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Liquid Crystals

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Liquid crystals comprising hydrogen-bonded organic acids
II. Heterodimers in mixed mesogenic acids

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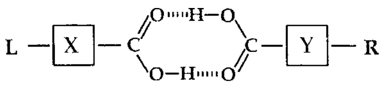
Nematic mesophase stability, as determined by the excess mesophase range in mixtures of organic acids (supramesogen derived from *para*-substituted phenyl, 4-substituted cyclohexane and bicyclo[2.2.2]octane carboxylic acids), is increased in mixtures of disparate species—mixed acids with differing substituent sizes (different supramesogen tail lengths) and different acid types (aliphatic and aromatic supramesogen cores). These trends enable one to estimate contributions to mesophase stability stemming from tail disparity and core differences, contributions that appear to carry over into analogous covalent mesogens. IR measurements of solid mixtures of acids suggest that the heterodimer acids population dominates, and deuterium NMR studies of labelled acids in the nematic phase emphasize the dynamic character of this class of supramesogens: dimer lifetimes are shorter than microseconds.

1. Introduction

The hydrogen bonds (H-bonds) in cyclic dimers of organic acids promote calamitic liquid crystallinity because of the extended, retilinear geometry associated with the 'supramesogen' (i). In part I of this study, Kang and Samulski considered H-bonded supramesogens comprising non-mesogenic precursor acids [1]. In part I of this study the mesophase stability was shown to be sensitive to the mesogen tail lengths in binary mixtures of a variety of non-mesogenic, *para*-substituted benzoic acids ($X = Y =$ phenyl). The findings suggested that a hetero-dimer, a cyclic, H-bonded supramesogen comprising the two different acids ($L \neq R = -C_nH_{2n+1}$), played an important role in the mesophases exhibited by the binary mixtures. Here we extend those studies to mixtures of (mesogenic) H-bonded acids having the same length tails but with different chemical constitutions, and to mixtures of different acids ($X \neq Y$) derived from aromatic and aliphatic moieties. For the latter we consider the mesophase behaviour of binary mixtures of three classes of organic acids in this study: *para*-substituted phenyl, 4-substituted cyclohexane and bicyclo[2.2.2]octane carboxylic acids.



(*i*)

Herein our goal is to examine: (1) the role of substituent differences in mixtures of acids with the same tail length but different chemical constitutions (e.g. 'five-atom tails' in aromatic acids with $L \neq R$, obtained by mixing *para*-substituted benzoic acids having tails $-C_5H_{11}$, $-OC_4H_9$, and $-NH(C_4H_9)$; (2) effects when the acid core (X, Y) is varied (e.g. aromatic versus aliphatic) with both equivalent ($L = R$) and non-equivalent ($L \neq R$) tail lengths. IR studies of mixtures of aromatic and aliphatic ring acids suggest that the heterodimer plays a dominant role in stabilizing the mesophase in these mixtures. Deuterium NMR experiments give additional insights into the dynamical nature of the H-bonded dimer mesogens [2, 3].

2. Experimental

All compounds were obtained from Aldrich Chemical Co., and were recrystallized from acetone and acetone/methanol cosolvents. Binary mixtures of all materials examined in the present study were prepared by simple mechanical stirring of the components at a temperature above the melting point. A polarizing microscope (Nikon Microphot FX) equipped with a Linkam hot stage was

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used for visual observations. DSC measurements were performed on a Seiko DSC 120; a heating rate of 10°C min^{-1} and a cooling rate of 5 or 10°C min^{-1} were used.

Mid-infrared spectra were recorded on a Bio-Rad FTS-6000 interferometer with a cryogenic MCT detector; the sample chamber was equipped with a Grase-Specac heatable cell with an automatic temperature controller. The accuracy of temperature measurements was approximately ±0.1°C. All the spectra were recorded at a resolution of 4 cm^{-1}. The sample was sandwiched between two KBr plates located in the electrical heating jacket connected to a temperature controller.

^{2}H NMR spectra of deuterium-exchanged acids of *p*-pentylbenzoic acid-d (5BA-d_1), *t*-4-pentylcyclohexane-1-carboxylic acid-d (5CHA-d_1), and the eqimolar mixture of 5BA-d_1 : 5CHA-d_1 were measured within the nematic temperature ranges, 368–392 K, 320–369 K, and 310–383 K, respectively, in steps of 5 degrees. In order to obtain information on the motional freedom of acid molecules in the nematic phase, spectra of deutrated benzoic acid-d_5 (BA-d_5) dissolved (10 mol%) in these three nematogenic acids were recorded within the nematic temperature ranges. The NMR measurements were carried out on a Bruker 500 MHz spectrometer.

