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Crystal Structures of TXC$_8$-TTF (X=Se,Te)

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The crystal structures of TSeC$_8$–TTF and TTeC$_8$–TTF were determined by X-ray analysis. The molecules in both compounds have chair-like forms and take columnar structures. The distance between the least-squares planes of the central skeleton along the stacking axis in the TSeC$_8$–TTF crystal is nearly equal to that of the TTeC$_8$–TTF crystal. This result is consistent with the fact that the electrical resistivities for both single crystals are of the same order.

TTC$_n$–TTF (tetrakis(alkylthio)tetrathiafulvalene) compounds are very unique organic semiconductors with low electrical resistivities as single-component compounds.1,2) Long alkyl chains assemble TTC$_n$–TTF molecules in a fashion such that the central π-systems can pile up one after the other very tightly (Molecular Fastener Effect). As a systematic extension of the Fastener Effect, TTeC$_n$–TTFs and TSeC$_n$–TTFs were designed with the aim to increase the intermolecular interactions and dimensionality by replacing the outer S atoms with other chalcogen atoms, such as Se or Te. We have already found that TTeC$_1$–TTF and TSeC$_1$–TTF (low-melting point phase) crystals have tight intercolumnar zigzag chains between chalcogen atoms and reveal rather low resistivities (TTeC$_1$–TTF: 8.1×10^4 Ω cm3) and TSeC$_1$–TTF (low-melting point phase): 1.0×10^6 Ω cm4–5)) along the stacking axis.

In this paper we present the structures of the TSeC$_8$–TTF and TTeC$_8$–TTF crystals and discuss the influence of molecular packing and overlap by replacing the larger chalcogen atoms, compared with those of TTC$_8$–TTF.6)

Experimental

The syntheses of these materials were reported in a preceding paper.4,7) Orange plate-like crystals of TSeC$_8$–TTF were crystallized from a mixed solvent of hexane and benzene, and dark-orange plate-like crystals of TTeC$_8$–TTF were obtained from an acetone solution.

For TSeC$_8$–TTF, crystal data: $C_{38}H_{68}S_4Se_4$, F.W.=969.06, triclinic, space group $P\bar{1}$, a=8.211(5), b=25.45(1), c=5.473(2) Å, α=90.30(4), β=92.70(4), γ=92.50(5)°, V=1142(1) Å^3, Z=1, D_x=1.41 g cm^{-3}, and μ(Mo $K\alpha$)=33.79 cm^{-1}, crystal size: $0.2\times0.02\times0.3$ mm^3. Intensity data were measured by the θ–2θ scan technique on a Rigaku AFC-5 four-circle diffractometer with graphite monochromatized Mo $K\alpha$ radiation. A total of 4507 reflections ($2\theta<50°$) were measured and corrected by a Gaussian Integration procedure for absorption effects. (The intensities of standard reflections ($50°<2\theta<60°$) were gradually decreased (total decrease was 14%). The crystal may be damaged by the X-ray radiation.) The crystal structure was solved by the direct method (MULTAN 78 program system8)) and refined by the block-diagonal least-squares procedure using 1145 independent reflections ($|F_o|>3\sigma(|F_o|)$). The final R=0.073, R_w=0.071 $\{w=[\sigma(F_o)^2+(0.015\,F_o)^2]^{-1}\}$ and $(\Delta/\sigma)_{max}$=0.69. The residual in the final difference Fourier synthesis were $\Delta\rho_{max}$=1.2 e Å^{-3} and $\Delta\rho_{min}$=−0.5 e Å^{-3}.

For TTeC$_8$–TTF, crystal data: $C_{38}H_{68}S_4Te_4$, F.W.=1163.62, triclinic, space group $P\bar{1}$, a=9.143(6), b=23.25(2), c=5.734(7) Å, α=92.30(8), β=97.76(9), γ=90.04(6)°, V=1207(15) Å^3, Z=1, D_x=1.60 g cm^{-3} and μ(Mo $K\alpha$)=25.88 cm^{-1}, crystal size: $0.1\times0.1\times0.4$ mm^3. 7640 reflections were measured on an Enraf–Nonius CAD4 diffratometer with graphite-monochromatized Mo$K\alpha$ radiation ($2\theta<60°$) by the ω–2θ scan technique. The structure was solved by the Patterson method and refined by the block-diagonal least-squares procedure by using 1656 independent reflections ($|F_o|>3\sigma(|F_o|)$). Since the intensities of standard reflections were gradually decreased (the total decrease was 28.7%) during the measurement, the R value was 0.110 and R_w was 0.129 in spite of the decay correction. The weighting scheme was $\{w=[\sigma(F_o)^2+(0.015F_o)^2]^{-1}\}$. Anisotropic thermal parameters were adopted for all non-hydrogen atoms, and hydrogen atoms were refined isotropically. (The structures have not been resolved for possible disorder of the terminal octyl chains.) The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.9) The calculations were carried out on a HITAC M-680H computer with the UNICSIII program system10) (for TSeC$_8$–TTF and TTeC$_8$–TTF) and a Micro VAX II computer with the SDP software package11) (for TTeC$_8$–TTF).

