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Structure of Tri-*p*-tolylphosphine Oxide Hemihydrate, $\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3\text{O}\cdot\frac{1}{2}\text{H}_2\text{O}$

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Abstract. $\text{C}_{21}\text{H}_{21}\text{OP}\cdot\frac{1}{2}\text{H}_2\text{O}$, $M_r = 329.4$, monoclinic, $C2/c$, $a = 16.192(3)$, $b = 12.382(2)$, $c = 19.353(3)$ Å, $\beta = 104.990(10)^\circ$, $V = 3748.0(10)$ Å³, $Z = 8$, $D_x = 1.167$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.147$ mm⁻¹, $F(000) = 1400$, $T = 295$ K, $R = 0.0686$, $wR = 0.0429$ for all 1757 unique data and $R = 0.0354$, $wR = 0.0348$ for those 1083 data with $F_o > 6.0\sigma(F_o)$. The central P atom has a distorted tetrahedral environment, with $\text{P}=\text{O} = 1.482(3)$ Å and $\text{P}-\text{C} = 1.798(3)$ – $1.799(3)$ Å. Average $\text{O}-\text{P}-\text{C} = 112.9^\circ$ and average $\text{C}-\text{P}-\text{C} = 105.8^\circ$. The O atom of the water molecule lies on a crystallographic twofold axis and is linked by hydrogen bonds to two tri-*p*-tolylphosphine oxide molecules with $\text{O}\cdots\text{O}(\text{water}) = 2.810(4)$ Å.

Experimental. A clear crystal with approximate dimensions $0.25 \times 0.30 \times 0.45$ mm was aligned on a Siemens *R3m/V* diffractometer. Determination of the unit-cell parameters and the orientation matrix and data collection ($\text{Mo } K\alpha$; $2\theta = 5.0 \rightarrow 40.0^\circ$; maximum $\sin\theta/\lambda = 0.539$ Å⁻¹) were performed using the *P3* program package (Siemens Analytical X-ray Instruments, Inc., 1989). Data were collected for the entire sphere by the coupled $\theta(\text{crystal})$ – $2\theta(\text{counter})$ scan ($h = -15 \rightarrow 15$, $k = -11 \rightarrow 11$, $l = -18 \rightarrow 18$). Three standard reflections were collected after each batch of 97 reflections; no significant fluctuations in their intensities were noted. A total of 7016 data were collected, and were corrected for Lorentz and polarization factors and for the effects of absorption (minimum and maximum transmission factors were 0.8894 and 0.9139, respectively). These data were merged to

produce 1757 independent reflections ($R_{\text{int}} = 3.30\%$). Axial photographs indicated that the crystal belonged to the *C*-centered subset of the monoclinic system. The systematic absences of hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$ indicated the possible space groups as *Cc* or *C2/c*. Intensity statistics clearly favored the centrosymmetric case. The space group *C2/c* (C_{2h}^6 ; No. 15) was assumed and confirmed by the successful solution and refinement of the structure in this higher symmetry space group.

All crystallographic calculations were carried out on a VAX3100 workstation with the use of the Siemens *SHELXTL-Plus* program set (Sheldrick, 1990). The analytical scattering factors for the neutral atoms were corrected for the f' and f'' components of anomalous dispersion using the values compiled in *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–101, 148–150). The structure was solved by a combination of direct methods and difference Fourier techniques. Refinement led to convergence [$(\Delta/\sigma)_{\text{max}} = 0.001$] with $R = 6.86\%$, $wR = 4.29\%$ and GOF = 1.42 for 1757 independent reflections and 239 variables [$R = 3.54\%$, $wR = 3.48\%$ for those 1083 reflections with $F_o > 6.0\sigma(F_o)$]. The quantity minimized was $\sum w(F_o - |F_c|)^2$, where $w^{-1} = \sigma^2(F) + 0.0001F^2$.

All non-H atoms were refined anisotropically, and the H atoms of the *p*-tolyl groups were included in calculated positions with $\text{C}-\text{H} = 0.96$ Å (Churchill, 1973). The positional and isotropic thermal parameters of the unique H atom of the H_2O molecule were refined. A final difference Fourier synthesis showed features only in the range 0.20 to -0.18 e Å⁻³. Final

Table 1. Atomic coordinates ($\times 10^4$) and displacement coefficients ($\text{\AA}^2 \times 10^3$)

Equivalent isotropic U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. H(1s) was refined isotropically.

