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Intramolecular hydrogen bond assisted planarization and self-assembly of simple disc-shaped molecules in mesophases†

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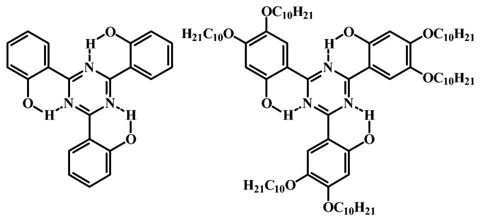
Two novel disc-shaped compounds (1, 2) with strong intramolecular hydrogen bonds were prepared and characterized; compound 2 showed a thermotropic mesophase as characterised by polarized optical microscopy, DSC and X-ray diffraction studies.

The design and synthesis of well-defined nanoscale architectures *via* self-assembly[1] and self-organization[2] is of great interest in materials research.[3] Weak interactions such as hydrogen bonding and van der Waals forces play a crucial role in controlling the molecular organization in liquid crystalline materials. Anisotropic dispersion forces are crucial and fundamental to the organization of liquid crystal phases. In addition, other potentially weak interactions such as hydrogen bonding have also been used to induce or modify mesomorphic behaviour.[4–7] In discotic supramolecular liquid crystals, intermolecular[8] or intramolecular hydrogen bonding[9,10] has been used to induce mesophase properties. It was our goal to design simple disc-shaped molecules with smaller cores formed through strong intramolecular hydrogen bonding and investigate the self-assembly in the mesophase.

Compounds **1** and **2** (Scheme 1) were synthesized (ESI†) using a Suzuki coupling reaction. 1,3,5-Trichlorotriazine was coupled with an unsubstituted or substituted phenylboronic acid molecule to yield compounds **1** and **2**, respectively.

The ^{1}H NMR spectra of compounds **1** and **2** showed sharp peaks due to the presence of phenolic –OH groups at 12.58 ppm in DMSO-d$_6$ (**1**) and at 13.25 ppm in CDCl$_3$ (**2**) (Fig. 1). A stable six-membered ring can be formed through intramolecular hydrogen bonds (see Scheme 1), which lead to the planarization of the aromatic core. Thus the observed downfield shift in the NMR peak of the phenolic –OH group in both compounds is due to intramolecular and not intermolecular hydrogen bonds.



Scheme 1 Molecular structures of the two disc-shaped molecules 2,4,6-tris(2-hydroxyphenyl)-1,3,5-triazine (**1**) and 2,4,6-tris(2-hydroxy-4,5-bis(decyloxyphenyl))-1,3,5-triazine (**2**). Potential hydrogen bonds are shown as dotted lines.

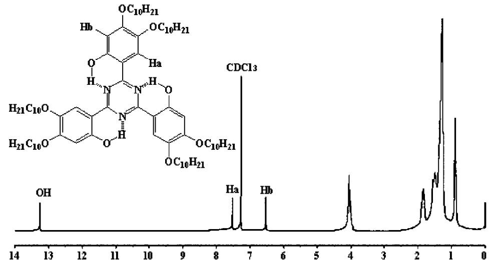


Fig. 1 ^{1}H NMR spectrum of compound **2** in CDCl$_3$ at room temperature.

To demonstrate the formation of intramolecular hydrogen bonds in compounds **1** and **2**, we synthesized a linear model compound **3** (Fig. 2) with similar hydrogen bond donor and acceptor moieties.

Compound **3** was synthesized (ESI†) using palladium (Pd) catalyzed coupling of diboronic acid obtained from 2,5-dibromo-1,4-dibenzyloxyhydroquinone and 2-bromopyridine. Single crystal X-ray diffraction studies‡ of the crystals obtained from toluene solution of compound **3** clearly revealed the presence of intramolecular hydrogen bonds between hydroxyl groups and pyridyl nitrogen atoms (Fig. 2B). The short distance between N and O atoms (2.56 Å), short N···H hydrogen bond (1.658 Å) and relatively long O–H bond (0.963 Å) indicate strong intramolecular hydrogen bond formation in the crystal lattice. The observed interplanar angle between the hydroquinol ring and the pyridine ring is very small (4.7°), which indicates planarization of the molecule (Fig. 2C). In the ^{1}H NMR spectrum of compound **3** in DMSO-d$_6$, solution, the peak due to the O–H proton was downfield shifted to 13.85 ppm, indicating strong hydrogen bond formation in solution. Since the NMR signals of –OH groups in compounds **1**, **2** and **3** are comparable in solution and the crystal lattice of compound **3** showed a planar structure, a planar geometry can be assigned to compounds **1** and **2**.

Thermal properties of the compounds were examined using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Both compounds showed high thermal stability in TGA measurements. Compound **1** showed a clear melting point at 315 °C with no mesophase properties. A preheated sample of compound **2** was used to run a DSC at a rate of 5 °C min^{-1} for heating and cooling cycles (Fig. 3). Upon heating, a distinctive transition from crystalline phase to mesophase was observed at 111 °C with an enthalpy change of 33.2 kJ mol^{-1}. Another exothermic peak observed at the clearing temperature of 173 °C (ΔH = 14.0 kJ mol^{-1}) indicated a transition from the mesophase to the isotropic phase. Compound **2** showed a broad mesophase range of *ca.* 62 °C.

