6,7-Dimethyl-2-(trifluoromethyl)-4*H*-pyrazolo[1,5-*a*]benzimidazole (6f): white crystals, 98% yield, mp 212–213 °C (methanol–water); ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.65 (ws, 1 H, NH), 7.69 (s, 1 H, H-5), 7.31 (s, 1 H, H-8), 6.29 (s, 1 H, H-3), 2.35 (s, 6 H, Ar-Me); IR (KBr) 1570 cm^{-1}. Anal. Calcd for $C_{12}H_{10}F_3N_3$: C, 56.98; H, 3.98; N, 16.16. Found: C, 57.00; H, 3.74; N, 16.55.

2,3-Tetramethylene-4*H*-pyrazolo[1,5-*a*]benzimidazole (6g): brown crystals, 80% yield, mp 287–288 °C dec (methanol–water); ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.20 (s, 1 H, NH), 7.60 (dd, J = 7.54 Hz, 1 H, H-5), 7.35 (dd, J = 7.54 Hz, 1 H, H-8), 7.15 (m, 2 H, H-6, H-7), 2.70 (m, 2 H, CH_2), 2.58 (m, 2 H, CH_2), 1.79 (m, 4 H, CH_2CH_2); IR (KBr) 1620 cm^{-1}. Anal. Calcd for $C_{13}H_{13}N_3$: C, 73.90; H, 6.20; N, 19.89. Found: C, 73.78; H, 6.18; N, 20.03.

2,3-Tetramethylene-6,7-dimethyl-4*H*-pyrazolo[1,5-*a*]benzimidazole (6h): brown crystals, 92% yield, mp > 300 °C (methanol); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.16 (s, 1 H, H-5), 7.25 (s, 1 H, H-8), 2.61 (m, 2 H, CH_2), 2.50 (overlapped m, 2 H, CH_2), 2.33 (s, 6 H, Ar-Me), 1.74 (m, 4 H, CH_2CH_2); IR (KBr) 1650, 1570 cm^{-1}. Anal. Calcd for $C_{15}H_{17}N_3$: C, 75.27; H, 7.16; N, 17.56. Found: C, 75.48; H, 6.96; N, 17.38.

2,3-Dimethyl-4*H*-pyrazolo[1,5-*a*]benzimidazole (6i): brown crystals, 85% yield, mp 299–300 °C dec (methanol); ^{1}H NMR (60 MHz, DMSO-d_6) δ 11.2 (ws, 1 H, H-4), 7.7 (m, 1 H, H-5), 7.3 (m, 3 H, H-6, H-7, H-8), 2.3 (s, 3 H, Me), 2.1 (s, 3 H, Me); IR (KBr) 1620 cm^{-1}. Anal. Calcd for $C_{11}H_{11}N_3$: C, 71.32; H, 5.98; N, 22.68. Found: C, 71.08; H, 6.09; N, 22.30.

2,3,6,7-Tetramethyl-4*H*-pyrazolo[1,5-*a*]benzimidazole (6j): brown crystals, 88% yield, mp > 300 °C (ethanol); ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.24 (s, 1 H, H-5), 6.88 (s, 1 H, H-8), 2.32 (s, 6 H, Ar-Me), 2.29 (s, 3 H, Me), 2.00 (s, 3 H, Me); IR (KBr) 1630 cm^{-1}. Anal. Calcd for $C_{13}H_{15}N_3$: C, 73.20; H, 7.08; N, 19.70. Found: C, 73.45; H, 6.96; N, 19.60.

Acknowledgment. This work was supported by the Spanish CICYT (PA86-0317). C. R. also is indebted to CONACYT and SEP (México) for a grant.

Registry No. **1a**, 91323-05-6; **1b**, 121361-06-6; **1c**, 130436-32-7; **1d**, 130436-33-8; **1e**, 130436-34-9; **1f**, 130436-35-0; **1g**, 130436-36-1; **1h**, 130436-37-2; **1i**, 130436-38-3; **1j**, 130436-39-4; **1k**, 130436-40-7; **1l**, 130436-41-8; **2a**, 130436-42-9; **2b**, 130436-43-0; **2c**, 130436-44-1; **2d**, 130436-45-2; **3a**, 53745-42-9; **3b**, 130436-46-3; **3d**, 130436-47-4; **3e**, 130436-48-5; **3f**, 130436-49-6; **3g**, 130436-50-9; **3h**, 130436-51-0; **3i**, 130436-52-1; **4j**, 130436-53-2; **4k**, 130436-54-3; **5a**, 130436-55-4; **5b**, 130436-56-5; **5c**, 130436-57-6; **5d**, 130436-58-7; **6a**, 22501-82-2; **6b**, 130436-59-8; **6d**, 130436-60-1; **6e**, 130436-61-2; **6f**, 130436-62-3; **6g**, 130436-63-4; **6h**, 130436-64-5; **6i**, 130436-65-6; **6j**, 130436-66-7; 1,2-diaminobenzimidazole, 29540-87-2; 5,6-dimethyl-1,2-diaminobenzimidazole, 60882-73-7; 1-amino-2-(methylamino)-benzimidazole, 107879-46-9.

Synthesis and Reactions of 1,3,4,6-Tetra-2-thienylthieno[3,4-*c*]thiophene

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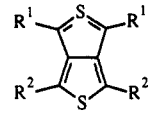
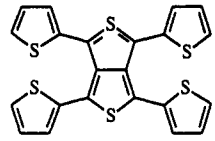
1,3,4,6-Tetra-2-thienylthieno[3,4-*c*]thiophene (**1f**) was synthesized from di-2-thenoylmethane after five steps. The cycloaddition reaction of **1f** with *N*-phenylmaleimide yielded a pair of exo (major) and endo (minor) adducts **7** and **8**, whose structures were assigned on the basis of the difference in the reactivity toward *m*-chloroperbenzoic acid. The reaction of **1f** with phenyl vinyl sulfoxide, dimethyl acetylenedicarboxylate, and di-2-thenoylacetylene gave benzo[*c*]thiophene derivatives **13**, **15**, and **16**, respectively.

