Synthesis and properties of some novel fluoro-substituted liquid crystals that contain phenyl and cyclohexyl rings linked by ethynyl units

Bing Chen Corresponding author[a]; Guixiang Sun[a]; Shouyi Xu[a]

[a] Department of Chemistry, Tsinghua University, Beijing, 100084, PR China

PLEASE SCROLL DOWN FOR ARTICLE

Synthesis and properties of some novel fluoro-substituted liquid crystals that contain phenyl and cyclohexyl rings linked by ethynyl units

BING CHEN*, GUIXIANG SUN and SHOUYI XU

Department of Chemistry, Tsinghua University, Beijing, 100084, PR China

Seven homologous series of some novel fluoro-substituted liquid crystals that contain phenyl and cyclohexyl or bicyclohexyl rings linked by ethynyl units were prepared and characterized. Textural observations by polarizing microscopy and DSC measurements of the phase transitions show that most of these compounds are thermotropic liquid crystals with a nematic phase or nematic, smectic A and smectic B phases; series **A**, **C′** and **D′** exhibit only a wide temperature range (>90°C) nematic phase. The mesomorphic phase stabilities of the four series **A′**, **B′**, **C′** and **D′** are higher than their thermal stabilities. For these compounds, no clearing points were observed before decomposition. The dielectric anisotropy ($\Delta\varepsilon$) and birefringence (Δn) of some target compounds were determined. These compounds exhibit moderate $\Delta\varepsilon$ and large Δn.

1. Introduction

High birefringence (Δn) liquid crystals are particularly useful not only in conventional display devices such as STN-LCDs, but also in flat panel liquid crystal displays such as PDLCDs, cholesterics, holographic switching devices and directional reflectors, that operate by reflecting or scattering mechanisms [1–6]. In addition, these materials are thought to have application potential in laser beam steering and infrared spatial modulators [7, 8]. As a result of these applications, a number of high Δn liquid crystalline compounds [9–13] have been studied in recent years. Within the framework of the single band model [14], the Δn of a liquid crystalline compound is determined mainly by its molecular conjugation, differential oscillator strength and order parameter. Molecules that contain high polarizability groups with high electron density, such as benzene rings or acetylene linking groups, will therefore have a large optical anisotropy.
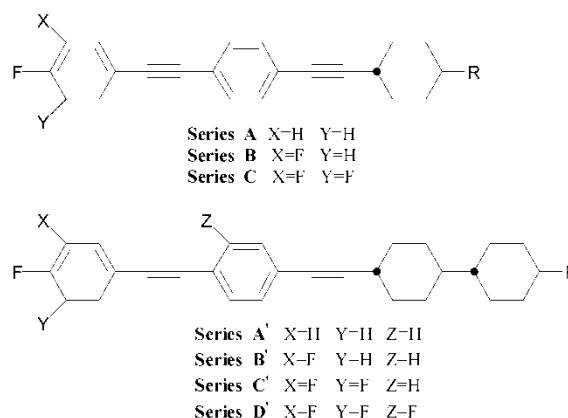
It is known that the fluorine atom is ideal in that it combines the properties of having a large electronegativity and small size so that fluorination has a dramatic effect on the properties of liquid crystal molecules, for example, giving reduced viscosity and adjusted dielectric anisotropy. Although cyclohexyl or bicyclohexyl groups in liquid crystal molecules may be disadvantageous to obtaining high birefringence materials, at the

same time they can reduce viscosity, increase the clearing point and enhance solubility. Thus in order to obtain high birefringence liquid crystal materials with good general properties, under the condition that the liquid crystal molecules designed have a long linear conjugation length, this study introduced a cyclohexyl or a bicyclohexyl group into a molecular core and synthesized new fluorinated liquid crystals. The general structures studied are shown in scheme 1.

2. Experimental
2.1. *Characterization techniques*

The structures of the final products and intermediates were confirmed by infrared spectroscopy (Nicolet 560 spectrophotometer), ^{1}H NMR spectroscopy (Bruker

Series A	X=H Y=H
Series B	X=F Y=H
Series C	X=F Y=F

Series A′	X=H Y=H Z=H
Series B′	X=F Y=H Z=H
Series C′	X=F Y=F Z=H
Series D′	X=F Y=F Z=F

Scheme 1. The structures of the target compounds.

*Author for correspondence;
e-mail: chenbing00@mails.tsinghua.edu.cn

300 spectrometer, with spectra recorded in CDCl$_3$ using TMS as an internal standard; the *J* values are given in Hz), and by mass spectroscopy (AEIMS-50 SD90 spectrometer). The purity of each final compound (tables 1 and 2) was determined by HPLC (Hypersil OD52 C18 Reverse Phase Column 250 × 4.6 mm) and all were found to be >99% pure. Elemental analysis for carbon and hydrogen was conducted on a Heraeus CHN-O-Rapid elemental analyser. The phase transition temperatures of the target compounds were determined by polarizing optical microscopy using an Olympus PM-10AD microscope fitted with a Mettler FP-80 heating stage and an FP-82 control unit, and by differential scanning calorimetry (Mettler DTA TA-2010 DSC, with a heating and cooling rate of 10°C min^{-1}). Phase identification was made by comparing the observed textures with those reported in the literature [15, 16]. Decomposition temperatures were determined on a 2050 Thermogravimetric Analyser.

2.2. Synthesis

The synthesis of the target molecules is outlined in scheme 2. All homologues were prepared using the same methods, therefore the general experimental procedures are illustrated using compounds A_2, B_2, C_2, A'_2, B'_2, C'_2, D'_2 as examples.

2.2.1. Trans-4-ethylcyclohexylmethanol (2a)

A solution of **1a** (78.0 g, 0.5 mol) in dry THF (400 ml) was added dropwise to a stirred suspension of LiAlH$_4$ (38.0 g, 1.0 mol) in dry THF (400 ml) below 0°C. The reaction mixture was stirred for 2 h at room temperature. A solution of potassium sodium tartrate (84 g, 0.4 mol) in H$_2$O (300 ml) was added dropwise to the reaction mixture; the mixture was filtered, and the insoluble fraction washed with THF. The combined organic layer was dried (Na$_2$SO$_4$). The solvent was removed *in vacuo*, and the residue purified by distillation under reduced pressure. Yield 63.1 g (88.9%), b.p. 78–80°C/0.5 mm Hg. ^{1}H NMR (δ): 0.85–1.19 (10H, m), 1.23–1.33 (2H, m), 1.67–1.79 (4H, m), 3.44–3.46 (2H, d, *J* = 6.3). IR v_{max} (film, cm^{-1}): 3266, 2908, 2844, 1452, 1376, 1222, 1072, 977, 894, 757.

