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## Liquid Crystals

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# A highly ordered hydrogen-bonded network

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Self-assembled, hydrogen bonded, supramolecular complexes based on the interaction of pyridine with carboxylic acids have been synthesized. These contain different proportions of a compound with two terminal benzoic acid residues and a pentaerythritol-based tetra-pyridyl. They have been investigated for possible mesomorphic properties. Surprisingly for a tetrahedral pentaerythritol-based complex, a mesophase was observed with a grainy microscopic texture, which was fluid and could be sheared. The mesogenic unit is formed on hydrogen bonding complexation between the pyridyl residues and the carboxylic acid residues. Infrared spectra, as a function of the temperature, were recorded for the 1:1 complex; these show pyridyl complexation and changes on isotropisation. These changes are discussed in terms of the hydrogen bonding. Fibres could be drawn from the (mesophase) melt, supporting a polymeric, extended-chain structure for the complexes.

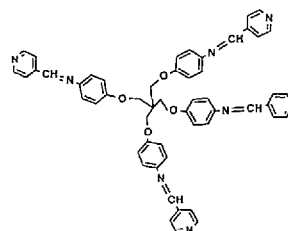
## 1. Introduction

The hydrogen bonding interaction between aromatic carboxylic acids and pyridines has previously been described for the formation of small molecule dimeric complexes [1]. The construction of mesogenic molecules [2, 3] in such a manner, and the relation between hydrogen bonding and liquid crystallinity involved in low molar mass materials has also been extensively investigated [4-6]. The association of difunctional species into long 'supramolecular' chains is also possible and has been described in the case of dicarboxylic acids [7], but has been relatively little studied for heteromeric hydrogen bonding. Recently, the liquid crystalline, chain-extended, 'polymeric' complex of bis-pyridyl with a dicarboxylic acid has been described [8]. It is known from work on polymer blends [9] that the pyridine-carboxylic acid complexation, with a formation constant of about 500, involves a stronger hydrogen bond than that in the corresponding carboxylic acid dimers, and it is therefore possible that supramolecular chains can be formed, in principle, with a reasonably high number of units linked together by hydrogen bonding.

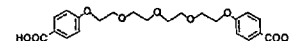
The tetrahedral pentaerythritol-based tetra-pyridyl molecule is a semi-flexible unit, which has the potential to be 'cross-linked' by hydrogen bonding complexation in more than one dimension when mixed with a suitable di-acid, for example, an aromatic dicarboxylic acid, so giving a 'supramolecular network'. However, from molecular modelling, it can be shown that the flexibility about the  $-\text{CH}_2-\text{O}-$  linkages of the pentaerythritol core is

sufficient for the molecule to adopt a conformation which is not tetrahedral, and it can essentially exist as a one-dimensional rod (calamitic) with pyridyl at each of the four ends which lie together in two pairs.

Here we describe a liquid crystalline, hydrogen bonded complex formed from the tetra-pyridyl (1) and the flexible chain di-acid (2) shown below.



Tetra-pyridyl (1)



Dicarboxylic acid (2)

The ethylene oxide chain between the benzoic acid units was chosen because it functions as a highly flexible spacer.

## 2. Experimental

All starting materials were obtained from the Aldrich Chemical Co. The tetra-pyridyl compound 1 was formed from a tetra-phenylamine precursor, as follows: Pentaerythritol and 4-nitrophenol were interacted using diethyl azodicarboxylate coupling [10] to give  $\text{C}(\text{CH}_2-\text{O}-\text{Ph}-\text{NO}_2)_4$  in high yield; this was reduced to the tetra-amine in DMF by Pd on carbon using ammonium formate as hydrogen source [11]. This product with pyridine

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Thermal transition data for mesomorphic compounds from POM and DSC.

Complex	Solid-mesophase/ $^{\circ}\text{C}$	DSC transitions/ $^{\circ}\text{C}$	Mesophase-isotropic/ $^{\circ}\text{C}$
1:1	70	116, 138, 163	170
1:2	158		182.5
2:1	73 (Not mesogenic)		

4-carboxaldehyde (and a little acetic acid as catalyst) gave the Schiffs base product in the normal way. Overall yield 75 per cent. Transmission temperatures: crystal 156–8 $^{\circ}\text{C}$  isotropic; cools to a glass. Elemental analysis: calculated C 74.30, H 5.14, 13.08 per cent; found C 74.50, H 5.38, N 12.96 per cent. IR: 1628, 1596, 1505, 1235, 1045, 837, 816  $\text{cm}^{-1}$ . NMR ( $\text{CDCl}_3$ ): 4.38 (s, 2 H), 7.0 (d, 2 H), 7.21 (d, 2 H), 8.5 (s, 1 H), 8.0 (d, 2 H), 8.90 (d, 2 H).

