

DESIGN AND SYNTHESIS OF POLYHETEROTETRAHETERAFULVALENES,  
METAL 1,2-DIHETEROLENES, AND THEIR LOW-DIMENSIONAL CONDUCTING  
AND SUPERCONDUCTING SALTS

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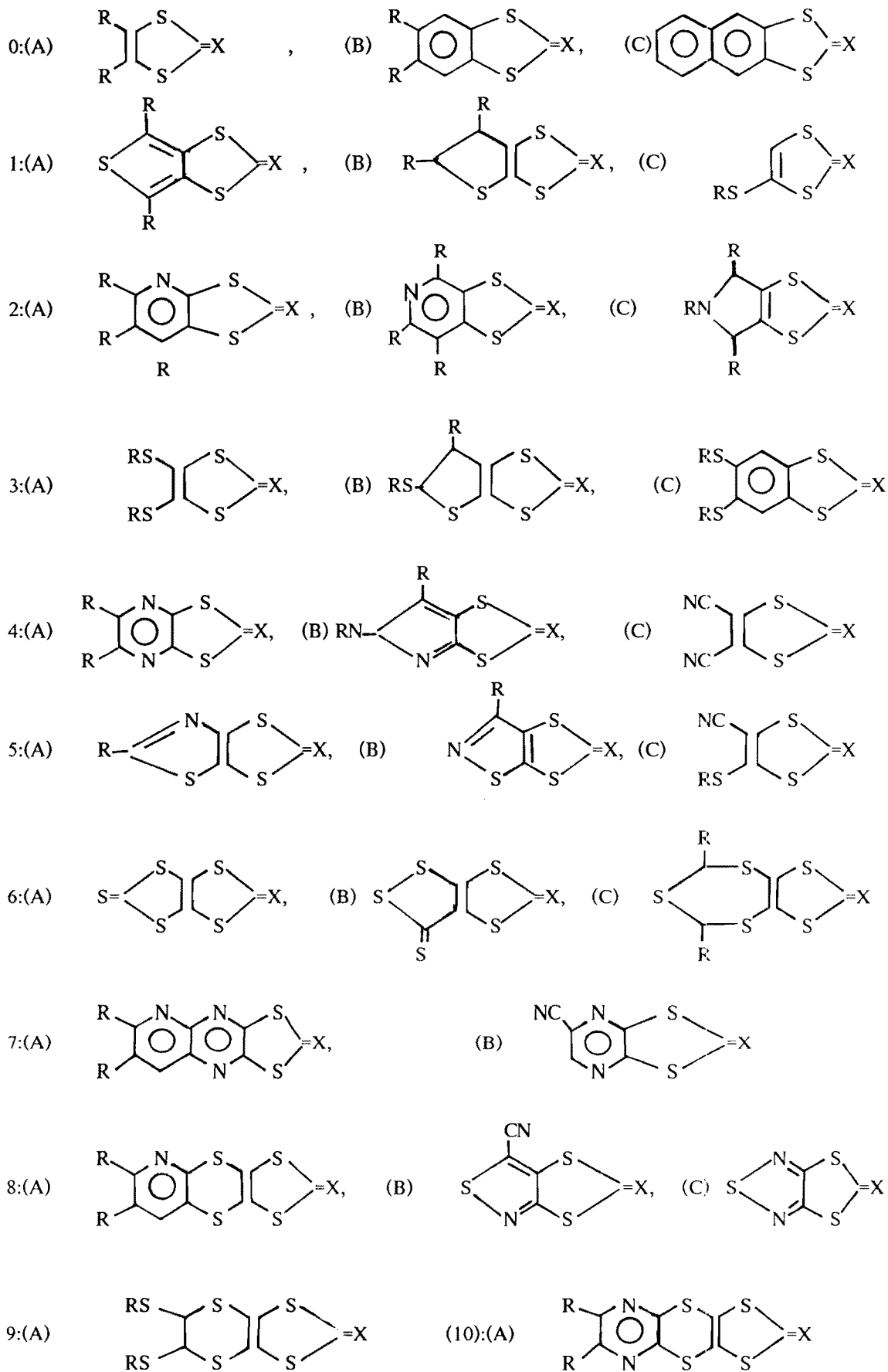
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INTRODUCTION

Most of the known organic and metalloorganic crystalline conductors (and superconductors) have been based on the tetrathiafulvalene derivatives, transition-metal 1,2-dithiolenes and selenium- or tellurium- analogs [1]-[5]. The synthesis and physicochemical properties of these compounds reported by 1988 are summarized in a number of excellent review articles [6]-[12]. Recent work concerning synthesis and physicochemical properties of these and similar compounds, is described in refs [13]-[56] and in references cited therein. Generally, 2-thioxo-1,3-dithioles and selenium or tellurium analogs have been used as starting materials for preparation of both tetraheterafulvalenes and metal 1,2-diheterolenes. For a systematic investigation, we have divided the simplest 2-thioxo-1,3-dithioles in classes, based on the number and the nature of the additional heteroatoms to the thioxo-dithiole group (see [41]). Table 1 shows examples of the simplest 2-thioxo-1,3-dithioles divided in classes: Class 0 contains compounds without additional heteroatoms; Class 1 contains compounds with a sulfur heteroatom in an additional ring or chain; Class 2 contains compounds with a nitrogen heteroatom in an additional ring or chain; and so on. One can design similar classification tables for the selenium, tellurium, oxygen and nitrogen analogs, as well as for their self- or cross-coupling products (polyheterotetraheterafulvalenes) and for the corresponding metal 1,2-heterolenes and similar compounds [57]-[60]. The addition of groups and heteroatoms to the tetraheterofulvalene core or to the metal 1,2-diheterolene core play an important role in the chemical and physicochemical properties of these compounds (see for example [6]). Also, they play an important role in the crystal structure and physical properties of the corresponding charge transfer complexes (CTC), cation radical salts (CRS) and cation deficient metal 1,2-diheterolenes (CDMD) (see for example [4]).

During the last ten years, a number of low-dimensional conducting crystals, based on oxygen-, sulfur-, selenium- and nitrogen- containing molecules have been investigated in our institute, and in a collaboration of our institute with others [20], [37]-[41], [61]-[98]. In this paper we report on new tetraheterafulvalenes and metal 1,2-diheterolenes, and discuss general synthetic methods which have been developed and applied recently for the preparation of this kind of compounds. Also,

Table 1. Examples of simple 2-thioxo-1,3-dithioles (X=S)



R=H,CH<sub>3</sub>,CF<sub>3</sub>,etc, 2R=CH<sub>2</sub>, CH<sub>2</sub>-CH<sub>2</sub> etc

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we briefly discuss the synthesis, structure and properties of some conducting crystalline salts based on these compounds.

## DESIGN OF NEW COMPOUNDS

Starting from the compounds given in Table 1, and selenium, tellurium, oxygen, and nitrogen analogs, one can design the preparation of a large number of tetraheterofulvalenes ( $\pi$ -donors) (all possible binary combinations of compounds of Table 1 as well as O, Se, N and Te analogs), and metal 1,2-diheterolenes ( $\pi$ -acceptors), and a very large number of their CTC, CRS and CDMD, which means a very large number of low-dimensional conducting crystals. The design of new tetraheterofulvalenes and metal 1,2-diheterolenes depends on the kind of products needed, namely, crystalline conductors or superconductors [1]-[4], conducting Langmuir-Blodgett films [16], [30],[31],[46], ferromagnetic organic metals [58],[60], materials for nonlinear optics [60], etc. At present, our interest is in the preparation of crystalline conductors and superconductors. Consequently, before we design and prepare new tetraheterofulvalenes and metal 1,2-diheterolenes, we should take into account all the current literature on organic conductors and superconductors based on already known compounds.

