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Synthesis, supramolecular structure and liquid crystalline behaviour of hydrazide-modified 4-methoxyazobenzene derivatives

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Novel hydrazide-modified 4-methoxyazobenzene derivatives, namely 4-{*n*-[4-(4-methoxyphenylazo)phenoxy] alkoxy} benzoic acid hydrazide (D_n, n=3,6,10), were synthesized and characterized. The FTIR spectra of the D_n compounds were examined in the range 3500–1000 cm^{-1} at different temperatures, and two different kinds of hydrogen-bonded supramolecular structure are proposed. The length as well as the parity of the alkyl spacer in D_n play key roles in determining both the supramolecular structure and the liquid crystalline properties. D_6 and D_{10} are monotropic nematic liquid crystals, while D_3, is a non-mesomorphic material. The melting temperatures of D_n are higher than those of the 4-{*n*-[4-(4-methoxyphenylazo)phenoxy] alkoxy}benzoic ethyl esters (C_n, n=3,6,10) due to the formation of hydrogen bonds.

1. Introduction

Hydrogen bonding is a key interaction in the process of molecular aggregation and recognition in nature, and it can be used to design and assemble supramolecular architectures. Kato and Frechet [1] and Lehn *et al.* [2] have reported a new type of thermotropic supramolecular liquid crystal obtained by molecular recognition processes through intermolecular hydrogen bonds. Such studies provide excellent examples of specific molecular recognition. After these findings, many liquid crystalline materials, including low molar mass liquid crystals [3] and main chain [4] or side chain [5] liquid crystalline polymers, have been prepared using intermolecular hydrogen bonds.

It is well known that hydrogen bonds may be formed between carboxyl (–C=O) and amide (–NH) 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 [6–8]. Jonas *et al.* [9] have investigated a novel system based on hydrazide derivatives of single chain diacetylene lipids, both theoretically and experimentally, and the unique hydrogen bonding pattern of the hydrazide headgroup was described. Our intention is to prepare a novel type of molecule possessing a hydrazide headgroup, to build supramolecular polymers possessing mesomorphic behaviour. Besides the hydrogen bonding between the carbonyl oxygen and the hydrogen of the amide nitrogen, there is also a hydrogen bonding interaction of the terminal amine hydrogens and their free electron pairs. Two points may be noted. First, the system contains only one component and the molecules should form a pseudo-side chain liquid crystalline polymer in which polymer backbone is formed through intermolecular hydrogen bonding between –NH, –C=O and –NH_2 groups. Second, the molecules might exhibit mesogenic behaviour due to the $\pi - \pi$ stacking of 4-methoxyazobenzene groups.

2. Experimental

2.1. *Synthesis of compounds D_n*

The synthetic route to the D_n compounds is given in the scheme. The following are typical synthetic processes.

The intermediates B_n were first prepared using diazotization and Williamson etherification reactions [10, 11].

2.1.1. 4-{3-[4-(4-Methoxyphenylazo)phenoxy]propoxy} benzoic ethyl ester (C_3). A mixture of 3.52 g (0.0212 mol) of 4-hydroxybenzoic acid ethyl ester, 7.39 g (0.0212 mol) of compound B_3, 11.89 g of anhydrous potassium carbonate, 0.3 g of KI and

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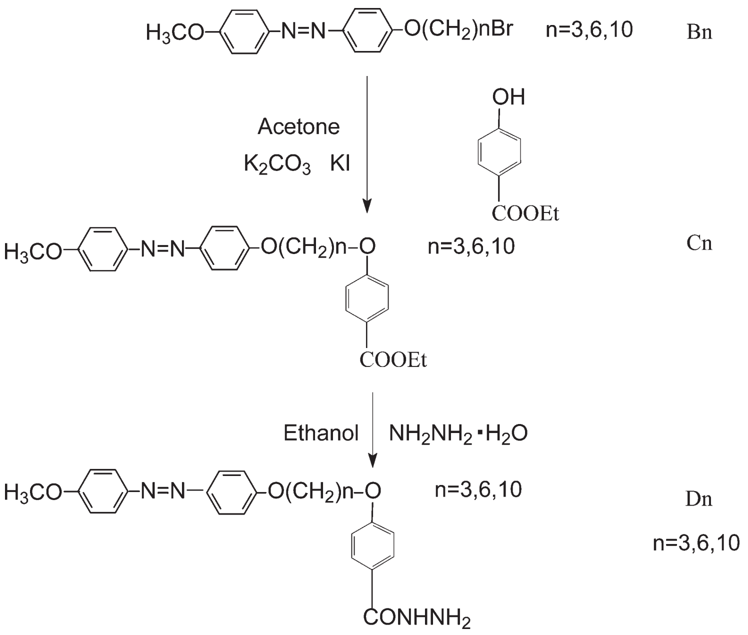