2.2.2. Trans, trans-4-ethylcyclohexylcyclohexylmethanol (2e)

The experimental procedure was the same as for the preparation of compound **2a**. The following quantities were used: compound **1e** (119 g, 0.5 mol) and LiAlH$_4$ (38.0 g, 1.0 mol). The product was purified by recrystallization from aqueous ethanol. Yield 101.9 g (91.2%),

m.p. 121.3°C. ^{1}H NMR (δ): 0.83–1.21 (16H, m), 1.26–1.39 (2H, m), 1.66–1.82 (8H, m), 3.45–3.48 (2H, d, *J* = 6.4). IR v_{max} (KBr disc, cm^{-1}): 3339, 2958, 2921, 2863, 1436, 1224, 1042, 981, 876, 775.

2.2.3. Trans-4-ethylcyclohexylmethanal (3a)

A solution of compound **2a** (61.2 g, 0.43 mol) in dry CH$_2$Cl$_2$ (150 ml) was added to a stirred suspension of pyridinium chlorochromate (PCC, 139.2 g, 0.64 mol) in dry CH$_2$Cl$_2$ (400 ml) at room temperature. The reaction mixture was stirred for 2 h, and then dry ether (500 ml) was added, and the mixture stirred for 5 min. The mixture stood for 1 h, and the solution was then poured off. The insoluble residue was washed with dry ether (3 × 100 ml). The combined organic solution was concentrated, and the residue purified by distillation under reduced pressure. Yield 50.4 g (82.5%), b.p. 61–63°C/ 5 mm Hg. ^{1}H NMR (δ): 0.83–1.22 (8H, m), 1.25–1.46 (2H, m), 1.79–1.83 (2H, m), 1.97–2.01 (2H, m), 2.18–2.26 (1H, m), 9.68 (1H, d, *J* = 6.8). IR v_{max} (film, cm^{-1}): 2921, 2850, 1697, 1448, 1419, 1317, 1263, 1000, 958, 896, 748.

### 2.2.4. Trans,trans-4-ethylcyclohexylcyclohexylmethanal (3e)

The experimental procedure was the same as for the preparation of compound **3a**. The following quantities were used: compound **2e** (89.6 g, 0.4 mol) and PCC (130.5 g, 0.6 mol). Yield 75.4 g (84.2%), b.p. 120–122°C/ 1.1 mm Hg. ^{1}H NMR (δ): 0.81–1.24 (14H, m), 1.27–1.46 (2H, m), 1.75–1.84 (6H, m), 1.98–2.03 (2H, m), 2.19–2.26 (1H, m), 9.66 (1H, d, *J* = 6.8). IR v_{max} (film, cm^{-1}): 2921, 2850, 1697, 1444, 1419, 1259, 993, 970, 900, 748.

2.2.5. Trans-4-ethylcyclohexyl-β,β'-dibromoethene (4a)

Triphenylphosphine (190.1 g, 0.73 mol) was added in portions to a stirred mixture of carbon tetrabromide (240.7 g, 0.73 mol) and zinc (47.4 g, 0.73 mol) in dry CH$_2$Cl$_2$ (600 ml). The suspension was stirred for 24 h at room temperature. Then compound **3a** (50.4 g, 0.36 mol) was added, and the mixture stirred for 3 h. The reaction mixture was filtered, the solvent was removed *in vacuo*, and the residue purified by distillation under reduced pressure. Yield 81.5 g (76.5%), b.p. 98–100°C/1 mm Hg. ^{1}H NMR (δ): 0.86–1.18 (8H, m), 1.21–1.28 (2H, m), 1.77–1.81 (4H, m), 2.17–2.28 (1H, m), 6.20–6.23 (1H, d, *J* = 9.0). IR v_{max} (film, cm^{-1}): 2992, 2923, 2850, 1618, 1448, 1376, 1079, 898, 835, 767.

2.2.6. Trans,trans-4-ethylcyclohexylcyclohexyl-β,β'-dibromoethene (4e)

The experimental procedure was the same as for the preparation of compound **4a**. The following quantities
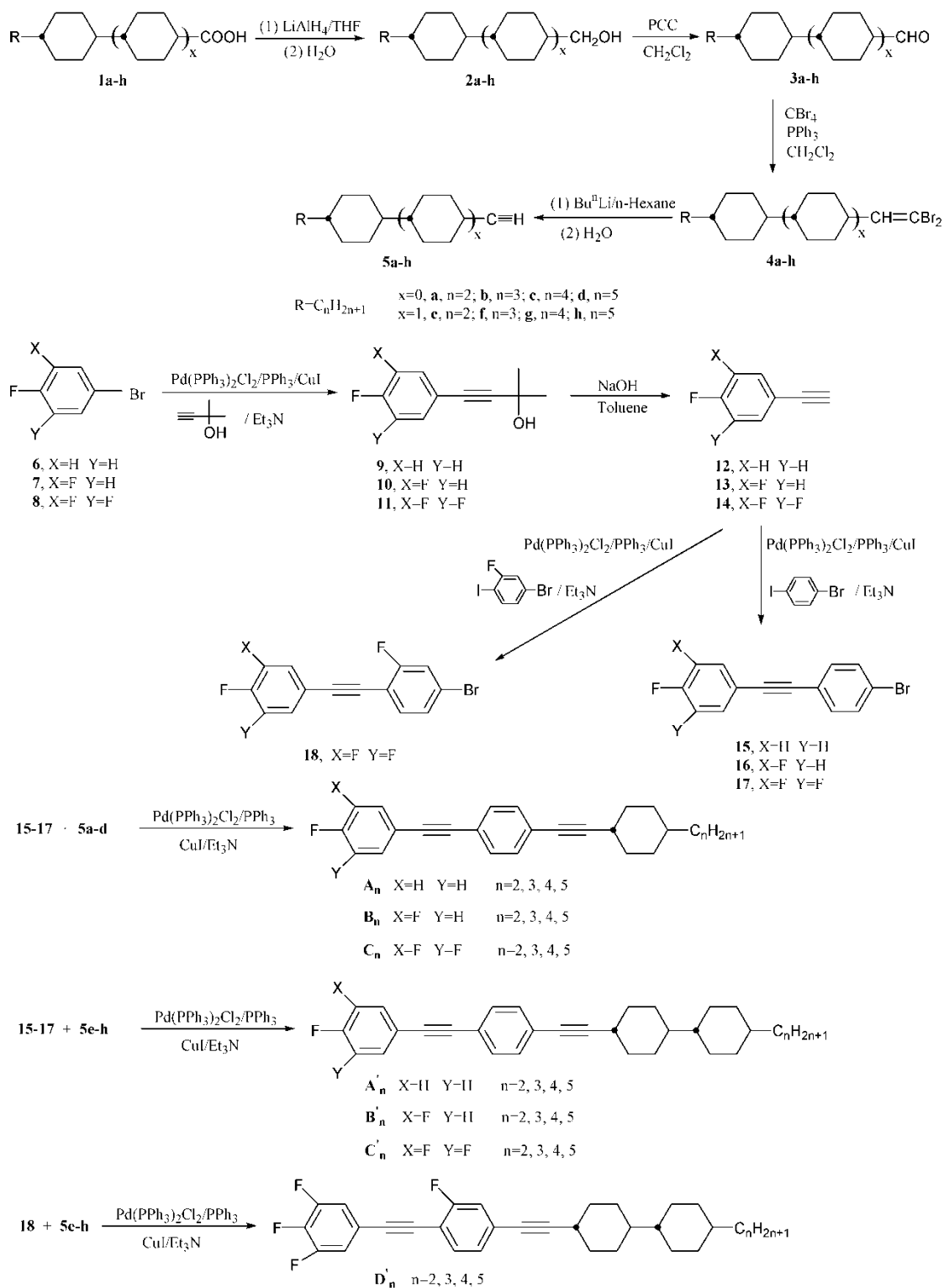
Scheme 2.   Synthetic route to the target compounds.

