Crystal Structures and Electrical Properties of $TSeC_n$-TTF (n=2 and 4)

Ping WANG, Takehiko MORI, Chikako NAKANO, Yusei MARUYAMA, Hiroo INOKUCHI,* Naoko IWASAWA,† Hideki YAMOCHI,† Hatsumi URAYAMA,† and Gunzi SAITO†

Institute for Molecular Science, Myodaiji, Okazaki 444

†The Institute for Solid State Physics, The University of Tokyo, Roppongi, Tokyo 106

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An organic compound $TSeC_n$-TTF [tetrakis(alkylseleno) tetrathiafulvalenes] with n=2, crystallizes in the monoclinic space group $P2_1/a$, a=23.218(5), b=8.960(3), c=10.489(3) Å, β=96.61(2)°, V=2168(1) Å^3, and Z=4; the compound with n=4 crystallizes in the triclinic space group $P\bar{1}$, a=9.198(1), b=10.539(2), c=8.248(2) Å, α=113.16(2), β=96.02(2), γ=90.61(2)°, V=729.9(3) Å^3 and Z=1. The molecule with n=2 has a bent structure, like a boat; and the molecule with n=4 has a structure in which each of the four alkyl chains is stretched towards different directions. The temperature dependence of electrical resistivity and the charge-carrier mobility have been measured, and the resistivities at room temperature are $\rho_a/\rho_b/\rho_c$=3.3×10^9/2.0×10^9/6.0×10^{11} and 2.2×10^{11}/1.0×10^{11}/1.3×10^{11} (Ω cm) for $TSeC_2$-TTF and $TSeC_4$-TTF, respectively. The quite isotropic character in the resistivities of a $TSeC_4$-TTF crystal may originate from its rather strange molecular structure.

Nowadays relatively high conductivities have been realized even in one-component organic materials under the presence of the columnar structures with the effective overlaps of π orbitals between molecules.[1] The physicochemical studies on the organic materials with long alkyl chains, such as TTC_n-TTF, $TTeC_n$-TTF, and $TSeC_n$-TTF (n=1—18)[2-4] have been widely carried out. A new function named as "molecular fastener effect" has been found. Comparing with TTC_n-TTF and $TTeC_n$-TTF, the electrical and thermal properties of $TSeC_n$-TTF series for large n ($n\geqq 8$) are similar to those of TTC_n-TTF and $TTeC_n$-TTF, in which the intermolecular interactions associated with alkyl chains play an important role. For the compounds with small n ($n\leqq 7$), the electrical and thermal properties of $TSeC_n$-TTF series are just in between TTC_n-TTF and $TTeC_n$-TTF series, in which the intermolecular interactions between chalcogen atoms and between C_6S_4 parts play an important role. In the present paper, we report the results of the single crystal X-ray structure analysis, the electrical conductivities and the charge-carrier mobilities of $TSeC_n$-TTF with n=2 and 4.

Experimental

Single crystals of $TSeC_2$-TTF and $TSeC_4$-TTF were prepared by a slow cooling method in a hexane solution. Dark yellow $TSeC_2$-TTF crystals were grown in a plate-like form after several days. For $TSeC_4$-TTF keeping the solution in a refrigerator for several days, dark red crystals were obtained in a block-like form.

