

Photoinduced cholesteric helix inversion in some systems containing chiral α,β -unsaturated ketones

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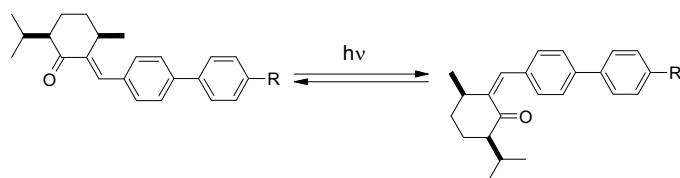
Cholesteric helix inversion induced with UV irradiation has been revealed in the liquid crystal (LC) system based on nematic 4-pentyl-4'-cyanobiphenyl (5CB) which contains left-handed helix inducing chiral dopant of 3(*R*)-methyl-6-arylidencyclohexanone series. A further irradiation results in increasing right-handed helical twisting in the system till photostationary state is reached. The twisting extent in this state exceeds three times that in the initial mixture and remains unchanged under further UV light action. The effect under consideration must be caused by reversible photochemical *E,Z*-isomerization of the chiral dopant molecules. This was proven by preparative photochemical synthesis of the corresponding *Z*-isomer and independent study of its properties as a chiral dopant in 5CB. It is shown that a principal difference exists between photoinduced changes in the LC systems containing chiral α,β -unsaturated ketones, 3(*R*)-methylcyclohexanone and (+)-isomenthone derivatives.

Обнаружена фотоиндуцированная УФ облучением инверсия знака холестерической спирали в жидкокристаллической системе на основе нематического 4-пентил-4'-цианобифенила (5ЦБ), содержащей хиральную добавку серии левозакручивающих 3(*R*)-метил-6-арилденциклогексанонов. Продолжение облучения после точки инверсии усиливает правое закручивание в системе до достижения фотостационарного состояния. В этом состоянии степень холестерического закручивания превышает в три раза таковое для исходной смеси и не изменяется при дальнейшем продолжительном действии света. Обнаруженный эффект обусловлен обратимой фотохимической *E-Z* изомеризацией, что доказано препаративным фотохимическим синтезом соответствующего *Z*-изомера и независимым изучением его поведения как хиральной добавки в 5ЦБ. Показано принципиальное отличие фотоиндуцированных изменений в системах, содержащих хиральные α,β -ненасыщенные кетоны, производные 3(*R*)-метилциклогексанона и (+)-изоментона.

Photoinduced changes in liquid crystalline (LC) systems with helical supramolecular structure offer promising applications for optical recording devices, ultra-violet (UV) radiation detection, color filters for reflective cholesteric liquid crystal displays elaboration as well as for photoswitching realization (see, e.g., [1–4]). Systems exhibiting the effect of photoinduced cholesteric helix inversion, which is relatively rare and occurs due to reversible photoisomerization

of a chiral dopant, are also of great interest [2]. As chiral dopants being capable for *E,Z*-photoisomerization either in isotropic organic solvents [5] or in LC media [6–8] α,β -unsaturated ketones, isomenthone arylidene derivatives **1** have been systematically studied.

Helical twisting power (HTP) of the *Z*-isomers of such compounds differs essentially from that for initial *E*-isomers. This fact offers a principal possibility for their use in optical information recording.



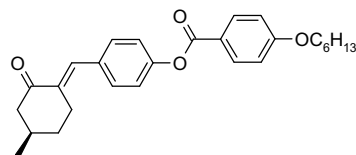
E-1

Z-1

R = H (a); OC_nH_{2n+1}, n = 1 (b), 7 (c), 8 (d)

