Synthesis and mesomorphic properties of super high birefringence isothiocyanato bistolane liquid crystals

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Four series of high birefringence bistolane liquid crystals containing isothiocyanato termal groups were synthesized and characterized. As well as the phenyl group, both biphenyl and naphthyl moieties were introduced to enhance the birefringence. These bistolane compounds exhibit reasonably low melting points and high birefringence of 0.5–0.8. A eutectic mixture was formulated from these compounds exhibiting a wide nematic range, high figure-of-merit and low viscosity.

1. Introduction

High birefringence (Δn) liquid crystals (LCs) are useful not only in conventional display devices such as STN-LCDs, but also in scattering-type PDLCDs as a reflective LCD, and in spatial light modulators. They are also of interest as componens of LCDs; for example, compensation films for improving the viewing angle, reflectors and polarizers. A number of LCs have been studied for these applications [1–3].

It is well known that high Δn values can be achieved by increasing the molecular conjugation length [2]; a considerable number of π-conjugated compounds have been developed as high Δn LCs [4]. Molecules that contain highly polarizable groups with high electron densislay, such as benzene rings or acetylene linking groups, will therefore have large optical anisotropies. Tolane-based LCs exhibit reasonably high Δn, low viscosity and good chemical, photo and thermal stability [5]. Bistolane LCs show birefringences greater than 0.3 in the visible spectrum and as a result have attracted particular attention [6–16]. The same properties are also found for isothiocyanates (NCS) [17]. Therefore, coupling of the tolane and NCS groups could lead to high optical and large dielectric anisotropies while preserving a relatively low viscosity [18]. Several molecular structures with high Δn values, e.g. diphenyldiacetylene [19, 20], naphthalene tolanes [21] and thiophenyldiacetylene [22–24] have been widely studied. The Δn values of these compounds were reported in the range of 0.4–0.6; however, the diacetylene compounds have in adequate UV and thermal stabilities, and thus their application is limited [25].

In this paper, we report the synthesis procedures and physical properties of highly birefringent bistolane LCs having a terminal isothiocyanato group. Phenyl, biphenyl and naphthyl moieties linked by an ethynyl unit were applied as the core structure. Lateral methyl substitution in the middle phenyl ring significantly reduces the melting temperatures of bistolane LCs [14]. By introducing different laterally substituted short alkyl chains and fluorine at various positions, the synthesized compounds were characterized with low melting point, relatively low viscosity, and high optical anisotropy, ready for immediate practical applications.

2. Experimental

2.1. *Characterization techniques*

^{1}H NMR spectra were measured with a Varian 300 MHz spectrometer. Infrared spectra were obtained using a Perkin-Elmer Spectrum One spectrophotometer in the range of 400–4000 cm^{-1}. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Pyris Diamond DSC instrument at a heating rate of 10°C min^{-1}. A Carl-Zeiss Axiophot polarizing microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor was used to observe the mesomorphic textures. The molecular mass and elemental analysis results were obtained from a T-200 GC/MS spectrometer and Heraeus CHN-OS RAPID instrument, respectively.

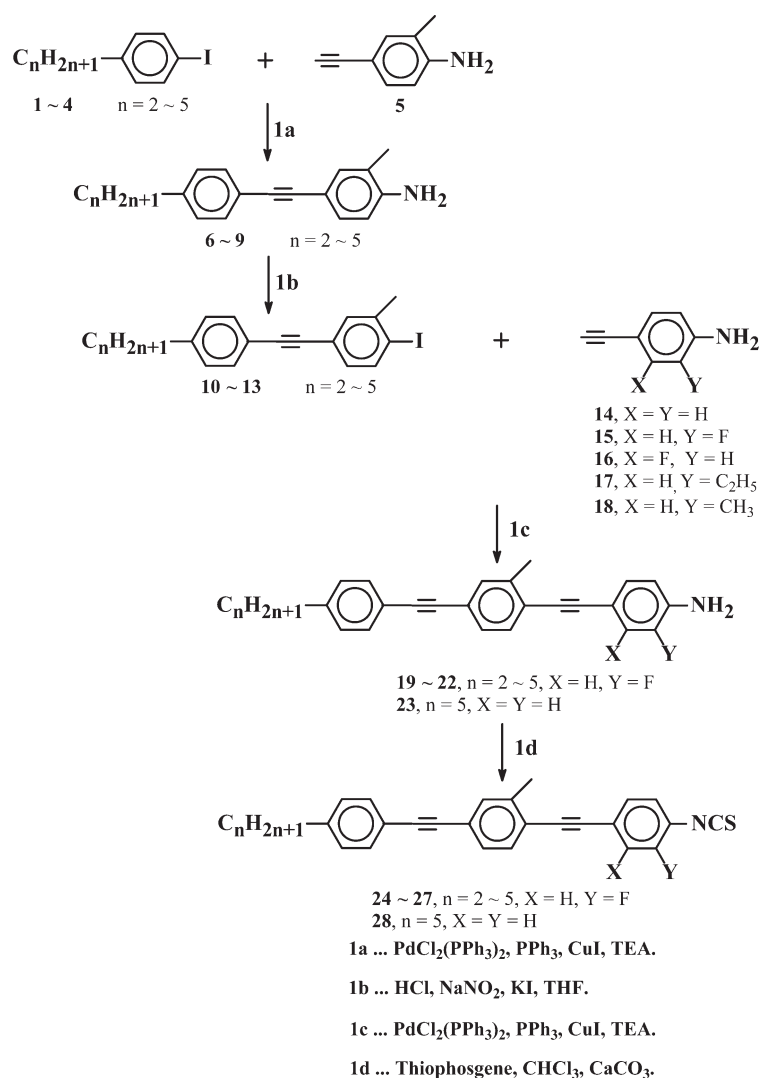*Corresponding author. Email: cshsu@mail.nctu.edu.tw

For electro-optic measurements, homogenous cells with cell gap $d \sim 8 \, \mu m$ were used. An a.c. voltage with 1 kHz square waves was used to drive the LC cell, whose inner surfaces were coated with indium tin oxide (ITO) electrodes. On top of the ITO, the substrate was covered with a thin polyimide alignment film. The cell was placed on a heating/cooling stage with a temperature stability of 0.2°C. Commercial LCs ZLI-1565 and E-63 (from Merck) were used as the host. A conventional guest–host method was applied to extrapolate the Δn value at $T \sim 23.5$°C.

