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N,*N*′-Dimethyl-*N*″-(trichloroacetyl)-phosphoramide

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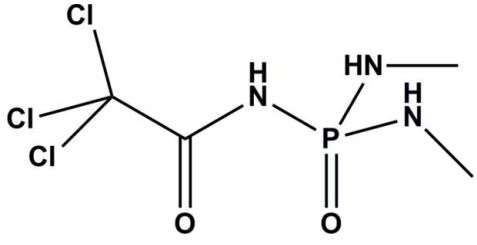
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; disorder in main residue; R factor = 0.077; wR factor = 0.195; data-to-parameter ratio = 12.2.

In the title compound, $C_4H_9Cl_3N_3O_2P$ or $CCl_3C(O)NHP(O)(NHCH_3)_2$, the P atom has a strongly distorted tetrahedral geometry due to the formation of intermolecular strong hydrogen bonds involving the N atoms. In the crystal, N—H···O=P and N—H···O=C hydrogen bonds connect the molecules into a two-dimensional array parallel to (100). An intramolecular P···O contact [P···O = 2.975 (3) Å] is observed. The CCl_3 group is rotationally disordered, with occupancies of 0.60 (3) and 0.40 (3)

Related literature

For the use of carbacylamidophosphates as potential new ligands for metal ions, see: Skopenko *et al.* (2004); Znovjyak *et al.* (2009); Yizhak *et al.* (2013); Gubina *et al.* (2009). For their biological activity, see: Amirkhanov *et al.* (1996); Rebrova *et al.* (1984). For P=O and C=O bond lengths, see: Mizrahi & Modro (1982); Amirkhanov *et al.* (1997); Gubina & Amirkhanov (2000). For the preparation of trichloroacetylamidophosphoric acid dichloranhydride, see: Kirsanov & Derkach (1956).



Experimental

Crystal data

$C_4H_9Cl_3N_3O_2P$
M_r = 268.46
Monoclinic, $P2_1/c$
a = 10.231 (2) Å
b = 8.754 (2) Å
c = 12.826 (3) Å
β = 101.27 (3)°
V = 1126.6 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.93 mm^{-1}
T = 293 K
0.4 × 0.3 × 0.3 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
3806 measured reflections
1908 independent reflections
1419 reflections with $I > 2\sigma(I)$
R_{int} = 0.060
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.077
$wR(F^2)$ = 0.195
S = 1.08
1908 reflections
157 parameters
33 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.82 e Å^{-3}
$\Delta\rho_{min}$ = −0.77 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.81 (3)	2.00 (4)	2.782 (5)	164 (5)
N3—H3···O1^{i}	0.81 (3)	2.21 (4)	2.953 (4)	153 (4)
N2—H2···O2^{ii}	0.81 (3)	2.38 (4)	3.077 (5)	146 (6)

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1995); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2520).

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supporting information

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N,*N*′-Dimethyl-*N*′′-(trichloroacetyl)phosphoramide

Vladimir Ovchynnikov

S1. Introduction

Carbacylamidophosphates of the general formula RC(O)NHP(O)R′$_2$ are potential new ligands for metal ions (Skopenko *et al.*, 2004; Znovjyak *et al.*, 2009; Gubina *et al.*, 2009). Many of these compounds also show biological activity (Amirkhanov *et al.*, 1996, Rebrova *et al.*, 1984). This work reports the structure of N,N′-Dimethyl-N′′-trichloracetyl-phosphoramide ($C_4H_9N_3O_2PCl_3$) (**I**).

S2. Experimental

S2.1. Synthesis and crystallization

The dichloranhydride of trichloroacetylamidophosphoric acid was prepared according to the method reported by Kirsanov (Kirsanov & Derkach, 1956). The dioxane solution (200 ml) of dichloranhydride of trichloroacetylamido-phosphoric acid (27.9 g, 0.1 mol) was placed in a three-neck round-bottomed flask and cooled by ice to 268 K. Then the dry methylamine was bubbled through the dioxane solution of $CCl_3C(O)NHP(O)Cl_2$ under stirring until the solution became alkaline. The temperature was not allowed to rise above 278 K. The stirring was continued for 1 h and the solution was left under ambient conditions. H_2NCH_3·HCl was filtered off after 12 h and the filtrate was evaporated. The oily precipitate of I was added to acetone which led to the formation of a white crystalline powder (yield 80%). White crystals suitable for X-ray analysis were obtained from slow evaporation of a 2-propanol solution.

