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An Isomeric Series of Thiophene-Fused Tetracyanoquinodimethanes. I.[#] Preparation and Physico-Chemical Properties

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Four isomeric benzodithiophene analogs of 11,11,12,12-tetracyano-9,10-anthraquinodimethane have been prepared via a $TiCl_4$ mediated condensation of the corresponding quinone and malononitrile. The reduction potential of these isomers was interpreted in terms of the resonance energies for the neutral and radical anion species. These new acceptor compounds, except for 4,8-bis(dicyanomethylene)-4,8-dihydrobenzo[1,2-*c*:4,5-*c*′]-dithiophene, formed crystalline charge-transfer complexes with tetrathiafulvalene, among which the complex of 4,8-bis(dicyanomethylene)-4,8-dihydrobenzo[1,2-*b*:4,5-*b*′]dithiophene particularly exhibited a high room-temperature conductivity of 4.78 S cm^{-1}.

Tetracyanoquinodimethane (TCNQ) has been widely used as an acceptor compound to form highly conducting charge-transfer complexes.[1] One particular aspect in the design of new TCNQ-type acceptors is the π-system extension. An extension of conjugated system could be of great importance in reducing the intramolecular Coulombic repulsion, and thereby enhancing the conductivities of the anion radical salts.[2] In this context, a variety of π-acceptors that have a larger size than that of TCNQ have been synthesized;[3] 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ) is such an extended conjugated analog of TCNQ.[4–6] The charge-transfer complexes of TCAQ, however, are insulators, owing to the nonplanar structure of TCAQ resulting from the steric interaction between the dicyanomethylene groups and the peri-hydrogen atoms.[6] This disadvantage is overcome by the annelation of heterocyclic π-systems bearing no peri-hydrogen atoms.[7]

We now describe the synthesis and properties of an isomeric series of thiophene-fused TCNQ acceptors, i. e. 4,8-bis(dicyanomethylene)-4,8-dihydrobenzo[1,2-*b*: 4,5-*b*′] (**1**), [1,2-*b*: 4,5-*b*′] (**2**), [1,2-*b*: 4,5-*c*′] (**3**), and [1,2-*c*: 4,5-*c*′]dithiophene (**4**). The electronic and steric properties of these isomeric compounds, which are regarded as being dithiophene analogs of TCAQ, have been found to depend on the mode of fusion of the two thiophene units in the molecule.

Results and Discussion

Synthesis. The synthesis of **1**—**4** was based on a methodology first developed by Hünig for the synthesis of TCAQ.[5] Thus, the corresponding precursor quinone[8] **5**—**8** was treated, respectively, with malononitrile in the presence of titanium tetrachloride and pyridine.[6] The crude product was chromatographed on a silica-gel column followed by recrystallization from acetonitrile to afford the desired compound in 15—37% yields. In the preparation of **1** and **2**, compounds **9** and **10**, due to the condensation of malononitrile only to one carbonyl group of the two, were isolated as co-products in 15 and 12%, respectively.

The structural assignement of **10** was established on the basis of the ^{1}H NMR spectrta: The peri-proton located close to the dicyanomethylene group resonates in a low field at around δ=8.5, whereas that close to the carbonyl group exhibits a high-field shift up to δ=ca. 7.8, as observed for compound **9** (δ=7.81 or 7.76). Therefore, the doublet signal at δ=7.84 ppm of **10** corresponds to a β proton of the thiophene ring, excluding the possibility of structure **11**.

