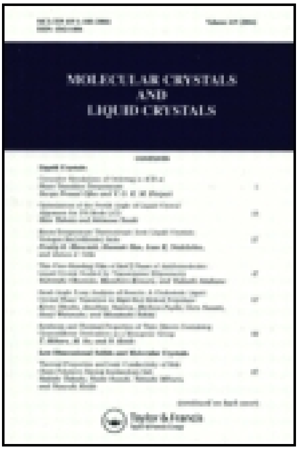

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

New N-Arylidene (S)-1-Phenylethylamines as the Components of Induced Short-Pitch Cholesterics

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To cite this article: L. A. Kutulya, G. P. Semenkova, N. I. Shkolnikova, V. V. Vashchenko, L. L. Ostis, V. M. Sorokin & A. G. Kozachenko (2001): New N-Arylidene (S)-1-Phenylethylamines as the Components of Induced Short-Pitch Cholesterics, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 357:1, 43-54

To link to this article: http://dx.doi.org/10.1080/10587250108028243

Mol. Cryst. Liq. Cryst., Vol. 357, pp. 43-54
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Printed in Malaysia

New N-Arylidene (S)-1-Phenylethylamines as the Components of Induced Short-Pitch Cholesterics

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(Received November 23, 1999; In final form April 05, 2000)

New N-arylidene (S)-1-phenylethylamines with ester group in arylidene fragment have been synthesized. The chiral dopants helical twisting power and temperature dependence of the induced cholesteric helical pitch in LC systems based on 4-pentyl-4′-cyanobiphenyl have been studied as well as selective light reflection spectra and their temperature dependences for systems including nematic E63 (Merck) and new chiral components. An influence of the chiral dopant molecular structure on the mentioned characteristics of LC systems investigated was revealed. The induced cholesteric compositions with temperature-independent selective light reflection in visible range have been obtained.

Keywords: N-arylidene (S)-1-phenylethylamines; chiral compounds; helical twisting power; induced short-pitch cholesterics; selective light reflection spectra; helical pitch temperature dependence

INTRODUCTION

The elaboration of short-pitch chiral nematic compositions is of importance for development of bistable LC devices based on diffractive properties of surface stabilized cholesteric texture [1]. Moreover, the temperature independence of induced helical pitch is a crucial factor and one of main requirements for LC materials to operate in such kind electrooptical devices. In this connection, taking into account data on the chiral components molecular structure effect on characteristics of induced cholesteric (N^*) systems (see, e.g., [2–13]), we synthesized two series of new N-arylidene (S)-1-phenylethylamines **1** and **2**:

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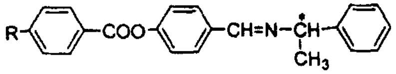
* Corresponding Author.



1, R = H, C_nH_{2n+1} (n = 1 – 4);

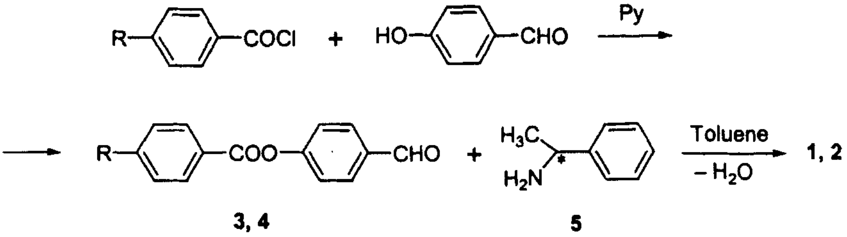
2, R = OC_mH_{2m+1} (m = 1 – 3, 5, 10)

The helical twisting power (β) of chiral dopants (CD) **1**, **2** and temperature dependences of the induced N^* helical pitch (*P*) for LC systems based on 4-pentyl-4′-cyanobiphenyl (5CB) were studied. Moreover, the selective light reflection spectra as well as their temperature dependences for systems containing E63 nematic liquid crystal (Merck) and the chiral dopants mentioned were obtained.

EXPERIMENTAL

Materials

The studied chiral compounds **1** and **2** were synthesized by refluxing of corresponding aldehydes **3** and **4** with a small excess of (S)-1-phenylethylamine **5** (see Scheme 1) in toluene under azeotropic water removal during 1 – 1.5 hours as described in [6]. The interaction completeness was checked up by thin-layer chromatography using Silufol UV254 plates.



