



# Crystal structure of 1,3-di-*tert*-butyl-2-chloro-1,3,2-diazaphosphorinane – a saturated six-membered phosphorus nitrogen heterocycle with a partially flattened chair conformation and a long P<sup>III</sup>—Cl bond

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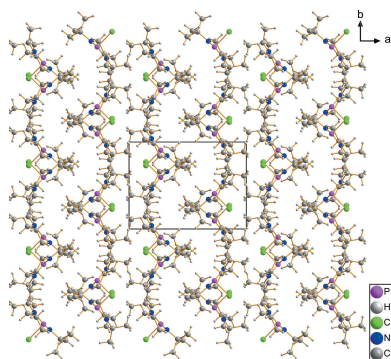
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Colourless blocks of 1,3-di-*tert*-butyl-2-chloro-1,3,2-diazaphosphorinane, C<sub>11</sub>H<sub>24</sub>ClN<sub>2</sub>P (**1**), were obtained by sublimation *in vacuo* slightly above room temperature. The asymmetric unit of the monoclinic crystal structure of the six-membered *N*-heterocyclic compound is defined by one molecule in a general position. The six-membered ring of the molecule adopts a cyclohexane-like chair conformation; the chair at one side is to some extent flattened as a result of the approximately trigonal-planar coordination of both nitrogen atoms. In detail, this modified chair conformation is characterized by an angle of 53.07 (15)° between the plane defined by the three carbon atoms and the best plane of the two nitrogen atoms and the two carbon atoms bound to them, and an angle of 27.96 (7)° between the latter plane and the plane defined by the nitrogen and phosphorus atoms. The *tert*-butyl groups are oriented equatorially and the chloro substituent is oriented axially. The P—Cl bond length of 2.2869 (6) Å is substantially longer than the P—Cl single-bond length in PCl<sub>3</sub> [2.034 Å; Galy & Enjalbert (1982). *J. Solid State Chem.* **44**, 1–23]. Inspection of the intermolecular distances gives no evidence for interactions stronger than van der Waals forces. The closest contact is between the Cl atom and a methylene group of a neighbouring molecule with a Cl⋯C distance of 3.7134 (18) Å, excluding a significant influence on the P—Cl bonding.

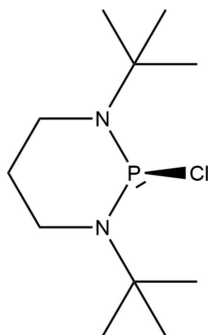
## 1. Chemical context

Over the past two decades, *P*-chlorofunctionalized *N*-heterocyclic phosphanes (NHPCls) received considerable attention, mainly as precursors of *N*-heterocyclic phosphonium ions (NHPs) that are valence isoelectronic compounds of the well-known *N*-heterocyclic carbenes (NHCs) (Papke *et al.*, 2017), but also as educts of tetrakis(amino)diphosphanes (*e.g.* Bezombes *et al.*, 2004; Blum *et al.*, 2016; Edge *et al.*, 2009; Frank *et al.*, 1996), some of which reversibly dissociate to stable phosphinyl radicals ('jack-in-the-box dipnictines'; Hinchley *et al.*, 2001), and as starting materials in the synthesis of mixed-valent tetrakis(amino)tetrachosphetes (Breuers *et al.*, 2015; Frank *et al.*, 1996). Furthermore, NHPCls and NHPs have been used as ligands in transition metal complexes (Thomas *et al.*, 2018), some of which have a potential application in catalysis (Gatien *et al.*, 2018). In the context of NHP chemistry, the majority of compounds are five-membered cycles, and especially *P*-chlorofunctionalized 1,3,2-diazaphospholenes (Denk *et al.*, 1996; Carmalt & Lomeli, 1997)



