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Crystal Structures and Molecular Packing of Tetrakis(alkylthio)-tetrathiafulvalene (TTC$_n$-TTF); Part I (n=3,4,6)

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The crystal structures of tetrakis(alkylthio)tetrathiafulvalene TTC$_n$–TTF (n=3, 4, 6) were determined by X-ray analysis. The structures of TTC$_n$–TTF drastically changed between n=3 and 4. The TTC$_3$–TTF molecule has a boat-like shape, like that of TTC$_1$–TTF and TTC$_2$–TTF. On the other hand, the TTC$_4$–TTF and TTC$_6$–TTF molecules have chair-like shapes, like that of TTC$_5$–TTF, and columnar structures with intermolecular effective overlaps between the central π-systems. These results can explain the drastic change in the electrical properties between n=3 and 4.

Studies concerning organic conductors have recently progressed, not only regarding charge-transfer complexes, but also regarding one-component organic materials. Tetrakis(alkylthio)tetrathiafulvalenes (abbreviated as TTC$_n$–TTFs), which have a central tetrathio-TTF(C$_6$S$_8$) π-system and a side alkyl chain system, were synthesized; their physical properties have been widely investigated as unique single-component organic semiconductors. Though such properties as the absorption spectra and redox potentials of a molecule in solution were independent on the carbon number (n) of the alkyl chain, the electrical and thermal properties of molecular assemblies in the solid state obviously changed, depending on n.[1,2] In particular, the compounds with small n ($1 \leqq n \leqq 3$) showed high resistivities (ca. 10^{10} Ω cm), while those with large n showed remarkably low resistivities ($4 \leqq n \leqq 9$: ca. 10^7 Ω cm, $n \geqq 10$: ca. $10^5 \Omega$ cm).[3] Thus, the intermolecular interactions between the alkyl groups of long-chain compounds must play an important role in the generation of high electrical conduction.

In this paper we report on the results concerning the crystal structures of short-chain compounds of TTC$_n$–TTF (n=3, 4, 6), and discuss changes in the electrical resistivity between n=3 and 4.

Experimental

The synthetic procedures of TTC$_n$–TTF compounds (n=1—18) were reported in a previous paper.[4,5] Single crystals of TTC$_n$–TTF (n=3, 4, 6) were prepared by recrystallization from mixed solvents of hexane and ethanol. Yellow plates for n=3 and orange needles for n=4, 6 were obtained. Crystal data and details concerning the experiments are given in Table 1. Intensity data for n=4, 6 were collected at 24 and 0 °C, since these melting points are close to room temperature (n=4: 24.6 °C, n=6: 28.6 °C).[6] Especially, in the case of n=4, although the intensity variation of monitored reflections was ca. 4%, the reflection intensities are rather weak in the range of high angles (40 °<2θ<60 °)) at room temperature. For the other crystals, the intensity variation of standard reflections was less than 5%. The reflections were collected by a Gaussian Integration procedure for absorption effects. The crystal structures were solved by the Patterson method (for n=4) and the direct method (MULTAN 82 program system[7]) (for n=3 and 6), and were refined by a block-diagonal least-sqaures procedure $\{w=[\sigma(F_o)^2+(0.015\,F_o)^2]^{-1}\}$. The H-atom positions of TTC$_4$–TTF and TTC$_6$–TTF measured at 24 °C were calculated, and those of the other crystals were derived from difference Fourier maps. Anisotropic thermal parameters were adopted for all non-hydrogen atoms; the hydrogen atoms were refined isotropically. The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[8] The calculations were carried out on a HITAC M-680H computer using ther UNICS III program system[9] (for n=4) and a MicroVAX II computer with the Enraf-Nonius SDP programs[10] (for n=3 and 6).

Results

TTC$_3$-TTF: The final atomic coordinates and thermal temperature factors are listed in Table 2.[11] The molecular structure is a boat-like form (Fig. 1(a)). The two propyl groups attached to S(5) and S(6) elongate nearly perpendicular to the central C$_6$S$_8$ group. The other propyl groups attached to S(7) and S(8) are almost parallel to the C$_6$S$_8$ group. The central skeleton is non-planar, and the tilt angles are 35.89(3)° and 37.69(3)° (Fig. 1(b)).

