Direct Syntheses of Tetrathiafulvalene and Bis(ethylenedithio)tetrathiafulvalene By a Non-Coupling Route from 1,4,5,8-Tetrathianaphthalene

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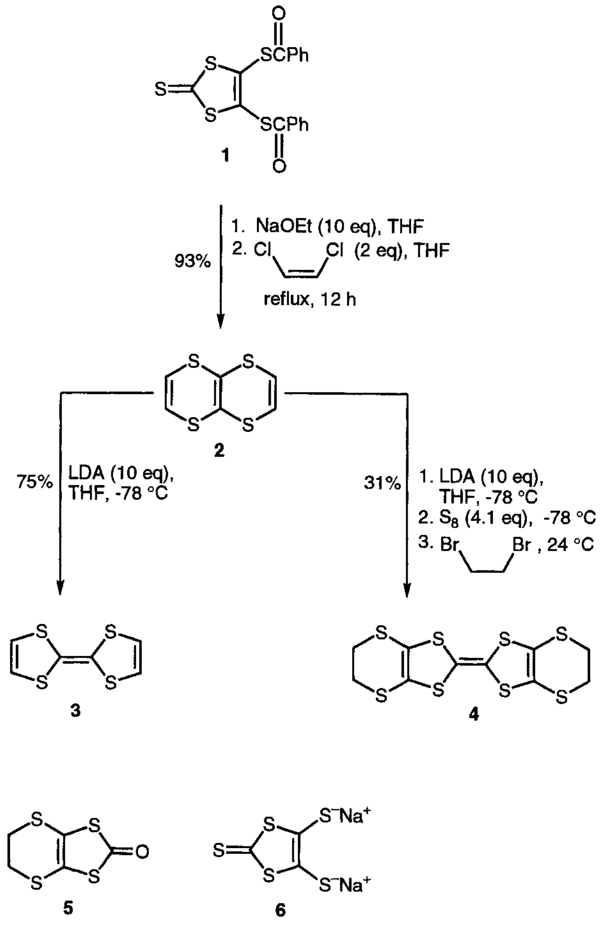
1,4,5,8-Tetrathianaphthalene (**2**, TTN; 1,4,5,8-tetrathiatetralin) has been synthesized in one step from 4,5-bis(benzoylthio)-1,3-dithiole-2-thione (**1**) and *cis*-dichloroethylene in high yield. TTN (**2**) is readily converted into tetrathiafulvalene (**3**, TTF) upon tetralithiation or bis(ethylenedithio)tetrathiafulvalene (**4**, BEDT-TTF) upon tetralithiation, sulfur insertion into the carbon–lithium bond pairs and subsequent capping of the reactive intermediate with 1,2-dibromoethane. The rearrangement of TTN allows for a facile synthesis of TTF and a novel non-coupling route to BEDT-TTF.

BEDT-TTF (2,2′-bi-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]-dithiinylidene) has been used in the preparation of at least 20 superconductors, thereby comprising the bulk of known organic superconducting molecular solids.[1,2] The most common syntheses of BEDT-TTF involve the multistep formation of 2-oxo-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin (**5**), which is coupled by refluxing in trialkyl phosphite/solvent.[3–5] Recently, Becher has reported a method whereby the precursor is coupled and then functionalized in order to yield BEDT-TTF.[6] In each case, a multistep procedure involving coupling is implemented. Alternative synthetic methods could facilitate the syntheses of known donors like BEDT-TTF or lead to the production of new materials sensitive to the coupling procedure.

Here we describe syntheses of TTF and BEDT-TTF which offer the following advantages: (i) easily attainable from inexpensive starting materials; (ii) short number of reaction steps; (iii) a precursor that is easily rearranged into TTF or BEDT-TTF.

The syntheses of TTN and BEDT-TTF are outlined in the Scheme. 4,5-Bis(benzoylthio)-1,3-dithiole-2-thione (**1**) was prepared according to published procedures.[7] TTN was originally synthesized by Cava, involving a multistep procedure starting with disodium 1,3-dithiole-2-thione-4,5-dithiolate (**6**) derived from the alkoxide ester cleavage of **1**, and culminating in a chromatographic separation.[8] More recently, TTN was prepared from **6** by refluxing with *cis*-dichloroethylene.[9] The disodium salt **6** was precipitated from a large volume of diethyl ether and was filtered using the Schlenk technique being stable under argon in the dark for only a few days.[7] Our synthesis comprises the coaddition of **1** and *cis*-dichloroethylene into gently refluxing THF containing dissolved excess sodium ethoxide. Presumably, **1** is cleaved at the thioester linkages, and the 1,3-dithiole-2-thione ring is ring opened to give byproducts $PhCO_2Et$ and $(EtO)_2C{=}S$, respectively, as well as the reactive tetrasodium salt of ethylenetetrathiolate. The ethylenetetrathiolate is nucleophilic enough to add *cis*-dichloroethylene 'side-on' to give a high yield of TTN. It should be noted that the other apparant isomer available upon addition (**3**, tetrathiafulvalene) is not detected by TLC or upon workup (NMR). The reaction provides a high yield (93 %) of TTN in a one-step reaction eliminating the need for air sensitive Schlenk techniques.



