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

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**To cite this Article** Shkolnikova, N. I. , Kutulya, L. A. , Pivnenko, N. S. , Roshal, A. D. and Semenkova, G. P.(2007) 'New (*S*)-1-phenylethylamine *N*-arylidene derivatives as chiral dopants to liquid crystalline systems', Liquid Crystals, 34: 10, 1193 — 1200

**To link to this Article: DOI:** 10.1080/02678290701640249

**URL:** http://dx.doi.org/10.1080/02678290701640249

*Liquid Crystals*, Vol. 34, No. 10, October 2007, 1193–1200

# New (*S*)-1-phenylethylamine *N*-arylidene derivatives as chiral dopants to liquid crystalline systems

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(*Received 24 March 2007; in final form 6 July 2007; accepted 14 August 2007*)

New chiral *N*-arylidene (*S*)-1-phenylethylamines with a 4,4″-biphenylene group in the central path of the rigid core were synthesized and their mesomorphic properties investigated. The helical twisting power and the temperature dependences of the helical pitch and the selective light reflection were analysed for several liquid crystalline systems based on 4-pentyl-4′-cyanobiphenyl, E63 (Merck) and 4-(*n*-hexyloxy)phenyl 4′-(*n*-butyl)benzoate containing new chiral components. The chiral compounds investigated induce helical ordering effectively in all the host materials and have significant potential for applications. The results obtained for the new chiral compounds are compared with those for some previously studied similar chiral additives.

## 1. Introduction

The search for induced cholesteric liquid crystal (LC) systems with certain characteristics has attracted considerable attention due to their use in different LC devices operating via the effect of selective light reflection in visible range of the spectrum [1, 2]. To obtain an induced chiral nematic phase with a short-pitch macrostructural helix, a chiral component (CC) dissolved in a nematic needs to possess the high helical twisting power (HTP). Different chiral additives exhibit different abilities to twist a nematic. The results for atropoisomers as chiral compounds, summarized by Gottarelli and Spada [3, 4], indicated that the most typical structural feature of such dopants associated with high HTP is the presence of two (or more) (quasi-) planar moieties chiraly disposed one with respect to the other(s). A considerable increase in the HTP for axially chiral compounds, namely, binaphthyls, has been observed under the stipulation of existence in their molecular structure of di- and quadri- rigid rod-like substituents containing a mesogenic core [5]. The HTP of the CCs with a single chiral centre is defined by many factors, such as (i) the difference of four substituents at the chiral centre in volume and polarization characteristics, as well as the extension of $\pi$-electronic fragment [6]; (ii) the molecular shape of preferential conformers (quasi-cylindrical or quasi-spherical) [7]; (iii) the peculiarities of the rigid core structure, in particular, the nature of the ring in the nearest surrounding of the chiral centre [8]; (iv) the distance of the chiral centre from the rigid aromatic core [9].

For many applications it is also important that the helical pitch or the maximum of the selective light reflection should have the certain temperature dependences [2, 10, 11]. Different factors have been discussed in the literature to be responsible for the change of the helical pitch with the temperature, such as the change of the concentration ratios of conformers with the different HTP for flexible chiral dopants [12, 13], the influence of the temperature dependence of elastic constants of selected nematic [14], the peculiarities of the conformational structure around the chiral centre in CC molecules [15], among others.

To obtain an induced cholesteric with a short-pitch structure, besides a high HTP, the CC must also have good solubility in the nematic as well as induce no other phases (smectic, for example) when mixed with the nematic in a certain concentration range. The latter ability of the CC can be associated with its inherent mesomorphic properties.

Thus, there is only piecemeal information reflecting what kind of modification in the molecular structure of the CC with a single chiral centre needs to be made to achieve desirable characteristics as a whole.

In this work we present the results of investigations concerning properties of new chiral *N*-arylidene (*S*)-1-phenylethylamines (CCs **1**, figure 1), i.e. their inherent

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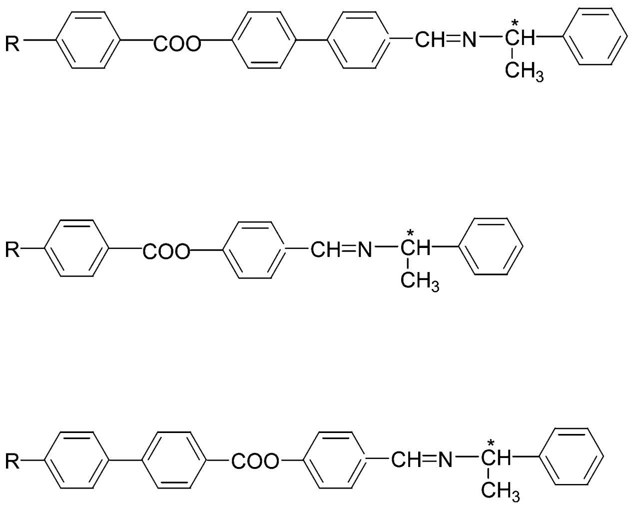
*Liquid Crystals*
ISSN 0267-8292 print/ISSN 1366-5855 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290701640249



**1** R = $OCH_3$ (**a**); $OC_2H_5$ (**b**); $OC_3H_7$ (**c**); $OC_5H_{11}$ (**e**); $OC_6H_{13}$ (**f**); $OC_7H_{15}$ (**g**); $OC_8H_{17}$ (**h**); $OC_9H_{19}$ (**i**); $OC_{10}H_{21}$ (**j**).

