Synthesis and Thiophene Ring Opening Reaction of [2]Paracyclo[2](2,5)- and -(2,4)thiophenophanes

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Dithia[3]paracyclo[3](2,4)- and -(2,5)thiophenophanes ⟨dithia-[3.3](2,4)- and -(2,5)PTP⟩ (**3**, **7**, **9**) are obtained by the coupling reaction of the corresponding bis(chloromethyl)- and bis(mercaptomethyl)arenes. Desulfurization of the dithia[3.3]PTPs **3**, **7**, **9** by photolysis affords the thia[2.3]PTPs **15**, **16**, **17** and [2.2]PTPs **14**, **18**, **19**, **20**. The pyrolysis of the disulfone **12** gives the symmetrical thiophenophane **13**. The dynamics of the ring inversion, the UV spectra, and the reductive ring opening with Raney-Ni (W-7) of the obtained PTPs are discussed.

We have recently reported[1] on the synthesis of all possible isomers (four types) of [2]metacyclo[2]thiophenophanes and their conformations. Although [2]paracyclo[2]thiophenophanes ([2.2]PTP) are expected to display novel properties, due to their stacked and closed aromatic rings[2], there are only a few reports[3] on the synthesis of [2.2](2,5)PTP, but none of [3.3]PTP and [2.2](2,4)PTP. The other reported [2]paracyclo[2]-heterophanes which contain a five-membered heteroaromatic ring include [2]paracyclo[2](2,5)-furanophane[3,4] [2]paracyclo[2](2,5)-pyrrolophane[5], and [2]paracyclo[2](3,5)isoxazolophane[6]; thus, there are only a few investigations concerned with this system. The reductive opening of one thiophene ring of [2.2]PTPs[7] affords substituted [7]-[8,9] and [8]paracyclophanes[4a,4b,10].

In this paper we report on the synthesis of [2.2](2,5)- and (2,4)PTPs via dithia[3.3](2,5)- and (2,4)PTPs as well as on the investigation of the ring inversion of this system.

Results and Discussion

A. Synthesis of Dithia[3.3]PTPs

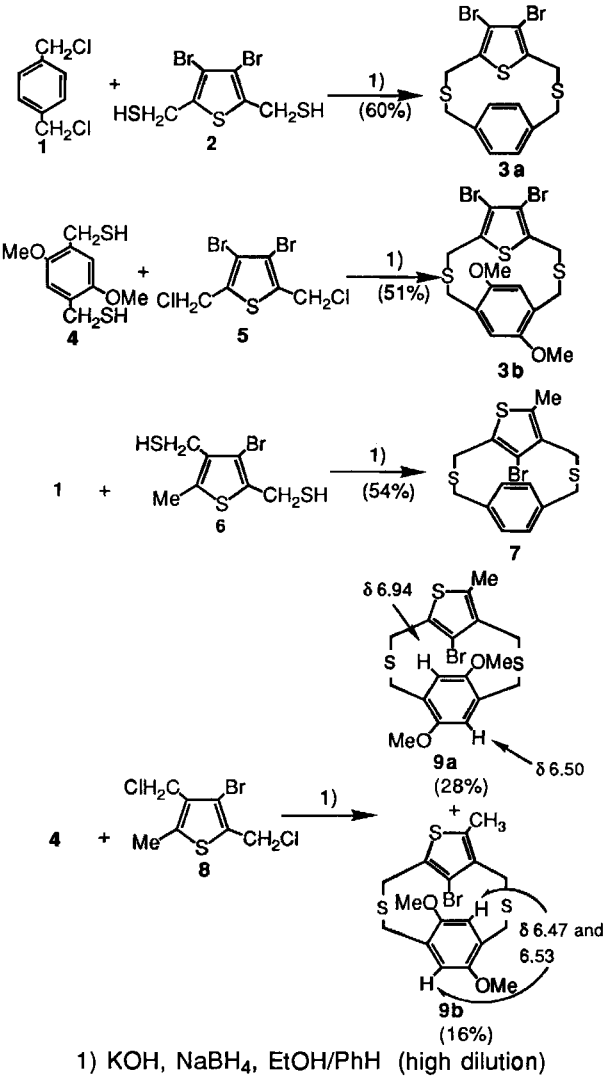
The dithia [3.3](2,5)- and -(2,4)PTPs are synthesized by coupling the corresponding bis(chloromethyl)arenes (**1**, **5**[1], **8**[1]) with bis(mercaptomethyl)arenes (**2**[1], **4**[11], **6**[1]) as shown in Scheme 1. The dithia [3.3]PTPs **3a**, **3b**, and **7** are obtained as single isomers, while dithia [3.3](2,4)PTP (**9**) is obtained as a mixture of two conformational isomers.

The bromine atoms of the dithia[3.3](2,4)PTPs **7** and **9** are reduced by lithiation to give the corresponding dithia-[3.3](2,4)PTPs **10** and **11** as shown in Scheme 2.

B. Desulfurization of Dithia[3.3]PTPs

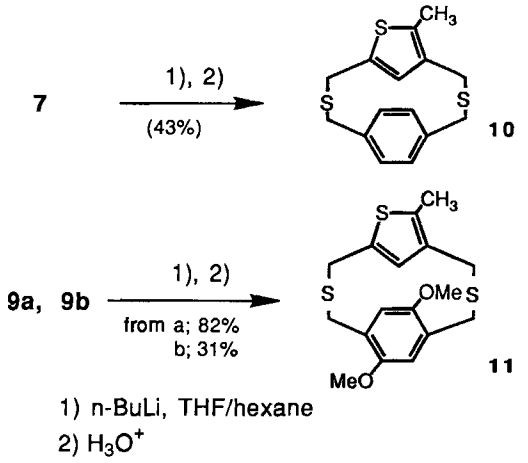
Desulfurization of dithia[3.3]PTPs is effected either by pyrolysis[12] of dithia[3.3]PTP tetraoxides or photolysis[13] of dithia[3.3]PTPs in trimethyl phosphite.

