(2-Methylidene-1,3-dithiolo[4,5-*d*])tetrathiafulvalene (DT-TTF): New Unsymmetrical TTFs condensed with 1,3-Dithiol-2-ylidene Moieties

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The synthesis and properties of the unsymmetrical tetrathiafulvalenes condensed with 1,3-dithiol-2-ylidene moieties are described; the electrical properties of several cation radical salts are also presented.

The structural feature of organic superconductors based on bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) is a two-dimensional arrangement of BEDT-TTF molecules through a S···S intermolecular interaction.[1] From this point of view modification of BEDT-TTF[2] is of particular interest for the development of new two-dimensional organic metals and superconductors.[3] Very recently we have succeeded in the synthesis of several alkyl derivatives of bis(2-methylidene-1,3-dithiolo[4,5-*d*])tetrathiafulvalene (BDT-TTF), which are TTFs condensed with two 1,3-dithiol-2-ylidene moieties instead of the ethylenedithio substituents in BEDT-TTF.[4] Among these BDT-TTFs, tetramethyl-BDT-TTF **1a** is expected to form conducting salts with more enhanced dimensionality than BEDT-TTF. However, **1a** is not suitable to prepare the cation radical salts owing to its extreme insolubility in common organic solvents. In this context synthesis of the unsymmetrical derivative of **1a** seems to be available in order to overcome its solubility problem. Furthermore, such unsymmetrical donors have also received current interest because several organic superconductors based on unsymmetrical dimethyl(ethylenedithio)diselenadithiafulvalene (DMET)[5] and methylenedithiotetrathiafulvalene (MDT-TTF) donors[6] have recently been prepared. In this communication we report the synthesis of the unsymmetrical TTF derivative possessing a half unit of **1a** (MeDT-TTFs, **2**), and characterization of their redox behaviour and electrical properties of the cation radical salts of the ethylenedithio derivative of **2**.†

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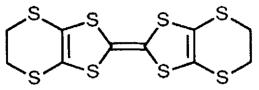
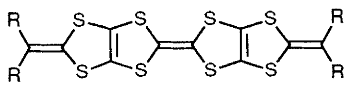
† Very recently the selenium analogues of DT-TTFs have also been prepared by Kato *et al.* (S. Aonuma, Y. Okano, H. Sawa, R. Kato and H. Kobayashi, *J. Chem. Soc., Chem. Commun.*, in the press)

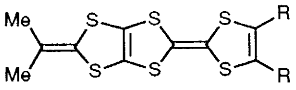


BEDT-TTF



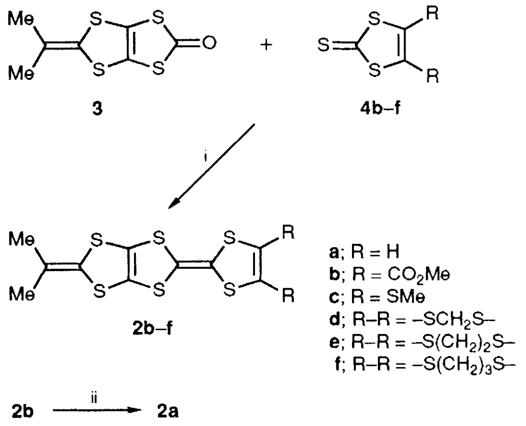
BDT-TTF

1a; R = Me
1b; R = Et
1c; R = n-Pr
1d; R–R = –$(CH_2)_4$–



DT-TTF

2a; R = H
2b; R = CO_2Me
2c; R = SMe
2d; R–R = –SCH_2S–
2e; R–R = –$S(CH_2)_2S$–
2f ; R–R = –$S(CH_2)_3S$–



Scheme 1 *Reagents and conditions*: i, $P(OEt)_3$, 75–80 °C, 2 h; ii, $LiBr\cdot H_2O$ (10 eq. mol), HMPA (hexamethylphosphoramide), 95 °C, 0.5 h and 110 °C, 1 h

