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A series of new type of benzo[*b*]thiophene-fused 1,4-benzoquinones and their tetracyanoquinodimethane derivatives were synthesized. The cyclic voltammetric data of new type quinones and tetracyanoquinodimethane derivatives displayed different behavior. All new quinones exhibit two reduction waves corresponding to the radical anion and dianion. On the other hand, most tetracyanoquinodimethane derivatives display a singlewave reduction to the dianion. The benzo[*b*]thiophene moiety fused tetracyanoquinodimethane derivatives reveal more negative reduction potentials than that of tetracyanoquinodimethane.

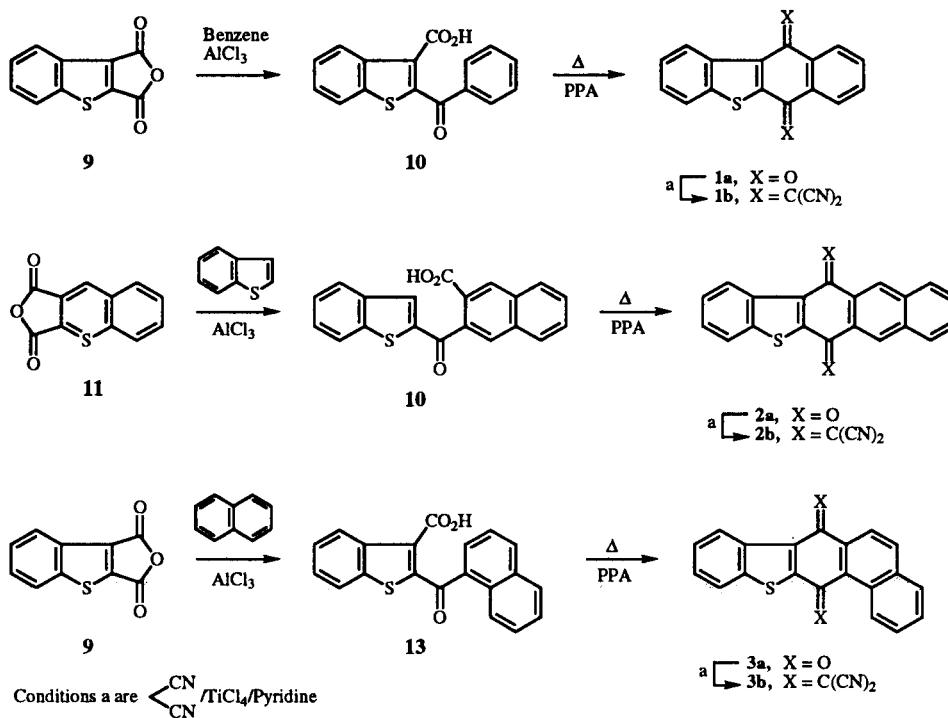
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Introduction.

Tetracyanoquinodimethane and their derivatives have been reported as a good acceptor to form good charge transfer complexes with donors [1-3]. Some of these complexes showed good conductivity at low temperature [4]. Tetracyanoanthraquinodimethane, which is a tetracyanoquinodimethane derivative fused with two benzene rings, has been reported as a good acceptor to form charge transfer complexes [5-9]. A series of thiophene fused tetracyanoquinodimethane derivatives have been reported [10,11] as π -extended systems and their modification by Kobayashi and coworker's research group. They reported that thiophene fused *N,N'*-dicyanoquinodiimine derivatives also formed charge transfer complexes with cuprous iodide which showed good conductive properties [12]. Hanack

reported the synthesis and electrochemical properties of 15,15,16,16-tetracyano-6,13-pentacenequinodimethane as a π -extended derivative of tetracyanoquinodimethane [13]. In spite of π -extension by fusing two naphthalene rings, 15,15,16,16-tetracyano-6,13-pentacenequinodimethane showed poorer electron-acceptor property than tetracyanoanthraquinodimethane. In this case, the extension of π -system only causes decrease of Coulomb repulsion. Furthermore, Seoane and his research group pointed out the relationship between the acceptor ability and molecular planarity of π -extended tetracyanoquinodimethane type acceptors [14]. And it is also pointed out that the large size of the sulfur atom increases the intrastack and interstack interactions and the conductivity and stabilization of the metallic state are enhanced [11,14]. These points of view

Scheme 1



prompted us to study a series of new π -extended tetracyanoquinodimethane type acceptors fused by benzo[*b*]thiophene. We now report the synthesis and electrochemical properties of π -extended 1,4-benzoquinone and tetracyanoquinodimethane derivatives containing benzo[*b*]thiophene ring.

