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Crystal Structures of an Axially and an Equatorially Oriented 2-(Aryloxy)-2-oxy-1,3,2-dioxaphosphorinane

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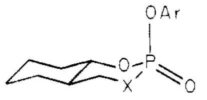
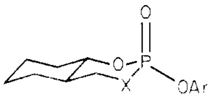
Single-crystal X-ray analysis of 2-(2,4-dinitrophenoxy)-2-oxo-*trans*-5,6-tetramethylene-1,3,2-dioxaphosphorinane (**3**) and 2-(*p*-methoxyphenoxy)-2-oxo-*trans*-5,6-tetramethylene-1,3,2-dioxaphosphorinane (**4**) reveals a chair conformation in each case. **3** crystallizes in the monoclinic space group $P2_1/c$ with a = 12.214 (3) Å, b = 6.304 (3) Å, c = 20.229 (7) Å, β = 96.42 (2)°, and Z = 4. The structure was refined to R = 0.041 and R_w = 0.055. For **4**, the monoclinic space group $P2_1/n$ was obtained with a = 8.615 (3) Å, b = 11.485 (3) Å, c = 14.419 (2) Å, β = 92.25 (2)°, and Z = 4. The structure was refined to R = 0.043 and R_w = 0.054. The solid-state structure of **3** agrees with the solution-state structure obtained by NMR. For **4**, solution-state NMR results indicated a mixture of chair and twist-boat. A small energy difference exists between these two conformers. A more flattened chair is obtained for **3** at the flap containing the phosphorus atom. The dihedral angle at the O–O "hinge" is 146.0° for **3** and 133.5° for **4**. The extent of bond angle coupling to ester torsional angles, greater in the axial triester **3** compared to the equatorial triester **4**, is in agreement with previous results.

Introduction

Gorenstein[2,3] carried out detailed configurational and conformational analyses of isomeric 2-(aryloxy)-1,3-dioxa-2-phospha-*trans*-decalin systems (substituted dioxaphosphorinanes), **1a** and **1b**, and related oxazaphosphorinanes, **2a** and **2b**, on the basis of ^{1}H NMR coupling data and ^{31}P and ^{13}C NMR spectra. This led to the identification of their solution structures.



1a (X = O), 2a (X = NH)



1b (X = O), 2b (X = NH)

All of the derivatives containing an axial aryloxy group (**1a**, **2a**) are indicated to be in a chair conformation while NMR data on the phosphorinanes containing equatorial aryloxy groups (**1b**, **2b**) support a variation in structural type from chair (Ar = *p*-NO_2Ph for **1a**) to an equilibrium between chair and twist-boat conformations (Ar = Ph, *p*-MeOPh, *p*-NO_2Ph for **1b**) to exclusively twist-boats (Ar = 2,4-dinitrophenyl for **1b**; Ar = *p*-NO_2Ph for **2b**).

The phosphorinanes that are able to assume twist-boat conformations (**1b**, **2b**) hydrolyze somewhat faster than epimers containing axial aryloxy groups (**1a**, **2a**).[3] Combined with thermodynamic data[3] on ground-state energies and the observation[3] of 100% inversion of configuration in the displacement for Ar = 2,4-dinitrophenyl (**1b**) and *p*-NO_2Ph (**2b**), ground-state destabilization of these equatorial derivatives is supported as the principal rate-determining factor.

In order to gain confirmation of ground-state geometries, it is of interest to carry out single-crystal X-ray analyses. So far, the solid-state structure of phosphorinane **1b** having an equatorial phenoxy group has been reported.[4] We report additional X-ray studies on 2-(2,4-dinitrophenoxy)-2-oxo-*trans*-5,6-tetramethylene-1,3,2-dioxaphosphorinane (**3**) and 2-(*p*-methoxyphenoxy)-2-oxo-*trans*-5,6-tetramethylene-1,3,2-dioxaphosphorinane (**4**). The former contains an axial aryloxy group, and the latter, an equatorial aryloxy group.

