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Design and characterization of novel supramolecular liquid crystals involving multiple hydrogen bonds

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A novel type of liquid crystalline system, namely 5-[4-(4-methoxyphenylazo)phenyloxyalkyloxy]-isophthalic acidhydrazides (**D*n***, *n* = 3, 6, 10) was designed and synthesized. The FTIR spectra of the **D*n*** compounds were examined in the range 4000–1000 cm^{-1} at different temperatures. The results showed that the stretching vibration frequencies of the NH and C=O groups, and the NH_2 deformation shifted to lower frequencies with decrease of temperature, while out-of-plane NH bending shifted slightly to higher frequency. Intermolecular hydrogen bonding between NH, NH_2 and C=O groups is proposed and the schematic supramolecular **D*n*** structure is given. This may explain the higher **D*n*** transitional temperatures and their smectic phase behaviour compared with that of 5-[4-(4-methoxyphenylazo)phenyloxyalkyloxy]-isophthalic acid diethyl esters.

1. Introduction

Hydrogen bonding is one of the key interactions in the process of molecular aggregation and recognition in nature [1] and it can be used to design and assemble supramolecular architectures. Side chain [2, 3], main chain [4, 5] and network [6] polymers with liquid crystalline properties have been built by supramolecular self-assembly through the formation of hydrogen bonds between different components. Frechet, and coworkers [2, 6, 7] and others [3] have used single hydrogen bonds to attach liquid crystalline groups to hydrogen-bonding polymer backbones. Kato *et al.* demonstrated that novel supramolecular liquid crystals are formed, through a pyridyl/carboxyl group hydrogen bond, when two kinds of organic molecule possessing either a pyridyl group as a hydrogen acceptor or a carboxyl group as a hydrogen donor are mixed [7, 8]. Griffin *et al.* [9, 10] reported that binary mixtures of bolas form organic compounds, bearing either two carboxyl groups or two pyridyl groups at both molecular termini, give rise to a supramolecular polymer through the formation of hydrogen bonds; the resulting hydrogen-bonded materials exhibit properties similar to those of conventional linear polymers formed through covalent bonds. In some other cases, simple surfactants are hydrogen-bonded to polymer backbones to create ordered mesomorphic materials [11, 12].

It is well known that hydrogen bonds may be formed between carboxyl (C=O) and amide (N–H) groups in poly(amide)s. Hydrogen bond formation between a carboxylate acceptor and a urea donor, and in some similar systems, was also reported recently [13–15]. Our intention has been to prepare a novel family of molecules possessing both carboxyl group as a hydrogen acceptor and amide as a hydrogen donor at each molecular terminus as shown in figure 1, to build a supramolecular network possessing mesomorphic behaviour. Three points may be noted. First, the system contains only one component and the molecules should form a polymer-like structure due to intermolecular hydrogen bonding between N–H, NH_2 groups and/or the C=O group. Second, the molecules should exhibit mesogenic behaviour due to the π–π stacking of *p*-methoxy azobenzene groups, and their liquid crystalline behaviour should be similar to that of side chain liquid crystalline polymers formed through a covalent bond. Third, the molecules should

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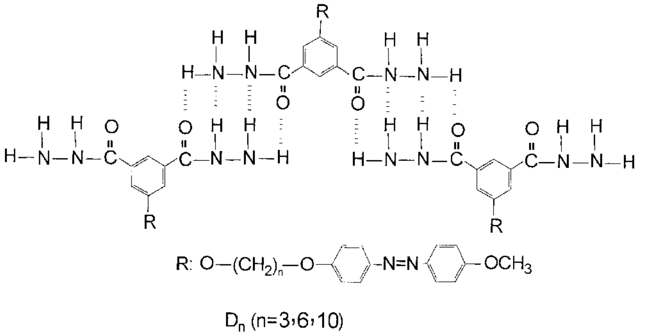


Figure 1. The molecular structure of **D*n*** compounds.

respond to different stimuli such as light, due to the *E*/*Z* transformation of azobenzene, and environmental factors such as the properties of the media in which the starting molecules are dissolved.

The present paper deals with the preparation from single components and characterization of mesomorphic behaviour of this supramolecular system.

