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Light induced shifts of ferroelectric mesophase transitions

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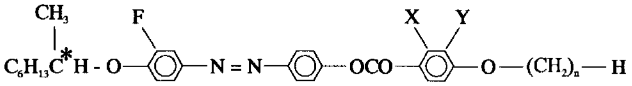
Several series of recently synthesized chiral azobenzene liquid crystals exhibit transitions driven by both illumination and temperature: some compounds can be 'melted' from the SmC* phase to the isotropic phase by increasing illumination only; according to the phase sequences, SmA, TGBA, N*, and blue phases are also involved in such behaviour. The observed phenomena are reversible and transition temperatures are reproducible in identical light conditions. Some specific transitions have been studied. Their temperatures can be lowered to 10 degrees below the dark transition values by increasing the illumination of samples. Under illumination, those transitions exhibit first order behaviour.

1. Introduction

Liquid crystal properties that are modified or enhanced photochemically have become of great interest. Most papers deal with mixtures of liquid crystals and dyes or chiral dopants [1–5].

The results of the present work concern pure liquid crystals. Their phase sequences and thermal responses depend strongly upon visible irradiation intensity. The compounds studied belong to three chiral azobenzene series [6] exhibiting ferroelectric mesophases, TGB and blue phases. The general structure of the molecules is:



where $X = Y =$ H: nA series, $X =$ H, $Y =$ F: nFA series, $X = Y =$ F: nF$_2$A series.

The phase sequences of the various compounds were determined by differential scanning calorimetry (DSC) and confirmed by microscopic observations with very low illumination. These sequences are given below in table 1.

The properties described in the present paper result from the behaviour of the chemical group PhN=NPh. The amount of *cis-trans*-isomerization of the double bond depends on the irradiation. In the *trans*-configuration the molecules are mesogenic while in the *cis*-configuration they are not and can even be seen as impurities in the liquid crystalline phases [7]. Such *cis-trans*-isomerization explains the photosensitive properties of some liquid crystalline polymers as well. In those materials, these properties stimulate much current research activity [8, 9].

Table 1. Phase sequences of the photosensitive compounds.

	Transition temperatures °C												
Compound	Cr		SmC*		SmA		TGB		N*		BP		I
7A	•	73.9			•	108.5	•	110.5	•	129.5	•	131.0	•
10A	•	76.4	•	103.6	•	119.3	•	120.6	•	125.9	•	127.0	•
7FA	•	66.5			•	93.5	•	98.4	•	113.8	•	114.8	•
8FA	•	85.9			•	102.3	•	107.1	•	115.6	•	116.8	•
10FA	•	88.1	•	102.8			•	103.0	•	111.0	•	112.1	•
12F$_2$A	•	57.6	•	106.6					•	114.0	•	115.2	•

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2. General features of photosensitivity

The properties described were established by polarizing microscopy used in transmission. The temperature control was obtained with a Mettler FP5 heating stage. The irradiation was produced by a halogen lamp (OSRAM, 100 W). The light variations were controlled through modifications of the condenser diaphragm aperture and through modifications of the applied voltage. Real values of irradiation were determined with a luxmeter. Its entry window was put against the lower face of the Mettler stage.

Investigations were made on different samples such as prismatic wedges with rubbed faces or flat drops on rubbed glasses, but mainly using thin cells made from microscope slides and cover slides. Since the degree of *cis-trans*-isomerization depends upon the light penetration depth, all the results quoted have been obtained either with constant thickness cells or by looking always at the same part of a prismatic sample.

All the pure compounds studied are photosensitive. Consider a cell placed upon a small aluminium (Al) sheet, in such a way that one part only of the observation field is crossed by incident light. In darkness, a given phase is chosen by checking the 'dark' temperature. When the light is put on, from the current level used for microscopic observations, the texture is quickly modified (within 10 s). The illuminated part of the sample 'melts' into one of the following phases of the sequence, as if the temperature had been increased. Table 2 gives some examples of irradiation intensities required to reach the various phases of some of the compounds. These values are obtained by increasing the illumination very slowly. According to the selected dark temperature, the isotropic liquid phase is not always accessible with the greatest intensity of the microscope lamp.

The TGBA and N* phases can be reached according to the imposed irradiation when starting from the SmA phase of 8FA. If the Al sheet is then removed both parts of the sample look different. The part which was previously hidden exhibits the former phase while the illuminated one shows the texture of the other phase. Simultaneous observations of both textures—hidden and illuminated—have to be performed under very weak irradiation so that the hidden texture is not modified during observation. On the other hand, the first illuminated texture evolves as the illumination is reduced. Those different behaviours of the two parts of the observation field are the reason why photographs of both textures together are not available. As soon as the light intensity is increased to the current level required by the camera, the whole sample quickly assumes the texture of the illuminated part.

