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Liquid Crystals

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Novel glass-forming liquid crystals. II. Systems containing 1-phenyl-2-(6-cyanonaphth-2-yl)ethyne as a high optical birefringence moiety

Hongqin Shi^a; Shaw H. Chen^b

^a Department of Chemical Engineering, Gavett Hall, University of Rochester, Rochester, New York, U.S.A. ^b Laboratory for Laser Energetics, University of Rochester, Rochester, New York, U.S.A.

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Novel glass-forming liquid crystals

II. Systems containing 1-phenyl-2-(6-cyanonaphth-2-yl)ethyne as a high optical birefringence moiety

by HONGQIN SHI and SHAW H. CHEN*

Department of Chemical Engineering, Gavett Hall, University of Rochester,
Rochester, New York 14627-0166, U.S.A.; and
Laboratory for Laser Energetics, University of Rochester, 250 East River Road,
Rochester, New York 14623-1299, U.S.A.

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A new series of glass-forming molecular materials have been synthesized that incorporate 1-phenyl-2-(6-cyanonaphth-2-yl)ethyne as the high optical birefringence nematogenic moiety and a diphenylacetylenic group as part of the chiral moiety containing (*S*)-(–)-1-phenylethanol. To facilitate the preparation of chiral nematic systems, the key intermediate, i.e. 1,3,5-cyclohexanetricarboxylic anhydride chloride, was synthesized and characterized. The thermotropic and optical properties of all products and the blends prepared therefrom were characterized by polarizing optical microscopy, differential scanning calorimetry, and UV-VIS-NIR spectrophotometry. It was found that all the resultant molecular materials readily form glasses with a T_g of around 60°C while showing no residual crystallinity below T_g or tendency toward crystallization by heating above T_g . Furthermore, binary blends showed a decreasing degree of miscibility at an increasing extent of structural dissimilarity with the all-chiral/all-nematic systems exhibiting significant phase separation at a chiral mole fraction of 0.16.

1. Introduction

Because of inherent optical anisotropy due to mesogenic ordering, liquid crystals have emerged as a technologically important class of materials potentially applicable to a wide range of electro-optical, optoelectronic, and optical information storage technologies [1–3]. To ensure long-term stability of desired mesogenic alignments, several approaches have been explored: (i) vitrification of thermally annealed liquid crystalline polymers, which has become a well-known technique, (ii) *in situ* photopolymerization of prealigned monomers [4–6] and (iii) low molar mass glass-forming liquid crystals [7–15]. We have been actively pursuing the third approach in view of the relative ease of processing into a large, uniform area due to the low melt viscosity and the possibility of inducing reversible phase/mesophase transitions, a versatility not permitted by the *in situ* polymerization approach.

Although a few low molar mass glass-forming liquid crystals have been reported in the literature, it remains unclear what structural features are conducive to achieving mesomorphic ordering without introducing crystallinity, which in general is undesirable for practical

applications. Since theoretical or computational methodologies do not promise any predictive tools for molecular design purposes in the foreseeable future, we have undertaken an experimental approach to glass-forming abilities of thermotropic liquid crystals through material synthesis and characterization. One objective is to enrich an empirical database which will serve as the basis for improving the understanding of vitrification and mesophase formation by low molar mass compounds.

In the first paper in this series [16], we reported nematic systems containing cyanotolan, cyanobiphenyl, and methoxybiphenylbenzoate mesogenic groups as well as chiral nematic systems, containing one of the above mesogens plus chiral moieties including (*S*)-(–)-1-phenylethylamine, (*S*)-(+)–1,3-butanediol, or (1*R*, 3*S*)-(+)–camphoric acid. The present work was designed to test the feasibility of employing a recently reported high optical birefringence nematogen [17] and a new chiral group containing diphenylacetylenic group to form nematic and chiral nematic glass-forming liquid crystals. A generic methodology was also established for the synthesis of cyclic chiral nematic systems using 1,3,5-cyclohexanetricarboxylic anhydride chloride as the intermediate. The thermotropic/optical properties and the miscibility between the resultant liquid crystals were all

* Author for correspondence.

characterized by polarizing optical microscopy, differential scanning calorimetry (DSC), and UV-VIS-NIR spectrophotometry.

2. Experimental

2.1. Reagents and chemicals

4-Iodophenol (99 per cent), 3,4-dihydro-2*H*-pyran (97 per cent), (trimethylsilyl)acetylene (98 per cent), copper(I) iodide (99.999 per cent), bis(triphenylphosphine)palladium(II) chloride (98 per cent), oxalyl chloride (98 per cent), pyridinium toluene-4-sulphonate, PPTS (98 per cent), diethyl azodicarboxylate, DEAD (> 90 per cent), triphenylphosphine, PPh₃ (99 per cent), 2-bromoethanol (95 per cent), (*S*)-(-)-1-phenylethanol (99 per cent), 6-methoxy-2-naphthonitrile (98 per cent), boron tribromide (1.0 M solution in methylene chloride), caesium carbonate (99.9 per cent), *N*-phenyltrifluoromethanesulphonimide (i.e. *N*-phenyltriflamide) (99 per cent), 4-iodobenzoyl chloride (97 per cent), thionyl chloride (99 per cent), 4-(dimethylamino)pyridine (99 per cent), acetic anhydride (99.2 per cent), 1,3,5-cyclohexanetricarboxylic acid (99 per cent, *cis* isomer and a mixture of *cis* and *trans* isomers), and silica gel (40 μm flash chromatography packing), were all used as received from Aldrich Chemical Company. Solvent THF (100.0 per cent, J. T. Baker) was dried by refluxing over sodium spheres in the presence of benzophenone, and methylene chloride (> 99.5 per cent, J. T. Baker) was dried by distillation over calcium hydride.