2.2. Synthesis

The compounds **1–5**, **14–18**, **29–30** and **39–40** were prepared by reported methods [14, 26]. As mentioned above, a large variety of high birefringence compound structures has been investigated. However, in all cases the synthesis of the final materials is greatly facilitated by the use of a palladium-catalysed cross-coupling reaction [27–33]; in the synthesis of some materials this synthesis procedure is virtually essential. Scheme 1 shows the synthesis of several isothiocyanato-substituted bistolanes containing alkyl groups; scheme 2 shows the synthesis of analogues containing alkoxy groups; scheme 3 shows the synthesis of similar compounds containing the biphenyl moiety; and scheme 4 shows the introduction of the naphthyl moiety.

Despite the development of the palladium-catalysed cross-coupling reaction to high levels, their exceptional versatility and their extreme tolerance to a wide range of functional groups, attempted couplings involving isothiocyanato substituents resulted in failure [34]. The

Scheme 1. Synthesis of compounds **24–28**.

2a ... PdCl$_2$(PPh$_3$)$_2$, PPh$_3$, CuI, TEA.

2b ... HCl, NaNO$_2$, KI, THF.

2c ... PdCl$_2$(PPh$_3$)$_2$, PPh$_3$, CuI, TEA.

2d ... Thiophosgene, CHCl$_3$, CaCO$_3$.
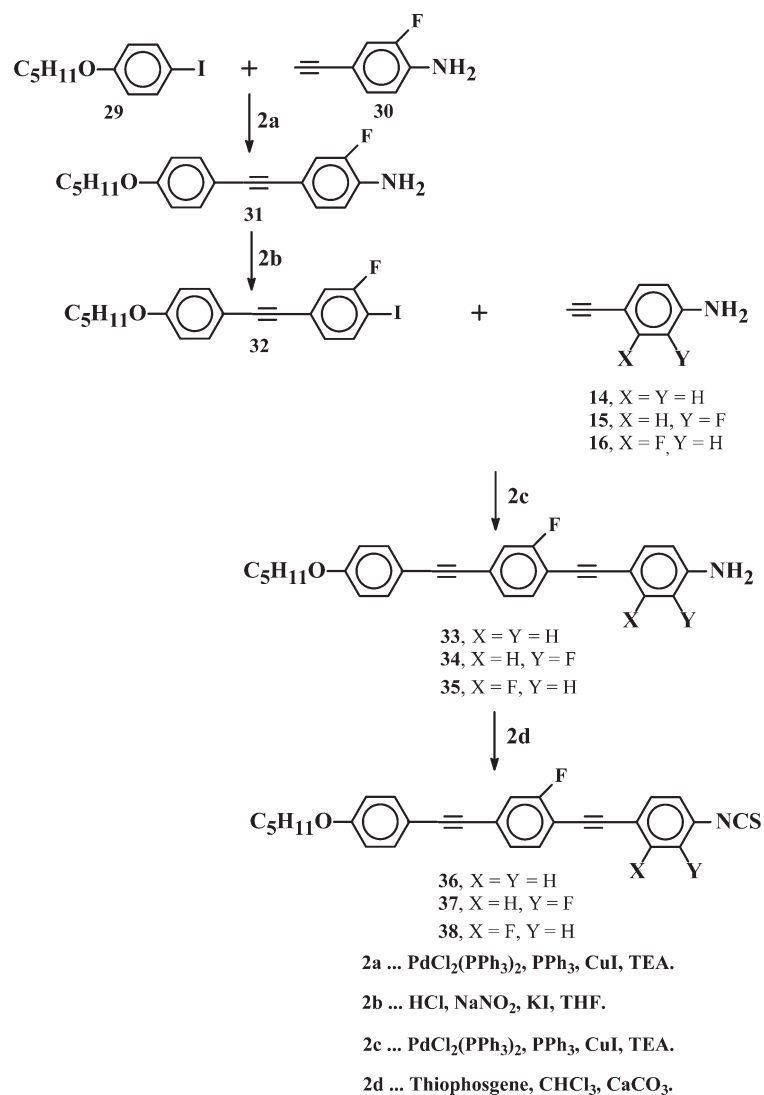
Scheme 2. Synthesis of compounds **36–38**.

use of thiophosgene and chloroform on an aromatic amine in the presence of aqueous calcium carbonate is a very useful and efficient method of introducing the isothiocyanato group [34, 35] and this method has been used in this research.

**2.2.1. 1-(4-Pentylphenyl)-2-(4-amino-3-methylphenyl)-acetylene,** 9**.** Compound **4** (2.74 g, 10 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.14 g, 0.2 mmol), triphenylphosphine (0.2 g, 0.8 mmol), copper(I) iodide (0.08 g, 0.4 mmol) and dry triethylamine (150 ml) were mixed and stirred at room temperature for 30 min under nitrogen. A solution of compound **5** (1.44 g, 11 mmol) dissolved in 75 ml of triethylamime was added dropwise and the mixture stirred at 70°C for 24 h. After cooling to room temperature, the mixture was filtered and filtrate concentrated *in vacuo* to remove triethylamine. The

crude product was dissolved in diethyl ether and extracted with aqueous ammonium chloride solution. The organic phase was then washed with saturated aqueous sodium chloride and dried over MgSO$_4$. The crude product was isolated by evaporating the solvent, and purified by column chromatography using ethyl acetate/*n*-hexane = 1/4 as eluant to give a deep yellow solid; yield 2.0 g (72%). ^{1}H NMR (δ, CDCl$_3$): 0.87–0.92 (t, 3H), 1.25–1.34 (m, 4H), 1.56–1.63 (m, 2H), 2.10 (s, 3H), 2.58–2.61 (t, 2H), 3.71 (s, 2H), 6.72–7.42 (m, 7H). IR (KBr) v_{max} (cm^{-1}): 3392, 3180, 2960, 2923, 2860, 2220, 1640, 1462, 1380, 1247, 1070, 823. MS *m/z* 402 (M$^+$), 345.