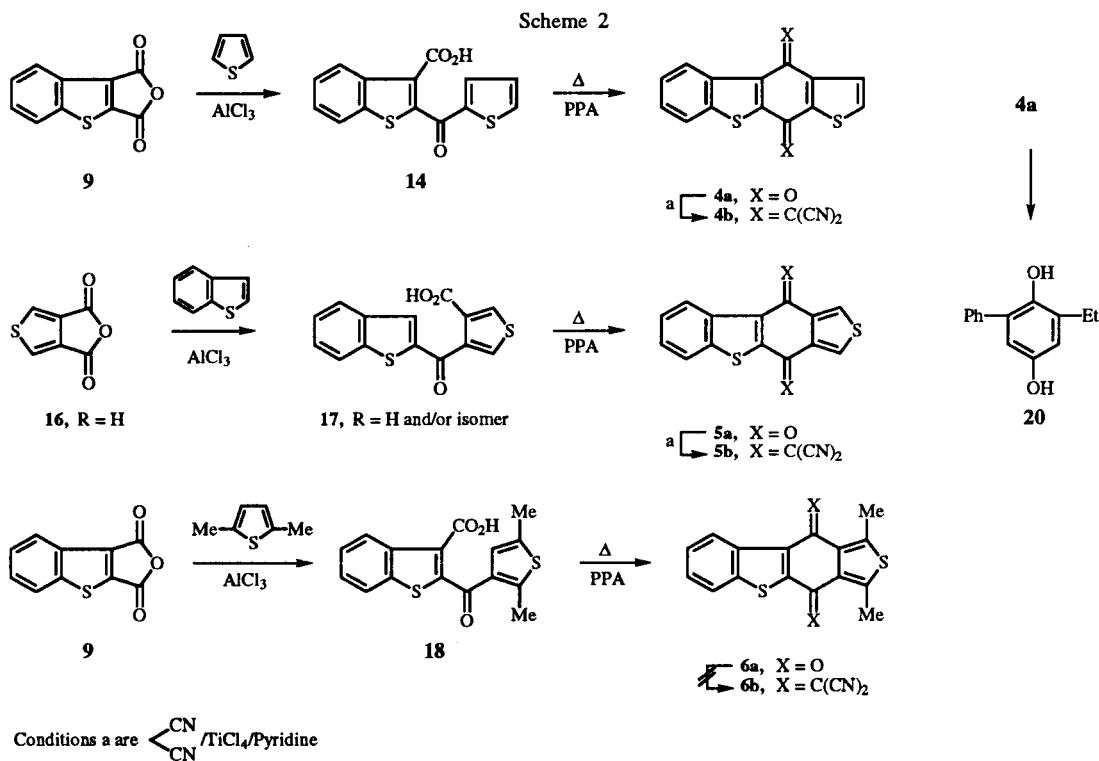
Result and Discussion.

Preparations.

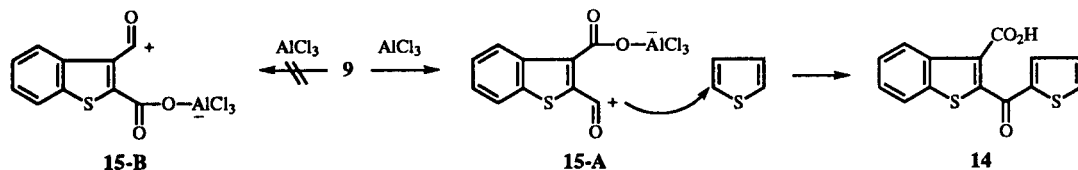
The synthesis of the new benzo[*b*]thiophene fused quinone derivatives consisted of multiple steps. The preparation of benzo[*b*]thieno[2,3-*b*]-1,4-naphthoquinone (**1a**) was carried out by cyclization of carboxylic acid **10**, obtained by the Friedel-Crafts reaction from benzo[*b*]thiophene-2,3-dicarboxylic anhydride (**9**) [15] with benzene (Scheme 1). The quinone (**2a**), in which naphthalene and benzo[*b*]thiophene were fused at the 2,3-position and at the 5,6-position to 1,4-benzoquinone was synthesized by the cyclization of 2-(3'-benzo[*b*]thiophenylcarbonyl)naphthalene-3-carboxylic acid and/or 2-(2'-benzo[*b*]thiophenylcarbonyl)naphthalene-3-carboxylic acid (**12**) which was prepared by Friedel-Crafts reaction of benzo[*b*]thiophene with naphthalene-2,3-dicarboxylic acid anhydride. The synthesis of benzo[*b*]thieno[2,3-*b*]-1,4-dinaphthoquinone (**3a**) was also carried out by the same cyclization reaction of 2-(1'-naphthylcarbonyl)-benzo[*b*]thiophene-3-carboxylic acid (**13**), obtained by the Friedel-Craft reaction of **9** with naphthalene.

The thieno[3',4':4,5]-4,10-dihydrobenzo[1,2-*b*]benzo[*b*]thiophene-4,10-dione (**4a**) was prepared by cyclization of

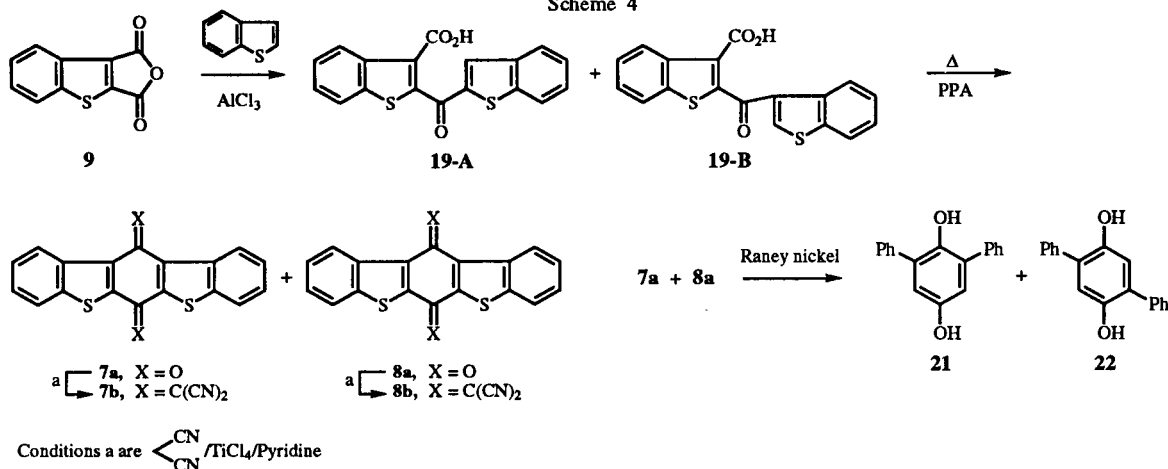
2-(2'-thenoyl)benzo[*b*]thiophene-3-carboxylic acid (**14**) [16]. But the structure of this quinone (**4a**) has not been determined by means of ^1H nmr spectroscopy. The structure of **4a** was confirmed by the fact that the reduction of **4a** with Raney nickel gave 2-ethyl-6-phenyl-1,4-dihydrobenzoquinone as an only product. This result indicated that the reaction of **9** with aluminum chloride gave the more stable cation **15-A** exclusively which attacked at the 2-position of thiophene to give 2-(2'-thenoyl)benzo[*b*]thiophene-3-carboxylic acid (**14**) as a single product. The cation **15-A** must react with aromatic compounds in other Friedel-Crafts reactions, which were accomplished by using **9** and aluminum chloride. In order to investigate the effectiveness of orientation of thiophene ring addition to basic parent framework (1,4-dihydrobenzo[1,2-*b*][1]benzothiophene-1,4-dione), different types of quinones **5a**, **6a** were prepared from the corresponding carboxylic acids **17**, **18**. Compound **17** was obtained by a combination reaction of 3,4-thiophenedicarboxylic anhydride (**16**) [17] with benzo[*b*]thiophene and **18** by the reaction of **9** with benzo[*b*]thiophene. In contrast to carboxylic acid **14**, the ring closure reaction of and/or a mixture of carboxylic acid **19**, which were prepared by the Friedel-Crafts reaction of **9** with benzo[*b*]thiophene, gave an inseparable 1:1 mixture of two quinone isomers **7a** and **8a** [18]. We attempted to obtain **8a** by the pyrolysis of **9** [19]. However, unfortunately pyrolysis gave a 1:3 mixture of **7a** and **8a**. The mechanism of the Friedel-Crafts reaction of **9** with benzo[*b*]thiophene can be explained by the



