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Supramolecular liquid crystals induced by intermolecular hydrogen bonding between benzoic acid and 4-(alkoxyphenylazo)pyridines

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Supramolecular liquid crystalline complexes have been obtained from binary mixtures of 4-(alkoxyphenylazo)pyridines and 4-octyloxylbenzoic acid. None of the pyridine-based derivatives is mesomorphic, but the hydrogen-bonded complexes are. Their liquid crystalline properties were investigated by DSC, polarizing optical microscopy, FTIR spectroscopy and powder X-ray diffraction. The complexes exhibit enantiotropic smectic C phases.

1. Introduction

Hydrogen bonding plays an important role in molecular recognition and self-assembly [1]. Over the last decade, a number of supramolecular mesogenic materials have been obtained by molecular self-assembly through hydrogen bonding [2]. Much earlier, Jones and co-workers found that hydrogen bonding in 4-substituted benzoic acids stabilized liquid crystal behaviour [3], but the components were identical and hence this was not an example of molecular recognition. Kato and Fréchet expanded this concept to include mixtures of differing components and obtained liquid crystals from binary mixtures of 4-alkoxybenzoic acids and pyridine-based derivatives [4]. The guest–host effect has found application in two important areas, one in obtaining information concerning the electronic spectra of dyes, and the other in the construction of colour or black–white electro-optical displays [5]. Guest–host liquid crystal displays have many advantages, such as higher image brightness and lower cost. Azo-based dyes can improve the viewing angle and the order parameter in guest–host liquid crystal displays, and can be used to obtain full colour reflective displays. However there are problems with guest–host systems such as solubility, stability and viscosity [6, 7]. If the azo dye was itself a liquid crystal this may resolve these problems, at least to some extent. In addition, azo-based liquid crystals have attracted considerable attention as a result of application potential in optical storage systems [8, 9]. Azo-based dye liquid crystals constructed via intermolecular hydrogen bonding form a potentially useful source of new materials; but there are few reports in this area [10]. The aim of this work was to obtain new azo-based dye liquid crystals using 4-(alkoxyphenylazo)pyridines as hydrogen bond acceptors and 4-octyloxylbenzoic acid as the hydrogen bond donor (see the scheme).

2. Results and discussion

2.1. *Synthesis*

The 4-(alkoxyphenylazo)pyridines (nPAP, $n = 10$, 12, 14, 16, 18, where n is the number of carbon atoms in the alkoxy chain) were synthesized by the reaction between an alkyl bromide and 4-hydroxyphenylazopyridine at room temperature in DMF [11]. 4-Octyloxybenzoic acid (OBA) was prepared using a literature method [12]. All the synthesized compounds were characterized by mass spectroscopy, ^{1}H NMR spectroscopy and elemental analysis.

2.2. *Preparation of the hydrogen-bonded complexes*

The hydrogen-bonded complexes were prepared by the slow solvent evaporation of a THF solution containing a 1 : 1 molar ratio of the hydrogen bond donor and acceptor units.

2.3. *FTIR spectroscopy*

Infrared spectroscopy was used to identify hydrogen bonding in the complexes. The existence of bands at around 2500 and 1950 cm^{-1} together with the absence of a band at 3000 cm^{-1} clearly indicates the formation of a 1 : 1 hydrogen-bonded complex.

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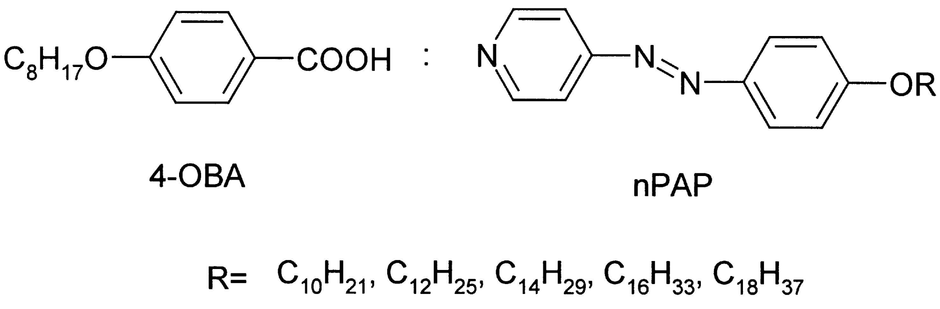


Scheme. Molecular structures of the compounds studied and their acronyms.

