Novel Crown Ethers by Oxidative Cycloaddition of Thiopheno Crown Ethers

YuanQiang Li,[a] Thies Thiemann,[b] Tsuyoshi Sawada[b] and Masashi Tashiro*[,b]
[a] *Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-koh-en, Kasuga-shi, Fukuoka 816, Japan*
[b] *Research Institute of Advanced Material, Kyushu University, 6-1 Kasuga-koh-en, Kasuga-shi, Fukuoka 816, Japan*

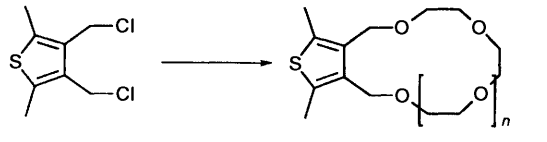
The synthesis of the thiopheno crown ethers **4** is described. The oxidative cycloaddition of these and the known thiopheno crown ethers **2** with *N*-phenylmaleimide is reported. The resulting sulfoxy-bridged cycloadducts **15** and **16** are transformed oxidatively into the phthalimido crown ethers **14** and **17**. An X-ray crystal-structural analysis of the cycloadduct **16b** is provided. The complexation behaviour of the crown ethers towards alkali-metal and silver cations is investigated.

In the last few years some work has appeared on the synthesis and properties of thiophene-containing crown ethers.[1-3] In view of recent work on polythiophenes, thiophene-containing crown ethers show some promise as subunits in conducting polymers.[4] On the whole, however, publications in this area are scarce. In particular, little is known about mixed thiopheno–benzo[2] or thiopheno–heteroareno[5] crown ethers and their complexation behaviour.

Lately we have been studying a mild, oxidative cycloaddition of thiophenes with electron-poor alkenes and alkynes.[6] First reported by Torssell[7] and Fallis[8] for the cycloaddition of dimethylthiophenes, we have found this reaction applicable to a wide range of electron-donor-substituted thiophene systems. In molecules with more than one thiophene unit, a sucessive cycloaddition with equal or non-equal dienophiles is possible. This reaction should make thiopheno crown ethers attractive precursors for the construction of mixed thiopheno–benzo crown ethers and also for benzo crown ethers, where the benzo units are substituted. Furthermore, owing to the intermediacy of a sulfoxy-bridged compound in the reaction sequence and the above mentioned possibility of a successive cycloaddition, it is conceivable that the effect of these consecutive changes of the structure on the complexing ability of the molecules may be amenable to study.

Results and Discussion

Preparation of the Novel Thiopheno Crown Ethers and their Oxidative Cycloaddition.—The thiopheno crown ethers **2a/b** were prepared by the reaction of 3,4-bis(chloromethyl)-2,5-dimethylthiophene **1** with disodium salts of polyethylene glycols according to the procedure of Reinhoudt[9] (Scheme 1).



1 2 $n = 1,2$

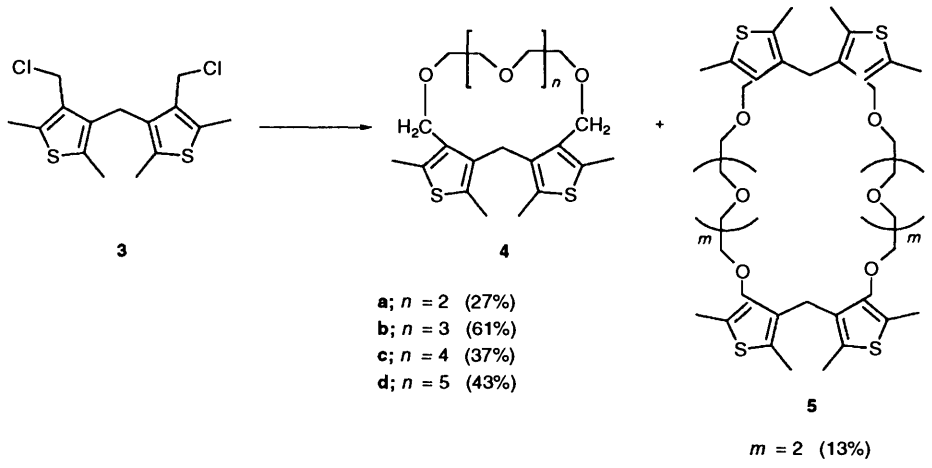
Scheme 1 *Reagents:* $HO(CH_2CH_2O)_{n+2}H$, NaH, THF

Similarly, compounds **4a–d** were prepared from dichloride **3** (Scheme 2). Only in the reaction of compound **3** with triethylene glycol (**3** ⟶ **4a**, $n = 2$) was a dimer, in this case compound **5**, also isolated. Dimers have been known to form in reactions of this type.[1,2,9] Compound **7**,[10] which was used as a model compound for the oxidative cycloaddition of thiopheno ethers, was synthesized by acid-catalysed etherification of the dialcohol **6** (Scheme 3). Compound **7** is a very stable oxocine. It is also formed as a by-product in the hydrolysis of dichloride **3** ($CaCO_3$, 1,4-dioxane) and was the only isolable product in the attempted dimesylation of diol **6** (methanesulfonyl chloride, pyridine).

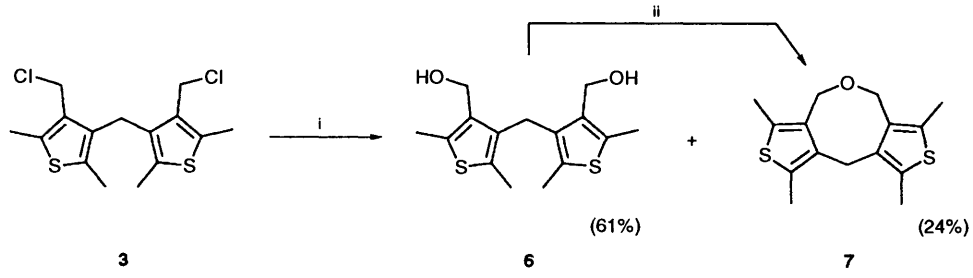
The first oxidative cycloadditions were carried out with tricycle **7** (Scheme 4). Compound **7** reacts with both *N*-phenylmaleimides **9a/b** and dimethyl acetylenedicarboxylate **8** upon addition of *m*-chloroperbenzoic acid (MCPBA) to the reaction mixture. It is thought that, in this oxidative cycloaddition, the thiophene is initially oxidized to a thiophene *S*-monoxide. This reactive intermediate, representative analogues of which have already been isolated under similar conditions,[11] then cycloadds in a formal [4+2] cycloaddition. While in the primary cycloadduct of the thiophene *S*-monoxide with acetylenes, such as diester **8**, SO is extruded oxidatively under the reaction conditions and an aromatic product, **10**, is formed, the cycloaddition of compound **7** with alkenes, such as maleimides **9**, yields bridged sulfoxides **11**. The SO bridge in these compounds can be extruded oxidatively with potassium permanganate under phase-transfer conditions (PTC) at room temperature,[12] and the aromatic products **12** are formed (Scheme 5).

