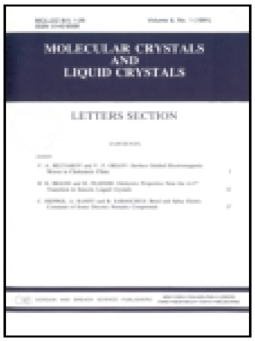


Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Structural Aspects and Host Effects of the Chirality Transfer by Mesogenic Substituted Aminoalcohols

Monika Bauer, Lutz Hartmann, Sophie Krüger, Frank Kuschel & Wolfgang Weissflog

To cite this article: Monika Bauer, Lutz Hartmann, Sophie Krüger, Frank Kuschel & Wolfgang Weissflog (2016) Structural Aspects and Host Effects of the Chirality Transfer by Mesogenic Substituted Aminoalcohols, Molecular Crystals and Liquid Crystals, 626:1, 1-11, DOI: 10.1080/15421406.2015.1106214

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1106214

Published online: 22 Mar 2016.

Submit your article to this journal

Article views: 121

View related articles

View Crossmark data

Full Terms & Conditions of access and use can be found at
http://www.tandfonline.com/action/journalInformation?journalCode=gmcl20

Download by: [College of Business Education] **Date:** 22 December 2016, At: 13:22

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2016, VOL. 626, 1–11
http://dx.doi.org/10.1080/15421406.2015.1106214

Structural Aspects and Host Effects of the Chirality Transfer by Mesogenic Substituted Aminoalcohols

Monika Bauer[a], Lutz Hartmann[a], Sophie Krüger[a], Frank Kuschel[a],
and Wolfgang Weissflog[b]

[a]Fraunhofer Research Institution for Polymeric Materials and Composites PYCO, Teltow, Germany; [b]Institute of Physical Chemistry, Martin-Luther University Halle-Wittenberg, Halle, Germany

ABSTRACT
In continuation of the investigations on chiral dopants derived from the aminoalcohols ephedrine and pseudoephedrine as chiral bivalent structure elements, a series of new agents bearing very different substituents has been synthesized. The products turned out to be suited for preparation of short-pitch chiral liquid crystalline (LC) phases and were characterized by measuring their helical twisting power (HTP) in nematic host mixtures. In particular cases, structural features on the molecular level of dopants in relation to host constitution will be discussed. On the other hand, macroscopic properties, such as dynamic and dielectric data of achiral host systems, have been considered to find out practically useful guidelines for tailoring chiral LC guest–host systems. The studies include recording of nuclear magnetic resonance (NMR) spectra to study the dependence of helicity induction on the configuration of stereogenic center. Further, some photostability tests of cholesteric mixtures reflecting light in the visible range have been undertaken with regard to exploiting these dopants in electro-optic liquid crystal devices such as cholesteric bistable displays.

KEYWORDS
Chiral aminoalcohols; dielectric spectroscopy; dynamic properties; NMR; photostability

1. Introduction

Chiral doping agents play an important role for the preparation of helically ordered liquid crystalline (LC) phases using achiral host compounds or mixtures. Most prominent examples are the reorganization of nematic compounds into cholesteric (chiral nematic) LC phases (CLC) [1], including the preparation of blue phase (BP) materials [2] and smectic C systems into ferroelectric ones [3]. By this doping procedure, the variety of optically active LC materials created from achiral systems has been enormously extended. First, a principal reason for considerable interest arises from the endeavor to understand the induction of phase chirality even at very low numbers of chiral guest particles. As an extreme example, one guest molecule of a bis-chelated imine-alkoxytitanium complex is sufficient for converting 740 molecules inside the nematic phase of 4-n-butyl-N-(4-methoxy-benzylidene)aniline (MBBA) into the cholesteric one [4]. Second, a series of important electro-optic applications require chiral twisting agents such as bistable LC displays (LCDs) fabricated from either cholesteric (CLCDs) [5] or surface-stabilized smectic C* phases (FLCDs) [6].

