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# An infrared study of hydrogen bond stability in benzoic acid–*trans*-1,2-bis(4-pyridyl)ethylene complexes in the solid state and the implications for the design of supramolecular polymers

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Derivatives of benzoic acid were complexed with *trans*-1,2-bis(4-pyridyl)ethylene. Infrared spectroscopy was used to confirm complexation and a correlation was found between the value of $\nu$-C=O for the complex in the solid state and the p$K_a$ of the benzoic acid derivative. The stabilities of the hydrogen bonds in the complexes were investigated by temperature dependent infrared spectroscopy. It was found that all of the complexes behaved in a similar way, the hydrogen bonds remained intact until the melting point of the complex was reached. The implications for the design of supramolecular polymers are discussed.

## Introduction

The concepts of supramolecular chemistry are increasingly being used in the design and synthesis of novel organic materials.[1] The simple association of two complementary compounds, through non-covalent interactions, can be used to create materials with new properties which are not possessed by either of the components alone. For instance, liquid crystalline materials can be prepared from non-liquid crystalline compounds in this manner.[2] Extension of these ideas has led to the concept of supramolecular polymers, arrays of small molecules held together in extended structures by non-covalent interactions.[3] Lehn and co-workers reported the design and synthesis of the first such system, a main chain liquid crystalline supramolecular polymer, in which the molecules were associated through hydrogen bonding.[3b] Since this initial study other hydrogen bonded systems have been investigated. Perhaps the simplest system of this type is based on the complexation of carboxylic acids with pyridines. In an extensive series of papers, Kato and Fréchet have exploited this hydrogen bonded system in the construction of small molecule liquid crystals[4] and subsequently extended these ideas to the conversion of non-liquid crystalline polymers into liquid crystalline materials.[5] The carboxylic acid–pyridine system has also been used to prepare main chain supramolecular liquid crystalline[6] and non-liquid crystalline[6d] polymers and network structures in which the hydrogen bond was responsible for chain extension. Network systems of this type have shown history dependent properties and displayed properties typical of small molecules at elevated temperatures, such as low viscosity, but properties more typical of polymers at lower temperatures, including glass transitions and fibre formation.[6d] Glass transitions and fibre formation from main chain supramolecular polymers, in which a carboxylic acid–pyridine hydrogen bond was responsible for chain extension, have also been reported.[3g] Stadler has developed thermoplastic elastomers which rely on hydrogen bonding between long polymer chains.[7]

The ability to form chain extended structures is crucial to the properties of supramolecular polymeric systems. The properties of the material in the liquid phase and in solution depend on the magnitude of the association between the monomer units. For instance, higher viscosity liquid phases and solutions would be expected for systems in which the monomers were more strongly associated with one another and lower viscosity liquids and solutions for more weakly associated monomers. Consequently, increasing the number of hydrogen bonds between the monomer units leads to higher viscosity liquid phases and solutions and properties typically associated with conventional polymers.[8] The properties of the solid state also rely on the ability of the monomers to associate into extended structures through non-covalent interactions. However, in contrast to the liquid phase and in solution, the magnitude of the non-covalent interactions which are responsible for chain extension will only be important if overcoming these intermolecular forces determines the properties of the solid state. For instance, if the material is heated and the interactions responsible for chain extension remain intact until the liquid phase then the thermal behaviour of the material must be determined principally by the other intermolecular forces and there would be no particular advantage in increasing the magnitude of the non-covalent interactions leading to chain extension. Thus, even the single hydrogen bond between a carboxylic acid and a pyridine would be adequate for the formation of chain extended structures in the solid phase at temperatures below the melting point of the material.

The complexation of benzoic acid derivatives with pyridine derivatives has frequently been used in the synthesis of supramolecular polymers.[3e–g,4–6] Since a variety of simple benzoic acid derivatives were readily available, complexes could be prepared in which the strength of the acid varied and the effects of temperature on the hydrogen bond stability in these complexes could be studied.