Electrochemical Redox Properties. The cyclic voltammetric data of a series of the thiophene-fused TCNQs are summarized in Tabel 1 together with those of a series of the corresponding quinones **5**—**8**. All of those quinonoid acceptors exhibit two single-electron reduction waves. TCAQ and other highly distorted TCNQ derivatives[9] have been known to exhibit a single-wave, two-electron reduction; they can thus be reduced

Table 1. Cyclic Voltammetric Data for **1**—**10**[a)]

Compd	E_1/V	E_2/V	$\Delta E=E_1-E_2$/V
1	+0.03	−0.24	0.27
2	+0.01	−0.25	0.26
3	−0.24	−0.45	0.21
4	−0.59	−0.77	0.18
5	−0.67	−1.33	0.66
6	−0.66	−1.32	0.66
7	−0.94	−1.57	0.63
8	−1.38	−1.90	0.52
9	−0.23	−0.67	0.44
10	−0.25	−0.69	0.44

a) V vs. SCE, measured in a 0.1 M solution of Et_4NClO_4 in acetonitrile.

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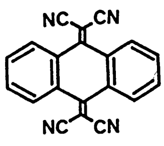
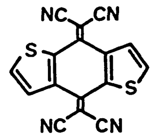
[#] For Part II in this series; see p. 2173 of this volume.



TCAQ



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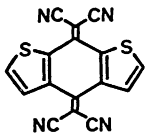

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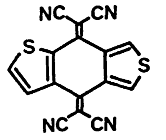

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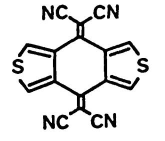

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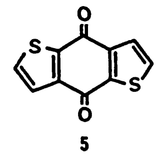

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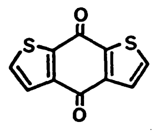

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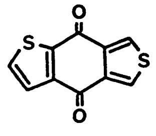

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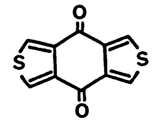

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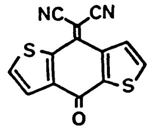

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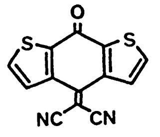

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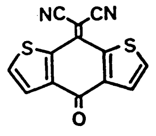

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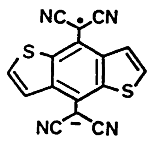
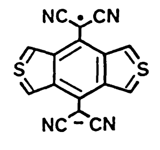


1'



4'

directly to the dianion species.[5,6] In the thiophene-fused TCNQs, however, the occurrence of two single-electron reductions, even in **4**, which is considered to be most highly distorted among the four isomers, suggests that the steric interactions caused by the four peri-hydrogen atoms of the thiophene rings of **4** and the dicyanomethylene moiety are significantly reduced, compared with those involved in the peri-hydrogen atoms of TCAQ.[10]

The first reduction potential decreases in the order **4**>**3**>**2**>**1** for the TCNQ series and **8**>**7**>**6**>**5** for the quinone series; compound **1** is an excellent electron acceptor. These trends could be rationalized on the basis of the resonance stabilities of the radical anions. Upon a one-electron reduction acceptor **1** becomes endowed with an aromatic sextet, as represented in canonical structure **1'**. In contrast to **1** the radical anion of **4** may be represented by formula **4'**, involving tetravalent sulfur. Such non-classical Kekulé thiophenes are unstable compared with classical Kekulé thiophenes,[11] although a few have been isolated,[12] including the benzo[1,2-*c*:4,5-*c'*]dithiophene ring system.[13] A non-classical condensed thiophene unit can also be generated in one of its resonance contributions of **3**.

The above interpretation was rather quantitatively verified by the concept of the resonance energy. The one-elctron reduction potential is correlated with the free-energy loss which is experienced in the formation of the anion radical species. For structurally related compounds this energy can be formulated as the π-resonance energy difference (ΔRE) between the neutral and radical anion species. The values for ΔRE of the thiophene-fused TCNQ series have been computed on the basis of Aihara's criterion using a general Hückel molecular orbital program.[14] The ΔRE values are given in Table

Table 2. Resonance Energy[a,b] for the Neutral (RE) and Radical Anion ($RE^{\bar{\cdot}}$) Species of **1**—**4**

Compd	RE (Neutral)	$RE^{\bar{\cdot}}$ (Radical anion)	$RE-RE^{\bar{\cdot}}$
1	0.2951	0.3314	0.036
2	0.2945	0.3307	0.036
3	0.2869	0.2927	0.006
4	0.2769	0.2812	0.004
TCNQ	0.0854	0.1442	0.0588

a) β unit. b) Hückel parameters used for calculation; $h_N=0.5$, $k_{C\equiv N}=1.4$, $h_S=1.2$, $k_{C\text{-}S}=0.65$.

