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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### THE NMR SPECTROSCOPY AND X-RAY CRYSTAL STRUCTURE DETERMINATION OF TWO ISOMERIC FORMS OF THE DIOXODIPHOSPHORUS MACROCYCLE 5,13-DIPHENYL-1,9-DIOXA-5,13-DIPHOSPHACYCLOHEXADECANE-5,13-DIOXIDE

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# THE NMR SPECTROSCOPY AND X-RAY CRYSTAL STRUCTURE DETERMINATION OF TWO ISOMERIC FORMS OF THE DIOXODIPHOSPHORUS MACROCYCLE 5,13-DIPHENYL-1,9-DIOXA-5,13-DIPHOSPHACYCLOHEXADECANE-5,13-DIOXIDE

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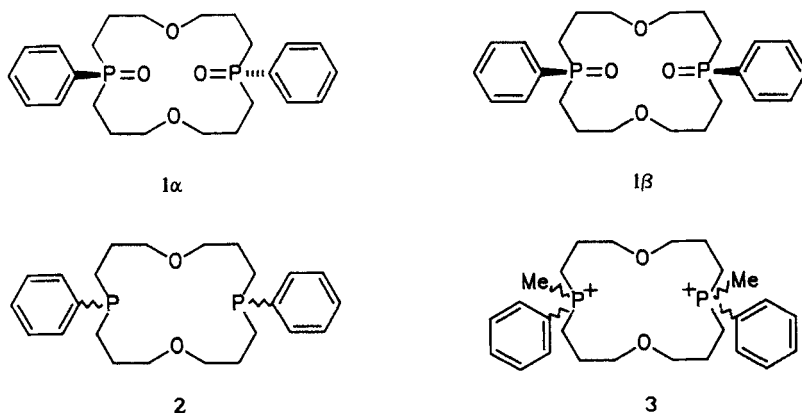
*(Received January 18, 1994)*

Single crystal X-ray structure analysis confirms the existence of two geometrical isomers of 5,13-diphenyl-1,9-dioxa-5,13-diphosphacyclohexadecane. In the solid state, the *trans* isomer has exact  $C_2$  symmetry while the *cis* isomer shows virtual  $C_2$  symmetry. Pairs of oxygen donor atoms are directed to opposite sides of the macrocycle in each ligand; in the *cis*-isomer, the phosphine oxide oxygens lie on the same side of the macrocycle, opposite to the ring ether oxygens while in the *trans*-isomer one phosphine oxide and one ether oxygen lie opposite to their symmetry-related counterparts. In solution, each isomer is identifiable by  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR but analysis of mixtures in the latter case is complicated by concentration-dependent chemical shifts.

**Key words:** Phosphine oxide; macrocycle; *cis*-, *trans*-isomerism; X-ray structure.

## INTRODUCTION

Polyheteroatomic macrocycles have been studied for many years and current widespread interest in these systems stems from their potential as ligands in, for example, catalytic processes<sup>1</sup> and metal extraction.<sup>2,3</sup> We earlier reported a recurrent method for controlled synthesis of macrocyclic polyheteroatomic diphosphine ligands which allowed stepwise introduction of different bridges between the phosphorus atoms,<sup>4</sup> facilitating the design of 'tailor-made' ligands with predetermined numbers and types of donor atoms and ring sizes. Selective cleavage of the phosphorus-carbon bonds in bisphosphonium salts was obtained by alkaline hydrolysis and ring closure was achieved in high dilution conditions. The intermediate phosphine oxides obtained at this stage occurred in approximately equal proportions of *cis*- and *trans*-stereoisomers, the distance between the two phosphorus atoms overcoming any steric influence directing the reaction towards one or other isomer. However for the dioxo compound (**1**) it was demonstrated that the pure isomers, (**1 $\alpha$** ) and (**1 $\beta$** ), can be separated by silica column chromatography,<sup>4</sup> allowing isolation of stereo-



chemically pure products in the subsequent generation of the dioxophosphine (**2**) and the dioxophosphonium (**3**) macrocycles of the crown-ether type. At the time of the original work it was not possible to assign *cis*- and *trans*-isomers due to the very small differences in the NMR and IR spectra observed for the two forms (**1α**) and (**1β**). For the interpretation of the results in our current studies of the selectivity of these and related ligands for 'hard' cations it is important to identify the individual isomers.

