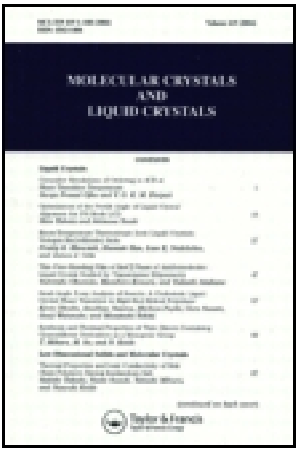

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An Influence of the Fluorosubstitution and the Spacer Length on Helical Twisting Power of Chiral Three Ring Esters with Perfluorinated Alkanoyloxy Unit in a Terminal Chain

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An Influence of the Fluorosubstitution and the Spacer Length on Helical Twisting Power of Chiral Three Ring Esters with Perfluorinated Alkanoyloxy Unit in a Terminal Chain

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Chiral liquid crystal phases have been attracting great interest in the past years because of their unique optical properties, such as: selective light reflection, optical dichroizm, ferro- and antiferroelectric behavior. One of the most popular ways of obtaining such materials is an addition of chiral dopants with high helical twisting power to the achiral liquid crystal mixtures. The aim of this paper is to investigate the dependence of helical twisting power on the spacer length and fluorosubstitution in recently prepared chiral three-ring esters with perfluorinated alkanoyloxy unit in a terminal chain.

Keywords Antiferroelectric phase; cholesteric phase; Helical Pitch; Helical Twisting Power

1. Introduction

Modification of non-chiral liquid crystalline mixtures with chiral dopants is one of the easiest ways of obtaining chiral liquid crystal materials for technological applications such as display devices and optical filters [1]. Since the pitch changes with the concentration of the chiral dopant, it is an effective method to control such parameters as selective light reflection and helix sense [2]. In recent years more interest is taken towards obtaining chiral materials and controlling their properties. Information about the influence of structural conditions on formation of helical pitch in non-chiral liquid crystalline materials is a topic that still needs more research. The variety of interactions occurring during the transfer of chirality from a single molecule of optically active dopant to non-chiral liquid crystal mixture makes applicable theoretical models hard to obtain.

This situation is responsible for the fact that dependence between the ability to create the helical pitch and a dopant molecular structure has been determined only for a few groups of compounds. The aim of this paper is to research correlations between Helical Twisting Power and molecular parameters of compounds with

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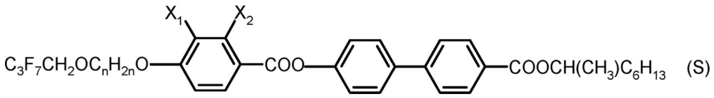
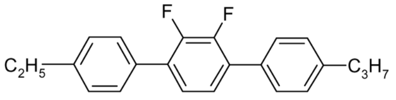
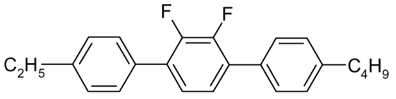
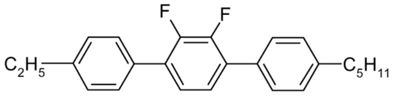
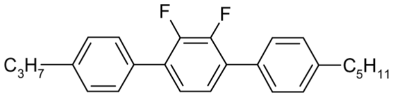
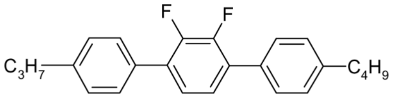
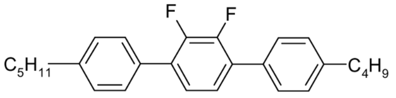
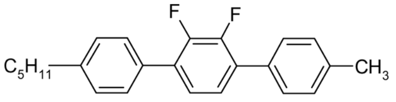
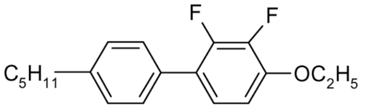
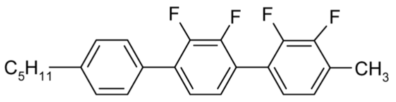
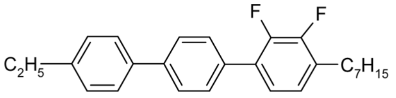


Figure 1. Structure of chiral dopants used where n = 2–7; $X_1 = X_2 = F$ or H, $X_1 = F$ and $X_2 = H$ or $X_1 = H$ and $X_2 = F$.

