HRMS calcd for $C_{11}H_{14}O$ (M - OH) 162.1045, found 162.1045.

6-Hydroxy-3,3-dimethyl-1,7-octadien-4-one (30) was prepared on a 5-mmolar scale according to the General Procedure for directed aldol condensations (vide supra) from 3,3-dimethyl-4-penten-2-one[15] and acrolein. The crude product was filtered over SiO_2 with EtOAc/hexanes, 1:3, and bulb-to-bulb distilled to obtained 0.56 g (67%) of **30** as a colorless liquid: oven temperature 50–55 °C (0.75 Torr); ^1H NMR δ 5.89 (m, 1 H, 2-H), 5.84 (m, 1 H, 7-H), 5.28, 5.18, 5.17, 5.12 (each m, 1 H, 1,8-H), 4.52 (m, 1 H, 6-H), 3.18 (d, J = 3.5 Hz, 1 H, OH), 2.72, 2.67 (AB q, J = 18 Hz, both parts split into d with J = 4 and 8 Hz, 2 H, 5-H), 1.24 (s, 6 H, CH_3); ^{13}C NMR δ 213.5 (s), 141.8 (d, J = 156 Hz), 139.1 (d, J = 154 Hz), 114.9 (t), 114.8 (t), 68.6 (d, J = 146 Hz), 50.9 (s), 43.8 (t, J = 126 Hz), 23.2 (q, J = 128 Hz); IR ν 3447, 1707, 1636, 1073, 994, 922 cm^{-1}; MS m/z (%) 169 (0.5, M + H), 150 (0.5), 99 (10), 81 (100), 43 (100); HRMS calcd for $C_{10}H_{14}O$ (M - H_2O) 150.1045, found 150.1044.

3,3-Dimethyl-1,5,7-octatrien-4-one (31) was prepared from **30** on a 2.9-mmolar scale in 25% yield by method B (vide supra) or on a 2.3-mmolar scale in 71% yield by method C as a yellow liquid: oven temperature 65 °C (10 Torr); ^1H NMR δ 7.24 (dd, J = 11, 14.5 Hz, 1 H, 6-H), 6.50 (d, J = 15 Hz, 1 H, 5-H), 6.45 (m, 1 H, 7-H), 5.92 (m, 1 H, 2-H), 5.65 (m, 1 H, 8c-H), 5.52 (m, 1 H, 8t-H), 5.18 (m, 2 H, 1-H), 1.25 (s, 6 H, CH_3); IR ν 1686, 1619, 1590, 1266, 1076, 1011, 920 cm^{-1}; MS m/z (%) 150 (2.5), 135 (1), 81 (100), 69 (19), 53 (36); HRMS calcd for $C_{10}H_{14}O$ 150.1045, found 150.1045.

3,3-Dimethyl-1,5,7-octatrien-4-ol (32) was prepared from **31** by the General Procedure for $LiAlH_4$ reductions (vide supra) on a 0.3-mmolar scale in 97% yield: oven temperature 80–85 °C (9 Torr); ^1H NMR δ 6.35 (m, 1 H, 7-H), 6.24 (dd, J = 10.5, 15 Hz, 1 H, 6-H), 5.86 (m, 1 H, 2-H), 5.73 (dd, J = 7, 15 Hz, 1 H, 5-H), 5.22 (m, 1 H, 8c-H), 5.13 (m, 1 H, 1t-H), 5.10 (m, 1 H, 8t-H), 5.08 (m, 1 H, 1c-H), 3.85 (br d, J = 6.5 Hz, 1 H, 4-H), 1.64 (br s, 1 H, OH), 1.03, 1.01 (each s, 3 H, CH_3); ^{13}C NMR δ 144.6 (d, J = 151 Hz), 136.2 (d, J = 151 Hz), 132.9 (d, J = 152 Hz), 132.4 (d, J = 153 Hz), 116.8 (t, J = 157 Hz), 112.9 (t, J = 156 Hz), 78.5 (d, J = 144 Hz), 41.3 (s), 23.2 (q, J = 126 Hz), 16.9 (q, J = 126 Hz); IR ν 3409, 1640, 1603, 1096, 1005, 911 cm^{-1}; MS m/z (%) 151 (0.5, M - H), 135 (1), 83 (27), 69 (64), 59 (75), 45 (100); HRMS calcd for $C_{10}H_{15}$ (M - OH) 135.1174, found 135.1174.

Thermal rearrangement of 32 was conducted on a 0.16-mmolar scale at 195 °C for 16.5 h as described in the General Procedure for intramolecular Diels–Alder reactions (vide supra). Chromatography on SiO_2 with EtOAc/hexanes, 1:12, yielded 2.0 mg (8%) of a product, followed by 5.5 mg (22%) of starting material. The product was assumed to be **6-methyl-3-vinyl-5-heptenal (33)** on the basis of the following ^1H NMR spectrum: δ 9.71 (t, J = 2.5 Hz, 1 H, CHO), 5.74 (m, 1 H, vinyl-CH_2), 5.09 (br t, overlapping, 1 H, 5-H), 5.04 (m, 1 H, cis-H of vinyl-CH_2), 5.03 (m, 1 H, trans-H of vinyl-CH_2), 2.67 (br quint, J = 7 Hz, 1 H, 3-H), 2.47, 2.38 (AB q, J = 14.5 Hz, both parts split into dd with J = 2, 5.5 Hz and 2.5, 8 Hz, 2 H, 2-H), 2.10 (t, J = 7 Hz, 2 H, 4-H), 1.70, 1.59 (each s, 3 H, CH_3).

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Supplementary Material Available: Selected ^1H and ^{13}C NMR spectra and an X-ray structure analysis of **27** (90 pages). Ordering information is given on any current masthead page.

Synthesis and Conformation of Dithia[3]metacyclo[3]thiophenophanes and [2]Metacyclo[2]thiophenophanes

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Dithia[3]metacyclo[3]- -(2,3)-, -(2,4)-, -(2,5)-, and -(3,4)thiophenophanes were prepared by dithiol bis-alkylations and were oxidized with *m*-chloroperbenzoic acid to the corresponding tetraoxides. Pyrolysis of the tetraoxides under a reduced pressure gave the corresponding [2]metacyclo[2]thiophenophanes together with many unexpected compounds. The conformations of the obtained products are also discussed.

Although many heterophanes and some metacyclo- and paracycloheterophanes such as metacyclopyridinophanes[1] have been prepared and their physical properties investigated,[2] there are only a few reports[3] about [*n*]metacyclo[*n*]heterophanes which contain 5-membered aromatic rings. Since [2]metacyclo[2]thiophenophanes ([2.2]phanes) have not yet been reported, the properties and the reactions of these compounds are still unknown. It has been previously reported that[4] [2.2]metacyclophanes could be easily prepared and that these compounds show novel reactivities and chemical structures.

There are four possible isomers of [2.2]phanes: (2,3)-phane, (2,4)phane, (2,5)phane, and (3,4)phane as shown in Figure 1.

Although these phanes could be important synthetic intermediates for the preparation of the corresponding [*n*]metacyclophanes by the reductive thiophene ring-opening reaction and are interesting compounds in the field of organic physical chemistry, their preparation and

(1) (a) Vögtle, F. *Tetrahedron Lett* **1968**, 3623. (b) Vögtle, F.; Effler, A. H. *Chem. Ber.* **1969**, *102*, 3071. (c) Fletcher, J. R.; Sutherland, I. O. *J. Chem. Soc., Chem. Commun.* **1969**, 1504. (d) Boekelheide, V.; Pepperdine, W. *J. Am. Chem. Soc.* **1970**, *92*, 3684. (e) Vögtle, F.; Neumann, P. *Tetrahedron* **1970**, *26*, 5299. (f) Bruhin, J.; Kneubühler, W., Jenny, W. *Chimia* **1973**, *27*, 277. (g) Higuchi, H.; Tani, K.; Otsubo, T.; Sakata, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 4027. (h) Przybilla, K. J.; Vögtle, F. *Chem. Ber.* **1989**, *122*, 347.

(2) Reviews, see: (a) Newkome, G. R.; Sauer, J. D.; Roper, J. M.; Hager, D. C. *Chem. Rev.* **1977**, *77*, 513. (b) *Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic Press: New York, **1983**; Vols. I and II.

(3) (a) Dithia[3]metacyclo[3](2,5)thiophenophane: Vögtle, F.; Lichtenthaler, R. *Chem. Ztg.* **1970**, *94*, 727. (b) Dithia[3]metacyclo[3]-(3,5)oxazolophane: Mashraqui, S. H.; Keehn, P. M. *J. Org. Chem.* **1983**, *48*, 1341. (c) [3]Metacyclo[3](2,5)thiopheno- and -furanophane: Miyahara, Y.; Inazu, T.; Yoshino, T. *Tetrahedron Lett.* **1984**, *25*, 415. Shinmyozu, T.; Hirai, Y.; Inazu, T., *J. Org. Chem.* **1986**, *51*, 1551.

(4) For example: (a) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1981**, *46*, 1543. (b) Tashiro, M.; Mataka, S.; Takezaki, Y.; Takeshita, M.; Arimura, T.; Tsuge, A.; Yamato, T. *J. Org. Chem.* **1989**, *54*, 451.

0022-3263/91/1956-2837$02.50/0

Table I. Yields and Conformations of Dithia[3.3]phanes and Their Tetraoxide Derivatives

	thiophene ring		benzene ring			yield (%)			
(*m*, *n*)	R_1	R_2	R_3	R_4	no.	**6**	**7**	route	anti:syn[a]
(2, 3)	4-H	5-COOEt	Me	t-Bu	**a**	16	83	A	–
	4-H	5-COOEt	OMe	t-Bu	**b**	33	81	A	–
	4-H	5-COOEt	H	H	**c**	11	84	A	–
(2, 4)	3-Me	5-Br	Me	t-Bu	**d**	46	91	A	5:1
	3-Me	5-Br	OMe	t-Bu	**e**	59	89	A	1:19[d]
	3-Me	5-Br	H	H	**f**	43	90	B	–
	3-Me	5-Br	NO_2	H	**g**	32	–	B	1:25
	3-Me	5-H	Me	t-Bu	**h**	57	87	C	–
	3-Me	5-H	OMe	t-Bu	**i**	53,[b] 97[c]	89	C	–
	3-Me	5-H	H	H	**j**	72	84	C	–
	$3,5\text{-Me}_2$		Me	t-Bu	**k**	21	–	D	5:1
(2, 5)	$3,4\text{-H}_2$		Me	t-Bu	**l**	60	84	A	–
	$3,4\text{-H}_2$		OMe	t-Bu	**m**	43	91	A	–
	$3,4\text{-Br}_2$		Me	t-Bu	**n**	69	81	A	6:1
	$3,4\text{-Br}_2$		OMe	t-Bu	**o**	55	94	A	–
	$3,4\text{-Br}_2$		H	H	**p**	44	100	B	–
	$3,4\text{-Br}_2$		NO_2	H	**q**	23	86	B	–
	$3,4\text{-Br}_2$		F	H	**r**	46	97	B	–
(3, 4)	$2,5\text{-Me}_2$		Me	t-Bu	**s**	54	87	A	–
	$2,5\text{-Me}_2$		OMe	t-Bu	**t**	39	84	A	–
	$2,5\text{-Me}_2$		H	H	**u**	53	81	B	–

[a] The ratios were determined from ^1H NMR spectra of **6** at room temperature; thus conformational changes may occur rapidly at room temperature. [b] From *syn*-**6e**. [c] From *anti*-**6e**. [d] Isolated.

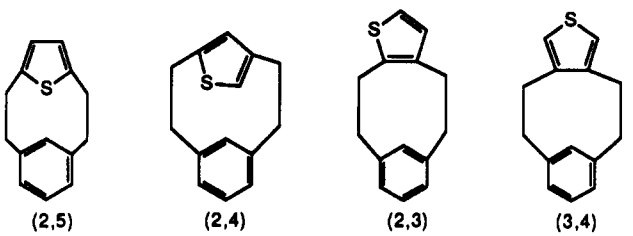


Figure 1. Isomers of [2]metacyclo[2](*m*,*n*)thiophenophanes.

chemistry have not yet been reported.