**2** R = $CH_3$ (**a**); $C_2H_5$ (**b**); $C_3H_7$ (**c**); $C_4H_9$ (**d**); $OCH_3$ (**e**); $OC_2H_5$ (**f**); $OC_3H_7$ (**g**); $OC_5H_{11}$ (**h**); $OC_{10}H_{21}$ (**i**).

**3** R = $CH_3$ (**a**); $C_4H_9$ (**d**); $C_5H_{11}$ (**e**); $C_6H_{13}$ (**f**); $C_7H_{15}$ (**g**); $C_8H_{17}$ (**h**); $C_9H_{19}$ (**i**); $C_{10}H_{21}$ (**j**).

Figure 1. Structures of CCs **1**–**3**.

mesomorphism, the HTPs in different nematic solvents and the temperature dependences of the helical pitch and the maximum wavelength of the selective light reflection. The influence of different fragments in the molecular structure of the new CCs on mentioned characteristics is discussed in comparison with their structurally similar analogues (CCs **2**–**3**, figure 1) studied previously [16, 17].

As nematic host materials, 4-pentyl-4′-cyanobiphenyl (5CB), E63 (Merck) and 4-(*n*-hexyloxy)phenyl 4′-(*n*-butyl)benzoate (nematic **III**) were used.

## 2. Experimental

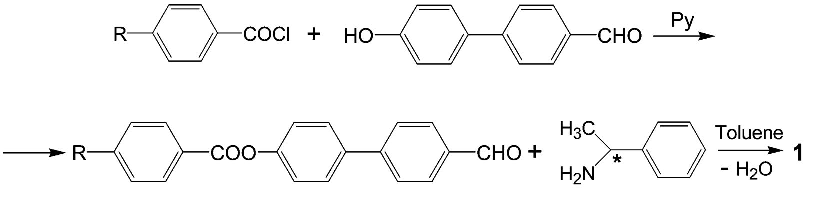
### 2.1. *Materials*

The compounds of series **1** were prepared by refluxing the corresponding aldehydes **4** with a small excess of (*S*)-1-phenylethylamines **5** in toluene under azeotropic water removal, similarly to that described elsewhere [18] (see scheme 1). Intermediate aldehydes **4** were synthesized similarly to compounds described previously [18].

Products **1** were purified by recrystallization from hexane or heptane. The structures of the new CCs **1** were determined by IR, $^1$H NMR and $^{13}$C NMR spectroscopy (using a Perkin Elmer RX1 FT-IR, in $CCl_4$, a Varian Mercury VX-200, 200 MHz, in $CDCl_3$, and a Varian Mercury-400, 400 MHz, in $CDCl_3$, respectively, see table 1). Mass spectra were recorded on a Varian 1200L using electron ionization method (IE); see table 1.

For CC **1a**: $^1$H NMR ($CDCl_3$) $\delta$: 1.619 (d, 3H, $CH_3$), 3.902 (s, 3H, $OCH_3$), 4.574 (q, 1H, C*H), 8.183–7.000 (m, 17H, aromatic), 8.416 (s, 1H, N=CH); $^{13}$C NMR ($CDCl_3$) $\delta$: 24.9, 55.6, 69.8, 113.9, 121.8, 122.2, 126.7, 126.8, 127.2, 128.2, 128.4, 128.8, 132.4, 135.4, 138.1, 142.5, 145.2, 150.8, 159.0, 164.0, 164.9.

For CC **1b**: $^1$H NMR ($CDCl_3$) $\delta$: 1.465 (t, 3H, $CH_3$), 1.613 (d, 3H, $CH_3$), 4.131 (q, 2H, $OCH_2$), 4.572 (q, 1H, C*H), 8.165–6.979 (m, 17H, aromatic), 8.413 (s, 1H, N=CH); $^{13}$C NMR ($CDCl_3$) $\delta$: 14.7, 24.9, 63.8, 69.8, 114.3, 121.5, 122.2, 126.7, 126.8, 127.2, 128.2, 128.5, 128.8, 132.4, 135.5, 138.1, 142.5, 145.2, 150.9, 159.0, 163.4, 165.0.



**4** **5**

Scheme 1. The synthesis of CCs **1**.

Table 1. Mass spectrometry, IR data and the optical rotation of CCs **1**.

| CC | R | MS: ($M^+$) | IR/cm$^{-1}$ (in $CCl_4$) | | | $[\alpha]_D^{20}$, $CHCl_3$ | $[\alpha_{molar}]_D^{20} \times 10^{-4}$, $CHCl_3$ |
|---|---|---|---|---|---|---|---|
| | | | $\nu_{C=O}$ | $\nu_{C=N}$ | $\nu_{C\text{–}O\text{–}Alk}$ | | |
| **1a** | $OCH_3$ | 435 | 1732 | 1634 | 1257 | 91.59 | 3.99 |
| **1b** | $OC_2H_5$ | 449 | 1731 | 1640 | 1256 | 88.30 | 3.97 |
| **1c** | $OC_3H_7$ | 463 | 1730 | 1644 | 1255 | 85.78 | 3.98 |
| **1e** | $OC_5H_{11}$ | 491 | 1729 | 1641 | 1255 | 80.26 | 3.95 |
| **1f** | $OC_6H_{13}$ | 505 | 1730 | 1644 | 1252 | 79.26 | 4.01 |
| **1g** | $OC_7H_{15}$ | 519 | 1725 | 1639 | 1258 | 77.56 | 4.03 |
| **1h** | $OC_8H_{17}$ | 533 | 1731 | 1641 | 1259 | 75.27 | 4.02 |
| **1i** | $OC_9H_{19}$ | 547 | 1730 | 1638 | 1259 | 74.80 | 4.10 |
| **1j** | $OC_{10}H_{21}$ | 561 | 1729 | 1642 | 1261 | 68.71 | 3.86 |