2.2.2. 1-(4-Pentylphenyl)-2-(4-iodo-3-methylphenyl)-acetylene, 13**.** Compound **9** (1.95 g, 7 mmol) was dissolved in THF (10 ml) and cooled to 0°C in an ice
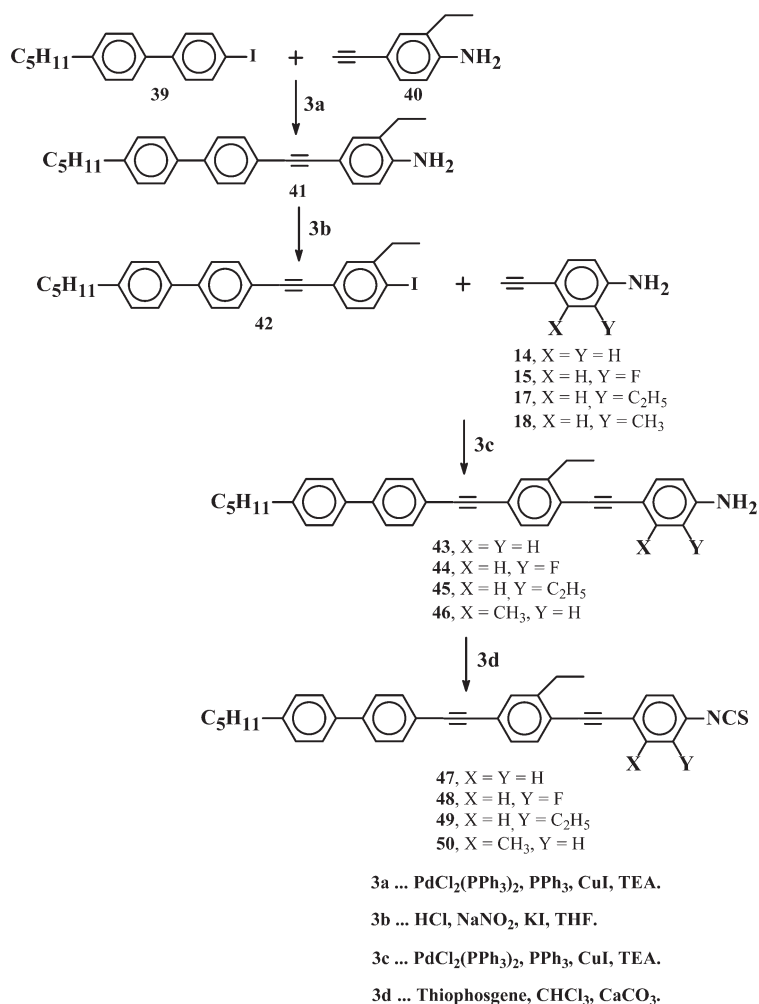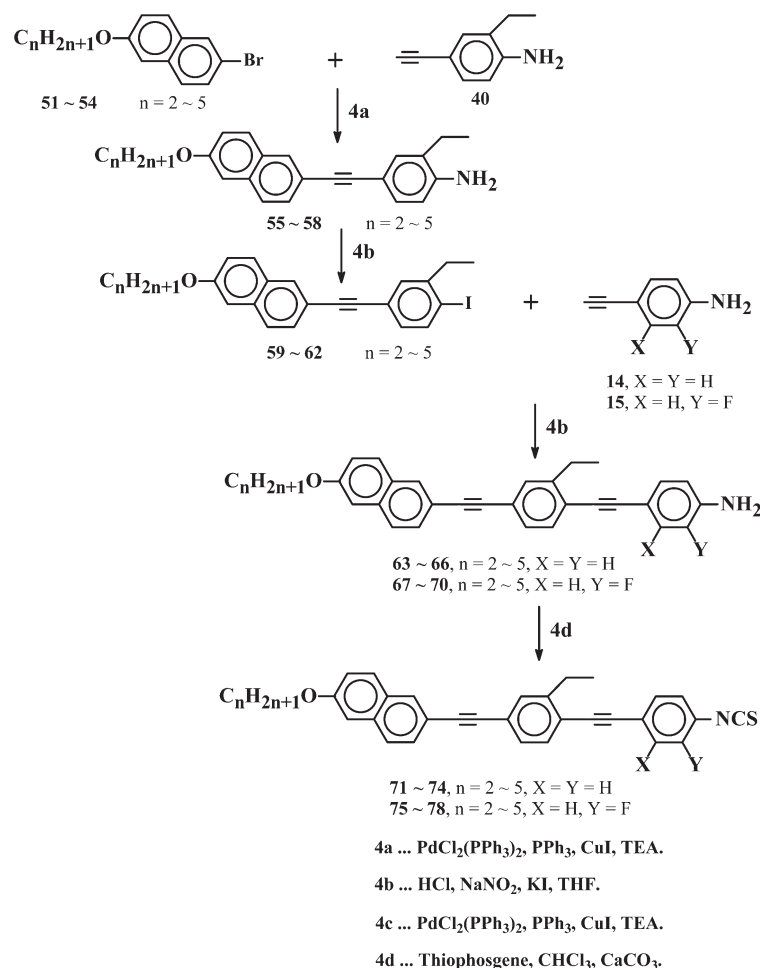
Scheme 3.   Synthesis of compounds **47–50**.