Scheme. Synthetic route for D_n compounds.

200 ml of dry acetone was heated under reflux for 30 h. After cooling to room temperature, the mixture was poured into an excess of ice water, and the precipitate recrystallized from anhydrous ethanol; yield 78%, m.p. 130–131°C. ^{1}H NMR (400 MHz, CDCl3), (ppm, from TMS): 1.36–1.39 (t, 3H, –C–CH_3), 2.31–2.34 (m, 2H, –C–CH_2–C–), 3.89 (s, 3H, –Ar–O–CH_3), 4.23–4.26 (m, 4H, –O–CH_2–C–), 4.32–4.37 (m, 4H, –O–$\underline{CH_2}$-CH_3), 6.93–6.95 (m, 2H, Ar–H, *m*-to, –COO–), 6.99–7.02 (m, 4H, Ar–H, *m*-to –N=N–), 7.88–7.91, (m, 4H, Ar–H, *o*-to –N=N–), 7.88–8.01 (m, 2H, Ar–H, *o*–to, –COO–). FTIR (KBr, pellet, cm^{-1}): 2948, 2931,2879 (–CH_2–, $\nu_{\alpha s}$ and ν_s), 2837 (–CH3, ν_s), 1713 (–C=O–, ν), 1601, 1497 (aromatic, $\nu_{C\text{-}C}$), 1469 (–CH_3, δ), 1314 (Ar–N, $\nu_{C\text{-}N}$), 1246, 1054 (Ar–O–C, ν), 1168, 1147 (O–CH_2, ν_s), 840 (aromatic, ν_{CH}).

Compounds C_6 and C_{10} were similarly synthesized and characterized. C_6: yield 80%, m.p. 131–131.5°C. C_{10}: Yield 85%, m.p. 127–128°C.

2.1.2. 4-{3-[4-(4-Methoxyphenylazo)phenoxy]propoxy} benzoic acid hydrazide (D_3). A mixture of 1.1188 g (0.0026 mol) of compounds C_3 and an excess of hydrazine monohydrate was dissolved in anhydrous alcohol and heated under reflux for 30 h. After the reaction was complete, the precipitate was filtered, washed with water, then recrystallized from ethanol and dried under vacuum; yield 70%, m.p. 190–191°C. ^{1}H NMR (400MHz, d_6-DMSO), (ppm, from TMS): 2.20–2.25 (m, 2H,–C–CH_2–C–), 3.86 (s, 3H, –Ar–O–CH_3), 4.20–4.26 (m, 4H, –O–CH_2–C–), 4.40–4.41 (d, 2H, –CO–N–NH_2), 6.99–7.02 (m, 2H, Ar–H, *m*-to –CON–), 7.11–7.15 (m, 4H, Ar–H, *m*-to –N=N–), 7.77–7.80, (m, 4H, Ar–H, *o*-to –N=N–), 7.80–7.85 (m, 2H, Ar–H, *o*-to –CON–), 9.61 (s, 1H, –CO–$\underline{NH}$–NH_2). FTIR (KBr, pellet, cm^{-1}): 3303, 3265, 3183 (–NH–, $\nu_{N\text{-}H}$), 2952, 2883, 2839 (–CH_2–, ν_s), 1648 (–C=O–, $\nu_{C\text{-}O}$), 1602, 1500 (aromatic, $\nu_{C=C}$), 1534 ($\nu_{C\text{-}N}$+δ_{NH}); 1466 (–CH_3, δ), 1301 (Ar–N, $\nu_{C\text{-}N}$), 1251, 1026 (Ar–O–C, ν), 1148, 1108, 1057 (–NH_2, γ_{NH2}), 838 (aromatic, ν_{CH}), 547 (aromatic, δ_{CH}). Elemental analysis: found, N 13.64, C 66.04, H 5.81; calcd for $C_{23}H_{24}N_4O_4$, N 13.33, C 65.70, H 5.75%.

