

# Pressure effect on the electrical conductivity and superconductivity of $\beta$ -(BDA-TTP) $_2$ I $_3$

Jun-ichi Yamada,<sup>\*a</sup> Kazuya Fujimoto,<sup>a</sup> Hiroki Akutsu,<sup>a</sup> Shin'ichi Nakatsuji,<sup>a</sup> Akira Miyazaki,<sup>b</sup> Masashi Aimitsu,<sup>b</sup> Satoshi Kudo,<sup>b</sup> Toshiaki Enoki<sup>b</sup> and Koichi Kikuchi<sup>c</sup>

Received (in Cambridge, UK) 29th November 2005, Accepted 20th January 2006

First published as an Advance Article on the web 16th February 2006

DOI: 10.1039/b516909g

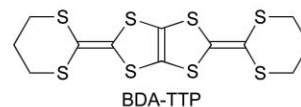
The pressure-induced electrical conductivity properties of  $\beta$ -(BDA-TTP) $_2$ I $_3$  have been investigated; the salt exhibits a dramatic change in the conductivity behaviour above *ca.* 10 kbar and undergoes a superconducting transition with an onset near 10 K.

The achievement of organic superconductivity is a major topic in the field of molecular conductors.<sup>1</sup> We have found that the  $\pi$ -electron donor BDA-TTP [2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene] gives the pressure-induced superconductors  $\beta$ -(BDA-TTP) $_2$ MCl $_4$  (M = Fe and Ga)<sup>2</sup> as well as the ambient-pressure superconductors  $\beta$ -(BDA-TTP) $_2$ X (X = SbF $_6$ , AsF $_6$  and PF $_6$ ).<sup>3</sup> The FeCl $_4$  and GaCl $_4$  salts of BDA-TTP at ambient pressure undergo metal-insulator (MI) transitions; however, by applying moderate pressures of less than 4.5 kbar, the MI transitions are suppressed and superconductivity appears in both salts.<sup>4</sup> Such a large pressure dependence is thought to originate from the conformational flexibility of BDA-TTP. Namely, a flapping motion of the two trimethylene end groups of BDA-TTP with respect to the molecular plane allows the outer dithiane rings to adopt various kinds of chair conformations. For instance, these end groups of BDA-TTP in  $\beta$ -(BDA-TTP) $_2$ MCl $_4$  (M = Fe and Ga) are bonded to the molecular plane from the same side,<sup>2a,5</sup> whereas those in  $\beta$ -(BDA-TTP) $_2$ X (X = SbF $_6$ , AsF $_6$  and PF $_6$ ) are found with opposite orientation with respect to the molecular plane: the same can be said for BDA-TTP in the neutral state.<sup>3</sup> An analogous situation can be encountered in the BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] conductors, in which, however, two twist conformations, *viz.*, the so-called eclipsed and staggered conformations, are present in the BEDT-TTF donor molecule.<sup>1a,b</sup> It is therefore expected that compared to the conformational change in BEDT-TTF by a twisting motion of the two ethylene end groups, that in BDA-TTP by a flapping motion leads to further varied physical properties under moderate pressures. This expectation prompted us to investigate the pressure-induced electrical conducting behaviour of other BDA-TTP salts. Herein, we describe what change in the transport properties of (BDA-TTP) $_2$ I $_3$  is brought about by application of pressure.

