Supramolecular chiral liquid crystals. The liquid crystalline behaviour of mixtures of 4,4′-bipyridyl and 4-[(*S*)-(−)-2-methylbutoxy]benzoic acid

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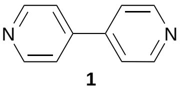
The thermal behaviour of binary mixtures of 4,4′-bipyridyl and 4-[(*S*)-(−)-2-methylbutoxy]benzoic acid has been investigated. The two components are not liquid crystalline. By comparison, mixtures containing between 0.1 and 0.5 mole fraction of 4,4′-bipyridyl exhibit mesogenic behaviour; specifically, chiral nematic, blue and smectic A phases are observed. The induced mesogenic behaviour is attributed to the formation of elongated hydrogen bonded complexes and this view is supported by infrared spectroscopy. The crystal structure of the complex containing 0.3 mole fraction of 4,4′-bipyridyl was determined using X-ray diffraction. This confirmed the formation of linear hydrogen bonded complexes in which two acid fragments are attached to a central 4,4′-bipyridyl core and supports the view that such complexes are responsible for the liquid crystalline behaviour of these mixtures.

A conventional low molar mass liquid crystal comprises molecules consisting of a semi-rigid anisometric core attached to which are normally one or two alkyl chains.[1] In essence it is the anisotropic interactions between the cores which give rise to liquid crystalline behaviour, while the role of the alkyl chains is largely to reduce the melting point of the material. The mesogenic core often contains phenyl rings connected *via* short unsaturated linkages.[1] In recent years, however, increasing research activity has focused on materials in which the core is assembled *via* noncovalent bonding,[2–4] although this is by no means a new concept; for example, some forty years ago Gray and Jones attributed the mesogenic behaviour of the 4-alkyloxybenzoic acids to the formation of hydrogen bonded dimers.[5] The novelty of the recent work lies with the use of hetero-intermolecular bonds in order to assemble the mesogenic core, *i.e.* the two interacting molecules are not identical, and such studies provide excellent examples of specific molecular recognition.[6,7] In addition, the two interacting molecules need not be, and indeed are often not, mesogenic although the resulting complex is liquid crystalline. This amplification of a specific molecular interaction into a macroscopic observable phenomenon is a central theme of supramolecular chemistry.[6,7] The most commonly used interaction for the construction of supramolecular liquid crystals is the hydrogen bond and of particular significance have been the studies reported by Kato and Fréchet describing the use of hydrogen bond formation between pyridyl and carboxylic acid fragments.[4] There is now a wealth of literature describing this class of hydrogen bonded mesogens,[2,4] but surprisingly few of these reports consider the induction of technologically relevant chiral phases.[8–12] Thus, we have characterised the thermal behaviour of mixtures of 4,4′-bipyridyl **1** and 4-[(*S*)-(−)-2-methylbutoxy] benzoic acid **2**. This particular system was chosen for study because Kato, Fréchet and their co-workers have shown that mixtures of 4,4′-bipyridyl and substituted benzoic acids exhibit induced or enhanced liquid crystalline behaviour.[13,14]



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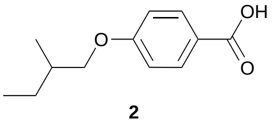

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Results and Discussion

The transition temperatures of the mixtures of 4,4′-bipyridyl and 4-[(*S*)-(−)-2-methylbutoxy]benzoic acid are listed in Table 1. The two pure components are not mesogenic. By contrast, the mixtures containing between 0.10 and 0.50 mole fraction of 4,4′-bipyridyl do exhibit liquid crystalline behaviour. Phase identification was performed using polarised light microscopy; clear characteristic textures were obtained for smectic A, chiral nematic and blue phases.[15,16] The entropy changes associated with the transitions support the phase assignments shown in Table 1. The mixtures containing 0.10 and 0.20 mole fraction of 4,4′-bipyridyl exhibit a blue phase; identical platelet textures were observed for both mixtures (see Plate 1). To the best of our knowledge, this is only the second reported example of the observation of blue phases in hydrogen bonded complexes.[11] Mixtures containing greater than 0.50 mole fraction of 4,4′-bipyridyl were not mesogenic, although miscibility was observed across the complete composition range.

