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A LIQUID CRYSTAL COMPOSITION COMPRISING DIESTER (S)

The present invention is related to liquid crystal materials.

Liquid crystal materials are well known organic materials comprising single compounds or mixtures of compounds which display phases, known as liquid crystal phases or mesophases, having a degree of molecular ordering intermediate between that of the fully ordered crystalline solid state and the fully disordered isotropic liquid state.

Electro-optical devices incorporating liquid crystal materials are well known and widely used as digital displays in such applications as watches, calculators and digital voltmeters and are finding use in more complex devices such as colour switches and displays. All of these devices utilise the optical contrast obtained when an electric field is applied across a thin insulating film of suitable liquid crystal material. The molecules of the material (in a liquid crystal phase at the temperature of operation) are re-orientated by the field causing a change in an optical property of the part of the film where the field is applied, eg a change in ambient light scattering or transmissivity.

There are several known types of electro-optical effect which are utilised in liquid crystal devices and one type is based on the use of "two-frequency" materials. "Two-frequency" materials may be defined as materials in which an electro-optical effect is obtained by applying to the liquid crystal device (ie across the liquid crystal material), either simultaneously

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or in sequence, electrical signals of two or more distinct frequencies such that at least one of the frequencies is below the cross-over frequency f_0 of the material (as defined below) and at least one is above f_0 .

5 Devices which are used as or are suitable for use as two-frequency devices, ie devices which may employ two-frequency materials, are as described in the following prior art references:

- (1) 'Liquid Crystal Displays and Colour Switches' by
10 M G Clark: Displays Vol 1 pages 17-24 (1979).
- (2) 'Fast switching twisted nematic electro-optical shutter and colour filter' by E P Raynes and I A Shanks: Electronics Letters Vol 10 pages 114-115, 1975.
- (3) 'Multi-colour displays using a liquid crystal colour
15 switch' by I A Shanks: AGARD Conference Proceedings Vol 167 pages 18.1-18.11 (1975).
- (4) 'Frequency addressed liquid crystal field effect' by H Bücher, R T Klingbiel and J P Van Meter: Applied Physics Letters, Volume 25 pages 186-188 (1974).
- 20 (5) UK Patent Specification No. 1,463,979.
- (6) UK Patent Specification No. 1,469,638.
- (7) UK Patent Specification No. 1,477,478.
- (8) UK Patent Specification No. GB 2,042,202A.

Known two-frequency devices may make use of one of the
25 following kinds of two-frequency effects:

- (i) multiplexing of liquid crystal displays either by modulating a signal at a frequency below f_0 while applying a constant signal above f_0 , or by modulating a signal above f_0 while applying a constant signal below f_0 , or by modulating
30 signals both above and below f_0 ; it is well known to those skilled in the art that higher levels of multiplexing can be

attained by these techniques than are possible with signals of a single frequency;

5 (ii) operation as liquid crystal shutters in which the liquid crystal device is switched into one state by application of a burst of electrical signals at a frequency below f_0 and back to its other state by application of a burst at a frequency above f_0 . In this way the shutter may be switched faster than if the natural relaxation time were limiting one of the transitions;

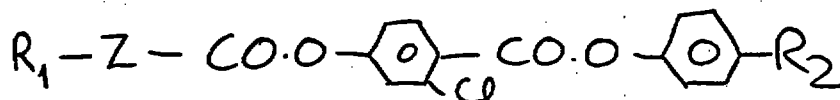
10 (iii) operation as liquid crystal shutters of the type as in (ii) above which are switched repetitively; such shutters may be used, for example, in frame-sequential displays as disclosed in UK Patent Specification No. GB 2,042,202A.

15 Two-frequency liquid crystal materials which have been used in known devices have consisted either of (i) materials of a single family type which have a high viscosity (and therefore a relatively slow electro-optical response) and also a liquid crystalline temperature range giving restricted temperatures of operation; (ii) materials which are mixtures which include a
20 component of relatively poor chemical stability or are coloured, eg yellow; or (iii) materials which are mixtures of compounds which do not show adequate dielectric switching properties.

25 It is an object of the present invention to provide a liquid crystal two-frequency material having an improved combination of properties.

