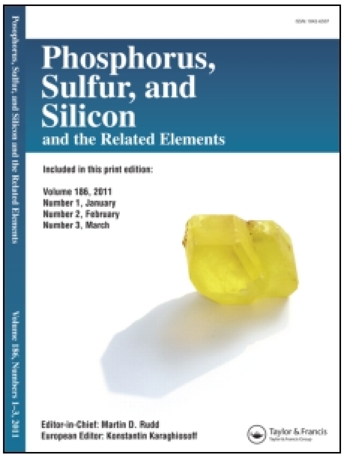

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2-O-METHYLXYLITAN CYCLOPHOSPHITES

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2-O-METHYLXYLITAN CYCLOPHOSPHITES

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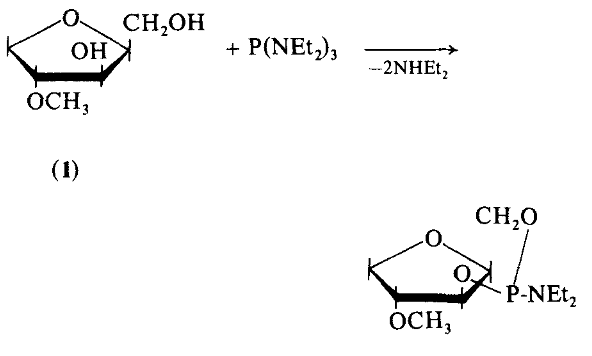
Two pairs of stereometric bicyclic 1,3,2-dioxaphosphorinans have been synthesized from 2-O-methylxylitan. The products have been isolated and their chemical properties studied. ^{1}H, ^{13}C, ^{31}P NMR and x-ray data have been used to determine the configurations and the conformational preference of the compounds.

It has been shown previously[1] that xylitan is easily phosphorylated at the primary hydroxyl with formation of hydrogen phosphonites. In the present work we reacted 2-O-methylxylitan (**1**) containing a β-diol system with di- and trifunctional derivatives of phosphorous acid in order to synthesize cyclophosphites. The latter are important for stereochemical studies and may be useful as models of more complicated cyclic phosphorus-containing carbohydrates that are being extensively studied at present.[2]

2-O-Methylxylitanylidene phosphorodiethylamidite (**2**) was obtained by interaction of equimolar quantities of (**1**) and phosphorous hexaethyltriamide:

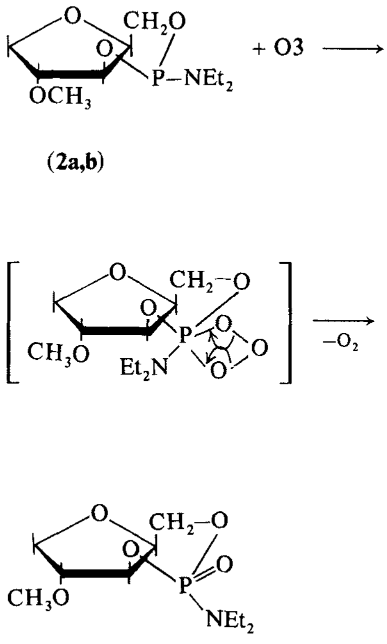


(**1**)

(**2a,b**)

^{13}C and ^{31}P NMR spectra revealed two stereoisomeric forms (Table I). The thermodynamically more stable isomer (**2a**)‡ exhibits ^{31}P resonance in relatively lower field and has a higher P–C^{4} vicinal coupling constant. Therefore, by analogy with 2-dialkylamino-1,3,2-dioxaphosphorinans,[3] a cis configuration with equatorial orientation of the amido group should be assigned to it.

Under the action of ozone or nitrogen oxide the equilibrium mixture of two isomers is oxidized with formation of a single isomer of 2-O-methylxylitanylidene diethylphosphoroamidate (**3a**). Therefore, interaction of both isomers with ozone proceeds with commensurable rates via an intermediate, presumably common for both isomers:



(**2a,b**)

(**3a**)

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‡ Here and below "a" designates isomers with $\delta^{31}P$ in relatively lower fields.

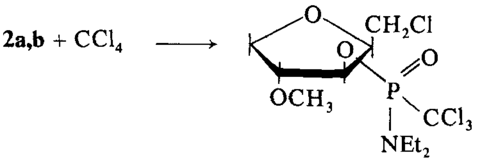
TABLE I

^{13}C and ^{31}P chemical shifts and ^{13}C-^{31}P spin coupling constants*[a]

