Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(*R*)-Dimethyl [(2-chlorophenyl)hydroxymethyl]phosphonate

M. Nawaz Tahir,[a] Nurcan Acar,[b] Hamza Yilmaz,[b] Muhammad Danish[c] and Dinçer Ülkü[d]*

[a]University of Sargodha, Department of Physics, Sagrodha, Pakistan, [b]University of Ankara, Department of Chemistry, Faculty of Science, Ankara, Turkey, [c]University of Sargodha, Department of Chemistry, Sargodha, Pakistan, and [d]Hacettepe University, Department of Physics Engineering, Beytepe 06532, Ankara, Turkey
Correspondence e-mail: dmntahir_uos@yahoo.com

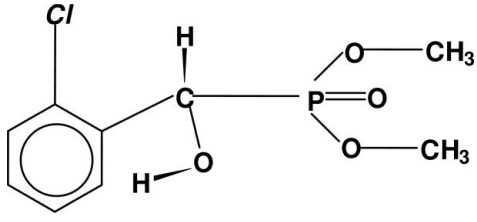
Received 11 July 2007; accepted 9 August 2007

Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.006 Å; R factor = 0.039; wR factor = 0.113; data-to-parameter ratio = 9.6.

In the crystal structure of the title compound, $C_9H_{12}ClO_4P$, the distorted tetrahedral geometry around the P atom consists of three phosphonate O atoms and one C atom of the benzyl group. The bond angles around phosphorus are in the range 101.76 (15)–116.18 (17)°. The P—O single-bond lengths are nearly equal [1.569 (3) Å], while the P=O double-bond length is 1.469 (3) Å. There exists strong intermolecular hydrogen bonding between the hydroxy group and an O atom of the phosphonate group of a symmetry-related molecule. Owing to intermolecular hydrogen bonding, a one-dimensional polymeric network is formed, extending along the crystallographic *b* axis.

Related literature

For related literature, see: Fang *et al.* (2006); Liu *et al.* (1995); Patel *et al.* (1990); Stowasser *et al.* (1992); Tahir *et al.* (1996).



Experimental

Crystal data

$C_9H_{12}ClO_4P$
M_r = 250.61
Orthorhombic, $P2_12_12_1$
a = 7.5670 (12) Å
b = 7.9230 (13) Å
c = 19.0420 (12) Å
V = 1141.6 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.47 mm^{-1}
T = 295 K
0.25 × 0.2 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: empirical (using intensity measurements) via ψ scans (*MolEN*; Fair, 1990)
T_{min} = 0.885, T_{max} = 0.954
1361 measured reflections
1314 independent reflections
1119 reflections with $I > 2\sigma(I)$
R_{int} = 0.012
3 standard reflections
frequency: 120 min
intensity decay: −2.5%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.113
S = 1.10
1314 reflections
137 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter: −0.13 (17)

Table 1
Selected geometric parameters (Å, °).

Cl1—C2	1.748 (4)	O1—C7	1.417 (4)
P1—O2	1.469 (3)	O3—C8	1.396 (5)
P1—O4	1.568 (3)	O4—C9	1.436 (5)
P1—O3	1.569 (3)	C1—C7	1.506 (5)
P1—C7	1.822 (3)		
O2—P1—O4	113.93 (18)	O2—P1—C7	116.18 (17)
O2—P1—O3	114.62 (18)	O4—P1—C7	101.76 (15)
O4—P1—O3	104.59 (19)	O3—P1—C7	104.22 (17)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^{i}	0.82	1.93	2.743 (4)	171
C7—H7···Cl1	0.98	2.57	3.100 (4)	114
C7—H7···O1^{i}	0.98	2.56	3.494 (5)	159

Symmetry code: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, -z$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Version 1.70.01; Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2031).

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supplementary materials

Acta Cryst. (2007). E**63**, o3817-o3818 [**doi:10.1107/S1600536807039499**]

(*R*)-Dimethyl [(2-chlorophenyl)hydroxymethyl]phosphonate

M. N. Tahir, N. Acar, H. Yilmaz, M. Danish and D. Ülkü

Comment

α-Hydroxy phosphonates are a subject of increasing interest because these compounds inhibit various enzymes like renin (Patel *et al.*, 1990) and HIV protease (Stowasser *et al.*, 1992).

