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Electrical Conductivities of Tetrakis(alkylthio)tetrathiafulvalene (TTC$_n$-TTF) and Tetrakis(alkyltelluro)tetrathiafulvalene (TTeC$_n$-TTF)

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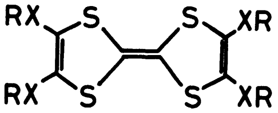
Electrical conductivities have been measured for TTC$_n$-TTF and TTeC$_n$-TTF. In the case of TTC$_n$-TTF, the compounds with short alkyl chains (n=1—3) show the high resistivities above 10^{10} Ω cm, while the resistivities of the compounds with long alkyl chains ($n \geqslant 4$) decrease to 10^6—10^7 Ω cm. The relatively low resistivities of the compounds with long alkyl chains are attributed to the considerable reduction in intermolecular distance between adjacent TTF skeletons caused by intermolecular interactions through alkyl chain groups taking into account the results of their crystal structures, thermal properties and densities. As for TTeC$_n$-TTF compounds, the carbon number dependence of resistivity is almost similar to that of TTC$_n$-TTF in the range of large n ($n \geqslant 8$). Exceptionally, TTeC$_1$-TTF exhibits noticeably low resistivity of 6.9×10^4 Ω cm. X-Ray diffraction study confirms that the high conductivity of TTeC$_1$-TTF is caused by the formation of zigzag Te chains due to the presence of strong intermolecular Te–Te atomic contacts.

Since the discovery of a metallic conductivity in TTF-TCNQ, many interests have been devoted to organic conductors with TTF derivative donors. A large number of organic metals are found in charge-transfer complexes with TTF derivative donors such as TMTTF (tetramethyl-TTF), HMTTF (hexamethylene-TTF), and BEDT-TTF (bis(ethylenedithio)-TTF)) complexes. Tetrakis(alkylthio)tetrathiafulvalene (abbreviated as TTC$_n$-TTF) used in this work is one of these derivatives, which is obtained by the introduction of four alkylthio substitutional groups to a TTF skeleton, as shown in Fig. 1. Some of charge-transfer complexes with TTC$_1$-TTF have been investigated$^{1)}$ and an iodine complex with a composition of (TTC$_1$-TTF)$(I_3)_{0.823}$ shows a metallic conductivity.$^{2,3)}$ Besides the studies related to CT complexes, TTC$_n$-TTF attracts interests in anomalous electrical property as a single component organic solid which does not belong to charge-transfer complexes, because of its good electrical conduction.$^{4)}$ TTC$_n$-TTF consists of a conjugated part of tetrathio-TTF (C_6S_8) moiety and an aliphatic part of four alkyl chain groups. It is interesting to investigate systematically how the conjugated and the aliphatic parts affect the physical properties of TTC$_n$-TTF's by changing the carbon number of alkyl group. Moreover, it is easy to extend our system by replacing sulfur atoms with other chalcogen atoms such as selenium or tellurium having bigger van der Waals radius. This strategy will enable to increase the magnitudes of intermolecular interactions and enhance the conductivity. We have reported the novel crystal structure, high electrical conductivity and low ionization energy of TTC$_9$-TTF compound,$^{4,5)}$ which are supposed to be associated with the reduction in intermolecular distance between TTF skeletons caused by the function of intermolecular interactions between alkyl chains. In this work, we present the experimental results of electrical conductivities of TTC$_n$-TTF and tetrakis(alkyltelluro)tetrathiafulvalene (abbreviated as TTeC$_n$-TTF). The origins of relatively low resistivities for the compounds with long alkyl chains are discussed in connection with crystal structures and the other physical properties such as thermal properties, densities, and ionization energies. Furthermore, the differences of electrical properties between TTC$_n$-TTF and TTeC$_n$-TTF are also discussed according to intermolecular interactions.



$R=C_nH_{2n+1}$

X=S : TTC$_n$-TTF
Te : TTeC$_n$-TTF

Fig. 1. The molecular structure of TTC$_n$-TTF and TTeC$_n$-TTF.

