

# Mesomorphic and dielectric properties of esters useful for formulation of nematic mixtures for dual frequency addressing system

D. ZIOBRO<sup>\*1</sup>, P. KULA<sup>1</sup>, J. DZIADUSZEK<sup>1</sup>, M. FILIPOWICZ<sup>1</sup>, R. DĄBROWSKI<sup>1</sup>, J. PARKA<sup>2</sup>, J. CZUB<sup>3</sup>, S. URBAN<sup>3</sup>, and S.T. WU<sup>4</sup>

<sup>1</sup>Institute of Chemistry, Military University of Technology, 2 Kaliskiego Str., 00-908 Warsaw, Poland

<sup>2</sup>Institute of Applied Physics, Military University of Technology, 2 Kaliskiego Str., 00-908 Warsaw, Poland

<sup>3</sup>Institute of Physics, Jagellonian University, 4 Reymonta Str., 30-059 Cracow, Poland

<sup>4</sup>College of Optics CREOL, University of Florida, Orlando, FL 32816, USA

*Mesomorphic and dielectric properties of three homologous series of two and three ring fluorosubstituted esters are described. They are 4-cyano-3-fluorophenyl 4-alkoxy-2-fluorobenzoates, 4-cyano-3-fluorophenyl 4-(4-alkylbenzoyloxy)-2-fluorobenzoates and 3-fluoro-4-cyanophenyl, or 3-fluoro-4-isothiocyanatophenyl or 3,4-difluorophenyl 4'-alkyl-2,3-difluoro-biphenyl-4-carboxylates. The compounds exhibit the nematic mesophase accompanied by the smectic A or smectic C mesophase in some cases. Most of them show strong dependence of the dielectric anisotropy  $\Delta\epsilon$  upon frequency, at low frequencies  $\Delta\epsilon$  reaches a value  $\sim 200$ , while at high frequencies a small negative dielectric anisotropy appears.*

**Keywords:** liquid crystal, dual-frequency addressing, fluorosubstituted esters, isothiocyanato esters.

## 1. Introduction

The aim of our research was to prepare nematic liquid crystal compounds with very large positive dielectric anisotropy ( $\Delta\epsilon > 0$ ) at low frequency and having ability to become dielectrically negative ( $\Delta\epsilon < 0$ ) at higher frequency. Such materials are very useful to formulate LC mixtures for low voltage driven displays as well as for dual frequency addressing modes [1]. Such system allows the LC to be driven parallel to the applied electric field using a low frequency waveform in the positive  $\Delta\epsilon$  regime, and perpendicular to it using a high frequency waveform in the negative  $\Delta\epsilon$  regime [2].

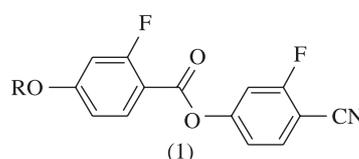
Fluoro-substituted liquid crystals are interesting because they generally exhibit excellent properties compared with the corresponding non-substituted compounds, such as lower ability to form smectic phases, lower voltage threshold and higher specific resistance [3].

The lateral location of fluorosubstituents in a liquid crystal molecule has been the most widely investigated mainly because of its reduction of the melting point. The study of lateral fluorosubstitution influence on mesophase behaviour was first conducted for two rings terminal cyanosubstituted esters (4-cyanophenyl 4-pentylbenzoates) and their homologues. A one (4-cyano-3-fluorophenyl 4-pentylbenzoates) and two lateral (the second lateral fluorine atom on the other side of the molecule) fluorosubstituent (4-cyano-3,5-difluorophenyl 4-pentylbenzoates) in comparison to the parent unsubstituted system reduces the  $T_{N-I}$  value by around 30°C.

The first fluorosubstituent (4-cyano-3-fluorophenyl 4-pentylbenzoates) confers a slight enhancement to the positive dielectric anisotropy, while the second fluorosubstituent (4-cyano-3,5-difluorophenyl 4-pentylbenzoates) provides a very high positive dielectric anisotropy. Either compounds do not have the appropriate  $T_{N-I}$  value to be major components of nematic mixtures for displays [4].