The crystal structure analysis was carried out with a Rigaku automated four-circle X-ray diffractometer AFC-5R and AFC-5 for $TSeC_2$-TTF and $TSeC_4$-TTF, respectively. For the compound of $TSeC_2$-TTF the crystal data is: $C_{14}H_{20}S_4Se_4$, F.W. 631.84, monoclinic, space group $P2_1/a$, a=23.218(5), b=8.960(3), c=10.489(3)Å, β=96.61(2)°, V=2168(1)Å^3, Z=4, D_x=1.937 g cm^{-3} and μ(Mo $K\alpha$)=70.671 cm^{-1}. Intensity data were measured by the θ-2θ scan technique on the diffractometer with graphite monochromatized Mo $K\alpha$ radiation ($2\theta<60°$). The structure was solved by the direct method using MULTAN 78 program system[5] and refined by the block-diagonal least-squares procedure using 1354 independent reflections $|F_o|>3\sigma(|F_o|)$. After absorption correction the refinement was limited to a final R value of 0.079. Anisotropic thermal parameters were adopted for all nonhydrogen atoms, and the hydrogen atoms were refined isotropically. For the compound of $TSeC_4$-TTF, the crystal data is: $C_{22}H_{36}S_4Se_4$, F.W. 743.84, triclinic, space group $P\bar{1}$, a=9.198(1), b=10.539(2), c=8.248(2) Å, α=113.16(2), β=96.02(2), γ=90.61(2)°, V=729.9(3)Å^3, Z=1, D_x=1.69 g cm^{-3}, μ(Mo $K\alpha$)=52.609 cm^{-1}. Intensity data were measured by the θ-2θ scan technique on the diffractometer with graphite monochromatized Mo $K\alpha$ radiation ($2\theta<60°$). The structure was solved also by the direct method using MULTAN 78 program system[5] and refined by the block-diagonal least-squares procedure using 2743 independent reflections $|F_o|>3\sigma(|F_o|)$. The refinement was limited to a final R value of 0.065. Anisotropic thermal parameters were adopted for all nonhydrogen atoms, and the hydrogen atoms were refined isotropically.[10]

The electrical resistivities were measured by a two probe method from room temperature to just above the each melting point under a vacuum of 10^{-4} Pa to avoid an oxidation effect. The electrical contacts to the specimen crystals were made with gold paint. The mobilities were measured by a time-of-flight method for charge carriers generated by irradiation from a pulsed nitrogen laser.

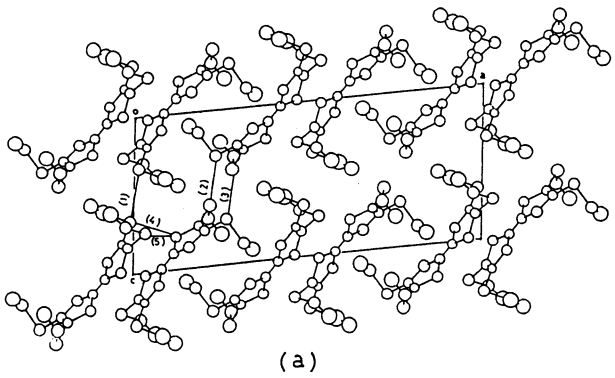
Results and Discussion

$TSeC_2$-TTF. The atomic coordinates are listed in Table 1. The crystal structure is shown in Figs. 1 and 2. Along the a axis, the $TSeC_2$-TTF molecules are stacked with overlapping as shown in Fig. 2(b), where the distance between the two C_2S_4 molecular planes is 3.41 Å. The shortest intermolecular S-S contact is 3.72(1) Å (Fig. 1b) which is a little longer than the sum of the van der Waals radii (3.70 Å). The shortest intermolecular S-Se contact is 3.804(8) Å, which is a little shorter than the sum of the van der Waals radii (3.85 Å). Along the c axis the shortest intermolecular Se-Se distance between the neighboring two molecules is 3.618(5) Å, which is much shorter than the sum of the van der Waals radii (4.00 Å) (Fig. 1). The molecule has a bent structure like a boat (Figs. 3(a) and(b)), and

Table 1. Positional Parameters and Equivalent Isotropic Thermal Parameters of $TSeC_2$-TTF

Positional parameters (×10**4) and equivalent isotropic temperature factors (HAMILTON, 1959).