Table 1 Redox potentials of **1a–f** in PhCN [V *vs.* SCE (saturated calomel electrode), Pt electrode, 25 °C]

Compound	E_1	E_2	E_3	$E_2 - E_1$
2a	+0.45	+0.76	+1.41[a]	0.37
2b	+0.62	+0.91	+1.51[a]	0.29
2c	+0.50	+0.75	+1.39[a]	0.25
2d	+0.51	+0.83	—	0.32
2e	+0.51	+0.79	+1.39[a]	0.28
2f	+0.50	+0.78	+1.45[a]	0.28
1b	+0.52	+0.73	+1.27[a,b]	0.21

[a] Irreversible step. Anodic peak potentials. [b] Two-electron transfer process.

The new unsymmetrical donors **2b–f** were synthesized as shown in Scheme 1. Isopropylidene-1,3-dithiolo[4,5-*d*]-1,3-dithiol-2-one **3** and 2 equimolar amounts of the appropriate 1,3-dithiole-2-thiones **4b–f** were allowed to react in neat triethylphosphite at 75–80 °C for 2 h under argon atmosphere. The precipitates were filtered off and then were column chromatographed on silica gel with CS_2–n-hexane (1 : 1, v/v) as the eluent. In all cases, the main products were the target molecules, and the symmetrical ones **5b–f** were obtained as minor products while **1a** was not obtained at all. The unsubstituted derivative of **2**(**2a**) was prepared by treatment of **2b** with an excess of $LiBr\cdot H_2O$ in HMPA at 90–100 °C in 67% yield.‡

The cyclic voltammetries of **2** were carried out by using tetra-n-butylammonium perchlorate as a supporting electrolyte in benzonitrile. All of these donors showed two pairs of reversible redox waves and one pair of irreversible waves except for **2d** which showed only two reversible waves. The redox potentials are summarized in Table 1 together with those of tetraethyl-BDT-TTF **1b** instead of **1a**. The first oxidation potentials (E_1) of **2a, b** were between those of corresponding symmetrical donors (**1b** and **5a**, **b**), as is often the case with most unsymmetrical donors.[7] While the E_1 values of **2c–f** were almost equal to those of **1b** and **5c–f**.

Preparation of cation radical salts with various inorganic acceptors was examined, and ClO_4^- and IBr_2^- salts of the ethylenedithio derivatives **2d** were obtained. Preliminary experiments on electrical properties of these salts revealed that the room temperature conductivities were 15 and 0.47 S cm^{-1} for ClO_4^- and IBr_2^- salts, respectively, both of which exhibited metallic conductive behaviour down to 88 K. We are currently engaged in preparation of superior quality single crystals suitable for X-ray crystallographic analysis and detailed investigations on the electrical properties at low temperature.

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‡ *Selective data* for the DT-TTF compounds. **1a**: 67% yield; reddish brown microcrystals; m.p. 167 °C (decomp.); ^1H NMR δ 1.72 (6H, s), 6.30 (2H, s); MS *m/z* 320 (M^-). **1b**: 67% yield; purple microcrystals; m.p. 212 °C (decomp.); ^1H NMR δ 1.72 (6H, s), 3.85 (6H, s); MS *m/z* 436 (M^+). **1c**: 47% yield; orange plates; m.p. 164–166 °C (decomp.); ^1H NMR δ 1.72 (6H, s), 2.42 (6H, s); MS *m/z* 412 (M^+). **1d**: 36% yield; gold microcrystals; m.p. 195 °C (decomp.); ^1H NMR δ 1.72 (6H, s), 4.94 (2H, s); MS *m/z* 396 (M^+). **1e**: 37% yield; m.p. 201 °C (decomp.), ^1H NMR δ 1.72 (6H, s), 3.29 (4H, s); MS *m/z* 410 (M^+). **1f**: 23% yield; orange microcrystals; m.p. 200–202 °C (decomp.); ^1H NMR δ 1.72 (6H, s), 2.76 (6H, m); MS *m/z* 424 (M^+).