Scheme 1



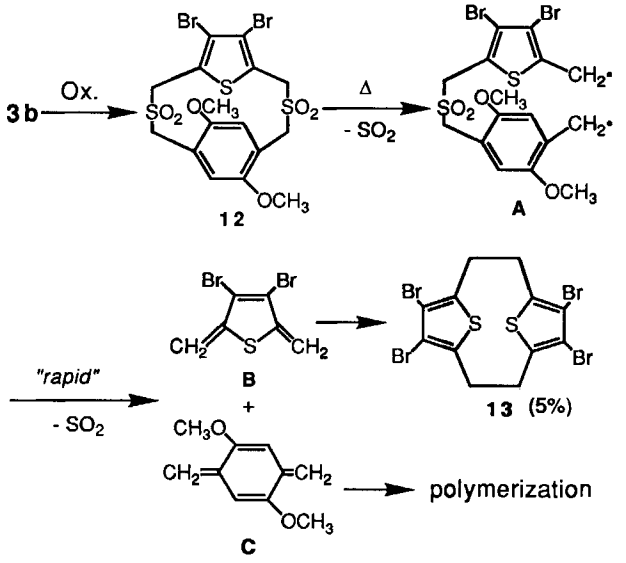
  0009–2940/91/0606–1403 $ 3.50+.25/0

Scheme 2



The pyrolysis of the tetraoxide derivative **12** affords the symmetrical thiophenophane **13** together with a large amount of polymer. The desired [2.2](2,5)PTP **14** and symmetrical [2.2]paracyclophane are not obtained under this conditions (480°C, 0.4–1,2 Torr). The formation of **13** is due to fast desulfonation of the intermediate **A** (Scheme 3).

Scheme 3

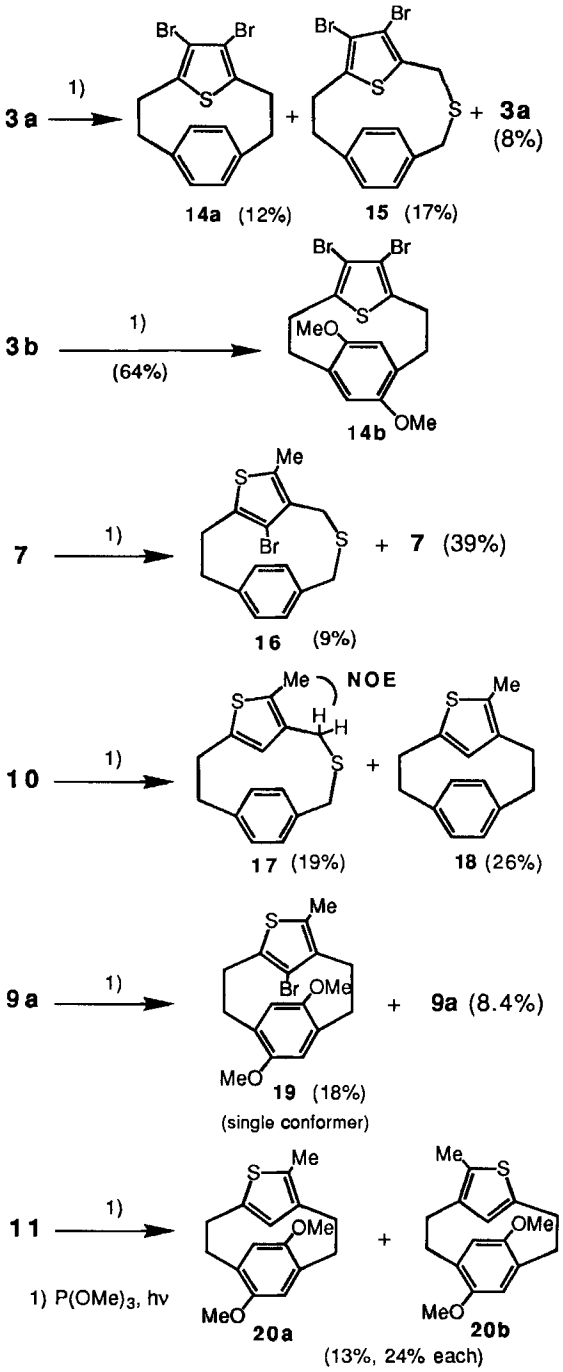


Since attempts to synthesize [2.2]PTP by the pyrolysis of the corresponding disulfones have failed, the photodesulfurization of dithia[3.3]PTPs has been carried out. Photodesulfurization of the dithia[3.3](2,5)PTP **3a** in trimethyl phosphite affords the desired [2.2](2,5)PTP **14a** together with thia[2.3](2,5)PTP **15** and starting material. In contrast, irradiation of the dimethoxy derivative **3b** under the same conditions gives only [2.2](2,5)PTP **14b** (Scheme 4).

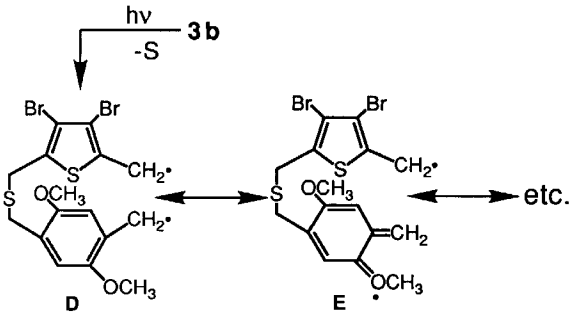
The high reactivity of **3b** results from the stabilization of the diradical intermediate (**D, E**) by the mesomeric effect of the methoxy group as shown in Scheme 5.

The photodesulfurization of **7** gives only thia [2.3]PTP **16**, while that of **10** under the same condition affords thia[2.3]PTP **17** and the desired [2.2](2,4)PTP **18**. The structures of **16** and **17** have been determined by an NOE spectrum of **17**: a remarkable NOE was observed between one of the methylene protons (δ = 3.43) near the sulfur atom and the methyl protons (Scheme 4). It is supposed to have obtained only one of the two possible isomers of the thia[3.2]phane due to the difference between the stability of the 2-thenyl and 3-thenyl radicals. The difference of the reactivity of these dithia[3.3]PTPs may also be due to the steric repulsion between the bromine atom and the benzene ring.

