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CRYSTAL STRUCTURES AND ELECTROCHEMICAL PROPERTIES OF ORGANIC DONORS, BMDT-TTF AND BEDSe-TSeF. TWO MODIFICATIONS OF BEDT-TTF

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Almost planar BMDT-TTF molecules form a side-by-side one-dimensional array along the [101] direction, while BEDSe-TSeF molecules are non-planar and dimerized. Electrochemical studies reveal two oxidation waves of BMDT-TTF at potentials similar to those of BEDT-TTF, and BEDSe-TSeF shows one oxidation wave at a potential higher than the second oxidation of BEDT-TTF.

The organic donor BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) has provided the first S-based organic superconductors.[1] We have pointed out that the BEDT-TTF compounds are characterized by the transverse S...S interaction which is closely related to the incorporated six-membered heterorings.[2] Chemical modification of the BEDT-TTF molecule is of special interest. In this paper, we report crystal structures and electrochemical properties of two BEDT-TTF modifications, BMDT-TTF (bis(methylenedithio)tetrathiafulvalene) with the incorporated five-membered heterorings, and the selenium analogue BEDSe-TSeF (bis(ethylenediseleno)tetraselenafulvalene).

The synthesis of BMDT-TTF is described in Ref. 3 and BEDSe-TSeF was synthesized according to the method of Lee et al.[4] In both cases, single crystals suitable for X-ray structure analyses were obtained by recrystallization from carbon disulfide. Crystal data: BMDT-TTF, $C_8H_4S_8$, monoclinic, space group $P2_1/c$, a=4.172(1), b=24.203(5), c=6.581(1) Å, β=112.59(1)°, V=613.6 Å^3, Z=2. BEDSe-TSeF, $C_{10}H_8Se_8$, monoclinic, space group $P2_1/c$, a=6.783(1), b=14.235(4), c=17.555(5) Å, β=109.20(2)°, V=1600.7 Å^3, Z=4.

Intensities were measured on a Rigaku automated four-circle diffractometer with Mo Kα radiation up to 2θ=65° for BMDT-TTF, and 2θ=60° for BEDSe-TSeF. Numbers of the independent reflections ($|Fo|>3\sigma(|Fo|)$) are 1775 for BMDT-TTF and 2612 for BEDSe-TSeF. The structures were solved by the direct method and refined to conventional R value of 0.043 for BMDT-TTF and 0.061 for BEDSe-TSeF. The final atomic coordinates are given in Table 1.

The BMDT-TTF molecule, except hydrogen atoms, is almost planar . In the crystal, the BMDT-TTF molecules stack uniformly along the a axis. The normal to

Table 1. Fractional atomic coordinates (x 10^4) with their estimated standard derivations for (a) BMDT-TTF and (b) BEDSe-TSeF

(a)

	x	y	z
S1	647(4)	673(0)	-2050(2)
S2	3444(4)	485(1)	2797(2)
S3	3640(3)	1850(0)	-1262(2)
S4	6490(3)	1652(0)	3553(2)
C1	830(12)	240(2)	155(6)
C2	3072(11)	1196(2)	-340(7)
C3	4324(11)	1112(2)	1830(6)
C4	7149(12)	2016(2)	1324(8)

(b)

	x	y	z
SE1	2527(2)	1155(1)	5173(1)
SE2	6375(2)	1438(1)	4547(1)
SE3	38(3)	-130(1)	3490(1)
SE4	3853(2)	181(1)	2859(1)
SE5	4096(3)	2794(1)	6497(1)
SE6	8269(3)	3100(1)	5809(1)
SE7	-2994(3)	-892(2)	1849(1)
SE8	1397(3)	-507(2)	1079(1)
C1	3612(22)	956(10)	4329(9)
C2	2696(20)	429(11)	3675(8)
C3	4495(23)	2107(12)	5643(8)
C4	6062(25)	2233(11)	5374(9)
C5	-242(26)	-406(11)	2388(8)
C6	1247(22)	-262(12)	2130(7)
C7	6987(35)	2760(24)	7233(13)
C8	8660(39)	2837(20)	6953(12)
C9	-2889(29)	-853(18)	760(11)
C10	-1046(34)	-131(17)	655(12)

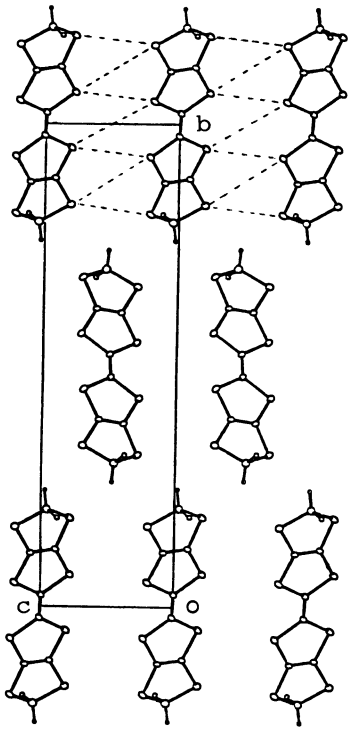


Fig. 1. Crystal structure of BMDT-TTF.

