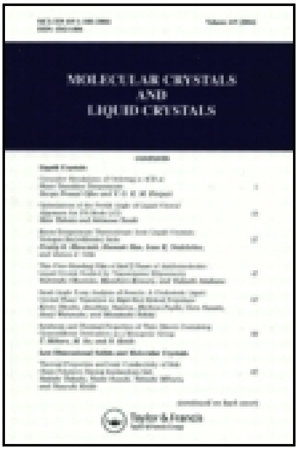

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Photo-induced Inversion of the Cholesteric Helix in Systems Containing 3(R)-Methylcyclohexanone 6-Arylidene Derivatives

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Induced cholesteric systems which were based on 4-pentyl-4′-cyanobiphenyl and contained 3(R)-methylcyclohexanone 6-arylidene derivatives as chiral dopants showed the helix inversion under UV light exposure due to the effective E-Z photo-isomerization of the dopant. Rather high twist extent produced during this process remained invariable under the subsequent irradiation or at elevated temperatures. The effect observed was driven by the sign and value difference in helical twisting powers of E- and Z-isomers of 3(R)-methylcyclohexanone derivatives. The cholesteric mixtures containing Z-isomers of 3(R)-methylcyclohexanone derivatives exhibited the selective visible light reflection.

Keywords: α,β-unsaturated ketones; chiral dopants; *E*-*Z*-isomerization; helix inversion; induced cholesteric; liquid crystals; selective visible light reflection

INTRODUCTION

Photo-induced effects in cholesteric and ferroelectric liquid crystalline (LC) compositions attract great interest due to the promising application prospects (see for example [1–7]). Such effects are commonly associated with photochemical transformations of components, either a LC host or a guest compound. Photochromic azobenzene derivatives possessing capability for *trans*-*cis* photo-isomerization have been the

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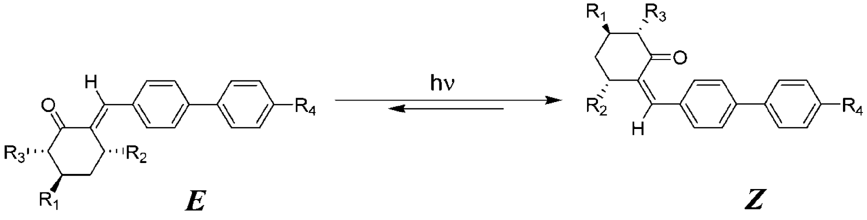

1: $R_1 = H$, $R_2 = CH_3$, $R_3 = CH(CH_3)_2$;

2: $R_1 = CH_3$, $R_2 = R_3 = H$; $R_4 = H$ (**a**), OC_6H_{13} (**b**), OC_7H_{15} (**c**), $p\text{-}C_6H_4\text{–}C_6H_{13}$ (**d**).

SCHEME

subject of a wide range of investigations as photosensitive components of LC systems (for example, [2,3,8–11]). Some possibilities of tuning the cholesteric helical pitch by the means of the *trans-cis* photoisomerization have been also discussed [3,11].

Photoisomerising α,β-unsaturated ketones have been studied to a lesser degree in the LC systems with induced supramolecular helical structures. Ambidextrous chiral thioindigo dopants belong to this type of components [4]. Ferroelectric LC systems containing these dopants showed photo-induced inversion of the spontaneous polarization. In this context, cyclohexanone arylidene derivatives are of significant importance. *E*-isomers of such compounds, e.g., (1*R*,4*R*)-*p*-menthane-3-one derivatives **1**, have been shown to be effective chiral dopants for the nematic host systems [12]. However, their use is limited due to an essential *E*-*Z*-photoisomerization (Scheme) [13]. *Z*-isomers of **1** that possess very low helical twisting power (HTP) prevail in the photostationary state of the induced cholesteric systems [14,15]. Thus, a drastic decrease in twist extent occurs under UV irradiation of the host systems which contain compounds **1**.

One way to overcome this problem is to search for the more stable α,β-unsaturated ketones with high HTP. The first steps on this direction were made in [16]. Photostationary states obtained by UV irradiation of some methylcyclohexanone arylidene derivatives were shown to possess twist extent even higher than the initial *E*-isomers do. In this work we present the detailed investigation of 3(*R*)-methylcyclohexanone arylidene derivatives **2** that promote the cholesteric helix inversion in mixtures with the 4-cyano-4′-pentylbiphenyl (5CB) under UV-irradiation.

