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Communications to the Editor

Structure of a Hydrogen-Bonded Liquid-Crystalline Network

L. M. Wilson*

Melville Laboratory for Polymer Synthesis, University of Cambridge, Pembroke Street, Cambridge CB2 3RA, U.K.

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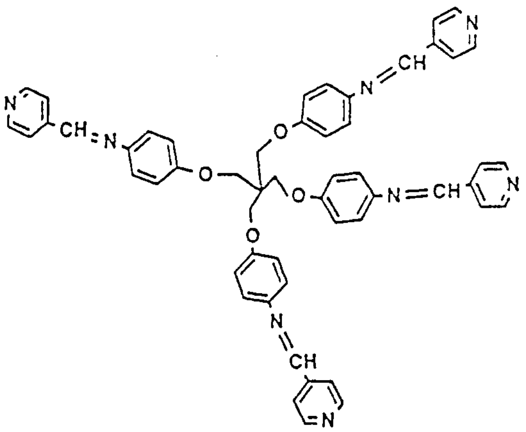
Introduction. The hydrogen-bonding interaction between aromatic carboxylic acids and pyridines has been described for the formation of small molecule dimer complexes.[1] The construction of mesogenic molecules[2,3] and the relation between hydrogen bonding and liquid crystallinity involved in low molar mass materials have 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 bispyridyl with 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, forms 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.

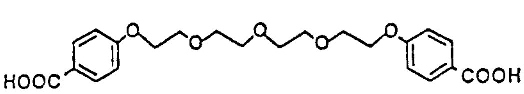
The tetrahedral pentaerythritol-based tetrapyridyl molecule is a "semiflexible" unit, having some rotation about the ether bonds, and has the potential to be "cross-linked" by hydrogen-bonding complexation of the pyridyls in more than one dimension when mixed with a suitable diacid, e.g., an aromatic dicarboxylic acid, thus giving a "supramolecular network". However, from molecular modeling it can be shown that the flexibility about the $-CH_2O-$ linkages of the pentaerythritol core is sufficient for the molecule to adopt a conformation which is not tetrahedral and can be essentially a one-dimensional rodlike (calamitic) conformation with two pyridyles at each end. Here we describe a liquid-crystalline hydrogen-bonded complex formed from the tetrapyridyl and the flexible chain diacid shown which were investigated by DSC, polarizing optical microscopy (POM), and X-ray diffraction (XRD).

Experimental Section. Pentaerythritol (1.36 g) and 4-nitrophenol (6.13 g, 10% excess) in dry THF were reacted using diethyl azodicarboxylate[10] (7.66 g and 11.5 g of PPh_3) at room temperature to give $C(CH_2OPhNO_2)_4$ in high yield, which was reduced to the tetraamine at 80–85 °C for 4–6 h in DMF by 10% Pd on carbon (0.7 g) with continuous addition of an excess of dry ammonium formate as the hydrogen source.[11]

This tetraamine (2 g) was reacted with 4-pyridinecarboxaldehyde (2.05 g, 20% excess) at room temperature in ethyl alcohol with a small amount of acetic acid to give the Schiff base tetrapyridyl product. Overall yield: 75%. Elem anal. Calcd: C, 74.30; H, 5.14; N, 13.08. Found: C, 74.50; H, 5.38; N, 12.96. IR: 1628, 1596, 1505, 1235, 1045, 837, 816 cm^{-1}. NMR ($CDCl_3$): 4.38 (s, 2H), 7.0 (d, 2H), 7.21 (d, 2H), 8.5 (s, 1H), 8.0 (d, 2H), 8.90 (d, 2H). MP: crystal, 156–8 °C; isotropic, cools to glass.



tetrapyridyl **1**



dicarboxylic acid **2**

The [(oxydiethoxyethylene)dioxy]bis(4-benzoic acid) was obtained as in ref 8. MP: solid, 187 °C; isotropic. IR (KBr disk): hydroxyl, 2600–3000 cm^{-1}; carbonyl, 1686 cm^{-1}.

The complexes were obtained as described in ref 8, by heating the stirred mixture of components in an oil bath to 180 °C for 2–4 min under nitrogen.

For the complexes of compounds 1 and 2, all characterization was consistent with assigned structures. See the discussion for DSC data.

