

Spinal Columnar Liquid Crystals: Polymeric Octasubstituted μ -Oxo-(phthalocyaninato)tin(IV)¹

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An octa-alkylsubstituted derivative of dihydroxo-tin(IV) phthalocyanine is shown to form columnar liquid crystals; polycondensation of the dihydroxo-tin(IV) derivative leads to a spinal columnar mesophase by formation of oxystannyl links between the macrocyclic units.

Phthalocyanines substituted with long alkane chains have been shown to form columnar (discotic) liquid crystals over extended temperature ranges.²⁻⁴ In this paper, the formation of polymeric liquid crystals whose backbone is composed of μ -oxo-(phthalocyaninato)tin(IV) units is described for the first time (Figure 1).

The dihydrogen derivative of octadodecyloxymethyl substituted phthalocyanine² [(C₁₂H₂₅OCH₂)₈PcH₂] was treated with SnCl₂ in refluxing pentanol in the presence of sodium pentanoate to give (C₁₂H₂₅OCH₂)₈PcSn in quantitative yield. The latter was treated with H₂O₂ to yield (C₁₂H₂₅OCH₂)₈Pc-Sn(OH)₂·2H₂O (1).[†] The liquid crystalline properties of (1) were studied by polarized light microscopy, differential scanning calorimetry, and X-ray diffraction at small angles. A transition is observed at 59 °C ($\Delta H = 3.6$ cal/g; 1 cal = 4.184 J) from a highly ordered crystalline phase (the 12 first diffraction rings of the X-ray pattern can be indexed assuming an orthorhombic structure with $a = 45.4$ and $b = 30.6$ Å) to a liquid crystalline phase. In this case, the inner rings indicate a rectangular packing of the columns with $a = 25.2$ and $b = 30.7$ Å. Simultaneously, the two intense and narrow peaks centred at 4.4 and 3.85 Å are converted into diffuse halos. The first signal is probably related to inter-alkane chain spacing while the second one may be associated with intermetallic distance within the columns by reference to previous work.^{1,4} At 95 °C ($\Delta H = 0.8$ cal/g), a new texture slowly appears which in turn yields an isotropic liquid at 114 °C ($\Delta H = 4.3$ cal/g). The intermediate phase is probably associated with the departure of water molecules present in the starting material. The fluid isotropic liquid slowly transforms into a highly viscous partially anisotropic mass with a change of colour from green to yellow-green. This new phase has been characterized by ¹H n.m.r., u.v.-visible, and i.r. spectroscopy. All methods

indicate the formation of oxystannyl polymers^{5,6} by comparison with previously described unsubstituted or tetrasubstituted⁷ (PcSnO)_x derivatives. The two characteristic i.r. bands, at 620 and 700 cm⁻¹, disappear upon heating⁶ (Figure 2). The birefringent domains become clear forming an isotropic liquid at temperatures higher than 290 °C depending on the heat treatment. At such high temperatures, the dodecyl side chains are in a quasi-molten state and the polymeric chains must therefore form a mesophase.

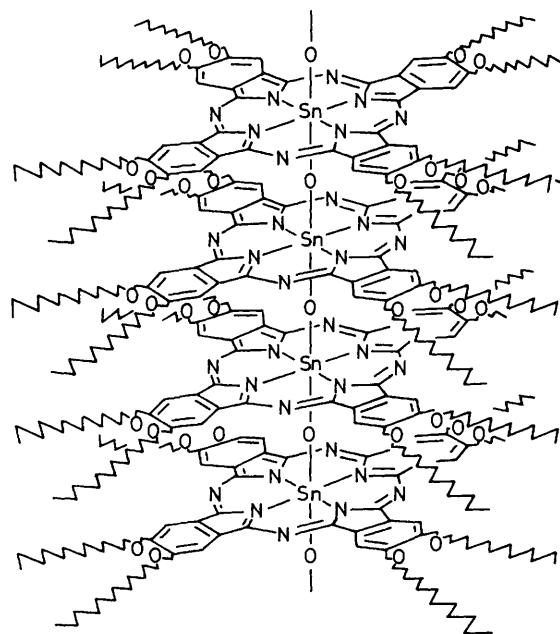


Figure 1. The polymeric octasubstituted μ -oxo-(phthalocyaninato)tin(IV) derivatives.

