Crystal and Molecular Structure of 4-Methyl-4-*p*-nitrobenzyl-4-phosphoniatetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane Bromide

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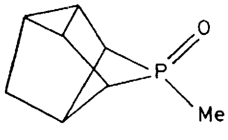
Crystals of the title compound are triclinic, space group $P\bar{1}$, $Z = 2$, $a = 6.750(3)$, $b = 8.705(3)$, $c = 12.961(5)$ Å, $\alpha = 91.60(3)$, $\beta = 95.02(4)$, $\gamma = 89.27(3)°$. The structure was solved by the heavy-atom technique, and refined by block-diagonal least-squares methods to R 0.056 for 1 440 independent reflections. The internal angles of the phosphetan ring are 87.3, 74.8, 87.5, and 90.3°; the ring is puckered with a dihedral angle of 46.6°. The crystals were twinned, and the two twins were related by a two-fold rotation about a, which superimposed $0kl$ and $0k\bar{l}$. The twinning did not seriously limit the accuracy of the analysis.

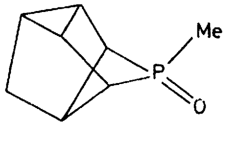
OVER the past decade the four-membered heterocycle containing a single phosphorus atom (phosphetan) has received considerable attention.[1] The angular constraints in this chemical system provide a structural asset for studying phosphorus stereochemistry, especially where pseudorotational processes[2] are involved. A ring methyl substituent bearing a *cis*- or *trans*-relationship to a functional group on phosphorus provides a convenient probe for following stereochemical changes (retention and inversion) about the phosphorus in chemical reactions.[1,3]

X-Ray studies have provided confirmation of stereochemical assignments and important physical data in a number of phosphetan derivatives,[4] which have been used extensively in interpreting detailed ^{13}C n.m.r. spectra.[5] However, all the *X*-ray work to date has been carried out on systems which are conformationally mobile in solution.

Cremer *et al.* recently described the synthesis, stereochemistry, and reactions of a rather novel molecule which contains a phosphetan ring system, 4-methyl-4-phosphatetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane 4-oxide,[6] which can exist as either the *exo* (Ia) (m.p. 156—157 °C) or *endo* (Ib) (m.p. 71—74 °C) isomer. The rigid nature of the entire molecule containing the phosphetan ring in a fixed conformation, provides a unique structure for ^{13}C n.m.r. studies (*e.g.* dihedral angular dependence of ^{31}P–^{13}C coupling constants).

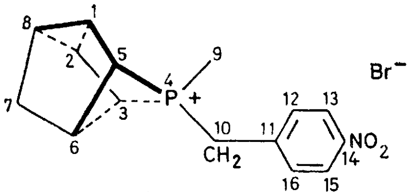


exo-isomer (m.p. 156 -157°)
(Ia)



endo-isomer (m.p. 71-74°)
(Ib)

In view of the interesting stereochemistry of this tetracyclic phosphetan oxide and the remarkably rapid rate of ring-opening observed on base treatment of this heterocycle,[6] a complete *X*-ray study was undertaken. As the *p*-nitrobenzylphosphonium bromide (II) formed crystals suitable for analysis, this was selected for study. The tetracyclic oxide (Ia) has been undergoing *X*-ray investigation for some time; unfortunately because of twinned crystals and other problems, this work has not been completed.[6]



(II)

EXPERIMENTAL

Crystal Data.—$C_{15}H_{17}BrNO_2P$, $M = 354.2$. Triclinic, $a = 6.750(3)$, $b = 8.705(3)$, $c = 12.961(5)$ Å, $\alpha = 91.60(3)$, $\beta = 95.02(4)$, $\gamma = 89.27(3)°$, $U = 758.3(5)$ Å^3, D_m (by flotation) 1.54, $Z = 2$, $D_c = 1.55$ g cm^{-3}, $F(000) = 360$. Space group $P\bar{1}$ (No. 2). Mo-K_α radiation, $\lambda = 0.710\ 73$ Å; μ(Mo-K_α) = 29.79 cm^{-1}.