There is, however, a serious difficulty associated with the essentially higher efficiency of photoreaction in $E \rightarrow Z$ direction than in $Z \rightarrow E$ one [5]. This causes a substantial enrichment of the rapidly achievable photostationary state with the photoproduct having low HTP. Furthermore, small difference in the UV spectra of the isomers [5] does not allow selection of an UV region suitable for an effective reverse photochemical process. A comparable efficiency of the direct and reverse reactions could only be achieved by use of a triplet sensitising dye [5]. However, there are some problems concerning the choice of such a sensitizer as well as unavoidable negative influence of this compound as a non-mesomorphic dopant on isotropic phase transition temperature and mesomorphic range of the LC mixture [9]. Search and investigation of new LC systems containing chiral α,β -unsaturated ketones capable of photoisomerization and possessing other ratios of quantum yields for the direct and reverse reactions as well as other HTP ratios between photoisomers is actual problem now. Among these systems, those potentially possessing photoinduced cholesteric helix inversion are of special interest. Some preconditions for the realisation of this effect follow from the results of recent investigations [6, 7, 10]. For some of the E - and Z -isomers of **1** series, HTP signs in nematic N -(4-methoxybenzylidene)-4-butylaniline (MBBA) are opposite [6, 7]. A similar effect was observed recently for the ester derivative of 3(R)-methyl-6-arylidene cyclohexanone **2** [10].

However, intermediate states of these systems under UV irradiation have not been

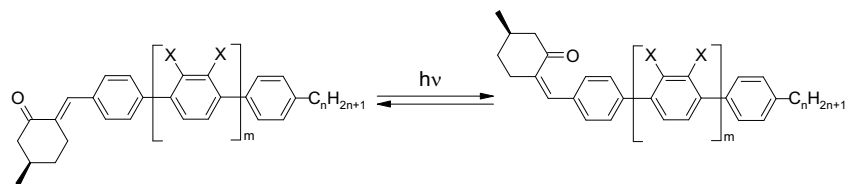


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studied in [6, 7, 10]. Moreover, selection of ester **2** as the subject of investigation is somewhat incorrect, since similar compounds are known to be capable of secondary photochemical changes [11].

In this work, for more detailed investigation of UV irradiation influence on a magnitude and sign of the helical twist in induced cholesteric systems based on the nematic 4'-pentyl-4-cyanobiphenyl (5CB), compounds **3** being analogues of **2** containing no ester group were chosen as chiral dopants.

The syntheses of compounds **3** were described in detail [12]. Studying of them by the spectral method (UV range) in dilute solutions (10^{-5} – 10^{-4} mole/l) in acetonitrile combined with high performance liquid chromatography (HPLC) analyses was carried out in the manner similar to that described for compounds **1** in [5]. The results obtained have shown that compounds **3** undergo photochemical E - Z isomerisation at the same efficiency as arylidene derivatives of (+)-isomenthone **1** studied before (Table 1) [5]. In accordance with conclusions of [5], the similar extent of the photoisomerisation should be also expected for these compounds in LC solutions. However, the behaviour of the induced helical pitch for systems containing chiral dopants of series **1** and **3** was turned out to be quite different.



E-3

Z-3

m = 0, n = 0 (a), 6 (b), 7 (c); m = 1, X = H, n = 6 (d); m = 1, X = F, n = 5 (e)

Table 1. Spectral and photochemical parameters of CDs **1** and **3** in organic solvents (*n*-octane for **1** [5, 11] and **3a** and acetonitrile for **3b, c** unless otherwise noted) *

CDs	$\nu_{max}, \text{cm}^{-1}(\epsilon)$		$\Phi_E(\epsilon_{\lambda^*})$	$\Phi_Z(\epsilon_{\lambda^*})$	Φ_E/Φ_Z	α_E
	<i>E</i> -isomer	<i>Z</i> -isomer				
1a	33480	34780	0.32	0.08	4.0	0.11
	(26100)	(23330)	(21710)	(11340)		
1b	32340	33820	0.25	0.07	3.6	0.16
	(28710)	(26470)	(28470)	(19880)		
1c	32040	33480	0.32	0.05	6.4	0.094
	(28700)	(20780)	(28680)	(19680)		
1d	32120	33580	0.35	0.05	7.0	0.095
	(26220)	(24100)	(26150)	(19700)		
3a	32540	34200	0.31	0.07	4.2	0.11
	(28530)		(27710)	(15050)		
3c	31380	33620	–	–	–	–
	(30025)		(26990)**	(29410)	(22640)**	
3d	31060	32460	0.33	0.08	4.1	0.19
	(45420)		(42730)	(40675)		
3e	32320	33760	0.28	0.08	3.5	0.15
	(46040)		(45520)	(30300)		

