Supramolecular dimeric liquid crystals. The liquid crystalline behaviour of mixtures of a-(4-pyridyloxy)-ν-[4-(4-butylphenylazo)phenoxy]alkanes and 4-octyloxybenzoic acid

**Marc J. Wallage and Corrie T. Imrie***

Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, UK AB24 3UE

The thermal behaviour of binary mixtures of 1-(4-pyridyloxy)-5-[4-(4-butylphenylazo)phenoxy]pentane (Bu-azo-5-Pyr) and 1-(4-pyridyloxy)-6-[4-(butylphenylazo)phenoxy]hexane (Bu-azo-6-Pyr) with 4-octyloxybenzoic acid is reported. Both systems are miscible over the complete composition range; this miscibility is attributed to the formation of a hydrogen bond between the unlike species, a view confirmed by IR spectroscopy. Bu-azo-5-Pyr and Bu-azo-6-Pyr do not exhibit liquid crystallinity but enhanced liquid crystal behaviour is observed for the mixtures with the acid. In particular, smectic A behaviour is injected into the phase diagrams of both systems. The clearing temperatures of the mixtures containing Bu-azo-6-Pyr are considerably higher than those for the analogous mixture containing Bu-azo-5-Pyr. In addition, the entropy change associated with the clearing transition for the equimolar mixture containing Bu-azo-6-Pyr is significantly higher than that for the analogous mixture containing Bu-azo-5-Pyr. These observations strongly suggest the formation of a supramolecular dimeric liquid crystal. For the Bu-azo-6-Pyr-based system the specific molecular interaction between the pyridyl and acid fragments has not only strongly enhanced the liquid crystalline behaviour but also increased the degree of molecular ordering.

In recent years increasing research activity has focused on liquid crystalline systems consisting of supramolecular complexes assembled *via* noncovalent interactions[1-3] but this is by no means a new idea. Indeed, some forty years ago Gray and Jones[4] attributed the liquid crystalline behaviour of the 4-alkyl- and 4-alkoxy-benzoic acids to hydrogen bonded dimers rather than to discrete molecular units. The novelty of the recent work, however, is that the two interacting species are not identical and a hetero-intermolecular bond is used to assemble the liquid crystal unit. Furthermore, the two interacting molecules need not be, and are often not, liquid crystalline individually but the resulting supramolecular complex is mesogenic. This amplification of a specific molecular interaction into a macroscopically observable phenomenon, in this case liquid crystallinity, is very much a central theme in supramolecular chemistry.[5,6]

The most commonly used interaction in assembling liquid crystalline complexes is the hydrogen bond[1-3] and particular interest has centred on mixtures of molecules containing pyridyl and carboxylic acid fragments.[2] In these mixtures the pyridyl unit serves as the hydrogen bond acceptor and the carboxylic acid as the hydrogen bond donor. The focus of much of this research has been the role of the hetero-hydrogen bond in determining the transition temperatures and phase behaviour of the system. In comparison, complex formation has not been used in an attempt to manipulate the degree of molecular ordering within the mesophase. In order to investigate this possibility we have now characterised the thermal behaviour of mixtures of two a-(4-pyridyloxy)-ν-[4-(4-butylphenylazo)phenoxy]alkanes, **1** and **2**, with 4-octyloxybenzoic acid, **3**. The acronyms used to refer to **1** and **2** are Bu-azo-5-Pyr and Bu-azo-6-Pyr, respectively. These particular structures were chosen because the analogous covalently bonded structures containing two mesogenic groups linked *via* a flexible spacer, the so-called dimeric liquid crystals, are known to exhibit mesophases in which the degree of molecular order is critically dependent on the length and parity of the alkyl spacer.
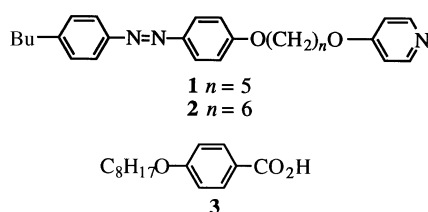

Experimental

Bu-azo-5-Pyr, **1**, and Bu-azo-6-Pyr, **2**, were prepared using the synthetic route shown in Scheme 1.