2. A fairly good correlation is seen between the experimentally observed reduction potentials and the computed ΔRE values. McDowell has employed an analogous treatment for the keto-enol equilibrium position in the benzodithiophene analogs of anthrone;[15] the calculated delocalization energy difference between two tautomeric forms could explain the equilibrium positions.

The difference ($\Delta E = E_1 - E_2$) between the half-wave potentials for the first and second reductions decreases upon going from the quinones **5**—**8** to the dicyanoquinonoids **9**, **10**, and further to the tetracyanoquinonoids **1**—**4**. These findings clearly indicate that the tetracyanoquinonoids possess a smaller electrostatic repulsion and better charge delocalization than do the quinones. Thus, the displacement of the carbonyl group with the dicyanomethylene group brings about an expanded π-conjugation.

The ΔE values among the isomeric TCNQ series increase in the order **4**<**3**<**2**≃**1**. A similar trend is also observed for the quinone series, which has no steric congestion in the molecule. It thus seems likely that the intramolecular Coulombic repulsion is reduced, since the two polarizable sulfur atoms in the molecule are located further apart in the molecular framework.

A closer examination of Table 1 may reveal the steric effect produced by the replacement of the two carbonyl groups in the quinones to the dicyanomethylene functions. The difference of the second reduction potential (E_2) between the quinone series and the TCNQ series for each isomer is almost constant for four isomers (**1**—**5**: 1.09, **2**—**6**: 1.07, **3**—**7**: 1.12, **4**—**8**: 1.13 V). It can be reasoned that the steric interactions are relieved in the radical anion, as well as in the dianion, due to a single-bond character endowed to the exocyclic double bond by reduction.[6] Thus, the above-mentioned differences in the second reduction potential (E_2) are ascribable solely to the electronic effects brought about by replacing the carbonyl group with a dicyanomethylene group. On the other hand, the difference in the first reduction potential (E_1) between the quinone series and the TCNQ series depends on the mode of the fusion of the thiophene rings (**1**—**5**: 0.64, **2**—**6**: 0.65, **3**—**7**: 0.70, **4**—**8**: 0.79 V); in particular, a large difference is observed between **4** and **8**. Such a large shift may be viewed as

