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Synthesis, Properties, and Structures of 1,2 : 5,6-Bis(ethylenedithio)pyracylene and Its Radical Cation Salts

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1,2 : 5,6-Bis(ethylenedithio)pyracylene (**2**) was synthesized as an example of molecular design for a polyaromatic condensed-type donor with two ethylenedithio groups at the periphery. The redox potential of **2** indicates that this heterocycle is a reversible two-stage redox system with low oxidation potentials, which enhances the donor ability. This donor was readily oxidized to afford single crystal radical cation salts with hexafluorophosphate (PF_6^-) and triiodide (I_3^-) by electrocrystallization. The crystal structures of the radical cation salts, $(\mathbf{2})_3(PF_6)_2$ and $(\mathbf{2})_2I_3$, show segregated stacks of donors and anions. The I_3 salt presents a two-dimensional sheet along the *ab* plane similar to I_3 salt of bis(ethylenedithio)tetrathiafulvalene.

Since the discovery of the metallic character of the charge-transfer complex between tetrathiafulvalene (TTF, **3**) and 7, 7, 8, 8- tetracyanoquinodimethane (TCNQ), many organic materials with metallic characteristics have been explored.[1)] The chemical modification of the TTF type donor led to organic superconductors, the radical cation salts of bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF, **4**).[2)] Various arenes substituted with chalcogenes have been also explored as good donors for organic molecular metals.[1,3)]

Buckminsterfullerene (C_{60}) has generated an explosion of research activity in various fields of science.[4)] C_{60} is made up of a number of pyracylene units in the cluster and pyracylene (**1** in Chart 1) is a prototype anti-aromatic molecule with a planar 12-π periphery.[5a)] Therefore, the reactivity and properties of **1** and its derivatives are of considerable interest. However, the chemistry of **1** has not been explored due to its difficult preparation.[5)] On the other hand, it is well known that radical cation salts of **4** are superconductors[6)] with T_c values as high as 11.6 K.[7)] The relation between the chemical structures of 1,2 : 5,6-bis(ethylenedithio)-pyracylene (**2**) and **4** can be considered in such a way that **2** is obtained from **4** by substitution of the four sulfur atoms with two paris of butadiene linkages without degradation of the π-conjugation. Presumably, **2** is a good candidate for making organic conductors. In this paper a novel synthesis and some physical properties of **2** and its radical cation salts are reported.

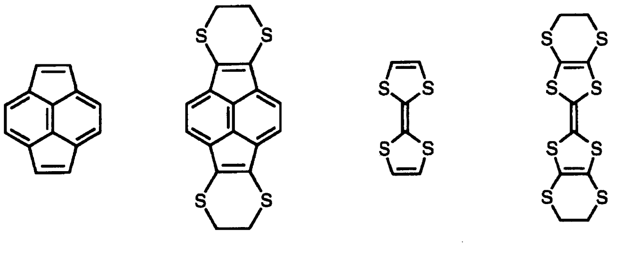
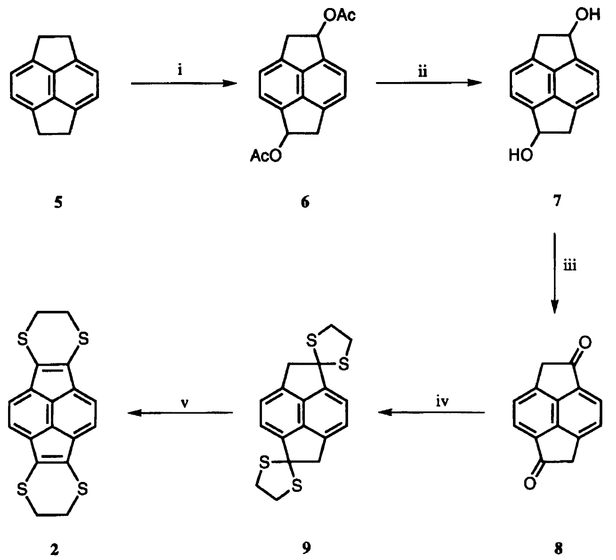

1 **2** **3** **4**

Chart 1.

Results and Discussion

Synthesis and Properties of 2: The synthesis of 1,2 : 5,6-bis(ethylenedithio)pyracylene (**2**) was done according to Scheme 1. The key step is the conversion of 1,5-pyracenedione (2,6-dihydro-1,5-pyracylenedione) (**8**)[8)] into **2** via dithioacetalization with 1,2-ethanedithiol and the subsequent ring-expansion reaction on treatment with tellurium tetrachloride ($TeCl_4$).[9)] Although the ring expansion of the dithiolane ring can be done by other reagents such as N-chlorosuccinimide (NCS) or halogens,[10)] pyracylene is too reactive to tolerate NCS and related reagents. This method has been used for the preparation of **2**. The ^{1}H NMR signals of **2** in $CDCl_3$ appeared at $\delta = 3.27$ and 6.39 ppm, which indicated some paramagnetic ring current, and the ^{13}C NMR signals were observed at δ=26.79, 119.97, 125.99, 129.56, and 140.36. When D_2SO_4 solvent was used, the signals were moved to lower fields (^{1}H NMR δ=3.92, 8.93, ^{13}C NMR δ=26.92, 121.31, 131.40, 138.49, 171.44). Thus, **2** was readily oxidized to the dication state merely by dissolution in D_2SO_4. Cyclic voltammetry of **2** [PhCN/*n*-Bu_4NClO_4 at room temperature: scan rate, 50 mV s^{-1}; electrode, Pt] had two reversible oxidation waves ($E^1_{1/2}$ +0.43 and $E^2_{1/2}$ +0.75) at potentials comparable to that of tetrathiafulvalene (**3**). This indicates that **2** is an even better donor than **4**,



Scheme 1. Reagents and conditions: i, Pb_3O_4, AcOH, 60 °C, 12 h, 62%; ii, NaOH, H_2O–EtOH, reflux, 2 h, 84%; iii, CrO_3, AcOH, room temperature, 4 h, 60%; iv, $(CH_2SH)_2$, $AlCl_3$, CH_2Cl_2, room temperature, 6 h, 52%; v, $TeCl_4$, C_6H_6, room temperature, 4 h, 56%.

which is attributed to the multistage redox system of pyracylene.[11] The redox potentials of **2**, **3**, and **4** are summarized in Table 1, where the solvent (MeCN) for **3** and **4** was inadequate for **2** because of its poor dissolving power. The difference between the first and second oxidation potentials of **2** is considerably smaller than that of **3** or **4**, which indicates the decrease of coulombic repulsion in the dication of **2**.