2.4. *Thermal properties of OBA, nPAP and the OBA : nPAP complexes*

The complexes formed via hydrogen bonding between OBA and *n*PAP show very interesting liquid crystalline properties. No *n*PAP compound is mesomorphic, and all melt directly to the isotropic liquid at about 70°C; OBA shows enantiotropic SmC (101–107°C) and nematic (107–147°C) phases. However, all the complexes show only an enantiotropic SmC phase and crystal-to-crystal phase transitions during heating and cooling (see figure 1). The liquid crystalline properties of the complexes were studied by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). They all show polymorphism, and the smectic phase exhibited a blurred schlieren texture, when viewed by POM. The melting and clearing points of all complexes are little changed as the length of the alkoxy chains increases (see table 1).

2.5. *X-ray diffraction studies of the complexes*

To corroborate the characterization of the liquid crystal phases, the OBA : 10PAP and OBA : 12PAP complexes were studied by X-ray diffraction (XRD). Figure 2 shows diffractograms of OBA : 10PAP at 110°C on heating and 105°C on cooling. A weak and broad reflection in the wide angle and a strong, sharp reflection in the small angle, corresponding to $d = 0.466$ and 4.01 nm respectively, are seen and are characteristic of a smectic phase. The calculated length of the OBA : 10PAP complex is 4.19 nm. Thus the small angle reflection corresponds to the layer spacing in the smectic phase, and the wide angle reflection to the intermolecular separation. The calculated length of the OBA : 10PAP complex is larger than the smectic layer spacing *d*, and this confirms the assignment of a smectic C phase.

The XRD data for OBA : 12PAP (figure 3) are similar to those for OBA : 10PAP, with a sharp, strong peak at small angle and a weak, diffuse peak at the wide angle. The layer spacing is 3.83 nm, smaller than that seen for OBA : 10PAP. Thus, the tilt of the molecules with respect to the layer normal increases on increasing the molecular length in the smectic C phase.

3. Experimental

3.1. *4-Hydroxyazopyridine*

4-Hydroxyazopyridine was prepared from 4-aminopyridine and phenol. Thus, to a solution of $NaNO_2$ (4.0 g) in water (20 ml), phenol (5 g) in 10% NaOH solution (45 ml) was added and the mixture was cooled

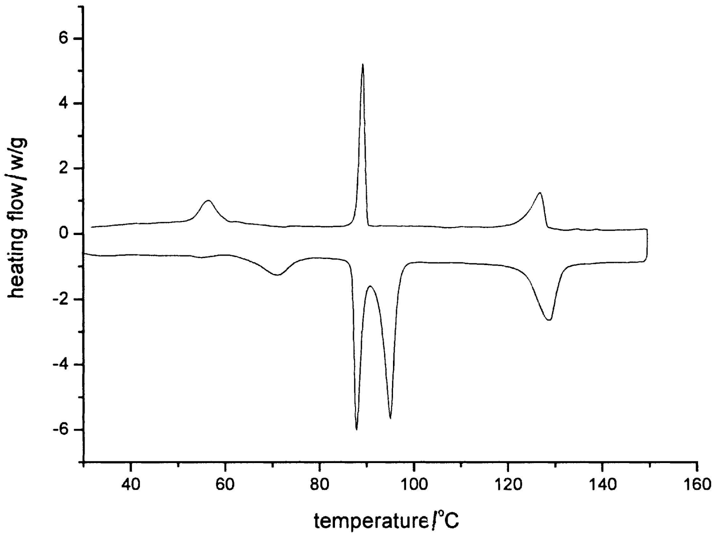
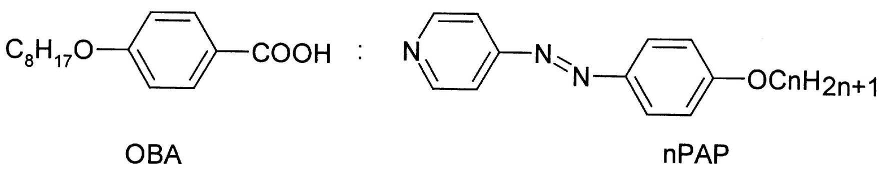


Figure 1. DSC curves of the OBA : 10PAP complex.

