

Structure of 2-Methoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane 2-Sulfide

BY P. VAN NUFFEL, A. T. H. LENSTRA AND H. J. GEISE

University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium

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Abstract

$C_6H_{13}O_3PS$ is monoclinic, $P2_1/c$, with $Z = 4$, $a = 10.673$ (5), $b = 6.502$ (4), $c = 13.502$ (4) Å, $\beta = 93.73$ (3)°, $D_{calc} = 1.394$ Mg m⁻³. Reflections were collected at 223 K on a computer-automated diffractometer. The structure was solved using intensities that were corrected by the French & Wilson [*Acta Cryst.* (1978), A34, 517–525] method, and refined by block-diagonal least-squares analysis to a final $R_w = 0.0446$ for 2742 independent reflections. The phosphate ring adopts a chair conformation with the methoxy group in an axial position; geometrical parameters are compared with those of the analogous 2-oxide and 2-selenide derivatives.

Introduction and experimental

Substituted cyclic phosphate compounds are well suited for the study of the influence of the anomeric effect (Altona, 1964; Romers, Altona, Buys & Havinga, 1969; David, Eisenstein, Hehre, Salem & Hoffman, 1973; Hudson & Verkade, 1975; Jeffrey, Pople, Binkley & Vishveshwara, 1978; Williams, Scarsdale, Schäfer & Geise, 1980) upon the geometry of molecules.

Suitable single crystals of the title compound (abbreviated TIOPOS) were obtained by slow evaporation of an ether–petroleum ether (50/50) solution at 253 K.

Reflections were measured on an Enraf–Nonius CAD-4 diffractometer using Zr-filtered Mo $K\alpha$ radiation. A total of 2745 independent reflections ($0^\circ < \theta < 30^\circ$) were collected using a pure ω scan. The crystal was cooled to 223 K with a stream of cold N₂ gas because it decays rapidly under the influence of air.

Intensities were corrected for Lorentz and polarization factors; in view of the low absorption coefficient ($\mu = 0.472$ mm⁻¹) and the size of the crystal ($0.4 \times 0.25 \times 0.1$ mm) no absorption correction was applied.

Structure determination and refinement

The structure was solved by conventional Patterson and (difference) Fourier techniques. The structural

parameters were refined in four different ways (Table 1). In the first two refinements we used intensities and a weighting scheme that were obtained directly from the original set of measurements. The two final models did not show any significant differences. Even with a cut-off value of zero, 219 reflections could not be used in the refinement process, because they have a negative intensity, resulting from the standard background–peak–background computations.

Studying the influence of the anomeric effect on molecules, small differences between the ‘normal’ value of bond lengths or valence angles and the actual ones are of decisive importance. To eliminate a systematic error, if any, due to the neglect of these negative intensities, we decided to apply the procedure of French & Wilson (1978) to our original data.

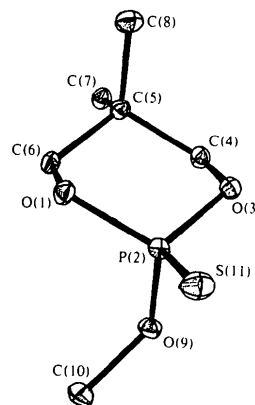


Fig. 1. Numbering of the atoms and conformation of the molecule.

Table 1. Some features of the different refinements

	(1)	(2)	(3)	(4)
French & Wilson correction	No	No	Yes	Yes
Weighting scheme	Counting statistics	Counting statistics	Counting statistics	Counting statistics
Cut-off	$I > 3.0\sigma(I)$	$I > 0.0\sigma(I)$	$I > 3.0\sigma(I)$	$I > 0.0\sigma(I)$
Number of reflections in least-squares*	2213	2526	2173	2742
Weighted R value† for observed reflections	0.0448	0.0450	0.0443	0.0446

* Total number of reflections measured: 2745.

