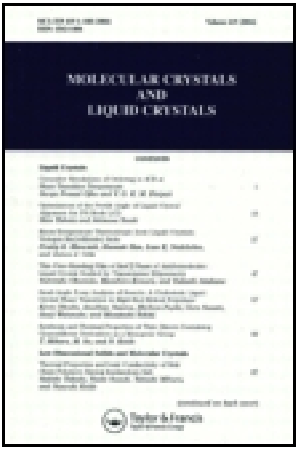

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New Mdlecuiar Conducpors: Variation on the Bedtttf Skeleton

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NEW MOLECULAR CONDUCTORS : VARIATION ON THE BEDTTTF SKELETON

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ABSTRACT New organic conductors obtained by modification of the BEDTTTF molecule are presented. The synthesis of these compounds is detailed and some physical properties are given.

The discovery of superconductivity at ambient pressure has been one of the most exciting improvements in the field of organic conductors[1]. Most of these studies have been devoted to the TMTCF (tetramethyltetrathia(selena)fulvalene) series. Unfortunatly the transition temperature of the superconductivity never rises well above one Kelvin in this series.

A few years ago significant advances were obtained using a new organic donor : the bis(ethylenedithio-)tetrathiafulvalene (BEDTTTF)[2]. The BEDTTTF salts exhibit a wide variety of behavior, several of them showing superconductivity. For instance one phase of $(BEDTTTF)_2I_3$ becomes superconducting around 8K[3] at ambient pressure.

The common structural feature of the TMTCF salts is a zig-zag stacking of the organic molecules, leading to cavities where the anions lie. This structural packing gives a quasi one dimensional character to the electronic properties of these compounds. On the other hand the presence of four more sulfur atoms in the BEDTTTF drastically enhances the interactions between neighbouring molecules giving rise to a behavior of higher dimensionality[4]. This enhancement of the dimensionality seems to be one of the origins of the interesting properties of the BEDTTTF salts but prevents the characteristic stacking of the organic molecules. Thus the BEDTTTF salts generally crystallize in many phases of different stoichiometries and structural arrangements[5] and it is very hard to obtain selective crystallization of the most interesting phases.

One way to avoid this problem is to modulate the transverse interactions : this may be done by modifying the shape of the organic donor. We will present in this communication the synthesis and properties of new molecules derived from the BEDTTTF skeleton.

One possible modification is to change the ethylendithio side groups to other alkyldithio groups and we have synthesized the bis(methylenedithio-)tetrathiafulvalene (see table 1). Another possibility is to synthezise unsymmetrical molecules by altering one half of the BEDTTTF[6]. By judicious choice of the second half of the molecule we can adjust its size and the distance between neighbours. Two examples of unsymmetrical donors we have studied are given table 1.

CHEMICAL PREPARATION

The synthesis of these compounds is achieved by coupling the corresponding thiones. The first step of this synthesis is thus the preparation of the thiones. The 1,3-dithiole-2 thiones (8) and (9) have been prepared using the already published method[7]. The synthesis of the other thiones is described figure 1.

The 4,5(ethylenedithio)-1,3-dithiol-2-thione (2) is readily obtained reducing carbon disulfide by metallic sodium in presence of dimethylformamide followed by cyclisation of the blood red dithiolate intermediate (1) with dibromoethane[8]. Unfortunatly this very simple method fails to prepare the 4,5(methylenedithio)-1,3-dithiol-2-thione (4). The latter thione has been obtained in an indirect way. The addition of $ZnBr_2$ to the dithiolate (1) gives the

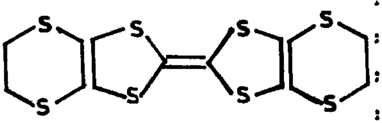
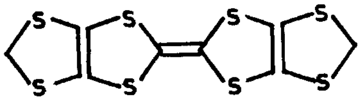
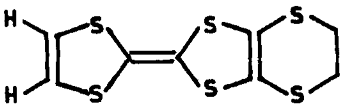
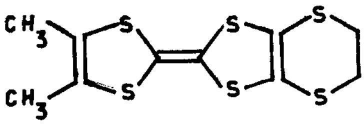
	Bis(EthyleneDiThio) TetraThiaFulvalene (6) BEDTTTF
	Bis(MethyleneDiThio) TetraThiaFulvalene (7) BMDTTTF
	EthyleneDiThio TetraThiaFulvalene (10) EDTTTF
	DiMethyl(EthyleneDiThio) TetraThiaFulvalene (11) DMEDTTTF

