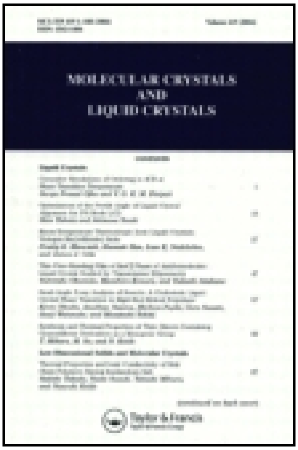

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New Chiral Dopant Possessing High Twisting Power

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New Chiral Dopant Possessing High Twisting Power

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We have synthesized and investigated a new chiral dopant. It belongs to the derivatives of p*-terphenyldicarboxylic acid and has twisting power in the smectic C^* mixture much higher than any chiral compound of this series known before. The ferroelectric liquid crystal mixtures on the base of achiral SmC matrix and the new chiral dopant have been elaborated and there optical and electro-optical properties were investigated.*

Keywords: chiral dopant; ferroelectric liquid crystal; helical pitch; helix wave vector; terphenyldicarboxylic acid derivative

INTRODUCTION

The most appropriate and cheep method to obtain ferroelectric liquid crystal (FLC) multicomponent composition with desirable properties is to admix a chiral dopant or a composition of the dopants into an achiral smectic C matrix [1,2]. This method allows to simplify the problem of FLC's creation by dividing it into two stages: the first stage is elaboration of the achiral matrix possessing required properties such

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as phase sequence, a broad temperature range of smectic C phase, rotational viscosity γ_φ, molecular tilt angle θ, etc. The second one is a choice of the chiral dopant providing an intended magnitude of the spontaneous polarization P_s and a proper helical pitch p_0, depending on the type of the used electro-optical effect.

The structure of a chiral dopant should be chosen so, that its introduction into a smectic C matrix would not considerably change the matrix fundamental parameters, especially the temperature range of smectic C phase. One of the most appropriate chemical class in this sense are derivatives of *p*-terphenyl-dicarboxylic acid [3–5], which even being non-mesogenic can enlarge the temperature range of C* phase of the mixtures, when they are added to achiral smectic C matrix.

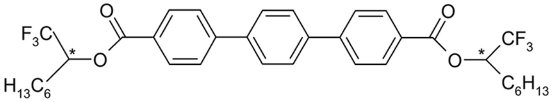
Chiral derivatives of *p*-terphenyl-dicarboxylic acid possess rather high helical twisting power both in nematic and smectic C* phases [3]. That was the reason why due to these chiral dopants the helical pitch of the smectic C* phase less than 1 μm was observed for the first time. Moreover, electro-optical mode of deformed helix ferroelectric (DHF) liquid crystal was recognized as a very suitable operation mode of low voltage and fast switching (the response time is less than 200 μs) liquid crystalline light shutters [6].

All FLC mixtures, elaborated before for applications with DHF-effect, have the helical pitch, which provides the selective light reflection in the visible spectral range, so, the helical pitch, obviously, was more than 400 nm. That was a reason why the light scattering accompanied the electro-optical response of the DHF cells placed between two crossed polarizers [7]. The contrast ratio of the light shutters was restricted by this light scattering, therefore a shift of the p_0 magnitude down to the UV spectral range is desirable to improve the optical quality of the DHF cells via suppression of the light scattering.

This paper is concerning with the synthesis and investigation of a new chiral dopant that belongs to the derivatives of terphenyl-dicarboxylic acid also but has twisting power much higher than any of chiral compound of this series [3–5] known before.

SYNTHESES

The chemical structure of the new dopant (*R,R*)-*bis*-(1,1,1-trifluorooct-2-yl)-4,4″-terphenyldicarboxylate (FOTDA) is shown below.



Synthesis of this dopant is accomplished as depicted in Figure 1.

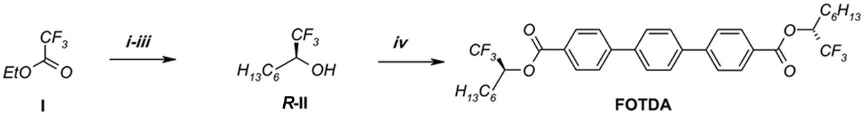


FIGURE 1 Scheme of FOTDA synthesis, where i: $C_6H_{13}MgBr$, Et_2O, reflux 4 h; ii: chloroacetyl chloride, pyridine, Et_2O/benzene; iii: lipase from Candida rugosa, phosphate buffer pH 7.28, 38°C, 12 h; iv: 4,4″-terphenyl dicarboxylic acid dichloranhydride, pyridine/toluene, reflux.S)-1,1,1-trifluorooctan-2-ol (S-II) was obtained by three-stage synthesis starting from ethyl trifluoroacetate (I). I was subjected to one-pot Grignard addition/reduction sequence which results in formation of racemic alcohol (II) [8]. Optically active S-II was obtained in 36% yield (>98% ee) by enzymatic kinetic resolution of chloroacetic ester of racemic-II similarly to the method described in the work [7]. Reaction of S-II and 4,4″-terphenyl dicarboxylic acid dichloride gives target compound FOTDA (III) in 23% yield.

