

## TETRAHETERAFULVALENES AS PRECURSORS OF CONDUCTING MATERIALS

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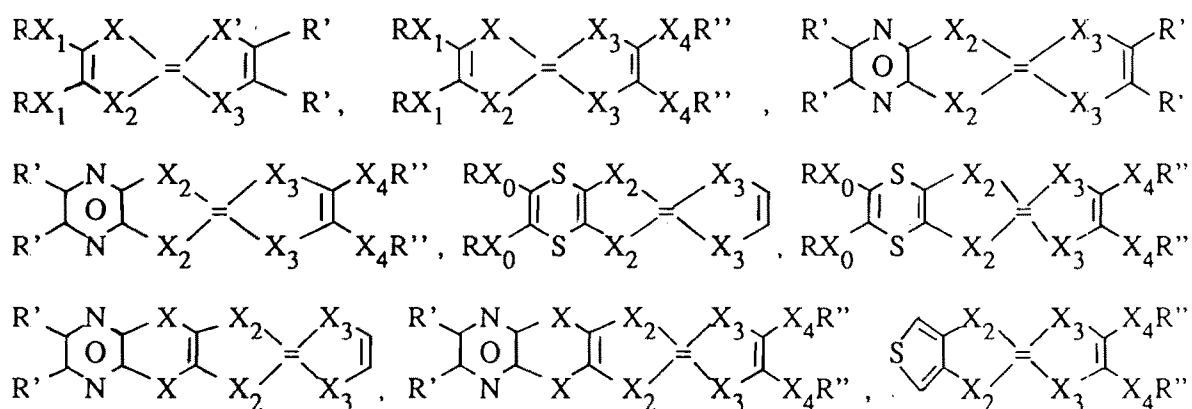
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### ABSTRACT

Methods for preparation of tetraheterafulvalenes containing O, S, Se, N as additional heteroatoms and some of their conducting products are described. Also, results concerning stoichiometry, structures, and physical properties are briefly discussed.

### INTRODUCTION

During the last five years, a number of conducting crystals based on oxygen-, sulfur-, selenium- and nitrogen-containing tetrachalcogeno-fulvalenes has been prepared and investigated in our institute and in a collaboration of our institute with others [1-15]. In this paper we report methods for preparation of tetraheterafulvalenes mainly of the following general formulas



(where  $X_1, X_4 = O, S, Se$ ;  $X_2, X_3, X_0, X, X' = S, Se$ ;  $R' = H, CH_3$  etc,  $R, R'' = CH_3, 2R, 2R'' = CH_2, CH_2CH_2, 2RX_1 = -S-N=CH-, -N=CH-CH=CH-$  etc) which are  $\pi$ -donors, as well as methods for preparation of conducting materials based on these donors and the corresponding symmetrical ones. Also, results concerning stoichiometry, structures and physical properties of these donors and their conducting products are briefly discussed and used for the design of new compounds.