4-Butyl-4′-hydroxyazobenzene, 4

Compound **4** was prepared as described in detail elsewhere.[7]

1-Bromo-5-[4-(4-butylphenylazo)phenoxy]pentane, 5

Compound **5** was prepared using the method described by Attard *et al.* elsewhere.[8] Thus, a mixture containing **4** (4.5 g, 17.6 mmol), 1,5-dibromopentane (40.6 g, 176 mmol) and potassium carbonate (20.68 g, 150 mmol) in acetone (100 ml) was refluxed with stirring overnight. The reaction mixture was allowed to cool, filtered and the acetone removed using a rotary evaporator. Light petroleum (bp 40–60 °C) (300 ml)
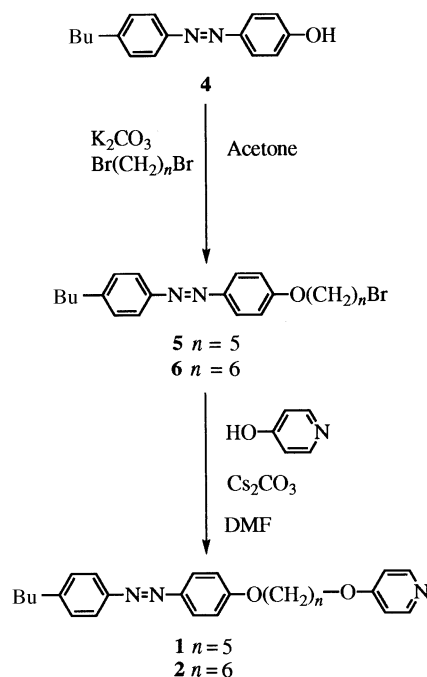
Scheme 1

was added to the organic extracts and the solution cooled to −20 °C for *ca.* 2–3 h. The resulting precipitate was collected, washed with light petroleum and dried under vacuum. The product was recrystallised from ethanol. Yield: 3.93 g, 55%. d_H (CDCl$_3$; *J* values in Hz throughout) 7.9, 7.8, 7.3, 7.0 (m, aromatic, 8H), 4.1 (t, ArOCH_2, 2H, *J* 6.3), 3.4 (t, CH_2Br, 2H, *J* 6.7), 2.7 (t, ArCH_2, 2H, *J* 7.8), 1.3–2.0 [m, CH$_3$CH_2CH_2, OCH$_2$CH_2)$_3$CH$_2$Br, 10H], 1.0 (t, CH$_3$, 3H, *J* 7.3).

1-Bromo-6-[4-(4-butylphenylazo)phenoxy]hexane, 6

Compound **6** was prepared using the procedure described for **5**. Yield: 5.54 g, 71%. d_H (CDCl$_3$) 7.9, 7.8, 7.3, 7.0 (m, aromatic, 8H), 4.0 (t, ArOCH_2, 2H, *J* 6.4), 3.4 (m, CH$_2$Br, 2H), 2.7 (t, ArCH_2, 2H, *J* 7.6), 1.3–2.0 [m, CH$_3$CH_2CH_2, OCH$_2$(CH_2)$_4$CH$_2$Br, 12H], 0.9 (t, CH$_3$, 3H, *J* 7.3).

Bu-azo-5-Pyr, 1

A mixture containing **5** (3.8 g, 9.5 mmol), 4-hydroxypyridine (0.92 g, 9.7 mmol) and caesium carbonate (15.6 g, 47.7 mmol) in *N,N*-dimethylformamide (DMF) (50 ml) was refluxed with stirring overnight. The reaction mixture was allowed to cool, poured into ice cold water (1 l) and stirred for *ca.* 30 min. The mixture was extracted with chloroform; the organic layer was washed with water, dried and the chloroform removed using a rotary evaporator. The crude product was passed through silica gel using acetone as the eluent. Yield: 0.6 g, 14.9%. Mp 85–86 °C. d_H (CDCl$_3$) 8.4, 7.9, 7.3, 6.9 (m, aromatic, 12H), 4.0 (m, 2 ArOCH_2, 4H), 2.7 (t, ArCH_2, 2H, *J* 7.6), 1.2–2.0 [m, (CH$_2$)$_3$, CH$_2$CH_2, 10H], 1.0 (t, CH$_3$, 3H, *J* 7.3).

Bu-azo-6-Pyr, 2

Bu-azo-6-Pyr was prepared using the procedure described for Bu-azo-5-Pyr. Yield 0.53 g, 9.7%. Mp 118–120 °C. d_H (CDCl$_3$) 8.4, 7.8, 7.3, 7.0, 6.8 (m, aromatic, 12H), 4.0 (m, ArOCH_2, 4H), 2.7 (t, ArCH_2, 2H, *J* 7.6), 1.3–1.9 [t, (CH$_2$)$_4$, CH$_2$CH_2, 12H], 0.9 (t, CH$_3$, 3H, *J* 7.3).