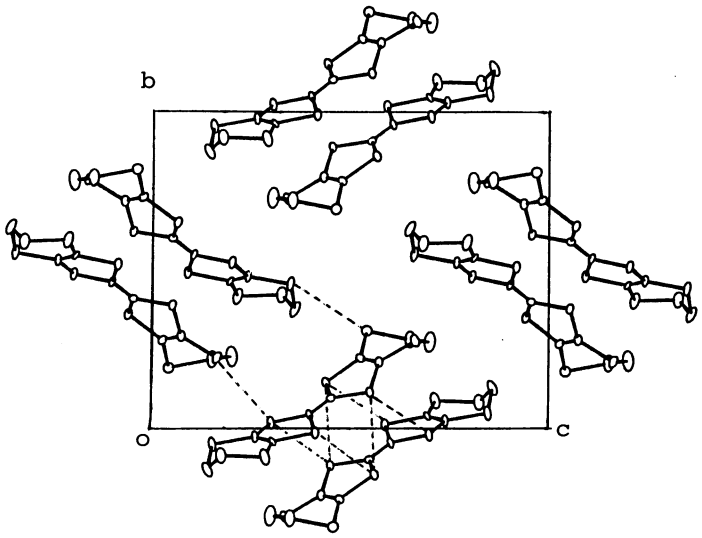
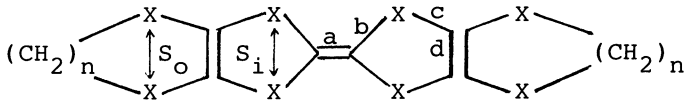


Fig. 2. Crystal structure of BEDSe-TSeF.

Table 2. Comparison of mean bond lengths (Å) and S_o/S_i ratios of BEDT-TTF, BMDT-TTF and BEDSe-TSeF. The bond lengths b,c, and d are average values, with an approximated D_{2h} symmetry



	X	n
BMDT-TTF	S	1
BEDT-TTF	S	2
BPDT-TTF	S	3
BEDSe-TSeF	Se	2

	a	b	c	d	S_o/S_i
BEDT-TTF	1.319	1.758	1.754	1.332	1.16
BMDT-TTF	1.327	1.766	1.738	1.334	0.99
BEDSe-TSeF	1.339	1.893	1.908	1.290	1.13

the BMDT-TTF molecular plane is tilted 24° with respect to the a axis. The interplanar stacking distance is 3.80 Å. The mode of intermolecular overlapping is the "ring-double bond" type which is frequently observed in the conductive cation radical salts of the TTF-type organic donor.[5] None of the S...S distances between adjacent molecules in the stack is shorter than the van der Waals distance (3.70 Å). The most interesting feature of the molecular packing is the transverse intermolecular S...S contacts shorter than the van der Waals distance (3.57-3.62 Å), which lead to a side-by-side one-dimensional array of the BMDT-TTF molecules along the [101] direction (Fig. 1; in all Figs., intermolecular chalcogen-chalcogen distances shorter than the van der Waals distance are indicated by dashed lines). Compared to BEDT-TTF, the transverse S...S interaction is enhanced in BMDT-TTF.

BEDSe-TSeF and BEDT-TTF are isomorphous.[6] The crystal of BEDSe-TSeF contains dimers of BEDSe-TSeF molecules (Fig. 2). The mode of intra-dimer molecular overlapping is "ring-double bond" type. The BEDSe-TSeF molecule is non-planar. The molecule contains three tetraselenaethylene planes with dihedral angles of 164.9° and 166.7° to each other. Compared to BEDT-TTF, the crystal of BEDSe-TSeF increases in the number of the intra- and inter-dimer chalcogen-chalcogen contacts shorter than the van der Waals distance (3.54-4.00 Å). The BEDSe-TSeF molecules align along the a axis with transverse Se...Se contacts (Fig. 3). This side-by-side molecular arrangement is the most characteristic feature of the cation radical salts of BEDT-TTF.

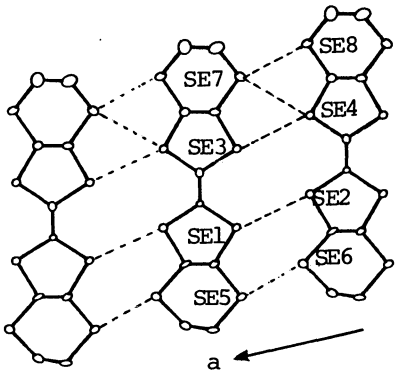


Fig. 3. Side-by-side arrangement of BEDSe-TSeF.

