Liquid Crystals

Hydrogen-Bonded Banana Liquid Crystals**

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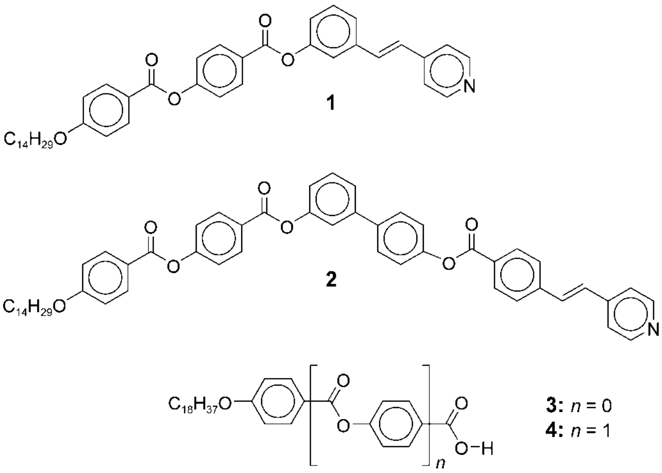
There are numerous examples in nature that demonstrate the crucial role of hydrogen bonds. Through imitation of this phenomenon, hydrogen bonds have been used to good effect by researchers to achieve specific synthetic targets.[1] Fields such as supramolecular chemistry and materials science are indebted to this strategy,[2] and important breakthroughs have been achieved by exploiting these inter- or intramolecular "*strong and directional, and… lovely*"[3] interactions. Liquid crystals, which are related to both of the aforementioned fields, are another example of the attractive possibilities of this interaction.[4] Mesomorphic properties result from a suitable combination of the shape of a molecule and the magnitude and direction of interactions between the molecules. Hydrogen bonding, through self-assembly, has been used to order thermotropic and lyotropic liquid crystals in which the magnitude and the direction of the interactions have been appropriate to maintain order within the fluid state. Calamitic and columnar mesophases of low or high molecular-weight materials have been stabilized with this approach. Such systems have also been obtained by the use of either mesogenic or non-liquid-crystalline moieties.

In 1996, a new type of mesogenic material appeared in the field of liquid crystals: the so-called "banana-compounds".[5] These mesomorphic materials are of interest from both an academic and a practical point of view.[6] These systems form a distinct class of liquid-crystalline compounds as they give rise to new types of mesophases that do not have analogues among classical calamitic phases. Interestingly, some of these compounds exhibit the unique feature of forming polar ordered mesophases with achiral molecules to provide antiferroelectric, ferroelectric or nonlinear optical responses—often with exceptional values for the relevant parameters.[7] Herein, we report a study that addresses a pertinent question that has not successfully been answered to date: is it possible to stabilize this type of mesophase through hydrogen bonding interactions? On the basis of the following results, the answer to this question is a resounding yes!

Having taken into account the structural molecular requirements that 1) govern these new macroscopic liquid-crystal phase arrangements[5] and 2) allow appropriate H bonded complexation, we focused our interests on the V-shaped H acceptor structures **1** and **2** shown in Scheme 1 and two benzoic acid derivatives of varying lengths as the H donor moieties **3** and **4**. The V-shaped 4′-stilbazoles (**1** and **2**) were prepared according to the synthetic route outlined in Scheme 2 (see also Supporting Information), and the acids (**3** and **4**) were prepared according to literature methods.[8] The synthesis of the desired bent complexes required the two components (H donor and H acceptor) to be mixed in precise equimolecular proportions in a common solvent (THF) followed by removal of the solvent. The formation of the complex was easily confirmed through polarizing optical microscopy measurements; the solid samples melted cleanly without the appearance of biphasic regions, which would otherwise have indicated the presence of nonstoichiometric complexes.



Scheme 1. General structures of the H acceptors (**1** and **2**) and H donors (**3** and **4**).