bath. Aqueous HCl (0.8 g, 21.0 mmol) was added and the mixture stirred for 30 min. Sodium nitrite (0.63 g, 9.1 mmol) dissolved in 5 ml of water was slowly added to the reaction mixture which was stirred for a further 30 min. After checking that the pH of the reaction mixture was acidic, potassium iodide (1.71 g, 10.5 mmol) dissolved in 8 ml of water was added, maintaining a temperature of 0–5°C. After stirring for 3 h at 0–5°C the reaction mixture was slowly heated to 45°C and held for 5 min. It was then cooled, treated with aqueous sodium thiosulphate solution and extracted with *n*-hexane. The organic phase was washed with saturated aqueous sodium chloride and dried over MgSO$_4$. The crude product was isolated by evaporating the solvent and purified by column chromatography using ethyl acetate/*n*-hexane = 1/10 as eluent to give a yellow liquid; yield 2.15 g (79%). ^{1}H NMR (δ, CDCl$_3$): 0.89–0.93 (t, 3H),

1.25–1.38 (m, 4H), 1.58–1.63 (m, 2H), 2.43 (s, 3H), 2.57–2.62 (t, 2H), 6.96–7.60 (m, 7H). IR (KBr) ν_{max} (cm^{-1}): 2980, 2935, 2870, 2200, 1640, 1450, 1366, 1254, 1113, 843. MS *m/z* 277 (M$^+$), 220.

2.2.3.   2-Methyl-{4-[2-(4-pentylphenyl)-1-ethynyl]-1-ethyny}-3-fluoroaminobistolane, 22.

By following the procedure for compound **9** and using **13** and 1**5** as starting materials, compound **22** was obtained as a deep yellow solid; yield 1.18 g (60%). ^{1}H NMR (δ, CDCl$_3$): 0.89–0.92 (t, 3H), 1.24–1.32 (m, 4H), 1.58–1.63 (m, 2H), 2.46 (s, 3H), 2.56–2.62 (t, 2H), 3.68 (s, 2H), 6.52–7.42 (m, 10H). IR (KBr) ν_{max} (cm^{-1}): 3376, 3120, 2930, 2903, 2880, 2210, 1650, 1460, 1377, 1240, 1170, 833.

2.2.4.   2-Methyl-{4-[2-(4-pentylphenyl)-1-ethynyl]-1-ethyny}-3-fluoroisothiocyanatobistolane, 27.

Compound **22** (1.1 g, 2.5 mmol) was dissolved in 15 ml of chloroform

Scheme 4. Synthesis of compounds **71–78**.

and added to a stirred, cooled (0°C) mixture of water (10 ml) calcium carbonate (0.39 g, 3.8 mmol), chloroform (8 ml) and thiophosgene (0.38 g, 3.3 mmol); stirring at 0°C was continued for 4 h. The stirred mixture was allowed to come to room temperature, heated to 45°C and held for 20 min, then poured into water. The aqueous layer was washed with dichloromethane; the combined organic extracts were washed with 1% aqueous HCl, then washed with water, brine and dried (MgSO$_4$). The crude product was isolated by evaporating the solvent, then purified by column chromatography using ethyl acetate/*n*-hexane=1/10 as eluent to give a white solid; yield 0.81 g (80%). ^{1}H NMR (δ, CDCl$_3$): 0.86–0.91 (t, 3H), 1.25–1.32 (m, 4H), 1.59–1.63 (m, 2H), 2.47 (s, 3H), 2.58–2.63 (t, 3H), 7.11–7.44 (m, 10H). ^{13}C NMR (δ, CDCl$_3$): 14.0, 20.5, 22.5, 30.9, 31.4, 35.9, 88.5, 90.9, 91.6, 92.7, 119.0, 119.2, 120.1, 120.3, 121.8, 123.4, 123.5, 124.0, 126.3, 128.0, 128.5, 128.8, 131.5, 131.9, 132.5, 140.3, 143.7, 156.4, 159.8. IR (KBr) v_{max} (cm^{-1}): 2950,

2926, 2855, 2212, 2046, 1659, 1510, 1411, 1271, 1035, 835. MS *m/z* 437 (M$^+$), 380. Elemental analysis: calc. for C$_{29}$H$_{24}$FNS, C 79.60, H 5.53, N 3.20; found, C 79.72, H 5.46, N 3.23%.

2.2.5. 1-(4-Pentylbiphenyl)-2-(4-amino-3-ethylphenyl)-acetylene, 41.

By following the procedure for compound **9** and using **39** and **40** as starting materials, compound **41** was obtained as a deep yellow solid; yield 2.6 g (70%). ^{1}H NMR (δ, CDCl$_3$): 0.91–0.93 (m, 6H), 1.26–1.37 (m, 4H), 1.63–1.65 (m, 2H), 2.62–2.68 (t, 2H), 2.84–2.89 (q, 2H), 3.82 (s, 2H), 7.13–7.75 (m, 11H). IR (KBr) v_{max} (cm^{-1}): 3363, 3150, 2959, 2927, 2869, 2199, 1661, 1619, 1502, 1463, 1312, 1240, 1004, 891.

2.2.6. 1-(4-Pentylbiphenyl)-2-(4-iodo-3-ethylphenyl)-acetylene, 42.

By following the procedure for compound **13** and using **41** as starting material, compound **42** was obtained as a yellow solid; yield 1.57g (82%). ^{1}H NMR (δ, CDCl$_3$): 0.87–0.91 (t, 3H),

1.19–1.24 (t, 3H), 1.28–1.35 (m, 4H), 1.61–1.66 (m, 2H), 2.61–2.66 (t, 2H), 2.70–2.75 (q, 2H), 7.01–7.79 (m, 7H). IR (KBr) v_{max} (cm^{-1}): 2955, 2925, 2853, 2210, 1632, 1514, 1495, 1462, 1388, 1260, 1225, 1134, 887.

