

With the exception of the six amino H atoms, all atoms in this structure lie in two parallel mirror planes at $\pm \frac{1}{4}c$. The planar TAG cations are stacked directly over one another in adjacent layers 3.109 (1) Å apart; the Cl⁻ anions are stacked in alternate layers 6.218 (1) Å apart. The closest interionic contacts between layers occur among the amino groups of the TAG cations and the Cl⁻ ions. The distance between the amino N atom and a Cl⁻ ion N(2)—Cl is 3.684 (2) Å. Although this interatomic distance is shorter than the 3.692 Å reported by Okaya & Pepinsky (1957), it is still larger than would be observed if hydrogen bonding were involved. In view of this, only van der Waals and Coulombic forces operate between adjacent layers of ions.

Within any layer, each Cl⁻ ion is surrounded by three TAG cations and is hydrogen bonded to three nearest-neighbor guanidinium N atoms with N(1)—Cl 3.158 (3) Å. Each Cl⁻ also has three nearest-neighbor amino groups with N atoms [N(2)—Cl] at a distance of 3.579 (3) Å as compared to 3.596 Å reported by Okaya & Pepinsky (1957).

The TAG cation (Fig. 1) displays C_{3h} symmetry with a C—N(1) bond length of 1.325 (2) Å and an

N(1)—N(2) bond length of 1.411 (4) Å which agree with the mean bond lengths of 1.322 (6) and 1.406 (5) Å observed in TAGN for C—N(1) and N(1)—N(2), respectively.

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Structure of the Ammonium Salt of *cis*-4-Methyl-2-oxido-1,3,2-dioxaphosphorinane 2-Sulphide, NH₄⁺.C₄H₈O₃PS⁻

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Abstract. $M_r = 185.2$, orthorhombic, *Pccn*, $a = 18.154$ (6), $b = 13.973$ (6), $c = 7.047$ (1) Å, $U = 1787.6$ Å³, $Z = 8$, $D_x = 1.38$ Mg m⁻³, *Mo Kα*, $\lambda = 0.71069$ Å, $\mu = 0.439$ cm⁻¹, $F(000) = 784$, $T = 295$ K, $R = 0.054$, $R_w = 0.051$, for 906 observed reflections. The structure comprises discrete C₄H₈O₃PS⁻ and NH₄⁺ ions bonded by N—H...O hydrogen bonds into dimers around the twofold axis.

Introduction. The title compound was synthesized by Mikołajczyk & Łuczak (1972) during their systematic studies of geometric isomerism in cyclic five- and six-membered phosphorus monothioacid derivatives, occurring when the molecule contains at least one

asymmetric centre at a ring carbon atom. The chemical background of this class of compounds has been described elsewhere (Bartczak, 1983). The present investigation was undertaken, as part of our systematic studies on the conformation and crystal chemistry of the 1,3,2-dioxaphosphorinane ring, to determine the localization of the negative charge in the molecule, *i.e.* whether the NH₄⁺ ion is linked to the sulphur or to the oxygen atom.

Experimental. Sample kindly supplied by Professor M. Mikołajczyk of the Centre of Molecular and Macromolecular Studies of the Polish Academy of Sciences in Łódź. Good colourless crystals grown from *n*-propanol–*n*-hexane 1:1 mixture by slow evaporation; preliminary Weissenberg and oscillation photographs

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showed systematic extinctions consistent uniquely with *Pccn* (No. 56, $0kl$, $l=2n+1$; $h0l$, $l=2n+1$; $hk0$, $h+k=2n+1$; $h00$, $h=2n+1$; $0k0$, $k=2n+1$; $00l$, $l=2n+1$); prismatic crystal, ca 0.3 mm edge, 1068 reflections measured, CAD-4 diffractometer (graphite monochromator, Mo $K\alpha$ radiation), 906 with $F_o > 3\sigma(F_o)$, Lp correction, not absorption, max. $hkl = 19, 15, 7$.