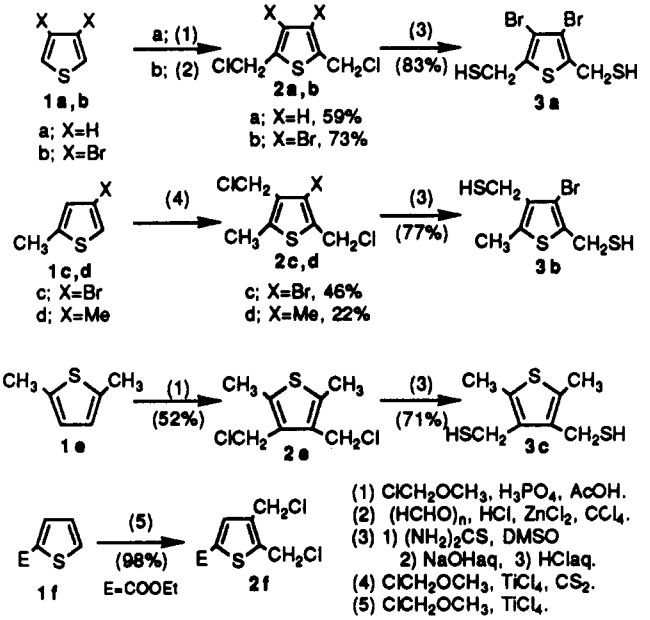
We undertook the preparation of the above types of [2.2]phanes from the corresponding dithia[3]metacyclo[3]thiophenophanes (dithia[3.3]phanes). The conformations of these compounds are discussed herein.

Results and Discussion

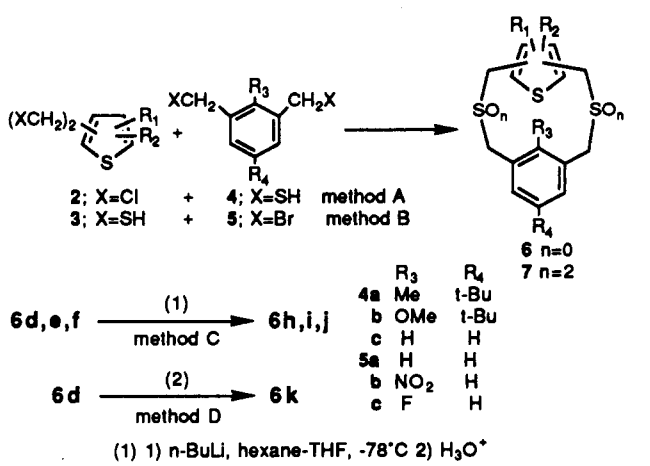
I. Preparation. Preparation of Bis(chloromethyl)- and Bis(mercaptomethyl)thiophenes. The preparative routes of the title compounds are shown in Scheme I.

Compounds **1b**,[5] **1c**,[6] and **1f**[7] were prepared from **1a** according to previously reported methods, whereas compound **1d**[8] was obtained by methylation of **1c** using MeMgI with $Ni(dppp)Cl_2$.[9] Chloromethylations of **1a**, **1b**, **1c**, **1d**, **1e**, and **1f** were carried out under conditions described in Scheme I to afford the desired bis(chloromethyl)thiophenes **2a**, **2b**, **2c**, **2d**, **2e**, and **2f**, respectively, whereas, the chloromethylation of **1a** and **1e** with chloromethyl methyl ether in the presence of phosphoric acid in acetic acid was a more convenient method than the previously reported one.[10,11] Although **2b** was stable, **2a** was too labile to handle in the usual experimental conditions. Bis(mercaptomethyl)thiophenes (**3a**, **3b**, and **3c**[12]) were ob-

Scheme I

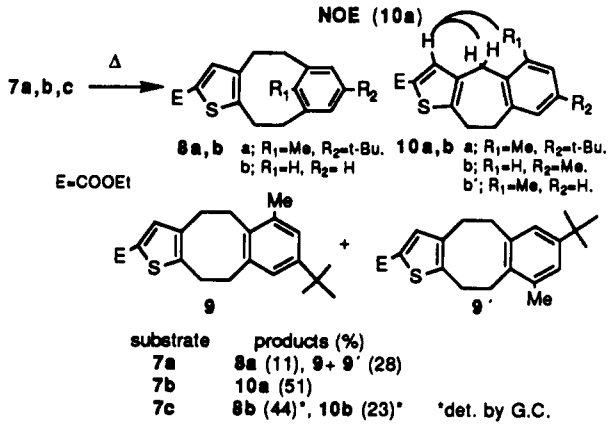


Scheme II



(5) Steinkopf, W.; Jacob, H.; Pentz, H. *Ann.* **1934**, *512*, 136.
(6) Gol'dfalb, Ya. L.; Vol'kenstein, Yu. B.; Lopatin, B. V. *Zh. Oshch. Khim.* **1964**, *34(3)*, 969; *Chem. Abstr.* **1964**, *61*, 629c.
(7) Weinstein, B. *J. Am. Chem. Soc.* **1955**, *77*, 6709.
(8) Janda, M.; Srogl, J.; Stibor, I.; Nemec, M.; Vopatrná, P. *Synthesis* **1972**, 545.
(9) (a) Kumada, M.; Tamao, K.; Sumitani, K. *Org. Synth.* **1978**, *58*, 127. (b) Pham, C. V.; Mark, H. B., Jr.; Zimmer, H. *Synth. Commun.* **1986**, *16*, 689.
(10) Griffing, J. M.; Salisbury, L. F. *J. Am. Chem. Soc.*, **1948**, *70*, 3416.
(11) Gaerther, R.; Tonkyn, R. G. *J. Am. Chem. Soc.* **1951**, *73*, 5872.

Scheme III



tained in good yield from the corresponding (chloromethyl)thiophenes **2b**, **2c**, and **2e** by the usual manner.[13]

Preparation of Dithia[3]metacyclo[3]thiophenophanes. Dithia[3.3]phanes and their tetraoxide derivatives were prepared by the routes shown in Scheme II and their yields are given in Table I.

The coupling reactions of bis(chloromethyl)thiophene **1f** with bis(mercaptomethyl)benzenes **4a–c** were carried out under high dilution conditions[4a] to afford the expected dithia[3.3](2,3)phanes, **6a–c**, together with a large amount of resinous materials. Their conformation will be discussed in a later section.

The oxidation of **6a–c** with *m*-chloroperoxybenzoic acid (*m*-CPBA) in CH_2Cl_2 afforded the corresponding tetraoxides **7a–c**, respectively. The coupling reactions of **2c** with **4a,b** afforded the corresponding dithia[3.3](2,4)-phanes **6d,e**. Similarly the reactions of **3b** with **5a,b**[14] gave **6f,g**, respectively, but the coupling reaction of **2d** and **4a** afforded a complex mixture.

Compounds **6h–j** were obtained by reduction of the Br atom of **6d–f** via lithiation using butyllithium at −78 °C. Interestingly, the yield from *syn*-**6e** was better than that from *anti*-**6e**. Stabilization of the intermediate anion by chelation of lithium to the oxygen atom of the methoxy group is proposed. The unstable **6k** was obtained from **6d** via methylation following lithiation.

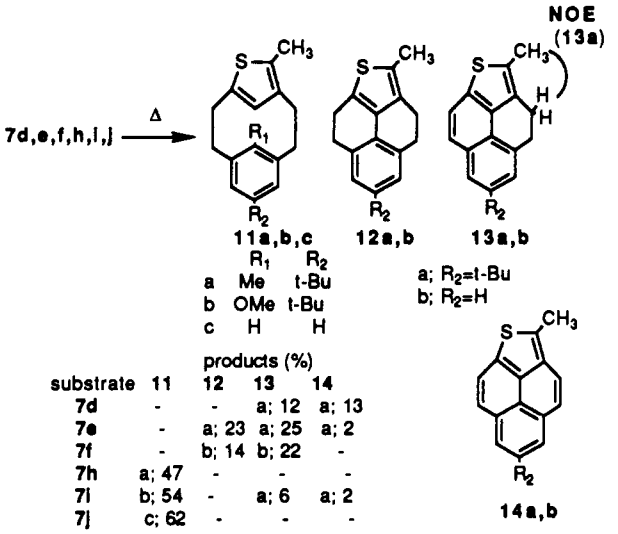
The preparations of dithia[3.3](2,5)- and -(3,4)phanes and their tetraoxides are also summarized in Scheme II. Bis(bromomethyl)benzene **5c** was synthesized in similar manner to that described in the literature ref 15.

Pyrolyses of Dithia[3.3]phane Tetraoxides. Pyrolyses of **7** were carried out under reduced pressure (480 °C, 0.4–0.8 Torr) in order to obtain the corresponding [2.2]-phanes.

[A] (2,3)Phanes. The results are summarized in Scheme III.

As shown in Scheme III, the expected [2.2]phanes **8a** and **8b** were obtained together with benzo[5,6]cycloocta-[1,2-*b*]thiophene (**9**) and benzo[4,5]cyclohepta[1,2-*b*]-thiophene[16] (**10**) by the pyrolysis of **7a** and **7c**, respectively. The desired [2.2]phane **8c** was obtained from a mixture of **8b** and **10b** by fractional gas chromatography, but **10c** was obtained as a mixture of the 7-methyl (**b**) and 5-methyl derivatives (**b'**). [2.2](2,3)Phanes **8** are the first heteroaromatic analogues of [2.2]orthometacyclophane, are expected to be highly strained molecules, and were not isolated until 1989.[17] This is the first synthesis of the unsymmetrical [2.2]orthometa type cyclophane. Pyrolysis of **7b** afforded only **10a** whose structure was determined from NOE spectra as shown in Scheme III. The pathway to the unexpected products, **9** and **10**, will be discussed later.

Scheme IV



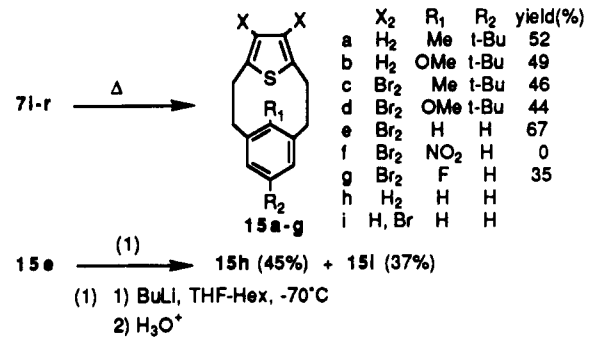
[B] (2,4)Phanes. Pyrolysis of **7h–j** afforded the expected [2.2](2,4)phanes, **11a–c**, as main products. However, **7d–f** afforded phenaleno[1,9-*bc*]thiophenes[18] (**12**, **13**, and **14**) as main products (Scheme IV). The structure of **13a** was determined from an NOE spectrum which was observed between the 1-methyl and 9-methylene protons.

The pyrolysis would proceed via a radical intermediate to give the tetrahydrophenalenothiophene **12**, which was oxidized with Br or R radicals to afford the dihydro derivative **13**. Further oxidation of **13** afforded **14**.

Also when **11b** was treated with BBr_3 in CH_2Cl_2 at room temperature, **12a** and **13a** were obtained in 34% and 3% yield, respectively. In contrast to the pyrolysis of **7d–f** described above, the reaction of **11b** with BBr_3 would proceed via cation intermediates to produce **12a** and **13a**.