2.2. Synthesis of glass-forming low molar mass molecular materials

Four glass-forming low molar mass compounds depicted as **I** through **IV** in figure 1 were synthesized according to schemes I through III following the experimental procedures as described below. Note that compound **IV** was synthesized from **II-4** following scheme I with procedures similar to those for compound **I** from **I-8**.

2.2.1. Compound I

I-1: A solution of 4-iodophenol (74.4 g) and dihydropyran (84.1 g) in anhydrous methylene chloride (800 ml) containing pyridinium toluene-4-sulphonate, PPTS, (17.5 g) was stirred at room temperature for 5 h. The solution was diluted with ether and washed several times with half-saturated brine to remove the catalyst. Upon evaporation of the solvent, recrystallization from ethanol was accomplished to yield compound **I-1** (90 g, 85 per cent).

I-2: To a mixture of compound **I-1** (25 g) and (trimethylsilyl)acetylene (12 g) in triethylamine (300 ml) were added bis(triphenylphosphine)palladium dichloride (1 g) and copper(I) iodide (0.133 g). The reaction mixture

was stirred under nitrogen at room temperature for 3 h, and the solvent was removed under reduced pressure. The residue was extracted with petroleum ether (500 ml), and the solution was filtered, washed with water and then dried over anhydrous MgSO₄. Upon evaporating the solvent *in vacuo*, the residue was purified by flash chromatography using 1 : 15 diethyl ether/petroleum ether as the eluent. The pale yellowish solid was recrystallized from ethanol to yield compound **I-2** (15 g, 66 per cent).

I-3: 5.0 g compound **I-2** and anhydrous potassium carbonate (1.0 g) were dissolved in 100 ml methanol and stirred for 2 h. The solvent was then evaporated off, and the residue was dissolved in 200 ml petroleum ether followed by washing with water and drying over anhydrous MgSO₄. Recrystallization from ethanol gave compound **I-3** (3.62 g, 98 per cent).

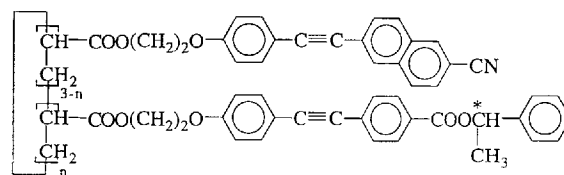
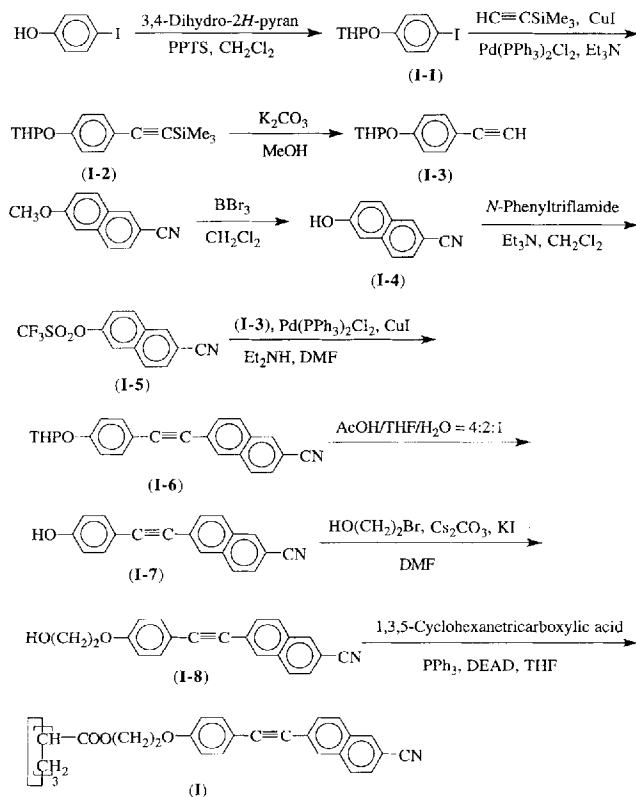
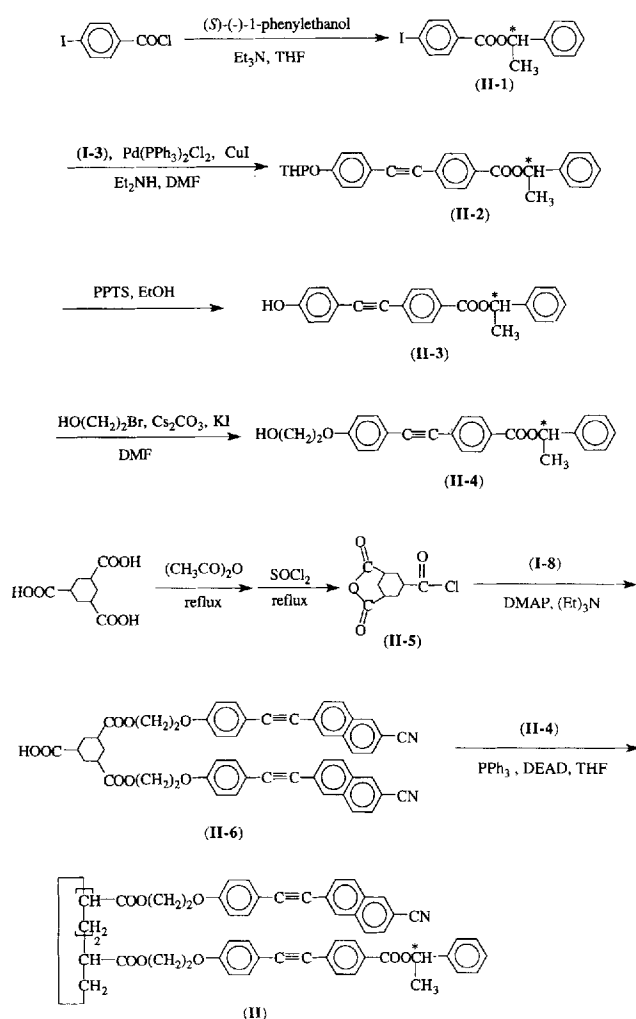


