4,5-Methylenedithio-4′,5′-ethylenedithiotetrathiafulvalene: a New, Unsymmetrical Electron Donor

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The synthesis, characterization, and *X*-ray crystal structure of a new, unsymmetrical donor in the bis(ethylenedithio)tetrathiafulvalene family are presented.

As part of our broad programme on the study of synthetic metals,[1] we are presently focussing on producing systematic variations in the interstack S · · · S interactions in materials related to bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF).[2] Such interactions, pivotal in suppressing instabilities inherent to low-dimensional systems, are responsible for the formation of extensive 2-dimensional S · · · S sheet networks in (BEDT-TTF)$_2$X salts, X = monovalent anion, which exhibit a rich variety of structural phases and electrical properties. Previous work from this laboratory has demonstrated the possibility of tuning the interstack S · · · S distances in these salts by employing linear anions of different lengths, the outcome of which is dramatically manifested in the solid state properties, particularly the superconducting transition temperatures.† An analogous tuning of the S · · · S interactions is, in principle, possible with the replacement of ethylene bridges in BEDT-TTF by methylene bridges (BMDT-TTF) and by propylene bridges (BPDT-TTF). However, such an approach has not been as fruitful since BMDT-TTF has yielded mostly 1 : 1 and 3 : 1 salts that are semiconductors and/or insulators[3,4] while BPDT-TTF, with the bulkier propylene bridges, has provided principally one-dimensional conductors and semiconductors.[3,5]

We surmised that between the two extremes of molecular modifications represented by BMDT-TTF and BPDT-TTF, there might be an intermediate regime, somewhat similar to BEDT-TTF, in terms of molecular features (planarity, bulk and disposition of bridging groups, *etc.*) to which molecular packing modes and hence solid state properties are quite sensitive. We thought that the unsymmetrical donors MET (**1**), MPT (**2**), and EPT (**3**)[6] might provide access to this intermediate regime. Furthermore, there is a substantial current interest[7] in the study of radical-cation salts of unsymmetrical donors since they were found to possess greater metallic character than their symmetrical counterparts.[8,9] We herein report the synthesis, characterization, and *X*-ray structure determination of the donor (**1**).

The key intermediates in our synthesis are the dithiodithiolones (**4**) and (**5**), which are conveniently prepared from the 'zincate'[10] by alkylation with the appropriate dibromoalkane, followed by oxidation with mercury(II) acetate (Scheme 1). Cross-coupling of (**4**) and (**5**) in neat, refluxing trimethyl phosphite provided the unsymmetrical donor MET along with

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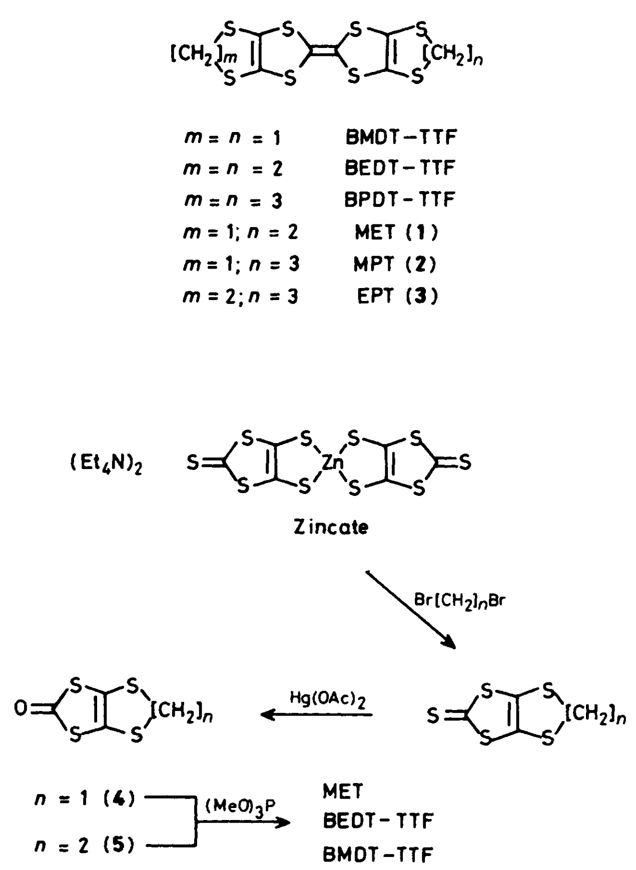
† Anion X, anion length in Å, ambient-pressure superconducting transition temperature (unless otherwise indicated) T_c: I_3^-, 10.14, 1.5 K (8 K under pressure); AuI_2^-, 9.42, 5 K; IBr_2^-, 9.3, 2.8 K, respectively.



