

CHIRAL CRYSTALLINE-LIQUID 2,5-DISUBSTITUTED 1,3,4-
THIADIAZOLES WITH EXTENDED SMECTIC C-PHASES

The invention relates to chiral liquid crystals, preferably with extended smectic C-phases for crystalline liquid mixtures for electrooptical arrangement for modulating transmitted or reflected light and for the coloured or black-and-white display of figures, symbols and moving or non-moving images.

It is known that crystalline liquid substances can be used for modulating light and for displaying measured values or for reproducing information. These methods are based on the fact that the preferred orientation of thin layers of crystalline liquid substances can be altered by the application of an electrical field. The change in preferred orientation of crystalline liquid substances is combined with a variation in optical behaviour (double refraction, rotatory power, light absorption). According to the initial orientation, the dielectric and optical anisotropy, the conductivity, spontaneous polarisation, dichroism and also the strength, direction and frequency of the applied electrical field which can be achieved by special pre-treatment of the electrodes or by the addition of suitable substances, so different types of electrooptical effects are observed and can be technically exploited (M. Tobias:

International Handbook of Liquid Crystal Displays 1975-76, Ovum Ltd., London; G. Meier, E. Sackmann, J.G. Grabmeyer: Applications of Liquid Crystals, Springer-Verlag Berlin-Heidelberg-New York 1975; N.A. Clark, S.T. Lagerwall: Applied Physics Lett. 36, 899 (1980)).

For example, one known method is based on the fact that by applying an electrical field to a substance with an optically active smectic C-phase the mean direction of the longitudinal axes of the molecules can be varied by double the tilt angle.

The rapid change-over which occurs thereby can, for instance for irradiated light, (with the aid of polarisation) be observed as a marked variation in intensity.

For the industrial application of ferroelectric smectic C-phases, the substances used must meet certain conditions such as for example

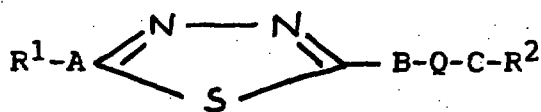
- extended optically active smectic C-phases,
- chemical stability and
- a negative dielectric and anisotropy.

Since almost exclusively mixtures are used for industrial applications, it is necessary to find mixture components which on the one hand have high conversion temperatures of the smectic C-phase to different phases and, on the other,

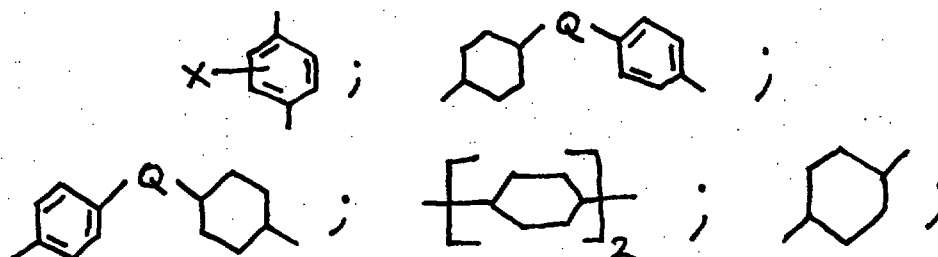
have no additional crystalline liquid phases at lower temperatures, including the sub-cooled range. It is not absolutely essential that these components themselves be optically active. They are required only to form optically active mixtures when mixed with optically active Sc-phases or other optically active substances.

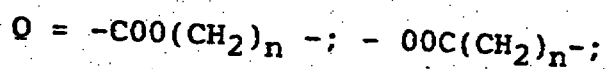
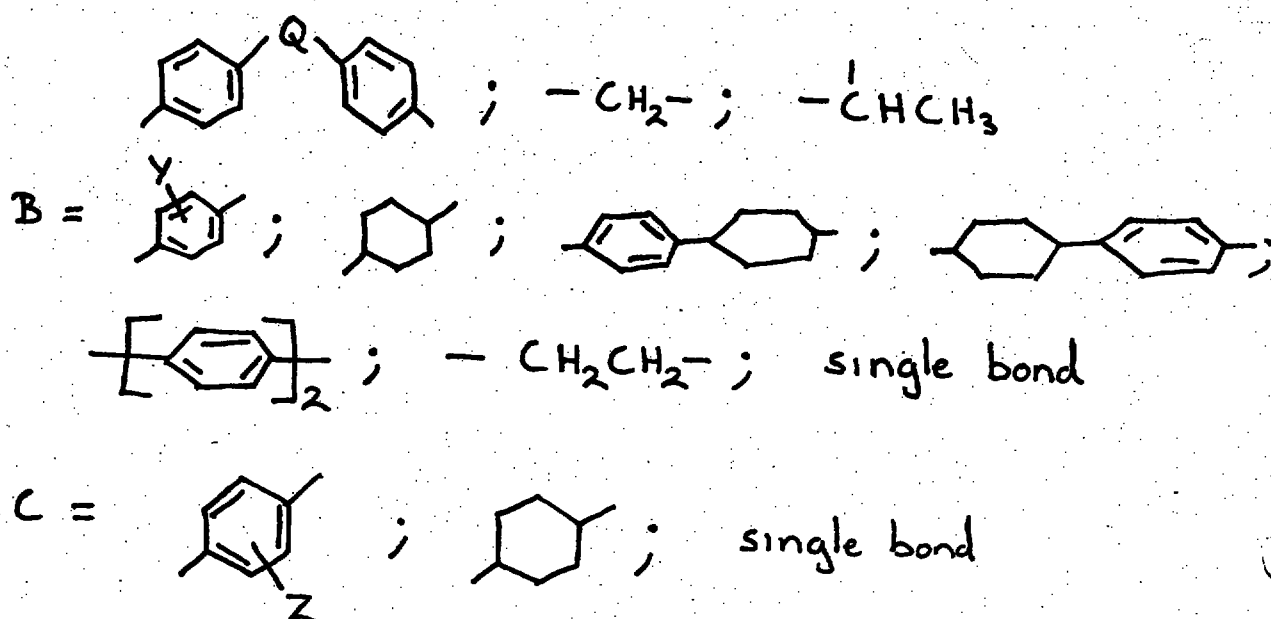
The object of the invention is to provide new liquid-crystalline substances for mixtures of liquid-crystalline substances for electrooptical applications with an extended temperature range.

