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Syntheses, Structures, and Properties of 2,3,6,7-Tetrathiabenzo[1,3-*cd*:4,6-*c'd'*]dipentalene and Its Methyl, Ethyl, Methylthio, and Ethylthio Derivatives: Novel Fused Polynuclear Heteroarenes

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The title heteroarene (TBD) isoelectronic with perylene was synthesized by way of a dimerization of thieno[2,3-*b*]thiophene. In addition, 1,4,5,8-tetramethyl, tetraethyl, tetrakis (methylthio), and tetrakis (ethylthio) derivatives were readily obtained from TBD. An X-ray crystallographic analysis of TBD demonstrated that the molecular structure is quite planar and symmetrical, but strained in the bond angles. The crystal structure comprises herringbone-type column stacking with intercolumnar heteroatomic interactions. TBD showed the same oxidation potential as did perylene, and like perylene, formed an iodine complex with a relatively high electrical conductivity of 0.11 S cm^{-1}. On the other hand, all of the TBD derivatives gave poorly conductive iodine complexes. In addition, TBD and the derivatives formed charge-transfer complexes with strong electron acceptors, such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF$_4$), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), and 1,1,2,3,4,4-hexacyano-1,3-butadiene (HCBD). These π-complexes, however, were mostly of low conductivity. The electrolyses of TBP gave powdery conductive polymers, whereas those of tetrakis (methylthio) TBD gave crystalline radical cation salts with conductivities of the order of 10^{-3} S cm^{-1}.

Perylene (**1**) gave halogen complexes, being the first organic solids to exhibit high electrical conductivity (Chart 1).[1] In addition, **1** formed radical-cation salts which qualified as low-dimensional organic metals.[2] The unusual interesting properties of **1** are based on the relatively low ionization potential for a hydrocarbon.[3] Recent attention concerning the design of organic metals has been focused on the development of novel heteroaromatic compounds, which behave as superior electron donors.[4—6] Heteroatoms incorporated in the heteroarenes serve to induce much polarization in the molecule, and to enhance intermolecular interactions, thus facilitating the formation of conductive molecular complexes. From this standpoint, Wudl et al. reported an isoelectronic heterocyclic analogue of perylene, 2,7-dithiabenzo[1,3-*cd*:4,6-*c'd'*]diindene (**2**), which formed an iodine complex that is very similar to the known perylene-iodine solid.[7] We have rather focused on 2,3,6,7-tetrathiabenzo[1,3-*cd*:4,6-*c'd'*]dipentalene (**3**), abbreviated as TBD below, as another isoelectronic heterocycle, in which all of the perimetric rings are replaced by thiophenes. It has been proposed that suitable electron-donor components for organic metals satisfy some requirements, such as high symmetry, high planarity, high polarizability, low ionization potential, and strong intermolecular interaction.[8—11] On the basis of these criteria, TBD might be more interesting as a potential electron donor. We report here on the syntheses, structures, and some properties of TBD **3** as well as its 1,4,5,8-tetramethyl, tetraethyl, tetrakis(methylthio), and tetrakis(ethylthio) derivatives **4**—**7**.[12]

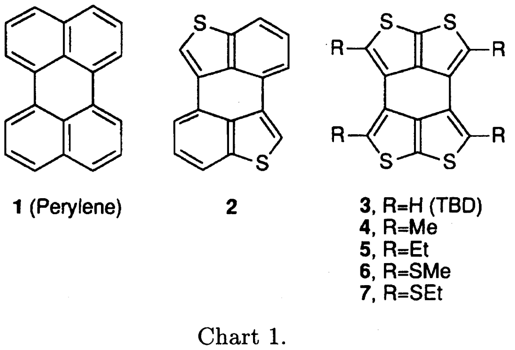
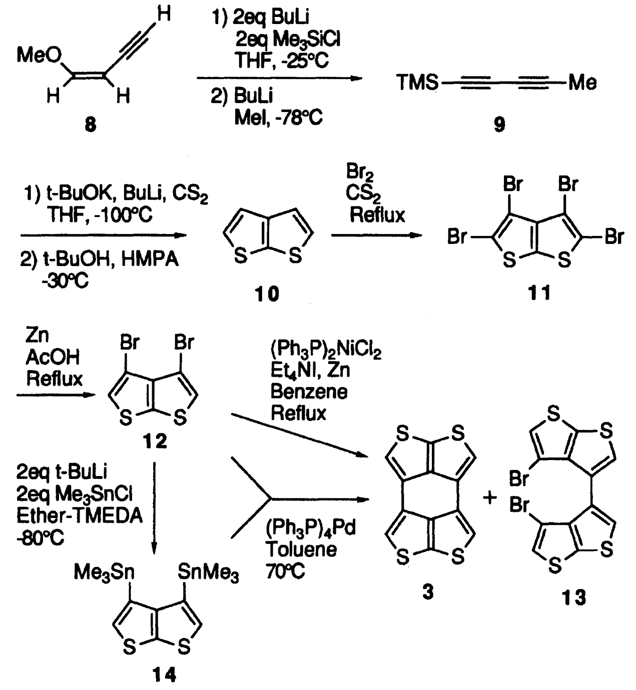


Chart 1.

As the simplest approach to TBD, we designed a dimerization of thieno[2,3-*b*]thiophene (**10**) at the two β-positions. In this strategy, a large-scale preparation of **10** as a key intermediate was at first necessary. The previous synthesis of **10** was carried out by utilizing a multistep sequence starting with 3-bromothiophene, according to a method of Gronowitz and Persson.[13] However, De Jong and Brandsma recently reported a novel synthetic method using a double ring-closure reaction of trimethylsilyl-1,3-pentadiyne (**9**) with carbon disulfide under basic conditions (Scheme 1).[14] The present study adopted this simple approach, since the starting material **9** turned out to be available in one pot from commercial 1-methoxyl-1-buten-3-yne (**8**) by a modification of the synthetic method for 1,4-bis(trimethylsilyl)-1,3-butadiyne according to Zweifel and Rajagopalan.[15] Thieno[2,3-*b*]thiophene (**10**), thus obtained, was converted via 2,3,4,5-tetrabromothieno[2,3-*b*]thiophene (**11**) to 3,4-dibromothieno[2,3-*b*]thiophene (**12**).[16] A conventional reductive coupling of **12** with catalytic bis(triphenylphosphine)nickel(II) chloride, excess active zinc, and tetraethylammonium iodide in

