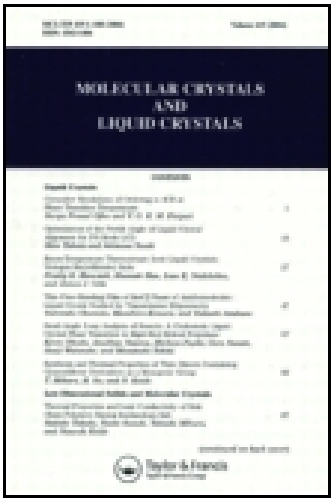


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Liquid Crystal Property of New Fluoro Coumarin Carboxylates

Kittappa M. Mahadevan [a], Hosanagara N. Harishkumar [a], Jagadeesh N. Masagalli [a] & Hosapalya T. Srinivasa [b]

[a] Department of Post Graduate Studies and Research in Chemistry, School of Chemical Sciences, Kuvempu University, Shankaraghatta, Karnataka, India

[b] Raman Research Institute, Bangalore, Karnataka, India

Published online: 22 Jan 2013.

To cite this article: Kittappa M. Mahadevan, Hosanagara N. Harishkumar, Jagadeesh N. Masagalli & Hosapalya T. Srinivasa (2013) Synthesis and Liquid Crystal Property of New Fluoro Coumarin Carboxylates, Molecular Crystals and Liquid Crystals, 570:1, 20-35, DOI: 10.1080/15421406.2012.704824

To link to this article: http://dx.doi.org/10.1080/15421406.2012.704824

Mol. Cryst. Liq. Cryst., Vol. 570: pp. 20–35, 2013

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.704824

Synthesis and Liquid Crystal Property of New Fluoro Coumarin Carboxylates

KITTAPPA M. MAHADEVAN,[1,*] HOSANAGARA N. HARISHKUMAR,[1] JAGADEESH N. MASAGALLI,[1] AND HOSAPALYA T. SRINIVASA[2]

[1]Department of Post Graduate Studies and Research in Chemistry, School of Chemical Sciences, Kuvempu University, Shankaraghatta, Karnataka, India
[2]Raman Research Institute, Bangalore, Karnataka, India

New liquid crystalline 4-alkoxyphenyl-coumarin-3-carboxylates ***6a–e, 7a–g, 8a–e,*** *and* ***9a–e*** *were prepared by reacting various coumarin-3-carboxylic acids* ***5a–d*** *with 4-(alkoxy) phenols* ***4a–g*** *in the presence of 1(3-dimethylaminopropyl-3-ethylcarbodiimide/dimethyl amino pyridine (EDCI/DMAP) as a coupling agent. The structures of the new coumarin derivatives were confirmed by spectral analysis and the liquid crystalline property was established by polarizing optical microscope and by differential scanning calorimetric techniques. The diethyl amine and morpholine were taken as electron-donating and –CF_3 as electron-withdrawing groups at the seventh position of the coumarin-3-carboxylic acids to check the mesomorphic property in all new 4-alkoxyphenyl-coumarin-3-carboxylates. Among them, only 4-alkoxyphenyl-7-triflouromethyl-coumarin-3-carboxylates* ***7a–g*** *exhibited liquid crystalline SmA phase.*

Keywords 4-Alkoxyphenyl-coumarin-3-carboxylate; fluorinated coumarins; focal conic texture; liquid crystal; mesophase

Introduction

Coumarin derivatives exhibit unique photochemical and photophysical properties, hence they become useful in various applications like brightening agents [1] and organic light-emitting diodes (LED) [2], etc. 7-(dimethylamino)-4-methyl coumarin dye doped in mesoporous organosilica (PMO) has been reported as a light-harvesting antenna [3]. Liquid crystalline polymers linked with coumarin moieties have been reported as a new kind of photoalignment layer for liquid crystals in which the photodimerization of the coumarin unit occurs by exposure to UV light, and hence the direction of orientation of the liquid crystals could be adjusted by the polarization direction of the irradiated light [4,5].

Recently, Yanqing Tian et al. [6] have reported the cyclic tetramethyltetrasiloxanes containing coumarin moieties for liquid crystalline property in which the thermal properties of the cyclic tetramethyltetrasiloxanes depend on the nature of the length of the tail ester group at the third position in coumarin moiety. Further, the addition of coumarin units into

*Address correspondence to Kittappa M. Mahadevan, Department of Post Graduate Studies and Research in Chemistry, School of Chemical Sciences, Kuvempu University, Shankaraghatta 577 451, Karnataka, India. Tel.: 0091-9164621170; Fax: 0091 8282 256255. E-mail: mahadevan@kuvempu.ac.in

the polymer/oligomer backbones and nanostructured block copolymers were reported to control the liquid crystal properties of the polymers [4] in which the length and position of tail groups and spacers on the coumarin units affect the liquid crystalline properties. Recently, Haruko Takechi et al. [7] have also studied the mesomorphic and crystalline properties of 7-(diethyl amino)-3-phenylcoumarin-3-alkylcarboxylates. Similarly, several coumarin derivatives have also been reported to exhibit liquid crystal properties and hence possess many related applications [8–10].

Hence, based on our experience in the synthesis of coumarins and other heterocycles [11–33] in this paper, we focused on the synthesis, characterization, and evaluation of liquid crystal property of suitably designed 4-alkoxyphenyl-7-substituted coumarin-3-carboxylates 6a–e, 7a–g, 8a–e, and 9a–e as a new class of compounds.

Experimental

All the chemicals used were of analytical grade. Melting points were recorded in an open capillary and are uncorrected. Purity of the compounds were checked by TLC on silica gel and purified by column chromatography on silica gel (230–400) mesh and as well as by the crystallization method. The structures of newly synthesized compounds were determined by using infrared (IR) spectroscopy (Shimadzu FTIR-8400 spectrophotometer), ^{1}H NMR, ^{13}C NMR, DEPT-135 (Bruker 400 spectrometer), LC-MS, and elemental analysis (Carlo-Erba1106 analyzer). The transition temperature and the associated enthalpy value for all compounds were determined by using differential scanning calorimetry (DSC) (Perkin-Elmer, Model Pyris 1). The textures of mesophase were observed by using a polarizing optical microscope (POM) (Olympus BX50) equipped with a heating stage (Mettler FP82HT) and a central processor (Mettler FP90).

A Typical Procedure for the Synthesis of 2-Oxo-2H-chromene-3-carboxylic acid-4-octyloxy-phenylester (6a)

A mixture of coumarin-3-carboxylic acid **5a** (1 g, 5.25 mmol), 1(3-dimethylaminopropyl-3-ethylcarbodiimide. hydrochloride) (EDCI) (1.1 g, 5.78 mmol), and mole equivalent of DMAP (dimethyl amino pyridine, 0.70 g, 5.78 mmol) were taken in dichloromethane. To this reaction mixture, the 4-alkoxy phenol **4a** (1.28 g, 5.78 mmol) was added, stirred at room temperature for 5 h, and the progress of the reaction was monitored by TLC (ethyl acetate: pet ether 1:1). After the completion of the reaction, the reaction mass was diluted with water and extracted with DCM (25 mL × 2). The organic layer was washed with saturated brine solution and dried over anhydrous sodium sulfate. The crude product (**6a**) thus obtained was purified by column chromatography by using ethyl acetate: petroleum ether (2:8) as eluent followed by recrystallization by ethanol. The 600 mg of yield was obtained as white solid.

The synthesis of intermediate 1-(benzyloxy)-4-alkoxybenzenes **3a–g** and 4-(alkoxy) phenols **4a–g** were reported in literature [36–38] and used here as key intermediates for the synthesis of the new 4-alkoxyphenyl-coumarin-3-carboxylates **6a–e**, **7a–g**, **8a–e**, and **9a–e** compounds to study their liquid crystal properties.