3. Results and discussion

3.1. *Thermodynamic studies*

In figure 1 we show the nematic mesophase ranges in equimolar binary mixtures of three pairs of organic acids with 'five-atom' tails denoted left (*L*) and right (*R*) for each acid in the pair illustrated in (i). The observed Cr–N and N–I transitions for the binary mixtures ($L \neq R$, entries b, d, and f) are intermediate between those of the pure acids ($L = R$, entries a, c, and e). That is, no unusual (de-)stabilizing influences are exhibited by the mixtures when hetero atoms units (–O– and –NH– in 4OBA and 4NBA, respectively) replace a $-CH_2-$ unit in 5BA to construct equivalent length *para*-substituted benzoic acid tails. In part I of this study, mixtures of (non-mesogenic) benzoic acids with different length tails showed increased nematic phase stability as the disparity in tail lengths increased. The same phenomenon is observed for the three types of benzoic acid tails (e.g. in binary mixtures of the five-atom tail acids 5BA, 4OBA and 4NBA with the *n*OBA homologous series). We illustrate this using the excess nematic mesophase stability, $N_{\mathrm{ex}} = [N_{mn} - (N_{mm} + N_{nn})/2]$, which is obtained by reducing the observed nematic range for a given binary mixture containing different tail lengths, N_{mn} (°C), by the average nematic range of the pure components, N_{mm} and N_{nn} (°C). N_{ex} gives a quantitative measure of the relative stability of mesophases as a function of the tail length disparity for acids in binary mixtures.

Figure 2 shows the excess nematic thermal stability of equimolar mixtures of the 'host' acid, *n*OBA, with 'guest' acids, (*a*) 5BA, (*b*) 4OBA and (*c*) 4NBA, respectively. The data is qualitatively the same for all three guest acids: N_{ex} increases as the tail length of the *n*OBA host decreases or increases relative to the 5-atom tail of each respective guest acid. When the guest and host acid tail lengths are equivalent (i.e. in the equimolar mixtures 5BA:4OBA, 4OBA:4OBA and 4NBA:4OBA), the nematic range is smallest. For all three guest acids in *n*OBA hosts, the mesophase range increases monotonically for $n > 4$ and $n < 4$. Neither 1OBA nor 2OBA exhibit mesophases, hence mixtures with these acids do not attenuate the value of N_{ex} ($N_{mm} = 0$). This may partially account for the observation that binary mixtures with 1OBA as the host show the broadest mesophases.

Figure 3 shows the effect of mixing the acid core units *X* and *Y*, that is, mixing aromatic benzoic acids with

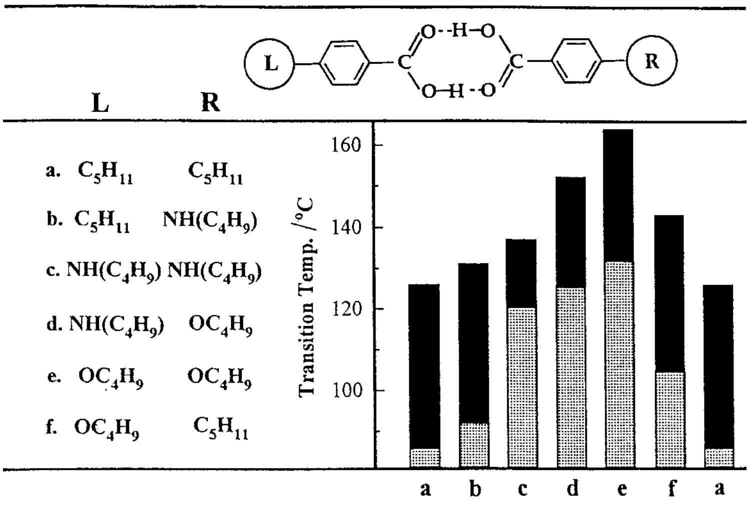


Figure 1. Transition temperatures and nematic mesophase ranges (dark solid shading) for pure ($L = R$; a, c, e) and 1 : 1 binary mixtures ($L \neq R$; b, d, f) of dimer mesogens with 5-atom tails *L* and *R*, where *L* and *R* represent $-C_5H_{11}$, $-NH(C_4H_9)$ or $-OC_4H_9$.

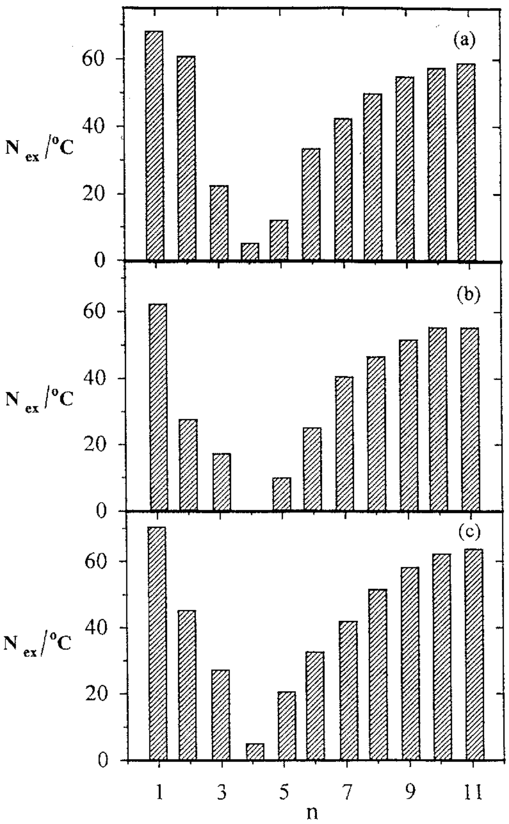


Figure 2. The excess nematic mesophase stability, N_{ex}, for three 'guest' acids 5BA, 4OBA, and 4NBA, plotted for equimolar binary mixtures wherein the 'host' acids are the homologous series *n*OBA. The N_{ex} is shown versus the number of carbon atoms, *n*, in the *n*OBA tail.

cyclic aliphatic acids at constant tail length. In five-atom tails ($L = R = -C_5H_{11}$), the mixing of acids having aromatic phenylene cores with acids based on aliphatic cores (cyclohexane and bicyclo[2.2.2]octane) broadens the mesophase range relative to that of the pure acids. (The 4-pentylbicyclo[2.2.2]octane-1-carboxylic acid is nonmesogenic; entry e figure 3.)