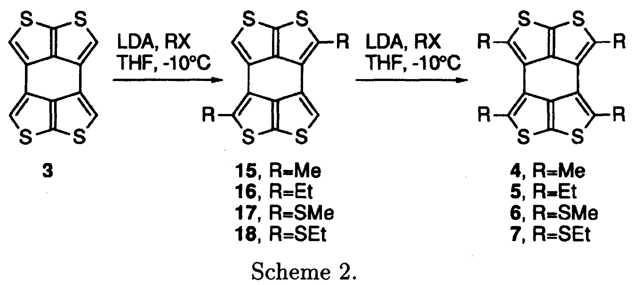


Scheme 1.

refluxing benzene[17] gave only 4,4′-dibromo-3,3′-bi[thieno[2,3-*b*]thiophene] (**13**) in the reaction mixture (maximum yield 28%). However, increasing the quantity of the nickel reagent formed the desired TBD, whose yield was optimized up to 14%. As an alternative, **12** was converted to 3,4-bis(trimethylstannyl)thieno[2,3-*b*]-thiophene (**14**) in 60% yield; a coupling reaction of **12** and **14** in the presence of catalytic tetrakis(triphenylphosphine)palladium in toluene at 70 °C gave TBD in 13% yield.

The TBD derivatives **4**—**7** were prepared by lithiation of **3** with lithium diisopropylamide (LDA) followed by a treatment with the corresponding alkyl iodide or dialkyl disulfide (Scheme 2). However, direct tetralithiation of **3** was difficult, even if excess LDA was used. The reaction stopped at dilithiation, forming the 1,5-disubstituted derivatives **15**—**18**. The repeated treatments with **15**—**18** gave the tetrasubstituted derivatives **4**—**7** in high yields.

TBD, though its molecular model suffers from a severe strain, is very stable and crystallizes in the form of faint brown needles from carbon disulfide. It sublimes at around 270 °C at atmospheric pressure and does not melt up to 300 °C in a sealed tube. Simple ^{1}H and ^{13}C NMR spectra support its highly symmetrical structure. It is not as colored as perylene, but its electronic absorption spectrum exhibits marked bathochromic and hyperchromic shifts, as compared with that of thieno[2,3-*b*]thiophene (**10**). This reflects the extended *peri*-conjugation of TBD (Fig. 1). Although the spectra of methyl and ethyl derivatives **4** and **5** are almost the same as that of TBD, those of methylthio and ethylthio derivatives **6** and **7** exhibit additional bathochromic shifts (Table 1).



Scheme 2.

The molecular structures of TBD and methylthio derivative **6** as well as 3,4-dibromothieno[2,3-*b*]thiophene (**12**), as a reference, were revealed by X-ray crystallographic analyses. The ORTEP drawings are shown in Fig. 2. The crystal data are summarized in Table 2, the bond distances and angles in Table 3, and the atomic coordinates in Table 4. The geometry of TBD is quite planar and has a center of symmetry. The perimetric five-membered rings suffer from considerable strain, which is more marked in bond angles than in bond lengths, as compared with the structure of **12**. As a result, the central six-membered ring is greatly deformed from a regular hexagon in contrast to the molecular structure of perylene.[18] As is often found for polynuclear arenes, the crystal structure of perylene is packed with independent dimer units. On the other hand, that of TBD comprises a herringbone type of stacking columns (Fig. 3). Some nonbonded S–S close contacts are observed between the adjacent stacked columns of TBD, which are shorter than van der Waals distance (3.6 Å). These strong heteroatomic interactions are, thus, understandable to facilitate a herringbone-type crystal packing for TBD.

The parent skeleton of methylthio derivative **6** is almost the same as that of TBD, and the diagonal two of the four methylthio groups lie parallel to the plane to make a conjugation; the remaining two, however, lie perpendicular to the plane (Fig. 4). The very close distance (3.27 Å) between the sulfur atoms of the neigh-

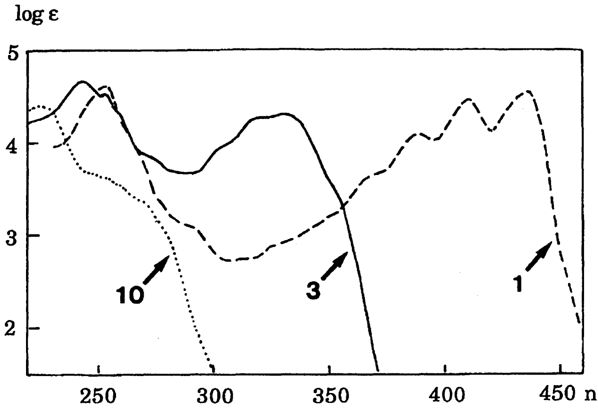


Fig. 1. Electronic spectra of perylene (**1**), TBD (**3**), and thieno[2,3-*b*]thiophene (**10**) in tetrahydrofuran.

Table 1. Half-Wave Oxidation Potentials and Electronic Absorption Data of Perylene (**1**), TBD (**3**), Its Derivatives **4**—**7**, and Thieno[2,3-*b*]thiophene (**10**)

Compd	$E_{1/2}$/V[a)]	$\lambda_{\max}$(log ε)/nm[b)]
1	+1.00	253.5 (4.63), 388 (4.11), 410 (4.45), 436.5 (4.56)
3	+1.01	242 (4.67), 253.5 (4.53), 329.5 (4.34)
4	+0.93	
5	+0.92	245 (4.53), 262.5 (4.48), 320 (4.25), 333.5 (4.28)
6	+0.88	254 (4.50), 283.5 (4.42), 370.5 (4.28)
7	+0.89	228 (4.27), 253 (4.58), 282 (4.46), 370 (4.28)
10	>+1.5	225 (4.41), 248 (3.70), 255 (3.65), 260 (3.56)

a) Cyclic voltammetry was measured with Pt working and counter electrodes at scan rate 100 mV s^{-1} in benzonitrile solution containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte at room temperature. b) In tetrahydrofuran. The electronic spectrum of **4** could not be measured because of its poor solubility in tetrahydrofuran.

