

$C_4S_8^{2-}$ and $C_{16}S_{18}^{4-}$: Intermediates in the Synthesis of Poly(Carbon Sulfide)

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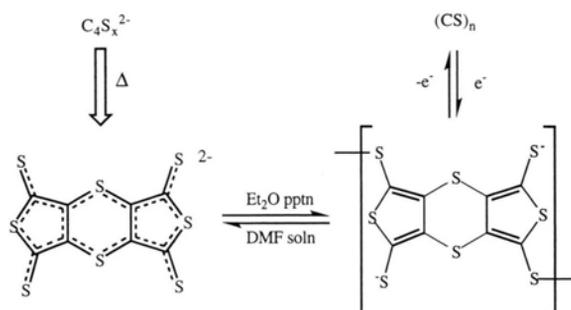
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Sulfur, Carbon Sulfides, Inorganic Polymer,
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$(PPN)_2C_{16}S_{18}$ was obtained by the addition of PPN^+Cl^- to a methanolic extract of $Na_2C_4S_x$, derived from the reaction of $C_6S_8O_2$ and NaOMe. Centrosymmetric $C_{16}S_{18}^{4-}$ consists of thiophene units unsymmetrically fused to two 1,4-dithiin rings. Solutions of $C_{16}S_{18}^{4-}$ convert to $C_8S_8^{2-}$ with heating. When C_4S_x ($x \sim 8$) is reduced by Na/ NH_3 followed by extraction and crystallization, one obtains the bicyclic polysulfide $C_4S_8^{2-}$, crystallized as its PPH_4^+ salt.

The chemistry of inorganic polymers is a topical theme [1]. Our most recent contribution to this area involved the preparation of crystalline forms of carbon monosulfide *via* the condensation of sulfided butadiene precursors [2]. An important aspect of that work was the use of kinetically stable C_4 building blocks to give carbon sulfides with identifiable C_4 subunits (Scheme 1).

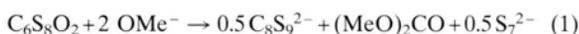


Scheme 1

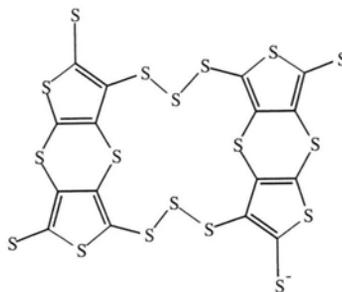
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In contrast to our method, materials produced by usual solvothermal processes bear only coincidental resemblance to their precursors [3]. The use of kinetically stable $C_nS_m^{2-}$ precursors lends a degree of predictability to the design of inorganic materials [4]. The building block approach [5] also facilitates mechanistic studies on the assembly process. In the course of these mechanistic efforts we have isolated a salt of $C_{16}S_{18}^{4-}$, the largest known carbon sulfide.

The polymer $(C_8S_8^{2-})_n$ (**1**) is obtained in a two step process starting with the base hydrolysis of the tricyclic bis(dithiocarbonate) $C_6S_8O_2$ [6] which gives $Na_2C_4S_n$ [1]. Addition of PPh_4Cl to these solutions gives $(PPh_4)_2C_4S_n$ which upon heating at $80^\circ C$ is converted in **1** [1]. The PPh_4^+ salt of $C_4S_n^{2-}$ does not crystallize well, but the corresponding PPN^+ salt gives well-formed black crystals. The crystallographic analysis confirms that this material has the empirical formula $(PPN)C_4S_{4.5}$ which indicates that the base hydrolysis of the $C_6S_8O_2$ proceeds according to eq (1).



With the formula $C_{16}S_{18}^{4-}$, **2** is the largest carbon sulfide to be characterized (Fig. 1). It consists of two $C_8S_8^{2-}$ subunits linked by trisulfide chains. All atoms in the centrosymmetric species obey the octet rule provided that negative charges are assigned to the four terminal S atoms:



Like **1**, anion **2** is built up from condensed thiophene tetrathiolate units. The connectivities in **1** and **2** differ, although the formula, charge, and the general topology of the $C_8S_8^{2-}$ subunits are similar. In **1**, the C_8S_8 unit has idealized D_{2h} symmetry by virtue of the symmetrical fusion of the thiophenetetrathiolates at the 3,4-positions. In contrast, the two thiophene units in **2** are not fused equivalently to the central dithiin – both 3,4 and 2,3 fusions are observed. Since **2** is obtained under