The invention is based on the problem of finding suitable mixture components with an extended status range of the smectic C-phase, negative dielectric anisotropy and the quality of forming optically active phases when in mixture. According to the invention, chiral preferably smectic phase forming crystalline liquid 2,5 disubstituted 1,3,4-thiadiazoles of general formula I.



in which A =





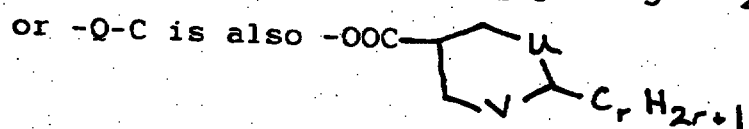
single bond

in which $n = 0 \dots 4$

X, Y, Z = independently of one another -H, -CN, -Cl

-Br, F

-OCH₃, -OC₂H₅, -CH₃, -C₂H₅



in which U, V = 0,0; 0,S; S,S

and $r = 1 \dots 12$

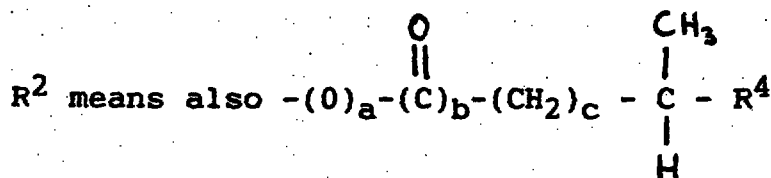
or -Q-C- is a single bond,

if $R^2 = -\text{OOCR}^3$ or

$-\text{COOR}^3$

and R^1 , R^2 and R^3 represent in each case straight-chain or

branched alkyl chains having 2 to 20 C-atoms in which one CH₂ group which is not adjacent to a heteroatom may be replaced by O, S, -OOC-, -COO-, -OOCO- or -CH=CH-



in which $R^4 = -C_mH_{2m+1}$, $-OC_{m-1}H_{2m-1}$

and $m = 2$ to 16

$a, b = 0$ or 1

$c = 0$ to 6

provided that the thiadiazole ring is not directly substituted by a heteroatom. The invention also provides for the use of such material in quantities use of these substances in quantities of 0.1 to 80 mol % in crystalline liquid mixture with extended smectic C-phases of a negative dielectric anisotropy and capable of forming optically active phases and which may also contain other crystalline liquid or non-crystalline liquid substances, for the modulation of transmitted or reflected light as well as for reproducing digits, symbols and images.

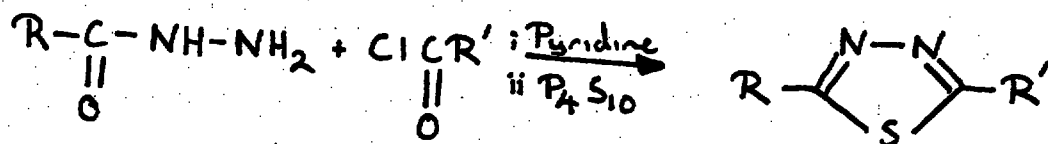
The 2,5-disubstituted 1,3,4-thiadiazoles according to the invention have broad chiral S₀ existence areas with low melting temperatures and in particular high clarification temperatures.

The new substances are stable under heat, irradiation by

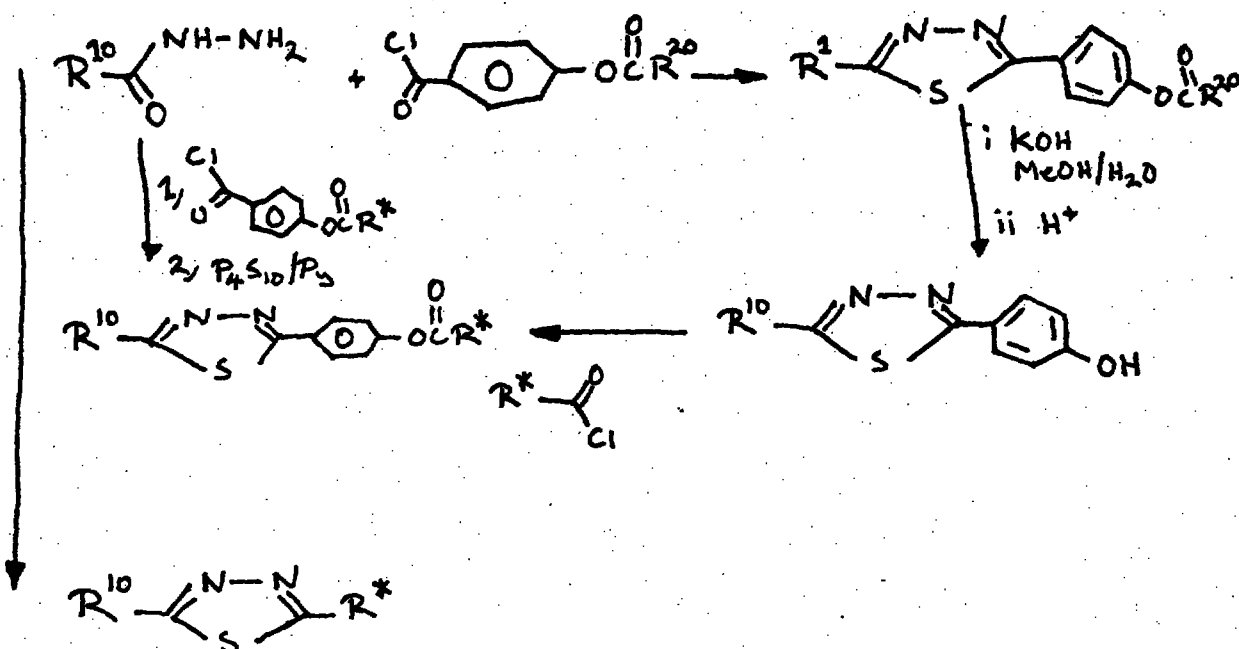
visible and ultra-violet light and electrical direct current and alternating current fields. In contrast to the hitherto known derivatives of 2,5 disubstituted thiadiazoles (Flussige Kristalle in Tabellen II pp. 359-361), they have broad smectic C-phase ranges.

