Tetrahedron Letters No. 31, pp 2655 - 2658, 1974. Pergamon Press. Printed in Great Britain.

CRYSTAL AND MOLECULAR STRUCTURE OF 2,5,5-TRIMETHYL-2-THIONO-1,3,2-DIOXAPHOSPHORINANE

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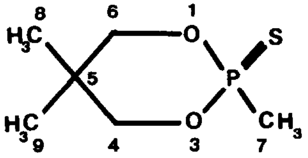
(Received in UK 10 June 1974; accepted for publication 19 June 1974)

In connection with investigations directed toward the study of the thermodynamical stability of 1,3,2-dioxaphosphorinanes [1], we have been interested in the nmr and stereochemistry of the 2-thiono-1,3,2-dioxaphosphorinanes [2].

Although several unsubstituted or 5,5-disubstituted 2-oxo-1,3,2-dioxaphosphorinanes have been studied by X-ray diffraction technique [3], there has been no X-ray studies concerning the 2-thiono-1,3,2-dioxaphosphorinanes. We wish to report here the X-ray structure determination of the 2,5,5-trimethyl-2-thiono-1,3,2-dioxaphosphorinane.



2,5,5-Trimethyl-2-thiono-1,3,2-dioxaphosphorinane

The 2,5,5-trimethyl-2-thiono-1,3,2-dioxaphosphorinane was readily synthesized by reacting methylphosphonothioic dichloride (Ethyl Corporation) and 2,2-dimethyl-1,3-propanediol (Aldrich). The crystals used in this investigation were recrystallized from warm cyclohexane. Due to slight decomposition under X-ray irradiation, the crystal was sealed in thin-walled capillary tube for data collection.

The crystals are orthorhombic, space group $P2_12_12_1$ (hoo, oko and ool absent for h, k or l odd). Other crystal data are summarized in Table 1.

TABLE I

2,5,5-Trimethyl-2-thiono-1,3,2-dioxaphosphorinane $C_6H_{13}O_2PS$ orthorhombic space group

F.W. = 180.21
F(000) = 96
$P2_12_12_1$
D_m = 1.23(5)
D_x = 1.285

a = 10.969 ± 0.001
b = 14.656 ± 0.001
c = 5.797 ± 0.001
V = 931.936 $Å^3$
Z = 4

The crystal used for measuring intensities was mounted about the c axis. The intensities of 1071 independent reflections (3°< θ < 70°) were recorded using Ni-filtered CuK_α radiation on a four circle Siemens diffractometer. The $2\,\bar{9}\,1$ reflection was checked periodically. It showed no drop-off in intensity during the data collection experiment. The structure was solved by direct methods with the program MULTAN [4]. Least-squares refinment, using the ORFLS program [5] (P,O,C,S anisotropic) has reached an R index ($R = \sum | F_o - F_c | / \sum | F_o |$) of 0.06 for 992 reflections.

Tables II and III give the bond distances and the bond angles with their standard deviations.

TABLE II

Bond distances (Å)		Standard deviations ($X.10^3$) are given in parenthese	
$P - O_1$	1.586 (4)	$O_1 - C_6$	1.468 (7)
$P - O_3$	1.582 (4)	$O_3 - C_4$	1.472 (7)
$P - S$	1.933 (2)	$C_4 - C_5$	1.530 (8)
$P - C_7$	1.772 (7)	$C_5 - C_6$	1.537 (8)
$C_5 - C_8$	1.536 (8)	$C_5 - C_9$	1.549 (7)

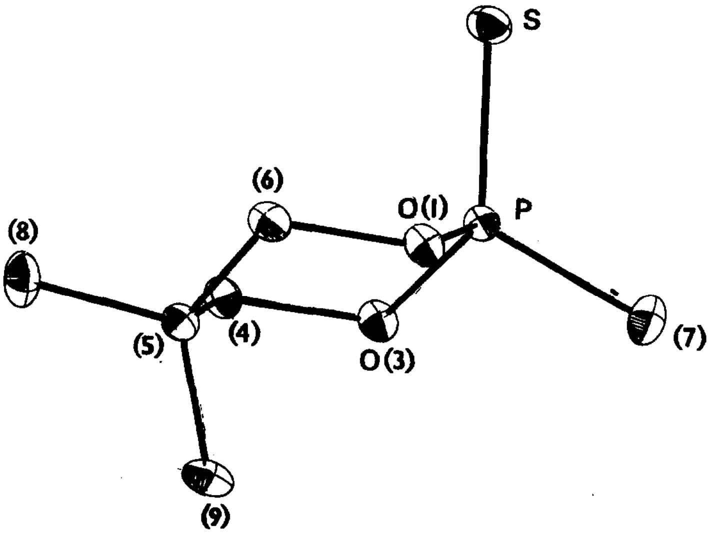
TABLE III

Bond angles (°)		Standard deviations are given in parenthese	
$O_1 - P - S$	115.1 (0.2)	$O_1 - C_6 - C_5$	111.1 (0.4)
$O_3 - P - S$	114.0 (0.2)	$O_3 - C_4 - C_5$	110.8 (0.5)
$O_1 - P - C_7$	102.7 (0.3)	$C_4 - C_5 - C_6$	108.7 (0.4)
$O_3 - P - C_7$	103.2 (0.3)	$C_4 - C_5 - C_8$	107.3 (0.5)
$S - P - C_7$	116.7 (0.3)	$C_6 - C_5 - C_8$	108.1 (0.5)
$O_1 - P - O_3$	103.5 (0.2)	$C_6 - C_5 - C_9$	109.3 (0.5)
$P - O_1 - C_6$	115.5 (0.4)	$C_4 - C_5 - C_9$	111.2 (0.5)
$P - O_3 - C_4$	115.9 (0.3)	$C_8 - C_5 - C_9$	112.2 (0.5)

The ring adopts a chair conformation (figure). The P=S bond points in the axial direction and the methyl group is in equatorial position. It must be pointed out that in all the 2-oxo-dioxaphosphorinanes reported in reference (3), the P=O bond is equatorial. Least-squares planes calculation shows that atoms P, S, C(7), C(5), C(8) and C(9) are almost planar (deviations : 0.003, -0.007, 0.005, -0.002 and 0.003 Å respectively). Atoms O(1), O(3), C(4) and C(6) are 1.242, -1.251, 1.244 and -1.244 Å away from this plane. The dihedral angle between the plane formed by P, O(1), O(3) and the least-squares planes through the atoms O(1), O(3), C(4) and C(6) is 45°7, while that formed between the C(4), C(5), C(6) plane and the least-squares plane is 51°9. Thus, the flattening out of this 2-thiono-1,3,2-dioxaphosphorinane is smaller than the one found in the 2-oxo-1,3,2-dioxaphosphorinane rings [3].

The P=S bond distances measured by X-ray diffraction and which range from 1.98 Å to 1.85 Å [6,7] may differ significantly from the P=S value reported here (1.933 Å). The other bond lengths agree with those found in 2-oxo-1,3,2-dioxaphosphorinanes. There are no intermolecular contacts short enough to affect the conformation of the ring.

The X-ray structure determination of other 2-R-2-thiono-1,3,2-dioxaphosphorinanes (R = Cl, O C_6H_5) which are predicted as having an equatorial P=S bond orientation in a low electric permeability medium is now under way.



Aknowledgments : We thank Mr. M. Thomas for his technical assistance in using the Siemens diffractometer of the Laue Langevin Institute ; computer assistance from D. Tordjman is also highly appreciated.

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