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Liquid Crystals

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Synthesis and mesomorphic properties of α -methylstilbene-based liquid crystals

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Synthesis and mesomorphic properties of α -methylstilbene-based liquid crystals

Chin-Yen Chang^a, Kang-Wei Ho^a, Chain-Shu Hsu^{a*}, Chih-Hung Lin^b, Sebastian Gauza^c and Shin-Tson Wu^c

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Six series of α -methylstilbene-based liquid crystals, i.e. 4-(4-alkylphenyl)-4'-amino- α -methylstilbenes (**2a–e**), 4-(4-alkylphenyl)-4'-cyano- α -methylstilbenes (**3a–e**), 4-(4-alkylphenyl)-4'-isothiocyanato- α -methylstilbenes (**4a–e**), 4'-(*trans*-4-alkylcyclohexyl)-4-fluoro- α -methylstilbenes (**5a–e**), 4'-(*trans*-4-alkylcyclohexyl)-4-amino- α -methylstilbenes (**7a–e**) and 4'-(*trans*-4-alkylcyclohexyl)-4-isothiocyanato- α -methylstilbenes (**8a–e**) were synthesised. All of these α -methylstilbene-based compounds exhibit an enantiotropic nematic phase. Some of the 4-(4-alkylphenyl)-4'-isothiocyanato- α -methylstilbenes with longer alkyl chains exhibit a smectic A phase. All of the liquid crystals obtained exhibit a wide nematic range and high birefringence of 0.16–0.46. Both series of isothiocyanato-based, liquid crystal compounds **4a–e** and **8a–e** containing α -methylstilbenes revealed much lower melting points and clearing temperatures than their cyano and amino homologues.

Keywords: α -methylstilbene liquid crystals; isothiocyanato liquid crystals; high birefringence

1. Introduction

Liquid crystals (LCs), which exhibit high birefringence (Δn), low viscosity, large LC range, small heat fusion enthalpy and good stability are essential for both display and optical applications. From the Schroder–Van Laar equation (1, 2), the individual LC components possessing a low melting temperature and high clearing point, and small heat fusion enthalpy are better candidates for widening the nematic range of the eutectic mixture. Highly birefringent LCs are attractive materials for applications in reflective type LC displays (3), infrared spatial light modulators (4), polymer-dispersed LCs (5), holographic switching devices (6), polarisers and directional reflectors (7, 8) and laser beam steering devices (9). Furthermore, they are also used in super-twisted nematic (STN) displays for faster response times.

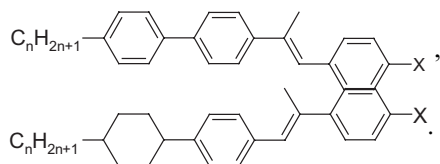
The high birefringence molecular structures, such as diphenyldiacetylene (10, 11), bistolane (12–15), naphthalene tolanes (16), thiophenyldiacetylene (17, 18) and diacetylene compounds (19) have been studied. The birefringence of these LCs is in the range of 0.4–0.6. From the single band model (20), the Δn of a LC is mainly determined by its molecular conjugation, differential oscillator strength and order parameter. It is well known that a high Δn value can be achieved by increasing the molecular conjugation length (21). However, a general problem of these highly conjugated molecules is that their melting points are usually very high. A major technical challenge in Δn LC studies is how to reduce the melting

temperature. In our previous work, we reported the study of the lateral substituted tolane (22, 23) and the stilbene LCs (24), which contained an isothiocyanato end group. As the result, the substitution of a methyl group is a major ingredient to decreasing the melting temperature. In addition, we reported the biphenyl-tolane materials with isothiocyanato and fluoride end groups displaying high Δn values but high transition temperatures (25). In 2002, the synthesis of fluorinated stilbene–tolane LCs was reported by Spells and coworkers (26). However, these molecules show high melting points above 200°C. Recently, we synthesised a series of α -methylstilbene–tolane LCs (27). The α -methylstilbene moiety has a performed effect on their phase transitions; both melting and clearing temperatures decrease dramatically.

In this study, we demonstrate the synthesis of LC materials with an α -methylstilbene core and isothiocyanato end group to decrease their transition temperatures and increase their Δn values. Six series of α -methylstilbene-based LCs were prepared by palladium-catalysed Heck coupling of aryl bromide with α -methylstilbene derivatives. The Heck reaction was reported by Heck (28, 29). The detailed mechanism of the Heck reaction was reported by Meijere and Meyer (30). The α -methylstilbene group and terminal cyclohexyl structure play an important role in lowering the melting point and clearing temperature of the obtained LCs. The mesomorphic property as well as

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birefringence of the synthesised LCs is discussed. The general chemical structure is shown below:



Here, n is limited from 2 to 6 and $X = \text{NH}_2$, NCS, CN or F.