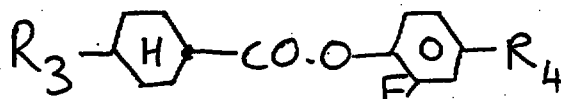
According to the present invention in a first aspect a composition suitable for use as a liquid crystal material in a two-frequency switching device comprises:

i. a first component A having at room temperature and at low frequencies a positive dielectric anisotropy and consisting of one or more compounds having a general formula:



wherein R_1 and R_2 are independently n-alkyl groups having from 3 to 7 carbon atoms; and Z is selected from 1,4 phenylene, trans-1,4-cyclohexyl and 2,6-naphthyl; and

ii. a second component B having a low viscosity and consisting of one or more compounds having a general formula:



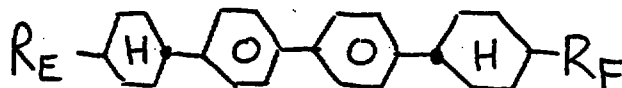
wherein R_3 and R_4 are independently n-alkyl groups having from 3 to 7 carbon atoms, the cross-over frequency of the composition being not greater than 20kHz at 20°C.

Preferably, component A comprises from 50 to 60% by weight of the composition.

The composition may additionally comprise:

iii. a high clearing point additive, component C, forming up to 20% by weight of the composition.

An example of such a composition is one where component A forms up to 60% by weight, component B forms from 35 to 40% by weight of the composition and component C forms up to 20% by weight of the composition, component C preferably being a compound of formula:

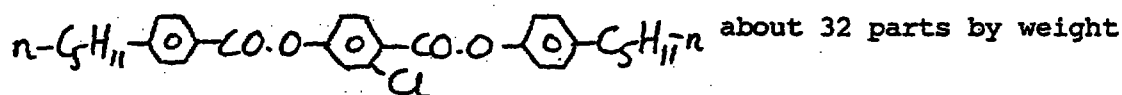
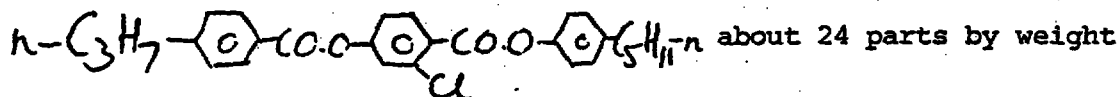


wherein R_E and R_F are independently n-alkyl groups containing from 3 to 7 carbons.

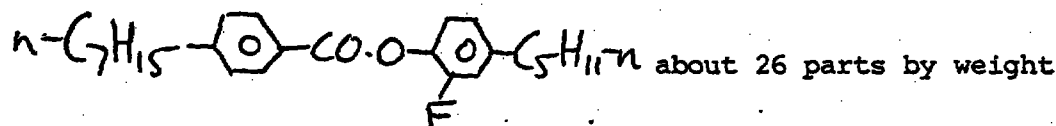
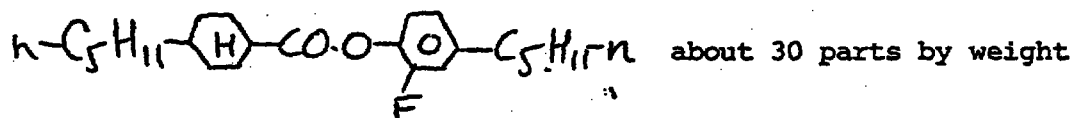
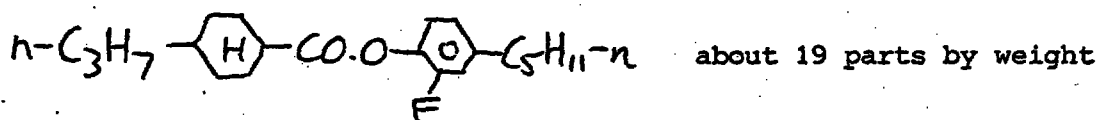
The relative proportions of component A and component B in the composition according to the first aspect of the invention are selected so that the mixture has the desired property, ie a cross-over frequency not greater than 20 kHz and preferably also a viscosity less than 100 cps at 20°C.

'Cross-over frequency' is the frequency of electrical signals applied to a liquid crystal material at which the dielectric anisotropy of the material changes from positive to negative.