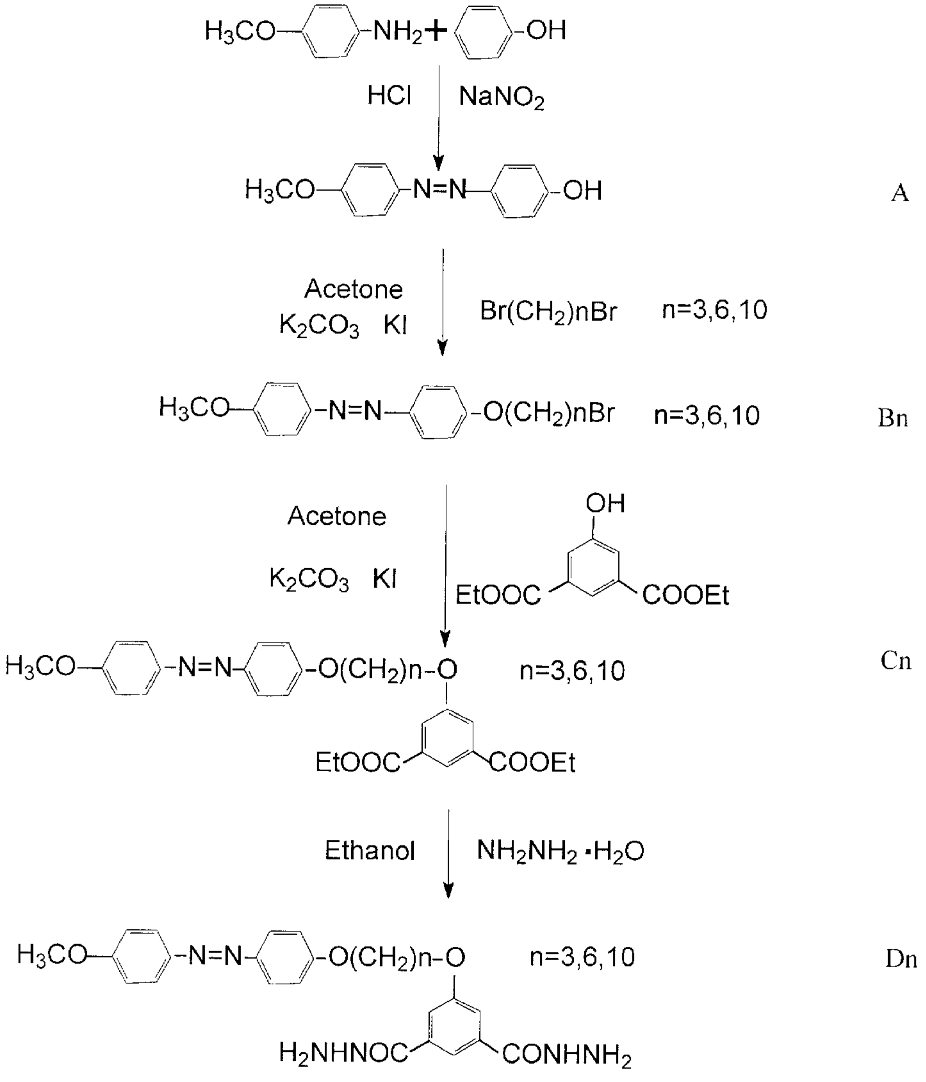
2. Experimental

2.1. *Synthesis of compounds* ***D*n**

The synthetic route to compounds **D*n*** is given in the scheme. Typical synthetic procedures are given below.

2.1.1. *4-(4-Methoxyphenylazo)phenol (A)*

The compound **A** was prepared through the coupling of diazotized aniline with phenol as described elsewhere [13]. Yield 88%, m.p. 142–143°C. FTIR (KBr, cm^{-1}): 3414 (–OH, ν_s); 2846 ($-\mathrm{CH}_3$, ν_s); 1599, 1496, 1439 (aromatic $\nu_{\mathrm{C\text{-}C}}$); 1465 ($-\mathrm{CH}_3$, δ); 845 (aromatic $\nu_{\mathrm{C\text{-}H}}$). ^{1}H NMR (400 MHz, CDCl_3), (ppm, from TMS): 3.88 (s, 3H, $-\mathrm{OCH}_3$), 6.97–7.01 (m, 4H, Ar–H, *m* to –N=N–), 7.85–7.88 (m, 4H, Ar–H, *o* to –N=N–).



Scheme.

2.1.2. *1-Bromo-[4-(4-methoxyphenylazo)phenyloxy]-hexane (**B6**)*

B6 was synthesized by a Williamson etherification [13]. Yield 85%, m.p. 105–106°C. FTIR (KBr, cm^{-1}): 2937, 2861 ($-CH_2-$, ν_{as}; $-CH_3$, ν_s); 1601, 1579, 1498, 1447 (aromatic, $\nu_{C\text{-}C}$); 1466 ($-CH_3$, CH_2, δ); 1245, 1030 (Ar$-$O$-$C, ν); 1147, 1109 (O$-CH_2$, ν_s); 843 (aromatic, ν_{CH}); 644 (C$-$Br, ν_s). ^{1}H NMR (400 MHz, $CDCl_3$), (ppm, from TMS): 1.55 (m, 4H, $-C-C-CH_2-CH_2-C-C-$), 1.87 (m, 4H, $-C-CH_2-C-C-CH_2-C-$), 3.43–3.46 (t, 2H, $-C-CH_2Br$), 3.87 (s, 3H, $-Ar-O-CH_3$), 4.06–4.09 (t, 2H, $-O-CH_2-C-$), 6.98–7.01 (m, 4H, Ar$-$H, *m* to $-N{=}N-$), 7.85–7.89 (m, 4H, Ar$-$H, *o* to $-N{=}N-$).