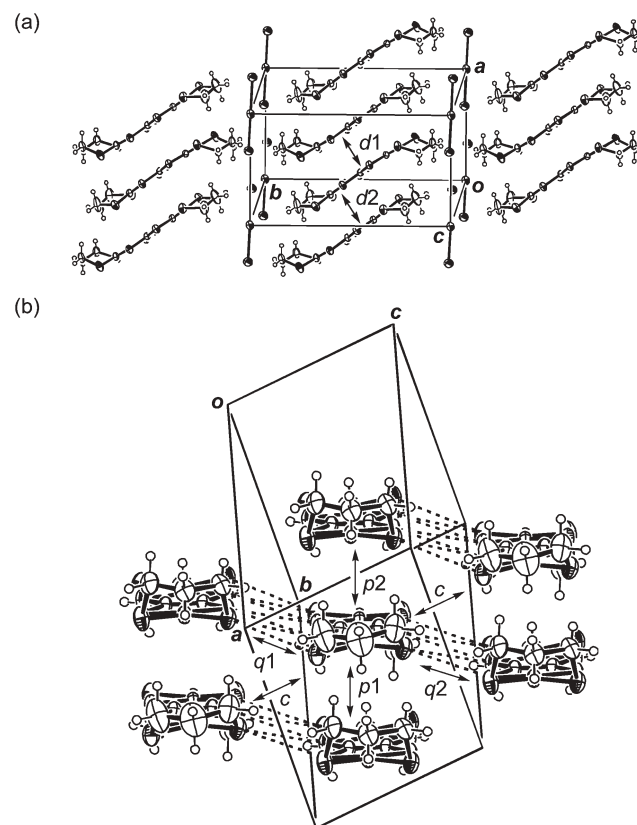
<sup>a</sup>Department of Material Science, Graduate School of Material Science, University of Hyogo, 3-2-1 Kouto, Kamigori-cho, Ako-gun, Hyogo 678-1297, Japan. E-mail: yamada@sci.u-hyogo.ac.jp; Fax: +81-791-58-0164; Tel: +81-791-58-0162

<sup>b</sup>Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8551, Japan

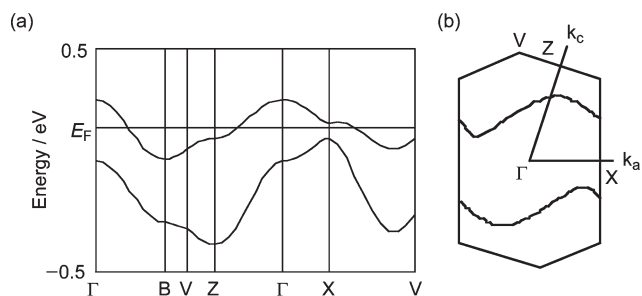
<sup>c</sup>Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan



As reported by us earlier,<sup>6</sup> (BDA-TTP) $_2$ I $_3$  exhibits semiconducting behaviour with an activation energy of 54 meV. To gain an insight into the derivation of the structure–property relationship, single-crystal X-ray structure determination was undertaken.<sup>†</sup> The salt consists of alternate layers of BDA-TTP donor molecules arranged in the  $\beta$ -packing mode and layers of I $_3^-$  anions (Fig. 1a).



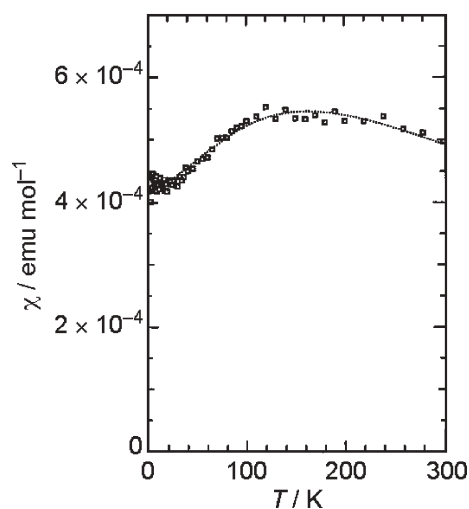
**Fig. 1** (a) Crystal structure of  $\beta$ -(BDA-TTP) $_2$ I $_3$ . Interplanar distances  $d1$  and  $d2$  are 3.65 and 3.49 Å, respectively. (b) Donor arrangement in  $\beta$ -(BDA-TTP) $_2$ I $_3$ . Short S...S contacts (<3.70 Å) are shown by broken lines. Intermolecular overlap integrals  $p1$ ,  $p2$ ,  $c$ ,  $q1$  and  $q2$  ( $\times 10^{-3}$ ) are 13.7, 5.02, -6.75, 0.20 and -5.28, respectively.