In tricycle **7** only one thiophene moiety reacts in the initial cycloaddition. Cycloaddition of isolated sulfoxides **11** with *N*-phenylmaleimide **9a** under the same conditions leads to an inseparable mixture of products. Compound **12**, on the other hand, readily cycloadds one more molecular equivalent of *N*-phenylmaleimide **9a** to give compound **13** (Scheme 5).

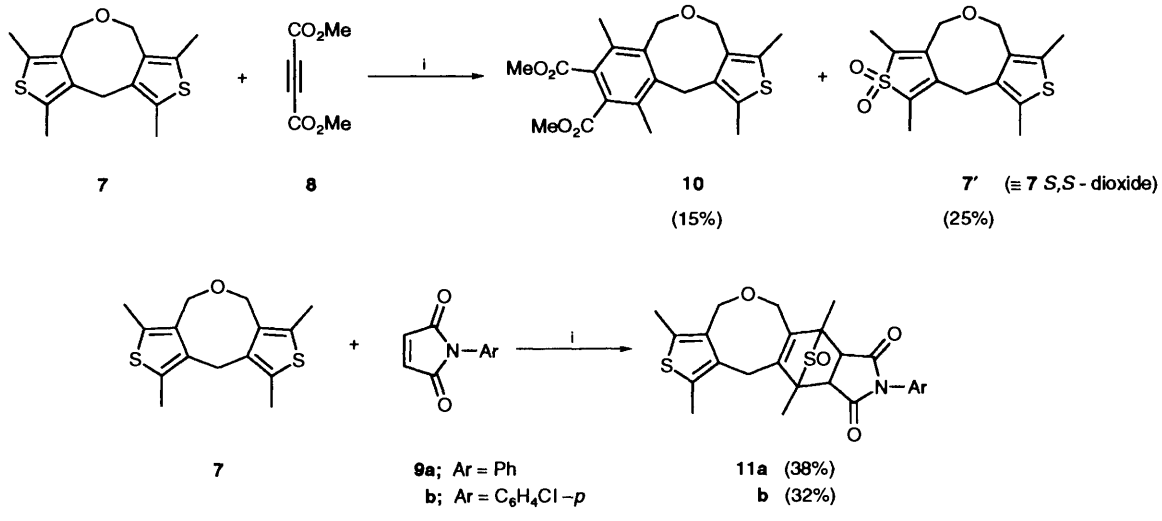
Crown ethers **2a/b** and **4a–d** react with *N*-phenylmaleimide **9a** under oxidative conditions to give the corresponding sulfoxy-bridged cycloadducts **15a/b** and **16a–d** (Schemes 6 and 7). In the case of substrates **2a/b** small amounts of the SO-extruded aromatics **14a/b** are also formed. Although this is not mentioned by Fallis,[8] small amounts of SO-extruded aromatized products are also formed in the oxidative cycloaddition of 2,5-dimethylthiophene and other substituted thiophenes with alkenes. The cycloadducts are *endo*-products, the lone pair (on sulfur) of the SO moiety being on the same side as the newly formed double bond of the cycloadduct, as could be ascertained by an X-ray crystal structural analysis of compound **16b** (Fig. 1). This stereochemistry was found in all of the SO-bridged cycloadducts formed in the oxidative cycloaddition of thiophenes with alkenes both Fallis[8] and we[6,13] have looked at crystallographically. The crown ethers **15a/b** and **16b–d** can be transformed into the benzo thiopheno crown ethers **14a/b** and **17a–c** by oxidative extrusion of SO under the same conditions as for extrusion from adducts **11** (Scheme 7).



Scheme 2 *Reagents:* $HO(CH_2CH_2O)_{n+1}H$, NaH, THF



Scheme 3 *Reagents:* i, $CaCO_3$ (aq.), 1,4-dioxane; ii, H_3PO_4



Scheme 4 *Reagents and conditions:* i, MCPBA, CH_2Cl_2, 0 °C

Complexation.—The complexing behaviour of some thiopheno crown ethers has been studied.[1,14] The complexation of thiopheno crown ethers with alkali metals {in the form of trichloro(ethylene)platinum[II] salts} has been investigated extensively by Reinhoudt *et al.*[15] We were interested to compare the complexing behaviour of thiopheno crown ethers with two thiopheno subunits with published results[1] for similar thiapheno crown ethers with one thiophene moiety. Furthermore, we wanted to see what effect the exchange of a thiophene moiety (*e.g.*, in compound **4b**) for an acceptor-substituted 7-thiabicyclo[2.2.1]heptene substructure (as in compound **16b**) or an acceptor-substituted benzo unit (as in compound **17a**) would have on the complexation behaviour of the corresponding crown ethers towards alkali cations. For this purpose the extractabilities for alkali ions was compared for the compounds **4b–d**, **5**, **14**/**15b**, **16b**/**c**, **17a** and **18**[1] (see Table 1) by using Pedersen's extraction method.[16] Also, the complexation behaviour towards Ag^+ was investigated.

The thiophene crown ethers **4c** and **4d** show moderate complexation of alkali cations, but very little selectivity, with a slight preference of the larger crown ether (**4d**) for the larger cation (Cs^+) as compared with crown **4c** (preference for the smaller Rb^+). They are similar to the thiopheno analogue of a 23-crown-7 **18**[1] in their complexation of alkali cations. The good complexation behaviour of crown **4c** (and to a lesser extent, crown **4d**) towards Ag^+ is of interest. This selectivity for Ag^+ is especially marked for crown **4b**, which shows poor complexation of alkali cations. The complexing ability for Ag^+ decreases with increasing ring size of the crown ether (**4b** > **4c** > **4d**). The smaller crown **4a**, on the other hand,

shows virtually no ability to complex Ag^+. Compounds **5**, **14b**/**15b** and **17a**, however, also show selectivities towards Ag^+. Whether a thiophene unit is directly involved in the complexation of Ag^+ in crowns **4b–4d**, **5** and **17a** is currently being investigated. The selectivities for Ag^+ of compounds **14b**/**15b** is less readily understood.

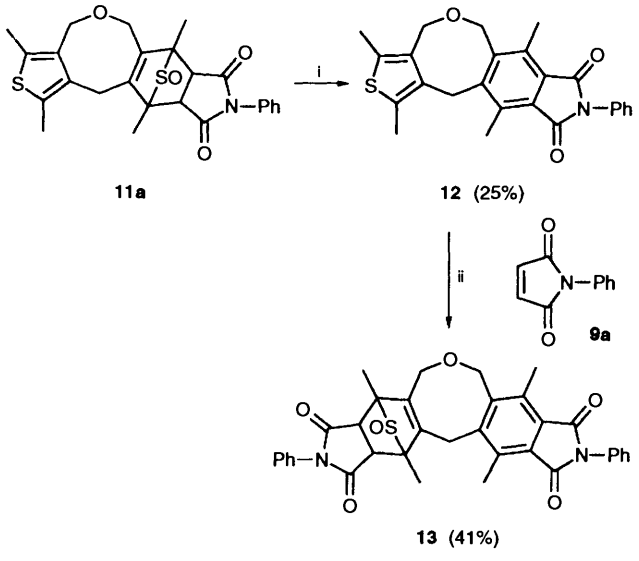
The primary cycloadducts of thiopheno crown ethers with maleimides show low extractabilities for alkali cations (**14b**, **16b** and **16c**), as also do the SO-extruded products, the tetracycle **15b**, and the mixed benzo thiopheno crown ether **17b**.

