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Study of the effect of hydrogen bonding on the phase behaviour of *p*-nitro azobenzene derivatives with hydrophilic tails

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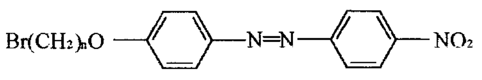
The infrared spectra of *N*-*n*-(4-nitrophenyl)azophenyloxyalkyldiethanolamines (C*n*) are examined in the range of 4000–400 cm^{-1} at different temperatures and the assignment of the fundamental vibrations given. Based on (1) the localization of the broad absorption band at 3456 cm^{-1}, and (2) attribution of the associated OH bands centred at 1410–1390, 1100, and 650–634 cm^{-1} to, respectively δOH deformation, νC–O stretching and γOH out-of-plane bending, intermolecular hydrogen bonding between OH groups in the crystalline, liquid crystalline and isotropic states is proposed. By considering the results of FTIR, WAXD and DSC measurements, the molecular arrangment of C10 in its smectic A phase as consisting of hydrogen bonding and strong interaction between dipolar groups (NO_2) is proposed. This may explain the high stability and high orientational ordering property of C*n* compounds in the liquid crystalline state compared with that of *n*-bromo-1-[4-(4-nitrophenyl)azophenyl] oxyalkanes (B*n*).

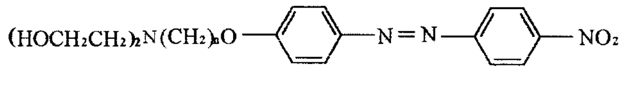
1. Introduction

Hydrogen bonding is one of the key interactions in the process of molecular aggregation and recognition in nature [1]; the use of hydrogen bonding in molecular design may widen the applicability of organic materials. Jeffrey [2] reviewed carbohydrate liquid crystals (LCs) and discussed the role of the hydrogen bond in the formation of LC phases. Recently, T. Kato *et al.* [3–5] found that a novel family of liquid crystalline materials could be built through intermolecular hydrogen bonding between independent and different components. A hydrogen bonded complex prepared in this way exhibited a nematic phase with high thermal stability due to the formation of an extended mesogen through hydrogen bonding. Studies on amphiphilic diols also revealed [6] that hydrogen bonding between neighbouring molecules was responsible for the occurrence of metastable liquid crystalline phases in the water-free state of amphiphilic alkane-1,2-diols; here the hydroxyl groups are organized in long hydrogen bonded networks arranged in double layers forming parallel and equidistant sheets separated by the hydrophobic alkyl chains.

p-Nitroazobenzene derivatives have been studied by many workers [7, 8] investigating the nonlinear optical effect due to the delocalized π-electron system arising from electron donor, acceptor and aromatic rings. Recently, we reported [9] the synthesis and characterization of a new class of *p*-nitroazobenzene liquid crystals with varying length of hydrophilic tails (OH groups), which will be used to prepare cross-linkable linear liquid crystalline polyesters. In the present study, Fourier transform infrared (FTIR) spectroscopy was used to study the hydrogen bond and to understand the phase behaviour of azo type LCs with hydrophilic tails. The molecular structures of these compounds is given in figure 1.



Bn (n = 3, 5, 6, 8, 10)



Cn (n = 3, 5, 6, 10)

Figure 1. The molecular structures of monomers B*n* and C*n*.

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2. Experimental

2.1. *Synthesis of the liquid crystals*

Liquid crystalline compounds with different lengths of hydrophilic tails, namely, *N*-*n*-(4-nitrophenyl)-azophenyloxyalkyldiethanolamine (C*n*), were prepared through a substitution reaction between a *n*-bromo-1-[4-(4-nitrophenyl)azophenyl] oxyalkane (B*n*) and a diethanolamine. Details of the preparation and characterization results were given in a previous paper [9].

2.2. *Characterization*

FTIR spectra were recorded with a BIO-RAD FTS-7 spectrometer. The samples were cast on a KBr window from chloroform solution to form thin films and another KBr window was placed on top. The sandwiched sample cell was held on a temperature controlled hot stage.

