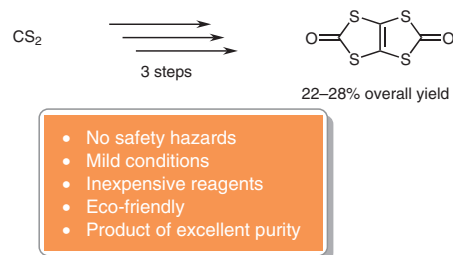# [1,3]-Dithiolo-[4,5-d][1,3-dithiole]-2,5-dione

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CS$_2$ →→→   3 steps   [product structure]

22–28% overall yield

- No safety hazards
- Mild conditions
- Inexpensive reagents
- Eco-friendly
- Product of excellent purity

Abstract   A safe, three-step reaction sequence to [1,3]-dithiolo-[4,5-d][1,3-dithiole]-2,5-dione starting from carbon disulfide is presented. Optimized reaction conditions, rigorous purification, and full characterization of all intermediates provide reproducibly a final product of superior quality with a melting point of 181 °C (dec.).

Key words   1,3,4,6-tetrathiapentalene-2,5-dione, thiapendione, 1,1,2,2-tetrathioethene, thermoelectricity, 2-oxo-1,3-dithiole-4,5-dithiolate, dmid

The importance of [1,3]-dithiolo-[4,5-d][1,3-dithiole]-2,5-dione (**1**; 1,3,4,6-tetrathiapentalene-2,5-dione or thiapendione, TPD for short), as synthetic building block for the preparation of organic solids with exciting physical properties, is paramount. TPD is used as precursor to bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET for short), the parent compound of many superconducting radical cation salts.[1,2]

ET can be obtained from **1** after two or three reaction steps, respectively, in good yield and excellent purity. The procedure is safe, operationally simple, and applicable to the preparation of other 4,5-disubstituted 1,3-dithiol-2-ones.[3a,b]

TPD is also the parent of linearly fused TTF analogues, the radical cation salts of which may display a metallic temperature dependence of the electrical conductivity or even superconducting properties.[4]

Compound **1** and aldehydes undergo a phosphite-mediated coupling reaction to 2,5-disubstituted tetrathiapentalenes, which can be transformed in a unique oxidative polymerization process to polymeric, vinylogous tetrathiafulvalenes.[5] Owing to their high sulfur content, such polymeric TTF derivatives could be of interest for the development of new materials with high refractive indices.[6]

TPD (**1**) has been employed extensively for the preparation of metal chelate complexes with the ligand 2-oxo-1,3-dithiole-4,5-dithiolate (dmid).[7] Cleavage of both rings of **1** gave closely related metal coordination polymers with interesting solid-state properties.[8,9]

Since a few years, macromolecular compounds based on the 1,1,2,2-tetrathioethene tetraanion and nickel as central metal have received enormous attention as starting materials for the manufacturing of high-performance thermoelectric materials.[10]

A recent publication on the use of **1** as precursor to thermoelectric devices emphasizes the need to use reagents of the highest purity possibly to avoid detrimental interferences and states this explicitly.[11] TPD is reported to be an off-white, crystalline solid. From commercial suppliers, it is an odorous, yellow powder that qualitatively darkens faster when treated with methoxide, thus necessitating its purification and recrystallization prior to performing the synthesis.[11]

The electrochemical behavior and the vibrational spectra of **1** were studied,[12,13] and the crystal structure was determined,[14] nevertheless reliable physicochemical data on **1** remain scarce. The reported melting points of **1** range from 121 °C to 181 °C (see Table 1), hence, purity and yields reported in the literature require clarification. In view of its synthetic relevance, **1** is a commercially available compound (Merck Aldrich, TCI, various Chinese suppliers), albeit at prohibitive cost, if needed continuously and in larger quantities.

