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## Liquid Crystals

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# Liquid crystals comprising hydrogen-bonded organic acids

## I. Mixtures of non-mesogenic acids

SEUNG KOO KANG and EDWARD T. SAMULSKI\*

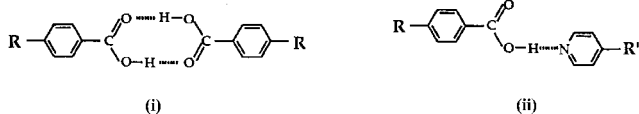
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Stable nematic phases are reported for binary mixtures of *p*-alkylbenzoic acids (*n*BA; where *n* = 1,2,3 denotes methyl, ethyl and propyl), *p*-alkoxybenzoic acids (*n*OBA, *n* = 1,2), and *p*-fluorobenzoic acid, which separately do not exhibit liquid crystalline phases. The mesophase stability increases in equimolar mixtures of acids having incommensurate lengths; the larger the difference in the tail substituents in the mixed organic acids, the broader the nematic phase. The trends in excess nematic range exhibited by the H-bonded supramesogens in binary mixtures parallels the behaviour of covalent mesogens. This is indicative of an influence of heterodimers comprising H-bonded pairs of the two different acids in equimolar mixtures of the non-mesogenic acids. It would appear that dimerized organic acids constitute a viable molecular-structural 'bread-board' for rapid screening for potential mesogen constituents

### 1. Introduction

The hydrogen bond (H-bond) is an important agent for engineering directional elements into supramolecular assemblies of noncovalently-connected molecules [1]. Recent examples of these assemblies range from soluble, 3-dimensional 'capsules' [2] to solid, non-centrosymmetric, 2-dimensional films [3]. Perhaps the earliest example of the unique geometrical ramifications of H-bonding in supramolecular organization is the work of Jones and co-workers who, starting some seventy years ago, showed that certain H-bonded dimers of organic acids (i) exhibit liquid crystallinity in their melts [4]. Interest in the relationship



between H-bond formation and mesomorphism continues, and in the last decade Kato and coworkers have exploited H-bonding between aromatic acids and the 4-substituted pyridyl group (ii) to stabilize low molar mass mesophases in binary mixtures [5], in mixtures with polymeric components [6], and most recently in chiral, mesomorphic networks comprising non-mesogenic precursors [7].

In all of these liquid crystalline melts of H-bonded supramolecules, it is the rectilinear, (cyclic) H-bonding

between the components in an extended geometry—the anisometric supramolecule's shape—that underlies the propensity for liquid crystal (LC) formation in such dimeric 'supramesogens' [8]. However, LC formation driven by anisotropic excluded volume interactions emanating from the shapes of H-bonded supramesogens such as i and ii is not the complete story. In the simplest examples of mesomorphic H-bonded dimers, *para*-substituted benzoic acids (i), the substituent *R*—the mesogen's 'tail'—must be sufficiently long/flexible in order to observe liquid crystallinity in melts at ambient pressure: in *p*-alkyl benzoic acids for example, LC formation is observed only for four-carbon (*R* = *n*-butyl) or longer length alkyl tail-substituted acids. Herein we examine binary mixtures of *para*-substituted 'short-tail' benzoic acids which separately do not exhibit LC phases. We find that even for marginally different pairs of non-mesogenic acids (e.g. *p*-methylbenzoic acid and *p*-ethylbenzoic acid), nematic phases are evident over a wide range of compositions in their binary mixtures. We report representative phase diagrams (determined by differential scanning calorimetry and optical microscopy) for binary mixtures of a variety of non-mesogenic acids, and emphasize how the disparity of the substituents—the difference in tail-lengths—in *para*-substituted benzoic acids influences the mesophase stability. The findings suggest that a hetero-dimer, a cyclic, H-bonded supramesogen comprising the two different non-mesogenic acids, plays an important role in the mesophases exhibited by the binary mixtures.

