May, 1989] © *1989 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **62**, *1547—1555 (1989)* 1547

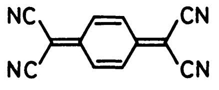
Novel Electron Acceptors Bearing a Heteroquinonoid System. II. Synthesis and Conductive Complexes of 2,5-Bis(dicyanomethylene)-2,5-dihydrothieno-[3,2-*b*]thiophene, 2,6-Bis(dicyanomethylene)-2,6-dihydrodithieno[3,2-*b*:2′,3′-*d*]thiophene, and Their Derivatives

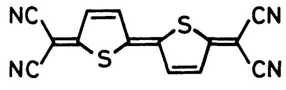
Koji Yui, Hideki Ishida, Yoshio Aso, Tetsuo Otsubo, Fumio Ogura,*
Atsushi Kawamoto,† and Jiro Tanaka†
Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Saijo, Higashi-Hiroshima 724
†Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

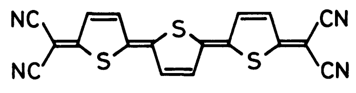
(Received November 19, 1988)

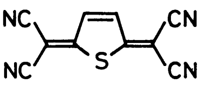
Novel heteroquinonoid compounds as potential electron acceptors, 2,5-bis(dicyanomethylene)-2,5-dihydrothieno[3,2-*b*]thiophene (**4a**), 3,6-dibromo derivative, 2,6-bis(dicyanomethylene)-2,6-dihydrodithieno[3,2-*b*:2′,3′-*d*]thiophene, 3,5-dibromo derivative, and 4,4-dioxide were synthesized by the action of tetracyanoethylene oxide or by a Pd(0)-catalyzed substitution reaction with sodium dicyanomethanide on the corresponding α,α'-dihalo-substituted fused thiophenes. They show effectively diminished on-site Coulomb repulsion owing to the extensive conjugation, and most of their molecular complexes with various electron donors exhibit very high electrical conductivities up to metallic region. In addition, X-ray crystallographic analysis of the complex of **4a** with bis(ethylenedithio)tetrathiafulvalene has elucidated that sulfur atoms embedded in **4a** molecule are capable of inducing a significant intermolecular interaction, forming a sheet-like network structure.

Intermolecular interactions of heteroatoms often play an important role on molecular assemblies. In particular, interstack contacts of chalcogen atoms in the cation radical salts of two organic electron donors, tetramethyltetraselenafulvalene and bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF), served to suppress typical Peierls-type insulating transitions, leading to the discovery of first organic superconductors.[1] On the other hand, similar multi-dimensionality based on chalcogen atoms has been designed for electron acceptors. Yamashita's and Kobayashi's groups have independently examined the condensation effect of heterocyclic rings on an excellent electron acceptor, 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ).[2] Our previous work has developed novel electron acceptors (**1**, its derivatives, and **2**) as extensively conjugated homologues of 2,5-bis(dicyanomethylene)-2,5-dihydrothiophene (**3**).[3] These acceptors have advantages of inducing not only increasing intermolecular interactions due to the sulfur atoms embedded in the quinonoid system but also very small on-site Coulomb repulsion due to the extensive conjugation, accordingly forming highly conductive molecular complexes.

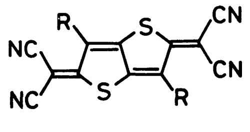

TCNQ

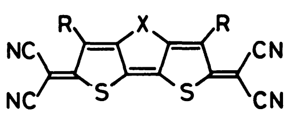

1

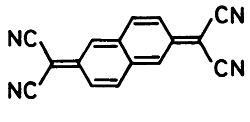

2


3

Our present aim is to study condensed homologues of **3** as another potential acceptors. 2,5-Bis(dicyanomethylene)-2,5-dihydrothieno[3,2-*b*]thiophene (**4a**) is the first molecule of the series and isoelectronic with 11,11,12,12-tetracyano-2,6-naphthoquinodimethane (TNAP), which has better accepting properties, that is, smaller on-site Coulomb repulsion, larger electron affinity, and higher polarizability than TCNQ.[4] A benzenoid compound corresponding to 2,6-bis(dicyanomethylene)-2,6-dihydrodithieno[3,2-*b*:2′,3′-*d*]thiophene (**5a**) is hitherto unknown. Now we wish to report the syntheses of **4a** and **5a** and their conductive molecular complexes as well as those of **4b** and **5b**—**c**.[5] In addition, the crystal structure of **4a**·BEDT-TTF complex is described, in which the sulfur atoms embedded in the quinonoid conjugation system are capable of inducing a significant intermolecular interaction.[6]

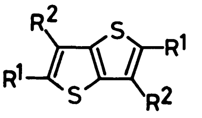

4a : R = H
4b : R = Br


5a : X = S, R = H
5b : X = S, R = Br
5c : $X = -\overset{O_2}{S}-$, R = H
5d : $X = -\overset{O}{S}-$, R = H

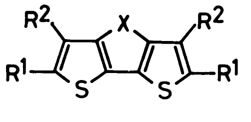

TNAP

Results and Discussion

Synthesis. *Gronowitz reaction* which refers to a conversion of 2,5-dihalogenothiophene into **3** by a pyrolytic reaction with tetracyanoethylene oxide (TCNEO)[7] was successfully applicable toward bi- and terthiophene systems to synthesize the corresponding heteroquinonoid compounds **1** and **2**.[5] We found that a similar procedure was equally well-applicable toward fused thieno- and dithienothiophene systems. 2,5-Dibromothieno[3,2-*b*]thiophene (**6a**) was treated with an excess of TCNEO at 167 °C of refluxing 1,3-dibromopropane for 2 h to afford **4a** in 36% yield. When accomplished at 131 °C of refluxing 1,2-dibromoethane as done in the synthesis of **1**, **2**, and **3**, the reaction proceeded very slowly and resulted in a lower yield (23%) of **4a**. On the other hand, Gronowitz reaction of 2,6-dibromodithieno[3,2-*b*:2′,3′-*d*]thiophene (**7a**) in refluxing 1,2-dibromoethane for 1.5 h simply produced a 39% yield of **5a**.



