CONDUCTING AND SUPERCONDUCTING SALTS BASED ON SOME SYMMETRICAL AND UNSYMMETRICAL DONORS

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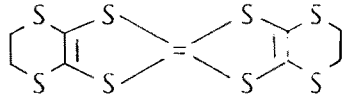
ABSTRACT

Conducting and superconducting salts based on bis(ethylenedithio)tetrathiafulvalene, ehtylenedithioselenatrithiafulvalene, ethylenedioxyethylenedithiotetrathiafulvalene, and ethylenedioxyvinylenedithiotetrathiafulvalene were prepared and studied.

INTRODUCTION

In recent papers of refs. [1-4] the preparation and physical properties of conducting and superconducting salts based on some symmetrical and unsymmetrical tetrachalcogenafulvalenes (π-donors) as well as on some metal 1,2-dithiolenes have been reported. In this paper we report the preparation and investigation of some conducting salts based on the π-donors: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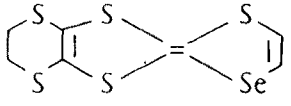
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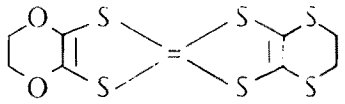
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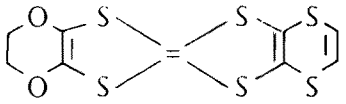
(4).

EXPERIMENTAL

Compounds (1), (3), (4) were prepared by methods reported in [5-8]. Compound (2) was prepared by treatment of 4,5-ethylenedithio-1,3- dithiole-2-one and 1,3- thiaseleno-2-one with triethyl phosphite followed by column chromatography separation (silica gel- carbon disulfide) [8]. τ-$(4)_2I_3(I_3)_y$ ($y \approx 1$) was prepared by method reported in [1]. β-$(2)_2IBr_2$ was prepared by electrocrystaflization of (2) in the presence of Bu_4NIBr_2 in dichloromethane. All the following salts were prepared by electrocrystallization in 1,1,2-trichloroethane containing 18-crown-6. $\varkappa$-$(1)_2I_3$ was prepared from ET(1) in the presence of KSeCN and CuI. By this method, in contrast to that reported in [9], almost all the crystals were found to be of the $\varkappa$-phase. $(1)_2Ag_x[N(CN)_2]_yBr_z$ was prepared from (1) in the presence of $AgN(CN)_2$ [10] and KBr. $(1)_2Cu_2(CN)_3$ was prepared from (1) in the presence of $NaN(CN)_2$ and CuCN. $(1)_2Cu_2(SCN)_y(CN)_z$ was prepared from (1) in the presence of KSCN and CuCN. $(3)_2Cu(SCN)_2$ was prepared from (3) in presence of KSCN and CuSCN [1]. Measurements were performed by instrumentation reported in [1-5].

RESULTS AND DISCUSSION

$\varkappa$-$(1)_2I_3$ or $\varkappa$-$(ET)_2I_3$

This salt crystallizes as brown-black plates in the monoclinic system space group $P2_1/c$ [9]. At ambient pressure, the temperature dependence of the normalized resistivity (ϱ/ϱ_{RT}) of crystals obtained by the method reported here is close to that reported by others [9]. Fig. 1 shows the temp. dependence of ϱ/ϱ_{RT} at ambient pressure and under a pressure of 2.3 kbar.

