

been reported (McKenney, Struck, Hildreth & Fryling, 1987). The structure of the next compound in this series, 1,4-butanediammonium dinitrate has also been reported (Jaskólski & Olovsson, 1989).

This work was supported in part by the Office of Naval Research, Mechanics Division.

References

- JASKÓLSKI, M. & OLOVSSON, I. (1989). *Acta Cryst.* **B45**, 78–85.
 MCKENNEY, R. L. JR, STRUCK, S. R., HILDRETH, R. A. & FRYLING, J. A. (1987). *J. Energ. Mater.* **5**, 1–25.
 SHELDRICK, G. M. (1980). *SHELXTL80. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Univ. of Göttingen, Germany.

Acta Cryst. (1991). **C47**, 2715–2716

Monoclinic Triphenylphosphine Oxide Hemihydrate

BY PAUL W. BAURES*

SmithKline Beecham Pharmaceuticals L-950, 709 Swedeland Road, King of Prussia, PA 19406, USA

(Received 4 February 1991; accepted 2 April 1991)

Abstract. $C_{18}H_{15}OP \cdot \frac{1}{2}H_2O$, $M_r = 287.30$, monoclinic, $C2/c$, $a = 19.423$ (5), $b = 8.478$ (5), $c = 18.327$ (5) Å, $\beta = 90.67$ (2)°, $V = 3017.7$ (9) Å³, $Z = 8$, $D_x = 1.265$ g cm⁻³, $\lambda(Cu K\alpha) = 1.5418$ Å, $\mu = 15.746$ cm⁻¹, $F(000) = 1208$, $T = 223$ K, $R = 0.050$ for 1734 reflections with $I > 3\sigma(I)$. The water O atoms sit on a crystallographic twofold axis and are linked by hydrogen bonds to two of the oxide molecules with O...O \cdots W distances of 2.910 (3) Å and an O...H—O \cdots W angle of 172.5 (4)°. The torsion angles between the plane of a phenyl ring and the plane generated by the atoms O, P and the *ipso* C atom in the corresponding ring are 66.21, 27.69 and 11.61° for rings C1—C6, C7—C12 and C13—C18, respectively.

Experimental. A crystal of the title compound was obtained from an attempted co-crystallization with an *N,N'*-unsymmetrically disubstituted urea. The crystal measured 0.70 × 0.20 × 0.08 mm and was mounted on a glass fiber using an epoxy resin. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Cu $K\alpha$ radiation. Lattice parameters and their e.s.d.'s were derived from the setting angles of 25 reflections ($30 < 2\theta < 35^\circ$). The space group was unambiguously determined from the systematic absences (hkl : $h + k = 2n$; $h0l$: $h, l = 2n$). 3014 reflections ($2 < 2\theta < 135^\circ$; $0 < h < 23$, $0 < k < 10$, $-21 < l < 21$) were collected using variable speed ω - 2θ scans. Three reflections ($\bar{8}47$, 937 , $6, \bar{2}, 11$) showed only random variation in intensities over 42.5 h of exposure time. Data were

corrected for Lorentz and polarization effects. Symmetry equivalent data were averaged, $R_{int} = 0.044$. The structure was solved *via* direct methods using the program *SHELXS86* (Sheldrick, 1985). The refinement was carried out using full-matrix least squares on F employing 1734 reflections with $I > 3\sigma(I)$. Unless otherwise noted, all programs were from a locally modified version of the *SDP* (Frenz, 1979) software. H atoms were found in a difference Fourier map and were refined with fixed thermal parameters equal to 1.3 times their non-H-atom counterparts. An empirical absorption correction was applied using *DIFABS* (Walker & Stuart, 1983) with a θ dependent correction. The min. correction was 0.672 and the max. correction was 1.452. The average correction was 1.009. No extinction correction was applied. Convergence with anisotropic thermal parameters for the non-H atoms and fixed isotropic thermal parameters for the H atoms was achieved at $R = 0.050$, $wR = 0.065$, $w = 1/\sigma^2(F)$ with $\sigma^2(F)$ given by the expression $[\sigma^2(I_o) + (0.05F)^2]$, 1734 reflections, 234 variables, $S = 1.574$, $(\Delta/\sigma)_{max} = 0.03$. A final difference Fourier map showed no features outside the range ± 0.25 e Å⁻³. Values of the neutral-atom scattering factors were taken from Cromer (1974). Atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are given in Table.† Bond lengths and angles are given in Table 2. Fig. 1 shows an *ORTEP* (Johnson, 1965) drawing of the molecule.