Using the same method, **B3** and **B10** were synthesized and their structures confirmed.

2.1.3. *5-[4-(4-Methoxyphenylazo)phenyloxyhexyloxy]-isophthalic acid diethyl ester (**C6**)*

A mixture of 6.22 g of 5-hydroxyisophthalic acid diethyl ester (0.026 mol), 10.17 g of **B6** (0.026 mol), 15 g of anhydrous potassium carbonate, and 100 ml of dry acetone was heated under reflux for 24 h. After cooling to room temperature, the mixture was poured into excess of ice water, and the precipitate recrystallized from anhydrous alcohol. Yield 85%, m.p. 101–102°C. FTIR (KBr, cm^{-1}): 2941, 2868 ($-CH_2-$, ν_{as}; $-CH_3$, ν_s); 1722 ($-C{=}O-$, ν); 1595, 1500 (aromatic, $\nu_{C\text{-}C}$); 1448 ($-CH_3$, $-CH_2-$, δ); 1371, 1313 (Ar$-$N, $\nu_{C\text{-}N}$); 1244, 1036 (Ar$-$O$-$C, ν); 1138, 1117 (O$-CH_2$, ν_s); 847 (aromatic, ν_{CH}). ^{1}H NMR (400 MHz, $CDCl_3$), (ppm, from TMS): 1.39–1.43 (t, 6H, $-C-CH_3$), 1.58 (m, 4H, $-C-C-CH_2-CH_2-C-C-$), 1.86 (m, 4H, $-C-CH_2-C-C-CH_2-C-$), 3.88 (s, 3H, $-Ar-O-CH_3$), 4.04–4.07 (m, 4H, $-O-CH_2-C-$), 4.37–4.43 (m, 4H, $-O-\underline{CH_2}-CH_3$), 6.98–7.01 (m, 4H, Ar$-$H, *m* to $-N{=}N-$), 7.74–7.75 (d, 2H, Ar$-$H, *o* to $-O-$), 7.85–7.89 (m, 4H, Ar$-$H, *o* to $-N{=}N-$), 8.27 (s, 1H, Ar$-$H, *o* to $-COO-$).

Compounds **C3** and **C10** were similarly synthesized and characterized.

2.1.4. *5-[4-(4-Methoxyphenylazo)phenyloxypropyloxy]-isophthalic acid diethyl ester (**C3**)*

Yield 85%, m.p. 98–99°C. FTIR (KBr, pellet, cm^{-1}): 2985, 2937 ($-CH_2-$, ν_{as}; $-CH_3$, ν_s); 1720 ($-C{=}O-$, ν); 1596, 1500, 1440 (aromatic, $\nu_{C\text{-}C}$); 1469 ($-CH_3$, $-CH_2-$, δ); 1371, 1311 (Ar$-$N, $\nu_{C\text{-}N}$); 1245, 1029 (Ar$-$O$-$C, ν); 1147, 1105 (O$-CH_2$, ν_s); 845 (aromatic, ν_{CH}). ^{1}H NMR (400 MHz, $CDCl_3$), (ppm, from TMS): 1.39–1.43 (t, 6H, $-C-CH_3$), 2.31–2.35 (m, 2H, $-C-CH_2-C-$), 3.88 (s, 3H, $-Ar-O-CH_3$), 4.24–4.30 (m, 4H, $-O-CH_2-C-$), 4.37–4.43 (m, 4H, $-O-\underline{CH_2}-CH_3$), 6.98–7.03 (m, 4H, Ar$-$H, *m* to $-N{=}N-$), 7.77–7.78 (d, 2H, Ar$-$H, *o* to $-O-$), 7.86–7.89 (m, 4H, Ar$-$H, *o* to $-N{=}N-$), 8.28 (s, 1H, Ar$-$H, *o* to $-COO-$).

2.1.5. *5-[4-(4-Methoxyphenylazo)phenyloxydecyloxy]-isophthalic acid diethyl ester (**C10**)*