The observed mesophase was fully characterized using polarizing optical microscopy (POM) and variable temperature X-ray diffraction studies. Compound **2** was heated to its

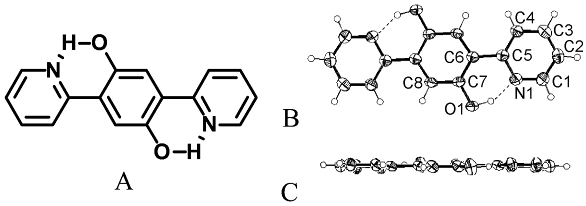


Fig. 2 Molecular structure of compound **3** (A) and its single crystal structure, top view (B) and side view (C). Hydrogen bonds are marked as dotted lines.

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† Electronic supplementary information (ESI) available: synthetic procedures for compounds **1**–**3** and crystallographic details for **3**. See http://www.rsc.org/suppdata/cc/b2/b201742c/

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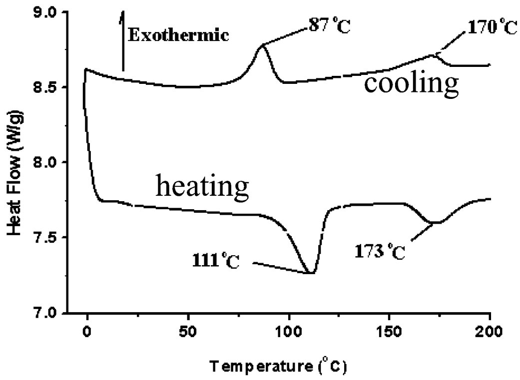
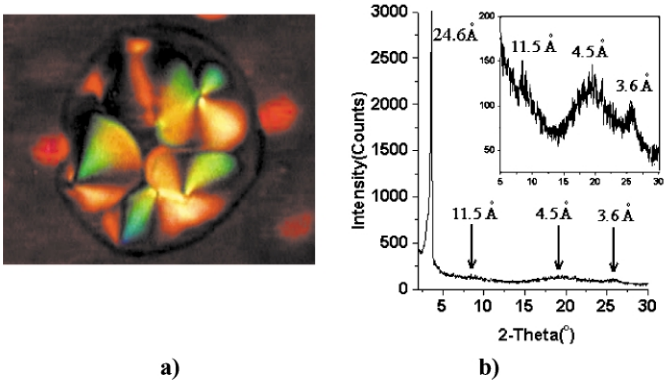


Fig. 3 DSC heating and cooling traces of compound **2** (5 °C min^{-1}).

clearing temperature (> 175 °C), where it became a transparent isotropic liquid. It was slowly cooled from the melt to room temperature at a rate of 1 °C min^{-1}. A strong birefringent, shearable fan-shaped texture was observed under crossed polarizers at 170 °C and persisted up to 87 °C (Fig. 4(a)).

The X-ray diffraction pattern (Fig. 4(b)) of compound **2** at 140 °C can be assigned as follows: 2.46 nm (10), 1.15 nm (20), 0.45 nm (liquid correlations between the molten side chain) and 0.36 nm (core to core).[11] Since the (10) peak of the 2D lattice is broad, it is not possible to identify the (11) peak position. From the optical texture and the X-ray diffraction data, it is difficult to rule out the various possibilities such as hexagonal and rectangular arrangements of molecules in the mesophase.[12,13]

In conclusion, we report the synthesis and characterization of simple disc-shaped molecules with mesophase properties induced by strong intramolecular hydrogen bonds. ^{1}H NMR spectra revealed intramolecular hydrogen bonding in all three compounds (**1**, **2** and **3**), similar to that observed in the crystal lattice of compound **3**. Thus a planar structure for compounds **1** and **2** is confirmed. Compound **2** showed mesophase characteristics as illustrated by DSC, POM and variable temperature X-ray diffraction studies. Further investigations with similar compounds are underway in our laboratory to elucidate the exact nature of the mesophase.



a) b)

Fig. 4 Characterization of the mesophase using polarized optical microscopy and X-ray diffraction studies: (a) optical texture at 160 °C, (b) X-ray diffraction pattern of compound **2** at 140 °C.

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Notes and references

‡ *Crystal data* for compound **3**: crystallized from toluene, $C_{16}H_{12}N_2O_2$, M = 264.28, monoclinic, space group $P2_1/n$, a = 6.0888(4), b = 5.6584(4), c = 17.924(1) Å, V = 617.48(7) Å^3, Z = 2, D_c = 1.421 g cm^{-3}, μ(Mo-Kα) = 0.096 mm^{-1}, T = 223 K, The structure, refined on F^2, converged for 1083 unique reflections (2979 measured, R_{int} = 0.055) to give $R1$ = 0.043 for which $I > 2\sigma(I)$ and $wR2$ = 0.122 for all reflections and goodness-of-fit = 1.003. CCDC reference number 179960. See http://www.rsc.org/suppdata/cc/b2/b201742c/ for crystallographic data in CIF or other electronic format.

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