

## Macrocyclic Liquid Crystals from Functionalised Thioether Crowns: the Single-crystal X-Ray Structures of *cis*- and *trans*-R<sub>2</sub>[14]aneS<sub>4</sub> (R = O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>OMe-4)

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The syntheses of *cis* and *trans* oligobenzoate ester derivatives R<sub>2</sub>[14]aneS<sub>4</sub> are described; the structures of the *cis* and *trans* derivatives for R = O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>OMe-4 are dominated by intermolecular packing between benzoate ester units, while the *cis* and *trans* derivatives for R = O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>OC<sub>8</sub>H<sub>17</sub>-4)-4 both show nematic mesophases.

The majority of macrocyclic liquid crystals that have been reported are based upon phthalocyanines and porphyrins.<sup>1</sup> There are few published reports on the synthesis of macrocyclic liquid crystals from functionalised saturated aza systems,<sup>2–5</sup> and none from homoleptic derivatised thioether crowns.<sup>6</sup> Lehn<sup>2</sup> and Ringsdorf<sup>3</sup> have reported the formation of tubular mesophases using functionalised hexaaza macrocycles confirming that polyaza macrocycles can indeed form mesophases incorporating ion channels. More recently, Lattermann and coworkers have reported functionalised [14]aneN<sub>4</sub> and [9]aneN<sub>3</sub> species that form discotic mesophases.<sup>4</sup> Unlike aza macrocycles which can be readily functionalised at N-donors, functionalisation of homoleptic thioether crowns has to be undertaken at the C-backbone.<sup>7,8</sup> We report herein the first examples of mesophase formation from derivatised homoleptic thioether crowns.

Our approach has been based on the separation of *cis* and *trans* (HO)<sub>2</sub>[14]aneS<sub>4</sub><sup>8</sup> by fractional crystallisation and subsequent esterification with mesogenic oligobenzoate ester groups. The advantage of this methodology is that it allows the direct synthesis of stereochemically pure products.<sup>6</sup> A range of oligobenzoate ester groups was prepared by coupling of aryl acid chlorides with phenols in the presence of DMAP [DMAP = 4-(*N,N'*-dimethylamino)pyridine].<sup>9</sup> Esterification of (HO)<sub>2</sub>[14]aneS<sub>4</sub> was achieved either by reaction with carboxylic acids in the presence of toluene-*p*-sulfonic acid-pyridine-DCC<sup>10</sup> (DCC = *N,N'*-dicyclohexylcarbodiimide), or by reaction with the anhydrides. This led to the desired macrocyclic diesters R<sub>2</sub>[14]aneS<sub>4</sub> (Fig. 1) in overall yields of some 40–80%.

In order to determine the packing and the conformation of the macrocyclic crown in these polyphenylester derivatives, crystals of both *trans*- and *cis*-R<sub>2</sub>[14]aneS<sub>4</sub> (R = O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>OMe-4) were grown from CH<sub>2</sub>Cl<sub>2</sub>-EtOH and CH<sub>2</sub>Cl<sub>2</sub>-acetone, respectively. The single crystal X-ray structure<sup>‡</sup> of the *trans* isomer **1** shows [Fig. 2(a)] the phenyl rings lying orthogonal to the plane of the macrocyclic ring which adopts a [3434] conformation, as observed for [14]aneS<sub>4</sub> as the

metal-free ligand.<sup>11</sup> The packing in the solid state is dominated by stacking of benzoate ester units [Fig. 2(b)]. The single-crystal X-ray structure of the *cis* isomer **2** also shows [Fig. 3(a)] the phenyl rings orthogonal to the general plane of the macrocyclic ring. However, for this isomer the crown thioether adopts a distorted [223223] conformation in which the ring is bent round to form a calix-type structure. Interestingly, a similar conformation is observed for [14]aneS<sub>4</sub> in the tetrahedral Cu<sup>I</sup> complex [Cu([14]aneS<sub>4</sub>)]<sup>+</sup>.<sup>12</sup> The distortion of the crown ring to a [223223] conformation in **2** enables the *cis*-functionalised phenyl rings to adopt positions as far apart from one another as possible on opposite sides of the thioether ring. This is similar to the positions of the benzoate ester moieties in the *trans* isomer **1**. Thus, in these structures the conformation of the macrocyclic ring in the solid state appears to be determined by interactions between the aromatic rings of the benzoate ester groups [Fig. 3(b)].<sup>13</sup> For **1**, ring–ring C–C distances vary from 3.763 to 3.839 Å, while for **2** the variation is 3.516–3.856 Å.