Yield 85%, m.p. 102–103°C. FTIR (KBr, pellet, cm^{-1}): 2931, 2852 ($-CH_2-$, ν_{as}; $-CH_3$, ν_s); 1722 ($-C{=}O-$, ν); 1601, 1500, 1446 (aromatic, $\nu_{C\text{-}C}$); 1462 ($-CH_3$, $-CH_2-$, δ); 1369, 1313 (Ar$-$N, $\nu_{C\text{-}N}$); 1240, 1025 (Ar$-$O$-$C, ν); 1143, 1108 (O$-CH_2$, ν_s); 845 (aromatic, ν_{CH}). ^{1}H NMR (400 MHz, $CDCl_3$), (ppm, from TMS): 1.41–1.43 (t, 6H, $-C-CH_3$), 1.35–1.48 (broad, 8H, $-C-C-C-(CH_2)_4-C-C-C-$), 1.78–1.84 (broad, 4H, $-C-\underline{CH_2}-(CH_2)_4-\underline{CH_2}-C-$), 3.89 (s, 3H, $-Ar-O-CH_3$), 4.02–4.06 (m, 4H, $-O-CH_2-C-$), 4.37–4.43 (m, 4H, $-O-\underline{CH_2}-CH_3$), 6.98–7.01 (m, 4H, Ar$-$H, *m* to $-N{=}N-$), 7.74–7.75 (d, 2H, Ar$-$H, *o* to $-O-$), 7.85–7.89 (m, 4H, Ar$-$H, *o* to $-N{=}N-$), 8.26 (s, 1H, Ar$-$H, *o* to $-COO-$).

2.1.6. *5-[4-(4-Methoxyphenylazo)phenyloxyhexyloxy]-isophthalic acidhydrazide (**D6**)*

A mixture of 9.72 g of **C6** (0.018 mol), and an excess amount of hydrazine monohydrate was dissolved in anhydrous alcohol; the mixture was then heated under reflux for 48 h. After the reaction was finished, the precipitate was filtered, washed with ethanol, and dried under vacuum. Yield 80%, m.p. 216–217°C. FTIR (KBr, cm^{-1}): 3323, 3263 ($-NH-$, $\nu_{N\text{-}H}$); 2939, 2866 ($-CH_2-$, ν_{as}; $-CH_3$, ν_s); 1641 ($-C{=}O-$, ν_s); 1629 ($-NH_2$, δ_{NH2}), 1592, 1504, 1466 (aromatic $\nu_{C\text{-}C}$); 1315 (Ar$-$N, $\nu_{C\text{-}N}$); 1248, 1036 (Ar$-$O$-$C, ν); 1149. 1111 (O$-CH_2$, ν_s); 843 (aromatic ν_{CH}). ^{1}H NMR (400 MHz, $CDCl_3$), (ppm, from TMS): 1.52 (m, 4H, $-C-C-CH_2-CH_2-C-C-$), 1.78 (m, 4H, $-C-CH_2-C-C-CH_2-C-$), 3.86 (s, 3H, $-Ar-O-CH_3$), 4.05–4.10 (m, 4H, $-O-CH_2-C-$), 4.54 (m, 4H, $-CO-N-NH_2$), 7.09–7.12 (m, 4H, Ar$-$H, *m* to $-N{=}N-$), 7.46–7.47 (d, 2H, Ar$-$H, *o* to $-O-$), 7.81–7.85 (m, 4H, Ar$-$H, *o* to $-N{=}N-$), 7.85 (s, 1H, Ar$-$H, *o* to $-CON-$), 9.78 (s, 2H, $-CO-\underline{NH}-NH_2$).

Using the same method, compounds **D3** and **D10** were successfully synthesized.

2.1.7. *5-[4-(4-Methoxyphenylazo)phenyloxypropyloxy]-isophthalic acidhydrazide (**D3**)*

Yield 78%, decomposed before m.p. FTIR (KBr, pellet, cm^{-1}): 3309 ($-NH-$, $\nu_{N\text{-}H}$); 2958, 2935 ($-CH_2-$, ν_s; $-CH_3$, ν_{as}); 1630 ($-C{=}O-$, $\nu_{C\text{-}O}$); 1595, 1502 (aromatic $\nu_{C\text{-}C}$); 1464 ($-CH_3$, $-CH_2-$, δ); 1354, 1313 (Ar$-$N, $\nu_{C\text{-}N}$); 1248, 1026 (Ar$-$O$-$C, ν); 1149, 1061 (O$-CH_2$, ν_s); 841 (aromatic, ν_{CH}). ^{1}H NMR (400 MHz, DMSO), (ppm, from TMS): 2.23–2.26 (m, 2H, $-C-CH_2-C-$), 3.85 (s, 3H, $-Ar-O-CH_3$), 4.25–4.26 (m, 4H, $-O-CH_2-C-$), 4.57 (broad, 4H, $-CO-N-NH_2$), 7.10–7.16 (m, 4H, Ar$-$H, *m* to $-N{=}N-$), 7.51–7.52 (d, 2H, Ar$-$H, *o* to $-O-$), 7.83–7.85 (m, 4H, Ar$-$H, *o* to $-N{=}N-$), 7.87 (s, 1H, Ar$-$H, *o* to $-CON-$), 9.81 (s, 2H, $-CO-\underline{NH}-NH_2$).