To our surprise various samples of (I) obtained in different batches have had some optical activity indicating that either the mechanism favours one conformer, or, two optical isomers prefer to crystallize separately in unequal proportions. Hence, we determined the crystal structure.

As can be seen on *ORTEP* diagram (Fig. 1.) the crystal investigated contains only the *R*-isomer. The P-atom adopts a distorted tetrahedral configuration: the bond angles aroud it being in the range 101.76 (15)°-116.18 (17)°. These values are closer to ideal like reported earlier (Fang *et al.*, 2006) than those of dimethyl[α-(benzylamino)-*p*-chlorobenzyl]phosphonate (Liu *et al.*, 1995). The geometry about P-atom is exactly similar to (Fang *et al.*, 2006), however, all the bond distances around P-atom are all larger. The bond distance P1—C7 [1.822 (3) Å] is smaller compared to the value [1.860 (4) Å], in our reported structure (Tahir *et al.*, 1996). There exist a strong inter-molecular hydrogen bonding between O1—H1 (hydroxy group) and O2^{i}(x + 1/2, −y + 1/2, −z). Another inter-molecular hydrogen bonding exists between C7—H7 and O1(x + 1/2, −y + 1/2, −z) which forms eight membered group (C7,O1,H1,O2^{i},P1^{i},C7^{i},O1^{i},H7). There also exists an intre-molecular hydrogen bonding between C7—H7···Cl1. Due to inter-molecular hydrogen bonding one-dimensional polymeric network is formed extending to crystallographic *b* axis (Fig. 2). The closest approach between polymeric chains is among C6 and C9 (x, y + 1, z) [3.387 (6) Å]. The Flack parameter −0.13 (17) [Flack, 1983] clearly indicates the *R*-configuration of the title compound.

Experimental

1.41 g (10 mmole) of *o*-chlorobenzaldehyde was disolved in an equivalent amount (1.10 g) of neat dimethylphosphonate in the presence of an equal mixture (2.5 g + 2.5 g) of KF and ψ-Al_2O_3. The mixture was kept at room temperature for 48 h. The product was extracted twice with 20 ml portions of a dichloromethane-methanol mixture (1:1). After the evaporation of the solvant on a rotary evaporator, the oily residue was redisolved in a mixture of diethyl ether and acetone (3:1) and recrystallized in this medium. M·P: (83–86 °C); yield: 40 percent %.

Refinement

H atoms to the C-atoms of the phenyl ring were bonded geometrically 0.930 Å, while the H-atom attached to C7 is at a distance of 0.98 Å. Thermal parameter of all these H atoms was taken 1.2 times of the corresponding atoms. The thermal parameter of H-atoms geometrically bonded to CH_3 groups [0.960 Å] and H-atom of OH [0.80 Å] was taken 1.5 times of the corresponding atom. Regarding data: Some reflections could not be recovered from flopy at back back home and also zero track of used hard disk damaged.

Figures

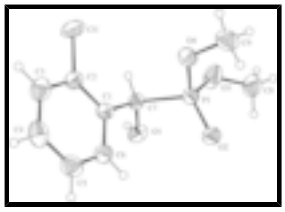

Fig. 1. *ORTEP* drawing of the title compound with the atom numbering scheme. The thermal ellpsoids are drawn at the 30% probability level. H-atoms are shown by small circles of arbitrary radii.

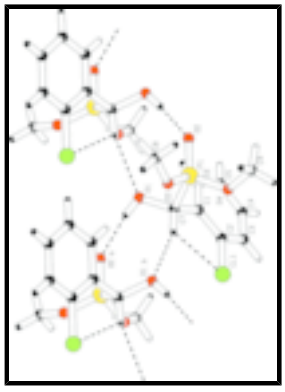

Fig. 2. The packing figure (*PLATON*: Spek, 2003) showing the mechanism of hydrogen bonding.