The sample used was recrystallized from acetonitrile as yellow needles, m.p. 206—208 °C (Found: C, 50.6; H, 5.0; Br, 22.5. $C_{15}H_{17}NO_2PBr$ requires C, 50.87; H, 4.84; Br, 22.56%). The ^{13}C n.m.r. spectrum ($CDCl_3$) was consistent with the structure of (II): δ (downfield from tetramethylsilane) 147.60 [4.0 Hz, C(14)], 138.52 [8.9 Hz, C(11)], 131.38 [4.9 Hz, C(12)], 124.47 [2.1 Hz, C(13)], 44.21 [52.8 Hz, C(3) and C(5)], 40.85 [14.0 Hz, C(6)], 34.26 [22.9 Hz, C(7)], 30.11 [30.5 Hz, C(10)], 26.89 [31.4 Hz, C(8)], 15.23 [5.5 Hz, C(1) and (2)], and 8.45 [35.4 Hz, C(9)]; ^{31}P–^{13}C coupling constants are in square brackets.

A crystal *ca.* 0.22 × 0.15 × 0.35 mm^3 was used for intensity measurement. From the photographs of the crystal it appeared that the spots were not well formed and the background intensity was also greater than normal. This crystal, which was the best of several examined, was accepted for data collection. Cell constants were obtained by least-squares refinement of 15 reflections.

The intensities were measured by graphite-monochromated Mo-K_α radiation on a Syntex $P\bar{1}$ diffractometer at a

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[1] Chem. Soc. Specialist Periodical Reports, 'Organophosphorus Chemistry,' ed. S. Trippett, vols. 1—7, 1970—1976.

[2] F. H. Westheimer, *Accounts Chem. Res.*, 1968, **1**, 70.

[3] S. E. Cremer and B. C. Trivedi, *J. Amer. Chem. Soc.*, 1969, **91**, 7200.

[4] D. D. Swank and C. N. Caughlan, *Chem. Comm.*, 1968, 1051; C. Moret and L. M. Trefonas, *J. Amer. Chem. Soc.*, 1969, **91**, 2255; Mazhar-ul-Haque, *J. Chem. Soc.* (*B*), 1970, 934, 938; 1971, 117.

[5] G. A. Gray and S. E. Cremer, *J. Org. Chem.*, 1972, **37**, 3458, 3470; G. A. Gray, S. E. Cremer, and K. Marsi, *J. Amer. Chem. Soc.*, 1976, **98**, 2109.

[6] S. E. Cremer, F. R. Farr, P. W. Kremer, and H. Wang, *J.C.S. Chem. Comm.*, 1975, 374.

take-off angle of 3°. The intensities of 2 671 independent reflections ($2\theta \leqslant 50°$) were measured by use of the θ—2θ scan technique with a variable scan rate of 4—24° min^{-1}, background counts were taken at each end of the scan range. Of these 1 745 reflections were considered to be observed, having $I \geqslant 3\sigma(I)$. Three standard reflections, measured periodically, showed no significant change in their intensities during data collection. Lorentz and polarization corrections were applied. Atomic scattering factors were taken from ref. 7, except those for hydrogen which were taken from ref. 8.

Structure Determination and Refinement.—The structure was solved by means of a three-dimensional Patterson function, and the heavy-atom method. Two cycles of isotropic least-squares refinement of the bromide ion and phosphorus atom only, gave R 0.35. The remaining non-hydrogen atoms were located from a three-dimensional Fourier map. Four cycles of block-diagonal isotropic refinement of all these atoms gave R 0.178. The structure was then refined anisotropically, thereby reducing R to 0.168. A difference-Fourier at this stage showed twelve extra peaks, which made no chemical sense: six had the same y and z co-ordinates as the bromide ion, and the other six had the same y and z co-ordinates as the phosphorus atom.