In figure 4 we illustrate the behaviour when *n*OBA host acids ($n = 1$–8) are mixed with guests derived from aliphatic pentyl-substituted acids (*t*-4-pentylcyclohexane-1-carboxylic acid (5CHA) and 4-pentylbicyclo[2.2.2]-octane-1-carboxylic acid (5BOA), figures 4(*a*) and 4(*b*) respectively, and with the aromatic acid *p*-pentylbenzoic acid 5BA, figure 4(*c*). In the latter mixtures, N_{ex} reflects the enhancement (for $n \neq 5$) derived from unequal tail lengths. In figures 4(*a*) and 4(*b*), the increased N_{ex} consists of two contributions, unequal cores in conjunction with unequal tails. In figures 4(*a*) and 4(*b*) we show with the horizontal bars the contribution from tail disparity derived from figure 4(*c*); the fraction of N_{ex} over and above the contribution from tail disparity is essentially constant, independent of host tail length for $n > 1$, and we attribute this to the excess mesophase range associated with mixing inequivalent cores.

Similar trends are apparent in structurally analogous covalent mesogens. Figure 5 shows the effect of mixing the aliphatic/aromatic character of core rings in covalent hydroquinone-*bis*-(4-ethylbenzoate or 4-cyclohexanecarboxylate) mesogens [4] at fixed tail length $L = R = -C_2H_5$. The asymmetric mesogen with an aromatic ring on one end and an aliphatic cyclohexane on the other

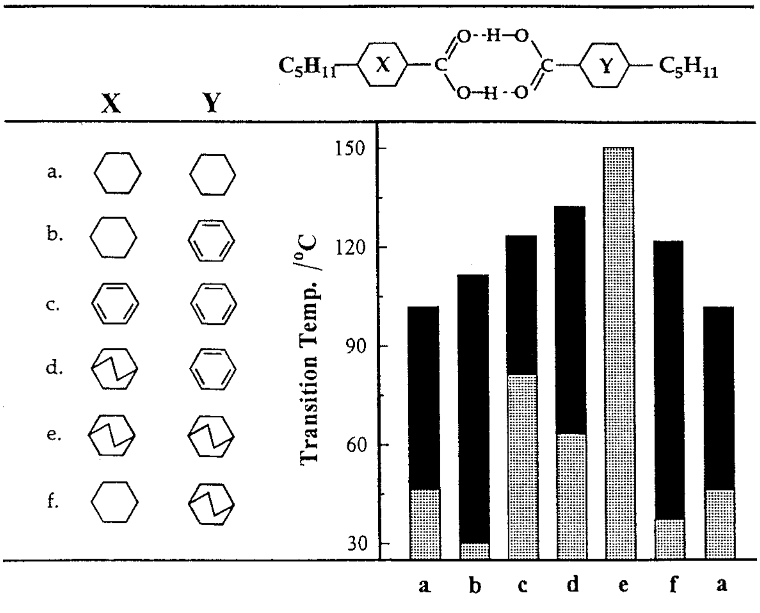


Figure 3. Transition temperatures and nematic mesophase ranges (dark solid shading) for pure and 1 : 1 binary mixtures of dimer mesogens with equivalent 5-atom tails $L = R = C_5H_{11}$ as a function of acid core structures.

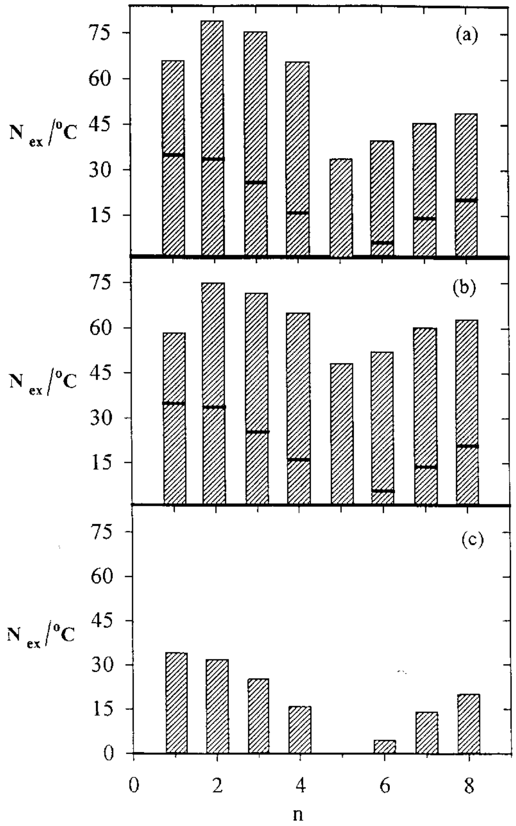


Figure 4. Excess nematic ranges for equimolar binary mixtures of mesogenic acids of: (*a*) *t*-4-pentylcyclohexane-1-carboxylic acid (5CHA) with *n*OBA hosts; (*b*) 4-pentylbicyclo-[2.2.2]octane-1-carboxylic acid (5BOA) with *n*OBA hosts; (*c*) *p*-pentylbenzoic acid (5BA) with *n*OBA hosts.

