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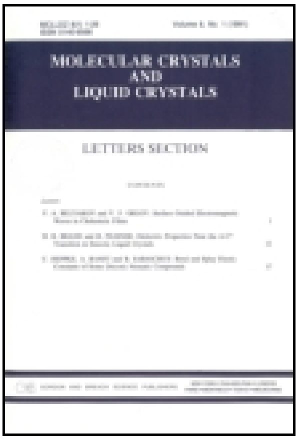

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Chiral Induction in Liquid Crystals with Dopants Derived from 1-Phenyl-2-Aminoalcohols

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New chiral additives derived from 1-phenyl-2-aminoalcohols have been prepared and tested. Especially ephedrine and pseudoephedrine as chiral auxiliaries with two asymmetric C atoms offer functional groups of divergent reactivity. Dopants prepared by acylation with promesogenic agents can be used in various electro-optic devices. A specific utilization concerns bistable cholesteric liquid crystal displays with stacked double layer construction in order to enhance the luminance of reflected light. Further, the solubility in nematic mixtures, the long term phase behavior, the dopant's impact on textures and phase behavior, the electro-optic response and the photostability of cholesteric mixtures have been investigated.

Keywords: Aminoalcohols; bistable displays; cholesteric; dopants; photostability

1. Introduction

To generate twisted structures in liquid crystalline (LC) phases, the chirality transfer by chiral dopants to an achiral LC material is a frequently used procedure. Depending on the ratio between induced helical pitch length p and wavelength λ of the visible light, different fields of electro-optic application are of interest. Long pitch systems ($p>>\lambda$) are generated in twisted or supertwisted nematic (TN, STN) LC displays (LCDs) to prevent regions with reverse twist. Intermediate pitch lengths systems ($p\approx \lambda$) are of interest for preparing cholesteric (chiral nematic) mixtures to be used in low-power display panels, e.g., in bistable cholesteric LC displays (CLCDs) with memory holding properties [1]. Although there is a large number of chiral nematic compounds, doping of achiral nematic host mixtures by chiral agents [2] is the commonly used option to meet the specific properties of practically usable materials. These dopants must fulfill several requirements: Priority have a sufficiently high helical twisting power (HTP), an adequate solubility in the host, a wide temperature region of (meta-) stable switching states and photostability. Concerning HTP, in order to minimize changes of the electro-optic properties of the host mixture by added dopants (e.g.,

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dielectric anisotropy, viscosity, phase sequence), a high degree of twist caused by a small amount of chiral admixture is essential. Therefore, the availability of dopants with high HTP values is of practical interest. Usually, the HTP is defined as

$$\mathrm{HTP} = \left(\frac{dp^{-1}}{dc}\right)_{c=0} \approx \frac{1}{pc} = \frac{\overline{n}}{\lambda_{\min} c}, \tag{1}$$

where p is the pitch length of the helix and c the dopant concentration. Mostly, HTP is related to the weight fraction w of the dopant (HTP_w), but sometimes it is related to the molar fraction x of the dopant [3,4]. Of course, HTP_x can be highly different from HTP_w, especially in case of large molar mass deviations between dopant and host material. There are several reports on synthetic nonsteroid dopants with exceptionally high HTP values [4], but admittedly without verification of their practical applicability in devices. Moreover, in many cases, a strong dependence of HTP values on the host matrix material has been observed relativizing reported data [5–7]. A crucial problem concerns the long-term phase stability of cholesteric solutions at room temperature and at low temperatures (e.g., –15°C). Many of the twist agents known for inducing efficiently helicity precipitate from cholesteric solution at convenient concentration [5,6]. Therefore, chiral dopants with low melting points and minor crystallization tendency should be favored. Due to these preconditions, the number of applicable chiral substances is severely limited and tradeoffs must be made. A further concern is the availability of dopant pairs having identical chemical constitution, but opposite configuration (e.g., enantiomers). Such compounds are used among others in CLCDs of double layer construction consisting of stacked cells with opposite handedness of cholesteric helices to enhance the optical contrast [8]. A single cell filled with a cholesteric mixture in the planar state reflects only circular polarized light with the handedness of its polarization equal to that of the helical structure. Circular polarized light of opposite handedness transmits without losses. This transmitted light may contribute to the luminance of reflected light by using double layer displays where the two cells are filled with cholesteric mixtures of opposite handedness.

