

Synthesis of Bis(ethylenedithio)dithiadiazafulvalenes (BEDT-DTDAF) and Generation of Charge-Transfer Complexes with Tetracyanoquinodimethane

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Abstract: The synthesis of bis(ethylenedithio)dithiadiazafulvalenes (BEDT-DTDAFs), in four steps via 4,5-(ethylenedithio)thiazole and 3-alkyl-4,5-(ethylenedithio)thiazolium salts, and the generation of conducting charge-transfer complexes from a new type of dithiadiazafulvalene and tetracyanoquinodimethane are reported.

Key words: carbenes, complexes, heterocycles, organic metals, fulvalenes

Tetraheterafulvalenes, such as TTF, TSeF, TTeF, and DTDAF, are widely used for the preparation of organic metals and organic superconductors.^{1–8} So far, many modified variants to the four parent compounds have been synthesized. One of the most noteworthy modifications of the tetrathiafulvalene (TTF) core is bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF, Figure 1), in which two-dimensional conductivity was observed.⁹ Moreover, organic superconductors are most commonly prepared from BEDT-TTF.

Dithiadiazafulvalenes (DTDAFs, Figure 1), which contain two nitrogen atoms in the tetraheterafulvalene core, are especially good electron donors ($E_{\text{HOMO}} = -3.916$ eV).¹⁰ Despite this fact DTDAFs are among the less explored tetraheterafulvalenes due to their oxygen sensitivity,¹¹ which makes synthesis of many of them very challenging.

To the best of our knowledge, DTDAF with four sulfur or selenium atoms at the ends of the π -system, i.e. the diaza-BEDT-TTF analogue, has not been previously synthesized and its electric properties have not been explored.

In this paper we wish to report the first synthesis of bis(ethylenedithio)dithiadiazafulvalenes (BEDT-DTDAFs). The reaction of thiazolium salts with base is

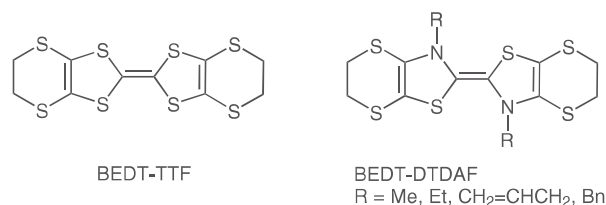


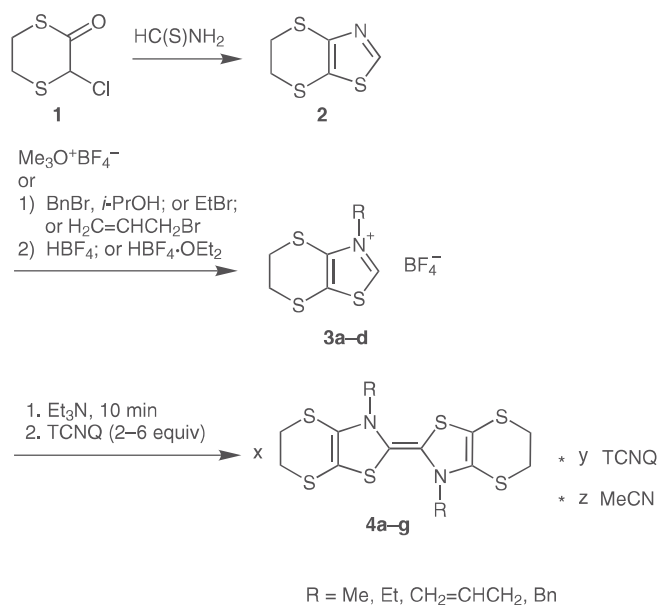
Figure 1

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Scheme 1

one of the most commonly used methods for the preparation of dithiadiazafulvalenes,⁸ hence the key intermediates for the preparation of BEDT-DTDAFs are the respective thiazolium salts **3a–d**.

We applied a modified Hantzsch synthesis to the preparation of 5,6-dihydro[1,4]dithiino[2,3-*d*]thiazole (**2**). 3-Chloro-1,4-dithiane-2-one (**1**) was prepared according to a procedure described by Larsen and Lenoir.¹² Reaction of **1** with freshly prepared thioformamide affords **2** in moderate yields (Scheme 1). Of course, Hantzsch's synthesis has been applied to the preparation of thiazoles from α -halocarbonyl compounds and thioamides, and it is well known that reaction of α -halo esters with thioamides leads to thiazol-4(*5H*)-ones rather than to thiazoles.¹³ Fortunately in our case the dehydration process was faster than 1,4-dithiane ring opening.

In the next step we alkylated **2** with alkyl bromides, followed by treatment with tetrafluoroboric acid, or trimethylxonium tetrafluoroborate to give thiazolium tetrafluoroborate salts **3a–d**. The thiazolium salts could also be synthesized in one step by reaction of **1** with substituted thioformamides; we obtained thiazolium salts in this manner only in the case of 3-benzyl-5,6-dihydro[1,4]dithiino[2,3-*d*]thiazol-3-ium tetrafluoroborate (**3b**), but the yield did not exceed 12%. Phenylthioformamide in reaction with **1** did not give a thiazolium salt.