least-squares plane defined by the atoms N(1), C(2), N(3), C(4), C(5), C(6), N(7), C(8) and N(9) is $0{\cdot}661x + 0{\cdot}214y - 0{\cdot}719z + 0{\cdot}458 = 0$, where x, y, z are Cartesian coordinates in Å. Atoms C(5) and C(6) have the maximum deviations from the plane of −0·018 (4) and +0·018 (5) Å, respectively, and the displacements of C(10) and N(17) are 0·104 (5) and 0·066 (4) Å, respectively.

The phenyl ring is planar. Its normal equation is $-0{\cdot}737x - 0{\cdot}409y - 0{\cdot}539z + 3{\cdot}467 = 0$. The dihedral angle between this plane and the purine system is 100·8°. The torsion angles C(4)—N(3)—C(10)—C(11) and N(3)—C(10)—C(11)—C(12) are −64·0 (5) and 113·6 (5)°, respectively.

The C(6)—N(17) bond length is short at 1·331 (6) Å. By comparison, the C_{ar}—NH_2 bond in aniline is 1·402 Å (Lister, Tyler, Hog & Larsen, 1974), whilst its length in *N*,*N*-dimethyladenine is 1·355 Å (Dahl, 1987). Consequently, form (III) describes the observed structure most accurately and confirms the correct interpretation of the NMR spectral data. The geometry of the five-membered ring suggests delocalization of the negative charge over all five atoms. However, the length of the C(5)—C(4), C(5)—C(6) and C(5)—N(7) bonds [1·409 (6), 1·399 (7) and 1·378 (6) Å] may be indicative of higher electron density at C(5).

Stacking interactions in the crystal structure are observed between the Cl atom and the purine system (Fig. 2). The distance from the Cl atom to the heterocyclic plane is 3·25 Å. All other intermolecular contacts correspond to sums of van der Waals radii (Zefirov & Zorkii, 1976).

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Triphenylphosphine: a Redetermination

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Abstract. $C_{18}H_{15}P$, $M_r = 262{\cdot}3$, monoclinic, $P2_1/a$, $a = 11{\cdot}329\ (3)$, $b = 14{\cdot}915\ (4)$, $c = 8{\cdot}440\ (1)$ Å, $\beta = 92{\cdot}12\ (2)°$, $V = 1\,425\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}22$ g cm^{-3}, Mo $K\alpha$, $\bar{\lambda} = 0{\cdot}71069$ Å, $\mu = 1{\cdot}70$ cm^{-1}, $T = 200$ K, $F(000) = 552$, $R = 0{\cdot}038$ for 2135 unique observed reflections. The crystal structure of the title compound has been redetermined, to improved precision, using diffractometer data at reduced temperature. The average P—C distance is 1·831 Å, and C—P—C angle is 102·8° (e.s.d.'s on individual parameters being 0·002 Å and 0·1°, respectively). The improved precision allows identification of several distortions, such as C—C bond-length variations, in the phenyl rings.

Introduction. Triphenylphosphine, PPh_3, and its derivatives have found widespread use as ligands in transition-metal chemistry, notably in homogeneous catalysis. The single-crystal X-ray structure of triphenylphosphine was reported in 1964 (Daly, 1964). As part of a general study on the geometric deformations in tertiary phosphine complexes (Orpen & Connelly, 1990; Dunne & Orpen 1990) precise values for the mean P—C bond length and C—P—C bond angle in the uncomplexed ligand were required. The structure determined by Daly using photographic techniques, with the visual estimation of reflection intensities, was refined to a crystallographic R factor of 0·101. Thus, there existed a need for a (low-

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temperature) structure determination with improved precision, which this study fulfils.