Preferably Component A comprises the following compounds preferably in the following mixture:



Preferably, Component B comprises the following compounds preferably in the following mixture:



It has been found that compositions according to the first aspect of the present invention unexpectedly shows a favourable combination of the following properties for use as two-frequency switching materials:

liquid crystalline temperature range;

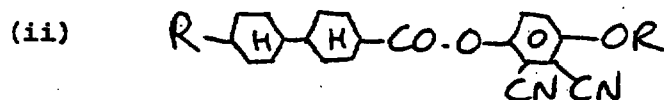
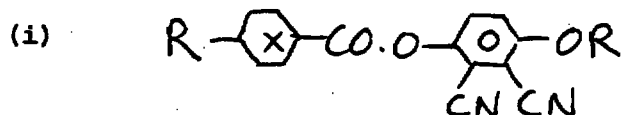
viscosity;

stability and

dielectric switching properties (eg cross-over frequency); lack of colouration, ie they are colourless.

'Strongly negative' compounds, which may be used as additives to the compositions of components A and B, are compounds

having a negative dielectric anisotropy having a magnitude greater than 3, eg

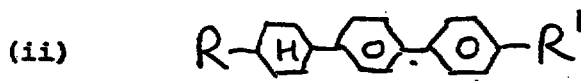


where R = alkyl and is or .

'High clearing point additive' as mentioned above means one or more compounds having a liquid crystal to isotropic liquid transition at high temperatures eg above 150°C. Examples are compounds having the following generalised formulae:



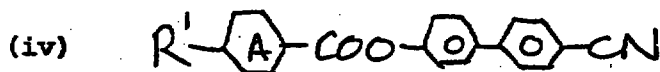
Formula Q1



Formula Q2



Formula Q3



Formula Q4

where the groups R are the same or different n-alkyl groups and the groups R' are alkyl or alkoxy groups which may be the same or different, where is a trans-1,4-disubstituted cyclohexane ring or a 1,4-disubstituted benzene ring.

The composition according to the first aspect of the present invention may be a nematic liquid crystal material which is used in its nematic mesophase in two-frequency applications, but it could also be a smectic material used in its smectic mesophase in such applications.

Mixtures of liquid crystal materials may be formed in a known way, eg by heating the components above the mixture clearing point and then stirring for a time (eg 5 mins) at that temperature before allowing the material to cool.

According to the present invention in a second aspect a liquid crystal device includes two dielectric substrates at least one of which is optically transparent, a layer of liquid crystal material sandwiched between the substrates and electrodes on the inner surfaces of the substrates to enable an electric field to be applied across the layer of liquid crystal material to provide an electro-optic effect therein, characterised in that the liquid crystal material consists of or includes a composition according to the first aspect, the device including means for switching the frequency of electric fields applied between electrodes on the respective substrate inner surfaces to cause the dielectric anisotropy of liquid crystal material to be switched between states giving different optical response.

The general construction and operation of devices of the kind to which those of the second aspect belong are known per se. The device according to the second aspect may be any known two-frequency switching device, eg any of those as described in the prior art references given above.

Examples of the composition and properties of mixtures embodying the first aspect of the invention will now be given. In these examples, where the properties given were all measured at 20°C, the following symbols are used:

- % = component percentage by weight.
- N-I = nematic liquid crystal to isotropic liquid transition temperature (clearing point).
- $\epsilon_{||LF}$ = dielectric constant measured parallel to the average molecular axis (director) of an aligned liquid crystal at low frequencies ($\ll f_0$).
- $\epsilon_{||HF}$ = permittivity measured parallel to the average molecular alignment axis of an aligned liquid crystal at high frequencies ($\gg f_0$).

$\epsilon_{\perp}$ = permittivity measured perpendicular to the average molecular alignment axis of an aligned liquid crystal.

$$\Delta\epsilon_{LF} = \epsilon_{||LF} - \epsilon_{\perp}$$

$$\Delta\epsilon_{HF} = \epsilon_{||HF} - \epsilon_{\perp}$$

f_0 = cross-over frequency (as explained above).

η = viscosity.

Δn = birefringence.

