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***Original Article***

# FLUORINATED BIPHENYLPYRIMIDINE AS A POSSIBLE MATRIX FOR FERROELECTRIC LIQUID CRYSTAL MIXTURES

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**ABSTRACT**

The results of the synthesis and study of a new fluorinated achiral smectic C liquid crystal, namely, 2-(3-fluoro-4'-pentylbiphenyl-4-yl)-5-hexylpyrimidine, are presented. The possibility to use this compound as a matrix for ferroelectric liquid crystal (FLC) mixtures is evaluated. Two mixtures have been prepared: one (**FLC-691-F**) is based on new fluorinated compound and another (**FLC-691**) on its non-fluorinated analogue. The diester of optically active 2-octanol and terphenyldicarboxylic acid was used as a chiral dopant for both mixtures. Investigation of these FLC mixtures parameters: phase transition temperatures, helix pitch, spontaneous polarization and tilt angle show significant influence of fluorine atom. When comparing the phase sequence of **FLC-691** and **FLC-691-F** mixtures, one can note that in the fluorine containing mixture an additional smectic A phase arises. At the same temperatures, the helix pitch of **FLC-691-F** is 2 – 2.5 times less than the helix pitch of **FLC-691**. The tilt angle of **FLC-691-F** is much smaller than that of **FLC-691** but its value approaches the optimal value of 22.5 degrees, which ensures maximum light transmittance of electro-optical cells. At the same time the presence of fluorine atom in the matrix is a reason for the decrease of the mixture spontaneous polarization and a significant decrease (almost 4 times) in the driving voltage of electro-optical light shutters. As a result, it was shown that the fluorinated matrix provides new possibilities for controlling the mixture parameters.

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***Научная статья***
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# ФТОРИРОВАННЫЙ БИФЕНИЛПИРИМИДИН КАК ВОЗМОЖНАЯ МАТРИЦА ДЛЯ ЖИДКОКРИСТАЛЛИЧЕСКИХ СЕГНЕТОЭЛЕКТРИЧЕСКИХ СМЕСЕЙ

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шаг спирали

**АННОТАЦИЯ**

Сообщается о синтезе и исследовании нового фторированного ахирального смектического С жидкого кристалла, а именно 2-(3-фтор-4'-пентилбифенил-4-ил)-5-гексилпиримидина. Проведена оценка возможности использования этого соединения в качестве матрицы для смесевого сегнетоэлектрического жидкого кристалла (СЖК). Были приготовлены две смеси: одна (**FLC-691-F**) на основе нового фторированного соединения и другая (**FLC-691**) на его нефторированном аналоге. В качестве хиральной добавки для обеих смесей использовали диэфир оптически активного 2-октанола и терфенилдикарбоновой кислоты. Исследование параметров смесей СЖК: температурной последовательности фазовых переходов, шага спирали, спонтанной поляризации и угла наклона показывает большое влияние атома фтора. При сравнении последовательности фаз смесей **FLC-691** и **FLC-691-F** можно отметить, что во фторсодержащей смеси возникает дополнительная смектическая А-фаза. Шаг спирали **FLC-691-F** в 2-2,5 раза меньше при тех же температурах, чем шаг спирали **FLC-691**. Угол наклона **FLC-691-F** значительно меньше, чем у **FLC-691**, но его величина приближается к оптимальному значению 22,5 градуса, что обеспечивает максимальное светопропускание оптико-электронных ячеек. В то же время наличие атома фтора в матрице является причиной уменьшения спонтанной поляризации смеси и значительного уменьшения (почти в 4 раза) управляющего напряжения электрооптических световых затворов. В результате было показано, что фторированная матрица дает новые возможности управления параметрами смеси.

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## Introduction

Smectic C* ferroelectric liquid crystals (FLCs) provide two or three orders of magnitude faster response time as compared with nematic liquid crystals (NLCs), and therefore, they attract attention of scientists and engineers due to their potential use in photonic devices operating in the microsecond or even in sub-microsecond range [1–3].