CONTACT Lutz Hartmann ✉ lutz.hartmann@pyco.fraunhofer.de 🖃 Fraunhofer PYCO Kantstr. 55 D-14513 Teltow, Germany
© 2016 Taylor & Francis Group, LLC

Historically, relative simple natural products, e.g. l-menthol [7], have been used as dopants. Since then, a huge number of chiral additives of miscellaneous chemical provenience and different induction efficiency have been synthesized; for a general survey see Eelkema and Feringa [8]. Considering application aspects, particularly with regard to electro-optic LC devices, such additives have to fulfil predefined specifications. These are mainly directed at high chirality transfer efficiency, sufficient solubility in the host material even at low temperatures and chemical as well as photostability. Special aspects concern the use of dopants with opposite handedness for color variation in CLCDs [9] and of pairs of identical chemical constitution but different configuration for contrast enhancement in monochrome multilayer CLCDs [10]. Tests revealed that only the fewest compounds recommended in the literature meet the requirements of application under stringent conditions [11].

Therefore, the search for suitable additives to formulate chiral LC phases is still an actual challenge. For that, it is desirable to access commercially obtainable auxiliaries to broaden the chiral basis. Apart from derivatives of carbohydrates [12], tartaric acid [13], and bi-2-naphthol [14], enantiomerically pure pharmaceutical products, especially nonsteroidal anti-inflammatory [15] or sympathomimetic drugs, such as the amphetamines [16, 17], have attracted rising interest.

For in-depth studies of structure–activity relationships, we synthesized further derivatives of ephedrine and pseudoephedrine with systematically altered promesogenic substituents. The target substances have been investigated as solutes in an achiral nematic mixture with regard to substituent effects, for instance the distance between chiral centers and LC cores, on the molar helical twisting power, HTP_x [16]. Dynamic and dielectric properties of different common nematic mixtures were related to their aptitude for helix formation by doping. Further, attempts have been made to improve the UV stability of doped systems.

2. Experimental

2.1. *Materials*

The molecular structure of the investigated dopants is characterized by enantiomerically pure 1-phenyl-2-aminoalcohols as central chiral units endowed with two asymmetric C atoms and equipped with two substituents R^1 and R^2 in N, O positions. The target dopants were prepared via simultaneous or sequential acylation of the starting aminoalcohols with mesogen affine acid chlorides [16].

Figure 1 illustrates the linking of R^1 and R^2 tails to the chiral center; see also Bauer et al. [17]. Some of the carboxylic acids used for the acylation of respective aminoalcohols were in stock or commercially available: trans-(4-n-pentylcyclohexane)carboxylic acid [18],

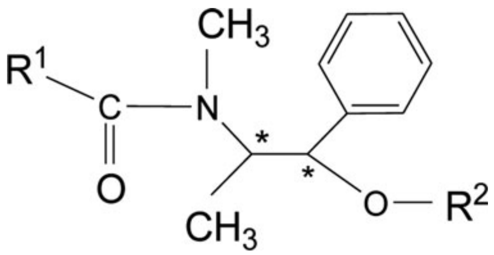


Figure 1. General formula of target dopants.

4-cyanobenzoic acid (Aldrich), 4′-cyano(1,1′-biphenyl)-4-carboxylic acid (ABCR), all-trans-4′-n-pentyl-bicyclohexyl-4-carboxylic acid (Synthon), 9-fluorenecarboxylic acid, and (S)-2-(6-methoxy-2-naphthyl)propionic acid (Naproxen^{TM}) (Aldrich). Others were re-synthesized according to the recipes given in the literature: 4-(4-cyanobenzoyloxy)benzoic acid [19], 3-(4-(cyanobenzoyloxy)benzoyloxy)benzoic acid [20], 2,5-bis(4-n-propyloxybenzoyloxy)benzoic acid [21], 4-(2,2-dicyanoethylene)benzoic acid from 4-formylbenzoic acid, and malononitrile as described in [22]. 3,5-bis(6-(4′-cyanobiphenyl-4-oxy)hexyloxy)benzoic acid was prepared in variation of a known pathway [23]: 4′-hydroxybiphenyl-4-carbonitril → 4′-(6-bromohexyloxy)biphenyl-4-carbonitril (Cr (N 66°C) 67°C I; where Cr = crystalline, N = nematic, I = isotropic) → 3,5-bis(6-(4′-cyanobiphenyl-4-oxy)hexyloxy)benzoic acid methylester (Cr (N 78°C) 104°C I) → target acid (Cr (N 117°C) 169–172°C I). 4-(4-(5-n-heptyl-2-pyrimidinyl)phenoxycarbonyl)benzoic acid (Cr 196–199°C N 278–280°C I) was obtained by the Steglich esterification of 4-(2-(5-n-heptylpyrimidinyl))phenol with 4-formylbenzoic acid followed by oxidation with sodium chlorite [24].

