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3-*tert*-Butyl-9,10-dihydro-9,10-*o*-benzeno-9-phosphaanthracene

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Abstract. $C_{23}H_{21}P$, monoclinic, $P2_1/n$, $a = 8{\cdot}573$ (5), $b = 17{\cdot}180$ (5), $c = 12{\cdot}809$ (3) Å, $\beta = 100{\cdot}88$ (2)°, $Z = 4$. Final R for 2522 observed reflexions 0·075. The average P—C distance is 1·843 (2) Å and the average C—P—C angle 94·5 (6)°. The *tert*-butyl group shows rotational disorder.

Introduction. The investigation of the title compound (TBPT), a *tert*-butyl derivative of phosphatriptycene, was undertaken to obtain information about the geometry around the P atom. The crystal structure determination of phosphatriptycene itself (Freijee & Stam, 1980) did not yield reliable results because of orientational disorder. The disorder is such that a fraction of the molecular sites in the ideal ordered structure are occupied by molecules rotated by 180° about a quasi-twofold axis perpendicular to the P—C axis of the molecule. In TBPT the quasi-twofold axes are suppressed by the substituent so that the same kind of disorder becomes impossible. 2522 reflexions with $I > 2\sigma(I)$ were collected on a Nonius CAD-4 diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. The structure was solved with *SIMPEL* (Overbeek & Schenk, 1978). The solution could only be obtained after rescaling the parity groups to $\langle E^2\rangle = 1$. During the refinement it became apparent that the *tert*-butyl group showed rotational disorder. Fig. 1 gives an idea of the disorder. It was not possible to obtain a model which satisfactorily accounts for the disorder. Finally, four isotropic partial-weight C atoms were introduced for each of the methyl groups with population parameters 0·5, 0·2, 0·2 and 0·1. In a ΔF synthesis the H atoms attached to the phosphatriptycene skeleton were clearly present whilst there were indications for the H atoms of the *tert*-butyl group of weight 0·5. Block-diagonal least-squares refinement, anisotropic for the non-hydrogen atoms of the phosphatriptycene moiety, isotropic for the disordered C atoms of the *tert*-butyl group and for the H atoms attached to the phosphatriptycene skeleton, led to a final R of 0·075. The H atoms of the *tert*-butyl group with weight 0·5 were introduced with fixed parameters at their calculated positions. A weighting scheme $w = 1/(1{\cdot}36 + F_o + 0{\cdot}024F_o^2)$ was used. Anomalous dispersion for P was taken into account and an extinction correction

$$F_c^{\rm corr} = F_c\left(1 + g\frac{1+\cos^4 2\theta}{1+\cos^2 2\theta}\cdot\frac{1}{\sin\theta}F_c^2\right)^{-1/4}$$

was applied resulting in a final value for g of $8{\cdot}5 \times 10^{-5}$. The final coordinates are listed in Table 1.†

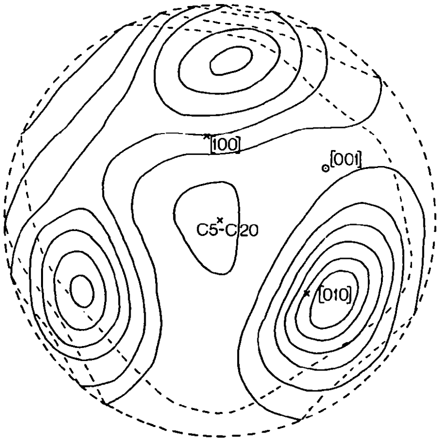

Fig. 1. Stereographic projection of the electron density of a sphere of radius 1·5 Å on to a plane perpendicular to the line C(5)–C(20).