* $\nu_{max}(\epsilon)$ is reciprocal wavelengths (extinction) in maximum of the wavelength $\pi\pi^*$ -absorption band, $\Phi_E(\epsilon_{\lambda^*})$ and $\Phi_Z(\epsilon_{\lambda^*})$ are quantum yields of the forward (*E*–*Z*) and backward (*Z*–*E*) photoisomerisation (extinctions for the respective isomers on the wavelength of excitation taken as 313 nm), α_E is mole fraction of the initial *E*-isomer in photostationary mixture (on HPLC data),

** measured in *n*-octane for *Z*-**3b**

The photoisomerisation of chiral compound **3c** in LC medium was studied by the irradiation of a chiral-nematic mixture prepared by the usual method when a chiral dopant is dissolved in the isotropic phase of a nematic (5CB, in our case) and cooled down to the cholesteric state. A high-pressure mercury lamp DRK-120 was used as the UV light source. The helical pitch, *P*, of the cholesteric mixture under study and its changes during irradiation were measured using the conventional Grandjean-Cano technique as described in the previous report [13]. The wedge-shaped cell was put in a specially constructed hot-stage arrangement which had a $\pm 0.5^\circ$ temperature control accuracy. A ratio between *E*- and *Z*-isomers in photostationary state was determined by analysis of the cholesteric mixture dissolved in chloroform using HPLC method (a Bishoff Lambda 1010 chromatograph, Pron-tosil 120-5-C18 ace-EPS column).

The reverse pitch, P^{-1} (as the twist measure) dependence on irradiation time for LC composition of 5CB with chiral dopant **3c** (the dopant mole fraction 0.0238) is

Table 2. Helical twisting power (β) of compounds of **1** and **3** series in 4'-pentyl-4-cyanobiphenyl

Chiral dopant	$\beta, \mu\text{m}^{-1}$	
	<i>E</i> -isomer	<i>Z</i> -isomer
1a	-36.9 ± 1.3 [6]	≤ 0 [6]
1c	-44.3 ± 1.8 [6]	-1.5 [8]
3b	–	37.5 ± 1.9
3c	-9.9 ± 0.3 [14]	36.8^*

* estimated by using equation (2).

shown in Fig. 1a. The P^{-1} value decreases steeply during the initial irradiation period that corresponds to the unwinding helix, reaches zero (the inversion point), and then rises up to the P^{-1} constant value of $0.77 \mu\text{m}^{-1}$ that corresponds to a rather small *P* value ($1.30 \mu\text{m}$). This helical pitch value remains unchanged under the following UV light action over a long period of

time (during 10 h) that confirms reaching photostationary state.

Such an influence of UV radiation on the P^{-1} value can be elucidated if suppose that the initial *E*-isomer and forming *Z*-one induce in nematic 5CB cholesteric helices of the opposite signs and determined twist extent, P^{-1} , is the weighted-average value:

$$P^{-1} = C_{total}(X_E\beta_E + X_Z\beta_Z), \quad (1)$$

where β_E , β_Z and X_E , X_Z are HTP values and mole fractions of *E*- and *Z*-isomers in the cholesteric mixture, respectively ($X_E + X_Z = 1$).

Using the reverse pitch value measured for the mixture in the photostationary state ($P^{-1} = 0.77 \mu\text{m}^{-1}$) and mole fractions of *E*- and *Z*-isomers according to HPLC analysis for this mixture ($X_E = 0.064$, $X_Z = 0.932$), at $C_{total} = 0.0238$ mole fractions) as well as measured β value for *E*-isomer **3c** (β_E is $-9.9 \pm 0.3 \mu\text{m}^{-1}/\text{mole fractions}$ [14], we estimated hypothetical HTP for the respective *Z*-form (*Z-3c*) as possible photoproduct, on Eq.(2):

$$\beta_Z = (P^{-1} - C_{total}X_E\beta_E)/C_{total}X_Z. \quad (2)$$

The $|\beta_Z|$ value calculated by this method exceeds the initial $|\beta_E|$ more than by three times (Table 2).