Careful examination of the observed and calculated structure factors revealed that all bad ΔF values occurred on layers $0kl$ and $3kl$ and were positive, indicating that the scales of these two layers were high relative to others. At this stage it was decided to refine the scale factors individually for $h = 0$—7, as well as the co-ordinates and anisotropic temperature factors of all the atoms. This gave R 0.086. A difference-Fourier map at this stage revealed all 17 hydrogen atom positions. Four more cycles were carried out including all the hydrogens as fixed atoms, each of which was given an isotropic B factor 0.5 Å^2 greater than the equivalent isotropic value for its parent carbon atom. A Hughes-type weighting scheme[9] of the form $\sqrt{w} = 1$ for $|F_o| \leqslant 18$, $\sqrt{w} = 18/|F_o|$ for $|F_o| > 18$ was used. The R value, based on the 1 745 reflections, was 0.075. A difference-Fourier map showed no significant peaks. Allowance for anomalous dispersion for bromide ion and phosphorus atom was applied.

From this refinement it was found that the scale factor of the $0kl$ layer was *ca.* 40% lower relative to the others. An agreement analysis was run on the data and it was found that the R values of all the layer lines were in good agreement, except the $3kl$ layer which was 0.163. These results indicated twinning in the crystal. It was not noticed from the photographs, although it was apparent that the spots were not well formed.

It is clear that the two twin components are related by a two-fold rotation about a which superimposes $0kl$ and $0\bar{k}l$. As a result the diffractometer measured the intensities of both twins in this layer, but only one twin on layers $h = 1$ and 2. If the volumes of the twins are equal the measured intensities of $0kl$ are twice as strong as they should be, so that the $|F_o|$ values are $\sqrt{2}$ times the correct value, *i.e.* 41% up as is found. In view of this it was considered justifiable to adjust the $0kl$ scale factor.

The $3kl$ layer presents quite a different problem. In Figure 1 the reciprocal lattice of one twin component is represented by solid lines and solid circles; the other by broken lines and open circles. The solid and open circles lie very close together on the $3kl$ layer; in fact only 0.0113 r.l.u. apart. Figure 2 shows that the adjacent circles are those for different reflections, namely $3kl$ and $3k(\overline{l+1})$ which have different intensities. It is very likely that part at least of the unwanted reciprocal lattice point was incorporated into the scan made by the diffractometer, so that the observed intensities are generally, but erratically, high. Moreover, it is likely that the fraction (α) of the unwanted reflection which was included in any measurement would vary from one part of the reciprocal space to

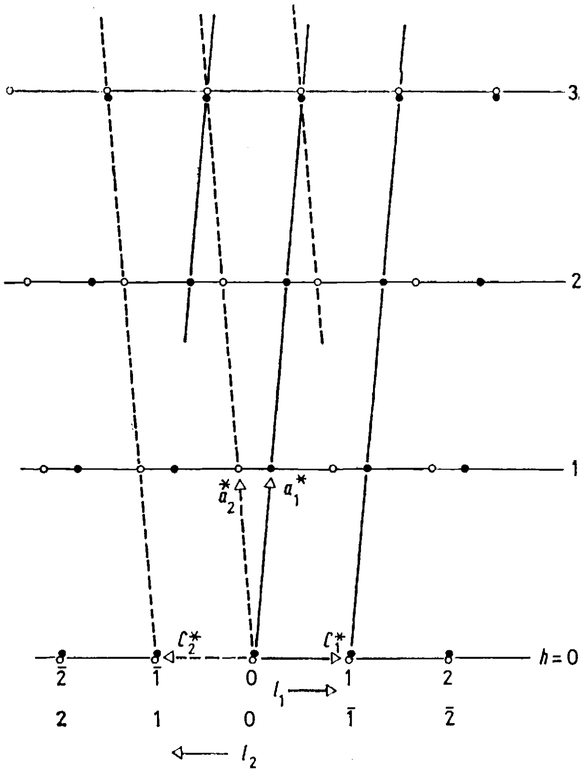

FIGURE 1 The superposition of the two twin reciprocal lattices (solid and open circles on layers $h = 0$ and 3 are deliberately displaced to avoid obliteration)