## RESULTS AND DISCUSSION

X-ray single crystal analysis of both isomers has now established that the original **1α** is the *trans*-isomer illustrated in Figure 1a, and correspondingly, **1β** is the *cis*-isomer shown in Figure 2a. Despite many attempts, only fine 'hair-like' crystals of the *cis*-isomer **1β** could be isolated which gave very poor diffraction resulting in relatively high estimated standard deviations on all parameters. Therefore detailed discussion of the bond lengths in this isomer is of little value. Nevertheless the overall features of both molecules are well established and the identity of the isomers has been demonstrated unambiguously. The *trans*-isomer (**1α**) has exact crystallographic  $C_i$  symmetry with the two equivalent phosphorus-bonded oxygen atoms O(2a) and O(2a') on opposite sides of the molecule, and the ring atom O(1a) is directed to the same side as O(2a) and correspondingly O(1a') lies on the other side. In contrast, the *cis*-isomer (**1β**) has virtual  $C_2$  symmetry (Figure 2a); again the oxygen atoms are directed in pairs—the phosphorus-bonded atoms O(2a) and O(2b) are both the same side of the molecule with the ring atoms O(1a) and O(1b) both on the other side. Thus, while the ring O-donors are in an endodentate orientation in both isomers, the disposition of pairs of oxygen donors to opposing sides of the macrocycle indicates that the ligand is not fully preorganised for binding a single metal ion in its cavity. Presumably dipole-dipole repulsions between lone pairs of the oxygen donor atoms and the steric demands of the alkyl bridges preclude such dispositions of the donor atoms in the uncomplexed ligand. However, the flexibility of the alkyl framework of the macrocycle is expected to allow significant

