Oxidative Cycloaddition of Thiophenophanes – [*n*](2.5)Parathiophenophane (*n* = 8,10–12,14), [8](2,4)Metathiophenophane and [2.2](2,5)Parametathiophenophane

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The oxidative cycloaddition of 3,4-dibromo-[*n*](2,5)thiophenophanes **12b–e** and (2,4)[8]thiophenophane **16** with dienophiles gave stereoselectively O=S-bridged cycloadducts **18**, **19** and **24**. The X-ray analysis of cycloadduct **18a** shows it to have a rigid conformation. The molecules can be regarded as a new series of paddlanes. Under the same oxidative conditions, 3,4-dibromo-[8](2,5)thiophenophane (**12a**) gave the two dimers **29** and **30**. The results of the X-ray analysis of **29** are discussed.

One of the interesting topics of research in cyclophane chemistry has been the Diels-Alder reaction of cyclophanes as a measure of the aromaticity of the systems.[1] It is known that [2.2]paracyclophane can undergo a [4+2]-cycloaddition with dicyanoacetylene and monocyanoacetylene because of strain activation in the phane systems.[2] Heterocyclophanes, such as furanophanes, also undergo Diels-Alder reactions with the furan units acting as diene components to give cycloadducts.[3] Little is known about the reactivity of thiophenophanes, and to the best of our knowledge there is only one example of a cycloaddition of a thiophenophane. It has been shown that [8](2,5)thiophenophane (**1**) cycloadds to dicyanoacetylene (**2**) at 160°C to give dicyano-substituted [8]paracyclophane (**3**) in low yield (Scheme 1).[4] For the most part thiophenes are poor dienes.[5] The authors have found that thiophenes, when oxidised at low temperatures with *meta*-chloroperoxybenzoic acid (*m*-CPBA) especially in the presence of a Lewis acid catalyst, such as $BF_3 \cdot Et_2O$,[6a] yield thiophene *S*-monoxides as rather stable dienes. These can be cycloadded to dienophiles (**5**) either in situ or in a second process to give O=S-bridged [4+2]-cycloadducts[6] (**6**) in fair to high yields (Scheme 2). These bicyclo[2.2.1]heptene *S*-oxides can be transformed selectively in a later step to the corresponding aromatic compounds[6c][6d][7] or to cyclohexadienes[7] upon extrusion of the O=S bridge. This easy sequence of reactions mimicking the Diels-Alder reaction of thiophenes themselves, but at low temperatures, should open a way for the reaction of thiophenophanes under identical conditions to produce novel, multifunctionalised cyclophanes. A further point of interest in the study of the possibilities of oxidative cycloadditions of thiophenophanes was whether ring strain of phane systems would have any effect on the oxidation of the thiophene core units to thiophene *S*-monoxides, on the stability of the thiophene *S*-monoxides and their reactivity as diene components in the cycloaddition reactions.

At first, a series of thiophenophanes has been synthesised. It is known that [8](2,5)thiophenophanes can be prepared from 1,4-cyclododecanedione by the Paal-Knorr method.[8] However, starting from cyclotetradecane-1,4-dione and using the same method, [10](2,5)thiophenophane could not be synthesised.[9] Here, we report a convenient route to 3,4-dibromo-[*n*](2,5)thiophenophanes **12** as shown in Scheme 3. The precursors in this synthesis are 3,4-dibromo-2,5-bis(bromomethyl)thiophene (**9a**) and 3,4-dibromo-2,5-bis(mercaptomethyl)thiophene (**9b**)[10], which in a coupling reaction give the dithiathiophenophanes **10**. **9a** can easily be prepared by bromination of 2,5-dimethylthiophene in high yield.[11] The introduction of the bromo substituents at the 3,4-positions in **9b** stabilises the 2,5-bis(mercaptomethyl)thiophene, and the use of **9a** as precursor is superior to using 3,4-dibromo-2,5-bis(chloromethyl)thiophene, for the preparation of which HCl gas is needed.[10] The thiophenophanes **12** (*n* = 8, 10–12, 14) were synthesised by the pyrolysis of the disulfones **11**, which had been obtained by the oxidation of the corresponding dithiathiophenophanes **10**. 3-Bromo-5-methyl[8](2,4)metathiophenophane (**16**) was prepared as shown in Scheme 4. The coupling reaction of 3-bromo-2,4-bis(chloromethyl)thiophene (**13**)[10] with 1,6-bis(mercapto)hexane was followed by oxidation of **14** and subsequent pyrolysis of **15** to give **16**.

The ^{1}H-NMR spectra of **12b–e** show that the thiophenophanes (*n* = 10–12, 14) are symmetric compounds. The signals of the four α-methylene protons of these compounds appear as simple triplets, indicating that the hydrocarbon

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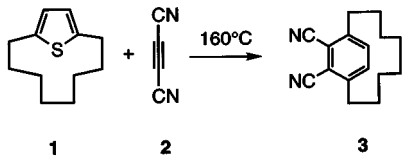
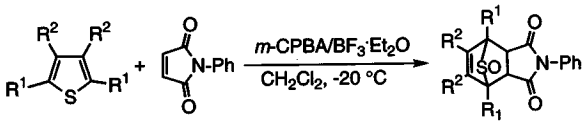
Scheme 1



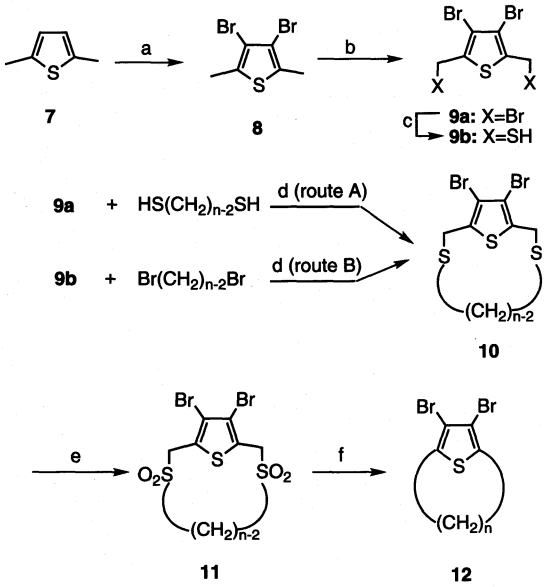
R. Helder 1974[4]

Scheme 2



R^1 = Me,
R^2 = Me, Cl, Br

Scheme 3. The synthesis of 3,4-dibromo-[*n*](2,5)thiophenophanes

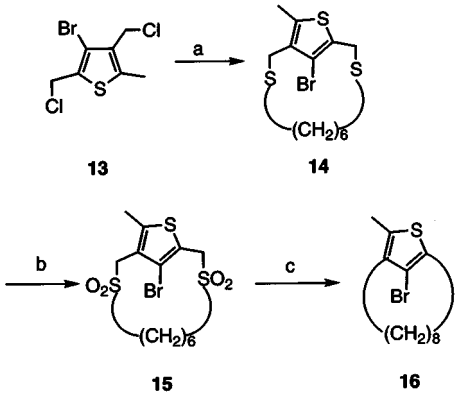


		Yield (%)		
	n	**10** (route)	**11**	**12**
a	8	60 (A)	94	50
b	10	54 (B)	90	55
c	11	47 (B)	92	50
d	12	53 (B)	87	54
e	14	66 (B)	94	67

a: Br_2 (2.2 equiv.), CH_2Cl_2. – b: Br_2 (2.2 equiv.), CH_2Cl_2. – c: (i) H_2NCSNH_2, KOH, EtOH, (ii) HCl. – d: KOH, EtOH. – e: *m*-CPBA, CH_2Cl_2. – f: Pyrolysis.

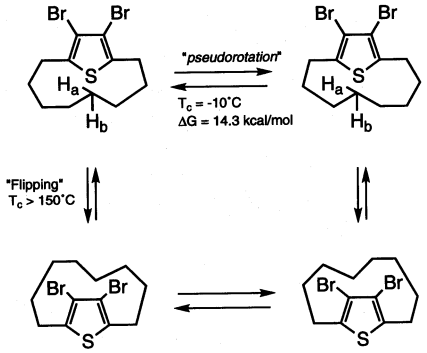
chain moves freely around the thiophene ring. On the other hand, the ^{1}H-NMR spectrum of **12a** shows it to be non-symmetric. Two α-methylene protons show a six-line signal as a doublet-triplet system at δ = 3.16, the other two α-methylene protons show multiplets at δ = 2.45. The two protons of the chain's centre carbon atom are shifted high-field to δ = 0. This indicates that the protons are within the magnetic anisotropy due to the aromatic system and are held above the aromatic ring. It also shows that the chain is confined to one side only of the thiophene ring. A dynamic ^{1}H-NMR study on **12a** (270 MHz) shows that the two methylene protons in the chain's centre exhibit pseudorotation at room temperature.[12] (Figure 1). The signals of these two protons coalesce at −10°C. At −70°C one of the proton signals, formerly at δ = 0.01, is shifted to δ = −1.80. At this temperature the pseudorotation is stopped. These findings are in accordance with the results found for [8](2,5)thiophenophane (**1**), which shows similar phenomena in the dynamic ^{1}H-NMR investigation.[8a]

Scheme 4



a: $HS[CH_2]_6SH$, $NaBH_4$, EtOH (60%). – b: *m*-CPBA, CH_2Cl_2 (94%). – c: Pyrolysis (63%).

Figure 1. Ring-flipping of **12a**



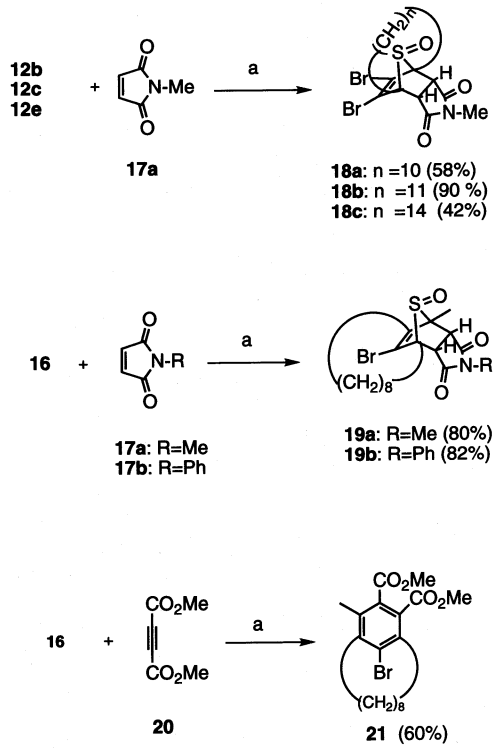
The UV spectra of the dibromo[*n*](2,5)thiophenophanes **12b**–**e** (*n* = 10–12, 14) show very little differences to the UV spectrum of 3,4-dibromo-2,5-dimethylthiophene (**8**) with λ_{max} = 204 and 244 nm, but a bathochromic shift of λ_{max} could be found in **12a** with λ_{max} = 208 and 252 nm. This is a good indication of the strain in **12a**.

