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Novel high birefringent isothiocyanates based on quaterphenyl and phenylethynyltolane molecular cores

Jakub Herman[a]*, Jerzy Dziaduszek[a], Roman Dąbrowski[a], Jerzy Kędzierski[a], Krystian Kowiorski[a], Venkata Sai Dasari[b], Surajit Dhara[b] and Przemysław Kula[a]

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We report the synthesis of new laterally alkyl substituted high birefringent quaterphenyl and phenylethynyltolane liquid crystals with isothiocyanate terminal group. The thermal and optical properties such as birefringence are measured and discussed based on their molecular structures. The compounds exhibit birefringence (Δn) in the range of 0.44–0.63, and are expected to be appropriate components of high birefringent nematic mixtures for various applications.

Keywords: high birefringence; nematic; isothiocyanate; tolane derivative

1. Introduction

High birefringence (Δn) liquid crystals (LCs) play an important role not only among conventional display devices but also in laser beam steering [1] and tunable-focus lenses [2]. Despite a great number of visible range applications [3–8], liquid crystal birefringence is also saturated in the IR region as reported by Wu [9]. Finally, compounds with increased birefringence gained a huge importance for radio frequency applications in the GHz and THz part of the spectrum [10,11]. Studies of LCs in the millimetre and terahertz ranges have been demonstrated and followed by different liquid crystal-based devices [12–16].

The birefringence of a liquid crystal is mainly determined by the π-electron conjugation of the molecular core, thus the more linearly conjugated liquid crystal would exhibit the larger optical anisotropy [17]. High Δn values can be obtained by increasing the molecular conjugation length and designing the proper molecular shape. Representative functional groups that contribute to the molecular conjugation length include unsaturated rings (benzene, naphthyl, thiophene) and unsaturated bonds. Nevertheless high melting temperature, increased viscosity and degraded photo stability are the major concerns for high Δn liquid crystals. Reduced UV stability is caused by increased UV absorption as well as intrinsic reactivity of the triple bond of compounds with elongated π-electron system. That forces a special protection of these materials form direct UV exposure. Despite the fact that application of high birefringent liquid crystals can be limited in visible and ultraviolet regions, they can be successfully utilised for long-wavelength radio frequency applications (GHz/THz frequencies) [12–16].

High melting temperatures, enthalpies, and increased viscosity is often a consequence of the elongated molecular structures of the high birefringent compounds. While the conjugation length increase leads to high melting points, high Δn liquid crystals show a poor solubility, when eutectic mixtures are to be formed. If melting temperatures as well as enthalpies can be successfully improved (lowered) by introducing into molecule various lateral alkyl substitution, that viscosity may still reach high values. An efficient way to reduce it is the elevated temperature operation applied for these compounds. Introduction of a number of lateral substituents across the long axis of the liquid crystalline molecule is a conventional method for the design of physico-chemical properties. The lateral fluorine substitution has an ability to reduce viscosity and increase the dielectric anisotropy [18]. But the most effective way for lowering melting point is the insertion of the lateral alkyl group, to widen the molecular width [19].

Continuing our interest in the design of new medium to high birefringent LCs [20,21], we have been focused in this paper, on the synthesis of the isothiocyanate quaterphenyl and phenylethynyltolane species, as the promising components of high birefringent liquid crystal applicable mixtures, with the common formulas given in Figure 1.

Compounds possessing four phenyl ring system (quaterphenyl) laterally substituted by one or few substituents in chosen rings were the object of low attention so far, mainly due to the extremely high melting

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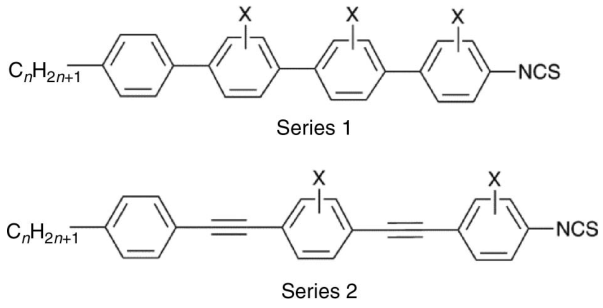


