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Synthesis and Properties of 1,8-Di(2-thienyl)-, 1,8-Bis(5,2'-bithiophene-2-yl)-, 1,8-Bis(5,2':5',2"-terthiophene-2-yl)-, and 1,8-Bis(5,2':5',2":5",2"'-quaterthiophene-2-yl)naphthalenes and Related Compounds

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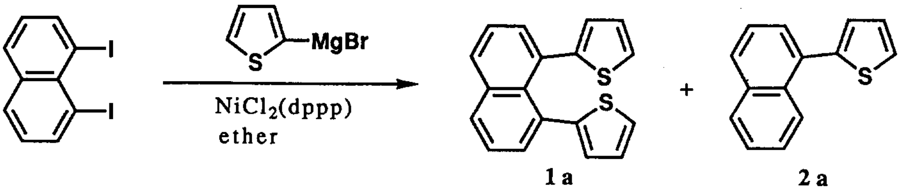
Abstract: 1,8-Di(2-thienyl)-, 1,8-bis(5,2'-bithiophene-2-yl)-, 1,8-bis(5,2':5',2"-terthiophene-2-yl)-, and 1,8-bis-(5,2':5',2":5",2"'-quaterthiophene-2-yl)naphthalenes (**1a**, **1b**, **1c**, and **1d**, respectively) were synthesized starting from 1,8-dibromonaphthalene by application of $NiCl_2$(dppp)-catalyzed coupling of aryl bromides with thienylmagnesium bromides. For comparison with these compounds, 1-(2-thienyl)-, 1-(5,2'-bithiophene-2-yl)-, 1-(5,2':5',2"-terthiophene-2-yl)-, and 1-(5,2':5',2":5",2"'-quaterthiophene-2-yl)naphthalenes (**2a-d**) were also prepared. Inspection of ^1H and ^{13}C NMR and UV/Vis data of **1a-d** and **2a-d** including X-ray single crystal structure data of **1b** suggests that the planes of two oligothiophene units of **1a-d** are approximately parallel to each other and are at large angles to the naphthalene ring. In accordance with these findings, CV oxidation potential data show that the radical cations formed from **1a-d** are stabilized by intramolecular electron transfer interaction of the two oligothiophene units.

Oligothiophenes are attractive building blocks for molecular electronic devices. It has been reported that field-effect transistors (FET's) could be processed easily by successive vacuum evaporations of α-conjugated oligothiophenes on thermally grown SiO_2 layers.[1] Recently, several molecules which have two perpendicular oligothiophene units bisected through a spiro carbon atom have been synthesized with expectation of obtaining new molecular switches.[2] As another approach directed toward molecular devices, thin solid films, in which oligothiophene units are cofacially stacked each other, have been also obtained by using Langmuir-Blodgett techniques.[3]

We can expect that two functional units with a planar structure on the peri positions of naphthalenes would be placed cofacially in close proximity because of steric demand and thus interact with each other to produce additional new interesting physico-chemical properties. In fact, an X-ray single crystal structure analysis of 1,8-diphenylnaphthalene revealed that approximately parallel planes of the two phenyls are at an angle of approximately 70° to the plane of the naphthalene ring.[4] Furthermore, it has been reported very recently that the variance of the barrier to aryl-naphthalene bond rotation of 1,8-diarylnaphthalenes is interpreted in terms of a through-space polar/π interaction between the two aryl units.[5] It is also known that a series of 1-aryl-8-tropylionaphthalene cations show the intramolecular charge-transfer (CT) bands between aryl and tropylium moieties.[6] In this connection, we have become interested in the synthesis and properties of 1,8-di(2-thienyl)-, 1,8-bis(5,2'-bithiophene-2-yl)-, 1,8-bis(5,2':5',2"-terthiophene-2-yl)-, and 1,8-bis(5,2':5',2":5",2'"-quaterthiophene-2-yl)naphthalenes (**1a**, **1b**, **1c**, and **1d**, respectively) which carry two oligothiophene units that would be placed cofacially on the peri positions.[7]

The method of our choice for the preparation of **1a-d** is the [1,3-bis(diphenylphosphino)propane]-nickel(II) chloride [$NiCl_2$(dppp)]-catalyzed coupling of aryl halides with arylmagnesium halides.[8] We thus first attempted the preparation of 1,8-di(2-thienyl)naphthalene (**1a**) by $NiCl_2$(dppp)-catalyzed coupling of 1,8-diiodonaphthalene with 2-thienylmagnesium bromide (Scheme 1). Unfortunately, however, the reaction carried out in refluxing ether gave 1-(2-thienyl)naphthalene (**2a**) (61%) as the major product and the desired **1a** (12%) as a minor product.



Scheme 1

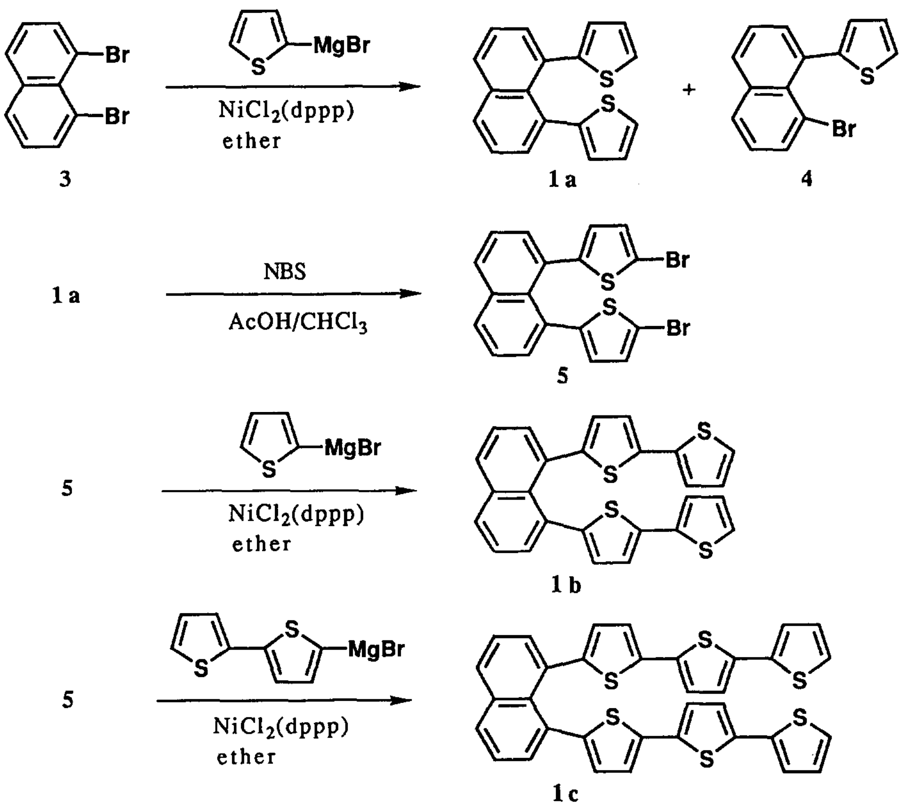
We therefore next planned to use 1,8-dibromonaphthalene (**3**) instead of the diiodo compound as the starting material. Reported syntheses of **3** are laborious and are not suitable for a large scale synthesis.[9] We therefore developed a new synthesis which involves the diazotization of easily obtainable naphtho[1,8-*de*]-triazine[10] followed by treatment with copper(I) bromide. The new method provides 25 g of 1,8-dibromonaphthalene in a single run in 37% overall yield starting from 1,8-diaminonaphthalene.

