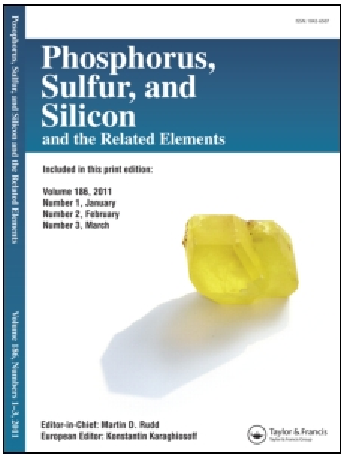

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DEVELOPMENTS OF PERI-DICHALCOGEN-BRIDGED FUSED AROMATIC HYDROCARBONS AS NOVEL ELECTRON DONORS FORMING CONDUCTIVE MOLECULAR COMPLEXES

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The developments of novel non-TTF type electron donors forming conductive molecular complexes are presented, especially focussing on methyl-substituted tetrachalcogeno-naphthalenes, anthracenes, and tetracenes. These compounds have been designed chiefly to possess advantageous characteristics, such as strong donating ability, enhanced solubility, and marked heteroatomic interaction, all of which are essential to electron donors forming organic metals. As a result, they formed a large number of conductive molecular complexes and radical cation salts. In particular, the NO_3^-, BF_4^-, and Cl^- salts of the dimethyl tetraselenoanthracene showed high room temperature conductivities of 440, 450, and 700 Scm^{-1}, respectively, with metallic behavior. Furthermore, the Br^- salt of the dimethyl tetratelluroanthracene showed an extraordinarily high conductivity of 1300 Scm^{-1}.

Keywords: organic conductor; molecular complex; radical cation salt; electron donor

INTRODUCTION

Conductive organic materials are a major subject of current interest. Since the historic discovery of the TTF-TCNQ complex as an unusual one-dimensional synthetic metal,[1] highly conductive materials and superconductors have been developed mainly from tetrathiafulvalene (TTF) and related compounds.[2] Thus, structural modifications of TTF have been extensively studied according to the two basic principles: replacement of chalcogen atoms and introduction of functional groups (Fig. 1).[3] In fact, TSF and TTeF were found to form more conductive charge-transfer complexes with TCNQ.[4] In addition, TMTSF led to the discovery of the first organic superconductor, and BEDT-TTF to the development of numerous high-temperature organic superconductors.[2]

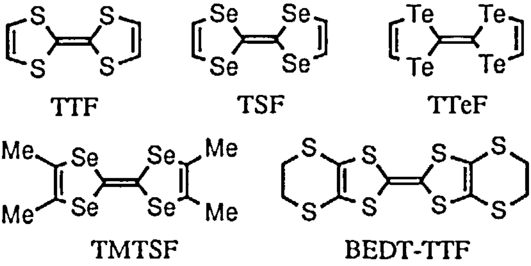


FIGURE 1 TTF variants

Only a limited number of non-TTF type electron donors forming organic metals have been known. In order to make a major breakthrough in the field of conductive organic materials, it is desirable to develop non-TTF types of superior electron donors. One of prototypical non-TTF type electron donors is tetrathiotetracene (TTT), which is a stronger donor than TTF and also forms a conductive TCNQ complex.[5] The strong donating ability of TTT is ascribable to the gain of aromaticity in the two heterocyclic rings but also in the two outer benzo rings in the oxidation states (Fig. 2). However, it has a great disadvantage of poor solubility in common solvents, so its extensive complexation study is very limited.