EXAMPLE 1MIXTURE 1

Component	%	N-I (°C)
$n\text{-C}_4\text{H}_9\text{---}\text{C}_6\text{H}_4\text{---COO---C}_6\text{H}_3\text{(Cl)---COO---C}_6\text{H}_4\text{---C}_5\text{H}_{11}\text{---}n$	29	
$n\text{-C}_5\text{H}_{11}\text{---C}_6\text{H}_4\text{---COO---C}_6\text{H}_3\text{(Cl)---COO---C}_6\text{H}_4\text{---C}_5\text{H}_{11}\text{---}n$	31	
$n\text{-C}_3\text{H}_7\text{---C}_6\text{H}_4\text{(H)---COO---C}_6\text{H}_3\text{(F)---COO---C}_6\text{H}_4\text{---C}_5\text{H}_{11}\text{---}n$	10	80
$n\text{-C}_5\text{H}_{11}\text{---C}_6\text{H}_4\text{(H)---COO---C}_6\text{H}_3\text{(F)---COO---C}_6\text{H}_4\text{---C}_5\text{H}_{11}\text{---}n$	16	
$n\text{-C}_7\text{H}_{15}\text{---C}_6\text{H}_4\text{(H)---COO---C}_6\text{H}_3\text{(F)---COO---C}_6\text{H}_4\text{---C}_5\text{H}_{11}\text{---}n$	14	

PROPERTIES OF MIXTURE 1

$$\Delta n = 0.12$$

$$\epsilon_{\text{LLF}} = 8.2$$

$$\epsilon_{\text{LHF}} = 3.6$$

$$\epsilon_{\text{L}} = 5.5$$

$$\Delta\epsilon_{\text{LF}} = +2.7$$

$$\Delta\epsilon_{\text{HF}} = -1.9$$

$$f_0 = 9.0 \text{ kHz}$$

$$\eta = 90 \text{ cps}$$

EXAMPLE 2MIXTURE 2

Component	%	N-I (°C)
$n\text{-C}_4\text{H}_9\text{-}\langle\text{O}\rangle\text{-COO-}\langle\text{O}\rangle_{\text{Cl}}\text{-COO-}\langle\text{O}\rangle\text{-C}_5\text{H}_{11}\text{-}n$	27	
$n\text{-C}_5\text{H}_{11}\text{-}\langle\text{O}\rangle\text{-COO-}\langle\text{O}\rangle_{\text{Cl}}\text{-COO-}\langle\text{O}\rangle\text{-C}_5\text{H}_{11}\text{-}n$	29	
$n\text{-C}_3\text{H}_7\text{-}\langle\text{H}\rangle\text{-COO-}\langle\text{O}\rangle_{\text{F}}\text{-C}_5\text{H}_{11}\text{-}n$	9.5	93
$n\text{-C}_5\text{H}_{11}\text{-}\langle\text{H}\rangle\text{-COO-}\langle\text{O}\rangle_{\text{F}}\text{-C}_5\text{H}_{11}\text{-}n$	15	
$n\text{-C}_7\text{H}_{15}\text{-}\langle\text{H}\rangle\text{-COO-}\langle\text{O}\rangle_{\text{F}}\text{-C}_5\text{H}_{11}\text{-}n$	13	
$n\text{-C}_5\text{H}_{11}\text{-}\langle\text{H}\rangle\text{-}\langle\text{O}\rangle\text{-}\langle\text{O}\rangle_{\text{F}}\text{-}\langle\text{H}\rangle\text{-C}_3\text{H}_7\text{-}n$	6.5	

PROPERTIES OF MIXTURE 2

Δn	=	0.12
ϵ_{ILF}	=	7.7
ϵ_{IHF}	=	3.3
$\epsilon_{\perp}$	=	5.3
$\Delta\epsilon_{\text{LF}}$	=	+2.4
$\Delta\epsilon_{\text{HF}}$	=	-2.0
f_0	=	6.0 kHz
η	=	96 cps

