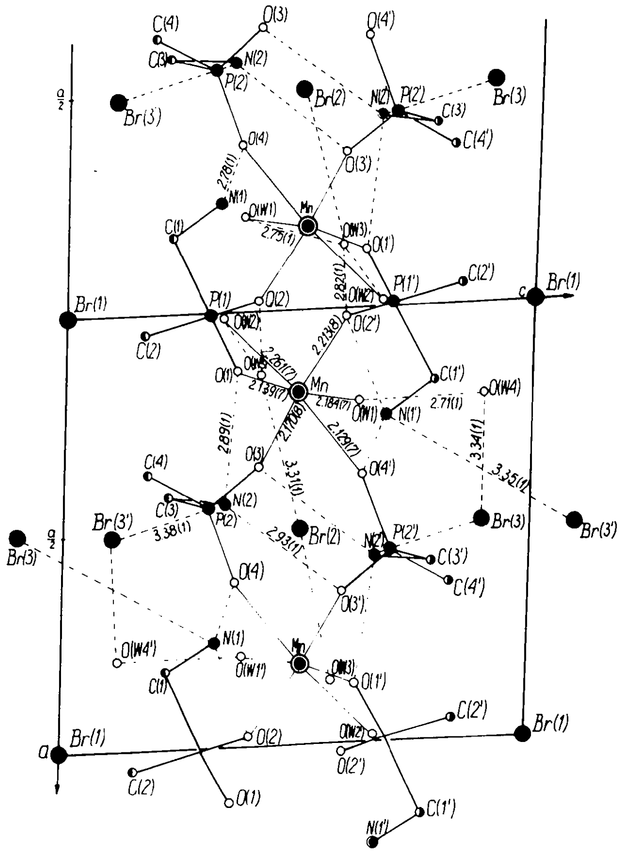

Fig. 2. The crystal structure viewed along **b**. The possible hydrogen bonds are represented by broken lines.

atoms have not been determined, some of the interatomic distances may be considered as hydrogen bonds. The structure viewed down **b** is shown in Fig. 2. The various hydrogen-bond distances are presented in Table 3. All four water molecules enter into hydrogen-bond formation. O(*W*1) and O(*W*2), and O(1), O(2), O(3) and O(4) of the phosphinic groups are coordinated to Mn and also form hydrogen bonds. Uncoordinated O(*W*3) and O(*W*4) take part in the hydrogen bonds with Br and the O atoms of other water molecules and the phosphinic group. The amino group in molecules I and II is also involved in hydrogen-bond formation. Short intermolecular contacts are listed in Table 3.

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Racemic *O*-Methylphenylphosphinylacetic Acid

By Z. Gałdecki and M. L. Główka

Institute of General Chemistry, Technical University, 36 Żwirki, 90-924 Łódź, Poland

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Abstract. (±)-Ph(MeO)P(O)CH_2COOH, monoclinic, $P2_1/c$, $a = 9{\cdot}552\,(5)$, $b = 9{\cdot}072\,(5)$, $c = 11{\cdot}882\,(6)$ Å, $\beta = 92{\cdot}25\,(8)°$, $D_o = 1{\cdot}37$, $D_c(\text{for } Z = 4) = 1{\cdot}374$ g cm^{-3}, $\mu(\text{Cu } K\alpha) = 22{\cdot}6$ cm^{-1}. The symbolic addition procedure and full-matrix least-squares refinement led to the final R of 0·058 for 1473 independent reflexions (Weissenberg photographs, Ni-filtered Cu $K\alpha$ radiation). The molecules form dimers utilizing the O atom of the phosphoryl group.

Introduction. The structure of the title compound has been solved as part of the programme on the X-ray study of phosphinylacetic acid derivatives. These optically active compounds, obtained and resolved by Michalski & Musierowicz (1967), are particularly interesting for explaining the mechanism of stereospecific synthesis. The (−) enantiomer is at present under examination.