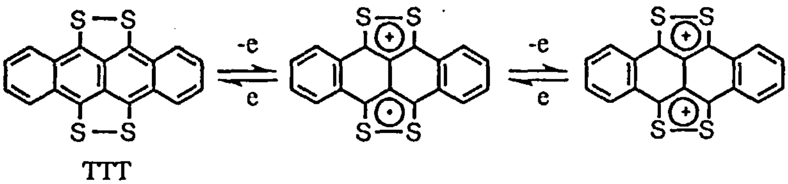


FIGURE 2 Redox process of TTT

In the TTT series, replacement of chalcogen atoms has been likewise studied: the selenium (TST) and the tellurium analogue (TTeT) were synthesized by Balodis group[6] and Sandmann group,[7] respectively. However, they have poorer solubilities and are more intractable. The unsymmetrical TST was also prepared, which has a donor ability comparable to that of the sym-TST.[8]

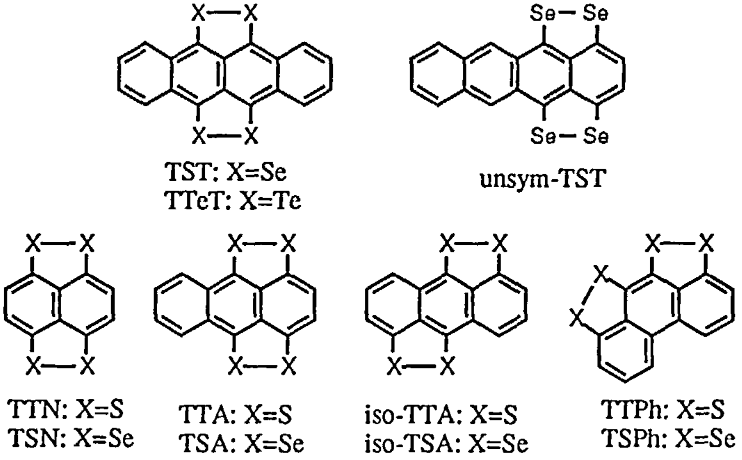
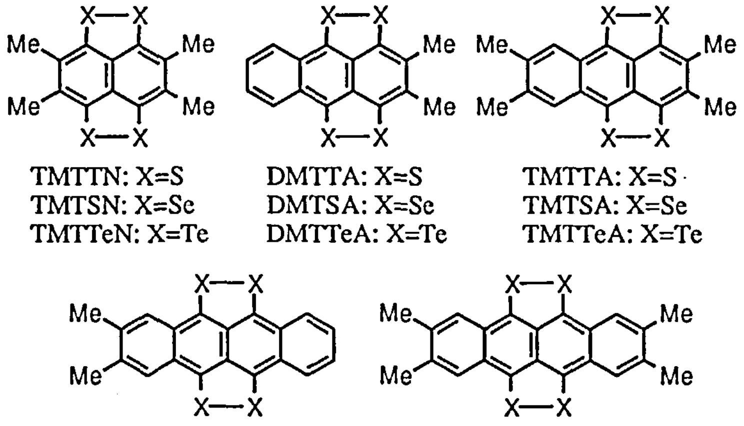


FIGURE 3 TTT variants

In order to study a potential of TTT, more tractable TTT type electron donors are required. Some structural modifications on the TTT structure have been thus carried out, and the principal change is to lower homologues, such as TTN,[9] TTA,[10] iso-TTA,[11] and TTPh (Fig. 3).[12] As expected, these lower homologues have enhanced solubilities, but suffer a considerable decrease in donor ability, because of decreasing gain of aromaticity in their oxidation states. The selenium variants, TSN,[13] TSA,[14] iso-TSA,[11] and TSPh,[12] were also studied, but again encountered the solubility problem. In addition, the tellurium ones with severer solubility remained unknown. The decreasing donor abilities proved fatal for the formation of charge-transfer complexes, and thus these compounds gave only few conductive complexes.[9,15] An exception is TTPh and TSPh bearing a unique interactive structure with the close arrangement of the two heterocyclic rings, which have a capacity to form conductive charge-transfer complexes.[12]

In order to overcome both of the two problems caused by the structural changes of TTT, that is, the decreasing donor abilities of the lower homologues and the low solubilities of the selenium- and tellurium-containing variants, we have focused on introduction of methyl groups into these molecular systems (Fig. 4). This article reviews such successful modifications of peri-dichalcogen bridged