Scheme 3



Scheme 4



following idea: the cation 9-A attacked both at the 2- and 3-positions of benzo[*b*]thiophene to give a 2:1 mixture of carboxylic acids 19-A and 19-B. Yuldashev has reported the same results on Friedel-Crafts acylation of benzo[*b*]thiophene [20]. These structures were confirmed by the following fact that the reduction of the mixture of quinones by Raney-nickel gave a 2:1 mixture of 2,6-diphenyl-1,4-dihydroquinone (21) and 2,5-diphenyl-1,4-dihydroquinone (22) [21]. In spite of many efforts to isolate each quinone by recrystallization or hplc separation, these two quinone compounds have not been isolated.

Reflux for 20 hours of 1a under a nitrogen atmosphere in pyridine with malononitrile did not provide 1b. To a solution of 1a and malononitrile in dichloromethane titanium tetrachloride was added followed by pyridine at 0° with stirring at room temperature. After the usual work up, 11,11,12,12-tetracyanobenzo[*b*]naphtho[2,3-*d*]thienoquinodimethane (1b) was obtained as orange needles in 71% yields. As shown in Table 1, 2b and 3b were prepared in low yield under the same reaction conditions used for the synthesis of 1b from 1a. The reaction of quinone 4a, in which the thiophene ring and the benzo[*b*]thiophene ring are fused to 1,4-benzothiophene, gave 4b in low yield (18%). The reaction of 5a with malononitrile gave 5b in 48% yields. In case of 6a, the reaction with malononitrile gave no tetracyano compound 6b. The steric hindrance caused by the two methyl groups at positions 1 and 3 of 6a inhibiting the approach of

Table 1
New acceptor Molecules

Compound	λ_{max} nm (log ϵ)	$\nu_{\text{CN}}, \text{cm}^{-1}$	mp, °C	yield, %
1a	366 (3.7)		222-224	80
2a	408 (3.9)		>360	36
3a	398 (3.8)		209-212	78
4a	386 (3.7)		205-209	92
5a	361 (4.5)		256-258	55
6a	366 (3.9)		237-240	22
7a+8a	398 (3.9)		257-260	64
1b	375 (3.8)	2215	312-315	71
2b	440 (4.1) sh	2224	300	29
3b	430 (4.1)	2225	290-292	10
4b	430 (4.4)	2250	340-341	18
5b	392 (4.1)	2220	>360	48
7b+8b	430 (4.4)	2250	>360	36

malononitrile to the quinone may be the reason of this result. Repeated attempts to isolate 7b and 8b failed. The yields and some physical properties of all tetracyanoquinodimethane derivatives from the corresponding quinones are listed in Table 1.

The uv spectra of the quinones prepared and the tetracyanoquinodimethane derivatives, which are recorded in Table 1, suggest that these compounds are far from planar [7,9,13,14]. The stretching vibrations of the conjugated cyano groups in the ir spectra of the tetracyanoquinodimethane derivatives were observed at 2210-2250 cm^{-1} , and which also support that molecular distortion of those compounds [14].

Table 2
Cyclic Voltammetry Data of New Acceptors (V vs SCE) [a]

Compound	$E^1_{1/2}$ V	$E^2_{1/2}$ V	ΔE , V
1a	-0.61	-1.29	0.68
2a	-0.70	-1.18	0.48
3a	-0.45	-1.15	0.7
4a	-0.45	-1.15	0.7
5a	-0.85	-1.36	0.51
6a	-0.88	-1.44	0.56
7a+8a	-0.38	-1.08	0.7
1b	-0.08	-0.08	0
2b	-0.18	-0.18	0
3b	-0.07	-0.07	0
4b	+0.11	-0.03	0.14
5b	-0.19	-0.19	0
7b+8b	+0.09	+0.09	0

[a] Versus Ag wire as a Ag/Ag⁺ reference electrode; electrolyte Bu₄N⁺ClO₄⁻; solvent acetonitrile; scan rate 100 m Vs⁻¹.

Electrochemistry.

