

N-[Bis(dimethylamino)phosphinoyl]-2,2,2-trichloroacetamide

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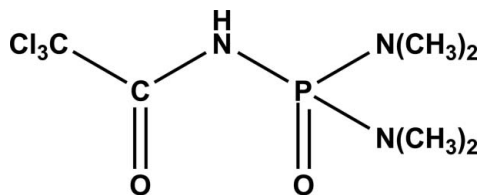
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.001$ Å; R factor = 0.030; wR factor = 0.072; data-to-parameter ratio = 39.1.

In the title compound, $\text{C}_6\text{H}_{13}\text{Cl}_3\text{N}_3\text{O}_2\text{P}$ or $\text{CCl}_3\text{C}(\text{O})\text{NH}-\text{P}(\text{O})(\text{N}(\text{CH}_3)_2)_2$, the phosphinoyl group is synclinal to the carbonyl group and acts as an acceptor for an intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond from the amide group as the donor.

Related literature

For the biological and pharmacological properties of carbacylamidophosphate derivatives, see: Adams *et al.* (2002); Grimes *et al.* (2008). For structural and conformation studies of related molecules, see: Gholivand *et al.* (2008*a,b*); Skopenko *et al.* (2004); Znovjyak *et al.* (2009*a,b*). For details of the synthesis, see: Kirsanov & Derkach (1956). For P—O bond lengths in compounds with amide substituents close to phosphorus atoms, see: Rebrova *et al.* (1982).



Experimental

Crystal data

$\text{C}_6\text{H}_{13}\text{Cl}_3\text{N}_3\text{O}_2\text{P}$

$M_r = 296.51$

Orthorhombic, $Pbca$

$a = 15.794$ (3) Å

$b = 15.820$ (3) Å

$c = 9.739$ (2) Å

$V = 2433.4$ (8) Å³

$Z = 8$

Mo $K\alpha$ radiation

$\mu = 0.87$ mm⁻¹

$T = 100$ K

$0.60 \times 0.40 \times 0.20$ mm

Data collection

Oxford Diffraction Xcalibur Sapphire2 (large Be window) diffractometer

Absorption correction: Gaussian (Coppens *et al.*, 1965)

$T_{\min} = 0.624$, $T_{\max} = 0.845$

35140 measured reflections

5631 independent reflections

4869 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.072$

$S = 1.15$

5631 reflections

144 parameters

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 0.46$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.40$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1N}\cdots\text{O1}^i$	0.828 (16)	1.968 (16)	2.7586 (11)	159.3 (16)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; 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, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: JH2144).

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supplementary materials

Acta Cryst. (2010). E66, o1102 [doi:10.1107/S1600536810013589]

***N*-[Bis(dimethylamino)phosphinoyl]-2,2,2-trichloroacetamide**

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Comment

P, N-substituted analogues of β -diketones – carbacylamidophosphates (CAPH), which comprise C(O)NHP(O) structural fragment, have attracted attention because of their using in pharmacology, as insecticides, pesticides and ureas inhibitor (Adams *et al.*, 2002; Grimes *et al.*, 2008). A variety of new coordination compounds with *s*-, *p*-, *d*- and *f*-metals based on the CAPH have been synthesized and characterized up to date (Skopenko *et al.*, 2004; Znovjyak *et al.*, 2009a). Thus, the syntheses and structure analysis of CAPH have been of increased interest (Gholivand *et al.*, 2008a). In this paper we report the crystal structure of a new CAPH – *N*-[bis(dimethylamino)phosphinoyl]-2,2,2-trichloroacetamide (**1**).