At the same time, a monotonous decrease of P^{-1} value (i.e. unwinding helix) under irradiation is typical of (+)-isomenthone derivatives **1** (see Fig. 1b). That is consistent with a much lower HTP of *Z*-isomers for these compounds [6, 7]. The photostationary mixture of 5CB with chiral dopant **3c** is proved to be stable not only under the prolonged UV light irradiation, but also against a thermal effect. The helical pitch value for this mixture remained unchanged after its heating at 100° during one hour followed by cooling down to the cholesteric state.

The formation of photodimers (**4a** and **4b**) as products of [2+2]-cycloaddition

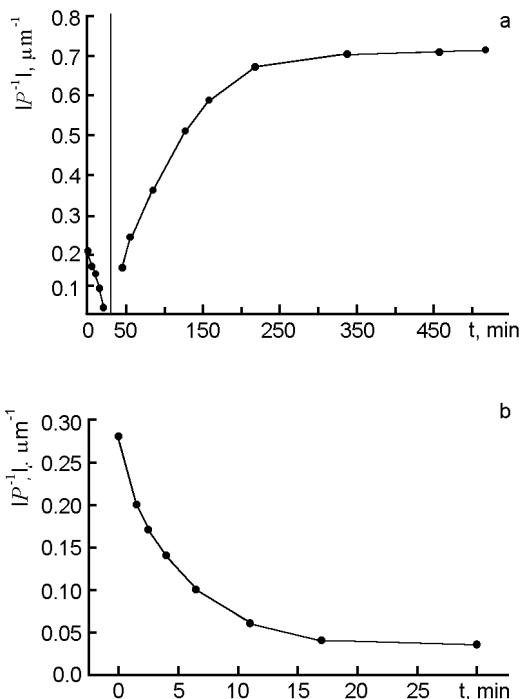


Fig.1. Reverse cholesteric pitch P^{-1} vs. irradiation time for the mixtures of 0.0238 mole fractions of **3c** in 5CB (a) and **1a-5CB** (b) [7].

should be noted to be also possible besides *E-Z*-isomerisation under UV irradiation of α,β -unsaturated ketones.

Such a process is known to run efficiently under irradiation in both crystalline examples [15] and solutions [16]. Since a possibility of the similar photoinduced reaction for compounds **3** cannot be excluded fully, in contrast to (+)-isomenthone derivatives **1** [5, 7], a detailed nature clarification of the phototransformation product for *E*-isomer **3c** is quite necessary. In this connection, the photoreaction product for compound *E-3b* being a more available but the nearest homologue of *E-3c* was investigated. It was prepared by irradiation of the

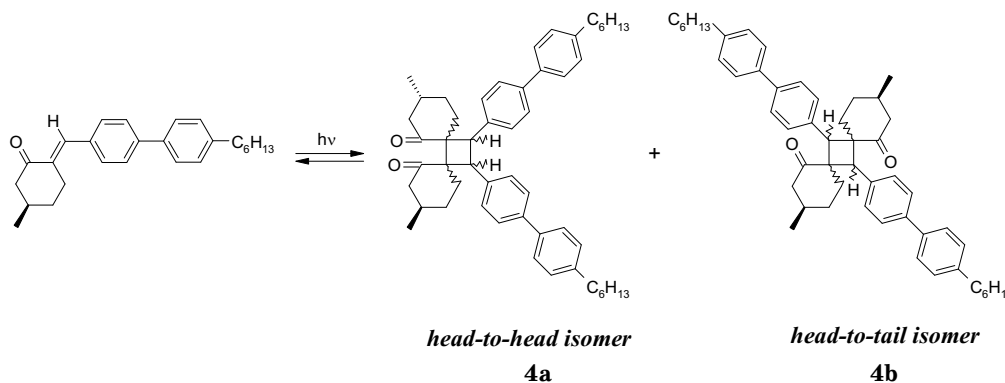
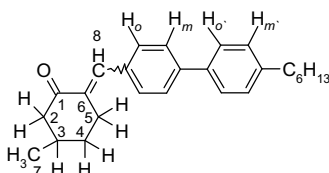


Table 3. Chemical shifts (δ) and difference in the ^1H NMR spectra of *E*- and *Z*-isomers of compound **3b** in CDCl_3 

