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Liquid Crystals

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Synthesis and mesomorphic properties of three- and four-ring liquid crystals containing cyclohexyl, phenyl and pyridyl units

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Two series of 4-(3-alkoxycarbonylpyridyl-6-ethynyl)phenyl *trans*-4-*n*-alkylcyclohexylcarboxylates and 4-(3-alkoxycarbonylpyridyl-6-ethynyl)phenyl 4-(*trans*-4-*n*-alkylcyclohexyl)benzoates have been prepared. Their mesmorphic properties were observed and measured by polarizing optical microscopy and differential scanning calorimetry. The relationship between structures and properties is discussed, showing that the ferroelectric phase can be observed when chiral terminal chains exist.

1. Introduction

With the development of liquid crystals science and technology, more and more new mesogens have been prepared and studied. Mesogens with only one phenyl ring, which were used first, were replaced by mesogens containing other aromatic or aliphatic rings, such as cyclohexyl, pyridyl, dioxane, etc. Mesogens containing the *trans*-1,4-cyclohexyl ring have been popularly used in many fields. Because of the presence of the nitrogen atom, there is less symmetry in mesogens bearing the pyridyl unit, so they have lower melting points than similar mesogens containing phenyl [1–3]; on the other hand, they possess a high birefringence and many other good advantages [4, 5]. In order to meet the higher quality requirements for materials and observe the relationship between structures and properties, we have combined these two important rings into one molecule. In this paper, the synthesis and the mesomorphic behaviours of novel mesogens containing *trans*-1,4-cyclohexyl, phenyl and pyridyl units are reported; their structures are shown in scheme 1.

2. Experimental

2.1. *Synthesis*

The paths to the target mesogens are outlined in scheme 2. First, 6-chloroniacin was reacted with a normal or branched alkanol in the presence of 1,3-dicyclohexylcarbodiimide (DCC) and *N*,*N*-dimethylaminopyridine (DMAP) as catalyst in anhydrous tetrafuran (THF) solution to obtain 3-alkoxycarbonyl-6-chloropyridine (**1-*n***). Then came the coupling reaction between **1-*n*** and trimethylsilylacetylene under the catalysis of bis(triphenylphosphine)palladium dichloride and copper(I) iodide in anhydrous triethylamine solution; treatment with tetrabutylaminium fluoride (TBAF) in anhydrous THF solution then gave the 3-alkoxycarbonylpyridyl-6-acetylene (**2-*n***).

Trans-4-alkylcyclohexylcarboxylic acid and 4-(*trans*-4-alkylcyclohexyl)benzoic acid were reacted with 4-iodophenol in a similar procedure to that used in the synthesis of compounds **1-*n***, giving 4-iodophenyl *trans*-4-alkylcyclohexylcarboxylate (**3-*m***) and 4-iodophenyl 4-(*trans*-4-alkylcyclohexyl)benzoate (**4-*m***). Finally **3-*m*** and **4-*m*** were coupled with **2-*n***, as in the synthesis of compounds **2-*n***, giving target compounds 4-(3-alkoxycarbonylpyridyl-6-ethynyl)phenyl *trans*-4-alkylcyclohexylcarboxylates (**A-*nm***) and 4-(3-alkoxycarbonylpyridyl-6-ethynyl)phenyl 4-(*trans*-4-alkylcyclohexyl)benzoates (**B-*nm***).

2.2. *Analysis*

The structures of the final products and intermediates were elucidated by a variety of spectral methods. IR spectra were recorded on a PE-983G spectrophotometer, using KBr pellets for solids, or films of liquids. ^{1}H NMR spectra with tetramethylsilane (TMS) as internal standard and ^{19}F NMR spectra with trifluoroacetic acid (TFA) as external standard were recorded on a Bruker 300 spectrometer (300 MHz), a Varian EM360L spectrometer (60 MHz) or a FX-90Q spectrometer (90 MHz). For ^{19}F NMR spectra the high field was positive. MS spectra were measured with a Finnigan-4021 spectroscope using electrical ionization. The phase transition temperatures of the target compounds were measured visually by polarizing optical microscopy (POM) using a polarizing microscope (Olympus PM-6) fitted with a heating stage (Mettler FP-80) and control unit (FP-82); and by differential scanning calorimetry (DSC, Shimadzu

