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STEREOCHEMISTRY OF ORGANOPHOSPHORUS CYCLIC COMPOUNDS—XV[1]

SYNTHESIS OF TETRAMETHYLAMMONIUM SALT OF 2-OXO-2-THIO-1,3,2-OXAZAPHOSPHORINAN AND ITS CRYSTAL AND MOLECULAR STRUCTURES

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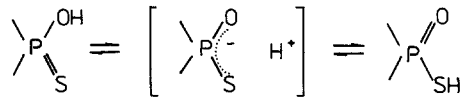
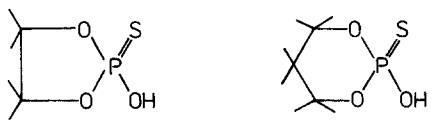
Abstract—2-Hydroxy-1,3,2-oxazaphosphorinan-2-thione (**5**) was prepared by alkaline hydrolysis of 2-chloro-1,3,2-oxazaphosphorinan-2-thione (**6**). Treatment of the latter with sodium methoxide afforded the 2-methoxy-derivative **7** from which the tetramethylammonium salt of the thioacid **5** was obtained by the action of trimethylamine. The structure of this salt has been determined by the direct method and refined by least-squares to R = 0.0734, a = 12.303(4), b = 9.041(3), c = 10.419(2)Å, space group $P2_12_12_1$. The 2-oxo-2-thio-1,3,2-oxazaphosphorinanyl anion is in the chair form with the exocyclic S and O atoms in an axial and equatorial position, respectively. An intermolecular H-bond between S and the endo-cyclic N atom is present in the solid-state structure.

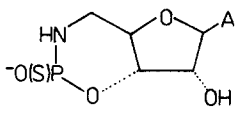
Phosphorus monothioacids, as a result of their high reactivity and the ambident character of the monothioacid anion, are convenient starting materials for the synthesis of a variety of phosphoryl and thiophosphoryl compounds.[2]



Recently, emphasis has centered on cyclic 5- and 6-membered phosphorus monothioacids which play a significant role in chemical and biochemical studies.[3–5]



In contrast to the widely investigated cyclic thioacids, in which phosphorus is a part of the 1,3,2-dioxaphospholan and 1,3,2-dioxaphosphorinan system, those containing the 1,3,2-oxazaphosphorinan ring are relatively unknown. The only examples of such thioacids are cyclic thionucleotides **1** and **2** prepared in the form of two diastereoisomers by Jastorff and Baer[6] and Morr and Ernst,[7] respectively.



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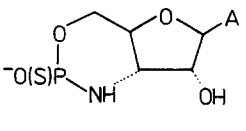

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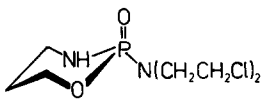

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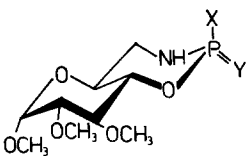

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The 1,3,2-oxazaphosphorinan ring system has recently attracted considerable attention because of its presence in antitumor agent cyclophosphamide (**3**)[8] and its congeners as well as in connection with the fact that 2-substituted 1,3,2-oxazaphosphorinan-2-ones and 1,3,2-oxazaphosphorinan-2-thiones **4** condensed with the carbohydrate moiety became important precursors to other chiral phosphates and thiophosphates.[9]

We report the synthesis of 2-hydroxy - 1,3,2 - oxazaphosphorinan - 2 - thione (**5**) and an X-ray analysis of its tetramethylammonium salt which was carried out in order to determine the conformation of the oxazaphosphorinan ring and particularly to establish the conformational preferences for the phosphorus monothioacid anion in this ring system.

