

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

The invention relates to non-chiral liquid crystals, preferably with extended smectic C-phases for crystalline liquid mixtures for electrooptical arrangements for modulating the 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

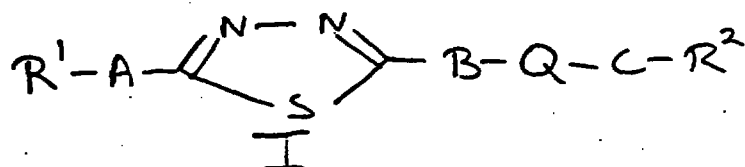
- extended optically active smectic C-phases,
- chemical stability and
- a negative dielectric and anisotropy.

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.

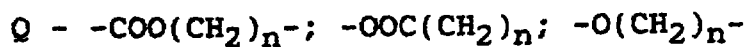
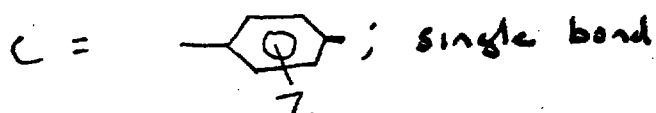
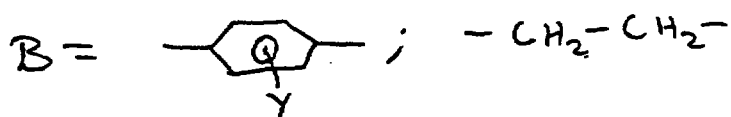
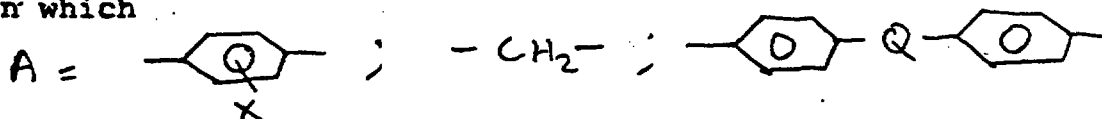
The object of the invention is to provide new liquid crystalline substances for mixtures of liquid-crystalline substances for electrooptical applications with an extended temperature range.

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 there is provided Achiral crystalline liquid 2,5-disubstituted 1,3,4-thiadiazole of general formula I



in which



$\text{---}(\text{CH}_2)_n\text{O} \text{---}$; single bond; provided that where Q is single bond C is $\text{---} \text{C}_6\text{H}_4 \text{---} \text{Q} \text{---} \text{Z}$

in which $n = 0 \dots 4$

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

and R^1 , R^2 and 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 $-CH=CH-$ or where $BQCR^2$ is

is $\text{---} \text{C}_6\text{H}_4 \text{---} OH$, $\text{---} \text{C}_6\text{H}_4 \text{---} CO_2CH_3$ or $\text{---} \text{C}_6\text{H}_4 \text{---} O_2CCH_3$

and wherein R^1 and $BQCR^2$ are different from one another.

In mixtures with one another as well as with other crystalline liquid or non-crystalline liquid substances, they are suitable for use in rapidly switching optoelectronic components having memory properties.

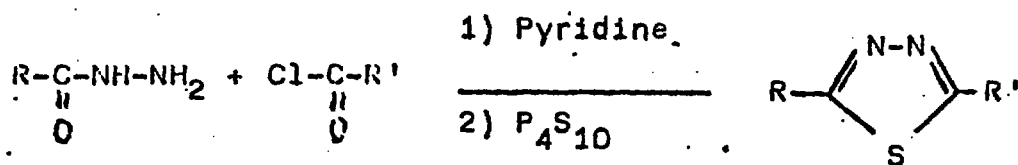
The 2,5-disubstituted 1,3,4-thiadiazoles according to the invention have broad chiral Sm existence areas with low melting temperatures and in particular high clarification temperatures.