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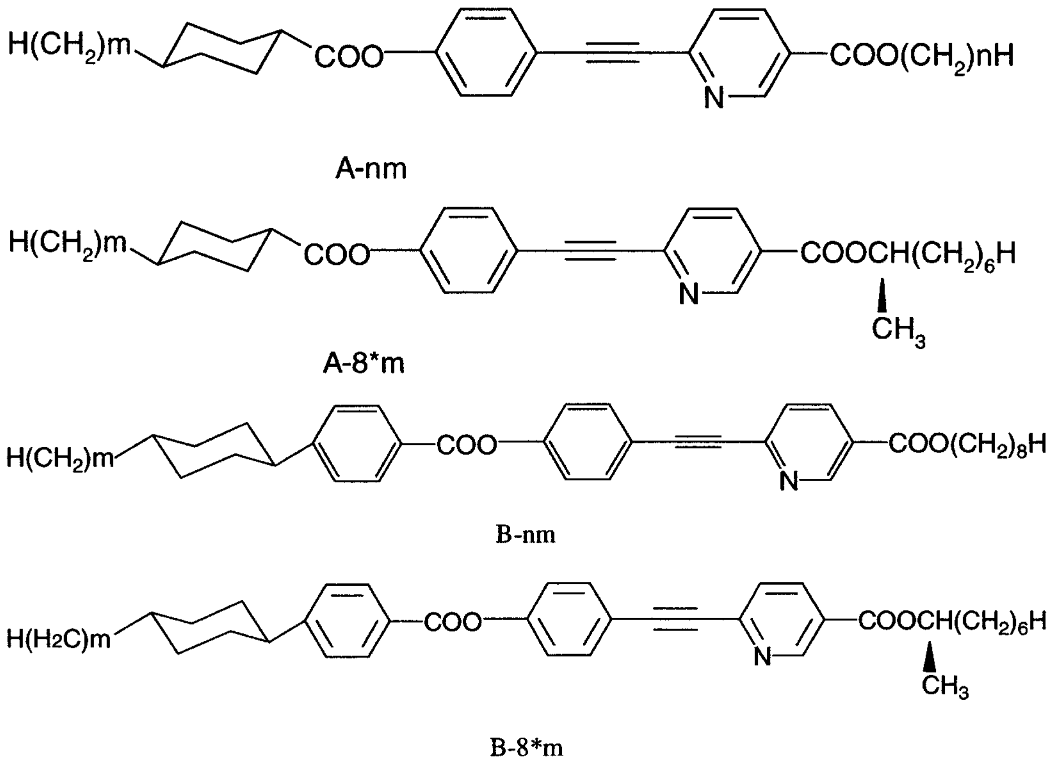


Scheme 1.

DSC-50 calorimeter with a data system, heating and cooling rate 5°C min^{-1}). The transition temperatures reported in this paper were the peak values of the transition on DSC traces. Phase identification was made by comparing the observed textures with those reported in the literature [6, 7].