Spectroscopic Details 2-Oxo-2H-chromene-3-carboxylic acid-4-octyloxy-phenylester (6a)

Yield: 94%; mp: 114°C–118°C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.06 (s, 1H), 8.0 (dd, J = 1.20 Hz, 1.6 Hz, 1H), 7.78–7.825 (m, 1H), 7.44–7.50 (m, 2H), 7.16–7.20

(m, 2H), 6.99–7.02 (m, 2H), 3.99 (t, $J = 6.4$ Hz, 2H), 1.69–1.75 (m, 2H), 1.40–1.45 (m, 2H), 1.29–1.33 (m, 8H), 0.86–0.88 (m, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 161.84, 157.02, 156.36, 155.25, 150.65, 144.00, 135.46, 131.04, 125.46, 123.04, 118.32, 117.13, 116.73, 115.53, 68.31, 31.71, 29.21, 29.14, 26.00, 22.55, 14.43 ppm; IR(KBr): $v =$ 1726(aromatic C=O) cm^{-1}, 1759(ester C=O) cm^{-1}; GCMS = 394.1; elemental analysis calcd for $C_{24}H_{26}O_5$ = C, 73.08, H, 6.64% Found: C, 73.66, H, 6.66%.

2-Oxo-2H-chromene-3-carboxylic acid-4-decyloxy-phenylester (6b)

Yield: 96%; mp: 98°C–101°C; ^{1}H NMR(400 MHz, DMSO-d_6): $\delta = 9.05$ (s, 1H), 7.99 (d, $J = 7.60$ Hz, 1H), 7.77–7.81 (m, 1H), 7.44–7.50 (m, 2H), 7.18 (d, $J = 8.8$ Hz, 2H), 7.0 (d, $J = 9.20$ Hz, 2H), 3.98 (t, $J = 6.40$ Hz, 2H), 1.69–1.71 (m, 2H), 1.39–1.44 (m, 2H), 1.27–1.35 (m, 12H), 0.87 (t, $J = 6.40$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 161.97, 157.17, 155.44, 149.68, 143.79, 134.76, 129.71, 124.96, 122.24, 117.87, 117.72, 116.93, 115.11, 68.46, 31.90, 29.58, 29.40, 29.32, 26.05, 22.68, 14.11 ppm; IR(KBr): $v =$ 1728(aromatic C=O) cm^{-1}, 1755(ester C=O) cm^{-1}; GCMS = 422.2; elemental analysis calcd for $C_{26}H_{30}O_5$ = C, 73.91, H, 7.16% Found: C, 73.92, H, 7.18%.

2-Oxo-2H-chromene-3-carboxylic acid-4-dodecyloxy-phenylester (6c)

Yield: 95%; mp: 89°C–92°C; ^{1}H NMR(400 MHz, $CDCl_3$): $\delta = 8.71$ (s, 1H), 7.64–7.71 (m, 2H), 7.34–7.41 (m, 2H), 7.12–7.15 (m, 2H), 6.91–6.93 (m, 2H), 3.96 (t, $J = 6.4$ Hz, 2H), 1.74–1.80 (m, 2H), 1.47–1.43 (m, 2H), 1.27–1.35 (m, 16H), 0.88 (t, $J = 6.8$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 161.97, 157.17, 156.44, 155.45, 149.69, 143.79, 134.77, 129.71, 124.97, 122.24, 117.87, 117.71, 116.93, 115.11, 68.46, 31.92, 29.64, 29.60, 29.40, 29.35, 29.38, 26.05, 22.69, 14.12 ppm; IR(KBr): $v = 1728$(aromatic C=O) cm^{-1}, 1758(ester C=O) cm^{-1}; GCMS = 450.3; elemental analysis calcd for $C_{28}H_{34}O_5$ = C, 74.64, H, 7.61% Found: C, 74.65, H, 7.61%.

2-Oxo-2H-chromene-3-carboxylic acid-4-tetracyloxy-phenylester (6d)

Yield: 98%; mp: 95°C–97°C; ^{1}H NMR(400 MHz, DMSO-d_6): $\delta = 9.05$ (s, 1H), 8.0 (d, $J = 8.0$ Hz, 1H), 7.78–7.82 (m, 1H), 7.44–7.50 (m, 2H), 7.18 (d, $J = 8.8$ Hz, 2H), 7.01 (d, $J = 8.80$ Hz, 2H), 3.99 (t, $J = 6.40$ Hz, 2H), 1.69–1.74 (m, 2H), 1.41–1.43 (m, 2H), 1.29 (m, 18H), 0.87 (t, $J = 6.0$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 161.98, 157.16, 156.45, 155.48, 149.70, 143.81, 134.77, 129.71, 124.97, 122.26, 117.88, 117.72, 116.94, 115.11, 68.46, 31.95, 29.64, 29.62, 29.40, 29.35, 30.38, 26.06, 22.69, 14.14 ppm; IR(KBr): $v = 1727$(aromatic C=O) cm^{-1}, 1759(ester C=O) cm^{-1}; GCMS = 478; elemental analysis calcd for $C_{30}H_{38}O_5$ = C, 75.28, H, 8.00% Found: C, 75.29, H, 8.01%.

2-Oxo-2H-chromene-3-carboxylic acid-4-octadecyloxy-phenylester (6e)

Yield: 93%; mp: 95°C–99°C; ^{1}H NMR(400 MHz, $CDCl_3$): $\delta = 8.71$ (s, 1H), 7.64–7.71 (m, 2H), 7.35–7.42 (m, 2H), 7.12–7.15 (m, 2H), 6.91–6.94 (m, 2H), 3.96 (t, $J = 8.0$ Hz, 2H), 1.74–1.81 (m, 2H), 1.42–1.47 (m, 2H), 1.26 (m, 28H), 0.88 (t, $J = 8.0$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 161.96, 157.17, 156.44, 155.45, 149.68, 143.79, 134.77, 129.71, 124.96, 122.24, 117.71, 116.93, 115.10, 68.46, 31.93, 29.70, 29.61, 29.41, 29.37, 29.28, 26.05, 22.69, 14.12 ppm; IR(KBr): $v = 1726$(aromatic C=O) cm^{-1}, 1759(ester

C=O) cm^{-1}; GCMS = 534.3; elemental analysis calcd for $C_{34}H_{46}O_5$ = C, 76.37, H, 8.67% Found: C, 76.39, H, 8.68%.

2-Oxo-7-trifluoromethyl-2H-chromene-3-carboxylic acid-4-butoxy-pheynylester (7a)

Yield: 94%; mp: 190°C–191°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.69 (s, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.6 (s, 1H), 7.61 (d, 8.0 Hz, 1H), 7.12–7.16 (m, 2H), 6.91–6.95 (m, 2H), 3.97 (t, J = 6.4 Hz, 2H), 1.74–1.81 (m, 2H), 1.46–1.54 (m, 2H), 1.00 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 161.42, 157.30, 155.33, 154.92, 147.95, 143.63, 136.39, 136.03, 135.69, 135.39, 130.39, 124.22, 122.12, 121.47, 120.22, 120.11, 115.15, 114.36, 31.30, 19.23, 13.83 ppm; IR(KBr): v = 1728(aromatic C=O) cm^{-1}, 1757(ester C=O) cm^{-1}; LCMS m/z = 406.36; elemental analysis calcd for $C_{21}H_{17}F_3O_5$ = C, 62.07, H, 4.2% Found: C, 61.90, H, 4.1%.

