Facile Syntheses of 4-(2-Cyanoethylthio)-1,3-dithiole-2-thione and New Electron Donors with Two TTF Units and Compounds with Bis(1,3-dithiole-2-thione) Groups

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Abstract: The synthetic conditions for the preparation of 4-(2-cyanoethylthio)-1,3-dithiole-2-thione (1) from TBA₂[Zn(dmit)₂] were studied. Compound 1 was used to synthesize new electron donors with two tetraethylfulvalene (TTF) units. Other interesting compounds that are good precursors for tetraethylfulvalenophanes were also easily prepared from TBA₂[Zn(dmit)₂].

Key words: electron donors, tetraethylfulvalene, cyclophane, 1,3-dithiole-2-thione, 1,3-dithiole-2-thione-4,5-dithiolate

As the key compound for the preparation of tetraethylfulvalene (TTF) derivatives, 4,5-bis(alkylthio)-1,3-dithiole-2-thiones can be conventionally synthesized from the zinc complex of 1,3-dithiole-2-thione-4,5-dithiolate (TBA₂[Zn(dmit)₂], TBA: tetrabutylammonium) or the anion of 1,3-dithiole-2-thione-4,5-dithiolate generated in situ. In comparison, its analogue, 4-(2-cyanoethylthio)-1,3-dithiole-2-thione is not easily accessible. We have just recently reported that 4-alkylthio-1,3-dithiole-2-thione can be synthesized easily starting from TBA₂[Zn(dmit)₂] and electrophilic reagents such as 3-bromopropionitrile in the presence of pyridine hydrochloride. Since 2-cyanoethyl is a good protecting group for thiolates, 4-(2-cyanoethylthio)-1,3-dithiole-2-thione (1) is a suitable precursor for the preparation of new electron donors (Figure 1). For example, 1 can be converted easily to 4-(2-cyanoethylthio)-1,3-dithiole-2-one (2) with Hg(OAc)₂, and new electron donor molecules such as 3 and 4 with 2-cyanoethyl group can be prepared through the cross-coupling of 2 and 4,5-ethylenedithio-1,3-dithiole-2-thione and 4,5-bis(merthiolylthio)-1,3-dithiole-2-thione, respectively, in the presence of trialkyl phosphite.

By removal of the 2-cyanoethyl group from 3 and 4 and subsequently reaction with bis-electrophilic reagents, new electron donors such as 5–9 (Figure 1) with two TTF units can be obtained from the easily accessible reactants in a rather straightforward way. These electron donors are interesting for studies of organic conductors since higher than one dimensional and different stoichiometric charge-transfer complexes may result from them. In particular, they may be useful for the construction of molecular spin-ladder systems. It is expected that other organic ammonium salts can be also used for the reaction to generate compound 1.

It was assumed that 4,5-dimercapto-1,3-dithiole-2-thione (10) was the important intermediate compound for the formation of 1 starting from TBA₂[Zn(dmit)₂] and 3-bromopropionitrile as shown in Scheme 1. But, when the reaction was performed in the presence of four equivalents of acids such as acetic acid and p-toluenesulfonic acid, compound 1 was not detected in the reaction mixture. By reducing the amounts of acids, only 4,5-bis(2-cyanoethylthio)-1,3-dithiole-2-thione (11) separated out in rather low yield and again compound 1 was not found in the reaction mixture. Thus, it may be inferred that pyridine hydrochloride would be a suitable reagent, while it is a mild acid and its conjugate base—the pyridine is a mild base, and is essential for the reaction to generate 1 (Scheme 1). Besides pyridine hydrochloride, several commercially available ammonium salts and the mixture of sodium acetate and acetic acid (in 1:1 molar ratio) were tried for the reaction under the same condition as in the case of pyridine hydrochloride (see Table 1). For comparison, the yields of 1 and 11 generated from the reaction (Scheme 1) in the presence of pyridine hydrochloride were also included in Table 1. In the cases of ammonium chloride and the mixture of sodium acetate and acetic acid, compound 1 was not formed and only compound 11 was obtained in a low yield. This may be attributed to the low solubilities of ammonium chloride and sodium acetate in the reaction medium (MeCN). But, it may be also due to the weak acidic character of ammonium chloride and weak basic character of sodium acetate. On the contrary, the results indicated that the hydrochloride salts of triethylamine, aniline and p-diaminobenzene can be employed for the reaction (Scheme 1) to induce the formation of 1. It is expected that other organic ammonium salts can be also used for the reaction to generate compound 1.
As an example, the effect of the quantity of pyridine hydrochloride used on the yield of 1 was studied (Table 1). When the molar ratio of pyridine hydrochloride versus TBA₂[Zn(dmit)₂] was less than four, the yield of 1 was lower and more 11 was produced. But, if the molar ratio of pyridine hydrochloride versus TBA₂[Zn(dmit)₂] was larger than four, the yield of 1 was not increased largely. The optimal molar ratio was about four. This may be explained as following: four equivalents of pyridine hydrochloride probably converted most of the TBA₂[Zn(dmit)₂] into 10 and liberate the free base (pyridine) which may be involved in the further reaction of 10 to generate 1. If limited amounts of pyridine hydrochloride were used, probably TBA₂[Zn(dmit)₂] was only partially transformed into 10, and the rest of TBA₂[Zn(dmit)₂] will react directly with 3-bromopropionitrile to give 11. Consequently, the yield of 1 will be lowered. In short, compound 1 can be synthesized from the easily accessible reactants with four equivalents of an organic ammonium salt in ca. 70% yield.