For CC **1c**: $^1H$ NMR ($CDCl_3$) $\delta$: 1.071 (t, 3H, $CH_3$), 1.615 (d, 3H, $CH_3$), 1.860 (m, 2H, $CH_2$), 4.019 (t, 2H, $OCH_2$), 4.573 (q, 1H, C*H), 8.188–6.962 (m, 17H, aromatic), 8.417 (s, 1H, N=CH); $^{13}C$ NMR ($CDCl_3$) $\delta$: 14.5, 22.5, 24.9, 68.0, 69.8, 114.3, 121.4, 122.2, 126.7, 126.8, 127.2, 128.2, 128.4, 128.8, 132.3, 135.4, 138.1, 142.5, 145.2, 150.9, 159.0, 163.6, 165.0.

For CC **1e**: $^1H$ NMR ($CDCl_3$) $\delta$: 0.953 (t, 3H), 1.437 (m, 4H, $2CH_2$), 1.619 (d, 3H, $CH_3$), 1.837 (m, 2H, $CH_2$), 4.051 (t, 2H, $OCH_2$), 4.574 (q, 1H, C*H), 8.164–6.981 (m, 17H, aromatic), 8.416 (s, 1H, N=CH); $^{13}C$ NMR ($CDCl_3$) $\delta$: 14.0, 22.5, 24.9, 28.1, 28.8, 68.3, 69.8, 114.3, 121.4, 122.2, 126.6, 126.8, 127.2, 128.2, 128.4, 128.8, 132.3, 135.4, 138.1, 142.5, 145.2, 150.9, 159.0, 163.6, 165.0.

For CC **1f**: $^1H$ NMR ($CDCl_3$) $\delta$: 0.924 (t, 3H), 1.527–1.314 (m, 6H, $3CH_2$), 1.617 (d, 3H, $CH_3$), 1.831 (m, 2H, $CH_2$), 4.053 (t, 2H, $OCH_2$), 4.573 (q, 1H, C*H), 8.189–6.962 (m, 17H, aromatic), 8.418 (s, 1H, N=CH); $^{13}C$ NMR ($CDCl_3$) $\delta$: 14.0, 22.6, 24.6, 25.7, 29.1, 31.6, 68.3, 69.8, 114.3, 121.4, 122.2, 126.6, 126.8, 127.2, 128.2, 128.4, 128.8, 132.3, 135.4, 138.1, 142.5, 142.5, 150.9, 159.0, 163.6, 165.0.

For CC **1g**: $^1H$ NMR ($CDCl_3$) $\delta$: 0.879 (t, 3H), 1.520–1.272 (m, 8H, $4CH_2$), 1.617 (d, 3H, $CH_3$), 1.826 (m, 2H, $CH_2$), 4.046 (t, 2H, $OCH_2$), 4.570 (q, 1H, C*H), 8.183–6.956 (m, 17H, aromatic), 8.415 (s, 1H, N=CH); $^{13}C$ NMR ($CDCl_3$) $\delta$: 14.1, 22.6, 24.8, 25.9, 29.0, 29.1, 31.8, 68.3, 69.8, 114.3, 121.4, 122.2, 126.6, 126.8, 127.2, 128.2, 128.4, 128.7, 132.3, 135.4, 138.0, 142.5, 145.2, 150.8, 159.0, 163.6, 165.0.

For CC **1h**: $^1H$ NMR ($CDCl_3$) $\delta$: 0.897 (t, 3H), 1.522–1.274 (m, 10H, $5CH_2$), 1.618 (d, 3H, $CH_3$), 1.828 (m, 2H, $CH_2$), 4.051 (t, 2H, $OCH_2$), 4.574 (q, 1H, C*H), 8.187–6.960 (m, 17H, aromatic), 8.412 (s, 1H, N=CH); $^{13}C$ NMR ($CDCl_3$) $\delta$: 14.1, 22.7, 24.9, 26.0, 29.1, 29.2, 29.3, 31.8, 68.3, 69.8, 114.3, 121.4, 122.2, 126.6, 16.8, 127.2, 128.2, 128.4, 128.7, 132.3, 135.4, 138.0, 142.5, 145.2, 150.8, 159.0, 163.6, 164.9.

For CC **1i**: $^1H$ NMR ($CDCl_3$) $\delta$: 0.890 (t, 3H), 1.521–1.285 (m, 12H, $6CH_2$), 1.616 (d, 3H, $CH_3$), 1.827 (m, 2H, $CH_2$), 4.048 (t, 2H, $OCH_2$), 4.572 (q, 1H, C*H), 8.184–6.958 (m, 17H, aromatic), 8.415 (s, 1H, N=CH); $^{13}C$ NMR ($CDCl_3$) $\delta$: 14.1, 22.7, 24.9, 26.0, 29.1, 29.3, 29.4, 29.5, 31.9, 68.4, 69.8, 114.3, 121.4, 122.2, 126.7, 127.2, 128.2, 128.4, 128.8, 132.3, 135.4, 138.1, 142.5, 145.2, 150.9, 159.0, 163.6, 165.0.