Discussion. The atomic numbering and the shape of the molecule are indicated in Fig. 2. The bond lengths and angles are listed in Table 2. The three P—C distances do not differ significantly and average 1·843 (2) Å. The average CPC angle is 94·5 (6)°. The average internal and external PCC angles are 116·3 (2) and 123·7 (9)° respectively. In Table 3 these values are compared with the corresponding values for triphenylphosphine (TPP) (Daly, 1964), diphosphatriptycene (DPT) (Schomburg

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† Lists of structure factors, isotropic thermal parameters for disordered C atoms and anisotropic for P and remaining C atoms and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35042 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

& Sheldrick, 1975) and 9,10-dihydro-2,7-dimethyl-9,10-*o*-(*m*-methyl)benzeno-9-aza-10-phosphaanthracene (PAT) (Schomburg & Sheldrick, 1976). The C—P—C angle varies with the nature of the bridgehead atom *X* opposite P. This angle is largest in TPP where there is no constraint from a second bridgehead atom and decreases with the length of the *X*—C bond (P—C 1·84, C—C 1·53, N—C 1·44 Å). For the three triptycene structures DPT, TBPT and PAT, decrease of the C—P—C angle is coupled with decrease of the P—C length. TPP, however, falls outside this scheme, so clearly the bond angle is not the only determining factor. The benzene rings in TBPT are planar within the limits of accuracy.

Table 1. *Fractional atomic coordinates* (P × 10^5, C × 10^4) *with their e.s.d.'s in parentheses*

	x	*y*	*z*	Population parameter	B_{eq} (Å^2)
P	84265 (11)	45402 (5)	19741 (9)		4·6
C(1)	8484 (4)	5611 (3)	2058 (3)		3·8
C(2)	7376 (4)	5956 (2)	2565 (3)		4·1
C(3)	7330 (5)	6764 (2)	2626 (3)		4·6
C(4)	8429 (5)	7208 (3)	2208 (3)		4·7
C(5)	9566 (4)	6865 (2)	1708 (3)		4·0
C(6)	9569 (4)	6061 (2)	1629 (3)		4·0
C(7)	8365 (5)	4398 (3)	3393 (4)		4·6
C(8)	7309 (5)	4870 (3)	3813 (3)		4·4
C(9)	7218 (6)	4812 (3)	4884 (4)		6·1
C(10)	8179 (7)	4296 (4)	5525 (4)		7·3
C(11)	9192 (7)	3828 (4)	5121 (5)		8·2
C(12)	9317 (5)	3874 (3)	4057 (5)		6·4
C(13)	6255 (5)	4476 (2)	1553 (3)		4·0
C(14)	5361 (4)	4926 (2)	2124 (3)		3·9
C(15)	3714 (5)	4895 (3)	1860 (4)		4·7
C(16)	2972 (5)	4420 (3)	1049 (4)		5·7
C(17)	3848 (6)	3988 (3)	479 (4)		5·9
C(18)	5503 (5)	4005 (2)	733 (4)		5·0
C(19)	6305 (4)	5437 (2)	3029 (3)		3·7
C(20)	10777 (5)	7361 (2)	1256 (3)		5·0
C(21)*A*	10600 (9)	8220 (5)	1423 (6)	0·5	
C(22)*A*	12475 (10)	7086 (5)	1720 (7)	0·5	
C(23)*A*	10530 (10)	7204 (5)	34 (7)	0·5	
C(21)*B*	1018 (3)	818 (2)	101 (2)	0·2	
C(22)*B*	1230 (3)	730 (3)	219 (2)	0·2	
C(23)*B*	1120 (3)	700 (1)	28 (2)	0·2	
C(21)*C*	1116 (2)	820 (2)	178 (2)	0·2	
C(22)*C*	1216 (3)	698 (2)	113 (2)	0·2	
C(23)*C*	995 (4)	748 (2)	−8 (2)	0·2	
C(21)*D*	1186 (7)	769 (4)	237 (5)	0·1	
C(22)*D*	1187 (4)	694 (2)	64 (3)	0·1	
C(23)*D*	962 (8)	797 (4)	31 (6)	0·1	

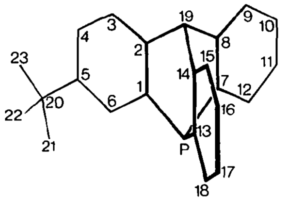

Fig. 2. Numbering of the atoms and shape of the molecule.

