Structure of 1,2,5-Trihydroxy-2,5-dimethylphospholane 1-Oxide, $C_6H_{13}O_4P$

By Z. Gałdecki and T. J. Bartczak

Institute of General Chemistry, Technical University of Łódź, 90–924 Łódź, Poland

W. M. Wolf*†

Chemical Crystallography Laboratory, University of Oxford, Oxford OX1 3PD, England

and H. Krawczyk and P. Majewski

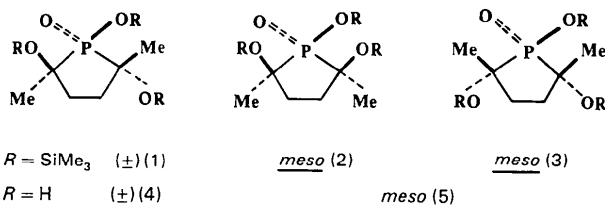*Institute of Organic Chemistry, Technical University of Łódź, 90–924 Łódź, Poland*

Abstract. $M_r = 180 \cdot 16$, orthorhombic, $P2_12_12_1$, $a = 6 \cdot 743$ (2), $b = 10 \cdot 419$ (2), $c = 12 \cdot 406$ (3) Å, $V = 871 \cdot 6$ (6) Å³, $Z = 4$, $D_m = 1 \cdot 35$, $D_x = 1 \cdot 36$ g cm⁻³, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 2 \cdot 9$ cm⁻¹, $F(000) = 384$, room temperature, $R = 0 \cdot 032$ for 1279 independent reflections. Extensive hydrogen bonding links molecules in a three-dimensional network. The phospholane ring is puckered so that it adopts a conformation intermediate between an envelope and a half-chair. The bond lengths and angles of the phospholane ring are normal, with the endocyclic C—P—C angle smaller than the other valency angles around phosphorus.

Introduction. The present work is a continuation of our investigations on the conformational and electronic properties of compounds incorporating a phospholane ring (Gałdecki & Główka, 1980, 1981; Gałdecki, 1981). The title compound has been prepared in the course of studies on the annulation of 2,5-hexanedione with bis(trimethylsilyl) hypophosphite and trimethylsilyl chloride (Bodalski, 1983). This reaction gave a mixture of diastereomeric heterocyclic esters (1), (2) and (3) in the ratio 4·5:1:1, respectively. Hydrolysis of the individual cyclization products results in the selective formation of the corresponding acids, (4) or (5).

$R = SiMe_3$ (±)(1)
$R = H$ (±)(4)

meso (2)

meso (3)

meso (5)

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* Author to whom all correspondence should be addressed.
† Permanent address: Institute of General Chemistry, Technical University of Łódź, Żwirki 36, 90–924 Łódź, Poland.

The relative stereochemistry of the diastereomeric esters (1) and (3) has been explicitly assigned on the basis of ¹H NMR spectra. Contrary to the *cis* isomers, different chemical shifts of the respective methyl groups could be unequivocally assigned to their *trans* configurations. However, the relative configurations of the acids (4) and (5) could not be confirmed in this way. We wish to report herein a single-crystal X-ray analysis of the acid (4).

Experimental. Colourless crystals grown by slow evaporation from methanol–ethyl acetate, 1:1. D_m by flotation in aqueous KI. Two specimens cut from two best looking prisms, sealed in Lindemann-glass capillaries, examined using oscillation and Weissenberg photographs, best crystal dimensions $0 \cdot 3 \times 0 \cdot 4 \times 0 \cdot 6$ mm, CAD-4F automated diffractometer, graphite-monochromated Mo $K\alpha$ radiation; accurate cell dimensions by least-squares calculations from angular settings of 25 reflections, $9 < \theta < 16°$, $\theta/2\theta$ scan mode; 3 standard reflections, variation $<3\%$; 2223 reflections measured, 1834 unique reflections with $\theta \le 30°$, hkl $-1,9$; $-1,14$; $-1,17$, $R_{int} = 0 \cdot 026$, no absorption correction, 1279 reflections with $I > 3\sigma(I)$ observed and used in further calculations; direct methods, refinement on F by standard full-matrix least squares and difference electron density syntheses; isotropic least-squares refinement gave $R = 0 \cdot 105$; all H atoms located on difference Fourier map after two cycles of anisotropic refinement, positional parameters included in last stages of refinement, temperature factors assumed equal to isotropic thermal parameters of parent non-hydrogen atoms and not refined; Waser-type constraints (Waser, 1963) applied, O—H $0 \cdot 95$ Å, e.s.d. $0 \cdot 01$ Å, difference in mean-square displacement along bond $0 \cdot 01$ Å², e.s.d. $0 \cdot 01$ Å²; corrections for anomalous dispersion applied for all non-hydrogen atoms; final weighting scheme (Carruthers & Watkin, 1979) $w = A_0 T_0(x) + A_1 T_1(x) + A_2 T_2(x)$, $A_0 = 15 \cdot 3$,

