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O,O′-Di-*p*-tolylpyrophosphoric bis(dimethylamide)

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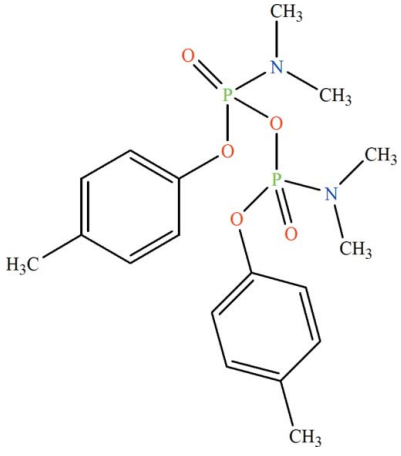
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.005 Å; R factor = 0.052; wR factor = 0.124; data-to-parameter ratio = 19.2.

The title compound, $C_{18}H_{26}N_2O_5P_2$, was obtained accidently from the reaction between *N*,*N*-dimethylphosphoramidochloridic acid 4-methyl phenyl ester, $NaNO_2$ and 18-crown-6 in acetonitrile under reflux conditions. The asymmetric unit contains one half-molecule, the complete molecule being generated by crystallographic twofold symmetry, with the bridging O atom lying on the rotation axis. The P atoms exhibit a tetrahedral coordination and are bridged *via* one O atom [P—O—P angle = 130.00 (19)°].

Related literature

For related structures, see: Ghadimi *et al.* (2007, 2009); Pourayoubi *et al.* (2007).



Experimental

Crystal data

$C_{18}H_{26}N_2O_5P_2$
M_r = 412.35
Monoclinic, $C2/c$
a = 26.484 (5) Å
b = 7.4195 (15) Å
c = 11.096 (2) Å
β = 112.949 (4)°
V = 2007.8 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.25 mm^{-1}
T = 100 K
0.50 × 0.25 × 0.10 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.930, T_{max} = 0.978
6483 measured reflections
2415 independent reflections
1763 reflections with $I > 2\sigma(I)$
R_{int} = 0.039

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.124
S = 0.94
2415 reflections
126 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Support of this investigation by Imam Hossein University is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2328).

References

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supplementary materials

Acta Cryst. (2010). E**66**, o450 [**doi:10.1107/S1600536810002692**]

***O*,*O*'-Di-*p*-tolylpyrophosphoric bis(dimethylamide)**

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Comment

Following our previous works about amido phosphoric acid esters with general formula $[(CH_3)_2N][p\text{-}CH_3—C_6H_4—O]P(O)X$ [for example X = $NHCH(CH_3)_2$ (Pourayoubi *et al.*, 2007) and $NHC(CH_3)_3$ (Ghadimi *et al.*, 2009)], we report here on the synthesis and crystal structure of title compound, $[(CH_3)_2N][p\text{-}CH_3—C_6H_4—O]P(O)(O)P(O)[O—C_6H_4\text{-}p\text{-}CH_3][N(CH_3)_2]$. The asymmetric unit contains one half-molecule, the complete molecule (Fig. 1) being generated by a twofold rotation axis. The phosphorous atoms exhibit a tetrahedral coordination and are bridged *via* one O atom (P—O—P angle = 130.0 (2)°). The bond angles around the P atoms are in the range of 94.25 (12)° (for O1—P1—O2 angle) to 117.71 (12)° (for O3—P1—O1 angle). The nitrogen atom indicates some deviation from planarity, the sum of the surrounding angles around N atom being about 353.3°.

Experimental

$[(CH_3)_2N]P(O)Cl[O—C_6H_4\text{-}p\text{-}CH_3]$ was synthesized according to the literature method (Ghadimi *et al.*, 2007). The title compound was prepared according to the following procedure: A mixture of $[(CH_3)_2N]P(O)Cl[O—C_6H_4\text{-}p\text{-}CH_3]$ (0.82 g, 3.5 mmol), $NaNO_2$ (0.24 g, 3.5 mmol) and 18-crown-6 (0.20 g) in acetonitrile (30 ml) was refluxed for 4 h and then filtered. The solvent was removed under vacuum and the solid recrystallized in a mixture of chloroform and n-hexane to produce single crystals after a slow evaporation at room temperature. IR (KBr, cm^{-1}): 2995, 2900, 2880, 2820, 1850, 1580, 1480, 1440, 1300, 1235, 1250, 1185, 1100, 990, 940, 730.