(entry b) shows a broadened mesophase range relative to the symmetric mesogens (entries a and c). Even greater mesophase stability is imparted to the covalent three-ring mesogen when the aromatic/aliphatic core-ring asymmetry is present with unequal tail lengths (entry d). The symmetric $L=R=-C_4H_9$ cyclohexyl mesogen—hydroquinone-*bis*-(4-butylbenzoate) or (4-cyclohexane-carboxylate), H4C—is shown to help gauge the significance of the increased stability of the asymmetric mesogen.

3.2. *Infra-red studies*

The fact that the observed mesophase trends in the covalent mesogen parallel those in binary mixtures of (asymmetric) acids, suggests that in the latter the H-bonded heterodimer could play a dominant role. If purely statistical associations accounted for the observations in mixed acids, we would anticipate 25 mol % of each of the homodimers to be occluded when the binary mixtures solidify. We explore the role of hetero- versus homo-dimer formation in mixtures of H-bonded acids using IR spectroscopy. IR studies focused on the carbonyl stretching region (1600–1800 cm^{-1}) wherein the signature of the cyclic dimer is an infrared band at ~ 1685 cm^{-1} [5]. The free C=O stretch of the free 'monomer' has a characteristic frequency of ~ 1750 cm^{-1} [6]. In figure 6 we show the temperature dependence of the carbonyl stretch region for 5BA. In figure 6 (*a*) the transition from crystal to nematic is signified by an abrupt and qualitative change from a two-component absorption band (with components at 1682.0 and 1699.0 cm^{-1}) in the Cr phase, to a single absorption (1692 cm^{-1}) in the nematic. The band at ~ 1610 cm^{-1} is a characteristic band due to phenyl ring stretching. With increasing temperature there is a continuous evolution of the spectra through the N–I transition with a slowly growing shoulder (~ 1735 cm^{-1}) characteristic of free acid monomer, figure 6 (*b*). There is no significant increase in the monomer concentration at the N–I transition as reported earlier by Kato *et al.* [7]. Note

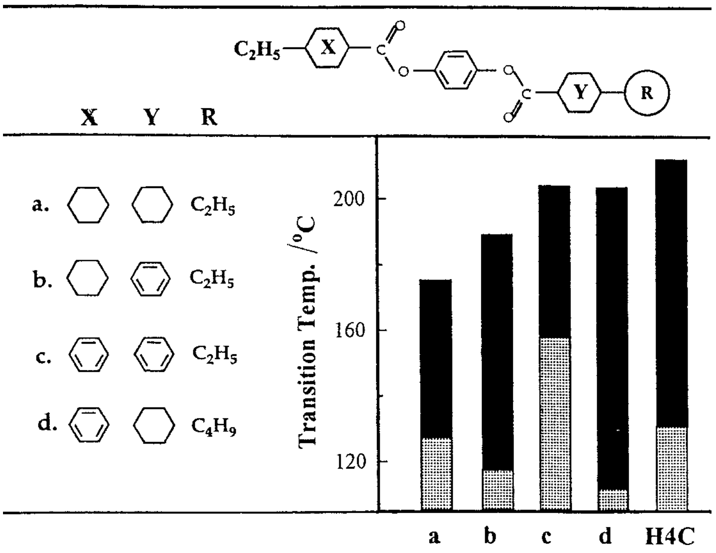


Figure 5. Transition temperatures and nematic mesophase ranges for covalent hydroquinone-bis(4-ethylbenzoate or 4-cyclohexanecarboxylate), with equivalent 2-atom tails $L=R=-C_2H_5$ and variable outer ring (core) structures (a–c) and core plus tail inequivalence (d, $L=-C_2H_5$, $R=-C_4H_9$); H4C is the symmetric mesogen hydroquinone-*bis*-(4-butylbenzoate or 4-cyclohexanecarboxylate).

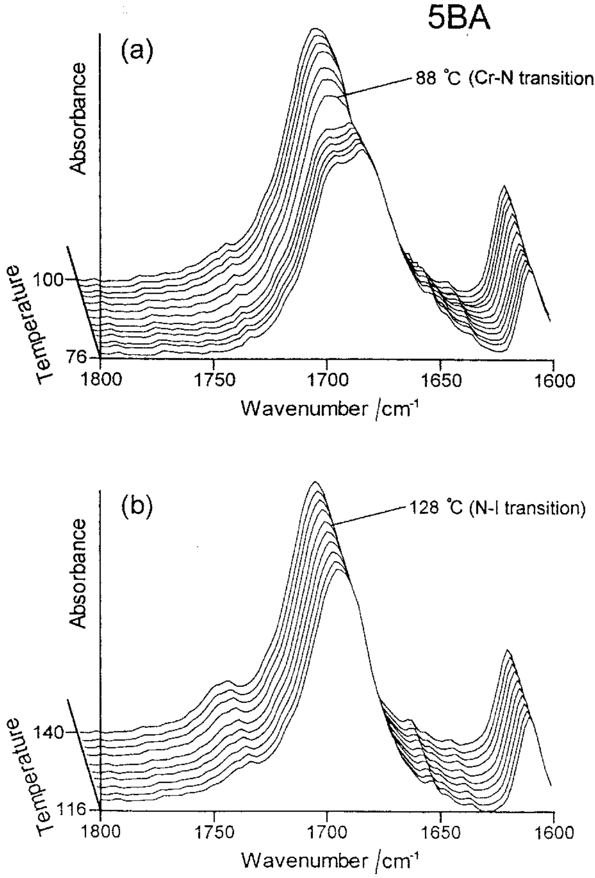


Figure 6. IR spectra of *p*-pentylbenzoic acid (5BA) versus temperature. (*a*) Spectra spanning the Cr–N transition (88°C); (*b*) spectra spanning the N–I transition (128° C).