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have gained a widespread use as precursors for 1,3,2-diazaphospholenium cations (the most prominent class of NHPs) that are weak  $\sigma$ -donors and strong  $\pi$ -acceptors (Caputo *et al.*, 2008; Tuononen *et al.*, 2007). A limited number of structurally characterized examples is known for the class of *P*-chlorofunctionalized four-membered NHPCLs  $\text{Cl}-\text{P}(\text{NR})_2 > E$  and the related NHPs. The fourth ring member  $>E$ , joining the class-defining  $\text{Cl}-\text{P}(\text{NR})_2$  fragment, is an  $>\text{SiR}_2$  group in most cases (*e.g.* Breuers & Frank, 2016; Gün *et al.*, 2017; Mo *et al.*, 2018; Mo & Frank, 2019; Veith *et al.*, 1988) but some compounds containing  $>\text{C}=\text{N}-R$  (Brazeau *et al.*, 2012),  $>\text{B}-\text{Ph}$  (Konu *et al.*, 2008) and  $>\text{As}-\text{Cl}$  (Hinz *et al.*, 2015) have also been synthesized and structurally characterized. In contrast to the aforementioned compounds with four- and five-membered rings, six-membered NHPs and NHPCLs are less present in recent publications, although 2-chloro-1,3,2-diazaphosphorinanes  $\text{H}_2\text{C}(\text{CH}_2\text{NR})_2 > \text{P}-\text{Cl}$ , for instance, have been known since the early 1970s (Maryanoff & Hutchins, 1972; Nifant'ev *et al.*, 1977). Temperature-dependent dynamical NMR investigations showed that in solution these substances are not subject to a fast conformation change, like the ring-inversion process of cyclohexane, and that in the predominant conformation the chloro substituent is expected to be in the axial position and the residues on the nitrogen atoms are oriented 'diequatorial'. This gives rise to a quite complex  $^1\text{H-NMR}$  spectrum with an  $AA'KK'QTX$  pattern ( $X = \text{P}$ ,  $AA'KK' = \text{C}_4$  and  $\text{C}_6$  protons,  $Q$  and  $T = \text{C}_5$  protons; Hutchins *et al.*, 1972). Furthermore, the number and position of the signals in the  $^1\text{H-NMR}$  spectrum are dependent on concentration, which was attributed to intermolecular chlorine-exchange mechanisms. Even though this parent class of six-membered NHPCLs has been known for quite some time, no crystal structure analysis has thus far been reported. Herein, we present the crystal structure of the title compound that allows for a structural comparison with the most closely related four- or five-membered NHPCLs known, on one hand, and with phospho- and 1,3,2-dioxaphosphacyclohexane derivatives, on the other hand.



## 2. Structural commentary

The molecular structure of **1** in the crystal is shown in Fig. 1. The molecule does not suffer from conformational disorder, which is often recognized in the solids of saturated *N*-heterocyclic compounds. The main characteristics of the

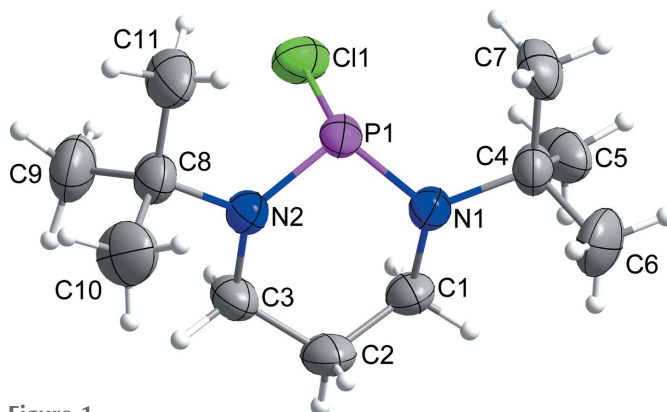


Figure 1

Diagram of the molecular structure of compound **1** in the crystal displaying the atom-labelling scheme. Anisotropic displacement ellipsoids are drawn at the 50% probability level, the radii of hydrogen atoms are chosen arbitrarily.

molecule are: (i) the partially flattened chair conformation of the central six-membered heterocycle (displayed in more detail in Fig. 2) with an angle of  $53.07(15)^\circ$  between the plane defined by the carbon atoms and the best plane of  $\text{C1}$ ,  $\text{C3}$ ,  $\text{N1}$  and  $\text{N2}$ , and an angle of  $27.96(7)^\circ$  between the latter plane and the plane defined by the nitrogen and phosphorus atoms; (ii) the equatorial orientation of both *tert*-butyl groups, enforced by the approximate trigonal-planar coordination of the nitrogen atoms [sums of angles  $356.2(\text{N1})$  and  $355.8(\text{N2})$ ], in combination with the axial orientation of the chloro substituent (Fig. 2) [out of plane angle:  $106.83(5)^\circ$ ]; (iii) the length of the  $\text{P1}-\text{Cl1}$  bond,  $2.2869(6) \text{ \AA}$ , is substantially longer than the standard single bond ( $2.02 \text{ \AA}$ ; Brown, 2016) and the longest bond found in a six-membered NHPCL so far. The  $\text{P}-\text{N}$  bond lengths [ $\text{P1}-\text{N1} = 1.6584(14)$  and  $\text{P1}-\text{N2} = 1.6519(14) \text{ \AA}$ ] are significantly smaller than the standard single-bond length [ $\text{P}-\text{N} = 1.704(4) \text{ \AA}$ ; Brown & Altermatt,