2.2.7. 2-Ethyl-{4-[2-(4-pentylbiphenyl)-1-ethynyl]-1-ethyny}-2-methylaminobistolane, 46. By following the procedure for compound **9** and using **42** and **18** as starting materials, compound **46** was obtained as a yellow solid; yield 1.0 g (63%). ^{1}H NMR (δ, CDCl$_3$): 0.88–0.93 (t, 3H), 1.25–1.37 (m, 7H), 1.63–1.68 (m, 2H), 2.17 (s, 3H), 2.62–2.67 (q, 2H), 2.84–2.92 (t, 2H), 3.79 (s, 2H), 7.01–7.79 (m, 14H). IR (KBr) v_{max} (cm^{-1}): 3357, 2923, 2851, 2213, 1631, 1467, 1355, 1052, 892. MS *m/z* 481 (M$^+$), 466.

2.2.8. 2-Ethyl-{4-[2-(4-pentylbiphenyl)-1-ethynyl]-1-ethyny}-2-methylisothiocyanatobistolane, 50. By following the procedure for compound **27** and using **46** as starting material, compound **50** was obtained as a white solid; yield 0.71 g (81%). ^{1}H NMR (δ, CDCl$_3$): 0.86–0.93 (t, 3H), 1.25–1.37 (m, 4H), 1.63–1.68 (m, 2H), 2.17 (s, 3H), 2.62–2.67 (t, 2H), 2.84–2.92 (q, 2H) 7.01–7.79 (m, 14H). ^{13}C NMR (δ, CDCl$_3$): 14.0, 14.6, 18.3, 22.5, 27.6, 31.1, 31.5, 35.6, 89.6, 89.9, 91.1, 93.6, 121.6, 121.9, 122.3, 123.6, 126.1, 126.8, 128.9, 130.0, 130.2, 131.1, 132.0, 132.1, 133.5, 135.2, 136.3, 137.5, 141.1, 142.7, 146.2. IR (KBr) v_{max} (cm^{-1}): 2964, 2926, 2196, 2070, 1659, 1463, 1408, 1261, 1094, 833. MS *m/z* 523 (M$^+$), 508. Elemental analysis: calc. for C$_{37}$H$_{33}$NS, C 84.85, H 6.35, N 2.67; found, C 84.69, H 6.42, N 2.72%.

2.2.9. 2-Bromo-6-ethoxynaphthalene, 51. 6-Bromo-2-naphthol (10.0 g, 44.82 mmol), bromoethane (6.35 g, 58.79 mmol), potassium carbonate (12.39 g, 89.64 mmol), potassium iodide (1.48 g, 8.91 mmol) and acetonitrile (80 ml) were mixed and heated under reflux with constant stirring for more than 16 h. The solvent was removed under vacuum and the reaction mixture poured into water. The product was extracted with ether (3 × 40 ml) and treated with dilute hydrochloric acid, washed with water and dried. The crude product was purified by column chromatography using hexane as eluent to give a white solid **51**; yield 11.2 g (99.5%). ^{1}H NMR (δ, CDCl$_3$): 1.20–1.70 (t, 3H), 3.80–4.30 (t, 2H), 7.05–7.88 (m, 6H). IR (KBr) v_{max} (cm^{-1}): 2963, 2938, 1265, 1064, 852.

2.2.10. 4-[2-(6-Ethoxy-2-naphthyl)-1-ethynyl]-2-ethylaniline, 55. By following the procedure for compound **9** and using **51** and **40** as starting materials, compound **55** was obtained as a brown solid; yield: 6.46 g (51.4%). ^{1}H NMR δ=1.30–1.50 (t, 3H), 2.45–2.52 (q, 2H), 3.78 (s,

2H), 4.0–4.20 (q, 2H), 7.06–7.91 (m, 9H). IR (KBr) v_{max} (cm^{-1}): 3359, 3059, 2980, 2934, 2210, 1622, 1599, 1471, 1385, 1256, 1041, 858.

2.2.11. 2-[2-(3-Ethyl-4-iodophenyl)-1-ethynyl]-6-ethoxy-naphthalene, 59. By following the procedure for compound **13** and using **55** as starting material, compound **59** was obtained as a yellow solid; yield 5.31 g (65.5%). ^{1}H NMR δ=1.13–1.26 (t, 3H), 1.30–1.50 (t, 3H), 2.45–2.52(q, 2H), 4.00–4.20 (q, 2H), 7.07–7.91 (m, 9H). IR (KBr) v_{max} (cm^{-1}): 2920, 2197, 1626, 1480, 1390, 1258, 1017, 856.

2.2.12. 2-Ethyl-{4-[2-(6-ethoxy-2-naphthyl)-1-ethynyl]}-4′-amino-3′-fluorobistolane, 67. By following the procedure for compound **9** and using **59** and **15** as starting materials, compound **67** was obtained as a brown solid; yield 3.04 g (59.8%). ^{1}H NMR δ=1.23–1.32 (t, 3H), 1.44–1.50 (t, 3H), 2.81–2.89 (q, 2H), 3.89 (s, 2H), 4.10–4.17 (q, 2H), 7.09–7.95 (m, 12H). IR (KBr) v_{max} (cm^{-1}): 3337, 2962, 2205, 1630, 1471, 1384, 1254, 1041, 856.