It is well known that compounds based on 2-thioxo-1,3-dithioles of Class 0 and Class 1 gave 1-dimensional conductors (see for example [5],[8]). However, 1-dimensional metallic systems are unstable and exhibit a metal-to-semiconductor transition at lower temperatures. The dimensionality can be increased by incorporating sulfur, selenium, tellurium or nitrogen atoms into the  $\pi$ -donor or  $\pi$ -acceptor molecule [4], [25],[14],[87],[88],[55]. By this modification, a superconducting ground state was found to be stabilized in salts with varying degrees of anisotropy. Thus, some salts of the type  $(\text{TMTSF})_2\text{X}$  ( $\text{X}=\text{PF}_6, \text{ClO}_4$  etc) based on the (selenium containing)  $\pi$ -donor molecules of tetramethyltetraselenafulvalene (TMTSF), were found to be quasi-1-dimensional superconductors (see for example [2]), while the salts of the type  $\beta\text{-(BEDTTTF)}_2\text{X}$  ( $\text{X}=\text{I}_3, \text{AuI}_2, \text{IBr}_2$ , etc) based on the (sulfur containing)  $\pi$ -donor molecules of bis(ethylenedithio)tetrathiafulvalene (BEDTTTF), were found to be 2-dimensional superconductors (see for example [1]-[4]). The compound  $(\text{Me}_4\text{N})[\text{Ni}(\text{dmit})_2]_2$  based on the (sulfur containing)  $\pi$ -acceptor molecules of bis(4,5-dimercapto-1,3-dithiole-2-thione)nickelate  $[\text{Ni}(\text{dmit})_2]$  was found to be a 2-dimensional superconductor, while  $(\text{TTF})[\text{Ni}(\text{dmit})_2]_2$  was found to be a quasi-1-dimensional superconductor (see ref.[1] and refs [33]-[35] cited therein). The salts  $(\text{DMET})_2\text{X}$  ( $\text{X}=\text{I}_3, \text{IBr}_2$  etc) and  $(\text{MDTTTF})_2\text{AuI}_2$  based on the unsymmetrical  $\pi$ -donor molecules of dimethyl(ethylenedithio)diselenadithiafulvalene (DMET) and methylenedithiotetrathiafulvalene (MDTTTF) were found to be 2-dimensional superconductors (see ref [94] and refs therein, [98]-[100]). The salts  $(\text{DMtTfSF})_2\text{X}$  ( $\text{X}=\text{ClO}_4, \text{PF}_6, \text{AsF}_6$ ) [101],  $(\text{EDTTTF})_2\text{IBr}_2$ , and  $(\text{EDTDSDTF})_2\text{IBr}_2$  [94], [98] based on the unsymmetrical  $\pi$ -donor molecules of dimethyl(trimethylene)tetraselenafulvalene (DMtTfSF), ethylenedithiotetrathiafulvalene (EDTTTF) and ethylenedithiodiselenadithiafulvalene (EDTDSDTF) were found to remain metallic down to very low temperatures. Also, some compounds of the type  $(\text{BEDO-TTF})_x\text{X}$  based on the symmetrical donor bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF) were found to be metallic down to low temperatures [19]; BEDO-TTF is better donor than BEDTTTF. The compounds TMTSF, BEDTTTF, DMET, MDTTTF, EDTTTF, DMtTfSF, and  $\text{M}(\text{dmit})_2$ , which gave good conductors or superconductors,

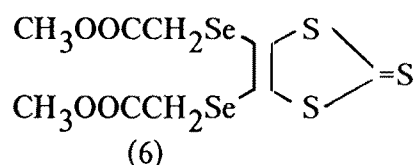
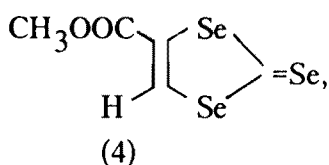
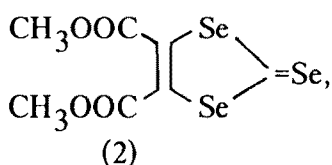
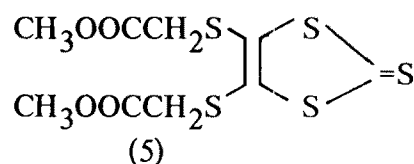
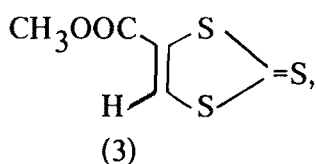
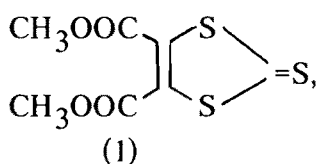
were found to be fairly good  $\pi$ -donors and  $\pi$ -acceptors [6],[47], [101], [102], respectively. The half-wave oxidation potentials of  $\pi$ -donors showed that the donor capacity decreases from tetrathiafulvalene to the corresponding tetrasenafulvalene and increases again for the corresponding tetratellurafulvalene [6],[14]. The  $\pi$ -donor capacity of tetraheterafulvalenes and  $\pi$ -acceptor capacity of metal 1,2-diheterolenes depends also on the nature of additional groups(chains or rings). Groups such as alkyls, cycloalkyls and thioalkyls are electron-donating groups, while groups such as trifluoromethyl, nitriles and esters are electron-withdrawing substituents. Addition of methyl groups, for example, increases the donor capacity in TTF, while addition of nitrile groups decreases the donor capacity in TTF (see for example [6]). The addition of a benzene- or vinylenedithio-group to the TTF-core increases the extent of its  $\pi$ -electron system, and the electron-donor capacity of the obtained (planar) TTFs then decreases, compared with the unsubstituted TTF [6], [36]. The addition of a pyrazine-(or a pyridine-, etc.) group decreases the  $\pi$ -electron donor capacity, but increases the ability for the formation of intermolecular contacts (and consequently of 2-or 3-dimensional systems) in the salts of (planar) TTFs [38],[73],[87], [88]. Similar effects have been discussed for the  $\pi$ -acceptor molecules of metal 1,2-diheterolenes. It was observed that, in metal 1,2-diheterolenes with a small cation (such as Li, Na, Me<sub>4</sub>N,) the intermolecular contacts are strong and consequently good conductors (cation-deficient metal 1,2-diheterolenes) can be obtained (see [44],[47],[50],[53],[55],[63],[64],[83],[86] and refs therein).

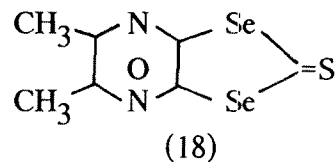
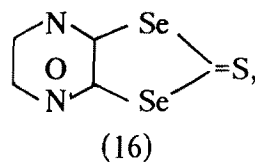
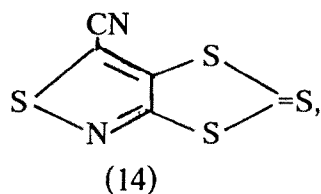
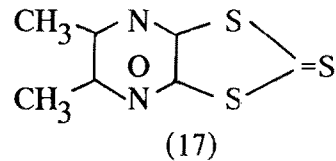
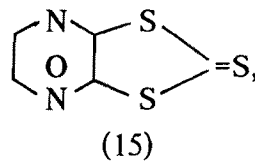
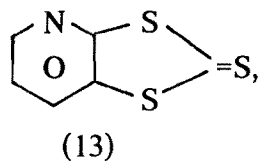
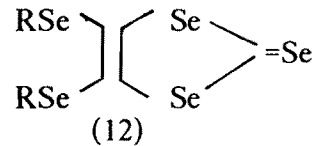
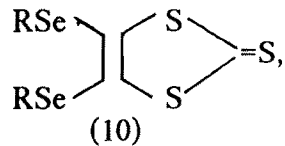
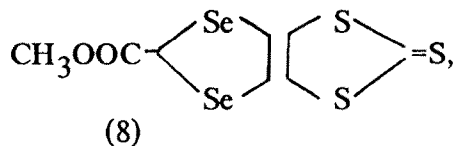
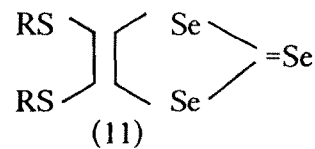
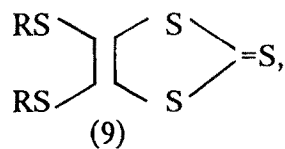
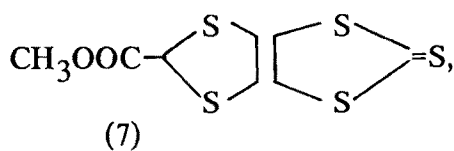
Tetraheterafulvalenes, such as bis(ethylenediseleno)tetrathiafulvalene, bis (methylenediseleno) tetrathiafulvalene, tetratellurafulvalenes, which are rich in selenium or tellurium hetero-atoms, showed two oxidation potentials, with values close to those of BEDTTF, and a few of them gave highly conducting complexes (see [14],[25],[32] and refs therein). However, the low solubility in common organic solvents of these  $\pi$ -donors seriously hampers crystal-growing efforts, and often results in poor crystal quality [14] [32].

Taking into account the above statement, we suggest the design and synthesis of symmetrical or unsymmetrical (planar) tetraheterafulvalenes poor in selenium or tellurium heteroatoms, and (small cation-) metal 1,2-diheterolenes fairly rich in sulfur, selenium, (tellurium) or nitrogen heteroatoms, to obtain good conductors or superconductors.

