

Synthesis, Stereochemistry, and Molecular and Crystal Structure of *exo*-3-Phenyl-3-phosphabicyclo[3.2.1]oct-6-ene 3-Oxide

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The syntheses of both the title compound and the *endo*-3-phenyl isomer are described. The isomer assignments were made on the basis of n.m.r. studies and confirmed by a crystal-structure analysis of the *exo*-3-phenyl compound. The crystals of $C_{13}H_{15}OP$ are triclinic, space group $P\bar{1}$, $Z = 2$, with unit cell dimensions $a = 5.973(2)$, $b = 10.496(2)$, $c = 10.699(2)$ Å, $\alpha = 120.27(2)$, $\beta = 104.12(2)$, and $\gamma = 77.60(2)^\circ$. The structure was solved by the heavy-atom method from diffractometer data and refined to an R value of 0.030. The phosphorinane ring adopts a chair conformation which is substantially flattened at the phosphorus end. The ring conformation, bond lengths, and valence and torsional angles are compared with those in several bicyclic[3.2.1] and monocyclic systems reported in the literature.

THE synthesis, stereochemistry, and reactions of phosphorinanes (parent substance as well as the oxide, sulphide, and phosphorinanium salt derivatives) have received considerable attention in the recent literature.^{1,2} As a consequence of the interest in this area and in an effort to understand the chemistry of these systems, a number of crystal structures have been reported.^{2,3}

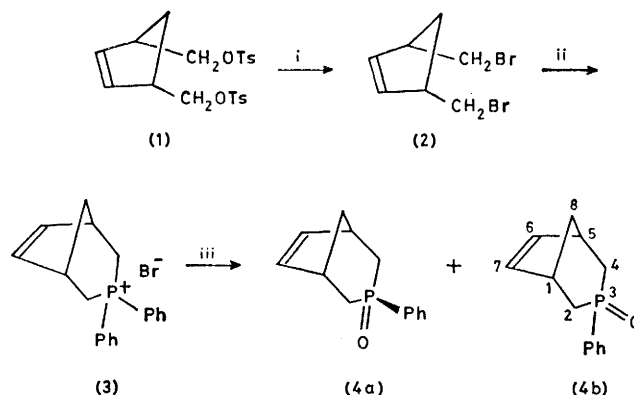
The purpose of the X-ray diffraction study of crystals of the title compound was to confirm the *endo* versus *exo* disposition of the 3-phenyl substituents, obtain torsion angles, and establish the total geometry of the molecule, especially the degree of puckering in the six-membered ring.

We are currently carrying out an investigation of the stereochemistry of aqueous base hydrolysis of substituted phosphoniabicyclo[3.2.1]-oct-6-ene and -octane bromides. Studies on phosphorinanium salts have produced results that are somewhat complex.^{1a,b} A detailed description of the molecular geometry of the mono- and bi-cyclic compounds should eventually aid in the interpretation of the data. In related work, we and others have attempted to establish a relationship of $^{31}P \cdots ^1H$ and $^{31}P \cdots ^{13}C$ coupling constants with geometry^{1c,4} (Karplus equation) as well as evidence of the γ -shift effect.⁵ In all cases we anticipate that an extensive data base of X-ray crystal structure results will be of benefit.

EXPERIMENTAL

Synthesis.—The preparation of the title substance (4a) began with *cis*-3,5-bis(bromomethyl)cyclopentene (2) which in turn was synthesized from *cis*-3,5-bis-*p*-tolylsulphonyloxymethylcyclopentene (1) which has been described elsewhere.⁶ Subsequent conversion of the dibromide to the phosphonium bromide heterocycle (3) was conveniently effected with trimethylsilyldiphenylphosphine, a reagent not previously used for this type of transformation. We found this reagent to be particularly convenient since it could be prepared, distilled, and stored prior to use; in addition, the ring closure went smoothly at 110° (refluxing toluene). In our hands we regard the silylphosphine as an improvement over

tetraphenylbiphosphine which was prepared *in situ* and employed for similar ring closures (180°, refluxing *o*-dichlorobenzene).⁷ Treatment of the diphenylphosphorinanium salt (3) with an aqueous solution of sodium hydroxide gave a mixture of the *endo*- and *exo*-3-phenyl-3-phosphabicyclo[3.2.1]oct-6-ene 3-oxides (4b and a). The isomeric oxides were separated by fractional recrystallization from cyclohexane. A summary of these reactions is shown (Scheme).