Figure 1. Chemical structures of glass-forming compounds **I** to **IV**. **I**, $n = 0$; **II**, $n = 1$; **III**, $n = 2$; **IV**, $n = 3$.



Scheme 1.



Scheme 2.

I-4: A solution of boron tribromide in dry methylene chloride (1 M, 100 ml, 100 mmol) was added dropwise to a stirred, cooled (-78°C) solution of 6-methoxy-2-naphthonitrile (10.0, 54.6 mmol) in dry methylene chloride under argon. The stirred mixture was allowed to warm to room temperature over a period of 9 h. The mixture was cooled to -10°C , water was added slowly, and the solid was collected by filtration. Recrystallization from ethanol gave compound **I-4** (8.8 g, 95 per cent).

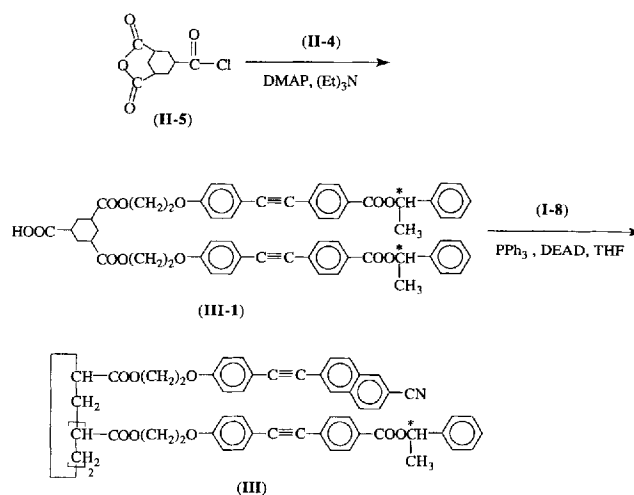
I-5: A solution of *N*-phenyltriflamide (19 g, 53.2 mmol) in dry methylene chloride (200 ml) was added dropwise to a stirred, cooled (-78°C) solution of compound **I-4** (8 g, 47.3 mmol) in dry methylene chloride (200 ml) and dry triethylamine (14 ml, 100 mmol) under argon. The stirred mixture was allowed to warm to room temperature overnight. The mixture was washed with aqueous sodium carbonate, and the separated aqueous layer was washed with methylene chloride. The combined organic extracts

were washed with water and dried with MgSO_4 . The solvent was removed *in vacuo* and the residue was purified by flash column chromatography with methylene chloride as the eluent. The obtained product was recrystallized from ethanol/water to give **I-5** (13.5 g, 95 per cent).

I-6: Dimethylformamide (115 ml) and diethylamine (67 ml) were added successively into a mixture of compound **I-5** (10 g, 33.2 mmol), compound **I-3** (6.71 g, 33.2 mmol), bis(triphenylphosphine)palladium(II) chloride (0.466 g, 0.664 mmol) and copper(I) iodide (0.252 g, 1.33 mmol). The mixture was stirred for 1 h at room temperature under argon. The solution was diluted with water and extracted with methylene chloride (3×200 ml). The combined extracts were washed with aqueous solution of sodium carbonate and then dried with MgSO_4 . The solvent was evaporated *in vacuo*. The residue was purified by flash chromatography with methylene chloride as the eluent. The crude product was recrystallized from ethanol/ethyl acetate to give compound **I-6** (9.8 g, 84 per cent).

I-7: Tetrahydrofuran (40 ml), water (20 ml) and acetic acid (80 ml) were successively added to compound **I-6**. The mixture was stirred at 60°C for 4 h. The solvent was partly removed *in vacuo*, and compound **I-7** was recrystallized from the remaining solvent (6.5 g, 95 per cent).

I-8: To a solution containing compound **I-7** (1.5 g, 5.6 mmol), caesium carbonate (1.82 g, 5.6 mmol), and a few crystal of potassium iodide in dimethylformamide (10 ml) was added dropwise 2-bromoethanol (0.47 ml, 5.6 mmol) at 80°C . The reaction mixture was stirred at 80°C for 24 h before dilution with methylene chloride (100 ml). The solution was washed with water and dried with MgSO_4 . The solvent was removed *in vacuo*, and the residue was purified by flash chromatography with methylene chloride/acetone (10:1) as the eluent. The



Scheme 3.

crude product was recrystallized from ethanol to give compound **I-8** (1.06 g, 61 per cent).

I: To a stirred solution containing compound **I-8** (0.5 g, 1.60 mmol), triphenylphosphine (0.419 g, 1.60 mmol), and 1,3,5-cyclohexanetricarboxylic acid (75 per cent *cis* and 25 per cent *trans*, 0.105 g, 0.48 mmol) in dry tetrahydrofuran (10 ml) was added dropwise a solution of diethyl azodicarboxylate (0.196 ml, 1.60 mmol) in dry tetrahydrofuran (10 ml) under argon atmosphere. The reaction mixture was stirred for 3 h before evaporating off the solvent. The residue was purified by flash chromatography with methylene chloride/acetone (40:1) as the eluent. The crude product was dissolved in methylene chloride (2 ml) and precipitated from methanol to give compound **I** (0.48 g, 91 per cent).

