CHEMISTRY LETTERS, pp. 559-562, 1987.

Molecular Structure of a New Multi-Sulfur π-Donor Molecule, Bis(vinylenedithio)tetrathiafulvalene, VT and Crystal and Electronic Structures of VT_2PF_6

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Multi-sulfur π-donor molecule, bis(vinylenedithio)tetrathiafulvalene, VT, is non-planar. Examination of crystal and electronic band structures revealed the one-dimensional nature of VT_2PF_6.

To date, several ambient organic superconductors have been found and the transition temperature of the organic superconductor has been enhanced up to 8 K.¹⁾ However, only a little is known about the way to obtain the molecular superconductors. Contrary to the first organic superconductor, Bechgaard salt with a one-dimensional (1D) open Fermi surface, the second ambient organic superconductor, β-(BEDT-TTF)$_2I_3$ and related compounds have strongly 2D electronic properties.²⁾ The recent report on the superconducting system of θ-(BEDT-TTF)$_2(I_3)_{1-x}(AuI_2)_x$ has suggested the existence of the ideally 2D electron gas in the organic system.³⁾

Very recently, a series of new molecular conductors based on multi-sulfur π-donor molecule, bis(vinylenedithio)tetrathiafulvalene (abbreviated hereafter as VT) have been synthesized and characterized.⁴⁾ In this paper, we will report molecular and crystal structures of neutral VT and VT_2PF_6.

The crystal of neutral VT is orange-colored. The crystal data determined by a Rigaku four-circle diffractometer are: $C_{10}H_4S_8$, monoclinic, space group $P2_1/c$, a=6.468(2), b=11.277(3), c=12.879(2) Å, β=134.42(2)°. V=671.0 Å^3, Z=2. Using the 1455 independent reflections ($|F_o|>3\sigma(|F_o|)$, $2\theta<60°$(Mo Kα)), the structure was solved by the direct method and refined to the final R-value of 0.043. The atomic coordinates are listed in Table 1.

The black crystals of VT_2PF_6 were obtained electrochemically. The crystal data are: $(C_{10}H_4S_8)_2PF_6$, triclinic, space group $P\bar{1}$, a=16.652(4), b=7.408(2), c=6.448(2) Å, α=100.05(2), β=103.44(2), γ=96.74(2)°, V=751.2 Å^3, Z=1. The number of the independent reflections ($|F_o|>3\sigma(|F_o|)$, $2\theta<60°$(Mo Kα)) is 3277. The R-value was reduced to 0.049. The final atomic coordinates are listed in Table 2.

The crystal structure of the neutral VT molecule is shown in Fig. 1. The VT molecules are on the centers of symmetry. The molecule is non-planar (Fig. 2). VT molecules are arranged side-by-side along a. The intermolecular short S···S contacts less than the van der Waals distance (3.70 Å) are found only along this direction (Fig. 3).

The crystal structure of VT_2PF_6 resembles those of $(TMTSF)_2PF_6$, $(TMTTF)_2PF_6$ and α-$(BEDT\text{-}TTF)_2PF_6$.5-7) Only one VT molecule is crystallographically independent and PF_6^- anion is on the inversion center (Fig. 4). Although the non-planarity of VT is reduced in the semication state ($VT^{1/2+}$) (see Fig. 5), the molecule can not be regarded as a planar molecule owing to the folded structure of the six-membered heterorings. The close side-by-side arrangement of the molecules commonly found in the crystals of molecular conductors based on the multi-sulfur π-molecules such as BEDT-TTF and BMDT-TTF2)also exists in VT_2PF_6. The intermolecular short S···S contacts are found along c. The shortest distance (S(7)(x,y,z)···S(8)(x,y,z-1)) is 3.43 Å, approximately equal to the shortest S···S distances in the BEDT-TTF compounds. Contrary to the BEDT-TTF compounds without close molecular stacking, VT_2PF_6 has diadic columns of VT along b. The shortest S···S distance along b is 3.55 Å (S(2)(x,y,z)···S(7)(x,y,z)). We have already pointed out that the "old criterion" on the design of the molecular metals, which requires the planarity of the molecule, must be revised.8) Again it should be stressed that the planarity of the molecule is not an indespensable requirement for the design of the molecular conductors.

