

An Investigation of the Hydrogen Bonding in Liquid-crystal Systems using Variable-temperature Electronic Spectroscopy

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Variable-temperature electronic spectroscopy on the mesomorphic hydrogen-bonded complex between 4-decyloxy-4'-stilbazole and 2,4-dinitrophenol shows that the higher energy ionic hydrogen-bonded state corresponding to proton transfer is significantly populated through the mesophase, and the mesophase provides an additional stabilisation for this state, by virtue of its microscopic structure; the clearing of the smectic A phase is shown not to be driven by hydrogen-bond rupture.

In recent years there has been an increasing interest in the use of hydrogen bonding for the construction of new liquid crystals. Lehn and coworkers¹ have described the use of complex, but complementary molecules in the formation of mesogenic species, while Kato *et al.*² have shown how mesomorphism can be induced by a single hydrogen bond in mixtures of pyridyl and benzoic acid derivatives. We have also studied induced and enhanced mesomorphism in many pyridyl-benzoic acid adducts³ and have additionally shown that the pyridyl-phenol interaction can still produce complexes that display an induced mesomorphism⁴ despite the generally weaker nature of this hydrogen bond.

In order to learn what possibilities hydrogen bonding can bring to liquid crystals, a number of important questions concerning the nature and role of the hydrogen bond must be addressed. One such fundamental question is to what extent changes in the hydrogen bonding affect the transition temperatures if at all. For example, on clearing, is it the hydrogen-bonded complex that undergoes the transition from mesophase to isotropic liquid, or is clearing driven by a rupture of the hydrogen bond and a dissociation into less mesogenic constituent parts? To answer some of these questions we have initiated variable-temperature infrared and solid-state MAS NMR studies on various mesomorphic pyridyl-phenol derivatives. Here however, we report on the results of some preliminary studies using variable-temperature electronic spectroscopy.

Our study was performed using the one-to-one adduct of 4-decyloxy-4'-stilbazole and 2,4-dinitrophenol (Fig. 1). The homologous series of these complexes show monotropic nematic phases at short alkoxy chain lengths and enantiotropic smectic A phases for longer derivatives. The phase behaviour of these mixtures is very different from that shown by the components; 4-alkoxy-4'-stilbazoles⁵ show a narrow range of smectic B and crystal smectic E phases before clearing typically at about 90 °C; 2,4-dinitrophenol simply melts at 108 °C.

Unlike most of the other hydrogen-bonded systems we have examined, these materials are a golden yellow in colour. This is in stark contrast to the components. Thus, the stilbazoles are cream coloured; $\lambda_{\text{max}}(\text{thf})$ 326 nm, and 2,4-dinitrophenol is a pale yellow; $\lambda_{\text{max}}(\text{thf})$ 295(sh), 340(sh) nm. Since the nature of the hydrogen bond greatly affects atoms in each conjugated chromophore (the nitrogen in the stilbazole and the oxygen of the phenol) both of these parts experience a large shift in the position of their absorption maxima making the complexes ideal for investigations by electronic spectroscopy.

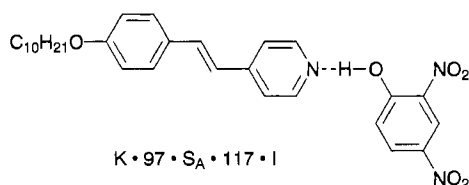


Fig. 1 The hydrogen-bonded complex 4-decyloxy-4'-stilbazole...2,4-dinitrophenol and its mesomorphism

Studies on hydrogen bonding and protonation have been correlated with the aqueous acidities of the components.⁶ It is found that generally for a difference in $\text{p}K_{\text{a}}$ of more than about 4, proton transfer occurs generating the ionic species. The $\Delta\text{p}K_{\text{a}}$ of the components in our complex is between 1 and 2, which places it firmly as a non-ionic, normal hydrogen-bonded situation. Nevertheless, it is useful to consider the electronic spectra of the ionic components; thus, decyloxystilbazolium hydrogen chloride is bright yellow having a $\lambda_{\text{max}}(\text{thf})$ at 368 nm, and potassium 2,4-dinitrophenolate is bright orange, $\lambda_{\text{max}}(\text{thf})$ 363 and 424 nm. It should be realised that comparison of solution with solid-state spectra and the use of aqueous acidities are far from ideal as these may not directly correlate with our observations in the solid state, but they nevertheless provide a useful place from which to start.