Table 2. *Bond lengths* (Å) *and angles* (°)

P—C(1)	1·843 (5)	C(8)—C(19)	1·540 (6)
P—C(7)	1·844 (6)	C(9)—C(10)	1·372 (8)
P—C(13)	1·841 (4)	C(10)—C(11)	1·356 (9)
C(1)—C(2)	1·381 (4)	C(11)—C(12)	1·389 (10)
C(1)—C(6)	1·399 (6)	C(13)—C(14)	1·390 (6)
C(2)—C(3)	1·391 (5)	C(13)—C(18)	1·385 (6)
C(2)—C(19)	1·482 (6)	C(14)—C(15)	1·390 (6)
C(3)—C(4)	1·395 (7)	C(14)—C(19)	1·554 (5)
C(4)—C(5)	1·394 (6)	C(15)—C(16)	1·379 (7)
C(5)—C(6)	1·385 (5)	C(16)—C(17)	1·362 (8)
C(5)—C(20)	1·538 (6)	C(17)—C(18)	1·395 (7)
C(7)—C(8)	1·397 (7)	C(20)—C(21)*A*	1·503 (9)
C(7)—C(12)	1·392 (7)	C(20)—C(22)*A*	1·539 (9)
C(8)—C(9)	1·392 (7)	C(20)—C(23)*A*	1·563 (9)
C(1)PC(7)	94·6 (2)	C(9)C(10)C(11)	120·7 (5)
C(1)PC(13)	95·2 (2)	C(10)C(11)C(12)	120·9 (6)
C(7)PC(13)	93·7 (2)	C(7)C(12)C(11)	119·4 (5)
PC(1)C(2)	116·3 (3)	PC(13)C(14)	116·1 (3)
PC(1)C(6)	122·8 (4)	PC(13)C(18)	123·9 (4)
C(2)C(1)C(6)	121·0 (4)	C(14)C(13)C(18)	120·0 (4)
C(1)C(2)C(3)	118·9 (4)	C(13)C(14)C(15)	119·1 (4)
C(1)C(2)C(19)	117·6 (3)	C(13)C(14)C(19)	116·5 (4)
C(3)C(2)C(19)	123·5 (4)	C(15)C(14)C(19)	124·4 (4)
C(2)C(3)C(4)	119·7 (4)	C(14)C(15)C(16)	120·6 (5)
C(3)C(4)C(5)	121·8 (5)	C(15)C(16)C(17)	120·3 (5)
C(4)C(5)C(6)	117·8 (4)	C(16)C(17)C(18)	120·2 (4)
C(4)C(5)C(20)	121·3 (4)	C(13)C(18)C(17)	119·8 (5)
C(6)C(5)C(20)	121·0 (4)	C(2)C(19)C(8)	109·2 (3)
C(1)C(6)C(5)	120·8 (4)	C(2)C(19)C(14)	108·4 (3)
PC(7)C(8)	116·4 (4)	C(8)C(19)C(14)	106·1 (3)
PC(7)C(12)	124·4 (4)	C(5)C(20)C(21)*A*	113·4 (5)
C(8)C(7)C(12)	119·2 (5)	C(5)C(20)C(22)*A*	109·9 (5)
C(7)C(8)C(9)	119·9 (5)	C(5)C(20)C(23)*A*	107·9 (5)
C(7)C(8)C(19)	116·1 (4)	C(21)*A*C(20)C(22)*A*	111·1 (5)
C(9)C(8)C(19)	124·0 (4)	C(21)*A*C(20)C(23)*A*	108·3 (5)
C(8)C(9)C(10)	119·8 (5)	C(22)*A*C(20)C(23)*A*	105·9 (6)

Table 3. *Average* P—C *distances* (Å) *and* CPC *and* PCC *angles* (°)

	$\langle \mathrm{P{-}C} \rangle$	$\langle \mathrm{CPC} \rangle$	$\langle \mathrm{PCC} \rangle_{\mathrm{int}}$	$\langle \mathrm{PCC} \rangle_{\mathrm{ext}}$
DPT	1·845 (2)	97·0 (2)	120·3 (3)	120·8 (2)
TBPT	1·838 (6)	94·6 (7)	116·4 (3)	123·8 (8)
PAT	1·823 (8)	93·3 (3)	115·6 (4)	124·0 (4)
TPP	1·828	103·0	116·1	124·0

Table 4. *Distances* (Å) *of the bridgehead atoms from the planes of the benzene rings and angles* (°) *between the benzene rings*

(I) = C(1)–C(6), (II) = C(7)–C(12), (III) = C(13)–C(18). E.s.d.'s are 2–3 × 10^{-3} for P, 4 × 10^{-3} for C and 8 × 10^{-3} Å for N.