Preparation of Radical Cation Salts: The radical cation salts of **2** with inorganic acceptors such as ClO_4^-, BF_4^-, PF_6^-, and I_3^- were prepared on a platinum electrode by a low current electrooxidation (4 $\mu A\,cm^{-2}$) in CH_2Cl_2 solution containing n-Bu_4NX ($X=ClO_4^-$, BF_4^-, PF_6^-, and I_3^-). The radical cation salts of **2** with hexafluorophosphate (PF_6^-) and triiodide (I_3^-) anion were obtained as single crystals by electrocrystallization, which were suitable for X-ray diffraction. The composition of the salts were found to be $(\mathbf{2})_3(PF_6)_2$ and $(\mathbf{2})_2I_3$ by elemental analyses, respectively.

On the other hand, the radical cation salts with ClO_4^- or BF_4^- grown on the anode were not suitable for X-ray diffraction. The composition of the salts could not be identified clearly by elemental analyses and their compressed pellet conductivities were 10^{-3} to 10^{-4} S cm^{-1}.

Table 1. Redox Potentials $E_{1/2}$ (V vs. SCE) of **2**, **3**, and **4**

Compound	First $E_{1/2}$	Second $E_{1/2}$	ΔE
$\mathbf{2}^{a)}$	0.43	0.75	0.32
$\mathbf{3}^{b)}$	0.35	0.75	0.40
$\mathbf{4}^{b)}$	0.54	0.96	0.42

a) In PhCN/n-Bu_4NClO_4 at room temperature: scan rate, 50 mV s^{-1}: electrode, Pt. b) Ref. 11. measured in MeCN.

Structure of 2: The crystal data, atomic numbering scheme, and atomic coordinates of **2** and its salts are shown in Table 2, Fig. 1, Tables 3, 5, and 7, respectively. The bond lengths, angles, and molecular structure of **2** are given in Table 4 and Fig. 2, respectively. Molecule **2** is centrosymmetric and essentially planar similar to the parent pyracylene;[5b] the maximum atomic deviation from the molecular plane is 0.575 Å for C(9). The carbon atoms in the ethylenedithio moiety are conformationally disordered, so the quality of the bond parameters for this group is rather poor in comparison to the others.

The shortest intermolecular S···S contact ($d_1 =$ 3.684(3) Å) is slightly shorter than the sum of van der Waals radii (3.7 Å).[12] The molecular packing of **2** has a unique three-dimensional donor network (Fig. 3). This crystal structure is quite different from that of **4**.[13]

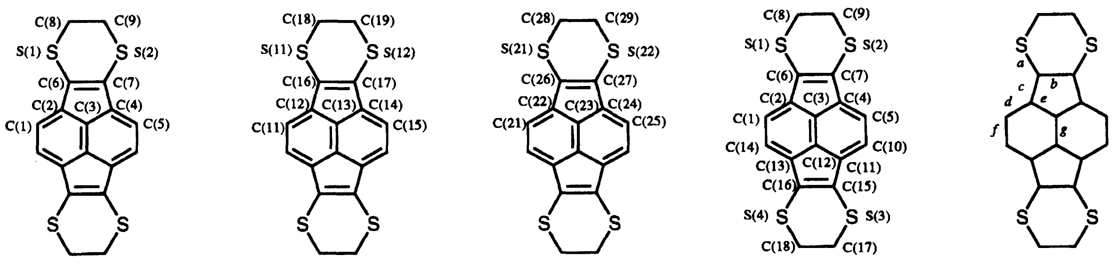
Structure of $(\mathbf{2})_3(\mathbf{PF_6})_2$: The bond parameters of $(\mathbf{2})_3(PF_6)_2$ are given in Table 6. The salt shows a segregated columnar stack of donor and anion units along the c axis, the donors being on the center of symmetry (Fig. 4). The donor column is composed of the three kinds of molecules $\mathbf{2}\alpha$, $\mathbf{2}\beta$ and $\mathbf{2}\gamma$ (Figs. 4 and 5). All the three molecules are almost planar with maximum deviations of 0.460 ($\mathbf{2}\alpha$, C(8)), 0.720 ($\mathbf{2}\beta$, C(18)), and 0.748 Å ($\mathbf{2}\gamma$, C(29)). In contrast to the neutral **2** with disordered ethylene group, all the ethylene conformations in $\mathbf{2}\alpha$, $\mathbf{2}\beta$, and $\mathbf{2}\gamma$ are ordered. Two donors ($\mathbf{2}\beta$ and $\mathbf{2}\gamma$) are almost in the same direction, and the other ($\mathbf{2}\alpha$) is oriented about 75° from these, as shown in Fig. 6.

The donor molecules are classified into two types by the bond lengths. A significant difference is seen in the lengths of a, b, and c bonds (Fig. 1) in $\mathbf{2}\alpha$, $\mathbf{2}\beta$, and $\mathbf{2}\gamma$ (Table 9). The bond lengths of the naphthalene skeletons (d, e, f, and g) are not changed so greatly. The bonds a and c of $\mathbf{2}\alpha$ are considerably longer than those of $\mathbf{2}\beta$ and $\mathbf{2}\gamma$, but the bond b of the former is shorter than those of the latters. The molecular dimension of $\mathbf{2}\alpha$ is similar to that of the neutral molecule **2**.

To realize this result, the π-molecular orbitals were calculated by a simple Hückel theory[14] adopting $\alpha_S = \alpha_C + 1.11\beta_{C\text{–}C}$ and $\beta_{C\text{–}S} = 0.69\beta_{C\text{–}C}$.[15] The bond orders estimated for 22π-electron system of the neutral state of **2** are compared with those for the mono cationic state (21π-electron system) in Table 9. The larger the bond order, the shorter the corresponding bond length.[16] The respective changes of a, b and c bonds, between $\mathbf{2}\alpha$ (and neutral **2**) and $\mathbf{2}\beta$ (and $\mathbf{2}\gamma$), can be explained with those in the bond orders of neutral and monocationic states. Therefore, the two donors ($\mathbf{2}\beta$ and $\mathbf{2}\gamma$) are presumed to be monocationic (charge=+1) state and other

Table 2. Crystal Data, Details of Data Collection and Refinement of **2** and Its Radical Cation Salts