It has been found that chiral dopants of an identical chemical structure but with opposite handedness are more suited to fabricate such displays than the combination of dopants with chemically different structure and opposite chirality [9–14]. This is due to the deviating properties (birefringence, temperature dependence of HTP, etc.) in case of chemically differing dopants leading to limitations of operational conditions. However, due to restrictions in terms of HTP, stability, and price, many of the potentially suited enantiomeric additives are not to be recommended. This also includes mesogenic esters of substituted 1,2-ethandiols [15], tetraaryl-1,3-dioxolane-4,5-dimethanols [16] (TADDOLs, instability of solutions at low temperatures [5]) as well as bi-2-naphthol-based chiral compounds (low photostability) [17]. Therefore, the objective of our work was to study new chiral additives derived from stereoisomeric ephedrine analogues 1-aryl-2-aminoalcohols. The motivation for choosing these chiral auxiliaries as starting material was the easy access because of their incidence in a substantial number of bioactive natural products and their use as resolving agents in stereochemistry. Moreover, enantiomerically pure ephedrines and pseudoephedrines are competitively priced synthetic compounds.

A specific feature of these auxiliaries with two stereocenters is their bifunctionality characterized by different reactivity, especially against carbonyl reagents. A large number of corresponding derivatives has been prepared and studied for a long time [18], preferentially with respect to their pharmacological relevance [19]. Particularly well investigated

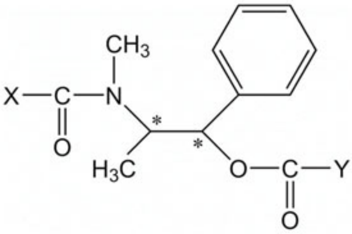


Figure 1. Basic chemical structure of the dopants **I**.

examples are O,N-diacetyl- and O,N-dibenzoylephedrines [20,21]. Also O,N-dipicolinoylpseudoephedrine was used as catalyst for stereoselective reductions [22]. However, according to our knowledge, there is no information about chirality transfer of related compounds to liquid crystalline phases.

2. Experimental Procedure

2.1 Materials

The general formula of the substituted chiral 1-phenyl-2-aminoalcohols **I** is illustrated in Fig. 1. To prepare the dopants we employed achiral promesogenic carboxylic acid chlorides [23] for the simultaneous or sequential acylation of the respective aminoalcohols following known procedures [24,25]. Compounds with identical acyl moieties **Ia**, **Ib** were synthesized by simultaneous acylation using two equivalents of the acid chlorides. Experience has shown that monoacylation of the related amino alcohols takes place preferentially at the amino group [22]. Therefore, to obtain products bearing two different substituents in N,O position (**Ic**–**Ie**), in a first step the appropriate N-acylated intermediates were prepared by selective acylation followed by esterification of the OH group. The integral structural parts of the synthesized dopants including the configuration of the initial aminoalcohols are summarized in Table 1. For example, the structure of (1R,2R)-2-(N-(4-trans-n-pentyl-cyclohexylcarbonyl)methylamino)-1-(4′-cyano-1,1′-biphenyl-4-carbonyloxy)-1-phenyl-propane (**Id**) is given in Fig. 2.

Nearly all synthesized twist agents were obtained as white solids or amber waxes with very low crystallization tendency. Microscopic contact preparations with a nematic partner

