Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3-Chloromethyl-5-methoxy-4-methoxycarbonyl-3-oxo-2,3-dihydro-[1,3]oxaphosphole monohydrate

Ciptadi Ciptadi,[a] Henri Jean Cristau,[a] Yves Alain Bekro,[a]‡ Monique Tillard[b] and David Virieux[a]*

[a]Laboratoire de Chimie Organique, UMR CNRS 5076, Ecole Nationale Supérieure de Chimie de Montpellier, 8, rue de l'école normale, 34296 Montpellier Cédex 5, France, and [b]Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques, UMR 5072 CC15, Université de Montpellier II, Sciences et Techniques du Languedoc, 2 Place Eugène Bataillon, 34095 Montpellier Cédex 5, France

‡ Current address: Université d'Abobo-Adjamé, 02BP801, Abidjan 02, République de Côte d'Ivoire

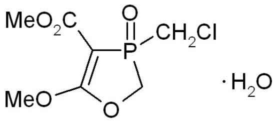
Correspondence e-mail: virieux@cit.enscm.fr

Received 18 November 2003
Accepted 28 November 2003
Online 19 December 2003

The title compound crystallizes as a monohydrate, $C_7H_{10}PO_5Cl{\cdot}H_2O$. In the crystal structure, two symmetry-related oxaphosphole molecules are linked through hydrogen bonds with the water molecule of crystallization.

Comment

The title compound, (I), is a completely original and highly functionalized phosphorus heterocycle (Manz *et al.*, 1997; Kozlov & Sedlov, 1968; Trishin *et al.*, 1995) with potential biological activity as an agrochemical (Kafarski & Lejczak, 1991). It was obtained by an unusual cyclization reaction using bis(chloromethyl)phosphinic chloride as a 1,2-dielectrophile and dimethyl malonate as a 1,3-dinucleophile. The combination of these two reagents in the presence of two equivalents of sodium hydride in tetrahydrofuran led to the formation of the phosphorus heterocycle.



The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. Compound (I) crystallizes incorporating a water molecule, which is tightly linked to the oxaphosphole through hydrogen bonding. The bonds lengths are close to those generally found in similar compounds: P—C bonds range from 1.755 (2) to 1.838 (2) Å, C—O single bonds are in the range 1.300 (2)–1.456 (2) Å, while the C═O distance is 1.207 (2) Å. In the

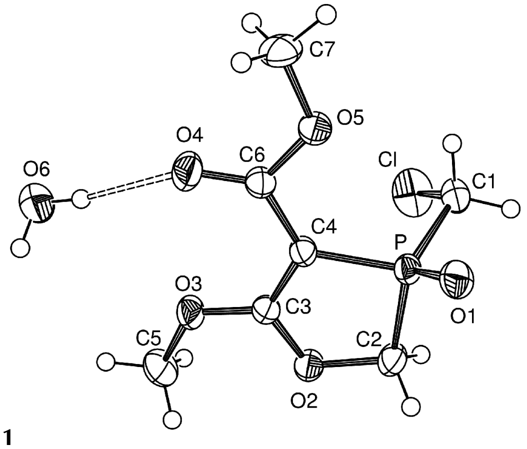


Figure 1
The molecular structure of the title compound, (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. The H atoms are shown as spheres of arbitrary radius and the hydrogen bond as double dashed lines.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.044
wR factor = 0.132
Data-to-parameter ratio = 21.6

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

DOI: 10.1107/S1600536803027351

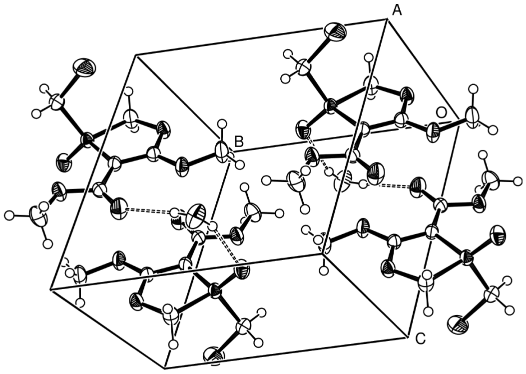


Figure 2
Crystal packing diagram of the title compound, (I). Hydrogen bonds are indicated as double dashed lines.

crystal structure, the packing of the molecules is stabilized by weak O—H···O hydrogen bonds [O···O = 2.894 (2) Å] involving the carbonyl group and an H atom of the water molecule (Taft *et al.*, 1996). Details are given in Fig. 2 and Table 2. The water molecule is also involved, through its second H atom, in a weak hydrogen bond [O···O = 2.863 (2) Å] with atom O1 on the phosphorus. The O···O distances and also O···H···O angles are comparable to those found in water for weak hydrogen bonding. The positions of all of the atoms in the molecule (except for O1, C1 and Cl, which are out of plane) deviate by less than 0.06 Å from the mean plane. This indicates that the molecule is almost flat, which is consistent with a strong conjugation of the sp^2 system involving the olefinic ester and the O atoms of the alkoxy groups (methoxy and heterocycle).