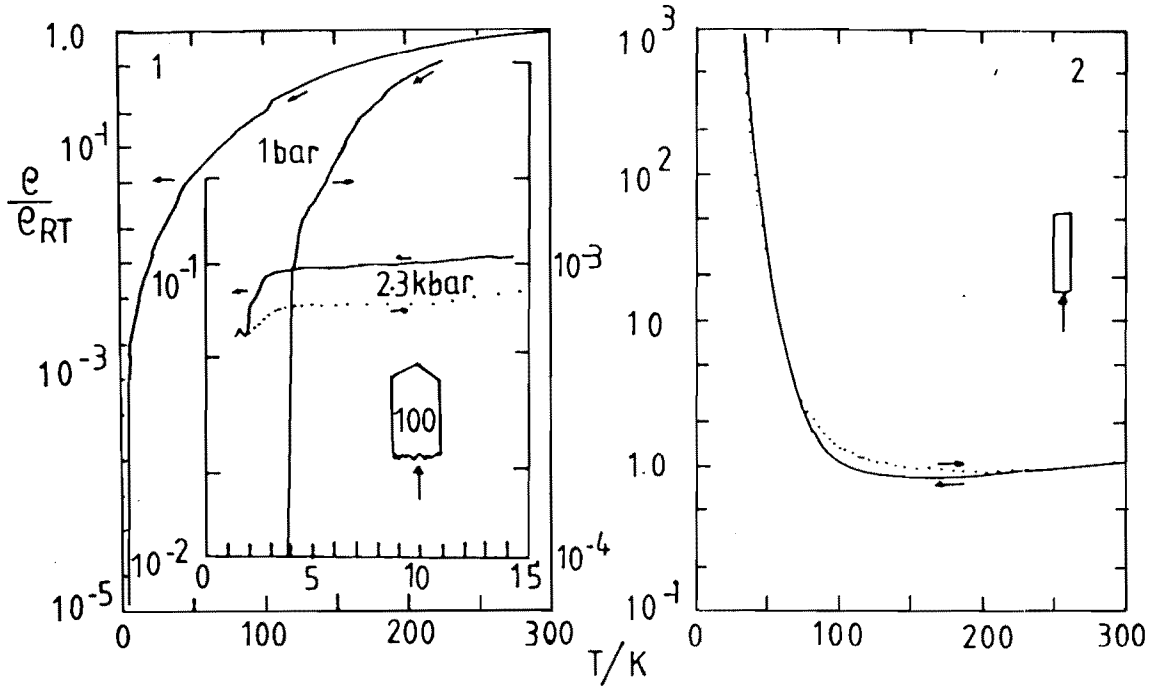

Fig. 1. Temperature dependence of normalized resistivity of x-$(ET)_2I_3$ measured along the arrow direction, at ambient pressure and under a pressure of 2.3 kbar.
Fig. 2. Same as Fig.1 but for $(1)_2Ag_x[N(CN)_2]_yBr_z$, at ambient pressure.

$(1)_2Ag_x[N(CN)_2]_yBr_z$ or $(ET)_2Ag_x[N(CN)_2]_yBr_z$

This salt crystallizes as thin brown-black plates. The crystals were not suitable for crystallographic analysis. The temperature dependence of normalized resistivity is shown in Fig.2. The salt is metallic around the room temperature and becomes insulator at $\approx$160 K.

x-$(1)_2Cu_2(CN)_3$ or x-$(ET)_2Cu_2(CN)_3$

Because of the elemental chemical analysis results (C 28.06, H 2.20, N 5.85, S 53.87), this salt was firstly considered to be $(ET)_2Cu_x[N(CN)_2]_y$ $(CN)_z(H_2O)_n$ with x=y=z=1, n=2 but crystallographic analysis showed that x=2, y=n=0, z=3. It crystallizes as brown-black rhomboid-shaped plates in the monoclinic system, space group $P2_1/c$, with a=16.143, b=8.549, c=13.253 Å , β=112.33°, V=1691.9 Å^3, Z=2, R=7.66%. It is isostructural to x-$(ET)_2I_3$. Fig.3 shows the projection of structure on the ab-plane. The conducting organic layers (ET-cations) are sandwiched between the insulating anion layers ($Cu_2(CN)_3$-polyanion). Similar results have been reported by the authors of ref.[11] from crystals of $(1)_2$ $Cu_2(CN)_3$ prepared independently by alternative methods, but they found that the crystals were semiconductive at ambient pressure around the room temperature. Geiser et al [11] found that the crystals became superconductive under a pressure of 1.5 kbar. The crystals obtained by method reported here showed a 2-D- metallic behaviour at room temperature (with σ_{RT}=20-40 S/cm), in accordance to the band structure calculations [11]. The temperature dependence of the normalized resistivity at ambient pressure and under a pressure of 1.9 kbar in the region 2-300 K is shown in Fig.4. One can see that at 5K under ambient pressure the resistivity shows a rapid drop,while under a pressure of 1.9 kbar the resistivity decreases smoothly down to ~ 2K. ESR measurements with a magnetic field perpendicular to (100) face of a single crystal showed an almost constant line width (~50G) for T>100T, which decreases below about 100 K [12]. The results are similar to those of x-$(ET)_2Hg_3Cl_8$ [13]. Physical properties at lower temperature will be reported elsewhere. Very recently we were informed that similar results have been obtained by others [14].

