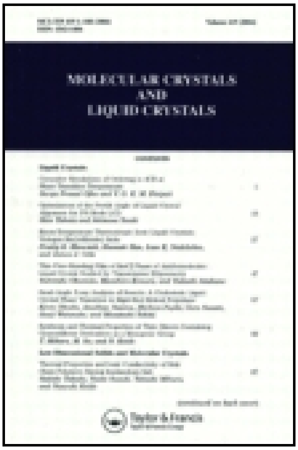


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Electrical Properties of DT-TTF Salts

Hideki Fujiwara [a] , Takeshi Miura [a] , Yohji Misaki [a] , Tokio Yamabe [a] , Takehiko Mori [b] , Hatsumi Mori [c] & Shoji Tanaka [c]

[a] Division of Molecular Engineering, Faculty of Engineering, Kyoto University, Kyoto, 606-01, Japan

[b] Department of Organic and Polymeric Materials, Faculty of Engineering, Tokyo Institute of Technology, O-okayama, Tokyo, 152, Japan

[c] International Superconductivity Technology Center, Shinonome, Tokyo, 135, Japan

To cite this article: Hideki Fujiwara , Takeshi Miura , Yohji Misaki , Tokio Yamabe , Takehiko Mori , Hatsumi Mori & Shoji Tanaka (1996): Electrical Properties of DT-TTF Salts, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 284:1, 329-336

To link to this article: http://dx.doi.org/10.1080/10587259608037935

*Mol. Cryst. Liq. Cryst.*, 1996, Vol. 284, pp. 329–336
Reprints available directly from the publisher
Photocopying permitted by license only

# ELECTRICAL PROPERTIES OF DT-TTF SALTS

HIDEKI FUJIWARA, TAKESHI MIURA, YOHJI MISAKI, and
TOKIO YAMABE
Division of Molecular Engineering, Faculty of Engineering, Kyoto University,
Kyoto 606-01, Japan

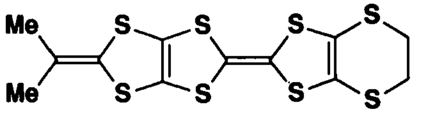
TAKEHIKO MORI
Department of Organic and Polymeric Materials, Faculty of Engineering, Tokyo
Institute of Technology, O-okayama, Tokyo 152, Japan

HATSUMI MORI, and SHOJI TANAKA
International Superconductivity Technology Center, Shinonome, Tokyo 135,
Japan

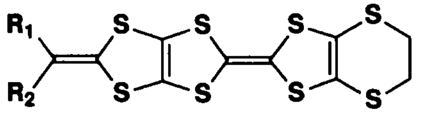
Abstract Several cation radical salts of MeEtDTET, EtDTET and CPDTET were prepared. Many of them showed metallic conducting behavior down to 1.4-4.2 K. X-ray crystal structure analysis of $(CPDTET)_2(SbF_6)_{0.87}$ revealed that this salt has a two-dimensional "κ-type" arrangement of donor molecules.

## INTRODUCTION

The discoveries of organic superconductors based on multisulfur unsymmetrical donors (MDT-TTF,[1] DMET[2]) have stimulated the interest for development of new class of unsymmetrical donors for organic metals stable down to low temperatures. Recently we have focused on 1,3-dithiol-2-ylidene group as a promising substituent for realizing two-dimensional arrangement of donor molecules in the conducting salts,[3] and many unsymmetrical TTF derivatives fused with 1,3-dithiol-2-ylidenes (DT-TTF) have been prepared.[3-5] Among them 2-isopropylidene-1,3-dithiolo[4,5-*d*]ethylenedithio-TTF (MeDTET) has yielded several cation radical salts showing metallic conductive behavior down to low temperature, and X-ray crystal structure analysis of $(MeDTET)_3PF_6TCE_x$ reveals that it has "κ-type" arrangement of donors in the conducting sheet.[6] In this context, investigation on electrical properties of cation radical salts based on the other DT-TTF donors is of considerable interest. Herein we report the synthesis of new DTET-TTFs (MeEtDTET and EtDTET) and electrical properties of cation radical salts of several DTET-TTFs. Furthermore crystal and band structures of $(CPDTET)_2(SbF_6)_{0.87}$ are described.



