Ethylenedioxytetrathiafulvalenes: New Unsymmetrical π-Donors

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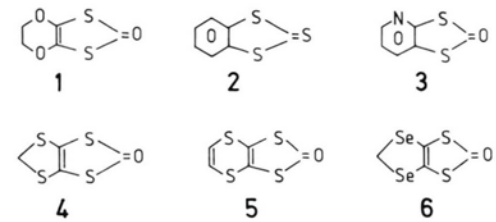
Tetrathiafulvalenes, π-Donors, Organic Conductors

Ethylenedioxybenzotetrathiafulvalene (EDOBTTF), ethylenedioxypyridino[4,5-b]tetrathiafulvalene (EDOP[4,5-b]TTF), ethylenedioxymethylenedithiotetrathiafulvalene (EDOMDTTTF), ethylenedioxyvinylenedithiotetrathiafulvalene (EDOVDTTTF), and ethylenedioxomethylenediselenotetrathiafulvalene (EDOMDSTTF) have been prepared and characterized analytically and spectroscopically.

Since the discovery of superconductivity in $(DMET)_2X$ (X = $AuBr_2$, AuI_2, I_3 *etc.*) [1] and $(MDTTTF)_2AuI_2$ [2] based on the unsymmetrical π-donor molecules DMET (= dimethyl-ethylenedithio-diselenadithiafulvalene) and MDTTTF (= methylenedithiotetrathiafulvalene), respectively, several trials have been done in order to obtain new superconducting materials using unsymmetrical π-donor molecules [3–7]. While the unsymmetrical π-donor DMET could be prepared by cross-coupling of 4,5-ethylenedithio-3,1-dithiole-2-one and dimethyl-1,3-diselenole-2-selone with triethyl phosphite followed by high performance liquid chromatography separation, such a strategy was unsuccessful in the case of MDTTTF [8] and similar compounds [5, 6]. In the case of pyridine- and pyrazine-containing tetraheterofulvalenes the separation of the cross-coupling product from the self-coupling subproducts can be performed easily by column chromatography [9, 10], because of the widely varying polarity of these compounds. In this paper we report the preparation of some new unsymmetrical π-donors based on 4,5-ethylenedioxy-1,3-dithiole-2-one (**1**) [3, 11]. The new compounds **1-2, 1-3, 1-4, 1-5,** and **1-6** were prepared by cross-coupling of **1** with **2** [12], **3** [13], **4** [2–4], **5** [14] and **6** [2–4], respectively, *via* triethyl phosphite, $(EtO)_3P$, according to Scheme 1, followed by silica gel column chromatography separation.



Experimental

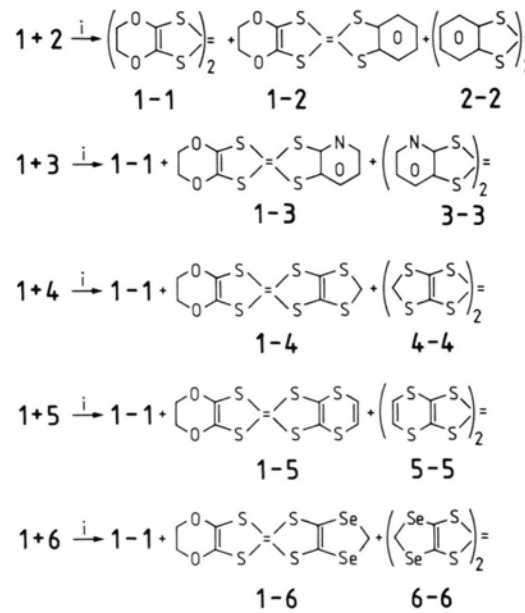
Reagents and apparatus

Reagents and apparatus described in our previous papers [3, 8–10, 13] as well as reagents described in [12] were used.

Preparation of ethylenedioxybenzotetrathiafulvalene **1-2** *and similar compounds* **1-3–1-6**

A solution of **1** (342 mg 2 mmol) and **2** (368 mg, 2 mmol) in triethylphosphite (10 ml) was heated at ~150 °C for 5 h with stirring under a nitrogen atmosphere.

The mixture was concentrated to dryness and the residue was dissolved in benzene cyclohexane (1:1) and subjected to a silica gel column chromatography (1 m) eluting with benzene cyclohexane (1:1). The initial yellow band yielded **2-2** (6 mg)



i = $(EtO)_3P$, ≈150 °C, N_2

Scheme 1.