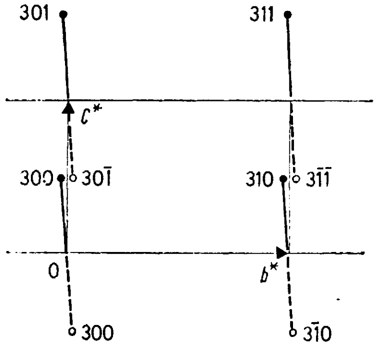

FIGURE 2 A view down [100] on to the $3kl$ net. The vectors represented by solid and broken lines are steeply inclined to the paper and pass each other closely at the $3kl$ and $3\bar{k}(\overline{l+1})$ points (the separation of these points has been exaggerated for clarity)

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[7] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[8] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[9] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

another and depends on the inclination between the reciprocal lattice vector and the vector joining nearly coincident twin points (this is almost parallel to b^*).

If we assume the twins have equal values, the measured intensity is:

$$I(3kl) = k[|F(3kl)^2| + \alpha|F(3\bar{k}(\overline{l+1})^2|],$$

where k is a little over unity for observed data since the intensities of the $0kl$ and $3kl$ layers are enhanced by twinning. As k is unknown, and the calculation of α depends on the small differences, between the large quantities, $I(3kl)$ and $|F(3kl^2)|$, one cannot estimate α reliably. If, however, we calculate

$$\sqrt{I(3kl)}\,[1 + |F(3\bar{k}(\overline{l+1})/F(3kl)|^2]^{-1/2},$$

this scales the observed $|F|$ values down assuming $\alpha \simeq 1$, *i.e.* that both twins contribute fully. This correction was applied to all the $3kl$ reflections for which $|F_o|$ was appreciably $>|F_c|$. For most of the terms the agreement was very good, but it was not always so, and for the terms where $|F_o| \leqslant |F_c|$ the correction made matters worse. For these α is probably small. It was also apparent from these results that α was largest for the reflections whose reciprocal lattice vectors have a major component parallel to b^*.

The layers $h = 4$ and 5 present no problems, but we must consider $h = 6$. There are not many of these terms in our list and their $|F_o|$ and $|F_c|$ values appear to agree pretty well. This is doubtless because the separation of the twins is now 0.0226 r.l.u. which makes overlap a little less likely. The $7kl$ layer again presents no problem.

In view of the above considerations, two modes of refinement were tried. First, all $3kl$ reflections for which $|F_o|$ was appreciably $>|F_c|$ were modified and the refinement gave R 0.064 for 1 745 reflections.

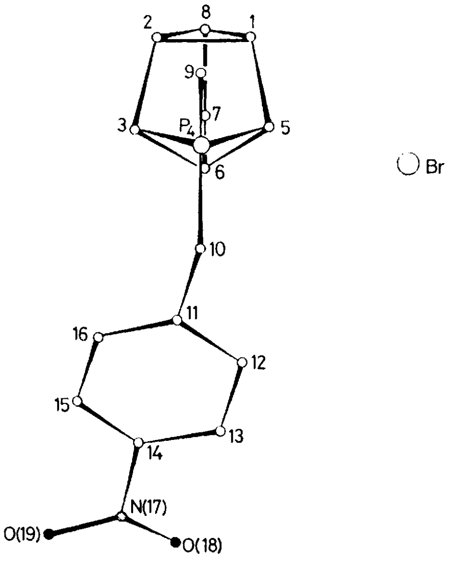

FIGURE 3 Molecule of 4-methyl-4-*p*-nitrobenzyl-4-phosphoniatetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane bromide, showing the atom numbering scheme used

Secondly, the entire $3kl$ layer was removed from the data set and the refinement gave R 0.056 for 1 440 reflections. All final geometry is based on these co-ordinates. The R value for the $3kl$ data from a separate run was 0.163. The three values of bond lengths for the three refinements differed only for 11 bonds and never by >0.01 Å.