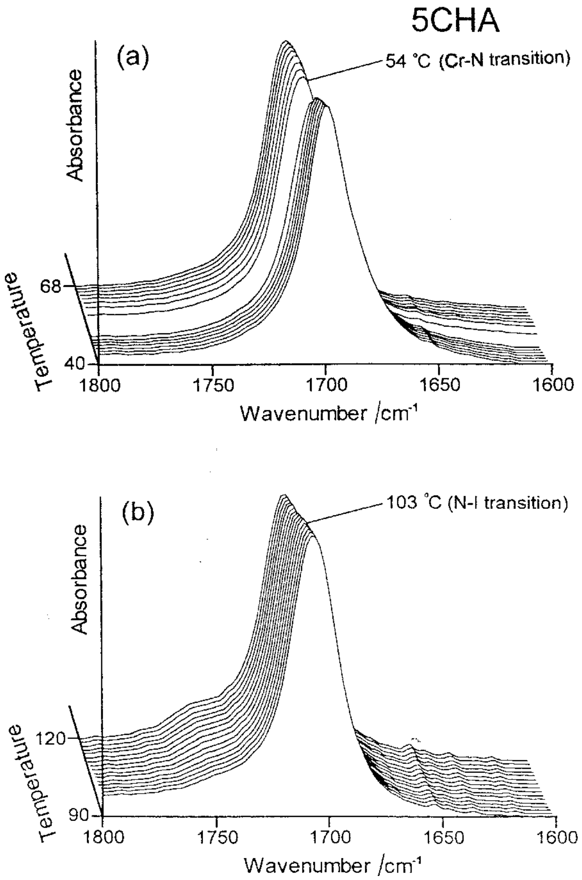


Figure 7. IR spectra of *t*-4-pentylcyclohexane-1-carboxylic acid (5CHA) versus temperature. (*a*) Spectra spanning the Cr–N transition (54°C); (*b*) spectra spanning the N–I transition (103°C).

however, the temperature range of 6OBA considered by the latter group was considerably higher, with $T_{\mathrm{NI}} = 153^{\circ}\mathrm{C}$.

Figure 7 shows the analogous behaviour of the aliphatic acid 5CHA. At the Cr–N transition there is an abrupt change in the carbonyl stretch (from 1697.5 cm^{-1} to 1703.0 cm^{-1}); there is no perceptible change at the N–I transition. At these lower temperatures there is only a modest amount of free monomer acid in evidence (i.e. the low intensity shoulder at $\sim$1735 cm^{-1}). We do not observe as much free acid for 5BA in the fluid phases as reported earlier by Kato [7] *et al.* for 6OBA. However, the nematic range for 6OBA (106–153°C) is considerably higher than that for 5BA (88–128°C) and the equilibria should shift to the free acid with increasing temperature.

In the equimolar binary mixture of 5BA:5CHA, the bandshape in the solid is a single broad Gaussian and the shift in the carbonyl stretch at the Cr–I transition, figure 8 (*a*), is less pronounced in the mixture than in the pure component acids, see figures 6 (*a*) and 7 (*a*). At higher temperatures, figure 8 (*b*), there are only marginal changes in the spectra across the N–I transition.

In figure 9 we consider in more detail the carbonyl stretch band in the solid state. Figure 9 (*a*) contrasts the bandshapes of the pure components 5BA and 5CHA with observations for the equimolar mixture. If the pure components 5BA and 5CHA were present in the solid state of the equimolar mixture, we would anticipate a spectrum corresponding to that shown in figure 8 (*b*). The 'double pellet' spectrum is obtained by placing KBr pellets of the pure components in series in the IR beam. This 'double pellet' spectrum can be decomposed—dotted lines in figure 9 (*b*), see table 1—into contributions from 5CHA (1697.5 cm^{-1}) and a two-component band for 5BA (5BA1 at 1682.0 cm^{-1} and 5BA2 at 1699.0 cm^{-1}). These ideal components can then be used to analyse the experimental spectrum of the equimolar 5BA:5CHA solid, figure 9 (*c*). In figure 9 (*c*) the experimental spectrum is decomposed into contributions from the heterodimer and the pure components (table 2). This analysis suggests that contributions from the pure components constitute less than 10% of the experimental bandshape. That is, the pure components are present in less than the statistically

