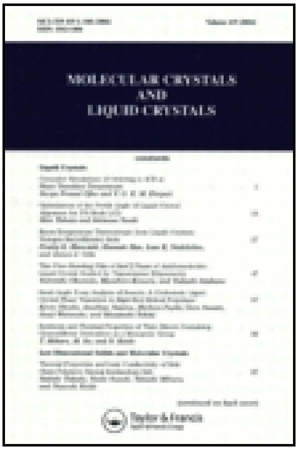

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Effect of Chiral Dopants Molecular Structure on Temperature Dependencies of Induced Cholesteric Helical Pitch

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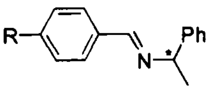
Effect of the chiral dopants molecular structure on the kind of the temperature dependencies of the induced cholesteric helical pitch has been studied for LC systems on the base of 4-pentyl-4'-cyanobiphenyl or 4-methoxybenzylidene-4-butylaniline including chiral *S*,α-phenylethylamine and *E*-1*R*,4*R*-2-(4-phenylbenzylidene)-*p*-menthane-3-one derivatives. The established correlations and their possible reasons have been discussed.

Keywords: induced cholesteric systems; the helical pitch temperature dependence; effect of chiral dopant molecular structure; *S*,α-phenylethylamine and *E*-1*R*,4*R*-2-(4-phenylbenzylidene)-*p*-menthane-3-one derivatives

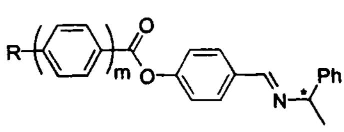
INTRODUCTION

Temperature dependence of helical pitch *P*(*T*) is an important characteristic of induced cholesteric systems. Such dependencies have been obtained for many chiral nematics and smectics [1] as well as for some induced cholesteric systems including non-chiral nematic and chiral dopant (see, e.g. [2-6]). However, the effect of chiral dopants molecular structure on this characteristic is still scantily studied for systematic series of dopants. The considerable distinction between temperature dependencies of the *P* value has been revealed for the LC systems including *E*- and *Z*-isomers of 1*R*,4*R*-2-(4-methoxyphenyl)benzylidene-*p*-menthan-3-one as chiral dopants [7, 8]. A slight reduction of *P* value with temperature rise has been observed for the systems containing *E*-isomer. In contrast, in the case of the systems with *Z*-isomer the induced helix untwists as the temperature increases. Besides, much lower helical twisting power (β) of *Z*-isomer as compared with that for *E*-form has been shown [7-9]. Distinctions in *P(T)* dependence kind as well as in β values can be seen for induced cholesteric LC containing (–)-menthole esters and tigogenin derivatives as chiral dopants [2]. An increase of the *P* value with temperature has been noticed for LC systems including some low-twisting chiral dopants N-arylidene *S*,α-phenylethylamine series [10, 11]. Low-anisometric quasi spherical molecular shape that these dopants possess [11] seems us to be of importance.

In this work, *P*(*T*) dependencies are described for the induced cholesteric systems on the base of 4-pentyl-4'-cyanobiphenyl (5CB) and, in some cases, on the base of 4-methoxybenzylidene-4-butylaniline (MBBA) including *S*,α-phenylethylamine (**1**–**3**) and *E*-1*R*,4*R*-2-(4-phenylbenzylidene)-*p*-menthane-3-one (**4**–**6**) derivatives as chiral dopants.

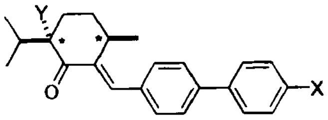


1, R = CH_3COO(**a**)
R = Ph(**b**)



2, m = 1; R = H(**a**), CH_3(**b**), C_4H_9(**c**), OCH_3(**d**), $OC_{10}H_{21}$(**e**)

3, m = 2; R = H(**a**), C_nH_{2n+1}, n = 1(**b**), 5(**c**), 7(**d**), 8(**e**), 9(**f**), 10(**g**), 11(**h**)



4, Y = H; **5**, Y = CH_3; **6**, Y = Br
X = H (**a**), OCH_3(**b**), OC_5H_{11}(**c**), OC_6H_{13}(**d**)

