# organic compounds

## N,N-Dimethyl O-p-tolyl phosphoramido-cyanidate

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The P—N bond in the title compound, $C_{10}H_{13}N_2O_2P$, is shorter [at 1.6104 (15) Å] than a normal P—N single bond. The N atom deviates slightly from the plane of the three atoms to which it is bonded. The sum of the angles surrounding this N atom is 358°. In the crystal structure, weak C—H···O hydrogen bonds link molecules into one-dimensional chains along the $a$-axis direction.

## Related literature

For a review of organophosphorus compounds as used as pesticides, see: Fulton & Key (2001). For related literature, see: Corbridge (1995); Ghadimi *et al.* (2007); Munro *et al.* (1994); du Plessis *et al.* (1982).
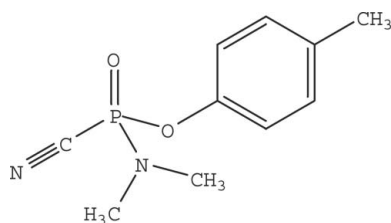


## Experimental

### Crystal data

$C_{10}H_{13}N_2O_2P$
$M_r = 224.19$
Triclinic, $P1$
$a = 6.0322$ (9) Å
$b = 6.8532$ (10) Å
$c = 7.3820$ (11) Å
$\alpha = 105.604$ (3)°
$\beta = 95.800$ (3)°
$\gamma = 106.802$ (3)°
$V = 276.03$ (7) Å$^3$
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.23$ mm$^{-1}$
$T = 100$ (2) K
$0.60 \times 0.12 \times 0.10$ mm

### Data collection

Bruker APEXII diffractometer
Absorption correction: none
3289 measured reflections
2791 independent reflections
2688 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.084$
$S = 1.04$
2791 reflections
139 parameters
3 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.48$ e Å$^{-3}$
$\Delta\rho_{min} = -0.41$ e Å$^{-3}$
Absolute structure: Flack (1983), 1332 Friedel pairs
Flack parameter: −0.03 (7)

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C7—H7A···O1$^i$ | 0.95 | 2.50 | 3.441 (2) | 174 |

Symmetry code: (i) $x - 1, y, z$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; 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*.

## References

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**supplementary materials**

## N,N-Dimethyl *O-p*-tolyl phosphoramidocyanidate

## S. Ghadimi, A. A. E. Valmoozi and M. Pourayoubi

### Comment

Organophosphorus compounds (henceforth OPs for convenience) are one of the most widely used classes of pesticides in the world (Fulton & Key, 2001). For some phosphoramido acid, esters inhibiting acetylcholinesterase (AChE) activity was reported, resulting in an accumulation of acetylcholine (ACh) in neural and non-neural tissues (Ghadimi *et al.*, 2007). Tabun (*O*-ethyl *N,N*-dimethyl-phosphoramidocyanidate, $(CH_3)_2NP(O)CN(OC_2H_5)$) is one of the well known nerve agent with very high toxicity (Munro *et al.*, 1994). The crystal structure of dimethyl *N*-phenylphosphoramidate has already been reported (du Plessis *et al.*, 1982). In this work, the synthesis and crystal structure of $(CH_3)2NP(O)CN(p—OC_6H_4—CH_3)$ is presented. The molecular structure of the title compound is shown in Fig. 1 Four different groups are linked to atom P1 giving a distorted tetrahedral configuration. The bond angles around P atom are in the range of 101.14 (8)° [O2—P1—C1] to 118.26 (7)° [O1—P1—O2]. The O atom (of the 4-$CH_3$—$C_6H_4$—O group) has sp2 character (P1—O2—C2= 119.88 (10)°). The P1—O2 bond length (1.5799 (13) Å) is smaller than a P—O normal single bond length (1.64 Å, Corbridge, 1995). Also, the P—N bond length (1.6104 (15) Å) is shorter than the normal P—N single bond length (1.77 Å, Corbridge, 1995). The N atom in the title molecule indicates a slight deviation from planarity. This fact can be shown by the torsion angle P1—C9—C10—N1, which is *ca* 9.07°. Furthermore, sum of the surrounding angles around N atom is 358.01° which is less than that for an sp2 hybridized atom. The P1—C1 bond length is longer than the P—N and P—O bond lengths (1.8096 (18) Å) and the cyanide group has nearly linear configuration (N2—C1—P1 = 175.43 (17)°). Each molecule is surrounded with by neighboring molecules *via* weak C—H···O interactions leading to a 1-D chain in the network. A view of the unit cell packing of title compound is given in Figure 2.
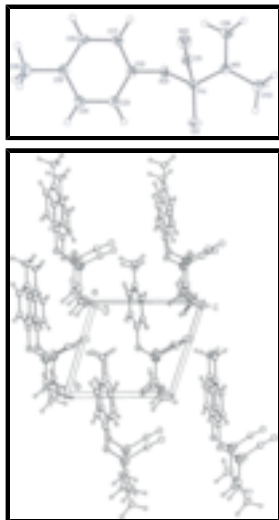
### Experimental

