OXIDATIVE CYCLOADDITION OF MOLECULES WITH MULTIPLE THIOPHENE CORES

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Abstract- The oxidative cycloaddition of molecules with multiple thienyl-units to alkynes and alkenes is described. The reaction proceeds at room temperature. Yields can be increased upon the use of $BF_3 \cdot Et_2O$. Intermediates of the reaction are thiophene-*S*-oxides. An examplary isolation of a thiophene-*S*-oxide (**16**) in this series and its subsequent cycloaddition are shown. In the case of the oxidative cycloaddition of the thiophenes with alkenes 7-thiabicyclo[2.2.1]heptene-*S*-oxides (*cf.*, **9**) are formed. An X-Ray crystal structural analysis of **9a-H** indicates the cycloaddition to be stereoselective (*syn-endo*). The SO-bridge in these bicyclic subunits could be extruded both thermally and oxidatively under PTC-conditions at room temperature. The products are novel orthocyclophanes.

INTRODUCTION

Donor-substituted thiophenes, when oxidized with peracids, undergo formal [4 + 2] cycloaddition reactions with electron-poor dienophiles. Thus, already Prochazka[1] noted that in the preparation of 2,5-dimethylthiophene-*S*,*S*-dioxide from 2,5-dimethylthiophene by oxidation with peracids side-products were formed, derived from the formal cycloaddition of an intermediate thiophene-*S*-monoxide. Thereafter, Torssell[2] and Fallis[3] reported on the cycloaddition of 2,5-dimethylthiophene with a number of electron-poor dienophiles such as *p*-benzoquinone and *N*-phenylmaleimide. We have found this mild, oxidative cycloaddition reaction to be applicable to a number of electron-donor substituted thiophene systems,[4,5] *albeit* limited as to the choice of dienophile.[6,7] Here, the possibility of transforming one or more thienyl-units in multi-core structures will be shown. Reactions depend on the amount of oxidizing agent used and on whether BF_3 is present. Reactions can be run in such a way that the only by-products are the recyclable starting thiophene precursors. An application of the reaction can be seen in cyclophane chemistry.

RESULTS AND DISCUSSION

In our recent interest in thiophene-containing macrocycles and cyclophanes[8] as versatile reaction precursors we have looked at the thiophene-moiety as a potential precursor for functionalised arene-subunits. In this context, the thermal [4 + 2] cycloaddition reaction of thiophene-*S*,*S*-dioxides with

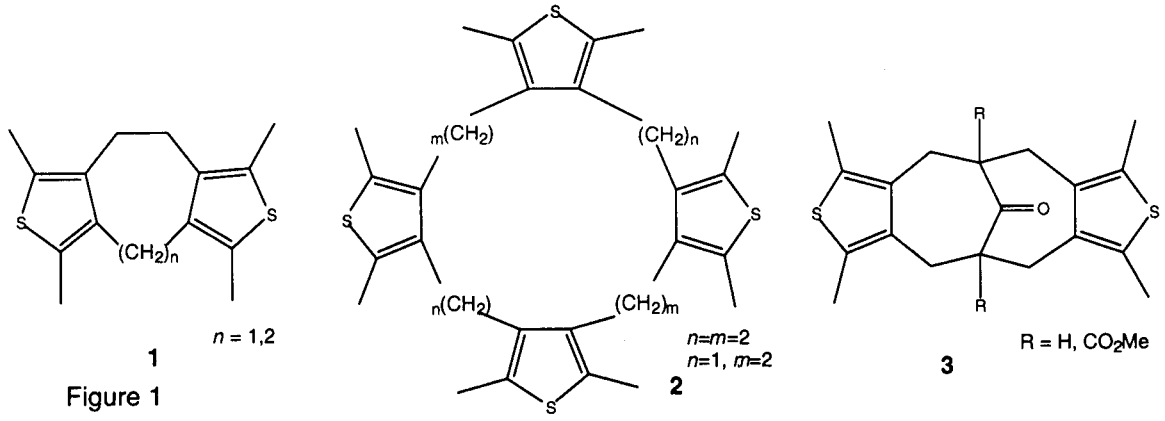
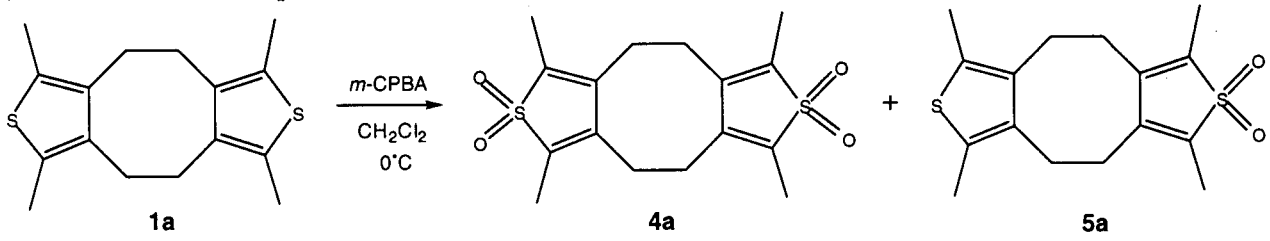


Figure 1

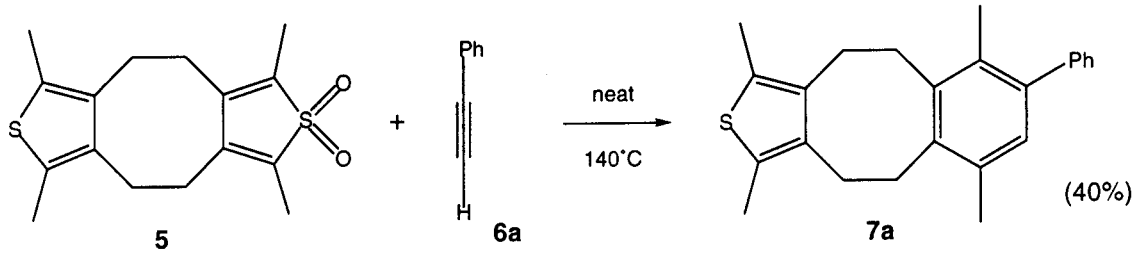
acetylenes, which has been the object of intensive study,[9] comes to mind. While thiophene-*S*,*S*-dioxides are usually easily available from the corresponding thiophenes, the thermal cycloaddition reactions themselves often require quite elevated temperatures. Thus, readily accessible tetramethylorthothiophenophanes (**1a/1b**)[10] (Figure 1) can be oxidized by *meta*-chloroperbenzoic acid (*m*-CPBA) to the thiophene-*S*,*S*-dioxides (**5a/5b**) and the thiophene-*S*,*S*,*S*,'*S*-'tetroxides (**4a/4b**) (Scheme



Scheme 1

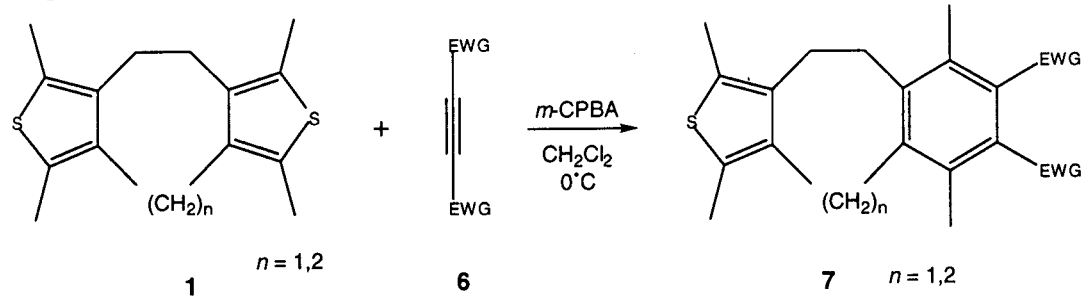
1), depending on the amount of *m*-CPBA used. Unfortunately, however, both thiophene-*S*,*S*-dioxides are relatively unreactive towards cycloaddition reactions with alkynes and alkenes. Thus, **5a** gives the cycloadduct (**7**) upon reaction with phenylacetylene (**6a**) only at 140°C (Scheme 2). On the other hand the thiophene-*S*,*S*,*S*',*S*'-tetroxide (**4a**) does not react with either phenylacetylene[11] or more electron-poor alkynes such as dimethyl acetylenedicarboxylate (**6b**) at temperatures up to 200°C. In part this is due to its poor solubility in normal organic solvents. Where **4a** is soluble at elevated temperatures, such as in DMSO, the solvents are not suitable for the cycloaddition reactions at those high temperatures. These results prompted us to look for a milder alternative and to turn to a *one pot* oxidation, cycloaddition reaction of **1** itself.