were used: compound **3e** (66.6 g, 0.3 mol), triphenylpho-sphine (156.2 g, 0.6 mol), carbon tetrabromide (197.8 g, 0.6 mol) and zinc (38.9 g, 0.6 mol). The product was purified by column chromatography (silica gel, *n*-hexane). Yield 88.8 g (78.2%), m.p. 43.2°C. ^{1}H NMR (δ): 0.83–1.19 (14H, m), 1.22–1.28 (2H, m), 1.71–1.83

(8H, m), 2.18–2.28 (1H, m), 6.22–6.25 (1H, d, $J = 9.0$). IR v_{max} (KBr disc, cm^{-1}): 2919, 2873, 1589, 1483, 1440, 1311, 1189, 995, 763.

2.2.7. *Trans-4-ethylcyclohexylethyne* (**5a**)

A solution of *n*-butyllithium in *n*-hexane (308.6 ml, 0.56 mol) was added dropwise to a stirred solution of compound **4a** (81.5 g, 0.28 mol) in dry THF (600 ml) at −78°C under nitrogen. The reaction mixture was stirred for 2 h at −78°C, and then it was warmed to room temperature. Water (400 ml) was added to the reaction mixture. The product was extracted into *n*-hexane (2×200 ml) and the combined organic layers were washed with water (2×200 ml) and then dried (Na$_2$SO$_4$). The solvent was removed *in vacuo*, and the residue purified by distillation under reduced pressure. Yield 27.2 g (71.5%), b.p. 36–38°C/1.1 mm Hg. ^{1}H NMR (δ): 0.85–1.20 (8H, m), 1.25–1.40 (2H, m), 1.65–1.76 (3H, m), 1.97–2.02 (2H, m), 2.09–2.18 (1H, m). IR v_{max} (film, cm^{-1}): 3297, 2929, 2871, 2109, 1508, 1488, 1378, 1072, 838, 642.

2.2.8. *Trans,trans-4-ethylcyclohexylcyclohexylethyne* (**5e**)

The experimental procedure was the same as for the preparation of compound **5a**. The following quantities were used: compound **4e** (75.6 g, 0.2 mol) and *n*-butyllithium in *n*-hexane (220.4 ml, 0.4 mol). Yield 29.9 g (68.8%), b.p. 122–124°C/1.1 mm Hg. ^{1}H NMR (δ): 0.81–1.22 (14H, m), 1.26–1.40 (2H, m), 1.63–1.78 (7H, m), 1.97–2.03 (2H, m), 2.09 –2.19 (1H, m). IR v_{max} (film, cm^{-1}): 3274, 2923, 2850, 2109, 1446, 1375, 952, 894, 663.

2.2.9. *2-Methyl-4-4′-fluorophenyl-3-butyne-2-ol* (**9**)

A solution of **6** (35.0 g, 0.2 mol), dichlorobis-(triphenylphosphine)palladium (0.6 g, 0.85 mmol), CuI (0.6 g, 3.1 mmol), triphenylphosphine (1.2 g, 4.9 mmol) and triethylamine (70 ml) in ethyl acetate (170 ml) was degassed by introducing nitrogen, and then 2-methyl-3-butyne-2-ol (16.2 g, 0.2 mol) was added to the mixture. The reaction mixture was stirred at 60–65°C for 8 h. After cooling to room temperature it was filtered, and the insoluble fraction washed with ethyl acetate. The combined organic layer was dried (Na$_2$SO$_4$). The solvent was removed *in vacuo*, and the residue purified by distillation under reduced pressure. Yield 28.1 g (78.9%), b.p. 96–98°C/2 mm Hg. IR v_{max} (film, cm^{-1}): 3272, 2975, 2923, 2228, 1602, 1506, 1446, 1224, 1155, 835.

2.2.10. *2-Methyl-4-3′,4′-difluorophenyl-3-butyne-2-ol* (**10**)

The experimental procedure was the same as for the preparation of compound **9**. The following quantities

were used: compound **7** (38.6 g, 0.2 mol) and 2-methyl-3-butyne-2-ol (16.2 g, 0.2 mol). Yield 32.3 g (83.7%), b.p. 90–92°C/0.5 mm Hg. IR v_{max} (film, cm^{-1}): 3347, 2983, 2935, 2226, 1598, 1517, 1421, 1265, 1166, 875.

2.2.11. *2-Methyl-4-3′,4′,5′-trifluorophenyl-3-butyne-2-ol* (**11**)

The experimental procedure was the same as for the preparation of compound **9**. The following quantities were used: compound **8** (42.2 g, 0.2 mol) and 2-methyl-3-butyne-2-ol (16.2 g, 0.2 mol). Yield 34.1 g (80.8%), m.p. 39.4°C. IR v_{max} (KBr disc, cm^{-1}): 3365, 2991, 2938, 2222, 1621, 1525, 1431, 1280, 1156, 866.

