

## Synthesis and Phase-transfer Property of Macrocyclic Polythiaether Sulphoxides

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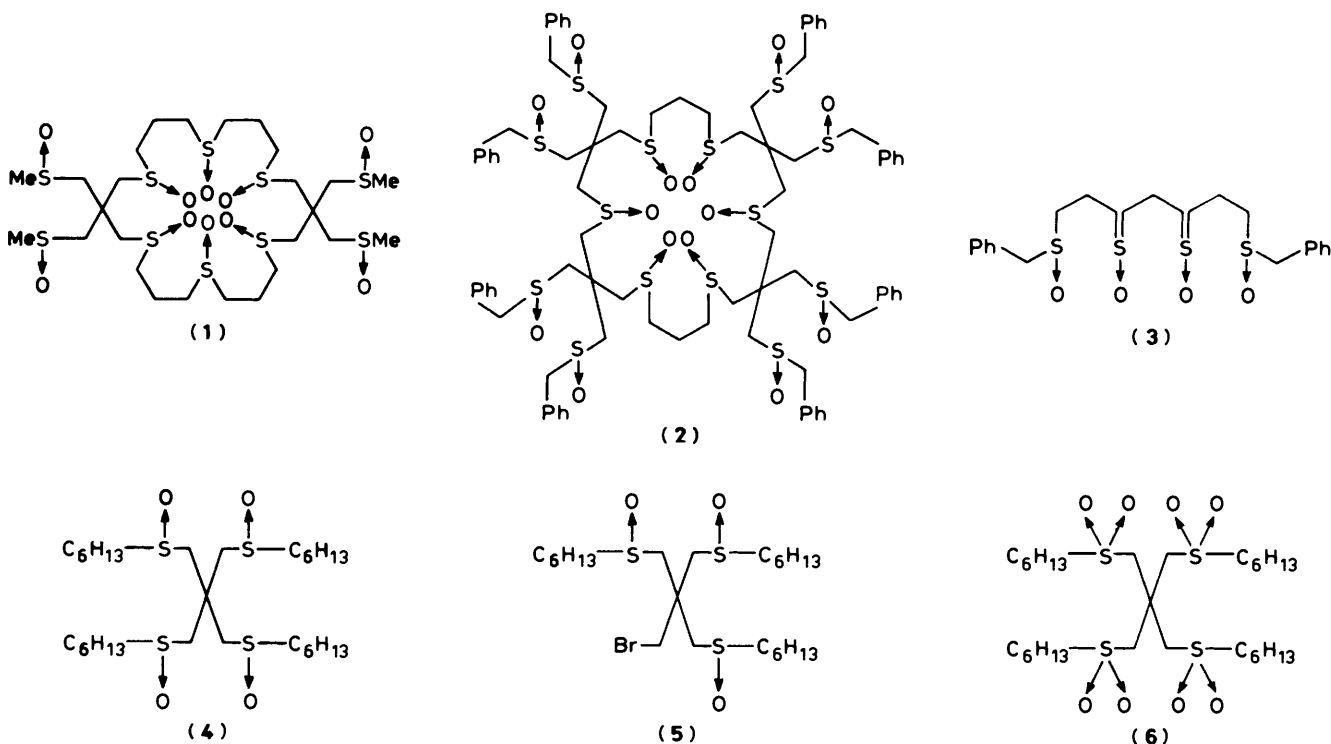
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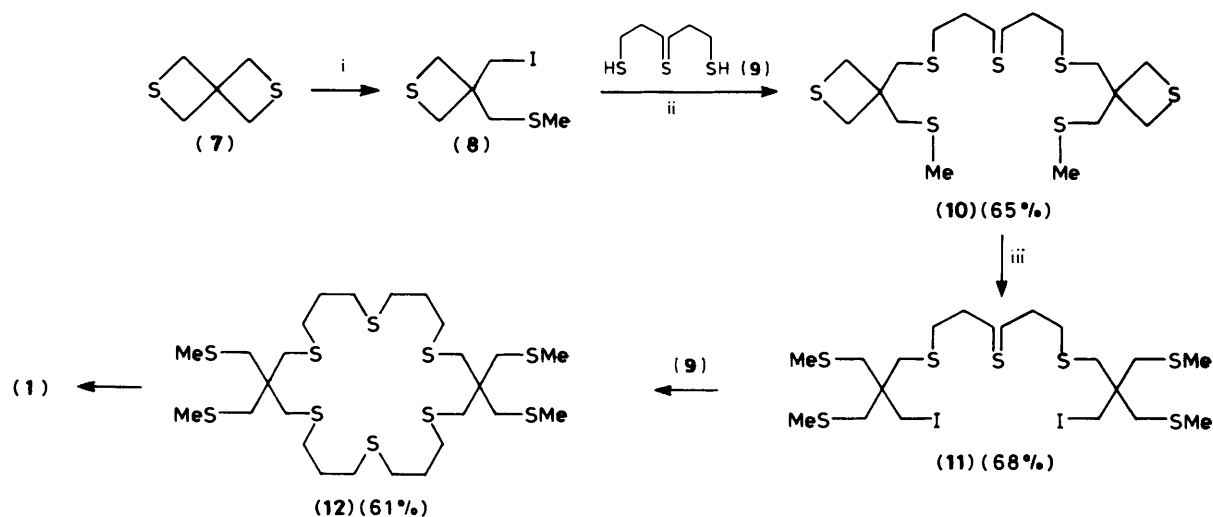
New macrocyclic polythiaethers with alkylthio side chains have been prepared in good yields starting from 2,6-dithiaspiro[3.3]heptane. The corresponding polysulphoxides were also prepared by the general oxidation method. The macrocyclic polythiaether sulphoxide with benzylsulphinyl side chains was found to be an excellent phase-transfer catalyst which promotes alkylation of benzyl methyl ketone with alkyl halides in a liquid-liquid two-phase system.