$A_1 = 20 \cdot 1$, $A_2 = 6 \cdot 3$, $T_i(x)$ is the ith Chebyshev series, $x = F_o/F_{omax}$; refinement converged with $R = 0 \cdot 032$, $wR = 0 \cdot 039$, $S = 0 \cdot 010$, max. $\Delta/\sigma = 1 \cdot 1$ for x coordinate of H(4), max. height in final difference Fourier map ca $0 \cdot 3$ e Å^{-3}; scattering factors from *Los Alamos Scientific Report* (Cromer & Mann, 1968). Anomalous-dispersion parameters from *International Tables for X-ray Crystallography* (1974). All calculations carried out on the University of Oxford Chemical Crystallography Laboratory VAX 11/750 computer using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), *CRYSTALS* (Watkin & Carruthers, 1981) and *CHEMGRAF* (Davies, 1981).*

Discussion. A view of the molecule with atom labelling is given in Fig. 1. Final atomic coordinates are summarized in Table 1, bond lengths and angles in Table 2.

Hydroxyl groups attached to atoms C(1) and C(4) are *trans* with respect to the pholane ring. The torsion angles and asymmetry parameters (Duax & Norton, 1975) clearly show that the ring is puckered, so that two dominating pseudosymmetry elements are observed: a mirror plane perpendicular to the P(1)—C(4) bond and a twofold axis passing through the P(1) atom, Fig. 2. The dihedral angle between the C(1)-C(2)C(3) plane and the least-squares mean plane C(1)P(1)C(4)C(3) [deviations in Å from this plane are, respectively, $-0 \cdot 07$ (4), $0 \cdot 05$ (4), $-0 \cdot 06$ (4), $0 \cdot 08$ (4)] is $50 \cdot 7$ (8)°. This indicates that the conformation of the ring is intermediate between an envelope and a half-chair.

The observed bond lengths and valency angles are in good agreement with those found in other pholane derivatives (van der Helm, Washecheck, Burks & Ealick, 1976; Stults & Moedritzer, 1979; Day, Husebye, Deiters & Holmes, 1980, and references cited above) and will not be discussed in detail. The C—P—C angle of $98 \cdot 0$ (1)° is significantly less than the other valency angles around phosphorus. Such a decrease of the endocyclic phosphorus angle is usually observed in pholane rings.

Apart from the hydrogen bonds,* no intermolecular distance is significantly shorter than the sum of the respective van der Waals radii.
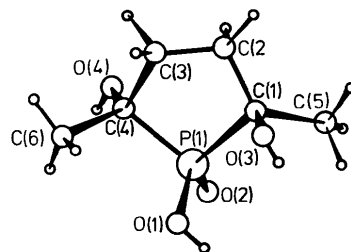
Fig. 1. View of the molecule showing the non-hydrogen-atom numbering.

Table 1. *Fractional atomic coordinates with their e.s.d.'s in parentheses and* U_{eq}

$$U_{eq} = (U_1 U_2 U_3)^{1/3}.$$

	x	y	z	$U_{eq}(\text{Å}^2)$
P(1)	0·0257 (1)	0·1234 (1)	0·4433 (1)	0·0260
O(1)	0·1591 (3)	0·2006 (2)	0·3630 (2)	0·0397
O(2)	−0·0358 (3)	0·2006 (2)	0·5396 (2)	0·0362
O(3)	0·2851 (3)	−0·0660 (2)	0·3986 (2)	0·0428
O(4)	−0·3579 (3)	0·0662 (2)	0·4335 (2)	0·0384
C(1)	0·1447 (4)	−0·0311 (3)	0·4793 (3)	0·0328
C(2)	−0·0310 (5)	−0·1229 (3)	0·4639 (3)	0·0431
C(3)	−0·1339 (5)	−0·0855 (3)	0·3598 (3)	0·0405
C(4)	−0·1861 (4)	0·0579 (3)	0·3655 (2)	0·0330
C(5)	0·2340 (6)	−0·0318 (4)	0·5917 (3)	0·0509
C(6)	−0·2229 (7)	0·1229 (6)	0·2577 (3)	0·0574