2. Experimental details

2.1 Materials

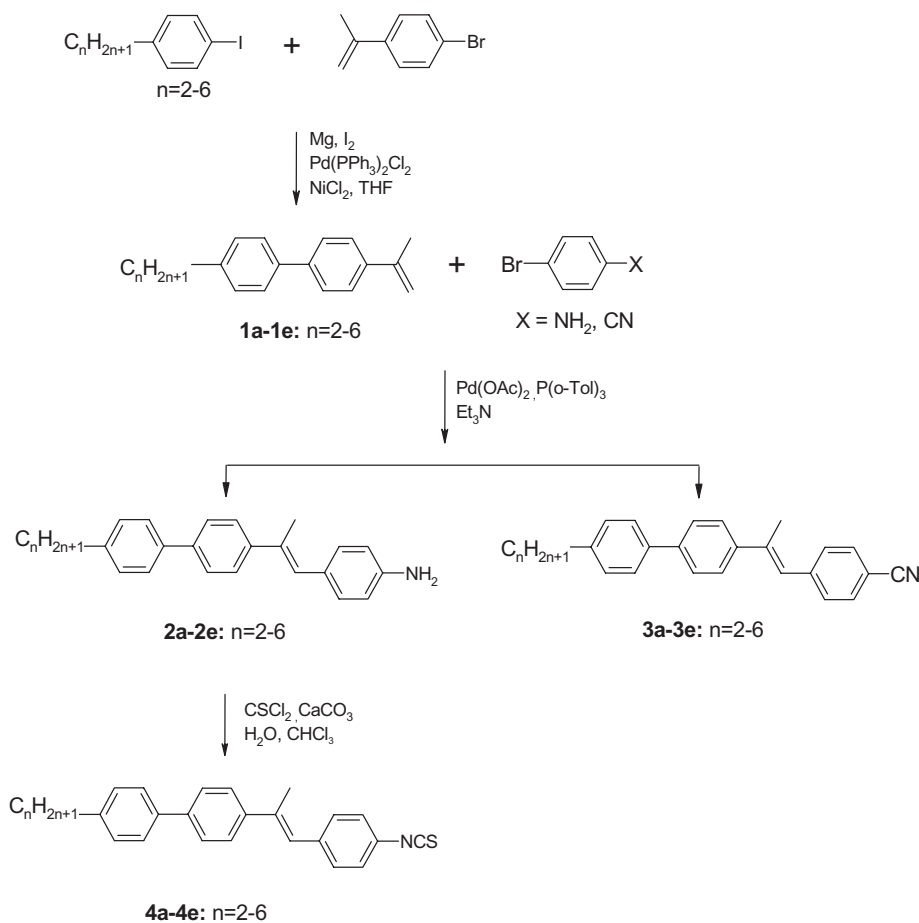
4-Fluoro- α -methylstyrene, 4-bromo- α -methylstyrene, 4-alkyl-1-iodobenzene, 4-bromoaniline, 4-iodoaniline, 4-bromo-1-cyanobenzene, palladium acetate, tri-(*o*-tolyl)phosphine and other reagents were purchased from Sigma-Aldrich and used as received. Dichloromethane and triethylamine were dried over CaH_2 . Tetrahydrofuran (THF) was dried over LiAlH_4 and distilled before use. We synthesised 4-(*trans*-4-alkylcyclohexyl)-1-iodobenzenes according to the previous literature reported by our laboratory (31).

2.2 Characterisation

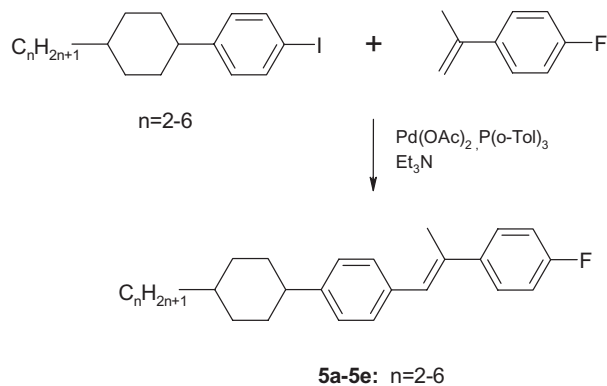
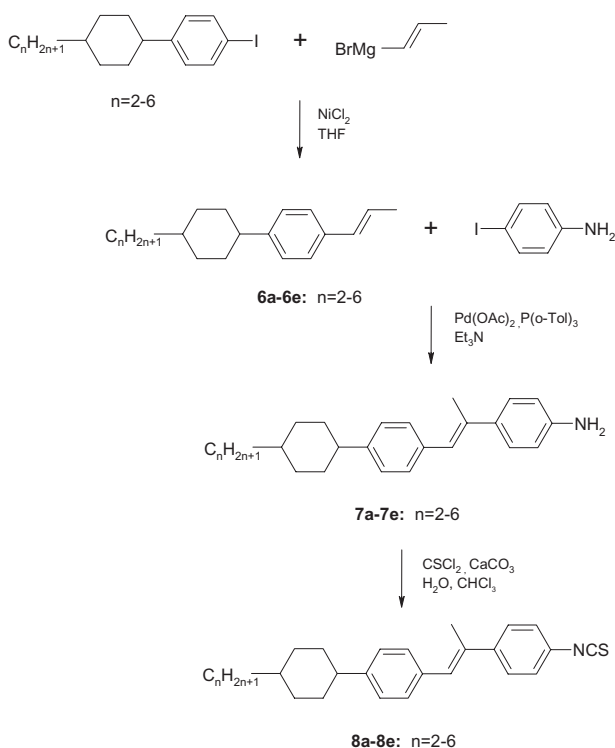
Proton nuclear magnetic resonance (^1H NMR) spectra (300 MHz) were recorded on a Varian VXR-300 spectrometer. Thermal transitions and thermodynamic parameters were determined by using a Seiko SSC/6200 differential scanning calorimeter equipped with a liquid nitrogen cooling accessory. Heating and cooling rates were 5°C min^{-1} . Transition temperatures reported here were collected during the second heating and cooling scans. A Carl Zeiss Axiphot optical polarising microscope equipped with a Mettler FP 82 hot stage and a FP 80 central processor was used to observe thermal transitions and analyse the anisotropic textures. The birefringence was measured by a Perkin-Elmer lambda-9 spectrophotometer with a He-Ne laser at 23°C in 633 nm.

