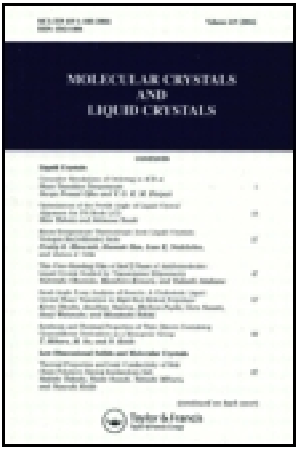

Molecular Crystals and Liquid Crystals
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Three Dimensional Conducting Solids: $(BPTTF)_2 BF_4$, $(BPTTF)_3 (ReO_4)_2$, (BPTTF) Clo_4 [where BPTTF=bis (pyrazino) tetrathiafulvalene] and Similar Compounds

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THREE DIMENSIONAL CONDUCTING SOLIDS: $(BPTTF)_2BF_4$, $(BPTTF)_3(ReO_4)_2$, $(BPTTF)ClO_4$ [where BPTTF=bis (pyrazino) tetrathiafulvalene] AND SIMILAR COMPOUNDS.

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The electrical properties of the title compounds were studied for a wide range of temperature. They indicate that the compounds are anisotropic at room temperature and become almost isotropic at low temperatures.

The observation of ambient pressure superconductivity in the salts $(TMTSF)_2ClO_4$ and $(BEDT\text{-}TTF)_2I_3$ has increased interest in the solid state properties of the simple salts of organic sulfur or selenium containing donors [1]-[3]. A feature of the existing compounds is the short interstack S-S or Se-Se distances leading to a two dimensional network of sulfur or selenium interactions. These interstack interactions appear vital in preserving the metallic state down to low temperatures. One way to increase these interstack interactions is to extend the molecular framework and include additional heteroatoms. Recently, the preparation of new types of organic donors, bis (pyrazino)tetrathiafulvalene(BPTTF) and some of its substituted derivatives, has been reported [4]. With this TTF-type donor it is possible to evaluate the effect of the incorporation of nitrogen heteroatoms on the interstack interactions.

In this paper the electrical properties of $(BPTTF)_2BF_4$, $(BPTTF)_3(ReO_4)_2$, $(BPTTF)ClO_4$ and similar compounds are described. These compounds were prepared [4] by the electrocrystallization of BPTTF (1.55×10^{-3}M) and Bu_4NX (5×10^{-3}M), $X=BF_4$, ReO_4, ClO_4 etc. in CH_2Cl_2 using platinum electrode at 1μA/cm^2 and 22°C. The crystals were washed with CH_2Cl_2 and dried; they had a copper - black lustrus appearence. The compounds $(BPTTF)Br_3$, $(BPTTF)IBr_2$ and similar compounds with bis(dimethylpyrazino) tetrathiafulvalene(BDMPTTF), bis(quinoxalino)tetrathiafulvalene(BQTTF) and bis(dimethylquinoxalino)tetrathiafulvalene(BDMQTTF) as donors were prepared by a similar method [4]. The crystals of $(BPTTF)_2BF_4$ were of the shape* illustrated in Fig.1.

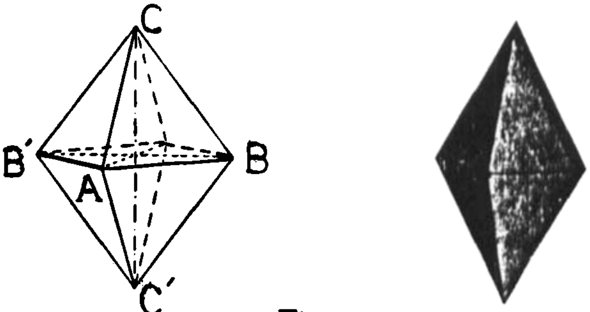

Fig.1

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*CC′was the grow up direction, namely perpedicular to the surface of the platinum electrode.

