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4-Methylphenyl (dimethylamido)-(isopropylamido)phosphate

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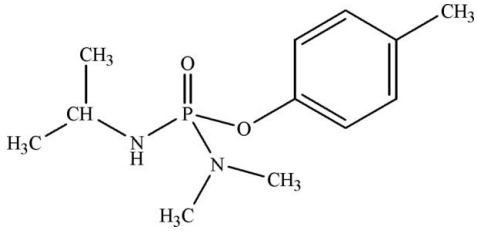
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.005 Å; R factor = 0.057; wR factor = 0.093; data-to-parameter ratio = 18.0.

In the title compound, $C_{12}H_{21}N_2O_2P$, the P—N bond lengths of 1.617 (2) and 1.645 (3) Å are shorter than a normal P—N single bond. The sum of the bond angles around the phosphoramide N atoms of 353° indicates their sp^2-hybridization. Molecules are linked *via* N—H···O=P hydrogen bonds into a one-dimensional chain parallel to the *c* axis.

Related literature

For related literature, see: Corbridge (1995); Ekstrom *et al.* (2006); Fest & Schmidt (1982); Ghadimi *et al.* (2007); Singh (1999).



Experimental

Crystal data

$C_{12}H_{21}N_2O_2P$
M_r = 256.28
Monoclinic, $P2_1/c$
a = 16.711 (5) Å
b = 8.306 (2) Å
c = 10.425 (3) Å
β = 101.963 (9)°
V = 1415.6 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.19 mm^{-1}
T = 100 (2) K
0.21 × 0.09 × 0.08 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*APEX2*; Bruker, 2005)
T_{min} = 0.963, T_{max} = 0.987
6264 measured reflections
2779 independent reflections
1418 reflections with $I > 2\sigma(I)$
R_{int} = 0.107

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.093
S = 1.00
2779 reflections
154 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O1^{i}	0.91	1.96	2.849 (4)	169

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2098).

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supplementary materials

Acta Cryst. (2007). E**63**, o4093 [**doi:10.1107/S1600536807045679**]

4-Methylphenyl (dimethylamido)(isopropylamido)phosphate

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Comment

Acetylcholinesterase (AChE) enzyme inhibition by organophosphorus (OPs) compounds is well known (Ekstrom *et al.*, 2006). It is generally governed by intramolecular properties (lipophilicity, electronic, steric) and three-dimensional structure of OPs (Singh, 1999). The range of herbicides which can be derived from OPs is very large indeed. For example, *Amiprofos-methyl* [*O*-methyl *O*-(4-methyl-2-nitrophenyl) *N*-isopropyl phosphoramidothioate] is a herbicidal organophosphate (Fest & Schmidt, 1982). In our previous work, we reported on the structure of *N,N*-dimethyl *O*-*p*-tolyl phosphoramidocyanidate (Ghadimi *et al.*, 2007). Here, we report the synthesis and crystal structure of the title compound. The four different groups linked to P atom give rise to a distorted tetrahedral configuration (Figure 1). The bond angles around P atom are in the range of 102.76 (14)° [for O2—P1—N2 amgle] to 114.77 (14)° [for the O1—P1—N2 angle]. The P1—O2 bond length [1.607 (2) Å] is shorter than the P—O single bond length (1.64 Å; Corbridge, 1995). Also, the P—N bond lengths [P1—N1 = 1.645 (3) Å and P1—N2 = 1.617 (2) Å] are shorter than the P—N single bond length (1.77 Å; Corbridge, 1995). The sum of the surrounding angles around N1 nad N2 (about 353°) points to sp^2 hybridization for the nitrogen atoms. Molecules are linked *via* N—H···O=P hydrogen bonds (Table 1, Fig. 2|) into one-dimensional chains parallel to the *c* axis.

Experimental

To a solution of *N,N*-dimethyl phosphoramidochloridic acid 4-methyl phenyl ester (0.82 g, 3.51 mmol) in 30 ml dry chloroform, isoprophylamine (0.41 g, 7.02 mmol) was added slowly and solution stirred at 273 K for 5 h. The solvent was evaporated in vacuum. Then the product was washed with water to remove $[(CH_3)_2CHNH_3]Cl$. After drying, the product was crystallized from chloroform at room temperature.