SCHEME Reagents: i, $LiBr-(CH_3)_2CO$, heat; ii, $Ph_2PSiMe_3-C_7H_8$, heat; iii, $NaOH-H_2O$, heat

General Conditions.— ^{13}C and ^{31}P n.m.r. spectra were measured with a JEOL FX-60 Q Fourier-transform spectrometer; 1H n.m.r. spectra were recorded with a Varian A-60A spectrometer; in all cases chemical shifts are expressed in δ values and were measured in $CDCl_3$ solution. M.p.s are reported as determined with a Thomas-Hoover apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Manipulation of air- and moisture-sensitive compounds was conducted in a glove-box under dry nitrogen.

***cis*-3,5-Bis(bromomethyl)cyclopentene (2).**—To anhydrous lithium bromide (133 g, 1.53 mol) in dry acetone (1.7 l), *cis*-3,5-bis-*p*-tolylsulphonyloxymethylcyclopentene (231 g, 0.53 mol)⁶ was added and the mixture heated at reflux for 8 h. The acetone was evaporated and cold water (700 ml) added; the mixture was then extracted with pentane (2 × 500 ml). The pentane was dried (Na_2SO_4) and

evaporated and the residue distilled (123 g, 92%), b.p. 65–70° at 0.1 mmHg (Found: C, 33.3; H, 4.15. $C_7H_{10}Br_2$ requires C, 33.1; H, 3.95%) δ_C 34.48 [C(4)], 37.72 (CH_2Br), 47.94 [C(3) and (5)], and 133.70 p.p.m. [C(1) and (2)]; δ_H 1–1.6 (1 H, m), 2.1–2.7 (1 H, m), 2.9–3.4 (2 H, m, allyl), 3.4 (4 H, m, J_{HCH_2} 6 Hz), and 5.75 (2 H, s, vinyl).

3,3-Diphenyl-3-phosphoniabicyclo[3.2.1]oct-6-ene Bromide (3).—To dry toluene (100 ml) under nitrogen and heated at reflux temperature were added separately and simultaneously *cis*-3,5-bis(bromomethyl)cyclopentene (20 g, 0.08 mol) and trimethylsilyldiphenylsilane⁸ (33 g, 0.13 mol) over 1 h. After another 1 h, a precipitate formed. The mixture was heated (reflux) for 4 days, cooled, and the solid product filtered and dried *in vacuo* (28 g, 73%). The salt was purified by recrystallization from ethyl acetate-acetonitrile, m.p. 223–226°. On several occasions material of m.p. 204–206° was obtained; since the ^{13}C n.m.r. spectra of material of either m.p. were identical, the variation in m.p. may reflect different crystalline forms. Moreover, aqueous base hydrolysis of either substance gave the same phosphine oxide product. The phosphonium salt gave a satisfactory elemental analysis (Found: C, 63.35; H, 5.65. $C_{19}H_{20}BrP$ requires C, 63.5; H, 5.6%); δ 7.2–8.3 (10 H, m, aromatic), 6.0 (2 H, s, vinyl), and 2.0–4.2 (8 H, m, aliphatic).

endo- and exo-3-Phenyl-3-phosphabicyclo[3.2.1]oct-6-ene 3-Oxide (4a and b).—To 10% aqueous sodium hydroxide solution (400 ml) was added 3,3-diphenyl-3-phosphoniabicyclo[3.2.1]oct-6-ene bromide (3) (80 g, 0.22 mol) and the mixture was allowed to reflux for 30 min. The brown, oily product was then extracted with CH_2Cl_2 (3 × 75 ml). The CH_2Cl_2 was evaporated to give a solid brown mixture of the oxides (46 g, 95%); the 1H n.m.r. indicated a 4 : 1 ratio of the *endo* : *exo* isomers.

Fractional recrystallization from cyclohexane gave the *exo*-3-phenyl as the less soluble isomer, m.p. 170–173°; the product was purified further by sublimation (*in vacuo*) (Found: C, 71.6; H, 7.1. $C_{13}H_{15}OP$ requires C, 71.55; H, 6.95%), δ_H 7.2–8.0 (5 H, m, aromatic), 6.27 (2 H, s, vinyl), 2.7–3.5 (2 H, two broad peaks, allyl), and 1.6–2.6 (6 H, m, aliphatic). The *endo*-3-phenyl isomer was the more soluble and hygroscopic compound. It was isolated from the mother liquors after repeated recrystallization, m.p. 79–81° (Found: C, 71.75; H, 7.15%), δ_H 7.3–8.0 (5 H, m, aromatic), 5.97 (2 H, s, vinyl), 2.6–3.5 (2 H, two broad peaks, allyl), and 1.9–2.6 (6 H, m, aliphatic).