	2	(**2**)$_3$(PF$_6$)$_2$	(**2**)$_2$I$_3$
Formula	$C_{18}H_{12}S_4$	$C_{54}H_{36}S_{12}P_2F_{12}$	$C_{36}H_{24}S_8I_3$
Fw	356.53	1359.53	1093.78
Crystal system	Rhombohedral	Monoclinic	Monoclinic
Space group	$R\bar{3}(h)$	$C2/c$	$P2_1/a$
a/Å	21.165(1)	32.53(2)	10.617(4)
b/Å	21.165(1)	10.250(3)	10.580(3)
c/Å	9.1388(6)	22.550(8)	16.428(2)
α/°	90	90	90
β/°	90	133.50(2)	98.95(2)
γ/°	120	90	90
V/Å^3	3545.1(4)	5454(7)	1823(1)
Z	9	4	2
D_{calcd}/g cm^{-1}	1.503	1.655	1.993
Crystal size/mm^3	0.12×0.12×0.25	0.50×0.38×0.23	0.45×0.12×0.25
No. of unique reflections	1229	6623	4428
No. of observations (I>3σ(I))	824	2759	2144
No. of variables	128	434	215
R	0.053	0.045	0.036
R_w	0.056	0.043	0.033



Neural 2 and 2α in (2)$_3$(PF$_6$)$_2$

2β in (2)$_3$(PF$_6$)$_2$

2γ in (2)$_3$(PF$_6$)$_2$

2 in (2)$_2$I$_3$

Fig. 1. Atomic numbering scheme for neutral **2**, **2**(α, β, γ) in (**2**)$_3$(PF$_6$)$_2$ and **2** in (**2**)$_2$I$_3$, and definition of bonds used in Table 9.

Table 3. Fractional Atomic Coordinates of Non-hydrogen Atoms for **2** with Estimated Standard Deviations in Parentheses

Atom	x	y	z
S(1)	0.5630(1)	0.23631(8)	0.0803(2)
S(2)	0.3939(1)	0.1104(1)	0.2413(2)
C(1)	0.6098(3)	0.1135(3)	−0.0754(6)
C(2)	0.5492(3)	0.1012(3)	0.0032(6)
C(3)	0.4964(3)	0.0273(3)	0.0270(6)
C(4)	0.4360(3)	0.0170(3)	0.1075(5)
C(5)	0.3821(3)	−0.0548(3)	0.1300(6)
C(6)	0.5179(3)	0.1413(3)	0.0790(6)
C(7)	0.4525(3)	0.0924(3)	0.1415(6)
C(8)	0.5097(8)	0.2567(6)	0.199(1)
C(9)	0.4316(7)	0.2076(7)	0.184(2)

one (**2**α) corresponds to neutral molecule **2**.

The intermolecular S(11)···S(21) (d_5=3.276(3) Å), C(12)···C(22), (3.382(6) Å) and C(13)···C(23) (3.292(6) Å) contacts shorter than the respective sums of van der Waals radii are observed between **2**β and **2**γ. Pertinent S···S contacts and distances between the least-squares

Table 4. Bond Lengths and Angles for **2**

Bond length/Å		Bond angle/°	
S(1)–C(6)	1.743(5)	C(6)–S(1)–C(8)	103.7(4)
S(1)–C(8)	1.765(9)	C(7)–S(2)–C(9)	97.8(4)
S(2)–C(7)	1.730(5)	C(2)–C(1)–C(5)	121.5(5)
S(2)–C(9)	1.87(1)	C(1)–C(2)–C(3)	116.0(5)
C(1)–C(2)	1.375(7)	C(1)–C(2)–C(6)	140.8(5)
C(1)–C(5)	1.472(8)	C(3)–C(2)–C(6)	103.2(4)
C(2)–C(3)	1.412(7)	C(2)–C(3)–C(3)	122.1(6)
C(2)–C(6)	1.484(7)	C(2)–C(3)–C(4)	114.3(4)
C(3)–C(3)	1.335(9)	C(3)–C(3)–C(4)	123.6(6)
C(3)–C(4)	1.393(7)	C(3)–C(4)–C(5)	115.9(5)
C(4)–C(5)	1.386(7)	C(3)–C(4)–C(7)	103.8(5)
C(4)–C(7)	1.486(7)	C(5)–C(4)–C(7)	140.3(5)
C(6)–C(7)	1.370(7)	C(1)–C(5)–C(4)	120.8(5)
C(8)–C(9)	1.45(2)	S(1)–C(6)–C(2)	121.2(4)
		S(1)–C(6)–C(7)	129.2(4)
		C(2)–C(6)–C(7)	109.5(5)
		S(2)–C(7)–C(4)	122.6(4)
		S(2)–C(7)–C(6)	128.2(4)
		C(4)–C(7)–C(6)	109.2(4)
		S(1)–C(8)–C(9)	114(1)
		S(2)–C(9)–C(8)	117.9(9)

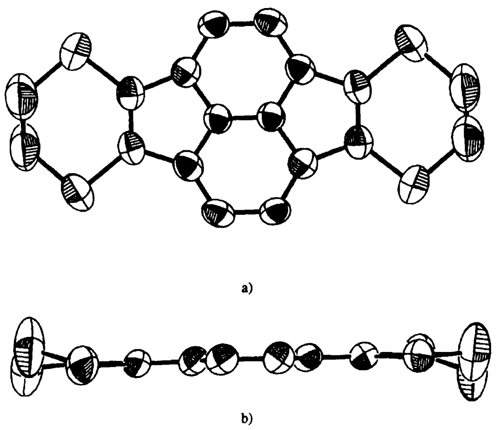


Fig. 2. Molecular structure of neutral **2**. The hydrogen atoms are omitted. The view direction is a) perpendicular and b) parallel to the molecular plane.

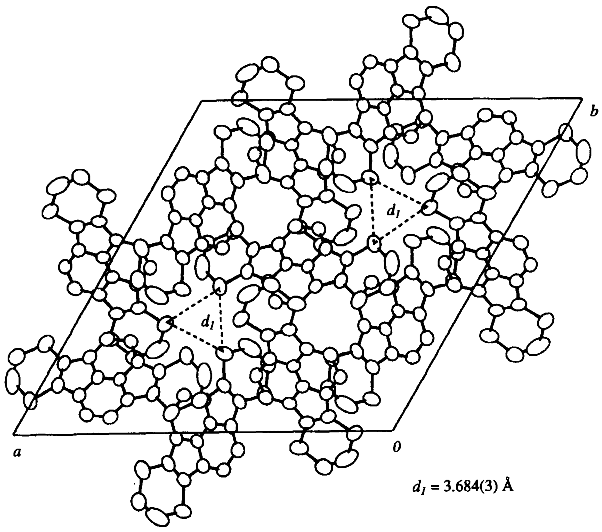


Fig. 3. Molecular packing of neutral **2** viewed along the *c* axis. The hydrogen atoms are omitted.