Compound		^{13}C								^{31}P
		C^1	C^2	C^3	C^4	C^5	OCH_3	C^6	C^7	
(7)	δ	74.2	78.5	78.4	82.2	61.4	—	—	—	—
(1)	δ	71.6	88.0	75.2	82.0	61.5	57.6	—	—	—
(8)	δ	74.2	76.0	76.6	81.2	67.7	—	92.4	—	—
(9)	δ	73.2	86.2	74.3	80.0	67.4	57.8	92.3	—	—
(2a)	δ	72.5	87.9	77.8	75.1	63.6	58.1	38.7	15.8	+142
	J	<1.0	3.2	3.4	11.0	7.0	—	22.0	—	
(2b)	δ	70.8	87.8	77.9	76.1	62.3	58.1	39.2	15.5	+131
	J	1.6	2.2	3.8	6.0	<1.0	—	22.8		
(3a)	δ	72.6	86.6	79.7	73.5	66.1	57.3	40.2	14.7	+3.7
	J	<1.0	10.0	5.3	6.4	5.0	—	5.4	<1.0	—
(4)	δ	72.3	84.7	80.9	79.6	40.6	57.5	40.6	13.9	+12.5
	J	<1.0	2.0	6.5	7.0	<1.0	—	2.3	1.6	—
(6a)	δ	73.1	86.9	82.4	74.2	67.3	58.5	—	—	+1.5
	J	<1.0	7.8	7.0	8.1	5.0	—			
(6b)	δ	72.6	87.7	82.9	74.4	68.2	58.6	—	—	−4.0
	J	<1.0	3.8	8.3	12.2	7.2	—	—		

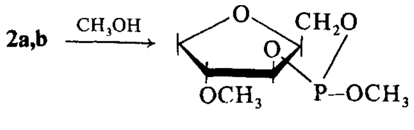
[a] ^{31}P chemical shifts are positive downfield from the standard.

Interaction of (**2**) with carbon tetrachloride proceeds according to the Arbusov scheme with formation of 5-chloro-5-desoxy-2-O-methylxylitanyl 3-trichloromethylphosphonodiethylamidate (**4**). As follows from NMR spectra the six-membered ring opens only at the C^5—O bond. A signal with δ = 40.6 ppm corresponding to chloromethyl carbon is observed in the ^{13}C spectrum.[4]



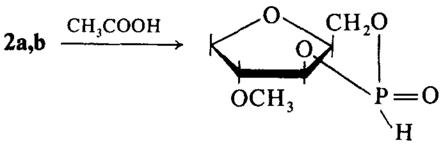
(**4**)

Methanolysis of (**2**) leads to the formation of a mixture of two isomeric methyl phosphites (**5**) that is impossible to separate as the isomers have close chromatographic mobilities and boiling points. Similar derivatives were obtained recently from xylitan and triethylphosphite.[5]



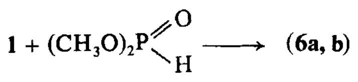
(**5**)

Acidolysis of (**2**) also yields a mixture of two stereoisomeric 2-O-methylxylitanylidene hydrogen phosphites (**6**) differing in boiling points and the characteristics of ^{31}P and ^{13}C NMR spectra (Table 1).



(**6**)

Independent synthesis of hydrogen phosphites (**6**) was carried out by ester exchange of 2-O-methylxylitan (**1**) with dimethyl phosphite.

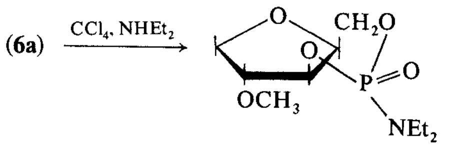


$$\mathbf{1} + (CH_3O)_2P(=O)H \longrightarrow (\mathbf{6a,b})$$

The presence of two stereoisomers (**6a**) and (**6b**) in a ratio similar to that observed after acidolysis of amidophosphite 2 was established by the method of ^{31}P and ^{13}C NMR. On storing, the raw product (**6**) crystallizes and the concentration of (**6a**) increases. Isomer (**6b**) is isolated by distillation of the raw product and gradually converts into (**6a**). Distillation of (**6a**) leads to a mixture of both isomers with approximately equal content of each. Several days after dissolution of (**6a**) in chloroform, equilibrium is reached with (**6a**:**6b**) ≈1 : 1.

The isomers of (**6**) are highly reactive. They are easily hydrolyzed to produce phosphorous acid and 2-O-methylxylitan. Alcoholysis by an excess of alcohol also results in opening of the six-membered ring.

Interaction of (**6a**) with carbon tetrachloride, according to Atherton and Todd,[6] proceeds with formation of a mixture of stereoisomeric (**3**).