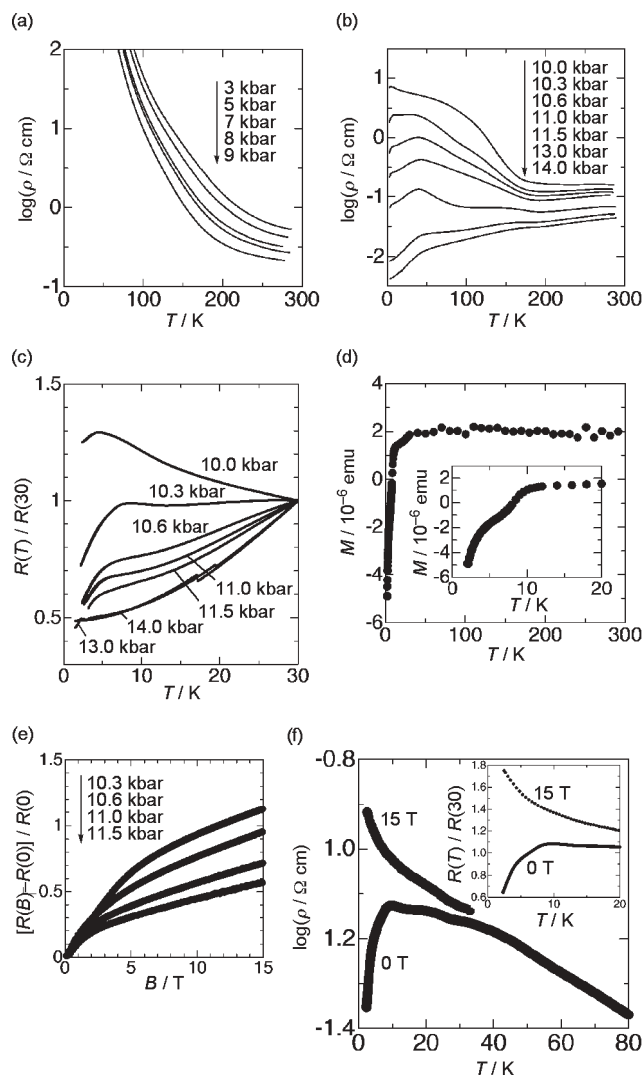
**Fig. 2** (a) Band structure and (b) Fermi surface of  $\beta$ -(BDA-TTP) $_2$ I $_3$ .

In the donor layer, the conformation of BDA-TTP, including the orientation of the two trimethylene end groups with respect to the molecular plane, belongs to the same category as found in  $\beta$ -(BDA-TTP) $_2$ X (X = SbF $_6$ , AsF $_6$  and PF $_6$ ). BDA-TTP molecules are dimerized with interplanar distances of 3.65 and 3.49 Å to form a stack along the *a*-axis. Intermolecular S $\cdots$ S contacts shorter than the van der Waals distance (3.70 Å) occur between donor stacks rather than within a donor stack (Fig. 1b). The overlap integrals between the HOMO's of adjacent donor molecules were calculated on the basis of the extended Hückel method.<sup>7</sup> A comparison of the intrastack overlap integral of *p*1 to *p*2 in  $\beta$ -(BDA-TTP) $_2$ I $_3$  (2.73) with the corresponding ratios in  $\beta$ -(BDA-TTP) $_2$ MCl $_4$  (M = Fe, 1.07; M = Ga, 1.10)<sup>2a,5</sup> indicates a much larger dimerization of donor molecules in  $\beta$ -(BDA-TTP) $_2$ I $_3$ . The tight-binding band calculation led to a one-dimensional (1D) electronic structure and an open Fermi surface along the intrastacking *a*-direction (Fig. 2), which would be responsible for the semiconducting behaviour.