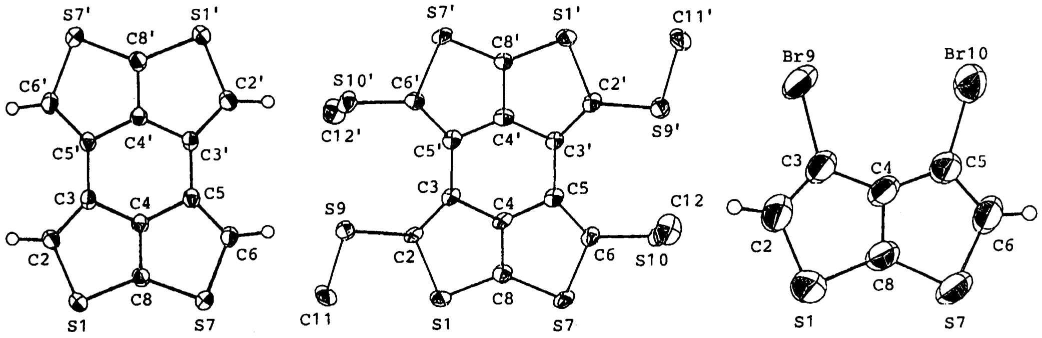


Fig. 2. ORTEP drawings and atomic numbering of TBD (**3**), methylthio derivative (**6**), and 3,4-dibromothieno[2,3-*b*]thiophene (**12**).

Table 2. Crystal Data of TBD (**3**), Methylthio Derivative (**6**), **6**·DDQ Complex, and Dibromothieno[2,3-*b*]thiophene (**12**)

Compound	TBD	**6**	**6**·DDQ	**12**
Formula	$C_{12}H_4S_4$	$C_{16}H_{12}S_8$	$C_{24}H_{12}S_8N_2O_2Cl_2$	$C_6H_2S_2Br_2$
Fw	276.43	460.75	687.76	298.02
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Monoclinic
Space group	*Pcab*	$P2_12_12_1$	$P\bar{1}$	$P2_1/n$
a/Å	15.029 (3)	24.193 (2)	9.566 (1)	4.003 (1)
b/Å	5.1793 (7)	14.158 (1)	10.265 (1)	11.686 (1)
c/Å	13.380 (3)	5.2133 (3)	7.571 (1)	17.359 (2)
α/°	90	90	93.40 (1)	90
β/°	90	90	114.87 (1)	90.87 (1)
γ/°	90	90	101.31 (1)	90
Z	4	4	1	4
Crystal size/mm^3	0.20×0.17×0.12	0.50×0.20×0.05	0.33×0.10×0.02	0.38×0.10×0.05
Radiation	Mo *Kα*	Cu *Kα*	Cu *Kα*	Cu *Kα*
Abs correction	None	Analytical	Analytical	Analytical
No. of data	1044	1641	2003	1286
R	0.033	0.045	0.049	0.037

boring methylthio groups presumably brings about a repulsion of their lone-pair electrons, which forces the one group to take the nonconjugated conformation. The skeletal sulfurs of **6**, like TBD, showed strong intercolumnar interactions, while the functional sulfur atoms do not participate in such interactions.

The cyclic voltammogram of TBD showed one reversible redox wave with a half-wave potential at +1.01 V vs. an Ag/AgCl standard electrode in benzonitrile containing tetrabutylammonium perchlorate as supporting electrolyte. This value is considerably lower than that (>+1.5 V) of thieno[2,3-*b*]thiophene, but equal to that (+1.00 V) of perylene (Table 1). This indicates that replacing two adjacent carbon atoms of perylene by a sulfur atom has almost no effect on the HCMO energy level.[19)] The repetitive cycling soon changed the

Table 3. Intramolecular Bond Lengths and Angles with Estimated Standard Deviations in Parentheses for TBD (**3**), Methylthio Derivative (**6**), **6**·DDQ Complex, and Dibromothieno[2,3-*b*]thiophene (**12**)

Bond lengths/Å	TBD	**6**		**6**·DDQ	**12**
S1–C2	1.750 (2)	1.775 (7),	1.764 (7)	1.744 (4)	1.726 (6)
S1–C8	1.728 (2)	1.716 (6),	1.720 (6)	1.710 (3)	1.712 (5)
C2–C3	1.368 (3)	1.371 (8),	1.384 (9)	1.381 (3)	1.358 (8)
C3–C4	1.436 (3)	1.448 (9),	1.431 (9)	1.440 (5)	1.429 (7)
C4–C5	1.436 (3)	1.450 (8),	1.447 (9)	1.439 (4)	1.429 (7)
C4–C8	1.366 (3)	1.375 (10),	1.390 (10)	1.370 (4)	1.374 (7)
C5–C6	1.364 (3)	1.366 (10),	1.379 (10)	1.394 (5)	1.355 (7)
C6–S7	1.745 (2)	1.770 (7),	1.767 (7)	1.755 (3)	1.728 (6)
S7–C8	1.728 (2)	1.708 (7),	1.702 (7)	1.722 (4)	1.711 (5)
C3–C5′	1.464 (3)	1.457 (9),	1.453 (9)	1.461 (4)	—
C2–S9	—	1.752 (6),	1.756 (6)	1.745 (3)	—
C6–S10	—	1.742 (6),	1.737 (6)	1.738 (3)	—
S9–C11	—	1.810 (8),	1.821 (9)	1.806 (5)	—
S10–C12	—	1.833 (9),	1.829 (8)	1.801 (6)	—
C3–Br9	—	—		—	1.870 (5)
C5–Br10	—	—		—	1.871 (5)
Bond angles/°					
S1–C2–C3	112.8 (2)	112.5 (5),	112.7 (5)	112.9 (3)	112.5 (4)
C2–C3–C4	110.3 (2)	110.1 (6),	109.9 (6)	109.8 (3)	112.7 (5)
C3–C4–C5	130.7 (2)	131.5 (6),	131.6 (6)	131.3 (3)	138.6 (4)
C3–C4–C8	114.7 (2)	114.6 (5),	115.2 (6)	114.0 (2)	110.8 (4)
C4–C5–C6	110.3 (2)	110.1 (6),	110.3 (6)	110.1 (3)	112.7 (5)
C4–C8–S1	111.1 (2)	111.6 (5),	110.8 (5)	112.1 (3)	113.5 (4)
C4–C8–S7	111.1 (2)	112.4 (5),	112.7 (5)	111.6 (2)	113.8 (4)
C5–C4–C8	114.6 (2)	113.9 (6),	113.3 (6)	114.7 (3)	110.6 (4)
C5–C6–S7	113.1 (2)	113.0 (5),	112.8 (5)	112.2 (2)	112.8 (4)
C6–S7–C8	90.9 (1)	90.7 (3),	91.0 (3)	91.5 (2)	90.2 (3)
S7–C8–S1	137.8 (1)	136.0 (5),	136.4 (5)	136.3 (2)	132.8 (3)
C8–S1–C2	91.0 (1)	91.1 (3),	91.4 (3)	91.1 (2)	90.5 (3)
C2–C3–C5′ (Br9)	135.3 (2)	136.1 (6),	135.5 (6)	135.9 (3)	121.5 (4)
C4–C3–C5′ (Br9)	114.4 (2)	113.8 (5),	114.6 (5)	114.2 (2)	125.8 (4)
C4–C5–C3′ (Br10)	114.8 (2)	114.1 (5),	114.5 (6)	114.2 (2)	126.0 (4)
C6–C5–C3′ (Br10)	134.9 (2)	135.9 (6),	135.2 (6)	135.4 (2)	121.2 (4)
S1–C2–S9	—	116.6 (4),	116.8 (4)	114.9 (2)	—
C3–C2–S9	—	130.9 (5),	130.4 (6)	132.1 (3)	—
C5–C6–S10	—	133.0 (5),	132.7 (5)	129.4 (2)	—
S7–C6–S10	—	114.0 (4),	114.5 (4)	118.3 (2)	—
S2–S9–C11	—	102.0 (3),	101.9 (3)	101.5 (2)	—
C6–S10–C12	—	100.2 (3),	101.2 (3)	102.8 (2)	—