Preparation and properties of numerous macrocyclic polyoxaethers (crown ethers) have been extensively reported. However, only a limited number of macrocyclic polythiaethers<sup>1</sup> and mixed aza-oxa-thia macrocyclic compounds containing four or more sulphur atoms in the ring<sup>2</sup> have been synthesized. Although the crown ethers co-ordinate strongly with alkali or alkaline earth metal cations, the thia and mixed oxa-thia macrocycles exhibit lower selectivity and less ability to co-ordinate to alkali or alkaline earth metal cations;<sup>2</sup> in contrast, macrocyclic polythiaethers exhibit substantial co-ordinational ability in selectively binding to heavy metals such as copper and mercury. This agrees with the hard and soft acids and bases theory.<sup>3</sup> If polysulphur functional groups are present in one molecule, the activity of the functional groups is cumulative. One such group of sulphur compounds is the polythiacrown ether series and their derivatives. Since the synthesis of macrocyclic polythiaethers is not easy and the yields of product

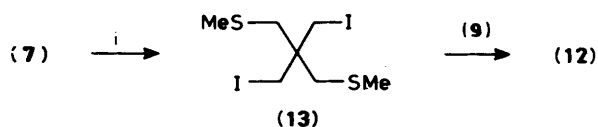
are generally poor, a simple and improved method of their preparation is desirable. Recently, Kellogg *et al.* has reported an improved procedure to make polythiacrown ethers by using  $\text{Cs}^+$  as a template.<sup>4</sup>

Although macrocyclic polyoxaethers (crown ethers) have been widely utilized as phase-transfer catalysts, there is no clear-cut example of these reactions using macrocyclic polysulphides or polysulphoxides. Recently, we have found that tetrakis-(alkylsulphinylmethyl)methanes as one of the polypodant analogues is an effective phase-transfer catalyst in  $\text{S}_{\text{N}}2$  type nucleophilic substitutions and alkylations.<sup>5</sup> Since thiacycrown ethers or sulphoxides should be more effective than the corresponding open-chain derivatives as phase transfer catalysts, we have prepared a new type of macrocyclic polythiaether sulphoxide which contains additional sulphinyl side chains as lariat arms, and have tested them as catalysts for two-phase alkylations.



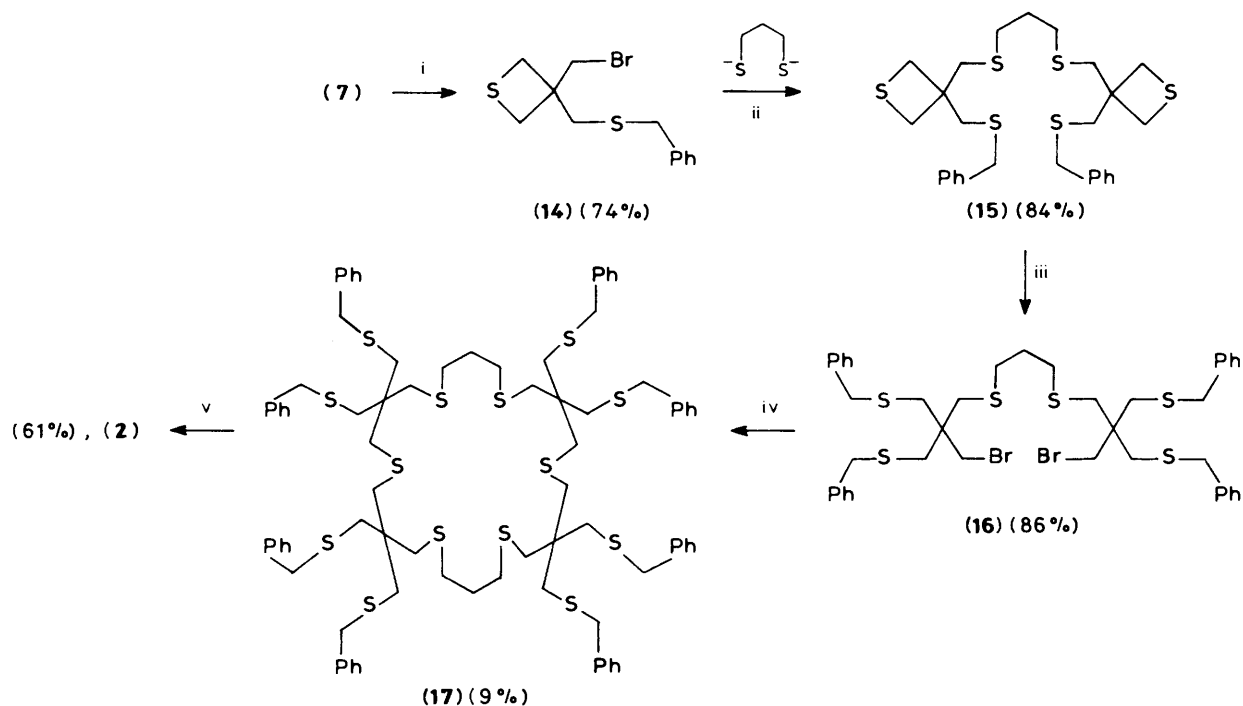


**Scheme 1A.** Reagents: i, MeI (1 equiv.)-C<sub>6</sub>H<sub>6</sub>-EtOH-heat, 12 h; ii, NaOEt-EtOH-C<sub>6</sub>H<sub>6</sub>-reflux, 5 h; iii, MeI-C<sub>6</sub>H<sub>6</sub>-EtOH, 70 °C, 16 h; iv, C<sub>6</sub>H<sub>6</sub>-EtOH-reflux, 10 h



