Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

N,*N*-Dimethyl-*N*′,*N*″-diphenylphosphoric triamide

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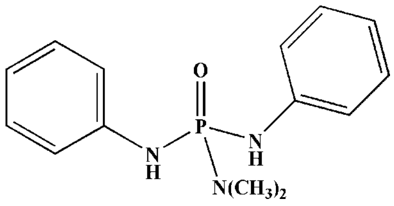
Received 27 October 2011; accepted 1 November 2011

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.028; wR factor = 0.084; data-to-parameter ratio = 12.2.

In the title compound, $C_{14}H_{18}N_3OP$, a crystallographic mirror plane bisects the molecule (the C,N,C atoms of the dimethylamido moiety and the P=O unit lie on the mirror plane). The P atom has a distorted tetrahedral geometry; the bond angles at P are in the range 98.98 (11)–115.28 (7)°. In the crystal, the O atom of the P=O group acts as a double hydrogen-bond acceptor for two symmetry-equivalent N—H⋯O hydrogen bonds, building [001] chains containing $R_2^1(6)$ loops.

Related literature

For bond lengths and angles in compounds having a $[(N)P(O)(N)_2]$ skeleton, see: Sabbaghi *et al.* (2011). For the double hydrogen-bond acceptor capability of the phosphoryl group, see: Pourayoubi *et al.* (2011).



Experimental

Crystal data

$C_{14}H_{18}N_3OP$
M_r = 275.28
Orthorhombic, $Cmc2_1$
a = 15.501 (3) Å
b = 10.8569 (17) Å
c = 8.1579 (13) Å
V = 1372.9 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.20 mm^{-1}
T = 100 K
0.60 × 0.15 × 0.13 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.891, T_{max} = 0.975
5356 measured reflections
1317 independent reflections
1272 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.084
S = 1.04
1317 reflections
108 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Absolute structure: Flack (1983), 604 Friedel pairs
Flack parameter: −0.11 (10)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1A⋯O1^i	0.88	2.22	2.982 (2)	145

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

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: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXTL* and *enCIFer* (Allen *et al.*, 2004).

Support of this investigation by the Ferdowsi University of Mashhad is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6483).

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supporting information

Acta Cryst. (2011). E**67**, o3220 [https://doi.org/10.1107/S1600536811046058]

N,*N*-Dimethyl-*N*′,*N*′′-diphenylphosphoric triamide

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S1. Comment

The title molecule, Fig. 1, has crystallographically imposed mirror symmetry. In the $(CH_3)_2NP(O)$ unit, the O—P—N—C torsion angles, showing the orientations of the methyl groups with respect to the phosphoryl group, are 0.0 and 180.0°.

The P═O and P—N bond lengths and the C—N—P bond angles match those found for the other compounds having a $[(N)P(O)(N)_2]$ skeleton (Sabbaghi *et al.*, 2011).

The tetrahedral geometry of the phosphorus atom is significantly distorted as it has been noted for the other phosphoric triamides: the bond angles at the P atom vary in the range from 98.98 (11) [N1^i—P1—N1; symmetry code (i): -x, y, z] to 115.28 (7)° [O1—P1—N1].

The O atom of the P═O group acts as a double hydrogen-bond acceptor (Pourayoubi *et al.*, 2011) to form the $[N—H]_2\cdots O(P)$ grouping within a 1-D hydrogen-bonded arrangement along the *c* axis (Fig. 2, Table 1).

S2. Experimental

Synthesis of $((CH_3)_2N)P(O)Cl_2$: $[(CH_3)_2NH_2]Cl$ (0.184 mol) and $P(O)Cl_3$ (0.552 mol) were refluxed for 8 h and afterwards the excess of $P(O)Cl_3$ was removed in vacuum.

Synthesis of title compound: to a solution of $((CH_3)_2N)P(O)Cl_2$ (3.7 mmol) in CH_3CN (15 ml), a solution of aniline (14.8 mmol) in CH_3CN (25 ml) was added at 273 K. After 4 h stirring, the solvent was removed and product was washed with deionized water and recrystallized from CH_3CN at room temperature to yield colourless rods.

S3. Refinement

The H4, H11, H12 and H13 were found in difference Fourier maps and refined with isotropic displacement parameters. The others hydrogen atom positions of the C-H and N-H units were calculated and refined in a riding-model with appropriate HFIX command in SHELXL-97.