## Results and discussion

Crystallisation of a 2 : 1 molar mixture of benzoic acid derivative and *trans*-1,2-bis(4-pyridyl)ethylene gave complexes **1–8**, see Fig. 1. $^1$H NMR spectra of the complexes in DMSO-d$_6$ and elemental analysis were consistent with a 2 : 1 molar ratio of benzoic acid derivative: *trans*-1,2-bis(4-pyridyl)ethylene.

Confirmation that complexation had occurred was most easily obtained by comparing the infrared spectrum of the complex with that of the corresponding benzoic acid derivative. It has been observed previously[9] that complexation between a pyridine and a benzoic acid causes the broad OH absorption between 3000–3500 cm$^{-1}$ to be replaced by two new absorptions at ~2500 and ~1900 cm$^{-1}$. These new absorptions have been interpreted as corresponding to double-minimum type

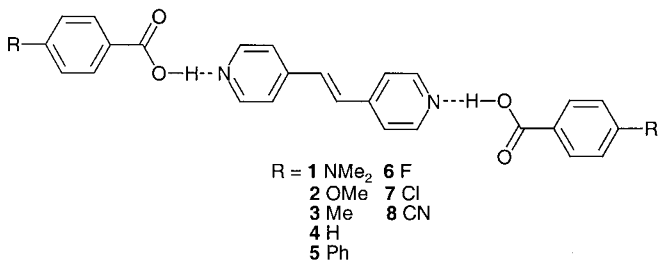

**Fig. 1** 4-Substituted benzoic acid–*trans*-1,2-bis(4-pyridyl)ethylene complexes.

hydrogen bonds.[9] It has been proposed[9] that hydrogen bonds of this type are formed between benzoic acid and pyridine derivatives when the difference between the $pK_a$ of the acid and that of the protonated pyridine is less than 3.75. Since the $pK_a$ of protonated *trans*-1,2-bis(4-pyridyl)ethylene[10] has been determined as 5.82 and the $pK_a$s of the benzoic acid derivatives[11] in this study are between 3.51 and 5.00 all the hydrogen bonds should be of the double-minimum type. A second feature which is associated with the formation of hydrogen bonds of this type is that the carbonyl absorption is found to shift to higher wavenumbers compared with the parent benzoic acid dimer.[9] These band changes were observed in the infrared spectra of complexes **1–8**. Only a single absorption was observed for *ν*-C=O in the solid state indicating that a single state was present for the hydrogen bonds in each of these complexes, whilst the band changes confirmed that the hydrogen bonds in the complexes were all of the same type. A plot of *ν*-C=O for the complexes **1–8** against the published values for the $pK_a$ of the benzoic acid derivatives at 25 °C in water[11] showed a correlation, see Fig. 2. It can be concluded from this correlation that the hydrogen bonding groups were in similar environments in the solid state and that the differences in the values observed for *ν*-C=O in the complexes were principally a result of electron donation or withdrawal by the different substituents attached to the aromatic ring of the benzoic acid. Consequently, it can be assumed that the strengths of the hydrogen bonds in the complexes in the solid state are determined by the nature of the benzoic acid substituent. Similar infrared studies of the complexation between various carboxylic acids and 1-methylimidazole in solution have recently been reported and are consistent with the results reported here.[12]

Further evidence for complexation comes from the melting points of the complexes. Complexes **1**, **4–8** had sharp melting points which were between those of *trans*-1,2-bis(4-pyridyl)ethylene and the acid, whilst **3** had a sharp melting point which was higher than either component. Interestingly **2** was found to be liquid crystalline, a nematic phase being present between 170.5–187 °C. The mesophase was characterised by optical microscopy. The temperature of the crystal to nematic transition was between the melting points of *trans*-1,2-bis(4-pyridyl)ethylene and *p*-anisic acid whilst the nematic to isotropic transition was higher than the melting points of either of these components. Both of these transitions were sharp. Neither of the components of complex **2** forms liquid crystalline phases alone. Many liquid crystalline complexes have been reported which rely on the hydrogen bonding of a benzoic acid and a pyridine to form the mesogen.[3e–g,4–6] The presence of a liquid crystalline phase for complex **2** is strong evidence for complex formation. Thus, the thermal behaviours of **1–8** are consistent with hydrogen bonding between the benzoic acid derivative and *trans*-1,2-bis(4-pyridyl)ethylene. In contrast to the infrared spectral data no correlation was found between the melting points of the complexes and the $pK_a$s of the acids.