Using the same method, compounds D_6 and D_{10} were successfully synthesized and their structures confirmed by IR and NMR. D_6: yield 65%, m.p. 190–191°C. Elemental analysis: found, N 11.75, C 67.14, H 6.69; calcd for $C_{26}H_{30}N_4O_4$, N 12.11, C 67.51, H 6.54%. D_{10}: Yield 60%, m.p. 177–178°C. Elemental analysis: found, N 10.71, C 69.50, H 7.27; calcd for $C_{30}H_{38}N_4O_4$, N 10.80, C 69.47, H 7.38%.

2.2. *Characterization*

The ^{1}H NMR spectra of the compounds were recorded with a Varian Unity 400 spectrometer (400 MHz), using deuteriated chloroform ($CDCl_3$) or d_6-DMSO as solvent, and tetramethylsilane (TMS) as an internal chemical shift reference. FTIR spectra were recorded with a Perkin Elmer Spectrum One B instrument. Samples for general study were pressed tablets of mixtures 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 plate. This sandwiched sample cell was held on a hot stage, with temperature control within 1°C. Elemental analyses were carried out on a ThermoQuest Italia S.P.A. FlashEA1112 apparatus.

The thermal properties of the compounds were investigated with a Mettler-Toled. DSC821^e instrument. The rate of heating and cooling was 10°C min^{-1}; the weight of the sample was about 2 mg, and indium and zinc were used for calibration. The peak maximum was taken as the phase transition temperature. Optical textures were observed by polarizing optical microscopy (POM) using a Leica DMLP microscope equipped with a Leitz 350 heating stage. Wide angle X-ray diffraction (WAXD) measurements were conducted with a Rigaku D/max 2500 PC X-ray generator, and a flat plate camera using Cu-K$_\alpha$ (λ=0.154 nm) radiation.

3. Results and discussion

3.1. *Synthesis*

The synthesis of compounds D_n consisted of four steps, involving the azo-coupling of phenol with 4-methoxyaniline, Williamson etherification with dibromoalkane and ethyl 4-hydroxybenzoate, and finally the hydrazidation of the C_n ethyl esters.

3.2. *FTIR analysis and the supramolecular structure of* D_n

3.2.1. Temperature-dependent IR spectra and the supramolecular structure of D_{10} and D_6. Temperature-dependent IR spectra can provide valuable information concerning thermally induced structural changes in hydrogen-bonded materials. Figure 1 (*a*) shows the IR spectra of D_{10} in the region 3500–1000 cm^{-1} measured at different temperatures on cooling from the isotropic phase. The presence of the broad band features in the 3500–3100 cm^{-1} region at 60°C (a) and their shift to higher wavenumbers at 190°C (e) indicate that strong intermolecular hydrogen bonding exists in D_{10} at low temperatures [12, 13]. The band at 3294 cm^{-1} is attributed to the N–H stretching mode of the hydrogen-bonded amide group overlapping with the antisymmetric stretching mode of the hydrogen-bonded NH_2 group, which splits into two bands at 3434 and 3328 cm^{-1} at 190°C (e). These two bands are tentatively assigned to the N–H stretching mode of the free amide group and the antisymmetric stretching mode of the free NH_2 group [14]. The band at 3205 cm^{-1} results from the Fermi resonance band between the symmetric stretching mode of the hydrogen-bonded NH_2 group and the overtone of its bending mode, which shift to 3216 cm^{-1} at 190°C. The four bands at 2936, 2921, 2876 and 2852 cm^{-1} are attributed to the antisymmetric and symmetric stretching modes of CH_3 and CH_2, respectively.