6a : $R^1 = Br$, $R^2 = H$
6b : $R^1 = R^2 = Br$
6c : $R^1 = R^2 = H$



7a : $X = S$, $R^1 = Br$, $R^2 = H$
7b : $X = S$, $R^1 = R^2 = Br$
7c : $X = -\overset{O_2}{S}-$, $R^1 = Br$, $R^2 = H$
7d : $X = -\overset{O}{S}-$, $R^1 = Br$, $R^2 = H$

2,3,5,6-Tetrabromothieno[3,2-*b*]thiophene (**6b**) and 2,3,6,7-tetrabromodithieno[3,2-*b*:2′,3′-*d*]thiophene (**7b**) were prepared in 87% and 94% yields by the treatment of thieno[3,2-*b*]thiophene (**6c**) and **7a**, respectively with a large excess of bromine in refluxing carbon disulfide. These tetrabromides **6b** and **7b** were allowed to react with TCNEO in refluxing 1,3-dibromopropane containing an excess of copper(I) bromide to afford 3,6-dibromo-2,5-bis(dicyanomethylene)-2,5-dihydrothieno[3,2-*b*]thiophene (**4b**) in 40% yield and 3,5-dibromo-2,6-bis(dicyanomethylene)-2,6-dihydrodithieno[3,2-*b*:2′,3′-*d*]thiophene (**5b**) in 27% yield, respectively.

Oxidation of **7a** with 2 equiv of *m*-chloroperbenzoic acid (MCPBA) in refluxing dichloromethane gave 2,6-dibromodithieno[3,2-*b*:2′,3′-*d*]thiophene 4,4-dioxide (**7c**) in 46% yield. The subsequent Gronowitz reaction of this sulfone **7c** in refluxing 1,3-dibromopropane afforded 2,6-bis(dicyanomethylene)-2,6-dihydrodithieno[3,2-*b*:2′,3′-*d*]thiophene 4,4-dioxide (**5c**) in 34% yield. When **7a** was oxidized with 1.2 equivalent of MCPBA at 0 °C, 2,6-dibromodithieno[3,2-*b*:2′,3′-*d*]thiophene 4-oxide (**7d**) was obtained as a major product in 46% yield together with **7c** (25%). In contrast to the above sulfone, TCNEO treatment of sulfoxide **7d** did not afford the corresponding heteroquinonoid acceptor **5d** but **5a** in 26% yield. The mechanism of this deoxygenation remains unclarified yet.

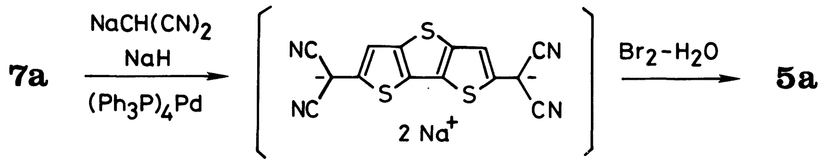
An alternative reaction used to synthesize **1** and **2** is nucleophilic substitution reaction of the precursory dibromides by sodium dicyanomethanide in refluxing 1,2-dimethoxyethane containing a catalytic amount of tetrakis(triphenylphosphine)palladium(0), followed by oxidation with bromine water. Scheme 1 shows a similar sequence of preparing **5a** in overall yield of 78%, whereas this procedure failed to synthesize **4a**, **5c**, and **5d**.

Redox Property. The redox behavior of acceptors **4a**, **b** and **5a**—**c** was determined by cyclic voltammetry in dichloromethane. Table 1 summarizes their half-wave reduction potentials together with those of **3** and TCNQ. All of these acceptors show two pairs of reversible redox waves. The first half-wave potentials ($E^1_{1/2}$) of **4a** and **5a** are comparable to that of **3**, indicating that the extension of heteroquinonoid skelton *in a condensed manner* is not capable of improving the electron accepting ability of **3**. As shown in Fig. 1, the longest wavelength maxima in the electronic absorption spectra of **3**, **4a**, and **5a** are bathochromically shifted largely with extending the conjugation system (**3**: $\lambda_{max}(\varepsilon)$ 330 (6400), 400 (18000), and 421 (20300); **4a**: 444 (66400) and 470 (71000); **5a**: 263

Table 1. Half-Wave Reduction Potentials[a]

Acceptor	$E^1_{1/2}$	$E^2_{1/2}$	ΔE/V
4a	0.06	−0.36	0.42
4b	0.25	−0.13	0.38
5a	0.05	−0.23	0.28
5b	0.16	−0.11	0.27
5c	0.28	−0.05	0.33
3	0.07	−0.54	0.61
TCNQ	0.25	−0.47	0.72

a) Cyclic voltammetry was carried out at RT in dichloromethane containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate using Ag/AgCl as a reference electrode and platinum as a working electrode at a scan rate of 100 mV s^{-1}.



Scheme 1.

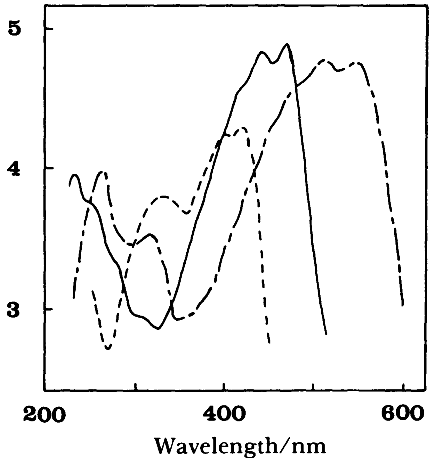


Fig. 1. Electronic spectra of **3** (-----), **4a**, (——), and **5a** (–––) in dichloromethane.

Table 2. Conductivities of Acceptors

Acceptor	Conductivity[a]/S cm^{-1}
4a	6.7×10^{-9}
4b	1.1×10^{-7}
5a	5.6×10^{-7}
5b	2.8×10^{-7}
5c	5.5×10^{-8}
3	$<10^{-11}$
TCNQ	8.1×10^{-10}

a) Measured on compressed pellets with a two-probe method at RT.