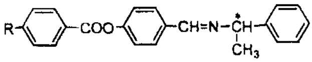
SCHEME 1

The products obtained were purified by recrystallization from hexane. Their purity was checked by high performance liquid chromatography (HPLC). Structures of the compounds obtained have been proved by IR and NMR ^1H spectra (Specord M80 and Varian VXR-300 spectrometers, respectively). The yield, melting point, specific optical rotation ($[\alpha]_D^{20}$) as well as elemental analysis data for the compounds prepared are listed in the Table I. The main IR and NMR ^1H spectral characteristics of the compounds **1** and **2** are presented in the Table II.

TABLE I Characteristics of new N-arylidene (*S*)-1-phenylethylamines **1** and **2**

	R	*Yield (%)*	*M.p. (°C)*	$[\alpha]_D^{20}$ $CHCl_3$	*Elemental analysis*			
					Formular	*C% (calcd)*	*H% (calcd)*	*N% (calcd)*
1a[6]	H	56	95–97	71.7	$C_{22}H_{19}NO_2$	80.19 (80.22)	5.76 (5.81)	4.18 (4.25)
1b[18]	CH_3	65	81.5–82.5	82.7	$C_{23}H_{21}NO_2$	80.50 (80.44)	6.18 (6.16)	4.15 (4.08)
1c	C_2H_5	62	72–72.5	80.0	$C_{24}H_{23}NO_2$	80.69 (80.64)	6.53 (6.49)	4.01 (3.92)
1d	C_3H_7	80	69.5–71	72.1	$C_{25}H_{25}NO_2$	80.74 (80.83)	6.74 (6.78)	3.70 (3.77)
1e	C_4H_9	65	57–59	79.4	$C_{26}H_{27}NO_2$	80.95 (81.01)	7.01 (7.06)	3.58 (3.63)
2a[18]	OCH_3	62	91–92	80.8	$C_{23}H_{21}NO_3$	76.92 (76.86)	5.95 (5.89)	4.05 (3.90)
2b	OC_2H_5	80	70.5–72	80.1	$C_{24}H_{23}NO_3$	77.25 (77.19)	6.30 (6.21)	3.67 (3.75)
2c	OC_3H_7	76	93–94.5	71.8	$C_{25}H_{25}NO_3$	77.42 (77.50)	6.44 (6.50)	3.70 (3.61)
2d	OC_5H_{11}	79	100.5–102	68.8	$C_{27}H_{29}NO_3$	78.12 (78.04)	7.11 (7.03)	3.30 (3.37)
2e[6]	$OC_{10}H_{21}$	78	81.5–82	54.2	$C_{32}H_{39}NO_3$	79.09 (79.14)	8.03 (8.09)	2.79 (2.88)

TABLE II IR and NMR ^1H data for some N-arylidene (*S*)-1-phenylethylamines **1** and **2**



	R	*IR, cm⁻¹ (in CCl₄)*		*δ, ppm (³J, Hz) in CDCl₃*ᵃ			
		$\nu_{C=O}$	$\nu_{C=N}$	*=CH, s, 1H*	*CH₃, d, 3H*	*C*H, quart., 1H*	*R*
1a	H	1746	1649	–	–	–	–
1b	CH_3	1742	1650	8.37	1.60 (6.7)	4.55 (6.5)	2.44, s, 3H
1c	C_2H_5	1743	1649	8.39	1.60 (6.6)	4.56 (6.6)	1.29, t, 3H (7.7) 2.75 q, 2H (7.7)
1d	C_3H_7	1742	1650	–	–	–	–
1e	C_4H_9	1743	1649	–	–	–	–
2a	OCH_3	1739	1650	8.38	1.60 (6.7)	4.56 (6.8)	3.89 (s)
2b	OC_2H_5	1739	1650	8.38	1.60 (6.6)	4.56 (6.5)	1.46, t, 3H (7.0) 4.12 q, 2H (7.0)
2c	OC_3H_7	1738	1650	–	–	–	–
2d	OC_5H_{11}	1738	1648	8.38	1.61 (6.6)	4.56 (6.6)	0.95, t, 3H (7.0); 1.44, m, 4H; 1.83, m, 2H 4.04, t, 2H (6.5)
2e	$OC_{10}H_{21}$	1739	1649	–	–	–	–

a. The aromatic protons appears as set of multiplets of 13H in 7.2 – 8.15 ppm region for compounds **1b**, **1c** and 6.90 – 8.18 ppm region for compounds **2a**, **2b**, **2d**.