EXPERIMENTAL

NMR ^{1}H spectra were recorded on a Jeol JNM-LA 400 FT or a Varian VXR-300 spectrometer. Mass spectra were recorded on a MI-1201E FAB spectrometer. The analyses of reaction mixtures and the determination of purity for target compounds were carried out by high performance liquid chromatography (HPLC) using a Bischoff HPLC system equipped with Prontosil 120–5-C18 ac*E*-EPS reversed phase column. 70–100 vol.% acetonitrile-water mixtures served as an eluent.

Compounds **2** were synthesised as *E*-isomers according to the procedure described in [17] and then were subjected to the UV-irradiation.

E-Z-photoisomerization of (E)-2-(4-arylbenzylidene)-(5R)-methylcyclohexanones

General procedure. Solution of the *E*-isomer (0.8 mmol) in heptane (100 mL) was UV irradiated while stirring until the HPLC revealed the photostationary state was reached. Heptane was evaporated and the residue was recrystallized from the minimal amount of methanol at −5°C thus giving corresponding *Z*-isomer.

(Z)-2-(4-phenylbenzylidene)-(5R)-methylcyclohexanone Z-2a

Yield 14%. Melting point 70–71°C (from methanol). NMR ^{1}H ($CDCl_3$, 400 MHz): 7.58 (d, 2H), 7.52 (d, 2H), 7.42 (m, 4H), 7.34 (m, 1H), 6.43 (s, 1H), 2.71 (m, 1H, *J*–14.4, 4.2, 3.4, 0.5 Hz), 2.63 (m, 1H, *J*–14.0, 4.1, 1.9 Hz), 2.58 (m, 1H, *J*–14.3, 11.9, 4.2, 2.0 Hz), 2.27 (m, 1H, *J*–14.0, 11.5 Hz), 2.12 (m, 1H, *J* 11.5, 10.9, 6.5, 4.1, 3.7, Hz), 2.02 (m, 1H, *J*–12.9, 4.2, 3.7, 3.4, 1.9 Hz), 1.56 (m, 1H, *J*–12.9, 11.9, 10.9, 4.2 Hz), 1.08 (d, 3H, *J* 6.5 Hz).

(Z)-2-(4-(4-hexylphenyl)benzylidene)-(5R)-methylcyclohexanone Z-2b

Yield 36%. Melting point 42.5–43°C (from methanol). NMR ^{1}H ($CDCl_3$, 300 MHz): 7.50 (d, 2H), 7.49 (d, 2H), 7.40 (d, 2H), 7.24 (d, 2H), 6.42 (s, 1H), 2.70 (m, 1H, *J*–14.4, 4.9, 4.1, 1.1 Hz), 2.56 (m, 1H, *J*–13.7, 4.4, 2.2 Hz), 2.51 (m, 1H, *J*–14.4, 11.3, 4.2, 2.0 Hz), 2.20 (m, 1H, *J*–13.7, 11.5 Hz), 2.13 (m, 2H), 1.94 (m, 1H, *J*–13.1, 4.9, 4.2, 3.4, 2.2 Hz), 1,61 (m, 2H), 1.49 (m, 1H, *J*–13.1, 11.5, 11.3, 4.1 Hz), 1.36 (m, 6H), 1.01 (d, 3H), 0.90 (t, 3H).

Measurement of the Properties of LC Mixtures

Induced helical pitch values were measured by the Grandgean-Cano method as described before [18]. HTP signs were determined as described in [19]. Selective light reflection spectra were measured in the planar oriented LC samples on a Hitachi M30 spectrophotometer. Photochemical studies in the LC media were carried out by dissolving the corresponding chiral dopant in the isotropic phase of 5CB followed by UV irradiation of mixture obtained with DRSh-120 high pressure mercury lamp. Helical pitch values were measured at the various irradiation times as described above. *E*-*Z* isomeric ratios at the photostationary state were determined by the HPLC analysis of the cholesteric mixture using ethyl acetate as an eluent.