Experimental

The synthetic procedures of TTC$_n$-TTF and TTeC$_n$-TTF compounds (n=1—18) were reported in the previous papers.$^{1,6)}$ The purification of these compounds was performed by column chromatography with silica gel and recrystallization. The purity was checked by thin-layer chromatography. Single crystals of TTC$_n$-TTF with n=1—11 were prepared by recrystallization in a mixed solution of hexane and methanol or acetone and methanol. Crystals of

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Table 1. Resistivities and Activation Energies of TTC$_n$-TTF

Compound	$\rho_{RT}$$^{a)}$/Ω cm	E_a/eV
TTC$_1$-TTF	2.9×10^{10}	0.38
TTC$_2$-TTF	1.2×10^{10}	0.29
TTC$_3$-TTF	9.6×10^{9}	0.52
TTC$_4$-TTF	6.2×10^{6}	0.22
TTC$_5$-TTF	6.4×10^{7}	0.29
TTC$_6$-TTF	3.0×10^{7}	0.28
TTC$_7$-TTF	3.8×10^{7}	0.26
TTC$_8$-TTF	7.0×10^{7}	0.21
TTC$_9$-TTF	5.0×10^{7}	0.21
TTC$_{10}$-TTF	3.7×10^{5}	0.13
TTC$_{11}$-TTF	5.6×10^{5}	0.17
TTC$_{12}$-TTF	5.3×10^{7}	0.25
TTC$_{13}$-TTF	2.3×10^{6}	0.24
TTC$_{14}$-TTF	7.8×10^{7}	0.33
TTC$_{15}$-TTF	2.9×10^{6}	0.24
TTC$_{16}$-TTF	9.9×10^{6}	0.28
TTC$_{17}$-TTF	1.6×10^{7}	0.26
TTC$_{18}$-TTF	6.8×10^{9}	0.48

a) Single crystals for the compounds with $n=1$—11 and compaction pellets for the compounds with $n=12$—18. The measurements for the crystals were performed along the long axis of the crystal.

TTC$_n$-TTF were mainly grown as needle-like crystals except thick plates of n=1, 2, and 9. The colors of the samples were yellow for n=1, 3, and 18 and orange for the other compounds. Single crystals of TTeC$_n$-TTF with n=1, 2, 8, and 9 were obtained as needle-like crystals with dark orange color. Electrical conductivity was measured by a two-probe method between room temperature and a temperature just above a melting point under a vacuum of $\approx10^{-4}$ Pa to avoid an oxidation effect. In the case of the compounds with n=12—18 for TTC$_n$-TTF and the compounds with n=13—18 for TTeC$_n$-TTF which are difficult to be crystallized as single crystals, conductivity was measured with compaction pellets.

Results and Discussion

TTC$_n$-TTF. The results of resistivities at room temperature ρ_{RT} and activation energies E_a for semiconductive TTC$_n$-TTF compounds are summarized in Table 1. Figure 2 shows the correlation between the carbon number n of alkyl group and log ρ_{RT} or E_a for the single crystal samples with n=1—11. The resistivities of the compounds with n=1—3 are very high (above 10^{10} Ω cm), while those of the compounds with $n\geqslant4$ decrease to 10^5—10^7 Ω cm except n=18 with $\approx10^{10}$ Ω cm. Especially, the resistivity values of 3.7×10^5 and 5.6×10^5 Ω cm for TTC$_{10}$-TTF and TTC$_{11}$-TTF, respectively, are remarkably low among single component organic solids ever observed (TTT (tetrathiotetracene) single crystal was reported to have the lowest resistivity 1.5×10^5 Ω cm among the organic solids including sulfur atoms though there have been arguments against the result because of the possibility of extrinsic features associated with the complex formation with oxygen[7]). The n dependence of the activation energies is correlated to that of room temperature resistivities as seen in Fig. 2, where TTC$_{10}$-TTF with a minimum resistivity corresponds to a minimum activation energy E_a=0.13 eV.