Despite the nonmesomorphic nature of both of the H acceptor compounds studied, all of the complexes were liquid crystalline over temperature ranges that were different to the ranges at which the carboxylic acids displayed calamitic phases (Table 1). More interestingly, the complexes exhibit textural features which are identical to those reported[8,9] and observed by us for SmCP (smectic C polar) mesophases. A schlieren texture and highly birefringent domains were observed upon cooling the sample from the isotropic liquid (Figure 1 a). From a structure–activity point of view, the larger the number of aromatic rings, the broader and more stable the mesophases are. Furthermore, hysteresis of the solidification processes of around 20 degrees was also observed.

The stability of the hydrogen bonding that leads to these banana complexes was also examined. The IR spectra of these materials (KBr pellets) show features that are characteristic of pyridine–carboxylic acid complexes.[4b,10] Thus, the forma-

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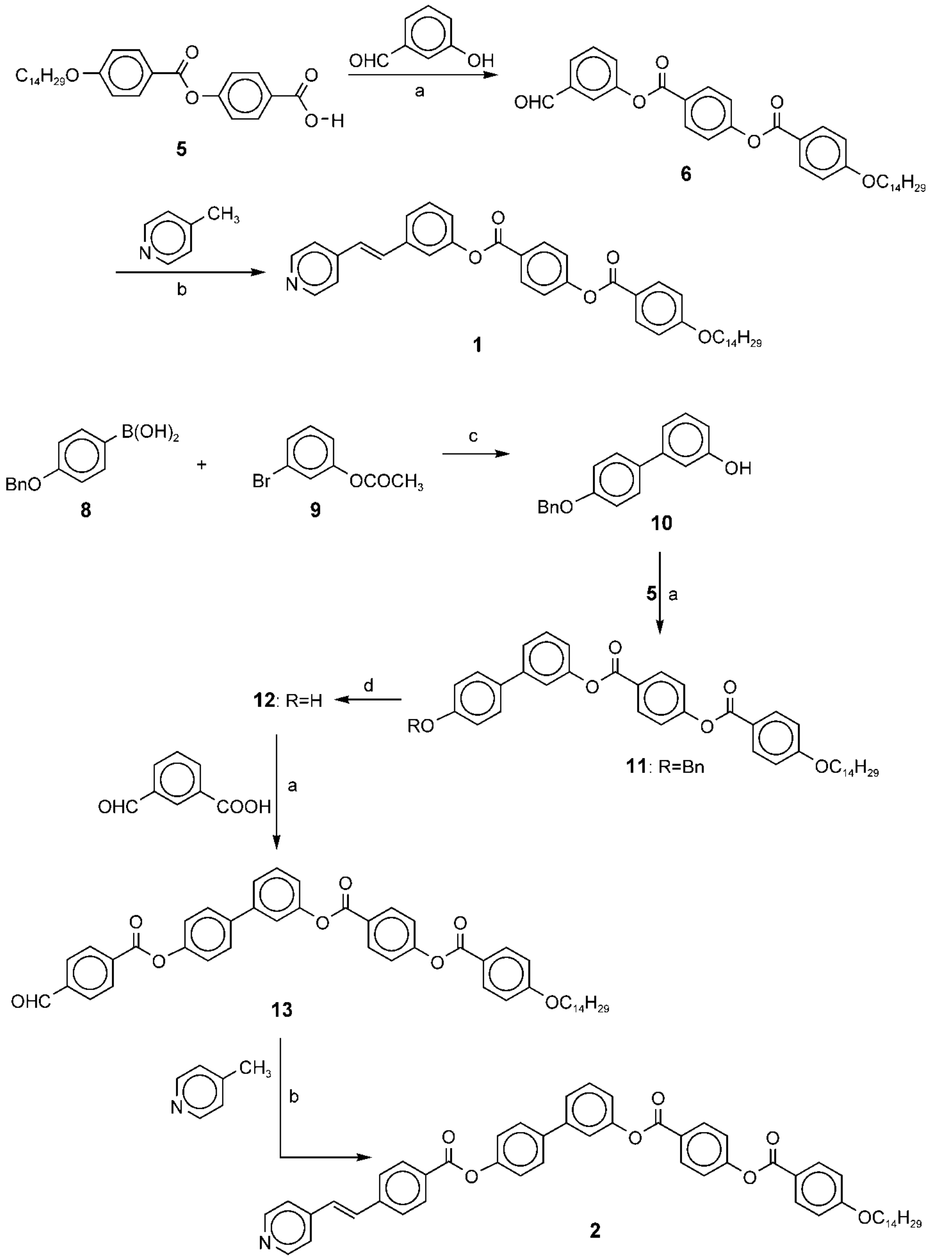
tion of the H bond is detected through the modification of the O–H stretching band of the acid. The complexes exhibit two absorptions at ≈2500 and $1950\,cm^{-1}$ which correspond to the O–H···N(Py) interaction, whereas carboxylic acid dimers exhibit a band (O–H) at $\approx 2650\,cm^{-1}$. On the other hand, an absorption band at $1683\,cm^{-1}$ which also corresponds to the acid dimers was not detected for the bent complexes. Furthermore, variable-temperature IR spectra were recorded for all of the complexes and these reveal that a carbonyl band, which arises from the dissociation of the hydrogen bonding, is not observed in either the crystalline phase or the mesophase.

