Temperature independent threshold voltage for an electrooptic effect

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Temperature independent threshold voltage for an electrooptic effect (*)

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Résumé. — Normalement la tension seuil de l'effet de transition cholestérique-nématique se réduit considérablement si la température monte. Cette dépendance de la température peut être compensée en utilisant des phases cholestériques induites dont le pas hélicoïdal diminue suffisamment si la température monte. La dépendance souhaitée du pas de l'hélice en fonction de la température est obtenue en mélangeant à la phase nématique deux composés chiraux de signe contraire.
Nous présentons ici des résultats obtenus sur des mélanges nématiques E 8 et S 1132 dopés avec les composés chiraux CB 15 et S 811, les valeurs de pas obtenues étant 3-5 µm. La tension seuil mesurée pour des épaisseurs de couches de 23,5 µm et 13 µm respectivement et pour des alignements homéotropes se révèle être constante à ± 3 % dans une gamme de température de 50 K.

Abstract. — The threshold voltage of the cholesteric-nematic phase change effect in general decreases considerably with increasing temperature. The temperature dependence for the threshold voltage can be compensated by using an induced cholesteric phase with a helix pitch decreasing sufficiently with increasing temperature. The appropriate temperature dependence of the pitch can be obtained if the nematic phase is doped with two chiral compounds which induce opposite sign of the helix screw sense when used separately.
The efficacy of this method was investigated for the two nematic mixtures E 8 and S 1132 to which the two chiral compounds CB 15 and S 811 had been added, the induced pitch values being 3-5 µm. The threshold voltage measured in samples of 23.5 µm and 13 µm thickness using homeotropic boundary conditions are found to be constant within ± 3 % over a temperature range of 50 K.

1. **Introduction.** — Electrooptical effects exhibited by liquid crystals generally show a strong decrease of the threshold voltage with increasing temperature. This is disadvantageous for display applications especially for multiplex operation, as is also the case for the cholesteric-nematic phase change effect [1, 2].

Compared with the electrooptical effects using nematic phases, the threshold voltage is not only dependent on the elastic and dielectric constants, but also on the reciprocal pitch of the cholesteric structure [3, 4]. Thus, by varying the pitch temperature coefficient without substantially affecting the other physical constants the temperature dependence of the threshold voltage is also influenced. Normally, nematic phases with positive dielectric anisotropy in which a cholesteric structure is induced by adding a chiral compound are used for the phase change effect. The induced cholesteric phases usually exhibit an increase of the pitch with increasing temperature [5] thus additionally magnifying the decrease of the threshold voltage.

We have recently shown that it is possible to considerably vary the temperature dependence of the pitch of induced cholesteric phases by adding two appropriate chiral compounds, each of which induces a different helical screw sense when used alone [6].

It is the purpose of this study to investigate to what extent the temperature dependence of the threshold voltage of the phase change effect can be compensated using this method.

2. **Experimental.** — Commercially available nematic phases E 8 (BDH, Poole, Great Britain), a mixture of cyanobiphenyles and -terphenyles, and S 1132 (E. Merck, Darmstadt, Germany), a mixture of phenylcyclohexanes and one biphenylcyclohexane were used without further purification. The nematic temperature range is reported to be − 11 to 70 °C

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and − 8 to 60 °C respectively. To induce the cholesteric structure the two chiral compounds 4-cyano-4'-(2-methylbutyl)-biphenyle (CB 15, BDH), and octyl-2-oxy-4-(4'-n-hexyloxy-benzoyloxy)-benzoate (S 811, E. Merck) were used. Earlier measurements [6, 7] with the nematic phase N 4 (E. Merck) have shown that the additives CB 15 and S 811 induce right-handed and left-handed helix structures respectively, each producing the highest helical twisting power of the compounds studied. The concentration was chosen such that, at room temperature, a pitch of approximately 4.5 μm was induced in each of the four cholesteric phases.

The helix pitch and screw sense were determined by the modified Grandjean-Cano method [7, 8].

