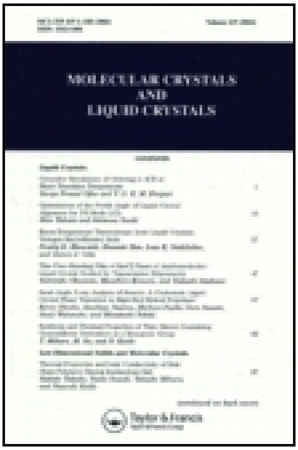

Molecular Crystals and Liquid Crystals

Photoinduced Effects in Liquid Crystal Systems Containing Chiral α,β-Unsaturated Ketones

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Photoinduced changes have been revealed and summarized for liquid crystalline (LC) systems with helical supramolecular structures induced with chiral α,β-unsaturated ketones. The photoinduced inversion of a helix sign was ascertained for LC mixtures containing 3R-methylcyclohexanone arylidene derivatives. This effect is accompanied with an essential enhancement of the helical twist in the photostationary state and its invariability under the following prolonged UV irradiation. For ferroelectric LC, the photoinduced inversion of a spontaneous polarization sign and a concomitant increase in its absolute value and in the smectic tilt angle are observed. The E–Z photoisomerization of chiral compounds is established to be responsible for the effects discovered.

Keywords: chiral dopants; induced cholesteric and ferroelectric liquid crystals; photoinduced effects

INTRODUCTION

Various changes in macroscopic properties of liquid crystalline (LC) sys-tems caused by photochemical transformations of their

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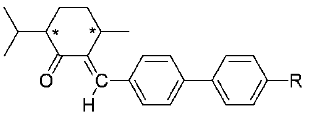
components attracted much attention rather long ago. Photoalignment effects in LC [1,2], light-induced switching in photochromic ferroelectric LC (FLC) by ultraviolet light at a fixed field polarity [3,4], and possibilities for data optical recording and storage [5,6] are the incomplete list of photoinduced effects which are of significant importance from both fundamental and applied points of view. As photoisomerizing chiral components of induced cholesteric LC compositions, α,β-unsaturated ketones, specifically (+)-isomenthone derivatives, are well known as well as some photoinduced effect provoked by them. For the first time, the effect of a long wavelength shift of the selective light reflection band under laser irradiation of a LC composition based on 4-pentyl-4′-cyanobiphenyl as a nematic solvent with a chiral dopant belonging to (+)-isomenthone arylidene derivatives was reported in [7]. Later, the *E*–*Z* photoisomerization was established to be responsible for this effect [8–11].

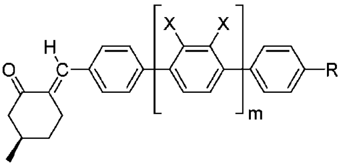
Initial *E*-isomers of chiral compounds (CCs), (+)-isomenthone arylidene derivatives, were shown [8,9] to possess a much higher helical twisting power (HTP, β) than *Z*-isomers as photoproducts ($\beta \approx 0$) [8,9]. The forward *E*→*Z* isomerization was revealed by the spectral method (UV) [10] to occur with a higher quantum yield (Φ_E) and, therefore, to prevail over the backward *Z*→*E* photoreaction (Φ_Z) in isotropic organic solutions. In LC systems, such a relationship between Φ_E and Φ_Z values causes an increased fraction of the *Z*-isomer in the photostationary state and, as a result, lowers the twist extent [8,9,11]. Qualitatively similar results were obtained in [12,13] for some new (+)-isomenthone derivatives as well as isomeric arylidene methylcyclohexanones.

Photoinduced changes in FLC are also of great interest. Two main types of photoinduced changes in these systems are known, *vis*., the inversion of a spontaneous polarization (*P*s) sign provoked due to the phototransformation of a chiral dopant [4] and changes in ferroelectric parameters coupled with the photoisomerization of host phase molecules at a photostabile chiral compound [3].

In this work, we summarize the results of our investigations concerning photoinduced effects in LC systems containing CCs. Two types of LC were studied, *vis*., induced cholesteric systems “nematic – CC” and induced ferroelectric compositions “achiral smectic-*C* – CC”. On the other hand, two types of CCs such as arylidene derivatives of 1*R*,4*R*-isomenthone (**1**) and 3*R*-methylcyclohexanone (**2**) were used in these investigations.