The X-ray diffraction patterns of the three complexes in their mesophases are very similar. In the wide-angle region there is diffuse scattering, whereas in the small-angle regions there are sharp layer reflections up to third order (Table 2 and Figure 2). This indicates well-defined layer structures for the liquid-crystalline phase in all cases; that is, the complexes arrange themselves in smectic phases without in-plane order. The estimated length of the "molecules" (67–76 Å) is larger than the interlayer distances measured and indicates tilted arrangements of the complexes in the liquid-crystalline phase with angles of around 39–45°.

An attractive feature of the SmCP mesophase is its switching response under electric fields.[5b,6,7a,9] This behavior was investigated for our H bonded materials: 5-μm ITO (indium tin oxide)-coated cells were filled with the samples and their switching behavior was studied. On slow cooling from the isotropic liquid, a texture with focal-conics containing fringe patterns and some circular domains was perfectly visible. The direction of the extinction brushes coincides with the polarizer and the analyzer (see Figure 1 b). Application of direct current (d.c.) fields causes the brushes to rotate (see Figures 1 c and d). The higher the field, the larger the tilt of the extinction brushes (with a saturation value around 45°). All these facts are consistent with a SmCP mesophase in which molecules are organized in layers and tilted. The tilt alternates from layer to layer to give rise to an anticlinic and antiferroelectric SmC_AP_A structure. Under a high enough d.c. field, the structure becomes a synclinic ferroelectric SmC_SP_F structure.[6,9] Moreover, upon application of triangular-wave fields, all these complexes show a tristable switching process typical of an antiferroelectric response. Figure 3 shows a typical plot of the inversion of



Scheme 2. Synthetic routes to the H acceptors **1** and **2**. a) DCC, DMAP, CH_2Cl_2; b) $(CH_3CO)_2O$; c) $Pd[P(Ph)_3]_4$, $NaHCO_3$, DME; d) $Pd(OH)_2/C$, cyclohexene, EtOH. DCC = Dicyclohexyl carbodiimide, DMAP = dimethylaminopyridine, DME = 1,2-dimethoxyethane.

Table 1: Thermal properties of the H donors, H acceptors and the complexes studied.