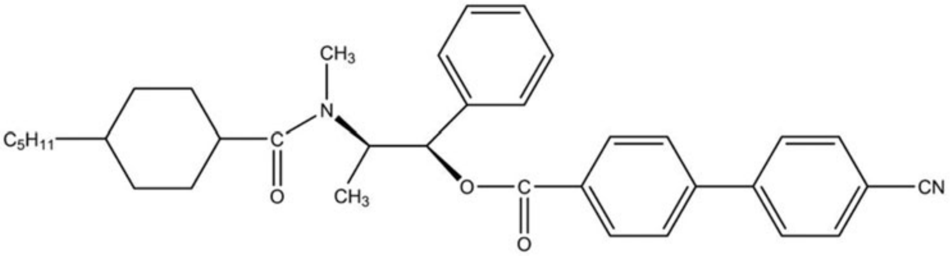
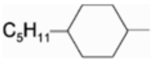
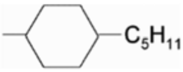
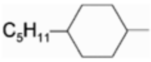
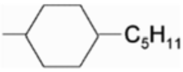
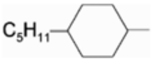
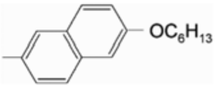
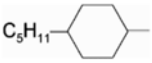
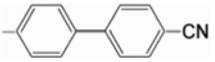
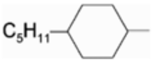
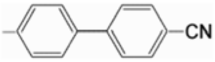


Figure 2. Chemical structure of the dopant **Id**.

Table 1. Structural constituents of chiral dopants **I** (cf. Fig. 1). **A** denotes the configuration of the starting amino alcohol

Code	X	**A**	Y
Ia		(1R,2S)−(−)	
Ib		(1S,2S)−(+)	
Ic		(1R,2R)−(−)	
Id		(1R,2R)−(−)	
Ie		(1S,2S)−(+)	

as preliminary qualitative check were performed to test the dopant properties (chiral transfer capability, mixing behavior). All of the diacylated products were miscible with commonly used nematic host mixtures, such as ZOC-1020XX (Chisso), E7, MDA-00-1795, and MLC-6650 (Merck).

2.2 Methods

The thermal phase behavior of dopants and mixtures has been examined by polarization microscopy using a Nikon Labophot 2 equipped with a Linkam THMS 600E heating stage. HTP values and the screw sense of the generated cholesteric phases were measured with the Grandjean–Cano method using planoconvex cylindrical lenses (Thorlabs) putting the sample on cleaned and rubbed quartz slides. For this purpose, cholesteric mixtures containing about 1 wt% of the dopants **Ia**–**Ie** in MLC-6650 as common nematic host (optical anisotropy Δn (20°C) $= 0.1498$, dielectric anisotropy $\Delta\varepsilon$ (20°C) $= 52.6$, mean nematic-isotropic transition temperature 90°C) were prepared. As an independent method to estimate HTP for given mixture compositions (cf. Table 3), the relation $\lambda_{\min} = \bar{n}\, p$ valid for coinciding viewing and incidence angles may be applied [26]. $\lambda_{\min}$ is the wavelength of the reflected circularly polarized light and $\bar{n}$ is the mean refractive index. For our MLC-6650-based solutions $\bar{n} \approx 1.57$ is assumed.

For reference studies, cholesteric mixtures from MLC-6650 and the already known twist agents **IIa**–**IIe** (Table 2) with reflection maxima located in the visible region have also been prepared. CB15 (**IIa**) was purchased from Merck KGaA. The synthesis of the other compounds **IIb**-**IIe** was described earlier [5]. Table 3 summarizes the composition of all samples investigated together with the wavelength $\lambda_{\min}$ of the transmittance minimum.

Test devices of bistable cholesteric liquid crystal displays were made using glass cells (E.H.C. Co., Ltd, Tokyo/Japan, cell spacing 3 μm, patterned ITO, without alignment layer). Stacked CLCDs have been prepared by combining two cells containing cholesteric mixtures of various handedness and by placing a droplet of glycerol as immersion liquid between

Table 2. Chiral dopants **II**. Note that **IIe** denotes a mixture of 2 TADDOLs

Code	Dopant
IIa	(S)-4-cyano-4′-(2-methylbutyl)biphenyl (CB15)
IIb	(4R,5R)-2-(4-biphenyl)-1,3-dioxolane-4,5-dicarboxylic acid dimethyl ester
IIc	1,4:3,6-dianhydro-D-sorbit-2.5-di-(6-n-hexyloxy-2-naphthoic acid)ester
IId	2,2′-bis(4′-n-pentyl-cyclohexyl-4-ylcarbonyloxy)-1,1′-binaphthyl
IIe	(4R,5R)-2,2-dimethyl-α,α,α',α'-tetra(phenanthr-9-yl)-1,3-dioxolane-4,5-dimethanol +(4R,5R)-2,2-dimethyl-α,α,α',α'-tetra(naphth-1-yl)-1,3-dioxolane-4,5-dimethanol

the cells in order to reduce parasitic reflections, e.g., at air/glass interfaces. The electro-optic switching characteristics of these CLCDs were determined using a display measuring system DMS 505 from Autronic-Melchers.