4-Octyloxybenzoic acid, 3

4-Octyloxybenzoic acid (Aldrich) was recrystallised from ethanol prior to use. The transition temperatures were in good agreement with those reported elsewhere:[9] crystal–smectic C, 101 °C, smectic C–nematic, 108 °C, and nematic–isotropic, 147 °C.

Preparation of complexes

The mixtures were prepared by codissolving the components in pyridine and the solvent allowed to evaporate slowly. The complexes were dried under vacuum for at least 24 h prior to characterisation.

Characterisation

The proposed structures of all the compounds were verified using ^{1}H NMR and IR spectroscopy. ^{1}H NMR spectra were measured in CDCl$_3$ on a Bruker AC-F 250 MHz NMR spectrometer. IR spectra were recorded using a Nicolet 205 FTIR spectrometer.

Thermal characterisation

The thermal behaviour of the materials was characterised by differential scanning calorimetry using a Mettler-Toledo DSC 820 system equipped with an intracooler accessory and calibrated using an indium standard. The heating and cooling rates in all cases were 10 °C min^{-1}. Phase identification was performed by polarised light microscopy using an Olympus BH-2 optical microscope equipped with a Linkam THMS 600 heating stage and TMS 91 control unit.

Results and Discussion

Bu-azo-5-Pyr–4-octyloxybenzoic acid mixtures

Bu-azo-5-Pyr and 4-octyloxybenzoic acid were miscible over the complete composition range and this was presumably attributable to the formation of a hydrogen bond between the unlike components in the mixture. This view was supported by IR spectroscopy; specifically, the spectra of the complexes contain bands centred at *ca.* 2490 and 1900 cm^{-1}, indicative of strong hydrogen bonding.[10–13] In addition, the carbonyl band has a shoulder at *ca.* 1690 cm^{-1}, a characteristic value for free carbonyl groups. Representative IR spectra of the individual components and the equimolar complex are shown as Fig. 1. Unfortunately, the complexity of the spectrum of the complex is such that it prevents even a semi-quantitative assessment of the equilibrium constant for the formation of the complex.

The dependence of the transition temperatures determined using differential scanning calorimetry on the mole fraction of Bu-azo-5-Pyr in the mixture is shown in Fig. 2. Bu-azo-5-Pyr melts directly into the isotropic phase at 89 °C and can be supercooled to *ca.* 70 °C without the observation of liquid crystallinity. Similarly, the mixtures containing greater than 0.5 mol fraction of Bu-azo-5-Pyr do not exhibit liquid crystalline behaviour. In comparison, the remaining mixtures are liquid crystalline; specifically nematic, smectic C and smectic A phases are observed. These phases were identified on the basis of the observation of clear characteristic optical textures when viewed through the polarised light microscope.[14,15] Specifically,
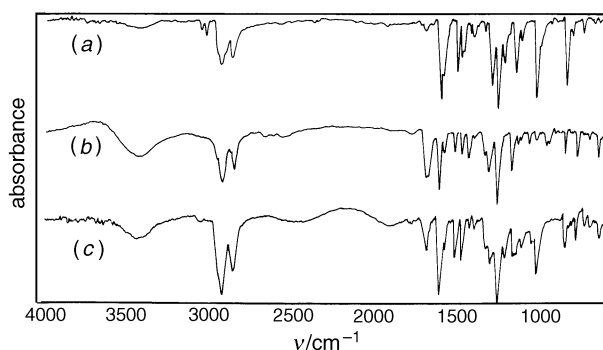

Fig. 1 IR spectra of (*a*) Bu-azo-5-Pyr, (*b*) 4-octyloxybenzoic acid and (*c*) the equimolar complex
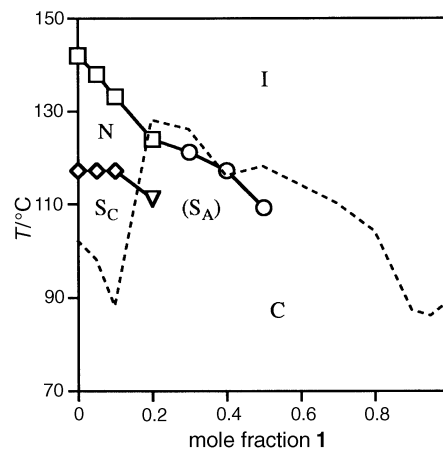

