N-(2-Chloro-2,2-difluoroacetyl)-N',N''-diisopropylphosphoric triamide

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In the title compound, $C_8H_{17}ClF_2N_3O_2P$, the phosphoryl group and the NH unit of the C(O)NHP(O) moiety adopt a *syn* conformation with respect to each other. The P atom is in a tetrahedral coordination environment and the environment of the N atom of the C(O)NHP(O) moiety is essentially planar. In the crystal, adjacent molecules are linked *via* N—H···O=P and N—H···O=C hydrogen bonds, building $R_2^2(8)$ and $R_2^2(12)$ rings in a linear arrangement parallel to [110].

Related literature

For metal complexes of phosphoryl donor ligands, see: Gholivand *et al.* (2010). For a phosphoric triamide compound having a C(=O)NHP(=O) skeleton, see: Pourayoubi *et al.* (2010). For hydrogen-bond motifs, see: Etter *et al.* (1990); Bernstein *et al.* (1995). For the synthesis of the starting material, $CClF_2C(O)NHP(O)Cl_2$, see: Iriarte *et al.* (2008).
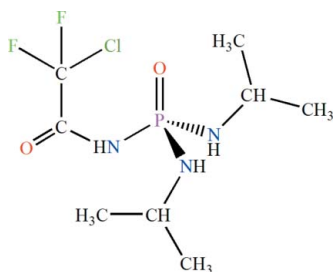
Experimental

Crystal data

$C_8H_{17}ClF_2N_3O_2P$
$M_r = 291.67$

Triclinic, $P\overline{1}$
$a = 8.1993$ (7) Å
$b = 9.6735$ (9) Å
$c = 9.8331$ (9) Å
$\alpha = 99.784$ (2)°
$\beta = 105.999$ (2)°
$\gamma = 110.770$ (2)°
$V = 669.18$ (10) Å^3

$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.42$ mm^{-1}
$T = 100$ K
$0.26 \times 0.19 \times 0.16$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.602$, $T_{max} = 0.750$

9089 measured reflections
4218 independent reflections
3337 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.095$
$S = 1.04$
4218 reflections

158 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^i	0.88	1.87	2.7295 (13)	164
N3—H3···O1^{ii}	0.85	2.14	2.9645 (14)	163

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

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supplementary materials

N-(2-Chloro-2,2-difluoroacetyl)-*N'*,*N''*-diisopropylphosphoric triamide

M. Pourayoubi and **A. Saneei**

Comment

Carbacylamidophosphates with a –C(O)NHP(O)- skeleton have attracted attention because of their roles as the *O,O'*-donor ligands for metal complexation (Gholivand *et al.*, 2010). Following our previous works about phosphorus compounds containing C(O)NHP(O) moiety such as P(O)[NHC(O)C$_6$H$_3$(2,6-F$_2$)][NHC(CH$_3$)$_3$]$_2$ (Pourayoubi *et al.*, 2010), we report here on the synthesis and crystal structure of P(O)[NHC(O)CClF$_2$][NH(C$_3$H$_7$)]$_2$. Single crystals of title compound were obtained from a solution of CH$_3$OH and CH$_3$CN after a slow evaporation at room temperature.

The phosphoryl group and NH unit are *syn* to each other and the phosphorus atom has a slightly distorted tetrahedral configuration (Fig. 1). The bond angles around the P atom are in the range of 103.30 (6)° to 119.69 (6)°. The P—N2 and P—N3 bonds (with bond lengths of 1.6262 (12) Å and 1.6190 (11) Å) are shorter than the P—N1 bond (1.7039 (11) Å). The environment of nitrogen N1 atom is essentially planar. The P=O bond length of 1.4768 (9) Å is standard for phosphoramidate compounds.

In the crystal structure, adjacent molecules are linked *via* N—H···O =P and N—H···O =C hydrogen bonds, building R_2^2(8) and R_2^2(12) rings (Etter *et al.*, 1990; Bernstein *et al.*, 1995) in a linear arrangement parallel to the *ab* plane in the direction of [110] axis (Table 1, Fig. 2).

Experimental

Synthesis of CClF$_2$C(O)NHP(O)Cl$_2$ CClF$_2$C(O)NHP(O)Cl$_2$ was prepared according to procedure reported by Iriarte *et al.* (2008) from a reaction between phosphorus pentachloride (16.91 mmol) and CClF$_2$C(O)NH$_2$ (16.91 mmol) in dry CCl$_4$ at 358 K (3 h) and then the treatment of formic acid (16.91 mmol) at ice bath temperature; then removing of solvent in vacuum to yield CClF$_2$C(O)NHP(O)Cl$_2$.

