Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Yarmolenko, S. N. , Kutulya, L. A. , Vashchenko, V. V. and Chepeleva, L. V.(1994) 'Photosensitive chiral dopants with high twisting power', Liquid Crystals, 16: 5, 877 — 882

To link to this Article: DOI: 10.1080/02678299408027858

URL: http://dx.doi.org/10.1080/02678299408027858

LIQUID CRYSTALS, 1994, VOL. 16, NO. 5, 877–882

Photosensitive chiral dopants with high twisting power†

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(Received 14 July 1992; accepted 3 August 1993

Quantitative investigations of *E*,*Z*-photoisomerization of chiral dopants (−)-2-arylidene-*p*-menthanones were carried out using solvents of different nature and various liquid crystalline matrices.

Liquid crystalline systems (LCS) with helical supermolecular structures induced by chiral photosensitive dopants present interesting perspectives for optical data processing. Therefore the investigation of chiral (−)-2-arylidene-*p*-menthane-3-ones (**I**) with a high twisting power that provide the possibility of obtaining induced cholesteric systems with selective light reflection in the visible spectral region should be rewarding [1, 2].

The effect of a long wavelength shift of the selective light reflection band under laser irradiation of a LC based on 4-pentyl-4′-cyanobiphenyl (5CB) as nematic solvent with a chiral dopant (**Ia**) was recently reported [3]. Presumably, the effect observed is due to photoisomerization of the chiral dopant and a corresponding decrease in its twisting power. We have carried out a photochemical investigation of some chiral dopants (**I**) in order to elucidate the possible mechanism of this process.

(−)-2-Arylidene-*p*-menthanones (**I**) have an exocyclic double bond C=C which is able to isomerize. It is also known that compounds of such a structure do not form photo-dimers, and the photo-steady state equilibrium of photoisomerization is shifted to the *Z*-isomer [4].

Changes observed in the electronic absorption spectra of solutions (**Ia–e**) during irradiation (see figure 1) are similar to those for the *cis–trans*-photoisomerization of α,β-unsaturated ketones [4, 5]. Precise isosbestic points remained over a long irradiation exposure in solvents for different concentrations (10^{-5}–10^{-2} mol l^{-1}) and data from liquid and gas–liquid chromatography indicated the presence of only one product of photoreaction. During irradiation a carbonyl group band ($\nu_{C=O}$) in the IR spectra of the initial compounds (**I**) decreased and a new band with 6–12 cm^{-1} higher frequency appeared, while the rest of the spectra was unchanged.

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† Presented at the Fourteenth International Liquid Crystal Conference, 21–26 June 1992, University of Pisa, Italy.

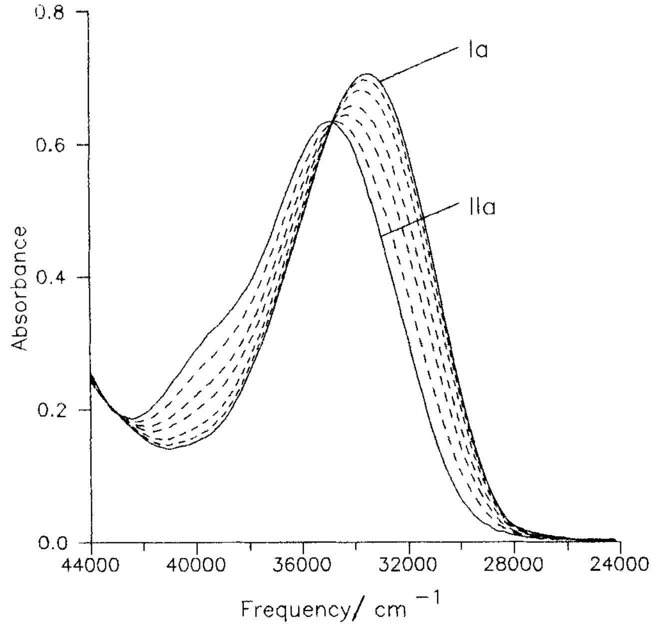
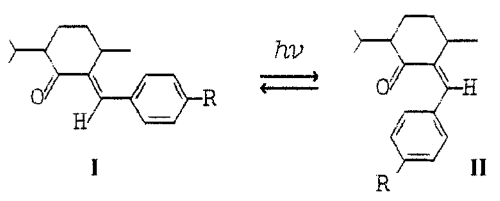


