

IV-K Systematic Study of Organic Conductors

Thanks to the systematic view to structure-property relationship studied particularly in BEDT-TTF-based conductors, recently our understanding of organic conductors has made a great progress. We have investigated charge ordered phases of molecular conductors, and have shown what kinds of charge ordered patterns are stable depending on the crystal structures. We have extended our molecular-orbital-calculation-based estimation of intermolecular interactions in organic conductors to π d-systems containing magnetic anions, and have discussed magnetic interactions J from the orbital overlaps. From the concept of "universal phase diagram" in the θ -phase, we can predict metal-insulator transition temperatures of a large number of organic conductors. We have applied this rule to tetrathiapentalene (TTP) compounds, verifying that this rule holds to these compounds with some shift of the metal-insulator boundary owing to the small U . We have prepared selenium containing TTP compounds, which have shown lower transition temperatures than the sulfur analogs. We also have shown that substitution of TTP donors with long alkyl chains such as ethylthio groups leads to preferable crystal structures, improving the balance of soft terminal parts and the extended core part of the long TTP molecules.

IV-K-1 Estimation of Off-Site Coulomb Integrals and Phase Diagrams of Charge Ordered States in the θ -Phase Organic Conductors

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Intermolecular Coulomb repulsion, V , of the highest occupied molecular orbitals (HOMO) of BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) is calculated for various molecular geometries. The bare V is a quantity that is easily estimated under the point charge approximation. As far as the screened V in actual crystals is proportional to the calculated bare V , the usual θ -phase prefers the horizontal or diagonal stripe, whereas the vertical stripe becomes comparatively stable in the limit of the small dihedral angle (in the metallic limit) (Figure 1). The phase diagrams of the θ -phase are discussed under the combination of the static charge distribution (the atomic limit) and the Stoner model (the extended Stoner model). The model contains two order parameters: the spin polarization, S_z , and the charge order, $n-1/2$. This model explains why the insulating state of the Rb salt below 190 K is a paramagnetic charge-ordered state, while the Cs salt has a different insulating phase below 20 K. The lattice dimerization of the Rb salt can be explained only from V .

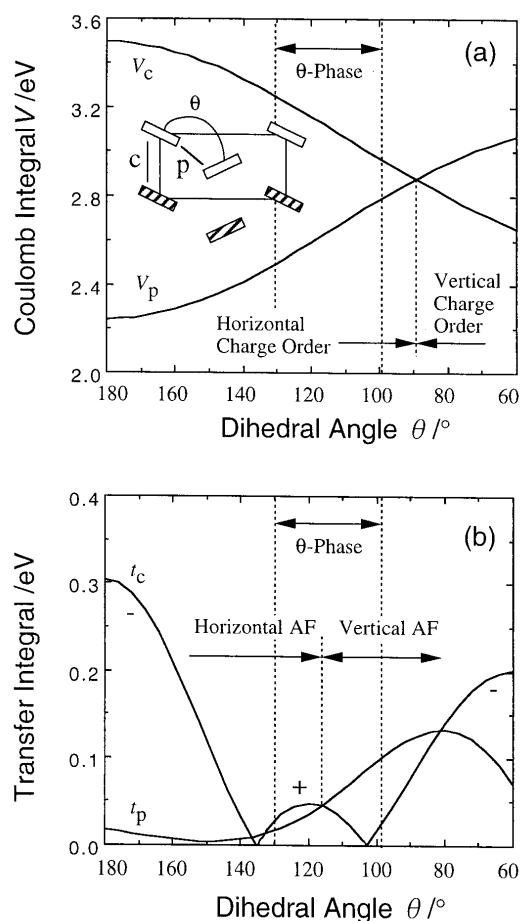


Figure 1. (a) Intermolecular Coulomb integrals, V , and (b) transfer integrals, t , between HOMO of two tilted BEDT-TTF molecules, calculated as a function of the dihedral angle, θ , in the θ -phase.

