*Data collection*

Siemens SMART CCD area-detector diffractometer
$\omega$ scans
Absorption correction: none
12 365 measured reflections
4651 independent reflections
2922 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.045$
$\theta_{\rm max} = 28.5°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 23$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.180$
$S = 1.142$
4208 reflections
245 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0589P)^2 + 0.7524P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.20$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.17$ e Å$^{-3}$
Extinction correction: *SHELXTL* (Sheldrick, 1997)
Extinction coefficient: 0.0040 (12)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å)*

| | | | |
|---|---|---|---|
| O1—C11 | 1.221 (3) | C4—C10 | 1.402 (4) |
| O2—C18 | 1.364 (3) | C5—C6 | 1.388 (5) |
| O2—C1 | 1.407 (3) | C5—C10 | 1.450 (4) |
| O3—C18 | 1.199 (3) | C6—C7 | 1.376 (5) |
| C1—C2 | 1.378 (3) | C7—C8 | 1.406 (5) |
| C1—C9 | 1.402 (3) | C8—C9 | 1.454 (4) |
| C2—C3 | 1.410 (3) | C9—C10 | 1.412 (3) |
| C2—C11 | 1.493 (3) | C11—C12 | 1.495 (3) |
| C3—C4 | 1.364 (3) | C18—C19 | 1.479 (3) |

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

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| C21—H21$\cdots$O3$^{\rm i}$ | 0.93 | 2.52 | 3.398 (4) | 156 |

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

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different $\varphi$ angle (0, 88 and 180°) for the crystal and each exposure of 10 s covered 0.3° in $\omega$. The crystal-to-detector distance was 4 cm and the detector swing angle was −35°. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the intensity of duplicate reflections, and was found to be negligible.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1396). Services for accessing these data are described at the back of the journal.

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# 2-Hydroxy-5-methyl-2-oxo-6-phenyl-4-phosphonomethyl-1,4,2-oxazoniaphosphorinane†

JEAN-FRANÇOIS SAINT-CLAIR,[a] FABRICE SIMÉON,[a] DIDIER VILLEMIN[a] AND MARIE-THÉRÈSE AVERBUCH-POUCHOT[b]

[a]*Ecole Nationale Supérieure d'Ingénieurs de Caen (ISMRA), Université de Caen, UMR CNRS 6507, 6 Boulevard du Maréchal Juin, 14050 Caen, France, and* [b]*LEDSS, UMR CNRS 5616, Université Joseph Fourier, BP53, 38041 Grenoble CEDEX 9, France. E-mail: marie-therese.averbuch@ujf-grenoble.fr*

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## Abstract

The title compound, $C_{11}H_{17}NO_6P_2$, crystallizes as a racemic zwitterion in the space group $Pca2_1$. The molecules are interlinked by O—H$\cdots$O and N—H$\cdots$O hydrogen bonds.

## Comment

Our ongoing investigation of aminophosphonates as supports for organic–inorganic materials (Ortiz-Avila *et al.*, 1994) led us to study procedures to prepare new achiral and chiral compounds of this kind. Moreover, these compounds are known either as analogues of natural amino acids exhibiting biological activities (Engel, 1977, 1987) or for their extraordinary chelating properties (Schwarzenbach *et al.*, 1948).

The main route to these compounds is a Mannich-type reaction first used by Fields (1952), but Moedritzer & Irani (1966) improved this reaction so that it proceeds almost quantitatively in most cases. Benzylamine

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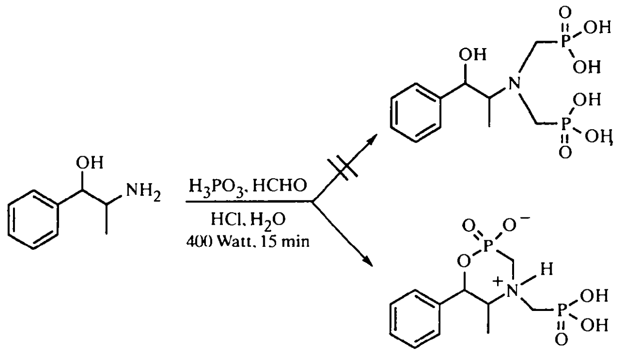
† Zwitterionic name: 5-methyl-2-oxido-2-oxo-6-phenyl-1,4,2-oxazoniaphosphorinan-4-ylmethylphosphonic acid.

and phenethylamine gave the corresponding phosphonic acids in very good yields in a monomode cavity, but, surprisingly, many unexpected results were observed when using some chiral compounds, such as (*R*)-butanolamine and (+)- or (−)-pseudoephedrines. Thus, no product crystallized directly when (+)- or (−)-norephedrine was irradiated, while racemic norephedrine gave a 60% yield of precipitate after 15 min of irradiation. The main spectroscopic characteristic of the title compound, (1), is the presence of two distinctive peaks in the $^{31}$P NMR spectrum. This lack of symmetry, also observed in the $^{13}$C NMR spectrum, led us to undertake the determination of the structure of (1).



