

Low viscosity, high birefringence liquid crystalline compounds and mixtures

R. DĄBROWSKI*, J. DZIADUSZEK¹, A. ZIÓŁEK¹, Ł. SZCZUCIŃSKI¹, Z. STOLARZ¹,
 G. SASNOUSKI², V. BEZBORODOV², W. LAPANIK², S. GAUZA³, and S.T. WU³

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

²Institute of Applied Physics Problems, 220064 Minsk, Belarus

³College of Optics/CREOL, University of Central Florida, Orlando, FL 32816, USA

Two types of fast switching mixtures with high positive dielectric anisotropy were described. The first type, with a birefringence below 0.3, was designed for devices operating at room or lower temperatures and the second one, with a birefringence higher than 0.3 for devices operating at elevated temperatures.

Keywords: isothiocyanatobiphenyls, isothiocyanatoterphenyls, isothiocyanatotolanes, phase transitions, nematic high birefringence mixtures.

1. Introduction

Liquid crystals (LCs) with large birefringence $\Delta n \geq 0.3$ are needed for many photonic applications to obtain fast operating shutters, broad range filters, and holographic devices [1,2].

Good quality thin cells are now available, and many manufacturers have reported display devices with a cell gap below 6 μm [3]. Therefore, interest in high birefringence nematic materials has increased.

The birefringence of LCs is mainly determined by π -electron conjugation length, molecular shape, linking group, and terminal groups. Benzene rings and double and triple bond systems lead to highly conjugated compounds. Major drawbacks of such highly conjugated structures are usually observed, high melting temperature and strong smectogeny. The isothiocyanates as compounds with the high Δn seem to be more suitable than other polar ones because of lower viscosity. Many isothiocyanato (NCS) compounds have been prepared and described recently [4–7] but mainly alkoxy derivatives were presented.

To improve their mesogenic properties, linear molecules having a NCS group in one terminal position of the rigid core of the molecule and alkyl group in the other end were laterally substituted with F or Cl atom or CH_3 group. To distinguish differences in the molecules rigid core, we set up two series (1 and 2) of structures shown in Table 1. Such structures greatly reduce melting temperature and viscosity and lead to the compounds with a high positive dielectric anisotropy.

2. Experimental

The refractive indices of single compounds of the formula 1–2 at temperature 20°C were extrapolated from guest-host systems of 5, 10, and 15 wt. % of the investigated compounds doped into mixture of Demus' esters. The refractive indices of the mixtures of series 1711 were measured directly using an Abbe refractometer, while of series 1631, 1658, 1659, 1680, and 1734 were obtained from measuring the phase retardation of the homogenous cell and calculation from the formula

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

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

$$\tau_0 = \gamma_1 d^2 / K_{11} \pi^2$$

The dielectric constants were obtained from a direct measurement using an HP4192A bridge. Threshold voltage and the elastic constants K_{11} , K_{33} were measured using a LCAS II system from LC Vision.

