C₈S₈²⁻ and C₁₆S₁₈¹⁺: Intermediates in the Synthesis of Poly(Carbon Sulfide)

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(PPN)₂C₈S₈ was obtained by the addition of PPN⁺Cl⁻ to a methanolic extract of Na₂C₈S₈, derived from the reaction of C₈S₈O₂ and NaOMe. Centrosymmetric C₁₆S₁₈ consists of thiophene units unsymmetrically fused to two 1,4-dithiin rings. Solutions of C₁₆S₁₈ convert to C₈S₈⁺ with heating. When C₈S₈ (x ~ 8) is reduced by Na/NH₃ followed by extraction and crystallization, one obtains the bicyclic polysulfide C₄S₈⁺, crystallized as its PPh₄⁺ 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 C₆ building blocks to give carbon sulfides with identifiable C₄ subunits (Scheme 1).

In contrast to our method, materials produced by usual solvothermal processes bear only coincidental resemblance to their precursors [3]. The use of kinetically stable C₈S₈⁺ 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 C₁₆S₁₈⁺, the largest known carbon sulfide.

The polymer (C₈S₈⁺)ₙ (1) is obtained in a two step process starting with the base hydrolysis of the tricyclic bis(dithiocarbonate) C₈S₈O₂ [6] which gives Na₂C₈S₈ [1]. Addition of PPh₄Cl to these solutions gives (PPh₄)₂C₈S₈ which upon heating at 80 °C is converted in 1 [1]. The PPh₄⁺ salt of C₈S₈⁺ 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)C₈S₈ which indicates that the base hydrolysis of the C₈S₈O₂ proceeds according to eq (1).

C₈S₈O₂ + 2 OMe⁻ → 0.5C₈S₈₂⁻ + (MeO)₂CO + 0.5S₅²⁻  (1)

With the formula C₁₆S₁₈⁺, 2 is the largest carbon sulfide to be characterized (Fig. 1). It consists of two C₈S₈⁺ 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 C₈S₈⁺ subunits are similar. In 1, the C₈S₈ unit has idealized D₃h symmetry by virtue of the symmetrical fusion of the thiophenotetrathiocarbonates 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

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Fig. 1. Two views of the $\text{C}_{16}\text{S}_{18}^{4-}$ (2) anion in $(\text{PPN})_4\text{C}_{16}\text{S}_{18}$ with thermal ellipsoids drawn at the 50% probability level. Selected distances (Å): $\text{S1}-\text{C4}, 1.734(5)$; $\text{S3}-\text{C7}, 1.749(5)$; $\text{S4}-\text{C4}, 1.751(5)$; $\text{S6}-\text{C5}, 1.695(5)$; $\text{S7}-\text{C2}, 1.756(5)$; $\text{S9}-\text{C8}, 1.771(5)$; $\text{C3}-\text{C4}, 1.435(7)$; $\text{C7}-\text{C8}, 1.734(5)$; $\text{S3}-\text{C7}, 1.785(5)$; $\text{S5}-\text{C1}, 1.695(5)$; $\text{S6}-\text{C5}, 1.734(5)$; $\text{S6}-\text{C8}, 1.759(5)$; $\text{S7}-\text{C5}, 1.756(5)$; $\text{S7}-\text{C2}, 1.767(5)$; $\text{S8}-\text{C3}, 1.767(5)$; $\text{S8}-\text{C6}, 1.771(5)$; $\text{S9}-\text{C8}, 1.676(5)$; $\text{C1}-\text{C2}, 1.378(7)$; $\text{C2}-\text{C3}, 1.415(6)$; $\text{C3}-\text{C4}, 1.387(6)$; $\text{C5}-\text{C6}, 1.358(6)$; $\text{C6}-\text{C7}, 1.435(7)$; $\text{C7}-\text{C8}, 1.412(6)$. Selected angles (°): $\text{C4}-\text{S1}-\text{C4}, 93.1(2)$; $\text{C5}-\text{S6}-\text{C8}, 94.0(2)$; $\text{C5}-\text{S7}-\text{C2}, 99.4(2)$; $\text{C3}-\text{S8}-\text{C6}, 100.0(2)$. The bending angle of the central 1,4-dithiin ring is 41.4(2)°.