In some cases, the afforded crude products were crystalline and could be refined by recrystallization. The melting temperatures are listed in Table 1 together with the structure of substituents R^1, R^2, and the configuration of starting aminoalcohols (A). Otherwise, the end products were obtained as vitreous solids or waxes after column chromatographic separation by elution with toluene/ethyl acetate of graded mixing ratio. Generally, these showed a very low crystallization tendency.

As a common nematic host, a multi-component mixture MLC-6650 (Merck) has been used. To study the dependence of HTP_x of a given dopant on host medium, four other proved nematic room temperature mixtures were involved: ZOC-5217XX (JNC Co.), E7 (Merck), Mi3, and Mi5. The composition and properties of the last two are given in Table 2. For HTP_x calculation in the case of commercial mixtures with unknown composition (MLC-6650, ZOC-5217XX), a mean molar mass of 300 g/mol has been assumed.

The commonly used twisting agents CB15 and ZLI-4571 (Merck) served for comparing photostability tests.

2.2. *Methods*

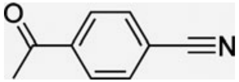
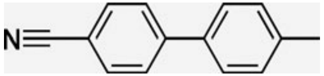
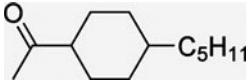
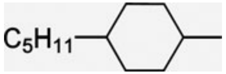
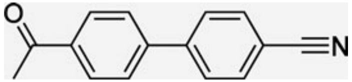
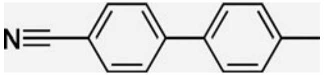
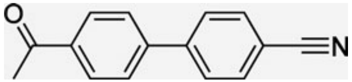
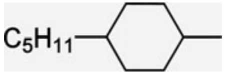
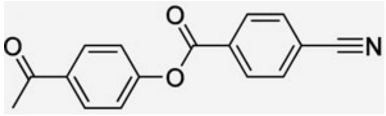
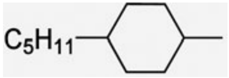
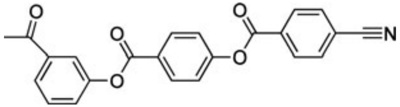
To observe the mixing behavior, phase transitions, and properties of the dopant-induced cholesterics, a polarization microscope Nikon Labophot 2, equipped with a Linkam THMS 600E heating stage, was used.

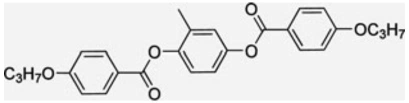
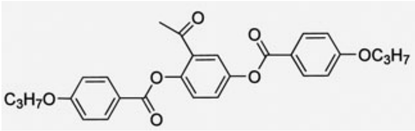
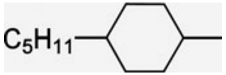
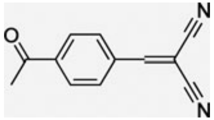
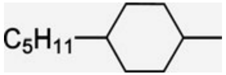
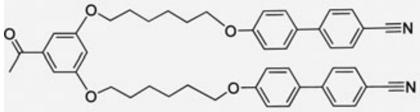
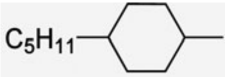
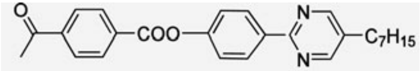
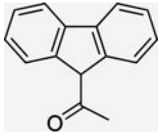
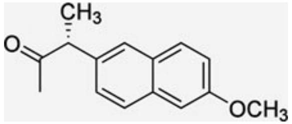
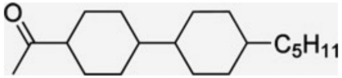
From the position and shift of disclination lines formed in wedge glass cells (E.H.C.) filled with solutions of about 1 wt% of dopant in nematic host, the screw sense [27] of helical structures, their pitch p, and its temperature dependence were determined. With $HTP_x = (dp^{-1}/dx)_{x=0} \approx 1/(px)$ (x is dopant's molar fraction), the HTP_x was estimated for each compound.

The structures of intermediates and products were analyzed using ^1H and ^{13}C NMR spectroscopy (Agilent 500 MHz, solvent $CDCl_3$) and FTIR spectroscopy (Nicolet 5700 equipped with an ATR-unit, Thermo Fisher Scientific Inc.).