Introduction

Although thieno[3,4-*c*]thiophenes, so-called "nonclassical" thienothiophenes, have been attracting much attention,[1] only a few thieno[3,4-*c*]thiophenes are known. The pioneering work in this field was done by Cava and co-workers, who reported the generation of transient 2,6-dimethyl (**1b**) and 2,6-bis(methoxycarbonyl) (**1c**)[2] and the synthesis of the first isolable 1,3,4,6-tetraphenyl derivatives (**1d**).[3] Afterward the synthesis and some reactions of an alternative type of thieno[3,4-*c*]-thiophenes, 1,3,4,6-tetrakis(alkylthio)thieno[3,4-*c*]-thiophenes (**1e**) were reported by Yoneda and co-workers.[4]





1a: $R^1 = R^2 = H$
b: $R^1 = CH_3$, $R^2 = H$
c: $R^1 = CO_2Me$, $R^2 = H$
d: $R^1 = R^2 = Ph$
e: $R^1 = R^2 = SR$

1f

Only recently we also reported the generation and characterization of the parent thieno[3,4-*c*]thiophene (**1a**).[5]

The title compound **1f** is of interest from the viewpoints of not only expanding the knowledge of thieno[3,4-*c*]-thiophenes but its chemical and physical properties because **1f** is formally composed by fusion of two molecules of α-terthiophenes at their central thiophene rings. α-Terthiophene is a compound of current interest due to its biological activities and as a starting material of electroconductive thiophene polymer.[6] We report here the

(1) (a) Cava, M. P.; Lakshmikantham, M. V. *Acc. Chem. Res.* **1975**, *8*, 139. (b) Litvinov, V. P.; Gol'dfarb, Ya. L. *Adv. Heterocycl. Chem.* **1976**, *19*, 123. (3) Cava, M. P.; Lakshmikantham, M. V. In *Comprehensive Heterocyclic Chemistry*; Bird, C. W., Cheeseman, G. W. H., Eds.; Pergamon Press: New York, 1984; Vol. 4, p 1037.

(2) (a) Cava, M. P.; Pollack, N. M. *J. Am. Chem. Soc.* **1967**, *89*, 3639. (b) Cava, M. P.; Pollack, N. M.; Dieterle, G. A. *Ibid.* **1973**, *95*, 2558.

(3) (a) Cava, M. P.; Husbands, G. E. M. *J. Am. Chem. Soc.* **1969**, *91*, 3952. (b) Cava, M. P.; Behforouz, M.; Husbands, G. E. M.; Srinivasan, M. *Ibid.* **1973**, *95*, 2561.

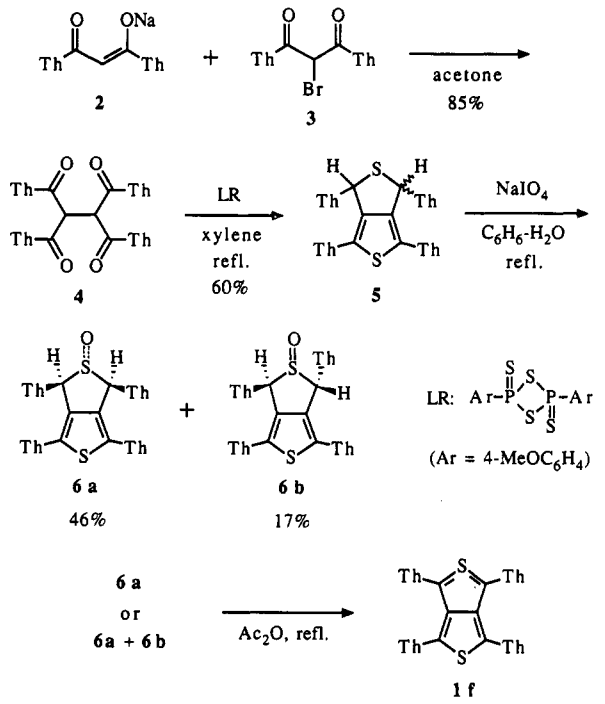
(4) (a) Yoneda, S.; Ozaki, K.; Inoue, T.; Sugimoto, A.; Yanagi, K.; Minobe, M. *J. Am. Chem. Soc.* **1985**, *107*, 5801. (b) Yoneda, S.; Tsubouchi, A.; Ozaki, K. *Nippon Kagaku Kaishi* **1987**, 1328. (c) Tsubouchi, A.; Matsumura, N.; Inoue, H.; Hamasaki, N.; Yoneda, S.; Yanagi, K. *J. Chem. Soc., Chem. Commun.* **1989**, 223. (d) Yoneda, S.; Ozaki, K.; Tsubouchi, A.; Kojima, H. *J. Heterocycl. Chem.* **1988**, *25*, 559. (e) Kobayashi, T.; Ozaki, K.; Yoneda, S. *J. Am. Chem. Soc.* **1988**, *110*, 1793.

(5) Nakayama, J.; Ishii, A.; Kobayashi, Y.; Hoshino, M. *J. Chem. Soc., Chem. Commun.* **1988**, 959.

(6) Nakayama, J.; Konishi, T.; Hoshino, M. *Heterocycles* **1988**, *27*, 1731. See also references cited therein.

0022-3263/91/1956-0078$02.50/0

Scheme I



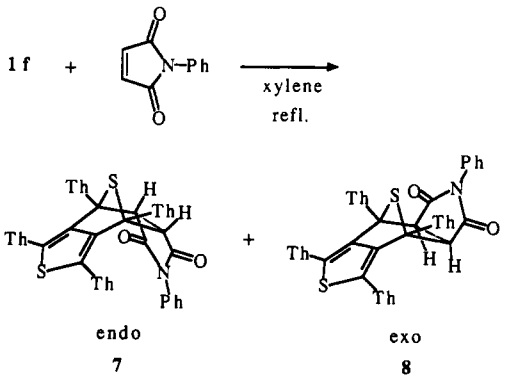
synthesis and some chemical and physical properties of **1f** (hereafter, Th denotes 2-thienyl in this paper).