TABLE 1 : Chemical formula of studied compounds

zinc complex (3)[8]. The reaction of this complex with di-

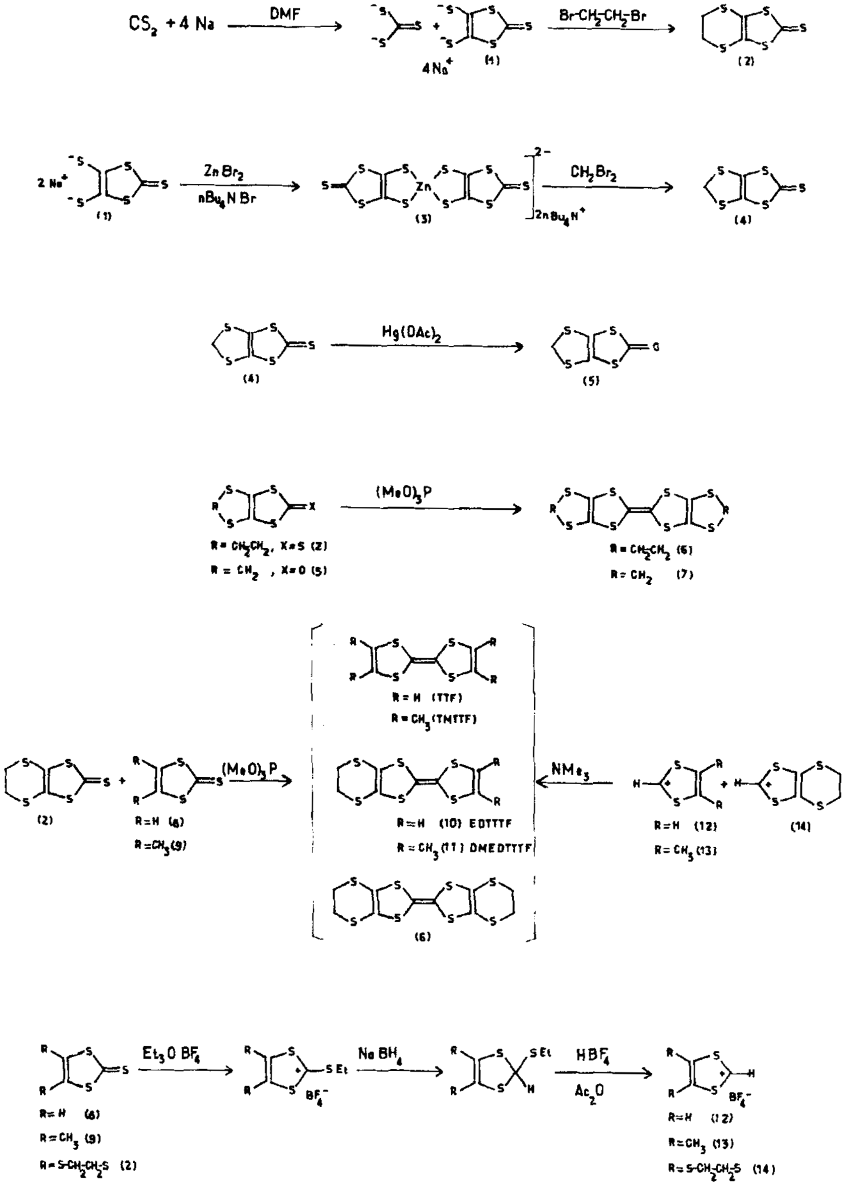


Figure 1 : Chemical routes to the desired compounds

bromomethane in acetone at room temperature for seven days leads to the expected compound with a global yield of 30%.

