JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

pubs.acs.org/JACS

Uniaxial Strain Orientation Dependence of Superconducting Transition Temperature (T_c) and Critical Superconducting Pressure (P_c) in β-(BDA-TTP)$_2$I$_3$

Koichi Kikuchi,*[†] Takayuki Isono,[†] Masayuki Kojima,[†] Haruo Yoshimoto,[†] Takeshi Kodama,[†] Wataru Fujita,[†] Keiichi Yokogawa,[‡] Harukazu Yoshino,[‡] Keizo Murata,[‡] Takayuki Kaihatsu,[§] Hiroki Akutsu,[§] and Jun-ichi Yamada*[§]

[†]Department of Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo 192-0937, Japan

[‡]Graduate School of Science, Osaka City University, Osaka 558-8585, Japan

[§]Department of Material Science, Graduate School of Material Science, University of Hyogo, 3-2-1 Kouto, Kamigori-cho, Ako-gun, Hyogo 678-1297, Japan

S Supporting Information

ABSTRACT: Dependence of the superconducting transition temperature (T_c) and critial superconducting pressure (P_c) of the pressure-induced superconductor β-(BDA-TTP)$_2$I$_3$ [BDA-TTP = 2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene] on the orientation of uniaxial strain has been investigated. On the basis of the overlap between the upper and lower bands in the energy dispersion curve, the pressure orientation is thought to change the half-filled band to the quarter-filled one. The observed variations in T_c and P_c are explained by considering the degree of application of the pressure and the degree of contribution of the effective electronic correlation at uniaxial strains with different orientations parallel to the conducting donor layer.

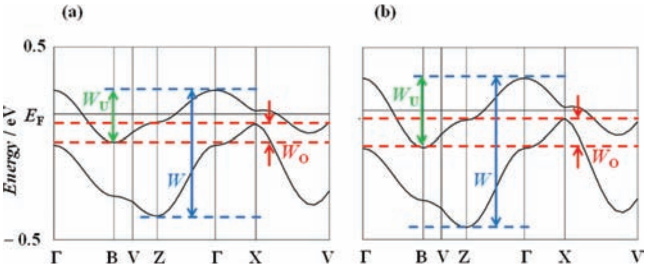

Figure 1. Band structures of β-(BDA-TTP)$_2$I$_3$ (a) at ambient pressure and (b) at a hydrostatic pressure of 7.5 kbar. The values of W, W_U, and W_O at ambient pressure are 0.65, 0.27, and 0.09 eV, respectively, whereas those at a hydrostatic pressure of 7.5 kbar are 0.78, 0.36, and 0.15 eV, respectively.

Since the discovery of TMTSF (tetramethyltetraselenafulvalene) superconductors followed by BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] superconductors,[1] the issue of controlling the superconducting transition temperature (T_c) in layered organic superconductors remains a major challenge in the research of organic superconductivity, though the settlement of this issue would serve as a guide to the production of new high-T_c superconductors. On the basis of their band structures, layered organic superconductors are roughly divided into two categories: the half-filled band system and the quarter-filled one.[2] In both systems, the T_c's are very sensitive to pressure and the electronic states are also changed by pressure. In the case of many layered organic superconductors with the half-filled band system, with increasing pressure, the Mott insulating ground state is suppressed and then the superconducting state appears.[3] On the other hand, in the case of layered organic superconductors with the quarter-filled band system, the pressure enables the charge ordering insulating state to change into the superconducting state.[4] Therefore, the application of pressure plays an important role in inducing organic superconductivity. In addition to the hydrostatic-pressure application with an isotropic pressure effect, the uniaxial strain method with modification of the intermolecular distance along a desired direction is a powerful tool for the research of organic superconductors.[5,6] Here we report what changes take place in the T_c and critial superconducting pressure (P_c) of the pressure-induced superconductor β-(BDA-TTP)$_2$I$_3$ by making fine adjustments to the orientation of applying uniaxial strain.