2-Oxo-7-trifluoromethyl-2H-chromene-3-carboxylic acid-4-hexyloxy-pheynylester (7b)

Yield: 92%; mp: 166°C–170°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (s, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.64 (s, 1H), 7.61 (d, J = 1.2 Hz, 1H),7.12–7.15 (m, 1H), 6.91–6.94 (m, 2H), 3.89 (t, J = 6.80 Hz, 2H), 1.75–1.80 (m, 2H), 1.44–1.47 (m, 2H), 1.26–1.32 (m, 6H), 0.87–0.91 (m, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 161.44, 157.20, 155.40, 155.09, 148.01, 143.59, 135.49, 136.03, 136.69, 135.44, 131.39, 125.22, 123.12, 121.37, 120.22, 120.10, 115.13, 114.68, 32.34, 19.03, 13.93 ppm; IR(KBr): v = 1726(aromatic C=O) cm^{-1}, 1755(ester C=O) cm^{-1}; LCMS m/z = 435(M+1); elemental analysis calcd for $C_{23}H_{21}F_3O_5$ = C, 63.59, H, 4.87% Found: C, 63.52, H, 4.89%.

2-Oxo-7-trifluoromethyl-2H-chromemene-3-carboxylic acid-4-decyloxy-phenylester (7c)

Yield: 96%; mp: 144°C–146°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69 (s, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.64 (s, 1H), 7.61 (d, J = 8.0, 1H),7.13–7.15 (m, 1H), 6.91–6.94 (m, 1H), 6.81(s, 2H), 3.87–3.97 (m, 2H), 1.71–1.80 (m, 2H), 1.39–1.47 (m, 2H), 1.26–1.31 (m, 12H), 0.87–0.91 (t, J = 6.4, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 161.43, 157.34, 155.36, 154.99, 147.95, 143.65, 130.42, 122.14, 121.48, 120.24, 120.12, 115.18, 114.44, 68.49, 31.82, 29.36, 32.25, 26.44, 22.76, 14.10 ppm; IR(KBr): v = 1725(aromatic C=O) cm^{-1}, 1756(ester C=O) cm^{-1}; LCMS m/z = 491(M+1); elemental analysis calcd for $C_{27}H_{29}F_3O_5$ = C, 66.11, H, 5.96% Found: C, 66.10, H, 5.76%.

2-Oxo-7-trifluoromethyl-2H-chromene-3-carboxylic acid-4-dodecyloxy-phenylester (7d)

Yield: 95%; mp: 134°C–138°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69 (s, 1H), 7.79 (d, J = 8.40 Hz, 1H), 7.64 (s, 1H), 7.60 (d, J = 1.20 Hz, 1H), 7.11–7.14 (m, 2H), 6.91–6.94 (m, 2H), 3.95 (t, J = 6.40 Hz, 2H), 1.75–1.82 (m, 2H), 1.42–1.48 (m, 2H), 1.27–1.37 (m, 16H), 0.88 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 161.41, 157.30, 155.35, 154.91, 147.98, 136.35, 136.02, 135.68, 135.35, 130.43, 124.22, 122.12, 121.47, 120.23, 120.08, 115.15, 114.38, 114.35, 68.47, 31.92, 29.64, 29.60, 29.40, 29.35, 29.26, 26.04, 22.69, 14.11 ppm; IR(KBr): v = 1726(aromatic C=O) cm^{-1}, 1759(ester C=O) cm^{-1}; elemental analysis calcd for $C_{29}H_{33}F_3O_5$ = C, 67.17, H, 6.41% Found: C, 67.18, H, 6.43%.

2-Oxo-7-trifluoromethyl-2H-chromene-3-carboxylic acid-4-tetradecyloxy-phenylester (7e)

Yield: 93%; mp: 128°C–130°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.70$ (s, 1H), 7.64–7.71 (m, 1H), 7.34–7.41 (m, 1H), 7.13 (m, 2H), 6.90–6.93 (m, 1H), 6.81 (s, 2H), 3.89 (t, $J = 6.40$ Hz, 2H), 1.72–1.78 (m, 2H), 1.41–1.45 (m, 2H), 1.26–1.31 (m, 20H), 0.88 (t, $J = 6.8$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 161.41, 157.17, 156.43, 155.45, 153.22, 149.68, 143,79, 134.76, 129.70, 124.96, 122.24, 117.87, 117.72, 116.94, 115.41, 115.11, 68.70, 68.46, 31.93, 29.67, 29.60, 29.42, 29.36, 26.07, 22.69, 14.12 ppm; IR(KBr): $v = 1727$(aromatic C=O) cm^{-1}, 1758(ester C=O) cm^{-1}; LCMS $m/z = 547$; elemental analysis calcd for $C_{31}H_{37}F_3O_5$ = C, 68.12, H, 6.82% Found: C, 68.15, H, 6.84%.

2-Oxo-7-trifluoromethyl-2H-chromene-3-carboxylic acid-4-hexadecyloxy-phenylester (7f)

Yield: 98%; mp: 124°C–127°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.69$ (s, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.64 (s, 1H), 7.61 (d, $J = 1.20$ Hz, 1H), 7.13–7.15 (m, 2H), 6.91–6.93 (m, 2H), 3.95 (t, $J = 8.0$ Hz, 2H), 1.75–1.80 (m, 2H), 1.42–1.49 (m, 2H), 1.26–1.34 (m, 24H), 0.88 (t, $J = 6.4$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 161.41, 157.30, 155.32, 154.91, 147.94, 143.62, 136.37, 136.03, 135.69, 135.34, 130.38, 124.21, 122.10, 121.46, 120.21, 120.11, 115.15, 114.39, 114.362, 68.47, 31.92, 26.03, 22.68, 14.10 ppm; IR(KBr): $v = 1726$(aromatic C=O) cm^{-1}, 1753(ester C=O) cm^{-1}; LCMS $m/z = 575$(M+1); elemental analysis calcd for $C_{33}H_{41}F_3O_5$ = C 68.97, H, 7.19% Found: C, 68.58, H, 8.33%.

2-Oxo-7-trifluoromethyl-2H-chromene-3carboxylic acid-4-octadecyloxy-phenylester (7g)

Yield: 94%; mp: 122°C–125°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.69$ (s, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.65 (s, 1H), 7.60 (d, $J = 1.20$ Hz, 1H), 7.14 (d, $J = 2.40$, 2H), 6.92 (d, $J = 2.40$, 2H), 3.95 (t, $J = 6.80$ Hz, 2H), 1.75–1.80 (m, 2H), 1.44–1.48 (m, 2H), 1.26–1.34 (m, 28H), 0.88 (t, $J = 6.4$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 161.42, 157.30, 155.33, 154.92, 147.96, 143.63, 136.03, 135.70, 130.40, 124.22, 122.12, 121.47, 120.22, 120.11, 115.15, 114.40, 68.48, 31.93, 29.70, 29.61, 29.40, 29.37, 29.26, 26.04, 22.69, 14.11 ppm; IR(KBr): $v = 1725$(aromatic C=O) cm^{-1}, 1753(ester C=O) cm^{-1}; LCMS $m/z = 603$(M+1); elemental analysis calcd for $C_{35}H_{45}F_3O_5$ = C, 69.75, H, 7.53% Found: C, 69.77, H, 7.51%.

7-Morpholin-4yl-2-oxo-2H-chromene-3-carboxylic acid-4-octyloxy-phenyl ester (8a)

Yield: 97%; mp: 147°C–148°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.61$ (s, 1H), 7.46 (d, $J = 9.20$ Hz, 1H), 7.10 (d, $J = 2.4$ Hz, 2H), 6.89–6.92 (m, 2H), 6.82 (dd, $J = 2.40$, 8.80 Hz, 1H), 6.68 (d, $J = 2.40$ Hz, 1H), 3.94 (t, $J = 6.8$ Hz, 2H), 3.85 (t, $J = 4.8$ Hz, 4H), 3.40 (t, $J = 4.8$ Hz, 4H), 1.71–1.81 (m, 2H), 1.41–1.47 (m, 2H), 1.23–1.34 (m, 8H), 0.88–0.90 (m, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 162.70, 158.20, 157.52, 156.95, 155.66, 149.92, 144.03, 131.02, 128.71, 122.41, 116.04, 115.58, 115.04, 114.67, 111.28, 110.79, 109.65, 99.45, 68.44, 66.30, 47.03, 31.82, 29.36, 29.28, 29.24, 26.05, 22.65, 14.09 ppm; IR(KBr): $v = 1728$(aromatic C=O) cm^{-1}, 1755(ester C=O) cm^{-1}; GCMS = 480; elemental analysis calcd for $C_{28}H_{33}NO_6$ = C, 70.13, H, 6.94, N, 2.92% Found: C, 70.15, H, 6.96, N, 2.93%.