IV-K-2 Estimation of π -d Interactions in Organic Conductors Including Magnetic Anions

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Magnetic interactions in organic conductors including magnetic anions, such as λ -(BETS)₂FeCl₄ and κ -(BETS)₂FeCl₄ [X = Cl and Br], are estimated from the intermolecular overlap integrals: the overlaps

between anions for J_{dd} , and those between anions and donors for $J_{\pi d}$. From this, the most stable spin alignments are decided, and such quantities as the Neel and Weiss temperatures, as well as the magnitude of spin polarization on the π -molecules are evaluated on the basis of the mean-field theory of πd -systems. The calculation is extended to several other πd -conductors, which are classified depending on the magnitudes of the direct dd - and indirect πd -interactions (Figure 1).

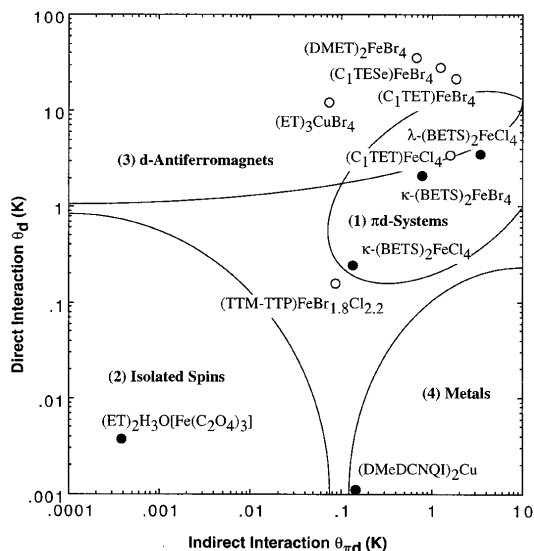


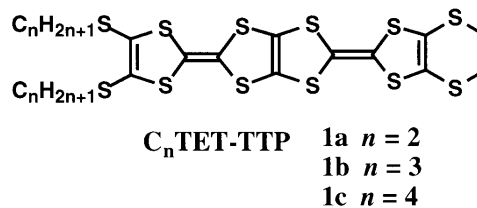
Figure 1. Calculated contributions of direct and indirect interactions to the Weiss temperatures. The closed circles designate metallic compounds at low temperatures.

IV-K-3 Tetrathiapentalene Derivatives with Long Alkyl Chains

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[Bull. Chem. Soc. Jpn. **74**, 59 (2001)]

Bis-fused π -electron donors having alkylthio chains, C_n TET-TTP (2-[4,5-bis(alkylthio)-1,3-dithiol-2-ylidene]-5-(4,5-ethylenedithio-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene; $n = 2-4$) have been synthesized. C_2 TET-TTP (**1a**) forms radical-cation salts with BF_4^- and ClO_4^- , which are metallic ($\sigma_{rt} = 900-2500 \text{ Scm}^{-1}$) down to helium temperatures. The I_3 salts of C_3 TET-TTP (**1b**) and C_4 TET-TTP (**1c**) are semi-conductive from room temperature ($\sigma_{rt} = 0.04$ and 0.025 Scm^{-1} , respectively). $(C_2\text{TET-TTP})_2ClO_4$ has uniform stacks of the donors, and has an elliptical Fermi surface characteristic of two-dimensional metals. $(C_4\text{TET-TTP})I_3$ is dimeric, and can be regarded as a band insulator. These crystal structures demonstrate the tendency that the long alkyl chains increase the anion content, and stabilize the usual stacking structure as well as the dimerization.

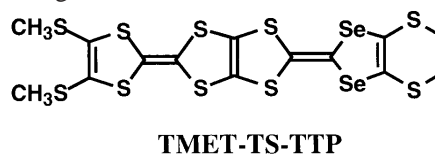


IV-K-4 TCNQ Complex with θ -Type Donor Arrangement: $(\text{TMET-TS-TTP})_2(\text{TCNQ})$

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[Adv. Mater. **12**, 983 (2000)]

A new tetrathiapentalene donor with selenium atoms, TMET-TS-TTP is prepared. $(\text{TMET-TS-TTP})_2(\text{TCNQ})$ has θ -type donor arrangement with a comparatively small dihedral angle (118°), and TCNQ acts as an isolated anion. This complex undergoes a metal insulator transition at 120 K accompanied by the broadening of the ESR intensity, suggesting an antiferromagnetic order.