From earlier experiments with thiopheno crown ethers[4] it was evident that in principle thiophene-units of macrocycles could be cycloadded to alkenes and alkynes when treated with *m*-CPBA. Prerequisite for the reaction to proceed is that the substituents should not be electron-withdrawing as there are limitations as to the thiophenes that can be oxidized at room temperature or at slightly elevated temperature. Thus, it is known that electron withdrawing functional groups hinder the oxidation of thiophene derivatives.[1,9,12]



Scheme 2 *Cycloaddition of a Thiophene-S,S-dioxide at Elevated Temperatures*

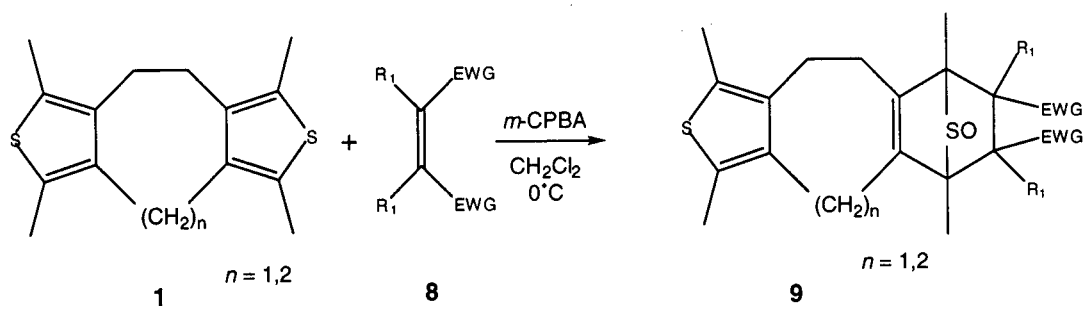
When applying the oxidative cycloaddition reaction to tetramethylorthothiophenophanes (**1**), it is possible to obtain cycloadducts of type (**6**) electron-deficient alkynes at 0°C (Scheme 3). The reaction is thought to proceed *via* an intermediate thiophene-*S*-monoxide,[13] which functions as the actual diene[14]



for **7b-d**: $n = 2$
7b: EWG = CO_2Me; **7c** : EWG = (CO)-Ph-*p*-Bu^t; **7d**: EWG^1 = (CO)Ph, EWG^2 = CO_2Me
7e: EWG = CO_2Me; $n = 1$

Scheme 3 *Oxidative Cycloaddition of Orthothiophenophanes with Alkynes*

in the cycloaddition. The corresponding thiophene-*S*,*S*-dioxides do not cycloadd under the conditions used (0°C). The primary cycloadducts formed aromatize, probably with the extrusion of sulfur monoxide.



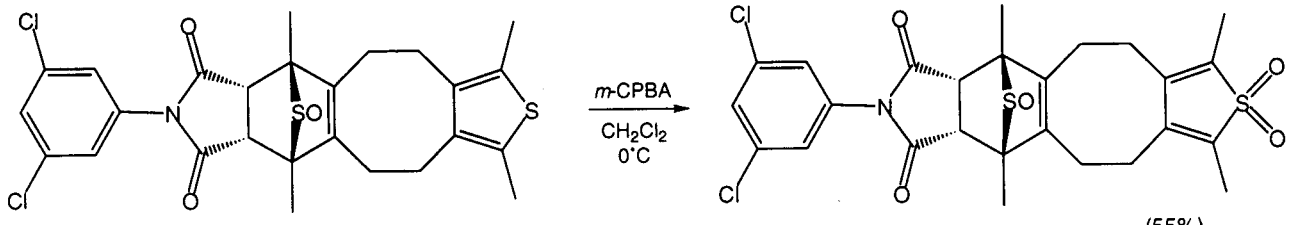
for **1/8a-d**: $n = 2$, R_1 = H; **8/9a**: EWG, EWG ≡ N-Ph-R ; **8/9b**: O ; **8/9c**: EWG^1=EWG^2=CO_2Bu^n

8/9d: EWG^1 = SO_2Ph; EWG^2 = H; **8/9e** R_1 = EWG = CN; for **9a-H**, R = H; **9a-Cl**, R = *p*-Cl

Scheme 4 *Oxidative Cycloaddition of Orthothiophenophanes with Alkenes*

A second pathway with an initial oxidation of the SO-bridge of the primary cycloadducts to an SO_2-

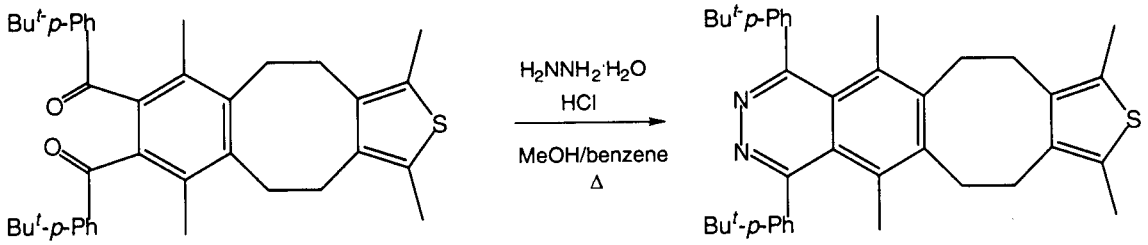
bridge with a subsequent release of SO_2 is disfavored as the oxidation of the SO-bridge of the corresponding cycloadduct (**9a-Cl$_2$**) (see Scheme 5) was found to proceed only very slowly under the conditions used. Thus, when cycloadduct (**9a-Cl$_2$**)[14] was oxidized further with *m*-CPBA, only the thiophene-*S*,*S*-dioxide (**10**) could be isolated. It is believed that in such cases the thiophene-moiety is preferably oxidized and that the SO-bridge is not affected.



9a-Cl$_2$ **10** (55%)

Scheme 5

1 cycloadd to electron-poor alkenes, giving the SO-bridged compounds (**9**) (Scheme 4). 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 (**9a-H**) (Figure 2). This stereochemistry was found in all of the SO-bridged cycloadducts formed in the oxidative cycloaddition of thiophenes with alkenes, both Fallis[3] and we[5,7,14] have looked at crystallographically.

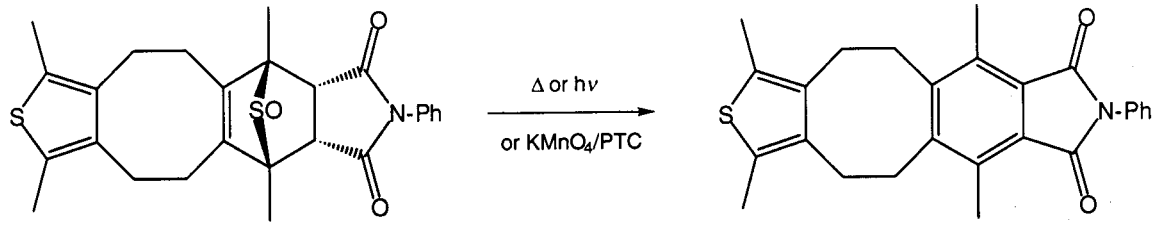


7c **11** (82%)

Scheme 6

Orthothiophenophanes such as **7c** can be transformed further by standard methods. An example towards orthophanes with more extended π-systems is shown in Scheme 6.

The SO-bridge of the cycloadducts formed with alkenes can be extruded thermally, photochemically,[4] electrochemically[15] or oxidatively under phase transfer conditions (PTC) (Scheme 7).[5,16]



9a **7f**

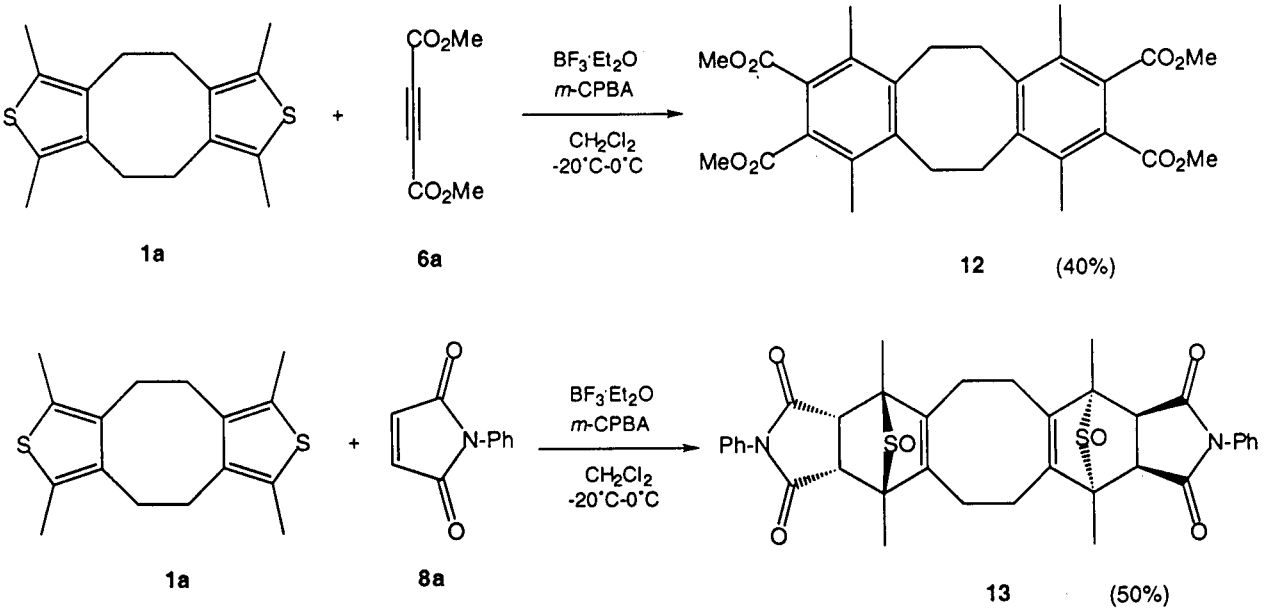
Scheme 7

The SO-bridged cycloadducts (**9**) are thermally more stable than the corresponding cycloadducts of 2,5-dimethylthiophene. The SO-extrusion temperatures for cycloadducts (**9**) have been ascertained by

thermal gravimetry (TG) to be at about 250°C. An extrusion of the SO-bridge in **9a-H** and **9a-Cl** was undertaken on a preparative scale at 250°C and gave aromatized orthocyclophanes (**7f**) and (**7g**).

