

[(4,4-Dimethyl-2-oxo-1,3-oxazolidin-3-yl)methyl]phosphonic acid

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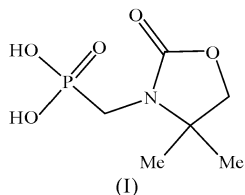
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The title compound, C₆H₁₂NO₅P, was synthesized as an intermediate phase in a search for new *N*-(phosphonomethyl)glycine derivatives. The molecules are held together by O—H···O hydrogen bonds, forming chains along the *b* axis in the crystal structure. The observed molecular structure is compared with that calculated by the density functional theory method.

Comment

The herbicidal activities of derivatives of *N*-(phosphonomethyl)glycine (glyphosate) were reported by Baird *et al.* (1971). These compounds have also been effective in suppressing tumour growth and have been investigated as potential lead compounds with anticancer, antiviral and antibacterial activities (Kafarski & Lejczak, 1991; Alonso *et al.*, 2000; Camden, 1999, 2000). Recently, we synthesized a series of five new α -aminophosphonic acids and investigated their genotoxic and antiproliferative activities (Naydenova *et al.*, 2006). Among the aforesaid five compounds, only for compound (I) were we able to obtain crystals suitable for X-ray diffraction. In this paper, we report the crystal structure of (I) and compare its geometric parameters with those optimized by density functional theory (DFT) calculations. Such a



comparison is required in order to verify whether the DFT method could be employed for investigating the molecular structures of the other four compounds in the series.

The molecular structure of (I) is shown in Fig. 1. The structural features of the oxazolidin-2-one ring are comparable with those of similar ring compounds (Rios *et al.*, 2002; Eknoian *et al.*, 1998). The ring has an envelope conformation, with atom C4 deviating by 0.416 (6) Å from the plane defined by the other four atoms (N3/C2/O1/C5). The P1—C8 bond length of 1.811 (4) Å and the N3—C8—P1 angle of 113.5 (2)° are comparable with the corresponding values found for the glyphosate molecule [1.817 (3) Å and 111.7 (2)°, respectively; Sheldrick & Morr (1981)]. The similarity in P1—O4 and P1—O5 bond distances (Table 1) corresponds to the fact that there is no transfer of a H atom from the acid group to the N atom.

Symmetrically equivalent molecules, generated by a 2₁ screw axis, are linked through O—H···O hydrogen bonds (Table 2), forming a chain parallel to the *b* axis (Fig. 2). In the chain, the molecules face one another in such a way that the phosphonic acid groups form the inner side of the chain, whereas the oxazolidin-2-one groups are outside it. Additional weak C—H···O interactions link the chains into 'pseudo-layers' parallel to the (100) plane. It is worth noting that polar interactions exist inside the pseudo-layers, whereas non-polar interactions are found outside them.

The values of the bond lengths and angles calculated by the DFT method are in good agreement with the experimental data (Table 1), the differences not exceeding 0.06 Å for the bond lengths and 3° for the valence angles. This shows that an envelope conformation of the oxazolidin-2-one ring is most

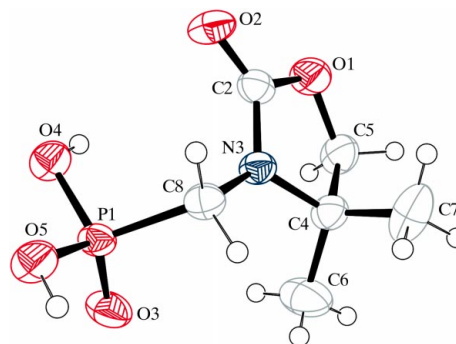


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

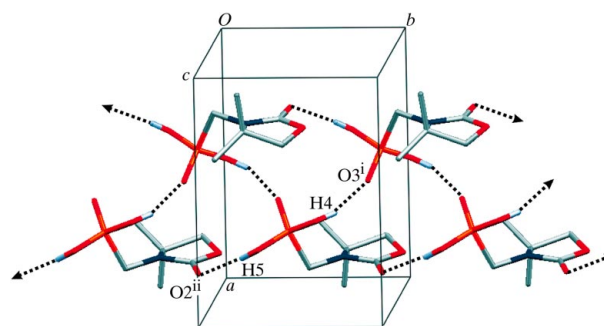


Figure 2

A view of the chain of (I) along the *b* axis. H atoms have been omitted except for those involved in O—H···O hydrogen bonds (dotted lines). [Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $x, y - 1, z$].

probable, with atom C4 displaced by 0.322 Å from the least-squares plane formed by the other four atoms. The major difference between the computed and experimental structures is in the value of the N3–C8–P1–O4 torsion angle [–78.2 and –63.6 (3)°, respectively]. Consequently, the intramolecular interaction between the oxazolidinone and phosphonic acid parts, O4–H4···O2, is more pronounced in the calculated structure than in the experimental one [O4–O2 = 2.727 and 3.250 (4) Å, respectively].