2.2.2. Compound II

II-1: To a solution of 4-iodobenzoyl chloride (5.0 g, 18.8 mmol) in dry tetrahydrofuran (40 ml) was added a solution of (*S*)-(-)-1-phenylethanol (2.29 g, 18.8 mmol) in tetrahydrofuran (20 ml) and triethylamine (2.62 ml, 18.8 mmol) at room temperature. The mixture was stirred for 4 h before dilution with methylene chloride (200 ml). The solution was washed with water and then dried over anhydrous MgSO₄. After removing the solvent *in vacuo*, the solid product **II-1** emerged from the residual viscous liquid (5.9 g, 89 per cent).

II-2: Dimethylformamide (30 ml) and diethylamine (15 ml) were added successively into a mixture of compound **II-1** (4.90 g, 13.9 mmol), compound **I-3** (2.81 g, 13.9 mmol), bis(triphenylphosphine)palladium(II) chloride (0.195 g, 0.278 mmol) and copper(I) iodide (0.105 g, 0.557 mmol). The mixture was stirred for 1 h at room temperature under argon. The solution was diluted with water and extracted with methylene chloride (3 × 50 ml). The combined extracts were washed with aqueous solution of sodium chloride and then dried with MgSO₄. The solvent was evaporated *in vacuo*. The residue was purified by flash chromatography with methylene chloride as the eluent. The product was further purified by recrystallization from ethanol/ethyl acetate to give compound **II-2** (4.8 g, 81 per cent).

II-3: A solution of compound **II-2** (4.5 g, 10.6 mmol) and pyridinium *p*-toluenesulfonate (5.0 g, 19.9 mmol) in ethanol (50 ml) was stirred at 60°C for 4 h before dilution with methylene chloride (100 ml). The solution was washed with aqueous sodium chloride solution and water and then dried with MgSO₄. The solvent was removed *in vacuo*. The residue was purified by flash chromatography with methylene chloride/acetone (10:1) as the eluent to give compound **II-3** (3.5 g, 97 per cent).

II-4: To a solution containing compound **II-3** (1.5 g, 4.39 mmol), caesium carbonate (1.42 g, 4.39 mmol) and a few crystal of potassium iodide in dimethylformamide

(10 ml) was added dropwise 2-iodoethanol (0.34 ml, 4.39 mmol) at 80°C. The reaction mixture was stirred at 80°C for 24 h and diluted with methylene chloride (100 ml). The solution was washed with water and dried with MgSO₄. The solvent was removed *in vacuo* and the residue was purified by flash chromatography with methylene chloride/acetone (10:1) as the eluent. The obtained product was recrystallized from ethanol to give compound **II-4** (0.7 g, 41 per cent).

II-5: 1,3,5-Cyclohexanetricarboxylic acid (*cis*, 10.0 g, 46.3 mmol) was heated at reflux with acetic anhydride (100 ml) for 24 h. The solvent was then distilled off and removed completely under high vacuum. After the residue was refluxed with thionyl chloride (40 ml) for 12 h, the excess thionyl chloride was distilled out and removed under vacuum. Crude product was obtained by vacuum distillation (2 mm Hg, 160°C). Recrystallization from dry toluene gave compound **II-5** (5.32 g, 53 per cent).

II-6: Dry triethylamine (0.134 ml, 0.96 mmol) was added to a solution of compound **II-5** (0.104 g, 0.48 mmol), compound **I-8** (0.3 g, 0.96 mmol) and 4-(dimethylamino)pyridine (DMAP) (0.006 g, 0.048 mmol) in dry THF (15 ml). After stirring for 24 h under a nitrogen atmosphere, the reaction mixture was diluted with methylene chloride (50 ml) and neutralized with hydrochloric acid. The organic layer was washed with half-saturated brine and then dried over MgSO₄. The solvent was removed *in vacuo*, and the solid residue was purified by flash chromatography with methylene chloride/methanol (9:1) as the eluent to give compound **II-6** (0.306 g, 78 per cent).

II: To a stirred solution containing compound **II-6** (0.133 g, 0.165 mmol), compound **II-4** (0.064 g, 0.165 mmol) and triphenylphosphine (0.048 g, 0.18 mmol) in dry tetrahydrofuran (10 ml) was added dropwise a solution of diethyl azodicarboxylate (0.022 ml, 0.18 mmol) in dry tetrahydrofuran (10 ml) under an argon atmosphere. The reaction mixture was stirred for 3 h before evaporating off the solvent. The solid residue was purified by flash chromatography with methylene chloride/acetone (40:1) as the eluent. The crude product was dissolved in methylene chloride (2 ml) for precipitation from methanol to give compound **II** (0.172 g, 88 per cent).

2.2.3. Compound III

III-1: To a solution of compound **II-5** (0.061 g, 0.282 mmol), compound **II-4** (0.218 g, 0.564 mmol) and 4-(dimethylamino)pyridine (DMAP) (0.004 g, 0.033 mmol) in dry THF (15 ml) was added dry triethylamine (0.079 ml, 0.564 mmol). After stirring for 24 h under a nitrogen atmosphere, the reaction mixture was diluted with methylene chloride (50 ml) and neutralized with hydrochloric acid. The organic layer was washed

with half-saturated brine and then dried over MgSO_4 . The solvent was removed *in vacuo* and the residue was purified by flash chromatography with methylene chloride/methanol (9:1) as the eluent to yield compound **III-1** (0.191 g, 71 per cent).