The substances can be used to particular advantage in mixtures with one another as well as with other ferroelectric crystalline liquid substances, for the induction of ferroelectrical properties into non-chiral compounds with smectic mesophases as well as for the induction of smectic C-phases.

A further advantage of the substances according to the invention resides in the fact that where many representatives are concerned, even with sub-cooling, no additional smectic phases occur below the smectic C-phase. The substances are accessible by per se known procedures by the reaction of carboxylic acid hydrazides with carboxylic acid chlorides, particularly chiral 4-alkyloxy-benzoyl chlorides or achiral 4-acyloxy-benzoyl chlorides and subsequent sulphurization with P_4S_{10} in organic solvents, particularly pyridine, or in the absence of this latter:



The reaction of achiral 4-acyloxy-benzoyl chlorides with carboxylic acid hydrazides results in achiral 2-subst.-4-(4-acyloxyphenyl)-thiadiazoles which are first saponified to the corresponding phenols in accordance with the following reaction diagram after which they are again esterified with chiral carboxylic acids directly or via their acid chloride.



This scheme is illustrative and can give rise to compounds not of the invention

The chiral carboxylic acids are produced for example

-by oxidation of chiral alcohols (such as for instance (S)-isoamylalcohol)

-by asymmetric synthesis, e.g. by means of chiral oxazolones

- or chiral imides
- by etherification of 4-hydroxybenzoic acid with chiral alkyl halides or tosylates.
- by esterification of 4-hydroxybenzaldehyde with chiral carboxylic acids and subsequent oxidation or by direct esterification of 4-hydroxybenzoic acid
- by alkylation of chiral -hydroxycarboxylic acids (e.g. lactic acids) and their derivatives.

Examples of the invention of preparation of starting materials and comparative examples

Example 1

(S)-2-(4-n-octyloxyphenyl)-5-[4-(2-methylbutanoyloxy)-phenyl]-thiadiazole.

A solution of 2.64 g (0.01 mol) 4-n-octyloxybenzoic acid hydrazide in 30 ml absolute pyridine was blended drop-wise with 2.4 g (0.01 mol) (S)-4-(2-methylbutanoyloxy)-benzoic acid chloride at 0 to 5°C accompanied by agitation. Afterwards, the reaction mixture is stirred for 45 minutes at 0°C, and then for 45 minutes at 20°C and then for 3 hours at 80°C.

After being allowed to cool to room temperature, 3 g P_4S_1 are added and after the exothermal reaction has died away, the result is stirred for 1 hour at 80°C and for 12 hours at 100°C. After cooling to room temperature, the reaction mixture has ethanol added to it after which it is poured into 200 ml iced water.

The solution is neutralised with aqueous NaOH and the

product of reaction extracted by a vacuum, washed with H_2O and recrystallised from ethanol.

Yield: 2.8g = 60% of the theory.

Further compounds were synthesised by this procedure (see Table 1,3).

Example 2

(S)-2-(2-methylpropyl)-5-(4-n-octyloxyphenyl)-thiadiazole (compound 1/2)

In accordance with the procedure set out in Example 1, 2.64 g (0.01 mol) 4-n-octyloxybenzoic acid hydrazide was reacted with 1.20 g (0.01 mol) (S)-2-methylbutyryl chloride.

Yield: 2.7 g 74% of the theory

= 0.0074 mol

Example 3

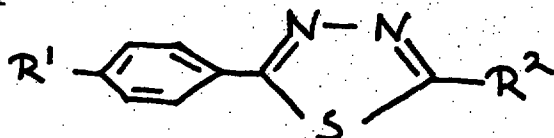
(S)-2-[4-(hexyloxypropanoyloxy)-phenyl]-5-(4-n-pentyloxyphenyl)-thiadiazole

0.36 g (1 mmol) 2-(4-n-pentyloxyphenyl)-5-(4-hydroxyphenyl)-thiadiazole; 2.6 g (1.5 mmol) (S)-hexyloxypropanoic acid, 0.4 g (1.3 mmol) EDC methiodide and 10 mg DMAP were suspended in 5 ml CH_2Cl_2 and agitated for 20 hours at room temperature. The resulting solution is diluted with 100 ml CH_2Cl_2 ; washed twice with 100 ml H_2O and once with 100 ml 5% $NaHCO_3$ solution, the solvent distilled off in a rotary evaporator and the residue recrystallised from ethanol.