In the lower spectral region, the two bands at 1479 and 1464 cm^{-1} in (a) are assigned to CH_2 scissoring modes, which are sensitive to the intermolecular interaction of alkyl chains. The two CH_2 scissoring bands merge into one band at 1468 cm^{-1} at 190°C (e). The bands centred at 1650 and 1625 cm^{-1} are attributed to hydrogen-bonded C=O stretching modes and NH_2 bending modes, which at 190°C shift to 1670 and 1621 cm^{-1}, respectively. In addition, the bands at 1602 and 1498 cm^{-1} are ascribed to the vibration modes of the phenyl ring, and the strong band at 1246 cm^{-1} to the stretching mode of Ar–O–C in D_{10}. The assignments of bands to characteristic vibrations of D_{10} are listed in table 1, which is based on the related literature [9, 12–15]. The spectral changes were reversible upon heating and cooling across the melting points, suggesting that hydrogen bonds between –C=O, –NH and $-NH_2$ groups exists in phases other than the isotropic state.

Compound D_6 shows IR spectra similar to those of D_{10}. Based on the IR analysis of D_{10} and D_6 and on the literature [9, 14, 15], a schematic representation of the supramolecular structures of D_{10} and D_6, showing the hydrogen bonding interaction, is given in figure 2 (*a*). Two kinds of hydrogen bonding in D_{10} and D_6 are formed: (i) the hydrogen bonding between carbonyl and amide groups, and (ii) the hydrogen bonding interaction between terminal amine hydrogens and their free electron pairs. The $-NH_2$ group acts simultaneously as a hydrogen donor and acceptor. The supramolecular pseudo-side chain liquid crystalline polymers are built through double intermolecular hydrogen bonding between –C=O, –NH and $-NH_2$ groups.

3.2.2. Temperature-dependent IR spectra and the supramolecular structure of D_3. Figure 1 (*b*) shows IR spectra of D_3 in the 3500–1000 cm^{-1} region measured at (f) 60°C and (g) 210°C on heating; and over a temperature range 200–100°C (a–e) on cooling. It can be seen that the band centred at 1670 cm^{-1} at 150°C shifts to 1650 cm^{-1} at 140°C, which indicates that the –C=O group is involved in hydrogen bond formation. The bands at 3434 and 3328 cm^{-1} shift to 3262 and 3181 cm^{-1}, respectively, within the same temperature region, showing that the hydrogen bond involving the