	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$
P(1)	3911 (1)	2486 (1)	3960 (1)	73 (1)
O(1)	4442 (2)	2463 (2)	3441 (1)	108 (1)
C(11)	3072 (2)	1491 (3)	3769 (2)	60 (2)
C(12)	2766 (2)	1000 (3)	4290 (2)	63 (2)
C(13)	2099 (2)	273 (3)	4117 (2)	67 (2)
C(14)	1716 (2)	17 (3)	3421 (3)	72 (2)
C(15)	2033 (3)	486 (4)	2899 (2)	95 (2)
C(16)	2698 (3)	1210 (3)	3069 (2)	91 (2)
C(17)	962 (3)	-742 (4)	3239 (3)	114 (3)
C(21)	4517 (2)	2232 (3)	4863 (2)	63 (2)
C(22)	4324 (2)	2667 (3)	5455 (2)	74 (2)
C(23)	4785 (3)	2410 (3)	6139 (2)	83 (2)
C(24)	5457 (3)	1702 (4)	6258 (3)	88 (2)
C(25)	5661 (3)	1262 (3)	5671 (4)	103 (3)
C(26)	5202 (3)	1515 (3)	4979 (3)	90 (2)
C(27)	5975 (3)	1429 (6)	7019 (3)	135 (3)
C(31)	3393 (3)	3766 (3)	3983 (2)	65 (2)
C(32)	2513 (3)	3894 (3)	3793 (2)	73 (2)
C(33)	2142 (3)	4892 (4)	3789 (2)	81 (2)
C(34)	2629 (3)	5815 (3)	3975 (2)	78 (2)
C(35)	3506 (3)	5688 (3)	4169 (2)	81 (2)
C(36)	3886 (3)	4696 (3)	4171 (2)	75 (2)
C(37)	2216 (4)	6909 (4)	3966 (3)	114 (3)
O(1s)	5000	1086 (5)	2500	157 (4)
H(1s)	4967 (38)	1496 (43)	2145 (25)	180 (26)

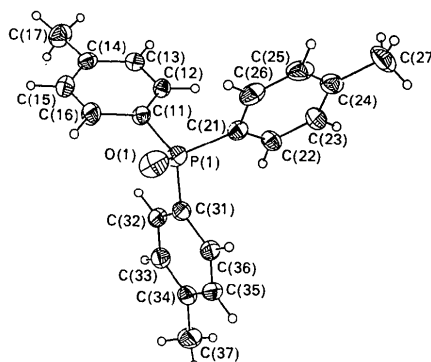
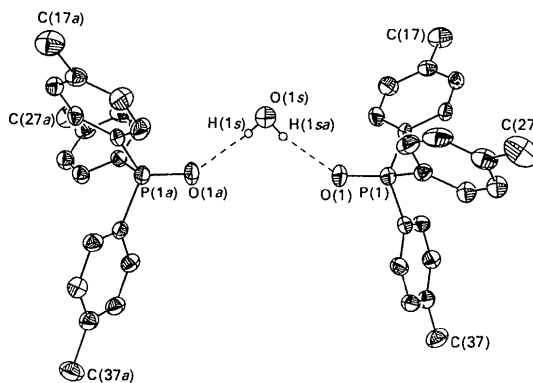
atomic coordinates appear in Table 1.* The crystal consists of an ordered array of $\text{O}=\text{P}(p\text{-tolyl})_3$ molecules and H_2O molecules of solvation in a ratio of 2:1. A perspective view of the $\text{O}=\text{P}(p\text{-tolyl})_3$ molecule, with the atomic numbering scheme, is shown in Fig. 1 (ORTEPII; Johnson, 1976). Fig. 2 shows the contents of two adjacent asymmetric units, with a crystallographic twofold axis running through the O atom of the H_2O molecule of solvation. Selected bond lengths and bond angles are collected in Table 2.