Yield: 0.35 g = 70% of the theory.

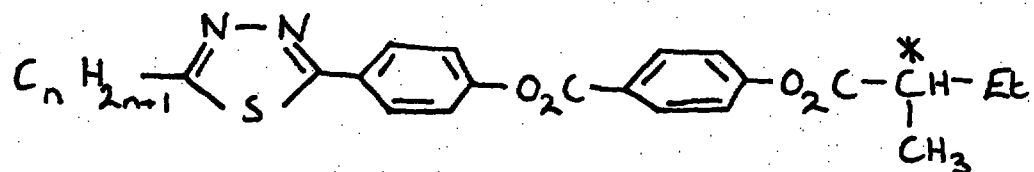
Further compounds were synthesised in accordance with this procedure (see Table 1, 2, 3).

TABLE 1

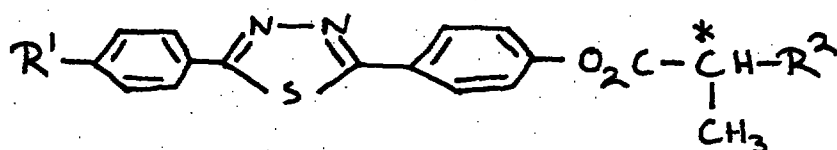


No.	R ₁	R ₂	C	S _A	is
1/1	C ₆ H ₁₃ O-C [*] -C(=O)- CH ₃	-C ₉ H ₁₉	.		
1/2	C ₈ H ₁₇ O-	-CH [*] -C ₂ H ₅ CH ₃	. 52	(. 19)	.
1/3	C ₂ H ₅ -CH [*] -C(=O)- CH ₃	-C ₇ H ₁₅	. 53.5	- -	.
1/4	CH ₃ O-CH [*] -C(=O)- CH ₃	-C ₇ H ₁₅	. 55	- -	.
1/5	C ₆ H ₁₃ O-CH [*] -C(=O)- CH ₃	-C ₂ H ₅	. 75	(. 01)	.

C = crystalline solid
 S_A, S_C = smectic A-, C-phase
 CH = cholesterolin phase
 is = isotropic-liquid

TABLE 2

No.	n	C	S _C	S _A	CH	is
2/1	7	. 103	. 115	-	-	. 166 .
2/2	9					

TABLE 3

No.	R ¹	R ²	C	S _C	CH	is
3/1	C ₁₀ H ₂₁	Et	. 126	. 140	-	- .
3/2	C ₁₀ H ₂₁	OMe	. 108	. 139	. 139.5	.
3/3	C ₁₀ H ₂₁	OC ₆ H ₁₃	. 110	. 121	-	- .
3/4	C ₅ H ₁₁ O	Et	. 155	. 101	. 163	.
3/5	C ₅ H ₁₁ O	OMe	. 96	. 155	. 165	.
3/6	C ₅ H ₁₁ O	OC ₆ H ₁₃	. 93	. 138	-	- .
3/7	C ₅ H ₁₁ O	OC ₁₀ H ₂₁	. 92	. 133	-	- .

	R ¹	R ²	12			
3/8	C ₈ H ₁₇ O	OC ₆ H ₁₃	. 89	. 163	-	-
3/9	C ₈ H ₁₇ O	OC ₆ H ₁₃	. 85	. 143.5	-	-
3/10	C ₈ H ₁₇ O	OC ₁₀ H ₂₁	. 80	. 134.5	-	-
3/11	C ₉ H ₁₉ O	OCH ₃	. 101	. 163	. 166	.
3/12	C ₉ H ₁₉ O	OC ₆ H ₁₃	. 70	. 144.5	-	-

EXAMPLE 4 (Comparative)

Production of 2-(4-n-octyloxyphenyl)-5-(4-[trans-4-n-propylcyclohexylpropionyloxyl]phenyl)-1,3,4-thiadiazole

0.01 mol (3.82 g) 2-(4-n-octyloxyphenyl)-5-(4-hydroxyphenyl)-1,3,4-thiadiazole are suspended in 15 ml absolute toluene and, after the addition of 10 ml triethylamine and 100 mg 4-dimethyl-aminopyridine, are with agitation reacted with 0.011 mol (2.38g) 3-(trans-4-n-propylcyclohexyl)-propionyl chloride. The mixture is agitated for 12 hours at room temperature and for 2 hours at 80°C. After cooling to room temperature, the reaction solution is diluted with 100 ml ether and washed once with 100 ml H₂O, once with 100 ml 5% NaHCO₃ solution and once again with 100 ml H₂O. After drying over Na₂SO₄, the solvent is distilled off at the rotary evaporator. The residue is recrystallised from ethanol and methanol to constancy of conversion temperatures.

Yield: 4.2 g (0.0075 mol) = 75% of the theory.

Production of 2-(4-n-octyloxyphenyl)-5-(4-acetoxyphenyl)-1,3,4-thiadiazole

0.1 mol (26.4 g) 4-n-octyloxybenzoic acid hydrazide is dissolved in 300 ml absolute pyridine and reacted with 0.1 mol (19.8 g) 4-acetoxybenzoyl chloride drop-wise with agitation and at 0 to 5°C. Now the reaction mixture is allowed slowly to heat to room temperature after which it is agitated for 2 hours at 20°C and then for 2 hours to 70°C.

After being allowed to cool to room temperature, the reaction mixture is poured into 1 litre of iced water. The precipitate is washed with H₂O and recrystallised once from ethanol.