In trying to generate mesomorphic derivatives of (HO)<sub>2</sub>[14]aneS<sub>4</sub> we decided to investigate systematically diesters of mono- di- and tri-benzoate esters, especially as there was evidence that porphyrins could be substituted in the 5 and 15 positions with alkoxyphenyl groups to generate mesomorphic compounds.<sup>14</sup> Both triester derivatives **3** and **4** led to mesomorphic species (Scheme 1). Thus, the nematic phase, readily identified by its classical *Schlieren* texture, was monotropic for the *trans* derivative **3** (Fig. 4) and enantiotropic for the *cis* derivative **4**, although clearing was accompanied by extensive decomposition at ca. 240 °C in the latter. Clearly, these transition temperatures are rather higher than we would wish, and we are now pursuing strategies to lower crystal lattice energy and transition temperatures.

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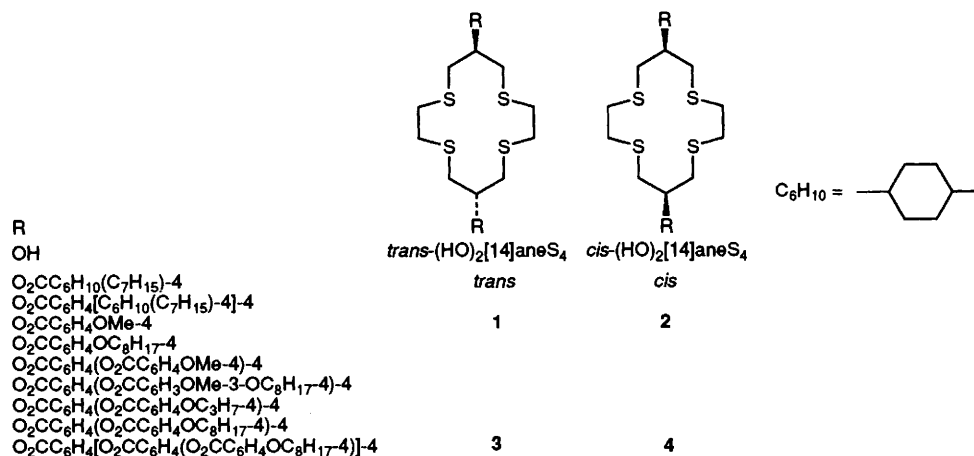
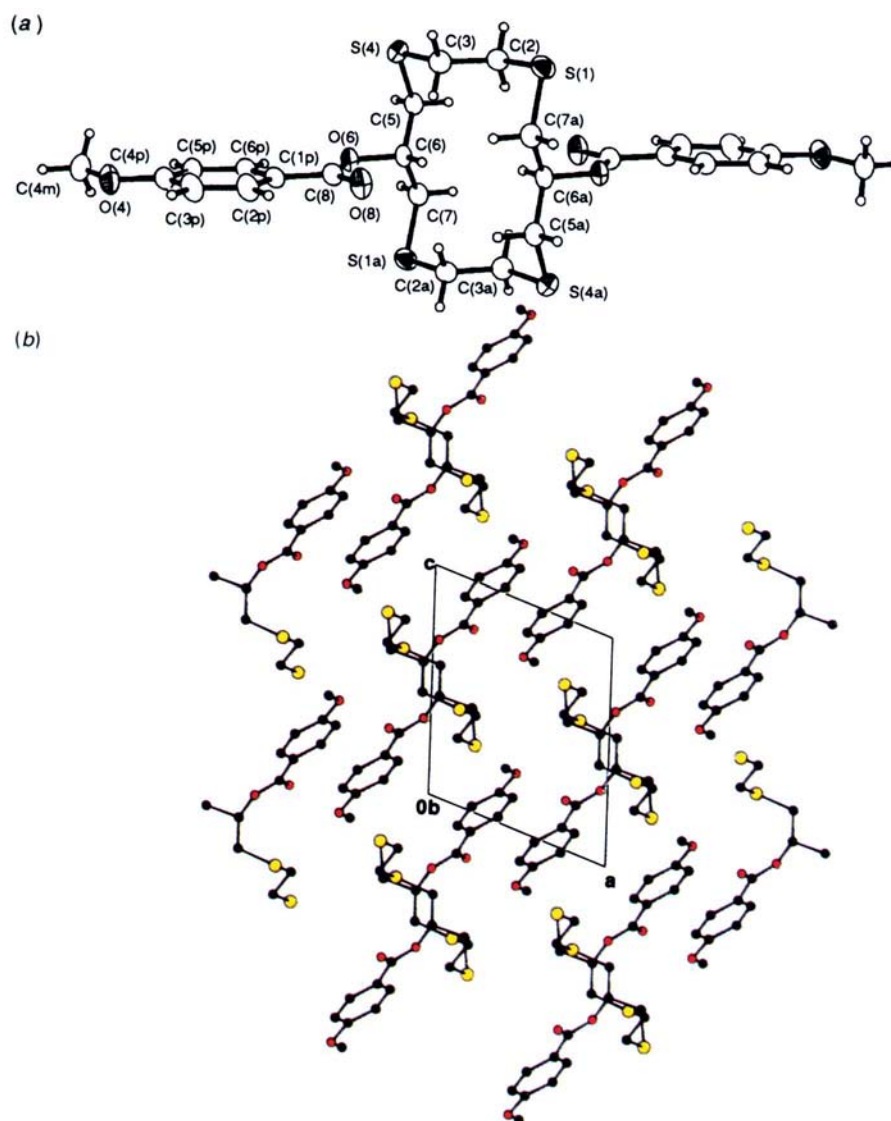
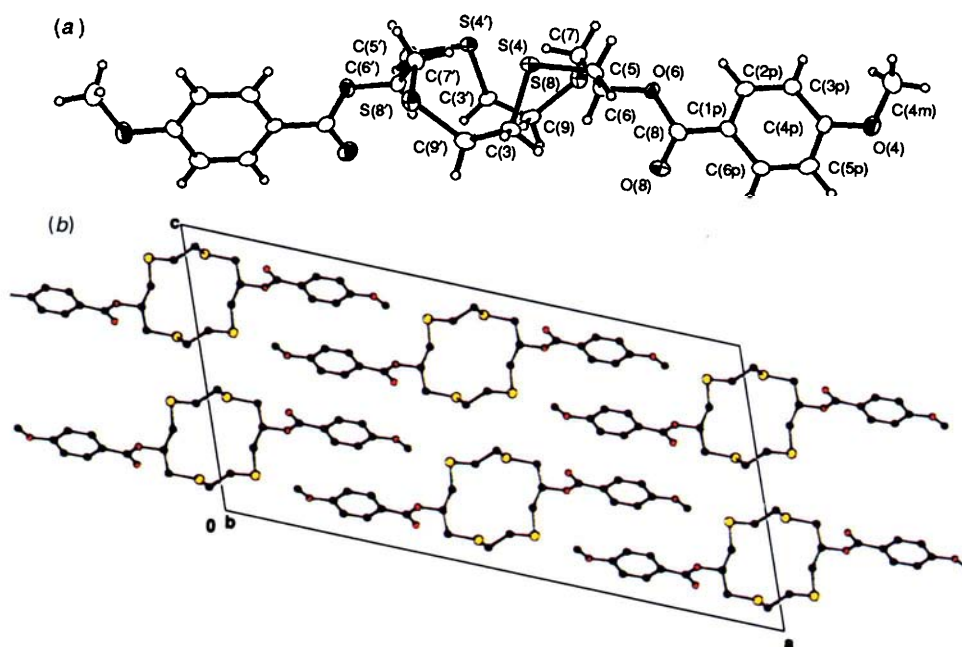


