N-(3-Nitrophenyl)-1-oxo-2,6,7-trioxa-1-phospha-bicyclo[2.2.2]octane-4-carboxamide dimethyl-formamide solvate

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In the crystal structure of the title compound, $C_{11}H_{11}N_2O_7P$, the carboxamide molecule and the solvent molecule of crystallization each possess mirror symmetry; for the former, the mirror plane bisects the two-ring $OP(OCH_2)_3C$ cage. The packing is stabilized by an intermolecular N—H⋯O hydrogen bond and a number of C—H⋯O hydrogen bonds.

Comment

Caged bicyclic phosphates are widely used as flame retardants, resin stabilizers and oil adducts. They have created great interest and many studies on these compounds have been reported (Allen *et al.*, 1995; Li *et al.*, 2002). We report here the structure of a new bicyclic phosphate cage compound, namely (3-nitro-phenyl)-1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane-4-carboxamide, that crystallizes as the dimethyl-formamide solvate, (I).


(I)
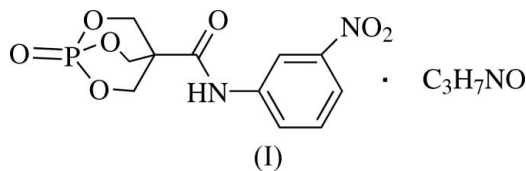
The molecular structure of (I) is illustrated in Fig. 1, and selected bond distances and angles are given in Table 1. The terminal P=O bond length is 1.446 (2) Å and the average bridging P—O distance is 1.562 (1) Å. The majority of the bond distances and angles are, within experimental error, similar to those in other trialkyl phosphates (Nimrod *et al.*, 1968; Liu *et al.*, 1992). The O—P—O bond angles, which range from *ca* 104 to 115°, are different from the unstrained angles (*ca* 104 and 120°, respectively) in dibenzyl hydrogen phosphate, which can be assumed to be representative of strainless angles of this type (Dunitz & Rollett, 1956). Some strain is also present in the P—O—C angles [average value 115.4 (1)°]. The configuration around phosphorus is therefore distorted tetrahedral.

In the crystal structure (Fig. 2), the nitro group N2/O6/O7 and dimethylformamide molecule are coplanar with the arene ring. Atom O8 of the dimethylformamide molecule is involved in an intermolecular N1—H1⋯O8 hydrogen bond (Fig. 2 and Table 2). The molecules stack in columns parallel to the *b* axis direction and are linked by a series of C—H⋯O hydrogen bonds (Table 2).

Experimental

A dry three-necked round-bottom flask was charged with 3-nitrophenylamine (2 mmol), 1-oxa-1-phosphatrioxabicyclo[2,2,2]-
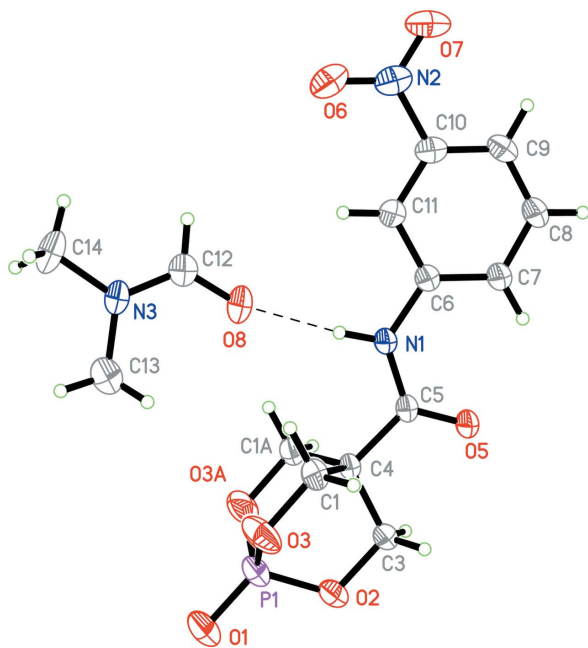
Figure 1
A view of the molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level. The intermolecular N1—H1···O8 hydrogen bond is indicated by a dashed line. [Symmetry code: (A) $x, \frac{1}{2} - y, z$.]

octane-4-chlorocarbinyl (2 mmol) and acetone (20 ml). The mixture was stirred and triethylamine (2.2 mmol), dissolved in acetone, was added dropwise over a period of 0.5 h. The reaction mixture was stirred for 0.5 h at room temperature and then refluxed for another 2 h. The product obtained was filtered off, washed thoroughly with water, and recrystallized from dimethylformamide and water (1:4 v/v). Single crystals were obtained by slow evaporation of a solution in dimethylformamide and water (1:4 v/v).