The variable-temperature electronic spectroscopy experiment was performed as follows: A drop of a concentrated solution of the adduct in tetrahydrofuran was sandwiched between two glass microscope coverslips. Heating the sample to about 60 °C for 10 min allowed the solvent to evaporate, leaving a thin microcrystalline film of the adduct. Solid-state ¹³C MAS NMR of the adduct obtained from a similar tetrahydrofuran solution showed no solvent to be present in the sample. The use of glass as a substrate limited the spectroscopy to wavelengths >310 nm. The sample was first mounted on a heated stage connected to a Mettler FP90 control processor, and then aligned between fibre-optic cables. The electronic spectra were recorded in transmission, using a Photal-Otsuka Electronics Deuterium Lamp MC-962A, and a Spectromultichannel photodetector, MCPD-100. The sample was heated at rates of 1 or 4 °C min⁻¹ and spectra were recorded every 0.33 or 1 °C respectively. Reproducible spectra were obtained, once the sample had been allowed to return to the original crystalline state. (Note: this material is easily supercooled and a wait of some minutes is usually required before crystallisation occurs.)

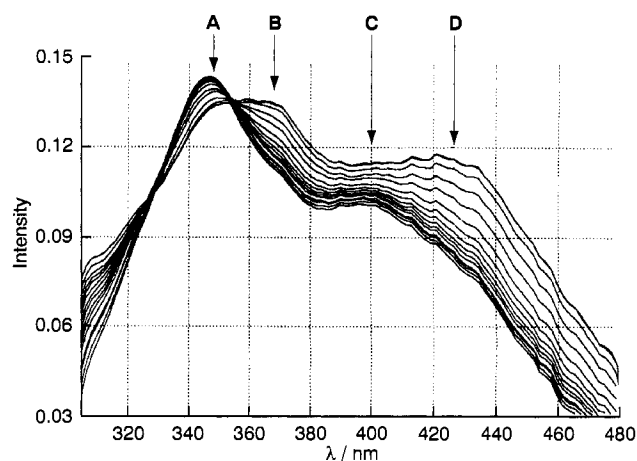


Fig. 2 Electronic spectra of the adduct for temperatures from 90 to 118 °C, as it passes from the crystal through the smectic A phase and into isotropic state

The spectra obtained on a heating run from 90 to 118 °C are shown in Fig. 2. The interpretation of these results starts with the assignment of the spectra. The two peaks in the lower temperature spectrum (see the curve at 90 °C in Fig. 2) at 348 (A) and 400 nm (B) correspond to the stilbazole and phenol respectively in the normal hydrogen-bonded form of the adduct [Fig. 3(a)]. Upon heating, one of the major changes in the spectra is the appearance of two new bands B at 368 nm and D at 426 nm. These are attributed to the ionic form of the adduct [Fig. 3(b)] and correspond to the hydrogen-bonded stilbazolium and phenate ions respectively.

These results are in agreement with an asymmetric double-well potential, where heating the sample gives a thermal population of the higher energy ionic state. Indeed the occurrence of isobestic points at 328 and 335 nm strongly suggests the existence of only two species and thus a single equilibrium. Since both the stilbazole and stilbazolium have similar absorption coefficients we can say a near 50% population of the two states is observed in the smectic A phase from about 114 °C.