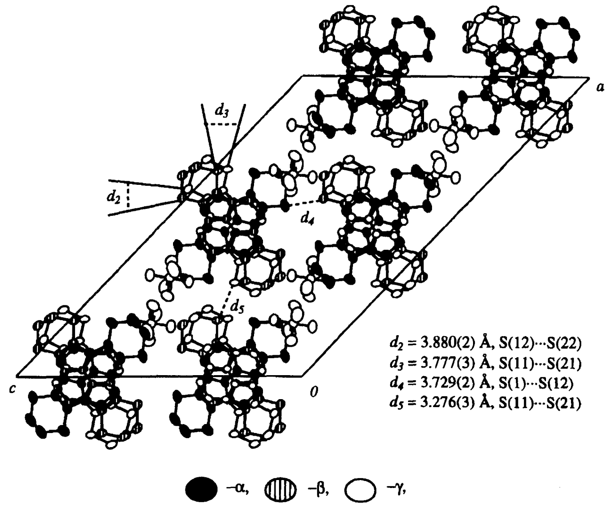


Fig. 4. Molecular packing of $(\mathbf{2})_3(PF_6)_2$ viewed along the *b* axis.

Table 5. Fractional Atomic Coordinates of Non-hydrogen Atoms for $(\mathbf{2})_3(PF_6)_2$ with Estimated Standard Deviations in Parentheses

Atom	*x*	*y*	*z*
S(1)	−0.06767(7)	0.7609(2)	0.3713(1)
S(2)	−0.17693(6)	0.7481(2)	0.1549(1)
S(11)	−0.18452(5)	0.4398(2)	0.01583(8)
S(12)	−0.09300(6)	0.4333(2)	−0.01658(8)
S(21)	0.18986(5)	0.0808(2)	0.45215(8)
S(22)	0.12288(6)	0.0639(2)	0.52514(7)
P(1)	0.17478(6)	0.2420(2)	0.20623(8)
F(1)	0.1641(1)	0.2619(3)	0.1271(2)
F(2)	0.1175(1)	0.1697(5)	0.1561(2)
F(3)	0.1869(1)	0.2214(4)	0.2871(2)
F(4)	0.2047(2)	0.1079(4)	0.2220(2)
F(5)	0.2340(1)	0.3106(4)	0.2588(2)
F(6)	0.1466(2)	0.3767(4)	0.1917(3)
C(1)	0.0512(2)	0.7537(5)	0.3962(3)
C(2)	−0.0055(2)	0.7530(5)	0.3262(3)
C(3)	−0.0196(2)	0.7516(5)	0.2519(3)
C(4)	−0.0775(2)	0.7512(5)	0.1832(3)
C(5)	−0.0935(2)	0.7519(5)	0.1083(3)
C(6)	−0.0619(2)	0.7544(5)	0.3003(3)
C(7)	−0.1041(2)	0.7515(5)	0.2163(3)
C(8)	−0.1422(3)	0.7991(9)	0.3041(5)
C(9)	−0.1802(3)	0.7183(9)	0.2308(5)
C(11)	−0.0853(2)	0.4201(5)	0.2290(3)
C(12)	−0.0785(2)	0.4170(4)	0.1750(3)
C(13)	−0.0223(2)	0.4127(4)	0.2096(2)
C(14)	−0.0171(2)	0.4173(4)	0.1531(3)
C(15)	0.0373(2)	0.4197(5)	0.1843(3)
C(16)	−0.1123(2)	0.4228(5)	0.0874(3)
C(17)	−0.0757(2)	0.4231(5)	0.0738(3)
C(18)	−0.1976(2)	0.5005(6)	−0.0713(3)
C(19)	−0.1697(2)	0.4231(7)	−0.0920(3)
C(21)	0.0731(2)	0.0854(5)	0.2435(3)
C(22)	0.0764(2)	0.0888(4)	0.3079(3)
C(23)	0.0253(2)	0.0918(4)	0.2886(2)
C(24)	0.0304(2)	0.0878(5)	0.3557(3)
C(25)	−0.0195(2)	0.0851(5)	0.3391(3)
C(26)	0.1190(2)	0.0857(5)	0.3976(3)
C(27)	0.0919(2)	0.0826(4)	0.4261(3)
C(28)	0.2222(2)	0.0881(7)	0.5568(3)
C(29)	0.1928(2)	0.0063(6)	0.5736(4)

planes are shown in Figs. 4 and 5, respectively. True, there are the short S···S contacts between the columns and the C···C one within the column, but the interaction between the cationic donors **2**β and **2**γ is insulated by the insertion of neutral **2**α. This structural feature is consistent with the low electrical conductive nature (10^{-5} S cm^{-1}, compressed pellet conductivity).

Structure of $(\mathbf{2})_2I_3$: The bond parameters and crystal structure of $(\mathbf{2})_2I_3$ are shown in Table 8 and Fig. 7, respectively. This crystal structure is similar to that of κ-(BEDT-TTF)$_2$I$_3$, which shows superconductivity at normal pressure.[13] The I_3^- anion is on an inversion center and located between the donor sheets related by inversion to each other. The donor and anion sheets are arranged alternately along the *c* axis. The donor sheet is composed of the inversion pair. The di-

