

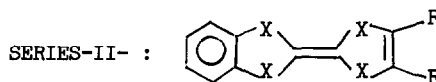
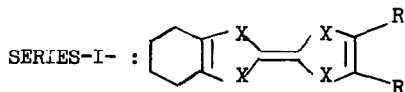
**NEW RADICAL-CATION SALTS CONTAINING
AN UNSYMMETRICALLY SUBSTITUTED TTF OR TSF
TYPE π -DONOR. SYNTHESIS AND CHARACTERIZATION**

J.M. FABRE, A.K. GOUASMLA, L. GIRAL
Laboratoire de Chimie Structurale Organique
U.S.T.L., Place Eugène Bataillon
34060 MONTPELLIER CEDEX

D. CHASSEAU
Chemical Crystallography Laboratory 9, Parks Road OXFORD U.K.
(Permanent address : Laboratoire de Cristallographie L.A. 144
UNIVERSITE DE BORDEAUX I 33405 TALENCE)

ABSTRACT : A number of unsymmetrically substituted tetraheterofulvalenes have been prepared. Their half wave potentials have been measured by cyclic voltammetry and compared with that of TTF. Their perchlorate and hexafluorophosphate salts have been electrochemically synthesized and their electrical properties studied. Some structural data are also given.

Since the discovery of highly conducting materials in the tetrathiafulvalene (TTF) and tetraselenafulvalene (TSF) families, much effort has been devoted in the synthesis of donor molecules producing salts with metallic properties (1). Recently, we have reported that radical cation salts of unsymmetrically alkylated TTF and TSF showed higher conductivities than their symmetrical analogues (2, 3). Considering these points, we have synthesized a number of unsymmetrically substituted TTF and TSF. Two series containing a benzo or a cyclohexyl group have been prepared.



X = Se ; 1 : R = H ; 2 : R = (CH₂)₃

X = S ; 5 : R = (CH₂)₄ ; 6 : R = H

X = S ; 3 : R = H ; 4 : R = (CH₂)₃

7 : R = CH₃ ; 8 : R = (CH₂)₃

- SYNTHESIS. -

Several methods of preparing the "unsymmetrical" tetrathiafulvalenes have been reported (4). We used the one based on the WITTIG-TYPE reaction described by CAVA (5). As earlier mentioned (6), the intrinsic instability of the ylid, formed as an intermediate in such a reaction, leads to a mixture in which the unsymmetrical species is the major product. The latter is easily separated by column chromatography (SiO₂-CS₂). The selenium derivatives 1 and 2 have been prepared by a cross-coupling method (4) using the appropriate 1,3-diselenole 2-selones as intermediate. Their separation was performed as described above. The half wave potentials of each π -donor prepared are summarized in table I.

TABLE - I - Half wave potentials of each unsymmetrically substituted tetraselena and tetrathiafulvalene prepared.

	CHTSF	CPCHTSF	CHTTF	CPCHTTF	BCHTTF	BTTF	BDMTTF	BCPTTF
N°	1	2	3	4	5	6	7	8
Redox $E_{1/2}^1$	580	500	420	340	530	600	500	535
Pot. (mV) $E_{1/2}^1$	955	900	840	825	1000	940	960	980

- Half wave potentials were measured by cyclic voltammetry : Pt/Pt/SCE : (TBAP - 1,1,2 trichloroethane, 0.1 M) : scan rate : 100 mV/s; $E_{1/2}^1$ (TTF) = 480 mV.
- The elemental analysis (C, H, S, Se) are consistent with each proposed formula.
- The $^1\text{H-NMR}$ data and melting points have already been published (7).

The salts were prepared in THF - NBu_4X by the well known electro-oxidation procedure (8) using a constant current of about 10 μA . For each TTF, TSF, two cases were systematically investigated considering the anion symmetry. Perchlorate and hexafluorophosphate were chosen as non centro-symmetric and centro-symmetric anions respectively. In addition, other salts were prepared in particular cases. According to the elemental analysis all the salts displayed a 2 : 1 stoichiometry.

- ELECTRICAL CONDUCTIVITY. -

The conductivity measurements were carried out by the usual four probe technique (9) on either the compressed pellets of the salt or their single crystals when it was possible to obtain them. The results are reported in table II.

TABLE II. Values of electrical conductivity measured at room temperature ($\Omega^{-1} \text{cm}^{-1}$).

	SERIES-I-		SERIES-II-			
	3	4	5	6	7(a)	8(b)
	CHTTF	CPCHTTF	BCHTTF	BTTF	BDMTTF	BCPTTF
ClO_4	0.6	2.10^{-5}	0.1^*	3.10^{-2}	2.10^{-4}	10^{-2**}
PF_6	1	—	1.10^{-3}	1^*	3.10^{-4}	10

single crystals obtained as very fine needles* or as very thin platelets**.

(a) : $(\text{BDMTTF})_2 \text{X}$ (X = ReO_4 : $= 2.10^{-5} \Omega^{-1} \text{cm}^{-1}$; X = AsF_6 : insulating)

(b) : $(\text{BCPTTF})_2 \text{X}$ (X = BF_4 : $= 3.10^{-2} \Omega^{-1} \text{cm}^{-1}$; X = AsF_6 : $= 3.5 \Omega^{-1} \text{cm}^{-1}$).