The dependence of the transition temperatures on the mole fraction of 4,4′-bipyridyl in the mixture is shown in Fig. 1. The most striking feature of this phase diagram is the strong induction of liquid crystallinity for mixtures containing between 0.10 and 0.50 mole fraction of 4,4′-bipyridyl. Indeed, the mixture containing 0.05 mole fraction of 4,4′-bipyridyl could be supercooled to *ca.* 100 °C prior to crystallisation without the observation of liquid crystallinity while the isotropic phase of the mixture containing 0.60 mole fraction of 4,4′-bipyridyl could be supercooled to *ca.* 90 °C before crystallisation occurred. The strong induction of liquid crystallinity for this binary system presumably arises from the formation of a linear, hydrogen bonded complex between the two components. This view is supported by infrared spectroscopy; specifically, the spectra of the complexes contain bands centred at *ca.* 2490 and 1900 cm^{-1}, indicative of strong hydrogen bonding.[17–20] In addition, the carbonyl band is shifted to 1693 cm^{-1}, a characteristic value for free carbonyl groups.

4,4′-Bipyridyl is a difunctional hydrogen bond acceptor and thus it would be expected that the formation of the hydrogen bonded complex would be maximised for the mixture containing 0.33 mole fraction of 4,4′-bipyridyl and 0.67 mole fraction of the monofunctional hydrogen bond donor, 4-[(*S*)-(−)-2-methylbutoxy]benzoic acid. If the clearing temperature of the mixture simply reflected the interaction strength parameter

Table 1 Transition temperatures and the entropies associated with the clearing transition for mixtures of 4,4′-bipyridyl and 4-[(*S*)-(−)-2-methylbutyloxy] benzoic acid

mole fraction of 4,4′-bipyridyl	transition temperature/°C						$\Delta S/R$
	C–I[a]	S_A–N*[b]	N*–BP[c]	BP–I[c]	N*–I[d]	S_A–I[d]	
0.00	110.5						
0.10	105.2		104.7	105.6			0.16
0.20	142.4	126[d]		134.8[e]			1.21
0.30	142.5	132			134.8		1.12
0.40	136.0					134.1	1.10
0.50	141.4					133.3	0.90
0.60	142.0						
0.70	118.8						
0.80	118.8						
0.90	107.5						
1.00	112.2						

[a]Extracted from reheating DSC trace, heating rate = 5 °C min^{-1}. [b]Measured using optical microscopy. [c]Extracted from cooling DSC trace, cooling rate = 0.2 °C min^{-1}. [d]Extracted from cooling DSC trace, cooling rate = 5 °C min^{-1}. [e]Combined N*–BP–I transition.

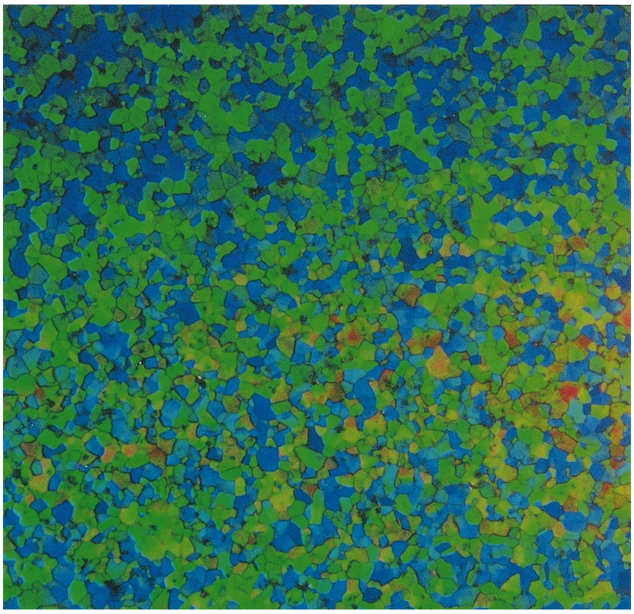

Plate 1 The platelet texture of the blue phase exhibited by the mixture containing 0.20 mole fraction of 4,4′-bipyridyl