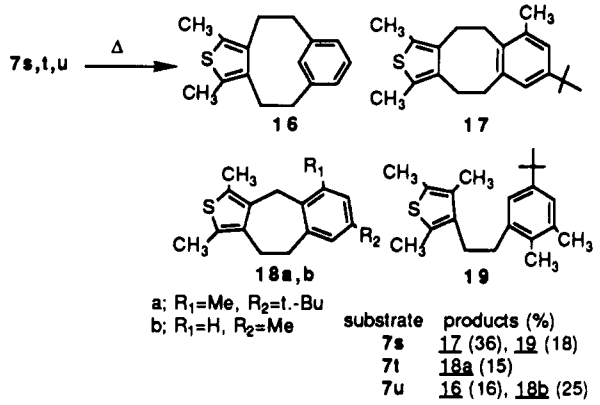
[C] (2,5)Phanes. The expected [2.2](2,5)phanes **15** were obtained by pyrolyses of the corresponding dithia[3.3]-phane tetraoxides, **7l–r**, as shown in Scheme V. However, **7q** did not afford any of the corresponding **15f**. In order

Scheme V

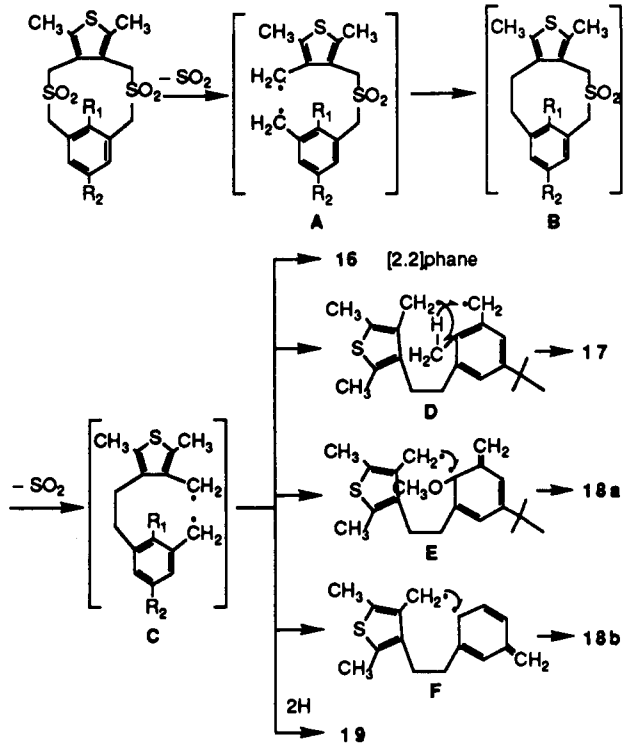


(12) Gol'dfalb, Ya. L.; Kondakova, M. S.; Krasnyanskaya, E. A.; Vinogradova, M. A., *Izv. Akad. Nauk SSSR, Ser. Khim.* **1964**, *12*, 2182; *Chem. Abstr.* **1965**, *62*, 9136h.
(13) Tashiro, M.; Yamato, T. *Org. Prep. Proc. Int.* **1981**, *13(1)*, 1.
(14) Vögtle, F.; Grütze, J.; Nätscher, R.; Wieder, W.; Weber, E.; Grün, R. *Chem. Ber.* **1975**, *108*, 1694.
(15) Yamato, T.; Arimura, T.; Tashiro M. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1.
(16) Majchrzak, M. W. *J. Heterocycl. Chem.* **1985**, *22*, 1203.
(17) Bodwell, G.; Ernst, L.; Haenel, M. W.; Hopf, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 455.
(18) (a) Tominaga, Y.; Castle, R. N.; Lee, M. L. *J. Heterocycl. Chem.* **1981**, *18*, 977. (b) Tominaga, Y.; Castle, R. N.; Lee, M. L. *J. Heterocycl. Chem.* **1982**, *19*, 1125.

Scheme VI



Scheme VII



to obtain **15h** from **15e**, the reduction of **15e** via lithiation was carried out since preparation of **15e** was easier than that of **15h**. However, reduction of **15e** afforded the monobromo derivative **15i** and expected **15h** in 37% and 45% yield, respectively.

[D] (3,4)Phanes. As shown in Scheme VI, the expected [2.2](3,4)phane **16** was only obtained from the corresponding **7u** and that the cyclooctene derivative, **17**, or cycloheptene derivatives,[19] **15**, were formed as major products. Although **19** could not be isolated, its formation and structure are proposed based on their GC–mass spectra.

Cyclooctene and cycloheptene derivatives were also found in the case of the (2,3)phanes as already mentioned. A reasonable reaction mechanism for the formation of such unexpected compounds is shown in Scheme VII.

Biradical C might be formed via intermediates, A and B, and then a radical coupling reaction of intermediate C would afford the desired **16**. The cyclooctene derivative (**17**) might also be formed by radical coupling with a methyl group following migration of radical via intermediate D. The cycloheptene derivatives would arise by radical coupling of the intermediates E and F which should be generated from C. The ethane derivative (**19**) is formed by reduction of the intermediate C.

(19) Ames, D. E.; Ribeiro, O. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1390.

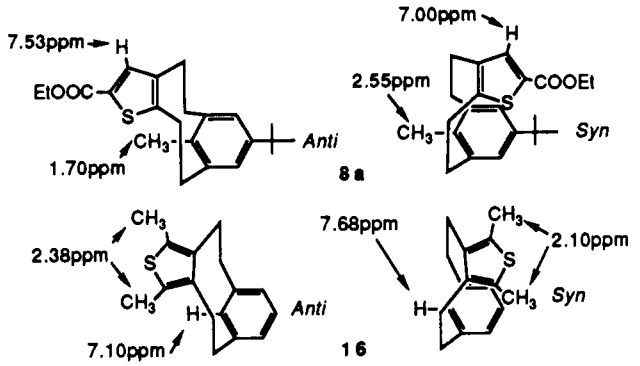


Figure 2. Conformations of [2.2](2,3)- and -(3,4)phanes.

A similar reaction pathway is proposed for the formation of **9** and **10** from the corresponding **7a–c**. However, in this case, the first radical cleavage should be highly selective since **7a–c** are unsymmetrical molecules.

II. Conformation. In dithia[3.3]- and -[2.2]metacyclophane derivatives, it is easy to determine whether they exist as syn or anti conformer, because the protons at the internal positions are expected to shift to high field from the shielding effect of the opposite benzene rings in the anti conformer. However, such shielding effects have not yet been investigated for dithia[3]metacyclo[3]thiophenophanes and [2]metacyclo[2]thiophenophanes. The study of shielding effect of the thiophene ring on the protons at the opposite benzene ring should be an interesting NMR problem.

The conformations of dithia[3.3]phanes at 25 °C are summarized in Table I.

[A] (2,3)Phane. Compound **6a** seems to exist as the anti conformer, because its internal methyl is observed at 1.85 ppm which is shifted 0.25 ppm higher from 4-*tert*-butyltoluene. In contrast, **6b** is assigned as the syn conformer because the *tert*-butyl group is shifted to 1.09 ppm by the opposite thiophene ring. The methylene bridge of **6c** is observed as four singlets, so both the C–S–C wobble[19] and rotation of the ring occur at room temperature. However, at room temperature, it might be anti rich because the proton at the inner position is observed at high field (6.25 ppm). In contrast, the smaller macrocycles, [2.2]phane **8a** and **8b**, were obtained as mixtures of syn and anti conformers (**8a**, syn:anti = 8:1; **8b**, syn:anti = 4:3) whose ratios were determined by their ^{1}H NMR spectra at 25 °C. It was not possible to separate the individual conformers. As shown in Figure 2, the methyl proton of the *anti*-**8a** appears at 1.70 ppm, which is 0.85 ppm higher than that of the *syn*-**8a** while the proton on the thiophene ring of syn conformer is found at 0.53 ppm higher field than that of anti. The difference of the conformer ratios between **8a** and **8b** might result from steric hindrance between the inner group (methyl and proton) and the thiophene ring.

[B] (2,4)Phane: Dithia[3.3]phanes with a Br group in their inner position were obtained as mixtures of anti and syn conformers except for **6f**. Ring flipping may occur at room temperature, and it is not obvious whether the proton at the inner position is shielded. In the case of **6e**, the anti and syn conformers were separated. Since the conformers of **6d,g** could not be isolated, the conformer ratios were determined from their ^{1}H NMR spectra. The protons of the benzene ring of *anti*-**6d** are seen at 7.13 and 7.14 ppm,

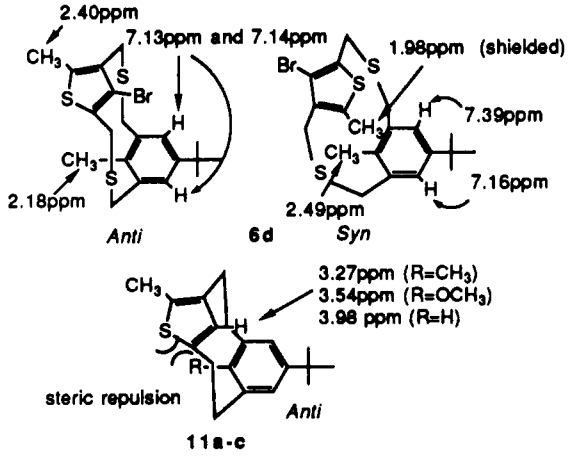


Figure 3. Conformations of dithia[3.3]- and -[2.2](2,4)phanes.

and those of the syn conformer occur at 7.16 and 7.39 ppm. This finding suggests that one of them is deshielded by the sulfur atom of the opposite thiophene ring. The methyl protons on the thiophene ring of the syn conformer is shifted to 1.98 ppm as shown in Figure 3. On the other hand, the conformationl change of compounds **6h–j** seems to occur at room temperature, and compounds **6h** and **6i** seem to be anti and syn conformers, respectively. The methylene bridge of **6j** is observed as four singlets at room temperature, so the C–S–C wobble and ring rotation freely occur at room temperature.

In contrast, no conformational changes were observable in the smaller [2.2](2,4)phanes (**11a–c**), and they should be anti conformers because the inner protons of the thiophene ring appear between 3.27 and 3.98 ppm (Figure 3), which values result from the high field shift caused by the anisotropy of the benzene rings. Interestingly, the internal protons of the thiophene ring are shifted to higher field as the size of the internal group on the benzene ring increased. This result can be explained by steric repulsion between the thiophene ring and the internal group of the benzene ring as shown in Figure 3.

[C] (2,5)Phanes. Conformational changes occurred freely in almost all of the dithia[3.3](2,5)phanes, and they seem to be syn conformers except for **6n** which exists as a mixture of the syn and the anti conformers (6:1) as shown in Table I. But the conformation of **6q,r**, which has no protons at the inner position, is not clear. The protons of the methylene bridge of **6p** is observed as one singlet and two doublets. This result means that one side of the C–S–C wobble of **6p** occurred and the other was slow on the NMR time scale at room temperature. This is one of its interesting physical characteristics because of its unsymmetrical structure.

The methyl protons at the inner position of the smaller [2.2](2,5)phane **15a** resonate at 1.96 ppm, which is only 0.14 ppm higher field than the ring methyl group of *tert*-butyltoluene, so it is not clear whether they are shielded. We carried out an X-ray crystallographic analysis of the dibromo derivative (**15c**). The ORTEP drawing showed that this [2.2]phane adopts the anti conformation (Figure 4). From the sectional view, the thiophene ring is bent like an envelope and the benzene ring boatlike. Previously, the crystal structures of [2.2]metacyclophane[21] (MCP) and [2.2](2,5)thiophenophane[22] (TPP) were reported, and their aromatic rings are bent like a boat and envelope, respectively. The degrees of each angle and distances which express how the aromatic rings are distorted are shown in Table II. From the results, it might be concluded that although the thiophene and benzene rings of **15c** are expected to be different in structure from the corresponding benzene ring of MCP and thiophene ring of TPP, respectively, the distortions of the benzene ring and thiophene ring of **15c** are almost the same as those of MCP and TPP.

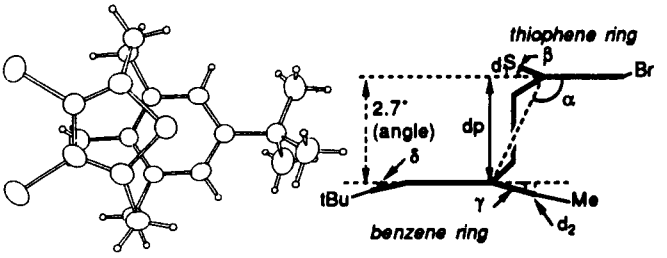


Figure 4. ORTEP and sectional view of **15c**.

