rings of CE1S, PGE$_1$ (Spek, 1977), PGE$_2$ (DeTitta *et al.*, 1980), and PGF$_{2\beta}$ (DeTitta *et al.*, 1980) adopt C(12) envelope conformations. The cyclopentyl ring of PGF$_{2I}$ (Chidester & Duchamp, 1974) adopts a C(9) envelope conformation. The two independent conformers of PGF$_{2\alpha}$ (Langs *et al.*, 1977) adopt envelope conformations, one a C(8) envelope and the other a C(9) envelope. The cyclopentyl ring of PGF$_{1\beta}$ (Abrahamsson, 1963) adopts a half-chair conformation. The cyclopentenyl rings of PGB$_1$ (DeTitta *et al.*, 1979) and of PGA$_1$ in both the monoclinic (DeTitta *et al.*, 1979) and orthorhombic (Edmonds & Duax, 1975) forms adopt relatively flat conformations.

In summary, the structural features of CE1S show both similarities and differences to those of previously reported prostaglandin structures. The relevance of solid-state, three-dimensional structural features to the solution properties of conformationally labile molecules, such as the prostaglandins, has been excessively discounted in the past. However, studies by Anderson and coworkers (Leovey & Anderson, 1975) suggest that the general structural features of PGF$_{2\alpha}$ in the crystalline state are maintained in solution. Circular dichroism spectra of aqueous PGF$_{2\alpha}$ are consistent with the 'hairpin' conformation for the chromophore defined by the C(5) through C(16) portion of the molecule. Lanthanide-induced shift NMR data are inconsistent with either an 'L-shape' or an extended conformation for the molecule. Also, the conformational specificities of the PGF$_{2\alpha}$ and PGE$_2$ receptors have been recently discussed in terms of the 'hairpin' alignment of the molecules (Anderson *et al.*, 1981). These data suggest that the structural features revealed by single-crystal diffraction are maintained by prostaglandin molecules in solution and are thus relevant to the solution properties. Until evidence to the contrary arises, we must likewise assume the conformation of CE1S determined by this study is descriptive of its favored conformation in solution.

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Structure of *endo*-3-Phenyl-3λ^5-phosphabicyclo[3.2.1]oct-6-ene 3-Oxide, $C_{13}H_{15}OP$

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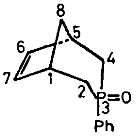
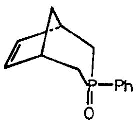
(*Received* 7 *September* 1982; *accepted* 16 *November* 1982)

Abstract. $M_r = 218{\cdot}2$, orthorhombic, space group *Pbca*, $a = 9{\cdot}122\,(4)$, $b = 12{\cdot}960\,(3)$, $c = 19{\cdot}446\,(2)$ Å, $U = 2298{\cdot}9$ Å^3, $Z = 8$, $D_x = 1{\cdot}261$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}202$ mm^{-1}, $F(000) = 928$. Final $R = 0{\cdot}035$ for 880 observed reflections. The phosphorinane ring adopts a chair conformation which is flattened at the phosphorus end. The ring conformation, bond lengths and valence and torsion angles are compared with those in the *exo*-3-phenyl isomer.

Introduction. In a previous study, the synthesis of both the title compound (I) and its *exo*-3-phenyl isomer (II) were described (Haque, Horne, Cremer & Most, 1981). The isomer assignments were made on the basis of NMR studies and confirmed by a crystal-structure analysis of the *exo*-3-phenyl compound. The purpose of



(I)



(II)

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the present study was to perform a crystal-structure analysis of the *endo*-3-phenyl compound, obtain torsion angles, establish the total geometry of the molecule, especially the degree of puckering in the six-membered ring, and to make a comparison with the *exo*-isomer.

Experimental. Crystal *ca* 0·38 × 0·45 × 0·90 mm enclosed in a Lindemann-glass capillary due to hygroscopic nature of the compound, Enraf–Nonius CAD-4 diffractometer, take-off angle 5°, Mo $K\alpha$ radiation filtered by a square-graphite-crystal monochromator, cell dimensions and their standard deviations derived by least-squares analysis of 25 accurately centered reflections; intensities of 2376 reflections (to $\theta < 25°$) measured by ω–2θ scans and background counts taken on each side of the peak, intensities of three standard reflections measured every 9000 s showed no significant change during data collection, crystal orientation monitored every 50 reflections, 880 reflections considered observed with $I > 3{\cdot}0\,\sigma(I)$, Lorentz and polarization corrections applied; form factors for non-H atoms from Cromer & Mann (1968) and for H atoms from Stewart, Davidson & Simpson (1965), anomalous terms for phosphorus included; all calculations carried out on the University of Petroleum and Minerals IBM 3033 computer, structure solved by direct methods with *SHELX* 76 (Sheldrick, 1976); isotropic full-matrix least-squares refinement and one cycle of anisotropic refinement reduced R to 0·079 and a difference map at this stage revealed all H atoms; further refinement of non-H atoms anisotropically and H atoms isotropically reduced R to a final value of 0·035, weighting scheme based on counting statistics used, $w = 1{\cdot}41(\sigma^2|F_o| + 0{\cdot}000323F_o^2)^{-1}$, $\sum w\Delta^2$ minimized, $R_w = 0{\cdot}034$; a final difference map showed no significant features.

