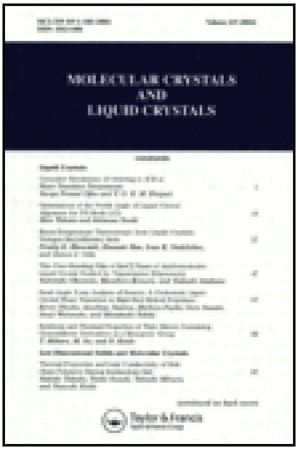

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Low Temperature and High Pressure (1.7K & 7 10^2 MPa) Structure of the First Superconducting Organic Salt $(TMTSF)_2PF_6$

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Low Temperature and High Pressure (1.7K & 7 10^2 MPa) Structure of the First Superconducting Organic Salt $(TMTSF)_2$ PF_6

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The neutron ($\lambda = 1.1750$Å) high pressure (7 10^2MPa) and low temperature (1.7K) structure of $(TMTSF)_2PF_6$ (Di(2,3,6,7-tetramethyl-1,4,5,8-tetraselenafulvalenium hexafluorophosphate; $2(C_{10}H_{12}Se_4)^{1/2+}$, PF_6^-, Mr = 1041.06) is reported. The lattice is triclinic $P\bar{1}$ and cell parameters:

a = 6.980(8), b = 7.581(3), c = 13.264(4)Å,
α = 84.17(3), β = 88.04(7), γ = 70.30(6)°
V = 657Å^3

The geometry of the TMTSF stacks changes little under constraint exception made for a shortening in the interplanar spacing. For the titled compound at 7 10^2 MPa a temperature decrease from 300K to 4K is equivalent to the effect of an extra 2 10^2MPa applied pressure. However temperature (rather than pressure) is responsible for a small change in the transverse shift of adjacent TMTSF molecules in a same column. Similarly pressure has little effect on the PF_6^- anion disorder at a given temperature.

If the low temperature TMTSF packing of $(TMTSF)_2PF_6$ (superconducting below ≃1.2K and above 9.5 10^2 MPa) is compared to that of $(TMTSF)_2$ ClO_4 (superconducting below ≃1,2K at ambient pressure), the *intrachain* interactions are found to be very similar. On the contrary, the low temperature strength of the *interchain* interactions in the PF_6^- salt requires an extra high pressure constraint to reach that observed in the ClO_4^- salt at ambient pressure.

Keywords: organic superconductors, structure, low dimensional solids

INTRODUCTION

Charge transfer $(TMTSF)_2^+ X^-$ salts (TMTSF = tetramethyltetraselenafulvalene, X^- = small anions) are known to undergo various instabilities especially towards a superconducting state; these transitions occur at low temperature and above a critical pressure which depends strongly of the nature of the anion. (For a review: see reference 1). Temperature as well as pressure are thus important parameters in the study of these compounds. For example, $(TMTSF)_2PF_6$ exhibits at $T_c = 11.5K$ a metal-insulator transition. Below T_c, the insulating ground state is found to be antiferromagnetic (spin density wave) while superconductivity occurs only below $T_{sc} = 1.2K$ under pressure.

All compounds in this family are isostructural.[2] They crystallize in the triclinic $P\bar{1}$ space group with very similar lattice constants. The quasi planar TMTSF units stack along the *a* direction and form *a*,*b* layers spaced by anions. Such a two-dimensional selenium network is well characterized by both intra and interchain Se-Se distances[3] which are some of the relevant parameters involved in theoretical models describing the competition of the various instabilities over the whole temperature and pressure range available to experiments.

Special interest has been focussed on the variation of these interactions under constraint. Most of the low temperature structure determinations have been performed on salts with non centrosymmetric anions such as $X^- = ReO_4^-$ [4,5] ClO_4^-[6] in which anion ordering may distort the TMTSF packing. Under pressure, only a few structural investigations have been published. All concerned centrosymmetric anions e.g.: $X^- = AsF_6^-$[7]. However the thermal expansion (4K to 295K) and the isothermal compressibility (from 10^{-1} to 16 10^2MPa) structures of the PF_6 salt have been recently described.[8] The latter temperature and/or pressure structural data set is presently the most complete one obtained on a $(TMTSF)_2$ X compound. It shows that varying temperature or pressure leads to a similar evolution of the TMTSF packing, the major aspects of which are:

(1) a shortening of intra and interchain distances $((1/d)/(\partial d/\partial T))_P$ and $((1/d)/(\partial d/\partial P))_T$ (in the ratio 1:1.5) which shows that the bidimensional character of this compound is apparently increased when either cooling or applying pressure.

(2) Se-Se distances obtained at T = 4K were found to be equivalent to those corresponding to an 8.10^2MPa applied pressure.

In this paper, we present structural data on $(TMTSF)_2 PF_6$ obtained both at low temperature and under high pressure: (1.7K & 7 10^2MPa).

