

Structure of Guanidinium 1,2,3,4-Tetrathio-cyclo-tetraphosphate

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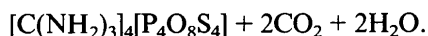
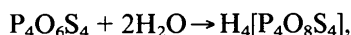
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Abstract. $[\text{C}(\text{NH}_2)_3]_4[\text{P}_4\text{O}_8\text{S}_4]$, $M_r = 620.46$, monoclinic, $P2_1/n$, $a = 10.894$ (8), $b = 13.126$ (8), $c = 8.919$ (6) Å, $\beta = 105.74$ (5)°, $V = 1227$ (3) Å³, $Z = 2$, $D_m = 1.64$, $D_x = 1.678$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $\mu = 0.693$ mm⁻¹, $F(000) = 640$, $T = 293$ K, final $R = 0.027$ for 2356 independent reflections. The $\text{P}_4\text{O}_8\text{S}_4$ ring anions are centrosymmetric. Among the four external S atoms two belonging to two successive P atoms are located above the ring plane while the two remaining ones are below. The two independent P atoms of the ring have a highly distorted tetrahedral coordination involving three O atoms and one S atom. The guanidinium cations, forming planar groups, are connected to the phosphoric ring anions by weak hydrogen bonds.

Introduction. Tetrathio-cyclo-tetraphosphates were first prepared in 1978 (Wolf & Meisel, 1978). Up to now the crystal structures of sodium tetrathio-cyclo-tetraphosphate hexahydrate (Ilyukhin, Kalinin, Kuvshinova & Tananaev, 1981), caesium tetrathio-cyclo-tetraphosphate (Ilyukhin, Kalinin, Kuvshinova & Tananaev, 1982) and barium tetrathio-cyclo-tetraphosphate decahydrate (Nikolaev & Kuvshinova, 1987) have been determined. The present work is part of a systematic investigation of chemical and structural data of cyclic thiophosphates.

Experimental. The title compound was prepared by slowly adding guanidinium carbonate to a cooled solution of tetrathio-cyclo-tetraphosphoric acid which was obtained by careful dissolution of the phosphorus oxide sulfide $\text{P}_4\text{O}_6\text{S}_4$ in water at 273–278 K (Kuvshinova, Wolf & Meisel, 1984).

The reaction is:



The guanidinium salt, which has relatively low solubility in water, was obtained as colorless crystals of about 1 mm in length by evaporation at room temperature. It was recrystallized once from water to obtain good quality crystals. The compound is stable at room temperature. Prismatic crystal: $0.32 \times 0.48 \times 0.48$ mm. Experimental density by pycnometry (paraffin oil). Philips PW 1100 diffractometer, graphite monochromator. Systematic absences $h0l$: $h + l = 2n$; $0k0$: $k = 2n$. 18 reflections ($12 < \theta < 16^\circ$) for refining the unit-cell dimensions. $\omega/2\theta$ scan, scan width 1.20° , scan speed $0.03^\circ \text{ s}^{-1}$, total background measuring time 10 s. Two intensity and orientation reflections ($\bar{4}44$ and $4\bar{4}\bar{4}$) every 2 h without significant variation. 3553 measured reflections ($3 < \theta < 35^\circ$). Range of hkl : $h - 16 \rightarrow 16$, $k 0 \rightarrow 20$, $l 0 \rightarrow 12$. Total number of independent reflections 3339. Lorentz and polarization corrections, no absorption correction. Crystal structure solved by direct methods (*MULTAN77*; Main, Lessinger, Woolfson, Germain & Declercq, 1977). Anisotropic full-matrix least-squares refinement (on F), isotropic for H atoms.