In the crystal packing molecules of **1** are linked to each other by intermolecular hydrogen bonds (N–H \cdots O), where amide nitrogen atom of one molecule acts as donor and oxygen atom of phosphinoyl group of neighboring molecule acts as acceptor (Fig. 2). The bond distance P(1)—O(1) (1.478 (1) Å) is typical for compounds with amide substituents close to phosphorus atoms (Rebrova *et al.*, 1982) and CAPH (Znovjyak *et al.*, 2009b). The values of C(1)—O(2) and C(1)—N(1) are 1.215 (1) Å and 1.355 (1) Å, respectively and close to the corresponding values of the CAPH (Gholivand *et al.*, 2008b). The P(1)—N(1) (1.714 (1) Å) distance in **1** is longer on average by 0.08 Å than P—N bond distances between amide substituents and phosphorus atoms (P(1)—N(2), P(1)—N(3)). The geometry around the phosphorus atom in **1** can be described as a distorted tetrahedron and which is similar to early reported CAPH. The O(1)—P(1)—N(1) angle value is close to near tetrahedral one (109.61 (4)°), while other O—P—N angels have values 113.19 (4)° and 116.53 (4)°, that may be explained by the repulsion between amide substituents and PO group. Fragment O(2)—C(1)—N(1)—P(1) is close to planarity (the torsion angle is -176.6°).

Experimental

The dichloranhydride of trichloroacetylamidophosphoric acid (CCl₃C(O)NHP(O)Cl₂) was prepared according to the method reported by Kirsanov (Kirsanov *et al.*, 1956).

The dioxane solution (200 ml) of CCl₃C(O)NHP(O)Cl₂ (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 dimethylamine (18.03 g, 0.4 mol) was bubbled through the dioxane solution of CCl₃C(O)NHP(O)Cl₂ 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. HN(CH₃)₂HCl was filtered off after 12 h and the filtrate was evaporated. The oily precipitate of **1** was isolated and recrystallized from 2-propanol which led to formation of white crystalline powder (yield 80%). White needle-shaped crystals suitable for X-ray analysis were formed over a period of 5 days from the 2-propanol/hexane solution. IR (KBr pellet, cm⁻¹): 3070 (ν (NH)), 1715 (ν (CO)), 1205 (ν (PO)), 1000 (ν (PN_{amine})), 867 (ν (PN_{amide})), 676 (ν (CCl)).

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 $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R-factors based on ALL data will be even larger.

Figures

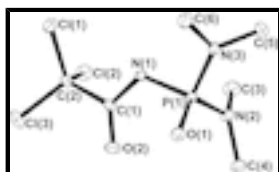


Fig. 1. Structural representation of **1** with atom numbering scheme and 50% probability thermal ellipsoid. The hydrogen atoms are omitted for clarity.

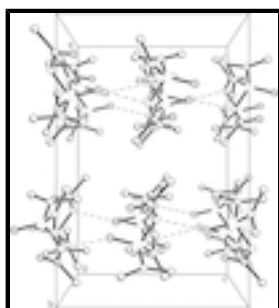


Fig. 2. A projection of packing diagram of the title compound along the y direction. Hydrogen bonds are indicated by dashed lines. H and Cl atoms are omitted for clarity.

N-[Bis(dimethylamino)phosphinoyl]-2,2,2-trichloroacetamide

Crystal data

$C_6H_{13}Cl_3N_3O_2P$

$M_r = 296.51$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 15.794(3) \text{ \AA}$

$b = 15.820(3) \text{ \AA}$

$c = 9.739(2) \text{ \AA}$

$V = 2433.4(8) \text{ \AA}^3$

$Z = 8$

$F(000) = 1216$

$D_x = 1.619 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 35140 reflections

$\theta = 3.6\text{--}36.1^\circ$

$\mu = 0.87 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Block, white

$0.60 \times 0.40 \times 0.20 \text{ mm}$

Data collection

Oxford Diffraction Xcalibur Sapphire2 (large Be window) diffractometer

5631 independent reflections

Radiation source: Enhance (Mo) X-ray Source graphite

4869 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

Detector resolution: 8.3359 pixels mm⁻¹ $\theta_{\max} = 36.1^\circ$, $\theta_{\min} = 3.6^\circ$
 ω scans $h = -26 \rightarrow 26$
 Absorption correction: gaussian $k = -25 \rightarrow 25$
 Coppens et al. (1965) $l = -12 \rightarrow 15$
 $T_{\min} = 0.624$, $T_{\max} = 0.845$
 35140 measured reflections