Scheme

TTN is a very useful starting material for other organic metals. Yoshida et al. reported that TTN could be electrochemically oxidized into tetrathiafulvalene.[10] More recently Anzai et al. stated that TTN could be converted into tetrathiafulvalene in 70 % yield via reaction with lithium diisopropylamide (LDA, >4 equiv).[11] We have subsequently verified the Anzai reaction and demonstrate that tetralithiated TTN can also be used to prepare BEDT-TTF. Upon tetralithiation of TTN with LDA at −78 °C in THF under N_2, elemental sulfur (sublimed, 4.1 equiv) was added to the reaction flask and warmed slowly to room temperature. The addition of excess 1,2-dibromoethane produced polymeric ethyl bridged tetrathiafulvalenetetrathiolate polymers/oligomers as well as BEDT-TTF. Simple Soxhlet extraction with carbon disulfide provided pure BEDT-TTF. The conversion of

TTN into BEDT-TTF is less an alternative synthesis of BEDT-TTF than a demonstration that inexpensive/easily attainable TTN can be used to synthesize tetrasubstituted tetrathiafulvalenes. Along with BEDT-TTF, we have successfully converted TTN into tetrakis(methylthio)tetrathiafulvalene,[11] tetrakis(benzylthio)tetrathiafulvalene[5] and tetrakis(cyanoethylthio)tetrathiafulvalene,[6] thereby demonstrating the potential scope of this synthetic method. The reaction scheme follows a number of studies on the reactivity of tetralithiated tetrathiafulvalene.[12-17] Chalcogen insertion into tetralithiated TTF can often give tetrachalcogenolato-TTF's, which can be alkylated with alkyl halides to give functionalized TTF tetrathioles.[12-17] Alkylation of tetrakis(chalcogeno)TTF's with alkyl dihalides to obtain BEDT-TTF and mixed chalcogen analogues was found not to be possible except for the modified synthesis of BEDSe-TTF[17] or when protecting groups were employed for chalcogen analogues of BEDT-TTF.[15]

The purification of BEDT-TTF has also been explored in this synthesis. BEDT-TTF is insoluble or poorly soluble in common solvents but it has been recrystallized from large volumes of chloroform or chlorobenzene.[3-5] We have found that homogeneous crystals (rods, 0.5 × 0.1 mm) can be obtained upon cooling from hot sulfolane (100 °C). Much larger homogeneous crystals (rods, 1.4 × 0.2 mm) were sequestered from hot thiophene upon slow cooling.

Because of the poor solubility of BEDT-TTF, solution NMR studies have been restricted to the proton site. We have been able to obtain solution ^{13}C NMR pertinent to our isomerization dependent synthesis using deuterated nitrobenzene as a lock solvent. At 80 °C, enough BEDT-TTF dissolves in $C_6D_5NO_2$ to obtain a singlet at $\delta = 30.62$ corresponding to the 4 equivalent ethyl carbons. Although differentiation between TTN and TTF required a 40 second delay between pulses to observe the central quaternary carbon peaks (assignments confirmed from undecoupled spectra), a 100 second relaxation delay failed to reveal any quaternary peaks in BEDT-TTF. The addition of chromium(III) acetylacetonate (5 mg) to a saturated BEDT-TTF/deuteronitrobenzene solution in a 5 mm tube (80 °C) revealed the 2 central quaternary carbon's peak at $\delta = 114.41$ using only a 5 second delay between pulses. The other 4 equivalent quaternary carbon's signal is buried in the lock solvent peaks as determined by solids NMR studies of related alkyl substituted tetrathiafulvalene tetrathioles.[18]

In summary, herein we have shown a simple synthesis of 1,4,5,8-tetrathianaphthalene: a valuable precursor that can be easily converted into tetrathiafulvalene or bis(ethylenedithio)tetrathiafulvalene. The utility of this method may be explored for the isomerization of other tetrachalcogenonaphthalenes.[19,20]

Melting points were obtained from Mel-Temp 2 apparatus and are uncorrected. NMR spectra were recorded on a Bruker MSL 300 spectrometer. Mass spectra were obtained from a Finnegan Mat TSQ 70. IR spectra were recorded with a BioRad 40S spectrometer. THF was distilled over Na/benzophenone prior to use.