Table II. Angles and Distances of [2.2]Phanes

	mcp[a]	tpp[a]	15c
d_1 (Å)	–	0.20	0.199
d_2 (Å)	0.143	–	0.161
d_p (Å)	2.295	2.63	2.62
α (deg)	–	–	114.9
β (deg)	–	–	9.7
γ (deg)	11.8	–	13.0
δ (deg)	3.4	–	2.6

[a] mcp = [2.2]metacyclophane. tpp = [2.2](2,5)thiophenophane.

[D] (3,4)Phanes. The dithia[3.3](3,4)phanes seem to be syn conformers since the protons of each inner group (methyl, methoxy, H), especially **6u** whose inner proton is observed at 8.21 ppm, are shifted to low field, but the conformational change may occur at room temperature. The methylene proton of **6u** appears as two singlets, hence the C–S–C wobble of **6u** occurs at room temperature. [2.2]Phane (**16**) was obtained as a mixture of syn and anti conformers (2:1) as shown in Figure 2. The reported [2.2]orthometacyclophane was a syn:anti = 4:1 mixture.[20] The steric hinderence between methyl group and benzene ring might cause **16** to be richer in the anti conformation than [2.2]orthometacyclophane.

Experimental Section

All melting points and boiling points are uncorrected. IR (KBr), JASCO IR-700; ^{1}H NMR, JEOL GSX-270 (270 MHz) in $CDCl_3$, TMS as reference; ^{19}F NMR, JEOL FX-100 (100 MHz) in $CDCl_3$, using C_6F_6 as reference; UV, Hitachi 220A spectrophotometer; MS, JEOL JMS-01-SG-2; EA, Hitachi 026 CHN analyzer or Yanaco MT-5. X-ray analysis was performed using CAD4 (ENRAF-NONIUS) at The Center of Advanced Instrumental Analysis, Kyushu University.

2,4-Dimethylthiophene (1d). To a freshly prepared solution 12.5 g (75 mmol) of methylmagnesium iodide in 23 mL of diethyl ether was added 10.7 g (60 mmol) of 4-bromo-2-methylthiophene (**1c**) and 90 mg (0.19 mmol) of nickel 1,3-bis(diphenylphosphino)propane,[9] and the mixture was heated at reflux under nitrogen for 22 h. The reaction mixture was poured into 2% HCl, and the organic phase was separated and washed with brine. After the mixture was dried ($MgSO_4$), the solvent was evaporated in vacuo. Fractional distillation of the residue afforded 4.4 g (66%) of **1d**, and 3.2 g (30%) of **1c** was recovered. **1c**: colorless oil; bp 140–142 °C (lit.[8] bp 144 °C).

2,5-Bis(chloromethyl)thiophene (2a). A solution of 20.0 g (0.24 mol) of thiophene, 50.0 g (0.63 mol) of chloromethyl methyl ether, 25 mL of H_3PO_4, and 140 mL of acetic acid was stirred for 15 h at room temperature. The reaction mixture was poured into 500 mL of ice–water, and the organic products were extracted

(20) See ref 2b, Chapter 4, Part 1, p 239.
(21) Brown, C. J. *J. Chem. Soc.* **1953**, 3278.
(22) Pahor, N. B.; Calligagaris, M.; Randaccio, L. *J. Chem. Soc., Perkin Trans. 2* **1978**, 42.
(23) Sone, T. *Nippon Kagaku Kaishi* **1965**, *86*, 1185.

with diethyl ether. The extracts were washed with water and dried ($MgSO_4$). The solvent was evaporated in vacuo and distillation under reduced pressure afforded 17.4 g (40%) of **2a**: colorless oil; bp 83 °C (1.3 Torr) (lit.[11] bp 106 °C (5 Torr)).

3-Bromo-2,4-bis(chloromethyl)-5-methylthiophene (2c). To a cold solution of 54 g (0.67 mol) of chloromethyl methyl ether and 48 g (0.25 mol) of $TiCl_4$ in 200 mL of CS_2 was added dropwise a solution of 30 g (0.17 mol) of **1c** in 20 mL of CS_2 for 30 min, and the mixture was stirred for 30 min at room temperature. The reaction mixture was poured into 500 mL of ice–water and extracted with 300 mL of dichloromethane. After the organic phase was washed with brine, the extracts were dried ($MgSO_4$). The solvents were evaporated in vacuo, and the residue was leached three times with 100 mL of refluxing hexane. The leachates were evaporated in vacuo, and recrystallization from petroleum ether afforded 26 g (56%) of **2c**: colorless needles (petroleum ether); mp 78.0–79.0 °C; IR (KBr) ν (cm^{-1}) 1256, 921, 634; ^1H NMR ($CDCl_3$) δ 2.50 (3 H, s), 4.52 (2 H, s), 4.72 (2 H, s); MS *m/e* 272, 274, 276 [M^+]. Anal. Calcd for $C_7H_7BrCl_2S$: C, 30.68; H, 2.57. Found: C, 30.38; H, 2.65.

2,4-Bis(chloromethyl)-3,5-dimethylthiophene (2d) was obtained from **2d** in 22% yield as described above for **2c**: colorless prisms (petroleum ether); mp 47.5–49.0 °C; IR (KBr) ν (cm^{-1}) 1439, 1394, 1254, 1202; ^1H NMR ($CDCl_3$) δ 2.22 (3 H, s), 2.44 (3 H, s), 4.46 (2 H, s), 4.68 (2 H, s); MS *m/e* 208, 210, 212 [M^+]. Anal. Calcd for $C_8H_{10}Cl_2S$: C, 45.95; H, 4.82. Found: C, 45.81; H, 4.80.

Ethyl 2,3-Bis(chloromethyl)thiophene-5-carboxylate (2f). To a mixture of 32 g (0.20 mol) of ethyl 2-thiophenecarboxylate[7] **10** and 80 g (1.0 mol) of chloromethyl methyl ether (1.0 mol) was added dropwise 60 g (0.30 mol) of $TiCl_4$ over 40 min cooled in an ice–water bath, and this mixture was stirred for 3 h at room temperature. To this mixture was added 200 mL of CH_2Cl_2, and this solution was poured into ice–water. The organic phase was washed with brine, dried ($MgSO_4$), and evaporated in vacuo. Recrystallization of the residue from hexane afforded 50 g (98%) of **2f**: colorless needles (hexane); mp 60.0–61.0 °C; IR (KBr) ν (cm^{-1}) 1714, 1256, 699; ^1H NMR ($CDCl_3$) δ 1.40 (3 H, t, J = 9 Hz), 4.40 (2 H, q, J = 9 Hz), 4.65 (2 H, s), 4.86 (2 H, s), 7.83 (1 H, s); MS *m/e* 252, 254, 256 [M^+]. Anal. Calcd for $C_9H_{10}Cl_2O_2S$: C, 42.70; H, 3.98. Found: C, 42.45; H, 3.90.

3,4-Dibromo-2,5-bis(mercaptomethyl)thiophene (3a). A solution of 6.8 g (20 mmol) of 2,5-bis(chloromethyl)-3,4-dibromothiophene[23] and 3.8 g (50 mmol) of thiourea in 50 mL of DMSO was stirred 14 h under N_2 at room temperature. The reaction mixture was poured into 100 mL of 5% aqueous NaOH solution and stirred for 1 h. The solution was acidified with 10% HCl, and the precipitate was extracted with $CHCl_3$. The organic layer was washed twice with brine and dried ($MgSO_4$). The solvent was evaporated in vacuo, and recrystallization of the residue from hexane afforded 5.6 g (83%) of **3a**: colorless prisms (hexane); mp 51.5–54.5 °C; IR (KBr) ν (cm^{-1}) 2544, 1412, 1310, 1250, 1131, 981, 694; ^1H NMR ($CDCl_3$) δ 2.08 (2 H, t, J = 8 Hz), 3.85 (4 H, d, J = 8 Hz); MS *m/e* 332, 334, 336 [M^+]. Anal. Calcd for $C_6H_6Br_2S_3$: C, 21.57; H, 1.81. Found: C, 21.74; H, 2.01.

3-Bromo-2,4-bis(mercaptomethyl)-5-methylthiophene (3b) was obtained from **2c** in 77% yield as described above for **3a**: colorless needles (hexane); mp 48.0–49.0 °C; IR (KBr) ν (cm^{-1}) 2538, 1243, 968, 701, 648; ^1H NMR ($CDCl_3$) δ 1.80 (1 H, t, J = 8 Hz), 2.01 (1 H, t, J = 8 Hz), 2.40 (3 H, s), 3.60 (2 H, d, J = 8 Hz), 3.78 (2 H, d, J = 8 Hz); MS *m/e* 268, 270 [M^+]. Anal. Calcd for $C_7H_9BrS_3$: C, 31.23; H, 3.37. Found: C, 31.41; H, 3.43.

3,4-Bis(mercaptomethyl)-2,5-dimethylthiophene (3c) was obtained from **2e** in 71% yield as described above for **3a**: colorless prisms (hexane); mp 31.0–32.0 °C (lit.[12] mp 39 °C).

Representative Synthesis for Dithia[3.3]phanes (Routes A and B). Ethyl 6-*tert*-Butyl-9-methyl-2,11-dithia[3]metacyclo[3](2,3)thiophenophane-15-carboxylate (6a). To a refluxing solution of 11.0 g (0.20 mmol) of KOH and 1.0 g (25 mmol) of $NaBH_4$ in 4 L of ethanol was added dropwise a solution of 12.7 g (50 mmol) of **2f** and 12.0 g (50 mmol) of dithiol **4a**[15] in 300 mL of ethanol benzene (1:1) over 24 h. The solvent was distilled off, and the residue was poured into ice–water. The mixture was extracted with CH_2Cl_2, the extracts were washed with brine and dried ($MgSO_4$), and the solvent was evaporated in vacuo. The residue was separated on silica gel column chromatography, and recrystallization of CH_2Cl_2 eluent from hexane afforded 3.2 g (15%) of **6a**: colorless prisms (ethanol); mp 145.0–146.0 °C; IR (KBr) ν (cm^{-1}) 2954, 1705, 1247, 1072; ^1H NMR ($CDCl_3$) δ 1.27 (9 H, s), 1.36 (3 H, t, J = 7 Hz), 1.85 (3 H, s), 2.70 (1 H, d, J = 16 Hz), 2.84 (1 H, d, J = 16 Hz), 3.13 (1 H, d, J = 16 Hz), 3.34 (1 H, d, J = 16 Hz), 3.68 (1 H, d, J = 12 Hz), 3.71 (1 H, d, J = 12 Hz), 4.16 (1 H, d, J = 12 Hz), 4.26 (1 H, d, J = 12 Hz), 4.31 (2 H, q, J = 7 Hz), 7.18 (1 H, s), 7.19 (1 H, s), 7.68 (1 H, s); MS *m/e* 420 [M^+]. Anal. Calcd for $C_{22}H_{28}O_2S_3$: C, 62.82; H, 6.71. Found: C, 62.78; H, 6.79.

The dithia[3.3]phanes described below were prepared in a similar manner described above for **6a**.

Ethyl 6-*tert*-Butyl-9-methoxy-2,11-dithia[3]metacyclo[3](2,3)thiophenophane-15-carboxylate (6b): colorless prisms (ethanol); mp 170.0–171.5 °C; IR (KBr) ν (cm^{-1}) 2960, 1702, 1251, 1069, 1009; ^1H NMR ($CDCl_3$) δ 1.09 (9 H, s), 1.30 (3 H, t, J = 7 Hz), 3.18 (1 H, d, J = 16 Hz), 3.37 (2 H, d, J = 16 Hz), 3.44 (1 H, d, J = 16 Hz), 3.68 (3 H, s), 3.78 (1 H, d, J = 16 Hz), 4.11–4.32 (4 H, m), 4.41 (2 H, t, J = 12 Hz), 6.99 (2 H, s), 7.43 (1 H, s); MS *m/e* 436 [M^+]. Anal. Calcd for $C_{22}H_{28}O_3S_3$: C, 60.51; H, 6.46. Found: C, 60.30; H, 6.48.