Table 1. The 1781 nematic mixture composition

Compound structure	Weight ratio (%)
	9
	13
	19
	8
	9
	13
	6
	12
	6
	5

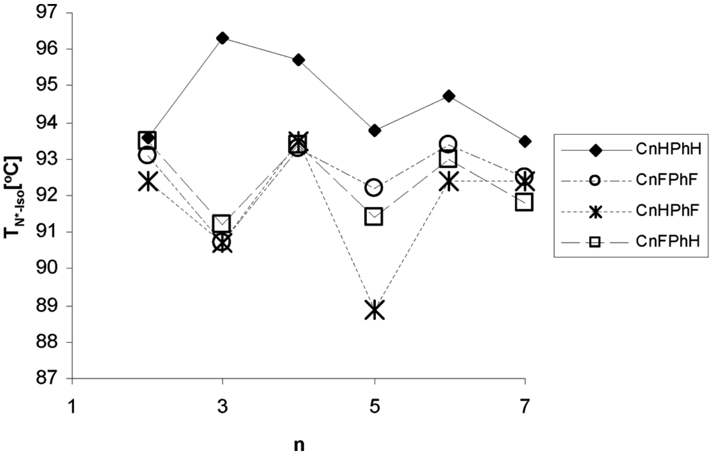
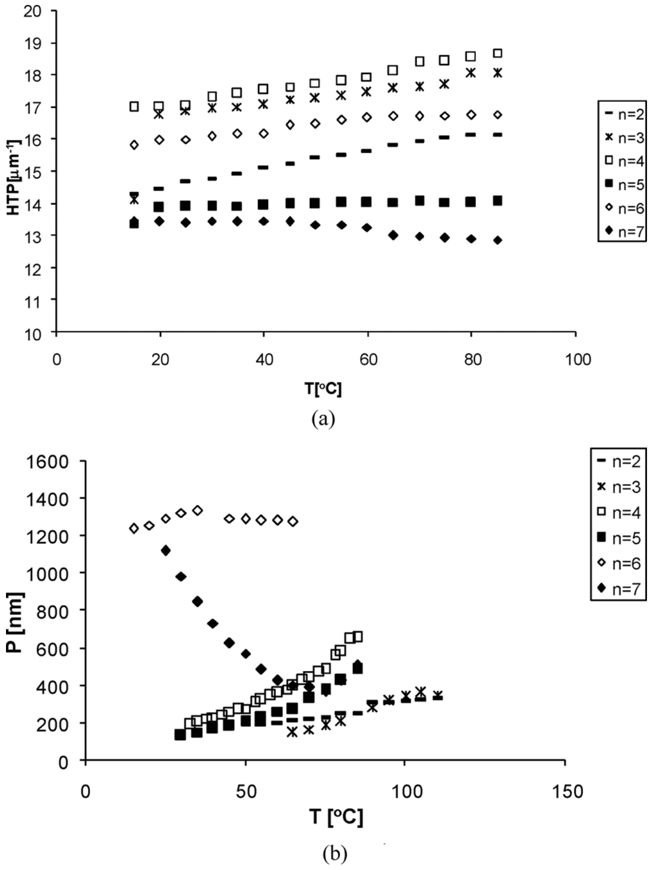


Figure 2. Dependence of the transition temperature between cholesteric and isotropic phases on a chiral dopant fluorosubstitution and spacer length.



(a)

(b)

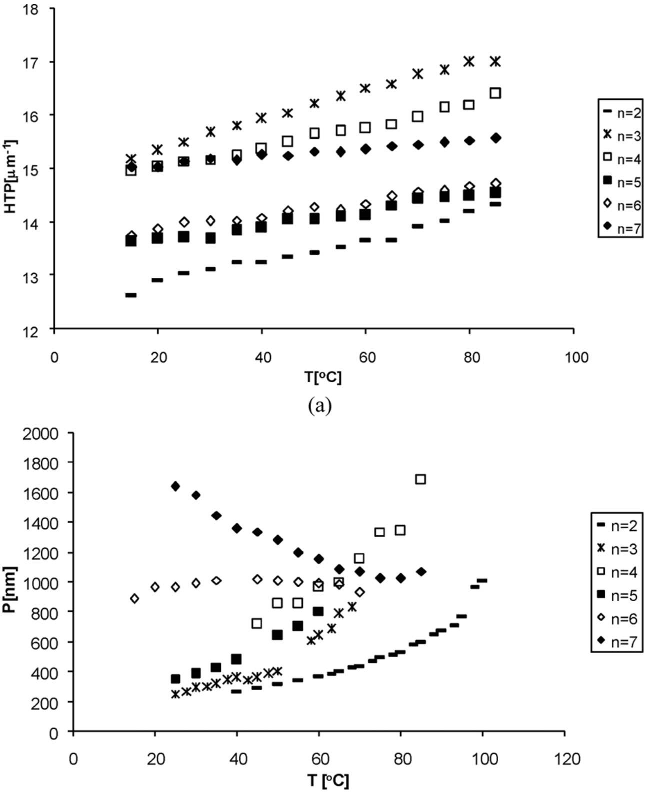
Figure 3. (a) Temperature dependence of HTP for $X_1 = X_2 = H$ substitution and (b) temperature dependence of helical pitch of pure compounds for $X_1 = X_2 = H$ substitution [7,8].