There are several intermolecular S···S contacts between two molecules related to the inversion center in this crystal (Fig. 2). The shortest S···S distance is 3.775(1)Å, which is the nearly same as twice the van der Waals radius. In the other directions the molecule has many van der Waals contacts between the C atoms of the propyl chains. The distance between the central C$_6$S$_8$ groups along the c-axis is greater than 5Å, since the two propyl chains is a molecule elongate nearly perpendicular to the central skeleton.

TTC$_4$-TTF: The atomic coordinates and thermal

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Table 1. Crystal Data

	TTC$_3$–TTF	TTC$_4$–TTF		TTC$_6$–TTF	
	$C_{18}H_{28}S_8$	$C_{22}H_{36}S_8$		$C_{30}H_{52}S_8$	
F. W.	500.94	557.04		669.25	
Temperature/K	297	297	273	297	273
Crystal size/mm^3	(0.3×0.1×0.4)	(0.3×0.1×0.4)	(0.2×0.03×0.3)	(0.1×0.03×0.6)	(0.1×0.03×0.4)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	12.136(1)	9.029(7)	9.021(1)	18.47(1)	18.431(3)
b/Å	13.156(1)	14.658(9)	14.575(1)	18.516(8)	18.458(4)
c/Å	7.942(1)	5.397(4)	5.389(1)	5.498(4)	5.475(2)
α/°	101.77(1)	97.98(5)	98.22(1)	98.55(5)	98.50(2)
β/°	98.15(1)	94.05(6)	94.27(2)	89.98(6)	89.98(2)
γ/°	94.29(1)	92.63(6)	92.27(1)	93.28(4)	93.66(1)
V/Å^3	1222(3)	704.1(9)	698(2)	1856(16)	1838(6)
Z	2	1	1	2	2
d_{cal}/g cm^{-3}	1.362	1.314	1.324	1.198	1.210
X-Ray	Cu $K\alpha$	Mo $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
μ(X-ray)/cm^{-1}	67.02	6.188	59.16	45.23	45.67
Scan mode	ω–2θ	θ–2θ	ω–2θ	ω–2θ	ω–2θ
$2\theta_{max}$/°	120	40	120	120	120
Diffractometer	Enraf–Nonius CAD4	Rigaku AFC-5	Enraf–Nonius CAD4	Enraf–Nonius CAD4	Enraf–Nonius CAD4
Reflections measured	3866	1806	2328	6100	5450
Reflections used ($\lvert F_o\rvert>3\sigma(\lvert F_o\rvert)$)	3179	518	1933	3672	3302
R	0.037	0.038	0.048	0.063	0.062
R_w	0.053	0.049	0.066	0.080	0.073
$(\Delta/\sigma)_{max}$	0.51	0.44	0.78	0.78	0.98
Residual density/eÅ^{-3}	0.3 to −0.2	0.2 to −0.3	0.5 to −0.4	0.6 to −0.3	0.7 to −0.3

Table 2. Positional Parameters (×10^4) and Equivalent Isotropic Thermal Parameters of TTC$_3$–TTF

Atom	x	y	z	B_{eq}/Å^2
S(1)	3321(1)	2428(1)	3041(1)	4.8
S(2)	1979(1)	−850(1)	1019(1)	4.8
S(3)	4200(1)	198(1)	2714(1)	4.7
S(4)	1038(1)	1501(1)	1479(1)	5.0
S(5)	274(1)	3564(1)	1012(2)	6.0
S(6)	2964(1)	−2910(1)	−197(1)	4.8
S(7)	5345(1)	−1746(1)	1713(2)	6.0
S(8)	2887(1)	4575(1)	2517(1)	5.6
C(1)	2431(3)	1284(3)	2089(5)	4.2
C(2)	2804(3)	335(3)	1930(5)	4.2
C(3)	3134(3)	−1582(2)	794(5)	4.0
C(4)	4141(3)	−1103(2)	1571(4)	4.0
C(5)	2419(3)	3256(3)	2210(5)	4.4
C(6)	1370(3)	2835(3)	1517(5)	4.6
C(7)	2409(3)	−2860(3)	−2450(5)	5.2
C(8)	3316(3)	−2439(3)	−3299(6)	6.2
C(9)	2933(4)	−2357(4)	−5144(6)	7.5
C(10)	6479(3)	−716(3)	2424(5)	5.0
C(11)	7547(3)	−1188(3)	2776(6)	5.9
C(12)	8540(3)	−385(4)	3503(7)	7.6
C(13)	4371(3)	4531(3)	2436(5)	5.1
C(14)	4921(3)	5611(3)	2529(5)	5.4
C(15)	6154(3)	5621(3)	2519(6)	6.0
C(16)	10(3)	3269(4)	−1315(6)	6.6
C(17)	899(4)	3748(4)	−2140(6)	6.8
C(18)	609(5)	3596(6)	−4052(8)	10.1

