Synthesis and Structure of [2$_4$](2,3,4,5)Thiophenophane (Superthiophenophane)

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The synthesis of [2$_4$](2,3,4,5)thiophenophane (superthiophenophane) (1), the first "ultimate" heterophane, was accomplished in five steps from 3,4-bis(chloromethyl)-2,5-dimethylthiophene. In the respective ^{13}C NMR spectra, the signals due to the thiophene ring carbons of 1 appear at lower field than do those of the corresponding carbons of 2,10-dithia[3.2.2.3](2,3,4,5)thiophenophane (5). This shift is elucidated as a compression effect between facial p-orbitals of the thiophene carbons. The UV spectra of the two thiophenophanes are, however, almost identical. The results of X-ray crystallographic analysis show that 1 is a more strained molecule than 5.

Introduction

The synthesis and characterization of many multibridged cyclophanes have been described.[1] These cyclophanes, the ultimate cyclophanes, in which all possible positions of the two benzene rings bridged by alkyl chains, are called "superphanes".[2] The first synthesis of [2$_6$]superphane was reported by Boekelheide and co-workers in 1979.[3] Since then, there have been many reports of the synthesis and characterization of the superphane.[4] Superphanes which incorporate aromatic rings other than benzene have also been described. For example, the synthesis and the structure of [4$_5$]superferrocenophane has only recently been reported.[5] Such compounds display interesting spectra and novel reactivities.[3,4] Syntheses of heterophanes have also been reported.[6] A few multibridged pyridinophanes are known.[7,8] However, multibridged heterophanes which incorporate five-membered heteroaromatic rings have not been described. This fact prompted us to synthesize [2$_4$](2,3,4,5)thiophenophane (superthiophenophane) (1), which is both the first example of a multibridged heterophane which incorporates five-membered rings and the first example of a superheterophane.

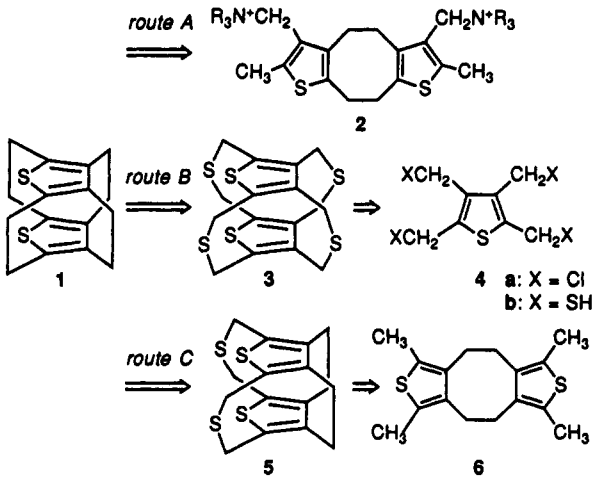
Results and Discussion

Synthesis of Superthiophenophane. It was expected that the synthesis of 1 would be accomplished by one of the three routes depicted in Scheme I.

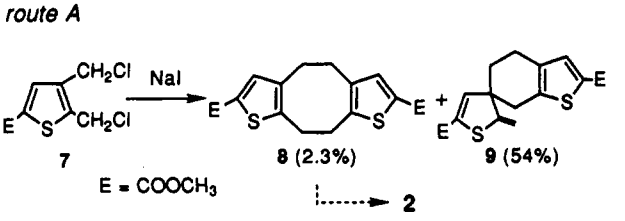
Route A. Dimerization of methyl 2,3-bis(chloromethyl)thiophene-5-carboxylate (7) on treatment with NaI afforded the corresponding [2.2](2,3)thiophenophane 8, which could be regarded as a precursor of the [2.2](2,3)-thiophenophane 2, but in only 2.3% yield. The spiro dimer 9 was the main product (Scheme II).[8] Because of the yield of 2 was so low, we gave up plans to synthesize 1 via route A.

Route B. Tetrakis(chloromethyl)thiophene (4a), a potential precursor of the tetrathiathiophenophane 3, was obtained by the chloromethylation of both thiophene (10) and 2-acetylthiophene (11) (Scheme III). Unfortunately, treatment of 4a with Na_2S under various conditions[9] af-

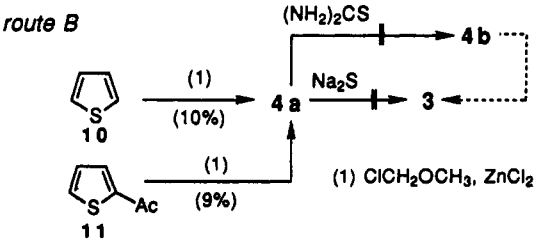
Scheme I



Scheme II



Scheme III



(1) For reviews, see: (a) Boekelheide, V. *Acc. Chem. Res.* **1980**, *13*, 65. (b) Kleinschroth, J.; Hopf, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 468. (c) Hopf, H. *Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic Press: New York, 1983; Chapter 9, p 521.