Amazingly, a detailed experimental procedure for the preparation of **1** including a full account of the purification and characterization of all intermediates and the final product TPD has never been disclosed.
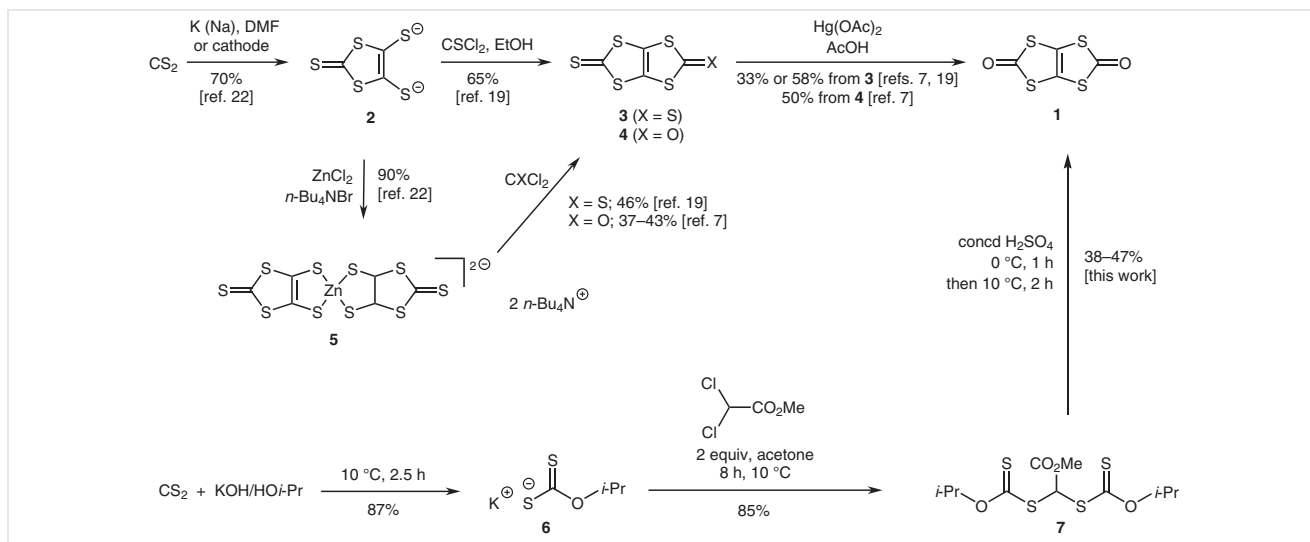
Scheme 1 Synthetic pathways to 1,3,4,6-tetrathiapentalene-2,5-dione (**1**)

For our investigations into the solid-state properties of TTF-based (super)conductors and oligo-/polymeric vinylogous TTF analogues as well as for application-oriented research,[5,15,16] we would like to depend on a reliable, safe, and environmentally friendly protocol for the continuous supply of compound **1** as precursor and key synthetic block. Accordingly, we wish to describe here a detailed protocol for the preparation of [1,3]-dithiolo-[4,5-*d*][1,3-dithiole]-2,5-dione (**1**). The approach is based on work communicated earlier,[17,18] and has been selected to avoid the potentially hazardous reduction of carbon disulfide, the use of mercury-based desulfurizing agents, and the constraints imposed by an electrochemical reduction process.

The synthesis of thiapendione was reported more or less simultaneously in 1977 by three different teams in preliminary communications.[7,17,19] Synthetic routes to the title compound together with the yields of individual reaction steps are depicted in Scheme 1. Overall yields, melting points, and selected analytical data of various approaches are summarized in Table 1.

Unsuccessful attempts to reduce CS_2 with sodium amalgam were reported as early as 1927.[20] Some fifty years later it was found that the electrochemical reduction of carbon disulfide yields actually the 1,3-dithiole-2-thione-4,5-dithiolate dianion **2** together with the trithiocarbonate dianion CS_3^{2-},[21] thus opening up a potential synthetic route to the title compound. In practice, the electrochemical reduction of carbon disulfide is limited to relatively small batch sizes.

The reduction of CS_2 with alkaline metals requires the presence of anhydrous DMF (or other aprotic co-solvents) to be of any preparative value and provides **2** in a yield of around 70%.[22,23]

The potential explosion hazard incurred by the reduction of CS_2 with group 1 elements, in particular potassium, restricts the choice of reducing agents to sodium.[23,24] Dianion **2** is known to undergo a thermal rearrangement to the corresponding 1,2-dithiole-3-thione.[25,26]

Treatment of **2** with thiophosgene and subsequent desulfurization of thione **3** with mercury(II) acetate/glacial acetic acid furnishes the title compound **1** after three reaction steps in a yield of 38%.[19] Similarly, reaction of the chelate complex **5** with phosgene or thiophosgene gives the

Table 1 Overall Yields and Melting Points of Thiapendione **1** as Reported in the Literature and this Work

Overall yield of **1** (%)	Mp (dec.) (°C)	Reference
38[a]	179–181	19
70–80[b]	150	17
57–65[c]	179–181	18
15/22[d]	176–180	7
42[b]	121–123	27
26–32[e]	174–181	this work
22–28[f]	174–181	this work

[a] The overall yield was calculated for CS_2 as starting compound. The yield of intermediate **2** was given as current efficiency = current yield for the cathodic reaction of CS_2.[19]
[b] As the authors did not disclose the source of precursor **6**, the overall yields refer to a two-step reaction sequence starting with xanthate **6**.
[c] Later, the same authors applied different reaction conditions, obtained lower yields, but a higher melting point.
[d] For details see text.
[e] The overall yields are based on xanthate **6** as starting compound and consider the actual product content of **7** (80%).
[f] The overall yields are given for CS_2 as starting product and consider the actual product content of **7**.

thiocarbonate **3** or **4**. Subsequent desulfurization with mercury(II) acetate provides **1** in overall yield of 15 and 22%, respectively (see Scheme 1).[7]

An alternative approach starts with the preparation of potassium isopropylxanthate (**6**) and gives **1** after alkylation with dichloroacetic acid methyl ester and subsequent cyclization of the resulting bisxanthate **7** in concentrated sulfuric acid.