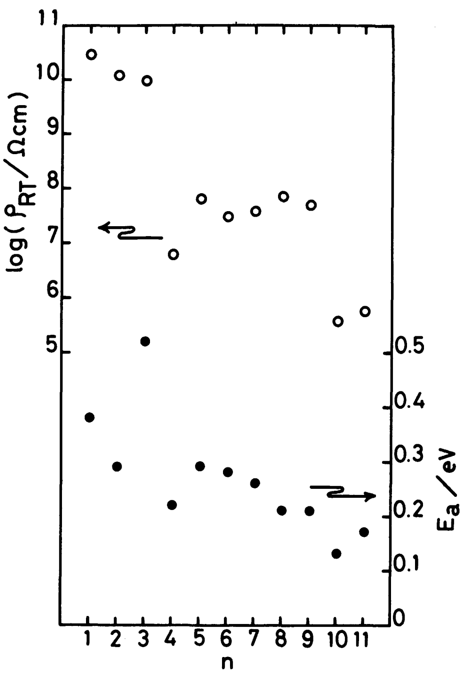

Fig. 2. The correlation between the carbon number n of alkyl group and logρ_{RT} or E_a for the single crystals of TTC$_n$-TTF (n=1—11).

Up to now the crystal structures are presented for the compounds with n=1, 2, 4, 5, 9, and 10.[8,9] The central C$_6$S$_8$ moieties of n=1 and 2 are nonplanar and the molecular structure has a boat form. The intermolecular interactions between adjacent C$_6$S$_8$ 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 resistivities of n=1 and 2 can be understood taking account of this fact. On the contrary, C$_6$S$_8$ moieties of n=4, 5, 9, and 10 are planar and the molecular structure has a chair form. The intermolecular overlaps between adjacent π systems are effectively large because there exists columnar stacking structures consisting of the conjugated π systems which are not found in TTC$_1$-TTF and TTC$_2$-TTF. Thus the compounds with $n\geqslant4$ show the relatively low resistivities due to the crystal structures which are favorable for electron transport. The remarkable enhancement of the conductivity with increasing n can be explained by the fact that TTC$_9$-TTF and TTC$_{10}$-TTF have the short interplanar distance of 3.49 Å between adjacent C$_6$S$_8$

Table 2. Anisotropies of Resistivities of TTC_n-TTF

Compound	ρ_x[a)]/Ω cm	ρ_y[b)]/Ω cm	ρ_z[c)]/Ω cm
TTC_1-TTF	2.9×10^{10}	1.7×10^{11}	2.7×10^{12}
TTC_2-TTF	1.2×10^{10}	1.2×10^{10}	1.4×10^{14}
TTC_9-TTF	5.0×10^{7} d)	1.2×10^{8} d)	2.9×10^{13} d)

a) Parallel to the long axis of the crystal. b) Perpendicular to the x-direction in the broad face of the crystal. c) Perpendicular to the x-direction and to the broad face of the crystal. d) The directions x, y, and z correspond to the c-, a-, and b-axes, respectively, in the crystal data.

Table 3. Resistivities and Activation Energies of $TTeC_n$-TTF

Compound	ρ_{RT}[a)]/Ω cm	E_a/eV
$TTeC_1$-TTF	6.9×10^{4}	0.25
$TTeC_2$-TTF	2.3×10^{9}	0.47
$TTeC_8$-TTF	1.7×10^{6}	0.24
$TTeC_9$-TTF	2.0×10^{6}	0.21
$TTeC_{13}$-TTF	1.1×10^{8}	0.41
$TTeC_{14}$-TTF	2.6×10^{8}	0.48
$TTeC_{15}$-TTF	1.7×10^{8}	0.43
$TTeC_{16}$-TTF	1.2×10^{8}	0.49
$TTeC_{17}$-TTF	1.4×10^{8}	0.43
$TTeC_{18}$-TTF	3.5×10^{8}	0.47

a) Single crystals for the compounds with $n=1$—9 and compaction pellets for the compounds with $n=13$—18. The measurements for the crystals were performed along the long axis of the crystal.

moieties which is considerably reduced in comparison with 3.73 Å in TTC_5-TTF (The difference in the observed resistivities between TTC_9-TTF and TTC_{10}-TTF with the same interplanar distance of 3.49 Å is considered to be caused by the difference in the magnitude of the transfer integrals between adjacent molecules which are easily changed by subtle difference in crystal structures.) These facts concerning crystal structures confirm that the remarkably low resistivities in the compounds with long alkyl chains are accomplished by strong intermolecular interactions due to the reduction in the intermolecular distance between adjacent C_6S_8 moieties.