voltammogram to two redox waves at +0.74 and +1.10 V, depositing a black polymeric material on the working electrode.[20] The same material was also formed by potentiostatic polymerization at +1.05 V, or galvanostatic polymerization at 1 μA in benzonitrile solution. Since **3** has four reactive sites for polymerization, it must take a complex network structure. The elemental analysis (C, 45.57; H, 1.05%) suggested that it was doped by 40% with the counter ion ClO_4^-. Its electrical conductivity, measured on a compressed pellet at room temperature, was 0.06 S cm^{-1}. The electrolysis using tetrabutylammonium tetrafluoroborate, as the supporting electrolyte, also gave a black material of the same conductivity (C, 47.05; H, 1.01%, doping level 0.35). All of the tetra-substituted derivatives **4**—**6**, on the other hand, exhibited reproducible redox cycles regarding voltammetry, due to a blocking of the reactive sites by the substituents. In addition, the substituents serve to lower the oxidation potentials (see also Table 1).

TBD, like perylene and **2**, formed fine black crystals from a chlorobenzene solution containing an equimolar amount of iodine. The complex had a 1 : 1 stoichiometry of TBD to iodine, and showed a relatively high electrical conductivity of 0.11 S cm^{-1}. The TBD derivatives **4**—**7** also formed iodine complexes, which were, however, less conductive (Table 5). In addition, TBD formed charge-transfer complexes with strong electron acceptors, such as TCNQ, $TCNQF_4$, DDQ, and HCBD. On the other hand, the TBD derivatives complexed only $TCNQF_4$ and DDQ, though they possess equal or lower oxidation potentials. These π-complexes were mostly poorly conductive. The conductivities of the charge-

Table 4. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2)

Atom	x	y	z	B_{eq}
TBD				
S (1)	0.20256 (3)	0.3583 (1)	0.07130 (3)	2.20 (1)
C (2)	0.14603 (14)	0.1026 (4)	0.12859 (15)	1.99 (4)
C (3)	0.07232 (13)	0.0262 (4)	0.07639 (14)	1.68 (4)
C (4)	0.06306 (13)	0.1770 (4)	−0.01302 (14)	1.69 (4)
C (5)	−0.00280 (13)	0.1682 (4)	−0.09062 (15)	1.70 (3)
C (6)	0.01576 (14)	0.3474 (4)	−0.16234 (15)	1.96 (4)
S (7)	0.11097 (3)	0.5282 (1)	−0.13635 (3)	2.22 (1)
C (8)	0.12730 (13)	0.3604 (4)	−0.02631 (15)	1.89 (4)
H (2)	0.170 (2)	0.031 (6)	0.191 (3)	1.99
H (6)	−0.016 (2)	0.385 (6)	−0.221 (2)	1.96
Compound **6**				
S (1)	0.42786 (6)	0.4641 (1)	0.1226 (4)	2.25 (9)
C (2)	0.41043 (23)	0.5422 (4)	0.3782 (14)	1.68 (16)
C (3)	0.45501 (23)	0.5931 (4)	0.4652 (14)	1.50 (16)
C (4)	0.50421 (23)	0.5663 (4)	0.3245 (13)	1.59 (17)
C (5)	0.56109 (23)	0.5980 (4)	0.3454 (15)	1.68 (16)
C (6)	0.59311 (25)	0.5520 (4)	0.1686 (15)	1.98 (18)
S (7)	0.55504 (6)	0.4719 (1)	−0.0252 (4)	2.18 (9)
C (8)	0.49577 (25)	0.4990 (4)	0.1369 (15)	2.02 (17)
S (9)	0.34136 (6)	0.5411 (1)	0.4793 (4)	2.31 (9)
S (10)	0.66366 (6)	0.5542 (1)	0.1022 (4)	2.42 (9)
C (11)	0.30775 (26)	0.4781 (5)	0.2193 (17)	2.99 (21)
C (12)	0.68876 (29)	0.4697 (6)	0.3439 (20)	3.77 (23)
S (1′)	0.59826 (6)	0.7965 (1)	0.8902 (4)	2.16 (9)
C (2′)	0.61546 (25)	0.7186 (4)	0.6368 (15)	1.82 (17)
C (3′)	0.57012 (23)	0.6698 (4)	0.5422 (14)	1.63 (17)
C (4′)	0.52146 (25)	0.6974 (4)	0.6793 (15)	1.89 (18)
C (5′)	0.46478 (23)	0.6650 (4)	0.6619 (15)	1.72 (17)
C (6′)	0.43262 (25)	0.7104 (4)	0.8428 (15)	1.85 (17)
S (7′)	0.47054 (6)	0.7923 (1)	1.0310 (4)	2.12 (9)
C (8′)	0.52960 (25)	0.7657 (4)	0.8688 (15)	1.96 (17)
S (9′)	0.68477 (6)	0.7179 (1)	0.5373 (4)	2.53 (9)
S (10′)	0.36253 (6)	0.7054 (1)	0.9137 (4)	2.33 (9)
C (11′)	0.71843 (28)	0.7833 (6)	0.7954 (17)	3.48 (22)
C (12′)	0.33399 (28)	0.7846 (5)	0.6679 (18)	3.11 (21)

transfer complexes are mainly dependent on the degree of charge transfer and the stacking form of the donor and acceptor. The nitrile vibrational frequencies of the TCNQ and TCNQF$_4$ complexes are observed in the range of 2218—2226 cm^{-1}, which are situated between those of neutral TCNQ (2232 cm^{-1}) and sodium salt (2174 cm^{-1}) or of TCNQF$_4$ (2234 cm^{-1}) and sodium salt (2201 cm^{-1}), indicating an appropriate partial charge transfer.[21)] The carbonyl vibrational frequencies (1640—1650 cm^{-1}) of the DDQ complexes are also shifted, as compared with neutral DDQ (1678 cm^{-1}); the partial charge transfer is supported by an X-ray analysis of the **6**·DDQ complex, in which the molecular dimension of the donor **6** changes by complexation (Table 3). On the other hand, Figure 4 clearly shows that the crystal structure of the **6**·DDQ complex assumes a mixed stacking of alternative donors and acceptors, though the DDQ molecules are disordered by a partial interchange of the Cl and CN groups. The low conductivities are thus due to the unfavorable mixed stacking form.