Compounds	Phase transition[a,b] [°C] (ΔH [$kJ\,mol^{-1}$])
1	K 108.2 (56.2) I
2	K 168.9 (37.0) I
3	K 104.6 (53.5) SmC 125.0 (7.9) I
4	K 101.6 (30.7) SmC 206.5 (13.8) I
1·3	K 98.2 (58.6) SmCP 118.8 (29.6) I
1·4	K 82.9 (59.3) SmCP 142.6 (26.1) I
2·3	K 117.9 (19.0) SmCP 173.8 (28.7) I

[a] Data determined by DSC at a scanning rate of $10\,°C\,min^{-1}$. [b] K: crystalline; SmC: smectic C mesophase; SmCP: smectic C polar mesophase; I: isotropic liquid phase.

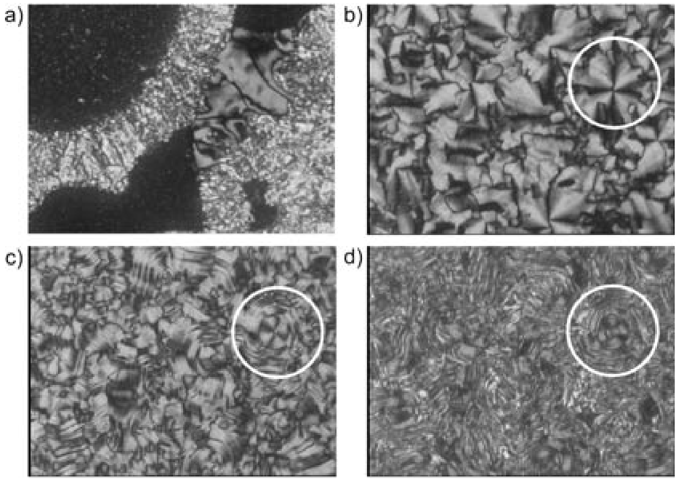


Figure 1. Textures of the mesophase SmCP: a) Complex **2·3** at 144 °C, uncoated cell; b) complex **1·3** at 100 °C, $V=0$, coated cell; c) complex **1·3** at 100 °C, $V=70$ (d.c.), coated cell; d) complex **1·3** at 100 °C, $V=100$ (d.c.), coated cell. The orientation of the extinction brushes is seen clearly in the circles indicated.

Table 2: X-ray data for the complexes studied.

Complex	Measured spacings [Å]	Miller index	Layer thickness [Å]
1·3	52.2 (vs)[a]	001	*d*: 52.05
	26.3 (w)	002	
	17.25 (m)	003	
1·4	50.5 (vs)	001	*d*: 51.04
	25.7 (m)	002	
	17.1 (m)	003	
2·3	61.6 (vs)	001	*d*: 61.6
	30.8 (m)	002	

[a] Intensity of the reflection: vs: very strong; w: weak; m: medium.

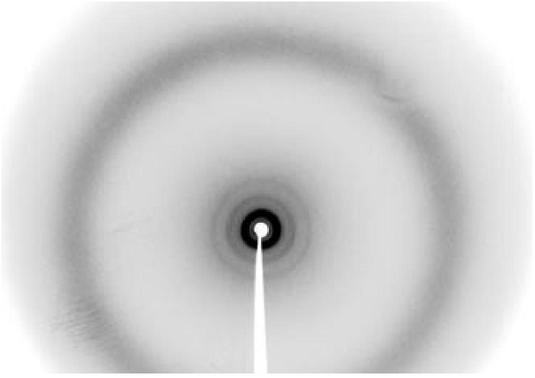


Figure 2. X-ray diffraction pattern of complex **1·4** at 120 °C in the SmCP mesophase.

the polarization current. Two peaks for each half-period are clearly visible. The integration of these peaks[11] gives a value around 200 nC cm^{-2} for the dielectric polarization for all of the complexes.

