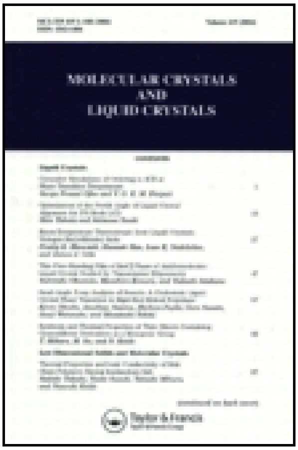

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Mesomorphic Behaviour of Hemin Based Porphyrin Liquid Crystals: Structure and Temperature Dependent Intracolumnar Order

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Mesomorphic Behaviour of Hemin Based Porphyrin Liquid Crystals: Structure and Temperature Dependent Intracolumnar Order

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A series of porphyrin liquid crystals derived from natural product hemin has been synthesized and its mesomorphic behaviour has been characterized. Free base compounds show a temperature dependent mesophase intracolumnar order, feature that is not observed in the related zinc compounds. This behaviour is tentatively attributed to conformational changes of the flexible parts of the molecule. Semiempirical calculations and energetical considerations that seem to support this hypothesis are presented.

Keywords: discotic liquid crystals; intracolumnar order; porphyrin; semiempirical calculations

INTRODUCTION

The porphyrin ring has been succesfully used as an aromatic core for the preparation of mesogenic compounds [1], specially for the synthesis of discotic molecules [2]. Its liquid crystal behaviour can be tuned either through the number and length of the side alkyl chains or through the substitution pattern (*meso*- or β-substitution). Thus, a wide variety of mesophases can be obtained, from nematic (N) to columnar (Col_x). But the synthesis of this kind of compounds usually proceeds through the condensation of pyrroles and aldehydes [3], which implies low yields and difficult purification. In the last years our group has been interested in the synthesis of liquid crystals from

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natural and commercially available hemin (ferriprotoporphyrin IX chloride, **1**) [4,5], in which the porphyrin ring is already formed. This paper presents a series of hemin based compounds that display hexagonal columnar mesophases.

EXPERIMENTAL

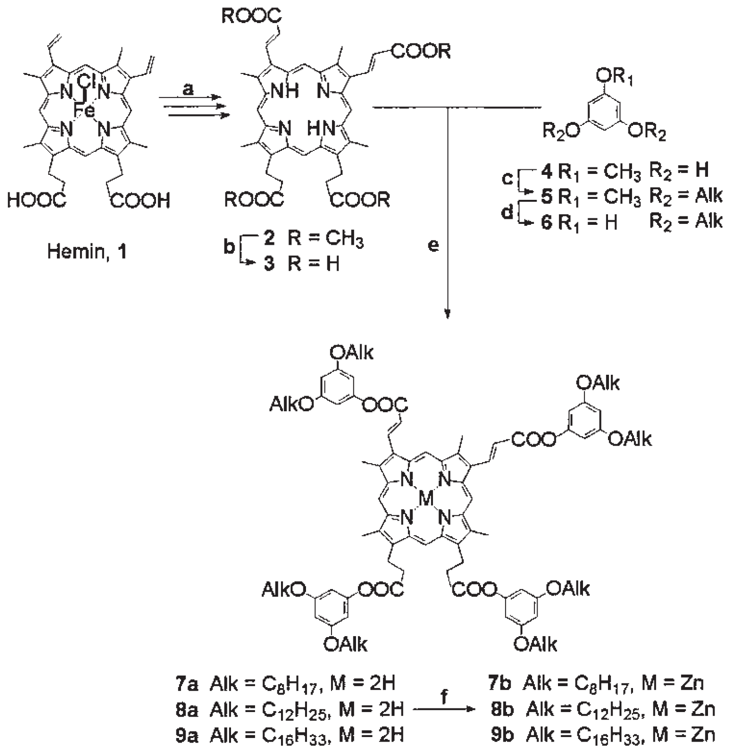
The synthesis of the hemin based liquid crystals was carried out following the previously reported procedure [5]. POM observation was performed using a Nikon Eclipse polarizing microscope equiped with a Linkam THMS 600 hot stage and a Linkam CI 93 programmable temperature controller. DSC were recorded using a Mettler-Toledo DSC821 module at a scan rate of 10 $^{\circ}\mathrm{C\,min^{-1}}$ under a nitrogen flow. X-Ray diffractograms were recorded using either an image plate with Kiesig geometry or a Debye-Scherrer Inel CPS-120, with their corresponding temperature controlling devices. AM1 semiempirical calculations were performed on a PC computer using the GaussView 3.0/Gaussian 03 Revision B.04 software package [6] with the default optimization parameters (Berny optimization algorithm without initial generation of force constants).

