

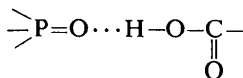
(±)-O-Methyl- α -phenylphosphinylpropionic Acid

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Abstract. $C_{10}H_{13}O_4P$, $M_r = 228.2$, orthorhombic, space group $Pbca$, $Z = 8$, $a = 11.112(4)$, $b = 14.019(5)$, $c = 14.021(5)$ Å, $V = 2185.75$ Å³, $D_m = 1.38$, $D_x = 1.385$ g cm⁻³, $F(000) = 960$, $\mu(\text{Cu } K\alpha) = 21.7$ cm⁻¹, $\mu_r = 0.50$. The structure was solved by direct methods (symbolic addition) and refined by full-matrix least-squares calculations, with anisotropic thermal parameters, to a final R value of 0.072 for 1510 independent intensities recorded on Weissenberg photographs (Cu $K\alpha$ radiation). The molecules form chains by means of strong hydrogen bonds



parallel to the z axis. All the H atoms have been located on difference Fourier maps.

Introduction. The present study is a continuation of a series of investigations on the structure and hydrogen bonding in *O*-methylphenylphosphinylacetic acid derivatives (Galdecki & Głowska, 1977, 1978). Phosphine oxides may form molecular complexes with acids (Hadži, 1962). So far only two such complexes of triphenylphosphine oxide with strong organic acids have been examined by X-ray techniques (Golič & Kaučič, 1976; Declercq, Germain, Putzeys, Rona & Van Meerssche, 1974). Similar hydrogen bonds are formed in the crystals we have examined but the situation here is more complex because of the presence of both hydrogen acceptor (P=O) and donor (C–OH) groups in the same molecule.

Crystals in the form of prisms were obtained by slow cooling of a saturated solution in a hot mixture of acetone and water. The unit-cell dimensions were first calculated from high-order reflections on Weissenberg photographs and refined from single-crystal diffractometer measurements. Multiple-film, equi-inclination Weissenberg photographs (Cu $K\alpha$ radiation) of the levels $0kl \dots 6kl$ were taken from a spherical crystal of diameter 0.46 mm, and interlevel scale factors were calculated from the $h0l$ and $h1l$ reflections. Systematic absences $0kl$, k odd, $h0l$, l odd, and $hk0$, h odd indicated the space group explicitly. Intensities of 1510 reflections were recorded and estimated visually. The data were corrected for spherical absorption (*International Tables for X-ray Crystallography*, 1959). All

calculations were processed with the XRAY 70 system (Stewart, Kundell & Baldwin, 1970). The scattering factors for P, O and C were taken from Doyle & Turner (1968) and for H from *International Tables for X-ray Crystallography* (1962).

The structure was determined by symbolic addition (program PHASE of the XRAY 70 system) based on $250 E > 1.5$. The basic difficulty in determining the structure was that normalized structure factors with l odd were all too small to contribute to the Σ_2 relationships. The resulting E map showed an additional mirror plane perpendicular to the b axis at $\frac{1}{4}$. Four E 's with l odd were included in the symbolic addition procedure by increasing the number of 'generators' from 50 to 80 and by decreasing the minimum acceptable probability to 0.9. The phases of 224 E were determined but the E map had the same slightly deformed mirror-plane symmetry. The positions of seven atoms were found with difficulty on the basis of the higher peaks of symmetry-dependent pairs (by plane m). A difference Fourier synthesis showed a further three atoms. Although the positions of the peaks did not differ more than 0.05 Å from the final coordinates we failed to find further atoms. In this situation we temporarily increased the E value for seven reflections with l odd to include them in the Σ_2 relationships and the direct structure determination was repeated. The first E map based on 202 reflections with known phases (with $P \geq 0.94$) revealed only four atoms [P, O(1), O(2) and C(7)] but successive use of Fourier and difference Fourier syntheses allowed us to locate the remaining non-hydrogen atoms ($R = 0.395$). The true values of F_o were restored for the seven modified reflections. Least-squares calculations were tried directly but the agreement factor increased rapidly during refinement when the interlayer scale factors were not fixed. After one cycle of least-squares calculations for this model without scale-factor refinement ($R = 0.28$) further calculations ran easily. Four cycles of full-matrix refinement with isotropic, followed by four cycles with anisotropic, thermal parameters resulted in $R = 0.072$ ($R_w = 0.106$). In the last two cycles 227 'less-thans' and 21 observed reflections with $|w\Delta F| \geq 0.8$ were not included in the refinement. The weighting scheme applied was $w^{-1} = 10 + |F| + 0.02|F|^2$. The final difference Fourier map revealed the positions of all the H atoms (Table 2), which were not refined.