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

temperature factors at 0 °C are listed in Table 3.[11] The molecular structure is a chair-like form, and is centrosymmetric (Fig. 3(a) and 3(b)). One zigzag chain of the butyl group elongates almost perpendicularly, while the other chain is slightly bent. The crystal structure is very similar to that of TTC$_5$–TTF.[3] The molecules are stacked so as to make a columnar structure along the c-axis (Fig. 3(b)) with an overlapping mode (Fig. 3(c)). The central

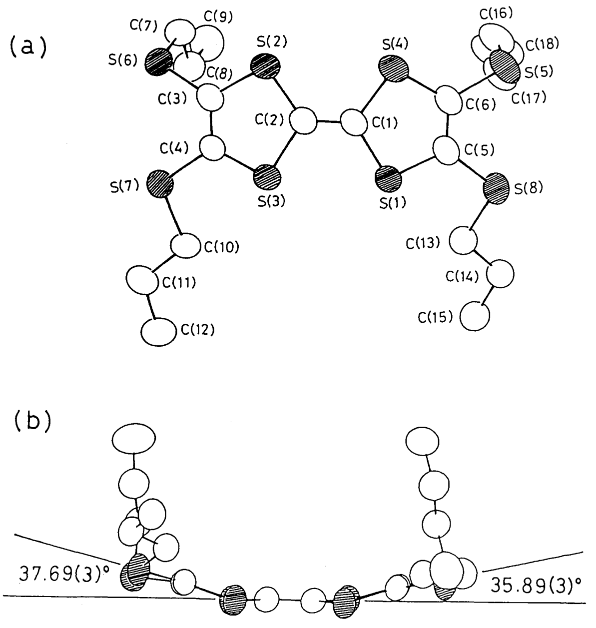

Fig. 1. Molecular structure of TTC$_3$–TTF (a) and side view (b).

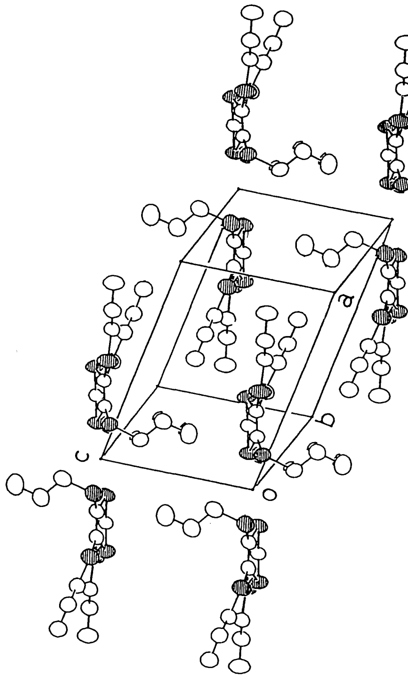

Fig. 2. Crystal structure of TTC$_3$-TTF.

Table 3. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Temperature Factors of TTC$_4$-TTF (0 °C)

Atom	*x*	*y*	*z*	B_{eq}/Å^2
S(1)	2301(1)	125(1)	1688(2)	3.0
S(2)	−452(1)	965(1)	3324(2)	2.8
S(3)	4186(1)	1161(1)	6136(2)	3.4
S(4)	1120(1)	2141(1)	7873(2)	3.4
C(1)	387(4)	227(2)	1015(7)	2.5
C(2)	2472(4)	976(3)	4380(7)	2.7
C(3)	1212(4)	1361(2)	5108(6)	2.6
C(4)	5433(4)	1430(3)	3810(8)	3.8
C(5)	5149(5)	2370(3)	2867(8)	3.9
C(6)	6360(5)	2625(3)	1213(9)	4.5
C(7)	6067(7)	3497(4)	156(11)	6.6
C(8)	−76(5)	2997(3)	6774(8)	3.9
C(9)	497(6)	3478(3)	4702(8)	4.5
C(10)	1894(7)	4081(4)	5473(10)	5.8
C(11)	2423(8)	4544(4)	3347(12)	7.5