7-Morpholin-4yl-2-oxo-2H-chromene-3-carboxylic acid-4-decyloxy-phenylester (8b)

Yield: 83%; mp: 150°C–152°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.63$ (s, 1H), 7.48 (d, $J = 8.80$ Hz, 1H), 7.27 (s, 2H), 7.11–7.13 (m, 2H), 6.91 (t, $J = 2.16$ Hz, 1H), 6.69 (d, $J = 2$ Hz, 1H), 3.88 (t, $J = 9.72$ Hz, 4H), 3.42 (t, $J = 9.80$ Hz, 4H), 1.79–1.82 (m, 3H), 1.75–1.77 (m, 3H), 1.44–1.46 (m, 12H), 0.89 (t, $J = 4.0$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 149.91, 158.22, 131.02, 122.41, 115.42, 115.04, 111.27, 109.67, 115.04, 99.48, 68.70, 68.44, 66.31, 47.03, 31.92, 26.05, 22.69, 14.11 ppm; IR(KBr): $\nu = 1728$(aromatic C=O) cm^{-1}, 1759(ester C=O) cm^{-1}; elemental analysis calcd for $C_{30}H_{37}NO_6$ = C, 70.98, H, 7.35, N, 2.76% Found: C, 70.99, H, 7.36%, N, 2.78%.

7-Morpholin-4yl-2-oxo-2H-chromene-3-carboxylic acid-4-dodecyloxy-phenylester (8c)

Yield: 87%; mp: 161°C–163°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.62$ (s, 1H), 7.48 (d, $J = 9.20$ Hz, 1H), 7.13 (d, $J = 4.00$ Hz, 2H), 6.92 (d, $J = 4.40$ Hz, 2H), 6.83 (d, $J = 4.80$ Hz, 2H), 3.88 (t, $J = 5.20$ Hz, 4H), 3.42 (t, $J = 4.80$ Hz, 4H), 1.75–1.80 (m, 3H), 1.46–1.50 (m, 3H), 1.42–1.46 (m, 16H), 0.89 (t, $J = 1.20$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 158.19, 156.94, 149.86, 131.00, 122.40, 115.02, 111.24, 109.66, 99.47, 68.44, 66.31, 47.04, 31.93, 29.70, 29.41, 29.36, 26.05, 22.69, 14.12 ppm; IR(KBr): $\nu = 1726$(aromatic C=O) cm^{-1}, 1758(ester C=O) cm^{-1}; GCMS = 535; elemental analysis calcd for $C_{32}H_{41}NO_6$ = C, 71.75, H, 7.71, N, 2.61% Found: C, 71.79, H, 7.72, N, 2.62%.

7-Morpholin-4yl-2-oxo-2H-chromene-3-carboxylic acid-4-tetradecyloxy-phenylester (8d)

Yield: 89%; mp: 142°C–145°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.63$ (s, 1H), 7.48 (d, $J = 8.8$ Hz, 1H), 7.12 (d, $J = 2.4$Hz, 2H), 6.92 (d, $J = 2.4$ Hz, 1H), 6.9 (s, 1H), 6.83 (d, $J = 4.0$ Hz, 2H), 3.90 (t, $J = 6.8$ Hz, 4H), 3.40 (t, $J = 6.4$ Hz, 4H), 1.75–1.79 (m, 3H), 1.46–1.50 (m, 23H), 0.90 (t, $J = 1.20$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 162.71, 156.86, 149.91, 144.03, 131.02, 128.74, 122.44, 116.04, 115.58, 115.04, 0.69, 111.30, 110.80, 109.65, 46.69, 44.67, 32.47, 47.04, 31.87, 29.38, 29.28, 29.36, 26.05, 22.69, 14.11 ppm; IR(KBr): $\nu = 1726$(aromatic C=O) cm^{-1}, 1758(ester C=O) cm^{-1}; elemental analysis calcd for $C_{34}H_{45}NO_6$ = C, 72.44, H, 8.05, N, 2.48% Found: C, 72.45, H, 8.06, N, 2.49%.

7-Morpholin-4yl-2-oxo-2H-chromene-3-carboxylic acid-4-octadecyloxy-phenylester (8e)

Yield: 95%; mp: 150°C–154°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.61$ (s, 1H), 7.47 (d, $J = 8.8$ Hz, 1H), 7.11 (dd, $J = 2.40$, 6.80 Hz, 2H), 6.90 (dd, $J = 2.00$, 6.80 Hz, 2H), 6.84 (d, $J = 2.4$ Hz, 1H), 6.69 (d, $J = 2.4$ Hz, 1H), 3.95 (t, $J = 6.4$ Hz, 4H), 3.42 (t, $J = 4.8$ Hz, 4H), 1.74–1.80 (m, 2H), 1.42–1.47 (m, 2H), 1.26–1.32 (m, 30H), 0.88 (t, $J = 6.4$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 158.21, 156.95, 149.89, 131.0, 122.41, 115.03, 111.26, 109.67, 99.48, 68.44, 66.31, 47.04, 31.93, 26.05, 22.69, 14.12 ppm; IR(KBr): $\nu =$ 1728(aromatic C=O) cm^{-1}, 1753(ester C=O) cm^{-1}; LCMS $m/z = 620$(M+1); elemental analysis calcd for $C_{38}H_{53}NO_6$ = C, 73.63, H, 8.62, N, 2.26% Found: C, 73.65, H, 8.64, N, 2.27%.

7-Diethylamino-4yl-2-oxo-2H-chromene-3-carboxylic acid-4-octyloxy-phenylester (9a)

Yield: 97%; mp: 108°C–112°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.58$ (s, 1H), 7.39 (d, $J =$ 9.20 Hz, 1H), 7.11 (dd, $J = 2.40$, 6.80 Hz, 2H), 6.90 (dd, $J = 2.00$, 6.80 Hz, 2H), 6.63 (dd, $J = 2.40$, 9.00 Hz, 1H), 6.50 (d, $J = 2.40$ Hz, 1H), 3.95 (t, $J = 6.80$ Hz, 2H), 3.44–3.46 (m, 4H), 1.76–1.81 (m, 2H), 1.43–1.47 (m, 2H), 1.32–1.34 (m, 14H), 0.90 (t, $J = 3.20$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 163.14, 158.79, 158.05, 156.83, 153.24, 150.09, 144.20, 131.32, 122.52, 114.99, 109.68, 107.95, 107.81, 96.80, 68.42, 45.17, 31.82, 29.37, 29.30, 29.24, 26.05, 22.66, 14.10, 12.45 ppm; IR(KBr): $\nu = 1728$(aromatic C=O) cm^{-1}, 1757(ester C=O) cm^{-1}; LCMS $m/z = 466$(M+1); elemental analysis calcd for $C_{28}H_{35}NO_5$ = C, 72.23, H, 7.58, N, 3.01% Found: C, 72.24, H, 7.59, N, 3.03%.