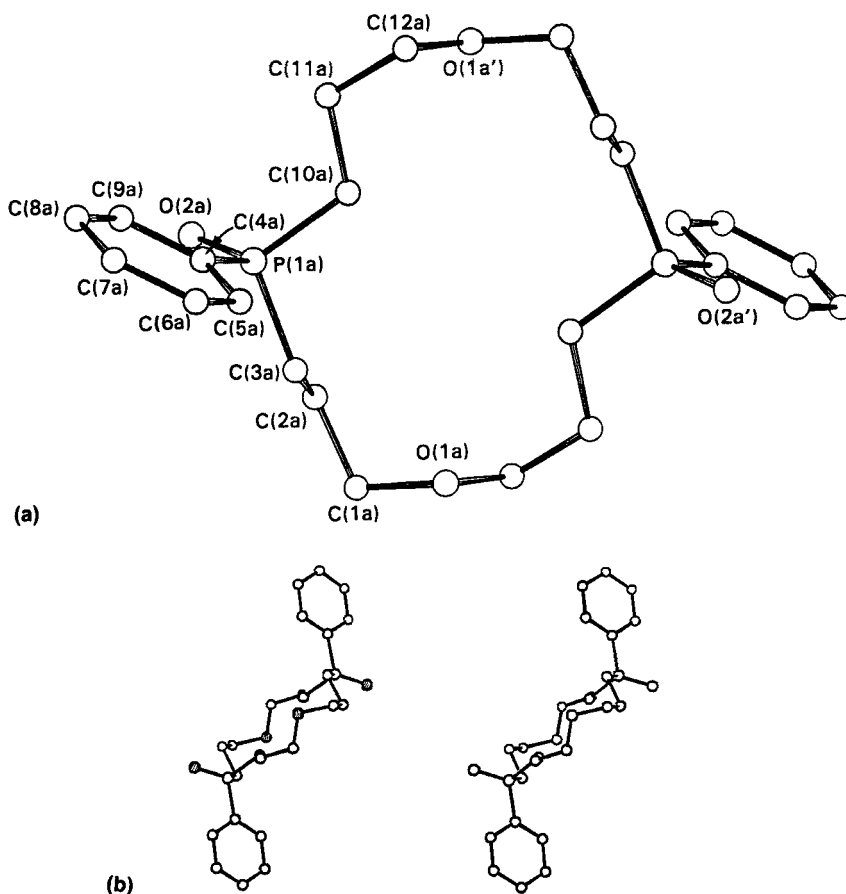


FIGURE 1 (a) The structure of centrosymmetric *trans*-5,13-diphenyl-1,9-dioxo-5,13-diphosphacyclohexadecane (**1a**) showing the atomic numbering scheme; (b) a 'sideways-on' stereoview showing the disposition of the O-donors (shaded) of the macrocycle.

freedom for the macrocyclic conformation which may result in distinctly different arrangements of donor atoms in the complexed and uncomplexed ligands.

Although the difference in the carbon-13 and phosphorus-31 NMR spectra of the two isomers is small it proved possible to distinguish discrete signals from each isomer in spectra of mixtures containing different proportions of the *cis*- and *trans*-isomers. In particular, as might be expected from  $^{31}\text{P}$  nuclei in such similar environments, direct integration of peak areas in the  $^{31}\text{P}$  spectrum of a mixture of isomers gives, in principle, a quantitative assay of the *cis:trans* proportions (Table I).

However, the  $^{31}\text{P}$  chemical shifts of both isomers show some concentration dependence and, as separations of signals due to the respective isomers are small, the relative positions of signals due to *cis* and *trans* isomers 'cross-over' and assignments on the basis of shift are inappropriate. Interestingly, isomerically pure samples of each macrocycle can be reliably identified by melting point.

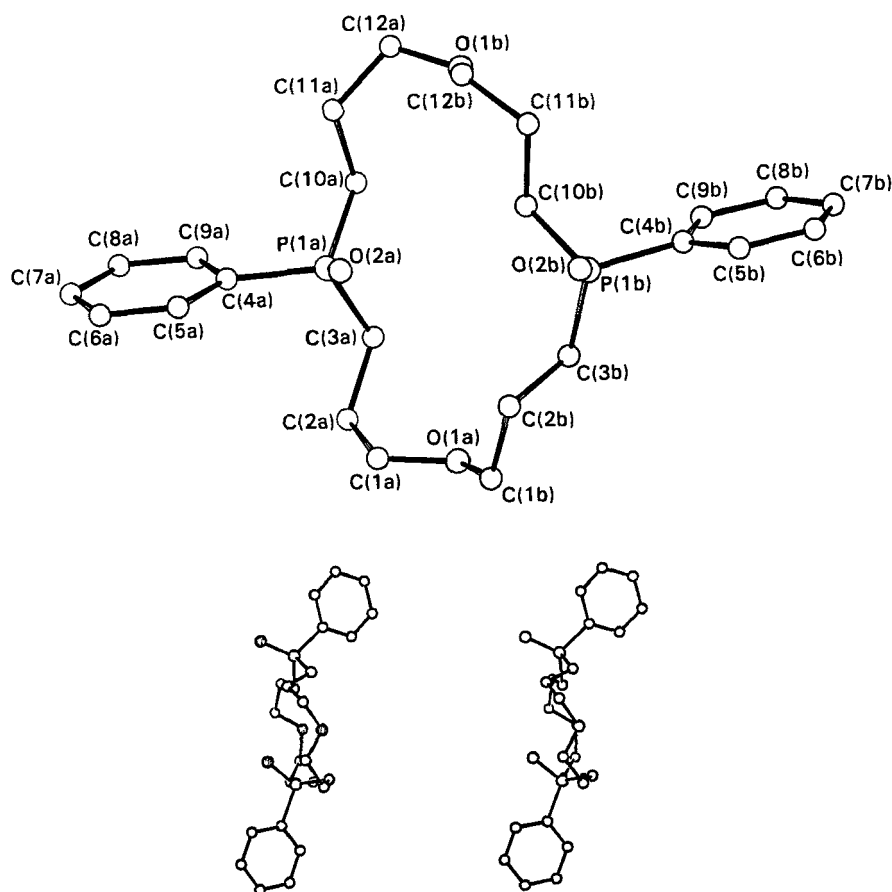


FIGURE 2 (a) The structure of *cis*-5,13-diphenyl-1,9-dioxo-5,13-diphosphacyclohexadecane (**1β**) showing the atomic numbering scheme; (b) a 'sideways-on' stereoview showing the disposition of the O-donors (shaded) of the macrocycle.