Scheme 4



Scheme 5

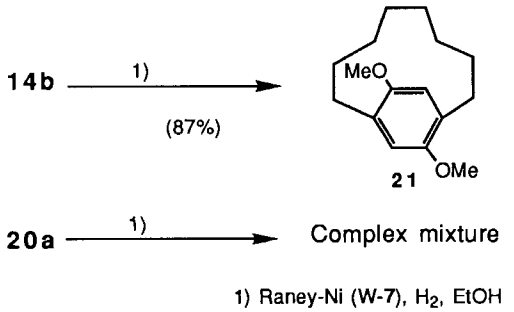


The photodesulfurization of the dimethoxy derivative *syn*-**9a** affords **19** as the single isomer of [2.2]PTP, but in low yield. In contrast, the same reaction of dithia[3.3]PTP **11** gives the two isomeric [2.2]phanes **20a** and **b** (Scheme 4).

C. Reductive Ring Opening Reaction of [2.2]PTPs

The reductive ring opening reaction of [2.2]PTPs is carried out under the same conditions as described in ref.[7]. The reduction of **14b** affords the dimethoxy[8]paracyclophane **21**. On the other hand, that of **20a** furnishes an inseparable mixture (Scheme 6).

Scheme 6



D. Ring Inversion of PTPs

The ^{1}H-NMR spectrum of the benzene protons of **3a** shows a singlet (4 protons) at 27°C. Therefore, a ring inversion of **3a** occurs at this temperature. Similarly, benzene protons of **3b** appear as a singlet (2 H), and also the thiophene ring protons of **3b** flip freely. The signals of the benzene protons of **3a** and **3b** coalesce at −35 and −32°C (270 MHz) as shown in Table 1. Since the estimated activation energy barriers ($\Delta G_c^{\neq}$) calculated from Δν (Hz) and the coalescence temperature (K)[14] are almost the same (11 kcal mol^{-1}), there is no relationship between the energy barrier of the flipping motion and the substituent on the benzene ring in this system.

The ^{1}H-NMR spectrum of the benzene protons of dithia[3.3](2,4)PTP **7** shows four kinds of double doublets (each 1 H) at 27°C. The signals do not coalesce below 120°C. Thus, the activation energy of **7** is above 20 kcal mol^{-1}. The coupling of **4** with **8** affords two conformational isomers of dithia[3.3](2,4)phanes (**9a** and **9b**), which are easily separated by the high energy barrier to flipping motion[15]. The assignments of these compounds are shown in Scheme 1. It is assumed that the signal of one benzene proton of **9a** (*syn*) is shifted to lower field owing to an anisotropy of the sulfur atom of the opposite thiophene ring[1]. The ^{1}H-NMR spectra of **10** and **11** at 27°C exhibit two doublets (each 2 H) and two singlets (each 1 H) for the benzene rings, respectively. These spectra show that obviously a flipping of the thiophene ring of **10** occurs. These signals do not broaden above −90°C. Figure 1 shows the ring flipping system of dithia[3.3](2,4)PTP. Ring flipping only occurs in **10** with a small substituent but not in **7** with a bulky group. The difference of the energy barriers between dithia[3.3](2,5)- and -(2,4)PTP is assumed to be caused by the bulkiness of the sulfur atoms of dithia[3.3](2,5)PTPs.

Table 1. Energy barrier of flipping of PTPs

PTPs	T_c (°C)	Δν (Hz)	$\Delta G_c^{\neq}$ (kcal mol^{-1})
3a[a]	-35	189	11
3b[a]	-32	188	11
10[a]	< -90	-	-
15[b]	> 120	36	>20
17[c]	0	152	13

[a] In [D_6]acetone. — [b] In [D_5]nitrobenzene. — [c] In $CDCl_3$.

The dynamic ^{1}H-NMR spectrum of thia[2.3](2,4)PTP **17** shows the coalescence of its benzene protons at 0°C, and the estimated energy barrier is 13 kcal mol^{-1}. In contrast, the signals of the benzene protons of thia[2.3](2,5)PTP **15** do not coalesce below 120°C, and the energy barrier of flipping of **15** is above 20 kcal mol^{-1}, which is higher than that of **17**. This fact resembles that of dithia[3.3]PTP.

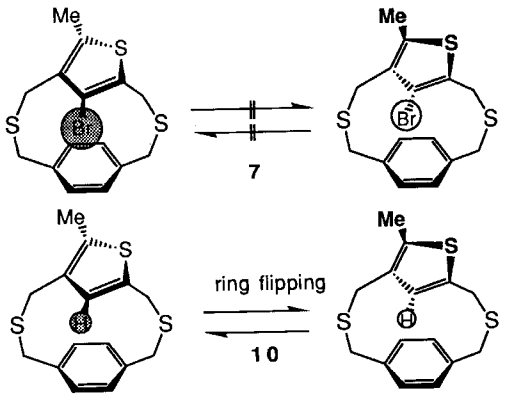


Figure 1. Ring flipping of dithia[3.3](2,4)PTPs

The ^{1}H-NMR spectra of [2.2]PTPs show no ring flipping at 27°C within the NMR time scale. [2.2](2,4)PTPs **20a** and **20b** are separated because of their conformational rigidity[15]. Nevertheless, the structure of these conformations is still unclear.

Although the conformation of [2.2](2,5)thiophenophane **13** is still obscure, **13** is supposed to be the *anti*-conformer due to steric repulsion between Br atoms.