## 2-THIOXO-1,3-DITHIOLES AND SELENIUM ANALOGS

2-Thioxo-1,3-dithioles and selenium analogs have been usually used as starting materials for the syntheses of both tetraheterafulvalenes and metal 1,2-diheterolenes. In this section, we describe methods of preparation and some properties of the following compounds, (1)-(18):

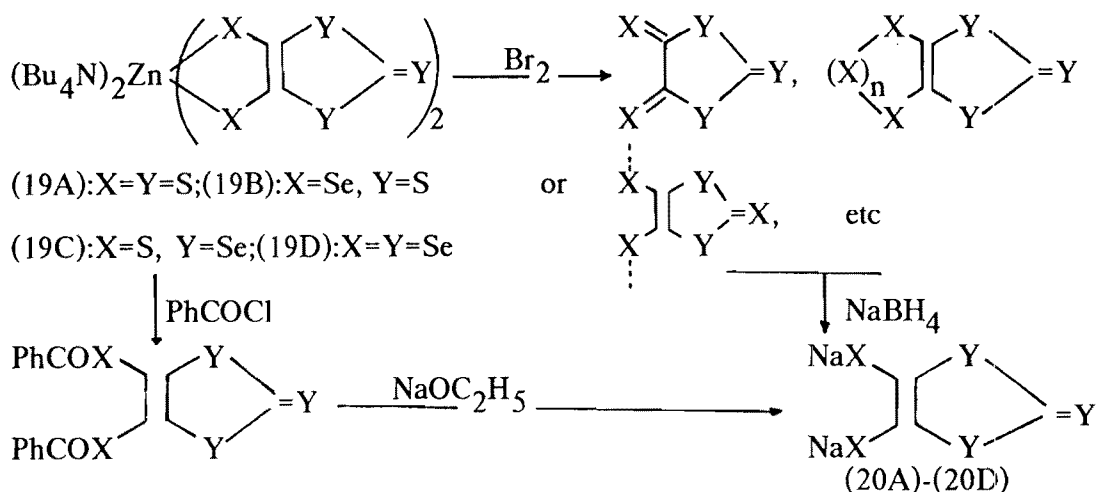




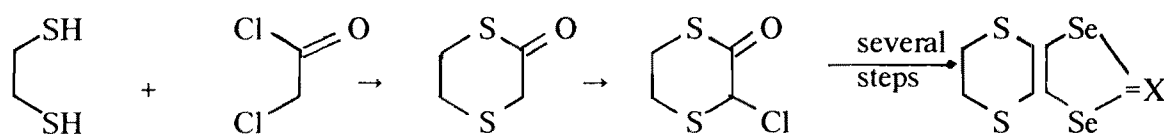
(a):R=CH<sub>3</sub>, (b):2R=CH<sub>2</sub>, (c):2R=CH<sub>2</sub>CH<sub>2</sub>, (d):2R=CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>  
 (e):2R=CH(CH<sub>3</sub>)CH<sub>2</sub>, (f):2R=CH(CH<sub>3</sub>)CH(CH<sub>3</sub>), (g):2R=CH=CH

4,5-Bis(methylcarboxy)-1,3-dithiole-2-thione (1) and its selenium analog (2) were known years ago (see ref [11] cited in ref [37] here and ref [30] cited in ref [20] here). They have been prepared by treatment of ethylene trithiocarbonate and selenium analog, respectively, with dimethyl acetylenedicarboxylate in toluene at reflux temperature. Methylcarboxyl-1,3-dithiole-2-thione(3)[103] and selenium-analog (4) [104], have been prepared by treatment of ethylene trithiocarbonate and selenium analog, respectively, with methyl propiolate in toluene at reflux temperature for several hours followed by silica gel column chromatography separation (C<sub>6</sub>H<sub>6</sub>-cyclohexane 1:1).

Compounds (5) [40], (6) [104], (7) [39], (8) [104], (9a)-(9f) [76], [79], (10a)-(10f) [25],[29], [41],[43], [104], (11a)-(11f) [105], [106], (12a)-(12f) [105]-[107] have been prepared by treatment of the corresponding tetrabutylammonium salt of zinc 1,2-dithiolates and selenium analogs (19A)-(19D) [79],[41] [106] or the Hg-[65] or Ni-[25] analogs with the corresponding alkyl halide ([79],[39]-[41],[106] and refs therein). Disodium 4,5-dithiolates and selenium analogs (20A)-(20D) should be used instead of (19A)-(19D) for the preparation of (9g), (10g), (11g) and (12g) (see refs [5],[6] cited in ref [20] here). Compounds (9f), (10f) can be also prepared from (20A), (20B), respectively, by a two-step sequence (treatment with the sulfate diester of (R,R)-butane-2,3-diol in MeOH and cyclization on heating in THF) (see ref[8] cited in ref [39] here). Compounds (20A)-(20D) can be prepared from the corresponding zincates (19A)-(19D) according to Scheme 1 [53], [63], [106]. However, compounds (19c) and (20c) have not been isolated yet in a pure form, [106]. For the preparation of the corresponding compounds (11) in a pure form, the method reported in ref [105] has been used. This method has been applied only in the case of 2R=CH<sub>2</sub>CH<sub>2</sub>, according to Scheme 2[105], [106],[22]. Also, it has been applied for the preparation of (9c) as an alternative method [22].



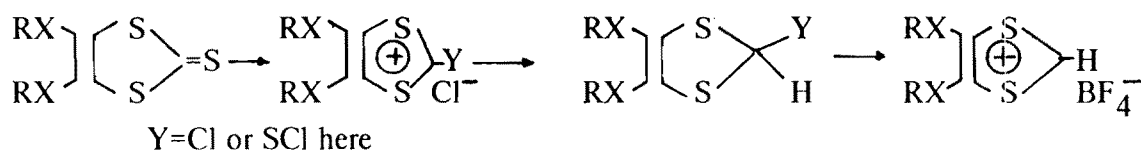
Scheme 1



Scheme 2

Compound (13) has been prepared from 2-chloro-3-nitropyridine by a four-step sequence (treatment with NaHS, reduction with tin(II)chloride, diazotization with nitrous acid and treatment with carbon disulfide at 220°C)[72],[85]. Compound (14) has been prepared by treatment of disodium 5-cyanoisothiazoledithiolate with thiophosgene [83], [86]. Compounds (15)-(17) have been prepared by a two-step sequence (treatment with KHS or NaHSe and reaction with thiophosgene) [78],[82]. Reactions with phosgene yielded the corresponding -2-ones [78],[82],[83],[86]. Compounds (15),(17) have been prepared also, by treatment of 2,3-dichloropyrazine and 2,3-dichloro-5,6-dimethylpyrazine, respectively, with potassium trithiocarbonate [78].

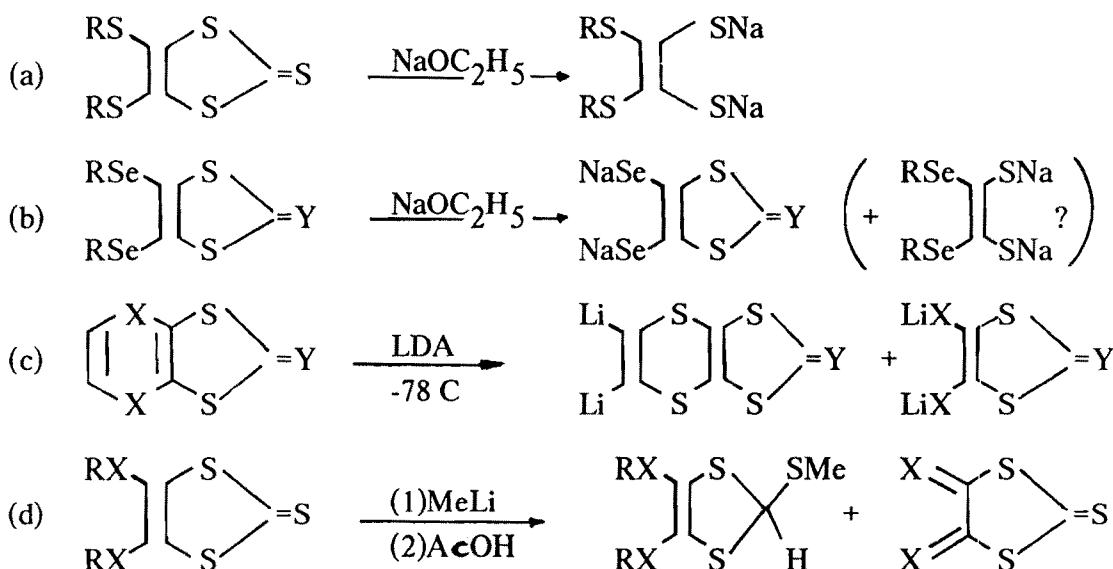
Compounds (1)-(18) are soluble in common organic solvents (dichloromethane, chloroform, benzene, etc), and they can be transformed easily to the 2-oxo-1,3-dithioles and 2-oxo-1,3-diselenoles, by treatment with mercury acetate in CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>COOH or CHCl<sub>3</sub>-CH<sub>3</sub>COOH mixtures (see for example [39]-[42]). They can be also converted to the corresponding selenones by a three-step sequence: reaction with methyl fluorosulfonate, treatment with morpholine, and reaction with hydrogen selenide (see ref [110] cited in ref [7] here). Compounds (7)-(10) can be converted to the corresponding 1,2-dithiolium salts by a three-step sequence reaction with sulfur dichloride, reduction with sodium borohydride, and reaction with fluoro-boric acid) according to Scheme 3 [39]:



Scheme 3

These salts can be prepared by a four-step sequence (methylation with dimethyl sulfate, treatment with fluoroboric acid, reduction with sodium borohydride and reaction with fluoroboric acid) [6],[39].

