The Chemistry of C_6S_{10}: a Channel Structure for $C_6S_{10}(CS_2)_{0.5}$ and Access to the Versatile DMAD·C_3S_4O (DMAD = dimethylacetylenedicarboxylate)

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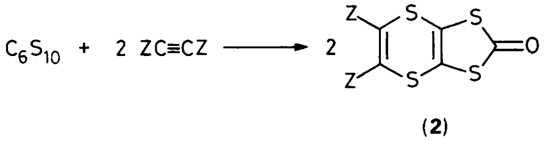
Treatment of $(Et_4N)_2[Zn(C_3S_5)_2]$ with SO_2Cl_2 gives molecular C_6S_{10} (1), structurally characterized as (1)·$(CS_2)_{0.5}$, which has a channel structure; a two step conversion affords bicyclic tetrathiaindenone $OC_3S_4{\cdot}C_2(CO_2Me)_2$ which is used to make new alkenedithiolate derivatives.

The carbon sulphides are a lightly studied family of molecular compounds with simple stoicheiometries. In our previous contribution to this area we described the sequence $[Zn(C_3S_5)_2]^{2-} \rightarrow (C_5H_5)_2TiC_3S_5 \rightarrow C_3S_8 + C_6S_{12}$.[1] We now report the preparation of the new carbon sulphide C_6S_{10} directly from the zinc reagent.[2] Preliminary experiments show that C_6S_{10} is a useful precursor to dithiacyclopentenone derivatives.

Compound (1), C_6S_{10}, was prepared as follows. An acetonitrile solution of SO_2Cl_2 (379 mg, 2.81 mmol in 50 ml) was added dropwise to a −40 °C solution containing $(Et_4N)_2[Zn(C_3S_5)_2]^2$ (1 g, 1.405 mmol) in acetonitrile (100 ml). Gas was evolved and an orange precipitate quickly formed. After warming the reaction mixture to room temperature, the solids were filtered and washed with acetonitrile, methanol, and water. Compound (1) was extracted from this crude product with CS_2 (300 ml), evaporation of which gave a 46% yield of analytically pure orange microcrystals of the CS_2 solvate.† The relative proportion of the CS_2-insoluble fraction increased when the reaction was conducted at higher temperatures. The insoluble material was an uncharacterized carbon sulphide tentatively formulated as $[C_3S_x]_n$. We propose that the synthesis of (1) proceeds according to equation (1).

$$Zn(C_3S_5)_2{}^{2-} + 2\,SO_2Cl_2 \rightarrow ZnCl_4{}^{2-} + C_6S_{10} + 2\,SO_2 \qquad (1)$$

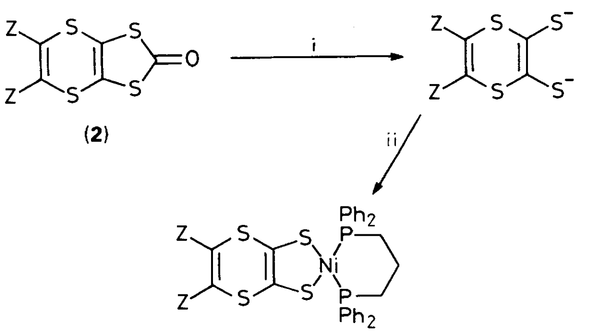
Compound (1) is soluble in CS_2 (275 mg/100 ml). Reverse phase HPLC on C_{18}-silica gel distinguishes it from S_8, C_3S_8, and C_6S_{12}. Its IR spectrum is very simple with a weak $\nu_{C=C}$ (1504 cm^{-1}), strong $\nu_{C=S}$ (1056 cm^{-1}), and moderately intense ν_{S-S} (505, 467, 447 cm^{-1}). The molecular structure‡ of the CS_2 solvate of (1) confirms the presence of two planar C_3S_5 subunits interconnected by persulphide bonds. Centrosymmetry is crystallographically imposed. The S_4 and the C_3S_5 planes are connected by 101° angles (Figure 1). The monoclinic lattice of (1)·$(CS_2)_{0.5}$ consists of layers formed by stacking of C_3S_5 rings (distance between C_3S_5 rings is *ca.* 3.5 Å) such that each C_6S_{10} molecule engages in π-π-interactions with four other C_6S_{10} molecules. The sheets thus formed are joined by S· · ·S contacts (3.83 Å) between thione groups. This interconnection pattern defines an array of infinite channels along the *c* axis in which CS_2 molecules half occupy symmetry related sites with co-ordinates (0, 1/2, 0), (1/2, 0, 1/2), (0, 1/2, 1/2), and (1/2, 0, 0) (Figure 2).