Thermal properties were determined with a Perkin Elmer DSC-7 instrument, with heating and cooling rates of 10°C min^{-1}.

Optical texture observations were performed with a Leitz-Wetzlar optical microscope equipped with a hot stage.

Wide angle X-ray diffraction (WAXD) measurements were conducted on a Philips X-ray generator (PW1700), using nickel filtrated CuK$_\alpha$ radiation.

3. Results and discussion

3.1. *Liquid crystalline properties of compounds Cn and Bn*

Table 1 shows the thermal properties of the two series of monomers B*n* and C*n* [9]. The transition temperatures were taken as the peak temperatures of the endotherms on heating and exotherms on cooling. On heating, smectic A (SmA) phases were clearly observed for C*n* compounds with $n = 5$, 6, and 10; on cooling, SmA phases were observed for C*n* with $n = 3$, 5, 6, and 10. The fan-like optical morphology for C10 shown in figure 2 confirmed the existence of the SmA phase. No liquid crystalline behaviour was observed for B*n* with $n = 2$, 3, 4, 5, 6, 8 and 10 on heating; nematic phases were found for B*n* with $n = 6$, 8, and 10 on cooling.

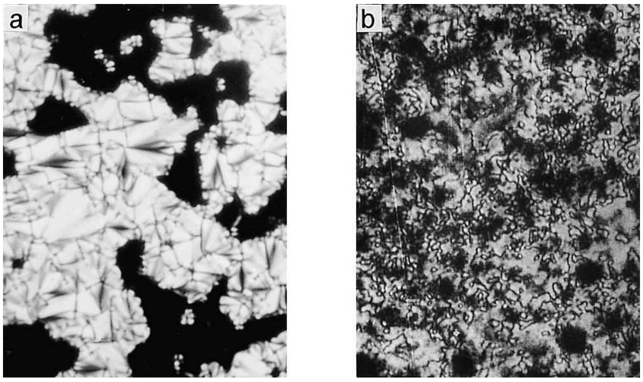

Figure 2. The optical texture of C10 at 104°C (*a*) and B8 at 68°C (*b*).

From the above analysis, it can be concluded that compounds with the same core structure but different polar tails (–OH and –Br) show different phase behaviour. C*n* compounds exhibit enantiotropic SmA phases for $n = 5$, 6, and 10; monotropic SmA for $n = 3$. Only monotropic nematic phases for B*n* with $n = 6$, 8, and 10 were found. Compared with B*n* compounds, the SmA phases of C*n* compounds with different lengths of terminal group showed high thermal stability.

3.2. *Hydrogen bond formation in Cn compounds*

The molecular structure of C*n* compounds suggest that hydrogen bonding might occur between OH groups or between OH and NO_2 groups. In order to know the exact interaction and to understand the difference in phase behaviour between B*n* and C*n* compounds, an FTIR spectroscopic study on C*n* at different temperatures was performed. Figure 3 shows the FTIR spectrum of C10 at room temperature and the assignments of the bands are listed in table 2, based on the established frequencies for IR bands [10].

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

Compounds	Heating	Cooling
B3	Cr 134 I	I 114 Cr
B5	Cr 122 I	I 102 Cr
B6	Cr 90 I	I 71 N 70 Cr
B8	Cr 78 I	I 71 N 54 Cr
B10	Cr 81 I	I 70 N 56 Cr
C3	Cr 126 I	I 119 (3.09) SmA 115 (25) Cr
C5	Cr 89 (62.6) SmA 125 (4.8) I	I 124 (5.28) SmA 68 (13.8) Cr
C6	Cr 67 (8.8) SmA 119 (4.41) I	I 117 (4.48) SmA 62 (9.0) Cr
C8		
C10	Cr 70 (36.7) SmA 114 (5.37) I	I 111 (6.06) SmA 59 (14.58) Cr