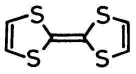
(9270), 315 (3000), 511 (60300), and 549 (59800) nm). These facts imply that such an extension does not lower the π-LUMO level of the heteroquinonoid acceptors but raises π-HOMO level, so that the energy gap between their HOMO and LUMO decreases in the order of the extensive acceptors. The differences (ΔE) between $E^1_{1/2}$ and $E^2_{1/2}$ values decrease as the quinonoid conjugation extend. This demonstrates that such an extension certainly cotributes to diminution of on-site Coulomb repulsion in dianion state. This effect, however, is not so conspicuous as that of the extension *in a linear manner* seen in molecule **1**, in which ΔE value is down to 0.23 V.[5]

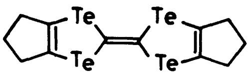
Two bromo substituents on **4b** and **5b** fairly enhance the electron-accepting power. The dibromide **4b**, as a result, is as strong an acceptor as TCNQ. The ΔE values of **4b** and **5b** are also diminished.

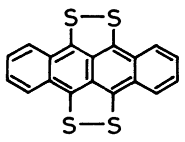
The accepting ability of **5a** is markedly strengthened by the conversion into the dioxide **5c** whose $E^1_{1/2}$ value is higher than that of TCNQ. The ΔE value of **5c**, however, becomes a little larger than that of **5a**, indicating that the sulfonation is not available for diminution of on-site Coulomb repulsion.

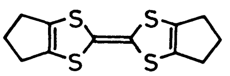
Table 2 shows electrical conductivities on pellet samples of neutral organic compounds. All new acceptors are relatively conductive in contrast to almost insulating behavior of **3**, being probably due to an increasing intermolecular contacts of the present extensive systems.

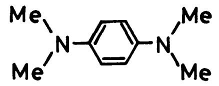
Charge-Transfer Salts. These acceptors did form a variety of molecular complexes with known electron donors such as tetrathiafulvalene (TTF), 5,6:11,12-bis(dithio)naphthacene (so-called tetrathiotetracene, TTT), bis(trimethylene)tetrathiafulvalene (HMTTF), *N,N,N′,N′*-tetramethylphenylenediamine (TMPDA), tetraphenylbipyranylidene (TPBP), bis(trimethylene)-tetratellurafulvalene (HMTTeF), 5,6-dihydroacenaphtho[5,6-*cd*]-1,2-ditellurole (ADTe), and BEDT-TTF. They are mostly of 1:1 stoichiometry, but some are of 2:1 rich in either donor or acceptor and include a solvent used for complexation. Table 3 summarizes the physical properties of these isolated complexes.

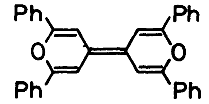

TTF

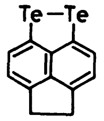

HMTTeF

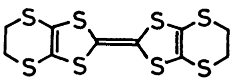

TTT


HMTTF


TMPDA


TPBP


ADTe


BEDT-TTF

Acceptors **1**, **2**, and **3** formed CT complexes only with strong electron donors such as TTF, TTT, HMTTeF, and TPBP, and the conductivities of the resulting complexes increased with the extensive conjugation of the acceptor.[5,8] On the other hand, **4a**, having the almost same accepting ability as **1**—**3**, formed complexes with all the other donors except ADTe. In this regard, **3a** of a condensed conjugated type is superior to acceptors **1** and **2** of a linear conjugated type. Moreover, most of the complexes showed very high electrical conductivities as measured on a compressed pellet at room temperature. In particular, the HMTTeF complex recorded the highest value of 140 S cm^{-1}. The BEDT-TTF and TTT complexes, however, exhibited exceptionally low

Table 3. Charge-Transfer Salts Composed of **4a**, **b**, and **5a**—**c**

Complex or salt[a]	Appearance	Found (Calcd)[b]/%			ν_{CN}[c]/cm^{-1}	dp[d]/°C	Conductivity[e] /S cm^{-1}
		C	H	N			
4a·TTF[f]	Black fine needles	46.33; (45.94;	1.39; 1.28;	11.90 11.90)	2199	157	13
4a·TTT	Green powder	57.37; (58.23;	1.51; 1.63;	8.11 9.05)	2216	228	1.9×10^{-7}[g]
(**4a**)$_2$·TMPDA[f]	Black powder	57.56; (58.60;	2.69; 2.89;	19.15 20.10)	2196	165	5.0×10^{-3}[g]
4a·HMTTF	Black fine needles	52.10; (52.34;	2.32; 2.56;	9.39 10.17)	2201	>300	4.7
(**4a**)$_2$·TPBP·CB	Deep violet fine needles	69.17; (69.40;	2.72; 3.00;	10.03 10.12)	2195	>300	2.7
4a·HMTTeF	Black fine needles	30.88; (30.90;	1.51; 1.51;	5.68 6.01)	2200	>300	140
4a·BEDT-TTF	Black leaflets	40.30; (40.59;	1.26; 1.55;	7.89 8.61)	2223	254	6.9×10^{-10}[g]
4b·TTF	Black needles	34.35; (34.40;	0.59; 0.64;	8.88 8.92)	2195	175	11
4b·(TTT)$_2$	Dark green fine needles	51.14; (51.06;	1.19; 1.43;	4.66 4.96)	2194	>300	3.1
4b·TMPDA	Dark blue fine cryst	44.62; (44.91;	2.50; 2.74;	13.21 14.28)	2193	157	2.0×10^{-1}
4b·HMTTF·(CB)$_{0.5}$	Black needles	42.67; (42.40;	1.89; 1.91;	7.42 7.33)	2192	160	7.5
4b·(HMTTeF)$_2$	Greenish brown fine cryst	25.47; (24.60;	1.83; 1.38;	3.22 3.19)	2192	222	170
4b·ADTe	Deep blue powder	34.60; (34.67;	0.93; 0.97;	6.12 6.74)	2200	298	3.7
4b·BEDT-TTF	Dark green fine needles	32.60; (32.67;	1.72; 1.00;	6.66 6.93)	2220	241	7.0×10^{-8}[g]
5a·TTF[f]	Deep green powder	45.65; (45.61;	1.33; 1.15;	10.45 10.64)	2198	184	2.3
5a·(TTT)$_2$	Black powder	56.95; (58.45;	1.45; 1.77;	5.75 5.45)	2172[i]	256	3.0
(**5a**)$_2$·TPBP	Dark green powder	66.42; (67.25;	2.61; 2.55;	9.47 10.12)	2202	>300	6.2×10^{-1}
5a·HMTTeF	Dark brown powder	31.43; (31.58;	1.47; 1.43;	5.38 5.66)	2200	277	20
5b·TTF	Greenish brown powder	36.01; (35.09;	0.68; 0.59;	8.01 8.18)	2205	245	23
5b·TTT	Dark green powder	46.13; (46.16;	0.97; 0.97;	6.60 6.73)	2194	>300	5.8
(**5b**)$_2$·HMTTF	Deep green powder	38.05; (38.60;	1.30; 0.97;	9.30 9.00)	2205	242	2.3
(**5b**)$_2$·TMPDA	Deep green fine needles	40.59; (40.59;	1.43; 1.43;	12.00 12.46)	2197	213	2.4
(**5b**)$_2$·TPBP	Dark green powder	53.19; (52.26;	1.79; 1.70;	7.10 7.86)	2190	>300	4.9
5b·HMTTeF	Black powder	27.38; (27.23;	0.91; 1.05;	4.60 4.89)	2192	244	14
5b·(ADTe)$_2$	Dark brown powder	34.88; (35.25;	1.42; 1.25;	5.03 4.33)	2192	238	2.3×10^{-1}
5c·TTF	Brown fine needles	43.61; (43.00;	1.76; 1.08;	10.20 10.02)	2192	262	1.2×10^{-2}
5c·(TTT)$_2$	Deep violet powder	55.65; (56.69;	1.48; 1.71;	5.22 5.29)	2193	285	2.1
5c·TPBP	Golden brown powder	70.24; (70.40;	3.41; 3.20;	6.25 6.84)	2192	295	7.7×10^{-6}[g]
5c·(HMTTeF)$_2$	Violet powder	27.63; (27.04;	2.00; 1.55;	2.99 3.32)	2192	210	7.7
4a·Na$_{0.7}$[f]	Black needles	51.39; (51.04;	0.70; 0.71;	19.32 19.84)	2204	>300	3.1×10^{-3}
4a·K$_{0.6}$[f]	Black powder	50.07; (49.74;	2.10; 0.70;	18.78 19.34)	2195	255	1.9

