

Supramolecular liquid crystals with columnar mesophases through self-assembly of carboxylic acids around a tribasic core

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The self-assembly of long chain alkoxy-substituted benzoic acids around tribasic core **1** provides a simple and flexible way to supramolecular liquid crystals with columnar mesophases.

During the last years several groups have developed a number of supramolecular approaches to the preparation of liquid crystals with columnar mesophases.¹ Disc-shaped mesogens can result, for example, from the association of a varying number of amphiphilic molecules whose incompatible polar and non-polar parts segregate on a microscopic scale. Micro-segregation is seen as an important driving force in the formation of smectic, columnar and cubic phases; the type of liquid-crystalline phase depends on the curvature of the interface.² Typical examples for columnar systems are Lattermann's monoaryl esters of *cis,cis*-1,3,5-cyclohexanetriol,³ Praefcke's inositol derivatives,⁴ Tschierske's laterally substituted terphenyls,² and Percec's taper-shaped benzo-crown ethers.⁵ The dimerisation of mesogenic benzamides,⁶ of phenanthridinones,⁷ the trimerisation of phthalhydrazides,⁸ complexes of a 2,4,6-triaryl-amino-1,3,5-triazine with benzoic acids,⁹ and complexes of certain pyridine derivatives with carboxylic acids^{10,11} illustrate how the discotic unit can be made up of a defined number of components that are held together by hydrogen bonding. Non-covalent complexation between non-identical components has so far led to columnar phases in only a few exceptional cases.^{9–11}

We have recently described that non-covalent complexes are readily obtained from carboxylic acids and tris(imidazoline) base **1**; these are held together by hydrogen bonds and salt bridges in non-polar solvents.¹² Two X-ray crystal structures indicated that such carboxylic acid complexes have an almost disc-like flat shape and therefore fulfill one of the structural requirements for discotic liquid crystals.^{12a,13} Here, we report a new type of supramolecular liquid crystal based on the assembly of benzoic acids, which are substituted with a sufficient number of long alkoxy side chains, around a tribasic core **1**.

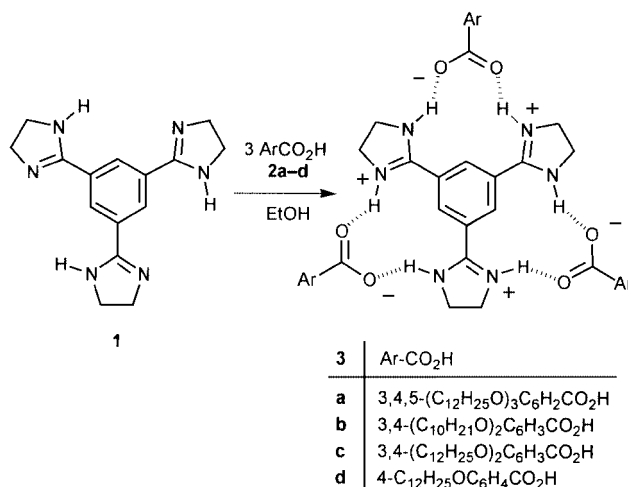
Long chain alkoxy-substituted benzoic acids **2a–d**¹⁴ and tris(imidazoline) base **1**¹² were prepared as described in the literature. All compounds were used after extensive purification, which included gradient sublimation of **1** at 310 °C/10^{−4} mbar. Complexes **3a–d** were prepared by dissolution of the respective benzoic acid **2a–d** (3 equiv.) and base **1** (1 equiv.) in hot ethanol (*ca.* 80 mL per mmol of **1**). The hot solution was filtered and, if necessary, concentrated until the still warm solution became cloudy. The salts crystallised in analytically pure form upon standing at room temperature (Scheme 1). All complexes gave satisfactory ¹H NMR, ¹³C NMR, IR and elemental analysis data.

As might be expected from multiple substitution with long-chain alkoxy groups, complexes **3a–c** showed high solubility in non-polar organic solvents, such as chloroform (solubility

typically > 200 mg mL^{−1}), toluene, or even hexane, whereas polar solvents (DMSO, alcohols) were generally found to be non-solvents. The diagnostic downfield ¹H NMR chemical shifts for the NH signal ($\delta_{\text{H}} \approx 13$) as well as for the singlet assigned to the core's aromatic protons ($\delta_{\text{H}} \approx 10.1$ in CDCl₃ or C₆D₆) emphasised that the equilibrium between the salt and its ionic components lies on the side of the hydrogen-bonded 3:1 complex in non-polar solvents.¹² No evidence for dissociation was observed for any of the carboxylic acid complexes in chloroform solutions at concentrations > 10^{−5} M. It is therefore expected that dissociation is even more unfavourable in the condensed phase.

Although neither **1** nor benzoic acids **2** are mesogenic, differential scanning calorimetry (DSC) and polarising optical microscope (POM) experiments confirmed that complexes **3a–c** transform to birefringent, shearable liquid-crystalline mesophases at *ca.* 80 °C (Table 1). The clearing temperatures of the mesophases of all three complexes were above 200 °C. Crystal-mesophase melting transitions exhibited large enthalpic changes (138 J g^{−1} for **3c**), whereas enthalpies for the clearing transition from the mesophase to the isotropic liquid were much smaller (17 J g^{−1} for **3c**) albeit still considerably higher than for a typical smectic phase.

