

Synthesis and Crystal Structure of New Tetrathiafulvalene Derivatives Incorporated into Thiacycrown Ether Macrocycles

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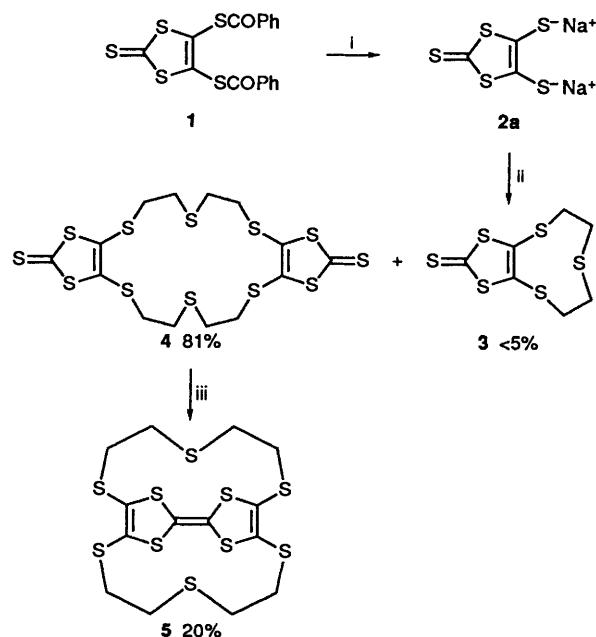
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Condensation of 2-thioxo-1,3-dithiole-4,5-dithiolate dianion **2** with 1,5-dibromo-3-thiapentane gave largely the 2:2 macrocycle **4** which could be converted into the novel tetrathiafulvalene-cage macrocycle **5** on treatment with triethyl phosphite. Treatment of the dithiolate dianion **2** with 1,9-dibromo-3,7-dithianonane gave the 1:1 macrocycle **6** which could be converted into the planar tetrathiafulvalene derivative **7**. The cyclic voltammogram of **7** showed a marked response on the addition of silver perchlorate, but no response when alkali metal perchlorates were added. Crystal structures of macrocycles **3** and **5** are also reported.

Tetrathiafulvalene (TTF) derivatives have been intensively investigated in recent years because of their ability to form charge transfer compounds and their potential as conductors and superconductors.¹ We have recently reported the synthesis of several macrocycles incorporating the 4,5-dithio-1,3-dithiole-2-thione unit and related macrocycles incorporating TTF units,² in attempts to prepare novel materials featuring TTF moieties within metal binding ligand systems, since it was expected that these materials would exhibit altered electrochemical properties in the presence of suitable metal cations. Of particular interest in this regard have been TTF-crown type compounds incorporating oxo- and aza-crown ether ligands,^{2b,d} which show alkali-metal binding properties.³ In addition, these compounds undergo two reversible oxidations in common with other TTFs, and show shifts in their oxidation potentials (of the order of 100 mV) when certain alkali metal cations are added to the electrochemical cell.³ Poly-sulfur crown-type compounds are known to give 'softer' ligands which should preferentially complex to transition metal cations.⁴ Although much work has been reported on thiacycrowns,^{5,6} there are to date no reports of such crown compounds incorporating electroactive units. We now report the synthesis and properties of two new TTFs **5** and **7** incorporated into thiacycrown structures, one of which shows a pronounced change in oxidation potentials, as measured using cyclic voltammetry, in the presence of silver cations.



