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Synthesis of Fluorosubstituted Three Ring Esters and Their Dielectric Properties

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Laterally substituted by fluorine atoms 4-cyanophenyl 4-(4-pentylbenzoyloxy)-benzoates have been prepared and their phase transition temperatures, enthalpies and dielectric properties upon frequency were evaluated. The novel compounds exhibit a broad range of nematic mesophase, large positive dielectric anisotropy changing sign at low frequency. They are convenient components of LC mixtures for dual frequency addressing devices.

Keywords: cyano and fluorosubstituted ester; dual-frequency addressing; high positive dielectric anisotropy; liquid crystal; nematic

1. INTRODUCTION

The applicability of liquid crystals (LC) in different electro-optical devices depend on some important parameters, such as: wide range of mesophase, low melting point, low viscosity, high clearing point and sometimes large dielectric anisotropy.

The introduction of a terminal cyano group (-CN) into a molecule results in positive anisotropy of such compounds. Among them derivatives of 4-cyanophenyl 4-(4-alkylbenzoyloxy)-benzoates have wide nematic ranges and lower melting points than 4-(4-alkoxybenzoyloxy) benzoates [1–6]. Both families show large positive dielectric anisotropy at low frequency and it becomes negative at moderate frequency. Therefore they are interesting as components for dual frequency LC materials [7–9].

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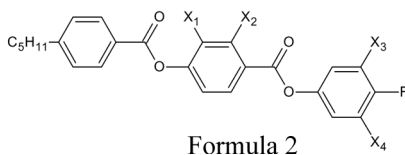
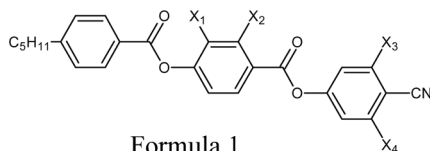
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Liquid crystals with a fluorine atom in the lateral positions of the molecule are interesting because they generally exhibit better properties compared with the corresponding non-substituted compounds, such as lower ability to form smectic phases, lower threshold voltage and bigger dielectric anisotropy ($\Delta\epsilon$) [10].

Their dependence of the $\Delta\epsilon$ upon frequency: at low frequencies $\Delta\epsilon$ reaches value ~ 50 , while at high frequencies a moderate negative dielectric anisotropy appears and crossover ($\epsilon_{||} = \epsilon_{\perp}$) is observed at low frequency. In our research we continued the preparation of nematic liquid crystalline compounds with large positive dielectric anisotropy ($\Delta\epsilon \gg 0$) at low frequency and having ability to become dielectrically negative ($\Delta\epsilon < 0$) at higher frequency. They are useful for the formulation of LC mixtures for low voltage driven displays as well as for dual frequency addressing modes. Such systems allow the LC to be driven parallel to the applied field using a low frequency waveform in the positive $\Delta\epsilon$ regime, and perpendicular to it using a higher frequency waveform in the negative $\Delta\epsilon$ regime [11]. This allow to shorten the off time for displays and other photonic devices [12–15].

In our previous paper we described the cyanophenyl esters with longer terminal chain (octyl- and octyloxy-) and fluorine atoms substituted to benzene rings in lateral position having moderate melting enthalpies, which were increased with the number of fluorine atoms [6]. In another paper we described mesomorphic and dielectric properties of homologous series of 4-cyano-3-fluorophenyl 4-(4-alkylbenzoyloxy)-2-fluorobenzoates [9], which exhibit a wide range of the nematic phase. These compounds have dipole moments of polar groups (CN, COO, F) followed with the same direction what leads to very large dielectric anisotropy and strong decreasing the resistivity of the compounds. According to Demus calculation [16] $\Delta\epsilon > 9$ involves increasing number of ions in higher temperature region.