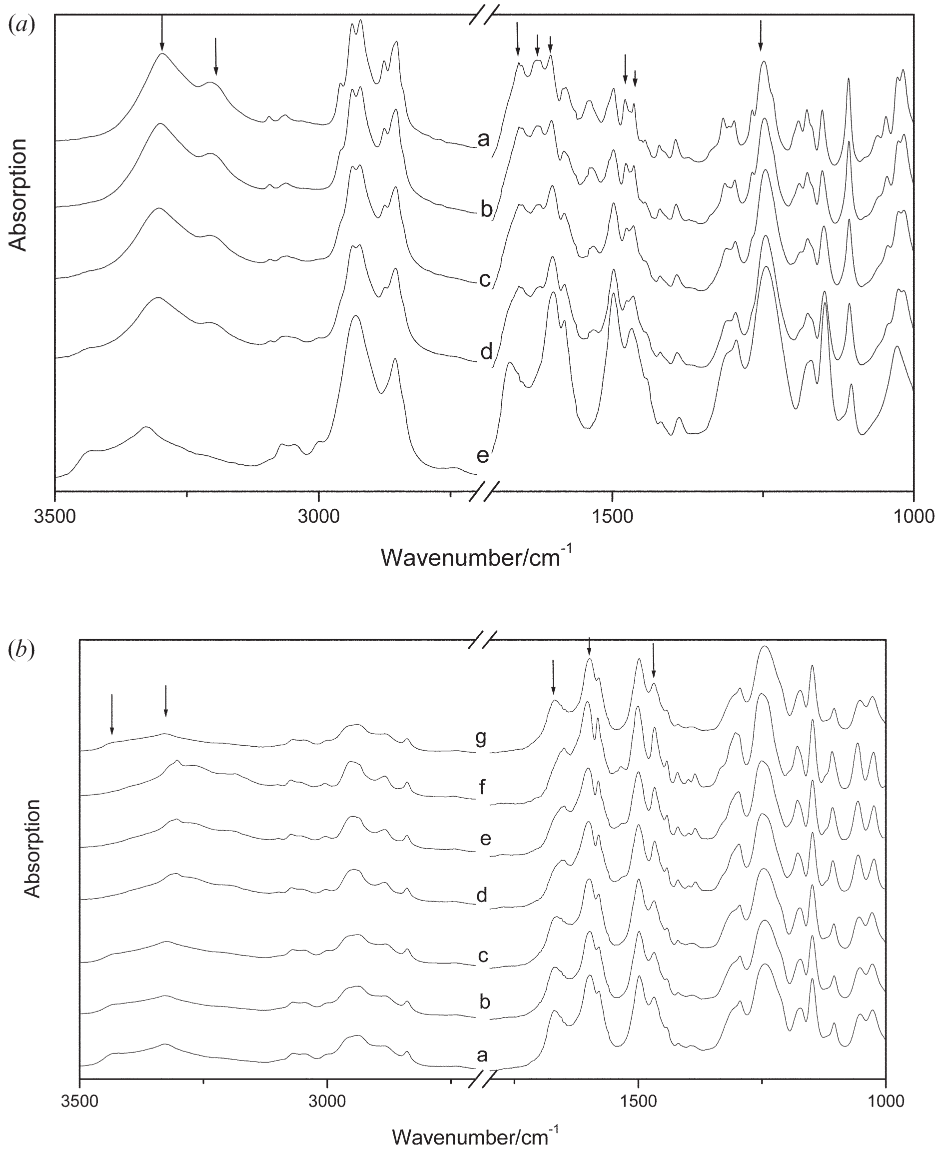

Figure 1. (*a*) FTIR spectra of D_{10} in the range 3500–1000 cm^{-1}at various temperatures on cooling: (a) 60°C, (b) 100°C, (c) 150°C, (d) 160°C (e) 190°C, (*b*) FTIR spectra of D_3 in the range 3500–1000 cm^{-1} at various temperatures: (a) 200°C, (b) 180°C, (c) 150°C, (d) 140°C (e) 100°C on cooling; (f) 60°C (g) 210°C on heating.

–NH_2 group is also formed at this temperature. Based on two-dimensional correlation spectra [14], the –NH of the amide group may not participate in the hydrogen bond formation in D_3.

A comparison of band intensity changes of the phenyl ring around 1600 and 1500 cm^{-1} between figures 1 (*a*) and (*b*) shows less change for D_3 than for D_{10}. As mentioned already, significant intensity changes of these bands are attributed to thermally induced structural variations of $\pi - \pi$ stacking among the aromatic groups in D_{10} [16]. Therefore, the slight intensity changes for the phenyl ring in D_3 indicate that no strong $\pi - \pi$ stacking exists among the aromatic groups. It should also be noted that there is no strong temperature dependence of intensity of the Ar–O–C stretching bands at 1244 cm^{-1} in D_3, figure 1 (*b*) indicating that the rotational freedom of Ar–O–C changes little in either melting or crystallization of D_3. That is, the rotational freedom of Ar–O–C is relatively high and the packing of the aromatic groups is not tight in either the crystalline or isotropic phases of D_3. It can be concluded that both the length and the parity of the alkyl spacer in D_n play important roles in the type of supramolecular structure. Combining the FTIR analysis of D_3 with literature results [14], it is reasonable to propose a supramolecular structure for D_3 as shown in

Table 1. Frequencies (cm^{-1}) of the observed IR spectra and the corresponding assignment to characteristic vibrations of D_{10}.