Table 1. Final atomic coordinates and B_{eq} for non-H atoms with *e.s.d.*'s in parentheses

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$			$B_{\text{eq}}(\text{Å}^2)$
	<i>x</i>	<i>y</i>	<i>z</i>	
P(1)	0.33926 (5)	0.97389 (4)	0.10181 (6)	2.056 (9)
P(2)	0.10996 (5)	0.59211 (4)	0.65987 (6)	1.962 (8)
S(1)	0.26837 (6)	0.35444 (5)	0.41089 (7)	3.08 (1)
S(2)	0.26096 (5)	0.10585 (5)	0.64228 (7)	3.04 (1)
O(E1)	0.3053 (1)	0.0698 (1)	0.1715 (2)	2.84 (3)
O(E2)	0.0799 (2)	0.6818 (1)	0.5538 (2)	2.69 (3)
O(L12)	0.1426 (1)	0.4943 (1)	0.5687 (2)	2.36 (3)
O(L21)	0.5162 (1)	0.0522 (1)	0.7986 (2)	2.59 (3)
C(1)	0.5960 (2)	0.1849 (2)	0.4097 (3)	2.81 (4)
C(2)	-0.0049 (2)	0.9247 (2)	0.7159 (3)	2.76 (4)
N(11)	-0.0032 (2)	0.6344 (2)	0.0550 (3)	3.95 (5)
N(21)	0.5857 (2)	0.2099 (2)	0.2637 (3)	3.90 (5)
N(31)	0.7001 (2)	0.2103 (2)	0.5197 (2)	3.66 (4)
N(12)	0.0791 (2)	0.8948 (2)	0.6433 (3)	3.60 (4)
N(22)	0.0014 (2)	0.9809 (2)	0.2314 (3)	3.93 (5)
N(32)	0.4078 (2)	0.6385 (2)	0.2370 (3)	3.48 (4)

Table 2. Main interatomic distances (Å), bond angles (°) and hydrogen bonds (Å, °) in guanidinium tetrathio-cyclo-tetraphosphate

P ₄ O ₈ S ₄ ring anion				
P(1)SO ₃ tetrahedron				
P(1)	S(1)	O(E1)	O(L12)	O(L21)
S(1)	1.9427 (8)	2.976 (2)	2.876 (2)	2.926 (2)
O(E1)	119.37 (8)	1.495 (2)	2.560 (2)	2.478 (2)
O(L12)	107.84 (6)	111.17 (9)	1.608 (2)	2.504 (2)
O(L21)	110.04 (7)	105.29 (8)	101.70 (8)	1.621 (1)
P(2)SO ₃ tetrahedron				
P(2)	S(2)	O(E2)	O(L12)	O(L21)
S(2)	1.9436 (7)	2.966 (1)	2.903 (1)	2.840 (1)
O(E2)	118.91 (6)	1.490 (2)	2.548 (2)	2.543 (2)
O(L12)	109.15 (6)	110.49 (9)	1.611 (2)	2.466 (2)
O(L21)	105.95 (6)	110.46 (9)	100.18 (9)	1.605 (2)
P(1)—P(2)	2.9811 (7)	P(1)—P(2)—P(1)	95.61 (2)	
P(1)—P(2)	2.9768 (8)	P(2)—P(1)—P(2)	84.39 (2)	
P(1)—O(L12)—P(2)	135.3 (1)			
P(1)—O(L21)—P(2)	135.1 (1)			
Guanidinium groups				
(I)				
C(1)—N(11)	1.316 (4)	N(11)—C(1)—N(21)	119.8 (2)	
C(1)—N(21)	1.318 (3)	N(11)—C(1)—N(31)	120.5 (2)	
C(1)—N(31)	1.325 (3)	N(21)—C(1)—N(31)	119.7 (2)	
(II)				
C(2)—N(12)	1.316 (3)	N(12)—C(2)—N(22)	119.9 (2)	
C(2)—N(22)	1.321 (3)	N(12)—C(2)—N(32)	120.5 (2)	
C(2)—N(32)	1.313 (3)	N(22)—C(2)—N(32)	119.6 (2)	
Hydrogen bonds				
N—H...O(S)	N—H	H...O(S)	N—O(S)	N—H...O(S)
N(11)—H(1N11)...O(E1)	0.85 (2)	2.07 (2)	2.909 (2)	168 (3)
N(11)—H(2N11)...O(L21)	0.86 (3)	2.47 (3)	3.243 (3)	161 (3)
N(21)—H(1N21)...S(2)	0.89 (3)	2.62 (3)	3.434 (3)	153 (2)
N(21)—H(2N21)...O(E2)	0.84 (3)	2.17 (3)	2.939 (2)	151 (3)
N(31)—H(1N31)...O(E2)	0.81 (3)	2.21 (3)	3.006 (3)	166 (3)
N(31)—H(2N31)...S(1)	0.90 (3)	2.57 (3)	3.470 (2)	171 (3)
N(12)—H(1N12)...O(E2)	0.82 (3)	2.09 (3)	2.907 (3)	173 (3)
N(12)—H(2N12)...S(2)	0.82 (3)	2.64 (3)	3.408 (2)	157 (3)
N(22)—H(1N22)...S(1)	0.88 (3)	2.66 (3)	3.519 (3)	165 (3)
N(22)—H(2N22)...S(2)	0.79 (3)	2.81 (3)	3.533 (3)	154 (3)
N(32)—H(1N32)...O(E1)	0.93 (3)	1.88 (3)	2.810 (3)	178 (3)
N(32)—H(2N32)...S(1)	0.77 (3)	2.87 (3)	3.476 (2)	137 (3)