Oxidative Cycloaddition of Thiophenes

The oxidative cycloaddition was carried out by oxidizing the thiophenophanes with *m*-CPBA under $BF_3 \cdot Et_2O$ catalysis and in the presence of a dienophile (Scheme 5). All of these reactions were run at −20 to 0°C. The oxidative

cycloaddition of dibromo[*n*](2,5)thiophenophanes **12** (*n* = 10, 11, 14) with *N*-methylmaleimide gave thiatricyclo[*n*.2.2.-1]alkene *S*-oxides as cycloadducts **18** in 42−90% yield. The oxidative cycloaddition of **16** with *N*-methylmaleimide and *N*-phenylmaleimide gave O=S-bridged cycloadducts **19a** and **19b** in 80% and 82% yield, respectively. The reaction of **16** with dimethyl acetylenedicarboxylate (**20**) gave [8]metacyclophane **21** in 60% yield.

Scheme 5



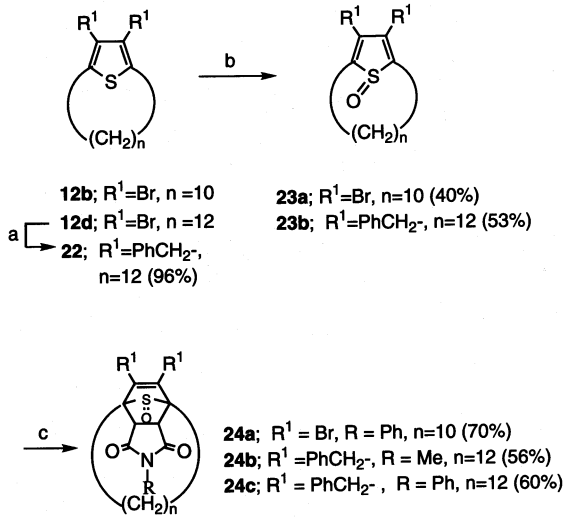
a: *m*-CPBA, $BF_3 \cdot Et_2O$, CH_2Cl_2, −20 to 0°C.

The ^{1}H-NMR spectra of the cycloadducts **18a−c** show that the methylene chain of these molecules are not freely movable. It is very likely that they take a rigid conformation. This is different from the [8](2,5)furanophane analogs.[13] In the spectrum of **18a**, the well-resolved signals of the α-methylene protons appear as two separate doublet/doublet/doublet (ddd) signals at δ = 2.05 and 2.60.

The same could be observed in **18b** and **18c**. These molecules can be regarded as a new type of compounds in the paddlane series.[14]

As we have found in an earlier study of the oxidative cycloaddition of simpler thiophenes, the reaction can be carried out using either of two methods, the one-pot procedure, as introduced above, or the two-step procedure. It is known that when substituted thiophenes are oxidized in the presence of $BF_3 \cdot Et_2O$, thiophene *S*-monoxides can be isolated as rather stable compounds in solution,[6a] and in some cases, often with bulky substituents, they can even be isolated as stable compounds.[6a,15] In the oxidation of 3,4-dibromo[12](2,5)thiophenophane (**12d**) and 3,4-dibenzyl[12](2,5)thiophenophane (**22**) with *m*-CPBA under $BF_3 \cdot Et_2O$ catalysis, the [12]thiophenophane *S*-monoxides **23a** and **23b** could be isolated. At room temperature, these thiophenophane *S*-monoxides are stable over longer periods of time. They react with *N*-phenyl- or *N*-methylmaleimide at room temperature to give cycloadducts **24** in reasonable yield.

Scheme 6



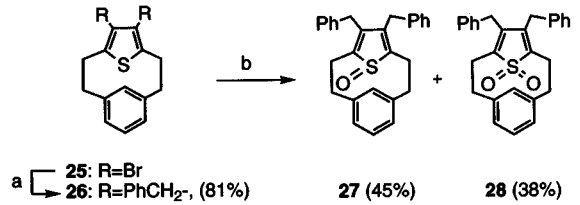
a: $PhCH_2MgBr$, $[(C_6H_5)_2P]NiCl_2$, ether. − b: *m*-CPBA, $BF_3 \cdot Et_2O$, −20 to −10°C. − c: **17a** or **17b**, CH_2Cl_2.

Thiophenophanes of smaller ring size do not undergo the oxidative cycloaddition reaction. Thus, **26** yields thiophenophane *S*-monoxide **27** upon oxidation with the corresponding thiophenophane *S*,*S*-dioxide as a competing product. However, **27** is not a reactive diene in the [4+2]-cycloaddition reaction. Furthermore, reaction of **26** with alkenes in a one-pot reaction to form the corresponding cycloadducts is not possible. Also, 1,11-Dibromo[8](2,5)thiophenophane **12a** does not undergo the oxidative cycloaddition reaction. Interestingly, two dimeric compounds, **29** and **30**, are formed in the reaction. The structures of these dimers have been confirmed by ^{1}H-NMR, IR, mass spectra, and X-ray analyses. The mechanism of the formation of **29** and **30** has not been totally clarified as of yet. However, it is supposed that the dimers **29** and **30** are formed in a radical mechanism. It is known that in the presence of Lewis acids, peroxides can generate the OH radical **31**.[16] A possible mechanism that is based on the generation of OH radicals is shown in Scheme 9. The OH radical **31**, generated from an *m*-CPBA/$BF_3 \cdot Et_2O$ system, reacts with **12a** to generate radical **A**. Radical **A** reacts with a second equivalent of **12a** to give the dimer **29**. On the other hand, a small amount of the starting material **12a** is oxidised to the thiophene *S*-monoxide **26**, which reacts with radical **A** to give **30** as the product.

X-ray Crystallographic Analyses

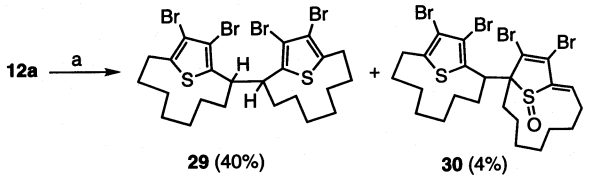
The ORTEP drawing of the cycloadduct **18a** is shown in Figure 2. The cycloadduct **18a** is the *endo* product, the lone pair at the sulphur atom being on the same side as the newly formed double bond of the cycloadduct. This means that the O=S moiety is directed to the approaching imide

Scheme 7



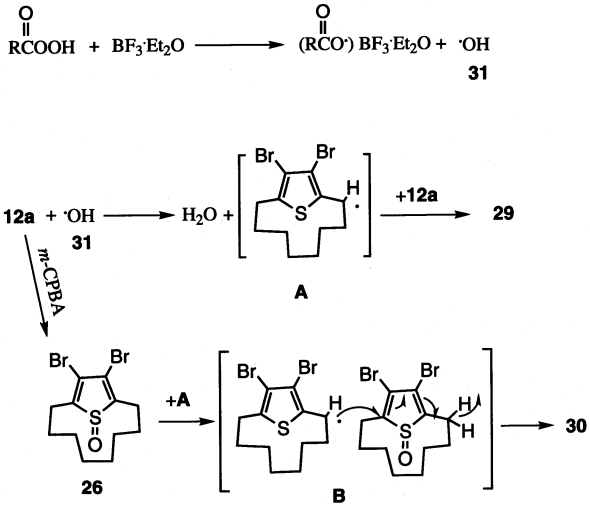
a: $PhCH_2MgBr$, $[(C_6H_5)_2P]NiCl_2$, ether. − b: *m*-CPBA, $BF_3 \cdot Et_2O$, −20 to −10°C.

Scheme 8



a: *m*-CPBA, $BF_3 \cdot Et_2O$, CH_2Cl_2, −20−0°C.

Scheme 9. Possible mechanism of the formation of **29** and **30**

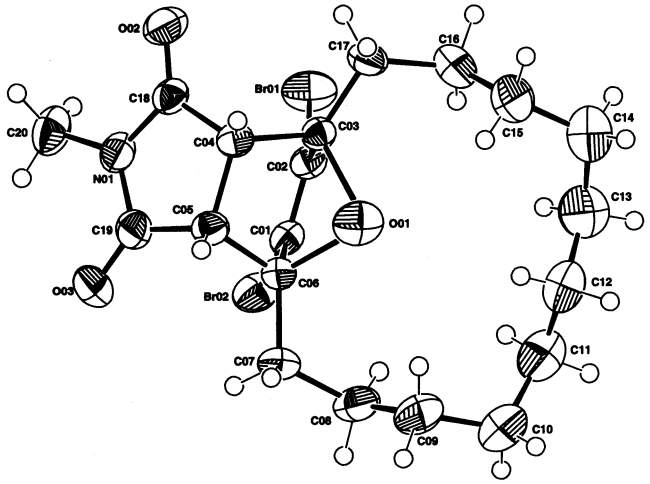


during the cycloaddition reaction. This stereoselectivity is in accordance with the cycloaddition of simpler thiophenes,[6a][6c][17] the stereoselectivity of which can be explained by the Cieplak effect.[15c][18] Selected bond angles and atomic distances can be found in Figure 2.

In comparison to [10](2,5)thiophenophane, cycloadduct **18a** is much more rigid. The ten-carbon chain shows some distortion in terms of the C−C−C bond angles. The angles of the sp^3-hybridized carbon atoms of the chain are widened to 113−120°, except for that of C11−C12−C13 which measures 111.1°. The bond angles of C10−C11−C12 and C14−C15−C16 are 118.3° and 117.1°, respectively. The largest bond angle is C10−C11−C12 with 120°.

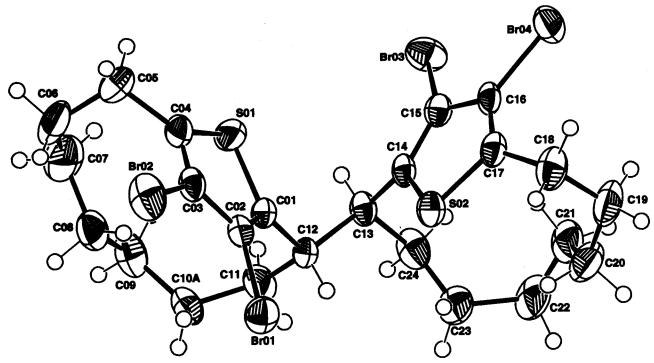
The ORTEP drawing of cycloadduct **29a** is shown in Figure 3. It clearly shows that both thiophene rings are no longer planar, but are distorted by 4.1° (S1−C1−C2−C3) and 4.5° (S2−C14−C15−C16), respectively. Furthermore, the vicinal ring carbon atoms C5 and C12 are far from the median plane of the thiophene system (S1−C1−C2−

Figure 2. ORTEP drawing of **18a**[a]



[a] Selected atomic distances [Å] and bond angles [°]: C(7)−C(8) 1.544(6), C(8)−C(9) 1.513(7), C(9)−C(10) 1.525(8), C(10)−C(11) 1.495(9), C(11)−C(12) 1.519(9), C(13)−C(14) 1.469(10), C(14)−C(15) 1.513(9), C(15)−C(16) 1.513(9), C(16)−C(17) 1.546(6); C(2)−C(1)−C(6) 112.0(3), C(2)−C(1)−Br(2) 125.1(3); C(6)−C(1)−Br(2) 122.3(2), C(1)−C(2)−C(3) 111.3(3), C(2)−C(3)−C(17) 118.2(3), C(2)−C(3)−C(4) 117.7(3), C(2)−C(3)−S(1) 97.5(2), C(17)−C(3)−S(1) 112.6(2), C(4)−C(3)−S(1) 100.4(2), C(1)−C(6)−C(7) 118.7(3), C(1)−C(6)−C(5) 107.4(3), C(7)−C(6)−C(5) 116.4(3), C(6)−C(7)−C(8) 113.7(3), C(9)−C(8)−C(7) 113.2(4), C(8)−C(9)−C(10) 114.2(5), C(11)−C(10)−C(9) 114.3(5), C(10)−C(11)−C(12) 118.3(6), C(11)−C(12)−C(13) 111.1(7), C(14)−C(13)−C(12) 120.3(8), C(13)−C(14)−C(15) 116.7(5), C(15)−C(16)−C(17) 115.4(4), C(3)−C(17)−C(16) 113.1(3).