EXPERIMENTAL

NMR ^1H spectra were recorded on a Varian Mercury VX-200 (200 MHz) spectrometer in $CDCl_3$ or DMSO d-6 using signal of residual protons as inner standard. Mass spectra were recorded on a Varian 1200 L GC-MS instrument either in GC-MS mode or with the use of direct exposure probe (DEP) method with EI at 70 eV. HPLC analyses were performed on a Bischoff HPLC system equipped with 2.0 × 250 mm Prontosil 120–5-C18H reversed phase column using acetonitrile as eluent; for preparative HPLC separation the 20 × 200 mm Prontosil 120–10-C18H reversed phase column was used. Elemental analyses were performed with EA-3000 analyser (Eurovector, Italy). Optical rotation was measured using SU-4 polarimeter in 10 cm cell.

The melting point of FOTDA was evaluated using a Mettler FP-51 apparatus with a Leitz polarizing microscope, DSC measurements were done by means of Perkin-Elmer deferential scanning calorimeter.

The helical pitch p_0 of mixtures of the new dopant FOTDA with a specially developed for this case achiral smectic C matrix was detected from the measurements of vertically aligned FLC layers transmittance, Figure 2. The achiral SmC matrix consists of phenyl- and biphenyl-pyrimidine derivatives. The measurements were done with the spectrometer “Ocean optics.” Taking into account that the alteration period of the smectic C* helical structure in effective birefringence index is equal to $p_0/2$, we evaluated a minimum of the transmittance due to the light selective reflection on the helical

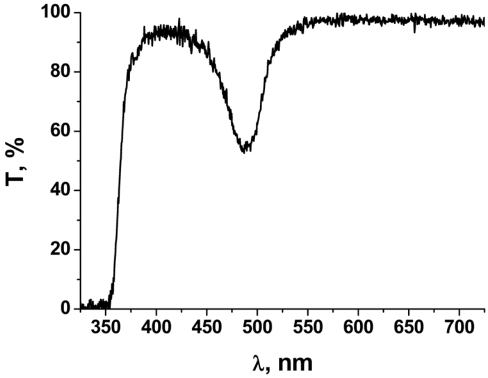


FIGURE 2 Transmittance spectrum of vertically aligned FLC layer with thickness is 20 μm, measured at temperature T = 18°C. The FLC mixture based on the achiral smectic C matrix and contains 14.3 mole percent of FOTDA.

structure that corresponds to the wavelength λ_{min}:

$$\lambda_{\min} = \frac{p_0}{2} \cdot n \cdot \cos\xi, \tag{1}$$

where n is averaged FLC birefringence index, ξ is the angle between the FLC helix axes and the metrical light propagation direction.

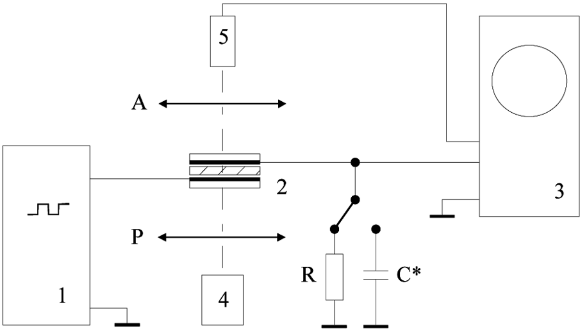


FIGURE 3 The design of experimental electro-optical set-up: 1 – generator, 2 – FLC cell placed on a rotating table, 3 – oscilloscope, 4 – He-Ne laser, 5 – a photo-diode, A – analyzer, P – polarizer, R – a resistance for registration of the polarization reversal current, C* – a capacitor for integrating of the polarization reversal current.

Electro-optical measurements of the FOTDA mixtures with the smectic C achiral martix were carried out using an ordinary electro-optical set-up (Fig. 3) based on He-Ne laser, Hewlett Packard Infinum oscilloscope and rotating table for adjusting of angular position of FLC cells placed between crossed polarizers. A programmed generator WFG-400 was used to generate electrical pulses sequences. A resistance R and a capacitor C* were used to control the polarization reversal current.