The formation of the radical cation salts of the TBD derivatives was attempted by galvanostatic electrocrystallization (5 μA) in 1,1,2-trichloroethane containing tetrabutylammonium perchlorate or hexafluorophosphate. However, the resulting salts did not separate out and were unstable to isolate; only the ClO$_4$ and PF$_6$ salts of methylthio derivative **6** were isolated as stable fine black crystals. These salts had electrical conductivities of the order of 10^{-3} S cm^{-1}.

Experimental

General. The melting points are uncorrected. All chemicals and solvents were of reagent grade. Elemental analyses were measured by Mr. Hideaki Iwatani, Microanalytical Laboratory in Department of Applied Chemistry, Faculty of Engineering, Hiroshima University. ^{1}H NMR spectra were recorded on a JEOL PMX-60 spectrometer (60 MHz) and ^{13}C NMR on a JEOL EX-270 (67.8 MHz) using tetramethylsilane as an internal standard. IR spectra

Table 4. (Continued)

Atom	x	y	z	$B_{\rm eq}$
6·DDQ complex				
S (1)	0.07762 (9)	0.35646 (9)	0.6575 (1)	3.26 (11)
C (2)	0.24638 (35)	0.29627 (31)	0.7058 (5)	2.86 (15)
C (3)	0.38439 (34)	0.38395 (29)	0.8439 (4)	2.51 (14)
C (4)	0.34749 (34)	0.50002 (29)	0.9141 (4)	2.62 (14)
C (5)	0.44700 (34)	0.61494 (29)	1.0632 (4)	2.43 (14)
C (6)	0.35521 (35)	0.69931 (31)	1.0838 (5)	2.90 (14)
S (7)	0.15298 (9)	0.63781 (7)	0.9218 (1)	3.38 (11)
C (8)	0.18923 (35)	0.49831 (32)	0.8271 (5)	2.94 (14)
S (9)	0.20942 (10)	0.13498 (9)	0.5827 (1)	3.86 (11)
S (10)	0.41449 (10)	0.85355 (9)	1.2345 (1)	3.89 (11)
C (11)	0.20919 (57)	0.03345 (43)	0.7695 (7)	5.20 (19)
C (12)	0.22856 (53)	0.88608 (47)	1.2065 (8)	5.19 (19)
C (13)	−0.33551 (44)	0.48933 (46)	0.5733 (6)	5.18 (18)
C (14)	−0.37853 (47)	0.60456 (49)	0.6435 (6)	4.84 (18)
C (15)	−0.53016 (46)	0.61457 (47)	0.5778 (6)	5.12 (18)
O (16)	−0.19918 (29)	0.47893 (32)	0.6357 (4)	5.90 (15)
Cl (17a)	−0.21164 (80)	0.74354 (92)	0.8386 (12)	4.80 (24)
Cl (17b)	−0.56416 (57)	0.77126 (53)	0.6844 (7)	4.78 (16)
C (18a)	−0.25914 (175)	0.68492 (124)	0.7692 (19)	4.57 (54)
C (18b)	−0.58210 (130)	0.70506 (111)	0.6300 (17)	4.25 (36)
N (19a)	−0.16365 (239)	0.77195 (298)	0.8770 (40)	5.27 (73)
N (19b)	−0.61377 (156)	0.79193 (169)	0.6842 (25)	5.89 (45)
H (11a)	0.314 (6)	0.060 (5)	0.876 (7)	4.74
H (11b)	0.121 (6)	0.044 (5)	0.792 (7)	4.74
H (11c)	0.178 (6)	−0.060 (5)	0.703 (7)	4.74
H (12a)	0.167 (6)	0.903 (5)	1.075 (7)	4.55
H (12b)	0.252 (6)	0.968 (5)	1.281 (7)	4.55
H (12c)	0.176 (6)	0.823 (5)	1.256 (7)	4.55
Compound **12**				
S (1)	0.7005 (4)	0.45026 (11)	0.41172 (9)	6.06 (5)
C (2)	0.7494 (15)	0.40874 (49)	0.31707 (32)	5.73 (15)
C (3)	0.8969 (13)	0.30452 (44)	0.31083 (26)	4.79 (12)
C (4)	0.9745 (12)	0.25433 (35)	0.38402 (26)	4.46 (12)
C (5)	1.1265 (13)	0.15265 (41)	0.41398 (28)	4.70 (12)
C (6)	1.1360 (15)	0.15024 (49)	0.49205 (32)	5.40 (14)
S (7)	0.9663 (4)	0.27162 (13)	0.53278 (6)	5.97 (5)
C (8)	0.8784 (13)	0.32503 (41)	0.44295 (28)	4.95 (13)
Br (9)	0.9890 (2)	0.24030 (5)	0.21481 (2)	6.14 (4)
Br (10)	1.2936 (2)	0.03111 (5)	0.35588 (2)	5.74 (4)
H (2)	0.753 (16)	0.467 (6)	0.276 (5)	5.73
H (6)	1.195 (14)	0.093 (7)	0.525 (4)	4.94

were taken on a Hitachi 260-30 spectrometer with a KBr disk or neat method. MS spectra were measured at 70 eV on a Shimadzu QP-1000A spectrometer using a direct insertion technique. Electronic spectra were recorded on a Shimadzu UV-160 spectrometer. Cyclic voltammetry was carried out on a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 function generator.

Trimethylsilyl-1,3-pentadiyne (9). Into a stirred solution of (*Z*)-1-methoxybuten-3-yne (**8**) (6.8 ml, 75 mmol) in dry THF (75 ml) at −25 °C under an argon atmosphere was slowly added a 1.5 M *n*-BuLi hexane solution (100 ml, 150 mmol) (1 M=1 mol dm^{-3}) and, 1h later, trimethylsilyl chloride (19 ml, 150 mmol). The mixture was stirred at room temperature and again cooled to −25 °C. After the further addition of a 1.5 M *n*-BuLi hexane solution (50 ml, 75 mmol), it was stirred for 2 h, and cooled to −78 °C. A solution of methyl iodide (4.7 ml, 75 mmol) in dry THF (50 ml) was added, and the mixture was stirred overnight.