structure presented in Figure 1, such as spacer length and the type of the rigid core fluorosubstitution. Helical Twisting Power temperature dependence will be calculated according to the equation HTP (μm^{-1}) = 1/(Pcr), where P (μm) is the helical pitch length, c (mol/mol) is the molar ratio of a chiral dopant and r is the enantiomeric excess [3–5]. Helical pitch was measured using of selective reflection method and calculated in accordance with the equation $P = \lambda_{max}/n$ where λ_{max} (μm) is the selectively reflected light wavelength, and n is the average refractive index. All of the investigated compounds have antiferroelectric phase SmC_A^*, most of them have also SmC* phase and some of them SmA* phase [6]. Their helical pitch in smectic phases and HTP in nematic phase will be compared in this paper.

2. Materials

Compounds with the chiral structure presented on Figure 1 [6] have been used as chiral dopants.

Nematic material mixture 1781 (Table 1) with negative dielectric anisotropy and the nematic-isotropic transition at 94.8°C and melting point below 0°C has been used as a host.



(a)

(b)

Figure 4. (a) Temperature dependence of HTP for $X_1 = X_2 = F$ substitution and (b) temperature dependence of helical pitch of pure compounds for $X_1 = X_2 = F$ substitution [7,8].

3. Experimental

Mixtures with all of chiral compounds of 10% weight ratio have been prepared. Cholesteric–isotropic transitions have been determined by means of texture observations under a polarizing microscope with heating stage.

Figure 1 shows the dependence of cholesteric–isotropic transition phase transition temperatures length of the alkyl chain within chiral dopant. The results for mixtures with 10% weigh ratio of optically active dopants are presented. It can be observed that unsubstituted dopants give the highest transition temperatures, which are higher than the isotropic transition temperature of pure 1781 mixture (94,8°C). In all other homologous series they are lower than 94,8°C. This can be caused by the similarity of structures between fluorosubstituted dopants and molecules of the nematic base mixture.

Selective reflection measurements were conducted with UV-3600 Shimadzu spectrophotometer using Peltier cells and temperature controller. Measurements were carried out in cooling stage with 5°C step. The helical pitch temperature dependence was published previously [7,8].

Figure 1a shows the temperature dependence of HTP for homologous series with $X_1 = X_2 = H$.

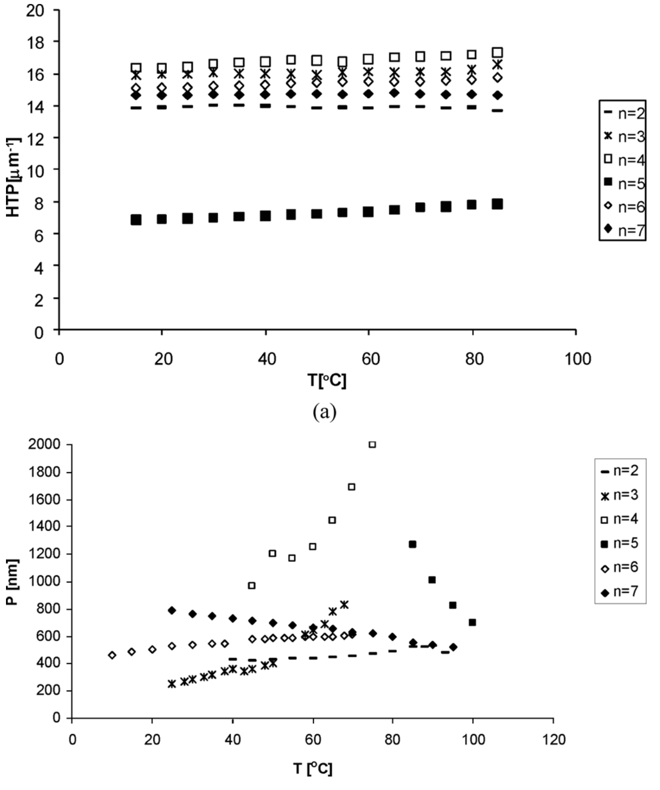
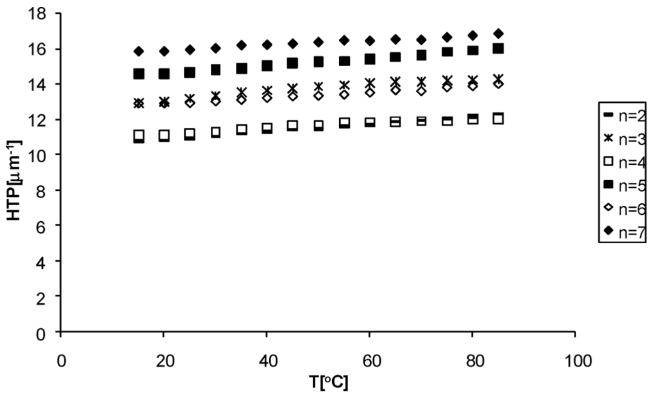