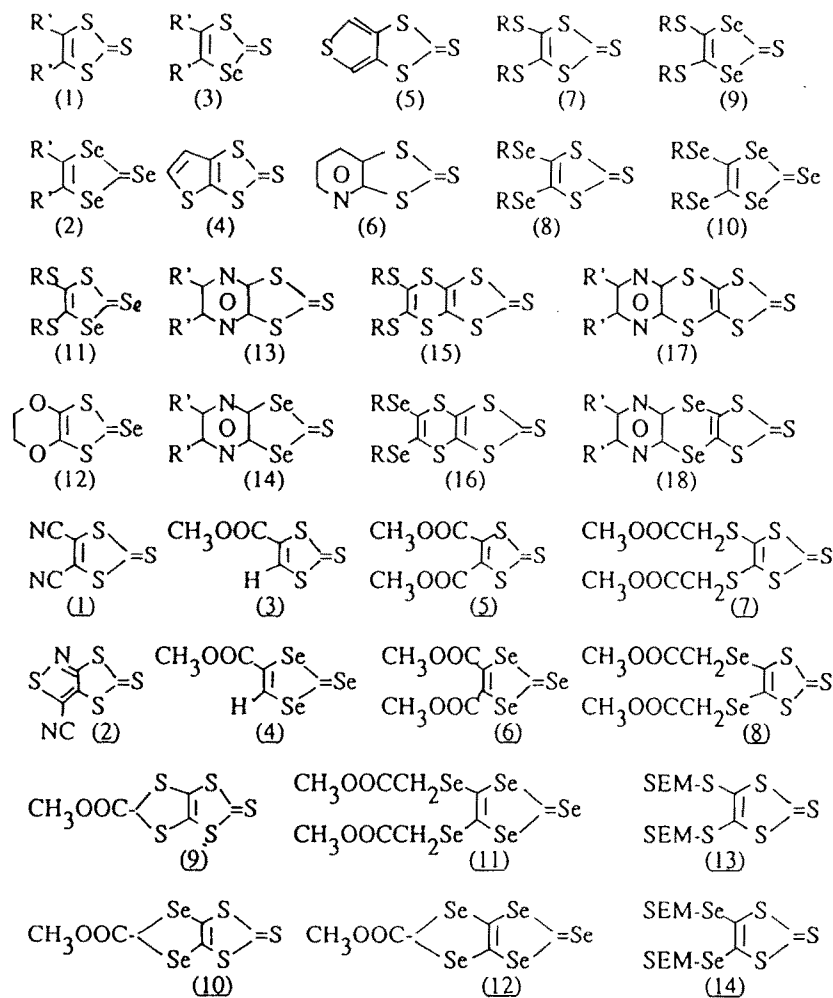
### STARTING MATERIALS

2-Thio-1,3-dithioles, 2-thio-1,3-diselenoles, etc, compounds (1)-(18) and (1)-(14), which are listed in Table I [1-3, 11-15], were used as starting materials for preparation of tetraheterafulvalenes. Compounds (1)-(14) are functionalized. Also, some compounds containing  $>C=O, >C=S, -SCH=CHS-, -SeCH_2-CH_2Se-$ , etc are functionalized. Compounds (1)-(18) and (1)-(2) can be used for preparation of transition metal 1,2-diheterolenes, organometallic compounds which also are precursors of conducting materials (see for example [1,2]).

### TETRAHETERAFULVALENES

Most of the known tetraheterafulvalenes have been prepared by self-coupling or cross-coupling of compounds of Table I, via triethyl phosphite. There is a large number of binary combinations of (1)-(18), but only 125 of them were actually prepared and studied in our laboratory. Usually, compounds (1)-(18) were firstly transformed to the 2-oxo-1,3-dithioles or 2-oxo-1,3-diselenoles with mercury acetate, in order to increase the yield of coupling-products. A number of unsymmetrical tetraheterafulvalenes were prepared by cross-coupling reaction (A+B) of

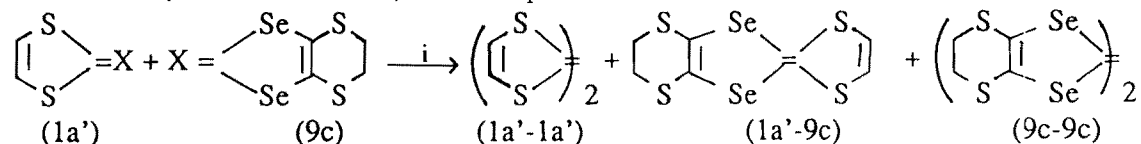
Table I. Starting materials



(a'): R' = H, (b'): R' = CH<sub>3</sub>, (c'): 2R' = CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, (d'): 2R' = CH=CH-CH=CH, etc.; (a): R = CH<sub>3</sub>, (b): 2R = CH<sub>2</sub>, (c): 2R = CH<sub>2</sub>CH<sub>2</sub>, (d): 2R = CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, (e): 2R = CH(CH<sub>3</sub>)CH<sub>2</sub>, (f): 2R = CH(CH<sub>3</sub>)CH(CH<sub>3</sub>), (g): 2R = CH=CH, (h): 2R = >C=O, (i): 2R = >C=S, (j): R = C<sub>18</sub>H<sub>37</sub> etc; SEM = (CH<sub>3</sub>)<sub>3</sub>Si(CH<sub>2</sub>)<sub>2</sub>OCH<sub>2</sub>