Figure 1. UV spectra of compound (**Ia**), changing under irradiation (dashed lines, $\lambda^* = 313$ nm, solvent – *n*-octane) and of the *Z*-isomer (**IIa**).



R = Ph(**a**), OMe(**b**), NMe_2(**c**), Cl(**d**), CN(**e**), NO_2(**f**).

These experimental data suggest that *E*,*Z*-photoisomerization of the compounds (**I**) occurs in their solutions during irradiation. To confirm this assumption, a photoproduct (**IIa**) was isolated. Its Z-configuration corresponds with a ^1H NMR spectrum in which the peak for the arylidene proton =CH δ 6·31 ppm) is considerably shifted upfield in comparison with the initial *E*-isomer (δ 7·09 ppm in CD_2Cl_2) and with similar data for *E*,*Z*-isomeric structures [6].

High frequency shifts of the carbonyl group band shown by *Z*-isomers compared with corresponding *E*-forms (table 1) indicate the considerable non-planarity of the cinnamoyl fragment of the compounds (**II**).

The energy increase in the long wavelength band of the UV spectra of the compounds (**II**) compared with (**I**) also indicates the non-planarity of the *Z*-isomers. However, extinction coefficients of the long wavelength bands in the spectra of the *Z*-isomers are only 1·1–1·6 times lower than those for corresponding *E*-forms, while for 2-arylidenecyclohexanones, this ratio is 2·2–2·6 [4, 6]. Similarly, the difference in $\nu_{C=O}$ of (**I**) and (**II**) is essentially lower than the values (20–26 cm^{-1}) for corresponding isomers of 2-benzylidenecyclohexanones [6] (table 1). These data indicate that non-planarity of the π-electronic systems (**I**) and (**II**) differs less than in the case of the *E*- and *Z*-forms of 2-benzylidenecylohexanones. Non-planar geometry of the cinnamoyl fragment of *E*-isomer (**Ia**) in both liquid and crystalline phases has also been reported [7, 8].

Z-isomers are rather stable compounds, and no thermally excited Z,E-isomerization was found when heating the solutions up to 80°C. Z-forms, unlike *cis*-α,β-unsaturated ketones [9], are fixed in acidic solvents (up to 30 per cent H_2SO_4) and they do not undergo rearrangement [6].

Compounds (**I**) and (**II**) when dissolved in nematic LCS show different twisting powers. For example, values of the twisting power (β) for E-isomer (**Ia**) in 4-methoxybenzylidene-4′-butylaniline and in 5CB are $-41\cdot9\pm1\cdot4$ [2] and $-36\cdot9\pm1\cdot3$, respectively, and for the corresponding Z-isomer are $+8\cdot8\pm0\cdot3$ and $-1\cdot1\pm0\cdot2\,\mu m^{-1}$ mole fraction, respectively. Such a considerable difference in twisting power is caused apparently by the different shapes of molecules (**Ia**) and (**IIa**): the E-isomer has an anisometric *quasi*-cylindric form [1, 8] and the Z-isomer is presumably *quasi*-spheric.

A decrease in the twisting power of (**I**) due to photoisomerization must result in an increase in the helical pitch of the induced cholesteric phase during irradiation. The dependence of the inverse helical pitch on irradiation exposure times for (**I**) was obtained for a mixture of *trans*-4-*n*-butyl- and *trans*-4-*n*-hexyl-cyclohexane-carboxylic acids in the ratio 1 : 1 and in 5CB matrices (figure 2). Photoequilibrium is reached after long irradiation times. A ratio of the isomers in this state can be determined using a helical pitch value P

$$P^{-1}=\sum \beta_i C_i,$$

where C_i is the concentration of each form. For photoequilibrium in 5CB we obtained a ratio $E/Z=14/86$. To determine a cause for such a strong shift of the photo-steady state equilibrium to the Z-form, we have measured quantum yields of photoisomerization.