Ethyl 2,11-Dithia[3]metacyclo[3](2,3)thiophenophane-15-carboxylate (6c): colorless prisms (hexane); mp 120.0–121.0 °C; IR (KBr) ν (cm^{-1}) 1699, 1450, 1249, 1073; ^1H NMR ($CDCl_3$) δ 1.39 (3 H, t, J = 7 Hz), 3.03 (2 H, s), 3.16 (2 H, s), 3.71 (2 H, s), 3.82 (2 H, s), 4.35 (2 H, q, J = 7 Hz), 6.25 (1 H, s), 7.20–7.35 (3 H, m), 7.84 (1 H, s); MS *m/e* 350 [M^+]; UV (cyclohexane) λ_{max} (nm) (log ϵ) 251 (3.91), 284 (3.96). Anal. Calcd for $C_{17}H_{18}O_2S_3$: C, 58.25; H, 5.18. Found: C, 58.02; H, 5.26.

17-Bromo-6-*tert*-butyl-9,14-dimethyl-2,11-dithia[3]metacyclo[3](2,4)thiophenophane (6d): colorless prisms (ethanol); mp 144.5–146.5 °C; IR (KBr) ν (cm^{-1}) 2956, 1412, 1220, 908, 877, 749; ^1H NMR ($CDCl_3$) δ (anti) 1.31 (9 H, s), 2.20 (3 H, s), 2.42 (3 H, s), 3.54 (1 H, d, J = 15 Hz), 3.64 (2 H, t, J = 14 Hz), 3.67 (1 H, d, J = 15 Hz), 3.69 (1 H, d, J = 14 Hz), 3.97 (1 H, d, J = 15 Hz), 4.06 (1 H, d, J = 14 Hz), 4.35 (1 H, d, J = 14 Hz), 4.41 (1 H, d, J = 14 Hz), 7.13 (1 H, d, J = 2 Hz), 7.14 (1 H, d, J = 2 Hz); (syn) 1.32 (9 H, s), 1.98 (3 H, s), 2.49 (3 H, s), 3.53–4.04 (8 H), 7.15 (1 H, d, J = 2 Hz), 7.39 (1 H, d, J = 2 Hz); MS *m/e* 440, 442 [M^+]. Anal. Calcd for $C_{20}H_{25}BrS_3$: C, 54.40; H, 5.71. Found: C, 54.66; H, 5.78.

17-Bromo-6-*tert*-butyl-9-methoxy-14-methyl-2,11-dithia[3]metacyclo[3](2,4)thiophenophane (6e). *syn*-**6e** (56%): colorless prisms (hexane); mp 138.0–139.0 °C; IR (KBr) ν (cm^{-1}) 2960, 1478, 1203, 1013; ^1H NMR ($CDCl_3$) δ 1.30 (9 H, s), 2.17 (3 H, s), 3.33 (2 H, d, J = 13 Hz), 3.35 (1 H, d, J = 16 Hz), 3.38 (1 H, d, J = 13 Hz), 3.53 (3 H, s), 4.15 (1 H, d, J = 15 Hz), 4.26 (1 H, d, J = 14 Hz), 4.39 (1 H, d, J = 14 Hz), 4.47 (1 H, d, J = 16 Hz), 7.03 (1 H, d, J = 3 Hz), 7.23 (1 H, d, J = 3 Hz); MS *m/e* 456, 458 [M^+]; UV (cyclohexane) λ_{max} (nm) (log ϵ) 264 (3.61). Anal. Calcd for $C_{20}H_{25}BrS_3O$: C, 52.50; H, 5.51. Found: C, 52.57; H, 5.43.

anti-**6e** (3%): colorless prisms (methanol); mp 128.0–131.0 °C; IR (KBr) ν (cm^{-1}) 2960, 1480, 1203, 1102, 1021; ^1H NMR ($CDCl_3$) δ 1.33 (9 H, s), 2.50 (3 H, s), 3.37 (3 H, s), 3.37 (1 H, d, J = 15 Hz), 3.47 (1 H, d, J = 13 Hz), 3.60 (1 H, d, J = 15 Hz), 3.62 (1 H, d, J = 13 Hz), 3.77 (1 H, d, J = 14 Hz), 3.82 (1 H, d, J = 15 Hz), 3.94 (1 H, d, J = 13 Hz), 4.23 (1 H, d, J = 13 Hz), 7.22 (1 H, d, J = 2 Hz), 7.30 (1 H, d, J = 2 Hz); MS *m/e* 456, 458 [M^+]; UV (cyclohexane) λ_{max} (nm) (log ϵ) 263 (3.78). Anal. Calcd for $C_{20}H_{25}BrS_3O$: C, 52.50; H, 5.51. Found: C, 52.49; H, 5.54.

17-Bromo-14-methyl-2,11-dithia[3]metacyclo[3](2,4)thiophenophane (6f): colorless prisms (benzene–ethanol); mp 138.0–141.0 °C; IR (KBr) ν (cm^{-1}) 1439, 1416, 1219, 791, 722; ^1H NMR ($CDCl_3$) δ 2.11 (3 H, s), 3.62 (1 H, d, J = 15 Hz), 3.71 (2 H, d, J = 16 Hz), 3.77 (2 H, d, J = 16 Hz), 3.85 (1 H, d, J = 15 Hz), 3.93 (1 H, d, J = 16 Hz), 4.49 (1 H, d, J = 15 Hz), 7.03–7.14 (4 H, m); MS *m/e* 370, 372 [M^+]. Anal. Calcd for $C_{15}H_{15}BrS_3$: C, 48.51; H, 4.07. Found: C, 48.45; H, 4.32.

17-Bromo-14-methyl-9-nitro-2,11-dithia[3]metacyclo[3](2,4)thiophenophane (6g): pale yellow prisms (benzene); mp 228.0–231.0 °C dec; IR (KBr) ν (cm^{-1}) 1521, 1402, 1345, 1220, 856; ^1H NMR ($CDCl_3$) δ (syn) 2.19 (3 H, s), 3.43 (1 H, d, J = 15 Hz), 3.50 (1 H, d, J = 14 Hz), 3.65 (1 H, d, J = 16 Hz), 3.76 (1 H, d, J = 17 Hz), 4.09 (1 H, d, J = 15 Hz), 4.12 (1 H, d, J = 17 Hz), 4.73 (1 H, d, J = 14 Hz), 4.96 (1 H, d, J = 16 Hz), 7.25–7.36 (2 H, m), 7.55–7.57 (1 H, m); (anti) 2.49 (3 H, s), 3.63–4.36 (8 H),

7.16–7.20 (2 H, m), 7.42–7.45 (1 H, m); MS *m/e* 415, 417 [M$^+$]. Anal. Calcd for $C_{15}H_{14}BrNO_2S_3$: C, 43.27; H, 3.39; N, 3.36. Found: C, 43.50; H, 3.55; N, 3.38.

6-*tert*-Butyl-8-methyl-2,11-dithia[3]metacyclo[3](2,5)thiophenophane (6l): colorless prisms (ethanol); mp 66.0–68.0 °C; IR (KBr) ν (cm^{-1}) 2960, 1481, 1360, 1231, 1027, 794; ^{1}H NMR ($CDCl_3$) δ 1.25 (9 H, s), 2.36 (3 H, br s), 2.81 (4 H, s), 2.92 (4 H, s), 5.83 (2 H, s), 6.81 (2 H, s); MS *m/e* 348 [M$^+$]; UV (cyclohexane) λ_{max} (nm) (log ϵ) 270 (3.59). Anal. Calcd for $C_{19}H_{24}S_3$: C, 65.47; H, 6.94. Found: C, 65.56; H, 7.07.

6-*tert*-Butyl-8-methoxy-2,11-dithia[3]metacyclo[3](2,5)thiophenophane (6m): colorless prisms (ethanol–benzene); mp 106.5–108.5 °C; IR (KBr) ν (cm^{-1}) 2944, 1478, 1107, 1013, 802; ^{1}H NMR ($CDCl_3$) δ (ppm) 1.30 (9 H, s), 3.53 (2 H, d, J = 15 Hz), 3.78 (2 H, d, J = 15 Hz), 3.88 (2 H, d, J = 15 Hz), 4.07 (2 H, d, J = 15 Hz), 3.54 (3 H, s), 6.12 (2 H, s), 7.26 (2 H, s); MS *m/e* 364 [M$^+$]. Anal. Calcd for $C_{19}H_{24}OS_3$: C, 62.59; H, 6.63. Found: C, 62.44; H, 6.85.

6-*tert*-Butyl-14,15-dibromo-2,11-dithia-9-methyl[3]metacyclo[3](2,5)thiophenophane (6n): colorless prisms (ethanol–benzene); mp 195.5–203.0 °C; IR (KBr) ν (cm^{-1}) 2960, 1480, 1290, 1131; ^{1}H NMR ($CDCl_3$) δ (syn) 1.29 (9 H, s), 2.41 (3 H, s), 3.67 (2 H, d, J = 16 Hz), 3.87 (2 H, d, J = 16 Hz), 3.89 (2 H, d, J = 15 Hz), 3.95 (2 H, d, J = 15 Hz), 6.97 (2 H, s); (anti) 1.29 (9 H, s), 1.54 (3 H, s), 3.78 (4 H, br s), 3.79 (4 H, br s), 7.36 (2 H, s); MS *m/e* 504, 506, 508 [M$^+$]. Anal. Calcd for $C_{19}H_{22}Br_2S_3$: C, 45.07; H, 4.38. Found: C, 45.24; H, 4.40.

6-*tert*-Butyl-14,15-dibromo-2,11-dithia-9-methoxy[3]metacyclo[3](2,5)thiophenophane (6o): colorless prisms (ethanol–benzene); mp 165.5–167.0 °C; IR (KBr) ν (cm^{-1}) 2950, 1477, 1255, 1007, 916; ^{1}H NMR ($CDCl_3$) δ 1.31 (9 H, s), 3.59 (3 H, s), 3.59 (2 H, d, J = 15 Hz), 3.73 (2 H, d, J = 16 Hz), 3.83 (2 H, d, J = 16 Hz), 4.07 (2 H, d, J = 15 Hz), 7.13 (2 H, s); MS *m/e* 520, 522, 524 [M$^+$]. Anal. Calcd for $C_{19}H_{22}Br_2OS_3$: C, 43.69, H, 4.24. Found: C, 43.89; H, 4.48.

14,15-Dibromo-2,11-dithia[3]metacyclo[3](2,5)thiophenophane (6p): colorless prisms (benzene); mp 193.0–194.5 °C; IR (KBr) ν (cm^{-1}) 1396, 1302, 1126, 896, 711; ^{1}H NMR ($CDCl_3$) δ 3.77 (2 H, d, J = 15 Hz), 3.79 (4 H, s), 4.03 (2 H, d, J = 15 Hz), 6.87 (1 H, s), 7.01–7.14 (3 H, m); MS *m/e* 434, 436, 438 [M$^+$]; UV (cyclohexane) λ_{max} (nm) (log ϵ) 270 (3.65). Anal. Calcd for $C_{14}H_{12}Br_2S_3$: C, 38.54; H, 2.77. Found: C, 38.77; H, 2.87.

14,15-Dibromo-2,11-dithia-9-nitro[3]metacyclo[3](2,5)thiophenophane (6q): pale yellow prisms (benzene); mp 210.0–211.0 °C; IR (KBr) ν (cm^{-1}) 1513, 1345, 1225, 1122, 725; ^{1}H NMR ($CDCl_3$) δ 3.71 (2 H, d, J = 15 Hz), 3.83 (2 H, d, J = 16 Hz), 3.91 (2 H, d, J = 16 Hz), 4.38 (2 H, d, J = 15 Hz), 7.28–7.38 (3 H, m); MS *m/e* 479, 481, 483 [M$^+$]. Anal. Calcd for $C_{14}H_{11}Br_2NO_2S_3$: C, 34.94; H, 2.30; N, 2.91. Found: C, 35.07; H, 2.39; N, 2.49.