An initial note claimed a yield of 70–80% for this three-step reaction sequence,[17] albeit the melting point reported was much lower than that of **1** prepared differently (see Table 1). Later, in another protocol, the same authors communicated a higher melting point, but significantly lower yields of **1**, without accounting for the obvious discrepancies.[18] A Chinese team revisited the same synthetic procedure, unfortunately without providing any details on analytical characterizations of intermediate and final product.[27] The overall yield reported amounts to around 42% of **1**, whereas the melting point of 121–123 °C appears to be abnormally low, when compared to other work (see Table 1).

Herein, we show that the experimentally simple, safe, three-step reaction sequence starting from carbon disulfide provides the title compound as an off-white, odorless solid of analytical purity. To elaborate a reliable experimental protocol, the reaction conditions for all individual steps have been checked repeatedly for reproducibility. Particular care has been taken to obtain complete spectroscopic and thermoanalytical data on intermediates and rigorously purified final products. A factorial 2^3 design approach was employed to explore the reaction conditions for the final cyclization step and to optimize yield and purity of the target compound **1**.

The first step of the reaction sequence starts with the preparation of potassium isopropylxanthate (**6**) from carbon disulfide and potassium hydroxide/*i*-PrOH. Compound **6** can be obtained in excellent yield on a molar scale. Crude **6** may contain small amounts (1–2%) of bright red impurities, which consist mainly of hydrated potassium carbonate, a typical by-product resulting from the hydrolysis of **6**; the red color is assigned tentatively to the presence of trithiocarbonates.[28] Purification through recrystallization or extraction gives **6** of analytical purity. The synthesis of **6** has been known for a long time,[29] a comprehensive characterization has been lacking, though. Like all xanthates, **6** is air- and moisture-sensitive and has only a limited shelf lifetime.

Treatment of **6** with dichloroacetic acid methyl ester in anhydrous acetone or acetonitrile at 10 °C or ambient temperature gave bisxanthate **7** as a transparent, yellow oil in a nominal yield of 85%. A higher reaction temperature (≥60 °C) reduced this value to 65% and resulted in a reddish coloration of the product. The latter finding is in line with observations made by Liu et al.,[27] and contrasts the quantitative yield reported earlier for this alkylation.[17] Regardless of the reaction temperature, the products obtained were not uniform as evidenced by TLC, NMR, and LC-MS assays. The averaged actual content of **7** varied as a function of T between 60 (T = 60 °C) and 80 mass% (T = 20 °C), respectively, as evidenced by quantitative ^{1}H NMR spectroscopy.

Compound **7** decomposes with evolution of gaseous products above temperatures of 130 to 135 °C (DSC) and cannot be distilled without degradation. The observed thermal instability is interpreted as propensity of **7** to undergo elimination reactions of the Chugaeff-type. An attempted high vacuum distillation (bp 36 °C/1.5×10^{-2} mbar) avoided thermal deterioration of **7** but failed to give a uniform product.

Similarly, attempted purifications of intermediate **7** by flash chromatography were unsuccessful. A chromatographically uniform product fraction contained not more than 80% of **7**, as shown by quantitative ^{1}H NMR assay. NMR spectroscopic data did not allow for an unambiguous identification of by-products. More obvious side reactions, such as the formal interchange of the thione sulfur and the ester oxygen of **7**, as anticipated for a Miyazaki–Neumann–Kwart rearrangement are not corroborated by the observed spectral features.[30]

A subsequent UHPLC-MS analysis confirmed the presence of target molecule **7** as main product, a result in line with quantitative NMR experiments. HRMS data allowed for the identification of a by-product with the empirical formula $C_{11}H_{18}O_4S_3$, albeit available spectroscopic information did not allow us to assign unambiguously a structure to the latter. As a scale-up of the chromatographic separation conditions is not accomplished readily, precursor **7** was used without further purification for the next reaction step.

