Acta Cryst. (1978). B**34**, 2938–2940

Enantiomeric *O*-Methylphenylphosphinylacetic Acid

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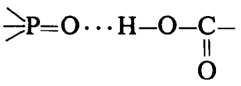
(*Received* 28 *November* 1977; *accepted* 17 *April* 1978)

Abstract. $C_9H_{11}O_4P$, $M_r = 214\cdot16$, tetragonal, space group $P4_12_12$, $Z = 8$, $a = 8\cdot19$ (1), $c = 31\cdot19$ (4) Å, $V = 2092\cdot1$ Å^3, $D_m = 1\cdot37$, $D_x = 1\cdot363$ g cm^{-3}, $F(000) = 896$, μ(Cu $K\alpha$) = 22·6 cm^{-1}. The structure was solved by direct methods (*MULTAN*) and refined by full-matrix least-squares calculations with anisotropic thermal parameters to a final R value of 0·074 for 1416 independent intensities collected on a Weissenberg camera. Strong hydrogen bonds (2·57 Å) connect the molecules in chains.



$$>P{=}O\cdots H{-}O{-}\underset{\underset{O}{\|}}{C}{-}$$

The lengths P=O, P–O and mean P–C bond are 1·49, 1·57 and 1·80 Å. O=P–O and mean O=P–C angles are 116 and 113° while O–P–C valency angles are 108 and 99°.

Introduction. The structure of enantiomeric *O*-methylphenylphosphinylacetic acid has been solved as a part of our X-ray study of optically active compounds with an asymmetric P atom. Michalski & Musierowicz (1967) obtained and resolved a number of phosphinylacetic acid derivatives, which are suitable models for studying various aspects of steric control in the formation of new asymmetric centres at carbon atoms adjacent to asymmetric P atoms. For this reason the crystal structures of enantiomeric *O*-methylphenylphosphinylacetic acid (present study) and *O*-methyl-α-phenylphosphinylpropionic acid (Gałdecki & Główka, 1977*b*), obtained by methylation of the former, have been examined. The structure of the racemic crystal has already been determined (Gałdecki & Główka, 1977*a*). The absolute configuration of the (–) enantiomer was determined on the basis of diffractometer intensity measurements, as a result of a small anomalous dispersion effect causing differences in the intensities recorded on the photographs. We are also interested in the geometry of the hydrogen bonding in crystals of compounds containing phosphoryl and carboxyl groups in the same molecule. As reported earlier (Hadži, 1962), phosphine oxides form molecular complexes with acids. Two such complexes of Ph_3PO with trichloroacetic acid (Golič & Kaučič, 1976) and dimethylmalonic acid (Declercq, Germain, Putzeys, Rona & Van Meerssche, 1974) have been isolated and their crystal structures solved by X-ray methods. Similar P=O···H–O hydrogen bonds are formed by phosphonylacetic acid derivatives.

Colourless, transparent crystals were obtained as prisms from acetone and water. Unit-cell dimensions were calculated from high-order reflections on Weissenberg photographs. 1416 reflections were collected on the photographs (equi-inclination Weissenberg and multiple-film method) by means of Ni-filtered Cu radiation. Seven levels $0kl\ldots6kl$ were taken from a spherical crystal of diameter 0·46 mm. The intensities of the reflections were estimated visually. The data were corrected for absorption (*International Tables for X-ray Crystallography*, 1959).

The structure of the enantiomeric *O*-methylphenylphosphinylacetic acid has been solved by means of the program *MULTAN* (Germain, Main & Woolfson, 1971). Further calculations were processed using the XRAY 70 system (Stewart, Kundell & Baldwin, 1970). Scattering factors for P, O and C were taken from Doyle & Turner (1968) and for H from *International Tables for X-ray Crystallography* (1962).