Based on a combination of these factors we were prepared some new compounds belonging to the three ring esters family with the general formulas:

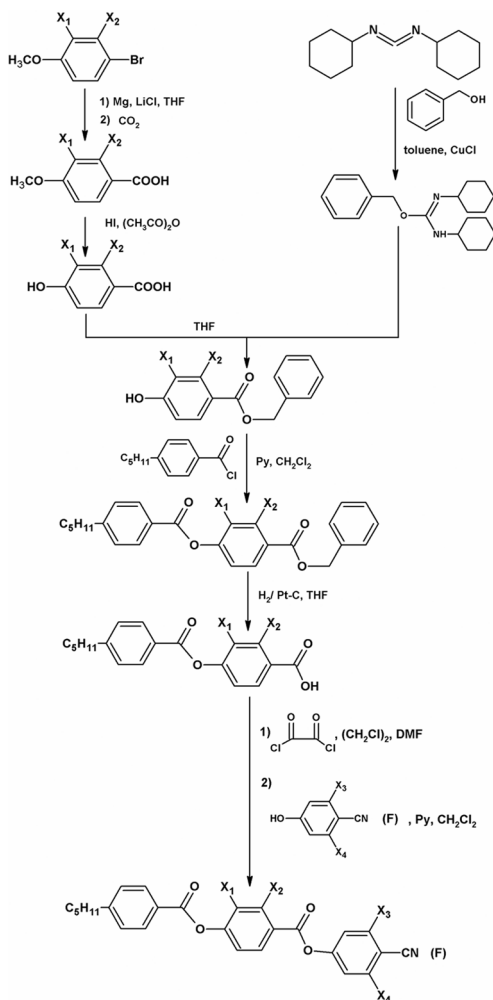


where: $X_1 = F$ is pending in the opposite direction to the other polar groups X_2 , X_3 , X_4 being F or H.

The presence of fluorine atoms in lateral position of molecules increases both values of electric permittivity constants (ϵ_{\perp} and ϵ_{\parallel}). Fluorine atom in position X_1 gives input mainly to ϵ_{\perp} value, while X_3 and X_4 to ϵ_{\parallel} value.

2. SYNTHESIS

The routes of synthesis of compounds 1a–e and 2 are presented on Scheme 1.



SCHEME 1 Synthetic route of compounds of the series 1 (-CN) and 2 (-F).

Synthesis details are described in the experimental part. The characteristic feature of the used method is protecting the carboxylic group in the 4-hydroxybenzoic acid by benzyl group from benzyl isourea, which more selectively and in mild condition and higher yield forms the ester bond by direct treating dicyclohexyl carbodiimide [16]. The needed dicyclohexyl benzyl isourea is prepared easily in the presence of small amount of cuprum chloride [17]. The compound may be additively purified and also stored long time without decomposition in closed bottle.

The structures of the final products and intermediates were confirmed by IR, PMR and GC-MS(EI) (Agilent 6890 N) chromatograph system with mass detector (Agilent MSD 5973 N) and HPLC-PDA-MS(API-ESI) (Shimadzu Prominence LC20) chromatograph system with diode array detector (SPD-M20A) and mass detector (LCMS-2010EV). In the experimental part only data of mass spectroscopy are listed, because this method gives more exact information about structure of the compounds. The route of synthesis leads to the well defined product without any doubts.

3. PHASE TRANSITIONS

Temperatures and enthalpies of phase transitions were measured by SETARAM 141 DSC instrument in heating and cooling cycles with scanning rate 2°C/min. The data of temperatures and enthalpies of phase transitions of synthesized compounds are given in Table 1.

TABLE 1 Phase Transitions Temperatures (Onset Point, from DSC Measurment) [°C] (Upper Row) and Enthalpies Transition [kJ/mol] (Lower Row) of the Compounds of Series 1 and 2

No.	X ₁	X ₂	X ₃	X ₄	Cr	SmA	N	I
1a	H	H	H	H	*	121.0	240.9	
						30.5	1.0	
						125.0 ^[15]	270.0 ^[15]	
1b	F	H	H	H	*	120.3	222.4	
						27.7	1.4	*
						105.3	196.7	
1c	F	H	F	H	*	30.2	0.8	*
						108.9	169.3	
						29.8	0.6	*
1d	F	H	F	F	*	86.4	200.9	
						26.5	0.9	*
						90.3	134.3	
Ie ^[9]	H	F	F	H	*	90.3	(95.9) [#]	
						29.6	(0.4)	*
2	F	H	F	H	*			

[#]monotropic phase.

