Chinese Chemical Letters Vol. 13, No. 8, pp 725 – 728, 2002
http://www.imm.ac.cn/journal/ccl/html


# The Inorganic-free Organic Conductor α′-$(ET)_2C_6H_4(SO_3)_2$ : Its Synthesis, Structure, and Conductivity

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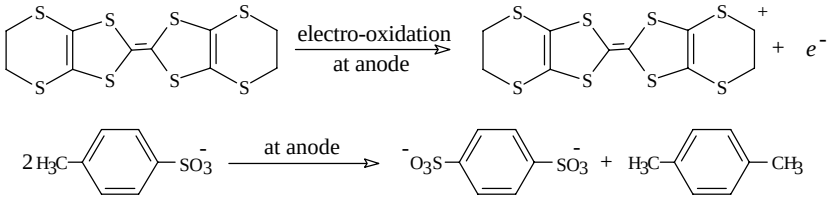
**Abstract:** A new ET based cation radical salt, α′-$(ET)_2C_6H_4(SO_3)_2$ (ET = bis(ethylenedithio) tetrathiafulvalene) has been synthesized by oxidative electro-crystallization and the crystal structure determined to be in monoclinic system, *P*2/*n* space group. Its resistivity-temperature curve shows a semi-conductive behavior with a discontinuation at about 150K.

**Keywords:** ET, synthesis, structure, conductivity.

Having more than twenty years' glory, ET series still keep the most promising family in various kinds of organic conductors. Most of ET based molecular conductors consist of organic cationic $ET^{+0.5}$ radical and certain anionic inorganic component such as the superconductor κ-$(ET)_2Cu[N(CN)_2]Cl$ ($T_C$ = 12.8K, 0.3kbar)[1]. Recently, the first purely organic superconductor β″-$(ET)_2SF_5CH_2CF_2SO_3$ ($T_C$ = 5.2K)[2] has been reported, which aroused our interest on this kind of inorganic-free organic conductors, and consequently the title organic conductors has been synthesized in our laboratory.

## Synthesis and Structure

At a constant current of 1.5 A, the brown black plate-like single crystals were grown by electro-chemical oxidation of ET in the presence of *p*-$CH_3C_6H_4SO_3Na$ and 18-crown-6 ether in 1,2-dichloroethane solvent in a course of 30 days. The oxidation process may be as follows:

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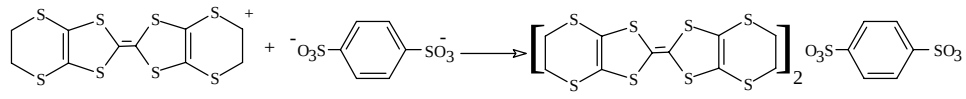


IR spectra data: (C-H) 2915m, 2848w; (C=C) 1626m, (S=C) 1257s, 1184s, 1010s, 673m, (ring def.) 878m, 562m, 455s $cm^{-1}$.

The X-ray diffraction data of the single crystal were collected on a Bruker P4 four-circle diffractometer and the structure was resolved by using SHELX-97 programs. The unit cell parameters: $\alpha$ = 7.7937(17) Å, $b$ = 6.6989(11) Å, $c$ = 34.422(7) Å, = 91.135(12) ; $V$ = 1796.8(6) $Å^3$, Z = 4.

**Figure 1** View along the *b* axis of the unit cell

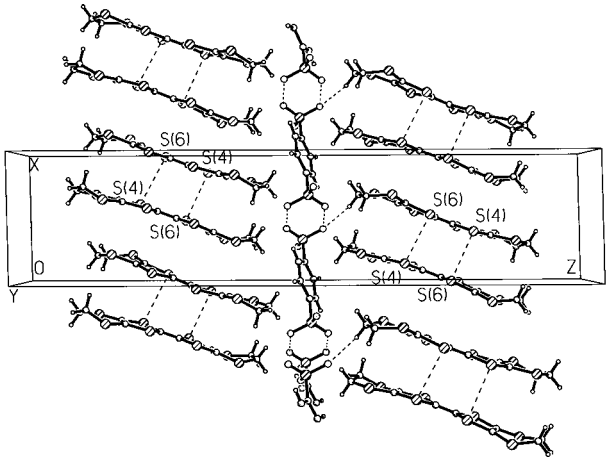
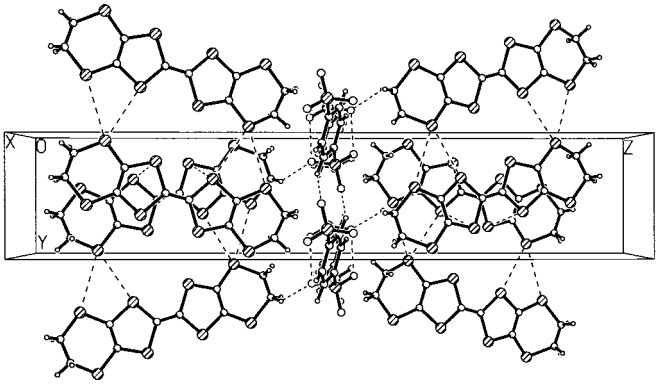



