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3-n-Alkyl-6-[4-n-Alkyloxy-Phenyl] -1,2,4,5-Tetra-Zines - New Stable Dyestuffs With Liquid-Crystalline Properties

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3-n-ALKYL-6-[4-n-ALKYLOXY-PHENYL]-1,2,4,5-TETRAZINES - NEW STABLE DYESTUFFS WITH LIQUID-CRYSTALLINE PROPERTIES

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Abstract: Some liquid crystalline 3-n-alkyl-6-[4-n-alkyloxy-phenyl]-1,2,4,5-tetrazines were synthesized. The substances show an intensive red violet colour and are stable under UV irradiation. Possible applications for colour switching displays are presented.

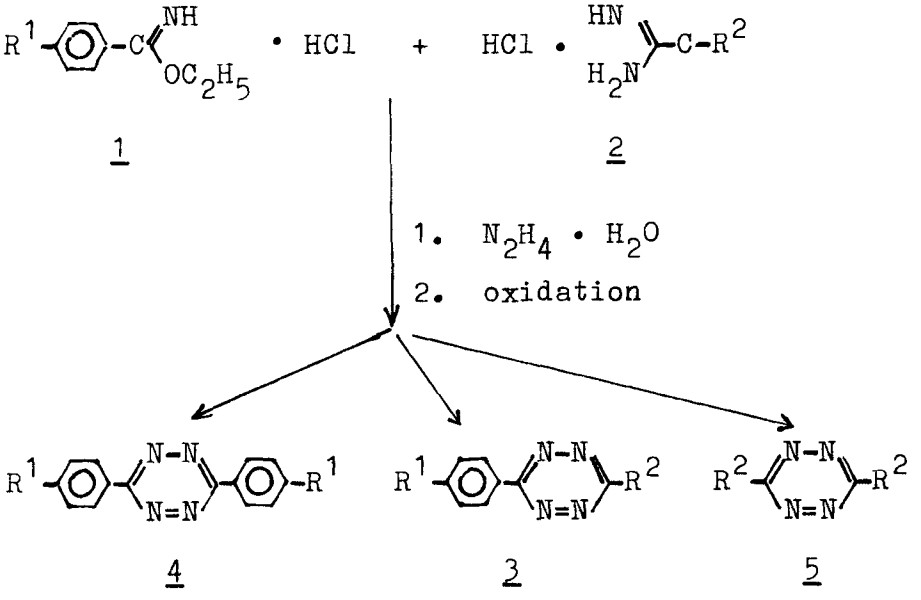
INTRODUCTION

More than ten years ago the guest host effect was proposed as a new principle for colour switching displays [1]. Despite the quick advances in liquid crystal research and technology the guest host effect till now did not establish among those effects which are realized in a large technical scale. This fact is due mainly to the low light stability and the poor solubility of the available dyestuffs. In order to find new dyestuffs with technically useful properties we tried to combine the colour absorption with liquid crystalline properties. Our efforts started from the tetrazine ring which is known to

absorb in the visible region of the spectrum [2].

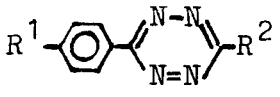
SYNTHESIS

We obtained 3-n-alkyl-6-[4-n-alkyloxy-phenyl]-1,2,4,5-tetrazines 3 in yields of 30 - 80 % by reaction of substituted benzimidoester hydrochlorides 1 with aliphatic amidinehydrochlorides 2 in the presence of hydrazine hydrate (80 %) and following oxidation with sodium nitrite according to the scheme:



The byproducts 4 and 5 are separated by recrystallisation. The transition temperatures of some synthesized tetrazines are given in table 1. As seen from the table the substances exhibit nematic, smectic A and smectic C phases in a relatively low temperature region.

TABLE 1



No	R^1	R^2	Cr	S_C	S_A	N	Is
1	C_4H_9O	C_5H_{11}	. 55	- -	- -	. 59	.
2	C_4H_9O	C_6H_{13}	. 49	(. 43)	- -	. 57	.
3	C_4H_9O	C_7H_{15}	. 47	(. 43.5)	- -	. 62	.
4	$C_5H_{11}O$	C_4H_9	. 48	- -	. 49	- -	.
5	$C_5H_{11}O$	C_5H_{11}	. 60	- -	- -	(. 59.5)	.
6	$C_5H_{11}O$	C_6H_{13}	. 65	- -	- -	(. 58.5)	.
7	$C_5H_{11}O$	C_7H_{15}	. 49	. 52.5	- -	. 63	.
8	$C_6H_{13}O$	C_5H_{11}	. 55	- -	. 68	- -	.
9	$C_6H_{13}O$	C_7H_{15}	. 58	. 67	. 74	. 76	.

Cr : solid crystal

S_A, S_C: smectic A, C

N : nematic

Is : isotropic

The numbers are the transition temperatures (°C).

Brackets denote monotropic phases.

