# The Synthesis, Stereochemistry, and Crystal Structure of *exo*-3-*p*-Nitrobenzyl-*endo*-3-phenyl-3-phosphoniabicyclo[3.2.1]octane Bromide

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The synthesis of the title compound is described. $C_{20}H_{23}BrNO_2P$ crystallizes in the monoclinic space group $P2_1/c$ with cell constants $a$ = 12.934(1), $b$ = 8.996(1), $c$ = 17.622(3) Å, $\beta$ = 106.74(1)°, $Z$ = 4. The structure was solved by the heavy-atom method and refined to an $R$ value of 0.046. The phosphorinanium ring adopts a chair conformation which is substantially flattened at the phosphorus end. The study confirmed the *endo*- and *exo*-disposition of phenyl and *p*-nitrophenyl substituents, respectively. The ring conformation, bond lengths, and angles as well as torsional angles are compared to calculated values of the silicon analogue; there is close similarity.

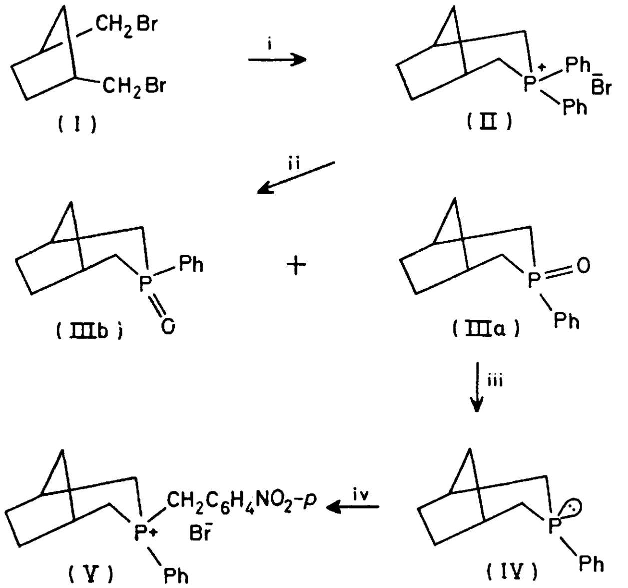
THE stereochemistry of hydroxide ion attack on phosphonium salts to give the phosphine oxide varies from complete inversion about phosphorus in acyclic salts [1] to complete retention in the four-membered ring heterocycle [2] (phosphetanium salt) and five-membered ring [3] (phospholanium salt). More complex stereochemical results are obtained for the phosphorinanium (six-membered ring) heterocycles.[4] A complete understanding of the latter system requires detailed information of the conformational disposition of the six-membered ring.

Our interest in the stereochemistry of base decomposition of phosphonium salts prompted us to investigate a bicyclic [3.2.1] structure in which the six-membered ring is conformationally restricted by the presence of a $-CH_2-CH_2-$ bridge. Both the parent hydrocarbon (bicyclo[3.2.1]octane) [5] and heteroatomic analogues [6] have been subject to theoretical calculation. Extensive n.m.r. studies of the substituted hydrocarbon have also been made in an attempt to access conformational preference.[7] Flattening of the six-membered ring has been implied in a number of cases.[7]

The purpose of the current study was to establish the configuration of the substituents about phosphorus in the title compound. This compound together with its *endo*-3-*p*-nitrobenzyl isomer constitutes part of a larger series of variously substituted phosphoniabicyclo[3.2.1]-octane and -oct-6-ene bromides which are being subjected to aqueous sodium hydroxide decomposition.[8] We anticipate that the stereochemical outcome of these reactions will be sensitive to conformational factors and the steric environment about phosphorus. Furthermore, the results of the $X$-ray determination provide a conformational picture which can be compared to the theoretical calculations on similar molecules.[5,6] The degree of ring flattening was of special concern in this study.

## EXPERIMENTAL

*Synthesis*.—The route to the title compound (V) is shown in the Scheme. In each step there is a close analogy in the literature for the type of transformation. Details are provided in the Experimental section. Each of the conversions (IIIa) ⟶ (IV) and (IV) ⟶ (V) is assumed to go with retention of configuration about phosphorus; adequate precedent supports this contention.[3,9] Thus, establishment of the *endo*- and *exo*-substituents in compound (V) by this $X$-ray study serves to identify the phenyl group as *endo* in structures (IIIa) and (IV).



SCHEME Reagents: i, $Ph_2PSiMe_3-PhCH_3-\Delta$; ii, $NaOH-H_2O-\Delta$; iii, $PhSiH_3$; iv, $p\text{-}NO_2C_6H_4CH_2Br$

*General Conditions*.—N.m.r. spectra were measured with a JEOL FX-60 QD Fourier transform spectrometer; 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-1,3-*Bis(bromomethyl)cyclopentane* (I).—The starting compound, *cis*-1,3-bis-(*p*-tolylsulphonyloxy)cyclopentane was prepared by modification of the preparation described by Birch and Dean,[10] m.p. 108—110.5° (lit.,[10] 108.5—109°).