14,15-Dibromo-2,11-dithia-9-fluoro[3]metacyclo[3](2,5)thiophenophane (6r): colorless prisms (ethanol–benzene); mp 154.0–158.0 °C; IR (KBr) ν (cm^{-1}) 1461, 1305, 914, 741; ^{1}H NMR ($CDCl_3$) δ 3.63 (2 H, d, J = 15 Hz), 3.78 (4 H, s), 4.03 (2 H, d, J = 15 Hz), 6.72–7.23 (3 H, m); ^{19}F NMR ($CDCl_3$) δ 46.95 (t, J = 7 Hz); MS *m/e* 452, 454, 456 [M$^+$]. Anal. Calcd for $C_{14}H_{11}Br_2FS_3$: C, 37.02; H, 2.44. Found: C, 37.43; H, 2.74.

6-*tert*-Butyl-9,14,16-trimethyl-2,11-dithia[3]metacyclo[3](3,4)thiophenophane (6s): colorless prisms (ethanol); mp 137.0–143.0 °C; IR (KBr) ν (cm^{-1}) 2960, 1483, 1438, 1243, 1174; ^{1}H NMR ($CDCl_3$) δ 1.31 (9 H, s), 1.94 (2 H, d, J = 13 Hz), 2.29 (6 H, s), 2.48 (3 H, s), 3.34 (2 H, d, J = 13 Hz), 3.78 (2 H, d, J = 13 Hz), 4.03 (2 H, d, J = 13 Hz), 7.06 (2 H, s); MS *m/e* 376 [M$^+$]. Anal. Calcd for $C_{21}H_{28}S_3$: C, 66.97; H, 7.49. Found: C, 66.89; H, 7.71.

6-*tert*-Butyl-9-methoxy-14,16-dimethyl-2,11-dithia[3]metacyclo[3](3,4)thiophenophane (6t): colorless prisms (ethanol); mp 180.0–182.0 °C IR (KBr) ν (cm^{-1}) 2960, 1485, 1203, 1098, 1005, 640; ^{1}H NMR ($CDCl_3$) δ 1.20 (9 H, s), 2.17 (6 H, s), 2.76 (2 H, d, J = 14 Hz), 3.54 (2 H, d, J = 14 Hz), 3.65 (2 H, d, J = 12 Hz), 3.69 (3 H, s), 4.13 (2 H, d, J = 12 Hz), 7.15 (2 H, s); MS *m/e* 392 [M$^+$]. Anal. Calcd for $C_{21}H_{28}OS_3$: C, 64.24; H, 7.19. Found: C, 64.01; H, 7.46.

14,16-Dimethyl-2,11-dithia[3]metacyclo[3](3,4)thiophenophane (6u): colorless prisms (ethanol–benzene); mp 151.0–152.0 °C IR (KBr) ν (cm^{-1}) 1605, 1443, 1173, 767; ^{1}H NMR ($CDCl_3$) δ 2.40 (6 H, s) 3.14 (4 H, s), 3.87 (4 H, s), 7.11–7.30 (3 H, m), 8.21 (1 H, s); MS *m/e* 306 [M$^+$]; UV (cyclohexane) λ_{max} (nm) (log ϵ) 249 (3.92) (shoulder). Anal. Calcd for $C_{16}H_{18}S_3$: C, 62.70; H, 5.92. Found: C, 62.92, H, 5.93.

Representive Reduction of Br Atom of 6d–f (Route C). 6-*tert*-Butyl-9,14-dimethyl-2,11-dithia[3]metacyclo[3](2,4)thiophenophane (6h). To a solution of 1.1 g (2.5 mmol) of **6d** in 15 mL of dry THF under N_2 at −70 °C was added dropwise a solution of 2.0 mL (3.2 mmol) of 1.6 M *n*-BuLi in hexane, and the mixture was stirred for 30 min at this temperature; 2.0 mL of 10% HCl was added the mixture, and the temperature rose to room temperature. The mixture was extracted with Et_2O, and the organic layer was washed with brine and dried ($MgSO_4$). The solvent was evaporated in vacuo, and the residue was separated on silica gel column chromatography. Recrystallization of the eluent (hexane–chloroform, 3:1) from methanol afforded 520 mg (57%) of **6h**: colorless prisms (methanol); mp 94.5–95.5 °C; IR (KBr) ν (cm^{-1}) 2962, 1482, 1361, 883; ^{1}H NMR ($CDCl_3$) δ 1.28 (9 H, s), 2.15 (3 H, s), 2.30 (3 H, s), 3.44 (1 H, d, J = 16 Hz), 3.50 (1 H, d, J = 16 Hz), 3.66 (1 H, d, J = 16 Hz), 3.79 (1 H, d, J = 16 Hz), 3.83 (1 H, d, J = 14 Hz), 3.94 (1 H, d, J = 14 Hz), 3.99 (1 H, d, J = 14 Hz), 4.04 (1 H, d, J = 14 Hz), 5.65 (1 H, s), 7.02 (2 H, s); MS *m/e* 362 [M$^+$]. Anal. Calcd for $C_{20}H_{26}S_3$: C, 66.25; H, 7.23. Found: C, 66.43; H, 7.24.

The products described below were also prepared in a similar manner described above for **6h**.

6-*tert*-Butyl-9-methoxy-14-methyl-2,11-dithia[3]metacyclo[3](2,4)thiophenophane (6i): colorless prisms (methanol); mp 133.0–134.5 °C; IR (KBr) ν (cm^{-1}) 2960, 1480, 1202, 1007, 878; ^{1}H NMR ($CDCl_3$) δ 1.26 (9 H, s), 2.12 (3 H, s), 3.41 (1 H, d, J = 14 Hz), 3.45 (1 H, d, J = 14 Hz), 3.50 (1 H, d, J = 14 Hz), 3.62 (3 H, s), 3.72 (1 H, d, J = 15 Hz), 3.77 (1 H, d, J = 14 Hz), 4.11 (1 H, d, J = 14 Hz), 4.11 (1 H, d, J = 15 Hz), 4.21 (1 H, d, J = 14 Hz), 6.70 (1 H, s), 7.08 (1 H, d, J = 2 Hz), 7.16 (1 H, d, J = 2 Hz); MS *m/e* 378 [M$^+$]. Anal. Calcd for $C_{20}H_{26}OS_3$: C, 63.45; H, 6.92. Found: C, 63.46; H, 6.88.

14-Methyl-2,11-dithia[3]metacyclo[3](2,4)thiophenophane (6j): colorless prisms (hexane); mp 123.0–125.0 °C; IR (KBr) ν (cm^{-1}) 1444, 1411, 1219, 1153, 846, 721; ^{1}H NMR ($CDCl_3$) δ 2.07 (3 H, s), 3.60 (2 H, s), 3.74 (2 H, s), 3.82 (2 H, s), 3.97 (2 H, s), 6.63 (1 H, s), 6.90–6.95 (2 H, m), 7.04–7.11 (2 H, m); MS *m/e* 292 [M$^+$]. Anal. Calcd for $C_{15}H_{16}S_3$: C, 61.60; H, 5.51. Found: C, 61.62; H, 5.64.

Methylation of 6d (Route D). To a solution of 440 mg (1.0 mmol) of **6d** in 25 mL of dry THF was added 0.70 mL (1.1 mmol) of *n*-BuLi in hexane at −70 °C under N_2. The mixture was stirred for 30 min at this temperature, and 150 mg (1.2 mmol) of Me_2SO_4 was added to the mixture and stirred until the temperature rose room temperature. The reaction mixture was poured into water, and the organics were extracted with Et_2O and washed with sodium hydrogen carbonate solution and brine. After the mixture was dried ($MgSO_4$), the solvent was evaporated in vacuo. The residue was separated on silica gel column chromatography, and recrystallization of hexane–benzene (4:1) eluent from methanol afforded 92 mg (25%) of **6k**.

6-*tert*-Butyl-9,14,17-trimethyl-2,11-dithia[3]metacyclo[3](2,4)thiophenophane (6k): colorless prisms (methanol); mp 130.5–133.5 °C; IR (KBr) ν (cm^{-1}) 2960, 1478, 1216, 870, 748; ^{1}H NMR ($CDCl_3$) δ (syn) 1.31 (9 H, s), 2.10 (3 H, s), 2.28 (3 H, s), 2.33 (3 H, s), 3.56 (1 H, d, J = 15 Hz), 3.70 (1 H, d, J = 16 Hz), 3.74 (2 H, d, J = 15 Hz), 3.80 (1 H, d, J = 17 Hz), 3.92 (1 H, d, J = 15 Hz), 4.21 (1 H, d, J = 15 Hz), 4.24 (1 H, d, J = 16 Hz), 7.01 (1 H, d, J = 2 Hz), 7.12 (1 H, d, J = 2 Hz); (anti) 1.26 (3 H, s), 1.28 (3 H, s), 1.30 (9 H, s), 2.04 (3 H, s), 3.47–4.27 (8 H, m), 6.87 (1 H, d, J = 2 Hz), 7.11 (1 H, d, J = 2 Hz); MS *m/e* 376 [M$^+$]. Anal. Calcd for $C_{21}H_{28}S_3$: C, 66.97; H, 7.49. Found: C, 66.99; H, 7.44.

Representive Oxidation for the Dithia[3.3]phanes. To a solution of 0.84 g (2.0 mmol) of **6a** in 40 mL of CH_2Cl_2 was added gradually 2.2 g (10 mmol) of 80% *m*-CPBA, and the mixture was stirred for 12 h at room temperature. The reaction mixture was poured into 20 mL of 2% aqueous NaOH solution, and the organic phase was separated. After being washed with brine, the organic phase was dried ($MgSO_4$) and evaporated in vacuo. Recrystallization of the residue from ethanol afforded 800 mg (83%) of **7a**.

The details of spectra (IR, NMR, MS) and elemental analyses of tetraoxides **7** are shown in supplementary material.

7a: colorless prisms (EtOH); mp 234.0–235.5 °C dec.
7b: colorless plates (EtOH); mp 240.0–242.0 °C.
7c: colorless plates (EtOH–PhH); mp 265.0–270.0 °C dec.
7d: colorless plates (PhH); mp 280.0–290.0 °C dec.
7e: colorless prisms (PhH); mp 320.0–322.0 °C dec.
7f: colorless needles ($CHCl_3$); mp 285 °C dec.
7h: colorless prisms (EtOH–PhH); mp 248.0–251.0 °C dec.
7i: colorless prisms (EtOH); mp 307.0–310.5 °C dec.
7j: colorless prisms ($CHCl_3$); mp 320 °C dec.
7l: colorless prisms ($CHCl_3$); mp 215 °C dec.
7m: colorless prisms (EtOH–PhH); mp 300 °C dec.
7n: colorless prisms (EtOH–PhH); mp 278.0–281.0 °C dec.
7o: colorless prisms (PhH); mp 285.0–288.0 °C dec.
7p: colorless prisms; mp 295 °C dec.
7q: colorless needles; mp 280 °C dec.
7r: colorless needles; ($CHCl_3$); mp 270 °C dec.
7s: colorless prisms (PhH); mp 267.0–270.0 °C dec.
7t: colorless prisms (PhH); mp 258.0–260.0 °C dec.
7u: colorless prisms ($CHCl_3$); mp 309.0–312.0 °C dec.

Pyrolysis of Dithia[3.3]phanes *S,S,S',S'*-Tetraoxide. The pyrolyses were carried out in a manner similar to that described in the literature.[4a] Products were extracted with CH_2Cl_2, and the ash was filtered. The solvent was evaporated, the residue was separated on silica gel column chromatography, and a mixture of hexane and CH_2Cl_2 (2:1) eluent afforded **8a** (11%) and **9** + **9'** (28%).

Ethyl 5-*tert*-Butyl-8-methyl[2]metacyclo[2](2,3)thiophenophane-13-carboxylate (8a): colorless oil; IR (KBr) ν (cm^{-1}) 2960, 1712, 1248, 1073, 754; ^1H NMR ($CDCl_3$) δ (syn) 1.04 (9 H, s), 2.55 (3 H, s), 6.26 (1 H, d, J = 2 Hz), 6.36 (1 H, d, J = 2 Hz), 7.01 (1 H, s); (anti) 0.90 (9 H, s), 1.73 (3 H, s), 5.93 (1 H, s), 6.05 (1 H, s) 7.53 (1 H, s); (common signal) 1.23–1.46 (4 H, m), 2.27–2.95 (4 H, m), 3.21–3.32 (1 H, m), 3.53–3.68 (2 H, m), 4.18–4.35 (2 H, m); MS m/e calcd for $C_{22}H_{28}O_2S$ 356.1809, obsd 356.1804 [M^+].

