

## Conjugated 'Tris'-tetrathiafulvalenes

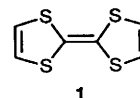
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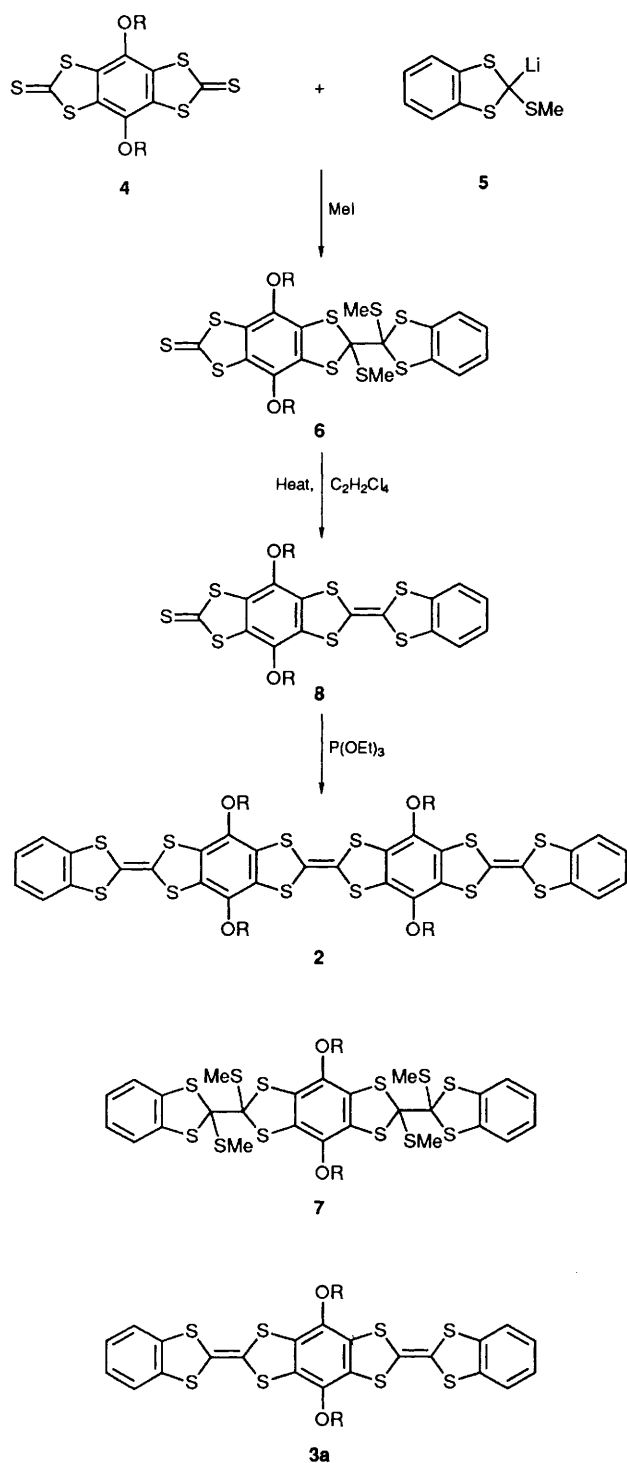
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The synthesis of an extended donor system containing three tetrathiafulvalene (TTF) moieties in full  $\pi$ -conjugation and its doping with several electron acceptors are described.

The magnitude of the electrical conductivity in organic charge-transfer (CT) complexes is controlled by the superstructure arising from the arrangement of the single molecule in the crystalline solid. Depending on the prevailing superstructure, the whole conductivity spectrum, from insulating to superconducting materials, can be covered, for example, with tetrathiafulvalene (TTF) **1** derivatives.<sup>1-3</sup> In many cases a

metal-insulator transition occurs at low temperatures, which is known as Peierls distortion.<sup>4</sup> Keeping these structure-function relationships in mind, we have synthesized a donor





Scheme 1

with an extended  $\pi$ -system containing three TTF subunits, aiming to increase further the dimensionality of the CT process in the donor molecule.

The synthetic route given in Scheme 1 was carried out initially with the ethoxylated substrates **4a**.<sup>5</sup> The insolubility of the reaction product **2a** severely inhibited a full characteriza-

tion. However, elemental analysis of **2a** obtained from coupling of **8a** is in agreement with the proposed structure and the IR spectra of **2a** and the structurally related **3a** exhibit a striking similarity.

In order to investigate the influence of an extension of the  $\pi$ -systems on the physical properties we synthesized the hexoxylated tris-TTF **2b**. The lengthening of the alkyl chains in **2b** leads to a markedly improved solubility, making this tris-fulvalene amenable to full spectroscopic investigations.

The preparation of **2** is accomplished by the addition of 4,8-dialkoxy-1,3,5,7-tetrathia-s-indacene-2,6-dithiones **4** to one equivalent of 2-lithio-2-methylthio-benzo-1,3-dithiole **5**<sup>6</sup> in tetrahydrofuran ( $-78^\circ\text{C}$ , argon), furnishing the hexathio-orthoalates **6** (yield: 39%). An inverse addition technique is essential in this case to suppress formation of the bis-adducts **7**. Warming of the mono-adducts **6** in 1,1,2,2-tetrachloroethane results in the extrusion of dimethyl disulphide ( $130^\circ\text{C}$ ), producing the TTF derivatives **8**<sup>7</sup> (yield: 87%). These intermediates, which themselves can be envisaged as donors suitable for the preparation of CT complexes, contain one terminal trithiocarbonate moiety, which allows for the formation of higher functionalized tetrathiafulvalenes. Heating the 'fulvalene thiones' **8** in triethyl phosphite leads to the symmetrical coupling of **8** and formation of the title compounds **2**,<sup>8</sup> highly polarisable molecules. The yield of the coupling step is 28% [**2b**:  $^1\text{H}$  NMR,  $\delta_{\text{H}}$  0.94 (t, 12H), 1.33–1.62 (m, 16H), 1.78 (q, 8H) and 3.95 (t, 8H);  $^{13}\text{C}$  NMR,  $\delta_{\text{C}}$  14.9, 22.6, 25.5, 30.2, 31.5, 72.5, 110.4, 111.6, 121.7, 125.8, 128.9, 136.7 and 142.2].

While the TTF 'dimer' **3** can be charged reversibly up to the tetra-cation in four separate potential steps,<sup>5</sup> the 'trimer' **2** can be oxidized to a hexa-cation. A cyclic voltammetric investigation of these oxidation processes will be published elsewhere.<sup>9</sup>

Addition of electron acceptors such as iodine, dichlorodicyano-*p*-benzoquinone (DDQ) or tetrafluoro-tetracyano-*p*-quinodimethane (TCNQ-F<sub>4</sub>) to solutions of **2b** in methylene chloride leads to the formation of deeply coloured CT complexes whose elemental analyses indicate a 1:2 stoichiometry. The room temperature conductivity of the DDQ complex (compressed pellet) amounts to  $10^{-1} \text{ S cm}^{-1}$ . Under identical experimental conditions the room temperature conductivity of **2b** is one order of magnitude greater than that of **3**. Radical cation salts of **2b** may be available by electrocrystallisation. Experiments to obtain these salts are under way.

Financial support by the Fonds der Chemie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Received, 3rd July 1990; Com. 0/03003A

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