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Supramolecular main chain liquid crystalline polymers utilizing azopyridine derivatives

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A series of main chain liquid crystalline polymers were formed through intermolecular hydrogen bonding between a functionalized bisazopyridine phenol and aromatic bisacids. The behaviour of these complexes was studied through differential scanning calorimetry and thermal polarizing optical microscopy. The presence of the hydrogen bonds was confirmed through infrared spectroscopy. These complexes formed thermotropic mesophases. The phases were determined to be nematic in nature from the schlieren textures of the optical micrographs. As the length of flexible spacer groups separating the mesogenic portions increased, the clearing temperatures of the mesophases decreased. As the length of the rigid component increased, the clearing temperature increased. A new bisacid species based on 2-hydroxy-6-naphthoic acid was used to increase clearing temperatures while remaining within an acceptable temperature window.

1. Introduction

The application of non-covalent or supramolecular interactions, such as hydrogen bonding, to form liquid crystals is an area of considerable scientific interest [1–7]. Hydrogen bonding has been used to form small molecule liquid crystals [1, 8], as well as main chain [9–11] and side chain [12, 13] mesogenic polymers; and calamitic [1–13], discotic [14–17] and banana-shaped [18] liquid crystals. One of the most commonly used associations is the benzoic acid and pyridine assembly. The resulting hydrogen bond is linear and strong enough to maintain structure at the temperatures needed to form a thermotropic mesogen.

Aoki and co-workers [18] reported the synthesis and application of 4-(4'-hydroxyphenylazo)pyridine in supramolecular polymers using aliphatic carboxylic acids. Other studies have used the azopyridine group to form side chain liquid crystalline polymers [19], small molecule liquid crystals [20] and metallomesogens [21]. Each of these studies confirmed that derivatives of 4-(4'-hydroxyphenylazo)pyridine are capable of forming stable mesophases through supramolecular assemblies.

Here we report the application of azopyridine-based ethers and esters towards the formation of supramolecular main chain liquid crystalline polymers. The length

of the mesogen varies in these systems, as does that of the spacer groups between the mesogens. We also report the synthesis of a new hydrogen bond donor for these supramolecular systems based on naphthoic acids.

2. Results and discussion

2.1. Synthesis

4-(4'-Hydroxyphenylazo)pyridine (AzP) was synthesized through the diazotization of 4-aminopyridine followed by an electrophilic aromatic substitution coupling with phenoxide [18]. Alkylation of AzP by the oligoethyleneglycoxy bistosylate was carried out using cesium carbonate in acetone in 50–75% yields. These molecules are denoted *n* AZO, in which *n* represents the number of ethyleneglycoxy repeat units found in the oligomer (*n*=3, 4 or 5). The bisacids (3 BA, 4 BA, 5 BA) were synthesized according to literature procedures. The bisnaphthoic acid species (4 NBA, 5 NBA) were synthesized through similar methodologies in 78% yield. Adipoyl and suberoyl bisazopyridine esters (AZO ADP, AZO SUB) were synthesized by reacting the appropriate bisacid halide with AzP in dichloromethane in 40–50% yield. The extended mesogen azoester systems were synthesized through the formation of the acid halide of a bisbenzoic acid using thionyl chloride with pyridine, followed by reaction with AzP in dry dichloromethane to form the ester in

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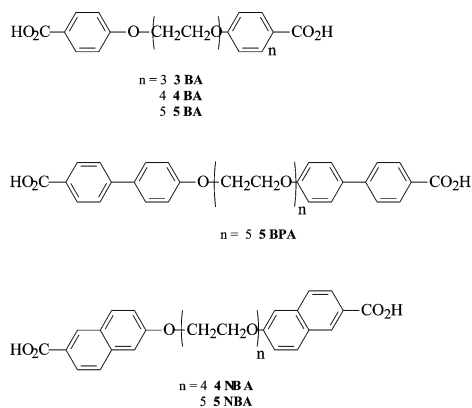
26% yield. Scheme 1 displays the molecules used in this study.

