Science, under Contract W-31-109-Eng-38.

Registry No. $(TMTSF)_2{\cdot}BF_4^-$, 73731-79-0; $(TMTSF)_2{\cdot}ClO_4^-$, 77273-54-2; $(TMTSF)_2{\cdot}FO_3S^-$, 81259-79-2; $(TMTSF)_2{\cdot}ReO_4^-$, 80531-49-3; $(TMTSF)_2{\cdot}PF_6^-$, 73261-24-2; $(TMTSF)_2{\cdot}BrO_4^-$, 81259-81-6; $(TMTSF)_2{\cdot}AsF_6^-$, 73731-75-6.

Supplementary Material Available: Full structural details for the $(TMTSF)_2X$ salts reported herein including source and reference diffraction data used in this work, plane dimerization distances (D_1 and D_2), interstack Se–Se contact distances (d_7, d_8, and d_9), and plots of known unit cell volumes versus derived ionic volumes (T = 298 and 125 K) (6 pages). Ordering information is given on any current masthead page.

Characterization of the Interchain Se···Se Interaction in $(TMTSF)_2X$ by Band Electronic Structure

Myung-Hwan Whangbo,*[†1a] Jack M. Williams,*[1b]
Mark A. Beno,[1b] and Jay R. Dorfman[‡1a]

Department of Chemistry, North Carolina State University
Raleigh, North Carolina 27650
Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439

Received August 23, 1982

Crystal structures of $(TMTSF)_2X$ salts exhibit a systematic decrease in the interchain Se···Se separations upon decreasing the unit cell volume or upon lowering temperature.[2] Such structural changes hold important information concerning how the interchain Se···Se separation is related to the magnitude of the interchain Se···Se interactions. To explore this relationship, we examined the electronic structures of $(TMTSF)_2X$ (X^- = AsF_6^-, BF_4^-, BrO_4^-, ClO_4^-, FSO_3^-, $H_2F_3^-$, PF_6^-, and ReO_4^-) by performing the tight-binding band calculations based upon the extended Hückel method.[3] Our calculations on all $(TMTSF)_2X$ compounds employed their crystal structures determined at 298 K and at 120–125 K.[2,4] Actual band-structure calculations for each $(TMTSF)_2X$ salt were carried out on a two-dimensional sheet of TSF molecules,[5] as reported elsewhere.[6,7]

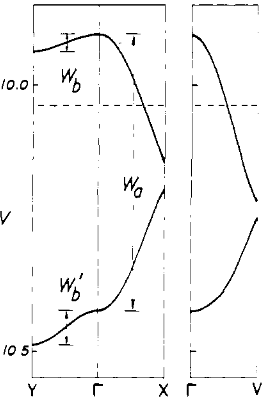


Figure 1. Band structure of a two-dimensional sheet of TSF molecules. The symbols Γ, X, Y, and V refer to the points in the Brillouin zone,[6] whose coordinates are expressed in fractions of the reciprocal vectors a^* and b^* as follows: Γ = (0.0, 0.0), X = (0.5, 0.0), Y = (0.0, 0.5), and V = (0.5, 0.5). The Fermi level is indicated by the dashed line.

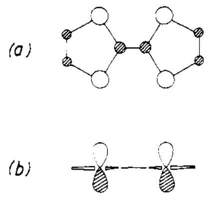
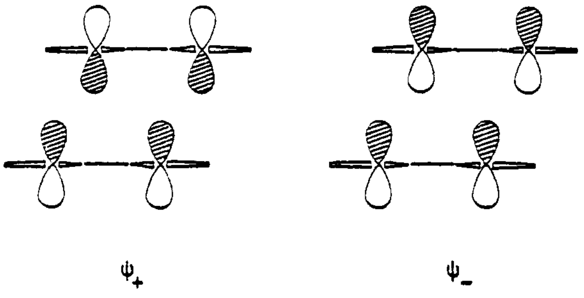


Figure 2. Schematic representations of the HOMO of a TSF molecule. The Se 4p and C 2p orbitals are projected onto the molecular plane in a. The side view of the HOMO is given in b, where only the Se 4p orbitals are shown for simplicity.