The cyclic voltammetry measurements of the new compounds were carried out in acetonitrile at room temperature with tetrabutylammonium perchlorate as the supporting electrolyte. The half-wave redox potentials of π -extended 1,4-benzoquinone derivatives and tetracyanoquinodimethane type derivatives are summarized in Table 2. All new quinones exhibit two reduction waves corresponding to the radical anion and dianion. On the other hand, the tetracyano tetracyanoquinodimethane-type compounds **1b**, **2b**, **3b**, **5b** and the mixture of **7b** and **8b** show a two-electron single wave reduction to the dianion. The redox wave in these compounds is indicative of an overall process leading to their dianion ($A + 2e \rightleftharpoons A^{2-}$). It has been reported that tetracyanoanthraquinodimethane exhibits a single-wave, two-electron reduction to the dianion because of its highly distorted structure [5,7,9,13,14]. But these new π -extended tetracyanoquinodimethane derivatives exhibited good reduction potentials in comparison with that of tetracyanoanthraquinodimethane. These results suggest that the structures of these new type π -expanded acceptors were less distorted than tetracyanoanthraquinodimethane. The acceptors **1b** and **6b**, in which the benzene rings are directly fused to the tetracyanoquinodimethane ring, showed a little higher redox potential in respect to the others. These results can be explained by the ring distortion caused by steric repulsion between the cyano group and the hydrogen atom at the peri-positions [5,13,14]. The mixture of **7b** and **8b**, which is two benzothiophenes added to the tetracyanoquinodimethane derivative, showed excellent acceptor properties. ($E^1_{1/2} = E^2_{1/2} = +0.09$ eV). The effects of direct fusion of the thiophene rings at the 2,3-position by two benzo[*b*]thiophenes to the tetracyanoquinodimethane parent frame was found to be very useful to decrease the reduction potential of tetracyanoquinodimethane. Only **4b** exhibits two quasi reversible wave

reduction to the dianion ($E^1_{1/2} = +0.11$, $E^2_{1/2} = -0.03$ eV). Compound **4b** exhibits the most positive first reduction potential and the radical anion of **4b** was stabilized by two thiophene rings. Comparison of the reduction potential of **4b** with that of **5b** suggested that fusion at the 2,3 positions of thiophene was more effective than fusion at the 3,4 positions when thiophene was introduced to improve the reduction properties of tetracyanoquinodimethane derivatives. Replacing the benzene ring with the thiophene ring leads to better acceptors, which is due to the extension of the π -system and to reduction of steric repulsion between the cyano group and the hydrogen atom at the peri-position of fused benzene ring. Many attempt to make charge transfer complexes using donors are now in progress.

EXPERIMENTAL

All of the melting points are uncorrected. The ¹H nmr spectra were recorded on a JEOL EX-270 spectrometer at 270 MHz, using TMS as an internal reference. The ir and mass spectra (70 eV) were recorded on Hitachi EPI-S2 and JEOL AX-350 spectrometers, respectively. Cyclic voltammograms: were measured by a potentiostat equipped with a function generator and a XY recorder. Benzo[*b*]thiophene-2,3-dicarboxylic acid was synthesized by the method reported in the literature [22].

Benzo[*b*]thiophene-2,3-dicarboxylic Anhydride (**9**).

The solution of benzo[*b*]thiophene-2,3-dicarboxylic acid (10.0 g, 45 mmoles) in acetic anhydride (9 ml) was refluxed for 2 hours and cooled to room temperature. The crystals were filtered and recrystallized from benzene to give **9** (7.9 g, 86%), yellow needles, mp 181°; ¹H-nmr (DMSO-*d*₆): δ 7.49-7.60 (m, 2H), 8.00-8.11 (m, 2H); ir: 1830 cm⁻¹, 1770 cm⁻¹, ν C=O; ms: 204 (M⁺, 33).

Anal. Calcd. for C₁₀H₄O₃S: C, 58.83; H, 1.98. Found: C, 58.52; H, 1.80.

General Procedure for the Preparation of Carboxylic Acids **10**, **13**, **14**, **18** and **19**.

2-Benzoylbenzo[*b*]thiophene-3-carboxylic Acid (**10**).

To a benzene (180 ml) solution of carboxylic anhydride **9** (6.1 g, 30 mmoles) was added aluminum chloride (8.0 g) with ice cooling. The mixture was refluxed for 3 hours and poured into water. The solvent was removed by steam distillation, and the residual solid was collected by filtration. The solid was dissolved in 20% aqueous sodium carbonate and filtered, the filtrate was acidified with concentrated hydrochloric acid to give **10** as a colorless precipitate, 7.4 g (63%), mp 199-201°; ¹H-nmr (DMSO-*d*₆): δ 7.40-7.70 (m, 6H), 7.77 (dd, 1H, *J* = 1.0, 7.2 Hz), 8.16 (d, *J* = 7.6 Hz); ir: 1680 cm⁻¹, ν C=O; ms: 282 (M⁺, 100).

Anal. Calcd. for C₁₆H₁₀O₃S: C, 68.07; H, 3.57. Found: C, 67.81; H, 3.44.

2-(1'-Naphthylcarbonyl)benzo[*b*]thiophene-3-carboxylic Acid (**13**).

Carboxylic acid (**13**) was obtained by the reaction of carboxylic acid anhydride **9** with naphthalene in 67% yield, colorless powder, mp 225-227°; ¹H-nmr (DMSO-*d*₆): δ 7.64-7.89

(m, 4H), 8.13 (d, $J = 8.2$ Hz, 1H), 8.22-8.34 (m, 2H), 8.49 (d, $J = 8.9$ Hz, 1H), 8.70-8.76 (m, 1H), 9.63 (d, $J = 8.6$ Hz, 1H); ir: 1680 cm^{-1} , 1660 cm^{-1} , $\nu \text{C}=\text{O}$; ms: 332 (M^+ , 100).

Anal. Calcd. for $\text{C}_{20}\text{H}_{12}\text{O}_3\text{S}\cdot\text{H}_2\text{O}$: C, 68.55; H, 4.03. Found: C, 68.81; H, 4.15.

2-(2'-Thenoyl)benzo[b]thiophene-3-carboxylic Acid (14).

Carboxylic acid **14** was obtained by the reaction of carboxylic acid anhydride **9** with thiophene in 70% yield, colorless needles, mp 176-178°; ^1H -nmr (DMSO- d_6): δ 7.18 (dd, 1H, thiophene proton, $J = 3.6, 5.0$ Hz), 7.40-7.61 (m, 4H), 8.08-8.18 (m, 2H); ir: 1690 cm^{-1} , 1670 cm^{-1} , $\nu \text{C}=\text{O}$; ms: 288 (M^+ , 100).

