4,5-Ethylenedioxy-4′,5′-ethylenedithiotetrathiafulvalene (EOET): a New Unsymmetrical Electron Donor

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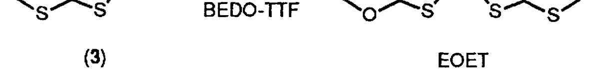
The synthesis, characterization, electrochemical properties, and preliminary *X*-ray structural data of the title electron donor, a hybrid of bis(ethylenedithio)tetrathiafulvalene and bis(ethylenedioxy)tetrathiafulvalene, are presented.

Among the various tetrathiafulvalene (TTF) derivatives, bis(ethylenedithio)tetrathiafulvalene (BEDT–TTF or ET) has recently emerged as an important electron donor because of its ability to form two-dimensional electrical conductors and superconductors. It has yielded the largest number of superconducting and metallic cation-radicals salts compared with other electron donors,[1] including that with the highest known superconducting transition temperature for an organic superconductor, κ-(BEDT–TTF)$_2$Cu(NCS)$_2$, $T_c = 10.4$ K.[2,3] Therefore, various chemical modifications of BEDT–TTF, obtained by replacement of all or some sulphur atoms with other chalcogens,[4,5] and ethylene end groups with other alkanediyl groups,[6] are of great interest from the viewpoint of 'molecular engineering' of solid-state properties. Additionally, because of the recent discoveries of superconductivity in cation-radical salts of *unsymmetrical* TTF derivatives, dimethylethylenedithiodiselenodithiafulvalene (DMET)[7] and methylenedithiotetrathiafulvalene (MDT–TTF,[8] it is now well established that the occurrence of superconductivity is not limited to the cation-radical salts of *symmetrical* TTF derivatives. We recently suggested that *unsymmetrical* TTF derivatives, since they have an intrinsic tendency to form centrosymmetric dimers, may be good candidates for preparing cation-radical salts with a κ-type molecular packing arrangement [molecular dimers which are arranged nearly orthogonal to each other, as in κ-(BEDT–TTF)$_2$Cu(NCS)$_2$], which appears to be the most promising structural type in the design of new organic metals and superconductors.[9] These considerations, and our recent discovery[10] of ambient pressure superconductivity at ~1.0 K in (BEDO–TTF)$_3$Cu$_2$(NCS)$_3$, have prompted us to synthesize the title *unsymmetrical* donor, EOET, which is a hybrid of BEDT–TTF and BEDO–TTF.[5] In this communication, we report its preparation, characterization by spectral and preliminary *X*-ray diffraction data, and electrochemical properties.

The synthesis (Scheme 1) of the unsymmetrical donor EOET was achieved by (MeO)$_3$P-mediated cross-coupling of 4,5-ethylenedioxy-1,3-dithiole-2-thione (**2**) and 4,5-ethylenedithio-1,3-dithiole-2-one (**3**).[11] The thione (**2**) was pre-



Scheme 1. *Reagents and conditions*: i, NaSH·H$_2$O, EtOH–AcOH; ii, (MeO)$_3$P, 65 °C, 5 h; iii, flash chromatography.

Table 1. Unit cell data for EOET, BEDT–TTF, and BEDO–TTF.

Compound	Space group	*Z*	*a*/Å	*b*/Å	*c*/Å	β/°	*U*/Å^3
EOET	$P2_1/c$	4	6.473(3)	14.231(6)	16.239(9)	110.71(4)	1399(1)
BEDT–TTF[a]	$P2_1/c$	4	6.614(11)	13.985(2)	16.646(3)	109.55(2)	1450(2)
BEDO–TTF[b]	$P2_12_12_1$	4	7.515(2)	7.627(2)	21.794(5)		1249.2(5)

[a] Ref. 13. [b] Ref. 5.

pared from the corresponding iminium salt (**1**)[5] by reaction with commercially available sodium hydrosulphide hydrate in ethanol–acetic acid mixture.† A mixture of (**2**) and (**3**), in a 3 : 2 molar ratio, was treated with freshly distilled $(MeO)_3P$ at 65 °C for 5 h. Flash chromatography of the product (silica gel; CS_2)[12] yielded EOET as an orange–red solid (yield 54% based on random coupling) m.p. 184—185 °C (decomp.); IR (KBr), $\nu_{max.}$ 1643m, 1159s, 1084w, and 771w cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.259 (4H) and 3.291 (4H); ^{252}Cf plasma desorption mass spectrum (PD MS), *m/z* 352 (M^+), 324 ($M^+ - C_2H_4$), and 236 ($M^+ - C_4H_4S_2$).

The cyclic voltammogram of EOET (Pt working electrode; 0.1 M Bu_4NPF_6 in CH_2Cl_2) showed two reversible redox waves, whose half-wave potentials were 0.01 and 0.43 V (*vs.* Ag/Ag$^+$ reference electrode). These values are midway between the corresponding half-wave potentials of BEDT–TTF (0.07 and 0.48 V) and BEDO–TTF (−0.04 and 0.37 V) measured under identical conditions.

X-Ray diffraction studies on several crystals of EOET, which show a great tendency for twinning, reveal that they are isostructural with BEDT–TTF,[13] but not with BEDO–TTF,[5] based on the cell constants (see Table 1) and a preliminary survey of intensity data obtained from a twinned crystal. The unit cell volume of EOET is *ca.* 4% less than that of BEDT–TTF. Because of the twinning found in the crystals of EOET investigated so far, we have been unable to obtain full structural details.

We are currently engaged in the preparation, structural studies, and investigation of electrical properties of cation-radical salts of EOET, and these results will be reported shortly.

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† In addition to the dimethyliminium salt (**1**), we have also prepared and used the corresponding piperidine-iminium salt in the synthesis of (**2**).