Experimental Section

Synthesis. The (dinitrophenoxy)dioxaphosphorinane **3** was prepared by the addition of sodium 2,4-dinitrophenoxide to a toluene solution of 2-chloro-2-oxo-5,6-tetramethylene-1,3,2-dioxaphosphorinane.[3] Separation of isomers on a silica gel column and recrystallization from ethyl acetate gave the axial isomer **3**, mp 127–130 °C. The chlorodioxaphosphorinane is obtained from the reaction of phosphorus oxychloride with *trans*-2-(hydroxymethyl)-1-cyclohexanol in ether solution.[3] The latter compound may be prepared from cyclohexene and paraformaldehyde.

The (*p*-methoxyphenoxy)dioxaphosphorinane **4** was prepared[3] by the addition of sodium *p*-methoxyphenoxide to a toluene solution of 2-chloro-2-oxo-5,6-tetramethylene-1,3,2-dioxaphosphorinane. Purification by column chromatography and recrystallization from ethyl acetate–isopropyl ether gave the equatorial isomer **4**, mp 111–114 °C.

All X-ray crystallographic studies were done on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1)$ = 0.709 30 Å, $\lambda(K\alpha_2)$ = 0.713 59 Å) at an ambient temperature of 23 ± 2 °C. Crystals were mounted inside sealed thin-walled glass capillaries as a precaution against moisture sensitivity. Details of the experimental and computational procedures have been described previously.[5]

Crystal Data for $C_{13}H_{15}O_8N_2P$ (3): colorless crystal cut from a large brick-shaped crystal, 0.35 × 0.35 × 0.35 mm; space group, uniquely determined, $P2_1/c$ [C^5_{2h}–No. 14],[6] Z = 4, a = 12.214 (3) Å, b = 6.304 (3) Å, c = 20.229 (7) Å, β = 96.42 (2)°, $\mu(\text{Mo } K\bar{\alpha})$ = 0.233 mm^{-1}. A total of 3876 independent reflections ($+h,+k,\pm l$) were measured by using the θ–2θ scan mode for $2° \leq 2\theta(\text{Mo } K\bar{\alpha}) \leq 55°$. No corrections were made for absorption.

Crystal Data for $C_{14}H_{19}O_5P$ (4): colorless crystal, irregular, cut from a polycrystalline mass, approximately 0.25 × 0.25 × 0.38 mm; space group, uniquely determined, $P2_1/n$ (alternate setting of $P2_1/c$), Z = 4, a = 8.615 (3) Å, b = 11.485 (3) Å, c = 14.419 (2) Å, β = 92.25 (2)°, $\mu(\text{Mo } K\bar{\alpha})$ = 0.215 mm^{-1}. A total of 2493 independent reflections ($+h,+k,\pm l$) were measured by using the θ–2θ scan mode for $2° \leq 2\theta(\text{Mo } K\bar{\alpha}) \leq 50°$. No corrections were made for absorption.

Both structures were solved by using direct methods (MULTAN) and were refined (anisotropic non-hydrogen atoms; fixed isotropic H atoms) by using full-matrix least squares.[7] For **3**, H atom coordinates were calculated and updated as refinement converged so that the final C–H bond lengths were 0.98 Å. Calculable H atoms for **4** were treated in the same fashion, while coordinates for the three methyl H atoms were obtained from a difference Fourier synthesis. For **3**, the final agreement factors[8] were R = 0.041, R_w = 0.055, and GOF = 1.56

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[1] (a) University of Massachusetts. (b) University of Illinois, Chicago Circle.

[2] Gorenstein, D. G.; Rowell, R. *J. Am. Chem. Soc.* **1979**, *101*, 4925.

[3] Gorenstein, D. G.; Rowell, R.; Findlay, J. *J. Am. Chem. Soc.* **1980**, *102*, 5077.

[4] Van Nuffel, P.; Lenstra, A. T. H.; Geise, H. J. *Bull. Soc. Chim. Belg.* **1982**, *91*, 43.

[5] Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.

[6] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, p 99.

[7] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$. Mean atomic scattering factors were taken from: Reference 6, 1974; Vol. IV, pp 72–98. Real and imaginary dispersion corrections for O and P were taken from the same source, pp 149–150.