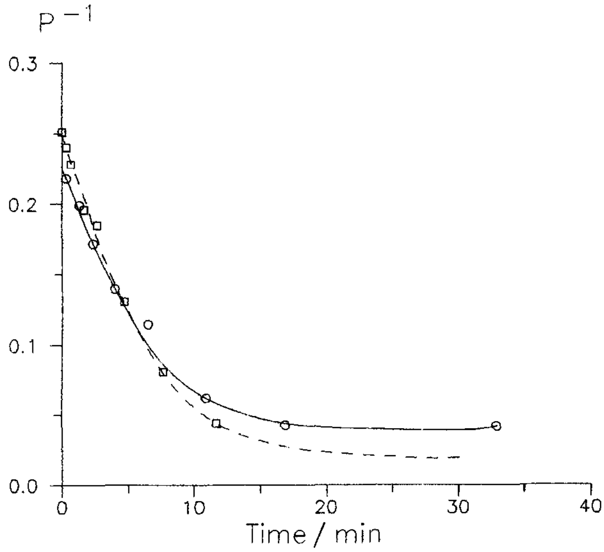


Figure 2. Dependence of inverse helical pitch on irradiation exposure for (−)2-(4-phenylbenzylidene)-*p*-menthan-3-one in 5CB (——) and in a mixture of *trans*-4-*n*-butyl- and *trans*-4-*n*-hexyl-cyclohexane-carboxylic acids (– – –).

The isomerization is photo-reversible because irradiation of the mixture in photo-equilibrium at the *Z*-isomer absorption maximum leads to an increase in *E*-form concentration. The rate of reversible *E*,*Z*-isomerization is described by the equation

$$-\frac{dC_E}{dt}=\frac{I_t}{V}\frac{(1-10^{-D_t})}{D_t}(\varphi_E D_E-\varphi_Z D_Z),$$

where I_t is the intensity of the exciting light, D_t is the absorbance at the excitation wavelength, D_E and D_Z are proportionate absorbancies of the *E*- and *Z*-forms, and φ_E and φ_Z are quantum yields for the forward and backward reactions. In the absence of other photoreactions, the equation has the following form:

$$-\frac{d\alpha_t}{dt}=\frac{l}{V}[\alpha_t Q_t(\varphi_E\varepsilon_E+\varphi_Z\varepsilon_Z)-\varphi_Z\varepsilon_Z Q_t],$$

where α_t is the fractional conversion, l is the length of the cell, V is the volume of the solution, ε_E and ε_Z are extinction coefficients of the *E*- and *Z*-forms at the excitation wavelength, and $Q_t=I_t(1-10^{-D_t})/D_t$ is the light absorbed after a time *t*. After integration, a linear equation is obtained

$$\frac{V}{l}\frac{1-\alpha_t}{\int Q_t dt}=(\varphi_E\varepsilon_E+\varphi_Z\varepsilon_Z)\frac{\int\alpha_t Q_t dt}{\int Q_t dt}-\varphi_Z\varepsilon_Z$$

from which φ_E and φ_Z can be determined (see table 1). As the UV spectrum of the photo-product is unknown, we determined them from a photo-steady state condition

$$\alpha_{t\to\infty}=\frac{\varepsilon_Z\varphi_Z}{\varepsilon_E\varphi_E+\varepsilon_Z\varphi_Z}.$$

As the UV spectra of nitro derivatives (**If**) and (**IIf**) nearly coincided, we could not determine φ_E and φ_Z for them. The photoequilibrium mixture composition and the proportion of the quantum yields were estimated from IR spectra obtained using CCl_4.