(1)-(18) via triethyl phosphite, followed by column-chromatography separation of cross-coupling product (AB) from the self-coupling byproducts (AA, BB).

$A + B \xrightarrow{i} AA + AB + BB$ , for example:



with X=O, instead of S gives (1a'-9c) in a good yield;  $i=(EtO)_3P$ , ~ 150 °C, N<sub>2</sub>.

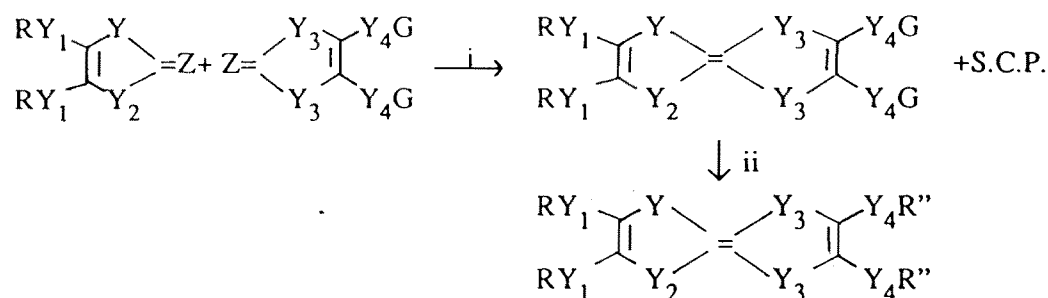
Scheme 1

The separation is effective, if there is a considerable difference in the R<sub>F</sub>-values of the self-coupling byproducts. R<sub>F</sub> depends on the nature of the additional group. It was found [12] that the R<sub>F</sub>-value of cross-coupling product (AB) is

$$R_F(AB) \approx \frac{1}{2} [R_F(AA) + R_F(BB)] \quad (1).$$

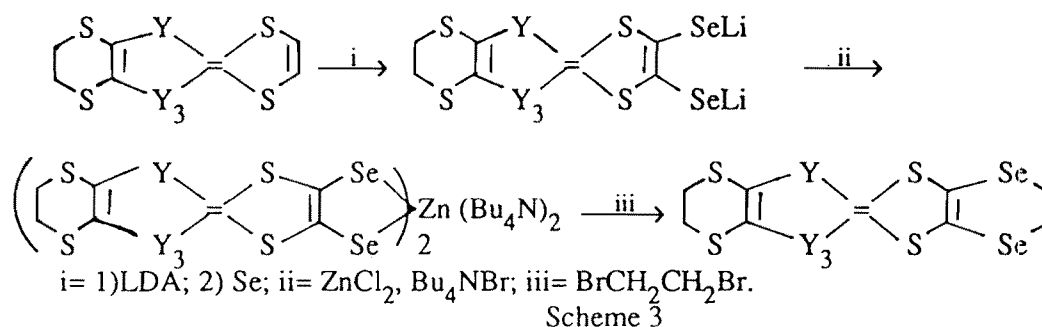
This means that the cross-coupling product will be found in the second fraction of the column. In the cases in which the separation is not possible, because of the small difference of R<sub>F</sub>-values,

functionalized compounds are used and the required tetraheterafulvalenes can be obtained according to the procedures of Scheme 2 [1,2,10,16] and Scheme 3 [13,17].