Spectra of the dielectric loss ε'' of all nematic hosts in a frequency range of 10^7 Hz to 5×10^{-2} Hz were recorded at 20°C by a Novocontrol Concept 80 System. Sample capacitors were prepared by placing a droplet of nematic mixtures on a brass electrode with a diameter of 20 mm. The second electrode (10-mm diameter) was separated by glass fiber spacers (diameter

Table 1. Constituents of dopants (cf. Fig. 1).

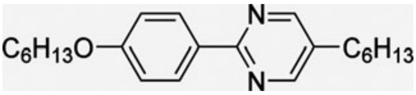
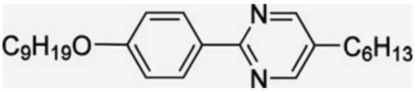
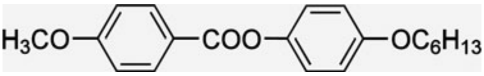
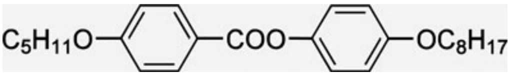
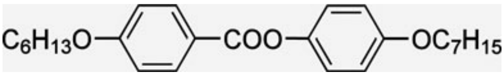
Code	R^1	A*	R^2	M_p (°C)
I		(1S,2S) – (+)		94–96
II		(1R,2R) – (–)		127–129
III		(1R,2S) – (–)		50–53
IV		(1R,2R) – (–)		109–113
V		(1R,2R) – (–)		
VI		(1R,2R)– (–)		

VII		(1R,2R) – (–)		79–81
VIII		(1R,2R) – (–)		
IX		(1S,2S) – (+)		
X		(1R,2R) – (–)		110–113
XI		(1R,2R) – (–)		
XII		(1S,2S) – (+)		126–128
XIII		(1R,2R) – (–)		81–82

---

*A denotes the configuration of chiral aminoalcohols.

Table 2. Properties of nematic hosts Mi3 and Mi5.

Code	Structure	Mol (%)	Thermal properties (°C)	Lit.
Mi3		68.5	Cr 4 N 60 Is	[25]
		31.5		
Mi5		24	Cr 5–10 N 68 Is	[26]
		27		
		12		
		37		

100 µm) placed into liquid samples. The relaxation times $\tau_{\max}$ listed in Table 4 were determined by fitting to the data a superposition of a conductivity contribution and model functions according to [28].

Bulk viscosities based on torsional shear flow were measured using a Dynamic Rotary Rheometer SR200 (Rheometrics, Inc.) with unaligned samples at 20°C. The results served solely as comparative data for selected basic host mixtures; see Table 4.

The experimental setup for photostability tests has been described previously [16]. The recording of transmittance spectra was confined to the middle of the sample area to minimize oxidation and humidity effects.

3. Results and Discussion

The $\mathrm{HTP_x}$ data obtained microscopically at room temperature are listed in Table 3.

Generally, compared with the $\mathrm{HTP_x}$ values of standard chiral dopants in MLC-6650 (S-4′-(2-methylbutyl)-4-cyanobiphenyl (CB15) 5.7 $\mu\mathrm{m}^{-1}$ [17]; 1,4;3,6-dianhydro-D-sorbit-2,5-di-(6-n-hexyloxy-2-naphthoic acid)ester 114 $\mu\mathrm{m}^{-1}$ [11]), the listed values appear to be in an acceptable range.

Table 3. $\mathrm{HTP_x}$ values of dopants listed in Table 1 in the nematic host MLC-6650 at 20°C.

Code	$\mathrm{HTP_x}$ ($\mu\mathrm{m}^{-1}$)	Code	$\mathrm{HTP_x}$ ($\mu\mathrm{m}^{-1}$)
I	−12	VIII	−59
II	−40	IX	15
III	−42	X	−104
IV	29	XI	23
V	−89	XII	−3
VI	−22	XIII	−66
VII	28		