**Figure 2** View along the *a* axis of the unit cell



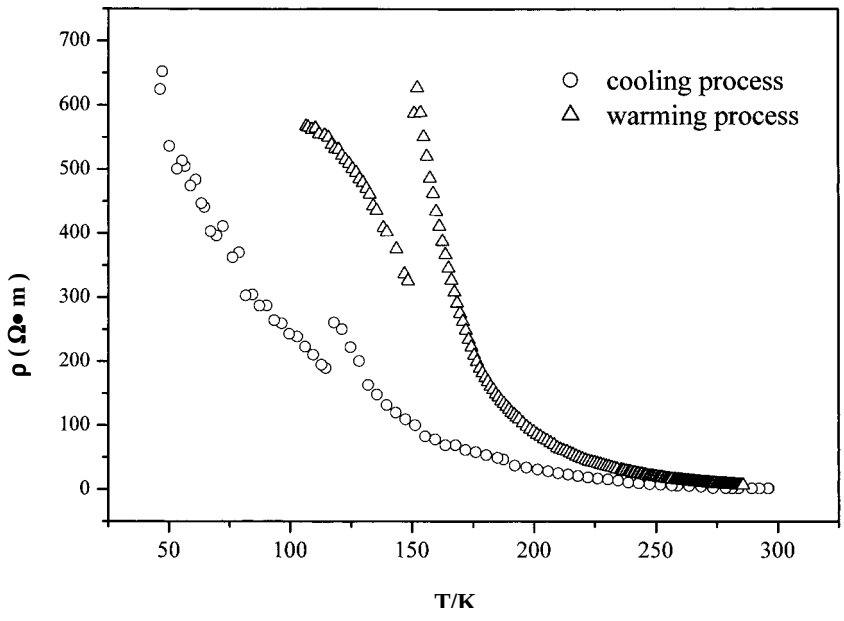
As shown in **Figure 1** and **Figure 2**, the dimerised $ET^+$ radicals are stacked to form staggered face-to-face columns along the α-axis direction, and another kind of side-by-side uniform one-dimensional chains are in the b-axis direction. By comparing the S…S distances, we concluded that the intermolecular interactions between $ET^+$ radicals in the *b*-axis direction (side-by-side type) may be much stronger than those in α-axis direction (face-to-face type). So α′-$(ET)_2C_6H_4(SO_3)_2$ may be classified into one-dimensional molecular conductors.

$C_6H_4(SO_3)_2^{2+}$ counter ions are also arranged along a-axis with some O…O short intermolecular contacts. Finally, layers of $ET^+$ radicals and $C_6H_4S_2O_6^{2-}$ counter anions alternate to form sandwiched structure along the *c*-direction.

**Conductivity**

Both of warming and cooling processes demonstrate a semiconductive behavior of α′-$(ET)_2C_6H_4(SO_3)_2$ as shown in **Figure 3** (the temperature data in warming process are more accurate in our experimental set-up). The triangle symbol indicates the warming process and the circle symbol indicates the cooling process

**Figure 3** Resistivity -temperature curve of α′-$(BEDT\text{-}TTF)_2C_6H_4(SO_3)_2$.




The room temperature conductivity of α′-$(ET)_2C_6H_4(SO_3)_2$ was measured to be 0.5913 $\Omega^{-1}$ $m^{-1}$. One noticeable feature of the -*T* curve in **Figure 3** is the discontinuation of resistivity at a certain temperature, this may correspond to a certain phase transition. Calculated from the -*T* curve of warming process, the activation energy of the crystal is 0.027 eV (From 100 K to 150 K) and becomes 0.2472 eV (above

150 K).

## Acknowledgments

This project was supported by a grant for the State Key Program of China and by the National Natural Science Foundation of China (No.20172034), and also supported by the open laboratory of organic solid of Institute of Chemistry of the Chinese Academy of Science.

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Received 9 November, 2001