β-(BDA-TTP)$_2$I$_3$ exhibits superconductivity with a rather high resistive T_c of 9.5 K under a hydrostatic pressure of 9.7 kbar.[7] The temperature dependence of the susceptibility explained by the one-dimensional antiferromagnetic Heisenberg model[7] and the infrared and Raman spectroscopic study[8] indicate that the ground state of β-(BDA-TTP)$_2$I$_3$ at ambient pressure is a Mott insulator with the half-filled band system, although there is an overlap between the upper and lower bands in the energy dispersion curve calculated by the extended Hückel method[9] as shown in Figure 1a, where W, W_U, and W_O stand for the total bandwidth of the upper and lower bands, the bandwidth of the upper band, and the overlap between the upper and lower bands, respectively. The values of W and W_U are essential to the control of the effective electronic correlation, because the effective electronic correlation is given by U/W and V/W, where U and V are the on-site and intersite Coulomb repulsions, respectively, in the quarter-filled band system, and is expressed as U/W_U and V/W_U in the

Received: August 5, 2011
Published: November 10, 2011

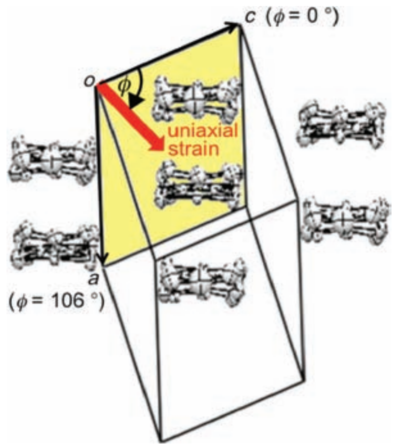

Figure 2. Donor arrangement in β-(BDA-TTP)$_2$I$_3$ and definition of the orientation of uniaxial strain in the *ac* plane. According to the definition, the orientations of the *c*-axis, *a*-axis, and −*a*-axis strains are assigned as $\phi = 0°$, 106°, and −74°, respectively.

half-filled band system. Our X-ray structural study of β-(BDA-TTP)$_2$I$_3$ under a hydrostatic pressure of 7.5 kbar[10] revealed that (i) the two outer dithiane rings of BDA-TTF adopt nonequivalent chair conformations (the respective dihedral angles around the corresponding intermolecular sulfur-to-sulfur axes are 51.3° and 29.2°, see Supplemental Figure S1), (ii) the conformation of BDA-TTP is slightly difference from that at ambient pressure, and (iii) the dimerization of BDA-TTP molecules is smaller than that at ambient pressure (Supplemental Figure S2). Introduction of such a structural flexibility into the design of new donor molecules would be useful for the control of the effective electron correlation leading to the superconducting state.[11] In addition, the overlap W_O increases (Figure 1b) with a reduction of about 4% in the unit cell volume [917.2(11) Å^3][12] compared to that [953.9(2) Å^3][7] at ambient pressure. The result implies that the ground state of the salt tends to change from the half-filled band into the quarter-filled one under applied pressure, because a large value of W_O is seen in the quarter-filled band structure.[4b]

We investigated the temperature dependence of the resistivity of β-(BDA-TTP)$_2$I$_3$ by applying uniaxial strains along the crystallographic *a*-, *b*-, and *c*-axes as well as different directions in the conducting *ac* plane to find favorable pressure orientations for inducing superconductivity. The orientation of uniaxial strain in the *ac* plane is defined by the angle ϕ from the *c*-axis fixed as a reference axis (Figure 2). Figure 3a−c shows the resistivity of the salt as a function of temperature under uniaxial strains parallel to the *a*-, *b*-, and *c*-axes, respectively. Under the *a*-axis strains up to 12 kbar, increase of resistivity began to be suppressed in a low temperature region at 7, 8, 9, and 10 kbar, and the salt behaved like a metal from 50 to 10 K under 12 kbar. On the other hand, under the *b*-axis strains, the insulating behavior of the salt remained unaltered at all pressures up to 12 kbar. Under the *c*-axis strains up to 10 kbar, a drop in resistivity appeared with an onset at 8.5 K under 8.5 kbar. The onset temperature of the resistivity drop increased up to 10.5 K at 9.5 kbar but decreased slightly to 9.5 K at 10 kbar. We observed a recovery of the resistance in the resistivity measurement of another single crystal by application of a uniaxal strain of 10 kbar with $\phi = \sim 7°$ under applied magnetic fields (Figure 4), so the drop in resistivity observed by applying the *c*-axis strain can be attributed to a superconducting transition. It was consequently found that the resistive T_c under the *c*-axis strain rises by 1 K compared to that (9.5 K) under hydrostatic pressure.