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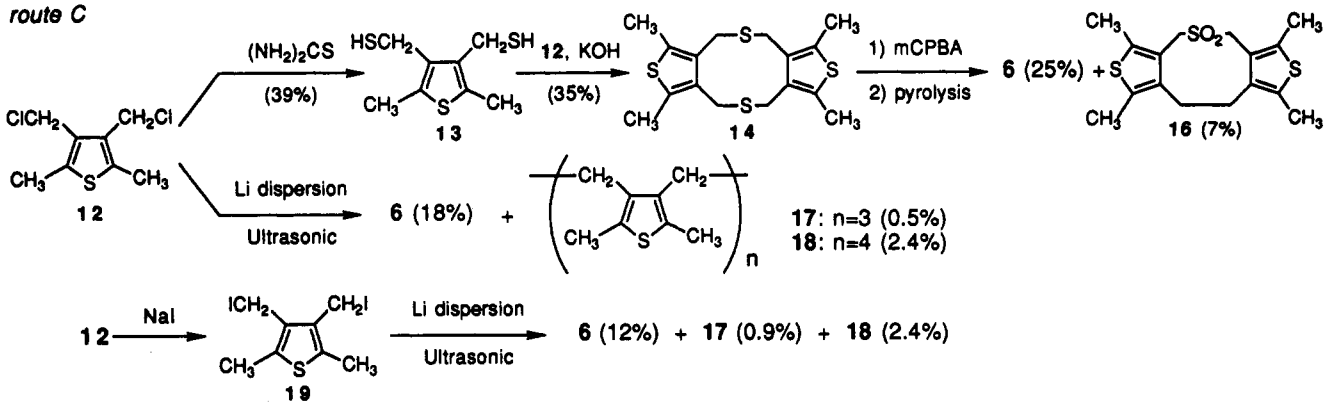
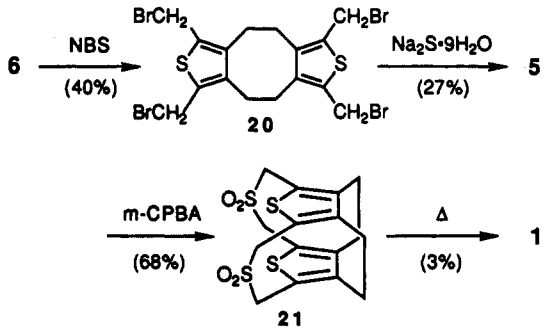
Scheme IV



Scheme V



forded no **3**. Attempts to thiolate **4a** by treating it with thiourea were also unsuccessful. The results indicate that route B could not be used for to prepare **1**.

Route C. A potential precursor of the dithiathiophenophane **5**, the [2.2](3,4)thiophenophane **6**, was synthesized in two ways: by the desulfurization of the dithia[3.3]phane **14** and by the coupling[10] of the chloromethylthiophene **12**[11] on treatment with Li (Scheme IV). Thus, the coupling of **12** and the (mercaptomethyl)thiophene **13** afforded dithia[3.3](3,4)thiophenophane **14** in 35% yield. Pyrolysis[12] of the disulfone **15** gave the [2.2](3,4)thiophenophane **6** (25%) and the monosulfone **16** (7%). The overall yield of **6** from **12** was only 3.3% (four steps). On the other hand, the coupling of **12** on treatment with lithium dispersion while the reaction mixture was irradiated with ultrasound[10] afforded **6**, the trimer **17**, and the tetramer **18** in yields of 18%, 0.5%, and 2.4%, respectively. Therefore, the latter method was used to prepare **6**. Although higher selectivity toward **6** was expected in the coupling of (iodomethyl)thiophene **19** with Li, a similar result was obtained.

Treatment of **6** with NBS in CH_2Cl_2 afforded the tetrakis(bromomethyl)thiophenophane **20** in 40% yield. Intramolecular cyclization of **20** on treatment with Na_2S in CH_2Cl_2/MeOH afforded the 2,10-dithia[3.2.2.3]thiophenophane **5** in 27% yield. Pyrolysis of the tetraoxide **21** (obtained in 68% yield by m-CPBA-oxidation of **5**) at 480 °C (1.5 Torr) afforded the superthiophenophane **1** in 3% yield (Scheme V).

