Ethylenedioxytetrathiafulvalenes: New Unsymmetrical \( \sigma \)-Donors


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Tetrathiafulvalenes, \( \sigma \)-Donors, Organic Conductors

Ethylenedioxybenzotetrathiafulvalene (EDOBTTF), ethylenedioxy-4,5-bijtetrathiаfulvalene (EDOP[4,5-b]TTF), ethylenedioxy-methylendithiotetrathiafulvalene (EDOMDTTTF), ethylenedioxyvinylendithiotetrathiafulvalene (EDOVDTTTF), and ethylenedioxomethylendiselenotetrathiafulvalene (EDOMSTTTF) have been prepared and characterized analytically and spectroscopically.

Since the discovery of superconductivity in ethylenedioxy-benzotetrathiafulvalene (EDOB-TTF) [1] and methylendithio-diselenotetrathiafulvalene (MDTTTF) [2], based on the unsymmetrical \( \sigma \)-donor molecules DMT (dimethyl-ethylenedithio-diselenanithiafulvalene) and MDTTF (= methylenedithiotetrathiafulvalene), respectively, several trials have been done in order to obtain new superconducting materials with unsymmetrical \( \sigma \)-donor molecules [3−7]. While the unsymmetrical \( \sigma \)-donor DM ET could be prepared by cross-coupling of 1,3-dithiolate with triethyl phosphite followed by column chromatography separation. Since the discovery of superconductivity in

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)

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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.

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 1.

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 \( \pi \)-donors. They react with TCNQ (tetracyanoquinodimethane), which is a \( \pi \)-acceptor, to give crystalline charge transfer complexes (CTC). The compound 1-2, TCNQ was found to be an insulator, while the compounds 1-3, TCNQ, 1-4, TCNQ, 1-5, TCNQ and 1-6, 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 \( \pi \)-donor was obtained. Using the new \( \pi \)-donors (D) a number of cation radical salts (CRS) of the type D\( \_X \) (where X = I\( _3 \), IBr\( _2 \), AuI\( _3 \), 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 \( \pi \)-donors 1-2–1-6 and of their CTC and CRS will be reported elsewhere.

We thank Dr. C. W. Mayer and J. S. Zambounis for recording mass spectra.

Table I. Preparative, analytical\( ^a \) and UV-spectral data\( ^b \) of 1-2–1-6.

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

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