(*R*)-Dimethyl [(2-chlorophenyl)hydroxymethyl]phosphonate

Crystal data

$C_9H_{12}ClO_4P$	$D_x = 1.458$ Mg m^{-3}
$M_r = 250.61$	Melting point: 83-86 K
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 25 reflections
$a = 7.5670$ (12) Å	$\theta = 10.6$–$18.5°$
$b = 7.9230$ (13) Å	$\mu = 0.47$ mm^{-1}
$c = 19.0420$ (12) Å	$T = 295$ K
$V = 1141.6$ (3) Å^3	Prism, colourless
$Z = 4$	0.25 × 0.2 × 0.15 mm
$F_{000} = 520$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{max} = 26.3°$
$\omega/2\theta$ scans	$\theta_{min} = 2.8°$
Absorption correction: empirical (using intensity measurements) via ψ scans (MolEN; Fair, 1990) ?	$h = 0\rightarrow9$
$T_{min} = 0.885$, $T_{max} = 0.954$	$k = 0\rightarrow9$
1361 measured reflections	$l = -23\rightarrow23$
1314 independent reflections	3 standard reflections
1119 reflections with $I > 2\sigma(I)$	every 120 min

R_{int} = 0.012

intensity decay: −2.5%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.039

$wR(F^2)$ = 0.113

S = 1.10

1314 reflections

137 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 0.40 e Å^{-3}

$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Extinction correction: none

Absolute structure: Flack (1983), number of Friedel pairs?

Flack parameter: −0.13 (17)

Special details

Experimental. the structure was solved by Patterson method using *SHELX86*. The whole molecule was recognized.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.56770 (15)	0.23649 (19)	0.17150 (7)	0.0795 (4)
P1	0.17377 (12)	0.01006 (12)	0.04711 (5)	0.0473 (3)
O1	0.1972 (4)	0.3210 (3)	0.00635 (13)	0.0574 (7)
H1	0.2771	0.3722	−0.0135	0.086*
O2	−0.0201 (3)	0.0013 (3)	0.04521 (15)	0.0598 (7)
O3	0.2678 (4)	−0.0579 (5)	−0.02068 (17)	0.0851 (11)
O4	0.2591 (4)	−0.0924 (3)	0.10882 (16)	0.0677 (8)
C1	0.2247 (5)	0.2842 (4)	0.13248 (18)	0.0435 (8)
C2	0.3483 (5)	0.2960 (5)	0.18634 (19)	0.0503 (8)
C3	0.3055 (7)	0.3590 (6)	0.2521 (2)	0.0681 (12)
H3	0.3909	0.3647	0.2871	0.082*
C4	0.1361 (7)	0.4132 (6)	0.2651 (2)	0.0711 (13)
H4	0.1068	0.4575	0.3087	0.085*
C5	0.0103 (6)	0.4015 (6)	0.2133 (2)	0.0678 (11)
H5	−0.1051	0.4353	0.2226	0.081*
C6	0.0532 (5)	0.3401 (5)	0.1477 (2)	0.0551 (9)
H6	−0.0330	0.3357	0.1130	0.066*
C7	0.2690 (5)	0.2188 (4)	0.06033 (16)	0.0442 (7)
H7	0.3977	0.2127	0.0550	0.053*