Figure 3. ORTEP drawing of **29**[a]



[a] Selected bond angles [°] and dihedral angles between the planes [°]: C(2)−C(1)−C(12) 130.0(5), C(1)−C(2)−C(3) 113.3(5), C(2)−C(3)−C(4) 113.8(5), C(2)−C(1)−S(12) 109.5(5), C(12)−C(1)−S(1) 120.2(4), C(5)−C(6)−C(7) 116.7(7), C(6)−C(7)−C(8) 115.1(7), C(7)−C(8)−C(9) 115.3(6), C(8)−C(9)−C(10A) 113.2(6), C(9)−C(10A)−C(11) 116.1(6), C(10A)−C(11)−C(12) 121.0(6), C(1)−C(12)−C(13) 111.1(5), C(1)−C(12)−C(11) 111.9(4), C(11)−C(12)−C(13) 110.3(4); S(1)−C(1)−C(2)−C(3) 4.3(5), C(11)−C(2)−C(3)−C(4) −0.2(6), C(2)−C(3)−C(4)−C(5) 157.1(5), C(12)−C(1)−C(2)−C(3) −169.0(5), C(2)−C(3)−C(4)−S(1) −4.0(6), C(3)−C(4)−C(5)−C(6) −71.5(9), S(1)−C(4)−C(5)−C(6) 88.4(7), C(4)−C(5)−C(6)−C(7) −53.0(10), C(5)−C(6)−C(7)−C(8) 86.4(9), C(6)−C(7)−C(8)−C(9) −154.4(6), C(7)−C(8)−C(9)−C(10A) 150.7(6), C(8)−C(9)−C(10A)−C(11) 8.8(13), C(9)−C(10A)−C(11)−C(12) 95.5(8), C(2)−C(1)−C(12)−C(13) −135.3(5), S(1)−C(1)−C(12)−C(13) 52.1(5), C(2)−C(1)−C(12)−C(11) 101.0(6), C(13)−C(14)−C(15)−C(16) −160.5(4), S(2)−C(14)−C(15)−C(16) 4.5(5), C(15)−C(16)−C(17)−C(18) 158.1(5), C(15)−C(16)−C(17)−S(23) −4.4(5), C(12)−C(1)−C(2)−C(3) −169.0(5).

C3−C4), with the torsional angle C2−C3−C4−C5 being 157.1°. The eight-carbon chains are distorted in terms of bond angles (C−C−C). Some of the angles of the formally sp^3-hybridised carbon atoms are widened. Thus, the angle of C5−C6−C7 is 116.7°, that of C6−C7−C8 is 115.1°, and that of C7−C8−C9 is 115.3°. The distance between C8 and the thiophene ring (S1−C1−C2−C3−C4) is 3.05 Å, between C21 and the thiophene ring (S2−C14−C15−C16−C17) is 3.13 Å. This small distance can be explained by the compressed structure due to the non-bonded interaction between the thiophene ring and the short aliphatic bridge. This is also in accordance with the ^{1}H-NMR spectrum of [8](2,5)thiophenophane (**12a**), which indicates a non-symmetrical structure with two protons in close proximity to the thiophene ring.

Experimental Section

General: Melting points are uncorrected. Infrared spectra were measured with JASCO IR-700 and Nippon Denshi JIR-AQ2OM machines. ^{1}H- and ^{13}C-NMR spectra were recorded with a JOEL EX-270 spectrometer. The chemical shifts are relative to TMS (solvent $CDCl_3$, unless noted otherwise). Mass spectra were measured with a JMS-01-SG-2 spectrometer (EI, 70 eV). UV spectra were recorded in ethanol with a Hitachi 22A spectrophotometer. Commercially available *meta*-chloroperbenzoic acid was purified before use.[20]

3,4-Dibromo-2,5-bis(bromomethyl)thiophene (**9a**): To a stirred solution of 2,5-dibromothiophene (**7**) (10.0 g, 0.089 mol) in CH_2Cl_2 (20 ml), cooled to −18°C, a solution of Br_2 (58.0 g, 0.37 mol) in CH_2Cl_2 (30 ml) was added. After the reaction mixture had been stirred for 2 h, the solvent was distilled and the residue was separated by column chromatography on silica gel (hexane) to give **9a** (34.47 g, 0.08 mol, yield 90%) as light yellow crystals, m.p. 116−118°C (hexane). − IR (KBr): ν = 2520 cm^{-1}, 2478, 1420, 1310, 1295, 1160, 1110, 1020. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 4.64 (s, 4 H, 2 × $BrCH_2$). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 25,21, 116,07, 135,81. − MS (70 eV); *m/z*: 432 (M^+[$^{81}Br_4$]), 430 (M^+[$^{79}Br^{81}Br_3$]), 428 (M^+[$^{79}Br_2{}^{81}Br_2$]), 426 (M^+[$^{79}Br_3{}^{81}Br$]), 424 (M^+[$^{79}Br_4$]). − $C_8H_4Br_4S$ (427.7): calcd. C 16.85; H 9.42; found C 16.86; H 9.06.

12,13-Dibromo-2,9-dithia[10](2,5)thiophenophane (**10a**). − *General Procedure A:* To a refluxing solution of KOH (2.8 g, 50 mmol) in EtOH (3 l) was added dropwise a solution of 1,6-dimercaptohexane (1.86 g, 12.4 mmol) and **9a** (1.8 g, 5.39 mmol) in benzene (300 ml) over 20 h. The solvent was distilled off, and the residue was poured into ice-cold water (200 ml). The mixture was extracted with dichloromethane (3 × 50 ml), the extracts were washed with brine and dried with anhydrous $MgSO_4$. The solvent was evaporated in vacuo. The residue was separated by column chromatography on silica gel (hexane) to give **10a** (3.1 g, 2.7 mmol, 60%), m.p. 151°C (hexane). − IR (KBr): ν = 2950 cm^{-1}, 2916, 2848, 1455, 1413, 1310, 1237, 1128. − ^{1}H NMR ($CDCl_3$): δ = 1.22 (m, 8 H, $[CH_2]_4$), 2.60 (t, 4 H, ^3J = 7.3 Hz, 2 × $[CH_2]_4CH_2S$), 3.85 (s, 4 H, 2 × thienyl-CH_2S). − ^{13}C NMR ($CDCl_3$): δ = 25.82, 29.06, 31.81, 31.93, 112.86, 136.73. − MS (70 eV); *m/z* (%): 418 (M^+[$^{81}Br_2$], 17), 416 (M^+[$^{79}Br^{81}Br$], 32), 414 (M^+[$^{79}Br_2$], 14). − $C_{12}H_{16}Br_2S_3$ (416.27): calcd. C 34.63, H 3.87; found C 35.18, H 3.89.

14,15-Dibromo-2,11-dithia[12](2,5)thiophenophane (**10b**): Using procedure A, KOH (1.5 g, 26.8 mmol), $NaBH_4$ (190 mg, 5 mmol) in EtOH (3 l) were allowed to react with 1,8-dibromooctane (1.47 g, 5.39 mmol) and **9b**[8] (1.8 g, 5.39 mmol) in PhH/EtOH (1:1, v/v) (100 ml) to give **10b** (1.2 g, 2.7 mmol, 54%) as colorless prisms, m.p. 91−92°C (hexane). − IR (KBr): ν = 2920 cm^{-1}, 2846, 1518, 1457, 1439, 1409, 1300, 1231, 1150, 902. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.20 (m, 4 H, 2 × CH_2), 1.37 (m, 4 H, 2 × CH_2), 1.51 (m, 4 H, 2 × CH_2), 2.58 (t, J = 7.1 Hz, 4 H, 2 × CH_2CH_2S), 3.85 (s, 4 H, 2 × thienyl-CH_2S). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 26.50 (t), 26.61 (t), 27.69 (t), 31.63 (t, CH_2S), 31.72 (t, CH_2S), 112.04 (s), 137.91 (s). − MS (70 eV); *m/z* (%): 446 (M^+[$^{81}Br_2$], 34), 444 (M^+[$^{79}Br^{81}Br$], 56), 442 (M^+[$^{79}Br_2$], 24). − $C_{14}H_{20}Br_2S_3$ (444.30): calcd. C 37.85, H 4.54; found C 37.88, H 4.68.

15,16-Dibromo-2,12-dithia[13](2,5)thiophenophane (**10c**): Using procedure A, KOH (1.3 g, 23.2 mmol), $NaBH_4$ (190 mg, 5 mmol) in EtOH (3 l) were allowed to react with 1,9-dibromononane (1.70 g, 5.99 mmol) and **9b**[8] (2.0 g, 6.0 mmol) in PhH/EtOH (1:1, v/v) (200 ml). Column chromatography on silica gel (hexane/toluene, 1:1) gave **10c** (1.3 g, 2.9 mmol, 47%) as colorless prisms, m.p. 70−71°C (hexane). − IR (KBr): ν = 2930 cm^{-1}, 1298. − ^{1}H NMR ($CDCl_3$): δ = 1.24 (m, 6 H, $[CH_2]_3$), 1.34 (m, 4 H, 2 × CH_2), 1.56 (m, 4 H, 2 × CH_2, 2.56 (t, ^3J = 7.4 Hz, 4 H, 2 × CH_2CH_2S), 3.86 (s, 4 H, 2 × thienyl-CH_2S). − ^{13}C NMR ($CDCl_3$): δ = 26.47, 26.81 (2 C), 27.71, 31.56, 31.79, 111.86, 138.10. − MS (70 eV); *m/z* (%): 460 (M^+[$^{81}Br_2$]), 458 (M^+[$^{79}Br^{81}Br$]), 456 (M^+[$^{79}Br_2$]). − $C_{15}H_{22}Br_2S_3$ (458.33): calcd. C 39.31, H 4.84; found C 39.55, H 4.69.

