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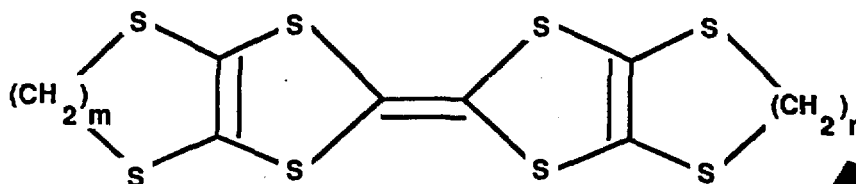
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**4,5-METHYLENEDITHIO-4',5'-PROPYLENEDITHIOTETRATHIAFULVALENE (MPT) AND
4,5-ETHYLENEDITHIO-4',5'-PROPYLENEDITHIOTETRATHIAFULVALENE (EPT)**

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Abstract The title electron donors, unsymmetrical analogs of Bis(ethylenedithio)tetrathiafulvalene, are synthesized. The utility of ²⁵²Cf Plasma Desorption Mass Spectrometry in the characterization and purity determinations is also reported.

Cation-radical salts derived from bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or simply ET) have recently attracted a great deal of attention due to the discovery of superconductivity in at least 8 salts with T_c 's ranging from 1 to 8 K.² Some structural features that are characteristic of these salts are-- a) 2-dimensional S...S contacts resulting in the formation of S...S sheet networks, b) donor sheets alternating with layers of linear trihalide anions and c) anions residing in a cavity of -CH₂- groups, with several short anion...H contacts. Employing anions of different lengths, it was possible to systematically tune the S...S contact distances, which directly influence the bandwidths and hence the density of states at the Fermi level. As a result, the superconducting transition temperature T_c was directly controllable by varying the length of the anion. Complementary to this anion-based tuning of the S...S network and the electrical properties is an approach wherein the number of -CH₂- units in the ET molecule are systematically varied. This should result in -CH₂- cavities of *different size and shape* with the attendant possibility of crystal engineering in these materials aimed towards new conductors and superconductors. With this motivation, we are currently studying cation-radical salts of ET-related donors with a differing number of -CH₂- units on the bridging groups. While the syntheses of symmetrical donors BPDT-TTF³ and BMDT-TTF⁴ were first reported nine years ago, the unsymmetrical donors EPT⁵ and MET⁶ were realized only recently. We herein report the synthesis and properties of the remaining member of the series, MPT, and present an alternate, expeditious synthesis for EPT.



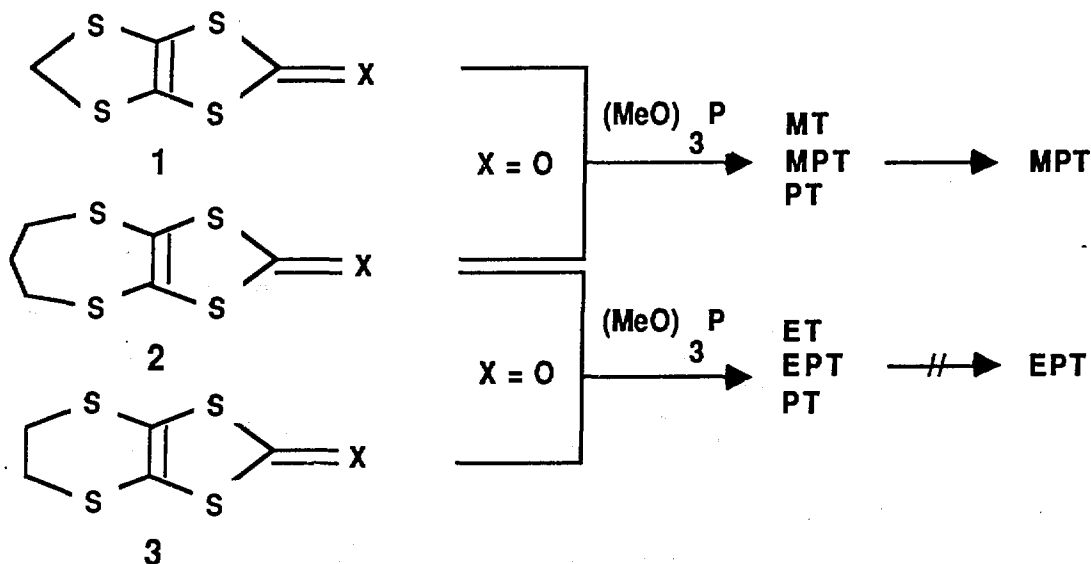
$m = n = 1$	BMDT-TTF (MT)	$m = 1 ; n = 2$	MET
$m = n = 2$	BEDT-TTF (ET)	$m = 1 ; n = 3$	MPT
$m = n = 3$	BPDT-TTF (PT)	$m = 2 ; n = 3$	EPT