2.2.12. *4-Fluorophenylethyne* (**12**)

NaOH (8.0 g, 0.2 mol) was added to a solution of compound **9** (25.1 g, 0.14 mol) in toluene (300 ml). The reaction mixture was heated under reflux for 4 h, it was then cooled to room temperature and filtered. The organic solution was dried (Na$_2$SO$_4$); toluene was removed *in vacuo*. The crude product was purified by distillation. Yield 11.6 g (68.8%), b.p. 126–128°C/760 mm Hg. IR v_{max} (film, cm^{-1}): 3297, 2137, 1602, 1515, 1446, 1157, 838, 528.

2.2.13. *3,4-Difluorophenylethyne* (**13**)

The experimental procedure was the same as for the preparation of compound **12**. The following quantities were used: compound **10** (27.6 g, 0.14 mol) and NaOH (8.0 g, 0.2 mol). Yield 13.8 g (71.2%), b.p. 129–131°C/760 mm Hg. IR v_{max} (film, cm^{-1}): 3312, 2140, 1605, 1511, 1452, 1147, 845, 556.

2.2.14. *3,4,5-Trifluorophenylethyne* (**14**)

The experimental procedure was the same as for the preparation of compound **12**. The following quantities were used: compound **11** (29.5 g, 0.14 mol) and NaOH (8.0 g, 0.2 mol). Yield 14.2 g (65.8%), b.p. 136–138°C/760 mm Hg. IR v_{max} (film, cm^{-1}): 3318, 2139, 1599, 1517, 1453, 1141, 843, 557.

2.2.15. *4-Bromo-4′-fluorodiphenylethyne* (**15**)

The experimental procedure was similar to that used for the preparation of compound **9**. The following quantities were used: compound **12** (9.6 g, 0.08 mmol) and 1-bromo-4-iodobenzene (22.7 g, 0.08 mol). The crude product was purified by column chromatography (silica gel, *n*-hexane). Yield 18.1 g (82.4%), m.p. 106.7°C. IR v_{max} (KBr disc, cm^{-1}): 1907, 1598, 1510, 1224, 1006, 837, 515.

2.2.16. *4-Bromo-3',4'-difluorodiphenylethyne (16)*

The experimental procedure was the same as for the preparation of compound **15**. The following quantities were used: compound **13** (11.0 g, 0.08 mol) and 1-bromo-4-iodobenzene (22.7 g, 0.08 mol). Yield 18.6 g (80.1%), m.p. 93.8°C. IR v_{max} (KBr disc, cm^{-1}): 1905, 1598, 1517, 1225, 1008, 839, 520.

2.2.17. *4-Bromo-3',4',5'-trifluorodiphenylethyne (17)*

The experimental procedure was the same as for the preparation of compound **15**. The following quantities were used: compound **14** (12.5 g, 0.08 mol) and 1-bromo-4-iodobenzene (22.7 g, 0.08 mol). Yield 18.9 g (75.9%), m.p. 81.9°C. IR v_{max} (KBr disc, cm^{-1}): 1907, 1610, 1525, 1257, 1008, 815, 526.

2.2.18. *4-Bromo-3-fluoro-3',4',5'-trifluorodiphenylethyne (18)*

The experimental procedure was the same as for the preparation of compound **15**. The following quantities were used: compound **14** (12.5 g, 0.08 mol) and 1-bromo-3-fluoro-4-iodobenzene (24.1 g, 0.08 mol). Yield 20.8 g (78.9%), m.p. 68.4°C. IR v_{max} (KBr disc, cm^{-1}): 1897, 1610, 1525, 1213, 1043, 823, 524.

2.2.19. *1-[(4-Fluorophenyl)ethynyl] -4-[(trans-4-ethyl-cyclohexyl)ethynyl]benzene (A_2)*

The experimental procedure was similar to that used for the preparation of compound **9**. The following quantities were used: compound **15** (0.55 g, 2.0 mmol) and **5a** (0.26 g, 2.0 mmol). The product was purified by column chromatography (silica gel, *n*-hexane) and then recrystallized from ethanol. Yield 0.32 g (53.6%); elemental analysis(%), calc. (found) for $C_{24}H_{23}F$: C 87.27 (87.12), H 6.97 (7.02); m.p. 104.9°C. ^{1}H NMR (δ): 0.86–1.21 (8H, m), 1.36–1.41 (2H, m), 1.74–1.78 (2H, m), 1.98–2.03 (2H, m), 2.32–2.35 (1H, m) 6.97–7.47 (8H, m). IR v_{max} (KBr disc, cm^{-1}): 2958, 2923, 2852, 2217, 1515, 1446, 1222, 1157, 838, 528. MS (*m/z*): 330 (M$^+$), 248 (100%), 233, 222.

2.2.20. *1-[(3,4-Difluorophenyl)ethynyl] -4-[(trans-4-ethylcyclohexyl)ethynyl]benzene (B_2)*

The experimental procedure was the same as for the preparation of compound A_2. The following quantities were used: compound **16** (0.59 g, 2.0 mmol) and **5a** (0.26 g, 2.0 mmol). Yield 0.47 g (62.1%); elemental analysis, calc. (found) for $C_{24}H_{22}F_2$: C 82.76 (82.71), H 6.32 (6.26); m.p. 120.3°C. ^{1}H NMR (δ): 0.86–1.25 (8H, m), 1.41–1.45 (2H, m), 1.78–1.83 (2H, m), 2.03–2.07 (2H, m), 2.35–2.39 (1H, m), 7.11 –7.42 (7H, m). IR v_{max} (KBr disc, cm^{-1}): 2960, 2927, 2850, 2217, 1594, 1517, 1418, 1326, 948, 825, 545. MS (*m/z*): 348 (M$^+$), 266 (100%), 251, 238.

2.2.21. *1-[(3,4,5-Trifluorophenyl)ethynyl] -4-[(trans-4-ethylcyclohexyl)ethynyl]benzene (C_2)*

The experimental procedure was the same as for the preparation of compound A_2. The following quantities were used: **17** (0.62 g, 2.0 mmol) and **5a** (0.26 g, 2.0 mmol). Yield 0.39 g (49.3%); elemental analysis, calc. (found) for $C_{24}H_{21}F_3$: C 78.69 (78.61), H 5.74 (5.76); m.p. 130.2°C. ^{1}H NMR (δ): 0.85–1.24 (8H, m), 1.40–1.45 (2H, m), 1.78–1.83 (2H, m), 2.02–2.06 (2H, m), 2.36–2.40 (1H, m), 7.10–7.42 (6H, m). IR v_{max} (KBr disc, cm^{-1}): 2931, 2850, 2215, 1594, 1529, 1428, 1376, 978, 831, 547. MS (*m/z*): 366 (M$^+$), 284 (100%), 269, 256.