Fig. 1 Oligobenzoate ester derivatives of [14]aneS<sub>4</sub>



**Fig. 2** View of the structure (a) and packing (b) of *trans*-R<sub>2</sub>[14]aneS<sub>4</sub> (R = O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>OMe-4) **1** with numbering scheme adopted. C: black O: red S: yellow



**Fig. 3** View of the structure (a) and packing (b) of *cis*-R<sub>2</sub>[14]aneS<sub>4</sub> (R = O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>OMe-4) **2** with numbering scheme adopted. C: black O: red S: yellow

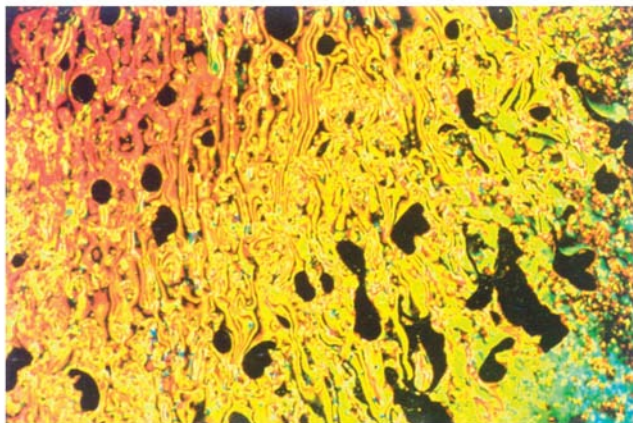
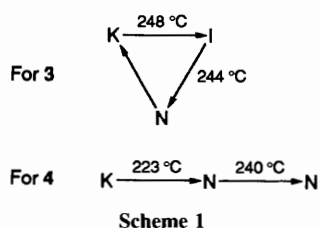


Fig. 4 Plate of nematic mesophase of 3



### Footnote

† D. W. B. is Sir Edward Frankland Fellow of the Royal Society of Chemistry, 1994/95.

