

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

Mehrdad Pourayoubi,<sup>a</sup> Saied Ghadimi<sup>b\*</sup> and Ali Asghar Ebrahimi Valmoozi<sup>b</sup>

<sup>a</sup>Department of Chemistry, Ferdowsi University of Mashhad, Mashhad, 91779, Iran, and <sup>b</sup>Department of Chemistry, Imam Hossein University, P.O. Box 16575-347, Tehran, Iran

Correspondence e-mail: ghadimi\_saied@yahoo.com

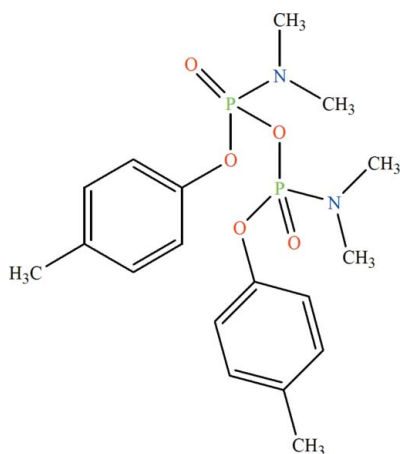
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.052;  $wR$  factor = 0.124; data-to-parameter ratio = 19.2.

The title compound,  $\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_5\text{P}_2$ , was obtained accidentally from the reaction between *N,N*-dimethylphosphoramido-chloridic acid 4-methyl phenyl ester,  $\text{NaNO}_2$  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 [ $\text{P}-\text{O}-\text{P}$  angle =  $130.00$  ( $19^\circ$ )].

### Related literature

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



### Experimental

#### Crystal data

$\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_5\text{P}_2$   
 $M_r = 412.35$   
 Monoclinic,  $C2/c$   
 $a = 26.484$  (5) Å  
 $b = 7.4195$  (15) Å  
 $c = 11.096$  (2) Å  
 $\beta = 112.949$  (4)°

$V = 2007.8$  (7) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.25$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.50 \times 0.25 \times 0.10$  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  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.039$

#### 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<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.37$  e Å<sup>-3</sup>

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

- Bruker (2005). *SADABS*, *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Ghadimi, S., Pourayoubi, M. & Valmoozi, A. A. E. (2009). *Z. Naturforsch. Teil B*, **64**, 565–569.  
 Ghadimi, S., Valmoozi, A. A. E. & Pourayoubi, M. (2007). *Z. Kristallogr. New Cryst. Struct.* **222**, 339–340.  
 Pourayoubi, M., Ghadimi, S. & Valmoozi, A. A. E. (2007). *Acta Cryst.* **E63**, o4093.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

**supplementary materials**

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

**M. Pourayoubi, S. Ghadimi and A. A. Ebrahimi Valmoozi**

### **Comment**

Following our previous works about amido phosphoric acid esters with general formula  $[(\text{CH}_3)_2\text{N}][p\text{-CH}_3\text{-C}_6\text{H}_4\text{-O}]\text{P}(\text{O})\text{X}$  [for example  $\text{X} = \text{NHCH}(\text{CH}_3)_2$  (Pourayoubi *et al.*, 2007) and  $\text{NHC}(\text{CH}_3)_3$  (Ghadimi *et al.*, 2009)], we report here on the synthesis and crystal structure of title compound,  $[(\text{CH}_3)_2\text{N}][p\text{-CH}_3\text{-C}_6\text{H}_4\text{-O}]\text{P}(\text{O})(\text{O})\text{P}(\text{O})[\text{O}-\text{C}_6\text{H}_4\text{-}i>p\text{-CH}_3][\text{N}(\text{CH}_3)_2]$ . 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 ( $\text{P}-\text{O}-\text{P}$  angle =  $130.0(2)^\circ$ ). The bond angles around the P atoms are in the range of  $94.25(12)^\circ$  (for  $\text{O1}-\text{P1}-\text{O2}$  angle) to  $117.71(12)^\circ$  (for  $\text{O3}-\text{P1}-\text{O1}$  angle). The nitrogen atom indicates some deviation from planarity, the sum of the surrounding angles around N atom being about  $353.3^\circ$ .

### **Experimental**

$[(\text{CH}_3)_2\text{N}]\text{P}(\text{O})\text{Cl}[\text{O}-\text{C}_6\text{H}_4\text{-}i>p\text{-CH}_3]$  was synthesized according to the literature method (Ghadimi *et al.*, 2007). The title compound was prepared according to the following procedure: A mixture of  $[(\text{CH}_3)_2\text{N}]\text{P}(\text{O})\text{Cl}[\text{O}-\text{C}_6\text{H}_4\text{-}i>p\text{-CH}_3]$  (0.82 g, 3.5 mmol),  $\text{NaNO}_2$  (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,  $\text{cm}^{-1}$ ): 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  $\text{Uiso}(\text{H})$  parameters equal to  $1.2 \text{ Ueq}(\text{Ci})$ , for methyl groups equal to  $1.5 \text{ Ueq}(\text{Cii})$ , where  $\text{U}(\text{Ci})$  and  $\text{U}(\text{Cii})$  are respectively the equivalent thermal parameters of the carbon atoms to which corresponding H atoms are bonded.

### **Figures**

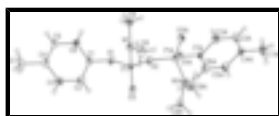


Fig. 1. Molecular view (50 % probability level) of the title compound. Symmetry code A:  $-x, y, -z+1/2$ .

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### *Crystal data*

$\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_5\text{P}_2$

$F(000) = 872$

# supplementary materials

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$$M_r = 412.35$$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$$a = 26.484\ (5)\ \text{\AA}$$

$$b = 7.4195\ (15)\ \text{\AA}$$

$$c = 11.096\ (2)\ \text{\AA}$$

$$\beta = 112.949\ (4)^\circ$$

$$V = 2007.8\ (7)\ \text{\AA}^3$$

$$Z = 4$$

$$D_x = 1.364\ \text{Mg m}^{-3}$$

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

Cell parameters from 1898 reflections

$$\theta = 2.9\text{--}30.7^\circ$$

$$\mu = 0.25\ \text{mm}^{-1}$$

$$T = 100\ \text{K}$$

Plate, colorless

$$0.50 \times 0.25 \times 0.10\ \text{mm}$$

## Data collection

Bruker APEXII CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube  
graphite

phi and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2005)

$$T_{\min} = 0.930, T_{\max} = 0.978$$

6483 measured reflections

2415 independent reflections

1763 reflections with  $I > 2\sigma(I)$

$$R_{\text{int}} = 0.039$$

$$\theta_{\max} = 28.0^\circ, \theta_{\min} = 1.7^\circ$$

$$h = -34 \rightarrow 21$$

$$k = -9 \rightarrow 9$$

$$l = -14 \rightarrow 14$$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.052$$

$$wR(F^2) = 0.124$$

$$S = 0.94$$

2415 reflections

126 parameters

0 restraints

Primary atom site location: structure-invariant direct  
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring  
sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.013P)^2 + 16.2989P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.002$$

$$\Delta\rho_{\max} = 0.34\ \text{e \AA}^{-3}$$

$$\Delta\rho_{\min} = -0.37\ \text{e \AA}^{-3}$$

## 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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
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)

# supplementary materials

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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 <sup>i</sup>	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 <sup>i</sup>	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 <sup>i</sup>	66.93 (11)	O1—C1—C2—C3	175.5 (3)
O1—P1—O2—P1 <sup>i</sup>	-170.64 (9)	C1—C2—C3—C4	0.2 (5)
N1—P1—O2—P1 <sup>i</sup>	-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