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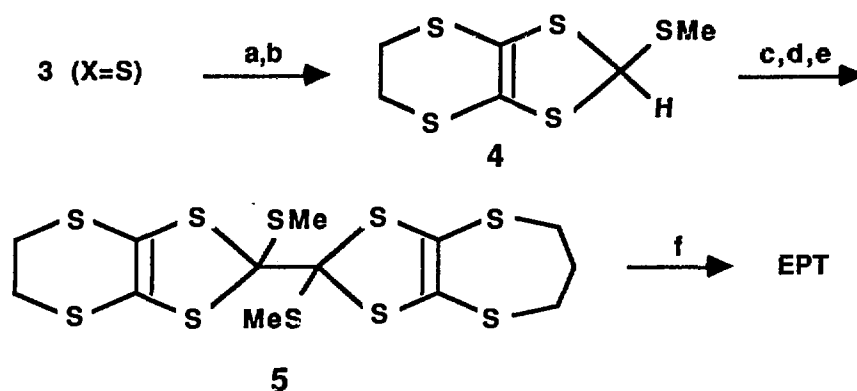
While the preparation of MPT by $(\text{MeO})_3\text{P}$ -mediated cross-coupling of 1,3-dithiole-2-ones **1** and **2** ($\text{X} = \text{O}$) followed by flash chromatographic separation (Silica, CS_2) posed no problems (Scheme I),⁷ such was not the case with EPT. Separation of EPT by chromatography or by fractional crystallization of the mixture (ET, EPT and PT) was unsuccessful. We then turned to the method depicted in Scheme II, by which symmetrical as well as unsymmetrical tetrathiafulvalenes can be accessed from the corresponding hexathioorthoalates.^{8,9,10}

Scheme I



Reaction of thione **3** ($\text{X}=\text{S}$) with excess MeLi in THF at -60°C followed by acidification resulted in the formation of trithioorthoformate **4** in ca. 75% yield. Successive treatment of purified **4** in THF at -60°C with $n\text{-BuLi}$ (0.95 equivalents), thione **2** ($\text{X}=\text{S}$, 1 equivalent) and MeI (excess) each after 1h intervals, provided the hexathioorthoalate **5**, which was easily separated from unreacted **4** and other minor byproducts by column chromatography in ca. 70% yield (ca. 95% based on recovered **4**). Although Lindsay and his coworkers claim the superiority of acid-catalyzed conversion of hexathioorthoalates to tetrathiafulvalenes⁹ over the conventional pyrolytic method,¹⁰ we find the reverse to be true in the case of **5**. Our attempts at *p*-toluenesulfonic acid-catalyzed conversion of **5** to EPT resulted in extensive decomposition to a dark blue product, presumably 1,3-dithiolium salts arising out of central C-C bond cleavage. On the other hand, refluxing a solution of **5** in 1,1,2-trichloroethane for several hours (reaction monitored by TLC, silica, CS_2) followed by cooling to 0°C precipitated EPT in 79% yield, virtually uncontaminated with symmetrical analogs ET and PT.^{11,12} This represents a shorter and more efficient alternative for the synthesis of EPT compared to the method described by Misumi and coworkers.⁵