Figure 1. General formulas for compounds of series 1 and 2 wherein: X = methyl, ethyl, fluorine, chlorine and $n = 3.5$.

temperatures of known compounds. Such a molecular core together with an appropriate substitution can affect Δn values up to 0.43–0.45 [22]. From the other side, both non-polar and polar phenylethynyltolane species gained a bigger interest as the promising high birefringent materials [18,23–27]. Especially polar phenylethynyltolane derivatives seem to be a desirable for many potential applications. Polar compounds reported so far consist either of fluorine atom or cyano group as a terminal groups [19]; Liao et al reported also some derivatives with isothiocyanate polar group [27]. These compounds exhibit not only satisfactory $\Delta\varepsilon$ values, but also very high birefringence ($\Delta n \sim 0.5$) in the visible spectral region.

Cyano (CN) and isothiocyanate (NCS) groups are two commonly employed polar groups used for elongating the molecular conjugation [28]. Many investigations conducted recently and in the past by our and other laboratories show that liquid crystalline isothiocyanates are attractive LCs from the application point of view [29], followed by proposals of high Δn mixtures [30]. Comparing the physico-chemical properties of analogous isothiocyanate compounds with those consisting of cyano group, the latter are more viscous and possess a larger dipole moments, caused by the very strong dipole moment of the carbon–nitrogen triple bond. Therefore, the isothiocyanates exhibit lower dielectric anisotropy than the cyano compounds, but their birefringence Δn is much higher [31]. Based on our experience and reasons mentioned above, we synthesised some isothiocyanate compounds with several lateral substitution. Moreover the discussion about optimal number of lateral substituents, their optimal position in molecular core, their shape and length is presented.

2. Experimental

The phase transition temperatures and enthalpy data were determined by polarising optical microscopy (POM) with an OLYMPUS BX51 equipped with a Linkam hot stage THMS-600 and differential scanning calorimeter (SETARAM DSC 141) during heating/cooling cycles (rate, 2 degrees/min). The purity of synthesised compounds were determined by thin layer chromatography (TLC), SHIMADZU GCMS-QP2010s series gas chromatograph equipped with quadrupole mass analyser (MS), high performance liquid chromatography HPLC-PDA-MS (APCI-ESI-dual source) Schimadzu LCMS 2010EV equipped with polychromatic UV-VIS detector and MS (ESI/APCI) analyser. Proton (^{1}H) nuclear magnetic resonance (NMR) spectra in $CDCl_3$ were collected using a Varian 500 spectrometer.

General synthetic methods of investigated compounds of series 1 and 2 are given in Schemes 1 and 2. For the series with quaterphenyl unit, 4-*n*-alkylphenylboronic acids were used as a starting materials. Suzuki–Miyaura hetero cross-coupling reaction was the major incorporated during synthesis of quaterphenyl rigid core, while Sonogashira–Hagihara coupling was predominant for the synthesis of phenylethynyltolane unit. Here 4-*n*-alkylphenylacetylene and 4-iodo-3-alkylaniline were used as starting reagents. Introduction of the NCS polar group into molecules in all cases was carried out at the last step with thiophosgene as a reactant. Experimental procedures are given below.