Anal. Calcd. for $\text{C}_{14}\text{H}_8\text{O}_3\text{S}_2\cdot\text{H}_2\text{O}$: C, 54.91; H, 3.29. Found: C, 54.92; H, 3.29.

2-(2,5-Dimethyl-3-thenoyl)benzo[b]thiophene-3-carboxylic Acid (18).

Carboxylic acid **18** was obtained by the reaction of carboxylic acid anhydride **9** with 2,5-dimethylthiophene in 76% yield, brown powder, mp 198-201°; ^1H -nmr (DMSO- d_6): δ 2.29 (s, 3H, methyl), 2.56 (s, 3H, methyl), 6.62 (s, 1H, thiophene proton), 7.42-7.62 (m, 3H), 8.13 (dd, 1H, $J = 1.0, 7.3$ Hz); ir: 1690 cm^{-1} , $\nu \text{C}=\text{O}$; ms: 316 (M^+ , 100).

Anal. Calcd. for $\text{C}_{16}\text{H}_{11}\text{O}_3\text{S}_2$: C, 64.40; H, 3.38. Found: C, 64.37; H, 3.11.

2-(2-Benzo[b]thienylcarbonyl)benzo[b]thiophene-3-carboxylic Acid (19-a) and 2-(3'-Benzo[b]thienylcarbonyl)benzo[b]thiophene-3-carboxylic Acid (19-b).

The mixture of carboxylic acids **19-a** and **19-b** was obtained by the reaction of carboxylic acid anhydride **9** with benzo[b]thiophene in 70% yield, colorless needles, mp 176-178°; ^1H -nmr (DMSO- d_6): δ 7.30-7.60 (m, 5H), 7.98-8.09 (m, 2H), 8.11 (s, 1H, thiophene proton), 8.75 (dd, 1H, $J = 1.0, 7.3$ Hz); ir: 1690 cm^{-1} , 1680 cm^{-1} , $\nu \text{C}=\text{O}$; ms: 338 (M^+ , 100).

Anal. Calcd. for $\text{C}_{18}\text{H}_{10}\text{O}_3\text{S}_2\cdot\text{H}_2\text{O}$: C, 60.65; H, 3.9. Found: C, 60.36; H, 3.68.

3-(2'-Benzo[b]thienylcarbonyl)thiophene-2-carboxylic Acid (12-a) and 3-(3'-Benzo[b]thienylcarbonyl)thiophene-2-carboxylic Acid (12-b).

The mixture of carboxylic acids **12-a** and **12-b** was obtained by the reaction of 2,3-naphthalenedicarboxylic acid anhydride (**11**) with benzo[b]thiophene in 93% yield, colorless powder, mp 253-255°; ^1H -nmr (DMSO- d_6): δ 7.33-8.70 (m, 11H); ir: 1697 cm^{-1} , 1655 cm^{-1} , $\nu \text{C}=\text{O}$; ms: 332 (M^+ , 100).

Anal. Calcd. for $\text{C}_{20}\text{H}_{12}\text{O}_3\text{S}\cdot\text{H}_2\text{O}$: C, 68.55; H, 4.03. Found: C, 68.62; H, 4.22.

4-(2'-Benzo[b]thienylcarbonyl)thiophene-3-carboxylic Acid (17-a) and 4-(3'-Benzo[b]thienylcarbonyl)thiophene-3-carboxylic Acid (17-b).

The 4:1 mixture of carboxylic acids **17-a** and **17-b** was obtained by the reaction of 3,4-thiophenecarboxylic acid anhydride (**16**) [**17**] with benzo[b]thiophene in 69% yield. The ratio of **17-a** and **17-b** was determined by the method of integration of ^1H nmr spectra, pale yellow powder, mp 145-151°; ^1H -nmr (DMSO- d_6): δ 7.52-7.69 (m, 2H), 7.95 (s, 1H, 2' of **17-b**), 8.08 (d, 1H, 2 or 5 proton of thiophene of **17-a**, $J = 3.2$ Hz), 8.19 (d, 1H, 2 or 5 proton of thiophene of **17-b**, $J = 3.2$ Hz), 8.20 (dd, 4' or 7' of benzo[b]thiophene, $J = 8.0, 1.4$ Hz), 8.39 (s, 1H, 3' proton of benzothiophene of **17-a**),

8.43 (d, 1H, 2 or 5 proton of thiophene of **17-a**), 8.47 (d, 1H, 2 or 5 proton of thiophene of **17-b**), 8.69 (dd, 1H, 4' of 7' of benzo[b]thiophene, $J = 8.3, 1.4$ Hz); ir: 1680 cm^{-1} , $\nu \text{C}=\text{O}$; ms: 288 (M^+ , 100).

Anal. Calcd. for $\text{C}_{14}\text{H}_8\text{O}_3\text{S}_2\cdot\text{H}_2\text{O}$: C, 54.89; H, 3.29. Found: C, 54.92; H, 2.99.

General Procedure to Produce Quinone Compounds **1a**, **2a**, **3a**, **4a**, **5a**, **6a**, **7a** and **8a**.

[1]Benzothieno[2,3-*b*]-1,4-naphthoquinone (**1a**).

Carboxylic acid **10** (2.8 g, 10 mmoles) was dissolved in polyphosphoric acid (20 g) and the solution was heated at 100° for 2 hours then cooled to room temperature. The reaction mixture was poured into ice water (50 ml). The precipitate was collected by filtration and washed with 10% aqueous sodium carbonate solution and water. Recrystallization from benzene gave **11** as yellow needles 2.1 g (80%), mp 222-224°; ^1H -nmr (DMSO- d_6): δ 7.65-7.70 (m, 2H), 7.87-7.98 (m, 2H), 8.14-8.28 (m, 3H), 8.79-8.84 (m, 1H); ir: 1670 cm^{-1} , $\nu \text{C}=\text{O}$, 1600 cm^{-1} , $\nu \text{C}=\text{C}$; uv: (acetonitrile): λ_{max} 219 nm (ϵ 21400), λ_{max} 258 nm (ϵ 25800), λ_{max} 301 nm (ϵ 6370), and λ_{max} 366 nm (ϵ 4910); ms: 264 (M^+ , 100).