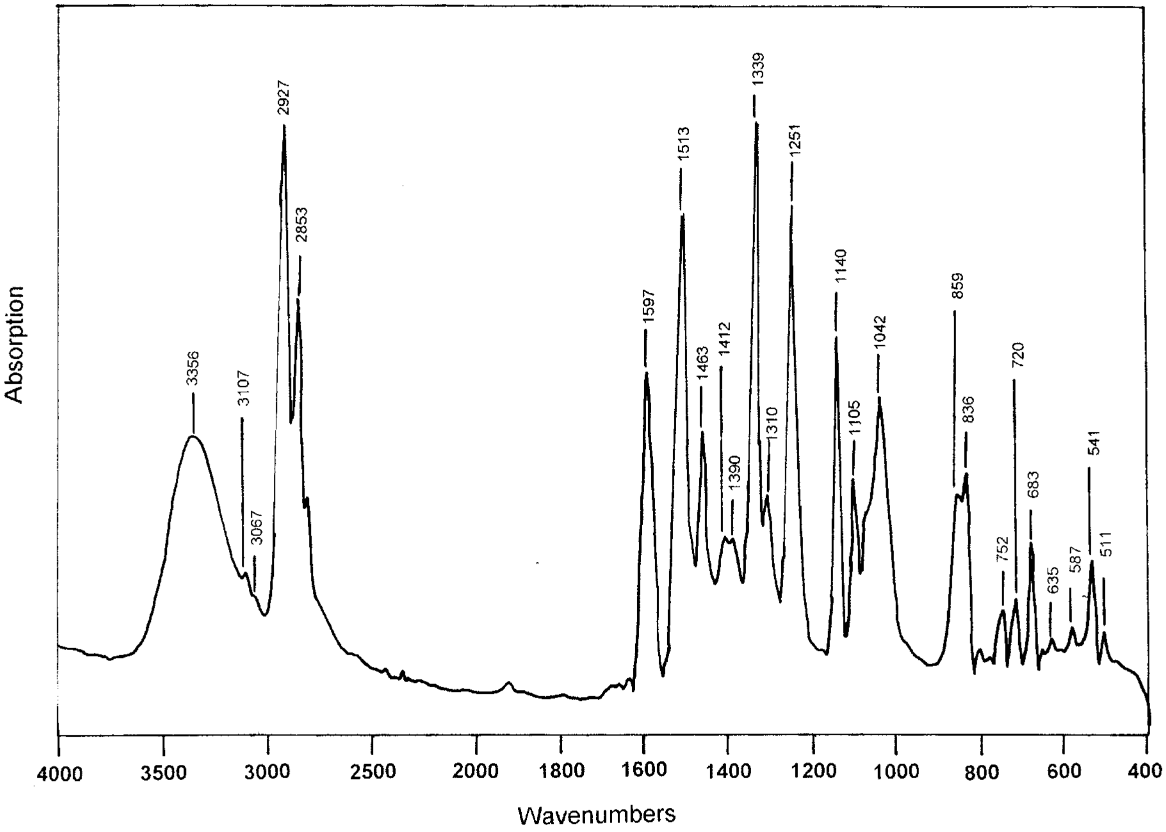

Figure 3. FTIR spectrum of C10 at room temperature.

Table 2. IR fundamental bands and their assignments for C10 at room temperature.

Bands/cm^{-1}	Assignment
3356	stretching vibration of associated OH groups
3107 and 3067	stretching vibration of C–H groups of aromatic rings
2927 and 2853	symmetric and asymmetric vibration of CH$_2$ groups
1597	stretching vibration of C=C of aromatic rings
1514	asymmetric vibration of NO$_2$
1463	deformation vibration of CH$_2$
1412 and 1390	stretching vibration of C–O coupled with in-plane bending of OH
1339	symmetric vibration of NO$_2$
1310	in-plane bending of OH
1251	stretching vibration of C–O–C coupled with deformation of OH
1140	stretching vibration of C–O
1105	stretching vibration of C–OH
1042	stretching vibration of C–O
859	stretching vibration of C–N
836	stretching vibration of C–H of aromatic rings
752	in-plane bending of C–NO$_2$
720	CH$_2$ rocking
684	folding vibration of aromatic rings
651 and 634	out-of-plane bending vibration of associated OH
587	
536	deformation vibration of C–C–O and in-plane rocking of CH$_2$