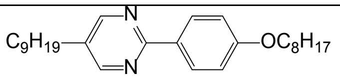
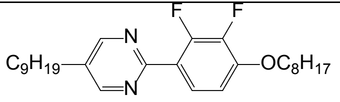
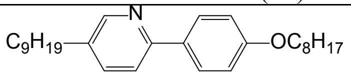
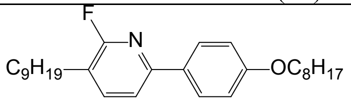
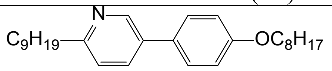
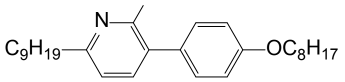
According to the literature [4, 5], the simplest method to create FLC compositions with the required properties is to add a chiral dopant into a non-chiral smectic C (SmC) matrix. It is necessary to elaborate a SmC matrix with the desired properties, such as relevant phase transitions sequence, low rotational viscosity, and appropriate molecular tilt angle. Finally, it is preferable to choose a chiral dopant that provides acceptable values of spontaneous polarization and helix pitch [6]. So, it is very important to choose the proper matrix and chiral dopant as well.

The phenyl and biphenyl pyrimidine derivatives were often used as achiral matrix for creation of FLC mixtures [7–11]. There are described biphenyl pyrimidines with optically active substituents, which have a wide smectic C* phase temperature range, a high spontaneous polarisation ($\boldsymbol{P_s}$) i.e., 500 nC/cm$^2$, and can be used as chiral dopants to achiral matrices [12]. It was noted [13] that melting points of compounds containing *p*-terphenyl core can be diminished by lateral substitution of hydrogen atoms in a core. In some cases, the use of fluorine substituent is efficient for these purposes [14–17].

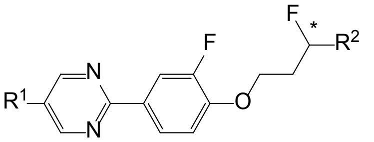
Design and study of fluorinated and non-fluorinated *p*-terphenyl-containing symmetric tetraesters are described in [18]. They were used as chiral components of ferroelectric liquid crystal materials working in deformed helix ferroelectric mode (DHF). The authors noted that core fluorination shows notable decrease in helix twisting power by 25–40 % depending on fluorine positions in the *p*-terphenyl core.

Applications and properties of fluorinated liquid crystals were described in the review [14]. Besides, the compounds with fluorinated *p*-terphenyl cores, fluorinated *trans*-1,4-disubstituited cyclohexylbiphenyls; three-ring structures based on *ortho*-difluorophenyls with a *trans*-1,4-disubstituted cyclohexane ring and derivatives of pyrimidine and pyridine were mentioned (see Table 1). According to Table.1, the insertion of fluorine in the molecules of phenyl pyridine or pyrimidine influences significantly the phase transition temperatures of LCs depending on the position of fluorine with respect to the nitrogen atoms in the molecule.

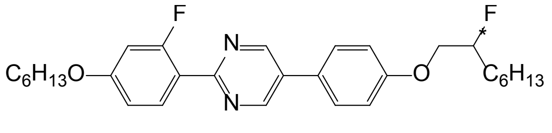
Table 1. **Phase transition temperatures of fluorinated and non-fluorinated phenyl pyrimidine and pyridine derivatives**

| |
|---|
| <br>Compound **A**<br>Cr 35.0 SmC 60.0 SmA 75.0 I (°C) |
| <br>Compound **B**<br>Cr 43.0 SmC 54.0 I (°C) |
| <br>Compound **C**<br>Cr 76.0.0 SmC 110.0 I (°C) |
| <br>Compound **D**<br>Cr 81.0 SmC 89.0 I (°C) |
| <br>Compound **E**<br>Cr 50.0 SmB 69.0 SmA 80.0 I (°C) |
| <br>Compound **F**<br>Cr 48.0 (SmA 40.0) I (°C) |

Compounds containing a fluorine atom in the benzene ring of phenyl- and biphenyl pyrimidines both in *meta*-position [19] to the pyrimidine fragment



and in *ortho*-position [20] were synthesized and studied.

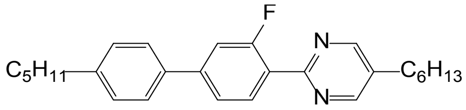


Fluorine is present in one of the side chains of both molecules as well.

The influence of fluorine on the SmC* helix pitch sign is mentioned in [20] but the authors failed to explain the mechanism of this phenomenon.

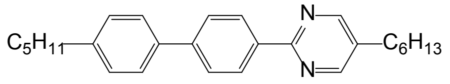
It has been shown in [21] that highly polar materials with multiple lateral fluorine substituents can have low melting points and, in some cases, generate a reasonably high smectic C-phase stability, which makes them suitable components in ferroelectric mixtures.