Refinement

The H atom of the NH group was found in a difference Fourier map and the remaining H atoms were placed in calculated positions. They were refined in riding model approximation with $U_{iso}(H) = 1.2U_{eq}(N,C)$ or $1.5U_{eq}(C)$ for methyl groups.

Figures

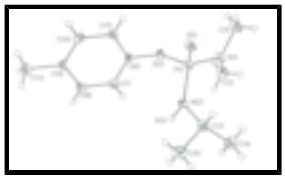

Fig. 1. The molecular structure of title compound showing the atom-numbering scheme. All non-H atoms are represented by 40% probability displacement ellipsoids.

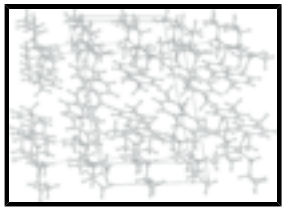

Fig. 2. A view of crystal packing of the title compound

4-Methylphenyl (dimethylamido)(isopropylamido)phosphate

Crystal data

$C_{12}H_{21}N_2O_2P$	F_{000} = 552
M_r = 256.28	D_x = 1.203 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 16.711 (5) Å	Cell parameters from 498 reflections
b = 8.306 (2) Å	θ = 3–20º
c = 10.425 (3) Å	μ = 0.19 mm^{-1}
β = 101.963 (9)º	T = 100 (2) K
V = 1415.6 (7) Å^3	Needle, colorless
Z = 4	0.21 × 0.09 × 0.08 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	2779 independent reflections
Radiation source: fine-focus sealed tube	1418 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.107
Detector resolution: 0 pixels mm^{-1}	θ_{max} = 26.0º
T = 100(2) K	θ_{min} = 1.3º
π and ω scans	h = −20→19
Absorption correction: multi-scan (APEX2; Bruker, 2005)	k = −10→8
T_{min} = 0.963, T_{max} = 0.987	l = −12→12
6264 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)]$ = 0.057	H-atom parameters constrained
$wR(F^2)$ = 0.093	$w = 1/[\sigma^2(F_o^2) + (0.01P)^2 + 0.01P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.00	$(\Delta/\sigma)_{max} < 0.001$
2779 reflections	$\Delta\rho_{max}$ = 0.27 e Å^{-3}
154 parameters	$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Primary atom site location: structure-invariant direct methods

Extinction correction: none

Special details

Experimental. ^{1}H NMR ($CDCl_3$, p.p.m.): 1.12 (d, 3H, $^3J_{H—H}$ = 6.5 Hz, isopropylamine-CH_3), 1.15 (d, 3H, $^3J_{H—H}$ = 6.4 Hz, isopropylamine-CH_3), 2.25 (s, 3 H, *p*-CH_3), 2.33 (b, 1H, NH), 2.68 (d, $^3J_{PNCH}$ = 10.1 Hz, 6H, $N(CH_3)_2$), 3.38–3.39 (m, 1H, isopropylamine-CH), 7.03 (m, 4 H, Ar—H); ^{13}C NMR ($CDCl_3$, p.p.m.): 20.64 (s, 1 C, *p*-CH_3), 25.27 (d, $^3J_{P—C}$ = 5.9 Hz, 1 C, isopropylamine-CH_3), 25.52 (d, $^3J_{P—C}$ = 5.3 Hz, 1 C, isopropylamine-CH_3), 36.96 (d, $^2J_{P—C}$ = 3.8 Hz, 2 C, $N(CH_3)_2$), 43.38 (s, 1 C, isopropylamine-CH), 119.92 (d, $^3J_{P—C}$ = 4.8 Hz, 2 C, C_{ortho}), 129.96 (s, 2 C, C_{meta}), 133.50 (s, 1 C, C_{para}), 149.12 (d, $^2J_{P—C}$ = 6.1 Hz, 1 C, C_{ipso}); $^{31}P\{^1H\}$ NMR ($CDCl_3$, p.p.m.): 13.70 (*s*); ^{31}P NMR ($CDCl_3$, p.p.m.): 13.70 (*m*). IR (KBr, cm^{-1}): 3210, 2949, 2940, 1599, 1499, 1455, 1297, 1227 (P=O), 1198, 1162, 1040, 985, 906, 816, 794, 705.