SnO_2 coated glass plates, treated with a benzoic lecithin solution to obtain a homeotropic alignment, together with 23.5 and 13 μm mylar spacers were used to measure the threshold voltage of the cholesteric-nematic phase change.

The sample was placed in the thermostated hot stage of a polarizing microscope. The sample temperature was measured using a thermocouple with a ± 0.1 °C accuracy. The transmitted light was measured with crossed polarizers using a photomultiplier and recorded on an x-y-plotter against the true rms value (Burr-Brown 4340) of the cell voltage at a frequency of 1 kHz.

The distance between the two glass plates forming the cell was considered to be uniform over the 3 mm diameter area detected by the photomultiplier since the cholesteric texture disappeared homogeneously with increasing voltage. With a scan speed of 4 V/min., the step function in the light intensity curve is sharp enough to enable the threshold voltage (measured at the foot of the step) to be adequately determined. However, below 0 °C the measurement error increases since the step slope decreases as the temperature is reduced.

3. **Theory.** — The threshold field E_c for the helical unwinding depends on the elastic twist constant k_{22}, the dielectric anisotropy $\Delta\varepsilon$, and the pitch p [3, 4]

$$E_c = \frac{\pi^2}{|p|} (k_{22}/\varepsilon_0 \Delta\varepsilon)^{1/2} . \quad (1)$$

In general the value of the square root decreases with increasing temperature. In order to obtain a temperature independent threshold field, the pitch magnitude must decrease as the temperature increases, which is not normally the case for induced cholesteric phases containing one chiral additive [5].

It is well known that, for a limited range of concentrations, the reciprocal pitch $1/p$ is proportional to the concentration of the chiral compounds added to the nematic phase

$$1/p = \sum_i h_i c_i \quad (2)$$

where h_i is the helical twisting power of the single chiral additive [9].

The temperature dependence of h_i can be expanded in a power series

$$h_i = \alpha_i + \beta_i t + \gamma_i t^2 + \cdots \quad (3)$$

Recently we have shown that the temperature dependence can be varied considerably if two chiral compounds are used, which induce helices with opposite sign when added separately to the nematic phase [6].

For a linear decrease of h_i with temperature, which is nearly true for most of the experiments, eqs. (3) and (2) result in eq. (4) for the addition of two chiral additives

$$1/p = \alpha^+ c^+ - |\alpha^-| c^- + (\beta^- c^- - |\beta^+| c^+) t \quad (4)$$

with $\alpha^+ > 0$, $\beta^+ < 0$ for a right-handed helix, and $\alpha^- < 0$, $\beta^- > 0$ for a left-handed helix.

If the relative slopes of the pitch curves differ from each other ($\alpha^+/\beta^+ \neq \alpha^-/\beta^-$) it is possible to produce a temperature independent pitch

$$d(1/p)/dt = 0 \quad \text{if} \quad c^+/c^- = \beta^-/|\beta^+| ,$$

as well as a helix inversion ($1/p = 0$) at the temperature t_n if

$$c^+/c^- = (|\alpha^-| - \beta^- t_n)/(\alpha^+ - |\beta^+| t_n)$$

simply by varying the concentration ratio c^+/c^- of the two chiral compounds. A decreasing pitch with increasing temperature can be obtained according to eq. (4) although an opposite slope is observed if each compound is added separately.

It is obvious from eqs. (1) and (2) that the threshold voltage U for a mixture with two chiral additives is the sum of the voltages of each mixture where only one chiral compound was used, multiplied by its helix pitch sign :

$$U = \sum_i \text{sgn}\,(p_i)\, U_i\, c_i . \quad (5)$$

The last equation shows that using this method, it is in principle not necessary to determine the size of the pitch.

4. **Results.** — The practicability of the method described in the preceding section was studied using the two commercial nematic mixtures, E 8 and S 1132 with the two chiral compounds CB 15 and S 811. The concentrations were chosen such that, at room temperature, a pitch of approximately 4.5 μm (Fig. 1) was induced in each of the four cholesteric phases (table I).