To study the photostability against high-intensity illumination, samples of planar oriented cholesteric mixtures made from MLC-6650 and different dopants were exposed. A solar simulation unit SOL 1200 (Hoenle) with a radiation intensity at sample position of 100 mW cm^{-2} has been used. The spectrum of the emitted light in the UV and visible range (295–780 nm) corresponds well to that of solar radiation. During sample exposition, the temperature was kept constant at 42°C. The samples were analyzed by recording the transmission spectra using an Ocean Optics USB2000+XR1-ES UV/VIS spectrometer. After cooling the samples to ambient temperature, the shift of the transmittance minima depending on illumination time was recorded. Generally, a lack of stability of cholesteric mixtures manifests as a shift of λ_{min} toward longer wavelengths.

3. Results and Discussion

The measured and calculated HTP values are listed in Table 4. Deviations between measured data and those estimated from λ_{min} may be due to the concentration dependence of

Table 3. Composition and transmittance minimum λ_{min} of the investigated cholesteric LC-mixtures with MLC-6650 as common host

Dopants in MLC-6650	Content of dopant/wt%	λ_{min}/nm
Ia	17	520
Ib	12.3	497
Ic	11	442
Id	4.9	618
Ie	5.1	611
IIa	33.7	712
IIb	12.5	560
IIc	4.5	518
IId	5.6	597
IIe	2.47 + 0.46	537

Table 4. HTP values of dopants **I** in the nematic host MLC-6650 at 25°C related to weight fraction (HTP$_{w(1)}$). The absolute value of HTP$_w$ was additionally estimated according to Eq. (1) (HTP$_{w(2)}$)

Dopant	HTP$_{w(1)}$/μm^{-1}	HTP$_{w(2)}$/μm^{-1}
Ia	−10	18
Ib	+22	26
Ic	−25	32
Id	−54	51
Ie	+55	51

HTP. Basically, the data reveal that the substitution of ephedrine by pseudoephedrine as stereogenic center leads to an enhanced twisting power (**Ia**, **Ib**). Further, the moderate HTP values of dopants with identical substituents X,Y (**Ia**, **Ib**) can be enhanced by acylation using unequal acyl moieties (**Ic**–**Ie**).

Exemplary, the properties of cholesteric mixtures prepared from dopants **Id** and **Ie** should be demonstrated. The planar oriented layer of a solution made up of 4.9 wt% **Id** in MLC-6650 forms a left-handed helical structure and reflects selectively light at 618 nm. An inverse helix is formed in corresponding mixtures containing 5.1 wt% of the enantiomeric dopant **Ie** with the transmittance minimum at 611 nm (Table 3). Hence, this dopant pair is suitable for the assembly of cholesteric double cell displays. It should be noted that the host MLC-6650 contains originally the commercial dopant S-811 (HTP = –13.8 μm^{-1}) at low concentration to prevent inverse twist in TN mode cells with $p >> \lambda$. This might explain that, compared with **Ie**, a slightly lower concentration of **Id** leads to almost the same value for $\lambda_{\min}$ (cf. Table 3).

To verify the merit of the stacked cell assembling, the transmission spectra of double layer displays fabricated from two sandwiched single cells containing either mixtures of identical or of opposite handedness of cholesteric helices are shown in Fig. 3. It is obvious that the superposition of cells prepared with opposite-handed dopants yields lower transmission (higher peak reflectance) in the spectral region fulfilling the Bragg condition for selective reflection. The effect of this sandwich structure may be improved by fine tuning the transmittance spectra through adjusting the concentration of the dopants and by further reduction of reflection loss.