Experimental. Colourless block (0·425 × 0·325 × 0·3 mm) grown from CH_2Cl_2/Et_2O solution at room temperature, Nicolet *P*3*m* diffractometer, 15 reflections centred ($28 < 2\theta < 30°$), graphite-monochromated Mo $K\alpha$ for data collection $2 < \theta < 25°$, temperature 200 K by Nicolet LT-1, θ–2θ scans in 96 steps, θ-scan width $(1·2 + 0·35\tan\theta)°$, 2837 data measured ($0 < h < 14$, $0 < k < 18$, $-11 < l < 11$), with no detectable decay or movement; systematic absences ($0k0$ $k = 2n+1$, $h0l$ $h = 2n+1$). 2521 unique data, $R_{\rm int} = 0·016$, 2135 reflections with $F > 3\sigma(F)$ retained, used for structure solution and refinement, no absorption correction. Known structure (Daly, 1964), blocked-cascade full-matrix least-squares refinement on F, $w = [\sigma^2(F) + 0·0006(F^2)]^{-1}$, anisotropic temperature factors for all non-H atoms; H atoms with common isotropic temperature factor; all atoms were refined without positional constraints. $R = 0·0380$, $wR = 0·0379$, $S = 1·526$; data:variable ratio 9·8:1, max. peak and min. trough in final ΔF synthesis 0·21 and $-0·22$ e Å^{-3}, respectively; max. shift/e.s.d. ratio in final cycle 0·010; complex neutral scattering factors for C, H, N, O from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computer program: *SHELXTL* (Sheldrick, 1985). Atomic coordinates and equivalent isotropic displacement parameters are given in Table 1.*

Discussion. Fig. 1 shows a perspective view of the molecule with the atomic labelling scheme; atoms C(11)–C(16) will be referred to as ring 1, atoms C(21)–C(26) as ring 2, and atoms C(31)–C(36) as ring 3. Selected bond lengths and angles are given in Table 2. The final R factor of 0·0380 and the improved e.s.d.'s for derived parameters indicate a more precise structure determination than the earlier study. For ease of comparison we have retained Daly's choice of non-standard space group. The structure consists of discrete molecules with no unusually short intermolecular contacts.

The P atom is, of course, tricoordinate, with the three P—C linkages folded back from the putative lone-pair site, giving the tetrahedral geometry and C—P—C angles less than 109·5°. The individual P—C bond lengths do not differ significantly; their mean value is 1·831 (2) Å, which may be compared with the value of 1·828 (3) Å reported by Daly (1964)

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3)

$U_{\rm eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U_{\rm eq}$
P	2110 (1)	367 (1)	1449 (1)	31 (1)
C(11)	3119 (1)	1323 (1)	1700 (2)	32 (1)
C(12)	4015 (2)	1544 (1)	688 (2)	42 (1)
C(13)	4722 (2)	2287 (1)	991 (3)	51 (1)
C(14)	4547 (2)	2820 (1)	2292 (3)	49 (1)
C(15)	3666 (2)	2609 (1)	3307 (3)	48 (1)
C(16)	2955 (2)	1871 (1)	3009 (2)	38 (1)
C(21)	2047 (2)	189 (1)	−695 (2)	32 (1)
C(22)	2898 (2)	−269 (1)	−1531 (2)	44 (1)
C(23)	2779 (2)	−354 (2)	−3164 (2)	54 (1)
C(24)	1816 (2)	4 (2)	−3966 (2)	56 (1)
C(25)	953 (2)	439 (1)	−3162 (2)	51 (1)
C(26)	1066 (2)	533 (1)	−1534 (2)	39 (1)
C(31)	3009 (2)	−587 (1)	2140 (2)	33 (1)
C(32)	4122 (2)	−512 (1)	2890 (2)	37 (1)
C(33)	4694 (2)	−1264 (1)	3501 (2)	46 (1)
C(34)	4175 (2)	−2095 (2)	3376 (3)	51 (1)
C(35)	3073 (2)	−2185 (2)	2626 (3)	53 (1)
C(36)	2501 (2)	−1437 (1)	2024 (3)	46 (1)