Based on the above observations and the previous results, the following mechanism was tentatively suggested for the unusual reaction of Zn(dmit)₂ ion (Scheme 2). Compound 10 was supposed to be the key intermediate. Probably with the help of pyridine, homo-cleavage of S–H bond generates radical intermediates 10a and 10b. From 10a, further cleavage of the neighboring S–H bond and intramolecular migration of hydrogen radical would lead to the radical intermediate 10c and free sulfur. This is in accordance with the separation of S₈ in the reaction mixture. Electron-transfer reaction between 10b and 10c.
should afford 4-thio-1,3-dithiole-2-thione anion (10d), which will react with suitable electrophilic reagents to produce the analogues of 1.

Since the 2-cyanoethyl group can be easily removed under basic condition, 1 is a potentially good starting compound for the synthesis of new electron donors and related interesting molecules. For instance, 1 was converted to 2 with Hg(OAc)₂, and 3 and 4 can be prepared by the conventional cross-coupling procedure effected by tri(isopropyl) phosphate in yields of 73 and 56%, respectively (Scheme 3). The deprotection of 2-cyanoethyl group resulted in the formation of the corresponding thiolates in situ, which subsequently reacted with bis-electrophilic reagents such as 1,2-dibromoethane to afford new electron donors with two TTF units 5–9. Analogues of these new electron donors were synthesized by different multi-step approaches. The oxidation potentials of these new electron donors were measured with cyclic voltammetry, and the results are summarized in Table 2. As examples, the cyclic voltammograms of 7 and 9 are shown in Figure 2. For 5, 6 and 7, three distinct redox-waves were observed. By comparing with the electrochemical behaviors of analogous electron donors described previously, the first two waves might correspond to two one-electron redox processes, and the third was probably due to a two-electron redox process. On the other hand, only two redox waves were detected for 8 and 9, which implied that the two TTF units were independent and they could be oxidized simultaneously. Investigations of their charge-transfer salts are in progress.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Redox Potentials of 3–9 Measured by Cyclic Voltammetry a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>E₁/₂(V)</td>
</tr>
<tr>
<td>3</td>
<td>0.49</td>
</tr>
<tr>
<td>4</td>
<td>0.52</td>
</tr>
<tr>
<td>5</td>
<td>0.37</td>
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<tr>
<td>6</td>
<td>0.38</td>
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<tr>
<td>7</td>
<td>0.40</td>
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<tr>
<td>8</td>
<td>0.44</td>
</tr>
<tr>
<td>9</td>
<td>0.46</td>
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a All measurements were performed in CH₂Cl₂ containing 0.1 M Bu₄NPF₆, with SCE as the reference electrode, platinum as working and counter electrodes.

Under similar conditions, TBA₂[Zn(dmit)₂] reacted directly with bis-electrophilic reagents such as 1,3-dibromopropane in the presence of pyridine hydrochloride to afford compounds 12 and 13 with bis(1,3-dithiole-2-thione) groups (see Scheme 4). The yields of 12 and 13...
were low (about 20%), which was probably due to the formation of compounds with only one 1,3-dithiole-2-thione group. Although the yields were not high, the present approach to compounds with bis(1,3-dithiole-2-thione) groups was rather simple in terms of the easiness to obtain the reactants and perform the reaction and separation in comparison with the synthetic method for their analogues. Efforts are underway to optimize the reaction condition and hence improve the yields. These compounds (e.g. 12 and 13) are good precursors for the tetrathiafulvalenophanes and other interesting molecules with TTF units. 

In summary, on the basis of our recent work, a facile and efficient approach to 1 was developed and the synthetic conditions were studied. Its synthetic applications were demonstrated by the efficient preparations of new electron donors 5-9 with two TTF units. Compounds like 12 and 13 with bis(1,3-dithiole-2-thione) groups can also be synthesized from TBA₂[Zn(dmit)₂] in a simple manner.

Melting points were measured with an XT4-100 microscope apparatus and are uncorrected. ¹H NMR spectra were recorded on Unity 200 (Varian) and Bruker 300 MHz instruments. IR spectra were recorded on a Pekin-Elmer 2000 FT-IR spectrometer. Mass spectra were recorded on AEI-MS50 for EI-MS, KYKY-ZH-P-5 for FAB-MS and Beflex III for TOF-MS. Elemental analyses were per-

Scheme 3 Synthesis of new electron donors 5-9

Figure 2 Cyclic voltammograms of 7 (left) and 9 (right)

Scheme 4 Synthesis of compounds 12 and 13
formed on a Carlo-Erba-1106 instrument. Cyclic voltammetric measurements were carried out on an EGDG PAR 370 system.