For the first time, we describe the combined effects of temperature and pressure on the molecular packing of a $(TMTSF)_2$ X compound. For clarity, the (300K & 10^{-1}MPa), (4K & 10^{-1} MPa), (300K & 9.8 10^2MPa) and (1.7K & 7 10^2MPa) data on $(TMTSF)_2$ PF_6 are abbreviated as RTP, LT, HP and LTHP respectively.

EXPERIMENTAL PART

The measurements were carried out at the Institut Laue-Langevin (Grenoble-France) on the normal beam (lifting counter technique) diffractometer D15 installed on an inclined thermal neutron beam tube at the High Flux Reactor. Experimental conditions were as follows: incoming beam wavelength of 1.1750 Å (Cu(331) monochromator in transmission), neutron flux at sample position $\simeq 7$ 10^6 n.cm^2.sec^{-1}. Low temperatures were achieved with a reservoir type helium cryostat and pressures with a clamp pressure cell[9] made of maraging steel (Marval 18) (Figure 1). The pressure transmitting medium was Fluorinert FC 75† since it does not crystallize at low temperature and pressure below 18 10^2MPa. The applied pressure was determined from the reading of a strain gauge bridge which

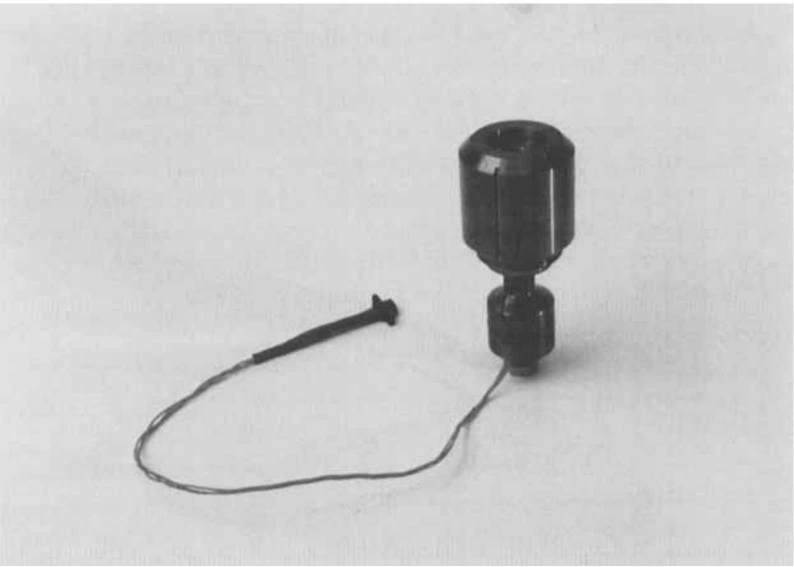

FIGURE 1 The clamp pressure cell made of maraging steel (ϕ_{inner} = 8 mm, ϕ_{outer} = 48 mm at sample level).

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†Fluorinert is a trade mark of 3M Company.

measures the deformation of the cell wall and has been calibrated against the lattice variations of NaCl.

The pressure was first increased up to 8 10^2MPa at room temperature and then the temperature was decreased. The latter pressure must be corrected from the pressure loss due to the thermal contraction of Fluorinert. At 1.7K, the correction is about 10^2MPa as previously checked by NaCl calibrations.[9] The experimental pressure at low temperature was thus $\simeq$7 10^2MPa.

Because of the high absorption ($\simeq$50%) of the incoming neutron beam by pressure cell and cryostat walls, the feasibility of such an experiment was conditioned by the availability of an unusually large crystal. The sample used was thus a hydrogenated (h_{24}) single crystal of 0.7 × 1.4 × 8.0 mm^3 but despite this, the average counting rate was relatively low.

Lattice parameters of $(TMTSF)_2PF_6$ at T = 1.7K & P = 7 10^2MPa computed from the observed diffraction angles of 15 strong Bragg reflections are:

$$a = 6.980(8)\ \text{Å},\ b = 7.581(3)\ \text{Å},\ c = 13.264(4)\ \text{Å}$$
$$\alpha = 84.17\ (3)\ ^\circ,\ \beta = 88.04\ (7)\ ^\circ,\ \gamma = 70.30\ (6)\ ^\circ$$
$$V = 657.4\ \text{Å}^3$$

The above values and the LT lattice parameters[8] made it possible to calculate the quasi isothermal compressibility of $(TMTSF)_2PF_6$ at 1.7-4K (Table I). The LT compressibilities along cell axes a, b and c are found to be respectively about 2.1, 2.8 and 4 times smaller than at 300K and thus the anisotropy of the elastic properties of the material increases upon cooling. It may be also noted that the compressibility along the stacking axis of the organic metal TTF.TCNQ is decreased by a factor 2.3 from 300K to 10K[10] a value slightly larger than that of 2.1 observed for the a axis of $(TMTSF)_2$ PF_6.