Synthesis of title compound To a solution of CClF$_2$C(O)NHP(O)Cl$_2$ (2.09 mmol) in dry CHCl$_3$, a solution of *N-iso*-propylamine (8.36 mmol) in dry CHCl$_3$ was added dropwise and stirred at 273 K. After 4 h, the solvent was evaporated at room temperature. The solid was washed with H$_2$O. The product was obtained after recrystallization from a methanol/acetonitrile mixture (4:1) after a slow evaporation at room temperature. **IR** (KBr, cm^{-1}): 3400, 3057, 2910, 2890, 2730, 1740 (C=O), 1500, 1260, 1218, 1165, 1118, 1095, 978, 920, 840, 738, 720.

Refinement

All H atoms attached to C atoms and the planar N1 atom were fixed geometrically and treated as riding with C—H = 0.98 Å (methyl) or 1.0 Å (methine) and N—H = 0.86 Å with U$_{iso}$(H) = 1.2U$_{eq}$(C$_{methine}$ or N) or U$_{iso}$(H) = 1.5U$_{eq}$(CH3). H atoms for N2 and N3 were located in difference Fourier maps and included in the subsequent refinement using restraints (N-H= 0.86 (1)Å with U$_{iso}$(H) = 1.5U$_{eq}$(N). In the last cycles of refinement they were treated as riding on their parent N atoms.
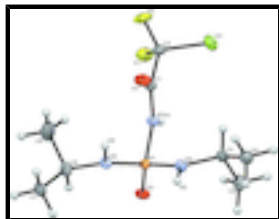
supplementary materials

Figures

Fig. 1. An *ORTEP*-style plot of title compound with the atom labeling scheme. Ellipsoids are shown at the 50% probability level. H atoms are represented as small spheres of arbitrary radii.
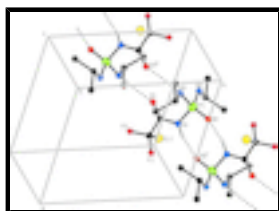

Fig. 2. Partial packing view showing the formation of the chain through N-H⋯O hydrogen bonds which are shown as dashed lines. H atoms not involved in hydrogen bondings have been omitted for the sake of clarity. [Symmetry codes: (i) -*x*+1, -*y*+2, -*z*; (ii) -*x*, -*y*+1, -*z*]

N-(2-Chloro-2,2-difluoroacetyl)-*N'*,*N''*- diisopropylphosphoric triamide

Crystal data

$C_8H_{17}ClF_2N_3O_2P$	$Z = 2$
$M_r = 291.67$	$F(000) = 304$
Triclinic, $P\overline{1}$	$D_x = 1.448$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.1993$ (7) Å	Cell parameters from 2867 reflections
$b = 9.6735$ (9) Å	$\theta = 2.3–30.9°$
$c = 9.8331$ (9) Å	$\mu = 0.42$ mm^{-1}
$\alpha = 99.784$ (2)°	$T = 100$ K
$\beta = 105.999$ (2)°	Prizm, colorless
$\gamma = 110.770$ (2)°	$0.26 \times 0.19 \times 0.16$ mm
$V = 669.18$ (10) Å^3	

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	4218 independent reflections
Radiation source: fine-focus sealed tube	3337 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.024$
φ and ω scans	$\theta_{max} = 31.0°$, $\theta_{min} = 2.3°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$h = -11 \rightarrow 11$
$T_{min} = 0.602$, $T_{max} = 0.750$	$k = -14 \rightarrow 14$
9089 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods

Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.036$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.095$	H-atom parameters constrained
$S = 1.04$	$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.0127P]$ where $P = (F_o^2 + 2F_c^2)/3$
4218 reflections	$(\Delta/\sigma)_{max} < 0.001$
158 parameters	$\Delta\rho_{max} = 0.56$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.30$ 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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, convention-al 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. 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.