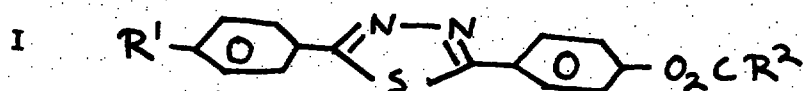
Yield: 38 g (0.09 mol) = 90% of the theory.

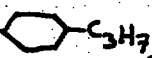
0.05 mol (21.3 g) of the resultant N-(4-n-octyloxybenzoyl)-N'-(4-acetoxybenzoyl)-hydrazine are dissolved in 150 ml pyridine and reacted with 15 g P₄S₁₀ under agitation.

After abatement of the exothermal reaction, the mixture is heated for 2 hours to 80°C and then agitated for a further 12 hours at 100°C. After cooling to room temperature, 50 ml ethanol are added and the reaction mixture poured into 1 litre of iced water. The resultant solution is neutralised with 10% caustic soda solution and the product extracted by a vacuum. The reaction product is thoroughly washed with water and recrystallised from ethanol or methanol.

Yield 18.1 g (0.0426 mol) = 85% of the theory.

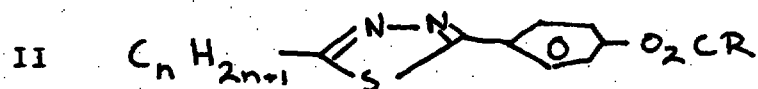
The following substances are obtained in a similar manner

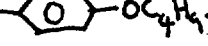
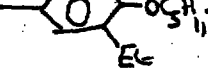


No.	R ¹	R ²	C	S	S	S	N	is
I 1	C ₁₀ H ₂₁	CH ₃	. 117	-	-	. 134	-	. 183
I 2	C ₁₀ H ₂₁	OC ₇ H ₁₅	. 80	-	-	. 153	-	. 157
I 3	C ₁₀ H ₂₁	OC ₄ H ₉	. 64	-	-	. 146	-	. 166
I 4	OC ₅ H ₁₁	C ₂ H ₅	. 118	-	-	. 161	-	. 225
I 5	OC ₅ H ₁₁	OC ₄ H ₉	. 95	-	-	. 141	-	. 196
I 6	OC ₈ H ₁₇	CH ₃	. 116	-	-	. 170	-	. 213
I 7	OC ₈ H ₁₇	C ₂ H ₅	. 113	-	-	. 169	-	. 209
I 8	OC ₉ H ₁₇	C ₉ H ₁₉	. 90	-	-	. 194	-	-
I 9	OC ₉ H ₁₇	CH ₂ OC ₇ H ₁₅	. 87	-	-	. 197	-	-
I 10	OC ₉ H ₁₇	C ₂ H ₄ -  -C ₃ H ₇	90(.75)	-	-	. 216	-	. 249
I 11	OC ₈ H ₁₇	CH ₂ -  -C ₃ H ₇	130	-	-	. 202	-	. 204
I 12	OC ₉ H ₁₇	CH(CH ₃)C ₉ H ₁₇	. 65 (.64)	-	-	. 135	-	-
I 13	OC ₉ H ₁₉	OC ₇ H ₁₅	. 83	-	-	. 174	-	. 183
I 14	OC ₉ H ₁₉	OC ₉ H ₁₉	. 94	-	-	. 198	-	-
I 15	OC ₉ H ₁₉	OC ₄ H ₉	. 87	-	-	. 168	-	. 186

S - smectic phase not identified in greater detail

(e.g. in case I 10 S_G), N- nematic
Compounds I 10, I 11, and I 12 are of the invention.



No.	n	R	C	S	S	S	N	is
II	15		$C_{10}H_{21}$. 104	-	-	. 121	. 135 . 146	.
II	27		$C_{10}H_{21}$. 105	-	-	. 140	. 141 . 143	.
II	37		OC_8H_{17} . 100	-	-	. 159	- - . 171	.
II	49		$C_{10}H_{21}$. 103	-	-	. 143	- - - -	.
II	59		OC_8H_{17} . 98	-	-	. 166	- - . 170	.
II	69		OC_4H_9 . 105	-	-	. 133	- - . 173	.
II	79		OC_5H_{11} . 81	-	-	. 85	- - . 99	.
II	89		C_3H_7 . 77	-	-	. 81	. 89 - -	.
II	99		C_2H_5 . 72	-	-	. 119	. 142 - -	.
II	109		C_2H_5 . 83	. 105	. 112	. 130	- -	.

Compounds II 8, II 9 and II 10 are of the invention

Example 5 (Comparative)

Production of 2-n-nonyl-5-4(4-methoxycarbonylphenyl)-1,3,4-thiadiazole.

0.1 mol (18.6 g) decanoic acid hydrazide is reacted in accordance with Example 4 with 0.1 mol (18.9 g) methoxycarbonyl-benzoyl chloride to produce N-decanoyl-N'-(4-methoxycarbonyl-benzoyl)-hydrazine.

0.05 mol (18.6 g) of the resultant diacylhydrazine are

reacted with 15 g P_4S_{10} in accordance with Example 4.

Yield: 15.0 g (0.041 mol) = 82% of the theory.

Mp: 114°C.

Production of 4-(2-n-nonyl-1,3 4-thiadiazole-5-yl)-benzoic acid.

0.02 mol (7.4 g) 2-nonyl-5-(4-methoxycarbonylphenyl)-1,3,4-thiadiazole are added to a solution of 0.2 mol (11.2 g) KOH in 400 ml methanol and heated for 2 hours until boiling. The solvent is distilled off at the rotary evaporator and the residue dissolved in 200 ml H_2O and acidulated with concentrated hydrochloric acid. The precipitate formed is extracted with a vacuum and recrystallised from ethanol.