(1)

The crystallographic study of (1) shows that the crystal has a zwitterion structure with localization of the negative charge on the methylenephosphonic group *A* (the methylenephosphonic group taking part in the formation of the heterocycle is denoted as *A* and the second methylenephosphonic group as *B*). As shown in Fig. 1, the oxazaphosphorinane ring adopts a chair conformation, as previously observed both in the 4-phosphonomethyl- and 4-hydroxyethyl-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinanes (Makaranets *et al.*, 1987). It is also worth noting that in group *B* the distances are those expected for protonated units in classical aminophosphonic acids: 1.488 (2) Å for the P2═O5 double bond, 1.532 (2) and 1.539 (2) Å for the P—OH single bonds, and 1.816 (2) Å for the P—C single bond (Table 1). Deprotonation and participation of group *A* in the heterocycle influence mainly the length of the P1—O1 bond [1.588 (1) Å] which becomes longer than the usual single bond. On the other hand, the P—O bonds involving atoms O2 [1.478 (1) Å] and O3 [1.498 (1) Å] of group *A* are formally intermediate between single P—O$^-$ and P═O double bonds, but, in fact, do not differ from the P═O distance in group *B*. The P—C distances of groups *A* and *B* are very similar [P1—C2 1.812 (2) and P2—C1 1.816 (2) Å]. All these observations agree with the distances reported previously for 4-phosphonomethyl-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinane (Makaranets *et al.*, 1987).

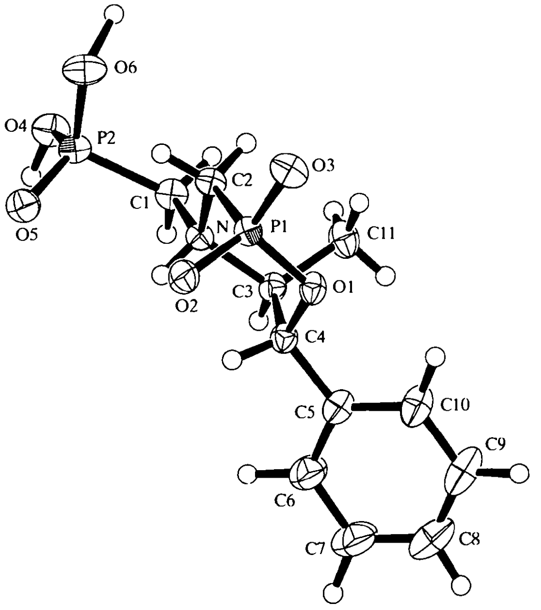


Fig. 1. *ORTEP*II drawing (Johnson, 1976) of the title compound with 45% probability displacement ellipsoids.

As can be inferred from the geometry of the molecule, no intramolecular hydrogen bond is observed in this atomic arrangement, but three intermolecular hydrogen bonds exist. They build a two-dimensional network parallel to the *ac* plane. It should be noted that, among these three hydrogen bonds, one of them, O6—H11···O3, is almost symmetrical, whereas the other two are normal (Table 2). One can also observe that these bonds link two enantiomeric molecules *via* H16 and H17, and two identical ones *via* H11. These observations are in agreement with the fact that crystallization was possible with the racemic mixture, but was not possible with optically pure norephedrine.

## Experimental

An aqueous solution (4 ml of water) of phosphorous acid (20 mmol, 1.64 g) in hydrochloric acid (37 wt% in water, 4 ml) was added to norephedrine (10 mmol, 1.80 g) stored in a quartz tube. The mixture was irradiated for 5 min at 200 W [irradiation was performed in an MES-focused microwave cavity TE$_{01}$ at 2450 MHz with a universal generator MES 73-800 (Villemin & Sauvaget, 1994; Villemin & Martin, 1995)]. Formaldehyde (37 wt% in water, 40 mmol, 3.24 ml) was then added rapidly. The mixture was refluxed under microwave irradiation at 400 W for 8 min and irradiation was stopped when crystallization was observed. The mixture was filtered and the white powder obtained was washed with ethanol and water. Recrystallization from pure water gave 2.03 g (60%) of pure (1) [m.p. = 526–528 K (darkens)]. $^1$H NMR ($D_2O$, $K_2CO_3$): 1.17 (*d*, 3H, $CH_3$, $^3J$ = 7.2 Hz), 3.35–3.83 (*m*, 4H, $CH_2$), 4.18 (*qd*, 1H, CH—$CH_3$, $^3J$ = 3.1, $^3J$ = 7.2 Hz), 5.90 (*d*, 1H, CH—Ph, $^3J$ = 3.1 Hz), 7.40–7.55 p.p.m. (*m*, 5H, $CH_{arom}$);

