Synthesis and crystal structure of the tetraalkylammonium salts of 1,2,3,4-tetramercapto-1,2,3,4-tetrathioxotetraphosphetane based on white phosphorus

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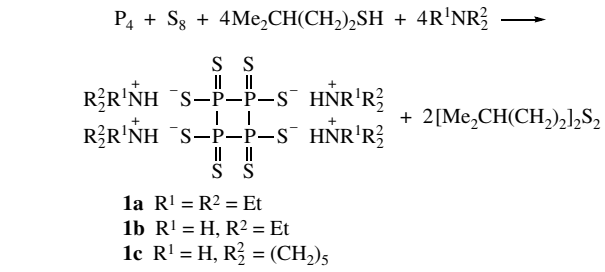
The reaction of P_4 with sulfur, 3-methylbutane-1-thiol and alkylamines yields tetraalkylammonium salts of tetraphosphetane previously unknown; the crystal structure of the tetrakis(triethylammonium) salt of 1,2,3,4-tetramercapto-1,2,3,4-tetrathioxotetraphosphetane is determined by X-ray diffraction analysis.

The well-known methods for obtaining tetraphosphetanes[1] are based on the reactions of dihalo(organo)phosphines with lithium, sodium and metal hydrides as reducing agents, the reaction of phenylphosphine with sulfur, and the interaction of white phosphorus with alkylmagnesium bromides and alkylbromides.

In this work, the synthesis of new tetraphosphetanes from white phosphorus and elemental sulfur with a thiol in the presence of amines was studied. We found that, in the interaction of P_4 with sulfur, 3-methylbutane-1-thiol and alkylamines (diethylamine, triethylamine and piperidine), the precipitates of tetraalkylammonium salts of 1,2,3,4-tetramercapto-1,2,3,4-tetrathioxotetraphosphetane **1a–c**† were obtained when the reaction mixtures were kept at room temperature for 15 h. (Note that a similar reaction of P_4 with sulfur and alcohols in the presence of amines affords ammonium salts of dialkyldithiophosphoric acids).[2]



1a $R^1 = R^2 = Et$
1b $R^1 = H$, $R^2 = Et$
1c $R^1 = H$, $R^2_2 = (CH_2)_5$

Previously unknown tetraphosphetane salts **1a–c**, which were isolated, were light yellow crystalline compounds. The yields were 18 (**1a**), 20 (**1b**) and 25% (**1c**). The structures of **1a–c** were confirmed by NMR (^{1}H, ^{31}P) and IR spectroscopy and elemental analysis.‡ The ^{31}P signals were observed in the salts obtained at 122–125.1 ppm. Crystals are soluble in polar solvents, stable in the air and water at temperatures up to 45 °C.

The crystal structure of tetrakis(triethylammonium) salt of 1,2,3,4-tetramercapto-1,2,3,4-tetrathioxotetraphosphetane **1a** was determined by X-ray diffraction.§ The asymmetric part of the unit cell contains two triethylamine molecules and half of the 1,2,3,4-tetramercapto-1,2,3,4-tetrathioxotetraphosphetane moiety located in the centre of symmetry (Figure 1). When refining the crystalline structure, it was established that one ethyl group of the triethylamine molecule is disordered in two positions with the occupancies of 0.72 and 0.28 [in Figure 1, one of the positions of C(2B) and C(3B) atoms is shown]. In the molecule, the P–P and P=S bond lengths are 2.308 and 1.983 Å, respectively, when the standard values are 2.256 and 1.954 Å, respectively.[3]

Two types of intermolecular interactions, including N–H···S and C–H···S, have been observed in the crystal of compound **1a**. Centrosymmetric tetraphosphetane moieties are connected with four triethylamine molecules by strong hydrogen bonds between protons H(1A) and H(1B) of the triethylamine molecules and sulfur S(4), S(1) atoms, respectively {*d*[H(1A)···S(4)] 2.18 Å, ∠[N(1A)–H(1A)···S(4)] 169° and d[H(1B)···S(1)] 2.41 Å, ∠[N(1B)–H(1B)···S(1)] 173°}. Owing to the appearance of additional H(41B)···S(3) and H(51A)···S(1) interactions (Figure 2), the supramolecular 1D chains in a crystal are formed along the