To anhydrous lithium bromide (125 g, 1.4 mol) in dry acetone (1 000 ml), the bistosylate (216 g, 0.5 mol) was added and the mixture heated at reflux for 4 days. The mixture was cooled and the lithium toluenesulphonate filtered and washed with acetone. The combined organic phases were evaporated and the concentrate added to water (1 000 ml). The product was extracted with pentane. The pentane was dried ($Na_2SO_4$) and evaporated and the bis(bromomethyl)cyclopentane distilled (109 g, 85%), b.p. 58—60° at 0.1 mmHg (Found: C, 32.9; H, 4.7; Br, 62.6. $C_7H_{12}Br_2$ requires C, 32.85; H, 4.75; Br, 62.45%); $\delta_C$ ($CDCl_3$) 30.62 [C(4), C(5)], 37.90 [C(2)], 38.39 ($CH_2$-Br), and 42.27 p.p.m. [C(1), C(3)].

3,3-*Diphenyl*-3-*phosphoniabicyclo*[3.2.1]*octane Bromide* (II).—This compound was prepared by treatment of *cis*-1,3-bis(bromomethyl)cyclopentane by a modification of a similar reaction described by Marsi [11] which had been originally reported by Maerkl.[12] To dry toluene (90 ml) at reflux in a 300 ml flask equipped with a reflux condenser and magnetic stirrer were added the above dibromide (10 g, 0.04 mol) and trimethylsilyldiphenylphosphine (15 g, 0.06 mol); [13] the two reagents were added dropwise and simultaneously over 2 h through separate addition funnels. Additional trimethylsilydiphenylphosphine (3 g) was added after 15 h, and the mixture heated for an additional 15 h. The reaction was cooled and filtered to give a solid (12.2 g, 67%). The *product* was recrystallized from water, m.p. 228—230° (Found: C, 62.9; H, 6.1. $C_{19}H_{22}BrP$ requires C, 63.15; H, 6.15%); $\delta$($CDCl_3$) 7.5—8.3 (10 H, m, aromatic) and 1.1—4.2 (12 H, m, aliphatic).

endo-3-*Phenyl*-3-*phosphabicyclo*[3.2.1]*octane* 3-*Oxide* (IIIa).—To an aqueous 20% sodium hydroxide solution (360 ml), 3,3-diphenyl-3-phosphoniabicyclo[3.2.1]octane bromide (57 g, 0.16 mol) was added and the mixture heated at reflux for 5 h. The brown, oily product was then extracted with methylene chloride (3 × 75 ml). The organic extract was dried ($Na_2SO_4$) and evaporated to give a crude mixture (33 g, 95%) of the *endo*- and *exo*-phenyl oxide isomers (3 : 1). The isomer ratio was determined from the relative areas of the following peaks in the $^{13}C$ n.m.r. spectra: (IIIa) $\delta$ 35.66 [60.1 Hz, C(2), C(4)] and 38.77 p.p.m. [8.2 Hz, C(8)]; (IIIb) $\delta$ 38.65 [61.1 Hz, C(2), C(4)], and 39.55 p.p.m. [6.4 Hz, C(8)]. The $^{31}P-^{13}C$ coupling and assignment are in parentheses. The *endo*-phenyl isomer was isolated by fractional recrystallization of the mixture from cyclohexane; the endo-*isomer* crystallized out first, m.p. 92—94° (Found: C, 70.75; H, 7.75. $C_{13}H_{17}OP$ requires C, 70.9; H, 7.8%); $\delta$ 7.1—8.2 (5 H, m, aromatic and 1.0—3.2 (12 H, m, aliphatic).

endo-3-*Phenyl*-3-*phosphabicyclo*[3.2.1]*octane* (IV).—A heterogeneous mixture of phenylsilane (4.5 g, 0.04 mol) and the *endo*-phenylphosphine oxide (3 g, 0.02 mol; 95% isomer purity) was heated to 45—55° for 12 h under nitrogen. As reduction took place, gas evolution occurred and the mixture became homogeneous. The mixture was cooled to 0 °C and deoxygenated 20% sodium hydroxide solution (30 ml) was added dropwise over 2 h. The product was extracted with benzene and the benzene washed with water (2 × 25 ml). The benzene was dried ($MgSO_4$) and evaporated to give the phosphine (90% isomer purity). The isomer ratio was determined from the relative areas of the following peaks in the $^{13}C$ n.m.r. spectrum: (IV) $\delta$ 39.70 p.p.m. [1.7 Hz, C(8)]; *exo*-phenyl isomer $\delta$ 41.25 p.p.m. [6.1 Hz, C(8)]. Purification by distillation was avoided since heating tends to convert the *endo*-phenyl isomer to the more stable *exo*-isomer. The phosphine could be reconverted to the parent oxide by oxidation with t-butyl hydrogen peroxide.

exo-3-p-*Nitrobenzyl*-endo-3-*phenyl*-3-*phosphoniabicyclo*-[3.2.1]*octane Bromide* (V).—The phosphabicyclo[3.2.1]octane [2.1 g, 0.01 mol) was combined with *p*-nitrobenzyl bromide (2.45 g, 0.012 mol) in ether (20 ml). The mixture was allowed to stand for 48 h. The precipitate was filtered off and washed with ether and benzene to give the desired *phosphonium salt* (3 g, 70%), m.p. 247—249° (Found: C, 57.5; H, 5.65. $C_{20}H_{23}BrNO_2P$ requires C, 57.15; H, 5.5%); $\delta$($CDCl_3$) 7.2—8.3 (9 H, m, aromatic), 5.05 (2 H, d, *J* 16.5 Hz, $PCH_2$), and 0.8—3.9 (12 H, m); $\delta_C$ ($CDCl_3$) 37.25 [5.4 Hz, C(8)], 33.24, [6.3 Hz, C(1), C(5)], 33.09 [43.4 Hz, C(15)], 28.48 [1.9 Hz, C(6), C(7)] 24.61 [43.4 Hz, C(2), C(4)], 118.77 [75.5 Hz, C(9)], 131.6 [9.0 Hz, C(10), C(14)], 129.6 [11.9 Hz, C(11), C(13)], 134.06 [3.2 Hz, C(12)], 135.9 [9.4 Hz, C(16)], 130.9 [5.3 Hz, C(17), C(21)], 122.2 [3.5 Hz, C(18), C(20)], and 147.0 p.p.m. [4.4 Hz, C(19)]; $^{31}P-^{13}C$ coupling constants are in square brackets.