Isomer Assignments based on N.M.R. Spectra.—Comparison of 1H , ^{13}C , or ^{31}P n.m.r. chemical shifts in a set of isomers frequently permits stereochemical assignments to be made.^{16,2c,9} The vinyl protons in (4a and b) are at δ 6.25 and 5.94, respectively. Molecular models suggest that a phenyl ring in the *endo*-position (4b) must adopt an orientation more or less parallel to the C(6)–C(7) bond and would thus shield the vinyl protons. Similarly, previous reports¹⁰ indicate that an *endo*-P=O group (4a) should, if anything, have a deshielding effect. The relative ^{31}P shifts of δ 28.53 (4a) and 30.89 (4b)* are also consistent with the ^{31}P chemical shifts of *cis*- and *trans*-4-*t*-butyl-1-phenylphosphorinane 1-oxides (29.99 and 28.19 p.p.m., respectively) reported by Marsi.^{2c}

Further confirmation of the assigned isomers was obtained from the effect of a lanthanide shift reagent $Eu(fod)_3$ on both the 1H and ^{13}C chemical shifts; the reagent most likely co-ordinates with the oxygen in the phosphine

oxides.¹⁰ On addition of 0.76 equivalents of shift reagent per equivalent of (4b), the vinyl protons shift by 1.28 p.p.m. (downfield) whereas in (4a), the resultant downfield shift is 2.75 p.p.m. Likewise, on addition of one equivalent of $Eu(fod)_3$ to (4a and b) in $CDCl_3$ solution, the vinyl carbons shifted downfield by 5.70 and 2.43 p.p.m., respectively. The results are consistent with the closer proximity of the P=O group to the vinyl protons (or carbons) in the *exo*-phenyl isomer (4a).

Crystal Data.—*exo*- $C_{13}H_{15}PO$ (4a), $M = 218.2$, m.p. 170–173 °C. Triclinic, $a = 5.973(2)$, $b = 10.496(2)$, $c = 10.669(2)$ Å, $\alpha = 120.27(2)$, $\beta = 104.12(2)$, $\gamma = 77.60(2)^\circ$, $U = 556.8$ Å³, $D_m = 1.31$, $Z = 2$, $D_c = 1.301$ g cm⁻³, $F(000) = 232$. Mo- K_α radiation, $\lambda = 0.71073$ Å, $\mu(Mo-K_\alpha) = 2.3$ cm⁻¹, space group $P\bar{1}$.

Accurate cell dimensions and their standard deviations were determined from a least-squares refinement of the angular settings of 25 accurately centred reflections on an Enraf-Nonius CAD-4 diffractometer. Data were collected on the diffractometer at a take-off angle of 5° with Mo- K_α radiation monochromated by a square graphite crystal. Intensities of independent reflections (to $\theta \leq 25^\circ$) were measured by the ω – 2θ scan technique using the ZIGZAG routine and background counts were taken on each side of the peak. The intensities of three standard reflections were measured every 90 reflections and showed no significant variation during data collection. A total of 1513 out of 1954 reflections were considered observed, having $I > 3\sigma(I)$. The data were corrected for Lorentz and polarization effects. Form factors for non-hydrogen atoms were taken from ref. 11 and for hydrogen atoms from ref. 12. Anomalous terms for phosphorus were included.¹³

All calculations were carried out on the University of Petroleum and Minerals IBM 370/158 computer using N.R.C. crystallographic programs.¹⁴

The structure was solved from a Fourier map phased on the phosphorus atom, which revealed all non-hydrogen atoms of the molecule. Block-diagonal least-squares refinement with isotropic temperature factors gave $R = 0.112$ for the observed reflections. All hydrogen atoms were located from a difference Fourier map, and further refinement of non-hydrogen atoms anisotropically and hydrogen atoms isotropically reduced R to 0.030. A Hughes-type weighting scheme¹⁵ of the form $w = 1$ for $|F_o| \leq 14$, $\sqrt{w} = 14/|F_o|$ for $|F_o| > 14$ was used. A final difference-Fourier map was flat.

RESULTS AND DISCUSSION

Figure 1 is an ORTEP¹⁶ drawing illustrating 50% probability ellipsoids for non-hydrogen atoms, and Figure 2 shows the packing of the molecules. The atomic coordinates of non-hydrogen and hydrogen atoms are listed in Tables 1 and 2, respectively. Interatomic distances and valence angles are given in Table 3. Anisotropic thermal parameters, and observed and calculated structure factors are listed in Supplementary Publication No. SUP 23063 (4 pp) †.

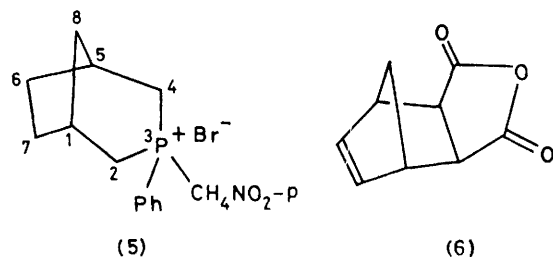
The only reasonably closely analogous phosphorus-containing bicyclo[3.2.1] compound whose X-ray structure has been reported¹⁷ and can, therefore, be used for comparison is *exo*-3-*p*-nitrobenzyl-*endo*-3-phenyl-3-

* The ^{31}P n.m.r. shifts with a positive sign are downfield from 85 H_3PO_4 (reference standard).