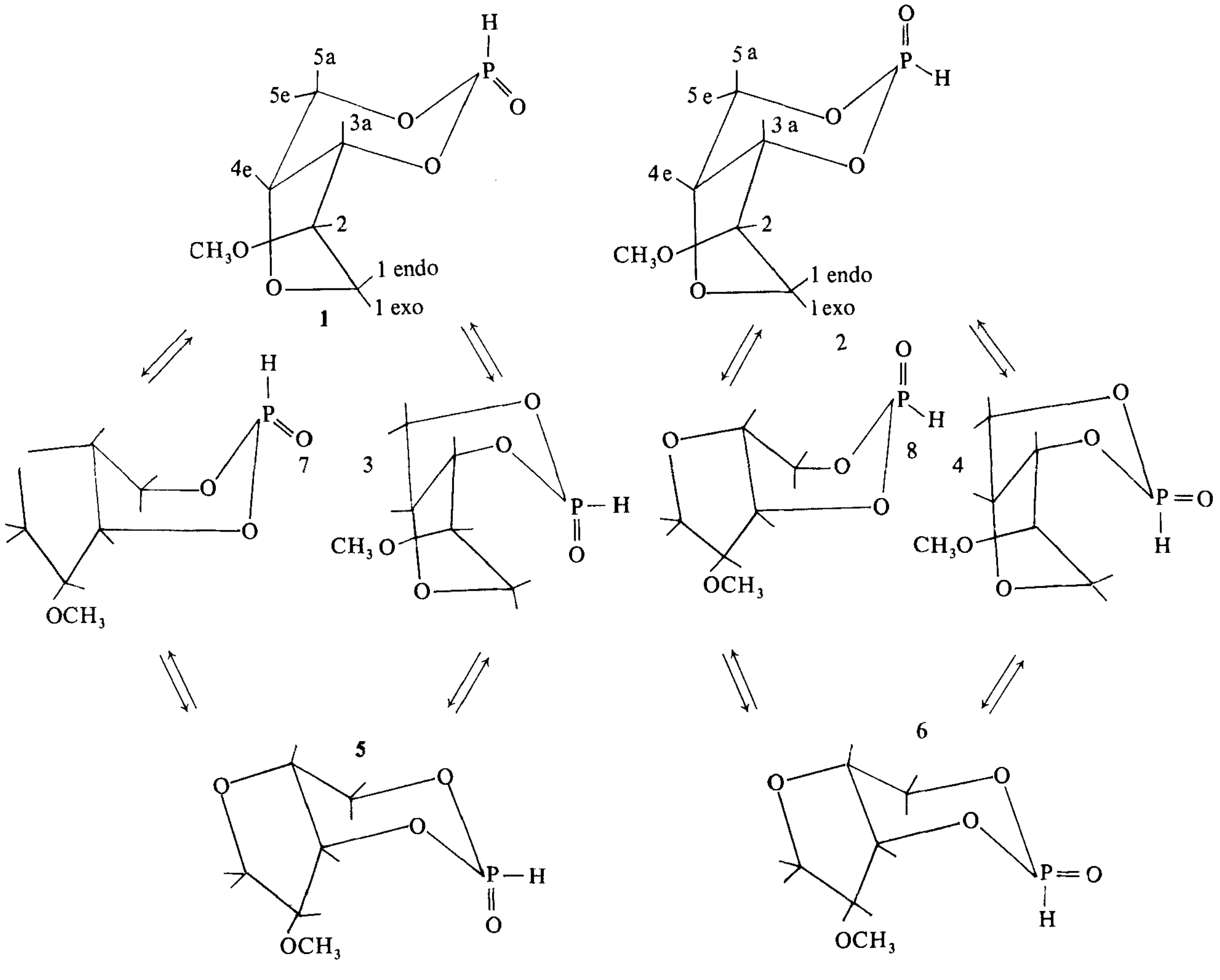
(**3a, b**)

Isomer (**3a**) was extracted from raw (**3**) with ether and was shown to be identical to the product obtained by oxidation of (**2**).

The ^{13}C NMR spectra of xylitan (**7**), 5,6-methylenexylitan (**8**) and 2-O-methyl-5,6-methylenexylitan (**9**) as model structures for assigning ^{13}C NMR signals were studied.

Stereochemical investigation of the compounds prepared was carried out by NMR and x-ray techniques. The Dreiding molecular model for (**6**) revealed that two isomers are possible, each existing in four conformations (see below).

Conformational analysis was carried out on the basis of ^{1}H, ^{13}C and ^{31}P NMR spectra, in particular of ^{1}H–^{1}H, ^{1}H–^{31}P and ^{13}C–^{31}P coupling constants. PMR spectra of (**6a**) and of a mixture of (**6a**) and (**6b**) are presented in Figure 1. To simplify the spectra, double heteronuclear ^{1}H–{^{31}P} resonance