*Crystal Data*.—$C_{20}H_{23}BrNO_2P$, $M = 420.3$. Monoclinic, $a = 12.934(1)$, $b = 8.966(1)$, $c = 17.622(3)$ Å, $\beta = 106.74(1)°$, $U = 1\,956.9$ Å$^3$, $D_m$ (by flotation) = 1.43 g cm$^{-3}$, $Z = 4$, $D_c = 1.427$ g cm$^{-3}$, Space group $P2_1/c$; Mo-$K_\alpha$ radiation, $\lambda = 0.710\,73$ Å, $\mu$(Mo-$K_\alpha$) = 23.20 cm$^{-1}$, $F(000) = 864$.

The Enraf–Nonius program SEARCH was used to obtain 25 reflections, which were then used in the program INDEX to obtain approximate cell dimensions. Accurate cell dimensions and their standard deviations were obtained by least-squares refinement of these 25 accurately centred reflections.

A crystal of *ca.* 0.25 × 0.30 × 0.5 mm$^3$ was used for intensity measurements on an Enraf–Nonius CAD-4 diffractometer controlled by a PDP8/A computer at a take-off angle of 5° with Mo-$K_\alpha$ radiation filtered by a square graphite crystal monochromator. 3 454 Independent reflections (to $\theta \leqslant 25°$) were measured by $\omega-(\frac{1}{6})2\theta$ scan technique using the ZIGZAG routine; 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 change in intensities during data collection. A total of 2 006 reflections were considered observed having $I > 3\sigma(I)$. Lorentz and polarization corrections were applied as usual. Form factors for non-hydrogen atoms were taken from ref. 14 and for hydrogen atoms from ref. 15. Anomalous terms for bromine and phosphorus were included.

All calculations were carried out on the University of Petroleum and Minerals IBM 370/158 Computer using N.R.C. crystallographic programs.[16]

The structure was solved by the heavy-atom method. A Fourier map phased on the bromide ion and phosphorus atom revealed all non-hydrogen atoms of the molecule. Block diagonal least-squares refinement with isotropic temperature factors gave *R* 0.122 for the observed reflections; anisotropic temperature factors reduced *R* to 0.064. All the hydrogen atoms were located from a difference synthesis and further refinement of non-hydrogen atoms anisotropically and hydrogen atoms isotropically reduced *R* to 0.046. A Hughes type weighting scheme [17] of the form $w = 1$ for $|F_o| \leqslant 20$, $\sqrt{w} = 20/|F_o|$ for $|F_o| > 20$ was used. A final difference map was flat except for a few peaks of *ca.* 0.6 Å$^{-3}$ in the vicinity of bromide and phosphorus.

## RESULTS AND DISCUSSION

Figure 1 is an ORTEP [18] drawing illustrating the 30% probability ellipsoids for the non-hydrogen atoms and Figure 2 showing the packing of the molecules. Figure 3 shows the atomic numbering. The atomic co-ordinates of non-hydrogen atoms and hydrogen atoms are given in Tables 1 and 2. Interatomic distances and valence angles are given in Table 3. Torsion angles and intermolecular contacts $<3.6$ Å are given in Tables 4 and 5 respectively. In Table 6 the bond and torsion angles of (V) are compared with silabicyclo[3.2.1]octane. Anisotropic thermal parameters, and observed and calculated structure factors are listed in Supplementary Publication No. SUP 22841 (6 pp.) *

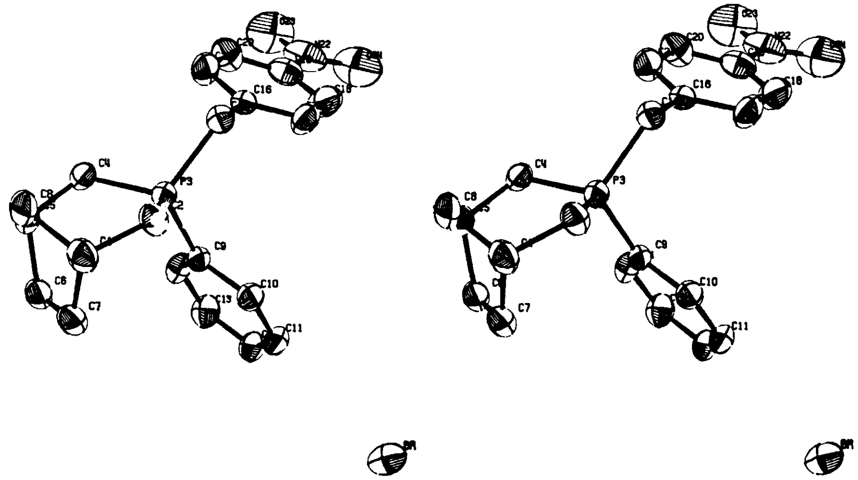


FIGURE 1 Stereopair of *exo*-3-*p*-nitrobenzyl-*endo*-3-phenyl-3-phosphoniabicyclo[3.2.1]octane bromide

Although several structural studies have been published on six-membered ring phosphines [19] and their oxides,[20] no comparable phosphonium salt has been measured which would serve as a basis of comparison with the title substance.