1 R = H (**a**); OCH_3 (**b**); OC_7H_{15} (**c**)

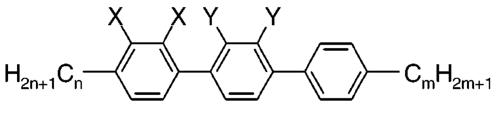


2 m = 0, R = H (**a**), C_6H_{13} (**b**); C_7H_{15} (**c**);
m = 1, X = H, R = C_6H_{13} (**d**);
m = 1, X = F; R = C_5H_{11} (**e**)

To ascertain the capability of some new α,β-unsaturated ketones **1** and **2** for the $E \rightleftharpoons Z$ photoisomerization as a possible origin of photoinduced effects in LC, UV spectra of their solution in isotropic organic solvents were studied similarly to [10].

EXPERIMENTAL

The syntheses of CCs **1**, **2** were described in [8,10,11,14]. 4-(*n*Pentyl)-4′-cyanobiphenyl (5CB) was used as a nematic host phase. The prepared LC mixtures were exposed to irradiation using a high-pressure mercury lamp DRSh-120 as a UV light source. At certain intervals of time, samples of the irradiated mixture were placed into a ready wedge-shaped cell for the determination of the induced helical pitch (*P*). The *P* and β values as well as twist signs for LC systems were determined by the Grandjean – Cano method analogously to [15]. As *SmC* achiral host phases, the mixtures of phenylbenzoate derivatives $C_mH_{2m+1}OC_6H_4COOC_6H_4OC_nH_{2n+1}$ (n = 6; m = 8, 10) (1:1) (matrix **3**) and of laterally fluorinated terphenyls (matrix **4**) were used.



n = 5, m = 7, X = F, Y = H
n = 5, m = 7, X = H, Y = F
n = 7, m = 5, X = F, Y = H

matrix **4**

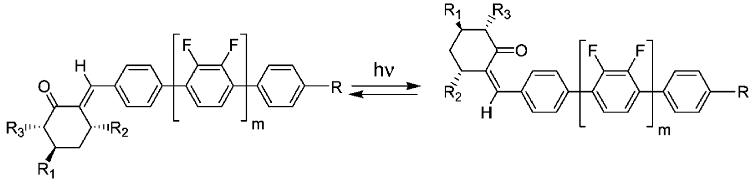
Host systems possessed the following phase transition temperatures, respectively [16]: *I* 89.5 *N* 76 *SmA* 70 *SmC Cr* (**3**) and *I* 121.7 *N* 97 *SmA* 89 *SmC* 13 *Cr* (**4**)

RESULTS AND DISCUSSION

Photoisomerization of *α,β*-Unsaturated Ketones in Isotropic Solutions

In Figure 1, the results of a spectral investigation are shown for CC **2c**. The observed changes in the UV spectra of this CC under irradiation are quite similar to those for CCs of type **1** studied earlier [10].

In both cases, the presence of two sharp isosbestic points gives evidence for the existent photochemical equilibrium in the studied solutions according to the general scheme:



