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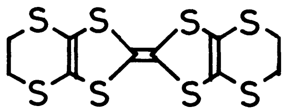
SYNTHESIS OF BIS(DIMETHYLVINYLENEDITHIO)TETRATHIAFULVALENE, BDMVDT-TTF

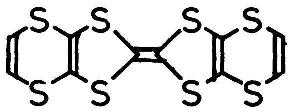
Kazuhiko INOUE, Yoshihiko TASAKA, Osamu YAMAZAKI,
Takashi NOGAMI,* and Hiroshi MIKAWA†
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamada-oka, Suita, Osaka 565
† Department of Environment and Safety Engineering,
Faculty of Engineering, Fukui Institute of
Technology, Gakuen-cho, Fukui 910

The title compound was synthesized as an attractive donor molecule for highly conductive organic salts. This molecule has an analogous structure to BEDT-TTF with possibly more planar structure.

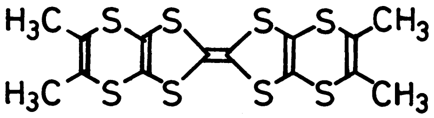
The studies on the organic superconductors have been made extensively in these few years. Several organic salts of BEDT-TTF were found to be superconductive under pressure and under ambient pressure.[1, 2] The superconductive transition temperature as high as 8 K has now been realized.[3] Since BEDT-TTF has two ethylene units at the both sides of the molecule, it is a nonplanar molecule.[4] Most of the donor molecules which give highly conductive organic complexes are planar. The replacement of the ethylene units of BEDT-TTF with carbon-carbon double bonds would give more planar donor molecule.[5]



BEDT-TTF



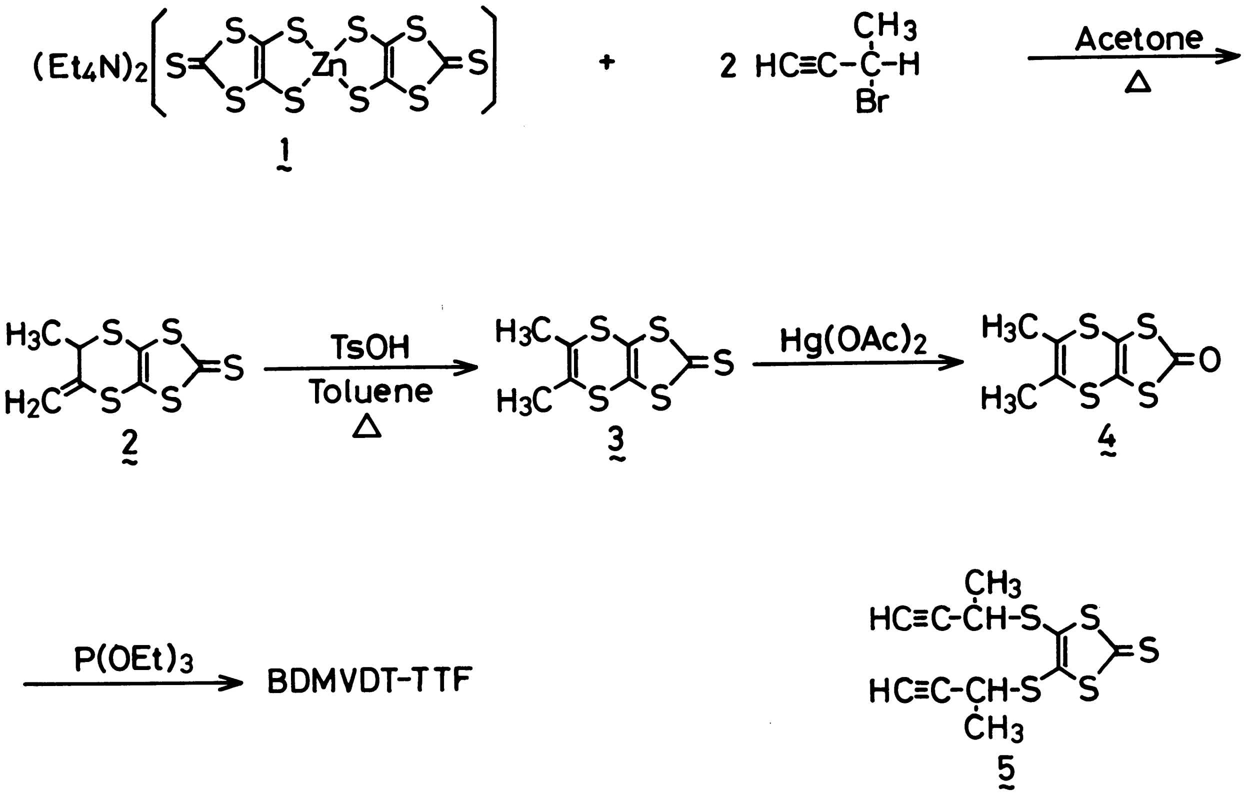
BVDT-TTF



BDMVDT-TTF

Schumaker et al. reported the syntheses of bis(vinylenedithio)tetrathiafulvalene (BVDT-TTF) and bis(dimethylvinylenedithio)tetrathiafulvalene (BDMVDT-TTF) without detailed description of the synthetic procedures.[6] We have synthesized

BDMVDT-TTF by four-step reactions as shown below.



