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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.041
 wR factor = 0.115
Data-to-parameter ratio = 13.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.***N*-(2-Nitrophenyl)-1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-carboxamide**

In the title compound, $\text{C}_{11}\text{H}_{11}\text{N}_2\text{O}_7\text{P}$, compression of the P—O—C angles is observed, suggesting that some strain is probably present. The configuration around phosphorus is distorted tetrahedral. In the crystal structure, N—H···O and C—H···O hydrogen-bond contacts and van der Waals forces stabilize the packing of the compound.

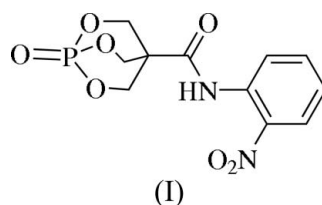
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Comment

Cage bicyclic phosphates have attracted much interest and many investigations have been reported (Allen *et al.*, 1995; Li *et al.*, 2002). It is found that cage bicyclic phosphates and their derivatives can serve as effective flame retardants in some polymers. They can produce less toxic gas and smoke compared with halogen-containing fire retardants. Therefore, they are recognized as environmentally friendly flame retardants. We report here the structure of a new cage bicyclic phosphate, namely *N*-(2-nitrophenyl)-1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-carboxamide, (I).



The molecular structure of (I) is illustrated in Fig. 1. The terminal O=P bond distance is 1.447 (2) Å and the average bridging P—O distance is 1.566 (3) Å. The O=P bond length is shorter than that of O—P, because of the presence of π -bonding. The bond distances and angles are within experimental error of those in the other trialkyl phosphates whose structures are known (Nimrod *et al.*, 1968; Liu *et al.*, 1992). The O—P—O and P—O—C bond angles (about 104 and 115°, respectively) are different from the unstrained angle (about 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 evidence of strain is present in (I) in the P—O—C angles of 115°. The configuration around phosphorus is distorted tetrahedral.

In the crystal structure, the nitro group N2/O6/O7 is almost coplanar with the arene ring. Atom O6 of the nitro group is involved in an intramolecular N1—H1···O6 hydrogen bond and an intermolecular C2—H2A···O6ⁱ hydrogen bond [symmetry code: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$]. The molecules are further loosely aggregated into a three-dimensional molecular network *via* a relatively weak C—H···O hydrogen bond (Table 2). A packing diagram is shown in Fig. 2.

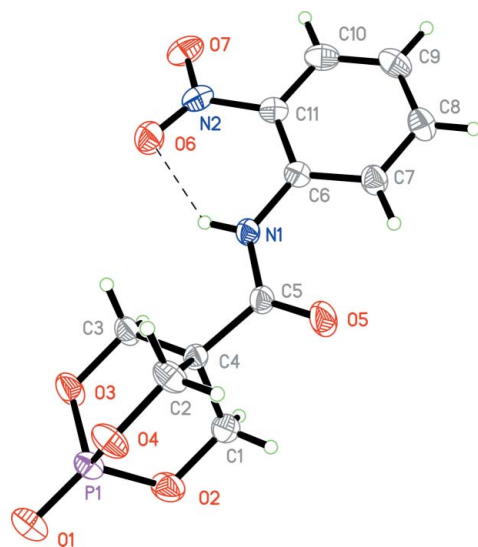


Figure 1

A view of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The intramolecular N1—H1...O6 hydrogen bond is indicated by a dashed line.

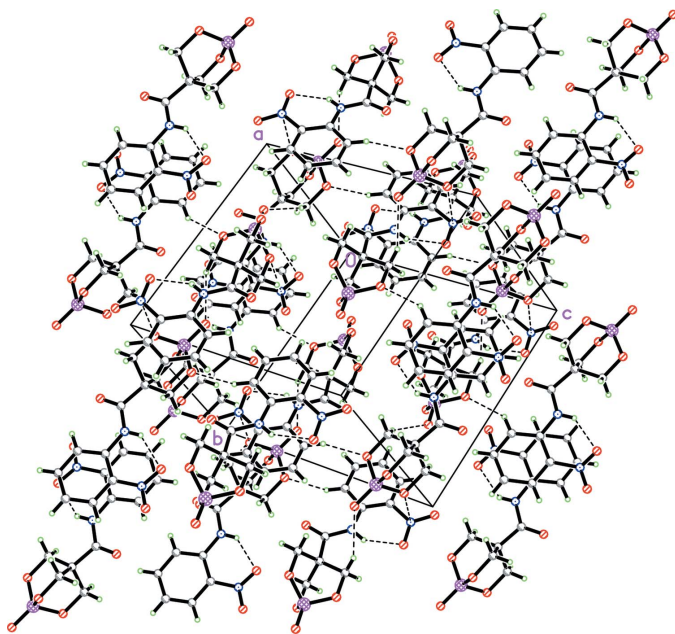


Figure 2

The packing of (I), showing hydrogen-bond interactions as dashed lines.