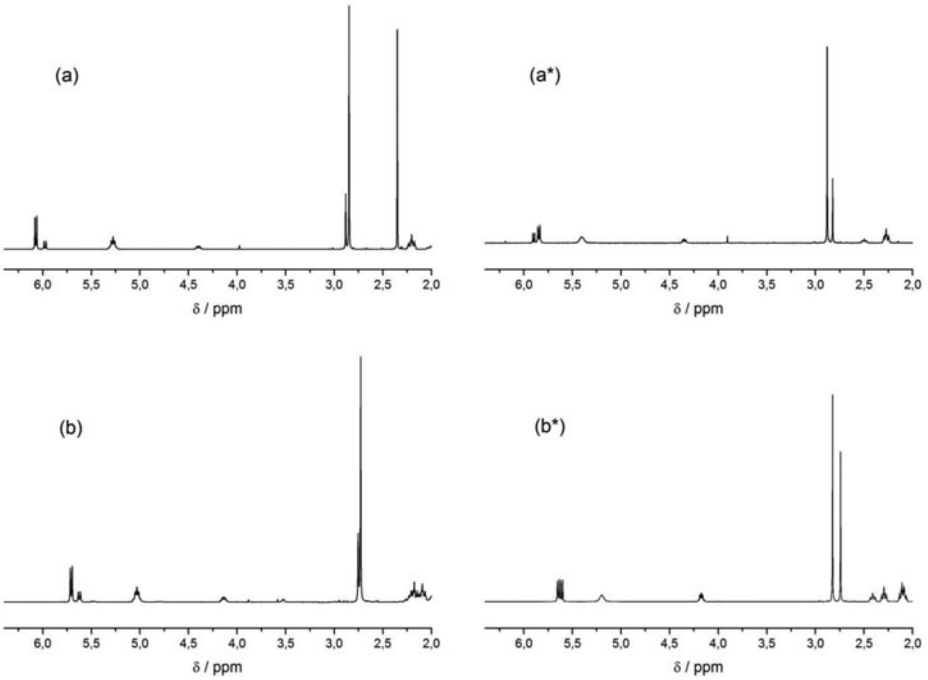
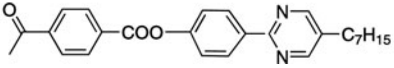


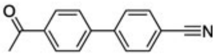
Figure 2. NMR spectra of diastereomeric dopant pairs: (a) “(1R,2S)-2-(N-(4-trans-n-pentylcyclohexylcarbonyl)methylamino)-1-(4′-cyano-1,1′-biphenyl-4-carbonyloxy)-1-phenylpropane (**III**), (a*) “the diastereomeric analog (1R,2R) – (–) [16], (b) “(1R,2S)-2-(N-(4-trans-n-pentylcyclohexylcarbonyl)-methylamino)-1-(4-trans-n-pentylcyclohexylcarbonyloxy)-1-phenylpropane [17], (b*) “the diastereomeric analog (1S,2S) – (+) [17]. For a better overview, only the range between 2 ppm and 6.7 ppm is presented.”

With respect to the twisting power, it seems to be reasonable to discuss the following different interfering factors:

1. The effect of the configuration of central chiral unit demonstrated, for instance, by the substitution of ephedrine by its diastereomer pseudoephedrine. As the comparison of **III** (configuration (1R,2S) – (–)) with the diastereomeric isomers ((1R,2R) – (–) and (1S,2S) – (+); **Id** and **Ie** in [16]) shows, this substitution yields a considerable increase in HTP_x from $-42\ \mu m^{-1}$ to $-99\ \mu m^{-1}$ and $100\ \mu m^{-1}$, respectively.
   Nuclear magnetic resonance (NMR) studies display that the replacement is connected with a change in conformational dynamics, especially with respect to relative stability and exchange rates of rotamers attributed to the hindered rotation around the -N-CO- partial double bond [17]. As revealed in Fig. 2 (a/a* and b/b*), the intensity ratio of unequal double signals at ~2.8 ppm and ~5.9 ppm is reversed by the alteration of stereogenic centers. Furthermore, the difference in resonance frequencies of conjugated peaks at ~2.8 ppm (NCH_3) increases with the substitution of ephedrine by pseudoephedrine core: From 14 Hz to 29 Hz (Fig. 2(a) and (a*)) and from 10 Hz to 41 Hz (Fig. 2(b) and (b*)).
2. The structure and position of promesogenic substituents at the same chiral core.
   (i) By exchange of the N- and O-substituents of dopant **II** (cyanobiphenyl unit in N-position) leading to an isomeric compound bearing cyanobiphenyl unit in O-position (**Id** in [16]), a distinct rise of HTP_x from $-40\ \mu m^{-1}$ to $-99\ \mu m^{-1}$ is observed.