The Spectra of the Superthiophenophane. The superthiophenophane **1** (colorless prisms from hexane) melts at 229–231 °C and decomposes at 315 °C.

Table I. Chemical Shifts of the Thiophene Ring Carbon of Thiophenophanes[a]

thiophenophane	thiophene carbon (δ, ppm)	Δδ (ppm)	
6	127.6, 137.3	0	
5	136.1, 138.4	−1–11	0
1	143.4, 145.8	6–18	5–9

[a] In $CDCl_3$, 27 °C, 68 MHz.

Table II. λ_{max} in the UV Spectra of the Thiophenophanes

thiophenophane[a]	λ_{max} (nm) (log ε)	thiophenophane[a]	λ_{max} (nm) (log ε)
22[b] (CH)	240 (3.85)	1 (CH)	268 (3.91)
6 (CH)	244 (4.05)	1 (CL)	270 (3.95)
5 (CH)	266 (3.40)		

[a] CH = in cyclohexane, CL = in $CHCl_3$. [b] 22: tetramethylthiophene.

Table III. Interplanar Distances and Torsional Angles in the Thiophenophanes 5 and 1

	5	1
d_1 (Å)	2.671	2.598
d_2 (Å)	3.223	2.757
d_3 (Å)	3.866	3.244
α (deg)	25.5	7.2
β (deg)	2.3	8.6
γ (deg)	10	24
δ (deg)	13	21

The ^1H NMR spectrum of a $CDCl_3$ solution of **1** at 27 °C shows four 4 H multiplets (AA'BB') which are assignable to the protons of the ethylene bridges. These four distinct signals suggest that the wobble[11,13] motions of ethylene bridges are restricted on the NMR time scale at this temperature. Because the ^1H NMR spectrum of the dithiathiophenophane **5** shows two doublets and two multiplets, the "wobbling" of the bridges of **5** is also slow.

The ^{13}C NMR spectrum of **1** shows signals due to two aliphatic carbons (26.71 and 30.09 ppm) and to two thiophene ring carbons (143.38 and 145.81 ppm) (Table I). The signals due to the thiophene carbons of **1** appear at about 7 ppm lower field than do those of **5** and at −1 to 11 ppm lower field than do those of **6**. These shifts can be explained in terms of the steric compression effect[14]

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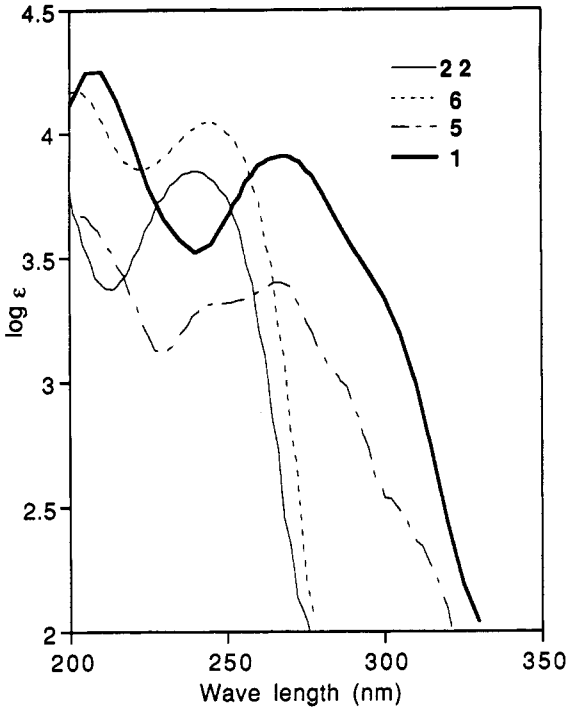

Figure 1. UV spectra of the thiophenophanes in cyclohexane solution.

between the p-orbitals of the thiophene ring carbons of thiophenophanes.

The UV spectra of the thiophenophanes are shown in Figure 1. A remarkable bathochromic shift (22 nm, λ_{max}) in the spectra of both **1** and **5** became evident when the spectra were compared with those of **6** and tetramethylthiophene (**22**) (Table II). The shift is evidence of either a transannular interaction[6b] of the two thiophene rings, an increased distortion of the planes of the two rings, or both. Interestingly, λ_{max} in the spectrum of **1** is only 1 nm greater than λ_{max} in the spectrum of **5**. Why this is so is still obscure because the intensity of the transannular interaction of the thiophene rings is probably similar in **1** and **5**.

