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Crowned Tetrathiafulvalene Derivatives

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Synopsis. A new type of tetrathiafulvalene derivatives, fused with crown ethers, was prepared, which did not form a complex with sodium cation or TCNQ acceptor but readily with silver cation.

With an attempt to develop the new character of tetrathiafulvalene (TTF) by use of a functional heterocyclic ring, we have studied novel TTF derivatives **1** and **2** which are fused with crown ethers. Complexation with metal cation at the crown ligand might make some influence on the donor character of the TTF.

The metallic[1] or electrochemical[2] reduction of carbon disulfide in aprotic media provides a synthetic entry for the preparation of thio-substituted derivatives of TTF.[3] Thus, sodium 2-thioxo-1,3-dithiole-4,5-dithiolate **4**, generated in situ by reduction of carbon disulfide with sodium in dry *N,N*-dimethylformamide, was allowed to react with methyl iodide to give 4,5-bis(methylthio)-1,3-dithiole-2-thione **5** in 70% yield.[1] On the other hand, a similar treatment of the dianion **4** with tetraethylene glycol ditosylate gave crown-fused 1,3-dithiole-2-thione **6** in only 0.8% yield as well as its dimer **7** in rather higher yield (6.5%). The yield of the key compound **6** was fairly increased up to 14% by effecting the reaction under a high dilution technique. Subsequently, heating of **6** at 110°C in triethyl phosphite resulted in self-coupling to bis-crowned tetrathiafulvalene **1** in 44% yield. A cross reaction of two 1,3-dithiole-2-thiones **5** and **6** led to a mixture of **1** (31%), **2** (21%), and **3**[4] (13%), which were readily separated from one another by column chromatography. Another type of crowned tetrathiafulvalene **8** was, in addition, prepared in a very low yield (2.9%) by a similar cross reaction of **5** and **7**.

The cyclic voltammograms of TTF derivatives **1**, **2**, and **3** exhibit two reversible oxidation waves due to TTF, whose half-wave potentials are situated at 0.521 and 0.748 V for **1**, at 0.509 and 0.757 V for **2**, and at 0.498 and 0.805 V for **3** *vs.* a silver reference electrode in dichloromethane. The almost identical voltammetric behaviors indicate that their π-donor abilities are nearly equal. However, crowned TTF **1** and **2**, in contrast to **3**,[3] did not form crystalline charge-transfer complexes with tetracyanoquinodimethane (TCNQ). The steric requirement of the crown ligand seems to prevent the complexation of the TTF. In addition, the crown ligand failed to complex sodium salts such as $\mathrm{Na^+TCNQ^{\overline{\cdot}}}$ and NaSCN. However, crowned TTF **1** and **2** strongly interacted with silver nitrate, forming crystalline 1:2 and 1:1 complexes, respectively. The electrical conductivities of these complexes are relatively low; σ_{RT} (compressed pellet) $6\times10^{-9}\ \Omega^{-1}\mathrm{cm}^{-1}$ for $2\mathrm{AgNO_3}$ complex of **1** and $4\times10^{-7}\ \Omega^{-1}\mathrm{cm}^{-1}$ for $\mathrm{AgNO_3}$ complex of **2**.

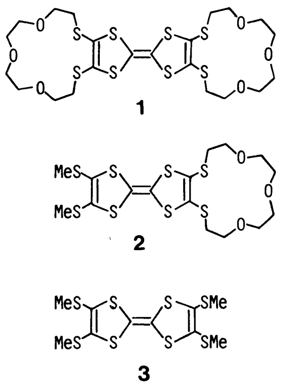

Fig. 1.

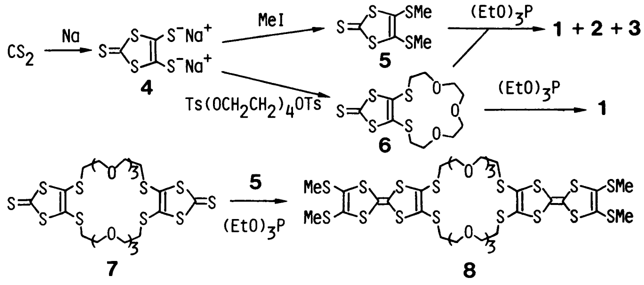

Fig. 2.

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Experimental

NMR spectra were determined on a JEOL PMX-60 spectrometer (60 MHz), MS spectra on a JEOL JMS-DX 300 spectrometer at 70 eV using a direct insertion technique, and IR spectra on a Hitachi 260-30 spectrophotometer. Cyclic voltammetry was made at 100 mVsec^{-1} scan rate in 2 mV dichloromethane solution with added tetrabutylammonium perchlorate by a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 functional generator using a Ag/AgCl reference electrode, a glassy carbon working electrode, and a platinum counter electrode. Electrical conductivity was measured on a compressed pellet with a two probe method.