C_6S_8 group is coplaner; the distance between the least-squares planes of the adjacent C_6S_8 skeletons along the stacking axis is 3.62Å (at 24 °C) and 3.60Å (at 0 °C), respectively. The shortest intracolumnar S⋯S contact is 3.659(5)Å (at 24 °C) and 3.641(1)Å (at 0 °C), respectively (Fig. 4(c)). This value is slightly shorter than twice the van der Waals radius (3.7Å). The intercolumnar S⋯S distances along the [101] direction (the S⋯S distance is 3.834(6)Å (at 24 °C) and 3.819(2)Å (at 0 °C), respectively) are longer than the intracolumnar distance. The molecules have some intra- and intercolumnar interchain interactions (the shortest C⋯C distance is 4.09(2)Å) (Fig. 4).

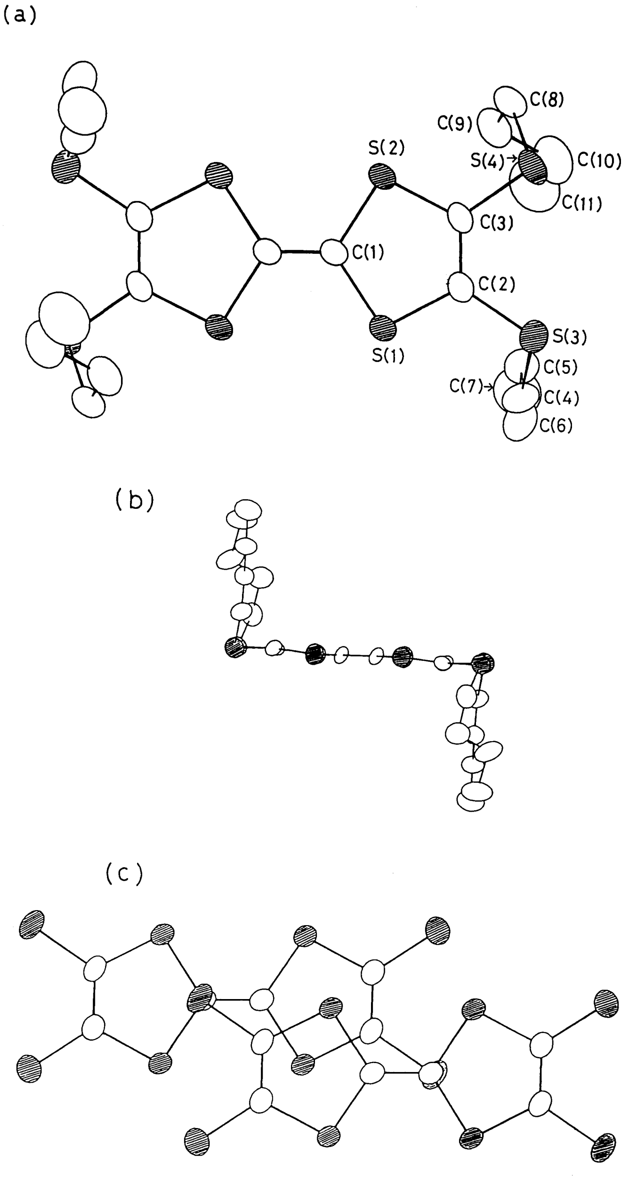

Fig. 3. Molecular structure of TTC$_4$-TTF (a), side view (b), and mode of overlap along the stacking axis (c) (0 °C).

TTC$_6$-TTF: The final atomic parameters at 0 °C are listed in Table 4.[11] There are two independent molecules (A and B) in the crystals, each of which has a crystallographic center of inversion (at (0, 0, 0) and (1/2, 0, 1/2)). Both molecules have a similar chair-like form. For each molecule, the central C_6S_8 skeleton is planer. One hexyl zigzag chain is nearly perpendicular to the central skeleton, while the other chain is slightly bent (Fig. 5(a) and 5(b)). These two molecules (A and B) form two kinds of columns (A and B, respectively) in the crystal. The overlapping modes are almost the same as in both columns (Fig. 5(c)). The distance between the least-squares planes of the adjacent C_6S_8 skeletons along the stacking axis in column A is the same as that in column B (3.59Å at 24 °C and 3.57Å at 0 °C), and is much