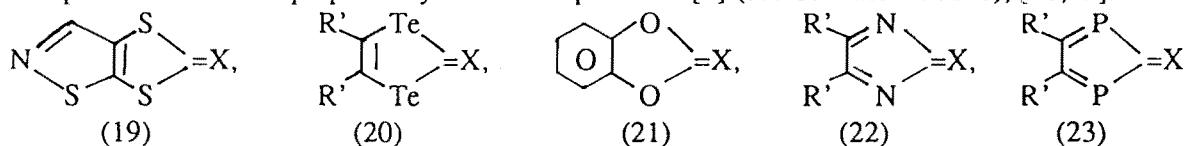
Here Z, Y<sub>1</sub>=O, S, Se; Y, Y<sub>2</sub>, Y<sub>3</sub>, Y<sub>4</sub>=S, Se; R, R''=alkyl-group, etc; RY<sub>1</sub>=H-, CH<sub>3</sub>-, etc; 2RY<sub>1</sub>=-N=CH-CH=CH-, -N=CH-CH=N-, etc; 2R=R''X<sub>0</sub>C=CX<sub>0</sub>R'', pyrazine-group, etc; R''Y<sub>4</sub>=H- or 2R''Y<sub>4</sub>=-S-N=CH-, etc; i=(EtO)<sub>3</sub>P, ~150°C, N<sub>2</sub> or (EtO)<sub>3</sub>P + C<sub>6</sub>H<sub>6</sub>, Δ, N<sub>2</sub>; S.C.P.= self coupling products; GY<sub>4</sub>=CH<sub>3</sub>OOC- → H- (or 1GY<sub>4</sub>=CH<sub>3</sub>OOC- and 1GY<sub>4</sub>=H-) → 2H-, with ii=LiBr+HMPA, ~150 °C, N<sub>2</sub>; G= CH<sub>3</sub>OOCCH<sub>2</sub>- → CH<sub>3</sub>-, and 2G=CH<sub>3</sub>OOCCH< → CH<sub>2</sub><, with ii=LiBr+HMPA, ~150 °C, N<sub>2</sub>; G= (CH<sub>3</sub>)<sub>3</sub>Si(CH<sub>2</sub>)<sub>2</sub>OCH<sub>2</sub>- → R'', with ii=Bu<sub>4</sub>NF+BrR''-R''Br; GY<sub>4</sub>=CN → H-, and 2GY<sub>4</sub>=-N-S-C(CN)= → -S-N=CH-, with ii= 1)KOH, 2) HCl, 3) DMF, Δ; etc

Scheme 2



Scheme 3

The following compounds are not known, but tetraheterafulvalene derivatives based on these compounds have been prepared by methods reported in [2] (see Scheme 2 above), [18,19].



Tetraheterafulvalenes (X<sub>2</sub>, X<sub>3</sub>, X, X'=O, S, Se, Te) are π-donor molecules. The π-donor capacity depends strongly on the nature of the additional heterogroups (see for example [1,10]). Tetraheterafulvalenes (22-22) and (23-23) are π-acceptors [19]. It was found that the values of half-wave oxidation potentials (HWOP) of unsymmetrical tetraheterafulvalenes are the average of the values of HWOP of the corresponding symmetrical ones [4,5,10,11], namely:

$$E_{1/2}^i(\text{AB}) = \frac{1}{2} [E_{1/2}^i(\text{AA}) + E_{1/2}^i(\text{BB})] \quad (2).$$

Values of HWOP of some tetrachalogenafulvalenes (donors) are listed in Table II [5,10,20].