The reaction of **3** with 2-thienylmagnesium bromide catalyzed by the foregoing reagent satisfactorily gave **1a** in an improved yield (36%) in addition to 1-bromo-8-(2-thienyl)naphthalene (**4**) in 30% yield (Scheme 2). The reaction of **4** with 2-thienylmagnesium bromide also afforded **1a** in 36% yield with recovery of **4** in 55% yield.

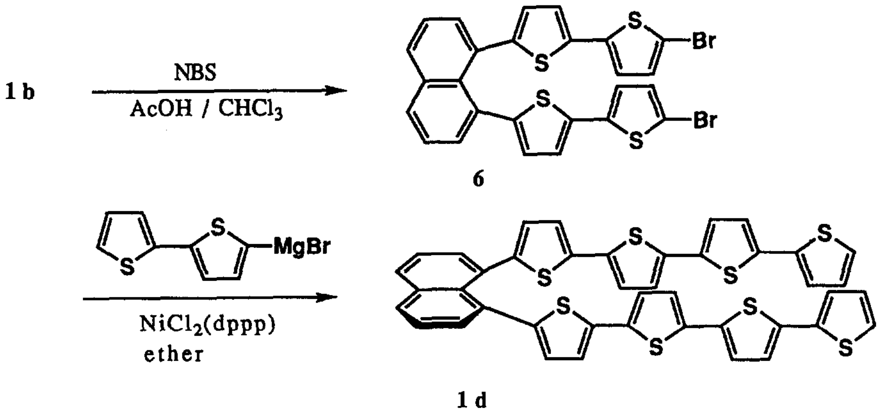
Bromination of **1a** with 2 equiv of *N*-bromosuccinimide (NBS) gave the dibromide **5** in 63% yield. The $NiCl_2$(dppp)-catalyzed coupling of **5** with 2-thienylmagnesium bromide in refluxing ether afforded expected 1,8-bis(5,2'-bithiophene-2-yl)naphthalene (**1b**) in 77% yield as pale-yellow crystals. Similarly the reaction of **5** with 5,2'-bithiophene-2-ylmagnesium bromide in the presence of $NiCl_2$(dppp) in refluxing ether provided 1,8-bis(5,2':5',2"-terthiophene-2-yl)naphthalene (**1c**) in 62% yield as yellow crystals. The above reaction carried out in refluxing tetrahydrofuran did not give the expected **1c**.

2-Bromo-5,2':5',2"-terthiophene did not give the corresponding Grignard reagent, which is required for the preparation of 1,8-bis(5,2':5',2":5",2'"-quaterthiophene-2-yl)naphthalene (**1d**) from **5**. 5,2':5',2"-Terthiophene-2-yllithium is easily prepared by lithiation of α-terthiophene.[11] However, the use of this lithium reagent for Pd^0-catalyzed[12] coupling with **5** gave a complex mixture from which any expected **1d** was not isolated. Finally the desired **1d** was prepared in 20% yield by the coupling of 5,2'-bithiophene-2-ylmagnesium bromide with the dibromide **6**, which is obtainable by bromination of **1b** in 78% yield (Scheme 3). Compound **1d** is a dark-brown powder and is practically insoluble in common organic solvents.

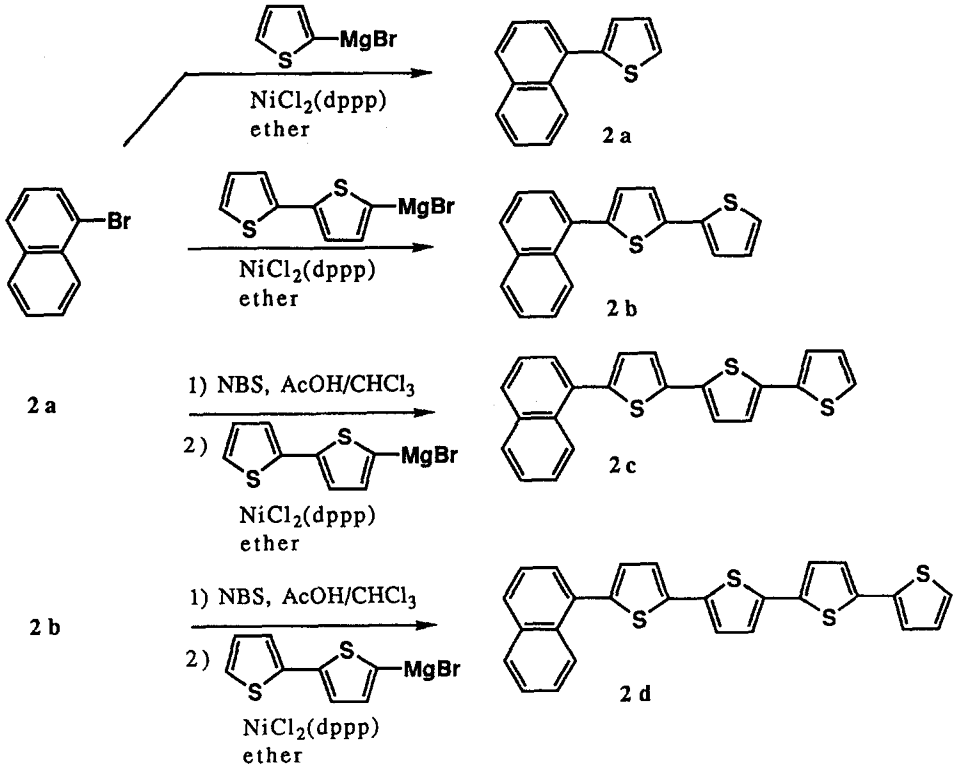
For comparison with **1a-d**, monosubstituted naphthalene derivatives **2a-d** were also synthesized (Scheme 4). The $NiCl_2$(dppp)-catalyzed coupling of 1-bromonaphthalene with 2-thienylmagnesium bromide