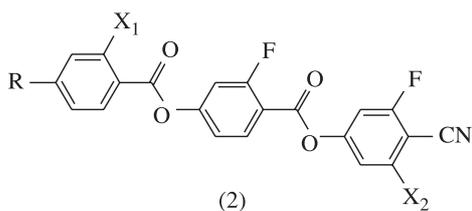
Several years ago two and three ring cyanoesters were also the objects of interest because some of them exhibit a smectic  $A_d$  and a reentrant nematic phase [5–7]. The smectic  $A_d$  phase is a one of few subphases of the smectic A phase, which is called “partially bilayer smectic” [8]. The two and three ring cyanoesters are the basis for new mixtures forming induced  $A_d$  systems [9]. Recently, the cyanoesters with the longer terminal chain (octyl- and octyloxy-) and fluorine atoms substituted in lateral position were obtained. The fluorine atom bonded to the same ring as cyano or alkoxy group were depressed stronger the stability of mesophase range than the fluorine atom at a central ring. The values of melting enthalpies were moderate and they increased with the number of fluorine atoms [10].

We have been prepared some compounds belonging to two and three ring esters with general formulae

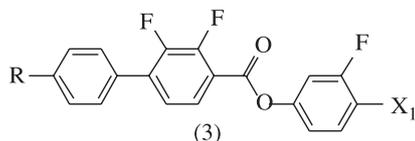


where R = C<sub>4</sub>H<sub>9</sub>, C<sub>8</sub>H<sub>17</sub>

\* e-mail: dziobro@wat.edu.pl



where R = C<sub>3</sub>H<sub>7</sub>, C<sub>4</sub>H<sub>9</sub>O, C<sub>4</sub>H<sub>9</sub>, C<sub>5</sub>H<sub>11</sub>; X<sub>1</sub>, X<sub>2</sub> = H, F



where R = C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>, C<sub>4</sub>H<sub>9</sub>; X<sub>1</sub> = CN, NCS, F.

The routes and experimental details of synthesis of compounds 1, 2, and 3 will be published in other paper [11].

## 2. Phase transitions

Temperatures and enthalpies of phase transitions were measured by SETARAM 141 DSC instrument in heating and cooling cycles with a scanning rate of 2°C/min. The obtained data of their phase transitions and enthalpies are given in Tables 1, 2, and 3.

Table 1. Phase transition temperatures (°C) (upper row) from DSC observations and enthalpies (kJ/mol) (lower row) of series 1.

No.	R	Cr	N	I
1a	C <sub>4</sub> H <sub>9</sub> [12]	*	57.8	(21.5)
			27.7	(0.2)
1b	C <sub>8</sub> H <sub>17</sub> [10]	*	62.5	(40.8)
			37.1	(0.3)

( ) monotropic transition

Both of 4-cyano-3-fluorophenyl 4-alkoxy-2-fluorobenzoates exhibit monotropic nematic phase as it was previously reported [10,12], but 4-cyano-3-fluorophenyl 4-octyloxy-2-fluorobenzoate (1b) in a higher temperature region than 4-cyano-3-fluorophenyl 4-butyloxy-2-fluorobenzoate (1a).

Table 2. Phase transition temperatures (°C) (upper row) from DSC observations and enthalpies (kJ/mol) (lower row) of series 2.

No.	R	X <sub>1</sub>	X <sub>2</sub>	Cr	SmC	N	I
2a	C <sub>3</sub> H <sub>7</sub>	H	H	*	94.5		214.5
					25.6	–	0.6
2b	C <sub>3</sub> H <sub>7</sub>	H	F	*	109.6	156.2	189.4
					25.4	0.7	0.8
2c	C <sub>4</sub> H <sub>9</sub> O	F	H	*	123.0		222.8
					38.0	–	0.9
2d	C <sub>4</sub> H <sub>9</sub>	H	H	*	105.3		200.4
					35.4	–	1.1
2e	C <sub>4</sub> H <sub>9</sub>	H	F	*	115.0	137.1	175.7
					35.8	0.03	0.8
2f	C <sub>5</sub> H <sub>11</sub>	H	H	*	86.4		200.9
					26.5	–	0.9

In series of 4-cyano-3-fluorophenyl 4-(4-alkylbenzoxy)-2-fluorobenzoates having one fluorine atom (compounds 2a, 2c, 2d, and 2f) in the terminal position only nematic phase is observed, while analogues with two fluorine atoms in the 3,5 positions to cyano group (compounds 2b and 2e) show also smectic C phase in broad temperature range. The butyl derivative (compounds 2d and 2e) have higher melting points than the propyl and pentyl chain and butyloxy chain involves higher melting points than others. They all have wide range of mesophase.