Ring closure reactions of substituted isopropyldithiocarbonates in strong mineral acids such as $HClO_4$ or H_2SO_4 are known to give 1,3-dithiol-2-ones in good to excellent yields.[31] In certain cases, however, the cyclization fails or proceeds with poor yields only.[3a,32]

Cyclization of bisxanthate **7** in concentrated sulfuric acid as described in the literature provided **1** only in unsatisfactory yields.[17,18,27] Attempts to replace sulfuric acid with polyphosphoric or methanesulfonic acid proved unsuccessful; for safety reasons the use of large quantities of concentrated perchloric acid was not pursued.

A factorial 2^3 design approach with reaction temperature, addition time of reactant **7**, and overall reaction (residence) time as variables and the reaction yield as response was employed to explore and to improve possibly reaction conditions and the final yield of the title compound.

Attempts to monitor the progress of cyclization and to determine the in situ yield of **1** via quantitative UV/Vis spectroscopy or quantitative FT-IR assay (KBr pellets) gave not fully satisfactory results since the errors of measurement are non-negligible. Therefore, only reaction yields referring to recrystallized **1** were used as pertinent response.

The optimization approach suggests that only the overall residence time in concentrated sulfuric acid has a significant influence on the yield of the cyclization reaction, while the other parameters appear to be of little, if any influence.

The solid obtained after neutralization and drying of the reaction mixture is a complex mixture as evidenced by TLC, LC-MS, quantitative UV/Vis, and IR assays. Unidentified, red, soluble by-products can account for more than the half of the mass of the crude product.

Recrystallization of crude **1** from acidified glacial acetic acid with addition of charcoal gave by far the best results in terms of purity and yields. FT-IR spectroscopy turned out to be a valuable tool to monitor the purification process.

Typical cyclization yields using optimized reaction conditions amount to 38–47%. Analytically pure **1** consists of off-white, ivory-colored needle-type crystals. The compound does not display a defined, sharp melting point, but melts with decomposition between 174 and 181 °C. The first value indicates the begin of a color change from off-white to red-brown, while the latter value refers to the formation of a homogeneous, black melt (end point). These findings are in line with those of previous work and explain the large temperature interval reported in the literature.[7]

Obviously, melting points as low as 123 or 150 °C as reported by other groups cannot refer to the same product.[17,27]

It should be recalled that the melting of a pure compound relates to a reversible first order transition usually associated with a well-defined fusion temperature and enthalpy. By contrast, melting with decomposition refers to a somewhat ill-defined, thermodynamically irreversible process, which depends usually on the heating rate employed.[33] Therefore, in the present case, melting point determinations are not the method of choice to monitor the progress of the purification process or to check reliably the purity of **1**.

Differential Scanning Calorimetry (DSC) measurements on pure samples of **1** gave sharp, endothermic signals with extrapolated onset temperatures of 181.5 to 181.7 °C taken as melting point equivalents (decomposition).

The overall yields of **1** reported in the present work are far from being fully satisfactory (for a summary, see Table 1), but still acceptable in view of the constraints encountered in the effort to construct sulfur-rich heterocycles such as the title compound. Contrary to alternative procedures, there are no inherent methodological restrictions, there is no concern about safety issues and no need to handle extremely toxic or otherwise problematic chemicals. Liu et al. reported higher nominal yields,[27] in view of the melting point reported, however, the relevance of these figure remains questionable. Similarly, the yield claimed by the IBM team is remarkable,[17] but cannot refer to pure products in view of the melting point given.

In conclusion, the present work provides the first comprehensive, detailed, and reproducible experimental approach to 1,3,4,6-tetrathiapentalene-2,5-dione of high purity, indispensable for the use of **1** in the development of modern, advanced materials. Intermediate **7** could be obtained only as product of technical grade purity (80%). The presence of by-products reduces the overall yield and incurs losses during workup. This is the price to be paid for a final product of excellent purity. The experimental protocol reported here includes full analytical characterization data of all intermediates and the final product of the reaction sequence. The thermal behavior of **1** was investigated in detail in order to clarify the issue of widely diverging melting points reported in earlier work.

