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The first liquid-crystalline, expanded porphyrins†

Jonathan L. Sessler,*^{*a*} Wyeth Callaway,^{*a*} Stephen P. Dudek,^{*a*} Richard W. Date,^{*b*} Vincent Lynch^{*a*} and Duncan W. Bruce*^{*b*}

 ^a Department of Chemistry and Biochemistry, Institute for Cellular and Molecular Biology, The University of Texas at Austin, Austin, TX 78712-0165, USA. E-mail: sessler@mail.utexas.edu; Fax: 1-512-471-7550
^b Department of Chemistry, University of Exeter, Stocker Road, Exeter, UK EX4 4QD. E-mail: d.bruce@exeter.ac.uk; Fax: 44 1392263434

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Aliphatic derivatives of hydrazinophyrin, a new type of tetrapyrrolic macrocycle prepared by the condensation of 2,5-diformylpyrroles with hydrazine, exhibit liquid crystalline properties as judged from polarising optical microscopy; these hydrazinophyrins appear to be the first mesogens derived from an expanded porphyrin core.

Functionalised liquid crystals are key components in displays, optoelectronic devices, and a wide variety of optical sensors.1 Although most of the liquid crystals in current use are calamitic, considerable effort has been devoted to investigating the properties of discotic mesogens. Two of the more popular cores for discotic mesogens are the tetrapyrrolic macrocycles porphyrin² and phthalocyanine,³ and many groups have used these cores to prepare a variety of liquid crystals with columnar mesophases. This success has led us to consider using expanded porphyrins to produce liquid crystals. Expanded porphyrins are oligopyrrolic macrocycles that have ring sizes larger than porphyrin, incorporate more than four heterocyclic subunits, or have a greater number of π -electrons within their (generally) conjugated peripheries.⁴ Much of the interest in expanded porphyrins comes from their unusual optical properties (e.g., red-shifted absorption bands). However, expanded porphyrins have also been shown to coordinate cations of the transition metal,5 lanthanide,6 and actinide7 series, as well as acting as novel anion binding agents.^{4,8} Expanded porphyrins have thus attracted attention in a range of application areas, that run the gamut from optical sensors^{7,8} to pharmaceuticals.⁹ To the best of our knowledge, however, expanded porphyrins have not yet been incorporated into liquid crystals. As a first step towards developing expanded porphyrin-based liquid crystals, we present here the synthesis of a new tetrapyrrolic macrocycle, 'hydrazinophyrin' (1).

Hydrazinophyrins **1a–d** were synthesised by the acidcatalysed condensation of 3,4-dialkoxy-2,5-diformylpyrroles¹⁰ with one equivalent of hydrazine (Scheme 1), and were fully characterised by standard techniques. Yields for this key macrocyclisation step ranged from 30 to 60%. In our hands, only the '4 + 4' condensation product was observed, although other groups have obtained only the '2 + 2' product under related conditions.^{11,12}



† Electronic supplementary information (ESI) available: synthetic procedures, hydrazinophyrin characterisation, and crystal structure data. See http://www.rsc.org/suppdata/cc/b3/b307901p/ Hydrazinophyrins are dark red in solution with high extinction coefficients typical of fully conjugated expanded porphyrins. For example, an extinction coefficient of 3×10^5 cm⁻¹ M⁻¹ is seen for the 419 nm Soret-like absorption of **1a** in CH₂Cl₂. On the other hand, the free-base form of hydrazinophyrin contains a 32 π -electron periphery and is therefore best viewed as being non-aromatic or, possibly anti-aromatic, as judged by the small downfield shifts of the pyrrolic NH protons. Techniques for calculating and mapping ring currents in porphyrins and expanded porphyrins are now available¹³ and could, in due course, be used to analyse the electronic nature of **1a** in more detail.