The BEDTTTF (6) is obtained by coupling the corresponding thiones in refluxing neat trimethylphosphite. This reaction gives only poor yield in the case of BMDTTTF (7). For this compound the coupling step is better starting from the corresponding cetone (5) obtained by reaction of mercuric acetate with the thione (4)[10]. Two ways can be followed to prepare the unsymmetrical molecules. The first one is the coupling of the two different thiones in refluxing trimethylphosphite. The second one is the coupling of the dithiolium salts (12 and 13 with 14) using trimethylamine. These dithiolium salts are obtained in three steps from the thiones : alkylation, reduction and desulfuration[11]. Both these methods yield random coupling and lead in addition to the expected unsymmetrical product the two symmetrical ones. The separation of the compounds is achieved using flash chromatography on silica gel with CS_2 as eluant. The desired purity is obtained after several runs.

The radical cation salts of these compounds are obtained by the classical electrochemical method. The results are summarized table 2. The obtained crystals are either needles or plate like and, at least for the unsymmetrical donors, seem not to be polyphasic. Unfortunatly we encounter some difficulties in the growing of DMEDTTTF crystals.

PHYSICAL CHARACTERIZATION

The salts stoichiometry (given table 2) has been checked using electronic microprobe and Weissenberg photographs for several compounds.

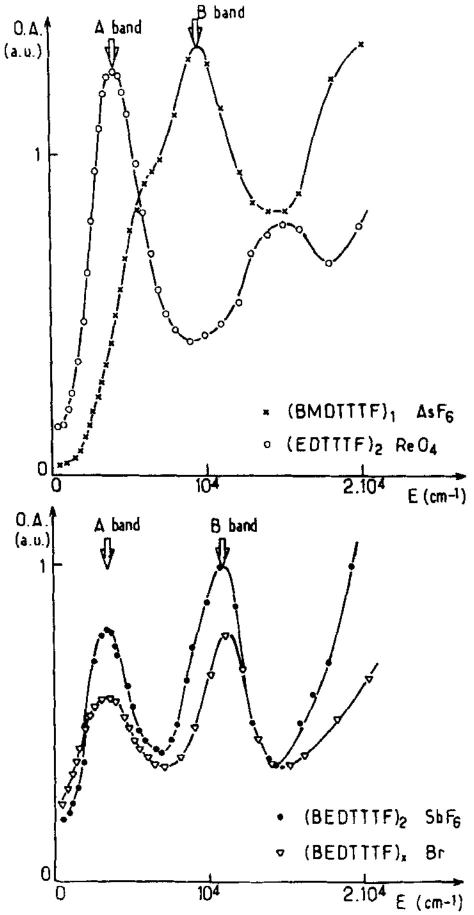


Figure 2 : Electronic absorption spectra of four studied salts

The optical absorption experiments in I.R. and visible spectra are fundamental for characterizing the elementary excitations in these solids. It has been shown [14] that two types of charge transfer bands occur : one absorption band around 4000 cm^{-1} for mixed valence salts (A band) and one other band just above 8000 cm^{-1} for fully ionized salts (B band). The exact positions of these electronic bands change slightly with the involved blocks.

Using the classical technique of dilute compounds in a KBr pellet, have obtained the results presented figure. 2 for the different compounds [15].

i) $(BMDTTTF)_2SbF_6$ presents a strong B peak with a shoulder on the low energy side, the origin of which is not clarified. This is in agreement with the semi-conducting behavior observed in this salt (stoichiometry 1-1) ;

ii) $(EDTTTF)_2ReO_4$ exhibits a strong A peak without any apparent B type absorption band (the absorption band above 12000 cm^{-1} is associated with an intramolecular electronic transition). This behavior is typical of conducting salts with 2-1 stoichiometry as TMTTF and DMtTTF salts [15].

iii) BEDTTTF salts : the two salts present simultaneously both the A and B absorption bands. This situation seems to be a new one and is not explained yet.

The electrical conductivity has been measured along the growth axis using the classical four probe method. The room temperature values are given table 2. The BMDTTTF salts seem to be poor conductors. All the samples of this donor show very low room temperature conductivity and behave as semiconductors. It is noticeable that these salts do not present the classical 2/1 stoichiometry. In the same way $(DMEDTTTF)_2SbF_6$ show an electrical conductivity of about $10^{-3}\Omega^{-1}cm^{-1}$ and semiconducting behavior.

