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Tris(2-imidazolyl)phosphine Hemihydrate

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Abstract. $C_9H_9N_6P.\frac{1}{2}H_2O$, $M_r = 241.2$, monoclinic, $C2/c$, $a = 13.822\,(4)$, $b = 8.0133\,(8)$, $c = 21.843\,(3)$ Å, $\beta = 105.41\,(2)°$, $V = 2332.4\,(9)$ Å^3, $Z = 8$, $D_m = 1.37\,(2)$, $D_x = 1.374$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1.540598$ Å, $\mu = 2.00$ mm^{-1}, $F(000) = 1000$, $T = 295\,(1)$ K, $R = 0.0904$, $wR = 0.0662$ for 1724 unique reflections and 180 parameters. Bond lengths and angles are close to normal but the PC—NH distances [average 1.323, range 1.316 (5)–1.329 (5) Å] are shorter than the PC—N distances [average 1.341, range 1.333 (5)–1.342 (5) Å]. The conformation of the molecule is determined by the water molecule which hydrogen bonds pairs of phosphine molecules together.

Introduction. Early attempts by us to produce the title compound by the literature method (Curtis & Brown, 1980) gave instead bis(2-imidazolyl)phosphinic acid (Howard-Lock, Lock, Penny & Turner, 1989). By coincidence the only common published data for the two compounds, namely the NMR spectra and melting points, were the same. Discussions with R. S. Brown revealed that the published general preparative procedure had to be modified for the title compound.† To fully characterize the title compound we have determined its structure. Colourless crystals were grown from methanol solution.

Experimental. Density by suspension in a dichloromethane–chloroform mixture. Crystal chosen for diffraction: plate 0.08 × 0.15 × 0.42 mm. Unit-cell parameters refined by least-squares fit of positional parameters for 20 reflections, $50.2 < 2\theta < 76.5°$, on a Rigaku AFC6R rotating-anode diffractometer, running at 50 kV and 50 mA with the use of graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1.540598$ Å at 295 K). Intensities $0 \le h \le 16$, $0 \le k \le 9$, $-25 \le l \le 25$ ($2\theta_{\text{max}} = 120°$) measured by an ω–2θ scan technique at a scan rate of 32.0° min^{-1} in 2θ. Total background time to scan ratio was 1:1. Methods of treating intensities have been described (Hughes, Krishnamachari, Lock, Powell & Turner, 1977; Lippert, Lock, Rosenberg & Zvagulis, 1977). Three standard reflections collected every 150 reflections ($3\bar{1}\bar{1}$, $R_{\text{merge}} = 0.030$; $40\bar{2}$, 0.036; $1\bar{1}4$, 0.033) showed no instrument instability or crystal decay. 1959 reflections measured, zonal reflections averaged to give 1724 independent reflections, $R_{\text{int}} = 0.0307$. Reflections with $3\sigma_I \ge I \ge -3\sigma_I$ (708) treated by the method of French & Wilson (1978). Lp corrections were made, as was a correction for absorption by the empirical method (North, Phillips & Mathews, 1968) (absorption correction factors $1.144 \le A^* \le 1.706$). Structure solved by direct methods based on 247 reflections with $|E| > 1.2$ and 50 sets of starting phases (Gilmore, 1984). H atoms located from difference map. Anisotropic full-matrix least-squares refinement minimized $\sum w(|F_o| - |F_c|)^2$, $w = (\sigma_F{}^2 + 0.0005F_o{}^2)^{-1}$. Scale, positional parameters for all atoms, anisotropic temperature factors for non-H atoms varied, 180 parameters. H atoms refined with fixed temperature factors. Final $R = 0.0904$, $wR = 0.0662$, $S = 1.031$. The large value of R is caused by the number of reflections with $I < 3\sigma_I$. Refinement ended when $(\Delta/\sigma)_{\text{max}} = 0.004$. Final difference map

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† Lists of structure factors, anisotropic thermal parameters, intramolecular bond lengths and angles involving H atoms, best planes and dihedral angles and a description of the preparative procedure have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54509 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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revealed electron density maximum 0.35, minimum -0.35 e Å^{-3}. Scattering factors from Cromer & Waber (1974). Corrections for anomalous dispersion made for P (Cromer & Ibers, 1974). Calculations employed *XTAL* (Stewart & Hall, 1983), *SHELX76* (Sheldrick, 1976) and *SNOOPI* (Davies, 1983) program systems on a VAX 8650 computer. Atomic positional parameters and U_{eq} values are given in Table 1.*

Table 1. *Atomic positional coordinates* (P, N, O, C × 10^4, H × 10^3) *and temperature factors* (Å^2 × 10^3)

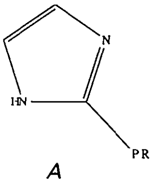
$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)$. H atoms were given fixed isotropic temperature factors $U = 0.080$ Å^2.