2.3 Synthesis

Scheme 1 outlines the synthetic procedures for 4-(4-alkylphenyl)-4'-4'-amino- α -methylstilbenes (**2a-e**), 4-(4-alkylphenyl)-4'-4'-cyano- α -methylstilbenes (**3a-e**), 4-(4-alkylphenyl)-4'-isothiocyanato- α -methylstilbenes



Scheme 1. Synthesis of compounds **2a-e**, **3a-e** and **4a-e**.

Scheme 2. Synthesis of compounds **5a-e**.Scheme 3. Synthesis of compounds **7a-e** and **8a-e**.

(4a-e). Schemes 2 and 3 outline the synthetic procedures used to prepare 4-(*trans*-4-alkylcyclohexyl)-4'-fluoro- α -methylstilbenes (**5a-e**), 4-(*trans*-4-alkylcyclohexyl)-4'-amino- α -methylstilbenes (**7a-e**) and 4'-(*trans*-4-alkylcyclohexyl)-4-isothio-cyanato- α -methylstilbenes (**8a-e**).

2.3.1 4-(4-Alkylphenyl)- α -methylstyrene (**1a-e**)

Compounds **1a-e** were prepared by the coupling reaction of 4-alkyliodobenzene with Grignard reagent of 4-bromo- α -methylstyrene (**32**). The synthesis of compound **1a** is described below.

Magnesium (1.4 g, 60 mmol) was charged into a flask under nitrogen, ethyl bromide (0.3 g, 2.7 mmol) in 1 ml of THF was added in order to activate the metal. After the solution was heated to 60°C, a solution of 4-bromo- α -methylstyrene (5.9 g, 30 mmol) in 20 ml of THF was added dropwise over 10 minutes. The reaction mixture was refluxed for 15 minutes and stirred without heating for another 45 minutes to form a Grignard reagent of 4-bromo- α -methylstyrene. 4-Bromo-1-ethyl benzene (6.1 g, 33 mmol), NiCl₂ (0.1 g) and THF (20 ml) were charged into a 100 ml flask, and the prepared Grignard reagent of 4-bromo- α -methylstyrene was added dropwise. The reaction mixture was heated at 55°C for 2 hours, and then cooled to room temperature. Diethyl ether (100 ml) and 1.4 M HCl (20 ml) were added to the flask. The organic layer was separated and dried over anhydrous MgSO₄. The solvent was removed *in vacuo* and purified by column chromatography (silical gel, with n-hexane as eluent) to yield 4.1 g (62%) of white crystals; mp = 130.4°C.

¹H NMR (CDCl₃, TMS, 300 MHz), δ = 1.17–1.23 (m, 3H), 2.24 (s, 3H), 2.60–2.67 (q, 2H), 5.06–5.08 (q, 1H), 5.39 (s, 1H), 7.19–7.22 (m, 2H), 7.47–7.53 (m, 6H).

2.3.2 4-(4-Alkylphenyl)-4'-amino- α -methylstilbene (**2a-e**) and 4-(4-alkylphenyl)-4'-cyano- α -methylstilbene (**3a-e**)

Compounds **2a-2e** and **3a-3e** were prepared by the Heck reaction of 4-(4-alkylphenyl)- α -methylstyrene (**1a-1e**) with 4-bromoaniline and 4-bromo-benzonitrile (**33**). The synthesis of compound **2a** is described below.

4-Ethyl- α -methylstyrene (1.5 g, 6.76 mmol), 4-bromoaniline (0.9 g, 5.63 mmol), palladium(II) acetate (13 mg, 0.06 mmol), tri(*o*-tolyl)phosphine (0.18 g, 0.6 mmol), triethylamine (4 ml) were dissolved in 8 ml of acetonitrile under nitrogen. The reaction mixture was heated at 110°C for 3 days. After cooling to room temperature, 10 ml of water was added. The mixture was extracted twice with 20 ml of CH₂Cl₂. The collected organic layer was dried over anhydrous MgSO₄. After solvent was removed *in vacuo*, the residue was purified by column chromatography (silical gel, ethyl acetate/n-hexane = 1/4 as eluent) to yield 0.59 g (34%) of yellowish crystals.