Results and Discussion

TSeC$_8$–TTF: The final atomic parameters are listed in Table 1.12) The molecule is centrosymmetric and has a chair-like form to make a columnar structure. Although the four octyl chains are bent to the central $C_6S_4Se_4$ skeletons (Fig. 1 (a)), the angle between the zigzag plane of the alkyl chain and the central plane is closer to 90° {chain A (C(1A)—C(8A)): 92.6°, chain B (C(1B)—C(8B)): 102.4°} than those in TTC$_8$–TTF.6) Although the octyl chains elongate to approximately the same direction, the C⋯C zigzag planes of the two neighboring octyl chains in a molecule (chain A and chain B) have an angle of 97°. The shortest intercolumnar C⋯C distance between the octyl chains is 3.84(4) Å and shorter than that of TTC$_8$–TTF (Form I).6) The octyl

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Table 1. Positional Parameters (×10⁴) and Equivalent Isotropic Thermal Parameters of the TSeC8–TTF

Atom	x	y	z	$B_{eq}{}^{a)}/\text{Å}^2$
Se(1)	−1144(3)	1253(1)	6838(4)	4.7
Se(2)	−4762(2)	726(1)	4131(4)	4.1
S(1)	552(6)	538(2)	3071(9)	3.9
S(2)	−2548(6)	87(2)	928(9)	4.0
C(1)	−409(20)	134(8)	843(31)	3.8
C(2)	−1254(21)	789(8)	4214(31)	4.0
C(3)	−2642(21)	522(8)	3236(31)	4.1
C(1A)	979(26)	1575(8)	6641(40)	5.9
C(2A)	1416(30)	1896(11)	4626(46)	8.5
C(3A)	804(32)	2401(10)	4714(43)	8.5
C(4A)	1396(32)	2749(10)	2711(50)	8.9
C(5A)	969(38)	3252(12)	2807(47)	10.9
C(6A)	1628(39)	3614(12)	809(56)	12.1
C(7A)	1391(50)	4163(16)	979(65)	16.9
C(8A)	2094(52)	4549(14)	−794(69)	18.7
C(1B)	−5240(22)	1200(8)	1354(31)	4.2
C(2B)	−4262(21)	1713(8)	1521(31)	3.7
C(3B)	−4695(23)	2059(8)	−655(35)	4.7
C(4B)	−3678(26)	2561(9)	−682(37)	6.0
C(5B)	−4181(31)	2926(9)	−2698(45)	7.5
C(6B)	−3232(36)	3433(11)	−2567(48)	10.0
C(7B)	−3870(43)	3778(12)	−4595(65)	13.9
C(8B)	−3127(51)	4310(18)	−4554(79)	20.0

a) $B_{eq}=\frac{4}{3}(\sum_i\sum_j B_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j)$.

chain directions, however, are not as parallel as are those in TTC8–TTF (Form I). The molecules stack uniformly along the c-axis (Fig. 1(b)). The overlapping mode (Fig. 1(c)) is similar to that of TTC8–TTF(especially Form II).[6] The terminal $C_2S_2Se_2$ part is slightly twisted from the central C_2S_4 part and the dihedral angle between the central C_2S_4 plane and the terminal $C_2S_2Se_2$ plane is 5.2(1)° (Fig. 1(d)) because of the large atomic radius of Se atom, compared with those of S and C atoms. The shortest intracolumnar intermolecular distances of S···S and Se···S are 3.586(9) Å and 3.891(7) Å, respectively. There is no shorter Se···Se contact within a column than 4 Å. The distance between the two least-squares planes of the central $C_6S_4Se_4$ skeletons along the stacking axis is 3.57 Å. Although the distance is longer than that of TTC8–TTF (3.43 and 3.50 Å for Form I at 0 °C and Form II at room temperature, respectively) because the Se atoms have a large atomic radius, it is significantly shorter than the sum of their van der Waals radii. In addition, there is intercolumnar Se···Se contact along the [101] direction (3.830(4) Å), which is shorter than twice the van der Waals radii (4.00 Å) (Fig. 1(c)).