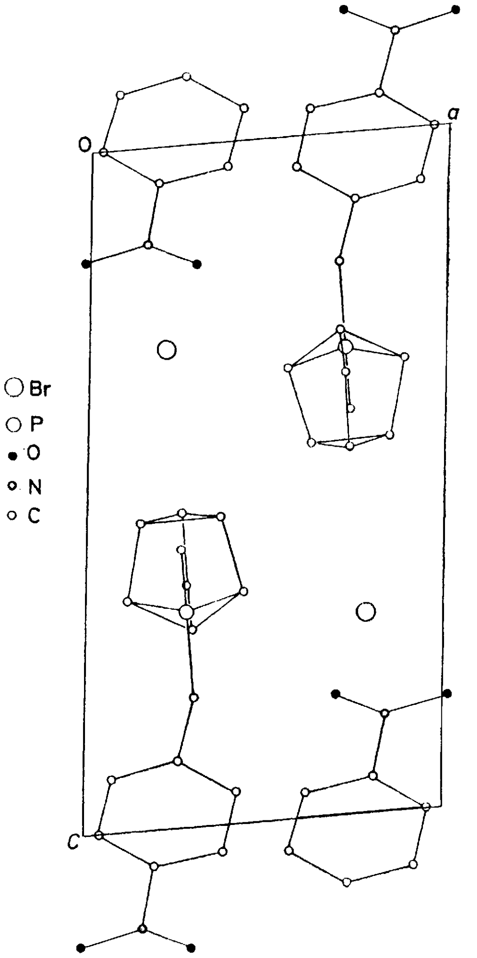

FIGURE 4 The [010] projection showing the packing of molecules

All calculations were carried out at the University of Petroleum and Minerals on an IBM 370/158 computer by means of the N.R.C. Crystallographic Programs.[10]

TABLE 1

Fractional co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses

Atom	x	y	z
Br	7 778(1)	5 716(1)	7 072(1)
C(1)	3 677(14)	1 949(10)	5 471(7)
C(2)	1 472(14)	1 916(10)	5 462(7)
C(3)	1 134(13)	2 287(9)	6 599(7)
P(4)	2 767(3)	3 924(2)	6 833(2)
C(5)	4 408(12)	2 297(9)	6 596(7)
C(6)	2 893(14)	1 270(9)	7 079(7)
C(7)	2 787(16)	−244(9)	6 446(7)
C(8)	2 594(15)	443(10)	5 398(7)
C(9)	2 577(14)	5 439(10)	5 948(7)
C(10)	3 017(14)	4 799(9)	8 123(7)
C(11)	2 639(14)	3 758(9)	8 987(6)
C(12)	4 238(14)	3 058(11)	9 551(7)
C(13)	3 894(17)	2 064(11)	10 340(7)
C(14)	1 985(16)	1 808(9)	10 547(7)
C(15)	362(15)	2 493(11)	10 009(7)
C(16)	715(14)	3 479(10)	9 225(7)
N(17)	1 582(18)	737(9)	11 367(6)
O(18)	2 979(19)	20(11)	11 771(8)
O(19)	−104(16)	622(10)	11 577(7)

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[10] F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Huber, N.R.C. Crystallographic Programs for the IBM 360 System, World List of Crystallographic Computer Programs, 2nd edn., Appendix, Oesthock, Utrecht, 1966, p. 52.

Figure 3 shows the structure and the atom numbering system used. Figure 4 shows the [010] projection of the structure. Table 1 lists final fractional co-ordinates for non-hydrogen atoms, Table 2 the co-ordinates of hydrogen atoms, Table 3 bond lengths and valence angles, and Table 4 intermolecular distances $\leqslant 3.6$ Å. Table 5 shows the agreement analysis for the three refinements and the final layer-line scales. Anisotropic thermal parameters, and observed and calculated structure factors are listed in Supplementary Publication No. SUP 22253 (6 pp.).*

TABLE 2

Hydrogen fractional co-ordinates ($\times 10^3$), derived from a ΔF map and unrefined