2a: IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3396, 3316, 3028, 1622, 1508; ¹H NMR (CDCl₃, TMS, 300 MHz), δ = 1.17–1.23 (t, 3H), 2.24 (s, 3H), 2.60–2.67 (q, 2H), 3.64 (br, 2H), 6.62–6.65 (d, 2H), 6.73 (s, 1H), 7.13–7.22 (m, 4H), 7.46–7.51 (m, 6H); MS m/z (M⁺) 313. Analysis calculated for C₂₃H₂₃N: C, 88.14; H, 7.40; N, 4.17; found C, 87.60; H, 7.67; N, 4.20.

2.3.3 4-(4-Alkylphenyl)-4'-isothiocyanato- α -methylstilbene (**4a-e**)

Compounds **4a-e** were prepared by isothiocyanation of 4-(4-ethyl phenyl)-4'-amino- α -methylstilbene (**2a-e**) (**24**). The synthesis of compound **4a** is described below.

Calcium carbonate (60 mg, 0.65 mmol) and thio-phosgen (0.07 g, 0.65 mmol) were dissolved in a mixed solvent of water (1 ml) and CHCl_3 (2 ml). The resulting solution was cooled to 0°C , and a solution of 4-(4-ethylphenyl)-4'-amino- α -methylstilbene (0.17 g, 0.54 mmol) in 6 ml of CHCl_3 was added. The reaction mixture was heated at 35°C for 1.5 hour and then poured into water. The aqueous solution was extracted twice with CH_2Cl_2 (10 ml). The collected organic layer was dried over anhydrous MgSO_4 . After the solvent was removed *in vacuo*, the residue was purified by column chromatography (silical gel, with n-hexane as eluent) to yield 0.19 g (99%) of white crystals.

4a: IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3431, 3025, 2081, 1596, 1499; ^1H NMR (CDCl_3 , TMS, 300 MHz), δ = 1.25–1.30(t, 3H), 2.30(s, 3H), 2.67–2.73(q, 2H), 6.83(s, 1H), 7.22–7.30(m, 4H), 7.34–7.37(d, 2H), 7.53–7.61(m, 6H); MS m/z (M^+) 355. Analysis calculated for $\text{C}_{24}\text{H}_{21}\text{NS}$: C, 81.09; H, 5.95; N, 3.94; found: C, 81.30; H, 6.13; N, 3.65.

2.3.4 4'-(Trans-4-alkyl-cyclohexyl)-4-fluoro- α -methylstilbene (**5a-e**)

Compounds **5a-e** were prepared by Heck reaction of 4-(*trans*-4-n-alkylcyclohexyl)-1-iodobenzene (**33**) and 4-fluoro- α -methylstyrene. The synthesis of compound **5b** is described below.

4-Fluoro- α -methylstyrene (0.9 g, 6.7 mmol), 4-(*trans*-4-n-propylcyclohexyl)-1-iodobenzene (1.8 g, 5.4 mmol), palladium(II) acetate (2.4 mg, 0.01 mmol), tri(*o*-tolyl)phosphine (6.6 mg, 0.22 mmol), triethylamine (4 ml) were dissolved in 8 ml of acetonitrile under nitrogen. The reaction mixture was heated at 110°C for 2 days. After cooling to room temperature, 10 ml of water was added. The mixture was extracted twice with 20 ml of CH_2Cl_2 . The collected organic layer was dried over anhydrous MgSO_4 . After solvent was removed *in vacuo*, the residue was purified by column chromatography (silical gel, with n-hexane as eluent) to yield 0.6 g (30%) of white crystals.

5b: IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2963, 2928, 2849, 1596, 1508, 1450, 1217, 969, 829; ^1H NMR (CDCl_3 , TMS, 300 MHz), δ = 0.85–1.95(m, 16H), 2.40–2.66(tt, 1H), 2.27(s, 3H), 6.74(s, 1H), 7.01–7.07(t, 2H), 7.19–7.22(d, 2H), 7.41–7.49(m, 4H); MS m/z (M^+) 336. Analysis calculated for $\text{C}_{23}\text{H}_{27}\text{F}$: C, 85.67; H, 8.69; found: C, 85.89; H, 8.77.

2.2.5 4-(Trans-4-n-alkylcyclohexyl)- β -methylstyrene (**6a-e**)

Compounds **6a-e** were prepared by the coupling reaction of 4-(*trans*-4-n-alkylcyclohexyl)-1-iodobenzene with isopropenylmagnesium bromide. The synthesis of compound **6a** is described below.

4-(*Trans*-4-n-ethylcyclohexyl)-1-iodobenzene (4.2 g, 13.5 mmol), NiCl_2 (0.1 g) and THF (20 ml) were stirred in a 100 ml flask, and isopropenylmagnesium bromide was added dropwise. The reaction mixture was heated at 55°C for 16 hours, and then cooled to room temperature. Diethyl ether (100 ml) and 1.4 N HCl (20 ml) were added to the flask. The organic layer was separated and dried with MgSO_4 . The solvent was removed *in vacuo* and purified by column chromatography (silical gel, with n-hexane as eluent) to yield 3.1 g (90%) of colourless liquid.