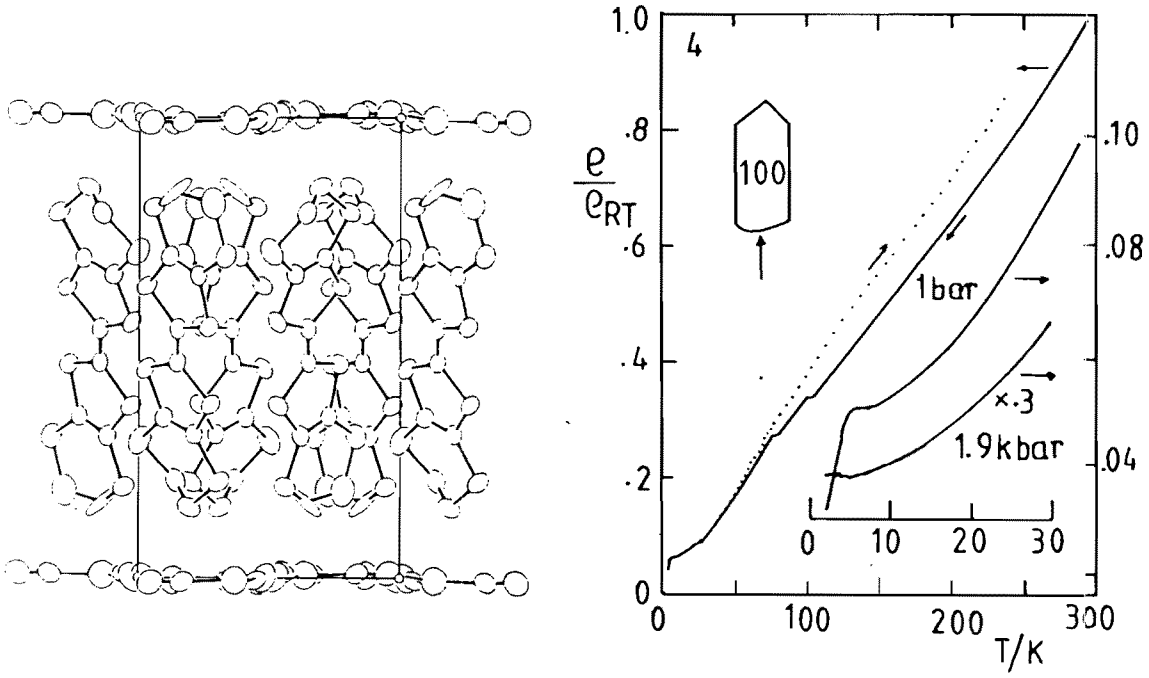

Fig. 3. Projection of structure of κ-$(ET)_2Cu_2(CN)_3$ on the ab-plane.
Fig. 4. Temperature dependence of normilized resistivity of κ-$(ET)_2Cu_2(CN)_3$.

$(1)_2Cu_2(SCN)_y(CN)_z$ or $(ET)_2Cu_2(SCN)_y(CN)_z$

This salt crystallizes as very thin brown needles. The stoichiometry y=1 and z=2 or y=2 and z=1 was estimated from the elemental chemical analysis. It is metallic and becomes semiconducting at ~110°K [4].

β-$(2)_2IBr_2$

This salt crystallizes as brown-black plates. Weissenberg diagrams showed that the salt is isostructural to β-$(EDTTTF)_2IBr_2$ and β-$(EDTDSDTF)_2IBr_2$ [15]. Fig. 5 shows the temperature dependence of the normalized resistivity. One can see that the salt remains metallic down to 2K. These results indicate that the substitution of one or two atoms of sulfur in the TTF-core by atoms of selenium does not affect the properties of the resulting salts.

$(3)_2Cu(SCN)_2$ or $(EDOEDTTTF)_2Cu(SCN)_2$

This salt crystallizes in small brown-black plates [1]. Fig.6 shows the temperature dependence of the normalized resistivity at ambient pressure and under pressure of 8 kbar. One can see that the salt is metallic and becomes semiconducting at 25K at ambient pressure [1] and at 15K under a pressure of 8kbar.