MeDTET

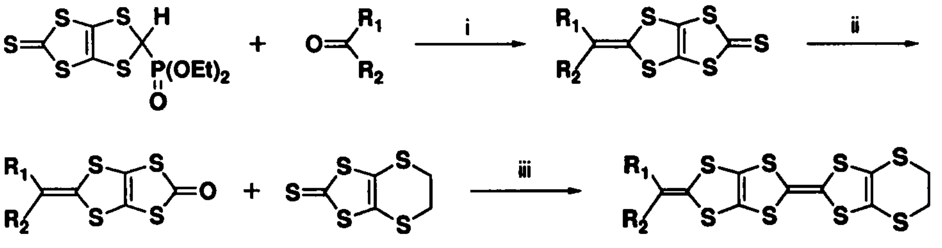


$R_1$ = Me, $R_2$ = Et; MeEtDTET
$R_1$ = $R_2$ = Et; EtDTET
$R_1$-$R_2$ = $-(CH_2)_4-$; CPDTET

## EXPERIMENTAL SECTION

Synthesis of CPDTET has been already reported.[4b] MeEtDTET and EtDTET were synthesized by the method similar to the synthesis of CPDTET as shown in Scheme I. Single crystals of cation radical salts were prepared by electrochemical oxidation in the presence of the corresponding tetra-*n*-butylammonium salts at a constant current of 0.3-0.5 μA/cm$^2$ in 1,1,2-trichloroethane (TCE), 1,2-dichloroethane (DCE) or chlorobenzene with a small amount of EtOH (10%, v/v) for about two weeks. The $I_3$ salts were obtained by mixing the hot solutions of donors and tetra-*n*-butylammonium triiodide in PhCl or TCE. The ratio between donor and anion was determined by energy dispersion spectroscopy (EDS) from the ratio of sulfur and elements designated in parenthesis in Table I. The electrical conductivity was measured by the four-probe technique on a single crystal.

A single crystal X-ray structure analysis was performed for a black platelike crystal of the $SbF_6$ salt of CPDTET. The crystal data: $(CPDTET)_2(SbF_6)_{0.87}$, Monoclinic, space group *Cc*, the lattice constants $a$ = 41.17(3), $b$ = 8.29(2), $c$ = 11.27(1) Å, $\beta$ = 100.0(1)°, $V$ = 3786(8) Å$^3$, Z = 4. The intensities were measured at



SCHEME I *Reagents and conditions*: i, 0.5 M LDA, THF, -78 °C, 20 min, ii, $Hg(OAc)_2$ (2 equiv.), $CHCl_3$-AcOH (1:1, v/v), room temp., 2h, iii, $P(OEt)_3$, 80 °C, 2h.

293 K on a Rigaku automated diffractometer (AFC-7R) equipped with monochromated Mo-$K\alpha$ radiation by the $\omega$-$2\theta$ scan technique. The structure was solved by the direct method (SHELXS86[7]) and refined by the full-matrix least-squares method. The final R ($R_w$) value was 0.049 (0.050) for the independent 1503 reflections ($I > 3.0\sigma(I)$).

## RESULTS AND DISCUSSION

### Conducting Properties of Cation Radical Salts

The electrical properties of cation radical salts of DTET-TTFs are summarized in Table I. The $PF_6$ and $AsF_6$ salts of MeEtDTET showed very high electrical conductivity of 450-1500 Scm$^{-1}$ at room temperature and metallic temperature dependence down to 1.4-4.2 K. As shown in Figure 1, both salts showed huge jumps of resistivity on cooling process as is observed in the $ClO_4$ salt of MeDTET,[6a] suggesting that metal to metal phase transition occurred. On the other hand, room temperature conductivity of $SbF_6$ and $I_3$ satls of EtDTET was relatively low ($10^0$ Scm$^{-1}$) compared to those of MeEtDTET salts. Both salts showed semiconductive behavior with large activation energies (~ 0.1 eV). It suggests that steric hindrance of two ethyl groups of EtDTET prevents effective intermolecular overlap of donors required for metallic electrical conduction.