The main idea of this work is to evaluate the possibility to use a new fluorine containing biphenyl pyrimidine derivative, namely 2-(3-fluoro-4'-pentylbiphenyl-4-yl)-5-hexylpyrimidine (compound **I**) as a matrix for FLC mixtures.



**I**

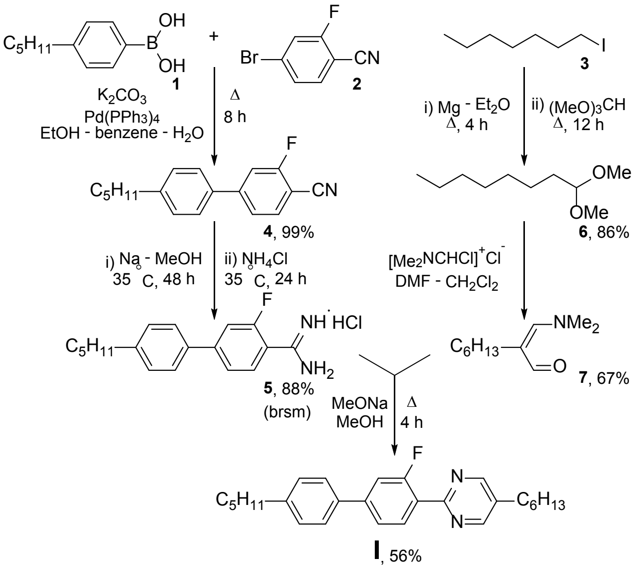
A goal was to study the influence of the fluorine substituent (which is at the *ortho*-position to the pyrimidine ring) on the helix pitch in the mixture with a non-mesogenic chiral dopant comparing it with non-fluorinated analogue – (4'-pentylbiphenyl-4-yl)-5-hexylpyrimidine (compound **II**). It was also planned to study the effect of the fluorinated matrix on the magnitude of spontaneous polarization and on the molecular tilt angle of the mixture.



**II**

## Experimental

A synthetic approach to biphenyl-pyrimidine **I** starting from commercially available 4-(*n*-pentyl)phenylboronic acid (**1**), 4-bromo-2-fluorobenzonitrile (**2**) and 1-iodoheptane (**3**) included five steps (*Scheme 1*). Initially, Suzuki cross-coupling between boronic acid **1** and bromide **2** afforded biphenylcarbonitrile **4** that was then transformed to amidine **5** via a base-catalyzed analogue of Pinner reaction. Meanwhile, iodide **3** was reacted with trimethyl orthoformate under Grignard reaction conditions resulting in acetal **6**, whose con-densation with Vilsmeier reagent gave rise to aminoacrolein **7**. Condensation of imidine **5** with aminoacrolein **7** provided desired biphenylpyrimidine **(I)**.



*Scheme 1*

### *Techniques and equipment*

NMR spectra were recorded on Bruker Avance 600 spectrometer at room temperature; the chemical shifts $\delta$ were measured in ppm with respect to solvent ($^1H$: $CDCl_3$, $\delta$ = 7.27 ppm; $CD_2Cl_2$, $\delta$ = 5.32 ppm; DMSO-$d_6$, $\delta$ = 2.50 ppm; $^{13}C$: $CDCl_3$, $\delta$ = 77.0 ppm; $CD_2Cl_2$, $\delta$ = 54.0 ppm; DMSO-$d_6$, $\delta$ = 39.5 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; m, multiplet. Coupling constants (*J*) are given in Hertz (Hz). Analytical thin layer chromatography (TLC) was carried out with silica gel plates (silica gel 60, F254, supported on aluminium) visualized with UV lamp (254 nm). Column chromatography was performed on silica gel 60 (230-400 mesh).

Phase transition temperatures were determined using Mettler Toledo hot stage HS82 and polarizing microscope Olympus BX53, which allows to take microphotographs of liquid crystal textures.

### *Synthesis of compound (I)*

4-(*n*-Pentyl)phenylboronic acid (**1**), 4-bromo-2-fluorobenzonitrile (**2**) and 1-iodoheptane (**3**) are commercially available materials.