Experimental

The reaction was carried out under nitrogen using Schlenk techniques. The solvents were dried by standard procedures, distilled and stored under nitrogen prior to use. All reactions were monitored by TLC (Merck, SIL G/UV254) or ^{31}P NMR. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC-200 or Avance-250 spectrometer and referenced to the solvent as internal standard. In a three-necked round-bottomed flask equipped with a magnetic stirrer, a condenser and a dropping funnel, 10.98 g (83.2 mmol, 1 equivalent) of dimethyl malonate in 20 ml of anhydrous THF was added dropwise to a suspension of 4.19 g (174.6 mmol, 2.1 equivalent) of sodium hydride (96%) in 200 ml of anhydrous THF at 253 K. Subsequently, when hydrogen gas had evolved, 15.09 g (83.2 mmol, 1 equivalent) of bis(chloromethyl)phosphinic chloride in 20 ml of THF was added slowly at 253 K without exceeding 273 K. The reaction was stirred for 2 h at room temperature. The reaction mixture was then concentrated, using a rotary evaporator to remove THF, and 100 ml of water was added. The solution was extracted three times with 50 ml of chloroform. The organic layers were dried over $MgSO_4$, and concentrated to afford a yellow oil which crystallized slowly. The resulting solid was filtered, washed with acetone to give the pure oxaphosphole (12.16 g, 50.6 mmol; 61% yield). Colourless plate-like crystals were obtained by crystallization from a hexane-ether mixture. M.p. 411–414 K; ^{31}P NMR ($CDCl_3$, 81.01 MHz): 49.28 p.p.m. (*s*) ^{1}H NMR ($CDCl_3$; 200.13 MHz): 3,72 (*s*, 3H, CH_3), 3,86 (*dd*, 1H, $^{2}J_{HH} = -14.1$ Hz, $^{2}J_{PH} = -9.2$ Hz, PCH_2Cl), 4,07 (*dd*, 1H, $^{2}J_{HH} = -14.1$ Hz, $^{2}J_{PH} = -10.3$ Hz, PCH_2Cl), 4.05 (*s*, 3H, CH_3), 4,53 (*dd*, 1H, $^{2}J_{HH} = -14.1$ Hz, $^{2}J_{PH} = -9.6$ Hz, PCH_2O), 4.71 p.p.m. (*d*, 1H, $^{2}J_{HH} = -14.1$ Hz, PCH_2O); ^{13}C NMR ($CDCl_3$, 50.32 MHz): 35.14 (*d*, $^{1}J_{PC} = 84.1$ Hz, PCH_2Cl), 51.00 (*s*, CH_3), 57.25 (*s*, CH_3), 66.87 (*d*, $^{1}J_{PC} = 66.2$ Hz, PCH_2O), 71.71 (*d*, $^{1}J_{PC} = 119.1$ Hz, PC=), 162.90 (*d*, $^{2}J_{PC} = 7.8$ Hz, CO_2Me), 174.91 p.p.m. [*d*, $^{2}J_{PC} = 33.1$ Hz, =C(OMe)]; MS FAB$^+$ (NBA Matrix): *m*/*z* = 241 (100%) ([*M*+H]$^+$), *m*/*z* = 209 (85%) ([*M*−MeO$^-$]$^+$).

Crystal data

$C_7H_{10}ClO_5P \cdot H_2O$
$M_r = 258.59$
Triclinic, $P\bar{1}$
a = 7.6307 (7) Å
b = 8.5404 (8) Å
c = 9.1204 (10) Å
α = 71.019 (9)°
β = 81.102 (8)°
γ = 72.999 (8)°
V = 536.32 (10) Å^3

Z = 2
$D_x = 1.601$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 9001 reflections
θ = 3.5–30.1°
μ = 0.51 mm^{-1}
T = 293 (2) K
Parallelepiped, colourless
0.4 × 0.3 × 0.2 mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
ω scans
Absorption correction: none
9001 measured reflections
3113 independent reflections

2695 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$
$\theta_{\rm max} = 30.1°$
h = −10 → 10
k = −12 → 11
l = −12 → 12

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.132$
S = 1.10
3113 reflections
144 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0758P)^2 + 0.1891P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.47$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.45$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

P—O1	1.4903 (12)	O3—C3	1.3001 (18)
P—C4	1.7549 (15)	O3—C5	1.451 (2)
P—C1	1.8099 (17)	O2—C3	1.3345 (17)
P—C2	1.8382 (17)	O2—C2	1.4558 (19)
Cl—C1	1.7709 (18)	O4—C6	1.2070 (19)
O5—C6	1.3437 (18)	C4—C3	1.371 (2)
O5—C7	1.441 (2)	C4—C6	1.453 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H2···O4$^{\rm i}$	0.84 (4)	2.06 (4)	2.894 (2)	171 (3)
O6—H1···O1$^{\rm ii}$	0.83 (3)	2.06 (4)	2.863 (2)	159 (3)

Symmetry codes: (i) *x*, *y* − 1, *z*; (ii) 1 − *x*, 1 − *y*, 1 − *z*.

H atoms attached to the C atoms were included in calculated positions and treated as riding atoms using *SHELXL*97 (Sheldrick, 1997) default parameters: C—H = 0.96–0.97 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. H atoms of the water molecule were located in a Fourier difference map and were refined isotropically.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2001); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97

(Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

References

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Kafarski, P. & Lejczak, B. (1991). *Phosphorus Sulfur Silicon*, **63**, 193–215.

Kozlov, E. S. & Sedlov, A. I. (1968). *J. Gen. Chem. USSR*, **38**, 1828–1830.

Manz, B., Bergsträsser, U., Kerth, J. & Maas, G. (1997). *Chem. Ber.*, **130**, 779–788.

Oxford Diffraction (2001). *CrysAlis CCD* and *CrysAlis RED*. Version 169. Oxford Diffraction Ltd, Abingdon, England.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen. Germany.

Taft, R. W., Berthelot, M., Laurence, C. & Leo, A. J. (1996). *Chemtech*, **26**, 20–29.

Trishin, Y. G., Vorob'ev, M. V. & Namestnikov, V. I. (1995). *Russ. J. Gen. Chem.* **65**, 144–145.