For preparation of the chiral imines **1** and **2**, (S)-1-phenylethylamine **5** with $[\alpha]_D^{20} = -39.8°$ was used, that answers to its 97.8 % enantiomeric purity as determined from the maximum value $[\alpha]_D^{20} = -40.7°$ obtained in [14] as well as achieved later in [15, 16]. Under the reaction conditions (heating in toluene), the starting product **5** does not change its specific optical rotation. Therefore, compounds **1** and **2** one can consider to possess the same high enantiomeric purity.

The intermediate aldehydes **3** and **4** were prepared by acylation of 4-hydroxybenzaldehyde using corresponding acylchlorides [6, 17].

Phase transition temperatures of the compounds **3b, d, e** and **4a, c – e** correspond to those given in [17]. No information on compounds **3c** and **4b** has been found. For these compounds prepared by us, m.p. 52 – 53°C, $\nu_{C=O}$ 1694, 1732 cm^{-1} for **3c** and m.p. 125–126°C, $\nu_{C=O}$ 1695, 1732 cm^{-1} for **4b** (in KBr in the both cases) have been determined.

The HPLC analysis was performed on liquid micro-column chromatograph "Milichrom 5–3" using a 2 × 80 mm Silasorb C18 reverse phase column and acetonitrile : water mixture (70 : 30) as the eluent.

Specific optical rotation was measured in $CHCl_3$ solutions at concentration $0.007 \div 0.015$ g/ml using SU polarimeter.

Conformational calculations of molecule **2c** were carried out by the molecular mechanics method with the MMX force field[19].

Measurements of Liquid Crystalline Systems Parameters

P values for LC systems studied at low CD concentrations (from 0.003 to 0.020 mole fraction) were measured using conventional Grandjean – Cano technique as described in the previous report [5]. The helical twisting power values were calculated from $\beta = (PC)^{-1}$ equation, where C is the CD mole fraction.

The selective light reflection spectra as well as their temperature dependences for short-pitch N^* systems including nematic E63 and the CD **1** or **2** (in concentrations presented in the Table III) were recorded using a Hitachi-330 spectrophotometer. The planar aligned samples were used (LC layer thickness was 10 μm). The P values for short-pitch N^* systems based on E63 were determined as $P = \lambda_{max}/n$. The CD helical twisting power in E63 was estimated as $\beta_m = n(\lambda_{max}C_m)^{-1}$, where C_m is CD mass fraction*, n is average refractive index. Here, n value 1.586 was taken according to [20].

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* The CD concentration cannot be expressed here in mole fractions because nature and receipt of components comprising commercial nematic E63 is unknown for us.

TABLE III Some characteristics of the N^* systems including chiral dopants **1** and **2**

	R	*5CB*		*E63*		
		-β, $\mu m^{-1} \times mol.fr^{-1}$	$dP/dT \times 10^4$ μm/degree	λ_{max}, nm, at 30 °C (C, mass %)	-β, $\mu m^{-1} \times mass\ fr^{-1}$	$d\lambda_{max}/dT \times 10^4$ μm/degree
1a	H	34.4 ± 1.5	+121 ± 14	–	–	–
1b	CH_3	34.9 ± 1.6	+18.7 ± 8.6	–	–	–
1c	C_2H_5	33.0 ± 1.2	+74.0 ± 9.6	538 (13.0)	22.8	+4.6 ± 0.3
1d	C_3H_7	31.2 ± 2.0	+52.1 ± 11	598 (12.7)	21.0	+5.8 ± 0.8
1e	C_4H_9	36.0 ± 1.8	+24.6 ± 2.8	490 (14.5)	22.5	+4.6 ± 0.4
2a	OCH_3	35.7 ± 1.8	+28.2 ± 6.8	509 (13.4)	23.4	0.0 ± 0.2
2b	OC_2H_5	35.5 ± 0.8	–47.3 ± 9.4	570 (12.7)	22.1	–0.1 ± 0.3
2c	OC_3H_7	35.2 ± 1.0	–34.2 ± 9.4	578 (12.9)	21.4	–0.4 ± 0.5
2d	OC_5H_{11}	37.2 ± 1.1	–115 ± 12	519 (15.1)	20.4	–5.2 ± 0.1
2e	$OC_{10}H_{21}$	40.4 ± 1.0	–130 ± 20	549 (16.6)	17.5	–12.4 ± 0.4

The sign of chiral dopants helical twisting power was determined in 5CB by measuring the *P* value for ternary mixture which contained both chiral compounds under study and a reference CD with known β value and sign, accounting additivity of 1/*P* value in such cases [5]. As the reference CD, (–)-2-(4-methoxybenzylidene)-*p*-menthane-3-one [3] was used. The identical twisting sign for the CD studied both in 5CB and in E63 was verified by contact method.