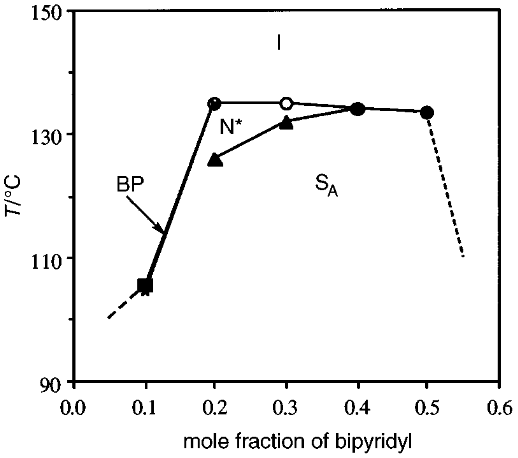

Fig. 1 Dependence of the transition temperatures on the mole fraction of 4,4′-bipyridyl for mixtures of 4-[(*S*)-(−)-2-methylbutyloxy]benzoic acid and 4,4′-bipyridyl. Melting temperatures have been omitted for the sake of clarity. Transitions: (×) blue phase–N*; (■) blue phase–I; (▲) S_A–N*; (⊗) blue phase–N*–I; (○) N*–I; (●) S_A–I.

between these complexes, a maximum in the clearing temperature curve would be expected at 0.33 mole fraction of 4,4-bipyridyl. Indeed, such behaviour was found for the binary phase diagrams of *trans*-1,2-bis(4-pyridyl)ethylene, a difunctional hydrogen bond acceptor, and the monofunctional hydrogen bond donors 4-methoxy-, 4-hexyloxy- and 4-butoxybenzoic acid.[14] In contrast to such expected behaviour, the clearing temperatures exhibited by the 4,4′-bipyridyl–4-[(*S*)-(−)-2-methylbutoxy]benzoic acid mixtures do not pass through a maximum on varying composition but instead the clearing temperature curve is rather flat (Fig. 1). We will return to this observation later.

The temperature range exhibited by the blue phase is reduced on increasing the concentration of 4,4′-bipyridyl and, indeed, a blue phase is not observed for the 0.30 mole fraction mixture; the molecular significance of this behaviour is unclear. The temperature range of the chiral nematic phase is also reduced on increasing the concentration of 4,4′-bipyridyl and the 0.40 and 0.50 mole fraction mixtures exhibit only a smectic A phase. This behaviour may be understood by considering the role played by the component in excess in determining phase structure and stability. For the mixture containing 0.30 mole fraction of 4,4′-bipyridyl the number of hydrogen bonds is maximised and a linear species, containing a central 4,4′-bipyridyl core attached to which are two terminal acid molecules, is formed; as we will see this view is supported by the X-ray diffraction study of the crystal phase exhibited by this mixture. The mixture exhibits a smectic A and a chiral nematic phase. Smectic phase formation may be thought of as a microphase separation in which the mesogenic cores form one region while the alkyl chains constitute another. Thus, the smectic A phase exhibited by the complex would be expected to exhibit a monolayer structure. If we now increase the mole fraction of 4,4′-bipyridyl in the mixture then the excess 4,4′-bipyridyl can readily be accommodated in the smectic layer in the largely aromatic domains. A dynamic equilibrium is presumably established in which fully complexed, mono-complexed and uncomplexed 4,4′-bipyridyl is present. The 4,4′-bipyridyl preferentially dissolved in the aromatic regions stabilises the microphase separation and the chiral nematic phase is extinguished. Conversely, if the acid component is in excess then hydrogen bonded acid dimers will be present. These dimeric species cannot be readily accommodated into the layered smectic structure, and hence destabilise the smectic phase relative to the chiral nematic phase. The similarity in the clearing temperatures for mixtures containing between 0.20 and 0.50 mole fraction of 4,4′-bipyridyl suggests that the stabilisation of the smectic phase by the presence of excess 4,4′-bipyridyl is similar to that of the nematic phase by excess acid.