All of the compounds were characterized on the basis of their spectral (^1H NMR, FTIR) data. Details are provided in §3. The hydrogen bond complexes were formed by thoroughly mixing equimolar quantities of the hydrogen bond donor and acceptor in the molten state for 2 min under an inert atmosphere. These mixtures were allowed to cool slowly to room temperature to form the liquid crystalline materials. Hydrogen bond formation was confirmed through infrared spectroscopy by the presence of two characteristic stretching bands (centred around 2500 and 1950 cm^{-1}).

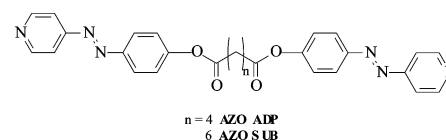
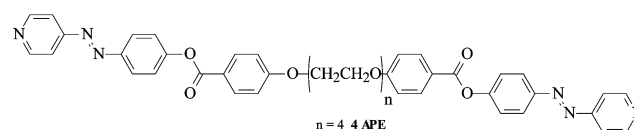
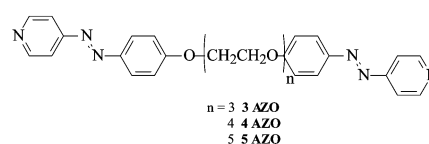
2.2. Thermal properties

A summary of all thermal transitions is presented in tables 1 and 2. A representative thermogram and thermal optical image are provided in figures 1 and 2, respectively. Because many of the assembled chain structures are monotropic in nature during the cooling phase, only the cooling cycle data from the thermograms is reported.

2.2.1. Azopyridine ether systems. The hydrogen bond complexes display largely monotropic nematic phases and transitions in differential scanning calorimetry (DSC) and thermal polarizing optical microscopy (TPOM). Phases were observed as the systems cooled from the isotropic melt through the formation of nematic droplets, which resolved into materials with a schlieran texture typical of the nematic phase. The phase transitions were repeatable over several heating/cooling cycles. While the biphenyl acid 5 BPA is itself liquid crystalline (I 249.0 N 222.7 Sm 219.5 Cr, $^{\circ}\text{C}$), the assembled mesogens display unique liquid crystalline characteristics. Increasing the length of the aromatic portions, and thereby increasing the rigidity of the mesogens, raises the transition temperatures and broadens the nematic range of the complexes. One difficulty encountered with the use of the biphenyl acid (5 BPA) was the high melting nature of the acid; several



Hydrogen Bond Donors



Hydrogen Bond Acceptors

Scheme 1. Materials used.

of the complexes degraded before any mesomorphism could be observed. In order to increase the mesogen length while maintaining a lower melting temperature, a

Table 1. Collected thermal phase transitions ($^{\circ}\text{C}$) for bisbenzoic acid derivatives. Cr=crystalline, N=nematic, I=isotropic, g=classification of the sample with no observed crystallization.

Azo compound	Bisacid		
	3BA	4BA	5 BA
3 AZO	I 172.5 N g	I 155.9 N 136.6 Cr	I 141.0 N 125.1 Cr
4 AZO	I 199.9 N 155.2 Cr	I 138.4 N 94.2 Cr	I 131.5 N 60.2 Cr
5 AZO	I 179.7 N 75.4 g	I 124.1 N 86.3 Cr	I 102.6 N 57.7 Cr
4 APE	I 216.5 N 155.8 Cr	I 220.9 N g	I 194.0 N g
AZO SUB	I 167.9 N 91.3 Cr	I 165.3 N g	I 148.2 N g
AZO ADP	N 217.6 N 118 Cr	I 203.1 N 85.9 Cr	I 186.2 N 132.5 Cr

Table 2. Collected thermal phase transitions (°C) for bisnaphthoic acid and biphenyl derivatives. Cr=crystalline, N=nematic, I=isotropic, g=classification of the sample with no observed crystallization.

Azo compound	Bisacid		
	5 BPA	4 NBA	5 NBA
3 AZO	I 225.3 N 134.2 Cr	I 176.7 N g	—
4 AZO	I 209.0 N 127.0 Cr	I 159.3 N g	I 142.7 N 40.4 Cr
5 AZO	—	—	—
4 APE	Dec ^a	—	—
AZOSUB	Dec	—	No transitions
AZO ADP	Dec	I 230.8 N g	I 212.4 N g

^aDecomposition ocamed.

pair of naphthoic acid species (4NBA, 5NBA) were synthesized. These species produced an intermediate set of transition temperatures between the single ring bisacids (3,4,5 BA) and the biphenyl acid species (5 BPA), as can be seen in tables 1 and 2.