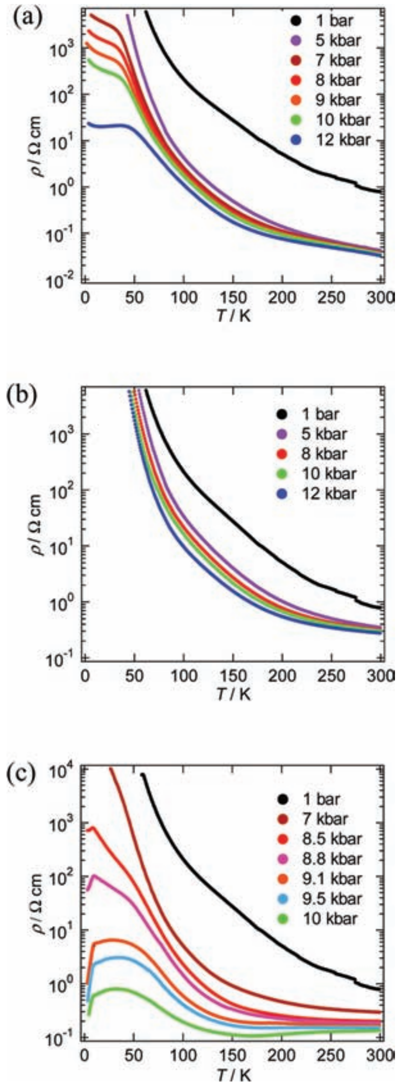

Figure 3. Temperature dependence of the resistivity of β-(BDA-TTP)$_2$I$_3$ under the (a) *a*-axis, (b) *b*-axis, and (c) *c*-axis strains.

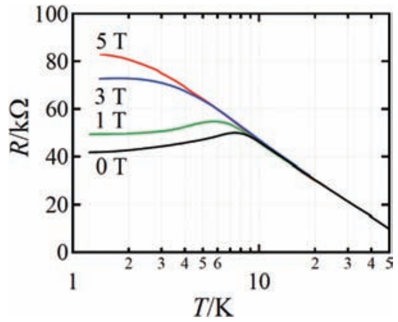

Figure 4. Magnetic-field dependence of the resistivity drop in β-(BDA-TTP)$_2$I$_3$ under a uniaxial strain of 10 kbar with $\phi = \sim 7°$. The magnetic field was applied along the crystallographic *b*-axis.

Figure 5a summarizes the pressure dependence of T_c in β-(BDA-TTP)$_2$I$_3$ by varying the orientation of uniaxial strain in the *ac* plane. Superconductivity was observed in the orientation

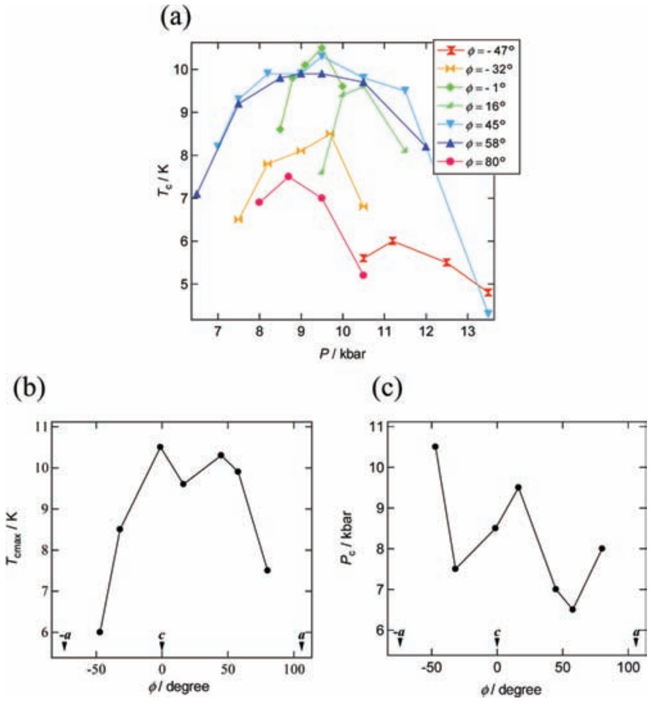

Figure 5. (a) Pressure dependence of T_c at different pressure orientations with φ = −47°, −32°, −1°, 16°, 45°, 58°, and 80°. (b) Pressure-orientation dependence of T_{cmax} and (c) pressure-orientation dependence of P_c in β-(BDA-TTP)$_2$I$_3$.