Figure 5. (a) Temperature dependence of HTP $X_1 = H$, $X_2 = F$ substitution and (b) temperature dependence of helical pitch of pure compounds for $X_1 = H$, $X_2 = F$ substitution [7,8].

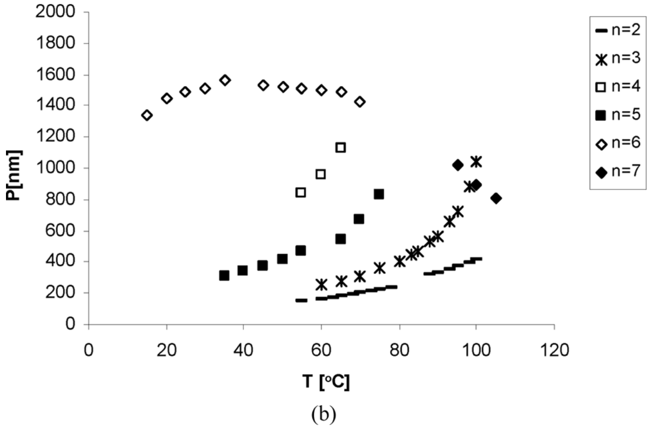
It is noticeable that HTP is the largest for the compound with 4 methylene groups in the alkyl chain and the smallest for the compound with 7 methylene groups. The HTP value seems to be higher for structures with high even numbers of carbon atoms in the alkyl chain. This fact is interesting if we compare this data with helical pitch values of pure compounds shown in Figure 1b. Pure compounds of extreme HTP values in nematic base have the most temperature-dependent helical pitch of all of the compounds in this homologous series. The helical pitch is increasing with temperature for the compound with 4 methylene groups and the helical pitch is decreasing with temperature for the compound with 7 methylene groups.

Figure 3a presents HTP values for homologous series with $X_1 = X_2 = F$ substitution.

For the compounds of this homologous series the highest and the lowest HTP values were calculated for the compounds with 3 and 2 carbon atoms in alkyl chain, respectively. Compounds with this type of substitution seem to show smaller HTP values than the previous homologous series. Comparison with pure compounds helical pitch measurements (Fig. 3b) indicates that both compounds with extreme HTP values have the lowest value of the helical pitch out of the compared compounds. If



(a)



(b)

Figure 6. (a) Temperature dependence of HTP for $X_1 = F$, $X_2 = H$ substitution and (b) temperature dependence of helical pitch of pure compounds for $X_1 = F$, $X_2 = H$ substitution.

we compare compounds in pairs even to odd n number (2 and 3, 4 and 5, 6 and 7), we will notice that the one with higher pitch value of one pair also exhibits higher HTP value.

In Figure 4a HTP values for monofluorosubstituted compounds with fluorine closer to ester group have been shown. A situation similar to difluorosubstituted homologous series occurs where pair of compounds with near odd and even numbers of methylene groups exhibit extreme values of HTP. The similarity is even higher when we compare pure compounds results for odd even pairs (Fig. 4b). The compound that possesses greater helical pitch has also the one out of a pair that has higher HTP.

HTP values for compounds with fluorine atom substituted closer to the spacer have been shown in Figure 5a. Two effects are visible, that odd number of methylene groups and larger alkyl chain groups promotes structures with higher Helical Twisting Power. This does not fully correspond with pure compounds helical pitch measurements, where it is the chain length that promotes larger P values (Fig. 5b).

4. Conclusions

For homologous series with different kinds of fluorosubstitution in rigid core, different kinds of HTP dependence on spacer length are observed. Comparison between HTP values in nematic phase and helical pitch of pure compounds in $\mathrm{SmC}_\mathrm{A}^*$ phase also does not give a clear correlation. The parameter that seems to have the dominating effect is the odd-even methylene group number in spacer chain, although in can be only traced with two neighboring members of most homologous series.

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