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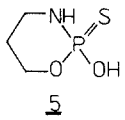

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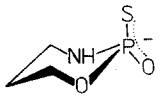
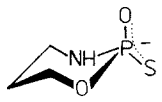


5a

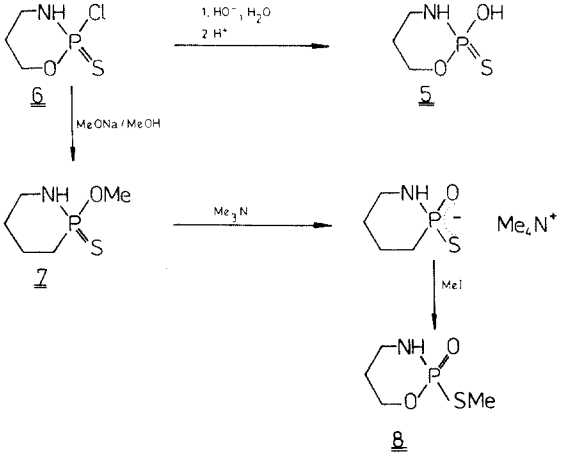


5b

An X-ray structural determination revealed that the solid state conformation of the 2 - oxo- -2 -thio - 1,3,2 - oxazaphosphorinanyl anion is **5a** and not the alternative chair conformation **5b**.

RESULTS AND DISCUSSION

Synthesis of 2 - *hydroxy* - 1,3,2 - *oxazaphosphorinan* - 2 - *thione* (**5**) *and its tetramethylammonium salt.* The cyclic thioacid **5** was obtained from the readily available 2 - chloro - 1,3,2 - oxazaphosphorinan - 2 - thione (**6**).[10] The free acid **5** obtained in moderate yield (42%) after acidification of the mixture and crystallisation had m.p. 168–172°. It was additionally characterized as dicyclohexylammonium salt (m.p. 186–191°). On the other hand, the chloride **6** was converted into 2 - methoxy - 1,3,2 - oxazaphosphorinan - 2 - thione (**7**). The thionoester **7** was, in turn, demethylated to give tetramethylammonium salt of the acid **5** (m.p. 218.5–221.5°). The reaction of this salt with an excess of methyl iodide afforded 2 - methylthio - 1,3,2 - oxazaphosphorinan - 2 - one (**8**). The reactions discussed above are summarised in Scheme.



The P atom in **5** is a center of chirality. Therefore, as could be expected on the basis of our earlier results,[11] the $^{31}P\{^1H\}$-NMR spectrum of the salt of **5** with optically active 1-(naphthyl)ethylamine shows two singlets of equal intensity due to the formation of two diastereoisomeric salts. Although the chemical shift difference is small, $\Delta\delta = 0.2$ Hz, the magnetic nonequivalence observed may be useful to follow the progress of optical resolution of the thioacid **5**.

†The structure factors and anisotropic thermal parameters and bond lengths involving H atoms are deposited with the British Library Lending Division as Supplementary Publication.

Crystal structure of tetramethylammonium 2 - *oxo* - 2 - *thio* - 1,3,2 - *oxazaphosphorinan.* An X-ray crystallographic analysis was performed on the tetramethylammonium salt of the thioacid **5** for two reasons. Firstly, it was interesting to determine the conformation of the 1,3,2-oxazaphosphorinan ring in the solid state especially in view of the fact that some recent reports[12] emphasized the propensity of this ring to undergo conformational changes from the normal chair form (found in the majority of cases)[13] to a twist form in response to steric or electronic demands of the substituents at P. Secondly, the determination of the structure of the compound under consideration could throw some light on the preferred configuration of the phosphorus monothioacid anion in this ring system.

The geometry of the 1,3,2-oxazaphosphorinan ring is shown in Fig. 1. Figure 2 shows the unit-cell contents. The final positional parameters with isotropic temperature factors are listed in Tables 1 and 2.† The bond lengths and angles are given in Tables 3 and 4.†

The 6-membered ring of the cyclid anion investigated has a chair conformation in which the exocyclic S and O atoms connected with P are in an axial and equatorial position, respectively. Thus, among two possible chair conformations for the 2 - oxo - 2 - thio - 1,3,2 - oxazaphosphorinanyl anion **5a** and **5b** the former exists in the solid state. The detailed information on the geometry of the 1,3,2-oxazaphosphorinan ring is given in Table 5. The differences $(\alpha - \beta)$ are chosen to illustrate the degree of distortion of the chair form from the ideal cyclohexane conformation ($\alpha = \beta \approx 55°$). In this regard the 1,3,2-oxazaphosphorinan ring is flattened at the P end as well as at the opposite ring C atom |C(2)|. The conformation of the 1,3,2-oxazaphosphorinan ring may also be described by its torsion angles (Table 6). The distorted tetrahedron around the P atom does not show considerable differences in relation to the literature data on that type of compounds.