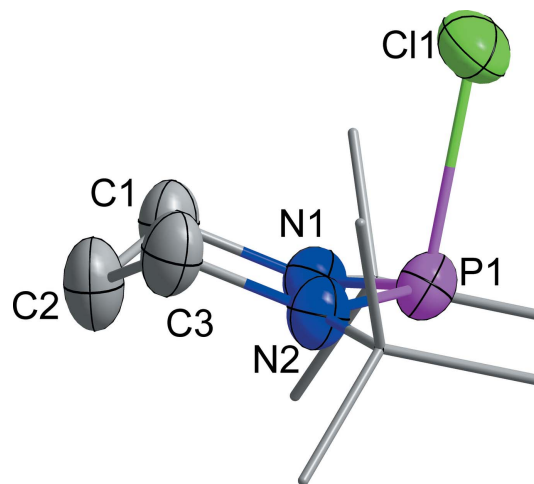


Figure 2

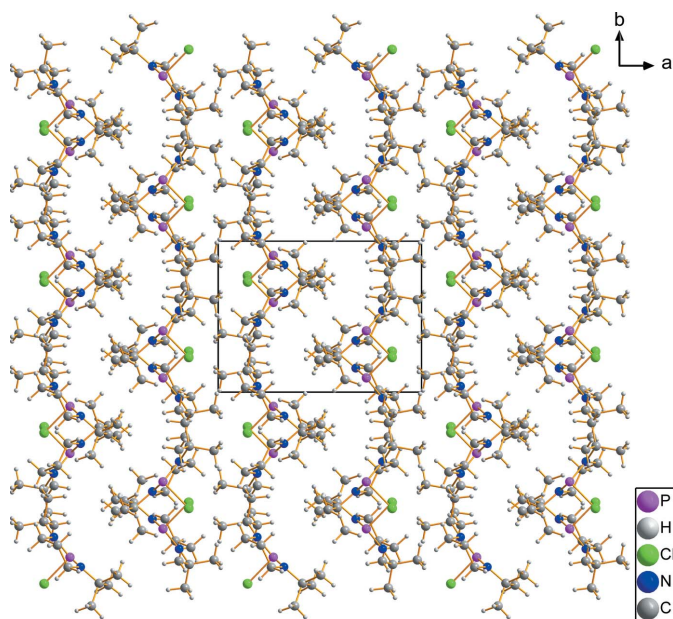
Chair conformation of the molecule (H atoms are omitted for clarity); note the cyclohexane-like conformation at the 'carbon-atom side' [folding angle  $53.07(15)^\circ$  as compared to  $54.5(6)^\circ$  in the ordered, monoclinic phase of  $\text{C}_6\text{H}_{12}$  (Kahn *et al.*, 1973)] and the 'semi-flattened' conformation [folding angle  $27.96(7)^\circ$ ] at the 'phosphorus/nitrogen-atom side'.

1985] and are close to the lower limit of the range found for NHPCls. The P–Cl bond is substantially longer than the P–Cl single-bond length in  $\text{PCl}_3$  (2.034 Å; Galy & Enjalbert, 1982). The closest related five-membered NHPCl, 2-chloro-1,3-di-*tert*-butyl-2,1,3-phosphadiazolidine ( $\text{CH}_2\text{N}^t\text{Bu}$ )<sub>2</sub>–P–Cl shows almost identical bonding at the phosphorus atom [P–N = 1.652 (2) and P–Cl = 2.3136 (7) Å; Denk *et al.*, 1999]. Unfortunately, a similar close relationship cannot be found among the known crystal structures of four-membered NHPCls and the closest related compound seems to be the *P*-chloro-substituted diazaphosphasiletidine Cl–P<(N<sup>t</sup>Bu)<sub>2</sub>>–SiMe<sub>2</sub> [P–N = 1.6815 (14) and P–Cl = 2.2498 (6) Å; Gün *et al.*, 2017].