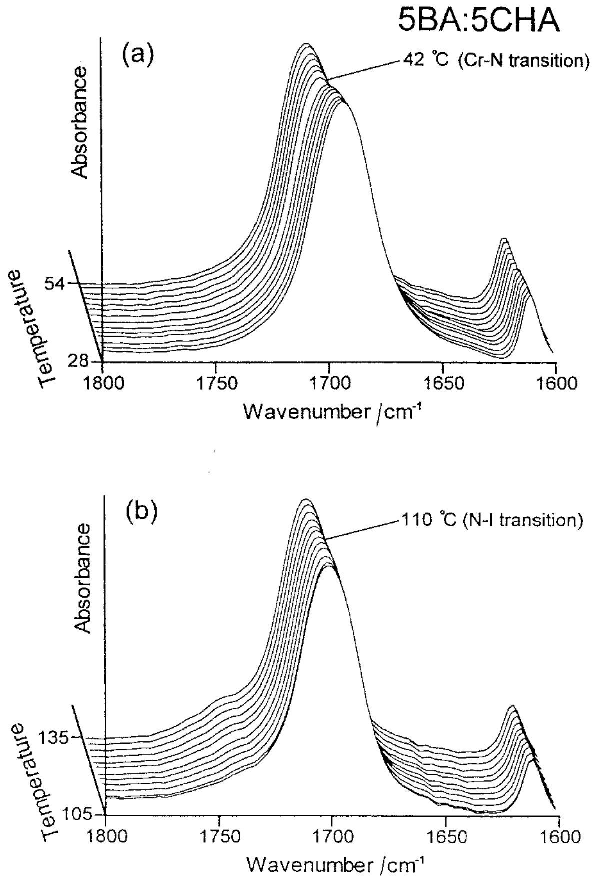


Figure 8. IR spectra of the binary 1 : 1 mixture *t*-4-pentylcyclohexane-1-carboxylic acid (5CHA) and *p*-pentylbenzoic acid (5BA) versus temperature. (*a*) Spectra spanning the Cr–N transition (42°C); (*b*) spectra spanning the N–I transition (110°C).

anticipated contribution (25 mol % each) implying that a heterodimer (ii) comprising both 5BA and 5CHA

(*ii*)

is the dominant species in the solid equimolar mixture of acids.

3.3. *NMR studies*

The IR studies of the solid mixture of acids suggest a static picture of the supramesogens such as the cyclic dimer depicted in (ii). The early deuterium NMR work by Rowell *et al.* [2] emphasized the dynamic nature of the mesophases consisting of H-bonded acids. We re-examined this aspect of supramesogens using deuterium NMR for two kinds of labels: (1) simple deuterium-exchanged acid protons (three mesophases: neat *p*-pentylbenzoic acid-d_1 (5BA-d_1), neat *trans*-4-pentylcyclohexane-1-carboxylic acid-d_1 (5CHA-d_1), and the eqimolar mixture of 5BA-d_1 : 5CHA-d_1); and (2) a covalent labelled 'probe molecule' benzoic acid-d_5 (BA-d_5) in the three unlabelled mesophases.

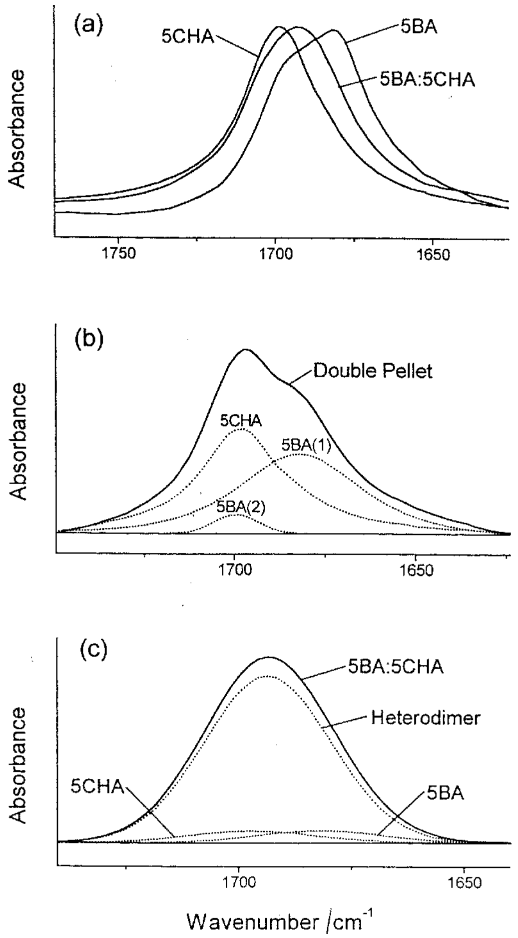


Figure 9. Room temperature IR spectra of the pure component acids and binary mixture of *t*-4-pentylcyclohexane-1-carboxylic acid (5CHA) and *p*-pentylbenzoic acid (5BA) in the solid (Cr) phase (*a*). In (*b*) the experimental (double pellet) spectrum of an ideal mixture of separate non-interacting acids 5BA and 5CHA is decomposed into Gaussian absorption. (*c*) Shows a similar decomposition of the 5BA : 5CHA equimolar experimental spectrum into contributions from the pure acids and the heterodimer comprising a cyclic H-bonded pair of both components.

Table 1. Curve fitting parameters of carbonyl peaks of *p*-pentylbenzoic acid at 25°C.

Peak centre /cm^{-1}	Fraction of area/%	Width at half height/cm^{-1}
1699.6	15.1	15.0
1682.0	84.9	30.0

Figure 10 shows sample deuterium NMR spectra of each type of label for equimolar mixtures of 5BA : 5CHA at the same reduced temperature ($T_{red} = T/T_{NI} \approx 0.90$).

Table 2. Curve fitting parameters of carbonyl peak of pure acids, *p*-pentylbenzoic acid (5BA) and *trans*-4-pentylcyclohexane carboxylic acid (5CHA), and their equimolar mixture at 25°C.