RESULTS AND DISCUSSION

Photo-induced Cholesteric Helix Inversion

Compound **2c** dissolved in nematic 5CB exhibited fast increase in helical pitch P at the beginning of the UV irradiation period. The twist extent P^{-1} decreased accordingly. During following irradiation P^{-1} reaches zero (the inversion point) and nematic ≪schlieren” texture is observed in a Grandgean-Cano cell. However, on further irradiation P^{-1} increased and, after a while, the system reached photostationary state which was indifferent to the subsequent UV light action (Fig. 1). The photostationary mixture obtained this way retained its properties even after maintaining the cell at 100°C during 1 h on air. The sign of the cholesteric helix in the photostationary mixture was found to be the opposite to the one observed before irradiation, i.e., the helix inversion takes place on UV irradiation in the mixture studied. HPLC analysis revealed the essential prevalence of the photoproduct (most likely the corresponding *Z*-isomer) without any other new substances. Similar behavior was observed for the solutions of **2d** in 5CB. Thus, the effect revealed appears to be independent of the arylidene structure of compounds **2**. On the contrary, for isomenthone arylidene derivatives **1** possessing molecular structure being quite similar to **2**, twist extent gradually decreased on irradiation [15]. This fact was shown to be a consequence of the effective *E*-*Z*-isomerization of **1** in both isotropic [13] and LC [14,15] states and the very low HTP of the corresponding *Z*-isomers. Since the UV spectra (the wavelengths of the absorption maxima and extinction coefficients) as well as quantum yields of the isomerization and compositions of photostationary mixtures for **1** and **2** [20,21] are quite similar, the difference observed in photochemical

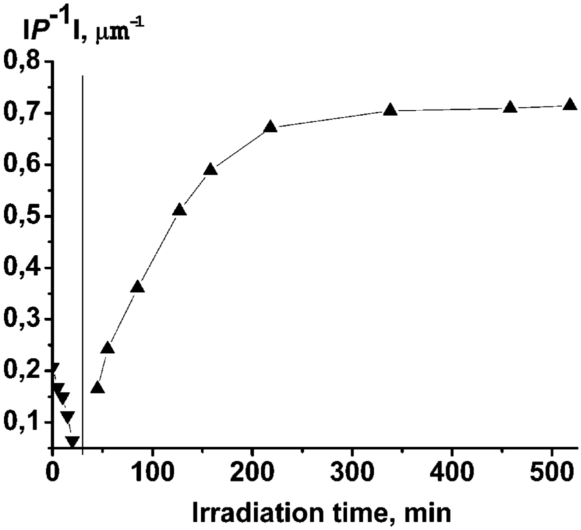

FIGURE 1 Dependence of twist extent value $|P^{-1}|$ on irradiation time for compound **2c** in 4-cyano-4′-pentylbiphenyl.

properties of the LC systems containing **1** and **2** could be related to the twisting properties of the corresponding *E*- and *Z*-isomers.

Helical Twisting Power of *Z*-isomers 2

Suppose that HTP signs of *Z*-isomers of **2c**,**d** are the opposite to the ones of corresponding *E*-forms and take into account that only two chiral substances are present in the photostationary mixture (HPLC), one can express twist extent P^{-1} as:

$$P^{-1} = C(\mathrm{X}_E\beta_E + \mathrm{X}_Z\beta_Z), \tag{1}$$

where C is the total concentration of the chiral dopant, X_E, X_Z are mole fractions of *E*- and *Z*- isomers determined from the HPLC experiments (0.932 and 0.064 correspondingly for **2c**, 0.792 and 0.208 for **2d**), and β_E and β_Z are HTPs of *E*- and *Z*- isomers. Values of β_E were determined experimentally for **2c**,**d** [17,21] (Table 1). From these data the HTP of the pure *Z*-isomer is calculated:

$$\beta_Z = (P^{-1} - \mathrm{CX}_E\beta_E)/\mathrm{CX}_Z. \tag{2}$$

We also can estimate β_Z values with Eq. (1) using quantum yields of the isomerization (Φ_E and Φ_Z are known from [20,21]) instead of X_E

TABLE 1 Helical Twisting Power (β) of the E-[6] and Z-Isomeric Arylidene Derivatives of (3R)-me-Thylcyclohexanone

Compound	β_E, μm^{-1}	β_Z, μm^{-1}
2a	-7.7 ± 0.5	31.3 ± 1.5
2b	-9.1 ± 0.7	37.4 ± 1.9 35^a
2c	-9.9 ± 0.3	35^b 38^c
2d	-10.5 ± 0.2	43^b