III: To a stirred solution containing compound **III-1** (0.140 g, 0.147 mmol), compound **I-8** (0.055 g, 0.176 mmol) and triphenylphosphine (0.039 g, 0.176 mmol) in dry tetrahydrofuran (10 ml) was added dropwise a solution of diethyl azodicarboxylate (0.018 ml, 0.176 mmol) in dry tetrahydrofuran (10 ml) under an argon atmosphere. The reaction mixture was stirred for 3 h before evaporating off the solvent. The residue was purified by flash chromatography with methylene chloride/acetone (40:1) as the eluent. The crude product was dissolved in methylene chloride (2 ml) for precipitation from methanol to give compound **III** (0.129 g, 70 per cent).

2.2.4. Compound IV

IV: To a stirred solution containing compound **II-4** (0.515 g, 1.334 mmol), 1,3,5-cyclohexanetricarboxylic acid (*cis*, 0.087 g, 0.404 mmol) and triphenylphosphine (0.35 g, 1.334 mmol) in dry tetrahydrofuran (10 ml) was added dropwise a solution of diethyl azodicarboxylate (0.163 ml, 0.1334 mmol) in dry tetrahydrofuran (10 ml) under an argon atmosphere. The reaction mixture was stirred for 3 h before evaporating off the solvent. The residue was purified by flash chromatography with methylene chloride/acetone (40:1) as the eluent. The crude product was dissolved in methylene chloride (2 ml) for precipitation from methanol to give compound **IV** (0.487 g, 91 per cent).

2.3. Characterization techniques

A Hitachi high performance liquid chromatography, HPLC, system comprising an L-2000 metering pump and an L-4200 UC-VIS absorbance detector equipped with an LiChrosorb[®] column (RP-18, 10 μm ,) was employed to determine the number of components and purity of the products. The purity levels of all final products were found to be better than 99 per cent based on HPLC analysis. Chemical structures of glassy nematics and chiral nematics were elucidated with elemental analysis (performed by Oneida Research Services, Inc. in Whitesboro, New York), the FTIR (Nicolet 20 SXC) and proton NMR (QE-300, GE) spectroscopic techniques. The chiral mole fractions in the chiral nematic systems were determined via an integration of appropriate proton NMR signals (typically 1 wt % in CDCl_3). Thermal transition temperatures were determined by differential scanning calorimetry, DSC (DuPont 910 interfaced with Thermal Analyst 2100 System at a nitrogen purge of $50 \text{ cm}^3 \text{ min}^{-1}$) with mesophase textures identified under a polarizing optical

microscope (Leitz Orthoplan-Pol) equipped with a hot stage (FP 82, Mettler) plus a central processor (FP 80, Mettler). For the determination of selective reflection wavelength, a spectrophotometer (Perkin-Elmer Lambda 9) was employed to gather a UV-VIS-NIR spectrum at room temperature on an optical element containing a chiral nematic material with a thickness on the order of 10 μm sandwiched between a pair of glass substrates (Corning 7059 near zero alkali baria alumina borosilicate glass with a refractive index of 1.53 at 589.3 nm). The optical element was first heated above the clearing temperature of the material followed by shearing to induce alignment and subsequently annealed at 95 per cent of its clearing temperature for 1 h.

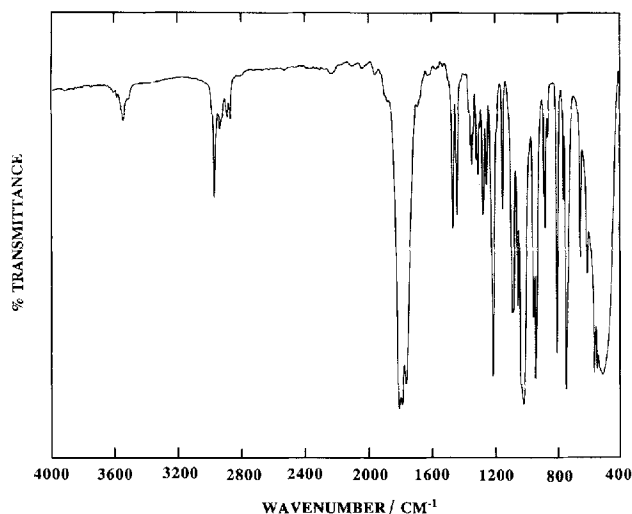


Figure 2. FTIR absorption spectrum of a thin film prepared from neat intermediate **II-5**.

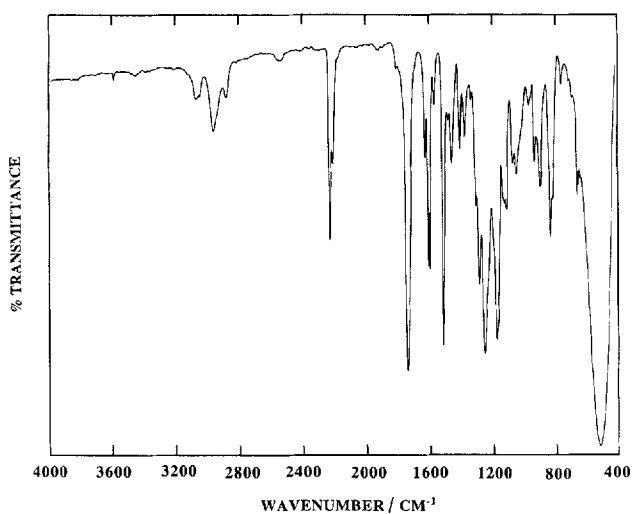


Figure 3. FTIR absorption spectrum of a thin film prepared from neat compound **I**.