E-isomer

Z-isomer

1 $m = 0; R_1 = H; R_2 = CH_3; R_3 = CH(CH_3)_2; R = OC_nH_{2n+1};$

2 $m = 0, 1; R_1 = CH_3; R_2 = R_3 = H; R = C_nH_{2n+1}.$

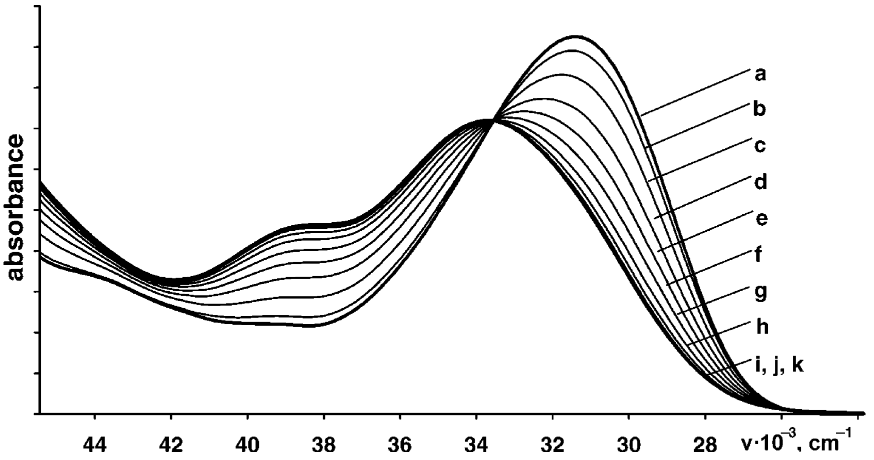


FIGURE 1 Photochemical *E–Z* transformation for compound **2c** (acetonitrile, excitation wavelength $\lambda^* = 313\,nm$): *a* is the spectrum of the initial *E*-isomer; *b – k* are the spectra of isomer mixtures after 5, 15, 30, 45, 65, 95, 130, 180, 250, and 400 min of irradiation, respectively.

TABLE 1 Spectral and Photochemical Parameters of CCs **1**, **2** in Isotropic Organic Solvents (*n*-octane for **1** and **2a** and acetonitrile for **2b-2e**)*

CD	$\nu_{\max}$ (ε)					
	E-isomer	*Z*-isomer	$\Phi_E(\varepsilon_{\lambda^*})$	$\Phi_Z(\varepsilon_{\lambda^*})$	Φ_E/Φ_Z	α_E
1a [10]	33480 (26100)	34780 (23330)	0.32 (21710)	0.08 (11340)	4.0	0.11
1b [10]	32340 (28710)	33820 (26470)	0.25 (28470)	0.07 (19880)	3.6	0.16
1c	32040 (28700)	33480 (20780)	0.32 (28680)	0.05 (19680)	6.4	0.094
2a	32540 (28530)	34200 (21330)	0.31 (27710)	0.07 (15050)	4.2	0.11
2b	31940 (25260)	33620 (25920)	–	–	–	
2c	31380 (30025)	33620** (26990)**	– (29410)	– (22460)**	–	–
2d	31060 (45420)	32460	0.33 (42730)	0.08 (40675)	4.1	0.19
2e	32320 (46040)	33760	0.28 (45520)	0.08 (30300)	3.5	0.15

*$\nu_{\max}(\varepsilon)$ is the reciprocal wavelength (extinction) in the maximum of the long-wavelength $\pi\pi^*$ band; Φ_E (ε_{λ^*}) and Φ_Z (ε_{λ^*}) are the quantum yields of forward (*E*–*Z*) and backward (*Z*–*E*) photoisomerizations (extinctions for isomers on the excitation wavelength); α_E is the *E*-isomer fraction in a photostationary mixture (on HPLC).

Measured in octane for the Z-isomer of **2b.

The close $\nu_{\max}$ of the *E*- and Z-isomers of CCs **1** and **2** (Table 1) testify to their identical phototransformations. This was also confirmed with preparative synthesis of the *Z*-isomer for **2b** and comparison of its UV and ^{1}H NMR spectral characteristics with those for *Z*-isomers of series **1**obtained earlier [9–11]. The results of quantitative determinations on the base of spectral and chromatographic (HPLC) analyses (Table 1) show that the efficiencies of the phototransformations for two types of CCs are equal rather than different. The photostationary states for both CCs are enriched with Z-isomers.

Photoinduced Changes in the Induced Helical Pitch of LC Systems (Nematic–Chiral Compound)

Although the phototransformations of CCs **1** and **2** in isotropic organic solvents occur similarly, quite different changes in the induced helical pitch are observed under UV irradiation of LC systems containing these chiral dopants. These distinctions are shown in Figure 2, *a* and *b*.

For the first mixture, UV irradiation involves a rapidly decreasing reverse pitch which asymptotically approaches zero (Fig. 2, *a*). Such a change conforms to the cholesteric helix unwinding due to the much lower HTP of the *Z*-isomer in comparison with that of the initial *E*-form. For the LC system with CC **2c**, the P^{-1} value