2.3. *3-n-Pentoxycarbonyl-6-chloropyridine (**1-5**)*

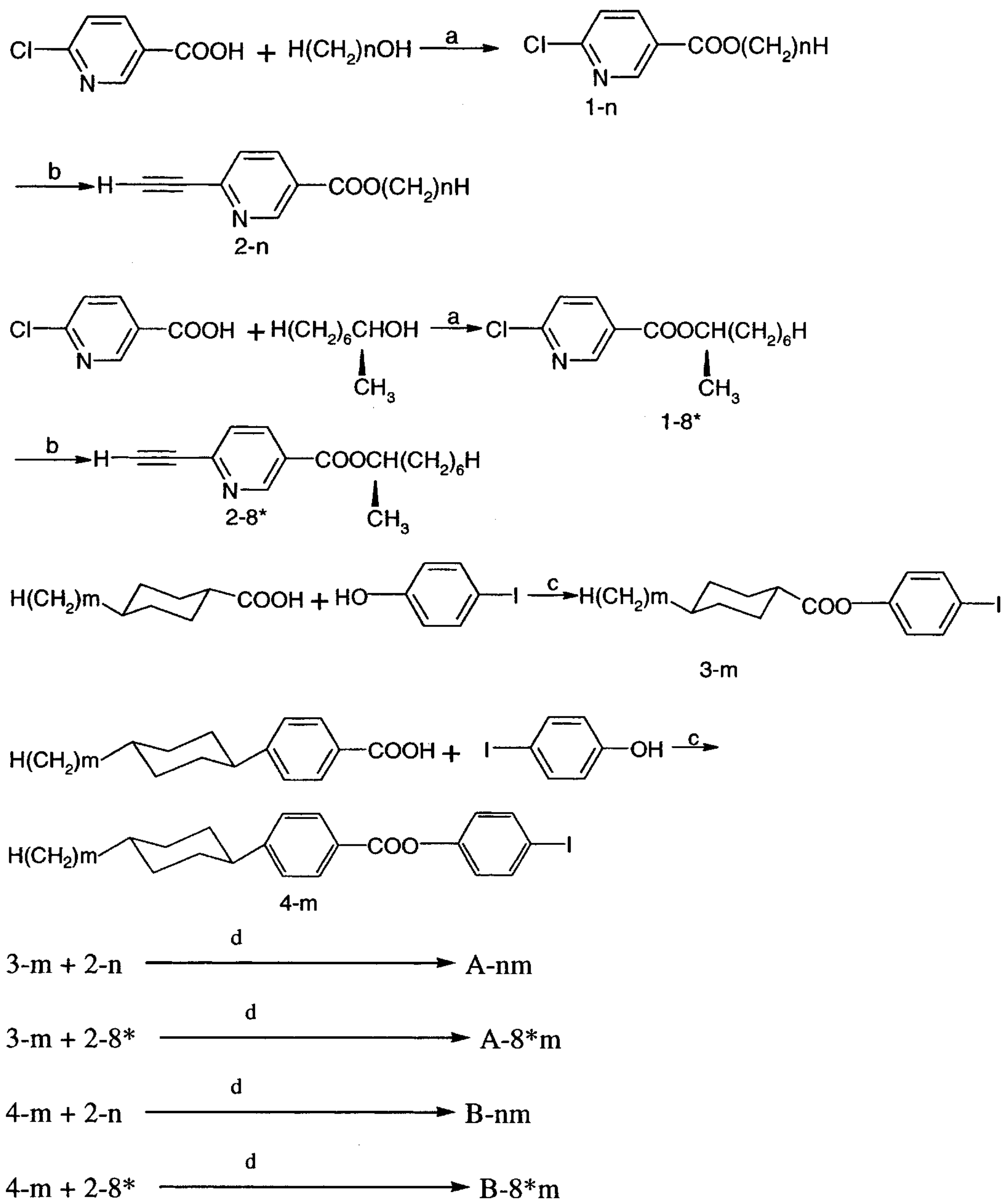
Under dry nitrogen, anhydrous tetrahydrogenfuran (40 ml) was added to a mixture of 6-chloroniacin (1.00 g, 6.29 mmol), *n*-pentanol (5.13 g, 50.34 mmol), DCC (1.46 g, 7.08 mmol) and DMAP (20 mg). The resulting mixture was stirred at room temperature for 48 h. The precipitate formed was filtered and washed with ether; the filtrate was washed with water, then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/ethyl acetate (20/1) as eluent. This gave a white solid; yield 1.073 g, 75%. ^{1}H NMR ($CDCl_3$/TMS) δ (ppm): 0.90 (t, 3H), 1.10–2.00 (m, 6H), 4.20 (t, 2H, $J = 6$ Hz), 7.25 (d, 1H, $J = 9$ Hz), 8.15 (d, 1H, $J = 9$ Hz), 8.90 (s, 1H).