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## 2. Experimental

All compounds were obtained from Aldrich Chemical Co., and were recrystallized from acetone and acetone/methanol mixtures. 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 used for visual observations. DSC measurements were performed on a Seiko DSC 120; a heating rate of  $10^{\circ}\text{C min}^{-1}$  and a cooling rate of 5 or  $10^{\circ}\text{C min}^{-1}$  was used.

## 3. Results and discussion

We consider six non-mesogenic organic acids in this study: three *p*-alkylbenzoic acids (*n*BA; where *n* = 1,2,3 denotes methyl, ethyl and propyl); two *p*-alkoxybenzoic acids, *p*-methoxybenzoic acid (1OBA) and *p*-ethoxybenzoic acid (2OBA); and *p*-fluorobenzoic acid (FBA). The crystal (Cr) to isotropic (I) melting transitions and associated heats and entropies for the neat acids are given in table 1; readily available pKa values of the acids are also tabulated. An even-odd alternation is apparent in the melting transitions of the *n*BA series; this alternation is displaced in the *n*OBA series due to the added oxygen atom in those tails.

Figure 1 shows two DSC traces of an equimolar physical mixture of crystals of 2BA with crystals of 3BA. In the 1st heating run, there is an endotherm corresponding to the melting of 2BA ( $111^{\circ}\text{C}$ ); this endotherm is complex as it is affected by the dissolution of 3BA into the 2BA melt. Despite the inhomogeneous nature of this initial melt in contrast to the pure acids, the mixture of H-bonded dimers nevertheless exhibits a nematic (N) mesophase which eventually transforms to the isotropic melt ( $\sim 123^{\circ}\text{C}$ ). After homogenizing via self-diffusion in the isotropic melt, the mixture more clearly shows I-N and N-Cr transitions (1st cooling trace). The 2nd heating and cooling runs show better-defined transitions (Cr-N at  $103^{\circ}\text{C}$  and N-I at  $119^{\circ}\text{C}$ ), indicative of a more homogeneous mixture of the two non-mesogenic components. Mixtures prepared by dissolution of the components and subsequent removal of the solvent exhibited similar behaviour.

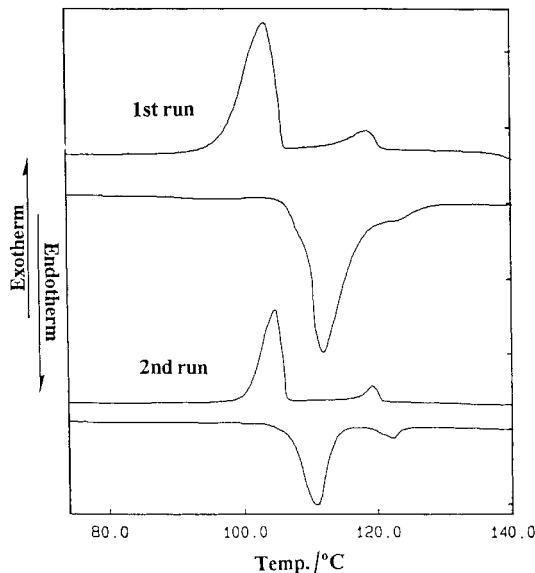


Figure 1. DSC traces of a binary mixture of *p*-ethylbenzoic acid (2BA) with *p*-*n*-propylbenzoic acid (3BA).