16,17-Dibromo-2,13-dithia[14](2,5)thiophenophane (**10d**): Using procedure A, KOH (1.5 g, 26.8 mmol), $NaBH_4$ (190 mg, 5 mmol) in EtOH (3 l) were allowed to react with 1,10-dibromodecane (1.8 g, 6 mmol) and **9b**[8] (2.0 g, 6.0 mmol) in PhH/EtOH (1:1, v/v) (200 ml). Column chromatography on silica gel (hexane/toluene, 1:1) gave **10d** (1.5 g, 3.2 mmol, 53%) as colorless prisms, m.p. 70−71°C (hexane). − IR (KBr): ν = 2950 cm^{-1}, 1440, 1410, 1300, 1230. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.28 (m, 8 H, 2 × $[CH_2]_2$), 1.34−1.41 (m, 4 H, 2 × CH_2), 1.62 (m, 4 H, 2 × CH_2), 2.58 (t, ^3J = 7.5 Hz, 4 H, 2 × CH_2CH_2S), 3.87 (s, 4 H, 2 × thienyl-CH_2S). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 26.47 (t), 27.23 (2 C) (t), 27.82 (t), 31.16 (t, CH_2S), 31.52 (CH_2S), 112.13 (s), 137.36 (s). − MS (70 eV); *m/z* (%): 476 (M^+[$^{81}Br_2$], 36), 474 (M^+[$^{79}Br^{81}Br$], 73), 472 (M^+[$^{79}Br_2$], 33), 195 (25). − $C_{16}H_{24}Br_2S_3$ (472.35): calcd. C 40.68, H 5.12; found C 40.67, H 5.20.

18,19-Dibromo-2,15-dithia[16](2,5)thiophenophane (**10e**): Using procedure A, KOH (2.2 g, 39.2 mmol), $NaBH_4$ (200 mg, 5.29 mmol) in EtOH (4 l) were allowed to react with 1,12-dibromododecane (2.95 g, 8.9 mmol) and **9b** (3.0 g, 8.9 mmol) in PhH/EtOH (1:1, v/v) (200 ml). Column chromatography on silica gel (hexane) gave **10e** (3.0 g, 5.98 mmol, 67%) as a colorless liquid. − IR (neat): ν = 2.924 cm^{-1}, 2852, 1674, 1459, 1300, 1233. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.20−1.40 (m, 14 H, 7 × CH_2), 1.61 (m, 6 H, $[CH_2]_3$), 2.56 (t, ^3J = 7.4 Hz, 4 H, 2 × CH_2CH_2S), 3.87 (s, 4 H, 2 × thienyl-CH_2S). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 27.01, 27.06, 27.17 (2 C), 27.69, 28.50, 30.96, 31.84, 112.24, 136.96. − MS (70 eV); *m/z* (%): 502 (M^+[$^{81}Br_2$], 14), 500 (M^+[$^{79}Br^{81}Br$], 23), 498 (M^+[$^{79}Br_2$], 10). − HRMS; *m/z*: calcd. for $C_{18}H_{28}Br_2S_3$ 501.9678, 499.9699, 497.9720; found 501.9667, 499.9719, 497.9716.

12,13-Dibromo-2,9-dithia[10](2,5)thiophenophane 2,2′,9,9′-Tetraoxide (**11a**). − *General Procedure B:* To a solution of **10a** (1.14 g, 2.74 mmol) in CH_2Cl_2 (200 ml) was added gradually *m*-CPBA (3.4 g, 70 w-%, 13.8 mmol), and the resulting mixture was stirred for 12 h at room temperature. The reaction mixture was poured into a mixture of a sat. aqueous $NaHCO_3$ (20 ml) solution and

CH_2Cl_2 (200 ml), and the organic phase was separated. The undissolved product was filtered, and the solid was washed thoroughly with water and ether to give **11a** (1.24 g, yield 94%) as colorless crystals, m.p. 330°C (dec.). – IR (KBr): ν = 2968 cm^{-1}, 1457, 1402, 1312 (SO_2), 1122 (SO_2). – MS (70 eV); *m/z* (%): 482 ($M^+[^{81}Br_2]$, 0.7), 478 ($M^+[^{79}Br_2]$, 0.8), 354 ($M^+[^{81}Br_2] - 2\ SO_2$, 8), 352 ($M^+[^{79}Br^{81}Br] - 2\ SO_2$, 20), 350 ($M^+[^{79}Br_2] - 2\ SO_2$, 8). – $C_{12}H_{16}Br_2O_4S_3$ (480.26): calcd. C 30.01, H 3.36; found C 29.23, H 3.34. – $C_{12}H_{16}Br_2O_4S_3$ (480.26): caldc. 481.8534, 479.8556, 477.8577; found 481.8562, 479.8585, 477.8562.

14,15-Dibromo-2,11-dithia[12](2,5)thiophenophane 2,2′,11,11′-Tetraoxide (**11b**): Using procedure B, **10b** (1.1 g, 2.48 mmol) in CH_2Cl_2 (40 ml) were allowed to react with *m*-CPBA (3.1 g, 70 w-%, 12.5 mmol) to give **11b** (1.26 g, 2.48 mmol, 90%) as colorless crystals, m.p. 279°C (dec.). – IR (KBr): ν = 2976 cm^{-1}, 2930, 2862, 1464, 1404, 1314, 1116, 913. – MS (70 eV); *m/z* (%): 510 ($M^+[^{81}Br_2]$), 508 ($M^+[^{79}Br^{81}Br]$), 506 ($M^+[^{79}Br_2]$), 382 ($M^+[^{81}Br_2] - 2\ SO_2$, 0.2), 380 ($M^+[^{79}Br^{81}Br] - 2\ SO_2$, 2.3), 378 ($M^+[^{79}Br_2] - 2\ SO_2$, 0.3). – $C_{14}H_{20}Br_2O_4S_3$ (508.32): calcd. C 33.08, H 3.97; found C 32.26, H 4.08. – HRMS; *m/z*: calcd. for $C_{14}H_{20}Br_2O_4S_3$ 509.8848, 507.8869, 505.8890; found 509.9928, 507.8833, 505.8874.

15,16-Dibromo-2,12-dithia[13](2,5)thiophenophane 2,2′,12,12′-Tetraoxide (**11c**): Using procedure B, **10 c** (1.30 g, 2.85 mmol) in CH_2Cl_2 (40 ml) were allowed to react with *m*-CPBA (3.4 g, 70 w-%, 13.8 mmol) to give **11c** (1.03 g, 2.62 mmol, 92%) as colorless crystals, m.p. 244–246°C (dec.). – IR (KBr): ν = 2924 cm^{-1}, 1459, 1404, 1310 (SO_2), 1144 (SO_2). – MS (70 eV); *m/z* (%): 396 ($M^+[^{81}Br_2] - 2\ SO_2$), 394 ($M^+[^{79}Br^{81}Br] - 2\ SO_2$), 392 ($M^+[^{79}Br_2] - 2\ SO_2$). – $C_{15}H_{22}Br_2O_4S_3$ (394.21): calcd. C 34.49, H 4.25; found C 33.49, H 4.19.

16,17-Dibromo-2,13-dithia[14](2,5)thiophenophane 2,2′,13,13′-Tetraoxide (**11d**): Using procedure B, **10d** (1.30 g, 2.75 mmol) in CH_2Cl_2 (40 ml) were allowed to react with *m*-CPBA (3.4 g, 70 w-%, 13.8 mmol) to give **11d** (1.28 g, 2.42 mmol, 87%) as colorless crystals, m.p. 255–257°C. – IR (KBr): ν = 2920 cm^{-1}, 2854, 1308 (SO_2), 1268, 1142 (SO_2). – MS (70 eV); *m/z* (%): 538 ($M^+[^{81}Br_2]$, 0.5), 536 ($M^+[^{79}Br^{81}Br]$, 0.9), 534 ($M^+[^{79}Br_2]$, 0.4), 410 ($M^+[^{81}Br_2] - 2\ SO_2$, 3.4), 408 ($M^+[^{79}Br^{81}Br] - 2\ SO_2$, 5.7), 406 ($M^+[^{79}Br_2] - 2\ SO_2$, 2.7). – $C_{16}H_{24}Br_2O_4S_3$ (536.35): calcd. C 35.83, H 4.51; found C 35.89, H 4.47.

18,19-Dibromo-2,15-dithia[16](2,5)thiophenophane 2,2′,15,15′-Tetraoxide (**11e**): Using procedure B, **10e** (1.0 g, 2.0 mmol) in CH_2Cl_2 (40 ml) were treated with *m*-CPBA (2.5 g, 70 w-%, 10.2 mmol) to give **11e** (1.05 g, 1.86 mmol, 93%) as colorless crystals, m.p. 256–257°C. – IR (KBr): ν = 2922 cm^{-1}, 1307 (SO_2), 1141 (SO_2). – MS (70 eV); *m/z* (%): 566 ($M^+[^{79}Br^{81}Br$), 562 ($M^+[^{79}Br_2]$), 438 ($M^+[^{81}Br_2] - 2\ SO_2$, 1.7), 436 ($M^+[^{79}Br^{81}Br] - 2\ SO_2$, 3.5), 434 ($M^+[^{79}Br_2] - 2\ SO_2$, 1.5). – $C_{18}H_{28}Br_2O_4S_3$ (564.42): calcd. 565.9475, 563.9496, 561.9516; found 565.9484, 563.9536, 561.9520.

3,4-Dibromo-[8](2,5)thiophenophane (**12a**). – *General Procedure C:* The pyrolysis of **11a** (1.1 g, 2.29 mmol) was carried out in a manner similar to that described in the literature[16]. After the pyrolysis, the organic material was extracted with CH_2Cl_2 (2 × 20 ml), and the ash was filtered. The solvent was evaporated, and the residue was subjected to column chromatography on silica gel (hexane) to give **12a** (0.38 g, 50%) as a colorless liquid. – IR (neat): ν = 2924 cm^{-1}, 2852, 1520, 1453, 1298. – ^1H NMR (270 MHz, $CDCl_3$): δ = 0.01 (m, 2 H, CH_2), 0.92 (m, 2 H, CH_2), 1.37 (m, 6 H, $[CH_2]_3$), 1.81 (m, 2 H, CH_2), 22.45 (m, 2 H, thienyl-CH_2), 3.16 (dt, *J* = 14.2 Hz, 4.3 Hz, 2 H, thienyl-CH_2). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 26.02, 28.57, 29.60, 31.03, 112.67, 139.53. – MS (70 eV); *m/z* (%): 354 ($M^+[^{81}Br_2]$, 10), 352 ($M^+[^{79}Br^{81}Br]$, 28), 350 ($M^+[^{79}Br_2]$, 7). – $C_{12}H_{16}Br_2S$ (352.13): calcd. C 40.93, H 4.58; found C 40.99, H 4.87. – HRMS; *m/z*: calcd. for $C_{12}H_{16}Br_2S$ 353.9298, 351.9319, 349.9339; found 353.9326, 351.9293, 349.9312. – UV (ethanol): λ_{max} (log ε) = 208 nm (4.01), 252 (3.75).

3,4-Dibromo-[10](2,5)thiophenophane (**12b**): The pyrolysis of **11b** (1.07 g, 2.11 mmol) was carried out as described for **12a** (procedure C) to yield **12b** (0.44 g, 1.16 mmol, 55%) as a colorless liquid. IR (neat): ν = 2926 cm^{-1}, 2854, 1459, 1350. – ^1H NMR (270 MHz, $CDCl_3$): δ = 0.76 (m, 4 H, 2 × CH_2), 1.11 (m, 4 H, 2 × CH_2), 1.36 (m, 4 H, 2 × CH_2), 1.67 (m, 4 H, 2 × CH_2), 2.81 (t, ^3J = 6.1 Hz, 4 H, 2 × thienyl-CH_2). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 25.30, 26.08, 26.91, 28.36, 29.74, 111.60, 138.58. – MS (70 eV); *m/z* (%): 382 ($M^+[^{81}Br_2]$, 30), 380 ($M^+[^{79}Br^{81}Br]$, 46), 378 ($M^+[^{79}Br_2]$, 30). – $C_{14}H_{20}Br_2S$ (380.19): calcd. C 44.23, H 5.30; found C 44.61, H 5.60. – UV (ethanol): λ_{max} (log ε) = 2.04 nm (4.00), 246 (3.86).