Results and Discussion

Synthesis and Physical Properties of Tetra-2-thienylthieno[3,4-*c*]thiophene (1f). For the synthesis of **1f**, a method used for **1d** was applied with a small modification (Scheme I).[3b] The reaction of the sodium salt (**2**) of di-2-thenoylmethane and bromodi-2-thenoylmethane (**3**) in acetone gave 1,1,2,2-tetra-2-thenoylethane (**4**) in 85% yield. The sulfurization of **4** by Lawesson's reagent (LR)[7] in refluxing xylene yielded two isomeric 1,3-dihydrothieno[3,4-*c*]thiophenes **5** in 60% yield. In the ^1H NMR spectrum, two kinds of methine protons appear at δ 5.87 and 6.06 in the ratio of 7:3. The separation of the isomers was so difficult by chromatographic means that the mixture, without further purification, was oxidized with $NaIO_4$ in refluxing benzene–water. After chromatographic purification, two sulfoxides **6a** and **6b** were obtained in 46 and 17% yield, respectively. In the ^1H NMR spectrum, the methine protons of cis sulfoxide **6a** appear at δ 5.46, while those of trans sulfoxide **6b**, which are nonequivalent, appear at δ 5.51 and 5.93. Pummerer dehydration of the cis sulfoxide **6a** in refluxing acetic anhydride gave desired **1f** in 68% yield. The use of a mixture of two sulfoxides also satisfactorily afforded **1f** (84%).

Thienothiophene **1f** is dark purple crystals (mp 187–188 °C, recrystallized from Ac_2O) and stable for a long time in air at room temperature. In the ^1H and ^{13}C NMR spectra, four 2-thienyls are equivalent and two kinds of carbons composing the thieno[3,4-*c*]thiophene skeleton appear at δ 116.49 and 141.63. In the UV–vis spectrum an intense absorption maximum appears at 576 nm (log ϵ 4.10) with a bathochromic shift of ca. 20 nm from that of **1d** (λ_{max} 553 nm). The redox potential was measured by the cyclic voltammetry to know the electron-donating property of **1f**. The measurament was carried out in the range from 0 to +1 V in dichloromethane, because of the low solubility of **1f** in other solvents. Thus, a reversible wave was observed and the redox potential was +0.61 V vs Ag/Ag^+.

Cycloaddition Reaction of 1f. The reaction of **1f** with *N*-phenylmaleimide (NPM) in refluxing xylene gave two isomeric 1:1 adducts **7** and **8** in 7 and 62% yield, respectively. Each isomer is stable in xylene at 140 °C, although



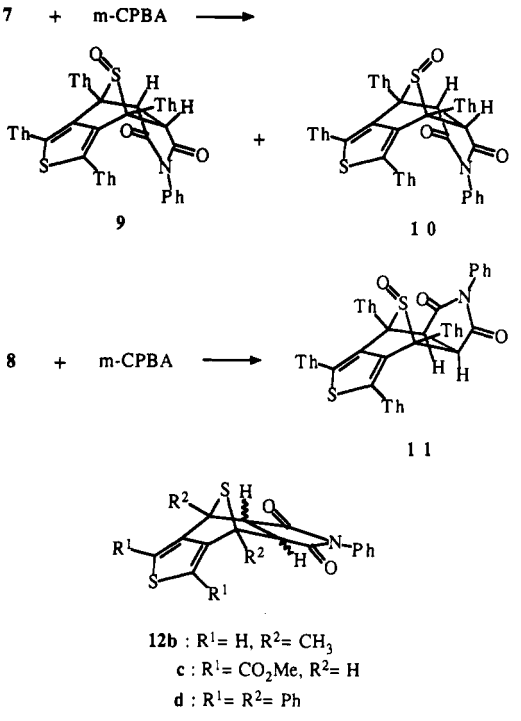
they decompose to **1f** and NPM when heated to above their melting points. The stereochemistry of the adducts was tentatively assigned on the basis of the difference in their reactivities toward *m*-chloroperbenzoic acid (*m*-CPBA). Thus, the reaction of endo isomer **7** with *m*-CPBA gave two isomeric sulfoxides **9** and **10**, the structures of which were assigned on the basis of the ^1H NMR chemical shifts of the exo protons; those of **10** resonate at lower field (δ 4.34) than those of **9** (δ 4.29) because of the larger deshielding effect of the syn sulfoxide group.[8] On the other hand, the reaction of exo isomer **8** with *m*-CPBA yielded sole sulfoxide **11**. These results are consistent with the following consideration: In the case of exo isomer **8**, the attack of *m*-CPBA takes place only from the opposite side of the *N*-phenylsuccimide ring to give a sole sulfoxide, while in the case of endo isomer **7** the steric interference due to exo protons is not so significant that two probable sulfoxides are given. Furthermore, although the protons α to the imide carbonyls of **9** and **10** resonate at lower field (δ 4.29 and 4.34, respectively) than those of **7** (δ 4.26) due to the deshielding effect of the sulfoxide bridge, the change of the chemical shifts of the corresponding protons between **8** and **11** are very small (δ 5.013 and 5.008, respectively) as expected from the structures of **8** and **11**.

By the way, Cava assingned the stereochemistry of the endo and exo adducts **12b–d**, formed by the reaction of **1b–d** with NPM, on the basis of the ^1H NMR data.[3b] That is to say, because of the deshielding effect of the sulfur bridge, the protons α to the imide carbonyls of an endo adduct appear at lower field than those of an exo adduct. If we follow this basis, our assignment of **7** and **8** is reverse. However, we believe that our assignment is supported by the experimental results mentioned above. The low-field shift of the endo protons of exo adduct **8** is probably due to the deshielding effect of a bridgehead 2-thienyl group,[3a] the rotation of which seems to be restricted considerably by another 2-thienyl group located at its peri position. Incidentally, the exo isomer **8** was formed as a major isomer. Since the consideration of the secondary orbital interaction between the frontier orbitals of thieno[3,4-*c*]thiophene[9] and NPM gives no prediction of the preference of the endo addition, this result is simply interpreted by

(7) (a) Pedersen, B. S.; Scheibye, S.; Nilsson, N. H.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 223. (b) For a recent review see: Cava, M. P.; Levinson, I. *Tetrahedron* **1985**, *41*, 5061.