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[12], the subsequent orange band yielded **1-2** (44 mg, 7% based on **1**) and the final red band yielded **1-1** (< 1 mg) [3, 11]. Compound **1-2** was purified by dissolving in dichloromethane and precipitation with hexane. It was found to be a red crystalline solid; m.p. = 175 °C; m.w. = 312 (mass spectrum). Fig. 1 shows the UV-visible spectrum of **1-2** as well as the spectra of **1-1** and **2-2** for comparison.

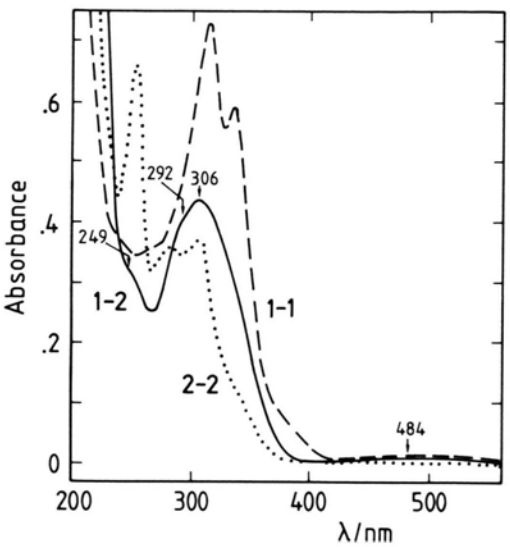

Fig. 1. UV-visible spectra of **1-1, 1-2, 2-2** in CH_3CN.

Compounds **1-3**–**1-6** were prepared by the same method except that the mixture obtained after treatment with triethyl phosphite was cooled to −10 °C and the precipitate was filtered off; the filtrate was concentrated and subjected to a column chromatography as in the previous case. A second crop may be obtained from the precipitate. Preparative, analytical and UV-spectral data are listed in Table I.

Results and Discussion

Coupling of **1** with each of the compounds **2**–**6** *via* triethyl phosphite afforded mixtures of the self-coupling products **1-1** and **2-2**–**6-6** with the cross-coupling products **1-2**–**1-6,** respectively. Because of the widely varying polarity of these compounds, the separation of each cross-coupling product from the corresponding self-coupling products was found to be easy. This procedure can be applied for the preparation of a large number of unsymmetrical tetraheterofulvalenes. The cross-coupling products were found to be good π-donors. They react with TCNQ (tetracyanoquinodimethane), which is a π-acceptor, to give crystalline charge transfer complexes (CTC). The compound **1-2**$_x$TCNQ was found to be an insulator, while the compounds **1-3**$_x$TCNQ, **1-4**$_x$TCNQ, **1-5**$_x$TCNQ and **1-6**$_x$TCNQ were found to be conducting solids. It should be noted that, in contrast to the self-coupling product BVDTTTF **5-5** [15], the corresponding cross-coupling product, EDOVDTTTF **1-5,** gave a CTC with TCNQ. This effect indicates that the substitution of an vinylenedithio group by an ethylenedioxy group decreases the half wave oxidation potentials, and consequently a better π-donor was obtained. Using the new π-donors (D) a number of cation radical salts (CRS) of the type D_xX (where X = I_3, IBr_2, AuI_2, BF_4 *etc.*) were prepared by chemical or electrochemical procedures (see for example [4]). These salts were found to be conducting solids. Details on the physical properties of the π-donors **1-2**–**1-6** and of their CTC and CRS will be reported elsewhere.

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Cpd.	Yield (%)	m.p. (°C)	C	H	S	λ/nm
1-2	7.0	175	46.05 (46.15)	2.48 (2.56)	42.60 (41.03)	306
1-3	5.6	206	42.15 (42.17)	2.16 (2.24)	41.29 (40.90)	287
1-4	3.9	171	31.87 (31.95)	1.67 (1.78)	56.87 (56.81)	325
1-5	4.5	194	34.14 (34.29)	1.76 (1.70)	54.67 (54.86)	323
1-6	< 1	218	25.21 (25.00)	1.27 (1.39)	29.43 (29.63)	312–320

Table I. Preparative, analytical[a] and UV-spectral data[b] of **1-2**–**1-6.**

[a] Analysis (%), calculated values are given in parentheses; [b] position of the strongest band in the UV-visible spectral range.

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