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Chiral Organic Compounds in Liquid Crystal Systems with Induced Helical Structure

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In this work, some of the most important characteristics of chiral compounds as components of the liquid crystal (LC) systems are discussed. These characteristics are the helical twisting power of chiral dopants (CDs) in the induced cholesteric (N^*) mesophases, the temperature dependence of the induced helical pitch (P) quantified by the dP/dT parameter and the influence of the CDs on the N^* mesophase thermal stability characterized by the dT_{iso}/dC parameter. The molecular structure influence on them for several systematic series of the N-arylidene derivatives of (*S*)-1-phenyl- and (*S*)-1-benzylethylamines as well as the chiral diastereomeric 2-arylidene-*p*-menthane-3-ones is considered.

Keywords: induced cholesteric mesophases; chiral dopants

INTRODUCTION

The induced cholesteric liquid crystals (LC) being the «achiral nematic LC – chiral dopant» composites (see, e.g.,[1 - 6]) are of great interest due to their use as materials for the development of different devices of the

information reflection.

This paper summarizes the most important regularities concerning the influence of the chiral dopants (CDs) molecular structure on macroscopic properties of the LC systems. These relations have been established by authors as a result of the researches of CDs systematic series including derivatives of the (*S*)-1-phenyl- and (*S*)-1-benzylethylamines and diastereomeric *p*-menthane-3-ones. Following points are discussed:

– the dependence of helical twisting power (HTP) of CDs on their molecular structure; structural requirements for strongly twisting CDs;

– the temperature dependence of the induced helical pitch (*P*) and regularities of its kind and of the quantitative characteristic (*dP/dT*) variation for the systematic series of CDs;

– the effect of CDs on the induced cholesteric mesophase (N*) thermal stability and dependence of this effect on the molecular structure.

In the most cases, CDs under study are non-mesogenic. Nematic 4-methoxybenzylidene-4'-butylaniline (MBBA) and 4-pentyl-4'-cyanobiphenyl (5CB) were used as LC matrixes.

EXPERIMENTAL

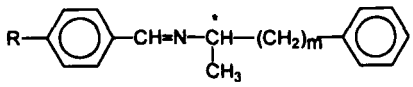
The synthesis of the studied CDs was described in [4, 7 - 9]. The *P* values for LC systems were measured by Grandjean – Cano method analogously to that described in the previous report [10]. The HTP (β) values were calculated from $\beta = (PC)^{-1}$ equation, where *C* is the CD mole fraction.

RESULTS AND DISCUSSION

Helical Twisting Power

An ability to induce the helical ordering in the nematic mesophase is the characteristic feature of chiral compounds only. Therefore, it is naturally to postulate that HTP is a function of the CD molecular chirality extent. In the case of CDs with the chiral center, the more difference of four substituents at one (in volume and polarization characteristics) the higher molecular chirality extent. Preferably, one substituent should be

an extended π-electronic grouping and the other, hydrogen atom. Two another substituents should be of an intermediate size and polarizability. The structures of the chain-like N-arylidene amines **1** and **2** correspond well to such requirements.



1 m = 0; **2** m = 1

As can be seen from the Table 1, the HTP of the compounds **1** is enhanced essentially as extension and polarizability of the substituent R increase in the following consequence:

$$CH_3COO < C_6H_5 < C_6H_5COO < C_6H_5C_6H_4COO$$

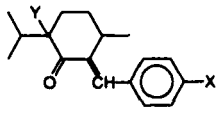
At the same time, the β value does not depend on the terminal alkyl chain length for both the CDs **1** and **2** ones.

TABLE 1 Helical twisting power for the compounds **1**, **2** in 5CB

R	$-\beta$, $\mu m^{-1} \cdot mol.fr.^{-1}$	
	1, m = 0	**2**, m = 1
CH_3COO	19.9 ± 1.2	–
C_6H_5	30.3 ± 1.7	31.0 ± 2.7
C_6H_5COO	34.4 ± 1.5	–
$C_6H_5C_6H_4COO$	39.7 ± 3.0	–
$C_nH_{2n+1}(C_6H_4)_2COO$		
n = 5	41.6 ± 1.2	32.5 ± 1.3
n = 6	42.5 ± 1.4	33.6 ± 1.8
n = 7	42.0 ± 3.7	33.4 ± 1.1
n = 8	42.4 ± 2.1	32.6 ± 2.4
n = 9	43.2 ± 2.2	32.8 ± 1.0
n = 10	41.4 ± 1.1	33.6 ± 0.8

Similar changes of HTP are observed also for 2-(4-X-benzylidene)-4-Y-*p*-menthane-3-ones **3**, **4** with the cyclic chiral fragment (Table 2). In these compounds series, any substituent X introduced into the *para*-position of the benzene ring causes a rise of HTP but the effect of the additional benzene ring (X = C_6H_5) or *para*-alkyloxyphenyl groups (X = $CH_3OC_6H_4$, $C_5H_{11}OC_6H_4$, $C_6H_{13}OC_6H_4$) is the most strong.