Crystal Structure of the Thiophenophanes. ORTEP drawings and sectional views of the thiophenophanes **5** and **1** are shown in Figures 2 and 3. The interplanar distances and distortional angles are listed in Table III. The angle between the planes of the two thiophene rings of **5** (α) is 25.5°, and the planes of the thiophene rings are only slightly distorted (β = 2.3°). However, the angle between the two thiophene rings of **1** (α) is only 7.2° (18.3° less) and the thiophene rings of **1** are more distorted as β = 8.6° (6.3° greater than in **5**). This is caused by steric repulsion between the two sulfur atoms of the thiophene ring of **1**. The torsional angles between the thiophene ring and the ethylene bridge of **5** are 10° and 13° at the 2- (γ) and 3-position (δ), respectively, and those of **1** are 24° (γ) (14° greater) and 21° (δ) (8° greater). The more distorted thiophene ring and the larger torsional angles between the rings and the bridges of superthiophenophane (**1**) show that **1** is more strained than **5**.

Table IV. Results of the X-ray Crystallographic Analysis of 5 and 1

	5	1
formula	$C_{16}H_{16}S_4$	$C_{16}H_{16}S_2$
formula weight	336.6	272.4
crystal system	monoclinic	orthorhombic
space group	$C2/c$	$P2_12_12$
Z value	4	2
a, Å	14.057 (6)	7.655 (1)
b, Å	7.214 (7)	11.715 (2)
c, Å	14.879 (6)	7.268 (2)
β, deg	104.42 (3)	-
V, Å^3	1461.28	651.68
d_{calcd}, g/cm^3	1.530	1.388
diffractometer	AFC5	CAD4
radiation	Cu Kα	Cu Kα
λ, Å	1.540598	1.54184
temp, °C	23.0	19.0
scan method	$2\theta - \omega$	$\omega - 2\theta$
2θ range, deg	$5 < 2\theta < 120$	$2 \leq 2\theta \leq 65$
no. of reflns		
measured	2139	687
observed	1813	603
solution method	direct method	direct method
software	TEXSAN ver. 2.0	SDP
R value	0.049	0.045 17
R_w value	0.066	0.055 09

Experimental Section

General. Melting points are uncorrected. IR (KBr): JASCO IR-700. ^{1}H and ^{13}C NMR: JEOL GSX-270 (270 and 68 MHz) in $CDCl_3$, TMS as reference. UV: Hitachi 220A spectrophotometer. MS: JEOL JMS-01-SG-2 (75 eV). EA: Yanaco MT-5. Dry THF was distilled from Na/benzophenone under N_2. Wako-gel C-300 or Merck silica gel 60 was used for column chromatography. The source of ultrasound was a Kaijo Denki CA2480-III (45 kW, 38 kHz).

2,3,4,5-Tetrakis(chloromethyl)thiophene (4a). To a mixture of 32 g (0.24 mol) of $ZnCl_2$, 100 g (1.2 mol) of $ClCH_2OCH_3$, and

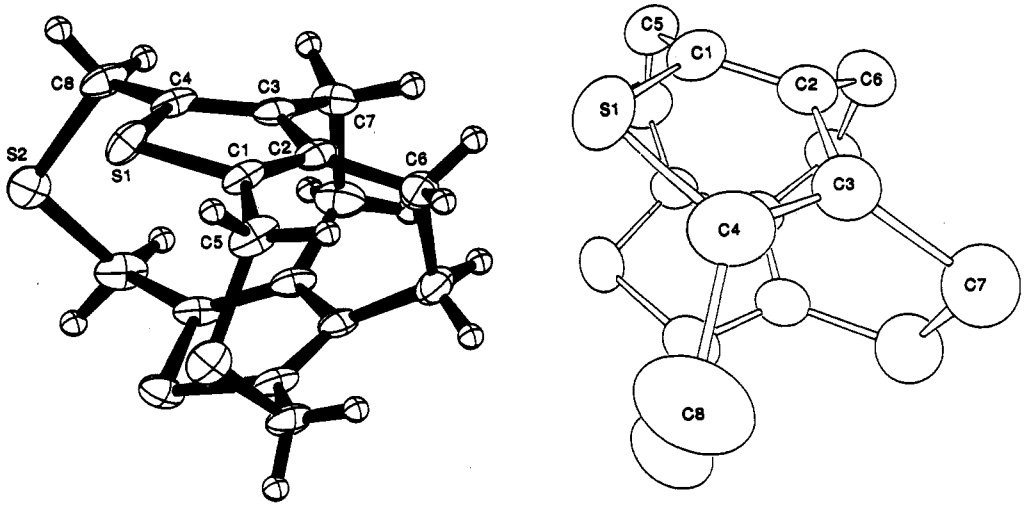

Figure 2. ORTEP drawings of thiophenophanes 5 and 1.