All compounds exhibit the nematic phase over a wide temperature range. Compound with cyano group in the terminal ring and having two fluorine atoms in position X_2 and X_3 (**1e**) has lower melting points than compounds with fluorine atoms in position X_1 and X_3 (**1c**, **1d**). Molecules with one (**1b**) or without fluorine atoms in benzene terminal rings (**1a**) have higher melting points than others, but show a nematic phase over the broader temperature range, because of their high clearing points. The fluorine atom in the position 2 (near carbonyl group) is more effective for decreasing the melting point than position 3 (near oxo group). The compound **1e** shows also large range of nematic phase, because of its low melting point. Exchanging the terminal cyano group (**1c**) for a fluorine atom (**2**) causes lowering melting points, but also narrowing temperature range of the nematic phase. The compound with fluoro group in the terminal position instead of a cyano group (**2**) exhibits also smectic A phase directly after melting, so it is well seen only during cooling cycle.

4. DIELECTRIC MEASUREMENTS

Dielectric measurements were performed on the HP4192A impedance analyzer in the frequency range of 10 kHz–30 MHz. The thickness of the samples was 0.7 mm. In the nematic phase the samples were oriented by a magnetic field of 0.8 T (the parallel and perpendicular to capacitor plates). The temperature was stabilized within ± 0.2 K. All measurements were carried out in the cooling runs, which sometimes led to a considerable supercooling of the N phase.

The principal permittivity components, $\varepsilon_{||}$ and ε_{\perp} , as well as the relaxation processes taking part in the nematic phase of compounds were studied for temperatures below 160°C. The dipole structure of molecules was analyzed. The relaxation times and activation barriers characterizing the principal molecular motions were determined. Figure 1 shows the static permittivities $\varepsilon_{||}$ and ε_{\perp} for three compounds: **1b**, **1c**, and **2**. Also substance **1e** was studied. However, in this case the parallel component reached a very high value (>200), rather typical for ferroelectric LCs. Because the substance shows a large ionic conductivity in spite of several re-crystallization procedures, it was assumed that the enormously large $\varepsilon_{||}$ was caused by the polarization due to free charges (so called Maxwell-Wagner effect [20]). Therefore, additional measurements for **1e** dissolved in a mixture having a small negative dielectric anisotropy (Demus' ester mixture), were performed [21]. In this way it was possible to calculate the permittivity components of pure **1e** substance which appeared to be ~ 60 at low

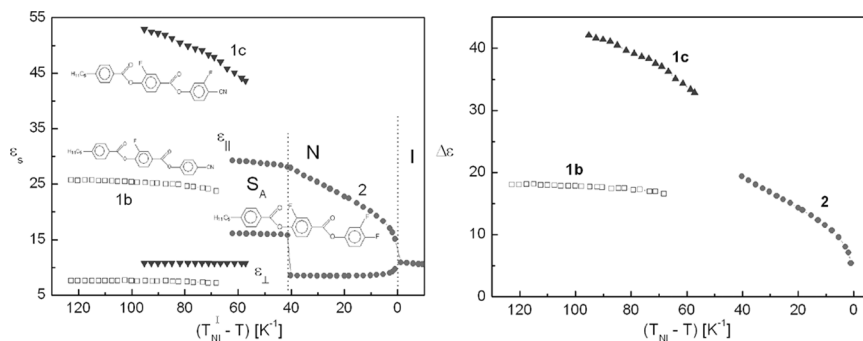


FIGURE 1 Dielectric permittivity tensor components in the nematic phase of three substances indicated (left) and the corresponding dielectric anisotropy (right). The shifted temperature scale is used because of very large differences in the clearing temperatures of particular substances (compare Table 1).

temperatures [21]. Also the substance **1d** exhibited very high permittivity, $\epsilon_{\parallel} > 300$, due to high ionic conductivity.