Table 6. Bond Lengths and Angles for $(\mathbf{2})_3(\mathrm{PF}_6)_2$

Bond length/Å		Bond angle/°	
(α)			
S(1)–C(6)	1.736(5)	C(6)–S(1)–C(8)	99.7(3)
S(1)–C(8)	1.808(7)	C(7)–S(2)–C(9)	100.7(3)
S(2)–C(7)	1.737(5)	C(2)–C(1)–C(5)	120.6(5)
S(2)–C(9)	1.814(7)	C(1)–C(2)–C(3)	116.8(4)
C(1)–C(2)	1.374(6)	C(1)–C(2)–C(6)	140.0(4)
C(1)–C(5)	1.450(7)	C(3)–C(2)–C(6)	103.3(4)
C(2)–C(3)	1.399(6)	C(2)–C(3)–C(3)	122.4(6)
C(2)–C(6)	1.493(6)	C(2)–C(3)–C(4)	114.2(4)
C(3)–C(3)	1.339(8)	C(3)–C(3)–C(4)	123.3(6)
C(3)–C(4)	1.389(6)	C(3)–C(4)–C(5)	116.3(4)
C(4)–C(5)	1.384(6)	C(3)–C(4)–C(7)	104.6(4)
C(4)–C(7)	1.479(6)	C(5)–C(4)–C(7)	139.1(5)
C(6)–C(7)	1.376(6)	C(1)–C(5)–C(4)	120.6(5)
C(8)–C(9)	1.46(1)	S(1)–C(6)–C(2)	121.5(4)
		S(1)–C(6)–C(7)	129.2(4)
		C(2)–C(6)–C(7)	109.3(4)
		S(2)–C(7)–C(4)	123.2(4)
		S(2)–C(7)–C(6)	128.2(4)
		C(4)–C(7)–C(6)	108.6(4)
		S(1)–C(8)–C(9)	115.4(6)
		S(2)–C(9)–C(8)	114.7(6)
(β)			
S(11)–C(16)	1.714(4)	C(16)–S(11)–C(18)	101.7(3)
S(11)–C(18)	1.809(6)	C(17)–S(12)–C(19)	103.1(3)
S(12)–C(17)	1.703(4)	C(12)–S(11)–C(15)	121.1(4)
S(12)–C(19)	1.812(6)	C(11)–C(12)–C(13)	116.6(4)
C(11)–C(12)	1.378(6)	C(11)–C(12)–C(16)	140.1(4)
C(11)–C(15)	1.434(6)	C(13)–C(12)–C(16)	103.3(4)
C(12)–C(13)	1.413(6)	C(12)–C(13)–C(13)	122.1(5)
C(12)–C(16)	1.459(6)	C(12)–C(13)–C(14)	114.7(4)
C(13)–C(13)	1.335(8)	C(13)–C(13)–C(14)	123.0(5)
C(13)–C(14)	1.396(6)	C(13)–C(14)–C(15)	116.8(4)
C(14)–C(15)	1.385(6)	C(13)–C(14)–C(17)	104.2(4)
C(14)–C(17)	1.463(6)	C(15)–C(14)–C(17)	138.9(4)
C(16)–C(17)	1.419(6)	C(11)–C(15)–C(14)	120.4(4)
C(18)–C(19)	1.504(8)	S(11)–C(16)–C(21)	127.4(3)
		S(11)–C(16)–C(17)	129.2(4)
		C(12)–C(16)–C(17)	109.4(4)
		S(12)–C(17)–C(14)	123.0(3)
		S(12)–C(17)–C(16)	128.6(3)
		C(14)–C(17)–C(16)	108.4(4)
		S(11)–C(18)–C(19)	114.5(4)
		S(12)–C(19)–C(18)	114.5(4)
(γ)			
S(21)–C(26)	1.711(4)	C(26)–S(21)–C(28)	102.9(3)
S(21)–C(28)	1.806(6)	C(27)–S(22)–C(29)	100.9(3)
S(22)–C(27)	1.716(4)	C(22)–S(21)–C(25)	120.9(4)
S(22)–C(29)	1.815(6)	C(21)–C(22)–C(23)	117.3(4)
C(21)–C(22)	1.378(6)	C(21)–C(22)–C(26)	140.0(4)
C(21)–C(25)	1.427(6)	C(23)–C(22)–C(26)	102.7(4)
C(22)–C(23)	1.400(6)	C(22)–C(23)–C(23)	122.5(5)
C(22)–C(26)	1.468(6)	C(22)–C(23)–C(24)	115.5(4)
C(23)–C(23)	1.341(8)	C(23)–C(23)–C(24)	121.9(5)
C(23)–C(24)	1.403(6)	C(23)–C(24)–C(25)	117.3(4)
C(24)–C(25)	1.393(6)	C(23)–C(24)–C(27)	103.3(4)
C(24)–C(27)	1.467(6)	C(25)–C(24)–C(27)	139.4(4)
C(26)–C(27)	1.403(6)	C(21)–C(25)–C(24)	120.1(4)
C(28)–C(29)	1.505(8)	S(21)–C(26)–C(22)	121.2(3)
		S(21)–C(26)–C(27)	129.0(3)
		C(22)–C(26)–C(27)	109.7(4)
		S(22)–C(27)–C(24)	123.6(3)
		S(22)–C(27)–C(26)	127.4(3)
		C(24)–C(27)–C(26)	108.8(4)
		S(21)–C(28)–C(29)	114.0(4)
		S(22)–C(29)–C(28)	114.6(4)

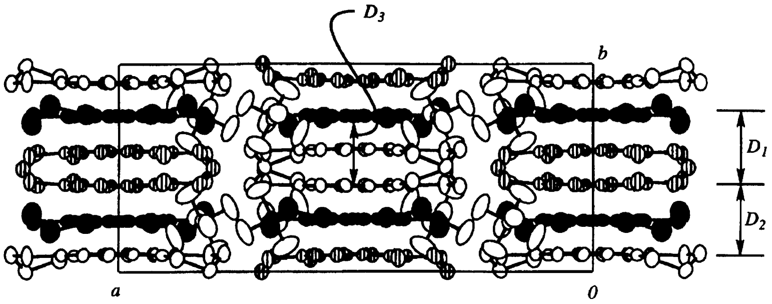
Table 7. Fractional Atomic Coordinates of Non-hydrogen Atoms for $(\mathbf{2})_2\mathrm{I}_3$ with Estimated Standard Deviations in Parentheses

Atom	x	y	z
I(1)	1/2	0	1/2
I(2)	0.39260(5)	−0.25066(5)	0.52376(3)
S(1)	−0.2472(2)	0.0283(2)	0.70460(9)
S(2)	0.0253(2)	0.2234(1)	0.7538(1)
S(3)	−0.0521(1)	0.1870(1)	1.25183(8)
S(4)	−0.3222(1)	−0.0095(2)	1.19979(9)
C(1)	−0.3189(5)	−0.0257(5)	0.9019(3)
C(2)	−0.2194(5)	0.0404(5)	0.8762(3)
C(3)	−0.1313(5)	0.0959(5)	0.9386(3)
C(4)	−0.0330(5)	0.1625(5)	0.9109(3)
C(5)	0.0568(5)	0.2186(5)	0.9696(3)
C(6)	−0.1698(5)	0.0753(5)	0.7997(3)
C(7)	−0.0609(5)	0.1489(5)	0.8201(3)
C(8)	−0.1390(6)	0.0836(6)	0.6385(3)
C(9)	−0.0887(7)	0.2163(6)	0.6597(3)
C(10)	0.0438(5)	0.2130(5)	1.0558(3)
C(11)	−0.0566(5)	0.1494(4)	1.0802(3)
C(12)	−0.1422(5)	0.0890(5)	1.0198(3)
C(13)	−0.2423(5)	0.0249(4)	1.0468(3)
C(14)	−0.3306(5)	−0.0328(5)	0.9876(3)
C(15)	−0.1111(5)	0.1232(5)	1.1569(3)
C(16)	−0.2200(5)	0.0483(5)	1.1369(3)
C(17)	−0.1914(6)	0.1748(6)	1.3019(4)
C(18)	−0.2473(6)	0.0449(6)	1.3010(3)