Proton	δ , ppm		$\Delta\delta$, ppm
	<i>E</i> -isomer	<i>Z</i> -isomer	
2-equatorial	2.13	2.27	0.14
2-equatorial	2.68	2.62	0.06
3	2.08	2.13	0.05
4-axial	1.38	1.62	0.29
4-equatorial	1.95	2.01	0.06
5-axial	2.71	2.59	-0.12
5-equatorial	3.13	2.70	-0.43
7CH ₃	1.07	1.08	0.01
8	7.61	6.42	-1.19
<i>o</i> -	7.50	7.50	0
<i>m</i> -	7.63	7.50	-0.13
<i>o'</i> -	7.62	7.50	-0.10
<i>m'</i> -	7.46	7.24	-0.22

respective *E*-form (***E*-3b**, 0.36 g) dissolved in heptane (100 ml) with non-filtered light of the high-pressure mercury lamp DRK-120 under mixing up to reaching photostationary state (control by HPLC). The solution obtained was evaporated to dryness and the residue was purified by the re-crystallisation from a minimal amount of methanol at -5°C . The purity (98.2 %) of the isolated photoproduct was checked by HPLC. Compound ***Z*-3b** is non-mesogenic, m.p. $42.5\text{--}43^\circ\text{C}$. The *Z*-isomer structure of this product was determined by ^1H NMR spectroscopy (Varian Mercury VX-200, 200 MHz, CDCl_3). The proton chemical shift values in spectra of the **3b** *E*- and *Z*-isomers differ significantly (Table 3). The highest absolute values $\Delta\delta$ are observed for the arylidene H(8) and equatorial H(5) protons. These distinctions are similar to established for *E*- and *Z*-isomers of compounds **1** [17]. At that, the resonance of the arylidene proton for the photoproduct under study ($\delta = 6.42$ ppm) is observed in the ranges being typical of *Z*-forms of other α,β -unsaturated ketones (δ 6.0 to 6.7 ppm [17–20]). It is of importance that the signal of this proton is shifted to the low field

with respect to the non-equivalent protons of the cyclobutane ring for the photodimer of type **4** (4.57 and 3.97 ppm) obtained starting from 2-benzylidene-6-benzylcyclohexanone [15]. Similarly, in the case of the photodimers of some aromatic α,β -unsaturated ketones [16], molecular structure of which was determined by X-ray analysis, the chemical shift of the cyclobutane proton nearest to benzene ring is 4.52 to 4.70 ppm. Such a position of the proton signals for the photodimers of type **4** differs significantly from the one for the phototransformation product of ***E*-3b**. Thus, it can be concluded from these data the photoproduct is indeed corresponding *Z*-isomer. As an additional proof, mass-spectrometric analysis performed in the liquid matrix of *m*-nitrobenzyl alcohol using the magnetic sector a mass spectrometer MI-1201E equipped with primary FAB ion source for generating a bombarding beam of argon atoms, has shown the photoproduct molecular mass ($[\text{M}+1]^+$, $m/z = 361$) coincident with that of the respective *Z*-isomer.

The magnitude and sign of HTP for obtained ***Z*-3b** were measured experimentally similar to as described in [13]. Its β value is positive and exceeds on absolute magnitude

that for the respective *E*-isomer. That experimental value is important to coincide uncommonly with the β value of *Z*-**3c** which was estimated above basing on the data on relation of isomers in photostationary state (Table 2). The somewhat different length of the terminal alkyl chain in molecules **3b** and **3c** does not influence HTP, as was observed for many series of chiral compounds (see, e.g. [13]).

This allows to conclude with the final word that *E,Z*-isomerization of compounds **3** occurs selectively when their solutions in isotropic (acetonitrile and heptane) as well as in nematic solvents (5CB) are UV irradiated. The selectivity extent is independent of the solvent concentration and nature. The formation of mixture of the *E*- and *Z*-isomers for **3** under UV irradiation of their 5CB solutions results in the cholesteric helix inversion. The helical pitch value in the photostationary state of such a system does not change under further UV light action. This makes these systems to be rather applicable for the photostable LC materials elaboration. High HTP of the *Z*-isomers of **3** in 5CB allows to reach selective visible light reflection, which can be used in the development of multicolour reflective cholesteric displays. Origins of the great difference revealed between HTP absolute values for the *Z*-isomers of compounds **1** and **3** are now under investigation.