C8	0.1895 (8)	−0.1584 (7)	−0.0722 (3)	0.0854 (15)
H8A	0.2745	−0.1832	−0.1082	0.128*
H8B	0.0911	−0.0993	−0.0924	0.128*
H8C	0.1489	−0.2618	−0.0514	0.128*
C9	0.2136 (6)	−0.2659 (6)	0.1212 (3)	0.0752 (13)
H9A	0.2786	−0.3072	0.1610	0.113*
H9B	0.2425	−0.3318	0.0805	0.113*
H9C	0.0892	−0.2745	0.1305	0.113*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0526 (6)	0.1012 (9)	0.0848 (7)	0.0123 (7)	−0.0213 (5)	0.0012 (7)
P1	0.0411 (5)	0.0440 (4)	0.0568 (5)	−0.0009 (4)	0.0001 (4)	−0.0005 (4)
O1	0.0495 (15)	0.0652 (16)	0.0574 (14)	−0.0111 (13)	−0.0051 (13)	0.0206 (12)
O2	0.0424 (13)	0.0495 (13)	0.0875 (17)	−0.0030 (12)	−0.0028 (13)	0.0068 (17)
O3	0.0605 (19)	0.108 (3)	0.087 (2)	−0.0166 (19)	0.0124 (17)	−0.044 (2)
O4	0.0700 (19)	0.0418 (13)	0.0913 (19)	0.0008 (14)	−0.0206 (16)	0.0101 (13)
C1	0.0437 (19)	0.0368 (15)	0.0501 (17)	−0.0043 (14)	−0.0008 (15)	0.0088 (14)
C2	0.050 (2)	0.0448 (18)	0.0564 (19)	−0.0040 (16)	−0.0059 (16)	0.0091 (16)
C3	0.081 (3)	0.069 (3)	0.055 (2)	−0.009 (3)	−0.009 (2)	0.0008 (19)
C4	0.092 (4)	0.065 (2)	0.057 (2)	−0.011 (3)	0.011 (2)	−0.010 (2)
C5	0.061 (3)	0.062 (2)	0.081 (3)	0.002 (2)	0.016 (2)	−0.004 (2)
C6	0.048 (2)	0.0504 (19)	0.067 (2)	−0.0044 (17)	0.0004 (19)	−0.0005 (17)
C7	0.0416 (17)	0.0436 (16)	0.0474 (17)	−0.0051 (15)	−0.0010 (14)	0.0031 (15)
C8	0.084 (3)	0.091 (3)	0.081 (3)	0.000 (3)	−0.008 (3)	−0.034 (3)
C9	0.066 (3)	0.054 (2)	0.106 (3)	0.003 (2)	0.002 (3)	0.019 (2)

Geometric parameters (Å, °)

Cl1—C2	1.748 (4)	C3—H3	0.9300
P1—O2	1.469 (3)	C4—C5	1.374 (7)
P1—O4	1.568 (3)	C4—H4	0.9300
P1—O3	1.569 (3)	C5—C6	1.379 (6)
P1—C7	1.822 (3)	C5—H5	0.9300
O1—C7	1.417 (4)	C6—H6	0.9300
O1—H1	0.8200	C7—H7	0.9800
O3—C8	1.396 (5)	C8—H8A	0.9600
O4—C9	1.436 (5)	C8—H8B	0.9600
C1—C2	1.392 (5)	C8—H8C	0.9600
C1—C6	1.401 (5)	C9—H9A	0.9600
C1—C7	1.506 (5)	C9—H9B	0.9600
C2—C3	1.386 (6)	C9—H9C	0.9600
C3—C4	1.374 (7)		
O2—P1—O4	113.93 (18)	C6—C5—H5	119.7
O2—P1—O3	114.62 (18)	C5—C6—C1	121.1 (4)
O4—P1—O3	104.59 (19)	C5—C6—H6	119.4
O2—P1—C7	116.18 (17)	C1—C6—H6	119.4

O4—P1—C7	101.76 (15)	O1—C7—C1	112.3 (3)
O3—P1—C7	104.22 (17)	O1—C7—P1	105.5 (2)
C7—O1—H1	109.5	C1—C7—P1	110.5 (2)
C8—O3—P1	125.5 (3)	O1—C7—H7	109.5
C9—O4—P1	121.3 (3)	C1—C7—H7	109.5
C2—C1—C6	116.7 (3)	P1—C7—H7	109.5
C2—C1—C7	123.1 (3)	O3—C8—H8A	109.5
C6—C1—C7	120.2 (3)	O3—C8—H8B	109.5
C3—C2—C1	122.2 (4)	H8A—C8—H8B	109.5
C3—C2—Cl1	117.7 (3)	O3—C8—H8C	109.5
C1—C2—Cl1	120.1 (3)	H8A—C8—H8C	109.5
C4—C3—C2	119.6 (4)	H8B—C8—H8C	109.5
C4—C3—H3	120.2	O4—C9—H9A	109.5
C2—C3—H3	120.2	O4—C9—H9B	109.5
C5—C4—C3	119.8 (4)	H9A—C9—H9B	109.5
C5—C4—H4	120.1	O4—C9—H9C	109.5
C3—C4—H4	120.1	H9A—C9—H9C	109.5
C4—C5—C6	120.7 (4)	H9B—C9—H9C	109.5
C4—C5—H5	119.7		
O2—P1—O3—C8	−16.2 (5)	C4—C5—C6—C1	1.6 (7)
O4—P1—O3—C8	109.3 (5)	C2—C1—C6—C5	−0.8 (6)
C7—P1—O3—C8	−144.3 (4)	C7—C1—C6—C5	−179.5 (4)
O2—P1—O4—C9	51.0 (4)	C2—C1—C7—O1	−134.9 (3)
O3—P1—O4—C9	−74.9 (4)	C6—C1—C7—O1	43.8 (4)
C7—P1—O4—C9	176.8 (3)	C2—C1—C7—P1	107.6 (3)
C6—C1—C2—C3	0.2 (5)	C6—C1—C7—P1	−73.7 (4)
C7—C1—C2—C3	178.9 (3)	O2—P1—C7—O1	−55.4 (3)
C6—C1—C2—Cl1	−177.7 (3)	O4—P1—C7—O1	−179.7 (2)
C7—C1—C2—Cl1	1.0 (5)	O3—P1—C7—O1	71.8 (3)
C1—C2—C3—C4	−0.4 (6)	O2—P1—C7—C1	66.3 (3)
Cl1—C2—C3—C4	177.6 (4)	O4—P1—C7—C1	−58.1 (3)
C2—C3—C4—C5	1.1 (7)	O3—P1—C7—C1	−166.6 (2)
C3—C4—C5—C6	−1.7 (7)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^{i}	0.82	1.93	2.743 (4)	171
C7—H7···Cl1	0.98	2.57	3.100 (4)	114
C7—H7···O1^{i}	0.98	2.56	3.494 (5)	159