Careful inspection of the data which had been measured without the discrimination of the reflections forbidden by the space group *Pccn* showed three symmetry-forbidden reflections with $I > 3\sigma(I)$. This prompted us at the start to try to solve the structure in space group *Pna2*, rather than in *Pccn*. The structure solved easily in *Pna2*, by direct methods with the *TANG* procedure of *SHELX76* (Sheldrick, 1976) and was refined anisotropically by standard difference-Fourier and least-squares techniques; $R = 0.047$, $R_w = 0.047$. However, the results were not entirely satisfactory, as the two molecules present in the asymmetric unit showed striking differences in the matching bond lengths and angles, although the general pattern was consistent with the literature data. The problem of solving and refining crystal structures in the space groups of unnecessarily low symmetry has been extensively reviewed recently (e.g. Schomaker & Marsh, 1979; Marsh & Schomaker, 1979). Therefore, we returned to the original centrosymmetric space group *Pccn*. Final refinements using F magnitudes converged with $R = 0.0537$ and $R_w = 0.0510$, $w = [\sigma^2(F_o) + 0.0136 F_o^2]^{-1}$; $(\Delta/\sigma)_{\max}$ for non-hydrogen atom = -0.53 for z coordinate of C(5); all ring hydrogen atoms refined in the 'riding model' (C-H = 1.08 Å); four H atoms of ammonium ion defined from a difference Fourier synthesis and refined isotropically; scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations performed with *SHELX76* (Sheldrick, 1976) and *XANADU* (Roberts & Sheldrick, 1975).*

Discussion. The molecular structure and atomic nomenclature are shown in Fig. 1. Final atomic coordinates and equivalent thermal parameters are given in Table 1. Intramolecular bond distances and angles are given in Table 2. Fig. 2 shows dihedral and torsion angles.

The structure consists of discrete NH_4^+ and $\text{C}_4\text{H}_8\text{O}_3\text{PS}^-$ ions bonded by a hydrogen bond $\text{O}(2)\cdots\text{H}(11') = 1.87(1)$ Å. The exocyclic phosphoryl $\text{O}(2)$ atom forms another hydrogen bond with a neighbouring complex: $\text{O}(2)\cdots\text{H}(12) = 1.94(1)$ Å

* Lists of structure factors, anisotropic thermal parameters, a packing diagram and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38685 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

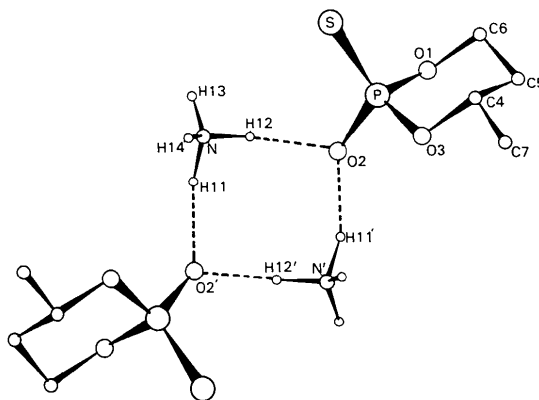


Fig. 1. The molecular structure and atomic numbering. A dimer is shown bonded by hydrogen bonds.

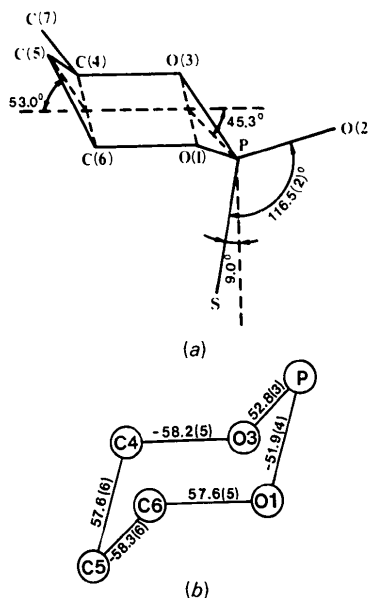


Fig. 2. (a) Dihedral angles ($^\circ$) in the 1,3,2-dioxaphosphorinane ring. (b) Torsional angles ($^\circ$).