To a solution of N, *N*-dimethyl phosphoramidochloridic acid 4-methyl phenyl ester (0.82 g, 3.5 mmol) in 30 ml dry acetonitrile KCN (0.45 g, 7 mmol) was added and stirred 4 h at 330 K. The mixture was cooled at room temperature, and filtered. The solvent was evaporated under vacuum. The solid product was washed with n-hexane and crystallized in hexane/ethyl acetate 9:1 at room temperature. $^1$H NMR ($CDCl_3$), δ(p.p.m.): 2.34 (s, 3 H, *p*-$CH_3$), 2.88 (d, 3JPNCH = 11.4 Hz, 6 H, NMe2), 7.10–7.21 (m, 4 H, Ar—H); $^{13}$C NMR ($CDCl_3$), δ(p.p.m.): 20.71 (s, 1 C, *p*-$CH_3$), 35.64 (s, 2 C, N($CH_3$)$_2$), 114.34 (d, 1JP-C = 186.8 Hz, 2 C, CN), 120.12 (d, 3JP-C = 4.90 Hz, 1 C, Cortho), 130.70 (s, 1 C, Cmeta), 136.32 (s, 1 C, Cpara), 146.32 (d, 2JP-C = 7.4 Hz, 1 C, Cipso); $^{31}$P{$^1$H} NMR δ (p.p.m.): −11.824 (*s*); $^{31}$P NMR, δ(p.p.m.): −11.94 to −11.71 (hept., 3JP-H = 11.3 Hz).

### Refinement

All hydrogen atoms were found in difference Fourier maps but were placed in calculated positions [C—H = 0.95–0.98 Å] and refined in the riding-model approximation with $U_{iso}(H)=1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups.