Table 1. Phase transition temperature (°C) and associated enthalpy changes ($J\,g^{-1}$ in parentheses) of the hydrogen-bonded OBA : *n*PAP complexes.



n = 10	$\mathrm{Cr} \xrightleftharpoons[56.6\ (5.44)]{71.1\ (6.73)} \mathrm{Cr''} \xrightarrow{87.9\ (62.21)} \mathrm{Cr'} \xrightarrow{95.1\ (37.99)} \mathrm{SmC} \xrightleftharpoons[126.8\ (19.58)]{128.7\ (22.03)} \mathrm{I}$ $\mathrm{SmC} \xrightarrow{89.3\ (70.80)} \mathrm{Cr''}$
n = 12	$\mathrm{Cr} \xrightleftharpoons[55.7\ (19.69)]{84.8\ (39.60)} \mathrm{Cr'} \xrightleftharpoons[82.4\ (43.33)]{92.3\ (40.21)} \mathrm{SmC} \xrightleftharpoons[126.2\ (19.58)]{128.0\ (22.03)} \mathrm{I}$
n = 14	$\mathrm{Cr} \xrightarrow{89.9\ (82.37)} \mathrm{SmC} \xrightleftharpoons[126.1\ (23.55)]{127.8\ (25.56)} \mathrm{I}$ $\mathrm{SmC} \xrightarrow{82.2\ (39.35)} \mathrm{Cr'} \xrightarrow{64.6\ (17.32)} \mathrm{Cr}$
n = 16	$\mathrm{Cr} \xrightleftharpoons[77.0\ (3.48)]{80.0\ (2.43)} \mathrm{Cr'} \xrightleftharpoons[88.7\ (65.69)]{92.9\ (71.61)} \mathrm{SmC} \xrightleftharpoons[123.1\ (25.96)]{125.8\ (26.90)} \mathrm{I}$
n = 18	$\mathrm{Cr} \xrightleftharpoons[68.2\ (9.46)]{77.9\ (6.99)} \mathrm{Cr'} \xrightleftharpoons[87.8\ (60.63)]{91.3\ (66.84)} \mathrm{SmC} \xrightleftharpoons[123.5\ (26.34)]{127.3\ (26.01)} \mathrm{I}$

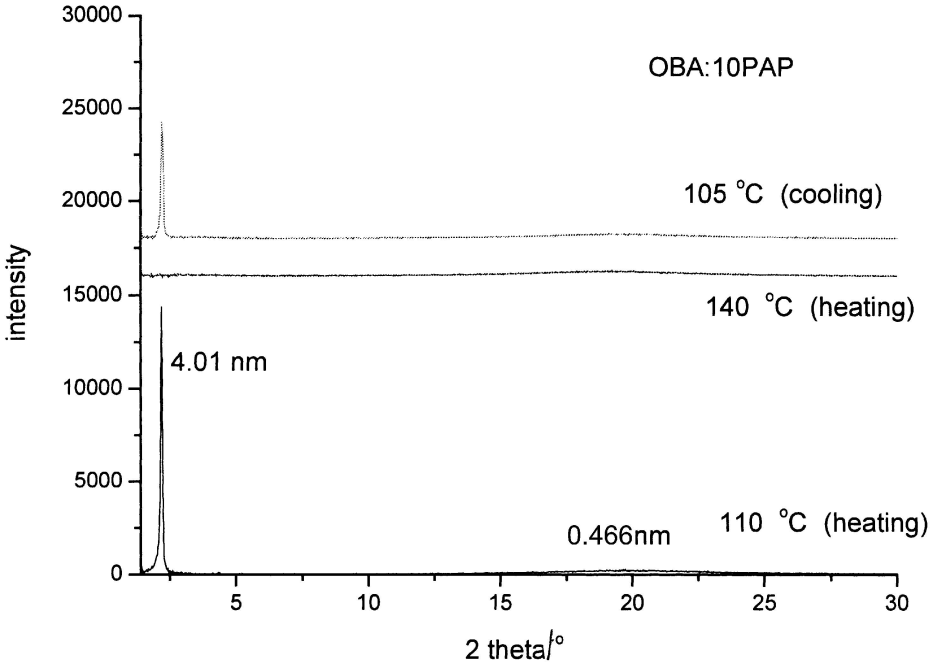


Figure 2. X-ray diffractograms for the OBA : 10PAP complex at different temperatures: 110°C (heating) smectic C phase; 140°C (heating) isotropic phase; 105°C (cooling) smectic C phase.