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 $F^2 > 2\text{sigma}(F^2)$ 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	0.21748 (6)	0.33403 (11)	0.82100 (9)	0.0181 (2)
O1	0.20364 (14)	0.3011 (2)	0.6793 (2)	0.0226 (6)
O2	0.30994 (14)	0.3037 (2)	0.8981 (2)	0.0179 (6)
N1	0.20238 (18)	0.5259 (3)	0.8471 (3)	0.0209 (7)
N2	0.16505 (16)	0.2225 (3)	0.9006 (3)	0.0178 (7)
H2	0.1838	0.2190	0.9885	0.021*
C1	0.2200 (2)	0.6460 (4)	0.7554 (4)	0.0310 (10)
H1A	0.1838	0.7389	0.7552	0.047*
H1B	0.2109	0.5995	0.6671	0.047*
H1C	0.2771	0.6807	0.7819	0.047*
C2	0.2109 (2)	0.5839 (4)	0.9817 (4)	0.0295 (10)
H2A	0.1754	0.6776	0.9827	0.044*
H2B	0.2679	0.6147	1.0163	0.044*
H2C	0.1951	0.4983	1.0362	0.044*
C3	0.0771 (2)	0.1973 (4)	0.8552 (3)	0.0226 (9)
H3A	0.0621	0.2266	0.7602	0.027*
C4	0.0277 (2)	0.3017 (4)	0.9294 (3)	0.0318 (10)
H4A	−0.0307	0.2786	0.8989	0.048*
H4B	0.0380	0.4155	0.9139	0.048*
H4C	0.0437	0.2786	1.0235	0.048*
C5	0.0583 (2)	0.0194 (4)	0.8689 (4)	0.0374 (12)
H5A	0.0879	−0.0446	0.8149	0.056*

H5B	−0.0006	0.0013	0.8398	0.056*
H5C	0.0755	−0.0130	0.9609	0.056*
C6	0.3447 (2)	0.1490 (4)	0.9015 (3)	0.0175 (8)
C7	0.3480 (2)	0.0556 (4)	1.0113 (3)	0.0205 (9)
H7A	0.3250	0.0934	1.0818	0.025*
C8	0.3849 (2)	−0.0936 (4)	1.0182 (4)	0.0232 (9)
H8A	0.3865	−0.1587	1.0936	0.028*
C9	0.4196 (2)	−0.1501 (4)	0.9174 (3)	0.0207 (8)
C10	0.4153 (2)	−0.0534 (4)	0.8082 (4)	0.0234 (9)
H10A	0.4384	−0.0905	0.7378	0.028*
C11	0.3777 (2)	0.0973 (4)	0.7989 (4)	0.0216 (9)
H11A	0.3751	0.1625	0.7232	0.026*
C12	0.4589 (2)	−0.3151 (4)	0.9248 (4)	0.0292 (9)
H12A	0.4816	−0.3330	0.8466	0.044*
H12B	0.4176	−0.3975	0.9295	0.044*
H12C	0.5028	−0.3215	1.0032	0.044*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0254 (6)	0.0142 (4)	0.0153 (5)	−0.0006 (5)	0.0058 (4)	0.0004 (5)
O1	0.0359 (16)	0.0207 (13)	0.0121 (13)	−0.0013 (11)	0.0068 (12)	0.0009 (11)
O2	0.0202 (14)	0.0117 (11)	0.0206 (14)	0.0012 (10)	0.0014 (11)	−0.0038 (11)
N1	0.033 (2)	0.0132 (14)	0.0159 (18)	0.0009 (14)	0.0048 (16)	0.0028 (14)
N2	0.0220 (18)	0.0200 (14)	0.0118 (16)	−0.0046 (13)	0.0039 (14)	0.0012 (13)
C1	0.043 (3)	0.0160 (17)	0.034 (2)	−0.0009 (19)	0.007 (2)	0.0012 (19)
C2	0.039 (3)	0.0219 (18)	0.029 (2)	0.0020 (18)	0.010 (2)	−0.0100 (18)
C3	0.023 (2)	0.028 (2)	0.017 (2)	−0.0006 (18)	0.0033 (18)	0.0026 (17)
C4	0.030 (2)	0.036 (2)	0.030 (2)	0.000 (2)	0.008 (2)	−0.001 (2)
C5	0.037 (3)	0.027 (2)	0.050 (3)	−0.0136 (19)	0.014 (3)	−0.013 (2)
C6	0.017 (2)	0.0136 (17)	0.023 (2)	0.0033 (16)	0.0056 (17)	−0.0037 (18)
C7	0.027 (2)	0.0175 (18)	0.018 (2)	−0.0015 (17)	0.0075 (18)	−0.0054 (17)
C8	0.026 (2)	0.0178 (18)	0.025 (2)	−0.0033 (17)	0.0036 (19)	0.0023 (17)
C9	0.020 (2)	0.0163 (17)	0.026 (2)	0.0027 (17)	0.0057 (18)	−0.0023 (18)
C10	0.025 (2)	0.028 (2)	0.019 (2)	0.0005 (17)	0.0089 (19)	−0.0066 (18)
C11	0.030 (2)	0.0151 (17)	0.022 (2)	0.0002 (17)	0.0086 (19)	0.0010 (17)
C12	0.030 (2)	0.0192 (19)	0.039 (2)	0.0032 (18)	0.007 (2)	−0.0010 (19)