TABLE I Low temperature (1.7-4K) quasi isothermal compressibility of $(TMTSF)_2PF_6$.

$$k_v = \left(\frac{-1}{V}\frac{\delta V}{\delta P}\right)_T \qquad k_l = \left(\frac{-1}{l}\frac{\delta l}{\delta P}\right)_T$$

		300K	1.7-4K
k_a	$(\times 10^4 MPa^{-1})$	0.41	0.20
k_b	$(\times 10^4 MPa^{-1})$	0.27	0.10
k_c	$(\times 10^4 MPa^{-1})$	0.25	0.06
$B = k_v^{-1}$	(MPa)	100 10^2	294 10^2

The intensities of 2159 independent Bragg reflections ($\sin\theta/\lambda <$ 0.7713 $Å^{-1}$) were collected by means of ω scans of 31 steps and with the angular width an experimental function of the Bragg angle θ. All reflections belong to the hkl reciprocal planes with $0 \leqslant h \leqslant 4$, $kmax \leqslant 11$, $lmax \leqslant 20$. Data reduction was performed with the help of the $\sigma(I)/(I)$ algorithm of Lehmann & Larsen.[11] Intensities were corrected for the Lorentz factor and for the absorption from the cell walls. (μ calculated = 1.25 cm^{-1}) to obtain structure factor (F_0).

The least square refinement of the structure was of the block diagonal type based on F_0 and with starting values the LT coordinates.[8] Atomic scattering factors were from Bacon.[12] Only isotropic atomic thermal parameters were used. All hydrogen atoms were refined. The final value of the reliability factor $R = \Sigma \, \|F_0| - |F_0\|/\Sigma|F_0|$ is $R \simeq 0.058$. The ratio of maximum least-squares shifts to error is found ($\Delta/\sigma \simeq 0..136$). Final coordinates are given in Table II; bond lengths and angles are displayed Figure 2.

STRUCTURE

As already observed in the case of the LT and HP structures of $(TMTSF)_2$ PF_6, there is no evidence for the loss of the inversion center at high pressure and low temperature. The LTHP structure was thus refined in the $P\bar{1}$ space group. The atom and interaction labelling initially used by Thorup[3] for the RTP structure of the compound is kept in the following. Side view of the stacks and projection in the b, c plane are displayed Figures 3a and 3b.

TMTSF Stacks: Combined effects of temperature and pressure do not significantly distort the zig-zag configuration of the RTP stacking. TMTSF units are still planar† and the angle between the *a* direction and the normal to the molecular TMTSF plane remains equal to 1.2°. The major effect on the overlap of adjacent molecules within a stack is a small change ($\simeq$0.03 Å) in the transverse shift parameters Δt (Table III). The latter change has been observed in the LT structure but not in the HP one and thus it appears to be a *typically low temperature effect*. As already observed at T = 4K, stacks are slightly dimerized (d_1 = 3.50 Å; d_2 = 3.48 Å). From data listed in Table III, the d_1 & d_2 shortening induced by lowering the temperature is

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†The mean plane is defined over C(3),C(13) and Se atoms. The largest deviation from planarity is found less than 0.02Å.

TABLE II Fractional coordinates (x,y,z) and isotropic thermal parameters (B) of atoms at (1.7K & 7 10^2MPa).

	X	Y	Z	B
Se(1)	3078(7)	3344(3)	6161(1)	.27(2)
Se(2)	1614(7)	7515(3)	5110(1)	.29(2)
Se(11)	3763(7)	1667(3)	3843(1)	.29(2)
Se(12)	2201(7)	5848(3)	2795(1)	.30(2)
C(1)	2334(9)	5360(3)	6997(2)	.34(2)
C(2)	1708(9)	7134(3)	6547(2)	.31(3)
C(3)	2526(9)	4929(3)	4942(1)	.30(3)
C(4)	1003(9)	8924(3)	7063(2)	.42(3)
C(5)	2509(9)	4754(3)	8116(2)	.47(3)
C(11)	3730(9)	2048(3)	2407(1)	.32(3)
C(12)	3074(9)	3830(3)	1959(2)	.32(3)
C(13)	2786(9)	4258(3)	4011(1)	.34(3)
C(14)	2883(9)	4415(3)	0829(2)	.38(3)
C(15)	4497(9)	0270(3)	1875(2)	.44(3)
H(101)	−055(2)	958(1)	699(1)	2.6(1)
H(102)	605(2)	−039(1)	199(1)	2.3(1)
H(103)	200(2)	598(1)	856(1)	1.4(1)
H(111)	157(2)	386(1)	833(1)	2.1(1)
H(112)	407(2)	396(1)	832(1)	2.1(1)
H(113)	141(2)	864(1)	787(1)	1.6(1)
H(121)	166(2)	993(1)	671(1)	1.8(1)
H(122)	146(3)	479(1)	059(1)	2.8(1)
H(123)	342(2)	559(1)	064(1)	1.8(1)
H(131)	384(2)	325(1)	041(1)	1.8(1)
H(132)	420(2)	057(1)	106(1)	1.5(1)
H(133)	377(2)	−073(1)	217(1)	2.04(1)
P	000(0)	000(0)	0000(0)	.41(5)
F(1)	0148(9)	−1237(4)	1074(2)	.44(3)
F(2)	2393(8)	−1039(4)	−0179(2)	.69(4)
F(3)	0497(9)	1593(4)	0548(2)	.55(4)