Table 4. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Temperature Factors of TTC$_6$–TTF (0 °C). The Atoms with A are in Column A and the Atoms with B are in Column B

Atom	x	y	z	$B_{eq}/Å^2$	Atom	x	y	z	$B_{eq}/Å^2$
S(1A)	279(1)	778(1)	−2566(4)	5.0	C(12A)	−2964(5)	1988(6)	1825(16)	4.9
S(2A)	−1124(1)	108(1)	−1139(5)	5.0	C(13A)	−2734(6)	2671(6)	3684(17)	5.6
S(3A)	−390(2)	1701(2)	−5860(5)	6.3	C(14A)	−3340(6)	2885(8)	5541(20)	7.2
S(4A)	−1991(1)	903(1)	−4432(4)	5.5	C(15A)	−3099(8)	3543(8)	7450(23)	8.2
S(1B)	5279(1)	777(1)	8346(4)	4.9	C(1B)	4827(4)	191(5)	5932(14)	3.5
S(2B)	3877(1)	108(1)	6248(4)	5.0	C(2B)	4485(5)	1070(5)	9841(16)	3.9
S(3B)	4610(2)	1702(2)	12565(5)	6.3	C(3B)	3851(5)	762(5)	8922(16)	3.9
S(4B)	3009(1)	903(1)	10331(4)	5.5	C(4B)	4917(8)	2531(7)	11203(27)	8.7
C(1A)	−170(4)	182(5)	−748(13)	3.5	C(5B)	4392(8)	2812(7)	9841(25)	8.7
C(2A)	−514(5)	1072(5)	−3773(14)	4.0	C(6B)	4662(9)	3525(8)	8864(27)	9.1
C(3A)	−1156(5)	761(5)	−3144(14)	4.0	C(7B)	4069(10)	3836(10)	7701(32)	11.6
C(4A)	−77(8)	2532(7)	−3679(26)	8.4	C(8B)	4199(15)	4532(12)	7059(46)	18.8
C(5A)	−609(8)	2817(7)	−2006(23)	8.8	C(9B)	3685(17)	4849(15)	6034(53)	23.3
C(6A)	−322(9)	3517(8)	−363(25)	9.1	C(10B)	2421(5)	1076(5)	7816(17)	4.5
C(7A)	−935(10)	3843(9)	1139(29)	11.0	C(11B)	2651(5)	1786(5)	6801(16)	4.4
C(8A)	−766(14)	4535(11)	2507(42)	17.8	C(12B)	2044(5)	1988(6)	5175(17)	4.8
C(9A)	−1343(17)	4851(15)	3808(51)	24.0	C(13B)	2268(5)	2670(6)	3987(17)	5.4
C(10A)	−2582(5)	1080(5)	−1758(16)	4.5	C(14B)	1163(6)	2983(8)	2371(23)	7.2
C(11A)	−2350(5)	1788(5)	−14(15)	4.4	C(15B)	1897(8)	3546(8)	1097(24)	8.6

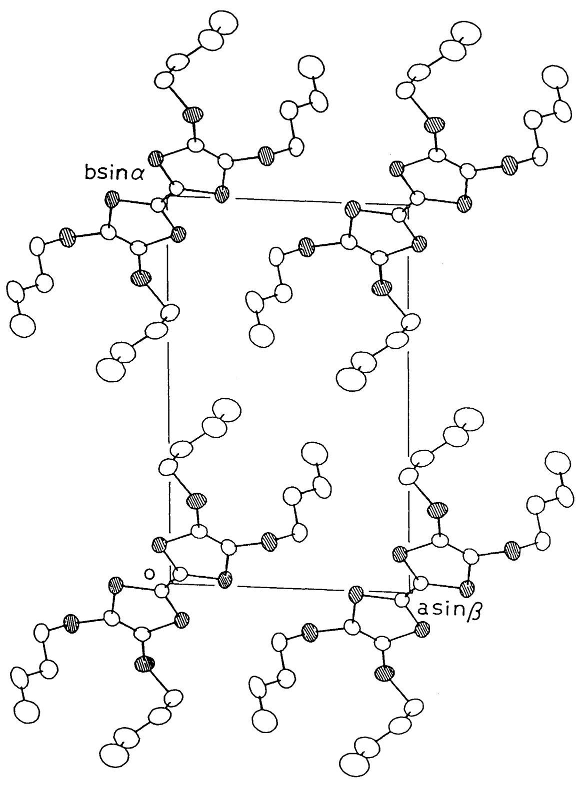

Fig. 4. Crystal structure of TTC$_4$–TTF (0 °C).