EXAMPLE 3MIXTURE 3

Component	%	N-I (°C)
$n\text{-C}_3\text{H}_7\text{---}\text{C}_6\text{H}_4\text{---COO---}\text{C}_6\text{H}_3(\text{Cl})\text{---COO---}\text{C}_6\text{H}_4\text{---C}_5\text{H}_{11}\text{---}n$	24	
$n\text{-C}_5\text{H}_{11}\text{---}\text{C}_6\text{H}_4\text{---COO---}\text{C}_6\text{H}_3(\text{Cl})\text{---COO---}\text{C}_6\text{H}_4\text{---C}_5\text{H}_{11}\text{---}n$	32	
$n\text{-C}_3\text{H}_7\text{---}\text{C}_6\text{H}_4\text{---COO---}\text{C}_6\text{H}_3(\text{F})\text{---COO---}\text{C}_6\text{H}_4\text{---C}_5\text{H}_{11}\text{---}n$	9.5	101
$n\text{-C}_5\text{H}_{11}\text{---}\text{C}_6\text{H}_4\text{---COO---}\text{C}_6\text{H}_3(\text{F})\text{---COO---}\text{C}_6\text{H}_4\text{---C}_5\text{H}_{11}\text{---}n$	15	
$n\text{-C}_7\text{H}_{15}\text{---}\text{C}_6\text{H}_4\text{---COO---}\text{C}_6\text{H}_3(\text{F})\text{---COO---}\text{C}_6\text{H}_4\text{---C}_5\text{H}_{11}\text{---}n$	13	
$n\text{-C}_5\text{H}_{11}\text{---}\text{C}_6\text{H}_4\text{---}\text{C}_6\text{H}_4\text{---}\text{C}_6\text{H}_4\text{---}\text{C}_6\text{H}_4\text{---C}_3\text{H}_7\text{---}n$	6.5	

PROPERTIES OF MIXTURE 3

$$\Delta n = 0.12$$

$$\epsilon_{\parallel \text{LF}} = 8.2$$

$$\epsilon_{\parallel \text{HF}} = 3.4$$

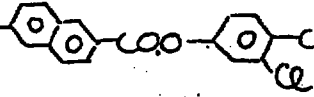
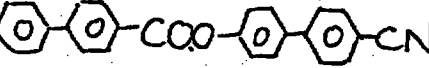
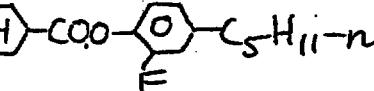
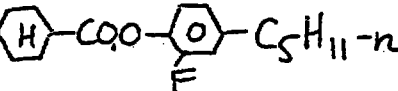
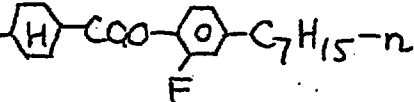
$$\epsilon_{\perp} = 5.2$$

$$\Delta \epsilon_{\text{LF}} = 3.0$$

$$\Delta \epsilon_{\text{HF}} = -1.8$$

$$f_0 = 4.5 \text{ kHz}$$

EXAMPLE 4MIXTURE 4

Component	%	N-I (°C)
$n\text{-C}_6\text{H}_{13}$ —  — C_5H_{11} —n <chem>CCCCCc1ccc(cc1)Oc2ccc(cc2)C(=O)Oc3ccc(cc3)C(=O)Oc4ccc(cc4)CCCC</chem>	20.0	
$n\text{-C}_7\text{H}_{15}$ —  —CN <chem>CCCCCc1ccc(cc1)Oc2ccc(cc2)C(=O)Oc3ccc(cc3)C#N</chem>	4.5	
$n\text{-C}_5\text{H}_{11}$ —  — C_5H_{11} —n <chem>CCCCCc1ccc(cc1)Oc2ccc(cc2)C(=O)Oc3ccc(cc3)F</chem>	26.5	73
$n\text{-C}_7\text{H}_{15}$ —  — C_5H_{11} —n <chem>CCCCCc1ccc(cc1)Oc2ccc(cc2)C(=O)Oc3ccc(cc3)F</chem>	26.5	
$n\text{-C}_7\text{H}_{15}$ —  — C_7H_{15} —n <chem>CCCCCc1ccc(cc1)Oc2ccc(cc2)C(=O)Oc3ccc(cc3)F</chem>	22.5	

PROPERTIES OF MIXTURE 4

η	=	45 cps
Δn	=	0.10
$\epsilon_{ LF}$	=	5.7
$\epsilon_{ HF}$	=	3.4
$\epsilon_{\perp}$	=	4.4
$\Delta\epsilon_{LF}$	=	+1.4
$\Delta\epsilon_{HF}$	=	-1.0
f_0	=	4 kHz

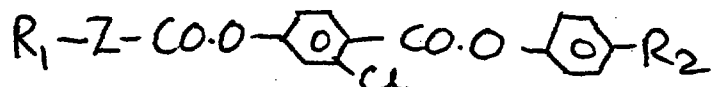
Compounds used in the above samples are known and some are commercially available.