TMTTN: X=S
TMTSN: X=Se
TMTTeN: X=Te

DMTTA: X=S
DMTSA: X=Se
DMTTeA: X=Te

TMTTA: X=S
TMTSA: X=Se
TMTTeA: X=Te

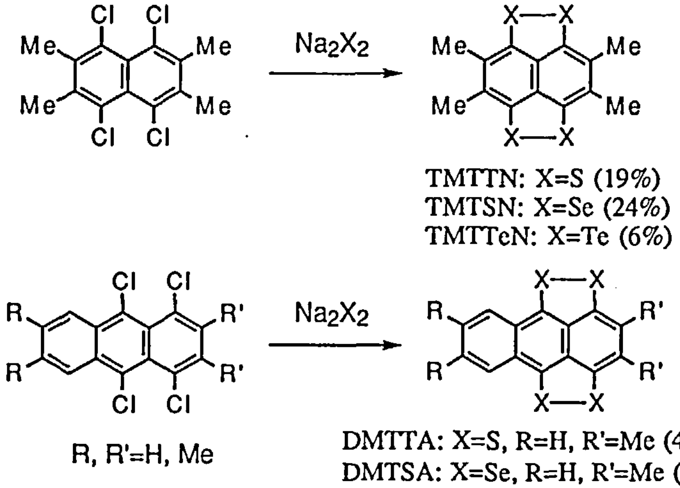
DMTTT: X=S
DMTST: X=Se

TMTTT: X=S
TMTST: X=Se

FIGURE 4 Methyl-substituted TTT type electron donors electron donors, which have been accomplished as a systematic program in our laboratory aimed at developing non-TTF type of superior electron donors since the late 1980s.

SYNTHESIS OF METHYL-SUBSTITUTED TETRACHALCOGENO-NAPHTHALENES, ANTHRACENES, AND TETRACENES

Scheme 1 shows the syntheses of the methyl derivatives of tetrachalcogenonaphthalenes[16] and tetrachalcogenoanthracenes.[17] The key substitution reactions of the corresponding tetrachloroarenes with sodium dichalcogenide in hexamethylphosphoric triamide, *N,N*-dimethylformamide, or 1,3-dimethyl-2-imidazolidinone at 100-150 °C



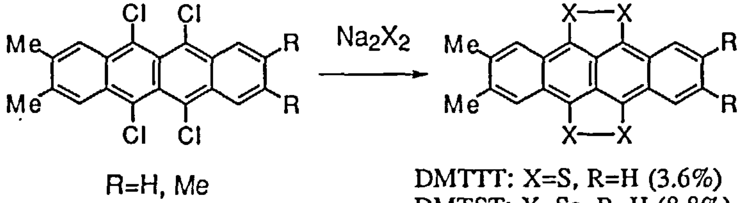
TMTTN: X=S (19%)
TMTSN: X=Se (24%)
TMTTeN: X=Te (6%)

R, R'=H, Me

DMTTA: X=S, R=H, R'=Me (43%)
DMTSA: X=Se, R=H, R'=Me (31%)
DMTTeA: X=Te, R=H, R'=Me (15%)
TMTTA: X=S, R=R'=Me (41%)
TMTSA: X=Se, R=R'=Me (29%)
TMTTeA: X=Te, R=R'=Me (14%)

SCHEME 1 Syntheses of methyl-substituted tetrachalcogenonaphthalenes and tetrachalcogenoanthracenes allowed smoothly the formation of the peri-dichalcogen bridged compounds. It may be noted that in these reactions, the tellurium derivatives were obtained despite poor yields.

The methyl derivatives of tetrachalcogenotetracenes were similarly synthesized, but troubled with very low yields (Scheme 2).[18] In this case, no tellurium compounds were obtained. Maruo and coworkers independently reported the synthesis of DMTTT.[19] During our research, a patent appeared to report an improved method applicable to the synthesis of the selenium compounds DMTST and TMTST.[20]



DMTTT: X=S, R=H (3.6%)
DMTST: X=Se, R=H (8.8%)
TMTTT: X=S, R=Me (6.2%)
TMTST: X=Se, R=Me (1.2%)