Scheme 2



Scheme 3

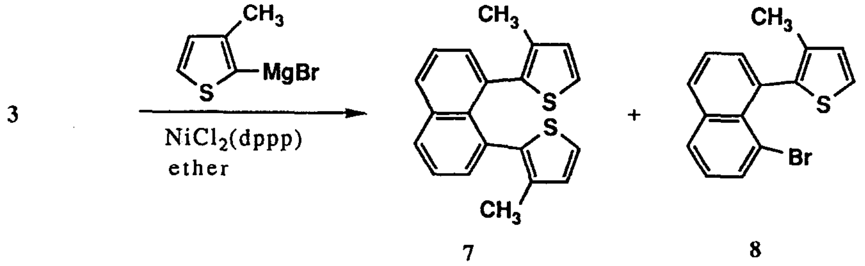


Scheme 4

afforded 1-(2-thienyl)naphthalene (**2a**) nearly quantitatively. Similarly the coupling of 1-bromonaphthalene with 5,2'-bithiophene-2-ylmagnesium bromide provided 1-(5,2'-bithiophene-2-yl)naphthalene (**2b**) in 87% yield. Bromination of **2a** with NBS followed by the coupling of the resulting bromide with 5,2'-bithiophene-2-ylmagnesium bromide gave 1-(5,2':5',2"-terthiophene-2-yl)naphthalene (**2c**) as yellow crystals in 61% overall yield. Similarly bromination of **2b** followed by coupling with the foregoing Grignard reagent led to 1-(5,2':5',2":5",2'"-quaterthiophene-2-yl)naphthalene (**2d**) as orange crystals in 54% overall yield, which is hardly soluble in common organic solvents.

Both ^1H and ^{13}C NMR data show that two thiophene rings of **1a** are equivalent, thus revealing that the naphthalene-to-thiophene bond is freely rotating at room temperature on NMR time scale, as is so for the naphthalene-to-benzene bond of 1,8-diphenylnaphthalene.[13] The barrier to the rotation about the naphthalene-to-bithiophene bond of **1b** would be comparable with that of **1a** because the outer thiophene rings are more remote each other than are the inner thiophene rings. In addition, the rotation about the thiophene-to-thiophene bonds of **1b** must be far faster than that about the naphthalene-to-thiophene bonds because the steric hindrance for the former process is smaller than that for the latter one. The same things would also hold for **1c** and **1d**. In fact, two oligothiophene units of **1b-d** appear equivalent in both ^1H and ^{13}C NMR spectra. The thiophene ring protons of **1a** at C-3 and C-4 appear at δ 6.43 and 6.58 ppm as doublet of doublet, while **2a** does not have any absorption at higher field than δ 7.00. This indicates that the preferred conformation of **1a** is the one in which two thiophene rings are approximately parallel to each other, but are not coplanar with the naphthalene ring, thus resulting in the shielding of the thiophene ring protons by ring current effect. The same conclusion on the preferred conformations of **1b-d** is also reached by inspecting chemical shift differences between **1b-d** and **2b-d**.

1,8-Di(*o*-tolyl)naphthalene is known to be separable into cis and trans atropisomers.[14] On the other hand, the methyl signal of 1,8-bis(3-methylthien-2-yl)naphthalene (**7**), the corresponding analog of the former, prepared by coupling of 1,8-dibromonaphthalene with 3-methylthien-2-ylmagnesium bromide in 35% yield (Scheme 5), appears at δ 1.75 ppm as a singlet above 40 °C. On lowering temperature, the singlet turns into two singlets (e.g., δ 1.86 and 1.74 ppm at -50 °C) attributable to cis and trans atropisomers, thereby the relative intensities depending on temperature: at 8 °C, 1:4.9; -15 °C, 1:5.1; -50 °C, 1:6.6. The major isomer whose methyl signal appears at a higher field should be assigned trans.[14] The calculated $\Delta G^\ddagger$ for the rotation about the naphthalene-to-thiophene bond is 15.4 kcal/mol, which is comparable with that of 1-phenyl-8-(*o*-tolyl)-naphthalene (14.7 kcal/mol)[5] but far smaller than that of 1,8-di(*o*-tolyl)naphthalene (24.1 kcal/mol).[14] These observations show that 2-thienyl behaves as a less bulky substituent than phenyl in the present system.



Scheme 5

In order to obtain further information about the geometry of **1a-d**, X-ray single crystal structure analyses of these molecules were planned. Good single crystals suitable for the analysis could be obtained for only **1b**. The molecular structure of **1b** is given in Fig. 1. Two bithiophene units are connected to the naphthalene ring in trans conformation and approximately parallel planes of the two inner thiophene rings of two bithiophene units are at an angle of 57° to the plane of the naphthalene ring. Although 2,2'-bithiophene and 5,2':5',2"-terthiophene exist in nearly planar form with C_{2h} and C_{2v} symmetries, respectively, in the crystalline state,[15] the planes of two thiophene rings of bithiophene units of **1b** are twisted with dihedral angles of 16° and 28°. The nonplanar structure of the bithiophene units of **1b** should be ascribed to packing effects in the crystal. Selected bond lengths (Å), bond angles (°), and torsion angles (°) are summarized in Table 1. Relatively small deviation of the bond angles C(9)-C(1)-C(11), C(9)-C(8)-C(19), and C(1)-C(9)-C(8) from 120°, keeping in mind that C(1)-C(9)-C(8) bond angles of the parent naphthalene and 1,8-dimethylnaphthalene are 121.5° and 127°, respectively,[16] is in harmony with coplanar structure of two thiophene units by which repulsion between them can be avoidable. Longer bond lengths of C(1)-C(11) and C(8)-C(19), 1.484 and 1.482 Å, respectively, than those between thiophene rings, 1.443 and 1.460 Å, indicate that the conjugation between naphthalene and thiophene rings are less effective than that between thiophene rings as expected from the molecular geometry.

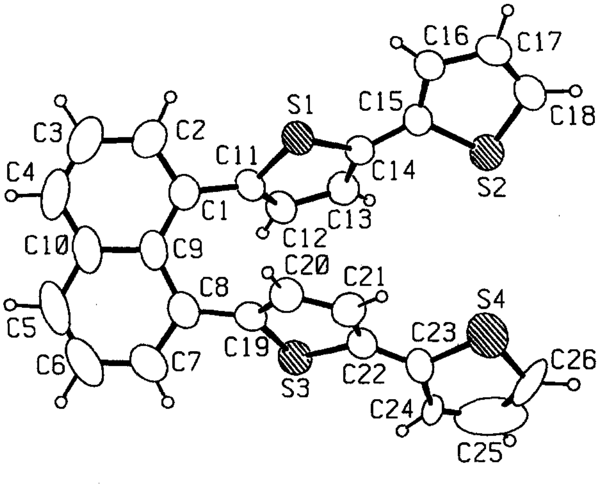


Fig. 1. ORTEP Drawing[17] of **1b** with Atom Numbering

Table 1. Selected Bond Length (Å), Bond Angle (°) and Torsion Angle (°)