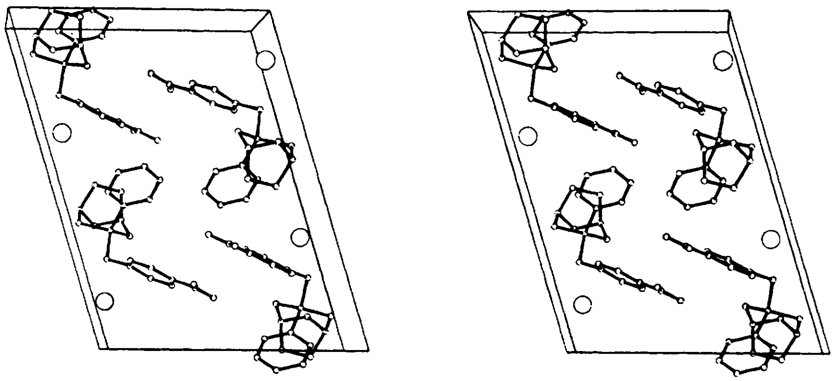
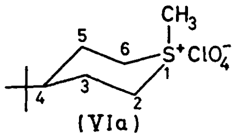
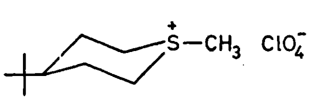


FIGURE 2 Stereopair showing the packing of molecules

Nevertheless there are several molecules which provide a useful basis for comparison. *X*-Ray structural analyses of both *cis*- and *trans*-4-t-butyl-*S*-methylthianium perchlorates (VIa and b) have been performed.[21] The torsional angles C(6)–S–C(2)–C(3) and S–C(2)–C(3)–C(4) are 64 and 69°, respectively, in (VIb) and 46 and 59°, respectively, in (VIa). Thus, the otherwise severe $S-CH_3$ non-bonded interaction with the axial C–H bonds at C(3) and C(5) is reduced by the flattening of the ring (an energetically ' cheap ' torsional change).[21] The torsional angles C(1)–C(2)–P(3)–C(4) and P(3)–C(4)–C(5)–C(6) of the phosphonium salt (V) are 31.2 (31.5) and 57.4° (58.5°) and more similar to those in (VIa) than in (VIb). In fact the six-membered ring in (V) is flattened more extensively, perhaps in order to avoid closeness of the *ortho*-hydrogens on the phenyl ring [H(10 and H(14)] with the equatorial protons on C(2) and C(4) (see Table 7). Even in the parent bicyclo-[3.2.1] hydrocarbon itself, the C(6)–C(7) bridge tends to force the axial bonds at C(1)–C(5) together which in turn lessens the puckering at C(2)–C(3)–C(4) and splays



(VIa)



(VIb)

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* See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1979, Index issue.

the axial bonds at C(2) and at C(4).[7] The splaying of the H(4)–C(4)–H(4′) angle (117°) in (V) is consistent with the expected flattening. However, the H(2)–C(2)–H(2′) angle is only 105°. At the present time we do not understand why both of these angles do not splay to an equal extent based on the symmetry of the system. It is also not obvious why the C(5)–C(8) bond length (1.507 Å) is so different from C(1)–C(8) (1.534 Å), since there is a parallel correspondence (based on symmetry) of the other bond lengths in this molecule.

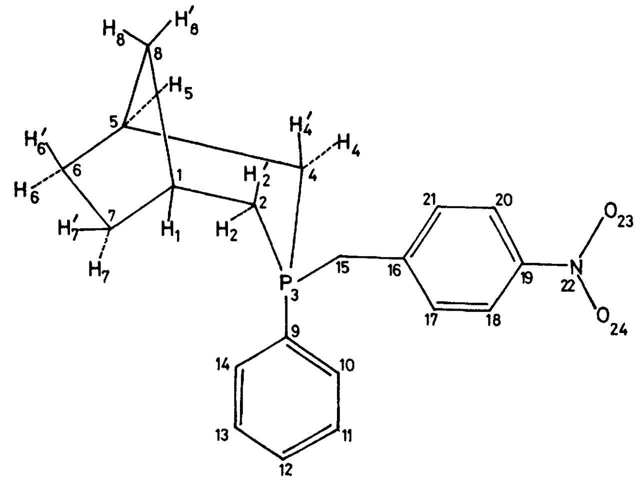

FIGURE 3 The structure and the atomic numbering

Perhaps the closest analogues of the phosphonium salt (V) are a series of silicon-substituted 3-silabicyclo[3.2.1]octanes which have been subject to calculations by force field methods.[6] The P–C bond lengths and C–P–C angles are generally similar to the corresponding Si–C bond lengths and C–Si–C angles. For comparison the silabicyclo[3.2.1]octane data are shown in Table 6. In nearly every instance the angular correspondence is well within 2°. Calculation on the *endo*-3-methyl- and 3,3-dimethyl-silabicyclo[3.2.1]octanes show results similar to the parent silane except for the torsional angle about C(1)–C(2)–C(3)–C(4) (21.5 and 22°, respectively) and C(3)–C(4)–C(5)–C(6) (63.9 and 64.5°, respectively) [6]. The presence of the tetrahederal axial $CH_3$–Si substituent causes increased ring flattening due to non-bonded interaction with the ethylene bridge.