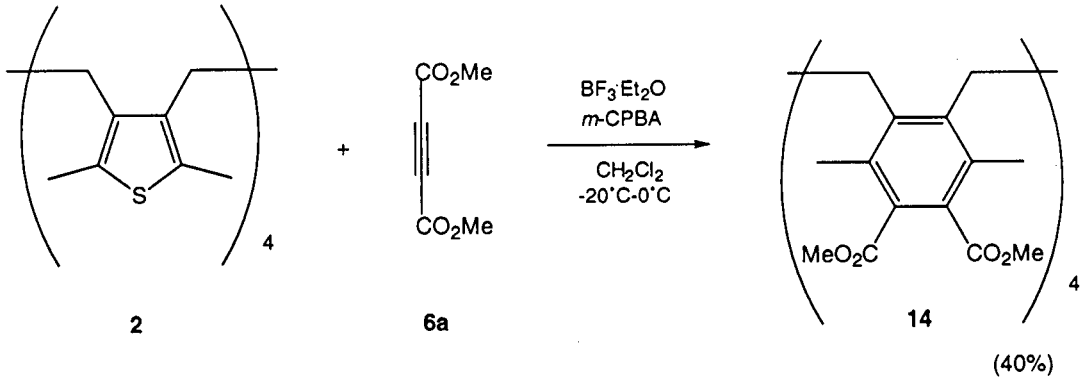
In principal, the SO-bridge in cycloadducts of type (**9**) can be extruded photochemically at room temperature. In the case of systems such as **9a-H** the turnover of the reaction is slow, relative to examined other 7-thiabicyclo[2.2.1]heptene *S*-oxides.[4] Whether this is due to an intramolecular triplet transfer[17] has not yet been clarified.

An effective method for the extrusion of the SO-bridge at room temperature is the oxidative reaction under PTC-conditions using $KMnO_4$ as oxidant and tributylbenzylammonium chloride (TBACl) as phase transfer catalyst. The aromatized orthocyclophanes such as **7f** can be isolated in acceptable yield.



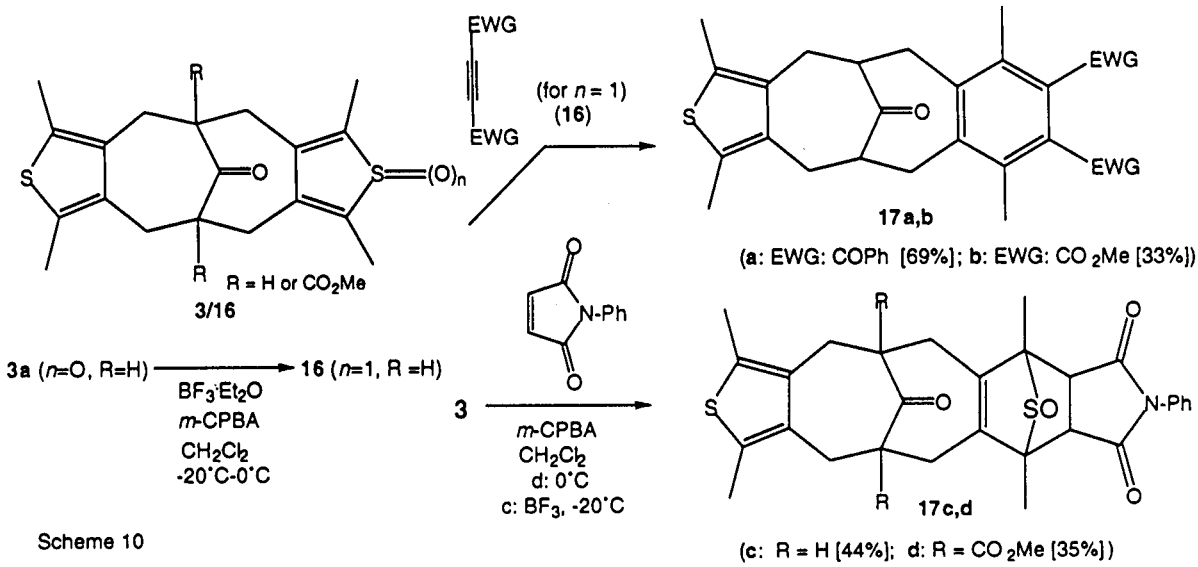
Scheme 8 *Double Cycloaddition Using $BF_3{\cdot}Et_2O$ as Lewis Acid*

The use of $BF_3{\cdot}Et_2O$ as Lewis acid catalyst in the oxidative cycloaddition of **1** leads to bisadducts (**12**) and (**13**) (Scheme 8). It could be shown that a second thienyl core can effectively compete for *m*-CPBA with an intermediary thiophene-*S*-monoxide subunit. Thus, a complexation of $BF_3{\cdot}Et_2O$ on the sulfoxy-moiety of the thiophene-*S*-monoxide subunit effectively shields it against further oxidation to thiophene-*S*,*S*-dioxide.



Scheme 9 *Quadruple Cycloaddition Using $BF_3{\cdot}Et_2O$ as Lewis Acid*

Larger amounts of oxidant and dienophile lead to a double cycloaddition and the isolation of **12** and **13**. Only one isomer of **13** can be isolated. It is believed that the two dienophiles add *anti* to one another. Simultaneous multiple additions can be undertaken with more than two thienyl-units in one molecule. In fact a quadruple cycloaddition is possible in the case of the four-thienyl-core cyclophane (**2a**) (n = m = 2) in 40% yield (Scheme 9). All of these reactions are run at temperatures of between -20°C and 0°C. A



Scheme 10

similar reaction of **2a** with dimethyl acetylenedicarboxylate without BF_3 as a catalyst gave a mono-adduct (**15**) only in mediocre yield.

A further system, where an oxidative cycloaddition can be carried out is the [3.3]orthothiophenophane (**3**) (Scheme 10).[18] Here, the orthothiophenophane-*S*-oxide (**16**) could be prepared selectively by oxidation in absence of a dienophile. Isolated **16** was then subjected to a [4+2] cycloaddition with acetylenes to give **17a,b**. Orthothiophenophanes (**17a,b**) are precursors of layered non-distorted interconnected π-systems (Figure 3).[19]

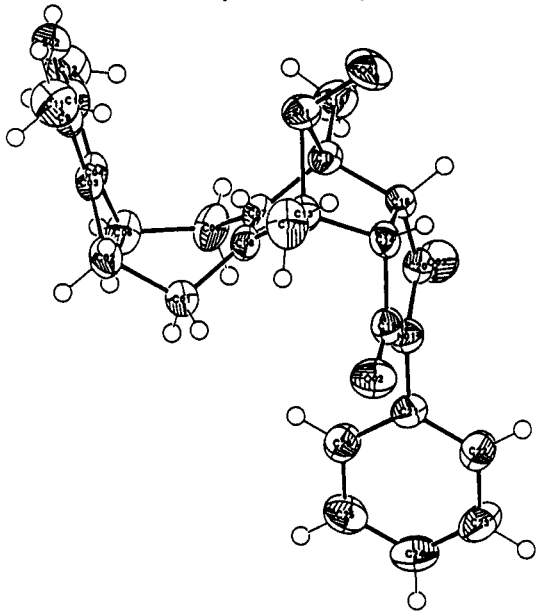


Figure 2. ORTEP drawing of **9a-H**.

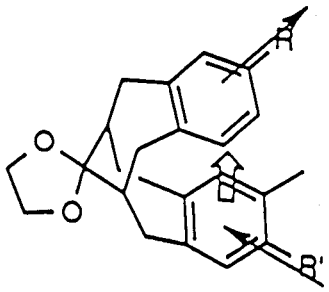


Figure 3.

Schematic of a layered rigid [3.3]orthocyclophane with donor and acceptor substituents.[19]

ACKNOWLEDGEMENT

The authors thank Ms. Yasuko Tanaka for providing us with mass and high resolution mass spectra.

EXPERIMENTAL

Mps were determined on a Multimurariken MELT THERMO and are uncorrected. IR spectra were measured on a JASCO-102 spectrophotometer. NMR spectra were recorded in $CDCl_3$ at 270 MHz (proton) and at 67.9 MHz (carbon-13) with a JEOL GSX-270 spectrometer with $SiMe_4$ as internal standard unless noted otherwise. *J*-Values are given in Hz. MS spectra were obtained on a JEOL JMS-01SG-2 mass spectrometer at 70 eV using a direct-inlet system. Column chromatography was carried out on silica gel (Wako gel, C-300). Thermal gravimetry was done on a Seiko SSC/5200 instrument in a temperature interval of between 20°C and 400°C with a gradient of 15°C/min.

The orthothiophenophanes (**1a/1b**),[10] (**2a**)[10](m=n=2)/(**2b**)[20](n=1,m=2) and (**3**, R = H, CO_2Me)[18] were obtained according to literature procedures.