The P–S bond length of 1.962(3)Å is longer than the normally observed length of the P=S bond being 1.94Å on the average[14] and it is much shorter than the length of the P–S bond lying between 2.08 to 2.14Å. On the other hand, the length of the P–O(1) bond is 1.475(6)Å showing a considerable shortening of this bond in relation to a single bond between P and O being 1.59Å on the average.[15] This situation seems to be typical for the monothioacid anion best described by two mesomeric forms in which the negative charge is delocalized between the S and O atoms.

The other bond lengths and angles in the 1,3,2-oxazaphosphorinan ring agree with the reported literature data. H atoms of the ring were localized geometrically. Isotropic refinements gave good temperature factors for all H atoms except for the H atom bound to N(1) (temp. factor 0.2226). The sum of the angles around the N atom is 350° and standard deviations of H(1)–N(1)–P (8.09°) and C(1)–N(1)–H(1) (9.2°) angles are very high. This proves the lability of the position of this H atom. The intermolecular distances indicate the existence of an intermolecular H–bond between S and the endocyclic N atom (3.596 Å). This finding brings in question the recent

Table 1. Positional parameters ($\times 10^4$) with isotropic temperature factors for the nonhydrogen atoms

Atom	x	y	z	B
P	103(1)	5302(2)	4429(1)	4.44(8)
S	526(2)	3229(2)	4674(2)	6.25(10)
O1	806(5)	6466(5)	4971(6)	6.33(25)
N1	-51(5)	5698(8)	2853(5)	5.51(29)
O2	-1086(4)	5558(8)	5011(5)	6.67(28)
C1	-1001(5)	4916(10)	2285(6)	5.57(33)
C2	-2066(6)	5243(10)	2993(7)	5.90(33)
C3	-1987(6)	4855(14)	4388(8)	7.08(44)
N2*	-1234(4)	-272(6)	6324(4)	3.91(19)
C21*	-1431(6)	-290(9)	4915(5)	5.16(29)
C22*	-1636(6)	1138(8)	6875(8)	5.61(33)
C23*	-1778(7)	-1572(8)	6939(8)	5.70(33)
C24*	-41(5)	-426(9)	6557(7)	5.14(31)

*refers to tetramethylammonium cation

Table 2. Hydrogen atom positional parameters ($\times 10^4$) with isotropic temperature factors

Atom	x	y	z	B
H1	141(158)	6681(126)	2367(153)	17.58(505)
H11	-1076(5)	5317(10)	1313(6)	8.51(105)
H12	-883(5)	3732(10)	2273(6)	8.51(105)
H21	-2711(6)	4605(10)	2561(7)	8.51(105)
H22	-2247(6)	6407(10)	2906(7)	8.51(105)
H31	-1893(6)	3672(14)	4474(8)	8.51(105)
H32	-2728(6)	5194(14)	4860(8)	8.51(105)
H211	-2249(6)	-370(9)	4543(5)	6.86(56)
H212	-945(6)	-1183(9)	4534(5)	6.86(56)
H213	-1081(6)	756(9)	4633(5)	6.86(56)
H221	-1430(6)	1079(8)	7882(8)	6.86(56)
H222	-2493(6)	1366(8)	6774(8)	6.86(56)
H223	-1172(6)	2011(8)	6426(8)	6.86(56)
H231	-2630(7)	-1292(8)	6899(8)	6.86(56)
H232	-1515(7)	-1603(8)	7928(8)	6.86(56)
H233	-1652(7)	-2643(8)	6505(8)	6.86(56)
H241	344(5)	543(9)	6157(7)	6.86(56)
H242	263(5)	-1403(9)	6080(7)	6.86(56)
H243	137(5)	-493(9)	7570(7)	6.86(56)