Discussion. Atomic parameters and their estimated standard deviations as obtained from the least-squares calculations are listed in Table 1. The bond lengths and angles, without correction for thermal vibration, are summarized in Table 3. Table 4 shows intermolecular contacts less than 3.5 Å between non-hydrogen atoms, except for the hydrogen bond O(1)⋯O(3). Table 5 gives the equation of the least-squares plane for the benzene ring and the deviations of some atoms from the plane.*

The asymmetric P and C(7) atoms have opposite configurations in each molecule. The molecules with the configuration *RS* alternate with those with the *SR* to form a hydrogen-bonded chain along the *z* axis (Fig. 1a). The P atom (Fig. 1b) is near the glide plane *c* ($y_p \sim$

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32882 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic coordinates ($\times 10^4$) for non-hydrogen atoms with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
P	1879 (1)	2472 (1)	1558 (1)
O(1)	2208 (3)	2045 (2)	2486 (2)
O(2)	940 (3)	1876 (2)	962 (2)
O(3)	2543 (4)	2414 (2)	-770 (2)
O(4)	3030 (4)	3872 (2)	-297 (2)
C(1)	1154 (5)	3607 (3)	1657 (3)
C(2)	218 (6)	3866 (3)	1068 (3)
C(3)	-358 (6)	4739 (4)	1187 (4)
C(4)	61 (8)	5369 (4)	1904 (5)
C(5)	1027 (6)	5114 (3)	2472 (4)
C(6)	1559 (6)	4230 (3)	2360 (3)
C(7)	3207 (5)	2580 (3)	820 (3)
C(8)	2935 (5)	3049 (3)	-133 (3)
C(9)	1187 (6)	886 (3)	705 (3)
C(10)	4215 (6)	3108 (4)	1350 (3)

Table 2. Positional parameters for hydrogen atoms as found from the difference Fourier map, and H-X (*X* = O, C) bond lengths

	<i>x</i>	<i>y</i>	<i>z</i>	Bonded to	Bond lengths (Å)
H(1)	0.240	0.235	0.145	O(3)	0.970
H(2)	0.027	0.341	0.048	O(1)	1.729
H(3)	0.111	0.509	0.083	C(2)	1.176
H(4)	0.040	0.605	0.206	C(3)	1.092
H(5)	0.139	0.543	0.311	C(4)	1.105
H(6)	0.227	0.406	0.288	C(5)	1.076
H(7)	0.350	0.190	0.063	C(6)	1.100
H(91)	0.175	0.093	0.018	C(7)	1.042
H(92)	0.184	0.055	0.012	C(9)	0.968
H(93)	0.053	0.053	0.047	C(9)	1.042
H(101)	0.396	0.375	0.146	C(9)	0.953
H(102)	0.459	0.280	0.180	C(10)	0.956
H(103)	0.500	0.310	0.085	C(10)	0.871
				C(10)	1.119

0.25). It causes the intensities of reflections with *l* odd to be small and was the source of the difficulty in the structure determination. The hydrogen bond O(1)⋯O(3) is 2.587 (1) Å, which agrees with the values found by Brown (1976) and in other papers [Gałdecki & Głowska (hereinafter GG), 1977, 1978]. The remaining bond lengths (Table 3) are in better agreement with the values found in racemic *O*-methyl-

Table 3. Bond lengths (Å) and angles (°), not corrected for thermal vibration, with their e.s.d.'s in parentheses