Discussion. Fig. 1 is an *ORTEP* drawing (Johnson, 1976) showing the molecule in perspective and Fig. 2 shows the packing arrangement in the crystal. Atomic positions are listed in Table 1,* and the bond lengths and angles involving non-H atoms are listed in Table 2. All intermolecular contacts are of the normal van der Waals type.

In the following discussion, the salient features of the *endo*-phenyl isomer (I) characterized in the present report will be compared with those of the *exo*-phenyl isomer (II) which formed the subject of a previous study (Haque *et al.*, 1981). In both isomers, the six-membered ring exists in a chair conformation, considerably flattened at the phosphorus end and with

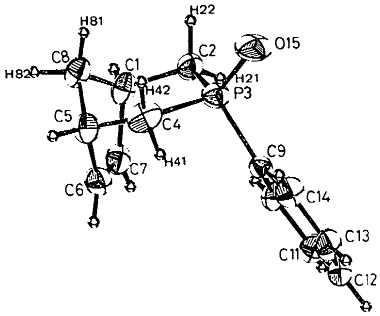

Fig. 1. Thermal ellipsoids at 30% probability and the atomic notation for *endo*-3-phenyl-3λ^5-phosphabicyclo[3.2.1]oct-6-ene 3-oxide.

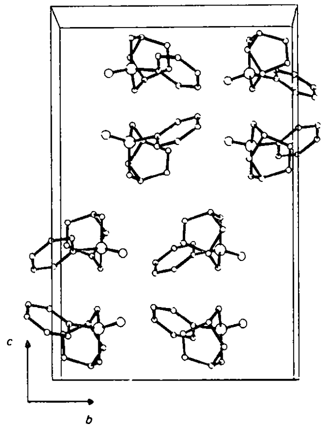

Fig. 2. The molecular packing arrangement.

Table 1. *Fractional coordinates* (×10⁴, ×10³ *for* H) *and isotropic temperature factors* (×10³)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}/U_{\rm iso}$(Å^2)
C(1)	970 (5)	1354 (3)	3468 (2)	59
C(2)	2339 (5)	1760 (4)	3093 (2)	58
P(3)	3964 (1)	1854 (1)	3626 (1)	56
C(4)	3314 (6)	1869 (3)	4511 (3)	71
C(5)	1756 (5)	1457 (3)	4617 (2)	65
C(6)	1664 (5)	359 (4)	4387 (3)	67
C(7)	1220 (4)	296 (4)	3756 (3)	62
C(8)	704 (4)	1968 (4)	4113 (2)	66
C(9)	5047 (4)	697 (3)	3517 (2)	46
C(10)	4688 (5)	−127 (3)	3105 (2)	56
C(11)	5639 (5)	−944 (4)	3009 (3)	67
C(12)	6977 (6)	−946 (4)	3339 (3)	71
C(13)	7350 (5)	−134 (5)	3747 (2)	71
C(14)	6420 (5)	692 (4)	3836 (2)	65
O(15)	4863 (3)	2776 (2)	3466 (2)	93
H(11)	20 (4)	139 (2)	318 (2)	48 (11)
H(21)	253 (4)	136 (3)	269 (2)	55 (11)
H(22)	217 (3)	249 (3)	296 (2)	55 (11)
H(41)	413 (5)	150 (3)	475 (2)	84 (15)
H(42)	341 (4)	256 (3)	460 (2)	77 (14)
H(51)	152 (4)	154 (2)	508 (2)	53 (11)
H(61)	195 (4)	−17 (3)	466 (2)	71 (14)
H(71)	118 (4)	−33 (3)	354 (2)	56 (11)
H(81)	89 (4)	270 (3)	409 (2)	52 (11)
H(82)	−28 (4)	190 (3)	429 (2)	79 (13)
H(101)	379 (4)	−13 (3)	289 (2)	55 (12)
H(111)	535 (4)	−152 (3)	269 (2)	85 (15)
H(121)	756 (5)	−152 (3)	325 (2)	103 (18)
H(131)	829 (5)	−9 (3)	400 (2)	86 (15)
H(141)	664 (4)	121 (3)	414 (2)	67 (14)

