Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Synthesis, Structure and Electrical Conductivity of $(BEDT\text{-}TTF)_X(BrO4)_Y$ Organic Metals

M. A. Beno [a], G. S. Blackman [a], P. C. W. Leung [a], K. D. Carlson [a], P. T. Copps [a] & Jack M. Williams [a]
[a] Chemistry and Materials Science and Technology Divisions, Argonne National Laboratory, Argonne, Illinois, 60439, .S.A.
Version of record first published: 17 Oct 2011.

To cite this article: M. A. Beno , G. S. Blackman , P. C. W. Leung , K. D. Carlson , P. T. Copps & Jack M. Williams (1985): Synthesis, Structure and Electrical Conductivity of $(BEDT\text{-}TTF)_X(BrO4)_Y$ Organic Metals, Molecular Crystals and Liquid Crystals, 119:1, 409-412

To link to this article: http://dx.doi.org/10.1080/00268948508075192

Mol. Cryst. Liq. Cryst. 1985, Vol. 119, pp. 409-412
0026-8941/85/1194-0409/$10.00/0

Printed in the United States of America

SYNTHESIS, STRUCTURE AND ELECTRICAL CONDUCTIVITY OF $(BEDT\text{-}TTF)_x(BrO_4)_y$ ORGANIC METALS

M. A. BENO, G. S. BLACKMAN, P. C. W. LEUNG, K. D. CARLSON, P. T. COPPS, AND JACK M. WILLIAMS
Chemistry and Materials Science and Technology Divisions, Argonne National Laboratory, Argonne, Illinois, 60439 U.S.A.

Abstract The electrochemical oxidation of BEDT-TTF (bis(ethylenedithio)-tetrathiafulvalene) in 1,1,2-trichloroethane solution in the presence of $(n\text{-}Bu_4N)BrO_4$ as supporting electrolyte produces three distinct morphologies: needles, thick plates, and thin plates. These crystal habits have been identified with different crystallographic phases: needles as $(BEDT\text{-}TTF)_2BrO_4$, thick plates as $(BEDT\text{-}TTF)_2(BrO_4)(TCE)_{0.5}$, and thin plates as $(BEDT\text{-}TTF)_3(BrO_4)_2$. The structural characterization and conductivity for these materials is presented.

INTRODUCTION

Research on BEDT-TTF organic metals has been stimulated by the discovery of metallic conductivity (to 1.4 K) in $(BEDT\text{-}TTF)_2(ClO_4)(1,1,2\text{-trichloroethane})_{0.5}$[1] and the subsequent report of pressure induced superconductivity in the non-solvated $(BEDT\text{-}TTF)_2(ReO_4)$, derivative ($T_c$ = 2 K, at $p > 4$ kbar).[2] The structural and electrical properties of the needle phase of $(BEDT\text{-}TTF)_2(BrO_4)$, isostructural with $(BEDT\text{-}TTF)_2(BrO_4)$ have been previously presented.[3] We report here the structural results for the two plate phases, $(BEDT\text{-}TTF)_2(BrO_4)(TCE)_{0.5}$, which is isostructural with $(BEDT\text{-}TTF)_2(ClO_4)(TCE)_{0.5}$,[4] and $(BEDT\text{-}TTF)_3(BrO_4)_2$ which is isostructural with the 3:2 ClO_4^- derivative.[5]

EXPERIMENTAL

Crystallographic and data collection parameters are given in Table I. The crystal structures were solved by direct methods (MULTAN) and refined with full-matrix least squares to the R-factors given in Table I. Four-probe conductivity measurements show that $(BEDT\text{-}TTF)_3(BrO_4)_2$ is metallic above 210 K and that the resistivity rises sharply below 50 K.

TABLE I Summary of Crystal Data, Data Collection Parameters, and Least-Squares Residuals for $(BEDT\text{-}TTF)_2BrO_4(TCE)_{0.5}$ and $(BEDT\text{-}TTF)_3(BrO_4)_2$

formula	$(C_{10}H_8S_8)_2BrO_4(C_2H_3Cl_3)_{0.5}$	$(C_{10}H_8S_8)_3(BrO_4)_2$
space group	$P\bar{1}$	$P\bar{1}$
Z	2	1
temperature	125±1K	298
lattice param.		
a, Å	7.656(2)	7.670(1) Å
b, Å	12.957(4)	9.550(2) Å
c, Å	18.590(2)	16.686(2) Å
α, deg.	109.6(2)	89.38(1)°
β, deg.	90.2(2)	87.02(1)°
γ, deg.	105.1(2)	83.87(1)°
V, Å^3	1668.4(8)	1213.6(5) Å
d_{calc}, g/cm^3	1.95	1.97 g/cm^3
cryst. size, mm	0.19 x 0.58 x 0.65	0.36 x 0.44 x 0.02
μ(MoKα), cm^{-1}	24.15	26.94
transmission factors	0.374-0.657	0.45 - 0.94
data collection instrument	Syntex $P2_1$ (graphite-monochromator) λ(MoKα) = 0.71073 Å	
scan method	θ-2θ, variable scan rate	ω-scans, variable rate
data collection range	0° < 2θ < 60°	$4^0 < 2\theta < 50^0$
no. of unique data	8070	4274
no. of unique data $F_o > 3\sigma(F_o)$	7297	3333
no. of param. refined	397	486
R^a	0.068	0.046
R_w^b	0.090	0.041
goodness of fit[c]	4.480	1.57