Table 3. (Continued)

Complex or salt[a]	Appearance	Found (Calcd)[b]/% C	H	N	ν_{CN}[c]/cm^{-1}	dp[d]/°C	Conductivity[e] /S cm^{-1}
(**4a**)$_3$·(n-Bu)$_4$N[f]	Black powder	59.82; (59.98;	3.80; 4.07;	16.48 17.49)	2170	279	6.3×10^{-4}
5a·Na[f,j]	Dark violet powder	44.13;	0.76;	14.27	2180	>300	5.3×10^{-1}
(**5a**)$_5$·(n-Bu)$_4$N[f]	Dark violet powder	54.71; (55.70;	2.88; 2.50;	14.14 15.86)	2183	273	1.9×10^{-1}
5c·Na[f]	Dark green powder	43.78; (44.56;	1.27; 0.53;	14.04 14.85)	2200	>300	1.1×10^{-4}[g]
5c·K[f]	Dark blue powder	42.77; (42.74;	0.67; 0.51;	14.21 14.24)	2192	>300	2.0×10^{-5}[g]

a) Obtained from chlorobenzene, which is abbreviated as CB when contained in the complex, unless otherwise described. b) Calculated as stoichiometry indicated for the complex. c) Measured with a KBr disk method unless otherwise mentioned. d) Decomposition point. e) Measured on compressed pellets at RT with a four-probe method unless otherwise described. f) Obtained from acetonitrile. g) Measured on compressed pellets with a two-probe method at RT. h) Obtained from benzonitrile. i) Measured with a Nujol mull method. j) Composition was not estimated by an elemental analysis of C, H, and N.

conductivities. The case of the BEDT-TTF complex is probably because of lack of charge transfer due to the weak electron-donating ability of BEDT-TTF, as indicated by no shift of the CN frequency of the complex relative to neutral **4a** (2223 cm^{-1}).[9] The case of the TTT complex may be ascribed to the formation of a Mot insulator due to the poor fit of a strong donor TTT to **4a**. Acceptor **4b** complexed all the given donors except TPBP. The resulting complexes, except the BEDT-TTF complex, had also very high conductivities including a marverously high value 170 S cm^{-1} of the HMTTeF complex for a pellet sample. It may be furthermore noted as a result of the elevated electron affinity of **4b** that the TTT, TMPDA,and BEDT-TTF complexes are considerably more conductive than the corresponding ones of **4a**. A similar but somewhat different situation is the case for more fused heteroquinonoid system **5**. Acceptor **5a** thus formed complexes with only four strong donors, TTF, TTT, TPBP, and HMTTeF, and its dibromo derivative **5b** with all the given donors. The latter complexes are generally more conductive than the former ones. On the other hand, sulfone acceptor **5c**, though the strongest of the present acceptors, complexed only just the same strong donors as did **5a**. In addition, the conductivities of **5c** complexes are not so high as those of the corresponding **5b** complexes. The sterical bulkiness of the sulfone moiety is realized to interfere crystallization with a conductive molecular arrangement on complexation.

Acceptors **4a**, **5a**, and **5c** were reduced with sodium iodide, potassium iodide, and tetrabutylammonium iodide to form the corresponding anion radical salts. The physical properties of these salts are also summarized in Table 3. Some of these salts are found to have mixed valences in the acceptor because of non-stoichiometric composition, and accordingly they show higher conductivities than the other salts with 1:1 composition.

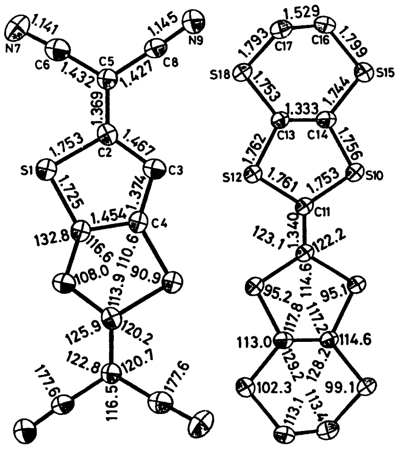
Table 4. Fractional Atomic Coordinates and Equivalent Temperature Factors (Å^2)