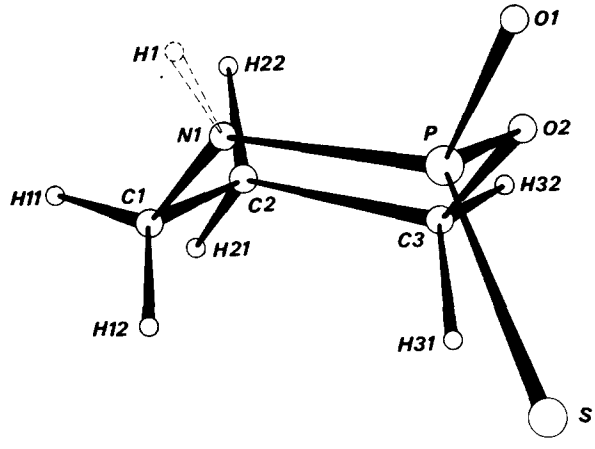


Fig. 1. Atom numbering scheme and solid state conformation of the 2-oxo-2-thio-1,3,2-oxazaphosphorinanyl anion.

Table 3. Bond lengths (Å)

P-S	1.962(3)	C(2)-C(3)	1.498(12)
P-O(1)	1.475(6)	C(3)-O(2)	1.433(10)
P-N(1)	1.675(5)	N(2)-C(21)	1.489(7)
P-O(2)	1.600(5)	N(2)-C(22)	1.483(9)
N(1)-C(1)	1.447(9)	N(2)-C(23)	1.497(9)
C(1)-C(2)	1.532(10)	N(2)-C(24)	1.493(8)

Table 3(a). Bond lengths involving hydrogen atoms (Å)

N(1)-H(1)	1.128(129)	C(22)-H(221)	1.080(12)
C(1)-H(11)	1.080(10)	C(22)-H(222)	1.080(11)
C(1)-H(12)	1.080(12)	C(22)-H(223)	1.080(11)
C(2)-H(21)	1.080(11)	C(23)-H(231)	1.080(12)
C(2)-H(22)	1.080(13)	C(23)-H(232)	1.080(11)
C(3)-H(31)	1.080(17)	C(23)-H(233)	1.080(10)
C(3)-H(32)	1.080(11)	C(24)-H(241)	1.080(11)
C(21)-H(211)	1.080(10)	C(24)-H(242)	1.080(11)
C(21)-H(212)	1.080(11)	C(24)-H(243)	1.080(10)
C(21(-H(213)	1.080(11)		