3,4-Dibromo-[11](2,5)thiophenophane (**12c**): The pyrolysis of **11c** (1.30 g, 2.50 mmol) was carried out as described for **12a** (procedure C) to yield **12c** (0.25 g, 0.628 mmol, 26%) as colorless prisms, m.p. 81–82°C (hexane). – IR (KBr): ν = 2922 cm^{-1}, 2854, 1461. – ^1H NMR ($CDCl_3$): δ = 0.87 (m, 2 H, CH_2), 1.23 (m, 12 H, 6 × CH_2), 1.65 (m, 4 H, 2 × CH_2), 2.86 (t, *J* = 5.9 Hz, 4 H, 2 × thienyl-CH_2). – ^{13}C NMR ($CDCl_3$): δ = 23.52, 25.30, 26.08, 26.90, 28.36, 27.74, 111.63, 138.58. – MS (70 eV); *m/z* (%): 396 ($M^+[^{81}Br_2]$,23), 394 ($M^+[^{79}Br^{81}Br]$, 51), 392 ($M^+[^{79}Br_2]$, 21). – $C_{15}H_{22}Br_2S$ (394.21): calcd. C 45.70, H 5.63; found C 46.20, H 5.62. – UV (ethanol): λ_{max} (log ε) = 204 nm (3.77), 246 (3.85).

3,4-Dibromo-[12](2,5)thiophenophane (**12d**): The pyrolysis of **11d** (1.0 g, 1.87 mmol) was carried out as described for **12a** (procedure C) to yield **12d** (0.41 g, 1.00 mmol, 54%) as colorless prisms, m.p. 69–71°C. – IR (KBr): ν = 2924 cm^{-1}, 2848, 1526, 1438, 1350, 1290. – ^1H NMR (270 MHz, $CDCl_3$): δ = 1.12 (s, 4 H, 2 × CH_2), 1.24 (m, 12 H, 6 × CH_2), 1.64 (m, 4 H, 2 × CH_2), 2.85 (t, *J* = 6.0 Hz, 4 H, thienyl-CH_2). – ^{13}C NMR ($CDCl_3$): δ = 25.21, 26.38, 27.05, 27.17, 28.81, 29.63, 111.25, 137.27. – MS (70 eV); *m/z* (%): 410 ($M^+[^{81}Br_2]$, 23), 408 ($M^+[^{79}Br^{81}Br]$, 53), 406 ($M^+[^{79}Br_2]$, 18). – $C_{16}H_{24}Br_2S$ (408.24): calcd. C 47.07, H 5.93; found C 47.68, H 6.21. – UV (ethanol): λ_{max} (log ε) = 204 nm (3.37), 2.46 (3.66).

3,4-Dibromo-[14](2,5)thiophenophane (**12e**): The pyrolysis of **11e** (0.94 g, 1.6 mmol) was carried out as described for **12a** (procedure C) to yield **12e** (0.48 g, 1.10 mmol, 67%) as a colorless liquid. – IR (neat): ν = 2924 cm^{-1}, 2854, 1526, 1459. – ^1H NMR (270 MHz, $CDCl_3$): δ = 1.22–1.30 (m, 20 H, 10 × CH_2), 1.64 (m, 4 H, 2 × CH_2), 2.85 (t, *J* = 5.9 Hz, 4 H, 2 × thienyl-CH_2). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 26.30, 26.58, 27.53, 27.62, 27.78, 28.73, 29.81, 111.23, 136.94. – MS (70 eV), *m/z* (%): 438 ($M^+[^{81}Br_2]$, 12), 436 ($M^+[^{79}Br^{81}Br]$, 20), 434 ($M^+[^{79}Br_2]$, 12). – $C_{18}H_{28}Br_2S$ (436.29): calcd. C 49.55, H 6.47; found C 49.86, H 6.15. – HRMS; *m/z*: calcd. for $C_{18}H_{28}Br_2S$ 438.0239, 436.0258, 434.0278; found 438.0264, 436.0236, 434.025. – UV (ethanol): λ_{max} (log ε) = 204 nm (2.81), 244 (3.76).

15-Bromo-13-methyl-2,9-dithia[10](2,4)thiophenophane (**14**): To a refluxing solution of KOH (2.2 g, 23.2 mmol) and $NaBH_4$ (200 mg, 5 mmol) in EtOH (4 l) was added dropwise a solution of 1,6-bis(mercapto)hexane (1.64 g, 10.95 mmol) and **13** (3.0 g, 10.95 mmol) in benzene (150 ml) over 12 h. The solvent was distilled off, and the residue was poured into ice-cold water (200 ml). The mixture was extracted with CH_2Cl_2 (3 × 30 ml), the collected organic phases were washed with brine and dried with anhydrous $MgSO_4$. The solvent was evaporated in vacuo, and the residue was separated by column chromatography on silica gel (hexane/ether, 10:1) to give

14 (2.3 g, 6.55 mmol, 60%) as colorless prisms, m.p. 117°C (hexane). – IR (KBr): ν = 2914 cm^{-1}, 1543, 1421, 1273, 1246, 1231, 1194, 1157, 1111. – ^1H NMR (270 MHz, $CDCl_3$): δ = 0.93–1.37 (m, 8 H, 4 × CH_2), 2.41–2.61 (m, 4 H, 2 × CH_2S), 2.49 (s, 3 H, CH_3), 3.57 (t, *J* = 15.0 Hz, 2 H, thienyl-CH_2S), 3.97 (d, *J* = 14.5 Hz, 1 H, thienyl-C*H*S), 4.31 (d, *J* = 14.5 Hz, 1 H, thienyl-C*H*S). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 14.38, 26.00, 26.20, 29.35, 29.58 (2 C), 30.41, 31.04, 31.13, 113.57, 132.78, 134.29, 136.08. – MS (70 eV); *m/z* (%): 352 (M^+[$^{79}Br^{81}Br$], 47), 350 (M^+[$^{79}Br_2$], 44). – $C_{13}H_{19}BrS_3$ (351.38): calcd. C 44.44, H 5.45; found C 44.63, H 5.66.

15-Bromo-13-methyl-2,9-dithia[10](2,4)thiophenophane 2,2,9,9-Tetraoxide (**15**): To a solution of **14** (1.08 g, 3.08 mmol) in CH_2Cl_2 (40 ml) was added gradually *m*-CPBA (3.8 g, 70 w-%, 15.4 mmol), and the mixture was stirred for 12 h at room temperature. The reaction mixture was poured into a mixture of sat. aqueous $NaHCO_3$ solution (40 ml) and CH_2Cl_2 (200 ml). The organic phase was separated, washed with brine and dried with anhydrous $MgSO_4$. The solvent was evaporated and the residue was washed with ether to afford **15** (1.20 g, 2.89 mmol, 94%) as colorless crystals, m.p. 277–278°C. – IR (KBr): ν = 2914 cm^{-1}, 1301 (SO_2), 1150, 1124 (SO_2). – MS (70 eV); *m/z* (%): 288 (M^+[$^{79}Br^{81}Br$] – 2 SO_2, 2.2), 286 (M^+[$^{79}Br_2$] – 2 SO_2, 1.5). – $C_{13}H_{19}BrO_4S_3$ (415.39): calcd. C 37.59, H 4.61; found C 37.60, H 4.73.

15-Bromo-13-methyl-[8](2,4)thiophenophane (**16**): The pyrolysis of **15** (2.3 g, 5.54 mmol) was carried out as described for **12a** (procedure C) to yield **16** (1.01 g, 3.52 mmol, 64%) as a colorless liquid. – IR (KBr): ν = 2924 cm^{-1}, 2854, 1545, 1442. – ^1H NMR ([D_8]toluene): δ = –0.1 (m, 1 H, CH_2CH_2), 0.33 (m, 1 H, CH_2CH_2), 0.97 (m, 4 H, 2 × CH_2), 1.25 (m, 2 H, CH_2), 1.58 (m, 2 H, CH_2), 1.86 (m, 2 H, CH_2), 2.00 (s, 3 H, CH_3), 2.43 (m, 2 H, thienyl-CH_2CH_2), 2.63 (ddd, ^3J = 4.62 Hz, ^3J = 11.87 Hz, ^2J = 14.00 Hz, 1 H, thienyl-CH_2CH_2), 2.84 (ddd, ^3J = 3.96 Hz, ^3J = 12.05 Hz, ^2J = 14.00 Hz, 1 H, thienyl-CH_2CH_2). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 13.68, 23.67, 24.20, 27.33, 27.31, 28.79, 29.24, 29.72, 33.44, 113.82, 130.55, 137.48, 138.42. – MS (70 eV); *m/z* (%): 288 (M^+[$^{79}Br^{81}Br$], 35), 286 (M^+[$^{79}Br_2$], 23). – HRMS; *m/z*: calcd. for $C_{13}H_{19}BrS$ 288.0370, 286.0391; found 288.0386, 286.0394. – UV (ethanol): λ_{max} (log ε) = 210 nm (3.81), 252 (3.74).

18,19-Dibromo-N-methyl-15-aza-20-thiatetracyclo[10.5.2.1.0^{13,17}]eicos-18-ene-14,16-dione 20-Oxide (**18a**). – *General Procedure D:* Under an inert gas and at –20°C, $BF_3 \cdot Et_2O$ (2 ml) was added to a solution of **12b** (130 mg, 0.34 mmol) and *N*-methylmaleimide (11 mg, 0.9 mmol) in dry CH_2Cl_2 (10 ml). The reaction mixture was stirred for 10 min at –20°C, then a solution of *m*-CPBA (110 mg, 0.64 mmol) in dry CH_2Cl_2 (10 ml) was slowly added. The reaction mixture was stirred for 1 h at –20°C, then for 3 h at 0–10°C. The suspension was poured into a mixture of conc. aq. $NaHCO_3$ solution (20 ml) and CH_2Cl_2 (40 ml) and stirred for 20 min at room temperature. The organic phase was separated and the aqueous phase extracted with CH_2Cl_2 (3 × 20 ml). The combined organic phases were washed with water and brine and dried with anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was separated by column chromatography on silica gel to give cycloadduct **18a** (90 mg, 0.18 mmol, 58%) as colorless prisms, m.p. 205–206°C (ether/hexane, 2:1). – IR (KBr): ν = 2928 cm^{-1}, 1775, 1700 (C=O), 1468, 1433, 1378, 1283, 1123, 1090 (SO), 1074 (SO). – ^1H NMR (270 MHz, $CDCl_3$): δ = 1.31 (m, 10 H, 5 × CH_2), 1.70 (m, 4 H, 2 × CH^a_2, 2 × C$H^a_2$$CH_2$CSO), 1.85 (m, 2 H, 2 × C$H^b_2$$CH_2$CSO), 2.05 (ddd, *J* = 4.0 Hz, 11.1 Hz, 15.8 Hz, 2 H, 2 × SOCCH^a_2), 2.60 (ddd, *J* = 3.3 Hz, 5.6 Hz, 15.8 Hz, 2 H, 2 × SOCCH^b_2), 2.87 (s, 3 H, CH_3), 3.71 (s, 2 H, 2 × COCH). – ^{13}C NMR (67.9 MHz, CD_2Cl_2): δ = 25.12, 25.45, 26.15, 26.68, 28.16, 28.97, 29.00, 52.52, 76.98, 173.65. – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 24.71, 25.34, 25.73, 27.80,28.60, 52.13, 77.00, 125.78, 173.37. – MS (70 eV); *m/z* (%): 509 (M^+[$^{81}Br_2$], 2), 507 (M^+[$^{79}Br^{81}Br$], 2), 505 (M^+[$^{79}Br_2$], 1). – HRMS; *m/z*: calcd. for $C_{19}H_{25}NBr_2O_3S$ 508.9884, 506.9902, 504.9922; found 508.9916, 506.9902, 504.9889.

