

## X-Ray Structural Characterization of a Thiolate Salt Displaying a Very Strong S–H⋯S Hydrogen Bond

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In attempting to prepare  $[\text{PPh}_4][\text{SCH}_2\text{CH}_2\text{SH}]$  **1** from  $\text{Na}[\text{SCH}_2\text{CH}_2\text{SH}]$  **2** and  $[\text{PPh}_4]\text{Cl}$ , the derived salt  $[\text{PPh}_4][\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SH}]$  **3** is produced in high yield, by a mechanism which is shown to involve the nucleophilic displacement of  $\text{HS}^-$  from the anion of **1**; the X-ray structure of **3** shows that pairs of the anions are coupled by very strong, almost linear S–H⋯S hydrogen bonds, with an S⋯S distance of 3.454(2) Å.

The potential importance of S–H⋯S bridge bonds in biological systems has been recognized for some time.<sup>1</sup> Such interactions can affect equilibrium configurations, redox potentials and reactivity. In spite of this, the number of well-characterized structures in which the hydrogen atom has been located, and its position refined, is very small. Generally the existence of these interactions has been inferred from S–H stretching frequencies and/or relatively short S⋯N interactions.<sup>2</sup> Krebs studied a series of dithiophosphinic acids which crystallize as H-bonded dimers and found S⋯S distances in the range 3.75–3.84 Å.<sup>2</sup> Earlier it had been predicted on theoretical grounds<sup>3</sup> that extremely strong symmetrical S⋯H⋯S bonds might exist with bond enthalpies of *ca.*

60 kJ mol<sup>-1</sup> and S⋯S distances of *ca.* 3.49 Å. In a study of  $[\text{NR}_4][\text{SH}] \cdot 2\text{H}_2\text{S}$ , the S⋯S distances were found to be similar to those in the dithiophosphinic acid structures.<sup>4</sup> More recently, Sellmann and coworkers<sup>5,6</sup> reported S–H⋯S bridges between coordinated  $\text{H}_2\text{S}$  and coordinated thiolate sulfur in the crystal structure of a ruthenium complex which crystallised as a centrosymmetric dimer. The S⋯S interaction here was 3.69 Å, and the S–H–S angle 153°.<sup>6</sup>

In attempting to prepare simple phosphonium thiolate salts for use in synthesizing metal complexes we reacted  $\text{Na}[\text{SCH}_2\text{CH}_2\text{SH}]$  **2** with  $[\text{PPh}_4]\text{Cl}$ , anticipating the product would be  $[\text{PPh}_4][\text{SCH}_2\text{CH}_2\text{SH}]$  **1**. Instead, the derived salt  $[\text{PPh}_4][\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SH}]$  **3** was produced in high

yield.† The X-ray crystal structure‡ of **3** (Fig. 1) shows that the anions are present in the structure as centrosymmetric dimers, which are linked in a head-to-tail fashion *via* hydrogen bonds. As might be anticipated, since the hydrogen bond is between a thiol hydrogen and the S atom of a free  $\text{RS}^-$ , this interaction is very strong. Indeed, based on the  $\text{S}\cdots\text{S}$  distance [3.454(2) Å] and the nearly linear geometry at hydrogen [the  $\text{S}-\text{H}\cdots\text{S}$  bond angle is 176(2)°] this appears to be a unique structure, especially since this is an intermolecular, rather than an intramolecular hydrogen bond. The only well characterized structure involving a shorter  $\text{S}\cdots\text{S}$  distance is in thiotropolone,<sup>2</sup> but this is due to the constrained intramolecular

† *Synthetic and spectroscopic data.* The reaction was carried out using standard Schlenk techniques. Sodium (0.23 g, 0.01 mol) and propan-2-ol (40  $\text{cm}^3$ ) were heated to 75 °C under nitrogen for 45 min to produce the required solution of sodium prop-2-oxide. After cooling to 20 °C,  $\text{HSCH}_2\text{CH}_2\text{SH}$  (2.0  $\text{cm}^3$ , 0.024 mol) was added *via* syringe. This mixture was allowed to cool to room temperature, then a propan-2-ol solution of  $[\text{PPh}_4]\text{Cl}$  (3.0 g, 0.008 mol) was added *via* a transfer tube, and the reaction continued for 12 h. After the reaction between  $[\text{PPh}_4]\text{Cl}$  and  $\text{NaSCH}_2\text{CH}_2\text{SH}$  was complete, the filtrate was evaporated to dryness, and extracted with MeCN to yield a pale-yellow crystalline solid which proved to be  $[\text{PPh}_4][\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SH}]$  **3** rather than the simple monoanionic salt,  $[\text{PPh}_4][\text{SCH}_2\text{CH}_2\text{S}^-]$ . Yield of **3** (after recrystallization twice from MeCN-Et<sub>2</sub>O), 2.6 g, 65% based on  $[\text{PPh}_4]\text{Cl}$ . <sup>1</sup>H NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  8.0–7.6 (m, 20 H), 2.59 (s, 8H), 1.60 (br s, 1H), [this latter (S–H) resonance was shown to be concentration dependent, varying between  $\delta$  2.5 and 1.6].

