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Key indicators

Single-crystal X-ray study
 $T = 120$ K
 Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.039
 wR factor = 0.097
 Data-to-parameter ratio = 16.1

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

N-(Diphenylphosphinoyl)hydroxylamine

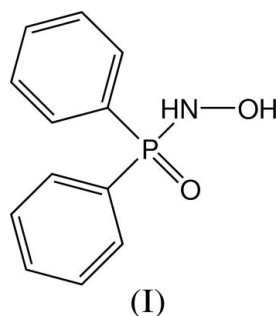
The title compound, $\text{C}_{12}\text{H}_{12}\text{NO}_2\text{P}$, is the first structurally studied phosphorus hydroxylamine derivative. The N atom is pyramidal. In the crystal structure, hydrogen bonds link molecules into double ribbons.

Received 23 October 2006

Accepted 26 October 2006

Comment

N-(Diphenylphosphinoyl)hydroxylamine, (I), and its analogues with different aryl and alkyl substituents, were synthesized by Harger (1983), and it has proved to be a useful intermediate in organic synthesis (Ware & King, 1999). No compound of this class has been previously studied by X-ray crystallography.



The molecular structure of (I) is shown in Fig. 1. The N atom is substantially pyramidal: the mean bond angle at it equals 112° . The geometry of the P—NH—OH group resembles that of S—NH—OH in the *N*-hydroxysulfonamides MeSO_2NHOH (Brink & Mattes, 1986) and PhSO_2NHOH (Scholz *et al.*, 1989), where the N atom is also pyramidal and the N—O distances are 1.437 (3) and 1.415 (6) Å, respectively. On the other hand, in $-\text{C}(=\text{O})-\text{NH}-\text{OH}$ units, the N atom usually has a planar configuration: out of 47 such structures present in the August 2006 update of the Cambridge Structural Database (Allen, 2002), only eight have a substantially pyramidal N atom. An electron-withdrawing hydroxyl group causes a small but significant lengthening of the P—N bond in (I) compared with the values of 1.630 (5) Å in $\text{Ph}_2\text{P}(=\text{O})\text{NH}_2$ (Oliva *et al.*, 1981, Schlecht *et al.*, 1998) and 1.642 (5) in $\text{Ph}_2\text{P}(=\text{O})\text{NHPH}$ (Priya *et al.*, 2005).

The molecule of (I), except for the hydroxyl group and the H atom attached to N, has an approximate local mirror plane which passes through the atoms P, O1 and N. The lone electron pair of the N atom lies in the same plane.

Both the amino and the hydroxyl groups form intermolecular hydrogen bonds with the phosphinoyl atom O2 (Table 2). These bonds link the molecules into an extended double ribbon running parallel to the *b* axis (Fig. 2).

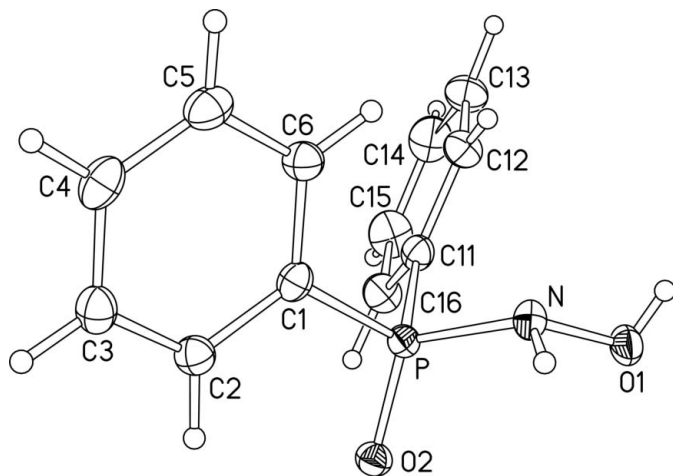


Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 50% probability level.