6a: ^1H NMR (CDCl_3 , TMS, 300 MHz), δ = 0.85–1.95(m, 17H), 2.40–2.66(tt, 1H), 6.94–6.97(d, 2H), 7.57–7.60(d, 2H).

2.3.6 4'-(Trans-4-alkylcyclohexyl)-4-amino- α -methylstilbene (**7a-e**)

Compounds **7a-e** were prepared by Heck reaction of 4'-(*trans*-4-alkyl-cyclohexyl)- β -methylstyrene with 4-iodoaniline. The synthesis of compound **7e** is described below.

4'-(*Trans*-4-hexylcyclohexyl)- β -methylstyrene (2.50 g, 8.79 mmol), 4-iodoaniline (1.92 g, 8.79 mmol), palladium(II) acetate (0.04 g, 0.18 mmol), tri(*o*-tolyl)phosphine (0.43 g, 1.41 mmol), triethylamine (4 ml) were dissolved in 8 ml of acetonitrile under nitrogen. The reaction mixture was heated at 110°C for 3 days. After cooling to room temperature, 10 ml of water was added. The mixture was extracted twice with diethyl ether (20 ml). The collected organic layer was dried over anhydrous MgSO_4 . After solvent was removed *in vacuo*, the residue was purified by column chromatography (silical gel, n-hexane and ethyl acetate (4:1) was used as eluent) to yield 0.43 g (13%) of white crystals.

7e: ^1H NMR (CDCl_3 , TMS, 300 MHz), δ = 0.85–1.95(m, 22H), 2.40–2.66(tt, 1H), 2.27(s, 3H), 3.70(br, 2H), 6.68–6.70(d, 2H), 6.74(s, 1H), 7.18–7.21(d, 2H), 7.26–7.29(d, 2H), 7.34–7.36(d, 2H).

2.3.7 4'-(Trans-4-alkylcyclohexyl)-4-isothiocyanato- α -methylstilbene (**8a-8e**)

Compounds **8a-e** were prepared by isothiocyanation of 4'-(*trans*-4-alkylcyclohexyl)-4-amino- α -methylstilbene (**7a-e**). The synthesis of compound **8e** is described below.

Calcium carbonate (0.2 g, 2 mmol) and thiophosgen (0.18 g, 1.6 mmol) were dissolved in a mixed solvent of water (3 ml) and CHCl_3 (2 ml). The resulting solution was cooled to 0°C , and a solution of 4'-(*trans*-4-hexyl-cyclohexyl)-4-amino- α -methylstilbene (0.50 g, 1.33 mmol) in 10 ml of CHCl_3 was added. The reaction mixture was heated to 35°C for 2 hours and then poured into water. The aqueous solution was extracted twice with CH_2Cl_2 (10 ml). The collected organic layer was dried over anhydrous MgSO_4 . After the solvent was removed *in vacuo*, the residue was purified by column chromatography (silical gel, n-hexane as eluent) to yield 0.5 g (90%) of white crystals.

8e: IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2963, 2919, 2840, 2090, 1508, 1427; ^1H NMR (CDCl_3 , TMS, 300 MHz), δ = 0.85–1.95 (m, 22H), 2.40–2.66 (tt, 1H), 2.27 (s, 3H), 6.81 (s, 1H), 7.20–7.30 (m, 6H), 7.48–7.51 (d, 2H); MS m/z (M^+) 417. Analysis calculated for $\text{C}_{28}\text{H}_{35}\text{NS}$: C, 80.52; H, 8.45; N, 3.35; found: C, 80.68; H, 8.48; N, 3.19.

3. Results and discussion

3.1 Thermal transitions and mesomorphic property

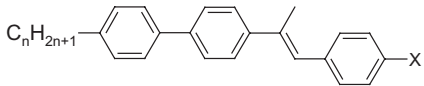
Table 1 reports the elemental analysis data of the synthesised α -methylstilbene-based LCs. The purities

of the listed LC compounds, which have been checked by high-performance liquid chromatography (HPLC), are higher than 99.0%. Table 2 summarises the phase transition temperatures and corresponding enthalpy changes of compounds **2a–e**, **3a–e** and **4a–e**. All compounds **2a–e** and **3a–e** exhibit an enantiotropic nematic phase. For the isocyanato compounds **4a–e**, both **4a** and **4b** with short alkyl chain show an enantiotropic nematic phase, while compounds **4c–e** with long alkyl chain exhibit both enantiotropic smectic A and nematic phases.

Compounds **2a–e**, **3a–e**, **4a–e** possess the same mesogenic core; the only difference is their terminal end groups. The melting points of amino series **2a–e** are in a range from 143.8 to 160.1°C , and their clearing points are in a range from 156.6 to 195.7°C . Both melting and clearing temperatures decrease as the alkyl chain length increases. Compound **2a** shows the highest clearing point of 195.7°C , and the widest temperature range (35.6°), of the nematic phase in this series. The cyano series **3a–e** showed much lower melting points which range from 91.6 to 138.8°C . Their clearing points are in a range from 179.9 to 251.5°C . Both melting and clearing temperatures decrease as the alkyl chain length increases (Figure 1). The compound **3d** showed the widest temperature range (127.3°) of the nematic phase in this series. The isothiocyanato series **4a–e** shows melting

Table 1. The elemental analysis data for α -methylstilbenes.