Scheme 1 Reagents and conditions: i, NaOEt, EtOH; ii, BrCH₂-CH₂SCH₁CH₂Br, EtOH; iii, (EtO)₃P, xylene, reflux

Results and Discussion

The synthesis of these novel TTFs, in common with the synthesis of our earlier reported TTF-containing macrocycles,² began with the dithiolate **2** readily generated *in situ* from the bis(benzoylthio ester) **1**.⁷ Addition of 1,5-dibromo-3-thiapentane to the disodium dithiolate **2a** (Scheme 1) gave the 2:2 macrocycle **4** in 81% yield along with a trace of the 1:1 adduct **3**. Crystals of **3** suitable for X-ray crystal structure determination (Fig. 1, Table 1) were obtained by slow evaporation of a solution in dichloromethane. As expected, based on our earlier work,² treatment of a solution of the 2:2 macrocycle **4**, in refluxing xylene, with triethyl phosphite, gave the TTF-cage macrocycle **5** as a crystalline material in 20% yield, from which a crystal structure was also successfully determined (Fig. 2, Table 2). A side-on view of **5** (Fig. 3) shows that the TTF unit is distorted away from its preferred planar

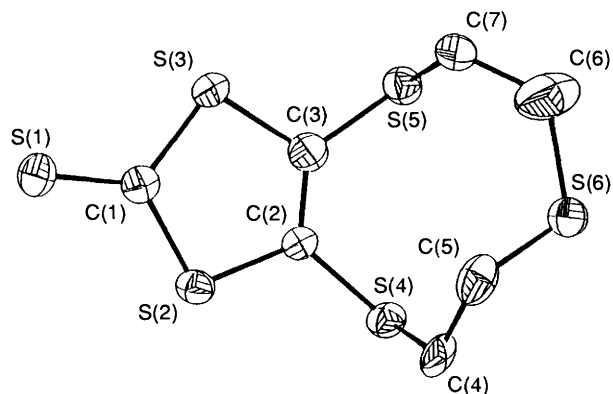
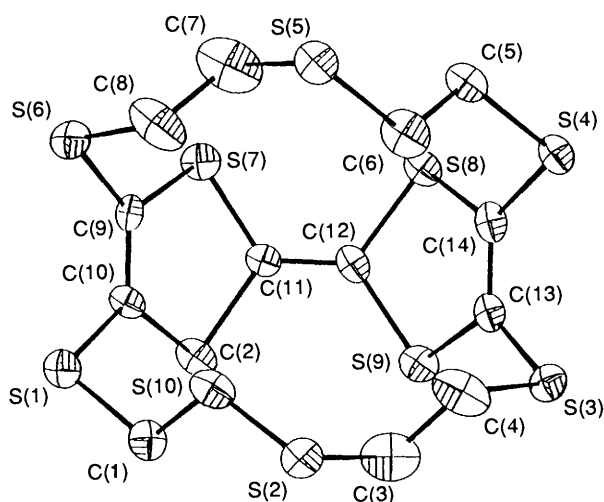
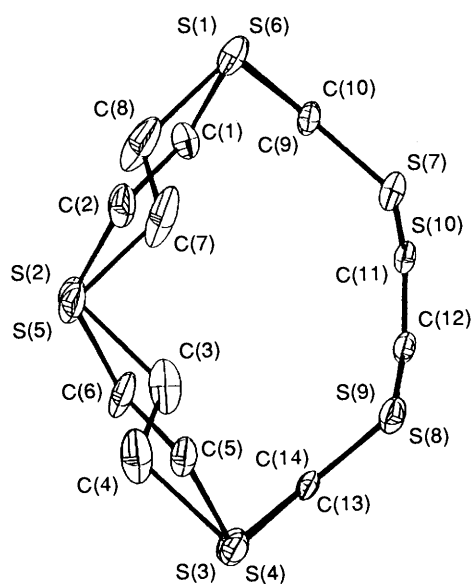


Fig. 1 Crystal structure of compound **3**

Table 1 Bond lengths (Å) and angles (°) for compound **3** (esd in parentheses)