	X	Y	Z	B_{eq}(Å**2)
Se1	9937(1)	1810(1)	8555(1)	4.6
Se2	7411(1)	4346(1)	9888(1)	4.6
S3	5178(2)	2146(1)	6995(2)	4.0
S4	7266(2)	−74(1)	6068(2)	3.8
C5	7921(6)	1566(5)	7623(7)	3.1
C6	5507(5)	441(5)	5641(7)	3.2
C7	6997(6)	2549(5)	8026(7)	3.3
C8	10488(6)	−89(6)	7636(8)	3.8
C9	12062(6)	−167(7)	8327(8)	4.0
C10	12546(7)	−1643(7)	7538(10)	5.1
C11	6875(7)	5454(6)	8516(9)	4.8
C12	7923(8)	5531(7)	7161(10)	5.7
C13	14124(8)	−1777(9)	8139(11)	6.5
C14	7466(10)	6258(8)	6212(11)	7.5
C15	8458(9)	6208(9)	4839(12)	7.1



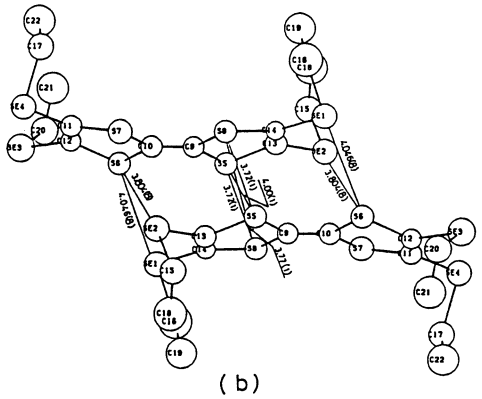
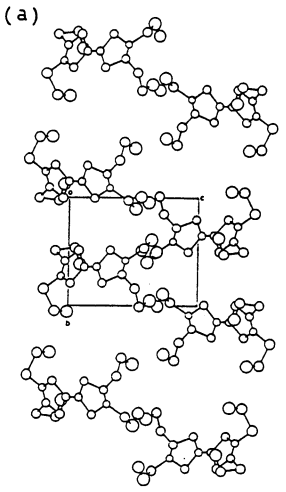


Fig. 1. Crystal structure of $TSeC_2$-TTF projected along the b axis (a) and the intermolecular interactions between two molecules along the a axis (b). [(1) 3.618(5), (2) 3.618(5), (3) 3.618(5), (4) 4.046(5), (5) 3.804(5)].

the dihedral angles between the optimal plane of the central C_2S_4 part and the planes of the two C_2Se_2 part are 8.5(2) and 12.0(2)°, respectively. The terminal Se-C-C bonds are strongly bent towards the central



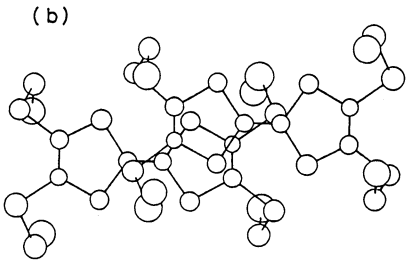


Fig. 2. Crystal structure of $TSeC_2$-TTF projected along the a axis(a) and the mode of overlaps of $TSeC_2$-TTF along the a axis (b).

plane and the molecules are overlapped along the stacking axis a.

The resistivities at room temperature are 3.3×10^9, 2.0×10^9, and 6.0×10^{11} (Ω cm) along the a, b, and c axis, respectively. The resistivity along the a axis is the same order as that along the b axis. The anisotropy between a or b and c directions is not so large, about 10^2, because of the absence of a special direction for easy electrical conduction. According to the crystal structure, it can be understood clearly. The easier axis for electrical conduction (ρ_a) corresponds to the stacking direction of C_6S_4 moiety (parallel to the a-axis), while the harder axis corresponds to the c-axis, where is almost no stacking but exist short Se-Se contacts (3.618(5)Å). These two factors give rise to the rather small anisotropy of about 10^2. Along the b-axis, adjacent $TSeC_2$-TTF molecules are arranged side by side which leads to about the same magnitude of ρ_b as ρ_a. The temperature dependence of the electrical resistivity along the a axis is shown in Fig. 4, in which the resistivity decreases with the temperature increase until the melting point, with an activation energy $E_a=3.7\times10^{-1}$ (eV).