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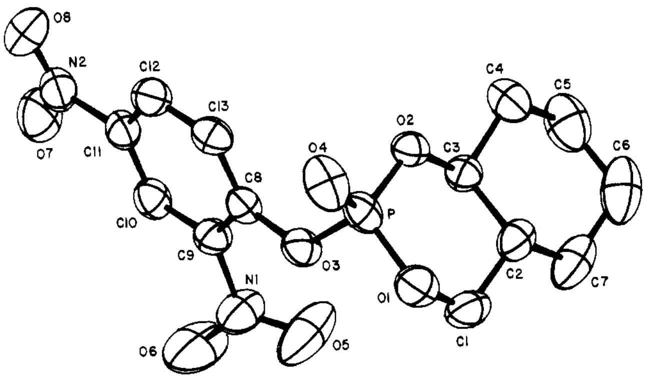

Figure 1. ORTEP plot of $(C_7H_{12}O_2)((NO_2)_2C_6H_3O)PO$ (**3**) with thermal ellipsoids at the 50% probability level. H atoms have been omitted for purposes of clarity.

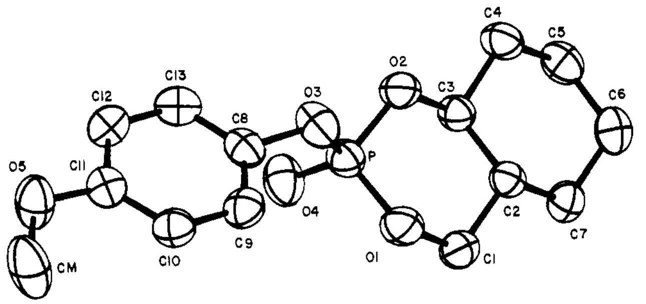

Figure 2. ORTEP plot of $(C_7H_{12}O_2)(CH_3OC_6H_4O)PO$ (**4**) with thermal ellipsoids at the 50% probability level. H atoms have been omitted for purposes of clarity. To facilitate comparisons of **3** and **4**, the molecule shown here is the inverse of that given in the coordinate list.

Table I. Atomic Coordinates in Crystalline $(C_7H_{12}O_2)((NO_2)_2C_6H_3O)PO$ (**3**)[a]

atom	10^4x	10^4y	10^4z
P	1714.7 (5)	8897 (1)	5693.1 (3)
O1	2016 (1)	10926 (3)	5314 (1)
O2	1131 (1)	7332 (3)	5176 (1)
O3	2930 (1)	7925 (3)	5883 (1)
O4	1114 (2)	9270 (3)	6259 (1)
O5	4726 (2)	7347 (4)	5304 (1)
O6	5970 (2)	5720 (5)	5909 (2)
O7	4964 (2)	−666 (3)	6959 (1)
O8	3508 (2)	−618 (4)	7469 (1)
N1	5019 (2)	6161 (4)	5749 (1)
N2	4110 (2)	163 (4)	7093 (1)
C1	2424 (2)	10660 (4)	4666 (2)
C2	1647 (2)	9305 (4)	4217 (1)
C3	1531 (2)	7116 (4)	4515 (1)
C4	713 (2)	5749 (5)	4102 (1)
C5	1065 (3)	5520 (6)	3401 (2)
C6	1201 (3)	7666 (7)	3085 (2)
C7	2017 (3)	9035 (5)	3518 (2)
C8	3169 (2)	5990 (4)	6170 (1)
C9	4202 (2)	5096 (4)	6111 (1)
C10	4511 (2)	3191 (4)	6409 (1)
C11	3778 (2)	2182 (4)	6771 (1)
C12	2756 (2)	3019 (4)	6845 (1)
C13	2453 (2)	4928 (4)	6541 (1)

[a] Numbers in parentheses are estimated standard deviations. Atoms are labeled to agree with Figure 1.

for the 2523 reflections having $I \geq 2\sigma_I$. For **4**, the corresponding values (1664 reflections) were $R = 0.043$, $R_w = 0.054$, and GOF = 1.44.