SYNTHESIS

The synthesis of liquid crystalline molecules from hemin is briefly described in Scheme 1 [5]. Hemin (**1**) was transformed into known compound **2** using the already known synthetic sequence [7]. Hydrolysis of the four methyl esters allowed the esterification of the 3,5-dialkyloxyphenols, obtained from 5-methoxyresorcinol (**4**) through etherification of the free hydroxy groups and selective cleavage of the methyl aryl ether. Formation of the aryl esters was carried out by first generation of the acyl chloride and reaction with the phenol in basic media, followed by a second esterification step using DCC as the coupling reagent. Metalation of the free base compounds (**7a–9a**) with zinc acetate in hot DMF furnished the corresponding zinc porphyrins (**7b–9b**).

LIQUID CRYSTAL BEHAVIOUR

The mesomorphism of the synthesized molecules was studied by means of polarized optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). Compounds were found to be liquid crystalline in wide temperature ranges that include room temperature (Fig. 1). For all the compounds the mesophase type



a. 4 steps, 71% overall, c. KOH, DME/H_2O, r.t., 92%, c. AlkBr, K_2CO_3, KI, DMF, 120 °C, 55-91%, d. EtSH, NaH, DMF, reflux, 70-77%, e. 1) $SOCl_2$, THF, r.t., 2) DMAP, Et_3N, CH_2Cl_2, r.t., 3) DCC, DMAP, CH_2Cl_2, r.t., 36-45% overall, f. $Zn(AcO)_2$, DMF,100-120 °C, 90-98%.

SCHEME 1 Synthesis of the porphyrin liquid crystal compounds based on hemin.

was determined to be hexagonal columnar (Col_h): the X-ray diffractograms showed a sharp peak in the low angle region and minor peaks at $1/\sqrt{3}$, $1/\sqrt{4}$, $1/\sqrt{7}, \ldots$ of the reciprocal distance assigned to the first peak, in addition to a broad peak at $2\theta = {\sim}20^\circ$ due to the molten alkyl side chains.

However, in addition to the influence that alkyl chain length and metalation could have on melting and clearing points, a further feature was noticed. While zinc compounds showed a highly ordered columnar structure in their whole mesophase range, free base compounds displayed two different mesophases differing in the intracolumnar order. At high temperatures, the XRD pattern showed a

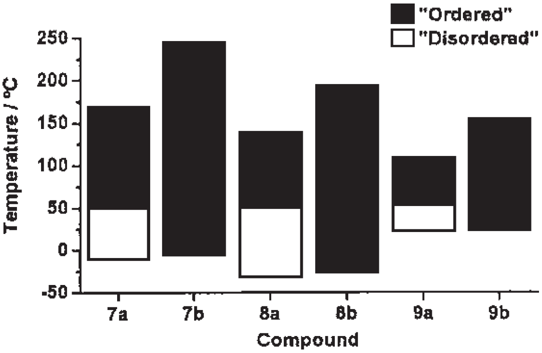


FIGURE 1 Mesomorphic temperature ranges of the synthesized compounds.

3.6 Å reflection indicative of a regular intracolumnar stacking. This reflection was not observed in the low temperature XRD pattern. The transition between "ordered" and "disordered" mesophases, at *ca.* 50°C, could be observed in the DSC measurements and also in the POM observations as a sudden change in the birefringence of the samples [5].