UV/Vis spectra were taken with a UV-3600 Plus UV/Vis/NIR spectrophotometer (Shimadzu), FT-IR data and ^{1}H and ^{13}C NMR were recorded with IFS 55 (Bruker) FT-IR and Inova 500 MHz (Varian) NMR spectrometers, respectively. Mass spectra were measured with Amazone Speed (ESI; Bruker) and 5977A-7890B (EI, Agilent) mass spectrometers, respectively, while an UPLC (U3000, Thermo Fisher Scientific) coupled to a quadrupole-TOF HRMS (Impact II, Bruker) was used for LC-MS. Chromatographic separations were performed with a Pure C 815 Flash system (Büchi) on Ecoflex columns packed with irregular silica gel 50 μm. Melting points were recorded with a M-565 apparatus (Büchi) and are uncorrected. Thermograms were recorded with a Pyris 1 Differential Scanning Calorimeter (PerkinElmer) at a heating rate of 10 K/min. KOH (powder; Merck), *i*-PrOH (anhyd, Acros), CS$_2$ (Aldrich), *t*-BuOMe (Aldrich), acetone (anhyd, Acros), methyl dichloroacetate, and concd H$_2$SO$_4$ (Aldrich) were used as received. The syntheses of potassium *O*-isopropyldithiocarbonate (**6**) and methyl 2,2-bis-(*O*-isopropyldithiocarboxy)acetate (**7**) were performed in inert atmosphere (argon).

Potassium *O*-Isopropyldithiocarbonate (6)

Finely powdered KOH (56 g, 1 mol) was suspended in anhyd *i*-PrOH (319 g, 5.3 mol) in a 1 L double-mantle reactor with mechanical stirrer connected to a cryothermostat and heated with stirring until a clear solution was formed (50 °C, 2.5 h). After cooling to 10 °C, CS$_2$ (76 g, 1 mol) was added slowly with stirring (1 h), which resulted in the formation of a reddish yellow, increasingly viscous reaction mixture. After the end of the addition, *t*-BuOMe (150 mL) was added and the reaction mixture was stirred (90 min) to complete precipitation of **6**. Bright red, viscous impurities were removed and *t*-BuOMe (200 mL) was added with stirring. After storage overnight (4 °C), the solid product was collected on a Büchner funnel, washed with *t*-BuOMe (5 × 50 mL), and dried in vacuo to give a reddish-yellow, crystalline solid in excellent yield (averaged yield of ten batches): 151.8 g (87%).

The purity of xanthate obtained according to above procedure is sufficient for further use, as spectroscopic and analytical data were satisfactory.

Hot extraction (*i*-PrOH, Knöfler–Böhm extractor, glass-cartridge with frit of porosity 0) was found to be an operationally simple and efficient procedure for the purification of larger quantities of crude xanthate (50 g). Extraction gave a product in excellent yield (>95%) and purity and allowed to remove insoluble, colored impurities (hydrated carbonate and minor trithiocarbonate).

Purified compound **6** is a pale-yellow solid sensitive to the presence of H_2O and O_2 and should be kept in inert atmosphere/vacuum. After storage for several months in standard sample vials, IR spectra showed a broad absorption at around 3500 cm^{-1}, indicating hydrolysis.

The product does not show a well-defined sharp melting point but starts to decompose above a temperature of around 220 °C (DSC). Classical melting point determinations show a first color change at around 205 °C, followed by gradual decomposition to a black melt between 215 and 220 °C; mp 215–220 °C (dec.).

IR (KBr): 2980, 2920, 2860, 1510, 1570 (s), 1185, 1150, 1150, 1050 (C=S, vs), 900 cm^{-1}.

^{1}H NMR (DMSO-d_6, 500 MHz): δ = 5.45 [sept, J = 6.25 Hz, 1 H, HC(CH$_3$)$_2$], 1.14 [d, J = 6.25 Hz, 6 H, HC(CH_3)$_2$].

^{13}C NMR (DMSO-d_6, 126 MHz): δ = 229.42 (C=S), 72.11 (HCO), 21.86 (CH$_3$).

MS (ESI): m/z (100%) = 134.9 [M$^-$ – K$^+$].

UV/Vis (MeOH): $λ_{max}$ (log ε) = 384 (1.73), 303.5 (4.27), 228 nm (4.02).

Anal. Calcd for C$_4$H$_7$KOS$_2$ (174.5): C, 27.56; H, 4.05. Found: C, 27.55; H, 4.03.

Methyl 2,2-Bis-(*O*-isopropyldithiocarboxy)acetate (7)

A solution of methyl dichloroacetate (49.16 g, 0.344 mol) in anhyd acetone (108 mL) was added dropwise with stirring under inert atmosphere to a suspension of potassium *O*-isopropyldithiocarbonate (**6**; 120 g, 0.688 mol) in anhyd acetone (480 mL) in a 1 L double-mantle reactor with mechanical stirrer connected to a cryothermostat (10 °C, 1 h). Xanthate **6** was prepared as described above and used without any further purification. Shortly after the beginning of the addition (ca. 30 min), a mildly exothermic reaction was observed. After the end of the addition, the reaction mixture was stirred at 10 °C (7 h) and left overnight at rt. The white precipitate (KCl) was removed by filtration and the solvent by evaporation. The resulting yellow oil was redissolved in hexane (300 mL) and filtered again. The solvent was stripped off at reduced pressure to give a light-yellow viscous liquid (average yield of ten batches: 103.9 g, 85%), which was used directly for the next reaction step.