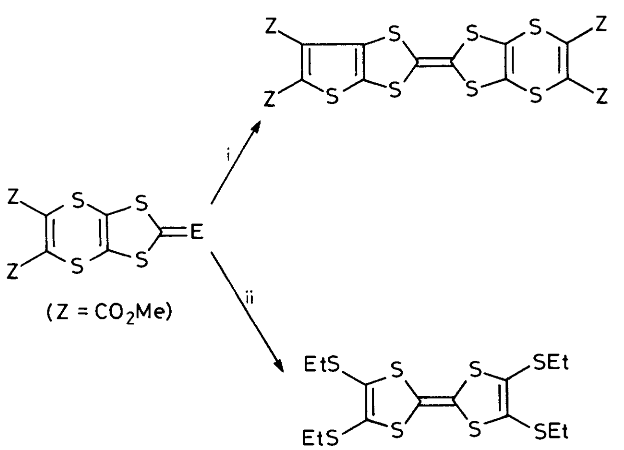
(2)

(Z = CO_2Me)

Scheme 1. *Reagents*: Bu_3P, Hg^{2+}.



Scheme 2. *Reagents and conditions*: i, 2 equiv. NaOMe in MeOH, 5 min; ii, $NiCl_2(dppp)$.



Scheme 3. *Reagents and conditions*: i, E=S, 3—4 equiv. PPh_3, toluene; ii, E=O, $P(OEt_3)$ neat.

Compound (1) is the oxidatively coupled dimer of $C_3S_5{}^{2-}$, also known as dmit.[3] As such (1) is chemically related to other 1,2,5,6-tetrathiacyclo-octadienes such as the dibenzo derivative $(1,2\text{-}C_6H_4)_2S_4$ and 1,2,5,6-$[(CF_3)_2C_2]_2S_4$, the dimer of 1,2-bis(trifluoromethyl)dithiete.[4] The disulphide character of (1) is indicated by its reaction with $(NEt_4)_2[Zn(C_3S_5)_2]$ and $VCl_3(thf)_3$ (thf = tetrahydrofuran) to give the recently reported $(Et_4N)_2[V(C_3S_5)_3]$ in 45% yield.[5]

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† Satisfactory analytical data were obtained. EI MS: 328 (M^+ − 2S)

‡ *Crystal data* for $C_6S_{10}{\cdot}1/2(CS_2)$: transparent orange columnar crystal, 0.2 × 0.2 × 0.60 mm, monoclinic, *C2/c* ($C_{2h}{}^6$ - No. 15); $a = 18.271(6)$, $b = 10.784(4)$, $c = 7.246(2)$ Å, $\beta = 95.26(2)°$, $U = 1422(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.011$ g cm^{-3}. Diffraction data: Enraf-Nonius CAD4 automated κ-axis diffractometer, Mo radiation ($K_\alpha = 0.71073$ Å). The crystal was mounted using oil (Paratone-N, Exxon) to a thin glass fibre and data were collected at −75 °C, range $2.0 < 2\theta < 46.0°$ for $\pm h - k - l$ ($h + k = 2n$) and corrected for dispersion, absorption, Lorentz, and polarization effects. Least-squares refinement of 881 reflections converged at $R = 0.020$ and $R_w = 0.025$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