Refinement

The H(C) atom positions were calculated. All hydrogen atoms were refined in isotropic approximation in riding model with the Uiso(H) parameters equal to 1.2 Ueq(Ci), for methyl groups equal to 1.5 Ueq(Cii), where U(Ci) and U(Cii) are respectively the equivalent thermal parameters of the carbon atoms to which corresponding H atoms are bonded.

Figures

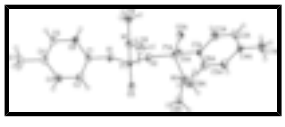


Fig. 1. Molecular view (50 % probability level) of the title compound. Symmetry code A: -x,y,-z+1/2.

***O*,*O*'-Di-*p*-tolylpyrophosphoric bis(dimethylamide)**

Crystal data

$C_{18}H_{26}N_2O_5P_2$ $F(000) = 872$

M_r = 412.35	D_x = 1.364 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 1898 reflections
a = 26.484 (5) Å	θ = 2.9–30.7°
b = 7.4195 (15) Å	μ = 0.25 mm^{-1}
c = 11.096 (2) Å	*T* = 100 K
β = 112.949 (4)°	Plate, colorless
V = 2007.8 (7) Å^3	0.50 × 0.25 × 0.10 mm
Z = 4	

Data collection

Bruker APEXII CCD area-detector diffractometer	2415 independent reflections
Radiation source: fine-focus sealed tube	1763 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.039
phi and ω scans	θ_{max} = 28.0°, θ_{min} = 1.7°
Absorption correction: multi-scan (SADABS; Bruker, 2005)	*h* = −34→21
T_{min} = 0.930, T_{max} = 0.978	*k* = −9→9
6483 measured reflections	*l* = −14→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
$R[F^2 > 2\sigma(F^2)]$ = 0.052	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.124	H-atom parameters constrained
S = 0.94	$w = 1/[\sigma^2(F_o^2) + (0.013P)^2 + 16.2989P]$ where $P = (F_o^2 + 2F_c^2)/3$
2415 reflections	$(\Delta/\sigma)_{max}$ = 0.002
126 parameters	$\Delta\rho_{max}$ = 0.34 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.37 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, 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}
P1	0.05951 (3)	0.15216 (10)	0.29554 (7)	0.01597 (17)
O1	0.08997 (8)	−0.0313 (3)	0.2957 (2)	0.0188 (4)
O2	0.0000	0.0607 (4)	0.2500	0.0198 (6)
O3	0.07504 (8)	0.2488 (3)	0.4196 (2)	0.0224 (5)
N1	0.06400 (10)	0.2733 (3)	0.1781 (2)	0.0192 (5)