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 thiadiazole flüssige kristalle in Table 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 achiral 4-acyloxy-benzoyl chlorides and subsequent sulphurization with P_4S_{10} in organic solvents, particularly pyridine, or in the absence of this latter:



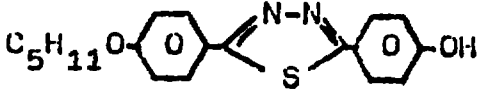
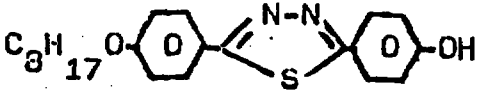
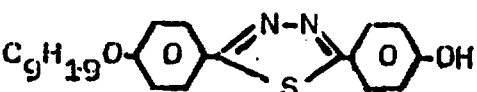
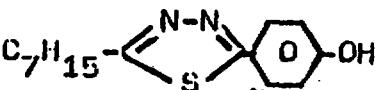
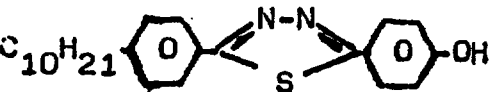
Example 1

2-(4-n-pentyloxyphenyl)-5-(4-hydroxyphenyl)-thiadiazole

4.0 g (0.01 mol) 2-(4-n-pentyloxyphenyl)-5-(4-acetyloxyphenyl)-thiadiazole were suspended in 40 ml methanol and reacted with a solution of 2 g KOH in 90 ml methanol. The mixture was heated for 2 hours under reflux. Then, the solvent was distilled off at a rotary evaporator and the residue dissolved in 50 ml H₂O. The solution was acidulated with 5% HCl, the resultant precipitate was extracted by a vacuum and recrystallised from ethanol.

Yield: 3.2 g 94% of the theory

The following compounds were synthesised in accordance with this procedure:

	Mp / °C /
	194
	
	193
	100-101
	152-153

Example 2

Production of 2-(4n-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.

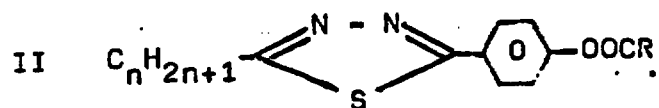
After being allowed to cool to room temperature, the reaction mixture is poured into 1 litre of iced water. The precipitate is washed with H₂O and recrystallised once from ethanol.

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

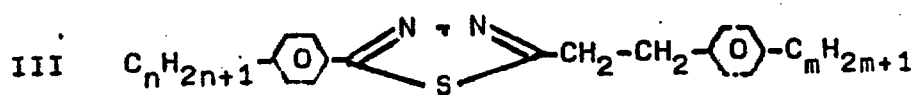
0.05 mol (21.3 g) of the resultant N-(4-n-octyloxybenzoyl)-N'-(4-acetoxybenzoyl)-hydrazine are dissolved in 150 ml pyridine and reacted with 15 g P₄S₁₀ under agitation.

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 productive reaction 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.



No.	n	R	C	S	S _C	S _A	N	1s
II 1	5	 -C ₁₀ H ₂₁	. 104	-	-	. 121	. 135	. 146 .
II 2	7	 -C ₁₀ H ₂₁	. 105	-	-	. 140	. 141	. 143 .
II 3	7	 -OC ₈ H ₁₇	. 100	-	-	. 159	-	. 171 .
II 4	9	 -C ₁₀ H ₂₁	. 103	-	-	. 143	-	- .
II 5	9	 -OC ₈ H ₁₇	. 98	-	-	. 166	-	. 170 .
II 6	9	 -OC ₄ H ₉	. 105	-	-	. 133	-	. 173 .
II 7	9	 -OC ₅ H ₁₁ C ₂ H ₅	. 81	-	-	. 85	-	. 99 .



No.	n	m	C	S _C	S _A	N	1s
III 1	6	4	. 56	. 89	. 123	-	- .

Example 3

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

0.1 mol (18.6 g) decanoic acid hydrazide are reacted in accordance with Example 2 with 0.1 mol (18.9 g) methoxycarbonylbenzoyl chloride to produce N-decanoyl-N'-(4-methoxycarbonylbenzoyl)-hydrazine.

0.05 mol (18.6 g) of the resultant diacylhydrazine are reacted with 15 g P_4S_{10} in accordance with Example 2

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-n-nonyl-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 at a rotary evaporator and the residue recrystallised from methanol until the conversion temperature attains constancy. Yield: 2.2 g (4.10⁻³ mol).