7-Diethylamino-4yl-2-oxo-2H-chromene-3-carboxylic acid-4-decylo-phenylester (9b)

Yield: 90%; mp: 106°C–110°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.59$ (s, 1H), 7.42 (d, $J = 8.8$ Hz, 1H), 7.11 (d, $J = 8.8$ Hz, 2H), 6.91 (t, $J = 8.4$ Hz, 2H), 6.71–6.68 (m, 1H), 6.55 (d, $J = 1.6$ Hz, 1H), 3.95 (t, $J = 6.8$ Hz, 2H), 3.50–3.44 (m, 4H), 1.81–1.74 (m, 2H), 1.47–1.42 (m, 2H), 1.32–1.24 (m, 18H), 0.878 (t, $J = 6.4$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 162.11, 158.77, 158.07, 156.84, 153.23, 150.08, 144.20, 131.31, 122.51, 114.97, 109.62, 107.90, 107.79, 96.77, 68.41, 45.16, 31.92, 29.70, 29.61, 29.41, 29.35, 29.30, 26.05, 22.67, 14.13, 12.44 ppm; IR(KBr): $\nu = 1726$(aromatic C=O) cm^{-1}, 1759(ester C=O) cm^{-1}; GCMS = 493.5; elemental analysis calcd for $C_{30}H_{39}NO_5$ = C, 72.99, H, 7.96, N, 2.84% Found: C, 73.01, H, 7.95, N, 2.83%.

7-Diethylamino-4yl-2-oxo-2H-chromene-3-carboxylic acid-4-dodecyloxy-phenylester (9c)

Yield: 94%; mp: 99°C–101°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.69$ (s, 1H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.64 (s, 1H), 7.60 (d, $J = 8.0$ Hz, 1H),7.16–7.12 (m, 2H), 6.94–6.90 (m, 2H), 3.96 (t, $J = 6.4$ Hz, 2H), 3.50–3.44(m, 4H), 1.75–1.82 (m, 2H), 1.42–1.47 (m, 2H), 1.32–1.28 (m, 22H), 0.88 (t, $J = 6.8$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 161.42, 157.31, 155.43, 154.92, 147.92, 143.62, 130.41, 122.13, 121.48, 120.24, 120.11, 115.17, 114.41, 68.49, 31.91, 29.58, 29.40, 29.31, 29.27, 26.05, 22.68, 14.11 ppm; IR(KBr): $\nu =$ 1726(aromatic C=O) cm^{-1}, 1753(ester C=O) cm^{-1}; GCMS = 521.2; elemental analysis calcd for $C_{32}H_{43}NO_5$ = C, 73.67, H, 8.31, N, 2.68% Found: C, 73.61, H, 8.29, N, 2.66%.

7-Diethylamino-4yl-2-oxo-2H-chromene-3-carboxylic acid-4-tetradecyloxy-phenylester (9d)

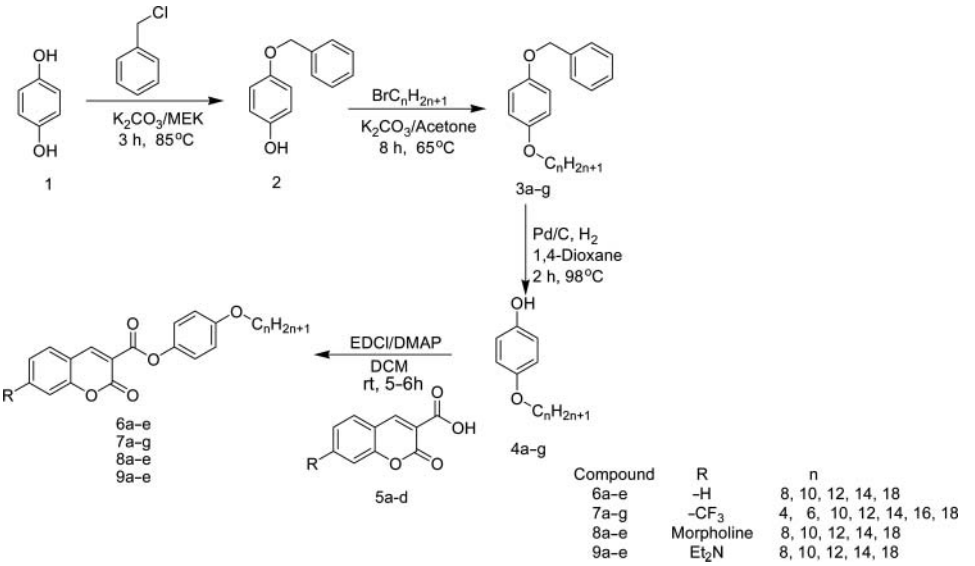
Yield: 97%; mp: 92°C–95°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.69$ (s, 1H), 7.40 (d, $J = 9.20$ Hz, 1H), 7.13 (d, $J = 2.0$ Hz, 2H), 6.91 (d, $J = 2.0$ Hz, 2H), 6.64 (dd, $J = 2.80$, 9.00 Hz, 1H), 6.50 (m, 1H), 3.95 (t, $J = 6.40$ Hz, 2H), 3.41–3.50 (m, 4H), 1.77–1.79 (m, 2H), 1.43–1.48 (m, 2H), 1.20–1.23 (m, 26H), 0.89 (t, $J = 6.8$ Hz, 3H) ppm; IR(KBr): $\nu =$ 1725(aromatic C=O) cm^{-1}, 1755(ester C=O) cm^{-1}; LCMS $m/z = 550$(M+1); elemental analysis calcd for $C_{34}H_{47}NO_5$ = C, 74.28, H, 8.62, N, 2.55% Found: C, 73.10, H, 8.61, N, 2.33%.

7-Diethylamino-4yl-2oxo-2H-chromene-3-carboxylic acid-4-octadecyloxy-phenylester (9e)

Yield: 93%; mp: 120°C–126°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.58$ (s, 1H), 7.39 (d, $J = 8.80$ Hz, 1H), 7.09–7.12 (m, 2H), 6.88–6.91 (m, 2H), 6.62 (dd, $J = 2.40$, 9.20 Hz, 1H), 6.49 (d, $J = 2.0$ Hz, 1H), 3.94 (t, $J = 6.40$ Hz, 2H), 3.46 (q, $J = 6.80$ Hz, 4H), 1.74–1.79 (m, 2H), 1.43–1.47 (m, 2H), 1.23–1.26 (m, 34H), 0.88 (t, $J = 7.20$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 163.12, 158.78, 158.06, 156.83, 153.24, 150.09, 144.20, 131.33, 122.51, 114.98, 109.69, 107.91, 107.80, 96.78, 68.42, 45.17, 31.93, 29.70, 29.61, 29.42, 29.36, 29.31, 26.06, 22.69, 14.12, 12.45 ppm; IR(KBr): $\nu = 1728$(aromatic C=O) cm^{-1}, 1753(ester C=O) cm^{-1}; LCMS $m/z = 606$(M+1); elemental analysis calcd for $C_{38}H_{55}NO_5$ = C, 75.33, H, 9.15, N, 2.31% Found: C, 74.98, H, 9.16, N, 2.30%.

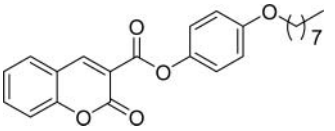
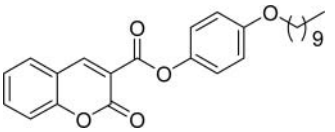
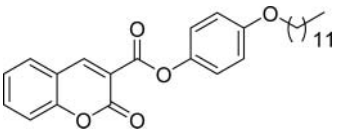
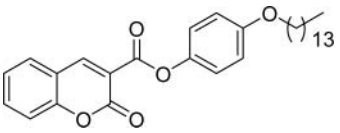
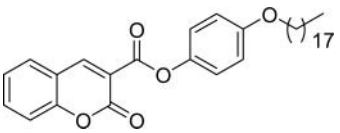
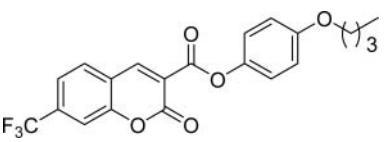
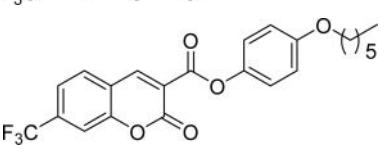
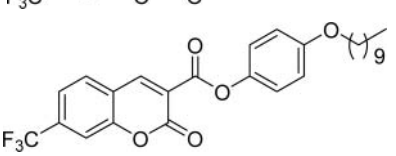
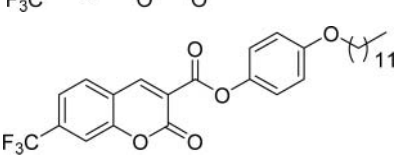
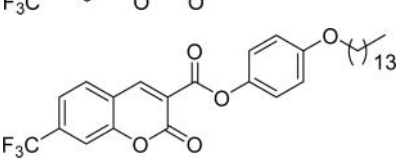
Results and Discussion

