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Thermotropic liquid-crystalline behaviour from mixtures of non-mesogenic molecules

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PRELIMINARY COMMUNICATIONS

Thermotropic liquid-crystalline behaviour from mixtures of non-mesogenic molecules

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A class of non-mesogenic molecules, which as mixtures exhibit monotropic nematic phases, is described.

Examples of binary mixtures of two mesogenic compounds or a mesogenic and a non-mesogenic compound which form new thermotropic liquid-crystalline phases are now well-known [1]. However, to our knowledge, there is only one report of non-mesogenic mixtures that form thermotropic liquid-crystalline phases [2]. Here, we present preliminary results for a class of compounds, 4-cyano-1-(4-alkyl-N-piperidino)benzenes (**I**), in which binary mixtures form monotropic nematic phases. The main experimental tools used to confirm the mesomorphism are differential scanning calorimetry (DSC) and polarized optical microscopy. In the DSC experiments, each sample was heated to 60°C (a temperature higher than the melting points of the individual components), cooled rapidly (*c.* $10°\mathrm{C\,min^{-1}}$) to the desired temperature, and then incubated for 10 min. Reported transition temperatures from DSC measurements correspond to the peak maxima of the thermograms from heating runs ($2°\mathrm{C\,min^{-1}}$).

The **I** series of compounds was synthesized by previously reported methods [3, 4] (see the reaction scheme) and were purified to ≥99 per cent homogeneity according to gas chromatographic analysis. IR, ^{1}H NMR, and ^{13}C NMR spectra are in accord with the structures of the compounds **I**. All of the compounds of structure **I** with $n = 4$–9 are solids at room temperature and, except for the $n = 6$ homologue, are not mesomorphic. The latter exhibits a monotropic nematic phase below 10°C [5]. The analogous phenylcyclohexanes (**II**) are known to exhibit enantiotropic nematic phases [6].

The $n = 4$ and $n = 7$ homologues of general structure **I** undergo solid–isotropic transitions at 42°C and 53°C, respectively (see figure 1). Their binary mixtures form a monotropic nematic phase that transforms slowly to a more stable solid phase. Figure 2(*a*) shows the microscopic texture of a 50/50 wt% mixture of $n = 4$ and $n = 7$ (designated **I**-47) after the sample had been cooled from the isotropic phase to -7°C, which is well below the isotropic–nematic transition temperature (8°C) of this composition. Figure 2 (*b*) shows the texture of the nematic phase of the sample near the clearing point. Both textures include centres with two and four brushes, characteristic of a nematic phase.

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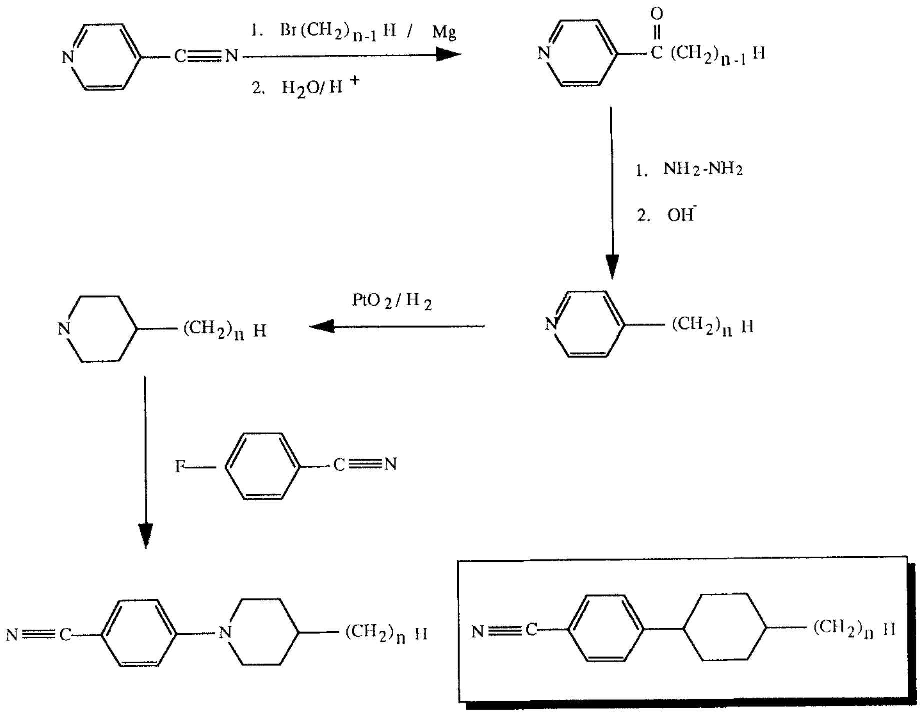

I II

The synthetic pathway for compounds of series I and II.