### CONDUCTING CRYSTALS

From the symmetrical and unsymmetrical tetrachalcogenafulvalenes a number of conducting crystals was prepared by chemical (rapid or slow precipitation or diffusion) and/or electroche-

Table II. Values of HWOP and  $\Delta E_{1/2}$  of some donors (in mV)\*

Donor	$E_{1/2}^1$	$E_{1/2}^2$	$\Delta E_{1/2}$	Donor	$E_{1/2}^1$	$E_{1/2}^2$	$\Delta E_{1/2}$
BO(12-12)	490	900	410	DMET(2b'-7c)	(575)	(962)	(387)
MDTTTF(1a'-7b)	535	915	380	S,S-DMBEDT(7c-7f)	(597)	(977)	(380)
TMTSF(2b'-2b')	550	950	400	ET(7c-7c)	600	980	380

\*0.025M  $Bu_4NPF_6$  in  $C_6H_5CN$  vs SCE; calculated values from eq.(2) are given in parentheses.

mical techniques [1,2,14]. The following reagents or supporting electrolytes were used: 1) salts with linear or quasi-linear anions; these are:  $Bu_4NI_3$ ,  $Bu_4NIBr_2$ ,  $Bu_4NAuI_2$ ,  $Bu_4NAuBr_2$ ,  $Bu_4NAu(CN)_2$ ,  $Bu_4NAg(CN)_2$  (in  $CH_2Cl_2$ ),  $CuSCN+KSCN$ ,  $CuCN+KSCN$  [3],  $CuI+KSeCN$ ,  $CuX +NaN(CN)_2$ ,  $AgN(CN)_2+KX$  ( $X=Cl, Br, CN$ ) [14] (in 1,1,2-trichloroethane + 18-crown-6) etc; 2) salts with planar or quasi-planar anions; these are:  $K_2Pt(CN)_4$ ,  $Bu_4NM(dmit)_2$ ,  $(Bu_4N)_2M(dcit)_2$  [21],  $TCNQ$  etc; 3) salts with tetrahedral anions:  $Bu_4NClO_4$ ,  $Bu_4NBF_4$ ; and 4) salts with octahedral anions:  $Bu_4NSbF_6$ ,  $Bu_4NPF_6$  and  $Bu_4NPbI_3$  (in  $CH_2Cl_2$ ).

Most of the crystals were found to be semiconducting and only few of them were found to be metallic or superconducting. The metallic and superconducting crystals are listed in Table III. In some cases the temperature of metal-insulator transition (MIT) decreases with increasing the pressure. From slow chemical reaction of  $ET(7c-7c)$  with  $Cu(SCN)_2$  in a stopped flask containing a small portion of  $CH_3CN$ , two kinds of crystals were obtained after one month: one superconducting ( $\alpha$ -phase) and another semiconducting. Sometimes, crystals with anion (or polyanion) different of that of supporting electrolyte have been obtained; electrochemical reaction of  $ET$  with  $CuI+KSeCN$ , for example, afforded  $\alpha-(ET)_2I_3$  instead  $(ET)_2Cu(SeCN)I$  [14]. Also, by changing the conditions of crystallization two or more than two phases can be obtained [4,12].