For CC **1j**: $^1H$ NMR ($CDCl_3$) $\delta$: 0.892 (t, 3H), 1.523–1.288 (m, 14H, $7CH_2$), 1.620 (d, 3H, $CH_3$), 1.829 (m, 2H, $CH_2$), 4.050 (t, 2H, $OCH_2$), 4.577 (q, 1H, C*H), 8.189–6.961 (m, 17H, aromatic), 8.417 (s, 1H, N=CH)m; $^{13}C$ NMR ($CDCl_3$) $\delta$: 14.1, 22.7, 24.8, 26.0, 29.1, 29.3, 29.4, 29.5, 29.6, 31.9, 68.3, 69.8, 114.3, 121.4, 122.2, 126.6, 126.8, 127.2, 128.2, 128.4, 128.7, 132.3, 135.4, 138.0, 142.5, 145.2, 150.8, 159.0, 163.6, 164.9.

The specific optical rotation, $[\alpha]_D^{20}$, of CCs **1** was measured using a Perkin Elmer-343 polarimeter. Values presented for the molar optical rotation, $[\alpha_{molar}]_D^{20}$, of CCs **1** with different length of the terminal substituent confirm essentially that the latter does not influence the optical rotation (see table 1), which is defined by peculiarities of the nearest surrounding of the chiral centre including the $\pi$-electronic fragment. The effect of different electronic polarizability ($\sigma$ or $\pi$) of one of substituents at the chiral centre on the optical rotation can be seen by the example of optically active mesogenic esters derived from benzene, bicyclo[2.2.2]octane and *p*-carborane carboxylic acids [8]. As can be seen from the data for CCs **1** (table 1) and CCs **2** [17] in comparison, the elongation of the $\pi$-electron fragment in one of substituents at the chiral centre by introduction of the oxygen atom and/or benzene ring yields somewhat increasing of values of $[\alpha]_D^{20}$.

## 2.2. *Measurement of liquid crystalline parameters*

Measurement of the melting points and texture studies of new chiral components were carried out using a polarizing optical microscope equipped with a heating stage within the accuracy of 0.5°C. Values of the induced helical pitch, $P$, were measured by the conventional Grandjean–Cano method as described elsewhere [19, 20]. A wedge-like sample consisting of glass plates and a polished wire was used to measure the distance between the Grandjean–Cano disclination lines. The thickness of the wire was determined by a calibrated scale of the microscope. The HTP (β) of the CCs **1** was calculated according to Gottarelli and Spada [3] as

$$\beta = (P_{Tred} C r)^{-1}, \tag{1}$$

where $C$ is the CC concentration, $P_{Tred}$ is the helical pitch at the reduced temperature $T_{red}$ [$T_{red}$=0.98$T_i$; $T_i$ is the temperature (in Kelvin) of the phase transition from the cholesteric (N*) to isotropic liquid (I)], $r$ is the enantiomeric purity (for all CCs $r$=1). The CC concentration in N* systems based on 5CB and nematic **III** was taken about 0.01–0.02 mole fraction. The Adams–Haas equation [21] was used for identification of the helix handedness in N* systems:

$$P^{-1} = C_1\beta_1 \pm C_2\beta_2, \tag{2}$$

where $\beta_1$, $C_1$ relate to the CC under study and $\beta_2$, $C_2$ relate to values for a reference CC with the known β value and sign of the helix handedness.

The spectra of the selective light reflection for short-pitch N* systems based on nematic E63 were obtained using a Perkin Elmer Lambda 35 UV/VIS spectrometer. Planar aligned samples were used; the thickness of the liquid-crystalline layer was 10 µm. The $P$ values for short-pitch N* systems were determined as

$$P = \lambda_{\max}/n, \tag{3}$$

where $n$ is the mean refractive index. The value of $n$=1.586 was taken for nematic E63 [22]. Concentrations of CCs **1**, **2** in systems based nematic E63 is expressed in weight per cent because an unknown exact composition of E63.

The $P(T)$ and $\lambda_{\max}(T)$ dependences were linear and characterized by the $dP/dT$ and $d\lambda_{\max}/dT$ parameters (correlation coefficients are 0.95–0.99).

## 3. Results and discussion

### 3.1. *Peculiarities of the chiral compound molecular structure*

The molecular structures of CCs **1**–**3** differ from each other in the central *N*-arylidene fragment and the terminal substituent. In the case of CCs **1**, two phenyl rings in the central part of molecule provide more effective molecular polarizability in comparison with CCs **2** and make the molecular structure somewhat more rigid compared with CCs **3**.

Chiral compounds **1**–**3** can be considered as conformationally homogeneous and anisometric chiral compounds. The *N*-arylidenephenylethylimine group could be expected to be the most "sensitive" fragment to lability (rotation around the N–C* bond) in the molecular structure of CCs **1**–**3**. However, according to our earlier calculations [23] by the quantum-chemical method based on the density functional theory, the internal rotation around the N–C* bond is characterized by the presence of three energy minima, the deepest of which corresponds to a quite anisometric *anticlinal* conformation (−*ac*, φ1=−122.2°, see figure 2). The energy of a synperiplanar form (*sp*, φ1=−6.8°) exceeds the energy of the preferential one by 2.4 kcal mol$^{-1}$. The value of the difference is the evidence of the dominance of conformations of a quite anisometric molecular shape of CCs **1** in LC solutions.