Related literature. The most recent crystallographic study of the related $\text{P}=\text{O}(\text{phenyl})_3$ was published by Spek (1987). Hydrogen bonding analogous to that in the present compound was found in the structure of $\text{P}=\text{O}(\text{phenyl})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ (Baures & Silverton, 1990); in the following discussion, corresponding values of bond lengths and angles from the structure of $\text{P}=\text{O}(\text{phenyl})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ are listed in parentheses for ease of comparison. The geometry about the P atoms is that of a slightly distorted tetrahedron. The $\text{O}-\text{P}-\text{C}$ angles were observed to be $\text{O}(1)-\text{P}(1)-\text{C}(11) = 112.8 (2)$, $\text{O}(1)-\text{P}(1)-\text{C}(21) = 112.9 (2)$ and $\text{O}(1)-\text{P}(1)-\text{C}(31) = 112.9 (2)^\circ$ [$111.6 (1)$, $111.8 (1)$, $112.5 (1)^\circ$]. The $\text{C}-\text{P}-\text{C}$ angles are slightly smaller than the $\text{O}-\text{P}-\text{C}$ angles, with $\text{C}(11)-\text{P}(1)-\text{C}(21) = 105.8 (2)$, $\text{C}(11)-\text{P}(1)-\text{C}(31) = 106.0 (2)$ and $\text{C}(21)-\text{P}(1)-\text{C}(31) = 105.7 (2)^\circ$ [$105.6 (1)$, $106.2 (1)$,

* Lists of anisotropic thermal parameters, H-atom positions and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55492 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1002]

Table 2. Bond lengths (\AA) and bond angles ($^\circ$)

P(1)—O(1)	1.482 (3)	P(1)—C(11)	1.799 (3)
P(1)—C(21)	1.798 (3)	P(1)—C(31)	1.799 (4)
C(11)—C(12)	1.376 (5)	C(11)—C(16)	1.379 (5)
C(12)—C(13)	1.378 (5)	C(13)—C(14)	1.368 (6)
C(14)—C(15)	1.373 (7)	C(14)—C(17)	1.509 (6)
C(15)—C(16)	1.374 (6)	C(21)—C(22)	1.372 (6)
C(21)—C(26)	1.394 (5)	C(22)—C(23)	1.379 (5)
C(23)—C(24)	1.369 (6)	C(24)—C(25)	1.374 (9)
C(24)—C(27)	1.532 (7)	C(25)—C(26)	1.389 (8)
C(31)—C(32)	1.385 (6)	C(31)—C(36)	1.395 (6)
C(32)—C(33)	1.373 (6)	C(33)—C(34)	1.382 (6)
C(34)—C(35)	1.381 (7)	C(34)—C(37)	1.509 (7)
C(35)—C(36)	1.374 (6)	O(1s)—H(1s)	0.846 (50)
O(1s)—H(1sa)	0.846 (50)		
O(1)—P(1)—C(11)	112.8 (2)	O(1)—P(1)—C(21)	112.9 (2)
C(11)—P(1)—C(21)	105.8 (2)	O(1)—P(1)—C(31)	112.9 (2)
C(11)—P(1)—C(31)	106.0 (2)	C(21)—P(1)—C(31)	105.7 (2)
P(1)—C(11)—C(12)	123.3 (3)	P(1)—C(11)—C(16)	119.4 (3)
C(12)—C(11)—C(16)	117.3 (3)	C(11)—C(12)—C(13)	121.3 (3)
C(12)—C(13)—C(14)	121.2 (4)	C(13)—C(14)—C(15)	117.8 (3)
C(13)—C(14)—C(17)	120.5 (4)	C(15)—C(14)—C(17)	121.7 (4)
C(14)—C(15)—C(16)	121.2 (4)	C(11)—C(16)—C(15)	121.3 (4)
P(1)—C(21)—C(22)	123.9 (3)	P(1)—C(21)—C(26)	118.7 (3)
C(22)—C(21)—C(26)	117.4 (4)	C(21)—C(22)—C(23)	121.7 (4)
C(22)—C(23)—C(24)	121.4 (4)	C(23)—C(24)—C(25)	117.6 (4)
C(23)—C(24)—C(27)	121.2 (5)	C(25)—C(24)—C(27)	121.2 (4)
C(24)—C(25)—C(26)	121.7 (4)	C(21)—C(26)—C(25)	120.2 (5)
P(1)—C(31)—C(32)	123.2 (3)	P(1)—C(31)—C(36)	119.6 (3)
C(32)—C(31)—C(36)	117.1 (4)	C(31)—C(32)—C(33)	121.5 (4)
C(32)—C(33)—C(34)	121.5 (4)	C(33)—C(34)—C(35)	117.0 (4)
C(33)—C(34)—C(37)	121.2 (5)	C(35)—C(34)—C(37)	121.8 (4)
C(34)—C(35)—C(36)	122.1 (4)	C(31)—C(36)—C(35)	120.8 (4)
H(1s)—O(1s)—H(1sa)	106.1 (71)		

Fig. 1. The tri-*p*-tolylphosphine oxide moiety, with H atoms included.Fig. 2. Hydrogen bonding in the $\text{P}(p\text{-tolyl})_3\text{O}\cdots(\text{H}_2\text{O})\cdots\text{O}(p\text{-tolyl})_3\text{P}$ unit. H atoms are shown only for the water molecule.