In order to study the effect of temperature on the hydrogen bonds in complexes **1–8** variable temperature infrared studies were carried out. The behaviours of all the complexes were similar. The nature of the hydrogen bonding in the complexes remained unchanged until the melting point was reached. In the case of **2** this was the nematic to isotropic transition. No broadening in the region 3000–3500 cm$^{-1}$, corresponding to uncomplexed acid, was observed. Above the melting point the 3000–3500 cm$^{-1}$ region showed broadening indicating that uncomplexed acid was now present, as acid dimers. The effect of temperature on the infrared spectrum of complex **4** (R = H) mp 141–142 °C is shown in Fig. 3. These observations are consistent with the hydrogen bonds within the complex remaining intact until the other intermolecular forces are overcome. Once these forces have been overcome the increased mobility in the isotropic liquid state allows exchange between the components and the formation of hydrogen bonded acid dimers. Kato and Fréchet carried out a variable temperature infrared study of a liquid crystalline complex with a hydrogen bond between a benzoic acid and a pyridine derivative.[13] Their findings are in agreement with those described in this work. They observed that uncomplexed acid was only observed in the isotropic liquid phase. In the mesophase the hydrogen bonding

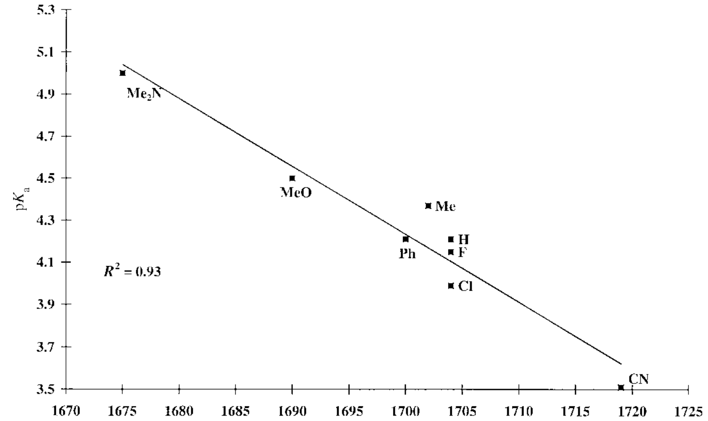

**Fig. 2** Variation of *ν*-C=O for complexes **1–8** in the solid state with the $pK_a$ of the benzoic acid derivatives.

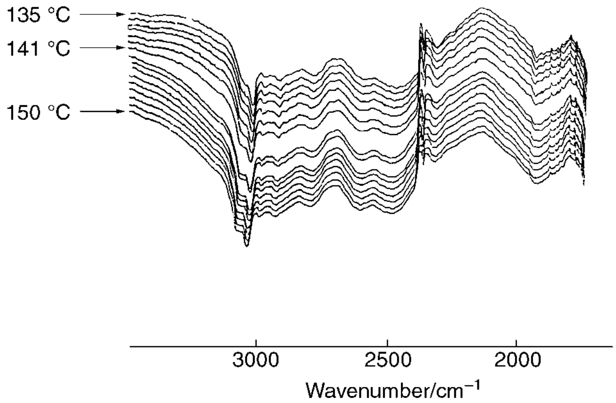

**Fig. 3** Infrared spectra for complex **4** recorded at 1 °C intervals between 135 and 150 °C.

within the complex remained intact. Solid state NMR studies of the molecular motions within two carboxylic acid–pyridine complexes, which are closely related to those described here, have recently been reported.[14] The differing thermal behaviour in these two complexes was attributed to differences in molecular motion as a result of intermolecular forces and packing rather than breaking of hydrogen bonds.