The crystal shape of $(BPTTF)_3(ReO_4)_2$ and $(BPTTF)ClO_4$ was close to that of $(BPTTF)_2BF_4$. The crystals of $(BPTTF)Br_3$, $(BPTTF)IBr_2$, $(BDMPTTF)I_3$, $(BDMPTTF)IBr_2$, $(BQTTF)Br_3$ and $(BDMQTTF)Br_3$ were obtained in the form of small cubes or platelets. Electrical conduction measurements were made in several crystal directions over the temperature range 300-100K. Measurements along the AB-direction were carried out with a two probe technique. All other measurements were carried out with a four-probe technique. Fig.2 shows the variation of conductivity (σ) with tempe-

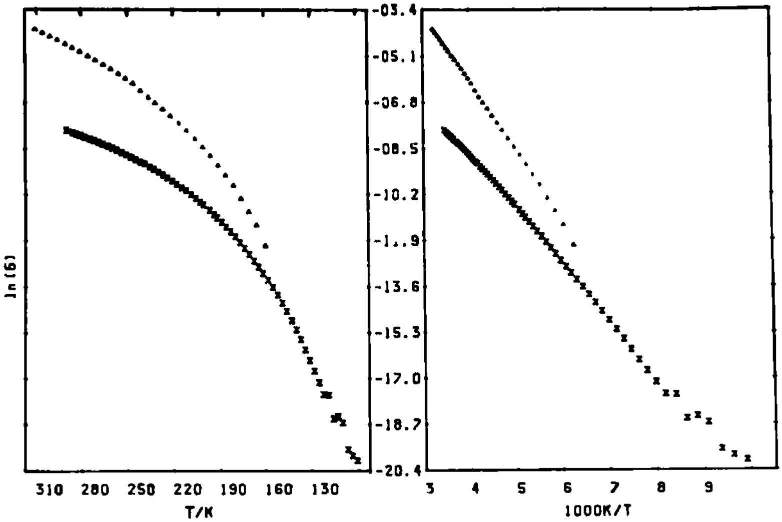

Fig.2. Variation of conductivity with temperature and inverse temperature for a single crystal of $(BPTTF)_2BF_4$ in CC'-(▲▲▲) and AB-(xxx) directions.

rature (T) and inverse temperature (1/T) for a single crystal of $(BPTTF)_2BF_4$ in CC′-and AB-directions, Fig.3 shows the variation of σ with T and 1/T for a single crystal of $(BPTTF)_3(ReO_4)_2$ in the CC′-direction, and Fig.4 shows the variation of σ with T and 1/T for a single crystal of $(BPTTF)ClO_4$ in the CC′-, BC- and AB-directions. The values of conductivity at room temperature (σ_{RT}) and the values of activation energy (E) are given in Table 1. One can see that the observed conductivity behaviour is very similar for all three compounds, which appear to be anisotropic and become almost isotropic at low temperatures. The activation energy and the conductivity in the AB-direction is smaller than in the CC′- direction. The three dimensional

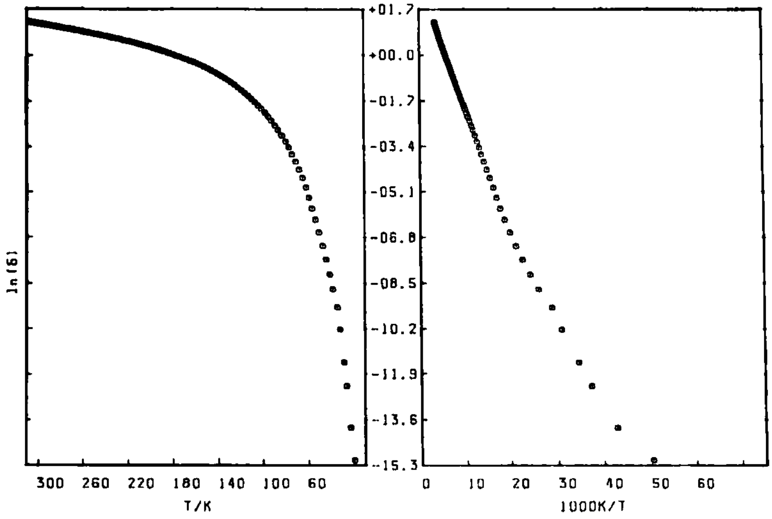

Fig.3. Same as Fig.2 but for a single crystal of $(BPTTF)_3(ReO_4)_2$ in CC′-direction.