In this paper, we prepared a series of four different liquid crystalline 4-alkoxyphenyl-coumarin-3-carboxylates **6a–e, 7a–g, 8a–e,** and **9a–e** by suitably modified synthetic pathway as shown in Scheme 1. In Scheme 1, initially the benzylation of hydroquinone was carried out by using benzyl chloride in the presence of dry potassium carbonate in methyl ethyl ketone as solvent to get the desired 4-(benzyloxy)phenol **2**. Further, the various 1-(benzyloxy)-4-alkoxybenzenes **3a–g** were prepared by reacting compound **2** with different bromoalkylhalides [34] in the presence of dry potassium carbonate in acetone. Further, the deprotection of benzyl group by hydrogenolysis [35] of compound **3** using Pd/C in 1,4-dioxane produced 4-(alkoxy) phenols **4a–g**. Finally, the required various 4-alkoxyphenyl-coumarin-3-carboxylates **6a–e, 7a–g, 8a–e,** and **9a–e** were synthesized by reacting compounds **4a–g** with various coumarin-3-carboxylic acids **5a–d** in the presence EDCI/DMAP as a coupling agent (Table 1).



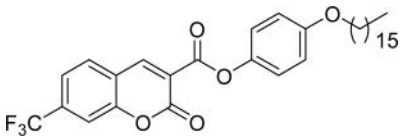
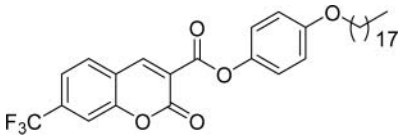
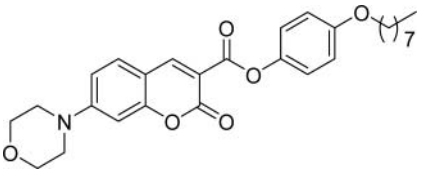
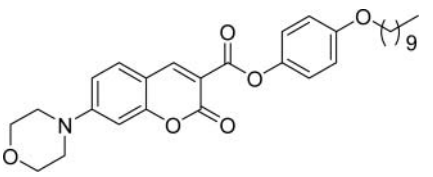
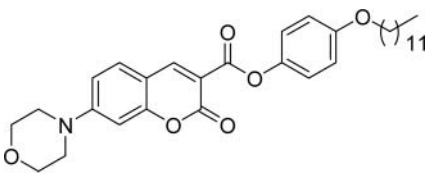
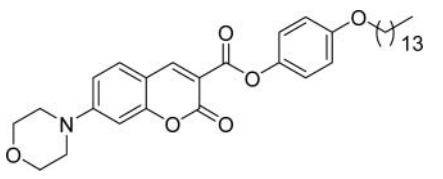
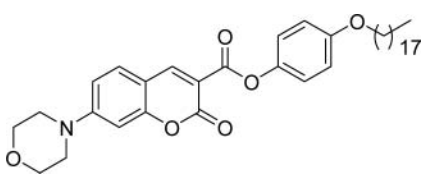
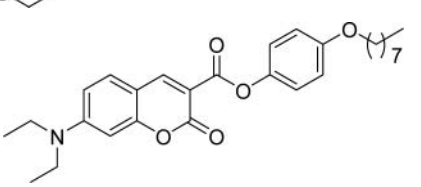
Scheme 1. Synthesis of 4-alkoxyphenyl-coumarin-3-carboxylates.

Table 1. Physical data of 4-alkoxyphenyl-coumarin-3-carboxylates **6a–e**, **7a–g**, **8a–e,** and **9a–e**

Entry	Products	Yields (%)[a]	MP°C
6a		94	114–118
6b		96	98–101
6c		95	89–92
6d		98	95–97
6e		93	95–99
7a		94	190–191
7b		92	166–170
7c		96	144–146
7d		95	134–138
7e		93	128–130

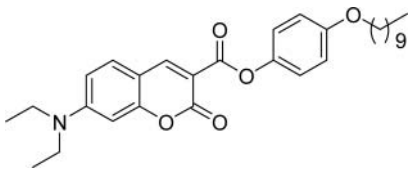
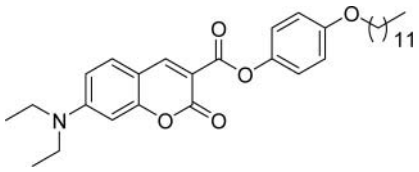
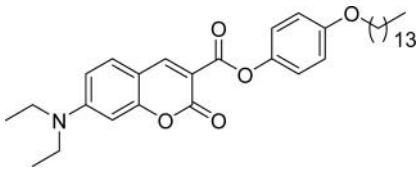
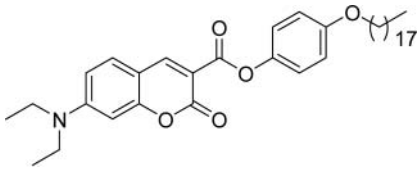
(Continued on next page)

Table 1. Physical data of 4-alkoxyphenyl-coumarin-3-carboxylates **6a–e**, **7a–g**, **8a–e,** and **9a–e** *(Continued)*

Entry	Products	Yields (%)[a]	MP°C
7f		98	124–127
7g		94	122–125
8a		97	147–148
8b		83	150–152
8c		87	161–163
8d		89	142–145
8e		95	150–154
9a		97	108–112

(Continued on next page)

Table 1. Physical data of 4-alkoxyphenyl-coumarin-3-carboxylates **6a–e**, **7a–g**, **8a–e,** and **9a–e** *(Continued)*

Entry	Products	Yields (%)[a]	MP°C
9b		90	106–110
9c		94	99–101
9d		97	92–95
9e		93	120–126

[a]Isolated yield.

Since the present work was mainly focused on investigation of liquid crystal properties of new 4-alkoxyphenyl-coumarin-3-carboxylate derivatives, the four different types of 4-alkoxyphenyl-coumarin-3-carboxylates **6a–e, 7a–g, 8a–e,** and **9a–e** were synthesized in which the morpholine, *N,N*-diethyl amine, and triflouromethane were present as electron-donating and electron-withdrawing groups on the seventh position of the coumarin moiety, while third position carries various long-chain 4-alkoxyphenyl groups. Interestingly, in a series, only the trifluoromethane group present at the seventh position on the 4-alkoxyphenyl-coumarin-3-carboxylates exhibited liquid crystal property as depicted in Fig. 1. All the new compounds were characterized by the IR, ^{1}H NMR, ^{13}C NMR, LC-MS, and elemental analysis.