^{a}Estimated by using Eq. (4); ^{b}Estimated by using Eq. (2); ^{c}Estimated by using Eq. (3).

and X_Z (Eq. (3)):

$$\beta_Z = (P^{-1} - C\Phi_E\beta_E)/C\Phi_Z. \quad (3)$$

The values of β_Z for **2c**,**d** estimated this way turned out to be more than four times higher in comparison to those of the E-forms (see Table 1). In order to confirm these results the HTP was measured in 5CB for the Z-isomers of compounds **2a**,**b** which were prepared according to [20,21]. The HTP was found to be in agreement with theoretical considerations expressed above. The cholesteric mixture consisting of 7.6 mol.% of compound **2b** in 5CB possessed selective visible light reflection with the maximum $\lambda_{\max}$ lying in the range 568–577 nm (depending on the temperature of measurements). The β_Z value could also be estimated from these data by using well-known Eq. (4):

$$\beta = n/\lambda_{\max}C, \quad (4)$$

where n is the average refraction index of LC taken as 1.5 (Table 1).

As it was noted above the HTP values for E- and Z-isomers of compounds **1** and **2** were rather different in spite of the similarities in structural and photochemical properties. Assuming that the helical twisting in induced cholesteric LC results from the balance between attractive and repulsive intermolecular interactions it is believed that twisting properties of the chiral dopant greatly depend on its molecular electronic and spatial structure. In this work we propose a qualitative model that describes the dependence of the HTP sign on the chiral dopant molecular structures for the α,β-unsaturated ketones **1** and **2** in the mixtures with 5CB.

Molecular attraction between the chiral dopant and nematic is in general determined by the dispersion forces and requires parallel arrangement of the aromatic cores of molecules. Repulsion is mainly caused by the intermolecular interactions of hydrogen atoms of benzene and cyclohexane rings of the chiral dopant and nematic; as a result, molecules of the nematic could not closely approach the cyclohexane ring of the dopant. Stereospecific repulsions could also take place between atoms of the benzene rings of the nematic and the methyl group at the chiral center of the dopant. Finally, repulsion of the uniformly charged atoms of different molecules should be taken into consideration.

For the *E*-**1** isomer, the chair conformation of the cyclohexanone ring with the axial methyl group is dominant both in solutions and in crystalline state [12]. We propose a model system, which consists of molecule **1** in the preferred chair conformation and two molecules of 5CB thereby representing the chiral dopant and its nearest nematic surroundings (Fig. 2). Nematic molecules are almost parallel to the aromatic core axis of the chiral dopant because this arrangement favors effective dispersion attraction. Moreover, two types of unfavorable steric and electrostatic interactions could be mentioned, namely, repulsion between the biphenyl fragment of the nematic molecule and the axial methyl group of the dopant and also repulsion between negative dipole ends of the nitrile and carbonyl groups of 5CB and the

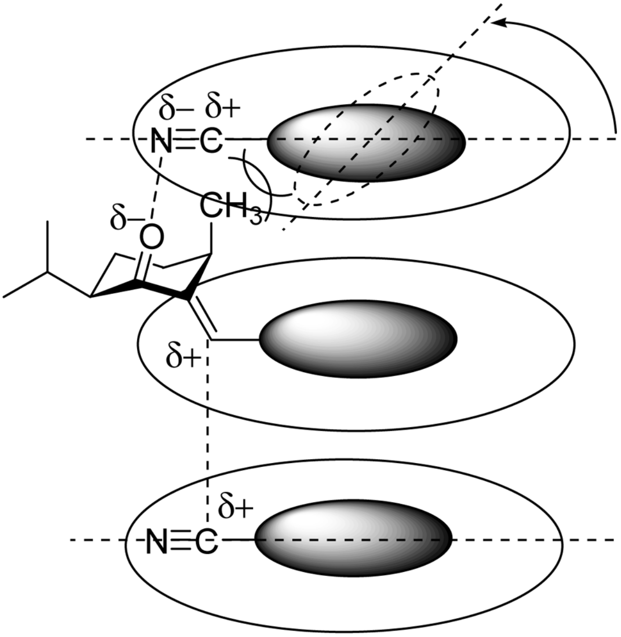

FIGURE 2 Model of helix induction in 5CB with *E*-isomers of isomenthone arylidene derivatives **1**. Aromatic cores are presented as ellipsoids.