The product is not uniform as evidenced by TLC [silica gel; CHCl$_3$/hexane (60:40), principal spot: R_f ≅ 0.58]. The actual content of **7** amounts on average to 80 mass%, as determined by quantitative ^{1}H NMR assays (internal standard: CH$_2$Br$_2$).

IR (ATR): 2980, 1740, 1450, 1570, 1540, 1255, 1080, 1020, 895 cm^{-1}.

^{1}H NMR (500 MHz, CDCl$_3$): δ = 5.99 (s, 1 H, SCHS), 5.70 [m, J = 6.25 Hz, 2 H, 2 × CH(CH$_3$)$_2$], 3.78 (s, 3 H, OCH$_3$), 1.37 [m, J = 6.25 Hz, 12 H, 2 × CH(CH_3)$_2$].

^{13}C NMR (126 MHz, CDCl$_3$): δ = 208.78 (C=S), 166.75 (C=O), 79.49 (HCO), 56.38 (OCH$_3$), 53.63 (SCHS), 21.08 (CH$_3$), 21.07 (CH$_3$).

MS (ESI): m/z = 365 [MNa$^+$], 343 [MH$^+$], 301 [MH$^+$ – C$_3$H$_6$], 259 [MH$^+$ – 2 × C$_3$H$_6$].

HRMS (ESI): m/z [MH$^+$] calcd for C$_{11}$H$_{19}$O$_4$S$_4$: 343.01607; found: 343.01586.

UV/Vis (hexane): $λ_{max}$ (log ε) = 348 (2.25), 283 (4.14), 220 (4.09), 196 nm (4.11).

[1,3]-Dithiolo-[4,5-*d*][1,3-dithiole]-2,5-dione (1)

Methyl 2,2-bis-(*O*-isopropyldithiocarboxy)acetate (**7**; 100 g, 0.29 mol) was dissolved in hexane (50 mL) and added dropwise via a syringe pump (1 h) to pre-cooled concd H$_2$SO$_4$ (540 mL, 0 °C) placed in a 1 L double-mantle reactor with mechanical stirrer connected to a cryothermostat. At the beginning of the addition, the reaction mixture was transparent and yellow, after around 50 min, the mixture became opaque and bright yellow. After the end of the addition, stirring was continued (2 h, 10 °C) and the homogenous reaction mixture was poured eventually in portions onto crushed ice (ca. 3.6 kg). The resulting suspension was stirred (10 min) and the ochre-colored precipitate collected on a Büchner funnel (fitted with acid-resistant glass-fiber filter paper). The solid obtained was washed thoroughly with H$_2$O (ca. 5 L) until the washings were neutral and give a negative reaction against aq BaCl$_2$. Drying in vacuo (12 h over silica gel and 18 h over P$_2$O$_5$) in the dark (product is light-sensitive!) provided a beige-brown, sticky solid. The crude product was suspended in a mixture of MeCN (500 mL) and concd H$_2$SO$_4$ (13 mL) and stirred (30 min) to remove soluble, red impurities. The mixture was collected on resistant filter paper to yield after drying (silica gel) an ochre-colored solid (60 g). The beige-brownish solid decomposed rapidly on standing (2–3 days). The solid was heated to reflux in a mixture of glacial AcOH (1450 mL), concd H$_2$SO$_4$ (6 mL), and charcoal (18 g), and filtered hot. Upon standing in the dark at rt, a precipitate formed which was collected on filter paper, rinsed with AcOH (5 mL), and dried in vacuo first over silica gel (12 h), then over solid KOH (48 h) to give a first crop of pure **1** as long, off-white needles; yield: 18.4 g (38%). Dilution of the mother liquor with half of the volume of demineralized H$_2$O gave a second crop of a fluffy, off-white crystalline solid (4.37 g), bringing the total yield of recrystallized product to 47%.

The calculation of the yield of the cyclization reaction is based on the actual reactant content (80%) of precursor **7** as outlined above.

Mp 174–181 °C (dec.); DSC (onset): 181.5–181.7 °C; a commercial sample (Sigma-Aldrich; Lot-Nr. EU 14213CQ) had mp 169–178 °C (dec.); DSC (onset): 180.3 °C.

IR (KBr): 1725, 1650 (C=O, vs), 986, 918, 720 cm^{-1} (s).

MS (EI, 70 eV): m/z = 208 (75, [M$^+$]), 180 (68), 152 (28), 120 (15), 88 (64), 76 (100).

UV/Vis (CH$_2$Cl$_2$): $λ_{max}$ (log ε) = 275 nm (3.77).