The tetraethyleneglycol diether from 4-hydroxybenzoic acid was obtained as in [8]. Crystal 187 $^{\circ}\text{C}$  isotropic. IR (KBr disc): hydroxyl, 2600–3000  $\text{cm}^{-1}$ ; carbonyl, 1686  $\text{cm}^{-1}$ .

The complexes of compounds **1** and **2** were obtained as described in [8] by mixing the components together in the molten state, all characterization was consistent with the assigned structures. See table for DSC data. GPC on solutions of these hydrogen bonded complexes would not give reliable 'polymer' molecular weights due to dissociation.

The measurements referred to above were performed on the following instruments: IR, Nicolet 510 spectrometer fitted with a Graseby Specac 5750 variable temperature IR cell and automatic temperature controller; NMR, Bruker WM 250 MHz spectrometer; DSC, Perkin-Elmer Series 7; Polarizing light microscopy, Leica Axioscope fitted with a Mettler FP82 micro-furnace. Elemental analyses were performed in the Department of Chemistry, University of Cambridge.

### 3. Results and discussion

The three complexes were yellow opaque solids, the colour typical for Schiffs bases. Neither of the starting materials, compounds **1** and **2**, show thermotropic mesophases and have melting points at 157 and 187 $^{\circ}\text{C}$ , respectively. The results of DSC for the 2:1 (ratio of pyridyl to carboxylic acid groups, i.e. 1:1 molar ratio of the tetra-pyridyl to the di-acid), 1:1 and 1:2 complexes (all second heating) are given in the table, together with polarizing optical microscopy (POM) data, and the DSC of the 1:1 complex is shown in figure 1. The 1:1 complex shows the most detail in the DSC, with a broad endotherm at 70–90 $^{\circ}\text{C}$ , followed by a small exotherm between 90 and 110 $^{\circ}\text{C}$ , followed by endothermic peaks at 138, 163 and 170 $^{\circ}\text{C}$  on the second heating. Thus there appears to be

melting, crystallization and re-melting between 70 and 138 $^{\circ}\text{C}$ . The major melting endotherms are at 163 and 170 $^{\circ}\text{C}$ . The first heating was performed up to 200 $^{\circ}\text{C}$  at the same heating rate (10 $^{\circ}\text{C min}^{-1}$ ) and was very similar in appearance to the second heating, although peaks were not quite as well resolved. On cooling only exotherms are seen between 65 and 118 $^{\circ}\text{C}$  (very broad), with a sharper peak at 87 $^{\circ}\text{C}$ . The isotropic to mesophase transition (on cooling) is therefore the broad exotherm between about 118 and 90 $^{\circ}\text{C}$ , corresponding with the POM observations. This complex shows a very large degree of supercooling and may have considerable difficulty on a molecular level in reorganizing from the isotropic state to the ordered mesophase. The POM indicated a shearable LC phase, between about and 170 $^{\circ}\text{C}$  on heating, with a high viscosity. The viscosity fell at the isotropization temperature (170 $^{\circ}\text{C}$ ), giving an easily shearable low viscosity liquid. The texture does not closely resemble any well-characterized liquid crystalline texture [12], although it may be smectic. The grainy appearance did not change appreciably on prolonged annealing and was similar to that of some liquid crystalline polymers. On cooling, the same texture was seen from about 114 $^{\circ}\text{C}$  and the mesophase was shearable down to about 60 $^{\circ}\text{C}$  (depending on the cooling rate).