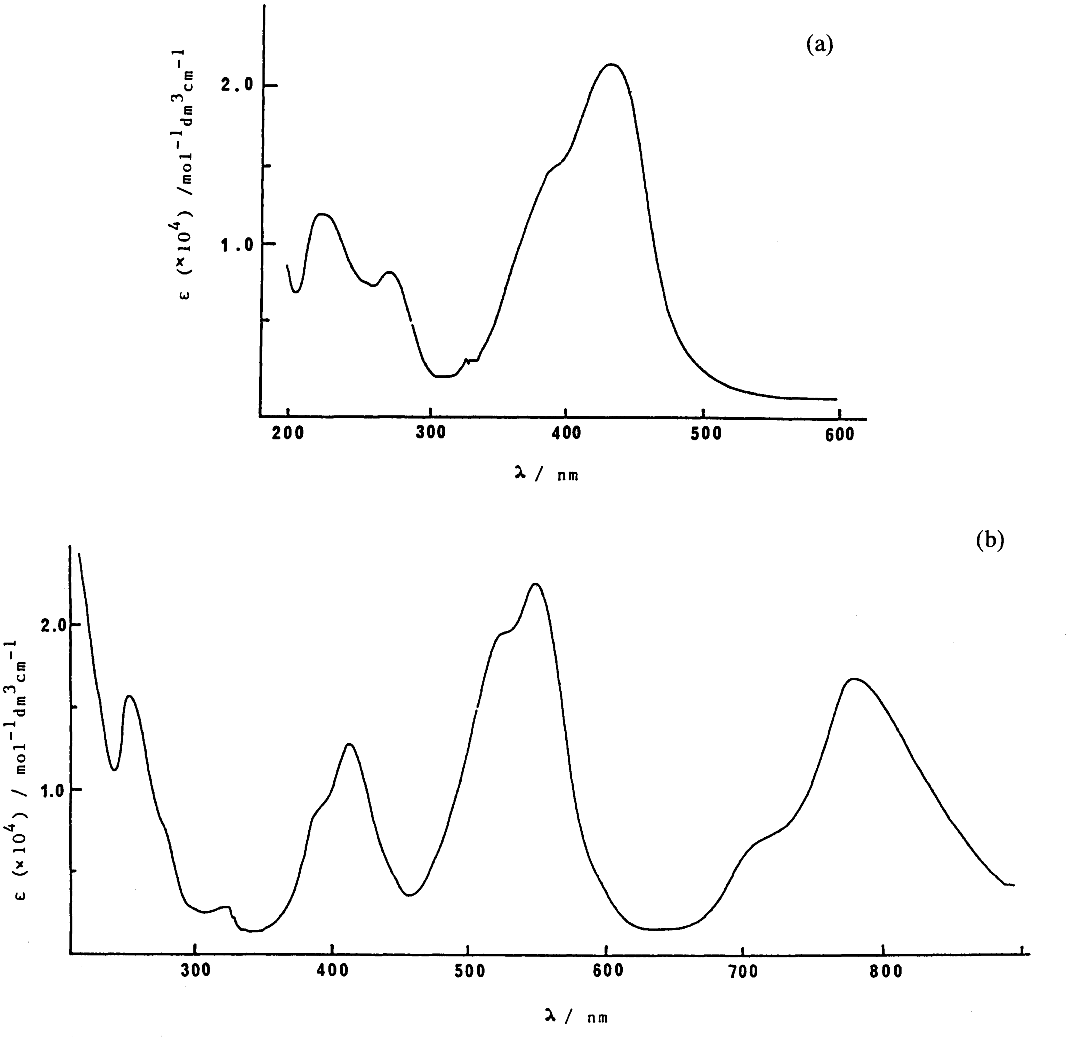


Fig. 1. UV-visible spectra of **1** (a) and anion radical of **1** (b) in an acetonitrile solution.

the result of a shift in the first reduction potential of the TCNQ to a more positive range than expected from electronic effects. The steric interaction exerted on neutral species of the isomer would be relieved in the anion radical species; it therefore acts as a driving force to undergo a one-electron reduction. However, the second wave from the radical anion to dianion would not gain a steric release, since the radical anion already has relief.

Electronic Spectra. The UV-visible spectral data of a series of thiophene-fused TCNQs are summarized in Table 3. The one-electron reduction of **1** by constant-potential electrolysis at +0.03 V vs. SCE produced a stable deep-red solution due to radical anion species (Fig. 1-b). This solution was electrochemically oxidized at +0.10 V vs. SCE to again give back an orange solution of the neutral **1** (Fig. 1-a). The radical anion species for the other isomers could be similarly produced by a stoichiometric one-electron reduction at constant potential. UV-visible spectral data for the radical anion species are also listed in Table 3.

The lowest electronic transition in the neutral molecules is successively blue-shifted upon going from **1** to **4**, although there is only a small difference between **1** and **2**. It has been known that the UV spectra of thieno[3,4-*b*]thiophene, constituted of nonclassical thiophene, is in marked contrast to those of thieno[2,3-*b*]thiophene and thieno[3,2-*b*]thiophene, which show a similar UV spectra of each other. This trend is also in line with the spectra observed in the precursor quinones,[15] and is presumably ascribable mostly to a successive rising of the LUMO energy levels in the order of **1**<**2**<**3**<**4**, as estimated from the electrochemical redox properties.