Atom	Attached to	*x*	*y*	*z*
H(1)	C(1)	484	188	504
H(2)	C(2)	16	182	504
H(3)	C(3)	−21	193	679
H(4)	C(5)	582	197	679
H(5)	C(6)	305	129	787
H(6)	C(7)	401	−92	658
H(7)	C(7)	161	−89	659
H(8)	C(8)	249	−19	473
H(9)	C(9)	250	525	525
H(10)	C(9)	173	627	624
H(11)	C(9)	395	587	592
H(12)	C(10)	203	569	814
H(13)	C(10)	438	523	825
H(14)	C(12)	567	322	935
H(15)	C(13)	501	153	1 077
H(16)	C(15)	−106	226	1 018
H(17)	C(16)	−41	405	881

TABLE 3

Bond lengths and valence angles with standard deviations in parentheses

(*a*) Distances (Å)

C(1)–C(2)	1.49(1)	C(7)–C(8)	1.49(1)
C(1)–C(5)	1.52(1)	C(10)–C(11)	1.50(1)
C(1)–C(8)	1.51(1)	C(11)–C(12)	1.39(1)
C(2)–C(3)	1.54(1)	C(11)–C(16)	1.39(1)
C(2)–C(8)	1.49(1)	C(12)–C(13)	1.39(1)
C(3)–P(4)	1.82(1)	C(13)–C(14)	1.36(1)
C(3)–C(6)	1.57(1)	C(14)–C(15)	1.38(1)
P(4)–C(5)	1.82(1)	C(14)–N(17)	1.48(1)
P(4)–C(9)	1.77(1)	C(15)–C(16)	1.39(1)
P(4)–C(10)	1.81(1)	N(17)–O(18)	1.21(1)
C(5)–C(6)	1.55(1)	N(17)–O(19)	1.20(1)
C(6)–C(7)	1.53(1)		

(*b*) Angles (°)

C(2)–C(1)–C(5)	104.7(7)	C(5)–C(6)–C(7)	106.8(7)
C(2)–C(1)–C(8)	59.5(6)	C(6)–C(7)–C(8)	97.1(7)
C(5)–C(1)–C(8)	109.3(7)	C(1)–C(8)–C(2)	59.7(6)
C(1)–C(2)–C(3)	102.6(7)	C(1)–C(8)–C(7)	108.1(8)
C(1)–C(2)–C(8)	60.8(6)	C(2)–C(8)–C(7)	108.5(8)
C(3)–C(2)–C(8)	109.2(7)	P(4)–C(10)–C(11)	115.5(8)
C(2)–C(3)–P(4)	99.5(6)	C(10)–C(11)–C(12)	119.6(8)
C(2)–C(3)–C(6)	96.2(7)	C(10)–C(11)–C(16)	120.7(8)
P(4)–C(3)–C(6)	87.3(5)	C(12)–C(11)–C(16)	119.7(8)
C(3)–P(4)–C(5)	74.8(5)	C(11)–C(12)–C(13)	119.9(9)
C(3)–P(4)–C(9)	118.9(4)	C(12)–C(13)–C(14)	118.8(9)
C(3)–P(4)–C(10)	118.2(4)	C(13)–C(14)–C(15)	122.9(9)
C(5)–P(4)–C(9)	119.0(4)	C(13)–C(14)–N(17)	119.8(9)
C(5)–P(4)–C(10)	116.7(4)	C(15)–C(14)–N(17)	117.3(8)
C(9)–P(4)–C(10)	107.0(4)	C(14)–C(15)–C(16)	118.0(9)
C(1)–C(5)–P(4)	98.4(6)	C(11)–C(16)–C(15)	120.8(9)
C(1)–C(5)–C(6)	96.4(7)	C(14)–N(17)–O(18)	117.6(9)
P(4)–C(5)–C(6)	87.5(5)	C(14)–N(17)–O(19)	117.8(9)
C(3)–C(6)–C(5)	90.3(6)	O(18)–N(17)–O(19)	124.6(9)
C(3)–C(6)–C(7)	105.6(7)		