2.4. *3-n-Pentoxycarbonylpyridyl-6-acetylene (**2-5**)*

Under dry nitrogen, anhydrous triethylamine (10 ml) was added to a mixture of compound **1-5** (1.05 g, 4.62 mmol), trimethylsilylacetylene (454 mg, 4.63 mmol), $Pd(PPh_3)_2Cl_2$ (20 mg), CuI (10 mg) and Et_3N (20 ml). The resulting mixture was stirred at 60°C for 24 h. The precipitate formed was filtered and washed with ether; the filtrate was washed with water, then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C) as the eluent. This gave a yellow liquid. TBAF (1.2 g, 4.60 mmol) was added to this liquid with 20 ml THF; the mixture was stirred for 30 min, then solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C) as the eluent. This gave a colourless liquid, yield 0.423 g, 42%. ^{1}H NMR ($CDCl_3$/TMS) δ (ppm): 0.60–2.00 (m, 9H), 3.25 (s, 1H), 4.30 (t, 2H, $J = 6$ Hz), 7.35 (d, 1H, $J = 9$ Hz), 8.05 (d, 1H, $J = 9$ Hz), 8.95 (s, 1H).

2.5. *4-(3-n-Pentoxycarbonylpyridyl-6-ethynyl)phenyl trans-4-propylcyclohexylcarboxylate (**A-53**)*

Under dry nitrogen, anhydrous triethylamine (10 ml) was added to a mixture of compound **2-5** (76 mg, 0.35 mmol), 4-iodophenyl *trans*-4-propylcyclohexylcarboxylate(**3-3**) (130 mg, 0.35 mmol), $Pd(PPh_3)_2Cl_2$ (15 mg), CuI (5 mg) and Et_3N (15 ml). The resulting mixture was stirred at 60°C for 24 h. The precipitate formed was filtered and washed with ether; the filtrate was washed with water, then dried over anhydrous sodium sulfate. The solvent



Reagents and conditions: (a) DCC, cat. DMAP, THF; (b) 1. trimethylsilylacetylene, Pd$(PPh_3)_2Cl_2$, CuI, Et_3N; 2. TBAF, THF; (c) DCC, cat. DMAP, THF; (d) Pd$(PPh_3)_2Cl_2$, CuI, Et_3N.

Scheme 2. Synthesis route.

was removed *in vacuo* and the residue purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20/1) as the eluent. This gave a white solid, which was recrystallized from acetone/methanol to give **A-53** as white flaky crystals; yield 122 mg, 76%. ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ (ppm): 0.85–2.13 (m, 25H), 2.46 (m, 1H), 4.34 (t, 2H, $J = 6.64$ Hz), 7.09 (d, 2H, $J = 8.41$ Hz), 7.57 (d, 1H, $J = 8.22$ Hz), 8.27 (dd, 1H, $J_1 = 8.12$ Hz, $J_2 = 1.83$ Hz), 9.19 (s, 1H). MS (*m*/*z*): 461 (M^+, 4.44). Analysis for $C_{29}H_{35}O_5N$: calc. C 75.46, H 7.64, N 3.03; found C 75.46, H 7.80, N 3.03%. IR (KBr, ν_{max}, cm^{-1}): 2956, 2926, 2860, 2217, 1757, 1718, 1587, 1503, 1466, 1374, 1281, 1205, 1154, 1121, 978, 854, 781.

2.6. *4-[(3-((S)-1-Methylheptoxycarbonylpyridyl)-6-ethynyl)phenyl] 4-(trans-4-n-pentylcyclohexyl)-benzoate (**B58***)*

Procedure as §2.5. ^{1}H NMR ($CDCl_3$/TMS, 90 MHz) δ H (ppm): 0.90 (t, 3H), 1.05–2.70 (m, 34H), 5.20 (m, 1H), 7.30 (d, 2H, $J = 9$ Hz), 7.35 (d, 2H, $J = 9$ Hz), 7.60 (d, 1H, $J = 9$ Hz), 7.65 (d, 2H, $J = 9$ Hz), 8.15 (d, 2H, $J = 9$ Hz), 8.30 (d, 1H, $J = 9$ Hz), 9.25 (s, 1H). MS 607 (M^+, 0.46). Analysis for $C_{40}H_{49}O_4N$: calc. C 79.04, H 8.13, N 2.30; found C 79.09, H 8.38, N 2.06%. IR (KBr, ν_{max}, cm^{-1}): 2922, 2854, 2220, 1746, 1714, 1589, 1508, 1377, 1268, 1209, 1122, 1062, 1014, 878, 780.