The improved reflectivity of double cell display devices filled with cholesteric mixtures of opposite handedness in the planar state is also revealed by their electro-optic characteristics in Fig. 4. The luminance is enhanced by a factor of almost 2, compared to single cells leading to brighter colors in double cell displays. On the other hand, the contrast ratio (i.e., the luminance ratio between the electrically switchable planar and focal-conic textures) remains almost unchanged since the luminance of reflected light in the focal-conic state of double cell displays increases likewise due to a doubled path length along which incident light is scattered.

Further experiments concern the long-term phase stability at low temperature. In thin layer glass cells filled with mixtures of **Id** and **Ie** in MLC-6650 of various dopant concentrations, no phase separation has been observed during storage at –15°C over 5 months.

Apart from the usual temperature dependence of $\lambda_{\min}$ [5], the textures and the phase behavior of doped mixtures become more and more influenced by the chiral admixture with

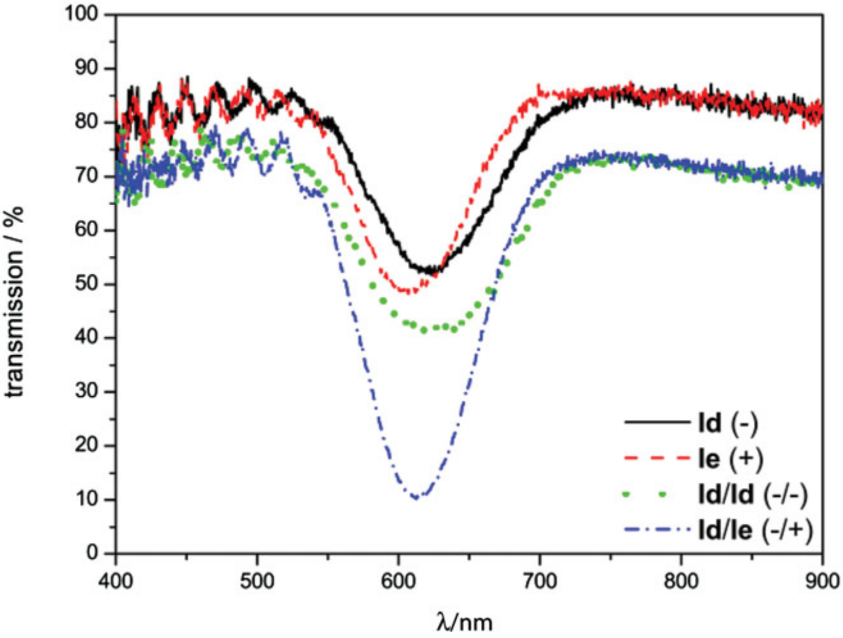


Figure 3. Transmission of single and double cells filled with cholesteric mixtures of indicated dopants in MLC-6650 with various handedness (cf. Table 3).