MATERIALS

Ethyl trifluoroacetate, *p*-terphenyl, bromohexane, magnesium fillings, chloroacetyl chloride, NaOH, KH_2PO_4, silica gel 0.035–0.070 mm (Acros), Lipase from *Candida rugosa*, type VII (Sigma) and all used solvents and acids are commercially available. All solvents were distilled and dried (if required) before the use. *n*-Hexylmagnesium bromide was obtained as described in [8]. 4,4″-Terphenyldicarboxylic acid dichloride was obtained from *p*-terphenyl according [10]. The *ee* of (*R*)-1,1,1-trifluorooctan-2-ol was estimated by comparison of optical rotation for the obtained sample $[\alpha]_D^{15}$ +28.3 (c = 2.34 $CHCl_3$) with lit. data $[\alpha]_D^{26}$ +26.3 (c = 1.04 $CHCl_3$) [11].

(R,R)-bis-(1,1,1-trifluorooct-2-yl)-4,4″-terphenyldicarboxylate (FOTDA). The solution of (*R*)-1,1,1-trifluorooctan-2-nol (2.9 g, 15.7 mmol) in 100 ml of toluene was added dropwise to the refluxed solution of 4,4″-terphenyldicarboxylic acid dichloranhydride, (2.13 g, 6.7 mmol) in 150 ml of dry toluene followed by addition of dry pyridine (20 ml). The reaction mixture was refluxed overnight and then concentrated in *vacuum*. The residue was flash-chromatographed on silica gel in hexane as eluent; fractions containing the desired product were concentrated in vacuum giving crude FOTDA as maize yellow oil which contains essential amount of impurities according to HPLC. Further purification by preparative HPLC followed by extraction with hot hexane via short plug of silica gel in the modified Soxlet apparatus, and low-temperature crystallization from MeOH gives FOTDA as white crystals in 23% yield.

Purity >99% (HPLC).

NMR ^1H ($CDCl_3$, δ, ppm, J/Hz): 8.17 (4H, d, 8.2 Hz), 7.74 (4H, d, 8.2 Hz), 7,74 (4H, s), 5.57 (2H, sext., 6.6 Hz), 1.90 (4H, d, 7.1 Hz), 1.33 (16H, m), 0.86 (6H, t, 6.3 Hz);

MS (m/z ($I_{rel.}$, %)):652 (6.9), 651 (37.1), 650 (100.0, M^+), 486 (3.8), 485 (18.2), 484 (34.6), 468 (12.6), 467 (45.1), 439 (5.0), 319 (18.7), 318 (74.1), 301 (21.5), 229 (13.3), 228 (34.8), 227 (14.8), 226 (17.6), 202 (6.0).

Melting point of compound FOTDA detected by microscope is 42.2°C.

Melting point of compound FOTDA detected via DCS is 42.12°C, melting heat is 3.9 kcal/M.

RESULTS AND DISCUSSION

It is known that in a mixture of nematic liquid crystals with a low concentration of a chiral dopant the helix wave vector q_0 is expressed by the following equation [3]:

$$q_0 = 2\pi/p_0 = \lambda_0 C_{ch} \tag{2}$$

where λ_0 is the twisting power of the mixture, p_0 is the helical pitch, C_{ch} is weight concentration of the dopant. We have found experimentally that $q_0(C_{ch})$ dependence of the binary mixture of 5CB with the dopant FOTDA can be described by the relationship (2) at $\lambda_0 \cong +0.4 \cdot 10^6\ (\text{m}\cdot\text{wt}\%)^{-1}$.

A dependence of the helical pitch p_0 on molar concentration C_{chm} of the chiral dopant FODTA $p_0(C_{chm})$ in its mixtures with the specially developed achiral smectic C multicomponent matrix has been measured as well (see Fig. 4). Evidently, $q_0(C_{chm})$ dependence (Fig. 4) exhibits a threshold in smectic C* phase. Similar behavior of the helical pitch was already reported before [12,13].

That means the equation (2) is not valid for smectic C* phase and origin of this fundamental phenomenon is still not clear. Analytical expression for $q_0(C_{chm})$ dependence in smectic C* phase can be written as:

$$q_0 = \frac{\lambda_{0m}}{2}\left[\left(C_{chm} - C_{chm}^{th}\right) + \left|C_{chm} - C_{chm}^{th}\right|\right], \tag{3}$$

where C_{chm}^{th} – is the threshold concentration, $\lambda_{0\text{m}}$ is the twisting power regarding the molar concentration of the chiral dopant. The experimental dependence $q_0(C_{chm})$ presented in Figure 4 can be described with the relationship (3) at $\lambda_{0\text{m}} = \cong +1.5 \cdot 10^6\ (\text{m}\cdot\text{mol}\%)^{-1}$. So, the twisting power is very high in comparison with any one reported before in smectic C* phase, see, for instance [3].