Tetramethyl[2.2](3,4)thiophenophane-*S*,*S*-dioxide (5a): A mixture of **1a** (310 mg, 1.12 mmol) and *m*-CPBA (600 mg, 80w%, 2.80 mmol) was stirred in chloroform (10 mL) at 0°C for 3 h and at rt for an additional 11 h. Then the reaction mixture was poured into aqueous saturated $NaHCO_3$ solution (50 mL) and quickly extracted with dichloromethane (CH_2Cl_2) (2 X 20 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed over silica gel (ether) to give **5a** (195 mg, 58%) as off-white crystals; mp 237°C (ether); *v* (KBr/cm^{-1}) 2880, 1620, 1480, 1440, 1380, 1180, 1060, 900 and 720; δ_H: 1.95 (6H, s, 2 CH_3), 2.23 (6H, s, 2 CH_3), 2.65 (4H, vt, ^3J = 6.7 Hz) and 2.83 (4H, vt, ^3J = 6.7 Hz); δ_C: 6.74, 12.72, 23.86, 24.67, 129.40, 131.43, 134.91 and 138.29; *m/z* 308 (M^+, 100), 243 (38) and 229 (62). *Anal.* Calcd for $C_{16}H_{20}O_2S_2$: C, 62.33; H, 6.46. Found: C, 61.73; H, 6.29.

When the amount of *m*-CPBA was increased, an appreciable amount of **4a** was formed. A mixture of **1a** (310 mg, 1.12 mmol) and *m*-CPBA (1.2 g, 80 w%, 5.60 mmol) was reacted accordingly in chloroform (10 mL) to give tetramethyl[2.2](3,4)thiophenophane-*S*,*S*,*S*',*S*'-tetroxide (**4a**) (155 mg, 42%) as colorless crystals, which are sparingly soluble in CH_2Cl_2 and were filtered off, after the reaction mixture was poured into saturated aqueous $NaHCO_3$ solution. (**4a**). mp > 300°C; *v* (KBr/cm^{-1}) 2900, 1483, 1450, 1280, 1167, 1102, 1041, 782 and 739; δ_H 2.07 (12H, s, 4 CH_3) and 2.66 (8H, br s); δ_C (DMSO-d_6) 2.00 (12H, s, 4 CH_3) and 2.86 (8H, s, 4 CH_2); δ_C (DMSO-d_6) 6.18, 21.73, 131.83 and 136.89; *m/z* 340 (M^+, 100). HRMS calcd for $C_{16}H_{21}O_4S_2$: 341.0881. Found: 341.0885 (FAB, 3-nitrobenzyl alcohol, MH^+).

4,7,12,14-Tetramethyl-5-phenyl-13-thiatricyclo[10.3.0.0^{4,9}]pentadecapenta-3,5,7,11,14-ene (7a): A mixture of **5a** (130 mg, 0.42 mmol) and phenylacetylene (**6a**) (500 mg, 4.9 mmol) was heated at 140°C for 2 h under an inert atmosphere. The remaining acetylene (**6a**) was evaporated *in vacuo*. Column chromatography on silica gel (hexane/ether 1:1) yields **7** (66 mg, 45%) as colorless crystals, mp 102 - 103°C; *v* (KBr/cm^{-1}) 2990, 1590, 1460, 1376, 1130, 870, 790 and 750; δ_H: 2.17 (3H, s, CH_3), 2.21 (3H, s, CH_3), 2.25 (3H, s, CH_3), 2.28 (3H, s, CH_3), 2.89 (4H, m), 3.10 (4H, m) and 7.20 - 7.45 (5H, m); δ_C (67.9

MHz, $CDCl_3$) δ_C: 12.76 (2C), 17.23, 20.52, 26.16, 26.25, 28.23, 28.53, 126.32, 127.34, 127.85, 129.47 (6C), 130.51, 132.74, 137.50, 138.76, 139.91, 140.32 and 143.09; *m/z* 346 (M^+, 100). HRMS calcd for $C_{24}H_{26}S$: 346.1755. Found: 346.1761.

Dimethyl 3,6,10,12-tetramethyl-11-thiatricyclo[9.3.0.0^{2,7}]tetradeca-2,4,6,10,13-pentaene-4,5-dicarboxylate (7e): To a solution of tetramethyl[2.1](3,4)thiophenophane (**1b**) (230 mg, 0.95 mmol) and dimethyl acetylenedicarboxylate (**6b**) (405 mg, 2.85 mmol) in CH_2Cl_2 (20 mL) was added dropwise a solution of purified *m*-CPBA (320 mg, 100 w%, 1.85 mmol) in CH_2Cl_2 (50 mL) at 0°C and over 3 h. The reaction was stirred for 1 h at 0°C and thereafter for 14 h at rt. Then it was poured into a saturated aqueous $NaHCO_3$ solution (20 mL). The aqueous phase was extracted with CH_2Cl_2 (3 X 10 mL), the organic phase was dried ($MgSO_4$) and concentrated. Chromatography on silica gel (hexane/ether 2:1) yielded **7e** (50 mg, 15%) as colorless prisms, mp 155.5 - 156.0°C (ether); ν (KBr/cm^{-1}) 2890, 1720, 1570, 1430, 1350, 1270, 1210, 1100, 1030, 960 and 730; δ_H: 2.14 (3H, s, CH_3), 2.36 (3H, s, CH_3), 2.37 (3H, s, CH_3), 2.42 (3H, s, CH_3), 2.73 (2H, vt, ^3J = 6.4 Hz), 3.24 (2H, vt, ^3J = 6.4 Hz), 3.82 (3H, s, OCH_3), 3.83 (3H, s, OCH_3) and 3.98 (2H, s); *m/z* 372 (M^+). *Anal.* Calcd for $C_{21}H_{24}O_4S$: C, 67.74; H, 6.45. Found C, 67.72; H, 6.46;

and *tetramethyl[2.1](3,4)orthothiophenophane-S,S-dioxide* (**5b**) (42 mg, 17%) as colorless prisms, mp 160°C (decomp); ν_{max} (KBr/cm^{-1}) 2950, 2870, 1630, 1470, 1440, 1110, 1060, 860, 760 and 730; δ_H: 2.05 (3H, s, CH_3), 2.08 (3H, s, CH_3), 2.21 (3H, s, CH_3), 2.34 (3H, s, CH_3), 2.79 (4H, s) and 3.55 (2H, s); δ_C: 6.83, 7.06, 13.08, 22,50, 24.94, 27.24, 53.46, 128.93, 129.81, 129.90, 130.87, 131.31, 133.19, 136.28 and 138.04; *m/z* 294 (M^+). *Anal.* Calcd for $C_{15}H_{18}O_2S_2$: C, 61.22; H, 6.12. Found C, 59.39; H, 6.05.

Dimethyl 4,7,12,14-tetramethyl-13-thiatricyclo[10.3.0.0^{3,8}]pentadeca-3,5,7,11,14-pentaene-5,6-dicarboxylate (7b): Tetramethyl[2.2](3,4)orthothiophenophane (**1a**) (310 mg, 1.12 mmol) and dimethyl acetylenedicarboxylate (**5b**) (405 mg, 2.85 mmol) were reacted as described above to yield **7b** (130 mg, 32 %) as colorless prisms, mp 175 - 176°C (ether); ν (KBr/cm^{-1}) 3000, 2850, 1730, 1435, 1215 and 1032; δ_H: 2.15 (6H, s, 2 CH_3), 2.20 (6H, s, 2 CH_3), 2.84 (4H, vt, J = 7.2 Hz), 3.10 (4H, vt, J = 7.2 Hz) and 3.82 (6H, s); δ_C: 12.72, 17.12, 25.88, 28.45, 52.22, 127.91, 130.31, 136.48, 142.93 and 169.70; *m/z* 386 (M^+), 354 and 339. *Anal.* Calcd for $C_{22}H_{26}O_4S$: C, 68.37; H, 6.78. Found C, 68.14; H, 6.73.

5,6-Bis(*p*-*tert*-butylbenzoyl)-4,7,12,14-tetramethyl-12-thiatricyclo-[10.3.0.0^{3,8}]pentadeca-3,5,7,-11,14-pentaene (7c): Tetramethyl[2.2](3,4)orthothiophenophane (**1a**) (310 mg, 1.12 mmol) and bis(*p*-*tert*-butylbenzoyl)acetylene (**6c**) (985 mg, 2.85 mmol) were reacted as described above to yield **7c** (245 mg, 38%) as colorless crystals, mp 180 – 181°C (hexane/ether); ν (KBr/cm^{-1}) 2970, 2870, 1675, 1601, 1560, 1403, 1220, 1182, 902; δ_H: 1.28 (18H, s, 2 Bu^t), 2.02 (6H, s, 2 CH_3), 2.16 (6H, s, 2 CH_3), 2.98 (4H, vt, J = 6.9 Hz), 3.18 (4H, vt, J = 6.9 Hz), 7.30 (4H, d, ^3J = 8.6 Hz) and 7.43 (4H, d, ^3J = 8.6 Hz); δ_C: 12.68, 17.60, 25.03, 27.18, 30.96, 35.00, 125.17, 127.74, 129.52, 129.95, 135.38, 136.24, 136.47, 140.48, 156.63 and 198.86; *m/z* 590 (M^+), 533, 399 and 161. *Anal.* Calcd for $C_{40}H_{46}O_2S$: C, 81.31; H, 7.85. Found: 81.20; H, 7.84.