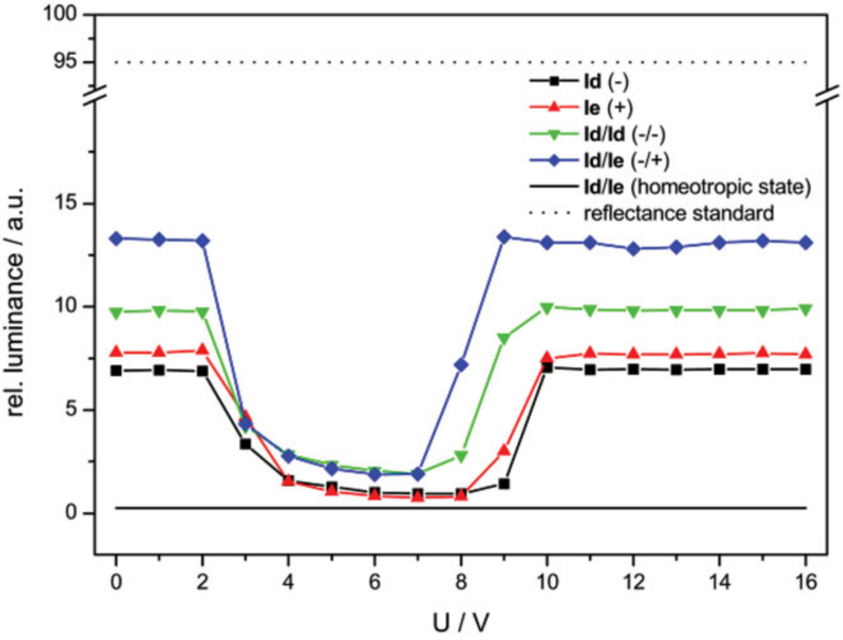


Figure 4. Electro-optic characteristics of single and double cells filled with cholesteric mixtures of indicated dopants in MLC-6650 with various helix handedness (cf. Table 3). All measurements refer to the luminance of a reflectance standard. The reflectance of a double cell in the homeotropic state is shown for comparison.

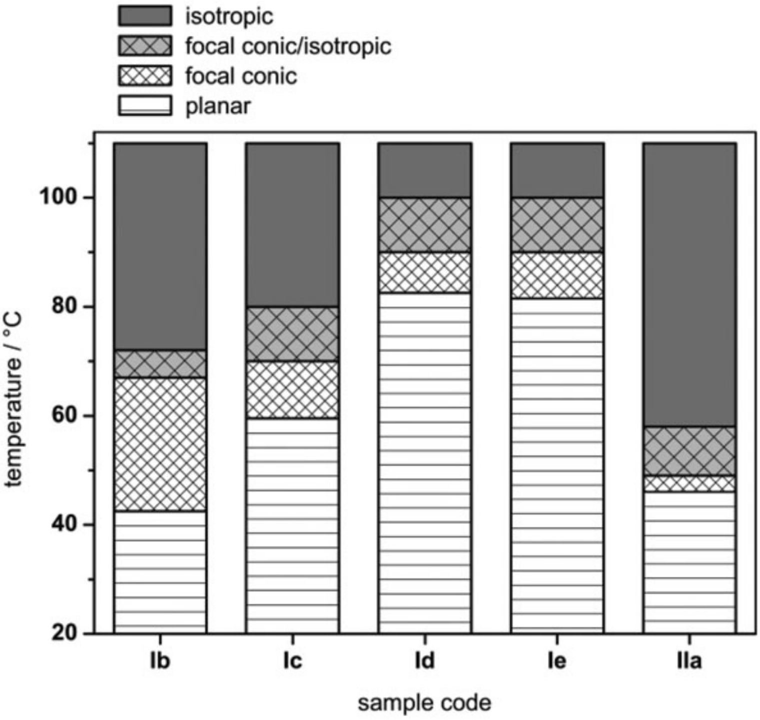


Figure 5. Temperature regions of planar and focal conic textures of cholesteric MLC-6650 based mixtures between untreated glass slides and the cholesteric-isotropic phase transition (cf. Tables 3 and 4).

increasing temperatures as indicated in Fig. 5. This point has also to be considered when selecting dopants for use in bistable cholesteric displays. Obviously, the temperature range of the metastable planar orientation with the helix axis-oriented normal to the substrate plane is the more extended the higher the HTP value is. When heating the cholesteric mixtures between untreated glass slides, a texture change from the planar to the stable focal conic orientation occurs within a relatively small temperature interval (Fig. 5). When cooling the samples below this interval, the reverse change is only possible by applying external fields (mechanical, electric or magnetic).

Photostability crucially affects the lifetime of LCDs. Aside from special applications using photoresponsive chiral dopants, such as data recording and storage by spatially resolved photochemical altering of the pitch [27], any light-induced bleaching or discoloration effects of the doped material in normal-mode CLCDs should be excluded. This is in particular true for projection displays. Therefore, irradiation tests are indispensable. Our samples (cf. Table 3) have been illuminated continually for 6 h with the results given in Fig. 6. For comparison and as benchmark, also cholesteric mixtures prepared from the familiar dopants **II** characterized by different photostability have been involved [5]. With the selection of these agents beginning from the frequently used and relatively stable CB15 up to TADDOLs known as highly photosensitive [5], a broad spectrum of photosensitivity should be covered. The most important finding in Fig. 6 concerns the excellent light stability of O,N-di(4-trans-n-pentylcyclohexylcarbonyl)ephedrines/pseudoephedrines **Ia** and **Ib**. Presumably, this is due to the lack of any conjugation between carbonyl groups

