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THE CRYSTAL STRUCTURE OF DI(2,3,6,7-TETRAMETHYL-1,4,5,8-TETRASELENAFULVALENIUM)TETRAFLUOROBORATE, $(TMTSF)_2BF_4$

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The crystals of $2C_{10}H_{12}Se_4^{1/2+}\cdot BF_4^-$ ($(TMTSF)_2BF_4$) belong to the triclinic system. The space group is $P\bar{1}$ and the lattice constants are: a=7.255(1), b=7.647(1), c=13.218(3) Å, α=82.23(2), β=87.15(2), γ=70.36(1)°, Z=1, V=688.10 Å^3. The nearly planar TMTSF groups stack in diadic columns along a. The intrastack and interstack contacts between Se atoms show the two-dimensional nature of the crystal.

Recent discovery of the organic superconductors has caused a great intrest.$^{1,2)}$ Although $(TMTSF)_2X$ compounds (X= PF_6,$^{3)}$ ClO_4,$^{4)}$ ReO_4,$^{4)}$ BrO_4,$^{5)}$ FSO_3,$^{5)}$ BF_4) are isomorphic, their physical properties differ from one another:$^{1,6,7)}$ $(TMTSF)_2PF_6$ has an antiferromagnetic ground state and transforms to a superconductive state at high pressure. $(TMTSF)_2ClO_4$ is a "zero-pressure organic superconductor" (T_c=1.2-1.4 K) and $(TMTSF)_2BF_4$ undergoes a metal-insulator transition at a fairly high temperature(~40K).

We have determined the crystal structure of $(TMTSF)_2BF_4$ at room temperature. The crystal belongs to the triclinic system and the space group is $P\bar{1}$. The lattice constants are: a=7.255(1), b=7.647(1), c=13.218(3) Å, α=82.23(2), β=87.15(2), γ=70.36(1)°. The 1525 significant reflections ($|F_o| > 3\sigma(|F_o|)$) were collected on a diffractometer with monochromated Mo Kα radiation up to 2θ=60°. The refinement of the structure was performed by the block-diagonal least-squares method. The final R factor is 0.085.

The structure is shown in Figs 1 and 2. The donor molecules stack along a to form a zig-zag column with a pseudotranslation of period a/2. The nearly planar TMTSF units are almost perpendicular to a (deviation 1.1°). The mode of intermolecular overlap is shown in Fig. 3. The similar "ring-double bond" type overlapping has been seen in (TMTSF)(TCNQ).[8] The atomic coordinates are given in Table 1.

The interplanar distances between adjacent TMTSF are 3.64±0.01 Å (TMTSF(A)...TMTSF(B)) and 3.61±0.01 Å (TMTSF(A)...TMTSF(C)), where A, B and C indicate the symmetry operations (see Fig. 1). The interplanar distances in the $(TMTSF)_2X$ structure reported to date are: 3.66 and 3.63 Å($(TMTSF)_2PF_6$[3]); 3.63 and 3.63 Å($(TMTSF)_2ClO_4$[4]); 3.64 and 3.64 Å($(TMTSF)_2ReO_4$[4]). The short interplanar distances in $(TMTSF)_2BF_4$ are considered to be due to the small size of the anion, which tends to make the TMTSF stacks compact. The volumes of the unit cells of $(TMTSF)_2X$ are; 714 Å^3(PF_6[3]); 710(ReO_4[4]); 707(BrO_4[5]); 694(ClO_4[4]); 688(BF_4). Since many $(TMTSF)_2X$ compounds become superconductors at high pressure , the small lattice spacing is considered to be favorable for realizing a