RESULTS AND DISCUSSION

Synthesized chiral compounds **1** and **2** induce the left-hand helix in both nematic matrices used. As follows from the Table III, the helical twisting power of these CD does not depend appreciably on the terminal alkyl or oxyalkyl substituent length.

The helical twisting power of CD **1** and **2** is sufficient to obtain LC mixtures based on E63 with selective light reflection in visible range at moderate dopant concentrations (12.7 ÷ 16.6 mass %, see Table III, column 5).

The *P*(*T*) dependences for all investigated LC systems 5CB – CD have been found to be linear at a good approximation (correlation coefficients are 0.95÷0.99) over the whole studied temperature range starting from 3 – 4° below the $N^* \rightarrow I$ phase transition (see Figure 1). These dependences were quantified using the *P*(*T*) function slope (the *dP*/*dT* values, Table III, column 4). In a similar way, temperature dependences of the selective light reflection λ_{max} in nematic E63 (see Figure 2) were characterized by the $d\lambda_{max}/dT$ parameter (Table III, column 7).

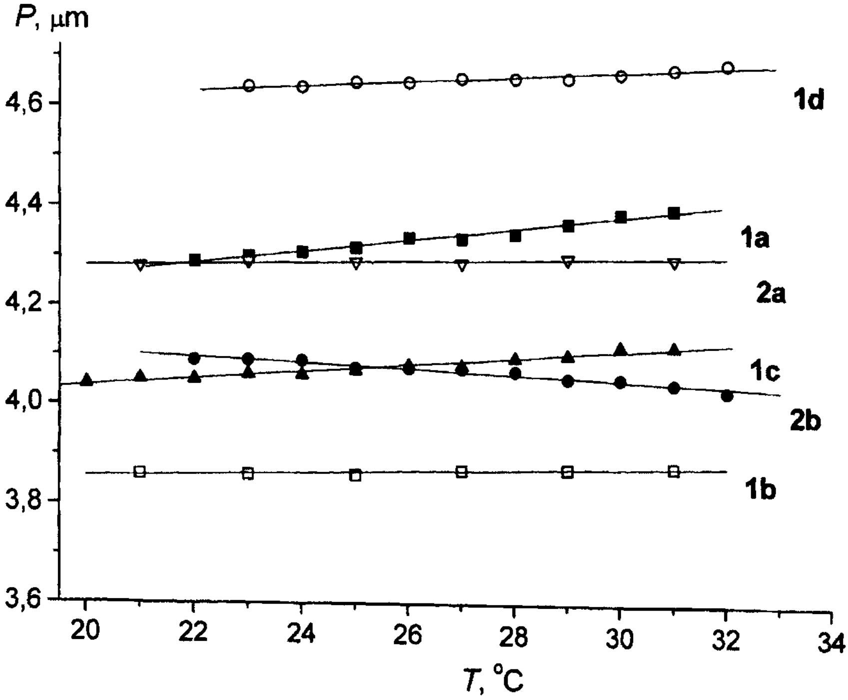


FIGURE 1 The temperature dependences of the induced helical pitch for LC systems based on 5CB containing chiral dopants of the **1** and **2** series. A number of curve corresponds that for the chiral compound in the Tables I – III

The substituent R in the CD molecule influences noticeably the temperature dependence character of induced helical pitch characterized by the sign and magnitude of dP/dT or $d\lambda_{max}/dT$. In the case of LC systems including CD **1a** – **1e** with R being H or alkyl and for CD **2a** (R is methoxy group), the P value increases or remains rather constant as the temperature rises ($dP/dT > 0$ or $d\lambda_{max}/dT \geq 0$). For 5CB-based LC systems, this effect is weakened considerably (dP/dT decreases) if the terminal hydrogen atom in the compound **1a** is replaced by an alkyl (CD **1b** – **1e**) or methoxy group (compound **2a**).