Compound	Elemental analysis: found (calculated)/%		
	C	H	N
2a	87.60 (88.14)	7.67 (7.40)	4.20 (4.17)
2b	87.75 (88.03)	7.70 (7.70)	4.04 (4.28)
2c	87.88 (87.93)	8.04 (7.97)	4.11 (4.10)
2d	87.70 (87.84)	8.19 (8.22)	3.85 (3.94)
2e	87.60 (87.75)	8.21 (8.45)	4.13 (3.79)
3a	89.01 (89.13)	6.78 (6.54)	4.16 (4.33)
3b	88.82 (88.98)	7.17 (6.87)	3.89 (4.15)
3c	88.90 (88.85)	7.34 (7.17)	3.62 (3.98)
3d	88.31 (88.72)	7.48 (7.45)	3.32 (3.83)
3e	88.16 (88.61)	7.62 (7.70)	3.79 (3.69)
4a	81.30 (81.09)	6.13 (5.95)	3.65 (3.94)
4b	81.31 (81.26)	6.30 (6.27)	3.52 (3.79)
4c	81.30 (81.42)	6.51 (6.57)	3.77 (3.65)
4d	81.58 (81.57)	6.90 (6.85)	3.40 (3.52)
4e	81.06 (81.71)	7.09 (7.10)	3.52 (3.40)
5a	85.89 (85.67)	8.37 (8.44)	
5b	85.68 (85.67)	8.77 (8.69)	
5c	85.86 (85.67)	8.97 (8.91)	
5d	85.49 (85.66)	9.34 (9.12)	
5e	85.83 (85.66)	9.18 (9.32)	
8a	79.39 (79.73)	7.56 (7.53)	3.50 (3.87)
8b	79.64 (79.95)	8.00 (7.78)	3.35 (3.73)
8c	80.32 (80.15)	8.03 (8.02)	3.36 (3.60)
8d	80.15 (80.35)	8.17 (8.24)	3.30 (3.47)
8e	80.68 (80.52)	8.48 (8.45)	3.19 (3.35)

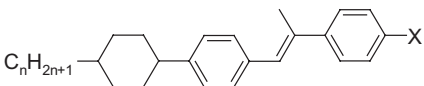
Table 2. Phase transition temperatures and corresponding enthalpy change for the compounds **2a–e**, **3a–e** and **4a–e**.


Heating T°C (Kcal mol ⁻¹)								
Compound	<i>n</i>	X	Cr	S _A	N	I		
2a	2	NH ₂	·	160.1 (5.13)	–	·	195.7 (0.13)	·
2b	3	NH ₂	·	149.3 (5.18)	–	·	175.4 (0.10)	·
2c	4	NH ₂	·	145.7 (5.94)	–	·	175.0 (0.08)	·
2d	5	NH ₂	·	147.3 (5.52)	–	·	174.3 (0.08)	·
2e	6	NH ₂	·	143.8 (5.85)	–	·	156.6 (0.05)	·
3a	2	CN	·	138.8 (5.64)	–	·	251.5 (0.33)	·
3b	3	CN	·	105.4 (2.32)	–	·	238.4 (0.07)	·
3c	4	CN	·	93.7 (3.43)	–	·	219.2 (0.18)	·
3d	5	CN	·	91.6 (2.58)	–	·	218.9 (0.14)	·
3e	6	CN	·	96.3 (3.77)	–	·	179.9 (0.08)	·
4a	2	NCS	·	120.1 (3.22)	–	·	232.3 (0.17)	·
4b	3	NCS	·	93.7 (1.48)	–	·	192.8 (0.05)	·
4c	4	NCS	·	92.0 (2.48)	·	119.2 (0.08)	·	226.0 (0.28)
4d	5	NCS	·	81.0 (1.20)	·	112.2 (0.06)	·	206.1 (0.17)
4e	6	NCS	·	86.2 (1.62)	·	135.0 (0.09)	·	211.6 (0.26)

points in a range from 81 to 120.1°C. Their melting points show an odd–even effect as chain length increases. Their clearing points are in a range from 232.3 to 192.8°C. The compound **4c** showed the widest mesomorphic temperature range (134°). Comparing the three series of LC compounds, their melting points follow the trend: **2a–e** > **3a–e** > **4a–e**. Basically the melting point relates to the dipole interaction between

LC molecules. Compounds **2a–e**, having an H-bonding due to the amino group, exhibit a higher melting point and larger melting enthalpy.

Table 3 reports the phase transition temperatures and corresponding enthalpy changes of compounds **5a–e**, **7a–e** and **8a–e**. All compounds **5a–e**, **7a–e** and **8a–e** with a cyclohexyl structure exhibit an enantiotropic nematic phase. Compounds **5a–e**, **7a–e** and **8a–e**

Table 3. Phase transition temperatures and corresponding enthalpy change for the compounds **5a–e**, **7a–e** and **8a–e**.