The phase diagram of the 2BA : 3BA mixtures is shown in figure 2. It was constructed from DSC observations (on cooling) and polarizing optical microscopy. Five distinct regions are apparent: an isotropic melt (I), homogeneous nematic phase (N, shaded region); a (complex) solid state where Cr, Cr' and Cr'' refer to the crystals associated with the 2BA : 3BA equimolar stoichiometric 50 : 50 mixture, pure 2BA, and pure 3BA, respectively; and isotropic and nematic phases in equilibrium with Cr'' on the 3BA-rich side of the phase diagram. Generally, eutectic behaviour is not observed; the calculated (Schroeder-van Laar equation) behaviour expected for the eutectic [9] is shown by the dotted line in the phase diagram (the calculated eutectic composition is 36 : 64 2BA : 3BA). Rather, we observe that small amounts of 3BA ( $\sim 10$  mol %) transform the 2BA-rich mixture into a nematic phase with a N-to-Cr + Cr' transition considerably higher than predicted for ideal mixing (dashed eutectic lines in figure 2). On the 3BA-rich side of the diagram, the N-to-Cr transition ( $103^{\circ}\text{C}$ ) appears to persist, indicative of the presence of an equimolar mixed crystal in the solid state together with

Table 1. Thermodynamic data for non-mesogenic benzoic acid derivatives.

Compound	$T_{mp}/^{\circ}\text{C}$	pKa	$\Delta H_f/\text{kJ mol}^{-1}$	$\Delta S_f/\text{kJ mol}^{-1} \text{K}^{-1}$
1BA (4-methylbenzoic acid)	176.0	4.36	15.0	33.5
2BA (4-ethylbenzoic acid)	107.0	4.35	13.2	34.7
3BA (4- <i>n</i> -propylbenzoic acid)	137.0	—	17.5	42.6
1OBA (4-methoxybenzoic acid)	176.0	4.49	24.2	54.0
2OBA (4-ethoxybenzoic acid)	192.0	4.80	28.9	60.0
FBA (4-fluorobenzoic acid)	178.0	4.14	20.9	46.4

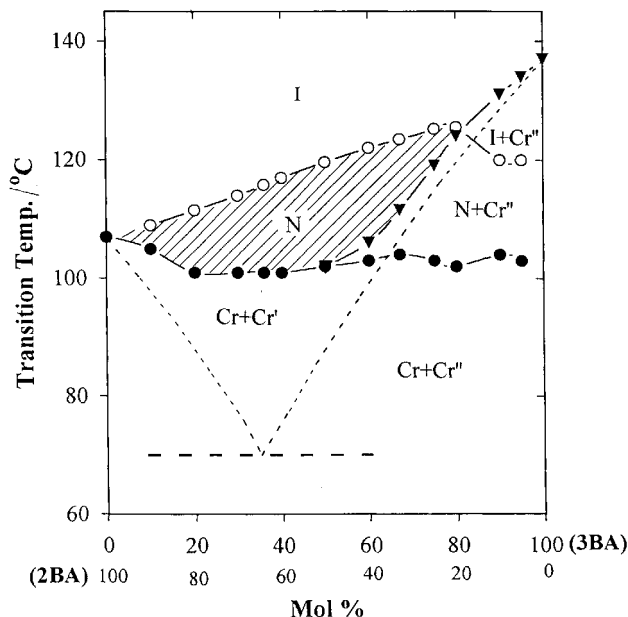


Figure 2. Phase diagram of the binary mixture of *p*-ethylbenzoic acid (2BA) with *p*-*n*-propylbenzoic acid (3BA). I and N represent the isotropic liquid and the nematic phases, respectively; Cr, Cr' and Cr'' refer to the crystal associated with the 2BA:3BA equimolar mixture, pure 2BA, and pure 3BA, respectively. The eutectic behaviour (dashed lines) is calculated from the Schroeder–van Laar equation.

occluded pure 3BA (Cr''). The latter Cr'' crystals are observed with polarizing microscopy as a separate phase in both the nematic and isotropic fluids in the 3BA-rich mixtures.