3.2.1. *Hydroxyl vibrations*

In the pure liquid or solid states, alcohols usually exhibit intermolecular hydrogen bonding. In the vapour state and in dilute solution in nonpolar solvents, alcohols exist essentially in the monomeric form (free –OH). In concentrated solutions or in mixtures, both free and bonded associated forms may be present [1]. Spectroscopic studies [11] on a series of normal primary or secondary alcohols indicated that association bands appear near 3300, 1410, 1330, 1110 and 670 cm^{-1}, whereas the monomer bands are found near 3640, 1250, 1080 and 200 cm^{-1}.

3.2.2. *νOH vibration*

The FTIR spectra of C10 at different temperatures are given in figure 4. Clearly, the frequency of the stretching vibration of OH groups (νOH) is shifted upwards with the increase of temperature, indicating the existence of hydrogen bonding. The plot of frequency versus temperature is given in figure 5; it can be seen that in the crystalline region, νOH frequency hardly changes before a large increase at T_{CrS}. A free hydroxyl stretching vibration centred at 3570 cm^{-1} appears above T_{SI}. This analysis confirms that (1) hydrogen bonding exists in the crystalline, liquid crystalline and isotropic phases, (2) no free hydroxyl groups exist in the crystalline or liquid crystalline phases. Besides the upward frequency shift of νOH, the half-width of νOH decreased with increase of temperature indicating a weakening of the hydrogen bond.

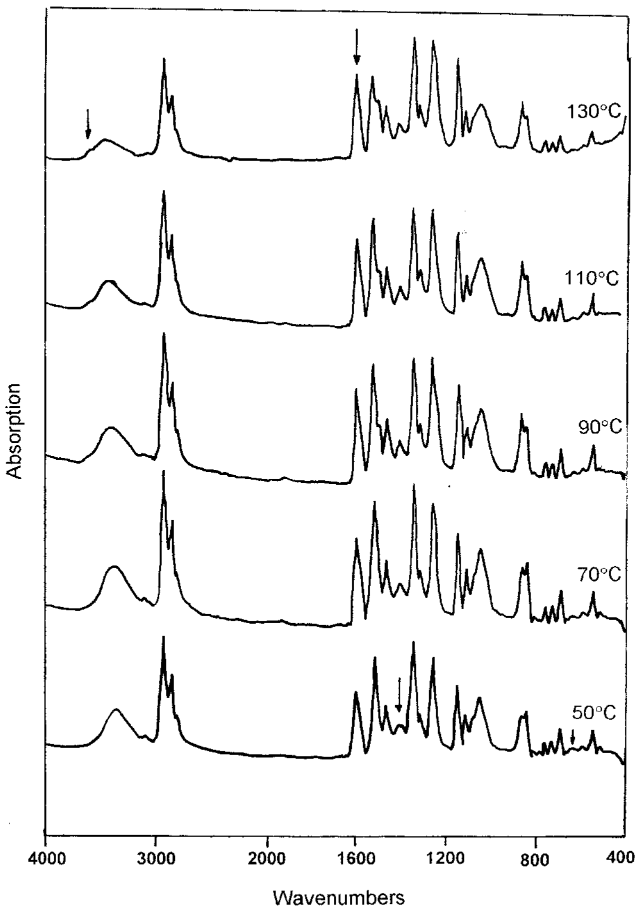

Figure 4. FTIR spectra of C10 at different temperatures.