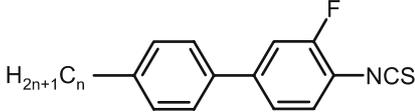
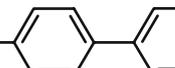
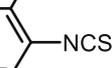
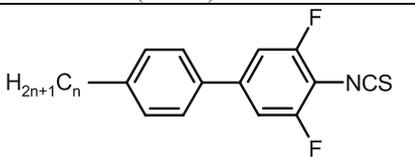
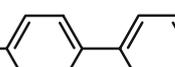
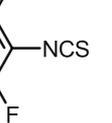
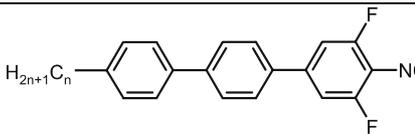
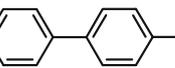
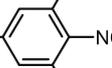
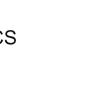
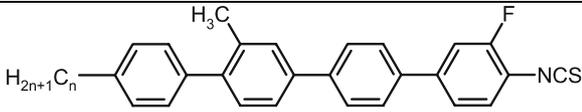
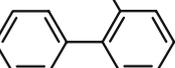
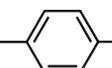
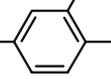
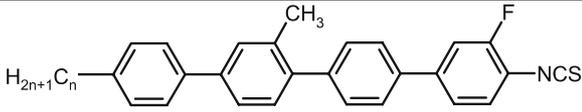
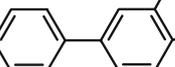
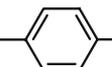
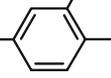
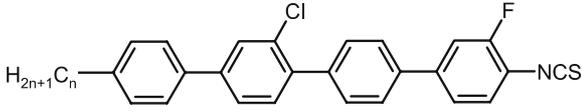
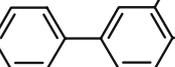
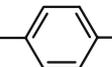
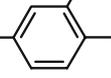
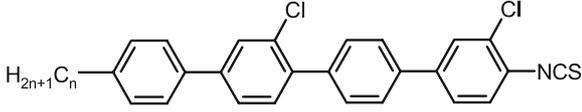
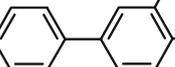
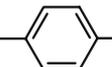
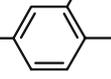
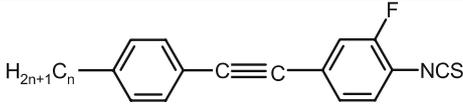
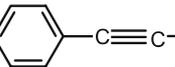
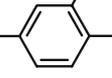
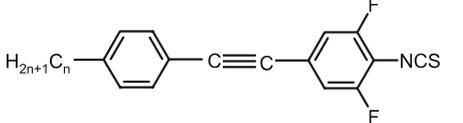
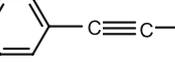
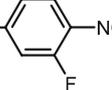
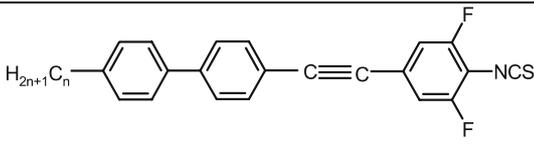
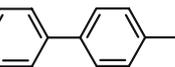
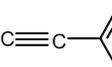
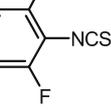
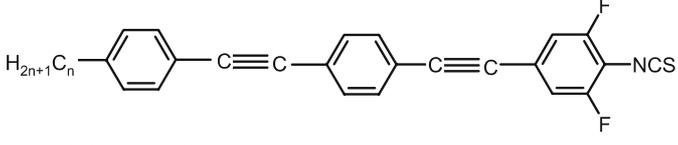
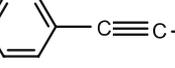
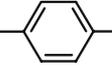
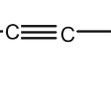
3. Results

Two-, three-, and four-ring compounds belonging to the series shown in Table 1 have been studied and characterized. Their phase transition temperatures [°C] and birefringences are given for the members with propyl or pentyl chain as illustration of their mesogenic and optical properties.

The compounds **1** were prepared by the coupling reaction of a boronic acid derivative with a haloaniline and compounds **2** were prepared by the coupling of an acetylene derivative with a haloaniline. The main difficulty dur-

* e-mail: rdabrowski@wat.edu.pl

Table 1. Structures, phase transition temperatures, and birefringence of the synthesized components.