When the light intensity is decreased to its lowest value, the sample returns gradually to the texture of the original phase determined by the 'dark' temperature.

3. Illumination–temperature phase diagrams

The above qualitative experiments show that the various phases of each compound can be reached by the combination of illumination and temperature. From microscopic observations on constant thickness samples ($\leqslant 5\,\mu m$), illumination–temperature (*Il–T*) phase diagrams can be drawn, and figures 1 and 2 give the *Il–T* phase diagrams of compounds 7A and 12F$_2$A. A given illumination is applied at a low temperature inside the first mesophase of the sequence (no noticeable shift of the Cr–LC transitions has been detected up to now). By heating the sample at $\sim 2°C\,min^{-1}$ the approximate transition temperatures are detected. Accurate values are then obtained by scanning up and down at appropriate temperature rates, owing to the good reversibility of the phase changes.

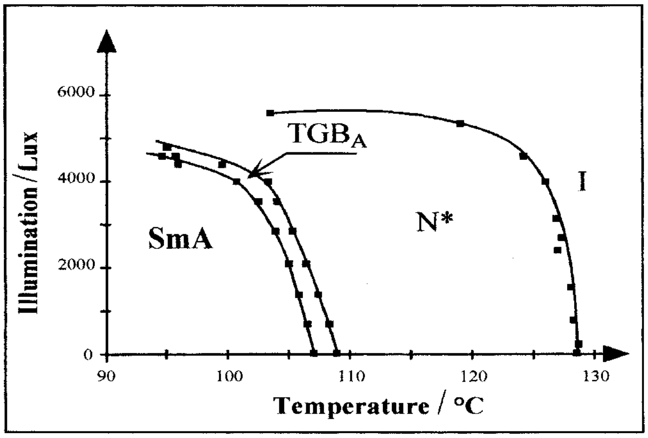


Figure 1. Illumination–temperature phase diagram for compound 7A.

Table 2. Irradiation intensities (lux) required for phase transitions at selected temperatures.

Compound	T_{dark}	SmC*		SmA		TGB		N*		I
7A	105			•	2100	•	3200	•	------------------	
12F$_2$A	105	•	1550					•	4600	•
8FA	101			•	2400	•	3100	•	------------------	
8FA	104					•	2400	•	5000	•

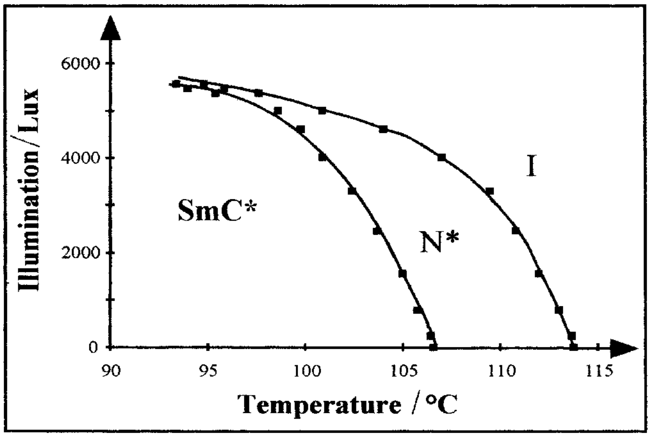


Figure 2. Illumination–temperature phase diagram for compound $12F_2A$.

Every transition of each sequence can be studied except the transition to the isotropic phase because this change often leads to disastrous modifications of characteristic sample textures. This transition is studied separately. From the isotropic phase, a slight illumination reduction induces the appearance of the blue phases of the sequences concerned. Then slow cooling allows the qualitative temperature range of the blue phase to develop. This range is wider for strong illumination than for weak. This behaviour is easily understood by looking at the curvature variations of the N*–I transition lines in the *Il–T* phase diagrams. This broadening of the temperature range under illumination would be useful for a detailed study of blue phases in the vicinity of their boundary transitions.

The curvature of the transition lines explains the photographs (figure 3) obtained with a slightly prismatic sample of 7A at the 'dark' temperature 106°C: when the illumination rises, the texture changes from the SmA phase up to the N* phase, by crossing the TGBA phase. Stronger illumination induces the formation of the isotropic phase. When the illumination decreases starting from N* phase, the TGBA phase appears and then the sample adopts the SmA texture with very low illumination. This behaviour obviously illustrates the above mentioned reversibility of the phase changes driven by light. In the same way, the succession of SmC*, N*, I phases is induced by increasing the illumination on a $12F_2A$ sample. For the various compounds the blue phases behave monotropically and appear only on reducing the illumination.