On heating the sample, we also notice an increase in absorption at both extremities of the spectrum, and from 121 °C upwards there is a deviation from the normal isobestic

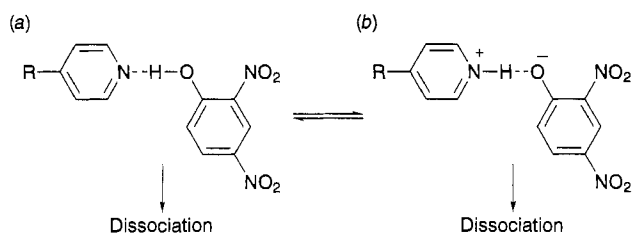


Fig. 3 Proton transfer between (a) the normal state of hydrogen bonding in the adduct and (b) the ionic hydrogen-bonded form

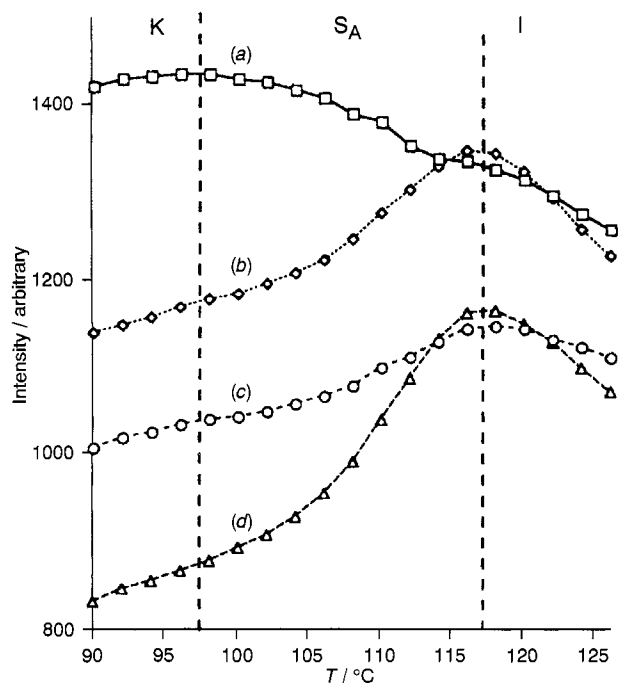


Fig. 4. Variation of the key transitions as a function of temperature: (a) 348 (□), (b) 368 (◇), (c) 400 (○) and (d) 426 nm (△)

behaviour, as spectra no longer cross at these points. From this we can say that below this temperature the spectral broadening is predominantly of thermal origin as the isobestic behaviour effectively rules out dissociation of the complex. Above this temperature, the deviation from ideal behaviour is caused by a breaking of the hydrogen bond and a dissociation into constituent parts. Thus, we can be sure that in this case, rupture of the hydrogen bond does not drive the isotropisation.

To obtain more information it is helpful to plot the intensities of the key transitions, A–D as a function of temperature and hence phase (Fig. 4). Upon isotropisation, there is a general reduction in the intensity of all transitions, which is probably accounted for in part by a broadening of the spectra with contributions from both thermal and dissociation-led effects. However, the transitions B and D corresponding to the ionic state are seen to decrease at a faster rate than the transitions A and C, indicating that the population of the ionic state in the smectic A phase is greater than expected in the case of a simple thermal population. We propose that the environment of the smectic A phase where there is a lamellar microphase separation of alkyl chains from the aryl cores, provides an additional stabilisation of the ionic hydrogen-bonded state, as here the hydrogen bond is predominantly surrounded by polarisable (aryl groups) and polarised (nitro groups) functionalities.

We conclude that in this case we observe a massive increase in the population of the ionic state as we pass through the smectic A phase, and that this is not simply due to a thermal population of the state but that the microscopic environment of the mesophase aids in the stabilisation of the ionic hydrogen bonded state.

We thank Dr David Apperly of the EPSRC Solid State NMR service and the EPSRC for a studentship to D. J. P.

Received, 10th July 1995; Com. 5104482K

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