2.2.22. *1-[(4-Fluorophenyl)ethynyl]-4-[trans-4-(trans-4-ethylcyclohexyl)cyclohexylethynyl]benzene (A'_2)*

The experimental procedure was the same as for the preparation of compound A_2. The following quantities were used: **15** (0.55 g, 2.0 mmol) and **5e** (0.44 g, 2.0 mmol). Yield 0.42 g (51.2%); elemental analysis, calc. (found) for $C_{30}H_{33}F$: C 87.38 (87.22), H 8.01 (8.05), m.p. 120.1°C. ^{1}H NMR (δ): 0.84–1.26 (14H, m), 1.39–1.43 (2H, m), 1.68–1.78 (6H, m), 2.05–2.09 (2H, m), 2.33–2.38 (1H, m), 7.01 –7.52 (8H, m). IR v_{max} (KBr disc, cm^{-1}): 2931, 2850, 2221, 1594, 1511, 1444, 1234, 1091, 837, 528. MS (*m/z*): 412 (M$^+$), 248 (100%), 233, 222.

2.2.23. *1-[(3,4-Difluorophenyl)ethynyl]-4-[trans-4-(trans-4-ethylcyclohexyl)cyclohexylethynyl]-benzene (B'_2)*

The experimental procedure was the same as for the preparation of compound A_2. The following quantities were used: **16** (0.59 g, 2.0 mmol) and **5e** (0.44 g, 2.0 mmol). Yield 0.35 g (40.8%); elemental analysis, calc. (found) for $C_{30}H_{32}F_2$: C 83.72 (83.63), H 7.44 (7.43); m.p. 107.8°C. ^{1}H NMR (δ): 0.81–1.25 (14H, m), 1.35–1.43 (2H, m), 1.68–1.78 (6H, m), 2.05–2.08 (2H, m), 2.34–2.38 (1H, m), 7.08 –7.42 (7H, m). IR v_{max} (KBr disc, cm^{-1}): 2910, 2850, 2221, 1596, 1519, 1272, 1419, 1101, 835, 548. MS (*m/z*): 430 (M$^+$), 266 (100%), 251, 238.

2.2.24. *1-[(3,4,5-Trifluorophenyl)ethynyl]-4-[trans-4-(trans-ethylcyclohexyl)cyclohexylethynyl]-benzene (C_2)*

The experimental procedure was the same as for the preparation of compound A_2. The following quantities were used: **17** (0.62 g, 2.0 mmol) and **5e** (0.44 g,

2.0 mmol). Yield 0.43 g (47.6%); elemental analysis, calc. (found) for $C_{30}H_{31}F_3$: C 80.36 (80.32), H 6.92 (7.01); m.p. 106.4°C. ^{1}H NMR (δ): 0.77–1.15 (14H, m), 1.32–1.50 (2H, m), 1.62–1.71 (6H, m), 1.98–2.02 (2H, m), 2.28–2.33 (1H, m) 7.03–7.36 (6H, m). IR v_{max} (KBr disc, cm^{-1}): 2931, 2850, 2217, 1610, 1529, 1430, 1255, 1053, 835, 549. MS (*m/z*): 448 (M$^+$), 284 (100%), 269, 256.

2.2.25. *1-[(3,4,5-trifluorophenyl)ethynyl]-2-fluoro-4-[trans-4-(trans-ethylcyclohexyl)cyclohexylethynyl]-benzene (D′$_2$)*

The experimental procedure was the same as for the preparation of compound A$_2$. The following quantities were used: **18** (0.66 g, 2.0 mmol) and **5e** (0.44 g, 2.0 mmol). Yield 0.47 g (50.2%); elemental analysis, calc. (found) for $C_{30}H_{30}F_4$: C 77.25 (77.23), H 6.44 (6.41); m.p. 105.8°C. ^{1}H NMR (δ): 0.86–1.33 (14H, m), 1.36–1.48 (2H, m), 1.69–1.79 (6H, m), 2.06–2.10 (2H, m), 2.29–2.36 (1H, m), 7.10 –7.40 (5H, m). IR v_{max} (KBr disc, cm^{-1}): 2925, 2850, 2219, 1610, 1529, 1429, 1276, 1047, 856, 524. MS (*m/z*): 466 (M$^+$), 302 (100%), 287, 204.

3. Results and discussion

The alkyl chain lengths of the seven homologous series reported here were restricted to $n = 2$–5.

The phase transition temperatures of series **A**, **B** and **C** are listed in table 1. Series **A** and **B** can be considered to be derived from the corresponding fluorinated tolanes [17]. All these compounds exhibited a liquid crystal phase owing to the increased length of the molecules. When two lateral *meta*-fluoro substitutions
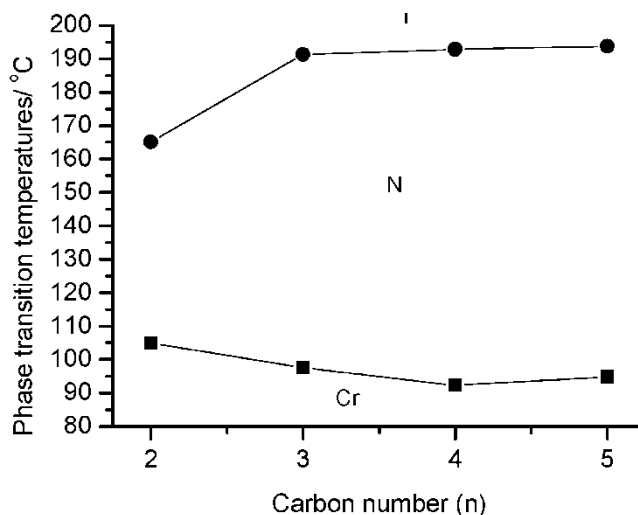

Figure 1. Dependence of transition temperatures on the number of carbon atoms in the alkyl chain for series **A**.

were introduced, to give series **C**, liquid crystal phases were not seen except for **C$_5$**. The only difference between series **A** compounds was the length of the terminal alkyl chains. Compounds **A$_3$**, **A$_4$** and **A$_5$** showed a wide nematic phase range (>94°C), and had similar melting and clearing points. When the terminal alkyl group was ethyl, compound **A$_2$** had a higher melting point and a lower clearing point than the other three homologues (see figure 1). This is mainly due to the rigidity of the ethyl unit in the molecule.