TABLE I Electrical properties of DTET-TTF•(Anion)$_x$.

| Donor | Anion | Solvent | x [a] | $\sigma_{rt}$ / Scm$^{-1}$ [b] | Conducting behavior [c] |
|---|---|---|---|---|---|
| MeEtDTET | $PF_6$ | DCE | 0.77 (P) | 1500 | M down to 1.4 K |
| | $AsF_6$ | TCE | 0.55 (As) | 480 | M down to 4.2 K |
| EtDTET | $SbF_6$ | DCE | 0.35 (Sb) | 5.1 | $E_a = 0.12$ eV |
| | $I_3$ | TCE | 0.25 (I) | 1.6 | $E_a = 0.10$ eV |
| CPDTET | $ClO_4$ | PhCl | 0.60 (Cl) | 0.037 | $E_a = 0.15$ eV |
| | $PF_6$ | PhCl | 0.42 (P) [d] | 0.015 | $E_a = 0.13$ eV |
| | $AsF_6$ | PhCl | 0.59 (As) | 27 | M down to 4.2 K |
| | $SbF_6$ | PhCl | 0.44 (X) [e] | 4.2 | $T_{M-I} \approx 200$ K |
| | $NbF_6$ | PhCl | 0.58 (Nb) | 140 | M down to 90 K [f] |
| | $TaF_6$ | PhCl | 0.37 (Ta) | 21 | $T_{M-I} \approx 140$ K |
| | $I_3$ | PhCl | 0.30(I) | 7.1 | M down to 4.2 K |

[a] Determined by the energy dispersion spectroscopy from the ratio of sulfur and the elements designated in parentheses. [b] Measured on a single crystal using four-probe method. [c] M designates metallic behavior. [d] Contains a solvent $(PhCl)_{0.22}$. [e] Determined by X-ray structure analysis. [f] Cracked at this temperature.

CPDTET yielded several high conducting cation radical salts also listed in Table I. The tetrahedral $ClO_4$ salt was a semiconductor with a large activation energy (0.15 eV). Most salts with octahedral anions showed metallic conductive behavior around room temperature (Figure 2). However, the $PF_6$ salt was exceptionally a semiconductor probably due to different crystal structure containing a small amount of chlorobenzene. Among the metallic salts with octahedral anions, the $AsF_6$ salt displayed metallic temper-

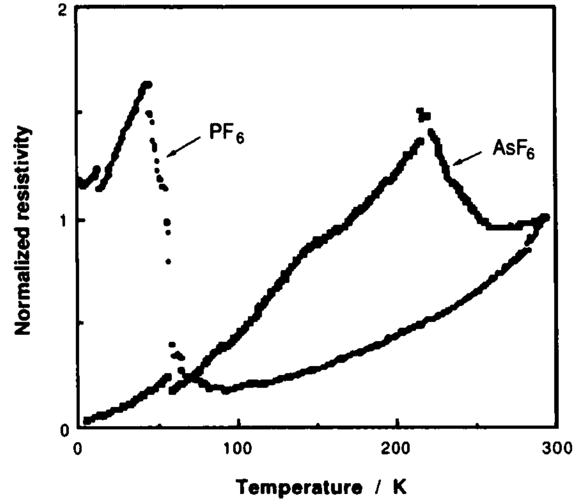


FIGURE 1 Temperature dependence of electrical conductivity of cation radical salts of MeEtDTET in the cooling run.

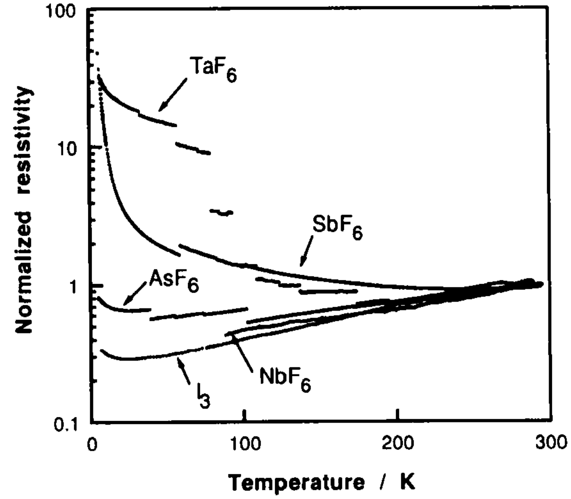


FIGURE 2 Temperature dependence of electrical conductivity of cation radical salts of CPDTET in the cooling run.

