

Unsymmetrically Substituted
Ethylenedioxytetrathiafulvalenes

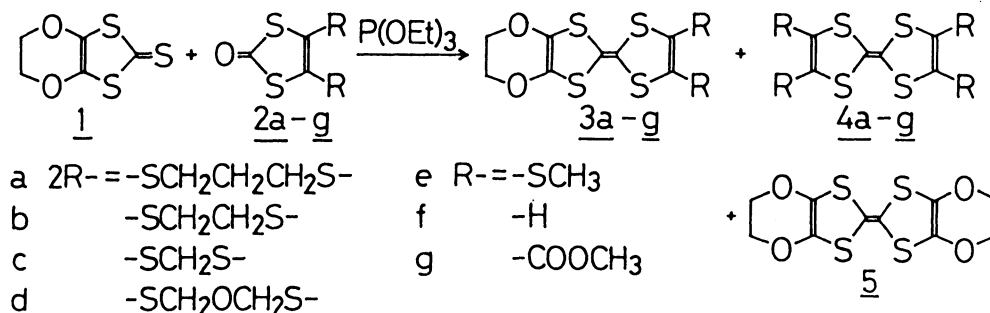
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Seven new electron donors, 4,5-ethylenedioxytetrathiafulvalenes where 4',5'-substituents are trimethylenedithio, ethylenedithio, methylenedithio, 2-oxatrimethylenedithio, methylthio, hydrogen and methyl carboxylate, are prepared, and their electrochemical properties are investigated.

A large number of chemical modifications of TTF (tetrathiafulvalene, 4f) have been investigated because their radical-cation salts show conducting and superconducting properties.¹⁾ Among them, recently prepared BEDO-TTF (bisethylenedioxy-TTF, 5) forms many highly conducting salts,^{2,3)} and its Cu(NCS)_x salt shows superconductivity.³⁾ Since the discoveries of superconductivity in radical-cation salts of unsymmetrical TTF have established that the occurrence of superconductivity is not limited to the salts of symmetrical TTF,^{4,5)} we have recently prepared an unsymmetrical donor EOET-TTF (ethylenedioxyethylenedithio-TTF, 3b),⁶⁾ and are investigating the physical and structural properties of its radical-cation salts.



Scheme 1.

In the present work, we report the preparation of several other unsymmetrical ethylenedioxy-TTF's whose other 4,5-positions are substituted by various substituents (3a-g). Papavassiliou et al. have recently reported the preparation of 3b and 3f.⁷⁾

The unsymmetrical donors (3a-g) were synthesized via phosphite mediated cross coupling of 4,5-ethylenedioxy-1,3-dithiole-2-thione (1)^{2,6,8)} and 1,3-dithiol-2-ones (2a-g)⁹⁻¹²⁾ as shown in Scheme 1. Molar ratios 1:1 to 1.5:1 of 1 and 2a-g were reacted in triethyl phosphite at 65 °C for 4 - 6 h. In the cases of 3a,b,d, the resulting solids were filtered off, and washed with hexane. In the other cases the phosphite was evaporated in vacuo. The unsymmetrical products (3a-g) were separated from the self-coupling products (4 and 5) on silica gel flash column chromatography using CH₂Cl₂ (for 3g) or CS₂ (for the others) as eluent, and recrystallized from CH₂Cl₂/hexane. The yields, properties, and spectroscopic data of these donors are listed in Tables 1 and 2.

The results of cyclic voltammogram of these unsymmetrical donors are summarized in Fig. 1, together with those of the corresponding symmetrical donors. All of these donors show two reversible waves. The redox potentials of unsymmetrical donors (3a-g) appear about midway between those of BEDO-TTF (5) and the corresponding symmetrical donors (4a-g). This rule holds even in the donor with the strongly electron-withdrawing substituent, methyl carboxylate (3g). Therefore, ΔE ($= {}^2E_{1/2} - {}^1E_{1/2}$) of the unsymmetrical donors, which is regarded as a measure of on-site Coulomb repulsion, remains in a similar magnitude to those of the corresponding symmetrical donors.