Fig. 3 shows the magnetic susceptibility of  $\beta$ -(BDA-TTP) $_2$ I $_3$  as a function of temperature at 0.1 T from 2 to 300 K. The susceptibility is well explained by the 1D antiferromagnetic Heisenberg model, giving a *J* value of -125(3) K and a spin concentration of 46(3)%.<sup>8</sup> This result implies the possibility of the occurrence of pressure-induced superconductivity in  $\beta$ -(BDA-TTP) $_2$ I $_3$ , because studies of the phase diagrams of TMTSF (tetramethyltetraselenafulvalene)<sup>9a</sup> and BEDT-TTF<sup>9b</sup>



**Fig. 3** Temperature dependence of the susceptibility of  $\beta$ -(BDA-TTP) $_2$ I $_3$ . The dotted line represents a theoretical curve for the 1D antiferromagnetic Heisenberg model with *J* = -125(3) K.



**Fig. 4** (a) Temperature dependence of the resistivity of  $\beta$ -(BAD-TTP) $_2$ I $_3$  at different pressures 3, 5, 7, 8 and 9 kbar from top to bottom. (b) Temperature dependence of the resistivity of  $\beta$ -(BAD-TTP) $_2$ I $_3$  at different pressures 10.0, 10.3, 10.6, 11.0, 11.5, 13.0 and 14.0 kbar from top to bottom. (c) Temperature dependence of the relative resistance of  $\beta$ -(BAD-TTP) $_2$ I $_3$  below 30 K under pressures of 10.0 to 14.0 kbar. (d) Temperature dependence of the magnetization for  $\beta$ -(BDA-TTP) $_2$ I $_3$  under a magnetic field of 0.1 T at 10 kbar. The inset shows the magnetization in the low-temperature region. (e) MR of  $\beta$ -(BDA-TTP) $_2$ I $_3$  at 1.6 K under different pressures 10.3, 10.6, 11.0 and 11.5 kbar from top to bottom. (f) Magnetic field dependence of the resistance drop in  $\beta$ -(BDA-TTP) $_2$ I $_3$  at 9.7 kbar. The inset shows the temperature dependence of the relative resistance in the low-temperature region at 0 and 15 T.

superconductors have shown that the superconducting state lies adjacent to the antiferromagnetic insulating state.

We investigated the pressure effect on the electrical transport properties of  $\beta$ -(BDA-TTP) $_2$ I $_3$  by applying hydrostatic pressures of up to 14 kbar.† The semiconducting behavior observed at ambient pressure remained almost unaltered under pressures of up to 9 kbar (Fig. 4a). Surprisingly, marked changes in the transport behavior took place above 10 kbar (Fig. 4b). At 10.0 kbar, the resistivity showed an almost temperature-independent value from room temperature, a change to semiconducting behavior below *ca.* 190 K and a drop with an onset at 4.5 K. In addition, the onset

temperature of the resistance drop reached 8.2 K by means of increasing the pressure by only 0.3 kbar (Fig. 4c); however, with further increases in the pressure, it decreased slowly and no resistance drop was observed at 14.0 kbar. In order to probe whether or not the resistance drop is attributable to a superconducting transition, we examined the Meissner effect of this salt. As shown in Fig. 4d, the salt at 10 kbar exhibited a sudden stepwise decrease in magnetization below 10.5 K under a magnetic field of 0.1 T.‡ Furthermore, magnetoresistance (MR) measurements at 1.6 K under pressures of 10.3 to 11.5 kbar indicated that the resistance was restored by increasing the magnetic field (Fig. 4e). Also, another sample at 9.7 kbar showed a stepwise resistance drop with an onset at 9.5 K, which completely disappeared by applying a magnetic field of 15 T (Fig. 4f). These results added to the superconductivity of this salt.