hedral angle between the neighboring donor molecules related by the glide plane symmetry is 67.0°. The inversion pairs form a two-dimensional sheet parallel to the *ab* plane. Ethylene conformations are ordered similar to **2** in the PF_6 salt, and the deviations of C(9) and C(17) atoms from the molecular plane are 0.827 and 0.968 Å, respectively. Average bond lengths *a* and *b* are intermediate between the respective bonds in the neutral **2** and cationic state ($\mathbf{2}\beta$ and $\mathbf{2}\gamma$ in the PF_6 salt), while *c*'s are not different. This result suggests that the ionicity of **2** in I_3 salt is 0.5, because the two molecules **2** are crystallographically equivalent.

There appear S···S contacts (d_6 and d_7 in Fig. 7) in the inversion pair and between the pairs (d_8 and d_9). C(2)···C(10) (3.356(7)), C(3)···C(11) (3.316(7)), C(3)···C(10) (3.395(7)), C(4)···C(12) (3.343(7)), C(5)···C(13) (3.280(7)), C(5)···C(12) (3.376(7)), C(7)···C(15) (3.400(7) Å) contacts are also observed in the donor sheet. The S···S contacts between the pairs are almost equal to the van der Waals contact, and the interplanar distance within the pair is 3.117 Å (Fig. 7). The single crystal conductivity of $(\mathbf{2})_2\mathrm{I}_3$ was 10^{-2} S cm^{-1} on *ab* plane at room temperature.

The radical cations having multiple chalcogen atoms at the periphery form a van der Waals S···S network, such as tris(ethylenedithio)benzene,[3a)] 1,4,7,10-tetrathiachrysene,[9b)] and 1,3,6,8-tetrakis(methylthio)pyrene.[3b)] In contrast to these the radical cation of **2** would tend to contact through van der Waals C···C interaction rather than the S···S interaction. The salt



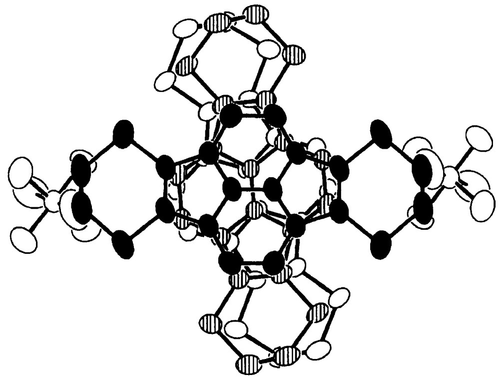
● –α, ◍ –β, ○ –γ,

D_1 = 3.327 Å (α···β)
D_2 = 3.357 Å (β···γ)
D_3 = 3.548 Å (γ···α)

Fig. 5. Molecular packing of $(\mathbf{2})_3(PF_6)_2$ viewed along the *c* axis.

Table 8. Bond Lengths and Angles for $(\mathbf{2})_2I_3$

Bond length/Å		Bond angle/°	
S(1)–C(6)	1.721(5)	C(6)–S(1)–C(8)	101.2(3)
S(1)–C(8)	1.797(7)	C(7)–S(3)–C(9)	99.9(3)
S(2)–C(7)	1.719(5)	C(15)–S(3)–C(17)	100.1(3)
S(2)–C(9)	1.810(7)	C(16)–S(4)–C(18)	102.1(3)
S(3)–C(15)	1.725(5)	C(2)–C(1)–C(14)	120.8(5)
S(3)–C(17)	1.805(6)	C(1)–C(2)–C(3)	116.2(5)
S(4)–C(16)	1.723(5)	C(1)–C(2)–C(6)	140.5(5)
S(4)–C(18)	1.821(6)	C(3)–C(2)–C(6)	103.4(4)
C(1)–C(2)	1.387(7)	C(2)–C(3)–C(4)	114.9(5)
C(1)–C(14)	1.434(7)	C(2)–C(3)–C(12)	123.1(5)
C(2)–C(3)	1.404(7)	C(4)–C(3)–C(12)	122.1(5)
C(2)–C(6)	1.483(7)	C(3)–C(4)–C(5)	117.4(5)
C(3)–C(4)	1.393(7)	C(3)–C(4)–C(7)	103.7(4)
C(3)–C(12)	1.358(7)	C(5)–C(4)–C(7)	138.9(5)
C(4)–C(5)	1.381(7)	C(4)–C(5)–C(10)	120.5(5)
C(4)–C(7)	1.481(7)	S(1)–C(6)–C(2)	121.0(4)
C(5)–C(10)	1.444(7)	S(1)–C(6)–C(7)	130.0(4)
C(6)–C(7)	1.391(7)	C(2)–C(6)–C(7)	109.0(4)
C(8)–C(9)	1.523(9)	S(2)–C(7)–C(4)	123.4(4)
C(10)–C(11)	1.372(7)	S(2)–C(7)–C(6)	127.4(4)
C(11)–C(12)	1.392(7)	C(4)–C(7)–C(6)	109.0(4)
C(11)–C(15)	1.493(7)	S(1)–C(8)–C(9)	113.4(4)
C(12)–C(13)	1.390(6)	S(2)–C(9)–C(8)	113.4(4)
C(13)–C(14)	1.383(7)	C(5)–C(10)–C(11)	120.2(5)
C(13)–C(16)	1.483(7)	C(10)–C(11)–C(12)	117.9(4)
C(15)–C(16)	1.398(7)	C(10)–C(11)–C(15)	139.3(5)
C(17)–C(18)	1.496(8)	C(12)–C(11)–C(15)	102.8(4)
		C(3)–C(12)–C(11)	122.0(5)
		C(3)–C(12)–C(13)	121.7(5)
		C(11)–C(12)–C(13)	116.3(5)
		C(12)–C(13)–C(14)	117.3(5)
		C(12)–C(13)–C(16)	103.0(4)
		C(14)–C(13)–C(16)	139.5(5)
		C(1)–C(14)–C(13)	120.9(5)
		S(3)–C(15)–C(11)	123.8(4)
		S(3)–C(15)–C(16)	127.3(4)
		C(11)–C(15)–C(16)	108.7(4)
		S(4)–C(16)–C(13)	121.5(4)
		S(4)–C(16)–C(15)	129.4(4)
		C(13)–C(16)–C(15)	109.1(4)
		S(3)–C(17)–C(18)	114.4(4)
		S(4)–C(18)–C(17)	114.5(4)



● –α, ◍ –β, ○ –γ,

Fig. 6. Mode of the molecular overlap of donors in $(\mathbf{2})_3(PF_6)_2$.