Compounds (1)-(18) should be purified, by gel column chromatography and /or recrystallization, before use. In the mass spectra of fairly pure compounds (9),(10), the presence of some decomposition products similar to those obtained by bromine-oxidation of (19)(see Scheme 1) and their isomers [66] has been observed. In the case where  $2R=CH_2$ , the contents have been found to be lower than those of the cases where  $2R=CH=CH$ ,  $CH_2CH_2$ . Also, compounds (9),(10) give several products in alkaline medium, depending on the nature of R and the conditions [21],[34],[45], [108] as it is shown in Scheme 4:



Scheme 4

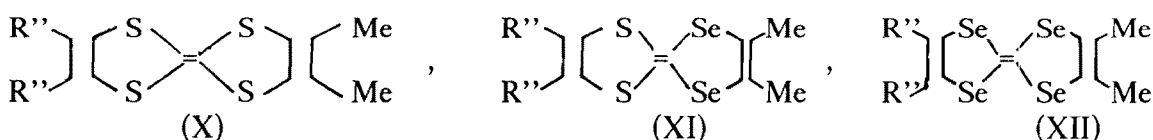
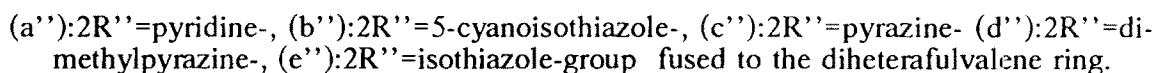
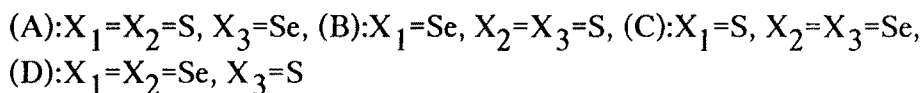
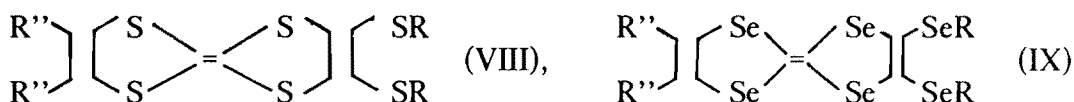
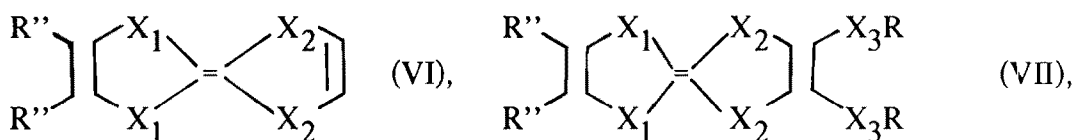
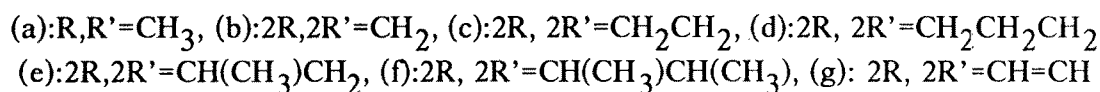
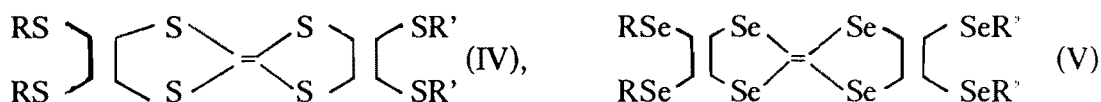
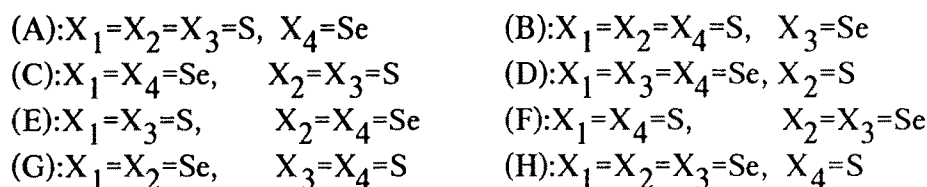
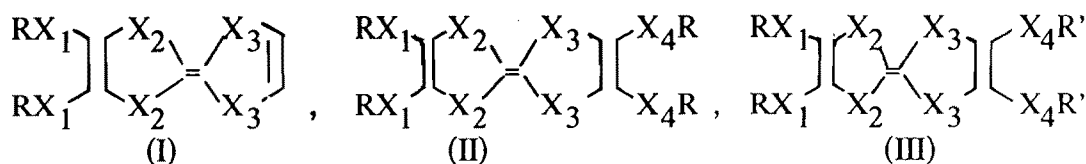
It has been elucidated that the products obtained from the routes (b)-(d) are not due to the presence of decomposition products in the samples of (9),(10).

#### POLYHETEROTETRAHETERAFULVALENES

A number of symmetrical polyheterotetraheterafulvalenes have been prepared by self-coupling reaction of the corresponding 2-thio-1,3-dithioles and selenium analogs via triethyl phosphite or other trivalent derivatives of phosphorous, in yields depending on the nature of the additional group and the reaction conditions (see for example [6], [7], [9]). It has been observed that 2-oxo-1,3-dithiols and 2-oxo-1,3-diselenoles give, in most cases, higher yields than the corresponding 2-thio- and 2-selenoxo-compounds, and the yield of cross-coupling products is higher than those of the self-coupling byproducts. Sometimes, coupling of 1,2-dithiolium salts (Scheme 3) or selenium analogs via triethylamine has been applied for the preparation of the corresponding tetraheterafulvalenes (see for example [6], [7], [39]). A number of sulfur [24], selenium [24], [32], [35] and tellurium [24]-containing symmetrical polyheterotetraheterafulvalenes have been prepared from the corresponding simplest tetraheterofulvalenes (TTF, TSF, TTeF) by a three-step sequence: lithiation with lithium diisopropylamide (LDA), chalcogene-addition and reaction with alkyl halide. A similar procedure has been applied for an oxygen-containing tetraheterafulvalene [32]. Some sulfur-[7], [78], selenium-[14], tellurium-[14] and nitrogen-containing [78] tetraheterafulvalenes have been prepared by

treatment of the corresponding dialkali dithiolates, as well as selenium- and tellurium- analogs with tetrachloroethylene.