	x(×10^4)	y(×10^4)	z(×10^4)	B_{eq}[a]
S1	646 (2)	590 (1)	2413 (2)	3.7 (1)
C2	870 (7)	1594 (4)	5146 (7)	2.6 (2)
C3	487 (8)	1287 (4)	6068 (8)	3.0 (2)
C4	−2 (8)	259 (4)	5936 (7)	2.8 (2)
C5	1398 (8)	2559 (4)	3690 (8)	2.8 (2)
C6	1684 (8)	2765 (4)	1747 (9)	3.5 (2)
N7	1869 (8)	2899 (4)	173 (8)	4.8 (2)
C8	1663 (8)	3407 (4)	5067 (8)	3.2 (2)
N9	1897 (8)	4108 (4)	6123 (7)	4.4 (2)
S10	4502 (2)	9118 (1)	2599 (2)	3.6 (1)
C11	4715 (7)	9518 (4)	157 (8)	2.8 (2)
S12	4184 (2)	8546 (1)	−1755 (2)	3.4 (1)
C13	3568 (7)	7579 (4)	−242 (8)	2.9 (2)
C14	3718 (8)	7841 (4)	1675 (8)	3.0 (2)
S15	3271 (3)	7086 (1)	3577 (2)	4.4 (1)
C16	2253 (11)	5875 (4)	2230 (10)	5.1 (2)
C17	3304 (10)	5652 (4)	639 (9)	4.2 (2)
S18	2842 (2)	6375 (1)	−1484 (2)	3.6 (1)

a) $B_{eq}=(4/3)\sum_{ij}\beta_{ij}(a_i\cdot a_j)$.

Molecular and Crystal Structure of 4a·BEDT-TTF Complex. An X-ray crystallographic analysis was undertaken to elucidate the function of the embedded sulfur atoms in the crystal structures of the present complexes. Most of the complexes, however, appeared as fine crystals or powders. Only the molecular complex of **4a** with BEDT-TTF gave a good single crystal being suitable for the analysis. The crystal is triclinic with space group $P\bar{1}$, the unit cell contains one donor and one acceptor, and each component is present on the crystallographic inversion center. Table 4 summarizes the final atomic parameters.

Figure 2 illustrates the molecular geometries of both components. Acceptor **4a** takes a planar conformation; the largest deviation from the least squares plane is 0.057 Å for the sulfur atoms. On the other hand, the structure of the BEDT-TTF molecule closely resembles those found in various cation radical salts of BEDT-TTF;[10] the TTF moiety keeps a planar conformation within 0.03 Å deviation and the terminal ethylene groups appreciably deviate from the optimal plane. The bond lengths of the TTF skelton can be used to estimate roughly the degree of charge transfer, ρ.[11] Table 5 shows a comparison of the present complex with neutral BEDT-TTF molecule[12] as a standard of $\rho=0$ and a cation radical salt α-(BEDT-TTF)$_2$PF$_6$[11] with $\rho=0.5$. The central C=C bond length (a) of the complex is between those of the neutral species and the salt, but the other C=C bond length (d) and C–S bond length (b and c) are quite identical to the corresponding ones of the neutral species. This indicates the degree of charge transfer in the present complex to be almost nil, as already judged from the examination of the nitrile stretching frequency.



4a BEDT-TTF

Fig. 2. Bond lengths and bond angles of **4a** and BEDT-TTF in this complex. Estimated standard deviations are 0.005—0.011 Å and 0.3—0.6° for lengths and angles, respectively.

Figure 3 shows the crystal structure viewed along the c axis (the transverse projection of the molecules) and along the orthogonal axis (the longitudinal projection of the molecules). The segregate stacking columns of both components are observed along the a axis, which is nearly perpendicular to the molecular planes, but the interplanar distances are as long as the unit length

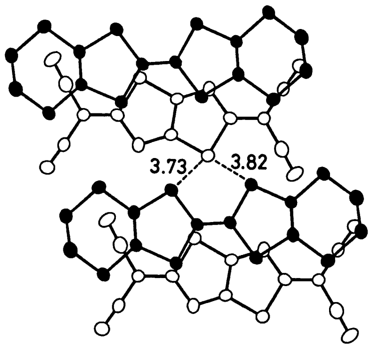
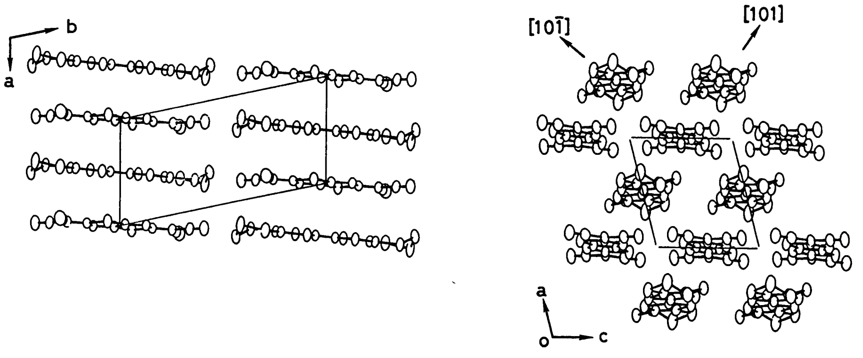


Fig. 4. The mode of the molecular overlap. The view direction is perpendicular to the molecular plane.

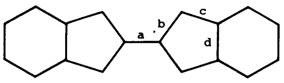


(a) (b)

Fig. 3. Crystal structures viewed (a) along c axis and (b) approximately along the long axis of the molecule.

Table 5. A Comparison of the Mean Bond Lengths (Å) of BEDT-TTF

Compound	ρ	a	b	c	d
BEDT-TTF[12]	0	1.319	1.753	1.755	1.328
α-(BEDT-TTF)$_2$PF$_6$[11]	0.5	1.365(4)	1.740(2)	1.750(2)	1.345(3)
Present complex	ca. 0	1.340(9)	1.757(6)	1.759(5)	1.333(8)



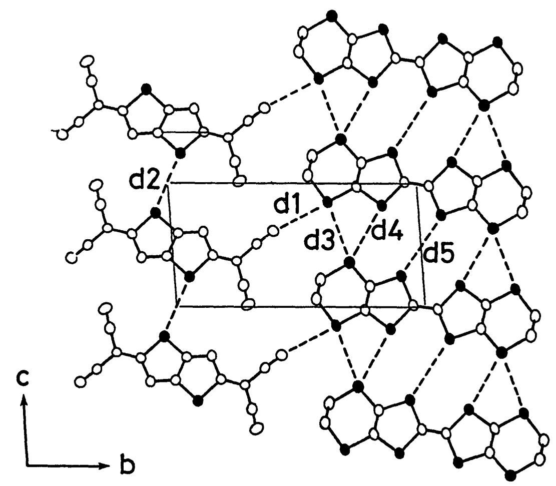


Fig. 5. Sheet-like net works in the (2$\bar{1}$0) plane. Some of short contacts: d1=3.33, d2=3.48, d3=3.64, d4=3.59, and d5=3.98 Å.