TABLE 1

Fractional co-ordinates ($\times 10^5$) for bromide and ($\times 10^4$) for others, with e.s.d.s in parentheses

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Br | 8 217(5) | 10 018(7) | 15 139(3) |
| C(1) | 9 095(5) | −1 055(6) | 5 599(3) |
| C(2) | 9 342(4) | 421(6) | 6 052(3) |
| P(3) | 8 184(1) | 1 192(1) | 6 291(1) |
| C(4) | 7 385(4) | −388(5) | 6 428(3) |
| C(5) | 7 481(4) | −1 717(6) | 5 900(3) |
| C(6) | 7 152(5) | −1 327(6) | 5 012(3) |
| C(7) | 8 182(5) | −918(6) | 4 816(3) |
| C(8) | 8 639(5) | −2 208(6) | 6 061(3) |
| C(9) | 7 406(4) | 2 418(5) | 5 536(2) |
| C(10) | 7 929(4) | 3 415(6) | 5 156(3) |
| C(11) | 7 347(5) | 4 392(6) | 4 601(3) |
| C(12) | 6 246(5) | 4 406(6) | 4 415(3) |
| C(13) | 5 716(4) | 3 470(7) | 4 786(4) |
| C(14) | 6 296(4) | 2 469(5) | 5 347(3) |
| C(15) | 8 715(4) | 2 246(6) | 7 189(3) |
| C(16) | 7 905(4) | 3 232(5) | 7 421(2) |
| C(17) | 7 910(5) | 4 756(7) | 7 291(3) |
| C(18) | 7 210(6) | 5 674(7) | 7 521(4) |
| C(19) | 6 495(4) | 5 080(7) | 7 867(3) |
| C(20) | 6 486(5) | 3 572(8) | 8 018(4) |
| C(21) | 7 208(5) | 2 648(6) | 7 799(3) |
| N(22) | 5 737(5) | 6 052(7) | 8 114(3) |
| O(23) | 5 099(4) | 5 478(8) | 8 407(4) |
| O(24) | 5 803(5) | 7 422(7) | 8 029(4) |

It would be of considerable interest in (V) to replace the *endo*-phenyl substituent ($sp^2$-C to P) with an alkyl group to see if the amount of ring flattening increased. In an extreme case (large, $sp^3$-hydridized *endo*-substituent and small *exo*-substituent) the six-membered ring could be forced to assume a boat or twist-boat conformation. Contrarily, replacement of the C(6)–C(7) bridge by a –CH=CH– unit should lead to increased puckering of the chair due to relief of the non-bonded *endo*-C(6)–H(6) [or C(7)–H(7)] repulsion.[22]

TABLE 2

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

| Atom | $x$ | $y$ | $z$ | $B$(Å$^2$) |
|---|---|---|---|---|
| H(1)[C(1)] | 980(4) | −137(5) | 547(3) | 5.3(12) |
| H(2)[C(2)] | 969(4) | 123(5) | 577(3) | 5.1(11) |
| H(2′)[C(2)] | 991(4) | 24(6) | 659(3) | 5.1(11) |
| H(4)[C(4)] | 671(4) | −5(6) | 632(3) | 4.9(10) |
| H(4′)[C(4)] | 774(5) | −64(6) | 696(3) | 6.9(14) |
| H(5)[C(5)] | 703(3) | −240(5) | 602(3) | 4.3(10) |
| H(6)[C(6)] | 660(4) | −54(6) | 487(3) | 6.6(14) |
| H(6′)[C(6)] | 683(4) | −216(6) | 477(3) | 6.6(13) |
| H(7)[C(7)] | 811(5) | 20(8) | 458(4) | 7.0(15) |
| H(7′)[C(7)] | 831(4) | −158(6) | 444(3) | 6.2(12) |
| H(8)[C(8)] | 901(4) | −222(6) | 663(3) | 5.6(12) |
| H(8′)[C(8)] | 867(4) | −317(6) | 578(3) | 5.8(12) |
| H(10)[C(10)] | 863(3) | 338(4) | 529(2) | 3.7(8) |
| H(11)[C(11)] | 775(5) | 514(8) | 441(4) | 7.1(6) |
| H(12)[C(12)] | 587(4) | 493(7) | 404(3) | 7.2(14) |
| H(13)[C(13)] | 497(4) | 344(6) | 464(3) | 5.7(12) |
| H(14)[C(14)] | 593(4) | 177(6) | 560(3) | 6.1(12) |
| H(15)[C(15)] | 923(4) | 280(6) | 708(3) | 5.4(11) |
| H(15′)[C(15)] | 900(4) | 154(6) | 759(3) | 4.6(10) |
| H(17)[C(17)] | 844(4) | 508(7) | 707(3) | 6.1(12) |
| H(18)[C(18)] | 719(5) | 645(8) | 738(4) | 7.4(17) |
| H(20)[C(20)] | 603(5) | 323(8) | 826(3) | 7.6(15) |
| H(21)[C(21)] | 721(4) | 161(7) | 790(3) | 6.4(13) |