Bond length (Å)		Bond angle (°)		Torsion angle (°)	
C(1)-C(2)	1.388(6)	C(1)-C(9)-C(8)	126.0(4)	C(1)-C(9)-C(10)-C(4)	-5.2(6)
C(1)-C(9)	1.425(6)	C(2)-C(1)-C(11)	116.9(4)	C(8)-C(9)-C(10)-C(5)	-6.0(6)
C(1)-C(11)	1.484(6)	C(7)-C(8)-C(19)	117.7(4)	C(11)-C(1)-C(9)-C(10)	-165.0(4)
C(7)-C(8)	1.380(6)	C(9)-C(1)-C(11)	123.4(4)	C(19)-C(8)-C(9)-C(10)	-169.6(4)
C(8)-C(9)	1.443(6)	C(9)-C(8)-C(19)	122.3(4)	C(9)-C(1)-C(11)-S(1)	-131.9(4)
C(8)-C(19)	1.482(6)			C(9)-C(8)-C(19)-S(3)	-124.3(4)
C(14)-C(15)	1.443(6)			S(1)-C(14)-C(15)-S(2)	-153.5(2)
C(22)-C(23)	1.460(6)			S(3)-C(22)-C(23)-S(4)	162.2(2)

UV/Vis spectra and CV oxidation potentials data of compounds **1a-d** and **2a-d** are summarized in Table 2. UV/Vis spectra for these compounds were measured in acetonitrile except **1d** determined in dichloromethane because of solubility problem. The molar extinction coefficients ε for these compounds increase with an increasing number of thiophene rings. The longest λ_{max} of **1a** is slightly longer than that of **2a**, whereas the longest λ_{max} for **1b-d** are shorter than those for the corresponding **2b-d**. These observations lead to the conclusion that **1a-d** exist in conformations where the thiophene units are approximately perpendicular to the naphthalene ring, which makes π-orbital overlap between naphthalene and thiophene units less effective, whereas for **2a-d** the conjugation between naphthalene ring and thiophene units is more effective because of the planar structure of the entire system. Again the same conclusion as that reached by NMR and X-ray analyses is derived.

Table 2. UV and Oxidation Potential Data of Naphthalenes **1a-d** and **2a-d**

Naphthalenes	λ_{max} (nm) (ε)	E^{ox} (V*)	Naphthalenes	λ_{max} (nm) (ε)	E^{ox} (V*)	Δ E^{ox} (2-1) (V)
1a	312 (8200)	0.96	**2a**	299 (9600)	1.02	0.06
1b	330 (32200)	0.66	**2b**	335 (20800)	0.75	0.09
1c	365 (52200)	0.50	**2c**	373 (32200)	0.62	0.12
1d	396 (78000)	0.41	**2d**	405 (43000)	0.59	0.18

*V *vs.* ferrocene/ferrocenium couple. $E_{1/2}$ (Ferrocene/Ferrocenium) : 0.09 V *vs.* Ag/Ag^+ in CH_3CN.
$E_{1/2}$ (Ferrocene/Ferrocenium) : -0.09 V *vs.* Ag/Ag^+ in THF.

The CV oxidation potential data were obtained with a platinum working electrode and 0.1 M electrolyte (tetrabutylammonium perchlorate) in acetonitrile except **1d** and **2d** in tetrahydrofuran because of solubility problem, and are corrected by the redox potentials for the ferrocene/ferrocenium couple. Every compound shows irreversible oxidation peaks because radical cations formed are very reactive and undergo polymerization as many thiophene derivatives do electro-polymerization.[18] In fact, a reddish-black film of polymeric materials was formed from **1d** on the Pt working electrode on many repeated scannings. E^{ox} decreases with an increasing number of thiophene rings without any exception. It is of particular interest that E^{ox} of **1a-d** are lower than those of the corresponding **2a-d**, regardless of the fact that the wavelengths of UV/Vis absorption maxima of **1a-d** are shorter than those of **2a-d**. Furthermore, E^{ox} differences between **1a** and **2a**, **1b** and **2b**, **1c** and **2c**, and **1d** and **2d** increase in this order along with an increasing number of thiophene rings. These observations strongly suggest that in **1a-d** the radical cation formed in one oligothiophene unit is stabilized by the participation of the other unit in the same molecule and that such stabilization is more effective in molecules having longer oligothiophene units. Finally the observed lower oxidation potentials of **1a-d** suggest the possibility that these compounds might serve as precursors for conducting polymers.

In conclusion we have succeeded in the preparation of naphthalene derivatives that carry two cofacially oriented α-oligothiophene units at the peri positions and are of interest from a view point of molecular devices because their radical cations are stabilized by electron transfer interaction between the two units.

EXPERIMENTAL

Melting points are uncorrected. NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) in $CDCl_3$ using tetramethylsilane as an internal standard. UV/Vis spectra were determined with a Shimadzu Model UV-2100 spectrophotometer. Mass spectra were recorded on a Shimadzu Model QP-2000 mass spectrometer. Elemental analyses were performed by the Chemical Analysis Center of Saitama University. Column chromatography was carried out using silica gel 60 (E. Merck, particle size 0.040-0.063 mm, 230-400 mesh ASTM).

1,8-Di(2-thienyl)naphthalene (1a) from 1,8-Diiodonaphthalene. A solution of 2-thienylmagnesium bromide, prepared from 4.16 g (25 mmol) of 2-bromothiophene and 0.61 g (25 mmol) of magnesium in 10 ml of ether, was added slowly by applying nitrogen gas pressure through a transfer tube and rubber septa to a stirred and ice-cooled mixture of 3.80 g (10 mmol) of 1,8-diiodonaphthalene and 20 mg of $NiCl_2$(dppp) in 100 ml of ether. The mixture was warmed slowly and then refluxed for 6 h. The reaction was quenched by addition of an aqueous solution of NH_4Cl and then ether (150 ml) was added. The organic layer was washed with water, dried over $MgSO_4$, and evaporated. The residue was chromatographed on a column of silca gel. Elution with hexane gave 1.28 g (61%) of 2-(1-naphthyl)thiophene (**2a**)[19] as a viscous oil and 0.35 g (12%) of **1a**: m.p. 104-105 °C (hexane); ^{1}H NMR δ 6.43 (dd, J=3.8 and 0.7 Hz, 2H), 6.58 (dd, J=5.0 and 3.8 Hz, 2H), 6.96 (dd, J=5.0 and 0.7 Hz, 2H), 7.44 (dd, J=8.0 and 7.2 Hz, 2H), 7.55 (dd, J=7.2 and 1.2 Hz, 2H), 7.84 (dd, J=8.0 and 1.2 Hz, 2H); ^{13}C NMR δ 123.94 (d), 125.05 (d), 126.07 (d), 127.60 (d), 129.17 (d), 130.53 (s), 132.33 (s), 132.43 (d), 135.37 (s), 144.14 (s); m/z 292 (M^+). Anal. Calcd for $C_{18}H_{12}S_2$: C, 73.93; H, 4.14. Found: C, 73.73; H, 4.23.