Heating T°C (Kcal mol ⁻¹)							
Compound	<i>n</i>	X	Cr	N	I		
5a	2	F	·	77.3 (4.65)	·	141.6 (0.10)	·
5b	3	F	·	81.8 (4.56)	·	166.9 (0.13)	·
5c	4	F	·	69.5 (5.79)	·	152.2 (0.14)	·
5d	5	F	·	63.4 (4.46)	·	138.5 (0.11)	·
5e	6	F	·	61.1 (5.26)	·	142.7 (0.14)	·
7a	2	NH ₂	·	87.6 (2.01)	·	113.8 (0.01)	·
7b	3	NH ₂	·	91.3 (2.13)	·	161.2 (0.05)	·
7c	4	NH ₂	·	71.0 (3.20)	·	170.3 (0.17)	·
7d	5	NH ₂	·	84.6 (3.74)	·	170.5 (0.08)	·
7e	6	NH ₂	·	75.1 (2.81)	·	139.5 (0.10)	·
8a	2	NCS	·	87.9 (2.90)	·	162.0 (0.01)	·
8b	3	NCS	·	87.1 (2.63)	·	185.0 (0.03)	·
8c	4	NCS	·	66.7 (1.94)	·	205.0 (0.01)	·
8d	5	NCS	·	73.6 (2.99)	·	213.3 (0.02)	·
8e	6	NCS	·	53.9 (2.31)	·	185.0 (0.01)	·

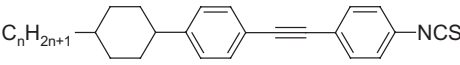
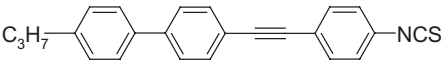
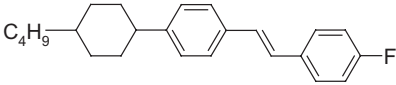
possess the same mesogenic core; the only difference is in their terminal end groups (Figure 2). The melting points of the fluorine series **5a–e** are in a range from 61.1 to 81.8°C, which exhibit an odd-even effect as the chain length increases. Their clearing temperatures are in a range from 138.5 to 166.9°C, which decreases as alkyl chain length increases. The compound **5b** showed the widest temperature range (85.1°) of nematic phase in this series. The melting points of the **7a–e** series are in a range from 71 and 91.3°C, which also exhibit an odd-even effect as chain length increases. Their clearing points are in a range from 113.8 to 170.5°C. The melting points of **8a–e** series are in a range from 53.9 to 87.9°C, which decrease as alkyl chain length increases. Their clearing points are in a range from 162 to 205°C. Compound **8d** showed the highest clearing point of 213.3°C, and the widest temperature range (139.7°) of the nematic phase in this series. Comparing the three series of compounds, their clearing points follow the trend: **8a–e** > **5a–e** > **7a–e**. The compounds **8a–e** turned out to have lower melting points and a wider mesomorphic temperature range among three series, since they contain both a cyclohexyl moiety and NCS end group. Comparing the mesomorphic properties of the **4a–e** and **8a–e** series, it seems that introducing the

cyclohexyl moiety to replace the phenyl ring decreases both melting and clearing temperatures and inhibits the formation of the smectic phase.

3.2 Effect of α -methylstilbene linking group

Table 4 lists the phase transitions of 4-alkylcyclohexyl-4'-isothiocyanato tolane (**n-CPTP-NCS**), 4-propylphenyl-4'-isothiocyanato tolane (**3-BPTP-NCS**), and 4'-(*trans*-4-butylcyclohexyl)-4-fluoro-stilbene (**4-CPDP-F**) LCs published by our laboratory (24, 25) and Spadlo *et al.* (34). Comparing the phase transition of **n-CPTP-NCS** compounds with that of **8a–d** and the phase transition of **3BPTP-NCS** with that of **4b**, it was seen that **8a–d** and **4b** show much lower melting and isotropic temperatures than those of the **n-CPTP-NCS** and **3BPTP-NCS** series. If we compare the phase transitions of **4-CPDP-F** with those of **5c**, the melting point of **5c** is 43.5° lower than that of **4-CPDP-F**. This proves that the α -methylstilbene moiety plays an important role in lowering the melting and isotropisation temperatures of the obtained LC compounds. Furthermore, it also inhibits the formation of the smectic phase.

Table 4. Phase transition temperatures and corresponding enthalpy change for the compounds **n-CPTP-NCS**, **3-BPTP-NCS** and **4CPDP-F**.

								
Heating T°C								
Compound	<i>n</i>	Cr	Sm	N	I			
2CPTP-NCS	2	.	140.2	–	–	.	243.0	.
3CPTP-NCS	3	.	137.2	–	–	.	265.4	.
4CPTP-NCS	4	.	106.9	.	139.9	.	257.4	.
5CPTP-NCS	5	.	119.5	.	147.6	.	254.9	.
								
Heating T°C								
Compound	<i>n</i>	Cr	SmA	N	I			
3BPTP-NCS	3	.	200.0	.	209.0	.	266.0	.
								