SCHEME 2 Syntheses of methyl-substituted tetrachalcogenotetracenes

DONOR ABILITIES AND SOLUBILITIES

Table I summarizes the half-wave oxidation potentials of a series of the tetrachalcogenoarenes. As already mentioned, the oxidation potentials increase in order of TTT, TTA, and TTN series. Methylation is, however, very effective in reducing the elevated oxidation potentials of the lower homologues TTA and TTN. In addition, remarkable is the tellurium effect. The sulfur and selenium compounds have nearly the same oxidation potentials, but the tellurium one has a much lower oxidation potential. It is thus worth noting that TMTTeN has a low

TABLE I Half-wave oxidation potentials (vs. Ag/AgCl)

Donor	$E_{1/2}(1)$/V	$E_{1/2}(2)$/V	ΔE/V
TTF	0.34	0.72	0.38
TTN	0.56	0.97	0.41
TSN	0.52	0.89	0.37
TMTTN	0.46	0.94	0.48
TMTSN	0.45	0.90	0.45
TMTTeN	0.31	0.73	0.42
TTA	0.36	0.75	0.39
TSA	0.35	0.71	0.36
DMTTA	0.32	0.73	0.41
DMTSA	0.31	0.72	0.41
DMTeA	0.20	0.63	0.43
TMTTA	0.26	0.69	0.43
TMTSA	0.26	0.68	0.42
TMTTeA	0.16	0.55	0.39
TTT	0.19	0.56	0.37
TST	0.21	0.58	0.37
DMTTT	0.13	0.52	0.39
DMTST	0.15	0.53	0.38
TMTTT	0.08	0.48	0.40
TMTST	0.10	0.48	0.38

oxidation potential comparable to that of TTF, and TMTTeA to that of TTT.

Introduction of methyl groups is expected to substantially enhance the solubilities of the tetrachalcogenoarenes. This is, however, not the case in the TTT series; for example the molar solubilities of TTT, DMTTT, and TMTTT in trichlorobenzene are 1.2 x 10^{-4}, 2.4 x 10^{-4}, and 1.5 x 10^{-4} mol dm^{-3}, respectively. On the other hand, it is very effective for the solubility enhancement of the lower homologues, as seen from a comparison of the solubilities of TTN (4.1×10^{-4} mol dm^{-3}) and TMTTN (5.5×10^{-3} mol dm^{-3}) in chloroform. In addition, dimethylation is more effective presumably on account of unsymmetrical topology than tetramethylation. For example, the molar solubilities of a series of TSA in chloroform are as follows: TSA 2.1×10^{-4}, DMTSA 3.1×10^{-3}, and TMTSA 3.2×10^{-4} mol dm^{-3}.

CHARGE-TRANSFER COMPLEXES

Owing to both the increasing donor ability and enhanced solubilities, the methyl-substituted tetrachalcogenoarenes are capable of forming a number of conductive charge-transfer complexes. Table II summarizes the selected charge-transfer complexes of the tetramethyl tetrachalcogenonaphthalenes.[16] Contrary to expectation, all the complexes have relatively low conductivities, and there is no significant difference in conductivity among the sulfur, selenium, and tellurium-containing complexes. It may be suspected that the low conductivities are mainly ascribed to the steric hindrance of the methyl groups of the donor molecules.

Such steric effect of methyl groups should be less effective in the

TABLE II Electrical conductivities of charge-transfer complexes of tetramethyl tetrachalcogenonaphthalenes[a]

Acceptor	TMTTN σ_{RT}/Scm^{-1}	TMTSN σ_{RT}/Scm^{-1}	TMTTeN σ_{RT}/Scm^{-1}
TCNQ	5.8×10^{-3}	2.4×10^{-3}	3.5×10^{-3}
$TCNQF_4$	2.6×10^{-8}	2.2×10^{-6}	2.6×10^{-5}
HCBD	4.5×10^{-3}	2.4×10^{-6}	5.0×10^{-7}
DDQ	6.8×10^{-8}	3.4×10^{-8}	1.9×10^{-4}

[a] Measured on a compressed pellet by a four-probe method.