	x	*y*	*z*	U_{eq}
P	8023 (1)	874 (1)	5615 (1)	37
C11	8336 (3)	−1142 (5)	5990 (2)	37
N12	8079 (3)	−2523 (4)	5644 (2)	48
C13	8390 (4)	−3819 (6)	6051 (2)	62
C14	8815 (4)	−3220 (6)	6626 (3)	63
N15	8783 (3)	−1520 (5)	6591 (2)	55
C21	9240 (3)	1871 (5)	5754 (2)	38
N22	9915 (3)	2199 (5)	6312 (2)	55
C23	10675 (4)	3019 (8)	6150 (3)	77
C24	10478 (4)	3156 (8)	5526 (2)	70
N25	9565 (3)	2441 (6)	5275 (1)	52
C31	7510 (3)	1918 (5)	6191 (2)	40
N32	7933 (3)	2130 (6)	6814 (2)	67
C33	7252 (5)	3004 (9)	7029 (3)	80
C34	6449 (4)	3315 (8)	6556 (3)	68
N35	6618 (3)	2625 (6)	6027 (2)	49
O	10000	685 (8)	7500	85
H13	827 (4)	−491 (7)	588 (2)	
H14	915 (4)	−383 (6)	697 (2)	
H15	907 (4)	−82 (6)	684 (2)	
H23	1118 (4)	334 (6)	644 (2)	
H24	1081 (4)	370 (6)	526 (2)	
H25	937 (5)	233 (8)	501 (3)	
H33	739 (4)	328 (6)	746 (3)	
H34	592 (4)	402 (6)	655 (2)	
H35	624 (4)	267 (7)	574 (3)	
HO	1009 (4)	133 (6)	722 (2)	

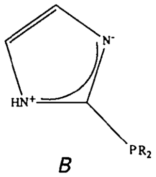
Table 2. *Selected interatomic distances* (Å), *angles* (°) *and hydrogen-bond interactions* (Å, °)

P—C11	1.811 (4)	N22—C23	1.364 (6)
P—C21	1.814 (4)	C23—C24	1.321 (7)
P—C31	1.807 (4)	C24—N25	1.362 (6)
C11—N12	1.333 (5)	N25—C21	1.324 (5)
N12—C13	1.360 (6)	C31—N32	1.342 (5)
C13—C14	1.327 (7)	N32—C33	1.353 (7)
C14—N15	1.364 (6)	C33—C34	1.324 (7)
N15—C11	1.329 (5)	C34—N35	1.355 (6)
C21—N22	1.348 (5)	N35—C31	1.316 (5)
C11—P—C21	102.6 (2)	C13—C14—N15	108.0 (5)
C11—P—C31	100.9 (2)	C14—N15—C11	106.0 (4)
C21—P—C31	101.4 (2)	N25—C21—N22	110.4 (4)
P—C11—N12	119.2 (3)	C21—N22—C23	104.8 (4)
P—C11—N15	130.0 (3)	N22—C23—C24	110.2 (5)
P—C21—N22	128.7 (3)	C23—C24—N25	107.2 (4)
P—C21—N25	120.9 (3)	C24—N25—C21	107.4 (4)
P—C31—N32	128.3 (3)	N35—C31—N32	110.2 (4)
P—C31—N35	121.5 (3)	C31—N32—C33	105.1 (4)
N15—C11—N12	110.7 (4)	N32—C33—C34	110.0 (5)
C11—N12—C13	105.9 (3)	C33—C34—N35	106.9 (5)
N12—C13—C14	109.0 (4)	C34—N35—C31	107.7 (4)
Hydrogen bonds			
O···N22	2.839 (5)	O—H	0.83 (4)
H···N22	2.06 (4)	O—H···N22	156 (5)
N15···O	2.850 (6)	N15—H15	0.81 (5)
H15···O	2.05 (5)	H15—H15···O	170 (5)

Discussion. The molecule is shown in Fig. 1 and bond distances and angles are given in Table 2. The bond angles in the imidazole rings agree well with those in imidazole (McMullen, Epstein, Ruble & Craven, 1979; Martinez-Carrera, 1966) and the unprotonated imidazole ring in bis(2-imidazolyl)-phosphinic acid (Howard-Lock *et al.*, 1989). Surprisingly, however, there are significant differences in bond lengths. In particular, the N*i*5—C*i*1 (*i* = 1–3) distances are shorter than the N*i*2–C*i*1 distances in the title compound, some significantly, and this is reflected in the averages [1.323, range 1.316 (5)–1.329 (5) Å *versus* 1.341, range 1.333 (5)–1.342 (5) Å]. This is the opposite to what is expected based on the idealized picture of imidazole, *A*, and to what is found in imidazole (McMullen *et al.*, 1979; Martinez-Carrera, 1966). It is also in contrast with the average values found in the phosphinic acid [1.351 (4), 1.359 (4) *versus* 1.332 (4), 1.334 (4) Å]. The carbon–carbon bonds (C*i*3—C*i*4) are also shorter [1.327 (7), 1.321 (7), 1.324 (7) Å], some significantly, than those observed in both imidazole [1.368 (1) Å] and the phosphinic acid [1.348 (4), 1.352 (4) Å]. It is as though the imidazole rings adopt a structure closer to *B*.