Anal. Calcd. for $\text{C}_{16}\text{H}_8\text{O}_2\text{S}$: C, 72.71; H, 3.05. Found: C, 72.51; H, 2.90.

[1]Benzothieno[2,3-*b*]-1,4-anthraquinone (**2a**).

Quinone **2a** was obtained from carboxylic acid **12** by the same procedure used for the synthesis of **1a**. Recrystallization from acetonitrile gave yellow needle in 36% yield, mp >300°; ^1H -nmr (deuteriochloroform): δ 7.60-7.80 (m, 4H), 8.00-8.06 (m, 1H), 8.10-8.16 (m, 2H), 8.76 (s, 1H), 8.79 (s, 1H), 8.97-9.03 (m, 1H); ir: 1664 cm^{-1} , $\nu \text{C}=\text{O}$; uv: (acetonitrile): λ_{max} 234 nm (ϵ 60500), λ_{max} 302 nm (ϵ 46400), and λ_{max} 408 nm (ϵ 8610); ms: 314 (M^+ , 100).

Anal. Calcd. for $\text{C}_{20}\text{H}_{10}\text{O}_2\text{S}$: C, 76.41; H, 3.21. Found: C, 76.80; H, 3.05.

[1]Benzothieno[2,3-*b*]-1,4-phenanthroquinone (**3a**).

Quinone **3a** was obtained from carboxylic acid **13** by the same procedure used for the synthesis of **1a**. Recrystallization from chlorobenzene gave orange needles in 78% yield, mp 209-212°; ^1H -nmr (DMSO- d_6): δ 7.64-7.89 (m, 4H), 8.13 (d, $J = 8.2$ Hz, 1H), 8.22-8.34 (m, 2H), 8.49 (d, $J = 8.9$ Hz, 1H), 8.70-8.76 (m, 1H), 9.63 (d, $J = 8.6$ Hz, 1H); ir: 1650 cm^{-1} , $\nu \text{C}=\text{O}$; uv: (acetonitrile): λ_{max} 233 nm (ϵ 42800), λ_{max} 292 nm (ϵ 38300), λ_{max} 343 nm (ϵ 8390), and λ_{max} 398 nm (ϵ 6820); ms: 314 (M^+ , 100).

Anal. Calcd. for $\text{C}_{20}\text{H}_{10}\text{O}_2\text{S}$: C, 76.41; H, 3.21. Found: C, 76.84; H, 2.94.

Thieno[3',2':4,5]-4,10-dihydrobenzo[1,2-*b*][1]benzothiophene-4,10-dione (**4a**).

Quinone **4a** was obtained from carboxylic acid **14** by the same procedure used for the synthesis of **1a**. Recrystallization with toluene gave orange needles in 92% yield, mp 205-209°; ^1H -nmr (DMSO- d_6): δ 7.60-7.70 (m, 3H), 8.18-8.24 (m, 2H), 8.66-8.76 (m, 1H); ir: 1660 cm^{-1} , $\nu \text{C}=\text{O}$; uv: (acetonitrile): λ_{max} 233 nm (ϵ 42800), λ_{max} 269 nm (ϵ 11300), λ_{max} 316 nm (ϵ 9420), and λ_{max} 386 nm (ϵ 5510); ms: 270 (M^+ , 100).

Anal. Calcd. for $\text{C}_{14}\text{H}_6\text{O}_2\text{S}_2$: C, 62.20; H, 2.24. Found: C, 61.98; H, 2.06.

Reduction of **4a** with Raney-nickel.

To suspension of freshly prepared Raney-nickel W7 (3 g) in ethanol (30 ml) was added a solution of **4a** (200 mg) in ethanol

(5 ml) and heated to reflux for 1 hour and the reaction mixture was filtered. After the ethanol was removed, the residue was chromatographed (silica gel/hexane-ethyl acetate = 3/1) to give 2-ethyl-6-phenyl-1,4-dihydrobenzoquinone (**20**) (90 mg, 57%), pale yellow oil; $^1\text{H-nmr}$ (deuteriochloroform): δ 1.21 (t, $J = 7.5$ Hz, 3H), 2.66 (q, $J = 7.5$ Hz, 2H), 3.82 (s, 1H, -OH), 6.57 (d, $J = 3.0$ Hz, 1H), 6.66 (d, $J = 3.0$ Hz, 1H), 7.25-7.55 (m, 6H, Ar-H and -OH); ir: 3398 cm^{-1} , ν O-H.

Anal. Calcd. for $\text{C}_{14}\text{H}_{14}\text{O}_2$: C, 78.48; H, 6.59. Found: C, 78.56; H, 6.33; ms: 214 (M^+ , 100).

4,10-dihydrothieno[3',4':4,5]benzo[1,2-*b*][1]benzothiophene-4,10-dione (**5a**).

Quinone (**5a**) was obtained from carboxylic acid **17** by the same procedure used for the synthesis of **1a**. Recrystallization with benzene gave yellow needle in 55% yield, mp 256-258°; $^1\text{H-nmr}$ (DMSO- d_6): δ 7.64-7.70 (m, 2H), 8.20-8.26 (m, 1H), 8.60 (d, $J = 3.0$ Hz, 1H, thiophene proton), 8.66 (d, $J = 3.0$ Hz, 1H, thiophene proton), 8.79-8.85 (m, 1H); ir: 1640 cm^{-1} , ν C=O; uv: (acetonitrile): λ_{max} 217 nm (ϵ 23800), λ_{max} 259 nm (ϵ 23500), λ_{max} 280 nm (ϵ 31000), and λ_{max} 361 nm (ϵ 7460); ms: 270 (M^+ , 100).