A more general comparison with other *P*-chloro-functionalized six-membered heterocyclic phosphorus compounds illustrates the P–Cl bond-length variation depending on the bonding situation in the heterocycle. Di-(3-methylindol-2-yl)chlorophosphine-4-bromophenylmethane (Mallov *et al.*, 2012), exhibits a planar coordination at the two carbon atoms next to the nitrogen atoms due to exoalkylene group bonding, with a P–Cl bond length of only 2.108 (2) Å. In 2-chloro-1,3,5,7-tetramethyl-4,6,8-trioxa-2-phosphaadamantane (Downing *et al.*, 2008), which can be considered as a chlorophosphorinane [(–CR)<sub>2</sub>>P–Cl] with an enforced chair conformation, P–Cl = 2.0754 (11) Å and in the 2-chloro-1,3,2-dioxaphosphorinane derivative [(–O)<sub>2</sub>>P–Cl] described by Pavan Kumar & Kumara Swamy (2007), P–Cl = 2.1227 (9) Å. Some examples of six-membered heterocycles with enforced ring flattening as a result of sterically demanding substituents (Brazeau *et al.*, 2012; Burford *et al.*, 2004; Holthausen *et al.*, 2016; Schranz *et al.*, 2000) and with flattening due to  $\pi$ -system involvement of the carbon atoms, such as 2-chloro-1,2,3,4-tetrahydro-1,3,2-diazaphosphonium salts (Lesikar *et al.*, 2007; Vidovic *et al.*, 2006), 2-chloro-5,6-benzo-1,3,2-diazaphosphorin-4-one (Sonnenburg *et al.*, 1997) and 2-chloro-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaphosphinines (Kozma *et al.*, 2015; Spinney *et al.*, 2007) all show significantly shorter P–Cl bonds compared to **1**, ranging from 2.072 (4) to 2.244 (3) Å. Further geometric details of **1** are given in the supporting information. C–C and C–N bond lengths, as well as endocyclic and exocyclic bond angles, are as expected taking into account the main structural characteristics given above. Finally it should be noted that the crystal structure determination described here confirms the suggestions of Hutchins *et al.* (1972) concerning the structure of 2-chloro-1,3,2-diazaphosphorinanes, derived by NMR spectroscopy.

### 3. Supramolecular features

Inspection of the intermolecular distances gives no evidence for interactions stronger than van der Waals forces in the crystal of **1**. The closest contact is given between Cl1 and the methylene group of the neighbouring molecule containing C1 at a Cl⋯C distance of 3.7134 (18) Å, symmetry related by the *c* glide plane (symmetry code:  $x, \frac{1}{2} - y, \frac{1}{2} + z$ ). Fig. 3 shows the packing of the molecules in the crystal. Space group-symmetry gives rise to an appealing wave-like pattern.



**Figure 3**  
Packing diagram of **1** (view direction  $[00\bar{1}]$ ) showing a wave-like pattern. Inspection of the intermolecular distances gives no evidence for interactions stronger than van der Waals forces and intermolecular influence on the P–Cl bonding can be excluded.