Refinement

Refinement on F^2 Primary atom site location: structure-invariant direct methods
 Least-squares matrix: full Secondary atom site location: difference Fourier map
 $R[F^2 > 2\sigma(F^2)] = 0.030$ Hydrogen site location: inferred from neighbouring sites
 $wR(F^2) = 0.072$ H atoms treated by a mixture of independent and constrained refinement
 $S = 1.15$ $w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 0.5268P]$
 5631 reflections where $P = (F_o^2 + 2F_c^2)/3$
 144 parameters $(\Delta/\sigma)_{\max} = 0.001$
 0 restraints $\Delta\rho_{\max} = 0.46 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.40 \text{ e } \text{\AA}^{-3}$

Special details

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

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
P1	0.285320 (15)	0.522358 (14)	0.42665 (2)	0.00982 (5)
C1	0.14518 (6)	0.60952 (6)	0.48883 (9)	0.01181 (14)
C2	0.06928 (6)	0.62610 (5)	0.58869 (9)	0.01177 (15)
Cl1	0.033556 (15)	0.534225 (14)	0.67522 (3)	0.01615 (5)
Cl2	0.104133 (16)	0.701650 (14)	0.71094 (2)	0.01672 (5)
Cl3	-0.015884 (16)	0.668869 (15)	0.49346 (3)	0.01985 (6)
O1	0.26191 (5)	0.51406 (5)	0.28033 (7)	0.01480 (12)
O2	0.15469 (5)	0.65692 (5)	0.39188 (8)	0.02050 (15)
N1	0.19672 (5)	0.54418 (5)	0.52192 (8)	0.01086 (13)
N2	0.35444 (5)	0.59761 (5)	0.45503 (8)	0.01341 (14)
N3	0.32000 (5)	0.43758 (5)	0.50197 (9)	0.01413 (14)
C3	0.36307 (7)	0.63290 (7)	0.59326 (10)	0.01877 (18)
H3A	0.3449	0.5908	0.6610	0.028*
H3B	0.3277	0.6835	0.6014	0.028*
H3C	0.4224	0.6479	0.6099	0.028*
C4	0.37770 (7)	0.65551 (6)	0.34435 (11)	0.01709 (17)