Electrochemical properties of BMDT-TTF, BEDT-TTF, BPDT-TTF and BEDSe-TSeF were studied by the cyclic voltammetry and the differential pulse polarography. The results are shown in Table 2. We used 1,1,2-trichloroethane, which is often used for the electrochemical crystallization, as solvent. The S-based donors (BMDT-, BEDT-, and BPDT-TTF) are oxidized in two one-electron steps. The first step is reversible for every compound. The second wave in the cyclic voltammogram of BPDT-TTF is reversible, and irreversible for BMDT-TTF and BEDT-TTF. The E_1 and E_2 (thus E_2-E_1) values are similar to each other for these S-based donors. Although low solubility of BEDSe-TSeF hampered its electrochemical study, the differential pulse polarography (sweep range; 0-1.5 V) showed one

Table 2. Electrochemical data of BMDT-, BEDT- and BPDT-TTF, and BEDSe-TSeF [a]

Compound	E_1	E_2	E_2-E_1
BMDT-TTF	0.57	0.77[b]	0.20
BEDT-TTF	0.55	0.85[b]	0.30
BPDT-TTF	0.57	0.88	0.31
BEDSe-TSeF	0.94		

a) Measured at a glassy carbon electrode in 1,1,2-trichloroethane, 0.1 M TBAP (volts vs. SCE); Temperature, 17 °C.
b) Irreversible; E_2 values were determined by differential pulse polarography, extrapolating the scan rate to 0 mV/s.

oxidation step at 0.94 V (vs. SCE). This value is higher than the E_2 value of BEDT-TTF. It is not confirmed whether this is a one- or two-electron step.

Both of BMDT-TTF and BEDSe-TSeF are modifications of BEDT-TTF. We consider the nature of these modifications in terms of structural and electronic features.

In the molecular conductors, even small structural modification of the constituent molecule would cause serious change of bulk properties. In the BEDT-TTF family, the S_o/S_i ratio (see Table 2) is an important structural factor, which is closely related to the dimensionality of the system.[7] The relation $S_o/S_i=1.0$ brings about two-dimensional molecular arrangements. Thus, in BMDT-TTF salts two-dimensional character of the system is enhanced.[3,7] The S_o/S_i ratio (>1.0) of BEDSe-TSeF is close to that of BEDT-TTF (Table 2), and the crystal of BEDSe-TSeF is isostructural with BEDT-TTF. These facts seem to promise that in the cation radical salts the molecular packings of BEDSe-TSeF cations will be very similar to those in the BEDT-TTF salts, provided the oxidation state is the same with that of BEDT-TTF. In addition, the replacement of S atoms by Se atoms will result in the enhanced intermolecular interaction.

The substitutions of the ethylene group in BEDT-TTF by the methylene or propylene group do not make serious difference of the E_1 and E_2 values, but the reversibility of the second oxidation indicates that the reactivity and stability of the dication are influenced. On the other hand, there is a great difference in electrochemical properties between BEDSe-TSeF and BEDT-TTF.

In BMDT-TTF and BEDSe-TSeF salts, the dimensionality of the system, one of the most important concepts provided by BEDT-TTF, will be enhanced by two differenct ways; the smoothing of the molecular shape in width ($S_o/S_i=1.0$) and the extension of the molecular orbital by the replacement of the chalcogen atom (S ⟶ Se).

References

1) S. S. P. Parkin, E. M. Engler, R. R. Schumaker, R. Lagier, V. Y. Lee, J. C. Scott, and R. L. Greene, Phys. Rev. Lett., 50, 270 (1983); E. B. Yagubskii, I. F. Shchegolev, V. N. Laukhin, P. A. Kononovich, M. V. Kartosovnik, A. V. Zvarykina, and L. I. Buravov, Pis'ma Zh. Eksp. Teor. Fiz., 39, 12 (1984).
2) H. Kobayashi, R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, G. Saito, T. Enoki, and H. Inokuchi, Mol. Cryst. Liq. Cryst., 107, 33 (1984).
3) R. Kato, A. Kobayashi, Y. Sasaki, and H. Kobayashi, Chem. Lett., 1984, 993.
4) V. Y. Lee, E. M. Engler, R. R. Schumaker, and S. S. P. Parkin, J. Chem. Soc., Chem. Commun., 1983, 235.
5) J. -J. Andre, A. Bieber, and F. Gautier, Ann. Phys., 1976, t. I, 145.
6) H. Kobayashi, A. Kobayashi, Y. Sasaki, G. Saito, and H. Inokuchi, submitted to Bull. Chem. Soc. Jpn.
7) R. Kato, H. Kobayashi, A. Kobayashi, and Y. Sasaki, Chem. Lett., 1984, 1693.

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