2.1.8. *5-[4-(4-Methoxyphenylazo)phenyloxy]decyloxy-isophthalic acidhydrazide (**D10**)*

Yield 79%, m.p. 181–182°C. FTIR (KBr, pellet, cm^{-1}): 3313 ($-NH-$, $\nu_{N\text{-}H}$); 2928, 2852 ($-CH_2-$, ν_{as}; $-CH_3$, ν_s); 1647 ($-C{=}O-$, $\nu_{C\text{-}O}$); 1595, 1502 (aromatic $\nu_{C\text{-}C}$); 1466 ($-CH_3$, $-CH_2-$, δ); 1319 (Ar–N, $\nu_{C\text{-}N}$); 1248, 1016 (Ar–O–C, ν); 1146, 1105 ($O-CH_2$, ν_s); 843 (aromatic, ν_{CH}). ^1H NMR (400 MHz, DMSO), (ppm, from TMS): 1.27–1.42 (broad, 8H, $-C-C-C-(CH_2)_4-C-C-C-$), 1.74 (broad, 4H, $-C-\underline{CH_2}-(CH_2)_4-\underline{CH_2}-C-$), 3.85 (s, 3H, $-Ar-O-CH_3$), 4.05–4.10 (m, 4H, $-O-CH_2-C-$), 4.54 (broad, 4H, $-CO-N-NH_2$), 7.09–7.12 (m, 4H, Ar–H, *m* to $-N{=}N-$), 7.46–7.47 (t, 2H, Ar–H, *o* to $-O-$), 7.81–7.85 (m, 4H, Ar–H, *o* to $-N{=}N-$), 7.85 (s, 1H, Ar–H, *o* to $-CON-$), 9.79 (s, 2H, $-CO-\underline{NH}-NH_2$).

2.2. *Characterization*

The ^1H NMR spectra of the compounds were recorded with a Varian Unity 400 spectrometer (400 MHz), using deuteriated chloroform ($CDCl_3$) as solvent and tetramethylsilane (TMS) as an internal chemical shift reference. FTIR spectra were recorded with a Bruker IFS66v spectrometer; the samples for general study were pressed tablets with KBr. Samples for hydrogen bonding study were prepared by casting onto a KBr plate from a solution of the compound in chloroform to form a thin film, which was then covered with another KBr window. This sandwiched sample cell was held on a hot stage, temperature-controlled within 1°C.

The thermal properties of the compounds were investigated with a Perkin Elmer DSC-7 instrument. The rate of heating and cooling was 10°C min^{-1}; the weight of the sample was about 6.5 mg, and indium and zinc were used for calibration. The peak maximum was taken as the phase transition temperature. Optical texture were observed by a Leica DMLP polarizing optical microscope equipped with a Leitz 350 microscope heating stage.

3. Results and discussion

3.1. *Synthesis*

The synthesis of the **D*n*** compounds consists of four steps, involving the azo coupling of a phenol with *p*-methoxy aniline, Williamson etherifications with dibromoalkane, and 5-hydroxyisophthalic acid diethyl ester, and finally the dihydrazidation between hydrazine hydrate and the diethyl ester. The ^1H NMR spectrum as well as the attribution of the protons of **D6** given in figure 2 confirmed the proposed **D*n*** molecular structure.

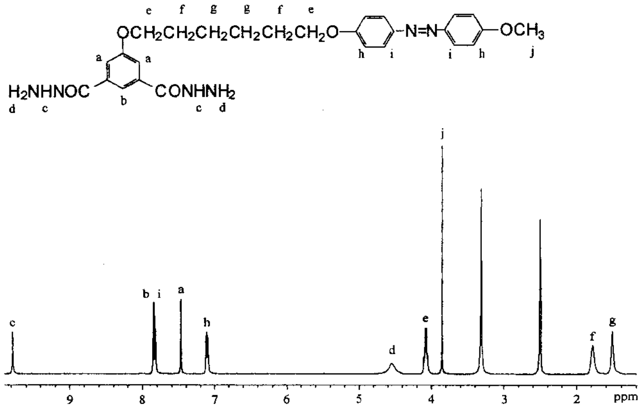


Figure 2. ^1H NMR spectrum of D6.

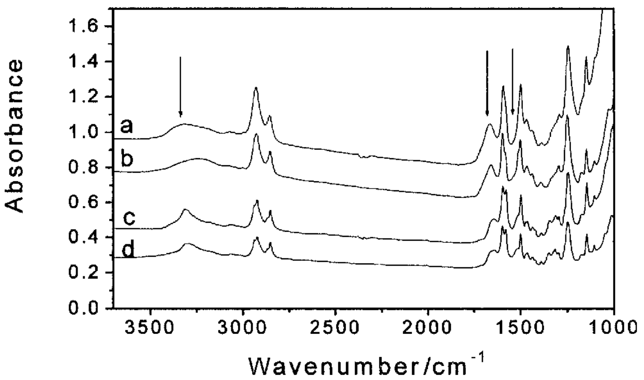


Figure 3. FTIR spectra of **D10** at different temperatures: (*a*) 200°C; (*b*) 25°C, cooled from 200°C; (*c*) 139°C, heating from 25°C for **D10** crystallized from ethanol; (*d*) 25°C, crystallized from ethanol.