Results and Discussion

Table II. Atomic Coordinates in Crystalline $(C_7H_{12}O_2)(CH_3OC_6H_4O)PO$ (**4**)[a]

atom	10^4x	10^4y	10^4z
P	3994 (1)	2713 (1)	5613 (1)
O1	3816 (3)	4055 (2)	5469 (2)
O2	3229 (3)	2462 (2)	6561 (2)
O3	2743 (3)	2191 (2)	4916 (2)
O4	5566 (3)	2269 (2)	5531 (2)
O5	4103 (3)	470 (2)	1461 (2)
C1	4397 (4)	4789 (3)	6243 (2)
C2	3610 (4)	4452 (3)	7126 (2)
C3	3835 (4)	3175 (3)	7346 (2)
C4	3022 (4)	2801 (3)	8202 (2)
C5	3616 (4)	3533 (3)	9037 (2)
C6	3466 (4)	4821 (3)	8843 (2)
C7	4242 (4)	5174 (3)	7954 (2)
C8	3161 (4)	1774 (3)	4029 (2)
C9	3002 (4)	2509 (3)	3287 (3)
C10	3311 (4)	2096 (3)	2408 (2)
C11	3780 (4)	956 (3)	2298 (2)
C12	3928 (4)	224 (3)	3062 (3)
C13	3620 (4)	633 (3)	3936 (2)
CM	4038 (5)	1211 (4)	667 (3)

[a] Numbers in parentheses are estimated standard deviations. Atoms are labeled to agree with Figure 2.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for $(C_7H_{12}O_2)((NO_2)_2C_6H_3O)PO$ (**3**)[a]

	Bond Lengths		
P–O1	1.557 (2)	C5–C6	1.513 (5)
P–O2	1.552 (2)	C6–C7	1.520 (5)
P–O3	1.612 (2)	C7–C2	1.541 (4)
P–O4	1.446 (2)	O3–C8	1.368 (3)
O1–C1	1.463 (4)	C9–N1	1.466 (3)
O2–C3	1.480 (3)	C11–N2	1.466 (3)
C1–C2	1.504 (4)	N1–O5	1.193 (3)
C2–C3	1.519 (3)	N1–O6	1.203 (3)
C3–C4	1.502 (3)	N2–O7	1.224 (3)
C4–C5	1.534 (4)	N2–O8	1.220 (3)
	Bond Angles		
O1–P–O2	107.9 (1)	C3–C4–C5	109.4 (2)
O1–P–O3	99.6 (1)	C4–C5–C6	111.2 (3)
O1–P–O4	115.1 (1)	C5–C6–C7	111.1 (3)
O2–P–O3	105.1 (1)	C6–C7–C2	110.6 (2)
O2–P–O4	113.7 (1)	O3–C8–C9	118.3 (2)
O3–P–O4	114.1 (1)	O3–C8–C13	122.9 (2)
P–O1–C1	118.0 (2)	C8–C9–N1	122.0 (2)
P–O2–C3	119.6 (1)	C10–C9–N1	116.7 (2)
P–O3–C8	125.9 (1)	C9–N1–O5	120.0 (2)
O1–C1–C2	110.6 (2)	C9–N1–O6	116.8 (2)
C1–C2–C3	110.9 (2)	O5–N1–O6	123.2 (3)
C2–C3–O2	109.3 (2)	C10–C11–N2	118.3 (2)
O2–C3–C4	106.9 (2)	C12–C11–N2	119.6 (2)
C1–C2–C7	112.7 (2)	C11–N2–O7	118.2 (2)
C7–C2–C3	108.3 (2)	C11–N2–O8	118.1 (3)
C2–C3–C4	112.7 (2)	O7–N2–O8	123.6 (3)

[a] Standard deviations in parentheses. Atoms are labeled to agree with Figure 1.

The atom-labeling scheme for **3** is shown in Figure 1. Atomic coordinates are given in Table I, while selected bond lengths and angles are given in Table III. For **4**, the corresponding information is given in Figure 2 and Tables II and IV. For both compounds, anisotropic thermal parameters and hydrogen atom parameters are provided as supplementary material.

Comparison of Solid- and Solution-State Structures. As can be seen in Figures 1 and 2, the fused-ring systems of both molecules have the same conformation, where the six-membered rings are in the chair form. For **3**, the dinitrophenoxy substituent is axially placed, and for **4**, the methoxyphenoxy substituent is in the equatorial position.

