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Syntheses and mesomorphic properties of laterally fluorinatedphenyl isothiocyanatotolanes and their high birefringent mixtures

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Syntheses and mesomorphic properties of di-, tri- and tetrafluorosubstituted 4'-(4-alkylphenyl)-4-isothiocyanatotolanes are described. Four fluorine substituted compounds in the position 2', 3', 3, and 5 show stronger nematic character than difluorosubstituted ones in the position 3, 5 or 2', 3'. Example of high birefringence nematic mixture and its properties are given.

Keywords: liquid crystals isothiocyanatophenyltolanes, fluorine substitution, phase transition, enthalpy transition, high birefringence nematic mixture.

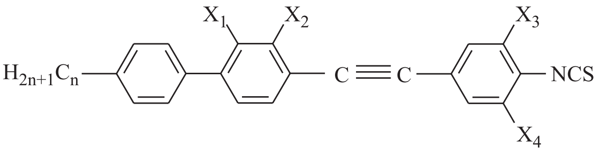
1. Introduction

High birefringence nematic liquid crystal mixtures have the potential application in many photonic areas. It has been proven that laser beam steering systems, working at infrared range of spectrum may greatly benefit from shrinking the cell gap when high birefringence materials are in use [1,2]. Also within visible region of spectrum it is possible to achieve response time of about 1 ms if 90 deg twisted nematic cell utilizing high birefringence mixture is applied [3,4]. Isothiocyanatotolanes and phenylisothiocyanatotolanes liquid crystalline compounds are the object of our interest because of their high birefringence. It results from extended π-electron conjugation through linear core of the molecules and highly polar terminal isothiocyanate group (NCS). The drawback of extended π-electron conjugation and linearity of the molecules is extensive smectogenity observed for tolane and phenyltolane isothiocyanates [5,6]. Strong smectogenity typically excludes LC single compounds from room temperature applications

To weaken smectogenity and suppress smectic phase at room temperature region we have synthesized isothiocyanatophenyl tolanes with one or two fluorine atoms in the terminal benzene ring near isothiocyanato group [5]. Such disubstituted compounds show high dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\|} - \varepsilon_{\perp}$ and the nematic phase in broader temperature range than observed for unsubstituted analogues.

Also, we observed that in most cases smectic phases are suppressed the most effectively in the case of lateral substitution in the central ring of a rigid molecular core (X_1 and X_2 of the Formula I).

Therefore we decided to prepare the compounds of Formula I, containing one or two fluorine atoms in central part of the molecules. Additionally, we included structures with lateral mono and difluorinated benzene ring linked with terminal NCS group (X_3 and X_4 of Formula I).



(I)

where (a) $X_1 = X_3 = F$ and $X_2 = X_4 = H$; (b) $X_1 = X_3 = X_4 = F$ and $X_2 = H$; (c) $X_1 = X_2 = F$ and $X_3 = X_4 = H$; (d) $X_1 = X_2 = F$ and $X_3 = F$ and $X_4 = H$; (e) $X_1 = X_2 = F$ and $X_3 = X_4 = F$.

Phase transition temperatures and transition enthalpies of the single compounds were measured to find a correlation between the position of lateral fluorination and mesomorphic properties of the compounds. Electro-optical and physical properties were measured to find application potential of differently fluorinated tolane and phenyltolane isothiocyanates synthesized for our experiment.

2. Experimental part

The methods of synthesis of the compounds of series 1(a)1(e) are given in Scheme 1.

4'-Alkyl-4-iodobiphenyls (A) were the starting reactants for all of the structures investigated. The preparation of (A) was different for the case of monofluorosubstituted compounds ($X_1 = F$, $X_2 = H$) and difluorosubstituted compounds ($X_1 = X_2 = F$). The monofluorosubstituted compounds A were prepared according to Scheme 2. The difluorosubstituted compounds were prepared from 1,2-difluoroben-