### 3.2. *Mesomorphic properties of CCs 1–3*

Usually weak-polar substances containing elongated *n*-alkyl or alkyloxy terminal chains have a tendency to form smectic phases [24]. The type of a smectic mesophase is mostly determined by the central fragment in the molecular structure of the substance (see, for example, Demus *et al.* [25, 26]). The new CCs **1** do not

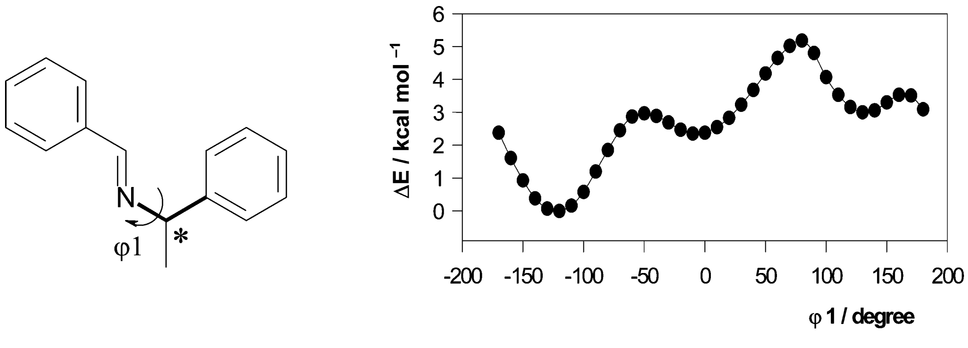


Figure 2. The energy change of *N*-benzylidenephenylethylamine vs. φ1 (DFT method).

exhibit rich mesomorphic properties. Only the high homologues (R=$OC_7H_{15}$, $OC_9H_{19}$, $OC_{10}H_{21}$) of series **1** exhibit the monotropic orthogonal smectic A* (SmA*) phase (see table 2) identified by a typical fan-shaped texture. The nonyloxy-substituted compound (CC **1i**), besides a narrow SmA* range, also exhibits a blue phase (BP). The BP was identified by the mosaic texture in the cell with untreated surfaces. The main factors in formation of blue phases are generally assumed to be a certain extent of chirality of the mesogenic compound as well as the elastic constants [27–30]. The high extent of molecular chirality of CCs **1** is confirmed by their quite high helical twisting power (see text below and tables 3–4).

Chiral compounds **2** do not reveal mesogenic states at all despite elongated *n*-alkyl or alkyloxy terminal substitutes. Not enough extended $\pi$-electron fragment in the molecular structure of CCs **2** and, correspondingly, their relatively low anisotropy of the molecular polarizability resulting in non-effective intermolecular dispersion interaction is a bar to exhibition of mesomorphic properties. The essential role of extended $\pi$-electronic system can be traced, in particular, using the data for esters of *p*-substituted benzoic and *p*-substituted diphenylcarbonic acids [25, 26].

The mesomorphic properties of CCs **3** were discussed thoroughly previously [18]. Here, it just should be noted that on increase of the length of the alkyl chain beginning from the R=$C_5H_{11}$ homologue (**3e**) the SmA* phase shows as a monotropic phase and from R=$C_7H_{15}$ (**3g**) as an enantiotropic one. Besides the SmA* phase, some homologues of series **3** exhibit the monotropic tilted smectic C* (SmC*) or the smectic E (SmE) phase (CCs **3j** and **3g**, respectively) [18].

The comparison of the mesomorphic properties of CCs **1** and **3** reveals that the addition of a benzene ring to the benzylidenimine group in the central part of molecules of CCs **1**, but not on the periphery as in case of CCs **3** (alkyldiphenyl fragment), leads to the crystal positional ordering of the centres of masses of molecules without forming intermediate smectic mesomorphic states. The position of the –COO– linking group in the molecular core of CCs **1** and **3** can also influence their smectogenic polymorphism.

Table 2. The phase transition temperatures (°C) of CCs **1** and **3**.