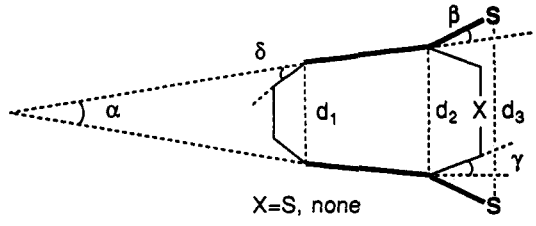

Figure 3. Sectional view of the thiophenophanes.

100 mL of $CHCl_3$ in an ice/water bath was added drop-by-drop a solution of 20 g (0.24 mol) of thiophene (**10**) in 20 mL of $CHCl_3$ over 15 min. The mixture was stirred for 6 h at rt, and then it was poured into ice/water. The organic phase was drawn off, washed with brine, and dried ($MgSO_4$). The solvent was evaporated, and the residue was subjected to column chromatography on silica gel (hexane). Concentration of the eluate and recrystallization of the residue afforded 6.7 g (24 mmol, 10%) of **4a**: colorless plates (hexane/PhH), mp 90 °C. IR: ν 1254, 1169, 1101, 682, 542 cm^{-1}. ^1H NMR: δ 4.60 (4 H, s), 4.70 (4 H, s). MS *m/e* 276, 278, 280, 282, 284 [M^+]. Anal. Calcd for $C_8H_8Cl_4S$: C, 34.56; H, 2.90. Found: C, 34.73; H, 2.91.

Compound **4a** (9% yield) was prepared from 2-acetylthiophene (**11**) in a manner similar to that described above.

5,7,13,15-Tetramethyl-2,10-dithia[3.3](3,4)thiophenophane (14). To a refluxing solution of 3.4 g (60 mmol) of KOH and 0.38 g (10 mmol) of $NaBH_4$ in 3.5 L of EtOH was added drop-by-drop a solution of 4.1 g (20 mmol) of 3,4-bis(chloromethyl)-2,5-dimethylthiophene (**12**)[11] and 4.0 g (20 mmol) of 2,5-dimethyl-3,4-bis(mercaptomethyl)thiophene (**13**)[15] in 200 mL of PhH/EtOH (1:1) over 24 h. The solvent was then distilled from the reaction mixture, and water was poured into the residue. The mixture was extracted with $CHCl_3$. The extract was washed with brine and dried ($MgSO_4$). The solvent was evaporated, and the residue was subjected to column chromatography on silica gel (hexane). Concentration of the eluate and recrystallization of the residue afforded 2.4 g (7.1 mmol, 35%) of **14** as colorless prisms (PhH/EtOH), mp 238-240 °C. IR: ν 1436, 1171, 739, 520 cm^{-1}. ^1H NMR: δ 2.43 (12 H, s), 3.58 (8 H, s). MS *m/e* 340 [M^+]. Anal. Calcd for $C_{16}H_{20}S_4$: C, 56.42; H, 5.92. Found: C, 56.66; H, 6.17.

5,7,13,15-Tetramethyl-2,10-dithia[3.3](3,4)thiophenophane 2,2,10,10-Tetraoxide (15). To a solution of 5.0 g (15 mmol) of **14** in 200 mL of CH_2Cl_2 was slowly added 21 g (120 mmol) of 80% *m*-CPBA. The mixture was stirred for 16 h at rt, and then 200 mL of MeOH was added. The precipitate that had formed was collected by filtration. The solid was washed with MeOH and hot $CHCl_3$ to afford 5.8 g (14 mmol, 98%) of **15** as a white powder, mp 290 °C dec. IR: ν 2922, 1701, 1439, 1320, 1240, 1126, 881, 826, 513, 462 cm^{-1}. Its ^1H NMR spectrum was not recorded because it was not soluble in any solvent tested. MS *m/e* 404 [M^+]. The tetroxide **15** was used at the next step without further purification.

Pyrolysis of 15. The pyrolysis of 500 mg (1.2 mmol) of **15** was carried out in a similar manner to that described in the literature,[12] at 550 °C (0.5–1.0 Torr). The product was extracted with CH_2Cl_2. The ash that was carried into the extract was removed by filteration. The solvent was evaporated from the filtrate, and the residue was subjected to column chromatography on silica gel (hexane/PhH (1:1)). Concentration of the first eluate and recrystallization of the residue afforded 82 mg (0.30 mmol, 25%) of **6**, and concentration of the second eluate and recrystallization of the residue afforded 30 mg (0.088 mmol, 7%) of **16**.