Reaction between  $\text{Na}[\text{SCH}_2\text{CH}_2\text{SH}]$  and  $[\text{PPh}_4][\text{SEt}]$ . Ethanedi-thiol (0.31  $\text{cm}^3$ , 0.0037 mol) was added to a solution of  $\text{NaOPr}^i$  in propan-2-ol (Na, 0.090 g, 0.0037 mol in propan-2-ol 35  $\text{cm}^3$ ). After stirring for 5 min, solid  $[\text{PPh}_4][\text{SEt}]$  (1.5 g, 0.0037 mol) was released into the Schlenk tube. The mixture was stirred for 12 h at room temp., then filtered and pumped to dryness. A small amount of the distillate (solvent plus any other volatiles) was collected in a cold trap for GC–MS analysis. Benzene was detected in this liquid. The solid residue was extracted with MeCN (50  $\text{cm}^3$ ) giving a slurry which was filtered and the solution evaporated to dryness. <sup>1</sup>H NMR analysis of a  $\text{CD}_3\text{CN}$  solution of the orange solid so produced showed a large number of resonances. Among these were signals due to  $\text{MeCH}_2\text{S}^-$  and  $-\text{SCH}_2\text{CH}_2\text{S}^-$ . Hydrolysis of a portion of the orange solid with 8 mol  $\text{dm}^{-3}$  HCl, followed by extraction with diethyl ether (3  $\times$  10  $\text{cm}^3$ ), drying over  $\text{MgSO}_4$ , and evaporation to 1  $\text{cm}^3$ , enabled the identification of the following species in a GC–MS analysis:  $\text{HSCH}_2\text{CH}_2\text{SCH}_2\text{Me}$ ,  $M^+ = 122$ ;  $\text{HSCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SH}$ ,  $M^+ = 154$ ;  $\text{HSCH}_2\text{CH}_2\text{SH}$ ,  $M^+ = 94$ ;  $\text{Ph}_3\text{PS}$ ,  $M^+ = 294$ ;  $\text{C}_6\text{H}_6$ ,  $M^+ = 78$ . Direct extraction of the orange solid with diethyl ether confirmed the presence of  $\text{Ph}_3\text{PS}$  in this solid fraction, again using GC–MS analysis and referring to an eight-peak spectral library.

‡ *Crystal data for 3:*  $[\text{PPh}_4][\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SH}]$ ,  $\text{C}_{28}\text{H}_{29}\text{PS}_3$ ,  $M = 492.69$ , triclinic, space group  $P\bar{1}$ , crystal size 0.20  $\times$  0.20  $\times$  0.40 mm,  $a = 10.414(3)$ ,  $b = 13.511(5)$ ,  $c = 9.380(7)$  Å,  $\alpha = 101.75(4)$ ,  $\beta = 94.59(4)$ ,  $\gamma = 85.15(2)^\circ$ ,  $V = 1284(1)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.273$  g  $\text{cm}^{-3}$ ,  $T = -102.0$  °C,  $F(000) = 520$ , and  $\mu(\text{Mo-K}\alpha) = 35.2$   $\text{cm}^{-1}$ ,  $R = 0.038$ ,  $R_w = 0.028$ .

Accurate cell dimensions and a crystal orientation matrix were determined on a Rigaku AFC6S diffractometer by a least-squares refinement of the setting angles of 23 reflections with  $\theta$  in the range 10–13°. Intensity data were collected by the  $\omega/2\theta$  scan method, using monochromatized Mo-K $\alpha$  radiation in the range  $2 < \theta < 25^\circ$ , with  $h$  0 to 12,  $k$  –15 to 15 and  $l$  –11 to 11. The intensities of 4823 reflections were measured (4550 unique,  $R_{\text{int}} = 2.81$ ), of which 3002 had  $I > 3\sigma(I)$ . Data were corrected for Lorentz, polarization effects, and an empirical absorption correction was applied; the correction coefficients were in the range 0.973 to 1.000.