1,6,8,13-Tetramethyl-16-phenyl-16-aza-7,19-dithiapentacyclo-[13.3.0.1^{1,13}.0^{2,12}.0^{5,9}]nonadeca-2:12,5,9-triene-15,17-dione 19-oxide (9a-H): To a solution of tetramethyl[2.2](3,4)orthothio-

phenophane (**1a**) (310 mg, 1.12 mmol) and *N*-phenylmaleimide (**8a-H**) (440 mg, 2.5 mmol) in dichloromethane (20 mL) was added dropwise a solution of *m*-CPBA (660 mg, 60 w%, 2.3 mmol) in dichloromethane (50 mL) at 0°C and over 3 h. The mixture was warmed to rt and was then poured into a solution of saturated aqueous $NaHCO_3$ (60 mL). The phases were separated and the aqueous layer was extracted with dichloromethane (3 X 5 mL). The collected organic phases were dried ($MgSO_4$) and concentrated *in vacuo*. Chromatography on silica gel (hexane/ether 1:2) yielded **9a-H** (178 mg, 34%) as colorless prisms, mp 232 - 234°C (ether); ν (KBr/cm^{-1}) 2965, 1775, 1715, 1500, 1450, 1380, 1180, 1100, 1065, 760, 705 and 640; δ_H: 1.63 (6H, s, 2 CH_3), 2.28 (6H, s, 2 CH_3), 2.43 (2H, m), 2.81 (4H, vt, ^3J = 8.7 Hz), 3.67 (2H, s), 7.06 (2H, m) and 7.43 (3H, m); δ_C: 12.92, 13.03, 25.01, 25.43, 51.07, 73.73, 126.29, 128.77, 128.84, 129.31, 131.59, 135.11, 136.12 and 174.66; *m/z* 465 (M^+). *Anal.* Calcd for $C_{26}H_{27}NO_3S_2$: C, 66.87; H, 5.94; N, 2.98. Found C, 67.10; H, 5.80; N, 3.01.

1,6,8,13-Tetramethyl-16-(*p*-chlorophenyl)-16-aza-7,19-dithiapentacyclo[13.3.0.1^{1,13}.0^{2,12}.0^{5,9}]nonadeca-2:12,5,9-triene-15,17-dione 19-oxide (9a-Cl): Analogously, **1a** (310 mg, 1.12 mmol) was reacted with *p*-chlorophenylmaleimide[21] (**8a-Cl**) (520 mg, 2.5 mmol) to give **9a-Cl** (210 mg, 36%) as colorless prisms, mp 219 - 220°C (ether); ν (KBr/cm^{-1}) 3075, 2960, 1710, 1485, 1380, 1185, 1050 and 805; δ_H: 1.63 (6H, s, 2 CH_3), 2.22 (6H, s, 2 CH_3), 2.42 (2H, m), 2.60 (2H, m), 2.83 (4H, vt, *J* = 6.7 Hz), 3.66 (2H, s), 7.02 (2H, d, ^3J = 8.9) and 7.42 (2H, d, ^3J = 8.9); δ_C: 12.92, 13.01, 25.03, 25.39, 52.05, 73.73, 127.42, 128.82, 129.38, 129.95, 134.61, 134.98, 136.08 and 174.41; *m/z* (FAB, 3-nitrobenzyl alcohol) 502 ([^{37}Cl]MH$^+$, 1.6) and 500 ([^{35}Cl]MH$^+$, 3.5). HRMS calcd for $C_{26}H_{27}NO_3{}^{35}ClS_2$: 500.1121. Found: 500.1123 (FAB, 3-nitrobenzyl alcohol: MH$^+$).

1,6,8,13-Tetramethyl-16-oxa-7,19-dithiapentacyclo[13.3.0.1^{1,13}.0^{2,12}.0^{5,9}]nonadeca-2:12,5,9-triene-15,17-dione 19-oxide (9b): Tetramethyl[2.2](3,4)orthothiophenophane (**1a**) (310 mg, 1.12 mmol) and maleic anhydride (245 mg, 2.50 mmol) in CH_2Cl_2 (20 mL) were reacted with *m*-CPBA (510 mg, 80 w%, 2.3 mmol) in CH_2Cl_2 (20 mL) as described above. Chromatography of the residue on silica gel (hexane/ether 1:2) gave **9b** (90 mg, 26%) as colorless prisms, mp 254 - 255°C (ether); ν (KBr/cm^{-1}) 2980, 2750, 1850, 1780, 1440, 1380, 1290, 1210, 1140, 1090, 940 and 910; δ_H: 1.60 (6H, s, 2 CH_3), 2.24 (6H, s, 2 CH_3), 2.55 - 2.64 (4H, m), 2.79 - 2.88 (4H, m) and 3.76 (2H, s); δ_C: 12.67, 12.90, 25.34, 25.41, 52.24, 74.12, 129.49, 134.28, 136.69 and 169.56; *m/z* 390 (M^+) and 342. *Anal.* Calcd for $C_{28}H_{40}O_5S_2$: C, 51.53; H, 5.64. Found C, 61.00; H, 5.76.

Dibutyl 5,7,12,15-tetramethyl-16-oxo-6,16-dithiatetracyclo[11.2.1.0^{1,11}.0^{4,8}]hexadeca-1:11,4,7-triene-13,14-dicarboxylate (9c): Tetramethyl[2.2](3,4)orthothiophenophane (**1a**) (270 mg, 0.97 mmol) and di-*n*-butyl maleate (590 mg, 2.58 mmol) in CH_2Cl_2 (20 mL) were reacted with *m*-CPBA (440 mg, 80 w%, 2.0 mmol) in CH_2Cl_2 (30 mL) as described above. Chromatography on silica gel (hexane/ether 1:2) gave **8c** (72 mg, 17%) as colorless prisms, mp 81 - 82°C (ether); ν (KBr/cm^{-1}) 2950, 2870, 1741, 1455, 1381, 1289, 1166, 1106, 1066 and 965; δ_H: 0.93 (6H, t, *J* = 6.8 Hz), 1.38 (4H, m), 1.58 (4H, m), 1.59 (6H, s, 2 CH_3), 2.24 (6H, s, 2 CH_3), 2.34 (2H, m), 2.82 (6H, m), 3.59 (2H, s), 3.91 - 4.07 (4H, m); δ_C: 12.90 (2C), 13.69, 19.13, 25.34, 25,51, 30.53, 52.92, 64.85, 72.22, 128.01, 135.74 and 170.73; *m/z* 520 (M^+), 472 and 371, *Anal.* Calcd for $C_{28}H_{40}NO_5S_2$: C, 64.62; H, 7.69. Found C, 64.69; H, 7.74;

and tetramethyl[2.2](3,4)orthothiophenophane-*S*,*S*-dioxide (**5a**) (100 mg, 34%).

5,7,12,15-Tetramethyl-14-phenylsulfonyl-6,16-dithiatetracyclo[11.2.1.0^{1,11}.0^{4,8}]hexadeca-1:11,4,7-triene 16-oxide (9d): Tetramethyl[2.2](3,4)orthothiophenophane (**1a**) (310 mg, 1.12 mmol) and phenyl vinyl sulfone (340 mg, 2.23 mmol) in CH_2Cl_2 (20 mL) were reacted with *m*-CPBA (580 mg, 80 w%, 2.6 mmol) in CH_2Cl_2 (30 mL) as described above. Chromatography on silica gel (hexane/ether 1:2) yielded **9d** (75 mg, 15%) as colorless needles, mp 196 - 197°C (ether); ν (KBr/cm^{-1}) 2880, 1450, 1310, 1150, 1090 and 1050; δ_H: 1.25 (3H, s, CH_3), 1.58 (3H, s, CH_3), 2.05 (1H, dd, ^3J = 3.1 and ^2J = 12.6), 2.33 (3H, s, CH_3), 2.34 (3H, s, CH_3), 2.19 - 2.35 (2H, m), 2.72 - 3.05 (6H, m), 3.88 (1H, dd ^4J = 2.3 and ^4J = 5.1), 7.05 - 7.67 (3H, m) and 7.82 - 7.87 (2H, m); δ_C 12.90, 13.40, 15.27, 19.28, 25.28, 25.37, 25.53, 36.67, 67.98, 69.11, 73.33, 127.85, 128,84, 129,37, 133.80, 134.93, 135.63, 135.90, 136.73 and 140.99; *m/z* 460 (M^+). *Anal.* Calcd for $C_{24}H_{28}O_3S_3$: C, 62.57; H, 6.13. Found: C, 62.41; H, 6.10.

13,13,14,14-Tetracyano-5,7,12,15-tetramethyl-6,16-dithiatetracyclo[11.2.1.0^{1,11}.0^{4,8}]hexadeca-1:11,4,7-triene 16-oxide (9e): Tetramethyl[2.2](3,4)orthothiophenophane (**1a**) (270 mg, 0.98 mmol) and tetracyanoethylene (347 mg, 2.7 mmol) in CH_2Cl_2 (20 mL) were reacted with *m*-CPBA (580 mg, 80 w%, 2.6 mmol) in CH_2Cl_2 (20 mL) as described above. Chromatography on silica gel (ether) gave **9e** (100 mg, 24%) as colorless prisms, mp 251°C (ether) (decomp); ν (KBr/cm^{-1}) 2940, 1550, 1450, 1384, 1120, 1090, 1030, 930, 765 and 720; δ_H: 1.85 (6H, s, 2 CH_3), 2.26 (6H, s, 2 CH_3), 2.50 (2H, m), 2.91 (2H, s) and 2.92 (6H, m); δ_C: 11.50, 12.97, 24.74, 25.32, 52.87, 78.38, 107.35, 129.52, 134.03 and 139.51; *m/z* 420 (M^+), 372 and 275. *Anal.* Calcd for $C_{22}H_{20}N_4OS_2$: C, 62.86; H, 4.76; N, 13.33. Found C, 62.54; H, 4.78; N, 12.74.