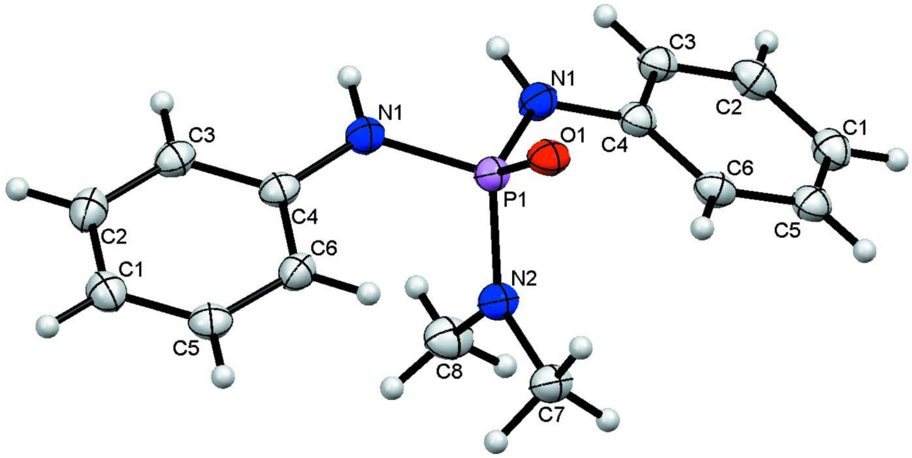

Figure 1

The molecular structure of the title compound with ellipsoids shown at the 50% probability level.

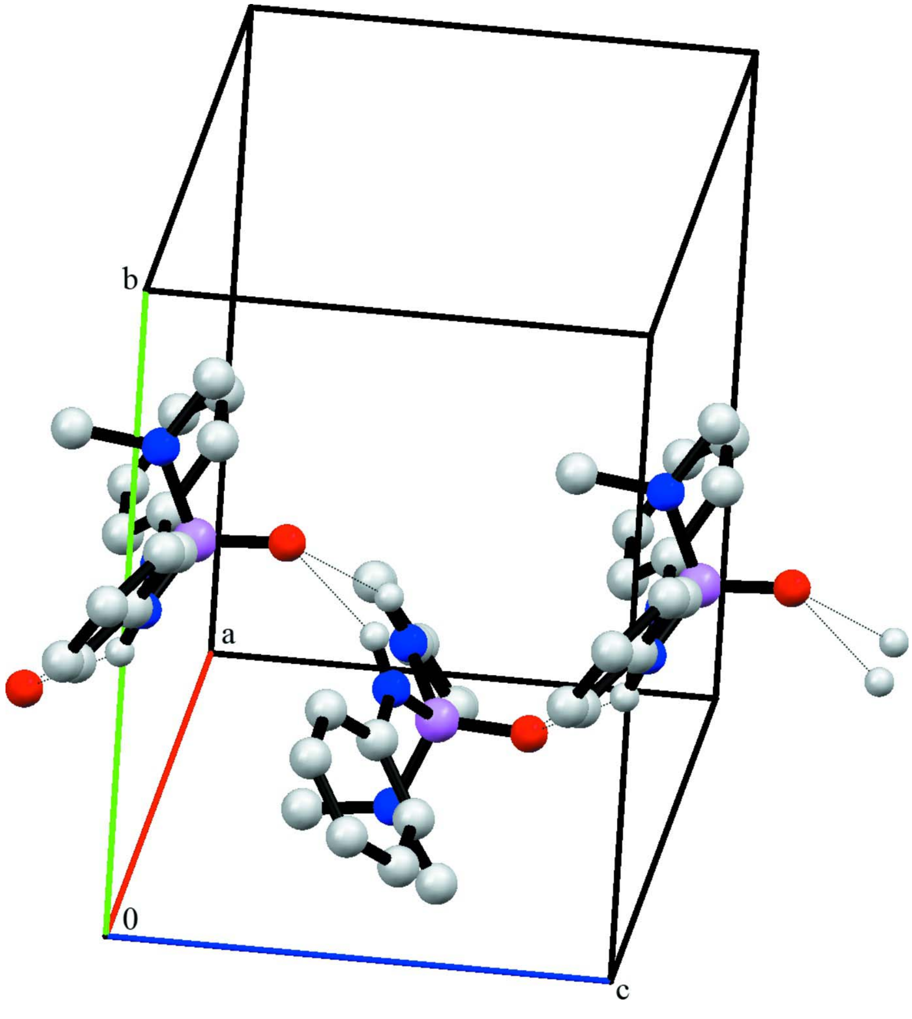

Figure 2

A view of the crystal packing showing the formation of 1-D arrangement through N—H···O hydrogen bonds (shown as dotted lines), carbon bound H atoms have been omitted for clarity.