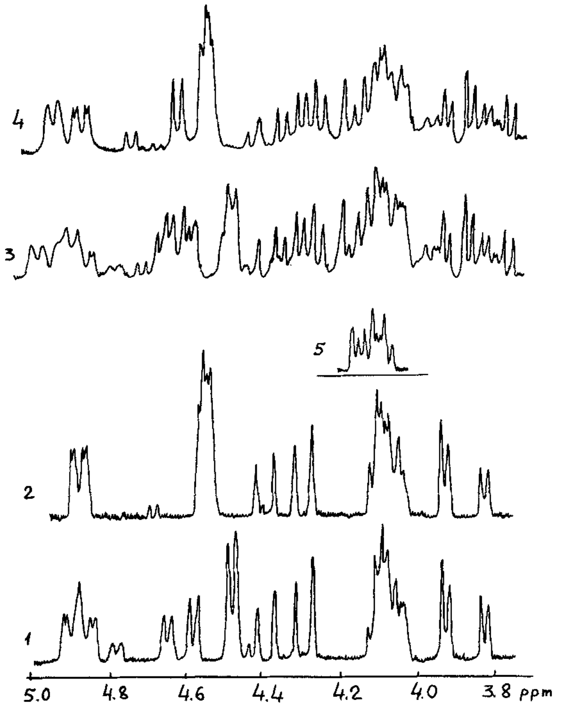


FIGURE 1 PMR spectra of (**6a**) (1, 2) and of a mixture of (**6a**) and (**6b**) (3–5); 1,3-spectra monoresonance, 2–5-spectra double ^1H-{^{31}P} resonance.

was used. Consider the spectrum of crystalline (**6a**). Two quartets with chemical shifts at 4.33 and 3.88 ppm that do not couple with phosphorus and have the same coupling constant of 10.0 Hz were assigned to two protons at C^1. An INDOR experiment while monitoring the lines of these two quartets shows that the signal of the H^2 proton is in a multiplet with δ 4.07 ppm. On the basis of coupling constants of H^2 with protons at C^1 and Karplus dependence[7] the signal at 4.33 ppm with $^3J_{HH} = 4.6$ Hz was assigned to the endo-proton and the signal at δ 3.88 ppm with $^3J_{HH}$ 1.8 Hz to the exo-proton. The AB-type spectrum at 4.55 ppm observed after phosphorus decoupling (spectrum 2) was assigned to two protons at C^5. The monoresonance spectrum of these protons is characterized by degeneration of one of the AB subspectra of the ABX system (X is ^{31}P) into a single line (it appears as a doublet due to coupling with H^4 and, therefore, a more precise designation of the spectrum is ABMX), which makes analysis more complicated. However, J_{AX} and J_{BX} can be determined from the chemical shifts δA and δB that are obtained from the ^1H-{^{31}P} spectrum (spectrum 2). The C^5 proton–phosphorus coupling constants of 21.8 and 4.0 Hz are in good agreement with similar constants for cyclic phosphites in the chair conformation[8] and permit assignment of the signal at 4.52 ppm to the axial proton and that at 4.58 ppm to the equatorial proton. From this assignment it also follows that non-chair conformations 3 and 7 that should have identical H^{5a}–P and H^{5e}–P coupling constants can be excluded. An INDOR experiment while monitoring the H^{5a} and H^{5e} lines revealed that a chemical shift H^4 is at 4.09 ppm and is overlapped with H^2. The remaining signal at δ 4.88 ppm was assigned to H^3. The missing spin coupling constants were determined from the PMR spectrum of (**6a**) in a toluene-chloroform (3 : 1) mixture (Figure 1, spectrum 5) that enhances the non-equivalence of H^2 and H^4. This spectrum also confirmed the assignments that H^4 occupies an equatorial position since the H^4–H^{5e} coupling constant was found to be 2.0 Hz, whereas for other arrangements of H^4 it should have been of the order of 10–12 Hz. Consequently conformation 5 of (**6a**) can be discarded. This conclusion conforms with the arrangement of the H^3. Its coupling constant due to interaction with phosphorus across three bonds of 3.6 Hz indicates axial orientation.[8] Thus, (**6a**) has a chair conformation corresponding to structures 1 and 2 that differ in the configuration of the hydrophosphoryl site.

Configurational assignment of (**6a**) and (**6b**) isomers was based on the comparison of chemical shifts of ^{31}P and ^1J(P–H) and ^{13}C–^{31}P coupling constants with corresponding data for monocyclic hydrogen phosphites,[9] the configurations of which have been reliably determined by various methods.[10] The crystalline (**6a**) isomer exhibiting ^{31}P resonance in lower field, smaller ^1J(P–H) value and smaller vicinal C^4–P coupling constant (Table 1) in relation to (**6b**) was assumed to be the cis-isomer (conformation 1).

Analysis of the PMR spectra of (**6b**) (Figure 1, spectra 3 and 4) was carried out in the same manner; the chemical shifts obtained and spin coupling constants are given in Table II. As can be seen the axial-axial interaction of vicinal H^4 and H^5 protons is absent and therefore conformations 6 and 8 of (**6b**) can be excluded. H–H coupling constants of (**6a**) and (**6b**) are almost identical, therefore conformations of both isomers in the region of the five-membered ring are similar.

