Investigations on benz[1,2]oxa-phosphinane derivatives

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The structures of two compounds, 3-[1-(2-hydroxyethyl-amino)ethylidene]-2-methoxy-3,4-dihydro-1,2λ^5-benzoxa-phosphinane-2,4-dione, $C_{13}H_{16}NO_5P$, and 3-[1-(2-hydroxy-ethylamino)ethylidene]-2-methoxy-6-methyl-3,4-dihydro-1,2λ^5-benzoxaphosphinane-2,4-dione, $C_{14}H_{18}NO_5P$, have been studied and compared. The oxophosphinane rings have a half-chair conformation and extra six- and five-membered rings are formed by intramolecular N—H$\cdots$O hydrogen bonds. An intermolecular O—H$\cdots$O hydrogen bond is also observed.

Comment

Aminophosphonic acids are synthetic analogues of natural amino acids, in which the carboxylic acid group is replaced by a phosphonic acid group. Aminophosphonic acids, their esters and their salts have attracted significant attention owing to their synthetic and biological value both as agrochemical (herbicides, pesticides and growth regulators in plants) and medical (antibiotics, antivirals and enzyme inhibitors) products with broad applications (Kalir & Kalir, 1996; Hudson & Pianka, 1996; Kukhar & Hudson, 1999).

In our previous work, we described the reaction of 2-methyl-4-oxo-4*H*-chromen-3-ylphosphonate, (I*a*), and 2,6-dimethyl-4-oxo-4*H*-chromen-3-ylphosphonate, (II*a*), with 2-hydroxyethylamine (Budzisz *et al.*, 2001). From this reaction, we obtained cyclic 2-aminophosphonic analogues of the chromone general structure, namely 3-[1-(2-hydroxyethyl-amino)ethylidene]-2-methoxy-3,4-dihydro-1,2λ^5-benzoxa-phosphinane-2,4-dione, (I), and 3-[1-(2-hydroxyethyl-amino)ethylidene]-2-methoxy-6-methyl-3,4-dihydro-1,2λ^5-benzoxaphosphinane-2,4-dione, (II) (Budzisz & Pastuszko, 1999; Budzisz *et al.*, 2001). The compounds obtained exhibited alkylation properties in an *in vitro* test with 4-(4-nitro-benzyl)pyridine (NBP) (Preussman *et al.*, 1969).

In a series of IR spectra determined in chloroform, the derivatives of benzo[1,2]oxaphosphinane in various concentrations (1–100 mmol) confirm the presence of a strong intramolecular hydrogen bond exhibiting a broad band at ν = 3430–3450 cm^{-1}.

The X-ray structural investigation of two derivatives of benz[1,2]oxaphosphinane has been carried out in a continuation of our studies (Budzisz *et al.*, 2001). The title structures, (I) and (II), consist of a benzene ring fused with an oxapho-sphinane ring. The hydroxyethylaminoethylidene group is attached at position 3 in both molecules. In (II), the benzene ring is substituted by a methyl group at position 6.
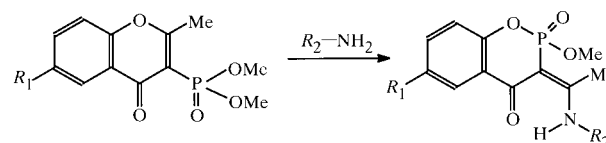
(I) R_1 = H, R_2 = CH_2CH_2OH
(II) R_1 = CH_3, R_2 = CH_2CH_2OH

The oxaphosphinane rings have half-chair conformations. The puckering parameters (Cremer & Pople, 1975) are Q_T = 0.383 (3) Å, φ_2 = 32.1 (8)° and θ_2 = 67.1 (7)° in (I), and Q_T = 0.360 (2) Å, φ_2 = 38.7 (5)° and θ_2 = 65.8 (7)° in (II), corresponding to the O1—P2—C3—C4—C10—C9 atom sequence, with a twofold pseudo-axis passing through the midpoints of the P2—O1 and C4—C10 bonds; asymmetry parameters (Nardelli, 1983) Δ_2 = 0.009 (2) for (I) and Δ_2 = 0.025 (1) for (II).