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H4A	0.3434	0.7070	0.3510	0.026*
H4B	0.3675	0.6282	0.2556	0.026*
H4C	0.4378	0.6702	0.3523	0.026*
C5	0.40306 (6)	0.42489 (7)	0.56243 (11)	0.01898 (18)
H5A	0.4371	0.4762	0.5507	0.028*
H5B	0.4313	0.3774	0.5169	0.028*
H5C	0.3969	0.4126	0.6605	0.028*
C6	0.26438 (7)	0.36368 (6)	0.51134 (12)	0.01950 (19)
H6A	0.2906	0.3158	0.4636	0.029*
H6B	0.2098	0.3767	0.4686	0.029*
H6C	0.2556	0.3491	0.6081	0.029*
H1N	0.1961 (10)	0.5241 (9)	0.6005 (17)	0.023 (4)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.01062 (9)	0.01090 (9)	0.00794 (9)	0.00005 (7)	0.00106 (7)	-0.00067 (7)
C1	0.0138 (4)	0.0121 (3)	0.0095 (3)	0.0019 (3)	-0.0007 (3)	-0.0001 (3)
C2	0.0123 (3)	0.0113 (3)	0.0117 (4)	0.0021 (3)	-0.0013 (3)	-0.0018 (3)
Cl1	0.01546 (10)	0.01469 (9)	0.01831 (11)	-0.00068 (7)	0.00464 (8)	0.00048 (7)
Cl2	0.02070 (10)	0.01642 (10)	0.01304 (10)	-0.00216 (7)	-0.00055 (8)	-0.00503 (7)
Cl3	0.01663 (10)	0.01936 (10)	0.02357 (12)	0.00705 (8)	-0.00704 (9)	-0.00265 (8)
O1	0.0174 (3)	0.0188 (3)	0.0082 (3)	-0.0010 (2)	0.0010 (2)	-0.0026 (2)
O2	0.0275 (4)	0.0196 (3)	0.0144 (3)	0.0069 (3)	0.0044 (3)	0.0073 (3)
N1	0.0119 (3)	0.0131 (3)	0.0076 (3)	0.0026 (2)	0.0013 (2)	0.0018 (2)
N2	0.0165 (3)	0.0145 (3)	0.0092 (3)	-0.0034 (3)	0.0001 (3)	-0.0002 (2)
N3	0.0116 (3)	0.0120 (3)	0.0188 (4)	0.0006 (2)	-0.0001 (3)	0.0027 (3)
C3	0.0226 (5)	0.0203 (4)	0.0134 (4)	-0.0056 (3)	-0.0021 (3)	-0.0032 (3)
C4	0.0195 (4)	0.0157 (4)	0.0160 (4)	-0.0041 (3)	0.0007 (3)	0.0031 (3)
C5	0.0147 (4)	0.0214 (4)	0.0208 (5)	0.0021 (3)	-0.0032 (4)	0.0047 (4)
C6	0.0177 (4)	0.0124 (4)	0.0284 (5)	-0.0003 (3)	0.0031 (4)	0.0013 (3)

Geometric parameters (\AA , $^\circ$)

P1—O1	1.4780 (8)	N3—C6	1.4652 (13)
P1—N3	1.6239 (8)	C3—H3A	0.9800
P1—N2	1.6388 (8)	C3—H3B	0.9800
P1—N1	1.7141 (8)	C3—H3C	0.9800
C1—O2	1.2151 (11)	C4—H4A	0.9800
C1—N1	1.3546 (12)	C4—H4B	0.9800
C1—C2	1.5658 (13)	C4—H4C	0.9800
C2—Cl3	1.7684 (9)	C5—H5A	0.9800
C2—Cl1	1.7723 (10)	C5—H5B	0.9800
C2—Cl2	1.7745 (9)	C5—H5C	0.9800
N1—H1N	0.828 (16)	C6—H6A	0.9800
N2—C4	1.4614 (13)	C6—H6B	0.9800
N2—C3	1.4637 (13)	C6—H6C	0.9800
N3—C5	1.4518 (13)		