For P–H vicinal constants in the six-membered ring the pattern is different. Isomer (**6b**) has higher H^{3a}–P and H^{5a}–P coupling constants and a lower

TABLE II

Chemical shifts (in $CHCl_3$, 10%) and spin coupling constants in PMR spectra of **(6a)**, **(6b)** and **(3a)**

Chemical shifts, ppm				Spin coupling constants, Hz			
No. of proton	**(6a)**	**(6b)**	**(3a)**		**(6a)**	**(6b)**	**(3a)**
1-endo	4.33	4.25	4.22	1-endo-1-exo	−10.0	−10.0	−9.2
1-exo	3.88	3.82	3.82	1-endo-2	4.6	5.0	4.0
2	4.07	4.07	3.92	1-exo-2	1.8	2.0	1.4
3a	4.88	4.95	4.94	2–3a	1.0	0.8	0.6
4e	4.09	4.10	3.87	3a–4e	3.0	2.8	2.3
5e	4.58	4.53	4.69	4e–5a	2.0	2.2	1.9
5a	4.52	4.68	4.44	4e–5e	2.1	2.4	2.4
O–CH_3	3.47	3.47	3.39	5a–5e	−13.3	−12.3	−13.0
N–CH_2	—	—	3.08	2–P	0	0	0
N...CH_3	—	—	1.10	3a–P	3.6	6.4	0.2
P–H	7.02	7.06		4e–P	2.2	0	0
				5a–P	4.0	5.6	2.7
				5e–P	21.8	13.6	20.3
				CH_3–CH_2			7.1
				P–CH_2			12.2
				P–H	688	734	—

H^{5e}–P constant as compared with **(6a)**, i.e. the coupling constants of phosphorus with axial and equatorial protons are somewhat equalized. This may be caused by the presence in conformational equilibrium of the trans-isomer **(6b)** along with chair structure 2 of appreciable amounts of boat structure 4, for which the P–H vicinal coupling constants should be identical due to the equality of dihedral POCH angles.[10] Data of ^{13}C NMR support this assumption. Increasing $^3J(C^4–P)$ and decreasing $^3J(C^2–P)$ constants in **(6b)** as compared with **(6a)** point to a decrease of dihedral C^4–C^3–O–P and C^2–C^3–O–P angles in **(6b)** which also may be explained by the presence of the boat conformation.

We made an attempt to quantitatively estimate the contribution of the boat structure in the conformational equilibrium of **(6b)**. Calculations based on the $^3J(C^4–P)$ constant and data for the dihedral angle 0°[5] (boat conformation) and dihedral angle 60° **(6a)**, chair conformation) gave a value of 26%. Thus, for **(6b)** the difference in conformation energy is ΔG°_{25} (chair → boat) = 0.6 kcal/mol. The value obtained is unusually small for cyclohexane derivatives and other heterocyclic systems. However, it is in agreement with data obtained for 1,3,2-dioxaphosphorinans.[10]

Configuration and conformation of phosphoroamidate **(3a)** were also investigated. Analysis of PMR spectra was carried out as described above, data are listed in Table II. Values of H–H and P–H coupling constants indicate an axial orientation of H^3 and equatorial orientation of H^4. The downfield shift of the ^{31}P resonance of **(3a)** relative to **(3b)** and the similar values of ^{13}C–^{31}P (C^2–P, C^3–P, C^4–P and C^5–P) coupling constants and of the corresponding constants for the cis-

TABLE III

Atom coordinates and isotropic temperature factors with their probable errors

	X	*Y*	*Z*	B_j Å
P	0.5005(4)	0.5741(3)	0.1535(1)	3.88(5)
O^1	0.7001(9)	0.5480(8)	0.1643(4)	4.9(2)
O^2	0.3951(10)	0.4162(9)	0.1191(3)	5.1(2)
O^3	0.4111(10)	0.6120(10)	0.2109(4)	5.8(2)
O^4	0.9657(11)	0.2764(10)	0.2179(4)	6.2(2)
O^5	0.6889(11)	0.2485(9)	0.1044(4)	5.6(2)
N	0.5398(12)	0.7069(10)	0.0985(4)	4.7(1)
C^2	0.8827(18)	0.3064(16)	0.1096(7)	6.5(3)
C^2	0.9108(15)	0.3825(13)	0.1750(5)	4.9(2)
C^3	0.7195(14)	0.4009(13)	0.1949(5)	4.5(2)
C^4O	0.5933(13)	0.2565(12)	0.1606(5)	4.5(2)
C^5	0.3985(14)	0.2641(13)	0.1522(6)	5.0(2)
C^6	0.0324(18)	0.3543(17)	0.2746(7)	6.8(3)
C^7	0.4447(17)	0.8443(15)	0.1020(6)	6.1(3)
C^8	0.2592(21)	0.8035(18)	0.0641(8)	8.3(4)
C^9	0.6294(17)	0.6914(15)	0.0380(5)	5.9(3)
C^{10}	0.8052(20)	0.8208(18)	0.0335(8)	8.1(4)