1,8-Dibromonaphthalene (3). An aqueous solution of 17.30 g (0.25 mol) of sodium nitrite was added slowly to a stirred suspension of 33.88 g (0.2 mol) of naphtho[1,8-*de*]triazine[10] in 500 ml of 6.9 M H_2SO_4 at -5 °C. After stirring for 2 h at -5 °C, a solution of 72.69 g (0.45 mol) of copper(I) bromide in 250 ml of 47% hydrobromic acid was added, and then the mixture was warmed to 85 °C and heated for 1 h at that temperature [the use of a 5-l beaker is recommended as a reaction vessel since steady foaming occurs during addition of copper(I) bromide and also on warming]. The dark brown suspension was cooled to room temperature and the pH was adjusted to ca. 7 by addition of sodium hydroxide pellets. The resulting precipitate was collected by filtration, washed with water many times, and then added to ether (ca. 1.5 l) and the insoluble materials were removed by filtration. The filtrate was dried over $MgSO_4$ and evaporated. The dark solid residue was chromatographed on a column of silica gel with hexane as the eluent and recrystallized from hexane to give 25.07 g (44%) of **3**, m.p. 108-109 °C (lit.[9] 108-109 °C).

1,8-Di(2-thienyl)naphthalene (1a). A solution of 2-thienylmagnesium bromide, prepared from 39.42 g (240 mmol) of 2-bromothiophene and 5.82 g (240 mmol) of magnesium in 70 ml of ether, was added slowly by applying nitrogen gas pressure to a stirred and ice-cooled mixture of 10.12 g (40 mmol) of **3** and 1.0 g of $NiCl_2$ (dppp) in 150 ml of ether through a transfer tube and rubber septa. The mixture was slowly warmed and refluxed for 8 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution. Ether (400 ml) was added to the mixture. The organic layer was washed with water, dried over $MgSO_4$, and evaporated. The crude product mixture thus obtained was chromatographed on a column of silica gel with hexane as the eluent to give 3.67 g (36%) of **1a** and 3.06 g (30%) of 1-bromo-8-(2-thienyl)naphthalene **4**: m.p. 71.5-72.5 °C (hexane); ^{1}H NMR δ 6.98 (dd, *J*=3.5 and 0.6 Hz, 1H), 7.07 (dd, *J*=3.6 and 3.5 Hz, 1H), 7.27 (t, *J*=7.8 Hz, 1H), 7.40 (dd, *J*=3.6 and 0.6 Hz, 1H), 7.46 (t, *J*=7.6 Hz, 1H), 7.59-7.61 (m, 1H), 7.8-7.89 (m, 3H); ^{13}C NMR δ 119.86 (s), 124.99 (d), 125.56 (d), 126.11 (d), 126.50 (d), 128.91 (d), 129.02 (d), 130.02 (d), 130.46 (s),132.05 (s), 132.70 (d), 134.20 (d), 135.92 (s), 142.83 (s); m/z 288, 290 (M$^+$). Anal. Calcd for $C_{14}H_9BrS$: C, 58.14; H, 3.14. Found: C, 58.12; H, 3.18.

1,8-Bis(5-bromothien-2-yl)naphthalene (5). To a stirred solution of 4.23 g (14.5 mmol) of **1a** in 50 ml of acetic acid and 50 ml of chloroform was added 5.22 g (29 mmol) of NBS in small portions. After stirring for 0.5 h at room temperature, the mixture was poured into ice-water and then chloroform (100 ml) was added. The organic layer was washed with aqueous $NaHCO_3$ solution and water, dried over $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel with hexane as the eluent and recrystallized from hexane to give 4.10 g (63%) of **5**: m.p. 141.5-142.5 °C ; 1H NMR δ 6.27 (d, *J*=3.5 Hz, 2H), 6.68 (d, *J*=3.5 Hz, 2H), 7.48-7.54 (m, 4H), 7.91-7.97 (m, 2H); ^{13}C NMR δ 110.95 (s), 125.18 (d), 128.06 (d), 129.45 (d), 129.97 (d), 130.62 (s), 131.07 (s), 132.60 (d), 135.32 (s), 145.52 (s); m/z 448, 450, 452 (M$^+$). Anal. Calcd for $C_{18}H_{10}Br_2S_2$: C, 48.02; H, 2.24. Found: C, 48.22; H, 2.34.

1,8-Bis(5,2'-bithiophene-2-yl)naphthalene (1b). A solution of 2-thienylmagnesium bromide, prepared from 1.67 g (10 mmol) of 2-bromothiophene and 0.24g (10 mmol) of magnesium in 10 ml of ether, was added to a stirred and ice-cooled mixture of 1.32 g (3 mmol) of **5** and 20 mg of $NiCl_2$ (dppp) in 100 ml of ether under nitrogen. The mixture was warmed slowly and refluxed for 9 h. After quenching the reaction by addition of a saturated aqueous NH_4Cl solution, the product was taken up by addition of CH_2Cl_2. The organic layer was washed with water, dried, evaporated, and chromatographed on a column of silica gel with hexane-toluene (8:2) as the eluent and recrystallized from hexane-toluene mixture to give 1.03 g (77%) of **1b**, m.p. 145-146°C ; ^{1}H NMR δ 6.41 (d, *J*=3.7 Hz, 2H), 6.71 (d, *J*=3.7 Hz, 2H), 6.96 (dd, *J*=5.1 and 3.6 Hz, 2H), 7.03 (dd, *J*=3.6 and 1.1 Hz, 2H), 7.15 (dd, *J*=5.1 and 1.1 Hz, 2H), 7.53 (dd, *J*=8.1 and 7.0 Hz, 2H), 7.62 (dd, *J*=7.0 and 1.4 Hz, 2H), 7.93 (dd, *J*=8.1 and 1.4 Hz, 2H); ^{13}C NMR δ 123.39 (d), 123.60 (d), 124.08 (d), 125.17 (d), 127.62 (d), 128.58 (d), 129.53 (d), 130.70 (s), 131.62 (s), 132.17 (d), 135.46 (s), 136.13 (s), 137.59 (s), 143.37 (s); m/z 456 (M$^+$). Anal. Calcd for $C_{26}H_{16}S_4$: C, 68.38; H, 3.53. Found: C, 68.35; H, 3.61.