Mixture of ethyl 7-*tert*-butyl-9-methyl-4,5,10,11-tetrahydrobenzo[5,6]cycloocta[1,2-*b*]thiophene-2-carboxylate (9) and ethyl 8-*tert*-butyl-6-methyl-4,5,10,11-tetrahydrobenzo-[5,6]cycloocta[1,2-*b*]thiophene-2-carboxylate (9'): ^1H NMR ($CDCl_3$) δ 1.28 (9 H, s), 1.35 (3 H, t, J = 7 Hz), 2.02 and 2.19 (3 H, s, 4:5), 2.72–3.13 (8 H, m), 4.31 (2 H, q, J = 7 Hz), 6.94, 6.97, 6.98, 7.38, 7.48, 7.54 (each 1 H, s); MS m/e calcd for $C_{22}H_{28}O_2S$ 356.1809, obsd. 356.1808.

Compounds described below were obtained in a similar manner to that described above for **8a**.

Ethyl 7-*tert*-butyl-9,10-dihydro-5-methyl-4*H*-benzo[4,5]-cyclohepta[1,2-*b*]thiophene-2-carboxylate (10a): colorless plates (methanol); mp 127.0–129.0 °C; IR (KBr) ν (cm^{-1}) 2960, 1698, 1461, 1251, 1070; ^1H NMR ($CDCl_3$) δ 1.30 (9 H, s), 1.34 (3 H, t, J = 7 Hz), 2.38 (3 H, s), 3.11–3.21 (4 H, m), 3.99 (2 H, s), 4.30 (2 H, q, J = 7 Hz), 7.06 (1 H, d, J = 2 Hz), 7.11 (1 H, d, J = 2 Hz), 7.50 (1 H, s); MS m/e 342 [M^+]. Anal. Calcd for $C_{21}H_{26}O_2S$: C, 73.64; H, 7.67. Found: C, 73.79; H, 7.63.

Ethyl [2]metacyclo[2](2,3)thiophenophane-13-carboxylate (8b): colorless oil; IR (KBr) ν (cm^{-1}) 2922, 1711, 1430, 1248, 1067; ^1H NMR ($CDCl_3$) δ (syn) 1.30 (3 H, t, J = 7 Hz), 1.46–1.56 (1 H, m), 2.35–2.52 (2 H, m), 2.87–3.07 (3 H, m), 3.44–3.58 (2 H, m), 4.23 (2 H, q, J = 7 Hz), 6.44 (1 H, d, J = 7 Hz), 6.50 (1 H, d, J = 7 Hz), 6.75 (1 H, t, J = 7 Hz), 7.08 (1 H, s), 7.61 (1 H, s); (anti) 1.40 (3 H, t, J = 7 Hz), 1.13–1.23 (1 H, m), 2.79–2.85 (2 H, m), 2.87–3.07 (4 H, m), 3.22–3.35 (1 H, m), 4.36 (2 H, q, J = 7 Hz), 6.79 (1 H, s), 6.91 (1 H, d, J = 7 Hz), 6.93 (1 H, d, J = 7 Hz), 7.26 (1 H, t, J = 7 Hz), 7.56 (1 H, s); MS m/e calcd for $C_{17}H_{18}O_2S$ 286.1027, obsd 286.1024 [M^+]; UV (cyclohexane) λ_{max} (nm) (log ϵ) 261 (3.75), 287 (3.75).

Ethyl 9,10-dihydro-7-methyl-4*H*-benzo[4,5]cyclohepta-[1,2-*b*]thiophene-2-carboxylate (10b) and ethyl 9,10-dihydro-5-methyl-4*H*-benzo[4,5]cyclohepta[1,2-*b*]thiophene-2-carboxylate (10b'): ^1H NMR ($CDCl_3$) (**10b**) δ 1.34 (3 H, t, J = 7 Hz), 2.38 (3 H, s), 3.12 (4 H, s?), 3.96 (2 H, s), 4.29 (2 H, q, J = 7 Hz), 6.96 (1 H, d, J = 7 Hz), 7.04–7.10 (2 H, m), 7.48 (1 H, s); (**10b'**) δ 1.33 (3 H, t, J = 7 Hz), 2.38 (3 H, s), 2.91–2.98 (2 H, m), 3.05–3.12 (2 H, m), 4.07 (2 H, s), 4.29 (2 H, q, J = 7 Hz), 7.04–7.10 (3 H, m), 7.38 (1 H, s); MS m/e calcd for $C_{17}H_{18}O_2S$ 286.1027, obsd 286.1025 [M^+].

6-*tert*-Butyl-3,4,8,9-tetrahydro-1-methylphenaleno[1,9-*bc*]thiophene (12a): colorless prisms (75% aqueous methanol); mp 109.5–110.5 °C; IR (KBr) ν (cm^{-1}) 2950, 1422, 1363, 1222, 876; ^1H NMR ($CDCl_3$) δ 1.32 (9 H, s), 2.35 (3 H, s), 2.72–2.77 (2 H, m), 2.88–2.94 (4 H, m), 2.98–3.04 (2 H, m), 7.08 (2 H, s); MS m/e 282 [M^+]; UV (cyclohexane) λ_{max} (nm) (log ϵ) 252 (4.27), 288 (4.09). Anal. Calcd for $C_{19}H_{22}S$: C, 80.80; H, 7.85. Found: C, 80.73; H, 7.78.

6-*tert*-Butyl-8,9-dihydro-1-methylphenaleno[1,9-*bc*]-thiophene (13a): colorless prisms (methanol); mp 110.5–115.0 °C; IR (KBr) ν (cm^{-1}) 2954, 1360, 1159, 873; ^1H NMR ($CDCl_3$) δ 1.43 (9 H, s), 2.56 (3 H, s), 3.08 (2 H, t, J = 8 Hz), 3.30 (2 H, t, J = 8 Hz), 7.46 (1 H, d, J = 2 Hz), 7.61 (1 H, d, J = 9 Hz), 7.69 (1 H, d, J = 2 Hz), 7.72 (1 H, d, J = 9 Hz); MS m/e 280 [M^+]; UV (cyclohexane) λ_{max} (nm) (log ϵ) 235 (4.46), 260 (4.42), 306 (4.00). Anal. Calcd for $C_{19}H_{20}S$: C, 81.38; H, 7.19. Found: C, 81.27; H, 7.34.

6-*tert*-Butyl-1-methylphenaleno[1,9-*bc*]thiophene (14a): pale green prisms (methanol); mp 122.0–125.0 °C; IR (KBr) ν (cm^{-1}) 2950, 1394, 874, 786, 694; ^1H NMR ($CDCl_3$) δ 1.52 (9 H, s), 2.92 (3 H, s), 7.48 (1 H, d, J = 9 Hz), 7.54 (1 H, d, J = 9 Hz), 7.85 (1 H, d, J = 9 Hz), 7.89 (1 H, d, J = 2 Hz), 7.99 (1 H, d, J = 9 Hz), 8.02 (1 H, d, J = 2 Hz); MS m/e 278 [M^+]; UV (cyclohexane) λ_{max} (nm) (log ϵ) 228 (4.35), 240 (4.35), 266 (4.32), 277 (4.47), 360 (4.25), 380 (4.23). Anal. Calcd for $C_{19}H_{18}S$: C, 81.97, H, 6.52. Found: C 81.56, H, 6.59.

3,4,8,9-Tetrahydro-1-methylphenaleno[1,9-*bc*]thiophene (12b): colorless plates (methanol); mp 65.0–67.0 °C; IR (KBr) ν (cm^{-1}) 2930, 1422, 1143, 760; ^1H NMR ($CDCl_3$) δ 2.36 (3 H, s), 2.75 (2 H, t, J = 7 Hz), 2.88–2.95 (4 H, m), 2.98–3.05 (2 H, m), 7.02–7.09 (3 H, m); MS m/e 226 [M^+]. Anal. Calcd for $C_{15}H_{14}S$: C, 79.60; H, 6.23. Found: C, 79.14; H, 6.44.

8,9-Dihydro-1-methylphenaleno[1,9-*bc*]thiophene (13b): colorless prisms (methanol); mp 55.0–57.0 °C; IR (KBr) ν (cm^{-1}) 2930, 1159, 817, 780, 678; ^1H NMR ($CDCl_3$) δ 2.57 (3 H, s), 3.09 (2 H, td, J = 8, 1 Hz), 3.31 (2 H, J = 8 Hz), 7.36 (1 H, dd, J = 7, 1 Hz), 7.41 (1 H, dd, J = 7, 7 Hz), 7.64 (1 H, d, J = 8 Hz), 7.74 (1 H, d, J = 7 Hz), 7.76 (1 H, d, J = 8 Hz); MS m/e 224 [M^+]. Anal. Calcd for $C_{15}H_{12}S$: C, 80.31; H, 5.39. Found: C, 80.03; H, 5.52.

5-*tert*-Butyl-8,12-dimethyl[2]metacyclo[2](2,4)thiophenophane (11a): colorless prisms (methanol); mp 68.0–71.0 °C; IR (KBr) ν (cm^{-1}) 2960, 2926, 1260, 1231, 908, 803; ^1H NMR ($CDCl_3$) δ 1.27 (3 H, s), 1.33 (9 H, s), 2.19–2.31 (1 H, m), 2.38 (3 H, s), 2.43–2.54 (1 H, m), 2.70–2.94 (4 H, m), 2.97–3.05 (2 H, m), 3.27 (1 H, s), 7.00 (1 H, d, J = 2 Hz), 7.03 (1 H, d, J = 2 Hz); MS m/e 298 [M^+]. Anal. Calcd for $C_{20}H_{26}S$: C, 80.48; H, 8.78. Found: C, 80.33; H, 8.87.

5-*tert*-Butyl-8-methoxy-12-methyl[2]metacyclo[2](2,4)-thiophenophane (11b): colorless prisms (75% aqueous methanol); mp 71.0–72.0 °C; IR (KBr) ν (cm^{-1}) 2960, 1477, 1291, 1240, 1199, 1024; ^1H NMR ($CDCl_3$) δ 1.33 (9 H, s), 2.11–2.22 (1 H, m), 2.33–2.44 (1 H, m), 2.37 (3 H, s), 2.52–2.85 (4 H, m), 2.92–3.02 (2 H, m), 3.20 (3 H, s), 3.54 (1 H, s), 6.99 (1 H, d, J = 2 Hz), 7.03 (1 H, d, J = 2 Hz); MS m/e 314 [M^+]. Anal. Calcd for $C_{20}H_{26}OS$: C, 76.38; H, 8.33. Found: C, 76.52; H, 8.37.

12-Methyl[2]metacyclo[2](2,4)thiophenophane (11c): colorless prisms (methanol); mp 41.0–44.0 °C; IR (KBr) δ (cm^{-1}) 2936, 1428, 1226, 783, 712, 566; ^1H NMR ($CDCl_3$) δ 2.14–2.41 (4 H, m), 2.43 (3 H, s), 2.87–3.07 (4 H, m), 3.98 (1 H, s), 4.77 (1 H, s), 6.97–7.04 (2 H, m), 7.16 (1 H, t, J = 8 Hz); MS m/e 228 [M^+]. Anal. Calcd for $C_{15}H_{16}S$: C, 78.90; H, 7.06. Found: C, 79.04; H, 7.08.

5-*tert*-Butyl-8-methyl[2]metacyclo[2](2,5)thiophenophane (15a): colorless prisms (75% aqueous methanol); mp 92.0–94.0 °C; IR (KBr) ν (cm^{-1}) 2954, 1478, 1185, 1028, 802, 589; ^1H NMR ($CDCl_3$) δ 1.34 (9 H, s), 1.96 (3 H, s), 2.20–3.34 (8 H, m), 6.68 (2 H, s), 6.95 (2 H, s); MS m/e 284 [M^+]; UV (cyclohexane) λ_{max} (nm) (log ϵ) = 215 (4.30), 277 (3.30). Anal. Calcd for $C_{19}H_{24}S$: C, 80.22; H, 8.50. Found: C, 80.33; H, 8.75.