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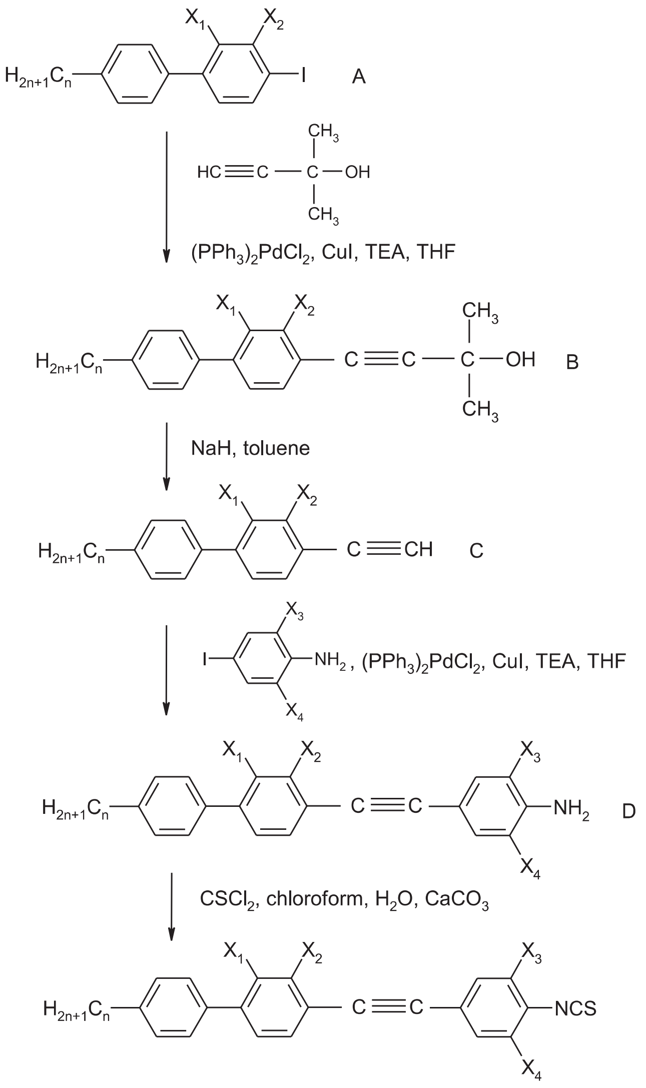


Scheme 1. The route of syntheses alkylphenyl isothiocyanatotolanes.

zene. Detailed synthesis route of difluorosubstituted compounds is discussed in Refs. 6, 8, and 10.

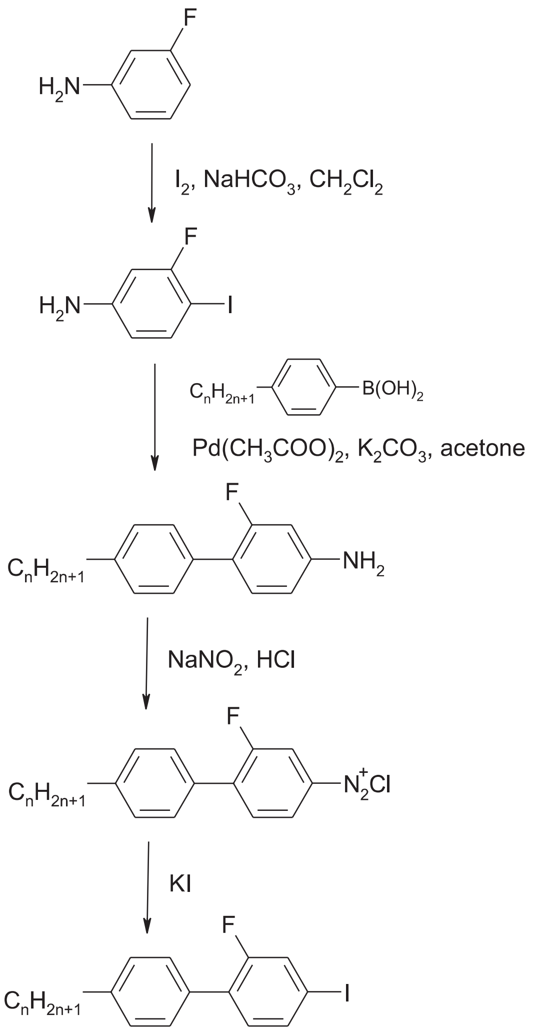
The phase transitions were observed by polarizing microscope OLYMPUS BX51 equipped with heating stage LINKAM THMS 600. Liquid crystal phases were identified from their specific texture patterns.