Fractional coordinates are × 10^3 for hydrogen atoms and × 10^4 for others. E.S.d's are given in parentheses.

nevertheless smaller under high pressure than at room pressure:

$$\left(\frac{1}{d}\frac{\partial d}{\partial T}\right)10^{-1}\text{MPa} \simeq 1.0\ 10^{-4}\ \text{K}^{-1};$$

$$\left(\frac{1}{d}\frac{\partial d}{\partial T}\right)7\ 10^{2}\text{MPa} \simeq 0.60\ 10^{-4}\ \text{K}^{-1}$$

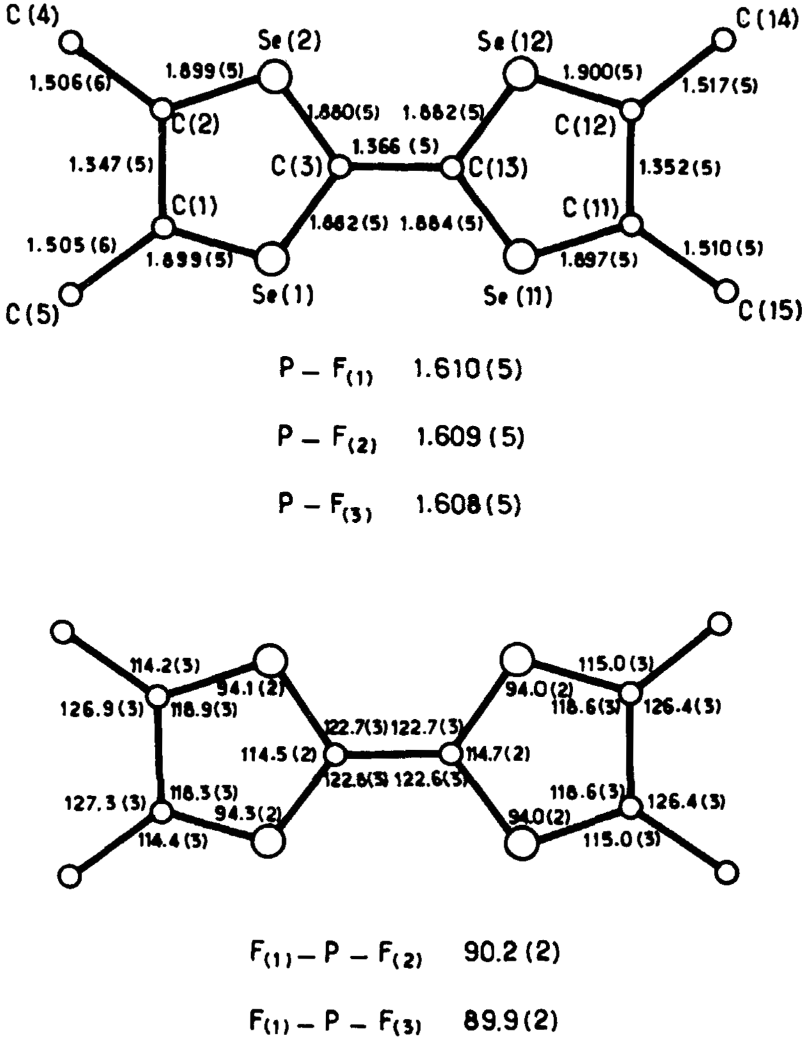


FIGURE 2 Bond lengths (Å) and angles (°) for the (TMTSF)$_2$PF$_6$ structure at (1.7K & 7 10^{2}MPa). E.s.d's are given in parentheses.

and thus induced temperature and pressure effects are not simply cumulative since the material becomes harder under constraint. Gallois *et al.*[8] have already reported that the interplanar distances are of similar lengths in the structures at (4K & 10^{-1}MPa) and (300K & 6.5 10^{2}MPa); we observe that interplanar distances at (1.7K & 7 10^{2}MPa)