4. Qualitative influence of the thickness

A quick examination of the photographs of 7A in figure 3 shows that texture changes start on the (left) side of small thickness when the light intensity is increased. By contrast, texture changes appear on the large (right) thickness side when illumination is reduced. This behaviour is clearly related to the penetration depth of photochemical isomerization of the azobenzene double bond. In particular, the relaxation to the *trans*-configuration is easier on the thick side of the sample when illumination decreases. For that reason lower phases of the sequences appear first for larger thicknesses before invading the whole sample. This influence of the thickness coupled to the dynamical behaviour of the occurrence of the transitions, as described in §5, explain the difficulties of comparing increasing and decreasing illumination values required for a transition at a selected temperature.

Detailed effects of thickness influence are currently under study.

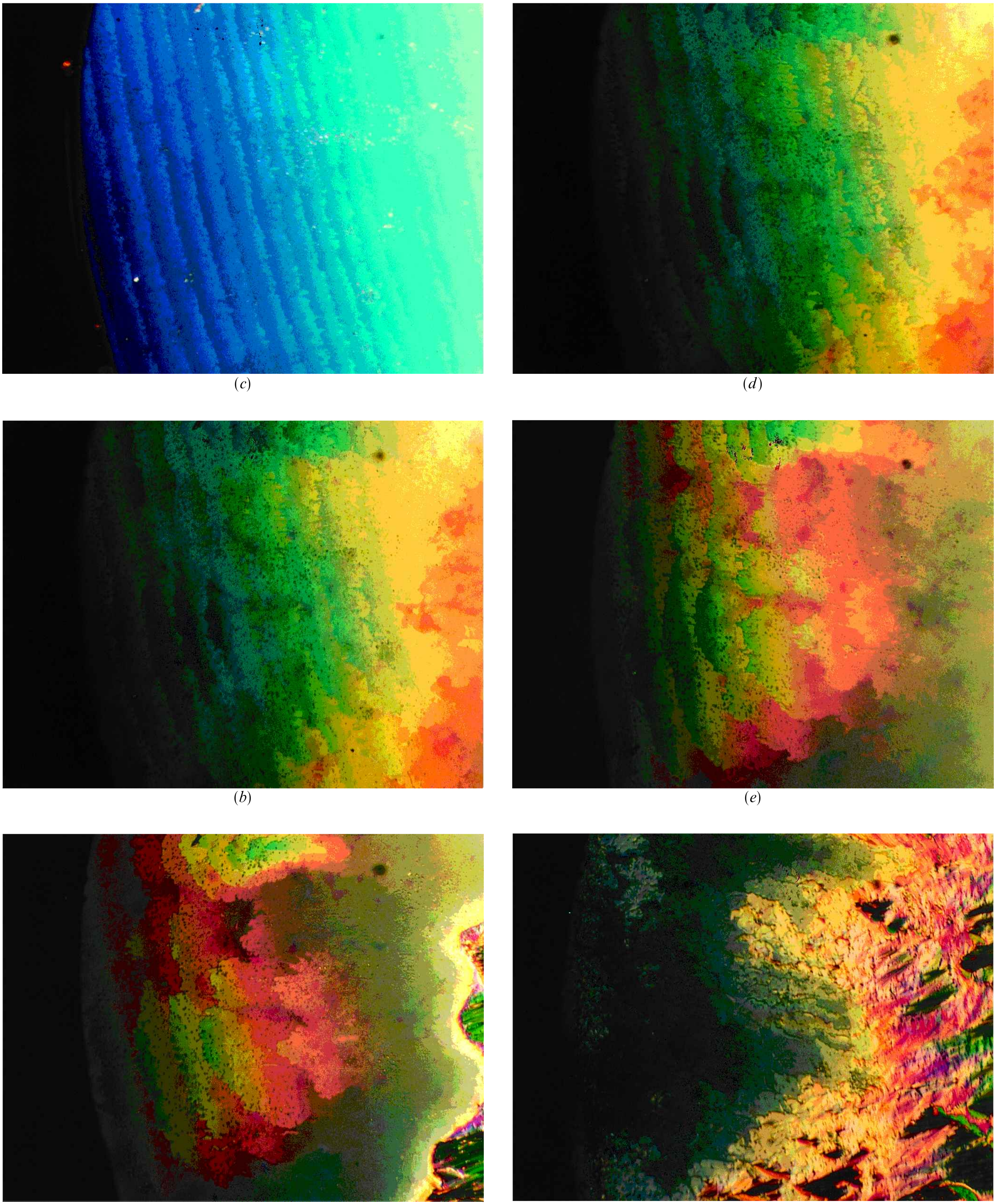
5. Transitions time delays

In accordance with the above remarks, all measurements were performed at constant thickness.