### 4. Database survey

A search of the Cambridge Structural Database (Version 5.40, November 2018 update; Groom *et al.*, 2016) for the heterocycle substructure of 2-chloro-1,3,2-diazaphosphorinanes (*i.e.* exclusively single bonds in the six-membered ring) yielded only one structure (DEHZOH; Mallov *et al.*, 2012). However, two of the ring carbon atoms are bonded to exoalkylene groups and are in planar coordination. A more general search allowing for alternative  $P^{\text{III}}$ -functionalization gave eight hits including  $N^1, N^{11}:N^4, N^8$ -bis( $\mu_2$ -methylphosphino)-1,4,8,11-tetraazacyclotetradecane (COLZUY; Hope *et al.*, 1984), 1,3-di-*tert*-butyl-2-triphenylsilyl-1,3,2-diazaphosphorinane (DODDUV; Nifant'ev *et al.*, 1985), the 1,3-di-*tert*-butyl-1,3,2-diazaphosphorinanyloxy)calix(4)arenes FEMLOZ and FEMLUF (Maslennikova *et al.*, 2004), ( $\eta^5$ -cyclopentadienyl)-dichloro(1,3-dimethyl-1,3,2-diazaphospholyl)titanium (LARTED; Nifant'ev *et al.*, 1991), the phosphatris(pyrrolyl)- and -(indolyl)methanes NEQBUG (Barnard & Mason, 2001*a*) and YETDIK (Barnard & Mason, 2001*b*) and finally 3-(*tert*-butyl)trimethylsilylamino-2,4-di-*tert*-butyl-1-[2-(1,3-di-*tert*-butyl-1,3,2-diazaphosphoridinyl)]imino-3-thio-1,2,4,3-thiadiazaphosphetidine (YOYEN; Wrackmeyer *et al.*, 1994). A search for *P*-chloro-functionalized six-membered ring compounds with any other three ring atoms joining the Cl–P<(NR)<sub>2</sub> fragment and allowing for any kind of bonding in the ring gave 16 hits including eight with three carbon atoms. In addition to DEHZOH mentioned before, these include 2-chloro-1-(2'-chloroethyl)-3-methyl-5,6-benzo-1,3,2-diazaphosphorin-4-one (MAMBUX; Sonnenburg *et al.*, 1997), the 2-chloro-1,3-diorganyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaphosphinines OGOXAL (Kozma *et al.*, 2015), REQKEE and TIPVIY



**Table 1**  
Experimental details.

Crystal data	
Chemical formula	C <sub>11</sub> H <sub>24</sub> ClN <sub>2</sub> P
<i>M<sub>r</sub></i>	250.74
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.5954 (5), 9.1549 (3), 12.9614 (6)
$\beta$ (°)	101.547 (3)
<i>V</i> (Å <sup>3</sup> )	1464.33 (10)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.35
Crystal size (mm)	0.48 × 0.28 × 0.25
Data collection	
Diffractometer	Stoe IPDS II
Absorption correction	Multi-scan ( <i>XPREP</i> ; Bruker, 2008)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.761, 0.929
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	16291, 3943, 3547
<i>R</i> <sub>int</sub>	0.050
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.686
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.048, 0.109, 1.01
No. of reflections	3943
No. of parameters	142
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.41, -0.21

Computer programs: *X-AREA* (Stoe & Cie, 2002), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b) and *DIAMOND* (Brandenburg, 2015).

(Spinney *et al.*, 2007) and the 1,3-bis(2,6-di-isopropylphenyl)-2-chloro-1,2,3,4-tetrahydro-1,3,2-diazaphosphonium salts NIJXUA (Lesikar *et al.*, 2007) and PENNUS (Vidovic *et al.*, 2006).

## 5. Synthesis and crystallization

The title compound was prepared under an argon atmosphere in oven-dried glassware using standard Schlenk techniques, modifying a published procedure (Nifant'ev *et al.*, 1977) by including a lithiation step. 3.75 g (20.1 mmol) of *N,N'*-di-*tert*-butyl-1,3-propanediamine were dissolved in a mixture of diethyl ether and *n*-hexane (35 ml/55 ml). 16 ml of an *n*-butyllithium solution (*c* = 2.5 mol l<sup>-1</sup> in *n*-hexane, 40 mmol) were slowly added at 263 K. Half an hour later, the reaction mixture was allowed to reach room temperature and the resulting pale-yellow suspension was stirred for 16 h. 2.92 g of PCl<sub>3</sub> (21.3 mmol) were added dropwise over a period of 15 minutes at 195 K. To complete the reaction, the yellow reaction mixture was stirred for another hour with cooling and finally for two h at room temperature. Subsequently, the LiCl precipitate was filtered off and, after removal of the solvent under reduced pressure, the crude product was obtained as a yellow solid. Colourless block-shaped crystals suitable for X-ray structure determination were obtained by sublimation in a vacuum (3·10<sup>-2</sup> mbar) at 313 K (30% yield; m.p. 327 K), by NMR analysis proved to be pure substance. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  3.16–3.07 (*m*, 4 H), 1.90–1.80 (*m*, 2 H), 1.34 [*d*, <sup>4</sup>*J*(H,P) = 3.5 Hz, 18H].