† See Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans.* 2, 1980, Index issue.

phosphoniabicyclo[3.2.1]octane bromide (5) (Table 4). The [3.2.1] ring system in both molecules approximates closely to a mirror plane, as can be gauged from Table 5.

Interestingly, the six-membered ring in both these



bicyclic compounds adopts a chair conformation which is considerably flattened at the phosphorus end and to a similar extent. Thus, the angles of (4a) between the least-squares plane C(1)-C(2)-C(4)-C(5) and the planes C(2)-P(3)-C(4) and C(1)-C(8)-C(5) are 31.1 and 70.0°, respectively. A least-squares plane calculation shows that C(1), C(2), C(4), and C(5) are virtually coplanar (deviation -0.001, 0.001, -0.001, and 0.001 Å, respec-

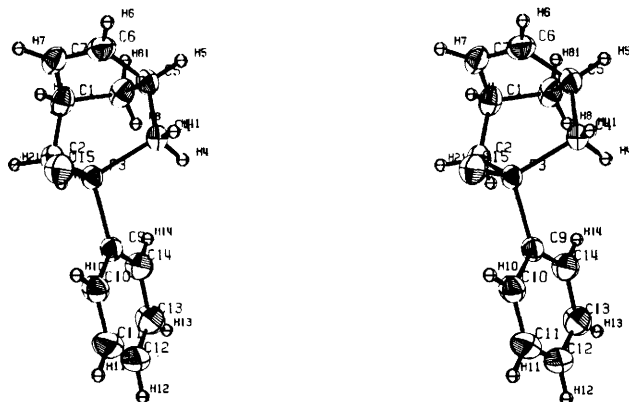


FIGURE 1 Stereopair for *exo*-3-phenyl-3-phosphabicyclo[3.2.1]oct-6-ene 3-oxide

tively), and P(3) C(8) are 0.57 and 0.90 Å below and above the plane, respectively.

The greater deviation in the torsional angles (last two entries in Table 4) of 6.2–6.3° can be readily accounted

to those in the *p*-nitrobenzylphosphonium salt derivative (5).

The plane of the aromatic ring in (4a) is essentially perpendicular to the planes C(1)-C(2)-C(4)-C(5) and C(1)-C(5)-C(6)-C(7), 89.8 and 88.7°, respectively. As a result the *ortho*-hydrogen [C(14)-H(14)] is 3.03, 2.60, and 2.54 Å from the axial C-H bonds at C(8), C(2), and C(4). In contrast, the *endo*-phenyl substituent in (5) is

TABLE 1

Fractional co-ordinates ($\times 10^4$) for non-hydrogen atoms with e.s.d.s in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	503(4)	3 479(3)	648(2)
C(2)	379(4)	2 108(3)	789(2)
P(3)	697(1)	2 529(1)	2 696(1)
C(4)	2 673(3)	3 948(2)	3 721(2)
C(5)	2 397(4)	4 989(2)	3 056(2)
C(6)	-109(4)	5 606(3)	2 849(3)
C(7)	-1 143(4)	4 767(3)	1 518(3)
C(8)	2 831(4)	4 101(3)	1 472(3)
C(9)	2 240(3)	896(2)	2 808(2)
C(10)	1 189(4)	246(2)	3 332(3)
C(11)	2 237(4)	-1 016(3)	3 416(3)
C(12)	4 359(4)	-1 659(3)	2 969(3)
C(13)	5 430(4)	-1 023(3)	2 450(3)
C(14)	4 407(4)	251(3)	2 377(3)
O(15)	-1 566(2)	2 917(2)	3 220(2)

not perpendicular to these same planes, and as a consequence intramolecular non-bonded interactions occur between its *ortho*-hydrogens and equatorial hydrogens bonded to C(2) and C(4).