60°C	190°C	Assignment
3294	3434	free amide sym stretching
	3328	NH_2 antisym stretching
3205	3216	Fermi resonance of NH_2 sym stretching and the overtone of NH_2 bending
2936	2930	CH_3 antisym stretching
2921	2930	CH_2 antisym stretching
2876	2855	CH_3 sym stretching
2852	2855	CH_2 sym stretching
1655	1670	amide I
1625	1620	NH_2 bending
1602	1598	phenyl ring stretching
1580	1580	phenyl ring stretching
1540		amide II
1498	1498	phenyl ring stretching
1479	1468	CH_2 scissoring
1464	1468	CH_2 scissoring
1317	1312	amide III
1246	1245	phenyl-O stretching
1152	1148	NH_2 scissoring
1108	1104	NH_2 scissoring
842	839	phenyl ring breathing

figure 2 (*b*). The supramolecular D_3 dimer is formed through intermolecular hydrogen bond between –C=O and $-NH_2$ groups.

3.3. *Phase transitional properties*

DSC curves for the D_n compounds in the course of heating and cooling are given in figure 3. It can be seen that there is only one endothermic peak for D_3, D_6 and D_{10} upon heating corresponding to their melting. During cooling, there is only one exothermic peak for D_3 corresponding to the isotropic–crystalline transition. Two exothermic peaks, corresponding to isotropic–liquid crystalline and liquid crystalline–crystalline transitions, were observed for D_6 and D_{10} during cooling. It can be concluded that D_6 and D_{10} exhibit monotropic liquid crystalline behaviour.

Figure 4 shows a POM photomicrograph of D_6 observed in the LC phase. The WAXD spectra of D_n (n=6,10) compounds in their liquid crystalline phases showed only one diffuse diffraction at $2\theta=20°$ corresponding to a *d*-spacing of 0.44 nm, which is characteristic of the nematic phase.

