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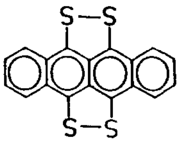
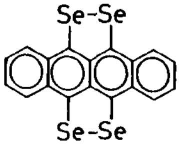
1,4,9,10-TETRATHIAANTHRACENE, A PROMISING DONOR MOLECULE FOR HIGHLY CONDUCTIVE ORGANIC COMPLEXES

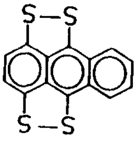
Shigeo Ohnishi, Takashi Nogami*, and Hiroshi Mikawa
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamadaoka, Suita, Osaka 565, Japan

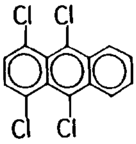
Summary: 1,4,9,10-Tetrathiaanthracene (TTA) was prepared, and the complex, TTA·$I_{1.2}$, showed the conductivity of 4.2 $(\Omega\ \mathrm{cm})^{-1}$.

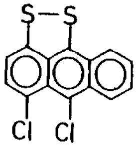
The complexes of 5,6,11,12-tetrathiatetracene (TTT) and its selenium analogue (TST) are known to give electrically conductive materials.[1-3] The donor molecules with similar structures to TTT or TST are promising candidates for the preparation of highly conductive organic complexes. 1,4,9,10-Tetrathiaanthracene (TTA) was synthesized by the reaction of 1,4,9,10-tetrachloroanthracene (TCA) with sulfur.[4] However, the yield by this method is low and not reproducible.[5] Thus, no property of TTA has been reported except for the esr spectrum of the cation radical of TTA in a solution. We have synthesized TTA by the reaction of TCA with sodium disulfide in N,N-dimethylformamide (DMF).[6]

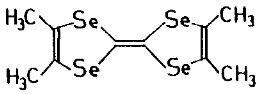

TTT


TST

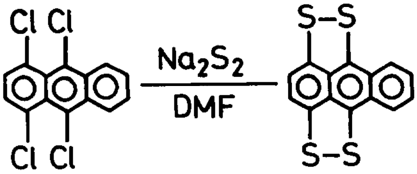

TTA


TCA


DCDTA


TMTSF

The synthesis of TCA was made by the procedures reported by us.[7] Equimolar amounts of sodium (1.4 g) and sulfur (1.94 g) were reacted in DMF (160 ml) at 100°C for one hour under nitrogen atmosphere. After the reaction, DMF (120 ml) solution of TCA (4 g) was added to the solution. The solution was refluxed for three hours under nitrogen atmosphere. After the reaction, the solvent was distilled out completely. The residue was washed with water, and dried in vacuo. Sublimation of the residue at 140 - 160°C in vacuo gave 1,9-dichloro-4,10-dithiaanthracene (DCDTA). Sublimation had been continued until no DCDTA was sublimed out. After that, sublimation at 200°C in vacuo, followed by a recrystallization from benzene gave TTA as violet needles (20 %



yield based on TCA).

TTA: Elemental analysis: Calcd for $C_{14}H_6S_4$ C, 55.60 %, H, 2.00 %, S, 42.40 %; found C, 55.96 %, H, 2.10 %, S, 41.86 %. U.V.: $\lambda_{max}^{CHCl_3}$/nm (log ε), 548 (3.98), 520 (3.93), 437 (3.71), 288 (4.36). Cyclic voltammetry (V vs SCE in benzonitrile solution of Bu_4NAsF_6): $E_{1/2}$ = 0.41 V, 0.85 V. Mp > 300°C.

The first and second oxidation potentials of TTA were almost the same as those of tetramethyltetraselenafulvalene (TMTSF)[8] or 1,4,9,10-tetraselenaanthracene (TSA).[9] The crystal, $TTA(PF_6)_{0.33}(TCE)_{0.96}$,[10] obtained by an electrochemical method[11] showed the resistivity of 4.4 x 10^3 Ω cm. The single crystal, $TTA\cdot I_{1.2}$, obtained by a gradual crystal growth from acetonitrile, showed the conductivity of 4.2 $(\Omega\ cm)^{-1}$ at a room temperature. Thus, TTA is a promising donor molecule for the highly conductive organic materials.

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(5) Private communication from Prof. F. Wudl.

(6) The isomer of TTA, 1,5,9,10-tetrathiaanthracene, and its selenium analogue were synthesized by six-step reactions. H. Endres, H. J. Keller, J. Queckborner, J. Veigel, and D. Schweitzer, *Mol. Cryst. Liq. Cryst.*, **86**, 111 (1982).
1,4,9,10-Tetraselenaanthracene was synthesized by us (see ref 7).

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(9) The oxidation potentials (vs SCE) of TMTSF and TSA are as follows. TMTSF: $E_{1/2}$ = 0.42 V, 0.81 V (from F. Wudl and E. A. Shalom, *J. Am. Chem. Soc.*, **104**, 1154 (1982)); TSA: $E_{1/2}$= 0.42 V, 0.84 V (from ref 7).

(10) TCE denotes 1,1,2-trichloroethane used as a solvent in the electrocrystallization.

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