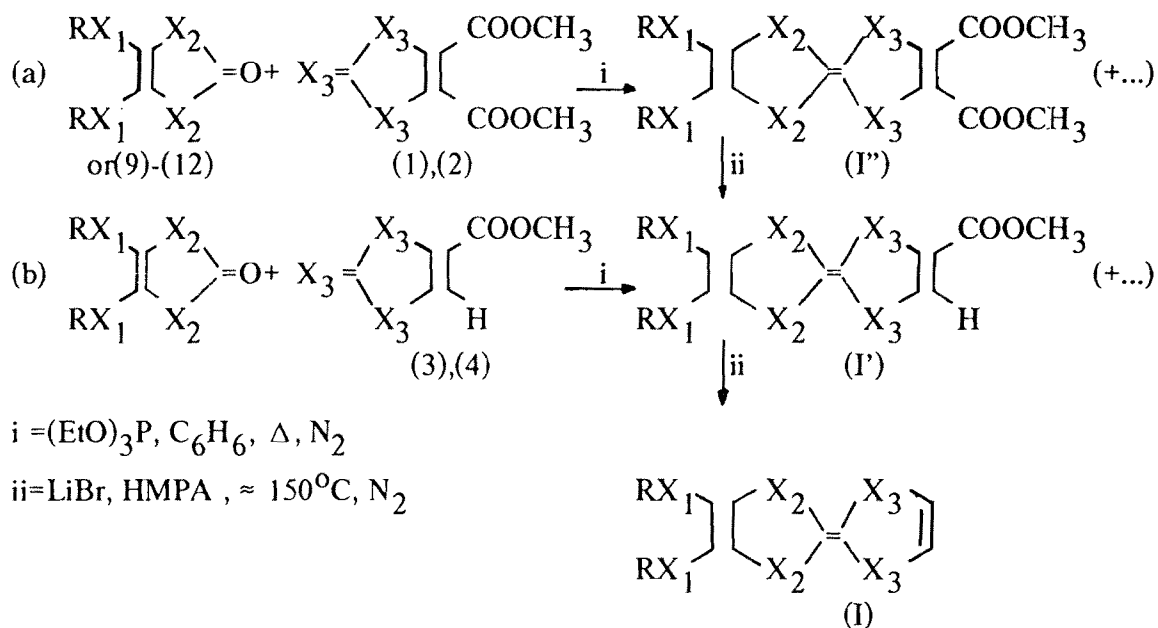
In this section we report methods for preparation of some unsymmetrical tetraheterafulvalenes of the following formulas, (I)-(XII):



A number of them have been prepared by cross-coupling reaction of materials (9)-(18), or the corresponding 2-oxo-1,3-dithioles and selenium-analogs, via triethyl phosphite. Because of the widely varying polarity of the cross-coupling products and the self-coupling byproducts, the separation by gel column chromatography is in most cases very easy (see [38],[74],[75],[78],[82],[83],[85],[86],[109]). Compounds (I)-(III) can be also prepared by this method, but the chromatography separation of the products is difficult (see refs [48], [59] cited in ref [38] here, [21]). To avoid these separation difficulties, a two- or three-step procedure, using one un-functionalized component and one component containing groups of highly polarity such as COOCH<sub>3</sub>, CN, has been applied (see [7], [20], [39]-[41] and refs therein).

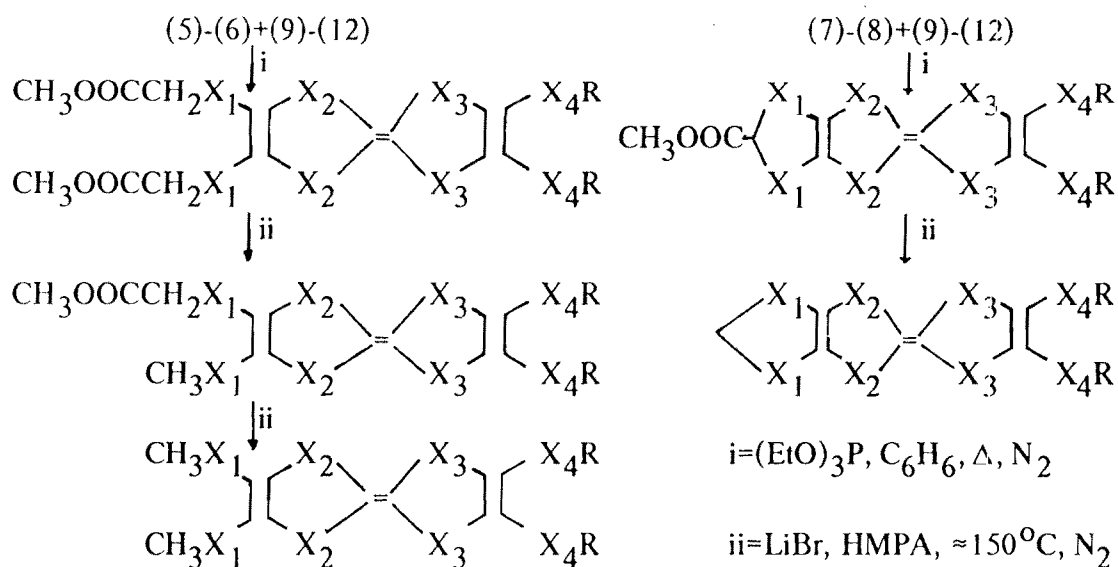


The functional groups should be eliminated, or modified, in the last step of the reaction procedure. Compounds of the type (I), for example, have been prepared from (9)-(12) and (1) - (4) according to the following Scheme 5 [20],[37], [41],[106]:



Scheme 5

It has been found that the yield of compounds of the type (VI), prepared by same procedure, is higher than that of the corresponding procedure using unfunctionalized components (:vinylene trithiocarbonate, vinylene triselenocarbonate [110] and (13)-(18)) [20], [38] [109]. Compounds similar to (I) and (VI) can be prepared by the same methods, using more complicated starting materials of Classes 9 [34], 10[78] (Table 1) and selenium analogs [36]. Also, using (5)-(8) and (9)-(12), tetraheterafulvalenes of the type (II)-(V) have been prepared by similar procedures (Scheme 6) [20], [39], [40], [106] [109]. Isothiazole-containing tetrathiafulvalenes of the type (VI) and (VIII) have been prepared, from the corresponding 5-cyanoisothiazole-containing tetrathiafulvalenes, by elimination of CN-group [86],

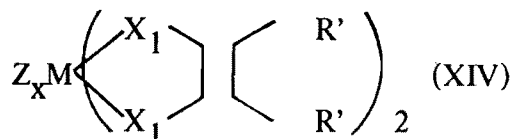
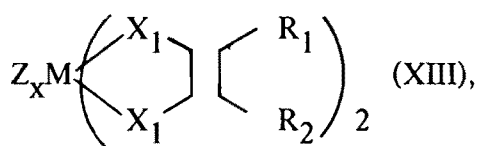


Scheme 6

[109]. Compounds of the type (III)-(V) have been prepared from 2-thioxo-1,3-dithiols by the trithioorthoformate procedure [21]: thiophilic addition of MeLi, acidification with AcOH, treatment with *n*-BuLi, addition of a second 2-thioxo-1,3-dithiols, followed by methylation with MeI, and thermolysis in organic solvents. They could be also prepared by a three-step procedure (lithiation with LDA, chalcogene-addition, treatment with alkylhalide) [20], which has been applied for the preparation of some symmetrical tetraheterafulvalenes [24],[32]. A number of subproducts, similar to those of Scheme 4, produced on the application of the last two procedures, are due to the alkaline reaction media. Also, impurities are due to the thermal isomerization of (20)[66],[79]. Sometimes, high-performance liquid chromatography, followed by recrystallization, is needed for a complete purification of the required tetraheterafulvalenes. The solutions of TTFs in organic solvents (CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> etc) are more or less unstable. It was observed, for example, that the NMR spectra of compounds (I)[41] in CDCl<sub>3</sub> do not show the band at ca δ: 6.33 (CH=CH) some days after the preparation of the solutions even in absence of oxygen. This means that a partial or complete transformation of TTFs to undesirable products takes place on standing of their solution for long time.

#### METAL 1,2-DIHETEROLENES

A number of metal 1,2-dithiolenes, mainly corresponding to 1,3-dithiols of Class 0 (Table 1), and selenium-, tellurium-, etc- analogs, have been described in refs [10]-[12] and refs therein. Recent work has been described in refs [48], [52], [54]. In this section we describe methods of preparation and properties of cation-rich salts of some metal 1,2-dithiolenes and selenium analogs, having ligands with additional heteroatoms (S,Se,N) to an additional ring or chain. These are compounds of the following formulas, (XIII)-(XXII),

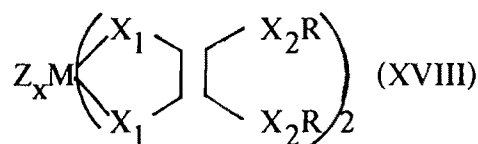
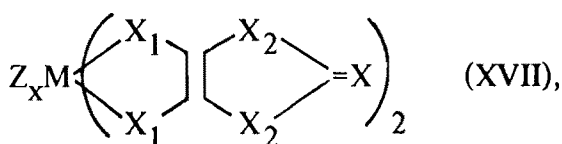
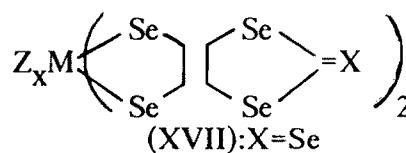
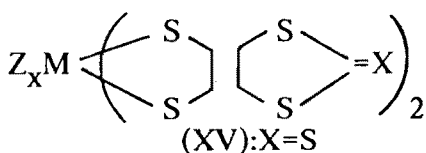