19,20-Dibromo-N-methyl-16-aza-21-thiatetracyclo[11.5.2.1.0^{14,18}]heneicos-19-ene-15,17-dione 21-Oxide (**18b**): To **12c** (120 mg, 0.30 mmol), $BF_3 \cdot Et_2O$ (2 ml), *N*-methylmaleimide (100 mg, 0.9 mmol) in CH_2Cl_2 (10 ml) was added *m*-CPBA (100 mg, 0.58 mmol) in CH_2Cl_2 (5 ml) as described for **18a** (procedure D) to yield **18b** (140 mg, 0.27 mmol, 89%) as colorless prisms, m.p. 230°C (ether). – IR (KBr): ν = 2932 cm^{-1}, 2850, 1773, 1699 (C=O), 1080 (SO), 1070 (SO). – ^1H NMR (270 MHz, $CDCl_3$): δ = 1.21–1.82 (m, 18 H, 9 × CH_2), 1.98 (ddd, *J* = 2.0 Hz, 9.6 Hz, 16.0 Hz, 2 H, 2 × SOCCH^a_2), 2.64 (ddd, *J* = 1.3 Hz, 8.5 Hz, 16.0 Hz, 2 H, 2 × SOCCH^b_2), 2.91 (s, 3 H, CH_3), 3.78 (s, 2 H, 2 × SOCCH). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 24.67, 25.12 (2 C), 25.32, 26.24, 27.26, 27.51, 52.31, 78.20, 125.70, 173.30. – MS (70 eV); *m/z* (%): 523 (M^+[$^{81}Br_2$]), 521 (M^+[$^{79}Br^{81}Br$]), 519 (M^+[$^{79}Br_2$]), 471 (M^+[$^{81}Br_2$] – SO), 473 (M^+[$^{79}Br^{81}Br$] – SO), 475 (M^+[$^{79}Br_2$] – SO). – $C_{20}H_{27}NBr_2O_3S$ (521.31): calcd. C 46.08, H 5.22, N 2.69; found C 45.81, H 5.04, N 2.79.

22,23-Dibromo-N-methyl-19-aza-24-thiatetracyclo[14.5.2.1.0^{17,21}]tetracos-22-ene-18,20-dione 24-Oxide (**18c**): To **12c** (250 mg, 0.57 mmol), $BF_3 \cdot Et_2O$ (2 ml), *N*-methylmaleimide (150 mg, 1.38 mmol) in CH_2Cl_2 (7 ml) was added *m*-CPBA (130 mg, 0.75 mmol) as described for **18a** (procedure D) to yield **18c** (140 mg, 0.24 mmol, 42%) as colorless prisms, m.p. 166–167°C (ether). – IR (KBr): ν = 2928 cm^{-1}, 2854, 1773, 1699 (C=O), 1092 (SO). – ^1H NMR (270 MHz, $CDCl_3$): δ = 1.26–1.98 (m, 22 H, 11 × CH_2), 1.71–1.82 (m, 2 H, CH_2), 1.89–1.99 (m, 2 H, 2 × SOCCH^a_2), 2.66–2.76 (m, 2 H, 2 × SOCCH^b_2), 2.91 (s, 3 H, NCH_3), 3.71 (s, 2 H, 2 × CHCO). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 26.15, 26.29 (2C), 28.27, 28.34, 28.41, 28.83, 29.36, 52.60, 81.21, 125.97, 174.29. – MS (70 eV); *m/z* (%): 517 (M^+[$^{81}Br_2$] – SO, 64), 515 (M^+[$^{79}Br^{81}Br$] – SO, 100), 513 (M^+[$^{79}Br_2$] – SO, 41). – $C_{23}H_{33}Br_2NO_3S$ (536.39): calcd. C 49.03, H 5.90, N 2.50; found C 49.29, H 5.83, N 2.54.

18-Bromo-N,1-dimethyl-14-aza-17-thiatetracyclo[9.5.1.1^{2,11}.$0^{12,16}$]hexadec-2:18-ene-13,15-dione 17-Oxide (**19a**): To **16** (110 mg, 0.38 mmol) $BF_3 \cdot Et_2O$ (2 ml), *N*-methylmaleimide (90 mg, 0.80 mmol) in CH_2Cl_2 (5 ml) was added *m*-CPBA (100 mg, 0.58 mmol) in CH_2Cl_2 (5 ml) as described for **18a** (procedure D) to yield **19a** (90 mg, 0.22 mmol, 57%) as colorless crystals, m.p. 151–152°C (CH_2Cl_2). – IR (KBr): ν = 2974 cm^{-1}, 2920, 2864, 1775, 1693 (C=O), 1461, 1435, 1384, 1282, 1080 (SO). – ^1H NMR (270 MHz, $CDCl_3$): δ = 0.88 (m, 1 H, CH_2), 1.09 (m, 1 H, CH_2), 1.26–1.57 (m, 8 H), 1.80 (s, 3 H, CH_3), 2.00 (m, 2 H, CH_2), 2.20 (m, 2 H, SOCCH_2), 2.51 (m, 2 H, C=CCH_2), 2.91 (s, 3 H, NCH_3), 3.69 (d, *J* = 7.3 Hz, 1 H, COCH), 3.81 (d, *J* = 7.3 Hz, 1 H, COCH). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 12.63, 21.76, 23.45, 25.39, 26.92, 28.00, 28.12, 28.19, 28.46, 28.95, 49.47, 55.79, 70.87, 81.74, 118.26, 146.74, 173.76, 175.33. – MS (70 eV); *m/z* (%): 367 (M^+[$^{79}Br^{81}Br$] – SO, 4), 365 (M^+[$^{79}Br_2$] – SO, 3). – $C_{18}H_{24}BrNO_3S$ (414.42): calcd. C 52.17, H 3.38; found C 51.95, H 5.76, N 3.57.

18-Bromo-1-methyl-N-phenyl-14-aza-17-thiatetracyclo[9.5.1.1^{2,11}.$0^{12,16}$]hexadec-2:18-ene-13,15-dione 17-Oxide (**19b**): To **16** (300 mg, 1.05 mmol), $BF_3 \cdot Et_2O$ (3 ml), *N*-phenylmaleimide (360 mg, 2.1 mmol) in CH_2Cl_2 (10 ml) was added *m*-CPBA (270 mg,

1.56 mmol) in CH_2Cl_2 (10 ml) as described for **18a** (procedure D) to yield **19b** (400 mg, 0.54 mmol, 80%) as colorless prisms, m.p. 219−220°C. − IR (KBr): ν = 2934 cm^{-1}, 1775, 1711 (C=O), 1499, 1384, 1182, 1090 (SO). − ^1H NMR (270 MHz, $CDCl_3$): δ = 1.37−1.64 (m, 10 H, 5 × CH_2), 1.85 (s, 3 H, CH_3), 2.20−2.28 (m, 4 H, $SOCCH_2CH_2$), 2.53−2.63 (m, 2 H, $C{=}CCH_2$), 3.87 (d, *J* = 7.4 Hz, 1 H, COCH), 3.97 (d, *J* = 7.4 Hz, 1 H, COCH), 7.23−7.26 (m, 2 H, aryl-*H*), 7.38−7.48 (m, 3 H, aryl-*H*). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 12.67, 21.85, 23.56, 27.06, 28.07, 28.18, 28.28, 28.54, 29.07, 48.45, 55.72, 71.10, 82.05, 118.54, 126.52, 128.82, 129.13, 131.62, 147.10, 172.61, 174.46. − MS (70 eV); *m/z* (%): 429 ($M^+[^{79}Br^{81}Br]$ − SO, 50), 427 ($M^+[^{79}Br_2]$ − SO, 48). − $C_{23}H_{26}BrNO_3S$ (476.23): calcd. C 57.98, H 5.50, N 2.94; found C 58.09, H 5.55, N 2.98.

Dimethyl 10-Bromo-14-methyl[8]metacyclophane-12,13-dicarboxylate (**21**): Under an inert gas and at −20°C, $BF_3 \cdot Et_2O$ (3 ml) was added to a solution of **16** (250 mg, 1.05 mmol) and **20** (360 mg, 2.54 mmol) in dry CH_2Cl_2 (1 ml). The reaction mixture was stirred for 10 min at −20°C, then a solution of *m*-CPBA (230 mg, 1.33 mmol) in dry CH_2Cl_2 (10 ml) was added slowly. The reaction mixture was stirred for 3 h at −20°C. The suspension was poured into a mixture of a conc. aqueous $NaHCO_3$ solution (30 ml) and CH_2Cl_2 (50 ml) and stirred for 20 min at room temperature. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 ml). The combined organic phases were washed with water and brine and dried with anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was separated by column chromatography on silica gel to give cycloadduct **21** (250 mg, 0.63 mmol, 60%) as a colorless liquid. − IR (neat): ν = 2948 cm^{-1}, 2858, 1737 (C=O), 1540, 1436, 1291, 1263, 1211. − ^1H NMR (270 MHz, $CDCl_3$): δ = 0.15 (m, 2 H, CH_2), 0.96 (m, 2 H, CH_2), 1.19 (m, 4 H, 2 × CH_2), 1.62 (m, 2 H, 2 × Ar-$CH_2CH^a_2$), 2.04 (m, 2 H, Ar-$CH_2CH^b_2$), 2.37 (s, 3 H, Ar-CH_3), 3.10 (m, 2 H, Ar-CH_2), 3.84 (s, 3 H, CO_2CH_3), 3.85 (s, 3 H, CO_2CH_3). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 16.82, 23.31, 23.56, 27.84, 28.02, 28.74, 30.17, 33.21, 33.46, 52.38, 53.47, 130.35, 130.71, 132.27, 133.17, 139.75, 145.30, 168.05, 168.66. − MS (70 eV); *m/z* (%): 398 $M^+[^{79}Br^{81}Br]$, 4), 396 ($M^+[^{79}Br_2]$, 4). − $C_{19}H_{25}BrO_4$ (397.31): calcd. C 57.44, H 6.34; found C 57.30, H 6.71. − HRMS; *m/z*: calcd. for $C_{19}H_{25}BrO_4$ 398.0918, 396.0936; found 398.0934, 396.0919.