TABLE IV

Bond lengths (Å) and their probable errors					
$P-O^1$	1.596(8)	C^2-O^4	1.43(2)	O^4-O^6	1.41(2)
$P-O^2$	1.587(8)	C^3-C^4	1.56(1)	$P-N$	1.621(9)
$P-O^3$	1.473(9)	C^3-O^1	1.47(1)	$N-C^7$	1.54(2)
C^1-C^2	1.53(2)	C^4-C^5	1.50(2)	C^7-C^8	1.58(2)
C^1-C^5	1.43(2)	C^4-O^5	1.41(1)	$N-C^9$	1.48(2)
C^2-C^3	1.55(2)	O^2-O^5	1.51(1)	C^9-C^{10}	1.51(2)
Bond angles and their probable errors					
C^1-P-O^2	103.8(5)	C^4-C^1	111.4(8)	$C^4-C^3-C^2$	109.9(9)
O^1-P-O^3	114.2(5)	$P-N-C^9$	115.5(8)	$C^2-C^5-C^4$	109.0(8)
O^1-P-N	101.3(5)	$O-N-C^7$	115.0(7)	$N-C^9-C^{10}$	109.0(9)
O^2-P-O^3	114.5(4)	C^9-N-C^7	114.6(9)	$C^3-C^2-O^4$	108.5(9)
O^2-P-N	104.2(5)	$O^5-C^4-O^3$	102.4(7)	$C^1-C^2-O^4$	109.4(9)
O^3-P-N	116.9(5)	$O^5-C^4-C^5$	114.6(9)	$C^3-C^2-O^1$	104.9(9)
$P-O^1-C^3$	119.2(6)	$C^3-C^4-C^5$	115.1(9)	$N-C^7-C^8$	111.9(9)
$P-O^2-C^5$	115.8(7)	$O^1-C^3-C^4$	108.9(9)	$O^5-C^1-C^2$	104.0(9)
$C^2-O^4-C^6$	111.2(9)	$O^1-C^3-C^2$	105.2(8)		

TABLE V

Mean-square planes

Atoms, the plane passes through	A	B	C	D	Displacements from the plane, Å
$P-O^1-C^3-C^4-C^5-O^2$	−3.12	0.86	19.40	1.69	$P(-0.22)$; $O^1(0.20)$; $C^3(-0.19)$; $C^4(0.20)$; $C^5(-0.25)$; $O^2(0.25)$; $O^3(-1.65)$; $N(0.86)$
$O^2-C^5-C^3-O^1$	−3.89	3.37	17.33	1.95	$O^2(0.02)$; $C^5(-0.02)$; $C^3(0.02)$; $O^1(0.034)$; $P(-0.69)$; $C^4(0.61)$
$C^1-C^2-C^4-O^5$	2.72	−8.11	7.18	0.66	$C^1(-0.05)$; $C^2(0.03)$; $C^4(-0.03)$; $O^5(0.05)$; $C^3(0.55)$
$C^1-C^2-C^3-O^5$	1.16	−7.46	10.89	0.02	$C^1(0.09)$; $C^2(-0.09)$; $C^3(0.06)$; $O^5(0.06)$; $C^4(-0.50)$
$C^1-C^2-O^5$	2.16	−7.99	8.36	0.38	$C^3(0.39)$; $C^4(-0.20)$; $C^5(+0.35)$

isomer of 4-methyl-2-dimethylamido-2-oxo-1,3,2-dioxaphosphorinan (where the amido group is arranged equatorially[4]) point to a structural similarity of phosphorinan rings in these compounds. Our deductions were confirmed by x-ray data for phosphoroamidate (**3a**). Coordinates of all atoms and temperature factors except for hydrogen are given in Table III. Bond lengths and bond angles with standard deviations are listed in Table IV. All values of bond-lengths and bond angles are typical of such compounds. Figure 2 shows a projection of the molecule on the (010) plane.