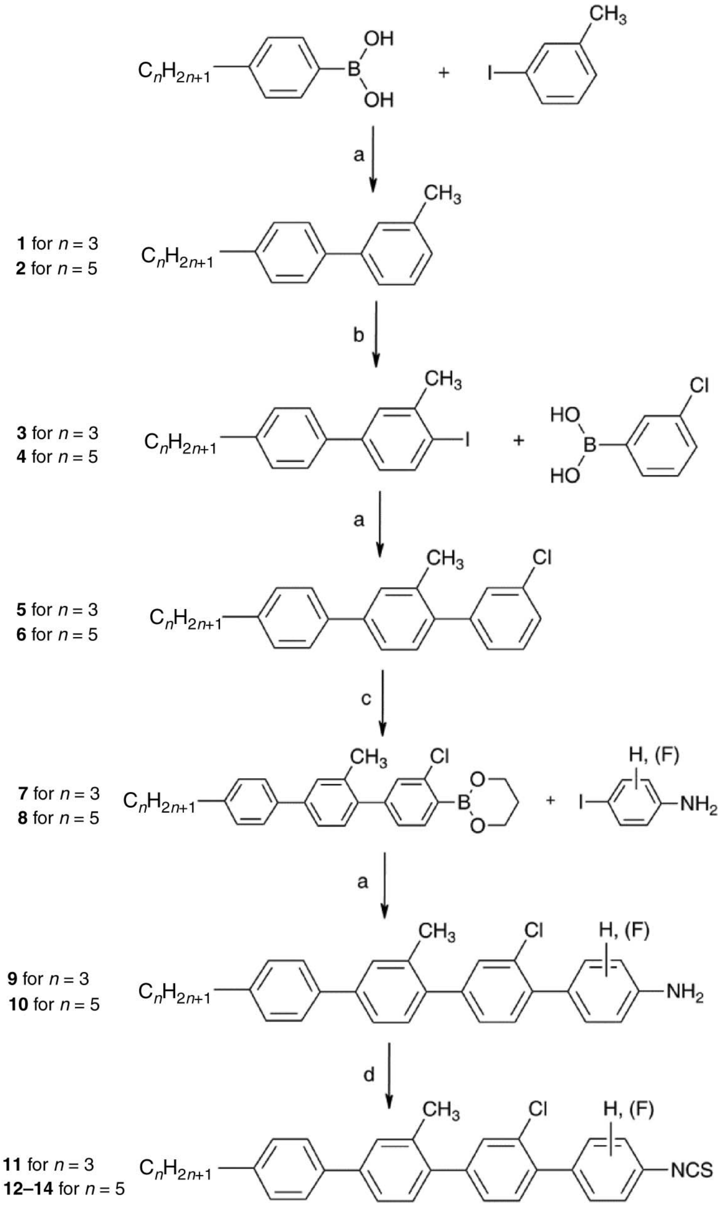
2.1 Synthetic procedures

2.1.1 4′-pentyl-3-methylbiphenyl (2) – Suzuki–Miyaura procedure

To the mixture of 4-pentylphenylboronic acid (85 g; 0.442 mol), 3-iodotoluene (80.3 g; 0.368 mol), K_2CO_3 (153 g; 1.1 mol) in 500 ml of acetone and 200 ml of water, all flushed with nitrogen, a 0.2 g (0.3% mol) of catalyst $PdCl_2$ was added. The reaction mixture was heated under reflux for 3 h. After reaction completion mixture was poured into 5% HCl solution. Crude product was extracted with hexane, washed with water, dried over $MgSO_4$. The hexane was evaporated and residue distilled at reduced pressure. Yield, 74.2 g (87%); b.p., 130°C (0.4 mmHg); MS(EI): 238 (M^+), 181, 166.

2.1.2 4′-pentyl-4-iodo-3-methylbiphenyl (4)

The mixture consisted of 4′-pentyl-3-methylbiphenyl **(2)** (73.6 g; 0.31 mol), I_2 (31.4 g; 0.124 mol), HIO_3 (11 g; 62 mmol), glacial acetic acid (350 ml), water (80 ml) and concentrated sulphuric acid (31 ml) was stirred for 3 h under reflux. The mixture was poured into Na_2SO_3 water solution. The product was extracted to dichloromethane, washed with water, dried over $MgSO_4$. Solvent was evaporated and the product was purified by column chromatography



Scheme 1. Synthetic route to quaterphenyl liquid crystals (series 1). Synthetic conditions: a – $Pd(OAc)_2$, K_2CO_3, Acetone, H_2O; b – I_2, HIO_3, H_2SO_4, CH_3COOH, H_2O; c – (1) sec-BuLi, THF, –75°C, (2) $B(OC_3H_7)_3$, –75°C, (3) H_3O^+, H_2O; d – $CSCl_2$, $CHCl_3$, H_2O.