TABLE I  
Phosphorus-31 nmr analysis of mixtures of *cis*- and *trans*-5,13-diphenyl-1,9-dioxo-5,13-diphosphacyclohexadecane (**1α** and **1β**)

	Pure sample		$\delta(^{31}\text{P})$ of mixture <sup>a</sup>	
	$\delta(^{31}\text{P})$	m. p.	(cis:trans)	
	ppm	°C	3:1	1:3
<i>Trans</i> ( <b>1α</b> )	41.7	170-171	41.4(15)	41.5(78)
<i>Cis</i> ( <b>1β</b> )	41.1	175-176	41.7(85)	42.0(22)

<sup>a</sup> Total concentration 80 mmol dm<sup>-3</sup> in CDCl<sub>3</sub>; chemical shift in ppm referenced to external *aqu.* H<sub>3</sub>PO<sub>4</sub>; relative peak heights are given in parentheses.

## EXPERIMENTAL

Melting points were determined using a Wild Leitz 350 apparatus. Infrared spectra were recorded on a Perkin Elmer 377 spectrophotometer from KBr pellets unless otherwise stated. Proton NMR were recorded on either Bruker AC200 or AC250 spectrometers;  $^1\text{H}$ -decoupled carbon-13 and phosphorus-31 spectra were obtained using a Bruker AC200. Chemical shifts are reported in ppm with respect to internal  $\text{SiMe}_4$  ( $^1\text{H}$  and  $^{13}\text{C}$ ) and external 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ). Microanalyses were carried out by the Service Central de Microanalyse, CNRS, Montpellier and mass spectra were recorded on a Jeol JMS-DX 300 spectrometer at the University of Montpellier.

**Preparation of cis- and trans-5,13-diphenyl-1,9-dioxo-5,13-diphosphacyclohexadecane-5,13-dioxide, 1 $\alpha$  and 1 $\beta$ .** The cyclic phosphine oxides were obtained from alkaline hydrolysis of 5,5,13,13-tetraphenyl-1,1,9,9-dioxo-5,13-diphosphonia-cyclohexadecane dibromide followed by column chromatography using a previously published procedure.<sup>4</sup>

**1 $\alpha$** —M.p. 170.5–171°C. Anal. Calcd. for  $\text{C}_{24}\text{H}_{34}\text{O}_4\text{P}_2$ : C, 64.28; H, 7.64; O, 14.27; Found: C, 64.03; H, 7.58; O 13.97%. M.S.:  $m/z$  448 (43%,  $\text{M}^+$ ), 168 (100%).  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ , 0.14 mol  $\text{dm}^{-3}$ ):  $\delta$ /ppm 1.65–2.40 (m, 16H); 3.35–3.65 (m, 8H); 7.45–7.60 (m, 6H); 7.65–7.80 (m, 4H).  $^{13}\text{C}$  NMR (50.3 MHz,  $\text{CDCl}_3$ , 0.35 mol  $\text{dm}^{-3}$ ):  $\delta$ /ppm 22.15 (d,  $^2J_{\text{PC}} = 3.7$  Hz,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ); 26.20 (d,  $^1J_{\text{PC}} = 69.0$  Hz,  $-\text{CH}_2\text{P}(\text{O})-$ ); 69.94 (d,  $^3J_{\text{PC}} = 12.0$  Hz,  $-\text{CH}_2\text{O}-$ ); 128.49 (d,  $^3J_{\text{PC}} = 11.1$  Hz,  $m\text{-Ph}$ ); 130.11 (d,  $^2J_{\text{PC}} = 8.8$  Hz,  $\sigma\text{-Ph}$ ); 131.43 (d,  $^4J_{\text{PC}} = 2.7$  Hz,  $p\text{-Ph}$ ); 132.67 (d,  $^1J_{\text{PC}} = 92.7$  Hz,  $i\text{-Ph}$ ).