No	Structure and phase transition temperatures	Δn
1a	 $H_{2n+1}C_n$ —  —  —NCS n = 5 Cr 31.0 (N 19.8) Iso	0.25
1b	 $H_{2n+1}C_n$ —  —  —NCS n = 5 Cr 13.1 Iso	
1c	 $H_{2n+1}C_n$ —  —  —  —NCS n = 3 Cr 95.3 SmA 107.5 N 187.1 Iso	0.33
1d	 $H_{2n+1}C_n$ —  —  —  —NCS n = 3 Cr 110 N 306 Iso	0.44
1e	 $H_{2n+1}C_n$ —  —  —  —NCS n = 5 Cr 115 N 283.5 Iso	0.43
1f	 $H_{2n+1}C_n$ —  —  —  —NCS n = 3 Cr 103 N 310 Iso	0.45
1g	 $H_{2n+1}C_n$ —  —  —  —NCS n = 3 Cr 145 N 272 Iso	0.45
2a	 $H_{2n+1}C_n$ —  —C≡C—  —NCS n = 5 Cr 49.0 (N 40.8) Iso	0.29
2b	 $H_{2n+1}C_n$ —  —C≡C—  —NCS n = 5 Cr 45 Iso	
2c	 $H_{2n+1}C_n$ —  —  —C≡C—  —NCS n = 5 Cr 61.4 (SmB 55.2) SmA 118.7 N 210.4 Iso	0.46
2d	 $H_{2n+1}C_n$ —  —C≡C—  —C≡C—  —NCS n = 4 Cr 163 N 243.2 Iso	

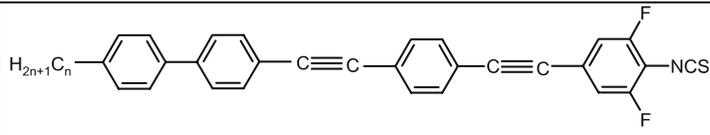
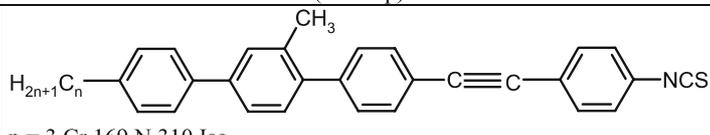
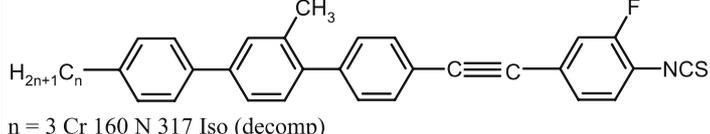
2e	 $H_{2n+1}C_n$ -phenyl-phenyl-C≡C-phenyl-C≡C-2,6-difluorophenyl-NCS	0.64
	n = 3 Cr 178 SmA 249.5 N 342 (decomp)	
2f	 $H_{2n+1}C_n$ -phenyl-2-methylphenyl-phenyl-C≡C-phenyl-NCS	0.54
	n = 3 Cr 169 N 310 Iso	
2g	 $H_{2n+1}C_n$ -phenyl-2-methylphenyl-phenyl-C≡C-2,6-difluorophenyl-NCS	0.54
	n = 3 Cr 160 N 317 Iso (decomp)	

Table 2. Physical properties of the nematic mixtures for low temperature operating devices.

	1280	1711	1711-A	1711-B	1711-C
Clearing point, (°C)	68–76	77–86	69–77	79–86	88–94
Viscosity ν (mm ² s ⁻¹) at 20°	12.6		17.9		
at 0°	33.5		49.4		
at -20°	147				
Δn (589 nm at 20°C)	0.1612	0.2406	0.2474	0.2777	0.2945
n_e	1.6698	1.7640	1.7756	1.881	1.8266
$\Delta\epsilon$	8.6	10.8	11.9	13.1	10.5
$\epsilon_{ }$	12.3	14.6	16.4	3.9	4.1
V_{10} (V)	2.0* 1.26	1.79* 1.15	1.74* 1.10	1.77* 1.17	1.90* 1.27
V_{50} (V)	2.26* 1.60	1.47	1.39	1.46	1.60
V_{90} (V)	2.66* 2.06	1.85	1.75	1.80	2.02
$p = V_{50}/V_{10}-1$	12.6* 27.6	27.6	25.6	24.7	25.3
$p = V_{90}/V_{10}-1$	32.2* 63.8	60.8	58.1	53.5	58.2
Temp. dep. (0–40°C) (%/°C)	0.3*				
Response time 20°					
t_{on} (ms)	4.8* 1.03	1.04	1.70	1.86	1.80
t_{off} (ms)	36* 4.50	4.33	5.97	5.80	4.75
K_{11} (pN)		17.2	17.8	21.3	19.6
K_{33} (pN)		20.4	20.7	24.6	23.1
FoM (μm ² /s)		6.0	6.2	5.5	5.2
γ_1 (mPs)		58	84	82	75
γ_1/K_{11} (ms/μm ²)		8.6	8.8	12.6	12.1
d (μm)	6.5* 1.7	1.6	1.62	1.67	1.62