EXPERIMENTAL

The studied compounds were synthesised as described in [11-14]. The measurement of *P* values was carried out by Grandjean–Cano method in a glass wedge-shaped cell which had a ± 0.5° temperature control accuracy. The chiral dopant mole fraction in LC solutions was from 0.003 to 0.008. In most cases, the $P(T)$ dependencies are almost linear over the whole studied temperature range (see Figures 1, 2). A sharp decrease of *P* just before N*→I phase transition is observed only for several compounds (see Figure 2a, curve **4b**, **4d**). However, even in these cases, 3–4° below the transition, $P(T)$ dependencies are linear in good approximation (correlation coefficients are 0.95–0.99). This peculiarity makes possible to quantify the effect of chiral dopant molecular structure on the dependence mentioned using the slope of $P_{rel}(T)$ function (the dP_{rel}/dT values, Tables I, II). Here, $P_{rel} = P/P_{Tiso-5}$ and P_{Tiso-5} is the *P* value at 5° below the phase transition N*→I. The use of the parameter P_{rel} is believed to be the most correct.

RESULTS AND DISCUSSION

In general, two types of $P(T)$ dependencies are observed for the systems studied: the *P* values increase or decrease with temperature (the dP_{rel}/dT values are positive or negative, respectively, see Figures 1, 2 and Tables I, II). Dependencies of the first type take place only for systems including the chiral dopants **1a**, **1b**, **2a–2d**, **5a**, **5b** (two last ones in MBBA). For other systems studied, the *P* value decreases as temperature rises.

As follows from Table I, in most cases the dP_{rel}/dT value decreases with increasing chiral dopant twisting power. Thus, an extension of the π-electronic fragment in *S*,α-phenylethylamine derivatives favours both the dP_{rel}/dT decrease and the helical twisting power increase (see Table I, compounds **1a** and **1b**, **2a** and **3a**, **2b** and **3b**). The dP_{rel}/dT value is also reduced as an alkyl or oxyalkyl substituent is introduced into compounds **2a**, **3a** (Table I) or **4a–6a** (Table II).

TABLE I Parameter dP_{rel}/dT (grad^{-1}) and helical twisting power (β, mμ^{-1} × mol.fr.$^{-1}$) for the chiral dopants 1–3 in 5CB

Compound	R	m	$dP_{rel}/dT \times 10^4$	$-\beta$ [10]
1a	CH_3COO	—	52 ± 8	19.9 ± 1.2
1b	C_6H_5	—	27 ± 3	30.3 ± 1.7
2a	H	1	17 ± 4	34.4 ± 1.5
2b	CH_3	1	4.8 ± 0.9	34.9 ± 1.6
2c	C_4H_9	1	6.0 ± 0.7	36.0 ± 1.8
2d	OCH_3	1	4.3 ± 0.9	35.7 ± 1.8
2e	$OC_{10}H_{21}$	1	-31 ± 4	40.4 ± 1.0
3a	H	2	-27.6 ± 0.6	39.7 ± 3.0
3b	CH_3	2	-48 ± 4	42.2 ± 2.9
3c	C_5H_{11}	2	-41 ± 6	41.6 ± 1.2
3d	C_7H_{15}	2	-58 ± 4	42.0 ± 3.7
3e	C_8H_{17}	2	-63 ± 9	42.4 ± 2.1
3f	C_9H_{19}	2	-60 ± 7	43.2 ± 2.2
3g	$C_{10}H_{21}$	2	-49 ± 5	41.4 ± 1.1
3h	$C_{11}H_{23}$	2	-35 ± 2	40.5 ± 1.7

In the case of the compounds **3**, as the number of carbon atoms (n) in terminal alkyl group increases, the dP_{rel}/dT parameter decreases and reaches a minimum at n = 7–9. A further alkyl elongation lead already to increase in this parameter (Table I). Moreover, in each series of 2-arylidene-*p*-menthane-3-one derivatives **4–6**, the replacement of OCH_3 by OC_5H_{11} group also results in the dP_{rel}/dT parameter decrease, however, the next homolog shows already the same or higher value (Table II). At the same time, no regular change of the helical twisting power is noted in the homologous series of the compounds **3–6** (Table I, II).