Colourless, transparent crystals were obtained from an acetone–water solution as thick needles, elongated along [010]. The systematic absences, *h*0*l* with *l* odd and 0*k*0 with *k* odd, indicated the space group explicitly. The unit-cell parameters were first calculated from high-order reflexions on Weissenberg and KFOR retigraph photographs; refinement was based on CAD-4 diffractometer measurements. Multiple-film, equi-inclination Weissenberg photographs of layers *h0l–h5l* were taken on a sphere of diameter 0·55 mm and interlayer scale factors were calculated from *hk*0 reflexions. Intensities of 1473 reflexions (about 63% of the accessible total) 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 atoms were taken from Doyle & Turner (1968) and for H from *International Tables for X-ray Crystallography* (1962).

The structure of the title compound has been determined by means of the symbolic addition procedure. The result reported in a preliminary communication (Gałdecki & Główka, 1976) was based on an E map for 160 E's $> 1{\cdot}5$ and on subsequent Fourier and difference Fourier syntheses ($R = 0{\cdot}33$).

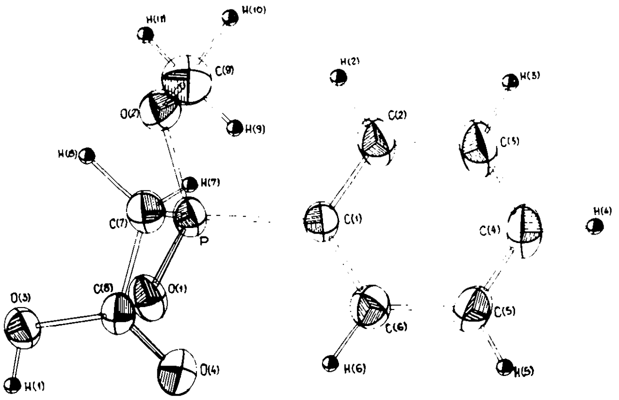

Fig. 1. A view of the molecule perpendicular to the benzene ring (vibration ellipsoids are at 40% probability for nonhydrogen atoms).

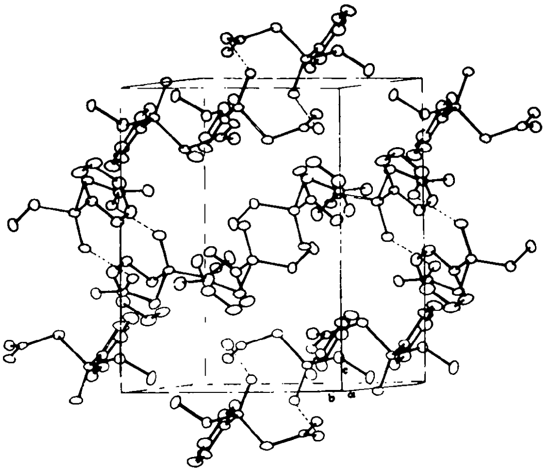

Fig. 2. A projection of the unit-cell contents with the hydrogen bond marked.

Full-matrix least-squares refinement of this model resulted in $R = 0{\cdot}077$ after four cycles with isotropic and a further three cycles with anisotropic thermal parameters ($w = 1$). The subsequent difference maps, alternating with refinement, revealed sites for all H atoms. Their inclusion reduced R to a final value of 0·058.* For the refinement the programs *CRYLSQ* and *ORFLS*, included in the XRAY 70 system, were used. The final weighting scheme applied was $w^{-1} = 7 + |F| + 0{\cdot}01|F|^2$. Maximum and mean values of Δ/σ in the final cycle were 2·12 and 0·33 respectively. Four reflexions with $w(|F_o| - |F_c|) > 0{\cdot}72$ were not included in the refinement.

Discussion. In the solid state, *O*-methylphenylphosphinylacetic acid molecules exist as dimers, utilizing the hydroxyl group and an O atom of the

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

	x	*y*	*z*
P	1780 (1)	2813 (2)	4098 (1)
O(1)	1537 (3)	2304 (4)	5252 (2)
O(2)	1274 (3)	4437 (5)	3832 (3)
O(3)	−773 (3)	157 (6)	3804 (3)
O(4)	1339 (3)	−681 (5)	3389 (3)
C(1)	3594 (4)	2726 (6)	3790 (3)
C(2)	4085 (5)	3429 (8)	2847 (4)
C(3)	−4508 (5)	3337 (9)	2617 (5)
C(4)	−3626 (5)	2531 (8)	3267 (4)
C(5)	−4082 (5)	1862 (7)	4211 (5)
C(6)	4518 (5)	1925 (7)	4482 (4)
C(7)	777 (5)	1827 (7)	3018 (4)
C(8)	488 (4)	270 (7)	3413 (3)
C(9)	1868 (9)	5644 (11)	4496 (7)