3,4-Dibenzyl-[12](2,5)thiophenophane (**22**): Under an inert gas and at room temperature, benzyl bromide (1.02 g, 6.0 mmol) was added by syringe to a suspension of magnesium (200 mg, 8.3 mmol) in diethyl ether (5 ml). The mixture was refluxed for 2 h. After the reaction mixture was cooled to room temperature, $NiCl_2(dppp)_2$ (16 mg, 0.025 mmol) and a solution of **12d** (750 mg, 1.84 mmol) in THF/ether (1:1) (10 ml) were added to the reaction mixture. The black mixture was heated to reflux for 12 h. Then it was hydrolysed in an ice bath with 10% HCl. The organic phase and ether extracts from the aqueous layer were combined, washed with water and dried with anhydrous $MgSO_4$. The solvent was evaporated in vacuo. The residue was separated by column chromatography on silica gel (hexane/ether, 6:1) to give **22** (740 mg, 1.72 mmol, 96%) as colorless prisms, m.p. 49−51°C. − IR (KBr): ν = 2924 cm^{-1}, 2850, 1604, 1494, 1454, 1073, 1029. − ^1H NMR (270 MHz, $CDCl_3$): δ = 1.26 (m, 16 H, 8 × CH_2), 1.54 (m, 4 H, 2 × CH_2), 2.73 (t, 4 H, *J* = 6.0 Hz thienyl-CH_2), 3.68 (s, 4 H, Ar-CH_2), 6.97 (m, 4 H, aryl-*H*), 7.12−7.32 (m, 6 H, aryl-*H*). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 25.50, 26.33, 27.37 (2C), 30.30, 32.45, 37.95, 125.66, 127.99, 128.19, 134.94, 137.32, 140.70. − MS (70 eV), *m/z* (%): 430 (M^+, 15). − $C_{30}H_{38}S$ (430.69): calcd. C 83.66, H 8.89; found C 84.10, H 8.64.

12,13-Dibromo-[10](2,5)thiophenophane S-Oxide (**23a**): Under an inert gas and at −20°C, $BF_3 \cdot Et_2O$ (1 ml) was added to a solution of **12b** (100 mg, 0.27 mmol) in CH_2Cl_2 (3 ml). The mixture was stirred for 10 min at −20°C. Thereafter a solution of *m*-CPBA (100 mg, 0.58 mmol) in dry CH_2Cl_2 (10 ml) was added dropwise and the mixture was stirred for 6 h at −20°C. Then the suspension was poured into a mixture of conc. aqueous $NaHCO_3$ (10 ml) and CH_2Cl_2 (30 ml) and stirred at room temperature for 20 min. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 ml). The combined organic phases were washed with water and brine and dried with anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was separated by column chromatography on silica gel (hexane/ether, 4:1) to give **23a** (50 mg, 0.13 mmol, 48%) as a colorless oil. − IR (neat): ν = 2928 cm^{-1}, 2856, 1578, 1461, 1078 (SO). − ^1H NMR (270 MHz, $CDCl_3$): δ = 0.84 (m, 2 H, CH_2), 1.11 (m, 4 H, 2 × CH_2), 1.42, (m, 4 H, 2 × CH_2), 1.63 (m, 4 H, 2 × CH_2), 1.91 (m, 2 H, thienyl oxide-CH_2CH_2), 2.83 (m, 4 H, thienyl oxide-CH_2). − ^{13}C NMR ($CDCl_3$): δ = 25.12, 25.66, 26.47, 27.80, 28.10, 120.36, 124.02, 148.19, 153.92. − FAB MS (6 keV); *m/z* (%): 399 ($MH^+[^{81}Br_2]$, 51), 397 ($MH^+[^{79}Br^{81}Br]$, 100), 395 ($MH^+[^{79}Br_2]$, 55). − FAB HRMS: calcd. for $C_{14}H_{20}Br_2OS$ 398.9639, 396.9660, 394.9680; found 398.9695, 396.9655, 394.9684.

3,4-Dibenzyl-[12](2,5)thiophenophane S-Oxide (**23b**): Under an inert gas and at −20°C, $BF_3 \cdot Et_2O$ (0.3 ml) was added to a solution of **22** (400 mg, 0.95 mmol) in CH_2Cl_2. The mixture was stirred for 10 min at −20°C. Thereafter a solution of *m*-CPBA (220 mg, 1.29 mmol) in dry CH_2Cl_2 (15 ml) was added dropwise and the mixture was stirred for 3 h at −20°C. Then the suspension was poured into a mixture of conc. $NaHCO_3$ solution (30 ml) and CH_2Cl_2 (50 ml) and stirred at room temperature for 20 min. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 ml). The combined organic phases were washed with water and brine and dried with anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was separated by column chromatography on silica gel (hexane/ether, 1:2) to give **23b** (220 mg, 0.33 mmol, 53%) as colorless prisms, m.p. 80−82°C (hexane). − IR (KBr): ν = 2926 cm^{-1}, 2854, 1603, 1494, 1455, 1045 (SO). − ^1H NMR (270 MHz, $CDCl_3$): δ = 1.29 (m, 16 H, 8 × CH_2), 1.58 (br. s, 2 H, thienyl-$CH_2CH^a_2$), 1.75 (br. s, 2 H, thienyl-$CH_2CH^b_2$), 2.60 (m, 2 H, thienyl-CH^a_2), 2.76 (m, 2 H, thienyl-CH^b_2), 3.47 (q, 4 H, *J* = 16.4 Hz, Ar-CH_2), 7.00 (m, 4 H, aryl-*H*), 7.25 (m, 6 H, aryl-*H*). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 24.87, 26.02, 26.76, 27.08, 27.85, 29.11, 32.09, 126.61, 127.92, 128.71, 137.61, 139.06, 148.10. − MS (70 eV); *m/z* (%): 447 (MH^+, 40), 430, 413. − $C_{30}H_{38}SO$ (446.69): calcd. C 80.67, H 8.57; found C 80.24, H 8.60.

18,19-Dibromo-N-phenyl-15-aza-20-thiatetracyclo[10.5.2.1.0^{13,17}]eicos-18-ene-14,16-dione 20-Oxide (**24a**): A solution of **23a** (70 mg, 0.176 mmol) and *N*-phenylmaleimide (60 mg, 0.354 mmol) in CH_2Cl_2 (3 ml) was stirred for 1 h. The solvent was evaporated in vacuo, and the residue was separated by column chromatography on silica gel (hexane/ether, 1:1.5) to give cycloadduct **24a** (70 mg, 0.123 mmol, 70%) as colorless needles, m.p. 199−200°C. − IR (KBr): ν = 2924 cm^{-1} (CH), 2846, 1775, 1709 (C=O), 1501, 1383, 1186, 1091 (SO). − ^1H NMR (270 MHz, $CDCl_3$): δ = 1.25 (m, 14 H, 7 × CH_2), 1.72−1.91 (m, 2 H, CH_2), 2.14 (m, 2 H, $SOCCH^a_2$), 2.70 (m, 2 H, $SOCCH^b_2$), 3.89 (s, 2 H, NCOCH), 7.19 (m, 2 H, aryl-*H*), 7.47 (m, 3 H, aryl-*H*). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 24.73, 25.44, 25.77, 27.89, 28.64, 52.13, 77.00, 125.62, 126.77, 129.11, 129.34, 131.37, 172.52. − MS (70 eV); *m/z* (%): 571 ($MH^+[^{81}Br_2]$, 5), 569 ($MH^+[^{79}Br^{81}Br]$, 21), 567 ($MH^+[^{79}Br_2]$, 5). − $C_{24}H_{27}BrNO_3S$ (569.36): calcd. C 50.63, H 4.78, N 2.46; found C 50.15, H 4.86, N 2.30. − HRMS; *m/z*: calcd. for $C_{24}H_{27}BrNO_3S$

571.0042, 569.0059, 567.0078; found 571.0018, 569.0049, 567.0056.

20,21-Dibenzyl-N-methyl-17-aza-22-thiatetracyclo[12.5.2.1.0^{15,19}]-docos-20-ene-16,18-dione 22-Oxide (**24b**): A solution of **23b** (30 mg, 0.067 mmol) and *N*-methylmaleimide (18 mg, 0.13 mmol) in benzene (3 ml) was refluxed for 1 h. The solvent was evaporated in vacuo, and the residue was separated by column chromatography on silica gel (hexane/ether, 1:2) to give cycloadduct **24b** (21 mg, 0.038 mmol, 56%) as colorless needles, m.p. 59−60°C. − IR (KBr): ν = 2960 cm^{-1}, 1729 (C=O), 1438, 1265, 1041 (SO). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.21−1.60 (m, 20 H, 10 × CH_2), 1.98 (m, 2 H, 2 × SOCC*H*$^a_2$), 2.58 (m, 2 H, 2 × SOCC*H*$^b_2$), 2.61 (s, 3 H, *N*CH_3), 3.50 (q, *J* = 13.5 Hz, 4 H, Ar-C*H*$_2$), 3.69 (s, 2 H, 2 × COCH), 7.04 (m, 4 H, aryl-*H*), 7.20−7.30 (m, 6 H, aryl-*H*). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 22.74, 24.78, 25.23, 26.27, 26.63, 26.94, 27.08, 33.19, 52.35, 77.20, 126.69, 128.57, 128.66, 128.82, 136.95, 137.72, 175.22. − MS (70 eV); *m*/*z* (%): 557 (M^+, 1), 509 (M^+ − SO, 78). − HRMS; *m*/*z*: calcd. for $C_{35}H_{43}NO_3S$ 557.2964; found 557.2964.

20,21-Dibenzyl-N-phenyl-17-aza-22-thiatetracyclo[12.5.2.1.0^{15,19}]-docos-20-ene-16,18-dione 22-Oxide (**24c**): A solution of **23b** (32 mg, 0.072 mmol) and *N*-phenylmaleimide (25 mg, 0.14 mmol) in benzene (3 ml) was refluxed for 1 h. The solvent was evaporated in vacuo, and the residue was separated by column chromatography on silica gel (hexane/ether, 1:1.5) to give cycloadduct **24c** (25 mg, 0.04 mmol, 60%) as colorless needles, m.p. 197−198°C. − IR (KBr): ν = 2924 cm^{-1} (C−H), 2848, 1778, 1714 (C=O), 1497, 1455, 1369, 1172, 1070 (SO). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.21−1.59 (m, 20 H, 10 × CH_2), 2.00 (m, 2 H, 2 × SOCC*H*$^a_2$), 2.62 (m, 2 H, 2 × SOCC*H*$^b_2$), 3.55 (q, *J* = 16.2 Hz, 4 H, Ar-C*H*$_2$), 3.87 (s, 2 H, 2 × COCH), 6.87−7.12 (m, 12 H, aryl-*H*), 7.39−7.45 (m, 3 H, aryl-*H*). − ^{13}C NMR (67.9 Hz, $CDCl_3$): δ = 16.50, 24.67, 26.31, 26.70, 27.01 (2 C), 33.44, 51.99, 77.20, 125.95, 126.56, 128.18, 128.54, 128.63, 128.75, 131.68, 136.57, 137.72, 174.23. − MS (70 eV); *m*/*z* (%): 619 (M^+, 9), 571 (6), 413 (M^+ − SO). − HRMS; *m*/*z*: calcd. for $C_{40}H_{45}NO_3S$ 619.3120; found 619.3120.