† The weighted R value is defined as

$$R_w = \frac{\sum w(|F_{obs}| - |F_{calc}|)^2}{\sum w|F_{obs}|^2}.$$

Table 2. *Positional parameters of TIOPOS in fractions of the cell edges*

The e.s.d.'s given in parentheses refer to the last significant digit. Isotropic temperature factors (\AA^2) of non-hydrogen atoms are calculated from the anisotropic temperature parameters assuming equal volume of the 50% probability region. All anisotropic thermal parameters were physically acceptable. H atom H(x_j) ($j = 1, 2, 3$) is attached to atom C(x).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso}
O(1)	0.1591 (1)	0.0886 (2)	0.2945 (1)	2.12
P(2)	0.21130 (5)	0.05022 (8)	0.18911 (4)	1.89
C(3)	0.3541 (1)	0.1120 (2)	0.2006 (1)	2.12
C(4)	0.3860 (2)	0.3069 (3)	0.2513 (1)	2.18
C(5)	0.3335 (2)	0.3161 (3)	0.3540 (1)	2.09
O(6)	0.1916 (2)	0.2845 (3)	0.3425 (1)	2.23
C(7)	0.3570 (2)	0.5316 (3)	0.3956 (2)	2.58
C(8)	0.3961 (2)	0.1552 (4)	0.4231 (2)	2.85
O(9)	0.1556 (1)	0.2289 (2)	0.1205 (1)	2.20
C(10)	0.0212 (2)	0.2499 (4)	0.1033 (2)	2.73
S(11)	0.18189 (5)	-0.22444 (9)	0.14318 (4)	2.67
H(41)	0.476 (2)	0.313 (3)	0.256 (2)	2.57
H(42)	0.361 (2)	0.420 (3)	0.212 (1)	1.98
H(61)	0.159 (2)	0.274 (3)	0.406 (1)	2.68
H(62)	0.153 (2)	0.392 (3)	0.303 (1)	1.62
H(71)	0.321 (2)	0.641 (4)	0.355 (2)	3.85
H(72)	0.446 (2)	0.562 (4)	0.402 (2)	4.39
H(73)	0.323 (2)	0.545 (4)	0.459 (2)	3.73
H(81)	0.483 (2)	0.177 (4)	0.432 (2)	3.68
H(82)	0.363 (2)	0.163 (3)	0.489 (1)	2.86
H(83)	0.377 (2)	0.021 (3)	0.399 (2)	3.18
H(101)	-0.011 (2)	0.142 (4)	0.058 (2)	4.88
H(102)	0.009 (2)	0.379 (4)	0.075 (2)	5.47
H(103)	-0.018 (2)	0.242 (4)	0.164 (2)	4.45

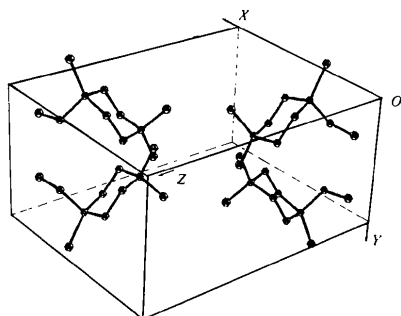


Fig. 2. The contents of one unit cell.

This procedure eliminates statistically the presence of a physical threshold in the data set by replacing negative intensities by their positive posterior value. Note that now with a cut-off of zero, only three reflections had to be rejected (because they were more negative than three times their e.s.d.). To our surprise the second set of refinements resulted in two sets of parameters which were in full agreement with our previous models. Even the Debye-Waller factors of the H atoms changed by no more than 0.3 times their e.s.d.

The structure reported here is the one in which 2742 reflections were used in the least-squares refinement.

Final positional parameters are listed in Table 2; the numbering of the atoms is depicted in Fig. 1 and the contents of one unit cell are shown in Fig. 2.†

Discussion

The phosphate ring has a chair conformation with the methoxy group in an axial position and the thiophosphoryl group in an equatorial position. A similar conformation was found for the 2-selenide (abbreviated SELOPOS) (Grand, Martin & Robert, 1975) and the 2-oxide derivatives (abbreviated OX-OPOS) (Van Nuffel, Lenstra & Geise, 1980) and is in agreement with the anomeric effect. This effect accounts for the stabilizing interaction of lone-pair orbitals with antibonding σ^* or π^* orbitals at adjacent atoms (Jeffrey, Pople & Radom, 1972; Radom, Hehre & Pople, 1972). Such an interaction is largest if the effective axis of the lone-pair orbital is in an *anti* position with respect to the bond into which electrons are being transferred. It is also strongly accentuated if this bond is polar and electron-withdrawing. Thus, the conformer with the largest number of lone pairs in an antiperiplanar position to electronegative groups is the most stable.

The methoxy group is assumed to be more electronegative than the $\text{P}=\text{O}$, $\text{P}=\text{S}$ or $\text{P}=\text{Se}$ group and thus the conformation with the methoxy group in an axial position (Fig. 3) is the most stable.

The anomeric description accounts for 12 conformations of 5,5-disubstituted 1,3,2-dioxaphosphorinane derivatives investigated by X-ray diffraction. Until now only one exception has been found in the crystalline state. 5,5-Dimethyl-2-phenyl-1,3,2-dioxaphosphorinane 2-oxide has been shown (Killean, Lawrence & Magennis, 1971) to have the phosphoryl group (more electronegative than the phenyl group) in an equatorial position. The occurrence of this unexpected conformer in the crystalline state may be due to stacking effects.

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35498 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

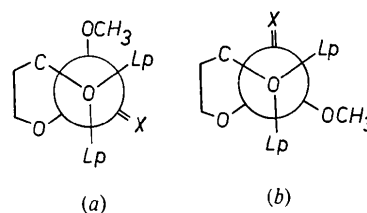


Fig. 3. Newman projection along a ring P-O bond for the conformation with $\text{P}=\text{X}$ in (a) equatorial and (b) axial position. X represents O, S or Se.