Two intramolecular hydrogen bonds, N32—H32$\cdots$O4 and N32—H32$\cdots$O35, are observed in both molecules which close
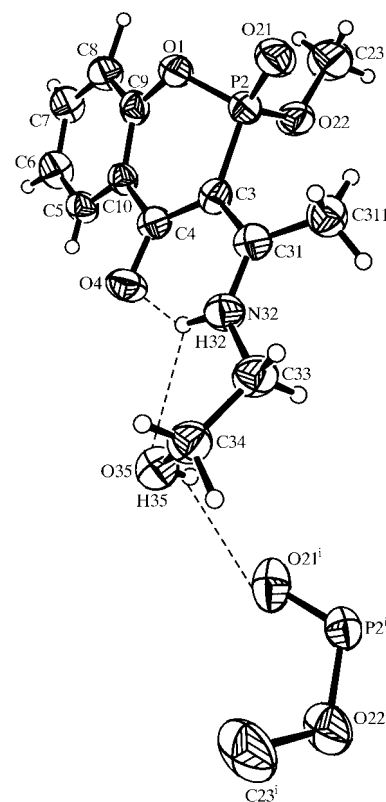

Figure 1
A perspective view of (I) showing hydrogen bonding to an adjacent molecule and the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. Symmetry codes are as given in Table 2.

the extra six- and five-membered rings, respectively. The six-membered rings are planar, whereas the conformation of the five-membered ring is a C34-deformed envelope in (I) and an N32-twist in (II) [asymmetry parameters (Nardelli, 1983): $\Delta_s = 0.04$ (1) for (I) and $\Delta_2 = 0.05$ (1) for (II)]. The puckering parameters (Cremer & Pople, 1975) are $q_2 = 0.42$ (1) Å and $\varphi_2 = -137$ (5)° in (I), and $q_2 = 0.49$ (1) Å and $\varphi_2 = -130$ (3)° in (II), corresponding to the C33—C34—O35—H32—N32 sequence.

The P atom has tetrahedral geometry slightly distorted towards trigonal pyramidal, with an elongated C3—P2 apical bond.

Bond distances and angles in both molecules are in good agreement with expected values (Allen *et al.*, 1987). The *ORTEX* (McArdle, 1995) drawings of molecules (I) and (II) with the atomic numbering scheme are given in Figs. 1 and 2, respectively.
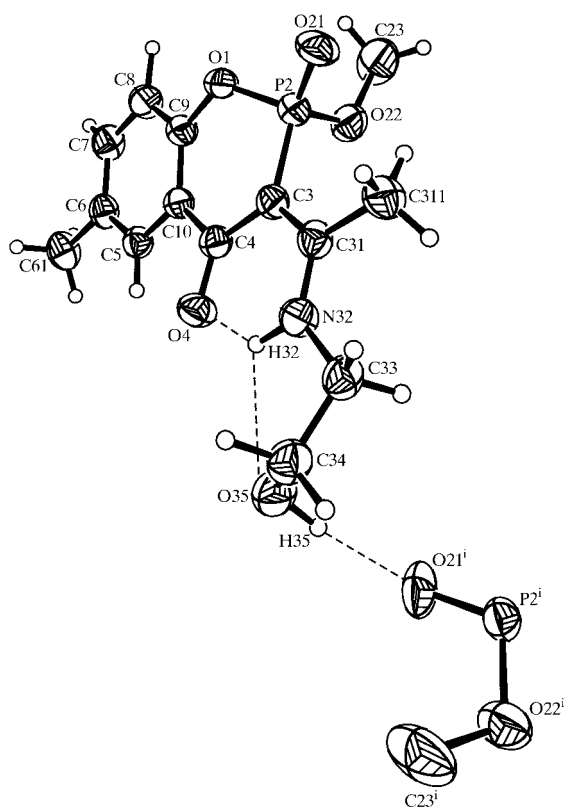

Figure 2
A perspective view of (II) showing hydrogen bonding to an adjacent molecule and the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. Symmetry codes are as given in Table 4.