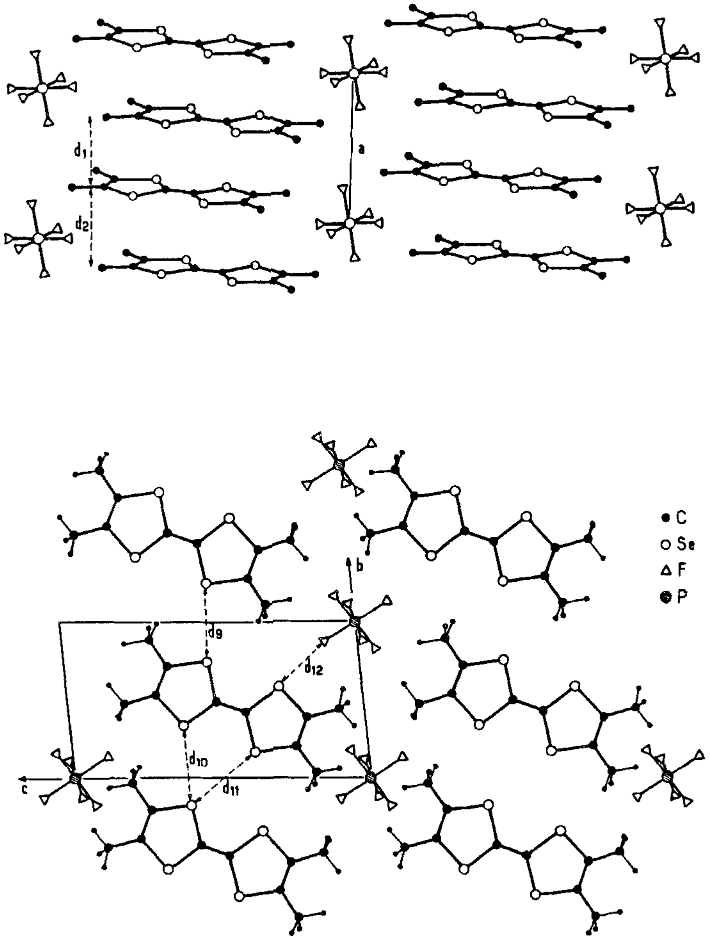


FIGURE 3 Structure of $(TMTSF)_2PF_6$: a) Side view of the stack. d_1 and d_2 are interplanar spacings. b) projection along the a axis. d_9, d_{10} and d_{11} label the shortest interchain Se. . .Se distances whereas d_{12} is the shortest Se. . .F distance.

are close to those at (300K & 9.8 10^2MPa). In other words, *as far as interplanar distances are concerned, a 300K to 4K temperature decrease under a constant pressure of 7 10^2MPa is equivalent to an increase of 2 10^2MPa only.*

Electrical conduction occurs mainly via the orbital overlap of Selenium atoms and thus clearly depends on the T and/or P induced changes in the stacking of TMTSF molecules. A simple picture to take into account variations in the main structural parameters (TMTSF molecular shifts: $\Delta l, \Delta t$; interplanar distances: d_1, d_2 and angles be-

TABLE III Interplanar distances (d_1,d_2), overlap parameters (Δt_i,Δl_i) and corresponding "intrastack overlap volumes" (V_1,V_2) in TMTSF stacks. – d_1 and d_2: distances between the mean molecular plane of a given (X,Y,Z) TMTSF molecule to a $1-X,1-Y,1-Z$) or ($-X,1-Y,1-Z$) adjacent one respectively.

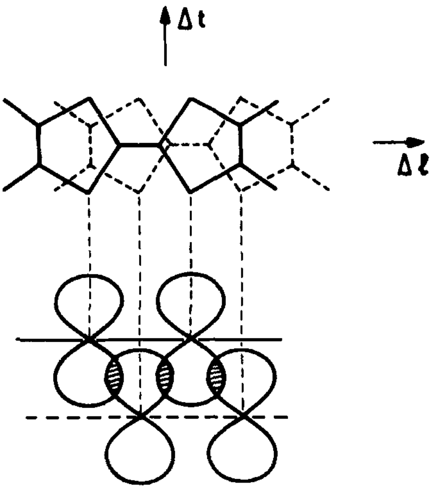
—d_3 to d_8; shortest intrastack Se-Se distances.

—Δ_{l1}, Δ_{l2}, Δ_{t1}, Δ_{t2} (in Å); relative shifts of molecular center of mass along (Δl) and across (Δt) the molecular elongation axis (see inset figure).

—V_1, V_2: intrastack molecular overlap volume of TMTSF dimers.

	300K (10^{-1}MPa)[a]	4K (10^{-1}MPa)[b]	6.5 10^{2}MPa (300K)[b]	9.8 10^{2}MPa (300K)[b]	1.7K (7 10^{2}MPa)[c]
*d*1 (Å)	3.66(1)	3.55(1)	3.56(1)	3.50(1)	3.50(1)
*d*2	3.63(1)	3.52(1)	3.56(1)	3.50(1)	3.48(1)
*d*3	4.044(2)	3.915(7)	3.958(3)	3.885(6)	3.872(4)
*d*4	3.983(2)	3.861(7)	3.891(3)	3.810(6)	3.815(4)
*d*5	4.067(2)	3.943(7)	3.979(3)	3.924(6)	3.893(4)
*d*6	3.874(2)	3.866(7)	3.817(3)	3.780(6)	3.765(4)
*d*7	3.927(2)	3.799(7)	3.872(3)	3.834(6)	3.828(4)
*d*8	4.133(2)	4.054(7)	4.061(3)	3.995(6)	4.004(4)
Δ*l*1	1.666(2)	1.648(2)	1.625(6)	1.56(1)	1.644(3)
Δ*t*1	0.033(2)	0.005(3)	0.055(7)	0.08(1)	0.002(4)
Δ*l*2	1.453(2)	1.469(2)	1.436(6)	1.43(1)	1.430(3)
Δ*t*2	0.052(2)	0.064(3)	0.064(7)	0.09(1)	0.078(4)
V1 (Å3)	1.176	1.93	1.75	2.20	2.500
V2	0.589	1.82	1.30	2.00	2.58