The synthesis of 1 was made by the reported procedures.[7] All of the succeeding reactions were conducted under nitrogen atmosphere. The first-step consists of a substitution reaction of 3-bromo-1-butyne[8] with 1, followed by cyclization reaction.[9, 10] One liter flask containing 350 ml of acetone was equipped with two dropping funnels and condenser. The dropping funnels contained acetone solution (70 ml) of 1 (3.6 g, 5 mmol) and acetone solution (60 ml) of 3-bromo-1-butyne (1.33 g, 10 mmol), respectively. After refluxing acetone in the flask, the acetone solutions of 1 and 3-bromo-1-butyne were dropped into the flask simultaneously during 3 h, and the mixture was refluxed further for 10 h. After cooling to room temperature, the residue was filtered off, and acetone was evaporated to give dark red oil. It was extracted with benzene, washed with water, and dried over sodium sulfate. Evaporation of benzene gave reddish-yellow oil. It was chromatographed on silica gel by using the mixed solvent of hexane and chloroform (4 : 1). The first yellow fraction contained 2 and 5. This mixture was chromatographed again on silica gel by using the mixed solvent of hexane and chloroform (6 : 1). The first yellow fraction gave pure 2 as a light yellow solid (50% yield based on 1). The use of the above dilution method is crucial for the synthesis of **2**. Without this method, **5** was obtained as a main product, and **2** could not be obtained.

The second step is the isomerization of **2** to **3**.[9, 10] Three hundred mg of **2** (1.2 mmol) was dissolved into toluene (30 ml). The solution was heated to 80 °C, and 456 mg of p-toluenesulfonic acid monohydrate (TsOH, 2.4 mmol) was added all at once. The solution turned black immediately, and it was refluxed for 1 h. After cooling to room temperature, TsOH was filtered off. The reddish brown solution was washed with water, then with aqueous sodium hydrogen carbonate, and finally with water, and dried over sodium sulfate. Evaporation of the solvent, followed by drying the residue under vacuum gave dark brown solid. It was recrystallized from acetonitrile to give yellow needles of **3** (50% yield).

Since the yield of BDMVDT-TTF from the coupling reaction of **3** with triethylphosphite was low, **3** was converted to **4** in the third-step reaction as follows. To the chloroform solution (10 ml) of **3** (100 mg, 0.4 mmol) was added 10 ml of acetic acid and 318 mg (1.0 mmol) of mercuric acetate, and the solution was stirred for 15 min at room temperature. The white precipitate was filtered off, and the filtrate was washed with water, then with aqueous sodium hydrogen carbonate, and finally with water, and dried over sodium sulfate. Evaporating the solvent gave **4** (82 mg, 88%). It was recrystallized from acetonitrile to give white needles of **4**.

The final-step of coupling reaction was made as follows. One hundred mg of **4** (0.43 mmol) was added to 3 ml of triethylphosphite (freshly distilled) and the solution was stirred at 100 - 105 °C for 2 h. After cooling to room temperature, the precipitate was collected, washed with methyl alcohol, and dried to give BDMVDT-TTF (90 mg, 96.6%). It was recrystallized from chloroform to give light yellow needles of BDMVDT-TTF.[11] The cyclic voltammetry of BDMVDT-TTF in THF (0.1 M $n\text{-Bu}_4\text{NClO}_4$, Pt electrode, 10 mV s^{-1}) exhibited one reversible wave: $E_{1/2}$ 0.80 V vs SCE. The electrochemical crystallization of BDMVDT-TTF is under way in order to obtain new conductive organic salts.

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11) Anal Found: C, 38.05; H, 2.61; S, 57.98%. Calcd for $C_{14}H_{12}S_8$: C, 38.50; H, 2.77; S, 58.73%. The poor agreement of the analyses will be caused by the difficulty to burn out BDMVDT-TTF due to the large content of sulfur. Mp 249 - 250 °C (dec). Mass 436 (M^+). λ_{max}^{THF} (log ε) 344 nm (3.52), 314 nm (3.50). ^{1}H-NMR δ 2.00.

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