E. UV Spectra of Dithia[3.3]-, Thia[2.3]-, and [2.2]PTPs

The UV spectra of (2,5)PTPs in cyclohexane are shown in Figure 2. A band of [3.3]PTP **3a** at 246 nm (log ε_{max} = 3.87) indicates a bathochromic shift as the strain increases and the distance between the two aromatic rings decreases as well as a band at 210 nm that is shifted to 228 nm in the spectrum of **14a**. These bathochromic shifts are ascribed to the transannular interaction between the thiophene ring and the benzene ring and the increase of the strain of these systems[16]. In contrast, in the case of the (2,4)PTP system,

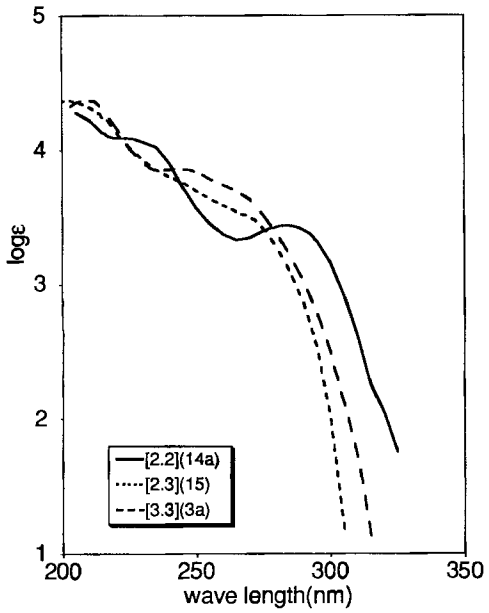


Figure 2. UV spectra of (2,5)PTPs **3a**, **14a**, and **15** (cyclohexane)

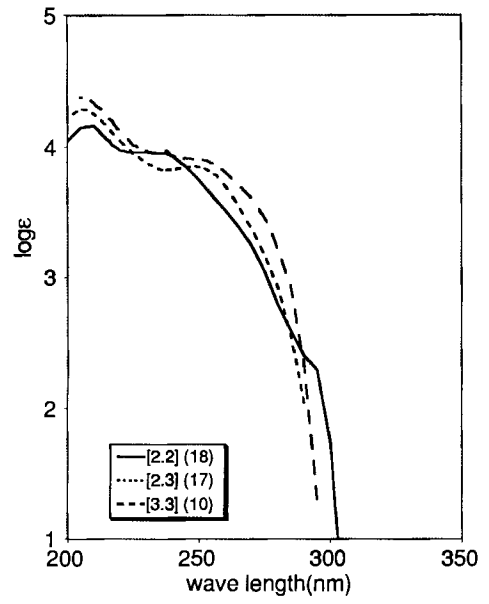


Figure 3. UV spectra of (2,4)PTPs **10**, **17**, and **18** (cyclohexane)

such phenomena have not been observed (Figure 3). The difference in the of UV behavior between (2,5)PTP and (2,4)PTP is supposed to be concerned with their modes of stacking.

Experimental

Melting points: uncorrected. – IR (KBr or NaCl): Jasco IR-700. – ^{1}H NMR: Jeol GSX-270, 270 MHz, in $CDCl_3$, TMS as reference. – UV: Hitachi 220A spectrophotometer. – MS: Jeol JMS-01-SG-2, EI (75 eV). – Elemental analyses: Yanaco MT-5.

Representative Synthesis of Dithia[3.3]phanes: To a refluxing solution of 2.2 g (40 mmol, 4 eq.) of potassium hydroxide and 190 mg of $NaBH_4$ (5 mmol, 0.5 eq.) in 3 l of ethanol was added dropwise a solution of 1.8 g of 1,4-bis(chloromethyl)benzene (**1**) (10 mmol) and 3.3 g of 3,4-dibromo-2,5-bis(mercaptomethyl)thiophene (**2**)[1] (10 mmol) in 100 ml of ethanol/benzene (1:1) for 24 h. The solvent was distilled off and the residue poured into icecold water. The mixture was extracted with dichloromethane and the extract washed with brine. The solution was dried with magnesium sulfate, and the solvent was evaporated in vacuo. The residue was subjected to column chromatography (silica gel, hexane/chloroform 2:1). From the eluate the solvents were removed by evaporation, and the residue was crystallized from methanol to afford 2.6 g of **3a** (6.0 mmol, 60%).

14,15-Dibromo-2,11-dithia[3]paracyclo[3](2,5)thiophenophane (**3a**): Colorless plates (methanol), m.p. 198.0–202.0°C. – IR (KBr): $\tilde{\nu}$ = [cm^{-1}] = 1508, 1407, 1299, 1202, 1135, 1096, 913, 858, 819, 750, 701, 669, 546. – ^{1}H NMR ($CDCl_3$): δ = 3.80 (4H, s), 3.96 (4H, s), 6.90 (4H, s). – MS (75 eV): *m/z* (%) = 434 (40) [M^+], 355 (18), 168 (28), 105 (100). – UV (cyclohexane): λ_{max} [nm] (logε) = 246 (3.87).

$C_{14}H_{12}Br_2S_3$ (436.3)
Calcd. C 38.54 H 2.77
Found C 38.91 H 3.02

14,15-Dibromo-6,9-dimethoxy-2,11-dithia[3]paracyclo[3](2,5)-thiophenophane (**3b**): A solution of 4.6 g of **4**[11] (20 mmol) and 6.8 g of **5**[18] (20 mmol) in 200 ml of ethanol/benzene (1:1) was added dropwise to a refluxing solution of 4.5 g of 80% potassium hydroxide (80 mmol) and 380 mg of sodium hydroxide (10 mmol) in ethanol (4 l) for 48 h. After workup, the residue was subjected to column chromatography (silica gel, hexane/chloroform 2:1). From the eluate the solvents were removed by evaporation, and the residue was crystallized from ethanol/hexane (3:1) to afford 5.0 g (51%) of **3b**; colorless needles (ethanol/benzene 3:1), m.p. 172.0–173.0°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2932, 1507, 1465, 1402, 1300, 1213, 1047, 917, 858, 686. – ^{1}H NMR ($CDCl_3$): δ = 3.43 (2H, d, *J* = 14 Hz), 3.73 (6H, s), 3.91 (2H, d, *J* = 14 Hz), 4.03 (2H, d, *J* = 14 Hz), 4.27 (2H, d, *J* = 14 Hz), 6.52 (2H, s). – MS (75 eV): *m/z* (%) = 494 (46) [M^+], 165 (100).