Table 4. Compilation of HTP_x values of dopants **X** and **Ie** [16] in five different nematic basic mixtures together with their viscosities η, dielectric relaxation times τ_{max}, and dielectric anisotropies $\Delta\varepsilon$ at 20°C

X: R2 =


Ie: R2 =


	ZOC-5217XX	E7	MLC-6650	Mi3	Mi5
η (mPas)	23.5	55	100	125	225
τ_{max} (s)	1.3×10^{-7}	5.9×10^{-8}	2.2×10^{-7}	1.7×10^{-6}	6×10^{-6}
$\Delta\varepsilon$	8.8 [33]	14.3 [34]	52.6 [34]	0.7* [35]	−0.7 [36]
X: HTP_x (μm^{-1})	−109	−108	−104	−44	−61
Ie: HTP_x (μm^{-1})	108	88	100	49	53

* estimated from $\Delta\varepsilon$ of pure mixing components

(ii) In accordance with the well-known experiences, e.g. [14], at a given R^1, with increasing longitudinal elongation of the second substituent, a clear rise in HTP_x is observed; compare R^2 in **I** (4-cyanophenyl) → **Id** (4′-cyano(1,1′-biphenyl) [16]) → **V** (4′-cyanobenzoyloxy-4-phenyl) → **X** (4-(4-(5-n-heptyl-2-pyrimidinyl)phenoxycarbonyl)phenyl) and **Ib** (trans-4-n-pentylcyclohexyl [16]) → **XIII** (all-trans-4-n-pentyl-1,1′-bicyclohexyl) (see Tables 1 and 3).

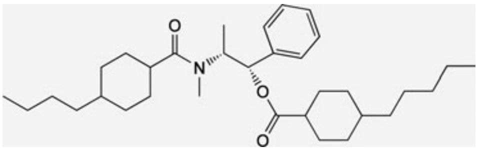
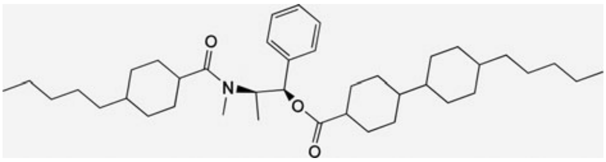
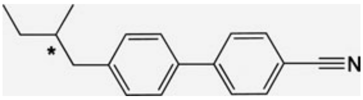
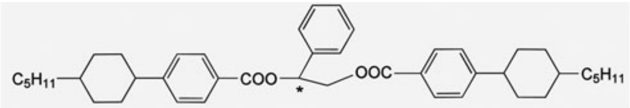
(iii) In case of lateral linking of a rod-like substituent R^2, a distinct reduction in chirality transfer is caused, see **VI** and **VII**.

(iv) An important factor is the distance between the promesogenic part of R^2 and the stereogenic center. The low HTP_x value of dopant **IX** is obviously due to C_6H_{12} spacers. The same has been observed with other dopant classes, e.g. with axially chiral binaphthyl derivatives [29].

3. Generally, far below the isotropization temperature, the helical twisting power of a dopant depends strongly on host LC [11, 17, 30, 31]. It is assumed that this dependence is governed by a favorable structural match between chiral dopant and host molecules via core–core interaction [30]. However, it seems that such specific interactions play a minor role, otherwise the minimal HTP_x of dopant **X** containing a pyrimidinylphenyl unit as solute in Mi3 is hard to understand (see Table 4). From the practical point of view, it is desirable to have correlations or at least rules of thumb involving macroscopic material data of hosts. According to this concern, HTP_x of two dopants with very different structure and polarity of substituent R^2 (**X** and **Ie** in [16]) dissolved in five different nematic basic mixtures has been measured. The results are given in Table 4 together with bulk viscosities η, dielectric anisotropies $\Delta\varepsilon$, and dielectric relaxation times τ_{max} of basic mixtures at 20°C. τ_{max} corresponds to the reorientation around long molecular axis, and is therefore a measure of molecular mobility in nematic hosts. Definitely, involving twist elastic constants K_{22} as well as rotational viscosities γ in this compilation should be reasonable. Unfortunately, for the mixtures in question, only few and strongly varying K_{22} and γ data are available. However, it seems that an approximate correlation exists between bulk and rotational viscosities [32].