[a] Thorup et al. (1981).
[b] Gallois et al. (1986).
[c] This work.



tween molecular planes) involved in the stacking description is to define an "intrastack overlap volume" of the Se atoms. For both dimers, the corresponding volumes (V_1 and V_2) are computed as the sum of all Se intrasack volumes of overlap,[13] the atoms being taken as spheres with radius slightly larger (2.1 Å) than the usual atomic van der Waals radius (r_{Se} = 2.0 Å).[14]

At room temperature, the calculated values of V_1 and V_2 (see Table III) strongly differ from one dimer to the other whilst, at low temperature, they are close to each other, independently of the applied pressure. Since the diadic character (d_1-d_2) is almost unchanged by T and P, the change in V_1, V_2 must be related to the low temperature behaviour of the overlap transverse components (Δl,Δt) mentioned above. Under constraint, V_1 and V_2 increase strongly. At T = 4K, they are found to be intermediate to that at 6.5 10^2MPa and 9.8 10^2MPa. At 1.7K & 7 10^2MPa, their variation from normal conditions are equivalent to the sum of those obtained when T and P effects are independently applied and thus for V_1 and V_2, T and P effects are cumulative.

Calculations performed on $(TMTSF)_2$ ClO_4 lead to similar results. V_1 and V_2 are very unequal at room temperature. ($V_{1\ 300K}$ = 1.21 Å^3, $V_{2\ 300K}$ = 0.74 Å^3) but are nearly equivalent at low temperature ($V_{1\ 7K}$ = 1.75 Å^3, $V_{2\ 7K}$ = 1.87 Å^3) and of the same order of magnitude of the LT values calculated for $(TMTSF)_2$ PF_6.

In other words, *the TMTSF stacking in the* PF_6^- and ClO_4^- *salt are similar at low temperature* (i.e. similar interplanar distances and identical modifications in the transverse overlap components).

TABLE IV Shortest interstack Se. . .Se and Se. . .F distances labelled in Figures 3b.

	300K (10^{-1}MPa)	4K (10^{-1}MPa)	6.5 10^2MPa (300K)	9.8 10^2MPa (300K)	1.7K (7 10^2MPa)
Interstack data.					
*d*9 (Å)	3.879(1)	3.711(7)	3.732(3)	3.657(6)	3.669(4)
V'1 (Å3)	0.328	0.753	0.694	0.925	0.885
*d*10 (Å)	3.934(1)	3.737(7)	3.777(3)	3.678(6)	3.695(4)
*d*11 (Å)	3.959(2)	3.859(7)	3.847(3)	3.753(6)	3.826(4)
V'2 (Å3)	0.642	1.729	1.528	2.351	1.700
Shortest Se . . . F distance					
*d*12 (Å)	3.233(7)	3.068(9)	3.123(13)	3.005(23)	3.036(6)

E.s.d's are given in parentheses.
V'_1 and V'_2 are the "interstack overlap volumes" between a (X,Y,Z) and a ($-X$,$2-Y$,$-1-Z$) or ($1-X$,$-Y$,$1-Z$) TMTSF molecule respectively.