OPTICAL AND ELECTROOPTICAL PROPERTIES

Similar to the liquid crystalline diphenyl-1,2, 4,5-tetrazines [3,4] the 3-n-alkyl-6-[4-n-alkyloxy-

phenyl]-1,2,4,5-tetrazines show an intensive red violet colour. The colour is due to a relatively weak absorption band of the $n \longrightarrow \pi^*$ transition of the tetrazine ring at 555 nm (λ = 550 l $mol^{-1} cm^{-1}$). The transition moment is oriented perpendicular to the molecule plane [2]. Therefore a planar oriented nematic sample of these tetrazines exhibits negative dichroism: Light polarized normal to the director is absorbed much larger than light polarized parallel to the director (see fig. 1). As seen from fig. 1, the dichroic ratio $E_\perp/E_\parallel$ of substance no 7 in a nematic matrix is about 4.5 at room temperature.

Because of the positive dielectric anisotropy the molecules are reoriented in field direction after applying a sufficiently strong electric field perpendicular to the director. When the incident light is polarized parallel to the director, the dielectric reorientation causes a strong absorption resp. a colour change from slightly pink to red violet.

On slowly cooling of the planar oriented nematic phase, the smectic C phase appears in a planar orientation, in which the director orientation is about the same as in the nematic phase. When an electric field is applied normal to the director, in the smectic C phase a colour change from pink to red violet occurs similar to the nematic phase due to a Freedericksz transition.

In table 2 the threshold voltage, the rise and decay times are given for the nematic and smectic C phase of substance no 7.

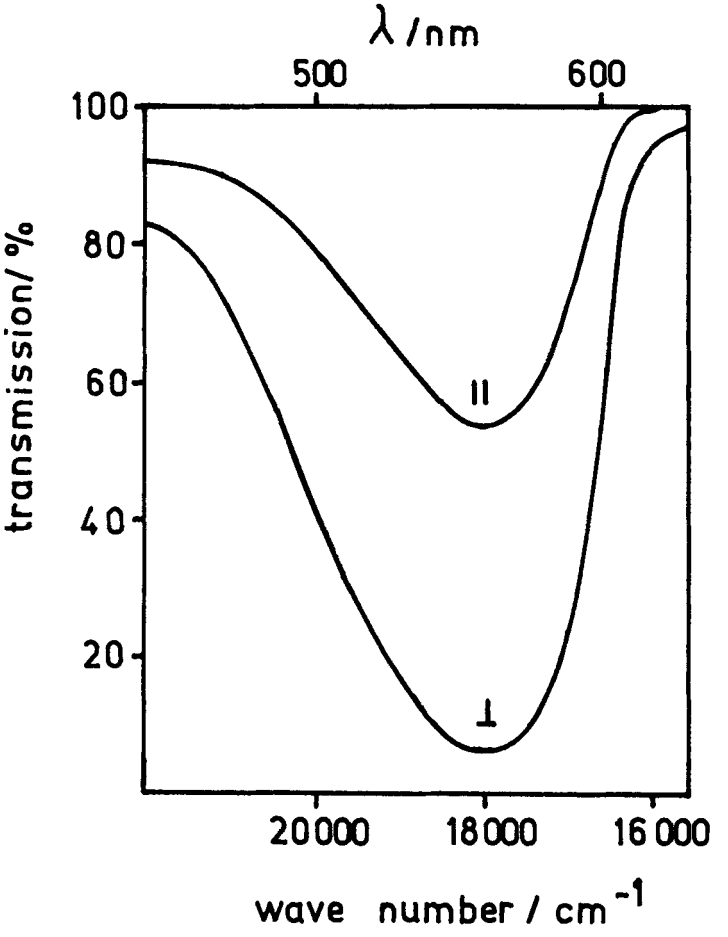


FIGURE 1: Transmission curve of 21 mole % substance no 7 in a planar oriented colourless nematic solvent (20 °C). Electric vector of light parallel (||) resp. normal (⊥) to the director. Layer thickness: 17 μm.

phase	$t/^{o}C$	U_{th}	U/U_{th}	t_{rise}/ms	t_{decay}/ms
N	56	10	3	18	110
S_C	50	14	3	29	46

TABLE 2: Threshold voltage, rise time and decay time of substance no 7 in the nematic and smectic C phase. Layer thickness: 10 μm.

The table shows that the decay time of the smectic C phase is distinctly shorter than in the nematic phase (see also [4,5]).

APPLICATIONS FOR ELECTROOPTICAL DISPLAYS

Planar oriented nematic or smectic C layers of the synthesized tetrazines can be used for field-induced colour switching displays preferably in the transient mode because of the strong colour saturation already in quite thin layers. A promising application is the use as guest material in a nematic host of high positive dielectric anisotropy. In spite of the relatively small extinction coefficient of the tetrazines, guest host cells may be produced with a high colour saturation because of the excellent solubility in nematic solvents. 10 - 20 % may be added to the nematic host without a remarkable change of melting or clearing points. It must be emphasized that the tetrazines show a high stability under light (also UV) irradiation.

The tetrazines may be used also for guest host systems containing two dichroic dyes with different

sign of dichroism [6]. For example 15 mole % of substance no 7 (negative dichroism) and 0.5 mole % of a yellow azo dye with positive dichroism are dissolved in a nematic host consisting of three homologous 4-cyanophenyl 4-n-alkylcyclohexane carboxylates [7]. When the incident light is polarized parallel to the director of the planar oriented sample, a strong yellow colour is observed in the field-off state. On applying an electric field a colour change to intensively red violet occurs.

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