Experimental

To a solution of 2-methyl-4-oxo-4*H*-chromen-3-ylphosphonate [for the preparation of (I)] or 2,6-dimethyl-4-oxo-4*H*-chromen-3-yl-phosphonate [for the preparation of (II)] in methanol was added a solution of ethanolamine in methanol. The mixture was left overnight at room temperature. The solvent was removed *in vacuo* and the crude products of (I) and (II) were purified by crystallization. Colourless crystals were obtained by slow evaporation from

methanol at room temperature (Budzisz & Pastuszko, 1999; Budzisz *et al.*, 2001). The reaction was carried out at room temperature in anhydrous methanol.

Compound (I)

Crystal data

$C_{13}H_{16}NO_5P$	Cu $K\alpha$ radiation
$M_r = 297.24$	Cell parameters from 25
Orthorhombic, $P2_12_12_1$	reflections
$a = 9.325$ (1) Å	$\theta = 26.9$–30.5°
$b = 9.662$ (1) Å	$\mu = 1.92$ mm^{-1}
$c = 15.619$ (2) Å	$T = 293$ (2) K
$V = 1407.4$ (1) Å^3	Prism, colourless
$Z = 4$	$0.2 \times 0.1 \times 0.1$ mm
$D_x = 1.403$ Mg m^{-3}	

Data collection

Rigaku AFC-5S diffractometer	$R_{int} = 0.064$
ω scans	$\theta_{max} = 66.0°$
Absorption correction: analytical	$h = -11 \rightarrow 11$
(de Meulenar & Tompa, 1965)	$k = -11 \rightarrow 9$
$T_{min} = 0.712$, $T_{max} = 0.841$	$l = -18 \rightarrow 18$
8498 measured reflections	3 standard reflections
1429 independent reflections (plus	frequency: 150 min
973 Friedel-related reflections)	intensity decay: <2%
1664 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = \{\exp[3(\sin\theta/\lambda)^2]\}/[\sigma^2(F_o^2)$
$R[F^2 > 2\sigma(F^2)] = 0.064$	$+ (0.1052P)^2]$ where $P =$
$wR(F^2) = 0.157$	$(F_o^2 + 2F_c^2)/3$
$S = 1.23$	$(\Delta/\sigma)_{max} = 0.051$
2402 reflections	$\Delta\rho_{max} = 0.42$ e Å^{-3}
224 parameters	$\Delta\rho_{min} = -0.62$ e Å^{-3}
H atoms treated by a mixture of	Absolute structure: Flack (1983)
independent and constrained	Flack parameter = 0.00 (5)
refinement	

Table 1
Selected geometric parameters (Å, °) for (I).

O1—C9	1.377 (6)	C4—O4	1.259 (6)
O1—P2	1.600 (3)	C4—C10	1.482 (6)
P2—O21	1.451 (4)	C9—C10	1.413 (6)
P2—O22	1.561 (4)	C31—N32	1.316 (6)
P2—C3	1.754 (5)	C31—C311	1.492 (8)
O22—C23	1.461 (6)	N32—C33	1.451 (6)
C3—C31	1.428 (6)	C33—C34	1.483 (8)
C3—C4	1.432 (7)	C34—O35	1.405 (7)
C9—O1—P2	120.9 (3)	O4—C4—C3	122.7 (4)
O21—P2—O22	113.7 (2)	O4—C4—C10	116.2 (4)
O21—P2—O1	107.7 (2)	C3—C4—C10	121.0 (4)
O22—P2—O1	104.9 (2)	C9—C10—C4	121.3 (4)
O21—P2—C3	119.3 (2)	N32—C31—C3	119.6 (5)
O22—P2—C3	105.3 (2)	N32—C31—C311	117.5 (5)
O1—P2—C3	104.6 (2)	C3—C31—C311	122.9 (4)
C23—O22—P2	119.6 (4)	C31—N32—C33	128.1 (5)
C31—C3—C4	122.0 (4)	N32—C33—C34	110.4 (5)
C31—C3—P2	120.4 (4)	O35—C34—C33	113.5 (5)
C4—C3—P2	117.6 (3)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N32—H32$\cdots$O4	0.97 (6)	1.76 (6)	2.601 (6)	143 (5)
N32—H32$\cdots$O35	0.97 (6)	2.46 (6)	2.797 (6)	100 (4)
O35—H35$\cdots$O21^i	0.68 (6)	2.25 (7)	2.790 (6)	137 (7)

Symmetry code: (i) $\frac{3}{2} - x, 1 - y, z - \frac{1}{2}$.