In conclusion, thiopheno crown ethers can be cycloadded oxidatively with electron-poor dienophiles at room temperature. In the cases studied the exchange of a thiophene unit in these crown ethers against an electon-acceptor-substituted thiabicyclo[2.2.1]heptene oxide substructure or a phthalimido unit led to a decrease of complexing ability of these structures for alkali cations. Some of the thiopheno crown ethers show high extractability towards Ag^+.

Table 1 Extraction of alkali metal picrates with thiopheno crown ethers[a]

Crown compound	Extractability (%)					
	Li^+	Na^+	K^+	Rb^+	Cs^+	Ag^+
14b	1	11	7	5	5	65
15b	0.3	4	2	1	3	47
5	1	3	21	27	27	57
4b	1	12	13	10	9	92
4c	3	10	63	67	64	80
4d	5	16	50	61	70	60
16b	3	4	2	3	3	14
16c	2	2	8	5	2	13
17a	3	4	4	9	4	36
18[1]	4	16	51	63	68	

[a] Measured by Pedersen's method[16] at 25 °C; aqueous phase: [picrate acid] = 7×10^{-5} mol dm^{-3}, [MNO_3] = 0.1 mol dm^{-3}; organic phase (CH_2Cl_2): [crown compound] = 7×10^{-4} mol dm^{-3}. Water–CH_2Cl_2 = 1.1 (v/v).



11a **12** (25%) **9a** **13** (41%)

Scheme 5 *Reagents and conditions:* i, $KMnO_4$, TBABr, CH_2Cl_2, room temp.; ii, MCPBA, CH_2Cl_2

Experimental

General.—M.p.s were determined on a Mitamurariken MELT THERMO and are uncorrected. IR spectra were measured on a JASCO-102 spectrometer. NMR spectra were recorded at 270 MHz (proton) and at 67.9 MHz (carbon-13) with a JEOL GSX-270 spectrometer with $SiMe_4$ as internal standard. *J*-Values are given in Hz. UV spectra were measured on a Hitachi 220 A spectrophotometer. Mass spectra were obtained on a JEOL JMS-O1SG-2 mass spectrometer at 70 eV using a direct-inlet system. Column chromatography was carried out on silica gel (Wako gel, C-300).

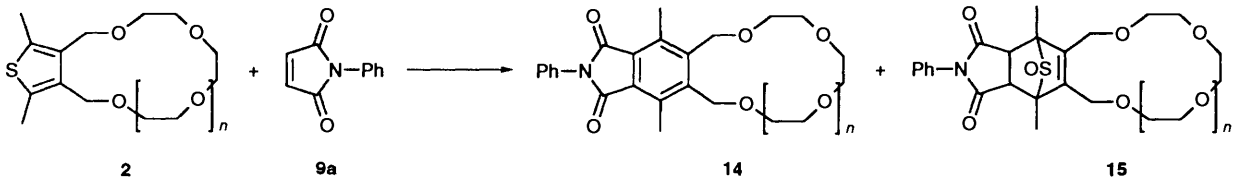
For the extractions (Table 1) spectroscopy grade dichloromethane (99.0%) was used.

The thiopheno crown ethers **2a** and **2b** were obtained according to literature procedures.[9]

Typical Preparation of the Thiopheno Crown Ethers **4**.—Sodium hydride (60% suspension in white oil; 1.0 g, 25 mmol) and triethylene glycol (0.9, 6 mmol) in dry tetrahydrofuran (THF) (100 cm^3) were stirred at 60 °C for 1 h. The solution was cooled to 25 °C and a solution of bis-(4-chloromethyl-2,5-dimethyl-3-thienyl)methane **3** (2.0 g, 6.0 mmol) in dry THF (120 cm^3) was added dropwise. The reaction mixture was stirred at 60 °C for 14 h. It was then cooled to 25 °C, and the precipitate formed was filtered off. The filtrate was concentrated at 40 °C and the residue was separated by column chromatography on silica gel with hexane–diethyl ether (1:2). First fraction, 4,6,21,23-*tetramethyl*-9,12,15,18-*tetraoxa*-5,22-*dithiatricyclo*-[18.3.0.$0^{3,7}$]*tricosa*-1(23),3,6,20-*tetraene* **4a** (0.67 g, 27%), m.p. 91–92 °C (Found: C, 61.3; H, 7.3. $C_{21}H_{30}O_4S_2$ requires C, 61.46; H, 7.37%); ν_{max}(KBr)/cm^{-1} 1440, 1120 and 1024; δ_H($CDCl_3$) 1.95 (6 H, s), 2.37 (6 H, s), 3.60–3.82 (12 H, m), 3.92 (2 H, s) and 4.40 (4 H, s); δ_C($CDCl_3$) 12.90 (2 C), 13.01 (2 C), 25.88, 65.16 (2 C), 69.25 (2 C), 70.40 (2 C), 71.03 (2 C), 129.92 (2 C), 132.94 (2 C), 134.37 (2 C) and 134.95 (2 C); *m*/*z* 410 (M^+, 64.1%), 260 (77.6) and 245 (100); second fraction, 4,6,21,23,27,29,44,46-*octamethyl*-9, 12,15,18,32,35,38,41-*octaoxa*-5,22,28,45-*tetrathiapentacyclo*[41.3.0.$0^{3,7}$.$0^{20,24}$.$0^{26,30}$]*hexatetraconta*-1(46),3,6,20,23,26,29,43-*octaene* **5** (0.63 g, 13%), oil (Found: C, 61.5; H, 7.5. $C_{42}H_{60}O_8S_4$ requires C, 61.46; H, 7.32%); ν_{max}(neat)/cm^{-1} 1456, 1350 and 1090; δ_H($CDCl_3$) 2.03 (12 H, s), 2.35 (12 H, s), 3.47–3.60 (24 H, m), 3.82 (4 H, s) and 4.29 (8 H, s); δ_C($CDCl_3$) 12.92 (4 C), 13.07 (4 C), 25.84 (2 C), 64.76 (4 C), 68.73 (4 C), 70.66 (8 C), 129.97 (4 C), 133.42 (4 C), 134.03 (4 C) and 134.54 (4 C); *m*/*z* 820 (M^+, 78.0%), 670 (22.1), 410 (30.1) and 260 (100).

Analogously were prepared tricycles **4b–4d**:

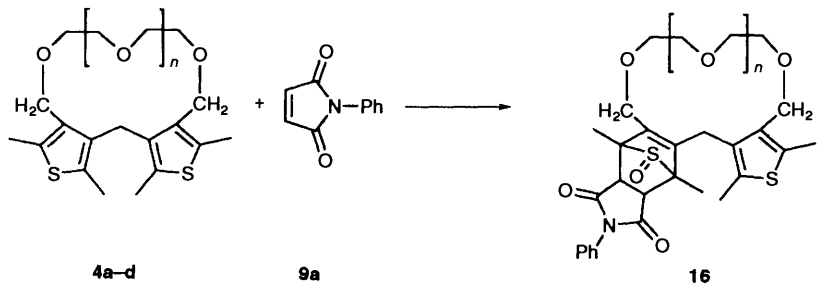
4,6,24,26-*Tetramethyl*-9,12,15,18,21-*pentaoxa*-5,25-*dithiatricyclo*[21.3.0.$0^{3,7}$]*hexacosa*-1(26),3,6,23-*tetraene* **4b** (61%), oil (Found: C, 61.3; H, 7.6. $C_{23}H_{34}O_5S_2$ requires C, 60.77; H,



2 **9a** **14** **15**

a; *n* = 1 (6%) (32%)
b; *n* = 2 (8%) (31%)

Scheme 6 *Reagents and conditions:* MCPBA, CH_2Cl_2, 0 °C



Scheme 7 *Reagents and conditions:* i, MCPBA, CH_2Cl_2, 0 °C; ii, $KMnO_4$, TBABr, CH_2Cl_2, room temp.