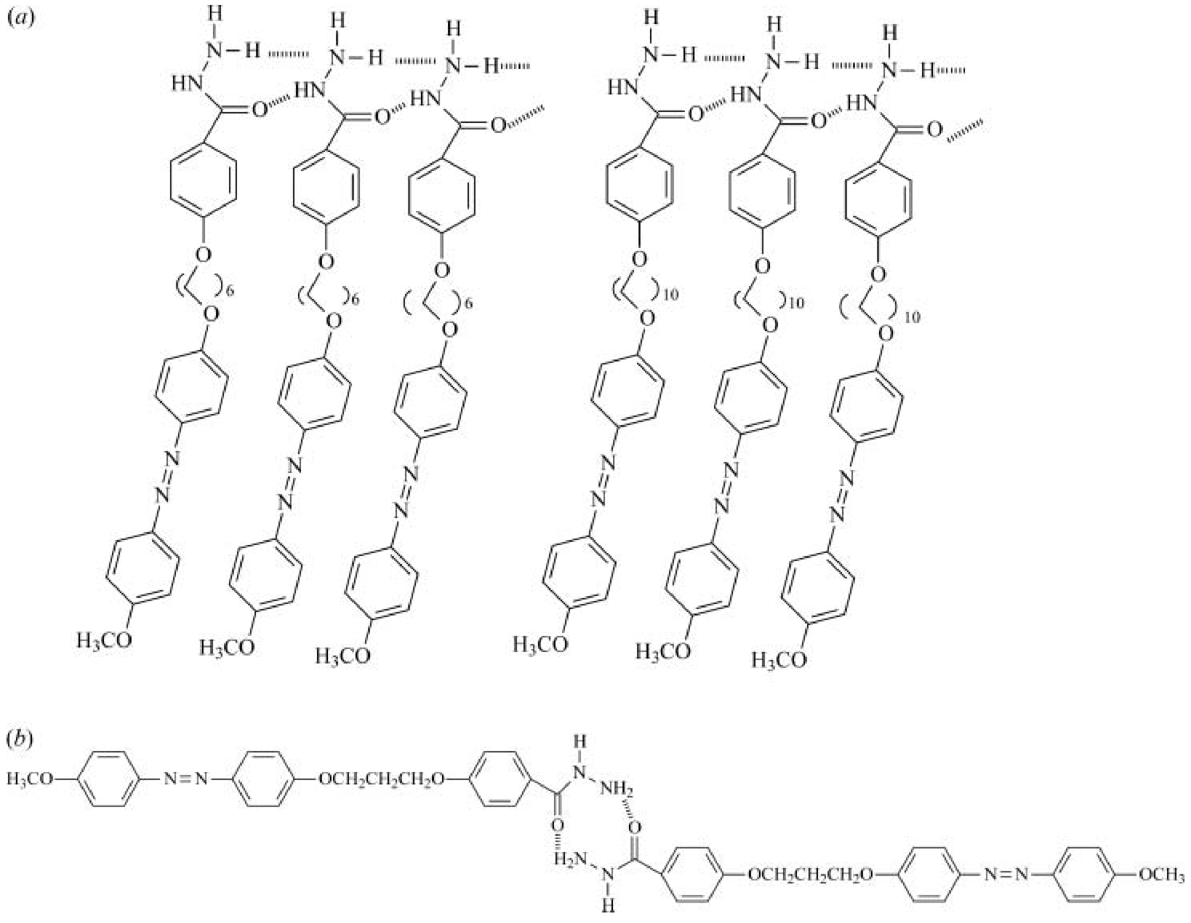

Figure 2. Schematic representation of the supramolecular structure of (*a*) D_6 and D_{10} (*b*) D_3.

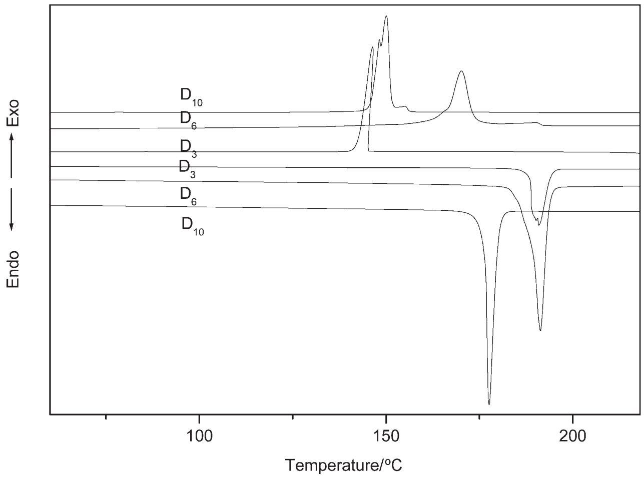

Figure 3. DSC curves of D_n compounds.

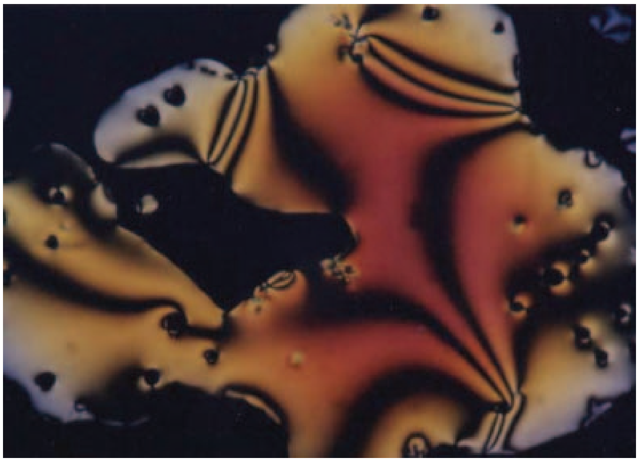

Figure 4. Polarizing optical photomicrographs (×200) of D_6 at 189°C.

Table 2. Transition temperatures (°C) and enthalpies of transition ($kJ\,mol^{-1}$, in parentheses) of D_n and C_n compounds: Cr=crystalline, N=nematic, I=isotropic phase.