The phosphorinanium ring adopts a chair conformation which is considerably flattened. The dihedral angles between C(1)–C(2)–C(4)–C(5) and C(2)–P(3)–C(4) and C(1)–C(8)–C(5) are 29.3 and 68.1°, respectively. A least-squares plane calculation shows that C(1), C(2), C(4), and C(5) are coplanar (deviation −0.003, 0.003, −0.002, and 0.003 Å, respectively). P(3) and C(8) are 0.532 and −0.882 Å away from this plane, respectively. The dihedral angles between the plane C(1)–C(2)–C(4)–C(5) and the phenyl and nitrobenzyl ring planes are 78.8 and 36.4°, respectively. The dihedral angles between C(1)–C(5)–C(6)–C(7) and the phenyl and nitrobenzyl ring planes are 33.4 and 77.5°, respectively. The 'opened' P(3)–C(15)–C(15) bond angle 114.9° provides the basis for the two aromatic

### Table 3

Bong length and angles with e.s.d.s in parentheses

(a) Distances (Å)

| | | | |
|---|---|---|---|
| C(1)–C(2) | 1.531(7) | C(10)–C(11) | 1.367(7) |
| C(1)–C(7) | 1.541(8) | C(10)–H(10) | 0.87(4) |
| C(1)–C(8) | 1.534(8) | C(11)–C(12) | 1.366(9) |
| C(1)–H(1) | 1.04(5) | C(11)–H(11) | 0.96(7) |
| C(2)–P(3) | 1.806(6) | C(12)–C(13) | 1.364(8) |
| C(2)–H(2) | 1.05(5) | C(12)–H(12) | 0.85(6) |
| C(2)–H(2′) | 1.03(5) | C(13)–C(14) | 1.385(8) |
| P(3)–C(4) | 1.809(5) | C(13)–H(13) | 0.92(6) |
| P(3)–C(9) | 1.795(4) | C(14)–H(14) | 0.96(5) |
| P(3)–C(15) | 1.812(5) | C(15)–C(16) | 1.507(7) |
| C(4)–C(5) | 1.538(7) | C(15)–H(15) | 0.90(5) |
| C(4)–H(4) | 0.90(5) | C(15)–H(15′) | 0.93(5) |
| C(4)–H(4′) | 0.94(6) | C(16)–C(17) | 1.385(8) |
| C(5)–C(6) | 1.539(7) | C(16)–C(21) | 1.370(8) |
| C(5)–C(8) | 1.507(9) | C(17)–C(18) | 1.369(9) |
| C(5)–H(5) | 0.91(5) | C(17)–H(17) | 0.93(6) |
| C(6)–C(7) | 1.515(9) | C(18)–C(19) | 1.354(9) |
| C(6)–H(6) | 0.98(6) | C(18)–H(18) | 0.84(7) |
| C(6)–H(6′) | 0.90(6) | C(19)–C(20) | 1.379(9) |
| C(7)–H(7) | 1.09(7) | C(19)–N(22) | 1.469(9) |
| C(7)–H(7′) | 0.94(5) | C(20)–C(21) | 1.384(9) |
| C(8)–H(8) | 0.99(5) | C(20)–H(20) | 0.88(6) |
| C(8)–H(8′) | 1.00(5) | C(21)–H(21) | 0.94(6) |
| C(9)–C(10) | 1.402(7) | N(22)–O(23) | 1.208(9) |
| C(9)–C(14) | 1.378(7) | N(22)–O(24) | 1.247(9) |

(b) Angles (°)