3. Results and discussion

It was demonstrated previously that a chiral nematic system can be readily synthesized by a stoichiometric control of chiral vs nematic precursors. However, with precursors **I-8** and **II-4** as depicted in schemes 1 and II, respectively, this approach was found to give a complex mixture that could not be adequately separated and purified. Thus, one unique feature of the present work is the preparation of 1,3,5-cyclohexanetricarboxylic anhydride chloride, i.e. **II-5**, serving as an intermediate for a facile synthesis of chiral nematic systems. The structure of **II-5** was verified with elemental analysis (see table 1) and FTIR spectrum shown in figure 2, in which the cyclic anhydride is identified by the C=O stretching bands at 1764 and 1808 cm^{-1} and acid chloride by the C=O stretching band 1788 cm^{-1} ; note that these identifications were made in accordance with [18]. The FTIR spectrum of compound **I** is reproduced in figure 3 to verify the presence of the C≡C and C≡N stretching bands at 2206 and 2225 cm^{-1} , respectively. The elemental analysis results, as compiled in table 1, and the proton NMR spectral data, as presented in table 2, are all consistent with the chemical structures depicted as compounds **I** to **IV** in figure 1.

Prior to determining the property of selective wavelength reflection inherent to cholesteric mesomorphism, it is of interest to inquire into the extent of light absorption in the visible region of the spectrum. Thus, UV spectra of compounds **I** and **IV** dissolved in methylene chloride at high dilution were collected in figure 4, thereby confirming the absence of light absorption above 380 nm. Thermotropic properties were characterized by a combi-

nation of hot stage polarizing optical microscopy and DSC with stability against thermal decomposition over relevant temperature range verified by TGA. Specifically, nematic and cholesteric mesomorphism was identified by threaded textures and oily streaks, respectively, under polarizing optical microscope. As a way to fine tune optical properties, compound **I** was blended with compounds **II**, **III** and **IV** at ratios yielding the desired chiral mole fraction, x (defined as the number of moles of chiral side arms divided by the sum of the number of moles of chiral side arms and that of nematic side arms), for both thermal and optical characterizations. Thermograms collected from the second heating scan at $20^\circ\text{C min}^{-1}$, following cooling from beyond the clearing point, T_c , to below T_g , are presented in figure 5 to 7. Key thermal data are compiled in table 3 to highlight the following observations:

- (i) All pure components and blends were found to form glasses with no residual crystallinity below T_g or tendency toward crystallization upon heating across and beyond T_g .
- (ii) Under hot stage polarizing optical microscope, compounds **I** and **II** showed nematic and cholesteric mesomorphism, respectively, between T_g and T_c , whereas compounds **III** and **IV** were found to be non-mesomorphic.
- (iii) Because of the greater degree of structural similarity in **I/II** than **I/III**, the former blend showed sharper clearing transitions than the latter, and both blends showed T_c decreasing with chiral content.

Table 1. Elemental analysis results (per cent) for intermediate **II-5** and compounds **I** to **IV**.

	Compound														
	I			II			III			IV			II-5		
	C	H	N	C	H	N	C	H	N	C	H	N	C	H	N
Calculated	78.47	4.63	3.81	77.68	4.94	2.39	76.98	5.21	1.12	76.36	5.45	0.00	49.88	4.16	0.00
Observed	78.06	4.61	3.72	77.68	4.98	2.32	76.80	5.27	1.05	76.57	5.60	0.01	49.97	4.20	0.00

Table 2. Proton NMR spectral data of compounds **I** to **IV** in CDCl_3 .

Compound I	Compound II	Compound III	Compound IV
1.60–3.04 [m, 9H, $-\text{CH}_2\text{CH}-$ on cyclohexane ring]	1.55–2.98 [m, 9H, $-\text{CH}_2\text{CH}-$ on cyclohexane ring and m, 3H, $-\text{CH}_3$]	1.60–3.00 [m, 9H, $-\text{CH}_2\text{CH}-$ on cyclohexane ring and m, 6H, $-\text{CH}_3$]	1.52–2.50 [m, 9H, $-\text{CH}_2\text{CH}-$ on cyclohexane ring and m, 9H, $-\text{CH}_3$]
4.25 [t, 6H, $-\text{CH}_2\text{O}-$]	4.17 [t, 6H, $-\text{CH}_2\text{O}-$]	4.20 [t, 6H, $-\text{CH}_2\text{O}-$]	4.18 [t, 6H, $-\text{CH}_2\text{O}-$]
4.50 [t, 6H, $-\text{CO}_2\text{CH}_2-$]	4.44 [t, 4H, $-\text{CO}_2\text{CH}_2-$]	4.45 [t, 4H, $-\text{CO}_2\text{CH}_2-$]	4.26 [t, 6H, $-\text{CO}_2\text{CH}_2-$]
6.94–8.22 [m, 30H, arom, ^1Hs]	4.50 [t, 2H, $-\text{CO}_2\text{CH}_2-$] 6.14 [m, 1H, $-\text{CO}_2\text{CH}-$] 6.88–8.16 [m, 33H, arom, ^1Hs]	4.50 [t, 2H, $-\text{CO}_2\text{CH}_2-$] 6.15 [m, 2H, $-\text{CO}_2\text{CH}-$] 6.89–8.20 [m, 36H, arom, ^1Hs]	6.14 [m, 3H, $-\text{CO}_2\text{CH}-$] 6.87–8.02 [m, 39H, arom, ^1Hs]

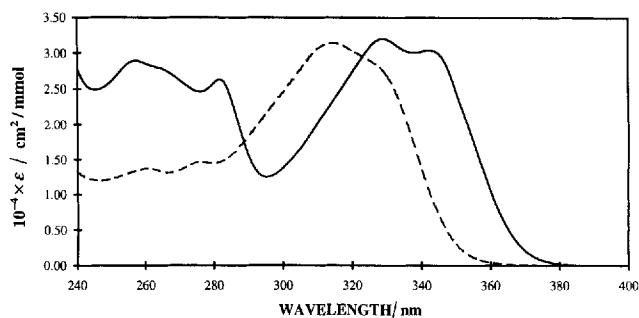


Figure 4. UV absorption spectra of compound **I**, solid curve, and **IV**, broken curve, dissolved in methylene chloride.