$C_{16}H_{16}Br_2O_2S_3$ (496.3)
Calcd. C 38.72 H 3.25
Found C 38.50 H 3.30

14-Bromo-16-methyl-2,11-dithia[3]paracyclo[3](2,4)thiophenophane (**7**): A solution of 1.8 g of **1** (10 mmol) and 2.7 g of **6**[1] (10 mmol) in 100 ml of ethanol/benzene (1:1) was added dropwise to a refluxing solution of 2.2 g of 80% potassium hydroxide (40 mmol) and 190 mg of sodium hydroxide (5 mmol) in ethanol (4 l) for 24 h. After workup, the residue was subjected to column chromatography (silica gel, hexane/dichloromethane 2:1). From the eluate the solvents were removed by evaporation, and the residue was crystallized from ethanol/benzene (1:1) to afford 2.0 g (54%) of **7**, colorless

prisms (ethanol/benzene 1:1), m.p. 153.0–155.0°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2900, 1544, 1510, 1429, 1192, 912, 813, 730, 684, 552. – ^{1}H NMR ($CDCl_3$): δ = 2.41 (3H, s), 3.46 (1H, dd, *J* = 1/16 Hz), 3.55 (1H, d, *J* = 15 Hz), 3.61 (1H, d, *J* = 16 Hz), 3.65 (1H, d, *J* = 15 Hz), 3.74 (1H, d, *J* = 15 Hz), 3.83 (1H, d, *J* = 15 Hz), 3.88 (2H, d, *J* = 16 Hz), 6.84 (1H, dd, *J* = 2/8 Hz), 6.97 (1H, dd, *J* = 2/8 Hz), 7.02 (1H, dd, *J* = 2/8 Hz), 7.13 (1H, dd, *J* = 2/8 Hz). – MS (75 eV): *m/z* (%) = 370 (89) [M^+], 203 (14).

$C_{15}H_{15}BrS_3$ (371.4)
Calcd. C 48.51 H 4.07
Found C 48.86 H 4.29

syn- (**9a**) *and anti-14-Bromo-5,8-dimethoxy-16-methyl-2,11-dithia[3]paracyclo[3](2,4)thiophenophane* (**9b**): A solution of 3.5 g of **4** (15 mmol) and 3.9 g of **8**[1] (15 mmol) in 100 ml of ethanol/benzene (1:1) was added dropwise to a refluxing solution of 3.4 g of 80% potassium hydroxide (60 mmol) and 380 mg of sodium hydroxide (8 mmol) in ethanol (4 l) for 30 h. After workup, the residue was subjected to column chromatography (silica gel, hexane/chloroform 2:1). After evaporation of the solvents crystallization of the residue of the first eluate from ethanol/benzene (1:1) and of the residue of the second eluate from ethanol/benzene (1:1) afforded 1.74 g (28%) of **9a** and 1.0 g (16%) of **9b**.

9a: Colorless prisms (ethanol/benzene 1:1), m.p. 184.0–185.5°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2942, 1510, 1466, 1401, 1319, 1229, 1208, 1047, 903, 853. – ^{1}H NMR ($CDCl_3$): δ = 2.39 (3H, s), 3.37 (1H, d, *J* = 14 Hz), 3.39 (1H, d, *J* = 16 Hz), 3.45 (1H, d, *J* = 15 Hz), 3.47 (1H, d, *J* = 15 Hz), 3.69 (3H, s), 3.79 (1H, d, *J* = 16 Hz), 3.84 (3H, s), 3.90 (1H, d, *J* = 15 Hz), 3.95 (1H, d, *J* = 15 Hz), 4.69 (1H, d, *J* = 14 Hz), 6.50 (1H, s), 6.94 (1H, s). – MS (75 eV): *m/z* (%) = 430 (90) [M^+], 165 (91).

$C_{17}H_{19}BrO_2S_3$ (431.4)
Calcd. C 47.33 H 4.44
Found C 47.36 H 4.42

9b: Colorless prisms (ethanol/benzene 1:1), m.p. 196.5–198.0°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2902, 1507, 1462, 1401, 1319, 1212, 1049, 915, 866, 689. – ^{1}H NMR ($CDCl_3$): δ = 2.46 (3H, s), 3.40 (1H, d, *J* = 16 Hz), 3.43 (2H, d, *J* = 15 Hz), 3.65 (1H, d, *J* = 15 Hz), 3.67 (3H, s), 3.77 (1H, d, *J* = 12 Hz), 3.79 (3H, s), 3.81 (1H, d, *J* = 15 Hz), 3.99 (1H, d, *J* = 12 Hz), 4.53 (1H, d, *J* = 15 Hz), 6.47 (1H, s), 6.53 (1H, s). – MS (75 eV): *m/z* (%) = 430 (95) [M^+], 165 (92).

$C_{17}H_{19}BrO_2S_3$ (431.4)
Calcd. C 47.33 H 4.44
Found C 47.72 H 4.45

Reduction of **7**: To a solution of 1.1 g of **7** (3.0 mmol) in 20 ml of dry THF under nitrogen at –70°C was added dropwise a solution of 2.5 ml of 1.6 M *n*-butyllithium in hexane (4.0 mmol). The mixture was stirred for 30 min. Then 2.0 ml of 10% hydrochloric acid (5.5 mmol) was added to the mixture and the temp. raised to room temp. The mixture was extracted with diethyl ether and the organic layer washed with brine and dried with magnesium sulfate. The solvent was evaporated in vacuo and the residue subjected to column chromatography (silica gel, hexane/chloroform 5:1). From the eluate the solvents were removed by evaporation, and the residue was crystallized from methanol to afford 380 mg (43%) of **10** (1.3 mmol).