S2.2. Refinement

H atoms of methyl groups were placed at calculated positions and treated as riding on the parent atoms, with U_{iso}(H) = 1.5 U_{eq}(C). H atoms of the amide group were located in a difference Fourier map and and further refined with similarity restraints for d(N—H) and U_{iso}(H) = 1.2U_{eq}(N). The CCl_3 group apperas rotationally disordered around the C1—C2 bond, with occupations of 0.60/0.40 (3)

S3. Results and discussion

In the title compound (**I**), the phosphorus environment has a strong distorted tetrahedral conformation due to the formation of strong N1—H1···O1 and N3—H3···O1 hydrogen bonds (Table 2, Fig.1). The N1—P—N3 angle has a value 98.72° and as a consequence there is an increase in the O1—P1—N3 and O1—P1—N1 angles (119.2° and 111.29°, respectively). The orientation of the C(O) and P(O) groups differs from the conformation of most CAF-ligands (Gubina & Amirkhanov, 2000), the angle between the O2C1N1 and N1PO1 planes having a value 57.3° (the pseudo-torsion angle O=C···P=O is -53.39°).

In the crystal, two intermolecular N–H···O=P hydrogen bonds connect molecules into a chain and a third N—H···O=C hydrogen bond connects the chains into a 2D array parallel to (100) (Fig.2). An intramolecular P···O contact is also present in the crystal [d(P···O) = 2.975 (3) Å], sorter than the sum of commonly accepted Van der Waals Radii (3.3 Å).

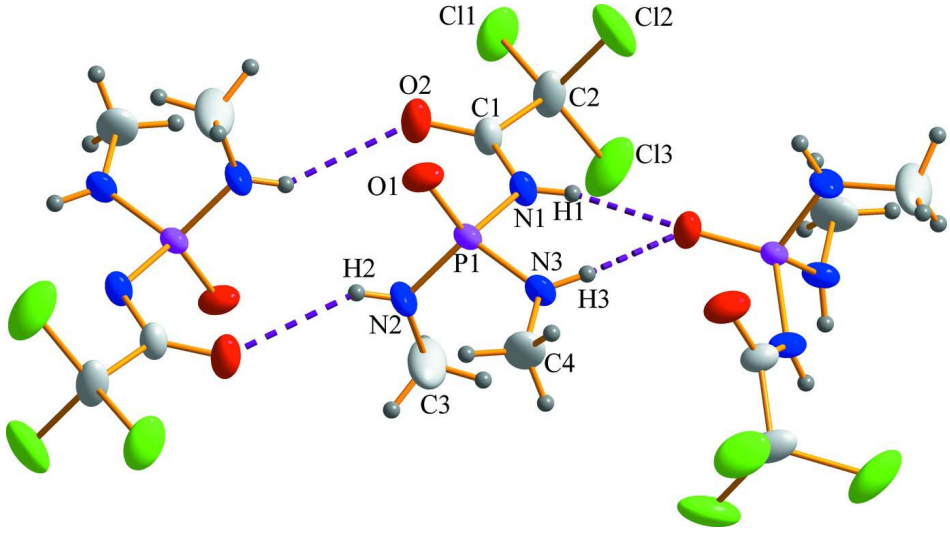

Figure 1

A view of the title compound (**I**) showing the atom-numbering scheme and the formation of three type of hydrogen bonds (dashed lines). Displacement ellipsoids drawn at a 30% probability level.

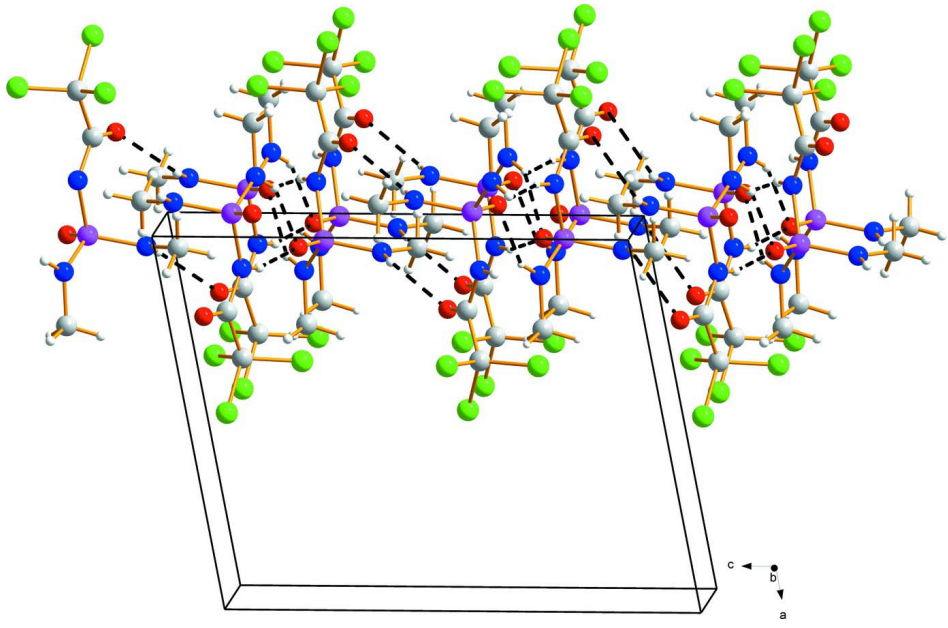

Figure 2

Packing view of (**I**) along the *b* axis. Only the major fraction of the CCl_3 group has been represented.