shorter than that of TTC$_5$–TTF (3.73Å).[3] The dihedral angle between the two central skeletons of the two adjacent columns is 81.6° (at 24 °C). The shortest intracolumnar S···S distance along the c-axis (3.731(3)Å at 24 °C and 3.710(3)Å at 0 °C) is nearly the same as twice the van der Waals radius. The intercolumnar S···S distances, however, are rather long (the shortest distances: 3.914(3)Å at 24 °C and 3.893(3)Å at 0 °C) compared with the intracolumnar contacts. Moreover, although a molecule has several intracolumnar interchain contacts (the shortest C···C distances: 3.94(1)Å at 24 °C and 3.91(1)Å at 0 °C) with the neighboring molecule, it has few intercolumnar C···C contacts of the alkyl chains (ths shortest distances: 3.93(3)Å at 24 °C and 0 °C) (Fig. 6).

Discussion

In the TTC$_3$–TTF crystal, the molecules have a boat-like structure, like in the TTC$_1$–TTF[12] and TTC$_2$–TTF[2] crystals. In the TTC$_1$–TTF crystal, the molecules have consecutive S···S contacts almost all along the molecular long axis (the shortest S···S distance is 3.478Å). Along the molecular short axis, however, the adjacent central skeletons are arranged almost perpendicularly to each other, and do not have short S···S distances.[13] In the TTC$_2$–TTF crystal, even though the molecules have short S···S contacts within a dimer (the shortest S···S distance is 3.552Å), the interdimer intermolecular S···S distances are nearly the same as twice the van der Waals radius.[2] In the TTC$_3$–TTF crystal, the two propyl chains in a molecule are largely bent, and the molecules mainly have C···C van der Waals contacts between the chains. Thus, in these boat-like structures, the extension of the overlaps of the central π-electron system is interrupted in terms of the alkyl groups.

On the other hand, the TTC$_4$–TTF and TTC$_6$–TTF molecules have chair-like shapes, and are similar to TTC$_5$–TTF. In both crystals, the alkyl chains elongate nearly perpendicular to the central C_6S_8 planes; the zigzag mode is not uniform (the Form III structure), compared with Form I and Form II of TTC$_8$–TTF.[14] Although the molecules have several intracolumnar C···C