The threshold voltage of the phase change effect, determined for 23.5 μm thick cells, is shown in figure 2. The results show that the threshold voltage

Table I. — $|p|\,U/d$-*values for the induced cholesteric phases investigated.*

	No.	c_{CB15}/wt.-%	c_{S811}/wt.-%	d/μm	$|p|\,U/d$								
					− 10 °C	0 °C	10 °C	20 °C	30 °C	40 °C	50 °C	60 °C	t_c/°C
E 8	Ia	2.79	—	23.5	3.25	2.77	2.51	2.42	2.44	2.47	2.46	2.31	68.3
	Ib	—	1.98	23.5	3.16	2.76	2.53	2.44	2.37	2.24	2.06	1.86	69.2
	Ic	6.84	6.33	23.5	3.20	2.75	2.52	2.43	2.36	2.29	2.14	—	59.1
S 1132	IIa	2.37	—	23.5	3.53	3.23	3.03	2.92	2.82	2.68	2.51	2.29	69.3
	IIb	—	1.63	23.5	3.56	3.31	3.07	2.92	2.83	2.78	2.71	2.13	69.2
	IIc	12.75	10.63	23.5	3.41	3.12	2.96	2.79	2.63	2.50	—	—	48.0
	IId	12.75	10.63	13	3.41	3.12	2.99	2.86	2.73	2.58	—	—	48.0

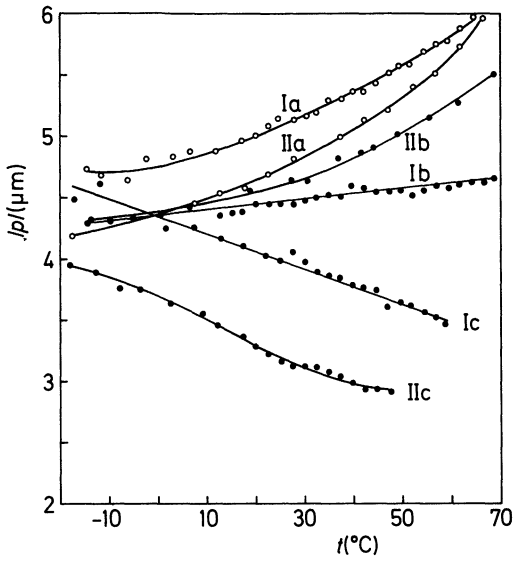

Fig. 1. — Temperature dependence of pitch (○ right-handed helix, ● left-handed helix) of the cholesteric phases induced in E 8 (Ia, b) and S 1132 (IIa, b) by one chiral compound CB 15 or S 811 and of the mixtures with temperature independent threshold voltage (Ic, IIc). For compositions see table I.

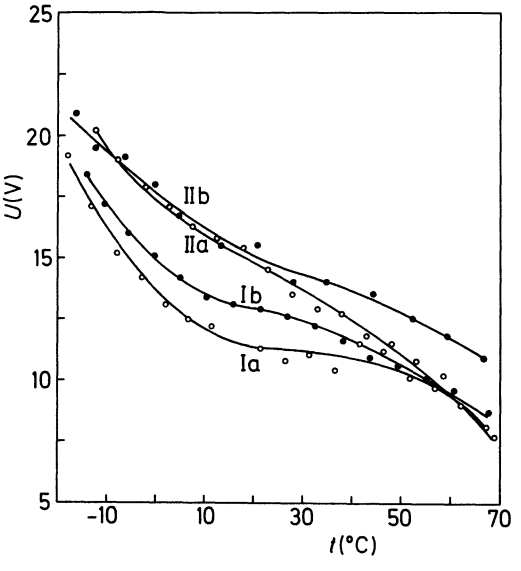

Fig. 2. — Temperature dependence of threshold voltage of the induced cholesteric phases obtained by the addition of one chiral compound. The cell thickness d was 23.5 μm.

decreases from 20 V to approximately 10 V over the temperature range from − 10 °C to 70 °C.

According to formula (1) the threshold voltage for the concentrations used depends only on the properties of the nematic host and not on those of the chiral compounds. Table I shows that the $|p|\,U/d$-values follow these predictions with an error limit of 5 % for both chiral compounds, though the temperature dependence of the pitch exhibits a considerably different behaviour.