The compounds studied have very high values of the dipole moment: 7.5 D, 8.5 D, 10.2 D, and 6.8 D for **1b**, **1c**, **1e**, and **2**, respectively [18]. According to the formula derived by Maier and Meier [22] $\Delta\epsilon(T) \sim (\mu^2/T) \cdot S(T)$, where $S(T)$ is the order parameter (other parameters constituting the formula show small temperature dependence and can be ignored). This relation can be used for discussing the data corresponding to various substances at the same $S(T)$ value and may be useful for $\Delta T = T_{NI} - T$ up to ~ 20 K, in which temperature range the order parameter behaves similarly for different compounds [23]. For the present substances ΔT is very large and one can note only that the observed trends are in qualitative agreement with the prediction of the Maier-Meier formula (Fig. 1, right picture).

All substances exhibit the crossover frequency at which the dielectric anisotropy $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ changes the sign from large positive at low frequencies, to negative ($-2 \div -5$) at moderate frequencies. Figure 2 presents examples of the measured dispersion spectra.

In Figure 3 the crossover frequency f_{co} versus temperature and $\ln f_{co}$ versus inverted temperature are presented which shows an activation character of the dependence.

The extrapolation crossover frequency for compound **1b** gives value below 1 kHz at 40°C.

The relaxation process observed for the parallel component of the permittivity can nicely be described by the semicircle in the $\epsilon'(\epsilon'')$ plot (Cole-Cole plot)—Figure 4. This means that the relaxation process corresponding to the molecular rotations around the short axes are

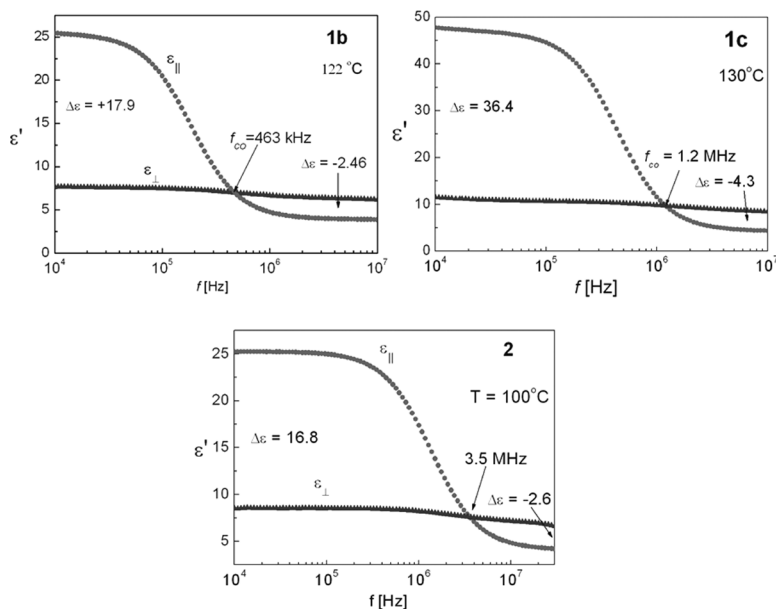


FIGURE 2 Dispersion spectra collected for two orientations of the samples with respect to the measuring field showing the change of the dielectric anisotropy.

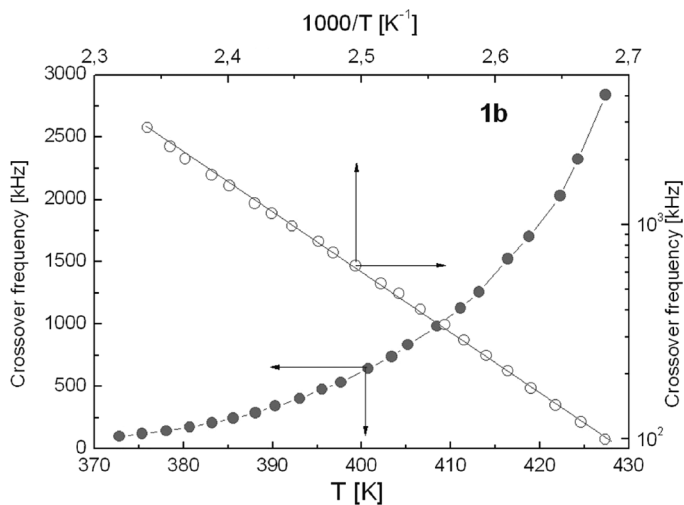


FIGURE 3 Temperature dependence of the cross-over frequency for **1b** presented in two scales.