16-Methyl-2,11-dithia[3]paracyclo[3](2,4)thiophenophane (**10**): Colorless plates (methanol), m.p. 103.0–106.0°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2898, 1510, 1432, 1222, 1199, 1142, 1118, 851, 721, 550. – ^{1}H NMR ($CDCl_3$): δ = 2.29 (3H, s), 3.49 (2H, s), 3.58 (2H, s), 3.82 (2H, s), 3.88 (2H, s), 5.26 (1H, s), 6.96 (2H, d, *J* = 8 Hz), 7.01 (2H, d, *J* = 8 Hz). – MS (75 eV): *m/z* (%) = 292 (84) [M^+], 125 (100). – UV (cyclohexane): λ_{max} [nm] (log ε) = 254 sh (3.90).

$C_{15}H_{16}S_3$ (292.5)
Calcd. C 61.60 H 5.51
Found C 61.59 H 6.00

5,8-Dimethoxy-16-methyl-2,11-dithia[3]paracyclo[3](2,4)thiophenophane (**11**): To a solution of 430 mg of **9a** (1.0 mmol) in 20 ml of dry THF was added 0.80 ml of 1.6 M *n*BuLi/hexane (1.3 mmol) at –70°C, and the mixture was stirred for 30 min. Then 1.0 ml of 10% HCl (2.7 mmol) was added. After workup, the residue was subjected to column chromatography (silica gel, hexane/dichloromethane). From the eluate the solvents were removed by evaporation, and the residue was crystallized from methanol to afford 290 mg (82%) of **11** (0.82 mmol); colorless prisms (hexane), m.p. 96.0–98.0°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2930, 1510, 1466, 1407, 1319, 1211, 1045, 858. – ^{1}H NMR ($CDCl_3$): δ = 2.28 (3H, s), 3.45 (1H, d, *J* = 16 Hz), 3.45 (1H, d, *J* = 14 Hz), 3.53 (1H, d, *J* = 13 Hz), 3.55 (1H, d, *J* = 15 Hz), 3.56 (1H, d, *J* = 15 Hz), 3.62 (1H, d, *J* = 16 Hz), 3.71 (3H, s), 3.75 (3H, s), 4.21 (1H, d, *J* = 14 Hz), 4.33 (1H, d, *J* = 13 Hz), 5.51 (1H, s), 6.53 (1H, s), 6.63 (1H, s). – MS (75 eV): *m/z* (%) = 352 (100) [M^+], 165 (49).

$C_{17}H_{20}O_2S_3$ (352.5)
Calcd. C 57.92 H 5.72
Found C 58.00 H 5.66

Oxidation of Dithia[3.3]phanes: To a solution of 1.98 g of **3b** (4.0 mmol) in 100 ml of dichloromethane was gradually added 4.3 g of 80% *m*-chloroperoxybenzoic acid (20.0 mmol). The reaction mixture was stirred at room temp. for 12 h and then poured into 100 ml of methanol. The white precipitate was filtered and washed with hot chloroform to afford quantitatively 2.24 g of **12**.

14,15-Dibromo-6,9-dimethoxy-2,11-dithia[3]paracyclo[3](2,5)-thiophenophane S,S,S',S'-Tetraoxide (**12**): Colorless prisms, m.p. 320.0°C (dec.). – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2938, 1514, 1401, 1312, 1270, 1222, 1169, 1152, 1113, 1040, 886, 509, 430. – A ^{1}H-NMR spectrum was not recorded because **12** is insoluble in any solvent. – MS (75 eV): *m/z* (%) = 558 (6) [M^+], 430 (9), 164 (100).

$C_{16}H_{16}Br_2O_6S_3$ (560.3)
Calcd. C 34.30 H 2.88
Found C 34.27 H 2.96

Pyrolysis of **12** (2.24 g, 4.0 mmol) was carried out in a similar manner as described in ref.[1]. The products were extracted with dichloromethane and ash was filtered off. The solvent was evaporated and the residue subjected to column chromatography (silica gel, hexane/chloroform 3:1). From the eluate the solvents were removed by evaporation, and the residue was crystallized from ethanol/benzene (1:1) to afford 53 mg (5%) of **13** (0.099 mmol).

4,5,11,12-Tetrabromo[2.2](2,5)thiophenophane (**13**): Colorless prisms (from ethanol/benzene 1:1), m.p. 240.0–243.0°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2920, 1285, 1204, 1179, 1015, 834, 814. – ^{1}H NMR ($CDCl_3$): δ = 2.99–3.11 (4H, m), 3.19–3.32 (4H, m). – MS (75 eV): *m/z* (%) = 533 (12) [M^+ + 1], 266 (49).

$C_{12}H_8Br_4S_2$ (535.9)
Calcd. C 26.89 H 1.50
Found C 27.29 H 1.70

Photodesulfurization of **3a**: A solution of 1.31 g of **3a** (3.0 mmol) in 200 ml of trimethyl phosphite was irradiated with a 100-W high-pressure mercury lamp at room temp. for 33 h under bubbling nitrogen. The solvent was distilled under reduced pressure, and 100 ml of water was added to the residue. The mixture was extracted with chloroform (3 × 50 ml), and the combined extracts

were washed with brine and dried with magnesium sulfate. The solvents were evaporated, and the residue was subjected to column chromatography (silica gel, hexane). After evaporation of the solvents, crystallization of the residue of first eluate from 80% methanol, of that of the second eluate from ethanol, and of that of the third eluate from ethanol afforded 130 mg (12%) of **14a** (0.35 mmol), 200 mg (17%) of **15** (0.50 mmol), and 100 mg (8%) of starting material, respectively.

12,13-Dibromo[2]paracyclo[2](2,5)thiophenophane (**14a**): Colorless prisms (80% methanol), m.p. 135.0–136.0°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2922, 1503, 1443, 1406, 1289, 1210, 1111, 994, 866, 795, 718, 642, 562, 516. – ^{1}H NMR ($CDCl_3$): δ = 2.69 (2H, ddd, *J* = 9/12/19 Hz), 3.11–3.32 (6H, m), 6.67–6.68 (2H, m), 7.10–7.11 (2H, m). – MS (75 eV): *m/z* (%) = 370 (6) [M^+], 266 (3), 104 (100). – UV (cyclohexane): λ_{max} [nm] (log ε) = 228 (4.08), 284 (3.44).