τ-$(4)_2(I_3)_1(I_3)_y$ or τ-$(EDOVDTTTF)_2(I_3)_1(I_3)_y$

This salt usually crystallizes as black plates with a golden lustre in the tetragonal system, space group $P\bar{4}2c$ [1]. Some thin crystals with a golden-green appeareance were found to have the same crystal structure. A stereoview of crystal structure is shown in Fig. 7 (see also [1]). One can see that the large axis of the donor molecules (4) is parallel to the c-axis. The donor molecules form extended layers parallel to the a- and b-axes at a=b=0.5. There is one I_3, which is well behaved, at the origin; the rest $(I_3)_y$ is disordered. There are intermolecular contacts between the S and O atoms of vinylenedithio- and ethylenedioxy-group, respectively, as well as contacts between the S atoms of the TTF-cores forming a 2-D· network perpendicular to the c-axis. The temperature dependence of the resistivity varies form crystal to

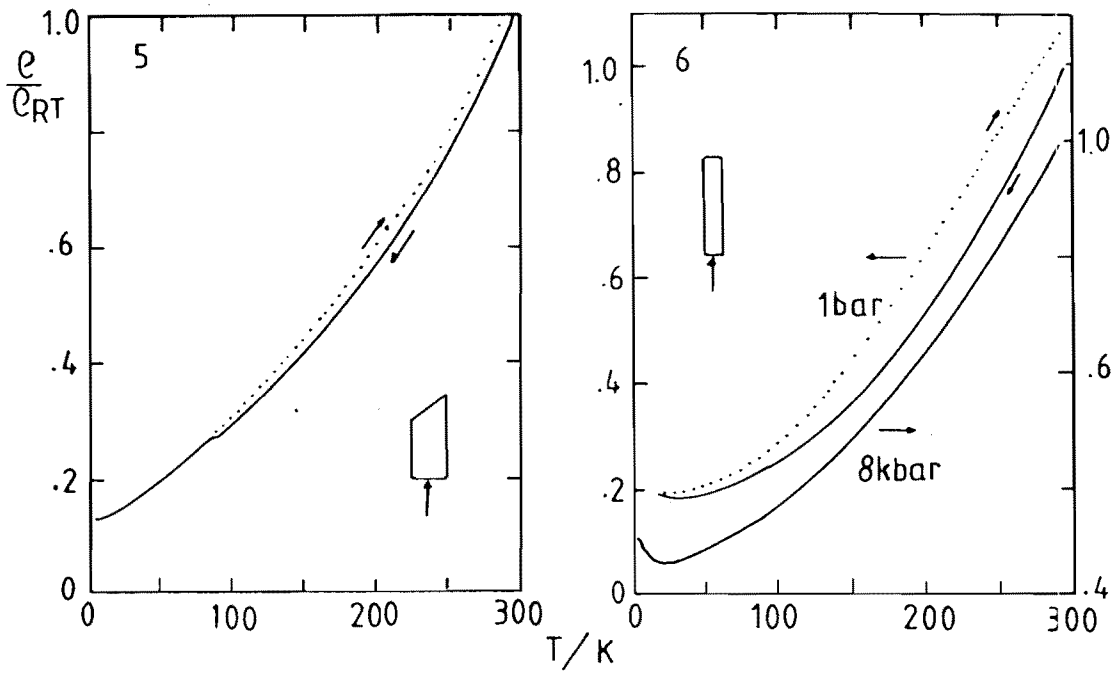

Fig.5. Temperature dependence of normalized resistivity of β-$(2)_2IBr_2$ at ambient pressure.
Fig. 6. Same as Fig. 5, but for $(3)_2Cu(SCN)_2$ at ambient pressure and under a pressure of 8kbar.