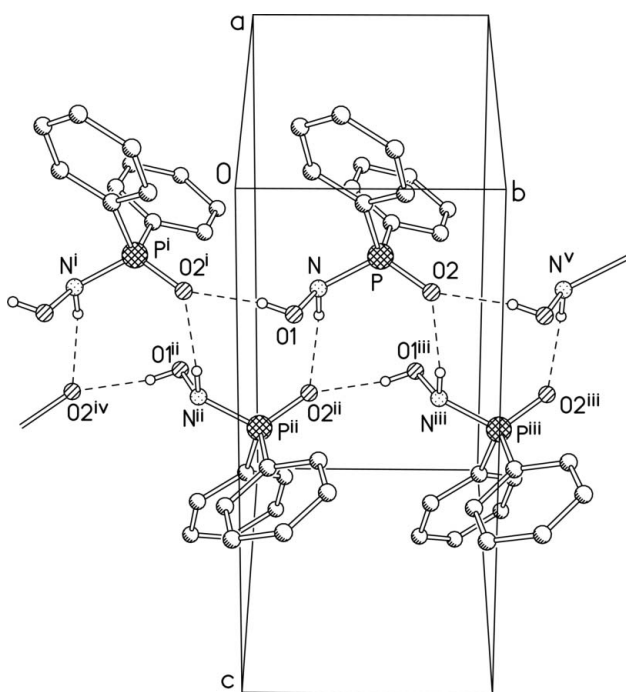


Figure 2
Part of the crystal structure of (I), with hydrogen bonds shown as dashed lines. [Symmetry codes: (i) $x, y - 1, z$, (ii) $1 - x, y - \frac{1}{2}, 1 - z$, (iii) $1 - x, y + \frac{1}{2}, 1 - z$, (iv) $1 - x, y - \frac{3}{2}, 1 - z$, (v) $x, y + 1, z$.]

Experimental

To a solution of *N,O*-bis(trimethylsilyl)hydroxylamine (1.790 g, 9.78 mmol) stirred at 273 K in anhydrous dichloromethane (8 ml), diphenylphosphinic chloride (1.52 ml, 7.83 mmol) was added dropwise. After 30 min, the solution was evaporated, the resulting oily solid resuspended in toluene (6 ml) and the white solid removed by filtration. The resulting solid was redissolved in anhydrous dichloromethane (8 ml) and methanol (0.8 g) and partially evaporated (*ca* 4 ml) after 1 h. The resulting solid suspension was removed by filtration and purified by recrystallization from methanol, yielding the product, (I), as white crystals (yield 0.953 g, 41.8%). The

compound has a m.p. (decomposition) at 400.9–404.7 K. However, although this temperature differs somewhat from the ranges of 418–419 K found by Harger (1983) and 416–418 K by Ware & King (1999), all spectroscopic and analytical properties were identical to those reported by these authors.

Crystal data

$C_{12}H_{12}NO_2P$
 $M_r = 233.20$
Monoclinic, $P2_1$
 $a = 8.5195(9) \text{ \AA}$
 $b = 5.7511(6) \text{ \AA}$
 $c = 11.958(1) \text{ \AA}$
 $\beta = 105.32(1)^\circ$
 $V = 565.1(1) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.371 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
 $\mu = 0.23 \text{ mm}^{-1}$
 $T = 120(2) \text{ K}$
Block, colourless
 $0.3 \times 0.2 \times 0.18 \text{ mm}$

Data collection

Bruker SMART 6K CCD area-detector diffractometer
 ω scans
Absorption correction: none
5264 measured reflections

3112 independent reflections
2826 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.024$
 $\theta_{max} = 30.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.097$
 $S = 0.99$
3112 reflections
193 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 0.1713P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.32 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.31 \text{ e \AA}^{-3}$
Absolute structure: Flack (1983), with 1314 Friedel pairs
Flack parameter: $-0.12(10)$

Table 1

Selected geometric parameters (\AA , $^\circ$).

