

Trianilinophosphine oxide

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Key indicators

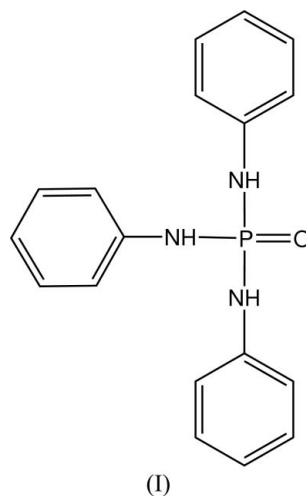
Single-crystal X-ray study
 $T = 297\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.049
 wR factor = 0.137
Data-to-parameter ratio = 15.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{18}\text{H}_{18}\text{N}_3\text{OP}$, was synthesized by the condensation of phosphoryl chloride with an excess of aniline. The P atom is in a distorted tetrahedral environment. The molecules are stabilized by a weak intramolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond and $\text{C}-\text{H}\cdots\pi$ interactions. The molecules are stacked along the b axis.

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Comment

Variation in P—N bond lengths has been observed in a survey of p -substituted phosphoric trianilides (Cameron *et al.*, 1976). We therefore decided to investigate the P—N bond lengths in the simple phosphoryl trianilide, (I), which was synthesized by the condensation of phosphoryl chloride and excess aniline.



All bond lengths in (I) show normal values (Allen *et al.*, 1987). In this simple phosphoryl trianilide system there is little difference in the P—N bond lengths (Table 1) compared with the reported P—N bond lengths for p -tolylphosphoryl triamide [*i.e.* 1.620 (7), 1.635 (7) and 1.669 (9) Å] and other similar compounds (Cameron *et al.*, 1976). This may be due to complete and equal overlap of the non-bonding p_z orbitals of all three $\text{N}sp^3$ atoms with an unoccupied d orbital on the P atom. This is further supported by the shorter phosphoryl $\text{P}=\text{O}$ bond length in (I) compared with those in the $\text{N},\text{N}',\text{N}''$ -tri- p -tolylphosphoryl triamide system [1.495 (8) Å; Cameron *et al.*, 1976]. The three N—P—N bond angles (Table 1) indicate that the P atom is in a distorted tetrahedral environment in order to minimize the steric interactions between the three aromatic rings.

The intramolecular $\text{C}14-\text{H}14A\cdots\text{O}1$ hydrogen bond generates an $S(6)$ graph-set motif (Bernstein *et al.*, 1995) and

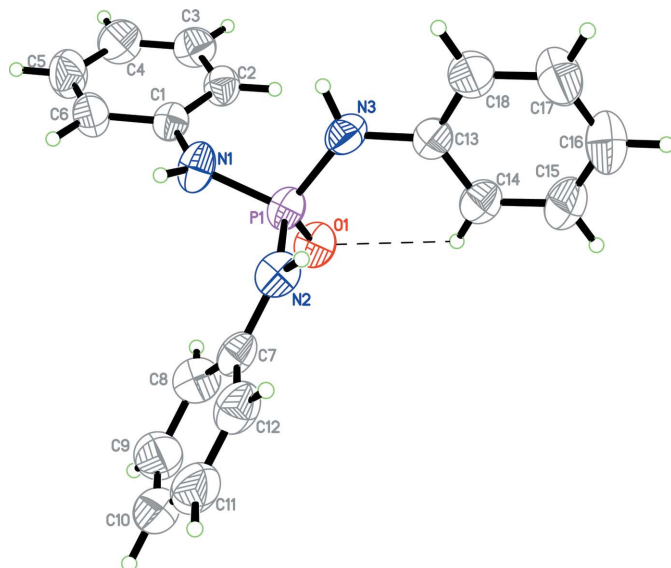


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. A dashed line indicates the intramolecular hydrogen bond.