† Lists of structure factors, anisotropic thermal parameters, least-squares planes, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54130 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Present address: Department of Medicinal Chemistry, 8-Health Sciences Unit F, 308 Harvard St S.E., Minneapolis, MN 55455, USA.

Table 1. Final positional parameters with e.s.d.'s in parentheses

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$B_{eq} (\text{\AA}^2)$
P	0.12465 (5)	0.0796 (1)	0.09912 (5)	4.04 (2)
O	0.0741 (1)	-0.0167 (3)	0.1396 (1)	4.91 (5)
OW	0.500	0.6930 (4)	0.750	6.77 (9)
C1	0.1403 (2)	0.0075 (4)	0.0083 (2)	3.94 (7)
C2	0.0861 (2)	0.0075 (5)	-0.0423 (2)	4.74 (8)
C3	0.0930 (2)	-0.0617 (5)	-0.1104 (2)	5.38 (9)
C4	0.1554 (2)	-0.1282 (5)	-0.1293 (2)	5.38 (9)
C5	0.2099 (2)	-0.1271 (5)	-0.0805 (2)	5.07 (8)
C6	0.2026 (2)	-0.0609 (4)	-0.0114 (2)	4.42 (7)
C7	0.0971 (2)	0.2806 (4)	0.0894 (2)	4.13 (7)
C8	0.0543 (2)	0.3435 (5)	0.1431 (2)	5.01 (8)
C9	0.0337 (2)	0.5006 (5)	0.1389 (2)	5.9 (1)
C10	0.5949 (2)	0.5945 (5)	0.0826 (3)	6.2 (1)
C11	0.0965 (2)	0.5347 (5)	0.0296 (2)	5.9 (1)
C12	0.1175 (2)	0.3777 (4)	0.0322 (2)	5.12 (9)
C13	0.2078 (2)	0.0847 (4)	0.1445 (2)	3.94 (7)
C14	0.2201 (2)	-0.0207 (4)	0.2013 (2)	4.92 (8)
C15	0.2833 (2)	-0.0196 (5)	0.2372 (2)	5.85 (9)
C16	0.3349 (2)	0.0825 (5)	0.2168 (2)	5.36 (9)
C17	0.3225 (2)	0.1863 (5)	0.1600 (2)	5.18 (9)
C18	0.2597 (2)	0.1877 (4)	0.1244 (2)	4.42 (7)

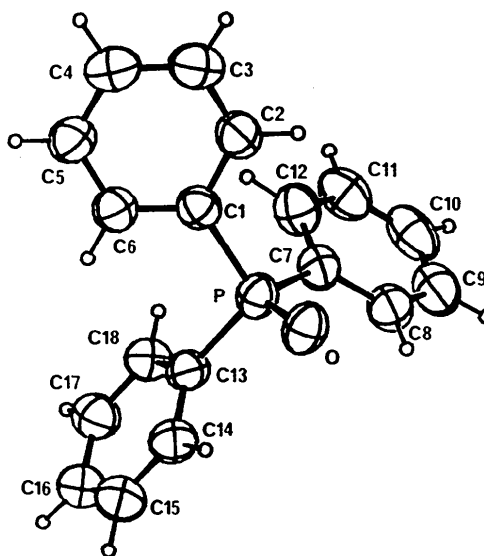


Fig. 1. ORTEP (Johnson, 1965) drawing of the title structure with the thermal ellipsoids drawn at the 50% level. The water of hydration has been omitted for clarity.