Anal. Calcd. for $\text{C}_{14}\text{H}_6\text{O}_2\text{S}_2$: C, 62.20; H, 2.24. Found: C, 62.37; H, 2.04.

4,10-Dihydro-1,3-dimethylthieno[3',4':4,5]benzo[1,2-*b*]benzothiophene-4,10-dione (**6a**).

Quinone **6a** was obtained from carboxylic acid **18** by the same procedure used for the synthesis of **1a**. Recrystallization from benzene gave an orange powder in 22% yield, mp 237-240°; $^1\text{H-nmr}$ (DMSO- d_6): δ 2.76 (s, 3H), 2.79 (s, 3H), 7.58-7.68 (m, 2H), 8.15-8.24 (m, 1H), 8.75-8.83 (m, 1H); ir: 1660 cm^{-1} , ν C=O; uv: (acetonitrile): λ_{max} 218 nm (ϵ 25300), λ_{max} 279 nm (ϵ 33000), and λ_{max} 366 nm (ϵ 8700); ms: 298 (M^+ , 100).

Anal. Calcd. for $\text{C}_{16}\text{H}_{10}\text{O}_2\text{S}_2$: C, 64.40; H, 3.38. Found: C, 64.37; H, 3.14.

6,12-Dihydrobenzo[1,2-*b*:4,5-*b'*]bis[1]benzothiophene-6,12-dione (**7a**) and 6,12-Dihydrobenzo[1,2-*b*:5,4-*b'*]bis[1]benzothiophene-6,12-dione (**8a**).

The mixture of quinones **7a** and **8a** were obtained from the mixture of carboxylic acids **19a** and **19b** by the same procedure used for the synthesis of **1a**. Recrystallization with chlorobenzene gave orange needles in 92% yield, mp 205-209°; $^1\text{H-nmr}$ (DMSO- d_6): δ 7.60-7.72 (m, 4H), 8.22-8.28 (m, 2H), 8.66-8.82 (m, 2H); ir: 1660 cm^{-1} , ν C=O; uv: (acetonitrile): λ_{max} 231 nm (ϵ 31700), λ_{max} 267 nm (ϵ 21000), λ_{max} 352 nm (ϵ 8550), and λ_{max} 398 nm (ϵ 7600); ms: 320 (M^+ , 100).

Anal. Calcd. for $\text{C}_{18}\text{H}_9\text{O}_2\text{S}_2$: C, 67.48; H, 2.52. Found: C, 67.85; H, 2.30.

Reduction of **7a** and **8a** with Raney Nickel.

To a suspension of freshly prepared Raney nickel W7 (3 g) in ethanol (30 ml) was added a solution of **7a** and **8a** (250 mg) in ethanol (5 ml) and heated to reflux for 1 hour and the reaction mixture was filtered. After ethanol was removed, the residue was chromatographed (Wako-silica gel 300/hexane-ethyl acetate = 3/1) to give 120 mg of a 1:1 mixture ($^1\text{H-nmr}$) of 2,6-diphenyl-1,4-dihydroquinone (**21**) and 2,5-diphenyl-1,4-dihydroquinone (**22**) [**21**]. The mixture was separated by means of medium-pressure column-chromatography (Merck Silica gel 60/ethyl acetate/hexane = 1/3) to give 60 mg (29%) of **21** and 50 mg (24%) of **22**.

Compound **21** was obtained as colorless crystals, mp 175-178°; $^1\text{H-nmr}$ (deuteriochloroform): δ 4.53 (s, -OH, 1H), 5.05 (s, -OH, 1H), 6.79 (s, ArH, 2H), 7.35-7.56 (m, 10H); ir (potassium bromide): 3327, 3059, 3030, 1597, 1458, 1431, 1207, 752 and 698 cm^{-1} ; ms: 262 (M^+ , 79).

Anal. Calcd. for $\text{C}_{18}\text{H}_{14}\text{O}_2$: C, 82.42; H, 5.38. Found: C, 82.55; H, 5.30.

Compound **22** was obtained as pale yellow crystals, mp 225-226°; $^1\text{H-nmr}$ (deuteriochloroform): δ 4.93 (s, -OH, 2H), 6.90 (s, ArH, 2H), 7.35-7.55 (m, 10H); ir (potassium bromide): 3409, 3053, 3034, 1596, 1485, 1410, 1184, 760 and 698 cm^{-1} ; ms: 262 (M^+ , 100).

Anal. Calcd. for $\text{C}_{18}\text{H}_{14}\text{O}_2$: C, 82.42; H, 5.38. Found: C, 82.45; H, 5.40.

General Procedure for the Synthesis of Tetracyano Compounds **1b**, **2b**, **3b**, **4b**, **5b** and **7b**, **8b**.

9,9,10,10-Tetracyano[1]benzothieno[2,3-*b*]-1,4-naphthoquinodimethane (**1**).

To a solution of quinone **1a** (1.0 g, 3.8 mmoles) and malononitrile (0.8 g, 12 mmoles) in dichloromethane (80 ml) was added titanium tetrachloride (4.5 ml) over a period of 30 m at 0° under nitrogen atmosphere and then was added pyridine (15 ml) over a period of 1 hour under the same conditions and the reaction mixture was stirred for 5 hours at room temperature. To this reaction mixture were added 10% aqueous hydrochloric acid (25 ml) and water (100 ml), and the mixture was extracted with benzene. The benzene extract was washed with water, dried, and concentrated. Chromatographic separation on silica gel (Wako C-200, chloroform/hexane = 1/1), followed by recrystallization from acetonitrile gave **1b** (0.97 g, 71%), pale orange prisms: mp 312-315°; ir: 2215 cm^{-1} , ν C $\equiv$ N; uv: (acetonitrile): λ_{sh} 362 nm (ϵ 4960), λ_{max} 285 nm (ϵ 5600), λ_{max} 338 nm (ϵ 5680), and λ_{max} 375 nm (ϵ 6670); $^1\text{H-nmr}$ (deuteriochloroform): δ 7.63-7.68 (m, 2H), 7.73-7.78 (m, 2H), 7.96-8.02 (m, 1H), 8.07-8.11 (m, 1H), 8.33-8.38 (m, 1H), 8.45-8.50 (m, 1H); ms: m/z 360 (M^+ , 14).

