(3S,8S)-3,8-Dimethyl-1,6-dioxa-4,9-diaza-5λ^5-phosphaspiro[4.4]nonane-2,7-dione

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.009 Å
R factor = 0.068
wR factor = 0.198
Data-to-parameter ratio = 9.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the the title compound, $C_6H_{11}N_2O_4P$, the P atom and the attached H atom lie on a crystallographic twofold axis. The molecule adopts a slightly distorted trigonal bipyramidal structure. The crystal structure involves intermolecular N—H···O hydrogen bonds.

Comment

The title compound, (I), was synthesized for a study of its biochemical activity. According to experimental evidence, this compound shows 63.6% rate inhibition to tyrosinase, an important enzyme in the formation of melanin which is widely distributed in microorganisms, animals and plants (Seo *et al.*, 2003). This type of compound and its analogs may afford new potent and efficient inhibitors of tyrosinase.

(I)
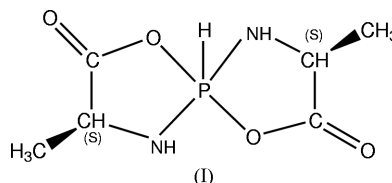
X-ray structural analysis revealed that the P atom and its attached H atom lie on a crystallographic twofold axis. The molecule adopts a slightly distorted trigonal bipyramidal structure, with the two O atoms in apical positions and the N atoms and H in equatorial positions, as shown in Fig. 1. The major distortion from the ideal angle of 120° occurs for N1—P—N1^i, which is 127.6 (4)° (symmetry code as in Table 1). This type of distortion is even more pronounced in the related compound, 1,6-dioxa-4,9-diaza-5-phosphaspiro[4.4]nonane, (II) (Meunier *et al.*, 1978), where the N—P—N angle is 130.8°.
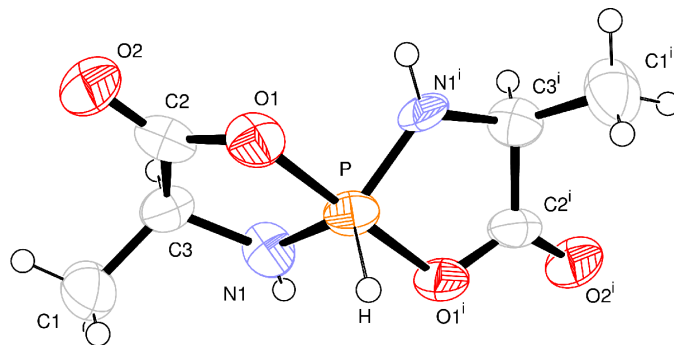

Figure 1
ORTEPII (Johnson, 1976) plot of the molecule. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. [Symmetry code: (i) $-x, -y, \frac{1}{2} + z$.]

The bond lengths and angles in (I) compares favourably with those in (II), which differs from (I) in that the rings are not substituted by methyl and keto groups. The crystal structure involves intermolecular N—H···O hydrogen bonds (Fig. 2 and Table 2).

Experimental

Following a general procedure (Garrigues *et al.*, 1977), phosphorus trichloride (10 mmol) was added to stirred L-alanine (20 mmol) in glycol dimethyl ether under a nitrogen atmosphere at room temperature. Triethylamine (4.2 ml) was then added dropwise to the solution at 263 K to induce the reaction; the solution was then stirred for two more hours. The solvent was removed under reduced pressure by rotary evaporation and the residue was washed rapidly with a sufficient quantity of water. The crude product was filtered off and recrystallized from acetone and petroleum ether (1:1).

Crystal data

$C_6H_{11}N_2O_4P$	Mo $K\alpha$ radiation
$M_r = 206.14$	Cell parameters from 25
Orthorhombic, $C222_1$	reflections
$a = 6.1138\ (12)$ Å	$\theta = 8$–$15°$
$b = 7.6933\ (15)$ Å	$\mu = 0.28$ mm^{-1}
$c = 19.824\ (4)$ Å	$T = 293\ (2)$ K
$V = 932.4\ (3)$ Å^3	Chunk, colorless
$Z = 4$	$0.15 \times 0.10 \times 0.08$ mm
$D_x = 1.468$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	430 reflections with $I > 2\sigma(I)$
ω–2θ scans	$\theta_{max} = 26.5°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = -7 \rightarrow 0$
	$k = 0 \rightarrow 9$
$T_{min} = 0.959$, $T_{max} = 0.978$	$l = -24 \rightarrow 0$
570 measured reflections	3 standard reflections
570 independent reflections	frequency: 60 min
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1249P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.069$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.198$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.07$	$\Delta\rho_{max} = 0.47$ e Å^{-3}
570 reflections	$\Delta\rho_{min} = -0.55$ e Å^{-3}
62 parameters	Extinction correction: *SHELXL*
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.010 (4)
	Absolute structure: Flack (1983), 0 Friedel pairs
	Flack parameter = 0.05 (6)

Table 1
Selected geometric parameters (Å, °).

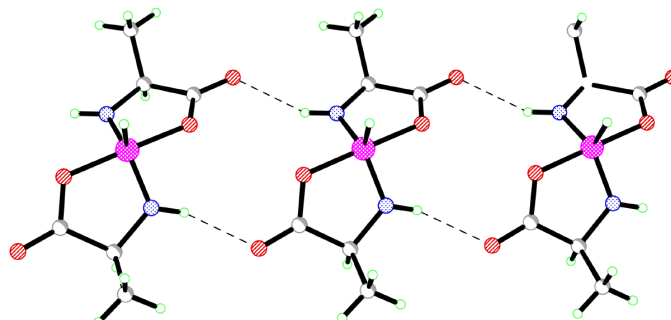|			
P—N1	1.622 (5)	O2—C2	1.206 (9)
P—O1	1.750 (5)	N1—C3	1.455 (9)
P—H	1.49 (9)	C3—C1	1.511 (9)
O1—C2	1.310 (8)	C3—C2	1.520 (9)
N1^i—P—N1	127.6 (4)	N1—C3—C1	113.1 (5)
N1—P—O1^i	90.4 (2)	N1—C3—C2	103.1 (5)
N1—P—O1	89.0 (3)	C1—C3—C2	111.6 (6)
O1^i—P—O1	178.6 (4)	O2—C2—O1	123.6 (6)
N1—P—H	116.2 (2)	O2—C2—C3	123.8 (6)
C2—O1—P	115.6 (4)	O1—C2—C3	112.6 (6)
C3—N1—P	119.5 (4)		

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

Figure 2
A view, approximately along the *b* axis, of the hydrogen bonds (dashed lines).

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1D···O2^{ii}	0.86	2.21	3.017 (7)	155

Symmetry code: (ii) $1 + x, y, z$.

The H atom attached to P was located and refined subject to the restraint P—H = 1.50 (10) Å. U_{iso}(H) was set equal to $1.2U_{eq}$(P). The other H atoms were positioned geometrically (C—H = 0.98 or 0.96 Å for tertiary and methyl H atoms, respectively, and N—H = 0.86 Å) and were included in the refinement in the riding-model approximation. U_{iso}(H) values were set equal to xU_{eq}(carrier atom), where x = 1.5 for methyl and x = 1.2 for the other H atoms. The absolute configuration of the compound was assigned by reference to an unchanging chiral centre in the synthetic procedure, and is confirmed by refinement of the Flack (1983) parameter.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1988); cell refinement: *CAD*-4 *software*; data reduction: *XCAD*4 (Harms, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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