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Macrocyclic liquid crystals

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The synthesis of macrocycle-containing liquid crystals is reviewed with particular emphasis on derivatives of synthetic aza crowns. The synthesis of the C-functionalized thioether crowns (HO)₂[14]aneS₄ and (HO)₂[16]aneS₄ is described, and their derivatization to give oligobenzoate esters discussed. The formation of mesogens and metallomesogens in these systems has been achieved, and structural studies have been utilized to probe ionophore and tail-group conformation(s). Structural studies of functionalized thioether crowns suggests a relationship between potential mesogen formation and the conformational flexibility of the incorporated crown thioether.

1. Introduction

Since the discovery of the cyanobiphenyl liquid crystals (Gray 1983), an international, multi-billion pound industry centred on liquid crystal displays has arisen. Such is the success of this industry that most households now own some device containing a liquid crystal, for example in a calculator or watch display. The display industry has been dominated for many years by the twisted nematic configuration, but continues to evolve with the realization of supertwisted nematic displays, surface-stabilized ferroelectric displays and, more recently, antiferroelectric and polymer-dispersed displays. Thus, the interplay between physicist, device engineer and chemist continues towards the goal of new and improved displays (Gray 1987). Despite the continued development of the display market, there has been a growing interest in non-display applications for liquid crystals and, in particular, for liquid crystals which might respond to a whole variety of external stimuli, generating what we might term *responsive mesophases*. A good example might be the use of the *E-Z* isomerism in azobenzenes to disrupt mesophase structures mechanically (figure 1) (Newton *et al.* 1995).

The search for mesogens of this type presents a variety of challenges to the synthetic chemist. Thus, recent years have seen the development of many new and interesting themes in the synthesis of liquid crystals, such as polycatenar mesogens (Maltête *et al.* 1993), metal-containing systems (Bruce 1992), flexibly linked dimeric species (Emsley *et al.* 1984), hydrogen-bonded mesogens (Kato *et al.* 1993; Bruce & Price 1994), low molar mass siloxane-containing systems (Coles *et al.* 1993) and

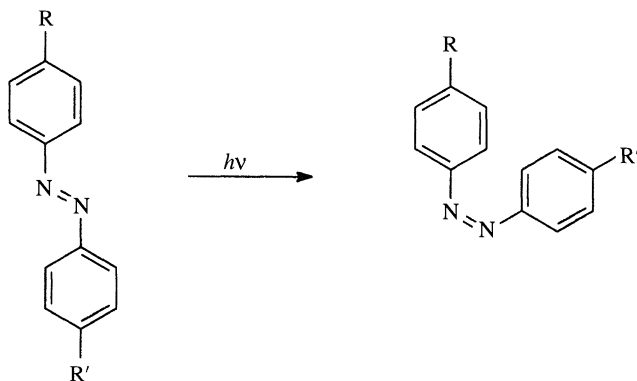
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Figure 1. Switching in *E-Z*-azobenzene mesogens.

potentially ferroelectric columnar species (Serrette & Swager 1993). One area which we believe holds substantial promise for the generation of responsive mesophases is that of macrocyclic liquid crystals.

Macrocycles are cyclic ligands incorporating N-, O-, S-, Se- or P-donor atoms that may bind to a variety of metal ions to form thermodynamically stable and kinetically inert complexes (Lindoy 1989; Vögtle 1994). The complexation of cations, and more recently anions, has driven research in macrocyclic chemistry towards *selective* complexation leading to new methodologies for sensing, for transport and removal of metal ions, and for the construction of new supramolecular arrays and materials. Thus, macrocyclic ionophores are designed receptor sites for the inclusion of metal ions and other guest species. The incorporation of macrocyclic ionophores within mesogenic materials is therefore a highly attractive methodology for the synthesis of responsive mesophases that can switch as a function of cation host, of redox change in the ligand and/or incorporated metal ion, and of photoactivation or luminescence. Our aims in this research are to synthesize new macrocyclic liquid crystal materials incorporating (selective) metal binding sites, which may subsequently show switching properties in terms of changes of redox, stereochemistry and/or magnetism.

2. N-donor macrocyclic liquid crystals

By far the bulk of the published work on macrocyclic liquid crystals has concentrated on phthalocyanines (Simon & Sirlin 1989) and to a lesser extent porphyrins (Shimizu *et al.* 1995). This work will not be extensively covered here, but a few general words are appropriate.

As might be expected from their shape, the mesomorphism of phthalocyanine and porphyrin liquid crystals is dominated by the formation of columnar phases (figure 2). In phthalocyanines, very low melting systems have been demonstrated (Weber *et al.* 1987) along with anisotropic conductivity (Berlabi *et al.* 1989) and spinally linked polymers (Sirlin *et al.* 1988). In porphyrins, photoconductivity has been observed (Shimizu *et al.* 1993) and, more recently, it has been shown that these disc-like molecules can be persuaded to exhibit rod-like mesomorphism by appropriate substitution in the 5- and 15- positions (Bruce *et al.* 1994).

Over the past ten years increasing interest in synthetic aza N-donor macrocyclic mesogens has developed. In 1985, Malthête *et al.* (1985) reported three macrocyclic liquid crystals, based on [18]aneN₆, [24]aneN₆O₂ and [27]aneN₆O₃ (figure 3) substi-

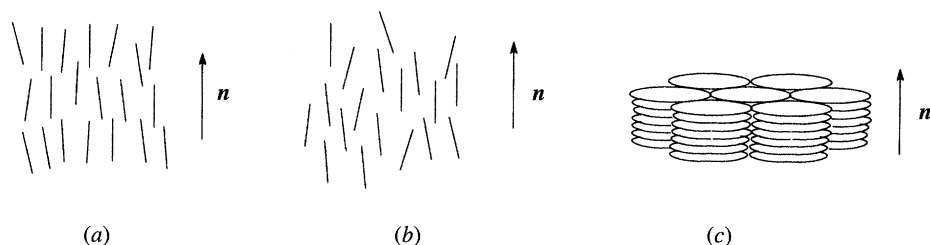


Figure 2. Schematic representations of (a) smectic, (b) nematic and (c) columnar liquid crystals.

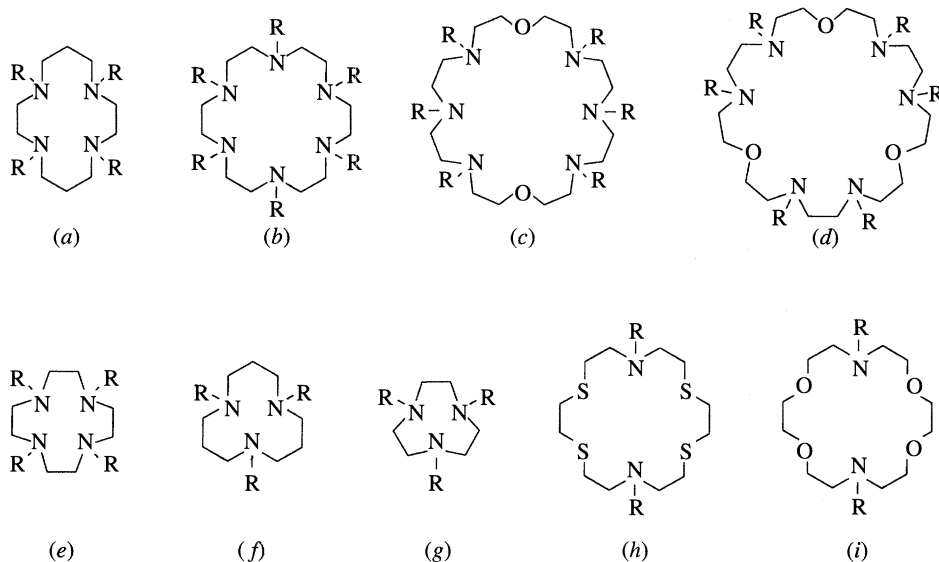


Figure 3. The *N*-substituted macrocycles: (a) [14]aneN₄; (b) [18]aneN₆; (c) [24]aneN₆O₂; (d) [27]aneN₆O₃; (e) [12]aneN₄; (f) [12]aneN₃; (g) [9]aneN₃; (h) [18]aneN₂S₄; and (i) [18]aneN₂O₄.

tuted at each nitrogen by an 4-dodecyloxybenzoyl group (figure 4, **I**, $n = 12$). Although X-ray studies could not unequivocally identify the mesophase as columnar, experiments on shear-aligned samples supported this assignment. This work was followed by reports from Ringsdorf's group (Mertesdorf & Ringsdorf 1989) on related systems based both on [18]aneN₆ and [14]aneN₄ (figure 3), in which the nitrogen atoms were functionalized with various peripheral groups. The ionophore [18]aneN₆ functionalized with 4-alkoxybenzoyl (figure 4, **I**) and 4-alkoxycinnamoyl (figure 4, **V**) groups afforded materials with columnar hexagonal mesophases. Interestingly, the corresponding derivatives of [14]aneN₄ did not show mesogen formation, while the use of 3,5-di(alkoxy)benzoyl (figure 4, **II**) or 3,4,5-tri(alkoxy)benzoyl (figure 4, **IV**) functionalization did not lead to mesophases with either macrocycle.