Anal. Calcd for C$_4$O$_2$S$_4$ (208.28): C, 23.06; S, 61.57; O, 15.36. Found: C, 22.98; S, 61.6; O, 15.6.

A commercial sample (Sigma-Aldrich; Lot-Nr. EU 14213CQ) gave: C, 23.08; S, 61.5.

Conflict of Interest

The authors declare no conflict of interest.

Funding Information

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1720891.

References

(1) Mizuno, A.; Garito, A.; Cava, M. P. *J. Chem. Soc., Chem. Commun.* **1978**, 18.

(2) For a recent review, see: Wosnitza, J. *J. Low Temp. Phys.* **2019**, *197*, 250.

(3) (a) Müller, H.; Ueba, Y. *Synthesis* **1993**, 853. (b) Müller, H.; Jouan, C.; Salhi, F. *Synth. Met.* **1997**, *85*, 1457.

(4) Misaki, Y. *Sci. Technol. Adv. Mater.* **2009**, *10*, 2.

(5) (a) Müller, H.; Salhi, F.; Divisia-Blohorn, B. *Tetrahedron Lett.* **1997**, *38*, 3215. (b) Müller, H.; Salhi, F.; Divisia-Blohorn, B.; Genoud, F.; Narayanan, T.; Lorenzen, M.; Ferrero, C. *Chem. Commun* **1999**, 1407. (c) Hapiot, P.; Salhi, F.; Divisia-Blohorn, B.; Müller, H. *J. Phys. Chem. A* **1999**, *103*, 11221.

(6) Boyd, D. A.; Nguyen, V. Q.; McClain, C. C.; Kung, F. H.; Baker, C. C.; Myers, J. D.; Hunt, M. P.; Kim, W.; Sanghera, J. S. *ACS Macro Lett.* **2019**, *8*, 113.

(7) (a) Poleschner, H.; John, W.; Kempe, G.; Hoyer, E.; Fanghänel, E. *Z. Chem.* **1978**, 345. (b) Poleschner, H.; John, W.; Hoppe, F.; Fanghänel, E. *J. Prakt. Chem.* **1983**, *325*, 957.

(8) (a) Vicente, R.; Ribas, J.; Cassoux, P.; Valade, L. *Synth. Met.* **1986**, *13*, 265. (b) Olk, R. M. W.; Dietzsch, W.; Köhler, K.; Kirmse, R.; Reinhold, J.; Hoyer, E.; Golic, L.; Olk, B. *Z. Anorg. Allg. Chem.* **1988**, *567*, 131. (c) Müller, H.; Puig Molina, A. P.; Narymbetov, B. Zh.; Zorina, L. V.; Khasanov, S. S.; Shibaeva, R. P. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1492.

(9) Xenikos, D. G.; Müller, H.; Jouan, C.; Sulpice, A.; Tholence, J. L. *Solid State Commun.* **1997**, *102*, 681.

(10) (a) Sun, Y.; Sheng, P.; Di, C.; Jiao, F.; Xu, W.; Qiu, D.; Zhu, D. B. *Adv. Mater.* **2012**, *24*, 932. (b) Sun, Y.; Qiu, L.; Tang, L.; Wang, H. G. H.; Zhang, F.; Xu, D. H. W.; Yue, P.; Guan, Y.; Jiao, F.; Sun, Y.; Tang, D.; Di, C.; Yi, Y.; Zhu, D. B. *Adv. Mater.* **2016**, *28*, 3351. (c) Menon, A. K.; Wolfe, R. M. W.; Kommandur, S.; Yee, S. K. *Adv. Funct. Mater.* **2018**, 1801620. (d) Toshima, N.; Oshima, K.; Shiraishi, Y. In *New Polymeric Materials Based on Element Blocks*; Chujo, Y., Ed.; Springer: Singapore, **2019**.

(11) Menon, A. K.; Wolfe, R. M. W.; Kommandur, S.; Yee, S. K. *Adv. Electron. Mater.* **2019**, 1800884.

(12) Falsig, M.; Lund, H. *Acta Chem. Scand., Ser. B* **1980**, *34*, 591.

(13) Ouyang, J.; Yakushi, K.; Kinoshita, T.; Nanbu, N.; Aoyagi, M.; Misaki, Y.; Tanaka, K. *Spectrochim. Acta. Part A* **2002**, *58*, 1643.

(14) Müller, H.; Averbuch, M.-T. *Acta Crysttallogr., Ser. C* **1998**, *55*, 590.

(15) Kartsovnik, M. V.; Zverev, V. N.; Andres, D.; Biberacher, W.; Helm, T.; Grigoriev, P. D.; Ramazashvili, R.; Kushch, N. D.; Müller, H. *Low Temp. Phys.* **2014**, *40*, 484.

