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Synthesis of Tetrakis(methylthio)bis(vinylenedithio)tetrathiafulvalene (TMTVT). TTF Derivative Possessing Twelve Sulfurs

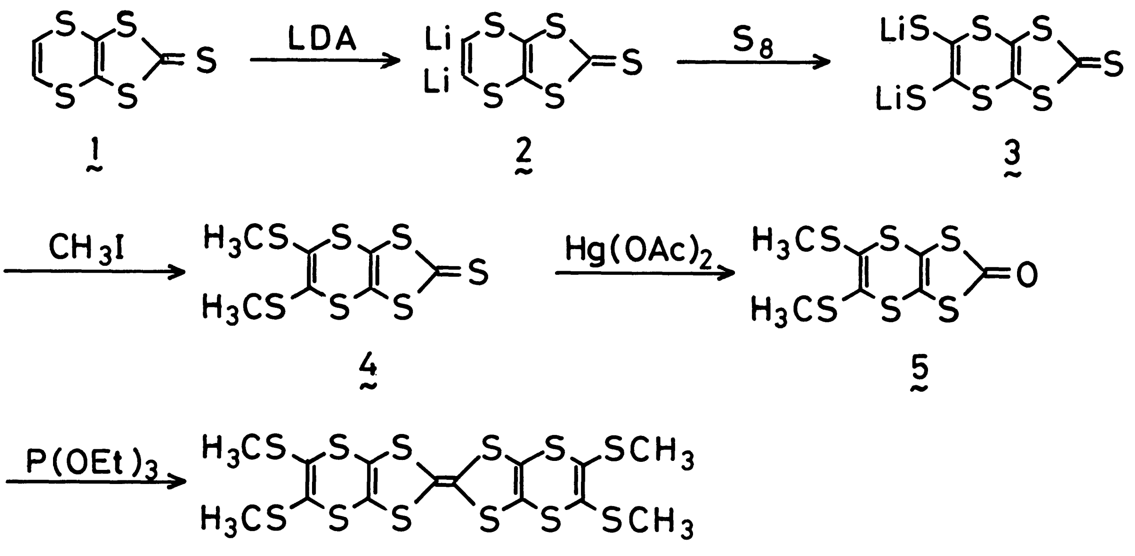
Hideyuki NAKANO, Tadashi NAKAMURA, Takashi NOGAMI,* and Yasuhiko SHIROTA
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamadaoka, Suita, Osaka 565

The title molecule (TMTVT) was synthesized as an attractive donor for highly conductive organic salts. TMTVT is the TTF derivative possessing the largest number of sulfurs in a molecule.

The studies on the highly conductive organic materials have attracted much attention especially since the discovery of organic superconductors in TMTSF-salts.1) The most characteristic property of the organic charge-transfer salts is their low-dimensional property. However, the low-dimensional system (especially one-dimensional system) is susceptible to a metal-insulator transition due to Peierls distortion. Therefore, increase in the dimensionality was pursued. One of the most successful results along this line was achieved for BEDT-TTF salts, and the trihalide salts gave ambient pressure organic superconductors.2,3) The two-dimensional properties of the BEDT-TTF salts arise partly from the presence of eight sulfurs in the donor site. We have synthesized tetrakis(methylthio)bis(vinylenedithio)tetrathiafulvalene (TMTVT), which has twelve sulfurs in a molecule. To our knowledge, TMTVT is the TTF derivative possessing the largest number of sulfurs.

The following reactions were performed under nitrogen atmosphere except for the reaction of 4 leading to 5. 4,5-(Vinylenedithio)-1,3-dithiole-2-thione (1) was synthesized by the reported method.4,5) To a THF solution of lithium diisopropylamide (LDA, 9.0 mmol) was added 1 (1.00 g, 4.5 mmol) at -78 °C, and the temperature of the solution was elevated slowly to room temperature with stirring, and the solution was stirred for another 2 h to give 2. It was cooled to -78 °C, sulfur (0.29 g, 9.04 mmol) was added, and the temperature of the solution was elevated slowly to room temperature. Stirring was continued for another 1 h to give 3. The solution was then cooled to -78 °C, methyl iodide (1.4 g, 10.1 mmol) was added, and the temperature of the solution was elevated slowly to room temperature. It was stirred for another 1 h. After evaporating the solvent, the residue was extracted with benzene, washed with water, and dried over Na_2SO_4. The crude product was chromatographed on silica gel by using a mixed solvent of hexane and chloroform (4 : 1) as an eluent, and the second yellow fraction gave 4 as yellow powder. It was recrystallized from hexane (0.475 g, 33.6% yield based on 1).

The conversion from 4 to 5 was made as follows. To a mixed solvent of acetic acid (50 ml) and chloroform (50 ml) was added 4 (0.5 g, 1.59 mmol) and mercury (II) acetate (1.013 g, 3.18 mmol), and the solution was stirred for 20 min at room temperature. It was washed with water, then with aqueous $NaHCO_3$, finally



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with water, and dried over Na_2SO_4. After evaporating the solvent, the residue was chromatographed on silica gel by using a mixed solvent of hexane and chloroform (1 : 1) as an eluent, and the second yellow fraction gave 5 as a pale yellow powder (0.24 g, 51% yield).

The coupling reaction of 5 to TMTVT was made as follows. The triethyl phosphite solution (1.8 ml) of 5 (0.18 g) was stirred at 110 °C for 2 h. The resulting red powder was collected, washed with methanol, and recrystallized from carbon tetrachloride to give TMTVT6) as red needles (0.115 g, 68% yield). The cyclic voltammetry of TMTVT gave single redox wave ($E_{1/2}$ = 0.83 V vs. SCE) in THF. The $E_{1/2}$ value is identical to that of bis(vinylenedithio)tetrathiafulvalene4) within the experimental error.

References

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6) Mp 200 °C (dec). Found: C, 29.92; H, 2.09; S, 67.99%. Calcd for $C_{14}H_{12}S_{12}$: C, 29.76; H, 2.14; S, 68.10%. Mass m/z 564 (M^+). ^1H-NMR (CS_2) δ = 2.40. λ_{max}^{THF}(log ε): 308 nm (4.33); 337 nm (4.30).

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