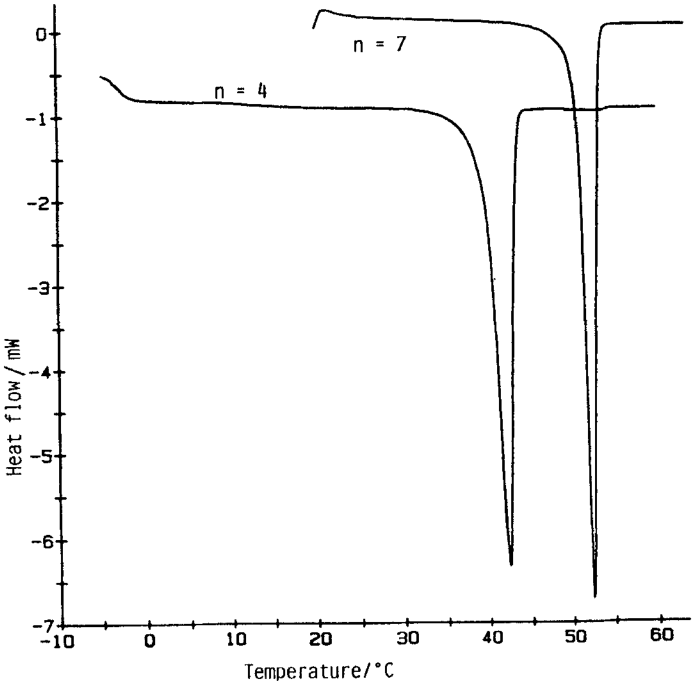

Figure 1. DSC heating thermograms ($2°C\,min^{-1}$) of $n=4$ ($\Delta H = 70\,J\,g^{-1}$) and $n=7$ ($\Delta H = 102\,J\,g^{-1}$) homologues of I.