All starting materials were obtained from Aldrich Chemical Co. Measurements were performed on the following instruments: IR, on a Nicolet 510M spectrometer fitted with a Graseby Specac 5750 variable-temperature IR cell and an automatic temperature controller; NMR, on a Bruker WM 250-MHz spectrometer; elemental analyses, in the Department of Chemistry, University of Cambridge; DSC, on a Perkin-Elmer Series 7; polarizing light microscopy, on a Leica axioscope fitted with a Mettler FP82 microfurnace. The X-ray diffraction measurements were performed on a Philips PW 1710 diffraction system. The samples were prepared by heating to the isotropic temperature and then cooling down to the mid-mesophase temperature, quenched in liquid nitrogen, and ground to powders for the X-ray measurements.

Results and Discussion. Although both of the starting materials, compounds 1 and 2, do not show thermotropic mesophases and have melting points at 157 and 187 °C, respectively, a mesophase is observed on hydrogen-bonding complexation between the two components. 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 °C, followed by a small exotherm between 90 and 110 °C, followed by a broad endotherm with peaks at 116, 138, 163, and 170 °C on the second heating at 10 °C/min (the first heating was performed to 200 °C at the same rate and was very similar in appearance). The endotherm–exotherm–endotherm appears to be typical melting re-

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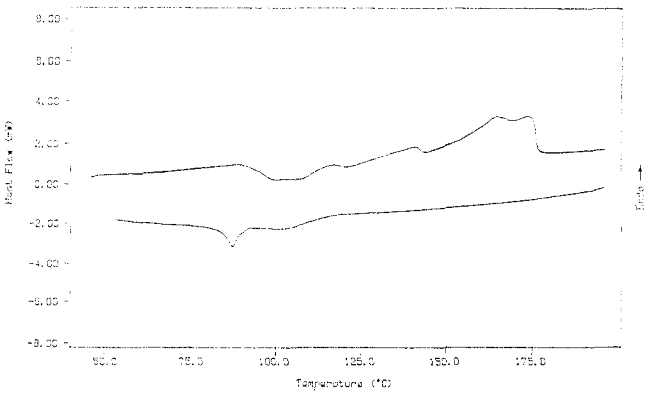


Figure 1. DSC second heating and cooling curves for the 1:1 complex.

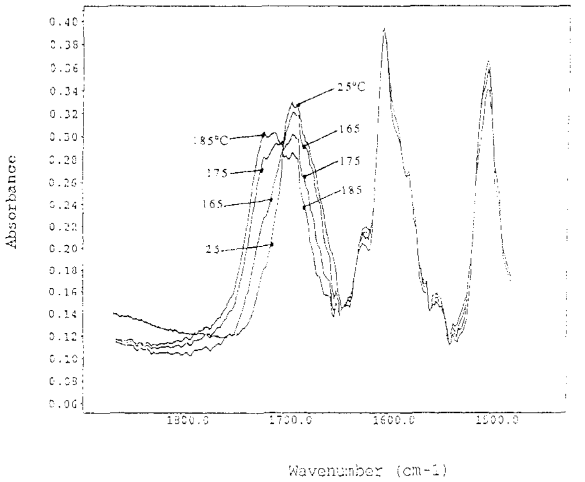


Figure 2. Series of IR scans (absorbance vs wavenumber) for the 1:1 complex, at 25, 165, 175, and 185 °C, showing the appearance of the peak at 1719 cm^{-1} and decreasing in absorbance at 1690 cm^{-1} as the temperature increases.

crystallization and remelting behavior between about 70 and 125 °C. On cooling, also at 10 °C/min a broad exotherm is seen between 118 and 60 °C (or less) and a sharper peak (with a shoulder) at 87 °C. The POM showed a soft shearable phase between about 70 and 170 °C, with a high viscosity, on heating. On cooling, the grainy texture appeared at 116–112 °C, corresponding to the broad DSC transition. The considerable undercooling compared to the transition at 170 °C indicates that the complex may have difficulty in rearranging from the isotropic temperature, probably due to the hydrogen bonding. At the isotropic temperature the viscosity fell, giving an easily shearable low viscosity liquid. The texture was grainy, as found in many polymeric systems, and 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.

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 °C, but on further heating some crystallization appeared to take place above 100 °C which disappeared at approximately 175 °C. The material then cooled to a solid isotropic glass. This complex therefore does not seem to have a thermotropic mesophase. The 1:2 (excess acid) complex showed a broad melting endotherm with the onset at approximately 160 °C in the DSC and with the peak at 182 °C, near the melting point of the diacid itself (187 °C). On heating, in the POM softening was observed from 158 °C, with the same texture as observed for the 1:1 complex. This texture remained until 182.5 °C, when the sample became completely isotropic.