To the best of our knowledge, no data (bond lengths and angles) are available for the bicyclo[3.2.1]oct-6-ene hydrocarbon analogue of (4a), though an X-ray crystal study of bicyclo[2.2.1]hept-5-ene-2,3-*exo*-dicarboxylic anhydride (6)¹⁸ provides useful comparative information. Thus the degree of puckering in the cyclopentene ring in (6) is 52.2° compared with cyclopentene itself (29.0°).¹⁹ The lower value in (4a) (38.7°) is not unexpected since the presence of the longer C(2)-P(3)-C(4) bridge does not exert the more stringent 'pincers' effect of the shorter two-carbon bridge in (6). The C(6)-C(7) double bond length in (4a) is 1.311(3) Å, which is significantly shorter than that of most double bonds, namely, 1.337(6) Å,²⁰ but comparable to that in (6),

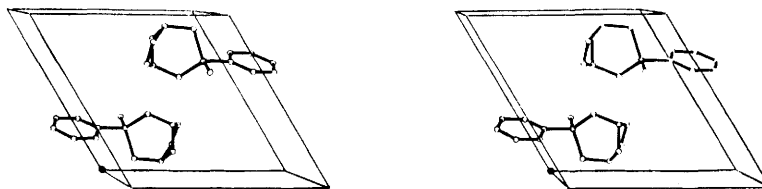


FIGURE 2 Stereopair showing the packing of molecules

for by the presence of the double bond in (4a). This shorter (sp^2-sp^2) bond necessarily (as seen from a simple Prentice-Hall framework molecular model) contracts torsion angles P(3)-C(2)-C(1)-C(7) and C(1)-C(8)-C(5)-C(6) and their symmetrical counterparts relative

1.320 Å. The bridge in (4a) also serves to contract the angles C(5)-C(6)-C(7) and C(1)-C(7)-C(6) (110.1, 111.3°) associated with the double bond; the corresponding angles in (6) are similarly contracted (107.6, 108.3°). Lastly, the one-carbon bridge angle C(1)-C(8)-C(5) is

TABLE 2

Factorial co-ordinates ($\times 10^3$) and isotropic temperature factors for hydrogen atoms, with e.s.d.s in parentheses

Atom	x	y	z	$B(\text{\AA}^2)$
H(1)[C(1)]	21(2)	323(2)	-37(2)	3.3(5)
H(2)[C(2)]	153(4)	132(3)	33(3)	4.6(5)
H(21)[C(2)]	-108(4)	172(3)	30(3)	4.2(5)
H(4)[C(4)]	424(3)	347(2)	375(2)	3.0(4)
H(41)[C(4)]	234(4)	450(2)	472(2)	3.3(5)
H(5)[C(5)]	335(4)	579(3)	368(2)	3.8(5)
H(6)[C(6)]	-84(5)	648(3)	363(3)	5.4(6)
H(7)[C(7)]	-269(4)	483(3)	113(3)	4.3(5)
H(8)[C(8)]	409(4)	330(2)	132(2)	3.3(5)
H(81)[C(8)]	307(4)	479(3)	115(2)	4.2(5)
H(10)[C(10)]	-22(4)	73(3)	363(3)	4.3(5)
H(11)[C(11)]	158(4)	-147(3)	379(3)	5.2(6)
H(12)[C(12)]	504(4)	-253(3)	304(3)	4.5(6)
H(13)[C(13)]	683(5)	-146(3)	217(3)	6.4(7)
H(14)[C(14)]	508(4)	73(3)	200(3)	4.2(5)

contracted to 102.1° , but not to the extent that is found in (6) (93.4°) or other bicyclo[2.2.1] systems* (92.0 — 93.2°) which are more highly strained.