Further studies on 4-alkoxycinnamoyl (figure 4, **V**) functionalized [18]aneN₆ macrocycles have confirmed (2 + 2)-photocycloaddition and *E-Z* isomerization of cinnamates in these materials (Mertesdorf *et al.* 1991). *E-Z* isomerization was found to be very rapid in these columnar mesophases, and this resulted in sufficient disruption to cause the sample to become isotropic. Similar studies on the glassy columnar phase obtained by cooling the columnar phase showed some evidence of *E-Z* isomerism but at a much slower rate (the mesophase texture persisted for about

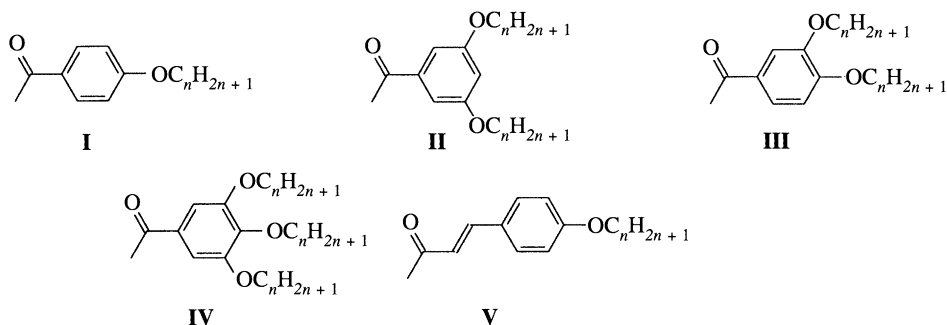


Figure 4. Auxilliaries (I–V) used in the *N*-substitution of aza macrocycles.

50 min), allowing time for the (2 + 2)-photocycloaddition to take place, as evidenced by oligomers identified by gel permeation chromatography. Cycloaddition was also seen when the macrocycles were dissolved in cyclohexane, in which they were expected to aggregate. Further studies of *N*-functionalized [18]ane N_6 systems have been reported (Idziak *et al.* 1991). These workers reported one new mesomorphic material. They went on to report the results of MM2 calculations on the Malthête [18]ane N_6 compound (figure 3) (Malthête *et al.* 1985) which led them to suggest that a rod-like structure was preferred and that, in fact, the mesophases of these materials were of the lamellar type. This hypothesis was shown to be incorrect in an elegant experiment reported by Malthête (1992), in which [18]ane N_6 was functionalized with 3-bromo-4-dodecyloxybenzoyl groups. The presence of the heavy atom (Br) allowed more data to be obtained in the X-ray scattering experiment, allowing the phase to be identified as columnar. The columnar structure of the original compounds was then established by miscibility studies (Malthête *et al.* 1992).

In 1989, Lattermann published the first in a series of papers looking at mesomorphic derivatives of aza macrocycles. As indicated above, Ringsdorf had previously reported that tetra-*N* substituted derivatives of [14]ane N_4 were not mesomorphic, having used 4-alkoxybenzoyl (figure 4, I), 3,5-di(alkoxy)benzoyl (figure 4, II), and 3,4,5-tri(alkoxy)benzoyl (figure 4, IV) groups for the functionalization. Lattermann's modification was to use a 3,4-di(decyloxy)benzoyl substituent (figure 4, III) which succeeded in generating unidentified columnar mesophases.

Ringsdorf had speculated (Mertesdorf & Ringsdorf 1989) that the lack of mesomorphism in his systems was probably due to the lower (two-fold) symmetry of the [14]ane N_4 systems compared to the (six-fold) symmetry of the [18]ane N_6 systems, leading to a more 'circular' shape in the latter. The lack of mesomorphism in the more highly substituted [18]ane N_6 systems was then addressed using arguments concerning the coverage of the macrocycle periphery by hydrocarbon chains. Lattermann showed that the arguments concerning the coverage of the periphery were reasonable, while those relating to the lower symmetry of the [14]ane N_4 macrocycles were probably, with hindsight, ill-founded. Thus, there is a very fine and subtle balance between the lack of effective coverage of the molecular periphery in the four-chain derivative (using 4-alkoxybenzoyl groups, figure 4, I) and its over-coverage in the twelve-chain derivative (using 3,4,5-tri(alkyloxy)benzoyl groups, figure 4, IV). The fact that 3,4-(dialkyloxy)benzoyl groups (figure 4, III) did however lead to mesomorphic materials while 3,5-disubstituted derivatives (figure 4, II) did not, was not explained, although the different effects exerted by the two groups in polycatenar systems was noted. Very recently, Ringsdorf and co-workers have confirmed that

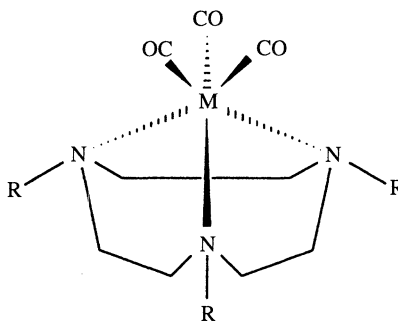


Figure 5. Structure of $[M(R_3[9]aneN_3)(CO)_3]$ ($M = Cr, Mo, W$).

3,4-di(alkoxy)benzoyl derivatives (figure 4, **III**) of $[12]aneN_4$ (figure 3) and related open-chain ligands form hexagonal columnar mesophases (Fischer *et al.* 1995). Related open-chain analogues have been also reported by Latterman (Stehani *et al.* 1994).

Having demonstrated the efficacy of 3,4-di(alkoxy)benzoyl groups (figure 4, **III**) with $[14]aneN_4$, Lattermann extended these studies and showed that they were also applicable with $[18]aneN_6$, $[12]aneN_3$ and $[9]aneN_3$ (figure 3) (Latterman *et al.* 1990). All of the compounds exhibited unidentified columnar phases, and the melting and clearing points for the latter two were rather low:

$$K \circ 37.5 \circ \phi \circ 59.5 \circ I,$$

$$K \circ 42.5 \circ \phi_1 \circ 43.5 \circ \phi_2 \circ 66 \circ I.$$

(The symbol ϕ signifies a columnar phase generated from a non-discotic molecule in common with the nomenclature used in polycatenar mesogens: K, crystal phase, I isotropic phase; temperatures quoted in $^{\circ}C$.)

An interesting point about these systems is that they take up water from the air. This tends to depress the melting point while leaving the clearing point unchanged, as the water is gradually lost on heating. Importantly, amide derivatives of aza macrocycles are poor metal receptors since the amide functions are relatively weak donors to metal ions. Therefore, in order to make stable metal complexes from these derivatized aza macrocycles, the amide group must be reduced to an amine. Interestingly, for derivatives of $[9]aneN_3$ formation of the amine species results in the loss of the mesomorphism of the free ligand (Latterman *et al.* 1992). Complexes of type $[M(R_3[9]aneN_3)(CO)_3]$ ($M = Cr, Mo, W$) (figure 5) were prepared by reaction of $[M(CO)_6]$ with the reduced amine ligand ($R_3[9]aneN_3$) (Schmidt *et al.* 1994), and, notably, all of the resultant complexes melted at about the same temperature into a columnar rectangular phase (ϕ_r , identified by X-ray methods), although the clearing points increased as $Cr (174.5^{\circ}C) < Mo (195^{\circ}C) < W (227.5^{\circ}C)$. The clearing enthalpies for the Cr and W complexes were effectively equal, although curiously, that for Mo was nearly 50% higher. The reduced $[9]aneN_3$ ligand also formed a complex on reaction with $Ni(NO_3)_2$; the resultant columnar mesophase which was formed on melting was described, on the basis of X-ray measurements and electron density calculations, as intermediate between a face-centred rectangular columnar mesophase and a lamello-columnar mesophase (Schmidt *et al.* 1992).