In conclusion, we have revealed that  $\beta$ -(BDA-TTP)<sub>2</sub>I<sub>3</sub> displays a dramatic divergence between the pressure-induced conducting behavior below 9 kbar and above 10 kbar. It is especially noteworthy that the superconducting transition temperature ( $T_c$ ) of  $\beta$ -(BDA-TTP)<sub>2</sub>I<sub>3</sub> increases with a slight increase in pressure and that the resistive or magnetic  $T_c$  around 10 kbar can be raised to about 10 K or above. A similar pressure effect on  $T_c$  prior to reaching its maximum has been found in high- $T_c$  organic superconductors such as  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl,<sup>10a</sup> its deuterated form  $\kappa$ -(d<sub>8</sub>-BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl<sup>10a</sup> and  $\lambda$ -(BETS)<sub>2</sub>GaBr<sub>1.5</sub>Cl<sub>2.5</sub> [BETS = bis(ethylenedithio)tetraselenafulvalene],<sup>10b</sup> all of which have  $T_c$ 's above 10 K.<sup>11</sup> On the other hand, we have failed to detect zero resistance in  $\beta$ -(BDA-TTP)<sub>2</sub>I<sub>3</sub> probably due to a small volume fraction in the observed superconducting state. Furthermore, it is very difficult in high-pressure experiments to exactly estimate the pressure loss during cooling, so we have been unable to know a pressure value suitable for observing the zero resistance or a sample-independent  $T_c$  in  $\beta$ -(BDA-TTP)<sub>2</sub>I<sub>3</sub>. However, there is a tendency for  $\beta$ -(BDA-TTP)<sub>2</sub>I<sub>3</sub> that when the  $T_c$  is higher, the magnitude of the resistance drop is larger. The realization of a superconducting state with a larger volume fraction and/or a higher  $T_c$  may, thus, require fine tuning of the pressure control or application of uniaxial strain. Work currently in progress is addressing this question.

This work was supported by MEXT (Nos. 15073102 and 15073211) and JSPS (No. 17550135).

## Notes and references

† Crystal data for (BDA-TTP)<sub>2</sub>I<sub>3</sub>: C<sub>24</sub>H<sub>24</sub>I<sub>3</sub>S<sub>16</sub>,  $M_r = 1206.13$ , triclinic, space group  $P\bar{1}$ ,  $a = 9.2460(9)$  Å,  $b = 16.792(2)$  Å,  $c = 6.4950(7)$  Å,  $\alpha = 95.263(9)^\circ$ ,  $\beta = 106.576(8)^\circ$ ,  $\gamma = 95.766(9)^\circ$ ,  $V = 953.9(2)$  Å<sup>3</sup>,  $Z = 1$ ,  $\rho_{\text{calcd}} = 2.099$  g cm<sup>-3</sup>,  $\mu = 3.354$  mm<sup>-1</sup>,  $2\theta_{\text{max}} = 55.1^\circ$ ,  $\lambda(\text{MoK}\alpha) = 0.7107$  Å,  $\omega$ - $2\theta$  scan mode,  $T = 296.2$  K, 4780 reflections, of which 4393 were independent and 3231 were included in the refinement [ $I > 3.0\sigma(I)$ ], data collected for Lorentzian and polarization effects; a  $\phi$ -scan absorption correction resulted

in transmission factors ranging from 0.562 to 1.000, solution by direct methods (SIR 92) and refinement on  $|F^2|$  by full-matrix least-squares procedures (teXsan for Windows ver. 1.06), 197 parameters, the non-H atoms were refined anisotropically, H atoms were included but not refined, final values  $R = 0.034$ ,  $wR = 0.034$ ,  $\text{GOF} = 1.91$ , maximum positive and negative peaks in  $\Delta F$  map were 1.59 and  $-1.26$  e Å<sup>-3</sup>, respectively. CCDC 289991. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b516909g

‡ Variable-temperature conductivity or magnetization measurements under hydrostatic pressure were carried out using a clamped Be–Cu pressure cell with a pressure medium of Daphne 7243 or 7373 oil (Idemitsu Co. Ltd.). Electrical conductivity was measured by the four-probe technique using gold wires attached to the single crystal with carbon paste.