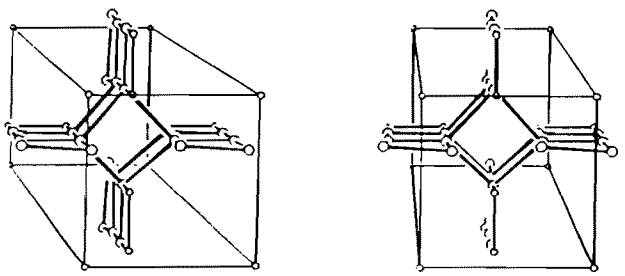

Fig.7. ORTEP stereoview of τ-(EDOVDT-TTF)$_2(I_3)(I_3)_y$ looking down the c- axis. For clarity only O (small cicles) and S(large cicles) atoms are shown.

crystal and depends on the orientation of the crystals. Fig. 8 shows the temperature dependence of normalized resistivity for six separate crystals. One can see that there is an anisotropy ρ(001)/ ρ[001]>1200 for T<80 K. The results are similar to those reported for ε-$(ET)_2(I_3)_1(I_8)_{0.5}$ [16]. It was observed ESR-signals are weak and become stronger after heating the crystals at 80 °C for several hours (line width=10 G) [12]. These results indicate that after heating a portion of I_3 goes out and the remaining crystals become more metallic.

Elemental chemical analysis showed that the value of y in salt τ-(EDOVDT-TTF)$_2(I_3)(I_3)_y$ is close to 1.0 [1], so the formal oxidation state of the donor molecule EDOVDT-TTF is close to +1.0. Most salts of donor molecules with +1 formal oxidation state are not metals [17].

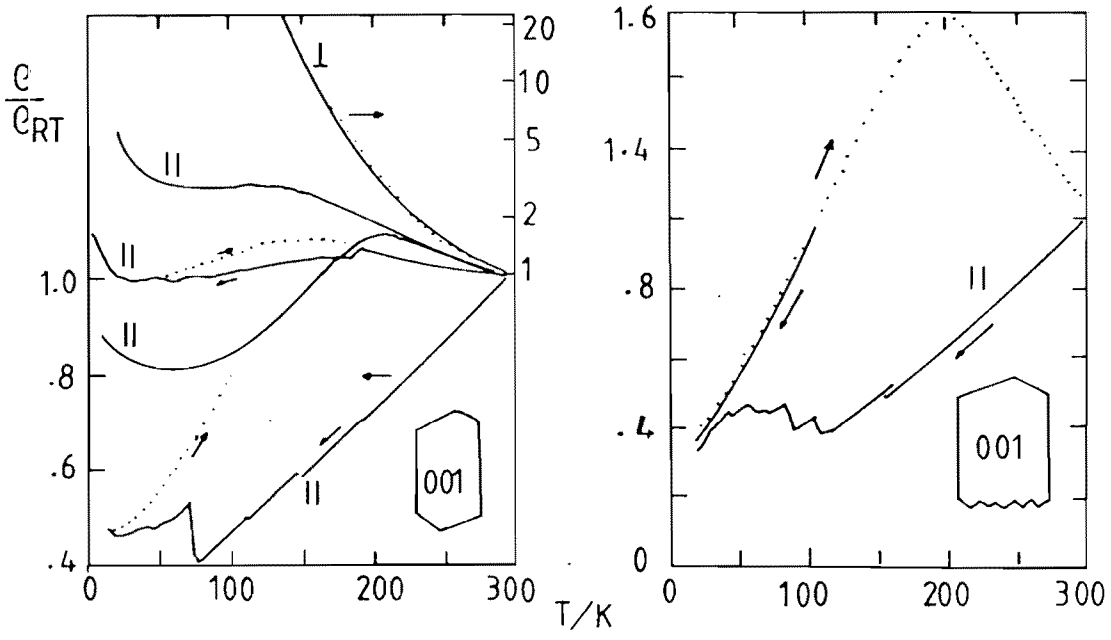

Fig. 8. Temperature dependence of ρ/ρ_{RT} for six crystals of τ-(EDOVDT-TTF)$_2$(I$_3$)$_1$(I$_3$)$_y$ in a direction parallel (I I) or perpendicular (⊥) to the ab-plane.

but, as it was shown above (see also [1,4]), τ-(EDOVDT-TTF)$_2$(I$_3$)$_1$(I$_3$)$_y$ exhibits a two dimensional metallic conductivity. In order to characterize this metallic property, we performed band electronic structure calculations on a single donor-molecule layer of the τ-phase salt by employing the extended Hückel tight- binding (EHTB) method [18]. Fig. 9 shows the dispersion relation of the highest-occupied band, where the dashed line represents the Fermi level corresponding to y=1.0. This band consists of two subbands, derived largely from the donor-molecule HOMO, since the donor-molecule layer contains two donors per unit cell. Both subbands are nearly flat along Γ →X and and Y →M. This dispersion characteristic originates from the "orthogonal" packing of donor molecules and the π-nature of the HOMO. Band orbital analysis will be described elsewhere.