C(1)–S(1)	1.626(9)	C(1)–S(2)	1.730(9)
C(2)–S(2)	1.742(9)	C(1)–S(3)	1.740(9)
C(3)–S(3)	1.761(8)	C(2)–S(4)	1.755(8)
C(4)–S(4)	1.809(9)	C(3)–S(5)	1.745(9)
C(7)–S(5)	1.811(10)	C(5)–S(6)	1.802(11)
C(6)–S(6)	1.803(12)	C(3)–C(2)	1.331(9)
C(5)–C(4)	1.512(13)	C(7)–C(6)	1.472(14)
C(2)–S(2)–C(1)	98.3(4)	C(3)–S(3)–C(1)	98.1(4)
C(4)–S(4)–C(2)	100.7(4)	C(7)–S(5)–C(3)	100.8(4)
C(6)–S(6)–C(5)	106.7(7)	S(2)–C(1)–S(1)	125.0(5)
S(3)–C(1)–S(1)	123.5(5)	S(3)–C(1)–S(2)	111.5(5)
S(4)–C(2)–S(2)	117.9(5)	C(3)–C(2)–S(2)	116.8(6)
C(3)–C(2)–S(4)	125.3(6)	S(5)–C(3)–S(3)	116.8(4)
C(2)–C(3)–S(3)	115.3(6)	C(2)–C(3)–S(5)	127.9(6)
C(5)–C(4)–S(4)	115.6(6)	C(4)–C(5)–S(6)	111.8(7)
C(7)–C(6)–S(6)	120.3(9)	C(6)–C(7)–S(5)	117.2(7)

**Fig. 2** Crystal structure of compound **5****Fig. 3** Crystal structure of **5** viewed side-on

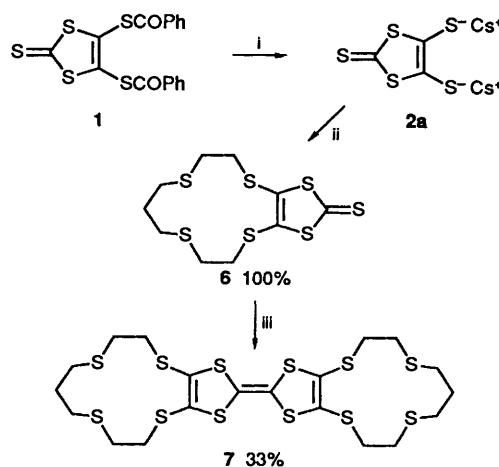
geometry as a result of the ring strain. We have reported previously on a series of related cage molecules with distorted TTF moieties² and we have been able to measure the oxidation potentials for these TTFs as compared with the degree of

Table 2 Bond lengths (Å) and angles (°) for compound **5**

C(1)–S(1)	1.804(13)	C(10)–S(1)	1.750(14)
C(2)–S(2)	1.817(14)	C(3)–S(2)	1.964(20)
C(4)–S(3)	1.988(19)	C(13)–S(3)	1.736(13)
C(5)–S(4)	1.845(13)	C(14)–S(4)	1.757(13)
C(6)–S(5)	1.821(13)	C(7)–S(5)	1.865(19)
C(8)–S(6)	1.882(19)	C(9)–S(6)	1.766(11)
C(9)–S(7)	1.773(14)	C(11)–S(7)	1.753(12)
C(12)–S(8)	1.780(13)	C(14)–S(8)	1.780(13)
C(12)–S(9)	1.765(13)	C(13)–S(9)	1.769(12)
C(10)–S(10)	1.764(12)	C(11)–S(10)	1.774(13)
C(2)–C(13)	1.486(16)	C(4)–C(3)	1.312(22)
C(6)–C(5)	1.479(17)	C(8)–C(7)	1.293(20)
C(10)–C(9)	1.335(15)	C(12)–C(11)	1.304(14)
C(14)–C(13)	1.356(15)		
C(10)–S(1)–C(1)	99.9(7)	C(3)–S(2)–C(2)	102.1(7)
C(13)–S(3)–C(4)	97.4(7)	C(14)–S(4)–C(5)	99.4(6)
C(7)–S(5)–C(6)	101.0(7)	C(9)–S(6)–C(8)	100.5(7)
C(11)–S(7)–C(9)	91.4(6)	C(14)–S(8)–C(12)	91.0(6)
C(13)–S(9)–C(12)	92.1(6)	C(11)–S(10)–C(10)	91.8(6)
C(2)–C(1)–S(1)	114.3(9)	C(1)–C(2)–S(2)	115.1(10)
C(4)–C(3)–S(2)	103.5(13)	C(3)–C(4)–S(3)	105.3(13)
C(6)–C(5)–S(4)	112.9(10)	C(5)–C(6)–S(5)	113.0(11)
C(8)–C(7)–S(5)	114.6(17)	C(7)–C(8)–S(6)	117.1(17)
S(7)–C(9)–S(6)	116.5(8)	C(10)–C(9)–S(6)	126.3(10)
C(10)–C(9)–S(7)	117.1(8)	S(10)–C(10)–S(1)	117.8(8)
C(9)–C(10)–S(1)	126.2(9)	C(9)–C(10)–S(10)	116.0(9)
S(10)–C(11)–S(7)	111.5(7)	C(12)–C(11)–S(7)	124.7(9)
C(12)–C(11)–S(10)	122.1(9)	S(9)–C(12)–S(8)	111.1(7)
C(11)–C(12)–S(8)	122.6(9)	C(11)–C(12)–S(9)	125.3(10)
S(9)–C(13)–S(3)	118.3(8)	C(14)–C(13)–S(3)	126.0(9)
C(14)–C(13)–S(9)	115.6(9)	S(8)–C(14)–S(4)	117.0(8)
C(13)–C(14)–S(4)	126.3(9)	C(13)–C(14)–S(8)	116.8(9)