**Scheme 1B.** Reagents: i, MeI (2 equiv.)-heat

out by the reaction of halides with sulphides at high dilution in basic media. However the synthesis of macrocyclic polythiaethers with side chains as functional groups is difficult by this method. Our alternative synthetic method for macrocyclic polythiaethers with alkylthio side chains is illustrated in Schemes 1 and 2. The new macrocyclic polythiaethers with alkylthio side chains (12) and (17) were prepared *via* the thietanes (8) and (14) starting from 2,6-dithiaspiro[3.3]heptane (7). The spiroheptane was easily obtained by reaction of 1,3-



**Scheme 2.** Reagents: i, PhCH<sub>2</sub>Br-C<sub>6</sub>H<sub>6</sub>-EtOH, 70 °C; ii, C<sub>6</sub>H<sub>6</sub>-EtOH; iii, PhCH<sub>2</sub>Br-C<sub>6</sub>H<sub>6</sub>-EtOH, 70 °C; iv, Na<sub>2</sub>S-BuOH-reflux; v, H<sub>2</sub>O<sub>2</sub>-AcOH-C<sub>6</sub>H<sub>6</sub>, room temperature

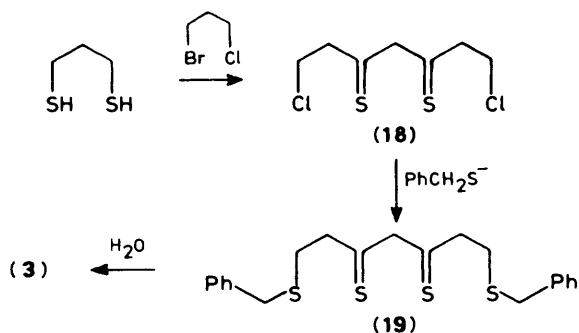
### Results and Discussion

There are several references in the literature to the preparation of macrocyclic polythiaethers containing four or more sulphur atoms.<sup>2</sup> In general, the final step for the ring closure is carried

dibromo-2,2-bis(bromomethyl)propane with sodium sulphide. 3-Iodomethyl-3-methylthiomethylthietane (8), which was obtained by treatment of 2,6-dithiaspiro[3.3]heptane (7) with 1 mol equiv. of methyl iodide, represents an interesting key

intermediate for the synthesis of macrocyclic polythiaethers bearing alkylthio side chains. An acyclic polythiaether bearing two thietane rings (**10**) was prepared in good yield by treatment of compound (**8**) with 4-thiaheptane-1,7-dithiol (**9**). The ring-opening reaction of the thietane ring in compound (**10**) with methyl iodide afforded the compound (**11**) in 68% yield. The macrocyclic polythiaether with alkylthio side chains (**12**) was synthesized in 61% yield by high-dilution cyclization from compound (**11**) and 4-thiaheptane-1,7-dithiol (**9**) [Experimental section method (a)]. Compound (**12**) could also be obtained by the following method (b) (see Experimental section); however, the yield from this method was low compared to that from method (a). Treatment of 2,6-dithiaspiro[3.3]heptane (**7**) with methyl iodide (2 mol equiv.) afforded the ring-opened product (**13**) with no evidence of sulphonium salts formation of the thietane groups. Macrocyclic compound (**12**) was prepared in 13% yield by high-dilution cyclization from (**13**) and 4-thiaheptane-1,7-dithiol (**9**) [method (b)].

The macrocyclic polythiaether (**17**) with eight pendant benzylthio groups was synthesized in a similar fashion starting with the spiroheptane (**7**) and benzyl bromide. The ring closure of compound (**16**) with sodium sulphide gave the new macrocyclic polythiaether (**17**). Formation of the monomeric and trimeric derivatives seems to be possible in this cyclization. Therefore, the number-average molecular weight ( $M_n$ ) of the macrocyclic sulphide (**17**) was determined by vapour pressure osmometry (v.p.o.) and the results indicated clearly that compound (**17**) is the dimeric product. The metal complexation properties of these materials will be reported elsewhere. The macrocyclic polythiaether sulphoxides (**1**) and (**2**) were obtained by the oxidation of the corresponding sulphides (**12**) and (**17**) with 30% aqueous hydrogen peroxide in acetic acid, resulting in diastereoisomeric mixtures respectively. 30% Aqueous hydrogen peroxide was also used to prepare the sulphoxide (**3**) by oxidation of the sulphide (**19**); the latter was prepared as shown in Scheme 3.



All assigned structures are consistent with the data derived from i.r.,  $^1\text{H}$  n.m.r., and mass spectroscopy, and elemental analysis.