		Distances of bridgehead atoms from benzene rings			Angles between benzene rings		
		(I)	(II)	(III)	(I)–(II)	(I)–(III)	(II)–(III)
TBPT	P	0·023	0·040	0·029	119·4	122·5	118·0
	C	0·093	0·003	0·005			
DPT	P	0·071	0·093	0·003	114·3	123·3	124·3
	P	0·093	0·071	0·003			
PAT	P	0·017	0·030	0·037	122·3	123·4	114·3
	N	0·034	0·112	0·078			
PAT	P	0·017	0·089	0·009	120·9	120·2	118·9
	N	0·005	0·047	0·052			

The molecule shows significant deviations from ideal threefold symmetry. The same appears to apply to DPT and PAT. In Table 4 the angles between the benzene rings and the deviations of the bridgehead atoms from the benzene rings are listed for TBPT, DPT and PAT.

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9,10-Dihydro-10-phenyl-9,10-*o*-benzeno-9-arsaanthracene

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Abstract. $C_{25}H_{17}As$, monoclinic, $P2_1/n$, a = 8·8392 (4), b = 20·477 (1), c = 10·082 (1) Å, β = 102·04 (1)°, Z = 4. Final R for 2799 independent reflexions 0·025. The As—C distances are 1·938 (3), 1·952 (3) and 1·955 (2) Å. The average C—As—C angle is 91·5°. The benzene rings are slightly folded as a result of intramolecular steric interaction.

Introduction. The investigation of the title compound, a derivative of arsatriptycene, was undertaken to obtain information about the geometry around the As atom. The crystal structure determination of arsatriptycene itself (Freijee & Stam, 1980) did not yield reliable results because of orientational disorder. The disorder is such that a fraction of the molecular sites in the ideal ordered structure are occupied by molecules rotated by 180° about a quasi-twofold axis perpendicular to the As–C axis of the molecules. In the title compound the quasi-twofold axes are suppressed by the substituent so that the same kind of disorder becomes impossible.

The title compound was prepared by Klebach & Bickelhaupt (1980). 2799 independent reflexions with $I > 2\sigma(I)$ were collected on a Nonius CAD-4 diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. No absorption correction was applied (crystal dimensions 0·2 × 0·2 × 0·4 mm; $\mu = 2{\cdot}59$ mm^{-1}). The structure was solved directly from an $(E^2 - 1)$ Patterson synthesis. Block-diagonal least-squares refinement, anisotropic for As and C, isotropic for H, resulted in R = 0·025. The H atoms were located in a ΔF synthesis. Anomalous dispersion of As was taken into account and a weighting scheme $w = 1/(4{\cdot}0 + F_o + 0{\cdot}015F_o^2)$ was used. An extinction correction

$$F_c^{\rm corr} = F_c\left(1 + g\,\frac{1+\cos^4 2\theta}{1+\cos^2 2\theta}\cdot\frac{1}{\sin 2\theta}\cdot F_c^2\right)^{-1/4}$$

(Larson, 1969) was included resulting in $g = 6{\cdot}7 \times 10^{-6}$. The final coordinates are listed in Table 1.†

Discussion. The atomic numbering and the shape of the molecule are indicated in Fig. 1. The bond distances and angles are given in Table 2. The three As—C bonds are not equal, As—C(1) [1·938 (3) Å] differing significantly from the other two [1·952 (3) and 1·955 (2) Å]. We have no explanation for this discrepancy, but it is interesting to note that the differences conform to the overall symmetry of the molecule (Fig. 1). The rather large differences between the three C—As—C angles reflect the flexibility of the rings with respect to the bridgehead atoms As and C(19) (see below). There is good agreement between corresponding bond lengths and angles in the three rings of the arsatriptycene moiety. The bond lengths show a significant trend: the inner bonds [average 1·430 (2) Å] are longer and the outer bonds [average 1·377 (2) Å] are shorter than the overall average of 1·390 Å.

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† Lists of structure factors, anisotropic thermal parameters for the non-hydrogen atoms and isotropic for the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35043 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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