It was quenched by addition of brine (400 ml), and extracted with ether. After the extract was dried (MgSO$_4$) and evaporated, distillation of the residue under reduced pressure gave a colorless oil (6.62 g, 65% yield), bp 80 °C/40 Torr (1 Torr=133.322 Pa) (lit,22) bp 36 °C/2 Torr); ^{1}H NMR (CDCl$_3$) δ=0.18 (s, 9H), 1.90 (s, 3H); IR (neat) 2100, 2230, 3000 cm^{-1}.

Thieno[2,3-*b*]thiophene (10). Into a suspension of potassium *t*-butoxide (28 g, 0.25 mol) in dry THF (200 ml) cooled at −100 °C was added 1.5 M *n*-BuLi hexane solution (136 ml, 0.20 mol) in an argon atmosphere; the mixture was stirred for 1 h at the temperature. Trimethylsilyl-1,3-pentadiyne (**9**) (14 g, 0.10 mol) was added at −80 °C; 1 h later, carbon disulfide was added at −100 °C. After 2 h of stirring, the temperature was raised to −30 °C, and a solution of *t*-butyl alcohol (19.4 ml, 0.21 mol) in dry HMPA

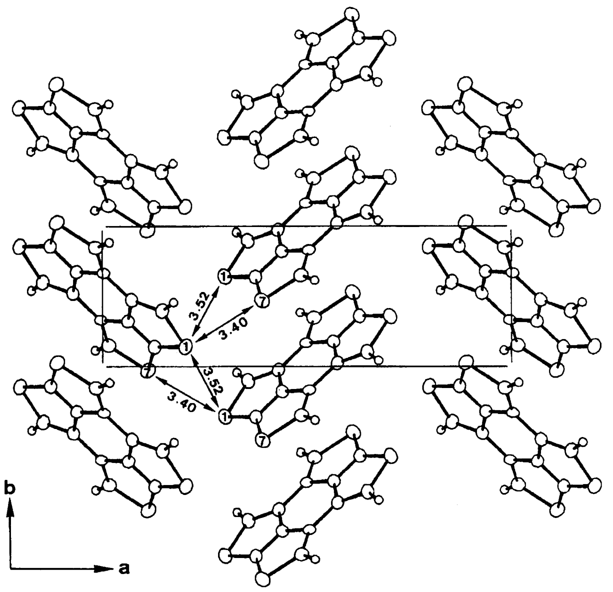


Fig. 3. Crystal structure of TBD (**3**) projected along the *c*-axis.

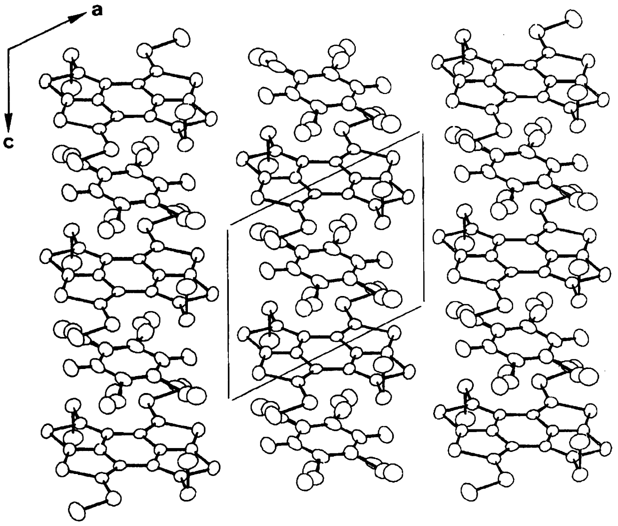


Fig. 4. Crystal structure of **6**•DDQ complex projected along the *a*-axis.

(100 ml) was added. The mixture was stirred at −30 °C for 3 h and at room temperature overnight, quenched with 0.2% hydrochloric acid (500 ml), and then extracted with ether. The extract was washed with brine, dried ($MgSO_4$), and evaporated. The residue was filtered through a short column of silica gel with hexane; the filtrate was distilled under reduced pressure to give a colorless oil (6.6 g, 47% yield), bp 64 °C/2 Torr (lit,[13]) bp 95 °C/10 Torr); ^{1}H NMR ($CDCl_3$) δ=7.06 (d, J=5.6 Hz, 2H), 7.16 (d, J=5.6 Hz, 2H); IR (neat) 3080, 3100 cm^{-1}.

2,3,4,5-Tetrabromothieno[2,3-*b*]thiophene (11). Into a solution of **10** (2.0 g, 14 mmol) in carbon disulfide was added bromine (6 ml, 120 mmol); the mixture was refluxed for 54 h. After 10% aq $NaHSO_3$ solution was added until the color of the excess bromine disappeared, the mixture was extracted with chloroform. The extract was washed with sat. aq $NaHCO_3$, dried ($MgSO_4$), and evaporated. The residue was recrystallized from hexane–dichloromethane to give colorless needles (5.6 g, 85% yield), mp 171 °C (lit,[23]) mp 172 °C); IR (KBr) 1485, 1450, 1140, 1000 cm^{-1}; MS *m*/*z* 452, 454, 456, 458, 460 (M$^+$).

3,4-Dibromothieno[2,3-*b*]thiophene (12). A mixture of **11** (5.5 g, 12 mmol), active zinc (2.8 g, 43 mmol), and acetic acid (30 ml) was refluxed for 3 h. After the addition of water, it was extracted with chloroform. The extract was washed with sat. aq $NaHCO_3$, dried ($MgSO_4$), and evaporated. The residue was purified by column chromatography on silica gel with hexane followed by recrystallization from hexane to give colorless needles (2.55 g, 71% yield), mp 132—133 °C (lit,[16]) mp 131 °C); ^{1}H NMR ($CDCl_3$) δ=7.23 (s); IR (KBr) 3100, 1480, 1238, 730 cm^{-1}; MS *m*/*z* 296, 298, 300 (M$^+$).