C1	0.14675 (11)	−0.0402 (4)	0.3240 (3)	0.0159 (6)
C2	0.18495 (13)	0.0402 (4)	0.4337 (3)	0.0237 (7)
H2A	0.1735	0.1112	0.4898	0.028*
C3	0.24040 (13)	0.0160 (4)	0.4612 (3)	0.0250 (7)
H3A	0.2669	0.0709	0.5369	0.030*
C4	0.25790 (12)	−0.0867 (4)	0.3802 (3)	0.0205 (6)
C5	0.21822 (12)	−0.1656 (4)	0.2707 (3)	0.0222 (6)
H5A	0.2294	−0.2372	0.2145	0.027*
C6	0.16261 (12)	−0.1427 (4)	0.2411 (3)	0.0205 (6)
H6A	0.1360	−0.1965	0.1652	0.025*
C7	0.31835 (12)	−0.1118 (5)	0.4103 (4)	0.0305 (8)
H7A	0.3238	−0.1263	0.3284	0.046*
H7B	0.3317	−0.2194	0.4647	0.046*
H7C	0.3387	−0.0059	0.4574	0.046*
C8	0.05658 (14)	0.4694 (4)	0.1789 (4)	0.0288 (7)
H8A	0.0723	0.5265	0.1217	0.043*
H8B	0.0751	0.5151	0.2683	0.043*
H8C	0.0174	0.4974	0.1472	0.043*
C9	0.04811 (13)	0.1948 (4)	0.0462 (3)	0.0239 (7)
H9A	0.0670	0.2590	−0.0013	0.036*
H9B	0.0084	0.2062	−0.0016	0.036*
H9C	0.0584	0.0672	0.0538	0.036*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0134 (3)	0.0175 (3)	0.0189 (4)	−0.0003 (3)	0.0084 (3)	−0.0005 (3)
O1	0.0150 (10)	0.0186 (10)	0.0268 (11)	−0.0006 (8)	0.0127 (9)	−0.0007 (9)
O2	0.0159 (14)	0.0197 (15)	0.0274 (16)	0.000	0.0123 (13)	0.000
O3	0.0209 (11)	0.0254 (11)	0.0212 (11)	0.0015 (9)	0.0087 (9)	−0.0031 (9)
N1	0.0183 (12)	0.0189 (12)	0.0216 (13)	−0.0024 (10)	0.0090 (11)	0.0008 (10)
C1	0.0142 (13)	0.0140 (12)	0.0219 (15)	−0.0007 (11)	0.0097 (11)	0.0043 (11)
C2	0.0247 (16)	0.0254 (15)	0.0223 (16)	0.0021 (13)	0.0104 (13)	−0.0029 (13)
C3	0.0200 (15)	0.0249 (15)	0.0247 (17)	−0.0016 (13)	0.0029 (13)	−0.0023 (13)
C4	0.0177 (14)	0.0172 (13)	0.0276 (16)	0.0010 (11)	0.0098 (13)	0.0077 (12)
C5	0.0208 (15)	0.0224 (15)	0.0266 (16)	0.0028 (12)	0.0127 (13)	−0.0007 (13)
C6	0.0206 (14)	0.0200 (14)	0.0221 (15)	−0.0004 (12)	0.0096 (12)	−0.0033 (12)
C7	0.0168 (15)	0.0286 (17)	0.042 (2)	0.0034 (13)	0.0075 (14)	0.0097 (15)
C8	0.0291 (17)	0.0205 (15)	0.0381 (19)	−0.0004 (13)	0.0147 (15)	0.0045 (14)

C9	0.0241 (15)	0.0279 (16)	0.0221 (16)	−0.0029 (13)	0.0115 (13)	0.0008 (13)

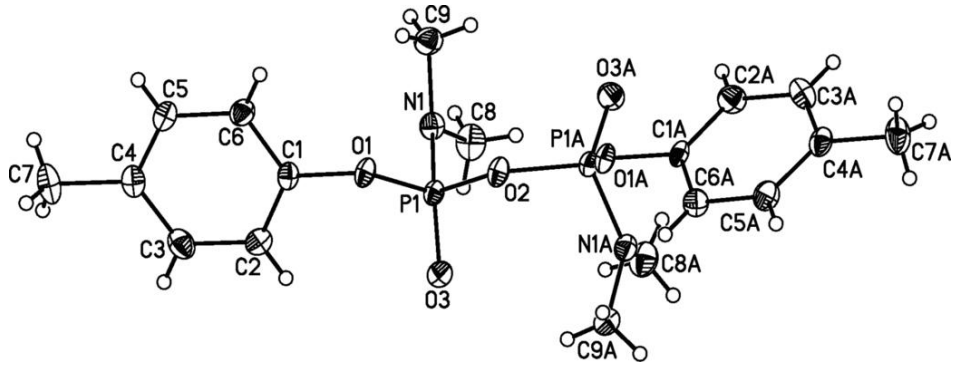
Geometric parameters (Å, °)