TABLE 2 Helical twisting power for the 2-(4-X-benzylidene)-4-Y-*p*-menthane-3-ones



3 Y = H; **4** Y = Br

X	$-\beta$, $\mu m^{-1} \cdot mol.fr.^{-1}$		
	Y = H (in MBBA)	Y = Br (in MBBA)	Y = H (in 5CB)
H	19.9 ± 3.1	23.0 ± 1.1	–
Cl	29.6 ± 2.1	30.5 ± 1.8	–
Br	32.6 ± 3.0	32.2 ± 1.0	28.0 ± 1.1
OCH_3	30.5 ± 1.1	32.8 ± 0.7	–
NO_2	35.3 ± 3.2	36.6 ± 3.1	–
C_6H_5	41.9 ± 1.4	44.5 ± 3.1	36.9 ± 0.6
$CH_3OC_6H_4$	48.9 ± 1.5	49.6 ± 1.9	40.1 ± 2.4
$C_5H_{11}OC_6H_4$	54.0 ± 4.0	52.4 ± 1.1	41.2 ± 2.9
$C_6H_{13}OC_6H_4$	52.7 ± 1.7	–	42.4 ± 2.4

It is of importance to take into account the peculiarity of the molecular spatial structure of the compounds **3**, **4** under consideration (Figure 1). Introduction of any substituent X in the *para*-position of the benzene ring increases their molecular anisometry in general.

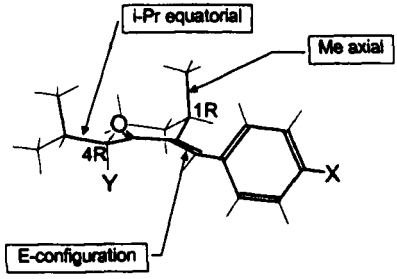
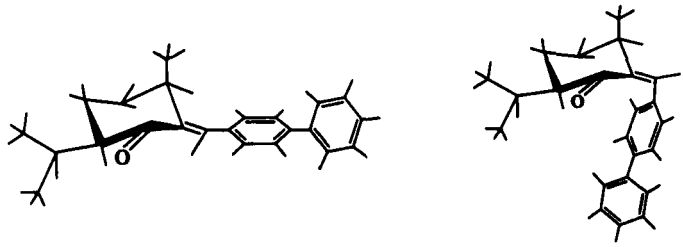


FIGURE 1 Spatial structure of the 2-(4-X-benzylidene)-4-Y-*p*-menthane-3-ones molecules according to data of [11 - 14].

Thus, the increase of both the π-electronic fragment extension and the molecular anisometry in general is favorable to the HTP rise. It

should be noted that the unsubstituted (–)-menthone exhibits very weak HTP: its |β| was estimated [4] as 0.7 $\mu m^{-1} \cdot mol.fract.^{-1}$.

Along with the mentioned formal criterion about the presence of an extensive π-electronic fragment (or any high polarizeable group) in CD molecules, the real spatial shape and conformational features should be taken into consideration. As an important example of the CD molecular shape influence on HTP, the significant difference in the β values for the *E*- and *Z*-isomers of some 2-arylidene-*p*-menthane-3-ones is illustrated in the Table 3. The *E*-isomers possess the more anisometric π-electronic fragment and more anisometric molecular shape (Figure 2). In contrast, the *Z*-form molecules are less anisometric; they possess a tightened shape. As a result, the |β| values for the *E*-isomers are higher significantly than those for *Z*- ones are (Table 3).



***E*-isomer** ***Z*-isomer**

FIGURE 2 The molecular structures of the 1*R*,4*R*-2-(4-phenylbenzylidene)-*p*-menthane-3-one *E*- and *Z*-isomers.