The phase transition temperatures (onset point) and enthalpies were measured with SETARAM DSC 141 microcalorimeter during heating cycles, heating rate 2 degrees/min.

An ordinary refractive index (n_o) was measured using an Abbe refractometr (Atago). A birefringence (Δn) was obtained from the phase retardation of the homogenous cell according to a formula [4]

$$\delta(V,T,\lambda) = 2\pi d \cdot \Delta n(V,T,\lambda)/\lambda$$

The free relaxation time (decay) of the controlled phase change was used to calculate the visco-elastic coefficient (γ_1/K_{11}) according to the following equation



Scheme 2. Route of synthesis 2-fluoro-4-iodo-4'-alkylbiphenyls.

$$\tau_o = \frac{\gamma_1 d^2}{\pi^2 K_{11}}.$$

The dielectric constants were obtained from a direct measurement using HP4192A bridge and LCASII automatic tester from LC Vision. LCAS instrument was also used for a threshold voltage measurement and the elastic constants K_{11}, K_{22}, and K_{33} estimation. Electronic spectra of the single compounds were registered on Carry UV-VIS spectrophotometer from a hexane solution.

3. Results

3.1. Mesomorphic properties

Mesomorphic properties of all investigated compounds are shown in Table 1. Difluorosubstituted in the central ring ($X_1 = X_2 = F$) compounds have distinctly lower melting temperatures than difluorosubstituted in the terminal ring ($X_3 = X_4 = F$) compounds if a short alkyl chain homologues are compared ($n = 2$ and 3). Longer alkyl chain homologues ($n = 5$) show the melting temperatures nearly the same (compounds 6 and 7, and 14 and 15, see Table 1).

Table 1. Phase transition [°C] – first line and enthalpy transition [kJ/mol^{-1}] – second line for alkylphenylisothiocyanatotolanes of formula (I).

No	n	X_1	X_2	X_3	X_4	Phase transition
1	2	H	H	F	F	Cr 121.3 N 233.6 Iso [Ref. 4] 41.0 0.61
2	2	F	F	F	H	Cr 72.8 (SmA 64.8) N 228.6 Iso 27.9 – 0.47
3	2	F	F	F	F	Cr 97.2 N 204.3 Iso 24.3 0.26
4	3	F	H	F	F	Cr 111.5 N 204.5 Iso 22.0 0.43
5	3	F	H	F	H	Cr 127.6 N 221.3 Iso 28.3 0.59
6	3	F	F	H	H	Cr 98.3 SmA 111.4 N 240 Iso (decomp) 25.2 0.08
7	3	H	H	F	F	Cr 121.4 N 229.7 Iso[Ref. 5] 19.5 0.64
8	3	F	F	F	H	Cr 80.5 SmA 95.2 N 236.5 Iso 24.0 0.05 0.58
9	3	F	F	F	F	Cr 89.0 (SmA 71) N 216 Iso 27.3 0.43
10	4	H	H	F	H	Cr 52.3 SmE 85.7 SmB 139.3 SmA181.3 N 241.5 Iso[Ref. 4] 10.5 1.90 0.6 0.50 0.50
11	4	H	H	F	F	Cr 62.3 SmA 105.3 N 212.7 Iso[Ref. 5] 23.2 0.035 0.43
12	4	F	H	F	H	Cr 68 SmA 79 N 197 Iso 18.01 0.13 0.45
13	4	F	H	F	F	Cr 66 N 172.5 Iso [Ref. 7]
14	5	F	F	H	H	Cr 69 SmA 150.3 N 233.1 Iso 24.1 0.052 0.65
15	5	H	H	F	F	Cr 61.4 (SmB 55.2) SmA 118.7 N 210.4 Iso[Ref. 5] 19.7 0.13 0.69
16	5	F	F	F	H	Cr 58 SmA 134.7 N 220 Iso 25.5 0.31 0.53
17	5	F	F	F	F	Cr 46.0 SmA 116.1 N 202.2 Iso 26.7 0.09 0.43