The valence band (i.e., the highest occupied band) of every $(TMTSF)_2X$ has the characteristic feature shown in Figure 1 for $(TMTSF)_2PF_6$ at 125 K. That is, the valence band consists of two overlapping bands.[6] With the formal oxidation of $(TMTSF)_2^+$ per unit cell, the valence band is one-quarter-empty because of the half-empty upper band and the completely filled lower band. The HOMO of each TSF molecule has large coefficients on Se 4p orbitals, as schematically shown in Figure 2. Two such HOMO's in each unit cell of $(TMTSF)_2X$ interact to form the in-phase and the out-of-phase combinations (ψ_+ and ψ_-, respectively). It is these orbitals ψ_+ and ψ_- that lead to the lower and the upper bands of Figure 1, respectively. The valence band of $(TMTSF)_2X$ may be characterized by three calculated parameters, i.e., the combined width W_a of the two overlapping bands along the chain direction (Γ → X), the width W_b of the upper band along the interchain direction (Γ → Y), and the width W_b' of the lower band along the interchain direction.



The magnitude of interaction between neighboring unit cells in a certain direction is proportional to the width of the resulting band in that direction. Therefore, both W_b and W_b' are associated

---

† Camille and Henry Dreyfus Teacher–Scholar (1980–1985).

‡ Present Address: Department of Chemistry, Harvard University, Cambridge, MA 02138.

(1) (a) North Carolina State University; (b) Argonne National Laboratory.

(2) Williams, J. M.; Beno, M. A.; Banovetz, L. M.; Braam, J. M.; Blackman, G. S.; Carlson, C. D.; Greer, D. L.; Loesing, D. M. *J. Am. Chem. Soc.*, preceding paper in this issue.

(3) (a) Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093. (b) Whangbo, M.-H.; Hoffmann, R.; Woodward, R. B. *Proc. R. Soc. London, Ser. A* **1979**, *366*, 23.

(4) The crystal structures of $(TMTSF)_2X$ used in our study were our own work and also taken from the following: (a) Thorp, N.; Rindorf, G.; Soling, H.; Bechgaard, K. *Acta Crystallogr. Sect. B* **1981**, *37B*, 1236. (b) Bechgaard, K.; Carneiro, K.; Rasmussen, F. B.; Olsen, M.; Rindorf, G.; Jacobsen, C. S.; Pedersen, H. J.; Scott, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2440. (c) Wudl, F. *Ibid.* **1981**, *103*, 7065. (d) Williams, J. M.; Beno, M. A.; Appelman, E. H.; Capriotti, J. M.; Wudl, F.; Aharon-Shalom, E.; Nalewajek, D. *Mol. Cryst. Liq. Cryst.* **1982**, *79*, 319. (e) Beno, M. A.; Williams, J. M.; Lee, M. M.; Cowan, D. O. *Solid State Commun.* **1982**, *44*, 1195. (f) Beno, M. A.; Blackman, G. S.; Williams, J. M.; Bechgaard, K. *Inorg. Chem.* **1982**, *21*, 3860. (g) Rindorf, G.; Soling, H.; Thorp, N., submitted for publication in *Acta Crystallogr., Sect B.*

(5) The acronyms TMTSF and TSF refer to tetramethyltetraselenafulvalene and tetraselenafulvalene, respectively.

(6) Whangbo, M.-H.; Walsh, W. M., Jr.; Haddon, R. C.; Wudl, F. *Solid State Commun.* **1982**, *43*, 637.

(7) The $H_{\mu\mu}$ value for Se 4p orbital was taken as −12.7 eV instead of −14.4 eV,[6] since the former reproduces the semimetallic property of $TiSe_2$.[8] However, these two parameters lead to band structures very similar in nature. The $H_{\mu\mu}$ value for Se 4d orbital was taken as −7.0 eV,[6] which provides a one-electron band structure consistent with the Shubnikov–de Haas data on $(TMTSF)_2PF_6$.[6,9,10] Calculations with and without Se 4d orbitals exhibit the same trends for the qualitative aspects of the interchain Se···Se interaction, although the intrachain and the interchain bandwidths are enhanced upon including Se 4d orbitals.[6] Thus we report only those results obtained without Se 4d orbitals, which should be regarded as a lower limit.[11]

(8) Ragavachari, K., private communication.