*3-Fluoro-4'-pentylbiphenyl-4-carbonitrile* (**4**) was synthesized mostly according to the previously reported procedure [22] except for solvent used and reaction time. $K_2CO_3$ (13.80 g, 100 mmol) was dissolved in $H_2O$ (30 mL) under stirring. To the resulting solution EtOH (45 mL) and benzene (90 mL) were added and this mixture was degassed via bubbling with Ar for 15 min. Then, 4-bromo-2-fluorobenzonitrile (**2**) (10.00 g, 50 mmol), 4-(*n*-pentyl)phenylboronic acid (**1**) (12.50 g, 65 mmol) and $Pd(PPh_3)_4$ (1.74 g, 1.5 mmol, 3 mol. %) were added subsequently. The reaction mixture was heated under reflux (ca. 65 °C) for 8 h, then cooled down to ambient temperature and poured into ice-water mixture (ca. 150 mL). The resulting mixture was extracted with ethyl acetate (3×50 mL), combined organic fractions were washed with brine (3×30 mL), dried with $Na_2SO_4$ and concentrated under reduced pressure. Residue was purified by column chromatography (eluent petroleum ether – ethyl acetate 9:1). Yield 13.16 g (99 %); yellowish oil.

$^1$H NMR ($CDCl_3$, 600 MHz) $\delta$ = 0.92 (t, $^3J$ = 7.0 Hz, 3H, $CH_3$), 1.33–1.41 (m, 4H, $CH_2$), 1.64–1.69 (m, 2H, $CH_2$), 2.66–2.69 (m, 2H, $CH_2$), 7.30–7.32 (m, 2H, Ar), 7.42 (dd, $^3J$ = 10.3, $^4J$ = 1.6 Hz, 1H, Ar), 7.48 (dd, $^3J$ = 8.0, $^4J$ = 1.6 Hz, 1H, Ar), 7.50–7.52 (m, 2H, Ar), 7.67 (dd, $^3J$ = 8.0, $^4J$ = 6.7 Hz, 1H, Ar).

$^{13}$C{$^1$H} NMR ($CDCl_3$, 150 MHz) $\delta$ = 13.8 ($CH_3$), 22.4 ($CH_2$), 30.8 ($CH_2$), 30.3 ($CH_2$), 35.4 ($CH_2$), 99.2 ($^2J_{CF}$ = 16 Hz, C), 114.0 (CN), 114.2 ($^2J_{CF}$ = 20 Hz, CH), 123.0 ($^3J_{CF}$ = 3 Hz, CH), 126.8 (2×CH), 129.1 (2×CH), 133.4 (CH), 135.0 ($^4J_{CF}$ = 2 Hz, C), 144.4 (C), 148.3 ($^3J_{CF}$ = 8 Hz, C), 163.3 ($^1J_{CF}$ = 258 Hz, C).

*3-Fluoro-4'-pentylbiphenyl-4-carboximidamide* (**5**) was synthesized according to the general procedure [23]. Nitrile **4** (5.862 g, 22.0 mmol) was dissolved in dry MeOH (300 mL) under stirring. The resulting solution was heated up to ca. 35 °C using an oil bath. Catalitic amount of Na (58 mg, 2.5 mmol) was added, and the reaction mixture stirred for 48 h. Then, $NH_4Cl$ (1.200 g, 22.4 mmol) was added, and the reaction was carried out under the stirring for additional 24 h. The reaction mixture was concentrated under reduced pressure and mixed with $Et_2O$ (30 mL). The precipitate was filtered off and washed with $Et_2O$ (2×30 mL). The filtrate was concentrated under reduced pressure giving the starting nitrile **4** (4.840 g, 18.1 mmol). The precipitate was redissolved in EtOH (60 mL) and filtered. The resulting filtrate was concentrated and dried under reduced pressure affording the desired product **5**. Yield 1.100 g (88 %); white solid.

$^1$H NMR (DMSO-$d_6$, 600 MHz) $\delta$ = 0.84 (t, $^3J$ = 7.0 Hz, 3H, $CH_3$), 1.22–1.32 (m, 4H, $CH_2$), 1.54–1.61 (m, 2H, $CH_2$), 2.58–2.61 (m, 2H, $CH_2$), 7.31 (d, $^3J$ = 8.2 Hz, 2H, Ar), 7.64 (br.s, 4H, NH), 7.70 (d, $^3J$ = 8.2 Hz, 2H, Ar), 7.70–7.73 (m, 1H, Ar), 7.75–7.78 (m, 2H, Ar).