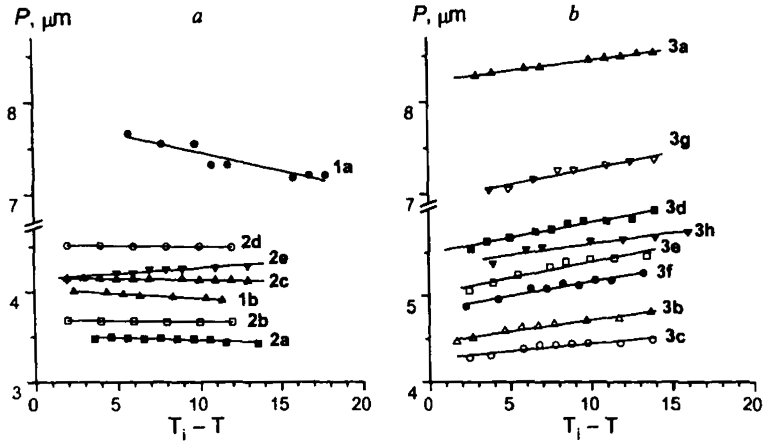


FIGURE 1 The temperature dependencies of the induced helical pitch for LC systems on the base of 5CB including the chiral dopants **1**, **2** (*a*) and **3** (*b*); the curve number corresponds to that of chiral dopant.

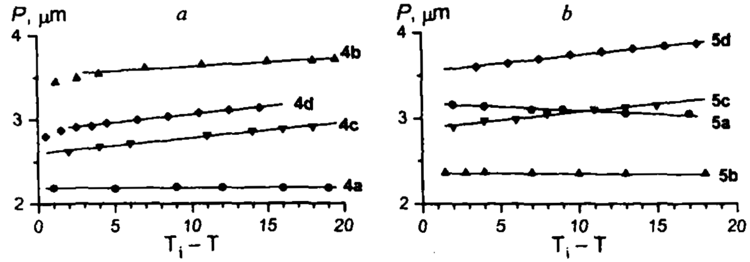


FIGURE 2 The temperature dependencies of the induced helical pitch for LC systems on the base of MBBA including the chiral dopants **4** (*a*) and **5** (*b*); the curve number corresponds to that of chiral dopant.

As shown in Table II, in each series of the LC systems based on MBBA which include the compounds **4–6** with the same substituent X, the dP_{rel}/dT value decreases in the sequence of Y: CH_3>H>Br. This trend is seen the most clearly for chiral dopants with X = H, OCH_3 (Table II). For the LC systems based on 5CB, the difference between dP_{rel}/dT parameter of compounds mentioned is levelled down significantly.

Taking into account the molecular structure characteristics obtained for compounds 1–6 by X-ray and molecular mechanics conformational analysis [11, 14–16], the $P(T)$ dependencies with the positive dP_{rel}/dT value may be concluded to be characteristic of the LC systems including chiral dopants with low-anisometric molecules. A low molecular anisometry has been shown to cause also low twisting power of chiral dopants [8–12, 17]. As the chiral dopant molecular anisometry is increased due to π-electronic skeleton extension or terminal alkyl (oxyalkyl) substituent incorporation, the dP_{rel}/dT value is reduced while the twisting power increases. The similar relation between the $P(T)$ dependence kind and chiral dopant molecular anisometry can be traced on the data of work [2].

TABLE II Parameter dP_{rel}/dT (grad^{-1}) and helical twisting power (β, mμ^{-1} × mol.fr.$^{-1}$) for the chiral dopants 4–6 in MBBA and 5CB.