The solid-state structure of **3** agrees with conclusions from NMR data[2,3] on the solution-state structure, indicating an axial orientation of the aryloxy group and a phosphorinane ring in a chair conformation. For **4**, solution NMR data[3] indicate

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(8) $R = \sum||F_o| - |F_c|| / \sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, and GOF $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where $N_v = 217$ and $N_o = 2523$ for **3** and $N_v = 181$ and $N_o = 1664$ for **4**.

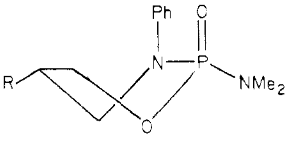
Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) in $(C_7H_{12}O_2)(CH_3OC_6H_4O)PO$ (4)[a]

Bond Lengths			
P–O1	1.563 (3)	C3–C4	1.506 (4)
P–O2	1.567 (2)	C4–C5	1.539 (5)
P–O3	1.565 (3)	C5–C6	1.510 (5)
P–O4	1.456 (3)	C6–C7	1.523 (5)
O1–C1	1.470 (4)	C7–C2	1.535 (5)
O2–C3	1.476 (4)	O3–C8	1.424 (4)
C1–C2	1.516 (4)	C11–O5	1.368 (4)
C2–C3	1.512 (4)	O5–CM	1.427 (5)

Bond Angles			
O1-P–O2	104.8 (1)	C1–C2-C7	111.0 (3)
O1-P–O3	103.3 (1)	C7–C2–C3	108.8 (3)
O1-P–O4	114.9 (1)	C2–C3–C4	112.9 (3)
O2-P–O3	100.8 (1)	C3–C4–C5	109.5 (3)
O2-P–O4	115.6 (2)	C4–C5–C6	111.5 (3)
O3-P–O4	115.6 (1)	C5–C6–C7	112.3 (3)
P–O1-C1	115.8 (2)	C6-C7–C2	110.9 (3)
P–O2-C3	114.8 (2)	O3–C8–C9	118.3 (3)
P–O3-C8	120.9 (2)	O3-C8–C13	119.4 (3)
O1-C1–C2	109.9 (3)	C10-C11-O5	124.0 (3)
C1–C2–C3	111.5 (3)	C12–C11–O5	115.9 (3)
C2-C3-O2	109.8 (3)	C11-O5-CM	117.5 (3)
O2–C3-C4	108.0 (3)		

[a] Standard deviations in parentheses. Atoms are labeled to agree with Figure 2.

a 50:50 mixture of chair and twist-boat conformers in $CDCl_3$, which increases to about 80% twist-boat in CH_3OH. This suggests the energy difference between the two conformers is quite small. As the X-ray results show, the chair form resulted on crystallization of **4**. This result parallels the X-ray study[4] of **1b** containing the unsubstituted phenoxy group, equatorially oriented. Here also, the chair form is observed. Similar to the conclusions from NMR data for **4**, approximately the same percentages of twist-boat and chair are indicated[3] in solution for the phenoxy derivative **1b**. The use of other crystallization techniques may provide a twist-boat conformation for crystallographic analysis. In the simpler phosphorinane systems, **5**[9] and **6**,[10] X-ray analyses have revealed twist-boat conformations. This same conformation is reported in solution for **6**.[10]



5 (R = Ph),[9] 6 (R = *t*-Bu)[10]

The near equality in energy indicated for the twist-boat and chair conformations of the *trans*-decalin systems, **1** and **2**, has been attributed[2] to a balance between an anomeric effect favoring the pseudoaxial orientation of the ester or amide group in the twist-boat and the 1,3-steric and eclipsing interactions favoring the chair conformation. Actually, the axial chair epimers are ~2 kcal/mol more stable than the equatorial chair epimers due to the anomeric effect.[2]

Further Structural Details. Although the nitro groups in **3** are essentially planar, they are rotated somewhat out of the plane of the phenyl ring, most probably to mitigate crowding. The dihedral angle between the plane of the nitro group containing N2 and the plane of the phenyl ring is 7.9°. For the nitro group containing N1, this value is 25.6°. Oxygen atoms O6, O7, and O8 are on the order of 2.4 Å away from the adjacent hydrogen atoms H10 and H12, which represents close contact in view of the van der Waals sum[11] of 2.6 Å for O and H. The distance between O5 and O3 is 2.625 (3) Å, which is less than the van der Waals sum of 2.8 Å.