Oxidation of 9a-Cl_2 - Preparation of 1,6,8,13-Tetramethyl-16-(*m*,*m*'-dichlorophenyl)-16-aza-7,19-dithiapentacyclo[13.3.0.1^{1,13}.0^{2,12}.0^{5,9}]nonadeca-2;12,5,9-triene-15,17-dione 7,7',19-trioxide (10): **9a-Cl_2** (670 mg, 1.27 mmol) and purified *m*-CPBA (1.0 g, 100 w%, 4.6 mmol) in CH_2Cl_2 (15 mL) were stirred at rt for 15 h. To the reaction mixture was given saturated aqueous $NaHCO_3$ (10 mL). The aqueous phase was extracted with CH_2Cl_2 (4 X 10 mL). The organic phase was dried over $MgSO_4$, concentrated *in vacuo* and the residue was chromatographed on silica gel to give **10** (390 mg, 55%) as a colorless solid, mp 264 - 266°C (ether); ν (KBr/cm^{-1}) 1778, 1719, 1558, 1445, 1100, 1070, 857, 800 and 750; δ_H: 1.67 (6H, s, 2 CH_3), 2.17 (6H, s, 2 CH_3), 2.37 - 2.47 (2H, m), 2.55 - 2.70 (2H, m), 2.75 (4H, m), 3.75 (2H, s), 7.05 (2H, m) and 7.40 (1H, m); δ_C: 6.79, 12.96, 23.31, 23.66, 51.03, 73.71, 124.51, 129.11, 132.79, 132.96, 135.51, 136.41, 136.71 and 173.67; *m/z* 569 (M^+[$^{37}Cl_2$]), 567 (M^+[$^{37}Cl^{35}Cl$]), 565 (M^+[$^{35}Cl_2$]) and 519 (M^+[$^{35}Cl^{37}Cl$]-SO). *Anal.* Calcd for $C_{26}H_{25}NO_5Cl_2S_2$: C, 55.12; H, 4.45. Found: C, 54.98; H, 4.41.

Oxidative Extrusion of SO-bridge - Preparation of 1,6,8,13-tetramethyl-16-phenyl-7-thia-tetracyclo[13.3.0.0^{2,12}.0^{5,9}]octadeca-1,5,8,12,14;18-pentaene-15,17-dione (7f): To **9a-H** (60 mg, 0.13 mmol) in CH_2Cl_2 (15 mL) was added dropwise at 0°C a solution of $KMnO_4$ (200 mg, 1.26 mmol) and benzyltributylammonium chloride (50 mg, 0.16 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 2 h at rt. Then a solution of sodium acetate in acetic acid (4 mL, pH 3) was added to the dark brown solution. The reaction mixture was extracted with CH_2Cl_2 (2 X 15 mL). The organic phase was neutralized with saturated aqueous $NaHCO_3$ solution, dried ($MgSO_4$) and concentrated. Filtration over

silica gel (ether/hexane 1:1) gave **7f** (32 mg, 60%) as colorless crystals, mp 183 - 185°C (ether); ν (KBr/cm^{-1}) 2950, 1770, 1710, 1600, 1500, 1460, 1380, 1260, 1120, 760, 740 and 690; δ_H: 2.20 (6H, s, 2 CH_3), 2.70 (6H, s, 2 CH_3), 2.95 (4H, vt, J = 6.8 Hz), 3.15 (4H, vt, J = 6.8 Hz) and 7.35 - 7.45 (5H, m); δ_C: 12.81, 13.73, 25.29, 27.48, 126.38, 127.21, 127.94, 128.85, 131.82, 134.34, 135.49, 147.33 and 168.46; *m/z* 415 (M^+). HRMS calcd for $C_{26}H_{26}NO_2S$: 416.1684. Found: 416.1694 (FAB, 2-nitrobenzyl alcohol: MH^+).

Thermal Extrusion of SO-bridge - Preparation of 1,6,8,13-tetramethyl-16-phenyl-7-thia-tetracyclo[13.3.0.0^{2,12}.0^{5,9}]octadeca-1,5,8,12,14;18-pentaene-15,17-dione (7f): **9a-H** (60 mg, 0.13 mmol) was placed in a flask and was heated in a sand-bath under argon to 250°C. The temperature was kept for 15 min. After the flask was cooled, the residue was taken up in chloroform and quickly filtrated over silica gel to give **7f** (46 mg, 85%).

Preparation of 1,6,8,13-Tetramethyl-16-(*p*-chlorophenyl-7-thiatetracyclo[13.3.0.0^{2,12}.0^{5,9}]octadeca-1,5,8,12,14;18-pentaene-15,17-dione (7g): **9a-Cl** (65 mg, 0.13 mmol) was dissolved in CH_2Cl_2 (20 mL), sand (500 mg) was added and the mixture was evaporated to dryness. **9a-Cl** adsorbed to the sand was transfered to a quartz-tube, the tube was evacuated (2 Torr) and then heated to 250°C for 10 min. After the tube was cooled, the residue was taken up in $CHCl_3$ (50 mL). The solution was filtered, concentrated *in vacuo* to leave a residue, which was chromatographed on silica gel (hexane/ether 2:1) to give **7g** (44 mg, 75%) as pale yellow crystals, mp 248 - 249°C (ether);ν (KBr/cm^{-1}) 2918, 1710, 1494, 1365, 1092, 834, 805 and 756; δ_H: 2.12 (s, 6H, 2 CH_3), 2.60 (s, 6H, 2 CH_3), 2.91 (t, 4H, ^3J = 7.4 Hz), 3.14 (t, 4H, ^3J = 7.4 Hz), 7.27 (d, 2H, ^3J = 8.9 Hz) and 7.37 (d, 2H, ^3J = 8.9 Hz); δ_C: 12.67, 13.89, 25.27, 27.42, 126.27, 128.09, 129.06, 130.57, 133.40, 134.50, 135.44, 147.55 and 168.14; *m/z* (FAB, 3-nitrobenzyl alcohol) 450 ([^{35}Cl]MH$^+$) and 452 ([^{37}Cl]MH$^+$). HRMS calcd for $C_{26}H_{25}NO_2{}^{35}ClS$: 450.1295 Found: 450.1271 (FAB, 3-nitrobenzyl alcohol, [^{35}Cl]MH$^+$); Calcd for $C_{26}H_{25}NO_2{}^{37}ClS$: 452.1275. Found: 452.1264 ([^{37}Cl]MH$^+$).

6,9-Bis(*p*-*tert*-butylphenyl)-7,8-diaza-17-thia-4,11,16,18-tetramethyltetracyclo[14.3.0.0^{3,12}.0^{5,10}]-nonadeca-3,5;10,6,8,11,15,18-heptaene (11): A mixture of **7c** (200 mg, 0.34 mmol), hydrazine hydrate (0.3 mL, 55 w% hydrazine, 3.4 mmol), hydrochloric acid, (conc., 0.1 mL) in a mixed solvent of MeOH (2 mL) / benzene (7 mL) was refluxed for 2 h. The reaction mixture was cooled, poured into water and extracted with ether. The organic phase was dried over $MgSO_4$, concentrated *in vacuo* and the residue was chromatographed over silica gel (ether) to give **11** (165 mg, 82%); ν (KBr/cm^{-1}) 2980, 1615, 1460, 1380, 1360, 1270, 1120 and 840; δ_H: 1.37 (18H, s, 2 Bu^t), 2.00 (6H, s, 2 CH_3), 2.17 (6H, s, 2 CH_3), 3.01 (4H, vt, ^3J = 7.4 Hz), 3.32 (4H, vt, ^3J = 7.4 Hz), 7.34 (4H, d, ^3J = 8.4 Hz) and 7.43 (4H, d, ^3J = 8.4 Hz); δ_C: 12.66, 20.40, 24.73, 27.85, 31.39, 34.70, 125.17, 126.83, 128.01, 129.14, 130.31, 135.56, 137.86, 144.70, 151.71 and 156.46; *m/z* 586 (M^+), 571 (M^+-CH_3) and 422. HRMS calcd for $C_{28}H_{32}O_8$: 587.3460. Found: 587.3466 (FAB, 3-nitrobenzyl alcohol: MH^+).