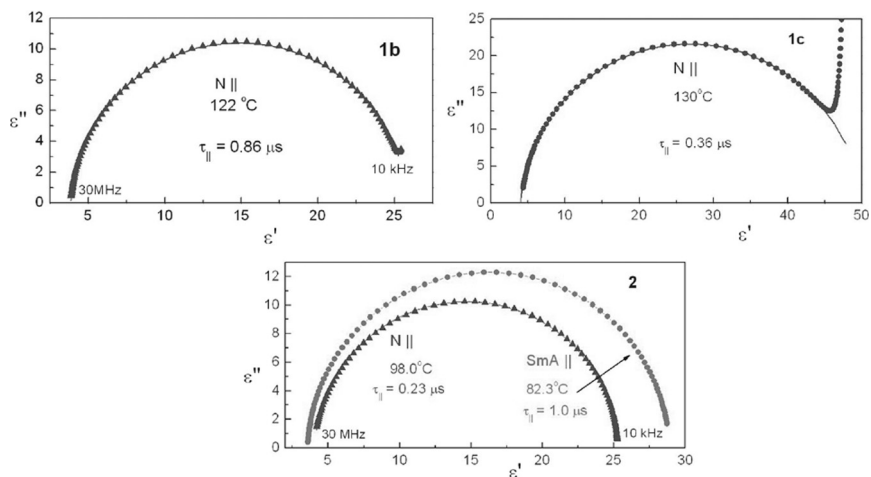


FIGURE 4 Cole-Cole plots from the relaxation spectra in the LC phases of three substances. For **1c** at low frequencies the conductivity gives pronounced effect.

well described by the Debye equation,

$$\varepsilon^*(\omega) - \varepsilon_\infty = \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau} \quad (1)$$

where ε_s and ε_∞ are the static and high frequency permittivities, respectively, τ is the relaxation time.

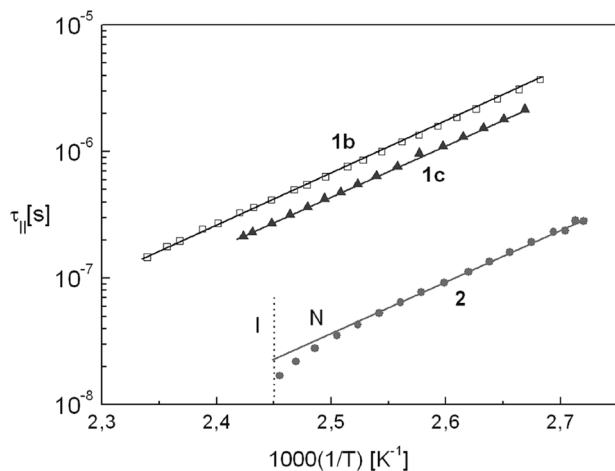


FIGURE 5 Activation plots for the nematic phase of three substances.

The relaxation time $\tau_{||}$ describes the flip-flop molecular motion around the short axis over the barrier $\Delta H_{||} = R(\partial \ln \tau_{||} / \partial T^{-1})$, R is gas constant – Figure 5. The slopes yield the activation barriers: 77.2 kJ/mol, 78.4 kJ/mol, and 81.6 kJ/mol (± 3 kJ/mol) for **1b**, **1c**, and **2**, respectively, which values are comparable to that determined by Heppke *et al.* [7] for substance **1a**.

6. EXPERIMENTAL

3-Fluoro-4-Methoxybenzoic Acid

The 500 ml round-bottom flask was charged with magnesium turnings (6.24 g, 260 mmol) and THF (10 ml). Then 4-bromo-2-fluoroanisole (33.5 ml, 260 mmol) in THF (250 ml) was added dropwise and the mixture was refluxed for 2 hours. After reactions completion, the mixture was cooled to -70°C on dry-ice bath, carbon dioxide was bubbled until temperature stopped increase and the reaction mixture was allowed to stand at room temperature overnight. Then the mixture was concentrated at low pressure, poured into water (100 ml), acidificated with 10% hydrochloric acid to pH=0 (~ 400 ml) and filtered. The crude product was crystallized from ethanol-water (4:1, 400 ml). Yield: 32.0 g (72.4%); $M_p = 214\text{--}217^{\circ}\text{C}$ ($M_p = 208\text{--}210^{\circ}\text{C}$ [24]); GC: 96.5%; MS: 170, 127, 99, 74, 45, 22.