† *General procedure for the preparation of tetraalkylammonium salts of 1,2,3,4-tetramercapto-1,2,3,4-tetrathioxotetraphosphetane* **1a–c**. An amine (32.7 mmol) was added dropwise to a stirred mixture of P_4 (32.3 mmol), sulfur (64.6 mmol) and 3-methylbutane-1-thiol (32.6 mmol) in MeCN (8 ml) at 15–30 °C. The mixture was stirred until the reaction was complete (complete conversion of P_4) ≈ 1–1.5 h. The reaction mixture was allowed to stand for 15 h at room temperature. Then, the precipitated crystals of **1a–c** were separated from the solution by decantation and washed with diethyl ether. The crystals obtained melted at 95–110 (decomp.) (**1a**), 152–168 (decomp.) (**1b**) or 195–208 °C (decomp.) (**1c**). The filtrate was evaporated and the residue was distilled. Diisoamyl disulfide was obtained, bp 125–127 °C (10 Torr), n_D^{20} 1.4870.[4]

‡ NMR spectra were measured on Bruker MSL-400 (162.0 MHz, ^{1}H) and Bruker CXP-100 (36.48 MHz, ^{31}P) spectrometers.

1a: ^{1}H NMR (CD_3OD) δ: 1.34–1.38 (t, 36H, Me), 3.2–3.38 (m, 24H, CH_2). ^{31}P NMR, δ: 122. IR (KBr, ν/cm^{-1}): 2670, 2490 (HN$^+$), 644, 559 [P(S)S]. Found (%): C, 36.61; H, 8.35; N, 7.11; P, 15.75; S, 32.16. Calc. for $C_{24}H_{64}N_4P_4S_8$ (%): C, 36.55; H, 8.12; N, 7.1; P, 15.7; S, 32.48.

1b: ^{1}H NMR (D_2O) δ: 1.23–1.27 (t, 24H, Me), 3.03–3.08 (m, 16H, CH_2). ^{31}P NMR, δ: 125.1. IR (KBr, ν/cm^{-1}): 2671, 2472 (HN$^+$), 659, 560 [P(S)S]. Found (%): C, 28.23; H, 6.24; N, 8.49; P, 18.76; S, 37.74. Calc. for $C_{16}H_{44}N_4P_4S_8$ (%): C, 28.5; H, 6.5; N, 8.33; P, 18.45; S, 38.1.

1c: ^{1}H NMR (D_2O) δ: 1.67–1.78 [m, 24H, $(CH_2)_3$], 3.16–3.19 [m, 16H, $N(CH_2)_2$]. ^{31}P NMR, δ: 123. IR (KBr, ν/cm^{-1}): 2612, 2472 (HN$^+$), 659, 565 [P(S)S]. Found (%): C, 33.45; H, 6.49; N, 7.54; P, 16.75; S, 34.99. Calc. for $C_{20}H_{48}N_4P_4S_8$ (%): C, 33.15; H, 6.6; N, 7.7; P, 17.1; S, 35.3.

§ *X-ray crystallography of* **1a**: $C_{24}H_{64}N_4P_4S_8$, M = 789.23, monoclinic, space group $P2_1/n$, a = 11.439(4), b = 10.784(2) and c = 16.116(4) Å, β = 98.39(2)°, V = 2045(1) Å^3, Z = 2, (anion in special position) d_{calc} = = 1.28 g cm^{-3}. Cell parameters and intensities of 3714 independent reflections (3536 with $I \geq 2\sigma$) were measured on an Enraf-Nonius CAD-4 diffractometer in the $\omega/2\theta$-scan mode, $\theta \leq 74.1°$, using CuKα radiation with a graphite monochromator. Data were corrected for the absorption effect (μMo 56.9 cm^{-1}). The structure was solved by a direct method using the SIR[5] program and refined by the full matrix least-squares using the SHELXL97[6] program. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the calculated position with the thermal parameters 30% larger than the atoms to which they are attached. Hydrogen atoms at nitrogen were revealed from the differences in the Fourier series and refined isotropically. The final residuals were R = 0.053, and R_w = 0.137. All calculations were performed on PC using the WinGX[7] program. Cell parameters, data collection and data reduction were performed on an Alpha Station 200 computer using the MoLEN[8] program. All figures and the analysis of intermolecular interactions were made using the PLATON[9] program.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 243023. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2005.