N,*N*′-Dimethyl-*N*″-(trichloroacetyl)phosphoramide

Crystal data

$C_4H_9Cl_3N_3O_2P$
M_r = 268.46
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 10.231 (2) Å
b = 8.754 (2) Å
c = 12.826 (3) Å
β = 101.27 (3)°
V = 1126.6 (4) Å^3
Z = 4
$F(000)$ = 544
D_x = 1.583 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2348 reflections
θ = 2.0–27.1°
μ = 0.93 mm^{-1}
T = 293 K
Block, colorless
0.4 × 0.3 × 0.3 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω/Θ scans
3806 measured reflections
1908 independent reflections
1419 reflections with $I > 2\sigma(I)$
R_{int} = 0.060
θ_{max} = 25.0°, θ_{min} = 2.0°
h = −12→12
k = 0→10
l = −15→15
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.077
$wR(F^2)$ = 0.195
S = 1.08
1908 reflections
157 parameters
33 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1369P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.82 e Å^{-3}
$\Delta\rho_{min}$ = −0.77 e Å^{-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 (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
P1	0.55195 (8)	0.17846 (12)	0.16971 (7)	0.0379 (4)	
Cl1	0.0184 (6)	0.1759 (10)	0.0571 (8)	0.098 (2)	0.60 (3)
Cl2	0.1528 (7)	0.2717 (16)	0.2675 (4)	0.108 (2)	0.60 (3)
Cl3	0.1588 (6)	0.4570 (7)	0.0816 (9)	0.114 (3)	0.60 (3)
Cl1A	0.0175 (8)	0.1557 (17)	0.0770 (15)	0.108 (5)	0.40 (3)
Cl2A	0.1466 (9)	0.321 (3)	0.2554 (10)	0.134 (5)	0.40 (3)
Cl3A	0.1524 (15)	0.434 (2)	0.050 (2)	0.185 (9)	0.40 (3)
O1	0.5607 (3)	0.0273 (4)	0.2191 (3)	0.0597 (8)	
O2	0.2813 (3)	0.0649 (4)	0.0732 (3)	0.0683 (10)	
N1	0.3994 (3)	0.2573 (4)	0.1646 (3)	0.0461 (8)	
H1	0.396 (5)	0.335 (5)	0.197 (4)	0.055*	
N2	0.5807 (5)	0.1646 (5)	0.0515 (3)	0.0668 (12)	
H2	0.602 (6)	0.080 (5)	0.036 (5)	0.080*	
N3	0.6418 (3)	0.3153 (4)	0.2290 (3)	0.0495 (9)	
H3	0.605 (4)	0.373 (6)	0.263 (3)	0.059*	

C1	0.2872 (4)	0.1851 (5)	0.1188 (3)	0.0508 (10)
C2	0.1579 (4)	0.2697 (6)	0.1287 (4)	0.0724 (15)
C3	0.5757 (12)	0.2923 (9)	−0.0197 (5)	0.130 (4)
H3A	0.6401	0.2781	−0.0641	0.195*
H3B	0.5954	0.3845	0.0208	0.195*
H3C	0.4882	0.2994	−0.0632	0.195*
C4	0.7862 (4)	0.3127 (8)	0.2458 (5)	0.0814 (17)
H4A	0.8171	0.4026	0.2152	0.122*
H4B	0.8145	0.2236	0.2126	0.122*
H4C	0.8226	0.3102	0.3207	0.122*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0356 (5)	0.0399 (6)	0.0419 (6)	0.0050 (3)	0.0166 (4)	0.0026 (4)
Cl1	0.049 (3)	0.089 (3)	0.137 (4)	−0.0087 (18)	−0.028 (3)	−0.040 (3)
Cl2	0.069 (3)	0.172 (6)	0.090 (3)	0.021 (3)	0.0296 (16)	−0.044 (4)
Cl3	0.059 (2)	0.058 (2)	0.198 (5)	0.0179 (14)	−0.041 (3)	−0.004 (3)
Cl1A	0.037 (3)	0.109 (7)	0.176 (9)	0.002 (3)	0.017 (4)	−0.075 (6)
Cl2A	0.040 (3)	0.161 (9)	0.208 (11)	−0.018 (4)	0.043 (4)	−0.130 (8)
Cl3A	0.116 (7)	0.096 (8)	0.292 (17)	0.032 (5)	−0.084 (9)	0.022 (9)
O1	0.0463 (14)	0.0482 (19)	0.086 (2)	0.0032 (12)	0.0153 (13)	0.0251 (16)
O2	0.0524 (17)	0.062 (2)	0.087 (2)	0.0047 (14)	0.0037 (15)	−0.0299 (18)
N1	0.0347 (15)	0.053 (2)	0.0496 (17)	0.0054 (14)	0.0070 (12)	−0.0148 (16)
N2	0.103 (3)	0.050 (3)	0.060 (2)	0.004 (2)	0.049 (2)	−0.0094 (19)
N3	0.0321 (16)	0.061 (2)	0.059 (2)	−0.0007 (13)	0.0171 (13)	−0.0123 (17)
C1	0.045 (2)	0.051 (3)	0.055 (2)	0.0054 (16)	0.0051 (17)	−0.0146 (19)
C2	0.039 (2)	0.072 (4)	0.099 (4)	0.006 (2)	−0.005 (2)	−0.034 (3)
C3	0.263 (11)	0.083 (5)	0.062 (3)	0.001 (6)	0.076 (5)	0.006 (3)
C4	0.038 (2)	0.090 (4)	0.119 (5)	−0.008 (2)	0.023 (2)	−0.016 (3)