Table 2. Bond distances (Å) and angles (°) of the TPPO fragment with e.s.d.'s in parentheses

P	O	1.482 (3)	C7	C12	1.395 (5)
P	C1	1.802 (3)	C8	C9	1.393 (6)
P	C7	1.795 (3)	C9	C10	1.371 (6)
P	C13	1.808 (3)	C10	C11	1.368 (6)
C1	C2	1.394 (5)	C11	C12	1.392 (5)
C1	C6	1.394 (5)	C13	C14	1.391 (5)
C2	C3	1.388 (5)	C13	C18	1.387 (5)
C3	C4	1.382 (6)	C14	C15	1.386 (6)
C4	C5	1.378 (5)	C15	C16	1.379 (6)
C5	C6	1.394 (5)	C16	C17	1.382 (5)
C7	C8	1.401 (5)	C17	C18	1.376 (5)

O	P	C1	113.3 (1)	P	C7	C12	123.2 (3)
O	P	C7	112.0 (2)	C8	C7	C12	118.7 (3)
O	P	C13	112.1 (1)	C7	C8	C9	119.8 (3)
C1	P	C7	106.5 (2)	C8	C9	C10	120.6 (4)
C1	P	C13	105.9 (2)	C9	C10	C11	120.3 (4)
C7	P	C13	106.7 (2)	C10	C11	C12	120.4 (4)
P	C1	C2	118.8 (3)	C7	C12	C11	120.3 (4)
P	C1	C6	122.5 (2)	P	C13	C14	118.3 (3)
C2	C1	C6	118.5 (3)	P	C13	C18	122.7 (2)
C1	C2	C3	121.3 (3)	C14	C13	C18	119.0 (3)
C2	C3	C4	119.4 (3)	C13	C14	C15	119.6 (3)
C3	C4	C5	120.3 (3)	C14	C15	C16	121.2 (4)
C4	C5	C6	120.4 (4)	C15	C16	C17	118.9 (4)
C1	C6	C5	120.1 (3)	C16	C17	C18	120.6 (4)
P	C7	C8	118.0 (3)	C13	C18	C17	120.7 (3)

Related literature. Triphenylphosphine oxide (TPPO) has been used as a crystallization aid with various substrates containing hydrogen-bond donors (Etter & Baures, 1988). There are three known anhydrous polymorphs of TPPO, an orthorhombic form (space group $Pbca$; Bandoli, Bortolozzo, Clemente, Croatto & Panattoni, 1970), a monoclinic modification [space group $P2_1/b$ (Gusev, Bokii, Afonia, Timofeeva, Kalinin & Struchkov, 1973) and $P2_1/a$ setting (Ruban & Zabel, 1976)] and a second monoclinic modification (space group $P2_1/c$; Spek, 1987). Cold temperature structures of the orthorhombic form (T

= 100 and 153 K) and of the first monoclinic form (T = 100 and 152 K) were reported by Brock, Schweizer & Dunitz (1985). A previously reported hemihydrate pseudopolymorph of TPPO is also known (Baures & Silvertown, 1990) as well as a hemiperhydrate pseudopolymorph (Thierbach, Huber & Preut, 1980).

The author thanks Dr Drake S. Eggleston for helpful discussion.

References

- BANDOLI, G., BORTOLOZZO, G., CLEMENTE, D. A., CROATTO, U. & PANATTONI, C. (1970). *J. Chem. Soc. A*, pp. 2778–2780.
- BAURES, P. W. & SILVERTON, J. V. (1990). *Acta Cryst. C46*, 715–717.
- BROCK, C. P., SCHWEIZER, W. B. & DUNITZ, J. D. (1985). *J. Am. Chem. Soc.* **107**, 6964–6970.
- CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, p. 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- ETTER, M. C. & BAURES, P. W. (1988). *J. Am. Chem. Soc.* **110**, 639–640.
- FRENZ, B. A. (1979). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.
- GUSEV, A. I., BOKII, N. G., AFONIA, N. N., TIMOFEEVA, T. V., KALININ, A. E. & STRUCHKOV, YU. T. (1973). *Zh. Strukt. Khim.* **14**, 115–125.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- RUBAN, G. & ZABEL, V. (1976). *Cryst. Struct. Commun.* **5**, 671–677.
- SHELDRIK, G. M. (1985). In *Crystallographic Computing 3*, edited by G. M. SHELDRIK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.
- SPEK, A. L. (1987). *Acta Cryst. C43*, 1233–1235.
- THIERBACH, D., HUBER, F. & PREUT, H. (1980). *Acta Cryst. B36*, 974–977.
- WALKER, N. & STUART, D. (1983). *Acta Cryst. A39*, 158–166.