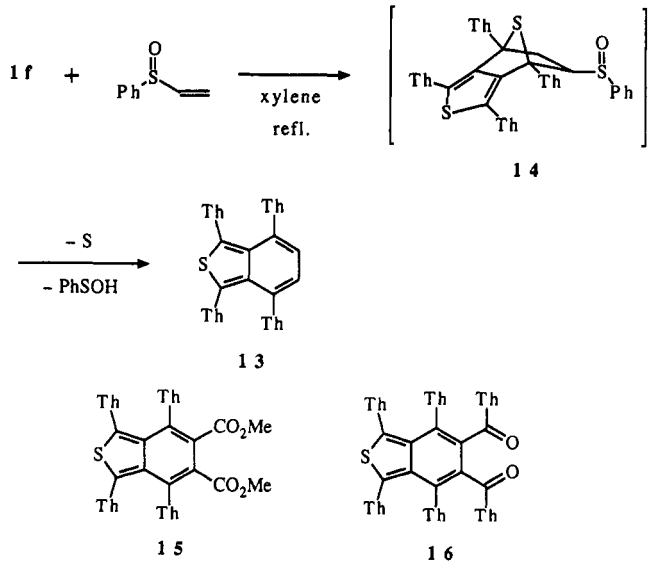
(8) Smith, D. J. H.; Finlay, J. D.; Hall, C. R. *J. Org. Chem.* **1979**, *44*, 4757.

(9) (a) Müller, C.; Schweig, A.; Cava, M. P.; Lakshmikantham, M. V. *J. Am. Chem. Soc.* **1976**, *98*, 7187. (b) Gleiter, R.; Bartetzko, R.; Brähler, G.; Bock, H. *J. Org. Chem.* **1978**, *43*, 3893.



the steric effect of 2-thienyl groups.

The reaction of **1f** with a large excess of phenyl vinyl sulfoxide (PVS) in refluxing xylene yielded tetra-2-thienylbenzo[*c*]thiophene (**13**) as yellow crystals, mp 272–273 °C, in 70% yield. Compound **13** is considered to be lead by the cycloaddition followed by the elimination of sulfur and benzenesulfenic acid from the initial adduct **14**. Similarly, the reaction of **1f** with dimethyl acetylenedicarboxylate (DMAD) and di-2-thenoylacetylene (DTA) gave benzo[*c*]thiophenes **15** and **16** as yellow crystals in 61 and 62% yield, respectively. Unlike the case of **1a**,[5]



the formation of the products derived from the further addition of PVS or DMAD to **13** or **15** was not observed. In any event, the rearomatization by loss of sulfur from an initial adduct is a common pathway in the reaction of thieno[3,4-*c*]thiophenes with acetylenic compounds.[3,4a]

Reaction of 1f with an Electron Acceptor. When dichloromethane solutions of **1f** and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were mixed at room temperature, brown powder (mp >360 °C) precipitated. The elemental analysis of the powder did not give the discrete ratio of **1f** to DDQ. Reaction of **1f** with tetracyanoquinodimethane or tetracyanotetrafluoroquinodimethane did not occur under similar conditions.

Experimental Section

General. Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H NMR spectra were obtained on a Bruker AM400 (400 MHz) or a JEOL FX-90Q (90 MHz) spectrometer and ^{13}C NMR spectra on a Bruker AM400 (100.6 MHz) or a JEOL FX-90Q (22.49 MHz) spectrometer using $CDCl_3$ as the solvent. IR spectra were taken on a Hitachi 270-50 spectrometer. UV–vis absorption spectra were taken on a Hitachi 340 spectrometer. Low- and high-resolution mass spectra were measured with a JEOL JMS-DX303 spectrometer operating at 70 eV in the EI mode. Dry column chromatography was performed with a 1:5 mixture of Merck Kieselgel 60 F_{254} (70–230 mesh) and Merck Kieselgel 60 (70–230 mesh) packed in a seamless cellulose tubing and visualized with a 254-nm UV lamp. Solutions were dried with anhydrous $MgSO_4$. Elemental analyses were performed by the Analytical Center of Saitama University, for which we thank Professor M. Sato, Mr. M. Kubo, and Mrs. E. Morikubo. Lawesson's reagent (LR) was prepared from anisole and phosphorus pentasulfide.[7a]

Di-2-thenoylmethane. This compound was prepared by the method used for dibenzoylmethane.[10] A solution of sodium ethoxide, prepared from sodium (1.79 g, 78 mmol) and anhydrous ethanol (40 mL), was added dropwise to a stirred mixture of 2-acetylthiophene (7.57 g, 60 mmol) and ethyl thiophene-2-carboxylate (29.05 g, 186 mmol) at 155 °C over a period of 1 h. After completion of the addition, the mixture was heated at that temperature for 0.5 h. The ethanol was removed under reduced pressure, and then the excess ethyl thiophene-2-carboxylate was removed in vacuo. The residual solid was treated with 85 mL of ice-cooled 4 M sulfuric acid and extracted with CH_2Cl_2 (2 × 100 mL). The combined extracts were washed with water, dried, and evaporated to a yellow solid. The solid was purified by sublimation at 100 °C (0.01 mmHg) to give 12.5 g (88%) of di-2-thenoylmethane:[11] mp 98 °C; ^{1}H NMR δ 6.52 (s, 1 H), 7.05–7.26 (m, 2 H), 7.53–7.80 (m, 4 H), 15.5 (br s, 1 H); IR (KBr) 3500, 3100, 1700–1500 (br), 1412, 1240, 1092, 1060, 850, 780, 752, 726, 700, 620, 562, 466 cm^{-1}.