dopant. Some reduction of the repulsive energy could be achieved if one nematic molecule (situated above chiral dopant) turns relatively the dopant long axis (Fig. 2). As a result, the positively charged nitrile carbon of this nematic molecule closes in the negatively charged carbonyl oxygen, and the 5CB molecule below the dopant is less affected by the unfavorable steric repulsion. Thus, spatial arrangements of two nematic molecules relatively the dopant could well explain the origin of left-handed twist in this system being in agreement with experimental data [12]. Since the second chiral center in *E*-**1** is distanced far from the arylidene fragment, it has insignificant effect on the HTP value of these compounds [12,16,22]. The propagation of the helical twist on the macroscopic level is believed to proceed through the elastic interactions between nematic molecules [23].

In solution *Z*-1 isomer exists as a 80:20 mixture of the inverted chair conformers [24]. Substantial repulsion between the nitrile group of the ≪above≫ nematic molecule and the axial methyl group of the chiral dopant may be expected for the host system containing this dopant in the dominant chair conformation. In similar way, the interactions between aromatic core of nematic molecule ≪above≫ and carbonyl oxygen of the dopant could also take place. These both interactions may be diminished if the nematic molecule ≪above≫ turns relatively to the dopant. As a result, the right-handed helix should be expected with repulsion interaction with ≪below≫ 5CB molecule considered insignificant (Fig. 3a). Minor chair conformer of *Z*-**1** contains equatorial methyl group [24] and carbonyl one is oriented down with respect to middle cyclohexanone plane. This structure feature adds to the significant repulsion between the nitrile nitrogen of the ≪below≫ nematic molecule and the carbonyl oxygen of dopant in providing an opportunity for turning both nematic molecules relatively the chiral dopant long axis (Fig. 3b). The HTP sign in this host system depends on relation between contributions of the interactions of the ≪above≫ and ≪below≫ 5CB molecules with the chiral dopant in the alternative conformations. Overall, the induced helix sign for *Z*-1 is determined by the relative concentrations of the inverted chair conformers of this dopant in the LC media and their HTP. Since, the alternative conformers of *Z*-1 produce opposite handed helices and the populations of the conformers are similar [24], the HTP value of the mixture should be close zero.

E-isomer of **2** has chair conformation with the equatorial methyl group preferred [25]. The methyl group in this conformation is distanced away from the π-electronic fragment, therefore its participation in interaction with nearest nematic molecules is believed to be insignificant [21]. As in the case of the *E*-**1**, repulsion between negative dipole

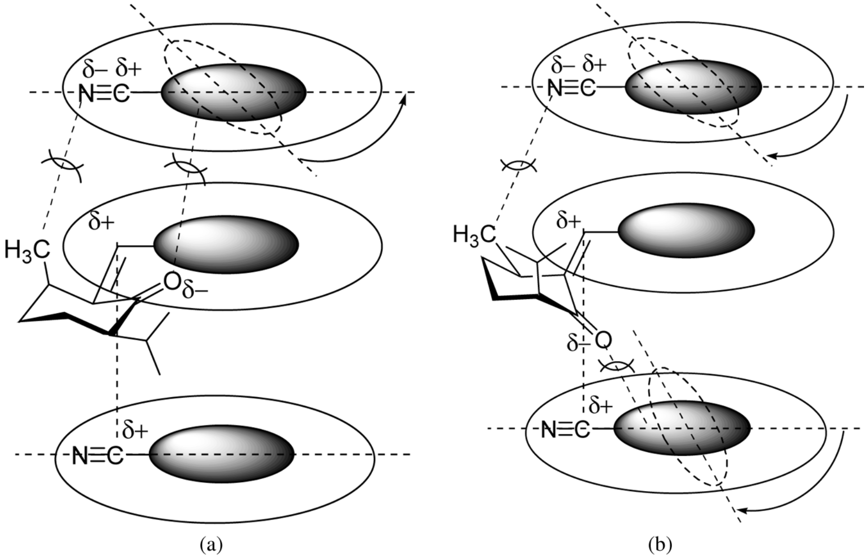

FIGURE 3 Model of helix induction in 5CB with major (*a*) and minor (*b*) conformers of *Z*-isomers of isomenthone arylidene derivatives **1**. Aromatic cores are presented as ellipsoids.

ends of the nitrile group of 5CB and the carbonyl group of the chiral dopant leads to the left-handed helical twist (Fig. 4a). The HTP signs for host systems containing *E*-**1** and *E*-**2** are the same (Table 1). The large difference in HTP values for the two types of chiral dopants is most likely due to the insignificant role of the equatorial methyl group of *E*-**2** in the repulsive interactions which promote the twist.