Yield: 5.8 g (0.017 mol) = 87% of the theory.

Mp: 255°C (decomp.).

Production of 4-(2-2-n-nonyl-1-1,3,4-thiadiazole-5-yl)benzoic acid-4-n-octyloxyphenylester:

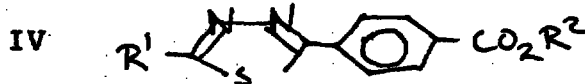
0.005 mol (1.66 g) 4-(2-n-nonyl-1,3,4-thiadiazole-5-yl)-benzoic acid are mixed with 5 ml thionyl chloride and heated for 2 hours until boiling. Afterwards, excess thionyl chloride is distilled off at the rotary evaporator and the residue is mixed with 0.006 mol (1.33 g) octyloxyphenyl, dissolved in 20 ml toluene, 5 ml triethylamine and 100 mg 4-dimethylaminopyridine.

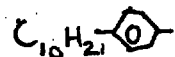
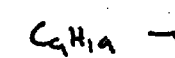
The reaction mixture is agitated for 12 hours at room temperature and for 2 hours at 80°C. After cooling to

room temperature, it is diluted with 100 ml ether and washed with 1 x 100 ml H₂O, 1 x 100 ml 5% NaHCO₃ solution and 1 x 100 ml H₂O. After drying with Na₂SO₄, the solvent is distilled off a rotary evaporator and the residue recrystallised from methanol until the conversion temperature attains constancy.

Yield: 2.2 g ($4 \cdot 10^{-3}$ mol).

As an example, the conversion temperatures of two compounds are given:



No.	¹ R	² R	C	S	S	N	I
IV1		CH ₃	140	-	-	224	-
IV2		OC ₃ H ₇	97	131	136	-	-

Example 6 (comparative)

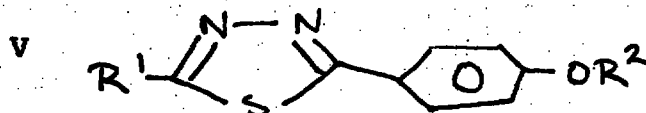
Production of 2-n-heptyl-5-[4-(4-n-heptylphenylmethylenoxy)-phenyl]-1,3,4-thiadiazole.

A mixture of 0.01 mol (2.76 g) 2-n-heptyl-5-(4-hydroxyphenyl)-1,3,4-thiadiazole, 0.015 mol (4.03 g) 4-n-heptylbenzylbromide, 50 ml acetone and 15 g K₂CO₃ are heated to reflux for 6 hours under agitation. After cooling of the reaction mixture, the solid precipitate is filtered off and carefully washed with 100 ml CHCl₃. The solution obtained is reduced at a rotary evaporator to the dry state and the residue recrystallised from acetone to

the point of constancy of the conversion temperature.

Yield: 3.9 g (0.013 mol) - 84% of the theory.

The following Table gives examples



No.	R ¹	R ²	C	S	S	S	N	is
V 1	C ₇ H ₁₅	CH ₂ -C ₆ H ₄ -C ₃ H ₇	109	-	-	-	165	-
V 2	C ₇ H ₁₅	CH ₂ -C ₆ H ₄ -OC ₂ H ₅	108	117	156	-	-	-
V 3	C ₇ H ₁₅	CH ₂ -C ₆ H ₄ -C ₇ H ₅	84	142	-	-	160	-
V 4	C ₇ H ₁₅	CH ₂ -C ₆ H ₄ -C ₇ H ₅	95	-	-	124	140	-

V1 and V3 are of the invention

Example 7

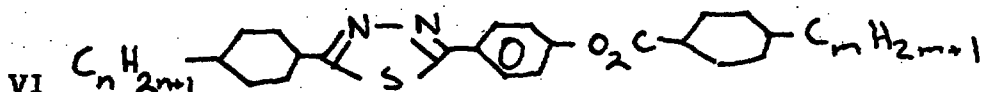
Production of 2-(trans-4-n-hexylcyclohexyl)-5-[4-(trans-4-n-hexylcyclohexylcarbonyloxy)-phenyl]-1,3,4-thiadiazole.

0.01 mol (1.52 g) 4-hydroxybenzoic acid hydrazide are reacted as in Example 4 with 0.025 mol (5.75 g) trans-4-n-hexylcyclohexanocarboxylic acid chloride to produce N-(trans-4-n-hexylcyclohexylcarbonyl)-N'-4-(trans-4-hexylcyclohexylcarbonyloxy)-benzoyl-hydrazine.

0.005 mol (2.7 g) of the diacylhydrazine thus obtained are reacted with 1.5 g P₄S₁₀ in accordance with Example 4.

Yield: 2.1 g = 78% of the theory.

The following Table gives examples



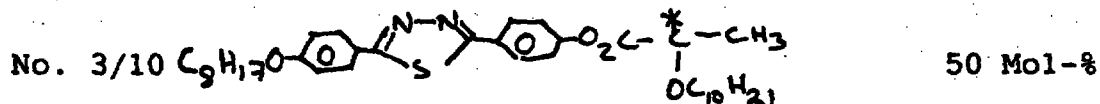
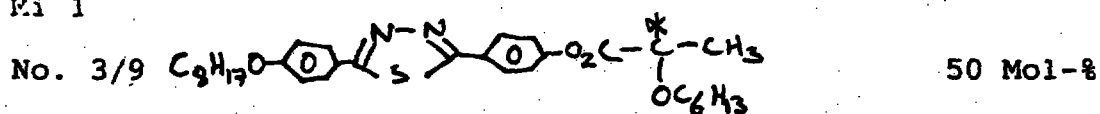
No.	n	m	C	S	N	is
VI 1	6	6	. 112	. 159	. 166	.
VI 2	8	8	. 105	. 161	- -	.