(7.205 Å) of the a axis. On the other hand, an alternate stacking arrangement is observed with a little face-to-face overlap along [101] or [10$\bar{1}$] direction, as illustrated in Fig. 4.

The intermolecular S···S contact distances (3.73 and 3.82 Å) between the alternately stacked components are slightly longer than the sum of van der Waals radius (3.70 Å). On the other hand, several short intermolecular contacts exist in (2$\bar{1}$0) plane, as shown in Fig. 5. The two components are separately arranged side by side along the transverse direction and alternately along the longitudinal direction, constituting a sheet-like network. In accordance with the structural features of various BEDT-TTF salts[10,11] and neutral BEDT-TTF,[12] the sulfur atoms of the ethylenedithio moiety in BEDT-TTF component play an important role on this side-by-side arrangement, that is, they strongly interact with the same kind of atom (3.64 Å) and the sulfur atoms (3.59 Å) of the 1,3-dithiole ring of the neighboring BEDT-TTF. In addition, they interact with the nitrogen atom of the acceptor with van der Waals contact (3.33 Å). On the other hand, there is no van der Waals contact between the sulfur atoms of the 1,3-dithiole rings (3.98 Å). Figure 5 also demonstrates that there exists a strong S···S interaction between the acceptors (3.48 Å). This indicates that the sulfur atoms embedded in the quinonoid conjugation system are capable of inducing multi-dimensionality in molecular complexes.

Conclusion

Novel compounds **4a**, **b** and **5a**—**c** of a fused conjugated type have been found to be superior electron acceptors with very small on-site Coulomb repulsion. They formed a variety of molecular complexes with π-electron donors, most of which exhibited high conductivities up to metallic bound. In particular, the HMTTeF complexes of **4a** and **4b** recorded 140 and 170 S cm^{-1}, respectively, marverously high for a pellet measurement at room temperature. The X-ray crystallographic analysis of **4a**·BEDT-TTF complex has elucidated that sulfur atoms embedded in the quinonoid conjugation contribute to intermolecular interactions in the crystal structure. Thus the present fused heteroquinonoid compounds are promising electron acceptors to design multi-dimensional organic metals directed towards a superconductor.

Experimental

General. Melting points are uncorrected. All solvents are of reagent grade. Electron donors used to prepare the molecular complexes, TTF,[13] TTT,[14] HMTTF,[15] TPBP,[16] BEDT-TTF,[17] and ADTe[18] were obtained according to the published procedures except commercially available TMPDA and HMTTeF. NMR spectra were recorded on a JEOL PMX-60 spectrometer (60 MHz) using tetramethylsilane as an internal standard. IR spectra were taken on a Hitachi 260-30 or a Perkin-Elmer 1600 FTIR spectrophotometer with a Nujol mull or a KBr disk method. MS spectra were measured on a Shimadzu GC-MS QP-1000A Mass spectrometer at 70 eV using a direct insertion technique. Electronic absorption spectra were recorded on a Shimadzu UV-160 spectrophotometer. Cyclic voltammetry was carried out on a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 function generator.

2,5-Bis(dicyanomethylene)-2,5-dihydrothieno[3,2-*b*]thiophene (4a). A mixture of **6a**[19] (838 mg, 2.81 mmol), TCNEO (1.61 g, 11.2 mmol), and dry 1,3-dibromopropane (21 cm^3) was heated under reflux for 2 h. The resulting solution was twice column-chromatographed on silica gel with dichloromethane, followed by recrystallization from acetonitrile to give **4a** (268 mg, 36%) as reddish brown needles: mp>300 °C; IR (KBr) 2223 (CN) and 1508 (C=C) cm^{-1}; MS *m/z* 266 (M$^+$, 100%); Anal. ($C_{12}H_2N_4S_2$) C, H, N.

2,3,5,6-Tetrabromothieno[3,2-*b*]thiophene (6b). A solution of bromine (2.4 cm^3, 49 mmol) in carbon disulfide (3 cm^3) was dropwise added to a solution of **6c** (200 mg, 1.43 mmol) in carbon disulfide (5 cm^3), and the mixture was heated under gentle reflux for 23 h. To the resulting suspension was carefully added a saturated sodium hydrogensulfite aqueous solution. The precipitated solid was collected by filtration, washed with water and ethanol, and dried in vacuo. The organic layer of the filtrate was washed with brine, 5% sodium hydrogencarbonate aqueous solution, and again brine, and dried over anhydrous magnesium sulfate. After concentration in vacuo, the residual solid was combined with the above precipitate, and recrystallized from benzene to give **6b** (567 mg, 87%) as colorless needles: mp 237—238.5 °C (in a sealed tube); Anal. ($C_6Br_4S_2$) C.

3,6-Dibromo-2,5-bis(dicyanomethylene)-2,5-dihydrothieno-[3,2-*b*]thiophene (4b). A mixture of **6b** (1.60 g, 3.50 mmol), TCNEO (5.04 g, 35.0 mmol), copper(I) bromide (3.51 g, 24.5 mmol), and dry 1,3-dibromopropane (70 cm^3) was heated under reflux for 4 h. The mixture was column-chromatographed on silica gel with dichloromethane, followed by recrystallization from chlorobenzene to give **4b** (627 mg, 40%) as purple micro prisms: mp>300 °C; IR (KBr) 2224 (CN) and 1508 (C=C) cm^{-1}; MS *m/z* 422 (M$^+$−2, 53%), 424 (M$^+$, 100%), and 426 (M^++2, 56%); Anal. ($C_{12}Br_2N_4S_2$) C, N.