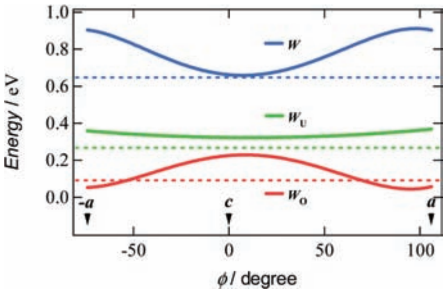

Figure 6. Pressure-orientation dependence of W, W_U, and W_O in β-(BDA-TTP)$_2$I$_3$. The values of W, W_U, and W_O at ambient pressure are indicated by the dotted lines.

angle range of −47° ≤ φ ≤ 80°; however, outside this range, no superconductivity was found. It should be noted that at the uniaxial strain with φ = 45° the T_c's varied from 4.3 to 10.3 K in a wide pressure range from 7 to 13.5 kbar and the P_c is lower than that (9.7 kbar) under hydrostatic pressure. Figure 5b and c depicts the plots of the maxima values of T_c (abbreviated as T_{cmax}) and the values of P_c, respectively, at different pressure orientations with φ = −47°, −32°, −1°, 16°, 45°, 58°, and 80°. The higher T_{cmax}'s from 8.5 to 10.5 K are recorded in the orientation angle range of −32° ≤ φ ≤ 58°, whereas the values of T_{cmax} decrease outside this range. The plots of P_c display a convex-shaped pressure-orientation dependence within the same orientation angle range, outside of which the values of P_c increase.

Taking account of the approximately 4% reduction of the unit cell volume by application of a hydrostatic pressure of 7.5 kbar, we calculated the tight binding band structures under uniaxial strains parallel to the *ac* plane by the extended Hückel method[9] based on the assumption that the distance between the BDA-TTP donor molecules along each uniaxial strain decreases by 5% with no change in the HOMO level of BDA-TTP at ambient pressure.[13] Figure 6 shows the curves of W, W_U, and W_O, which were obtained from the band calculations by varying the pressure orientation angle at an interval of 5° in the *ac* plane, together with the values of W, W_U, and W_O at ambient pressure. The value of W_O exhibits a gradual increase as φ approaches 0° (the direction of the *c*-axis) and a gradual decrease as φ comes close to 106° (the direction of the *a*-axis) and −74° (the direction of the −*a*-axis). A maximum value of W_O is observed at φ = 16° (the direction perpendicular to the *a*-axis). The variation of W_O suggests that the ground state of β-(BDA-TTP)$_2$I$_3$ is changed from the half-filled band into the quarter-filled one by applying the *c*-axis strain, whereas the half-filled band is dominant in the ground state of the salt under the *a*-axis strain. It is noteworthy that compared to the value of W_O at ambient pressure, larger values of W_O are observed in the orientation angle range in which higher T_{cmax}'s are recorded (Figure 5b). Therefore, the quarter-filled band system is likely to be favorable for the achievement of superconductivity in β-(BDA-TTP)$_2$I$_3$.

Application of pressure is generally thought to lead to an enhancement of the bandwidth and, consequently, to decrease the electron correlation.[14] In addition, a key parameter to control the ground state in the quarter-filled band system is proposed to be the effective electronic correlation U/W and V/W.[2] The ground state is in the metallic phase when the values of U/W and V/W are small, while the ground state is in the insulating phase when those are large. Superconductivity appears when U/W and V/W are in between. In the conducting *ac* plane of β-(BDA-TTP)$_2$I$_3$, the total bandwidth W exhibits a value close to the maximum value under the *a*-axis strain (Figure 6) and a minimum value at the uniaxial strain with φ = 16°. With decreasing W, the values of U/W and V/W increase, so that the achievement of superconductivity requires the increase of pressure. It is thus expected that the value of P_c shows a maximum around φ = 16° and decreases as the orientation angle moves away from φ = 16°. This prediction is in good agreement with the pressure-orientation dependence of P_c in the orientation angle range of −32° ≤ φ ≤ 58° (Figure 5c) where the ground state of β-(BDA-TTP)$_2$I$_3$ seems to be the quarter-filled band. At the pressure orientation angles of −47° and 80°, the ground states are close to the half-filled band, the values of P_c significantly increase (Figure 5c), and the values of T_{cmax} decrease (Figure 5b).