Sodium Salt of Di-2-thenoylmethane (2). NaOH (2 M, 50 mL) was added to a stirred solution of di-2-thenoylmethane (2.36 g, 10 mmol) in CH_2Cl_2. The resulting yellow solid was collected by filtration, air-dried, and finally dried in vacuo to give 2.53 g (98%) of **2**.

Bromodi-2-thenoylmethane (3). A mixture of di-2-thenoylmethane (2.36 g, 10 mmol) and potassium acetate (1.16 g, 12 mmol) in acetic acid (50 mL) was stirred until the mixture had become homogeneous. To this was added dropwise bromine (1.72 g, 11 mmol) at room temperature. After the addition, the mixture was stirred for 0.5 h and then diluted with water (100 mL). The resulting white solid was collected by filtration, washed with water, air-dried, and finally dried in vacuo to give 3.07 g (97%) of **2**: mp 112 °C (EtOH); ^{1}H NMR δ 6.10 (s, 1 H), 7.03–7.30 (m, 2 H), 7.66–7.92 (m, 4 H); 1679, 1658 cm^{-1} (C=O). Anal. Calcd for $C_{11}H_7BrO_2S_2$: C, 41.92; H, 2.24. Found: C, 41.81; H, 2.36.

1,1,2,2-Tetra-2-thenoylethane (4). To a mixture of sodium salt **2** (2.63 g, 10.2 mmol) and bromide **3** (3.15 g, 10.0 mmol) was added acetone (100 mL), and the mixture was stirred at a temperature of an ice–salt bath for 1 h and then at room temperature overnight. The resulting white precipitates were collected by filtration and washed with water and then with a small amount of acetone to give 4.01 g (85%) of **4**: white powder; mp 270 °C dec (acetone); ^{1}H NMR (DMSO-d_6) δ 6.23 (s, 2 H), 7.23 (dd, J = 4.7, 4.0 Hz, 4 H), 8.05 (d, J = 4.7 Hz, 4 H), 8.20 (d, J = 4.0 Hz, 4 H); IR (KBr) 1670 cm^{-1} (C=O); HRMS calcd for $C_{22}H_{14}O_4S_4$ m/z 469.9775, found 469.9790.

1,3,4,6-Tetra-2-thienyl-1*H*,3*H*-thieno[3,4-*c*]thiophenes (5). A mixture of **4** (1.81 g, 3.85 mmol) and Lawesson's reagent (3.43 g, 8.47 mmol) in anhydrous xylene (50 mL) was refluxed for 3 h.

(10) Mangini, A.; McElvain, S. M. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 251.
(11) Lintvedt, R. L.; Holtzclaw, H. F., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 2713.

The resulting mixture was cooled to room temperature, washed with aqueous $NaHCO_3$ and then with water, dried, and evaporated under reduced pressure. The residue was subjected to dry column chromatography (silica gel, CCl_4) to give 1.09 g (60%) of **5**. Compound **5** thus obtained was a mixture of cis and trans isomers in the ratio 7:3, which could not be separated by chromatographic means: ^1H NMR δ 5.87 (s, 1.4 H), 6.06 (s, 0.6 H), 6.68–7.17 (m, 12 H); MS m/z (relative intensity) 470 (M^+, 100), 437 (33), 386 (27), 373 (31); HRMS calcd for $C_{22}H_{14}S_6$ m/z 469.9420, found 469.9402.

1,3,4,6-Tetra-2-thienyl-1*H*,3*H*-thieno[3,4-*c*]thiophene 2-Oxides (6a and 6b). A solution of **5** (655 mg, 1.4 mmol) in benzene (35 mL) and a solution of $NaIO_4$ (450 mg, 2 mmol) in water (6 mL) were combined, and to this was added MeOH (35 mL). The mixture was heated under reflux for 8 h. Benzene (50 mL) and water (50 mL) were added to the mixture cooled to room temperature. The mixture was stirred for a short period, and the benzene layer was separated, washed with water, dried, and evaporated. The residual solid was subjected to dry column chromatography (silica gel, $CHCl_3$) to give 314 mg (46%) of the cis isomer **6a** and 115 mg (17%) of the trans isomer **6b**. **6a**: colorless crystals; mp 215–216 °C (CCl_4); ^1H NMR δ 5.46 (s, 2 H), 6.8–7.2 (m, 12 H); ^{13}C NMR δ 69.3, 125.6, 126.4, 127.1, 127.3, 127.7, 128.1, 131.2, 134.3, 135.6, 139.7; IR (KBr) 1040 cm^{-1} (S=O); UV-vis ($C_2H_4Cl_2$) λ_{max} (nm) (log ϵ) 366 (4.63), 258 (4.64); MS m/z (relative intensity) 486 (M^+, trace), 468 (72), 438 (100). Anal. Calcd for $C_{22}H_{14}OS_6$: C, 54.29; H, 2.90. Found: C, 54.37; H, 2.96. **6b**: colorless crystals; mp 194–195 °C (CCl_4); ^1H NMR δ 5.51 (s, 1 H), 5.93 (s, 1 H), 6.8–7.4 (m, 12 H); ^{13}C NMR δ 60.7, 65.6, 126.4, 126.5, 126.7, 126.8, 127.1, 127.51, 127.52, 127.58, 127.64, 127.65, 128.6, 129.4, 131.5, 131.96, 132.02, 133.6, 133.7, 134.7, 135.6, 135.8; IR (KBr) 1042 cm^{-1} (S=O); UV-vis ($C_2H_4Cl_2$) λ_{max} (nm) (log ϵ) 354 (4.64), 256 (4.68); MS m/z (relative intensity) 486 (M^+, trace), 468 (72), 438 (100).