Apart from the change in the 3.6 Å reflection, there were not great differences between the structures of the "ordered" and "disordered" mesophases, as judged from the DRX experiments [5]. The following hypothesis is then proposed: a rearrangement of the phenyl propionate chains of the molecules is responsible of the "ordered"-"disordered" transition, while the two acrylate chains are expected to stay coplanar to the porphyrin ring due to the intramolecular π-conjugation. Molecules in the "ordered" mesophase would have a planar conformation allowing good columnar stacking, but when the temperature is lowered, the propionate chains would rearrange towards a more stable conformation with a non planar shape, partially breaking the π-π stacking interactions between neighbouring molecules and reducing the intracolumnar order of the stack. In metalated porphyrins, the proposed rearrangement does not take place because the lower energy of the non planar coformation could not compensate the loss of stabilizing intermolecular π-π interactions, which are stronger due to the presence of the zinc atom in the centre of the porphyrin core [8].

COMPUTATIONAL CALCULATIONS

To test our hypothesis for the "ordered"-"disordered" transition, *in vacuo* AM1 semiempirical geometry optimizations were carried out

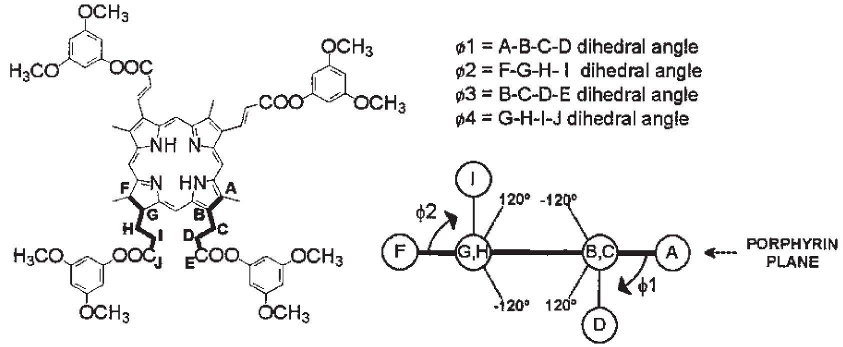


FIGURE 2 Structure of the methyl analogue used for the computational calculations, with the dihedral angles used for the propionic ester chain optimizations.

on the free base methyl analogue (M = 2H, Alk = CH_3) of the liquid crystal compounds. If the hypothetic planar structures were found to be away from the optimal conformations, the "ordered" mesophase would only exist if any kind of stabilizing factor (enhancement of intermolecular interactions and/or increase of the thermal energy) was capable to overcome the energetic cost; if there was not such overcome, molecules should tend to adopt the non planar optimal conformations that favour the formation of the "disordered" mesophase.

The conformational preferences of the molecule were explored through the optimization of geometries covering the possible conformations of

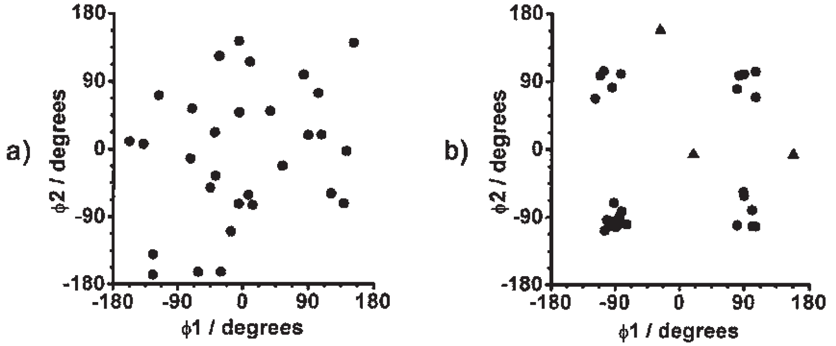


FIGURE 3 a) Initial conformations used in structure optimizations ($\phi 1$ and $\phi 2$ angles); b) AM1 optimized conformations ($\phi 1$ and $\phi 2$ angles). Filled circles: energetical optimum structures; filled triangles: planar structures.

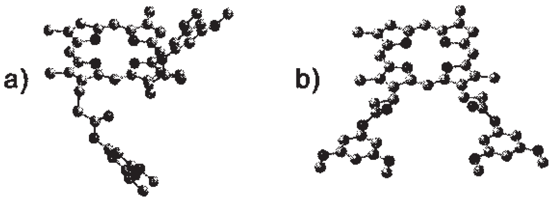


FIGURE 4 Examples of AM1 optimized structures. a) Out of plane conformation ($\phi1 = 103.1^\circ$, $\phi2 = -82.9^\circ$, $\phi3 = 89.7^\circ$, $\phi4 = 94.7^\circ$); b) Planar conformation ($\phi1 = -6.4^\circ$, $\phi2 = 19.3^\circ$, $\phi3 = 160.4^\circ$, $\phi4 = -175.3^\circ$). Acrylate ester chains have been omitted for clarity.