Crystal data

$C_{11}H_{11}N_2O_7P \cdot C_3H_7NO$	$D_x = 1.439$ Mg m^{-3}
$M_r = 387.28$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/m$	Cell parameters from 1715
$a = 11.052$ (2) Å	reflections
$b = 6.7210$ (15) Å	$\theta = 3.1$–$25.0°$
$c = 13.204$ (3) Å	$\mu = 0.20$ mm^{-1}
$\beta = 114.344$ (3)°	$T = 294$ (2) K
$V = 893.6$ (3) Å^3	Prism, yellow
$Z = 2$	$0.26 \times 0.22 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector	2006 independent reflections
diffractometer	1335 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.025$
Absorption correction: multi-scan	$\theta_{max} = 26.4°$
(*SADABS*; Sheldrick, 1996)	$h = -12 \rightarrow 13$
$T_{min} = 0.951$, $T_{max} = 0.962$	$k = -6 \rightarrow 8$
5100 measured reflections	$l = -16 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.043$	$+ 0.2629P]$
$wR(F^2) = 0.128$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} = 0.001$
2006 reflections	$\Delta\rho_{max} = 0.23$ e Å^{-3}
157 parameters	$\Delta\rho_{min} = -0.26$ e Å^{-3}
H atoms treated by a mixture of	Extinction correction: *SHELXL97*
independent and constrained	Extinction coefficient: 0.061 (6)
refinement	
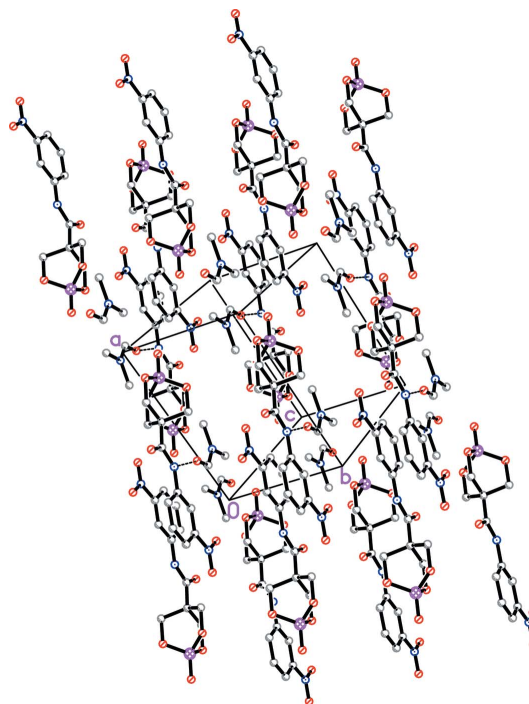
Figure 2
The crystal packing of compound (I), showing the N—H···O hydrogen-bonding interactions as dashed lines. H atoms have been omitted.

Table 1
Selected geometric parameters (Å, °).

P1—O1	1.446 (2)	P1—O3	1.5646 (18)
P1—O2	1.557 (2)		
O1—P1—O2	114.63 (14)	O3—P1—O3^i	103.45 (15)
O1—P1—O3	114.62 (8)	C3—O2—P1	115.21 (17)
O2—P1—O3	104.07 (9)	C1—O3—P1	115.58 (13)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O8	0.90 (3)	1.95 (3)	2.847 (3)	175 (3)
C1—H1C···O5^{ii}	0.97	2.40	3.311 (3)	157
C1—H1D···O8	0.97	2.57	3.439 (3)	149
C1—H1D···O7^{iii}	0.97	2.57	3.222 (3)	125
C7—H7···O5	0.93	2.25	2.851 (3)	122
C9—H9···O1^{iv}	0.93	2.54	3.194 (4)	128
C11—H11···O8	0.93	2.56	3.309 (4)	138

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

The H atom bonded to the atom N1 was located in a difference Fourier map and refined isotropically. The H atoms bonded to C atoms were positioned geometrically and included in the refinement in the riding-model approximation, with C–H = 0.93-0.97 Å and $U_{iso}(H) = 1.5U_{eq}(C_{methyl})$ and $U_{iso}(H) = 1.2U_{eq}(C_{aromatic}, C_{methylene})$. The H atoms of the solvent methyl groups are disordered over two positions, each of occupancy 0.5.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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