Mobility measurements for single crystals at room temperature have indicated that the electron and hole mobilities along the c axis are $\mu_c^e=1.7$ cm^2 V^{-1} s^{-1} and

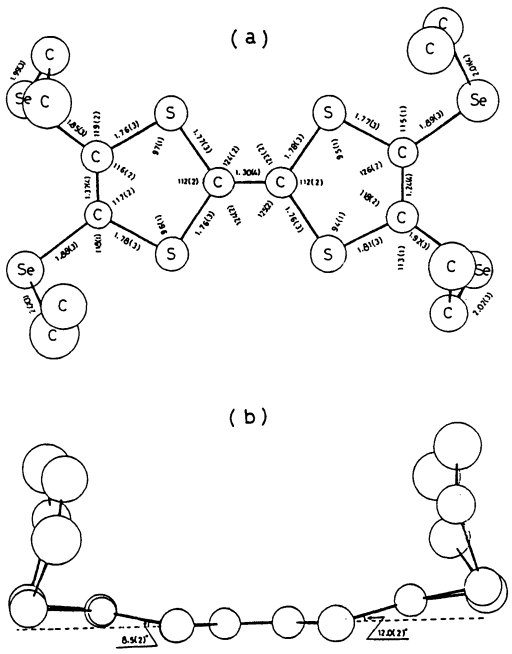


Fig. 3. Molecular structure of $TSeC_2$-TTF (a) and the side view (b).

μ_c^h=1.4 $cm^2V^{-1}s^{-1}$, respectively. Taking into account of the resistivity data, we can estimate fairly high mobilities along the a or b axis. The charge-carrier mobilities in an anthracene crystal are 0.3 and 1.5 $cm^2V^{-1}s^{-1}$ along the c and a or b axis, respectively. Comparing these values with the present data, we can conclude that the effect of chalcogen atoms is still important in $TSeC_2$-TTF crystals.

$TSeC_4$-TTF. The atomic coordinates are listed in Table 2. The crystal structure is shown in Fig. 5. The stacking axis with respect to the central molecular planes is c axis, along which the distance between the two molecular planes is as far as 4.82 Å, because the two isobutyl chains, which are just between the two molecular planes, are directed up and down from the optimal plane of the central S_4C_6 part, as shown in Figs. 5(b) and 6(b). The intermolecular interactions between adjacent C_6S_4 moieties are weak and can be described in terms of the van der Waals interactions because of the absence of discernible intermolecular overlaps between adjacent π systems. Therefore, the high resistivity along the stacking c axis can be understood by taking account of this fact. Along the b and a axis the interaction between two molecules is still rather weak, Fig. 5(c), so that no good conducting path can be formed in any direction. The distances between Se-Se, Se-S, Se-C, S-S, S-C, and C-C are all longer than the sum of van der Waals radii.

In the TYC_n-TTF family the $TSeC_4$-TTF molecule gives a quite special structure, neither of the chair nor boat form, in which the four isobutyl chains are almost perpendicular to each other. Such kind of molecular shape may lead to three dimensionally isotropic molecular packing form. Actually the electrical

Table 2. Posional Parameters and Equivalent Isotropic Thermal Parameters of $TSeC_4$-TTF

Positional parameters (×10**4)and equivalent isotropic temperature factors (HAMILTON, 1959).