In homologous series of 3-fluorophenyl 4'-alkyl-2,3-difluorobiphenyl-4-carboxylates, only nematic phase is observed in the case of the all cyano members (compounds 3a, 3c, 3f, 3h), while analogues isothiocyanato series show also smectic A phase in a broad temperature range (compounds 3b, 3d, 3g). 3,4-difluorophenyl 4'-propyl-2,3-difluorobiphenyl-4-carboxylate (compound 3e) exhibits also smectic A phase and shows the additional phase transition. Longer alkyl chain effectively decreases the melting points but more effectively in the case of isothiocyanato compounds and increases melting enthalpies in the case of cyano compounds. In isothiocyanato homologous series, longer alkyl chain increases the smectic A phase stabilities at higher temperatures.

## 3. Dielectric measurements

Dielectric measurements were performed with the aid of a HP4192A impedance analyzer in the frequency range of 100 Hz – 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 alignments). The temperature was stabilized within ±0.2 K. All measurements were carried out in the cooling runs but these sometimes led to a considerable supercooling. Due to high clearing temperatures of some substances, the measurements could not start from the isotropic phase.

Examples of temperature dependence of the static dielectric constants  $\epsilon_s$  are shown in Fig. 1. The  $\epsilon_s$  values correspond to the plateau of the permittivity  $\epsilon'(f)$  at low frequencies (compare Fig. 2) or were taken from the extrapolation of  $\epsilon'(f)$  to  $f = 0$  by means of the Cole-Cole plots.

Table 3. Phase transition temperatures (°C) (upper row) from DSC observations and enthalpies (kJ/mol) (lower row) of series 3.

No.	R	X <sub>1</sub>	Cr <sub>1</sub>	Cr <sub>2</sub>	SmA	N	I
3a	C <sub>2</sub> H <sub>5</sub>	CN	*	136.5 34.0	–	–	* 0.4
3b	C <sub>2</sub> H <sub>5</sub>	NCS	*	107.3 28.4	–	135.6 2.05	* 0.6
3c	C <sub>3</sub> H <sub>7</sub>	CN	*	106.9 33.3	–	–	* 0.6
3d	C <sub>3</sub> H <sub>7</sub>	NCS	*	103.2 30.9	–	147.9 1.42	* 0.6
3e	C <sub>3</sub> H <sub>7</sub>	F	*	83.1 18.8	* 89.2 <sup>#</sup> 6.5	106.3 4.0	* 0.3
3f	C <sub>4</sub> H <sub>9</sub>	CN	*	94.1 35.8	–	–	* 0.4
3g	C <sub>4</sub> H <sub>9</sub>	NCS	*	71.6 18.3	–	158.5 2.03	* 0.7
3h	C <sub>5</sub> H <sub>11</sub>	CN	*	92.3 38.3	–	–	* 0.4
3i	C <sub>5</sub> H <sub>11</sub>	NCS	*	82.7 28.9	–	163.6 1.3	* 0.7

<sup>#</sup> observed phase transition during heating cycles only

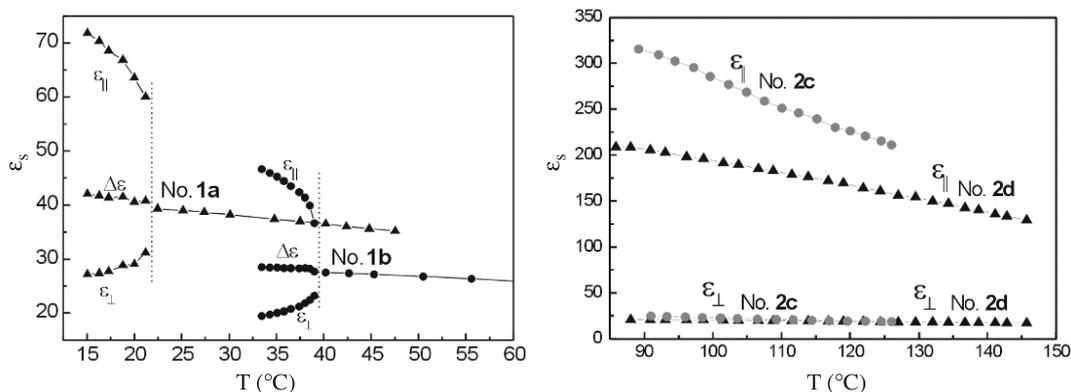


Fig. 1. Static permittivities vs. temperature for compounds 1a, 1b, 2c, and 2d.

