

Correlations between Molecular Motion in the Solid State and Liquid-crystalline Phase Transitions for Two Hydrogen-bonded Carboxylic Acid–Pyridyl Complexes

Melinda J. Duer,^{a*} Lynn F. Gladden,^b Anselm C. Griffin,^{*†c} Chetan P. Jariwala^c and E. Clare Stourton^a

^a Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW

^b Department of Chemical Engineering, University of Cambridge, Pembroke Street, Cambridge, UK CB2 3RA

^c Melville Laboratory for Polymer Synthesis, University of Cambridge, Pembroke Street, Cambridge, UK CB2 3RA

Studies of molecular motion can be used to probe intermolecular potentials and lead towards an understanding of the phase transitions of two hydrogen-bonded, carboxylic acid–pyridyl complexes.

We have recently begun a comparative study of the motional degrees of freedom available to similarly structured molecules in solids, some of which exhibit liquid-crystalline phase transitions, and some of which do not. Molecular motions are governed by the various intermolecular potentials, which operate to form the bulk solid structure. Thus, by studying molecular motion, we can probe the intermolecular potential. In turn, an understanding of the intermolecular potential is crucial to understanding the phase-transition properties of a material. Two molecules, illustrated in Fig. 1, have proved very interesting in this study. Both are examples of complexes formed by hydrogen bonding between a carboxylic acid (4-pentylbenzoic acid in **PH** and 4-pentylcyclohexanoic acid in **CH**) and a pyridyl, in this case, 1,2-bis-(4-pyridyl)ethane. Such complexes, including polymeric ones, have recently received attention^{1,2} because of the liquid-crystalline phases formed by many of them.

The complex **PH** undergoes transition to a smectic A liquid-crystalline phase at 420 K, a nematic phase at 440 K and isotropic phase at 452 K.¹ In contrast, **CH** forms no liquid-crystalline phases, but melts directly to an isotropic liquid at 404 K, a temperature which is well below that of even the first solid–fluid phase transition of **PH**.

We have obtained a detailed picture of the motional degrees of freedom available to both these complexes in their solid states over a range of temperatures, by employing several different one- and two-dimensional NMR techniques.

The motion in the aromatic regions of both complexes has been successfully studied by quantitative analysis^{3,4} of the spinning sideband patterns arising from the aromatic ¹³C signals in slow speed, magic angle spinning (MAS) experiments. Such analyses show that both the phenylene and pyridyl rings of the **PH** complex are essentially static on the NMR timescale up to a temperature of 363 K. Above this temperature however, both types of ring perform rapid (> 10⁵ Hz), 180° flips about their approximate two fold axes. This transitional temperature corresponds to a solid–solid phase transition as evidenced by the dsc curve for **PH**. The pyridyl rings of the **CH** complex are likewise static on the NMR timescale at 173 K, but above this temperature perform rotational liberations about their approximate two fold axes, the amplitude and rate of these liberations increasing with temperature (amplitude *ca.* 20° and rate *ca.* 200 kHz at 373 K). At 403 K, immediately below the mp for **CH** (404 K), the pyridyl rings undergo rapid (> 10⁵ Hz), unrestricted rotations about the approximate two fold axis.

The motion in the alkyl regions of both complexes has been studied with a two-dimensional NMR experiment (2DCSA).⁵ This experiment arranges that the ¹³C chemical shift anisotropy powder patterns for individual ¹³C sites are separated in one

spectral dimension (*F*1) according to the isotropic ¹³C chemical shift of each powder pattern in the other dimension (*F*2). The powder patterns in *F*1 can then be quantitatively analysed⁶ to reveal details of the motion of each individual ¹³C site. This is the first time that this technique has been applied to the study of molecular motion. The ¹³C chemical shift anisotropy powder patterns from such an experiment for the C₅ alkyl chain carbons in **PH** at 297 K (Fig. 2) are typical of those for static spins. On the other hand, those for the same region of the **CH** complex