Compound			MBBA		5CB	
	X	Y	$dP_{rel}/dT \times 10^4$	–β	$dP_{rel}/dT \times 10^4$	–β
4a	H	H	0.4 ± 2	41.9 ± 1.4	–39 ± 1	36.9 ± 0.6
4b	OCH_3	H	–28 ± 3	48.9 ± 1.5	–69 ± 3	40.1 ± 2.4
4c	OC_5H_{11}	H	–64 ± 2	54.0 ± 4.0	–110 ± 4	41.2 ± 2.9
4d	OC_6H_{13}	H	–64 ± 3	52.7 ± 1.7	–33 ± 2	42.4 ± 2.4
5a	H	CH_3	24 ± 3	37.8 ± 2.8	–38 ± 3	41.6 ± 2.3
5b	OCH_3	CH_3	3.5 ± 1	34.8 ± 1.0	–85 ± 4	30.6 ± 2.8
5c	OC_5H_{11}	CH_3	–65 ± 5	42.9 ± 3.3	—	—
5d	OC_6H_{13}	CH_3	–54 ± 2	47.5 ± 2.2	–88 ± 3	46.5 ± 2.0
6a	H	Br	–18 ± 3	44.5 ± 3.1	–40 ± 2	46.5 ± 1.2
6b	OCH_3	Br	–52 ± 5	49.6 ± 1.9	–119 ± 3	50.7 ± 1.2
6c	OC_5H_{11}	Br	–69 ± 6	52.4 ± 1.1	–138 ± 6	54.1 ± 1.6

As follows from Table I, the molecular anisometry increasing by the π-electronic skeleton extension influences both values of dP_{rel}/dT and β (cf. **1a** and **2a**, **2a** and **3a**, **2b** and **3b**) more significantly in comparison with the effect of terminal substituent incorporation (cf. **2a** and **2b–e**, **3a** and **3b–3h**).

Smaller dP_{rel}/dT values in MBBA for all compounds **4a–4d** (Y = H) as compared to those for **5a–5d** (Y = CH_3) having the same substituent X are in agreement with the molecular anisometry reduction in the compounds 4 due to replacement of hydrogen atom at the chiral centre C-4 by axial methyl group [14, 15]. However, negative and the lowest dP_{rel}/dT values for 4-bromo substituted compounds **6a–6c** (see Table II) do not correlate with low anisometry of their molecules. The C–Br bond in these molecules has been shown [16] to be axial similarly to methyl group in the case of chiral dopants **5a–5d**. Besides, Van-der-Waals radii of bromine atom and of methyl group are essentially equal. In spite of structure similarity of 4-methyl (**5**) and 4-bromo (**6**) derivatives, the observed difference between the dP_{rel}/dT values for these compounds reveals some specific effects caused by higher polarizability of the bromine atom as compared to that of the methyl group as well as by significant dipole moment of the C–Br bond.

It follows from theoretical models [18, 19] and experimental results [20] that the $P(T)$ dependence is defined by the change with temperature of the orientation ordering parameter and by temperature dependence of the elastic constant K_{22} associated therewith. In low concentration (0.2 to 0.4 %), chiral dopants having moderate or high molecular anisometry do not influence the ordering parameter and the K_{22} constants of the 5CB and MBBA [20]. For induced cholesterics containing those dopants, the reduction of the nematic K_{22} value with temperature rise favours the helical twisting (decrease of P value). Indeed, more negative dP_{rel}/dT values for the systems based on 5CB in comparison with those for the MBBA-based ones (having a weaker K_{22} *vs* T dependence [20]) containing the same chiral dopant are in well agreement with our considerations.

It may be assumed increase of *P* value with the temperature rise observed for LC systems with low-anisometric chiral dopants is caused by that such dopants disturb strongly the local ordering in the mesophase [11, 12, 21], thus hindering an effective formation of the cholesteric helix. The lowest helical twisting power of those dopants in the series studied (see Table I, compounds **1a, 1b**) agrees with that assumption. As the temperature increases, the mentioned effect strengthens obviously to a greater extent than the elastic constant K_{22} is reduced.

CONCLUSION

The chiral dopants molecular structure, particularly, their molecular anisometry, influences significantly the character of temperature dependence of the induced helical pitch. Chiral dopants having low-anisometric molecules cause the cholesteric helix to untwist as temperature increases. For LC systems including chiral dopants with high molecular anisometry, the *P* value decreases as temperature rises. Increasing of the dopant molecular anisometry by means of π-electronic skeleton extension affects most significantly the quantitative characteristic of the *P*(*T*) dependencies.

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