Table 2. *Hydrogen-atom parameters* ($\times 10^3$)

	x	*y*	*z*	U (Å^2)
H(1)	84 (6)	60 (9)	591 (5)	38 (3)
H(2)	336 (5)	400 (6)	232 (4)	50 (2)
H(3)	−429 (5)	389 (6)	187 (4)	54 (3)
H(4)	−269 (5)	263 (6)	311 (4)	50 (2)
H(5)	−344 (5)	138 (7)	474 (4)	57 (4)
H(6)	419 (5)	152 (6)	522 (4)	50 (3)
H(7)	121 (4)	183 (5)	236 (4)	31 (2)
H(8)	−14 (7)	250 (8)	278 (5)	95 (5)
H(9)	254 (13)	505 (14)	484 (11)	223 (13)
H(10)	246 (14)	657 (15)	430 (10)	198 (12)
H(11)	134 (11)	663 (13)	468 (9)	247 (11)

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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 32551 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

The mean value of the H–C distances is 1·00 (2) Å.

P–O(1)	1·474 (9)	C(1)–C(2)	1·387 (15)
P–O(2)	1·579 (28)	C(2)–C(3)	1·384 (11)
P–C(1)	1·786 (14)	C(3)–C(4)	1·338 (21)
P–C(7)	1·807 (31)	C(4)–C(5)	1·362 (16)
O(2)–C(9)	1·451 (48)	C(5)–C(6)	1·389 (12)
O(3)–C(8)	1·311 (17)	C(6)–C(1)	1·388 (14)
O(4)–C(8)	1·187 (36)	C(7)–C(8)	1·526 (22)
		O(1)···H(1)	1·866 (11)
O(1)–P–O(2)	114·8 (1·)	C(1)–C(2)–C(3)	119·6 (1·)
O(1)–P–C(1)	111·5 (1·)	C(2)–C(3)–C(4)	120·9 (1·)
O(1)–P–C(7)	114·0 (1·)	C(3)–C(4)–C(5)	120·3 (1·)
O(2)–P–C(1)	107·0 (1·)	C(4)–C(5)–C(6)	120·9 (1·)
O(2)–P–C(7)	99·8 (1·)	C(5)–C(6)–C(1)	118·7 (1·)
C(1)–P–C(7)	108·9 (1·)	C(6)–C(1)–C(2)	119·5 (1·)
P–O(2)–C(9)	119·0 (2·)	O(3)–C(8)–C(7)	111·3 (2·)
P–C(7)–C(8)	109·8 (1·)	O(3)–C(8)–O(4)	126·2 (2·)
P–C(1)–C(2)	120·5 (1·)	O(4)–C(8)–C(7)	122·4 (2·)
P–C(1)–C(6)	120·0 (1·)	O(3)–H(1)···O(1)	164·1 (1·)

Table 4. *Selected intermolecular distances* <3·5 Å

The first atom is at *x*,*y*,*z* and superscripts refer to equivalent positions: (i) $-x, 1-y, 1-z$, (ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$, (iii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

O(3)···C(8^{i})	3·330 (11)	O(2)···C(8^{iii})	3·189 (13)
C(5)···C(9^{i})	3·420 (38)	O(2)···O(3^{iii})	3·217 (14)
O(3)···O(4^{i})	3·433 (30)	C(4)···O(4^{iii})	3·408 (90)
O(1)···C(8^{i})	3·456 (35)	C(3)···O(4^{iii})	3·416 (69)
O(1)···C(7^{ii})	3·483 (56)	C(7)···O(4^{iii})	3·424 (27)