The upper and lower subbands of Fig.9 touch only at the Γ point. Therefore, when the overall band is half-filled (i.e., y=1.0), the Fermi surface is given by a single wave vector point (i.e., Γ). If y is smaller than 1.0, the formal oxidation state of EDOVDT-TTF is smaller than +1.0, so that the upper subband becomes partially filled. The Fermi surfaces calculated for y=0.9, 0.8 and 0.7 are shown in Fig.10. For $0.8 \leq y < 1.0$, the Fermi surface is an electron pocket centered at Γ and elongated along Γ →X and Γ →Y. For $y \leq 0.7$, the elongated parts of the electron pocket reach the Brillouin zone boundaries thereby creating "distorted squares" centered at M and its equivalent points. Obviously, the results are the same, if we consider that the portion of ordered (I$_3$)$_1$ decreases. Therefore, τ-(EDOVDT-TTF)$_2$(I$_3$)$_1$(I$_3$)$_y$ is predicted to be a 2D metal, in agreement with experiment. According to our EHTB calculations, the carriers of this salt are electrons. It would be interesting to perform thermopower and/or Hall effect measurement to confirm this prediction. Another interesting experiment to perform is Shubnikov-de Haas measurements, because the value of y can be estimated on the basis of the Fermi surface area inferred from these measurements.

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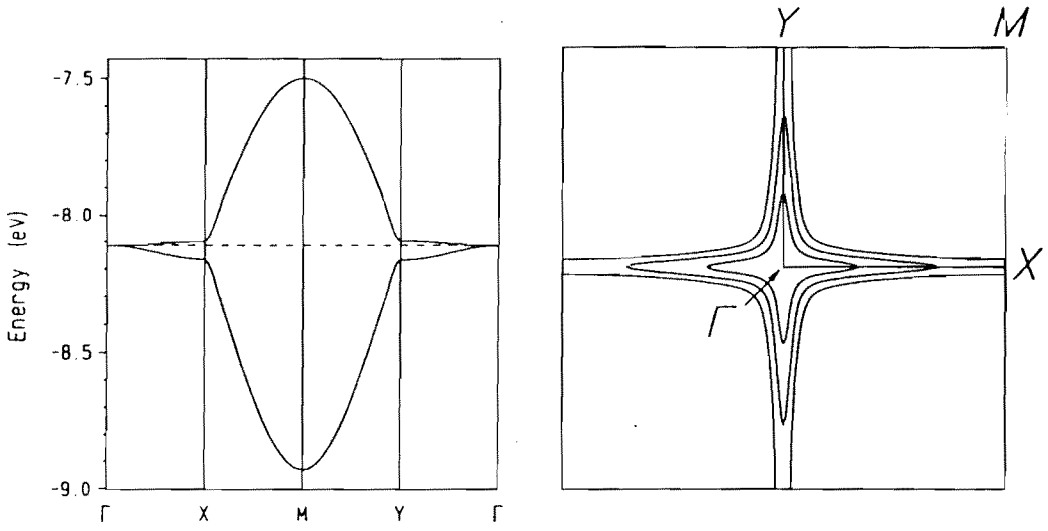

Fig.9. Dispersion relation of the highest-occupied band calculated for a donor-molecule layer of τ-(EDOVDT-TTF)$_2$(I$_3$)$_1$(I$_3$)$_y$, where Γ=(0, 0),X=a*/ 2, 0),Y=(0, b*/ 2) and M=(a*/ 2, b*/ 2). Dashed line represents the Fermi level for y=1.
Fig.10. Fermi surfaces of τ- (EDOVDT-TTF)$_2$(I$_3$)$_1$(I$_3$)$_y$ calculated for y=0.9, y=0.8, and y=0.7 represented as the innermost, the middle and the outermost contours, respectively.

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