| CC | R | Phase behaviour | CC | R | Phase behaviour |
|---|---|---|---|---|---|
| **1a** | $OCH_3$ | $\mathbf{C} \underset{111}{\overset{131.5}{\rightleftharpoons}} \mathbf{I}$ | **3a** | $CH_3$ | $\mathbf{C} \underset{126.9}{\overset{144.2}{\rightleftharpoons}} \mathbf{I}$ |
| **1b** | $OC_2H_5$ | $\mathbf{C} \underset{120}{\overset{131}{\rightleftharpoons}} \mathbf{I}$ | **3d** | $C_4H_9$ | $\mathbf{C} \underset{123.6}{\overset{146}{\rightleftharpoons}} \mathbf{I}$ |
| **1c** | $OC_3H_7$ | $\mathbf{C} \underset{143}{\overset{155}{\rightleftharpoons}} \mathbf{I}$ | **3e** | $C_5H_{11}$ | $\begin{tikzcd} \mathbf{C} \arrow[rr, "125.3"] & & \mathbf{I} \arrow[dl, "122.3"] \\ & \textbf{Sm A*} \arrow[ul, "103.9"] & \end{tikzcd}$ |
| **1e** | $OC_5H_{11}$ | $\mathbf{C} \underset{118}{\overset{129.5}{\rightleftharpoons}} \mathbf{I}$ | **3f** | $C_6H_{13}$ | $\begin{tikzcd} \mathbf{C} \arrow[rr, "128.3"] & & \mathbf{I} \arrow[dl, "115.6"] \\ & \textbf{Sm A*} \arrow[ul, "107.8"] & \end{tikzcd}$ |
| **1f** | $OC_6H_{13}$ | $\mathbf{C} \underset{109}{\overset{127}{\rightleftharpoons}} \mathbf{I}$ | **3g** | $C_7H_{15}$ | $\begin{tikzcd} \mathbf{C} \arrow[rr, "117.4"] & & \textbf{Sm A*} \arrow[dl, "96.1"] \arrow[r, shift left, "118.7"] & \mathbf{I} \arrow[l, shift left, "117.9"] \\ & \textbf{Sm E} \arrow[ul, "88.8"] & & \end{tikzcd}$ |
| **1g** | $OC_7H_{15}$ | $\begin{tikzcd} \mathbf{C} \arrow[rr, "124"] & & \mathbf{I} \arrow[dl, "108"] \\ & \textbf{Sm A*} \arrow[ul, "102"] & \end{tikzcd}$ | **3h** | $C_8H_{17}$ | $\mathbf{C} \underset{83.8}{\overset{108.9}{\rightleftharpoons}} \textbf{Sm A*} \underset{109.5}{\overset{110.3}{\rightleftharpoons}} \mathbf{I}$ |
| **1h** | $OC_8H_{17}$ | $\mathbf{C} \underset{118}{\overset{134}{\rightleftharpoons}} \mathbf{I}$ | **3i** | $C_9H_{19}$ | $\mathbf{C} \underset{76.2}{\overset{98}{\rightleftharpoons}} \textbf{Sm A*} \underset{106.5}{\overset{107.3}{\rightleftharpoons}} \mathbf{I}$ |
| **1i** | $OC_9H_{19}$ | $\begin{tikzcd} \mathbf{C} \arrow[r, shift left, "125"] & \mathbf{I} \arrow[l, shift left] \arrow[d, "112"] \\ \textbf{Sm A*} \arrow[u, "105"] & \textbf{BP} \arrow[l, "107"'] \end{tikzcd}$ | **3j** | $C_{10}H_{21}$ | $\begin{tikzcd} \mathbf{C} \arrow[rr, "96.1"] & & \textbf{Sm A*} \arrow[dl, "81.6"] \arrow[r, shift left, "104.6"] & \mathbf{I} \arrow[l, shift left, "102.6"] \\ & \textbf{Sm C*} \arrow[ul, "78.6"] & & \end{tikzcd}$ |
| **1j** | $OC_{10}H_{21}$ | $\begin{tikzcd} \mathbf{C} \arrow[rr, "120"] & & \mathbf{I} \arrow[dl, "109"] \\ & \textbf{Sm A*} \arrow[ul, "90"] & \end{tikzcd}$ | | | |

Table 3. The HTP (β) and *dP*/*dT* parameter in the systems based on 5CB doped with CCs **1**–**3**.

| CC | R | $-\beta/$ $\mu m^{-1}$ mol.fr.$^{-1}$ | $(dP/dT \times 10^4)/$ $\mu m\,K^{-1}$ | CC | R | $-\beta/$ $\mu m^{-1}$ mol.fr.$^{-1}$ | $(dP/dT \times 10^4)/$ $\mu m\,K^{-1}$ |
|---|---|---|---|---|---|---|---|
| **1a** | $OCH_3$ | 37.2 ± 4.2 | −113 ± 10 | **2d** | $C_4H_9$ | 36.0 ± 1.8 | +24.6 ± 2.8 |
| **1b** | $OC_2H_5$ | 41.1 ± 1.7 | −118 ± 31 | **2e** | $OCH_3$ | 35.7 ± 1.8 | +28.2 ± 6.8 |
| **1c** | $OC_3H_7$ | 39.8 ± 1.4 | −100 ± 10 | **2f** | $OC_2H_5$ | 35.5 ± 0.8 | −47.3 ± 9.4 |
| **1e** | $OC_5H_{11}$ | 41.5 ± 2.3 | −117 ± 34 | **2g** | $OC_3H_7$ | 35.2 ± 1.0 | −34.2 ± 9.4 |
| **1f** | $OC_6H_{13}$ | 40.2 ± 2.9 | −154 ± 48 | **2h** | $OC_5H_{11}$ | 37.2 ± 1.1 | −115 ± 12 |
| **1g** | $OC_7H_{15}$ | 42.7 ± 1.3 | −177 ± 46 | **2i** | $OC_{10}H_{21}$ | 40.4 ± 1.0 | −130 ± 20 |
| **1h** | $OC_8H_{17}$ | 41.1 ± 1.7 | −190 ± 29 | **3a** | $CH_3$ | 42.2 ± 2.9 | −263 ± 20 |
| **1i** | $OC_9H_{19}$ | 42.9 ± 0.9 | −144 ± 28 | **3g** | $C_7H_{15}$ | 42.0 ± 3.7 | −354 ± 26 |
| **1j** | $OC_{10}H_{21}$ | 40.8 ± 2.5 | −210 ± 50 | **3h** | $C_8H_{17}$ | 42.4 ± 2.1 | −371 ± 45 |
| **2a** | $CH_3$ | 34.9 ± 1.6 | +18.7 ± 8.6 | **3i** | $C_9H_{19}$ | 43.2 ± 2.2 | −330 ± 27 |
| **2b** | $C_2H_5$ | 33.0 ± 1.2 | +74.0 ± 9.6 | **3j** | $C_{10}H_{21}$ | 41.4 ± 1.1 | −346 ± 34 |
| **2c** | $C_3H_7$ | 31.2 ± 2.0 | +52.1 ± 11 | | | | |