5-*tert*-Butyl-8-methoxy[2]metacyclo[2](2,5)thiophenophane (15b): colorless plates (80% aqueous methanol); mp 82.5–83.0 °C; IR (KBr) ν (cm^{-1}) 2956, 1462, 1287, 1008, 795; ^1H NMR ($CDCl_3$) δ 1.35 (9 H, s), 2.20–3.28 (8 H, m), 3.24 (3 H, s), 6.72 (2 H, s), 6.93 (2 H, s); MS m/e 300 [M^+]. Anal. Calcd for $C_{19}H_{24}OS$: C, 75.95; H, 8.05. Found: C, 76.17; H, 8.21.

5-*tert*-Butyl-12,13-dibromo-8-methyl[2]metacyclo[2](2,5)thiophenophane (15c): colorless prisms (hexane); mp 174.5–175.0 °C; IR (KBr) δ (cm^{-1}) 2956, 1461, 997, 870, 844; ^1H NMR ($CDCl_3$) δ 1.33 (9 H, s), 1.96 (3 H, s), 2.41–2.52 (2 H, m), 2.69–2.76 (2 H, m), 3.17–3.36 (4 H, m), 6.97 (2 H, s); MS *m/e* 440, 442, 444 [M^+]. Anal. Calcd for $C_{19}H_{22}Br_2S$: C, 51.60; H, 5.01. Found: C, 51.82; H, 5.03.

5-*tert*-Butyl-12,13-dibromo-8-methoxy[2]metacyclo[2](2,5)thiophenophane (15d): colorless prisms (methanol); mp 118.0–120.0 °C; IR (KBr) ν (cm^{-1}) 2950, 1476, 1283, 1203, 1008; ^1H NMR ($CDCl_3$) δ 1.32 (9 H, s), 2.39–2.55 (4 H, m), 3.28–3.40 (4 H, m), 3.35 (3 H, s), 6.96 (2 H, s); MS *m/e* 456, 458, 460 [M^+]. Anal. Calcd for $C_{19}H_{22}Br_2OS$: C, 49.80; H, 4.84. Found: C, 50.09; H, 4.96.

12,13-Dibromo[2]metacyclo[2](2,5)thiophenophane (15e): colorless prisms (methanol); mp 124.5–125.0 °C; IR (KBr) ν (cm^{-1}) 2922, 1442, 1298, 1007, 795; ^1H NMR ($CDCl_3$) δ 2.35–2.47 (2 H, m), 2.66–2.84 (4 H, m), 3.29–3.49 (2 H, m), 5.97 (1 H, d, J = 1.5 Hz), 7.01 (2 H, dd, J = 1.5, 7.5 Hz), 7.20 (1 H, t, J = 7.5 Hz); MS *m/e* 370, 372, 374 [M^+]; UV (cyclohexane) λ_{max} (nm) (log ϵ) 282 (3.52). Anal. Calcd for $C_{14}H_{12}Br_2S$: C, 45.19; H, 3.25. Found: C, 45.38; H, 3.47.

12,13-Dibromo-8-fluoro[2]metacyclo[2](2,5)thiophenophane (15g): colorless prisms (methanol); mp 168.5–169.0 °C; IR (KBr) ν (cm^{-1}) 2934, 1456, 1179, 1011, 892, 790; ^1H NMR ($CDCl_3$) δ 2.39–2.62 (4 H, m), 3.28–3.42 (4 H, m), 6.95–7.02 (3 H, m); ^{19}F NMR ($CDCl_3$) δ 48.41 (s); MS *m/e* 388, 390, 392 [M^+]. Anal. Calcd for $C_{14}H_{11}Br_2FS$: C, 43.10; H, 2.84. Found: C, 43.53; H, 3.09.

6-*tert*-Butyl-1,4,10-trimethyl-2,3,8,9-tetrahydrobenzo[5,6]cycloocta[1,2-*c*]thiophene (17): colorless oil; IR (KBr) ν (cm^{-1}) 2954, 2918, 1478, 1362, 869; ^1H NMR ($CDCl_3$) δ 1.29 (9 H, s), 1.97 (3 H, d, J = 1 Hz), 2.15 (3 H, s), 2.28 (3 H, s), 2.58–2.62 (2 H, m), 2.64–2.75 (2 H, m), 2.99–3.02 (2 H, m), 3.09–3.12 (2 H, m), 6.96 (1 H, s), 6.96 (1 H, s); MS calcd for $C_{21}H_{28}S$ 312.1910, obsd 312.1913 [M^+].

1-(2,3,5-Trimethyl-2-thiopheneyl)-2-(5-*tert*-butyl-2,3-dimethylphenyl)ethane (19): determined by GC mass spectrum; MS *m/e* 139 (1266), 175 (134), 314 (235) [M^+].

7-*tert*-Butyl-9,10-dihydro-1,3,5-trimethyl-4*H*-benzo[4,5]cyclohepta[1,2-*c*]thiophene (18a): colorless prisms (methanol); mp 171.0–173.0 °C; IR (KBr) ν (cm^{-1}) 2960, 1485, 1148, 877; ^1H NMR ($CDCl_3$) δ 1.29 (9 H, s), 2.14 (3 H, s), 2.39 (3 H, s), 2.43 (3 H, s), 2.78 (2 H, t, J = 5 Hz), 3.19 (2 H, t, J = 5 Hz), 3.89 (2 H, s), 7.04 (1 H, d, J = 2 Hz), 7.07 (1 H, d, J = 2 Hz); MS *m/e* 298 [M^+]. Anal. Calcd for $C_{20}H_{26}S$: C, 80.48; H, 8.78. Found: C, 80.04; H, 8.96.

11,13-Dimethyl[2]metacyclo[2](3,4)thiophenophane (16): colorless prisms (methanol); mp 78.0–79.0 °C; IR (KBr) ν (cm^{-1}) 2912, 1431, 763, 722, 686, 483; ^1H NMR ($CDCl_3$) δ (syn) 2.10 (6 H, s), 2.40–2.49 (2 H, m), 2.75–2.90 (4 H, m), 3.29–3.36 (2 H, m), 6.44 (2 H, d, J = 7 Hz), 6.70 (1 H, t, J = 7 Hz), 7.68 (1 H, s); (anti) 1.15–1.25 (2 H, m), 2.38 (6 H, s), 2.62–2.68 (2 H, m), 2.75–2.90 (4 H, m), 6.90 (2 H, d, J = 7 Hz), 7.10 (1 H, s), 7.21 (1 H, t, J = 7 Hz); MS *m/e* 242 [M^+]; UV (cyclohexane) λ_{max} (nm) (log ϵ) 249 (3.84) (shoulder), 290 (2.79). Anal. Calcd for $C_{16}H_{18}S$: C, 79.29; H, 7.48. Found: C, 79.58; H, 7.52.

9,10-Dihydro-1,3,7-trimethyl-4*H*-benzo[4,5]cyclohepta[1,2-*c*]thiophene (18b): colorless oil; IR (KBr) ν (cm^{-1}) 2918, 1688, 1607, 1445, 1378; ^1H NMR ($CDCl_3$) δ 2.15 (3 H, s), 2.29 (3 H, s), 2.38 (3 H, s), 2.77 (2 H, t, J = 6 Hz), 3.05 (2 H, t, J = 6 Hz), 3.84 (2 H, s), 6.91–7.06 (3 H, m); MS calcd for $C_{16}H_{18}S$ 242.1128, obsd 242.1122 [M^+].

Treatment of 11b with BBr_3. To a solution of 100 mg (0.32 mmol) of **11b** in 6.0 mL of CH_2Cl_2 was added dropwise a solution of 400 mg (1.6 mmol) of BBr_3 in 1.0 mL of CH_2Cl_2, and the mixture was stirred 80 h at room temperature. The mixture was poured into ice–water, and the organic phase was separated, washed with brine, and dried ($MgSO_4$). After evaporation of the solvent, the residue was separated on silica gel column chromatography, and recrystallization of two fractions (hexane eluent) afforded 30 mg (34%) of **12a** and 3 mg (3%) of **13a**.

Reduction of 15e. To a solution of 100 mg (0.27 mmol) of **15e** in 5 mL of dry THF was added 1.0 mL (1.6 mmol) of 1.6 M *n*-BuLi in hexane at −70 °C, and the mixture was stirred for 1 h. To this reaction mixture was added 1.0 mL of 10% HCl, and the mixture was stirred for 1 h. The organics were extracted with Et_2O, washed with brine, and dried ($MgSO_4$). After evaporation of the solvent, the residue was separated on silica gel column chromatography, and recrystallization of two fractions (hexane eluent) afforded 29 mg (37%) of **15i** and 26 mg (45%) of **15h**.

[2]Metacyclo[2](2,5)thiophenophane (15h): colorless prisms (water–methanol); mp 97.5–99.0 °C; IR (KBr) ν (cm^{-1}) 2914, 2844, 1185, 915, 799; ^1H NMR ($CDCl_3$) δ 2.30–2.49 (4 H, m), 2.88–2.93 (2 H, m), 3.18–3.25 (2 H, m), 6.15 (1 H, t, J = 2 Hz), 6.88 (2 H, s), 6.97 (2 H, dd, J = 2, 7 Hz), 7.19 (1 H, t, J = 7 Hz); MS *m/e* 214 [M^+]. Anal. Calcd for $C_{14}H_{14}S$: C, 78.46; H, 6.58. Found: C, 78.41; H, 6.54.

12-Bromo[2]metacyclo[2](2,5)thiophenophane (15i): colorless prisms (water–methanol); mp 70.0–71.0 °C; IR (KBr) ν (cm^{-1}) 2918, 1163, 919, 791, 711, 545; ^1H NMR ($CDCl_3$) δ 2.30–2.46 (3 H, m), 2.66–2.83 (2 H, m), 2.92–2.97 (1 H, m), 3.15–3.30 (2 H, m), 6.14 (1 H, s), 6.85 (1 H, s), 6.98 (1 H, d, J = 7 Hz), 7.01 (1 H, d, J = 7 Hz), 7.20 (1 H, t, J = 7 Hz); MS *m/e* 292, 294 [M^+]. Anal. Calcd for $C_{14}H_{13}BrS \cdot {}^1/_5H_2O$: C, 56.65; H, 4.55. Found: C, 56.86; H, 4.56.

Crystallographic Section. 15c: $C_{19}H_{22}Br_2S$, Mw = 442.26; monoclinic; space group $P2_1/n$; a = 23.796 (6), b = 7.704 (1), and c = 9.870 (3) Å; α = 90.00°; β = 97.85°; γ = 90.00°; V = 1793 $Å^{-3}$; Z = 4; d_x = 1.642 g cm^{-3}.

Data collection: diffractometer, CAD4 (ENRAF-NONIUS); crystal size 0.2 × 0.2 × 0.2 mm; radiation, Mo Kα (0.710 73 Å), 26 mA, 50 kV; monochromator graphite; data collecting mode, $\omega - 2\theta$ scan, $2\theta_{max}$ = 56; reciprocal lattice segment, $-31 \le h \le 31$, $0 \le k \le 10$, $0 \le l \le 13$; number of reflections, 4887 (obserbed), 1904 ($I > 3\sigma(I)$); linear absorption coefficient, −0.0205%, spherical absorption collection was used (max 48.2%, min 49.1% transmission).

Structure analysis: solution direct method; method of refinement, full matrix, R = 0.029, R_w = 0.035; software, SDP (DEC PDP11/23 was used.).

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Supplementary Material Available: The spectral data (IR, NMR, MS) and elemental analyses of tetraoxides **7**, positional parameters and their estimated standard deviations and refined temperature factor expressions, bond distances, bond angles of X-ray crystallography of **6c**, *syn*- and *anti*-**6e**, **6j**, **6p**, **8b**, **11c**, **12a**, **13a**, **14a**, **15e**, and **16** (13 pages). Ordering information is given on any current masthead page.