Although no absolute correlation can be seen between the helix induction and the characteristic data of basic mixtures given in Table 4, some general tendencies are obvious. Thus, the chirality transfer will be facilitated by low bulk (rotational) viscosities and high molecular mobility. The results suggest that the twisting power of guest molecules is essentially controlled by the dynamic material parameters of host medium. On the other hand, minor differences between the HTP_x data at a given host medium suggest that specific molecular interactions are less involved.

Table 5. Content and resulting initial reflection wavelengths $\lambda_{min,0}$ of various dopants in CLC samples prepared with MLC-6650 as nematic basic mixture.

Code	Content (wt%)	$\lambda_{min,0}$ (nm)	Structure	
P1	12.3	497		PE-2Cy [17]
P2	7.7	587		**XIII**
P3	33.7	710		CB15
P4	7.0	560		ZLI-4571

An important criterion for the use of a material inducing helix structures in LC phases is light insensitivity [16, 37]. Especially the photo tuning of reflection notch of CLC mixtures containing photosensitive admixtures, such as azobenzene compounds, requires the availability of light-insensitive dopants [38]. It is expected that structures mainly comprising alicyclic ring systems possess a particular high photostability. This is confirmed by the results obtained with CLC samples prepared from MLC-6650 as common, photostable host [39] and four different dopants; see Tables 5 and 6. Except ZLI-4571, the sun simulator irradiation caused a red shift ($\Delta\lambda_R > 0$) of reflection notches relative to initial reflection wavelengths ($\lambda_{min,0}$). In comparison with familiar and commonly used twisting agents CB15 and ZLI-4571, the pseudoephedrines with substituents comprising cyclohexane units (P1 and P2) stand out due to a remarkably high light stability.

In conclusion, continuing the synthesis and characterization of mesogenic derivatized 1-phenyl-2-aminoalcohols to broaden the pool of practically usable chiral dopants for electro-optical applications, several new compounds are presented. Based on selected examples, the dependence of twisting ability on the configuration of stereogenic center, on the structure and

Table 6. Shift of reflection maximum $\Delta\lambda_R$ after a sun simulator illumination (100 mW cm^{-2}) for an exposure time t_{ex} as indicated.

	$\Delta\lambda_R$ (nm)			
t_{ex} (h)	P1	P2	P3	P4
6	4	6	25	−3
20	5	9	33	−32

position of pro-mesogenic substituents, and on the distance between LC promoting building units and the central chiral unit has been revealed. The compilation of macroscopic properties of achiral LC basic materials, such as dielectric anisotropies, viscosities, and dielectric relaxation times with their twistability by chiral dopants, yields a correlation to a certain extent. Compared with conventional twisting agents, photostability tests of cholesteric mixtures prepared with dopants containing mainly hydroaromatic ring structures showed an enhanced light insensitivity.

Acknowledgments

We are indebted to R. Stannarius (Magdeburg), H. Kresse (Halle), and M. Gwiazda (Teltow) for many useful hints and discussions. The authors also thank A. Fujita (JNC Co.) for supplying LC material.

Funding

Financial support by the German Federal Ministry of Economics and Technology within the aeronautical research project "INGA – Innovative Galley" (20K1103D) is highly acknowledged.