N,*N*-Dimethyl-*N*′,*N*′′-diphenylphosphoric triamide

Crystal data

$C_{14}H_{18}N_3OP$
$M_r = 275.28$
Orthorhombic, *Cmc*2₁
$a = 15.501$ (3) Å
$b = 10.8569$ (17) Å
$c = 8.1579$ (13) Å
$V = 1372.9$ (4) Å^3
$Z = 4$
$F(000) = 584$
$D_x = 1.332$ Mg m^{-3}
Melting point: NOT MEASURED K
Mo *Kα* radiation, $\lambda = 0.71073$ Å
Cell parameters from 3006 reflections
$\theta = 3.4$–25.5°
$\mu = 0.20$ mm^{-1}
$T = 100$ K
Rod, colourless
0.60 × 0.15 × 0.13 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.891$, $T_{max} = 0.975$
5356 measured reflections
1317 independent reflections
1272 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 25.5°$, $\theta_{min} = 2.3°$
$h = -18 \rightarrow 14$
$k = -13 \rightarrow 11$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.084$
$S = 1.04$
1317 reflections
108 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0623P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Absolute structure: Flack (1983), 604 Friedel pairs
Absolute structure parameter: −0.11 (10)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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, conventional *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}
H13	−0.0531 (17)	0.819 (2)	−0.158 (3)	0.043 (6)*
H11	0.0000	0.708 (4)	−0.186 (5)	0.052 (11)*
H12	0.0000	0.849 (4)	0.262 (6)	0.053 (11)*

H4	−0.0525 (13)	0.9247 (19)	0.112 (3)	0.028 (5)*
P1	0.0000	0.62183 (5)	0.12667 (6)	0.02090 (19)
O1	0.0000	0.63022 (15)	0.3089 (2)	0.0251 (4)
N1	0.08103 (10)	0.54350 (14)	0.0464 (2)	0.0254 (4)
H1A	0.0696	0.4706	0.0047	0.031*
N2	0.0000	0.76094 (19)	0.0485 (3)	0.0243 (5)
C1	0.34009 (13)	0.66067 (19)	0.0212 (2)	0.0271 (4)
H1	0.3986	0.6864	0.0142	0.033*
C2	0.31200 (13)	0.55744 (18)	−0.0645 (2)	0.0283 (4)
H2	0.3515	0.5125	−0.1303	0.034*
C3	0.22643 (11)	0.51958 (17)	−0.0546 (2)	0.0243 (4)
H3	0.2080	0.4485	−0.1128	0.029*
C4	0.16777 (13)	0.58505 (18)	0.0398 (2)	0.0232 (4)
C5	0.28212 (11)	0.72536 (16)	0.1165 (3)	0.0252 (4)
H5	0.3011	0.7954	0.1762	0.030*
C6	0.19609 (10)	0.68909 (16)	0.1260 (3)	0.0241 (4)
H6	0.1566	0.7349	0.1910	0.029*
C7	0.0000	0.8737 (2)	0.1449 (4)	0.0269 (6)
C8	0.0000	0.7773 (3)	−0.1284 (4)	0.0329 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0224 (3)	0.0191 (3)	0.0212 (3)	0.000	0.000	0.0002 (3)
O1	0.0304 (10)	0.0227 (9)	0.0221 (10)	0.000	0.000	0.0036 (7)
N1	0.0246 (8)	0.0218 (8)	0.0300 (8)	−0.0009 (6)	0.0010 (6)	−0.0034 (6)
N2	0.0304 (11)	0.0218 (11)	0.0208 (12)	0.000	0.000	−0.0001 (8)
C1	0.0239 (9)	0.0308 (10)	0.0265 (9)	0.0005 (8)	−0.0006 (8)	0.0058 (8)
C2	0.0286 (9)	0.0314 (10)	0.0248 (9)	0.0073 (8)	0.0025 (8)	0.0006 (8)
C3	0.0289 (9)	0.0215 (9)	0.0225 (9)	0.0025 (7)	−0.0021 (8)	0.0006 (7)
C4	0.0264 (9)	0.0208 (10)	0.0224 (10)	0.0021 (8)	−0.0024 (7)	0.0032 (7)
C5	0.0296 (8)	0.0230 (8)	0.0230 (9)	0.0005 (7)	−0.0033 (9)	0.0038 (8)
C6	0.0269 (8)	0.0226 (8)	0.0227 (7)	0.0043 (7)	0.0013 (8)	−0.0007 (8)
C7	0.0342 (13)	0.0224 (13)	0.0241 (14)	0.000	0.000	0.0001 (10)
C8	0.0446 (17)	0.0310 (16)	0.0232 (14)	0.000	0.000	0.0029 (12)