Unit weights. Final refinements with 2356 reflections corresponding to $I > 3\sigma_I$. Final $R = 0.027$ ($wR = 0.030$). For the total set of 3339 independent reflections the R value is 0.036. No extinction correction. $S = 0.729$. Max. $\Delta/\sigma = 0.03$. Max. peak height in final difference Fourier synthesis $0.405 \text{ e } \text{Å}^{-3}$. Scattering factors for neutral atoms and f' , f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV). Enraf-Nonius (1977) *SDP* used for all calculations. Computer used: MicroVAX.

Discussion. The final atomic coordinates are reported in Table 1.*

* Lists of structure factors, anisotropic thermal parameters for non-H atoms, H-atom coordinates, and bonds and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53117 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The P₄O₈S₄ ring anion. The tetrathio-cyclo-tetraphosphate anion is made up of a ring of four PO₃S tetrahedra sharing corners. This ring, being centrosymmetrical, consists of only two such PO₃S tetrahedra. These tetrahedra are strongly distorted, the longest vertex corresponding to the P—S bond. As expected the P—O bridging bonds (1.605–1.621 Å) are about 8% longer than the P—O terminal bonds (1.490–1.495 Å). Among the four external S atoms of the ring two belonging to two adjacent P atoms are located above the ring plane while the two remaining ones are below.

Compared with the P—S bond lengths found in ionic dithiophosphates (1.96–1.98 Å) and with the average P—S single-bond distance (2.03 Å) (Corbridge, 1974), the shortened P—S bonds (1.943–1.944 Å) observed in the title compound give some evidence for π character of the P—S bond caused by mesomeric bond distribution between the external P—O and P—S linkages.

The main geometrical features of the P₄O₈S₄ ring anion are reported in Table 2.

The guanidinium group. As can be seen from the N—C—N angles reported in Table 2 the guanidinium group is planar within the estimated errors. These angles are very close to the theoretical ones (119.7–120.5°) and their sum is 360°. The C—N bonds are almost identical (1.316–1.325 Å) and slightly shortened in comparison with those found in guanidinium carbonate (1.34 Å) (Adams & Small, 1974) and guanidinium diphosphate monohydrate (1.334 Å) (Adams & Ramdas, 1977).

A three-dimensional network of weak hydrogen bonds, whose geometrical features are reported in Table 2, connects the guanidinium groups and the P₄O₈S₄ anions.