distortion. Unfortunately, compound **5** proved to be insufficiently soluble in any suitable solvent to allow us to measure the oxidation potentials by cyclic voltammetry.

When the dithiolate **2b** was treated with 1,9-dibromo-3,7-dithianonane, under high dilution conditions, the 1:1 adduct **6** formed in quantitative yield (Scheme 2). Coupling of this

**Scheme 2** Reagents and conditions: i, CsCO₃, MeOH; ii, BrCH₂CH₂-S(CH₂)₃SCH₂CH₂Br, DMF; iii, (EtO)₃P, neat, 125 °C

material by heating in neat triethyl phosphite gave the tetrathiafulvalene derivative **7** in 33% yield as an orange solid. Cyclic voltammetry measurements in dichloromethane (0.1 mol dm⁻³ Bu₄NPF₆, Pt working electrode, 100 mV s⁻¹)* indicate that this novel TTF has two reversible oxidations at 0.53 and 0.89 V (relative to a SCE electrode) (Fig. 4). The addition of an

* Cyclic voltammetry experiments were carried out using a Schlumberger solartron with 1286 electrochemical interface.

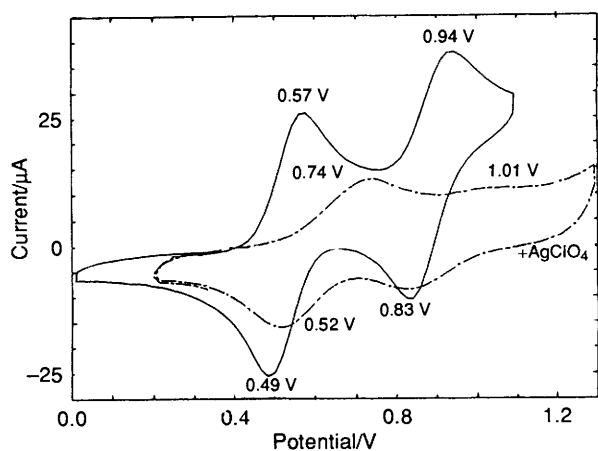
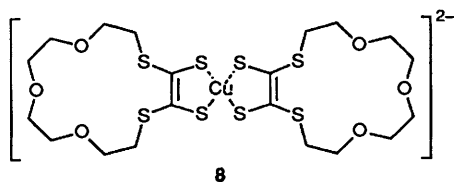