2.2.2. Aliphatic azopyridine ester systems. Aliphatic diesters were made using the hydroxyazopyridine and adipoyl chloride and suberoyl chloride to form 4-(4'-hydroxyphenylazo)pyridine adipate (AZO ADP) and 4-(4'-hydroxyphenylazo)pyridine suberate (AZO SUB). These systems melted at reasonable temperatures, and complexes formed using these hydrogen bond acceptors displayed liquid crystalline transitions. Larger, higher melting hydrogen bond donors (biphenyl acids in

particular) melted at too high a temperature and degraded the esters rather than forming liquid crystalline phases. The naphthoic acid species, however, displayed no such problem and were utilized to form liquid crystalline phases.

2.2.3. 4-(4'-Hydroxyphenylazo)pyridine benzoate systems. 4 APE melted at a considerably higher temperature than the corresponding ether systems and possessed mesogenic character itself (Cr 144.5 Sm 154.1 N 200.0 I 193.3 N 142.6 Cr, °C). It should be noted that any liquid crystalline behaviour observed in these complexes is independent from that of the parent azoester. The higher melting point made complexation with the hydrogen bond donors slightly more

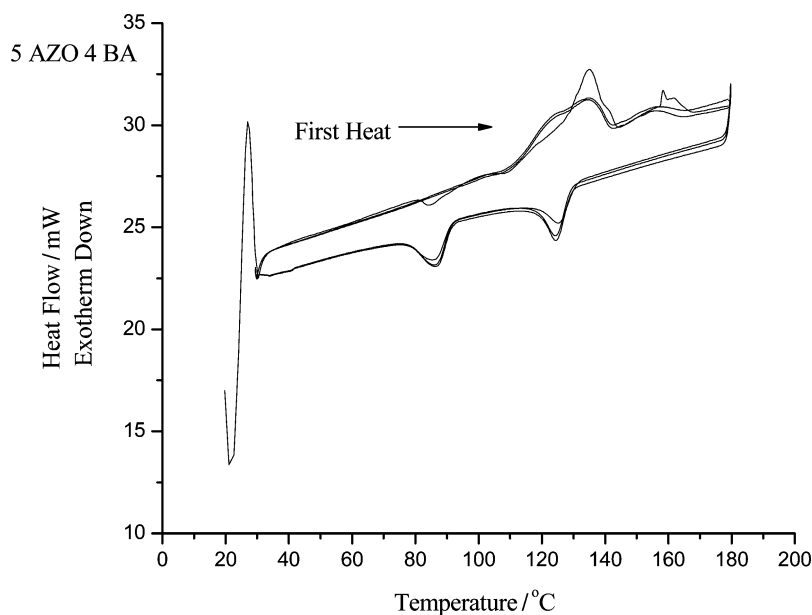


Figure 1. Differential scanning calorimetric thermogram for 5 AZO 4 BA.

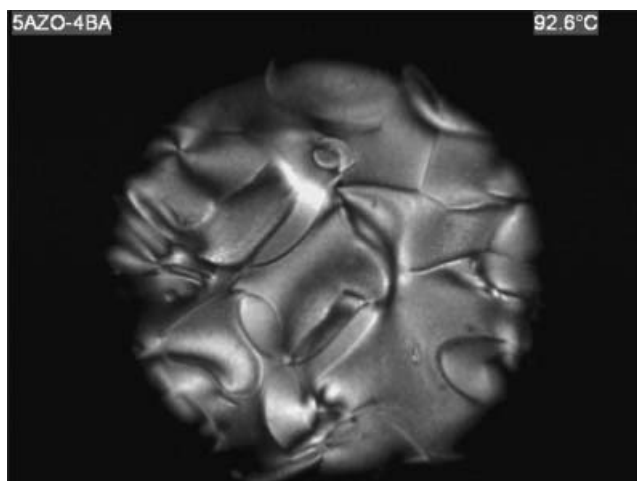


Figure 2. Thermal optical micrographs of 5AZO 4 BA.

problematic. Complexes with the simple bisacids showed higher temperature transitions than were observed in the ether systems, as was to be expected with the longer mesogens. When complexed with the biphenyl acid, the species melted at such a temperature that the liquid crystalline phase was never observed.