2.2.13. 2-Ethyl-{4-[2-(6-ethoxy-2-naphthyl)-1-ethynyl]}-3′-fluoro-4′-isothiocyanatobistolane, 75. By following the procedure for compound **27** and using **67** as starting material, compound **75** was obtained as a white solid; yield 2.51 g (76.3%). ^{1}H NMR δ=1.23–1.32 (t, 3H), 1.44–1.50 (t, 3H), 2.81–2.89 (q, 2H), 4.10–4.17 (q, 2H), 7.05–7.95 (m, 12H). ^{13}C NMR (δ, CDCl$_3$): 14.5, 14.8, 18.3, 27.6, 31.1, 63.5, 88.9, 90.7, 92.0, 92.3, 106.6, 118.9, 119.8, 120.5, 123.6, 124.2, 126.8, 128.0, 128.4, 128.8, 128.9, 129.3, 131.1, 131.4, 132.2, 134.3, 142.0, 146.4, 156.4, 158.0, 159.8. IR (KBr) v_{max} (cm^{-1}): 2923, 2195, 2093, 1622, 1475, 1390, 1256, 1040, 834. Elemental analysis: calc. for C$_{37}$H$_{33}$NS, C 78.29, H 4.84, N 2.95; found, C 78.27, H 4.66, N 2.95%.

3. Results and discussion
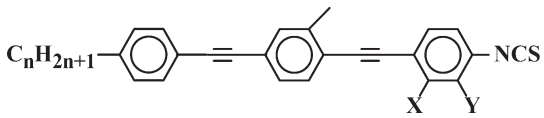
3.1. *Thermal transitions and mesomorphic properties*

The chemical structure, phase transition temperatures, associated enthalpies, and optical anisotropy values for the reported novel compounds and some known materials for comparison are shown in tables 1–5. Table 2 summarizes the phase transitions of compounds **24–28**. In all these bistolanes, a methyl lateral substituent was introduced at the cental phenyl ring to obtain lower melting point LCs. All these compounds exhibit an enantiotropic nematic phase. Compounds **24–27** contain the same terminal isothiocyanato group on the right-hand side and different alkyl chain length on the left. Their phase transitions are plotted against

Table 1.   Purity and elemental analysis data for some representative bistolanes.

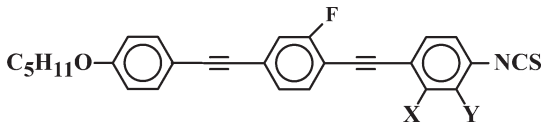| Compound	Purity/%	Elemental analysis, found (calc.)/%		
		C	H	N
24	99.0%	78.96(79.17)	4.59(4.40)	3.54(3.52)
25	99.0%	79.19(78.95)	4.92(5.06)	3.42(3.48)
26	98.6%	79.40(79.77)	5.24(4.96)	3.31(3.18)
27	99.1%	79.60(79.72)	5.53(5.46)	3.20(3.23)
28	98.7%	83.02(82.71)	6.01(6.22)	3.34(3.25)
36	98.4%	76.51(76.08)	5.04(5.39)	3.19(2.91)
37	98.8%	73.50(73.37)	4.63(5.02)	3.06(2.96)
38	98.8%	73.50(73.15)	4.63(4.74)	3.06(3.15)
47	99.0%	84.83(85.04)	6.13(6.01)	2.75(2.81)
48	99.0%	81.94(82.17)	5.73(5.74)	2.65(2.45)
49	98.8%	84.87(84.47)	6.56(6.50)	2.60(2.76)
50	99.1%	84.85(84.69)	6.35(6.42)	2.67(2.72)
71	99.0%	81.37(80.93)	5.07(5.06)	3.06(2.99)
72	99.3%	81.50(81.22)	5.34(5.36)	2.97(2.92)
73	99.3%	81.62(81.90)	5.60(5.43)	2.88(2.81)
74	99.0%	81.73(81.26)	5.85(6.04)	2.80(2.62)
75	99.4%	78.29(78.27)	4.84(4.66)	2.95(2.95)
76	98.6%	78.50(77.94)	4.94(5.22)	2.86(2.79)
77	99.0%	78.70(78.29)	5.20(5.07)	2.78(2.77)
78	98.6%	78.89(78.53)	5.45(5.61)	2.71(2.72)

the carbon number of the left-hand alkyl chain in figure 1. Both melting and clearing temperatures decrease gradually with increasing carbon number. Compound **28** contains similar structures to those of compound **27**, without an additional lateral fluoro group at the C-3 position of the right-hand phenyl ring. For comparison purposes, we synthesized compound **27** which contains a lateral fluoro group at the C-3 position of the phenyl ring. Its clearing point is lower than those of compound **28**. It seems that the lateral group can hinder molecular packing and thus decrease transition temperatures.
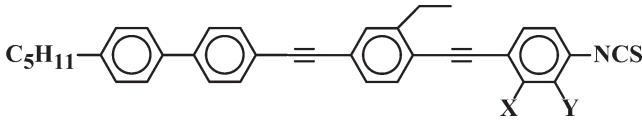
Table 3 lists the phase transition temperatures of compounds **36**–**38**. Their alkyl side chains were changed to the equivalent alkoxy groups. In all these bistolanes a fluoro lateral substituent was introduced at the central phenyl ring, and they all contain the same terminal iscthiocyanato group. Compound **36** exhibits enantiotropic nematic and smectic phases. The introduction of a lateral fluoro group at the C-3 position of the phenyl ring in compound **37** did not suppress the smectic phase by destroying the symmetry, in fact it enhanced the melting point to 150°C. The position of the fluorine atom was changed from C-3 to C-2 to provide a pure nematic phase in compound **38**; as expected, a wide nematic range from 127 to 259°C was obtained.

Table 2.   Phase transition temperature (°C) and corresponding enthalpy changes (kcal mol^{-1}) in parentheses, for compounds **24**–**28**. Cr=crystal, N=nematic, I=isotropic.