Experimental

A dry three-necked round-bottomed flask was charged with 2-nitrophenylamine (2 mmol), 4-chlorocarbinyl-1-oxa-1-phosphatrioxa-bicyclo[2.2.2]octane (2 mmol) and acetone (20 ml). To the stirred mixture, triethylamine (2.2 mmol) dissolved in acetone was added dropwise over a period of 0.5 h. After completion of triethylamine addition, the reaction mixture was stirred for 0.5 h at room temperature. The reaction mixture was then refluxed for another 2 h. The product was filtered off and washed thoroughly with water. The product was crystallized by slow evaporation from an *N,N*-dimethylformamide–water solution (1:4 *v/v*).

Crystal data

$C_{11}H_{11}N_2O_7P$
 $M_r = 314.19$
 Monoclinic, $P2_1/c$
 $a = 8.2381$ (14) Å
 $b = 12.269$ (2) Å
 $c = 12.937$ (2) Å
 $\beta = 105.075$ (3)°
 $V = 1262.6$ (4) Å³
 $Z = 4$

$D_x = 1.653$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2576 reflections
 $\theta = 2.3$ – 26.4 °
 $\mu = 0.26$ mm⁻¹
 $T = 293$ (2) K
 Prism, yellow
 $0.34 \times 0.28 \times 0.24$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.912$, $T_{\max} = 0.945$
 7022 measured reflections

2597 independent reflections
 1865 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 $\theta_{\max} = 26.4$ °
 $h = -7 \rightarrow 10$
 $k = -15 \rightarrow 13$
 $l = -16 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.115$
 $S = 1.05$
 2597 reflections
 195 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 0.5183P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.28$ e Å⁻³
 $\Delta\rho_{\min} = -0.31$ e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.043 (3)

Table 1

Selected geometric parameters (Å, °).

P1—O1	1.4472 (18)	P1—O2	1.5710 (19)
P1—O4	1.5637 (17)	O6—N2	1.231 (3)
P1—O3	1.5643 (18)	O7—N2	1.221 (2)
O1—P1—O4	114.72 (10)	C1—O2—P1	114.59 (14)
O1—P1—O3	114.18 (10)	C3—O3—P1	115.97 (13)
O4—P1—O3	104.62 (10)	C2—O4—P1	114.39 (13)
O1—P1—O2	114.69 (11)	O7—N2—O6	122.0 (2)
O4—P1—O2	103.41 (10)	O7—N2—C11	118.1 (2)
O3—P1—O2	103.90 (11)	O6—N2—C11	119.86 (18)
O7—N2—C11—C10	10.7 (3)	O7—N2—C11—C6	−168.6 (2)
O6—N2—C11—C10	−169.7 (2)	O6—N2—C11—C6	11.0 (3)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1...O6	0.82 (3)	1.97 (3)	2.632 (3)	138 (2)
N1—H1...N2	0.82 (3)	2.54 (2)	2.928 (3)	111 (2)
C2—H2A...O6 ⁱ	0.97	2.59	3.511 (3)	159
C3—H3B...O1 ⁱⁱ	0.97	2.50	3.351 (3)	147
C7—H7...O5	0.93	2.19	2.824 (3)	124
C7—H7...O3 ⁱ	0.93	2.42	3.216 (3)	144
C10—H10...O7	0.93	2.36	2.675 (3)	100

Symmetry codes: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $-x, y - \frac{1}{2}, -z + \frac{3}{2}$.

The H atom bonded to atom N1 was located in a difference Fourier map and refined isotropically. C-bound H atoms were included in the refinement in the riding-model approximation, with C—H = 0.93–0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1997); data reduction: *SAINTE*; 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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