$C_{14}H_{12}Br_2S$ (372.1)
Calcd. C 45.19 H 3.25
Found C 45.07 H 3.58

13,14-Dibromo-10-thia[2]paracyclo[3](2,5)thiophenophane (**15**): Colorless prisms (ethanol), m.p. 136.0–136.5°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2922, 1505, 1420, 1298, 1209, 1147, 993, 880, 847, 830, 810, 643, 544, 485. – ^{1}H NMR ($CDCl_3$): δ = 2.69 (1H, ddd, *J* = 8/10/14 Hz), 2.90–3.11 (2H, m), 3.32 (1H, ddd, *J* = 1/8/14 Hz), 3.76 (1H, d, *J* = 17 Hz), 3.84 (1H, d, *J* = 14 Hz), 3.91 (1H, d, *J* = 14 Hz), 4.14 (1H, d, *J* = 17 Hz), 6.13 (1H, dd, *J* = 2/8 Hz), 6.55 (1H, dd, *J* = 2/8 Hz), 7.10 (1H, dd, *J* = 2/8 Hz), 7.23 (1H, dd, *J* = 2/8 Hz). – MS (75 eV): *m/z* (%) = 402 (24) [M^+], 136 (100). – UV (cyclohexane): λ_{max} [nm] (log ε) = 270 sh (3.50).

$C_{14}H_{12}Br_2S_2$ (404.2)
Calcd. C 41.60 H 2.99
Found C 41.47 H 3.24

12,13-Dibromo-4,7-dimethoxy[2]paracyclo[2](2,5)thiophenophane (**14b**): A solution of 3.5 g of **3b** (7.0 mmol) in 200 ml of trimethyl phosphite was irradiated with a 100-W high-pressure mercury lamp at room temp. for 38 h under bubbling nitrogen. After workup, the residue was subjected to column chromatography (silica gel, hexane/dichloromethane 1:1). From the eluate the solvents were removed by evaporation, and the residue was recrystallized from methanol to afford 1.94 g (64%) of **14b**; colorless prisms (methanol), m.p. 116.0–118.5°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2988, 2926, 2824, 1498, 1461, 1396, 1292, 1211, 1105, 1043, 1000, 875, 853, 746, 628. – ^{1}H NMR ($CDCl_3$): δ = 2.71–2.93 (4H, m), 3.12–3.20 (1H, m), 3.30–3.47 (2H, m), 3.62 (3H, s), 3.71–3.79 (1H, m), 3.82 (3H, s), 6.01 (1H, s), 6.50 (1H, s). – MS (75 eV): *m/z* (%) = 430 (12) [M^+], 164 (100).

$C_{16}H_{16}Br_2O_2S$ (432.2)
Calcd. C 44.47 H 3.73
Found C 44.65 H 3.77

16-Bromo-13-methyl-10-thia[2]paracyclo[3](2,4)thiophenophane (**16**): A solution of 0.74 g of **7** in 150 ml of trimethyl phosphite was irradiated with a 100-W high-pressure mercury lamp at room temp. for 20 h under bubbling nitrogen. After workup, the residue was subjected to column chromatography (silica gel, hexane/dichloromethane 5:1). After evaporation of the solvents, crystallization of the residue of the first eluate from methanol and of that of the second eluate from ethanol/benzene (1:1) afforded 50 mg of **16a** (9%) and 290 mg of **7** (39%); **16**: Colorless prisms (methanol), m.p. 114.0–118.0°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2918, 1427, 1175, 923, 876, 839, 813, 744, 689, 603, 537, 501. – ^{1}H NMR ($CDCl_3$): δ = 2.39 (3H, s), 2.44–2.55 (1H, m), 2.73–2.81 (1H, m), 2.97–3.18 (2H, m), 3.41 (1H, d, *J* = 16 Hz), 3.66 (1H, d, *J* = 16 Hz), 3.76 (1H, d, *J* = 14 Hz), 3.84 (1H, d, *J* = 14 Hz), 6.66 (1H, dd, *J* = 2/8 Hz), 6.90 (1H, dd, *J* = 2/8 Hz), 7.05 (1H, dd, *J* = 2/8 Hz), 7.14 (1H, dd, *J* = 2/8 Hz). – MS (75 eV): *m/z* (%) = 338 (93) [M^+], 155 (71), 104 (51).

$C_{15}H_{15}BrS_2$ (339.3)
Calcd. C 53.10 H 4.46
Found C 53.28 H 4.63

13-Methyl-10-thia[2]paracyclo[3](2,4)thiophenophane (**17**) *and 12-Methyl[2]paracyclo[2](2,4)thiophenophane* (**18**): A solution of 0.29 g of **10** (1.0 mmol) in 50 ml of trimethyl phosphite was irradiated with a 100-W high-pressure mercury lamp at room temp. for 68 h under bubbling nitrogen. After workup, the residue was subjected to column chromatography (silica gel, hexane/dichloromethane 4:1). After evaporation of the solvents, the evaporation of the first eluate, crystallization of the residue of the second eluate from 80% methanol and of that of the third eluate afforded 60 mg of **18** (26%), 50 mg of **17** (19%), and 84 mg of **10** (29%); **17**: Colorless prisms (80% methanol), m.p. 72.0–76.0°C. – IR (KBr): [cm^{-1}] = 2926, 1647, 1505, 1409, 1245, 1159, 1088, 909, 850, 801, 599, 492, 456. – ^{1}H NMR ($CDCl_3$): δ = 2.26 (3H, s), 2.70 (2H, br. s), 2.80 (2H, br. s), 3.43 (2H, br. s), 3.80 (2H, br. s), 5.06 (1H, s), 6.64 (2H, br. s), 7.00 (2H, br. s). – MS (75 eV): *m/z* (%) = 260 (100) [M^+], 125 (90). – UV (cyclohexane): λ_{max} [nm] (log ε) = 249 sh (3.85).