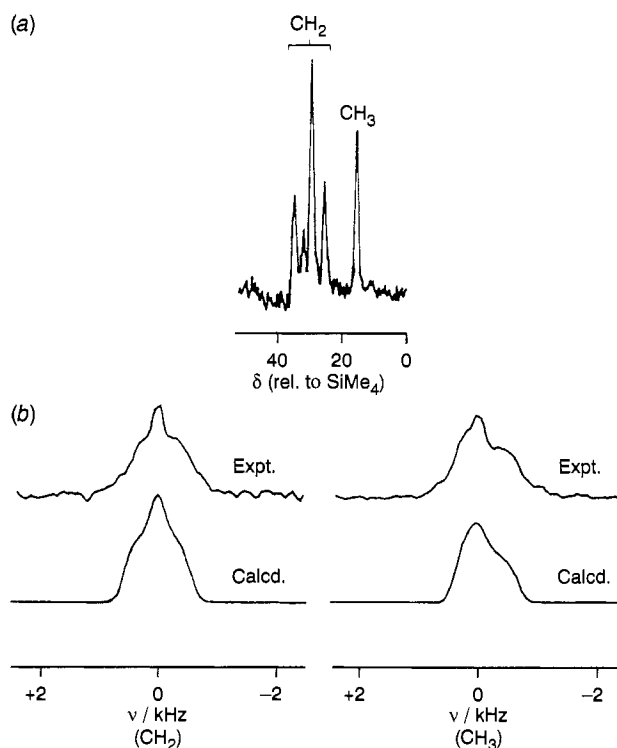


Fig. 2 The results of the 2DCSA NMR recorded for the **PH** complex at 297 K. (a) The projection in *F*2, the dimension containing isotropic ¹³C chemical shifts. (b) Top: a typical slice in *F*1 through C-3 methylene (CH₂) and methyl (CH₃) ¹³C peaks; bottom: simulated spectra. Experimental details: ¹³C frequency was 100.56 MHz and the ¹H frequency was 399.98 MHz. ¹H 90° pulse length, 4 μ s; ¹³C contact pulse; 10 ms; ¹³C 180° pulse length, 8 μ s; recycle delay 3 s. A ¹H decoupling field of 62.5 kHz was used during *t*₁ and *t*₂, 32 *t*₁ points and 2048 *t*₂ points were collected. The sample spinning rate (5 kHz) was controlled to better than ± 5 Hz by the standard Chemagnetics spinning controller. Linebroadening of 200 Hz was applied in *t*₁ prior to Fourier transformation.

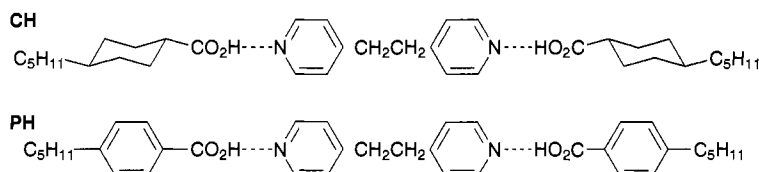


Fig. 1 The two carboxylic acid–pyridyl complexes used in this work. The cyclohexane ring in **CH** has a *trans* conformation.