The results described here show that the hydrogen bonds remain intact in the solid state at temperatures below the melting point of the complex, irrespective of the acidity of the benzoic acid derivative and hence the strength of the hydrogen bond. Amongst the properties which distinguish polymers from low molecular mass compounds are the tendency to form glasses and exhibit glass transitions, significantly different rheological behaviour and the ability to draw fibres from the melt and solution. There are very few supramolecular polymers which have been reported to possess any of these properties; the majority of such systems behave more like crystalline low molecular mass compounds. It is interesting to consider the results described here in light of previous studies which described supramolecular systems which exhibited some of the properties typically associated with polymers.

It has been found that oligotetrahydrofurans which were terminated with carboxylic acid functionalities exhibited changes in rheological properties, compared with similar compounds which were terminated with esters.[15] It was suggested that the dimerisation of the carboxylic acids in crystalline domains was responsible for the differences in behaviour. $^{13}$C CP/MAS NMR studies revealed that the carboxylic acids remained as dimers at elevated temperatures. Interestingly, the oligotetrahydrofuran linkers between the carboxylic acid groups were found to exist in both crystalline and amorphous regions and the presence of a glass transition was inferred. The association of a carboxylic acid with a pyridine derivative through hydrogen bonding is stronger than that of carboxylic acid dimerisation. The current study, which found that the hydrogen bonding remains intact in crystalline environments at temperatures below the melting point of the crystal, is therefore consistent with these observations. Telechelic oligo- and poly(dimethylsiloxanes) terminated with ureidopyrimidine groups associate through quadruple hydrogen bonding.[8] These very strong associations allowed these materials to form chain extended structures in both the solid and liquid phases and in solution, resulting in many of the properties of polymers. The oligomeric compound, which contained only 13 atoms in the spacer between the end groups, could be obtained in both crystalline and amorphous forms. The crystalline compound was found to behave in many respects like other low molecular weight organic compounds but the amorphous form displayed many properties commonly associated with conventional polymers. The mechanical properties were used to estimate a degree of polymerisation of $>100$ for this material. The principal factor affecting the chain extension appeared to be monomer purity. The complexation of molecules containing four pyridine groups with dicarboxylic acids also produced materials which exhibited polymeric properties.[6d] These materials relied on single hydrogen bonds for chain extension but were supramolecular networks rather than linear polymers. Interestingly, one of these materials when initially prepared from the melt exhibited properties similar to other low molecular mass crystals, but thermal cycling, which was accompanied by a reduction in crystallinity, led to the appearance of a glass transition. This behaviour was accounted for by changes in the conformation of the pyridine component. The other system of this type produced a material with a crystalline melting point and a glass transition.[6d] However, the crystalline regions did not form on cooling and crystallisation was induced as the sample was heated below its melting point. In both cases it seems likely that the conformational properties of the molecules bearing the pyridine groups led to difficulties in packing and hence crystallisation was inhibited. Consideration of the supramolecular systems which display polymeric properties suggests that whilst strong associations between the components of a supramolecular polymer are essential if the system is to possess polymeric properties in the liquid state and in solution, in the solid state the inhibition of crystallinity is far more important. Thus the pyridine–carboxylic acid system should be an effective means of chain extension in supramolecular polymers in the solid state. In the liquid state and in solution the lability of the single hydrogen bonds would result in the formation of low viscosity liquids and solutions offering potential processing advantages over conventional polymers. Experimental support comes from a main chain supramolecular polymer in which chain extension resulted from complexation between a pyridine and a carboxylic acid and in which crystallisation was inhibited.[3g] This linear system possessed a glass transition and fibres could be drawn from the melt.

Although the design and synthesis of supramolecular polymers are still at an early stage, systems with polymeric properties in the solid and liquid states and in solution have already been realised.[8] Perhaps more intriguing are the systems which have been shown to display properties typical of linear or network polymers in the solid state and yet behave more like low molecular mass materials in the liquid state and in solution.[3g,6d] The results of this study suggest that the carboxylic acid–pyridine complex is an effective system for the construction of supramolecular polymers of this type.