The effective electronic correlation U/W_U and V/W_U in the half-filled band system acts as a key parameter to control the ground state,[2] akin to the case of the quarter-filled band system. In the *ac* plane of β-(BDA-TTP)$_2$I$_3$, the values of the upper bandwidth W_U at different uniaxial strains are slightly larger than that at ambient pressure (Figure 6) and almost independent of φ. This pressure-orientation dependence of W_U differs from that of W, so it seems in the half-filled band system that a higher pressure is necessary for increase of W_U and hence for decrease of U/W_U and V/W_U to induce superconductivity. As mentioned above, the ground state of β-(BDA-TTP)$_2$I$_3$ is regarded as the half-filled band for the orientation of the *a*-axis strain, and we were actually unable to find superconductivity by applying the *a*-axis strains up to 12 kbar, though suppression of the resistivity increase and a metallic resistive behavior were observed (Figure 3a). There is therefore a possibility that further increases in the pressure along the *a*-axis induce superconductivity in β-(BDA-TTP)$_2$I$_3$ with the half-filled band.

In conclusion, we revealed variations in the T_c and P_c of the pressure-induced superconductor β-(BDA-TTP)$_2$I$_3$ by applying uniaxial strains with a variety of orientation angles in the conducting *ac* plane. Then we calculated the values of W, W_U, and W_O in the band structure of β-(BDA-TTP)$_2$I$_3$ under uniaxial strains, presumed the ground state of the salt by the variations of W_O, and elucidated the effects of both the pressure and the effective electronic correlation on the induction of superconductivity. This approach to study organic superconductivity demonstrates that the pressure orientation can change the ground state into another one, where the control of T_c is feasible by adjusting the value of uniaxial strain, considering the contribution of the effective electronic correlation. This work is thus the first example that realizes two competing insulating states depending on the pressure orientation in the same material, which is sure to shed light on the research of organic superconductors associated with those ground states. On the other hand, it remains to be proved that further application of the *a*-axis strain to β-(BDA-TTP)$_2$I$_3$ leads to superconductivity. Work currently in progress is addressing this issue.

ASSOCIATED CONTENT

Supporting Information. Experiment details of both the crystal structure determination under hydrostatic pressure and the resistivity measurement under uniaxial strain, Crystallographic information in CIF format for β-(BDA-TTP)$_2$I$_3$ under a hydrostatic pressure of 7.5 kbar. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

kikuchi-koichi@tmu.ac.jp; yamada@sci.u-hyogo.ac.jp

ACKNOWLEDGMENT

This work was supported by Grant-in-Aid for Scientific Research (B) (No. 21350080) and Grant-in-Aid for Scientific Research on Innovative Areas (No. 20110007) from the MEXT of Japan.

REFERENCES

(1) (a) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M.-H. *Organic Superconductors (Including Fullerenes): Synthesis, Structure, Properties and Theory*; Prentice Hall: Englewood Cliffs, NJ, 1992. (b) Ishiguro, T.; Yamaji, K.; Saito, G. *Organic Superconductors*, 2nd ed.; Fulde, P., Ed.; Springer Series in Solid-State Science, Vol. 88; Springer: Berlin, 1998. (c) *TTF Chemistry—Fundamentals and Applications of Tetrathiafulvalene*; Yamada, J., Sugimoto, T., Eds.; Kodansha & Springer: Tokyo, 2004. (d) *Chem. Rev.* **2004**, *104* (issue 11) (Molecular Conductors). (e) *J. Phys. Soc. Jpn.* **2006**, *75* (issue 5) (Organic Conductors).

(2) Seo, H.; Hotta, C.; Fukuyama, H. *Chem. Rev.* **2004**, *104*, 5005–5036.

(3) Miyagawa, K.; Kanoda, K.; Kawamoto, A. *Chem. Rev.* **2004**, *104*, 5635–5653.

(4) (a) Mori, H.; Tanaka, S.; Mori, T. *Phys. Rev. B* **1998**, *57*, 12023–12029. (b) Nishikawa, H.; Sato, Y.; Kikuchi, K.; Kodama, T.; Ikemoto, I.; Yamada, J.; Oshio, H.; Kondo, R.; Kagoshima, S. *Phys. Rev. B* **2005**, *72*, 052510-1–4.