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 $(\text{PPN})_4$ at 80 °C for 12 h (conditions used for the conversion of $(\text{PPh}_4)_2\text{C}_4\text{S}_4$ into 1 [1], gives the $\text{C}_8\text{S}_8^{2-}$ ion, which spontaneously polymerizes upon crystallization. This conversion was established by comparison of UV-Vis spectra of DMF solutions (wherein $(\text{C}_8\text{S}_8^{2-})_n$ is dissociated [1]) which allows unambiguous identification due to the fine structure in the range 300–820 nm ($\lambda_{\text{max}} = 332, 360$ (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 $\text{C}_4\text{S}_x$ $(6 \leq x \leq 8)$, itself obtained by the reaction of $\text{Na}_2\text{S}_x$ with hexachlorobutadiene [8]. Cation exchange with $\text{PPh}_4\text{Cl}$ gave $(\text{PPh}_4)_2\text{C}_4\text{S}_4$ which crystallizes from MeCN–Et$_2$O solution. The related PPN$^+$ salt was prepared analogously. These are salts of $\text{C}_8\text{S}_8^{2-}$ (3).

Crystallographic analysis of $(\text{PPh}_4)_2(3)$ 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$_2$S$_5$ 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 $\text{C}_4\text{S}_8^{2-}$. 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 $(\text{C}_8\text{S}_8^{2-})_n$ from sulfided butadienes involves the formation of thio-phenetetathiolate 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 C₄S₈₂⁻ (3) anion in (PPh₄)₂C₄S₈ with thermal ellipsoids drawn at the 25\% probability level. Selected distances (Å): S₁–Cl, 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 (°): 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); 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

\((\text{Ph}_3\text{P})_2[\text{C}_4\text{S}_8]\)

\(\text{C}_6\text{S}_6\) was prepared according to Fanghäl's procedure \[8\]. This material, 17.82 g, was reduced by 2 equiv of Na in 250 ml of \(\text{NH}_3\) at \(-33^\circ\text{C}\) for 1 h. The resulting dark brown colored solution was allowed to evaporate. Some of the resulting \(\text{Na}_2\text{C}_6\text{S}_{10}\), 0.286 g (~1 mmol) was dissolved in 30 ml of \(\text{H}_2\text{O}\). This solution was treated with a solution of 0.75 g of \(\text{Ph}_4\text{PCl}\) in 15 ml of water to give an orange brown solid. The solid was collected through filtration and then extracted into \(\text{CH}_3\text{CN}\) and the solution was filtered to remove any solids. The careful addition of \(\text{Et}_2\text{O}\) 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.

\((\text{PPN})_4[\text{C}_{16}\text{S}_{18}]\)

A suspension of 0.296 g (1 mmol) of \(\text{C}_6\text{S}_{10}\text{O}_2\) in 30 ml of \(\text{MeOH}\) was treated with a fresh solution of \(\text{NaOMe}\) in 10 ml of \(\text{MeOH}\) (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 \(\text{PPNCI}\) 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 \(\text{DMF}\), which was filtered to remove \(\text{NaCl}\). The product was crystallized by layering the DMF with \(\text{Et}_2\text{O}\) 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: \(\text{C}_{80}\text{H}_{60}\text{P}_4\text{S}_9\), \(\text{M} = 1461.72\), monoclinic, space group: \(P2_1/c\), \(a = 18.4124(2), \ b = 17.4764(2), \ c = 21.9473(2) \text{Å}, \ \beta = 92.494(1)\text{°}, \ V = 7055.6(1) \text{Å}^3, \ Z = 4, \ D_c = 1.378 \text{g/cm}^3, \ \mu = 0.421 \text{mm}^{-1}, \ \lambda(\text{Mo–K}_\alpha) = 0.71073 \text{Å}, \ 2\theta_{\text{max}} = 45\text{°}. 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. \(\text{C}_5\text{H}_{36}\text{P}_2\text{S}_8\), \(\text{M} = 983.26\), orthorhombic space group \(\text{Pbca}\), \(a = 15.5801(6), \ b = 19.9559(7), \ c = 30.671(1) \text{Å}, \ V = 9536.0(6) \text{Å}^3, \ Z = 8, \ D_c = 1.370 \text{g/cm}^3, \ \mu = 0.478 \text{mm}^{-1}, \ \lambda(\text{Mo–K}_\alpha) = 0.71073 \text{Å}, \ 2\theta_{\text{max}} = 40\text{°}. 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 \(\text{PPh}_4^+\) cations. Then non-hydrogen atoms on the anion were refined anisotropically. Final \(R = 7.15\% \ (wR_2 = 15.56\%)\).

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