The P(3)-C(2) and P(3)-C(4) distances [1.821 and

TABLE 3

Bond lengths and angles with e.s.d.s in parentheses

(a) Distances (\AA)			
C(1)-C(2)	1.538(4)	C(6)-C(7)	1.311(3)
C(1)-C(7)	1.505(4)	C(6)-H(6)	0.98(3)
C(1)-C(8)	1.532(3)	C(7)-H(7)	0.92(3)
C(1)-H(1)	0.96(2)	C(8)-H(8)	0.98(3)
C(2)-P(3)	1.821(2)	C(8)-H(81)	0.99(3)
C(2)-H(2)	0.96(3)	C(9)-C(10)	1.383(3)
C(2)-H(21)	0.95(3)	C(9)-C(14)	1.395(3)
P(3)-C(4)	1.814(2)	C(10)-C(11)	1.375(4)
P(3)-C(9)	1.810(3)	C(10)-H(10)	0.93(3)
P(3)-O(15)	1.486(2)	C(11)-C(12)	1.375(4)
C(4)-C(5)	1.540(4)	C(11)-H(11)	0.94(3)
C(4)-H(4)	0.96(2)	C(12)-C(13)	1.376(4)
C(4)-H(41)	0.97(2)	C(12)-H(12)	0.95(3)
C(5)-C(6)	1.508(4)	C(13)-C(14)	1.377(4)
C(5)-C(8)	1.522(3)	C(13)-H(13)	0.90(3)
C(5)-H(5)	0.96(3)	C(14)-H(14)	0.97(3)
(b) Angles ($^\circ$)			
C(2)-C(1)-C(7)	111.0(2)	C(5)-C(6)-C(7)	110.1(2)
C(2)-C(1)-C(8)	109.8(2)	C(5)-C(6)-H(6)	124(2)
C(2)-C(1)-H(1)	110(1)	C(7)-C(6)-H(6)	126(2)
C(7)-C(1)-C(8)	100.2(2)	C(1)-C(7)-C(6)	111.3(2)
C(7)-C(1)-H(1)	112(1)	C(1)-C(7)-H(7)	120(2)
C(8)-C(1)-H(1)	114(1)	C(6)-C(7)-H(7)	128(2)
C(1)-C(2)-P(3)	112.3(2)	C(1)-C(8)-C(5)	102.1(2)
C(1)-C(2)-H(2)	112(2)	C(1)-C(8)-H(8)	111(1)
C(1)-C(2)-H(21)	111(2)	C(1)-C(8)-H(81)	109(2)
P(3)-C(2)-H(2)	109(2)	C(5)-C(8)-H(8)	113(1)
P(3)-C(2)-H(21)	107(2)	C(5)-C(8)-H(81)	109(2)
H(2)-C(2)-H(21)	106(2)	H(8)-C(8)-H(81)	113(2)
C(2)-P(3)-C(4)	105.3(1)	P(3)-C(9)-C(10)	117.9(2)
C(2)-P(3)-C(9)	106.7(1)	P(3)-C(9)-C(14)	123.6(2)
C(2)-P(3)-O(15)	112.9(1)	C(10)-C(9)-C(14)	118.5(2)
C(4)-P(3)-C(9)	105.9(1)	C(9)-C(10)-C(11)	121.0(2)
C(4)-P(3)-O(15)	115.3(1)	C(9)-C(10)-H(10)	115(2)
C(9)-P(3)-O(15)	110.2(1)	C(11)-C(10)-H(10)	124(2)
P(3)-C(4)-C(5)	112.3(2)	C(10)-C(11)-C(12)	120.2(3)
P(3)-C(4)-H(4)	109(1)	C(10)-C(11)-H(11)	123(2)
P(3)-C(4)-H(41)	107(1)	C(12)-C(11)-H(11)	117(2)
C(5)-C(4)-H(4)	111(1)	C(11)-C(12)-C(13)	119.4(3)
C(5)-C(4)-H(41)	110(1)	C(11)-C(12)-H(12)	119(2)
H(4)-C(4)-H(41)	108(2)	C(13)-C(12)-H(12)	122(2)
C(4)-C(5)-C(6)	110.7(2)	C(12)-C(13)-C(14)	120.8(3)
C(4)-C(5)-C(8)	110.2(2)	C(12)-C(13)-H(13)	118(2)
C(4)-C(5)-H(5)	110(2)	C(14)-C(13)-H(13)	121(2)
C(6)-C(5)-C(8)	101.0(2)	C(9)-C(14)-C(13)	120.0(2)
C(6)-C(5)-H(5)	110(2)	C(9)-C(14)-H(14)	116(2)
C(8)-C(5)-H(5)	115(2)	C(13)-C(14)-H(14)	124(2)

1.814(2) \AA] are similar to those in (5) [1.806, 1.809(6) \AA], *trans*-4-*t*-butyl-1-phenylphosphorinane 1-oxide^{2c} (1.795 and 1.791 \AA), and *cis*-1-iodomethyl-1-phenylphospholanium iodide²¹ (1.82 and 1.81 \AA), but are significantly shorter than a 'normal' P-C bond of

TABLE 4

A comparison of valence and torsional angles ($^\circ$) in two bicyclo[3.2.1] systems, (4a) and (5)

Angle	(5)	(4a)	Average of difference
C(1)-C(2)-P(3)	112.9 (112.2)* ⁽⁴⁾	112.3 (112.3)* ⁽²⁾	0.3
C(2)-P(3)-C(4)	106.0(2)	105.3(1)	0.7
C(2)-C(1)-C(8)	111.1 (111.2) (5)	109.8 (110.2) (2)	1.2
C(1)-C(8)-C(5)	102.5 (5)	102.1 (2)	0.4
C(7)-C(1)-C(8)	103.0 (102.5) (4)	100.2 (101.0) (2)	2.2
C(4)-P(3)-C(2)-C(1)	31.2 (-31.5)* ⁽³⁾	33.3 (-33.5)* ⁽²⁾	2.2
P(3)-C(2)-C(1)-C(8)	-56.0 58.0 (3)	-58.8 (58.7) (2)	1.8
C(2)-C(1)-C(8)-C(5)	78.2 (-79.2) (4)	80.4 (-80.4) (2)	1.7
C(2)-C(1)-C(7)-C(6)	-93.3 (94.5) (5)	-93.0 92.5 (2)	1.7
C(6)-C(7)-C(1)-C(8)	26.5 (-25.6) (4)	23.7 (-23.5) (2)	2.5
P(3)-C(2)-C(1)-C(7)	58.5 (-57.4) (3)	52.1 (-51.2) (2)	6.3
C(7)-C(1)-C(8)-C(5)	-42.6 (42.9) (4)	-36.7 (36.5) (2)	6.2