1,3,4,6-Tetra-2-thienylthieno[3,4-*c*]thiophene (1f). The sulfoxide **6a** (195 mg, 0.4 mmol) was heated in acetic anhydride (5 mL) under reflux for 4 h under N_2. The resulting purple mixture was evaporated under reduced pressure, and the dark purple residue was chromatographed on a short column of silica gel. Elution with CCl_4 gave 127 mg (68%) of **1f** as a dark purple solid. The use of a mixture of **6a** and **6b** also satisfactorily afforded **1f** (84%). **1f**: dark purple crystals; mp 187–188 °C (Ac_2O); ^1H NMR δ 6.86 (dd, J = 3.7, 1.0 Hz, 4 H), 6.90 (dd, J = 5.1, 3.7 Hz, 4 H), 7.22 (dd, J = 5.1, 1.0 Hz, 4 H); ^{13}C NMR δ 116.49 (s), 126.15 (s), 127.16 (d), 128.06 (d), 134.05 (s), 141.63 (s); IR (KBr) 3100 (w), 1512 (w), 1218 (m), 850 (m), 830 (m), 814 (m), 688 (s), 490 (m) cm^{-1}; UV-vis ($C_2H_4Cl_2$) λ_{max} (nm) (log ϵ) 576 (4.10), 335 (sh, 3.73), 285 (4.32), 234 (4.24); MS m/z (relative intensity) 468 (M^+, 100), 436 (17); HRMS calcd for $C_{22}H_{12}S_6$ m/z 467.9264, found 467.9299. Anal. Calcd for $C_{22}H_{12}S_6$: C, 56.38; H, 2.58; S, 41.04. Found: C, 56.08; H, 2.79; S, 40.47.

Reaction of 1f with *N*-Phenylmaleimide (NPM). A mixture of **1f** (100 mg, 0.21 mmol) and NPM (37 mg, 0.21 mmol) in xylene (10 mL) was refluxed for 3 h under N_2. The mixture was evaporated under reduced pressure, and the residue was subjected to dry column chromatography (silica gel, CH_2Cl_2–CCl_4, 3:2) to give 83 mg (62%) of the exo adduct **8** and 9 mg (7%) of the endo adduct **7**. **8**: colorless crystals; mp 282–283 °C dec (CH_3CN–$CHCl_3$); ^1H NMR δ 5.01 (s, 2 H), 6.64–6.68 (m, 4 H), 6.86–6.90 (m, 4 H), 7.11 (dd, J = 4.8, 1.4 Hz, 2 H), 7.16 (d, J = 4.9 Hz, 2 H), 7.28–7.34 (m, 3 H), 7.64 (d, J = 2.8 Hz, 2 H); IR (KBr) 3100 (w), 2950 (w), 1720 (s), 1506 (m), 1384 (s), 1190 (s), 848 (m), 796 (m), 704 (s) cm^{-1}; MS m/z (relative intensity) 641 (M^+, 43), 468 (100). Anal. Calcd for $C_{32}H_{19}NO_2S_6$: C, 59.88; H, 2.98; N, 2.18. Found: C, 59.72; H, 3.07; N, 2.03. **7**: white solid; mp 252 °C dec (after chromatographic purification); ^1H NMR δ 4.26 (s, 2 H), 6.45 (dd, J = 3.6, 0.9 Hz, 2 H), 6.75 (dd, J = 5.1, 3.6 Hz, 2 H). 6.79 (dd, J = 5.0, 3.7 Hz, 2 H), 7.13–7.19 (m, 5 H), 7.29–7.37 (m, 4 H); MS m/z (relative intensity) 641 (M^+, 70), 468 (100); HRMS calcd for $C_{32}H_{19}NO_2S_6$ m/z 640.9741, found 640.9719.

Reaction of Endo Adduct 7 with *m*-CPBA. To a solution of **7** (9.9 mg, 0.015 mmol) in $CHCl_3$ (3 mL) was added *m*-CPBA (>70%, 4.0 mg, >0.016 mmol) in $CHCl_3$ at −50 °C. The solution was warmed to room temperature and stirred for 12 h. To the mixture were added CH_2Cl_2 and 10% Na_2CO_3. The organic layer was separated, dried, and evaporated. The yellow residue was subjected to dry column chromatography (silica gel, CH_2Cl_2) to give sulfoxides **9** (6.5 mg, 64%) and **10** (6.4 mg, containing impurities). **9**: yellow powder; mp 271–273 °C dec (CCl_4–CH_3CN); ^1H NMR δ 4.29 (s, 2 H), 6.52 (dd, J = 3.6, 1.0 Hz, 2 H), 6.74 (dd, J = 5.1, 3.6 Hz, 2 H), 6.85 (dd, J = 5.2, 3.7 Hz, 2 H), 7.17–7.21 (m, 6 H), 7.35–7.44 (m, 3 H), 7.64 (dd, J = 3.7, 1.0 Hz, 2 H); IR (KBr) 3065 (w), 2910 (m), 1704 (s), 1484 (m), 1364 (s), 1182 (s), 1078 (s, S=O), 822 (m), 682 (s); MS m/z (relative intensity) 657 (M^+, 7), 641 (7), 607 (100); HRMS calcd for $C_{32}H_{19}NO_3S_6$ m/z 656.9689, found 656.9699. **10**: yellow crystals, mp 263–266 °C dec (CCl_4–CH_3CN); ^1H NMR δ 4.34 (s, 2 H), 6.56, (dd, J = 3.6, 1.1 Hz, 2 H), 6.78 (dd, J = 5.2, 3.6 Hz, 2 H), 6.88 (dd, J = 5.2, 3.7 Hz, 2 H), 7.17–7.24 (m, 6 H), 7.34–7.38 (m, 3 H), 7.75 (dd, J = 3.7, 1.0 Hz, 2 H); IR (KBr) 3090 (w), 2900 (m), 1708 (s), 1482 (m), 1376 (s), 1186 (s), 1082 (s, S=O), 834 (m), 688 (s) cm^{-1}; MS m/z (relative intensity) 657 (M^+, 11), 641 (11), 607 (100); HRMS calcd for $C_{32}H_{19}NO_3S_6$ m/z 656.9689, found 656.9708.