Crowned 1,3-Dithiole-2-thione (6). Sodium (1.68 g, 73 mmol) was added into a solution of carbon disulfide (12 ml) and dry *N,N*-dimethylformamide (20 ml) under nitrogen. The mixture was gently refluxed with stirring overnight, and meanwhile sodium gradually dissolved to bring about a viscous dark red solution containing dianion **4**. It was then diluted with ethanol (55 ml, previously bubbled by nitrogen gas) and introduced into a dropping funnel through a needle bridge. A solution of tetraethylene glycol ditosylate (18.32 g, 36.5 mmol) in tetrahydrofuran (100 ml) was placed in another dropping funnel. Both the solutions were dropwise and simultaneously added into a stirred ethanol solution (250 ml) at 50°C under nitrogen. The addition took half a day, and heating was continued further overnight. After the resulting insoluble salt was removed by filtration, the filtrate was evaporated and extracted with dichloromethane. The extract was washed, dried (Na_2SO_4), and evaporated. The residual red oil was purified by flash chromatography on silica gel with 1:2 dichloromethane–ether and then gel-permeation liquid chromatography with chloroform, giving **6** (1.79 g, 14%), yellow columns from hexane–dichloromethane, mp 70—74 °C. ^1H NMR ($CDCl_3$): δ=3.04 (t, *J*=6 Hz, 4H, CH_2S), 3.66 (s, 8H, CH_2O), 3.77 (t, *J*=6 Hz, 4H, CH_2O). MS: *m/z* 356 (M^+). IR (KBr): 1055 (C=S), 1120 (C–O) cm^{-1}. Found: C, 36.78; H, 4.51%. Calcd for $C_{11}H_{16}O_3S_5$: C, 37.05; H, 4.52%.

The same reaction without the above dilution technique gave a mixture of **6** (0.8%) and **7** (6.5%). The dimer **7** was separated from **6** by liquid chromatography, yellow fine crystals from ethanol–dichloromethane, mp 84.5—85.5 °C. ^1H NMR ($CDCl_3$): δ=3.08 (t, *J*=6 Hz, 8H, CH_2S), 3.62 (s, 16H, CH_2O), 3.73 (t, *J*=6 Hz, 8H, CH_2O). MS: *m/z* 712 (M^+). IR (KBr): 1065 (C=S), 1120 (C–O) cm^{-1}. Found: C, 36.95; H, 4.50%. Calcd for $C_{22}H_{32}O_6S_{10}$: C, 37.05; H, 4.52%.

Bis-crowned TTF (1). Compound **6** (356 mg, 1.0 mmol) was heated in triethyl phosphite (2 ml) under nitrogen. The starting material completely dissolved with a rise of temperature, and orange microcrystals precipitated at 110 °C. After 30 min at 110 °C, the product **1** was collected by filtration and washed with hexane (142 mg, 44%), orange fine crystals from acetonitrile, mp 211—212 °C. ^1H NMR ($CDCl_3$): δ=2.99 (t, *J*=6 Hz, 8H, CH_2S), 3.65 (s, 16H, CH_2O), 3.74 (t, *J*=6 Hz, 8H, CH_2O). MS: *m/z* 648 (M^+). IR (KBr): 1120 (C–O) cm^{-1}. Found: C, 40.71; H, 4.85%. Calcd for $C_{22}H_{32}O_6S_8$: C, 40.72; H, 4.97%.

Mono-crowned TTF (2). A mixture of **5** (226 mg, 1.0 mmol) and **6** (356 mg, 1.0 mmol) was heated at 110 °C in triethyl phosphite (3 ml) for 30 min under nitrogen. After evaporation, the residue was chromatographed on silica gel to give a red eluate with dichloromethane and then two red eluates with 1:20 ether–dichloromethane. The first red eluate gave **3** (25 mg, 13%), orange columns from acetonitrile, mp 93—94 °C (lit,[3] 94.5—96 °C). The second red eluate gave **2** (108 mg, 21%), orange plates from ethanol–chloroform, mp 125—126 °C. ^1H NMR ($CDCl_3$): δ=2.43 (s, 6H, CH_3), 2.97 (t, *J*=6 Hz, 4H, CH_2S), 3.64 (s, 8H, CH_2O), 3.73 (t, *J*=6 Hz, 4H, CH_2O). MS: *m/z* 518 (M^+). IR (KBr): 1115 (C–O) cm^{-1}. Found: C, 36.90; H, 4.10%. Calcd for $C_{16}H_{22}O_3S_8$: C, 37.04; H, 4.27%. The third red eluate gave **1** (100 mg, 31%).

Crowned bis-TTF (8). Compound **7** (142 mg, 0.2 mmol) was heated together with **5** (180 mg, 0.8 mmol) in triethyl phosphite (2 ml) at 110 °C under nitrogen. The reaction mixture was worked up as described for **2**, giving **8** (6 mg, 2.9%), orange fine crystals from acetonitrile, mp 109—111 °C. ^1H NMR ($CDCl_3$) δ=2.43 (s, 12H, CH_3), 3.02 (t, *J*=6 Hz, 8H, CH_2S), 3.64 (s, 16H, CH_2O), 3.69 (t, *J*=6 Hz, 8H, CH_2O). IR (Neat): 1115 (C–O) cm^{-1}. Found: C, 37.19; H, 4.13%. Calcd for $C_{32}H_{44}O_6S_{16}$: C, 37.04; H, 4.27%.

Complexation with Silver Nitrate. A mixture of **2** (52 mg, 0.1 mmol) and silver nitrate (17 mg, 0.1 mmol) was dissolved in hot ethanol (*ca.* 20 ml). The clear solution was cooled in a refrigerator, giving reddish orange fine crystals of mono-crowned TTF·$AgNO_3$ complex (34 mg), dec. 150 °C with melt. IR (KBr): 1385 (NO_3), 1115 (C–O) cm^{-1}. Found: C, 27.87; H, 3.20; N, 1.63%. Calcd for $C_{16}H_{22}NO_6S_8Ag$: C, 27.90; H, 3.22; N, 2.03%.

Bis-crowned TTF·2$AgNO_3$ complex was prepared in a similar manner; orange fine crystals, dec. 218 °C with melt. IR (KBr): 1380 (NO_3), 1115 (C–O) cm^{-1}. Found: C, 27.02; H, 3.28; N, 2.60%. Calcd for $C_{22}H_{32}N_2O_{12}S_8Ag_2$: C, 26.72; H, 3.26; N, 2.83%.

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