P-O(1)	1.479 (1)	O(1)-P-O(2)	114.6 (2)
P-O(2)	1.577 (2)	O(1)-P-C(1)	113.7 (1)
P-C(1)	1.790 (1)	O(1)-P-C(7)	109.6 (8)
P-C(7)	1.808 (1)	O(2)-P-C(1)	102.4 (2)
O(2)-C(9)	1.459 (5)	O(2)-P-C(7)	106.4 (7)
C(1)-C(2)	1.376 (2)	C(1)-P-C(7)	109.7 (9)
C(2)-C(3)	1.391 (6)	P-O(2)-C(9)	120.6 (12)
C(3)-C(4)	1.417 (4)	P-C(1)-C(2)	121.8 (1)
C(4)-C(5)	1.383 (1)	P-C(1)-C(6)	117.8 (2)
C(5)-C(6)	1.383 (1)	P-C(7)-C(8)	112.1 (11)
C(6)-C(1)	1.392 (1)	P-C(7)-C(10)	111.0 (13)
C(7)-C(8)	1.519 (6)	C(1)-C(2)-C(3)	120.5 (5)
C(7)-C(10)	1.535 (4)	C(2)-C(3)-C(4)	118.9 (9)
C(8)-O(3)	1.335 (7)	C(3)-C(4)-C(5)	120.1 (6)
C(8)-O(4)	1.180 (5)	C(4)-C(5)-C(6)	119.9 (1)
		C(5)-C(6)-C(1)	120.2 (2)
		C(6)-C(1)-C(2)	120.3 (2)
		C(7)-C(8)-O(3)	111.4 (28)
		C(7)-C(8)-O(4)	125.2 (22)
		C(8)-C(7)-C(10)	111.2 (15)
		O(3)-C(8)-O(4)	123.4 (30)

Table 4. Selected intermolecular distances (Å) less than 3.5 Å

The first atom is at *x, y, z* and Roman numerals refer to equivalent positions:

(i) $x, \frac{1}{2} - y, \frac{1}{2} + z$, (ii) $\frac{1}{2} - x, \frac{1}{2} - y, z$, (iii) $\frac{1}{2} + x, \frac{1}{2} - y, -z$.

O(1)⋯O(4 ⁱ)	3.486	O(4)⋯C(9 ⁱⁱ)	3.272
O(1)⋯C(8 ⁱ)	3.438	O(3)⋯C(2 ⁱⁱⁱ)	3.498
C(5)⋯C(1 ⁱⁱ)	3.343		

Table 5. Deviations of some atoms from the benzene least-squares plane

The equation of the plane is expressed in direct space as $Px + Qy + Rz = S$, where $P = -7.1082$, $Q = -5.6902$, $R = 9.1519$, $S = -1.3630$.

Atoms defining least-squares plane	Other atoms	Deviations (Å)
C(1)		0.0043
C(2)		-0.0164
C(3)		0.0113
C(4)		0.0055
C(5)		-0.0174
C(6)		0.0126
	P	0.0477
	O(1)	0.9049
	O(2)	0.5108
	C(7)	-1.6377