***N*,*N*-Diphenyl-1,6,12,17-tetramethyl-9,20-diaza-23,24-dithiaheptacyclo[17.3.0.1^{1,17}.0^{2,16}.0^{5,13}.-0^{7,11}]tetracosa-(2,16;5,13)-diene-8,10,19,22-tetraone 23,24-dioxide (12)**: $BF_3{\cdot}Et_2O$ (2.0 mL, 16.3 mmol) was added to a solution of **1a** (300 mg, 1.1 mmol) and *N*-phenylmaleimide (**8a-H**) (750 mg, 4.35

mmol) in dry CH_2Cl_2 (10 mL) in an inert atmosphere and at -20°C. The reaction mixture was stirred for 10 min at -20°C. Then a solution of purified *m*-CPBA (600 mg, 100 w%, 3.48 mmol) in dry CH_2Cl_2 (20 mL) was added slowly. The reaction mixture was stirred for additional 3 h at -20°C. Then the suspension was poured into a mixture of saturated aqueous $NaHCO_3$ (20 mL) and CH_2Cl_2 (50 mL). The resulting mixture was stirred for 20 min at rt. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 X 20 mL). The combined organic phase was washed with water and brine and dried over $MgSO_4$. After removal of the solvent *in vacuo*, ether was added to the crude product mixture to give cycloadduct (**12**) (290 mg, 40%) as a mixture of two isomers. After crystallisation from CH_2Cl_2-ether the main product was obtained as light yellow crystals; mp 279 - 281°C (ether); ν (KBr/cm^{-1}) 1776, 1710, 1497, 1380, 1183, 1103 and 1069; δ_H: 1.59 (12H, s, 4 CH_3), 2.43 (8H, m), 3.72 (4H, s), 7.21 (4H, m) and 7.45 (6H, m); δ_C: 13.28, 25.19, 50.73, 73.78, 125.71, 128.88, 129.25, 131.25, 135.29 and 174.37; *m/z* 556 [M^+-2(SO)]. HRMS calcd for $C_{36}H_{34}N_2O_6S_2$: 654.1858. Found: 654.1846.

Tetramethyl 4,7,12,15-tetramethyltricyclo[10.4.0.0^{3,8}]hexadeca-3,5,7,11,13,15-hexaene-5,6,13,14-tetracarboxylate (13): $BF_3{\cdot}Et_2O$ (3.0 mL, 24.4 mmol) was added to a solution of **1a** (300 mg, 1.1 mmol) and dimethyl acetylenedicarboxylate (500 mg, 3.52 mmol) in dry CH_2Cl_2 (10 mL) under an inert atmosphere and at -20°C. The reaction mixture was stirred for 10 min at -20°C. Then a solution of purified *m*-CPBA (470 mg, 100 w%, 2.7 mmol) in dry CH_2Cl_2 (20 mL) was added slowly. The reaction mixture was stirred for another 3 h at -20°C. Then the suspension was poured into a mixture of saturated aqueous $NaHCO_3$ (20 mL) and CH_2Cl_2 (50 mL). The resulting mixture was stirred for 20 min at rt. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 X 20 mL). The combined organic phase was washed with water and brine and dried over $MgSO_4$. After the removal of the solvent *in vacuo*, ether was added to the crude mixture. The precipitate was filtered off to give **13** (180 mg, 34%) as colorless crystals, mp 282- 283°C (ether); ν (KBr/cm^{-1}) 2950, 1733, 1438, 1327, 1307 and 1288; δ_H: 2.28 (12H, s, 4 CH_3), 3.00 (8H, bs) and 3.82 (12H, s, 4 $COOCH_3$); *m/z* 465 (M^+-CH_3O), 450 (M^+-CH_3O-CH_4O) and 449. HRMS calcd for $C_{28}H_{32}O_8$: 496.2097. Found: 496.2089.

Dimethyl 4,6,11,13,18,21,26,28-octamethyl-5,12,27-trithiapentacyclo[24.3.0.0^{3,7}.0^{10,14}.0^{17,22}]nonacosa-3,6,10,13,17,19,21,25,28-nonaene 19,20-dicarboxylate (15): To a solution of octamethyl[2.2.2.2]orthothiophenophane (**2a**) (300 mg, 0.54 mmol) and dimethyl acetylene-dicarboxylate (**6b**) (200 mg, 1.4 mmol) in CH_2Cl_2 (20 mL) was added dropwise a solution of *m*-CPBA (80w%, 300 mg, 1.4 mmol) in CH_2Cl_2 (30 mL) at 0°C and over 3 h. The reaction mixture was stirred for 1 h at 0°C, for 14 h at rt. Then it was poured into saturated aqueous $NaHCO_3$ (20 mL). The aqueous phase was extracted with CH_2Cl_2 (3 X 10 mL). The organic phase was dried over $MgSO_4$ and concentrated. Chromatography on silica gel (hexane/ether: 1:2) yielded octamethyl[2.2.2.2]ortho-thiophenophane-*S*,*S*-dioxide (**15-SO**) (75 mg, 24%) as colorless crystals; mp 253 - 254°C (ether); ν (KBr/cm^{-1}) 2950, 1460, 1440, 1380, 1290, 1180, 1160, 780, 760, 740; δ_H: 1.80 (6H, s, 2 CH_3), 2.10 (6H, s, 2 CH_3), 2.25 (6H, s, 2 CH_3), 2.31 (6H, s, 2 CH_3), 2.30 (4H, m) and 2.50 - 2.70 (12H, m); δ_C: 12.80, 13.03, 13.29, 17.08, 25.01, 25.75, 27.18, 27.62, 129.61, 129.84, 136.20, 136.60, 136.71 and 137.14; *m/z* 584 (M^+). *Anal.* Calcd for $C_{32}H_{40}O_2S_4$: C, 66.75; H, 6.85. Found C, 66.59; H, 6.97;

and **15** (30 mg, 11%) as colorless crystals; mp 262 - 263°C (ether); ν (KBr/cm^{-1}) 2950, 1850, 1740, 1440, 1380, 1300 and 740; δ H: 1.93 (6H, s, 2 CH_3), 1.95 (6H, s, 2 CH_3), 2.40 (6H, s, 2 CH_3), 2.42 (6H, s, 2 CH_3), 2.50 - 2.60 (12 H, m), 2.90 (4H, m) and 3.90 (6H, s, 2 $COOCH_3$); δ_C: 13.05, 13.17, 13.36, 17.02, 26.59, 26.81, 27.19, 29.48, 129.14, 129.54, 129.88, 131.04, 132.36, 135.59, 136.63, 137.30, 141.87 and 163.00; *m/z* 662 (M^+). HRMS calcd for $C_{38}H_{46}O_4S_3$: 662.2558. Found: 662.2569.

2',5'-Dimethylthieno[*c*]-2',5'-dimethyl-*S*-oxothieno[*c*]bicyclo[4.4.1]undeca-3,8-dien-11-one (16). BF_3Et_2O (1.27 mL, 10.0 mmol) was added slowly to a solution of **3** (R=H) (330 mg, 1.0 mmol) in dry CH_2Cl_2 (5 mL) at -20°C and under an inert atmosphere. After 10 min, a solution of purified *m*-CPBA (225 mg, 100 w%, 1.3 mmol) was added dropwise to the reaction mixture. The resulting solution was stirred at -20°C for 2 h and then poured into a mixture of cold water (50 mL) and CH_2Cl_2 (50 mL) and stirred for 20 min. Thereafter the phases were separated, the aqueous phase extracted with ether (2 X 30 mL) and the collected organic phase washed with water (3 X 30 mL). The organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (CH_2Cl_2/EtOAc 1:1) to give **16** (138 mg, 40%) as a colorless solid; mp 233 - 266°C (ether) (decomp); ν (KBr/cm^{-1}) 2950, 2925, 2845, 1705, 1435, δ_H (two isomeric structures): 2.16 (s, 6H, 2 X CH_3, isomer A), 2.17 (s, 6H, 2 X CH_3, isomer B), 2.31 (s, 6H, 2 X CH_3, isomer B), 2.33 (s, 6H, 2 X CH_3, isomer A), 2.55 (m, 4H, both isomers), 2.83 – 3.12 (m, 6H, both isomers); *m/z* 346 (M^+, 8), 331 (M^+-CH_3, 29), 330 (M^+-[O], 77), 329 (M^+-[OH], 100). HRMS calcd for $C_{19}H_{22}O_2S_2$: 346.1060. Found: 346.1061.

3',4'-Dibenzoyl-2',5'-dimethylbenzo[*c*]-2',5'-dimethylthieno[*c*]bicyclo[4.4.1]undeca-3,8-dien-11-one (17a). A solution of **16** (100 mg, 0.29 mmol) and dibenzoylacetylene (**6e**) (135 mg, 0.58 mmol) in chloroform-d_3 ($CDCl_3$, 1 mL) was held at 60°C for 18 h. The reaction mixture was poured into water (30 mL) and extracted with $CHCl_3$ (4 X 20 mL). The collected organic phase was washed with water (3 X 20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel ($CHCl_3$) to give **17a** (103 mg, 69%) as a colorless solid; mp 103 - 107°C (ether); ν (KBr/cm^{-1}) 2910, 1690, 1655, 1590, 1585, 1435, 1305, 1275, 1200, 1170, 1015, 915, 880, 825, 750; δ_H: 2.04 (s, 6H, 2 X CH_3), 2.40 (s, 6H, 2 X CH_3), 2.65 – 3.13 (m, 10H), 7.32 – 7.38 (m, 4H, aryl-H), 7.47 – 7.53 (m, 2H, 2 X aryl-H), 7.63 (d, 4H, aryl-H, ^3J = 7.26 Hz); δ_C 13.39, 17.29, 27.84, 29.78, 52.33, 128.48, 129.72, 130.21, 131.44, 133.41, 133.55, 137.23, 137.75, 139.43; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 533 (MH^+, 45). HRMS calcd for $C_{35}H_{33}O_3S$: 533.2150. Found: 533.2159.