Geometric parameters (Å, °)

P1—O1	1.473 (2)	C4—H4B	0.9800
P1—O2	1.607 (2)	C4—H4C	0.9800
P1—N2	1.617 (2)	C5—H5A	0.9800
P1—N1	1.645 (3)	C5—H5B	0.9800
O2—C6	1.408 (3)	C5—H5C	0.9800
N1—C1	1.454 (4)	C6—C11	1.370 (4)
N1—C2	1.463 (4)	C6—C7	1.375 (4)
N2—C3	1.462 (4)	C7—C8	1.379 (4)
N2—H2	0.9055	C7—H7A	0.9500

C1—H1A	0.9800	C8—C9	1.384 (4)
C1—H1B	0.9800	C8—H8A	0.9500
C1—H1C	0.9800	C9—C10	1.383 (4)
C2—H2A	0.9800	C9—C12	1.514 (4)
C2—H2B	0.9800	C10—C11	1.394 (4)
C2—H2C	0.9800	C10—H10A	0.9500
C3—C4	1.517 (4)	C11—H11A	0.9500
C3—C5	1.524 (4)	C12—H12A	0.9800
C3—H3A	1.0000	C12—H12B	0.9800
C4—H4A	0.9800	C12—H12C	0.9800
O1—P1—O2	114.03 (13)	C3—C4—H4C	109.5
O1—P1—N2	114.77 (14)	H4A—C4—H4C	109.5
O2—P1—N2	102.76 (14)	H4B—C4—H4C	109.5
O1—P1—N1	110.38 (14)	C3—C5—H5A	109.5
O2—P1—N1	103.52 (14)	C3—C5—H5B	109.5
N2—P1—N1	110.63 (13)	H5A—C5—H5B	109.5
C6—O2—P1	120.3 (2)	C3—C5—H5C	109.5
C1—N1—C2	114.3 (3)	H5A—C5—H5C	109.5
C1—N1—P1	119.8 (2)	H5B—C5—H5C	109.5
C2—N1—P1	119.4 (2)	C11—C6—C7	121.4 (3)
C3—N2—P1	122.1 (2)	C11—C6—O2	119.8 (3)
C3—N2—H2	115.9	C7—C6—O2	118.8 (3)
P1—N2—H2	115.2	C6—C7—C8	119.4 (3)
N1—C1—H1A	109.5	C6—C7—H7A	120.3
N1—C1—H1B	109.5	C8—C7—H7A	120.3
H1A—C1—H1B	109.5	C7—C8—C9	121.3 (3)
N1—C1—H1C	109.5	C7—C8—H8A	119.4
H1A—C1—H1C	109.5	C9—C8—H8A	119.4
H1B—C1—H1C	109.5	C10—C9—C8	118.0 (3)
N1—C2—H2A	109.5	C10—C9—C12	121.1 (3)
N1—C2—H2B	109.5	C8—C9—C12	120.9 (3)
H2A—C2—H2B	109.5	C9—C10—C11	121.7 (3)
N1—C2—H2C	109.5	C9—C10—H10A	119.2
H2A—C2—H2C	109.5	C11—C10—H10A	119.2
H2B—C2—H2C	109.5	C6—C11—C10	118.3 (3)
N2—C3—C4	111.7 (3)	C6—C11—H11A	120.8
N2—C3—C5	108.8 (3)	C10—C11—H11A	120.8
C4—C3—C5	111.2 (3)	C9—C12—H12A	109.5
N2—C3—H3A	108.3	C9—C12—H12B	109.5
C4—C3—H3A	108.3	H12A—C12—H12B	109.5
C5—C3—H3A	108.3	C9—C12—H12C	109.5
C3—C4—H4A	109.5	H12A—C12—H12C	109.5
C3—C4—H4B	109.5	H12B—C12—H12C	109.5
H4A—C4—H4B	109.5		
O1—P1—O2—C6	−61.9 (2)	P1—N2—C3—C5	136.0 (2)
N2—P1—O2—C6	62.9 (2)	P1—O2—C6—C11	83.0 (3)
N1—P1—O2—C6	178.1 (2)	P1—O2—C6—C7	−99.9 (3)
O1—P1—N1—C1	−31.4 (3)	C11—C6—C7—C8	−0.3 (5)

