

8. Chiral Metals? A Chiral Substrate for Organic Conductors and Superconductors

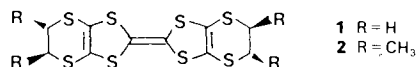
by John D. Wallis, Andreas Karrer, and Jack D. Dunitz*

Laboratorium für Organische Chemie, ETH-Zentrum, Universitätstrasse 16, CH 8092 Zürich

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Chiral metals are so far practically unknown. The synthesis of a chiral substrate for possible organic conductors and superconductors is described.

Almost nothing appears to be known about the properties of organic conductors or superconductors crystallizing in chiral space groups. In fact, the only chiral conducting solids we are aware of are metallic selenium and tellurium (both in space group $P3_121$ or enantiomorph) [1] and the organic metal, bis(tetraselenotetracene) iodide, $(TSeT)_2I$ [2], all based on achiral building blocks. It seems possible that the limitation to proper symmetry elements in a chiral conductor could be associated with the emergence of new properties, in particular those connected with interactions between applied electric and magnetic fields and their internal counterparts. To search for and study such properties in a systematic manner, it would obviously be very helpful to have chiral conducting materials where the chirality stems from the structure of the building blocks themselves and not merely from the manner in which they happen to be packed in the crystal. So far, all the substrates used in the preparation of organic metals have consisted of achiral molecules (mostly planar or nearly planar aromatic or heterocyclic molecules). One of the best known recent examples is the heterocyclic poly-sulfur containing compound bis(ethylene-dithio)tetrathiafulvalene **1** [3], often abbreviated to BEDT-TTF or sometimes to ET [4], which forms conducting salts of the type $(ET)_2X$. The corresponding tetramethylated compound **2** with *R,R* or *S,S* dimethylated bridges can occur as three



stereoisomers, an enantiomeric pair (with D_2 point symmetry) and a *meso*-form (with C_{2h} point symmetry). Moreover, in contrast to **1** where the six-membered rings are free to invert from one half-chair conformation to another, the introduction of the peripheral Me groups could inhibit this motion and thus play an important role in controlling the ordering of linear, tetrahedral, and octahedral anions in charge-transfer salts of **2** compared with **1**, hence influencing the conditions favorable for a transition to a superconducting phase [4]. We have now prepared one of the chiral isomers and report here on the synthesis and some preliminary observations.

The synthetic strategy is simple (*Scheme*). The novel cyclic sulfate diester **3** (from (*R,R*)-butane-2,3-diol) was reacted with dianion **4** [5] in MeOH to give a 1:1 adduct,

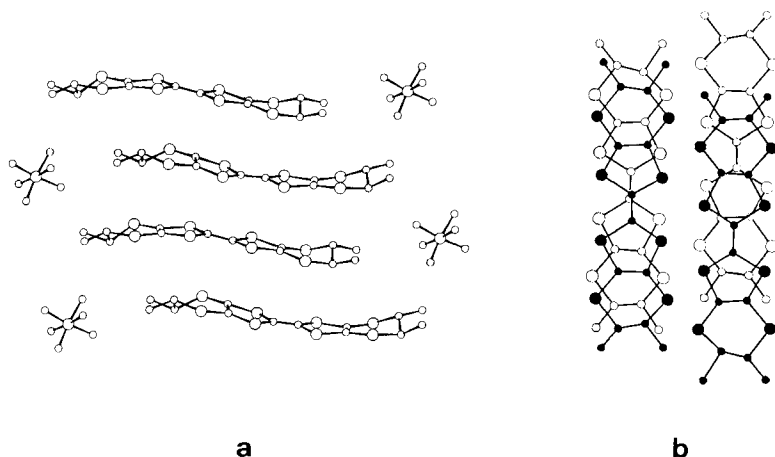
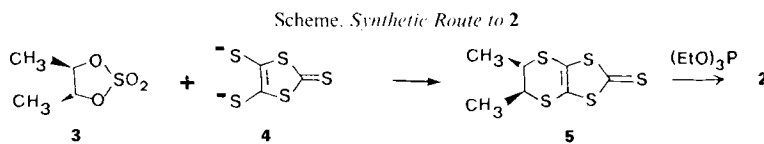


Fig. a) View of a molecular stack in the crystal structure of $(2)_2PF_6$. The stacking axis is b. b) The two types of overlap between adjacent molecules of **2** in this structure.

which cyclized on heating in THF to **5**. Dimerization of **5** with $(EtO)_3P$ then yielded **2**, obtained as extremely thin dendritic crystals and characterized by NMR, MS, and crystal-structure analysis of a conducting ($\sigma \approx 5\Omega^{-1}cm^{-1}$) PF_6^- salt¹⁾). The Fig. shows two views of the structure, which is very reminiscent of the structures of analogous ET complexes [4]. We have also carried through the corresponding synthesis, starting with the racemic diol.



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²⁾ Crystals of $(2)_2PF_6$ are triclinic, $a = 6.915$, $b = 8.085$, $c = 19.384$ Å, $\alpha = 82.66$, $\beta = 84.40$, $\gamma = 70.98^\circ$ at room temperature, space group $P1$, $Z = 1$. The present R factor is 0.061 for the 2271 reflections used in the structure analysis.