- (a) J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini and M.-H. Whangbo, *Organic Superconductors (Including Fullerenes)—Synthesis, Structure, Properties, and Theory*, Prentice Hall, Englewood Cliffs, NJ, 1992; (b) T. Ishiguro, K. Yamaji and G. Saito, *Organic Superconductors*, ed. P. Fulde, Springer, Berlin, 2nd ed, 1998; (c) *TTF Chemistry—Fundamentals and Applications of Tetrathiafulvalene*, ed. J. Yamada and T. Sugimoto, Kodansha & Springer, Tokyo, 2004; (d) thematic issue on Molecular Conductors, *Chem. Rev.*, 2004, **104**.
- (a) J. Yamada, T. Toita, H. Akutsu, S. Nakatsuji, H. Nishikawa, I. Ikemoto, K. Kikuchi, E. S. Choi, D. Graf and J. S. Brooks, *Chem. Commun.*, 2003, 2230; (b) E. S. Choi, D. Graf, J. S. Brooks, J. Yamada, H. Akutsu, K. Kikuchi and M. Tokumoto, *Phys. Rev. B*, 2004, **70**, 024517.
- J. Yamada, M. Watanabe, H. Akutsu, S. Nakatsuji, H. Nishikawa, I. Ikemoto and K. Kikuchi, *J. Am. Chem. Soc.*, 2001, **123**, 4174.
- For a recent study of the pressure effect on other molecular conductors, see: L. Beer, J. L. Brusso, R. C. Haddon, M. E. Itkis, H. Kleinke, A. A. Leitch, R. T. Oakley, R. W. Reed, J. F. Richardson, R. A. Secco and X. Yu, *J. Am. Chem. Soc.*, 2005, **127**, 18159.
- (a) J. Yamada, T. Toita, H. Akutsu, S. Nakatsuji, H. Nishikawa, I. Ikemoto and K. Kikuchi, *Chem. Commun.*, 2001, 2538; (b) K. Kikuchi, H. Nishikawa, I. Ikemoto, T. Toita, H. Akutsu, S. Nakatsuji and J. Yamada, *J. Solid State Chem.*, 2002, **168**, 503.
- J. Yamada, H. Akutsu, H. Nishikawa and K. Kikuchi, *Chem. Rev.*, 2004, **104**, 5057.
- For the parameters used for the calculation, see: T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 627.
- For the fit of the susceptibility, see: R. Clément, J. J. Girerd and I. Morgenstern-Badarau, *Inorg. Chem.*, 1980, **19**, 2852.
- (a) C. Bourbonnais and D. Jérôme, in *Advances in Synthetic Metals—Twenty Years of Progress in Science and Technology*, ed. P. Bernier, S. Lefrant and G. Bidan, Elsevier, Amsterdam, 1999, ch. 3; (b) K. Kanoda, *Physica C*, 1997, **282–287**, 299.
- (a) H. Ito, T. Ishiguro, M. Kubota and G. Saito, *J. Phys. Soc. Jpn.*, 1996, **65**, 2987 and references therein; (b) H. Kobayashi, H. Akutsu, E. Arai, H. Tanaka and A. Kobayashi, *Phys. Rev. B*, 1997, **56**, R8526.
- For other organic superconductors which show the pressure-induced increase of  $T_c$  in a wider pressure range, see: (a) J. E. Schirber, D. L. Overmyer, E. L. Venturini, H. H. Wang, K. D. Carlson, W. K. Kwok, S. Kleinjan and J. M. Williams, *Physica C*, 1989, **161**, 412; (b) L. Brossard, M. Ribault, L. Valade and P. Cassoux, *Phys. Rev. B*, 1990, **42**, 3935; (c) A. Kobayashi, H. Kim, Y. Sasaki, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita and W. Sasaki, *Chem. Lett.*, 1987, 1819; (d) H. Taniguchi, M. Miyashita, K. Uchiyama, K. Satoh, N. Mōri, H. Okamoto, K. Miyagawa, K. Kanoda, M. Hedo and Y. Uwatoko, *J. Phys. Soc. Jpn.*, 2003, **72**, 468.