Fig. 4 Cyclic voltammogram of compound 7 recorded in dichloromethane at a scan rate of 100 mV s^{-1} with Bu_4NPF_6 as electrolyte (—) and with excess AgClO_4 added (---)

excess of silver perchlorate to the electrochemical cell results in a pronounced change in the voltammogram, with both oxidation waves being shifted to higher potentials (0.74 and 1.01 V), while the reduction waves show little change.* An explanation consistent with these observations is that the thiocrown moieties of TTF 7 complex a silver cation, thus raising the potential of the first and second electron oxidations due to electron withdrawal from the TTF-unit. After the second oxidation and consequent formation of the TTF dication, the silver cation is expelled from the thiocrown due to charge repulsion and, consequently, the reduction of the dication occurs as for the uncomplexed TTF. Apparently the slow rate of silver complexation does not allow recomplexation between the first reduction and the second. It is also notable that the addition of lithium, sodium or potassium perchlorate to the electrochemical cell showed no effect. This observation indicates that the system is cation selective and that the change in oxidation potentials is indeed due to complexation and not as a result of ion-pairing effects. This system is comparable with the crown ether dithiolene complex 8 recently reported by Green⁸



for which cyclic voltammetry indicates that addition of sodium cations shifts the first oxidation wave and the corresponding reduction wave to higher potentials, but the second oxidation wave and corresponding reduction wave are unaffected, an observation consistent with decomplexation of the sodium cation before the second oxidation, but recomplexation before the second reduction. This suggests that the complexation–decomplexation of sodium cations in this system is considerably faster than the corresponding complexation–decomplexation of silver cations in our system, although Green used a slower scan rate (50 mV s^{-1}) and acetonitrile (in which macrocycle 7 is insoluble) as solvent, so that a direct comparison of these results is not possible.

* The possibility that redox reactions of silver itself are being observed in this voltammogram can be discounted since both the reduction potential for $\text{Ag}^+ \rightarrow \text{Ag}^0$ and the oxidation potential for $\text{Ag}^+ \rightarrow \text{Ag}^{2+}$ lie outside the potential range used.

Experimental

Mass spectra were recorded on a Varian MAT 311A. IR spectra were recorded on a Perkin-Elmer 1750 spectrometer in potassium bromide discs and ^1H NMR spectra on a Bruker AC 250 FT spectrometer; δ -values in ppm relative to TMS; J -values in Hz. PDMS spectra were obtained on a Bio-ion time of flight 10 K plasma desorption instrument.

1,5-Dibromo-3-thiapentane.—**Warning:** this is a mustard compound and must be handled with extreme caution. Hydrobromic acid (48% w/w solution in water, 30 cm^3) was added to a solution of 2,2'-thiodiethanol (10 g, 82 mmol) in water (20 cm^3) and the mixture warmed to 60°C for 1 h. The product was extracted into chloroform ($3 \times 50 \text{ cm}^3$) and the organic extracts were dried (Na_2SO_4). Removal of solvent and distillation under reduced pressure gave the dibromide as a white solid (11 g, 54%), b.p. $102\text{--}104^\circ\text{C}/1.8 \text{ mmHg}$ (lit.,⁹ $115^\circ\text{C}/6 \text{ mmHg}$), m.p. $31\text{--}33^\circ\text{C}$ (lit.,⁹ 31°C).