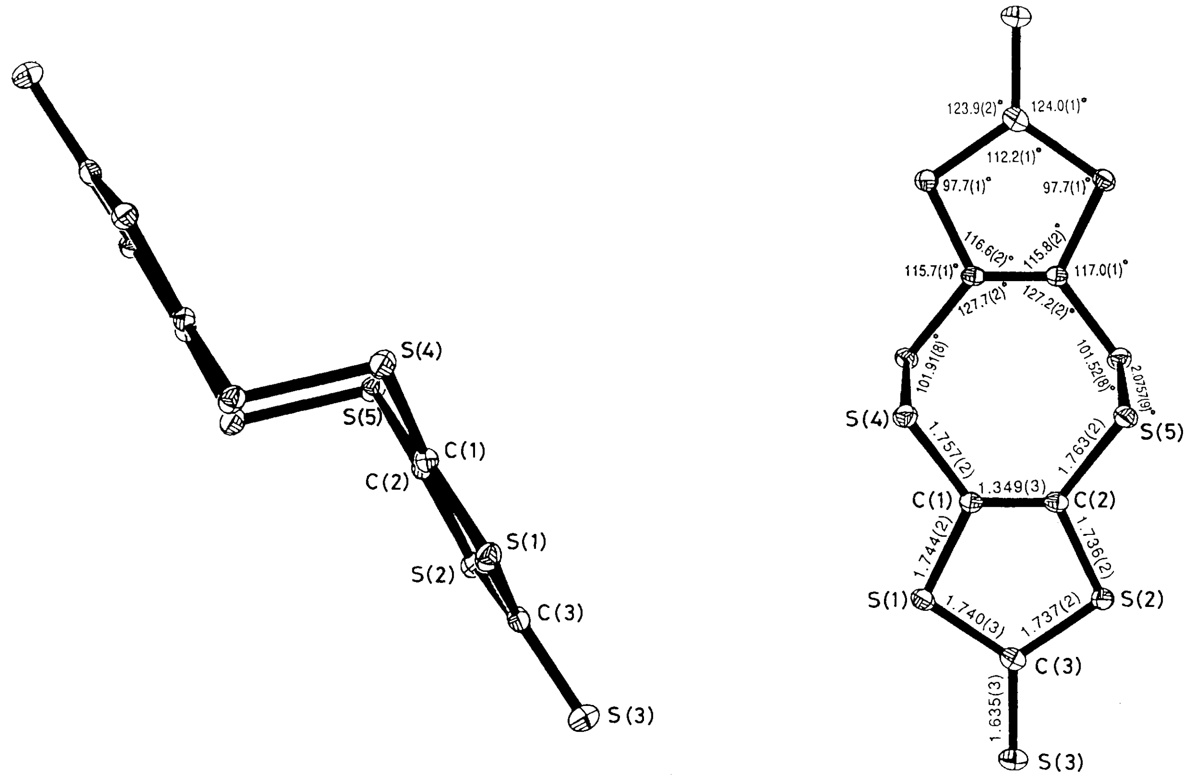

Figure 1. Molecular structure of C_6S_{10}.

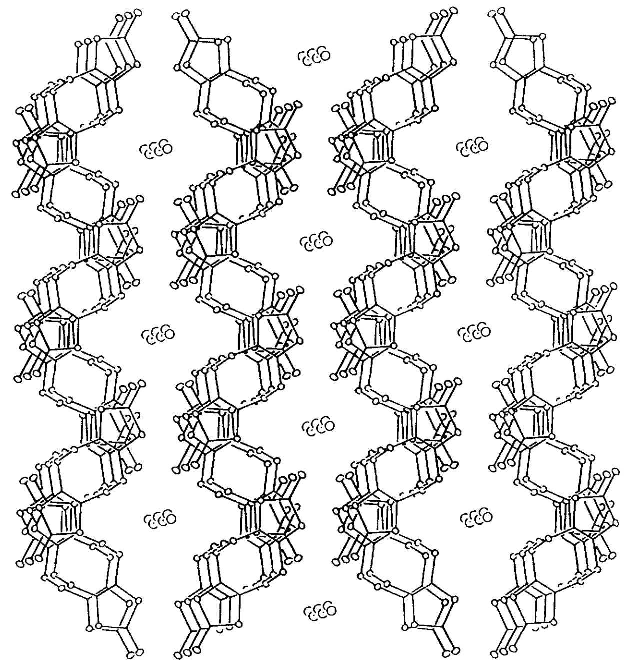

Figure 2. View of the $C_6S_{10}{\cdot}(CS_2)_{0.5}$ lattice looking approximately down the *c* axis.

Compound (**1**) is an excellent precursor to the tetrathiaindenethione *via* the PBu_3-catalysed reaction with two equiv. of dimethylacetylenedicarboxylate (DMAD) in CH_2Cl_2 at room temperature. The thione is obtained in 65% yield as yellow crystals after chromatography with SiO_2 and recrystallization from $CHCl_3/MeOH$ [also formed in this reaction is a compound $(DMAD)_2{\cdot}C_3S_5$ which will be described separately]. This improved[1] procedure can be conducted on a multigram scale and is not very sensitive to the purity of (**1**). For example the polymer $(C_3S_x)_n$ can be used in this synthesis. This thione is quantitatively converted to the carbonyl derivative (**2**) by treatment with an excess of $Hg(O_3CCF_3)_2$ (1.2 equiv.) in 5 : 1 $CHCl_3$–acetic acid [240 ml g^{-1} (**2**); 25 °C; 1 h] (Scheme 1). Compound (**2**)§ is a precursor to the alkenedithiolate abbreviated $DMAD{\cdot}C_2S_4^{2-}$, Scheme 2. The ligand chemistry of its half saturated analogue $C_2H_4{\cdot}C_2S_4^{2-}$ has been the subject of recent work by Bereman and co-workers.[6] Treatment of $DMAD{\cdot}C_2S_4^{2-}$ with $NiCl_2$ (dppp) [dppe = $1,3\text{-}(Ph_2P)_2C_3H_6$] affords the yellow green dithiolene complex $Ni(DMAD{\cdot}C_2S_4)(dppp)$. Preliminary studies suggest that this complexation method may be general.