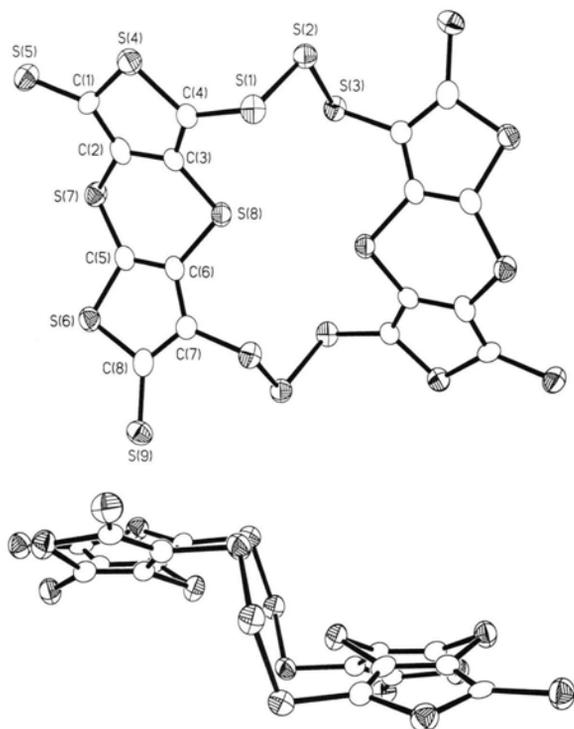
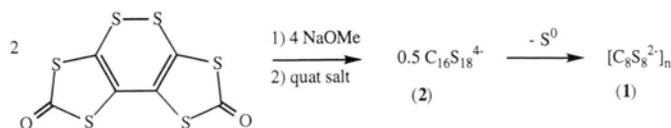


Fig. 1. Two views of the $C_{16}S_{18}^{4-}$ (**2**) anion in $(PPN)_4C_{16}S_{18}$ with thermal ellipsoids drawn at the 50% probability level. Selected distances (Å): S1–C4, 1.734(5); S3–C7, 1.749(5); S4–C4, 1.751(5); S4–C1, 1.785(5); S5–C1, 1.695(5); S6–C5, 1.734(5); S6–C8, 1.759(5); S7–C5, 1.756(5); S7–C2, 1.767(5); S8–C3, 1.767(5); S8–C6, 1.771(5); S9–C8, 1.676(5); C1–C2, 1.378(7); C2–C3, 1.415(6); C3–C4, 1.387(6); C5–C6, 1.358(6); C6–C7, 1.435(7); C7–C8, 1.412(6). Selected angles ($^\circ$): C4–S1–S2, 107.0(2); S3–S2–S1, 108.97(8); C7–S3–S2, 104.9(2); C4–S4–C1, 93.1(2); C5–S6–C8, 94.0(2); C5–S7–C2, 99.4(2); C3–S8–C6, 100.0(2). The bending angle of the central 1,4-dithiin ring is 41.4(2) $^\circ$.

mild conditions (no heating, only cation exchange), it is clear that the thiophene ring, also seen in **1**, forms under very mild conditions.

We confirmed that anion **2** is an efficient precursor to **1** (Scheme 2). Heating a methanolic suspension of $(PPN)_4$ **2** at 80 $^\circ$ C for 12 h (conditions used for the conversion of $(PPh_4)_2C_4S_x$ into **1** [1]), gives the $C_8S_8^{2-}$ ion, which spontaneously polymerizes upon crystallization. This conversion was established by comparison of UV-Vis spectra of DMF



Scheme 2

solutions (wherein $(C_8S_8^{2-})_n$ is dissociated [1]) which allows unambiguous identification due to the fine structure in the range 300–820 nm (λ_{max} = 332, 360 (sh), 428 (sh), 442, 596 nm).

The structure of an alternative, but less efficient precursor to **1** was also investigated. These results provide a fuller picture of the role that C:S stoichiometry plays in the condensation process. The second precursor is obtained by the sodium-ammonia reduction of C_4S_x ($6 \leq x \leq 8$), itself obtained by the reaction of Na_2S_5 with hexachlorobutadiene [8]. Cation exchange with PPh_4Cl gave $(PPh_4)_2C_4S_x$ which crystallizes from MeCN–Et₂O solution. The related PPN^+ salt was prepared analogously. These are salts of $C_4S_8^{2-}$ (**3**). Crystallographic analysis of $(PPh_4)_2$ (**3**) revealed a thiophene derivative where the 2,5 positions are occupied by terminal thiolato groups and the 3,4 positions are linked to a polysulfide chain (Fig. 2). This bicyclic species features a chair-shaped seven-membered C_2S_5 ring [9] fused to a planar thiophene. With S/C = 2, anion **3** is more sulfur-rich than **1** (S/C = 1); it is thus understandable that **3** converts to **1** less rapidly than does **2** (S/C = 1.125).

The results presented herein help to establish the condensation pathways from small precursors to polycarbon sulfides. At a conceptual level, the process finds some analogies in silicate condensation although redox process are more important for the carbon sulfides. We see that high S/C ratios inhibit the polymerization process due to the formation of polysulfido rings as seen in $C_4S_8^{2-}$. This may be important in the design of new materials derived from carbon sulfides since they should not be very S-rich. The synthesis of $(C_8S_8^{2-})_n$ from sulfided butadienes involves the formation of thiophenetetrathiolate derivatives which condense to give an unsymmetrical tricyclic dithiin which in turn rearranges in the final stages with elimination of elemental sulfur. While the lability of the S–S bonds was expected, we were surprised to find that the C–S bonds are readily made and broken. The ability of C–S bonds to anneal under mild conditions, together with the stability of the C–C bonds in the C_4 core, suggests that sulfided carbon compounds have further potential as building blocks in materials synthesis.