Reaction of Disodium 2-Thioxo-1,3-dithiole-4,5-dithiolate with 1,5-Dibromo-3-thiapentane.—1,5-Dibromo-3-thiapentane (0.61 g, 2.5 mmol) dissolved in dry ethanol (100 cm^3) was added over 2 h to a stirred solution of the dithiolate 2a, generated *in situ* from the dibenzoyl ester (1.0 g) by the addition of sodium ethoxide in dry ethanol (0.12 g Na in 30 cm^3 ethanol) under nitrogen. The reaction mixture was stirred overnight after which time the resulting yellow precipitate, which was only sparingly soluble in any solvent, was filtered off, washed with water, ethanol and then ether and vacuum dried. Recrystallisation from chloroform gave the 2:2 macrocycle 5,6,8,9,15,16,18,19-octahydrobis[1,3]dithiolo[4,5-*b*:4',5'-*k*][1,4,7,10,13,16]hexathiacyclooctadecene-2,12-dithione 4 (0.57 g, 81%), m.p. 110°C (decomp.); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2800, 1458, 1410, 1267, 1194 and 1060; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.15 (3 H, t, J 8) and 2.80 (3 H, t, J 8); m/z 568 (M^+ , 20%), 504 ($\text{M}^+ - \text{S}_2$, 5%) and 76 (CS_2 , 100%) (Found: C, 29.4; H, 2.7; S, 67.8. $\text{C}_{14}\text{H}_{16}\text{S}_{12}$ requires C, 29.57; H, 2.81; S, 67.60%).

Trace quantities of the 1:1 macrocycle 5,6,8,9-tetrahydro-1,3-dithiolo[4,5-*b*]trithiacyclononene-2-thione 3 could be isolated by applying a suspension of the crude reaction product (500 mg) in dichloromethane (6 cm^3) to a flash chromatography column [30 g of Merck Silica gel 60 ($40\text{--}63 \mu\text{m}$) in a column of internal diameter of 19 mm] and eluting with dichloromethane (500 cm^3). The volume of the collected dichloromethane solution was reduced to 150 cm^3 and then left to evaporate slowly whereupon yellow crystals suitable for X-ray analysis were deposited on the walls of the flask, m.p. $138\text{--}140^\circ\text{C}$ (Found: C, 29.3; H, 2.95. $\text{C}_7\text{H}_8\text{S}_6$ requires C, 29.57; H, 2.81%).

5,6,8,9,14,15,18-Octahydro-1,4:10,13-ethenotetrathioxy-1,4,7,10,13,16-hexathiaoctadecene.—Triethyl phosphite (2 cm^3 , 11.5 mmol) was added to a suspension of the macrocycle 4 (1.0 g, 1.9 mmol) in xylene (40 cm^3) and the mixture was refluxed for 4 h. The resulting brown crystalline material was filtered off, washed with ether and dried to give the macrocycle 5 (0.17 g, 20%), m.p. $130\text{--}132^\circ\text{C}$ (decomp.); m/z 504 (M^+ , 100%) (Found: C, 33.0; H, 4.2. $\text{C}_{14}\text{H}_{16}\text{S}_{10}$ requires C, 33.33; H, 3.17%). The macrocycle 5 proved to be extremely insoluble in all solvents tried which made further purification and a more accurate microanalysis impossible. However, the crystals obtained directly from the reaction were of sufficient quality to allow crystal structure determination.

1,9-Dibromo-3,7-dithianonane.¹⁰—**Warning:** this is a mustard compound and must be handled with extreme caution. Phosphorus tribromide (13.5 g, 50 mmol) was added dropwise, over 4 h, to a mixture of 3,7-dithianonane-1,9-diol¹¹ (12 g, 60 mmol) and dry pyridine (2 cm^3) at -10°C , with the

Table 3 Crystal data and details of data collection and refinement for Compounds 3 and 5

	Compound 3	Compound 5
Formula	C ₇ H ₈ S ₆	C ₁₄ H ₁₆ S ₁₀
<i>M</i>	284.54	504.94
Crystal system	Monoclinic	Triclinic
<i>a</i> /Å	5.18(1)	7.54(1)
<i>b</i> /Å	9.68(1)	9.92(1)
<i>c</i> /Å	22.39(1)	14.92(1)
α/°	90	84.70(2)
β/°	91.86(2)	75.36(2)
γ/°	90	67.65(2)
<i>V</i> /Å ³	1122.10	1000.64
θ range for cell/°	1.5–25	1.5–25
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>Z</i>	4	2
<i>D</i> _c /g cm ⁻³	1.68	1.68
<i>F</i> (000)	584	520
<i>v</i> (Mo-Kα)/Å	0.710 69	0.710 69
μ/cm ⁻¹	11.25	10.56
<i>T</i> /K	298	298
θ range for data/°	2.3–29.0	2.3–29.0
Total data measured	7641	4961
Total unique	2711	3187
Total observed	1969	1274
Significance test	<i>F</i> _o > 3σ(<i>F</i> _o)	<i>F</i> _o > 3σ(<i>F</i> _o)
No. of parameters	122	221
Weighting scheme	unit weight	<i>w</i> = 1/σ ² (<i>F</i> _o)
<i>R</i>	0.077	0.047
<i>wR</i>	0.073	0.051