The data obtained for the photoequilibrium mixture composition in acetonitrile corresponds to those for 5CB (table 2). Quantum yields of photoisomerization and the position of equilibrium do not depend upon the nature of the substituent (table 1), the solvent polarity or the excitation wavelength (table 2). Therefore, quantitative data on the photoisomerization process, obtained for dilute solutions of (**I**), can describe photo-reactions in liquid crystalline matrices of these substances to a good approximation. Based on the results of our investigation some conclusions about details of photoisomerization can be made.

The lowest excited singlet state of compounds (**Ia, b, d–f**) is $S^*_{n\pi}$; it manifests itself as a shoulder in a long wavelength part of the UV spectra. Effective transition $S_{n\pi^*}\to T_{\pi\pi^*}$ [5] leads apparently to $T_{\pi\pi^*}$ occupancy and thus to *E*,*Z*-isomerization. We have found that triplet donors sensitize a photoreaction. Therefore for (**I**) and (**II**), the photo-active state is triplet as is also the case for benzylidenecycloalkanones [4]. We have not found a photo-reduction of (**I**) and (**II**), which is characteristic for carbonyl compounds, that indicates the π,π^*-nature of the photo-active state [5]. If it is assumed that the excitation of (**I**) and (**II**) leads to occupation of a common photo-active 'phantom-triplet' state ($\tilde{T}$) [5], then a comparison of α_∞ values with extinctions of *E*- and *Z*-isomers at the excitation wavelength shows that kinetically the rate of the $E\to Z$ process is 1·5–2·2 times greater than that for $Z\to E$. Therefore, the high degree of photo-

Table 1. Quantum yields of E,Z-isomerization (λ^* 313 nm) and spectral characteristics of the compounds (**I**)–(**II**).

Compound†	R	$\nu_{max}(\varepsilon)$		$\nu_{C=O}$					
		E	Z	E	Z	$\varphi_E(\varepsilon^*_\lambda)$	$\varphi_Z(\varepsilon^*_\lambda)$	φ_E/φ_Z	α_∞
Ia	Ph	33480 (26100)	34780 (23330)	1686	1698	0·32 (21710)	0·11 (10970)	3·0	0·11
Ib	OCH_3	33580 (17730)	35900 (10870)	1685	1696	0·34 (14160)	0·12 (4660)	2·8	0·11
Ic	$N(CH_3)_2$	28700 (23530)	32120 (14100)	1679	1694	0·43 (13340)	0·10 (13730)	4·3	0·12
Id	Cl	35820 (17520)	37560 (13430)	1686	1698	0·31 (4550)	0·11 (1450)	2·8	0·10
Ie	CN	35800 (19940)	37020 (18520)	1686	1694	0·35 (4490)	0·15 (1340)	2·4	0·11
If	NO_2	33440 (15420)	—	1688	1694	—	—	2·5	0·29

† Solvent: *n*-octane; average error for $\varphi_E \approx 4$ per cent, $\varphi_E \approx 12$ per cent, $\alpha_\infty \approx 5$ per cent.

Table 2. Quantum yields of isomerization for compound **Ia** in various solvents and wavelengths of excitation (λ^*).

Solvent	λ^* nm	ε_E	ε_Z	φ_E	φ_Z	φ_E/φ_Z	α_∞
n-Octane	313	21710	10970	0·32	0·11	3·0	0·11
n-Octane	334	7860	2380	0·34	0·11	3·1	0·12
n-Octane	366	525	206	0·33	0·11	3·0	0·13
Acetonitrile	313	22260	10820	0·37	0·13	2·8	0·11
Methanol	313	26740	13200	0·30	0·09	3·3	0·10

transformation from (**I**) to (**II**) is due not only to differences in the absorption of the isomers, but also to different rates of transformation of the excited E- and Z-isomers into the $\tilde{T}$-state.

Thus, the E,Z-isomerization of chiral dopants can be used to create photochemically controlled liquid crystalline matrices with induced helical order.

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