Compound	n	X	Y	heating scan / cooling scan
24	2	H	F	Cr 162.8(3.04) N 216.8(0.03) I / I 193.8(0.02) N 103.8 (2.26) Cr
25	3	H	F	Cr 172.2(3.67) N 217.9(0.01) I / I 196.2(0.01) N 130.4 (3.05) Cr
26	4	H	F	Cr 130.1(2.79) N 202.8(0.05) I / I 202.2(0.04) N 71.1 (2.05) Cr
27	5	H	F	Cr 103.5(6.30) N 188.3(0.16) I / I 186.7(0.14) N 60.8 (6.50) Cr
28	5	H	H	Cr 103.1(5.81) N 225.0(0.22) I / I 223.5(0.24) N 79.7 (4.59) Cr

Table 3.   Phase transition temperatures (°C) and corresponding enthalpy changes (kcal mol^{-1}) in parentheses, for compounds **36**–**38**. Cr=crystal, Sm=smectic, N=nematic, I=isotropic.

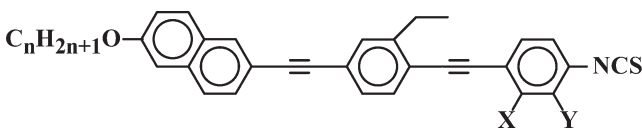| Compound	X	Y	heating scan / cooling scan
36	H	H	Cr$_1$ 96.0(0.98) Cr$_2$ 126.2(1.18) SmA 160.8(0.26) N 231.6(0.11) I / I 229.2(0.02) N 157.6(0.14) SmA 123.1(0.82) Cr$_2$ 60.8(0.57) Cr$_1$
37	H	F	Cr 150.9(9.14) SmA 174.9(0.20) N 231.6(0.29) I / I 245.9(0.13) N 160.8(0.18) SmA 117.5(8.76) Cr
38	F	H	Cr$_1$ 98.0(2.05) Cr$_2$ 126.6(2.01) N 259.2(0.01) I / I 252.8(0.01) N 70.4(1.24) Cr

Table 4. Phase transition temperatures (°C) and corresponding enthalpy changes (kcal mol^{-1}) in parentheses, for Compounds 47–50. Cr=crystal, N=nematic, I=isotropic.

C$_5$H$_{11}$—⟨◯⟩—⟨◯⟩—≡—⟨◯⟩—≡—⟨◯⟩—NCS (X, Y)

Compound	X	Y	heating scan / cooling scan
47	H	H	Cr 115.9(10.08) N 241.3(0.38) I I 234.8(0.21) N 89.7(15.44) Cr
48	H	F	Cr 107.3(10.82) N 241.4(0.22) I I 229.5(0.18) N 60.8(9.01) Cr
49	H	C$_2$H$_5$	Cr$_1$ 44.0(3.80)Cr$_2$ 80.3(8.90) N 225.6(2.09) I I 224.2(1.85) N 37.9(4.57) Cr
50	CH$_3$	H	Cr 114.7(42.90) N 240.9(0.29) I I 229.4(0.17) N 62.1(35.03) Cr

Table 4 lists the phase transition temperatures of isothiocyanato biphenyl-bistolanes 47–50. In this series a pentyl group was placed on the biphenyl ring, and different lateral groups were introduced on the right-hand side containing an isothiocyanato phenyl ring. All the listed compounds exhibit a pure nematic phase within the whole mesomprphic region. Moreover, the smectic phases which normally appear in NCS-based biphenyl tolanes or tolanes are completely suppressed. Such an unusual behaviour is believed to be due to the laterally substituted ethyl chain(s) and/or the single fluorine atom. The lateral substitutions increase molecular separation and break the molecular symmetry so that formation of the smectic phase is inhibited.

Table 5. Phase transition temperatures (°C) and corresponding enthalpy changes (kcal mol^{-1}) in parentheses, for compounds 71–78. Cr=crystal, N=nematic, I=isotropic.

C$_n$H$_{2n+1}$O—⟨◯◯⟩—≡—⟨◯⟩—≡—⟨◯⟩—NCS (X, Y)

| Compound	n	X	Y	heating scan / cooling scan
71	2	H	H	Cr 154.1(2.85) N 278.1(0.01) I I 274.9(−) N 114.5(0.71) Cr
72	3	H	H	Cr 137.9(4.25) N 279.5(0.2) I I 274.9(−) N 137.1(−) Cr
73	4	H	H	Cr 157.0(1.96) N 266.1(−) I I 247.7(−) N 104.0(−) Cr
74	5	H	H	Cr 119.9(2.0) N 187.2(−) I I 160.8(−) N 60.5(−) Cr
75	2	H	F	Cr 153.9(8.66) N 283.6(0.36) I I 282.8(−) N 144.6(5.94) Cr
76	3	H	F	Cr 144.4(2.78) N 277.7(−) I I 268.4(−) N 125.8(2.73) Cr
77	4	H	F	Cr 135.3(2.32) N 259.0(−) I I 255.3(−) N 78.9(0.26) Cr
78	5	H	F	Cr 122.3(3.32) N 237.3(0.13) I I 235.0(−) N 72.8(2.01) Cr

aOverlapped transition.
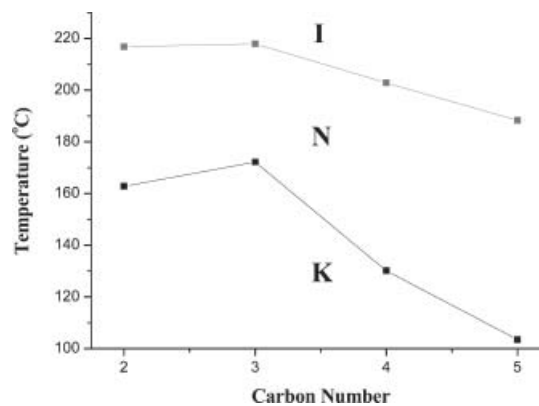
Figure 1. Dependence of transition temperatures on the number of alkyl chain carbon atoms for compounds 24–27.