TABLE 3 Helical twisting power for the 1*R*,4*R*-2-(4-X-benzylidene)- *p*-menthane-3-one *E*- and *Z*-isomers.

Isomer	X	–β, $\mu m^{-1} \cdot mol.fr.^{-1}$	
		MBBA	5CB
E	C_6H_5	–41.9 ± 1.4	–36.9 ± 0.6
Z	C_6H_5	+8.8 ± 0.3	–1.1 ± 0.2
E	$C_6H_4OCH_3$	–49.7 ± 2.2	–40.1 ± 2.4
Z	$C_6H_4OCH_3$	+15.1 ± 0.7	0
E	$C_6H_4OC_7H_{15}$	–	–44.3 ± 1.8
Z	$C_6H_4OC_7H_{15}$	–	–1.5 ± 2.5

Temperature Dependence of the Induced Helical Pitch

As a quantitative characteristic of the $P(T)$ dependence, the dP/dT parameter was used. This parameter was determined in the temperature range starting from 3 – 4° below the N*→I phase transition as that described in the work [15]. It was revealed that the kind of the $P(T)$ function as well as the dP/dT parameter depend on the chiral dopant molecular structure. Two types of the $P(T)$ dependencies were observed: the P value increases as temperature rises (the dP/dT values are positive) or the P value decreases with temperature (the dP/dT values are negative).

The data for systematical series of N-arylidene derivatives **1** of (*S*)-1-phenylethylamine are an example of the effect of the CD molecular structure, in particular of the molecular anisometry, on the dP/dT parameter (Table 4). In this series, the unsubstituted CD **1a** with the lowest anisometry exhibits the highest positive dP/dT value which decreases then as the molecular anisometry rises due to lengthening of the terminal alkyl group (CDs **1b** – **1e**). The highest negative dP/dT values are observed for CDs having the extensive three-ring N-arylidene fragment and the long terminal alkyl group (R = *p*-$XC_6H_4C_6H_4COO$, n = 7 – 10; CDs **1l** –**1o**).

A strong influence of the CD molecular shape on the $P(T)$ dependence kind can be seen also from the Figure 3 for compositions of MBBA with the 1*R*,4*R*-2-(4-methoxyphenylbenzylidene)-*p*-menthane-3-one *E*- and *Z*-isomers.

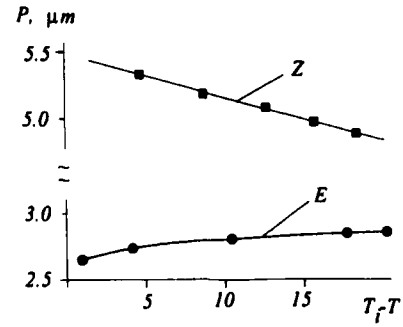


FIGURE 3 The dependences $P(T)$ for the mixtures of MBBA with the *E*- and *Z*-isomers of 1*R*,4*R*-2-(4-methoxyphenylbenzylidene)-*p*-menthane-3-one.

TABLE 4 Some characteristics of the chiral dopants **1** in LC compositions based on 5CB (R = *p*-XC_6H_4COO, CDs **1a** – **1j**; *p*-$XC_6H_4C_6H_4COO$, CDs **1i** –**1o**)

	X	$-\beta$ $\mu m^{-1}.mol.fr^{-1}$	$dP/dT \times 10^4$ μm/degree	Parameter A_{N^*}, degree/mol. %
1a	H	34.4 ± 1.5	121 ± 14	–1.88 ± 0.14
1b	CH_3	34.9 ± 1.6	18.7 ● 8.6	–1.38 ± 0.03
1c	C_2H_5	33.0 ± 1.2	74.0 ± 9.6	–1.42 ± 0.02
1d	C_3H_7	31.2 ± 2.0	52.1 ± 11	–
1e	C_4H_9	36.0 ± 1.8	24.6 ± 2.8	–1.60 ± 0.02
1f	OCH_3	35.7 ± 1.8	28.2 ± 6.8	–1.18 ± 0.04
1g	OC_2H_5	35.5 ± 0.8	–47.3 ± 9.4	–
1h	OC_3H_7	35.2 ± 1.0	–34.2 ± 9.4	–
1j	OC_5H_{11}	37.2 ± 1.1	–115 ± 12	–
1i	H	39.7 ± 3.0	–230 ± 5	–0.16 ± 0.10
1k	CH_3	42.2 ± 2.9	–263 ± 20	+0.48 ± 0.14
1l	C_7H_{15}	42.0 ± 3.7	–354 ± 26	+0.78 ± 0.06
1m	C_8H_{17}	42.4 ± 2.1	–371 ± 45	–
1n	C_9H_{19}	43.2 ± 2.2	–330 ± 27	+0.66 ± 0.09
1o	$C_{10}H_{21}$	41.4 ± 1.1	–346 ± 34	–