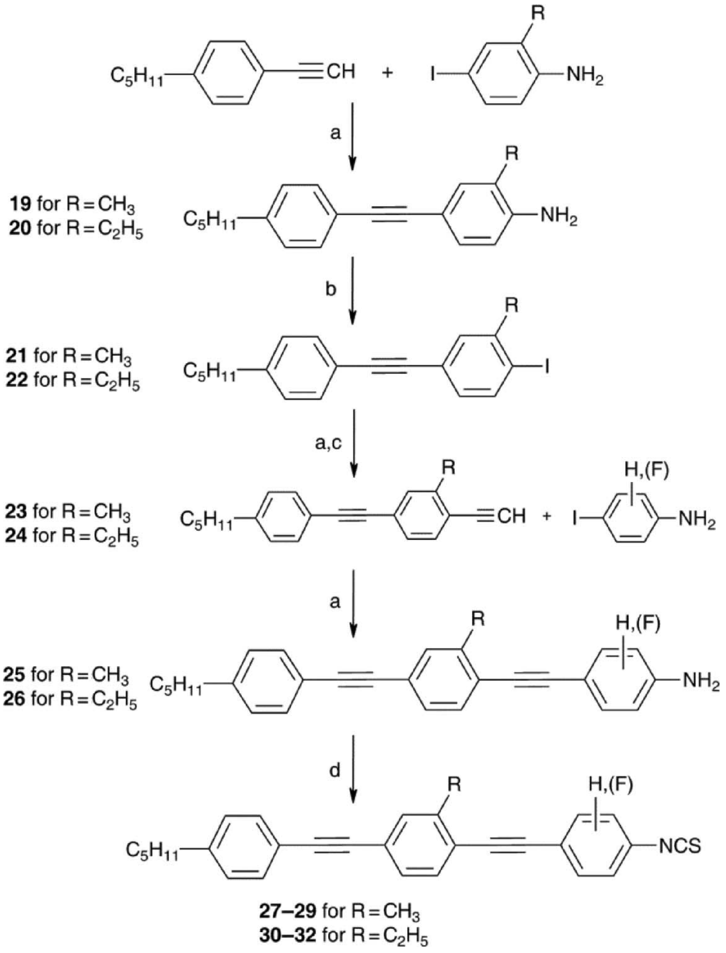
(silica gel) using hexane as eluent to give a deep yellow liquid; yield, 90.5 g (80%); MS(EI): 364 (M^+), 307, 165.

2.1.3 3-chloro-2′-methyl-4′′-pentyl-[1,1′:4′,1′′] terphenyl (6)

Compound **6** was prepared using a procedure similar to that described for synthesis of compound **2**. Product **6** was purified by column chromatography (silica gel) using hexane/methylene chloride as eluents to give yellow oil. Yield, 23.7 g (70%); MS(EI): 348 (M^+), 291, 239, 165.

2.1.4 2-(3-chloro-2′-methyl-4′′-pentyl-[1,1′:4′,1′′] terphenyl-4-yl)-1,3,2-dioxaborinane (8)

A solution of compound **6** (23.7 g; 68 mmol) in anhydrous Tetrahydrofuran (200 ml) was stirred and cooled to –75°C on a dry ice/acetone bath, all flushed with nitrogen. The sec-Butyllithium in cyclohexane-hexane solution (68 ml; 1.3 m) was added dropwise and stirred for 3 h. After that, the tripropyl borate (17.5 ml; 80 mmol) was added dropwise and temperature kept at –75°C. Stirring was continued while mixture was allowed to reach room temperature. Then solvents were evaporated and residue was poured