Compound 47 shows the highest transition temperature because of its right-hand side phenyl ring without lateral substitutents. In compound 48 a fluoro lateral substituent was introduced at the C-3 position of the right-hand side phenyl ring, reducing the melting point from 115.9 to 108°C. In compound 49 an ethyl group was introduced at the C-3 position of the right-hand side phenyl ring, and both melting and clearing points were reduced. In compound 50 a methyl lateral substituent was introduced at the C-2 position of the right-hand side phenyl ring; the resulting transition temperature was similar to that of compound 47.

Table 5 summarizes the phase transition temperatures of isothiocyanato naphthyl-bistolanes 71–78. In this series a pentyl group was placed on the biphenyl ring, and different lateral groups were introduced on the right-hand side containing an isothiocyanato phenyl ring. Compounds 71–74 contain the same terminal isothiocyanato group on the right-hand side phenyl ring and alkoxy chains of varying length on the naphthyl ring. Their phase transitions are plotted against the carbon number of the alkyl chain in
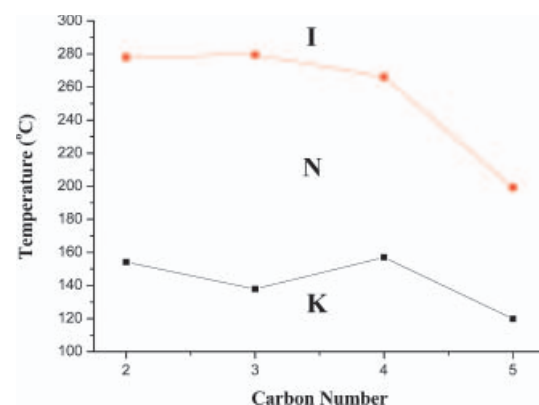

Figure 2. Dependence of transition temperatures on the number of alkyl chain carbon atoms for compounds 71–74.
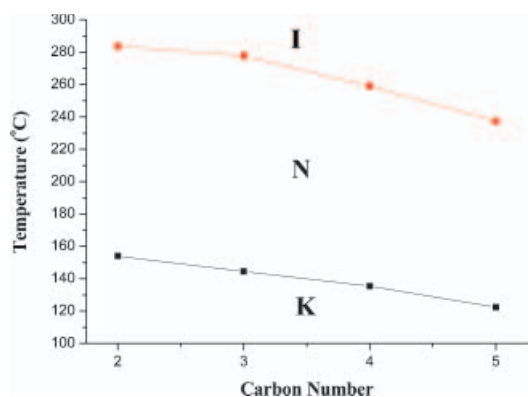
Figure 3. Dependence of transition temperatures on the number of alkyl chain carbon atoms for compounds **75–78**.

figure 2. It can be seen that melting points show an odd–even effect with increasing carbon number, while clearing temperatures decrease gradually. Compounds

75–78 contain similar structures to those of compounds **71–74**, with an additional lateral fluoro group at the C-3 position of the right-hand side phenyl ring. Both melting and clearing points decrease gradually with increasing carbon number, see figure 3. To reduce the transition temperatures further, a lateral fluoro group was introduced at the C-3 position of the right-hand side phenyl ring, but the transition temperatures of most of the compounds were not reduced as expected. Only the melting point of compound **76** was decreased to that of compound **72**, from 157.0 to 135.3°C.

3.2. *Optical anisotropy*

The Δn value, defined as the difference between the two principal refractive indices of a uniaxial material, was estimated by a guest–host method. The Δn value of a guest–host system can be approximated from the

Table 6. Δn value for single compound. Data calculated from guest-host systems.

Compound	Structure	Δn
28		0.47[a]
37		0.49[a]
38		0.49[a]
47		0.73[b]
48		0.67[b]
49		0.55[b]
50		0.62[b]
74		0.61[b]

[a]Host ZLI 1132. [b]Host mixture E-63.

following equation:

$$(\Delta n)_{\mathrm{gh}} = x(\Delta n)_{\mathrm{g}} + (1-x)(\Delta n)_{\mathrm{h}} \qquad (1)$$

where the subscripts g, h and gh denote guest, host, and guest–host cells, respectively; x is the concentration (in wt %) of the guest compound. By comparing the measured results for the guest–host mixtures with those of the host mixture, the Δn values of the guest compounds can be extrapolated.

The Δn values of some synthesized compounds are listed in table 6. Commercial LCs ZLI-1132 or E-63 was used as host mixture. It can be seen that the Δn values of these compounds are in the range 0.5 to 0.8. For those compounds with biphenyl and naphthyl moieties, the Δn value is higher than that for the corresponding phenyl moiety. This is because biphenyl and naphthyl moieties have a more extended electron conjugation than the phenyl moiety. The lateral substitutions affect the Δn values significantly. The Δn values of compounds **28**, **37** and **38**, were similar, approaching to 0.5. Compound **49** has the lowest birefringence among the compounds **47**–**50** due to its two laterally substituted ethyl chains, which would lead to a higher Δn value due to the molecular packing density effect. The Δn values of compounds **48**, **50** and **74** are 0.67, 0.62 and 0.61, respectively. Compound **47** has the highest Δn of 0.73 and is expected to be useful for PDLC, cholesteric display, and laser beam steering applications.

4. Conclusions

Four series of novel super high Δn bistolane laterally substituted liquid crystals with terminal isothiocyanato groups were synthesized. Lateral alkyl or fluoro groups were introduced to modify the LC properties. The extrapolated Δn of some of these compounds is greater than 0.7. Some of these compounds exhibit an odd–even effect in their phase transition temperatures. A eutectic mixture consisting of these compounds and some NCS tolanes was developed. The Δn value was determined by the guest–host method using a commercial LC as host matrix. Compounds containing biphenyl and naphthyl moieties have a high Δn value; compound **47** has the highest Δn of 0.73, making it a good candidate for many display applications.

Acknowledgement

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