**Phase-transfer Reactions Using Acyclic- or Cyclic-poly-sulphoxides.**—Several sulphoxides have been reported to catalyse two-phase alkylations.<sup>6</sup> In order to test the present sulphoxides as phase-transfer catalysts under liquid-liquid two-phase conditions, benzyl methyl ketone and alkyl halides in 50% aqueous sodium hydroxide were allowed to react in the presence of the sulphoxides (**2**)—(**6**). The sulphoxides used in the phase-transfer reactions are all mixtures of geometric isomers which were difficult to separate. Since these sulphoxides and, similarly, the unsubstituted crown sulphoxides are highly

**Table.** Liquid-liquid two-phase alkylations catalysed by various sulphoxides

$$\text{PhCH}_2\text{COMe} + \text{RX} \xrightarrow[50\% \text{ aqueous NaOH}]{\text{Catalyst}} \text{PhCH(R)COMe} + \text{NaX}$$

RX	Catalyst (mol%)	Temp. (°C)	Time (h)	Yield <sup>a</sup> (%)
EtI	( <b>2</b> ) (1.0)	R.t. <sup>c</sup>	0.9	92
EtI	( <b>4</b> ) (1.0)	R.t.	1.5	94
EtI	( <b>5</b> ) (1.0)	R.t.	2.0	91
EtI	( <b>6</b> ) (1.0)	R.t.	4.0	89
EtI	( <b>20</b> ) <sup>b</sup> (1.0)	R.t.	5.0	14
EtI	( <b>3</b> ) (1.0)	R.t.	5.0	9
BuI	( <b>4</b> ) (1.0)	R.t.	4.0	92
BuBr	( <b>21</b> ) <sup>c</sup> (5.0)	80	1.5	93
BuBr	( <b>22</b> ) <sup>d</sup> (1.0)	20	4.0	65

<sup>a</sup> By g.l.c. analysis. <sup>b</sup>  $\text{C}_{12}\text{H}_{25}\text{S}(\text{O})\text{C}_{12}\text{H}_{25}$ . <sup>c</sup> Dicyclohexyl-18-crown-6.<sup>7</sup> <sup>d</sup> Tributylhexadecylphosphonium bromide.<sup>8</sup> <sup>e</sup> R.t. = room temperature.

soluble in water, the presence of hydrophobic groups such as hexyl or benzyl are also necessary.

Inspection of the results obtained (see Table) reveals the following features characteristic of the reactions. The catalytic activity of the sulphoxide (**4**) as an octopus molecule is superior to those of the trisulphoxide (**5**) or sulphone (**6**). However, an acyclic polysulphoxide such as compound (**3**) was ineffective in promoting the reaction, probably because the geometry of the sulphoxide is an important factor. In this series, the sulphoxide (**2**) which has eight hydrophobic benzylsulphinyl groups was the most effective catalyst. We believe that the sulphinyl groups in the crown ring and those of the side chains function jointly. Apparently, the fixed geometry of the sulphinyl groups in compound (**2**) is much more effective in trapping cations than that of the open-chain analogues. Thus, the polythiacrown ether sulphoxides have been demonstrated to be powerful phase-transfer catalysts.

## Experimental

All m.p.s are uncorrected and were taken on a Yanako micro melting-point apparatus. I.r. spectra were obtained on a JASCO A-3 spectrophotometer and n.m.r. spectra were obtained on a Hitachi R-600 FT-NMR spectrometer or a JEOL LNM-MH-100 spectrometer in  $\text{CDCl}_3$  using  $\text{SiMe}_4$  as an internal standard. All the reactions were monitored by chromatography, namely t.l.c. (Merck Kieselgel 60-GF<sub>254</sub>), g.l.c. [Hitachi 163, using a 5% silicon GE SE-30 on  $\text{SiO}_2$  (60–80 mesh) or 2% silicon OV-1 Chromosorb W on  $\text{SiO}_2$  (80–100 mesh) column]. Silica gel used for column chromatography was Merck Kieselgel 60. Mass spectra were taken with a Hitachi RMU-6MG mass spectrometer. Elemental analyses were carried out by the Chemical Analysis Center in this University.

All reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co. Ltd., or Aldrich Chemical Co. The reagents used as reaction solvents were further purified by general methods.

**Preparation of the Polysulphoxides (1)–(3).**—The title compounds were prepared from the corresponding sulphides (**12**), (**17**), or (**19**) with hydrogen peroxide in acetic acid according to the general oxidation method. The yields, spectral data and elemental analyses are as follows.

Compound (**1**), yield 52%;  $\nu_{\text{max}}$  (KBr) 2 900 and 1 040  $\text{cm}^{-1}$ ;  $\delta$

2.31 (8 H, m, 4 × CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.73 (12 H, s, MeSO), 2.96 (16 H, m, 8 × CH<sub>2</sub>SO), and 3.48 (16 H, m, 8 × CH<sub>2</sub>SO).

Compound (2), yield 42%; m.p. 150–162 °C;  $v_{\max}$  (KBr) 1 030 cm<sup>-1</sup>;  $\delta$  2.20 (4 H, m, 2 × CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.85 (8 H, m, 2 × CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.30 (32 H, m, CH<sub>2</sub>SO), 3.95 (16 H, s, 8 × CH<sub>2</sub>Ph), and 7.20 (40 H, s, 8 × Ph) (Found: C, 55.6; H, 5.6; S, 25.1. C<sub>82</sub>H<sub>100</sub>O<sub>14</sub>S<sub>14</sub> requires C, 56.0; H, 5.7; S, 25.5%).

Compound (3), yield 68%; m.p. 190–194 °C;  $v_{\max}$  (KBr) 1 050 cm<sup>-1</sup>;  $\delta$  1.68 (6 H, quint, *J* 6 Hz, 3 × CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.80 (12 H, m, 6 × CH<sub>2</sub>SO), 4.50 (4 H, br s, 2 × CH<sub>2</sub>Ph), and 7.25 (10 H, s, 2 × Ph) (Found: C, 54.8; H, 6.4. C<sub>23</sub>H<sub>32</sub>O<sub>4</sub>S<sub>4</sub> requires C, 55.2; H, 6.4%).