Scheme 2. Synthetic route to phenylethynyltolane liquid crystals (series 2). Synthetic conditions: a – $PdCl_2(PPh_3)_2$, CuI, TEA, DBU, THF; b – HCl, dioxane, $NaNO_2$, KI; c – NaH, toluene; d –$CSCl_2$, $CaCO_3$, H_2O, $CHCl_3$.

into water and acidified with 10% HCl to pH ~ 2–3. Purification of boronic acid was continued by carrying out an esterification to cyclic boronic ester derivative **(8)** with subsequent amount of 1,3-propanediol (4.9 ml; 68 mmol) in toluene solution. Crude product was purified by column chromatography (silica gel, methylene chloride as eluent) to give yellow low melting crystals. Yield, 27.8 g (70% GC-MS purity); MS(EI): 432 (M^+), 375, 317, 239.

2.1.5 *2′-chloro-4-isothiocyanato-2″-methyl-4‴-pentyl-[1,1′:4′,1″:4″,1‴]-quaterphenyl (12)*

Compound **10** was synthesised using standard Suzuki–Miyaura cross-coupling protocol. The solid hydrochloride of **10** amine was filtered off, washed with cold acetone and then dissolved in chloroform (30 ml). The solution was dropped slowly to the mixture consisted of $CHCl_3$ (30 ml), water (30 ml) and thiophosgene (0.8 ml; 10.6 mmol) at 0–5°C. The mixture was stirred for 5 h at room temperature. The organic layer was separated, dried over $MgSO_4$, the solvent was evaporated and the solid residue was purified by column chromatography (silica gel) using boiling heptane as eluent to give white solid crystal, which was recrystallised from acetone. Yield, 1.7 g (50%); m.p., 107°C; MS(EI): 481 (M^+), 424, 392, 212. ^1H NMR (200MHz, $CDCl_3$) δ 7.53–7.51 (d, 2H, Ar–H); 7.48–7.46 (d, 2H, Ar–H); 7.37–7.32 (m, 5H, Ar–H); 7.29–7.26 (m, 5H, Ar–H); 2.67–2.62 (t, 2H, Ar–CH_2–); 2.39 (s, 3H, Ar–CH_3); 1.75–1.59 (m, 2H, –CH_2–); 1.39–1.26 (m, 4H, –CH_2CH_2-); 0.95–0.88 (t, 3H, –CH_3).

2.1.6 *2-methyl-4-[(4-pentylphenyl)ethynyl] aniline (19) – Sonogashira–Hagihara protocol*

To the mixture of 4-iodo-2-methylaniline (100 g; 0.43 mol), triethylamine (71 ml; 0.52 mol), 1, 8-Diazabicyclo[5.4.0]undec-7-ene (64 ml; 0.43 mol), anhydrous Tetrahydrofuran (500 ml), $PdCl_2(PPh_3)_2$ (5 g; 3% mol), CuI (2.5 g; 3% mol), a solution of 77.6 g (0.45 mol) 4-pentyl-1-ethynylbenzene in 200 ml of anhydrous Tetrahydrofuran was slowly added over 30 min at room temperature. A consequent exothermic reaction raised the temperature up to 50°C. The mixture was refluxed for 3 h, then cooled and poured into water. Crude product was extracted with toluene. Organic layer was washed with water, dried over $MgSO_4$ and filtrated. Toluene was evaporated under reduced pressure conditions and the residue was recrystallised form a hexane solution to give a brown crystals. Yield, 95 g (80%), m.p., 71.7–72.2°C; MS(EI): 277 (M^+), 220, 204.

2.1.7 1-iodo2-methyl-4-[(4-pentylphenyl)ethynyl] benzene (21)

To a solution of compound **19** in dioxane (250 ml), 100 mL of 30% HCl solution was added dropwise at 0–5°C. After that, aqueous solution of sodium nitrite (32.4 g; 0.47 mol) was added slowly and the mixture was stirred for 1 h, maintaining the temperature at the same level of 0–5°C. Finally the reaction mixture was treated with aqueous solution of 68.6 g of NaI. After the temperature of the mixture rose to room temperature, it was poured into a water solution of Na_2SO_3, then the product was extracted with toluene, washed with water, brine and dried over $MgSO_4$. Organic solvent was evaporated and the crude product was purified by column chromatography (silica gel, hexane as eluent) to give a deep brown liquid. MS(EI): 388 (M^+), 331, 261, 202.

