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On the mesomorphism of hydrogen bonded complexes formed between decyloxystilbazole and phthalic acid

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Preliminary Communications

On the mesomorphism of hydrogen bonded complexes formed between decyloxystilbazole and phthalic acid

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Further investigation of the mesomorphism of hydrogen bonded complexes formed between alkoxystilbazoles and benzenedicarboxylic acids has led to a reinterpretation of the phase behaviour. We have found unexpectedly that the most stable complex is at an equimolar ratio.

While hydrogen bonding has long been recognised as important in certain liquid crystal systems (e.g. the mesomorphism of carbohydrate liquid crystals [1] and of alkoxybenzoic acids [2]), it is only recently that the phenomenon has begun to be studied in a systematic way for the construction of liquid crystalline materials [3]. For example, the authors have described many low molar mass and polymeric systems using stilbazole derivatives as hydrogen bonding acceptors [4].

The basic strategy relies on the formation of a new supramolecular species by the formation of a hydrogen bonding interaction (figure 1). The new species then possesses mesomorphic behaviour distinct from either component.

Following the report [5] of a nematic phase in the putative bent 2:1 complex formed between *trans*-4-decyloxystilbazole, **10-OPhVPy**, and phthalic acid, **PA** (figure 2), we felt it appropriate to study this complex in greater detail as a prelude to an investigation of

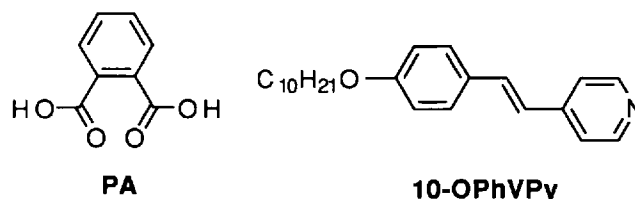


Figure 2. Structures of phthalic acid (**PA**) and decyloxystilbazole (**10-OPhVPy**).

structurally related systems. During the course of this work, it became apparent that the phase behaviour was more complicated than we had first thought, leading us to undertake a more thorough study of this complex, which we now report.

While the initial study had used pyridine as solvent for the preparation of the complex from its components, the present study used tetrahydrofuran (THF) on account of its greater volatility. For both solvents, we found that with **PA** and **10-OPhVPy**, complex formation was not complete after simply removing the solvent, unlike our observations with almost all other systems we have studied. Instead, thermal annealing was required to obtain reproducible mesomorphism. As we have seen no evidence in any other mesomorphic hydrogen bonded

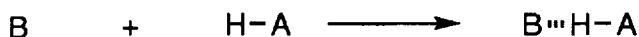


Figure 1. Schematic diagram showing formation of hydrogen bonded systems.

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system for solvent retention in the solid, we do not believe that this is at the heart of the need for thermal annealing, and further experiments are already underway to prove this point. On heating this complex, instead of the reported nematic mesophase, we observed an S_A phase, identified by its characteristic appearance using polarizing optical microscopy, and by measurements using low-angle X-ray scattering, where a sharp reflection was found at an angle corresponding to a layer spacing of 40.0 \AA and a diffuse reflection of 4.5 \AA corresponding to the side-to-side interactions.

Pure PA is non-mesomorphic, while **10-OPhVPy** exhibits both smectic B and crystal E phases, but only over a narrow temperature range [6]. From this we can see that a hydrogen bonding interaction between the two molecules has resulted in the formation of a new mesogenic species which exhibits a mesophase previously unobserved for either of the pure components.

For a complex between a dicarboxylic acid and a stilbazole, one would suppose that a 2:1 complex would result, utilising both carboxyl groups. In order to test this assumption, we constructed a binary phase diagram and found to our initial surprise that the stable complex was formed at an equimolar composition (figure 3). This is shown quite clearly, as the maximum mesophase stability is at this composition.