*Preparation of Tetrakis(hexylsulphinylmethyl)methane (4).*—The reaction of tetrakis(bromomethyl)methane with sodium hexane thiolate gave tetrakis(hexylthiomethyl)methane which was then treated with hydrogen peroxide to afford tetrakis(hexylsulphinylmethyl)methane (4) in 61% yield; m.p. 150–153 °C;  $v_{\max}$  (KBr) 1 050 cm<sup>-1</sup>;  $\delta$  0.90 (12 H, t, Me), 1.30 [32 H, m, 4 × (CH<sub>2</sub>)<sub>4</sub>], 2.80 (8 H, m, 4 × CH<sub>2</sub>SO), and 3.42 (8 H, m, CH<sub>2</sub>SO) (Found: C, 57.6; H, 10.0. C<sub>29</sub>H<sub>60</sub>O<sub>4</sub>S<sub>4</sub> requires C, 57.95; H, 10.1%).

*3-Bromomethyl-3,3,3-tris(hexylsulphinylmethyl)methane (5).*—Compound (5) was prepared in the following manner. A solution of 2,6-dithiaspiro[3.3]heptane (7) (3.96 g, 25 mmol) and hexyl bromide (5.45 g, 33 mmol) in benzene–ethanol (50 ml) was heated in a sealed tube at 120 °C for 11 h. The solvent was removed under reduced pressure. The residue was purified by distillation to afford 3-bromomethyl-3-(hexylthiomethyl)thietane, yield 4.3 g (51%), b.p. 160 °C at 3 mmHg;  $v_{\max}$  (neat) 2 920, 1 610, 1 420, and 1 240 cm<sup>-1</sup>;  $\delta$  0.93 (3 H, t, *J* 6 Hz, 2 × Me), 1.12–1.76 [8 H, m, (CH<sub>2</sub>)<sub>4</sub>], 2.62 (2 H, t, *J* 7 Hz, CH<sub>2</sub>S), 3.12 (6 H, br s, 3 × CH<sub>2</sub>S), and 3.86 (2 H, s, CH<sub>2</sub>Br) (Found: C, 44.4; H, 7.2. C<sub>11</sub>H<sub>21</sub>BrS<sub>2</sub> requires C, 44.4; H, 7.1%). A solution of 3-bromomethyl-3-(hexylthiomethyl)thietane (4.15 g, 14 mmol), hexanethiol (1.82 g, 15.4 mmol), and sodium metal (0.43 g, 18.5 mmol) in benzene–ethanol (100 ml) was refluxed for 12 h under N<sub>2</sub>. After removal of the solvent, the residue was extracted with chloroform. The residue was purified by silica gel column chromatography using hexane–benzene (1:1) as the eluant to give 3,3-bis(hexylthiomethyl)thietane (2.8 g, 60%);  $v_{\max}$  (neat) 2 900, 1 620, and 1 410 cm<sup>-1</sup>;  $\delta$  0.87 (6 H, t, *J* 15 Hz, Me), 1.13–1.75 [16 H, m, 2 × (CH<sub>2</sub>)<sub>4</sub>], 2.53 (4 H, t, *J* 7 Hz, 2 × CH<sub>2</sub>S), 2.89 (4 H, s, CH<sub>2</sub>S), and 2.96 (4 H, s, 2 × CH<sub>2</sub>S). A solution of 3,3-bis(hexylthiomethyl)thietane (2.2 g, 6.5 mmol) and hexyl bromide (1.2 g, 7.15 mmol) in benzene–ethanol (30 ml, 1:1) was heated in a sealed tube at 140 °C for 10 h after which time the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using hexane–benzene (1:1) as the eluant to give 3-bromomethyl-3,3,3-tris(hexylthiomethyl)methane (2.3 g, 71%);  $v_{\max}$  (neat) 2 910, 1 420, 1 250, and 820 cm<sup>-1</sup>;  $\delta$  0.90 (9 H, t, 3 × Me), 1.14–1.75 [24 H, m, 3 × (CH<sub>2</sub>)<sub>4</sub>], 2.53 (6 H, t, *J* 7 Hz, CH<sub>2</sub>S), 2.74 (6 H, s, 3 × CH<sub>2</sub>S), and 3.60 (2 H, s, CH<sub>2</sub>Br). The title compound (5) was prepared from the corresponding sulphide with hydrogen peroxide in acetic acid in 65% yield;  $v_{\max}$  (neat) 1 045 cm<sup>-1</sup>;  $\delta$  0.89 (9 H, t, 3 × Me), 1.12–1.77 [24 H, m, 3 × (CH<sub>2</sub>)<sub>4</sub>], 2.76 (6 H, m, CH<sub>2</sub>SO), 3.31 (6 H, m, CH<sub>2</sub>SO), and 4.05 (2 H, br s, CH<sub>2</sub>Br) (Found: C, 48.7; H, 8.3. C<sub>23</sub>H<sub>47</sub>BrO<sub>3</sub>S<sub>3</sub> requires C, 49.0; H, 8.4%).

Tetrakis(hexylsulphonylmethyl)methane (6) was obtained by oxidation of the corresponding sulphide with hydrogen peroxide in acetic acid in 71% yield, m.p. 85.0 °C (lit.<sup>9</sup> 85.5 °C);  $v_{\max}$  (neat) 2 900, 1 320, and 1 140 cm<sup>-1</sup>.