$(\mathbf{2})_2I_3$ is very stable at ambient temperature; the electrical conductivity is not changed for several months. These results support the potential utility of ethylenedithio-modified pyracylene **2** as a novel electron donor for constructing two-dimensional organic conductors.

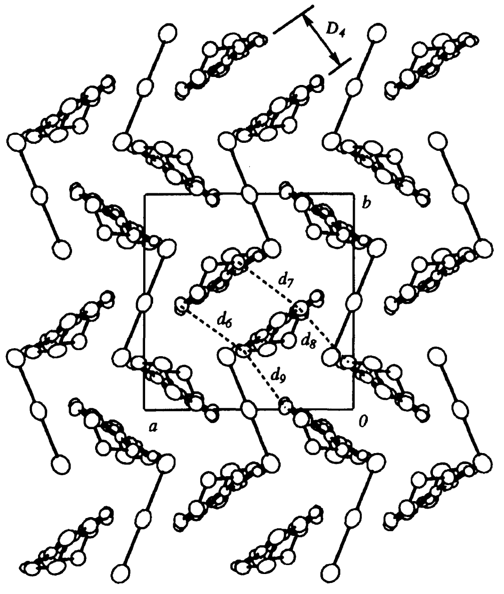
Experimental

General Methods. Melting points were obtained on a Yanaco micro melting point apparatus and are uncorrected. Proton and carbon nuclear magnetic resonance spectra (^{1}H and ^{13}C NMR) were recorded respectively at 270 and 67.8 MHz on a JEOL JNM-GSX270 FT-NMR spectrometer in $CDCl_3$ or D_2SO_4. TMS was used as an internal standard. All Chemical shifts are reported in parts per million (δ) relative to TMS. Ultraviolet-visible spectra were measured for MeCN or H_2SO_4 solution with Hitachi U-3200 spectrometer. Infrared spectra (KBr) were measured with a Hitachi 270-30 spectrophotometer. Mass spectra were taken on a Hitachi M-80B instrument operating at 20 eV. Microanalyses were done on a Perkin–Elmer 240C elemental analyzer. Pyracene (tetrahydropyracylene) (**5**) was prepared as previously reported.[5a)] All chemicals were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Kasei Kogyo Co., Ltd., and Aldrich Chemical Company, Inc. Solvent were dried over appropriate agents before use. Column chromatography was done on Wakogel C-200 (Wako Pure Chemical Industries, Ltd., abt. 200 mesh). The cyclic voltamme-

Table 9. The Average of Observed Bond Lengths and Bond Orders of **2** in Neutral State and in Radical Cation Salts

2	Neutral	$PF_6(\alpha)$	$PF_6(\beta)$	$PF_6(\gamma)$	I_3	Bond order[a)]	
						Neutral (22π)	Cationic (21π)
a	1.736	1.736	1.708	1.713	1.722	0.266	0.353
b	1.370	1.377	1.419	1.403	1.394	0.769	0.644
c	1.485	1.486	1.461	1.467	1.485	0.401	0.450
d	1.380	1.379	1.381	1.385	1.380	0.654	0.636
e	1.402	1.394	1.403	1.401	1.394	0.510	0.475
f	1.427	1.450	1.434	1.427	1.439	0.619	0.634
g	1.335	1.339	1.335	1.341	1.358	0.534	0.594

a) Bond orders were calculated by simple HMO method.[14,15)]



$D_4 = 3.117$ Å
$d_6 = 3.859(3)$ Å, S(2)···S(4)
$d_7 = 3.885(3)$ Å, S(1)···S(3)
$d_8 = 3.705(2)$ Å, S(2)···S(4)
$d_9 = 3.741(2)$ Å, S(1)···S(2)

Fig. 7. Molecular packing of $(\mathbf{2})_2I_3$ viewed along the *c* axis.

try was done at room temperature under nitrogen using a Yanagimoto P-1100.

1,5-Bisacetoxypyracene (Mixture with 1,6-Isomer) (6). **6** was prepared from **5** as previously reported.[17)] Compound **6** contained small amounts of 1,6-regio isomers. These mixtures were used for the next step without separation. The same product **2** was formed in the last step of the synthetic sequence. ^{1}H and ^{13}C NMR spectra of the main product are shown below: **6**; 58%, mp 190—200 °C (recryst. from hexane–CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ=2.10 (6H, s), 3.40 (2H, d, J=18.0 Hz), 3.92 (2H, dd, J=18.0 and 7.0 Hz), 6.68 (2H, d, J=7.0 Hz), 7.35 (2H, d, J=6.0 Hz), 7.54 (2H, d, J=6.0 Hz); ^{13}C NMR ($CDCl_3$) δ=21.20, 40.46, 77.40, 121.54, 123.86, 136.50, 137.93, 139.61, 171.08; IR (KBr) 2928, 1728, 1376, 1246, 1224, 1030, 822 cm^{-1}; MS (20 eV) m/z (rel intensity) 296 (M$^+$, 25), 237 (18), 211 (24).

1,5(1,6)-Pyracenediol (7) and 1,5(1,6)-Pyracenedione (8).[18)] To a solution of **6** (1 mmol) in ethanol (15 ml) was added sodium hydroxide (10%-15 ml) and the resultant mixture was refluxed for 4 h. The reaction mixture was extracted with CH_2Cl_2, and the organic layer was dried over sodium sulfate. The solution was evaporated under reduced pressure to leave a crude product (**7**). Compound **7** also contained small amounts of 1,6-regio isomers but was used for the next reaction without any purification for the above reason. **7**: 84%, mp >250 °C (recryst. from ethanol); IR (KBr) 3328, 2908, 1442, 1420, 1072, 1044, 846 cm^{-1}; MS (20 eV) m/z (rel intensity) 212 (M$^+$, 100), 165 (65), 139 (9). To a solution of **7** (2 mmol) in acetic acid (30 ml) was added chromium trioxide (3 mmol) in acetic acid (30 ml) dropwise and the resultant mixture was stirred for 4 h at room temperature. The reaction mixture was extracted with ether and the organic layer was dried over magnesium sulfate, evaporated under reduced pressure to give a crude product, which was purified by chromatography on silica gel to give **8**; 60%, mp>250 °C (recryst. from hexane–CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ=3.94 (4H, s), 7.55 (2H, s), 8.07 (2H, s); IR (KBr) 1780, 1715, 1393, 1340, 1270, 845 cm^{-1}; MS (20 eV) m/z (rel intensity) 208 (M$^+$, 100) 180 (47), 152 (80). Found C, 80.65; H, 3.99%. Calcd for $C_{14}H_8O_2$: C, 80.76; H, 3.87%.

