelectric liquid crystals for the production of rapid switching displays having storage properties for the display of digits, symbols and images.

It is known to use ferroelectric liquid crystals for the production of rapid switching displays having storage properties (N.A. Clark, S.T. Lagerwall, Appl. Phys. Lett. 36, 899 (1980)).

The number of ferroelectric liquid crystal compounds has greatly increased in recent times, but there are still no pure substances possessing optimum properties (S.T. Lagerwall, J. Wahl, N.A. Clark, Proceed. SID Symposium October 1985 San Diego USA; J.W. Goodby Science 231, 350 (1986), F. Dahl, S.T. Lagerwall, Ferroelectrics 58, 215 (1984), D. Demus, H. Zashke, Flüssige Kristalle in Tabellen ("Liquid Crystals in Tables") II, Leipzig 1984).

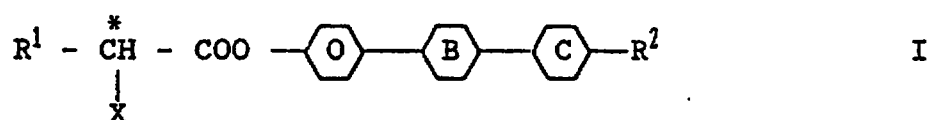
Many ferroelectric liquid crystals are chemically and thermally not very stable, possess high melting temperatures or their spontaneous polarization is not sufficient. On account of the too small dipole moments and the associated low spontaneous polarization, the derivatives of the 2-methyl-butyl group and other chiral-branched alkyl chains are unsuitable for practical use as a consequence of their too long switching times.

Other ferroelectric liquid crystals contain the azomethine grouping and as Schiff bases are not very stable against heat, moisture and acids. Some ferroelectric liquid crystals derived from chiral *d*-chloro carboxylic acids (J.W. Goodby et al, Proceed. of 1983 A.C.S. Meeting Las Vegas, Nevada 1982. Liquid Crystals and Ordered Fluids Volume 4 F 1) exhibit too high melting temperatures.

The objective of the present invention is rapid switching displays having storage properties, which contain chemically and thermally stable ferro-electric liquid crystalline substances.

The task of the invention is ferro-electric liquid crystals which can be used in rapid switching displays having storage properties.

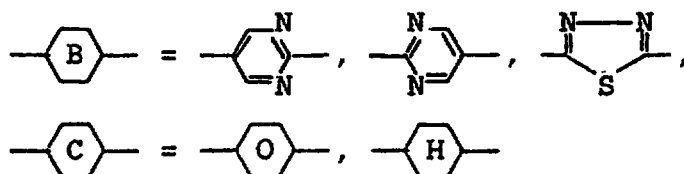
According to the invention there is provided ferro-electric derivatives of chiral acyclic halogen carboxylic acids in accordance with the general Formula I:



wherein $R^1 = \text{C}_l\text{H}_{2l+1}-$, $(\text{CH}_3)_2\text{CH}-$, $\text{C}_7\text{H}_5-\text{CH}(\text{CH}_3)-$,
 $(\text{CH}_3)_2\text{CH}-\text{CH}_2$

$R^2 = \text{C}_K\text{H}_{2K+1}-$, $\text{C}_K\text{H}_{2K+1}\text{O}-$, $\text{C}_K\text{H}_{2K+1}\text{S}-$, $\text{C}_K\text{H}_{2K+1}\text{CO}-$
 $\text{C}_K\text{H}_{2K+1}\text{COO}-$, $\text{C}_K\text{H}_{2K+1}\text{OOC}-$, $\text{C}_K\text{H}_{2K+1}\text{NH}-$

$l = 3 - 12$, $K = 1 - 12$

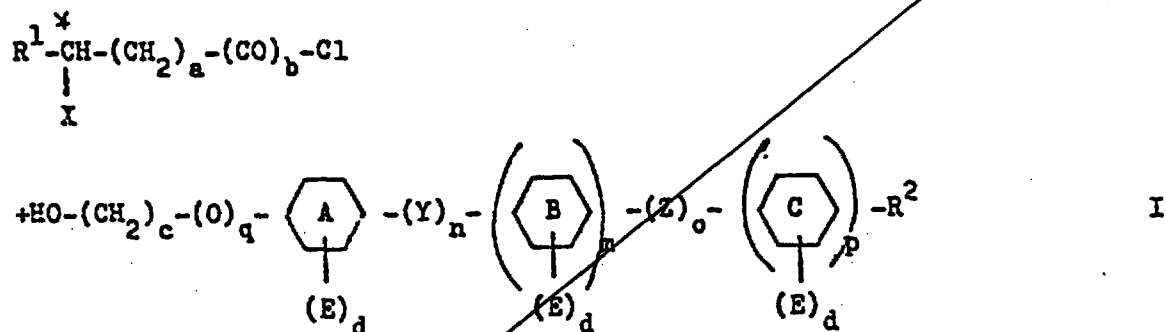


wherein X denotes Cl, Br,

with the limitation that if B is a pyrimidal ring, R^1 must be $\text{C}_7\text{H}_5-\overset{*}{\text{CH}}(\text{CH}_3)-$.