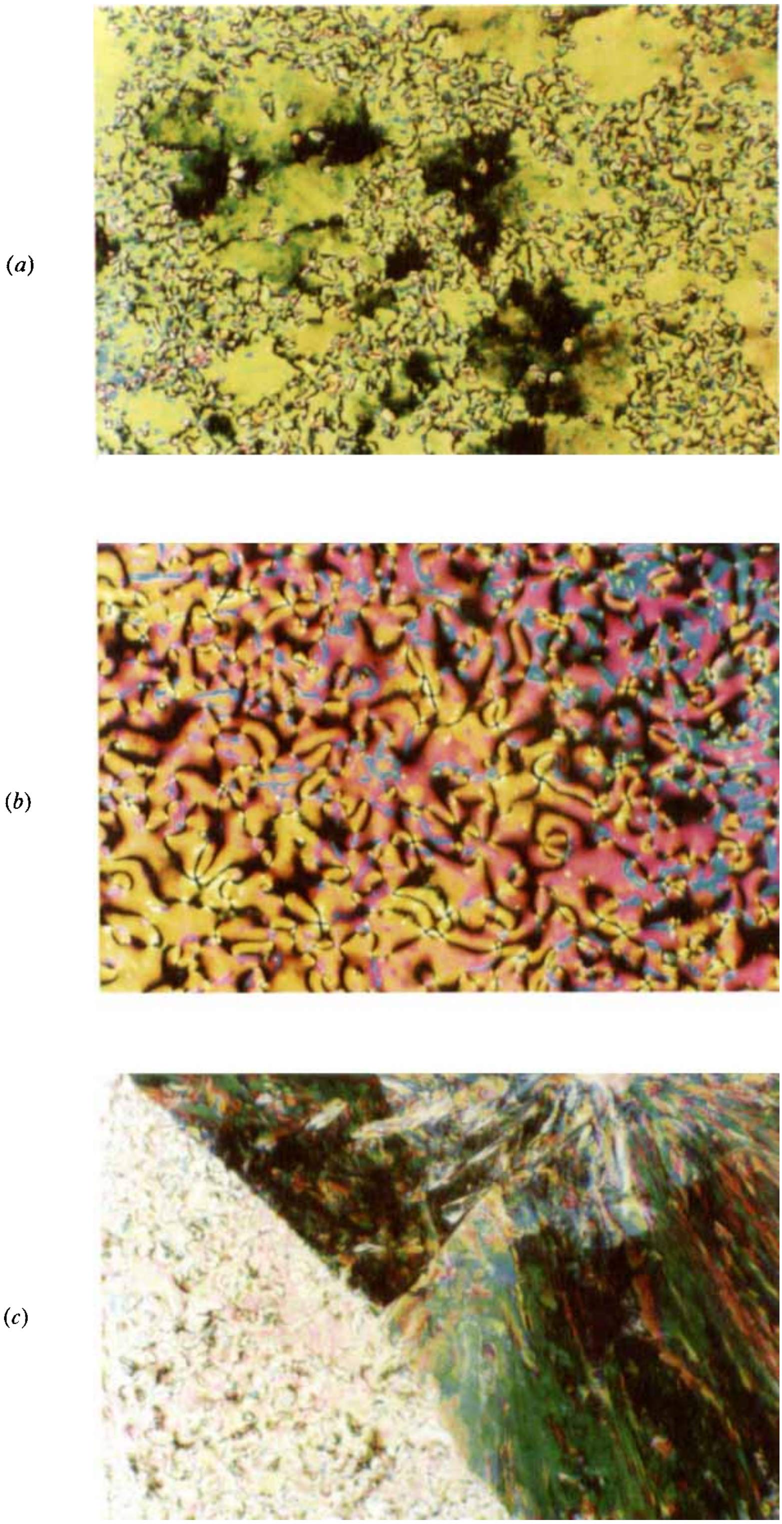

Figure 2. Optical micrographs of 50/50 wt% **I-47** through crossed polarizers (magnification × 510). (*a*) Cooled to −7°C; (*b*) heated to *c.* 8°C; (*c*) cooled to −14°C, showing the coexistence of the nematic phase (lower half), the eutectic solid (centre), and phase separated solid (lighter semi-circle at top). With time, the nematic transforms completely to the eutectic solid.

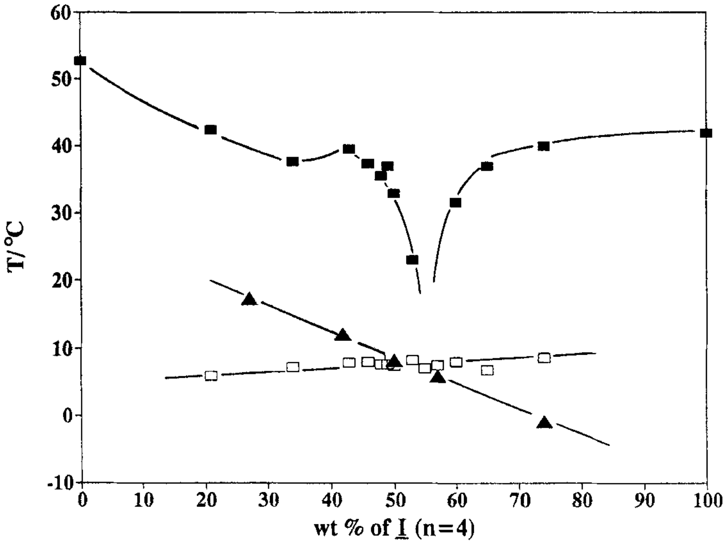

Figure 3. Phase diagram of I-47: □, eutectic melting point; ▲, nematic clearing point; ■, solid–isotropic transition.