Four cycles of a full-matrix least-squares refinement (program *CRYLSQ* of the XRAY system) of the positional and isotropic thermal parameters resulted in $R = 0\cdot126$. A further five cycles of refinement with anisotropic parameters reduced R to 0·074. The mean and maximum values of Δ/σ (the ratio of the change in atomic parameter to its standard deviation) in the final cycle were 0·43 and 1·5 respectively. A difference Fourier synthesis showed the five H atoms connected to the benzene ring and the H atom of the carboxyl group, but these were not used in the refinement (the C–H bond lengths differ considerably from the mean value). The final weighting scheme applied was $w^{-1} = 10 + |F| + 0\cdot03|F|^2$. Eleven reflections with $w(|F_o - F_c|) \geq 1\cdot0$ were not included in last two cycles of the refinement.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33557 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Final atomic parameters are reported in Table 1, while Fig. 1 shows a molecule of enantiomeric *O*-methylphenylphosphinylacetic acid viewed normal to the *xz* plane with the numbering system used. The packing of molecules is shown in Fig. 2. The molecules form chains by means of strong intermolecular hydrogen bonds between phosphoryl and carboxyl groups. The axes of the chains are nearly perpendicular to the [001] direction. The O(1)···O(3) distance is 2·57 Å which agrees well with the values found in molecular complexes of triphenylphosphine oxide with dimethylmalonic acid, 2·52 and 2·58 Å (Declercq, Germain, Putzeys, Rona & Van Meerssche, 1974), and trichloroacetic acid, 2·50 Å (Golič & Kaučič, 1976), as well as those in racemic *O*-methylphenylphosphinylacetic acid, 2·62 Å (Gałdecki & Główka, 1977*a*), racemic *O*-methyl-α-phenylphosphinylpropionic acid, 2·59 Å (Gałdecki & Glowka, 1977*b*), and racemic 3-[benzyl-(phenyl)phosphinyl]-2-butenoic acid, 2·59 Å (Główka, 1978). The observed bond lengths and angles (Table 2) are similar to those found by the authors in other *O*-methylphenylphosphinylacetic acid derivatives (Gałdecki & Główka, 1977*a*,*b*). Shortening of the O(2)—C(9) bond length to 1·412 Å and increase of the P—O(2)—C(9) bond angle to 123° probably results from experimental errors affecting the position of C(9). A similar explanation accounts for the increase of the C(7)—C(8)—O(3) angle to 114·6° (the mean value found in the previously investigated phosphinylacetic acid derivatives being 111·4°) and the decrease of the O(3)—C(8)—O(4) angle to 122·2° (mean

Table 1. *Atomic coordinates* (×10⁴) *for the non-hydrogen atoms, with e.s.d.'s in parentheses*

	x	*y*	*z*
P	−140 (2)	6559 (2)	9559 (1)
O(1)	−300 (6)	6048 (5)	10015 (1)
O(2)	−1786 (5)	6740 (6)	9303 (1)
O(3)	3522 (6)	8880 (6)	9545 (1)
O(4)	2133 (6)	9070 (8)	10148 (1)
C(1)	1173 (6)	5236 (6)	9254 (1)
C(2)	1155 (7)	5297 (7)	8809 (1)
C(3)	2228 (8)	4338 (8)	8570 (2)
C(4)	3286 (8)	3226 (8)	8770 (2)
C(5)	3308 (9)	3217 (9)	9221 (2)
C(6)	2223 (8)	4153 (8)	9459 (2)
C(7)	611 (8)	8598 (7)	9501 (2)
C(8)	2152 (8)	8888 (7)	9767 (2)
C(9)	−3048 (10)	5567 (12)	9322 (3)

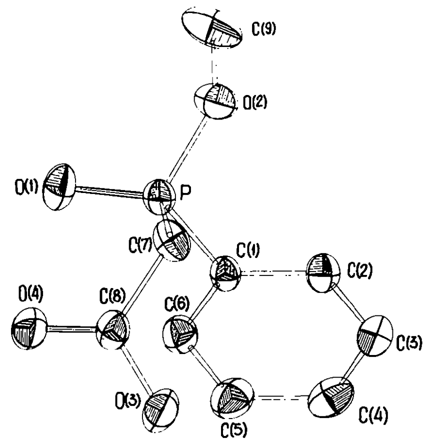

Fig. 1. View of the molecule normal to the *xz* plane (*ORTEP*, Johnson, 1965).

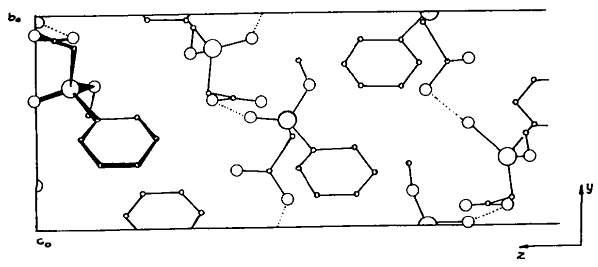

Fig. 2. The packing of the molecules.

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

P—O(1)	1·487 (1)	O(1)—P—O(2)	115·8 (4)
P—O(2)	1·575 (3)	O(1)—P—C(1)	112·9 (1)
P—C(1)	1·798 (1)	O(1)—P—C(7)	112·9 (3)
P—C(7)	1·789 (3)	O(2)—P—C(1)	107·5 (6)
O(2)—C(9)	1·412 (6)	O(2)—P—C(7)	98·9 (9)
C(1)—C(2)	1·389 (3)	C(1)—P—C(7)	107·7 (8)
C(2)—C(3)	1·396 (2)	P—O(2)—C(9)	122·7 (5)
C(3)—C(4)	1·352 (5)	P—C(1)—C(2)	120·0 (10)
C(4)—C(5)	1·407 (11)	P—C(1)—C(6)	120·8 (11)
C(5)—C(6)	1·388 (16)	P—C(7)—C(8)	112·0 (8)
C(6)—C(1)	1·390 (7)	C(1)—C(2)—C(3)	120·5 (7)
C(7)—C(8)	1·528 (8)	C(2)—C(3)—C(4)	120·1 (4)
C(8)—O(4)	1·197 (17)	C(3)—C(4)—C(5)	120·6 (5)
C(8)—O(3)	1·319 (12)	C(4)—C(5)—C(6)	119·4 (11)
		C(5)—C(6)—C(1)	120·2 (12)
		C(6)—C(1)—C(2)	119·2 (11)
		C(7)—C(8)—O(4)	123·1 (22)
		C(7)—C(8)—O(3)	114·6 (35)
		O(3)—C(8)—O(4)	122·2 (24)