It is surprising that compound 14, fluorinated in the middle benzene ring has higher clearing temperature and more stable smectic A phase than compound 15 with fluorination adjacent to the terminal NCS group. Introduction of a fluorine atom into position X_3 to the structure already difluorinated in the middle ring (compound 16) decreases smectogenity. Addition of two fluorine atoms in position X_3 and X_4 involves further decrease in smectogenity (compound 17). In the last case, also melting temperature drops distinctly. A similar behaviour is observed for the compounds with three carbons alkyl chain (compounds 6, 8, and 9). Tetrafluorinated compound 3 ($X_1 = X_2 = X_3 = X_4 = F$) with two carbons alkyl chain ($n = 2$) has the strongest nematic behaviour.

3.2. Electro-optical and physical properties

Electronic spectrum of compound 8 and compound 15 are compared in Fig. 1.

Fluorosubstituted in the middle ring compound 8 shows similar coefficient of molar absorbance to one observed for compound 15 substituted only the position 3,5. The maximum of absorption band and the edge of absorbance of the compound 15 are shifted slightly to the longer wavelength compared to compound 8.

Multicomponent mixtures 1760-2 and 1791 were formulated from two ring alkylisothiocyanatotolanes monosubstituted by fluorine atom in position 3 [5] and alkylphenyli-

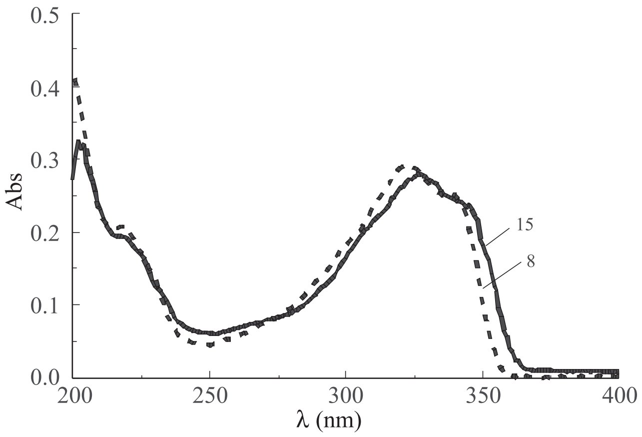


Fig. 1. Electronic spectrum of compounds 8 and 15.

Table 2. Nematic range and the physical and electrooptical properties of mixture 177–02 at 633 nm

	1760-2	**1791**
mp$_{(theor.)}$ [°C]	–7,5	<–10
cryst. temp. [°C]	–13	
N-SmA [°C]		
N-Iso [°C]	85,9	104,8–109
Δn at 633 nm	0,3582*	0,4011*
n_o at 633 nm	1,5435****	
n_e at 633 nm	1.9095	
$\Delta\varepsilon$	17,1**	
	16,7***	17,4***
$\varepsilon_{\parallel}$	22,0**	
	23,1***	23,6***
$\varepsilon_{\perp}$	4,9**	
	6,4***	6,2***
γ_1 [mPas]	143,0**	
γ_1/K_{11} [ms/μm^2]	8,70*	11,56*
FoM [μm^2/s]	14,75*	13,92*
K_{11} [pN]	22,0**	
K_{22} [pN]	13,2**	
K_{33} [pN]	23,2**	
V_{th} [V]	1,58**	

* – electrooptic measurements[4]
** – LCAS II measurements[4]
*** – direct dielectic permittivity measurements
**** – direct refractometric measurement
***** – combinated data from electrooptic and refractometric measurements [4]

sothiocyanatotolanes substituted by fluorine atoms in 3, 5 and 2', 3', 3, 5 positions described here.

Both presented mixtures show nematic phase in broad temperature range. A value of dielectric anisotropy of the mixture 1760-2 is relatively high with $\varepsilon_{\perp}$ value higher than reported earlier in Ref. 2, see the data in Tables 2 and 3. The birefringence measured for mixture 1791 is significantly higher than the one measured for 1760-2, which is partially a result of higher clearing temperature.

