

Tristram Chivers, James  
Grebinski, Masood Parvez\* and  
Zhiyong FuDepartment of Chemistry, The University of  
Calgary, 2500 University Drive NW, Calgary,  
Alberta, Canada T2N 1N4

Correspondence e-mail: parvez@ucalgary.ca

## Key indicators

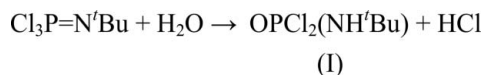
Single-crystal X-ray study  
 $T = 173$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.007$  Å  
 $R$  factor = 0.059  
 $wR$  factor = 0.165  
Data-to-parameter ratio = 23.2For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.*tert*-Butylamidodichlorophosphine oxideThe monomeric units in the title compound,  $\text{C}_4\text{H}_{10}\text{Cl}_2\text{NOP}$ , are linked together by  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds to give parallel linear strands along the  $b$  axis.

Received 5 July 2005

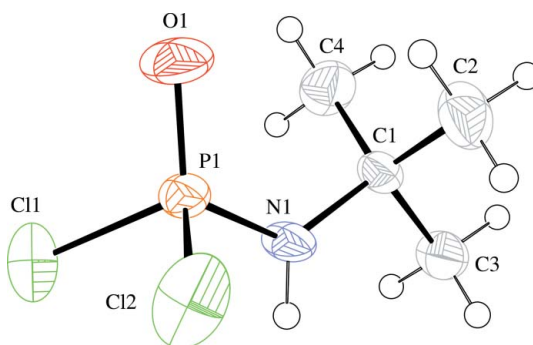
Accepted 6 July 2005

Online 13 July 2005

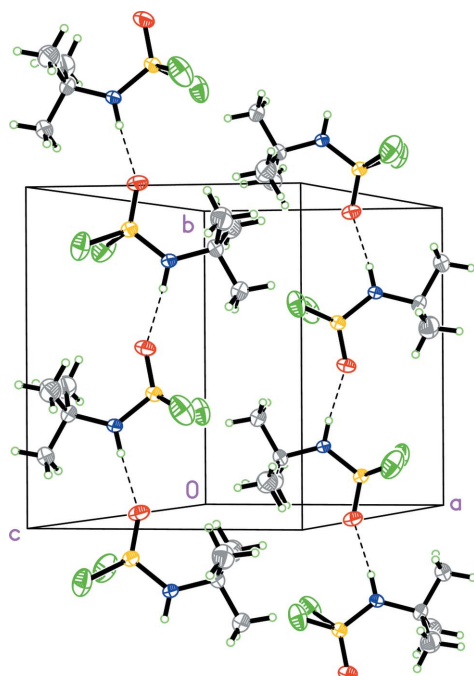
## Comment

Although the parent monoamidophosphoric acid  $\text{OP}(\text{OH})_2\text{NH}_2$  is well known (Emsley & Hall, 1976),  $N$ -substituted derivatives are not well characterized (Clark & Warren, 1963; Halmann & Lapidot, 1960). As part of our attempts to synthesize new  $N$ -substituted phosphoramidic acids, we investigated the reaction of *tert*-butylimidodichlorophosphorane with  $t\text{BuNH}_3\text{Cl}$  at 373 K for 24 h in the absence of a solvent. The monosubstituted derivative, (I), was isolated in *ca* 3% yield after sublimation. Compound (I) was obtained in a higher yield (23%) by exposing *tert*-butylimidodichlorophosphorane to moist air for 10 min.

The structure of (I) is composed of monomeric units (Fig. 1) linked together in parallel linear strands along the  $b$  axis by  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds (Fig. 2). The structure of  $\text{PO}(\text{NH}^t\text{Bu})_3$ , (II), also forms a one-dimensional chain through hydrogen-bonding but, in that case, there are three  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds to each O atom (Chivers *et al.*, 2003). Selected bond lengths and bond angles of (I) are listed in Table 1. The  $\text{P}=\text{O}$  double bond [ $\text{P}=\text{O} = 1.453$  (3) Å] is *ca* 0.02 Å shorter than that in (II). The greater  $\pi$ -bond character in (I) is attributed, in part, to the lower degree of hydrogen bonding per O atom. In addition, the two electronegative chlorine substituents on phosphorus in (I) will generate a more polar  $\text{P}^+-\text{O}^-$  bond, as reflected by the  $\text{P}-\text{N}$  bond length [ $\text{P}-\text{N} = 1.595$  (3) Å] which is *ca* 0.04 Å shorter than



**Figure 1**  
ORTEP (Johnson, 1976) drawing showing the monomeric unit of (I). Displacement ellipsoids are plotted at the 50% probability level.



**Figure 2**  
Packing diagram of the unit cell of (I). Hydrogen bonds are represented by dashed lines.

the mean P–N bond distance in (II). The unexpectedly large angle at N1 [C1–N1–P1 = 127.3 (3)°] presumably reflects the steric influence of the bulky *tert*-butyl substituent on N1.