TABLE 4

Intermolecular contacts $\leqslant 3.6$ Å, involving non-hydrogen atoms

$C(1) \cdots C(8^{I})$	3.49(1)	$C(7) \cdots O(19^{I})$	3.29(1)
$C(2) \cdots C(8^{I})$	3.53(1)	$C(8) \cdots C(8^{I})$	3.56(1)
$C(5) \cdots O(18^{I})$	3.34(1)	$C(14) \cdots O(19^{I})$	3.58(1)
$C(6) \cdots O(18^{I})$	3.25(1)	$C(15) \cdots N(17^{I})$	3.50(1)
$C(6) \cdots O(19^{I})$	3.18(1)	$C(15) \cdots O(19^{I})$	3.35(1)
$C(7) \cdots O(18^{I})$	3.52(1)	$C(16) \cdots C(16^{II})$	3.46(1)

Roman numeral superscripts denote the following equivalent positions, relative to the reference molecule at x, y, z:

I $-x, -y, -z$
II $-x, -y, -z + 1$

TABLE 5

Agreement analyses for three modes of refinements

h	R_1	R_2	R_3	S_F *
0	0.052	0.051	0.048	0.191
1	0.055	0.054	0.054	0.344
2	0.057	0.056	0.056	0.340
3	0.163	0.107		0.302
4	0.055	0.055	0.054	0.330
5	0.063	0.063	0.062	0.316
6	0.080	0.077	0.080	0.306
7	0.078	0.078	0.077	0.295

* S_F = final scale factor for intensities.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The phosphetan ring is puckered as expected, with atoms alternately above and below the least-squares plane through the ring atoms, C(3) and C(5) both being 0.24 Å above and P(4) and C(6) being 0.20 and 0.29 Å respectively below the plane. The dihedral angle between the planes C(3), P(4), C(5) and C(3), C(6), C(5) is 46.6°. This dihedral angle is almost double that found in other phosphetans, an increase which is probably due to the presence of the tetracyclic system. All other phosphetan derivatives whose structures have been determined by *X*-ray diffraction have almost identical puckering (dihedral angles 19.9—26.4).[4] The internal angle at the phosphorus is 74.8(4)°, which is significantly smaller than that found in other phosphetan derivatives (81.3—85.9°).[4] The internal angle opposite to phosphorus at C(6) is 90.3(6)°, and is significantly smaller than the comparable angle found in other phosphetan derivatives (100.0—103.1°).[4] The other two internal angles of the phosphetan ring are almost identical. The P–C distances in the phosphetan ring are identical [1.82(1) Å], and are significantly shorter than the sum of the covalent radii (1.87 Å);[11] they are also significantly shorter than the P–C bonds found in other phosphetan derivatives (1.83—1.94 Å),[4] but significantly longer than two recently reported distances [1.788(5) and 1.799(5) Å].[12] One C–C bond length in the phosphetan ring is as expected, the other is longer but does not differ significantly from previously reported values.[4] The P–C(benzyl) distance [1.81(1) Å] is in good agreement with values reported for this type of compound.[4,12]

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1977, Index issue.

[11] L. Pauling, ' The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1964, p. 224.

[12] A. Fitzgerald, J. A. Campbell, G. D. Smith, C. N. Caughlan, and S. E. Cremer, *J. Org. Chem.*, in the press.

In phosphatetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane most of the chemically equivalent bond lengths and valence angles are almost identical, though crystallography does not require this. The mean C–C length in the benzene ring is 1.383 Å, which is not much different from the standard value of (1.394 Å).[13] The internal angles of the benzene ring average 120.0°. All other bond lengths and valence angles agree well with accepted values.

Figure 4 shows the molecular packing projected down the *b* axis. There are twelve intermolecular contacts $\leqslant$3.6 Å (Table 4), all of which are less than the sum of the van der Waals' radii.

The *X*-ray structure confirms earlier assumptions as to the stereochemistry in the tetracyclic system.[6] The material in the present study was prepared by reduction of the corresponding oxide (m.p. 156—157 °C) with trichlorosilane, followed by quaternization with *p*-nitrobenzyl bromide. The reduction step proceeded with overall inversion around the phosphorus[6] and the quaternization reaction with retention.

The bond distances and angles obtained from the current study will be useful for correlation of lanthanide-shift effects on ^{13}C n.m.r. spectra. Initial studies of this kind on phosphetan oxides have been carried out.[12]

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