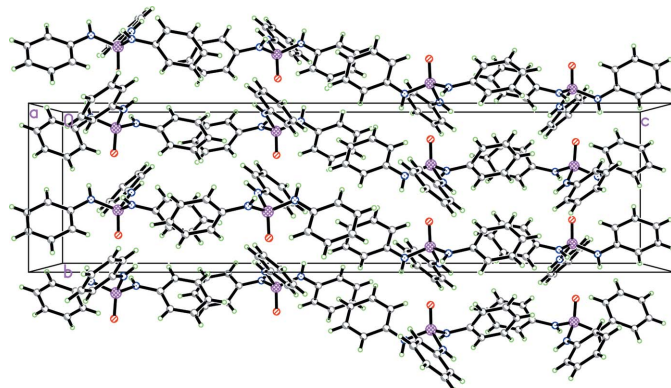


Figure 2
The crystal packing of (I), viewed down the *b* axis.

weak intermolecular C—H··· π interactions stabilize the structure (Table 2). The molecules are stacked along the *b* axis in parallel layers (Fig. 2).

Experimental

Phosphoryl chloride (1.5 ml, 0.98 mmol) was added dropwise to an excess of aniline (8 ml) at 273 K. After stirring for 20 min, the solid mass was filtered off, washed with dilute hydrochloric acid and crystallized from methanol to afford (I) (m.p. 546 K, 74% yield).

Crystal data

$C_{18}H_{18}N_3OP$
 $M_r = 323.32$
Orthorhombic, *Pbca*
 $a = 9.9173$ (8) Å
 $b = 9.2463$ (7) Å
 $c = 35.405$ (3) Å
 $V = 3246.6$ (4) Å³

$Z = 8$
 $D_x = 1.323$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 0.18$ mm⁻¹
 $T = 297$ (2) K
Block, colourless
0.41 × 0.33 × 0.24 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.931$, $T_{\max} = 0.959$

16288 measured reflections
3183 independent reflections
2735 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$
 $\theta_{\max} = 26.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.137$
 $S = 1.09$
3183 reflections
208 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0685P)^2 + 1.0693P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.18$ e Å⁻³
 $\Delta\rho_{\min} = -0.39$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

| | | | |
|----------|-------------|-----------|-------------|
| P1—O1 | 1.4672 (14) | P1—N3 | 1.6436 (18) |
| P1—N1 | 1.6368 (16) | P1—N2 | 1.6447 (17) |
| N1—P1—N3 | 105.06 (9) | C1—N1—P1 | 127.92 (13) |
| N1—P1—N2 | 105.16 (9) | C7—N2—P1 | 128.31 (14) |
| N3—P1—N2 | 103.58 (9) | C13—N3—P1 | 127.46 (14) |

Table 2

Hydrogen-bond geometry (Å, °).

Cg1 and Cg2 are the centroids rings C1—C6 and C7—C12, respectively.

| <i>D</i> —H··· <i>A</i> | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|-------------------------------|-------------|---------------|-----------------------|-------------------------|
| C14—H14A···O1 | 0.93 | 2.57 | 3.229 (3) | 128 |
| C3—H3B···Cg2 ⁱ | 0.93 | 3.05 | 3.3714 | 132 |
| C6—H6A···Cg1 ⁱⁱ | 0.93 | 3.17 | 3.3423 | 157 |
| C11—H11A···Cg2 ⁱⁱⁱ | 0.93 | 2.97 | 3.3258 | 117 |

Symmetry codes: (i) $-x + \frac{3}{2}, y - \frac{3}{2}, z$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, z$; (iii) $-x + \frac{5}{2}, y - \frac{1}{2}, z$.

H atoms were placed in calculated positions, with N—H distances of 0.86 Å and C—H distances of 0.93 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL, PARST (Nardelli, 1995) and PLATON (Spek, 2003).

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References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Cameron, T. S., Magee, M. G. & McLean, S. (1976). *Z. Naturforsch. B Chem. Sci.* **31**, 1295–1296.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

Sheldrick, G. M. (1996). *SADABS*. University of Gottingen, Germany.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison,
Wisconsin, USA.

Siemens (1996). *SMART* and *SAINTE*. Siemens Analytical X-ray Instruments
Inc., Madison, Wisconsin, USA.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.