1,4,5,8-Tetrathianaphthalene (2):
Fresh sodium (9.2 g, 400 mmol) was added to a 3-necked 2000 mL round bottom flask equipped with a stir bar, two 250 mL pressure equalizing funnels and a reflux column all under N_2. EtOH (200 mL) was added to the sodium through one of the addition funnels. After all of the sodium had reacted, THF (500 mL) was charged into the flask. 4,5-Bis(benzoylthio)-1,3-dithiole-2-thione (**1**; 16.24 g, 40 mmol) was dissolved in THF (250 mL) and added to one addition funnel, and *cis*-1,2-dichloroethylene (6.4 mL, 84 mmol) was dissolved in THF (250 mL) and added to the remaining dropping funnel. The two solutions were simultaneously added dropwise over a 4 h period to the NaOEt solution under gentle reflux with stirring. The thione **1** turned red upon reaction with the alkoxide solution, and the whole mixture turned yellow accompanied by a large amount of precipitate after allowing the reaction to reflux gently overnight. After cooling, H_2O (200 mL) was added to the flask, dissolving the precipitate and turning the solution a purple color. The THF (and some of the H_2O) was then removed by rotoevaporation to give a light brown-yellow solid. The solid was collected by vacuum filtration through a sintered glass funnel and washed with copious amounts of H_2O. The product was recrystallized from cyclohexane/hexane (5:3) to give yellow/orange crystals; yield: 7.60 g (93 %); mp 125–127 °C (Lit.[8] mp 125–126 °C).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 118.70$ (s, int. C=C), 125.39 (s, ext. C=C).

Tetrathiafulvalene (3).
BuLi (80 mL of a 2.5 M solution in hexanes, 200 mmol) was syringed (glass w/Teflon plunger) through a rubber septum into a solution of diisopropylamine (30 mL, 214 mmol) in anhyd THF (100 mL) in a 1000 mL round bottom flask with a stir bar at −78 °C (dry ice/propan-2-ol) under N_2 (purge through the rubber septum). After stirring the solution for 1 h, TTN (**2**; 4 g, 19.6 mmol) was dissolved in anhyd THF (400 mL) and added to a 500 mL pressure equalizing funnel and placed on top of the flask. N_2 was then transferred to the top of the funnel. The TTN was then added dropwise over a 4 h period to the LDA solution whereupon a brilliant yellow color persisted. The solution was stirred at −78 °C for 3 h and was then allowed to warm to 24 °C. After 30 min, H_2O (20 mL) was slowly added into the flask turning the mixture a yellow/amber color. The THF (and some of the H_2O) was then removed by rotoevaporation to give an orange/brown solid. The solid was collected by vacuum filtration through a glass sintered funnel and washed with copious amounts of H_2O. The product was recrystallized from cyclohexane/hexane (5:3) to afford orange/yellow crystals; yield: 2.98 g (75 %); mp 118–120 °C (Lit.[21] mp 119 °C).

^{13}C NMR ($CDCl_3$/TMS): $\delta = 110.10$ (s, int. C=C), 119.06 (s, ext. C=C).

Bis(ethylenedithio)tetrathiafulvalene (4):
TTN (4 g, 19.6 mmol) was tetralithiated exactly as described for the synthesis of **3**. After the solution of tetralithiated TTN was stirred at −78 °C for 3 h, the addition funnel was removed, and the N_2 (purge through a septum) was placed back in the round bottom flask. Sublimed sulfur (2.6 g, 81 mmol) was then added to the flask in one portion.[22] The resultant brown solution (solid materials) was stirred at −78 °C for 1 h and slowly allowed to warm to 24 °C overnight (Dewar kept in place w/o dry Ice replenishment). The following day, hexamethylphosphoric triamide (HMPA, 50 mL) was syringed into the flask at 24 °C.[17] One hour after HMPA addition, 1,2-dibromoethane (18 mL, 209 mmol) was slowly syringed (2 h) into the reaction flask quenching the reactive intermediates. Stirring was maintained for 1 d, whereupon the round bottom flask was condensed, and the solid orange-brown residue was Soxhlet-extracted with CS_2 (300 mL) to give an orange solution, which was subsequently rotoevaporated to give a bright red solid. BEDT-TTF was fully recrystallized from sulfolane (small crystals) or from thiophene (large crystals); yield: 2.30 g (31 %); mp 241–244 °C (dec.) (Lit.[4] mp 245–247 °C (dec.) The IR spectrum (KBr) was identical with an authentic sample (Aldrich).

^{13}C NMR ($C_6D_5NO_2$): $\delta = 30.62$ (s, CH_2CH_2), 114.41 (s, int. C=C), ext. C=C not visible (solvent).

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(22) Occasionally sulfur insertion can be difficult. If encountered, the sulfur can be dissolved in a minimal volume of CS_2 and then added to the reaction mixture.