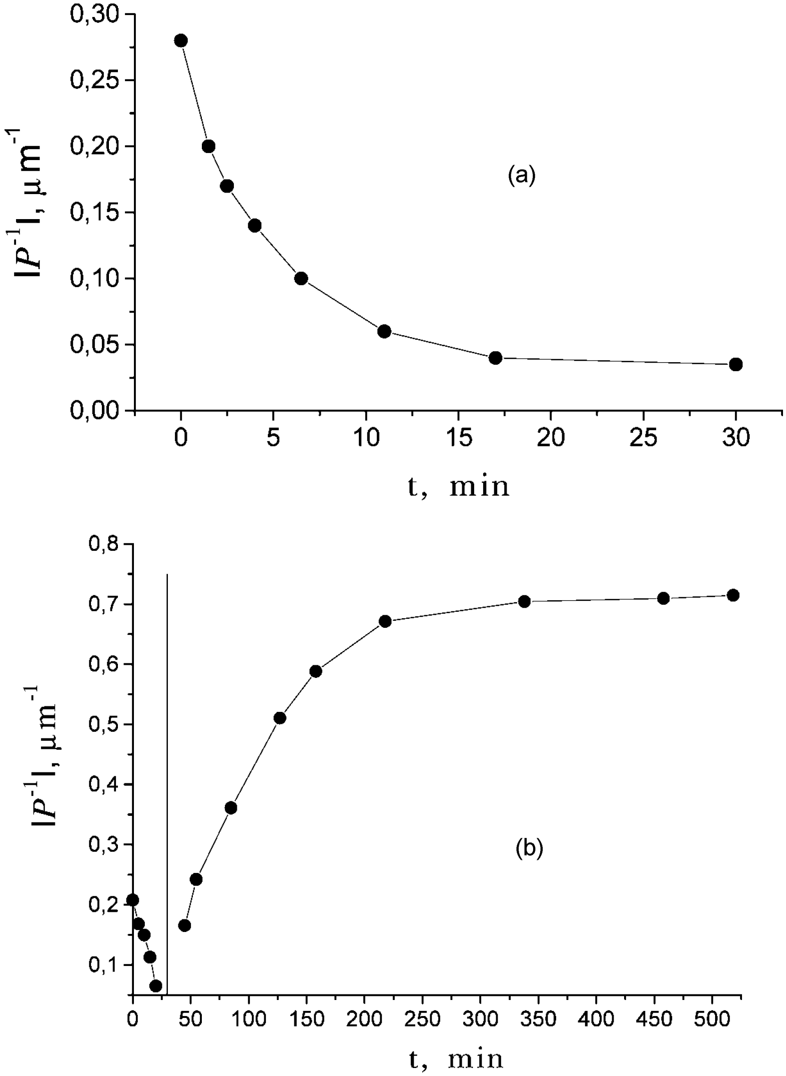


FIGURE 2 Reverse cholesteric pitch P^{-1} vs. irradiation time for 5CB–**1a** (*a*) [9] and 5CB–**2c** (*b*) mixtures.

rapidly decreases during the initial irradiation period, reaches zero (the inversion point), and then rises up to a constant magnitude (Fig. 2, *b*). This P^{-1} value exceeds the initial one by more than 3 times and remains invariable under the following UV light action over a long period of time (about 10 h), which confirms the reaching of the photostationary state.

Such a photoinduced effect observed for LC systems containing CCs **2** can be explained if we suppose that the initial *E*-isomer and the formed *Z*- one induce the cholesteric helices of opposite signs in 5CB. In this case, the HTP of the *Z*-isomer exceeds essentially those for the initial *E* one. That supposition was confirmed experimentally. In contrast to left-twisted *E*-isomer **2b** ($\beta = -9.1 \pm 0.7$ μm^{-1}/mol.fract.), the respective *Z*-form induces a right-hand cholesteric helix with $\beta = 37.5 \pm 1.9$ μm^{-1}/mol.fract., which exceeds those for the *E*-isomer by about 4 times. Moreover, this Z-isomer produces induced short-pitch cholesteric compositions with selective light reflection in the visible range. Thus, λ_{max} of the reflection band for the 5CB – Z-isomer of **2b** mixture (7.58 mol. % of **2b**) varies from 562 to 577 nm with the temperature (30.0 ÷ 20.0°C). This corresponds to $\beta = 35.2$–34.2 μm^{-1}/mol.fract.