(9) Kwak, J. F.; Schirber, J. E.; Greene, R. L.; Engler, E. M. *Phys. Rev. Lett.* **1981**, *46*, 1296.

(10) Horovitz, B.; Gutfreund, H.; Weger, M. *Solid State Commun.* **1981**, *39*, 541; *Mol. Cryst. Liq. Cryst.* **1982**, *79*, 155.

(11) (a) Grant, P. M. *Phys. Rev. B: Condens. Matter* **1982**, *26*, 6888. (b) Jacobsen, J. C.; Tanner, D. B.; Bechgaard, K. *Phys. Rev. Lett.* **1981**, *46*, 1142; *Mol. Cryst. Liq. Cryst.* **1982**, *79*, 25.

0002-7863/83/1505-0645$01.50/0 © 1983 American Chemical Society

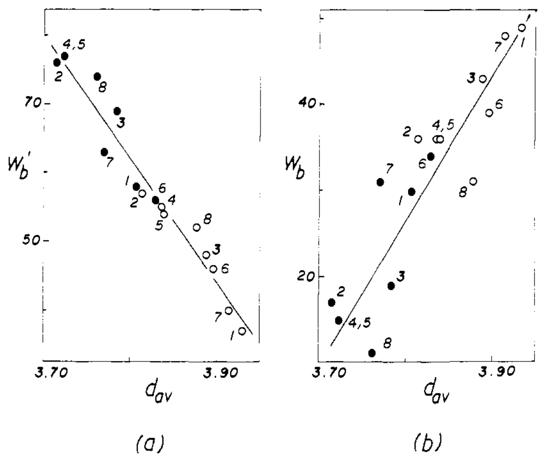


Figure 3. Calculated bandwidths W_b' and W_b of (TMTSF)$_2$X along the interchain direction plotted as a function of the experimental interchain Se···Se separation, $d_{av} = (d_9 + 2d_7)/3$: (a) W_b' vs. d_{av}, and (b) W_b vs. d_{av}, where the values of W_b' and W_b are given in meV and the value of d_{av} is in Å. The empty and filled circles refer to the data for the 298 K and the 120–125 K structures, respectively. The numbers **1**–**8** represent the anions X$^-$ of (TMTSF)$_2$X as follows: **1** = AsF$_6^-$, **2** = BF$_4^-$, **3** = BrO$_4^-$, **4** = ClO$_4^-$, **5** = FSO$_3^-$, **6** = H$_2$F$_3^-$, **7** = PF$_6$, and **8** = ReO$_4$.

with the magnitude of the interchain Se···Se interaction. The structural parameters relevant for describing the interchain Se···Se interactions are the two shortest interchain Se···Se separations d_9 and d_7 (see Figure 1 of ref 2). Between neighboring chains of TMTSF molecules, there occur one d_9 and two d_7 Se···Se contacts per TMTSF molecule. Since the Se 4p orbitals in the HOMO of each TMTSF have the same sign, all the Se 4p orbitals associated with the d_9 and d_7 Se···Se contacts can be chosen to have the same sign. Consequently, the weighted average of the interchain Se···Se separations $d_{av} = (d_9 + 2d_7)/3$ is a good experimental parameter to correlate with the calculated W_b' and W_b values. The plot of W_b' vs. d_{av} and that of W_b vs. d_{av} are respectively shown in Figure 3, which reveals that the lower band becomes wider but the upper band becomes narrower upon decreasing the interchain Se···Se separation.[12] Thus the magnitude of the interchain Se···Se interaction increases with the decrease in the interchain Se···Se separation according to the lower band, while the opposite is the case according to the upper band.