3.2. *FTIR analysis*

Temperature dependence FTIR spectra provide valuable information concerning thermally induced changes in hydrogen-bonded materials. Figure 3 shows the FTIR spectra of **D10** at different temperatures. The spectrum of **D10** at 191°C cooled from 200°C (melting point of **D10** is 172°C) is given in figure 3(*a*). The broad band at 3317 cm^{-1} is attributed to the N–H stretching vibration, and the band at 1668 cm^{-1}, the C=O stretching vibration overlapped with NH_2 deformation. Further cooling of **D10** from 200°C to room temperature, figure 3(*b*), causes steady downward frequency shifts of the above two bands from 3323 to 3243 cm^{-1} and from 1668 to 1660 cm^{-1}, respectively. These spectra change were completely reversible upon heating and cooling across the melting point, suggesting that the pseudopolymer network formed through multiple hydrogen bonding between C=O and NH and NH_2 groups in the course of the cooling cycle. The plot of N–H stretching vibration versus temperature is given in figure 4. The schematic representation of the supramolecular side chain liquid crystalline system involving multiple hydrogen bond formation is given in figure 1.

It is well established that the level of hydrogen bonding is determined to a significant extent not only by the

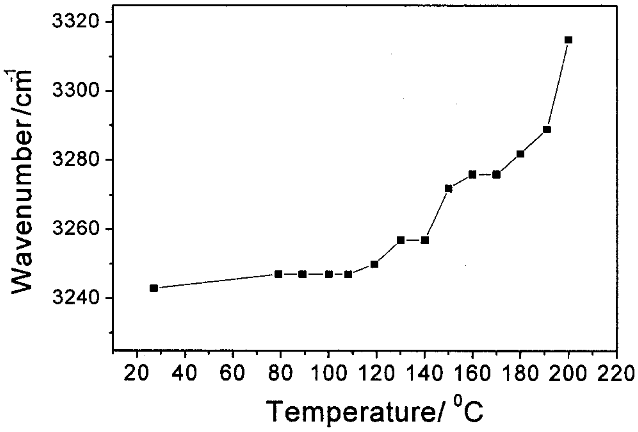


Figure 4. Plot of N–H stretching vibration of **D10** versus temperature.

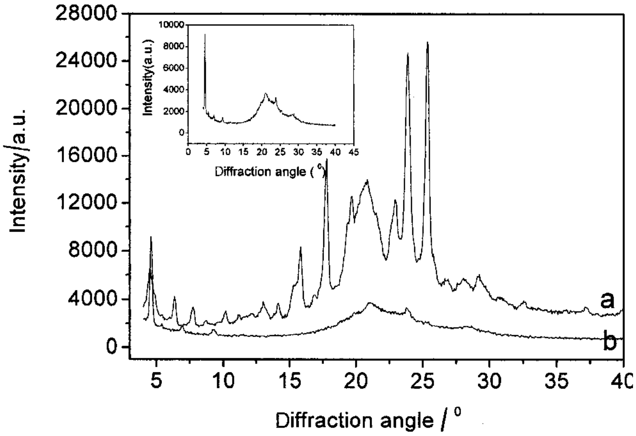


Figure 5. WAXD spectra of D10: (*a*) crystallized from ethanol; (*b*) crystallized from isotropic phase.

chemical structures of the molecules but also by environmental factors. To study the effect of environmental factors on its supramolecular assembly, **D10** was treated either by precipitating from ethanol or by cooling from its isotropic phase. The spectrum of **D10** precipitated from ethanol is given in figure 3 (*d*); bands centred at 3296 and 3313 cm^{-1} are attributed to the N–H stretching vibration, while those centred at 1662 and 1641 cm^{-1}, to the C=O stretching vibration and the NH_2 bending vibration, 1517 cm^{-1} to C–N stretching and out-of-plane NH bending, respectively. Compared with figure 3 (*b*) two N–H stretching vibration bands are observed; they are sharper and located at higher frequency, while the NH_2 bend vibration is at lower frequency, indicating that fewer and weaker hydrogen bonds were formed in the solvent-induced crystallization sample. These results suggested that in the process of precipitation of **D10** from ethanol, the solvent suppresses H-bond formation between **D10** molecules. No significant spectral changes were observed for **D10** crystallized from ethanol upon heating it to 140°C. Heating it across 140°C cause the disappearance of the 3296 cm^{-1} band, the broadening of the 3313 cm^{-1} band, and the upward frequency shift of the NH_2 bending vibration from 1641 cm^{-1} (140°C) to 1666 cm^{-1} (200°C), indicating that NH_2 groups are hydrogen-bonded above 140°C.