P1—O3	1.462 (2)	C4—C5	1.388 (4)
P1—O1	1.582 (2)	C4—C7	1.514 (4)
P1—O2	1.6059 (14)	C5—C6	1.389 (4)
P1—N1	1.625 (3)	C5—H5A	0.9500
O1—C1	1.413 (3)	C6—H6A	0.9500
O2—P1^{i}	1.6059 (14)	C7—H7A	0.9800
N1—C8	1.468 (4)	C7—H7B	0.9800
N1—C9	1.476 (4)	C7—H7C	0.9800
C1—C6	1.379 (4)	C8—H8A	0.9800
C1—C2	1.379 (4)	C8—H8B	0.9800
C2—C3	1.390 (4)	C8—H8C	0.9800
C2—H2A	0.9500	C9—H9A	0.9800
C3—C4	1.389 (4)	C9—H9B	0.9800
C3—H3A	0.9500	C9—H9C	0.9800
O3—P1—O1	117.71 (12)	C4—C5—H5A	119.1
O3—P1—O2	112.64 (10)	C6—C5—H5A	119.1
O1—P1—O2	94.25 (12)	C1—C6—C5	118.7 (3)
O3—P1—N1	113.71 (13)	C1—C6—H6A	120.6
O1—P1—N1	106.27 (12)	C5—C6—H6A	120.6
O2—P1—N1	110.55 (11)	C4—C7—H7A	109.5
C1—O1—P1	122.57 (17)	C4—C7—H7B	109.5
P1—O2—P1^{i}	130.00 (19)	H7A—C7—H7B	109.5
C8—N1—C9	114.2 (3)	C4—C7—H7C	109.5
C8—N1—P1	119.4 (2)	H7A—C7—H7C	109.5
C9—N1—P1	119.7 (2)	H7B—C7—H7C	109.5
C6—C1—C2	121.2 (3)	N1—C8—H8A	109.5
C6—C1—O1	116.9 (3)	N1—C8—H8B	109.5
C2—C1—O1	121.8 (3)	H8A—C8—H8B	109.5
C1—C2—C3	119.1 (3)	N1—C8—H8C	109.5
C1—C2—H2A	120.5	H8A—C8—H8C	109.5
C3—C2—H2A	120.5	H8B—C8—H8C	109.5
C4—C3—C2	121.3 (3)	N1—C9—H9A	109.5
C4—C3—H3A	119.4	N1—C9—H9B	109.5
C2—C3—H3A	119.4	H9A—C9—H9B	109.5
C5—C4—C3	117.9 (3)	N1—C9—H9C	109.5
C5—C4—C7	121.0 (3)	H9A—C9—H9C	109.5
C3—C4—C7	121.0 (3)	H9B—C9—H9C	109.5
C4—C5—C6	121.8 (3)		
O3—P1—O1—C1	−64.5 (2)	P1—O1—C1—C6	−133.6 (2)
O2—P1—O1—C1	177.1 (2)	P1—O1—C1—C2	50.4 (3)
N1—P1—O1—C1	64.3 (2)	C6—C1—C2—C3	−0.4 (5)
O3—P1—O2—P1^{i}	66.93 (11)	O1—C1—C2—C3	175.5 (3)
O1—P1—O2—P1^{i}	−170.64 (9)	C1—C2—C3—C4	0.2 (5)
N1—P1—O2—P1^{i}	−61.51 (10)	C2—C3—C4—C5	−0.3 (5)

O3—P1—N1—C8	−28.6 (3)	C2—C3—C4—C7	179.7 (3)
O1—P1—N1—C8	−159.7 (2)	C3—C4—C5—C6	0.5 (5)
O2—P1—N1—C8	99.2 (2)	C7—C4—C5—C6	−179.4 (3)
O3—P1—N1—C9	−178.3 (2)	C2—C1—C6—C5	0.7 (4)
O1—P1—N1—C9	50.6 (2)	O1—C1—C6—C5	−175.4 (3)
O2—P1—N1—C9	−50.4 (3)	C4—C5—C6—C1	−0.7 (5)

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

Fig. 1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C6
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C5A
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C2
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