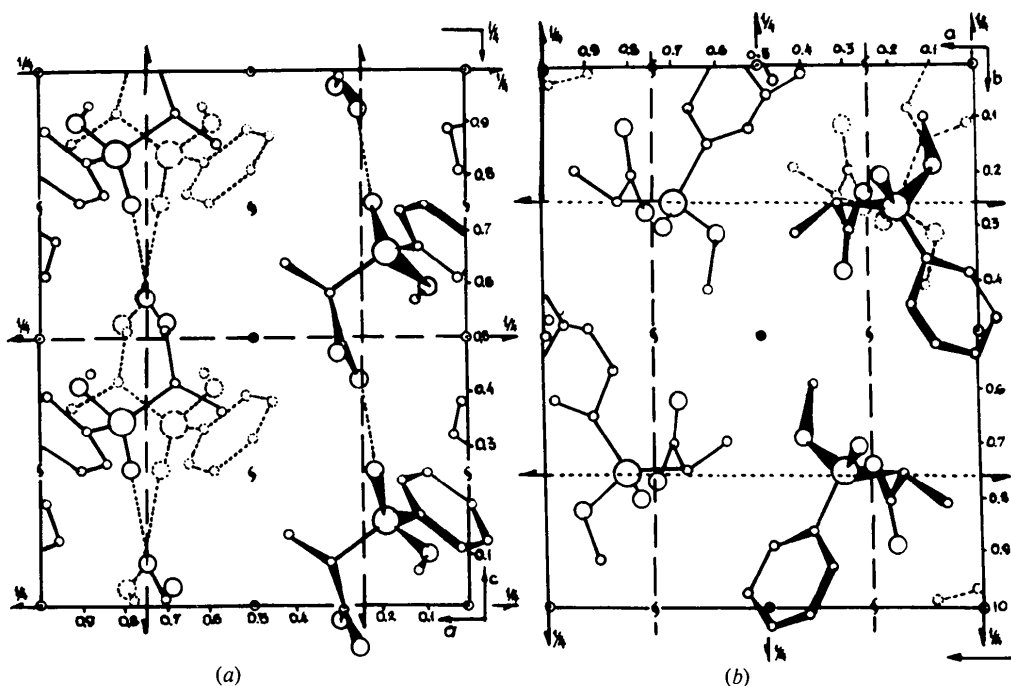


Fig. 1. The crystal structure of (\pm) -O-methyl- α -phenylphosphinylpropionic acid. (a) Hydrogen-bonded chain seen along [010]. (b) Position of the P atom (largest circle) in projection on the xy plane.

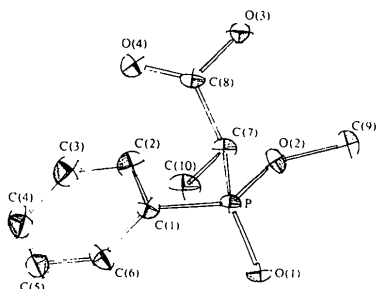


Fig. 2. View of the molecule perpendicular to the yz plane. Vibration ellipsoids were calculated with 40% probability (ORTEP, Johnson, 1965).

phenylphosphinylacetic acid (GG, 1977) than with those in the enantiomeric form (GG, 1978). Considerable differences occur in the geometry of the carboxyl group. C(7)–C(8) and C(8)–O(4) seem to be too short (1.519 and 1.180 Å), in contrast to C(8)–O(3), which is anomalously long (1.335 Å). Leiserowitz (1976) published bond lengths for a series of carboxylic acids none of which was as long as the observed C–O bond or as short as the observed C=O. These variations probably result from experimental errors affecting the position of C(8).

Views of the molecule and unit-cell contents are shown in Figs. 2 and 3 respectively.

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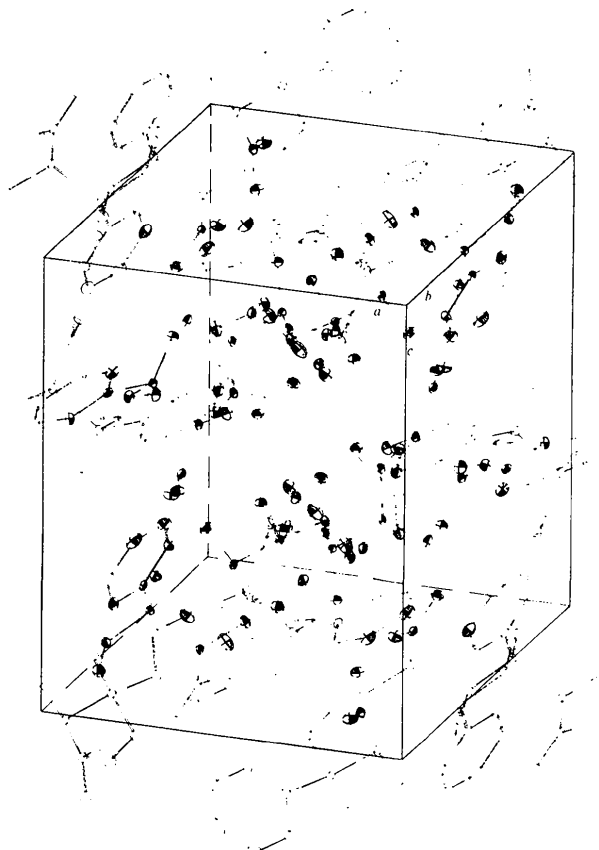


Fig. 3. Packing of molecules in the unit cell (ORTEP; Johnson, 1965).

