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ORGANIC METALS FROM CHIRAL BEDT-TTF DONORS

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ABSTRACT

We have recently described our project to prepare methylated BEDT-TTF derivatives in order to obtain different radical ion salts of these donors (1). Meanwhile we have obtained 7,7'-Dimethyl-BEDT-TTF ("DIET"), 7,8'-Dimethyl-BEDT-TTF ("DIET") and 7,7',8,8'-Tetramethyl-BEDT-TTF ("TMET") as isomeric mixtures and some of them in an "optically pure" form. The isomeric mixtures have been prepared as reported earlier (1) corresponding to the "classical" synthesis of BEDT-TTF (2). The optically pure compounds have been obtained starting from the optically pure 1,2-propanediol and 2,3-butanediol respectively, depicted on page 4.

RESULTS

The different donors were electrocrystallized under varying conditions. The following results have been obtained:
(i) DIET-salts could be crystallized with the counter ions FSO_3^-, CLO_4^-, HSO_4^-, IO_4^-, ReO_4^-, BF_4^-, $CF_3SO_3^-$, NO_3^-, Br_3^-, I_3^-, $[AuI_2]^-$ and PF_6^-. The salts (DIET)(BF_4) and (DIET)(FSO_3)have been prepared starting from an isomeric mixture and from the optically pure S,S and R,R-derivatives respectively. The crystals of the different preparations of (DIET)(BF_4) show the same structural features: Monoclinic, space group C 2/m, a = 5,240(9), b = 12,13(1), C = 14,20(1)Å, ß = 95.39(9)°. The symmetry of the unit cell and the

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position of the methyl groups show that only an average of the possible molecular orientations in the lattice is found by X-ray investigations. This means that the crystals are highly disordered. Figures 1 and 2 show the temperature dependence of the electrical conductivity for (DIET)(BF_4) obtained from the isomeric mixture (1) and from the pure S,S-derivative (fig. 2).

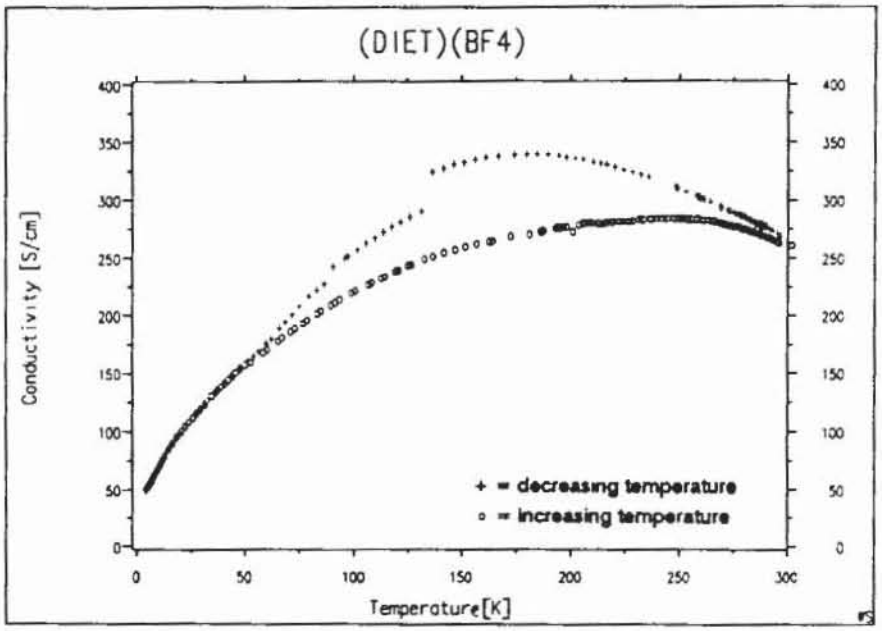


Fig. 1. Temperature dependence of the electrical conductivity of DIET-BF_4 from isomeric mixture of the donor