Other target compounds and intermediates have satisfactory elementary analyses and appropriate ^1H NMR, IR and MS spectral data.

3. Results and discussions

The phase transition behaviours of target compounds are summarized in the table. All the target compounds exhibit mesophases. Their mesomorphic properties are determined by their liquid crystalline core and two terminal chains. We note the terminal chains of cyclohexyl as R_L and terminal chains of pyridyl as R_R. When the carbon number of R_L is 2, only the nematic phase is observed; when the length of R_L is 3, smectic A and nematic phases both appear. With further increase of R_L, a monotropic or enantiotropic smectic E phase is observed. It can be seen from the table that only when R_L and R_R are of middle length ($R_L = 4$ or 5, $R_R = 6$ or 7), the smectic E phase is mostly stable; however, **A94** does not obey the rule, it exhibits an enantiotropic smectic E phase.

Figures 1 and 2 indicate the different effect of the two terminal chains. Figure 1 indicates the mesomorphic properties of series **A*n*5**; figure 2 describes the mesomorphic properties of series **A7*m***. We see the ascending dependence of clearing point on the parameter *m*, which is also seen in series **A6*m***, **A8*m*** and **A9*m***. A descending dependence of clearing points on the parameter *n* is seen, similarly in series **A*n*3** and **A*n*4**; but **A94** has a clearing point is higher than **A84**, for reasons that are not clear.

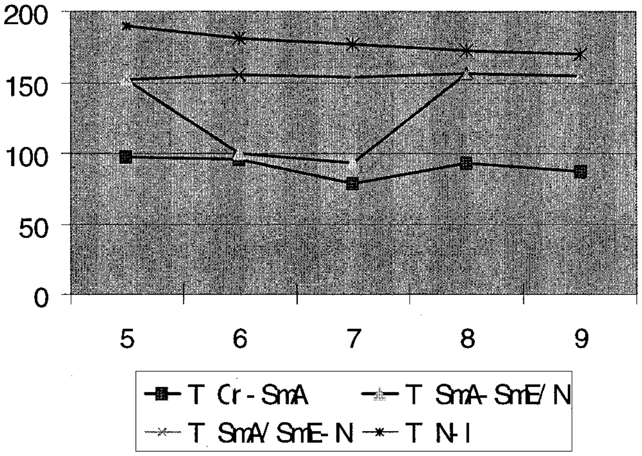


Figure 1. The transition behaviour of compounds **A*n*5**: dependence of transition temperatures on the length of the alkoxy R_R.

Table. Phase transitions of the target compounds. Cr = crystals; SmA = smectic A phase; SmE = smectic E phase; SmC* = chiral smectic C phase; N = nematic phase; I = isotropic liquid; Recr = recrystallization.