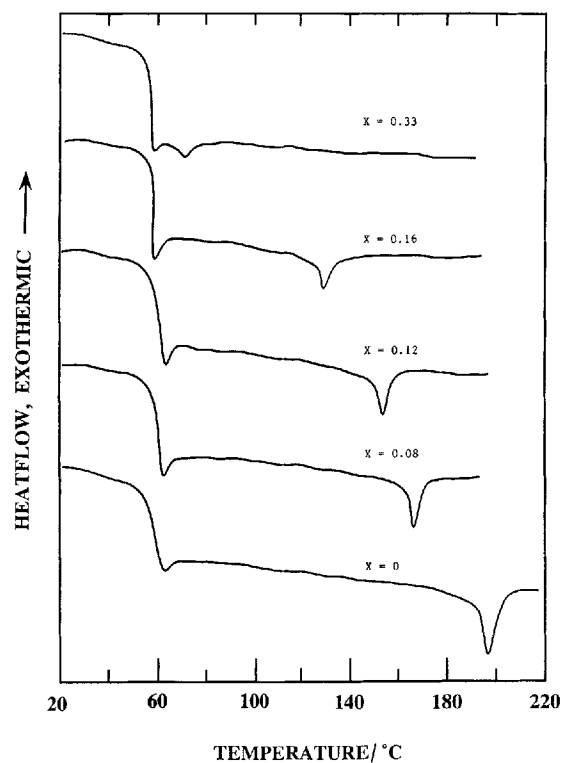


Figure 5. DSC thermogram of the **I/III** system, second heating scan at $20^\circ\text{C min}^{-1}$.

- (iv) The **I/III** system at $x = 0.16$ sheared at 120°C then annealed at 90°C yielded oily streaks across the entire optical element $1/2$ inch in diameter. However, a transition to cholesteric fan-shaped textures was observed upon annealing at 130°C for 1 h. In addition, small portions of excess non-mesogenic **III** seemed to have separated from the chiral-nematic blend as shown in figure 8(a).
- (v) The increased degree of structural dissimilarity in the **I/IV** system, in comparison to the other two blends, resulted in T_c being rather insensitive to chiral content, an indication of saturation at

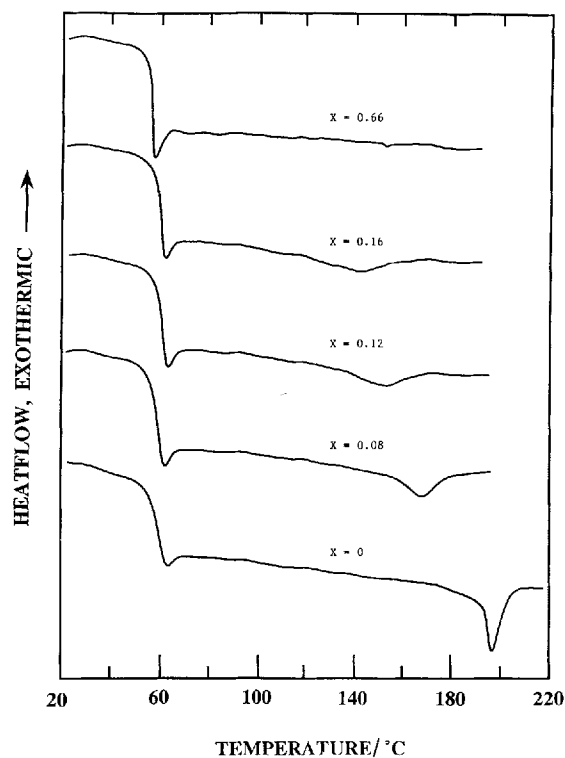


Figure 6. DSC thermogram of the **I/III** system, second heating scan at $20^\circ\text{C min}^{-1}$.

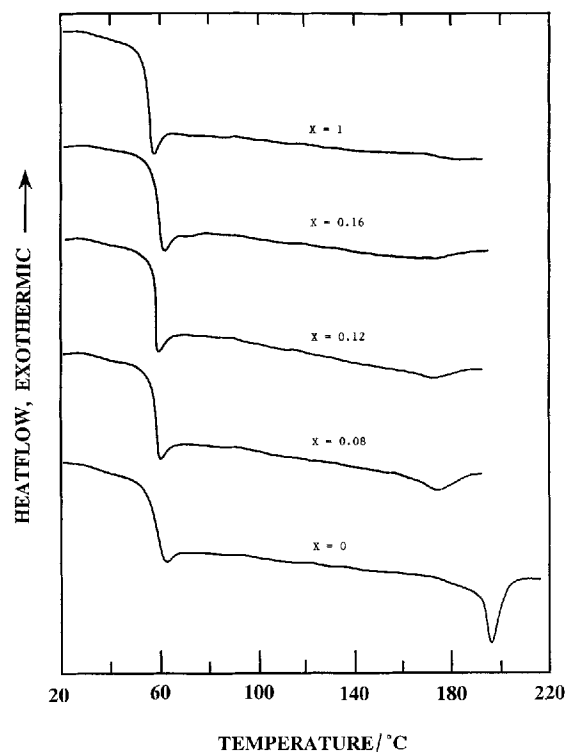


Figure 7. DSC thermogram of the **I/IV** system, second heating scan at $20^\circ\text{C min}^{-1}$.