For the nematic mixture S 1132 the physical parameters necessary to calculate the threshold voltage are known

$$(p = 3\,\mu\text{m},\ \Delta\varepsilon = 11.9,\ k_{22} = 5.8 \times 10^{-7}\,\text{dyn.}\,[10]).$$

Eq. (1) gives a $|p|\,U/d$ value of 2.33 V at 20 °C which is 15 % below the determined voltage. The reason might be our definition of the threshold voltage or the difference between the nominal and the real cell-thickness.

Figure 1 shows that the relative slopes of the pitch functions of CB 15 and S 811 are different taking the concentrations into account. This is true for the additives in E 8 (Ia, b) as well as in S 1132 (IIa, b). Thus, choosing an appropriate c^+/c^- — relationship according to eq. (4) should result in a decrease of the pitch with increasing temperature. Figure 1 shows that a weight relation of $c^+/c^- = 1.08$ in E 8 yields an almost linear pitch decrease with temperature, the slope of which is approximately opposite to that of $|p|\,U/d$ *vs.* t dependence in E 8 (table I). In S 1132, however, a $c^+/c^- = 1.20$ was necessary to achieve the same result.

Figure 3 shows the threshold voltage U obtained with these concentrations of the additives. With E 8 the threshold voltage is found to be constant within 3 % in the temperature range from 0 °C to 50 °C. With S 1132 a much higher total concentration of the additives of 23.38 wt.-% was used thereby reducing the clearing point of the mixture by about 20 K. In the remaining temperature range from − 5 °C to 40 °C, however, the threshold voltage was relatively constant. Using a cell thickness of 13 μm reduces the threshold voltage of the S 1132 sample (Fig. 3, IId) to nearly half its original value, this remaining

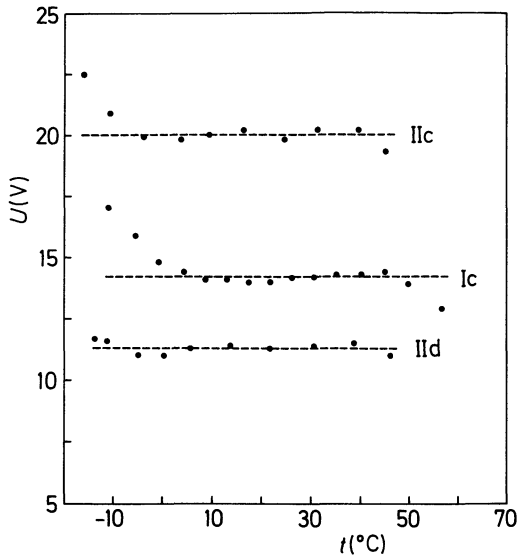

Fig. 3. — Threshold voltage of the induced cholesteric phases with compensated temperature dependence. The cell thickness d was 23.5 μm for Ic, IIc and 13 μm for IId.

constant within the same temperature range, as expected.

Calculations for the compensated mixtures yield $|p|\ U/d$-values (table I) which do not differ much from those evaluated for the single additives. Considering the high total concentration this result is rather remarkable.

In order to achieve a strong contrast together with a maximum brightness it is necessary to have a rather small pitch when using the phase change effect with an incorporated dye [11]. It can be assumed that for the dosage of S 1132 such a small value of the pitch has already been reached (Fig. 1). Similar results should be obtained by using higher concentrations in E 8 which, however, result not only in a further diminution of the clearing point but also in an increase of the threshold voltage.

According to eq. (5), it should be possible to calculate the threshold voltage of compounds with two chiral additives, assuming equal layer thickness, from the voltages of the cholesteric phases induced with single doping, without having to know the absolute pitch value. For the concentrations of CB 15 and S 811 given in table I, values of − 13.4 V (E 8) and − 19.2 V (S 1132) at 20 °C are obtained, the negative sign indicating a left-handed helix structure, which is in agreement with the measurements (Fig. 1). The absolute threshold voltages of 14.1 V (Ic) and 19.9 V (IIc) determined experimentally, show only a small discrepancy from the calculated values. However, using such methods, it is not possible to predict a constant threshold voltage over the given temperature range — even assuming different concentration ratios c^+/c^-. For finite layer thicknesses eq. (1) is an approximation. This may be the cause for the discrepancy between observed and calculated values of the threshold voltages.