Ringsdorf also investigated the effects of complexation on $[18]aneN_6$ hexafunctionalized with 4-tetradecyloxybenzoyl groups (figure 4, **I**, $n = 14$) and $[14]aneN_4$ tetrafunctionalized with 4-tetradecyloxybenzoyl groups (figure 4, **I**, $n = 14$) or 3,4-di(decyloxy)benzoyl groups (figure 4, **III**, $n = 10$) (Liebmann *et al.* 1991). In each

case, it was again necessary to reduce the amide groups to amines prior to complexation. Interestingly, the 2:1 ligand:metal complex resulting from the reaction of the functionalized [18]aneN₆ macrocycle with Co(NO₃)₂ gave rise to a columnar nematic phase *near room temperature*, while the same ligand gave an unidentified mesophase when complexed in a 1:1 ratio with Ni(NO₃)₂. Both of the [14]aneN₄ systems were complexed with Cu(NO₃)₂ and the four-chained macrocycle derivative gave rise to an unidentified mesophase, while the eight-chained macrocycle derivative was non-mesomorphic. Clearly there remains an element of trial and error in the design of such metallomesogens and in the understanding of intermolecular interactions that stabilize such phases.

Neve & Ghedini have reported a series of materials based on sulphur-containing macrocycles. These represent the first containing thioether donors, although functionalization occurs at N-donor centres and is therefore comparable with the preceding work described above. Initially, [18]aneN₂S₄ and [18]aneN₂O₄ (figure 3) were acylated at the nitrogen atoms with hexyloxybenzoyl (figure 4, **I**, $n = 6$) and dodecyloxybenzoyl (figure 4, **I**, $n = 12$) groups to give functionalized macrocycles which were non-mesomorphic (Neve & Ghedini 1993; He *et al.* 1990). However, introduction of Pd(II) into [18]aneN₂S₄ functionalized with dodecyloxybenzoyl groups led to mesomorphism. X-ray scattering studies implied that the mesophase was lamellar and the published optical textures are certainly consistent with those found in the lamellar phases of anhydrous ionic materials. Thus, importantly, the inclusion of a metal ion has led to the formation of a mesophase from a non-mesomorphic ligand. Subsequently, a wider range of these derivatized [18]aneN₂S₄ materials was synthesized, and their Cu(I) complexes obtained (Neve *et al.* 1994*a*). Again, the ligands were non-mesomorphic, but the complexes showed broad melting transitions to a mesophase whose viscosity decreased as the temperature was increased; the clearing transition was also somewhat sharper. X-ray studies in mesophase were carried out and although the data proved difficult to interpret unequivocally, it seems that the mesophase possessed an undulating ribbon structure based on a rectangular lattice, i.e. the phase was essentially lamellar. A derivative of [18]aneN₂S₄ was reacted with AgCF₃SO₃ and AgPF₆ to give Ag(I) complexes (Neve *et al.* 1995*a*). These complexes again showed a viscous birefringent mesophase which was investigated by X-ray scattering. The results implied an undulating bilayer mesophase, with a structure similar to that shown in figure 6, in which the metal-containing cations describe a 'U'-shaped motif. The same materials were also found to show lyotropic mesomorphism in acetonitrile at concentrations of between 15 and 35 wt% complex, giving a lamellar ripple phase (i.e. again, a modulated phase). If [18]aneN₂S₄ is acylated with an alkanoyl chloride instead of a benzoyl chloride derivative, the ligand is found again to be non-mesomorphic, but Ag(I) complexes with triflate counter-anion show evidence of lamellar phases, while those with a tosylate counter-anion show a viscous low-birefringence mesophase (Neve *et al.* 1995*b*).

The work of Neve & Ghedini, carried out in parallel with our own described below, clearly shows that addition of metal ions can have advantageous effects on mesophase formation and stability. The aim of our own work was to synthesize new thioether macrocyclic ligands functionalized with pendant mesogenic groups. In contrast to aza macrocycles, functionalization of thioether S-donor crowns requires a more involved synthetic approach in that attachment points have to be developed on the C-backbone or periphery of the ionophore since the S-donors themselves cannot be derivatized. However, since functionalization occurs at the C-backbone of the

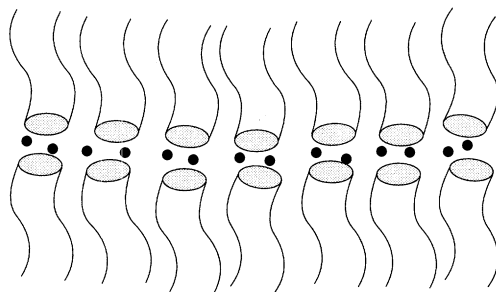
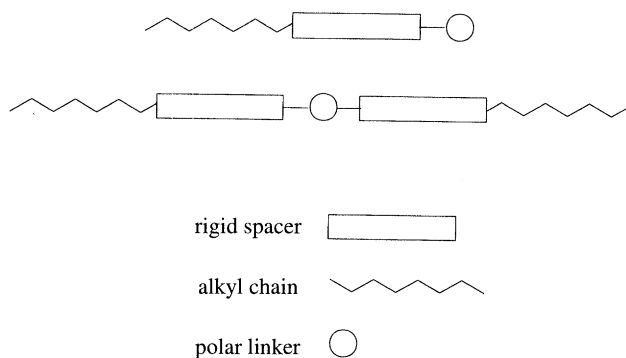
Figure 6. Undulating bilayer mesophase of $[\text{Ag}([18]\text{aneN}_2\text{S}_4)][\text{CF}_3\text{SO}_3]$.

Figure 7. Design of calamitic mesogens.

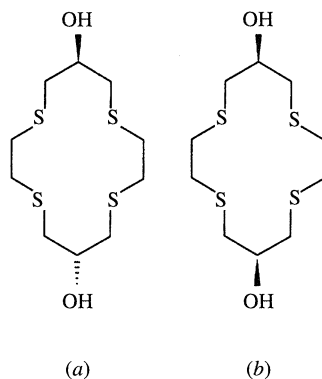
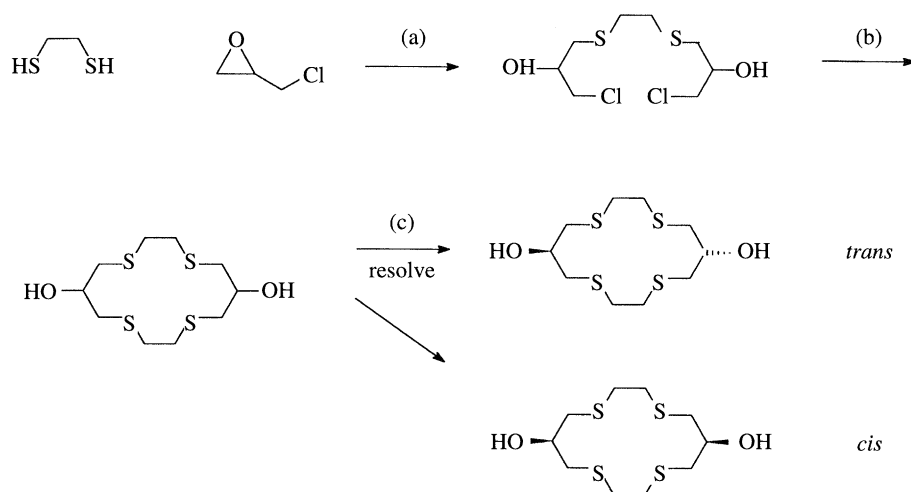
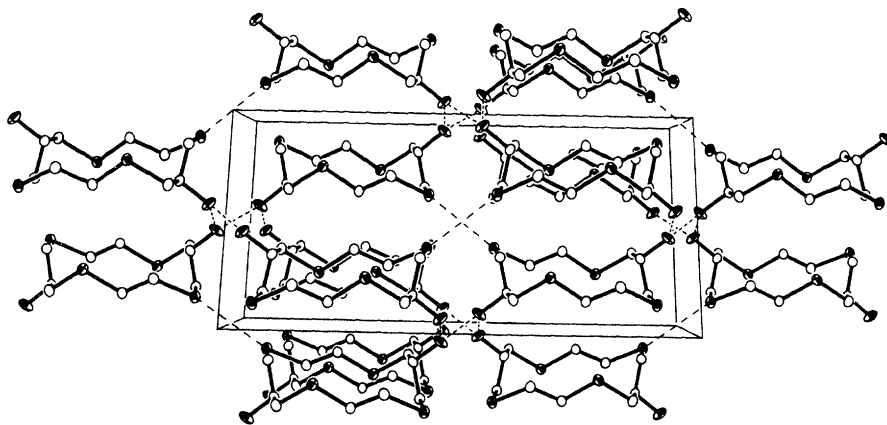
macrocycles, the thioether S-donors remain freely available for metal ion binding and complexation.