	X	Y	Z	B_{eq}(Å**2)
Se1	115(1)	4730(3)	3332(3)	5.0
Se2	−327(1)	8455(3)	2516(3)	4.8
Se3	2188(1)	8526(3)	−3900(3)	6.0
Se4	2667(1)	4954(3)	−2918(3)	4.9
S5	359(3)	7979(7)	175(6)	3.7
S6	1234(3)	7994(7)	−2086(7)	4.3
S7	1602(3)	4960(7)	−1375(7)	4.2
S8	741(3)	4920(6)	861(6)	3.9
C9	830(8)	6457(22)	−83(20)	2.5
C10	1167(8)	6482(22)	−1006(23)	3.2
C11	2050(10)	5968(24)	−2280(19)	3.1
C12	1817(10)	7323(28)	−2645(21)	3.9
C13	169(9)	7220(25)	1649(25)	3.8
C14	337(8)	5885(25)	1984(21)	2.8
C15	246(10)	10096(28)	2987(28)	5.0
C16	895(14)	4049(40)	4140(32)	8.2
C17	3203(13)	4745(27)	−1230(28)	5.7
C18	730(16)	9613(32)	3919(34)	8.4
C19	1258(13)	5144(40)	4571(30)	8.4
C20	2128(11)	10596(29)	−3162(28)	5.8
C21	2554(16)	10670(42)	−2007(30)	9.3
C22	3418(14)	6219(32)	−725(34)	8.1

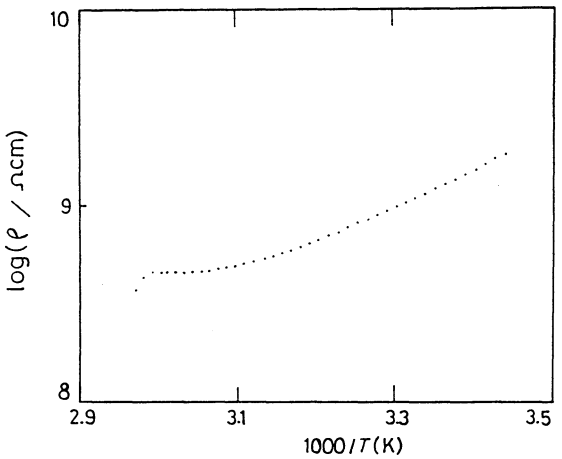
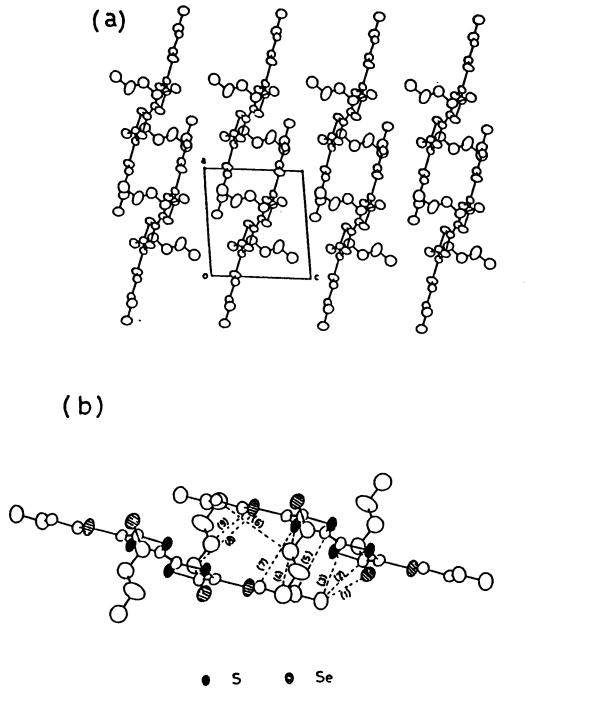


Fig. 4. The temperature dependence of electrical resistivity along the a axis for $TSeC_2$-TTF.

resistivities appear as 2.2×10^{11}, 1.0×10^{11}, and 1.3×10^{11} Ω cm along the a, b, and c axis, respectively, which clearly shows the isotropic character.