Z=Li,Na,etc; Bu<sub>4</sub>N,Me<sub>4</sub>N, etc; x=2,1; M=Zn,Hg,Ni, Pd etc

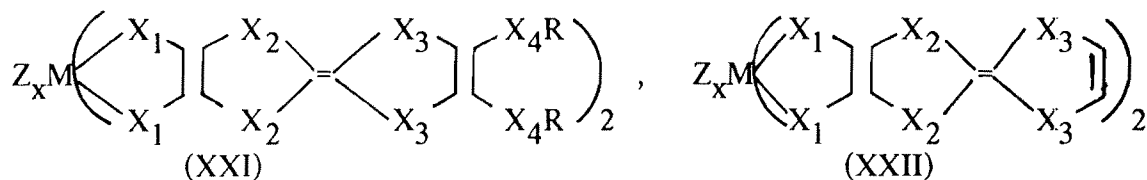
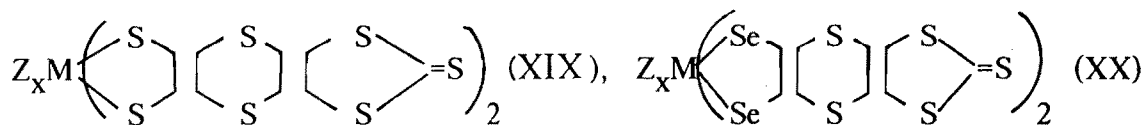
(A):X<sub>1</sub>=S, R<sub>1</sub>=R<sub>2</sub>=CN, (B): X<sub>1</sub>=S, R<sub>1</sub>=CN, R<sub>2</sub>=SCH<sub>3</sub>

(C):X<sub>1</sub>=Se, R<sub>1</sub>=R<sub>2</sub>=CN, (D):X<sub>1</sub>=S, R<sub>1</sub>+R<sub>2</sub>= S-S-C(=S)

(A'):X<sub>1</sub>=S, 2R'=pyridine-, (B'):X<sub>1</sub>=S, 2R'=5-cyanoisothiazole-, (C'):X<sub>1</sub>=S,2R'=pyrazine-group fused to the metal 1,2-dithiolate ring and similar with X<sub>1</sub>=Se.



(A):X<sub>1</sub>=Se, X<sub>2</sub>=X=S, (B):X<sub>1</sub>=S, X<sub>2</sub>=X=Se, (C):X<sub>1</sub>=X<sub>2</sub>=S, X=Se, (D):X<sub>1</sub>=X<sub>2</sub>=Se, X=S.

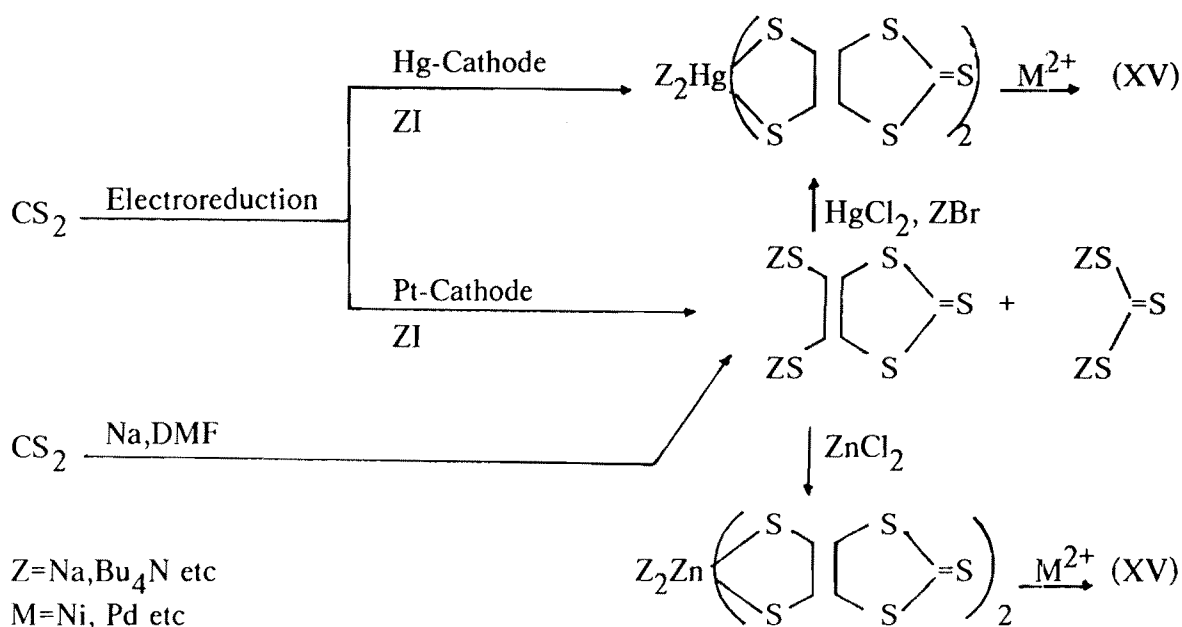


(A):  $X_1=X_2=X_3=\text{S}$ ,  $X_4=\text{Se}$ , (B):  $X_1=X_2=X_4=\text{S}$ ,  $X_3=\text{Se}$  etc

(a):  $\text{R}=\text{CH}_3$ , (b):  $2\text{R}=\text{CH}_2$ , (c):  $2\text{R}=\text{CH}_2\text{CH}_2$  etc

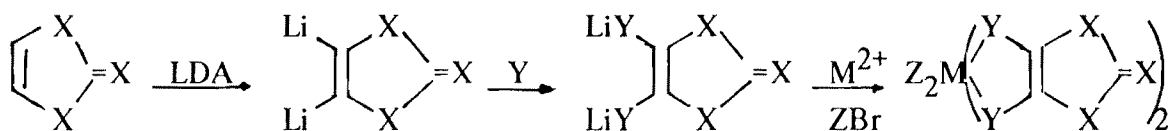
(i):  $2\text{R}=\text{O}$ , (ia):  $2\text{R}=\text{S}$ , etc

Compounds of the type (XIII) have been prepared from the corresponding disodium dithiolates, or 1,3-dithioles [11], [27],[79], and Se-analogs [111], by methods reported in refs [10] - [12]. Also, compounds of the type (XIV) have been prepared by similar methods [72], [78], [83], [85], [86], [112],[113]. Compounds of the type (XV) have been prepared by chemical or electrochemical reduction of carbon disulfide in dimethylformamide (DMF), followed by reaction with transition-metal salts according to Scheme 7 (see [61]-[65], [78] and refs cited therein). Selenium-



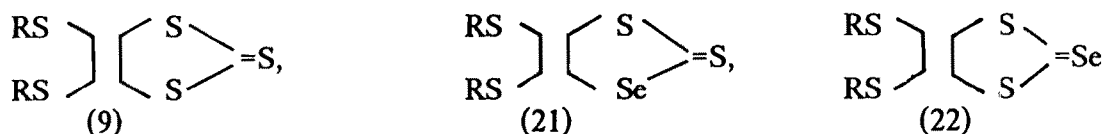
Scheme 7

analogues (XVI) have been prepared from carbon diselenide by similar methods (see [53], [62]-[65],[107]). Using  $\text{CSSe}$ , instead of carbon disulfide or carbon diselenide, a number of alloys have been obtained [53]. Compounds (XV), (XVII A) and (XVI) have been prepared from vinylene trithiocarbonate and vinylene triselenocarbonate, respectively, by a three-step procedure according to Scheme 8 (see [25],[29],[41],[106]). Attempts to prepare (XVII B)-(XVIID) and similar compounds