How sensitive the results are to the concentration ratio of the additives can be seen from figure 4. With additions of $c^+ = 8.91$ wt.-% and $c^- = 5.18$ wt.-% ($c^+/c^- = 1.72$) a helix inversion in E 8 occurs at 39 °C. At temperatures below and above these values the threshold voltage increases dramatically. However, even with the 125 μm wide cell, there is still a considerable temperature range exhibiting a homeotropic nematic structure throughout, i.e. no twisting of the nematic phases [12]. This causes the threshold field to vanish.

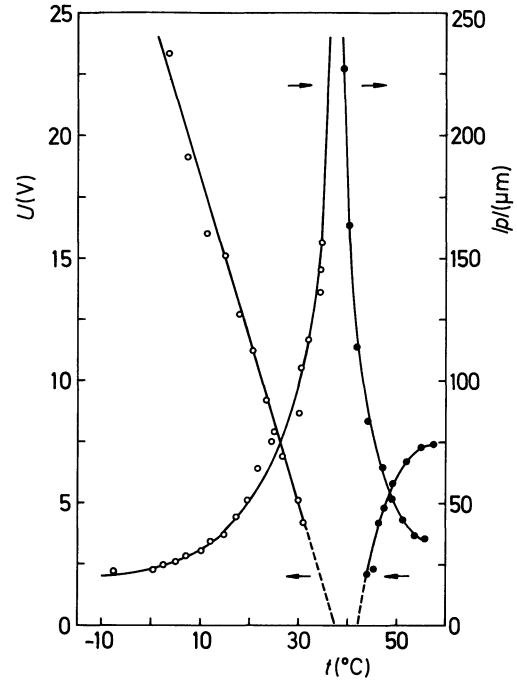

Fig. 4. — Threshold voltage measured with a cell thickness d of 125 μm and pitch *versus* temperature for an induced cholesteric mixture exhibiting a helix inversion at 39 °C (8.91 wt.-% CB 15 and 5.18 wt.-% S 811 in the nematic mixture E 8).

5. **Discussion.** — The results of the experiments described above show that by using two or more different chiral additives, induced cholesteric phases having a suitable pitch temperature coefficient can be generated such that the threshold voltage of the phase change effect is nearly temperature independent over a wide temperature range. This method is based on the fact that the temperature dependence of the pitch is not a universal function like the other physical parameters but depends on the type of the additive and the nematic host as shown in earlier experiments [13].

In nematic phases, however, the threshold voltages of electrooptical effects only depend on properties which are supposed to have a direct relation with the degree of order. It is only by choosing nematic phases with the clearing point well above the normal working temperature that the temperature dependence of the threshold voltage can be reduced. This has

already been extensively discussed for the Schadt-Helfrich effect [14].

In order to overcome the reverse twist in Schadt-Helfrich displays, induced cholesteric phases are frequently used having a threshold voltage, which depends on the induced pitch [15, 16]. Finding an appropriate temperature function for the pitch, which would lead to a Schadt-Helfrich effect threshold voltage which is independent of temperature, seems to be very difficult, because it is necessary to use rather large pitches (greater than 4-times the layer thickness). On the other hand it seems to be useful to apply two or more additives to induce a constant pitch in order to constitute a clear relation between pitch and layer thickness.

One of the main applications of the phase change effect in the future should be found in the use of dichroic dyes as additives. To achieve the highest possible contrast rather small pitches should be induced [11]. As the present paper shows, even in this case, it is possible to obtain a temperature independent threshold voltage, but because of the very high concentrations of the chiral additives needed, the clearing temperatures of the mixtures are considerably reduced. This is why it seems necessary to find new chiral additives with the highest possible helical twisting power for easier applications. These compounds should induce right- or left-handed helical structure with different relative temperature dependence if possible.

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