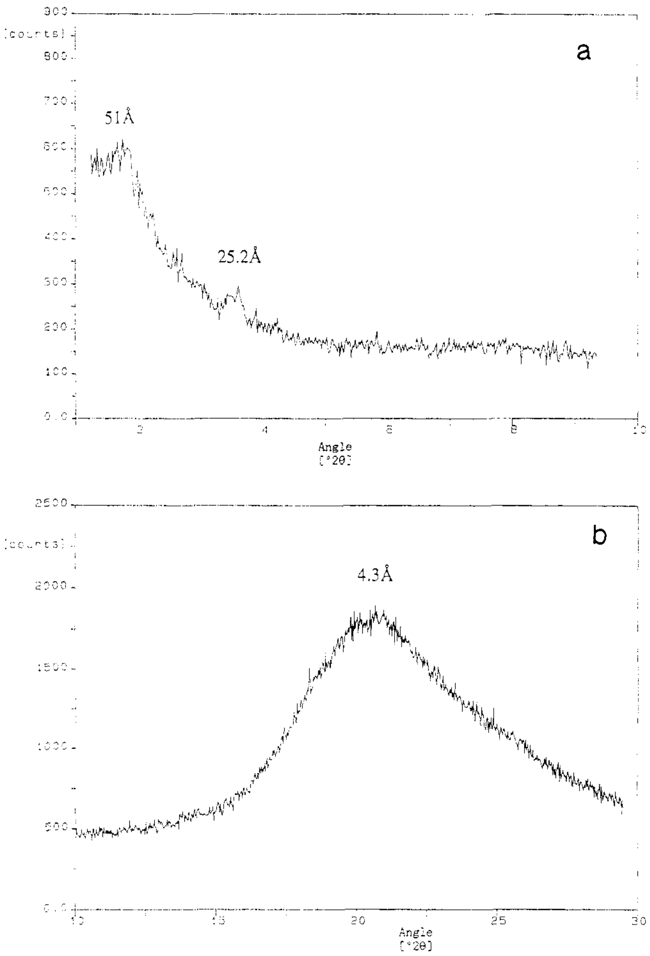
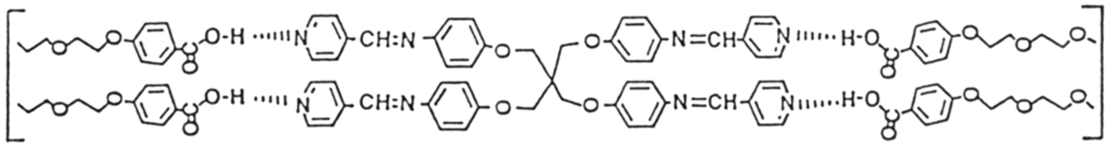


Figure 3. X-ray diffraction of the 1:1 complex in the mesophase, (a) low angle and (b) higher angle, intensity vs angle (2θ).

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. Peaks typical for hydrogen-bonded[1] hydroxyl are seen at 2500 and 1910 cm^{-1}. 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[13] absorbances at 2500 and 1910 cm^{-1} in the complex as the temperature is increased.

The frequency of the carbonyl is a strong indicator of the extent of proton transfer in the hydrogen-bonded complex.[9] The frequency of the carbonyl in the acid hydrogen-bonded dimer itself is 1686 cm^{-1}, while in the pyridyl complex it was observed at 1691 cm^{-1}, which shows the expected shift to higher frequency on pyridine complexation. However, the peak is quite broad, perhaps indicating splitting.[16] There was a clear splitting of the carbonyl peak from this (fairly broad) peak at 1691 cm^{-1} to peaks at 1691 and 1719 cm^{-1} as the temperature was increased and the average hydrogen bonding decreased. Figure 2 illustrates the change in the absorbance of the carbonyl region versus temperature. In this case there was a gradual increase from zero in the absorbance of the new peak at 1719 cm^{-1} from 165 °C onward, with the changeover in relative absorbance magnitudes at about 177 °C on heating. Below 165 °C there was practically no evidence of the peak at 1719 cm^{-1}. This was reversible, and on cooling the changeover in the magnitudes of the

Chart 1



absorbances was at about 145 °C, with no sign of the 1719 cm^{-1} peak below 125 °C. The temperature of this absorbance intensity crossover corresponds quite closely to the isotropization and change to low viscosity liquid for this complex, and therefore the low viscosity above this temperature could be due to the onset of breakup of the structure into smaller units, i.e., a high loss of the hydrogen bonding interactions which were effectively fixed at lower temperatures, giving a polymeric or extended 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 spend a proportion of their time "free" and not hydrogen bonded. The appearance of the carbonyl peak at 1719 cm^{-1} is then due to the free uncomplexed acid. 165 °C is actually the temperature at which the free acid was observed recently in a pyridyl–carboxylic acid complex.[16]