The fluoro-substituted esters of component B specified above are described in UK Patent Specification No. 2,063,250A and examples of the diesters of component A are described in UK Patent Specification No. 1,432,692.

CLAIMS

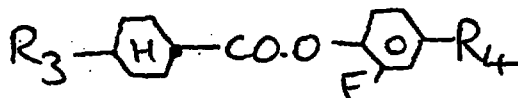
1. A composition suitable for use as a liquid crystal material in a two frequency switching device comprising:

i. a first component A having at room temperature and at low frequencies a positive dielectric anisotropy and consisting of one or more compounds having a general formula:



wherein R_1 and R_2 are independently n-alkyl groups having from 3 to 7 carbon atoms; and Z is selected from 1,4-phenylene, trans-1,4-cyclohexyl and 2,6-naphthyl; and

ii. a second component B having a low viscosity and consisting of one or more compounds having a general formula:



wherein R_3 and R_4 are independently n-alkyl groups having from 3 to 7 carbon atoms, the cross-over frequency of the composition being not greater than 20kHz at 20°C.

2. A composition as claimed in claim 1 and wherein component A forms up to 60% by weight of the composition.

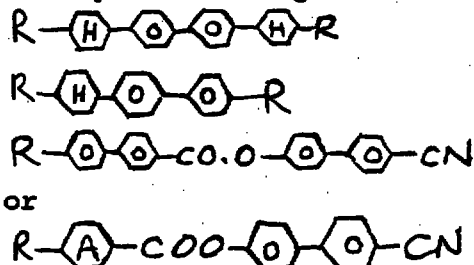
3. A composition as claimed in claim 1 or claim 2 and wherein the composition additionally comprises:

iii. a high clearing point additive, component C, forming up to 20% by weight of the composition.

4. A composition as claimed in claim 3, and wherein component A forms from 50 to 60% by weight, component B forms from 35 to 40% by weight and component C forms up to 10% by weight of the composition.



5. A composition as claimed in claim 3 and wherein component C comprises one or more compounds having a formula:



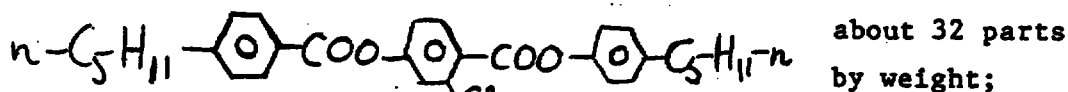
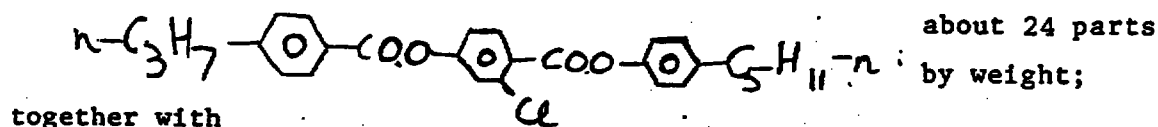
wherein each R is independently alkyl, each R' is independently alkyl or alkoxy and A represents either H or O .

6. A composition as claimed in claim 1 and which additionally comprises an additional component comprising one or more strongly negative compounds having a negative dielectric anisotropy with a magnitude greater than 3.