**Figures**





**N,N-Dimethyl O-p-tolyl phosphoramidocyanidate**

*Crystal data*

| | |
|---|---|
| $C_{10}H_{13}N_2O_2P$ | $Z = 1$ |
| $M_r = 224.19$ | $F_{000} = 118$ |
| Triclinic, $P1$ | $D_x = 1.349$ Mg m$^{-3}$ |
| Hall symbol: P 1 | Mo $K\alpha$ radiation<br>$\lambda = 0.71073$ Å |
| $a = 6.0322$ (9) Å | Cell parameters from 1809 reflections |
| $b = 6.8532$ (10) Å | $\theta = 2.9–33.7°$ |
| $c = 7.3820$ (11) Å | $\mu = 0.23$ mm$^{-1}$ |
| $\alpha = 105.604$ (3)° | $T = 100$ (2) K |
| $\beta = 95.800$ (3)° | Prism, colourless |
| $\gamma = 106.802$ (3)° | $0.60 \times 0.12 \times 0.10$ mm |
| $V = 276.03$ (7) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Bruker APEX II diffractometer | 2688 reflections with $I > 2\sigma(I)$ |
| Radiation source: fine-focus sealed tube | $R_{int} = 0.020$ |
| Monochromator: graphite | $\theta_{max} = 29.0°$ |
| $T = 100(2)$ K | $\theta_{min} = 2.9°$ |
| ω scans | $h = -8 \rightarrow 8$ |
| Absorption correction: none | $k = -9 \rightarrow 9$ |
| 3289 measured reflections | $l = -9 \rightarrow 10$ |
| 2791 independent reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.034$ | $w = 1/[\sigma^2(F_o^2) + (0.0486P)^2 + ]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.084$ | $(\Delta/\sigma)_{max} = 0.001$ |
| $S = 1.04$ | $\Delta\rho_{max} = 0.48$ e Å$^{-3}$ |
| 2791 reflections | $\Delta\rho_{min} = -0.41$ e Å$^{-3}$ |
| 139 parameters | Extinction correction: none |
| 3 restraints | Absolute structure: Flack (1983), 1332 Friedel pairs |
| Primary atom site location: structure-invariant direct methods | Flack parameter: −0.03 (7) |
| Secondary atom site location: difference Fourier map | |

*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$^2$ > 2sigma(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 | 0.82244 (6) | 0.58868 (5) | 0.72672 (5) | 0.01572 (11) |
| O1 | 1.0453 (2) | 0.5443 (2) | 0.7274 (2) | 0.0239 (3) |
| O2 | 0.6317 (2) | 0.48682 (18) | 0.53457 (17) | 0.0175 (2) |
| N1 | 0.8366 (2) | 0.8366 (2) | 0.7906 (2) | 0.0186 (3) |
| N2 | 0.5735 (3) | 0.4022 (3) | 0.9964 (2) | 0.0244 (3) |
| C1 | 0.6641 (3) | 0.4674 (3) | 0.8858 (3) | 0.0180 (3) |
| C2 | 0.5178 (3) | 0.2614 (3) | 0.4632 (2) | 0.0157 (3) |
| C3 | 0.6336 (3) | 0.1317 (3) | 0.3651 (2) | 0.0177 (3) |
| H3A | 0.7893 | 0.1921 | 0.3468 | 0.021* |
| C4 | 0.5173 (3) | −0.0891 (3) | 0.2938 (3) | 0.0193 (3) |
| H4A | 0.5943 | −0.1799 | 0.2255 | 0.023* |
| C5 | 0.2882 (3) | −0.1790 (3) | 0.3214 (2) | 0.0175 (3) |
| C6 | 0.1780 (3) | −0.0424 (3) | 0.4193 (3) | 0.0189 (3) |
| H6A | 0.0219 | −0.1013 | 0.4375 | 0.023* |
| C7 | 0.2907 (3) | 0.1783 (3) | 0.4912 (2) | 0.0179 (3) |
| H7A | 0.2136 | 0.2699 | 0.5580 | 0.021* |

| | | | | |
|---|---|---|---|---|
| C8 | 0.1680 (4) | −0.4192 (3) | 0.2471 (3) | 0.0246 (4) |
| H8A | 0.0071 | −0.4544 | 0.2726 | 0.037* |
| H8B | 0.2569 | −0.4885 | 0.3119 | 0.037* |
| H8C | 0.1618 | −0.4704 | 0.1087 | 0.037* |
| C9 | 0.6234 (3) | 0.8978 (3) | 0.7893 (3) | 0.0208 (4) |
| H9A | 0.6312 | 0.9986 | 0.7160 | 0.031* |
| H9B | 0.6118 | 0.9661 | 0.9213 | 0.031* |
| H9C | 0.4844 | 0.7695 | 0.7299 | 0.031* |
| C10 | 1.0552 (3) | 1.0079 (3) | 0.9003 (3) | 0.0246 (4) |
| H10A | 1.0802 | 1.1293 | 0.8498 | 0.037* |
| H10B | 1.1886 | 0.9538 | 0.8889 | 0.037* |
| H10C | 1.0430 | 1.0549 | 1.0354 | 0.037* |