In figure 3 the chemical differences between the ether-containing tail of 1OBA and the alkyl tail of 3BA give rise to a more symmetric phase diagram. In this binary mixture pure I and N phases are observed in equilibrium with Cr' and Cr'' at the extreme compositions. Again there does not appear to be coincidence between calculated eutectic behaviour—a 1OBA:3BA ratio of 69:31 is the computed eutectic point—and observations. In fact, the 50:50 mixture exhibits a wide nematic range. The percentages of Cr' or Cr'' in the fluid phases can be determined as a function of composition from DSC traces of the type shown in figure 4. In such traces, the crystallization exotherms (shaded) corresponding to crystalline acid phases occluded from the melt, are used with the measured heats of fusion of the pure acids ( $\Delta H_f$ ) to derive the amounts of Cr' and Cr'' in equilibrium with the I and N phases. The observations (figure 5) suggest that the 50:50 mixture is a uniquely stable composition: The fraction of occluded Cr' (Cr'') is linearly proportional to the excess of 1OBA (3BA) relative to the equimolar mixture. The full lines in figure 5 denote the ideal behaviour of the occluded acids calculated by

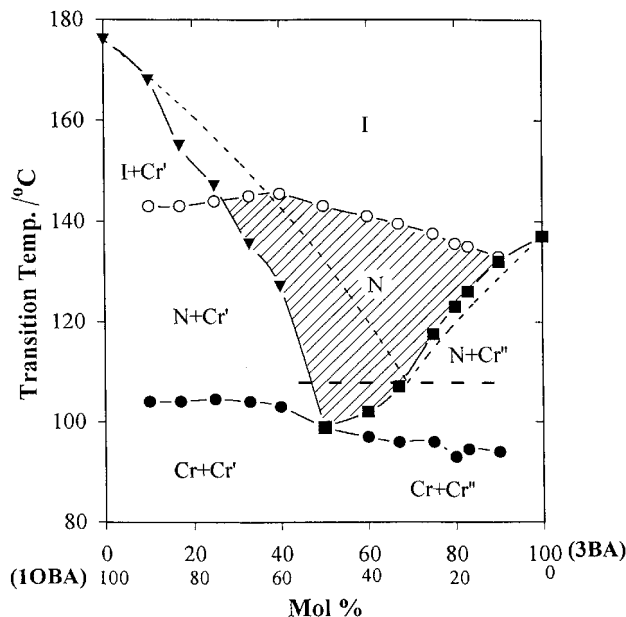


Figure 3. Phase diagram of the binary mixture of *p*-anisic acid (1OBA) with *p*-*n*-propylbenzoic acid (3BA). I and N represent the isotropic liquid and the nematic phases, respectively; Cr, Cr' and Cr'' refer to the crystalline phases associated with the 1OBA:3BA equimolar mixture, pure 1OBA, and pure 3BA, respectively. The eutectic behaviour (dashed lines) is calculated from the Schroeder–van Laar equation.

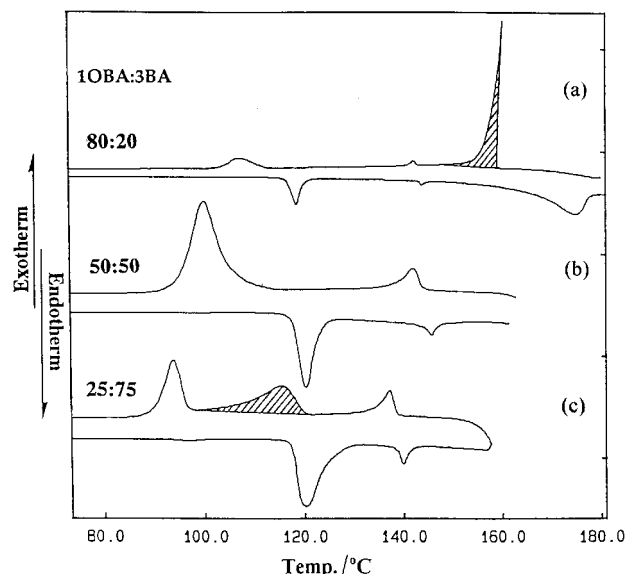


Figure 4. DSC traces of binary mixtures of *p*-anisic acid (1OBA) with *p*-*n*-propylbenzoic acid (3BA); (a) 80:20, (b) 50:50, and (c) 25:75 mol ratios of 1OBA:3BA. The shaded exotherms correspond to crystallization of the pure components occluded from the fluid (meso)phases.