## Experimental

*tert*-Butylimidoditrichlorophosphorane (1.65 g, 7.87 mmol) was exposed to air for 10 min and then the sample was stored under an atmosphere of nitrogen. After 24 h, clear colorless needle-like crystals were formed. X-ray quality single crystals of (I) (0.34 g, 1.79 mmol, 23% yield) were obtained by sublimation at 328 K at  $ca$   $10^{-3}$  Torr (m.p. = 379–381 K). Analysis calculated for  $C_4H_{10}Cl_2NOP$ : C 25.28, H 5.30, N, 7.37%; found: C 25.23, H 5.32, N 7.11%. NMR data ( $C_6D_6$ , 298 K):  $^1H$  NMR  $\delta$  0.99 (s, *t*Bu);  $^{13}C$  [ $^1H$ ] NMR:  $\delta$  30.62 [s,  $-C(CH_3)_3$ ], 55.79 [s,  $-C(CH_3)_3$ ];  $^{31}P$  [ $^1H$ ] NMR,  $\delta$  5.94 (s). IR ( $cm^{-1}$ ): 3180 (*m, br*, [ $\nu(N-H)$ ]), 1257 (*w, sh*, [ $\nu(P-N)$ ]), 1028 (*m*, [ $\nu(P=O)$ ]), 585 (*s*, [ $\nu(P-Cl)$ ]), 547 (*s*, [ $\nu(P-Cl)$ ]).

### Crystal data

$C_4H_{10}Cl_2NOP$	$D_x = 1.450$ Mg m $^{-3}$
$M_r = 190.00$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 6208 reflections
$a = 8.256$ (3) Å	$\theta = 3.3$ – $27.5^\circ$
$b = 10.219$ (5) Å	$\mu = 0.86$ mm $^{-1}$
$c = 11.053$ (5) Å	$T = 173$ (2) K
$\beta = 111.090$ (2)°	Prism, colorless
$V = 870.1$ (7) Å $^3$	$0.21 \times 0.08 \times 0.06$ mm
$Z = 4$	

### Data collection

Nonius KappaCCD diffractometer	1538 reflections with $I > 2\sigma(I)$
$\omega$ and $\varphi$ scans	$R_{int} = 0.034$
Absorption correction: multi-scan (SORTAV; Blessing, 1997)	$\theta_{max} = 27.5^\circ$
$T_{min} = 0.840$ , $T_{max} = 0.950$	$h = -10 \rightarrow 10$
6208 measured reflections	$k = -13 \rightarrow 11$
1970 independent reflections	$l = -14 \rightarrow 14$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 2.44P]$
$R[F^2 > 2\sigma(F^2)] = 0.059$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.165$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.08$	$\Delta\rho_{max} = 0.75$ e Å $^{-3}$
1970 reflections	$\Delta\rho_{min} = -0.46$ e Å $^{-3}$
85 parameters	H-atom parameters constrained

**Table 1**

Selected geometric parameters (Å, °).

P1–O1	1.453 (3)	P1–Cl2	2.0038 (17)
P1–N1	1.595 (3)	N1–C1	1.490 (5)
P1–Cl1	2.0025 (17)		
O1–P1–N1	116.98 (18)	N1–P1–Cl2	108.20 (15)
O1–P1–Cl1	111.76 (18)	Cl1–P1–Cl2	99.53 (8)
N1–P1–Cl1	106.53 (15)	Cl1–N1–P1	127.3 (3)
O1–P1–Cl2	112.28 (18)		

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1–H1 $\cdots$ O1 $^i$	0.88	1.95	2.820 (4)	168

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

H atoms were located in a difference Fourier synthesis and were included in the refinement at geometrically idealized positions, with N–H = 0.88 Å and C–H = 0.98 Å, and with  $U_{iso} = 1.2$  and 1.5 times  $U_{eq}$  of the parent N and C atoms, respectively. The final difference map was free of any chemically significant features.

Data collection: COLLECT (Hooft, 1998); cell refinement: DENZO (Otwinowski & Minor, 1997); data reduction: SCALEPACK (Otwinowski & Minor, 1997); program(s) used to solve structure: SIR92 (Altomare *et al.*, 1993); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97 (Sheldrick, 1997).

The authors acknowledge financial support from NSERC Canada and the Alberta Ingenuity Fund.

## References

- Altomare, A., Casciarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
- Chivers, T., Krahn, M., Schatte, G. & Parvez, M. (2003). *Inorg. Chem.* **42**, 3994–4005.
- Clark, V. M. & Warren, S. G. (1963). *Nature (London)*, **199**, 657–659.
- Emsley, J. & Hall, D. (1976). *The Chemistry of Phosphorus*, pp. 381–382. New York: John Wiley & Sons Inc.
- Halmann, M. & Lapidot, A. (1960). *J. Chem. Soc.* pp. 419–424.
- Hooft, R. (1998). COLLECT. Nonius BV, Delft, The Netherlands.
- Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (1997). SHELXL97. University of Göttingen, Germany.