For the mentioned above LC system containing the anisometric *E*-isomer, the *P* value changes with the temperature rise only very slight. In contrast, the essential increase of the helical pitch is observed for the composition with the *Z*-isomer possessing the less anisometric tightened molecular shape (see Figure 2).

We considered also the effect of the different molecular configurations of some 2-arylidene-*p*-menthane-3-ones **3** (1*R*,4*R*-*cis*- or 1*R*,4*S*-*trans*-) on their behavior in the N* mesophase. As one can see from the Table 5, the β value does not depend on the C-4 chiral center configuration (4R or 4S). However, the dP/dT parameter have the higher positive value for the system containing the 1*R*,4*S*-diastereomer than for the composition with 1*R*,4*R* one. This difference can be caused by the nice distinction of the CD molecular conformations: the 4-isopropyl

group is equatorial in the 1*R*,4*R*-diastereomer molecule and axial in the case of its 1*R*,4*S*-isomer. In one's part, the different orientation of the isopropyl group results in the essential distinction of the diastereomers molecular shape [8].

TABLE 5 The $|\beta|$ and dP/dT values for the some *p*-menthane-3-one derivatives with the different configurations

X	Configuration	$\|\beta\|$, $\mu m^{-1}.mol.fr^{-1}$	$dP/dT \times 10^4$, μm/degree
C_6H_5 *)	1*R*,4*R*	36.9 ± 0.6	–
C_6H_5 *)	1*R*,4*S*	39.8 ± 1.6	–
$COOCH_3$ **)	1*R*,4*R*	32.8 ± 1.6	61 ± 7
$COOCH_3$ **)	1*R*,4*S*	34.7 ± 1.0	110 ± 10

*) Data in MBBA. **) Data in 5CB.

Chiral Dopant Influence on the Thermal Stability of the Induced N* Mesophase

The parameter $A_{N^*} = dT_{iso}/dC$ (T_{iso} is the temperature of the N*→I phase transition; C is the CD concentration) was used as a quantitative characteristic of the CD influence on the thermal stability of the induced N* mesophase and, consequently, on its ordering extent in accordance with [4, 16, 17].

In a number of cases, we revealed the some relation between the change in the parameters A_{N^*} and dP/dT. So, for example, the essentially positive dP/dT values (untwisting of the cholesteric helix with the temperature rise) and simultaneously strong disordering effect (the negative A_{N^*} parameter) were obtained for the CDs of series 1 having low anisometric molecules (Table 4, CDs **1a** – **1f**). In contrast, both the negative dP/dT values and positive A_{N^*} parameter are observed for the LC systems containing the chiral compounds with the essentially high molecular anisometry (Table 4, CDs **1k** –**1o** with three-ring arylidene fragment). Some other examples of the analogous effect of the CDs molecular shape were presented in works [4,15]. One should note that the

A_{N^*} parameter is subjected to the essential influence of the terminal alkyl or oxyalkyl substituent, in contrast to the β values (see Table 4 and [18]).

CONCLUSION

The results of performed investigations allow to formulate the main requirements to the molecular structure of the chiral dopants having the chirality center and suitable for using as components of LC materials. The presence of the extensive fragment with the high polarizability in the chiral dopant molecule is necessary for obtaining of the strong twisting in the mesophase. Preferably, it should be the extensive π-electronic group that ensures the effective interaction of the chiral dopant with nematic environment and, as a result, the strong chiralizing influence.

The chiral dopants have to possess the high molecular chirality extent. For molecules with the chiral center, the more difference in volume and polarizing characteristics between four substituents at this center the higher chirality extent.

The anisometric quasi-cylindrical molecular shape of the chiral dopants is needed also. Chiral dopants possessing low anisometric quasi-spherical molecular shape exhibit the weak twisting power.

The presence of the terminal alkyl or oxyalkyl group in the chiral dopant molecule is of importance also, inasmuch as it favors the reduction of the disordering effect on the N* mesophase and the control of the temperature dependence of the induced helical pitch.

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