Compound	Heating	Cooling
C_3	Cr 131 (42.1) I	I 92 (39.91) Cr
C_6	Cr 131 (64.27) I	I 132 (3.20) N 115 (52.57) Cr
C_{10}	Cr 127 (90.89) I	I 109 (0.11) N 108 (82.02) Cr
D_3	Cr 191 (72.20) I	I 146 (56.15) Cr
D_6	Cr 191 (69.66) I	I 190 (0.88) N 170 (34.03) Cr
D_{10}	Cr 178 (92.77) I	I 155 (1.21) N 150 (57.77)

Combining the results of DSC, WAXD and POM, the phase transitional properties of D_n compounds during heating and cooling are summarized in table 2. For comparison, the thermal properties of C_n compounds are also listed. It can be seen that D_6 and D_{10} are monotropic nematic liquid crystals, while D_3 is non-mesomorphic. Thus both supramolecular structure and liquid crystalline behaviour are affected by the length of the alkyl spacers. The melting temperature (T_m) of D_n is much higher than that of the corresponding C_n. These results suggested that hydrogen bonding plays an important role in the stabilization of crystalline and mesomorphic phases.

4. Conclusion

Novel supramolecular liquid crystals containing the 4-methoxyazobenzone mesogenic group have been synthesized and characterized. The FTIR studies on D_n (n=3, 6, 10) revealed two kinds of hydrogen bonding pattern, depending on the length of alkyl spacer. For D_6 and D_{10}, through double intermolecular hydrogen bonding between –C=O, –NH and $–NH_2$ groups, supramolecular pseudo-side chain liquid crystalline polymers are constructed; while for D_3, a supramolecular dimer is formed through an intermolecular hydrogen bond between –C=O and $–NH_2$ groups. Both the length and the parity of the alkyl spacer in D_n play key roles in the supramolecular structure and liquid crystalline behaviour. D_6 and D_{10} are monotropic nematic liquid crystals, while D_3 is non-mesomorphic. The melting temperatures of D_n compounds are higher than those of the corresponding C_n ester derivatives due to the formation of hydrogen bonds.

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References

[1] T. Kato, J.M.J. Frechet. *J. Am. Chem. Soc.*, **111**, 8533 (1989).
[2] M.-J. Brienne, J. Gabrad, J.-M. Lehn, I. Stibor. *J. chem. Soc. chem. Commun.*, 1868 (1989).
[3] Y.S. Kang, H. Kim, W.C. Zin. *Liq. Cryst.*, **28**, 709 (2001).
[4] C. Alexander, C.P. Jariwala, C.M. Lee, A.C. Griffin. *Macromol. Symp.*, **77**, 283 (1994).
[5] T. Kato, M. Nakano, T. Moteki, T. Uryu, S. Ujie. *Macromolecules*, **28**, 8875 (1995).
[6] G. Maier, T. Gribet. *Polym. Mater. Sci. Eng.*, **84**, 297 (2001).
[7] B.J.B. Folmer, R.P. Subesma, R.M. Verstegen, J.A.J. Vanderrijt, E.W. Meijer. *Adv. Mater.*, **12**, 874 (2000).
[8] A.J. Myles, N.R. Branda. *J. Am. chem. Soc.*, **123**, 177 (2001).

[9] U. Jonas, K. Shah, S. Norvez, D.H. Charych. *J. Am. chem. Soc.*, **121**, 4580 (1999).

[10] M. Li, C.W. Guo, Y.Q. Wu. *Liq. Cryst.*, **29**, 1031 (2002).

[11] G.J. Wang, M. Li, M.M. Yu, C.W. Guo, X.F. Chen, G. Li, E.L. Zhou. *Liq. Cryst.*, **27**, 867 (2000).

[12] D. Lin-Vien, N.B. Colthup. *Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*. Academic Press (1999).

[13] B.J. Bulkin. *Advances in Infrared and Raman Spectroscopy*, vol. 8, p. 257, Heyden, New York (1991).

[14] H.H. Zhang, Y.Q. Wu, B.L. Bai, M. Li, *J. Phys. Chem. B* (submitted).

[15] Y.Q. Wu, Y.Q. Hao, M. Li, C.W. Guo, Y. Ozaki. *Appl. Spectrosc.*, **57**, 933 (2003).

[16] K. Aoki, M. Nakagawa, K. Ichimura. *J. Am. chem. Soc.*, **122**, 10997 (2000).