Figure 3 shows that, regardless of the temperature change, the data points for X$^-$ = BF$_4^-$, ClO$_4^-$, and FSO$_3^-$ are clearly separated out from those for X$^-$ = AsF$_6^-$ and PF$_6^-$. Such a feature is also obtained when the unit cell volumes of (TMTSF)$_2$X are plotted against the d_{av} values.[2] Along the interchain direction, the upper (lower) bands of the BF$_4^-$, ClO$_4^-$, and FSO$_3^-$ derivatives are narrower (wider) than the corresponding ones of the AsF$_6^-$ and PF$_6^-$ derivatives. Thus for the BF$_4^-$, ClO$_4^-$ and FSO$_3^-$ derivatives, it is expected that the density of states at the Fermi level is greater, the two sheets of the Fermi surface (see Figure 2a of ref 6) are less curved, but the overall interchain Se···Se interaction is stronger.[13] A high transition temperature T_c for superconductivity is likely to occur from a nearly half-filled narrow band.[14] However, such a band is also susceptible to electron localization.[15] The competition between superconductivity and electron localization is quite delicate. For example, (TMTSF)$_2$PF$_6$ undergoes a spin density wave (SDW) transition near 12 K at ambient pressure,[16] while an applied pressure of about 12 kbar suppresses this SDW transition and gives rise to superconductivity.[17] Thus it appears that under applied pressure the interchain Se···Se separations of (TMTSF)$_2$PF$_6$ become shortened and close to those of (TMTSF)$_2$ClO$_4$, a superconductor below 1.2 K at ambient pressure.[4b]

In summary, characterization of the interchain Se···Se interaction in (TMTSF)$_2$X requires at least two parameters, e.g., the interchain bandwidths of the two overlapping bands that arise from the two TMTSF HOMO's of each unit cell. The magnitudes of the interchain Se···Se interaction predicted from the widths of those two bands exhibit the opposite trends with respect to the change in the interchain Se···Se separations. This kind of complex behavior of the interchain Se···Se interaction might be responsible for the wealth of physical phenomena observed in (TMTSF)$_2$X.[18]

Acknowledgment. The work at North Carolina State University was supported by the Camille and Henry Dreyfus Foundation through a Teacher–Scholar Award to M.-H. W. The work at Argonne National Laboratory was supported by the U.S. Department of Energy, Office of Basic Energy Science, Division of Materials Science, under Contract W-31-109-Eng-38. We are thankful to Dr. P.M. Grant for communicating his work prior to publication.

Registry No. (TMTSF)$_2$AF$_6$, 73731-75-6; (TMTSF)$_2$BF$_4$, 73731-79-0; (TMTSF)$_2$BrO$_4$, 81259-81-6; (TMTSF)$_2$ClO$_4$, 77273-54-2; (TMTSF)$_2$FSO$_3$, 81259-79-2; (TMTSF)$_2$H$_2$F$_3$, 82979-12-2; (TMTSF)$_2$PF$_6$, 73261-24-2; (TMTSF)$_2$ReO$_4$, 80531-49-3; Se, 22541-48-6.

---

[12] The straight lines of Figure 3 may be used to approximate the relationship between W_b' and d_{av} and that between W_b and d_{av}, respectively. With W_b' and W_b in meV and d_{av} in Å, the linear equations are given as follows: $W_b' \simeq -180d_{av} + 746$; $W_b \simeq 167d_{av} - 608$. At 298 (120-125) K the intrachain bandwidths W_a of (TMTSF)$_2$X calculated without Se 4d orbitals are 0.463 (0.517), 0.449 (0.499), 0.446 (0.484), 0.452 (0.482), 0.448 (0.480), 0.522 (0.586), 0.463 (0.517), and 0.453 (0.497) eV for X$^-$ = AsF$_6^-$, BF$_4^-$, BrO$_4^-$, ClO$_4^-$, FSO$_3^-$, H$_2$F$_3^-$, PF$_6^-$, and ReO$_4^-$, respectively.