The conductivity of VT_2PF_6 is 20 S cm^{-1} at room temperature, comparable to the room-temperature conductivity of well-known ambient-pressure superconductor β-$(BEDT\text{-}TTF)_2I_3$. The system shows a metal-like behavior above ca. 180 K, below which the resistivity is activated ($E_a \simeq 0.055$ eV (T<100 K)).4) Since the conduction band is formed by the intermolecular overlapping of the highest occupied molecular orbital (HOMO), the intermolecular overlap integrals of HOMO (S) were calculated.9) The interaction along b (b1, b2 (see Table 3)) is much larger than the other interactions. In addition, b1 is almost equal to b2. So that the system can be regarded as approximately regular 1D system with the band anisotropy almost equal to that of the Bechgaard salt($t_{//}/t_{\perp} \simeq 10$). The tight-binding band structure was calculated, using the simple approximation t=ES, where t is the transfer integral and E is the proportional constant of the order of the energy of HOMO. The periodically waved Fermi planes, almost identical to those of $(TMTSF)_2X$ and $(TMTTF)_2X$ (X=ClO_4, PF_6,···) were obtained (Fig. 6). Despite of the resemblance of the Fermi surfaces obtained by the simple tight-binding band calculations, the electronic properties of $(TMTSF)_2X$ and $(TMTTF)_2X$ are different to each other. In view of the magnitudes of the transfer integrals, VT_2PF_6 resembles $(TMTTF)_2X$ rather than $(TMTSF)_2X$. However, it is a delicate problem to predict the physical properties of VT_2PF_6 on the analogy of the simple band structures of these systems. The doubling of the lattice constants of VT_2PF_6 below 170 K ((a,b,c) → (2a,2b,2c)) reminds us of the similar structure changes in $(TMTSF)_2X$ and $(TMTTF)_2X$. The details of the structural phase transition and the suppression of the metal-insulator transition of VT_2PF_6 at high pressure will be reported in the near future.

Table 1. Fractional atomic coordinates ($\times 10^4$) with their estimated standard deviations for neutral VT

Atom	x	y	z
S(1)	1477(2)	365(1)	2103(1)
S(2)	4386(2)	534(1)	1093(1)
S(3)	6071(2)	1813(1)	4791(1)
S(4)	9265(2)	1992(1)	3654(1)
C(1)	1196(8)	181(4)	654(4)
C(2)	4672(8)	1191(4)	3160(4)
C(3)	5962(8)	1280(4)	2693(4)
C(4)	11063(9)	1588(4)	5444(4)
C(5)	9793(9)	1522(4)	5905(4)

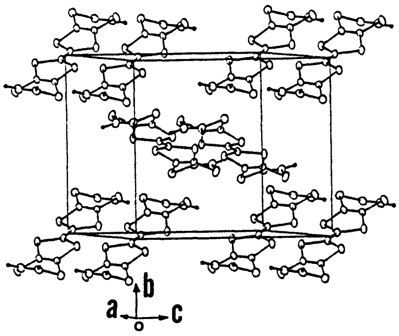


Fig. 1. Crystal structure of VT.

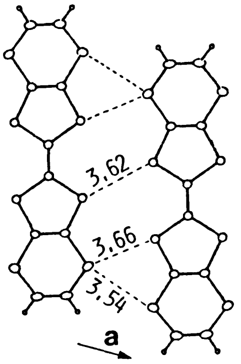


Fig. 3. Side-by-side arrangement of VT molecules in neutral VT.

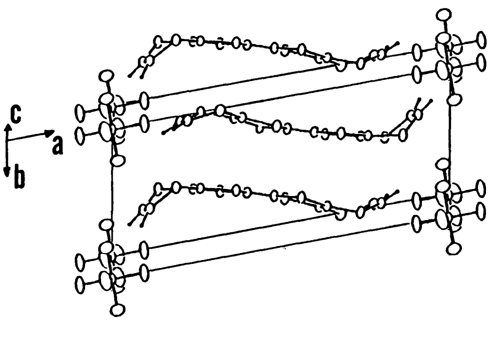


Fig. 4. Crystal structure of VT_2PF_6.

Table 2. Fractional atomic coordinates ($\times 10^4$) with their estimated standard deviations for $(VT)_2PF_6$

Atom	x	y	z
S(1)	6802(1)	3507(2)	50(2)
S(2)	6325(1)	4079(2)	4191(2)
S(3)	4879(1)	2137(3)	-2568(2)
S(4)	4384(1)	2704(2)	1548(2)
S(5)	8639(1)	4453(3)	2243(3)
S(6)	8103(1)	5141(3)	6876(2)
S(7)	3202(1)	270(3)	-5243(3)
S(8)	2618(1)	957(3)	-478(3)
C(1)	6007(3)	3413(9)	1367(9)
C(2)	5193(3)	2822(9)	261(9)
C(3)	7606(3)	4239(9)	2437(9)
C(4)	7390(3)	4508(9)	4318(9)
C(5)	3846(3)	1283(8)	-2666(9)
C(6)	3620(3)	1558(9)	-801(9)
C(7)	9089(4)	3535(10)	4516(11)
C(8)	8884(4)	3829(10)	6366(11)
C(9)	2229(4)	744(10)	-4894(11)
C(10)	2008(4)	1024(10)	-3059(11)
P	0	0	0
F(1)	168(4)	2154(8)	214(12)
F(2)	-953(3)	142(8)	-166(8)
F(3)	195(3)	305(9)	2548(7)