IV-K-5 Universal Phase Diagram of θ -Type TMET-TTP Salts

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[J. Phys. Soc. Jpn. **70**, 1642 (2001)]

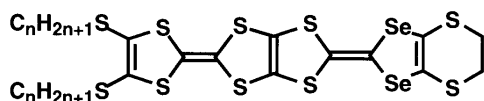
A new θ -type TMET-TTP salt $(\text{TMET-TTP})_2\text{HSO}_4$, which has smaller dihedral angle (116°), and has 2:1 composition, is prepared. This salt undergoes a metal insulator transition at around 100 K. The ESR measurement indicates that the low-temperature insulating state is paramagnetic. Thanks to this exceptional salt, a universal phase diagram of θ -type TTP salts can be discussed similarly to θ -type ET salts. In the θ -type ET salts, the universal phase diagram holds in the uniform quarter-filled band. However, our works in the θ -type TMET-TTP salts prove that the universal phase diagram is not largely influenced by the band-filling and the position of the Fermi energy.

IV-K-6 Selenium Analogs of Tetrathiapentalene Derivatives with Long Alkyl Chains

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[*Bull. Chem. Soc. Jpn.* **74**, 833 (2001)]

A novel selenium-containing bis-fused tetra-thiafulvalene donor, C₂TET-TS-TTP (2-[4,5-bis(ethylthio)-1,3-dithiol-2-ylidene]-5-(4,5-ethylenedithio-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene) has been synthesized. The ClO₄⁻, BF₄⁻, and PF₆⁻ salts of C₂TET-TS-TTP are isostructural, having β-type structures. These salts are essentially metallic down to low temperatures.

C₂TET-TS-TTP

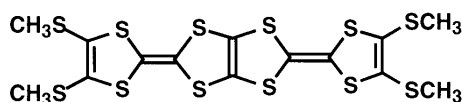
IV-K-7 1:1 Composition Organic Metal Including a Magnetic Counteranion, (TTM-TTP)FeBr_{1.8}Cl_{2.2}

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An organic donor, TTM-TTP forms 1:1 donor/anion salts with FeCl₄⁻ and FeBr₄⁻, (TTM-TTP)FeX₄(PhCl)_{0.5} (X = Cl and Br), which have one-dimensional dimerized columns and are insulators even at room temperature. In contrast, the salt with an alloyed anion, (TTM-TTP)FeBr_{1.8}Cl_{2.2}, shows high electrical conductivity of about 1000 Scm⁻¹ at room temperature and remains metallic down to 160 K. This salt has uniform, one-dimensional, donor columns. This is the first 1:1 donor/anion composition organic metal with a magnetic counteranion. These compounds exhibit weak magnetic interactions; the Weiss temperatures are around 1–3 K.



TTM-TTP

IV-K-8 Marginal Paramagnetic State of a One-Dimensional Half-Filled Alternating Chain in (TTM-TTP)Au₂

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[*J. Phys. Soc. Jpn.* **69**, 4066 (2000)]

(TTM-TTP)Au₂ has a dimerized structure along the donor stacking direction, and shows semiconducting behavior below room temperature. ESR, static magnetic susceptibility, and optical reflectance of this salt have

been measured to investigate the spin state and the electronic correlation. The ESR signal has been observed from room temperature to 3 K, and the spin susceptibility shows paramagnetic behavior with a rapid decrease below 10 K. The static magnetic susceptibility is paramagnetic and has an anomaly around 10 K in agreement with the ESR result. The chain axis optical reflectance spectra show clear optical gap in the mid-infrared region. An attempt is undertaken to analyze the optical spectrum by means of the one-dimensional dimerized Hubbard model, which suggests that the on-site Coulomb repulsion, *U*, is small and the spin polarization is located at the marginal paramagnetic boundary. These results indicate that this compound is not a band-insulator but the Mott insulator with a small spin gap.