108.8 (1)°]. The bond length P(1)—O(1) = 1.482 (3) Å [1.487 (2) Å], and the P—C bond lengths are P(1)—C(11) = 1.799 (3), P(1)—C(21) = 1.798 (3) and P(1)—C(31) = 1.799 (4) Å [1.796 (2), 1.797 (3), 1.806 (3) Å].

Both the O atom [O(1s), which lies on a twofold axis] and the H atom [H(1s)] of the solvent water molecule were found and their positions were refined. The distances O(1s)—H(1s) and O(1s)—H(1sa) are each 0.846 (50) Å. In the hydrogen bond O(1)⋯O(1s) = 2.810 (4) [2.856 (3)], O(1)⋯H(1s) = 2.05 (6) Å and P(1)—O(1)⋯H(1s) = 145.3 (1.5)°. The position and bond lengths involving the H atoms of the solvent molecule were not reported in the previous structural study of P=O(phenyl)₃·½H₂O.

Other related structures include (*o*-CH₃C₆H₄)₃PO (Cameron & Dahlen, 1975) and (*m*-CH₃C₆H₄)₃PO·H₂NSO₂(*p*-CH₃C₆H₄) (Ferguson, Lough & Glidewell, 1989).

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Low-Temperature Structures of *cis*-4-*tert*-Butylcyclohexyl *p*-Nitrobenzoate (1) and *trans*-4-*tert*-Butylcyclohexyl *p*-Nitrobenzoate (2)

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Abstract. *cis*- and *trans*-4-*tert*-Butylcyclohexyl *p*-nitrobenzoate, C₁₇H₂₃NO₄, *M_r* = 305.4. (1) *cis* isomer, triclinic, *P* $\bar{1}$, *a* = 6.3555 (7), *b* = 11.615 (4), *c* = 12.365 (4) Å, α = 111.44 (3), β = 100.06 (2), γ = 96.38 (2)°, *V* = 821.16 Å³, *Z* = 2, *D_x* = 1.23 Mg m⁻³, λ (Cu *K* α) = 1.5418 Å, μ = 0.66 mm⁻¹, *F*(000) = 328, *T* = 130 (2) K, *R* = 0.033 for 2237 unique observed reflections. (2) *trans* isomer, triclinic, *P* $\bar{1}$, *a* = 5.9963 (7), *b* = 15.511 (4), *c* = 17.244 (4) Å, α = 83.15 (2), β = 89.73 (1), γ = 87.94 (2)°, *V* = 1591.4 Å³, *Z* = 4, *D_x* = 1.27 Mg m⁻³, λ (Cu *K* α) = 1.5418 Å, μ = 0.64 mm⁻¹, *F*(000) = 656, *T* = 130 (2) K, *R* = 0.032 for 4504 unique observed reflections. Structure (2) consists of two independent molecules in the asymmetric unit, which have essentially identical conformations. In both structures the ester function adopts the preferred *Z* configuration. The axial C—OPNB (PNB = *p*-nitrobenzoate) bond

length in (1) is 1.473 (2) Å, which is slightly longer than the two equatorial C—OPNB bond lengths observed in (2) [C(1)—O(1) and C(1')—O(1')] for the two molecules are 1.463 (2) and 1.468 (2) Å, respectively].

Experimental. A Philips PW1100/20 diffractometer with graphite monochromator was used for data collection. Crystal temperatures were maintained at 130 (2) K with a Leybold-Heraeus nitrogen cooling device. Lattice parameters were determined from least-squares analysis of the setting angles of 25 reflections with 50 < 2 θ < 60°. Three check reflections measured every 120 min during data collection for (1) and (2) showed no significant decrease in intensity. Structure solution was by direct methods (*SHELXS86*, Sheldrick, 1985), ΔF synthesis and full-matrix least-squares refinement. Non-H atoms were refined with anisotropic displacement factors. H atoms were refined with isotropic thermal parameters. Weighting scheme $w = [\sigma^2(F) + (0.0005)F^2]^{-1}$.

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