The structure was solved by direct methods using SAPI91.<sup>9</sup> The refinement was done *via* full-matrix least-squares calculations, initially with isotropic and finally with anisotropic temperature factors for the non-hydrogen atoms. At an intermediate stage of the refinement, a difference map revealed all the hydrogen atoms which were included in the subsequent cycles with fixed isotropic temperature factors. All computer programs used in the study were part of the TEXSAN system.<sup>10</sup> Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

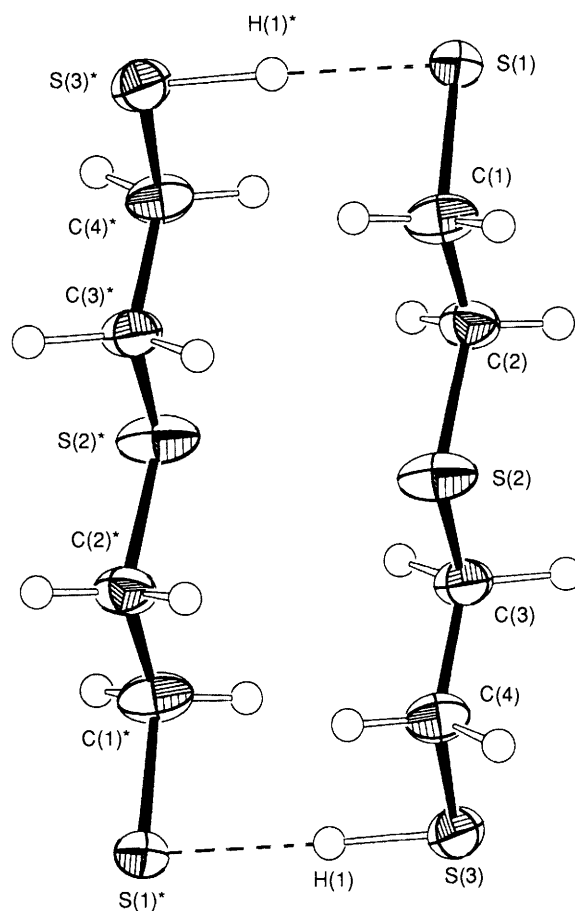
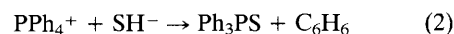
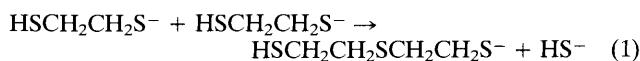


Fig. 1 ORTEP drawing of the centrosymmetric pairs of  $[\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SH}]^-$  anions in the crystal structure of **3**. Selected values of interatomic distances (Å) and angles (°):  $\text{S}(3)-\text{H}(1)$  1.47(3),  $\text{S}(1)^*\cdots\text{H}(1)$  1.98(3),  $\text{S}(1)^*\cdots\text{S}(3)$ , 3.454(2),  $\text{S}(2)\cdots\text{S}(2)^*$  4.75(1);  $\text{S}(1)^*-\text{H}(1)-\text{S}(3)$  176(2),  $\text{C}(4)-\text{S}(3)-\text{H}(1)$  97(1),  $\text{C}(1)-\text{S}(1)-\text{H}(1)^*$  87(1). Atoms are related to their \*equivalents through the symmetry operation  $-x, -y, 2-z$ .

geometry and furthermore, the bridge angle is 133°, well outside the range of  $175^\circ < \text{X}-\text{H}\cdots\text{Y} < 180^\circ$  which is typical of strong hydrogen bonds.<sup>7</sup> Contrary to the prediction that strong hydrogen bonds between sulfur atoms will be symmetric,<sup>3</sup> it will be noted that in **3** the thiol and thiolate sulfur atoms are distinct, with the individual S–H distances being 1.47(3) and 1.98(3) Å respectively. The  $\text{C}(1)-\text{S}(1)-\text{H}(1)$  bond angle is very close to 90°, suggesting that the H-acceptor orbital on S(1) is essentially pure p in character. Another notable feature of the structure is that the non-hydrogen atoms are almost coplanar.

The infrared spectrum of **3** shows weak absorptions at 2334 and 2375  $\text{cm}^{-1}$ , which we tentatively assign to  $\nu(\text{S}-\text{H})$  vibrations, lowered from 2545  $\text{cm}^{-1}$  reported for the free dithiol,<sup>8</sup> and similar in magnitude to those reported for dithiophosphinates.<sup>2</sup> These absorptions were found to be sensitive to sample preparation method, and for this compound would provide a poor criterion for ascertaining the strength of the S–H bond.

The mechanism of formation of the anion of **3** has been elucidated, and involves the following reactions [eqns. (1) and (2)]. The unexpected displacement of the poor leaving group



$\text{SH}^-$  is driven by the subsequent removal of this product in the reaction with the  $[\text{PPh}_4]^+$  cation. Both the by-products were

identified and in the presence of a second thiolate anion ( $\text{SEt}^-$ ), the expected mixture of products (**3** and  $\text{C}_2\text{H}_5\text{SCH}_2\text{CH}_2\text{S}^-$ ) was formed. Direct reaction between  $[\text{PPh}_4]\text{Cl}$  and  $\text{NaSH}$  in propan-2-ol was shown to give  $\text{PPh}_3\text{S}$  and benzene.

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