2-Fluoro-4-Hydroxybenzoic Acid

A mixture of ethyl 2-fluoro-4-hydroxy benzoate (40.0 g, 217 mmol), potassium hydroxide (50.0 ml, 0.9 mol) in water (0.1 l) and ethanol (0.5 l) was refluxed for 6 hours. When the reaction was complete (TLC) the reaction mixture was poured into diluted hydrochloric acid, stirred and concentrated at low pressure. The crude product crystallized from water (0.4 l). Yield: 31.5 g (90.3%); $M_p = 195\text{--}197^{\circ}\text{C}$ ($M_p = 204\text{--}205.5^{\circ}\text{C}$ [25]); GC: 90.3%; MS: 156, 139, 127, 119, 111, 99, 92, 83, 71, 64, 57, 45, 38, 31.

3-Fluoro-4-Hydroxybenzoic Acid

40% hydroiodic acid (94.8 ml, 411 mmol) was added dropwise to acetic anhydride (216 ml, 2.29 mol), stirred and cooled on water bath. When the addition was complete 3-fluoromethoxybenzoic acid (35.0 g, 206 mmol) was added and the reaction mixture was refluxed for 5 days. Then acetic acid was distilled off and then the solution of sodium hydrogen sulfate was added until an iodine was reduced. The crude product was crystallized twice from water (300 ml). Yield: 29.5 g

(91.9%); $M_p = 163\text{--}166^\circ\text{C}$ ($M_p = 162\text{--}163^\circ\text{C}$ [22]); GC: 96.4%; MS: 156, 139, 111, 83, 45, 19.

O-Benzyl N,N'-Dicyclohexylisourea

A mixture of N,N'-dicyclohexylcarbodiimide (25.0 g, 120 mmol), benzyl alcohol (13.3 ml, 128 mmol), toluene (40 ml) and a bit of copper (I) chloride was stirred at room temperature for 5 days. When the reaction was complete (TLC) hexane (250 ml) was added and mixture was passed through alumina pad. Filtrate was evaporated to dryness. Yield: 37.0 g (97.1%); ($B_p = 130^\circ\text{C}/0.0001\text{ Torr}$ [17]).

Benzyl 3-Fluoro-4-Hydroxybenzoate

A mixture of 3-fluoro-4-hydroxybenzoic acid (25.8 g, 165 mmol), O-benzyl N,N'-dicyclohexylisourea (49.4 g, 157 mmol) and dry THF (200 ml) was refluxed for 6 hours. The precipitate was filtered off and the filtrate was concentrated at low pressure. The crude product was crystallized from ethanol (300 ml) and then from hexane/toluene (2:1, 300 ml). Yield: 18.4 g (47.8%); $M_p = 89\text{--}93^\circ\text{C}$; GC: 98.0%; MS: 246, 224, 201, 168, 139, 116, 91, 65, 39.

Benzyl 2-Fluoro-4-Hydroxybenzoate

Benzyl 2-fluoro-4-hydroxybenzoate was obtained similar as 3-fluoro-4-hydroxybenzoate by reaction of 2-fluoro-4-hydroxybenzoic acid with O-benzyl N,N'-dicyclohexylisourea and dry THF. Yield: 26.8 g (49.1%); $M_p = 139\text{--}142^\circ\text{C}$; GC: 99.6%; MS: 246, 228, 201, 183, 165, 139, 111, 91, 65, 39.