2.1.8 1-ethynyl-2-methyl-4-[(4-pentylphenyl) ethynyl] benzene (23)

Compound **23** was obtained with standard Sonogashira protocol and then by the deprotection of carbon–carbon triple bond with catalytic amount of sodium hydride in anhydrous toluene. Product **23** does not crystallise and stay in form of dark oil. Yield, 15 g (72%); MS(EI): 286 (M^+), 229, 202.

2.1.9 4-[2-methyl-4-[(4-pentylphenyl)ethynyl] phenyl]ethynyl aniline (25)

Compound **25** was prepared using a procedure similar to that described for the synthesis of **19**. Product **25** was purified by recrystallisation from hexane to give deep brown crystals.

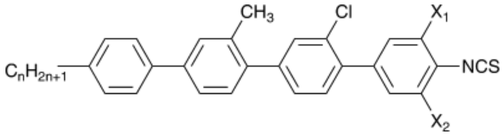
2.1.10 1-[(4-isothiocyanatophenyl)ethynyl]-2-methyl-4-[(4-pentylphenyl)ethynyl] benzene (27)

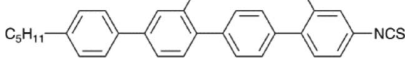
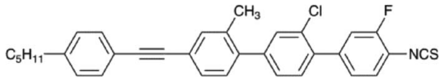
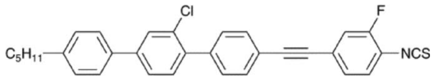
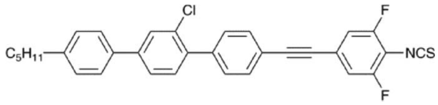
To the mixture of compound 4-[2-methyl-4-[(4-pentylphenyl)ethynyl]phenyl]ethynyl aniline ***(25)*** (6 g; 16 mmol), $CaCO_3$ (4 g; 40 mmol) in $CHCl_3$ (30 ml) and water (30 ml), the straight thiophosgene (1.9 ml; 24 mmol) was added slowly while stirring and maintaining temperature at 0–5°C. Then the mixture was stirred for 5 h at room temperature. The organic layer was separated, dried over $MgSO_4$ and the solvent was evaporated at lower pressure. Crude product was purified by column chromatography (silica gel, hexane as eluent) and recrystallised from acetone to give white crystals. Yield, 2.8 g (42%); m.p., 100°C; MS(EI): 419 (M^+), 362, 330, 302. ^1H NMR (200MHz, $CDCl_3$) δ 7.56–7.51 (m, 2H, Ar–H); 7.49–7.45 (m, 2H, Ar–H); 7.43–7.41 (m, 2H, Ar–H); 7.35–7.30 (m, 1H, Ar–H); 7.19–7.14 (m, 4H, Ar–H); 2.65–2.56 (t, 2H, Ar–CH_2-); 2.50 (s, 3H, Ar–CH_3); 1.69–1.58 (m, 2H, –CH_2–); 1.35–1.28 (m, 4H, –CH_2CH_2–); 0.93–0.86 (t, 3H, –CH_3).