The longest wavelength band of TCAQ has been reported to exhibit a pronounced blue-shift, as compared to that of TCNQ, in spite of its expanded π-conjugation. This observation strongly suggest a highly distorted structure for TCAQ.[6,16] For isoelectronic analogs **1**—**4**, however, no such large shift has been observed. Thus, the distortion in the thiophene-fused TCNQ isomers would be less severe than that in TCAQ.

Table 3. UV-Visible Spectra[a)] of **1**—**4** and Their Anion Radical[b)]

Compd	Neutral λ/nm (log ε)	Radical anion λ/nm (log ε)
1	433 (4.32)	785 (4.19)
	272 (3.88)	554 (4.37)
	224 (4.02)	423 (4.10)
		266 (4.19)
2	424 (4.41)	783 (4.06)
	260 (4.03)	533 (4.24)
	230 (4.21)	396 (3.93)
		340 (3.71)
		236 (4.42)
3	394 (4.40)	639 (4.51)
	277 (4.32)	388 (4.15)
	216 (4.17)	305 (4.02)
		271 (4.29)
4	357	588
	280	

a) nm in acetonitrile. b) Generated by electrochemical reduction.

Charge-Transfer Complexes. Acceptors **1**, **2**, and **3** afforded a 1 : 1 charge transfer complex with tetrathiafulvalene (TTF), whereas **4** produced no charge-transfer complex, probably due to the poor electron-accepting ability and/or the steric interaction.[17]

The room-temperature conductivities of the complexes were measured on compressed pellets by a standard two-probe technique and were found to be extremely high for **1**-TTF, 4.78 S cm^{-1}, and **2**-TTF, 0.89 S cm^{-1}. The conductivity of **3**-TTF, however, was low, below 10^{-6} S cm^{-1}. The crystal structures of these complexes are described in the following papers.[10]

Compound **1** was chemically reduced to an anion radical salt by treating with lithium iodide in acetonitrile, which was further converted to the tetraethylammonium salt by an ion-exchange reaction with tetraethylammonium perchlorate. The dark-blue prisms, thus obtained, exhibited a high conductivity of 0.46 S cm^{-1} at room temperature, as measured on a single crystal. The temperature dependence of the conductivity showed semiconduting behavior with an activation energy of 0.12 eV.

As revealed in several materials demonstrated herein, we believe that two isomers of thiophene-fused TCNQs, **1** and **2**, are promising precursors for synthetic metals.

Experimental

All of the melting points are uncorrected. The ^{1}H NMR spectra were recorded on JEOL GSX-270 and Varian EM-390 spectrometers in chloroform-*d* with TMS as the internal standard. The IR spectra were run on a JASCO A202 spectrophotometer. The UV spectra were recorded on a Hitachi U-3200 spectrophotometer. Cyclic voltammetric measurements were performed in a 0.1 M (1 M=1 mol dm^{-3}) solution of tetrabutylammonium perchlorate in acetonitrile. HPLC-grade acetonitrile was distilled from P_2O_5 before use. About 1 mM of a substrate was used, employing the Pt working and counter electrodes and a commercially available saturated calomel electrode (SCE) as a reference electrode. All potentials were determined under a N_2 atmosphere, using a standard two-component cell. Voltammograms were generated by utilizing a Hokuto Denki Model HA-301 potentiostat/galvanostat with a Riken Denki recorder.