3.3. *WAXD analysis*

The WAXD spectra of **D10**, crystallized from ethanol and molted, are given in figure 5. A prominent feature of WAXD patterns of **D10** from the molten state is that a broad peak appears at $2\theta > 20°$ for **D10** from its molten state, unlike the pattern from ethanol crystallization. Analogous diffraction patterns were obtained from **D6** from ethanol and from the molten state. These results suggest that the materials solidified from the molten state are not well crystallized and that the pseudopolymer structures are formed as a result of intermolecular hydrogen bond, which suppresses the regular arrangement of the mesogenic groups.

3.4. *Phase transition properties*

DSC analysis was used to study the thermal properties of **D*n*** compounds. Their phase transition properties are listed in table 1; for comparison, the thermal properties of **C*n*** compounds are also listed. Only one endothermic peak was observed upon heating **D10**, attributed to the melting of the crystals, while two endothermic peaks were observed for **D6**, corresponding to crystalline–crystalline and crystalline–isotropic transitions. The structural change at the crystalline–crystalline transition of **D6** during heating was discussed in detail by Wu *et al.* [17]. Only one exothermic peak was observed for **D6** and **D10**, corresponding to the isotropic–liquid crystalline transition. The corresponding enthalpies of the isotropic–liquid crystalline transition are 2.6 kJ mol^{-1} for **D6** and 3.1 kJ mol^{-1} for **D10**.

Polarizing optical microscopy was used to determine the LC phases; the textures of **D6** and **D10** in their LC phases are given in figure 6. The first appearance of

Table 1. Thermal transition properties of **D*n*** and **C*n*** compounds. Transition temperatures (°C) and the enthalpies of transition (kJ mol^{-1}, in parentheses): Cr, crystalline; Sm Smectic; I isotropic.

Compound	Heating	Cooling
C3	Cr 98 I	I 71 Cr
C6	Cr 101 I	I 84 Cr
C10	Cr 102 I	I 91 Cr
D3	decomposed	
D6	Cr_1 125 (58.7) Cr_2 214 (59.0) I	I 139 (2.6) SmA
D10	Cr 187 (73.4) I	I 178 (3.1) SmA

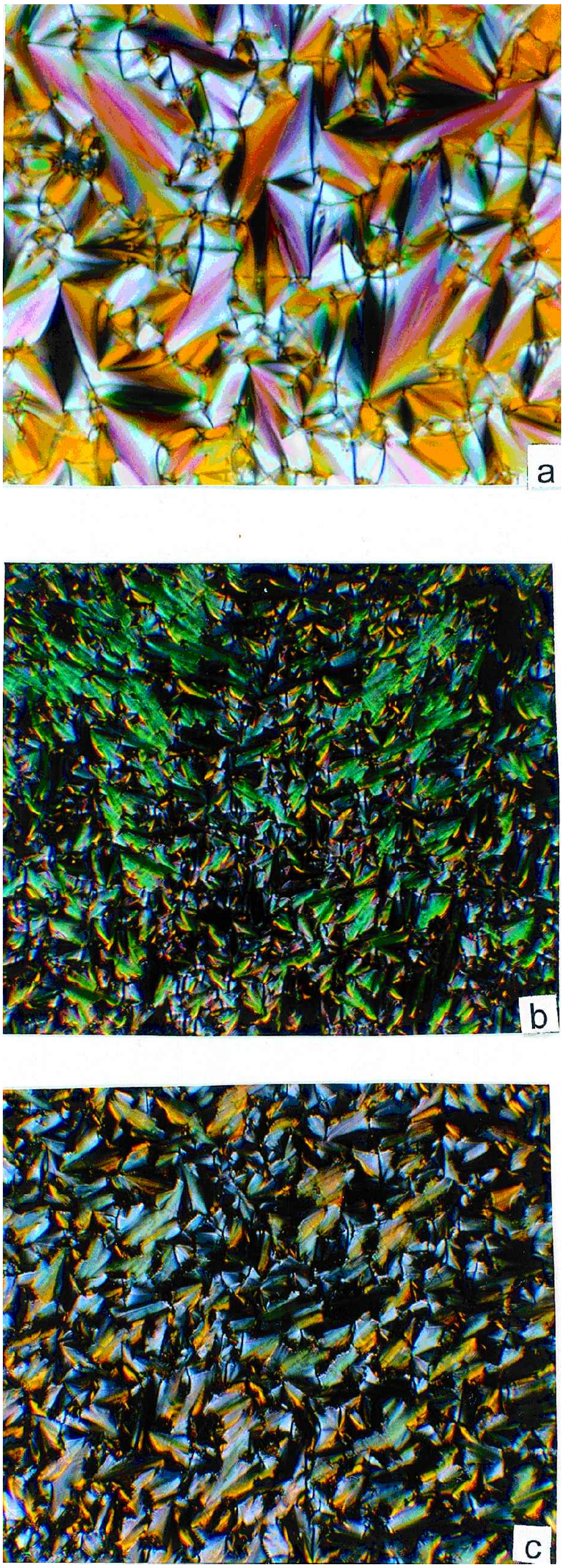


Figure 6. Polarizing optical photomicrograph of **D6** and **D10** (×200): (*a*) **D6** at 113°C; (*b*) **D10** at 150°C; (*c*) **D10** at 25°C.