Liquid Crystal Property

The new series of 4-alkoxyphenyl-coumarin-3-carboxylates **6a–e, 7a–g, 8a–e,** and **9a–e** were studied for liquid crystal property. The liquid crystal property was confirmed by the polarizing optical microscope. The highest electronegativity and smaller size of the fluorine atom led to high polar and less steric effect [8]. Hence, the presence of trifluoromethane group in compounds **7a–g** provides higher values of positive dielectric anisotropy, which

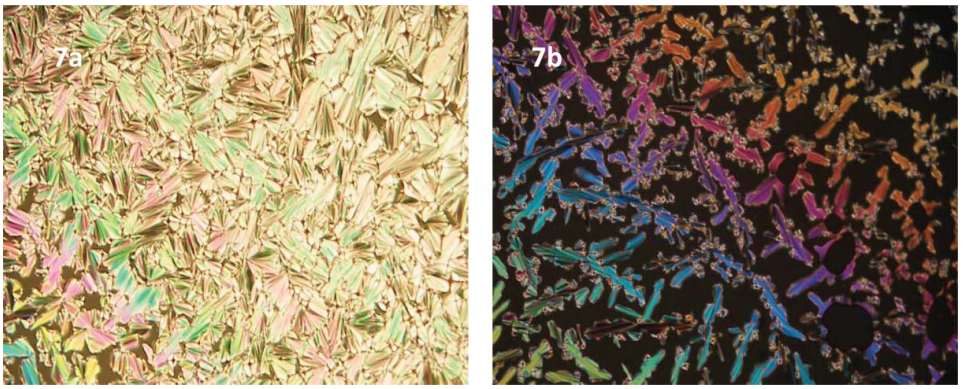


Figure 1. A typical focal conic texture from the isotropic phase for some selected 4-alkoxyphenyl-7-triflouromethyl-coumarin-3-carboxylates **7a** at 206.1°C and **7b** at 202.9°C.

could be the reason for the liquid crystalline property of 4-alkoxyphenyl-7-triflouromethyl-coumarin-3-carboxylates **7a–g**. From the results, we depicted that (Table 2) the fluorine atoms in $–CF_3$ effectively balance the polar effect in favor of steric factor, while substituent such as morpholine and *N,N*-diethyl amine present at the seventh position exhibited poor polarization power that may affect the formation of liquid crystal property in 4-alkoxyphenyl-7-CF_3-coumarin-3-carboxylates. Thus, the 4-alkoxyphenyl-coumarin-3-carboxylate containing—CF_3 substituent at the seventh position was found to form liquid crystals at various transition temperatures depending on the length of the 4-alkoxyphenyl chain (C_4 to C_{18}) on the third position of coumarin ring as shown in Fig. 3. It was observed that the liquid crystal property was reduced when chain length was increased in which the packing layer had been disturbed significantly and hence only 4-alkoxyphenyl-7-triflouromethyl-coumarin-3-carboxylates **7a–g** exhibited liquid crystalline property.

Further, the thermal study revealed that the 4-alkoxyphenyl-7-triflouromethyl-coumarin-3-carboxylates **7a–g** showed wide thermal range of mesophase with increasing

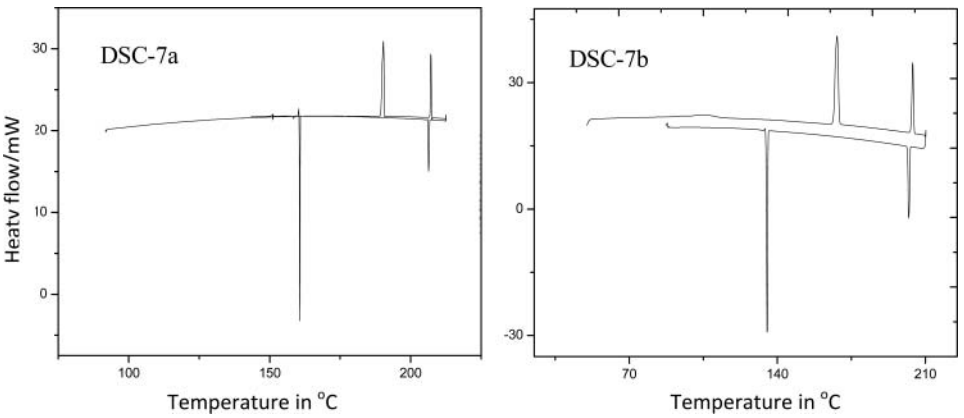


Figure 2. DSC thermograms of some selected compounds **7a** and **7b**.

Table 2. The transition temperatures (°C) and the associated enthalpy values (kJ mol^{-1}) (in italics) for compounds **6a**, **6e**, **7a–g,** and **8e**

Compound S. No./*n*	1st heating scan					1st cooling scan			
	R	State	Trans. temp.	Phase	Trans. temp.	State	Mp/enthalpy	Phase	Trans. temp.
6a 06	H	Cr	117.7/*102.6*	(—)	(—)	(I)	104.8/*104.5*	(—)	(—)
6e 18	H	Cr	120.4/*155.7*	(—)	(—)	(I)	108.1/*108.8*	(—)	(—)
7a 04	CF_3	Cr	190.3/*64.67*	SmA	207.1/*22.73*	(I)	206.4/*21.58*	SmA	160.6 /*52.72*
7b 06	CF_3	Cr	168.2/*56.73*	SmA	203.9/*22.64*	(I)	202.1/*22.20*	SmA	135.1/*47.57*
7c 10	CF_3	Cr	144.7/*39.27*	SmA	199.9/*20.90*	(I)	197.4/*20.90*	SmA	126.7/*41.28*
7d 12	CF_3	Cr	136.0/*35.08*	SmA	197.1/*21.86*	(I)	198.4/*21.45*	SmA	129.4/*41.73*
7e 14	CF_3	Cr	145.6/*45.48*	SmA	200.4/*21.86*	(I)	198.4/*21.45*	SmA	129.4/*41.73*
7f 16	CF_3	Cr	134.2/*31.60*	SmA	191.9/*19.96*	(I)	190.6/*19.68*	SmA	124.9/*31.10*
7g 18	CF_3	Cr	132.3/*29.58*	SmA	185.4/*18.50*	(I)	183.7/*18.15*	SmA	120.5/*44.17*
8e 18	Et_3N	Cr	125.2/*136.3*	(—)	(—)	(I)	98.1/*97.5*	(—)	(—)

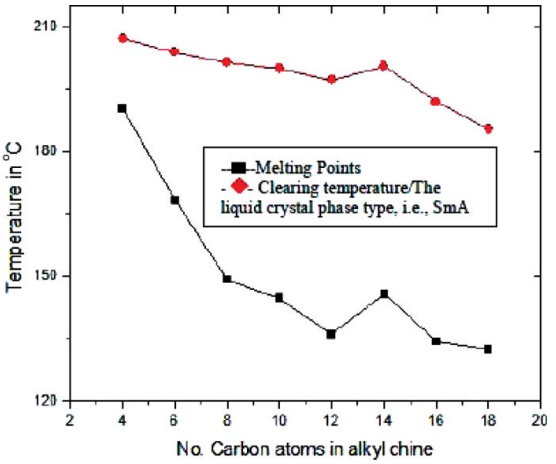


Figure 3. Transition temperatures/number of carbon atoms of compounds **7a–g**.

alkyl chain length as shown in Fig. 2. The smaller the chain length, the range of mesophase was less.

In the 4-alkoxyphenyl-7-triflouromethyl-coumarin-3-carboxylates **7a–g**, where $n = 4$ (**7a**), the crystal was melt at 190°C to form Smectic A phase, which stands up to 207°C and then it changes to isotropic form. The same was reversed on cooling, in which the compound **7a** showed mesophase from 206°C and then it attained crystalline phase at 160°C to give a long range of transition temperatures about 53°C. The typical texture is as shown in Fig. 2. When $n = 18$ (**7g**), the crystal melts at 132°C and then attains mesophase which stands up to 185°C to produce an isotropic phase. The same was observed while cooling the compound **7g** in which it showed mesophase from 184°C, and then it crystallized at 120°C to produce long transition temperature about 65°C when compared to shorter alkoxyphenyl chain (Fig. 2). A similar thermal stability was observed for compounds containing alkoxyphenyl chain from $n = 4$ to 18, respectively. The wide-range thermal stability and their enthalpy data for selected compounds are given in Table 2.

The graphs were plotted by using phase transition temperature versus carbon number of alkoxyphenyl groups as shown in Fig. 3.