TTeC8–TTF: The atomic parameters are listed in Table 2.[12] The molecular structure is a chair-like form, similar to that of TSeC8–TTF (Fig. 2(a)). The

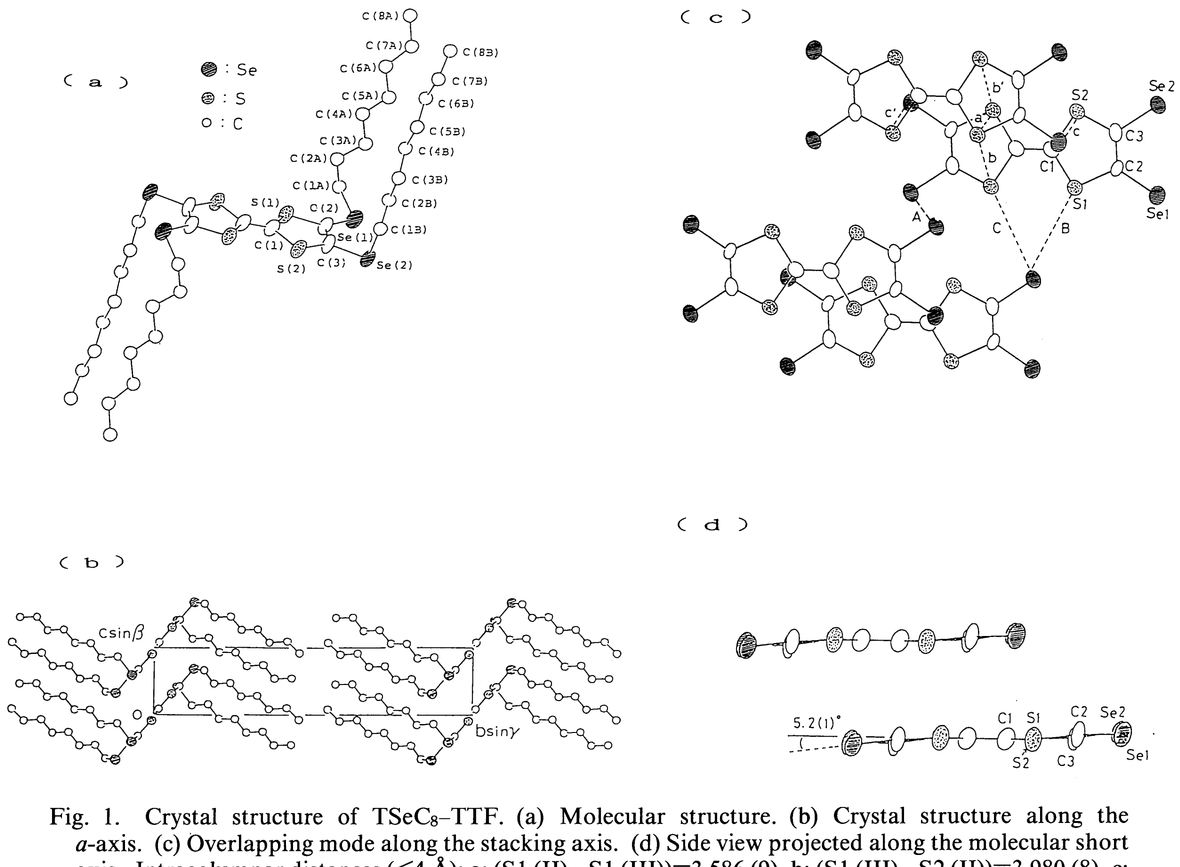

Fig. 1. Crystal structure of TSeC8–TTF. (a) Molecular structure. (b) Crystal structure along the a-axis. (c) Overlapping mode along the stacking axis. (d) Side view projected along the molecular short axis. Intracolumnar distances (<4 Å): a: (S1 (II)···S1 (III))=3.586 (9), b: (S1 (III)···S2 (II))=3.980 (8), c: (Se1 (III)···S2 (I))=3.891(7) Å. Intercolumnar distances (<4 Å): A: (Se2 (II)···Se2 (V))=3.830 (4), B: (Se2 (VI)···S1 (I))=3.870 (6), C: (Se2 (VI)···S2 (II))=3.973 (6) Å. Symmetry operations: I (x,y,z), II ($-x,-y,-z$), III ($x,y,1+z$), IV ($-x,-y,1-z$), V ($1+x,y,1+z$), VI ($1+x,y,z$).