Table 2. *Selected interatomic distances* (Å) *and angles* (°) *for* PPh_3

P—C(11)	1·834 (2)	P—C(21)	1·828 (2)
P—C(31)	1·832 (2)	C(11)—C(12)	1·391 (3)
C(11)—C(16)	1·392 (3)	C(12)—C(13)	1·386 (3)
C(13)—C(14)	1·376 (3)	C(14)—C(15)	1·376 (3)
C(15)—C(16)	1·381 (3)	C(21)—C(22)	1·394 (3)
C(21)—C(26)	1·393 (2)	C(22)—C(23)	1·386 (3)
C(23)—C(24)	1·370 (3)	C(24)—C(25)	1·374 (3)
C(25)—C(26)	1·382 (3)	C(31)—C(32)	1·394 (2)
C(31)—C(36)	1·395 (3)	C(32)—C(33)	1·385 (3)
C(33)—C(34)	1·375 (3)	C(34)—C(35)	1·385 (3)
C(35)—C(36)	1·378 (3)		

C(11)—P—C(21)	103·3 (1)	C(21)—P—C(31)	101·7 (1)
C(11)—P—C(31)	103·3 (1)	P—C(11)—C(16)	116·6 (1)
P—C(11)—C(12)	125·4 (1)	C(11)—C(12)—C(13)	120·4 (2)
C(12)—C(11)—C(16)	118·1 (2)	C(13)—C(14)—C(15)	119·6 (2)
C(12)—C(13)—C(14)	120·7 (2)	C(11)—C(16)—C(15)	121·2 (2)
C(14)—C(15)—C(16)	120·1 (2)	P—C(21)—C(26)	116·8 (1)
P—C(21)—C(22)	124·7 (1)	C(21)—C(22)—C(23)	120·3 (2)
C(22)—C(21)—C(26)	118·5 (2)	C(23)—C(24)—C(25)	120·5 (2)
C(22)—C(23)—C(24)	120·1 (2)	C(21)—C(26)—C(25)	120·7 (2)
C(24)—C(25)—C(26)	119·9 (2)	P—C(31)—C(36)	117·5 (1)
P—C(31)—C(32)	124·1 (1)	C(31)—C(32)—C(33)	120·5 (2)
C(32)—C(31)—C(36)	117·9 (2)	C(33)—C(34)—C(35)	119·9 (2)
C(32)—C(33)—C(34)	120·5 (2)	C(31)—C(36)—C(35)	121·5 (2)
C(34)—C(35)—C(36)	119·7 (2)		

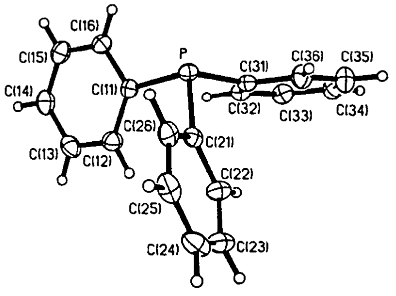

Fig. 1. View of PPh_3, with thermal ellipsoids representing 30% probability density.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53209 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and also with a mean of 1·828 Å for 2239 complexes with PPh_3 as a ligand to transition metals (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1989). The mean value of the three C—P—C bond angles is 102·8 (5)° and, as was also noted by Daly (1964), one of the angles is markedly smaller than the other two. The symmetry of the P, C(11), C(21), C(31) unit is therefore lowered from the ideal C_{3v} to approximately C_s symmetry. The C atoms of each phenyl ring are coplanar, with mean deviations from the plane of 0·0018 (ring 1), 0·0060 (ring 2) and 0·0019 Å (ring 3). The overall mean C—C bond length is 1·384 (2) Å, and the mean C—C—C bond angle 120·0 (2)°.