For compound *Z*-**2** the spatial structure of the chair conformation is not essentially different from that of *E*-**2**. In both cases preferable equatorial methyl group [26] is removed from the π-electronic fragment. Unlike the LC host system 5CB–*E*-**2**, the repulsion between the benzene ring of the nematic molecule positioned ≪above≫ and the carbonyl oxygen of the dopant and also repulsion between positively charged carbon of the nematic nitrile group and the uniformly charged carbon of the chiral dopant double bond play a vital part. These interactions lead to the right-handed twist (Fig. 4b) and the HTP signs for the *E*-**2** and *Z*-**2** must be opposite (Table 1). The large difference in HTP values for *E*-**2** and *Z*-**2** could be the consequence of the strengthening of the repulsive dipole-dipole interactions in the systems containing *Z*-isomers due to the carbonyl group being almost parallel to the aromatic cores of their molecules.

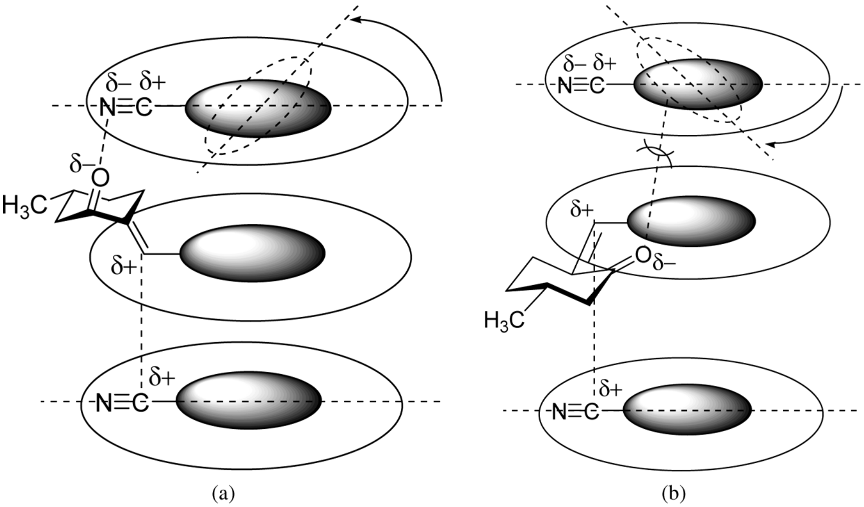

FIGURE 4 Model of helix induction in 5CB with *E*-(*a*) and *Z*-isomers (*b*) of arylidene derivatives of (3*R*)-methylcyclohexanone *2*. Aromatic cores are presented as ellipsoids.

This simple model explains origin of helical twist in LC host systems which contain α,β-unsaturated ketones with different molecular conformations, though it does not take into account some aspects of molecular motion in the LC compositions, particularly rotation of the molecule around the long axis. Nevertheless, the regularities established experimentally [16,22] for some close analogues of the chiral dopants studied in this work, e.g., isomeric methylcyclohexanone arylidene derivatives with ester linkage between benzene rings behave in agreement with the proposed model. The highest HTP value was determined for the compound being the analog of *E*-**1** without *iso*-propyl group. HTP for the corresponding *Z*-isomer was estimated to be much lower. For the *E*-compounds with the methyl group removed from the arylidene fragment, HTP values become lower, similar to *E*-**2a**,**b**, however, the twist extent increases remarkably on irradiation due to the corresponding *Z*-isomer formation.

CONCLUSION

The photo-induced inversion of the chlolesteric helix was observed during photochemical *E*–*Z*-isomerization of the 3(*R*)-methylcyclohexanone arylidene derivatives studied in 4-cyano-4′-pentylbiphenyl solutions. The opposite signs of twists caused by different isomers as well as four times higher value of the helical twisting power of the Z-isomer in comparison to that of the corresponding E-form are shown to be the driving factors in inversion of the cholesteric helix.

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