Sample	Peak centre /cm^{-1}	Fraction of area /%	Width of half height/cm^{-1}
5BA	1682.0	10.0	30.0
5CHA	1697.2	12.5	24.0
5BA : 5CHA	1693.5	77.5	36.0

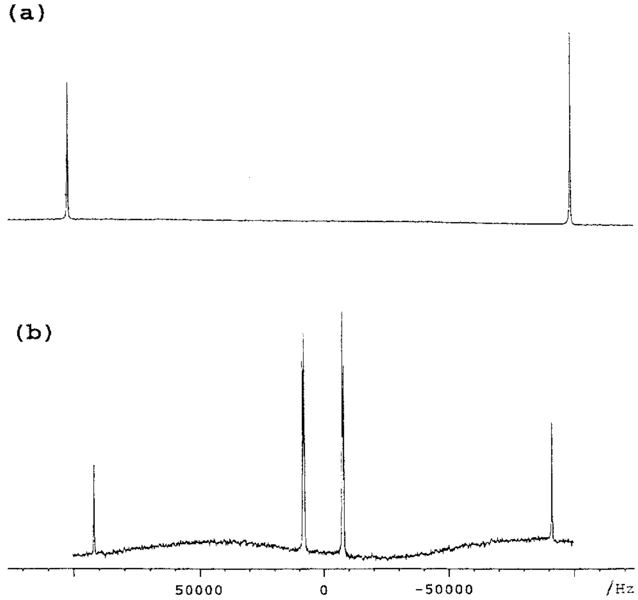


Figure 10. ^{2}H NMR spectra of (*a*) the eqimolar mixture of 5BA-d$_1$: 5CHA-d$_1$ and (*b*) the BA-d$_5$ dissolved in the eqimolar mixture of 5BA : 5CHA at 67°C.

The two sets of quadrupolar splittings with intensity ratios 4 : 1 for the BA-d$_5$ probe, figure 10 (*b*), stem from the two (geometrically) inequivalent sets of deuterons, the four *ortho* and *meta* deuterons and the single *para* deuteron. In both spectra in figure 10, the quadrupolar splittings indicate a 'single species' characterized by well-defined quadrupolar splitting(s) $\Delta\nu$. Each $\Delta\nu$ value is related to the orientational order of the local principal electric field gradient (efg), along the –O–D---O– H-bond for the deuterium exchanged acids 5BA-d$_1$: 5CHA-d$_1$ or the C–D covalent bonds in the probe BA-d$_5$, respectively. This splitting is defined by

$$\Delta\nu = (3\mathrm{eq}Q/2\pi h)S_{\mathrm{bond}}P_2(\cos\Omega) \qquad (1)$$

where the quadrupole coupling constant (3eq$Q/2\pi h$) is ~ 184 kHz for the –O–D---O– H-bond and ~ 193 kHz for the aromatic C–D [2]. $P_2(\cos\Omega) = 3(\cos^2\Omega - 1)/2$ where Ω is the angle between the nematic director and the magnetic field. Equation (1) together with knowledge of the internal geometry—the orientation of the bond efg with respect to the 'symmetry axis' of the supramesogen (or probe)—can be used to estimate the degree of supramolecular orientational order in the nematic phases of H-bonded acids.

In figure 11 (*a*) the $\Delta\nu$ values in the nematic phases of the deuterium exchanged pure acids and the equimolar mixture are shown versus reduced temperature. The $\Delta\nu$ values for pure 5CHA-d$_1$ are about a factor of two smaller than those observed for pure 5BA-d$_1$ (and the equimolar mixture of 5BA : 5CHA). This difference is anticipated, as aliphatic mesogens are known to have negative diamagnetic anisotropy ($\Delta\chi < 0$) and as a result, the director aligns normal to the magnetic field ($\Omega = 90°$ and $P_2(\cos\Omega) = -0.5$); the aromatic mesogens have $\Delta\chi > 0$ ($\Omega = 0°$ and $P_2(\cos\Omega) = 1.0$). It would appear that the aromatic character of the susceptibility in the 5BA : 5CHA mixture dominates, so that for the mixture, $\Delta\chi > 0$ and the $\Delta\nu$ values are similar to those found in the pure 5BA-d$_1$ where $\Omega = 0°$. Similar findings are observed when the deuterated probe BA-d$_5$ is used to ascertain the orientational order, figure 11 (*b*).

We examined the behaviour of the (covalent) probe BA-d$_5$ in the 5BA : 5CHA mixture, together with the behaviour of the labile acid deuteron in the mixture of acids 5BA-d$_1$: 5CHA-d$_1$, as the latter would appear to