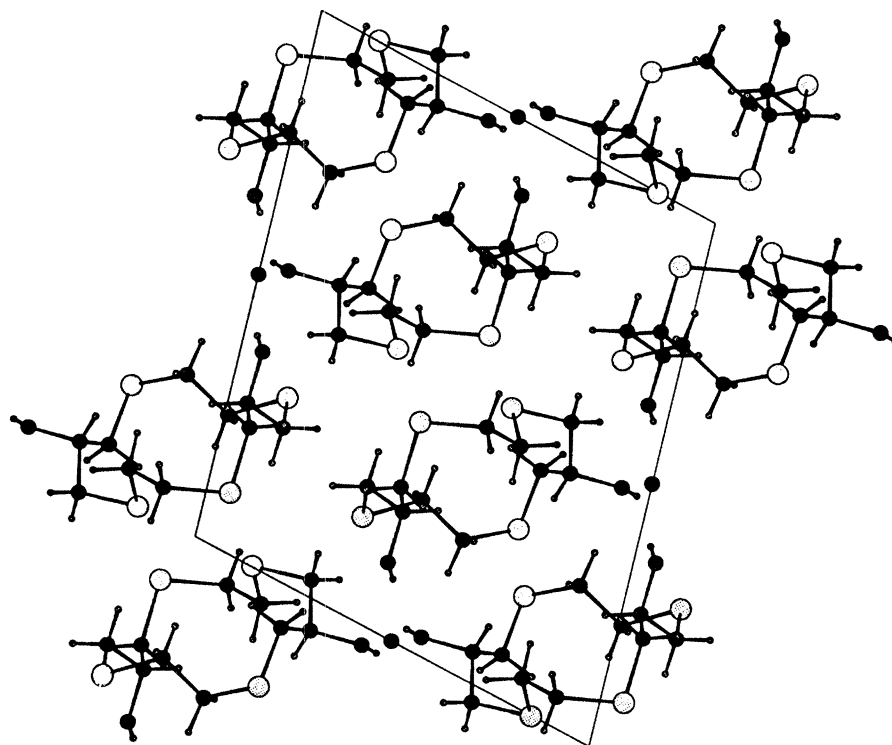
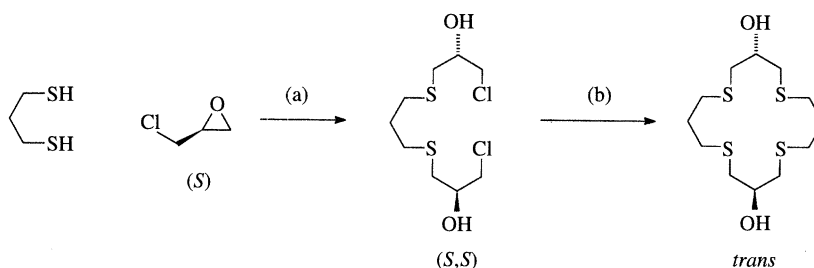
Very few examples of functionalized thioether crowns have been reported in the literature, and these are generally based upon *exo* alcohol (Pett *et al.* 1988; Smith *et al.* 1991) or keto (Edema *et al.* 1992; Edema *et al.* 1993a, b; Buter *et al.* 1991) groups. Our strategy for the design of calamitic (rod-like) mesogens is based on the covalent attachment of the macrocyclic linker *via* rigid spacer(s) to alkyl chains (figure 7).

3. Thioether macrocycles incorporating external alcohol groups

We prepared the tetrathioether ligand $(\text{HO})_2[14]\text{aneS}_4$ (figure 8) as a mixture of *cis* and *trans* isomers using a modification of the method of Rorabacher and co-workers (figure 9) (Pett *et al.* 1988). This synthesis involves mustard gas intermediates (as do many thioether ligand syntheses) and extensive chromatographic separations and recrystallizations. Thus, reaction of ethane-1,2-dithiol with (\pm) epichlorohydrin affords 1,10-dichloro-2,9-dihydroxy-4,7-dithiadecane (figure 9). Macrocyclization with one equivalent of ethane-1,2-dithiol with Cs_2CO_3 under high dilution conditions affords after chromatography the product as a 1:1 *cis-trans* mixture.

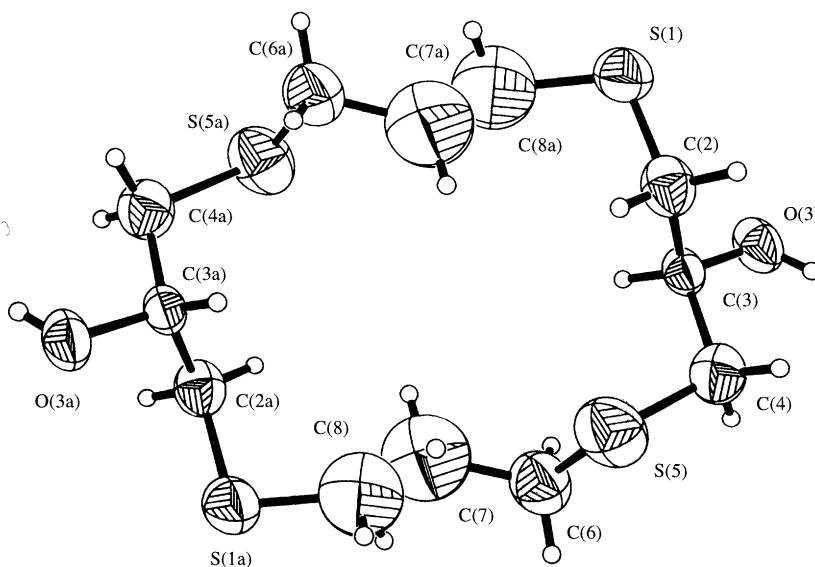
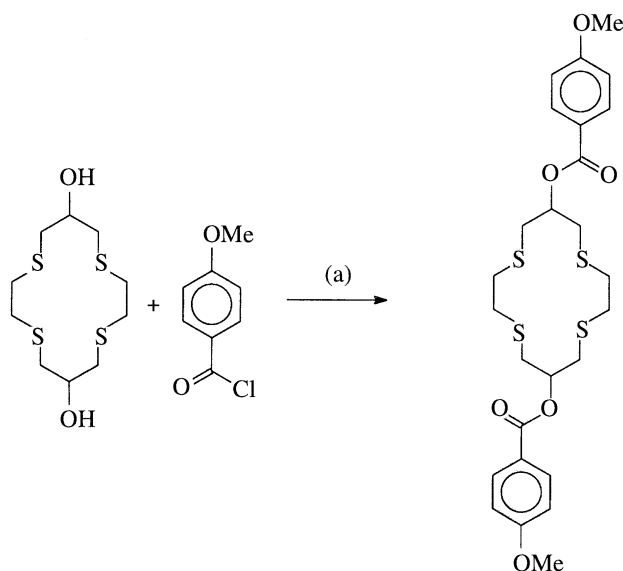
The advantage in preparing $(\text{HO})_2[14]\text{aneS}_4$ is that the *cis* and *trans* isomers can be resolved by careful recrystallization, the *trans* isomer being the less soluble. We confirmed complete resolution of the two diastereoisomers by ^1H and ^{13}C NMR spectroscopy, and a further insight was obtained from single-crystal X-ray studies. The *trans* isomer of $(\text{HO})_2[14]\text{aneS}_4$ (figure 10) crystallizes in a [3434] conformation with an interesting stacked arrangement of molecules in the lattice. An unusual

Figure 8. (a) *trans*-(HO)₂[14]aneS₄, (b) *cis*-(HO)₂[14]aneS₄.Figure 9. Synthesis of (HO)₂[14]aneS₄. Reagents: (a) EtOH, Et₃N; (b) DMF, HS(CH₂)₂SH, Cs₂CO₃; (c) EtOH.Figure 10. Structure of *trans*-(HO)₂[14]aneS₄.