(16) Müller, H.; Ueba, Y. (Sumitomo Electric Industries, Ltd.) EU Patent 0570927, **2003**.

(17) Schumaker, R. R.; Engler, E. M. *J. Am. Chem. Soc.* **1977**, *99*, 5521.

(18) Schumaker, R. R.; Lee, V. Y.; Engler, E. M. *J. Org. Chem.* **1984**, *49*, 565.

(19) Krug, W. P.; Bloch, A. N.; Cowan, D. O. *J. Chem. Soc., Chem. Commun.* **1977**, 660.

(20) Fetkenheuer, B.; Fetkenheuer, H.; Lecus, B. *Ber. Dtsch. Chem. Ges.* **1927**, *60*, 2528.

(21) (a) Wawzonek, S.; Heilmann, S. M. *J. Org. Chem.* **1974**, *39*, 511. (b) Bontempelli, G.; Magno, F.; Mazzochin, G.-A.; Seeber, R. *J. Electroanal. Chem.* **1975**, *63*, 231.

(22) (a) Steimecke, G.; Kirmse, R.; Hoyer, E. *Z. Chem.* **1975**, *15*, 28. (b) Steimecke, G.; Sieler, H.-J.; Kirmse, R.; Hoyer, E. *Phosphorus Sulfur* **1979**, *7*, 49.

(23) (a) Hartke, K.; Kissel, Th.; Quante, J.; Matusch, R. *Chem. Ber.* **1980**, *113*, 1898. (b) Varma, K. S.; Bury, A.; Harris, N. J.; Underhill, A. E. *Synthesis* **1987**, 837. (c) Reed, P. E.; Braam, J. M.; Sowa, L. M.; Barkhau, R. A.; Blackman, G. S.; Cox, D. D.; Ball, G. A.; Wang, H. H.; Williams, J. M. *Inorg. Synth.* **1989**, *26*, 386. (d) Hansen, T. K.; Becher, J.; Jørgensen, T.; Varma, K. S.; Khedekar, R.; Cava, M. P. *Org. Synth.* **1996**, *73*, 270. (e) Hansen, T. K.; Becher, J.; Jørgensen, T.; Varma, K. S.; Khedekar, R.; Cava, M. P. *Org. Synth. Coll. Vol. IX* **1998**; 203. (f) Wang, C.; Batsanov, A. S.; Bryce, M. R.; Howard, J. A. K. *Synthesis* **1998**, 1615.

(24) Moradpour, A.; Schumaker, R. R. *J. Chem. Educ.* **1986**, *63*, 1016.

(25) (a) Steimecke, G.; Sieler, H.-J.; Kirmse, R.; Dietzsch, W.; Hoyer, E. *Phosphorus Sulfur* **1982**, *12*, 237. (b) Beck, J.; Daniels, J.; Roloff, A.; Wagner, N. *Dalton Trans.* **2006**, 1174. (c) Even though reaction rates are appreciable only at elevated temperatures, a thermal transformation at lower temperatures cannot be excluded and may be another source of impurities. Solid state properties of synthetic metals are extremely susceptible to the presence of impurities at levels far below the detection limit of classical elemental analyses.[26]

(26) Müller, H.; Heidmann, C.-P.; Kellner, D.; Biberacher, W.; Andres, K. *Synth. Met.* **1990**, *39*, 261.

(27) Liu, S. G.; Wu, P. J.; Liu, Y. Q.; Zhu, D.-B. *Chin. Chem. Lett.* **1995**, *6*, 363.

(28) Schauenstein, E.; Treiber, E. *Melliand Textilber.* **1951**, *XXXII*, 44.

(29) Whitmore, W. F.; Lieber, E. D. *Ind. Eng. Chem.* **1935**, *7*, 127.

(30) (a) Frank, D.; Nieger, M.; Friedmann, C.; Lahann, J.; Bräse, S. *Isr. J. Chem.* **2012**, *52*, 143. (b) Zonta, C.; De Lucchi, O.; Volpicelli, R.; Cotarca, L. *Top. Curr. Chem.* **2007**, *275*, 131.

(31) Bhattacharya, A. K.; Hortmann, A. G. *J. Org. Chem.* **1974**, *39*, 95.

(32) Müller, H.; Fritz, H. P.; Nemetschek, R.; Hackl, R.; Biberacher, W.; Heidmann, C. P. *Z. Naturforsch., B* **1992**, *47*, 718.

(33) Rosenblum, E. I.; Taylor, W. S. *J. Pharm. Pharmacol.* **1954**, *6*, 656.