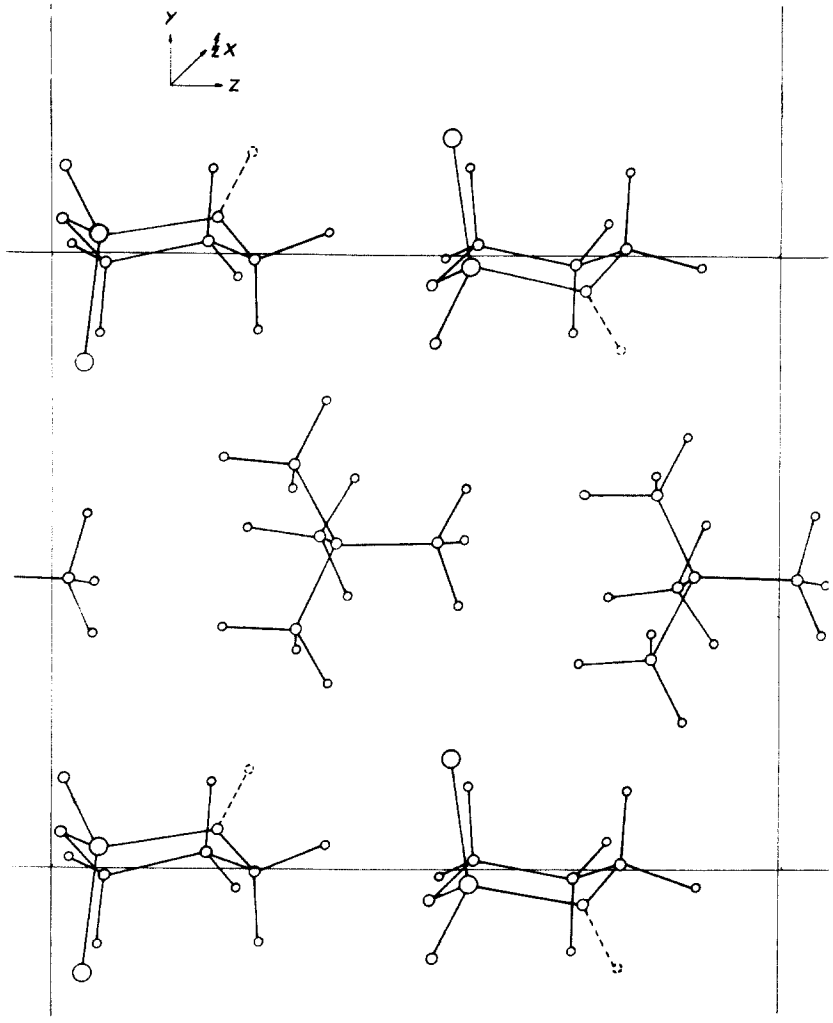


Fig. 2. The packing of the molecules of tetramethylammonium salt of **5** in the unit cell.

Table 4. Bond angles (°)

O(1)-P-S	118.4(2)	C(3)-C(2)-C(1)	111.5(6)
N(1)-P-S	108.1(3)	C(22)-N(2)-C(21)	109.7(5)
N(1)-P-O(1)	109.1(3)	C(23)-N(2)-C(21)	109.9(5)
O(2)-P-S	109.4(3)	C(23)-N(2)-C(22)	111.1(5)
O(2)-P-O(1)	106.7(3)	C(24)-N(2)-C(21)	108.6(5)
O(2)-P-N(1)	104.2(3)	C(24)-N(2)-C(22)	110.1(5)
C(1)-N(1)-P	115.1(5)	C(24)-N(2)-C(23)	107.3(5)
C(3)-O(2)-P	118.1(5)	H(1)-N(1)-P	123.7(80)
C(2)-C(1)-N(1)	114.3(6)	C(1)-N(1)-H(1)	110.9(92)
C(2)-C(3)-O(2)	112.7(7)		

Table 5. Ring geometry of 1.3.2-oxazaphosphorinane

Plane	Atom in the plane	Deviations from plane (Å)
(i)	N(1)	-0.008(3)
	O(2)	0.008(3)
	C(1)	0.008(3)
	C(3)	-0.008(4)
(ii)	P	0.0
	O(2)	0.0
	N(1)	0.0
(iii)	C(1)	0.0
	C(2)	0.0
	C(3)	0.0
(iiii)	P	0.0
	S	0.0
	O(1)	0.0

Angles between normals to planes (°)

α=(i)(ii)=40.16
β=(i)(iii)=48.26
γ=(i)(iiii)=89.61

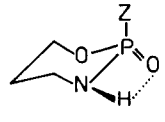
Equations of the planes

(i) $-0.3875\,X_o + 0.9002\,Y_o - 0.1986\,Z_o = 3.9980$
(ii) $0.2096\,X_o + 0.9686\,Y_o + 0.1335\,Z_o = 5.2849$
(iii) $0.3239\,X_o + 0.9239\,Y_o + 0.2039\,Z_o = 4.1938$
(iiii) $-0.5209\,X_o - 0.0285\,Y_o + 0.8531\,Z_o = 3.7344$

Table 6. Torsion angles (°)

N(1)-P-O(2)-C(3)	47.8(5)
P-O(2)-C(3)-C(2)	-56.1(4)
C(1)-C(2)-C(3)-O(2)	54.6(5)
N(1)-C(1)-C(2)-C(3)	-54.1(6)
P-N(1)-C(1)-C(2)	51.1(4)
O(2)-P-N(1)-C(1)	-44.6(4)

proposals[16] that the equatorially situated phosphoryl O atom in the 1,3,2-oxazaphosphorinan ring may form the intramolecular H-bond with the N–H ring grouping as shown below.



EXPERIMENTAL

^{1}H NMR spectra were measured with a Perkin–Elmer R-12B instrument with HMDSO as external standard. ^{31}P-NMR and ^{13}C-NMR spectra were recorded on a JEOL-INM FX60 spectrometer using 85% phosphoric acid as external standard and TMS as internal standard, respectively. Mass spectra were obtained on a GCMS-LKB 9000S instrument. M.ps and b.p. are uncorrected. All solvents were dried and purified by conventional methods. Compound **6** was prepared in 45% yield from thio-

phosphoryl chloride and 3-aminopropan-1-ol in accordance with Kildisheva *et al.*;[10] m.p. 84–86°; ^{1}H NMR ($CDCl_3$) δ 2.07–3.22 (2H, m, CCH_2C), 3.40–4.31 (2H, m, CH_2N), 4.51–5.33 (3H, m, NH and CH_2O); ^{31}P NMR (MeOH) δ 70.7; ^{13}C NMR ($CDCl_3$) δ 71.4 (C_6, $^2J_{CP}$ = 11.7 Hz), 42.5 (C_4, $^2J_{CP}$ = 5.9 Hz), 25.9 (C_5, $^3J_{CP}$ = 3.8 Hz).