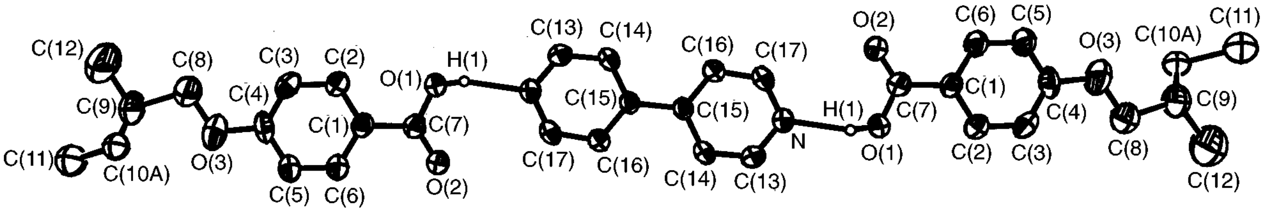

Fig. 2 The structure of the complex formed between 4-[(*S*)-(−)-2-methylbutoxy]benzoic acid and 4,4′-bipyridyl, showing the atom numbering scheme and ellipsoids at the 40% probability level

The 2:1 molar ratio of 4-butoxybenzoic acid and 4,4′-bipyridyl exhibits a smectic A–nematic transition at 150 °C and a nematic–isotropic transition at 159 °C.[13,14] The corresponding temperatures for the 4-[(*S*)-(−)-2-methylbutyloxy] benzoic acid–4,4′-bipyridyl complex are 132 and 135 °C, respectively. Thus chain branching has reduced the clearing temperature by 24 °C and the smectic A–nematic transition temperature by 18 °C. These reductions are smaller, however, than normally observed on the addition of a 2-methyl branch in conventional low molar mass liquid crystals,[21,22] but the generality of this observation must be tested for a wider range of materials.

The crystal structure of the 0.3 mole fraction bipyridyl complex was studied using X-ray diffraction; the space group used in the refinement was $P2_1/c$. The *R*-value for this analysis (0.112) is rather high but attributable to disorder within the crystal. The 'molecular' unit is essentially a linear hydrogen bonded complex consisting of a central 4,4′-bipyridyl core and two terminal 4-(2-methylbutoxy)benzoic acid molecules (see Fig. 2). The most interesting feature of the complex is the nature of the hydrogen bonding. The O(1)–H distance is 0.83 (±0.13) Å, the H–N distance is 1.88 (±0.13) Å and the O(1)–H–N bond angle is 161 (±12)°. Thus, these data support the view that the complex is assembled *via* hydrogen bonding rather than *via* salt formation.

The packing of the complexes is shown in Fig. 3 and 4. Both figures show layers of complexes viewed down *c*, one layer at $z/c=0$ (Fig. 3) and the other at $z/c=1/2$ (Fig. 4). In both figures the complexes are arranged head-to-tail to form infinite chains, but in Fig. 4 the chains are rotated by approximately 40° and translated by $b/2$ compared with Fig. 3. Thus the crystal consists of alternating layers of complexes propagated in the direction of *c*. A second feature common to Fig. 3 and 4 is the occurrence of ribbons of molecules lying side by side (*R* and *R*′). The stacking of the ribbons in the *c* direction creates blocks one molecule thick which lie perpendicular to *a*. The only interactions between adjacent ribbons within a layer, and therefore between the blocks, are the comparatively weak van der Waals forces between the alkyl chains of the acid fragments. This is very similar to the situation described for monoclininc zinc butanoate,[23] for which disorder in the stacking of double-sided parafinnic layers was clearly detectable. Thus there are grounds for anticipating disorder in the stacking of the parafinnic blocks in the crystal structure of the complex giving rise to the rather high *R*-factor.