Conclusion

A convenient approach to obtain series of 4-alkoxyphenyl-coumarin-3-carboxylates **6a–e, 7a–g, 8a–e,** and **9a–e** has been developed. The PMO studies strongly evidenced that all the trifluoromethane-substituted 4-alkoxyphenyl coumarin-3-carboxylates **7a–g** exhibited SmA phases.

Acknowledgments

The authors are thankful to Mrs. K. N. Vasuda, Raman Research Institute, Bangalore for providing DSC spectral data and Indian Institute of Science, Bangalore for spectral analysis.

References

[1] Zahradnik, M. (1992). *The Production and Application of Fluorescent Brightening Agents*, Wiley & Sons: Chichester.

[2] (a) Zhou, S., Jia, J., Gao, J. R., Han, L., Li, Y., & Sheng, W. (2010). *Dyes and Pigments*, *86*, 123–128. And reference cited in.
(b) Marice-Priscille, B., Bischoff, L., & Garbay, C. (2004). *Angew. Chem. Int. Ed.*, *43*, 3442–3436.
(c) Meng-Ting, L., Chia-Kuo, Y., Wen-Ping, Y., Hsian-Hung, C., Chi-Hung, L., Chih-Hung, T., & Chen, C. H. (2004). *Org. Lett.*, *6*(8), 1241–1244.
(d) Yi-Feng, Sun., Shu-Hong, Xu., Ren-Tao, Wu., Zhu-Yuan, Wang., Ze-Bao, Zheng., Ji-Kun, Li., & Yi-Ping, Cui. (2010). *Dyes and Pigments*, *87*(2), 109–118.

[3] Shinji, I., Osamu, O., Yasutomo, G., Kentaro, O., Masamichi, I., Ken-ichi, Y., Takao, T., & Tadasi, O. (2009). *Angew. Chem. Int. Ed.*, *48*, 4042–4046.

[4] Tian, Y., Akiyama, E., Nagase, Y., Kanazawa, A., Tsutsumi, O., & Ikeda, T. (2004). *J. Mater. Chem.*, *14*, 3524–3531.

[5] Tian, Y. Q., Akiyama, E., Nagase, Y., Kanazawa, A., Tsutsumi, O., & Ikeda, T. (2000). Macromol. *Chem. Phys.*, *201*, 1640–1652.

[6] Tian, Y. Q., Akiyama, E., & Nagase, Y. (2003). *J. Mater. Chem.*, *13*, 1253–1258.

[7] Takechi, H., Kubo, K., Takahashi, H., & Matsumoto, T. (2007). *J. Oleo. Sci.*, *56*(4), 195–200.

[8] Hird, M. (2007). *Chem. Soc. Rev*., *36*, 2070–2095.

[9] Trenor, S. R., Shultz, A. R., Love, B. J., & Long, T. E. (2004). *Chem. Rev.*, *104*(6), 3059–3077.

[10] Nakai, H., Takenaka, S., & Kusabayashi, S. (1983). *Bull. Chem. Soc. Jpn.*, *56*, 3571–3577.

[11] Harishkumar, H. N., Mahadevan, K. M., Kiran Kumar, H. C., & Satyanarayan, N. D. (2011). *A Org. Commun.*, *4*(2), 9–15.

[12] Harishkumar, H. N., Mahapatra, S., Venugopala, K. N., & Mahadevan, K. M. (2011). *Acta Cryst.*, *E67*, o2264.

[13] Rajesha, G., Mahadevan, K. M., Satyanarayan, N. D., & Bhojya Naik, H. S. (2011). Phosphorus, *Sulfur Silicon Relat. Elem.*, *186*, 1733–1743.

[14] Sudhakara, A., Jayadevappa, H., & Mahadevan, K. M. (2011). *Org. Chem.: Indian J.*, *7*(5).

[15] Goudarshivannanavar, B. C., Kiran Kumar, H. C., Jayadevappa, H., Mahadevan, K. M., & Satyanarayana, N. D. (2011). *Org. Chem.: Indian J.*, *7*(4), 228–235.

[16] Rajesha, G., Kiran Kumar, H. C., Bhojya Naik, H. S., & Mahadevan, K. M. (2011). *Org. Chem.: Indian J.*, *7*(6), 365–368.

[17] Rajesha, G., Kiran Kumar, H. C., Bhojya Naik, H. S., & Mahadevan, K. M. (2011). *S. Afr. J. Chem.*, *64*, 88–94.

[18] Varma, P. P., Srinivasa, A., & Mahadevan, K. M. (2011). *Synth. Commun.*, *41*, 2186–2194.

[19] Harishkumar, H. N., Vijaykumar, H., & Mahadevan, K. M. (2010). *Synth. Commun.*, *40*, 3281–3289.

[20] Varma, P. P., Sherigara, B. S., Mahadevan, K. M., & Vijaykumar, H. (2010). *Synth. Commun.*, *40*, 2220–2231.

[21] Rajesha, G., Bhojya Naik, H. S., Harishkumar, H. N., Hosamani, K. M., & Mahadevan, K. M. (2009). *Arkivoc.*, *ii*, 11–19.

[22] Kumara, T. H. S., Mahadevan, K. M., Harishkumar, H. N., Padmashali, B., & Naganagowda, G. (2009). *Phosphorus, Sulfur Silicon Relat. Elem.*, *184*, 1866–1879.

[23] Srinivasa, A., Mahadevan, K. M., Varma, P. P., & Sudhakara, A. (2009). *Phosphorus, Sulfur Silicon Relat. Elem.*, *184*, 1843–1853.

[24] Sudhakara, A., Jayadevappa, H., Mahadevan, K. M., & Vijaykumar, H. (2009). *Synth. Commun.*, *39*, 2506–2515.

[25] Sudhakara, A., Jayadevappa, H., Harishkumar, H. N., & Mahadevan, K. M. (2009). *Lett. Org. Chem.*, *6*, 159–164.

[26] Srinivasa, A., Mahadevan, K. M., & Vijaykumar, H. (2009). *Synth. Commun.*, *39*, 93–101.

[27] Varma, P. P., Sherigara, B. S., Mahadevan, K. M., & Vijaykumar, H. (2009). *Synth. Commun.*, *39*, 158–165.

[28] Srinivasa, A., Mahadevan, K. M., Kumara, T. H. S., & Vijaykumar, H. (2008). *Monatsh. Chem.*, *139*, 1475–1478.
[29] Srinivasa, A., Mahadevan, K. M., & Vijaykumar, H. (2008). *Monatsh. Chem.*, *139*, 255–259.
[30] Srinivasa, A., Mahadevan, K. M., Hosamani, K. M., & Vijaykumar, H. (2008). *Monatsh. Chem.*, *139*, 141–145.
[31] Kiran Kumar, H. C., Mahadevan, K. M., Varma, P. P., & Srinivasa, A. (2012). *Chin. J. Chem.*, *30*, 534–540.
[32] Harishkumar, H. N., Mahadevan, K. M., & Jagadeesh, N. M. (2012). *S. Afr. J. Chem.*, *65*, 5–9.
[33] Mahesh, A. G., Jayadevappa, H., Sudhakara, A., & Mahadevan, K. M. (2008). *Lett. Org. Chem.*, *5*, 628–632.
[34] Sadashiva, B. K., & Prasad, V. (1996). *J. Chem. Soc. Perkin Trans.*, *2*, 755–759.
[35] Radhika, S., Srinivasa, H. T., & Sadashiva, B. K. (2011). *Liq. Cryst.*, *38*(6), 785–792. And reference cited there in.
[36] Bisoyi, H. K., Srinivasa, H. T., & Kumar, S. (2009). *Beilstein J. Org. Chem.*, *5*, 52.
[37] Reddy, R. A., & Tschierske, C. (2006). *J. Mater. Chem.*, *16*, 907–961.
[38] Murata, C., Masuda, T., Kamochim, Y., Todoroki, K., Yoshida, H., Nohta, H., Yamaguchi, M., & Takadate, A. (2005). *Chem. Pharm. Bull.*, *53*, 750–758.