**1 $\beta$** —M.p. 175–176°C. Anal. Calcd. for  $\text{C}_{24}\text{H}_{34}\text{O}_4\text{P}_2$ : C, 64.28; H, 7.64; O, 14.27; Found: C, 64.14; H, 7.85; O 14.15%. M.S.:  $m/z$  448 (43%,  $\text{M}^+$ ), 168 (100%).  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ , 0.14 mol  $\text{dm}^{-3}$ ):  $\delta$ /ppm 1.65–2.35 (m, 16H); 3.45–3.65 (m, 8H); 7.45–7.60 (m, 6H); 7.65–7.80 (m, 4H).  $^{13}\text{C}$  NMR (50.3 MHz,  $\text{CDCl}_3$ , 0.35 mol  $\text{dm}^{-3}$ ):  $\delta$ /ppm 22.12 (d,  $^2J_{\text{PC}} = 3.8$  Hz,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ); 27.43 (d,  $^1J_{\text{PC}} = 69.1$  Hz,  $-\text{CH}_2\text{P}(\text{O})-$ ); 69.88 (d,  $^3J_{\text{PC}} = 11.3$  Hz,  $-\text{CH}_2\text{O}-$ ); 128.49 (d,  $^3J_{\text{PC}} = 11.1$  Hz,  $m\text{-Ph}$ ); 130.76 (d,  $^2J_{\text{PC}} = 8.8$  Hz,  $\sigma\text{-Ph}$ ); 131.41 (d,  $^4J_{\text{PC}} = 2.7$  Hz,  $p\text{-Ph}$ ); 132.96 (d,  $^1J_{\text{PC}} = 92.6$  Hz,  $i\text{-Ph}$ ).

**X-Ray Structure Determination—Crystal Data.** **1 $\alpha$** ,  $\text{C}_{24}\text{H}_{34}\text{O}_4\text{P}_2$ ,  $M = 448.45$ , monoclinic, space group  $P2_1/n$ ,  $a = 13.597(3)$ ,  $b = 5.728(2)$ ,  $c = 16.219(3)$  Å,  $\beta = 114.10(3)^\circ$ ,  $Z = 2$ ,  $D_c = 1.292$  g  $\text{cm}^{-3}$ ,  $F(000) = 480$ ,  $\mu(\text{Mo-K}\alpha) = 2.10$   $\text{cm}^{-1}$ . **1 $\beta$** ,  $\text{C}_{24}\text{H}_{34}\text{O}_4\text{P}_2$ ,  $M = 448.45$ , monoclinic, space group  $P2_1/n$ ,  $a = 17.973(3)$ ,  $b = 22.549(4)$ ,  $c = 5.662(2)$  Å,  $\beta = 95.86(2)^\circ$ ,  $Z = 4$ ,  $D_c = 1.305$  g  $\text{cm}^{-3}$ ,  $F(000) = 960$ ,  $\mu(\text{Mo-K}\alpha) = 2.10$   $\text{cm}^{-1}$ .

**Data collection.** Data were collected with a Philips PW1100 four circle diffractometer in the  $\theta$  range 3–23° for the colourless crystal of **1 $\alpha$**  (dimensions  $2.1 \times 2.8 \times 3.2$  mm) and in the range 3–21° for the colourless crystal of **1 $\beta$**  (dimensions  $2.1 \times 2.8 \times 3.2$  mm) by the method described previously.<sup>5</sup> A constant scan speed of  $0.05^\circ \text{ s}^{-1}$  and an  $\omega$ -scan width of  $0.90^\circ$  was used in each case. Three reference reflections were measured at 5 h intervals and showed no significant changes in intensities. The data

TABLE II

(a) Fractional atomic coordinates for *trans*-5,13-diphenyl-1,9-dioxo-5,13-diphosphacyclohexadecane (**1 $\alpha$** )