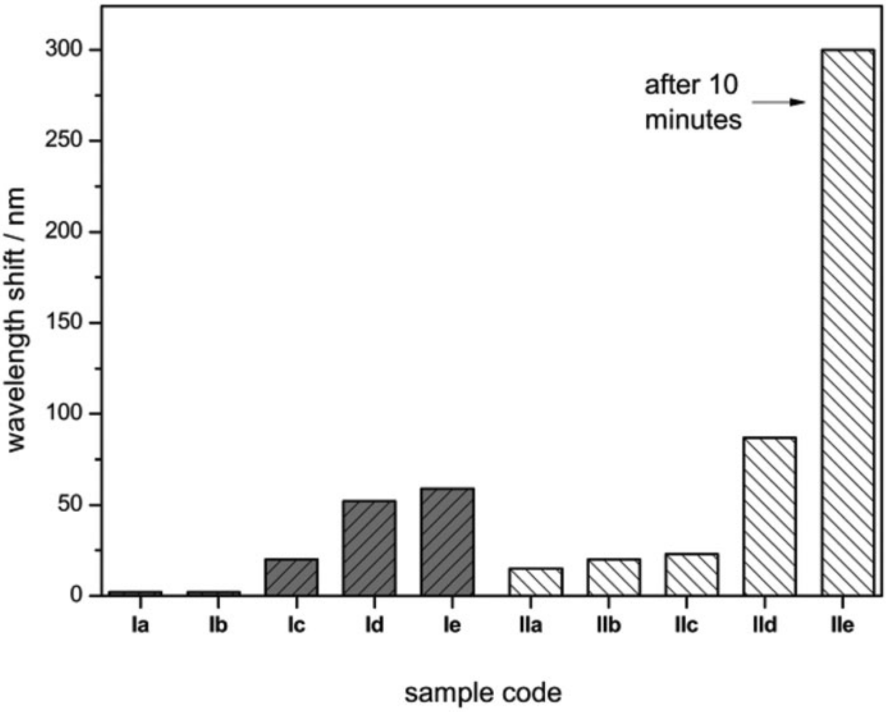


Figure 6. Shift of the transmission minimum $\lambda_{\min}$ after 6 h (except **IIe**) of sun simulator irradiation at 100 mW cm^{-2} for mixtures of the indicated dopants in MLC-6650 as common host (cf. Table 3).

(C=O) and C−C multiple bonds, such as given in aromatic rings, in these compounds [28]. This is confirmed by the comparably high stability of CB15 (**IIa**) and of the tartaric acid derivative **IIb**. In contrast, the overcrowding of aromatic rings in a dopant molecule as given in the binaphthols **IId** [17] and, as an extreme example, in TADDOLs **IIe**, degrades the photostability.

In summary, new chiral dopants derived from stereoisomeric 1-phenyl-2-aminoalcohols were used as twist agents to obtain helically arranged liquid crystalline mixtures from achiral host LC phases. Using the configuration diversity and bifunctionality of enantiomerically pure ephedrines and pseudoephedrines, the dopants have been prepared by acylation with promesogenic carboxylic acids. The capability of chirality transfer can be enhanced through substitution of ephedrine by pseudoephedrine as bichiral center as well as by using unequal acyl substituents of different polarity. The dopants are characterized by a satisfactory helical twisting power, a vanishing crystallization tendency as well as the practically important low-temperature phase stability of short-pitch cholesteric blends. The distinct influence of selected dopants on electro-optic characteristics and on textures and phase regions of the cholesteric mixtures has been demonstrated. Especially, the outstanding photostability of products with two alicyclic substituents should be emphasized. The dopants can thus fulfill the stringent requirements of practical operation conditions, e.g., as low twist chiral nematic systems in displays subjected to high luminous energy as well as in power-saving bistable cholesteric displays in stacked cell or combined layer configuration.

Acknowledgment

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