2 - *Hydroxy* - 1,3,2 - *oxazaphosphorinan* - 2 - *thione* (**5**). To a water soln of NaOH (0.8 g, 20 mmol) **6** (1.6 g, 9.3 mmol) was added portionwise at room temp. After 5 hr stirring the soln was acidified with conc HCl (4 ml) at 5–10°. The ppt was quickly filtered off and dried over P_2O_5 in a disiccator. The thioacid **5** obtained (0.6 g, 42%) was crystallised from MeOH, m.p. 168–172°. ^{31}P NMR (H_2O) δ 57.6, (aq NaOH) 56.5; ^{13}C-NMR (aq NaOH) δ 67.5 (C_6, $^2J_{CP}$ = 6.2 Hz), 41.3 (C_4, $^2J_{CP}$ = 3.9 Hz), 26.2 (C_5). (Found: C, 23.86; H, 5.59; P, 18.82, N, 8.72. Calc. for $C_3H_8NO_2PS$: C, 23.63; H, 5.26; P, 20.2; N, 9.15%).

Dicyclohexylammonium salt of **5** was prepared from **5** (2 g, 13.1 mmol) and dicyclohexylamine (2.37 g, 13.1 mmol) in ether (15 ml). The ppt (2.7 g) was crystallised from acetone-MeOH (2 : 1, 30 ml), m.p. 186–191° (Found: C, 54.01; H, 9.40; P, 10.06; N, 7.67. Calc. for $C_{15}H_{31}N_2O_2PS$: C, 53.90; H, 9.33; P, 9.26; N, 8.37%).

2-*Methoxy*-1,3,2-*oxazaphosphorinan*-2-*thione* (**7**). To a soln of NaOMe prepared from Na (0.2 g, 8.6 mmol) and MeOH (15 ml), **6** (1.39 g, 8.1 mmol) was added portionwise at 10–15° and the resulting mixture was stirred for 3 hr at room temp. and left to stand overnight. Then the soln was evaporated, the residue diluted with benzene (15 ml) and the benzene soln washed with water (2 × 15 ml). The water layer was extracted with benzene (15 ml). The combined organic soln was dried over $MgSO_4$ and evaporated. The crude **7** was distilled under reduced pressure (0.3 mm Hg; 140° bath temp.) to afford 0.9 g (67%) of the pure product; n_D^{23} 1.5291. ^{31}P NMR (CCl_4) δ 67.7; ^{1}H NMR ($CDCl_3$) δ 1.90–3.15 (2H, m, CCH_2C), 3.40–4.20 (2H, m, CH_2N), 4.24 (3H, d, CH_3O, $^3J_{HP}$ = 13.3 Hz), 4.51–5.29 (3H, m, CH_2O and NH); ^{13}C NMR ($CDCl_3$) δ 68.9 (C_6, $^2J_{CP}$ = 8.8 Hz), 41.1 (C_4, $^2J_{CP}$ = 5.9 Hz), 26.2 (C_5, $^3J_{CP}$ = 8.8 Hz), 52.9 (CH_3, $^2J_{CP}$ = 5.9 Hz), MS (70 eV) *m/e* 167 (M^+, 70%), 134 (50), 104 (22), 79 (26), 56 (100), 47 (24), 28 (30). (Found: C, 28.90; H, 6.34; N, 7.87, Calc. for $C_4H_{10}N_2OPS$: C, 28.74; H, 6.03; N, 8.37%).