Table 1. Positional parameters ($\times 10^4$) and equivalent U values ($\text{\AA}^2 \times 10^3$) for the non-hydrogen atoms

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
S	467 (1)	-1489 (1)	3497 (2)	52 (1)
P	1268 (1)	-809 (1)	2218 (2)	40 (1)
O(2)	1829 (2)	-1415 (3)	1221 (4)	50 (1)
N	1673 (3)	-3418 (4)	2197 (7)	51 (2)
O(1)	976 (2)	-56 (3)	680 (5)	59 (1)
O(3)	1707 (2)	-147 (2)	3682 (4)	46 (1)
C(4)	1308 (3)	679 (4)	4465 (8)	56 (2)
C(5)	1059 (3)	1308 (4)	2846 (9)	67 (2)
C(6)	577 (4)	768 (4)	1445 (9)	73 (2)
C(7)	1830 (5)	1154 (5)	5828 (12)	99 (3)

which produces a dimer (Fig. 1). There is also a longer bond O(2)⋯H(14) of 2.21 (1) Å. Similar dimeric arrangements are frequently observed, for example in the structure of the ammonium picrate complex with 1,10-phenanthroline (Jones, Milburn, Sawyer & Hughes, 1981). The 1,3,2-dioxaphosphorinane ring is a slightly distorted chair (Fig. 2). The asymmetry parameters (Duax & Norton, 1975) are: $C_s(P) = 0.7 (5)^\circ$ and $C_2[O(1), C(6)] = 5.7 (5)^\circ$. The S=P bond is situated axially to the ring and the P—O bond equatorially. The C(7) methyl group and the exocyclic oxygen atom are in a *cis* configuration, as expected by Mikołajczyk & Łuczak (1972). The geometry of the ring closely resembles those in similar structures of the dicyclohexylammonium salt of the title compound (Bartczak, 1983) and in 4-methyl-1,3,2-dioxaphosphorinane 2-oxide (Saenger & Mikołajczyk, 1972).

Table 2. Bond lengths (Å) and angles (°)

P—S	1.957 (2)	O(2)—P	1.499 (3)
O(1)—P	1.600 (3)	O(3)—P	1.599 (3)
C(6)—O(1)	1.463 (7)	C(4)—O(3)	1.470 (6)
C(5)—O(4)	1.509 (8)	C(7)—C(4)	1.504 (9)
C(6)—C(5)	1.520 (9)		
O(2)—P—S	116.5 (2)	O(1)—P—S	112.6 (2)
O(1)—P—O(2)	106.2 (2)	O(3)—P—S	110.7 (1)
O(3)—P—O(2)	106.9 (2)	O(3)—P—O(1)	102.8 (2)
C(6)—O(1)—P	115.5 (3)	C(4)—O(3)—P	116.8 (3)
C(5)—C(4)—O(3)	108.7 (4)	C(7)—C(4)—O(3)	106.0 (4)
C(7)—C(4)—C(5)	114.4 (5)	C(6)—C(5)—C(4)	111.9 (4)
C(5)—C(6)—O(1)	110.2 (4)		

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Structures of 7-Bromo-1,3-dihydro-5-(2-pyridyl)-2H-1,4-benzodiazepin-2-one (Bromazepam, C₁₄H₁₀BrN₃O) and 5-(2-Fluorophenyl)-1,3-dihydro-1-methyl-7-nitro-2H-1,4-benzodiazepin-2-one (Flunitrazepam, C₁₆H₁₂FN₃O₃)*

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Abstract. Bromazepam: $M_r = 316.2$, monoclinic, $P2_1/c$, $a = 10.304 (4)$, $b = 15.897 (5)$, $c = 8.122 (3)$ Å, $\beta = 106.8 (3)^\circ$, $U = 1273.6 \text{ \AA}^3$, $Z = 4$, $D_x = 1.649 \text{ Mg m}^{-3}$, $\mu(\text{Mo } K\alpha, \lambda = 0.71069 \text{ \AA}) = 3.13 \text{ mm}^{-1}$, $F(000) = 632$, room temperature, $R =$

All bonds and angles have typical values for this class of compounds and will not be discussed in detail.

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0.040 for 1470 observed reflections. Flunitrazepam: $M_r = 313.3$, monoclinic, $P2_1/n$, $a = 7.321 (1)$, $b = 13.668 (5)$, $c = 14.356 (5)$ Å, $\beta = 96.68 (2)^\circ$, $U = 1426.8 \text{ \AA}^3$, $Z = 4$, $D_x = 1.459 \text{ Mg m}^{-3}$, $\mu(\text{Mo } K\alpha, \lambda = 0.71069 \text{ \AA}) = 0.07 \text{ mm}^{-1}$, $F(000) = 648$, room temperature, $R = 0.054$ for 1017 observed reflections. In both molecules the seven-membered ring is in a boat conformation. The angle between the benzo moiety of

* Contribution from the Crystallography Unit, Universities of Aston and Birmingham.