Anal. Calcd. for $\text{C}_{22}\text{H}_8\text{N}_4\text{S}$: C, 73.31; H, 2.23; N, 15.55. Found: C, 73.03; H, 1.99; N, 15.37.

11,11,12,12-Tetracyano[1]benzothieno[2,3-*b*]-1,4-anthraquinodimethane (**2b**).

Compound **2b** was obtained from **2a** in 29% yield, orange powder, mp 300°; ir: 2224 cm^{-1} , ν C $\equiv$ N; uv: (acetonitrile): λ_{max} 267 nm (ϵ 29500), λ_{max} 320 nm (ϵ 26500), λ_{max} 384 nm (ϵ 17500); $^1\text{H-nmr}$ (deuteriochloroform): δ 7.61-7.71 (m, 2H), 7.74-7.83 (m, 2H), 7.97-8.13 (m, 4H), 8.79 (s, 1H), and 8.95 (s, 1H); ms: m/z 410 (M^+ , 100).

Anal. Calcd. for $\text{C}_{26}\text{H}_{10}\text{N}_4\text{S}$: C, 76.08; H, 2.46; N, 13.65. Found: C, 76.10; H, 2.40; N, 13.33.

11,11,12,12-Tetracyano[1]benzothieno[2,3-*b*]-1,4-dinaphthoquinodimethane (**3b**).

Compound **3b** was obtained from **3a** in 10% yield, orange powder, mp 290-292°; ir: 2225 cm^{-1} , ν C $\equiv$ N; uv: (acetonitrile): λ_{max} 260 nm (ϵ 21800), λ_{max} 330 nm (ϵ 22100), λ_{max} 390 nm (ϵ 17100), and λ_{max} 430 nm (ϵ 11900); $^1\text{H-nmr}$ (deuteriochloroform): δ = 7.57-7.86 (m, 4H), 7.97-8.05 (m, 2H), 8.07-8.16 (m, 2H), 8.22 (d, $J = 8.6$ Hz, 1H), and 8.40 (d, $J = 8.6$ Hz, 1H); ms: m/z 410 (M^+ , 100).

Anal. Calcd. for $C_{26}H_{10}N_4S$: C, 76.08; H, 2.46; N, 13.65. Found: C, 75.40; H, 2.20; N, 13.26.

4,10-Bis(dicyanomethylene)thieno[3',2':4,5]-4,10-dihydrobenzo-[1,2-b][1]benzothiophene (**4b**).

Compound **4b** was obtained from **4a** in 76% yield, red powder, mp 340-341°C; ir: 2250 cm^{-1} , ν C $\equiv$ N; uv: (acetonitrile): λ_{max} 269 nm (ϵ 15000), λ_{max} 305 nm (ϵ 10900), and λ_{max} 430 nm (ϵ 24900); 1H -nmr (deuteriochloroform): δ 7.59-7.65 (m, 2H), 7.78 (d, J = 5.3 Hz, 1H), 7.82 (d, J = 5.3 Hz, 1H), 7.92-7.98 (m, 1H), 8.91-8.98 (m, 1H); ms: m/z 366 (M^+ , 100).

Anal. Calcd. for $C_{20}H_6N_4S_2$: C, 65.55; H, 1.65; N, 15.29. Found: C, 65.15; H, 1.50; N, 15.51.

4,10-Bis(dicyanomethylene)thieno[3',4':4,5]-4,10-dihydrobenzo-[1,2-b][1]benzothiophene (**5b**).

Compound **5b** was obtained from **5a** in 48% yield, red powder, mp >360°C; ir: 2220 cm^{-1} , ν C $\equiv$ N; uv: (acetonitrile): λ_{max} 257 nm (ϵ 10400), λ_{max} 340 nm (ϵ 7830), and λ_{max} 392 nm (ϵ 12000); 1H -nmr (deuteriochloroform): δ 7.65-7.69 (m, 2H), 7.98-8.02 (m, 1H), 8.07-8.12 (m, 1H), 8.55 (d, J = 2.6 Hz, 1H, thiophene proton), 8.81 (d, J = 2.6 Hz, 1H, thiophene proton); ms: m/z 366 (M^+ , 100).

Anal. Calcd. for $C_{20}H_6N_4S_2$: C, 65.55; H, 1.65. Found: C, 65.02; H, 1.90.

6,12-Bis(dicyanomethylene)-6,12-dihydrobenzo[1,2-b:4,5-b']-bis[1]benzothiophene and 6,12-Bis(dicyanomethylene)-6,12-dihydrobenzo[1,2-b:5,4-b']bis[1]benzothiophene **7b** and **8b**.

A mixture of **7b** and **8b** were obtained from the mixture of **7a** and **8a** in 36% yield, orange powder, mp >360°C; ir: 2250 cm^{-1} , ν C $\equiv$ N; uv: (acetonitrile): λ_{max} 275 nm (ϵ 20000), λ_{max} 308 nm (ϵ 14100), λ_{max} 330 nm (ϵ 16000), and λ_{max} 430 nm (ϵ 25000); 1H -nmr (deuteriochloroform): δ 7.62-7.71 (m, 4H), 7.97-8.03 (m, 2H), 8.14-8.19 (m, 2H); ms: m/z 416 (M^+ , 73).

Anal. Calcd. for $C_{24}H_8N_4S_2$: C, 69.21; H, 1.94; N, 13.46. Found: C, 65.14; H, 1.66; N, 13.38.

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