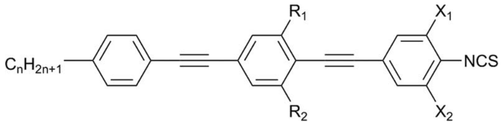
3. Results and discussion

The mesomorphic properties of prepared compounds are listed in Table 1. Final liquid crystals are white solids, show a simple mesophase sequence, and possess only nematic phases in broad temperature ranges. For the comparison of properties also other never reported so far fluorinated analogues (**15–18, 33–35**), synthesised in our lab too, are matched in Table 1. Compounds of series 1 (see Table 1) exhibit low melting temperatures, which are decreasing with the lengthening of alkyl terminal chain. It seems that substitution of quaterphenyl core with methyl group and chlorine/fluorine atoms simultaneously lower melting temperatures successfully. Additionally increasing number of fluorine atoms in quaterphenyl core decreases the clearing point of such compounds. Such substitution makes these mesogens easily supercooled to room temperatures. Introducing carbon–carbon triple bond inside quaterphenyl core (see compound **16**, Table 1) extends extra molecular conjugation leading to increased birefringence (Δn) without deterioration of liquid crystal properties. Until now only few mesogens with methyl lateral substitution based on phenylethynyltolane core were reported earlier [27]. Our results confirm that data. The interesting situation is that phase transition enthalpies are much lower than those of fluorine substituted homologues (see compounds **33–35,** Table 1). Alkyl lateral substitution widens molecular separation considerably comparing

Table 1. Phase transition temperatures and enthalpies (kJ/mol) of compounds measured by DSC method (onset point) in a heating cycle at 2°C/min.



No.	*n*	X_1	X_2	Phase transition **temperatures** [°C] (*enthalpy [kJ/mol]*)
11	3	H	H	Cr **148.6** *(42.6)* N **206.1** Iso
12	5	H	H	Cr **106.6** *(28.0)* N **161.9** Iso
13	5	F	H	Cr **86.3** *(24.9)* N **142.0** Iso
14	5	F	F	Cr **95.2** *(26.5)* N **117.0** Iso
15				Cr **77.3** *(28.7)* N **265.0** Iso
16				Cr **83.5** *(24.9)* N **211.9** Iso
17				Cr **114.7** *(32.8)* N >**300** Iso
18				Cr **95.9** *(33.6)* N **280.0** Iso



	n	R_1	R_2	X_1	X_2	
27	5	CH_3	H	H	H	Cr **101.1** *(24.2)* N **234.1** Iso
28	5	CH_3	H	F	H	Cr **107.7** *(27.1)* N **220.4** Iso
29	5	CH_3	H	F	F	Cr **99.5** *(23.7)* N **195.4** Iso
30	5	C_2H_5	H	H	H	Cr **76.6** *(24.6)* N **157.3** Iso
31	5	C_2H_5	H	F	H	Cr **73.0** *(29.3)* N **144.8** Iso
32	5	C_2H_5	H	F	F	Cr **115.9** *(38.9)* N **126.1** Iso
33	3	F	F	H	H	Cr **147.3** *(41.8)* N >**300.0** Iso
34	3	F	F	F	H	Cr **156.3** *(41.9)* N **253.2** Iso
35	4	H	H	F	F	Cr **165.0** *(40.9)* N **243.0** Iso

to other substituents leading to improvement of melting properties.

To measure the Δn values, a set of 5–20% wt. nematic guest–host systems were prepared. Mixtures were composed of investigated compounds and host nematic 1816 ($\Delta n = 0.220$ measured at 25°C for sodium line D) prepared in our lab (method a). As a second host in method b, known single compound nematic was applied.[1] The Δn values for investigated isothiocyanates can be extrapolated from guest–host mixtures results by comparison with host nematic system. For the birefringence measurements of guest–host mixtures, the method based on exploiting interference in a wedge cells of small apex angle was used [32,33], which is a modification of method described in [34]. Birefringence values, determined with this method are marked as method a, possess the systematic error of about 2% which appears due to low accuracy of determining the wedge geometry. The errors involved in the temperature determination are of about 0.3 K. Method b applied here uses the phase modulation technique to measure the birefringence of the sample [35]. The setup consists of two crossed Glan–Thompson (GT) polarisers, a photoelastic modulator (PEM), a He–Ne laser source and a detector. The plane polarised light after first GT polariser passes through PEM and sample where both are kept at 45° with respect to the first polariser. The light passes through the second GT polariser and then to a detector. The detector output is connected to a lock-in amplifier for the detection of the first and the second harmonics of the ac signal.