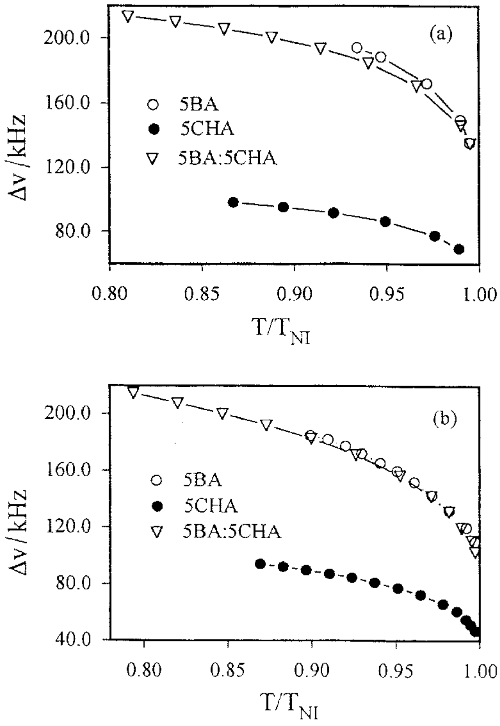
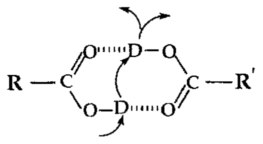
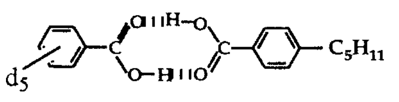


Figure 11. Temperature dependence of deuterium quadrupolar splittings (Hz) in the nematic temperature ranges. (*a*) Deuterium exchanged acids for neat acids and 5BA-d$_1$: 5CHA-d$_1$ mixture; (*b*) 10 mol % BA-d$_5$ dissolved in neat acids and 5BA : 5CHA mixture.

have an extra degree of motion, namely the chemical exchange associated with the deuteron diffusing from dimer to dimer in the melt:



This extra degree of motional freedom might be expected to readily average any intrinsic ordering differences between the three kinds of cyclic dimers in the melts—the two homodimers and a heterodimer—and thereby account for the single $\Delta\nu$, figure 10 (*a*). In the case of the covalent probe BA-d_5, we anticpate that the ordering of the *para*-deuteron would be different in the different cyclic dimers (iii–v):



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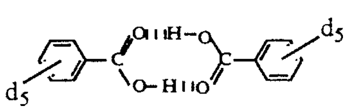

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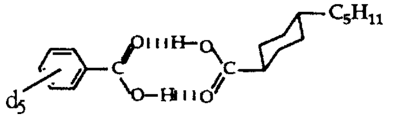


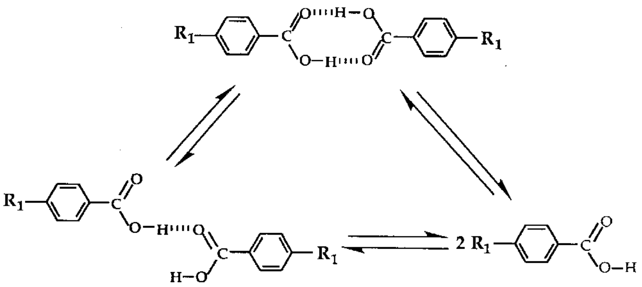
(*v*)

Unless there is very fast exchange to average the contributions of these three dimers, we expect to see the superposition of distinct splittings. This is not observed for the BA-d_5, figures 10 (*b*) and 11 (*b*), suggesting that on the relevant NMR timescale the probe must exchange among all conceivable dimer pairs. Such rapid interchange and effective averaging appears feasible; the magnitudes of the quadrupolar splittings observed here ($\Delta\nu \sim 200$ kHz) translate into a timescale $\tau \sim \Delta\nu^{-1} \sim 5 \times 10^{-6}$ s. If we assume that the self-diffusion of the probe in the mesophase is characterized by a diffusion constant $D \sim 10^{-7}\,\mathrm{cm^2\,s^{-1}}$, a root mean square distance $\langle x \rangle = (D\tau)^{1/2} \sim 700$ Å would be sampled on the NMR timescale τ. Hence our results support a picture of dynamic supramesogens—the lifetime of a cyclic dimer would appear to be much less than a few microseconds at the lowest temperatures accessible in the nematic mixtures.

4. Concluding remarks

In this study we extend the findings of part I [1] where we showed that binary mixtures of non-mesogenic acids exhibit mesophases. We show that for mesogenic acids containing the same length tails (five-atoms) but variable chemical constitution (cases where –O– and –NH– in 4OBA and 4NBA, respectively, replace a $-CH_2-$ unit in 5BA), the mesophase behaviour can be interpolated from observations carried out on the pure components (figure 1). Also, the dominance of tail length disparity in determining the phase stability of equimolar binary mixtures of 5BA, 4OBA and 4NBA guests in *n*OBA hosts, is similar to the findings in part I using mixtures of non-mesogenic acids: the larger the difference in tail lengths of the two acids, the larger the (excess) nematic thermal stability range (figure 2). Mixing the chemical constitution of the supramesogen 'core' by varying the chemical constitution of the H-bonded acid pairs (aromatics mixed with aliphatics) also enhances the mesophase stability (figure 3). The most dramatic enhancement of phase stability occurs with mixed acid cores having disparate tail lengths. These observations in binary mixtures of acids are qualitatively reflected in the behaviour of structurally related covalent mesogens.

In the melts of organic acids there are a variety of H-bonded 'supramolecules' and 'free' species, schematically illustrated by the equilibria below [8]:



The NMR findings suggest that the lifetime of these species is very short ($< 10^{-6}$ s), with no evidence for orientationally distinct supramolecules in the nematic phase. The dynamic complexity of these fluids appears to carry over into the solid state of binary acids: H-bonded homodimers and heterodimers do not exhibit simple statistical populations in the solid state. The IR evidence presented here suggests that the heterodimer dominates the population of supramesogens and determines the behaviour of these mixtures of H-bonded acids.

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