Table 2. Positional Parameters (×10^4) and Equivalent Isotropic Thermal Parameters of the TTeC$_8$–TTF

Atom	x	y	z	$B_{eq}$$^{a)}$/Å^2
Te(1)	4077(3)	733(1)	6784(5)	5.2
Te(2)	291(3)	1403(2)	7353(5)	5.6
S(1)	2194(9)	122(5)	2064(16)	4.1
S(2)	−691(9)	589(5)	2705(17)	4.5
C(1)	307(33)	141(16)	1016(51)	3.1
C(2)	2092(32)	600(19)	4427(61)	4.7
C(3)	809(37)	823(19)	4735(61)	4.6
C(1A)	5402(36)	1003(18)	4241(63)	4.2
C(2A)	4874(37)	1528(18)	3151(62)	4.4
C(3A)	5938(47)	1793(22)	1635(75)	6.8
C(4A)	5401(47)	2304(19)	251(76)	6.1
C(5A)	6712(58)	2587(25)	−1159(89)	8.7
C(6A)	6065(58)	3124(26)	−2351(100)	9.8
C(7A)	7192(65)	3333(29)	−3697(113)	11.9
C(8A)	6823(89)	3829(37)	−4976(146)	16.2
C(1B)	926(94)	2149(38)	5608(129)	17.1
C(2B)	739(82)	2371(28)	3714(109)	13.8
C(3B)	1130(85)	2988(32)	3146(99)	14.0
C(4B)	1256(108)	3182(40)	1316(188)	20.8
C(5B)	1973(79)	3819(29)	1161(118)	12.8
C(6B)	1232(116)	4136(44)	−337(203)	24.5
C(7B)	1954(90)	4597(42)	−1614(184)	21.6
C(8B)	3150(112)	4848(48)	−647(191)	25.3

a) $B_{eq}=\frac{4}{3}(\sum_i\sum_j B_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j)$.

four octyl chains elongate nearly perpendicular to the central skeleton; their zigzag mode is not uniform. The least-squares plane of the C···C zigzag (chain A: C(1A)—C(8A)) makes an angle of ca. 90° with the neighboring C···C plane (chain B: C(1B)—C(8B)), as can be seen in TSeC$_8$–TTF. The molecules stack uniformly along the c-axis (Fig. 2(b)). The distance between the two least-squares planes of the C$_6$S$_4$Te$_4$ skeletons along the stacking axis is 3.56 Å, approximately the same as that of TSeC$_8$–TTF. It may be caused by the fact that the mode of intracolumnar interatomic overlap and contacts are different from those of TSeC$_8$–TTF and TTC$_8$–TTF[6] (Fig. 2(c)) due to a steric repulsion between large Te atoms. The shortest intracolumnar Te···S and Te···C distances are 3.87(1) and 3.80(4) Å, respectively. The S···S and Te···Te distances, however, are rather longer than the sum of van der Waals radii. The terminal parts of the central skeleton are slightly twisted, like that of TSeC$_8$–TTF, and the dihedral angle between the central C$_2$S$_4$ plane and the terminal C$_2$S$_2$Te$_2$ plane is 2.9(2)°. Between the columns there is Te···S contact (3.94(1) Å), which is nearly equal to the sum of the van der Waals radii. The shortest intercolumnar Te···Te distance is 4.362(6) Å along the [101] direction which may not be a strong interaction.