Scheme II



a) Excess MeLi, THF, -60 °C b) AcOH c) n-BuLi, THF, -60 °C d) 2(X = S) e) MeI
f) 1,1,2-Trichloroethane, reflux

The presence of even small amounts of symmetrical analogs as impurities in the unsymmetrical donors will have drastic effects on the electrical properties of their radical-cation salts stemming from crystal defects, possible alloying etc. Therefore, we have used ^{252}Cf Plasma Desorption Mass Spectrometry¹³ for the identification and purity determination of the unsymmetrical donors. Advantages of this ionization technique over other ionization techniques such as electron impact, chemical ionization etc., are that no pre-vaporization prior to ionization is necessary, and that molecular ions are ejected directly from the solid sample which is held at ambient temperature. This is particularly important in this class of donors which have similar ionization potentials (*vide infra*) but often decompose when heated, prior to vaporization. For example, purified MET⁶ exhibited only its molecular ion cluster without any detectable peaks corresponding to both MT and ET in the ^{252}Cf PDMS spectrum. On the other hand, the electron impact spectrum of the same sample showed molecular ion clusters corresponding to all three species, presumably resulting from a disproportionation pathway.

Changes in the polymethylene bridging groups of ET are not expected to alter the redox properties of the donors significantly and the cyclic voltammetry data (Table 1) bears this out. Both ionization potentials and ΔE , which is a measure of on-site Coulomb energy, of all six electron donors are of essentially similar magnitude. Thus, the series of electron donors MT, ET, PT, MET, MPT and EPT should facilitate a systematic study of the relationship between electrical properties, and the changes in molecular packing in the solid state (dependent solely on the steric factors), and the $\text{CH}_2\cdots\text{anion}$ interactions (dependent on the spatial arrangement of $-\text{CH}_2-$ groups). We are currently engaged in the preparation, elucidation of structural features and determination of electrical properties of the cation-radical salts of this series of donors.

Table 1. Cyclic Voltammetric Data^a

	MT	ET	PT	MET	MPT	EPT
$E_{1/2}(1)$	0.10	0.07	0.10	0.07	0.08	0.11
$E_{1/2}(2)$	0.45	0.48	0.50	0.45	0.46	0.52
ΔE	0.35	0.41	0.40	0.33	0.38	0.41

^a in Volts vs. Ag/Ag⁺, at Pt disc, 0.1 M Bu₄NPF₆ in CH₂Cl₂, sweep rate 50mV/sec

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References and Notes

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7. MPT : m.p. 192-193°C (dec) ; ^1H NMR (CDCl_3), δ 4.94 (s, 2H), 2.69 (t, 4H), 2.40 (m, 2H) ; IR(KBr), 2989, 2878, 1411, 1396, 1385, 1275, 1236, 955, 901, 887, 866, 851, 816, 766 cm^{-1} ; ^{252}Cf PDMS, 384(M^+) ; Analysis, Element (Calc), Found, C (31.22), 30.72, H (2.10), 1.99, S (66.68), 66.59.
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11. Determined by TLC (Silica, CS_2) and ^{252}Cf Plasma Desorption Mass Spectrometry of the crude product.
12. EPT : m.p. 235-236°C (dec) ; ^1H NMR (CDCl_3) δ 3.29 (s, 4H), 2.69 (t, 4H), 2.40 (m, 2H) ; IR(KBr), 2963, 2920, 2882, 2818, 1408, 1394, 1275, 1236, 887, 771 cm^{-1} ; ^{252}Cf PDMS, 398 (M^+) ; Analysis, Element (Calc), Found, C(33.1-32.88, H (2.53), 2.52, S (64.33), 64.47.
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