The various phases of the compounds can be addressed by both illumination and temperature, i.e. the different transitions can be induced by illumination only. The stronger the illumination, the more the transition is shifted towards low temperatures. The time delays increase with the transition shifts. Figure 4 drawn for the SmC*–N* transition of $12F_2A$ is a striking example of the typical behaviour of the transitions vs. irradiation time. In darkness a temperature T_{IR} is fixed inside the existence range of the lower mesophase of the sequence. Then irradiation at the chosen level is applied and the time delay for the occurrence of the transition under study is measured. The temperature variation $T_D - T_{IR}$ is the shift between the 'dark' transition temperature T_D and the temperature T_{IR} of the transition under irradiation.

Time constants τ can be determined by fitting the curves (figure 4) with classical formulae of the type $y = a - b\exp(-t/\tau)$. The a and b values are very close to each other. The a value represents the greatest shift of the transition temperature that can be obtained with the applied illumination. It is clearly related to the illumination level. Similar behaviours are observed with the SmA–TGBA transitions of 8FA and 10A and with the N*–I transitions of $12F_2A$ and 7FA. For this latter type of transition, it must be noted that blue phases (monotropic) are involved in the transition mechanism. As mentioned, thickness dependence of the time constants is under study. Of course, a dynamical behaviour of the occurrence of transitions is also observed with decreasing illumination.

Finally, an initial homeotropic orientation of the samples makes determination of some transitions easier. However the evolution of transition shifts vs. time seems



(*c*) (*d*)

(*b*) (*e*)

(*a*) (*f*)

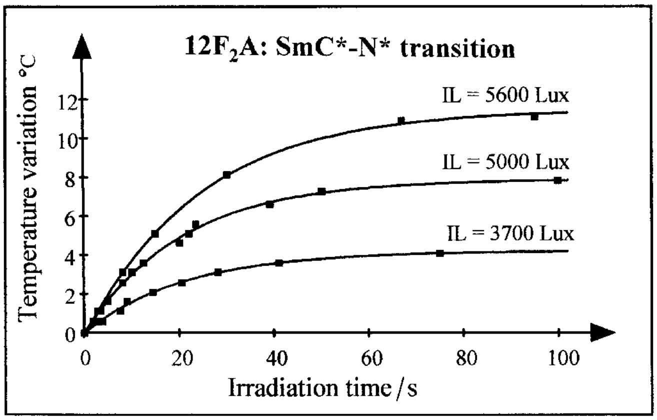


Figure 4. Shifts of the SmC*–N* transition temperature of 12F$_2$A versus time delay for various intensities of illumination; the sample had a planar alignment.

more complicated in this case, indicating the influence of molecular orientation in liquid crystal photochemical processes.

6. Conclusion

For the different members of three pure chiral azobenzene series, temperature shifts of ferroelectric mesophase transitions are induced by incident light. The occurrence of the various phases is driven by both irradiation level and temperature. Each compound's behaviour is well described by a new type of 'illumination–temperature' phase diagram.

At constant thickness, curves of transition temperature shifts vs. time can be drawn. Under illumination, the transitions behave as first order when the initial orientation of the sample is planar.

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Figure 3. Photographs showing the textural effects of increasing (*a*, *b*, *c*) and decreasing (*d*, *e*, *f*) illumination on a slightly prismatic sample of 7A. The temperature is constant for all the observations ($T = 106°C$). See also the *Il–T* phase diagram of compound 7A. (*a*) Weak illumination at 106°C: TGBA Cano steps appear; the SmA texture is still visible on the large thickness (right) side of the preparation. (*b*) At the TGBA–N* (*Il*–106°C) transition the N* texture appears on the small thickness (left) side. (*c*) Grandjean–Cano steps in the N* phase. (*d*) Illumination on the N* texture (*c*) is now reduced: the sample goes back to the N*–TGBA transition. Comparison with (*b*) provides evidence for the reversibility of the phenomena. (*e*) Within the (*Il*–106°C) range of the TGBA phase. (*f*) Below the TGBA–SmA (Il–106°C) transition: SmA texture is growing from the large thickness (right) side.