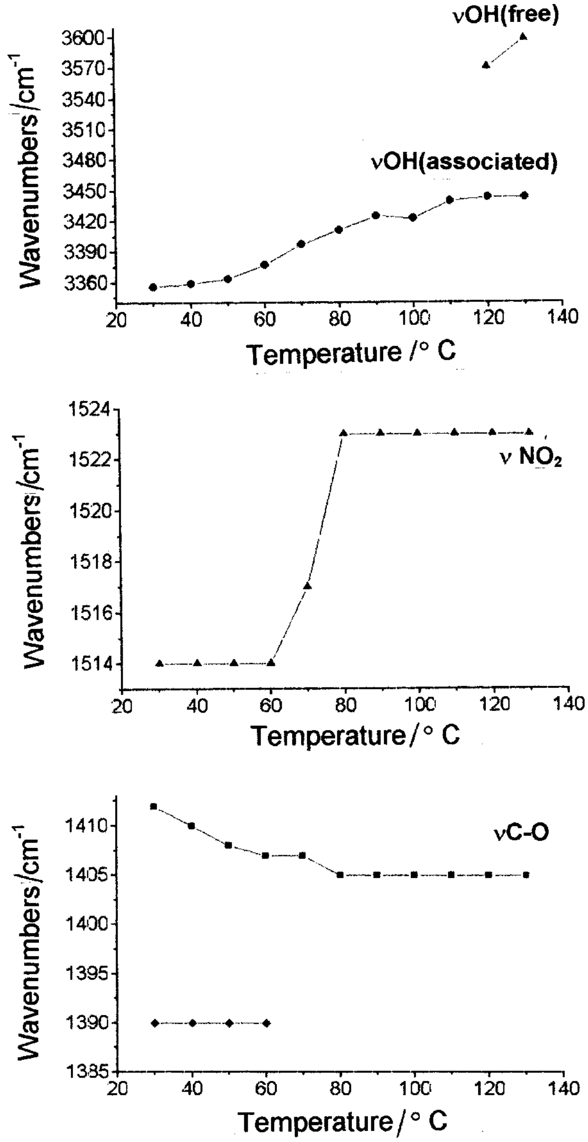

Figure 5. Plot of vibration frequencies versus temperature for different groups.

3.2.3. *γOH vibrations*

The intermolecular γOH association band has been observed as a doublet at 670–650 cm^{-1} in γ-hydroxybutyrates [12]. As for C10 the doublet at 630–650 cm^{-1} was attributed to the intermolecular γOH association band. As can be seen from figure 4, the γOH frequency changes little with temperature, while the intensity in the crystalline state is higher than in the liquid crystalline and isotropic states, indicating that the hydrogen bond is strongest in the crystalline state.

3.2.4. *δOH deformations*

Association bands occured in the IR spectra of C10 as a doublet at 1410–1390 cm^{-1}, consistent with the existence of strong intermolecular hydrogen bonding in the crystalline state. This doublet changed into a single band centred at 1407 cm^{-1} at temperatures higher than 80°C. The frequency change is given in figure 5; clearly, the δOH frequency shifts downwards with increase in temperature, again confirming the existence of intermolecular hydrogen bonding in C10.

3.2.5. *νC–OH vibrations*

Bands at 1105 and 1140 cm^{-1} corresponded respectively, to intermolecularly bonded OH and the stretching vibration mode (νC–O) [12]; no intramolecular hydrogen bonding of νC–O (centred at 1120 cm^{-1}) or free OH group vibration (centred at 1080 cm^{-1}) were observed. The frequencies of νC–O and νC–OH changed little with increase of temperature.

3.2.6. *νNO$_2$ vibrations*

Strong absorption bands at 1335 and 1514 cm^{-1} corresponded respectively to symmetric and asymmetric stretching vibration of NO$_2$ groups. Plots of νNO$_2$ versus temperature are given in figure 5. It can be seen that the frequency of ν_{as}NO$_2$ shifted upwards from 1513 cm^{-1} at temperatures below 70°C to 1523 cm^{-1} at temperatures higher than 80°C, suggesting that NO$_2$ acting as a proton acceptor participated in the forming of hydrogen bonding with OH groups. The hydrogen bonding between OH and NO$_2$ groups was stable in the crystalline state and destroyed at temperatures higher than T_{CrS}.