Reaction of Exo Adduct 8 with *m*-CPBA. To a solution of **8** (28.6 mg, 0.0446 mmol) in CH_2Cl_2 (5 mL) was added *m*-CPBA (>70%, 11.0 mg, >0.045 mmol) in CH_2Cl_2 (2 mL) at −50 °C. The solution was warmed to room temperature, and to this were added CH_2Cl_2 and aqueous $NaHCO_3$. The organic layer was separated, dried, and evaporated. The pale yellow residue was purified by dry column chromatography (silica gel, CH_2Cl_2) to give sulfoxide **11** (23.5 mg, 80%). **11**: yellow crystals; mp 290–291 °C dec (CH_3CN–CH_2Cl_2); ^1H NMR δ 5.01 (s, 2 H), 6.71 (dd, J = 4.8, 3.7 Hz, 2 H), 6.74 (dd, J = 3.7, 1.0 Hz, 2 H), 6.82–6.86 (m, 2 H), 6.94 (dd, J = 5.2, 3.7 Hz, 2 H), 7.19 (dd, J = 4.8, 1.0 Hz, 2 H), 7.23 (dd, J = 5.2, 0.8 Hz, 2 H), 7.28–7.34 (m, 3 H), 7.53 (dd, J = 3.7, 0.8 Hz, 2 H); IR (KBr) 2915 (w), 1724 (s), 1512 (w), 1384 (s), 1194 (s), 1098 (s, S=O), 858 (m), 702 (s) cm^{-1}; MS m/z (relative intensity) 657 (M^+, 13), 641 (trace), 609 (100), 462 (32); HRMS calcd for $C_{32}H_{19}NO_3S_6$ m/z 656.9689, found 656.9717. Anal. Calcd for $C_{32}H_{19}NO_3S_6$: C, 58.42; H, 2.91; N, 2.13. Found: C, 58.27; H, 2.96; N, 2.09.

Reaction of 1f with Phenyl Vinyl Sulfoxide (PVS). A mixture of **1f** (47.3 mg, 0.1 mmol) and PVS (80 mg, 0.52 mmol) in xylene (10 mL) was heated under reflux for 5 h under N_2. For the completion of the reaction, an additional amount of PVS (0.3 mmol) was added after 2 and 4 h, respectively. The mixture was evaporated under reduced pressure and purified by dry column chromatography (silica gel, CCl_4) to give 33 mg (70%) of 1,3,4,7-tetra-2-thienylbenzo[*c*]thiophene (**13**): yellow crystals; mp 272–273 °C (CH_2Cl_2–hexane); ^1H NMR δ 6.66 (dd, J = 3.4, 0.9 Hz, 2 H), 6.69–6.73 (m, 4 H), 6.76 (dd, J = 5.2, 3.4 Hz, 2 H), 7.11 (dd, J = 4.9, 1.1 Hz, 2 H), 7.16 (dd, J = 5.2, 0.9 Hz, 2 H), 7.18 (s, 2 H); ^{13}C NMR δ 124.8, 126.6, 126.82, 126.84, 127.5, 127.9, 128.36, 128.41, 128.8, 134.3, 135.5, 141.1, UV-vis (CH_2Cl_2) λ_{max} (nm) (log ϵ) 412 (4.35), 255 (4.70); m/z (relative intensity) 462 (M^+, 100), 429 (24). HRMS calcd for $C_{24}H_{14}S_5$ m/z 461.9699, found 461.9679.

Reaction of 1f with Dimethyl Acetylenedicarboxylate (DMAD). A mixture of **1f** (64.2 mg, 0.137 mmol) and DMAD (57.8 mg, 0.406 mmol) in xylene (10 mL) was refluxed for 9 h under N_2. For the completion of the reaction, an additional amount of DMAD (2 mmol) was added after 3 and 6 h, respectively. The mixture was evaporated under reduced pressure, and the residue was subjected to dry column chromatography (silica gel, CCl_4) to give 49 mg (61%) of 5,6-bis(methoxycarbonyl)-1,3,4,7-tetra-2-thienylbenzo[*c*]thiophene (**15**): yellow crystals; mp 277–277.5 °C (CH_2Cl_2–hexane); ^1H NMR δ 3.54 (s, 6 H), 6.58 (dd, J = 3.5, 0.9 Hz, 2 H), 6.72 (dd, J = 5.1, 3.5 Hz, 2 H), 6.74 (dd, J = 5.0, 3.5 Hz, 2 H), 6.85 (dd, J = 3.5, 1.0 Hz, 2 H), 7.14 (dd, J = 5.1, 0.9 Hz, 2 H), 7.16 (dd, J = 5.0, 1.0 Hz, 2 H); ^{13}C NMR δ 52.3 (q), 126.2 (d), 127.0 (d), 127.1 (d), 127.2 (d), 128.0 (d), 129.2 (d), 129.3 (d) 130.3 (s), 131.1 (s), 133.8 (s), 134.0 (s), 137.1 (s), 168.4 (s); IR (KBr) 1736 cm^{-1} (C=O); UV-vis (CH_2Cl_2) λ_{max} (nm) (log ϵ) 414 (4.36), 262 (4.87); MS m/z (relative intensity) 578 (M^+, 100); HRMS calcd for $C_{28}H_{18}O_4S_5$ m/z 577.9809, found 577.9811. Anal. Calcd for $C_{28}H_{18}O_4S_5$: C, 58.11; H, 3.13. Found: C, 58.04; H, 3.17.

Preparation of Di-2-thenoylacetylene (DTA). To a solution of 1,2-dibromo-1,2-di-2-thenoylethane[12] (0.364 g, 0.89 mmol) in CH_2Cl_2 (20 mL) was added a solution of triethylamine (0.365 g,

(12) Kooreman, H. J.; Wynberg, H. *Recueil* **1967**, *86*, 37.