[13] The upper (lower) band of Figure 1 is half (completely) filled. Thus the property representing all the electrons of the valence band is more influenced by the lower band.

[14] Krüger, E. *Phys. Status Solidi B* **1978**, *85*, 493.

[15] (a) Brandow, B. H. *Adv. Phys.* **1977**, *26*, 651. (b) Mott, N. F. "Metal-Insulator Transitions"; Barnes & Noble: New York, 1977. (c) Haas, C. "Current Topics in Materials Science"; Kaldis, E., Ed.; North-Holland; Amsterdam, 1979; Chapter 1. (d) Whangbo, M.-H. *Acc. Chem. Res.*, in press.

[16] (a) Bechgaard, K.; Jacobsen, C. S.; Mortensen, K.; Pedersen, H. J.; Thorup, N. *Solid State Commun.* **1980**, *33*, 1119. (b) Walsh, W. M., Jr.; Wudl, F.; Thomas G. A.; Nalewajek, D.; Hauser, J. J.; Lee, P. A.; Poehler, T. *Phys. Rev. Lett.* **1980**, *45*, 829. (c) Scott, J. C.; Pedersen, H. J.; Bechgaard, K. *Phys. Rev. Lett.* **1980**, *45*, 2125. (d) Chaikin, P. M.; Grunner, G.; Engler, E. M.; Greene, R. L. *Phys. Rev. Lett.* **1980**, *45*, 1874. (e) Chaikin, P. M.; Tiedje, T.; Bloch, A. N. *Solid State Commun.* **1982**, *41*, 739.

[17] (a) Jerome, D.; Mazaud, A.; Ribault, M.; Bechgaard, K. *J. Phys. Lett.* (*Paris*) **1980**, *41*, L95. (b) Andres, K.; Wudl, F.; McWhan, D. B.; Thomas, G. A.; Nalewajek, K.; Stevens, A. L. *Phys. Rev. Lett.* **1980**, *45*, 1449.

[18] A recent summary of experimental and theoretical results on (TMTSF)$_2$X salts is found in *Mol. Cryst. Liq. Cryst.* **1982**, *79*, 1-359.

Bacteriorhodopsins Containing Cyanine Dye Chromophores. Support for the External Point-Charge Model

Fadila Derguini, Charles G. Caldwell, Michael G. Motto, Valeria Balogh-Nair, and Koji Nakanishi*

Department of Chemistry, Columbia University
New York, New York 10027

Received October 6, 1982

Bacteriorhodopsin[1] (bR, MW ~27 000), the protein pigment of the purple membrane of *Halobacterium halobium*, functions as a light-driven proton pump.[2] Its single polypeptide chain,[3,4] which constitutes seven α-helical rods perpendicular to the membrane plane,[5] is bound through lysine-216[6-8] to *trans*-retinal

---

[1] Oesterhelt, D.; Stoeckenius, W. *Nature* (*London*) *New Biol.* **1971**, *233*, 149-152.

[2] Oesterhelt, D.; Stoeckenius, W. *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 2853-2857.

[3] Ovchinnikov, Yu. A.; Abdulaev, N. G.; Feigina, M. Yu.; Kiselev, A. V.; Lobanov, N. A. *FEBS Lett.* **1979**, *100*, 219-224.

[4] Khorana, H. G.; Gerber, G. E.; Herlihy, W. C.; Gray, C. P.; Anderegg, R. J.; Nihei, K.; Biemann, K. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 5046-5050.

[5] Unwin, P. N. T.; Henderson, R. *Nature* (*London*) **1975**, *257*, 28-32.

[6] Bayley, H.; Huang, K. S.; Radhakrishnan, R.; Ross, A. H.; Takagaki, Y.; Khorana, H. G. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 2225-2229.

[7] Lemke, H.-D.; Oesterhelt, D. *FEBS Lett.* **1981**, *128*, 255-260.

[8] Mullen, E.; Johnson, A. H; Akhtar, M. *FEBS Lett.* **1981**, *130*, 187-193.

© 1983 American Chemical Society