12,13-Dibenzylmetacyclo[2](2,5)thiophenophane (**26**): Under an inert gas and at room temperature benzyl bromide (1.02 g, 6 mmol) was added by syringe to a suspension of magnesium (200 mg, 8.3 mmol) in diethyl ether (5 ml). The resulting mixture was refluxed for 2 h. After the mixture was cooled to room temperature, $NiCl_2(dppp)_2$ (16 mg, 0.025 mmol) and a solution of **25** (740 mg, 2.0 mmol) in THF/ether (1:1) (10 ml) was added. The black mixture was heated to reflux for 12 h. Then it was hydrolyzed in an ice bath with 10% HCl solution. The organic phase and ether extracts from the aqueous layer were combined, washed with water, and dried with anhydrous $MgSO_4$. The solvent was evaporated in vacuo, and the residue was separated by column chromatography on silica gel (hexane/ether, 6:1) to give **26** (680 mg, 1.72 mmol, 87%) as colorless prisms, m.p. 135−137°C (hexane). − IR (KBr): ν = 3020 cm^{-1}, 2900, 1600, 1490, 1450, 1420, 1320, 1070, 1022, 930, 910. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.28−2.39 (m, 4 H, 2 × CH_2), 2.75−2.82 (m, 2 H, C*H*$^a_2$C*H*$^b_2$), 3.10−3.22 (m, 2 H, C*H*$^a_2$C*H*$^b_2$), 4.00 (s, 4 H, Ar-C*H*$_2$), 6.12 (s, 1 H, aryl-*H*), 6.98−7.25 (m, 13 H, aryl-*H*). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 31.84, 33.64, 37.81, 125.70, 126.02, 128.14, 128.35, 128.68, 130.58, 139.94, 140.27, 141.72, 141.96. − MS (70 eV); *m*/*z* (%): 394 (M^+, 100), 288 (51). − $C_{28}H_{26}S$ (394.57): calcd. C 85.23, H 6.64; found C 85.28, H 6.93.

12,13-Dibenzylmetacyclo[2](2,5)thiophenophane S-Oxide (**27**): Under an inert gas and at −20°C, $BF_3 \cdot Et_2O$ (0.26 ml) was added to a solution of **26** (280 mg, 0.71 mmol) in CH_2Cl_2 (5 ml). The mixture was stirred for 10 min at −20°C. Thereafter a solution of *m*-CPBA (180 mg, 1.04 mmol) in dry CH_2Cl_2 (15 ml) was added dropwise and the mixture was stirred for 3 h at −20°C. Then the suspension was poured into a mixture of a conc. solution of aqueous $NaHCO_3$ (30 ml) and CH_2Cl_2 (50 ml) and stirred at room temperature for 20 min. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 ml). The combined organic phasees were washed with water and brine and dried with anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was separated by colmun chromatography on silica gel to give **28** (140 mg, 3.3 mmol, 38%) as light yellow crystals, m.p. 153−155°C (ether) and **27** (110 mg, 2.67 mmol, 45%) as yellow crystals, m.p. 164−165°C (ether). − **28**: IR (KBr): ν = 2920 (C−H) cm^{-1}, 1603, 1495, 1452, 1433, 1291 (SO_2), 1133, (SO_2). − ^{1}H NMR ($CDCl_3$): δ = 2.56, (m, 4 H, 2 × CH_2), 2.80 (m, 4 H, 2 × CH_2), 3.74 (d, 2 H, *J* = 16.7 Hz, Ar-C*H*$_2$), 3.94 (d, *J* = 16.7 Hz, 2H Ar-C*H*$_2$), 7.10−7.29 (m, 14 H, aryl-*H*). − MS (70 eV); *m*/*z* (%): 426 (M^+, 1), 362 (19). − **27**: IR (KBr): ν = 2920 cm^{-1}, 1585, 1493, 1451, 1076 (SO). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.52−2.62 (m, 4 H, 2 × CH_2), 2.78−2.86 (m, 2 H, CH_2), 2.91−2.98 (m, 2 H, CH_2), 3.59 (d, *J* = 16.2 Hz, 2 H, Ar-C*H*$_2$), 3.72 (d, *J* 16.2 Hz, 2 H, Ar-C*H*$_2$), 6.86 (s, 1 H, aryl-*H*), 7.12−7.28 (m, 13 H, aryl-*H*). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 28.86, 33.26, 37.34, 126.74, 127.64, 128.30, 128.48, 128.75, 131.12, 134.39, 137.04, 141.10, 144.98, 154.81. − MS (70 eV); *m*/*z* (%): 410 (M^+, 10), 394, 378 (100). − HRMS; *m*/*z*: calcd. for $C_{28}H_{26}OS$ 410.1704; found 410.1713.

1,1′-Bi(10,11-dibromo-[8](2,5)thiophenophanyl) (**29**): Under an inert gas and at −20°C, $BF_3 \cdot Et_2O$ (2 ml) was added to a solution of **12a** (150 mg, 0.43 mmol) in dry CH_2Cl_2 (5 ml). The reaction mixture was stirred for 10 min at −20°C, then a solution of *m*-CPBA (130 mg, 0.77 mmol) in dry CH_2Cl_2 (7 ml) was added slowly. The reaction mixture was stirred for 5 h at −20°C. The suspension was poured into a mixture of a conc. aqueous $NaHCO_3$ solution (20 ml) and CH_2Cl_2 (30 ml) and stirred for 20 min at room temperature. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 ml). The combined organic phases were washed with water and brine and dried with anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was separated by column chromatography on silica gel (hexane) to give cycloadduct **29** (670 mg, 0.95 mmol, 43%) as colorless prisms, m.p. 192°C (hexane) and dimer **30** (6 mg, 0.008 mmol, 4%) as colorless crystals), m.p. 195−196°C (hexane). − **29**: IR (KBr): ν = 2922 cm^{-1}, 2850, 1440, 1260, 1060. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = −0.40 (br. s, 2 H), 0.98−1.63 (m, 22 H, 11 × CH_2), 2.46 (sept, 2 H, thienyl-CH_2C*H*$_2$), 3.14 (dt, ^3J = 3.2 Hz, ^2J = 14.3 Hz, 2 H), 3.63 (m, 2 H, 2 × CH). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 21.51, 26.61, 27.53, 28.43, 29.88, 30.87, 34.45, 44.26, 111.22, 113.67, 140.05, 142.62. − MS (70 eV); *m*/*z* (%): 706 (M^+[$^{81}Br_4$], 1.0), 704 (M^+[$^{81}Br_3{}^{79}Br$], 2.1), 702 (M^+[$^{81}Br_2{}^{79}Br2$], 3.7), 700 (M^+[$^{81}Br^{79}Br_3$], 1.9), 698 (M^+[$^{79}Br_4$], 0.4). − FAB MS (6 keV): 702.9 (MH^+). − $C_{24}H_{30}Br_4S_2$ (702.25): calcd. C 41.05, H 4.31; found C 41.21, H 4.41. − **30**: ^{1}H NMR (270 MHz, $CDCl_3$): δ = −0.70 (br. s, 1 H), 0.26 (m, 1 H), 0.85−1.84 (m, 19 H), 2.27 (m, 2 H), 2.60 (m, 2 H), 2.85 (m, 1 H), 3.17 (m, 1 H), 3.84 (dd, 1 H, *J* = 4.0 Hz, 12.0 Hz), 6.43 (dd, 1 H, *J* = 4.0 Hz, 12.0 Hz). − MS (70 eV); *m*/*z* (%): 722 (M^+[$^{81}Br_4$], 9), 720 (M^+[$^{81}Br_3{}^{79}Br$], 30), 718 (M^+[$^{81}Br_2{}^{79}Br_2$], 48), 716 (M^+[$^{81}Br^{79}Br_3$], 39), 714 (M^+[$^{79}Br_4$], 15). − HRMS; *m*/*z*: calcd. for $C_{24}H_{30}Br_4OS_2$ 722.8473, 720.8491, 718.8510, 716.8530, 714.8550; found 722.8480, 720.8467, 718.8508, 716.8497, 714.8539.

X-*ray Crystallographic Analysis of* **18a**: Intensity data were collected with an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods (SIR 92)[21]. All non-hydrogen atoms were located in the succeeding difference Fourier syntheses. Hydro-

Table 1. Experimental crystallographic details for **18a** and **29**

Compound	**18a**	**29**
Formula	$C_{20}H_{27}Br_2NO_3S$	$C_{24}H_{30}Br_4S_2$
M	521.31	702.24
Recrystallized from	ether/hexane	ether/hexane
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a [Å]	17.924(3)	10.543(2)
b [Å]	7.959(10)	15.420(1)
c [Å]	16.2890(10)	8.477(2)
α[°]	90	93.790(10)
β[°]	108.29(1)	106.850(10)
γ[°]	90	76.330(10)
V [Å^3]	2206.3(5)	1281.6(4)
$D_{calcd.}$ [g cm^{-3}]	1.569	1.820
Z	4	2
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
μ(Cu-K_α) [Å]	1.54184	1.54184
Crystal size [mm]	0.3 × 0.27 × 0.10	0.43 × 0.33 × 0.23
T [°C]	23±2	23±2
Absorption correction	empirical	empirical
Scan mode	ω-2θ	
Scan range (θ) [°]		2θ−42
Measured data	3904	4516
Unique data	3752	4339
Observed data	3394	3962
No. of parameters	245	282
Obs. criterion	$F_o \geq 2\sigma(F_o)$	$F_o \geq 2\sigma(F_o)$
R[a]	0.0437	0.0493
R_w[b]	0.124	0.1387
Residual density [e Å^{-3}]		0.891 to −0.870

[a] $R = [\Sigma||F_o| - |F_o||]/\Sigma|F_o|]$. − [b] $R_w = [\Sigma_w(|F_o| - |F_c|)^2]/\Sigma_w F_o^2]^{1/2}$.

gen atoms were located by calculation. H atoms with riding model, weighting scheme $w^{-1} = \sigma^2(F_o^2) + (0.0799\ P)^2 + 2.6887\ P$, where $3\ P = (F_o^2 + 2\ F_c^2)$. All non-hydorgen atoms treated anisotropically were refined by full-matrix least-squares calculation. 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[22]. The final cell parameters and specific data collection parameters are summarised in Table 1.

X-Ray Crystallographic Analysis of **29**: Intensity data were collected with an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods (SIR 92)[21]. All non-hydrogen atoms were located in the succeeding difference Fourier syntheses. Hydrogen atoms were located by calculation. H atoms with riding model, weighting scheme $w^{-1} = \sigma^2(F_o^2) + (0.0868\ P)^2 + 3.4202\ P$, where $3\ P = (F_o^2 + 2\ F_c^2)$. All non-hydrogen atoms treated anisotropically were refined by full-matrix least-squares calculation. 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[22]. The final cell parameters and specific data collection parameters are summarised in Table 1.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101500 (for **18a**) and -101501 (for **29**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code + (1223)336-033; E-mail: deposit@ccdc.cam.ac.uk).

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