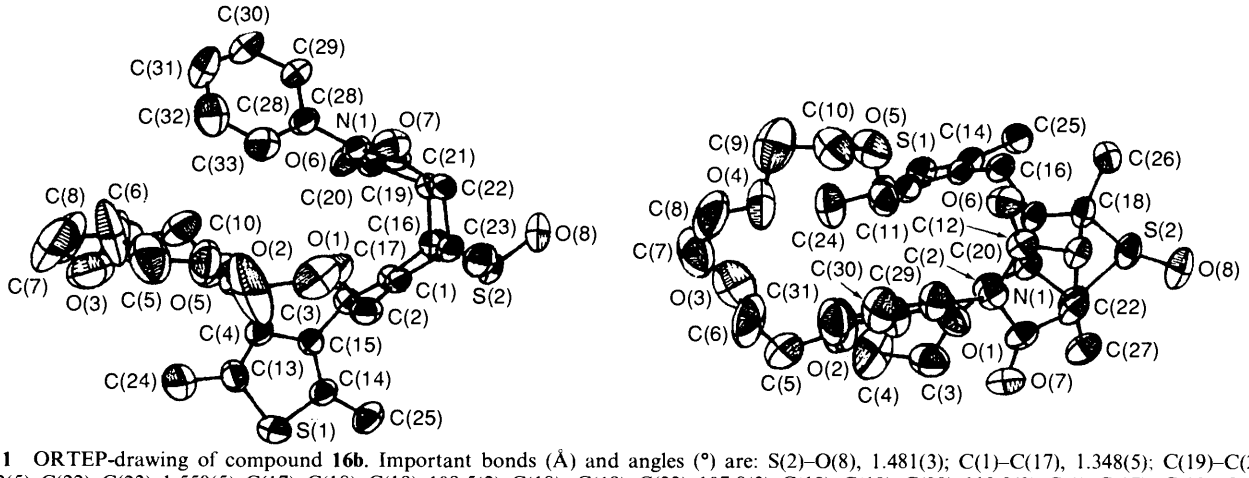
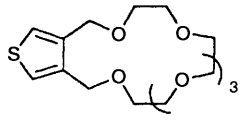


Fig. 1 ORTEP-drawing of compound **16b**. Important bonds (Å) and angles (°) are: S(2)–O(8), 1.481(3); C(1)–C(17), 1.348(5); C(19)–C(22), 1.512(5); C(22)–C(23), 1.550(5); C(17)–C(18)–C(19), 109.5(2); C(18)–C(19)–C(22), 107.8(3); C(18)–C(19)–C(20), 112.2(3); C(1)–C(17)–C(18)–C(19), −61.2(3); C(23)–S(2)–C(18)–C(19), 55.7(2). The crown 'handle' of compound **16b** exhibits a high degree of thermal motion at room temperature.



18[1]

7.58%); ν_{max}(neat)/cm^{-1} 1450, 1350 and 1112; δ_H($CDCl_3$) 1.99 (6 H, s), 2.38 (6 H, s), 3.54–3.78 (16 H, m), 3.86 (2 H, s) and 4.36 (4 H, s); δ_C($CDCl_3$) 12.96, 13.12, 25.98, 64.96, 69.31, 70.78, 70.89, 70.92, 129.91, 133.44, 134.34 and 134.63; *m/z* 454 (M^+, 27.0%), 260 (81.2).

4,6,27,29-*Tetramethyl*-9,12,15,18,21,24-*hexaoxa*-5,28-*dithiatricyclo*[24.3.0.0^{3,7}]*nonacosa*-1(29),3,6,26-*tetraene* **4c** (37%), oil (Found: C, 59.75; H, 7.6. $C_{25}H_{38}O_6S_2$ requires C, 60.21; H, 7.68%); ν_{max}(neat)/cm^{-1} 1460, 1355 and 1110br; δ_H($CDCl_3$) 2.04 (6 H, s), 2.37 (6 H, s), 3.44–3.53 (20 H, m), 3.84 (2 H, s) and 4.33 (4 H, s); δ_C($CDCl_3$) 12.98 (2 C), 13.10 (2 C), 25.90, 64.76 (2 C), 68.86 (2 C), 70.73 (8 C), 129.99 (2 C), 133.46 (2 C), 134.20 (2 C) and 134.63 (2 C); *m/z* 498 (M^+, 60.6%), 260 (100) and 245 (63.4).

4,6,30,32-*Tetramethyl*-9,12,15,18,21,24,27-*heptaoxa*-5,31-*dithiatricyclo*[27.3.0.0^{3,7}]*dotriaconta*-1(32),3,6,29-*tetraene* **4d** (43%), oil (Found: C, 59.5; H, 7.35. $C_{27}H_{42}O_7S_2$ requires C, 59.79; H, 7.74%); ν_{max}(neat)/cm^{-1} 1452, 1356 and 1120; δ_H($CDCl_3$) 2.04 (6 H, s), 2.37 (6 H, s), 3.61–3.68 (24 H, m), 3.83

(2 H, s) and 4.32 (2 H, s); $\delta_C(CDCl_3)$ 12.92 (2 C), 13.05 (2 C), 25.82, 64.74 (2 C), 68.77 (2 C), 70.69 (10 C), 129.97 (2 C), 133.39 (2 C), 134.05 (2 C) and 134.55 (2 C); *m/z* 542 (M^+, 23.5%), 262 (51.8) and 246 (100).

Preparation of 4,6,12,14-*Tetramethyl*-9-*oxa*-5,13-*dithiatricyclo*[9.3.0.0^{3,7}]*tetradeca*-1(14),3,6,11-*tetraene* **7**.—A solution of bis-(4-hydroxymethyl-2,5-dimethyl-3-thienyl)methane **6**[10] (0.5 g, 1.7 mmol) in benzene (120 cm^3) was added dropwise to a mixture of phosphoric acid (15 cm^3) and benzene (30 cm^3) during 5 h. The reaction mixture was stirred at 25 °C for 1 h, after which it was poured into cold water (50 cm^3). The mixture was extracted with diethyl ether (2 × 50 cm^3). The organic phase was washed carefully with cold water, dried ($MgSO_4$) and concentrated at 40 °C. The residue was separated by column chromatography on silica gel with hexane–diethyl ether (10:1) as eluent to give 4,6,12,14-tetramethyl-9-oxa-5,13-dithiatricyclo[9.3.0.0^{3,7}]tetradeca-1(14),3,6,11-tetraene **7** (0.4 g, 85%), m.p. 160–161 °C (lit.,[10] 154–155.5 °C) (Found: C, 64.6; H, 6.5. Calc. for $C_{15}H_{18}OS_2$: C, 64.75; H, 6.47%); ν_{max}(KBr)/cm^{-1} 2875, 1470, 1440, 1250, 1110, 1035 and 900; $\delta_H(CDCl_3)$ 2.28 (6 H, s), 2.40 (6 H, s), 3.77 (2 H, s) and 4.60 (4 H, br s); *m/z* 278 (M^+, 100%), 263 (78.3), 247 (20.8) and 125 (94.1).