The mesogen in this complex is the extended aromatic "rod" composed of the pyridylidene–aniline unit hydrogen bonded with the phenylcarboxylic acid group (this is the only rigid linear unit). The tetrapyridyl compound itself was not found to be liquid crystalline, 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 liquid-crystalline behavior, since the pentaerythritol core would be expected to have a tetrahedral conformation. But it was found from molecular modeling and from similar pentaerythritol-based liquid-crystalline small molecules[14,15] that such molecules could take an essentially "rodlike" linear shape, with the pyridyls pointing outward at the ends of the rod. The liquid-crystalline pentaerythritol-based molecules (without further flexible spacers to the mesogenic rods) contained three para-linked phenyl rings with one ester linkage in the mesogenic unit, while those that were not liquid-crystalline contained two or less rings.[15] The axial ratio of the pyridyl unit in this (uncomplexed) pentaerythritol compound is therefore less than the ratio found for the liquid-crystalline small molecules and therefore may be below the borderline for mesogenicity, but when complexed, it would be above the axial ratio limit and therefore could be mesogenic.

To confirm the extended chain conformation of the hydrogen-bonded complex postulated above, the mesophase structure of the complex was investigated by powder X-ray diffraction on a quenched sample of the 1:1 complex. This shows two low angle layer peaks at about 1.73 (weak) and 3.5° 2θ (very weak), corresponding to d spacings of 51 and 25.2 Å, as shown in Figure 3a. These show that there is indeed a layer structure and appear to correspond to the 001 and 002 smectic layer spacings. At higher angles there is a broad diffuse peak centered at a d spacing of about 4.3 Å. This shows fairly liquidlike ordering within the layers and is consistent with smectic A type layer ordering, as shown in Figure 3b. From molecular models the fully extended molecular repeat length (L) of the combined tetrapyridyl and diacid units is about 65 Å. The layer periodicity observed in the mesophase (about 51 Å) is thus less than the fully extended conformation, with d/L about 0.8, showing some tilting or disordering, probably in the rather long diacid units, but this layer spacing does confirm the extended structure of the hydrogen-bonded units. The most likely conformation giving rise to an anisotropic liquid-crystalline array is shown in Chart 1. This does in fact represent a "ladder"-type polymeric system.

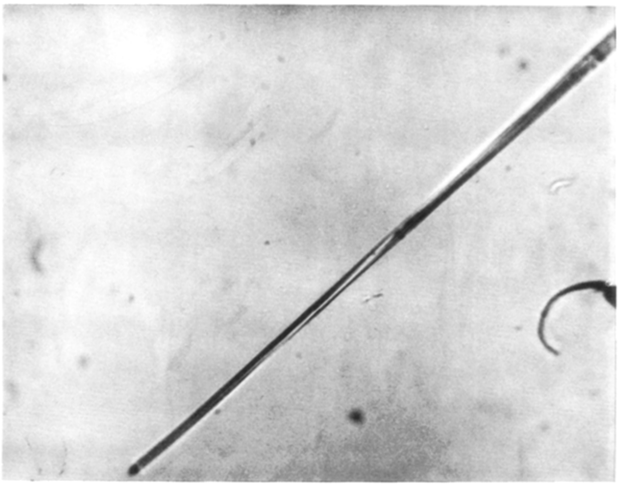


Figure 4. Photomicrograph of fiber drawn from the 1:1 complex. 100× magnification.

The decrease in average hydrogen bonding as the temperature increases would of course contribute to a decrease in the mesogenicity as the mesogen itself dissociates into its nonmesogenic components. Thus the disappearance of the texture and the transition to a low viscosity liquid coincide and are both due to dissociation of the hydrogen bonding at high temperature.

Fibers 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 supramolecular and polymeric in nature. The extended structure of the tetrapyridyl component (as shown above), having two pyridyls at each end, would help to counteract the reversible hydrogen-bonding dissociation dynamics and therefore help to form longer hydrogen-bonded supramolecular chains compared to a linear dipyridyl unit. Only one case of fiber formation has previously been observed.[17] In conclusion, the complex behaves like a supramolecular material at room temperature and above but as small molecules at higher temperatures. This property may be useful for some applications.

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