2,6-Bis(dicyanomethylene)-2,6-dihydrodithieno[3,2-*b*:2′,3′-*d*]thiophene (5a). A) Using TCNEO. A mixture of **7a** (354 mg, 1.00 mmol),[20] TCNEO (576 mg, 4.00 mmol), and dry 1,2-dibromoethane (16 cm^3) was heated under reflux for 1.5 h. The mixture was column-chromatographed on silica gel with dichloromethane, followed by recrystallization from acetonitrile to give **5a** (125 mg, 39%) as deep violet fine crystals: mp>300 °C; IR (KBr) 2219 (CN) and 1496 (C=C) cm^{-1}; MS *m/z* 322 (M^+, 100%); Anal. ($C_{14}H_2N_4S_3$) C, H, N.

B) Using Sodium Dicyanomethanide. Malononitrile (79 mg, 1.2 mmol) was added to an ice-cooled suspension of sodium hydride (96 mg, 2.4 mmol, 60% oily) in absolute 1,2-dimethoxyethane (4 cm^3) under nitrogen stream, and the mixture was stirred at RT for 20 min. To this solution was added **7a** (142 mg, 0.40 mmol) and tetrakis(triphenylphosphine)palladium(0) (46 mg, 0.04 mmol), and the mixture was heated under reflux for 2 h. The resulting solution was treated with saturated bromine water (15 cm^3) at 0 °C, and filtered on Hyflo Super-cel. The collected solid was extracted with boiling chlorobenzene, and recrystallized from chlorobenzene to give **5a** (101 mg, 78%).

2,3,6,7-Tetrabromodithieno[3,2-*b*:2′,3′-*d*]thiophene (7b). Bromine (2.1 cm^3, 41.2 mmol) was added to a solution of **7a** (1.91 g, 5.39 mmol) in carbon disulfide (40 cm^3), and the solution was heated at gentle reflux for 24 h. The solution was carefully treated with 10% sodium hydrogensulfite aqueous solution, and diluted with hexane. The resulting precipitate was collected by filtration, washed thoroughly with water and methanol, dried in vacuo, and recrystallized from chlorobenzene to give **7b** (2.59 g, 94%) as off-white leaflets: mp>300 °C; Anal. ($C_8Br_4S_3$) C.

3,5-Dibromo-2,6-bis(dicyanomethylene)-2,6-dihydrodithieno[3,2-*b*:2′,3′-*d*]thiophene (5b). A mixture of **7b** (2.10 g, 4.10 mmol), TCNEO (5.91 g, 41.0 mmol), copper(I) bromide (4.12 g, 28.7 mmol), and dry 1,3-dibromopropane (120 cm^3) was heated under reflux for 1.2 h. The reaction mixture was column-chromatographed on silica gel with dichloromethane, and recrystallized from chlorobenzene to give **5b** (530 mg, 27%) as deep green prisms: mp>300 °C; IR (KBr) 2221 (CN) and 1490 (C=C) cm^{-1}; MS *m/z* 478 (M^+−2, 50%), 480 (M^+, 100%), and 482 (M^++2, 62%); Anal. ($C_{14}Br_2N_4S_3$) C, N.

2,6-Dibromodithieno[3,2-*b*:2′,3′-*d*]thiophene 4,4-Dioxide (7c). MCPBA (216 mg, 1.00 mmol, 80% purity) was added to a solution of **7a** (177 mg, 0.500 mmol) in dichloromethane (15 cm^3), and the mixture was heated under gentle reflux for 2 d. The reaction mixture was poured into a concentrated sodium hydrogensulfite aqueous solution, and extracted with dichloromethane. The organic layer was washed with 5% sodium hydrogencarbonate aqueous solution and water, and dried over anhydrous magnesium sulfate. After concentration in vacuo, the residue was purified by column chromatography on silica gel with dichloromethane to give **7c** (90 mg, 47%): yellow prisms from chloroform; mp 248 °C (decomp); IR (KBr) 1348, 1303, 1282, 1154, 1132 (SO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.21 (s); Anal. ($C_8H_2Br_2O_2S_3$) C, H.

2,6-Bis(dicyanomethylene)-2,6-dihydrodithieno[3,2-*b*:2′,3′-*d*]thiophene 4,4-Dioxide (5c). A mixture of **7c** (1.47 g, 3.81 mmol), TCNEO (5.49 g, 38.1 mmol), and dry 1,3-dibromopropane (50 cm^3) was heated under reflux for 5 h. The reaction mixture was twice column-chromatographed on silica gel with dichloromethane–acetone (96:4 v/v), and recrystallized from acetonitrile to give **5c** (462 mg, 34%) as deep violet prisms: mp>300 °C; IR (KBr) 2222 (CN) and 1510 (C=C), 1343, 1323, 1172 (SO_2) cm^{-1}; MS *m/z* 354 (M^+, 100%); Anal. ($C_{14}H_2N_4O_2S_3$) C, H, N.

2,6-Dibromodithieno[3,2-*b*:2′,3′-*d*]thiophene 4-Oxide (7d). MCPBA (517 mg, 2.40 mmol, 80% purity) was added to a solution of **7a** (708 mg, 2.00 mmol) in chloroform (26 cm^3) at 0 °C. The mixture was stirred at 0 °C for 9 h and at RT for 4 h, poured into 10% sodium hydrogensulfite aqueous solution, and extracted with chloroform. The organic layer was washed with 5% sodium hydrogencarbonate aqueous solution and water, and dried over anhydrous magnesium sulfate. After concentration in vacuo, the residue was column-chromatographed on silica gel with chloroform to give **7c** (190 mg, 25%) and **7d** (340 mg, 46%): yellow crystals from hexane–chloroform; mp 172.5—174 °C; IR (KBr) 1052 (SO) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.34 (s); Anal. ($C_8H_2Br_2OS_3$) C, H.

Reaction of 7d with TCNEO. A mixture of **7d** (143 mg, 0.386 mmol), TCNEO (556 mg, 3.86 mmol), and dry 1,3-dibromopropane (7 cm^3) was heated under reflux for 2 h. The reaction mixture was worked up according to the procedure of Method A described in the synthesis of **5a**, and the yield was 26%.

Preparation of Molecular Complexes and Anion Radical Salts. All molecular complexes described in this report were each prepared by mixing saturated solutions of donor and acceptor in hot chlorobenzene, acetonitrile, or benzonitrile. All anion radical salts were obtained by the reaction of the acceptors with the corresponding metal iodide or tetrabutylammonium iodide in hot acetonitrile or benzonitrile. The complexes or salts precipitated out immediately or on cooling appropriately, and were collected by filtration and dried in vacuo.