In contrast, in the case of LC compositions based on both used nematic liquid crystals but containing chiral compounds **2b** – **2e** with oxyalkyl substituents, the P value decreases as the temperature rises ($dP/dT < 0$ or $d\lambda_{max}/dT < 0$). That effect becomes more pronounced as the oxyalkyl chain length in the CD molecule increases. Similar distinctions are observed also for the $d\lambda_{max}/dT$ parameter in the case of LC systems based on E63 (Table III). However, it should be noted

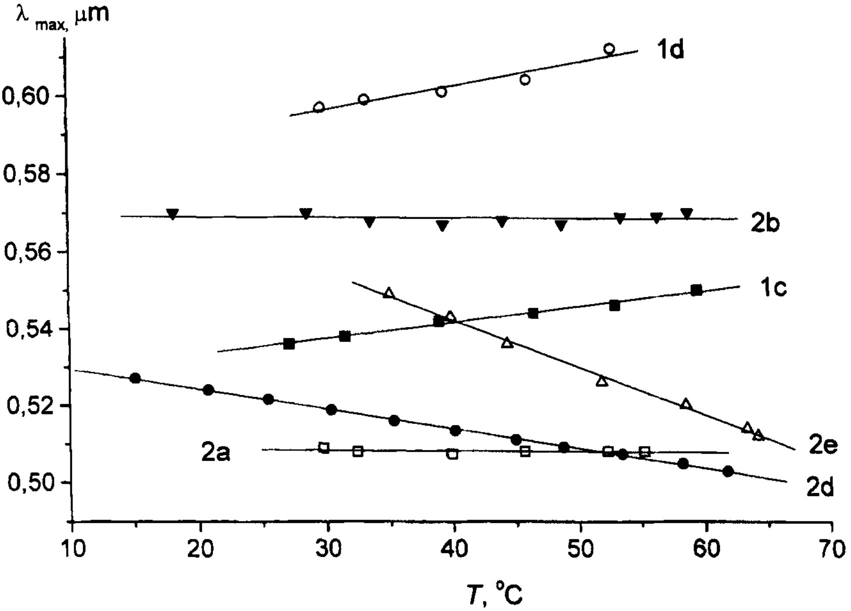


FIGURE 2 The temperature dependences of the selective light reflection λ_{max} for LC systems on the base E63 nematic containing chiral dopants of the **1** and **2** series. A number of curve corresponds that for the chiral compound in the Tables I – III

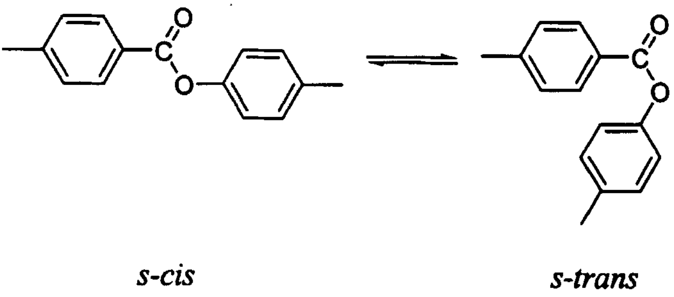
that for compositions E63 – CD **1c** – **1e** with alkyl substituents (C_2H_5 – C_4H_9), the parameter $d\lambda_{max}/dT$ is essentially independent of the alkyl chain length.

Molecules of compounds studied have chain-like structures and introduction or lengthening of the terminal alkyl group no doubt results in their anisometry increase. Then, the molecular anisometry variations in the studied CD series influence essentially the temperature dependence character of the induced helical pitch and dP/dT parameter as its quantitative characteristic. As one can see from the Table III, the least anisometric unsubstituted CD **1a** of the series studied exhibits the highest positive dP/dT value which decreases then as the molecular anisometry rises due to the terminal alkyl group lengthening (Table III, CD **1c** – **1e**). In the case of the compound **2b**, the dP/dT (or $d\lambda_{max}/dT$) parameter changes its sign and becomes then more negative as alkyl chain lengthens in the series **2** of alkyloxy substituted CD. Still more negative dP/dT values, namely $(-170 \div -370)\times10^{-4}$ μm/degree, were observed in 5CB for the analogs of compounds **1** containing three-ring benzoate fragment and, consequently, having more anisometric molecules [7].