$^{13}$C{$^1$H} NMR (DMSO-$d_6$, 150 MHz) $\delta$ = 14.0 ($CH_3$), 22.0 ($CH_2$), 30.6 ($CH_2$), 30.9 ($CH_2$), 34.8 ($CH_2$), 114.0 ($^2J_{CF}$ = 22 Hz, CH), 115.6 ($^2J_{CF}$ = 13 Hz, C), 122.5 ($^3J_{CF}$ = 3 Hz, CH), 127.0 (2×CH), 129.1 (2×CH), 130.7 (CH), 134.6 (C), 143.7 (C), 146.7 ($^3J_{CF}$ = 8 Hz, C), 159.5 ($^1J_{CF}$ = 253 Hz, C), 162.2 (C).

*1,1-Dimethoxyoctane* (**6**) [24] was synthesized according to the general procedure [25]. To a stirred suspension of magnesium turnings (7.61 g, 0.317 mol) in dry $Et_2O$ (30 mL), a solution of 1-iodoheptane (**3**) (52 mL, 0.317 mol) in dry $Et_2O$ (30 mL) was added dropwise at such a rate to maintain $Et_2O$ at gentle reflux. After adding 10 mL of the solution of **3**, the reaction mixture was diluted with additional portion of $Et_2O$ (130 mL). After that, the remaining solution of **3** was added dropwise. The mixture was heated under reflux for 4 h, then cooled down to ambient temperature and trimethyl orthoformate (35 mL, 0.317 mol) was added dropwise. The resulting mixture was heated under reflux for 12 h, allowed to cool to ambient temperature and poured onto ice-water mixture (150 mL). The $Et_2O$ layer was separated and the aqueous layer was extracted with ethyl acetate (2×50 mL). Combined organic fractions were washed with brine (2×50 mL), dried with $Na_2SO_4$ and concentrated under reduced pressure. The residue was distilled. Yield 47.45 g (86 %). Colorless liquid, b.p. 87–88 °C / 20 torr.

$^1$H NMR ($CD_2Cl_2$, 600 MHz) $\delta$ = 0.88 (t, $^3J$ = 7.0 Hz, 3H, $CH_3$), 1.25–1.33 (m, 10H, $CH_2$), 1.52–1.58 (m, 2H, $CH_2$), 3.27 (s, 6H, $OCH_3$), 4.31 (t, $^3J$ = 5.8 Hz, 1H, CH).

$^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 150 MHz) $\delta$ = 14.4 ($CH_3$), 23.3 ($CH_2$), 25.2 ($CH_2$), 29.8 ($CH_2$), 30.0 ($CH_2$), 30.3 ($CH_2$), 32.4 ($CH_2$), 53.0 (2×$OCH_3$), 105.3 (CH).

*2-[(Dimethylamino)methylidene]octanal* (**7**) was obtained according to the general procedure [26]. A solution of DMF (6.72 g, 92 mmol) in $CH_2Cl_2$ (10 mL) was added dropwise with stirring to a solution of $POCl_3$ (15.45 g, 101 mmol) in $CH_2Cl_2$ (10 mL) at 0 °C under Ar. The resulting mixture was stirred for 12 h at ambient temperature and then concentrated under reduced pressure. The residue was suspended in 1,2-dichloroethane (10 mL) and cooled down to 0 °C. To the resulting mixture, DMF (6.72 g, 92 mmol) and solution of 1,1-dimethoxyoctane (**6**) (8.00 g, 46 mmol) in 1,2-dichloroethane (10 mL) were added sequentially. The mixture was stirred at ambient temperature for 1 h, heated under reflux for 1 h, cooled down to ambient temperature, and poured onto mixture of $K_2CO_3$ (30 g) and ice (100 g). Then, additional $K_2CO_3$ and water were added under stirring until pH 10. The mixture was extracted with ethyl acetate (3×50 mL), combined organic fractions were washed with brine (5×50 mL), dried with $Na_2SO_4$ and concentrated under reduced pressure. The product **7** was purified by column chromatography (eluent petroleum ether – ethyl acetate 4:1). Yield 5.65 g (67 %); brown oil.

$^1$H NMR ($CD_2Cl_2$, 600 MHz) $\delta = 0.88$ (t, $^3J = 7.0$ Hz, 3H, $CH_3$), 1.25–1.40 (m, 8H, $CH_2$), 2.36–2.39 (m, 2H, $CH_2$), 3.13 (s, 6H, $NCH_3$), 6.47 (br.s, 1H, CH=), 8.84 (s, 1H, CHO).