to 0°C. The resulting solution was added to a cooled solution of 4-aminopyridine (6 g) in HCl solution (25 ml concentrated HCl: 16 ml water) with stirring for 10 min below 0°C. Subsequently, a saturated solution of Na_2CO_3 was added to adjust the pH of the mixture to about 6. A yellow dye formed and was filtered off; purification was difficult because of its low solubility. Yield of the crude product 75%.

3.2. *4-Decyloxylphenylazopyridine (10PAP)*

4-Hydroxyazopyridine (0.5 g) was dissolved in DMF (15 ml). To this, K_2CO_3 (0.69 g) was added as the base. 1-Bromodecane (0.8 g) was then added to the mixture, which was then strongly stirred for 72 h at room temperature. The mixture was then filtered and the filtrate was evaporated to remove the DMF. The residue was redissolved in chloroform (20 ml) and washed with water

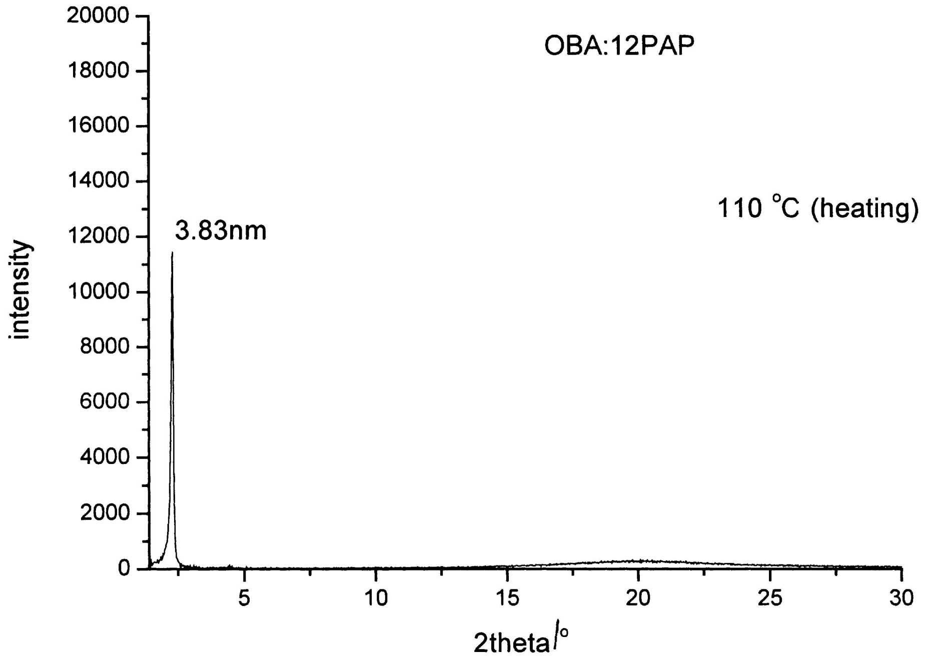


Figure 3. X-ray diffractogram for the OBA : 12PAP complex at 110°C (heating) smectic C phase.

(3 × 20 ml). The separated organic layer was dried over anhydrous calcium chloride overnight, filtered and the chloroform evaporated off . The residue was purified by column chromatography on silica gel (chloroform/acetone = 5/1 as eluent) to yield 0.6 g (55%) 10PAP.