The effect on the internal geometry of a phenyl ring caused by introducing a substitutent has been comprehensively studied [see for example Domenicano, Vaciago & Coulson (1975)]. The geometry may be described by the bond lengths *a*, *b* and *c*, and the angular parameters *w*, *x*, *y* and *z*, as shown in Fig. 2. Any primary distortion is such as to lower the symmetry of the C_6 ring from D_{6h} to approximately C_{2v}. An electropositive susbstituent will generally decrease the angle *w* at the *ipso* carbon from 120°, increase the endocyclic angles *x* and cause a lengthening of the *a* bonds with respect to the *b* bonds (Domenicano *et al.*, 1975). Table 3 lists the mean values of the bond lengths *a*, *b* and *c* and of the bond angles *w*, *x*, *y* and *z* for each phenyl ring in PPh_3. The three C—C—C angles at the *ipso* carbons, *w*, at 118·1 (2), 118·5 (2) and 117·9 (2)°, are significantly smaller than other internal angles, as predicted. The endocyclic *x* angles appear to be significantly larger than the values of *w*. The *a* bonds are also longer than the *b* bonds, which in turn are longer than the *c* bonds. Domenicano *et al.* (1975) reported a shortening, by 0·01–0·02 Å, of the *c* bonds. It is of course possible that this trend is an artefact of the effects of vibrational motion. This would lead to an attenuation of bond distances, which would be most severe for the outermost bonds, if each phenyl ring were 'wagging' about the P atom. The molecular geometry was therefore subjected to the rigid-body *TLS* analysis of Schomaker & Trueblood (1968). Applying a correction based on this analysis leads to a lengthening of the P—C bonds by 0·003–0·004 Å, whilst the C—C bonds become 0·002–0·003 Å longer. The trends along the series of *a*, *b* and *c* bond lengths (Table 3) are not erased, however.

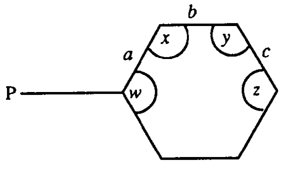

Fig. 2. Geometry definitions for a substituted phenyl ring.

Table 3. *Mean values and e.s.d.'s of the a, b and c bond lengths* (Å) *and w, x, y and z bond angles* (°) *in* PPh_3

Single observations for *w* and *z* are given with e.s.d.'s from the crystallographic least-squares refinement.

Ring	*a*	*b*	*c*	*w*	*x*	*y*	*z*
1	1·392 (1)	1·384 (4)	1·376 (3)	118·1 (2)	120·8 (6)	120·4 (4)	119·6 (2)
2	1·394 (1)	1·384 (3)	1·372 (3)	118·5 (2)	120·5 (3)	120·0 (1)	120·5 (2)
3	1·394 (1)	1·382 (5)	1·380 (7)	117·9 (2)	121·0 (7)	120·1 (6)	119·9 (2)

The vector normal to the $(C_{ipso})_3$ plane may be used to define a lone-pair 'direction', to which torsion angles defining the extent of phenyl ring rotation, ω_i, $i = 1$–3, may be referred (see Bye, Schweizer & Dunitz, 1982). The values obtained are ring 1, −155·0; ring 2, −153·4; ring 3, −120·6° and are equivalent to 25·0, 26·6 and 59·4° and indicate that one phenyl ring is rotated by over 30° more than the other two, destroying a regular propeller conformation of threefold symmetry. Daly (1964) noted a similar result using the normals to each ring. An analysis of many crystal structures (Bye *et al.*, 1982) has shown the equilibrium conformation of an isolated Z-PPh_3 fragment is a symmetric propeller, with all three phenyl rings rotated in the same sense and by about 40°. The closest intermolecular non-bonded contact is H(34)···H(25) at 2·553 Å (generated by the transformation $0{\cdot}5 - x$, $y - 0{\cdot}5$, $-z$), whilst ring 3 is involved in four other close contacts: C(31)···H(24) 2·956 (x, y, $1 + z$), C(33)···H(23) 2·975 (x, y, $1 + z$), H(34)···C(25) 3·024 ($0{\cdot}5 - x$, $-0{\cdot}5 + y$, $-z$), H(35)···C(26) 3·031 ($0{\cdot}5 - x$, $y - 0{\cdot}5$, $-z$) and C(32)···H(23) 3·041 Å (x, y, $1 + z$). These short intermolecular distances all involve an atom of ring 2 and one of ring 3, and may be a consequence of the increased rotation of ring 3 noted above.

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