Series **B** contained a lateral fluoro-substituent. Compound **B$_2$** exhibited a monotropoic nematic phase. The nematic phase ranges of compounds **B$_3$**, **B$_4$** and **B$_5$** were about 55°C. Figure 2 shows the plot of the phase transition temperature versus the carbon

Table 1. Transition temperatures (°C) of series **A**, **B** and **C**.

Compound	X	Y	n	Cr		N		I
A$_2$	H	H	2	●	104.9	●	165.2	●
A$_3$	H	H	3	●	97.6	●	193.3	●
A$_4$	H	H	4	●	92.2	●	192.9	●
A$_5$	H	H	5	●	94.8	●	193.8	●
B$_2$	F	H	2	●	120.3	●	(117.2)^a	●
B$_3$	F	H	3	●	99.5	●	156.6	●
B$_4$	F	H	4	●	95.5	●	155.1	●
B$_5$	F	H	5	●	94.7	●	152.1	●
C$_2$	F	F	2	●	130.2			●
C$_3$	F	F	3	●	118.4			●
C$_4$	F	F	4	●	112.5			●
C$_5$	F	F	5	●	102.1	●	119.6	●

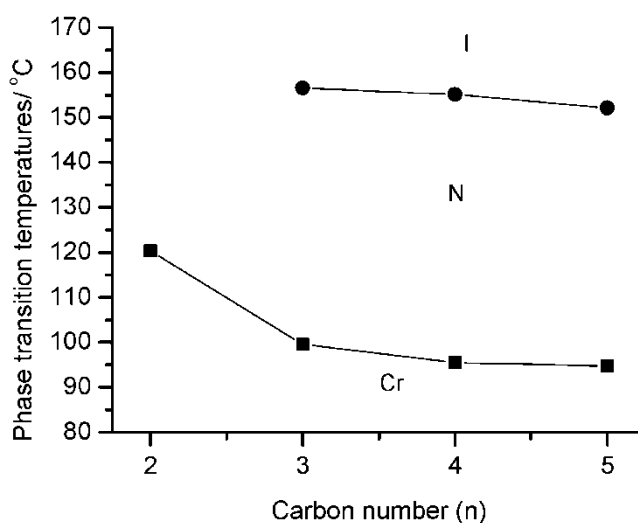^{a}( ) denotes a monotropic transition.

Figure 2. Dependence of transition temperatures on the number of carbon atoms in the alkyl chain for series **B**.
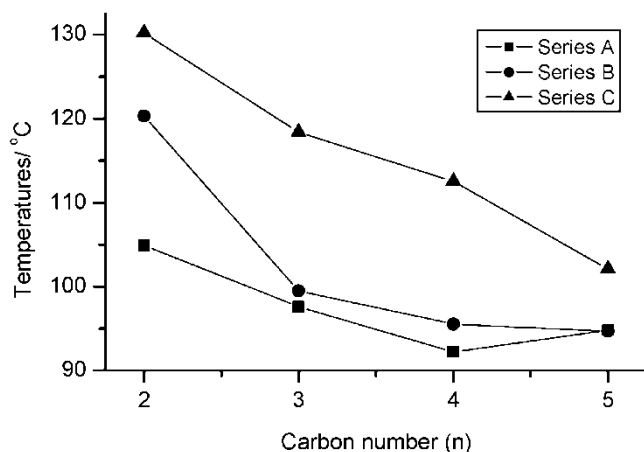
Figure 3. Melting points of cyclohexyl compounds.

number of the terminal alkyl chains and it also shows that neither the melting nor clearing points changed appreciably on increasing n except for those of B_2.

For compounds having two lateral fluoro substituents on the terminal phenyl ring, i.e. series **C** compounds, those with short alkyl chains exhibited no mesomorphic phase. When the carbon number increased to $n = 5$, C_5 showed a nematic phase with a narrow phase transition temperature range (only 17.5°C). Comparing the cyclohexyl compounds, the melting points of series **C** were higher than those of the corresponding series **A** and **B** compounds (see figure 3). With the gradual increase in the width of the mono-, di- and tri-fluoro-substituted molecules, the increased

intermolecular separation weakens the lateral molecular attractive forces; at the same time, the increased molecular polarity enhances the terminal molecular attractive force. Although both the lateral and terminal interactions can affect melting points, when the terminal alkyl groups are the same the terminal interactions of the molecules play a major role in determining the melting points of these compounds. The stronger the molecule's terminal interaction, the higher the melting point. Of the three series, series **C** compounds have the strongest terminal interactions, so their melting points are the highest. For example, the melting points of compounds A_3, B_3 and C_3 are 97.6, 99.5 and 118.4°C, respectively.

Table 2 summarizes the phase transition temperatures for series **A′**, **B′**, **C′** and **D′**. All these compounds contain a bicyclohexyl group in their molecular cores. Surprisingly, none exhibited clearing points. In the DSC traces of series **A′** and **B′**, three peaks were observed on heating from room temperature to 270°C, while for series **C′** and **D′**, only one peak was observed. Smectic B, smectic A and nematic phase textures for series **A′** and **B′** compounds were observed. Nematic textures for series **C′** and **D′** compounds were observed under a polarizing microscope on cooling; however, no transition from the nematic phase to isotropic liquid for any of these compounds was observed on heating to 270°C. Thermogravimetric analysis (TGA) showed series **A′**, **B′**, **C′** and **D′** compounds began to decompose at somewhat different temperatures (table 2). The results of DSC, TGA and polarizing microscopy studies

Table 2. Transition temperatures (°C) of series **A′**, **B′**, **C′** and **D′**.