3.3. *Molecular arrangment of Cn compounds in the liquid crystalline phase*

From the above analysis, it can be inferred that intermolecular hydrogen bonding between OH groups and between OH and NO$_2$ groups existed in the crystalline state. After melting of the three-dimensional-ordered crystalline lattice, the weak hydrogen bond between OH and NO$_2$ groups was destroyed, but the ordered clusters due to hydrogen bonding between OH groups remained until the temperature was high enough to partially destroy the hydrogen bonding. Thus, in the liquid crystalline and isotropic states, only intermolecular hydrogen bonding between OH groups existed. Considering the FTIR results, as well as the DSC, POM and WAXD measurements. The molecular arrangement of C10 in the liquid crystalline state is given in figure 7. The bilayer structure results from the (1) strong dipolar interaction between NO$_2$ groups, and (2) hydrogen bonding between OH groups from molecules in either the same or different layers, and forming long hydrogen bond networks in the liquid crystalline phase. The SmA phase thus formed possesses higher thermal stability than the ordinary system due to dipolar interaction. The proposed molecular arrangement is consistent with the WAXD results for C10 which indicated that its liquid crystalline phase was SmA$_D$ with a *d*-spacing of 4.42 nm and *d*/*L* ratio of 1.43.

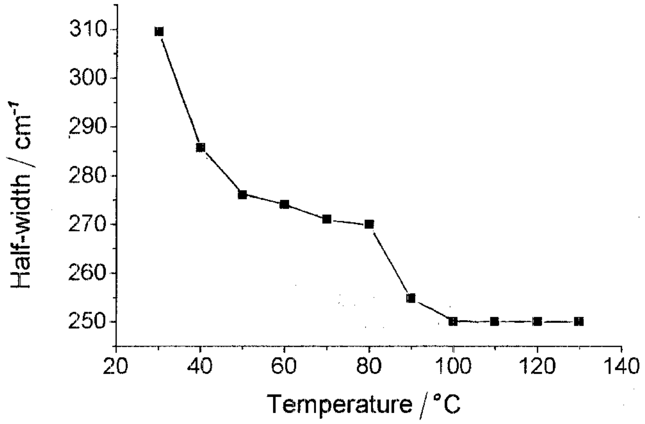

Figure 6. Plot of half-width of ν_sOH (associated) versus temperature.

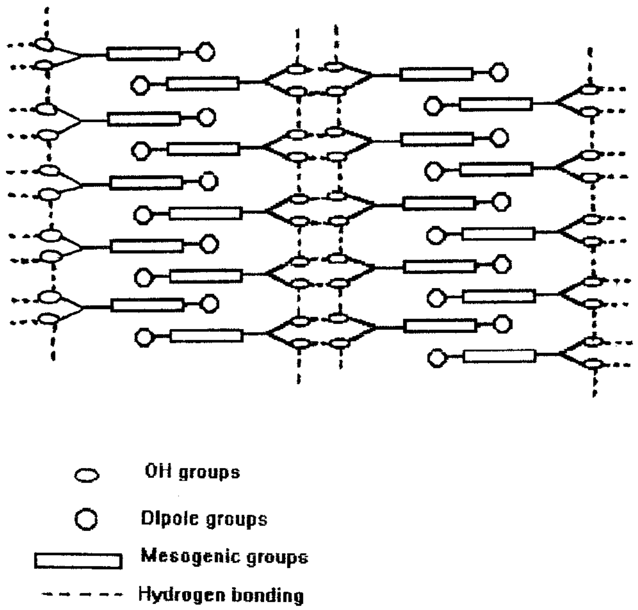

Figure 7. Schematic representation of the molecular arrangement of C10 showing the SmA phase.

4. Summary

An FTIR spectroscopic study on compound C10 was performed, the results showing the existence of intermolecular hydrogen bonding between OH groups in its crystalline, liquid crystalline and isotropic phases. Based on the results of FTIR, DSC, POM and WAXD analyses, a molecular arrangement for C10 resulting from hydrogen bonding between OH groups and strong dipolar interaction of NO_2 groups is proposed.

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