Thus, the results obtained confirm the assumption [7] that the chiral dopants molecular anisometry influences the temperature dependence character of the induced cholesteric helical pitch. It should be noted that different microscopical models of helical twisting in cholesteric LC (see, e.g., [13, 21 - 24]) explain either increase or decrease of *P* value as temperature rise. However, none of them predicts a smooth variation of the *dP/dT* parameter and its sign inversion as the CD molecular anisometry rise in the series of the structurally similar compounds.

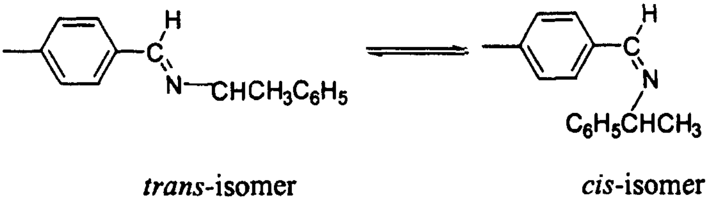
In general, regularities observed for the *dP/dT* parameter can be caused by different effects. On the one hand, conformational transformations of the CD molecules are possible. On the other hand, the CD introduction into LC can result in changes of the ordering extent and K_{22} elastic constant associated therewith.

For studied chiral compounds, *s-cis-* and *s-trans*-conformers of the ester fragment are capable to exist (see Scheme 2).



SCHEME 2

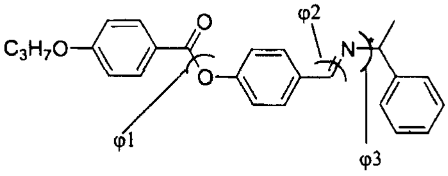
As it is well known from X-ray structure studies (see, e.g.,[25-27]), ester compounds in the crystals have preferable and more anisometric *s-cis*-conformation. The molecular mechanics simulations carried out by us (for example of the compounds **2c**) show that the energies of the mentioned conformers differ by more than 2 kcal/mole (see Table IV, respective conformers *a* – *d* and *e* – *h* having different torsion angle φ1 and like angles φ2 and φ3). Therefore, only a very slight shift of the conformational equilibrium position (Scheme 2) can be expected in the temperature range 20 – 60°C (increase of the minor *s-trans*-conformers fraction from 1.5 to 3.0 %, Table IV). It is also true for thermal *trans-cis* isomerization with respect to imine group (Scheme 3). In this case, *trans*-isomers *a* – *d* are much more energy preferable than *cis-* ones *j* – *k* (by more than 4 kcal/mole, see Table IV) which are absent practically in equilibrium system.



SCHEME 3

At last, it should be noted that conformational transformations associated with internal rotation about N-C* bond (torsion angle φ_3, Table IV) can take place, too. However, as it was shown in [6], these conformational transitions are not accompanied by any essential change in the molecular anisometry (or statistical molecular shape) and, consequently, in the CD helical twisting power.

TABLE IV Results of the conformational simulations for compound **2c**



	Conformer				*Mol. % of conformers at different temperatures*				
	E, kcal/mole	*Torsion angles*			*273 K*	*293 K*	*308 K*	*333 K*	*353 K*
		φ1	*φ2*	*φ3*					
a	54.00	−171	−179	−62	46.0	45.1	44.5	43.3	42.4
b	54.02	−169	−180	−152	44.4	43.6	43.0	42.0	41.2
c	55.16	−174	180	65	5.4	6.1	6.6	7.5	8.1
d	55.45	−171	−180	98	3.2	3.7	4.1	4.8	5.3
Total					99.0	98.5	98.2	97.6	97.0
e	56.29	14.4	180	−155	0.7	0.9	1.0	1.3	1.6
f	56.73	16.9	−179	−52	0.3	0.4	0.5	0.7	0.9
g	57.53	14.4	179	65	0.1	0.1	0.1	0.2	0.3
h	57.76	16	180	101	0.0	0.1	0.1	0.1	0.2
Total					1.1	1.5	1.7	2.3	3.0
j	59.55	−178	−1	−57	0.00	0.00	0.00	0.01	0.02
i	59.90	−177	−1	−152	0.00	0.00	0.00	0.01	0.01
k	61.68	−172	−3	84	0.00	0.00	0.00	0.00	0.00
Total					0.0	0.0	0.0	0.02	0.03