Table 4 Fractional atomic coordinates (× 10⁴) for compound 3

	<i>x</i>	<i>y</i>	<i>z</i>
S(1)	−3016(4)	−2042(2)	8378(1)
S(2)	1392(3)	−740(2)	9053(1)
S(3)	−451(4)	500(2)	7956(1)
S(4)	5495(3)	1381(2)	9306(1)
S(5)	3343(4)	2823(2)	7988(1)
S(6)	3594(6)	4719(2)	9261(1)
C(1)	−837(12)	−842(7)	8462(3)
C(2)	2950(12)	770(7)	8842(3)
C(3)	2133(12)	1351(6)	8331(3)
C(4)	3712(16)	2259(8)	9875(3)
C(5)	1903(16)	3386(9)	9652(4)
C(6)	1624(26)	5152(14)	8609(5)
C(7)	898(15)	4080(8)	8169(4)

temperature being maintained below 5 °C. After the addition, the reaction mixture was allowed to warm to room temperature and was stirred for 16 h; water (20 cm³) was added and the aqueous phase extracted with ether (3 × 100 cm³). The combined organic extracts were washed with saturated aqueous NaHCO₃ (2 × 100 cm³) and then sulfuric acid (2 mol dm⁻³; 100 cm³), dried (CaCl₂) and evaporated under reduced pressure to give the product as a yellow oil in quantitative yield which was used directly in the next reaction without further purification; δ_H(CDCl₃) 3.50 (4 H, m) and 2.93 (4 H, m), 2.67 (4 H, m) and 1.87 (2 H, quint); δ_C(CDCl₃) 33.97, 30.52, 30.24 and 28.80; *m/z* 322 (M⁺, 12%).

8H-5,6,9,10,12,13-Hexahydro-1,3-dithiolo[4,5-*e*][1,4,7,10]-tetrathiacyclotridecene-2-thione **6**.—1,9-Dibromo-3,7-dithianonane (5.0 g, 16 mmol), dissolved in dry dimethylformamide (50 cm³), was added over 10 h, *via* a syringe pump to a stirred solution of dicaesium 2-thioxo-1,3-dithiole-4,5-dithiolate, generated *in situ* from a suspension of the dibenzoyl ester (4.06 g) in dry methanol (80 cm³) by the addition of caesium carbonate (6 g, 20 mmol), under nitrogen. The reaction mixture

Table 5 Fractional atomic coordinates (× 10⁴) for compound 5

	<i>x</i>	<i>y</i>	<i>z</i>
S(1)	3239(4)	3856(3)	5129(2)
S(2)	8794(4)	199(3)	3921(2)
S(3)	7789(4)	−1522(3)	1513(2)
S(4)	7226(4)	1141(3)	−132(2)
S(5)	7907(5)	4804(3)	1082(2)
S(6)	2774(4)	6523(3)	3489(2)
S(7)	985(4)	4878(3)	2631(2)
S(8)	3032(4)	2433(3)	985(2)
S(9)	3498(4)	118(3)	2368(2)
S(10)	1449(4)	2573(3)	4015(2)
C(1)	5167(14)	2073(11)	4936(8)
C(2)	6831(15)	1984(12)	4129(9)
C(3)	7820(21)	−755(16)	3164(12)
C(4)	8774(21)	−619(18)	2316(11)
C(5)	7167(16)	2965(11)	75(8)
C(6)	7926(18)	3013(13)	888(9)
C(7)	5370(23)	5678(18)	1818(11)
C(8)	5292(25)	5781(18)	2686(10)
C(9)	2036(13)	5024(10)	3537(8)
C(10)	2258(14)	3967(11)	4169(7)
C(11)	1574(14)	3005(10)	2826(7)
C(12)	2419(14)	2007(11)	2180(7)
C(13)	5629(14)	−48(10)	1482(7)
C(14)	5405(14)	1025(11)	839(8)