As expected $DMAD{\cdot}C_3S_5$ and $DMAD{\cdot}C_3S_4O$ are precursors to tetrathiafulvalene (TTF) derivatives but the chemistry is unusual due to the intervening reactivity of the electrophilic alkene backbone. Thus treatment of refluxing toluene solutions of the thione with 3—4 equiv. of PPh_3 affords an unsymmetrical tetrathiafulvalene in 43—48% yield (Scheme 3). This unexpected product was characterized by elemental analysis and high resolution EI MS (m/z = 579.8583; calcd for M $C_{18}H_{12}O_8S_7$ = 579.8577). This compound is unreactive

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§ *Selected spectroscopic data* for $OC_3S_4C_2(CO_2Me)_2$: EI MS (70 eV): 322 (M^+), 294 (M^+ – CO); IR(KBr): $\nu_{C=O}$ = 1674, 1638, 1615 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.87. $NiS_4C_2(CO_2Me)_2(dppp){\cdot}CH_2Cl_2$: ^1H NMR (CD_2Cl_2) δ 2.20 (quintet, 2H), 2.44 (t, 4H), 3.71 [s, 6H, (OCH_3)], 5.33 [s, 2H, (CH_2Cl_2)], 7.35—7.57 (m, 20H); field desorption (FD) MS: m/z 766 (M^+). $C_{10}S_7(CO_2Me)_4$: EI MS: m/z 580 (M^+, 100), 548 (M^+ –S, 15), 522 (M^+ $-CO_2CH_2$, 15); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.96 (s, 3H), 3.88 (s, 3H), 3.85 (s, 6H). $C_6S_4(SEt)_4$: EI MS: 444 (M^+); ^1H NMR ($CDCl_3$) δ 2.85 (q, 8H), 1.32 (t, 12H). E_p(MeCN, TBAHFP, Ag/AgCl) 0.516, 0.833 V.

towards PPh_3 and the reaction of the thione with only one equivalent of PPh_3 gave only a poor yield of the TTF compound together with unreacted thione. The 500 MHz ^1H NMR spectrum of this material shows three methyl resonances in the ratio of 1 : 1 : 2. Characteristic of other TTF derivatives,[7] this compound undergoes two reversible 1e oxidations as shown by cyclic voltammetry (+0.811 and 1.185 V *vs.* Ag/AgCl in MeCN, 0.1 M Bu_4NPF_6).

Reaction of the oxo derivative (**2**) with $P(OEt)_3$ affords a 38% yield of $(EtS)_4(TTF)$,[8] a relative of the topical bis(ethylenedithiolato)tetrathiafulvalene.[9] We suggest that this reaction proceeds *via* an Arbusov rearrangement following attack of the phosphorus at the electrophilic CO_2Me-substituted alkene.

To summarize, the readily available compound $(Et_4N)_2[Zn(C_3S_5)_2]$ can be directly converted to C_6S_{10} which in turn is an excellent precursor to new alkene-1,2-dithiolates. The recent preparation[10] of a second isomer of $C_3S_5^{2-}$ presents further opportunities in binary carbon sulphide chemistry. These results will be described in a future report.

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References

1 X. Yang, T. B. Rauchfuss, and S. R. Wilson, *J. Am. Chem. Soc*, 1989, **111**, 3465.

2 G. Steimecke, H.-J. Sieler, R. Kirmse, and E. Hoyer, *Phosphorus Sulfur*, 1979, **7**, 49.

3 S. Alvarez, R. Vicente, and R. Hoffmann, *J. Am. Chem. Soc.*, 1985, **107**, 6253; M. Bousseau, L. Valade, J.-P. Legros, P. Cassoux, M. Garbauskas, and L. Interrante, *J. Am. Chem. Soc.*, 1986, **108**, 1908; W. E. Broderick, M. E. McGee, M. R. Godfrey, B. M. Hoffman, and J. A. Ibers, *Inorg. Chem.*, 1989, **28**, 2902.

4 C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Am. Chem. Soc.*, 1960, **82**, 1515.

5 G.-T. Matsubayashi, K. Akiba, and T. Tanaka, *Inorg. Chem.*, 1988, **27**, 4744.

6 J. H. Welch, R. D. Bereman, J. Bordner, W. Hatfield, and J. H. Helms, *Inorg. Chem.*, 1985, **24**, 2905.

7 W. Chen, M. P. Cava, M. A. Takassi, and R. M. Metzger, *J. Am. Chem. Soc.*, 1988, **110**, 790.

8 K. Imaeda, T. Enoki, Z. Shi, P. Wu, N. Okada, H. Yamochi, G. Saito, H. Inokuchi, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 3163; G. Saito, *Pure Appl. Chem.*, 1987, **59**, 999.

9 J. R. Ferraro and J. M. Williams, 'Introduction to Synthetic Electrical Conductors,' Academic Press, New York, 1987.

10 G. Steimecke, H.-J. Sieler, R. Kirmse, W. Dietzsch, and E. Hoyer, *Phosphorus Sulfur*, 1982, **12**, 237.