assuming that a stable, stoichiometric 50:50 complex persists in the non-stoichiometric compositions. Table 2 shows the heats and entropies of the Cr–N and N–I

Table 2. Phase transitions in the stoichiometric 1:1 mixtures of unlike non-mesogenic aromatic acids.

	$T_{CrN}$	$\Delta H_{CrN}/\text{kJ mol}^{-1}$	$\Delta S_{CrN}/\text{kJ mol}^{-1} \text{K}^{-1}$	$T_{NI}$	$\Delta H_{NI}/\text{kJ mol}^{-1}$	$\Delta S_{NI}/\text{kJ mol}^{-1} \text{K}^{-1}$
1BA/2BA	107.0	11.8	33.5	108.5		<sup>a</sup>
1BA/3BA	109.0	5.4	13.5	130.0	1.52	(4.11)
2BA/3BA	103.0	10.3	27.2	120.0	1.15	(2.99)
1OBA/1BA	137.0	14.3	34.6	138.0		<sup>a</sup>
1OBA/2BA	96.0	9.6	25.5	131.0	0.95	(2.36)
1OBA/3BA	91.0	12.4	33.2	143.0	1.78	(4.29)
FBA/1BA	144.0	12.6	30.3	—		—
FBA/2BA	82.0	5.5	15.5	106.0	1.96	(5.11)
FBA/3BA	92.0	10.9	29.5	122.0	0.98	(2.46)

<sup>a</sup> The heat of fusion ( $\Delta H_{NI}$ ) for nematic–isotropic transitions is convolved with  $\Delta H_{CrN}$  for nematic–crystal transitions because of the proximity of the transition ( $\sim 2^\circ\text{C}$ ).

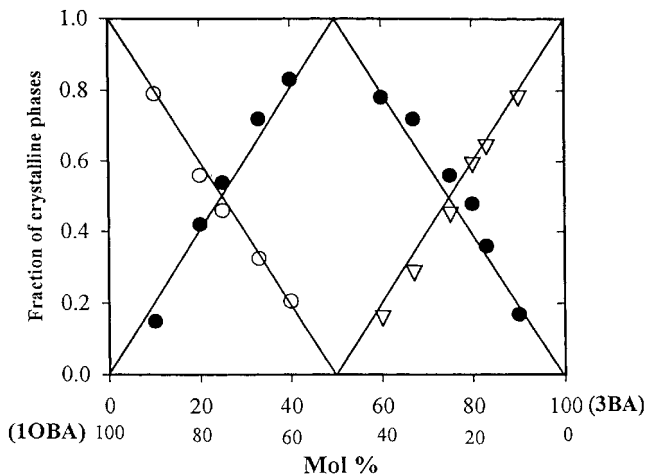


Figure 5. The fraction of Cr, the solid phase associated with the equimolar 1OBA:3BA mixtures (solid circles) derived from DSC traces of non-stoichiometric compositions of 1OBA and 2OBA is shown versus composition of the binary mixture; the two fractions Cr' and Cr'', respectively, are the fractions of occluded 1OBA (open circles) and 3BA (open triangles) found in the same non-stoichiometric binary mixtures. The data is derived from the heat of fusion of each (pure) component and crystallization exotherms such as shown in figure 4.

transitions for the equimolar mixtures of acids; with the exception of the FBA:1BA mixture (non-mesogenic) the behaviour is rather similar for all pairs of acids.