The 2:1 (excess pyridyl) complex showed no clear features in the DSC, with no peaks on second heating. In the POM it was found that this complex softened to a fluid isotropic phase at 73 $^{\circ}\text{C}$ , but on further heating some crystallization appeared to take place above 100 $^{\circ}\text{C}$ , with both isotropic liquid and crystallites present; the latter disappeared at approximately 175 $^{\circ}\text{C}$  (investigation of all the phases is continuing). The material then cooled to a solid isotropic glass. This complex therefore does not seem to form a thermotropic mesophase. The 1:2 (excess

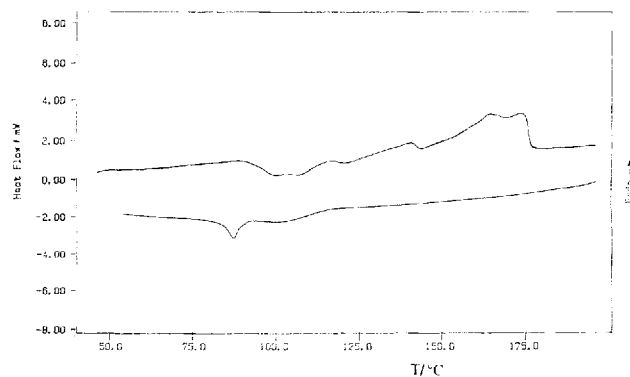
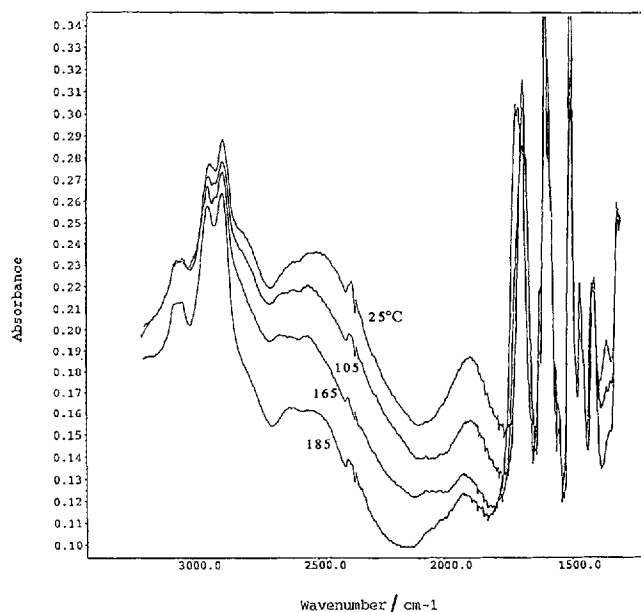


Figure 1. DSC second heating and cooling curves for the 1:1 complex.

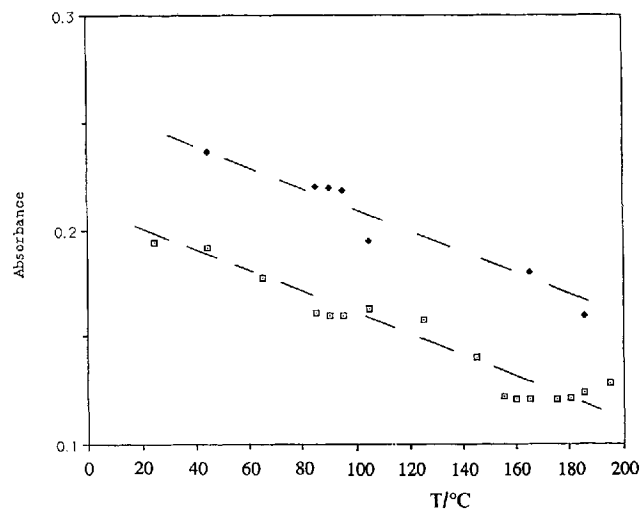
acid) complex showed a broad melting endotherm, with the onset at approximately 160°C in the DSC and with a peak at 182°C, near the melting point of the di-acid itself (187°C). On heating in the POM, softening was observed from 158°C, giving the same texture as that observed for the 1:1 complex. This texture remained until 182.5°C, when the sample became completely isotropic.

The complex with a 1:1 ratio of pyridyl to carboxylic acid showed the widest liquid crystalline temperature range. Therefore infrared spectra were run at different temperatures, from 25 to 195°C, to investigate the hydrogen bonding in the 1:1 complex. No peaks due to the uncomplexed starting material could be seen. The IR spectra show a gradual and continuous decrease in the average hydrogen bonding absorbances at 2500 and 1910  $\text{cm}^{-1}$  in the complex as the temperature is increased, with no clear discontinuities, as shown in figures 2 (a) and ((b)). Such a temperature effect on the hydrogen bonding has previously been observed in another pyridyl-carboxylic acid system [13].