Table 3. Comparison of the ring torsion angles ($^{\circ}$) in the 1,3,2-dioxaphosphorinane ring for OXOPOS, TIOPOS and SELOPOS

	OXOPOS	TIOPOS	SELOPOS
O(1)–P(2)–O(3)–C(4)	–43.0 (6)	–46.1 (5)	–44.0
P(2)–O(3)–C(4)–C(5)	51.7 (6)	54.5 (5)	53.4
O(3)–C(4)–C(5)–C(6)	–56.1 (6)	–56.9 (5)	–56.5
C(4)–C(5)–C(6)–O(1)	59.2 (6)	58.2 (5)	57.6
C(5)–C(6)–O(1)–P(2)	–56.1 (6)	–56.5 (5)	–55.1
C(6)–O(1)–P(2)–O(3)	45.4 (6)	47.1 (5)	45.2

Table 4. Comparison of angles ($^{\circ}$) between some least-squares planes for OXOPOS, TIOPOS and SELOPOS

	OXOPOS	TIOPOS	SELOPOS
α_1^*	38.3	40.3	38.5
α_2	51.3	51.7	51.5
β	48.2	64.9	62.3

* α_1 is the angle between the central plane [O(1)–O(3)–C(4)–C(6)] and the plane O(1)–P(2)–O(3), α_2 between the central plane [O(1)–O(3)–C(4)–C(6)] and the plane C(4)–C(5)–C(6), and β between the plane O(9)–X(11)–P(2)–C(5)–C(7)–C(8) and the plane P(2)–O(9)–C(10).

Majoral & Navech (1972) have demonstrated by IR spectroscopy that the anomerically stable conformer with P=O in an axial position is dominant in solution.

The attachment of electronegative atoms causes a loss of electron density around P. The anomeric effect compensates for this loss by back donation of electrons from O lone pairs into antibonding σ^* or π^* orbitals. This causes a flattening of the ring around P which can be seen from the ring torsion angles given in Table 3, or by comparing the angles α_1 and α_2 in Table 4.

Valence angles and bond lengths, listed in Tables 5 and 6 respectively, are normal, compared to those of other cyclic phosphates. The valence angles POC are near to 120° , indicating that the O atoms are sp^2 -like. This agrees with the idea that lone pairs on O are directionally non-equivalent. Nevertheless, the picture with sp^3 -hybridized lone pairs can be used as an operationally useful pattern of thinking that allows one to predict significant molecular properties. We note that the C–O bonds in the phosphate ring are significantly longer (average 1.466 Å) than those normally found in ethers and alcohols (1.43–1.44 Å). Similar elongations have been found in other anomeric systems; for example, acetals (Jeffrey, Pople, Binkley & Vishveshwara, 1978; Van de Mierop & Lenstra, 1978) and cyclic sulfites (Petit, Lenstra & Geise, 1978). This is a typical feature of anomeric centers.

Because the anomeric interaction of the ring O atoms is least with equatorially oriented groups, the substitution of Se or S by the more electronegative O

Table 5. Comparison of bond angles ($^{\circ}$) in OXOPOS, TIOPOS and SELOPOS (e.s.d.'s in parentheses)

	OXOPOS	TIOPOS	SELOPOS
P(2)–O(1)–C(6)	118.0 (3)	116.7 (2)	116.1 (3)
P(2)–O(3)–C(4)	118.0 (3)	117.3 (2)	117.6 (3)
O(1)–P(2)–O(3)	105.7 (2)	105.5 (1)	106.5 (2)
O(1)–P(2)–O(9)*	101.7 (2)	105.7 (1)	105.9 (2)
O(3)–P(2)–O(9)*	106.8 (2)	101.3 (1)	100.9 (2)
O(1)–P(2)=X*	114.5 (2)	112.3 (1)	112.3 (1)
O(3)–P(2)=X*	111.1 (2)	114.1 (1)	114.2 (2)
O(9)–P(2)=X	116.0 (2)	116.7 (1)	116.0 (1)
P(2)–O(9)–C(10)	122.5 (4)	119.7 (2)	120.7 (4)
O(3)–C(4)–C(5)	111.7 (4)	111.6 (2)	112.1 (5)
O(1)–C(6)–C(5)	111.4 (5)	111.6 (2)	112.0 (5)
C(4)–C(5)–C(6)	109.0 (5)	108.8 (2)	109.4 (5)
C(4)–C(5)–C(7)	110.3 (5)	108.0 (2)	107.7 (5)
C(4)–C(5)–C(8)	108.4 (4)	110.8 (3)	111.5 (5)
C(6)–C(5)–C(7)	110.2 (5)	107.5 (2)	108.3 (5)
C(6)–C(5)–C(8)	108.3 (5)	111.2 (3)	110.9 (5)
C(7)–C(5)–C(8)	110.5 (5)	110.5 (3)	108.9 (5)

* The asymmetry of these valence angles is due to the asymmetric position of the exocyclic methoxy group; in OXOPOS C(10) is on the same side of the plane P(2)–O(9)–X–C(5)–C(7)–C(8) as O(3); in TIOPOS and SELOPOS it is on the opposite side. Conversion of OXOPOS to the analogous asymmetry of TIOPOS and SELOPOS was impossible due to the noncentrosymmetric space-group symmetry $P2_12_1$ of OXOPOS.