Geometric parameters (Å, º)

P1—O1	1.489 (2)	C2—H2	0.9500
P1—N2	1.639 (2)	C3—C4	1.388 (3)
P1—N1^{i}	1.6521 (16)	C3—H3	0.9500
P1—N1	1.6522 (16)	C4—C6	1.401 (3)
N1—C4	1.419 (2)	C5—C6	1.393 (2)
N1—H1A	0.8800	C5—H5	0.9500
N2—C8	1.454 (3)	C6—H6	0.9500
N2—C7	1.455 (3)	C7—H12	0.99 (5)
C1—C5	1.380 (3)	C7—H4	1.02 (2)
C1—C2	1.391 (3)	C8—H13	0.97 (3)

C1—H1	0.9500	C8—H11	0.89 (4)
C2—C3	1.391 (3)		

O1—P1—N2	109.39 (11)	C4—C3—C2	120.39 (18)
O1—P1—N1^{i}	115.28 (7)	C4—C3—H3	119.8
N2—P1—N1^{i}	108.66 (8)	C2—C3—H3	119.8
O1—P1—N1	115.28 (7)	C3—C4—C6	119.10 (17)
N2—P1—N1	108.66 (8)	C3—C4—N1	118.62 (16)
N1^{i}—P1—N1	98.98 (11)	C6—C4—N1	122.28 (16)
C4—N1—P1	124.87 (13)	C1—C5—C6	120.74 (18)
C4—N1—H1A	117.6	C1—C5—H5	119.6
P1—N1—H1A	117.6	C6—C5—H5	119.6
C8—N2—C7	115.7 (2)	C5—C6—C4	119.99 (17)
C8—N2—P1	119.9 (2)	C5—C6—H6	120.0
C7—N2—P1	124.38 (19)	C4—C6—H6	120.0
C5—C1—C2	119.30 (18)	N2—C7—H12	107 (2)
C5—C1—H1	120.4	N2—C7—H4	108.2 (13)
C2—C1—H1	120.4	H12—C7—H4	113.7 (18)
C1—C2—C3	120.49 (18)	N2—C8—H13	107.6 (15)
C1—C2—H2	119.8	N2—C8—H11	115 (3)
C3—C2—H2	119.8	H13—C8—H11	105.1 (19)

O1—P1—N1—C4	−72.29 (16)	C1—C2—C3—C4	0.6 (3)
N2—P1—N1—C4	50.87 (18)	C2—C3—C4—C6	−0.5 (3)
N1^{i}—P1—N1—C4	164.16 (11)	C2—C3—C4—N1	179.88 (17)
O1—P1—N2—C8	180.0	P1—N1—C4—C3	−169.43 (13)
N1^{i}—P1—N2—C8	−53.37 (7)	P1—N1—C4—C6	11.0 (2)
N1—P1—N2—C8	53.37 (7)	C2—C1—C5—C6	−0.7 (3)
O1—P1—N2—C7	0.0	C1—C5—C6—C4	0.7 (3)
N1^{i}—P1—N2—C7	126.63 (7)	C3—C4—C6—C5	−0.1 (3)
N1—P1—N2—C7	−126.63 (7)	N1—C4—C6—C5	179.45 (18)
C5—C1—C2—C3	0.0 (3)		

Symmetry code: (i) −*x*, *y*, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1^{ii}	0.88	2.22	2.982 (2)	145

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