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

	x	y	z	U_{iso}*/U_{eq}
P1	0.23257 (4)	0.86972 (4)	0.03714 (4)	0.01390 (8)
Cl1	0.30477 (6)	0.56630 (4)	−0.36890 (4)	0.03081 (10)
F1	0.54717 (11)	0.63181 (10)	−0.11562 (10)	0.0284 (2)
F2	0.31465 (14)	0.40675 (9)	−0.19141 (11)	0.0322 (2)
O1	0.10801 (14)	0.52987 (10)	−0.10574 (11)	0.0238 (2)
O2	0.37834 (13)	1.03015 (10)	0.10823 (10)	0.0196 (2)
N1	0.33089 (14)	0.77459 (12)	−0.05183 (12)	0.0146 (2)
H1	0.4368	0.8292	−0.0609	0.018*
N2	0.03816 (15)	0.83557 (13)	−0.09290 (12)	0.0182 (2)
H2	−0.0483	0.8420	−0.0661	0.022*
N3	0.16459 (15)	0.79008 (12)	0.15566 (12)	0.0155 (2)
H3	0.0753	0.6993	0.1225	0.019*
C1	0.25344 (17)	0.61960 (14)	−0.10878 (14)	0.0153 (2)
C2	0.36184 (19)	0.55503 (15)	−0.18656 (15)	0.0192 (3)
C3	0.02381 (19)	0.84469 (16)	−0.24394 (15)	0.0201 (3)
H3A	0.0704	0.7721	−0.2874	0.024*
C4	−0.1816 (2)	0.78961 (18)	−0.33779 (16)	0.0259 (3)
H4A	−0.2525	0.6837	−0.3386	0.039*
H4B	−0.1939	0.7916	−0.4394	0.039*
H4C	−0.2309	0.8581	−0.2959	0.039*
C5	0.1427 (2)	1.00657 (18)	−0.24315 (16)	0.0262 (3)
H5A	0.2750	1.0341	−0.1889	0.039*
H5B	0.1051	1.0809	−0.1947	0.039*

H5C	0.1246	1.0090	−0.3453	0.039*
C6	0.29579 (18)	0.82087 (16)	0.30596 (15)	0.0208 (3)
H6A	0.3976	0.9277	0.3361	0.025*
C7	0.1941 (2)	0.81568 (18)	0.41385 (16)	0.0268 (3)
H7A	0.1366	0.8888	0.4081	0.040*
H7B	0.2834	0.8442	0.5148	0.040*
H7C	0.0965	0.7108	0.3884	0.040*
C8	0.3848 (3)	0.7080 (2)	0.3090 (2)	0.0390 (4)
H8A	0.4568	0.7195	0.2437	0.058*
H8B	0.2867	0.6020	0.2749	0.058*
H8C	0.4685	0.7294	0.4105	0.058*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.01625 (15)	0.00992 (14)	0.01683 (16)	0.00349 (11)	0.01039 (12)	0.00433 (11)
Cl1	0.0425 (2)	0.0345 (2)	0.02119 (18)	0.01780 (18)	0.01803 (16)	0.00824 (15)
F1	0.0208 (4)	0.0305 (5)	0.0358 (5)	0.0133 (4)	0.0117 (4)	0.0065 (4)
F2	0.0469 (6)	0.0162 (4)	0.0489 (6)	0.0186 (4)	0.0300 (5)	0.0147 (4)
O1	0.0247 (5)	0.0128 (4)	0.0318 (5)	0.0005 (4)	0.0187 (4)	0.0040 (4)
O2	0.0237 (5)	0.0115 (4)	0.0233 (5)	0.0026 (4)	0.0158 (4)	0.0030 (4)
N1	0.0148 (5)	0.0108 (5)	0.0195 (5)	0.0034 (4)	0.0109 (4)	0.0043 (4)
N2	0.0203 (5)	0.0223 (5)	0.0191 (5)	0.0112 (5)	0.0126 (4)	0.0091 (4)
N3	0.0153 (5)	0.0125 (5)	0.0161 (5)	0.0012 (4)	0.0081 (4)	0.0042 (4)
C1	0.0178 (6)	0.0119 (5)	0.0171 (6)	0.0054 (5)	0.0089 (5)	0.0047 (4)
C2	0.0243 (7)	0.0134 (6)	0.0246 (7)	0.0089 (5)	0.0131 (5)	0.0076 (5)
C3	0.0255 (7)	0.0244 (7)	0.0177 (6)	0.0151 (6)	0.0118 (5)	0.0076 (5)
C4	0.0262 (7)	0.0281 (7)	0.0222 (7)	0.0131 (6)	0.0066 (6)	0.0045 (6)
C5	0.0276 (7)	0.0329 (8)	0.0226 (7)	0.0121 (6)	0.0129 (6)	0.0148 (6)
C6	0.0176 (6)	0.0220 (6)	0.0180 (6)	0.0032 (5)	0.0057 (5)	0.0069 (5)
C7	0.0352 (8)	0.0334 (8)	0.0180 (6)	0.0181 (7)	0.0124 (6)	0.0099 (6)
C8	0.0395 (9)	0.0669 (12)	0.0355 (9)	0.0384 (9)	0.0212 (8)	0.0278 (9)

Geometric parameters (Å, °)