3,4-Bis(trimethylstannyl)thieno[2,3-*b*]thiophene (14). Into a solution of **12** (100 mg, 0.34 mmol), dry ether (10 ml), and TMEDA (0.3 ml) at −80 °C was dropwise added 1.2 M *t*-BuLi heptane solution (0.57 ml, 0.68 mmol) in an argon atmosphere, and the mixture was stirred for 30 min. A solution of trimethylstannyl chloride (137 mg, 0.68 mmol) in dry ether (1 ml) was added, and the stirring was continued for 1 h at −80 °C and then overnight at room temperature. After sat. aq NH_4Cl solution (20 ml) was added, the mixture was extracted with chloroform; the extract was washed with brine, dried ($MgSO_4$), and evaporated. The residue was purified by gel permeation liquid chromatography to give a brown oil (95 mg, 60% yield); ^{1}H NMR (CS_2) δ=0.38 (s, 18H), 7.23 (s, 2H); IR (neat) 2980, 2915 cm^{-1}; MS *m*/*z* 466 (M$^+$). Found: C, 30.85; H, 4.30%. Calcd for $C_{12}H_{14}S_2Sn_2$: C, 30.94; H, 4.33%.

2,3,6,7-Tetrathiabenzo[1,3-*cd*:4,6-*c′d′*]dipentalene (3). Method A. A mixture of **12** (500 mg, 1.68 mmol), bis(triphenylphosphine)nickel(II) dichloride (540 mg, 0.83 mmol), tetraethylammonium iodide (2.76 g, 10.7 mmol), and active zinc (1.42 g, 21.7 mmol) in dry benzene (15 ml) was refluxed for 28 h in an argon atmosphere. After filtration, the filtrate was evaporated. The residue was chromatographed on silica gel with carbon disulfide; the eluted yellow solid was washed with a 1 : 1 mixed solution (2 ml) of hexane and chloroform and recrystallized from carbon disulfide to give pale yellow needles of **3** (31 mg, 14% yield), mp>300°C; ^{1}H NMR (CS_2) δ=7.23 (s); ^{13}C NMR (DMSO-d_6) δ=121.95, 125.15, 132.98, 150.17; IR (KBr) 3100, 1421, 819, 740, 719, 693 cm^{-1}; MS *m*/*z* 276 (M$^+$, 100), 277 (16), 278 (19), 279 (2.7), 280 (1.5). Found: C, 51.91; H, 1.46%. Calcd for $C_{12}H_4S_4$: C, 52.14; H, 1.46%.

When a catalytic amount of bis(triphenylphosphine)-nickel(II) dichloride was used in the above reaction, 4,4′-dibromo-3,3′-bi[thieno[2,3-*b*]thiophene] (**13**) was obtained in 28% yield; white fine needles from hexane; mp 201—203 °C; ^{1}H NMR (CCl_4) δ=7.15 (s,2H), 7.25 (s,2H); IR (KBr) 3100, 1363, 1180, 735 cm^{-1}; MS *m*/*z* 434, 436, 438 (M$^+$). Found: C, 33.27; H, 0.92%. Calcd for $C_{12}H_4Br_2S_4$: C, 33.03; H, 1.04%.

Method B. A solution of **14** (50 mg, 0.11 mmol) and tetrakis(triphenylphosphine)palladium (0) (40 mg, 0.035 mmol) in toluene (10 ml) was stirred at 70 °C for 1 h under an argon atmosphere. A solution of **12** (33 mg, 0.11 mmol) in toluene (5 ml) was added over a period of 20 min; the reaction was continued for 2 d. Work-up was carried out as

Table 5. Charge-Transfer Complexes of TBD and Its Derivatives (**4**—**7**)

Complex	D : A	Appearance[a]	Dp	Found (Calcd)[b]			σ[c]	ν(CN,CO)
			°C	C	H	N	S cm^{-1}	cm^{-1}
TBD·I$_2$	1 : 1	Black powder	145	27.18	0.76	0	1.1×10^{-1}	
				(27.50	0.66	0)		
TBD·TCNQ	1 : 1	Dark blue needles	232	59.98	1.68	11.66	2.5×10^{-9}	2222
				(60.20	1.58	11.76)		
TBD·TCNQF$_4$	1 : 1	Black fine needles	191	52.16	0.73	10.14	1.5×10^{-8}	2221
				(52.17	0.73	10.14)		
TBD·DDQ	1 : 1	Dark green needles	191	47.72	0.80	5.56	1.2×10^{-7}	1650[e]
				(47.68	0.75	5.49)		
TBD·HCBD	1 : 1	Dark blue needles	177	54.98	0.84	17.49	1.6×10^{-7}	2218
				(54.95	0.80	17.45)		
4·I$_2$	1 : 0.43	Black needles[d]	110	43.51	3.27	0	4.1×10^{-7}	
				(43.51	2.74	0)		
4·TCNQF$_4$	1 : 1	Dark brown powder	164	54.45	2.24	8.83	4.9×10^{-7}	2226
				(55.25	1.99	9.20)		
5·TCNQF$_4$	1 : 1	Black needles	141	57.61	2.98	8.42	1.6×10^{-7}	2219
				(57.82	3.03	8.43)		
6·I$_2$	1 : 2	Black powder	110	19.25	1.49	0	1.0×10^{-6}	
				(19.85	1.25	0)		
6·TCNQF$_4$	1 : 1	Black needles	260	45.90	1.60	7.56	5.3×10^{-6}	2218
				(45.64	1.64	7.60)		
6·DDQ	1 : 1	Black needles	186	41.86	1.76	4.06	1.3×10^{-7}	1650[e]
				(41.90	1.76	4.07)		
7·I$_2$	1 : 4	Black powder	126	15.79	1.36	0	1.6×10^{-5}	
				(15.68	1.32	0)		
7·TCNQF$_4$	1 : 1	Black needles	224	48.47	2.45	6.94	2.9×10^{-9}	2223
				(48.47	2.54	7.06)		
7·DDQ	1 : 1	Black needles	146	45.16	2.64	3.54	2.0×10^{-9}	2224, 1640
				(45.21	2.71	3.77)		
6·ClO$_4$·TCE	1 : 1 : 2	Black fine needles[f]	127	28.96	2.16	0	6.4×10^{-3}	
				(29.04	2.19	0)		
6·PF$_6$·TCE	1 : 1 : 1	Black fine needles[f]	204	29.48	2.37	0	8.9×10^{-3}	
				(29.25	2.05	0)		

a) Obtained from chlorobenzene, unless otherwise stated. b) Calculated as stoichiometry indicated. c) Measured on compressed pellets with a two-probe or four-probe method at room temperature. d) Obtained from *o*-dichlorobenzene. e) Vague nitrile absorption. f) Obtained from electrocrystallization in 1,1,2-trichloroethane (TCE) including tetrabutylammonium perchlorate or hexafluorophosphate as supporting electrolyte.

described in Method A to give TBD (4.0 mg, 13% yield).