P–O2	1.4965 (15)	O1–N	1.441 (2)
P–N	1.6612 (18)	O1–H0	0.78 (4)
P–C11	1.797 (2)	N–H1	0.88 (3)
P–C1	1.797 (2)		
O2–P–N	118.76 (8)	C11–P–C1	110.90 (9)
O2–P–C11	110.42 (9)	O1–N–P	111.70 (13)
N–P–C11	103.62 (9)	O1–N–H1	105.9 (17)
O2–P–C1	111.73 (9)	P–N–H1	116.8 (19)
N–P–C1	100.79 (9)		

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H0 \cdots O2 ⁱ	0.78 (4)	1.93 (4)	2.685 (2)	163 (3)
N–H1 \cdots O2 ⁱⁱ	0.88 (3)	2.10 (3)	2.945 (2)	160 (2)

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

All H atoms were refined in an isotropic approximation, with C–H distances in the range 0.89 (4)–1.01 (3) \AA .

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors thank both the EPSRC and GlaxoSmithKline Pharmaceuticals for a CASE award (to AJB), and Dr A. S. Batsanov for advice.

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supporting information

Acta Cryst. (2006). E62, o5343–o5345 [https://doi.org/10.1107/S1600536806044862]

***N*-(Diphenylphosphinoyl)hydroxylamine**

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N*-(diphenylphosphinoyl)hydroxylamineCrystal data*

$C_{12}H_{12}NO_2P$

$M_r = 233.20$

Monoclinic, $P2_1$

Hall symbol: $P\ 2_1yb$

$a = 8.5195$ (9) Å

$b = 5.7511$ (6) Å

$c = 11.958$ (1) Å

$\beta = 105.32$ (1)°

$V = 565.1$ (1) Å³

$Z = 2$

$F(000) = 244$

$D_x = 1.371$ Mg m⁻³

Melting point: 402.8(19) K

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2257 reflections

$\theta = 2.5$ – 29.9 °

$\mu = 0.23$ mm⁻¹

$T = 120$ K

Block, colourless

$0.3 \times 0.2 \times 0.18$ mm

Data collection

Bruker SMART CCD 6 K area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 5.6 pixels mm⁻¹

ω scans

5264 measured reflections

3112 independent reflections

2826 reflections with $I > 2\sigma(I)$

$R_{int} = 0.024$

$\theta_{max} = 30.0$ °, $\theta_{min} = 1.8$ °

$h = -10 \rightarrow 11$

$k = -8 \rightarrow 8$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.097$

$S = 0.99$

3112 reflections

193 parameters

1 restraint

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 0.1713P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.32$ e Å⁻³

$\Delta\rho_{min} = -0.31$ e Å⁻³

Absolute structure: Flack (1983), with 1314 Friedel pairs

Absolute structure parameter: -0.12 (10)