The six-membered heterocycle has a practically undistorted chair conformation. Deviations of O^2, O^5, C^3 and O^1 atoms from the mean-square plane that passes through these atoms are within the range of probable errors (±0.02 Å) (Table V). Phosphorus and C^4 atoms are displaced from this plane by −0.69 Å and +0.61 Å, respectively. The phos-

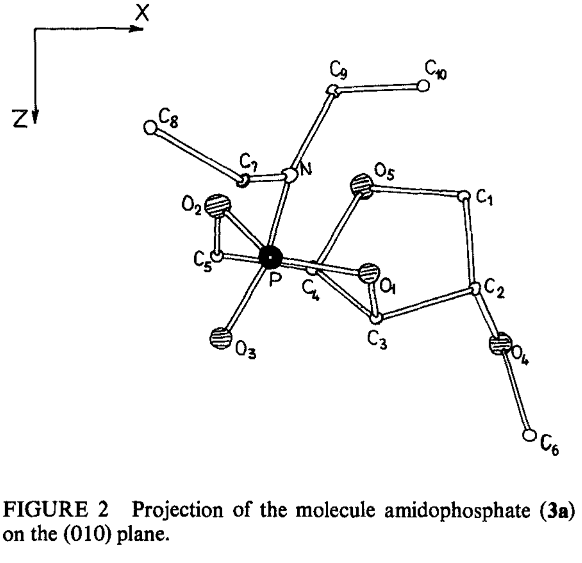


FIGURE 2 Projection of the molecule amidophosphate (**3a**) on the (010) plane.

phoryl oxygen O^3 is axial and the nitrogen atom is equatorial in relation to the ring plane (Table V).

In the pentafuranose ring the C^3 atom is shifted from the plane of the other four atoms by 0.55 Å in the same direction as O^5. C^4 is also (considerably) displaced (—0.50 Å) from the plane passing through the other four atoms of the ring (Table V). This may be explained by fusion of the six- and five-membered rings into a condensed system. C^3 is shifted by 0.39 Å from the plane passing through the remaining three atoms (C^1–C^2–O^5), i.e., twice the displacement of the C^4 atom (Table V). Thus, conformation of the pentafuranose ring may be considered as intermediate between $T_4{}^3$ and V^3, being closer to the first.

EXPERIMENTAL

Substances were chromatographed on a thin layer of Brockman II aluminum oxide or of KSK-grade silica gel. Chromatograms were developed with iodine vapors. The following systems were used: A—chloroform : methanol (9 : 1) and Al_2O_3; B—benzene : dioxane (1 : 1) and Al_2O_3; C—chloroform and Al_2O_3; D—chloroform : acetone (1 : 1) and silica gel; E—hexane : dioxane (1 : 1) and Al_2O_3; F—chloroform : methanol (9 : 1) and silica gel; G—benzene : tetrahydrofuran (1 : 1) and Al_2O_3; H—benzene : acetone (2 : 1) and Al_2O_3; I—chloroform : methanol : hexane (7 : 3 : 5) and Al_2O_3.

^{31}P NMR spectra were recorded on a JNM-4H100 instrument, against an 85% phosphoric acid as external standard. ^1H and ^{13}C spectra were recorded on a Varian XL-100-15 spectrometer. Chloroform was used as a solvent. ^{13}C spectra were recorded in the FT mode. Chemical shifts of ^{13}C were measured in relation to cyclohexane as an internal standard ($\delta C_6H_{12} = 27.5$ ppm) and are given in relation to TMS. Signal assignments in ^{13}C spectra were made on the basis of incomplete double resonance experiments and calculations of chemical shifts according to the additive scheme. Unequivocal assignment of ^{13}C signals of 5a was based on selective double $^{13}C - \{^1H\}$ resonance and results of PMR spectra analysis.

Crystals of 2-O-methylxylitane diethylamidocyclophosphate are monoclinic, space group P2 I/b, cell parameters: $a = 7.541$ (1); $b = 8.713$ (1); $c = 21.311$ (3); $\gamma = 104.37°$ (2), $z = 4$.

The three-dimensional set of intensities was obtained on an automatic diffractometer Y-290, MoK_α radiation, graphite monochromator. Integral intensities of reflections were measured by the ω-scanning technique. 1362 non-zero independent reflections with $(\sin \theta/\lambda)_{max} = 0.705$ were registered.

The structure was determined by the direct sign Sayer-Zachriansen-Cochran criterion using standard Rentgen-70 computer programs. Refinement was carried out isotropically by the least squares method using 1049 non-zero reflections up to $R = 0.119$.

2-O-Methylxylitanylidene phosphorodiethylamidite (**2**). 11.89 (gmol) of 1 and 19.81 (gmol) of phosphorous hexaethyltriamide were heated under reflux to 110° in an argon atmosphere. The reaction was monitored by the amount of diethylamine forming and by TLC. 15.3 ml of diethylamine was formed after 2 h. 20.69 g of the raw product (96%) was obtained, after distillation—70%. B.p. 88° (10^{-2} mm), n_D^{20} 1.4818, R_f 0.9 (B); 0.6 (E); *t* 0.8 (G). Found: C, 48.22; H, 8.12; N, 5.59; P, 12.59%, $C_{10}H_{20}NO_4P$. Calculated: C, 48.19; H, 8.02; N, 5.62; P, 12.40%.