These unsymmetrical donors form charge-transfer salts with

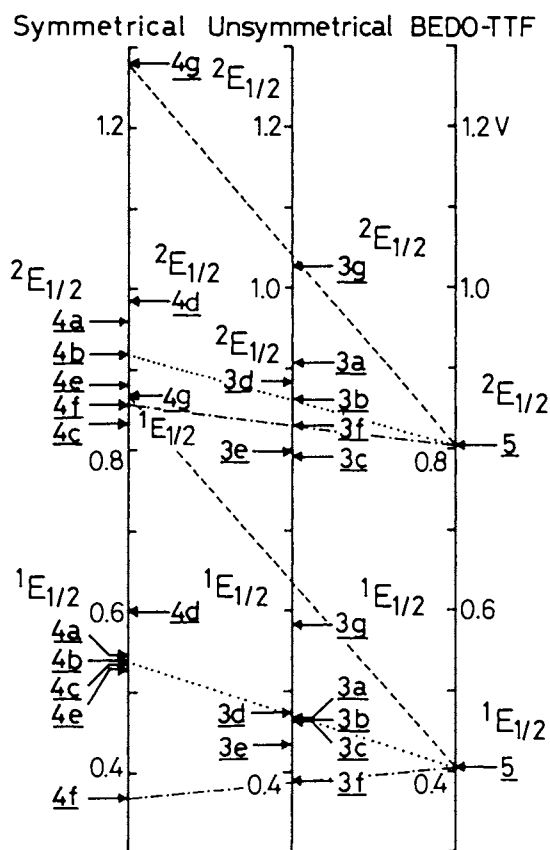


Fig. 1. Half-wave redox potentials (vs. Ag/AgCl reference electrode) of symmetrical and unsymmetrical TTF's, measured in Bu₄NPF₆/benzonitrile at a Pt working electrode.

Table 1. Yield, color, and melting point of the substituted ethylenedioxytetrathiafulvalenes

	Substituent	Yield ^{a)} /%	Color	Mp /°C
<u>3a</u>	Trimethylenedithio	59	Yellow orange	184 - 185 (dec.)
<u>3b</u>	Ethylenedithio	54	Red orange	184 - 185 (dec.) ^{b)}
<u>3c</u>	Methylenedithio	9	Rouge	161 - 163 (dec.)
<u>3d</u>	2-oxatrimethylene-dithio	58	Red orange	188 - 189 (dec.)
<u>3e</u>	methylthio	12	Red orange	73.7 - 74.1
<u>3f</u>	(unsubstituted)	3	Orange	91.0 - 91.5 ^{c)}
<u>3g</u>	methyl carboxylate	37	Black	122 - 123

a) Based on random coupling.

b) 192 °C in Ref. 7. c) 92 °C in Ref. 7.

Table 2. Spectroscopic data of unsymmetrical ethylenedioxy-TTF's

Product	Mass (M/Z=)	IR (KBr, cm ⁻¹)	¹ H NMR (CDCl ₃ , δ =)
<u>3a</u>	366,338,250,222, 194,106,88,76	1642m,1269w,1158s,1084w, 1012w,948w,890w,865w,771w	4.25(4H),2.69(4H), 2.40(2H)
<u>3b</u>	352,324,236,208, 148,88,76	1642m,1268w,1161s,1084w, 1012w,950w,863w,771w	4.26(4H),3.29(4H)
<u>3c</u>	338,310,254,222, 178,100,90,88,76	1654m,1268w,1163s,1082w, 1008w,949w,862w,764w	4.94(2H),4.26(4H)
<u>3d</u>	368,340,252,222, 100,88,76	1644m,1305m,1156s,1082w, 1039m,990w,945w,907m,863w	4.83(4H),4.26(4H)
<u>3e</u>	354,326,238,223, 150,118,88,76	1655m,1420w,1166s,1086w, 1014w,951w,899w,867w	4.24(4H),2.47(6H)
<u>3f</u>	262,234,146,102, 88,76	1655m,1163s,952w,795w	6.32(2H),4.24(4H)
<u>3g</u>	378,350,276,262, 192,88,76	1688m,1656s,1562m,1545m, 1528m,1438w,1301m,1215m, 1164s,1015m	4.26(4H),3.83(6H)

TCNQ (tetracyanoquinodimethane) and radical-cation salts with various anions. Their conducting and structural properties will be reported else-

where.

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