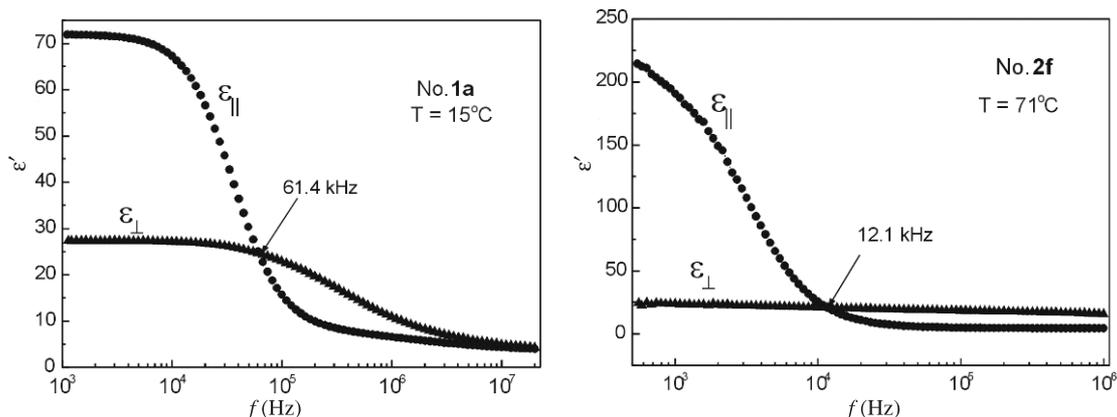


Fig. 2. Dependence of parallel and perpendicular permittivities on frequency for compounds 1a and 2f.

The substances studied are strongly polar with large longitudinal and transversal components of the dipole moment. Because the measuring capacitor was calibrated with the use of standard low polar liquids (with  $\epsilon$  up to 6) therefore the permittivities as large as 200–300 could be deter-

mined with low accuracy ( $\sim \pm 10\%$ ). As it can be seen in Fig. 1, one fragment added to formula 1 causes considerable increase in the parallel component of the permittivity while the perpendicular one persists practically unchanged.

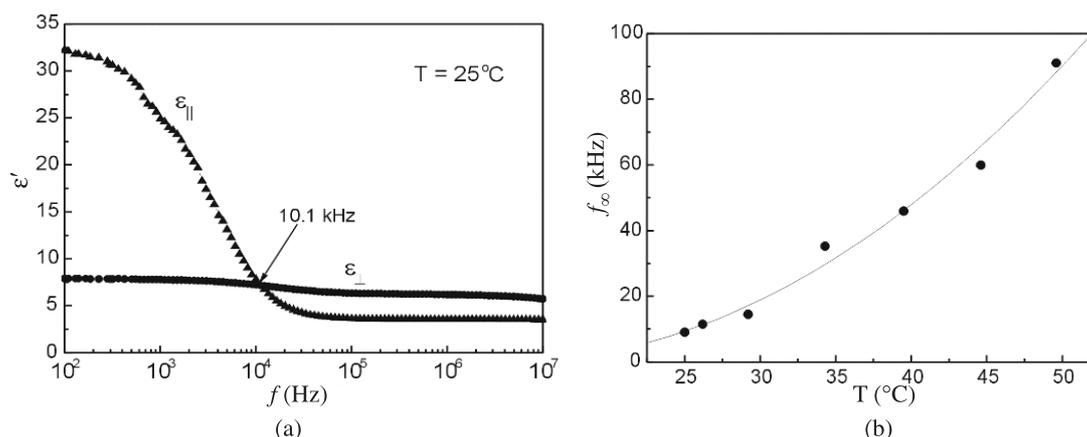


Fig. 3. Variation of dielectric permittivities with frequency of LC mixture composed in: 9.0 wt % of 4''-ethyl-2',3'-difluoro-4,5-propyl terphenyl, 13.0 wt % of 4''-ethyl-2',3'-difluoro-4-butyl terphenyl, 19.0 wt % of 4''-ethyl-2',3'-difluoro-4-pentyl terphenyl, 9.0 wt % of 4''-propyl-2',3'-difluoro-4-butyl terphenyl, 8.0 wt % of 4''-propyl-2',3'-difluoro-4-pentyl terphenyl, 13.0 wt % of 4''-butyl-2',3'-difluoro-4-pentyl terphenyl, 6.0 wt % of 4''-pentyl-2',3'-difluoro-4-methyl terphenyl, 5.0 wt % of 4''-heptyl-2',3'-difluoro-4-ethyl terphenyl, 6.0 wt % of 4''-methyl-2',3'-difluoro-4-pentyl terphenyl and 12.0 wt % of 4'-propyl 2,3-difluoro-4-ethoxybiphenyl doped by 20 wt % of compound 2f [Fig. 3(a)], and the temperature dependence of the crossover frequency  $f_{\infty}$  [Fig. 3(b)]. This amount is higher than results from eutectic composition calculation.