1,8-Bis(5,2':5',2"-terthiophene-2-yl)naphthalene (1c). A solution of 5,2'-bithiophene-2-yl-magnesium bromide, prepared from 2.45 g (10 mmol) of 5-bromo-2,2'-bithiophene and 0.25g (10 mmol) of magnesium in 15 ml of ether, was added to a stirred and ice-cooled mixture of 1.35 g (3 mmol) of **5** and 30 mg of $NiCl_2$(dppp) in 100 ml of ether. The mixture was warmed slowly, refluxed for 8 h, and treated as in the case of **1b**. Three recrystallizations of the crude product from cyclohexane gave 1.15 g (62%) of analytically pure **1c**: m.p. 170-172 °C(dec.); ^{1}H NMR δ 6.43 (d, *J*=3.7 Hz, 2H), 6.72 (d, *J*=3.7 Hz, 2H), 6.93-6.96 (m, 4H), 7.02 (d, *J*=3.7 Hz, 2H), 7.08 (dd, *J*=3.8 and 1.1 Hz, 2H), 7.17 (dd, *J*=5.0 and 1.1 Hz, 2H), 7.54 (dd, *J*=8.5 and 7.0 Hz, 2H), 7.63 (dd, *J*=7.0 and 1.2 Hz, 2H), 7.94 (dd, *J*=8.5 and 1.2 Hz, 2H); ^{13}C NMR δ 123.51 (d), 123.74 (d), 123.91(d), 124.20 (d), 125.21 (d), 127.79 (d), 128.70 (d), 129.65 (d), 130.73 (s), 131.74 (s), 132.18 (d), 135.47 (s), 135.98 (s), 136.11 (s), 136.38 (s), 137.26 (s), 143.64 (s); m/z 620 (M^+). Anal. Calcd for $C_{34}H_{20}S_6$: C, 65.77; H, 3.25. Found: C, 65.90; H, 3.51.

1,8-Bis(5'-bromo-5,2'-bithiophene-2-yl)naphthalene (6). To a stirred solution of 4.57 g (10 mmol) of **1b** in 50 ml of acetic acid and 250 ml of chloroform was added 3.59 g (20 mmol) of NBS in small portions. After stirring for 2 h at room temperature, the mixture was treated as in the case of **5**. The crude product was chromatographed on a column of silica gel and recrystallized from CCl_4 to give 4.79 g (78%) of **6**: m.p. 153-154 °C; ^1H NMR δ 6.41 (d, *J*=3.7 Hz, 2H), 6.65 (d, *J*=3.7 Hz, 2H), 6.77 (d, *J*=3.8 Hz, 2H), 6.92 (d, *J*=3.8 Hz, 2H), 7.53 (t, *J*=7.6 Hz, 2H), 7.60 (d, *J*=7.0 Hz, 2H), 7.94 (d, *J*=7.9 Hz, 2H); ^{13}C NMR δ 110.61 (s), 123.41 (d), 123.83 (d), 125.22 (d), 128.56 (d), 129.76 (d), 130.49 (d), 130.66 (s), 131.48 (s),132.25 (d), 135.36 (s), 135.43 (s), 138.97 (s), 143.99 (s); m/z 614, 616, 618 (M^+). Anal. Calcd for $C_{26}H_{14}Br_2S_4$: C, 50.82; H, 2.30. Found: C, 50.92; H, 2.49.

1,8-Bis(5,2':5',2":5",2"'-quaterthiophene-2-yl)naphthalene (1d). A solution of 5,2'-bithiophene-2-ylmagnesium bromide, prepared from 0.73 g (3 mmol) of 5-bromo-2,2'-bithiophene and 75 mg (3 mmol) of magnesium in 8 ml of ether, was added to a stirred and ice-cooled mixture of 0.61 g (1 mmol) of **6** and 10 mg of $NiCl_2$(dppp) in 70 ml of ether. The mixture was warmed slowly, refluxed for 12 h, and quenched by addition of a saturated aqueous NH_4Cl solution. Three recrystallizations of the crude product from toluene gave 0.15 g (20%) of **1d**: m.p. 238-240 °C; ^1H NMR δ 6.46 (d, *J*=3.6 Hz, 2H), 6.75 (d, *J*=3.6 Hz, 2H), 6.96 (d, *J*=3.7 Hz, 2H), 6.97-7.00 (m, 6H), 7.02 (d, *J*=3.7 Hz, 2H), 7.11 (d, *J*=2.9 Hz, 2H), 7.20 (d, *J*=5.2 Hz, 2H), 7.56 (t, *J*=7.6 Hz, 2H), 7.65 (d, *J*=5.8 Hz, 2H), 7.97 (d, *J*=8.2 Hz, 2H); m/z 784 (M^+). ^{13}C NMR spectrum could not be determined because of low solubility of the compound in organic solvents. Anal. Calcd for $C_{42}H_{24}S_8$: C, 64.25; H, 3.08. Found: C, 64.51; H, 3.30.

2-(1-Naphthyl)thiophene (2a). A solution of 2-thienylmagnesium bromide, prepared from 16.31 g (100 mmol) of 2-bromothiophene and 2.44 g (100 mmol) of magnesium in 50 ml of ether, was added to a stirred and ice-cooled mixture of 16.57 g (80 mmol) of 1-bromonaphthalene and 20 mg of $NiCl_2$ (dppp) in 100 ml of ether under nitrogen. The mixture was warmed slowly, refluxed for 8 h, and quenched by addition of a saturated aqueous NH_4Cl solution. The crude product was chromatographed on a column of silica gel with hexane as the eluent to give **2a** quantitatively. **2a**: b.p. 132 °C (0.5 mmHg) [lit.[19] 165 °C (1 mmHg)]; ^1H NMR δ 7.17 (dd, *J*=6.0 and 2.7 Hz, 1H), 7.24 (dd, *J*=2.7 and 1.0 Hz, 1H), 7.41 (dd, *J*=6.0 and 1.0 Hz, 1H), 7.45-7.51 (m, 3H), 7.54-7.57 (m, 1H), 7.83-7.89 (m, 2H), 8.20-8.23 (m, 1H); ^{13}C NMR δ 125.21 (d), 125.60 (d), 125.73 (d), 125.97 (d), 126.41 (d), 127.24 (d), 127.35 (d), 128.17 (d), 128.29 (d), 128.37 (d), 131.86 (s), 132.42 (s), 133.83 (s), 141.75 (s).

5-(1-Naphthyl)-2,2'-bithiophene (2b). A solution of 5,2'-bithiophene-2-ylmagnesium bromide, prepared from 4.89 g (20 mmol) of 5-bromo-2,2'-bithiophene and 0.49 g (20 mmol) of magnesium in 25 ml of ether, was added to a stirred and ice-cooled mixture of 2.91 g (14 mmol) of 1-bromonaphthalene and 30 mg of $NiCl_2$(dppp) in 50 ml of ether. The mixture was warmed slowly, refluxed for 6 h, and quenched by addition of a saturated aqueous NH_4Cl solution. The crude product was chromatographed on a column of silica gel with hexane as the eluent to give 3.57 g (87%) of **2b**: m.p. 99-100 °C (hexane); ^1H NMR δ 7.02-7.05 (m, 1H), 7.15 (d, *J*=3.6 Hz, 1H), 7.22-7.25 (m, 3H), 7.46-7.53 (m, 3H), 7.57-7.60 (m, 1H), 7.84-7.91 (m, 2H), 8.29-8.32 (m, 1H); ^{13}C NMR δ 123.67 (d), 123.95 (d), 124.38 (d), 125.25 (d), 125.63 (d), 126.06 (d), 126.52 (d), 127.83 (d), 128.00 (d), 128.05 (d), 128.36 (d), 128.53 (d), 131.65 (s), 131.98 (s), 133.89 (s), 137.31 (s), 137.61 (s), 140.75 (s); m/z 292 (M$^+$). Anal. Calcd for $C_{18}H_{12}S_2$: C, 73.93; H, 4.14. Found: C, 73.83; H, 4.21.