The frequency of the carbonyl group is a strong indicator of the extent of proton transfer in such a hydrogen bonded complex [9]. The frequency of the carbonyl group in the hydrogen bonded dimer of the acid itself is 1686  $\text{cm}^{-1}$ , while in the pyridyl complex it was observed at 1691  $\text{cm}^{-1}$ , showing the expected shift to higher frequency on pyridine complexation. However, the peak is quite broad, probably indicating splitting into peaks of slightly higher and lower frequency [14]. There was a clear splitting of the carbonyl peak from this (fairly broad) peak at 1691 to peaks at 1691 and 1719  $\text{cm}^{-1}$  as the temperature was increased and the 'time average' hydrogen bonding decreased. Figure 3 illustrates the change in the absorbance for the carbonyl region as a function of temperature. In this case there was gradual increase from zero in the absorbance of the new peak at 1719  $\text{cm}^{-1}$  from 165°C onwards, with a change over in relative absorbance magnitudes at about 177°C on heating. Below 165°C there was practically no evidence of the peak at 1719  $\text{cm}^{-1}$ . This process was reversible, and on cooling the change over in the magnitudes of the absorbances was at about 145°C, with no sign of the 1719  $\text{cm}^{-1}$  peak below 125°C. The temperature of this absorbance intensity cross-over corresponds quite closely to the isotropization temperature for this complex, and therefore it can be proposed that the low viscosity above this temperature could be due to the onset of break-up of the structure into smaller chains and units, i.e. a high degree of loss of the hydrogen bonding interactions, which were effectively fixed at lower temperatures, giving a 'polymeric' structure. To support this, a similar situation in side-chain polymers has been observed [13]. The rates of hydrogen bond formation and dissociation become so rapid that, at elevated temperatures, a significant fraction of carboxylic acid groups



(a)



(b)

Figure 2. (a) A series of IR scans (absorbance versus wavenumber) for the 1:1 complex, at 25, 105, 165, and 185°C, showing the decrease in absorbance at 2500 and 1910  $\text{cm}^{-1}$  as the temperature increases. (b) A plot of the absorbances at 2500 and 1910  $\text{cm}^{-1}$  versus temperature, showing the decrease in hydrogen bonding; absorbance:  $\square$ , 1910  $\text{cm}^{-1}$ ;  $\blacklozenge$ , 2500  $\text{cm}^{-1}$ .

spend a proportion of their time 'free' and not hydrogen bonded. The appearance of the carbonyl peak at 1719  $\text{cm}^{-1}$  is then due to the 'free' uncomplexed acid, since, on the short IR time-scale, a snapshot of the free acid while it is 'between' hydrogen bonds can be seen. By coincidence, 165°C is actually the temperature at which the free acid was observed recently in a pyridyl-carboxylic

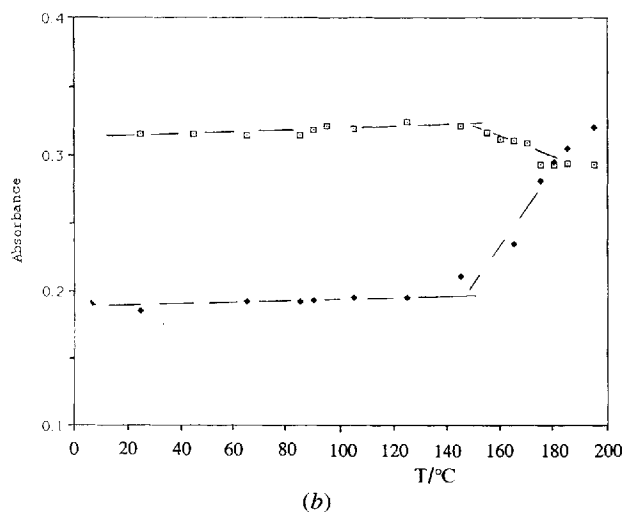
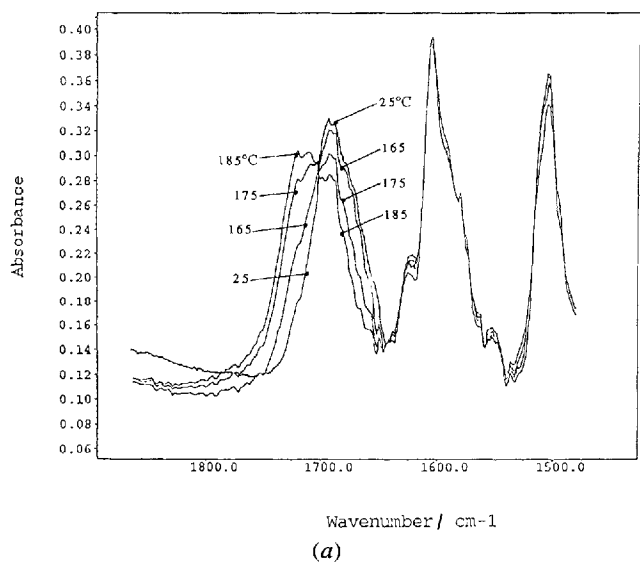
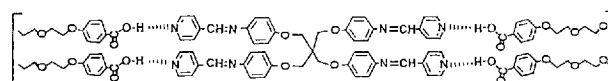