3. Experimental

3.1. Characterization

Phase transitions were observed using an Olympus BHT polarizing microscope equipped with a Mettler-Toledo FP82-HT thermal optical hotstage connected to a Mettler Toledo FP90 control unit. Differential scanning calorimetry thermograms were obtained from a Perkin-Elmer Pyris 1 DSC. A heating/cooling rate of $10^{\circ}\text{C min}^{-1}$ was used in both analyses. Infrared spectroscopy was carried out using a Nicolet Avatar 360 FTIR. ^1H and ^{13}C NMR spectra were recorded on a JEOL Eclipse 400 MHz FTNMR spectrometer using TMS as an internal standard.

3.2. Materials

Reagent grade reagents and solvents were used as received from suppliers. Spectrographic grade solvents were used for all measurements. The synthesis of AzP [18], 3, 4 and 5 BA [22], and 4 BPA [23] have been previously described.

3.2.1. General procedure for the preparation of ethyleneglycoxy-bis-4-(4'-hydroxyphenylazo)pyridine. 4-(4'-Hydroxyphenylazo)pyridine was mixed with the di-*p*-tosylate (2.2 to 1 molar ratio) of the appropriate

oligomeric ethyleneglycoxy chain with cesium carbonate (2.2 eq.) in acetone and heated under reflux for 48 h. The mixture was then cooled to room temperature, filtered and the solvent removed from the acetone fraction under reduced pressure. The resultant solid was recrystallized from methanol to afford the pure azopyridine ether.

3 AZO: 74% yield, m.p. 152–153°C. ^1H NMR: 8.76 (d, 4H pyridyl protons α -to nitrogen), 7.95 (d, 4 H pyridyl protons β -to nitrogen), 7.68 (d, 4H, phenol ring α -to azo group), 7.15 (d, 4 H phenol protons β -to azo group), 4.28 (t, 4 H, $\text{PhO}-\text{CH}_2\text{CH}_2\text{OCH}_2$), 3.89 (t, 4 H, $\text{PhO}-\text{CH}_2\text{CH}_2\text{OCH}_2$), 3.72 (s, 4 H, $\text{PhO}-\text{CH}_2\text{CH}_2\text{OCH}_2$). Anal: calc. for $\text{C}_{28}\text{H}_{28}\text{N}_6\text{O}_4$, C 65.61, H 5.51, N 16.39; found, C 65.38, H 5.73, N 16.21%.

4 AZO: 67% yield, m.p. 118–120°C. ^1H NMR: 8.76 (d, 4H pyridyl protons α -to nitrogen), 7.97 (d, 4 H pyridyl protons β -to nitrogen), 7.69 (d, 4H, phenol ring α -to azo group), 7.16 (d, 4 H phenol protons β -to azo group), 4.27 (t, 4 H, $\text{PhO}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$), 3.87 (t, 4 H, $\text{PhO}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$), 3.67 (t, 4 H, $\text{PhO}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$), 3.63 (t, 4 H, $\text{PhO}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$). Anal: calc. for $\text{C}_{30}\text{H}_{32}\text{N}_6\text{O}_5$, C 64.74, H 5.79, N 15.10; found, C 64.8, H 5.67, N 15.20%.

5 AZO: 52% yield, m.p. 74–76°C. ^1H NMR: 8.77 (d, 4H pyridyl protons α -to nitrogen), 7.95 (d, 4 H pyridyl protons β -to nitrogen), 7.68 (d, 4H, phenol ring α -to azo group), 7.14 (d, 4 H phenol protons β -to azo group), 4.28 (t, 4 H, $\text{PhO}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$), 3.88 (t, 4 H, $\text{PhO}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$), 3.66 (t, 4 H, $\text{PhO}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$), 3.63 (t, 4 H, $\text{PhO}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$), 3.56 (s, 4 H, $\text{PhO}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$). Anal: calc. for $\text{C}_{32}\text{H}_{36}\text{N}_6\text{O}_6$, C 63.99, H 6.04, N 13.99; found: C 64.21, H 6.13, N 13.67%.