The phase diagram of I-47 mixtures is shown in figure 3. Points on the solid to isotropic curves and the eutectic line were taken from DSC heating thermograms after the samples had been cooled to *c.* – 10°C from the isotropic phase and incubated there for 10 min. The nematic clearing curve is from optical microscopy of thin samples sandwiched between two glass plates which had been cooled from their isotropic phase to below the clearing point and then heated. A eutectic can be estimated at a composition of 55/45 wt% for $n=4$. A typical thermogram from slow cooling (1°C min^{-1}) and heating (2°C min^{-1}) of a 56/44 wt% mixture is shown in figure 4 (*a*). The reversible transition at 8°C is due to an isotropic–nematic transformation (optical microscopy). When this sample was incubated at $\leqslant -10$°C for a relatively long period of time (10–60 min, depending on the incubation temperature) the heating thermogram contained a large endotherm at 7·0°C, a small nematic–isotropic endotherm at *c.* 11°C, and a broad endotherm from melting of a small fraction of the sample that crystallized as, presumably, one neat component during the cooling to incubation to heating cycle (see figures 2 (*c*) and 4 (*b*). Due to this phase separation, the nematic phase is enriched in the $n=4$ component and its clearing point is observed at a higher temperature than expected. Partial phase separation was not present in the thin samples used to establish the nematic–isotropic temperature line in figure 3. The large endotherm at 7°C is from melting of the eutectic solid which emanates from the supercooled nematic phase. The birefringent optical patterns of the monotropic nematic phase can be distorted by tapping on the glass plates sandwiching the sample. In composition ranges far from the eutectic, tapping accelerates solidification of the nematic phase. Transition enthalpies from heating thermograms are consistent with these observations. The measured heat from the eutectic solid–nematic transitions of a eutectic composition sample of I-47 is *c.* 38 J g^{-1}, but varies somewhat between runs due to uncontrollable surface catalysed partial solidification; that of the nematic–isotropic transition is *c.* 2 J g^{-1}.

Our primary interest in this work is to deduce the effect of mesophase order on the dynamics of the amino-phenyl excited state bond rotation (i.e. twisted intramolecular charge transfer states [7]) of components of structure I. Future studies will be directed

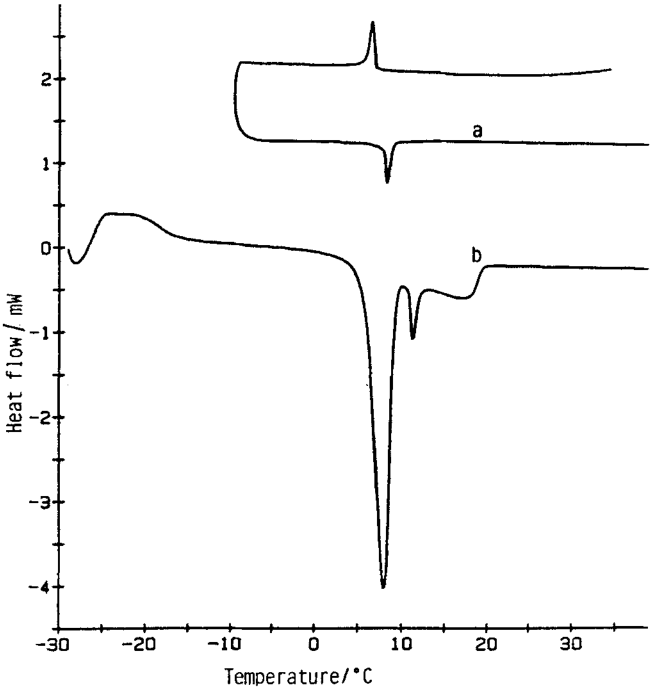

Figure 4. DSC thermograms of 56/44 wt% I-47; (*a*) cooling (1°C min^{-1}) and heating (2°C min^{-1}). (*b*) Heating (2°C min^{-1}) after the sample had been incubated at −30°C for 10 min.

toward that goal (using neat samples of compounds I and its solutions in enantiotropic liquid crystals) as well as understanding why only mixtures of the non-mesogenic compounds I yield a nematic phase when many pure homologues of structure II form enantiotropic nematic phases. The exchange of a C–H group for nitrogen must increase the conformational lability of the saturated ring and may allow stronger dipolar interactions between adjacent molecules. Clearly, subtle balancing of these and other forces dictate which phases can form and their relative stability. It is reasonable to assume that judicious changes in the structure of compounds I may lead to mixtures with enantiotropic phases and that other classes of molecules may behave like these compounds I. Not surprisingly, we have noted that some ternary mixtures of compounds I also form mesophases.

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