5-Bromo-2-(1-naphthyl)thiophene. To a stirred solution of 4.59 g (22 mmol) of **2a** in 50 ml of acetic acid and 50 ml of chloroform was added 3.94 g (22 mmol) of NBS in small portions. After stirring for 0.5 h at room temperature, the mixture was treated as in the case of **5**. The crude product was chromatographed on a column of silica gel to give 5-bromo-2-(1-naphthyl)thiophene quantitatively: ^{1}H NMR δ 6.98 (d, *J*=3.7 Hz, 1H), 7.12 (d, *J*=3.7 Hz, 1H), 7.45-7.53 (m, 4H), 7.85-7.90 (m, 2H), 8.17-8.19 (m, 1H); ^{13}C NMR δ 111.99 (s), 125.18 (d), 125.39 (d), 126.15 (d), 126.67 (d), 127.67 (d), 128.19 (d), 128.38 (d), 128.87 (d), 130.12 (d), 131.46 (s), 131.66 (s), 133.81 (s), 143.41 (s); m/z 288, 290 (M$^+$). Anal. Calcd for $C_{14}H_9BrS$: C, 58.15; H, 3.14. Found: C, 58.21; H, 3.23.

5-(1-Naphthyl)-2,2':5',2"-terthiophene (2c). A solution of 5,2'-bithiophene-2-ylmagnesium bromide, prepared from 1.47 g (6 mmol) of 5-bromo-2,2'-bithiophene and 0.15 g (6 mmol) of magnesium in 10 ml of ether, was added to a stirred and ice-cooled mixture of 1.19 g (4 mmol) of 5-bromo-2-(1-naphthyl)-thiophene and 10 mg of $NiCl_2$(dppp) in 20 ml of ether. The mixture was warmed slowly, refluxed for 6 h, and quenched by addition of a saturated aqueous NH_4Cl solution. Three recrystallizations of the crude product from cyclohexane gave 0.88 g (61%) of analytically pure **2c**: m.p. 109-111 °C ; ^{1}H NMR δ 7.00-7.02 (m, 1H), 7.08 (d, *J*=3.7 Hz, 1H), 7.10 (d, *J*=3.7 Hz, 1H), 7.14 (d, *J*=3.7 Hz, 1H), 7.16-7.20 (m, 2H), 7.22 (d, *J*=3.7 Hz, 1H), 7.45-7.52 (m, 3H), 7.57 (m, 1H), 7.82-7.89 (m, 2H), 8.28-8.31 (m, 1H); ^{13}C NMR δ 123.70 (d), 123.89 (d), 124.23 (d), 124.36 (d), 124.47 (d), 125.26 (d), 125.60 (d), 126.08 (d), 126.56 (d), 127.87 (d), 128.00 (d), 128.15 (d), 128.39 (d), 128.58 (d), 131.61 (s), 131.90 (s), 133.90 (s), 136.08 (s), 136.21 (s), 137.12 (s), 137.30 (s), 140.89 (s); m/z 374 (M$^+$). Anal. Calcd for $C_{22}H_{14}S_3$: C, 70.55; H, 3.77. Found: C, 70.28; H, 3.81.

5-Bromo-5'-(1-naphthyl)-2,2'-bithiophene. To a stirred solution of 2.94 g (10 mmol) of **2b** in 15 ml of acetic acid and 30 ml of chloroform was added 1.81 g (10 mmol) of NBS in small portions. After stirring for 1 h at room temperature, the mixture was treated as in the case of **5**. The crude product was recrystallized from hexane to give 3.11 g (83%) of 5-bromo-5'-(1-naphthyl)-2,2'-bithiophene: m.p. 93.5-94.5 °C ; ^{1}H NMR δ 6.94 (d, *J*=3.9 Hz, 1H), 6.98 (d, *J*=3.9 Hz, 1H), 7.13 (d, *J*=3.7 Hz, 1H), 7.16 (d, *J*=3.7 Hz, 1H), 7.46-7.52 (m, 3H), 7.55-7.57 (m, 1H), 7.84-7.90 (m, 2H), 8.25-8.28 (m, 1H); ^{13}C NMR δ 110.93 (s), 123.73 (d), 124.21 (d), 125.24 (d), 125.53 (d), 126.12 (d), 126.61 (d), 128.05 (d), 128.09 (d), 128.41 (d), 128.69 (d), 130.67 (d), 131.59 (s), 131.73 (s), 133.88 (s), 136.53 (s), 138.80 (s), 141.29 (s); m/z 370, 372 (M$^+$). Anal. Calcd for $C_{18}H_{11}BrS_2$: C, 58.22; H, 2.99. Found: C, 58.27; H, 3.08.

5-(1-Naphthyl)-2,2':5',2":5",2"'-qauterthiophene (2d). A solution of 5,2'-bithiophene-2-yl-magnesium bromide, prepared from 1.23 g (5 mmol) of 5-bromo-2,2'-bithiophene and 0.12g (5 mmol) of magnesium in 10 ml of ether, was added to a stirred and ice-cooled mixture of 1.09 g (3 mmol) of 5-bromo-5'-

(1-naphthyl)-2,2'-bithiophene and 10 mg of $NiCl_2$(dppp) in 30 ml of ether. The mixture was warmed slowly, refluxed for 6 h, and quenched by addition of a saturated aqueous NH_4Cl solution. Two recrystallizations of the crude product from toluene gave 0.87 g (65%) of analytically pure **2d**: m.p. 190-191 °C; ^1H NMR δ 7.02-7.04 (m, 1H), 7.04-7.23 (m, 8H), 7.45-7.52 (m, 3H), 7.60 (d, *J*=6.6 Hz, 1H), 7.87 (d, *J*=8.2 Hz, 1H), 7.90-7.92 (m, 1H), 8.30-8.32 (m, 1H); ^{13}C NMR δ 123.77 (d), 123.99 (d), 124.27 (d), 124.33 (d), 124.40 (d), 124.58 (d), 125.28 (d), 125.61 (d), 126.11 (d), 126.59 (d), 127.91 (d), 128.03 (d), 128.20 (d), 128.41 (d), 128.62 (d), 131.63 (s), 131.90 (s), 133.92 (s), 135.90 (s), 136.22 (s), 136.35 (s), 137.05 (s), 137.25 (s), 141.04 (s); m/z 456 (M^+). Anal. Calcd for $C_{26}H_{16}S_4$: C, 68.38; H, 3.53. Found: C, 68.54; H, 3.69.