$C_{15}H_{16}S_2$ (260.4)
Calcd. C 69.18 H 6.19
Found C 69.06 H 6.18

18: Colorless oil. – IR (NaCl): $\tilde{\nu}$ (cm^{-1}) = 2924, 2852, 1433, 1230, 1081, 897, 801, 728. – ^{1}H NMR ($CDCl_3$): δ = 2.25 (3H, s), 2.27–2.40 (1H, m), 2.49–2.78 (5H, m), 3.01–3.10 (2H, m), 4.82 (1H, s), 6.16 (1H, dd, *J* = 2/8 Hz), 6.36 (1H, dd, *J* = 2/8 Hz), 7.02 (1H, dd, *J* = 2/8 Hz), 7.12 (1H, dd, *J* = 2/8 Hz). – MS (75 eV): *m/z* (%) = 228.0970 (49) [M^+], (calcd. 228.0972 for $C_{15}H_{16}S$), 124 (100). – UV (cyclohexane): λ_{max} [nm] (log ε) = 235 sh (3.96).

14-Bromo-4,7-dimethoxy-12-methyl[2]paracyclo[2](2,4)thiophenophane (**19**): A solution of 220 mg of **9a** (0.50 mmol) in 50 ml of trimethyl phosphite was irradiated with a 100-W high-pressure mercury lamp at room temp. for 5 h under bubbling nitrogen. After workup, the residue was subjected to column chromatography (silica gel, hexane/dichloromethane 2:1). After evaporation of the solvents, crystallization of the residue of the first eluate from methanol and of that of the second eluate from ethanol/benzene (1:1) afforded 33 mg of **19** (18%) and 18 mg of **9a** (8.4%). – **19**: Colorless prisms (methanol), m.p. 130.5–132.5°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2922, 1497, 1463, 1396, 1315, 1208, 1175, 1046, 861, 796. – ^{1}H NMR ($CDCl_3$): δ = 2.34 (3H, s), 2.29–2.39 (1H, m), 2.57–2.86 (4H, m), 3.20–3.44 (3H, m), 3.58 (3H, s), 3.83 (3H, s), 5.95 (1H, s), 6.60 (1H, s). – MS (75 eV): *m/z* (%) = 366 (94) [M^+], 202 (83), 123 (54).

$C_{17}H_{19}BrO_2S + 1/5\,H_2O$ (370.9)
Calcd. C 55.05 H 5.27
Found C 54.96 H 5.14

anti- (**20a**) *and syn-4,7-Dimethoxy-12-methyl[2]paracyclo[2](2,4)thiophenophane* (**20b**): A solution of 350 mg of **11** (1.0 mmol) in 50 ml of trimethyl phosphite was irradiated with a 100-W high-pressure mercury lamp at room temp. for 4 h under bubbling nitrogen. After workup, the residue was subjected to column chromatography (silica gel, hexane/dichloromethane 5:3). After evaporation of the solvents, crystallization of the residue of the first eluate from methanol and of that of the second eluate from methanol afforded 68 mg of **20a** (24%) and 38 mg of **20b** (13%).

20a: Colorless prisms (methanol), m.p. 103.0–104.0°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2920, 1498, 1453, 1397, 1300, 1206, 1046, 882, 829. – ^{1}H NMR ($CDCl_3$): δ = 2.23 (3H, s), 2.27–2.47 (2H, m),

2.60–2.90 (4H, m), 3.27–3.52 (2H, m), 3.54 (3H, s), 3.85 (3H, s), 5.14 (1H, s), 5.85 (1H, s), 6.61 (1H, s). – MS (75 eV): *m/z* (%) = 288 (73) [M^+], 165 (47), 124 (100).

$C_{17}H_{20}O_2S$ (288.4)
Calcd. C 70.80 H 6.99
Found C 70.61 H 6.89

20b: Colorless prisms (methanol), m.p. 60.0–66.0°C. – IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2930, 1496, 1464, 1396, 1208, 1046, 515. – ^{1}H NMR ($CDCl_3$): δ = 2.21–2.39 (2H, m), 2.29 (3H, s), 2.59–2.78 (4H, m), 3.25–3.54 (2H, m), 3.51 (3H, s), 3.86 (3H, s), 5.10 (1H, s), 5.65 (1H, s), 6.50 (1H, s). – MS (75 eV): *m/z* (%) = 288 (100) [M^+], 165 (30), 124 (22).

$C_{17}H_{20}O_2S$ (288.4)
Calcd. C 70.80 H 6.99
Found C 70.46 H 6.97

Reductive Ring Opening Reactions of **14b**: A mixture of 860 mg of **14b** (2.0 mmol) and 20 ml of a Raney-Ni (W-7) ethanolic suspension[13] (ca. 26 mmol) was refluxed under hydrogen for 4 h. The reaction mixture was cooled to room temp. and the precipitate filtered off on Celite. After evaporation of the solvent, hexane was added to the residue and the precipitate filtered off. The filtrate was concentrated in vacuo and the residue subjected to column chromatography (silica gel, hexane/chloroform 2:1). From the eluate the solvents were evaporated, and the residue was recrystallized from methanol to afford 460 mg of **21** in 87% yield.

10,13-Dimethoxy[8]paracyclophane (**21**): Colorless prisms (methanol), m.p. 31.0–37.0°C. – IR (NaCl): $\tilde{\nu}$ [cm^{-1}] = 2926, 2854, 1724, 1504, 1465, 1402, 1208, 1047, 871. – ^{1}H NMR ($CDCl_3$): δ = –0.09 to 0.01 (2H, m), 0.58–0.81 (4H, m), 1.14–1.27 (2H, m), 1.48–1.58 (4H, m), 2.14–2.22 (2H, m), 3.18 (2H, dt, *J* = 5/18 Hz), 3.82 (6H, s), 6.62 (2H, s). – MS (75 eV): *m/z* (%) = 248.1774 (100) [M^+] (calcd. 248.1775 for $C_{16}H_{24}O_2$), 164 (57).

$C_{16}H_{24}O_2$ (248.4)
Calcd. C 77.37 H 9.74
Found C 76.82 H 9.75

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