References

[1] Buckingham, A. D., Ceasar, G. P., & Dunn, M. B. (1969). *Chem. Phys. Lett.*, *3*, 540.
[2] Yoshizawa, A. (2013). *RSC Adv.*, *3*, 25475.
[3] Hird, M. (2014). Designing Principles, Synthesis, and Properties of Smectic C Host Materials for Ferroelectric Liquid Crystals. In: *Handbook of Liquid Crystals*, Goodby, J.W., Collings, P.J., Kato, T., Tschierske, C., Gleeson, H., & Raynes, P. (Eds.), Vol. 8, 237-262. Wiley-VCH: Weinheim, Germany.
[4] Braun, M., Hahn, A., Engelmann, M., Fleischer, R., Frank, W., et al. (2005). *Chem. Eur. J.*, *11*, 3405.
[5] Greubel, W., Wolff, U., & Krüger, H. (1973). *Mol. Cryst. Liq. Cryst.*, *24*, 103.
[6] Clark, N. A., & Lagerwall, S. T. (1980). *Appl. Phys. Lett.*, *36*, 899.
[7] Stegemeyer, H., & Mainusch, K. J. (1970). *Chem. Phys. Lett.*, *6*, 5.
[8] Eelkema, R., & Feringa, B. L. (2006). *Org. Biomol. Chem.*, *4*, 3729.
[9] Liu, Y.-J., Wu, P.-C., & Lee, W. (2014). *Mol. Cryst. Liq. Cryst.*, *596*, 37.
[10] Makow, D. M. (1980). *Appl. Opt.*, *19*, 1274.
[11] Bauer, M., Boeffel, C., Kuschel, F., & Zaschke, H. (2006). *J. Soc. Inform. Display*, *14*, 805.
[12] Vill, V., Fischer, F., & Thiem, J. (1988). *Z. Naturforsch.*, *43a*, 1119.
[13] Kuball, H. G., Weiss, B., Beck, A. K., & Seebach, D. (1997). *Helvetica Chim. Acta*, *80*, 2507.
[14] Holzwarth, R., Bartsch, R., Cherkaoui, Z., & Solladie, G. (2004). *Chem. Eur. J.*, *10*, 3931.
[15] Jeeva, S., Cowling, S. J., Raynes, E. P., & Goodby, J. W. (2009). *Liq. Cryst.*, *36*, 1193.
[16] Kuschel, F., Hartmann, L., Bauer, M., & Weissflog, W. (2014). *Mol. Cryst. Liq. Cryst.*, *588*, 51.
[17] Bauer, M., Hartmann, L., Kleinpeter, E., Kuschel, F., Pithart, C., et al. (2015). *Mol. Cryst. Liq. Cryst.*, *608*, 14.
[18] Schubert, H., Uhlig, V., & Dehne, R. (1972). *Zeitschrift für Chem.*, *12*, 219.
[19] Davidson, P., & Strzelecki, L. (1988). *Liq. Cryst.*, *3*, 1583.
[20] Tamba, M. G., & Weissflog, W. (2015). Unpublished manuscript.
[21] Jacobi, A., Pirwitz, G., & Weissflog, W. (1998). *Proceedings of SPIE*, *3319*, 249.
[22] Gazit, A., Yaish, P., Gilon, C., & Levitzki, A. (1989). *J. Med. Chem.*, *32*, 2344.
[23] Kouwer, P. H. J., & Mehl, G. H. (2003). *Mol. Cryst. Liq. Cryst.*, *397*, 301.
[24] Achten, R., Koudijs, A., Giesbers, M., Marcelis, A. T. M., & Sudholter, E. J. R. (2005). *Liq. Cryst.*, *32*, 277.
[25] Zaschke, H., Schubert, H., Kuschel, F., Dinger, F., & Demus, D. (1971). Patent GDR No. WP 95892.
[26] Deutscher, H.-J., Weissflog, W., Demus, D., & Pelzl, G. (1970). Patent GDR No. WP 86269.
[27] Gerber, P. R. (1980). *Z. Naturforsch.*, *35a*, 619.
[28] Havriliak, S., & Negami, S. (1967). *Polymer*, *8*, 161.
[29] Goh, M., & Akagi, K. (2008). *Liq. Cryst.*, *35*, 953.
[30] Kobayashi, K., & Yoshizawa, A. (2007). *Liq. Cryst.*, *34*, 1455.

[31] Rejmer, W., Czuprynski, K., & Drzewinski, W. (2011). *Mol. Cryst. Liq. Cryst.*, *547*, 33.
[32] Junge, M. (1998). *Physical Properties of Liquid Crystals: VII. Viscosities of Nematic Liquid Crystal Materials*, Newsletter, Merck KGaA.
[33] *Preliminary data sheet: LIXON^{TM}*, JNC Co., 2015.
[34] *Technical data sheets: Licristal^{TM}*, Merck KGaA, 2008.
[35] Kresse, H., Schmidt, P., & Demus, D. (1975). *Phys. Status Solidi Appl. Res.*, *32*, 315.
[36] Kresse, H. (1973). Unpublished data.
[37] Wen, C. H., Gauza, S., & Wu, S. T. (2005). *J. Soc. Inform. Display*, *13*, 805.
[38] Hrozhyk, U. A., Serak, S. V., Tabiryan, N. V., & Bunnin, T. J. (2008). *J. Appl. Phys.*, *104*, 063102.
[39] Kuschel, F., Hartmann, L., & Bauer, M. (2010). *J. Appl. Polymer Sci.*, *117*, 1486.