Figure 6 illustrates how 1:1 equimolar mixtures of the non-mesogenic  $m\text{BA}:n\text{BA}$  (and  $m\text{OBA}:n\text{OBA}$ ) acids exhibit increasing mesophase stability with increasing disparity of tail lengths, that is, for  $m \neq n$ . As the difference between tail lengths ( $m - n$ ) increases, the nematic range is broadened. The  $T_{NI}$  and clearing points show evidence of odd–even effects stemming from the parity of the number of atoms in the tails. The most thermally robust phases are observed for the pairs with the most disparate tail lengths, i.e. 1BA:4BA (and 1OBA:4OBA). The relative stability of the  $n\text{OBA}$  mesophases as a

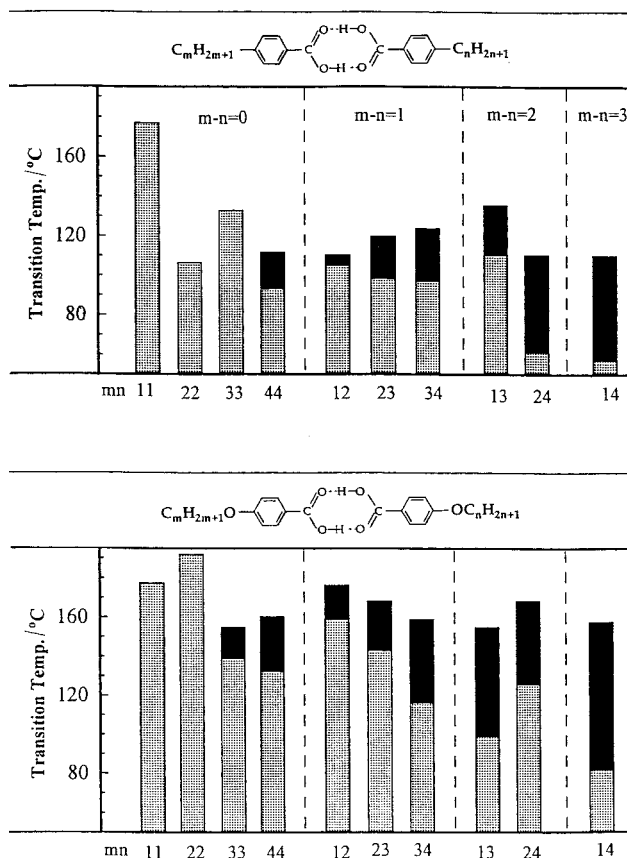


Figure 6. The transition temperature dependence on  $m$  and  $n$ , the numbers of aliphatic tail carbon atoms in the stoichiometric mixtures of  $p$ -alkylbenzoic acids (top) and  $p$ -alkoxybenzoic acids (bottom). The black and the dotted parts stand for the thermal ranges of nematic and crystal phase, respectively.

function of the tail length disparity is shown in figure 7 (top) in terms of the excess nematic thermal stability associated with the equimolar mixtures. This excess nematic mesophase stability,  $N_{ex} = [N_{mn} - (N_{mm} + N_{nn})/2]$ , is obtained by reducing the observed nematic range for