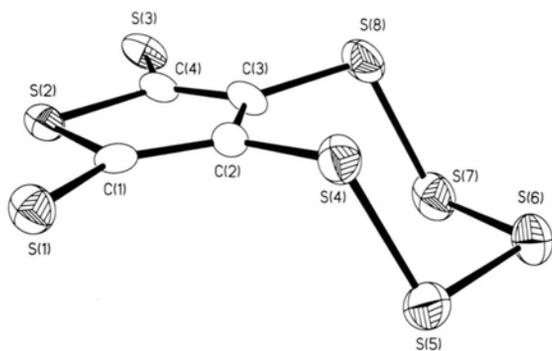


Fig. 2. Structure of the $C_4S_8^{2-}$ (**3**) anion in $(PPh_4)_2C_4S_8$ with thermal ellipsoids drawn at the 25% probability level. Selected distances (Å): S1–C1, 1.711(9); S2–C4, 1.760(9); S2–C2, 1.760(8); S3–C4, 1.718(9); S4–C2, 1.731(9); S8–C3, 1.737(9); C1–C2, 1.38(1); C2–C3, 1.46(1); C3–C4, 1.39(1); S–S (mean), 2.063(4). Selected angles ($^\circ$): C4–S2–C1, 95.0(4); C2–S4–S5, 105.5(3); S4–S5–S6, 106.1(2); S7–S6–S5, 105.1(2); S6–S7–S8, 103.5(2); C3–S8–S7, 105.0(3).

Experimental

$(Ph_4P)_2[C_4S_8]$

C_4S_6 was prepared according to Fanghanel's procedure [8]. This material, 17.82 g, was reduced by 2 equiv of Na in 250 ml of NH_3 at $-33^\circ C$ for 1 h. The resulting dark brown colored solution was allowed to evaporate. Some of the resulting $Na_2C_4S_8$, 0.286 g (~ 1 mmol) was dissolved in 30 ml of H_2O . This solution was treated with a solution of 0.75 g of Ph_4PCl in 15 ml of water to give an orange brown solid. The solid was collected through filtration and then extracted into CH_3CN and the solution was filtered to remove any solids. The careful addition of Et_2O gave large purple-red crystals. Yield: 0.682 g (69%). IR (KBr): 527, 688, 722, 750, 811, 942, 995, 1107, 1188, 1350, 1434, 1482, 1583, 3051 cm^{-1} . This material was identified by single crystal X-ray diffraction.

$(PPN)_4[C_{16}S_{18}]$

A suspension of 0.296 g (1 mmol) of $C_6S_6O_2$ in 30 ml of MeOH was treated with a fresh solution of NaOMe in 10 ml of MeOH (prepared from 0.092 g of Na). The orange suspension quickly dissolved to give a dark brown solution. After stirring for 3 days, 1.22 g of solid PPNCl was added. The solution was stirred for additional 24 h. Solvent was removed under reduced pressure to give a dark brown residue. This material was extracted into ~ 30 ml of DMF, which was filtered to remove NaCl. The product was crystallized by layering the

DMF with Et_2O to give dark brown plate-like crystals. Yield: 0.182 g (25%). IR (KBr): 498, 533, 542, 690, 722, 743, 795, 848, 966, 997, 1113, 1182, 1260, 1297, 1327, 1436, 1480, 1566, 1667, 3051 cm^{-1} . This material was identified by single crystal X-ray diffraction.

Crystallographic analysis of **2**

Diffraction data were collected at 198 K on a Siemens 3-circle platform diffractometer with CCD area detector. Crystal data for **2**: $C_{80}H_{60}N_2P_4S_9$, $M = 1461.72$, monoclinic, space group: $P2_1/c$, $a = 18.4124(2)$, $b = 17.4764(2)$, $c = 21.9473(2)$ Å, $\beta = 92.494(1)^\circ$, $V = 7055.6(1)$ Å³, $Z = 4$, $D_c = 1.378$ g/cm³, $\mu = 0.421$ mm⁻¹, $\lambda(Mo-K\alpha) = 0.71073$ Å, $2\theta_{max} = 45^\circ$. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 (SHELXL 93). All non-hydrogen atoms were refined anisotropically. Final $R = 5.35\%$ ($wR_2 = 9.07\%$).

Crystallographic analysis of **3**

Diffraction data were collected at 198 K on a Siemens 3-circle platform diffractometer with CCD area detector. $C_{52}H_{40}P_2S_8$, $M = 983.26$, orthorhombic space group $Pbca$, $a = 15.5801(6)$, $b = 19.9559(7)$, $c = 30.671(1)$ Å, $V = 9536.0(6)$ Å³, $Z = 8$, $D_c = 1.370$ g/cm⁻³, $\mu = 0.478$ mm⁻¹, $\lambda(Mo-K\alpha) = 0.71073$ Å, $2\theta_{max} = 40^\circ$. The structure was solved by direct methods and refined by full-matrix least squares on F^2 (SHELXL 93). There is some disorder in one of the PPh_4^+ cations. Then non-hydrogen atoms on the anion were refined anisotropically. Final $R = 7.15\%$ ($wR_2 = 15.56\%$)*.

Acknowledgements

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