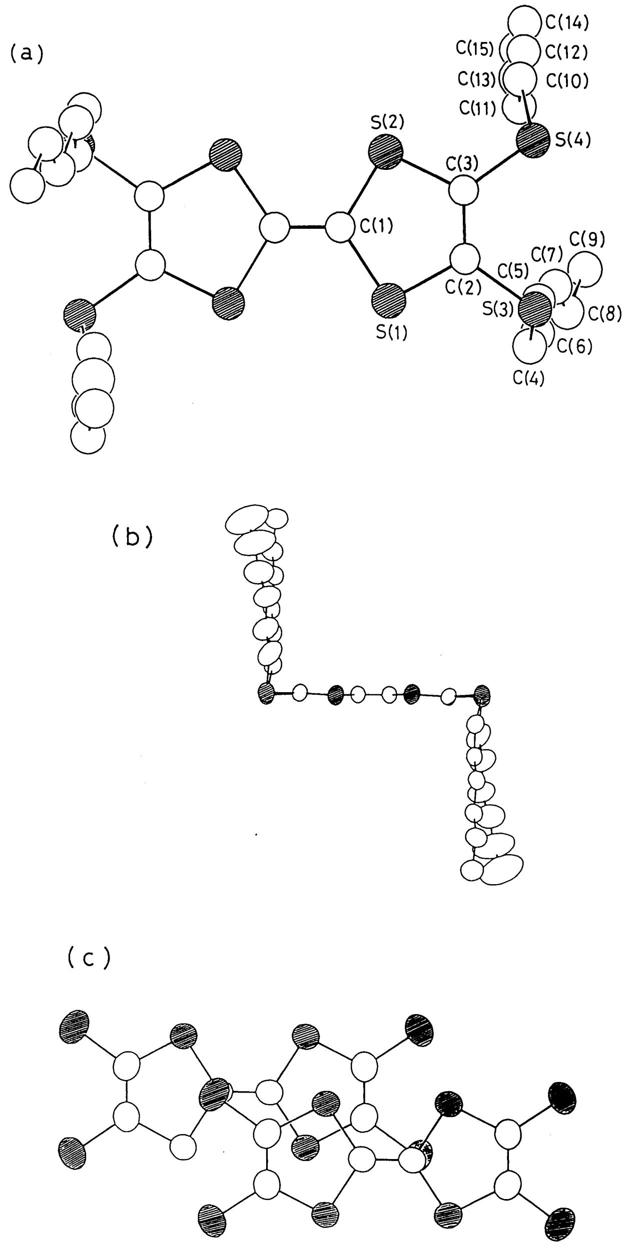

Fig. 5. Molecular structure of TTC$_6$–TTF (a), side view (b), and mode of overlap along the stacking axis (c) (0 °C).

contacts between their alkyl chains, they do not have many intercolumnar interchain contacts. On the other hand, in the TTC$_5$–TTF crystal, the molecules do not have any short intercolumnar S$\cdots$S contacts ($<$4Å), since the two alkyl chains in a molecule are slightly far from the perpendicular, and the chains interrupt the neighboring central skeletons to be close to each other along the molecular short axis. The distances between the least-squares C$_6$S$_8$ planes along the stacking axis are significantly shorter than the sum of van der Waals radii. In the TTC$_5$–TTF crystal, the interplanar distance is slightly longer than those in the TTC$_4$–TTF and TTC$_6$–TTF crystals, since the zigzag mode of the alkyl chains is rather irregular, and the van der Waals interactions between the neighboring chains seem to be weak. Moreover, the TTC$_6$–TTF molecule has a few intercolumnar interchain contacts, in spite of their longer alkyl chains, in comparison with those of the TTC$_4$–TTF and TTC$_5$–TTF molecules; this is because there are two kinds of columns and the molecules in these two columns make an angle of 81.6° in this crystal. Thus, in the TTC$_6$–TTF crystal, the shorter interplaner distance along the stacking axis may be mainly caused by intracolumnar van der Waals attractive interactions of their alkyl chains.

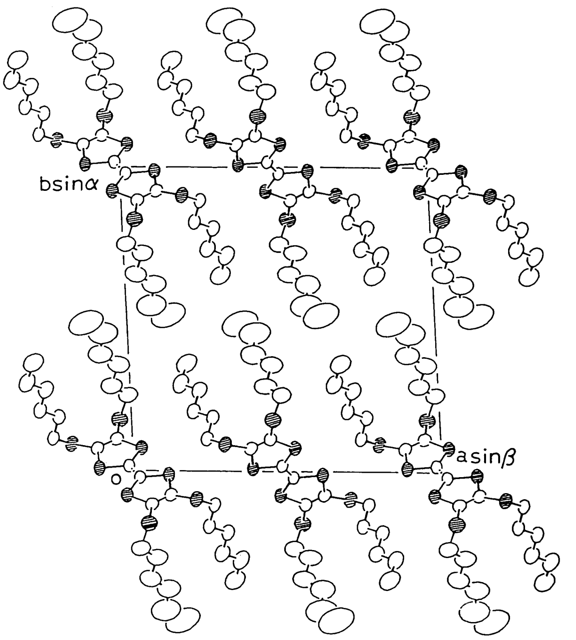

Fig. 6. Crystal structure of TTC$_6$–TTF (0 °C).

These results concerning crystal structure analysis imply that the electrical properties drastically change between n=3 and 4. Crystals which have molecular structures that are boat-like (n=1, 2, 3) reveal high electrical resistivities (ca. 10^{10} Ω cm); Form III crystals (n=4, 5, 6), however, show rather low resistivities (ca. 10^7 Ω cm) along the c-axis. Therefore, the chair-like molecules can make columnar structures which are favorable for electron transport along the stacking axis. However, these alkyl chains are not sufficiently long to have a uniform arrangement like that of n-alkane. Thus, in Form III crystals (n=4, 5, 6), the intercolumnar intermolecular contacts (S$\cdots$S, S$\cdots$C, C$\cdots$C) are not strong; this fact could be one of the reasons for their rather low melting points (n=4:24.6 °C; n=5:32.2 °C; n=6:28.6 °C).

Crystal structure analyses of the long-chain members will be reported and compared with these structures in our next paper (Part II).

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