Table 4. Some characteristics of the systems based on nematic **III** doped with CCs **1**.

| CC | R | $\lvert\beta\rvert/\mu m^{-1}$ mol.fr.$^{-1}$ | $(dP/dT \times 10^4)/\mu m\,K^{-1}$ | $\lambda_{max}$/nm at 34°C (*C*/mol.%) | $(d\lambda_{max}/dT)$/nm $K^{-1}$ |
|---|---|---|---|---|---|
| **1a** | $OCH_3$ | 25.6 ± 1.0 | −400 ± 60 | 588 (10.4) | −3.78 ± 0.56 |
| **1b** | $OC_2H_5$ | 27.2 ± 1.3 | −366 ± 53 | – | – |
| **1c** | $OC_3H_7$ | 28.4 ± 1.5 | −413 ± 73 | – | – |

### 3.3. *Characteristics of the N* systems doped with CCs 1–3*

The helical twisting power, β, and *dP*/*dT* values obtained for systems based on 5CB and nematic **III** doped with CCs **1** are listed below in tables 3–4. The new CCs **1** as well as CCs **2** and **3** induce the left-handed cholesteric helix in 5CB [16] identified experimentally.

As can be seen from table 3, the HTP values of CCs **1** as well as those of CCs **2** and **3** in the systems based on 5CB are rather high due to mainly high extent of chirality associated with the considerable difference of four substituents at the chiral centre in volume and polarization characteristics [6]. The greater the difference between the four substituents, the higher the extent of molecular chirality, as was shown, for example, for derivatives of (*S*)-1-phenylethylamine (CCs **2**, **3**), (*S*)-1-benzylethylamine and diastereomeric *p*-menthane-3-ones [6]. Here, it should be noted that the HTP values of CCs **1** are practically the same as those of CCs **3** ($\beta \approx 40\,\mu m^{-1}$ mol.fr.$^{-1}$, see table 3). The displacement of the benzene ring from the periphery (CCs **3**) to the central part (CCs **1**) in one of substituents at the chiral centre and, thereby, conservation of the extended $\pi$-electronic system in it, does not result in appreciable changes in the HTP values. Consequently, such a modification in the molecular structure of a CC can be used to achieve other purposes, for example, to change the *dP*/*dT* parameter without losses in the HTP. CCs **2** possess a somewhat lower extent of molecular chirality in comparison with CCs **1** and **3** due to noticeable reduction of polarization characteristics of one of substituents at the chiral centre and, correspondingly, exhibit lower HTP values ($\beta \approx 35\,\mu m^{-1}$ mol.fr.$^{-1}$, see table 3; see also Kutulya *et al.* [17]). The length of the terminal alkyl chain for all CCs **1**–**3** does not influence the HTP appreciably (see table 3) as it takes place in most cases (see, for example, Kutulya *et al.* [6]).

The *dP*/*dT* values for systems based on 5CB doped with CCs **1** are negative and have a tendency to decrease as the length of the terminal substitute increases. This confirms the established relationship between the molecular anisometry of CCs of allied series and the *dP*/*dT* parameter [23]. CCs **1** possessing relatively high-anisometric molecules cause the cholesteric helix to twist as temperature increases, whereas low-anisometric CCs **2** result in the opposite effect (the negative *dP*/*dT* parameter for systems doped with CCs **1** and positive for CCs **2**, see table 3). The effect of the displacement of the benzene ring in molecular structures of CCs **1** and **3** on the *dP*/*dT* parameter attracted our attention. The systems doped with CCs **3** exhibit much more negative *dP*/*dT* values (three times higher in absolute value than for CCs **1**, see table 3). So far as the molecular anisometry is only a tool to describe the influence of the anisotropy of molecular polarizability of a CC on the *dP*/*dT* parameter, qualitative changes in polarizability can be a reason of mentioned behaviour. Besides, some difference in molecular rigidity of CCs **1** and **3** and, consequently, their different interactions with molecules of the nematic are reflected on values of the *dP*/*dT* parameter.

The HTP values of CCs **1** in the systems based on nematic **III** are one and a half times lower in comparison with those in systems based 5CB with the same CCs (see table 4). Beside of the high extent of molecular chirality of a CC, another factor affecting the HTP values in N* systems is usually considered to be elastic constants, in particular, the twist elastic constant, $K_{22}$, of selected nematic [3, 31, 32]. The nematic **III** has less strong elastic properties in comparison with 5CB ($K_{22}$ is about $2.8 \times 10^{-12}$ N for some derivatives of oxyphenylbenzoate [33] and 3.2–$3.4 \times 10^{-12}$ N for 5CB [34–36]) and could be expected to be twisted more effectively. However, this was not revealed in the case of CCs **1**.