Example 8

By mixing a plurality of substances according to the invention together, the melting of the ferroelectrical crystalline liquid materials are lowered and the range of existence substantially widened.

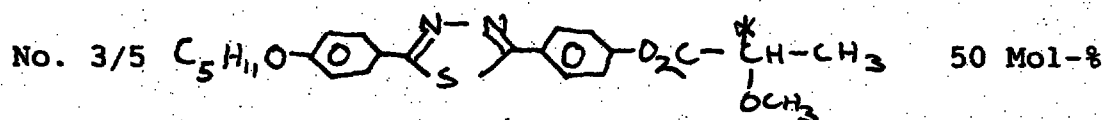
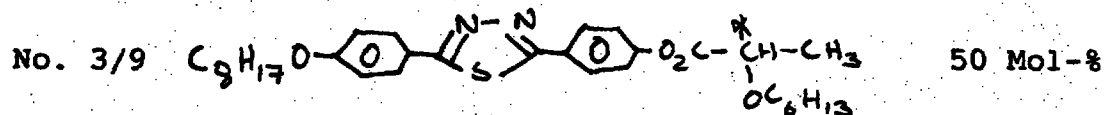
This is demonstrated by the following two mixtures:

Mi 1



C 60 - 65 S_C 133-134 Is

Mi 2

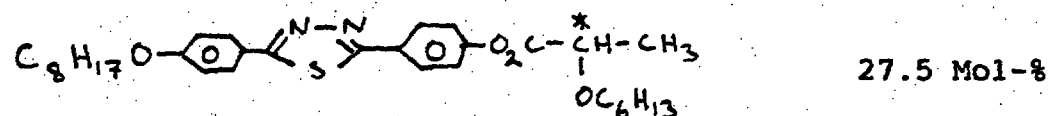
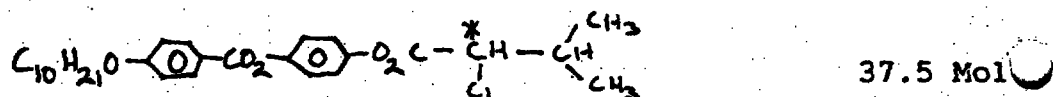
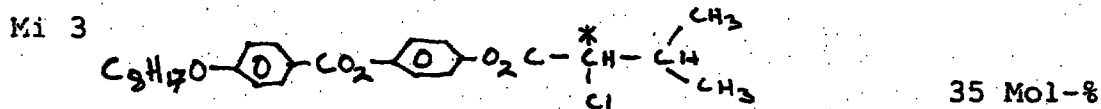


C 70 S_C^{*} 146-47 H^{*} 156-57 Is
Both these mixtures can be used in optoelectronic displays.

Example 9

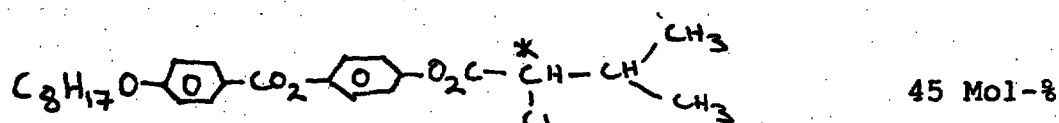
The properties of the substances according to the invention are substantially modified by mixture with further substances, preferably those which themselves have ferroelectrical smectic C*-phases or non-chiral C-phases.

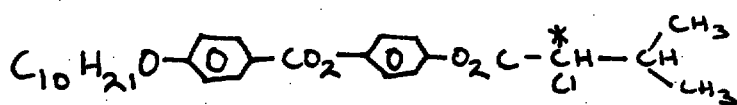
This should be demonstrated by the following three mixtures.