4,6,11,13-Tetramethyl[2.2](3,4)thiophenophane (6). Colorless prisms (hexane), mp 164.5–165 °C. IR: ν 2912, 2854, 2352, 1443, 1379, 1143, 909 cm^{-1}. ^1H NMR: δ 2.22 (12 H, s), 2.81 (8 H, s). UV (cyclohexane): λ_{max} (nm) (log ϵ) = 244 (4.05). MS *m/e* 276 [M^+]. Anal. Calcd for $C_{16}H_{20}S_2$: C, 69.51; H, 7.29. Found: C, 69.24; H, 7.18.

5,7,12,14-Tetramethyl-2-thia[3.2](3,4)thiophenophane 2,2-Dioxide (16). Colorless prisms ($CHCl_3$), mp 288 °C dec. IR: ν 1303, 1118, 879, 827, 448 cm^{-1}. ^1H NMR: δ 2.20–3.30 (4 H, br.s), 2.37 (6 H, s), 2.51 (6 H, s), 3.93 (4 H, s). MS *m/e* 340 [M^+]. Anal. Calcd for $C_{16}H_{20}O_2S_3$: C, 56.43; H, 5.92. Found: C, 56.38; H, 5.87.

Treatment of 12 with Li. To a suspension of 2.5 g (0.11 mol) of a 30% mineral oil dispersion of Li in 25 mL of dry THF under N_2 at rt was added, drop-by-drop, a solution of 10 g (48 mmol) of **12** in 100 mL of dry THF over 2 h. During the addition, the reaction mixture was irradiated with ultrasound. Ultrasonic irradiation was continued for 2 h, and then 20 mL of MeOH was slowly added to the mixture, cooling in an ice bath. Then 100 mL of benzene was added and the insoluble material that formed was filtered off. The filtrate was washed with water and brine and dried ($MgSO_4$). The solvent was evaporated, and the residue was extracted with refluxing hexane. The extract was concentrated, and the residue was subjected to column chromatography on silica gel (hexane; then hexane/PhH (1:1)). Concentration of the first eluate and recrystallization of the residue afforded 1.1 g (4.0 mmol, 18%) of **6**, and concentration of the second eluate and recrystallization of the residue afforded 160 mg (0.29 mmol, 2.4%) of **18**. The residue that remained after the extraction with hot hexane extract was also subjected to column chromatography on silica gel ($CHCl_3$). Concentration of the eluate and recrystallization of the residue afforded 33 mg (0.080 mmol, 0.5%) of **17**.

4,6,11,13,18,20-Hexamethyl[2.2.2](3,4)thiophenophane (17). Colorless prisms ($CHCl_3$), mp 370 °C dec. IR: ν 2912, 1470, 1437, 1145 cm^{-1}. ^1H NMR: δ 2.43 (18 H, s), 2.71 (12 H, s). MS *m/e* 414 [M^+]. Anal. Calcd for $C_{24}H_{30}S_3$: C, 69.51; H, 7.29. Found: C, 69.36; H, 7.24.

4,6,11,13,18,20,25,27-Octamethyl[2.2.2.2](3,4)thiophenophane (18). Colorless prisms (hexane/PhH), mp 265–266 °C. IR: ν 2912, 1447, 1144, 1101 cm^{-1}. ^1H NMR: δ 2.20 (24 H, s), 2.55 (16 H, s). MS *m/e* 552 [M^+]. Anal. Calcd for $C_{32}H_{40}S_4$: C, 69.51; H, 7.29. Found: C, 69.47; H, 7.30.

3,4-Bis(iodomethyl)-2,5-dimethylthiophene (19). A solution of 2.0 g (9.6 mmol) of **12** and 5.8 g (48 mmol) of NaI in 40 mL of acetone was stirred at rt for 16 h. The mixture was then poured into water, and the whole was extracted with CH_2Cl_2. The extract was washed with water and brine and was dried ($MgSO_4$). Evaporation of the solvent and recrystallization of the residue afforded 1.7 g (4.3 mmol, 46%) of **19** as colorless needles (hexane), mp 108–110 °C. IR: ν 2910, 1135, 542, 477 cm^{-1}. ^1H NMR: δ 2.23 (6 H, s), 4.28 (4 H, s). MS *m/e* 392 [M^+]. Anal. Calcd for $C_8H_{10}I_2S$: C, 24.51; H, 2.57. Found: C, 24.67; H, 2.80.