The same reduction in the HTP values was observed for the systems based on nematic **III** doped with CCs **2**–**3** [37]. Such unexpected behaviour needs be considered in the context of peculiarities of the molecular structure of nematic **III**. Nematic **III** being structurally similar to some more elongated phenylbenzoate derivatives exhibiting a smectic phase [for example, 4-(*n*-octyloxy)phenyl 4′-(*n*-hexyloxy)benzoate or 4-(*n*-hexyloxy)phenyl 4′-(*n*-octyloxy)benzoate] should be expected as a potential smectogen. Assuming the existence of smectic-like clusters of fluctuating nature in the N* phase in the systems based on nematic **III** we believe that the induction of helical ordering by a CC of series **1**–**3** occurs less effectively than in case of nematic 5CB. The *dP*/*dT* values in systems based on nematic **III** doped with CCs **1** are negative and very high in absolute value, which could be an indirect proof of the presence of smectic-like clusters. Small-angle X-ray scattering data [38, 39] confirm the existence of smectic-like clusters in the N* phase in the systems based on phenylbenzoate derivatives as host phases.

The HTP values of CCs **1** are high enough to obtain selective light reflection in the visible range of the spectrum at relatively moderate concentrations of the CCs in systems based on nematic E63 (14–16 wt% of CCs **1**, see table 5) as well as nematic **III** (10.4 mol.% or 12.5 wt% of CC **1a**, see table 4).

Since the temperature dependence of the mean refractive index, *n*, is negligible in the majority of cases, the influence of the molecular anisometry of allied CCs on the $d\lambda_{\max}/dT$ parameter is evident even at quite high concentrations of CCs. As follows from the $d\lambda_{\max}/dT$ parameter (tables 4–5), one can vary its value from positive to negative through zero with elongation sequentially of the $\pi$-electronic core of CCs **2** by means of addition of the oxygen atom and/or benzene ring, as well as by the lengthening of the terminal substituent (CCs **1**) provided the anisometric molecular shape is conserved.

## 4. Conclusions

New chiral (*S*)-1-phenylethylamine *N*-arylidene derivatives with a 4,4″-biphenylene group in the central path of the rigid core exhibit the monotropic orthogonal smectic A* phase in the presence of a long terminal substituent in their molecular structure. The new series of chiral compounds presented possess high helical twisting power and allow us to achieve selective light reflection in the visible range of the spectrum at concentrations of about 10–16% in selected nematic LCs. The character of the temperature dependences of the helical pitch as well as the selective light reflection for the systems studied can be controlled by variation of the chiral dopant anisometry, in agreement with correlations established previously. The observed unexpected reduced values of the helical twisting power for the new chiral *S*-1-phenylethylamine *N*-arylidene derivatives in nematic 4-(*n*-hexyloxy)phenyl 4′-(*n*-butyl)-benzoate arise from the presence of smectic-like clusters in these LC systems.

Table 5. The $\lambda_{\max}$ values of the selective light reflection (at 30°C) and the $d\lambda_{\max}/dT$ parameter for the systems based on E63 doped with CCs **1** and **2**.

| CC | R | $\lambda_{\max}$/nm (*C*/wt%) | $(d\lambda_{\max}/dT)$/nm K$^{-1}$ | CC | R | $\lambda_{\max}$/nm (*C*/wt%) | $(d\lambda_{\max}/dT)$/nm K$^{-1}$ |
|---|---|---|---|---|---|---|---|
| **1a** | $OCH_3$ | 449 (15.9) | $-0.8 \pm 0.2$ | **2b** | $C_2H_5$ | 538 (13.0) | $+0.46 \pm 0.03$ |
| **1b** | $OC_2H_5$ | 605 (14.2) | $-1.2 \pm 0.3$ | **2c** | $C_3H_7$ | 598 (12.7) | $+0.58 \pm 0.08$ |
| **1c** | $OC_3H_7$ | 609 (15.2) | $-1.5 \pm 0.1$ | **2d** | $C_4H_9$ | 490 (14.5) | $+0.46 \pm 0.04$ |
| **1e** | $OC_5H_{11}$ | 687 (14.7) | $-2.3 \pm 0.3$ | **2e** | $OCH_3$ | 555 (12.3) | $0.00 \pm 0.02$ |
| **1f** | $OC_6H_{13}$ | 705 (14.1) | $-2.3 \pm 0.4$ | **2f** | $OC_2H_5$ | 555 (13.0) | $-0.01 \pm 0.03$ |
| **1g** | $OC_7H_{15}$ | 707 (14.8) | $-2.8 \pm 0.1$ | **2g** | $OC_3H_7$ | 555 (13.5) | $-0.04 \pm 0.05$ |
| **1h** | $OC_8H_{17}$ | 721 (14.6) | $-2.7 \pm 0.2$ | **2h** | $OC_5H_{11}$ | 519 (15.1) | $-0.52 \pm 0.01$ |
| **1i** | $OC_9H_{19}$ | 764 (14.8) | $-3.0 \pm 0.1$ | **2i** | $OC_{10}H_{21}$ | 549 (16.6) | $-1.24 \pm 0.04$ |
| **1j** | $OC_{10}H_{21}$ | 708 (15.2) | $-3.8 \pm 0.4$ | | | | |

## Acknowledgements

The authors are grateful to Merck KGaA, Darmstadt, for a gift of nematic E63. The authors would like to thank Dr. A.V. Turov (T.G. Shevchenko Kiev National University) for the measurements of $^{13}$C NMR spectra of the chiral compounds.

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