Mesophases of discotic liquid crystals:influence of the lateral chain architecture

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Considerable scientific and technological effort has been recently devoted to discotic liquid crystals as potential candidates for applications as pressure sensors, light emitting diodes (LED), solar cells (solar battery chargers, flexible solar panels), field effect transistors, anisotropic conductors and display devices due to their capability to self-organize in columns. The columnar mesophase structure is determined not only by the structure of the molecular core, but also by the aliphatic side chains. In this work, the influence of the lateral aliphatic chains architecture is explored. Two new discotic molecules (Figure 1), based on a hazaazatryphenylene core (HATCONHR), having either six long linear alkyl chains (**1a**) or six short branched lateral chains (**1b**) have been synthesised. The thermotropic properties and the structure of the mesophases were studied by Polarized Optical Microscopy (POM), Differential Scanning Calorimetry (DSC) and Temperature-Resolved X-ray diffraction.

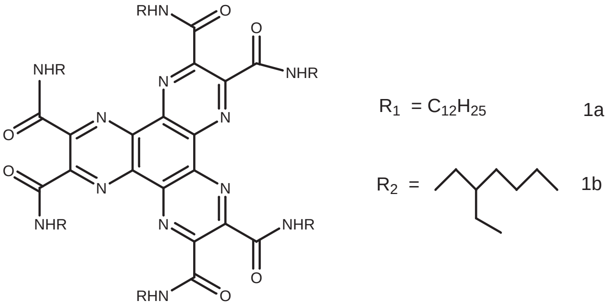

Figure 1: Molecular structure of the HATCONHR derivatives

For the molecule **1a** an endothermic peak is observed at 47°C and the associated enthalpy change is approx 24 J/g. The molecule **1b** present only a weak transition at about 176°C and the enhthalpy change is only 0.7 J/g. POM observations revealed birefringence of **1a, 1b** discotic molecules in the whole temperature range under investigation (RT up to the degradation temperature, approx 250°C), but no specific textures were observed.

X-ray diffraction experiments were performed on the X33 camera of the European Molecular Biology Laboratory at the storage ring DORIS III of the Deutschers Elektronen Syncrhroton (DESY), Hamburg. The X-ray diffraction patterns of the molecule **1a** (Figure 2) show a set of three reflections in the small-angle region, with reciprocal spacings being given by the ratio $1{:}\sqrt{3}{:}2$. These peaks are assigned to the (100), (110), (200) reflections of the hexagonal lattice [1]. In the wide-angle region, X-ray diffraction data displays two peaks. The first broad peak corresponds to the characteristic distance between the aliphatic side chains. The second one is assigned to the (001) reflection and reflects the intra-columnar stacking of the disks.The lattice parameter **1a**, was found to vary from 29.65 to 30.4 Å and increases by 5% in the phase transition region. This phase transition is probably due to the variation of the hydrogen bonds strength leading to the change of the lateral chain's conformation. Inter-columnar stacking of 3.2 Å was determined, which is, to our knowledge, the smallest value reported in the literature [2]. The calculated thermal expansion coefficients are $1.6.10^{-4}$ K^{-1} for the intra-columnar distance, $2.3.10^{-4}$ K^{-1} for the inter-columnar spacing and $3.2.10^{-4}K^{-1}$ for the characteristic distance between the aliphatic side-chains. The thermal expansion of the mesophase is, therefore, strongly anisotropic [3]

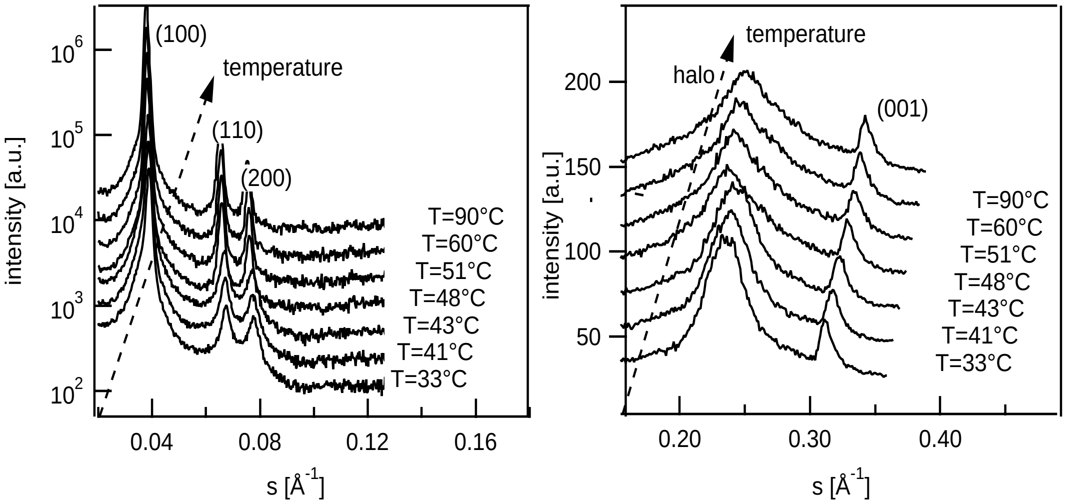

Figure 2: X-ray diffraction patterns acquired with two position sensitive detectors during heating at 10°C/min between 30 and 90°C.

The mesophase presented by compound **1b** can be indexed according to the oblique mesophase and the phase transition observed in the DSC at 176°C corresponds to a change in the symmetry of the unit cell (monolinic cell, 4P21-monoclinic cell, 7PA) [4]. It is worth noted that the intra-columnar order observed in the case of compound **1a** was not observed for compound **1b**.
The investigations have revealed that both the structure of the columnar phases of discogens, as well as the phase transition temperatures can be strongly modified for HATCONHR derivatives via the arhitecture of the lateral aliphatic chains.

References

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