4,8-Bis(dicyanomethylene)-4,8-dihydrobenzo[1,2-*b*: 4,5-*b*′]-dithiophene (1). Titanium tetrachloride (ca. 0.8 ml, 5.8 mmol) was added under nitrogen to a magnetically stirred solution of 4,8-dihydrobenzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-dione (0.635 g, 2.88 mmol) and malononitrile (3.80 g, 57.5 mmol) in a mixture of dry chloroform (200 ml) and pyridine (10 ml ca. equiv of the dione). The resulting orange suspension was stirred for 5 h at reflux. The reaction was worked up by adding water (400 ml). The insoluble solid was filtered off by using an aspirator and the organic layer was extracted by chloroform (200 ml×2), collected, and dried ($MgSO_4$). The solvent was removed in vacuo and the residue was chromatographed on silica gel with chloroform as an eluent. Mono-dicyanomethylene product **9** (0.115 g, 15%) at first, and then **1** (0.336 g, 37%) was eluted, respectively.

1: Red prisms, mp 332 °C (decomp); IR (Nujol) 2200 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.90 (2H, d, J=5.7 Hz), 8.54 (2H, d, J=5.7 Hz). Found: C, 60.70; H, 1.34; N, 17.73; S; 20.48%. Calcd for $C_{16}H_4N_4S_2$ C, 60.75; H, 1.27; N, 17.71; S, 20.27%.

8-Dicyanomethylene-4,8-dihydrobenzo[1,2-*b*: 4,5-*b*′]dithiophen-4-one (9): Orange red prisms, mp 217 °C decomp; IR (Nujol) 2220, 1658 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=8.53 (1H, d, J=5.5 Hz), 7.84 (1H, d, J=5.5 Hz), 7.81 (1H, d, J=5.5 Hz), 7.76 (1H, d, J=5.5 Hz). Found: C, 58.42; H, 1.40; N, 10.53%. Calcd for $C_{13}H_4ON_2S_2$: C, 58.19; H, 1.50; N, 10.44%.

Other three isomers were prepared from the corresponding quinone precursors by similar procedures to those described for **1**.

4,8-Bis(dicyanomethylene)-4,8-dihydrobenzo[1,2-*b*: 5,4-*b*′]-dithiophene (2): Orange-red prisms, mp 325 °C (decomp); IR (Nujol) 2210 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.91 (2H, d, J=5.7 Hz), 8.46 (2H, d, J=5.7 Hz). Found: C, 60.65; H, 1.56; N, 17.46; S, 20.50%. Calcd for $C_{16}H_4N_4S_2$: C, 60.75; H, 1.27; N, 17.71; S, 20.27%.

8-Dicyanomethylene-4,8-dihydrobenzo[1,2-*b*: 5,4-*b*′]dithiophen-4-one (10) as a co-product of **2** is characterized as follows: Orange red prisms, mp 236 °C (decomp); IR (Nujol) 2250, 1652 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=8.46 (2H, d, J=5.5 Hz), 7.84 (2H, d, J=5.5 Hz). Found: C, 58.12; H, 1.84; N, 10.28; S, 23.73%. Calcd for $C_{13}H_4ON_2S_2$: C, 58.19; H, 1.50; N, 10.44; S, 23.88%.

4,8-Bis(dicyanomethylene)-4,8-dihydrobenzo[1,2-*b*: 4,5-*c*′]-dithiophene (3): Golden-yellow needles, mp 307° (decomp); IR (Nujol) 2210 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=8.96 (1H, d, J=2.9 Hz), 8.87 (1H, d, J=2.9 Hz), 8.34 (1H, d, J=5.5 Hz), 7.92 (1H, d, J=5.5 Hz). Found: C, 60.56; H, 1.19; N, 17.84; S, 20.53%. Calcd for $C_{16}H_4N_4S_2$: C, 60.75; H, 1.27; N, 17.71; S, 20.27%.

4,8-Bis(dicyanomethylene)-4,8-dihydrobenzo[1,2-*c*: 4,5-*c*′]-dithiophene (4): Yellow needles, mp>320 °C; IR (Nujol) 2225 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=8.81 (4H, s). Found: C, 60.68; H, 1.44; N, 17.83; S, 20.58%. Calcd for $C_{16}H_4N_4S_2$: C, 60.75; H, 1.27; N, 17.71; S, 20.27%.

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