O1—P1—N3	116.53 (4)	N2—C3—H3A	109.5
O1—P1—N2	113.19 (4)	N2—C3—H3B	109.5
N3—P1—N2	107.40 (4)	H3A—C3—H3B	109.5
O1—P1—N1	109.61 (4)	N2—C3—H3C	109.5
N3—P1—N1	101.37 (4)	H3A—C3—H3C	109.5
N2—P1—N1	107.83 (4)	H3B—C3—H3C	109.5
O2—C1—N1	125.55 (9)	N2—C4—H4A	109.5
O2—C1—C2	118.29 (8)	N2—C4—H4B	109.5
N1—C1—C2	116.12 (8)	H4A—C4—H4B	109.5
C1—C2—C13	108.70 (6)	N2—C4—H4C	109.5
C1—C2—C11	113.68 (6)	H4A—C4—H4C	109.5
C13—C2—C11	108.72 (5)	H4B—C4—H4C	109.5
C1—C2—C12	106.98 (6)	N3—C5—H5A	109.5
C13—C2—C12	109.28 (5)	N3—C5—H5B	109.5
C11—C2—C12	109.40 (5)	H5A—C5—H5B	109.5
C1—N1—P1	121.03 (7)	N3—C5—H5C	109.5
C1—N1—H1N	120.3 (11)	H5A—C5—H5C	109.5
P1—N1—H1N	115.7 (11)	H5B—C5—H5C	109.5
C4—N2—C3	114.58 (8)	N3—C6—H6A	109.5
C4—N2—P1	119.89 (7)	N3—C6—H6B	109.5
C3—N2—P1	119.62 (7)	H6A—C6—H6B	109.5
C5—N3—C6	113.97 (8)	N3—C6—H6C	109.5
C5—N3—P1	127.02 (7)	H6A—C6—H6C	109.5
C6—N3—P1	119.00 (7)	H6B—C6—H6C	109.5
O2—C1—C2—C13	32.74 (11)	N3—P1—N2—C4	138.23 (8)
N1—C1—C2—C13	-149.48 (7)	N1—P1—N2—C4	-113.24 (8)
O2—C1—C2—C11	153.97 (8)	O1—P1—N2—C3	159.66 (7)
N1—C1—C2—C11	-28.25 (10)	N3—P1—N2—C3	-70.29 (8)
O2—C1—C2—C12	-85.16 (10)	N1—P1—N2—C3	38.24 (9)
N1—C1—C2—C12	92.62 (8)	O1—P1—N3—C5	118.05 (9)
O2—C1—N1—P1	1.02 (14)	N2—P1—N3—C5	-10.10 (10)
C2—C1—N1—P1	-176.58 (6)	N1—P1—N3—C5	-123.08 (9)
O1—P1—N1—C1	-53.07 (8)	O1—P1—N3—C6	-61.17 (9)
N3—P1—N1—C1	-176.80 (7)	N2—P1—N3—C6	170.68 (7)
N2—P1—N1—C1	70.54 (8)	N1—P1—N3—C6	57.70 (8)
O1—P1—N2—C4	8.18 (9)		

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>
N1—H1N···O1 ⁱ	0.828 (16)	1.968 (16)	2.7586 (11)	159.3 (16)

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

Fig. 1

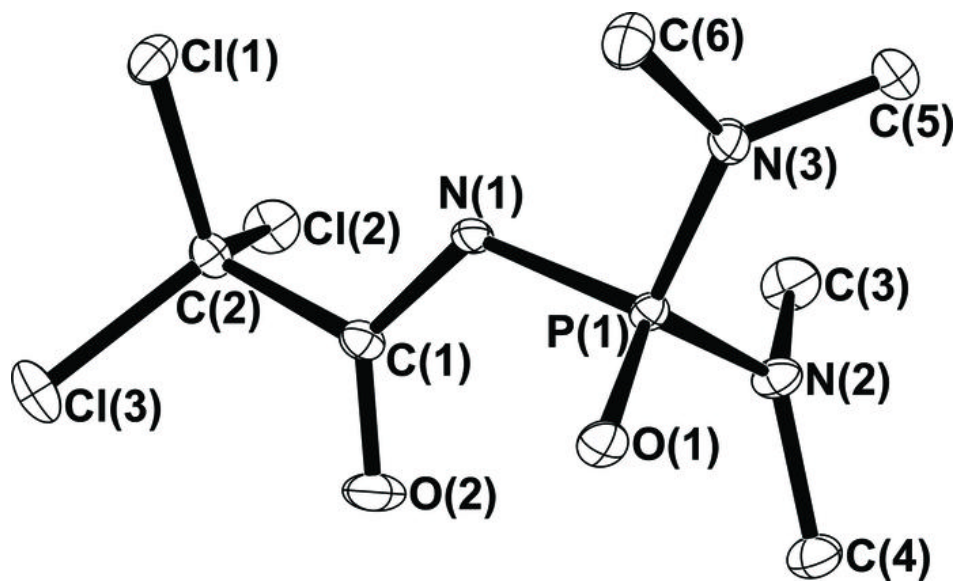


Fig. 2