was stirred overnight after which time the resulting yellow precipitate was filtered off and washed with water (500 cm³), methanol (100 cm³) and ether (100 cm³) to give the macrocycle **6**, which could be recrystallised from ethyl acetate–light petroleum, in quantitative yield (3.5 g), m.p. 152–153 °C; *v*_{max}(KBr)/cm⁻¹ 1055 (C=S); δ_H(CDCl₃) 3.29 (4 H, m), 2.90 (4 H, m), 2.80 (4 H, m) and 1.91 (2 H, m); δ_C(CDCl₃) 211.81, 135.42, 39.52, 35.07, 27.38 and 24.35; *m/z* 358 (M⁺, 4%) (isotopic substitution pattern was in accordance with C₁₀H₁₄S₇), 224 (M⁺ − C₅H₁₀S₂, 100%), 148 (C₆H₁₂S₂⁺, 34%) and 106 (C₃H₆S₂⁺, 97%) (Found: C, 33.7; H, 4.0; S, 62.2. C₁₀H₁₄S₇ requires C, 33.52; H, 3.91; S, 62.57%).

Bi(8H-5,6,9,10,12,13-hexahydro-1,3-dithiolo[4,5-*e*][1,4,7,10]-tetrathiacyclotridecene-2-ylidene) **7**.—The macrocycle **6** (0.2 g, 0.6 mmol) was suspended in freshly distilled triethyl phosphite (10 cm³) and the mixture heated to 125 °C for 45 min. After cooling, the excess of triethyl phosphite was distilled off at reduced pressure and methanol (10 cm³) was added. The resulting precipitate was filtered off and washed with methanol to give the tetrathiafulvalene derivative **7** as orange microcrystals (60 mg, 33%), m.p. 236–238 °C; *v*_{max}(KBr)/cm⁻¹ 1163; δ_H(CDCl₃) 3.24 (8 H, m), 2.80 (16 H, m) and 1.92 (14 H, m); *m/z* 652 (M⁺, 6.5%) (isotopic substitution pattern was in accordance with C₂₀H₂₈S₁₄), 592 (M⁺ − C₂H₄S), 148 (C₆H₁₂S₂⁺, 32%) and 106 (C₃H₆S₂⁺, 97%) (Found: M⁺, 651.8908. C₂₀H₂₈S₁₄ requires *M*, 651.8840).

X-ray Crystallography.—X-ray data for both compounds **3** and **5** were recorded using a FAST TV area detector diffractometer with graphite-monochromated Mo-K radiation (*v* = 0.710 69 Å), following previously described procedures.¹² The crystals of compound **3** were not of good quality and the specimen used showed higher than preferred mosaicity. Crystal data and details of the structure refinement are given in Table 3. One hemisphere of data was recorded for each sample. The structures were solved by direct methods (SHELXS-86)¹³ and refined by least squares techniques (SHELX-80).¹⁴ The data were corrected for absorption using the DIFABS¹⁵ procedure and hydrogens were included in idealised positions in each structure. Non-hydrogen atoms were refined aniso-

tropically. Atomic fractional coordinates are given in Tables 4 and 5; temperature factor coefficients, full lists of bond lengths and angles and F_o/F_c values have been deposited at the Cambridge Crystallographic Data Centre.*

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* For details of the CCDC scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1992, issue 1.

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