Figure 11. Structure of *cis*-(HO)₂[14]aneS₄.Figure 12. Synthesis of *trans*-(HO)₂[16]aneS₄. Reagents: (a) Et₃N, EtOH; (b) DMF, HS(CH₂)₃SH, Cs₂CO₃.

zig-zag hydrogen-bonded array via intermolecular interactions between external alcohol groups is observed, leading to the formation of channels through the structure with macrocycles packing on top of one another. This is consistent with the relative insolubility of the *trans* isomer. No extended H-bonding is observed for the *cis* form (figure 11), the *cis* isomer crystallizing as a hemihydrate with a more distorted macrocyclic conformation.

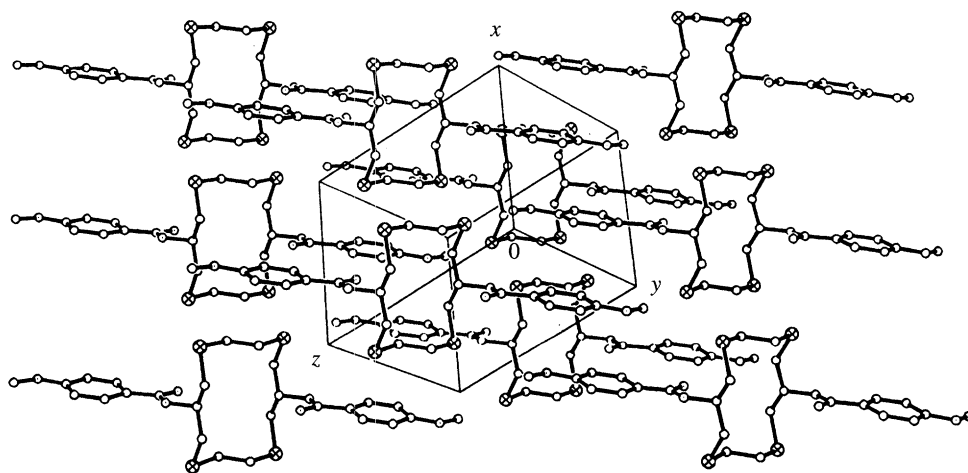
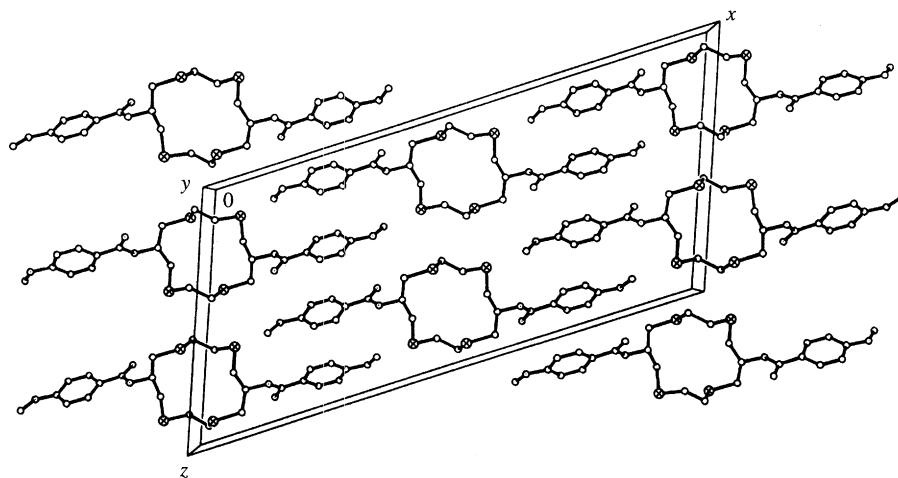
In contrast, a *cis-trans* mixture of (HO)₂[16]aneS₄ could not be resolved easily, either chromatographically or by fractional recrystallization. We therefore developed our own selective synthesis to *trans*-(HO)₂[16]aneS₄ using chiral epoxide. Pure *trans*-(HO)₂[16]aneS₄ was prepared by the reaction of propane-1,3-diol with (*S*)-epichlorohydrin to afford 1,11-dichloro-2*S*,10*S*-dihydroxy-4,8-dithiaundecane (figure 12). Subsequent cyclization under the high dilution conditions described above

Figure 13. Structure of *trans*-(HO)₂[16]aneS₄.Figure 14. Synthesis of (MeO-Ph-COO)₂[14]aneS₄. Reagents: (a) 4-dimethylaminopyridine, THF.

afforded *trans*-(HO)₂[16]aneS₄ in 30% yield. The *trans* stereochemistry of this material was confirmed crystallographically (figure 13).

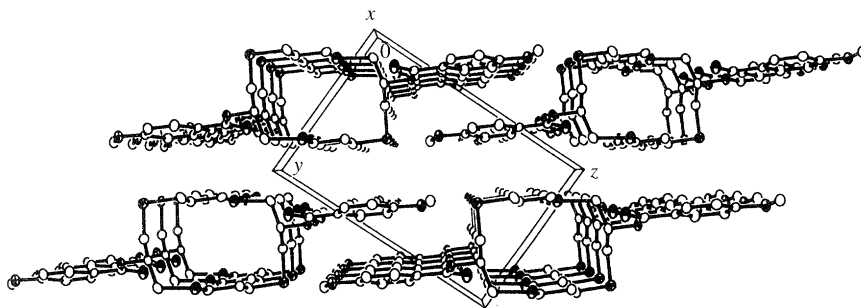
4. *p*-Methoxybenzoate derivatives of *cis*/*trans*-(HO)₂[14]aneS₄ and *trans*-(HO)₂[16]aneS₄

Reaction of *cis*- or *trans*-(HO)₂[14]aneS₄ with *p*-methoxybenzoyl chloride in the presence of DMAP (DMAP = *N,N*-dimethyl-4-aminopyridine) afforded the required

Figure 15. Structure of *trans*-(MeO-Ph-COO)₂[14]aneS₄.Figure 16. Structure of *cis*-(MeO-Ph-COO)₂[14]aneS₄.

bis-anisate esters in 70–90% yield (figure 14). Again the *cis* product was found to have a significantly greater solubility than that of the *trans* isomer. A similar reaction with *trans*-(HO)₂[16]aneS₄ yielded the bis-anisate in 75% yield.

Crystals of all three bis-anisates were grown and their single crystal X-ray structures determined (figures 15–17). In all three a common aromatic–aromatic π -stacking motif was observed. It was this interaction which determined the overall packing within the lattice, with the thioether macrocycle adopting a conformation to allow these interactions to occur. In the structure of the *cis*-(MeO-Ph-COO)₂[14]aneS₄ (figure 16), for example, the macrocycle, in common with *cis*-(HO)₂[14]aneS₄, adopted a distorted [223223] conformation. Thus, all three structures display a rod-like motif as required for calamitic mesophase formation.

Figure 17. Structure of *trans*-(MeO-Ph-COO)₂[16]aneS₄.

5. Mesogenic carboxylic acids

Mesogenic carboxylic acids were prepared as oligomers of *p*-hydroxybenzoic acid. *p*-Hydroxybenzoic acid was alkylated under basic conditions to afford *p*-alkoxybenzoic acids. Conversion to the acid chloride was effected by treatment with oxalyl chloride. Subsequent esterification with benzyl *p*-hydroxybenzoate followed by hydrogenolysis afforded the required ester-acids in good overall yield. Repeating the acid chloride-esterification-hydrogenolysis sequence gave diester-acids in moderate-to-excellent yield (figure 18). Other derivatives have been prepared by similar procedures with the incorporation of alkyl and alkoxy groups, and saturated functionalities such as *trans*-alkylcyclohexyl and *trans,trans*-alkyldicyclohexyl groups. It was found that with an increasing number of aromatic groups, these acids become more and more insoluble, with systems containing biphenyl or cyclohexyl-biphenyl functions being essentially unworkable. The incorporation of more than one alkoxy chain or cyclohexyl groups improved solubilities. The mesomorphism of these species will be reported separately.