In mixtures with one another and with other liquid crystalline substances or non-crystalline substances, they form ferro-electrical crystalline liquid phases and are suitable for use in displays.

The substances are produced according to a method which itself is known, ~~for example by esterification of chiral α -halogen carboxylic acids or~~ their derivatives with corresponding hydroxy compounds, according to the following arrangement:



The chiral α -halogen carboxylic acids are obtained by reaction of commercially obtainable chiral α -amino acids by decomposition of racemates of the α -halogen carboxylic acids or by asymmetrical synthesis. Other derivatives are produced by esterification with β -halogen carboxylic acids ~~or reaction with other chiral halogen alkyl derivatives.~~

As a consequence of the high dipole moments of the halogen alkyl derivatives, the substances possess a high spontaneous polarization and thus short switching times in optoelectronic displays.

Examples of embodiment

In tables 1 and 4, examples of particular substances according to the invention which may be used alone, in mixtures of them, or in mixtures of them with other known substances, are listed.

Tables 2 and 3 contain known substances, which may be used as mixture components with the substances of tables 1 and 4.

The following meanings are used:

- K = crystalline solid state
- S_C^* = ferroelectric smectic C-phase
- S_A, S_B = smectic A, B-phase
- CH = cholesterinic phase
- I = isotropic liquid phase
- N = nematic phase
- S_X = unclassified smectic phase

The numbers between the phase designations indicate equilibrium temperatures in °C.

Table 1

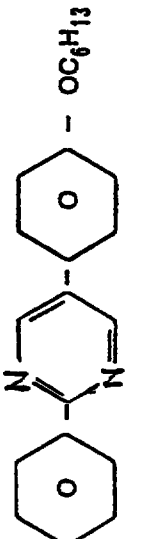
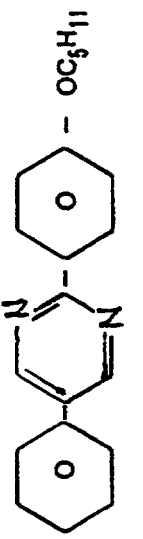
		K	S _x	Sc	SA	CH	I
Nr. 1	$ \begin{array}{c} \text{C}_2\text{H}_5 - \text{CH} - \text{CHCOO} - \text{OC}_6\text{H}_{13} \\ \quad \\ \text{CH}_3 \quad \text{C1} \end{array} $ 	140	-	-	190	-	.
Nr. 2	$ \begin{array}{c} \text{C}_2\text{H}_5 - \text{CH} - \text{CHCOO} - \text{OC}_6\text{H}_{11} \\ \quad \\ \text{CH}_3 \quad \text{C1} \end{array} $ 	153	-	-	172	185	.

Table 2

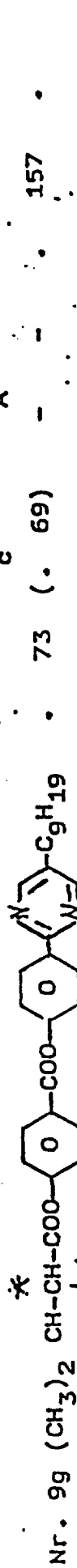
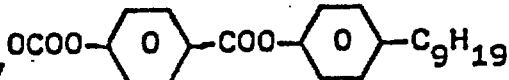
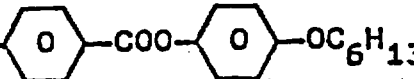
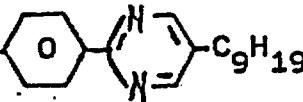
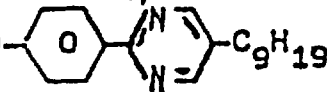
Nr.	Chemical structure	K	S_c	S_A	CH	I
Nr. 9g	$(CH_3)_2$ CH-CH-COO- 	73	(69)	-	157	.
Nr. 9h	$(CH_3)_2$ CH-CH-COO- 	87	154	-	188	.
Nr. 10	$(CH_3)_2$ CH-CH-COO- 	86	132	-	196	.
Nr. 11	$(CH_3)_2$ CH-CH-COO- 	49	58	-	72	BP74
Nr. 12	$(CH_3)_2$ CH-CH-COO- 	66	(45)	68	70	BP72
Nr. 13	$(CH_3)_2$ CH-CH-COO- 	62	(42)	69	-	.