$^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 150 MHz) $\delta = 14.0$ ($CH_3$), 22.6 ($CH_2$), 22.8 ($CH_2$), 29.3 ($CH_2$), 31.5 ($CH_2$), 31.8 ($CH_2$), 43.0 (2×$NCH_3$), 114.8 (C), 159.4 (CH), 191.2 (CHO).

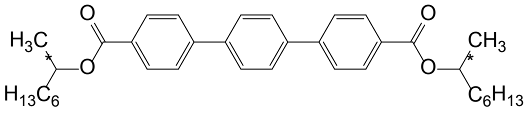
*2-(3-Fluoro-4’-pentylbiphenyl-4-yl)-5-hexylpyrimidine)* (**I**) was obtained according to the general procedure [27]. To the boiling suspension of amidine hydrochloride **5** (228 mg, 0.638 mmol) and aminoacrolein **7** (117 mg, 0.638 mmol) in dry MeOH (4 mL), a solution of MeONa, prepared from Na (21 mg, 0.893 mmol) and MeOH (1 ML), was added dropwise under stirring. The resulting mixture was heated under reflux for 4 h, cooled down to ambient temperature and concentrated under reduced pressure. The residue was dissolved in water (10 mL) and ethyl acetate (10 mL). Organic layer was separated and water layer was extracted with ethylacetate (3× 10 mL). Combined organic fractions were washed with brine (3×10 mL), dried with $Na_2SO_4$ and concentrated under reduced pressure. The product (**I**) was purified by column chromatography (eluent petroleum ether – ethyl acetate 10:1). Yield 145 mg (56 %), white crystals.

$^1$H NMR ($CDCl_3$, 600 MHz) $\delta = 0.91$ (t, $^3J = 7.1$ Hz, 3H, $CH_3$), 0.92 (t, $^3J = 7.1$ Hz, 3H, $CH_3$), 1.31–1.43 (m, 10H, $CH_2$), 1.65–1.72 (m, 4H, $CH_2$), 2.65–2.68 (m, 4H, $CH_2$), 7.28–7.30 (m, 2H, Ar), 7.45 (dd, $^3J$ = 12.5, $^4J$ = 1.8 Hz, 1H, Ar), 7.51 (dd, $^3J$ = 8.1, $^4J$ = 1.8 Hz, 1H, Ar), 7.57–7.59 (m, 2H, Ar), 8.13–8.16 (m, 1H, Ar), 8.72 (s, 2H, Ar).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz) $\delta = 14.0$ (2×$CH_3$), 22.5 (2×$CH_2$), 28.7 ($CH_2$), 30.2 ($CH_2$), 30.6 ($CH_2$), 31.1 ($CH_2$), 31.5 (2×$CH_2$), 35.6 ($CH_2$), 115.0 ($^2J_{CF}$ = 24 Hz, CH), 122.4 ($^4J_{CF}$ = 3 Hz, CH), 124.5 ($^2J_{CF}$ = 10 Hz, C), 126.9 (2×CH), 129.0 (2×CH), 132.0 ($^3J_{CF}$ = 2 Hz, CH), 133.0 (C), 136.5 (C), 143.3 (C), 144.8 ($^3J_{CF}$ = 9 Hz, C), 157.0 (2×CH), 160.9 ($^3J_{CF}$ = 5 Hz, C), 161.4 ($^1J_{CF}$ = 255 Hz, C).

*FLC mixtures preparation and investigation*

Two mixtures were prepared: **FLC-961-F** and **FLC-961**. Compound (**I**) was used as LC matrix for **FLC-961-F** and compound (**II**) – for **FLC-961**. The diester of optically active 2-octanol and terphenyldicarboxylic acid (**III**) [28] as a nonmesogenic chiral dopant was added in both mixtures. The matrix-dopant molar ratio was 3:1 when preparing both mixtures.



**III**

Investigation of both FLC mixtures parameters: helix pitch $p_0$, spontaneous polarization $P_s$ and tilt angle $\theta$ were carried out according to the described methods [8]. The electro-optical response shape of electro-optical cells based on FLC mixtures was recorded using RIGOL DS 1054 oscilloscope and evaluated by the Origin-2018 software.