* measured in the cell $d = 6.5 \mu\text{m}$.

ing the synthesis was to limit side reactions leading to autocoupling and generation of symmetrical hydrocarbons and diacetylenes. Detailed methods of synthesis are presented in other papers [8–10] and there are given the phase transitions for the other members of homologous series.

Two-ring monofluorosubstituted compounds **1a** and **2a** are low melting and low clearing mesogens, see example, while difluorosubstituted **1b** and **2b** are not mesogenic at room temperature. Three-ring compounds **1c** and **2c** have a broad nematic phase range and moderately high melting points, in the range of 50–100°C, and clearing points of about 200°C. Smectic phases are observed in three-ring substituted compounds, especially in series **2**, but at low temperatures only. Four-ring compounds except **1d-f** have very high melting points and are not useful for mixtures preparations. The birefringence of two-ring compounds **1** and **2** is between 0.25–0.3 and it increases to 0.65 for four-ring compound **2e** with two triple bonds.

The compounds of series **1** and **2** were used to prepare two types of nematic mixtures with high birefringence and large positive dielectric anisotropy, see Tables 2 and 3.

Isothiocyanates based mixture W-1280 with very fast switching, low melting point (below –40°C) and low viscosity [11] was used as a host mixture for series of 1711. The mixtures of 1711 were prepared by doping our host (W-1280) by the compounds **1a–1c** and **2a–2c** in increasing amount. Several quickly operating mixtures with birefringence growing up to 0.3 were prepared in such a way. They are capable to operate below room temperature. Our measurements proved that by using such composition enable us to obtain rise and fall time in the range of 1–2 ms and 4–5 ms respectively if thin (1.7 μm) cells are used. The second type of mixtures was prepared only from the compounds **1–2** without the host mixture previously mentioned. This shows birefringence up to 0.40 but the mixtures with higher birefringence up to 0.5 can be also formulated. Drawback of these mixtures is their increased viscosity. To describe switching performance of high birefringence mixtures we typically use figure-of-merit. It takes into one account birefringence and viscoelastic coefficient (γ_1/K_{11}) while a cell thickness is not critical.

$$FoM = \frac{\Delta n^2 \cdot K_1}{\gamma_1}$$

Although, increased viscosity of high birefringence mixtures, their figure-of-merit is much higher than the obtained for series 1711. A typical value is between 10 and 15. It suggests that switching times obtained for such mixtures should be very short if thin cell is in use. Our experiment with a very thin cell < 1.5 μm shows that this kind of mixture can switch very quickly at room or elevated temperatures, see Table 3.

4. Conclusions

Using the low-viscosity advantage of isothiocyanato compounds, high-birefringence and low to moderate viscosity mixtures showing short response times in thin cells can be

Table 3. Physical properties of high birefringence nematic mixture.