## Conclusions

A series of complexes were synthesised from benzoic acid derivatives and *trans*-1,2-bis(4-pyridyl)ethylene. The formation of hydrogen bonded complexes was confirmed by the band changes in the infrared spectra, compared with those of the uncomplexed components. Similar band changes in all of the complexes confirmed that the hydrogen bonds in each complex were of the double-minimum type. The values for $\nu$-C=O for the complexes in the solid state were found to correlate with the p$K_a$ of the benzoic acid derivative. The stability of the hydrogen bonds in each complex was studied by temperature dependent infrared spectroscopy. It was found that all of the complexes behaved in a similar way, the hydrogen bonds remained intact until the melting point of the complex was reached. This behaviour was consistent with other studies. It is suggested that the single hydrogen bond between a carboxylic acid and a pyridine derivative can be an effective means of chain extension in supramolecular polymers and allow such materials to exhibit polymeric properties in the solid state, providing that the hydrogen bonds remain intact in the solid state and the materials have a low crystallinity.

## Experimental

All starting materials were purchased from Aldrich Chemical Co. and were used as received. Melting points were determined on an Electrothermal IA9100 melting point apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet 510 FTIR instrument. A Graseby Specac P/N 5750 High Temperature Cell and a P/N 20130 Temperature Controller were used to obtain variable temperature infrared spectra. A Zeiss Axioskop polarising microscope equipped with a Linkam TMS 91/THMS 600 heating stage was used for optical microscopic studies. $^1$H NMR spectra in DMSO-$d_6$ were recorded on a Bruker 250 MHz Fourier Transform NMR spectrometer with TMS as an internal reference. Elemental analyses were performed by Medac Ltd., Brunel University, Uxbridge, Middlesex, UK UB8 3PH.

Complexes **1–8** were prepared by crystallisation from methanol, or alternatively by crystallisation from pyridine, drying in a vacuum oven at 60 °C, and recrystallisation from chloroform (THF–chloroform for **8**). The figures in brackets after $\nu_{max}$ for the complex are the values for the dimer of the corresponding benzoic acid derivative.

**1**: mp 220–221 °C (Found: C, 70.2; H, 6.3; N, 10.9. $C_{30}H_{32}N_4O_4$ requires C, 70.3; H, 6.3; N, 10.9%); $\nu_{max}$(KBr)/cm$^{-1}$ 1675 (1669).

**2**: mp K 170.5 N 187 I °C (Found: C, 68.7; H, 5.3; N, 5.7. $C_{28}H_{26}N_2O_6$ requires C, 69.1; H, 5.4; N, 5.8%); $\nu_{max}$(KBr)/cm$^{-1}$ 1690 (1686).

**3**: mp 183–185 °C (Found: C, 74.0; H, 5.8; N, 6.1. $C_{28}H_{26}N_2O_4$ requires C, 74.0; H, 5.8; N, 6.2%); $\nu_{max}$(KBr)/cm$^{-1}$ 1702 (1679).

**4**: mp 141–142 °C (Found: C, 73.2; H, 5.15; N, 6.6. $C_{26}H_{22}N_2O_4$ requires C, 73.2; H, 5.2; N, 6.6%); $\nu_{max}$(KBr)/cm$^{-1}$ 1704 (1686).

**5**: mp 172–173 °C (Found: C, 78.7; H, 5.2; N, 4.8. $C_{38}H_{30}N_2O_4$ requires C, 78.8; H, 5.2; N, 4.8%); $\nu_{max}$(KBr)/cm$^{-1}$ 1700 (1683).

**6**: mp 160–162 °C (Found: C, 67.4; H, 4.3; N, 6.0. $C_{26}H_{20}F_2N_2O_4$ requires C, 67.5; H, 4.4; N, 6.05%); $\nu_{max}$(KBr)/cm$^{-1}$ 1704 (1684).

**7**: mp 195–197 °C (Found: C, 63.0; H, 4.1; N, 5.8. $C_{26}H_{20}Cl_2N_2O_4$ requires C, 63.0; H, 4.1; N, 5.65%); $\nu_{max}$(KBr)/cm$^{-1}$ 1704 (1684).

**8**: mp 215–216 °C (Found: C, 70.5; H, 4.2; N, 11.65. $C_{28}H_{20}N_4O_4$ requires C, 70.6; H, 4.2; N, 11.75%); $\nu_{max}$(KBr)/cm$^{-1}$ 1717 (1702).

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