Fig. 2 Dependence of the transition temperatures on the mole fraction of Bu-azo-5-Pyr **1** for mixtures of Bu-azo-5-Pyr and 4-octyloxybenzoic acid. The broken line represents the melting point; (#) smectic A–isotropic transition; (↑) smectic C–nematic transition, (%) nematic–isotropic transition; (( ) smectic C–smectic A transition. C = crystal; N = nematic; S$_C$ = smectic C; S$_A$ = smectic A; I = isotropic. Crystal–crystal transitions have been omitted for the sake of clarity.

for the nematic phase a Schlieren texture was observed containing both types of point singularity and which flashed when subjected to mechanical stress, while for the smectic C phase a Schlieren texture was also observed but in which only one type of point singularity was evident. For the smectic A phase a focal conical fan texture was observed in coexistence with regions of homeotropic alignment.

The mixtures containing 0.05 and 0.1 mol fraction of Bu-azo-5-Pyr exhibit the same phase sequence as the pure acid, namely smectic C–nematic–isotropic. The nematic–isotropic transition temperature falls on increasing the concentration of Bu-azo-5-Pyr whereas the smectic C–nematic transition temperature appears to be insensitive to changes in composition. For the 0.2 mol fraction Bu-azo-5-Pyr mixture, a smectic A phase is injected between the smectic C and nematic phase. The mixtures containing 0.3, 0.4 and 0.5 mol fraction of Bu-azo-5-Pyr exhibited exclusively smectic A behaviour. Thus, increasing the concentration of Bu-azo-5-Pyr strongly promotes smectic A rather than nematic behaviour; we will return to this observation below.

The melting points of the Bu-azo-5-Pyr–4-octyloxybenzoic acid mixtures are typically significantly higher than those of the individual components, see Fig. 2. This behaviour strongly suggests that the unlike components exhibit a specific interaction. By comparison, the clearing temperature initially decreases in essentially a linear fashion on increasing the concentration of Bu-azo-5-Pyr, see Fig. 2. The extrapolation of the linear segment of the clearing temperature curve allows the virtual clearing temperature of Bu-azo-5-Pyr to be estimated at *ca.* 52 °C. The clearing temperatures for the 0.3, 0.4 and 0.5 mol fraction of Bu-azo-5-Pyr mixtures deviate in a positive sense away from a linear dependence on composition.

Bu-azo-6-Pyr–4-octyloxybenzoic acid mixtures

The dependence of the transition temperatures on the mole fraction of Bu-azo-6-Pyr in the mixtures is shown in Fig. 3. The phase assignments were performed using the arguments offered for the Bu-azo-5-Pyr-based mixtures. In addition, the IR spectra obtained for the mixtures were essentially identical to that shown in Fig. 1. The mixtures containing 0.05 and 0.1 mol fraction of Bu-azo-6-Pyr exhibit smectic C and nematic phases and the associated transition temperatures are similar to those of the pure acid. The 0.2 mol fraction of Bu-azo-6-Pyr mixture exhibits smectic C and A phases while the 0.3, 0.4 and 0.5 mol fraction mixtures exhibit exclusively smectic A behaviour. The 0.6 mol fraction mixture shows a smectic A
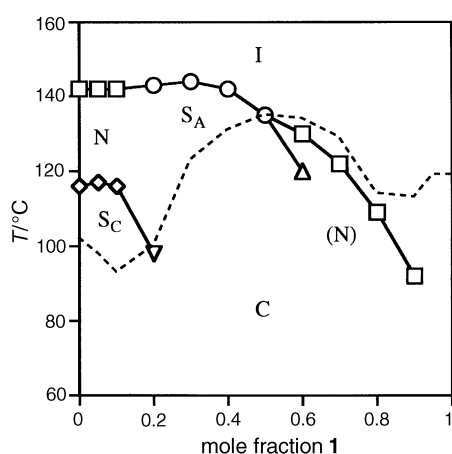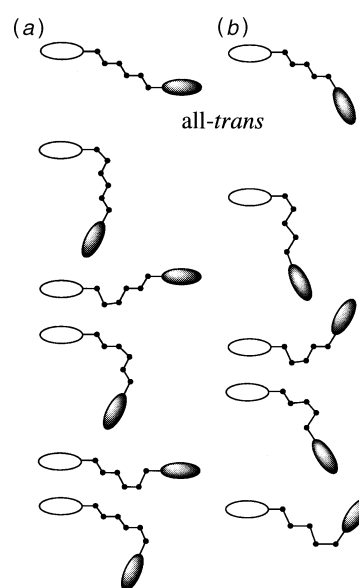
and a nematic phase whereas the 0.7, 0.8 and 0.9 mixture exhibit solely nematic behaviour. The 0.95 mixture and pure Bu-azo-6-Pyr do not exhibit liquid crystallinity. The virtual clearing temperature of Bu-azo-6-Pyr, estimated by extrapolating the clearing temperature curve, is *ca.* 74 °C.