Figure 3. (a) A series of IR scans (absorbance versus wavenumber) for the 1:1 complex, at 25, 165, 175 and 185°C, showing the appearance of the peak at  $1719\text{ cm}^{-1}$  and a small decrease in absorbance at  $1691\text{ cm}^{-1}$  as the temperature increases. (b) A plot of the absorbances at  $1719$  and  $1691\text{ cm}^{-1}$  versus temperature, showing the change in the carbonyl absorbances; absorbance:  $\square$ ,  $1691\text{ cm}^{-1}$ ;  $\blacklozenge$ ,  $1719\text{ cm}^{-1}$ .

acid complex [14]. The disappearance of the texture seen in the POM to give a low viscosity (isotropic) liquid coincides with this transition.

Moreover, the mesogen in this complex is the 'rod' composed of the pyridylideneaniline hydrogen bonded with the aromatic carboxyl group, since this is the only fairly rigid linear unit. The tetra-pyridyl compound itself was not found to be mesomorphic, although the axial ratio of its pyridyl units is fairly large (similar to stilbene). It may at first seem surprising that this complex can show

LC behaviour, since the pentaerythritol core would be expected to have a tetrahedral conformation. But as mentioned in the introduction, it was found from molecular modelling and from similar pentaerythritol based liquid crystalline small molecules [15, 16] that this molecule can assume an essentially 'rod-like' linear shape, with the pyridyls pointing outwards at the ends of the rod. The axial ratio of the pyridyl units in this (uncomplexed) pentaerythritol compound is also just below the borderline for mesogenic [16], but when complexed would be above the axial ratio limit and therefore mesogenic. This would be the most likely conformation giving rise to an anisotropic liquid crystalline array, as shown below. The decrease in average hydrogen bonding as the temperature increases would of course contribute to a decrease in the mesogenicity as the mesogen itself (composed of the hydrogen bonded pyridyl and carboxylic acid rod) dissociates to its non-mesogenic components. Thus the disappearance of the texture and the transition to a low viscosity liquid coincide and both are due to dissociation of the hydrogen bonding at high temperature.



Fibres could be drawn from the (mesophase) melt of the 1:1 complex, as shown in figure 4. This lends support to the idea that the material is essentially polymeric in nature. The extended structure of the tetra-pyridyl compound (as shown above), having two pyridyls at each end, would help to counteract the reversible hydrogen bonding

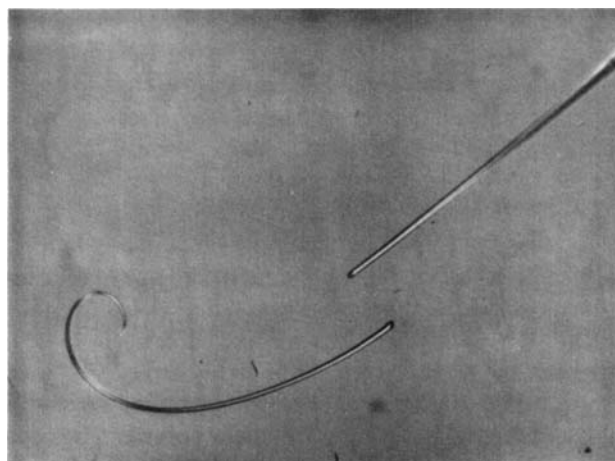


Figure 4. Photomicrograph of fibres drawn from the 1:1 complex.  $100\times$  magnification.

dissociation dynamics and therefore help to form longer hydrogen bonded supramolecular chains compared to a linear dipyrindyl unit. Only one case of fibre formation has previously been observed [17]. In conclusion, the complex behaves as a supramolecular material at room temperature and above, but the behaviour is consistent with small molecules at higher temperatures. This property may be useful for some applications.

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