O2—P1—N1—C1	91.1 (3)	O2—C6—C7—C8	−177.3 (3)
N2—P1—N1—C1	−159.5 (3)	C6—C7—C8—C9	0.9 (5)
O1—P1—N1—C2	178.5 (2)	C7—C8—C9—C10	−0.9 (5)
O2—P1—N1—C2	−59.1 (3)	C7—C8—C9—C12	−179.0 (3)
N2—P1—N1—C2	50.3 (3)	C8—C9—C10—C11	0.4 (5)
O1—P1—N2—C3	−48.3 (3)	C12—C9—C10—C11	178.6 (3)
O2—P1—N2—C3	−172.7 (2)	C7—C6—C11—C10	−0.1 (5)
N1—P1—N2—C3	77.4 (3)	O2—C6—C11—C10	176.9 (3)
P1—N2—C3—C4	−100.8 (3)	C9—C10—C11—C6	0.1 (5)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1^{i}	0.91	1.96	2.849 (4)	169

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

Fig. 1

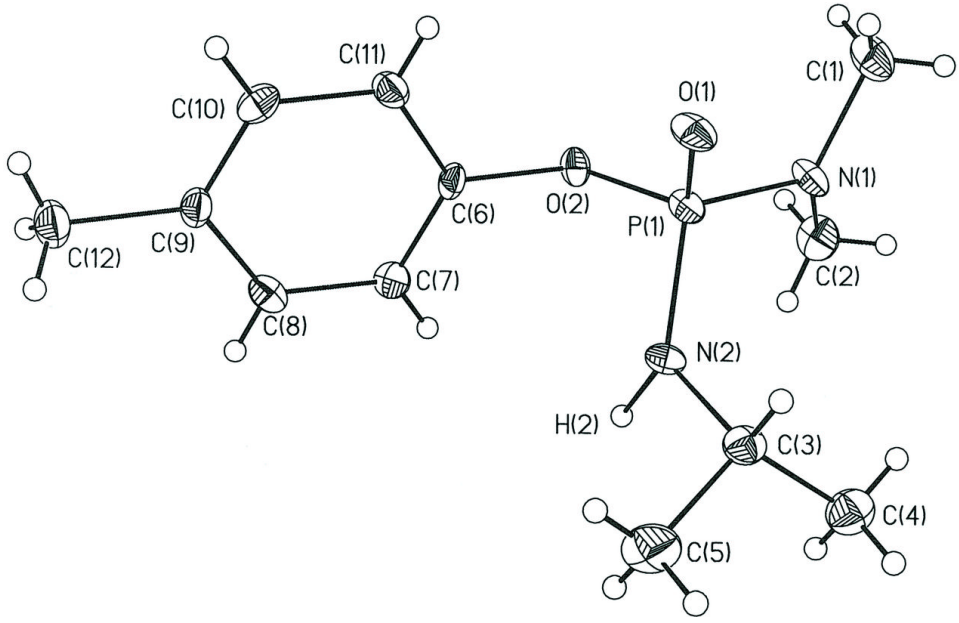

Fig. 2