Therefore, in $TSeC_n$-TTF system both the physical properties[4] and the molecular packing form have been much influenced by the length of alkyl chains and the chalcogen atoms. The higher resistivity of $TSeC_4$-TTF can be understood with the crystal structure. The shortest Se-Se distance, 4.03 Å, is considerably longer as compared with 3.618(5) Å in $TSeC_2$-TTF and the interplanar distance (4.82 Å) between C_6S_4 parts is also much longer than 3.41 Å in $TSeC_2$-TTF. The quite different physical properties between $TSeC_2$-TTF and $TSeC_4$-TTF can be ascribed to the different molecular



(1) C-Se 3.98(1) (4) C-S 3.844(7) (7) C-S 3.918(7)
(2) C-C 3.80(1) (5) C-C 3.90(1) (8) C-Se 3.947(6)
(3) C-C 3.93(1) (6) C-C 3.95(1) (8) C-Se 3.931(6)

Fig. 5. Crystal structure of $TSeC_4$-TTF projected along the b axis (a), the intermolecular interactions between two molecules along the c axis (b) and the crystal structure of $TSeC_4$-TTF projected along the c axis (c).

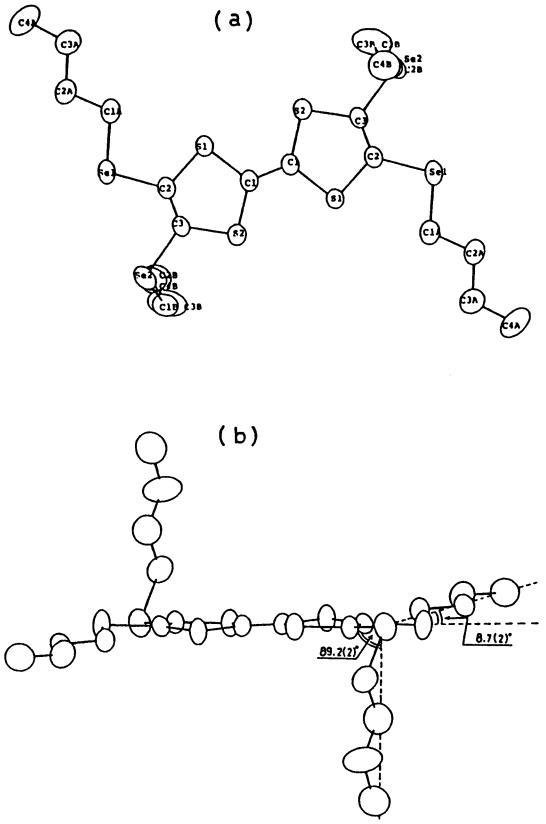


Fig. 6. Molecular structure of $TSeC_4$-TTF (a) and the side view (b). The interatomic distances and angles are shown in Table 3.

Table 3. The Interatomic Distances and Angles in the $TSeC_4$-TTF Compound

Distance (Å)			
C1-C1	1.362(6)	C1-S2	1.753(6)
S2-C3	1.761(6)	C3-C2	1.309(8)
C1-S1	1.757(6)	S1-C2	1.752(6)
C2-Se1	1.905(6)	Se1-C1A	1.944(6)
C1A-C2A	1.516(9)	C2A-C3A	1.52(9)
C3A-C4A	1.52(1)	C3-Se2	1.915(6)
Se2-C1B	1.955(8)	C1B-C2B	1.52(1)
C2B-C3B	1.51(1)	C3B-C4B	1.52(1)
Angle (°)			
S1-C1-S2	114.8(3)	C1-S1-C2	94.8(2)
C1-S2-C3	94.1(2)	S1-C2-C3	117.5(4)
S2-C3-C2	118.5(4)	S2-C3-Se2	116.7(3)
S1-C2-Se1	118.1(3)	C3-C2-Se1	124.4(4)
C2-C3-Se2	124.3(4)	C2-Se1-C1A	100.2(2)
Se1-C1A-C2A	110.1(4)	C1A-C2A-C3A	111.0(5)
C2A-C3A-C4A	113.3(5)	C3-Se2-C1B	98.5(3)
Se2-C1B-C2B	112.5(3)	C1B-C2B-C3B	109.1(7)
C2B-C3B-C4B	112.8(8)		