4,6,11,13-Tetrakis(bromoethyl)[2.2](3,4)thiophenophane (20). A solution of 1.6 g (5.8 mmol) of **6** and 5.2 g (29 mmol) of NBS in 150 mL of CH_2Cl_2 was stirred at rt for 2 h. The mixture was then poured into ice/water. The organic phase was drawn off, washed with brine, and dried ($MgSO_4$). The solvent was evaporated, and the residue was washed with CH_2Cl_2 (10 mL × 3) to give 1.4 g (2.4 mmol, 40%) of **20** as colorless prisms, mp 142 °C dec. IR: ν 1442, 1199, 900, 546 cm^{-1}. ^1H NMR: δ 3.09 (4 H, s), 4.61 (4 H, s). MS *m/e* 588, 590, 592, 594, 596 [M^+]. Anal. Calcd for $C_{16}H_{16}Br_4S_2$: C, 32.46; H, 2.27. Found: C, 32.10; H, 2.83.

2,10-Dithia[3.2.2.3](2,3,4,5)thiophenophane (5). To a vigorously stirred solution of 0.96 g (4.0 mmol) of $Na_2S{\cdot}9H_2O$ in 400 mL of MeOH/CH_2Cl_2 (3:1) at rt was added, drop-by-drop, a solution of 600 mg (1.0 mmol) of **20** in 400 mL of CH_2Cl_2 over 12 h. The mixture was stirred for an additional 36 h, and then water was added. The organic layer was drawn off and was washed with water and brine and dried ($MgSO_4$). The solvent was evaporated, and the residue was subjected to column chromatography on silica gel (hexane/PhH (1:1)). Concentration of the eluate and recrystallization of the residue afforded 90 mg (0.27 mmol, 27%) of **5** as colorless prisms (PhH), mp 255 °C dec. IR: ν 2956, 1475, 1408, 1248, 1096, 694 cm^{-1}. ^1H NMR: δ 2.65–2.84 (8 H, m, AA'BB', $-CH_2CH_2-$), 3.72 (4 H, d, J = 15 Hz, $-CH_2S-$), 4.13 (4 H, d, J = 15 Hz, $-CH_2S-$). ^{13}C NMR: δ 23.7, 30.8, 136.1, 138.4. UV ($CHCl_3$): λ_{max} (nm) (log ϵ) 266 (3.40), 242 (3.30, shoulder). MS *m/e* 336 [M^+]. Anal. Calcd for $C_{16}H_{16}S_4$: C, 57.10; H, 4.79. Found: C, 56.85; H, 4.90.

2,10-Dithia[3.2.2.3](2,3,4,5)thiophenophane 2,2,10,10-Tetraoxide (21). To a solution of 100 mg (0.30 mmol) of **5** in 50 mL of CH_2Cl_2 was added slowly 320 mg (1.8 mmol) of 80% *m*-CPBA. The mixture was stirred at rt for 12 h, and then the solvent was evaporated. The residue was washed with MeOH (10 mL × 3) to give 81 mg (0.20 mmol, 68%) of **21** as colorless needles (DMF/water), mp >300 °C. IR: ν 1304, 1132, 1117, 526, 505, 476

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cm^{-1}. ^{1}H NMR: δ 3.01–3.28 (8 H, m, AA'BB', $-CH_2CH_2-$), 4.07 (4 H, d, J = 15 Hz, $-CH_2S-$), 4.66 (4 H, d, J = 15 Hz, $-CH_2S-$); MS m/e 400 [M$^+$]. Anal. Calcd for $C_{16}H_{16}O_4S_4$: C, 47.98; H, 4.03. Found: C, 48.23; H, 4.18.

[2$_4$](2,3,4,5)Thiophenophane (Superthiophenophane) (1). The pyrolysis of 250 mg (0.63 mmol) of **21** was carried out in a manner similar to that described in the literature,[12] at 470 °C (1.5–2 Torr) for 5 min. The product was extracted with CH_2Cl_2. The ash that was carried into the extract was removed by filtration. The solvent was evaporated from the filtrate, and the residue was subjected to column chromatography on silica gel (hexane/CH_2Cl_2 (4:1)). Concentration of the eluate and recrystallization of the residue afforded 5.0 mg (0.018 mmol, 3%) of **1** as colorless prisms (hexane), mp 229–231 °C. IR: ν 2920, 1455, 1232, 1067, 532, 450 cm^{-1}. ^{1}H NMR: δ 2.46–2.88 (8 H, m, AA'BB', $-CH_2CH_2-$), 2.91–3.30 (8 H, m, AA'BB', $-CH_2CH_2-$); ^{13}C NMR: δ 26.7, 30.1, 143.4, 145.8. UV ($CHCl_3$): λ_{max} (nm) (log ε) 269 (3.95), 243 (3.79, shoulder). HRMS m/e 272.0693 [M$^+$] (100), calcd 272.0693 for $C_{16}H_{16}S_2$, 244 (17), 136 (73). Anal. Calcd for $C_{16}H_{16}S_2$: C, 70.54; H, 5.92. Found: C, 70.23; H, 5.93.