Atom	x	y	z
P(1a)	0.5197(3)	0.1444(6)	0.8568(2)
O(1a)	0.2297(5)	0.5055(16)	0.8820(4)
O(2a)	0.5289(6)	−0.1117(14)	0.8764(5)
C(1a)	0.2157(10)	0.2655(22)	0.8464(8)
C(2a)	0.3240(8)	0.1483(23)	0.8733(7)
C(3a)	0.3871(7)	0.2578(18)	0.8231(6)
C(5a)	0.5311(5)	0.4333(13)	0.7222(6)
C(6a)	0.5588(5)	0.4794(13)	0.6500(6)
C(7a)	0.6131(5)	0.3113(13)	0.6222(6)
C(8a)	0.6397(5)	0.0969(13)	0.6667(6)
C(9a)	0.6120(5)	0.0508(13)	0.7390(6)
C(4a)	0.5577(5)	0.2190(13)	0.7668(6)
C(10a)	0.5998(7)	0.3223(21)	0.9492(7)
C(11a)	0.7225(9)	0.2823(20)	0.9809(7)
C(12a)	0.7868(9)	0.4822(24)	1.0355(8)

TABLE II (*Continued*)  
 (b) Fractional atomic coordinates for *cis*-5,13-diphenyl-  
 1,9-dioxo-5,13-diphosphacyclohexadecane (**1 $\beta$** )

Atom	<i>x</i>	<i>y</i>	<i>z</i>
O(1a)	0.7124(7)	0.7573(5)	0.0488(22)
C(1a)	0.6850(8)	0.6988(6)	0.0386(31)
C(2a)	0.7108(7)	0.6638(6)	0.2573(30)
C(3a)	0.7943(6)	0.6574(5)	0.3071(26)
P(1a)	0.8366(3)	0.6057(3)	0.1382(15)
O(2a)	0.8366(4)	0.6188(3)	-0.1262(20)
C(5a)	0.7452(4)	0.5110(3)	-0.0161(20)
C(6a)	0.7097(4)	0.4569(3)	0.0136(20)
C(7a)	0.7200(4)	0.4276(3)	0.2315(20)
C(8a)	0.7658(4)	0.4525(3)	0.4197(20)
C(9a)	0.8012(4)	0.5066(3)	0.3900(20)
C(4a)	0.7909(4)	0.5359(3)	0.1721(20)
C(10a)	0.9260(4)	0.6001(6)	0.2838(23)
C(11a)	0.9808(6)	0.5633(6)	0.1627(34)
C(12a)	1.0596(7)	0.5862(6)	0.1849(32)
O(1b)	1.0651(6)	0.6440(5)	0.0954(22)
C(1b)	0.7064(6)	0.7881(7)	-0.1684(29)
C(2b)	0.7759(6)	0.7817(8)	-0.2928(26)
C(3b)	0.8450(5)	0.8081(6)	-0.1606(26)
P(1b)	0.9278(3)	0.7981(3)	-0.2883(15)
O(2b)	0.9228(3)	0.7947(3)	-0.5614(20)
C(5b)	1.0034(3)	0.9015(3)	-0.3476(20)
C(6b)	1.0491(3)	0.9495(3)	-0.2752(20)
C(7b)	1.0809(3)	0.9533(3)	-0.0405(20)
C(8b)	1.0670(3)	0.9092(3)	0.1219(20)
C(9b)	1.0213(3)	0.8612(3)	0.0495(20)
C(4b)	0.9895(3)	0.8573(3)	-0.1852(20)
C(10b)	0.9632(6)	0.7333(4)	-0.1561(29)
C(11b)	1.0361(8)	0.7112(6)	-0.2329(31)
C(12b)	1.0570(10)	0.6493(6)	-0.1532(24)

TABLE III  
 Selected bond lengths (Å) and angles (°) for *trans*-5,13-diphenyl-1,9-  
 dioxo-5,13-diphosphacyclohexadecane (**1 $\alpha$** )