The remaining 4-(alkoxyphenylazo)pyridines were prepared in a similar way. The yields ranged 55–61%. The elemental analysis data, mass spectra and melting points for the *n*PAP series are shown in table 2. All the *n*PAP compounds were characterized by ^{1}H NMR spectroscopy. Representative data for 18PAP: ^{1}H NMR (200 MHz, $CDCl_3$), δ 8.791 (d, 2H, $J = 5.9$ Hz, pyridine); 7.970 (d, 2H, $J = 8.5$ Hz, phenyl); 7.703 (d, 2H, $J = 6.0$ Hz); 7.033 (d, 2H, $J = 8.5$ Hz); 4.06 (t, 2H, $J = 6.5$ Hz, $-OCH_2-$); 1.833 (m, 2H, $-CH_2-$); 1.185–1.411 (m, 30H); 0.879 (t, 3H, $J = 6.3$ Hz).

3.3. *4-Octyloxylbenzoic acid (OBA)*

OBA was synthesized by the alkylation of 4-hydroxybenzoic acid with 1-bromooctane in ethanol, using KOH as base (heated at reflux for 4 h), and by subsequent acidification. The crude product was purified by recrystallization from ethanol/water (1/1); yield 80%. Elemental analysis: calc. for $C_{15}H_{22}O_3$ C 71.97, H 8.86; found C 71.87, H 8.877%.

4. Conclusion

In summary, we have prepared new azo-based dye liquid crystals constructed via intermolecular hydrogen bonding and studied their liquid crystalline properties. The results show that all the hydrogen-bonded complexes exhibit smectic C phases.

Table 2. Elemental analysis data, melting points and mass spectra for *n*PAP homologues.

			Elemental analysis (%)					
			Calculated			Found		
Compound	Melting point/°C	$M + 1/z$	C	H	N	C	H	N
10PAP	62.5–64.1	340	74.29	8.62	12.38	74.46	8.700	12.46
12PAP	69.2–71.0	368	75.15	9.06	11.44	75.22	9.191	11.37
14PAP	69.8–70.2	396	75.89	9.43	10.63	76.10	9.520	10.71
16PAP	76.2–78.7	424	76.54	9.76	9.92	77.02	9.798	10.09
18PAP	71.8–73.8	452	77.10	10.05	9.31	77.11	10.02	9.376

References

[1] Lehn, J. M., 1988, *Angew. Chem. int. Ed. Engl.*, **27,** 89.

[2] Constantinos, M. P., and Dimitris, T., 2001, *Liq. Cryst.*, **28,** 1127.

[3] (*a*) Bradfield, A. E., and Jones, B., 1929, *J. chem. Soc.*, 2660; (*b*) Gray, G. W., and Jones, B., 1953, *J. chem. Soc.*, 4179.

[4] Kato, T., and Fréchet, M. J., 1989, *J. Am. chem. Soc.*, **111,** 8533.

[5] John, G., and Lai, F. K., 1999, *J. mater. Chem.*, **9,** 2333.

[6] Matsui, M., Shirai, K., Tanaka, N., Funabiki, K., Muramatsu, H., Shibata, K., Abe, Y., and Ohgomori, Y., 1999, *J. mater. Chem.*, **9,** 2755.

[7] Bauman, D., and Moryson, H., 1997, *J. mol. Struct.*, **404,** 113.

[8] (*a*) Ruslim, C., and Ichimura, 1998, *Chem. Lett.*, 789; (*b*) Kozlovsky, M. V., Shibaev, V. P., Stakanov, A. I., Weyrauch, T., and Haase, W., 1998, *Liq. Cryst.*, **24,** 759.

[9] (*a*) Hermann, D. S., Rudquist, P., Ichiura, K., Kudo, K., Komitov, L., and Lagerwall, S. T., 1997, *Phys. Rev. E*, **55,** 2857; (*b*) Sasaki, T., Tkeda, T., and Ichimura, K., 1994, *J. Am. chem. Soc.*, **116,** 625.

[10] (*a*) Ajay, M. V., and Suresh, D., 2001, *Liq. Cryst.*, **28,** 259; (*b*) Li, L. L., and Je, L. L., *Liq. Cryst.*, 2001, **28,** 1513.

[11] Yam, V. W. W., Yang, Y., Yang, H. P., and Cheung, K. K., 1999, *Organometallics*, **18,** 5252.

[12] Jones, B., 1953, *J. chem. Soc.*, 1874.