Geometric parameters (Å, º)

P1—O1	1.462 (3)	N1—H1	0.81 (3)
P1—N2	1.605 (4)	N2—C3	1.437 (8)
P1—N3	1.608 (4)	N2—H2	0.81 (3)
P1—N1	1.696 (3)	N3—C4	1.451 (5)
Cl1—C2	1.744 (6)	N3—H3	0.81 (3)
Cl2—C2	1.791 (7)	C1—C2	1.544 (6)
Cl3—C2	1.748 (7)	C3—H3A	0.9600
Cl1A—C2	1.768 (8)	C3—H3B	0.9600
Cl2A—C2	1.710 (9)	C3—H3C	0.9600
Cl3A—C2	1.753 (9)	C4—H4A	0.9600
O2—C1	1.199 (5)	C4—H4B	0.9600
N1—C1	1.342 (5)	C4—H4C	0.9600
O1—P1—N2	109.5 (2)	C1—C2—Cl3A	106.1 (7)
O1—P1—N3	119.3 (2)	Cl2A—C2—Cl3A	109.4 (7)

N2—P1—N3	108.0 (2)	Cl1—C2—Cl3A	98.8 (8)
O1—P1—N1	111.30 (18)	C1—C2—Cl1A	110.2 (4)
N2—P1—N1	109.4 (2)	Cl2A—C2—Cl1A	107.6 (5)
N3—P1—N1	98.72 (18)	Cl3—C2—Cl1A	117.3 (7)
C1—N1—P1	121.8 (3)	Cl3A—C2—Cl1A	108.4 (6)
C1—N1—H1	120 (3)	C1—C2—Cl2	106.2 (4)
P1—N1—H1	118 (3)	Cl1—C2—Cl2	110.4 (5)
C3—N2—P1	123.4 (4)	Cl3—C2—Cl2	109.7 (5)
C3—N2—H2	122 (4)	Cl3A—C2—Cl2	124.1 (9)
P1—N2—H2	114 (4)	Cl1A—C2—Cl2	101.5 (6)
C4—N3—P1	122.0 (4)	N2—C3—H3A	109.5
C4—N3—H3	120 (3)	N2—C3—H3B	109.5
P1—N3—H3	116 (4)	H3A—C3—H3B	109.5
O2—C1—N1	125.7 (4)	N2—C3—H3C	109.5
O2—C1—C2	119.9 (4)	H3A—C3—H3C	109.5
N1—C1—C2	114.3 (4)	H3B—C3—H3C	109.5
C1—C2—Cl2A	115.0 (6)	N3—C4—H4A	109.5
C1—C2—Cl1	110.9 (4)	N3—C4—H4B	109.5
Cl2A—C2—Cl1	115.0 (5)	H4A—C4—H4B	109.5
C1—C2—Cl3	111.0 (4)	N3—C4—H4C	109.5
Cl2A—C2—Cl3	95.1 (8)	H4A—C4—H4C	109.5
Cl1—C2—Cl3	108.6 (5)	H4B—C4—H4C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.81 (3)	2.00 (4)	2.782 (5)	164 (5)
N3—H3···O1^{i}	0.81 (3)	2.21 (4)	2.953 (4)	153 (4)
N2—H2···O2^{ii}	0.81 (3)	2.38 (4)	3.077 (5)	146 (6)

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