Photoinduced Changes in Macroscopic Properties of Ferroelectric LC Systems (Achiral Smectic-*C*–Chiral Compound)

LC systems based on an achiral smectic-*C* host and containing CCs 1 were established to demonstrate rather effective ferroelectric parameters, *vis*., a high spontaneous polarization (*P*s) and a smectic-C^* tilt angle (θ) which depends on the CC concentration only weakly and possesses the optimal values of 22 ÷ 23° for several systems studied earlier [17]. The reversible photochemical $E \rightleftharpoons Z$ isomerization characteristic of α,β-unsaturated ketones 1 and 2 can be expected to provoke essential changes in the parameters of induced FLC containing such CCs. In this work, we studied the influence of UV irradiation on properties of the FLC systems containing CC 1c. In Figure 3, the *P*s temperature dependences for the initial FLC composition based on ester *SmC* 3 and the idem composition under irradiation are presented. Such a dependence shifted to lower *P*s absolute values already after 5 min of irradiation and, under the following light action *P*s, acqures the opposite, positive sign. Thus, the FLC system studied exhibits the photoinduced *P*s sign inversion. The same photoinduced effect was revealed to be characteristic also of the FLC composition *SmC* 4 – CC 1c (see Fig. 4).

The observed inversion of the *P*s sign is accompanied by an increase both in absolute *P*s and in smectic-*C* tilt angle values for irradiated FLC samples with different CC concentrations. Invariability of these parameters under prolonged light action after the photostationary state was also established.

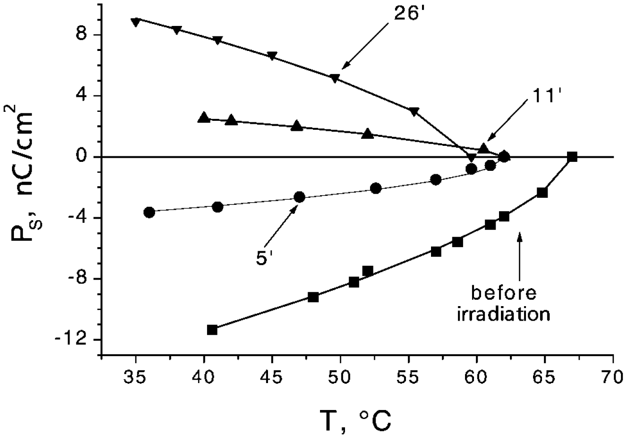


FIGURE 3 Spontaneous polarization, *P*s, vs. temperature for FLC system *Sm*C **3**–CC **1c** before irradiation and under irradiation during 5, 11, and 26 min with nonfiltered light of a mercury lamp DRSh-120 (8.02 mol. % of CC **1c**, 7 μm in thickness of a cell).

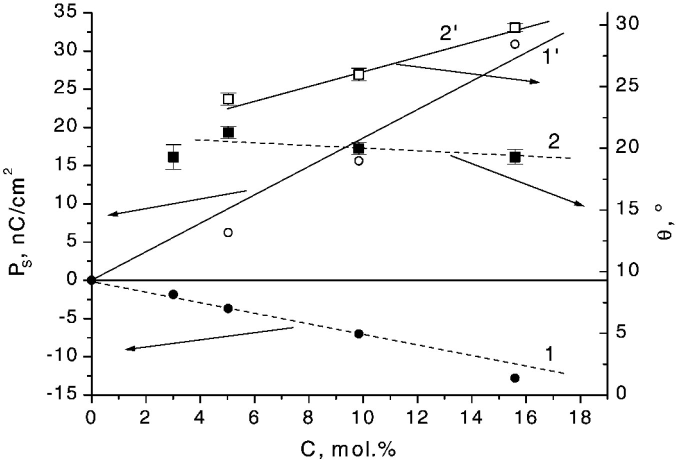


FIGURE 4 Concentration dependences of the *P*s (curves *1*, *1′*) and *θ* (curves *2*, *2′*) values for LC compositions *SmC* **4**–CC **1c** before and after irradiation during 1 h (dashed and solid lines, respectively).

CONCLUSION

Chiral *α*,*β*-unsaturated ketones, (+)-isomenthone and 3*R*-methylcyclohexanone derivatives, capable of *E*–*Z* photoisomerization, provoke photoinduced sign inversions of the cholesteric helix and spontaneous polarization in induced cholesteric and ferroelectric LC systems, respectively, which are accompanied with an essential improvement of the parameters of these LC materials.

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