| | | | |
|---|---|---|---|
| C(2)–C(1)–C(7) | 112.9(5) | H(8)–C(8)–H(8′) | 115(4) |
| C(2)–C(1)–C(8) | 111.1(5) | P(3)–C(9)–C(10) | 120.0(3) |
| C(2)–C(1)–H(1) | 106(3) | P(3)–C(9)–C(14) | 121.4(4) |
| C(7)–C(1)–C(8) | 102.5(4) | C(10)–C(9)–C(14) | 118.4(4) |
| C(7)–C(1)–H(1) | 109(3) | C(9)–C(10)–C(11) | 120.6(5) |
| C(8)–C(1)–H(1) | 115(3) | C(9)–C(10)–H(10) | 117(3) |
| C(1)–C(2)–P(3) | 112.9(4) | C(11)–C(10)–H(10) | 122(3) |
| C(1)–C(2)–H(2) | 114(3) | C(10)–C(11)–C(12) | 119.9(5) |
| C(1)–C(2)–H(2′) | 109(3) | C(10)–C(11)–H(11) | 117(4) |
| P(3)–C(2)–H(2) | 110(3) | C(12)–C(11)–H(11) | 123(4) |
| P(3)–C(2)–H(2′) | 106(3) | C(11)–C(12)–C(13) | 120.8(5) |
| H(2)–C(2)–H(2′) | 105(4) | C(11)–C(12)–H(12) | 122(4) |
| C(2)–P(3)–C(4) | 106.0(2) | C(13)–C(12)–H(12) | 117(4) |
| C(2)–P(3)–C(9) | 112.8(2) | C(12)–C(13)–C(14) | 119.8(5) |
| C(2)–P(3)–C(15) | 106.0(2) | C(12)–C(13)–H(13) | 121(3) |
| C(4)–P(3)–C(9) | 111.0(2) | C(14)–C(13)–H(13) | 119(3) |
| C(4)–P(3)–C(15) | 112.2(2) | C(9)–C(14)–C(13) | 120.4(5) |
| C(9)–P(3)–C(15) | 108.9(2) | C(9)–C(14)–H(14) | 119(3) |
| P(3)–C(4)–C(5) | 112.2(3) | C(13)–C(14)–H(14) | 121(3) |
| P(3)–C(4)–H(4) | 106(3) | P(3)–C(15)–C(16) | 114.9(3) |
| P(3)–C(4)–H(4′) | 101(4) | P(3)–C(15)–H(15) | 101(3) |
| C(5)–C(4)–H(4) | 112(3) | P(3)–C(15)–H(15′) | 105(3) |
| C(5)–C(4)–H(4′) | 108(4) | C(16)–C(15)–H(15) | 111(3) |
| H(4)–C(4)–H(4′) | 117(5) | C(16)–C(15)–H(15′) | 112(3) |
| C(4)–C(5)–C(6) | 113.1(4) | H(15)–C(15)–H(15′) | 113(4) |
| C(4)–C(5)–C(8) | 111.2(4) | C(15)–C(16)–C(17) | 119.9(5) |
| C(4)–C(5)–H(5) | 103(3) | C(15)–C(16)–C(21) | 120.4(5) |
| C(6)–C(5)–C(8) | 103.0(4) | C(17)–C(16)–C(21) | 119.5(5) |
| C(6)–C(5)–H(5) | 112(3) | C(16)–C(17)–C(18) | 120.6(6) |
| C(8)–C(5)–H(5) | 115(3) | C(16)–C(17)–H(17) | 115(3) |
| C(5)–C(6)–C(7) | 106.5(5) | C(18)–C(17)–H(17) | 125(4) |
| C(5)–C(6)–H(6) | 113(3) | C(17)–C(18)–C(19) | 119.5(6) |
| C(5)–C(6)–H(6′) | 105(4) | C(17)–C(18)–H(18) | 116(6) |
| C(7)–C(6)–H(6) | 113(3) | C(19)–C(18)–H(18) | 124(6) |
| C(7)–C(6)–H(6′) | 114(4) | C(18)–H(19)–C(20) | 121.2(6) |
| H(6)–C(6)–H(6) | 106(5) | C(18)–C(19)–N(22) | 120.1(6) |
| C(1)–C(7)–C(6) | 105.9(5) | C(20)–C(19)–N(22) | 118.7(5) |
| C(1)–C(7)–H(7) | 112(3) | C(19)–C(20)–C(21) | 119.3(6) |
| C(1)–C(7)–H(7′) | 110(3) | C(19)–C(20)–H(20) | 119(4) |
| C(6)–C(7)–H(7) | 110(3) | C(21)–C(20)–H(20) | 122(4) |
| C(6)–C(7)–H(7′) | 110(3) | C(16)–C(21)–C(20) | 119.9(5) |
| H(7)–C(7)–H(7′) | 109.(5) | C(16)–C(21)–H(21) | 120(4) |
| C(1)–C(8)–C(5) | 102.5(5) | C(20)–C(21)–H(21) | 120(4) |
| C(1)–C(8)–H(8) | 114(3) | C(19)–N(22)–O(23) | 118.1(6) |
| C(1)–C(8)–H(8′) | 104(3) | C(19)–N(22)–O(24) | 116.9(6) |
| C(5)–C(8)–H(8) | 111(3) | O(23)–N(22)–O(24) | 125.0(7) |
| C(5)–C(8)–H(8′) | 109(3) | | |

### Table 4

Torsion angles (°) with e.s.d.s in parentheses

| | |
|---|---|
| C(1)–C(2)–P(3)–C(4) | 31.2(2) |
| C(2)–P(3)–C(4)–C(5) | −31.5(3) |
| P(3)–C(4)–C(5)–C(8) | 58.0(3) |
| C(8)–C(1)–C(2)–P(3) | −56.0(3) |
| C(4)–C(5)–C(8)–C(1) | −79.2(4) |
| C(5)–C(8)–C(1)–C(2) | 78.2(5) |
| P(3)–C(4)–C(5)–C(6) | −57.4(3) |
| C(7)–C(1)–C(2)–P(3) | 58.5(3) |
| C(4)–C(5)–C(6)–C(7) | 94.5(4) |
| C(6)–C(7)–C(1)–C(2) | −93.3(5) |
| C(6)–C(7)–C(1)–C(8) | 26.5(5) |
| C(8)–C(5)–C(6)–C(7) | −25.6(4) |
| C(7)–C(1)–C(8)–C(5) | −42.6(4) |
| C(1)–C(8)–C(7)–C(6) | 42.2(9) |
| C(5)–C(6)–C(7)–C(1) | −0.8(5) |

### Table 5

Intermolecular contacts <3.6 Å involving non-hydrogen atoms

| Atoms * | | Atoms * | |
|---|---|---|---|
| C(4) ··· O(23$^{I}$) | 3.398(8) | C(7) ··· C(19$^{II}$) | 3.578(8) |
| C(6) ··· N(22$^{II}$) | 3.328(8) | C(13) ··· C(13$^{III}$) | 3.512(8) |
| C(6) . . . O(23$^{II}$) | 3.362(8) | C(20) . . . O(24$^{II}$) | 3.202(9) |
| C(6) ··· O(24$^{II}$) | 3.558(8) | | |

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

I, $1 - x, \frac{1}{2} + y, 1.5 - z$
III, $x, \frac{1}{2} - y, \frac{1}{2} + z$
III, $1 - x, 1 - y, 1 - z$

rings to be relatively non-parallel. The C(16)–C(15)–P(3)–C(9) torsion angle is 47.1°.