Heating T°C								
Compound		Cr	Sm	N	I			
4CPDP-F		.	113	.	118	.	206.7	.

Data obtained from Liao *et al.* (24), Lin *et al.* (25) and Spadlo *et al.* (34).

3.3 Optical anisotropy

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

$$(\Delta n)_{gh} = x(\Delta n)_g + (1 - x)(\Delta n)_h. \quad (1)$$

In Equation (1), the subscripts g, h and gh refer to guest, host and guest–host cells, respectively, and x is the concentration (in wt %) of the guest compound. The Δn value of the guest compounds can be deduced by the results of guest–host mixtures.

The Δn value of α -methylstilbene-based LC compounds are listed in Table 5. The commercial LC ZLI-1565 was used as a host. The Δn values are in the range 0.16 to 0.46. Compound **8c** containing isothiocyanato end group shows a Δn value of 0.25, which is higher than that of the fluoro compound **5d**. Compound **4b** containing an isothiocyanato end group also showed a higher Δn value of 0.46 than that of the cyano compound **3a**. This is because the isothiocyanato group has an elongated conjugation compared with the fluoro and cyano groups. Comparing Δn values of compound **4b** with those of **3BPTP-NCS** and **3BPDNCS**, these three compounds show very close Δn values. This

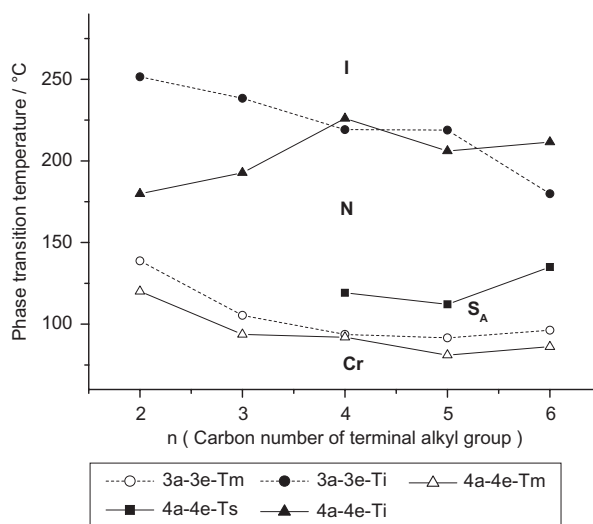


Figure 1. Melting and isotropic temperatures of compounds **3a–e**, **4a–e** as a function of the carbon number (n) of the alkyl group (27).

result proves that the conjugation lengths of tolane, stilbene and α -methylstilbene are similar. The compound **4b** which shows the highest Δn value is expected to be useful for polymer-dispersed liquid crystals, STN display and laser beam steering applications.

Table 5. The Δn values of some single compounds.

Compounds	Chemical structure	Δn
3a		0.36 ^a
4b		0.46 ^a
5b		0.16 ^a
8c		0.25 ^a
3BPTNCS		0.50 ^b
3BPDNCS		0.48 ^b

^aData calculated from the guest–host systems using host mixture ZLI-1565, $\Delta n = 0.12$ at 23.5°C.

^bData calculated from the guest–host systems using host mixture E44, at 23°C.

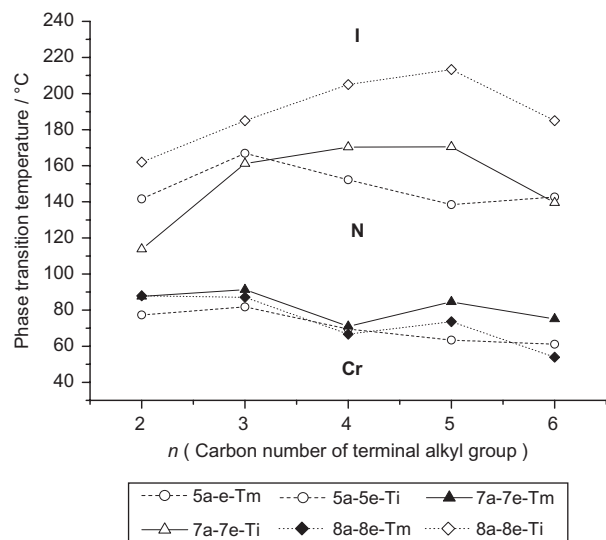


Figure 2. Melting and isotropic temperatures of compounds **5a–e**, **7a–e** and **8a–e** as a function of the carbon number (n) of the alkyl group (27).

4. Conclusion

Six series of high birefringence α -methylstilbene-based LCs were synthesised. All synthesised LCs revealed an enantiotropic nematic phase. The 4-alkylcyclohexyl- α -methylstilbene series showed much lower melting points than those of the 4-alkylphenyl- α -methylstilbene series. Those compounds, which contain both biphenyl and isothiocyanato moieties, have high Δn values. Compound **4b** has the highest Δn value at 0.46 and a wide nematic range (99.1°), which could make it a good candidate for many display applications. In this study we also synthesised the cyclohexyl containing α -methylstilbene LCs. These compounds, which show moderate Δn values and low melting temperature, are useful for formulating a high birefringent eutectic mixture.

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