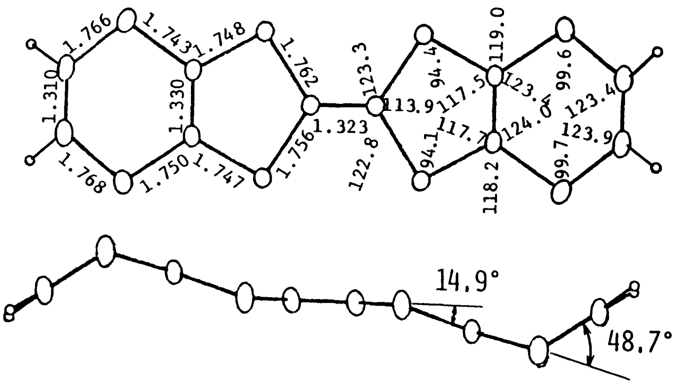


Fig. 2. Molecular structure of VT in neutral VT.

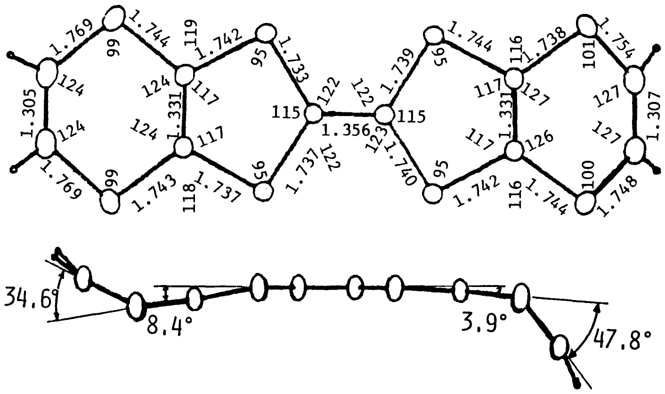
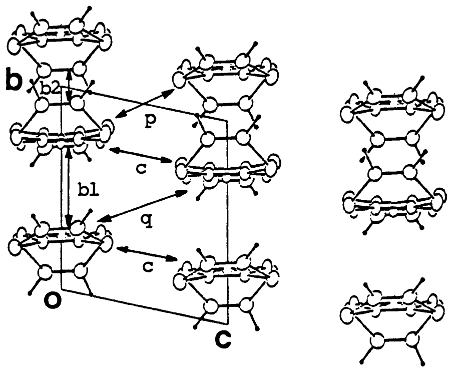


Fig. 5. Molecular structure of VT in VT_2PF_6.

Table 3. Intermolecular overlap integrals (S) of HOMO of VT

	S
b1	13.2×10^{-3}
b2	13.9
p	1.3
q	2.1
c	-1.4



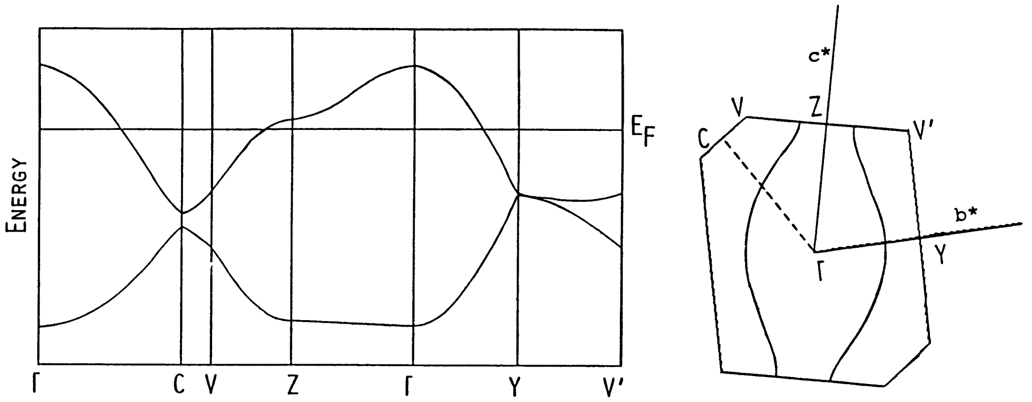


Fig. 6. Tight-binding band structure and Fermi surface of VT_2PF_6.

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9) In the calculation of the overlap integrals, the Slater exponents determined by Clementi were used (E. Clementi and C. Roetti, Atomic Data and Nuclear Data Tables, 14, 177 (1974).

(Received November 12, 1986)