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Supplementary Material Available: Tables of positional parameters, their estimated standard deviations, refined temperature factor expressions, bond distances, and bond angles of X-ray crystallographic study of thiophenophanes **5** and **1** (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Reactions of Spiro[2.4]hept-4-ene Derivatives with Tetracyanoethylene. Extensive Rearrangements Involving the Aza-Cope Process[1]

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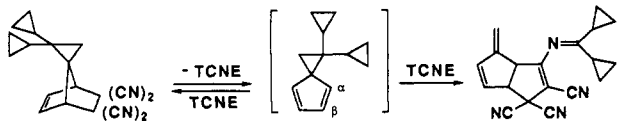
In CH_2Cl_2 or CH_3CN, 1,1-dicyclopropylspiro[2.4]hept-4-ene (**4a**) reacted readily with TCNE in a unique manner to give 4-[*N*-(dicyclopropylmethylene)amino]-6-methylenebicyclo[3.3.0]oct-3-ene-2,2,3-tricarbonitrile (**8a**), an imine after extensive rearrangements, and 3,3-dicyclopropylspiro[4.4]non-6-ene-1,1,2,2-tetracarbonitrile (**9a**), a [$_σ$2 + $_π$2] cycloadduct. In the reaction of 1-cyclopropyl-1-methyl derivative **4b**, 3-(1,1,2,2-tetracyanoethyl)-1-(2-cyclopropylallyl)cyclopentene (**10a**), formally a vinylogous homoene type adduct, was also produced in addition to **8b** and **9b**. The reaction of 1,1-dimethyl derivative **4c** produced **10b**, exclusively. The reaction of 1,1-dicyclopropylbenzo[*f*]spiro[2.4]hept-4-ene (**5a**) gave exclusively imine **11**, a benzoanalog of **8a**, whereas the reaction of saturated benzo derivatives **7** produced **15**, corresponding to **9**. The production of **8** (as well as **11**) and **10** might be depicted in a stepwise dipolar fashion, in which the first formed intermediate **17** will open its spiro-linked three-membered ring to give the second zwitterion **18**, which then either cyclizes to a nine-membered adduct **19** or undergoes a proton transfer to give **20**. **19** then undergoes aza-Cope rearrangement to afford **8**, and **20** ultimately tautomerizes to **10**. The parent spiroheptene **4d** gave merely a mixture of [$_π$2 + $_π$2] cycloadduct **14** and [$_σ$2 + $_π$2] cycloadduct **9c**. The formation of **8** and/or **10** is thus limited to occur in such vinylcyclopropanes that hold suitable pendant substituents which can provide greater stabilization to the zwitterionic intermediates. Even in the reaction of spiro[2.4]hepta-4,6-dienes with TCNE, 1,1-dicyclopropyl derivative **2a** produced a sizable amount of **3a**, corresponding to **8**, as well as **16a–16a'** in addition to the expected [$_π$4 + $_π$2] cycloadduct **1a**, whereas **2b–2c** produced simply the corresponding Diels–Alder adduct.

Introduction

In studying Diels–Alder reactions of spiro[2.4]hepta-4,6-diene derivatives, we have made the unexpected observation that Diels–Alder adduct **1a**, in which the spiro-linked cyclopropane is substituted by geminal cyclopropyl groups, undergoes isomerization at 50–80 °C to a bicyclic imine derivative **3a**.[2] Since this isomerization presumably



1a **2a** **3a**

proceeds via a retro-Diels–Alder reaction of **1a** followed by a reattack of tetracyanoethylene (TCNE) at the β position of spiroheptadiene **2a**,[2] we anticipated that the same type of transformation should occur with spiro[2.4]hept-4-enes **4**. In fact, the expected imine is formed readily in the reaction of *gem*-dicyclopropyl derivative **4a**, as well as in the reaction of its benzoanalog **5a**. In the

4a : $R^1 = R^2$ = c-Pr
4b : R^1 = c-Pr, R^2 = Me
4c : $R^1 = R^2$ = Me
4d : $R^1 = R^2$ = H

5a : R = c-Pr
5b : R = H

present paper, the results obtained in the reactions of **4a–d** and **5a–b**, as well as those of **2a–d**, are described, and the scope of the unique transformation to give the imine is presented.

Results and Discussion

Preparation of the Substrates. 2a–c were prepared in the reaction of appropriately substituted fulvenes[3] with

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(2) Nishida, S.; Asanuma, N.; Tsuji, T.; Imai, T. *Chem. Lett.* **1991**, 495.

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