Special details

Experimental. The data collection nominally covered a full sphere of reciprocal space, by a combination of 4 runs of narrow-frame ω scans (scan width 0.3 ° ω , 5 s exposure), every run at a different ϕ and/or 2θ angle. Crystal to detector distance 4.85 cm. 1798 unique reflections after merging Friedel equivalents.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
P	0.49405 (5)	0.54483 (9)	0.31719 (4)	0.01523 (11)
O1	0.34049 (18)	0.1992 (3)	0.37448 (14)	0.0215 (3)
H0	0.352 (3)	0.072 (7)	0.357 (2)	0.032 (8)*
O2	0.41802 (17)	0.7499 (3)	0.35948 (12)	0.0186 (3)
N	0.5009 (2)	0.2928 (3)	0.38621 (15)	0.0181 (3)
H1	0.549 (3)	0.293 (5)	0.461 (2)	0.027 (7)*
C1	0.7066 (2)	0.5917 (3)	0.32967 (16)	0.0173 (4)
C2	0.7774 (2)	0.8000 (4)	0.37769 (17)	0.0199 (4)
H2	0.708 (3)	0.916 (5)	0.407 (2)	0.027 (7)*
C3	0.9428 (3)	0.8397 (4)	0.38948 (18)	0.0225 (4)
H3	0.994 (3)	0.982 (6)	0.421 (2)	0.034 (8)*
C4	1.0360 (3)	0.6723 (4)	0.35245 (19)	0.0243 (4)
H4	1.148 (3)	0.688 (6)	0.357 (2)	0.034 (8)*
C5	0.9659 (3)	0.4657 (4)	0.3037 (2)	0.0246 (4)
H5	1.024 (4)	0.349 (6)	0.279 (3)	0.042 (8)*
C6	0.8007 (2)	0.4248 (4)	0.29228 (18)	0.0202 (4)
H6	0.753 (3)	0.281 (6)	0.261 (2)	0.032 (7)*
C11	0.3864 (2)	0.4761 (4)	0.17032 (17)	0.0188 (4)
C12	0.4124 (3)	0.2693 (4)	0.11705 (19)	0.0237 (4)
H12	0.490 (4)	0.166 (6)	0.161 (3)	0.040 (8)*
C13	0.3292 (3)	0.2269 (5)	0.0022 (2)	0.0303 (5)
H13	0.354 (4)	0.086 (6)	-0.032 (3)	0.042 (9)*
C14	0.2185 (3)	0.3873 (5)	-0.0585 (2)	0.0339 (6)
H14	0.155 (4)	0.361 (7)	-0.133 (3)	0.055 (10)*
C15	0.1895 (3)	0.5920 (5)	-0.0057 (2)	0.0330 (6)
H15	0.114 (4)	0.687 (6)	-0.048 (3)	0.045 (9)*
C16	0.2744 (3)	0.6370 (4)	0.10921 (19)	0.0253 (4)
H16	0.263 (3)	0.778 (6)	0.148 (2)	0.029 (7)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P	0.0159 (2)	0.0138 (2)	0.0163 (2)	0.0000 (2)	0.00476 (15)	-0.0004 (2)
O1	0.0194 (7)	0.0161 (7)	0.0313 (8)	-0.0018 (5)	0.0106 (6)	0.0004 (6)
O2	0.0190 (7)	0.0167 (7)	0.0207 (7)	0.0008 (5)	0.0060 (6)	-0.0018 (6)
N	0.0178 (8)	0.0167 (8)	0.0200 (8)	-0.0019 (6)	0.0055 (6)	0.0017 (6)
C1	0.0167 (8)	0.0200 (11)	0.0149 (8)	-0.0005 (7)	0.0038 (6)	0.0023 (7)
C2	0.0194 (9)	0.0208 (10)	0.0193 (9)	-0.0005 (8)	0.0049 (7)	-0.0009 (8)

C3	0.0225 (10)	0.0242 (10)	0.0197 (9)	-0.0043 (8)	0.0035 (8)	0.0012 (8)
C4	0.0176 (9)	0.0332 (12)	0.0217 (9)	-0.0009 (9)	0.0044 (8)	0.0053 (9)
C5	0.0229 (10)	0.0268 (11)	0.0262 (10)	0.0059 (8)	0.0100 (9)	0.0039 (9)
C6	0.0196 (9)	0.0199 (10)	0.0214 (9)	0.0011 (8)	0.0059 (8)	-0.0010 (8)
C11	0.0184 (9)	0.0206 (9)	0.0172 (8)	-0.0036 (7)	0.0046 (7)	-0.0014 (7)
C12	0.0259 (10)	0.0215 (10)	0.0237 (9)	-0.0018 (8)	0.0068 (8)	-0.0038 (9)
C13	0.0398 (13)	0.0291 (13)	0.0233 (10)	-0.0066 (10)	0.0105 (10)	-0.0098 (9)
C14	0.0402 (13)	0.0418 (15)	0.0167 (9)	-0.0110 (11)	0.0023 (10)	-0.0045 (10)
C15	0.0352 (12)	0.0355 (17)	0.0233 (10)	0.0010 (10)	-0.0013 (9)	0.0059 (10)
C16	0.0288 (11)	0.0237 (10)	0.0220 (10)	0.0005 (9)	0.0044 (9)	0.0020 (9)