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Positions of all hydrogen atoms were identified *via* subsequent  $\Delta F$  syntheses. In the refinement, a riding model was applied using idealized C–H bond lengths (0.98–0.99 Å) as well as H–C–H and C–C–H angles. In addition, the H atoms of the CH<sub>3</sub> groups were allowed to rotate around the neighbouring C–C bonds. The *U*<sub>iso</sub> values were set to 1.5*U*<sub>eq</sub>(C<sub>methyl</sub>) and 1.2*U*<sub>eq</sub>(C<sub>methylene</sub>).

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## supporting information

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## Crystal structure of 1,3-di-*tert*-butyl-2-chloro-1,3,2-diazaphosphorinane – a saturated six-membered phosphorus nitrogen heterocycle with a partially flattened chair conformation and a long P<sup>III</sup>—Cl bond

Erik Mecke and Walter Frank

### Computing details

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-AREA* (Stoe & Cie, 2002); program(s) used to solve structure: SHELXT (Sheldrick, 2015a4); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 2015); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015b).

### 1,3-Di-*tert*-butyl-2-chloro-1,3,2-diazaphosphinane

#### Crystal data

C<sub>11</sub>H<sub>24</sub>ClN<sub>2</sub>P

*M<sub>r</sub>* = 250.74

Monoclinic, *P*2<sub>1</sub>/*c*

*a* = 12.5954 (5) Å

*b* = 9.1549 (3) Å

*c* = 12.9614 (6) Å

β = 101.547 (3)°

*V* = 1464.33 (10) Å<sup>3</sup>

*Z* = 4

*F*(000) = 544

*D<sub>x</sub>* = 1.137 Mg m<sup>-3</sup>

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 20870 reflections

θ = 4.5–59.2°

μ = 0.35 mm<sup>-1</sup>

*T* = 173 K

Block, colourless

0.48 × 0.28 × 0.25 mm

#### Data collection

Stoe IPDS II  
diffractometer

ω-scans

Absorption correction: multi-scan  
(XPREP; Bruker, 2008)

*T<sub>min</sub>* = 0.761, *T<sub>max</sub>* = 0.929

16291 measured reflections

3943 independent reflections

3547 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.050

θ<sub>max</sub> = 29.2°, θ<sub>min</sub> = 2.7°

*h* = -17→17

*k* = -12→12

*l* = -17→17

#### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.048

*wR*(*F*<sup>2</sup>) = 0.109

*S* = 1.01

3943 reflections

142 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: difference Fourier map

H-atom parameters constrained

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0327*P*)<sup>2</sup> + 0.8644*P*]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

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

$$\Delta\rho_{\max} = 0.41 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$$

### Special details

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

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.85529 (4)	0.26976 (5)	0.83702 (4)	0.05736 (15)
P1	0.72874 (3)	0.09412 (5)	0.77742 (3)	0.03774 (11)
N1	0.67636 (11)	0.15879 (16)	0.65862 (11)	0.0411 (3)
N2	0.80820 (11)	-0.03915 (15)	0.75215 (11)	0.0390 (3)
C1	0.73831 (16)	0.1599 (2)	0.57350 (14)	0.0511 (4)
H11	0.7950	0.2362	0.5881	0.061*
H12	0.6892	0.1842	0.5060	0.061*
C2	0.79040 (18)	0.0142 (3)	0.56389 (15)	0.0579 (5)
H21	0.7332	-0.0608	0.5451	0.070*
H22	0.8314	0.0187	0.5063	0.070*
C3	0.86546 (15)	-0.0296 (2)	0.66384 (14)	0.0485 (4)
H31	0.8981	-0.1256	0.6538	0.058*
H32	0.9248	0.0428	0.6809	0.058*
C4	0.58516 (16)	0.2663 (2)	0.64533 (15)	0.0507 (4)
C5	0.6238 (2)	0.4171 (3)	0.6188 (2)	0.0810 (7)
H51	0.6437	0.4141	0.5495	0.122*
H52	0.6870	0.4457	0.6722	0.122*
H53	0.5654	0.4883	0.6176	0.122*
C6	0.49516 (19)	0.2120 (3)	0.5566 (2)	0.0804 (8)
H61	0.5245	0.1962	0.4930	0.121*
H62	0.4372	0.2850	0.5423	0.121*
H63	0.4660	0.1199	0.5777	0.121*
C7	0.5396 (2)	0.2788 (3)	0.7459 (2)	0.0756 (7)
H71	0.5958	0.3169	0.8030	0.113*
H72	0.5165	0.1822	0.7653	0.113*
H73	0.4774	0.3454	0.7337	0.113*
C8	0.85809 (15)	-0.1413 (2)	0.83911 (15)	0.0489 (4)
C9	0.97954 (16)	-0.1119 (3)	0.87176 (17)	0.0655 (6)
H91	1.0154	-0.1390	0.8141	0.098*
H92	1.0096	-0.1700	0.9343	0.098*
H93	0.9915	-0.0079	0.8879	0.098*
C10	0.8368 (3)	-0.2973 (2)	0.7984 (2)	0.0860 (8)
H101	0.7585	-0.3146	0.7800	0.129*
H102	0.8699	-0.3664	0.8533	0.129*
H103	0.8684	-0.3110	0.7359	0.129*
C11	0.80696 (18)	-0.1203 (3)	0.93605 (17)	0.0631 (6)