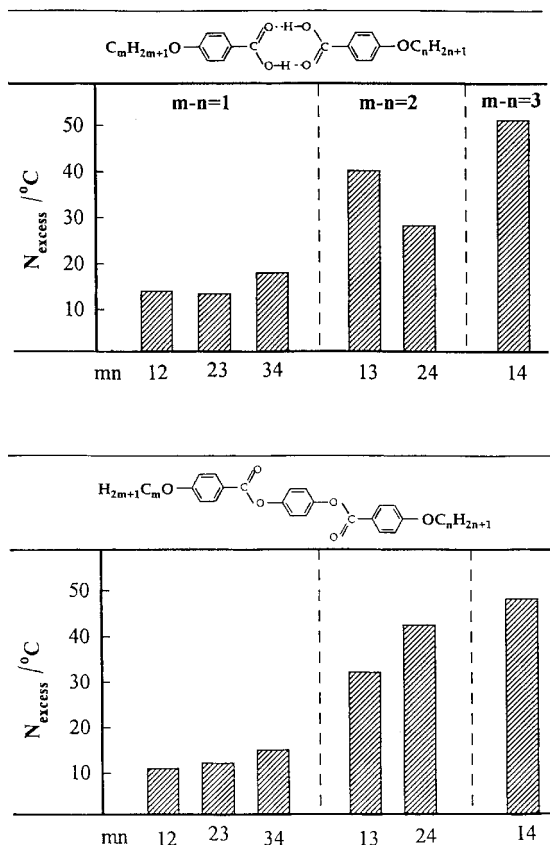
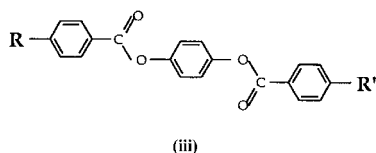


Figure 7. The excess nematic temperature range associated with equimolar mixtures of alkoxy acids  $m\text{OBA}:n\text{OBA}$  as a function of the difference in lengths of the aliphatic tails (top) are contrasted with observations in covalent bis(4-alkoxybenzoyloxy)benzene mesogens (bottom). Data for the latter transitions are from [10].

the binary mixture of different tail lengths,  $N_{mn}$  ( $^\circ\text{C}$ ), by the average nematic range of the pure components,  $N_{mm}$  and  $N_{nn}$  ( $^\circ\text{C}$ ). Also shown in figure 7 (bottom) is the behaviour of a similar homologous series in a related covalent mesogen, a series of bis(4-alkoxybenzoyloxy)benzenes (iii) with inequivalent tails [10]. Admittedly, the central



core of the covalent mesogen does not preserve the linearity in the cyclic acid supramesogen, nor are the dimensions of these two mesogenic cores equivalent. Also, there are extra degrees of isomeric freedom in the ester linkages in the covalent mesogen. Nevertheless, the behaviour of  $N_{\text{ex}}$  in the covalent mesogen with respect to tail length disparity parallels  $N_{\text{ex}}$  observed for the H-bonded supramesogens.

#### 4. Concluding remarks

The melts of pure organic acids are inherently complex as they are composed of a variety of equilibrating species: free acid, H-bonded cyclic dimers, and ill-defined open chain H-bonded polymers [11]. Moreover, the stability of the H-bond itself ( $5\text{--}10\text{ kcal mol}^{-1}$ ) limits its role in maintaining the anisometric dimer shapes in the supramesogen. Adding a second component (binary mixtures of acids) further complicates the already complex system. In particular, there is now the possibility of forming heterodimers—cyclic, H-bonded dimers between the two different components. The absence of simple eutectic behaviour when pairs of non-mesogenic acids are mixed, coupled with the observation of stable nematic phases for the binary mixtures suggests that the heterodimer may play a dominant role in LC formation in this class of supramesogens. Admittedly, there does not appear to be any significant microscopic driving force for heterodimer formation (e.g. no significant difference in pKa values; see table 1). There would be a configurational entropic gain for an apolar nematic phase composed of asymmetric mesogens (heterodimers) relative to that formed by symmetric mesogens (homodimers), but this should be similar for all heterodimer mesogens, independent of the disparity of tail lengths.