Specific insights into the structure of hydrazinophyrin came from an X-ray diffraction analysis of the free base of **1a**.[‡] The resulting structure (Fig. 1) revealed the presence of two molecules of methanol bound inside the central macrocyclic cavity. As expected for a fully conjugated system, the macrocycle is planar, with average torsional angles of $177.3 \pm$ 1.3° about the four hydrazines. The hydrazine units in the macrocycle are all in a *trans* configuration, while the system as a whole possesses C_2 symmetry. Proton NMR spectroscopy indicates that **1a** and its homologues retain a C_2 symmetry element in solution; in particular, two of the four imine signals and one of the two pyrrolic NH signals are shifted upfield



Fig. 1 Top and side views of the X-ray crystal structure of 1a. Two molecules of methanol are bound in the cavity. Thermal ellipsoids are scaled to the 50% probability level.

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relative to the others in $CDCl_3$. These shifts in the NMR spectrum lead us to suggest that two of the four pyrrolic protons are involved in intramolecular hydrogen bonding involving adjacent imine nitrogens. Consistent with this conclusion is the finding that in DMSO- d_6 , the NMR spectrum shows degenerate pyrrolic proton and imine proton signals, presumably because this solvent serves to break up the internal hydrogen bonding pattern.

The structure of **1a** led us to consider that hydrazinophyrin might represent a useful core for the generation of discotic liquid crystals. To test this hypothesis, three different long-chain 3,4-dialkoxy-2,5-diformylpyrroles were synthesised using slightly modified literature procedures.¹¹ These pyrroles were then condensed with hydrazine to form the corresponding hydrazinophyrins bearing eight alkoxy chains on the β -pyrrolic positions containing six (**1b**), ten (**1c**), and fourteen (**1d**) carbon atoms, respectively.

Compounds **1b** to **1d** were studied by polarising optical microscopy. It was found that they were solid at room temperature and rather immobile, although it was difficult to tell whether they were crystalline. However, at around 50 °C they became more mobile and were easy to spread around the slide some ten degrees later. The lack of a defined event in the DSC of these compounds suggests that the solid phase may then be a glass. On heating above 120 °C, all compounds started slowly to decompose and so it was not possible to define a meaningful clearing point, although most were entirely isotropic/decomposed by around 160 °C. Once more, no event was observed by DSC, supporting this assumption.

In terms of mesomorphism, it was apparent that once the materials had softened, the compound was in the mesophase as evidenced by the mobility and general birefringence observed by microscopy. The decomposition of the materials at elevated temperatures meant that textures could not be obtained on cooling the isotropic phase as is commonly carried out. Therefore the samples were heated to 90–100 °C, spread out and annealed for periods of around 1 h. In this way, micrographs such as that observed in Fig. 2 were obtained, showing clearly that the material is in a columnar phase, although it is not possible to determine the exact symmetry from this micrograph.

These systems appear to be the first reported expanded porphyrin-derived liquid crystals. Preliminary work suggests



Fig. 2 Polarising photomicrograph of the columnar mesophase of 1b taken at 95 $^\circ C$ on heating and after annealing for around 1 h.

that the protonated forms of **1a** are able to bind anions, such as chloride, with high affinity in aprotic media. It may be possible to incorporate liquid crystalline forms of hydrazinophyrin as an integral component in anion-sensing detectors. Separately, compounds **1b–d** define a useful starting point for the development of other types of expanded porphyrin-derived liquid crystals.

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Notes and references

‡ *Crystal data* for **1a**: (thin needles, $0.41 \times 0.11 \times 0.09$ mm): C₁₇H₂₂N₆O₅, *M* = 390.41, monoclinic, *a* = 7.4409(1), *b* = 13.4669(2), *c* = 19.1745(4) Å, *a* = 90, β = 90.1340(8), γ = 90°, *T* 153 K, *U* = 1921.39(6) Å³, *Z* = 4, μ (Mo-Kα) = 0.71073 Å, 8262 reflections collected, 4363 independent reflections (*R*(int) = 0.0264), *R*₁ = 0.0654, 0.1008 (all data), *wR*(*F*²) = 0.1412, 0.1528 (all data). CCDC 216305. See http://www.rsc.org/suppdata/ cc/b3/b307901p/ for crystallographic data in CIF or other electronic format.

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