Experimental

Compound (I) was prepared according to the method of Naydenova *et al.* (2006). Crystals of (I) suitable for single-crystal X-ray diffraction were grown as colourless needles by slow evaporation of an aqueous solution at 277 K.

Crystal data

C ₆ H ₁₂ NO ₅ P	Z = 4
M _r = 209.14	D _x = 1.502 Mg m ⁻³
Monoclinic, P2 ₁ /c	Mo Kα radiation
a = 9.2775 (13) Å	μ = 0.29 mm ⁻¹
b = 6.7213 (16) Å	T = 290 (2) K
c = 14.875 (2) Å	Prism, colourless
β = 94.614 (11)°	0.24 × 0.24 × 0.22 mm
V = 924.6 (3) Å ³	

Data collection

Enraf–Nonius CAD-4 diffractometer	R _{int} = 0.096
ω/2θ scans	θ _{max} = 30.0°
5096 measured reflections	3 standard reflections
2661 independent reflections	frequency: 120 min
1642 reflections with I > 2σ(I)	intensity decay: 1%

Refinement

Refinement on F ²	w = 1/[σ ² (F _o ²) + (0.0712P) ² + 1.849P]
R[F ² > 2σ(F ²)] = 0.067	where P = (F _o ² + 2F _c ²)/3
wR(F ²) = 0.192	(Δ/σ) _{max} < 0.001
S = 0.98	Δρ _{max} = 0.29 e Å ⁻³
2661 reflections	Δρ _{min} = –0.34 e Å ⁻³
118 parameters	
H-atom parameters constrained	

Methyl H atoms were constrained to an ideal geometry, with C–H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C), but were allowed to rotate freely about their parent C–C bonds. The other H atoms were placed in calculated positions, with methylene C–H = 0.97 Å and hydroxy O–H = 0.82 Å, and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C, O).

DFT calculations at the B3LYP/6311++G(d,p) level of theory using GAUSSIAN03 (Frisch *et al.*, 2004) were performed. Optimizations started from the X-ray geometry of (I) and were followed by optimization of all geometric variables (bond lengths and angles) with no symmetry constraints.

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1994); cell refinement: CAD-4 EXPRESS; data reduction: XCAD4 (Harms & Wocadlo, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and MERCURY (Macrae *et al.*, 2006); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Table 1

Comparison of geometric data for (I) from both experimental and DFT calculations (Å, °).

	Experimental	DFT
C2–N3	1.336 (4)	1.361
C4–N3	1.487 (4)	1.479
C8–N3	1.459 (4)	1.454
C8–P1	1.811 (4)	1.850
O3–P1	1.473 (3)	1.483
O4–P1	1.543 (3)	1.596
O5–P1	1.552 (3)	1.612
O2–C2–N3	127.7 (4)	127.03
C6–C4–C7	112.2 (4)	111.63
N3–C4–C5	98.1 (3)	98.49
N3–C8–P1	113.5 (2)	112.4
O3–P1–O4	113.82 (17)	113.8
O4–P1–O5	101.15 (14)	101.7
O5–P1–C8	104.69 (16)	102.24
O3–P1–C8–N3	62.0 (3)	58.87
O5–P1–C8–N3	–170.7 (2)	–175.95
P1–C8–N3–C2	91.6 (4)	70.08
C8–N3–C2–O2	–4.4 (6)	–6.42
O1–C2–N3–C4	9.9 (4)	5.00

Table 2

Hydrogen-bond geometry (Å, °).

D–H···A	D–H	H···A	D···A	D–H···A
O4–H4···O3 ⁱ	0.82	1.73	2.503 (4)	157
O5–H5···O2 ⁱⁱ	0.82	1.82	2.609 (4)	162
C5–H5A···O5 ⁱⁱⁱ	0.97	2.68	3.553 (4)	151
C6–H6B···O4 ⁱⁱⁱ	0.96	2.52	3.365 (4)	147

Symmetry codes: (i) –x + 1, y + ½, –z + ½; (ii) x, y – 1, z; (iii) x, –y + ½, z – ½.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB3021). Services for accessing these data are described at the back of the journal.

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