P1—O2	1.4768 (9)	C3—H3A	1.0000
P1—N3	1.6190 (11)	C4—H4A	0.9800
P1—N2	1.6262 (12)	C4—H4B	0.9800
P1—N1	1.7039 (11)	C4—H4C	0.9800
Cl1—C2	1.7566 (14)	C5—H5A	0.9800
F1—C2	1.3366 (16)	C5—H5B	0.9800
F2—C2	1.3351 (15)	C5—H5C	0.9800
O1—C1	1.2127 (15)	C6—C8	1.513 (2)
N1—C1	1.3447 (15)	C6—C7	1.5164 (19)
N1—H1	0.8800	C6—H6A	1.0000
N2—C3	1.4775 (17)	C7—H7A	0.9800
N2—H2	0.8390	C7—H7B	0.9800
N3—C6	1.4754 (17)	C7—H7C	0.9800
N3—H3	0.8536	C8—H8A	0.9800

C1—C2	1.5399 (17)	C8—H8B	0.9800
C3—C5	1.520 (2)	C8—H8C	0.9800
C3—C4	1.5207 (19)		
O2—P1—N3	112.27 (5)	C3—C4—H4A	109.5
O2—P1—N2	119.69 (6)	C3—C4—H4B	109.5
N3—P1—N2	103.94 (6)	H4A—C4—H4B	109.5
O2—P1—N1	105.13 (5)	C3—C4—H4C	109.5
N3—P1—N1	112.31 (5)	H4A—C4—H4C	109.5
N2—P1—N1	103.30 (6)	H4B—C4—H4C	109.5
C1—N1—P1	122.76 (9)	C3—C5—H5A	109.5
C1—N1—H1	118.6	C3—C5—H5B	109.5
P1—N1—H1	118.6	H5A—C5—H5B	109.5
C3—N2—P1	123.77 (9)	C3—C5—H5C	109.5
C3—N2—H2	116.2	H5A—C5—H5C	109.5
P1—N2—H2	117.0	H5B—C5—H5C	109.5
C6—N3—P1	121.89 (8)	N3—C6—C8	111.29 (12)
C6—N3—H3	112.7	N3—C6—C7	109.51 (11)
P1—N3—H3	117.9	C8—C6—C7	111.49 (12)
O1—C1—N1	126.01 (12)	N3—C6—H6A	108.1
O1—C1—C2	118.79 (11)	C8—C6—H6A	108.1
N1—C1—C2	115.19 (10)	C7—C6—H6A	108.1
F2—C2—F1	107.66 (11)	C6—C7—H7A	109.5
F2—C2—C1	109.72 (10)	C6—C7—H7B	109.5
F1—C2—C1	112.14 (11)	H7A—C7—H7B	109.5
F2—C2—Cl1	108.56 (10)	C6—C7—H7C	109.5
F1—C2—Cl1	108.94 (9)	H7A—C7—H7C	109.5
C1—C2—Cl1	109.74 (9)	H7B—C7—H7C	109.5
N2—C3—C5	111.99 (11)	C6—C8—H8A	109.5
N2—C3—C4	108.48 (11)	C6—C8—H8B	109.5
C5—C3—C4	112.00 (12)	H8A—C8—H8B	109.5
N2—C3—H3A	108.1	C6—C8—H8C	109.5
C5—C3—H3A	108.1	H8A—C8—H8C	109.5
C4—C3—H3A	108.1	H8B—C8—H8C	109.5
O2—P1—N1—C1	168.43 (10)	O1—C1—C2—F2	−22.92 (17)
N3—P1—N1—C1	46.05 (12)	N1—C1—C2—F2	158.19 (11)
N2—P1—N1—C1	−65.33 (11)	O1—C1—C2—F1	−142.50 (13)
O2—P1—N2—C3	72.29 (12)	N1—C1—C2—F1	38.60 (15)
N3—P1—N2—C3	−161.47 (10)	O1—C1—C2—Cl1	96.28 (13)
N1—P1—N2—C3	−44.04 (11)	N1—C1—C2—Cl1	−82.62 (12)
O2—P1—N3—C6	−36.29 (12)	P1—N2—C3—C5	−61.53 (14)
N2—P1—N3—C6	−167.07 (10)	P1—N2—C3—C4	174.35 (9)
N1—P1—N3—C6	81.94 (11)	P1—N3—C6—C8	−89.23 (13)
P1—N1—C1—O1	0.56 (19)	P1—N3—C6—C7	147.05 (10)
P1—N1—C1—C2	179.37 (9)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

N1—H1⋯O2^{i}	0.88	1.87	2.7295 (13)	164
N3—H3⋯O1^{ii}	0.85	2.14	2.9645 (14)	163

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

Fig. 1

Fig. 2