All compounds show a strong frequency dependence of the dielectric anisotropy  $\Delta\epsilon = \epsilon_{||} - \epsilon_{\perp}$  in the nematic phase. The very large positive dielectric anisotropy observed at low frequencies ( $\Delta\epsilon$  up to 300) becomes negative at higher frequencies, see Fig. 2. It happens due to the dispersion of the  $\epsilon_{||}(f)$  permittivity falling on the kilohertz range for these long molecules. The corresponding relaxation processes will be discussed in a separate paper.

The compounds series 1 and 2 allow us to formulate liquid crystalline mixtures for dual frequency mode because of change of the sign of dielectric anisotropy from  $\Delta\epsilon > 0$  to  $\Delta\epsilon < 0$ . The so-called crossover frequency can be as low as 10 kHz [Fig. 3(a)] and rapidly increases with a rising temperature, see Fig. 3(b).

## 4. Conclusions

The compounds of series 1 and 2 are very useful for formulation of nematic mixtures for dual frequency addressing system because they have large positive dielectric anisotropy and they change the sign of  $\Delta\epsilon$  at low frequency.

## Acknowledgements

The work was carried under grant No. OT00C01627.

## References

1. X. Liang, Y.Q. Lu, Y.H. Wu, F. Du, H.Y. Wang, and S.T. Wu, "Dual-frequency addressed variable optical attenuator with submillisecond response time", *Jpn. J. Appl. Phys.* **44**, 1292–1295 (2005).
2. P.D. Brimicombe, S.J. Elston, and E.P. Raynes, "A dual frequency addressed polymer stabilized pi-cell liquid crystal device", *Liq. Cryst.* **34**, 641–647 (2007).

3. S.S. Zhang, R. Ren, X.M. Li, Q. Li, X.Y. Song, and Q.L. Wei, "Synthesis and liquid crystalline properties of novel compounds containing a 3-fluoro-4-cyanophenoxy group", *Liq. Cryst.* **33**, 795–801 (2006).
4. M. Hird, "Fluorinated liquid crystals – properties and applications", *Chem. Soc. Rev.* **36**, 2070–2095 (2007) and cited references.
5. H.T. Nguen, "Polymorphism of mesogenic substances containing polar molecules. Part III. Molecular aspects", *J. Chim. Phys.* **80**, 83–98 (1983).
6. F. Hardouin, A.M. Levelut, M.F. Achard, and G. Sigaud, "Polymorphism of mesogenic substances containing polar molecules. Part I. Physical chemistry and structure", *J. Chim. Phys.* **80**, 53–64 (1983).
7. R. Dąbrowski and K. Czupryński, "Induced smectic and nematic phases and re-entrant phenomena", in *Modern Topics in Liquid Crystals*, pp. 125–160, edited by A. Buka, Word Scientific Publishing Co., 1997.
8. B.J. Ostrowski and M.A. Saidakhmetov, "X-ray study of modulated smectic A phase", *Mol. Cryst. Liq. Cryst.* **192**, 19–24 (1990).
9. M. Brodzik and R. Dąbrowski, "Induction of smectic Ad phase in mixtures of polar esters", *Mol. Cryst. Liq. Cryst.* **260**, 361–367 (1995).
10. B. Jankiewicz, W. Drzewiński, and R. Dąbrowski, "Two and three cyanoesters lateralny substituted with fluorine", *16 CLC Conf. Proc.*, Stare Jablonki, Poland, 21–28 (2005).
11. D. Ziobro, J. Dziaduszek, M. Filipowicz, R. Dąbrowski, J. Czub, and S. Urban, "Synthesis of fluorosubstituted esters and their dielectric properties", *Mol. Cryst. Liq. Cryst.* (in preparation, 2008).
12. W. Gray, M. Hird, D. Lacey, and K.J. Toyne, "The synthesis and transition temperatures of some fluoro-substituted 4-cyanophenyl and 4-cyanobiphenyl-4'-yl 4-pentyl- and 4-butoxybenzoates", *Mol. Cryst. Liq. Cryst.* **172**, 165–189 (1989).