	m	*n*	Transition temperatures/°C
A	2	7	Cr 107.8 N 153.4 I 153.2 N 98.6 Recr
A	2	8	Cr 110.1 N 145.6 I 145.2 N 102.3 Recr
A	3	5	Cr 88.8 SmA 113.4 N 189.7 I 189.1 N 111.5 SmA 74.5 Recr
A	3	6	Cr 92.9 SmA 123.8 N 180.9 I 180.3 N 122.7 SmA 81.0 Recr
A	3	7	Cr 88.0 SmA 119.9 N 175.1 I 174.9 N 119.4 SmA 73.1 Recr
A	3	8	Cr 89.5 SmA 125.0 N 170.6 I 170.2 N 125.7 SmA 78.1 Recr
A	3	9	Cr 82.1 SmA 125.6 N 167.0 I 166.0 N 125.1 SmA 71.3 Recr
A	4	5	Cr 91.3 SmA 137.5 N 187.6 I 186.7 N 135.7 SmA 89.6 SmE 71.5 Recr
A	4	6	Cr 94.9 SmE 106.2 SmA 140.1 N 177.5 I 176.8 N 139.2 SmA 89.9 SmE 74.7 Recr
A	4	7	Cr 81.1 SmE 91.1 SmA 139.1 N 174.3 I 174.2 N 138.6 SmA 82.6 SmE 65.9 Recr
A	4	8	Cr 94.9 SmA 142.5 N 169.7 I 169.2 N 141.8 SmA 79.7 SmE 68.8 Recr
A	4	9	Cr 93.1 SmE 102.7 SmA 140.1 N 177.5 I 177.0 N 139.4 SmA 89.9 SmE 72.9 Recr
A	5	5	Cr 97.8 SmA 152.5 N 189.5 I 188.9 N 151.7 SmA 97.9 SmE 78.5 Recr
A	5	6	Cr 95.7 SmE 99.7 SmA 155.7 N 181.6 I 180.9 N 155.1 SmA 95.7 SmE 70.1 Recr
A	5	7	Cr 78.8 SmE 93.3 SmA 154.0 N 176.9 I 176.7 N 153.8 SmA 89.9 SmE 66.9 Recr
A	5	8	Cr 93.0 SmA 156.1 N 173.3 I 173.0 N 155.8 SmA 88.5 SmE 71.0 Recr
A	5	9	Cr 86.8 SmA 154.7 N 170.3 I 169.8 N 153.8 SmA 84.9 SmE 63.1 Recr
A	3	8*	Cr 92.3 SmC* 113.3 I 112.5 SmC* 73.9 Recr
A	4	8*	Cr 95.7 SmC* 115.7 I 114.7 SmC* 83.5 SmE 73.3 Recr
A	5	8*	Cr 90.2 SmC* 121.4 I 120.6 SmC* 79.3 SmE 74.7 Recr
B	3	8	Cr 122.2 SmA 236.2 N 264.7 I 273.5 N 235.2 SmA 114.7 Recr
B	3	8*	Cr 122.2 SmC* 226.0 N 233.7 I 232.9 N 225.3 SmC* 106.4 Recr
B	5	8*	Cr 126.5 SmC* 218.5 I 217.4 SmC* 107.5 Recr

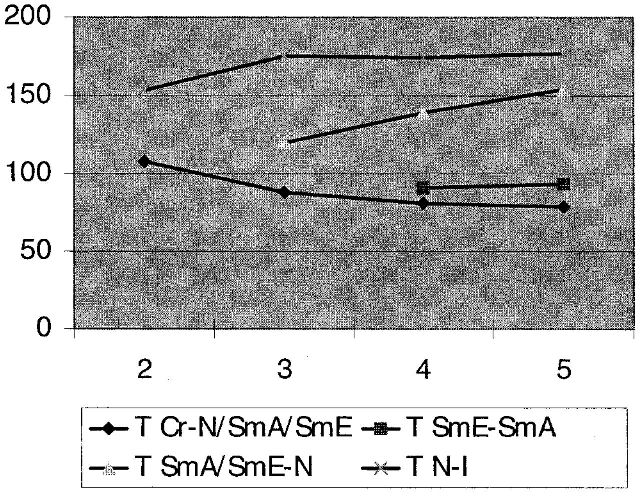


Figure 2. The transition behaviour of compounds **A7*m***: dependence of transition temperatures on the length of the alkoxy R_L.

When another phenyl was introduced into the liquid crystalline core, **B83** was prepared; it has much higher melting and clearing points than **A83**, and a wide mesophase range because of strong conjugation and a large length/width ratio. Because of potential application in ferroelectric liquid crystal displays, a chiral terminal chain was introduced into this structure and series **A8*_m_** and **B8*_m_** were prepared. A broad chiral smectic C phase (ferroelectric phase) was observed. In particular, **A8*3** and **B8*5** show only the SmC* phase.

In conclusion, the synthesis and mesomorphic properties of these new liquid crystals give us a better understanding of the structure–property relationships in liquid crystals. They also have potential application as display materials.

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