Table 3. Dispersion of ordinary index n_o of mixture 1760-2 measured by refractometric method at 25°C.

λ [nm]	n_o
656	1.5430
633	1.5453
589	1.5502
546	1.5566
486	1.5695
450	1.5830

The viscolastic coefficient shown by the mixtures is relatively low, therefore the value of Figure of Merit is high if compared to commercially available high birefringence LC mixtures [9]. Figure of Merit parameter is described by the following equation

$$FoM = \frac{\Delta n^2 K_{11}}{\gamma_1}.$$

Both, ordinary and extraordinary refractive indices (n_o and n_e) are very high. Only ordinary refractive index remains within Abbe refractometer measuring range. Therefore, value of extraordinary refractive index had to be calculated from electro-optical and refractometric measurements.

4. Conclusions

Four fluorine substituted 2', 3', 3, 5 alkylphenylisothiocyanatotolanes show stronger nematic character than difluorosubstituted compounds in the position 3, 5 or 2', 3'. They are promising components for the preparation of high birefringent nematic mixtures with improved value of $\Delta\varepsilon/\varepsilon_{\perp}$.

Acknowledgements

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References

1. J. Harriman, S. Gauza, S.T. Wu, D. Wick, B. Bagwell, T. Martinez, D. Payne, and S. Serati, "Transmissive spatial light modulators with high figure-of-merit liquid crystals for

foveated imaging applications", *Proc. SPIE* **6135**, 61350C (2006).

2. S. Gauza, C.H. Wen, S.T. Wu, R. Dąbrowski, C.S. Hsu, C.O. Catanescu, and L.C. Chien "High birefringence liquid crystals for photonic applications", *Proc. SPIE* **5947**, 51–64 (2005).
3. S. Gauza, X. Zhu, S.T. Wu, W. Piecek, and R. Dąbrowski, "Fast switching liquid crystals for colour-sequential LCDs", *J. Display Techn.* **3**, 250–252 (2007).
4. S. Gauza, S.T. Wu, A. Spadło, and R. Dąbrowski, "High performance room temperature nematic liquid crystals based on laterally fluorinated isothiocyanatotolanes", *J. Display Techn*. **2**, 247–253 (2006).
5. R. Dąbrowski, J. Przedmojski, A. Spadło, J. Dziaduszek, and M. Tykarska, "Features of the smectic phases in some strongly polar biphenyls and tolanes", *Phase Transit.* **77**, 1103–1110 (2004).
6. R. Dąbrowski, J. Dziaduszek, A. Ziółek, Ł. Szczuciński, Z. Stolarz, G. Sasnouski, V. Bezborodov, W. Lapanik, S. Gauza, and S.T. Wu, "Low viscosity, high birefringence liquid crystalline compounds and mixtures", *Opto-Electron. Rev.* **15**, 47–51 (2007).
7. A. Spadło, R. Dąbrowski, M. Filipowicz, M. Bogun, S. Gauza, and S.T. Wu, "Synthesis, mesomorphic and optical properties of 4'-alkyl-3,5-difluoro-4-isothiocyanatotolanes and 4'-alkylphenyl-3,5-difluoro-4-isothiocyanatotolanes", *Conf. Proc. 16th Conf. on Liquid Crystals*, Stare Jabłonki 2005, Poland, 53–58 (2007).
8. P. Kula, A. Spadło, J. Dziaduszek, and R. Dąbrowski, "Synthesis and mesomorphic properties of therphenyls", *Opto-Electron. Rev.*, **16**, 379–389 (2008).
9. S. Gauza, Y. Zhao, T. Le Cor, S.T. Wu, J. Dziaduszek, G. Sasnouski, R. Dąbrowski, and L. Chy Chien, "Enhancing birefringence by doping fluorinated phenyltolanes", *J. Display Techn.* **2**, 327–332 (2006).
10. R. Dąbrowski, J. Dziaduszek, and A. Ziółek, *Liq. Cryst.* (in preparation).