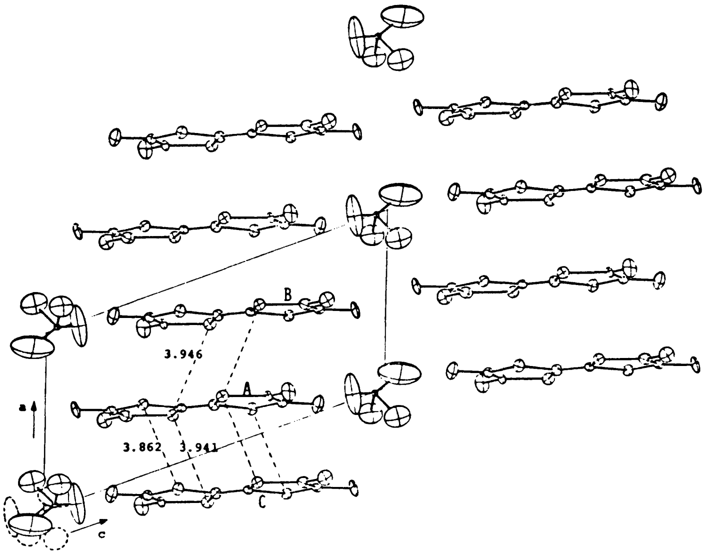

Fig. 1. Side-view of stack (tilted 10°) showing shorter distances (Se...Se)(Å) within a stack. Each contact between two TMTSF units occurs twice because of the inversion center midway between the units. The symmetry operations are: A(x,y,z), B(1-x,1-y,1-z) and C(-x,1-y,1-z). The BF_4 anions show disorder, taking one of the two possible positions randomly.

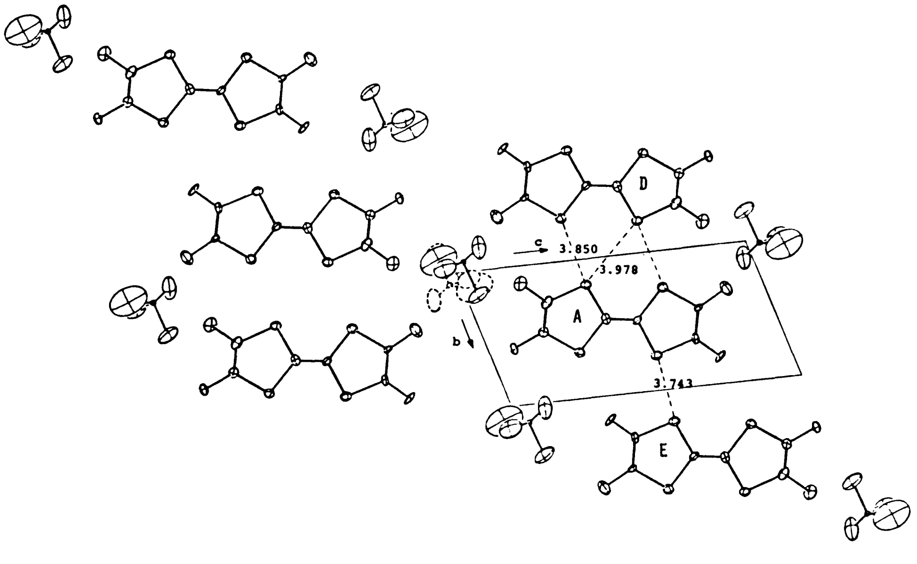

Fig. 2. View along a showing shorter interchain distances (Se...Se)(Å). The symmetry operations are: A(x,y,z), D(1-x,-y,1-z) and E(-x,2-y,1-z).

superconducting state. It has been pointed out that the critical pressure(Pc), above which the superconducting phase is stabilized, decreases with the lattice constant c.[9)] However, $(TMTSF)_2BF_4$ becomes an insulator at low temperature and ambient pressure,[6)] whose lattice constant c is smaller than that of zero-pressure superconductor, $(TMTSF)_2ClO_4$. Therefore, the relationship between Pc and c dose not hold for $(TMTSF)_2BF_4$.