The helical pitch of smectic C* mixtures can get UV region at concentration of the dopant more than 20 molar percents, see Figure 5. Actually, the mixtures exhibit no selective reflection in the visible spectral range; they look like completely white because the helical pitch is less than 400 nm. Nevertheless, DHF effect [6] manifests in the mixtures very pronounced. Even if the FLC layer thickness

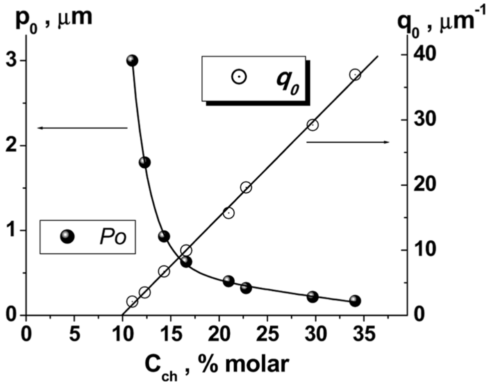


FIGURE 4 Dependencies of the helical pitch and the wave vector on molar concentration of FOTDA in mixtures with the achiral smectic C multicomponent matrix. Measurements were carried out at temperature interval from $A^* - C^*$ phase transition $(T_c - T) = 35^\circ C$.

is 1.5 μm the helix is not unwound at all and the cell demonstrates the response time $\tau_{0.1-0.9}$ that is independent on the applied voltage amplitude in the case it is less than critical amplitude U_c of the helix unwinding that corresponds to the peak in Figure 5.

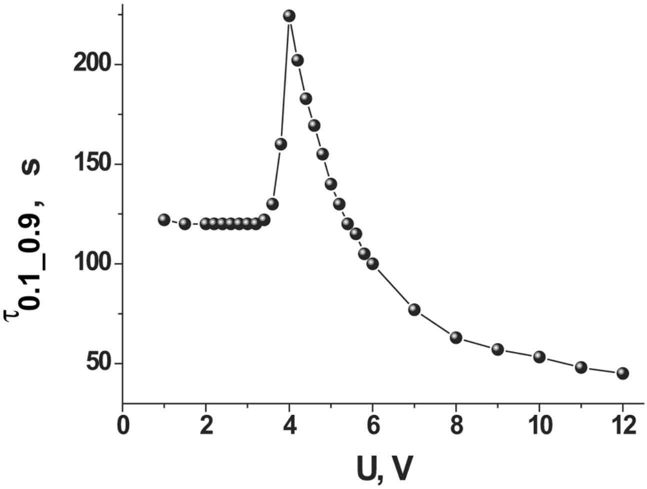


FIGURE 5 The electro-optical response time of 1.5 μm FLC cell based on the mixture of FOTDA (30% mol) and the achiral smectic C matrix (70% mol).

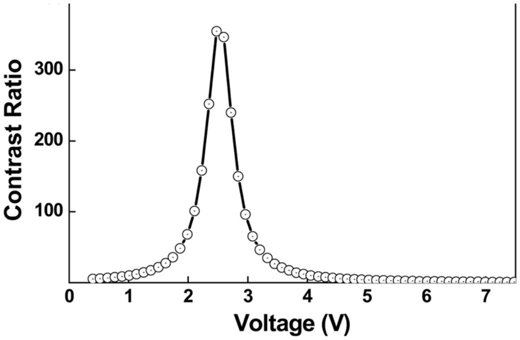


FIGURE 6 The contrast ratio of 1.5 μm DHF FLC cell based on the mixture of FOTDA (30% mol) and the achiral smectic C matrix (70% mol). Measurements have been carried out at $\lambda = 0.63\,\mu m$, the ac driving voltage frequency is 100 Hz.

The contrast ratio of DHF FLC cells based on very short helical pitch ($p_0 < 400\,nm$) can be rather high (more than 300:1, as it is shown in Fig. 6) due to the absence of the light scattering in the visible spectral range. It is evident advantage of the short helical pitch FLC's for electro-optical applications.

CONCLUSIONS

The new chiral non-mesogenic dopant possessing very high twisting power in smectic C* mixture was synthesized and investigated. It was shown experimentally that mixtures of the dopant with the achiral SmC matrix are ferroelectric liquid crystals which helical pitch is less than 400 nm in a broad temperature range. Possible advantages of the short helical pitch FLC's in electro-optical applications have been analyzed.

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