Mesophase stability increases in mixtures of covalent liquid crystals having incommensurate lengths, and mixtures of such LCs were frequently the materials of choice in early LC displays requiring a broad mesophase range. In the mixtures of non-mesogenic organic acids, incommensurate dimer length clearly affects mesophase stability. The larger the difference in the tail substituents for  $m \neq n$  in the binary mixture of organic acids, the broader the nematic phase (figure 6). As the inter- and intra-supramesogen chemistry is unchanged within a homologous series, the observed increase in mesophase stability with increasing  $(m-n)$  suggests that a packing/translational entropic stabilization underlies the propensity for liquid crystal formation in the mixtures of non-mesogenic acids. In particular, it would appear that in the lamellar-like crystals formed by aromatic acids [12], the variable lengths characteristic of mixtures of two different acids result in incommensurate defects in the packing of acid dimers; in turn, this suppresses crystal formation, i.e. the melting temperature is depressed in the mixed acids. Lastly, the trends in excess nematic range  $N_{\text{ex}}$  exhibited by the binary mixtures of alkoxybenzoic acids parallels the behaviour of  $N_{\text{ex}}$  observed in covalent bis(4-alkoxybenzoyloxy)benzene mesogens with inequivalent tails and we interpret this observation to be indicative of a dominant influence of heterodimers in these equimolar mixtures of non-mesogenic acids. In subsequent infrared studies we attempt to quantify the role of the heterodimer in such supramesogens [13].

In summary, despite the increased inherent complexity associated with mixtures, dimerized organic acids constitute a viable molecular-structural 'bread-board' for rapid screening of the propensity for mesophase formation when two structural motifs are juxtaposed in the form of H-bonded pairs. The resulting supramesogens can give insights into the engineering of specific properties into potential covalent mesogens.

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### References

- [1] LEHN, J.-M., 1995, *Supramolecular Chemistry: Concepts and Perspectives*, a personal account built upon the George Fisher Baker lectures in chemistry at Cornell University (Rome, New York: Accademia nazionale dei Lincei); WUEST, J. D., 1995, *Mesomolecules: from Molecules to Materials*, edited by G. D. Mendenhall, A. Greenberg and J. F. Liebman (New York: Chapman & Hall).
- [2] MARTIN, T., OBST, U., and REBEK JR., J., 1998, *Science*, **281**, 1842.
- [3] CAI, C., BÖSCH, M. M., TAO, Y., MÜLLER, B., GAN, Z., KÜNDIG, A., BOSSHARD, C., LIAKATAS, I., JÄGER, M., and GÜNTER, P., 1998, *J. Am. chem. Soc.*, **120**, 8563.
- [4] BRADFIELD, A. E., and JONES, B. J., 1929, *J. chem. Soc.*, 2660; JONES, B., 1935, *J. chem. Soc.*, 1874; BENNETT, G. M., and JONES, B., 1935, *J. chem. Soc.*, 240; GRAY, G. W., and JONES, B., 1953, *J. chem. Soc.*, 4179.
- [5] KATO, T., and FRÈCHET, J. M. J., 1989, *J. Am. chem. Soc.*, **111**, 8533.
- [6] KATO, T., and FRÈCHET, J. M. J., 1989, *Macromolecules*, **22**, 3819.
- [7] KIHARA, H., KATO, T., URYU, T., and FRÈCHET, J. M. J., 1998, *Liq. Cryst.*, **24**, 413.
- [8] PALEOS, C. M., and TSIOURVAS, D., 1995, *Angew. Chem. int. Ed. Engl.*, **34**, 159.
- [9] See for example, DEMUS, D., FIETKAU, C., SCHUBERT, R., and KEHLEN, H., 1974, *Mol. Cryst. liq. Cryst.*, **25**, 215.
- [10] THIEM, J., 1992, *Liquid Crystals*, Vol. IV-7-e (Berlin, Heidelberg Springer-Verlag), p. 130.
- [11] HADZI, D., and DETONI, S., 1979, *The Chemistry of Acid Derivatives Part 1*, edited by S. Patai (New York: John Wiley & Sons), p. 213; JEFFREY, G. A., 1997, *An Introduction to Hydrogen Bonding* (New York: Oxford University Press).
- [12] BRYAN, R. F., and FALLON, III, L., 1975, *J. chem. Soc. Perkin II*, 1175.
- [13] KANG, S. K., and SAMULSKI, E. T., 2000 (companion manuscript), *Liq. Cryst.*