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

IV

No.	R ¹	R ²	C	S _C	S _A	N	I
IV 1	C ₁₀ H ₂₁ -	-CH ₃	,140	-	-	, 224	- - .
IV 2	C ₉ H ₁₉ -	-OC ₈ H ₁₇	, 97	, 131	, 136	- -	. .

Example 4

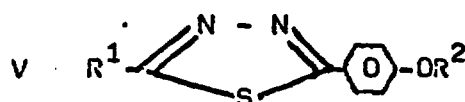
Production of 2-n-heptyl-5-[4-(4n-heptylphenylmethylenoxy)-phenyl]-1,3,4-thiadiazole

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-heptylbromide, 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 CHCl_3 . 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 temperatures.

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

The following Table gives examples



No.	R ¹	R ²	C	S	S _C	S _A	N	is
V 2	C ₇ H ₁₅	CH ₂ -  -OC ₆ H ₁₃	108	117	156	-	-	-
V 4	C ₇ H ₁₅	CH ₂ -  -C ₇ H ₁₅	95	-	124	140	-	-

Example 5

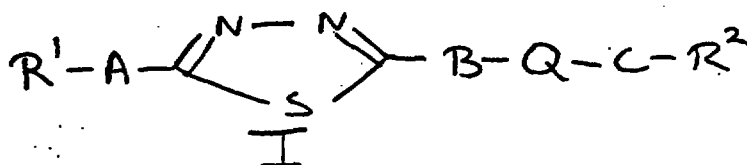
Widening of the S_C-phase area from 4-n-octyloxybenzoic acid-4'-n-pentyloxyphenylester (S 58 S_C 63 S_A 65 N 85 is) is demonstrated by the following Example: to 41.9% by mass of the said component, 12.4% of component no. I 7 were added; 23.3% of component II 3 and 22.4% of component II 5 were added. The mixture created melts at 40 to 45°C. The S_C-phase is now stable up to 100°C. The subsequent nematic phase clarifies at 132°C. Upon cooling, down to crystallisation at 32°C, no further phase conversion was observed below 100°C.

Example 6

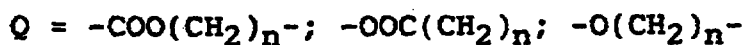
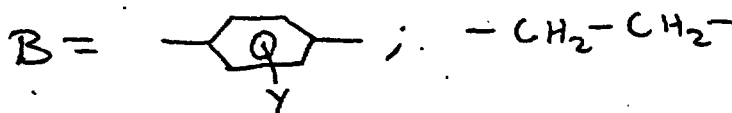
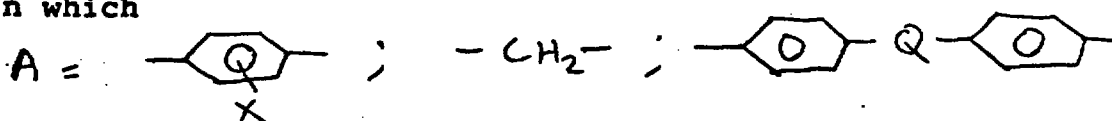
7.0% by mass tigogenin were added to the mixture in Example 5. The optically active C-phase converted to the cholesterolin phase at around 105°C . The optically active smectic C-phase was very readily detectable by its fan-like texture, interrupted by equidistant lines.

CLAIMS

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



in which



$-(CH_2)_nO-$; single bond; provided that where Q is single bond C is 

in which $n = 0 \dots 4$

X, Y, Z = independently of one another -H, -CN, -Cl, -Br, -F, $-OCH_3$, $-OC_2H_5$, $-CH_3$, $-C_2H_5$



and R^1 , R^2 and 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 $-CH=CH-$, or where $BQCR^2$

is $\text{---} \text{C}_6\text{H}_4 \text{---} OH$, $\text{---} \text{C}_6\text{H}_4 \text{---} CO_2CH_3$ or $\text{---} \text{C}_6\text{H}_4 \text{---} O_2CCH_3$

and wherein R^1A and $BQCR^2$ are different from one another.

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.
