

Pyrazino-methyl-ethylenedithio-tetrathiafulvalene, Precursor of τ -Phase Conductors

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Modifications of the previously reported methods of preparation of racemic pyrazino-methyl-ethylenedithio-tetrathiafulvalene, *i.e.*, 2-(5,6-dihydro-5-methyl-1,3-dithiolo[4,5-b][1,4]dithiin-2-ylidene)-1,3-dithiolo[4,5-b]pyrazine, and their cation radical salts with linear counter anions are reported. ESR spectra and preliminary X-ray diffraction measurements indicate that the salts crystallize in the τ -phase (tetragonal system).

Introduction

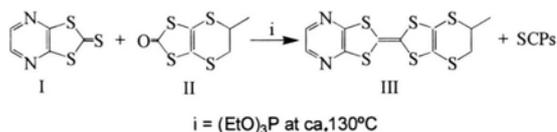
It has been found that the τ -phase crystals of some cation radical salts (τ -phase conductors) exhibit exceptional structural and physical properties, *e.g.*, crystallization in the tetragonal system, star-like Fermi surface, negative Hall coefficient and negative magnetoresistance at low fields as well as magnetoresistance oscillations at higher fields [1–6]. The τ -phase conductors are based on some unsymmetrical π -donor molecules, such as pyrazino-dimethyl-ethylenedithio-tetrathiafulvalene (P-DMEDT-TTF) with linear counter anions (*e.g.*, AuBr_2^- , AuI_2^- , IBr_2^-). A similar π -donor, pyrazino-methyl-ethylenedithio-tetrathiafulvalene (P-MEDT-TTF), *i.e.*, 2-(5,6-dihydro-5-methyl-1,3-dithiolo[4,5-b][1,4]dithiin-2-ylidene)-1,3-dithiolo[4,5-b]pyrazine, has been prepared and studied fifteen years ago [7, 8]. Using pyrazino-1,3-dithiole-2-thione and 4-methyl-ethylenedithio-1,3-dithiole-2-thione as starting materials, the donor P-MEDT-TTF had been obtained in a low yield (*ca.* 6%) [7, 8]. Upon electrocrystallization of this donor in the

presence of a linear-anion containing compound by a well known method [1, 9], which will be briefly described below, polycrystalline deposits of cation radical salts had been obtained [8].

In this paper, the preparation of P-MEDT-TTF and its cation radical salts with linear counter anions by modified methods is reported. By application of these methods, it was found that good crystals of τ -phase salts can be obtained.

Experimental

The π -donor P-MEDT-TTF (III) was prepared by the reaction procedure of Scheme 1. Pyrazino-2,3-dithiole-2-thione (I) was prepared by the method reported in [7, 8]. Racemic 4-methyl-ethylenedithio-1,3-dithiole-2-thione was prepared from $(\text{Bu}_4\text{N})_2\text{Zn}(\text{dmit})_2$ (where dmit is 1,3-dithiole-2-thione-4,5-dithiolate) by the method reported in [10, 11], in a yield of 70%. It was then converted to the corresponding ketone (II) in quantitative yield by a well known method using $\text{Hg}(\text{OAc})_2$ (see [1, 12]). A solution of compounds I (186 mg, 1 mmol) and II (222 mg, 1 mmol) in neat triethylphosphite (5 ml) was heated with stirring at *ca.* 100 °C for 1 h and then at *ca.* 130 °C for 3 h. Excess of triethylphosphite was distilled off under vacuum and the yellow-red solid mass was washed with methanol (2×3 ml) and air dried. The solid was purified by column chromatography (silica, CH_2Cl_2). The second orange-yellow fraction was collected, evaporated and dried in air to give 70 mg (19.5%) of the cross coupling product P-MEDT-TTF (III) as an orange polycrystalline solid. Recrystallization from CH_2Cl_2 –hexane yielded orange needles, m.p. 146–147 °C (lit. 145 °C [7, 8]). The first and third fractions yielded the self coupling products (SCPs) of II [10] and I [7, 8], respectively.



Scheme 1.

A standard H-cell equipped with Pt-electrodes was used for electrocrystallization of the cation radical salts [8, 9]. In the one compartment, a solution of 10–15 mg of the donor P-MEDT-TTF and



50–60 mg of Bu_4NX ($X = \text{AuBr}_2, \text{AuI}_2, \text{IBr}_2$) in 25 ml of CH_2Cl_2 was placed. In the other compartment, a solution of 50–60 mg of Bu_4NX in 25 ml of CH_2Cl_2 was placed. When the anode electrode was placed in the high donor concentration compartment (as in [9]), the electrocrystallization with a current of $0.6 \mu\text{A}$ gave polycrystalline deposits (flakes) of cation radical salt at the anode electrode, as it was reported previously [8]. When the anode electrode was placed in the low (or zero at the beginning) donor concentration compartment, the electrocrystallization was slower, but good crystals (tetragonal plates) were obtained in 10–15 d. The crystals obtained by this slightly modified method have the same morphology as the τ -phase salts based on P-DMEDT-TTF and similar π -donors [1–6].

All the salts of P-MEDT-TTF with linear counter anions exhibit broad ESR bands as in the cases of τ -phase salts based on P-DMEDT-TTF and similar π -donors [1, 6]. Moreover, preliminary X-ray diffraction measurements of the AuBr_2 based salt of P-MEDT-TTF gave a space group of tetragonal system (I4) with $a = 7.4$ and $c = 67.4 \text{ \AA}$. These data are close to those obtained for the corresponding salt of P-DMEDT-TTF [1, 6].

Results and Discussion

The racemic material 4-methyl-ethylenedithio-1,3-dithiole-2-one, precursor of P-MEDT-TTF can be obtained from $(\text{Bu}_4\text{N})_2\text{Zn}(\text{dmit})_2$ in good yield (ca. 70%) by a two-step reaction [10] (see also [11]), while the racemic material 4,5-dimethyl-ethylenedithio-1,3-dithiole-2-one, precursor of P-DMEDT-TTF has been obtained in a lower yield (ca. 29%) by a three-step reaction [6, 11]. The cross coupling product of the reaction of Scheme 1 (i.e., P-MEDT-TTF) was obtained in a yield of 19.5%. It is a racemic mixture of two enantiomers, since the starting material (II) is also a racemic mixture.

It was found that the π -donor P-MEDT-TTF with linear counter anions give salts of the τ -phase. The donor P-MEDT-TTF, instead of P-DMEDT-TTF, is suggested for the preparation and further investigation of τ -phase conductors. It is expected that the τ -phase salts based on P-MEDT-TTF should contain both isomers, as in the case of the recently reported τ -phase salts based on P-DMEDT-TTF [6,11].

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