TABLE III Electrical conductivities of charge-transfer complexes of methyl-substituted tetrachalcogenoanthracenes[a]

Acceptor	DMTTA	DMTSA	DMTTeA
	σ_{RT}/Scm^{-1}	σ_{RT}/Scm^{-1}	σ_{RT}/Scm^{-1}
TCNQ	9.6 x 10^{-1}	1.2	5.3 x 10^{-6}
DMTCNQ	9.5 x 10^{-1}	5.3 x 10^{-1}	1.2 x 10^{-3}
DMOTCNQ	2.2	5.0 x 10^{-7}	3.2 x 10^{-2}
TNAP	7.9	2.6 x 10^{-2}	4.9 x 10^{-2}
DCBT	1.5 x 10^{-6}	3.7	6.0
DBBS	7.1 x 10^{-1}	8.0	5.8
Acceptor	**TMTTA**	**TMTSA**	**TMTTeA**
	σ_{RT}/Scm^{-1}	σ_{RT}/Scm^{-1}	σ_{RT}/Scm^{-1}
TCNQ	5.0 x 10^{-2}	2.7 x 10^{-1}	1.8 x 10^{-6}
DMTCNQ	7.7 x 10^{-7}	1.2 x 10^{-5}	4.6 x 10^{-2}
DMOTCNQ	4.0 x 10^{-9}	1.0 x 10^{-8}	1.1 x 10^{-7}
TNAP	1.7	9.2 x 10^{-3}	6.0 x 10^{-1}
DCBT	6.0 x 10^{-3}	3.1 x 10^{-3}	2.3
DBBS	1.0 x 10^{-3}	8.1 x 10^{-4}	3.6

[a] Measured on a compressed pellet by a four-probe method.

charge-transfer complexes of the extensive donor systems. As shown in Table III, the conductivities of the methyl-substituted tetrachalcogenoanthracene complexes are much higher than the preceding naphthalene ones, although some complexes have still low conductivities.[17] The conductivities are not directly dependent on the donor or acceptor species but on their combinations. There is, however, a general tendency that the complexes of the tetramethyl anthracene donors are less conductive than the corresponding dimethyl ones, and especially it is remarkable in the complexes with 2,5-dimethyl derivative (DMTCNQ) and 2,5-dimethoxy derivative

(DMOTCNQ) of TCNQ relative to those with TCNQ and extensive electron acceptors, such as 9,9,10,10-tetracyano-2,6-naphthoquinodimethane (TNAP), 3,3'-dichloro-5,5'-bis(dicyanomethylene)-5,5'-dihydro-$\Delta^{2,2'}$-bithiophene (DCBT), and 3,3'-dibromo-5,5'-bis(dicyanomethylene)-5,5'-dihydro-$\Delta^{2,2'}$-biselenophene (DBBS). These results also suggest that some of the steric effect remains in the antracene series.

Table IV summarizes the conductivities of the methyl-substituted tetrachalcogenotetracene complexes.[18] In this case, the donors do not have enough solubilities to make good crystals, so the obtained complexes are microcrystalline, but all have high conductivities, meaning that there is no longer the steric effect of methyl groups on the complexation of the extensive tetracene system.

TABLE IV Electrical conductivities of charge-transfer complexes of methyl-substituted tetrachalcogenotetracenes[a]

Acceptor	DMTTT	DMTST	TMTTT	TMTST
	σ_{RT}/Scm^{-1}	σ_{RT}/Scm^{-1}	σ_{RT}/Scm^{-1}	σ_{RT}/Scm^{-1}
TCNQ	9.5×10^{-1}	6.6×10^{-1}	2.4×10^{-1}	6.6×10^{-1}
DMTCNQ	15	2.2	1.2	2.2
TNAP	8.7×10^{-1}	1.3×10^{-1}	1.1×10^{-2}	8.4×10^{-2}
DBBS	1.4	4.3	2.1×10^{-1}	5.5×10^{-1}

[a] Measured on a compressed pellet by a four-probe method.