As with the Bu-azo-5-Pyr-based mixtures, the melting points of the Bu-azo-6-Pyr-based mixtures tend to be significantly higher than expected on the basis of a linear variation of the melting point on composition, see Fig. 3, and again this is indicative of a specific interaction between the unlike components. The clearing temperatures for the Bu-azo-6-Pyr-based mixtures are also considerably higher than expected and smectic A behaviour is injected into the phase diagram.

Comparison of the systems

The estimated virtual transition temperature of Bu-azo-6-Pyr is *ca.* 22 °C higher than that for Bu-azo-5-Pyr. This difference is in accord with the pronounced alternation observed for conventional low molar mass mesogens containing a bulky group attached *via* a flexible alkyl spacer to the mesogenic core.[16–19] Thus, these estimated values are both self-consistent and reasonable. The miscibility observed for both systems implies that the hydrogen bond between the unlike components is more favourable than that present in the self-associated acid dimers. Furthermore, the strength of this hydrogen bond is sufficient to counteract the unfavourable entropic term which tends to promote phase separation.[9]

The smectic A–isotropic transition temperature for the equimolar mixture containing Bu-azo-6-Pyr, 135 °C, is considerably higher than that observed for the Bu-azo-5-Pyr-based mixture, 109 °C. This large difference, similar to that observed for conventional dimeric liquid crystals,[20,21] may be accounted for by considering the relative shapes of the complexes. Thus, for the Bu-azo-6-Pyr–acid complex the mesogenic groups are coparallel if the spacer is in the all-*trans* conformation, see Fig. 4(*a*); this arrangement reinforces the intramolecular orientational correlations between the mesogenic cores and, hence, enhances the clearing temperature. In contrast, for the Bu-azo-5-Pyr–acid complex when the spacer is in the all-*trans* conformation the mesogenic groups are constrained to lie at an angle with respect to each other, see Fig. 4(*b*), so reducing the clearing temperature. All the mixtures containing Bu-azo-6-Pyr exhibit higher clearing temperatures than the correspond-

Fig. 3 Dependence of the transition temperatures on the mole fraction of Bu-azo-6-Pyr **1** for mixtures of Bu-azo-6-Pyr and 4-octyloxybenzoic acid. Crystal–crystal transitions have been omitted for the sake of clarity. (◠) Smectic A–nematic transition; all other symbols are as defined in Fig. 2.


Fig. 4 Schematic representation of the effect on the shape of the complex on introducing a single *gauche* defect into the spacer for (*a*) an even-membered and (*b*) an odd-membered spacer

ing mixture containing Bu-azo-5-Pyr and this simply reflects the higher clearing temperature of the Bu-azo-6-Pyr–acid complex.