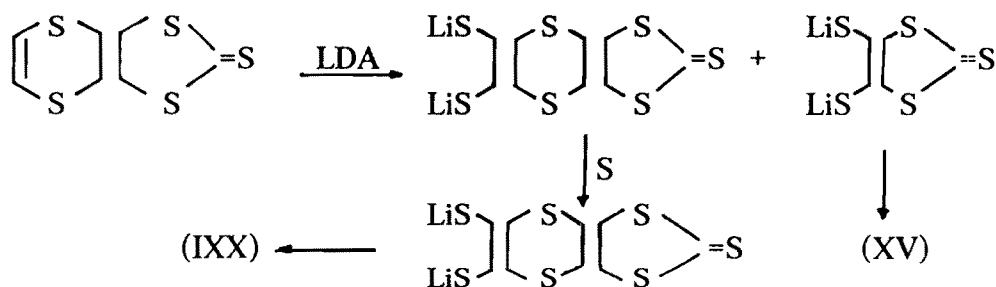


Scheme 8

from the corresponding vinylene trichalcogenocarbonate [114] by this method have been unsuccessful. Instead of them, a number of alloys with symmetrical or unsymmetrical molecules have been obtained [104]. The reason is that, in alkaline medium (LDA), a rearrangement of sulfur and selenium atoms takes place [104]. 1,3-Thiaselenole-2-thione, for example, can be isomerized to 1,3-dithiole-2-selenone, and vice versa [104],[114]. Treatment of the resulting alloys (M=Zn) with alkyl halides, followed by chromatographic separation, a number of compounds (9), (21), (22) etc have been obtained [104]. The isolation of these compounds shows the pres-



ence of the corresponding ligand in the considered alloy. Compounds (XV) and (XVIIA), with X=O, [49], [50],[64] instead of X=S, can be prepared by same procedure (Scheme 8) using 1,3-dithiole-2-one and 1,3-diselenole-2-one, respectively, instead of vinylene trithiocarbonate. Some compounds with formulas (XV)-(XVII) can be prepared from 4,5-vinylenedithio-1,3-dithiole-2-thione, 4,5-vinylenediseleno-1,3-dithiole-2-thione, etc by a two-step sequence: reaction with LDA (see Scheme 4c) followed by treatment of a transition metal salt with ZBr. A few of them can be prepared by an easier procedure from the ethylene-analogs (see Scheme 4b) [108]. Some compounds with formula (XVIII) have been prepared by treatment of the corresponding 1,3-dithioles and selenium-analogs with potassium ethoxide or potassium hydroxide, followed by treatment with a transition-metal salt in presence of ZBr [47] [76]. However, this method can not be applied for the preparation of (XVIII B) (see Scheme 4b). Instead, the compounds of the type (XVIIA) have been obtained [108]. Compounds of the type (XIX) can be isolated from the reaction products of 4,5-vinylenedithio-1,3-dithiole-2-thione with LDA, after sulfurization with sulfur, and treatment with a transition-metal salt in the presence of ZBr, according to the following Scheme 9 [34], [36],[45], [108]:



Scheme 9

Compounds of the type (XX) can be prepared by a similar procedure. However, in both of the last cases, the separation of (XIX) and (XX) from the byproducts (XVIII) is difficult [108]. Similar procedures have been applied for the preparation of (XXI), (XXII) and similar compounds (see [76], [77],[108],[115]) from the corresponding compounds of the type (I), (II) etc.

Purification of compounds (XIII)-(XXII) and conversion from a cation Z to an other Z', or from a metal to another one, can be performed by a three-step sequence: treatment with benzoyl chloride, reaction with sodium ethoxide and treatment with a transition metal salt in presence of ZBr or Z'Br. All the compounds of the type (XIII)-(XXII) can be transformed to the corresponding neutral compounds (x=0) after treatment with an oxidizing reagent (e.g. Br<sub>2</sub>) or by electrooxidation.

## CONDUCTING AND SUPERCONDUCTING SALTS

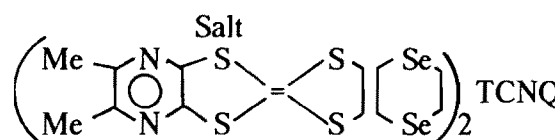
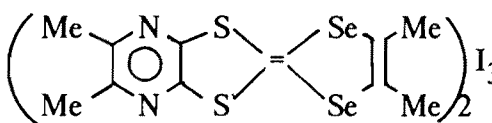
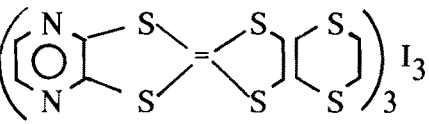
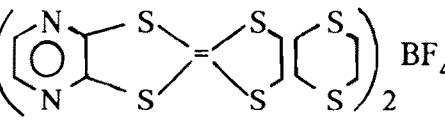
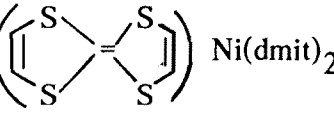
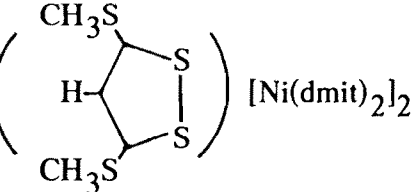
Using compounds of the type (I)-(XXVII), a number of charge-transfer complexes (CTC), cation-radical salts (CRS), and cation deficient metal 1,2-diheterolenes (CDMD) have been prepared [20], [37]-[41], [61]-[99], [108], [109], by chemical (direct reaction or diffusion) or electrochemical procedures, some of which are outlined in the following Scheme 10 :

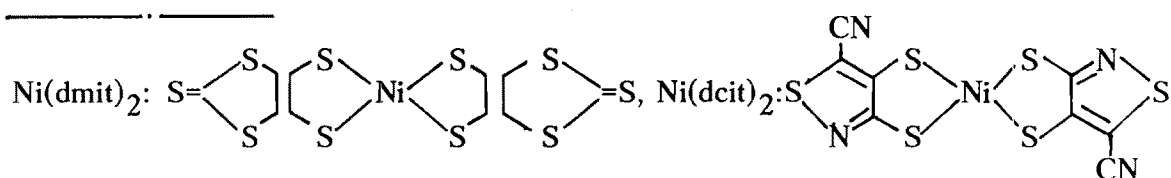
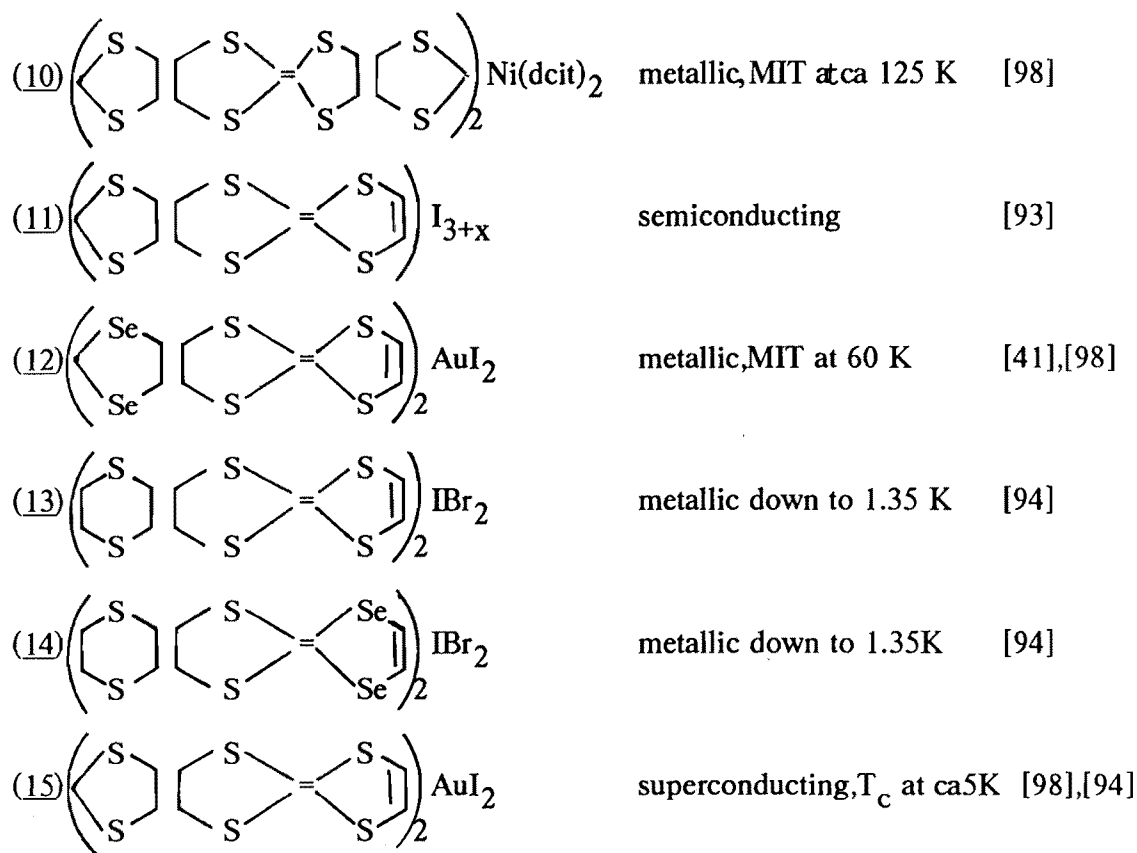
- (a)  $x\text{D} + \text{TCNQ} \rightarrow \text{D}_x\text{TCNQ}$  ( $x=0,5,1,2$ ; D=donor)  
 (b)  $x\text{D} + \text{I}_3^- \rightarrow \text{D}_x\text{I}_3$  ( $x=1,2$  etc)  
 (c)  $\text{ZX} + \text{X}' \rightarrow \text{ZX}' + \text{X}$  ;  $\text{ZX} + \text{KTCNQ} + \text{TCNQ} \rightarrow \text{Z}(\text{TCNQ})_2 + \text{KX}$   
 (d)  $\text{Z}_2\text{X} \rightarrow \text{Z}_1\text{X} \rightarrow \text{Z}_x\text{X}$  ( $1 > x > 0$ )  
 (e)  $\text{ZX} + (\text{TTF})\text{X}' \rightarrow \text{Z}(\text{TTF}) + \text{ZX}'$  (Z=cation)