A



B

We have no reasonable explanation for these observations. Structure *B* might be stabilized by hydrogen bonding in rings 1 and 2, but the effect is also observed in ring 3 where no hydrogen bonding is present. The P—C distances lie between those observed for the protonated and unprotonated rings in the phosphinic acid and are shorter than those observed in tris(2-pyridyl)phosphine (average 1.811 *versus* 1.837 Å) (Lock & Turner, 1987).

The molecule shows little tendency towards the chiral propeller arrangement often found in triarylphosphines. The imidazole rings are almost perpendicular to the C11–C21–C31 plane [ring 1 82.9 (2); ring 2 96.0 (2); ring 3 91.0 (2)°] and are thus at roughly 120° to each other [rings 1–2 118.4 (2);

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* See deposition footnote.

rings 1–3 121.1 (2); rings 2–3 120.5 (2)°]. If we consider the P atom to be at the 'top' of the molecule, the imidazole rings are oriented such that the protonated N atoms in rings 2 and 3 are 'up', whereas that on ring 1 is 'down'. For rings 1 and 2 this conformation is determined by the water molecule which is hydrogen bonded to these two rings, to N22 in ring 2 as a donor and to N15 in ring 1 as an acceptor. As can be seen in Fig. 2, because the water molecule is on a special position it binds two phosphine molecules together in discrete pairs. Interactions between phosphine pairs are van der Waals.

The conformation of ring 3 appears to be determined by the need to remove the steric interaction of H35 with H15. That there is some steric crowding is suggested by the P—C*i*1—N*i*2 and P—C*i*1—N*i*5 (*i* = 1–3) angles. In the phosphinic acid (Howard-Lock *et al.*, 1989) these angles were essentially the same [125.2 (2), 125.7 (2), *versus* 125.0 (2), 124.1 (2)°]. In the title compound the angles are roughly 120 and 129°. The larger angle is not exclusively associated with P—C*i*1—N*i*2 or P—C*i*1—N*i*5, but with the N atom which is 'down'. The larger angle appears to be caused by steric repulsion between the 'down' N atoms. The N22···N32 [3.211 (5) Å] and N15···N32 [3.237 (6) Å] distances are close to the van der Waals distances (Bondi, 1964). The N15···N22 distance [3.493 (6) Å] is somewhat longer than the van der Waals distance but there may be additional constraints imposed by the hydrogen bonding.

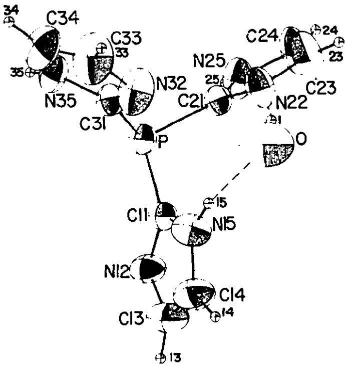

Fig. 1. The phosphine molecule and a water molecule, showing the atom numbering. H atoms are labelled by affixes only in smaller print. Hydrogen bonds are shown by broken lines.

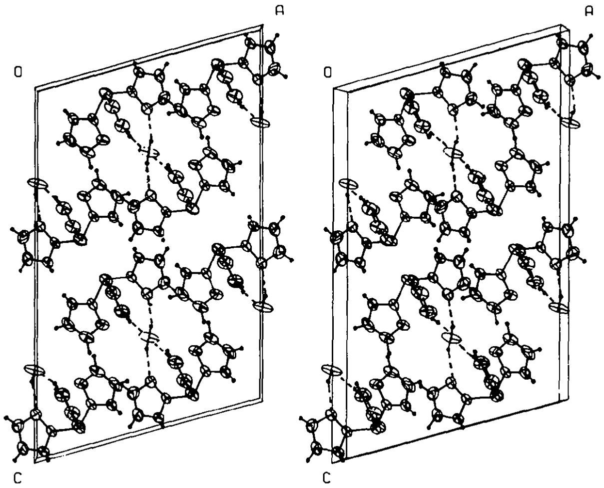

Fig. 2. The packing in the unit cell. **c** and **a*** are parallel to the sides and bottom of the page respectively and the view is down **b**. Hydrogen bonds are shown by broken lines.

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