The anisotropies of resistivities at room temperature for the compounds with $n=1$, 2, and 9 are summarized in Table 2. According to the structure analysis, TTC_9-TTF shows a large anisotropy $\rho_b/\rho_c\approx10^6$ as shown in Table 2 and the easy axis for electrical conduction (ρ_c) corresponds to the stacking direction of C_6S_8 moiety parallel to the c-axis, while the hard axis corresponds to the b-axis, in which direction adjacent TTC_9-TTF molecules face to each other through long alkyl chains elongated parallel to the b-axis. Along the a-axis, there exist strong S-S contacts which give rise to about the same magnitude of ρ_a to ρ_c. The investigation of resistivity just above the melting point (T_m=57 °C) shows that ρ_c increases to $\approx10^{12}$ Ω cm which is nearly equal to ρ_b in the crystal around T_m. This fact gives evidence that the regular stacks of the conjugated π systems parallel to the c-axis favorable to the good conduction is destroyed in liquid state. These results suggest the presence of the electrical conduction path associated with the large intermolecular overlaps and the short S-S contacts between adjacent π systems. On the other hand, TTC_1-TTF and TTC_2-TTF show a relatively small anisotropy (10^2—10^4) because of the absence of a special direction for easy electrical conduction.

Ultraviolet photoelectron spectroscopic studies presented that the compounds with long alkyl chains showed extraordinarily low ionization energies of 4.7—4.85 eV.[5)] Such low values can be explained by the enhancement of polarization energy through large intermolecular interactions due to the small intermolecular distance. The studies of the thermal property suggest that intermolecular interactions are dominated mainly by the van der Waals interaction of C_6S_8 moieties in the range of small n ($n\leqslant7$), while they are dominated mainly by alkyl chain groups in the range of large n.[10)] Taking into consideration of the results of crystal structures, the short interplanar distance for the compounds with large n is caused by these intermolecular interactions between alkyl chain groups, which is consistent with the following result of the density. The density measurements showed that the ratio of effective volumes of C_6S_8 moieties to those of alkyl chain groups for the compounds with $n\geqslant8$ decreased obviously as compared with the ratio of the compounds with $n<8$.[10)] This fact means that effective volumes of C_6S_8 moieties for the compounds with $n\geqslant8$ are effectively depressed by intermolecular interactions caused by long alkyl chains. These results suggest that intermolecular interactions through alkyl chain groups work to reduce the interplanar distance between adjacent C_6S_8 moieties, which leads to remarkably high conductivities of the compounds with long alkyl chains.