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $R_w = [w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

[c] goodness-of-fit = $[\Sigma w(|F_o|-|F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

DISCUSSION

These materials contain segrated stacks of donor and acceptor molecules possessing significant intermolecular S-S interactions (less than the van der Waals sum of 3.6 A) which form a 2-dimensional sheet network. For $(BEDT\text{-}TTF)_2(BrO_4)(TCE)_{0.5}$ the anions are ordered but a disordered solvent molecule is located at a center of symmetry in the unit cell (see Figure 1). Disorder is also observed in the ethylene carbon atoms of the BEDT-TTF molecule. However in the $(BEDT\text{-}TTF)_3(BrO_4)_2$ structure both the BEDT-TTF molecule and BrO_4^- anion are ordered (see Figure 2). The metal-insulator transition observed in the 3:2 phase is similar to the 190K M-I transition[5] observed in $(BEDT\text{-}TTF)_3(ClO_4)_2$.

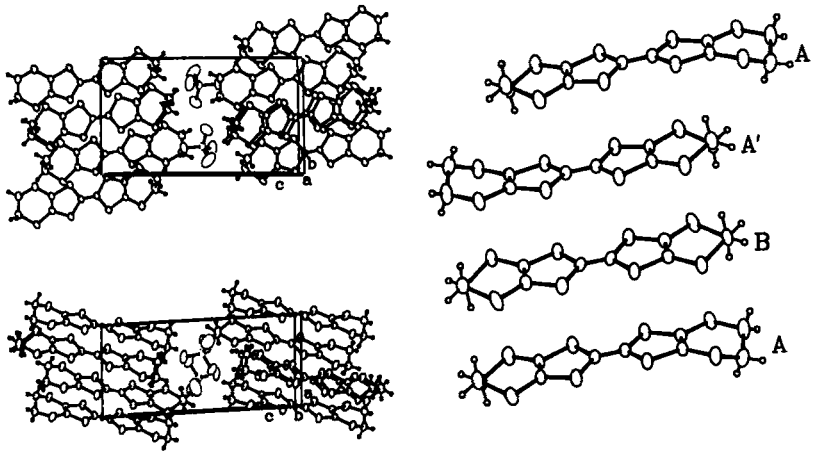

FIGURE 1 Unit cell and side-by-side arrangement of BEDT-TTF molecules in $(BEDT\text{-}TTF)_2(BrO_4)(TCE)_{0.5}$.

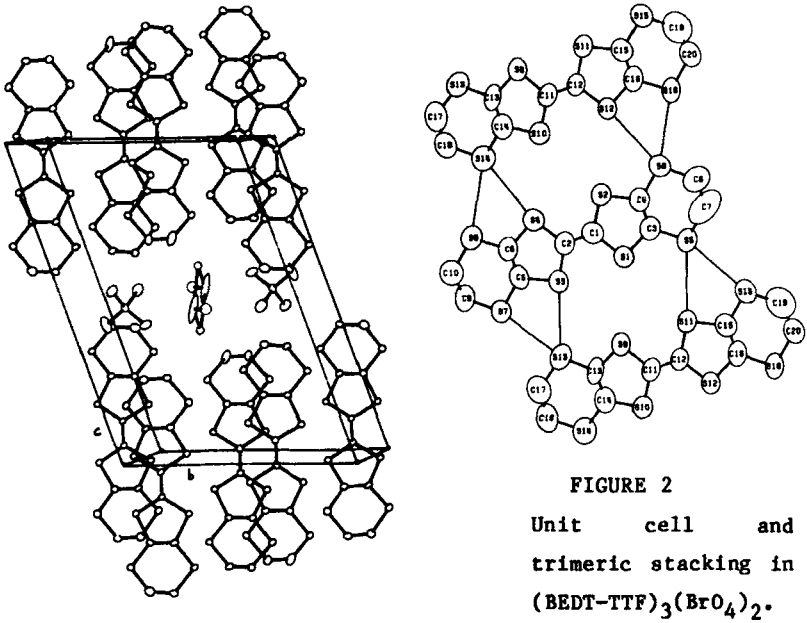

FIGURE 2
Unit cell and trimeric stacking in $(BEDT\text{-}TTF)_3(BrO_4)_2$.

Acknowledgment Work supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under Contract W-31-109-ENG-38.

REFERENCES

1. G. Saito, T. Enoki, K. Toriumi and H. Inokuchi, Solid State Commun., 42, 557 (1982).
2. S. S. P. Parkin, E. M. Engler, R. R. Shumaker, R. Lagier, V. Y. Lee, J. C. Scott and R. L. Green, Phys. Rev. Lett., 50, 270 (1983).
3. J. M. Williams, M. A. Beno, H. H. Wang, P. E. Reed, L. J. Azevedo and J. E. Schirber, Inorg. Chem., 23, 1790 (1984).
4. H. Kobayashi, A. Kobayashi, Y. Sasaki, G. Saito, T. Enoki and H. Inokuchi, J. Am. Chem. Soc., 105, 297 (1983).
5. H. Kobayashi, R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, G. Saito, T. Enoki and H. Inokuchi, Chem. Lett. 1984, 179.