*2,6-Dithiaspiro[3.3]heptane (7).*—To a solution of 1,3-dibromo-2,2-bis(bromomethyl)propane (31 g, 80 mmol) in

ethanol (600 ml) was added Na<sub>2</sub>S·9H<sub>2</sub>O (48 g, 200 mmol) in water (100 ml) and the mixture was refluxed for 10 h. The solvent was removed under reduced pressure and the residue was extracted with chloroform, and dried (MgSO<sub>4</sub>). After removal of the solvent, the residue was purified by silica-gel column chromatography using hexane–benzene (1:1) as the eluant or distillation to give compound (7) (6.5 g, 61%), m.p. 31–32 °C (lit.<sup>10</sup> 31.5 °C); b.p. 70–72 °C at 1 mmHg;  $\delta$  3.28 (8 H, s, CH<sub>2</sub>S).

*3-Iodomethyl-3-(methylthiomethyl)thietane (8).*—A mixture of the spiroheptane (7) (3.38 g, 25 mmol) and methyl iodide (3.55 g, 25 mmol) in benzene (40 ml) was heated in a sealed tube at 70 °C for 10 h. The solvent was removed under reduced pressure and the residue was purified by distillation to afford compound (8) in 63% yield, b.p. 110–113 °C at 2 mmHg;  $v_{\max}$  (neat) 2 900, 1 420, and 1 180 cm<sup>-1</sup>;  $\delta$  2.20 (3 H, s, MeS), 2.97 (6 H, s, 3 × CH<sub>2</sub>S), and 3.60 (2 H, s, CH<sub>2</sub>I) (Found: C, 26.1; H, 4.2. C<sub>6</sub>H<sub>11</sub>IS<sub>2</sub> requires C, 26.2; H, 4.3%).

*Synthesis of 4-Thiaheptane-1,7-dithiol (9).*—To a solution of 1-bromo-3-chloropropane (20 g, 127 mmol) in ethanol (110 ml) was added a mixture of sodium sulphide (18.3 g, 76 mmol) and water (40 ml). The reaction mixture was refluxed for 5 h, after which time the solvent was removed under reduced pressure. To a solution of the residue in ethanol (100 ml) was added thiourea (11.6 g, 152 mmol) and the mixture was refluxed for 24 h. The solution was concentrated, and potassium hydroxide (42 g, 599 mmol) in water (150 ml) was added to the residue; the mixture was then refluxed for 5 h under N<sub>2</sub>. The mixture was cooled in an ice–water bath and cooled aqueous sulphuric acid was added dropwise until the mixture became acidic. After the addition was complete, the reaction mixture was extracted with chloroform (3 ×) and the extracts were dried (MgSO<sub>4</sub>). After removal of the solvent, the residue was distilled under reduced pressure to afford the known<sup>11</sup> dithiol (9) as a liquid (7.7 g, 66%), b.p. 110.0–110.5 °C at 2.5 mmHg;  $v_{\max}$  (neat) 2 930, 2 550, 1 430, and 1 250 cm<sup>-1</sup>;  $\delta$  1.38 (2 H, t, *J* 8 Hz, 2 × SH), 1.92 (4 H, q, *J* 8 Hz, 2 × CH<sub>2</sub>), and 2.41–2.93 (8 H, m, 4 × CH<sub>2</sub>S).

*Synthesis of the Polythiaether (10).*—A mixture of sodium ethoxide (0.30 g, 13.2 mmol), 4-thiaheptane-1,7-dithiol (9) (1.0 g, 5.5 mmol), and 3-iodomethyl-3-methylthiomethylthietane (8) (2.74 g, 10 mmol) in benzene–ethanol (1:1; 40 ml), was refluxed for 5 h under N<sub>2</sub> after which time the solvent was removed under reduced pressure. The title compound was purified to afford a colourless oil by silica gel column chromatography using benzene–chloroform (1:1) as the eluant 1.55 g (66%),  $v_{\max}$  (neat) 2 900, 1 420, 1 170, and 750 cm<sup>-1</sup>;  $\delta$  1.88 (4 H, q, *J* 7 Hz, 2 × CH<sub>2</sub>), 2.19 (6 H, s, 2 × MeS), 2.65 (8 H, m, 4 × CH<sub>2</sub>S), and 3.00 (16 H, m, 8 × CH<sub>2</sub>S).

*Synthesis of the Polythiaether (11).*—A mixture of the polythiaether (10) (470 mg, 1 mmol) and methyl iodide (280 mg, 2 mmol) in benzene–ethanol (20 ml) was heated in a sealed tube at 70 °C for 18 h after which time the solvent was removed under reduced pressure. The title compound was purified by silica-gel column chromatography using benzene as the eluant, to afford a colourless oil (510 mg, 68%);  $v_{\max}$  (neat) 2 900, 1 420, and 1 180 cm<sup>-1</sup>;  $\delta$  1.97 (4 H, q, *J* 7 Hz, 2 × CH<sub>2</sub>), 2.28 (12 H, s, 4 × MeS), 2.78 (20 H, m, CH<sub>2</sub>S and CH<sub>2</sub>SMe), and 3.48 (4 H, s, 2 × CH<sub>2</sub>I) (Found: C, 32.0; H, 5.45. C<sub>20</sub>H<sub>40</sub>I<sub>2</sub>S<sub>7</sub> requires C, 31.65; H, 5.3%).