Table III. Some metallic (or superconducting) crystals \*

Crystal	$\sigma_{RT}$ (S/cm)	MIT(K)**	Crystal	$\sigma_{RT}$ (S/cm)	MIT(K)**
$\alpha$ -(1a'-7b) <sub>2</sub> AuI <sub>2</sub>	12-36	Tc=5K	(2b'-13a') <sub>2</sub> I <sub>3</sub>	~92	~120
$\beta$ -(2a'-7c) <sub>2</sub> IBr <sub>2</sub>	150-550	<0.05	(2b'-13a') <sub>2</sub> ClO <sub>4</sub>	44	~250
$\beta$ -(2a'-7c) <sub>2</sub> IBr <sub>2</sub>	>1600	<1.35	(7c-13a') <sub>2</sub> BF <sub>4</sub>	~21	~200
(1a'-7c) <sub>2</sub> AuI <sub>2</sub>	500	~125	$\alpha'$ -(7c-13a') <sub>3</sub> I <sub>3</sub>	30	~100
		(4.8kbar)20	$\beta'$ -(7c-13a') <sub>3</sub> I <sub>3</sub>	40	~170
(1a'-7c)AuBr <sub>2</sub>	~330	~140	(7c-14b') <sub>x</sub> ClO <sub>4</sub>	>1000	~70
		(13kbar)15	(7c-14b') <sub>x</sub> I <sub>3</sub>	>100	250
(1a'-7c) <sub>2</sub> Ag(CN) <sub>2</sub>	2-50	150			(12kbar)4
(1a'-7c) <sub>2</sub> SbF <sub>6</sub>	~120	200	(12-7c) <sub>2</sub> Cu(SCN) <sub>2</sub>	29	~25
(1a'-7c) <sub>x</sub> TCNQ	40	125			(8kbar)15
		(8.1 kbar)70	$\tau$ -(12-7g) <sub>2</sub> AuI <sub>2</sub> (AuI <sub>2</sub> ) <sub>-1</sub>	29	~25
(1a'-7g) <sub>2</sub> IBr <sub>2</sub>	~714	200	$\tau$ -(12-7g) <sub>2</sub> IBr <sub>2</sub> (IBr <sub>2</sub> ) <sub>-1</sub>	60	~70
	50		$\tau$ -(12-7g) <sub>2</sub> I <sub>3</sub> (I <sub>3</sub> ) <sub>-1</sub>	45	<15
(1a'-8b) <sub>2</sub> AuI <sub>2</sub>	305	~50	(7c-7c) <sub>2</sub> Cu <sub>2</sub> (SCN) <sub>x</sub> (CN) <sub>y</sub>	~40	~110
(1a'-7b) <sub>2</sub> Au(CN) <sub>2</sub>	160	30	$\alpha$ -(7c-7c) <sub>2</sub> Cu <sub>2</sub> (CN) <sub>3</sub>	~40	Tc = 4.5K?
(1a'-7c) <sub>x</sub> Cu(SCN) <sub>2</sub>	30	100	$\alpha$ -(7c-7c) <sub>2</sub> I <sub>3</sub>		Tc = 4K
(1a'-7f) <sub>2</sub> ClO <sub>4</sub>	~80	160	(7c-7c) <sub>2</sub> Ag <sub>x</sub> [N(CN) <sub>2</sub> ] <sub>y</sub> Br <sub>z</sub>	26	~160
(3a'-7c) <sub>2</sub> IBr <sub>2</sub>	~460	<2K	(7b-7b) <sub>x</sub> Ni(dcit) <sub>2</sub>	~40	~120
(1a'-7c) <sub>2</sub> PF <sub>6</sub>		100	$\alpha$ -(7c-7c) <sub>2</sub> Cu(NCS) <sub>2</sub>		Tc=9K

\* See refs. [4, 5, 8-10, 14] and refs. cited in [1,2]; MIT or critical temperature (Tc)

## CONDUCTING FILMS

Unsymmetrical tetrachalcogenafulvalenes [12] can be developed in thin films by the Langmuir-Blodgett (LB) [12,22] or by vacuum evaporation [23] technique. I<sub>2</sub>-doped films of (7c-7j), (7c-8j) [24] were found to be conductive.