3',4'-Biscarbomethoxy-2',5'-dimethylbenzo[*c*]-2',5'-dimethylthieno[*c*]bicyclo[4.4.1]undeca-3,8-dien-11-one (17b). A solution of **15** (50 mg, 0.14(5) mmol) and dimethyl acetylenedicarboxylate (40 µL, 0.33 mmol) in chloroform-d_3 ($CDCl_3$, 1 mL) was held at 60°C for 5 h. Thereafter, the reaction mixture was directly subjected to column chromatography on silica gel ($CHCl_3$) to give **17b** (20 mg, 33%) as a colorless solid, mp 179 - 181°C (ether); ν (KBr/cm^{-1}) 2950, 2918, 2850, 1734, 1211, 1030; δ_H: 2.20 (s, 6H, 2 X CH_3), 2.31 (s, 6H, 2 X CH_3), 2.49 – 2.64 (m, 4H), 2.73 (m, 2H), 2.85 – 3.15 (m, 4H), 3.77 (s, 6H, 2 X CO_2CH_3); δ_C: 13.35, 16.78, 27.80, 29.78, 52.11, 52.27, 131.05, 131.43, 133.24, 140.34, 140.56, 169.24, 214.79; m/z 440 (M^+, 100), 410 ([M^+-2XCH_3], 23), 409 (M^+-OCH_3, 80). HRMS calcd for $C_{25}H_{28}O_5S$: 440.1657. Found: 440.1657.

***N*-Phenyl-1,7,9,15-tetramethyl-21-oxo-18-aza-8,21-dithiahexacyclo[15.3.0.1.^{1,15}1.^{4,12}0.^{2,14}0.^{6,10}]docosa-2;14,6,9-trien-22-one (17c).** $BF_3{\cdot}Et_2O$ (1.5 mL, 12.2 mmol) was added to a solution of **3** (R = H) (175 mg, 0.53 mmol) and *N*-phenylmaleimide (**8a-H**) (276 mg,1.59 mmol) in dry CH_2Cl_2 (5 mL) under an inert atmosphere and at -20°C. The reaction mixture was stirred for 10 min at -20°C. Then a solution of purified *m*-CPBA (500 mg, 100 w%, 2.9 mmol) in dry CH_2Cl_2 (5 mL) was added slowly. The reaction mixture was stirred for 2 h at -20°C. Thereafter additional *m*-CPBA (250 mg, 1.45 mmol) was added and the solution stirred for another hour at -20°C. Then the suspension was poured into a mixture of saturated aqueous $NaHCO_3$ (20 mL) and CH_2Cl_2 (50 mL). The resulting mixture was stirred for 20 min at rt. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 X 20 mL). The combined organic phase was washed with water and brine and dried over $MgSO_4$. After the removal of the solvent *in vacuo*, the residue was subjected to column chromatography on silica gel (ether – ether/ethyl acetate 10:1) to give **17c** (121 mg, 44%), mp 263°C (ether); *v* (KBr/cm^{-1}) 2954, 1712, 1500, 1381, 1178, 1105, 1073, 754, 701; δ_H: (^{1}H-^{1}H-COSY) 1.72 (s, 6H, 2 X CH_3), 2.12 (m, 4H), 2.28 (s, 6H, 2 X CH_3), 2.63 (m, 2H), 2.86 (dd, 2H, ^2J = 15.5 Hz, ^3J = 5.6 Hz), 3.03 (m, 2H), 3.72 (s, 2H), 6.74 (dd, 2H, ^3J = 6.2 Hz, ^4J = 2.0 Hz), 7.40 - 7.50 (m, 3H); δ_C: 12.54, 13.30, 23.27, 28.98, 51.03, 52.02, 73.60, 126.39, 129.16, 129.59, 132.16, 132.72, 134.21, 138.09, 174.43, 212.86; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 520 (MH^+, 17.0), 471 (M^+-SO, 10.6); HRMS calcd for $C_{29}H_{30}NO_4S_2$: 520.1616. Found 520.1619 (FAB, 3-nitrobenzene, MH^+);

and the double adduct **17c-2** (79 mg, 21%) as a colorless solid, mp 247 - 248°C (ether); IR (KBr/cm^{-1}) *v* 2960, 1712, 1500, 1455, 1386, 1193, 1106, 1072, 764, 699; δ_H: 1.57 (s, 6H, 2 X CH_3), 1.73 (s, 6H, 2 X CH_3), 2.29 - 2.52 (m, 6H), 2.58 (dd, 2H, ^2J = 15.5 Hz, ^3J = 5.6 Hz), 2.98 (m, 2H), 4.11 (s, 2H), 4.13 (s, 2H), 7.12 (dd, 2H, ^3J = 6.4 Hz, ^4J = 2.2 Hz), 7.23 (dd, 2H, ^3J = 6.2 Hz, ^4J = 2.0 Hz), 7.37 - 7.55 (m, 6H); δ_C 13.21, 13.26, 29.15, 29.70, 50.35, 50.67, 50.89, 73.47, 73.53, 125.19, 126.39, 128.87, 129.07, 129.13, 129.49, 131.01, 131.32, 134.03, 134.30, 173.92, 174.12, 209.41; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 709 (MH^+, 9.5), 660 (M^+-SO, 2.1), 612 (M^+-2SO). *Anal.* Calcd for $C_{39}H_{36}N_2O_7S_2{\cdot}C_4H_8O_2$: C, 64.80; H, 5.56; N, 3.51. Found: C, 64.27; H, 5.75; N, 3.32.

Dimethyl *N*-phenyl-1,7,9,15-tetramethyl-21-oxo-18-aza-8,21-dithiahexacyclo[15.3.0.1.^{1,15}1.^{4,12}0.^{2,14}-0.^{6,10}]docosa-2;14,6,9-trien-22-one 4,12-dicarboxylate (17d). To **3** (R = CO_2Me) (150 mg, 0.33 mmol) and *N*-phenylmaleimide (**8a-H**) (150 mg, 0.86 mmol) in CH_2Cl_2 (3 mL) was added dropwise and at 0°C *m*-CPBA (200 mg, 60 w%, 0.70 mmol) in CH_2Cl_2 (7 mL) and the reaction was stirred for 24 h at rt. Thereafter the mixture was poured into saturated aqueous Na_2CO_3 solution, stirred and extracted with CH_2Cl_2 (2 X 50 mL). The organic solution was washed with water (30 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was taken up in CH_2Cl_2/Et_2O (1:1 v/v, 20 mL), whereupon a precipitate formed to give **17d** (73 mg, 35%) as a colorless solid. An analytical amount was recrystallized in ether; mp 284 - 285°C (ether); *v* (KBr/cm^{-1}) 2924, 1746, 1712, 1558, 1499, 1455, 1328, 1280, 1105, 952, 708; δ_H: 1.83 (s, 6H, 2 X CH_3), 2.23 (d, 2H, ^2J = 14.1 Hz), 2.27 (s, 6H, 2 X CH_3), 2.43 (d, 2H, ^2J = 14.1 Hz), 2.97 (d, 2H, ^2J = 15.8 Hz), 3.08 (d, 2H, ^2J = 15.8 Hz), 3.70 (2H, s), 3.81 (s, 6H, 2 X $COOCH_3$), (dd, 2H, ^3J = 8.3 Hz, ^4J = 1.5 Hz), 7.45 (m, 3H); δ_C 12.18, 13.24, 26.88, 32.83, 51.44,

52.70, 64.08, 74.11, 126.23, 129.06, 129.65, 131.25, 133.17, 137.55, 142.05, 172.02, 174.48, 207.20; MS (FAB, glycerin) *m/z* (%) 636 (MH^+, 0.4), 587 (MH^+-SO, 0.3); MS (FAB, 3-nitrobenzyl alcohol) 636 (MH^+, 3.9), 587 (M^+-SO, 1.6). *Anal.* Calcd for $C_{33}H_{33}NO_8S_2$: C, 62.35; H, 5.23; N, 2.20. Found C, 62.09; H, 5.33; N, 2.18.

Structure Determination of the Cycloadduct 9a-H. - Intensity data were collected on an Enraf-Nonius CAD4 diffractometer, ω-2Θ scan type, graphite-monochromatic CuKα radiation, λ = 1.541.84 Å. Of 4236 independent reflections collected in the range of $1 < \Theta > 65°$, 3570 reflections with $I_0 > 3\sigma(I_0)$ were taken as observed. The crystal did not show any significant decay during data collection. The structure was solved by direct methods (SIR 92)[22] and refined by full-matrix least-squares calculations. Hydrogen atoms treated isotropically were refined by full-matrix least-squares calculation. All calculations were performed with an IBM RISC System/6000 380 computer using SHELXL-93.[23] Using the scheme $w = 4F_o^2/\sigma^2(F_o^2)^2$ the final residuals are given as: R = 0.044, R_w = 0.107. The cell dimensions are: a = 11.98(7), b = 23.06(4), c = 8.90(5) Å, β = 110.6(10)°, V = 2304.4 (19) Å^3, space group $P2_1/n$, Z = 4, $D_{calc.}$ = 1.342 g cm^{-3}. The crystallographic data (excluding structure factors) for the structure reported has been deposited with the Cambridge Crystallographic Data Centre.*

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