ature dependence down to 4.2 K. The $SbF_6$ salt exhibited the metal to semiconductor transition, but its activation energy after the transition is considerably small (0.002 eV), indicating the resulting energy gap is very tiny. Furthermore, linear $I_3$ salt showed metallic conductive behavior down to 4.2 K, consequently indicating that the cyclopentanylidene ring of CPDTET does not disturb metallic conduction in contrast to the diethyl groups of EtDTET.

### Crystal Structure of $(CPDTET)_2(SbF_6)_{0.87}$

The unit cell contains two crystallographically independent CPDTET molecules. The population analysis indicates that the ratio of donor : anion is 2 : 0.87. As shown in Figure 3, the unit cell contains two sheets of donors which are related to each other by the translation vector of (1/2, 1/2, 0).

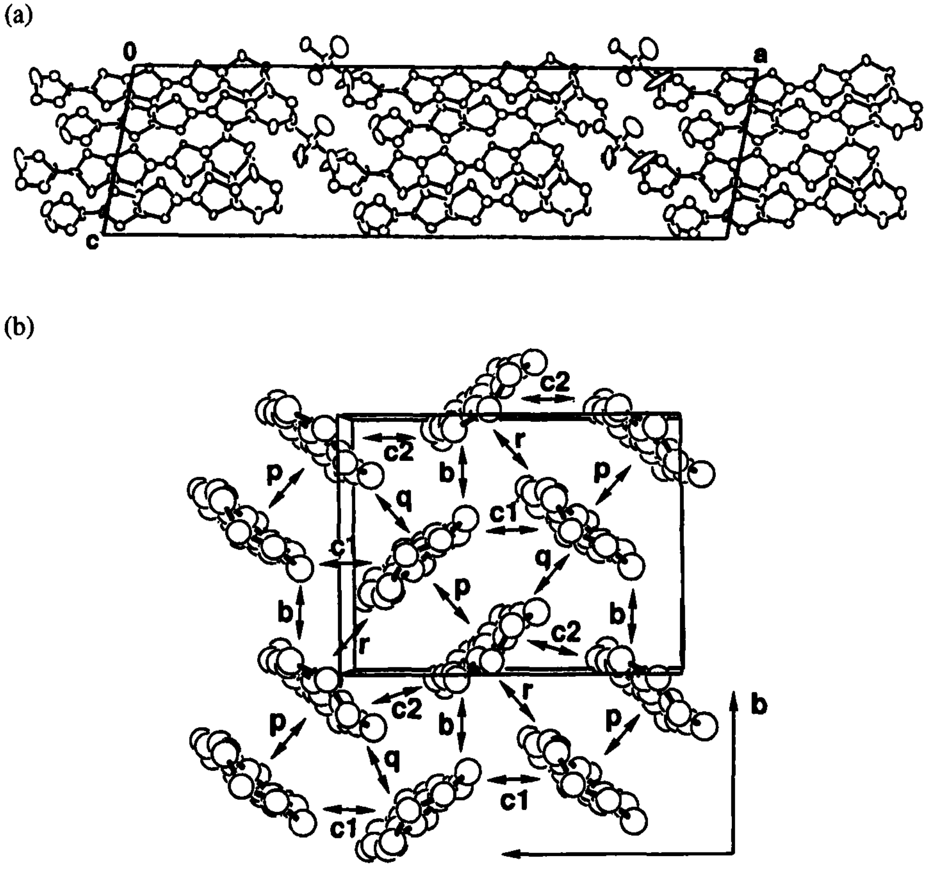


FIGURE 3 (a) Crystal structure viewed along b-axis and (b) donor arrangement of $(CPDTET)_2(SbF_6)_{0.87}$.