Table 3. *Intramolecular distances* (Å) *at least* 0·2 Å *less than the sum of the van der Waals radii, and intermolecular distances* (Å) *less than* 3·5 Å

Intramolecular		Intermolecular	
P···C(9)	2·623	O(4)···O(1$^{\text{i}}$)	3·287
P···C(8)	2·754	O(4)···C(6$^{\text{i}}$)	3·304
P···C(2)	2·768	C(8)···O(1$^{\text{i}}$)	3·329
P···C(6)	2·780	C(7)···O(4$^{\text{ii}}$)	3·342
O(1)···C(1)	2·743	O(4)···C(3$^{\text{iii}}$)	3·463
O(1)···C(7)	2·736	O(3)···C(2$^{\text{iv}}$)	3·494
O(1)···O(2)	2·595		
O(1)···O(3)	2·572		

(i) $\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{4}+z$, (ii) $y, \frac{1}{2}+x, 2-z$, (iii) $y-1, \frac{1}{2}+x, 2-z$, (iv) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{7}{2}-z$.

124°). The changes result from experimental errors affecting the position of C(8). The mean C—C bond length in the benzene ring, not corrected for thermal motion, is 1·39 Å. Valency angles on phosphorus differ greatly: O=P—O 116, O=P—C 113, O—P—C 107 and 99, and C—P—C 108°. Some inter- and intramolecular distances are given in Table 3.

The authors are indebted to Dr S. Musierowicz for pointing out the interesting features of this material and for supplying crystals. This research was supported by project MR.I-9 from the Polish Academy of Sciences.

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Acta Cryst. (1978). B**34**, 2940–2943

Structure of 2-*tert*-Butylimido-λ^4-thio-3,4-dihydro-3,3,5,8-tetramethyl-1(2*H*)-naphthalenone

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(*Received* 24 *February* 1978; *accepted* 15 *May* 1978)

Abstract. $C_{18}H_{25}NOS$, monoclinic, $P2_1/c$, a = 8·828 (2), b = 16·916 (4), c = 11·699 (3) Å, β = 110·17 (2)°, Z = 4, d_c = 1·173 g cm^{-3}. The final R = 0·044 (R_w = 0·038) for the 1776 observed X-ray reflections. In the thione–imide group ($>$C=S=N—) only the S—N bond is a full double bond as indicated by the bond lengths: C—S 1·646, S—N 1·558 Å. The angle C—S—N is 110·4°. Semi-empirical calculations lead to the following charge distribution: C —0·05, S 0·44, N —0·41.

Introduction. The structure determination of the title compound has been undertaken in order to verify the chemical structure derived from chemical and spectroscopic studies (Crossland, 1977) and to obtain structural information on the thione–imide group. A suitable crystalline specimen was kindly supplied by Dr I. Crossland, Technical University of Denmark. From this specimen a single crystal with dimensions 0·20 × 0·13 × 0·19 mm was selected and used for data collection on a computer-controlled diffractometer (CAD-4F) with graphite-monochromatized Mo $K\alpha$ radiation. The systematic extinctions and symmetry relations among the X-ray reflections were those of the centrosymmetric space group $P2_1/c$. Unit-cell parameters with e.s.d.'s were determined by least-squares techniques from diffractometer measurements on 25 single-crystal reflections having $\theta > 10°$. 2686 independent reflections with $\theta < 24°$ were collected by the conventional ω-scan technique. Of these reflections only the 1776 with $I_{\rm net}$ greater than $2\sigma(I_{\rm net})$ were considered as observed and used in the subsequent structural refinements. During the data collection a significant decay in intensities was observed for the selected reference reflections. Accordingly the collected intensities ($I_{\rm obs}$) were corrected by the function $I_{\rm corr} = I_{\rm obs}\exp(at^2 + bt)$, where t is the time parameter in seconds and where the constants $a = 1·5\ (3) \times 10^{-6}$ and $b = 3·8\ (9) \times 10^{-4}$ were determined by a least-squares treatment of the intensity decay observed for