Table V. Comparison of Bond Angles (deg) at Phosphorus for **3** and **4** with Values for Related Phosphorinane Triesters[a]

	axial ester (3)	equatorial ester (4)	av values[b] axial ester	av values[b] equatorial ester
O2–P–O3	105.1	100.8	105.9 ± 1.0	100.0 ± 0.8
O1–P–O3	99.6	103.3	101.7 ± 1.1	103.7 ± 2.6
O2–P–O1	107.9	104.8	106.2 ± 0.8	105.0 ± 0.3
O4–P–O3	114.1	115.6	115.5 ± 1.3	115.3 ± 0.7
O1–P–O4	115.1	114.9	113.1 ± 1.5	115.5 ± 1.0
O2–P–O4	113.7	115.6	113.1 ± 1.5	115.5 ± 1.0
Σ(R)OPO(R)	312.6	308.9	313.8	308.7
b = [Σ(R)OPO(R)]/3[c]	104.2	103.0	104.6	102.9
Σ(R)OP=O	342.9	346.1	341.7	346.1
a = [Σ(R)OP=O]/3[d]	114.3	115.4	113.9	115.4

[a] For **3**, the (R)O2-P–O3(R′) fragment is (*g*,*g*), and about (R)O1-P–O3(R′), it is (*g*,*t*). For **4**, owing to the retention of the O4 label for the phosphoryl oxygen, the (*g*,*g*) and (*g*,*t*) designations are reversed for these two fragments. However, these designations are not obeyed by **4**. [b] Represents average values from six crystal structures of phosphorinane triesters related to **3** and **4**. [c] The value of *b* is the average ester bond angle. [d] The value of *a* is the average phosphoryl ester angle.

Table VI. Torsional Angles for **3** and **4** (deg)

fragment	3	4[a]	fragment	3	4[a]
C3-O2-P-O3	66.4	160.6	C1-O1-P-O3	69.5	158.0
O2-P-O3-C8	61.4	153.5	O1-P–O3-C8	173.0	81.7

[a] See footnote *a* to Table V and the accompanying text.

The methoxy group in **4** is nearly coplanar with the phenyl ring. The dihedral angle between the plane defined by C11, O5, and CM and the plane of the phenyl group is 3.4°. The resulting crowding between the methyl group and H10 can be seen in the angles about C11. The angle C10–C11–O5 is opened to a value of 124.0 (3)°, while the angle O5–C11–C12 is compressed to 115.9 (3)°.

Comparison of dihedral angles between respective mean planes (Tables E and F, supplementary material) for **3** and **4** (Figure 3) shows that the *trans*-decalin structures are very similar. The largest difference exists at the O1–O2 hinge. A more flattened chair is seen for the dinitrophenoxy derivative **3**.

Examination of the bond distances shows the effect of the greater electron-withdrawing ability of the nitro groups compared to that of the methoxy substituent. The phenoxy O3–C8 distance in the former is considerably shorter in the dinitro compound, 1.368 (3) Å, compared to the case of the methoxy derivative, 1.424 (4) Å. The concentration of electron density indicated in the O3–C8 bond accounts for the longer P–O3 bond and shorter phosphoryl bond in **3** compared to those in **4**. The P–O3 distance in **3** is 1.612 (2) Å compared to 1.565 (3) Å for **4**. Greater π bonding is possible in the phosphoryl linkage P–O4 as this effect is lessened in the adjacent P–O3 bond in the dinitro compound **3**.