Oxidative Cycloaddition of Compound **7** *with Dimethyl Acetylenedicarboxylate* **8**.—To a solution of compound **7** (0.3 g, 1.1 mmol) and dimethyl acetylenedicarboxylate **8** (0.3 g, 2.1 mmol) in dichloromethane (10 cm^3) was added dropwise a solution of MCPBA (65 wt.%; 0.6 g, 2.3 mmol) in dichloromethane (20 cm^3) at 0 °C during 2 h. The reaction mixture was stirred at 25 °C for 2 h and was then poured into saturated aq. sodium hydrogen carbonate (10 cm^3). The phases were separated and the aqueous phase was extracted with dichloromethane (2 × 10 cm^3). The collected organic phases were dried ($MgSO_4$), and concentrated at 40 °C. The residue was separated by column chromatography on silica gel with diethyl ether–hexane (1:1) as eluent. Fraction 1, cycloadduct *dimethyl* 4,6,12,15-*tetramethyl*-9-*oxa*-5-*thiatricyclo*[9.4.0.0^{3,7}]*pentadeca*-1(15),3,6,11,13-*pentaene*-13,14-*dicarboxylate* **10** (60 mg, 15%), m.p. 168–169 °C (Found: C, 64.7; H, 6.1. $C_{21}H_{24}O_5S$ requires C, 64.93; H, 6.23%); ν_{max}(KBr)/cm^{-1} 1736, 1435, 1212 and 1030; $\delta_H(CDCl_3)$ 2.18 (3 H, s), 2.30 (3 H, s), 2.32 (3 H, s), 2.43 (3 H, s), 3.85 (3 H, s), 3.86 (3 H, s), 3.98 (2 H, s), 4.28 (2 H, s) and 5.04 (2 H, s); $\delta_C(CDCl_3)$ 12.65, 12.77, 12.90, 13.08, 26.16, 50.84, 50.92, 63.23, 65.34, 72.69, 74.02, 126.29, 128.86, 129.18, 130.35, 131.37, 131.41, 132.12, 132.67, 133.17, 137.91, 174.21 and 174.55; fraction 2 was the S,S-*dioxide* **7′** (84 mg, 25%) (Found: C, 57.9; H, 5.8. $C_{15}H_{18}O_3S_2$ requires C, 58.06; H, 5.81%); ν_{max}(KBr)/cm^{-1} 1440, 1285, 1170 and 1120; $\delta_H(CDCl_3)$ 1.98 (3 H, s), 2.19 (3 H, s), 2.29 (6 H, s), 3.69 (2 H, br s), 4.39 (2 H, br s) and 4.79 (2 H, br s); $\delta_C(CDCl_3)$ 6.85, 7.08, 12.78, 12.89, 25.18, 62.48 (br), 67.15 (br), 130.94, 131.05, 132.38 and 135.44.

Oxidative Cycloaddition of Compound **7** with N-*Phenylmaleimide* **9a**.—To a solution of compound **7** (0.30 g, 1.08 mmol) and *N*-phenylmaleimide **9a** (0.37 g, 2.16 mmol) in dichloromethane (20 cm^3) was added dropwise a solution of MCPBA (65 wt.%; 0.6 g, 2.4 mmol) in dichloromethane (20 cm^3) at 0 °C during 2 h. The reaction mixture was stirred at 25 °C for 5 h and was then poured into saturated aq. sodium hydrogen carbonate (10 cm^3). The phases were separated and the aqueous phase was extracted with dichloromethane (2 × 10 cm^3). The collected organic phases were collected, dried ($MgSO_4$) and concentrated at 40 °C. The residue was separated by column chromatography on silica gel with hexane–diethyl ether (1:3) as eluent to give 1,5,7,13-*tetramethyl*-16-*phenyl*-10-*oxa*-6,19-*dithia*-16-*azapentacyclo*[11.5.1.0^{2,12}.0^{4,8}.0^{14,18}]*nonadeca*-2(12),4,7-*triene*-15,17-*dione* 19-*oxide* **11a** (0.19 g, 38%), m.p. 231–233 °C (Found: C, 64.8; H, 5.5; N, 3.0. $C_{25}H_{25}NO_4S_2$ requires C, 64.24; H, 5.35; N, 3.00%); ν_{max}(KBr)/cm^{-1} 1715, 1380, 1185 and 1070; $\delta_H(CDCl_3)$ 1.75 (3 H, s), 1.87 (3 H, s), 2.20 (3 H, s), 2.25 (3 H, s), 3.49 (2 H, m), 3.79 (2 H, m), 4.13 (2 H, s), 4.46 (1 H, d, *J* 14), 4.59 (1 H, d, *J* 14), 6.95 (2 H, m) and 7.38–7.40 (3 H, m); $\delta_C(CDCl_3)$ 12.65, 12.78, 12.90, 13.08, 26.16, 50.84, 50.92, 63.23, 65.34, 72.68, 74.02, 126.29 (3 C), 128.86, 129.18 (3 C), 130.35, 131.41, 132.13, 132.67, 133.91, 174.21 and 174.55; *m/z* 467 (M^+, 29.0%), 419 (M^+ − SO, 100).

Analogously, by reaction of compound **7** with *N*-(*p*-chlorophenyl)maleimide **9b**, was prepared 16-(*p*-chlorophenyl-1,5,7,13-tetramethyl-10-oxa-6,19-dithia-16-azapentacyclo-[11.5.1.0^{2,12}.0^{4,8}.0^{14,18}]nonadeca-2(12),4,7-triene-15,17-dione 19-oxide **11b** (32%), m.p. 197–199 °C; ν_{max}(KBr)/cm^{-1} 1710, 1495, 1378, 1160 and 1064; $\delta_H(CDCl_3)$ 1.74 (3 H, s), 1.87 (3 H, s), 2.22 (3 H, s), 2.23 (3 H, s), 3.47 (2 H, m), 3.74 (1 H, d, *J* 8.3), 3.79 (1 H, d, *J* 8.3), 4.13 (1 H, d, *J* 15.5), 4.18 (1 H, d, *J* 15.5), 4.48 (1 H, d, *J* 14.1), 4.54 (1 H, d, *J* 14.1), 6.90 (2 H, m) and 7.36 (2 H, m); *m/z* 501 (M^+[^{35}Cl], 22.0%), 453 (M^+ − SO, 75.2), 423 (48.6) and 241 (56.4).