On the other hand the salts of EDTTTF are better conductors. The room temperature conductivity of these 2/1 salts is about 30 $\Omega^{-1}cm^{-1}$ for ClO_4 and ReO_4 and up to 1000 $\Omega^{-1}cm^{-1}$ for the PF_6 salt. This value is the highest found in sulfur compounds and is of the same order of magnitude as the best TMTSF salts. Moreover these EDTTTF salts are metallic at room temperature as shown by the temperature dependence of the conductivity curves given figure 3.

Anions / Organic Molecules	Br^-	ClO_4^-	ReO_4^-	PF_6^-	SbF_6^-
$(BEDTTTF)_x$ Stoichiometry RT conductivity ($\Omega^{-1}cm^{-1}$) RT behavior	needles x 100 metallic	•	•	Cf réf. 12 x = 2 15 semi-conductor	Cf réf. 13 x = 2 5 semi-conductor
$(EDTTTF)_x$ Stoichiometry RT conductivity ($\Omega^{-1}cm^{-1}$) RT behavior		small needles x = 2 30 metallic	needles x = 2 30 metallic	needles/plates x = 2 1000 metallic	microcrystals
$(DMEDTTTF)_x$ Stoichiometry RT conductivity ($\Omega^{-1}cm^{-1}$) RT behavior					† plates 10^{-3} semi-conductor
$(BMDTTTF)_x$ Stoichiometry RT conductivity ($\Omega^{-1}cm^{-1}$) RT behavior		needles x = 1 < 1 semi-conductor		powder x = 1	needles x = 1 < 1 semi-conductor

TABLE 2 : Physical data of several cation radical salts

• for a review see ref. 5 and references therein

† this sample has been prepared by J.P. MORAND.

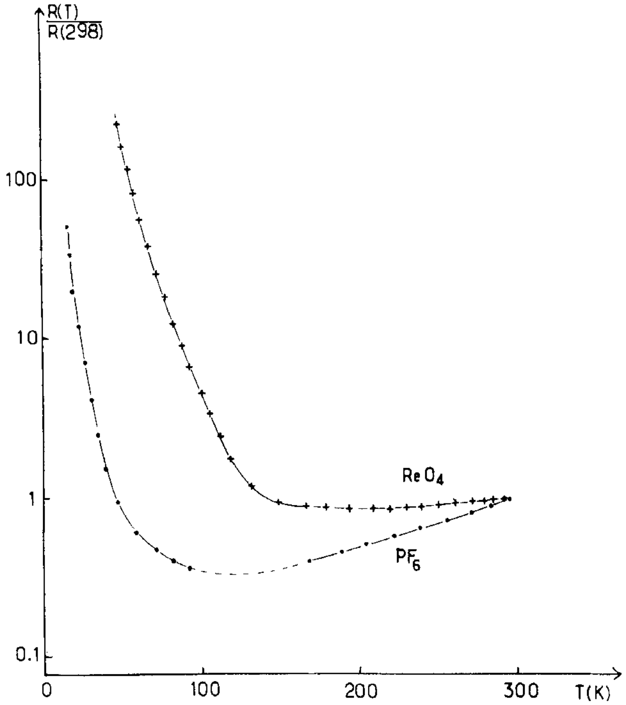


Figure 3 : Temperature dependence of the normalized resistivity for two (EDTTF)$_2$X *salts*

Unfortunatly the metallic behavior does not persist at low temperature. The electronic localization becomes dominating around 130K for (EDTTTF)$_2$ClO$_4$ and around 40K for (EDTTTF)$_2$PF$_6$. Moreover a slight anomaly has been detected in the logarithmic derivative curve of the conductivity of this latter compound at 35K. Nevertheless work is currently in progress in order to synthesize other salts of this very interesting donor and we hope to obtain salts with metallic behavior until very low temperature.

Whatever the difficulties in synthesizing unsymmetrical molecules, the results obtained with EDTTTF salts are in agreememnt with our hypothesis. The achievement of highly conducting samples needs the possibility of a modulation of the transverse interactions and one way to achieve this goal is to prepare unsymmetrical organic conductors.

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