Crystal Structure Analysis of 3a · BEDT-TTF. The intensities of X-ray diffractions were collected with a Rigaku automated diffractometer using Cu $K\alpha$ radiation monochromatized with a graphite plate. We obtained 1969 independent diffractions within 2θ=126° which had intensities larger than the statistical counting error, and used all of them for analysis. The dimension of the measured crystal was 0.50×0.40×0.01 mm^3. The crystal belonged to the triclinic system with the space group, $P\bar{1}$, crystal data being a=7.205(1), b=13.654(1), c=6.898(2) Å, α=91.76(1), β=103.85(2), γ=101.32(1)°, Z=1, and V=643.9(2) Å^3, D_{obs}=1.626, and D_{calcd}=1.679 g cm^{-3}. The structure was solved by the direct method combined with the Monte-Carlo method[21] for the selection of the initial set of phase. It was refined by the full-matrix least squares method after applying the absorption corrections.[22] Atomic scattering factors were taken from International Tables for X-ray Crystallography.[23] Anisotropic temperature factors were used for the refinement, and hydrogen atoms were not included in the refinement. The final R value was 0.073. Computations were carried out partly at the Information Processing Center of Hiroshima University and mainly at the Computation Center of Nagoya University using the library program of CRYSTAN system. Tables of structure factors and anisotropic thermal parameters are deposited as Document No. 8869 at the Office of the Editor of Bull. Chem. Soc. Jpn.

This work was partially supported by Grants-in-Aid for Scientific research Nos. 62550635 and 63604576 from the Ministry of Education, Science and Culture. The authors wish to thank Mr. Hideaki Iwatani, Hiroshima University, for elemental analysis.

References

1) For a review, see: J. M. Williams, M. A. Beno, H. H. Wang, P. C. W. Leung, T. J. Emge, U. Geiser, and K. D. Carlson, *Acc. Chem. Res.*, **18**, 261 (1985).

2) Y. Yamashita, T. Suzuki, T. Mukai, and G. Saito, *J. Chem. Soc., Chem. Commun.*, **1985**, 1044; K. Kobayashi and C. L. Gajurel, *ibid.*, **1986**, 1779.

3) K. Yui, Y. Aso, T. Otsubo, and F. Ogura, *J. Chem. Soc., Chem. Commun.*, **1987**, 1816.

4) J. Diekmann, W. R. Hertler, and R. E. Benson, *J. Org. Chem.*, **28**, 2719 (1963); D. J. Sandman and A. F. Garito, *ibid.*, **39**, 1165 (1974).

5) A preliminary result was published in the following paper: K. Yui, H. Ishida, Y. Aso, T. Otsubo, and F. Ogura, *Chem. Lett.*, **1987**, 2339.

6) A preliminary report has appeared in the following paper: Y. Aso, K. Yui, H. Ishida, T. Otsubo, F. Ogura, A. Kawamoto, and J. Tanaka, *Chem. Lett.*, **1988**, 1069.

7) S. Gronowitz and B. Uppström, *Acta Chem. Scand., Ser. B*, **28**, 981 (1974).

8) M. L. Kaplan, R. C. Haddon, F. B. Bramwell, F. Wudl, J. H. Marshall, D. O. Cowan, and S. Gronowitz, *J. Phys. Chem.*, **84**, 427 (1980).

9) J. S. Chappell, A. N. Bloch, W. A. Bryden, M. Maxfield, T. O. Poehler, and D. O. Cowan, *J. Am. Chem. Soc.*, **103**, 2442 (1981).

10) R. Kato, H. Kobayashi, A. Kobayashi, and Y. Sasaki, *Chem. Lett.*, **1984**, 1693; R. Kato, A. Kobayashi, Y. Sasaki, and H. Kobayashi, *ibid.*, **1984**, 993; K. Bender, I. Henning, D. Schweizer, K. Dietz, H. Endres, and H. J. Keller, *Mol. Cryst. Liq. Cryst.*, **108**, 359 (1984); H. Kobayashi, R. Kato, A. Kobayashi, G. Saito, M. Tokumoto, H. Anzai, and T. Ishiguro, *Chem. Lett.*, **1986**, 93.

11) H. Kobayashi, A. Kobayashi, Y. Sasaki, G. Saito, and H. Inokuchi, *Chem. Lett.*, **1984**, 183.

12) H. Kobayashi, A. Kobayashi, Y. Sasaki, G. Saito, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **59**, 301 (1986).

13) L. R. Melby, H. D. Hartzler, and W. A. Sheppard, *J. Org. Chem.*, **39**, 2456 (1974).

14) E. P. Goodings, D. A. Mitchard, and G. Owen, *J. Chem. Soc., Perkin Trans. 1*, **1972**, 1310.

15) H. K. Spencer, M. P. Cava, F. Yamagishi, and A. F. Garito, *J. Org. Chem.*, **41**, 730 (1976).

16) G. A. Reynolds, C. H. Chen, and J. A. Van Allan, *J. Org. Chem.*, **44**, 4456 (1979).

17) E. M. Engler, V. Y. Lee, R. R. Schumaker, S. S. P. Parkin, R. L. Greene, and J. C. Scott, *Mol. Cryst. Liq. Cryst.*, **107**, 19 (1984).

18) Y. Aso, K. Yui, T. Miyoshi, T. Otsubo, F. Ogura, and J. Tanaka, *Bull. Chem. Soc. Jpn.*, **61**, 2013 (1988).

19) A. Bugge, *Acta Chem. Scand.*, **23**, 2704 (1969).

20) G. F. Pedulli, M. Tiecco, M. Guerra, G. Martelli, and P. Zanirato, *J. Chem. Soc., Perkin Trans. 2*, **1978**, 212.

21) A. Furusaki, *Acta Crystallogr., Sect. A*, **35**, 220 (1979).

22) C. Katayama, N. Sakabe, and K. Sakabe, *Acta Crystallogr., Sect. A*, **28**, S207 (1972).

23) "International Tables for X-ray Crystallography," Kynoch Press, Birmingham, England (1974), Vol. IV.