phosphoryl group. The length of the hydrogen bond is 2·62 (1) Å, which agrees with values tabulated by Brown (1976). The O–H···O angle is 164 (1)°. The molecular structure and the numbering system are presented in Fig. 1 (Johnson, 1965). A projection of the unit-cell contents is shown in Fig. 2. The atomic parameters and their estimated standard deviations as obtained from the least-squares refinement are listed in Tables 1 and 2. The bond lengths and angles, not corrected for thermal vibration, are summarized in Table 3. The P–OCH_3 bond length (1·58 Å) is in agreement with the corresponding value in organic phosphates (Karle & Britts, 1966). The P=O and P–C bond lengths are 1·47 and 1·79 Å respectively; these values compare well with those found in dimethylphosphinic acid (Giordano & Ripamonti, 1967), di-*n*-nonylphosphinic acid (Bello, 1973), diphenylphosphinic acid (Fenske, Mattes, Löns & Tebbe, 1973) and 2-aminoethylphosphinic acid (Okaya, 1966). The mean C–C distance in the benzene ring is ~1·38 Å and the bond angles range from 119 to 121°. Only C(3)–C(4) is shorter (1·34 Å) but no correction has been made for thermal motion, which is significant. For example,

Table 5. *Deviations of some atoms* (*in* Å) *from the least-squares benzene plane*

The equation of the least-squares plane is given in the form $lx' + my' + nz' = d$, where $l = -0{\cdot}0399$, $m = 0{\cdot}8149$, $n = 0{\cdot}5783$, $d = 4{\cdot}3979$, and $x' = xa$ (similarly y' and z') in orthogonal ångström space.

Atoms defining least-squares plane	Other atoms	Deviations from plane
C(1)		0·1069
C(2)		−0·0387
C(3)		0·0594
C(4)		−0·1247
C(5)		0·0463
C(6)		−0·0492
	P	0·4519
	O(1)	0·8803
	O(2)	1·4962
	C(7)	−0·9852

Declercq, Germain, Putzeys, Rona & Van Meerssche (1974) have found the distances in the benzene ring to be 1·32 to 1·44 Å, and Konno & Saito (1973) found 1·34 to 1·40 Å for comparable data and similar compounds. The remaining bond lengths and angles are in agreement with previously determined structures, within the limits of errors. Some intermolecular distances <3·5 Å are given in Table 4. The equation of the least-squares benzene plane and deviations of some atoms from it are given in Table 5.

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Tetrakis(1-pyrazolyl)borato(triphenylphosphine)(carbonyl)(nitrosyl)molybdenum

BY E. RODULFO DE GIL, A. VALENTINA RIVERA AND HERMES NOGUERA

Departamento de Química, Facultad de Ciencias, Universidad de los Andes, Merida, Venezuela

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Abstract. $[(C_3H_3N_2)_4B]Mo[(C_6H_5)_3P](CO)(NO)$, triclinic, $P\bar{1}$, $a = 9{\cdot}058\,(5)$, $b = 13{\cdot}132\,(8)$, $c = 15{\cdot}020\,(8)$ Å; $\alpha = 86{\cdot}01\,(2)$, $\beta = 80{\cdot}26\,(2)$, $\gamma = 71{\cdot}65\,(2)^\circ$, $U = 1671$ Å^3; $Z = 2$, $D_x = 1{\cdot}38$ g cm^{-3}. The structure was determined by Patterson methods and refined to an R of 0·057 for 3759 unique diffractometer data. The coordination around Mo is distorted octahedral, around B it is tetrahedral and around P, distorted tetrahedral. The four pyrazolyl rings are planar, as are the phenyl rings.