Pyridine hydrochloride and 1,12-dibromodecane were purchased from Acros Chemicals. 1,11-Dibromo-3,6,9-trioxoundecane was synthesized from tetraethylene glycol, Ph$_3$P and CBr$_4$ with the conventional method. TBA[Zn(dmit)$_2$] was prepared according to Ref.\(^1\). All other chemicals and solvents were from Beijing Chemical Company, and were used as received. The petroleum ether used had a bp range of 60–90 °C.

4-(2-Cyanoethylthio)-1,3-dithiole-2-thione (1)

This was prepared as described in Ref. 3. Different organic amine salts as well as NH$_4$Cl and NaOAc/ACOH were tried and the results are summarized in Table 1.

4-(2-Cyanoethylthio)-1,3-dithiole-2-thione (1)

To a solution of compound 1\(^1\) (0.27 g, 1.23 mmol) in CH$_2$Cl$_2$ (45 mL) was added Hg(OAc)$_2$ (1.18 g, 3.69 mmol) and the mixture was stirred at 20 °C for 1 h. The white precipitate was removed by filtration through Celite and the filtrate was washed with CH$_2$Cl$_2$. The solvent was removed to afford compound 2 as a colorless powder; yield: 200 mg (80%); mp 56–57 °C.

IR (KBr): 2248 cm$^{-1}$ (C=S).

Anal. Calcd. for C$_{35}$H$_{52}$NOS$_3$: C, 35.29; H, 2.37; N, 6.77. Found: C, 35.45; H, 2.48; N, 6.89.

Yield: 92%; yellow oil.

IR (KBr): 2920, 2865, 1554, 1469, 1409 cm$^{-1}$.

1H NMR (CDCl$_3$): δ = 2.95 (s, 4 H, SCH$_2$), 4.05 (s, 4 H, S CH$_2$ S), 6.64 [s, 2 H, CH=CS(S)].

MS (TOF): $m/z$ = 756 (M$^+$).

Anal. Calcd. for C$_{24}$H$_{32}$S$_{14}$O$_3$: C, 35.38; H, 3.20.

9 Yield: 69%; red-brown powder; mp 88–89 °C.

IR (KBr): 2921, 2850, 1555, 1485, 1426 cm$^{-1}$.

1H NMR (CDCl$_3$): δ = 1.22–1.38 (m, 16 H, CH$_2$), 1.48–1.72 (m, 4 H, CH$_2$), 2.43 (s, 12 H, SCH$_2$), 2.74 (t, J = 7.6 Hz, 4 H, S CH$_2$ S), 6.33 [s, 2 H, CH=CS(S)].

MS (TOF): $m/z$ = 822 (M$^+$).

Anal. Calcd. for C$_{38}$H$_{32}$S$_{14}$O$_3$: C, 40.84; H, 4.65. Found: C, 41.27; H, 4.71.

Compound 12

To a solution of TBA[Zn(dmit)$_2$] (940 mg, 1.0 mmol) in MeCN (50 mL), were added 1,5-dibromopentane (0.14 mL, 1.0 mmol) and pyridine hydrochloride (462.2 mg, 4.0 mmol). The mixture was heated to 50–60 °C and stirred for 2 h at this temperature. The resulting mixture was filtered hot and the remaining solid was further washed with CH$_2$Cl$_2$ (3 x 20 mL) for complete extraction of the

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product. The combined filtrate and washings were decolorized by use of activated charcoal. After removal of the solvent, column chromatography of the crude reaction mixture on silica gel with CH₂Cl₂–petroleum ether (1:4, v/v) as eluent afforded compound 1 as a yellow solid (72 mg, 18%); mp 80–82 °C.

IR (KBr): 1432, 1060, 1046 cm⁻¹.

¹H NMR (CDCl₃): δ = 1.60–1.90 (m, 6 H, CH₂CH₂CH₂), 2.85 (t, J = 7.2 Hz, 4 H, SCH₂), 7.02 [s, 2 H, CH=CS(S)].

MS (EI): m/z = 400 (M⁺).

Anal. Calcd for C₁₁H₁₂S₈: C, 33.97; H, 3.02, Found: C, 32.59; H, 2.79.

Compound 13
This was prepared according to the same procedure as above; yield: 21%; yellow powder; mp 72–73 °C.

IR (KBr): 1413, 1331, 1264, 1186, 1061 cm⁻¹.

¹H NMR (CDCl₃): δ = 2.01 (quint, J = 7.4 Hz, 2 H, CH₂), 2.93 (t, J = 7.4 Hz, 4 H, SCH₂), 7.07 [s, 2 H, CH=CS(S)].

MS (EI): m/z = 372 (M⁺).


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References