H111	0.7286	-0.1367	0.9164	0.095*
H112	0.8208	-0.0205	0.9629	0.095*
H113	0.8388	-0.1902	0.9908	0.095*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C11	0.0692 (3)	0.0498 (3)	0.0529 (3)	-0.0125 (2)	0.0117 (2)	-0.0122 (2)
P1	0.0374 (2)	0.0386 (2)	0.0394 (2)	0.00313 (16)	0.01304 (15)	0.00418 (16)
N1	0.0410 (7)	0.0420 (7)	0.0407 (7)	0.0073 (6)	0.0093 (5)	0.0033 (6)
N2	0.0388 (7)	0.0362 (6)	0.0423 (7)	0.0030 (5)	0.0093 (5)	0.0012 (5)
C1	0.0553 (10)	0.0609 (11)	0.0386 (8)	0.0111 (9)	0.0133 (7)	0.0070 (8)
C2	0.0666 (12)	0.0672 (13)	0.0426 (9)	0.0142 (10)	0.0169 (9)	-0.0053 (9)
C3	0.0493 (9)	0.0537 (10)	0.0451 (9)	0.0109 (8)	0.0158 (7)	-0.0028 (8)
C4	0.0511 (10)	0.0481 (10)	0.0529 (10)	0.0149 (8)	0.0106 (8)	0.0062 (8)
C5	0.101 (2)	0.0493 (12)	0.0943 (18)	0.0181 (13)	0.0239 (15)	0.0167 (12)
C6	0.0526 (12)	0.098 (2)	0.0830 (16)	0.0202 (13)	-0.0058 (11)	-0.0045 (15)
C7	0.0733 (15)	0.0876 (17)	0.0719 (14)	0.0409 (14)	0.0291 (12)	0.0144 (13)
C8	0.0512 (10)	0.0434 (9)	0.0522 (10)	0.0103 (8)	0.0110 (8)	0.0108 (8)
C9	0.0477 (10)	0.0957 (17)	0.0521 (11)	0.0230 (11)	0.0076 (8)	0.0079 (11)
C10	0.115 (2)	0.0402 (11)	0.102 (2)	0.0101 (13)	0.0214 (17)	0.0085 (12)
C11	0.0636 (12)	0.0692 (13)	0.0612 (12)	0.0141 (10)	0.0234 (10)	0.0278 (10)

*Geometric parameters (Å, °)*

C11—P1	2.2869 (6)	C5—H53	0.9800
P1—N2	1.6519 (14)	C6—H61	0.9800
P1—N1	1.6584 (14)	C6—H62	0.9800
N1—C1	1.473 (2)	C6—H63	0.9800
N1—C4	1.496 (2)	C7—H71	0.9800
N2—C3	1.472 (2)	C7—H72	0.9800
N2—C8	1.502 (2)	C7—H73	0.9800
C1—C2	1.502 (3)	C8—C10	1.527 (3)
C1—H11	0.9900	C8—C9	1.527 (3)
C1—H12	0.9900	C8—C11	1.534 (3)
C2—C3	1.498 (3)	C9—H91	0.9800
C2—H21	0.9900	C9—H92	0.9800
C2—H22	0.9900	C9—H93	0.9800
C3—H31	0.9900	C10—H101	0.9800
C3—H32	0.9900	C10—H102	0.9800
C4—C5	1.526 (3)	C10—H103	0.9800
C4—C6	1.527 (3)	C11—H111	0.9800
C4—C7	1.529 (3)	C11—H112	0.9800
C5—H51	0.9800	C11—H113	0.9800
C5—H52	0.9800		
N2—P1—N1	102.93 (7)	H52—C5—H53	109.5
N2—P1—C11	100.22 (5)	C4—C6—H61	109.5