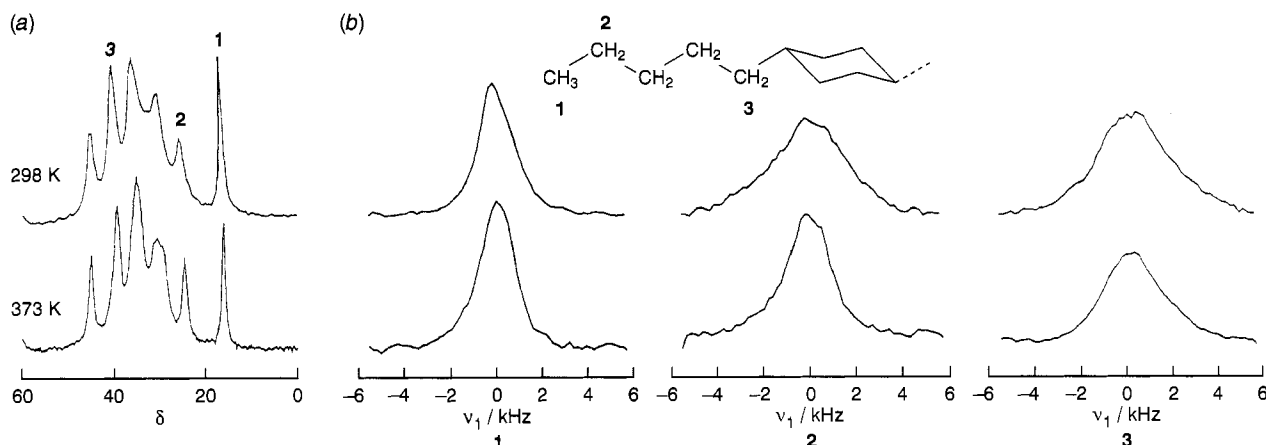


Fig. 3 The results of the 2DCSA NMR experiment recorded for the **CH** complex at 297 K and 373 K for the C_5H_{11} alkyl chain. (a) The projection in F_2 , the dimension containing isotropic ^{13}C chemical shifts. (b) Experimental slices in F_1 through the isotropic ^{13}C peaks at temperatures of 297 and 373 K. ^{13}C frequency, 100.56 MHz; 1H frequency, 399.98 MHz. 1H 90° pulse length, 4.6 μs ; ^{13}C contact pulse, 10 ms; ^{13}C 180° pulse length, 9.2 μs ; recycle delay 3 s. A 1H decoupling field of 48 kHz was used during t_1 and 54 kHz during t_2 . 32 t_1 points and 2048 t_2 points were collected. The sample spinning rate (4.5 kHz) was controlled to better than ± 5 Hz by the standard Chemagnetics spinning controller. Linebroadening of 500 Hz was applied in t_1 prior to Fourier transformation.

(Fig. 3) at the same temperature do not show any of the expected features for a chemical shift anisotropy powder pattern, *i.e.* resolved shoulders and horns. These powder patterns can be simulated by assuming the carbons in the C_5 alkyl chain undergo rotational diffusion about the C–C bonds at rates of the order of 5–10 kHz. The narrowing of the lineshapes at 373 K is due to more rapid motion (*ca.* 20–50 kHz). The same experiment demonstrates that the cyclohexylene ring is rigid at this temperature, which is to be expected, given the 1,4-*trans* substitution of the ring.

A further two-dimensional NMR experiment (WISE)⁷ was performed to confirm these results. This experiment allows the 1H lineshapes arising from 1H – 1H dipolar coupling for 1H spins in different regions of a molecule to be resolved. Partial averaging of the 1H – 1H dipolar interaction by molecular motion alters the width of these lines and allows qualitative assessment of the degree of motion. Such an experiment at 373 K on **PH** revealed that even at this higher temperature the C_5 alkyl chain in **PH** is rigid. This confirmed previous findings for **CH**.

In summary, the **PH** complex is essentially rigid on the NMR timescale up to 363 K, whereupon rapid, 180° flips of the phenylene and pyridyl rings begin, but the C_5 alkyl chain remains rigid. In **CH** diffusive rotational motions of the whole molecule are apparent above 173 K, their rate increasing with temperature.

The rigidity of the alkyl chain in **PH** is presumably due to tight molecular packing in this region of the molecule and is therefore highly likely to be lost on transition to a liquid-crystalline phase. This drastic change of mobility upon transition ensures a large (conformational) entropy change. In turn, this is precisely what is required for the existence of a stable liquid-crystalline phase.⁸ The temperature of a phase change T_{pc} is given by $T_{pc} = \Delta H_{pc} / \Delta S_{pc}$, where ΔH_{pc} and ΔS_{pc} are the enthalpy and entropy of the phase transition respectively. If the temperature of melting to an isotropic phase T_1 is to be distinct from that for the formation of a liquid-crystalline phase T_{lc} *i.e.* the liquid-crystalline phase is to have a separate existence, then T_{lc} must be as low as possible. This is achieved

if ΔS_{lc} is large. For the **CH** complex, where there is already considerable mobility in the solid phase, the change in (conformational) entropy upon transition to a fluid phase can only be relatively small and hence the formation of a liquid-crystalline phase unlikely. In turn, the differences in the molecular mobilities of **CH** and **PH** are likely to be related to differences in intermolecular packing.

We wish to acknowledge the Melville Laboratory Consortium for partial support of this work. M. J. D. wishes to thank the Royal Society and the SERC for their support, and E. C. S. thanks the EPSRC for a studentship.

Received, 1st June 1995; Com. 5/03519H

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† Present address: Department of Chemistry and Biochemistry, The University of Southern Mississippi, Box 5043, Hattiesburg, MS 39406-5043, USA.

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