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ANTHRA[1,9-cd:4,10-c'd']BIS[1,2]DISELENOLE, A NEW ELECTRON DONOR MOLECULE

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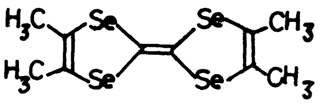
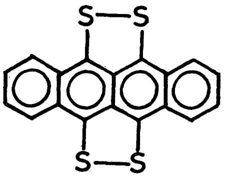
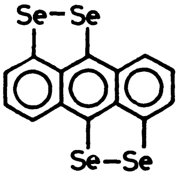
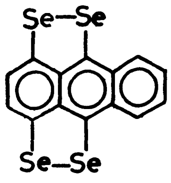
A new electron donor molecule, anthra[1,9-cd:4,10-c'd']bis[1,2]-diselenole, was synthesized. The charge-transfer complex formed between the donor and TCNQ showed the electrical conductivity of 1 $(\Omega\ \mathrm{cm})^{-1}$ for a compressed pellet sample.

The studies on the low-dimensional organic conductors have made a great progress in these few years. One-dimensional conductor undergoes Peierls transition at a low temperature to give rise to a metal-insulator transition. In order to realize superconductivity at a low temperature, interchain coupling must be introduced to suppress the Peierls instability. In fact, interchain coupling through selenium atoms was found to play an important role to the complexes of tetramethyltetraselenafulvalene (TMTSF), the first organic superconductors.1)

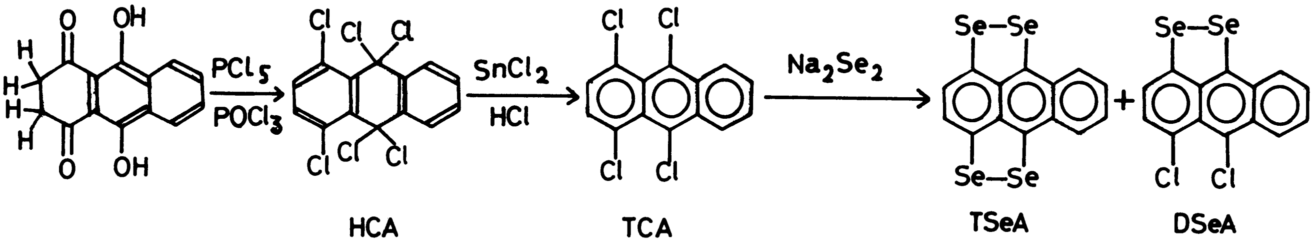

TMTSF


TTT


TSA


TSeA

In a search for other electron donor molecules effective to the interchain coupling, we drew attention to naphthaceno[5,6-cd:11,12-c'd']bis[1,2]dithiole (abbreviated to TTT) and its analogues.2) These molecules have four chalcogen atoms stretched out from the aromatic ring. The complexes including these donor molecules are expected to have strong interchain coupling through chalcogen atoms; this fact may result in the disappearance of Peierls transition owing to the presence of two-dimensional characters. The donor molecules with similar structure to TTT are expected to give highly conductive organic complexes down to low temperatures. New donor molecules, anthra[1,9-cd:5,10-c'd']bis[1,2]diselenole (TSA) and its sulfur analogue, have recently been prepared by six-step reactions, and $TSA\cdot I_{1.2}$ showed metallic behavior above 230 K;3) the metal-insulator transition could not be suppressed. We have now synthesized the isomer of TSA, anthra[1,9-cd:4,10-c'd']bis-[1,2]diselenole (TSeA) by the three-step reactions as shown below.



Although TSA and TSeA were obtained essentially by the same reactions of tetrachloroanthracene with sodium diselenide, TSeA could be obtained more easily.

The synthesis of 1,4,9,9,10,10-hexachloroanthracene (HCA) was made by the reported procedures.[4] 1,4,9,10-Tetrachloroanthracene (TCA) was synthesized by refluxing the solution containing glacial acetic acid (20 ml), hydrochloric acid (15 ml), HCA (3 g), and stannous chloride dihydrate (12.2 g) for ten min. TCA was purified by chromatography on alumina with benzene. TSeA was synthesized as follows. Equimolar amounts of sodium (0.7 g) and selenium (2.4 g) were reacted in N,N-dimethylformamide (80 ml) at 100°C under nitrogen atmosphere. After almost homogeneous solution had been obtained, TCA (2 g) was added to the solution. The solution was refluxed for eight h under nitrogen atmosphere. The solvent was distilled out completely. The residue was oxidized with formic acid, and then filtered. The cation radical of TSeA in the filtrate was reduced with aqueous $TiCl_3$ to give a dark brown powder. Sublimation of the powder at 170°C in vacuo gave 4,10-dichloroanthra-[1,9-cd][1,2]diselenole (DSeA) as a reddish brown powder. The sublimation had been continued until no DSeA was sublimed. The sublimation of the residue at 260°C in vacuo gave TSeA as a violet powder[5] (20 % yield based on TCA).

The complex of TSeA·TCNQ, obtained by mixing equimolar amounts of 1,2,4-trichlorobenzene solution of TSeA and TCNQ, showed the electrical conductivity of 1 $(\Omega\ cm)^{-1}$ for a compressed pellet sample.

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References

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2) H. Tanaka, T. Nogami, and H. Mikawa, Chem. Lett., 1982, 727; B. Hilti, C. W. Mayer, and G. Rihs, Solid State Commun., 41, 787 (1982).

3) H. Endres, H. J. Keller, J. Queckborner, J. Veigel, and D. Schweitzer, Mol. Cryst. Liq. Cryst., 86, 111 (1982).

4) L. A. Weinberger and R. Gerstl, US Patent, 3703533 (1972).

5) EA: Found, C, 34.59, H, 1.59 %. Calcd for $C_{14}H_6Se_4$, C, 34.31, H, 1.24 %. VI: $\lambda_{max}^{CH_3Cl}$ (log ε), 297 (4.20), 343 (3.46), 430 (3.57), 520 (3.93), 552 (4.05). Cyclic voltammetry (1,1,2-trichloroethane): $E_{1/2}$, 0.40, 1.0 V vs SCE. Mass: the intensities of the isotope peaks of molecular ions coincided completely with those obtained by computer calculation.

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