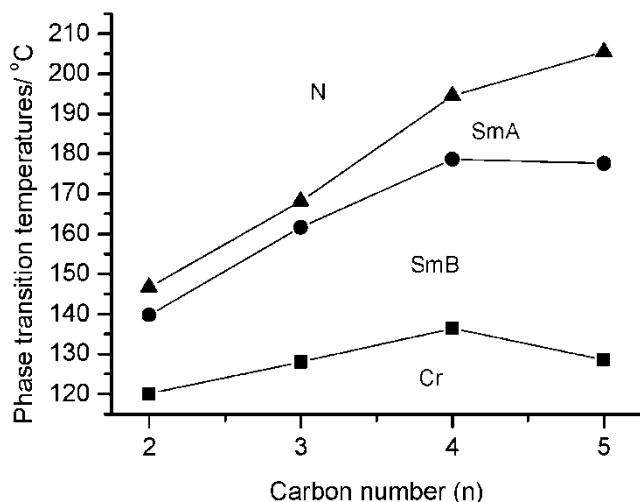| Compound	X	Y	Z	n	Cr		SmB		SmA		N	
A′₂	H	H	H	2	●	120.1	●	139.8	●	146.7	●	> 250
A′₃	H	H	H	3	●	128.1	●	161.7	●	168.2	●	> 250
A′₄	H	H	H	4	●	136.4	●	178.6	●	194.9	●	> 250
A′₅	H	H	H	5	●	128.6	●	177.6	●	205.4	●	> 250
B′₂	F	H	H	2	●	107.8	●	115.5	●	139.8	●	> 260
B′₃	F	H	H	3	●	116.4	●	137.5	●	160.0	●	> 260
B′₄	F	H	H	4	●	115.0	●	139.9	●	172.7	●	> 260
B′₅	F	H	H	5	●	109.4	●	142.9	●	174.1	●	> 260
C′₂	F	F	H	2	●	106.4					●	> 220
C′₃	F	F	H	3	●	111.2					●	> 220
C′₄	F	F	H	4	●	115.5					●	> 220
C′₅	F	F	H	5	●	110.6					●	> 220
D′₂	F	F	F	2	●	105.8					●	> 230
D′₃	F	F	F	3	●	99.2					●	> 230
D′₄	F	F	F	4	●	91.3					●	> 230
D′₅	F	F	F	5	●	77.9					●	> 230

Figure 4.   Dependence of transition temperatures on the number of carbon atoms in the alkyl chain for series **A**′.

indicate that the mesomorphic phase stability of these compounds is greater than their thermal stability.

The transition temperatures of series **A**′ are shown in figure 4. The data clearly show that the smectic B phase ranges of series **A**′ are wider than the corresponding smectic A phase ranges, and on increasing the alkyl chain length, both the smectic B and the smectic A phase ranges increase. As far as the transition temperatures of series **B**′ are concerned (see figure 5 and table 2), the smectic B and smectic A phase ranges are narrower than 35°C, while the nematic phase ranges are greater than 80°C. On increasing *n*, $T_{\text{SmA-N}}$ and $T_{\text{SmA-SmB}}$ of series **B**′ increased, whereas their melting points first increase, and then decrease. Series **B**′ compounds exhibit lower $T_{\text{SmA-N}}$, $T_{\text{SmA-SmB}}$ and
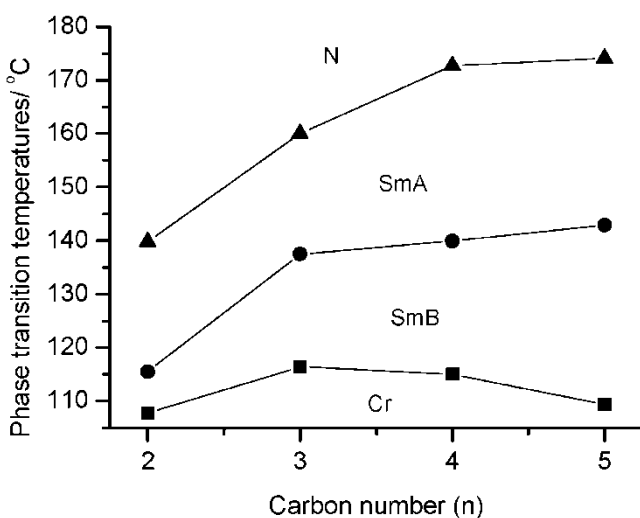
melting points than the corresponding series **A**′ compounds, presumably because the lateral fluoro substituent increases the molecular width and therefore weakens the attractive forces.

Moving to series **C**′, the phase behaviour is much simpler than for series **A**′ and **B**′. Thus a very wide nematic range ($> 100°C$) is exhibited; moreover their melting points are not very high (around 110°C). In order to reduce the melting points further, we introduced fluorine atoms to the middle phenyl ring of series **C**′ to obtain series **D**′. Comparing corresponding compounds of these two series, on increasing *n*, the difference in melting points between series **C**′ and **D**′ compounds increases (see table 2). For example, the melting points of compounds **C**′₂ and **D**′₂ are 106.4 and 105.8°C, respectively; while those of compounds **C**′₅ and **D**′₅ are 110.6 and 77.9°C, respectively. The nematic phase ranges of series **D**′ are also very wide ($> 120°C$).

Figure 6 shows the melting points of bicyclohexyl compounds. It is very interesting that on increasing the polarity and width of a molecule, the trend seen in the melting points is different from that for the cyclohexyl compounds (see figure 3). The melting points of series **A**′ are higher than those of the corresponding series **B**′, **C**′ and **D**′ compounds, which demonstrates that in competition with a molecule's terminal interaction, its lateral interactions may largely determine the melting points of bicyclohexyl compounds. Series **A**′ compounds, which have the largest length-to-breadth ratio, have the strongest lateral interaction among the four series, so their melting points are the highest. In contrast, series **D**′ compounds have the lowest melting points.

A comparison of the cyclohexyl compounds with the corresponding bicyclohexyl compounds (see tables 1 and 2) reveals that the replacement of a cyclohexyl ring
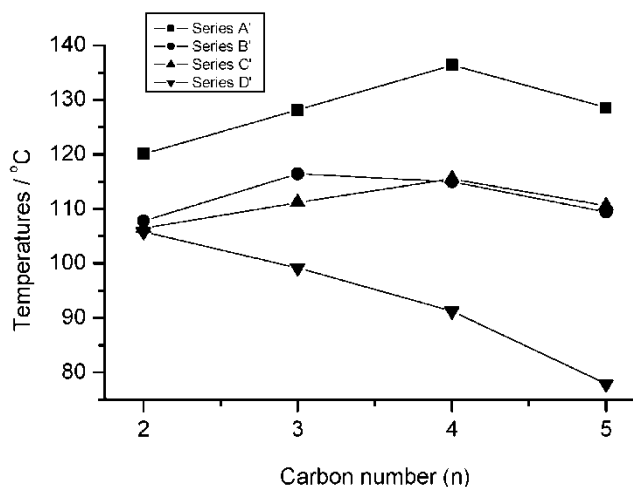

Figure 5.   Dependence of transition temperatures on the number of carbon atoms in the alkyl chain for series **B**′.