2-O-Methylxylitanylidene phosphorodiethylamidate (**3**). (a) A mixture of ozone and oxygen (0.75 vol.% of ozone) was passed through 2.51 g of (**2**) for 2 h. The reaction is exothermal and the temperature raised to 60°. The reaction was monitored by TLC and ^{31}P NMR. The product was distilled at 104° (10^{-2} mm). The yield was 2.65 g (80%). M.p. 55° from hexane), R_f 0.8 (A); 0.5 (B); 0.6 (G). Found: C, 44.95; H, 7.85; N, 5.24; P, 11.59%, $C_{10}H_{20}NO_5P$. Calculated: C, 45.20; H, 7.56; N, 5.28; P, 11.71%.

(b) 5.5 ml of diethylamine was added over a 40-min period to a mixture of 4.5 (gmol) of (**6a**), 10 ml of dry dioxane and 3.6 (gmol) of carbon tetrachloride at 40–50°C. The mixture was then stirred for an hour, the amine hydrochloride was filtered (2.2 g, 87%) and the filtrate evaporated. The residue, a yellow oily liquid, is a mixture of (**3a**) and (**3b**) (5.74 g, 94%). (**3a**) was isolated by extraction with absolute ether, yield 2.8 g (48%). M.p. 56° (from hexane). R_f 0.8 (A); 0.5 (B); 0.6 (C), $\delta^{31}P = 3.7$ ppm. The viscous residue, (**3b**), was washed with hot hexane or chromatographed on a Al_2O_3 column to remove traces of (**3a**). The yield was 4.0 g (52%), R_f 0.6 (A); 0.5 (B); 0.6 (C), $\delta^{31}P = +7.0$ ppm. Found: C, 44.85; H, 7.99; N, 5.25; P, 11.94%, $C_{10}H_{20}NO_5P$. Calculated; C, 45.20; H, 7.56; N, 5.28; P, 11.71%.

2-O-Methyl-6-chloro-5-desoxaxylitanye 3-trichloromethylphosphonodiethylamidate (**4**). 5 g of 2 (gmol) and 3.5 (gmol) of carbon tetrachloride were stirred for 20–30 min. The syrup obtained (n_D^{20} 1.4905) crystallizes after treatment with absolute hexane. The crystals were dried in a vacuum desiccator over P_2O_5. The yield was 8 g (90%), m.p. 62°. R_f 0.84 (A); 0.88 (B); 0.51 (D). Found: C, 32.63; H, 5.12; N, 3.50; P, 7.74%, $C_{11}H_{20}O_4PCl_4$. Calculated: C, 32.70: H, 4.95; N, 3.47; P, 7.69%.

2-O-Methylxylitanylidene methylphosphite (**5**). A mixture of 1 g of (**2**) (gmol) and 10 g of methanol were heated for 2 h at 70° in a flask equipped with a stirrer and a reflux condenser. After removing excessive material the product was distilled *in vacuo*. A mixture of isomers is obtained with a yield of 0.75 g (89%), b.p. 78° (10^{-2} mm), n_D^{20} 1.4630, R_f 0.94 (A); 0.9 (B). Found: C, 40.89; H, 6.24; P, 15.00%, $C_7H_{13}O_5P$. Calculated: C, 40.40; H, 6.25; P, 14.90%.

2-O-Methylxylitanylidene hydrogenphosphonite (**6**). (a) To a solution of 2 (gmol) of (**2**) in 6 ml of absolute ether 0.46 (gmol) of anhydrous (freezed out and distilled over P_2O_5) acetic acid was added drop-wise over a period of 10 min at 30–35°C. The mixture was stirred for 30 min and then stored for an hour at 50–60° under vacuum (4 mmHg) to remove diethylacetamide. The total yield of (**6a**) and (**6b**) was 1.39 g (90%). (**6b**) is isolated by distillation, b.p. 112° (10^{-2} mm), n_D^{20} 1.4750, R_f 0.8 (A). On storing it is converted into (**6a**), m.p. 86°, R_f 0.71 (A); 0.30 (B). Found: C, 36.97; H, 5.91; P, 16.05%, $C_6H_{11}O_5P$. Calculated: C, 37.11; H, 5.72; P, 14.97%.

(b) A mixture of 12.34 (gmol) of (**1**) and 9.17 (gmol) of dimethylphosphite was heated under reflux for 4 h at 125–130°. The reaction was monitored by the amount of alcohol formed, by the weight of the reaction mass and by TLC. A viscous colourless mixture of the isomers was obtained with a yield of 16.22 g (99.6%). The raw product (**6**) crystallizes on storing and the concentration of (**6a**) increases. (**6a**)—m.p. 86°, R_f 0.80 (A); 0.3 (D). (**6b**) is isolated by distillation, b.p. 111° (10^{-2}

mm), n_D^{20} 1.4715, R_f 0.80 (A); 0.3 (D), M.W. 194 (mass-spectrum). On storing it is converted into 5a. Found: C, 37.14; H, 5.75; P, 15.96%.

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