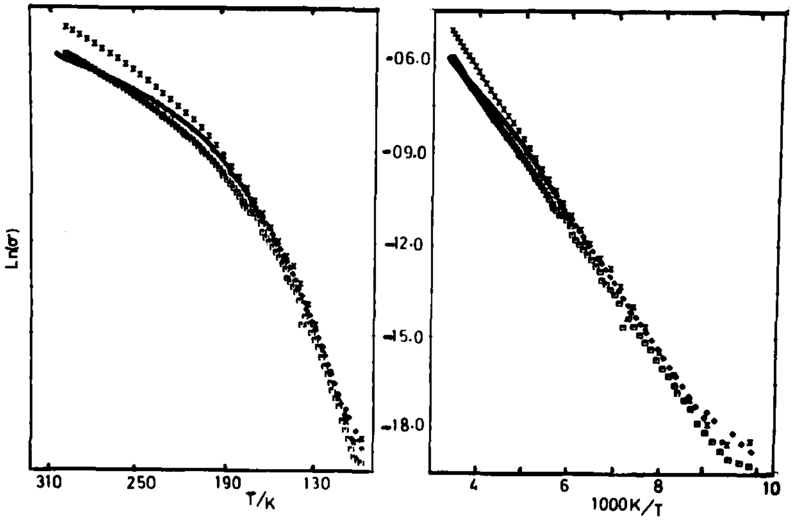

Fig.4. Same as Fig.2 but for a single crystal of (BPTTF) ClO_4 in CC′-(xxx), AC-(□□□) and AB-(◇◇◇) directions.

Table 1

	$(BPTTF)_2BF_4$	$(BPTTF)_3(ReO_4)_2$	$(BPTTF)ClO_4$
$\sigma_{RT}(\Omega^{-1}cm^{-1})$	$*1-2x10^{-2}$	$*1.5x10^{-3}$	$*3-8x10^{-3}$
E(meV) AC	——	——	190
E(meV) CC′	390	140	190
E(meV) AB	198/147**	——	130
Contact Material	Colloidal Graphite	Colloidal Silver	Colloidal Graphite

*The highest values, corresponding to the CC′-direction.
**Arrhenius plot displayed to linear regions between 290 and 230, also 230 and 150 K, for which the activation energies were 147 and 198 meV, respectively.

conduction behaviour was attributed to extensive interstack interactions. According to the crystal structure results [5] the AB-direction is close to the stacking direction, which involves partially overlapping molecules of BPTTF. In the stacking direction the S···S intermolecular distance is 3.64 Å in $(BPTTF)_2BF_4$ [5],while the corresponding van der Waals distance is 3.70 Å.The conductivity in CC´-direction is due to the interstack interactions.The S···N interstack intermolecular distance is 3.00 Å in $(BPTTF)_2BF_4$ [5],while the corresponding van der Waals distance is 3.35 Å and the S—N bond distance in $(SN)_x$ is 2.90 Å.The dc-conductivity of polycrystalline compressed discs of $(BPTTF)Br_3$,$(BPTTF)IBr_2$,$(BQTTF)Br_3$ and $(BDMQTTF)Br_3$ was found to be 10^{-6}-10^{-5} $\Omega^{-1}cm^{-1}$,while that of $(BDMPTTF)I_3$ and $(BDMPTTF)IBr_2$ was found to be 2-8x10^{-2} $\Omega^{-1}cm^{-1}$.Results of the conductivity measurements on single crystals of the last two compounds in crystallographic directions will be published in future.

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