[†] Overall yield: 95%. Satisfactory elemental analyses (C,H,N) were obtained.

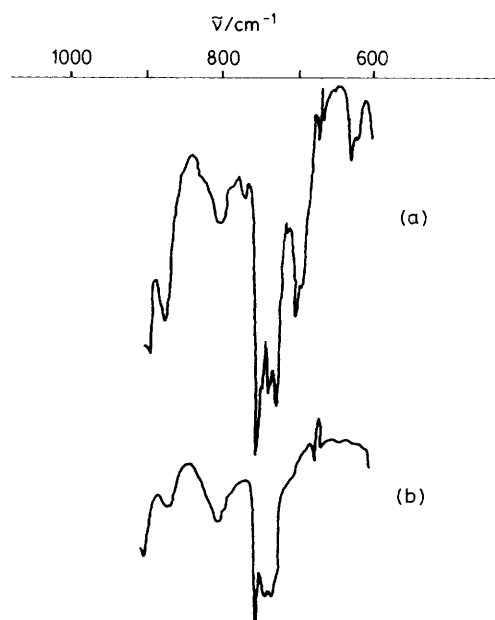


Figure 2. I.r. spectra of (a) $(C_{12}H_{25}OCH_2)_8PcSn(OH)_2$ and (b) after heating in air for a few hours at $140^\circ C$.

No other example of a polymeric mesophase with a similar structure has been described so far.‡ The term 'spinal columnar liquid crystal' is proposed for such polymers.

‡ Related systems with pendant disc shaped mesogenic side groups have been described.⁸ Disc-like mesogens have also been polycondensed with bifunctional derivatives to form polymers.^{9,10}

Further studies are under progress to determine the molecular weight of the polymers formed and the type of liquid crystalline organization they lead to.

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References

- 1 Work performed within the Groupe de Recherches sur les Matériaux Moléculaires (G.R.I.M.M.). For part 18 of the series Annelides, see D. Guillon, P. Weber, A. Skoulios, C. Piechocki, and J. Simon, *Mol. Cryst. Liq. Cryst.*, 1985, **130**, 223.
- 2 C. Piechocki and J. Simon, *Nouv. J. Chim.*, 1985, **9**, 159.
- 3 J. Simon, J.-J. André, and A. Skoulios, *Nouv. J. Chim.*, 1986, **10**, 295.
- 4 C. Piechocki, J. Simon, A. Skoulios, D. Guillon, and P. Weber, *J. Am. Chem. Soc.*, 1982, **104**, 5245; *Mol. Cryst. Liq. Cryst.*, 1983, **100**, 275.
- 5 W. J. Kroenke, L. E. Sutton, R. D. Joyner, and M. E. Kenney, *Inorg. Chem.*, 1963, **2**, 1064; 1962, **1**, 717.
- 6 C. W. Dirk, T. Inabe, K. F. Schoch, Jr., and T. J. Marks, *J. Am. Chem. Soc.*, 1983, **105**, 1539.
- 7 J. Metz, G. Pawlowski, and M. Hanack, *Z. Naturforsch., Teil B*, 1983, **38**, 378.
- 8 W. Kreuder and H. Ringsdorf, *Makromol. Chem. Rapid Commun.*, 1983, **4**, 807.
- 9 O. Herrmann-Schörrherr, J. H. Wendorff, W. Kreuder, and H. Ringsdorf, *Makromol. Chem. Rapid Commun.*, 1986, **7**, 97.
- 10 G. Wenz, *Makromol. Chem. Rapid Commun.*, 1985, **6**, 577.