*Atomic displacement parameters ($Å^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| P1 | 0.01261 (18) | 0.01389 (19) | 0.0204 (2) | 0.00529 (14) | 0.00426 (14) | 0.00354 (15) |
| O1 | 0.0163 (6) | 0.0243 (7) | 0.0313 (7) | 0.0107 (5) | 0.0062 (5) | 0.0044 (6) |
| O2 | 0.0189 (6) | 0.0122 (5) | 0.0206 (6) | 0.0049 (5) | 0.0032 (5) | 0.0045 (5) |
| N1 | 0.0151 (7) | 0.0142 (7) | 0.0258 (8) | 0.0049 (6) | 0.0048 (6) | 0.0050 (6) |
| N2 | 0.0245 (8) | 0.0232 (8) | 0.0241 (8) | 0.0062 (6) | 0.0058 (6) | 0.0066 (6) |
| C1 | 0.0168 (8) | 0.0139 (8) | 0.0213 (8) | 0.0056 (6) | 0.0010 (6) | 0.0027 (6) |
| C2 | 0.0168 (8) | 0.0140 (7) | 0.0159 (7) | 0.0046 (6) | 0.0018 (6) | 0.0052 (6) |
| C3 | 0.0152 (8) | 0.0181 (8) | 0.0188 (8) | 0.0047 (6) | 0.0050 (6) | 0.0045 (6) |
| C4 | 0.0211 (9) | 0.0180 (8) | 0.0193 (8) | 0.0084 (7) | 0.0054 (7) | 0.0038 (6) |
| C5 | 0.0173 (8) | 0.0173 (8) | 0.0168 (8) | 0.0051 (6) | −0.0006 (6) | 0.0056 (6) |
| C6 | 0.0130 (8) | 0.0210 (8) | 0.0224 (8) | 0.0049 (6) | 0.0028 (6) | 0.0076 (7) |
| C7 | 0.0163 (8) | 0.0193 (8) | 0.0187 (8) | 0.0085 (7) | 0.0024 (6) | 0.0046 (6) |
| C8 | 0.0222 (9) | 0.0156 (8) | 0.0311 (10) | 0.0030 (7) | −0.0009 (7) | 0.0050 (7) |
| C9 | 0.0209 (9) | 0.0184 (8) | 0.0247 (9) | 0.0111 (7) | 0.0031 (7) | 0.0048 (7) |
| C10 | 0.0168 (8) | 0.0197 (9) | 0.0293 (10) | 0.0011 (7) | 0.0036 (7) | 0.0005 (7) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| P1—O1 | 1.4613 (13) | C5—C6 | 1.390 (2) |
| P1—O2 | 1.5799 (13) | C5—C8 | 1.510 (2) |
| P1—N1 | 1.6104 (15) | C6—C7 | 1.390 (2) |
| P1—C1 | 1.8096 (18) | C6—H6A | 0.9500 |
| O2—C2 | 1.4181 (19) | C7—H7A | 0.9500 |
| N1—C9 | 1.463 (2) | C8—H8A | 0.9800 |
| N1—C10 | 1.467 (2) | C8—H8B | 0.9800 |
| N2—C1 | 1.145 (2) | C8—H8C | 0.9800 |
| C2—C7 | 1.383 (2) | C9—H9A | 0.9800 |
| C2—C3 | 1.385 (2) | C9—H9B | 0.9800 |
| C3—C4 | 1.394 (2) | C9—H9C | 0.9800 |
| C3—H3A | 0.9500 | C10—H10A | 0.9800 |
| C4—C5 | 1.401 (2) | C10—H10B | 0.9800 |
| C4—H4A | 0.9500 | C10—H10C | 0.9800 |