## Results and discussion

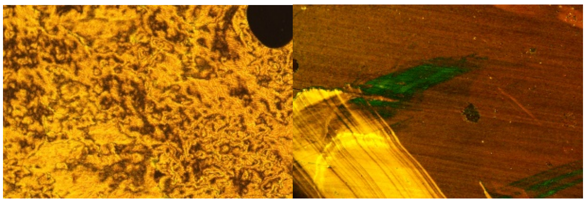
The phase transition temperatures of compounds (**I**), (**II**) and FLC mixtures: **FLC-691** and **FLC-691-F** are presented in the Table 2. The table illustrates that introduction of fluorine atom in the *ortho*-position with respect to pyrimidine ring does not influence considerably the transition temperature from crystal to smectic C-phase but dramatically diminishes clearing point and leads to enlarging of smectic phase temperature range due to disappearance of nematic phase. As a result of the change in the phase transitions sequence caused by the fluorine atom, the smectic C phase temperature range expands significantly. Specifically, the temperature range of the smectic C phase of compound **I** is 49.9–117.1 °C, while the same phase of compound **II** is observed only in the range of 54.0–81.7 °C (Table 2).

Table 2. **Phase transition temperatures of compounds I, II and the mixtures**

| Code | Cr–Cr$_1$ (◦C) | Cr–Sm (◦C) | Sm–N (◦C) | N–Iso SmC–Iso or SmA–Iso (◦C) |
|---|---|---|---|---|
| Compound (**I**) | | 48.9–49.9 SmC | – | 117.1 (SmC–Iso) |
| Compound (**II**) | 46.5 | 54.0 SmC | 81.7 | 163.0 |
| **FLC-691** | – | 38.9 SmC | – | 119.9 |
| **FLC-691-F** | – | 36.8 SmC<br>65.2 SmA | – | 83.5–85 (SmA–Iso) |

When comparing **FLC-691** and **FLC-691-F** mixtures, we can note that in the fluorine containing mixture an additional smectic A phase arises (see Table 2).

It is worth noting the influence of the fluorine atom on the alignment quality of individual compounds **I** and **II**, see Fig. 1. The compounds were inserted in between two glass substrates without any treatment of the last ones. Evidently, the fluorine containing compound **I** is aligned much better than compound **II**.



*a* *b*

*Fig. 1*. Microphotographs of smectic C phase textures of compounds **I** (*a*) and **II** (*b*) taken by the polarizing microscope with crossed polarizer and analyzer at 58 °C on cooling from isotropic phase. The images sizes are 300 × 200 μm

If we compare the mixtures **FLC-691** and **FLC-691-F** (see Fig. 2), one can see that the helix pitch of **FLC-691-F** is 2–2.5 times smaller at the same temperatures than the helix pitch of **FLC-691**. It is necessary to emphasize that it is the first case when in the mixtures of achiral smectic C matrices with the well-known chiral dopant (**III**) the subwavelength helix pitch is obtained. This impressive effect is provided only by the fluorinated matrix **I**.

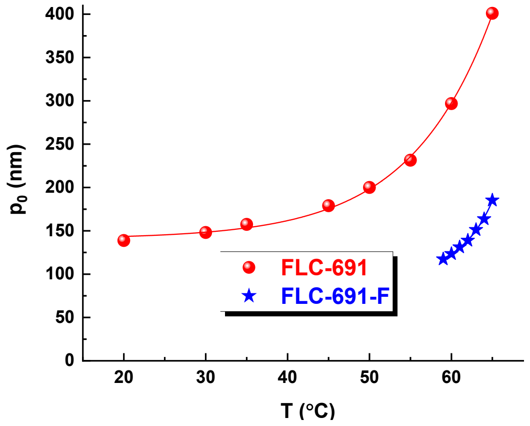


*Fig. 2*. Temperature dependences of helix pitch ($p_0$) for mixtures **FLC-691** (red balls) and **FLC-691-F** (blue stars)

Comparing temperature dependences of tilt angles θ for mixtures **FLC-691** and **FLC-691-F** (Fig. 3) elucidates that at the same temperature the tilt angle of **FLC-691-F** is much smaller than for **FLC-691**. At the same time, the tilt angle value approaches the optimal value of 22.5 deg., which ensures the maximum light transmittance of electro-optical cells [29].