1,8-Bis(3-methylthien-2-yl)naphthalene (7). A solution of 3-methylthien-2-ylmagnesium bromide, prepared from 17.73 g (100 mmol) of 2-bromo-3-methylthiophene and 2.44 g (100 mmol) of magnesium in 30 ml of ether, was added to a stirred and ice-cooled mixture of 7.15 g (25 mmol) of 1,8-dibromonaphthalene and 0.30 g of $NiCl_2$ (dppp) in 70 ml of ether. The mixture was warmed slowly, refluxed for 15 h, and quenched by addition of a saturated aqueous NH_4Cl solution. The crude product mixture was chromatographed on a column of silica gel with hexane as the eluent to give 2.73 g (35%) of **7** and 2.91g (38%) of 1-bromo-8-(3-methylthie-2-nyl)naphthalene (**8**). **7**: m.p. 119.5-121 °C (hexane); ^1H NMR δ 1.74 (s, 6H), 6.49 (d, *J*=3.8 Hz, 2H), 6.87 (d, *J*=3.8 Hz, 2H), 7.41 (d, *J*=6.9 Hz, 2H), 7.49 (t, *J*=7.6 Hz, 2H), 7.92 (d, *J*=8.1 Hz, 2H); ^{13}C NMR δ 14.97 (q), 122.01 (d), 124.97 (d), 128.90 (d), 129.26 (d), 132.05 (s), 132.57 (d), 134.83 (s), 137.84 (s) ; m/z 320 (M^+). Anal. Calcd for $C_{20}H_{16}S_2$: C, 74.96; H, 5.03. Found: C, 75.20; H, 5.13. **8**: b.p. 135-138 °C (0.25 mmHg); ^1H NMR δ 1.90 (s, 3H), 6.89 (d, *J*=5.1 1H), 7.25-7.34 (m, 2H), 7.48-7.56 (m, 2H), 7.82-7.92 (m, 3H); ^{13}C NMR δ 14.37 (q), 119.71 (d), 124.08 (d), 125.23 (d), 126.05 (d), 129.09 (d), 129.12 (d), 130.06 (d), 130.67 (s), 131.51 (s), 132.80 (d), 134.05 (d), 135.89 (s), 136.84 (s), 136.94 (s); m/z 302, 304 (M^+). Anal. Calcd for $C_{15}H_{11}BrS$: C, 59.42; H, 3.66. Found: C, 61.09; H, 3.88. HRMS calcd 301.9765, found 301.9766.

X-Ray Crystal Structure Determination; *crystal data*: $C_{26}H_{16}S_4$, $M_r = 456.7$, monoclinic, $P2_1/n$, $a = 17.773(2)$, $b = 7.300(1)$, $c = 16.827(2)$ Å, $\beta = 92.26(1)°$, $V = 2181.5(4)$ Å^3, $Z = 4$, $D_{calc} = 1.390$ gcm^{-3}, μ(Mo *K*α) = 0.429 mm^{-1}.

A yellow crystal of dimensions 0.40 x 0.40 x 0.30 mm was mounted on a Rigaku AFC-5 four-circle diffractometer equipped with a graphite monochromator. Cell parameters were refined by least squares based on 25 2θ values ($10 < \theta < 15°$) measured with Mo *K*α radiation ($\lambda = 0.71073$ Å). Intensity data were collected in the range $2 < \theta < 27.5°$ ($-23 < h < 23$, $0 < k < 9$, $0 < l < 21$) by θ-2θ scan mode. 5174 reflections were measured and 2935 unique reflections were obtained with $|F_o| > 3\sigma(|F_o|)$. After the absorption correction, the structure was solved by direct methods using *SHELXS*86.[20] The coordinates and anisotropic thermal parameters of the non-H atoms were refined by block-diagonal least squares to minimize the function, $\Sigma\omega(|F_o|-|F_c|)^2$ with weight $\omega^{-1} = \sigma(|Fo|)$. Hydrogen atoms were also included in the refinement. The calculations were carried out on a MIPS 3230 workstation with *XTAL*3.0.[21] The final *R* value was 0.068 and $R_\omega = 0.050$ for 2935 reflections. Atomic coordinates of the non-H atoms are listed in Table 3.

Table 3. Atomic Coordinates and Equivalent Isotropic Thermal Parameters

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
S(1)	0.11062(6)	0.6861(2)	0.51634(7)	0.0467(4)
S(2)	0.12273(7)	1.2166(2)	0.63000(8)	0.0638(5)
S(3)	0.38665(6)	0.7793(2)	0.51038(7)	0.0568(5)
S(4)	0.3366(1)	1.1052(3)	0.7149(1)	0.1077(8)
C(1)	0.1906(2)	0.4931(6)	0.4028(2)	0.044(2)
C(2)	0.1282(3)	0.4170(6)	0.3632(3)	0.056(2)
C(3)	0.1346(3)	0.2718(7)	0.3098(3)	0.071(2)
C(4)	0.2027(3)	0.2057(6)	0.2942(3)	0.070(2)
C(5)	0.3410(3)	0.1987(7)	0.3184(3)	0.080(2)
C(6)	0.4037(3)	0.2565(7)	0.3571(3)	0.090(3)
C(7)	0.3988(3)	0.3848(7)	0.4179(3)	0.074(2)
C(8)	0.3312(2)	0.4616(6)	0.4379(3)	0.051(2)
C(9)	0.2628(2)	0.4129(5)	0.3938(2)	0.045(2)
C(10)	0.2680(3)	0.2701(6)	0.3349(2)	0.058(2)
C(11)	0.1788(2)	0.6678(5)	0.4457(2)	0.042(2)
C(12)	0.2118(2)	0.8317(5)	0.4333(2)	0.043(2)
C(13)	0.1842(2)	0.9736(5)	0.4813(2)	0.044(2)
C(14)	0.1287(2)	0.9178(5)	0.5301(2)	0.039(1)
C(15)	0.0851(2)	1.0230(5)	0.5845(2)	0.040(1)
C(16)	0.0129(2)	0.9940(6)	0.6080(2)	0.045(2)
C(17)	−0.0108(2)	1.1296(6)	0.6613(3)	0.056(2)
C(18)	0.0415(3)	1.2576(7)	0.6787(3)	0.064(2)
C(19)	0.3313(2)	0.5828(6)	0.5086(3)	0.047(2)
C(20)	0.2945(2)	0.5671(6)	0.5767(3)	0.051(2)
C(21)	0.3084(2)	0.7122(6)	0.6303(2)	0.054(2)
C(22)	0.3571(2)	0.8412(6)	0.6036(2)	0.047(2)
C(23)	0.3835(2)	1.0135(6)	0.6388(3)	0.056(2)
C(24)	0.4443(2)	1.1299(5)	0.6188(2)	0.041(1)
C(25)	0.4481(3)	1.269(1)	0.6642(4)	0.132(3)
C(26)	0.3981(3)	1.2877(7)	0.7199(3)	0.104(3)

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