The arrangement of donors in the conducting sheet is similar to the two-dimensional κ-type BEDT-TTF salts. Several intermolecular S-S contacts shorter than the sum of van der Waals radii (3.70 Å) exist only between dimers and the shortest distance is 3.33 Å. The overlap mode in a dimer is so-called "ring-over-bond" manner and intradimer distance is 3.59 Å. Interestingly two cyclopentanylidene rings in the dimer situated on the same direction distinct from the case of other κ-type salts of unsymmetrical donors like (MeDTET)$_3$PF$_6$TCE$_x$,[6] (MDT-TTF)$_2$AuI$_2$,[1b] and (DMET)$_2$AuBr$_2$[2b] in which two donor molecules are dimerized in a head-to-tail manner (Figure 4).

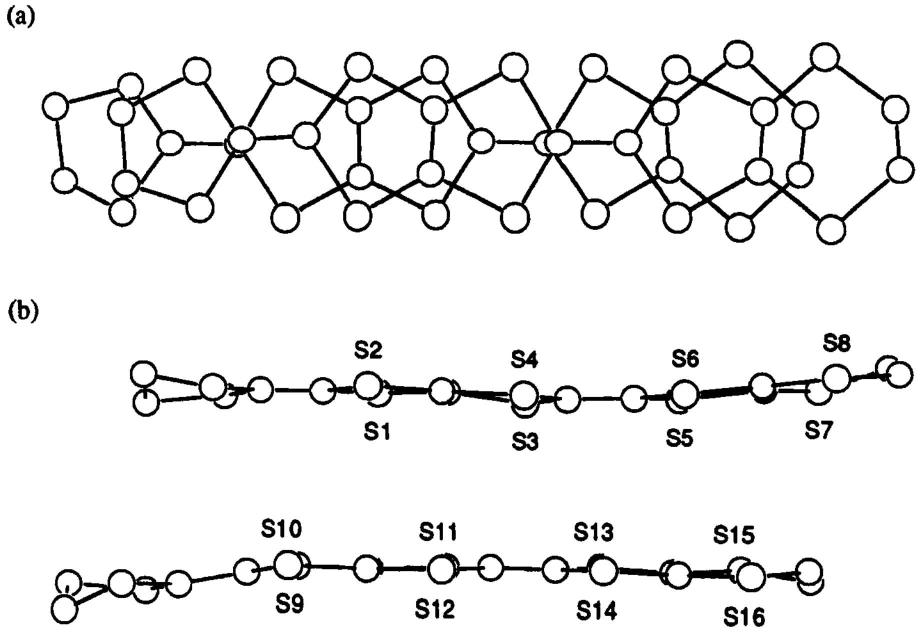


FIGURE 4 (a) Overlap mode in the dimer of (CPDTET)$_2$(SbF$_6$)$_{0.87}$ and (b) the side view.

## Band Structure of (CPDTET)$_2$(SbF$_6$)$_{0.87}$

The band structure of (CPDTET)$_2$(SbF$_6$)$_{0.87}$ was calculated by the tight-binding method based on the extended Hückel approximation on a donor layer (*bc* plane). The dispersion relation and Fermi surface is shown in Figure 5. The overlap integrals are p = 21.3, b = 13.7, q = 5.9, r = 2.8, c1 = -7.7, and c2 = $-4.3 \times 10^{-3}$ (see Figure 3). The intradimer overlap integral (p) is larger than that of (MeDTET)$_3$PF$_6$TCE$_x$ ($13.4 \times 10^{-3}$) probably due to the difference of the overlap mode discussed in the previous section.

The band structure and Fermi surface are quite similar to those of the κ-type BEDT-TTF salts and the band width (0.56 V) is nearly equal to that of (BEDT-TTF)$_2$Cu(NCS)$_2$[8] (0.59 eV) and is broader than that of (MeDTET)$_3$PF$_6$TCE$_x$ (0.47 V). As a result of existence of a *c*-glide plane, the band dispersion is degenerated on the ZM zone boundary. The Fermi surface is essentially two-dimensional circle but is folded and closed on the ZM boundary. The origin of the metal to semiconductor transition of this salt is not clear at present, but we would discuss it elsewhere.