Table 3

	K	S _c	S _A	N	T
Nr. 14 $C_8H_{17}OCOO-$  $-C_9H_{19}$	. 34	. 34	-	-	. 56
Nr. 15 $C_8H_{17}O-$  $-OC_6H_{13}$	. 55	. 66	-	-	. 89,5
Nr. 16 $C_8H_{17}O-$  $-C_9H_{19}$	. 33	. 56,5	. 74,5	-	-
Nr. 17 $C_6H_{13}O-$  $-C_9H_{19}$	. 24	. 43	. 69,5	. 70,5	.

The following examples provide production methods for starting materials for the invention:

Production of (S)-2-(4-(2-Chlor-3-methyl-butyryloxy)-phenyl)-5-(4-hexyloxyphenyl)-pyrimidine (no. 1)

A. 2-(4-hydroxyphenyl)-5-(4-hexyloxy-phenyl)-pyrimidine

0.01 mol of 4-hydroxybenzamidinium-hydrochloride and 0.01 mol of 3-dimethylamino-2-(4-hexyloxyphenyl)-N,N-dimethyl propene (2)-immoniumperchlorate are heated in 100 ml of triethylamine for 8 hours with reflux. After cooling, the mixture is poured onto ice/concentrated H_2SO_4 (200 g:25 ml), and the precipitate is sucked off and recrystallized several times from methanol.

Yield: 2.6 g (75% of theoretical value)

F: 155°C

B. (S)-2-(4-(2-Chlor-3-methyl-butyryloxy)-phenyl)-5-(4-hexyloxyphenyl)-pyrimidine.

To a solution of 0.005 mol 2-(4-hydroxyphenyl)-5-(4-hexyloxyphenyl)-pyrimidine, 0.6 ml triethylamine and 50 ml absolute toluene, 0.77 g/0.005 mol of (S)-2-Chloro-3-methylbutyryl chloride are added. (The acidic chloride was produced by the known method from the optically active amino acids).

The mixture is allowed to stand for one day at room temperature and is then heated for one hour at 80°C on a water bath. After filtering off the precipitate, the solvent is distilled out and the residue is recrystallized

several times from ethanol.

The yields are 60-70% of the theoretical value.

The liquid crystalline melt behaviour is given in the tables.

A. Production of (S)-(+)-3-hydroxy butane acid ethyl ester. 200g of fresh bakers' yeast are slurried with a 30°C hot solution of 300 g saccharose in 1.6 litre fresh water and lightly stirred at 30°C. After one hour, 0.15 mol of distilled acetoacetic ester are added with through stirring and the mixture is lightly stirred for 24 hours at 25-30°C. A 35°C hot solution of 200 g saccharose in 1 litre of water is then added by portions and, after one hour of thorough stirring, 0.15 mol of acetoacetic ester are again added. The mixture is stirred for 50 hours at 25-30°C. Sucking-off over kieselguhr is then carried out and the residue is washed twice with 100 ml water each time. The purified aqueous phases are saturated with NaCl and extracted five times with 500 ml ether each time. After separation and drying of the organic phase over Na₂SO₄, the product is concentrated on the rotary evaporator to 50-80 ml. Fractionated distillation of the residue provides (S)-(+)-3-hydroxy butane acid ethyl ester with a yield of 65-75% of theoretical value.

ee = 84% Kp₁₂ = 73°C

()D²⁵ = +36.2°

(CHCl₃ : C = 1.3)

B. Production of (R)-(-)-3-chlorobutane acid ethyl ester

0.07 mol of water-free ZnCl_2 are added to 0.24 mol of (S)-(+)-3-hydroxy butane acid ethyl ester in 100 ml benzene with stirring and exclusion of moisture. 0.72 mol of SOCl_2 are then added and stirred at room temperature for 2 days. The reaction mixture is then treated with saturated NaHCO_3 solution. After separation of the aqueous phase, drying is carried out with Na_2SO_4 , the solvent is distilled off and the residue is subjected to fractionated distillation. (R)-(-)-3-chlorobutane acid ethyl ester is obtained in a yield of 65%.