A very fine texture was observed during the first heating of complexes **3a–c**. Subsequent slow cooling (cooling rate ≤ 2 °C min^{−1}) from the isotropic melt led—after significant supercooling (*ca.* 15 °C for **3a**)—to the dendritic growth of homeotropic finger-like contours (Fig. 1) that are characteristic for columnar mesophase formation.¹⁵ Further cooling to room temperature again produced a fine-structured texture, and even the previously homeotropic regions finally showed birefringence. The thermal stability of the mesophases was, however,



Scheme 1

Table 1 Phase transition temperatures T and enthalpies ΔH of **3a–d** as determined by DSC^a

	3a		3b		3c		3d	
	K–M	M–I	K–M	M–I	K–M	M–I	K–K	K–I
First heating/ $^{\circ}\text{C}$	63	214	79 ^b	244	72	240	62	188
$\Delta H/\text{J g}^{-1}$	53	9	111	19	138	17	34	36

^a K: crystalline phase, M: mesophase, I: isotropic phase; heating and cooling rates $10\text{ }^{\circ}\text{C min}^{-1}$. ^b An additional endothermic transition with a peak at $71\text{ }^{\circ}\text{C}$ can be detected if the crystallised sample was dried at $<60\text{ }^{\circ}\text{C}$ prior to DSC measurements.

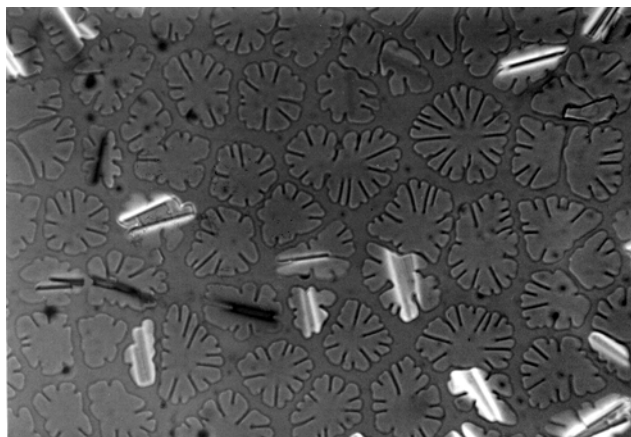


Fig. 1 Representative optical polarised micrograph showing the dendritic growth of homeotropic contours at $200\text{ }^{\circ}\text{C}$ after slow cooling of complex **3b** from the isotropic melt (polarisers not completely crossed).

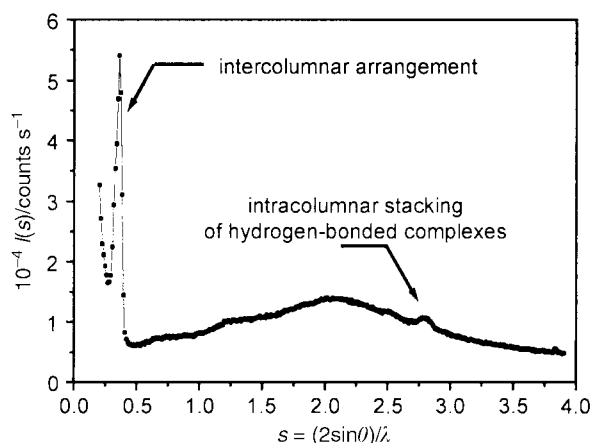


Fig. 2 Typical X-ray scattering diagram of hydrogen-bonded complex **3b** taken at $150\text{ }^{\circ}\text{C}$ in the mesophase region.

somewhat limited. After prolonged annealing at $170\text{ }^{\circ}\text{C}$ or heating at temperatures $>200\text{ }^{\circ}\text{C}$ for more than a few minutes, extended domains evolved which lacked birefringence and were surrounded by brown shades indicating decomposition of the textures. Interestingly, the liquid-crystalline domains of the 3,4-disubstituted **3b–c** were found to be larger than those of the symmetrical complex **3a**, both during the first heating process and subsequent cooling. Although complex **3d** became malleable upon heating above $70\text{ }^{\circ}\text{C}$, a single dodecyloxy group per benzoic acid unit was evidently insufficient to stabilise a liquid-crystalline phase.

X-Ray scattering experiments confirmed the presence of liquid-crystalline mesophases in the high temperature regime of complexes **3a–c**. Fig. 2 shows a typical scattering pattern with a maximum at low angles, corresponding to Bragg spacings in the range of 3–4 nm, a broad maximum due to liquid-like arrangement of the terminal alkyl chains and a well defined maximum at wide angles, corresponding to a Bragg spacing of 0.36 nm. The value of the Bragg spacing associated with the

scattering maximum at small angles clearly indicates that the scattering units are significantly larger compared to the dimensions of either the tribasic core or the benzoic acid derivatives. The Bragg spacing of 0.36 nm points towards a regular stacking of the aromatic components, a feature which is well known from structural studies on mesophases formed by covalently bonded discotic mesogens.¹⁶ The presence of only a single maximum at low angles in the scattering pattern from non-oriented systems does not allow an assignment of the specific type of columnar arrangement; however, we obtained reasonable estimates for the macroscopic density by assuming hexagonally ordered columns of regularly stacked hydrogen-bonded complexes. Further studies on the morphology using X-ray scattering and AFM are in progress.

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