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* Lists of structure factors, anisotropic thermal parameters, torsion angles, and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38241 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *involving non-*H *atoms with e.s.d.'s in parentheses*

C(1)–C(2)	1·538 (5)	C(5)–C(8)	1·523 (6)
C(1)–C(7)	1·499 (6)	C(6)–C(7)	1·295 (6)
C(1)–C(8)	1·506 (6)	C(9)–C(10)	1·374 (5)
C(2)–P(3)	1·812 (4)	C(9)–C(14)	1·398 (5)
P(3)–C(4)	1·822 (5)	C(10)–C(11)	1·381 (5)
P(3)–C(9)	1·808 (4)	C(11)–C(12)	1·379 (6)
P(3)–O(15)	1·482 (3)	C(12)–C(13)	1·361 (6)
C(4)–C(5)	1·532 (6)	C(13)–C(14)	1·377 (6)
C(5)–C(6)	1·494 (6)		
C(7)–C(1)–C(2)	111·5 (3)	C(6)–C(5)–C(8)	100·7 (4)
C(2)–C(1)–C(8)	110·2 (4)	C(5)–C(6)–C(7)	111·2 (5)
C(7)–C(1)–C(8)	101·3 (4)	C(1)–C(7)–C(6)	110·2 (5)
C(1)–C(2)–P(3)	114·6 (3)	C(1)–C(8)–C(5)	101·8 (4)
C(2)–P(3)–C(4)	105·9 (2)	P(3)–C(9)–C(10)	125·6 (3)
C(2)–P(3)–C(9)	108·9 (2)	P(3)–C(9)–C(14)	116·2 (3)
C(4)–P(3)–C(9)	107·3 (2)	C(10)–C(9)–C(14)	118·0 (4)
C(2)–P(3)–O(15)	112·8 (2)	C(9)–C(10)–C(11)	121·6 (4)
C(4)–P(3)–O(15)	111·7 (2)	C(10)–C(11)–C(12)	119·7 (5)
C(9)–P(3)–O(15)	110·0 (2)	C(11)–C(12)–C(13)	119·4 (5)
P(3)–C(4)–C(5)	115·2 (3)	C(12)–C(13)–C(14)	121·4 (5)
C(4)–C(5)–C(6)	110·1 (4)	C(9)–C(14)–C(13)	119·9 (5)
C(4)–C(5)–C(8)	110·2 (4)		

C(1), C(5), C(4), and C(2) effectively coplanar. In the *exo*-phenyl isomer the projection of the plane of the phenyl ring essentially bisects the C(2)—P(3)—C(4) bond angle, whereas the considerable steric crowding in the *endo*-isomer causes the phenyl group to assume an orientation which results in the projection of its plane falling roughly parallel with the P(3)—C(2) bond vector. As a consequence of this, non-bonded intramolecular interaction occurs between the *endo*-hydrogen bonded to C(2) and the *ortho*-hydrogen bonded to C(10), these H atoms being only 2·28 (5) Å apart.

Whilst the bond lengths and bond angles in the *exo* and *endo*-isomers show a close similarity, there are some interesting and significant differences in the torsion and flap angles.* Thus, the magnitude of the angle between the planes C(2)—P(3)—C(4) and C(1)—C(2)—C(4)—C(5) decreases from 31° in the *exo*-isomer to 17·9 (4)° in the *endo*-isomer, presumably due to the distorting forces induced by the intramolecular interaction between H(101) and H(21) mentioned in the previous paragraph. To our knowledge no other phosphorinane ring structure so far studied has exhibited such a degree of flattening at the phosphorus end. In addition, the [3.2.1] ring system which in the *exo*-isomer approximates closely to a mirror plane, shows less evidence of such symmetry in the *endo*-isomer, due also to this intramolecular interaction.

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* See previous footnote.

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N,N'-Diphenylhexanediamide (DPHD),* $C_{18}H_{20}N_2O_2$

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Abstract. $M_r = 296{\cdot}4$, orthorhombic, *Pbca*, $a = 15{\cdot}228\ (4)$, $b = 11{\cdot}265\ (3)$, $c = 9{\cdot}489\ (3)$ Å, $V = 1627{\cdot}8$ Å^3, $Z = 4$, $D_x = 1{\cdot}21$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}60$ mm^{-1}, $F(000) = 632$. Final $R = 4{\cdot}2\%$ for 686 observed reflexions. Molecules are connected by hydrogen bonds to four other molecules. The hydrogen-bonding scheme found is compared with that of related diamides. Two different types of hydrogen bonding are found. From the available data it is concluded that torsion angles can be influenced by hydrogen bonding.

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* The Structure of Model Compounds of Aromatic and Aromatic–Aliphatic Polyamides. IV. Part III: Harkema, van Hummel & Gaymans (1980).

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