Preparation of 4,6,12,18-*Tetramethyl*-15-*phenyl*-9-*oxa*-5-*thia*-15-*azatetracyclo*[9.7.0.0^{3,7},0^{13,17}]*octadeca*-1(18),3,6,11,13-*pentaene*-14,16-*dione* **12**.—To a solution of sulfoxide **11a** (0.9 g, 1.9 mmol) in dichloromethane (30 cm^3) was added a solution of potassium permanganate (0.35 g, 2.2 mmol) and tetrabutylammonium bromide (TBABr) (0.74 g, 2.3 mmol) in dichloromethane (30 cm^3). The resulting mixture was stirred for 5 h at 25 °C. Thereafter acetic acid (2 cm^3) and water (10 cm^3) were added, the phases were separated, and the aqueous phase was extracted with dichloromethane (2 × 10 cm^3). The collected organic phases were dried ($MgSO_4$), and concentrated at 40 °C. The residue was separated by column chromatography on silica gel with diethyl ether–hexane (2:1) to give 4,6,12,18-*tetramethyl*-15-*phenyl*-9-*oxa*-5-*thia*-15-*azatetracyclo*[9.7.0.0^{3,7}.0^{13,17}]*octadeca*-1(18),3,6,11,13-*pentaene*-14,16-*dione* **12** (0.2 g, 25%), m.p. 241–242 °C (Found: C, 72.05; H, 5.6; N, 3.3. $C_{25}H_{23}NO_3S$ requires C, 71.94; H, 5.52; N, 3.36%); ν_{max}(KBr)/cm^{-1} 1712, 1505 and 1364; $\delta_H(CDCl_3)$ 2.20 (3 H, s), 2.47 (3 H, s), 2.76 (3 H, s), 2.77 (3 H, s), 4.12 (2 H, s), 4.37 (2 H, s), 5.13 (2 H, s), 7.35–7.41 (3 H, m) and 7.45–7.51 (2 H, m).

1,5,11,17-*Tetramethyl*-8,20-*diphenyl*-14-*oxa*-23-*thia*-8,20-*diazahexacyclo*[15.5.1.0^{2,16}.0^{4,12}.0^{6,10}.0^{18,22}]*tricosa*-2(18),4(12),5,10-*tetraene*-7,9,19,21-*tetraone* 23-*oxide* **13** was prepared analogously to compound **11a**. Column chromatography of the crude product on silica gel with diethyl ether gave compound **13** (41%), m.p. 240–241 °C (Found: C, 68.9; H, 5.0; N, 4.50. $C_{35}H_{30}N_2O_6S$ requires C, 69.26; H, 4.98; N, 4.62%); ν_{max}(KBr)/cm^{-1}; $\delta_H(CDCl_3)$ 1.78 (3 H, s), 1.92 (3 H, s), 2.60 (3 H, s), 2.73 (3 H, s), 3.76–3.83 (4 H, m), 3.96 (2 H, s), 4.80 (1 H, d, *J* 13.5), 4.92 (1 H, d, *J* 13.5), 7.05 (2 H, m), 7.41 (6 H, m) and 7.55 (2 H, m); $\delta_C(CDCl_3)$ 12.72, 13.14, 13.25, 14.14, 28.77, 50.55, 51.07, 60.34, 63.37, 73.24, 74.20, 125.97, 126.81, 128.12, 129.06, 129.11, 131.25, 131.63, 133.96, 134.84, 135.76, 139.26, 141.24, 141.64, 167.48, 167.51, 174.07 and 174.29; *m/z* 606 (M^+, 15.0%), 558 (M^+ − SO, 76) and 528 (100).

Preparation of the Cycloadducts **15a/b**.—Compound **15a** was prepared analogously to its analogue **11a**. The crude product was separated by column chromatography on silica gel with diethyl ether. Fraction 1, 15,21-*dimethyl*-18-*phenyl*-3,6,9,12-*tetraoxa*-18-*azatricyclo*[12.7.0.0.^{16,20}]*henicosa*-1(21),14,16(20)-*triene*-17,19-*dione* **14a** (6.0%) m.p. 197–198 °C (Found: C, 67.4; H, 6.3; N, 3.3. $C_{24}H_{27}NO_6$ requires C, 67.76; H, 6.40; N, 3.29%); ν_{max}/cm^{-1} 1710, 1500, 1390 and 1130; $\delta_H(CDCl_3)$ 2.80 (6 H, s), 3.72–3.87 (12 H, m), 4.92 (4 H, s), 7.38–7.46 (3 H, m) and 7.48–7.52 (2 H, m); $\delta_C(CDCl_3)$ 13.44, 66.81, 69.85, 70.01, 72.04,

126.92, 127.92, 128.44, 128.95, 131.86, 137.03, 143.59 and 167.94; *m/z* 425 (M^+, 55.1%); further chromatography, with diethyl ether–methanol (97 : 3), gave fraction 2, 1,16-*dimethyl*-19-*phenyl*-4,7,10,13-*tetraoxa*-22-*thia*-19-*azatetracyclo*[14.5.1.$0^{2,15}$.$0^{17,21}$]-*docos*-2(15)-*ene*-18,20-*dione* **15a** (32%) m.p. 181–183 °C (Found: C, 60.0; H, 6.05; N, 2.9. $C_{24}H_{29}NO_7S$ requires C, 60.62; H, 6.15; N, 2.95%); ν_{max}(KBr)/cm^{-1} 1710, 1500, 1382 and 1100; δ_H($CDCl_3$) 1.82 (6 H, s), 3.57–3.68 (12 H, m), 3.78 (2 H, s), 4.32 (2 H, d, *J* 11.2), 4.42 (2 H, d, *J* 11.2), 7.25 (2 H, m) and 7.41–7.44 (3 H, m); *m/z* 475 (M^+, 29.6%), 427 (M^+ − SO, 100).

The analogous crown **15b** was prepared similarly. The crude product was separated by column chromatography on silica gel with diethyl ether. Fraction 1, 18,24-*dimethyl*-21-*phenyl*-3,6,9,12,15-*pentaoxa*-21-*azatricyclo*[15.7.0.$0^{19,23}$]*tetracosa*-1(24),17,19(23)-*triene*-20,22-*dione* **14b** (8%), m.p. 153–154 °C (Found: C, 66.4; H, 6.6; N, 3.4. $C_{26}H_{31}NO_7$ requires C, 66.51; H, 6.65; N, 3.36%); ν_{max}/cm^{-1} 1710, 1510, 1400 and 1110; δ_H($CDCl_3$) 2.81 (6 H, s), 3.69–3.83 (16 H, m), 4.84 (4 H, s) and 7.38–7.49 (5 H, m); δ_C($CDCl_3$) 13.66, 66.49, 70.66, 70.87, 71.01, 71.37, 126.93, 127.96, 128.41, 128.96, 131.84, 137.00, 143.54 and 167.92; *m/z* 469 (M^+, 5.0%), 292 (32.0) and 89 (100). Further chromatography, with diethyl ether–methanol (97 : 3), gave 1,19-*dimethyl*-22-*phenyl*-4,7,10,13,16-*pentaoxa*-25-*thia*-22-*azatetracyclo*[17.5.1.$0^{2,18}$.$0^{20,24}$]-*pentacosa*-2(18)-*ene*-21,23-*dione* **15b** (31%), m.p. 180–181 °C (Found: C, 60.2; H, 6.4; N, 3.0. $C_{26}H_{33}NO_8S$ requires C, 60.10; H, 6.40; N, 2.70%); ν_{max}(KBr)/cm^{-1} 1710, 1500, 1384 and 1120; δ_H($CDCl_3$) 1.83 (6 H, s), 3.56–3.65 (16 H, m), 3.78 (2 H, s), 4.27 (2 H, d, *J* 11.9), 4.34 (2 H, d, *J* 11.9), 7.22 (2 H, m) and 7.40 (3 H, m); δ_C($CDCl_3$) 12.58, 51.12, 64.51, 69.95, 70.62, 70.78, 71.41, 73.19, 126.77, 128.66, 128.98, 131.86, 136.85 and 173.91; *m/z* 519 (M^+, 2.9%), 471 (M^+ − SO, 100).