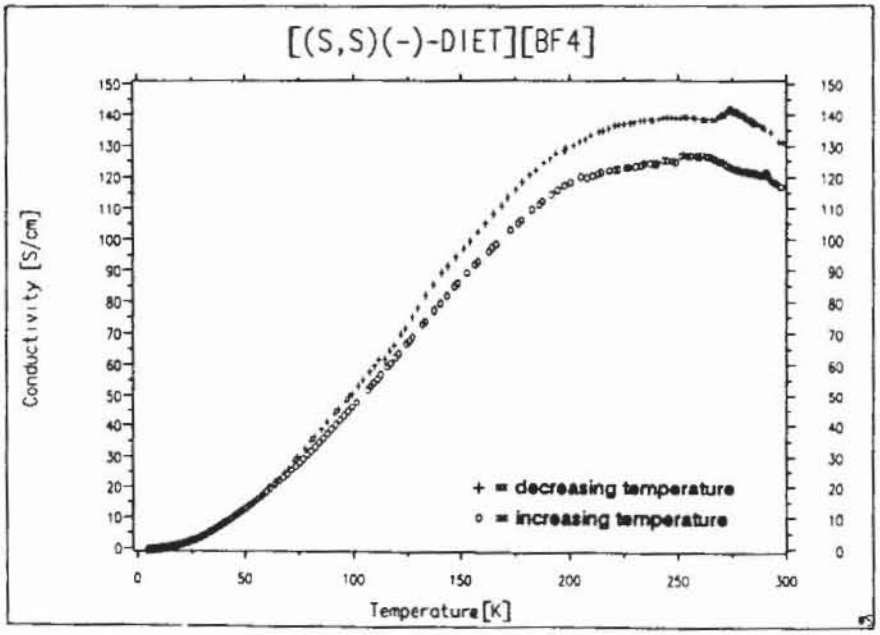


Fig. 2. Temperature dependence of the electrical conductivity of DIET-BF_4 from the S,S-derivative of DIET (crosses are data during cooling, circles during heating of the sample).

(ii) TMET-salts could be obtained with the counter ions PF_6^-, AsF_6^-, SbF_6^-, I_3^-, FSO_3^-, $CF_3SO_3^-$, ReO_4^-, ClO_4^-, BF_4^-. Starting from isomeric mixtures and using PF_6^- as counter ion results in a metallic and a semiconducting phase. In contrast to earlier investigations of the TMET/PF_6 system (3) we were able to isolate a <u>metallic</u> solid. X-ray investigations suggest that compounds of at least two different compositions $(TMET)_2PF_6$ and $(TMET)(PF_6)(C_6H_5Cl)$ respectively are obtained. The $(TMET)_2PF_6$ phase contains the achiral R,S,R,S-7,8,7',8'-Tetramethyl-BEDT-TTF molecules solely.
(Crystal data: Monoclinic space group $P2_1$, a = 5,057(3), b = 6,823(4), c = 33,44(2)Å, γ = 107,72(5)°, Z = 1). Figure 3 gives an impression of the arrangement of the molecules in the lattice. This structure is totally different compared to the earlier reported semiconducting $(TMET)_2PF_6$ phase (3).

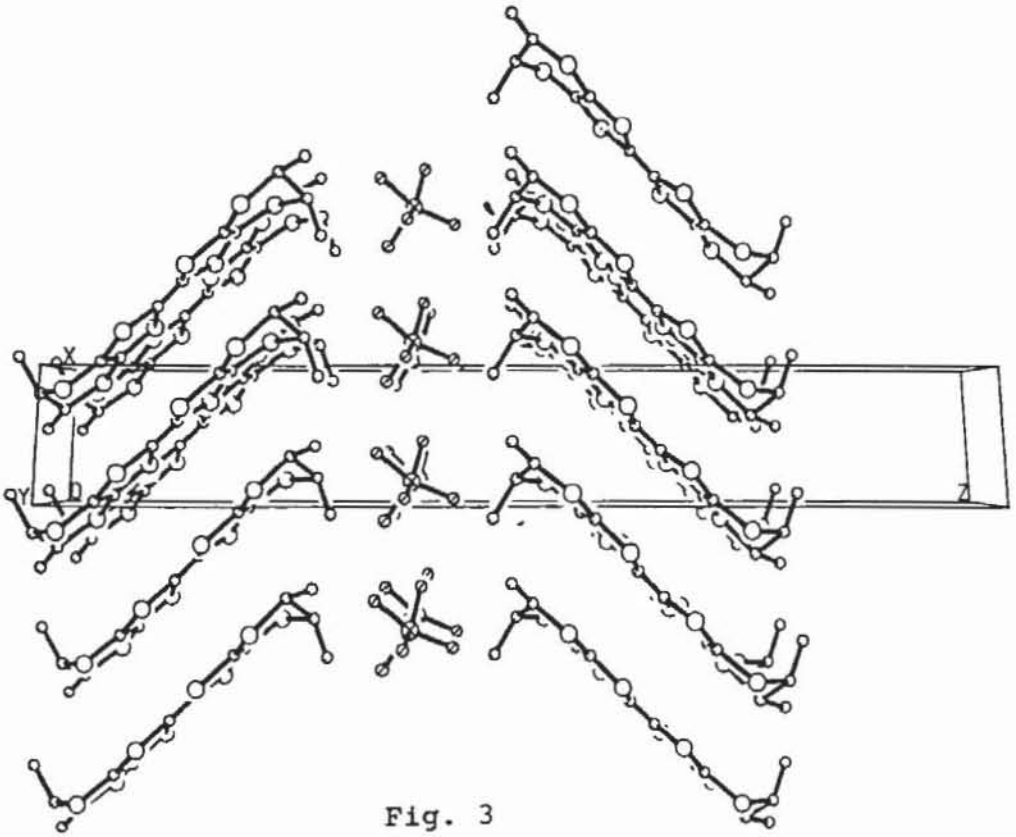


Fig. 3

Additionally we could characterize a 1:1 phase, which contains $(TMET)_2^{2+}$ dimers. The molecular ions of a pair are related to each other by a center of symmetry. So the crystal contains only the R,R,S,R-7,8,7',8'-TMET molecules paired directly with its enantiomer. Figure 4 presents the conformation of one $(TMET)_2^{2+}$ pair in this solid. Furthermore we could isolate an isostructural AsF_6^--pha-