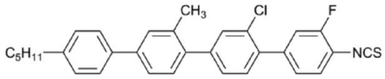
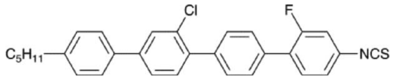
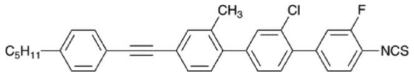
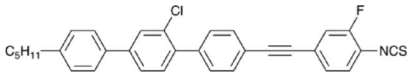
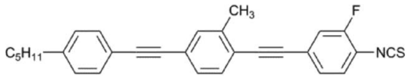
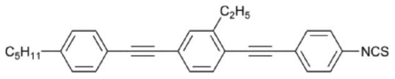
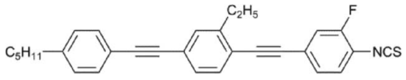
The birefringence of the sample is given by

$$\Delta n = \frac{\lambda}{2\pi d} \arctan \left[\frac{I_1 f}{I_2 f} \times \frac{J_2(A_0)}{J_1(A_0)} \right]$$

where λ is the wavelength of laser light, d is the cell thickness, I_{1f} and I_{2f} are the first and second harmonic signals measured by the lock-in amplifier, A_o is the retardation amplitude of the PEM and J_1 and J_2 are the first and second order Bessel functions. This method is very sensitive and capable of measuring retardation much less than a nanometer. The measurements were made as a function of temperature using an Instec temperature controller with an accuracy of 20 mK. The whole experiment was controlled by a computer.

Results of birefringence measurements for chosen structures are given in Table 2. The lowest values of birefringence are found for compounds with quaterphenyl core (compounds **13** and **15**). Four phenyl rings connected together and combined with the isothiocyante group generate Δn values in the range 0.44–0.45. Introduction of one triple carbon–carbon bond inside this core (compounds **16** and **17**) raised the birefringence above 0.5 level. Whereas phenylethynyltolane (bistolane) unit in connection with high polarisable polar NCS group show the highest values of Δn (compounds **28**, **30** and **31**). Results show strong conjugation effect of π-electron system especially inside bistolane unit, for which experimental results exceed the most the theoretical assumptions. This kind of structural sequence appears as a great advantage over quaterphenyl unit. The effect of carbon–carbon triple bond on birefringence increase can be noticed comparing values of quaterphenyl structures **13** and **15** with results obtained for **16** and **17**. Such bond helps to elongate π-electron system and increases birefringence values of about 0.09.

Table 2. Birefringence values of chosen structures extrapolated from guest–host systems (measured at 25°C) using wedge cells @589 nm[a] and phase modulation technique @633 nm[b].

No.	Structure	Δn^a	Δn^b
13		0.44	0.43
15		0.45	
16		0.53	0.52
17		0.55	
28		0.63	
30		0.63	0.62
31		0.62	

4. Conclusions

Two homologous serie of compounds exhibiting nematic phase in broad temperature range, from quaterphenyl and phenylethynyltolane families have been synthesised and characterised. Synthesised compounds are attractive to formulation of new high birefringent mixtures with broad temperature range of nematic phase. Careful selection of lateral substituent, their position and sequence among rigid cores of molecules have the biggest influence on the optimisation of mesogenic properties of liquid crystalline molecules. In our case, proper connection of these substituents in lateral positions allowed to reach reasonable levels both in melting temperatures and enthalpies, what is very important in mixture formulation. Further experiments confirmed valuable optical properties of investigated structures. New materials are characterised with the birefringence values from 0.44 for quaterphenyl core up to 0.63 for phenylethynyltolane core. Further work is now underway to further investigate the viscoelastic properties of prepared compounds.

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Note

1. 1,4-bis[(4-butylphenyl)ethynyl]-2-ethylbenzene, $T_{Cr–N}$ = 29.5°C, $T_{N\text{-}I}$ = 121.0°C, Δn = 0.37 (633 nm, 25°C).

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