	1631	1658	1659	1680	1734
N-Iso, (°C)	91–94	113–116	97–10	40	110–114
Cr-(N), (°C)	< –5	< 0	< 0	(–2)	(–3)
$\epsilon_{ }$	15.7	19.8	21.3	16.6	22.0
ϵ_{\perp}	3.9	4.2	4.6	5.0	4.4
$\Delta\epsilon$	11.8	15.6	16.7	11.6	17.6
Δn (633 nm)	0.3637	0.3800	0.3700	0.3064	0.3900
K_{11} (pN)	17.6	21	16	8.38	26.2
K_{33} (pN)	34.6	32	31	20.3	28.1
K_{33}/K_{11}	1.97	1.5	1.9	2.42	1.07
γ_1/K_{11} (ms/μm ²)	9.1	10.5	12.0	11.2	11.6
FoM (μm ² /s)	14.5	13.8	11.7	8.4	13.1
V_{10} (V)	1.7	1.6	1.4	1.2	1.7
λ (nm)	633	633	633	633	633
Temp. (°C)	25	25	25	25	25
Response time (20°C)					
t_{on} (ms)					1.86
t_{off}					3.90
d (μm)					1.52

formulated. Two types of such mixture with a positive dielectric anisotropy were demonstrated. The first one, with ability to operate, in the low temperature region shows value of FoM at the level of 2–5. The second type mixtures show FoM in the range of 10–15. Because their high birefringence, relatively thinner cell can be used for further reduce of the response time. The operating voltage can be minimized as a result of high value of dielectric anisotropy of this type of mixture.

Acknowledgements

The work was carried under the Project UCF Purchase Order No: 33893, project nr 0T00C01627 and NATO Programme Security Through Science, Collaborative Linkage Grant No. CBP.EAP.CLG 981323.

References

1. S.T. Wu and D.K. Yang, “Reflective liquid crystals displays”, Wiley-SID, Verlag, Weinheim, 2001.
2. S.T. Wu, C.S. Hsu, Y.Y. Chuang, and H. Cheng, *Jpn. J. Appl. Phys.* **39**, L38–L41 (2000).
3. P. Janssen, J.A. Shimizu, J. Dean, and R. Albu, “Design aspects of a scrolling colour LCOS display”, *Displays* **23**, 99–108 (2002).

4. S. Gauza, H. Wang, C.H. Wen, S.T. Wu, A.J. Seed, and R. Dąbrowski, "High birefringence isothiocyanato tolane liquid crystals", *Jpn. J. Appl. Phys.* **42**, 3463–3466 (2003).
5. A. Spadło, R. Dąbrowski, M. Filipowicz, Z. Stolarz, J. Przedmojski, S. Gauza, C.Y. Fan, and S.T. Wu, "Synthesis, mesomorphic and optic properties of isothiocyanatotolanes", *Liq. Cryst.* **30**, 191–198 (2003).
6. C.O. Catanescu, L.C. Chien, and S.T. Wu, "High birefringence nematic liquid crystals for display and telecom applications", *Mol. Cryst. Liq. Cryst.* **411**, 93–102 (2004).
7. S. Gauza, C.H. Wen, S.T. Wu, N. Janarthanan, and C.S. Hsu, "Super high birefringence isothiocyanato biphenyl-bistolane liquid crystals", *Jpn. J. Appl. Phys.* **43**, 7634–7638 (2004).
8. A. Spadło, R. Dąbrowski, M. Filipowicz, 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", *Proc. SPIE* in press.
9. A. Ziótek, R. Dąbrowski, A. Spadło, K. Kenig, P. Kula, S. Gauza, and S.T. Wu, "Synthesis and mesomorphic properties of fluoro – substituted isothiocyanatobiphenyls and isothiocyanatoterphenyls", *SPIE* in press, 2005.
10. R. Dąbrowski, J. Dziaduszek, A. Ziótek, Ł. Szczuciński, Z. Stolarz, G. Sasnouski, V. Bezbodov, W. Lapanik, S. Gauza, and S.T. Wu, "Preparation of compounds and mixtures with high optical anisotropy", *Mol. Cryst. Liq. Cryst.* in press.
11. Z. Stolarz, R. Dąbrowski, J. Parka, X. Huang, and W. Lapanik, "Low viscosity mixtures for TN and STN displays", *Proc. SPIE* **4147**, 41–48 (2000).