Preparation of 1,5,7,22-*Tetramethyl*-25-*phenyl*-10,13,16,19-*tetraoxa*-6,28-*dithia*-25-*azapentacyclo*[20.5.1.$0^{2,21}$.$0^{4,8}$.$0^{23,27}$]-*octacosa*-2(21),4,7-*triene*-24,26-*dione* 28-*oxide* **16a**.—To a solution of compound **4a** (0.41 g, 1.0 mmol) and *N*-phenylmaleimide **9b** (0.21 g, 1.2 mmol) in dichloromethane (10 cm^3) was added dropwise a solution of MCPBA (65 wt.%; 0.5 g, 2.1 mmol) at 0 °C during 1 h. The reaction mixture was stirred at 25 °C for 4 h and was then poured into saturated aq. sodium hydrogen carbonate (10 cm^3). The phases were separated and the aqueous phase was extracted with dichloromethane (2 × 10 cm^3). The combined organic phases were dried ($MgSO_4$), and concentrated at 40 °C. The residue was separated by column chromatography on silica gel with diethyl ether to give *title compound* **16a** (0.19 g, 31%), m.p. 109–111 °C (Found: C, 62.3; H, 6.7; N, 2.3. $C_{31}H_{37}NO_7S_2$ requires C, 62.08; H, 6.22; N, 2.34%); ν_{max}(KBr)/cm^{-1} 1713, 1380 and 1105; δ_H($CDCl_3$, COSY) 1.32 (3 H, s), 1.82 (3 H, s), 2.29 (3 H, s), 2.34 (3 H, s), 3.34 (1 H, d, *J* 16.5), 3.39–3.62 (13 H, m), 3.79 (1 H, d, *J* 8.3), 3.90 (1 H, d, *J* 11.1), 4.06 (1 H, d, *J* 16.5), 4.24 (1 H, d, *J* 12.2), 4.46 (1 H, d, *J* 12.2), 4.94 (1 H, d, *J* 11.1), 7.29–7.33 (2 H, m) and 7.40–7.45 (3 H, m); δ_C($CDCl_3$) 12.58, 12.98, 13.37, 13.50, 26.20, 51.20, 52.40, 64.44, 64.73, 68.54, 69.72, 69.85, 70.15, 70.23 (2 C), 71.19 (2 C), 73.17, 73.77, 127.13, 128.63, 128.99, 131.79, 131.86, 132.04, 133.37, 133.82, 133.93, 138.40, 173.62 and 174.77; *m/z* 599 (M^+, 28.0%), 551 (M^+ − SO, 42) and 401 (100).

Compounds **16b–16d** were similarly prepared.

1,5,7,25-*Tetramethyl*-28-*phenyl*-10,13,16,19,22-*pentaoxa*-6,31-*dithia*-28-*azapentacyclo*[23.5.1.$0^{2,24}$.$0^{4,8}$.$0^{26,30}$]*hentriaconta*-2(24),4,7-*triene*-27,29-*dione* 31-*oxide* **16b** (37%), m.p. 70–71 °C (Found: C, 61.4; H, 6.4; N, 2.6. $C_{33}H_{41}NO_8S_2$ requires C, 61.57; H, 6.42; N, 2.18%); ν_{max}(KBr)/cm^{-1} 1720, 1502, 1385 and 1110; δ_H($CDCl_3$) 1.54 (3 H, s), 1.82 (3 H, s), 2.13 (3 H, s), 2.38 (3 H, s), 3.36–3.60 (18 H, m), 3.70 (1 H, d, *J* 8.0), 3.79 (1 H, d, *J* 8.0), 3.87 (1 H, d, *J* 10.6), 4.04 (1 H, d, *J* 10.6), 4.34 (1 H, d, *J* 11.5), 4.39 (1 H, d, *J* 11.5), 7.26–7.29 (2 H, m) and 7.38–7.50 (3 H, m); δ_C($CDCl_3$) 12.47, 13.08, 13.39, 13.57, 51.09, 51.90, 63.49, 64.82, 69.02, 70.57, 70.82 (2 C), 70.91, 71.00 (2 C), 71.25, 73.37, 73.60, 76.57, 77.03, 77.23, 77.50, 126.75, 128.61, 129.02, 129.13, 131.53, 131.86, 132.95, 133.91, 134.50, 138.60, 173.74 and 174.70; *m/z* 643 (M^+, 24.3%), 595 (M^+ − SO, 30.8) and 401 (100).

1,5,7,28-*Tetramethyl*-31-*phenyl*-10,13,16,19,22,25-*hexaoxa*-6,34-*dithia*-31-*azapentacyclo*[26.5.1.$0^{2,27}$.$0^{4,8}$.$0^{29,33}$]*tetratriaconta*-2(27),4,7-*triene*-30,32-*dione* 34-*oxide* **16c** (35%), m.p. 128–129 °C (Found: C, 61.1; H, 6.6; N, 2.0. $C_{35}H_{45}NO_9S_2$ requires C, 61.14; H, 6.55; N, 2.04%); ν_{max}(KBr)/cm^{-1} 1710, 1500, 1380 and 1100; δ_H($CDCl_3$) 1.56 (3 H, s), 1.82 (3 H, s), 2.17 (3 H, s), 2.37 (3 H, s), 3.37–3.73 (22 H, m), 3.71 (1 H, d, *J* 7.9), 3.79 (1 H, d, *J* 7.9), 3.90 (1 H, d, *J* 10.9), 4.03 (1 H, d, *J* 10.9), 4.29 (1 H, d, *J* 11.9), 4.37 (1 H, d, *J* 11.9), 7.24–7.27 (2 H, m) and 7.35–7.49 (3 H, m); δ_C($CDCl_3$) 12.51, 13.08, 13.41, 13.48, 26.24, 51.10, 51.84, 63.50, 64.80, 68.95, 70.69, 70.78 (3 C), 70.85 (3 C), 70.92 (2 C), 73.37, 73.69, 126.64, 126.84, 128.68, 129.09 (2 C), 131.55, 131.71, 131.84, 133.15, 133.67, 134.66, 138.45, 173.69 and 174.68; *m/z* 639 (M^+ − SO, 8.0%).