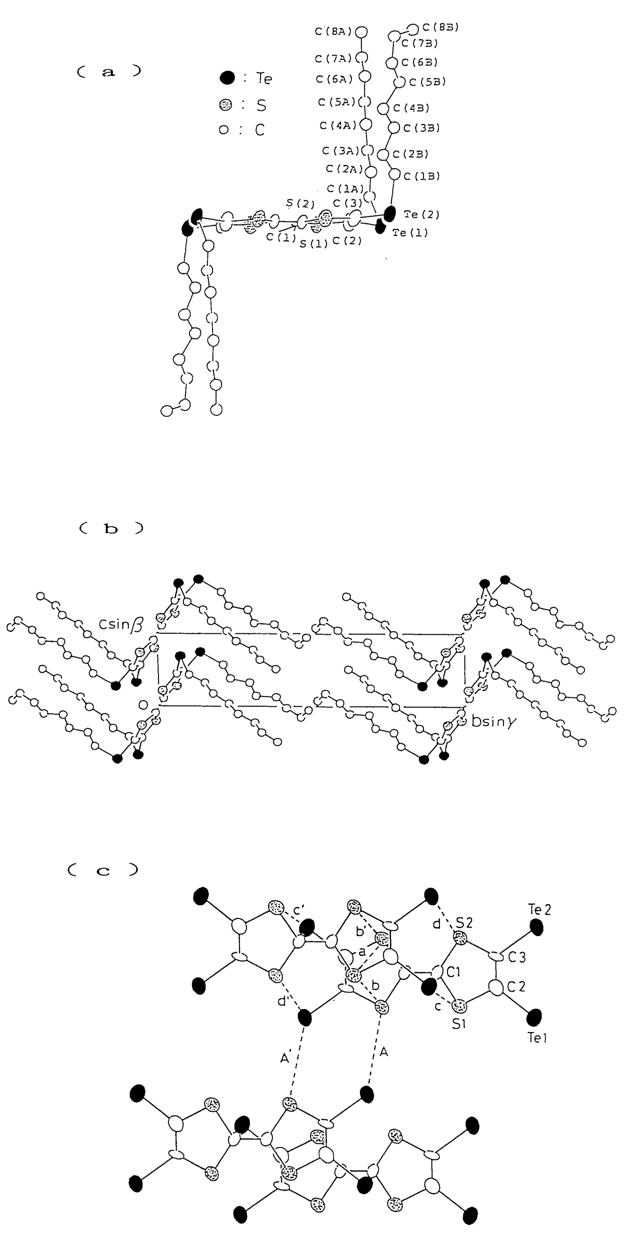

Fig. 2. Crystal structure of TTeC$_8$–TTF. (a) molecular structure. (b) Crystal structure along the a-axis. (c) Overlapping mode along the stacking axis. Intracolumnar distances (<4 Å): a: (S1(II)···S1(III)) =3.97(2), b: (S2(II)···S1(III)=3.90(2), c: (Te1(III)···S1(I))=3.87(1), d: (Te2(III)···S2(I))=3.98(1) Å. Intercolumnar distances (<4 Å): A: (Te2(IV)···S2(II))=3.94(1) Å. Symmetry operations: I (x,y,z), II ($-x$,$-y$,$-z$), III (x,y, 1+z), IV (1+x,y, 1+z).

In summary, long alkyl chains tend to pack like alkanes, since the chair-like form of the molecule is very effective to produce dense packing for alkyl chains in the crystal. In this packing, however, the chalcogen atoms cannot have strong intercolumnar contact in the direction of the molecular long axis, compared with TTeC$_1$–TTF and TSeC$_1$–TTF (L-phase). In the case of TSeC$_8$–TTF and TTeC$_8$–TTF, the molecules have chair-like shapes and the chalcogen atoms have intercolumnar interactions only nearly along the molecular short axis. Furthermore, although the octyl chains in both crystals are not very parallel to each other, compared with those of TTC$_8$–TTF (Form I), long octyl chains can have intermolecular interactions with van der Waals contacts.

These attractive forces can decrease the distance between the central π-electron systems along the stacking axis. In the case of $TSeC_8$–TTF and $TTeC_8$–TTF, although the interplanar distances along the stacking axis are a little larger than those of TTC_8–TTF crystals (Form I and Form II), they are significantly shorter than the sum of van der Waals radii of the chalcogen atoms and the Fastener Effect is thus effective in these crystals. The distance between the central least-squares planes in the $TTeC_8$–TTF crystal is almost equal to that in the $TSeC_8$–TTF crystal, in spite of including larger Te atoms, since the $C_6S_4Te_4$ skeletons overlap in a slightly different way in order to avoid the other chalcogen atoms (Te, S). This fact is consistent with the observed results that the electrical resistivity of the $TTeC_8$–TTF crystal (1.7×10^6 Ω cm) is nearly equal to that of the $TSeC_8$–TTF crystal (7.5×10^5 Ω cm).

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