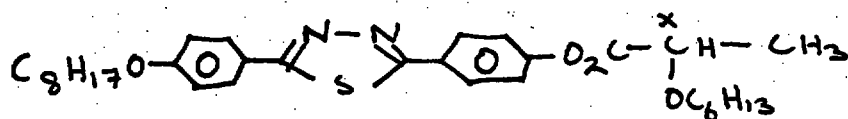
C 37 S_C^{*} 60 S_A 84 H^{*} 90 Is

Mi 4





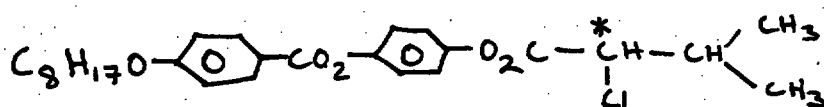
35 Mol-%



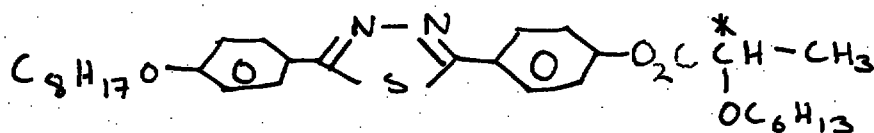
20 Mol-%

C 33 S_C^{*} 46 S_A 70 M^{*} 81,5 Is

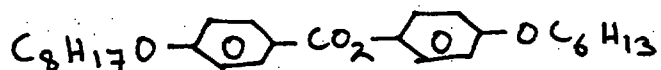
Mi 5



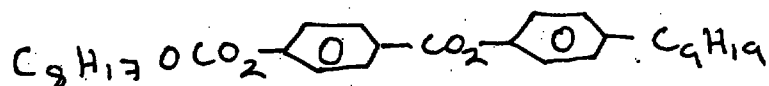
44 Mol-%



21 Mol-%



14 Mol-%



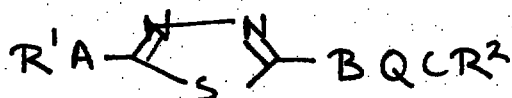
21 Mol-%

C 25 S_C^{*} 47 S_A 70 M^{*} 79 Is

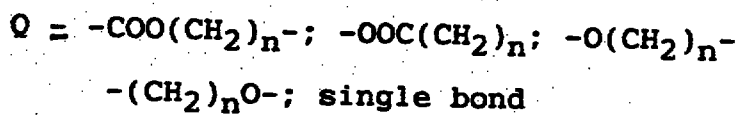
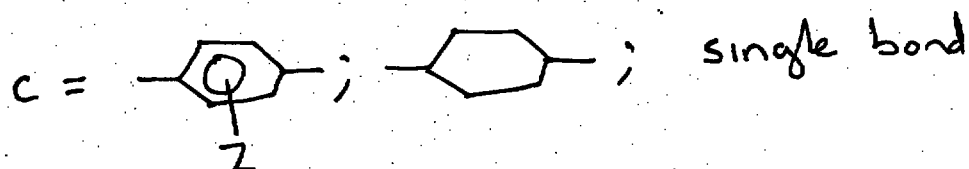
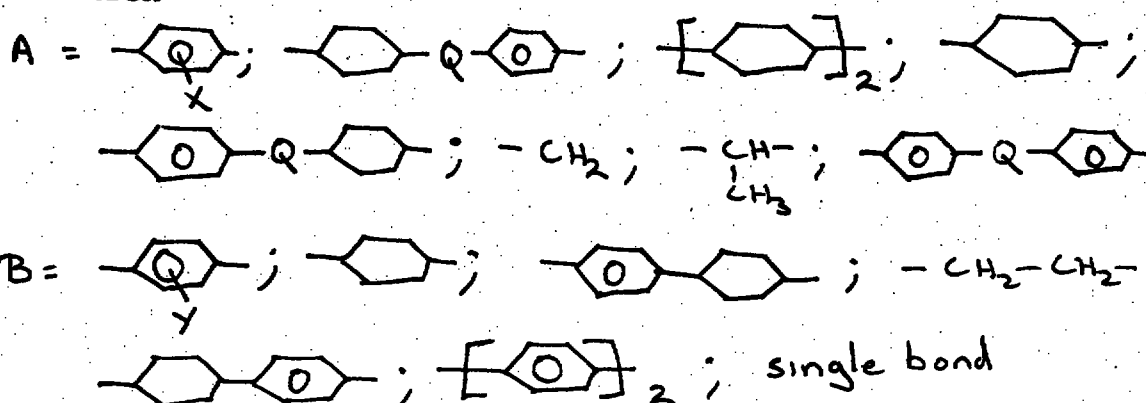
Also these mixtures are ideally suitable for use in displays.

CLAIMS

1. A chiral crystalline liquid 2,5-disubstituted 1,3,4-thiadiazole of general formula I

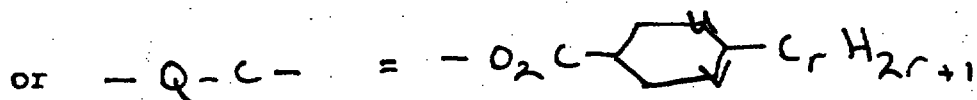


in which



in which $n = 0 \dots 4$

X, Y, Z = independently of one another -H, -CN, -Cl, -Br, -F, -OCH₃, -OC₂H₅, -CH₃, -C₂H₅

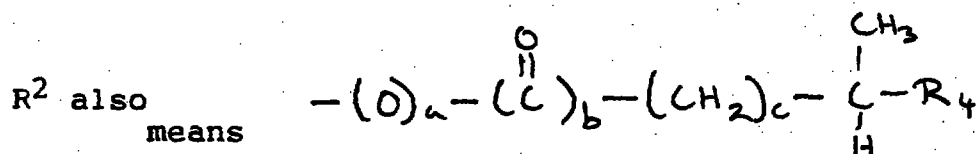


in which U, V = 0,0; 0,S; S,S and r = 1 ... 12

or -Q-C- is a single bond if $R^2 = -OOCR^3$

or $-COOR^3$

and R^1 , R^2 and R^3 are in each case straight chain or branched alkyl chains with 2 to 20 C-atoms in which a CH_2 group which is not adjacent a heteroatom can be replaced by O, S, $-OOC-$, $-COO-$, $-OOCO-$ or $-CH=CH-$,



in which $R^4 = -C_mH_{2m+1}$; $OC_{m-1}H_{2m-1}$

and $m = 2 - 16$

$a, b = 0$ or 1

$c = 0$ to 6

provided that the thiadiazole ring is not directly substituted by a heteroatom.

2. Use of the substances mentioned in Claim 1 in quantities of 0.1 to 80 mol % in crystalline liquid mixtures with extended smectic C-phases of a negative dielectric anisotropy and capable of forming optically active phases and which may also contain other crystalline liquid or non-crystalline liquid substances, for the modulation of transmitted or reflected light as well as



for reproducing digits, symbols and images.

3. Crystalline-liquid as claimed in Claim 1, substantially as described in any one of the examples disclosed herein.