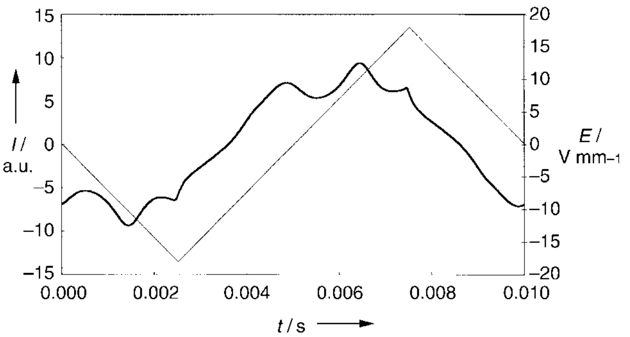


Figure 3. Polarization switching current of complex **1·3** under a triangular-wave electric field: 100 Hz, 36 Vpp µm^{-1} (5 µm-Linkam cell).

The presence of stilbazole structures in these materials also led us to assess their luminescent response, which, if present, would increase the multifunctional character of these novel systems. As an initial study, the one-photon-excited fluorescence emissions of these complexes were determined in solution (10^{-6} M in THF); representative results from these studies are shown in Figure 4. The H donor compounds or the H bonded complexes absorb at 310 nm (**1** and its complexes) or 320 nm (**2** and its complex) and they exhibit fluorescence emissions around 355 nm and 365 nm, respectively. A decrease in the absorptivity of the H donors is observed upon complexation. To determine the potential of the complexes as fluorescent materials, more in-depth studies of their luminescent behavior will be undertaken in a future project—particularly with respect to the novel SmCP mesophase as, to our knowledge, there is no precedence in the literature for this property in 'banana' liquid crystals.

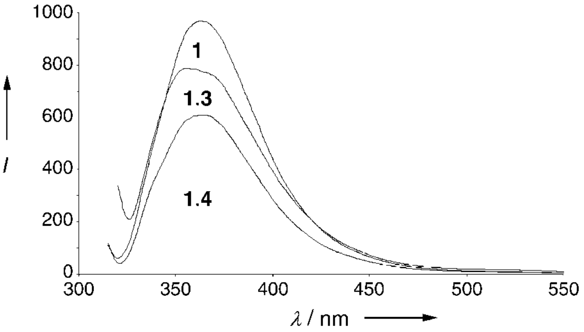
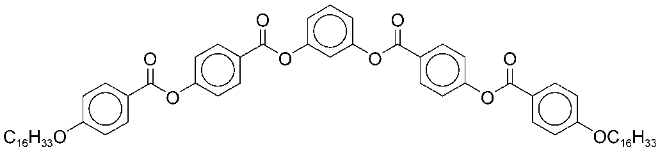


Figure 4. Fluorescence spectra of compound **1** and complexes **1·3** and **1·4** at room temperature in THF. Excitation wavelength 310 nm, emission wavelength 355 nm.

Although we were unable to find an example of a compound in the literature that could be considered as a covalent analogue of our bent complexes, we compared the mesomorphic properties of **1·3** with the longest related



K 110 °C SmCP 119 °C I

Scheme 3. 'Banana' ester compound for comparison with **1·3**.

'banana' ester reported by Pelzl's group[12] (Scheme 3). From the data obtained, we tentatively conclude that despite the slight difference in length in the two materials, the similarity in their thermal behavior is sufficiently close to acknowledge the formation of H bonded complexes as a useful strategy to design and, more interestingly, to identify new 'banana' liquid crystals. In an attempt to obtain new mesophases, as well as to approach different V-shaped structures by H bonding, the complexation of some pyridine structures with different carboxylic acids is currently in progress.

In summary, further evidence of the versatility of hydrogen bonding for the anisotropic self-organization of functional materials has been obtained. A successful method to obtain novel mesophases, namely the most studied SmCP liquid-crystalline phase, through H bonding interactions has been developed. More interestingly, the attractive electro-optical and dielectric responses of this polar phase were also determined for these noncovalent systems. Furthermore, these results indicate that these V-shaped H bonded structures are an easily obtained and attractive "testing bank", not only for the induction of different mesophases but also as a potential way to obtain different multifunctional 'banana' liquid crystals.

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