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

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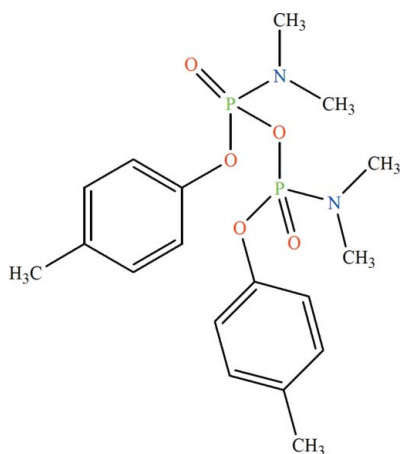
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.052; wR factor = 0.124; data-to-parameter ratio = 19.2.

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, 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°)].

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) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.25$ mm⁻¹
 $T = 100$ 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
 $\Delta\rho_{\text{max}} = 0.34$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.37$ 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).

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supporting information

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

Mehrdad Pourayoubi, Saied Ghadimi and Ali Asghar Ebrahimi Valmoozi

S1. 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, $[(\text{CH}_3)_2\text{N}][p\text{-CH}_3\text{-C}_6\text{H}_4\text{-O}]\text{P}(\text{O})(\text{O})\text{P}(\text{O})[\text{O}-\text{C}_6\text{H}_4\text{-}p\text{-CH}_3][\text{N}(\text{CH}_3)_2]$. 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 (P—O—P angle = $130.0(2)^\circ$). The bond angles around the P atoms are in the range of $94.25(12)^\circ$ (for O1—P1—O2 angle) to $117.71(12)^\circ$ (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° .

S2. Experimental

$[(\text{CH}_3)_2\text{N}]\text{P}(\text{O})\text{Cl}[\text{O}-\text{C}_6\text{H}_4\text{-}p\text{-CH}_3]$ was synthesized according to the literature method (Ghadimi *et al.*, 2007). The title compound was prepared according to the following procedure: A mixture of $[(\text{CH}_3)_2\text{N}]\text{P}(\text{O})\text{Cl}[\text{O}-\text{C}_6\text{H}_4\text{-}p\text{-CH}_3]$ (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.

S3. Refinement

The H(C) atom positions were calculated. All hydrogen atoms were refined in isotropic approximation in riding model with the $U_{\text{iso}}(\text{H})$ parameters equal to $1.2 U_{\text{eq}}(\text{C}_i)$, for methyl groups equal to $1.5 U_{\text{eq}}(\text{C}_{ii})$, where $U(\text{C}_i)$ and $U(\text{C}_{ii})$ are respectively the equivalent thermal parameters of the carbon atoms to which corresponding H atoms are bonded.

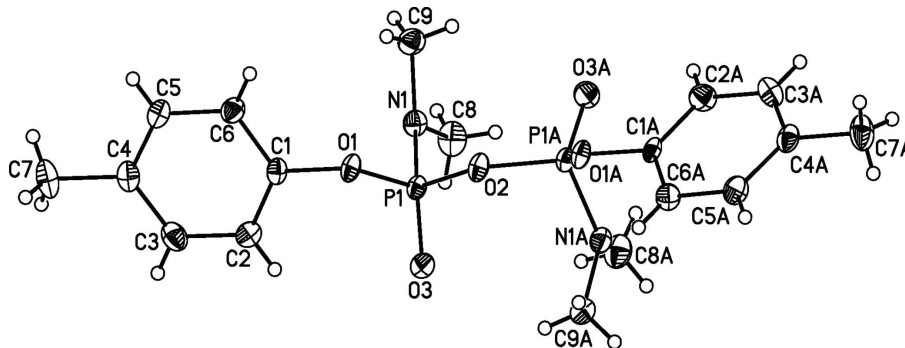


Figure 1

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

$C_{18}H_{26}N_2O_5P_2$

$M_r = 412.35$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

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

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

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

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

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

$Z = 4$

$F(000) = 872$

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

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 monochromator

phi and ω 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

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

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 (\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 (Å²)

| | 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 code: (i) $-x, y, -z+1/2$.