Table 2. WAXD results for **D6** and **D10** in their LC phases.

Sample	D_1/nm	D_2/nm	L/nm	D/L
D6	3.21	2.49	2.15	1.48
D10	3.84	1.92	2.65	1.42

bâtonnets followed by the appearance of a fan-like texture upon cooling from the isotropic phase confirm the existence of smectic A phases of **D6** and **D10**. Very interestingly, the liquid crystalline texture of **D6** and **D10** can be partially frozen-in on quenching the samples from their liquid crystalline phases to room temperature; this behaviour is very similar to that of polymer liquid crystals. These results suggested that the network formed through internal hydrogen bonds in **D*n*** suppresses the regular arrangement of the molecules.

The *d*-spacings of **D6** and **D10** in their LC phases are summarized in table 2. It can be seen that the *d*-spacings at lower diffraction angles are in range of $L < d < 2L$ (L is the calculated length of the mesogen including CH_2 group assuming that CH_2 is in the *trans*-form). As can be seen from table 1, no liquid crystalline phases were observed for **C*n*** compounds, and the **D*n*** melting points were much higher than the **C*n*** melting points. These results suggested that hydrogen bonding was involved in the formation of the mesomorphic phases.

4. Conclusion

Novel supramolecular liquid crystals containing the *p*-methoxyazobenzene mesogenic group have been designed and synthesized. FTIR spectroscopic studies showed that multiple intermolecular hydrogen bonding between N–H, NH_2, and C=O groups was formed in either their crystalline, liquid crystalline or isotropic phases. Highly stable liquid crystalline phases were observed for compounds **D6** and **D10**.

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References

[1] PIMENTAL, G. C., and MCCLELLAN, A. L., 1960, *The Hydrogen Bond* (San Francisco & London: W.H. Freeman).
[2] KATO, T., NAKANO, M., MOTEKI, T., URYU, T., and UJIIE, S., 1995, *Macromolecules*, **28,** 8875.
[3] (*a*) BAZUIN, C. G., BRANDYS, F. A., EVE, T. M., and PLANTE, M., 1994, *Macromol. Symp.*, **84,** 183; (*b*) TALROZE, R., KUPTSOV, S., SYCHEVA, T.,

BAZBORODOV, V., and PLATE, N., 1995, *Macromolecules*, **28,** 8689.

[4] ALEXANDER, C., JARIWALA, C. P., LEE, C. M., and GRIFFIN, A. C., 1994, *Macromol. Symp.*, **77,** 283.

[5] FOUQUEY, C., LEHN, J.-M., and LEVELUT, A. M., 1990, *Adv. Mater.*, **2,** 254.

[6] KATO, T., KIHARA, H., KUMAR, U., URYU, T., and FRECHET, J. M. J., 1994, *Angew Chem. int. Ed. Engl.*, **33,** 1644.

[7] KATO, T., and FRECHET, J. M. J., 1995, *Macromol. Symp.*, **98,** 311.

[8] KIHARA, H., KATO, T., URYU, T., and FRECHET, J. M. J., 1996, *Chem. Mater.*, **8,** 961.

[9] LEE, C.-M., JARIWALA, C. P., and GRIFFIN, A. C., 1994, *Polymer*, **35,** 4550.

[10] LEE, C.-M., and GRIFFIN, A. C., 1997, *Macromol. Symp.*, **117,** 281.

[11] RUOKALAINEN, J., BRINKE, G. TEN, IKKALA, O., TORKKELI, M., and SERIMAA, R., 1996, *Macromolecules*, **29,** 3409.

[12] RUOKALAINEN, J., SAARIAHO, M., IKKALA, O., BRINKE, G. TEN, THOMAS, E. L., TORKKELI, M., and SERIMAA, R., 1999, *Macromolecules*, **32,** 1152.

[13] MAIER, G., and GRIBET, T., 2001, *Polym. Mater. Sci. Eng.*, **84,** 297.

[14] FOLMER, B. J. B., SIJBESMA, R. P., VERSTEGEN, R. M., VAN DER RIJT, J. A. J., and MEIJER, E. W., 2000, *Adv. Mater.*, **12,** 874.

[15] MYLES, A. J., and BRANDA, N. R., 2001, *J. Am. chem. Soc.*, **123,** 177.

[16] WANG, G., LI, M., YU, M., GUO, C., LI, G., and ZHOU, E., 2000, *Liq. Cryst.*, **27,** 867.

[17] WU, Y., LI, M., GUO, C., and OZAKI, Y, *J. Phys. Chem* (submitted).