(5) For reviews, see: (a) Kagoshima, S.; Kondo, R. *Chem. Rev.* **2004**, *104*, 5593–5608. (b) Murata, K.; Kagoshima, S.; Yasuzuka, S.; Yoshino, H.; Kondo, R. *J. Phys. Soc. Jpn.* **2006**, *75*, 051015-1–15.

(6) For example, see: (a) Hirayama, T.; Manabe, K.; Akimoto, H.; Ishimoto, H.; Ito, H.; Ishiguro, T.; Mori, H.; Saito, G. *Czech. J. Phys.* **1996**, *46* (Suppl. S2), 813–814. (b) Maesato, M.; Kaga, Y.; Kondo, R.; Kagoshima, S. *Phys. Rev. B* **2001**, *64*, 155104-1–8. (c) Tajima, N.; Sugawara, S.; Tamura, M.; Nishio, Y.; Kajita, K. *J. Phys. Soc. Jpn.* **2006**, *75*, 051010-1–10. (d) Ito, H.; Ishihara, T.; Tanaka, H.; Kuroda, S.; Suzuki, T.; Onari, S.; Tanaka, Y.; Yamada, J.; Kikuchi, K. *Phys. Rev. B* **2008**, *78*, 172506-1–4.

(7) Yamada, J.; Fujimoto, K.; Akutsu, H.; Nakatsuji, S.; Miyazaki, A.; Aimatsu, M.; Kudo, S.; Enoki, T.; Kikuchi, K. *Chem. Commun.* **2006**, 1331–1333.

(8) Uruichi, M.; Nakano, C.; Tanaka, M.; Yakushi, K.; Kaihatsu, T.; Yamada, J. *Solid State Commun.* **2008**, *147*, 484–489.

(9) For the parameters used for the calculation, see: Mori, T.; Kobayashi, A.; Sasaki, Y.; Kobayashi, H.; Saito, G.; Inokuchi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 627–633. We calculated the band structures including the 3d orbitals of the sulfur atoms in BDA-TTP.

(10) The pressure value is a value at room temperature. For the pressure loss during cooling, see: (a) Murata, K.; Yoshino, H.; Yadav, H. O.; Honda, Y.; Shirakawa, N. *Rev. Sci. Instrum.* **1997**, *68*, 2490-1–4. (b) Yokogawa, K.; Murata, K.; Yoshino, H.; Aoyama, S. *Jpn. J. Appl. Phys.* **2007**, *46*, 3636–3639. (c) Murata, K.; Yokogawa, K.; Yoshino, H.; Klotz, S.; Munsch, P.; Irizawa, A.; Nishiyama, M.; Iizuka, K.; Nanba, T.; Okada, T.; Shiraga, Y.; Aoyama, S. *Rev. Sci. Instrum.* **2008**, *79*, 085101-1–6.

(11) (a) Yamada, J.; Watanabe, M.; Akutsu, H.; Nakatsuji, S.; Nishikawa, H.; Ikemoto, I.; Kikuchi, K. *J. Am. Chem. Soc.* **2001**, *123*, 4174–4180. (b) Choi, E. S.; Graf, D.; Brooks, J. S.; Yamada, J.; Akutsu, H.; Kikuchi, K.; Tokumoto, M. *Phys. Rev. B* **2004**, *70*, 024517-1–8.

(12) Crystallographic data for β-(BDATTP)$_2$I$_3$ under a hydrostatic pressure of 7.5 kbar: $C_{24}H_{24}S_{16}I_3$, triclinic, space group $P\bar{1}$, $a = 9.097(7)$ Å, $b = 16.659(8)$ Å, $c = 6.389(5)$ Å, $\alpha = 95.07(5)°$, $\beta = 106.06(4)°$, $\gamma = 96.44(5)°$, $V = 917.2(11)$ Å^3, $R = 0.0400$, $R_w = 0.0828$, GOF = 1.232.

(13) According to the assumption, the uniaxial strain along the *b*-axis in β-(BDA-TTP)$_2$I$_3$ elicits 5% reduction in the distance between the donor molecule and the anion, and the resulting band structure is the same as that at ambient pressure owing to no modification in the distance of the donor molecules responsible for the electrical conductivity.

(14) Kanoda, K. *J. Phys. Soc. Jpn.* **2006**, *75*, 051007-1–16.