Symmetry codes: (i) *x*+1/2, −*y*+1/2, −*z*.

Fig. 1

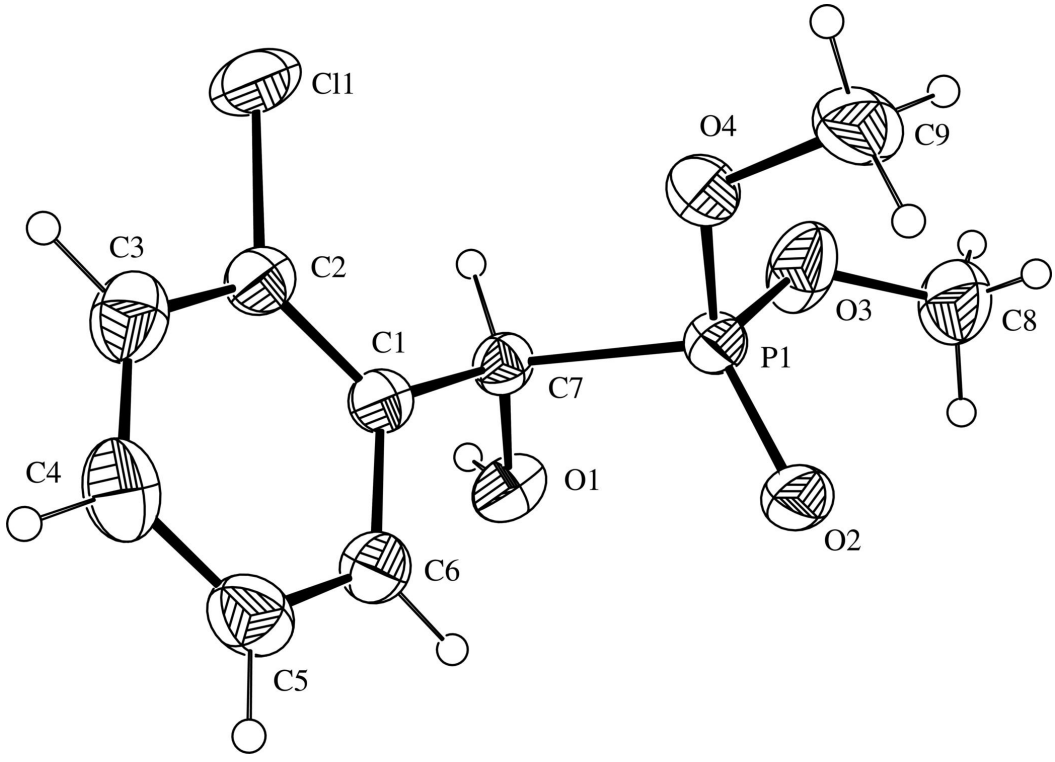

Fig. 2