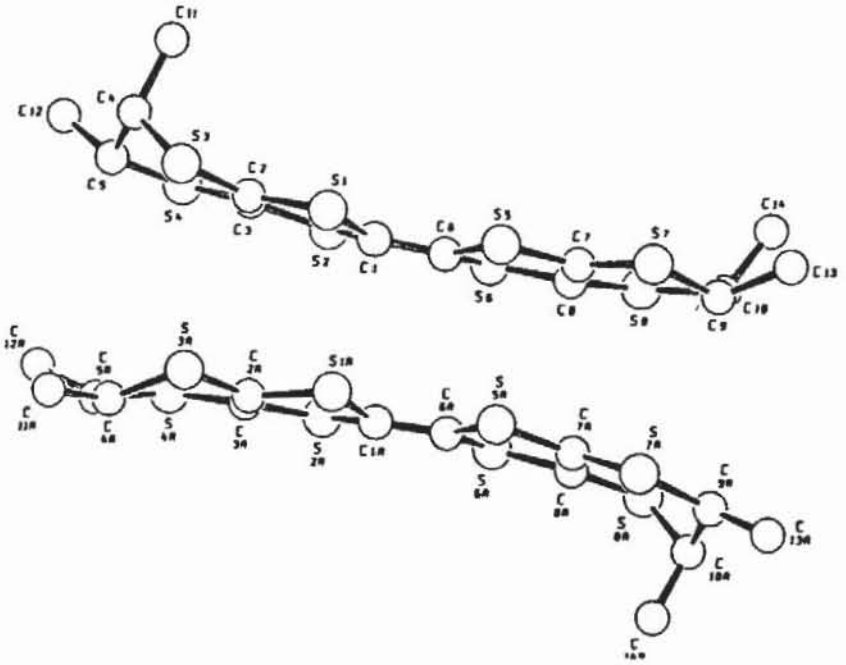
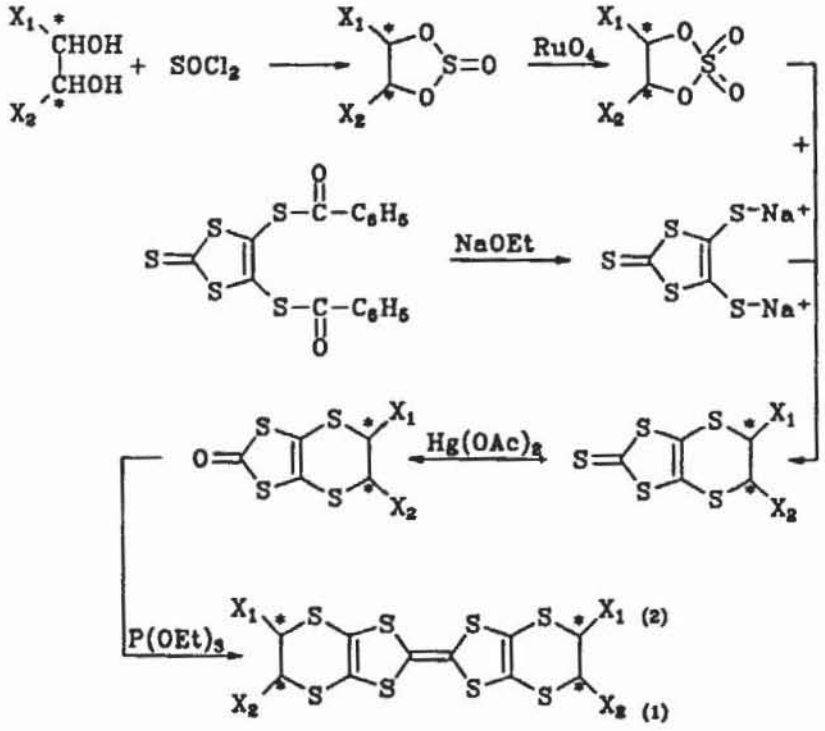


Fig. 4

se (composition $(C_{14}H_{16}S_8)AsF_6 \cdot C_6H_5Cl$: monoclinic space groups $P2_1$, a = 8,478(8), b = 19,06(2), c = 17,89(1)Å, ß = 91,02(7)°, Z = 4).



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