P(1a)–O(2a)	1.496(9)	P(1a)–C(3a)	1.779(10)
P(1a)–C(4a)	1.788(11)	P(1a)–C(10a)	1.772(10)
O(1a)–C(1a)	1.473(15)	C(1a)–C(2a)	1.512(17)
C(2a)–C(3a)	1.537(17)	C(5a)–C(6a)	1.395(14)
C(5a)–C(4a)	1.395(11)	C(6a)–C(7a)	1.395(12)
C(7a)–C(8a)	1.395(11)	C(8a)–C(9a)	1.395(14)
C(9a)–C(4a)	1.395(12)	C(10a)–C(11a)	1.550(15)
C(11a)–C(12a)	1.492(16)		
C(3a)–P(1a)–O(2a)	114.2(5)	C(4a)–P(1a)–O(2a)	112.4(5)
C(4a)–P(1a)–C(3a)	104.9(4)	C(10a)–P(1a)–O(2a)	114.5(5)
C(10a)–P(1a)–C(3a)	104.2(5)	C(10a)–P(1a)–C(4a)	105.7(5)
C(2a)–C(1a)–O(1a)	110.3(9)	C(3a)–C(2a)–C(1a)	111(1)
C(2a)–C(3a)–P(1a)	113.8(7)	C(4a)–C(5a)–C(6a)	120.0(8)
C(7a)–C(6a)–C(5a)	120.0(7)	C(8a)–C(7a)–C(6a)	120.0(9)
C(9a)–C(8a)–C(7a)	120.0(8)	C(4a)–C(9a)–C(8a)	120.0(7)
C(5a)–C(4a)–P(1a)	122.2(7)	C(9a)–C(4a)–P(1a)	117.8(6)
C(9a)–C(4a)–C(5a)	120.0(9)	C(11a)–C(10a)–P(1a)	113.7(8)
C(12a)–C(11a)–C(10a)	112(1)		

were corrected for Lorentz and polarisation factors and equivalent reflections were merged to give a total of 551 unique data with  $I > 3\sigma(I)$  for **1a** and 621 with  $I > 2.5\sigma(I)$  for **1b**.

**Structure solution and refinement.**<sup>6</sup> **1a**—All non-hydrogen atoms of the asymmetric unit of the molecule were located by direct methods. A difference-Fourier synthesis using low angle data ( $\sin \theta < 0.35$ ) revealed the positions of 6 of the 17 hydrogens in the asymmetric unit and the remainder of the hydrogen atoms were included in idealised positions (C—H 1.08 Å). Absorption corrections<sup>7</sup> were applied after refinement with isotropic thermal parameters for all non-hydrogen atoms. In the final cycles of full-matrix least squares refinement, the phosphorus and oxygen atoms were assigned anisotropic thermal parameters. Neutral scattering factors, corrected for the real and imaginary components of anomalous dispersion were used throughout.<sup>8</sup> Individual weights of  $1/\sigma^2(I)$  were assigned to each reflection and refinement converged at  $R$  0.0686 and  $R'$  0.0646 where  $R' = \Sigma ||F_o| - |F_c||w^{1/2} / \Sigma |F_o|w^{1/2}$ . Final atomic coordinates are listed in Table IIa, selected bond lengths and angles are given in Table III.

**1b**—All non-hydrogen atoms of the molecule were located by direct methods. To overcome the poor quality of the diffraction data, each set of corresponding bond lengths in the macrocyclic ring were constrained to a common (refined) free variable, phenyl rings in the structure were constrained to an idealized geometry (C—C 1.40 Å, C—C—C 120°) and all hydrogen atoms were included in idealized positions (C—H 1.08 Å). Absorption corrections<sup>7</sup> were applied after refinement with isotropic thermal parameters for all non-hydrogen atoms. In the final cycles of damped least squares refinement, the phosphorus and oxygen atoms were assigned anisotropic thermal parameters. Neutral scattering factors, corrected for the real and imaginary components of anomalous dispersion were used throughout.<sup>8</sup> Individual weights of  $1/\sigma^2(I)$  were assigned to each reflection and refinement converged at  $R$  0.1093 and  $R'$  0.0911. Final atomic coordinates are listed in Table II(b).

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

#### ACKNOWLEDGEMENTS

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