* Values in parentheses are the symmetrical counterparts on the farther side of the molecule, e.g. C(1)-C(2)-P(3) [C(5)-C(4)-P(3)] or C(4)-P(3)-C(2)-C(1) [C(2)-P(3)-C(4)-C(5)].

1.872 \AA . The P(3)-C(9) bond length of 1.810(3) \AA is comparable to (5) [1.795(4) \AA] and the average P-C (Ph) bond lengths found in other compounds containing tetrahedral phosphorus.²²⁻²⁵ The P(3)-O(15) bond length of 1.486(2) \AA is longer than the 'normal' P=O distance of 1.44 \AA , but agrees well with that in phosphetan 1-oxides

TABLE 5

Bond lengths (\AA)	$\langle \Delta/\sigma \rangle$		$\langle \Delta/\sigma \rangle$	
	(4a)	(5)	(4a)	(5)
Bond lengths (\AA)	3.5	3.5	2.0	1.2
Valence angles ($^\circ$)	4.0	1.7	2.0	1.1
Torsion angles ($^\circ$)	4.5	7	1.5	1.8

(1.471—1.494 \AA),^{22,24,26} *trans*-4-*t*-butyl-1-phenylphosphorane 1-oxide (1.483 \AA),^{2c} and trimethylphosphine oxide²⁷ (1.48 \AA , electron diffraction).

There is a parallel correspondence (based on symmetry) of the bond lengths (and angles) in (4a). The four sp^3 - sp^3 bonds have a mean of 1.533(4) \AA which is similar to the paraffinic value [1.541(3) \AA] quoted in ref. 19. The two sp^3 - sp^2 bonds [1.505(4), 1.508(4) \AA] are shorter than the 1.53(1) \AA reported,²⁰ but close to the 1.516 \AA in (6).

The mean C-C bond length in the phenyl ring is 1.380(4) \AA which agrees within experimental precision with the equivalent bond lengths in (5) [1.377(8) \AA],

* See references cited in ref. 17 for norbornane, norbornadiene, and cyclopentadiene dimer.

trans-4-*t*-butyl-1-phenylphosphorinan 1-oxide^{2c} (1.379 Å) and a phospholanium iodide²¹ [1.37(1) Å]. The internal angles of the aromatic ring average 119.98(2°).

The only intramolecular contact less than 3.5 Å is C(4) ··· O(15) (3.35 Å), which is a normal van der Waals contact.