$$K_{p16} = 68^\circ\text{C}$$

$$(d)_D^{25} = -14.36^\circ$$

$$(\text{CH}_{\text{Cl}_3}; C = 4.7)$$

C. Production of (R)-(-)-3-chlorobutyryl chloride

0.07 mol of (R)-(-)-3-chlorobutyric acid ethyl ester are thoroughly stirred with 100 ml of concentrated hydrochloric acid until a clear solution is obtained and are then kept for 3 days at $37-40^\circ\text{C}$ with light stirring. Dilution is then carried out with 100 ml water, followed by saturation with NaCl and extraction three times with 100 ml ether each time. After drying of the organic phase with Na_2SO_4 , the solvent is removed on the rotary evaporator and the residue subjected to fractionated distillation in vacuum. The yield of (R)-(-)-3-chlorobutane acid is 70-75% of theoretical value.

$$K_{p30} = 125^\circ\text{C}$$

0.06 mol of SOCl_2 are added to 0.04 mol (R)-(-)-3-chlorobutane acid and left to stand for 24 hours at room temperature with exclusion of moisture. The temperature of the mixture is then kept for $1\frac{1}{2}$ hours

at 42°C and the mixture is then subjected to fractionated distillation using an ice-cooled vessel.

Yield: 70-75% of theoretical value

$$Kp_{15} = 45^{\circ}\text{C}$$

$$(\alpha)_D^{25} = -13.7^{\circ}$$

$$(\text{CHCl}_3; c = 7.34)$$

D. Esterification of (R)-(-)-3-chlorobutyryl chloride with phenols and alcohols

In a 50 ml Erlenmeyer flask with CaCl_2 tube, 1.7×10^{-3} mol of the relevant alcohol or phenol are placed in 15-30 ml of THF. After cooling of the solution to -30°C , 2.13×10^{-3} mol (R)-(-)-3-chlorobutyryl chloride and 1.7×10^{-3} mol pyridine are added in succession with stirring. After stirring has been carried out for 10 minutes at -30°C , the reaction mixture is left to stand for 2 days at -20°C . The mixture is then added to 300 ml of ice-cold 5% hydrochloric acid.

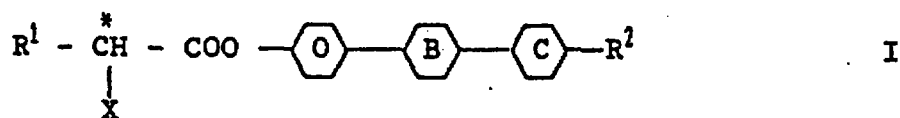
If the ester precipitates out, suction-off is carried out and recrystallization is carried out from methanol, hexane or benzene.

If the ester does not crystallize in the 5% hydrochloric acid solution, extraction with ether is carried out three times, followed by drying with Na_2SO_4 and subsequent distillation. The yield of the corresponding esters is 30-70% of the theoretical value.



CLAIMS:

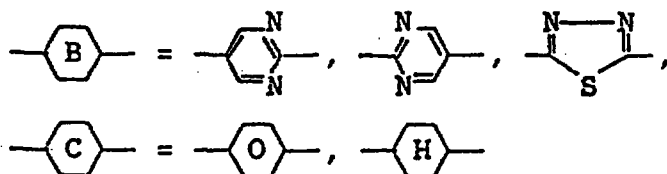
1. Ferro-electric crystalline-liquid derivatives of chiral acyclic halogen carboxylic acids of the general formula :



wherein $R^1 = C_2H_5-$, $(CH_3)_2CH-$, $C_2H_5-CH(CH_3)-$,
 $(CH_3)_2CH-CH_2-$

$R^2 = C_KH_{2K+1}-$, $C_KH_{2K+1}O-$, $C_KH_{2K+1}S-$, $C_KH_{2K+1}CO-$
 $C_KH_{2K+1}COO-$, $C_KH_{2K+1}OOC-$, $C_KH_{2K+1}NH-$

$l = 3 - 12$, $K = 1 - 12$



wherein X denotes Cl, Br,

with the limitation that if B is a pyrimidal ring, R^1 must be $C_2H_5-\overset{*}{CH}(CH_3)-$.

2. Ferro crystalline-liquid derivatives comprising a mixture of two or more compounds according to claim 1.

3. Ferro-electric crystalline-liquid derivatives comprising a mixture of one or more compounds according to claim 1 together with one or more known ferro-electric crystalline-liquid derivatives.

4. Ferro-electric crystalline-liquid derivatives



substantially as herein described in Table 1 or Table 4 above, alone, in a mixture of two or more of them, or in a mixture of one or more of them with a known ferro-electric crystalline liquid derivative.