The entropy change associated with the smectic A–isotropic transition, expressed as the dimensionless quantity $\Delta S/R$, for the equimolar mixture containing Bu-azo-6-Pyr, 3.61, is considerably larger than that for the Bu-azo-5-Pyr-based equimolar mixture, 1.65; these values have been calculated assuming the formation of a 1:1 complex. This dramatic difference in the entropy change associated with the clearing transition on adding just a single methylene unit is characteristic behaviour for conventional dimeric liquid crystals[20,21] and may be accounted for by considering the inherent flexibility of the spacer. Indeed, the rationalisation of the dependence of the clearing temperatures on the parity of the spacer considered just the all-*trans* conformation of the spacer which is clearly unrealistic. If instead we consider the effects of introducing a single *gauche* defect into the spacer and allow it to move sequentially along the chain, then there are still conformations of an even-membered spacer in which the mesogenic units lie coparallel, see Fig. 4(*a*). In comparison, all the conformations of the odd-membered spacer constrain the mesogenic units to lie at an angle with respect to each other, see Fig. 4(*b*). The smectic A phase is an anisotropic environment which selects the more elongated conformations in which the mesogens are coparallel. Thus, at the smectic A–isotropic transition, there is a greater change in the conformational distribution of an even-membered spacer than for an odd-membered spacer. Consequently, the conformational component of the overall smectic A–isotropic entropy change is higher for even-membered dimers, *i.e.* the equimolar Bu-azo-6-Pyr–acid mixture. We must remember, however, that are three main contributions to the overall entropy change, conformational, orientational and translational, and it is the subtle interplay of these that determines the overall value. Indeed, calculations suggest that the conformational component may only be a relatively small component of the overall entropy change.[21] Thus, further speculation on the molecular significance of the pronounced difference in the smectic A–isotropic entropy change between these supramolecular complexes must now await further investigation. It is apparent, however, that the specific molecular interaction between the pyridyl and acid fragments in the Bu-azo-6-Pyr–acid equimolar mixture is manifested at the macroscopic level not only by the induction of smectic A behaviour into the phase diagram but also by the high degree of molecular ordering within the mesophase. It should be noted that if the two components are simply miscible but exhibit non-ideal behaviour then the clearing entropy would not be so critically dependent on spacer length. The non-ideality in the transition temperatures of some liquid crystal mixtures is driven by an enthalpic term and the clearing entropy is essentially unaffected. Thus, the magnitude of the clearing entropies for the systems discussed here are indicative of complex formation.

The strong induction of smectic A behaviour in both phase diagrams, see Fig. 2 and 3, may be accounted for in terms of the relative tendencies of dimeric liquid crystals to form smectic phases and the probable local structure within the smectic phase. It has been shown that if the lengths of the terminal alkyl chains attached to a dimer exceed half the length of the flexible spacer, as, for example, in both equimolar complexes, then a monolayer smectic phase results.[21] The formation of this phase may be understood in terms of a microphase separation in which there exists three distinct regions: mesogenic groups, terminal alkyl chains and spacers, see Fig. 5(*a*). In these dimeric structures the terminal chains are simply too long to be accommodated within the region comprising the spacers. The driving force resulting in this phase separation may be considered as either energetic or entropic. Energetically, phase separation will occur if the mean of the core–core and chain–chain interactions is more favourable than the core–
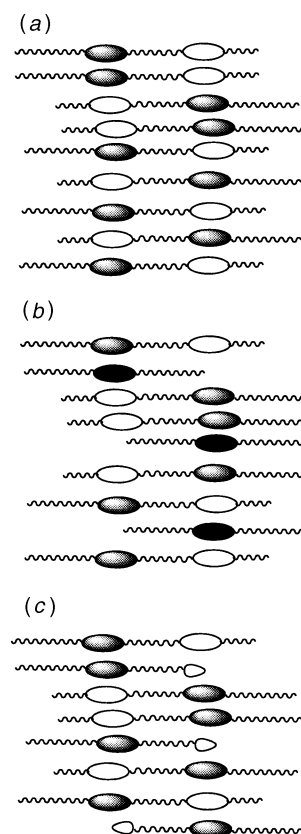
Fig. 5 Probable local packing arrangements in the smectic A phase for mixtures containing (*a*) an equimolar ratio of the two components, (*b*) an excess of the acid and (*c*) an excess of **1**. Shaded ellipses represent azobenzene, open ellipses represent hydrogen bonded mesogenic units, filled ellipses represent hydrogen bonded acid dimers and the pear-shape represents free pyridyl units.

chain interaction while entropically, the unfavourable interaction between a core and a chain which acts to order the chain drives phase separation. Thus, the equimolar complex would be expected to, and indeed does, exhibit smectic rather than nematic behaviour. If we now increase the mole fraction of the acid component then hydrogen bonded acid dimers will be present. Initially, these may be accommodated within the smectic phase structure, see Fig. 5(*b*), but as their concentration increases the terminal octyl chains, which are too long to be accommodated within the spacer domains, destabilise the smectic phase and nematic behaviour is observed. Conversely, if the Bu-azo-Pyr component is in excess than the packing density in the smectic phase is reduced, see Fig. 5(*c*), and again nematic behaviour is favoured.

Conclusion

In this study, we have seen that the phase behaviour and transition temperatures of mixtures **1** and **2** with **3** are determined by the formation of a hydrogen bond between the unlike components; this is quite general behaviour.[1–3] For the first time, however, we have shown how the degree of molecular order within the mesophase can also be controlled by hydrogen bonding at the molecular level.

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