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REFERENCES

- ¹ (a) K. L. Marsi and J. L. Jasperse, *J. Org. Chem.*, 1978, **43**, 760; (b) K. L. Marsi, J. L. Jasperse, F. M. Llort, and D. B. Kanne, *ibid.*, 1977, **42**, 1306; (c) J. J. Breen, S. O. Lee, and L. D. Quin, *ibid.*, 1975, **40**, 2245; (d) S. D. Venkataramu, G. D. Macdonell, W. R. Purdum, M. El-Deek, and K. D. Berlin, *Chem. Rev.*, 1977, **77**, 121.
- ² (a) A. T. McPhail, J. J. Breen, and L. D. Quin, *J. Am. Chem. Soc.*, 1971, **93**, 2574, on 1-phenylphosphorinan-4-one; (b) A. T. McPhail, J. J. Breen, J. H. Somers, J. C. H. Steele, jun., and L. D. Quin, *Chem. Commun.*, 1971, 1020, on 4,4-dimethoxy-1-phenylphosphorinan; (c) A. T. McPhail, P. A. Luhan, S. I. Featherman, and L. D. Quin, *J. Am. Chem. Soc.*, 1972, **94**, 2126, on *trans*-4-*t*-butyl-1-methylphosphorinan-4-ol; (d) L. D. Quin, A. T. McPhail, S. O. Lee, and K. D. Onan, *Tetrahedron Lett.*, 1974, 3473, on 4-substituted 1-methylphosphorinan-4-ol 1-sulphides; (e) G. D. Macdonell, K. D. Berlin, J. R. Baker, S. E. Ealick, D. Van der Helm, and K. L. Marsi, *J. Am. Chem. Soc.*, 1978, **100**, 4535, on *trans*-4-*t*-butyl-1-phenylphosphorinan 1-oxide.
- ³ J. C. Gallucci and R. Homes, *J. Am. Chem. Soc.*, 1980, **102**, 4379.
- ⁴ J. P. Albrand, D. Gagnaire, J. Martin, and J. B. Robert, *Bull. Soc. Chim. Fr.*, 1969, 40; G. A. Gray and S. E. Cremer, *J. Org. Chem.*, 1972, **37**, 3458, 3470; J. J. Breen, S. O. Lee, and L. D. Quin, *J. Org. Chem.*, 1975, **40**, 2245; A. Rudi and Y. Kashman, *Org. Magn. Reson.*, 1977, **10**, 245.
- ⁵ D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc.*, 1967, **89**, 5315; D. G. Gorenstein, *ibid.*, 1977, **99**, 2254; J. B. Stothers and C. T. Tan, *Can. J. Chem.*, 1976, **54**, 917.
- ⁶ C. A. Grab and H. R. Pfaender, *Helv. Chem. Acta*, 1970, **53**, 256.
- ⁷ K. L. Marsi, D. M. Lynch, and G. D. Homer, *J. Heterocycl. Chem.*, 1972, **9**, 331; G. Maerkl, *Angew. Chem. Int. Ed. Engl.*, 1963, **2**, 620.
- ⁸ W. Kuchen and H. Buchwald, *Chem. Ber.*, 1959, **92**, 227.
- ⁹ L. D. Quin and S. O. Lee, *J. Org. Chem.*, 1978, **43**, 1424; J. R. Wiseman and H. O. Krabbenhoft, *ibid.*, 1976, **41**, 589.
- ¹⁰ S. E. Cremer, F. R. Farr, P. W. Kremer, H. Hwang, G. A. Gray, and M. G. Newton, *J. Chem. Soc., Chem. Commun.*, 1975, 374; B. D. Cuddy, K. Treon, and B. J. Walker, *Tetrahedron Lett.*, 1971, 4433; O. Awerbouch and Y. Kashman, *Tetrahedron*, 1975, **31**, 33.
- ¹¹ D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 1965, **18**, 104.
- ¹² R. F. Stewart, E. R. Davidson, and S. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
- ¹³ D. T. Cromer, *Acta Crystallogr.*, 1965, **18**, 17.
- ¹⁴ F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Huber, 'N.R.C. Crystallographic Programs, World List of Crystallographic Computer Programs,' Oesthock, Utrecht, 1966, 2nd edn., Appendix, p. 52.
- ¹⁵ E. W. Hughes, *J. Am. Chem. Soc.*, 1941, **63**, 1737.
- ¹⁶ C. K. Johnson, ORTEP Report ORNL-5138, Oak Ridge National Laboratory, 1976.
- ¹⁷ Mazhar-ul-Haque, W. Horne, S. E. Cremer, P. W. Kremer, and J. T. Most, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1467.
- ¹⁸ G. Filippini, C. M. Gramaccioli, C. Rovere, and M. Simonetta, *Acta Crystallogr.*, 1972, **B28**, 2869, and references cited.
- ¹⁹ M. I. Davis and T. W. Muecke, *J. Phys. Chem.*, 1970, **74**, 1104.
- ²⁰ 'Molecular Structures and Dimensions,' eds. O. Kennard, D. G. Watson, F. H. Allen, N. W. Isaacs, W. D. S. Motherwell, R. C. Pettersson, and W. G. Town, 1972, Oesthock, Utrecht, vol. A1, p. S2.
- ²¹ A. Fitzgerald, G. D. Smith, C. N. Caughlan, K. L. Marsi, and F. B. Burns, *J. Org. Chem.*, 1976, **41**, 1155.
- ²² Mazhar-ul-Haque, *J. Chem. Soc. B*, 1970, 938.
- ²³ C. Moret and L. M. Trefonas, *J. Am. Chem. Soc.*, 1969, **91**, 2255.
- ²⁴ Mazhar-ul-Haque, *J. Chem. Soc. B*, 1971, 117.
- ²⁵ Mazhar-ul-Haque and C. N. Caughlan, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1101.
- ²⁶ Mazhar-ul-Haque, *J. Chem. Soc. B*, 1970, 711, 934.
- ²⁷ H. K. Wang, Forsvarets-forsking Intern. Rapport (Norway), 1960, I.R.-K-225. Bond lengths for P=O as short as 1.40 Å, D. Swank, C. N. Caughlan, F. Rameriz, O. P. Madan, and C. P. Smith, *J. Am. Chem. Soc.*, 1967, **89**, 6503, and as long as 1.5 Å, E. Sheffer and K. N. Trueblood, *Acta Crystallogr.*, 1965, **18**, 1067, have been reported.