Table 2. *Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

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P(1)—O(1)	1·564 (2)	C(1)—C(2)	1·534 (4)
P(1)—O(2)	1·498 (2)	C(1)—C(5)	1·518 (5)
P(1)—C(1)	1·853 (3)	C(2)—C(3)	1·518 (5)
P(1)—C(4)	1·854 (3)	C(3)—C(4)	1·536 (5)
O(3)—C(1)	1·425 (4)	C(4)—C(6)	1·520 (5)
O(4)—C(4)	1·436 (3)		
O(1)—P(1)—O(2)	113·0 (1)	O(3)—C(1)—C(5)	112·3 (2)
O(1)—P(1)—C(1)	110·5 (1)	C(2)—C(1)—C(5)	114·7 (3)
O(1)—P(1)—C(4)	107·5 (1)	C(1)—C(2)—C(3)	107·4 (3)
O(2)—P(1)—C(1)	113·2 (1)	C(2)—C(3)—C(4)	108·4 (3)
O(2)—P(1)—C(4)	113·5 (1)	P(1)—C(4)—O(4)	107·1 (2)
C(1)—P(1)—C(4)	98·0 (1)	P(1)—C(4)—C(3)	101·9 (2)
P(1)—C(1)—O(3)	109·9 (2)	P(1)—C(4)—C(6)	114·8 (3)
P(1)—C(1)—C(2)	100·2 (2)	O(4)—C(4)—C(3)	105·7 (2)
P(1)—C(1)—C(5)	113·4 (2)	O(4)—C(4)—C(6)	111·0 (3)
O(3)—C(1)—C(2)	105·4 (2)	C(3)—C(4)—C(6)	115·5 (3)
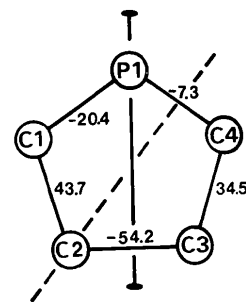
Fig. 2. The conformation of the pholane ring. Torsion angles in degrees with e.s.d.'s ca $0 \cdot 5°$. $C_2^{P(1)} = 11 \cdot 3$ (8)°; $C_s^{C(2)} = 12 \cdot 4$ (8)°, all other asymmetry parameters are greater than $C_s^{C(3)} = 29 \cdot 3$ (8)°.

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Structure of 1-Methylhydrazinium Trifluoroacetate, $CH_7N_2^+.C_2F_3O_2^-$

BY VALERY E. SHKLOVER AND YURI T. STRUCHKOV

Nesmeyanov Institute of Organoelement Compounds of the USSR Academy of Sciences, 28 Vavilov Street, Moscow B-334, USSR

Abstract. $M_r = 160.1$, monoclinic, $P2_1/c$, $a = 7.841$ (1), $b = 13.191$ (2), $c = 6.149$ (1) Å, $\beta = 92.80$ (1)°, $V = 635.2$ (2) Å³, $Z = 4$, $D_x = 1.674$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 2.03$ cm⁻¹, $F(000) = 328$, $T = 150$ K, $R = 0.049$ for 1308 reflections. The crystal is built up of $[F_3CCOO]^-$ anions and $[H_2NN(H_2)CH_3]^+$ cations, linked by N–H···O hydrogen bonds to form zigzag chains along the c axis. Several interionic contacts are less than the sum of the van der Waals radii. The bond lengths and angles of both ions differ slightly from those of the uncharged compounds in the manner expected.

Introduction. An X-ray study of 1-methylhydrazinium trifluoroacetate (I) was carried out in order to investigate the peculiarities of crystal packing and the hydrogen-bond system in the crystal of this salt.

Experimental. Transparent plate-shaped single crystal, $0.4 \times 0.4 \times 0.1$ mm. Unit-cell parameters from 24 reflections with $32 \leq 2\theta \leq 34°$. 1607 reflections measured ($0 \leq h \leq 8$, $0 \leq k \leq 17$, $-10 \leq l \leq 10$). Syntex $P2_1$ diffractometer (graphite monochromator, $\theta/2\theta$

scan, $2\theta_{max} = 55°$). No significant variation in intensities of 2 standard reflections (400, 080) measured every 100 reflections. No absorption or secondary-extinction corrections. Structure solved by direct methods (MULTAN; Germain, Main & Woolfson, 1971), revealing all nonhydrogen atoms. Refinement by full-matrix least squares with anisotropic thermal parameters for nonhydrogen atoms. 1308 independent reflections with $I \geq 2\sigma(I)$. $\sum w(|F_o| - |F_c|)^2$ minimized; $w = 1/[\sigma^2(F_o) + |F_o|^2]$. Scattering factors from International Tables for X-ray Crystallography (1974). Hydrogen atoms located by difference synthesis, refined isotropically. Final $R = 0.049$, $wR = 0.044$, max. $(\Delta/\sigma) = 0.5$, final electron density fluctuations ± 0.4 e Å⁻³. All calculations carried out with Eclipse S/200 computer using INEXTL programs (Gerr, Yanovsky & Struchkov, 1983).*