$TTeC_n$-TTF. $TTeC_n$-TTF compounds also have semiconductive characters and the results of their electrical resistivities at room temperature ρ_{RT} and activation energies E_a are summarized in Table 3. Single crystals were employed only in $n=1$, 2, 8, and 9 for the present resistivity measurement. The magnitude of the resistivity of 6.9×10^4 Ω cm for $TTeC_1$-TTF, which is the lowest in the series of $TTeC_n$-TTF, is lower than the minimum resistivity in the TTC_n-TTF system. Crystal structure analysis gives the knowledge to understand noticeably low resistivity of this compound.[11)] The central $C_6S_4Te_4$ moiety of $TTeC_1$-TTF is planar unlike TTC_1-TTF. $TTeC_1$-TTF molecules are stacked to form a column structure with the interplanar distance of 3.76 Å. Tellurium atoms between neighbouring columns form zigzag chains along the stacking axis of $TTeC_1$-TTF molecules. The shortest Te–Te distance between neighbouring columns is 3.64 Å, which is significantly smaller than the van der Waals distance 4.12 Å of Te atom. The network of the zigzag Te chains in this material is reminiscent of the crystal structure of inorganic pristine Te where strong interatomic interactions associated with a short Te–Te distance (2.84 Å) bring about high conductivity (1 Ω cm). Therefore, the strong Te–Te interactions of $TTeC_1$-TTF compound is considered to give noticeably high conductivity. The short Te–Te contact has been observed also in the crystal of HMTTeF (bis(trimethylene)tetratellurafulvalene),[12] where HMTTeF molecules form columns stacked alternately with Te–Te distances of 3.583 and 3.743 Å. The dimerization effect of HMTTeF may be unfavorable to realize good electrical conduction.[13] On the contrary, for $TTeC_1$-TTF, the uniform zigzag Te interchains network can contribute to accomplish noticeably high conductivity. $TTeC_1$-TTF reveals the well-conductive character even just above melting point (T_m=170 °C) with the resistivity of $\approx 10^7$ Ω cm. This fact means that the short range ordering of molecular stacking associated with intermolecular interactions still remain in the molten state because of strong interatomic interactions between tellurium atoms. $TTeC_2$-TTF is found to have higher resistivity than $TTeC_1$-TTF. The high resistivity of $TTeC_2$-TTF can be easily understood by crystal structure analysis,[11] which suggests that the shortest Te–Te distance 3.99 Å in $TTeC_2$-TTF is considerably large as compared with 3.64 Å in $TTeC_1$-TTF and the interplanar distance between $C_6S_4Te_4$ moieties is very large (4.2 Å). For the compounds with $n \geqslant 8$, the resistivity is in the similar range to that for TTC_n-TTF with $n \geqslant 8$. According to the results of thermal properties, the series of $TTeC_n$-TTF is divided into two subgroups depending on the length of alkyl chain, which are different from the series of TTC_n-TTF.[14] For the compounds with long alkyl chains ($n \geqslant 7$), similar to TTC_n-TTF, intermolecular interactions associated with long alkyl chains predominate molecular packing, leading to the reduction in the distance between the $C_6S_4Te_4$ π systems which can act to enhance electrical conduction. The behavior of the resistivity for the compounds with $n \geqslant 7$ can be explained along this line. For the compounds with $n<7$, which belong to the other subgroup, competition among three kinds of intermolecular interactions originating from alkyl chains, tellurium atoms and TTF π systems gives peculiar crystal structures depending on n. In the case of $TTeC_1$-TTF which has the shortest alkyl chains, strong intermolecular interaction between tellurium atoms plays an important role to determine a crystal structure and works to realize good electrical conduction as well as pristine tellurium.

Summary

The solid state properties of TTC_n-TTF and $TTeC_n$-TTF have been investigated by electrical conductivity measurement. In the case of TTC_n-TTF, the compounds with small n (n=1—3) show the high resistivities of above 10^{10} Ω cm, while those with large n ($n \geqslant 4$) show relatively low resistivities of 10^5—10^7 Ω cm. Especially, TTC_{10}-TTF and TTC_{11}-TTF show the remarkably low resistivities of 3.7×10^5 and 5.6×10^5 Ω cm, respectively. These values are exceptionally low among organic conductors which do not belong to charge-transfer complexes. The fairly good conductivities of the compounds with long alkyl chains are caused by the reduction in the distance between π systems of adjacent C_6S_8 moieties parallel to the stacking axis, which is accomplished by intermolecular van der Waals interactions through alkyl chain groups. The function of long alkyl chains for the reduction in the distance between the adjacent π systems can be called as "a molecular fastener effect". The optical band gaps are ≈ 2 eV for TTC_n-TTF compounds.[15] Thus the small activation energies of 0.1—0.3 eV from conductivity cannot be explained by a simple band picture for semiconducting materials. Electrical properties of $TTeC_n$-TTF are qualitatively same to those of TTC_n-TTF for the long alkyl chain compounds ($n \geqslant 8$). $TTeC_1$-TTF shows the lowest resistivity of 6.9×10^4 Ω cm among a series of TXC_n-TTF (X=S and Te). The noticeably high conductivity of this compound is considered to be caused by strong intermolecular interactions due to the presence of uniform zigzag Te chains similar to inorganic pristine Te.

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