3.6 mmol) in CH_2Cl_2 (2 mL) at 0 °C. The mixture was warmed to room temperature and stirred overnight. The mixture was washed with dilute HCL, aqueous Na_2CO_3, and water, in this order. The solution was dried and evaporated, and the residue was subjected to dry column chromatography (silica gel, CH_2Cl_2–CCl_4, 3:1) to give 0.121 g (55%) of DTA: colorless crystals; mp 137–138 °C (EtOH); ^1H NMR δ 7.23 (t, J = 4.4 Hz, 2 H), 7.83 (dd, J = 4.8, 0.9 Hz, 2 H), 8.04 (dd, J = 3.8, 0.9 Hz, 2 H); ^{13}C NMR δ 83.4 (s), 128.8 (d), 136.7 (d), 136.9 (d), 143.7 (s), 168.0 (s); IR (KBr) 1640 cm^{-1} (C=O); MS m/z (relative intensity) 246 (M^+, 45), 190 (29), 135 (28), 111 (100), 83 (18). Anal. Calcd for $C_{12}H_6O_2S_2$: C, 58.52; H, 2.46. Found: C, 58.37; H, 2.62.

Reaction of 1f with Di-2-thenoylacetylene (DTA). A mixture of **1f** (0.296g, 0.632 mmol) and DTA (0.187 g, 0.76 mmol) in xylene (50 mL) was refluxed for 6 h under N_2. The mixture was cooled to room temperature and evaporated. The dark-purple residue was subjected to dry column chromatography (silica gel, CH_2Cl_2–CCl_4, 1:1 and then 2:1) to give 41 mg of unreacted **1f** and 265 mg (62%) of 5,6-di-2-thenoyl-1,3,4,7-tetra-2-thienylbenzo[c]thiophene (**16**). **16**: yellow crystals; mp 310–311 °C (CH_2Cl_2–hexane); ^1H NMR δ 6.54 (br s, 2 682 (dd, J = 3.7, 0.9 Hz, 2 H), 6.71 (dd, J = 5.2, 3.7 Hz, 2 H), 6.85 (br s, 4 H), 6.95 (d, J = 4.2 Hz, 2 H), 7.15 (dd, J = 5.2, 0.9 Hz, 2 H), 7.34 (d, J = 3.2 Hz, 2 H), 7.45 (d, J = 4.6 Hz, 2 H); IR (KBr) 1660 cm^{-1} (C=O); UV-vis (CH_2Cl_2) λ_{max} (nm) (log ϵ) 423 (4.18), 295 (4.70), 250 (sh, 4.75); MS m/z (relative intensity) 682 (M^+, 100); HRMS calcd for $C_{34}H_{18}O_2S_7$ m/z 681.9352, found 681.9360. Anal. Calcd for $C_{34}H_{18}O_2S_7$: C, 59.80; H, 2.66. Found: C, 59.08; H, 2.80.

Reaction of 1f and 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). To a degassed solution of DDQ (19.4 mg, 0.085 mmol) in CH_2Cl_2 (10 mL) was added degassed solution of **1f** (40.0 mg, 0.085 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred at room temperature overnight. By filtration of the mixture, 8.3 mg of black precipitates were collected. Adding hexane to the filtrate yielded an additional amount (0.9 mg) of the brown powder: mp >360 °C. Anal. Found: C, 45.06; H, 1.64; N, 7.12.

Syntheses of Monometalated and Unsymmetrically Substituted Binuclear Phthalocyanines and a Pentanuclear Phthalocyanine by Solution and Polymer Support Methods

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Binuclear phthalocyanines in which two different phthalocyanine nuclei are covalently linked through five-atom bridges, derived from 2-ethyl-2-methylpropane-1,3-diol, are prepared. In the examples, one phthalocyanine ring is always substituted with neopentoxy substituents, while the other phthalocyanine ring is unsubstituted or contains *tert*-butyl substituents or a neopentoxy-substituted copper phthalocyanine, constituting a binuclear phthalocyanine in which only one ring is metalated. The precursor, 2-(2-(hydroxymethyl)-2-methylbutoxy)-9,16,23-trineopentoxyphthalocyanine was prepared in solution and also by solid-phase methods, using polymer-bound trityl chloride derived from a 1% divinylbenzene-co-styrene copolymer. A metal-free pentanuclear phthalocyanine, in which four phthalocyaninyl groups are covalently bound to the four benzo groups of a central phthalocyanine nucleus, is described and characterized by FAB mass spectroscopy. In some experiments some rare examples of demetalation of some zinc phthalocyanines are noted during phthalocyanine formation. A modified flash chromatography procedure proved to be useful for separating similarly substituted mononuclear phthalocyanines.

Using face-to-face porphyrin dimers, held together by a pair of covalent amide bridges[1,2] or by a single rigid aromatic bridge,[3,4] the four-electron reduction of dioxygen to water, without forming free hydrogen peroxide, has been achieved. In most examples, it was the dicobalt porphyrin dimers that were the active catalysts. Collman et al.[5] have shown that a mixed metal cobalt–silver cofacial porphyrin dimer may also be an interesting catalyst.

As the porphyrin dimer catalysts tend to decompose after several cycles, we have been attempting to find similar catalysts that would be more stable under similar conditions. To this end we have prepared, for the first time, a whole series of binuclear phthalocyanines[6-8] (Pcs), covalently linked by 5, 4, 3, 2, 1, 0 and "–1" bridges and a unique tetranuclear phthalocyanine.[9] To date, however, none of the multinuclear Pcs have achieved the desired four-electron of O_2, although the two-electron reduction of many of the multinuclear Pcs have been more efficient[9,10] relative to simple mononuclear Pcs. Perhaps, this fact is not too surprising as only a very few of the porphyrin dimers prepared by Collman's group[1,2] were good catalysts and it is difficult to predict the exact cofacial

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