the propionic ester chains. Starting structures were generated by the random choice of dihedral angles $\phi1$, $\phi2$, $\phi3$ and $\phi4$ (Fig. 2). Structures showing clashes between chains were discarded, specially those with the ($+120^\circ \leq \phi1 \leq +180^\circ$, $-180 \leq \phi2 \leq -120^\circ$) and the ($-180^\circ \leq \phi1 \leq -120^\circ, +120^\circ \leq \phi2 \leq +180^\circ$) values, for which clashes between methylene groups noted as D and I in Figure 2 are very significant. The initial conformations subjected to optimization are presented in Figure 3a.

Furthermore, planar geometries were also optimized with the restriction that the five aromatic rings (four phenyl rings, one porphyrin ring) should stand into the same plane, resembling the most favoured conformation of the molecules for the "ordered" mesophase.

The results obtained after the optimizations are presented in Figure 3b. As can be seen, the propionic ester chains tend to an out-of-plane conformation, with dihedral angles $\phi1$ and $\phi2$, which mainly drive the orientation of the chains, always being around $\pm 90^\circ$. On the other side, the planar conformations have very different dihedral angle values: all of them have a value around 0 or $\pm 180^\circ$. Examples of optimum and planar conformations are shown in Figure 4.

ENERGETIC CONSIDERATIONS

One of the conclusions that can be withdrawn from the AM1 semiempirical calculations is that the planar conformations of the molecule are not absolute energetic minimums. In fact, optimal structures have a calculated energy varying from –1088 to –1098 $\text{kJ} \cdot \text{mol}^{-1}$, while that of the planar structures is estimated between –1064 and –1069 $\text{kJ} \cdot \text{mol}^{-1}$, this is, 19–34 $\text{kJ} \cdot \text{mol}^{-1}$ higher.

Given these results, planar conformations of molecules in the "ordered" mesophase must be stabilized by some kind of intermolecular interactions, since they do not look able to permanently keep this geometry by themselves. If π stacking interactions are considered as the main intermolecular stabilizing contributions, the porphyrin-porphyrin stacking and two possible phenyl-phenyl stackings must be accounted for each molecule in order to balance the loss of stability when bringing the molecules away from the energy optimum.

From solution NMR studies, porphyrin-porphyrin interactions have been estimated to be up to $18\,\mathrm{kJ\cdot mol^{-1}}$ in free base molecules [9], and up to $48\,\mathrm{kJ\cdot mol^{-1}}$ in zinc porphyrins [10]. *In vacuo* computational calculations [11] suggest that phenyl-phenyl stacking can have an up to $10\,\mathrm{kJ\cdot mol^{-1}}$ stabilizing energy. Then the overall π-π stacking contributions can be estimated to be up to $38\,\mathrm{kJ\cdot mol^{-1}}$ in free base compounds and up to $68\,\mathrm{kJ\cdot mol^{-1}}$ in metalated ones. The first value is very similar to the energetic cost of the planar structure, while the second value clearly surpasses it.

The energetic data here presented seem to support the hypothesis for the “ordered”-“disordered” transition. Two factors, namely conformation of the propionic ester chains and intermolecular π-π stacking, would control the intracolumnar ordering and would oppose each other. In the free base compounds, the two factors might balance allowing variation in the intracolumnar order depending on temperature. At low temperatures molecules would tend towards conformational energetic minima which correspond to non planar structures. The formed columar stacks would not have a high degree of intracolumnar order due to the steric hindrance of the non planar conformations that do not allow an efficient intermolecular stacking. On the other hand, at high temperatures, the conformational restrictions of the planar structure would become less important and could be balanced by the improved intermolecular π-π stacking. Then a more ordered mesophase should be observed. In zinc porphyrins, stronger intermolecular stacking and therefore a higher stabilizing energy would allow the molecules to stay in the planar structure in the whole mesophase range. Rearrangement of the propionate chains would not be favoured since it would not balance the loss of the intermolecular interactions. Therefore only the “ordered” mesophase would be formed.

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