The interplanar distances suggest that the overlap between 2pπ orbitals of the C atoms is very small. Thus, the Se-Se contacts will play an important role in the formation of the conduction band. The short intrastack and interstack Se-Se contacts are given in Figs. 1 and 2, which show the two-dimensional Se-Se "sheet network". The Se-Se distance of 3.743 Å between TMTSF(A) and TMTSF(E) (see Fig. 2) is the shortest in the $(TMTSF)_2X$ structures ever reported. Although the conductivity parallel to the TMTSF stack ($\sigma_{/\!/}$) has been reported to be much larger than that perpendicular to it ($\sigma_\perp$) ($\sigma_{/\!/}/\sigma_\perp > 10^2$, at room temperature[6)]), interstack Se-Se distances are rather shorter than intrastack Se-Se distances. The one-dimensional conduction may be attributable to the anisotropy of the atomic orbital of Se.

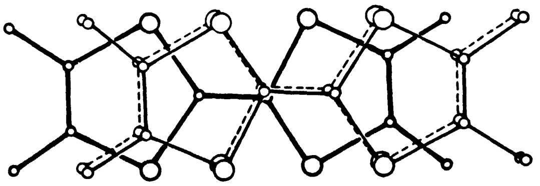

Fig. 3. TMTSF overlaps along the normal to the molecular plane. The dotted and solid lines denote the adjacent molecules above and below the molecule drawn with heavy lines.

Table 1. Final atomic parameters.
Values for fractional coordinates are multiplied by 10^4.

	X	Y	Z	$B_{eq}/\mathring{A}^2$ a)		X	Y	Z	$B_{eq}/\mathring{A}^2$
Se(1)	3740(4)	1695(3)	3821(2)	2.6(0.1)	C(7)	2196(34)	5457(29)	7000(16)	2.2(0.9)
Se(2)	2280(3)	5788(3)	2791(2)	2.5(0.1)	C(8)	1629(32)	7291(33)	6527(15)	2.4(1.0)
Se(3)	2970(4)	3443(3)	6150(2)	2.8(0.1)	C(9)	2320(53)	4853(51)	8107(23)	5.2(1.7)
Se(4)	1633(3)	7511(3)	5120(2)	2.8(0.1)	C(10)	952(53)	8933(36)	7072(24)	4.9(1.5)
C(1)	2800(30)	4239(33)	4014(16)	2.3(1.2)	B	208(488)	-577(337)	378(119)	16.2(20.6)
C(2)	3678(36)	2011(37)	2402(21)	3.4(1.5)	F(1)	271(80)	1461(63)	433(47)	9.0(3.2)
C(3)	3092(28)	3796(30)	1938(17)	2.2(1.1)	F(2)	1843(77)	-1068(71)	-290(50)	10.3(2.2)
C(4)	4403(40)	284(39)	1813(24)	4.2(1.7)	F(3)	554(125)	-1225(69)	1047(38)	15.5(4.4)
C(5)	2991(46)	4222(38)	817(18)	3.8(1.3)	F(4)	-716(103)	-802(140)	-350(107)	22.2(8.6)
C(6)	2520(33)	4947(29)	4961(17)	2.4(1.0)					

a) Equivalent isotropic temperature factor as defined by W. C. Hamilton (Acta Crystallogr., 12, 609 (1959).

The large thermal motion of the anion is a common structural feature of $(TMTSF)_2X$ compounds.$^{3-5)}$ Since the anions are on the center of symmetry, the orientation of the tetrahedral anion must be disordered. The ordering of the orientation of the anions produces a periodical potential and might change the electrical properties. In fact, the doubling of the unit cell along a has been observed at the metal-insulator transition temperature of $(TMTSF)_2ReO_4$.$^{4)}$ In $(TMTSF)_2BF_4$, disorder and/or thermal motion of BF_4^- is much larger than ClO_4^- in $(TMTSF)_2ClO_4$. The boron atom is not located on (0,0,0) (see Figs. 1 and 2). This may be due to the small size of the anion, which can move easily in a cavity produced by the TMTSF molecules.

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