References

1. T.Sagisaka, Y.Yokoyama, *Bull. Chem. Soc. Jap.*, **73**, 191 (2000).
2. C.Ruslim, K.Ichimura, *J. Mater. Chem.*, **12**, 3377 (2002).
3. L.Komitov, O.Tsutsumi, C.Ruslim, *J. Appl. Phys.*, **89**, 7745 (2001).
4. J.Z.Vlahakis, M.D.Wand, R.P.Lemieux, *J. Am. Chem. Soc.*, **125**, 6862 (2003).
5. S.N.Yarmolenko, L.V.Chepeleva, L.A.Kutulya et al., *Zh. Obshch. Khim.*, **65**, 145 (1995).
6. S.N.Yarmolenko, L.A.Kutulya, V.V.Vashchenko, L.V.Chepeleva, *Liq. Cryst.*, **16**, 877 (1994).
7. L.A.Kutulya, S.N.Yarmolenko, V.V.Vashchenko et al., *Zh. Fiz. Khim.*, **69**, 88 (1995).
8. L.A.Kutulya, V.V.Vashchenko, A.O.Doroshenko et al., *Proc. SPIE*, **4418**, 89 (2001).
9. L.A.Kutulya, I.B.Nemchenok, S.S.Oleinik, *Kristallographia*, **35**, 1242 (1990).
10. J.Lub, W.Ten Hoeve, W.P.M.Nijssen, *Liq. Cryst.*, **29**, 995 (2002).
11. L.V.Chepeleva, A.O.Doroshenko, T.G.Drushlyak et al., *Proc. SPIE*, **5257**, 71 (2003).
12. A.I.Krivoshey, L.A.Kutulya, V.V.Vashchenko et al., *Proc. SPIE*, **5257**, 13 (2003).
13. L.A.Kutulya, G.P.Semenkova, S.N.Yarmolenko et al., *Kristallografiya*, **38**, 183 (1993).
14. L.A.Kutulya, N.S.Pivnenko, N.I.Shkolnikova, *Zh. Struct. Khim.*, **45** (2004)
15. G.C.Forward, D.A.Whiting, *J. Chem. Soc. C*, 1868 (1969).
16. F.R.Cibin, N.Di Bello, G.Doddi et al., *Tetrahedron*, **59**, 9971 (2003).
17. N.S.Pivnenko, V.V.Vashchenko, L.A.Kutulya et al., *Russ. Chem. Bull.*, **50**, 1596 (2001).
18. A.Hassher, T.C.Mead, *Tetrahedron*, **20**, 2201 (1964).
19. D.Bass, H.Cerfontain, *Tetrahedron*, **33**, 1509 (1977).
20. E.Mena, P.Van de Witte, J.Lub, *Liq. Cryst.*, **27**, 929 (2000).

Фотоіндукована інверсія холестеричної спіралі у деяких системах, що містять хіральні α,β -ненасичені кетони

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Виявлено фотоіндуковану УФ опроміненням інверсію знаку холестеричної спіралі у рідкокристалічній системі на основі нематичного 4-пентил-4'-ціанобіфенілу (5ЦБ), яка містить хіральну домішку серії лівозакручуючих 3(*R*)-метил-6-ариліденциклогексанонів. Продовження опромінення після точки інверсії посилює праве закручування у системі до досягнення фотостаціонарного стану. У цьому стані ступінь холестеричного закручування перевищує втричі відповідний показник для вихідної суміші і не змінюється при подальшому тривалому впливі світла. Виявлений ефект обумовлений оборотною фотохімічною *E-Z* ізомеризацією, що доведено препаративним фотохімічним синтезом відповідного *Z*-ізомеру та незалежним дослідженням його поведінки як хіральної домішки в 5ЦБ. Показано принципову відмінність фотоіндукованих змін у системах, які містять хіральні α,β -ненасичені кетони, похідні 3(*R*)-метилциклогексанону та (+)-ізоментону.