Table 3. Thermotropic and optical properties of compounds **I** to **IV** and blends of **I** with **II**, **III** and **IV**.

System	x^\dagger	$T_g/^\circ\text{C}^\ddagger$	$\Delta C_p W \text{ g}^{-1}$	$T_c/^\circ\text{C}$	$\Delta H_c/\text{J g}^{-1}$	$\lambda_{\text{R}}/\text{nm} $
I	0.00	60	0.13	197	2.72	NA
II	0.33	61	0.16	72	0.34	¶
III	0.66	59	0.17	non-mesomorphic	NA	NA
IV	1.00	58	0.17	non-mesomorphic	NA	NA
I/II	0.16	62	0.15	135	1.00	508
	0.12	62	0.15	155	1.51	713
	0.08	62	0.15	169	1.36	1024
I/III	0.16	63	0.16	146	1.62	570
	0.12	62	0.15	155	1.28	709
	0.08	61	0.16	170	1.26	1116
I/IV	0.16	62	0.15	≈ 170	§	1611
	0.12	62	0.15	178	§	1611
	0.08	62	0.14	180	1.26	1631

† Chiral mole fraction in pure compounds or mixtures.

‡ Located at mid-point of step change.

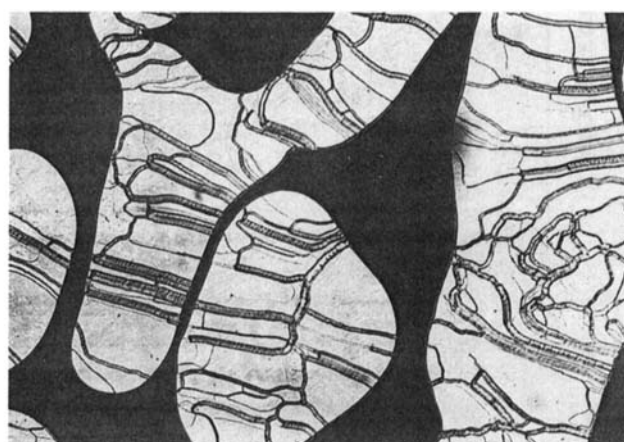
§ Clearing peaks too broad to quantify ΔH_c .

$||$ Located at the centre of the selective wavelength reflection band.

$¶$ Cholesteric mesophase identifiable under polarizing optical microscope but selective wavelength reflection band not observable on optical element with UV-VIS-NIR spectrophotometry because of the proximity of T_c to T_g .



(a)



(b)

Figure 8. Optical micrograph under polarizing optical microscope at a magnification factor of $\times 80$: (a) chiral-nematic mixture **I/III** at $x = 0.16$ annealed at 130°C for 1 h showing cholesteric fan-shaped texture with phase-separated nonmesogenic **III** which was absent when the element was first prepared by annealing at 90°C ; (b) chiral-nematic mixture **I/IV** at $x = 0.16$ annealed at 130°C for 1 h showing oily streaks coexisting with excess, non-mesogenic **IV**.

$x \approx 0.12$. To further support this point, an optical element was prepared using a mixture with an overall $x = 0.16$ and annealed at 130°C for 1 h before quenching to room temperature. The optical micrograph shown in figure 8 (b)) reveals the coexistence of oily streaks and amorphous regions due to excess compound **IV**, which is not the case with the **I/II** blend at x up to 0.16 or the **I/III** blend at x up to 0.12.

(vi) Observed values for the heat capacity change accompanying glass transition, ΔC_p , and the enthalpy of clearing, ΔH_c , of all the pure components and blends are close to previously reported glass-forming liquid crystals [16].

Optical elements prepared according to the procedures described in § 2 were characterized with UV-VIS-NIR

spectrophotometry to determine the selective reflection wavelength, λ_R , for compound I blended with compounds II, III and IV that exhibited cholesteric mesomorphism. The results are included in the last column of table 2. It is noted that λ_R in the visible region is readily achievable in both the I/II and I/III systems. In contrast, it was not possible to tune λ_R into the visible region with the I/IV system, suggesting a limitation on miscibility which is consistent with the comment made in (v) above.

4. Summary

A high optical birefringence nematogenic moiety, 1-phenyl-2-(6-cyanonaphth-2-yl)ethyne, and a chiral moiety comprising (S)-(-)-1-phenylethanol and diphenylacetylene were employed to synthesize a series of novel molecular materials. Although all-nematic and all-chiral systems were readily prepared, 1,3,5-cyclohexanetricarboxylic anhydride chloride was synthesized as an intermediate to facilitate the preparation of chiral-nematic systems. Characterizations of pure components and selected binary blends led to the following observations:

- (i) All pure components and blends were found to form glasses without residual crystallinity below T_g or a tendency to crystallize upon heating across T_g .
- (ii) Pure components containing two or three chiral side arms did not show mesomorphism, while the ones containing two and three nematic side arms showed cholesteric and nematic mesomorphism, respectively
- (iii) The miscibility between pure components was clearly dictated by structural similarity with the all-nematic/all-chiral system showing significant phase separation at a chiral mole fraction of 0.16 based on observations by polarizing optical microscopy, DSC and UV-VIS-NIR spectrophotometry.

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