RADICAL CATION SALTS

Radical cation salts are much more interesting than charge-transfer complexes, because the former have often presented epoch-making examples of extraordinarily high conductors and superconductors. Electrocrystallization using the methyl-substituted tetrachalcogenonaphthalene and anthracene compounds gave a number of radical cation

TABLE V Electrical conductivities of radical cation salts of tetramethyl tetrachalcogenonaphthalenes[a]

Anion	TMTTN	TMTSN	TMTTeN
	σ_{RT}/Scm^{-1}	σ_{RT}/Scm^{-1}	σ_{RT}/Scm^{-1}
I_3^-	11.8^s	11.3^s	2.1 x 10^{-4}
ClO_4^-	7.2 x $10^{-4\ s}$	3.9 x 10^{-6}	---------
BF_4^-	1.9 x 10^{-4}	7.1^s	---------
PF_6^-	1.6 x $10^{-1\ s}$	2.0 x $10^{-4\ s}$	---------
Cl^-	4.9 x 10^{-6}	1.6 x 10^{-3}	---------
Br^-	4.8 x 10^{-8}	1.2 x 10^{-2}	---------

[a] Measured on a compressed pellet or on a single crystal (with superscript of s) by a four-probe method.

salts. Table V shows the conductivities of the radical cation salts of the tetramethyl terachalcogenonaphthalenes.[16] Some of the sulfur- and selenium-containing salts are highly conductive, but the other ones are not so conductive. The methyl steric effect also may have some influence on the formation of the conductive radical cation salts as seen in the case of the above charge-transfer complexes.

Table VI shows the conductivities of the radical cation salts of the dimethyl tetrachalcogenoanthracenes.[21-25] All the salts of DMTTA are fairly conductive, but variable temperature measurements show semiconductive behavior. On the other hand, the salts of DMTSA, except for the PF_6^- and ASF_6^- ones, show much higher conductivities than the sulfur-containing salts.[21] In particular, the NO_3^-, BF_4^- ,[21,24] and Cl^-[22] salts have very high conductivities of 440, 450, and 700 Scm^{-1}, respectively, and are metallic. In every salt, a metal-to-insulator transition occurs at around 200 K.

It is worth noting that the stoichiometry of the donor and the counter ion for most of the DMTTA and DMTSA salts including the highly conductive NO_3 and BF_4 ones is 1:1. This is very unusual,

TABLE VI Stoichiometries and electrical conductivities of radical cation salts of dimethyl tetrachalcogenoanthracenes[a]

Donor	Anion	D:A	σ_{RT}/Scm^{-1}	E_a/eV
DMTTA	NO_3^-	1:1	4.4	0.065
DMTTA	BF_4^-	1:1	7.0	0.063
DMTTA	ClO_4^-	1:1	5.0×10^{-1}	0.072
DMTTA	PF_6^-	2:1	1.2×10^{-1}	0.072
DMTTA	AsF_6^-	2:1	1.9×10^{-1}	0.079
DMTSA	NO_3^-	1:1	440	metallic, $T_{M\text{-}I}$ 220 K
DMTSA	BF_4^-	1:1	450	metallic, $T_{M\text{-}I}$ 180 K
DMTSA	ClO_4^-	1:1	40	0.020
DMTSA	PF_6^-	1:1	6.5×10^{-1}	0.092
DMTSA	AsF_6^-	2:1	1.0×10^{-1}	0.117
DMTSA	Cl^-	2:1	700	metallic, $T_{M\text{-}I}$ 200 K
DMTTeA	BF_4^-	3:2	9.7×10^{-3}	0.17
DMTTeA	ClO_4^-	3:2	7.1×10^{-3}	0.16
DMTTeA	ReO_4^-	3:2	5.5×10^{-3}	0.16
DMTTeA	PF_6^-	5:1	5.6×10^{-2}	0.077
DMTTeA	AsF_6^-	5:1	1.2×10^{-1}	0.068
DMTTeA	Br^-	2:1	1300	0.010

[a] Conductivities were measured on a single crystal by a four-probe method.