1,5(1,6)-Pyracenedione Bis(ethylenedithioacetal) (9).[19)] To a solution of **8** (1 mmol) and ethanedithiol (2.2 mmol) in dichloromethane (30 ml) was added powdered $AlCl_3$ (0.35 mmol) and the resulting suspension was stirred for 4 h at room temperature. The reaction was quenched by the addition of 5% aqueous sodium hydrogen carbonate and the insoluble material was removed by filtration. The oraganic layer was separated, dried over sodium sulfate, and evaporated under reduced pressure to leave a crude product, which was purified by chromatography on silica gel to give **9**; 52%; mp>250 °C (recryst. from hexane–CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ=3.56—3.74 (8H, m), 4.22 (4H, s), 7.33 (2H, d, J=7.0 Hz), 7.55 (2H, d, J=7.0 Hz); IR (KBr) 2924, 1414, 1274, 1218, 996, 966, 840 760 cm^{-1}; MS (20 eV) m/z (rel intensity) 360 (M$^+$, 26), 332 (100), 304 (88), 272 (98), 240 (86). Found: C, 59.71; 4.54%. Calcd for $C_{18}H_{16}S_4$: C, 59.96; H, 4.47%.

Synthesis of 1,2 : 5,6-Bis(ethylenedithio)pyracylene (2).[9)] To a solution of **9** (0.5 mmol) in dichloromethane (10 ml) was added powdered $TeCl_4$ (2 mmol) and the resulting suspension was stirred for 4 h at room temperature. During the course of this procedure, free tellurium was separated as a black precipitate. The reaction was quenched by the addition of 5% aqueous sodium hydrogen carbonate and the insoluble material was removed by filtration. The organic layer was separated, dried over sodium sulfate, and evaporated under reduced pressure to leave a crude product, which was purified by chromatography on silica get to give **2**; 56%, mp 199—201 °C; ^{1}H NMR ($CDCl_3$) δ=3.27, (8H, s), 6.39 (4H, s); ^{13}C NMR ($CDCl_3$) δ=26.79, 119.97, 125.99, 129.56, 140.36; UV λ_{max} (MeCN) 499 (ε 1630), 471 (1610), 393 (29400), 373 (28200), 354 (19500), 278 (19300), 231 (46400), 210 nm (38500); UV λ_{max} (H_2SO_4) 834 (ε 18600), 501 (12600), 453 (47700), 430 (34400), 366 (14200), 309 (15800), 237 (21100), 208 nm (23000); IR (KBr) 2916, 1666, 1456, 1408, 1378 1286 1162, 1008, 836 cm^{-1}; MS (20 eV) m/z (rel intensity) 356 (M$^+$; 19), 328(14), 281(26), 207(100). HRMS (70 eV) Found: m/z 355.9824. Calcd for $C_{18}H_{12}S_4$: M, 355.9821. Found: C, 60.55; H, 3.23%. Calcd for $C_{18}H_{12}S_4$: C, 60.64; H, 3.39%.

Preparation of the Radical Cation Salts of 1,2 : 5,6-Bis(ethylenedithio)pyracylene (2). All the radical cation salts were prepared from a $(CH_2Cl)_2$ solution of the donor (**2**) and n-Bu_4NClO_4, n-Bu_4NBF_4, n-Bu_4NPF_6, or n-Bu_4NI_3 by an electrochemical method. The general procedure was as follows: A solution of **2** (0.05 mmol) in $(CH_2Cl)_2$ (30 ml) is treated with n-Bu_4NX (X=ClO_4, BF_4, PF_6, or I_3) (0.3 mmol), and the solution was cooled at −20 °C and electrolized between Pt plates with a current density of 4 μA cm^{-2}: $(\mathbf{2})_x(ClO_4)_y$, black powder, mp >250 °C. Found: C, 48.79; H, 2.90%. $(\mathbf{2})_x(BF_4)_y$, black powder, mp >250 °C. Found C, 49.20; H, 2.70%. Composition x and y could not be identified by elemental analyses.; $(\mathbf{2})_3(PF_6)_2$, black plates, mp >250 °C. Anal. Calcd for $C_{54}H_{36}S_{12}P_2F_{12}$: C, 47.71; H, 2.67%. Found: C, 47.77; H, 2.63%; $(\mathbf{2})_2I_3$, black plates, mp 215—220 °C decomp. Anal. Calcd for $C_{36}H_{24}S_8I_3$: C, 39.53; H, 2.21%. Found: C, 39.97; H, 2.16%.

Electrical Conductivity Measurement. The electrical conductivity for the compressed pellet was measured by a four-probe method. Electrical conductivities for the single crystal were measured by a two-probe method. Electrical contacts were done with gold paste.

Crystal Structures. The X-ray diffraction data were collected by using a Rigaku AFC-5R automated four-circle diffractometer with Cu or Mo $K\alpha$ radiation monochromatized by graphite (λ(Cu $K\alpha$)=1.54178 Å, 2θ–ω scans, $2\theta_{max}$=123° or λ(Mo $K\alpha$)=0.71069 Å, 2θ–ω scans, $2\theta_{max}$=55°). The structures were solved by a direct method using the MITHRIL program[20] and refined by the full-matrix least-squares method on F with weight $w=1/\sigma^2(F)$. An empirical absorption correction with ψ-scan method was used.[21] Anisotropic thermal parameters were used for the refinement of non-H atoms. The positions of certain H atoms were refined with isotropic thermal parameters. The positions of the other H atoms were calculated from positions of non-H atoms. Calculations were done on a VAX station 3200 computer with the TEXSAN program[22] which used the atomic scattering factors taken from "International Tables for X-Ray Crystallography"[23] and took anomalous dispersion into account. Tables of complete set of atomic parameters, structure factors, and anisotoropic thermal parameters are deposited as Document No. 68004 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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