6. Mesomorphic derivatives of *cis/trans* (HO)₂[14]aneS₄ and *trans*-(HO)₂[16]aneS₄

Initial attempts at the preparation of mesomorphic derivatives were thwarted by solubility incompatibilities of the *trans*- or *cis*-(HO)₂[14]aneS₄ and the mesogenic acid starting materials. Reaction of acid (**1**) with 1,3-dicyclohexylcarbodiimide (DCC) and toluene sulphonic acid in pyridine and *trans*- or *cis*-(HO)₂[14]aneS₄ gave the tetraester (**2**) in 30% yield (figure 19). Neither the *cis* nor *trans* isomers was mesomorphic:

$$\begin{aligned} \textit{trans} \text{ isomer } (\mathbf{2}): & \quad K \circ 196 \circ I, \\ \textit{cis} \text{ isomer } (\mathbf{2}): & \quad K \circ 165 \circ I. \end{aligned}$$

The above synthetic methodology however failed for the preparation of hexaester derivatives such as (**3**) (figure 19). A series of esterification procedures was attempted including:

- (i) acid chlorides plus DMAP;
 - (ii) DCC plus DMAP;
 - (iii) 2-chloro-1-methylpyridinium iodide and Bu₃N with *N, N'*-carbonyldiimidazole in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).
- All of these proved unsuccessful for the preparation of (**3**). Finally, good yields of the hexaesters (**3**) were obtained by reacting the diols with an excess of the acid

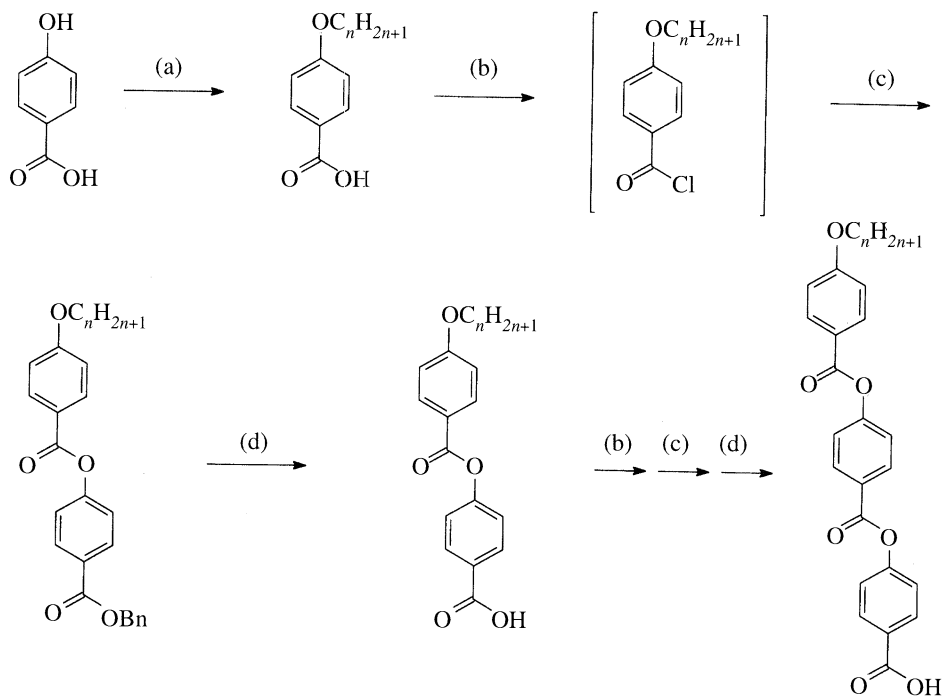


Figure 18. Synthesis of oligobenzoate esters. Reagents: (a) EtOH, KOH, $\text{BrC}_n\text{H}_{2n+1}$; (b) CH_2Cl_2 , $(\text{COCl})_2$, DMF (cat.); (c) CH_2Cl_2 , 4- $\text{HO-C}_6\text{H}_4\text{CO}_2\text{Bn}$, DMAP; (d) THF, $\text{H}_2/\text{Pd/C}$.

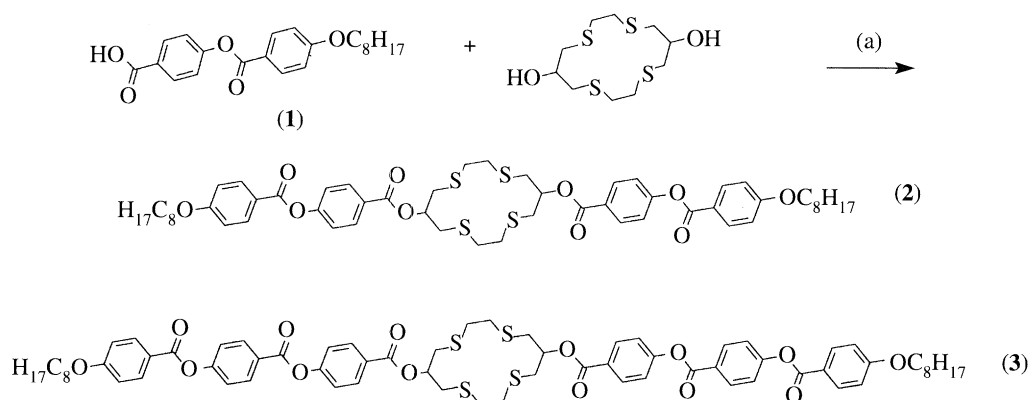


Figure 19. Oligobenzoate esters of $(\text{HO})_2[14]\text{aneS}_4$. Reagents: (a) Pyridine, DCC, $p\text{TSA}$.

anhydrides in the presence of Et_3N and 4-pyrrolidinopyridine (figure 20). The acid anhydrides were prepared in excellent yield by the reaction of the triethylammonium salt of the acid with bis-(2-oxo-3-oxazolidinyl)-phosphoramidic chloride (BOP.Cl) in THF. Although separation of the product from the excess carboxylic acid was time consuming, this method led to the formation of the desired macrocyclic ester (3) in 50–80% yield.

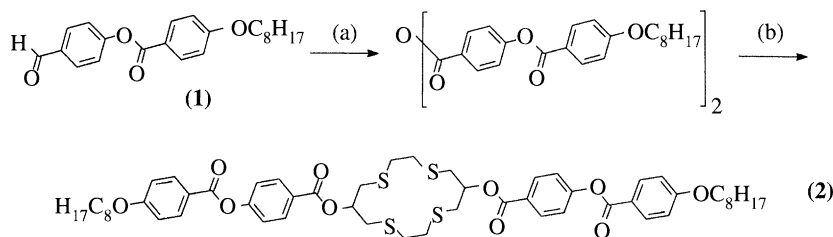


Figure 20. Oligobenzoate esters of $(\text{HO})_2[14]\text{aneS}_4$. Reagents: (a) THF, Et_3N , BOP.Cl; (b) THF, $(\text{HO})_2[14]\text{aneS}_4$, Et_3N , DMAP.

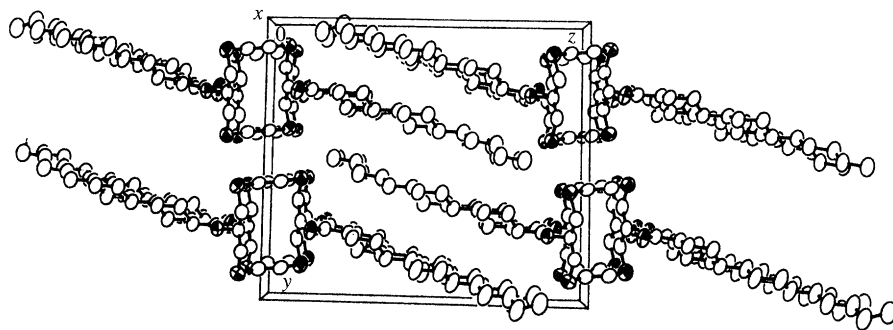
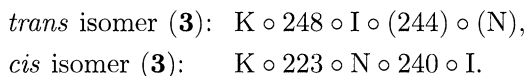


Figure 21. Structure of *trans*-($\text{C}_5\text{H}_{11}\text{-Cy-Cy-COO}$) $_2[14]\text{aneS}_4$.