We have also studied the change in smectic layer spacing with composition and temperature using low-angle X-ray scattering, and as expected for an orthogonal mesophase, we found that the spacing did not alter with temperature. However, unexpectedly we found that the layer spacing changed with composition, across the

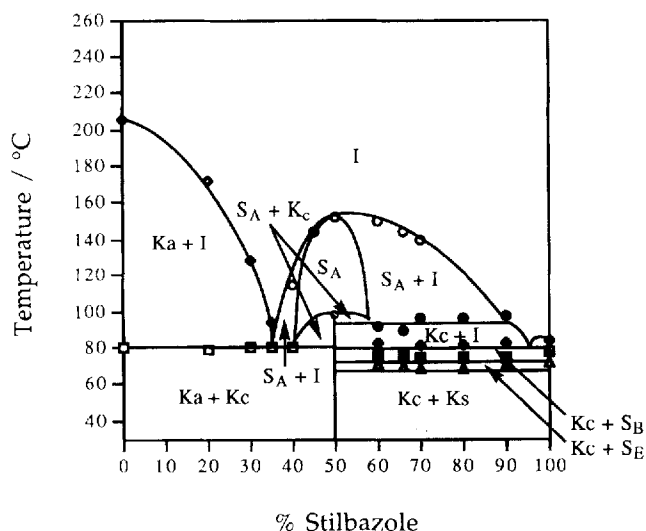


Figure 3. Binary phase diagram of phthalic acid complex: Ks: stilbazole, crystal; Ka: phthalic acid, crystal, Kc: crystal complex.

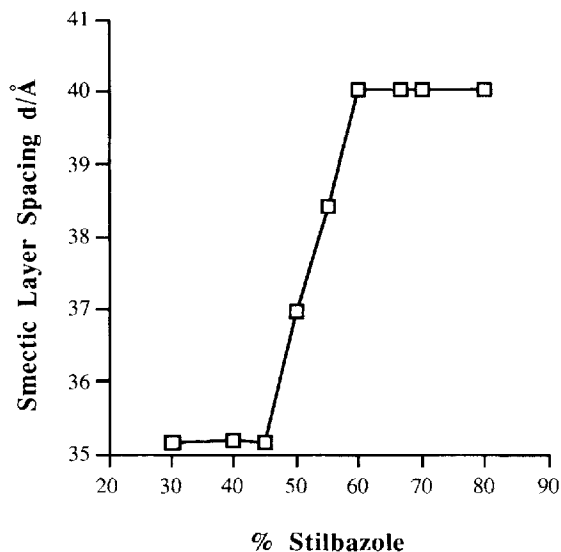


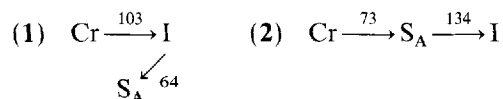
Figure 4. Change in layer spacing $d/\text{\AA}$, with composition at 120°C .

entire range of stability of the smectic state as a single phase, as shown in figure 4. The jump in the layer spacing from 35.2 to 40.0 \AA with increasing concentration of stilbazole indicates a change in the molecular arrangement within the layers with increasing concentration of **10-OPhVPy**. These results are under further investigation.

In trying to understand the stability of the equimolar complex, we have to rationalize the fact that the expected 2:1 complex is not formed, and then differentiate between the two possible equimolar stoichiometries—namely that we have either a 1:1 or a 2:2 complex. That a 2:1 complex is not formed, we attribute to the fact that the pK_a of the second carboxyl proton will change following hydrogen bond formation involving the first (cf. the pK_{a1} and pK_{a2} values of pure phthalic acid are 2.89 and 5.51, respectively), making the formation of the second hydrogen bond unfavourable [7]. Certainly in work carried out by Etter [8], it was found that when 2-aminopyridine, which has two equivalent hydrogen donor and acceptor sites was complexed with certain benzoic acids, a 1:1 complex was preferentially formed. The explanation given for this was the change in the accepting ability of the second ring nitrogen once the first had formed a hydrogen bond. In addition, we can consider the possibility that the second acid proton intramolecularly hydrogen bonds with the first carboxyl group, thus making it unavailable for complexation. Solid state NMR experiments are planned to test this hypothesis.

Distinguishing between the 1:1 and 2:2 complexes is more difficult. In the latter, we would assume that the

vacant carboxyl groups would simply associate into dimers, while in the former case we must assume that the vacant carboxyl groups remained vacant. In order to distinguish between these two possibilities, we have made the complexes between **10-OPhVPy** and monomethyl phthalate (**1**) and benzoic acid (**2**) at equimolar ratios. The phase behaviour is shown below (all temperatures in °C).



The layer spacing for **1** was found to be 33.7 Å and for **2** was found to be 35.0 Å, and both are comparable with the layer spacing for the phthalic acid complex with <45% decyloxystilbazole. This result indicates a similarity in the molecular arrangement within the layers, and is still under investigation.

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