Bond Angle Coupling to Torsional Angles. On the basis of molecular orbital calculations and analysis of X-ray crystallographic structures of neutral phosphate triesters, Gorenstein et al.[12] had proposed that O–P–O bond angles were coupled to R–O–P–O(R′) torsional angles. Rotation about the P–O ester bond from a gauche to a trans conformation is predicted

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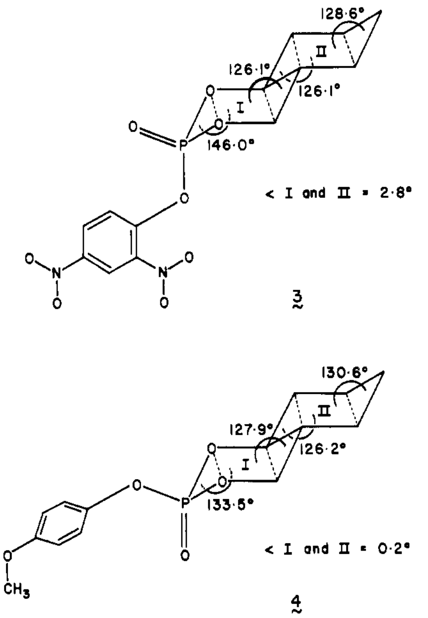


Figure 3. Schematic showing the dihedral angles at "hinges" in the *trans*-decalin system of **3** and **4**.

to result in a 5° reduction in the ester O–P–O bond angle.

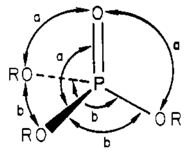
This coupling effect is borne out by the present X-ray results on **3** and **4**. For the axial ester (POX_{ax}) **3**, the O2–P–O3 angle of 105.1 (1)° is close to the average supported by previous X-ray results,[13a–d] 105.9 ± 1.0°, while the O1–P–O3 angle of 99.6 (1)° is just outside the average value for this angle observed in related structures, 101.7 ± 1.1°[13a–d] (Table V). The conformation about the (R)O2–P–O3(R′) structural fragment is gauche,gauche (*g,g*) and about the (R)O1–P–O3(R′) fragment is gauche,trans (*g,t*). Pertinent torsional angles are listed in Table VI.

For equatorial esters, similar though smaller coupling of bond and torsional angles exists. In cases where the bond angles deviate from predicted values, the dihedral angles about the (R)O1–P–O3(R′) or (R)O2–P–O3(R′) do not conform very well to the *g,g* or *g,t* description, respectively. Here, the corresponding average O–P–O angles are 103.7 ± 2.6 and 100.0 ± 0.8°.[4,13e,f] In the equatorial (POX_{eq}) ester **4**, these angles are 103.3 (1) and 100.8 (1)°, respectively. Even though the latter angles agree well with the average values in Table V, the torsional angles for **4** correspond more closely to *t,g* and *t,t* rather than *g,g* and *g,t* (Table VI).

Origin of ^{31}P Chemical Shift Differences between Axial and Equatorial Esters. Six-membered-ring phosphate triesters with an axial ester group have ^{31}P chemical shifts up to 6 ppm upfield from the isomeric phosphates with the ester group equatorial.[14] This chemical shift difference has been attributed to the O–P–O bond angle distortions that result from the torsional angle differences in the axial and equatorial esters as discussed in the previous sections.

As shown in Table V, the difference in the sum of the three ester angles for the related phosphorinanes is on the average 5.1° (313.8 vs. 308.7°, with the equatorial esters having smaller angles). For the axial ester **3** and equatorial ester **4** reported here, these sums (312.6 and 308.9°, respectively) agree well with the previous averages.

This decrease in ester O–P–O angles must, of course, be compensated by an increase in R(O)P=O bond angles as also shown in Table V and represented as



In the phosphorinane esters the bond angles are significantly distorted from tetrahedral values, and this distortion is greater for the equatorial esters. In these esters the ester bond angles (b) contract to an average of 103.0° while the phosphoryl ester angles increase to an average of 115.4° (Table V). Here also the respective values obtained for **3** and **4** agree closely with these average values. This further distortion from tetrahedral symmetry will lead to a hybridization change on phosphorus, which is quite likely responsible for the 4–6 ppm difference in epimeric ester ^{31}P chemical shifts.[14]

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Registry No. **3**, 74431-09-7; **4**, 74410-65-4.

Supplementary Material Available: Compilations of observed and calculated structure factor amplitudes and thermal parameters (Tables A and C), parameters for hydrogen atoms (Tables B and D), and least-squares planes (Tables E and F) for **3** and **4**, respectively (24 pages). Ordering information is given on any current masthead page.

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