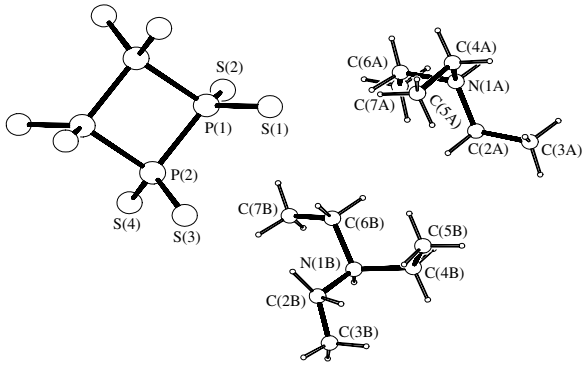


Figure 1 Crystal structure of compound **1a**. Selected bond lengths (Å) and angles (°): P(1)–S(2) 1.969(1), P(1)–S(1) 1.990(1), P(1)–P(2) 2.305(1), P(1)–P(2) (-*x* + 2, –*y* – 1, –*z* + 1) 2.311(1), P(2)–S(3) 1.978(1), P(2)–S(4) 1.993(1), N(1B)–C(2B) 1.473(8), N(1B)–C(4B) 1.490(6), N(1B)–C(6B) 1.533(7), N(1A)–C(2A) 1.477(7), N(1A)–C(4A) 1.493(7), N(1A)–C(6A) 1.539(7); S(2)–P(1)–S(1) 117.05(6), S(2)–P(1)–P(2) 114.53(5), S(1)–P(1)–P(2) 109.78(6), S(2)–P(1)–P(2) (–*x* + 2, –*y* – 1, –*z* + 1) 112.18(5), S(1)–P(1)–P(2) (–*x* + 2, –*y* – 1, –*z* + 1) 110.20(6), P(2)–P(1)–P(2) (–*x* + 2, –*y* – 1, –*z* + 1) 89.89(5), S(3)–P(2)–S(4) 117.42(6), S(3)–P(2)–P(1) 110.90(6), S(4)–P(2)–P(1) 112.77(5), S(3)–P(2)–P(1) (–*x* + 2, –*y* – 1, –*z* + 1) 111.98(6), S(4)–P(2)–P(1) (–*x* + 2, –*y* – 1, –*z* + 1) 110.45(6), P(1)–P(2)–P(1) (–*x* + 2, –*y* – 1, –*z* + 1) 90.11(5).

a axis. The parameters of C–H···S interactions are: *d*[H(41B)···S(3)] 2.87 Å, ∠[C(4B)–H(41B)···S(3)] 146° and *d*[H(51A)···S(1)] 2.78 Å, ∠[C(5A)–H(51A)···S(1)] 172°. Note that close contacts between the sulfur atoms of 1,2,3,4-tetramercapto-1,2,3,4-tetrathioxo-tetraphosphetane molecules have not been observed; the shortest distance between them is equal to 6.2 Å. Thus, from the point of view of charge distribution in the crystal, sphere-like associates are formed. The inner part of these spheres contains negatively charged 1,2,3,4-tetramercapto-1,2,3,4-tetrathioxotetraphosphetane anions, and the triethylamine cations form the external part. In terms of supramolecular structures, the mutual arrangement of the molecules in the crystal is characterised by the hexagonal packing of spherical suprastructures (Figure 3), which results in the loss of the chosen direction in the crystal and, possibly, its anisotropic properties. Note that, for more than 20 crystalline compounds from the Cambridge Crystallographic Database containing triethylamine cations, their distribution in a crystal is of a chain or lamellar type. The calculated packing coefficient in the crystal of compound **1a** is 0.67, which is close to the lower limit of this parameter for organic compounds.

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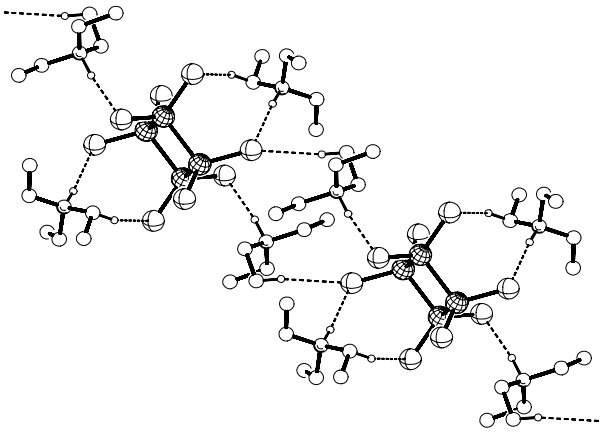

Figure 2 Hydrogen bonds in the crystal of compound **1a**. Hydrogen atoms with no H-bondings are omitted for clarity.

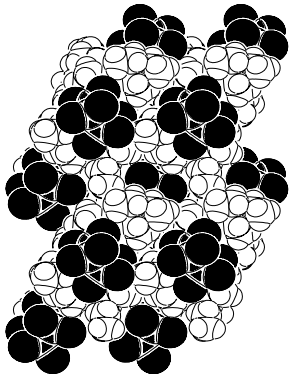

Figure 3 Crystal packing of compound **1a** in the van der Waals representation. The carbon, hydrogen and nitrogen atoms are represented by open circles; the phosphorus and sulfur atoms are represented by close circles.

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