Experimental

Materials

4,4′-Bipyridyl (98%) was obtained from Aldrich. 4-[(*S*)-(−)-2-Methylbutoxy]benzoic acid was synthesised using well documented procedures: specifically, (*S*)-(−)-2-methylbutan-1-ol was brominated using phosphorus tribromide to yield (*S*)-(−)-2-methyl-1-bromobutane, which was subsequently reacted with 4-hydroxybenzoic acid to give 4-[(*S*)-(−)-2-methylbutoxy]benzoic acid.[24]

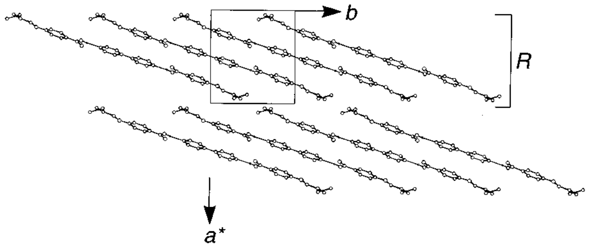

Fig. 3 A layer of molecules at $z/c=0$ viewed down *c*. Atoms are drawn as circles of arbitrary radius increasing in the order H<C<N<O. The cell edge *b* and [100] are indicated.

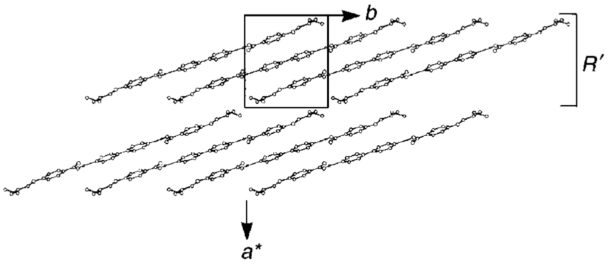

Fig. 4 As Fig. 3 except that the complexes are at $z/c=1/2$

Preparation of complexes

The mixtures were prepared by co-dissolving the components in hot EtOH. The cooled solution was allowed to evaporate to dryness over several days in a desiccator over activated silica gel. The desiccator was evacuated approximately every 12 h using a water pump. The crystals obtained were dried under vacuum.

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. Phase identification was performed by polarised light microscopy using an Olympus BH-2 optical microscope equipped with a Linkham THMS 600 heating stage and TMS 91 control unit.

Crystal structure determination

The crystal structure exhibited by the mixture containing 0.3 mole fraction of 4,4′-bipyridyl was determined by X-ray diffraction using a Nicolet *P*3 four-circle diffractometer with Mo-Kα radiation. Data collection and cell refinement were performed using Nicolet P3 software.[25] Data collection used 2θ scan rates of 5.33 ($I_p<150$) to 58.6° min^{-1} ($I_p>2500$), where I_p was the prescan intensity. Scan widths were 2.4 to 2.7° 2θ. Data reduction was performed using RDNIC.[26] The structure was solved by direct methods and refined by full-matrix least squares. All non-H, with the exception of C(10A), C(10B) and C(11), of the highly disordered 2-methylbutoxy terminal chains were refined anisotropically (atom numbers are defined in Fig. 2). Aromatic protons were placed in calculated positions with the C—H bond length at 0.95 Å and refined riding upon the C to which they were attached with separate group U_{iso} values for pyridyl and phenyl H [refined values 0.075(±0.016) and 0.058(±0.014) $Å^2$, respectively]. The hydroxy H (OH) was found in a difference map and refined isotropically in the usual manner [$U_{\mathrm{iso}} = 0.13(\pm 0.06)$ $Å^2$]. No attempt was made to position the alkyl protons because of the disorder apparent, particularly in the terminal ethyl group of the 4-(2-butoxy) residue, for which C(10A) and C(10B) represent two approximately equally occupied positions for the methylene carbon. The structure solution and refinement software used was SHELXS86[27] and SHELX76[28] and for molecular graphics PLOTAID[29] and ORTEX[30] were used.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/21.

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