Syntheses of TBD Derivatives (4—7). A typical procedure is described in the following preparation of 1,5-dimethyl-2,3,6,7-tetrathiabenzo[1,3-*cd*:4,6-*c′d′*]dipentalene (**15**). Into a solution of TBD (30 mg, 0.11 mmol) in dry THF (30 ml) cooled to −18 °C was added 1.0 M LDA THF solution (0.3 ml, 0.3 mmol) in an argon atmosphere; the mixture was stirred for 30 min at the temperature. Methyl iodide (0.1 ml, 1.6 mmol) was added, and the stirring was continued overnight at room temperature. After sat. aq NH$_4$Cl solution (30 ml) was added, the mixture was extracted with carbon disulfide; the extract was washed with brine, dried (MgSO$_4$), and evaporated. The residue was purified by column chromatography on silica gel with carbon disulfide followed by recrystallization from chlorobenzene to give faint brown needles (33 mg, 99% yield), mp 300 °C (decomp); ^{1}H NMR (CS$_2$) δ=2.66 (s,6H), 7.07 (s,2H); IR (KBr) 3090, 1420, 1370, 1075, 820 cm^{-1}; MS *m/z* 304 (M$^+$). Found: C, 55.16; H, 2.63%. Calcd for C$_{14}$H$_8$S$_4$: C, 55.23; H, 2.65%.

1,4,5,8-Tetramethyl-2,3,6,7-tetrathiabenzo[1,3-*cd*:4,6-*c′d′*]dipentalene (4): 60% yield: brown needles from chlorobenzene; mp>300°C; ^{1}H NMR (CS$_2$) δ=2.77 (s); IR (KBr) 2920, 2850, 1440, 1085, 795 cm^{-1}; MS *m/z* 332 (M$^+$). Found C, 57.74; H, 3.60%. Calcd for C$_{16}$H$_{12}$S$_4$: C, 57.79; H, 3.64%.

1,5-Diethyl-2,3,6,7-tetrathiabenzo[1,3-*cd*:4,6-*c′d′*]-dipentalene (16): 55% yield; pale-yellow powder from EtOH–CHCl$_3$; mp 138—139 °C; ^{1}H NMR (CS$_2$) δ=1.42 (t, *J*=7.5 Hz, 6H), 3.05 (q, *J*=7.5 Hz, 4H), 7.03 (s, 2H); IR (KBr) 3100, 2980, 2890 cm^{-1}; MS *m/z* 332 (M$^+$). Found: C, 57.69; H, 3.57%. Calcd for C$_{16}$H$_{12}$S$_4$: C, 57.79; H, 3.64%.

1,4,5,8-Tetraethyl-2,3,6,7-tetrathiabenzo[1,3-*cd*:4,6-*c′d′*]dipentalene (5): 67% yield; pale-yellow needles from chlorobenzene; mp 194—195.5 °C; ^{1}H NMR (CS$_2$) δ= 1.38 (t, *J*=7.5 Hz, 6H), 3.11 (t, *J*=7.5 Hz, 4H), IR (KBr) 2980 cm^{-1}; MS *m/z* 388 (M$^+$). Found: C, 61.80; H, 5.18%. Calcd for C$_{20}$H$_{20}$S$_4$: C, 61.81; H, 5.19%.

1,5-Bis(methylthio)-2,3,6,7-tetrathiabenzo[1,3-*cd*:4,6-*c′d′*]dipentalene (17): 58% yield; pale-yellow powder, mp 209—210 °C; ^{1}H NMR (CS$_2$) δ=2.52 (s, 6H), 7.70

(s, 2H); IR (KBr) 3080, 2920, 2850 cm^{-1}; MS *m/z* 368 (M$^+$). Found: C, 45.48; H, 2.19%. Calcd for $C_{14}H_8S_6$: C, 45.62; H, 2.19%.

1,4,5,8-Tetrakis(methylthio)-2,3,6,7-tetrathiabenzo-[1,3-*cd*:4,6-*c′d′*]dipentalene (6): 57% yield; pale-yellow needles from CS_2, mp 222.5—224 °C; ^{1}H NMR (CS_2) δ=2.52 (s); IR (KBr) 2920 cm^{-1}; MS *m/z* 460 (M$^+$). Found: C, 41.50; H, 2.57%. Calcd for $C_{16}H_{12}S_8$: C, 41.71; H, 2.63%.

1,5-Bis(ethylthio)-2,3,6,7-tetrathiabenzo[1,3-*cd*:4,6-*c′d′*]dipentalene (18): 56% yield; pale-yellow fine needles from hexane–chloroform; ^{1}H NMR (CS_2) δ=1.34 (t, J=7.3 Hz, 6H), 2.91 (q, J=7.3 Hz, 4H), 7.85 (s, 2H); IR (KBr) 3100, 2960, 2910 cm^{-1}; MS *m/z* 396 (M$^+$). Found: C, 48.43; H, 3.05%. Calcd for $C_{16}H_{12}S_6$: C, 48.45; H, 3.05%.

1,4,5,8-Tetrakis(ethylthio)-2,3,6,7-tetrathiabenzo-[1,3-*cd*:4,6-*c′d′*]dipentalene (7): 53% yield; pale-yellow fine needles from hexane–chloroform; ^{1}H NMR (CS_2) δ=1.28 (t, J=7.3 Hz, 6H), 2.91 (q, J=7.3 Hz, 4H); IR (KBr) 2970, 2930 cm^{-1}; MS *m/z* 516 (M$^+$). Found: C, 36.24; H, 1.66%. Calcd for $C_{20}H_{20}S_8$: C, 36.37; H, 1.74%.

Charge-Transfer Complexes. All of the charge-transfer complexes described in this report were prepared by mixing two hot saturated solutions of donor and acceptor in chlorobenzene or dichlorobenzene. The resulting complexes precipitated out upon cooling, and were collected by filtration, then dried.

Crystal Structures. The X-ray diffraction data were collected with a Rigaku automated diffractometer using Cu $K\alpha$ radiation monochromatized with a graphite plate. Independent reflections within $2\theta=126°$ ($|F_o|>3.0\sigma$ (F_o)) were used for analyses. The structures were solved by a direct method combined with the Monte-Carlo method for selecting the initial set of phase,[24] and refined by a full-matrix least-squares method.[25] Atomic scattering factors were taken from International Tables for X-ray Crystallography.[26] The anisotropic temperature factors were used for refinement. Tables of final atomic parameters, structure factors, and anisotropic thermal parameters are deposited as Document No. 66023 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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