*Synthesis of the Macrocycle (12).*—Method (a). To a stirred refluxing mixture of (11) (156 mg, 0.2 mmol) in benzene (30 ml) and sodium metal (21 mg, 0.9 mmol) in ethanol (30 ml) under N<sub>2</sub> was added dropwise over 2 h 4-thiaheptane-1,7-dithiol (9); the mixture was then refluxed for a further 10 h. After removal of

the solvent, the residue was extracted with chloroform. The title compound was purified by silica gel column chromatography using hexane-ethyl acetate (9:1) as the eluant to afford a colourless oil (82 mg, 61%);  $\nu_{\max}$  (neat) 2 900 and 1 420  $\text{cm}^{-1}$ ;  $\delta$  1.99 (8 H, q,  $J$  7 Hz, 4  $\times$   $\text{CH}_2$ ), 2.28 (12 H, s, 4  $\times$  MeS), and 2.60–3.22 (32 H, m,  $\text{CH}_2\text{S}$  and  $\text{CH}_2\text{SMe}$ ) (Found: C, 45.0; H, 7.6; S, 46.3.  $\text{C}_{26}\text{H}_{52}\text{S}_{10}$  requires C, 45.6; H, 7.6; S, 46.8%). The number-average molecular weight ( $M_n$ ) of the sulphide (12) was determined by vapour pressure osmometry (v.p.o.) CORONA-117 (Found:  $M_n$  662  $\pm$  33. Calc. for  $\text{C}_{26}\text{H}_{52}\text{S}_{10}$ :  $M$ , 684).

**Method (b).** To a solution of 2,2-bis(iodomethyl)-1,3-dimethylthiopropene (13) (19 g, 45.6 mmol) in benzene (1.5 l) and sodium metal (2.54 g, 110.4 mmol) in ethanol (1 l) was added 4-thiaheptane-1,7-dithiol (9) (9.14 g, 50.2 mmol) in ethanol-benzene (1:1, 100 ml). The mixture was refluxed for 40 h under  $\text{N}_2$ , after which time the solvent was removed under reduced pressure. The residue was subjected to silica gel column chromatography with hexane-ethyl acetate (9:1) as the eluant to afford the title macrocycle as a colourless oil (2.0 g, 13%), whose properties were identical to those described above.

**2,2-Bis(iodomethyl)-1,3-dimethylthiopropene (13).**—A mixture of 2,6-dithiaspiro[3.3]heptane (260 mg, 2 mmol) and methyl iodide (570 mg, 4 mmol) in benzene (10 ml) was heated in a sealed tube at 100  $^\circ\text{C}$  for 10 h after which time the solvent was removed under reduced pressure. The residue was purified by distillation to give the iodide (13), (78%), b.p. 135  $^\circ\text{C}$  at 1 mmHg;  $\delta$  2.19 (6 H, s, 2  $\times$  MeS), 2.72 (4 H, s, 2  $\times$   $\text{CH}_2\text{S}$ ), and 3.36 (4 H, s, 2  $\times$   $\text{CH}_2\text{I}$ ) (Found: C, 20.0; H, 3.35.  $\text{C}_7\text{H}_{14}\text{I}_2\text{S}_2$  requires C, 20.2; H, 3.4%).

**3-Benzylthiomethyl-3-bromomethylthietane (14).**—A mixture of 2,6-dithiaspiro[3.3]heptane (7) (9.5 g, 72 mmol) and benzyl bromide (13 g, 76 mmol) in benzene (50 ml) was heated in a sealed tube at 80  $^\circ\text{C}$  for 10 h after which time the solvent was removed under reduced pressure. The residue was purified by distillation to give the thietane (14) (14.7 g, 80%);  $\nu_{\max}$  (neat) 2 950, 1 490, 1 450, 1 420, 1 240, and 700  $\text{cm}^{-1}$ ;  $\delta$  2.88 (6 H, s, 3  $\times$   $\text{CH}_2\text{S}$ ), 3.67 (4 H,  $\text{CH}_2\text{Ph}$  and  $\text{CH}_2\text{Br}$ ), and 7.20 (5 H, s, Ph) (Found: C, 47.0; H, 5.0.  $\text{C}_{12}\text{H}_{15}\text{BrS}_2$  requires C, 47.5; H, 5.0%).

**Synthesis of the Polythiaether (15).**—A mixture of 3-benzylthiomethyl-3-bromomethylthietane (14) (10.5 g, 34.6 mmol) in benzene (150 ml), propane-1,3-dithiol (2.1 g, 19.1 mmol), and sodium metal (1 g, 43 mmol) in ethanol (200 ml) was refluxed for 8 h under  $\text{N}_2$ . After evaporation of the solvent, the residue was extracted with chloroform. The title compound was purified by silica gel column chromatography using benzene-hexane (1:1) as the eluant to afford a colourless oil (9.3 g, 84%);  $\nu_{\max}$  (neat) 2 900, 1 580, 1 490, 1 450, and 1 410  $\text{cm}^{-1}$ ;  $\delta$  1.87 (2 H, quint,  $J$  7 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 2.54 (4 H, s, 2  $\times$   $\text{CH}_2\text{Ph}$ ), 2.85 (16 H, m, 8  $\times$   $\text{CH}_2\text{S}$ ), 3.61 (4 H, s, 2  $\times$   $\text{CH}_2\text{Ph}$ ), and 7.20 (10 H, s, 2  $\times$  Ph).