Scheme 10

The salts, obtained by these methods, have been found have in several varying chemical compositions, crystal structures and physical properties, which depend in most cases on the counter ion and the conditions of crystallization. Table 2 gives the formulas of some salts, and information on their corresponding composition and

Table 2. Examples of some conducting and superconducting salts

Salt	Behavior	Refs
(1) 	semiconducting	[109]
(2) 	metallic, MIT at ca 120K	[89]
(3) 	metallic, MIT at ca 60K	[80]
(4) 	metallic, MIT at ca 180K	[84]
(5) 	semiconducting	[61],[62]
(6) 	semiconducting	[76]
(7) $\text{K}_2[\text{Ni}(\text{dmit})_2]_5$	semiconducting	[44],[63]-[65]
(8) $\text{Cs}[\text{Pd}(\text{dmit})_2]_2$	metallic, MIT at 60K	[44],[63][65]
(9) $(\text{Me}_4\text{N})_x[\text{Pd}(\text{dmit})_2]$	metallic MIT at ca 280K	[98]



electrical behavior. Crystal structure solutions, which have been performed in a number of salts, showed that there are strong intermolecular interactions due to the S--S, S--N, Se--Se, Se---S, Se---N contacts [95]-[97],[91],[87],[88] [80], [73]. Compound (1) behaves as a semiconductor, similar to those reported in ref [14b] and ref [15] cited therein, which are compounds of tellurium and selenium:(DMHM-TTeF)<sub>x</sub>TCNQ, (CpHMT-TSF)<sub>x</sub>TCNQ, (DMHM-TSF)<sub>2</sub>TCNQ. Compound (3) and similar compounds, reported in refs [75],[80], [87], have a composition 3:1. According to a treatment given in ref [116], in the case of salts with stoichiometry 2:1, 4:3 and 1.1:1, the anionic chains (A) provide an external potential on the organic stack (D) which corresponds to a Fermi wave vector  $q^A$  with values  $4k_F^D$ ,  $2k_F^D$  and  $\frac{4}{3}k_F^D$ , respectively [116]. In the case of 3:1 salts, it should be  $q^A \geq 6k_F^D$ . Compound (6) and similar compounds [66], [69], [76], [79] are semiconductors under ambient pressure, and are of the same stoichiometry as (Me<sub>4</sub>N) [Ni(dmit)<sub>2</sub>]<sub>2</sub> (:superconductor under pressure). Conductivity measurements under high pressure are required for this kind of salts. Compounds (13) and (14) which are isostructural with the  $\beta$ -(BEDTTTF)<sub>2</sub>X superconductors [4], are metallic down to 1.35 K. These compounds have a residual conductivity  $\sigma_{1.35K} > 10000 \Omega^{-1} \text{ cm}^{-1}$  [98]. According to the treatment reported in refs [117], [3], the superconductivity in organic systems requires a minimum residual conductivity of  $6000 \Omega^{-1} \text{ cm}^{-1}$ , a value consistent with the theoretical estimation based on the Anderson localization. Compounds (13) and (14) could be candidates for superconductivity as they fulfill

the above conditions. This means that conductivity measurements are required at lower temperatures. Compound (15) consists of unsymmetrical molecules of methylene dithiotetrathiafulvalene (MDTTTF) [20], [37]. Compound (15) and compounds (16),(17),(18) are almost isostructural at room temperature[94],[97], [99],[100], [118],[119]. They are superconducting crystals, which consist of tightly linked dimers almost orthogonally arranged, to form 2-dimensional S---S, or Se---S networks (see [94], [119] and refs therein).

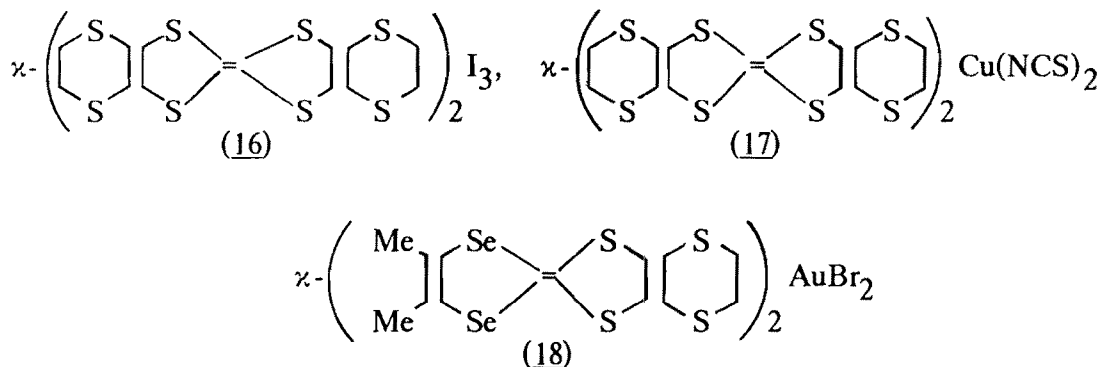


Fig.1 shows the temperature (T) dependence of resistivity ( $\rho$ ) of superconductors (15) [94], (16)[119], (17) [118] and (18) [99]. One can observe that the resistivity of (15) decreases smoothly with decreasing temperature down to superconducting transition temperature. This observation indicates that the crystal structure

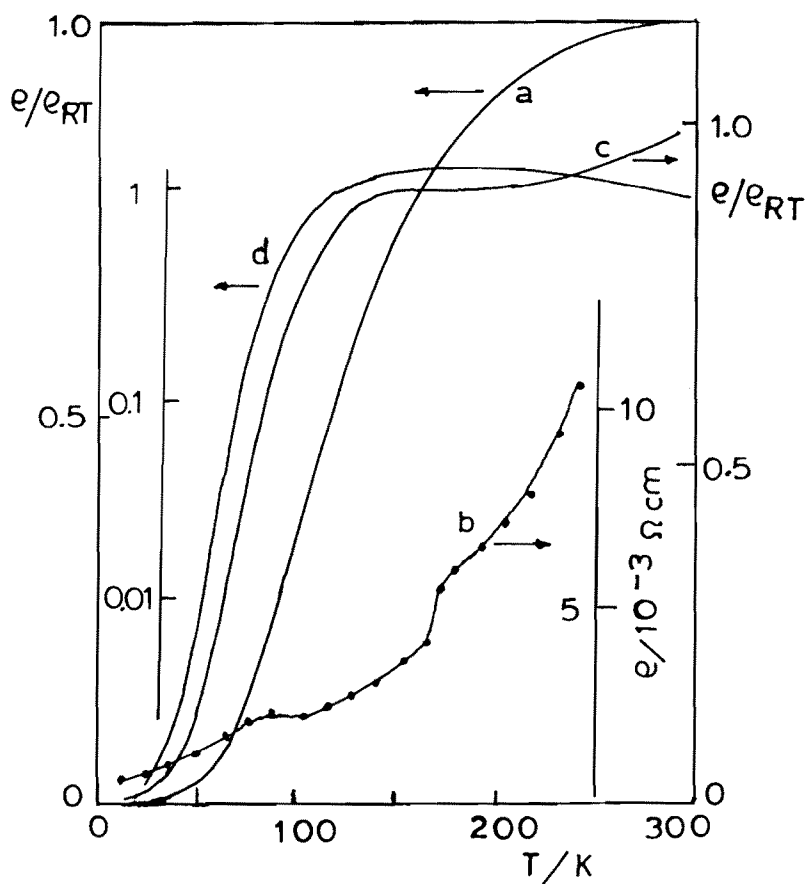


Fig. 1. Temperature dependence of resistivity of superconductors: (15)(a), (16)(b), (17)(c), and (18)(d) for  $T_c < T \leq T_{RT}$ .

remains the same as that at room temperature. These findings from the considered compound (15) firmly dispel the following two notions [8]:

- (1) symmetrical molecules are essential for designing new conductors and superconductors,
- (2) the molecules must be packed in regular stacks in the crystals of conductors and superconductors

#### ACKNOWLEDGEMENTS

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