BEDT-TTF and BMDT-TTF. MET was separated by flash chromatography[11] (silica gel, 1 : 1 hexanes–CS_2) and further purified by recrystallization ($CHCl_3$).[‡] T.l.c. (silica gel, 1 : 1 hexanes–CS_2) of this sample indicated no contamination with either BEDT-TTF or BMDT-TTF.

The cyclic voltammogram of MET (Pt working electrode, 0.1 M Bu_4NPF_6 in CH_2Cl_2) revealed two reversible redox waves at 0.07 and 0.45 V (*vs.* Ag/Ag^+ reference electrode) which are similar to those of BEDT-TTF (0.07 and 0.48 V) and BMDT-TTF (0.1 and 0.45 V) as determined by us under identical conditions.

The *X*-ray diffraction study[§] showed that MET crystallizes with the same space group as that of BEDT-TTF[12] but with a slightly smaller (by *ca.* 4%) unit cell volume. Thus, MET is clearly in a structural regime close to BEDT-TTF and, consequently, its radical-cation salts may possess molecular packing features similar to those of $(BEDT\text{-}TTF)_2X$ salts. The large thermal parameters observed at the ends of the molecule (Figure 1) appear to be due to a packing disorder in the crystal studied where a small fraction (<5%) of the MET molecules are packed into the unit cell with the positions of the methylene and ethylene bridges exchanged.

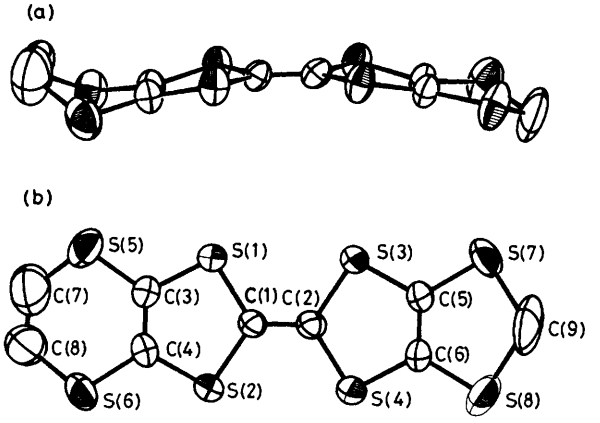


Figure 1. ORTEP Drawing of MET: (a), side view; (b) top view.

We are currently engaged in the preparation and investigation of electrical properties of radical-cation salts of MET.

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[‡] MET: m.p. 183.5—184 °C (decomp.); i.r. (KBr), 2990, 2959, 2913, 2853, 1422, 1408, 1384, 1284, 1255, 1173, 1128, 1091, 955, 919, 901, 889, 848, 768, and 682 cm^{-1}; ^1H n.m.r. ($CDCl_3$, relative to Me_4Si), δ 4.948 (2H) and 3.297 (4H); ^{252}Cf plasma desorption mass spectrum, *m/z* (rel. int.) 370 (100, M^+), 342 (25, $M^+ - C_2H_4$); elemental analyses were satisfactory.

[§] *Crystal data:* $C_9H_6S_8$, $M = 370.66$, monoclinic, space group $P2_1/n$, unit cell at 298 K: $a = 6.422(2)$, $b = 13.972(5)$, $c = 15.479(5)$ Å, $\beta = 92.45(3)°$, $U = 1387.6(8)$ Å^3, $D_c = 1.774(1)$ g/cm^3 for $Z = 4$. Data with $4.0° \leqslant 2\theta \leqslant 60°$ were collected on a Syntex $P2_1$ diffractometer with monochromated Mo-K_α radiation ($\bar{\lambda} = 0.71073$ Å) and corrected for Lorentz-polarization effects and absorption, $\mu_c = 12.10$ cm^{-1}. $R(F) = 0.069$ for 3164 reflections with $F_o \geqslant 3\sigma(F_o)$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.