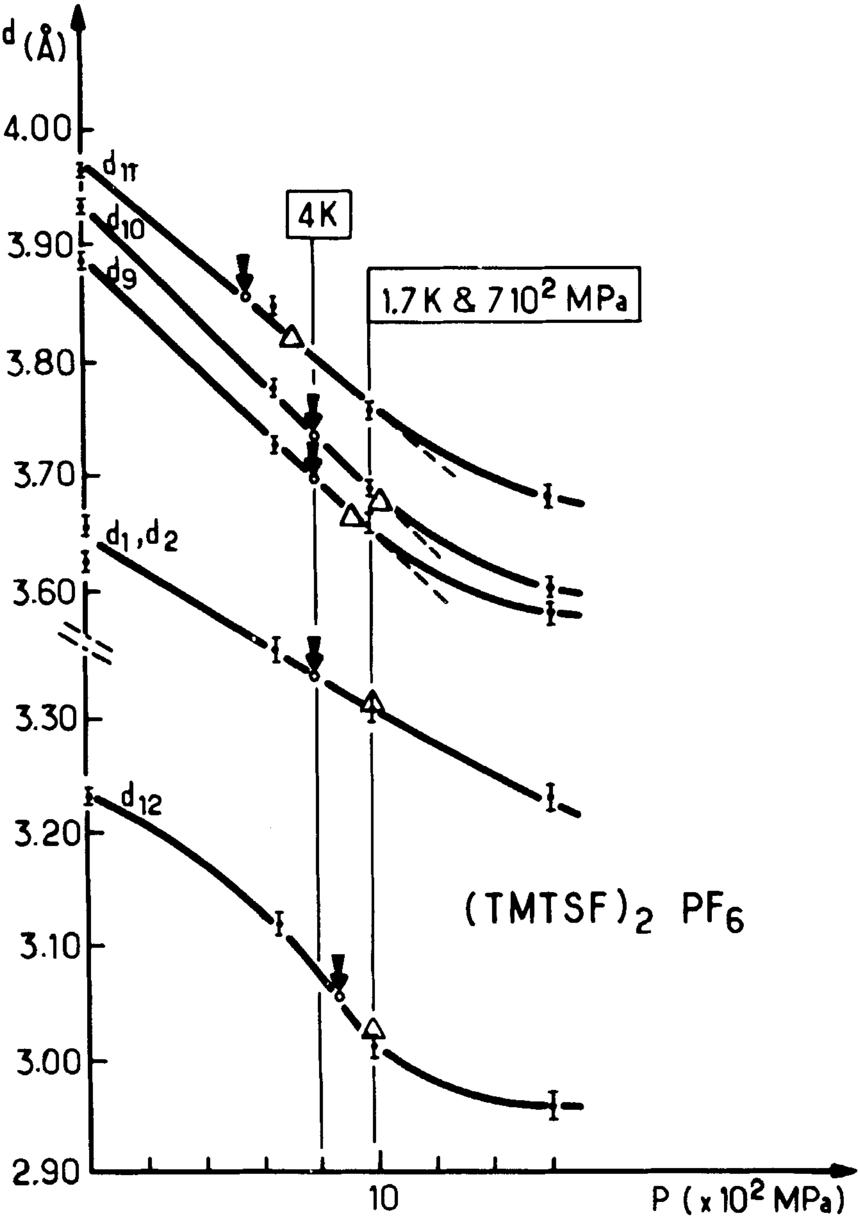


FIGURE 4 Pressure dependence of the shortest Se. . .Se and Se. . .F interactions labelled in Figure 2. Values at 16 10^{2}MPa are from recent X-Ray structural determinations which will be published elsewhere. Heavy arrows indicate the corresponding values observed at 4K under normal pressure and lights arrows are for the values at 1.7K & 7 10^{2}MPa.

TABLE V Observed values of the ϕ_i angles between a TMTSF molecular plane and the directions of the shortest Se. . .Se distances with the nearest TMTSF molecules. The latter distances (Å) are given in parentheses below the corresponding angles (°).

	300K (10^{-1}MPa)	4K (10^{-1}MPa)	6.5 10^2MPa (300K)	9.8 10^2MPa (300K)	1.7K 7.2 10^2MPa
ϕ1	18.44(3)	15.99(13)	17.73(5)	16.42(15)	15.62(6)
	|3.879(1)|	|3.711(6)|	|3.732(3)|	|3.651(5)|	|3.669(2)|
ϕ2	18.24(3)	14.97(12)	16.57(5)	15.57(15)	14.53(6)
	|3.934(1)|	|3.737(6)|	|3.777(2)|	|3.678(5)|	|3.695(2)|
ϕ3	35.73(3)	38.02(12)	36.90(5)	38.10(15)	38.26(6)
	|4.167(2)|	|4.156(7)|	|4.097(3)|	|4.156(8)|	|4.114(3)|
ϕ4	54.89(3)	53.41(10)	54.75(4)	54.32(12)	53.09(6)
	|5.941(2)|	|5.620(6)|	|5.721(3)|	|5.545(8)|	|5.540(3)|

Interchain interactions: The shortest Se-Se interchain distances in $(TMTSF)_2\ PF_6$ are listed in Table IV. The LTHP data are found to be nearly equivalent to that at 300K & 10.10^2MPa (Figure 4). The values of the isobar shortening at ambient pressure $((1/d)/(\partial d/\partial T))_{10^{-1}\mathrm{MPa}} \simeq 1.5\ 10^{-4}\mathrm{K}^{-1}$, and under high pressure $((1/d)/(\partial d/\partial T))_{7\ 10^2\mathrm{MPa}} \simeq 0.5\ 10^{-4}\mathrm{K}^{-1}$ confirm the small influence of temperature on the TMTSF packing as pressure is applied.

The ϕ_i angles† between the (X,Y,Z) TMTSF molecular plane and the shortest Se-Se interactions of the nearly TMTSF molecules are believed to be other pertinent structural parameters required for understanding the electrical properties of 1D organic conductors and superconductors.[15,16] The observed values for $(TMTSF)_2\ PF_6$ are reported in Table V. Their evolutions are very similar to those early mentioned when either temperature is reduced or when pressure is increased. Moreover it appears that the differences observed at low temperature between the PF_6^- and ClO_4^- salts[6,8] are reduced under pressure. In other words, the low temperature $(TMTSF)_2PF_6$ interchain interactions, geometrically characterized by larger Se-Se distances and ϕ_i angles evolve under pressure towards the 7K $(TMTSF)_2\ ClO_4$ configuration.

