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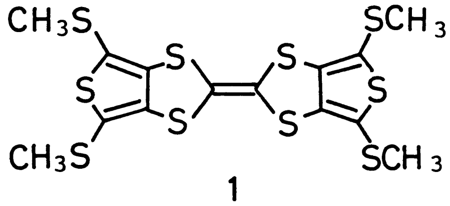
TETRAKIS(METHYLTHIO)-$\Delta^{2,2'}$-DITHIENO[3,4-d]-1,3-DITHIOLE. A NEW TTF-TYPE DONOR

Keiji KOBAYASHI

Department of Chemistry, College of Arts and Sciences,
The University of Tokyo, Komaba, Meguro-ku, Tokyo 153

The title compound, which is designed to increase the interstack interaction in the solid state, was synthesized as a new donor for conductive charge-transfer complexes.

Intensive current interest has been focussed on the organic charge-transfer complexes with high electrical conductivity, and in the chemistry of their donor and acceptor species. The incorporation of polarizable heteroatoms within the donor framework is regarded as one important aspect to design new donor molecules, as it could increase interchain interactions in the solid state and thus bring about the stable metallic state. In this context, annelation of thiophene rings on the tetrathiafulvalene system and its selenium and tellurium analogues is an interesting structural modification.[1,2] We present herein a promising new donor based on tetrathiafulvalene fused doubly to 3,4-position of 2,5-bis(methylthio)-thiophene, i. e., tetrakis(methylthio)-$\Delta^{2,2'}$-dithieno[3,4-d]-1,3-dithiole (1). The methylthio substituents are anticipated to allow an increase in interchain interactions.



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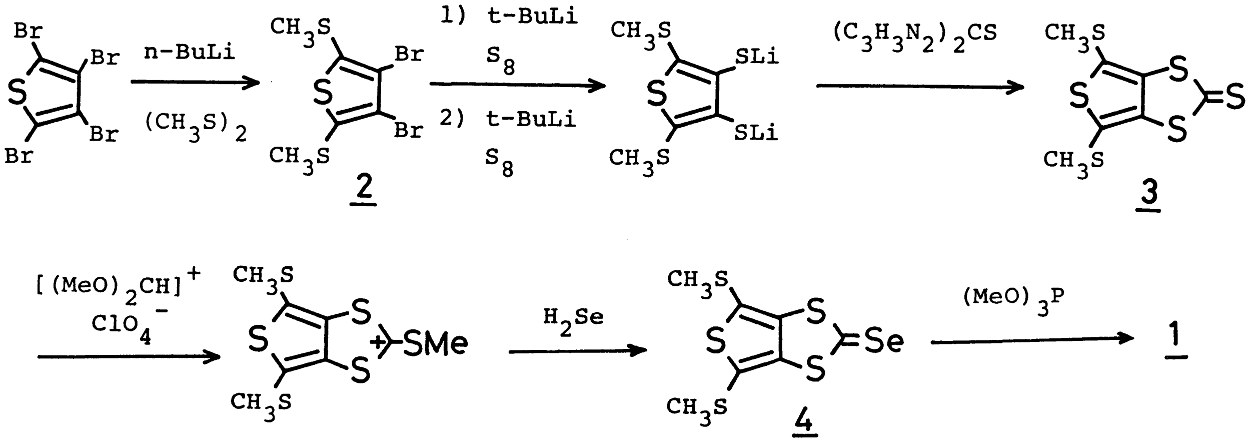
The reactions leading to 1 are based on the study by Cowan.[2] Tetrabromothiophene was allowed to react with n-butyllithium (2 equiv.) in THF and then with dimethyldisulfide (2 equiv.) for 1 h at -78 °C to afford 3,4-dibromo-2,5-bis(methylthio)-thiophene (2) in 73% yield as white needles [mp 65-66 °C. ^{1}H NMR ($CDCl_3$) δ 2.50]. Compound 2 was treated with t-butyllithium (2 equiv.) in THF under argon at -78 °C for 30 min; then elemental sulfur (1 equiv.) was added and the mixture was stirred for 2 h at -78 °C. The entire procedure was then repeated. After quenching with glacial acetic acid (3 equiv.) in THF, thiocarbonylbis(imidazole) (1 equiv.) in THF was added slowly at -78 °C. The solution was allowed to warm to room temperature in 5 h and stirred at that temperature overnight. Thus thione 3 was obtained in 45% yield as yellow needles [mp 133-135 °C. ^{1}H NMR ($CDCl_3$) δ 2.51].

Thione 3 was converted to the corresponding selenone 4, via methylation on the thione with dimethoxycarbenium tetrafluoroborate in dichloromethane at room temperature (2 h), followed by diluting with one volume of methanol and subsequent



addition of excess hydrogen selenide through the argon flow at room temperature. Selenone 4 was obtained in 61% yield as dark red needles [mp 143-144 °C. ^{1}H NMR ($CDCl_3$) δ 2.53].

The coupling of 4 was accomplished by heating a solution of 4 and excess trimethylphosphite in toluene at reflux under argon for 2 h. The crude product was recrystallized from chloroform to give 1 in 45% yield as yellow prisms [mp 183-184 °C. ^{1}H NMR ($CDCl_3$) δ 2.46. ^{13}C NMR ($CDCl_3$) δ 20.81, 118.45, 124.22, 140.28. Found: C, 33.42; H, 2.49; S, 63.96%. Calcd for $C_{14}H_{12}S_{10}$: C, 33.57; H, 2.41, S, 64.02%].

The cyclic voltammetry of 1 performed in CH_3CN (0.1 M n-Bu_4NClO_4, Pt-electrode 100 $mV^{-1}s$) exhibited two reversible one-electron oxidation waves at 0.87 and 1.16 V vs S. C. E. The small difference between the first and the second oxidation potential suggests that the intramolecular Coulomb repulsion energy is significantly decreased.

The preparation of charge-transfer complexes by electrochemical crystallization as well as diffusion method is now in progress. The high solubilities of 1 would provide a variety of possibilities for these preparations.

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