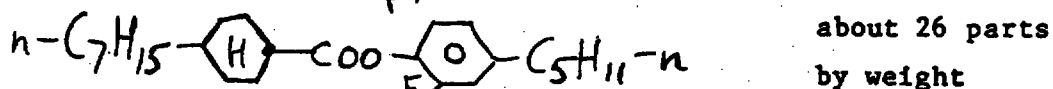
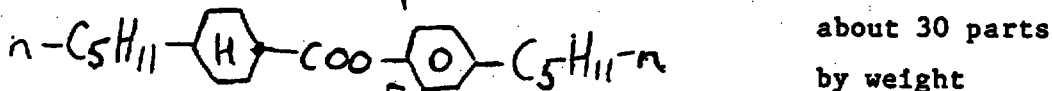
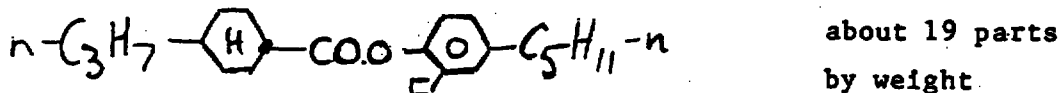
7. A composition as claimed in claim 1 and wherein Z is O , R_2 is $\text{n-C}_5\text{H}_{11}$ and R_1 is selected from $\text{n-C}_5\text{H}_{11}$ and $\text{n-C}_3\text{H}_7$.

8. A composition as claimed in claim 1 and wherein R_4 is $\text{n-C}_5\text{H}_{11}$ and R_3 is selected from $\text{n-C}_3\text{H}_7$, $\text{n-C}_5\text{H}_{11}$ and $\text{n-C}_7\text{H}_{15}$.

9. A composition as claimed in claim 1 and wherein component A comprises:



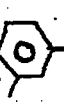
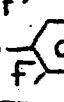
and wherein component B comprises:



10. A composition as claimed in claim 1 and which is a mixture of the following compounds in at least approximately the stated percentages by weight of the overall mixture:



Compound

$n-C_3H_7$ -  - COO -  - COO -  - $C_5H_{11}-n$	% 24
$n-C_5H_{11}$ -  - COO -  - COO -  - $C_5H_{11}-n$	32
$n-C_3H_7$ -  - COO -  - $C_5H_{11}-n$	9.5
$n-C_5H_{11}$ -  - COO -  - $C_5H_{11}-n$	15
$n-C_7H_{15}$ -  - COO -  - $C_5H_{11}-n$	13
$n-C_5H_{11}$ -  -  -  -  - C_3H_7-n	6.5

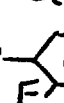
11. A composition as claimed in claim 1 and which is a mixture of the following compounds in at least approximately the stated percentages by weight of the overall mixture:

Compound

$n-C_4H_9$ -  - COO -  - COO -  - $C_5H_{11}-n$	% 27
$n-C_5H_{11}$ -  - COO -  - COO -  - $C_5H_{11}-n$	29
$n-C_3H_7$ -  - COO -  - $C_5H_{11}-n$	9.5
$n-C_5H_{11}$ -  - COO -  - $C_5H_{11}-n$	15
$n-C_7H_{15}$ -  - COO -  - $C_5H_{11}-n$	13
$n-C_5H_{11}$ -  -  -  -  - $C_5H_{11}-n$	6.5

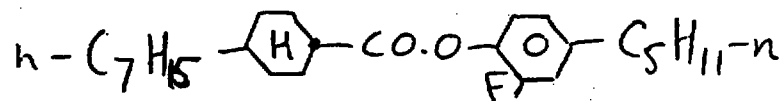
12. A composition as claimed in claim 1 and which is a mixture of the following compounds in at least approximately the stated percentages by weight of the overall mixture:

Compound

$n-C_4H_9$ -  - COO -  - COO -  - $C_5H_{11}-n$	% 29
$n-C_5H_{11}$ -  - COO -  - COO -  - $C_5H_{11}-n$	31
$n-C_3H_7$ -  - COO -  - $C_5H_{11}-n$	10
$n-C_5H_{11}$ -  - COO -  - $C_5H_{11}-n$	16



* C L M S *



13. A liquid crystal device comprising two dielectric substrates at least one of which is optically transparent, a layer of liquid crystal material sandwiched between the substrates and electrodes on the inner surfaces of the substrates to enable an electric field to be applied across the layer of liquid crystal material to provide an electro-optic effect therein, the device also including means for switching the frequency of electric fields applied between the electrodes on the respective substrate inner surfaces to cause the dielectric anisotropy of liquid crystal material to be switched between states giving different optical response, and wherein the improvement comprises the liquid crystal material being a composition as claimed in claim 1.