Figure 6.   Melting points of bicyclohexyl compounds.

Table 3. Dielectric anisotropy ($\Delta\varepsilon$) and birefringence (Δn) of selected compounds.

Compound	n	$\Delta\varepsilon$	Δn
$\mathbf{A_2}$	2	$+4.9$	0.34
$\mathbf{B_2}$	2	$+6.9$	0.33
$\mathbf{C_2}$	2	$+11.6$	0.30
$\mathbf{A'_2}$	2	$+4.5$	0.32
$\mathbf{B'_2}$	2	$+6.1$	0.30
$\mathbf{C'_2}$	2	$+9.2$	0.28
$\mathbf{D'_2}$	2	$+8.9$	0.27

with a bicyclohexyl ring enhances the mesomorphic phase stability and promotes the formation of smectic phases for mono-fluoro and di-fluoro substituted compounds. It is surprising that increasing the length of a molecular core does not always increase the melting point. For example, compounds $\mathbf{B'_2}$, $\mathbf{C'_2}$ and $\mathbf{C'_3}$ are more extended than the corresponding compounds $\mathbf{B_2}$, $\mathbf{C_2}$ and $\mathbf{C_3}$, but exhibit lower melting points.

In order to determine other properties of these compounds, seven compounds ($\mathbf{A_2}$, $\mathbf{B_2}$, $\mathbf{C_2}$, $\mathbf{A'_2}$, $\mathbf{B'_2}$, $\mathbf{C'_2}$ and $\mathbf{D'_2}$) were selected for the measurement of dielectric anisotropy and birefringence. The dielectric anisotropy and birefringence of these compounds were measured by a guest–host method [18]. The dielectric constant of TEB-3550 (liquid crystal mixture for TN-LCD, produced by Qinghua Yawang Liquid Crystal Materials Co. Ltd., China) and a mixture containing TEB-3550 and 10 wt% of each selected compound were measured at 20°C. The refractive indices of TEB-3550 and three mixtures containing TEB-3550 and 5, 10 and 15 wt% of each selected compound were measured at 20°C and 589 nm. The extrapolated dielectric anisotropy and birefringence values of each pure compound are shown in table 3. As can be seen from the table, the birefringence values of these compounds are high, between 0.27 and 0.34, while the dielectric anisotropy values for these compounds are moderate. The lateral fluoro substituent increases the width of the molecule so that the separation between neighbouring molecules is increased. This looser molecular packing leads to a slightly lower birefringence. The increase of molecular length can also reduce the birefringence slightly. Thus among these compounds, $\mathbf{A_2}$ has the largest birefringence, and $\mathbf{D'_2}$ has the lowest birefringence. Table 3 shows that with an increase in the number of fluorine atoms in a molecule, its polarity is enhanced gradually, and there is a corresponding increase in the compound's dielectric anisotropy.

4. Conclusion

We have synthesized 28 new compounds belonging to seven homologous series and studied their mesomorphic properties. The effect of alkyl chain length, and fluoro substitution, on the thermal behaviour for cyclohexyl and bicyclohexyl-containing compounds is discussed. The mesomorphic phase stability of four series, $\mathbf{A'}$, $\mathbf{B'}$, $\mathbf{C'}$ and $\mathbf{D'}$, is higher than their thermal stability. Series $\mathbf{A}$, $\mathbf{C'}$ and $\mathbf{D'}$ exhibit only a nematic phase with a very broad temperature range ($>90°C$), high birefringence (>0.27) and moderate dielectric anisotropy. These good general properties mean that these materials are very promising candidates for application in liquid crystal mixtures for high birefringence LCDs.

References

[1] FERGASON, J. L., 1985, *SID Tech. Dig.*, **16,** 68.
[2] YANG, D. K., DOANE, J. W., YANIV, Z., and GLASSER, J., 1994, *Appl. Phys. Lett.*, **64,** 1905.
[3] DOANE, J. W., VAZ, N. A., WU, B. G., and ZUMER, S., 1986, *Appl. Phys. Lett.*, **48,** 269.
[4] LI, J., HOKE, C., FREDLY, D. S., and BOS, P. J., 1996, *SID Dig '96*, 265.
[5] SUTHERLAND, R. L., NATARAJAN, L. V., TONDIGLIA, V. P., and BUNNING, T. J., 1993, *Chem. Mater.*, **5,** 1533.
[6] BOWLER, C. C., YUAN, H., and CRAWFORD, G. P., 1999, *Mol. Cryst. liq. Cryst.*, **331,** 209.
[7] MCMANAMOR, P. F., WATSON, E. A., DORSCHNER, T. A., and BARNES, L. J., 1993, *Opt. Eng.*, **32,** 2657.
[8] WU, S. T., EFORN, U., GRINBERG, J., and HESS, L. D., 1985, *SID Tech. Dig.*, **16,** 262.
[9] CAMPBELL, N. L., DUFFY, W. L. G., THOMAS, I., WILD, J. H., KELLY, S. M., BARTLE, K., O'NEILL, M., MINTER, V., and TUFFIN, R. P., 2002, *J. mater. Chem.*, **12,** 2706.
[10] SEKINE, C., FUJISAWA, K., IWAKURA, K., and MINAI, M., 2001, *Mol. Cryst. liq. Cryst.*, **364,** 711.
[11] HSU, C. S., SHYU, K. F., CHUANG, Y. Y., and WU, S. T., 2000, *Liq. Cryst.*, **27,** 283.
[12] WU, S. T., HSU, C. S., and SHYU, K. F., 1999, *Appl. Phys. Lett.*, **74,** 344.
[13] WU, S. T., MARGERUM, J. D., HO, M. S., FUNG, B. M., HSU, C. S., CHEN, S. M., and TSAI, K. T., 1995, *Mol. Cryst. liq. Cryst.*, **261,** 79.
[14] WU, S. T., 1986, *Phys. Rev. A*, **33,** 1270.
[15] DEMUS, D., and RICHTER, L., 1978, *Textures of Liquid Crystals* (New York: Weinheim).
[16] GRAY, G. W., and GOODBY, J. W., 1984, *Smectic Liquid Crystals: Textures and Structures* (Philadelphia Heyden).
[17] HSU, C. S., TSAY, K. T., CHANG, A. C., WANG, S. R., and WU, S. T., 1995, *Liq. Cryst.*, **19,** 409.
[18] KHOO, I. C., and WU, S. T., 1993, *Optics and Nonlinear Optics of Liquid Crystals* (Singapore: World Scientific).