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S,S-Dimethyl-N-(2-oxo-1-indoliny)sulfoximide

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Abstract. C₁₀H₁₂O₂N₂S, monoclinic, *P*2₁/*c*, *a* = 12.310 (2), *b* = 10.970 (2), *c* = 7.955 (1) Å, β = 93.93 (1)°, *Z* = 4, *V* = 1071.7 (4) Å³, *M_r* = 266.2, *D_x* = 1.65 g cm⁻³. The structure was solved by Patterson syntheses and refined to *R* = 0.049 for 3186 observed reflections.

Introduction. The title compound was obtained by Dr B. Marco (1975) in the course of the synthesis of 3,4-diketocinnoline derivatives (Lora-Tamayo, Marco &

Navarro, 1974). Organic chemists are interested in the mechanism of formation of these products and want to know the precise conformation, which is not clear from other techniques; thus the present work was undertaken. The intensities were measured from a 0.41 × 0.34 × 0.62 mm crystal on a Philips PW 1100 four-circle diffractometer, with graphite-monochromated Mo K_α radiation (λ = 0.7107 Å). The ω–2θ scan technique was employed. 4716 unique reflections were recorded up to θ = 35° of which 3186 were considered

Table 1. Final positional parameters and their standard deviations, and bond distances (Å) involving the hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>	C–H bond
S(1)	0.33743 (3)	0.55708 (3)	0.25159 (5)	H(5a)	0.254 (2)	0.091 (2)	0.377 (3)	0.97 (3)
O(4)	0.2877 (1)	0.5786 (1)	0.0839 (2)	H(5b)	0.307 (3)	0.111 (3)	0.199 (4)	0.99 (3)
N(2)	0.2789 (1)	0.4764 (1)	0.3800 (2)	H(7)	0.068 (3)	0.055 (3)	0.113 (4)	0.96 (4)
N(3)	0.2596 (1)	0.3580 (1)	0.3132 (2)	H(8)	−0.081 (3)	0.172 (4)	0.029 (5)	0.92 (4)
C(4)	0.3227 (1)	0.2588 (1)	0.3563 (2)	H(9)	−0.084 (3)	0.391 (3)	0.060 (4)	1.01 (3)
C(5)	0.2627 (1)	0.1472 (1)	0.2852 (2)	H(10)	0.074 (2)	0.472 (3)	0.193 (4)	0.84 (3)
C(6)	0.1575 (1)	0.1977 (1)	0.2101 (2)	H(12a)	0.502 (3)	0.568 (4)	0.160 (5)	0.96 (4)
C(7)	0.0674 (1)	0.1419 (2)	0.1312 (2)	H(12b)	0.461 (3)	0.426 (4)	0.168 (5)	0.98 (4)
C(8)	0.0216 (2)	0.2141 (2)	0.0768 (3)	H(12c)	0.507 (3)	0.499 (4)	0.334 (5)	0.96 (4)
C(9)	0.0192 (1)	0.3391 (2)	0.1003 (3)	H(13a)	0.289 (4)	0.726 (5)	0.365 (6)	0.87 (5)
C(10)	0.0720 (1)	0.3967 (2)	0.1770 (2)	H(13b)	0.396 (4)	0.753 (4)	0.290 (6)	1.04 (5)
C(11)	0.1586 (1)	0.3236 (1)	0.2308 (2)	H(13c)	0.401 (4)	0.684 (4)	0.458 (6)	0.92 (5)
C(12)	0.4705 (2)	0.5051 (2)	0.2241 (3)					
C(13)	0.3541 (3)	0.6939 (2)	0.3645 (3)					
O(14)	0.4110 (1)	0.2622 (1)	0.4376 (2)					