because a normal 1:1 radical cation salt with complete charge transfer is usually a Mott insulator, where electron migration is interfered by on-site coulombic repulsion. This can be best understood by a band model (Fig. 6): when the complete charge transfer occurs, the lower half of the HOMO band formed by a donor assembly is filled by electrons. The coulombic repulsion induces an energy gap U in the middle of the band. When the energy gap is large, the band system becomes a Mott

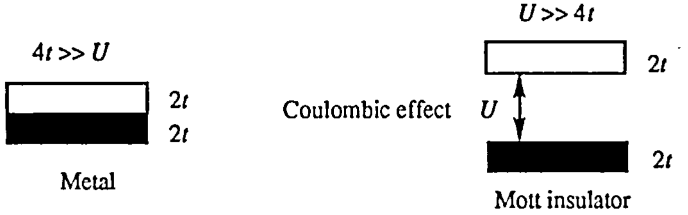


FIGURE 6 Energy band structures of the donor assembly of 1:1 complete charge-transfer complex. The boxes indicate the allowed energy states and the shaded areas indicate the regions filled with electrons (*t* : transfer integral; *U* : on-site coulombic repulsion).

insulator. On the other hand, when the coulombic energy is much less than transfer integral energy *4t*, the spliting is small, and the band system may remain metallic.

The coulombic repulsion energy of DMTSA is estimated not to be particularly small, because a gap between the first and second half-wave oxidation potentials of the donor is nearly the same as that of TTF (see Table I). The crystal structure of the BF_4 salt shows the main feature of uniform zigzag stacks of the DMTSA molecules with a good overlap (Fig. 7). The Se--Se distance between the stacking donors is 3.69 Å, shorter than the normal van der Waals contact (3.8 Å). Thus the metal-like property of the 1:1 salts is ascribed to large transfer integral rather than reduced *U*.[25]

Table 6 also summarizes the conductivities of the radical cation salts of DMTTeA.[23] The conductivities except the bromide one are not so high as those of the selenium-containing complexes. An exception is the bromide complex, which demonstrated an extraordinarily high conductivity of 1300 Scm^{-1}. Unfortunately, this showed not metallic but semiconductive behavior with a very low activation energy. An X-ray crystal structural analysis showed that the donors make stacking columns with sliding, and the Te--Te distance between the stacked donor molecules is 3.7 Å, which is very shorter than the normal van der Waals contact (4.1-4.4 Å). It can be thus concluded that the extraordinarily high conductivity is induced by the strong nonbonded Te--Te interaction.

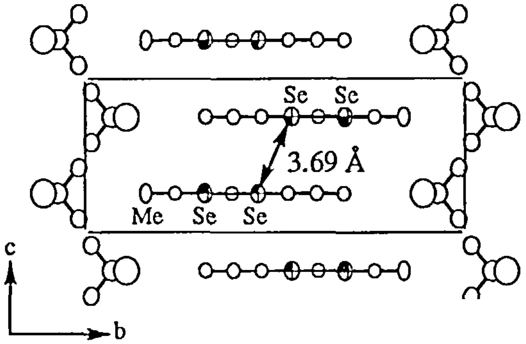


FIGURE 7 Crystal structure of the DMTSA•BF_4 salt projected along the a-axis.

CONCLUSIONS

Peri-dichalcogen bridged fused aromatic hydrocarbons represented by TTT have been successfully modified to better electron donors by methylation onto the aromatic systems. This modification is especially effective in the selenium- and tellurium-containing lower homologues. Among a series of the modified compounds, the dimethyl tetraseleno- and tetratelluro-anthracenes can behave as the most superior electron donors forming highly conductive molecular salts: the 2:1 Cl^- salt of the dimethyl tetraselenoanthracene shows 700 Scm^{-1}, and the 2:1 Br^- salt of the dimethyl tetratelluroanthracene 1300 Scm^{-1}. In addition, the dimethyl tetraselenoanthracene forms unusual 1:1 metallic salts with BF_4^- (σ_{RT}=450 Scm^{-1}) and NO_3^- (σ_{RT}=440 Scm^{-1}). The high conductivities of the above salts are ascribed to strong nonbonded Se--Se or Te--Te interactions between the stacked donors.

Acknowledgments

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