The compounds 1 and 2 were obtained in too small amount to be electrically measured. It is to be noted (table II), that some salts display a room temperature conductivity $< 1 \Omega^{-1} \text{cm}^{-1}$, especially as seen with $(\text{BCPTTF})_2 \text{AsF}_6$ and PF_6 . Generally TTF molecules containing a benzo-group as substituent give insulating or semiconducting salts. The temperature dependence of the normalized electrical conductivity of such AsF_6 and PF_6 salts are shown in figure I.

FIGURE-I- Temperature dependence of the normalized electrical conductivity of $(\text{BCPTTF})_2\text{PF}_6$; AsF_6 and $(\text{TMTTF})_2\text{PF}_6$ taken as reference.

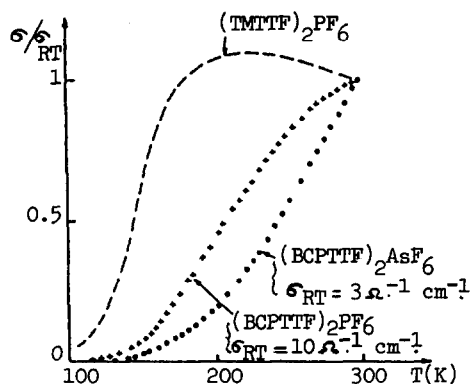
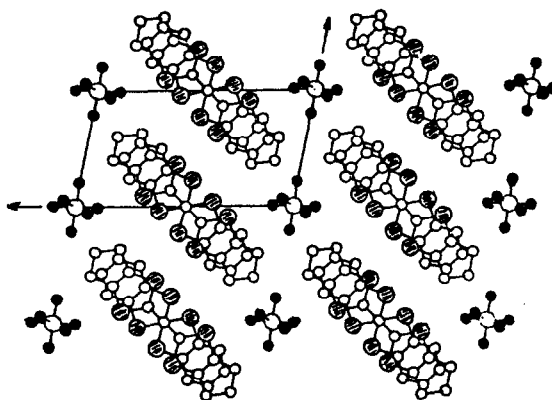


FIGURE-II- Crystal structure of $(\text{BCPTTF})_2\text{PF}_6$. Projection along the stacking axis (a-axis).

○ = C ; ● = S ; ● = F ; ○ = P.



The obtained data are compared with the results recorded for $(\text{TMTTF})_2\text{PF}_6$ (dashed line). In contrast with the broad maximum observed for $(\text{TMTTF})_2\text{PF}_6$, a semiconducting behavior is already present at room temperature for the BCPTTF salts. For the hexafluorophosphate, the curvature of $\sigma(T)$ near 300 K may be a precursor for a saturation of the conductivity at higher temperature. This effect is not seen for the hexafluoroarsenate salt indicating in this case a more pronounced tendency towards an activated resistivity which is in agreement with the lower room temperature conductivity observed for the $(\text{BCPTTF})_2\text{PF}_6$ salt.

- STRUCTURAL DATA. -

The conducting salt $(\text{BCPTTF})_2\text{PF}_6$ and AsF_6 are isomorphous and exhibit the following crystal data ($\text{Cu-K}\alpha$; $\lambda = 1.5418 \text{ \AA}$) :

$a = 7.137$; $b = 7.637$; $c = 17.736 \text{ \AA}$; $\alpha = 101.73$; $\beta = 91.26$; $\gamma = 99-68^\circ$; $V = 720.4 \text{ \AA}^3$.
for $(\text{BCPTTF})_2\text{PF}_6$.

$a = 7.141$; $b = 7.641$; $c = 13.837 \text{ \AA}$; $\alpha = 101.62$; $\beta = 91.57$; $\gamma = 99.03$; $V = 728.9 \text{ \AA}^3$.
for $(\text{BCPTTF})_2\text{AsF}_6$.

As reported in figure II, the crystal structure ($R = 0.052$) of $(\text{BCPTTF})_2\text{PF}_6$ shows columns of BCPTTF molecules stacked along the a-axis. The columns form sheets by translation along the b-direction. The PF_6 anions which separate each sheet along the c-axis, are localized on centers of symmetry. Within the columns the overlapping modes are quite similar to those observed in the $(\text{TMTTF})_2\text{X}$ series (10, 11). However, in contrast, the interchain S.....S distance is shorter (3.65 \AA ; 3.87 \AA) than in $(\text{TMTTF})_2\text{PF}_6$ (11).

According to the angle ($\psi = 22.7^\circ$; 32.7°) between the S...S direction and the BCPTTF molecular plane, it is predictable that the corresponding transfer integral will be weak (12). Such a result is not favorable to stabilize a metallic behavior with a decreasing temperature (2, 3).

In conclusion, a series of new radical cation salts involving unsymmetrical -donors of TTF and TSF type have been synthesized and their electrical properties studied. $(\text{BCPTTF})_2\text{PF}_6$ is the first example of a conducting salt in which the unsymmetrical -donor bears a benzo group. Its semiconducting behaviour can be explained considering both its structural and electronic characteristics. Quite generally the electrical behavior of $(\text{TMTTF})_2\text{X}$; $(\text{BPTTF})_2\text{X}$ salts, is understood in terms of continuous electronic localization below a given temperature T_p at which the maximum of the conductivity occurs (13). Our results (figure 1) indicate that the localization increases going from $(\text{TMTTF})_2\text{PF}_6$ to $(\text{BCPTTF})_2\text{PF}_6$ and $(\text{BPCTTF})_2\text{AsF}_6$. A more developed discussion including magnetic data and detailed structures will be given elsewhere.

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