1,5,7,31-*Tetramethyl*-34-*phenyl*-10,13,16,19,22,25,28-*heptaoxa*-6,37-*dithia*-34-*azapentacyclo*[29.5.1.$0^{2,30}$.$0^{4,8}$.$0^{32,36}$]-*heptatriaconta*-2(30),4,7-*triene*-33,35-*dione* 37-*oxide* **16d** (30%), m.p. 122–124 °C (Found: C, 61.1; H, 6.6; N, 2.0. $C_{37}H_{49}NO_{10}S_2$ requires C, 60.72; H, 6.75; N, 1.92%); ν_{max}(KBr)/cm^{-1} 1712, 1500, 1450 and 1292; δ_H($CDCl_3$) 1.54 (3 H, s), 1.82 (3 H, s), 2.19 (3 H, s), 2.36 (3 H, s), 3.34–3.65 (26 H, m), 3.69 (1 H, d, *J* 8.3), 3.78 (1 H, d, *J* 8.3), 3.89 (1 H, d, *J* 10.9), 4.12 (1 H, d, *J* 10.9), 4.26 (1 H, d, *J* 11.9), 4.34 (1 H, d, *J* 11.9) and 7.39–7.50 (5 H, m); *m/z* 731 (M^+, 22.0%), 683 (M^+ − SO, 13.2) and 401 (100).

Preparation of 4,6,24,30-*Tetramethyl*-27-*phenyl*-9,12,15,18,-21-*pentaoxa*-5-*thia*-27-*azatetracyclo*[21.7.0.$0^{3,7}$.$0^{25,29}$]*triaconta*-1(30),3,6,23,25(29)-*pentaene*-26,28-*dione* **17a**.—To a solution of compound **16b** (0.3 g, 0.47 mmol) in dichloromethane (30 cm^3) was added dropwise a solution of potassium permanganate [potassium manganate(VII)] (80 mg, 0.5 mmol) and TBABr (0.2 g, 0.6 mmol) in dichloromethane (20 cm^3). The resulting mixture was stirred at 25 °C for 3 h. Acetic acid (2 cm^3) and water (10 cm^3) were added. The phases were separated, and the aqueous phase was extracted with dichloromethane (2 × 10 cm^3). The combined organic phases were dried ($MgSO_4$), and concentrated at 40 °C. The crude product was separated by column chromatography on silica gel with diethyl ether to give title compound **17a** (0.1 g, 36%), m.p. 50–51 °C (Found: C, 66.1; H, 6.5; N, 2.7. $C_{33}H_{39}NO_7S$ requires C, 66.75; H, 6.58; N, 2.36%); ν_{max}(KBr)/cm^{-1} 1720, 1510, 1390 and 1150; δ_H($CDCl_3$) 1.84 (3 H, s), 2.38 (3 H, s), 2.59 (3 H, s), 2.84 (3 H, s), 3.59–3.76 (16 H, m), 4.27 (2 H, s), 4.37 (2 H, s), 4.73 (2 H, s), 7.36–7.47 (3 H, m) and 7.47–7.52 (2 H, m); δ_C($CDCl_3$) 13.06, 13.48, 13.85, 14.16, 29.76, 65.23, 66.86, 69.63, 70.49, 70.64, 70.76, 70.87, 71.18, 71.23, 71.37, 126.92 (2 C), 127.90, 128.16, 128.96 (2 C), 129.65, 131.91, 132.29, 133.85, 133.98, 136.60, 136.80, 137.34, 142.86, 147.29, 168.07 and 168.19; *m/z* 593 (M^+, 56.0%), 399 (78) and 384 (100).

Compounds **17b** and **17c** were prepared analogously.

4,6,27,33-*Tetramethyl*-30-*phenyl*-9,12,15,18,21,24-*hexaoxa*-55-*thia*-30-*azatetracyclo*[24.7.0.$0^{3,7}$.$0^{28,32}$]*tritriaconta*-1(33),3,6,26,28(32)-*pentaene*-29,31-*dione* **17b** (42%), oil; ν_{max}(KBr)/cm^{-1} 1718, 1385 and 1100br; δ_H($CDCl_3$) 1.73 (3 H, s), 2.38 (3 H, s), 2.62 (3 H, s), 2.83 (3 H, s), 3.57–3.71 (20 H, m), 4.26 (2 H, s), 4.36 (2 H, s), 4.69 (2 H, s) and 7.39–7.50 (5 H, m); δ_C($CDCl_3$) 13.06, 13.46, 13.84, 14.21, 29.60, 64.98, 66.74, 69.29, 70.35, 70.78 (8 C), 127.00, 127.90, 128.25, 128.95, 129.16 (2 C), 129.16, 129.72, 131.93, 132.41, 133.78, 133.96, 136.55, 136.84, 142.89 and 147.26, 168.04 and 168.14; *m/z* 637 (M^+) (Found: M^+, 637.2709. $C_{35}H_{43}NO_8S$ requires M, 637.2709).

4,6,30,36-*Tetramethyl*-33-*phenyl*-9,12,15,18,21,24,27-*heptaoxa*-5-*thia*-33-*azatetracyclo*[27.7.0.$0^{3,7}$.$0^{31,35}$]*hexatriaconta*-

1(36),3,6,29,31(35)-*pentaene*-32,34-*dione* **17c** (45%), oil; ν_{max}(KBr)/cm^{-1} 1770, 1715, 1600, 1380br and 1105br; δ_H($CDCl_3$) 1.71 (3 H, s), 2.39 (3 H, s), 2.62 (3 H, s), 2.83 (3 H, s), 3.58–3.72 (24 H, m), 4.25 (2 H, s), 4.37 (2 H, s), 4.69 (2 H, s), 7.38–7.42 (3 H, m) and 7.47–7.50 (2 H, m); δ_C($CDCl_3$) 13.39, 13.77, 13.98, 14.14, 29.54, 64.89, 66.72, 69.06, 69.87, 70.69 (10 C), 126.85, 126.92, 127.84, 128.16, 128.50, 128.64, 128.91, 129.68, 131.84, 131.97, 132.33, 133.60, 133.85, 136.51, 136.80, 142.73, 147.19, 167.85 and 168.12; *m/z* 681 (M^+) (Found: M^+, 681.2971. $C_{37}H_{47}NO_9S$ requires M, 681.2971).

Structure Determination of the Cycloadduct **16b**.—Intensity data were collected on an Enraf-Nonius CAD4 diffractometer, ω–2θ scan type, graphite-monochromatic Cu-Kα radiation, λ = 1.541 84 Å. Of 5892 independent reflections collected in the range $1 < \theta < 65°$, 4848 reflections with $I_0 > 3\sigma(I_0)$ were taken as observed. The crystal did not show any significant decay during data collection. Positional parameters were determined by direct methods (Monte Carlo method)[17] using MULTAN[18] and were refined by full-matrix least-squares calculations with all non-hydrogen atoms treated anisotropically and hydrogen atoms treated isotropically, using the scheme $w = 4F_0^2/\sigma^2(F_0^2)^2$ to give the final residuals: R = 7.34, R_w = 10.3.

The cell dimensions are: a = 11.90(2), b = 15.45(2), c = 9.13(2) Å, α = 98.16(1), β = 95.79(2), γ = 100.47(1)°, V = 1623 Å^3, space group = $P\bar{1}$, Z = 2, D_{calc} = 1.317 g cm^{-3}.

Fractional atomic coordinates, tables of bond lengths and angles, as well as anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.*

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