Tetramethylammonium salt of **5**. A mixture of **7** (0.81 g, 4.8 mmol) and Me_3N (2 ml) in benzene (15 ml) was kept at room temp. for 2 weeks (protected from light). The crystalline salt was filtered off, washed with benzene and dried over P_2O_5, 0.5 (46%), m.p. 218–221.5°. ^{1}H NMR (CD_3OD) δ 1.82–2.42 (2H, m, CCH_2C), 3.75 (14H, m, CH_2N and $(CH_3)_4N$), 4.34–5.11 (3H, m, CH_2O and NM); ^{31}P NMR (H_2O) δ 56.8 (Found: C, 37.15; H, 8.90; N, 12.26. Calc. for $C_7H_{19}N_2O_2PS$: C, 37.15; H, 8.46; N, 12.38%).

2-*Methylthio*-1,3,2-*oxazaphosphorinan*-2-*one* (**8**). A mixture of **5** prepared as above (0.67 g, 2.96 mmol) and MeI (2 ml) was dissolved in benzene (20 ml), refluxed for 4.5 hr and left to stand overnight. The residue was distilled under reduced pressure (0.4 mm Hg, 140° bath temp.) to give **8**, 0.3 g, (61%), n_D^{24} 1.5360. ^{1}H NMR ($CDCl_3$) δ 2.19–2.70 (2H, m, CCH_2C), 2.85 (3H, d, CH_3S, $^3J_{HP}$ = 14.0 Hz), 3.57–4.25 (2H, m, CH_2N), 4.65–5.27 (3H, m, CH_2O and NH); ^{31}P NMR ($CDCl_3$) δ 27.5; ^{13}C NMR ($CDCl_3$) δ 70.2 (C_6, $^2J_{CP}$ = 3.9 Hz); MS (70 eV) *m/e* 167 (M^+, 70%), 134 (50), 104 (22), 79 (26), 56 (100), 47 (24), 28 (30). (Found: C, 29.44; H, 6.59; P, 18.54. Calc. for $C_4H_{10}NO_2PS$: C, 28.74; H, 6.03; P, 18.53%).

X-Ray structure determination of tetramethylammonium salt of **5**

Crystal data. $C_7H_{19}N_2O_2PS$. M = 226.30. Orthorombic, a = 12.303(4), b = 9.041(3), c = 10.419(2)Å, V = 1158.9(6)Å^3, Z = 4, F(000) = 488, $\lambda(CuK_\alpha)$ = 1.54178Å, $\mu(CuK_\alpha)$ = 3.46 mm^{-1}; D_m = 1.303 Mg · m^{-3}, D_c = 1.297 Mg · m^{-3}, space group $P2_12_12_1$.

Crystallographic measurements and structure analysis. The crystals of the tetramethylammonium salt of **5** were recrystallised from n-BuOH. The crystals are sensitive to moisture.

The single crystal of approximate dimensions 0.2 × 0.2 × 0.3 mm was sealed into a Lindemann glass capillary tube. The space group was determined from Weissenberg photographs. The cell parameters and intensity data were collected on a Syntex $P2_1$ four-circle diffractometer by the use of graphite monochromated CuK_α radiation. Measurements were carried out in the $\theta - 2\theta$ scan mode for $2\theta \ll 115°$. A Lorentz polarization correction but no absorption $|\mu(CuK_\alpha) = 3.46\ mm^{-1}|$ correction was applied.

The structure was solved by direct method with $925 > 1.96\ \sigma$ (J) independent reflections. The refinement by full-matrix least-squares method with anisotropic temp. factors for all non-H atoms gave conventional R = 0.0916. Asymmetry parameters calculated for the 1,3,2-oxazaphosphorinan ring are: $\Delta C_S(P\text{–}C_2)$ = 3.4°, $\Delta C_2(C_2\text{–}C_3)$ = 2.7°.

The phase problem was solved by MULTAN-76 program using 177 normalised structure factors with $E \geq 1.2$. The refinement of the structure was carried out by the blocked full-matrix least-squares method (SHELX-76)[17] with anisotropic temperature factors for all non-H atoms. The H positions were refined with isotropic temperature parameters. The terminal value of $R_W = (\Sigma w^{1/2}\Delta/\Sigma w^{1/2}F_0^2) = 0.0874$ with R = 0.0734. The weights were given by $w = k|\delta^2(F_0) + gF_0^2|^{-1}$ where k and g were refined to 0.5011 and 0.004192, respectively. Complex neutral-atom scattering factors were employed.[18]

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