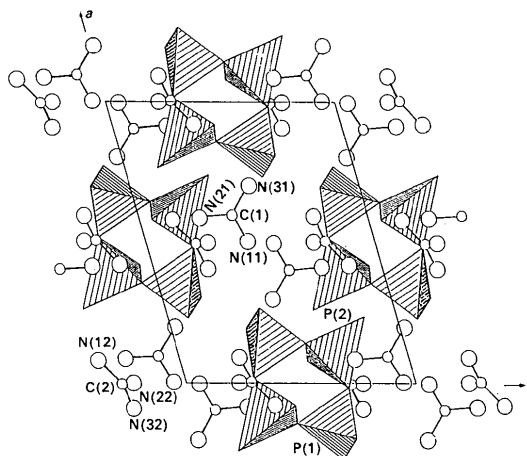


Fig. 1. Projection of the atomic arrangement of guanidinium tetrathio-cyclo-tetraphosphate along the b axis.

Fig. 1, generated with *STRUPLO84* (Fischer, 1985), shows a projection along the *b* axis of the atomic arrangement of this salt.

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Structure of (*E*)-Phenyl 2-Pyridyl Ketone Oxime

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Abstract. $C_{12}H_{10}N_2O$, $M_r = 198.2$, monoclinic, $C2/c$, $a = 16.246$ (3), $b = 8.423$ (1), $c = 17.383$ (3) Å, $\beta = 122.34$ (1)°, $V = 2009.7$ (1) Å³, $Z = 8$, $D_x = 1.31$, $D_m = 1.30$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 6.53$ cm⁻¹, $F(000) = 832$, $T = 295$ K, $R(F) = 0.045$ for 1357 independent reflections. The molecules form a unique centrosymmetric dimer, in which the OH group forms a bifurcated hydrogen bond with the pyridine N atom and the oxime N atom. The two oxime N atoms in the dimer have a short non-bonding contact 2.837 (4) Å.

Introduction. The crystal structure of the title compound was determined as part of our studies of ketone oxime derivatives (Taga & Miyasaka, 1987; Taga, Uchiyama, Machida & Miyasaka, 1988). One of the characteristics of an oxime compound is dimer formation through OH...N hydrogen bonds as observed in several oxime derivatives, e.g. *p*-nitrobenzaldehyde oxime (Brehm & Watson, 1972; Bachechi & Zambonelli, 1973), *p*-dimethylaminobenzaldehyde oxime (Bachechi & Zambonelli, 1972), 1-phenyl-1,2-propanedione 2-oxime (Saarinen, Korvenranta & Nasakkala, 1977) and carvoxime (Oonk & Kroon, 1976; Kroon, van Gurp, Oonk, Baert & Fouret, 1976). The hydrogen bonds are usually formed between the N—OH groups related by a center of symmetry. Stability of such a hydrogen-

bonding system was theoretically studied by Jeffrey, Ruble, McMullan, DeFrees & Pople (1981) and Jeffrey, Ruble & Pople (1982). The title ketone oxime forms a similar centrosymmetric dimer, but the hydrogen bonds are of a bifurcated type. This paper describes the details of the structure of the unique hydrogen-bonded dimer.

Experimental. Crystals from ethanol–water as colorless prisms; crystal dimensions 0.2 × 0.2 × 0.3 mm; density by flotation; Rigaku AFC-5RU diffractometer with graphite monochromator; cell dimensions by least-squares to fit 20 θ angles (16.2–28.3°); 1442 reflections ($0 \leq h \leq 18$, $0 \leq k \leq 9$, $-19 \leq l \leq 19$) collected within $2\theta < 120^\circ$; 2θ - ω scan mode; intensity fluctuation less than 2% for three standard reflections measured every 56 reflections; intensities corrected for Lorentz and polarization factors, but not for absorption; 1357 unique reflections with $F_o > 3\sigma(F_o)$ used for structure determination. Structure solved with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refined by full-matrix least squares based on F ; $w = [\sigma^2(F) + (0.023F)^2]^{-1}$; non-H atoms anisotropic, H atoms found in difference maps were isotropic; $R = 0.045$, $wR = 0.071$; $S = 1.4$; maximum parameter shift less than 0.05σ ; maximum residual density 0.25 e Å⁻³; atomic scattering factors from *International Tables*