Compound (II)

Crystal data

$C_{14}H_{18}NO_5P$	Cu $K\alpha$ radiation
$M_r = 311.26$	Cell parameters from 25
Orthorhombic, $P2_12_12_1$	reflections
$a = 11.071 (1)$ Å	$\theta = 22.5–28.3°$
$b = 16.190 (2)$ Å	$\mu = 1.80$ mm^{-1}
$c = 8.490 (1)$ Å	$T = 293 (2)$ K
$V = 1521.7 (3)$ Å^3	Prism, colourless
$Z = 4$	$0.6 \times 0.3 \times 0.3$ mm
$D_x = 1.359$ Mg m^{-3}	

Data collection

Rigaku AFC-5S diffractometer	$\theta_{max} = 72.7°$
ω scans	$h = 0 \rightarrow 13$
Absorption correction: analytical	$k = 0 \rightarrow 20$
(de Meulenar & Tompa, 1965)	$l = 0 \rightarrow 10$
$T_{min} = 0.505$, $T_{max} = 0.650$	3 standard reflections
1669 measured reflections	frequency: 150 min
1669 independent reflections	intensity decay: <2%
1450 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0636P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.097$	$(\Delta/\sigma)_{max} = 0.021$
$S = 1.02$	$\Delta\rho_{max} = 0.17$ e Å^{-3}
1669 reflections	$\Delta\rho_{min} = -0.20$ e Å^{-3}
230 parameters	Extinction correction: *SHELXL97*
H atoms treated by a mixture of	Extinction coefficient: 0.0055 (6)
independent and constrained	Absolute structure: Flack (1983)
refinement	Flack parameter = -0.01 (4)

Table 3
Selected geometric parameters (Å, °) for (II).

O1—C9	1.393 (3)	C4—O4	1.253 (3)
O1—P2	1.594 (2)	C4—C10	1.492 (4)
P2—O21	1.462 (2)	C9—C10	1.380 (4)
P2—O22	1.570 (2)	C31—N32	1.320 (4)
P2—C3	1.750 (3)	C31—C311	1.499 (4)
O22—C23	1.472 (4)	N32—C33	1.463 (4)
C3—C31	1.418 (4)	C33—C34	1.502 (5)
C3—C4	1.436 (4)	C34—O35	1.404 (4)
C9—O1—P2	121.11 (17)	O4—C4—C3	122.9 (3)
O21—P2—O22	114.48 (16)	O4—C4—C10	117.3 (2)
O21—P2—O1	107.20 (12)	C3—C4—C10	119.8 (3)
O22—P2—O1	104.79 (13)	C10—C9—O1	121.5 (3)
O21—P2—C3	119.37 (16)	C9—C10—C4	123.0 (2)
O22—P2—C3	104.52 (14)	N32—C31—C3	120.0 (3)
O1—P2—C3	105.23 (12)	N32—C31—C311	116.6 (3)
C23—O22—P2	118.4 (2)	C3—C31—C311	123.5 (3)
C31—C3—C4	121.2 (3)	C31—N32—C33	127.9 (3)
C31—C3—P2	120.9 (2)	N32—C33—C34	108.5 (3)
C4—C3—P2	117.8 (2)	O35—C34—C33	112.8 (3)

For both compounds, all methyl H atoms were constrained to their parent atoms as a rigid body (C—H = 0.96 Å). All other H atoms were located in difference maps and refined isotropically [C—H = 0.82 (6)–1.16 (7) Å for (I), and 0.93 (3)–1.09 (4) Å for (II)].

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N32—H32$\cdots$O4	1.05 (5)	1.71 (5)	2.575 (3)	136 (4)
N32—H32$\cdots$O35	1.05 (5)	2.39 (5)	2.801 (4)	102 (4)
O35—H35$\cdots$O21^i	0.94 (5)	1.87 (5)	2.768 (4)	162 (5)

Symmetry code: (i) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989*a*); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (1989*b*); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: *PARST*97 (Nardelli, 1996).

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