structure; one is in a boat form, and another is in the form in which each of the four alkyl chains are stretched towards different directions. The molecular structure of $TSeC_2$-TTF is similar to that of TTC_2-TTF,[6] both in boat form, and different from the chair form of $TTeC_2$-TTF.[7] The molecular structure of $TSeC_4$-TTF is not only different from that of TTC_4-TTF,[8] which is in a chair form, but also different from any other of the TYC_n-TTF family. It means that the selenium atoms play an important role to determine their crystal structures. Furthermore, although the intermolecular interactions in a $TSeC_4$-TTF crystal are rather weak just as stated above, it should be noted that they are almost isotropic. The three dimensionally isotropic character is rather unusual in the family of organic semiconductors or conductors, and in the history of developing organic conductors much efforts for increasing the dimensionality have been pursued. In this sense the molecular structure of $TSeC_4$-TTF may give a key to solve this problem, and the preparation of charge transfer complexes based on $TSeC_4$-TTF could give rise to a new type of organic conduc-

tors.

So far, three kinds of molecular structure, chair form, boat form and $TSeC_4$-TTF-like form, have been realized in TYC_n-TTF family. The chair form structure is favorable to decrease the distance between two molecular planes and build up a good conducting path along the stacking axis. The intermolecular overlaps between adjacent π systems are effectively large because there exists a columnar stacking consisting of the conjugated π systems, which can not be found in the crystals which have molecules of other structure forms. The compounds, such as TTC_n-TTF for n=4, 5, 7, 9, 10[6,8,9] and $TTeC_1$-TTF,[7] are in chair form structures and have relatively low resistivities in each own series. On the other hand, the boat form structure usually leads to a large interplane distance, in such compounds as $TSeC_2$-TTF, TTC_1-TTF, and TTC_2-TTF of which crystals have relatively high resistivities. In the case of $TSeC_4$-TTF-like form having rather weak intermolecular interactions, however, it is a good form to obtain a three dimensionally isotropic structure. If we can introduce much stronger intermolecular interactions to this system with keeping its isotropic character, for example, by applying a high pressure, we could obtain a new type of organic semiconductor. In the sense, the $TSeC_4$-TTF-like form has an unique significance.

In summary, we have analyzed the crystal structures of $TSeC_n$-TTF (n=2 and 4), and found out some specific factors to understand their properties. We have measured the electrical properties of both crystals and discussed them in correlation with their crystal structures. We are now proceeding with the preparation of charge-transfer complexes based on $TSeC_2$-TTF and $TSeC_4$-TTF.

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7) Y. Higuchi and N. Yasuoka, private communication, $TTeC_1$-TTF, monoclinic, $P2_1/n$, a=13.769(3), b=5.480(3), c=9.239(5) Å, β=90.49(1)°, chair form; $TTeC_2$-TTF, monoclinic, $P2_1/a$, a=14.017(4), b=9.021(2), c=9.239(5)Å, β= 104.34 (3)°, chair form.

8) C. Nakano, unpublished results, TTC_4-TTF triclinic $P\bar{1}$, a=9.029(7), b=14.658(9), c=5.397(4) Å, α=97.98(5), β=94.05(6), γ=92.63(6)°, chair form; TTC_7-TTF, monoclinic, $P2_1/a$, a=8.797(2), b=46.90(1), c=5.141(1) Å, β=103.89 (2)°, chair form.

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10) Tables of equations of the plane, anisotropic thermal parameters, F_o-F_c, coordinates of hydrogen atoms for the compounds of $TSeC_2$-TTF and $TSeC_4$-TTF, respectively, are deposited as Document No. 8834 at the Office of the Editor of Bull. Chem. Soc. Jpn. The atomic numbering in these Reference Tables ($TSeC_4$-TTF) is corresponding to that in the Fig. 6 of this paper as shown below: This Paper-Reference Table, C1-C6, C2-C5, C3-C7, S1-S4, S2-S3, Se1-Se1, Se2-Se2, C1A-C8, C2A-C9, C3A-C10, C4A-C13, C1B-C11, C2B-C12, C3B-C14, C4B-C15.