Benzyl 4-(4-pentylbenzoyloxy)-3-Fluorobenzoate

A 250 ml round-bottom flask was charged with benzyl 3-fluoro-4-hydroxybenzoate (18.3 g, 74 mmol), pyridine (12 ml, 149 mmol) and dry dichloromethane (150 ml). The 4-pentylbenzoyl chloride (15.1 ml, 74 mmol) was dropped. The reaction mixture was stirred and refluxed until the reaction was complete (TLC). After cooling to room temperature the reaction mixture was poured into diluted hydrochloric acid and stirred until the precipitate of pyridine hydrochloride was dissolved. Phases were separated. The water phase was extracted with dichloromethane ($3 \times 100\text{ ml}$). The combined organic fractions were washed with diluted hydrochloric acid ($3 \times 100\text{ ml}$) and water ($3 \times 100\text{ ml}$), dried over MgSO_4 and concentrated in vacuum. The crude product was purified by column chromatography ($\text{SiO}_2/\text{CH}_2\text{Cl}_2$)

obtaining colorless oil. Yield: 28.4 g (90.7%); GC: 93.7%; MS: 420, 399, 363, 355, 313, 281, 246, 207, 175, 139, 118, 91, 65, 41, 19.

Benzyl 4-(4-pentylbenzoyloxy)-2-Fluorobenzoate

Benzyl 4-(4-pentylbenzoyloxy)-2-fluorobenzoate was obtained similar as benzyl 4-(4-pentylbenzoyloxy)-3-fluorobenzoate by reaction of benzyl 2-fluoro-4-hydroxybenzoate and 4-pentylbenzoyl chloride with pyridine in dry dichloromethane. Yield: 15.4 g (75.2%); GC: 99.4%; MS: 420, 401, 374, 355, 335, 313, 269, 246, 226, 207, 175, 139, 118, 91, 65, 41, 20.

Benzyl 4-(4-pentylbenzoyloxy)-Benzoate

Benzyl 4-(4-pentylbenzoyloxy)-benzoate was obtained similar as benzyl 4-(4-pentylbenzoyloxy)-3-fluorobenzoate from benzyl 4-hydroxybenzoate and 4-pentylbenzoyl chloride with pyridine in dry dichloromethane. Yield: 35.4 g (88.1%).

4-(4-pentylbenzoyloxy)-3-Fluorobenzoic Acid

To the solution of benzyl 4-(4-pentylbenzoyloxy)-3-fluorobenzoate (28.5 g, 68 mmol) in THF (100 ml) 10% palladium on charcoal (1.5 g) was added. The reaction mixture was flushed with hydrogen, connected to gas burette filled with hydrogen and stirring was turn on. While hydrogen was consumed the temperature was increased. When reaction was completed (TLC), the reaction mixture was flushed with nitrogen, catalyst was filtered off and rinsed with THF (20 ml). The filtrate was evaporated and the dry residue was crystallized from ethanol (150 ml) and then from hexane/toluene (1:1, 200 ml).

Yield: 19.3 g (86.2%); Cr 180–185 N 208–213 Iso.

4-(4-pentylbenzoyloxy)-Benzoic Acid

4-(4-pentylbenzoyloxy)-benzoic acid was obtained similar as 4-(4-pentylbenzoyloxy)-3-fluorobenzoic acid by reaction of benzyl 4-(4-pentylbenzoyloxy)-benzoate with hydrogen and 10% palladium on charcoal in THF.

Yield: 27.2 g (99.0%); (Cr 152 N 272 Iso [26]).

4-(4-pentylbenzoyloxy)-2-Fluorobenzoic Acid

4-(4-pentylbenzoyloxy)-2-fluorobenzoic acid was obtained similar as 4-(4-pentylbenzoyloxy)-3-fluorobenzoic acid by reaction of benzyl

4-(4-pentylbenzoyloxy)-2-fluorobenzoate with hydrogen and 10% palladium on charcoal in THF.

Yield: 11.8 g (97.5%); Cr 107–109 N 224–225 Iso.