The P(3)–C(2) and P(3)–C(4) distances of 1.806(6) and 1.809(5) Å are almost identical but are significantly shorter than a normal P–C bond of 1.872 Å.[23] These distances compare well with 1.795(2) and 1.791(2) Å reported in *trans*-4-t-butyl-1-phenylphosphorinan 1-oxide[24] and with 1.82(1) and 1.81(1) Å found in *cis*-1-iodomethyl-3-methyl-1-phenylphospholanium iodide.[25] The P(3)–C(9) bond length of 1.795 Å agrees well with the average P–C(Ph) bond lengths found in other compounds containing tetravalent phosphorus.[26-29] The P(3)–C(15) bond length of 1.812(5) Å is in good agreement with values reported for this type of compound.[30]

The seven ($sp^3$–$sp^3$) bonds have a mean of 1.529(8) Å, which is appreciably lower than the value [1.541(3)] Å quoted in ref. 31. However, this value seems to be based on a large number of studies, not all of them of good accuracy. Our values compare well with that of 3-silabicyclo[3.2.1]octane.[6] The mean of nine valence angles at tetrahedral atoms is 108.9(5)°, which is closer to the ideal value of 109.5° than is usual in cyclopentane and cyclohexane systems, presumably in this case because of the stiffening constraints exerted by one ring on the other.

The mean C–C lengths in the phenyl and nitrobenzyl rings are 1.377(8) and 1.374(9) Å respectively, which are significantly shorter than the standard value of 1.395 Å[31] but these values agree well with 1.379 Å reported for *trans*-4-t-butyl-1-phenylphosphorinan 1-oxide[24] and

TABLE 6

Comparison of bond and torsional angles of (V) with 3-silabicyclo[3.2.1]octane

| Angle (°) | | Angle (°) | | Difference (°) |
|---|---|---|---|---|
| C(1)–C(2)–P(3) | 112.9 (112.2) * | C(1)–C(2)–Si | 112.4 | 0.15 |
| C(2)–P(3)–C(4) | 106.0 | C(2)–Si–C(4) | 105.6 | 0.5 |
| C(2)–C(1)–C(8) | 111.1 (111.2) | C(2)–C(1)–C(8) | 111.0 | 0.15 |
| C(2)–C(1)–C(7) | 112.9 (113.1) | C(2)–C(1)–C(7) | 112.3 | 0.7 |
| C(7)–C(1)–C(8) | 102.5 (103.0) | C(7)–C(1)–C(8) | 103.2 | 0.45 |
| C(1)–C(8)–C(5) | 102.5 | C(1)–C(8)–C(5) | 103.8 | 1.3 |
| C(1)–C(7)–C(6) | 105.9 (106.5) | C(1)–C(7)–C(6) | 106.4 | 0.2 |
| C(1)–C(8)–C(5)–C(6) | 42.2 (−42.6) | C(1)–C(8)–C(5)–C(6) | 39.7 | 2.7 |
| C(8)–C(5)–C(6)–C(7) | −25.6 (26.5 | C(8)–C(5)–C(6)–C(7) | 24.2 | 1.85 |
| P(3)–C(4)–C(5)–C(6) | −57.4 (58.5) | Si–C(4)–C(5)–C(6) | 59.5 | 1.55 |
| C(1)–C(7)–C(6)–C(5) | 0.8 | C(1)–C(7)–C(6)–C(5) | 0.1 | 0.7 |
| C(1)–C(2)–P(3)–C(4) | 31.2 (−31.5) | C(1)–C(2)–Si–C(4) | 32.0 | 0.65 |
| C(2)–C(1)–C(8)–C(5) | 78.2 (−79.2) | C(2)–C(1)–C(8)–C(5) | 78.7 | 0.5 |

* The value in parentheses represents the angular counter-part due to symmetry.

1.37(1) Å reported for *cis*-1-iodomethyl-3-methyl-1-phenylphospholanium iodide.[25] The internal angles of these rings average 120.0(5)°.

TABLE 7

Hydrogen intramolecular contacts $<2.40$ Å

| | | | |
|---|---|---|---|
| H(1) · · · H(7′) | 2.26(7) | H(6) · · · H(7) | 2.26(9) |
| H(1) · · · H(8′) | 2.34(8) | H(6′) · · · H(7′) | 2.21(8) |
| H(2) · · · H(10) | 2.37(6) | H(10) · · · H(11) | 2.27(8) |
| H(4) · · · H(5) | 2.24(7) | H(11) · · · H(12) | 2.34(9) |
| H(4) · · · H(14) | 2.14(7) | H(12) · · · H(13) | 2.23(8) |
| H(4′) · · · H(5) | 2.28(7) | H(13) · · · H(14) | 2.33(7) |
| H(4′) · · · H(8) | 2.36(8) | H(15) · · · H(17) | 2.28(8) |
| H(5) · · · H(6′) | 2.15(7) | H(17) · · · H(18) | 2.23(9) |
| H(5) · · · H(8′) | 2.37(7) | H(20) · · · H(21) | 2.32(9) |

The packing of these molecules is depicted in the ORTEP stereodiagram (Figure 2). There are seven-intermolecular contacts $<3.6$ Å. None of them is especially short and are normal van der Waals contacts.

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