3.2.2. Preparation of tetraethyleneglycoxy-bis-4-(4'-hydroxyphenylazo)pyridine benzoate. Tetraethyleneglycoxy bis-4-benzoic acid (1.19 g, 0.0027 mol) was heated under reflux in thionyl chloride (150 ml 2.05 mol) with a trace of pyridine for 120 min. Excess thionyl chloride was removed under reduced pressure and the remaining oil was immediately diluted with 100 ml of methylene chloride. To this solution 1.11 g (0.0056 mol) of 4-(4'-hydroxyphenylazo)pyridine in 100 ml of methylene chloride was added and the mixture stirred overnight. The reddish liquid was then distilled under reduced pressure to remove excess methylene chloride. A deep red solid was collected and recrystallized from methanol to provide 0.578 g of product (26% yield). Melting behaviour: Cr 144.5 Sm 154.1 N 200.0 I ($^{\circ}\text{C}$). ^1H NMR:

8.80 (d, 4H pyridyl protons α -to nitrogen), 8.13 (d, 4H, aromatic protons α -to carboxyl group), 8.01 (d, 4H, pyridyl protons β -to nitrogen), 7.69 (d, 4H, phenol ring α -to azo group), 7.37 (d, 4H, aromatic protons β -to carboxyl group), 7.16 (d, 4 H phenol protons β -to azo group), 4.21 (t, 4 H, PhO-CH₂CH₂OCH₂CH₂O-), 3.74 (t, 4 H, PhO-CH₂CH₂OCH₂CH₂O-), 3.69 (t, 4 H, PhO-CH₂CH₂OCH₂CH₂O-), 3.60 (t, 4 H, PhO-CH₂CH₂OCH₂CH₂O-). Anal: calc. for C₄₅H₄₃N₆O₉, C 66.57, H 5.34, N 10.35; found, C 66.16, H 5.12, N 9.70%.

3.2.3. Preparation of 4-(4'-hydroxyphenylazo)pyridine aliphatic esters (ADP AZO and SUB AZO). 4-(4'-Hydroxyphenylazo)pyridine was dissolved in 25 ml of methylene chloride and added dropwise to a solution containing half an equivalent of the appropriate diacid chloride in methylene chloride. The reaction was allowed to reflux with stirring for 30 min, and cooled to room temperature. Excess methylene chloride was removed under vacuum and the red solid was purified by column chromatography (silica gel/methanol) to provide the desired ester.

AZO ADP: 62% yield, m.p. 210–211.5°. ¹H NMR: 8.82 (d, 4H pyridyl protons α -to nitrogen), 8.02 (d, 4 H pyridyl protons β -to nitrogen), 7.75 (d, 4H, phenol ring α -to azo group), 7.31 (d, 4 H phenol protons β -to azo group), 2.7 (m, 4 H, CH₂ α -to carbonyl), 1.9 (m, 4H, CH₂ β -to carbonyl). Anal: calc. for C₂₉H₂₈N₆O₅, C 66.4, H 5.38, N 16.02; found, C 65.98, H 4.99, N 16.32%.

AZO SUB: 47% yield, m.p. 197–198°. ¹H NMR: 8.81 (d, 4H pyridyl protons α -to nitrogen), 8.01 (d, 4 H pyridyl protons β -to nitrogen), 7.69 (d, 4H, phenol ring α -to azo group), 7.26 (d, 4 H phenol protons β -to azo group), 2.65 (t, 4 H, CH₂ α -to carbonyl), 1.82 (m, 4H, CH₂ β -to carbonyl) 1.50 (m, 4H, CH₂ γ -to carbonyl). Anal: calc. for C₃₁H₃₂N₆O₄, C 67.38, H 5.84, N 15.21; found, C 66.89, H 5.77, N 15.40%.