The ligand **(3)** showed nematic mesophases as indicated:



Thus, the synthesis of a derivatized thioether macrocycle that showed liquid crystal activity has been achieved (Blake *et al.* 1994), and represents the first examples of homoleptic thioether liquid crystals. We note that, very recently, related stereochemically unresolved and non-mesomorphic derivatives have been reported by Neve & Ghedini (Neve & Ghedini 1994). We have also found that *trans*-($\text{HO})_2[16]\text{aneS}_4$ functionalized with $\text{OOC-Ph-OOC-Ph-OOC-Ph-OC}_8\text{H}_{17}$ shows nematic behaviour.

The above melting points were rather high and the liquid crystalline ranges narrow. However, these results do indicate the possibility of rendering non-liquid crystalline macrocyclic ionophores mesomorphic by the addition of sufficiently anisotropic substituents. It is now believed that the large 'tail' group is required since the macrocycle acts as a flexible spacer effectively decoupling the two ends of the molecule. Therefore, liquid crystallinity must derive from tail groups acting relatively independently of one another. Unfortunately, these hexaesters have proven to be rather insoluble and complexes have not been prepared.

Derivatization of $(\text{HO})_2[14]\text{aneS}_4$ with cyclohexyl groups was also investigated (figure 21), although these groups tended to increase the melting points of the resultant materials.

7. Mesomorphic transition metal complexes of macrocyclic tetrathioethers

As noted above, the tetraester derivatives (**2**) did not display any liquid crystalline phases due to insufficiently mesogenic tail groups, largely decoupled from one another by the flexible macrocycle. It was therefore of interest to determine the effects of incorporation of a metal centre within the macrocycle, which would lock the macrocycle thus coupling the two ends of the molecule together.

The reaction of *trans*-(**2**) with $[\text{Pd}(\text{MeCN})_4][\text{BF}_4]_2$ in $\text{CH}_3\text{CN}-\text{CHCl}_3$ solution yielded the *trans*-complex (**4**) (figure 22) in good yield. This material displayed a monotropic nematic phase with a melting point of 312°C and an excellent nematic range of $272-130^\circ\text{C}$. Significantly, the parent ligand simply melted at 196°C , while the *cis*-isomer of (**4**), prepared in an analogous method to the *trans*-isomer, was not mesomorphic and melted with some decomposition at 258°C . Thus, the synthesis of mesomorphic metal complexes from non-mesomorphic thioether crown ligands has also been realized.

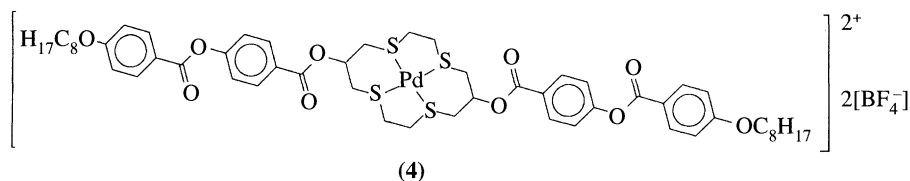


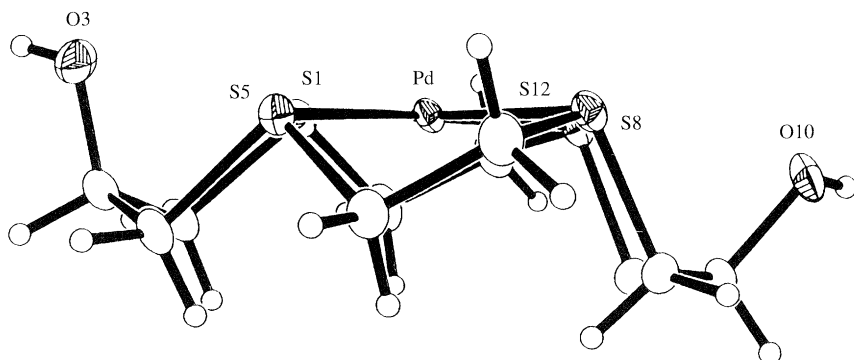
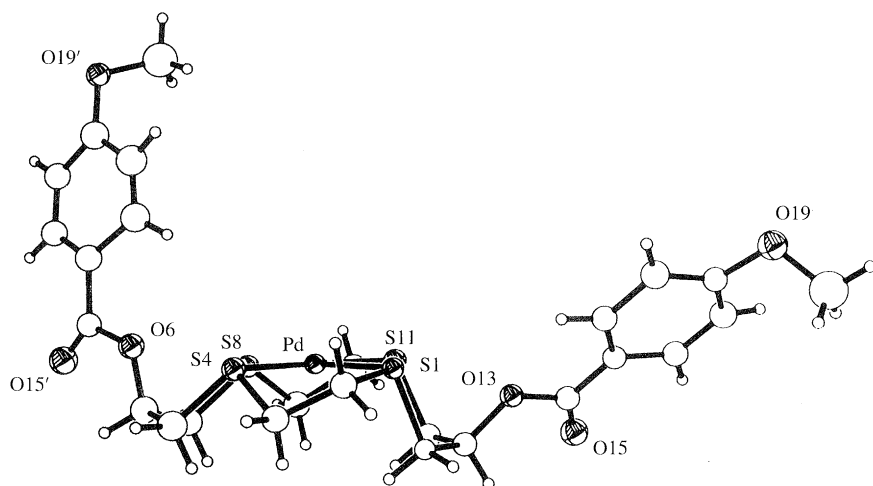
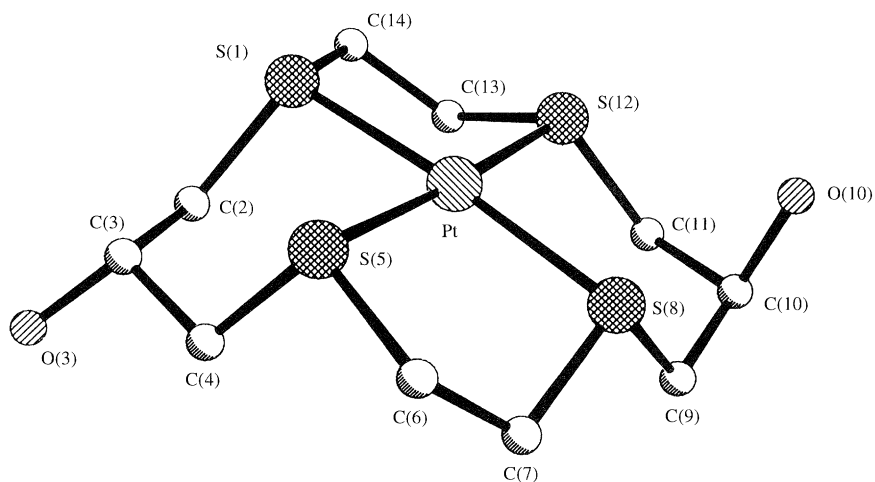
Figure 22. Pd(II) complex of the tetraester ligand (**2**).

trans isomer (**4**): $K \circ 312 \circ I \circ (272) \circ (N) \circ (130) \circ (K)$,

cis isomer (**4**): $K \circ 258 \circ I$.

This result has great significance for the way in which we think about these macrocyclic systems and, hence, for the direction of future work. The above results support the idea that in the metal-free macrocycles, the macrocycle is akin to a flexible spacer between the mesogenic oligo(ester) functions (cf. the flexibly spaced twin liquid crystals described by, for example, Luckhurst and co-workers (Emsley *et al.* 1984)). From our previous work on thioether crowns we know that the metal-free macrocycles are indeed highly flexible and may adopt a wide range of low-energy conformations (Blake & Schröder 1990; Blake *et al.* 1993). The two oligo(benzoyl ester) groups within our functionalized crowns are therefore effectively 'decoupled' from one another and so behave as two independent mesogenic tails. This explains why six benzoyl ester groups (three per side) are required to generate a mesomorphic metal-free macrocycle. A metal-free four-ring system such as (**2**) is therefore not mesomorphic as each side of the macrocycle is largely decoupled and is therefore not capable of stabilizing a mesophase independently. However, when Pd(II) is complexed to the central macrocycle, the ring becomes more 'locked', the inherent flexibility of the macrocycle is largely lost, and what was a pair of decoupled two-ring esters becomes a coupled five-ring mesogen which now has sufficient anisotropy to give rise to a mesophase. Therefore, it is clear that in these systems, liquid crystal phases are directly promoted by the addition of a metal ion.