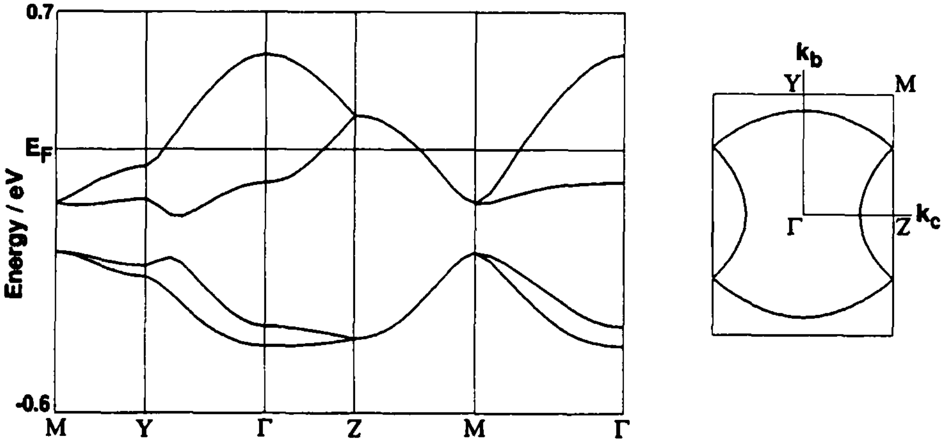


FIGURE 5 The energy dispersion and Fermi surface of (CPDTET)$_2$(SbF$_6$)$_{0.87}$.

## ACKNOWLEDGMENTS

This work is partially supported by Grant-in-Aid for Scientific Research No. 06243215 and No. 00063275 from the Ministry of Education, Science, and Culture of Japan. One of the authors (H. F.) is indebted to the JSPS Research Fellowships for Young Scientists.

## REFERENCES

1. (a) G. C. Papavassiliou, G. A. Mousdis, J. S. Zambounis, A. Terzis, A. Hountas, B. Hilti, C. W. Mayer, and J. Pfeiffer, Synth. Met., 27, B379 (1988).
(b) A. M. Kini, M. A. Beno, D. Son, H. H. Wang, K. D. Carlson, L. C. Porter, U. Welp, B. A. Vogt, J. M. Williams, D. Jung, M. Evain, M.-H. Whangbo, D. L. Overmyer, and J. E. Schirber, Solid State Commun., 69, 503 (1989)
2. (a) K. Kikuchi, M. Kikuchi, T. Namiki, K. Saito, I. Ikemoto, K. Murata, T. Ishiguro, and K. Kobayashi, Chem. Lett., 931 (1987).

(b) K. Kikuchi, Y. Honda, Y. Ishikawa, K. Saito, I. Ikemoto, K. Murata, H. Anzai, and T. Ishiguro, Solid State Commun., 66, 405 (1988).

3. (a) Y. Misaki, H. Nishikawa, K. Kawakami, T. Uehara, and T. Yamabe, Tetrahedron Lett., 33, 4321 (1992).
4. (a) Y. Misaki, H. Nishikawa, H. Fujiwara, K. Kawakami, T. Yamabe, H. Yamochi, and G. Saito, J. Chem. Soc., Chem. Commun., 1408 (1992).
   (b) Y. Misaki, K. Kawakami, H. Nishikawa, H. Fujiwara, T. Yamabe, and M. Shiro, Chem. Lett., 445 (1993).
5. S. Aonuma, Y. Okano, H. Sawa, R. Kato, and H. Kobayashi, J. Chem. Soc., Chem. Commun., 1193 (1992).
6. (a) Y. Misaki, H. Nishikawa, T. Yamabe, T. Mori, H. Inokuchi, H. Mori, and S. Tanaka, Chem. Lett., 1341 (1993).
   (b) Y. Misaki, H. Nishikawa, H. Fujiwara, T. Yamabe, T. Mori, H. Mori, and S. Tanaka, Synth. Met., 70, 1151 (1995).
7. G. M. Sheldrick, in Crystallographic Computing 3, (Oxford University Press, 1985) pp.175-189.
8. D. Jung, M. Evain, J. J. Novoa, M.-H. Whangbo, M. A. Beno, A. M. Kini, A. J. Schultz, J. M. Williams, and P. J. Nigrey, Inorg. Chem., 28, 4516 (1989).