3.2.4. Synthesis of methyl 2-hydroxy-6-naphthoate. 6-Hydroxy-2-naphthoic acid (5 g) was combined with 500 ml of methanol and 0.5 ml of sulphuric acid and heated under reflux for 24 h. The excess solvent was removed under reduced pressure and the remaining oil poured into 2 l of ice water. A white solid precipitated, was isolated by filtration and recrystallized from ethanol to provide 2.80 g of a greyish-tan solid; yield 52%, m.p. 153°C. ¹H NMR: 8.52 (s, 1H), 7.94 (d, 1H), 7.75 (d, 1H), 7.68 (d, 1 H), 7.38 (s, 1 H), 7.22 (d, 1H), 3.98 (2, 3H). Anal: calc. for C₁₂H₁₀O₃, C 71.28, H 4.98; found, C 70.98, H 5.04%.

3.2.5. General procedure for the preparation of ethyleneglycoxy-bis-2-(6-hydroxynaphthoic acid).

Methyl 2-hydroxy-6-naphthoate was mixed with the *p*-tosylate (2.2 to 1 molar ratio) of the appropriate oligomeric ethyleneglycoxy chain with cesium carbonate (2.2 eq.) in acetone and heated under reflux for 48 h. The mixture was cooled to room temperature, filtered and the solvent removed from the acetone fraction under reduced pressure. The remaining oil was mixed with 250 ml of a 10% potassium hydroxide in ethanol solution and heated under reflux for 3 h. The solution was cooled to room temperature and excess solvent removed under reduced pressure. The greyish-brown solid was then added to 4 l of water acidified with 250 ml of 12M hydrochloric acid. A grey precipitate was collected by filtration and recrystallized from ethanol. The resultant solid was recrystallized from ethanol to afford the pure bisacid.

4 NBA: 72 % yield, m.p. 184–185°C. ¹H NMR: 8.51 (s, 2H), 8.03 (d, 2H), 7.86 (d, 2H), 7.81 (d, 2 H), 7.39 (s, 2 H), 7.22 (d, 2H), 4.25 (t, 4 H, PhO-CH₂CH₂OCH₂CH₂O-), 3.88 (t, 4 H, PhO-CH₂CH₂OCH₂CH₂O-), 3.67 (t, 4 H, PhO-CH₂CH₂OCH₂CH₂O-), 3.61 (t, 4 H, PhO-CH₂CH₂OCH₂CH₂O-). Anal: calc. for C₃₀H₃₀O₉, C 67.41, H 5.66; found, C 67.33, H 5.41%.

5 NBA: 68% yield, m.p. 164–165°C. ¹H NMR: 8.52 (s, 2H), 8.01 (d, 2H), 7.90 (d, 2H), 7.85 (d, 2 H), 7.38 (s, 2 H), 7.22 (d, 2H), 4.22 (t, 4 H, PhO-CH₂CH₂OCH₂CH₂OCH₂-), 3.80 (t, 4 H, PhO-CH₂CH₂OCH₂CH₂OCH₂-), 3.55 (t, 4 H, PhO-CH₂CH₂OCH₂CH₂OCH₂-), 3.51 (t, 4 H, PhO-CH₂CH₂OCH₂CH₂OCH₂-), 3.33 (s, 4 H, PhO-CH₂CH₂OCH₂CH₂OCH₂-). Anal: calc. for C₃₂H₃₄O₁₀, C 66.43, H 5.92; found, C 66.49, H 6.18%.

4. Conclusions

A series of supramolecular main chain liquid crystalline polymers has been made from chains terminated with 4-(4'-hydroxyphenylazo)pyridine and benzoic acid species. These complexes display mainly nematic monotropic liquid crystalline behaviour (cooling cycle). An increase in the transition temperatures occurred as the mesogens increased in length. The transition temperatures also decreased as the flexibility of the spacer groups increased. The use of biphenyl acids, while useful for increasing the transition temperatures, in many cases led to melting points too high for LC transitions to be observed. The introduction of bisnaphthoic acid hydrogen bond donors provided longer mesogens and increased phase transition temperatures while remaining low enough that mesogenicity could be observed.

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