| | | | |
|---|---|---|---|
| O1—P1—O2 | 118.26 (7) | C5—C6—H6A | 119.2 |
| O1—P1—N1 | 117.32 (7) | C7—C6—H6A | 119.2 |
| O2—P1—N1 | 102.87 (7) | C2—C7—C6 | 118.46 (16) |
| O1—P1—C1 | 108.72 (8) | C2—C7—H7A | 120.8 |
| O2—P1—C1 | 101.14 (8) | C6—C7—H7A | 120.8 |
| N1—P1—C1 | 106.88 (8) | C5—C8—H8A | 109.5 |
| C2—O2—P1 | 119.88 (10) | C5—C8—H8B | 109.5 |
| C9—N1—C10 | 115.30 (14) | H8A—C8—H8B | 109.5 |
| C9—N1—P1 | 121.52 (11) | C5—C8—H8C | 109.5 |
| C10—N1—P1 | 121.19 (13) | H8A—C8—H8C | 109.5 |
| N2—C1—P1 | 175.43 (17) | H8B—C8—H8C | 109.5 |
| C7—C2—C3 | 121.95 (15) | N1—C9—H9A | 109.5 |
| C7—C2—O2 | 118.45 (15) | N1—C9—H9B | 109.5 |
| C3—C2—O2 | 119.60 (15) | H9A—C9—H9B | 109.5 |
| C2—C3—C4 | 118.69 (16) | N1—C9—H9C | 109.5 |
| C2—C3—H3A | 120.7 | H9A—C9—H9C | 109.5 |
| C4—C3—H3A | 120.7 | H9B—C9—H9C | 109.5 |
| C3—C4—C5 | 120.86 (16) | N1—C10—H10A | 109.5 |
| C3—C4—H4A | 119.6 | N1—C10—H10B | 109.5 |
| C5—C4—H4A | 119.6 | H10A—C10—H10B | 109.5 |
| C6—C5—C4 | 118.46 (16) | N1—C10—H10C | 109.5 |
| C6—C5—C8 | 121.62 (17) | H10A—C10—H10C | 109.5 |
| C4—C5—C8 | 119.92 (17) | H10B—C10—H10C | 109.5 |
| C5—C6—C7 | 121.58 (16) | | |
| O1—P1—O2—C2 | 67.61 (14) | C7—C2—C3—C4 | −0.3 (3) |
| N1—P1—O2—C2 | −161.29 (12) | O2—C2—C3—C4 | −179.12 (15) |
| C1—P1—O2—C2 | −50.89 (13) | C2—C3—C4—C5 | −0.4 (3) |
| O1—P1—N1—C9 | 178.18 (13) | C3—C4—C5—C6 | 0.9 (3) |
| O2—P1—N1—C9 | 46.52 (14) | C3—C4—C5—C8 | −178.47 (15) |
| C1—P1—N1—C9 | −59.52 (15) | C4—C5—C6—C7 | −0.8 (3) |
| O1—P1—N1—C10 | −18.64 (18) | C8—C5—C6—C7 | 178.61 (16) |
| O2—P1—N1—C10 | −150.30 (15) | C3—C2—C7—C6 | 0.5 (3) |
| C1—P1—N1—C10 | 103.65 (16) | O2—C2—C7—C6 | 179.28 (14) |
| P1—O2—C2—C7 | 101.96 (16) | C5—C6—C7—C2 | 0.1 (3) |
| P1—O2—C2—C3 | −79.22 (17) | | |

*Hydrogen-bond geometry (Å, °)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| C7—H7A···O1[i] | 0.95 | 2.50 | 3.441 (2) | 174 |

Symmetry codes: (i) *x*−1, *y*, *z*.

**Fig. 1**

**Fig. 2**