Geometric parameters (Å, °)

P—O2	1.4965 (15)	C5—C6	1.397 (3)
P—N	1.6612 (18)	C5—H5	0.93 (3)
P—C11	1.797 (2)	C6—H6	0.95 (3)
P—C1	1.797 (2)	C11—C16	1.390 (3)
O1—N	1.441 (2)	C11—C12	1.394 (3)
O1—H0	0.78 (4)	C12—C13	1.391 (3)
N—H1	0.88 (3)	C12—H12	0.94 (3)
C1—C2	1.395 (3)	C13—C14	1.380 (4)
C1—C6	1.398 (3)	C13—H13	0.96 (3)
C2—C3	1.397 (3)	C14—C15	1.389 (4)
C2—H2	1.01 (3)	C14—H14	0.92 (4)
C3—C4	1.393 (3)	C15—C16	1.397 (3)
C3—H3	0.96 (3)	C15—H15	0.89 (4)
C4—C5	1.387 (3)	C16—H16	0.95 (3)
C4—H4	0.95 (3)		
O2—P—N	118.76 (8)	C4—C5—H5	123 (2)
O2—P—C11	110.42 (9)	C6—C5—H5	117 (2)
N—P—C11	103.62 (9)	C5—C6—C1	120.1 (2)
O2—P—C1	111.73 (9)	C5—C6—H6	120.0 (17)
N—P—C1	100.79 (9)	C1—C6—H6	119.9 (17)
C11—P—C1	110.90 (9)	C16—C11—C12	119.82 (19)
N—O1—H0	101 (2)	C16—C11—P	118.00 (16)
O1—N—P	111.70 (13)	C12—C11—P	122.18 (16)
O1—N—H1	105.9 (17)	C13—C12—C11	120.0 (2)
P—N—H1	116.8 (19)	C13—C12—H12	123 (2)
C2—C1—C6	119.93 (19)	C11—C12—H12	117 (2)
C2—C1—P	118.67 (15)	C14—C13—C12	120.0 (2)
C6—C1—P	121.40 (15)	C14—C13—H13	122.9 (18)
C1—C2—C3	119.8 (2)	C12—C13—H13	117.1 (18)
C1—C2—H2	118.7 (16)	C13—C14—C15	120.4 (2)
C3—C2—H2	121.5 (16)	C13—C14—H14	123 (2)
C4—C3—C2	120.0 (2)	C15—C14—H14	117 (2)
C4—C3—H3	118.5 (17)	C14—C15—C16	119.7 (2)
C2—C3—H3	121.5 (17)	C14—C15—H15	117 (2)

C5—C4—C3	120.4 (2)	C16—C15—H15	123 (2)
C5—C4—H4	115.1 (19)	C11—C16—C15	119.9 (2)
C3—C4—H4	124.4 (19)	C11—C16—H16	116.8 (17)
C4—C5—C6	119.8 (2)	C15—C16—H16	123.2 (17)
O2—P—N—O1	65.74 (16)	C11—P—C1—C6	-54.62 (19)
C11—P—N—O1	-57.12 (15)	O2—P—C11—C16	12.1 (2)
C1—P—N—O1	-171.94 (13)	N—P—C11—C16	140.31 (17)
O2—P—C1—C2	1.63 (18)	C1—P—C11—C16	-112.30 (17)
N—P—C1—C2	-125.48 (16)	O2—P—C11—C12	-168.05 (16)
C11—P—C1—C2	125.29 (16)	N—P—C11—C12	-39.85 (19)
O2—P—C1—C6	-178.28 (15)	C1—P—C11—C12	67.54 (19)
N—P—C1—C6	54.61 (17)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H0...O2 ⁱ	0.78 (4)	1.93 (4)	2.685 (2)	163 (3)
N—H1...O2 ⁱⁱ	0.88 (3)	2.10 (3)	2.945 (2)	160 (2)

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+1, y-1/2, -z+1$.