## RESULTS AND DISCUSSION

A number of tetrachalcogenafulvalenes with several additional heterogroups or in other words a number of  $\pi$ -donors with a variety of HWOP-values has been prepared and studied in our laboratory. The HWOP-values of the donors, which gave superconducting crystals (see [1,25]), are listed in Table II. Recently, the preparation of unsymmetrical tetrachalcogenafulvalenes with HWOP-values close to those of Table II has been attempted. Some results are discussed here. (1a'-7c), (2a'-7c) and (3a'-7c) of which the HWOP-values [10] are in between those of (2a'-7b) and (7c-7c), gave (1a'-7c)<sub>2</sub>IBr<sub>2</sub>, (7a'-7c)<sub>2</sub>IBr<sub>2</sub> and (3a'-7c)<sub>2</sub>IBr<sub>2</sub>, respectively, conducting crystals (of  $\beta$ -phase), which remain metallic down to low temperatures (see Table III). Similar results are expected for (1a'-9c)<sub>2</sub>IBr<sub>2</sub> [20]. The HWOP-values of (7g-12) are close to those of (7c-7c) [10], but (7g-12) gave metallic (not superconducting) crystals. However, some tetrathiafulvalenes with at least one -SeCH<sub>2</sub>-CH<sub>2</sub>Se- or -SeCH<sub>2</sub>Se- [12] as additional heterogroup and HWOP-values close to those of (7c-7c) gave only semiconducting crystals. Some unsymmetrical tetrachalcogenafulvalenes with -N=CR'-CR'=N- as an additional heterogroup gave metallic crystals of stoichiometry 3:1 (donor / anion), while some with -OCH<sub>2</sub>-CH<sub>2</sub>O- gave 2-D- metallic crystals of the tetragonal system ( $\tau$ -phase) and stoichiometry 1:~1. Some -N=CR'-CR'=N- containing tetrachalcogenafulvalenes, of which the HWOP are higher than those of ET (7c-7c) [10], gave salts which remain metallic down to low temperatures (at least 4K) [26]. Unsymmetrical tetrathiafulvalenes with a long-chain alkyl-group (R=C<sub>18</sub>H<sub>37</sub>, etc) and HWOP-values lower of those of (7c-7c) gave conducting LB-films [22,24]. Some tetratellurafulvalenes (see Cowan et al [18]) and some rich in selenium tetrachalcogenafulvalenes (see [1, 27]), of which the HWOP-values are close to those of (7c-7c), gave conducting crystals. However, the low solubility of these donors in common organic solvents seriously hampers crystal growing efforts and often results in poor crystal quality. In these cases is not clear yet if the donor-molecules are planar at low temperatures. Substitution of the H-atoms of vinylenedithiotetrathiafulvalenes by a RX<sub>0</sub>C=CX<sub>0</sub>R (X<sub>0</sub>=S, Se) or -N=CH-CH=N-group does not affect drastically the HWOP-values of the  $\pi$ -donors. In some cases the resulting multiheterotetrathiafulvalenes were found to be nonplanar [13,28]. Tetraoxafulvalenes (X, X<sub>2</sub>, X<sub>3</sub>=O) are expected to have HWOP-values close to those of tetrachalcogenafulvalenes (X, X<sub>2</sub>, X<sub>3</sub>=S, Se). This means that new symmetrical or unsymmetrical tetraheterafulvalenes with X<sub>2</sub>, X<sub>3</sub>=O, S, Se will give good conductors. However, by today only one member of tetraoxafulvalenes, the dibenzotetraoxafulvalene, has been reported.

These results indicate that the substitution of one or two atoms of sulfur in the tetrathiafulvalene core (S<sub>2</sub>, S<sub>3</sub>) by atoms of selenium (or oxygen) could afford tetraheterafulvalenes with properties close to the corresponding tetrathiafulvalenes and consequently, in some cases, it could afford superconducting crystals.

In some cases ( $\kappa$ -,  $\theta$ -, etc phases) the cations and anions form separate layers; the cation (conducting) layers are sandwiched between the anion or polyanion (insulating or semiconducting) layers. A variety of polyanion structures was found. In the case of  $\tau$ -phase the anions form a pseudo-3-D- network, similar to that of  $\epsilon$ -(ET)<sub>2</sub>I<sub>3</sub>(I<sub>8</sub>)<sub>0.5</sub> [29]: mixed cation/ anion layers of composition 2:1 alternate with anion layers. (ET)<sub>1</sub>PbI<sub>3</sub>, which is a semiconductor, seems to have a cubic perovskite structure. Details on the preparation, crystal structures and physical properties of this kind of materials will be published elsewhere [14].

Work concerning conducting crystalline salts of recently prepared tetraheterafulvalenes [30] is in progress in our Institute. We believe that salts obtained from new tetraheterafulvalenes and/or new anions will lead to new findings in organic conductivity and superconductivity.

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