**Synthesis of the Polythiaether (16).**—A mixture of the polythiaether (15) (7.7 g, 14 mmol) and benzyl bromide (5.3 g, 30.8 mmol) in benzene-ethanol (350 ml) was heated in a sealed tube at 70  $^\circ\text{C}$  for 20 h after which time the solvent was removed under reduced pressure. The title compound was purified by silica gel column chromatography using benzene as eluant, to afford a colourless oil (10.8 g, 86%);  $\nu_{\max}$  (neat) 2 900, 2 850, 1 490, 1 450, and 1 420  $\text{cm}^{-1}$ ;  $\delta$  1.92 (2 H, quint,  $J$  6 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 2.61 (16 H, m, 8  $\times$   $\text{CH}_2\text{S}$ ), 3.52 (4 H, s, 2  $\times$   $\text{CH}_2\text{Br}$ ), 3.74 (8 H, s, 4  $\times$   $\text{CH}_2\text{Ph}$ ), and 7.26 (20 H, s, 4  $\times$  Ph).

**Synthesis of the Macrocycle (17).**—To a refluxing solution of sodium sulphide (0.72 g, 3.0 mmol) in butanol (30 ml), was

added dropwise, within 2 h, under  $\text{N}_2$  the dibromide (16) (2.2 g, 2.5 mmol); the mixture was refluxed for a further 15 h. After evaporation of the solvent, the residue was extracted with chloroform. The compound was purified by silica-gel column chromatography using benzene as the eluant, to afford a colourless oil (0.34 g, 9%);  $\nu_{\max}$  (neat) 2 900, 1 490, 1 450, and 1 420  $\text{cm}^{-1}$ ;  $\delta$  1.91 (4 H, m, 2  $\times$   $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 2.59 (40 H, m,  $\text{CH}_2\text{CH}_2\text{CH}_2$  and  $\text{CH}_2\text{S}$ ), 3.70 (16 H, s, 8  $\times$   $\text{CH}_2\text{Ph}$ ), and 7.22 (40 H, s, 8  $\times$  Ph) (Found: C, 64.0; H, 6.5.  $\text{C}_{82}\text{H}_{100}\text{S}_{14}$  requires C, 64.2; H, 6.5%). The number-average molecular weight ( $M_n$ ) of the sulphide (17) was determined by vapour pressure osmometry (v.p.o.) CORONA-117 (Found:  $M_n$  1 507  $\pm$  33. Calc. for  $\text{C}_{82}\text{H}_{100}\text{S}_{14}$ :  $M$ , 1 532), which can be distinguished clearly from other possible compounds e.g. monomer;  $\text{C}_4\text{H}_5\text{S}_7$ :  $M$ , 766; trimer;  $\text{C}_{123}\text{H}_{150}\text{S}_{21}$ :  $M$ , 2 298.

**1,11-Dichloro-4,8-dithiaundecane (18).**—To a stirred warm mixture (ca. 50  $^\circ\text{C}$ ) of propane-1,3-dithiol (4.3 g, 40 mmol) in benzene (50 ml) and sodium metal (1.84 g, 80 mmol) in ethanol (100 ml) was added 1-bromo-3-chloropropane within 30 min under  $\text{N}_2$ . The mixture was refluxed for 5 h after which time the solvent was removed under reduced pressure. The residue was extracted with chloroform, and the extract was dried ( $\text{MgSO}_4$ ). After removal of the solvent, the title compound was purified by silica gel column chromatography using hexane-benzene (1:1) as the eluant to afford a colourless liquid (6.34 g, 61%);  $\delta$  1.95 (6 H, m, 3  $\times$   $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 2.58 (8 H, m, 4  $\times$   $\text{CH}_2\text{S}$ ), and 3.58 (4 H, t,  $J$  6 Hz, 2  $\times$   $\text{CH}_2\text{Cl}$ ).

**1,15-Diphenyl-2,6,10,14-tetrathiapentadecane (19).**—1,11-Dichloro-4,8-dithiaundecane (18) (1.57 g, 6 mmol) in benzene-ethanol (50 ml) was added to a stirred, refluxing mixture of toluene- $\alpha$ -thiol (1.64 g, 13.2 mmol) in benzene (50 ml) and sodium metal (0.33 g, 14.5 mmol) in ethanol (100 ml) under  $\text{N}_2$ . The mixture was refluxed for 5 h, after which time the solvent was removed under reduced pressure. The residue was extracted with chloroform, and the extract was dried ( $\text{MgSO}_4$ ). After removal of the solvent, the title compound was purified by silica-gel column chromatography using hexane-benzene (3:7) as the eluant to afford a yellow liquid (1.92 g, 92%);  $\nu_{\max}$  (neat) 2 900, 1 490, 1 450, and 1 410  $\text{cm}^{-1}$ ;  $\delta$  1.72 (6 H, quint,  $J$  6 Hz, 3  $\times$   $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 2.46 (12 H, m, 6  $\times$   $\text{CH}_2\text{S}$ ), 3.56 (4 H, s, 2  $\times$   $\text{CH}_2\text{Ph}$ ), and 7.15 (10 H, s, 2  $\times$  Ph);  $m/z$  436 ( $M^+$ ) (Found: C, 63.2; H, 7.45.  $\text{C}_{23}\text{H}_{32}\text{S}_4$  requires C, 63.25; H, 7.4%).

**General Procedure for P.T.C. Reactions.**—The reactions were carried out in a two-necked reactor. To a mixture of benzyl methyl ketone (2 mmol), ethyl iodide (2.4 mmol) and the sulphoxide [e.g. (2), (3), (4), (5), and (6); 0.02 mmol] was added 50% aqueous sodium hydroxide. The mixture was stirred vigorously at room temperature. Small samples of the reaction mixture were withdrawn with a microsyringe at intervals, quenched with dilute HCl, and extracted with dichloromethane; the extract was monitored by g.l.c. When the reaction was finished, the yield of alkylated product was determined by g.l.c. analysis.

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