The minor *s-trans-* or *cis*-forms possess less anisometric (nearly quasi-spherical) molecular shape than preferable *s-cis* or *trans* ones and may be assumed to exhibit significantly lower helical twisting power. Here, an analogy can be expected with a great difference between helical twisting power of 2-arylidene-*p*-menthane-3-one *E*- and *Z*-isomers that has been established experimentally in[28]. Thus, the CD molecular transformations according to the Schemes 2 and/or 3 could cause only an increase of the induced helical pitch (an untwisting of the induced cholesteric helix) with temperature rise. However, this type of *P*(*T*) dependence is observed only for compounds **1a** – **1e** and **2a**. A change of *dP/dT* parameter sign observed for the chiral compounds **2b** – **2e** having structures similar to CD **1a** – **1e, 2a** and differing in terminal substituent only are not in agreement with assumption on an influence of conformational transformations on *P*(*T*) dependence in the case of investigated compounds. This assumption does not also allow to explain dependence of the *dP/dT* parameter on CD molecular anisometry.

Thus, it is unlikely that conformational changes of the benzoate fragment (Scheme 2) and/or thermal *trans-cis* isomerisation according to Scheme 3 as well as internal rotation around N-C* bond can stipulate the variations of the *dP/dT* parameter in compounds of **1** and **2** series.

At the same time, an influence of CD molecular structure on the ordering extent of induced cholesteric LC has been confirmed in experiment. Namely, a various effect on thermal stability of the induced cholesteric mesophases caused by different chiral compounds can be considered as such confirmation [4, 6, 18, 29]. According to [30], the isotropic transition temperature (T_i) characterizes the thermal stability of mesophase and, consequently, its ordering extent. An influence of the different chiral dopants on this characteristic of induced cholesteric mesophases has been quantified by the parameter dT_i/dC [4, 6, 18, 29, 31]. It has been shown that such parameter is subjected to change regularly with molecular anisometry variation for the systematical series of investigated chiral compounds. Generally, chiral compounds with positive *dP/dT* value or exhibiting a weakly pronounced *P*(*T*) dependence provoke an essential disordering effect on mesophase. In contrast, chiral dopants forming LC mixtures with essentially negative *dP/dT* parameter can enhance thermal stability of mesophases (dT_i/dC values are positive). For example, such behavior was observed for N-arylidene derivatives of (S)-1-phenyl- and (S)-1-benzylethylamines with three-ring arylidene fragment [18] having more anisometric molecules than in the case of CD **1** and **2**.

Taking into account all data mentioned as well as theoretical concepts [32, 33] concerning the influence of temperature-induced change of the orientation ordering parameter *S* and of the elastic constant K_{22} associated therewith on the *P*(*T*) dependence, it can be assumed that chiral dopant effect on these properties is of great importance, at least for LC systems studied.

It is of importance to note that the use of the CD **2a** – **2c** containing relatively short oxyalkyl groups (OCH_3 – OC_3H_7) permits to obtain induced cholesteric systems with temperature-independent helical pitch and selective light reflection in visible range. It should be noted that imines **1** and **2** having aliphatic substituent at nitrogen atom are photochemically stable in contrast to N-benzylideneaniline derivatives. As was examined by us, the values of helical pitch in the induced N^* mesophase were not subjected to change under irradiation of UV light source D_2 (~10 W/cm^2) at least during half an hour. This forms a prerequisite for practical application of the CD studied in electrooptical devices.

Preparation of other series chiral dopants having a moderate molecular anisometry and a sufficiently strong helical twisting power can be considered as a viable approach to elaboration of the short-pitch induced N^* materials with temperature-independent helical pitch.

CONCLUSION

New non-mesogenic chiral compounds, (S)-1-phenylethylamine N-arylidene derivatives with ester group in arylidene fragment possess a sufficient helical twisting power to obtain the short-pitch induced cholesteric systems. The terminal alkyl or alkyloxy substituent length in chiral dopant molecule affects the temperature dependence character of the induced N^* helical pitch P (increase or decrease of the P value with temperature rise) as well as that of selective light reflection λ_{max}. These phenomena may be assumed to result from changes mainly in ordering extent and elastic constant K_{22} of nematic solvent due to the chiral compound added.

Some of the new chiral compounds studied containing short terminal alkyloxy group (OCH_3, OC_2H_5, OC_3H_7) made it possible to develop induced cholesteric systems based on E63 nematic liquid crystals with temperature-independent helical pitch and selective light reflection in visible range.

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