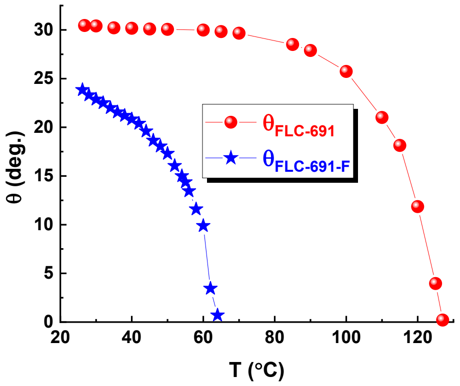


*Fig. 3*. Temperature dependences of tilt angles *θ* for mixtures **FLC-691** (red balls) and **FLC-691-F** (blue stars)

Introduction of fluorine atom significantly reduces the spontaneous polarization of **FLC-691-F** mixture compared to **FLC-691** mixture (Fig. 4). It is also necessary to note the very strong influence of fluorine atom on the temperature of the phase transition from ferroelectric smectic phase C* to paraelectric phase of mixtures. The criterion for this transition is the tendency of spontaneous polarization ($P_s$) and tilt angle θ to zero, which is illustrated in Figure 3 and 4.

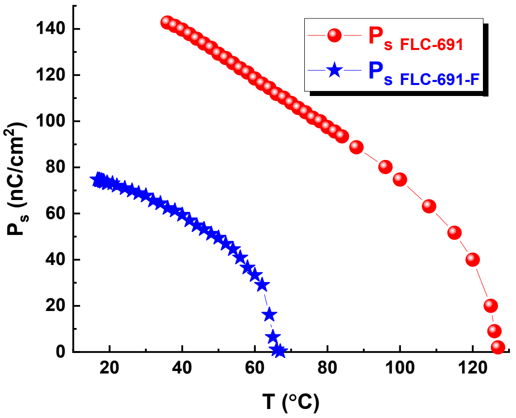


*Fig. 4*. Temperature dependences of spontaneous polarization $P_s$ for mixtures **FLC-691** (red balls) and **FLC-691-F** (blue stars)

The presence of fluorine atom in the structure of compound **I** is the reason for a significant decrease (almost 4 times) in the driving voltage *V* of electro-optical light shutters, see Fig. 5.

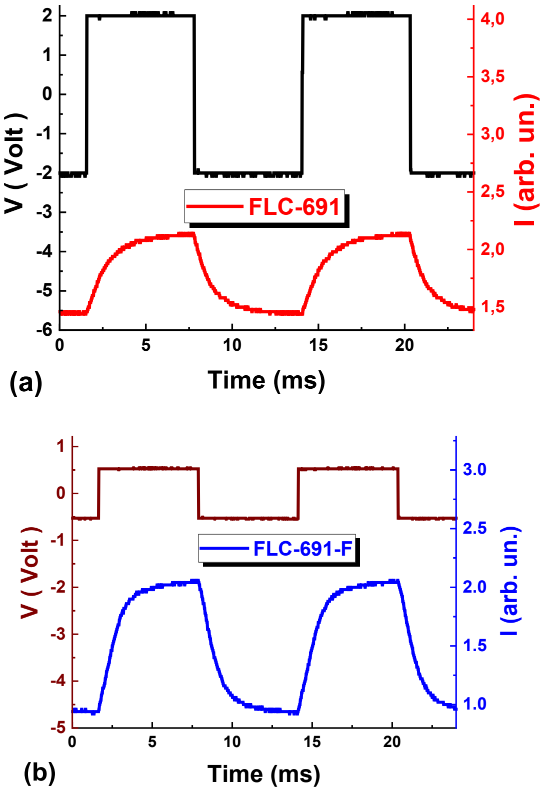


*Fig. 5*. Electro-optical responses (bottom lines) of FLC cells under applied voltage (top lines). The FLCs layer thickness is 1.6 μm: (*a*) **FLC-691**, (*b*) **FLC-691-F**. The measurements were carried out at 23 °C

## Conclusions

A new fluorinated achiral SmC compound, *2-(3-fluoro-4′-pentylbiphenyl-4-yl)-5-hexylpyrimidine)* (compound **I**), was synthesized and investigated for the first time as the SmC matrix for the liquid-crystal smectic C* ferroelectric mixture. It was shown that this matrix provides new possibilities for controlling the mixture parameters, primarily to reduce the helix pitch and the driving voltage of electro-optical light shutters. We are planning to continue this research.

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***Contribution of authors:***

[1]***Budynina E.M****. – carrying out and describing the synthesis of a new LC compound.*

[2]***Torgova S.I.*** *– preparation of the mixtures, measurement of phase transition temperatures of individual components and mixtures, writing text of the article.*

[3]***Kuznetsov A.V.*** *– conducting research, processing experimental data, preparing illustrations.*

[4]***Pozhidaev E.P****. – development of the concept of scientific work, research planning, editing text of the article.*

***The authors declare no conflicts of interests.***

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