4-Cyano-3-Fluorophenyl 4-(4-pentylbenzoyloxy)-3-Fluorobenzoate (1c)

To the suspension of 4-(4-pentylbenzoyloxy)-3-fluorobenzoic acid (4.8 g, 14 mmol) in dry dichloroethane (100 ml) oxalyl chloride (1.5 ml, 17 mmol) and one drop of N,N-dimethylformamide were added. The reaction mixture was stirred at room temperature until the evolution of gases stopped. The excess of oxalyl chloride was distilled off with dichloroethane (80 ml). After cooling to room temperature, pyridine (3.5 ml, 44 mmol), 4-cyano-3-fluorophenol (2.0 g, 14.5 mmol) and dichloromethane (80 ml) were added and the mixture was refluxed for 6 hours. Then reaction mixture was cooled to room temperature and poured into diluted hydrochloric acid (100 ml). Phases were separated. The water phase was extracted with dichloromethane (2 × 100 ml). The combined organic fractions were washed with diluted hydrochloric acid (3 × 100 ml), water (3 × 100 ml) and brine (100 ml), dried over MgSO₄ and concentrated at low pressure. The crude product was purified by column chromatography (SiO₂/CH₂Cl₂) and crystallized from ethanol/acetone (3:1, 100 ml). Yield: 5.6 g (85.5%); HPLC: 99.1%; MS: 448 [M-H]⁻, 387, 359, 329, 274, 207, 152, 136, 91.

4-Cyanophenyl 4-(4-pentylbenzoyloxy)-Benzoate (1a)

4-cyanophenyl 4-(4-pentylbenzoyloxy)-benzoate was obtained similar as 4-cyano-3-fluorophenyl 4-(4-pentylbenzoyloxy) 3-fluorobenzoate.

Yield: 25.3 g (70.0%); HPLC: 99.1%; MS: 412 [M-H]⁻, 357, 319, 283, 235, 163, 118, 62.

4-Cyanophenyl 4-(4-pentylbenzoyloxy)-3-Fluorobenzoate (1b)

4-cyanophenyl 4-(4-pentylbenzoyloxy)-3-fluorobenzoate was obtained similar as 4-cyano-3-fluorophenyl 4-(4-pentylbenzoyloxy)-3-fluorobenzoate.

Yield: 4.9 g (78.2%); HPLC: 99.6%; MS: 430 [M-H]⁻, 355, 329, 256, 235, 191, 118, 90.

4-Cyano-3,5-Difluorophenyl 4-(4-pentylbenzoyloxy)-3-Fluorobenzoate (1d)

4-cyano-3,5-difluorophenyl 4-(4-pentylbenzoyloxy)-3-fluorobenzoate was obtained similar as 4-cyano-3-fluorophenyl 4-(4-pentylbenzoyloxy)-3-fluorobenzoate.

Yield: 5.4 g (84.8%); HPLC: 99.9%; MS: 466 $[M-H]^-$, 417, 388, 292, 289, 221, 154, 142, 91.

4-Cyano-3-Fluorophenyl 4-(4-pentylbenzoyloxy)-2-Fluorobenzoate (1e)

4-cyano-3-fluorophenyl 4-(4-pentylbenzoyloxy)-2-fluorobenzoate was obtained similar as 4-cyano-3-fluorophenyl 4-(4-pentylbenzoyloxy)-3-fluorobenzoate.

Yield: 11.7 g (94.0%); HPLC: 97.5%; MS: 472 $[M-H]^-$, 399, 345, 293, 271, 207, 175, 113, 55.

3,4-Difluorophenyl 4-(4-pentylbenzoyloxy)-3-Fluorobenzoate (2)

3,4-difluorophenyl 4-(4-pentylbenzoyloxy)-3-fluorobenzoate was obtained similar as 4-cyano-3-fluorophenyl 4-(4-pentylbenzoyloxy)-3-fluorobenzoate.

Yield: 5.3 g (82.4%); HPLC: 99.1%; MS: 441 $[M-H]^-$, 395, 377, 329, 267, 191, 129, 91.

7. CONCLUSIONS

Laterally fluorosubstituted cyanophenyl 4-(4-pentylbenzoyloxy) benzoates have stronger dependence of parallel electric permittivity constant $\epsilon_{||}$ upon frequency than analogous fluorophenyl diester. The fluorosubstituted central ring in the position 2 leads to the compounds with the lower melting point and broader range of nematic phase than the substitution in the position 3, but both structures are good dopant to formulate mixtures with dual frequency addressing systems.

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