Relative shift components of TMTSF molecules (x and y across and along the TMTSF elongation axis respectively, z normal to the molecular plane) listed in Table VI lead to the ϕ_1 and ϕ_2 variations. They give evidence for shift of the $(-X,2-Y,1-Z)$ and

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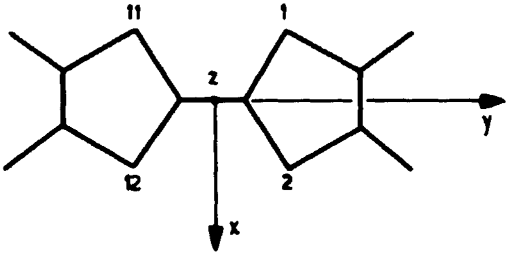
†Defined in more details in Reference 8.

TABLE VI Relative shift of TMTSF molecules under constraint ΔX, ΔY, ΔZ: components of the displacement of a given TMTSF molecule from its position under normal conditions towards the molecule (X,Y,Z). The directions are defined in the inset figure with respect to molecule I. All values are in Å. E.s.d's are less than 0.01 Å.



$\bar{I} + 2b + c$	$\Delta x = -0.12$	$\Delta x = -0.12$
	$\Delta y = -0.04$	$\Delta y = -0.04$
	$\Delta z = -0.19$	$\Delta z = -0.24$
$\bar{I} + a + c$	$\Delta x = 0.07$	$\Delta x = 0.13$
	$\Delta y = 0.06$	$\Delta y = 0.09$
	$\Delta z = 0.28$	$\Delta z = 0.32$

$(1-X,-Y,1-Z$, molecules towards the (X, Y,Z) unit under both applied constraints.

It is noteworthy that the orbital overlaps between selenium atoms of the nearest interstack TMTSF units will change since both Se-Se distances and angles describing all these interactions are highly dependent on constraint. To shed some lights on this latter point, we may calculate approximate "interstack overlap volumes" (V_1' and V_2') equal to the intersection volume of Se atomic spheres of adjacent (X,Y,Z) and $(-X,2-Y,1-Z)$ or $(1-X,-Y,1-Z)$ TMTSF units respectively. The resulting values of V_1' and V_2' (Table IV) exhibit similar increases under both T and P constraints. It may be also noted that V_1' is larger than V_2' although the short Se-Se distances involved in the formulation of V_1' and V_2' are one (d_9) for the former and three (d_{11} and two symmetry related d_{10}) for the latter.

Cation-Anion Interactions: Interactions between TMTSF stacks and PF_6 anions are enhanced by T and P effects and become significant. E.g. the LTHP structure shows a Se-F(1) distance ($d_{12}=3.02$ Å) shorter than the sum of atomic van der Waals radii ($r_{Se}+r_F=3.35$ Å) and close to the d_{12} value (3.00 Å) already observed at HP. Nevertheless, the latter shortening (Figure 4) is almost achieved at LT and thus temperature is the most relevant parameter in that case. This can be seen by looking to the shortest F. . .H—CH_2 distances between the TMTSF methyl group surrounding a PF_6 anion. In fact, they show no noticeable shortening from LT to LTHP (4K: 2.45 Å, 2.46 Å, 2.46 Å; 1.7K & 7 10^2 MPa: 2.45 Å, 2.47 Å, 2.46 Å). This leads to the conclusion that the volume of the anion cavity changes little from LT to LTHP since the Se-F and F. . .H—CH_2 interactions binding the anion to the surrounding TMTSF molecules are almost unchanged by pressure at low temperature. The *PF_6 anion* remains necessarily centrosymmetric since the P atom sits at the inversion center. *Its shape is no longer distorted at LTHP* as it was the case under normal conditions and presents an almost perfect octahedral shape. Bonds and angles are shown in Figure 2.

The thermal motion parameters (Table II) of all the fluorine atoms do not drastically decrease from LT to LTHP and remain in an almost similar ratio. The thermal motion of the anion is thus only slightly affected. This strongly supports the hypothesis of an almost complete freezing of the anion at LT[8] and confirms *the pre-eminent influence of temperature effects on the anionic structural behaviour.*

In conclusion, this high pressure and low temperature structural investigation of $(TMTSF)_2PF_6$ gives evidence of non-cumulative temperature and pressure effects on the TMTSF packing. In fact, at $T = 4K$, the pressure effect is strongly minimized as compared to room temperature. However it is still sufficient to induce enhanced intra and interchain Se-Se interactions which tend to give the same geometrical characteristic to the Selenium network in $(TMTSF)_2$ PF_6 at LTHP than to $(TMTSF)_2$ ClO_4 at LT. On the other hand, the anion-cation interactions and the anion thermal motion are found to be almost pressure independent at low temperature.

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