‡ Crystal data for *trans*-C<sub>26</sub>H<sub>32</sub>O<sub>6</sub>S<sub>4</sub> **1**, *M* = 568.8, triclinic, space group *P* $\bar{1}$ , with *a* = 8.2681(6), *b* = 9.2300(7), *c* = 10.1136(7) Å,  $\alpha$  = 102.633(5),  $\beta$  = 109.494(4),  $\gamma$  = 92.192(5)°, *V* = 704.7(3) Å<sup>3</sup> [from 2 $\theta$  values of 16 reflections measured at  $\pm\omega$  ( $2\theta$  = 30–32°,  $\lambda$  = 0.71073 Å), *T* = 295 K], *Z* = 1 (implying that the molecule lies across a crystallographic inversion centre), *D<sub>c</sub>* = 1.340 g cm<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 0.375 mm<sup>-1</sup>. A colourless lath (0.80 × 0.40 × 0.10 mm) was mounted on a Stoe Stadi-4 four-circle diffractometer. Data collection using Mo-K $\alpha$  X-radiation ( $\lambda$  = 0.71073 Å) gave 2556 absorption-corrected reflections [A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr. Sect. A*, 1968, **24**, 351] to  $2\theta_{\text{max}}$  = 50°, 2476 unique (*R<sub>int</sub>* 0.058), of which 1625 with *F* ≥ 4 $\sigma$ (*F*) were used in all calculations. Automatic direct methods [SHELXS-86: G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 1990, **46**, 467] located all non-H atoms, which were then refined anisotropically. H-atoms were located from a  $\Delta F$  synthesis and thereafter included in calculated positions [SHELXTL/PC: G. M. Sheldrick, University of Göttingen, 1990; Siemens Analytical X-Ray Instruments Inc., Madison, Wisconsin, USA]. At final convergence, *R* = 0.0338, *wR* = 0.0373, *S* = 1.470 for 165 parameters and the final  $\Delta F$  synthesis showed no feature beyond  $\pm 0.19$  e Å<sup>-3</sup>.

For *cis*-C<sub>26</sub>H<sub>32</sub>O<sub>6</sub>S<sub>4</sub> **2**, *M* = 568.8, monoclinic, space group *C2/c*, with *a* = 32.595(21), *b* = 5.349(3), *c* = 16.418(9) Å,  $\beta$  = 111.19(5)°, *V* = 2669(3) Å<sup>3</sup> [from 2 $\theta$  values of 27 reflections measured at  $\pm\omega$  ( $2\theta$  = 15–32°,  $\lambda$  = 0.71073 Å), *T* = 150 K], *Z* = 4 (implying that the molecule lies across a two-fold symmetry element), *D<sub>c</sub>* = 1.415 g cm<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 0.396 mm<sup>-1</sup>. A colourless column (0.45 × 0.15 × 0.15 mm) was mounted on a Stoe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device [J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105]. Data

collection using Mo-K $\alpha$  X-radiation ( $\lambda$  = 0.71073 Å) gave 1745 unique, absorption-corrected reflections [A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr. Sect. A*, 1968, **24**, 351] to  $2\theta_{\text{max}}$  = 45°, of which 1731 were used in all calculations. Automatic direct methods [SHELXS-86: G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 1990, **46**, 467] located all non-H atoms, which were then refined anisotropically. H-atoms were located from a  $\Delta F$  synthesis and thereafter included in calculated positions [SHELXL-93: G. M. Sheldrick, University of Göttingen, Germany, 1993]. At final convergence, *R*[*F* ≥ 4 $\sigma$ (*F*)] = 0.0626, *wR*[*F*<sup>2</sup>] = 0.2037, *S*[*F*<sup>2</sup>] = 1.061 for 165 parameters and the final  $\Delta F$  synthesis showed no feature beyond  $\pm 0.53$  e Å<sup>-3</sup>.

Molecular structures (SHELXTL) and crystal packing (CAME-RON, L. J. Pearce and D. J. Watkin, Chemical Crystallography Laboratory, University of Oxford, 1993) for **1** and **2** are illustrated in Fig. 2 and 3. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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