Table 1. *Atomic coordinates* (×10^4) *with standard deviations in parentheses*

	x	*y*	*z*		*x*	*y*	*z*
Mo	2887 (1)	1369 (1)	2379 (1)	N(14)	−299 (6)	−947 (3)	3502 (3)
P	1859 (1)	2896 (1)	1319 (1)	N(24)	−287 (8)	−1843 (5)	3103 (3)
B	669 (7)	−233 (4)	3085 (3)	C(34)	−1036 (8)	−2353 (5)	3712 (4)
N	3624 (6)	2147 (4)	3082 (3)	C(44)	−1531 (9)	−1817 (5)	4530 (4)
O(N)	4131 (7)	2589 (5)	3559 (4)	C(54)	−1060 (8)	−911 (4)	4384 (3)
C	4907 (7)	897 (4)	1709 (3)	C(15)	−301 (5)	3330 (3)	1430 (3)
O(C)	6213 (6)	538 (4)	1340 (4)	C(25)	−1060 (6)	2559 (4)	1407 (3)
N(11)	502 (5)	1705 (3)	3216 (3)	C(35)	−2662 (7)	2828 (5)	1541 (4)
N(21)	−260 (5)	949 (3)	3334 (3)	C(45)	−3582 (7)	3873 (6)	1699 (4)
C(31)	−1785 (8)	1409 (5)	3652 (4)	C(55)	−2848 (8)	4650 (5)	1726 (4)
C(41)	−2019 (7)	2476 (5)	3773 (4)	C(65)	−1223 (6)	4385 (4)	1583 (3)
C(51)	−574 (7)	2623 (4)	3497 (3)	C(16)	2459 (6)	2659 (3)	112 (3)
N(12)	2031 (5)	288 (3)	1643 (2)	C(26)	4047 (7)	2243 (4)	−236 (3)
N(22)	1079 (5)	−290 (3)	2057 (3)	C(36)	4519 (8)	2067 (4)	−1137 (4)
C(32)	727 (8)	−837 (5)	1420 (3)	C(46)	3438 (9)	2281 (5)	1711 (4)
C(42)	1502 (8)	−615 (5)	606 (3)	C(56)	1845 (9)	2696 (5)	−1386 (4)
C(52)	2277 (7)	84 (4)	771 (3)	C(66)	1371 (7)	2895 (4)	−482 (3)
N(13)	3309 (6)	−22 (3)	3293 (3)	C(17)	2255 (6)	4156 (3)	1443 (3)
N(23)	2226 (5)	−571 (3)	3480 (3)	C(27)	2021 (7)	4560 (4)	2302 (4)
C(33)	2789 (8)	−1423 (4)	4021 (4)	C(37)	2188 (8)	5544 (5)	2424 (4)
C(43)	4230 (9)	−1424 (5)	4192 (4)	C(47)	2642 (9)	6137 (5)	1696 (5)
C(53)	4511 (8)	−526 (5)	3721 (4)	C(57)	2919 (9)	5735 (5)	839 (5)
H(25)	−372 (11)	1747 (7)	1285 (6)	C(67)	2712 (7)	4758 (4)	710 (4)
H(35)	−3218 (13)	2225 (9)	1522 (7)	H(31)	−2520 (11)	1020 (12)	3830 (14)
H(45)	−4851 (13)	4082 (10)	1803 (8)	H(41)	−3040 (11)	2990 (13)	3920 (13)
H(55)	−3548 (13)	5461 (8)	1851 (8)	H(51)	−320 (13)	3310 (11)	3420 (12)
H(65)	−662 (11)	4991 (7)	1598 (6)	H(32)	150 (11)	−1340 (11)	1580 (12)
H(26)	4901 (12)	2064 (8)	207 (6)	H(42)	1220 (12)	−820 (13)	40 (8)
H(36)	5740 (14)	1751 (8)	−1394 (7)	H(52)	2760 (13)	430 (12)	320 (13)
H(46)	3819 (16)	2131 (8)	−2413 (7)	H(33)	2310 (13)	−1890 (12)	4310 (10)
H(56)	991 (15)	2868 (8)	−1835 (6)	H(43)	5020 (12)	−1880 (14)	4620 (9)
H(66)	148 (13)	3222 (8)	−230 (6)	H(53)	5450 (11)	−190 (13)	3770 (12)
H(27)	1684 (12)	4104 (7)	2870 (7)	H(34)	−1240 (13)	−3040 (11)	3640 (9)
H(37)	1980 (14)	5851 (8)	3087 (8)	H(44)	−2460 (11)	−1930 (12)	4990 (10)
H(47)	2787 (16)	6905 (8)	1795 (10)	H(54)	−1150 (12)	−350 (11)	4800 (11)
H(57)	3278 (16)	6190 (8)	273 (9)	H(67)	2910 (12)	4455 (7)	44 (7)