The ability to prepare pure *cis* and *trans* isomers of $(\text{HO})_2[14]\text{aneS}_4$ and $(\text{HO})_2[16]\text{aneS}_4$ now becomes of great significance. Interestingly, both *cis* and *trans* derivatives of (**3**) showed liquid crystal mesophases with very similar phase stability ($T_{\text{NI}}(\text{trans})$ 244°C , $T_{\text{NI}}(\text{cis})$ 240°C), which would imply that the structural

Figure 23. Structure of $[\text{Pd}(\text{cis}-(\text{HO})_2[14]\text{aneS}_4)]^{2+}$.Figure 24. Structure of $[\text{Pd}(\text{cis}-(\text{MeO-Ph-COO})_2[14]\text{aneS}_4)]^{2+}$.Figure 25. Structure of $[\text{Pt}(\text{trans}-(\text{HO})_2[14]\text{aneS}_4)]^{2+}$.

anisotropy of the mesophase species is similar in each case, something perhaps not expected in different isomers. A clue is provided by the structures of the *cis* and *trans* anisate esters (discussed above), where similar relative dispositions of the aromatic rings in the crystal packing is achieved by a change in the conformation of the macrocyclic ring. We suggest that in both *cis* and *trans* isomers, the stacking of benzoylester groups promotes an anisotropic structure leading to mesophase formation. Further, this mesogenic structure is maintained in the isotropic state as evidenced by the reversibility of T_{NI} . However, the isomerism becomes an important issue on complexation, as the conformation of the macrocyclic ring will become partially locked, suggesting that quite different mesomorphism may be observed in complexed *cis* and *trans* isomers. This is confirmed by the observation of mesomorphism in the Pd(II) complex of *trans*-(**2**), and the absence of mesomorphism for the Pd(II) complex of *cis*-(**2**). The results of the crystallographic studies on *cis*- and *trans*-(MeO-Ph-COO)₂[14]aneS₄ also suggest that lower melting materials may be obtained if the observed intermolecular interactions between phenyl ester groups can be disrupted, for example by lateral substitution.

We have undertaken structural studies on Pd(II) and Pt(II) complexes of functionalized thioether crowns in order to monitor the effects of complexation on the conformation(s) of these ionophores. The structures of $[M(cis - R_2[14]aneS_4)]^{2+}$ (R = OH, M = Pd (figure 23), Pt; R = OOC-Ph-OMe, M = Pd (figure 24)) confirm that these *cis*-isomer complexes have their functional groups disposed in such a way that linear rod-like structure cannot be clearly defined. In contrast, the structure of $[Pt(trans-(HO)_2[14]aneS_4)]^{2+}$ (figure 25) appears to place the OH groups in more advantageous positions with respect to the formation of rod-like structures. Unfortunately, at the time of writing we have not obtained a crystal structure of $[Pd(trans-(MeO-Ph-COO)_2[14]aneS_4)]^{2+}$ to verify these ideas.

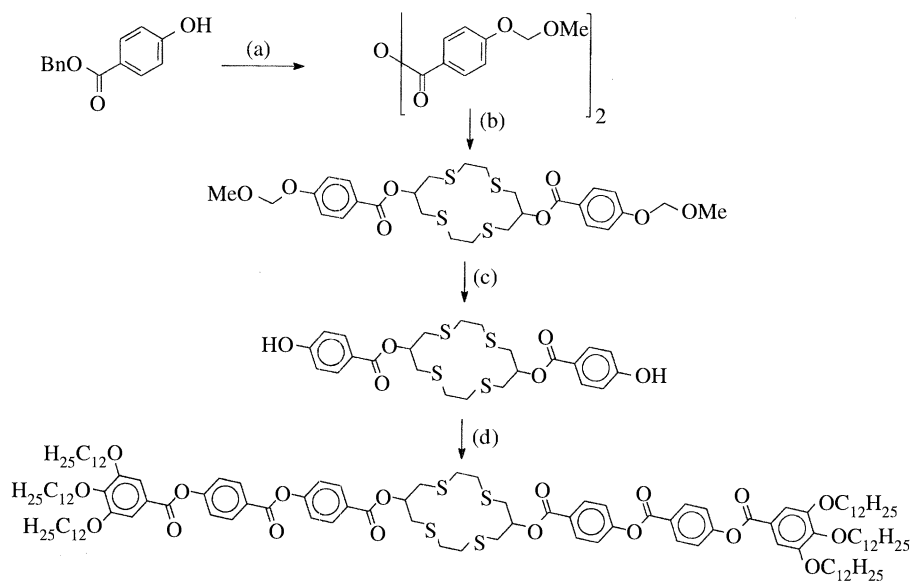
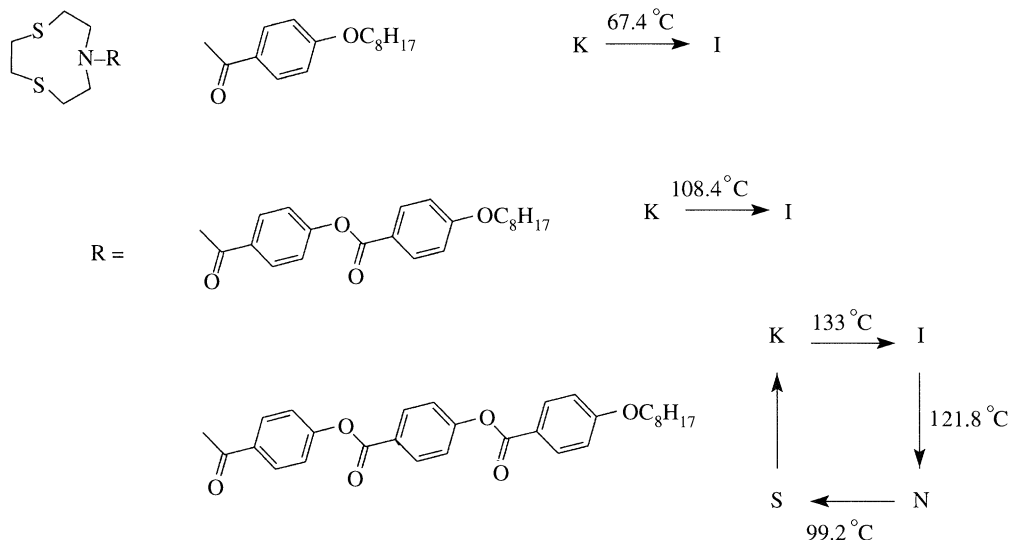
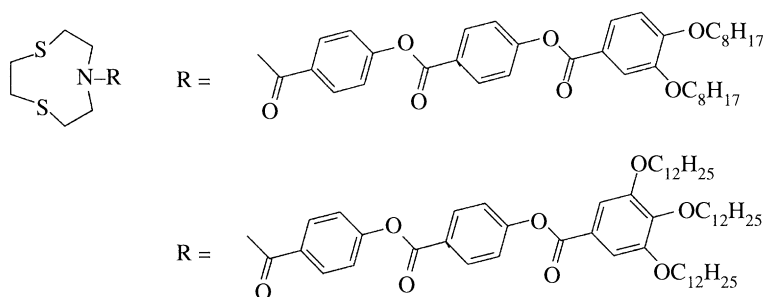


Figure 26. Synthesis of 3,4,5-substituted oligobenzoate derivatives of [14]aneS₄. Reagents: (a) CH₂(OMe)₂, *p*TSA, CHCl₃ 4 Å sieves (ii) H₂/Pd/C, (iii) BOP.Cl, Et₃N; (b) THF, (HO)₂[14]aneS₄, Et₃N, DMAP; (c) MeOH, dioxane, HCl (conc.); (d) CH₂Cl₂, O-[CO-C₆H₄-O₂C-C₆H₂-3,4,5-(OC₁₂H₂₅)₃]₂, Et₃N.

Figure 27. Oligobenzoate ester derivatives of [9]aneNS₂.Figure 28. Oligobenzoate ester derivatives of [9]aneNS₂.

8. Further developments

The development of synthetic strategies to other functionalized thioether crowns is now under investigation. Thus, we have prepared 3,4,5-trisubstituted oligo(benzoate) derivatives of [14]aneS₄ (figure 26) by the use of MOM (MOM = methoxymethylene) protecting groups to prepare a diphenolic derivative of [14]aneS₄ which reacts more readily than the parent (HO)₂[14]aneS₄ species. This and related substituted derivatives are now under investigation.

Likewise, derivatives of [9]aneNS₂ have been prepared and mesogen formation observed for triester derivatives. These data are summarized in figure 27 and 28.

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