$^{13}C$ NMR ($D_2O$, $K_2CO_3$): 3.22 (*s*, $CH_3$), 45.00 (*d*, $CH_2$—P), 47.00 (*d*, $CH_2$—P), 60.87 (*d*, CH—$CH_3$), 79.28 (*s*, CH—Ph), 125.98 (*s*, $^3C_{arom}$), 128.31 (*s*, $^4C_{arom}$), 128.93 (*s*, $^2C_{arom}$), 138.45 p.p.m. (*s*, $^1C_{arom}$); $^{31}P$ NMR ($D_2O$, $K_2CO_3$): 6.12 (*s*, P—cycle), 8.20 p.p.m. (*s*); IR ($cm^{-1}$, KBr): 3060 (*s*, OH), 2998 (*w*), 1332 (*w*), 1178 (*vs*, P═O), 1120 (*s*, P═O), 1082 (*vs*, P—O), 982 (*s*, P—O), 936 (*m*).

### *Crystal data*

$C_{11}H_{17}NO_6P_2$
$M_r = 321.21$
Orthorhombic
$Pca2_1$
$a = 14.361$ (2) Å
$b = 13.711$ (2) Å
$c = 7.475$ (2) Å
$V = 1471.9$ (4) Å$^3$
$Z = 4$
$D_x = 1.449$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 24 reflections
$\theta = 10.9–11.9°$
$\mu = 0.318$ mm$^{-1}$
$T = 293$ K
Elongated prism
0.31 × 0.29 × 0.26 mm
Colourless

### *Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega$–$2\theta$ scans
Absorption correction: none
2306 measured reflections
2306 independent reflections
1885 reflections with $I > 2\sigma(I)$

$\theta_{max} = 29.93°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 10$
2 standard reflections every 120 reflections intensity decay: 4.15%

### *Refinement*

Refinement on $F$
$R = 0.026$
$wR = 0.033$
$S = 1.836$
1885 reflections
180 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F_o) + 0.00016|F_o|^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.28$ e Å$^{-3}$
$\Delta\rho_{min} = -0.20$ e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| P1—O1 | 1.588 (1) | P2—O5 | 1.488 (2) |
| P1—O2 | 1.478 (1) | P2—O6 | 1.532 (2) |
| P1—O3 | 1.498 (1) | P2—C1 | 1.816 (2) |
| P1—C2 | 1.812 (2) | O1—C4 | 1.451 (2) |
| P2—O4 | 1.539 (2) | N—C2 | 1.502 (2) |
| O1—P1—O2 | 110.52 (7) | O5—P2—C1 | 107.95 (7) |
| O1—P1—O3 | 107.84 (7) | O6—P2—C1 | 108.88 (8) |
| O1—P1—C2 | 102.60 (7) | P1—O1—C4 | 113.7 (1) |
| O2—P1—O3 | 117.23 (8) | C2—N—C3 | 112.5 (1) |
| O2—P1—C2 | 109.56 (8) | P2—C1—N | 114.1 (1) |
| O3—P1—C2 | 108.06 (8) | P1—C2—N | 113.3 (1) |
| O4—P2—O5 | 116.93 (8) | N—C3—C11 | 112.5 (1) |
| O4—P2—O6 | 107.48 (8) | C4—C3—C11 | 114.2 (2) |
| O4—P2—C1 | 103.26 (8) | O1—C4—C3 | 108.6 (1) |
| O5—P2—O6 | 111.81 (9) | O1—C4—C5 | 110.6 (1) |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O4—H16···O5$^{i}$ | 0.96 | 1.58 | 2.517 (2) | 162 |
| O6—H11···O3$^{ii}$ | 1.18 | 1.26 | 2.432 (2) | 168 |
| N—H17···O2$^{i}$ | 0.93 | 1.78 | 2.629 (2) | 151 |

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

H atoms were located by difference Fourier syntheses.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1026). Services for accessing these data are described at the back of the journal.

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# 1,3,4,6-Tetrathiapentalene-2,5-dione

Harald Müller[a] and Marie-Thérèse Averbuch[b]

[a]*European Synchrotron Radiation Facility, BP 220, 38043 Grenoble, CEDEX 9, France, and* [b]*LEDSS, UMR CNRS 5616, Université Joseph Fourier, BP 53, 38041 Grenoble, CEDEX 9, France. E-mail: mueller@esrf.fr*

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## Abstract

The title compound, [1,3]dithiolo[4,5-*d*][1,3]dithiole-2,5-dione, $C_4O_2S_4$, is a sulfur heterocyclic system formally composed of a tetrathioethylene unit ($C_2S_4$) and two carbonyl groups. The bicyclic molecule is essentially planar and exhibits $D_{2h}$ symmetry, although