Table 6. Comparison of bond distances (Å) in OXOPOS, TIOPOS and SELOPOS (e.s.d.'s in parentheses)

	OXOPOS	TIOPOS	SELOPOS
P=X	1.444 (4)	1.910 (1)	2.055 (2)
P(2)–O(1)	1.567 (4)	1.581 (3)	1.565 (4)
P(2)–O(3)	1.565 (4)	1.574 (3)	1.568 (4)
O(1)–C(6)	1.450 (6)	1.461 (3)	1.454 (7)
O(3)–C(4)	1.472 (6)	1.470 (3)	1.490 (7)
C(4)–C(5)	1.516 (6)	1.530 (3)	1.478 (8)
C(6)–C(5)	1.532 (8)	1.526 (3)	1.524 (7)
C(5)–C(7)	1.537 (8)	1.524 (3)	1.531 (9)
C(5)–C(8)	1.529 (8)	1.526 (3)	1.490 (7)
P(2)–O(9)	1.565 (4)	1.578 (3)	1.588 (4)
O(9)–C(10)	1.428 (6)	1.445 (3)	1.429 (7)

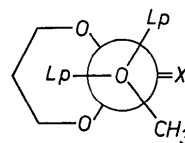


Fig. 4. Newman projection along the exocyclic P–O bond. X represents O, S or Se.

does not cause any significant differences in the geometrical parameters of the six-membered ring. Only O(9) can have an anomeric interaction with the P=X bond. The Newman projection in Fig. 4 shows that the methoxy group is directed away from the six-membered ring and takes a *gauche* position with respect to the

P=X bond (see angle β , Table 4). The anomeric stabilization from O(9) increases with increasing electronegativity of X. This explains the shortening of the P(2)–O(9) bond on going from SELOPOS to TIOPOS and OXOPOS.

The effect of increasing delocalization around O(9) can be seen from the angle P(2)–O(9)–C(10) which is significantly larger in OXOPOS compared to TIOPOS and SELOPOS.

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The Structure of Trimesic Acid, Its Hydrates and Complexes.

VI.* Glycine–Trimesic Acid Monohydrate, $\text{H}_3\text{N}^+\text{CH}_2\text{COO}^- \cdot \text{C}_9\text{H}_6\text{O}_6 \cdot \text{H}_2\text{O}$

BY F. H. HERBSTEIN, M. KAPON, ILANA MAOR AND G. M. REISNER

Department of Chemistry, Technion – Israel Institute of Technology, Haifa, Israel

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Abstract

The ternary adduct glycine–trimesic acid monohydrate is orthorhombic, $a = 7.971$ (5), $b = 24.615$ (10), $c = 6.476$ (5) Å, space group $Pna2_1$, $Z = 4$. The structure was solved by *MULTAN* and refined to $R = 4.42\%$, using 1570 reflections measured on a four-circle diffractometer with Mo $K\alpha$ radiation (graphite monochromator). The glycine is present in the zwitterionic form and the three moieties are joined together by a rather complicated three-dimensional arrangement of hydrogen bonds. These are all of standard dimensions except for the hydrogen bond between a carboxyl oxygen of glycine and a hydroxyl oxygen of trimesic acid; this is very short [$d(\text{O} \cdots \text{O}) = 2.464$ (3) Å] and

nearly symmetrical [$d(\text{O}_{\text{TMA}}-\text{H}) = 1.16$ (6) Å, $d(\text{O}_{\text{Gly}}^-\cdots\text{H}) = 1.31$ (6) Å]. This substance is classified as an acid salt in which the NH_3^+ group acts as cation and the two anions are the partially ionized carboxyl groups of trimesic acid and glycine.

1. Introduction

Aqueous solutions containing equimolar amounts of trimesic acid (1,3,5-benzenetricarboxylic acid; TMA) and glycine give crystals of the ternary complex glycine–trimesic acid monohydrate. Determination of the crystal structure shows that the glycine and TMA moieties are joined by a very short, nearly symmetrical hydrogen bond. Such bonds were first found in acid and basic salts of monobasic acids and monoacidic

* Part V: Herbstein & Kapon (1979).