N1—P1—C11	100.57 (6)	C4—C6—H62	109.5
C1—N1—C4	114.76 (14)	H61—C6—H62	109.5
C1—N1—P1	121.73 (11)	C4—C6—H63	109.5
C4—N1—P1	119.69 (12)	H61—C6—H63	109.5
C3—N2—C8	115.07 (13)	H62—C6—H63	109.5
C3—N2—P1	121.39 (12)	C4—C7—H71	109.5
C8—N2—P1	119.34 (11)	C4—C7—H72	109.5
N1—C1—C2	111.20 (16)	H71—C7—H72	109.5
N1—C1—H11	109.4	C4—C7—H73	109.5
C2—C1—H11	109.4	H71—C7—H73	109.5
N1—C1—H12	109.4	H72—C7—H73	109.5
C2—C1—H12	109.4	N2—C8—C10	107.76 (17)
H11—C1—H12	108.0	N2—C8—C9	110.10 (16)
C3—C2—C1	112.13 (16)	C10—C8—C9	110.9 (2)
C3—C2—H21	109.2	N2—C8—C11	110.81 (15)
C1—C2—H21	109.2	C10—C8—C11	109.06 (19)
C3—C2—H22	109.2	C9—C8—C11	108.19 (17)
C1—C2—H22	109.2	C8—C9—H91	109.5
H21—C2—H22	107.9	C8—C9—H92	109.5
N2—C3—C2	111.45 (15)	H91—C9—H92	109.5
N2—C3—H31	109.3	C8—C9—H93	109.5
C2—C3—H31	109.3	H91—C9—H93	109.5
N2—C3—H32	109.3	H92—C9—H93	109.5
C2—C3—H32	109.3	C8—C10—H101	109.5
H31—C3—H32	108.0	C8—C10—H102	109.5
N1—C4—C5	110.44 (17)	H101—C10—H102	109.5
N1—C4—C6	108.04 (17)	C8—C10—H103	109.5
C5—C4—C6	110.3 (2)	H101—C10—H103	109.5
N1—C4—C7	111.19 (15)	H102—C10—H103	109.5
C5—C4—C7	108.4 (2)	C8—C11—H111	109.5
C6—C4—C7	108.5 (2)	C8—C11—H112	109.5
C4—C5—H51	109.5	H111—C11—H112	109.5
C4—C5—H52	109.5	C8—C11—H113	109.5
H51—C5—H52	109.5	H111—C11—H113	109.5
C4—C5—H53	109.5	H112—C11—H113	109.5
H51—C5—H53	109.5		
N2—P1—N1—C1	-33.19 (16)	C1—C2—C3—N2	59.3 (2)
C11—P1—N1—C1	69.98 (15)	C1—N1—C4—C5	-48.7 (2)
N2—P1—N1—C4	170.01 (13)	P1—N1—C4—C5	109.66 (18)
C11—P1—N1—C4	-86.82 (14)	C1—N1—C4—C6	72.0 (2)
N1—P1—N2—C3	33.52 (15)	P1—N1—C4—C6	-129.63 (17)
C11—P1—N2—C3	-69.94 (13)	C1—N1—C4—C7	-169.02 (19)
N1—P1—N2—C8	-170.64 (13)	P1—N1—C4—C7	-10.7 (2)
C11—P1—N2—C8	85.90 (13)	C3—N2—C8—C10	-72.3 (2)
C4—N1—C1—C2	-153.99 (17)	P1—N2—C8—C10	130.43 (17)
P1—N1—C1—C2	48.1 (2)	C3—N2—C8—C9	48.8 (2)
N1—C1—C2—C3	-58.7 (2)	P1—N2—C8—C9	-108.48 (16)

C8—N2—C3—C2	154.03 (17)	C3—N2—C8—C11	168.49 (17)
P1—N2—C3—C2	-49.2 (2)	P1—N2—C8—C11	11.2 (2)

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