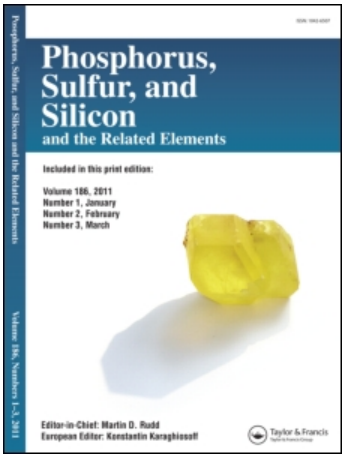

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X-RAY CRYSTALLOGRAPHIC STRUCTURES OF TWO POLYMORPHIC FORMS OF *CIS*-6-CARBOXY-2,10-DIOXA-1-PHOSPHABICYCLO-[4.4.0JDECANE 1-OXIDE

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X-RAY CRYSTALLOGRAPHIC STRUCTURES OF TWO POLYMORPHIC FORMS OF *cis*-6-CARBOXY-2,10-DIOXA-1-PHOSPHABICYCLO-[4.4.0]DECANE 1-OXIDE

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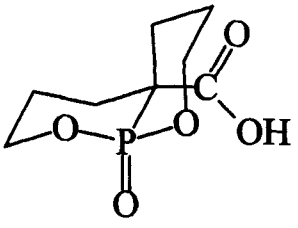
The title compound, *cis*-6-carboxy-2,10-dioxa-1-phosphabicyclo[4.4.0]decane 1-oxide (**4**), crystallizes in two different crystalline forms: **4a**, monoclinic, $P2_1/c$, a = 7.7702(5) Å, b = 7.1115(3) Å, c = 17.8577(10), β = 99.146(5)°, V = 974.46(10) Å^3, Z = 4, D_{calc} = 1.501 Mg m^{-3}, Cu Kα, λ = 1.54178 Å, μ = 2.51 mm^{-1}, F(000) = 464, T = 298(2) K, R = 0.041 and **4b**; orthorhombic, $P2_12_12_1$, a = 7.9188(8) Å, b = 10.8147(6) Å, c = 11.261(2), V = 964.4(3) Å^3, Z = 4, D_{calc} = 1.515 Mg m^{-3}, Cu Kα, λ = 1.54178 Å, μ = 2.54 mm^{-1}, F(000) = 464, T = 295(2)K, R = 0.046. In each form the structures are found to consist of two *cis*-fused six-membered rings, with each ring in the chair conformation. Both structures exhibit intermolecular hydrogen bonding of the form P=O· · ·H—O—C=O with **4a** in the form of dimers and **4b** in the form of helical chains. All corresponding bond lengths and angles are statistically the same for **4a** and **4b**. A significant difference in the orientation of the carboxy group in **4a** and **4b** was observed. This orientation of the carboxy group was investigated using molecular calculations at the PM3 level.

Key words: Polymorphic, bicyclic phosphonate, intermolecular hydrogen bonding, X-ray crystal structure, PM3 molecular calculation.

INTRODUCTION

Our interest in bicyclic phosphonates arose from the desire to develop a synthetic route to the previously unreported *trans*-fused isomer[1] of the parent compound *cis*-2,10-dioxa-1-phosphabicyclo[4.4.0]decane 1-oxide (**1**).[2,3,4] Since the two analogous model compounds, decalin and 2,10-dioxabicyclo[4.4.0]decane (**2**)[5,6] exist in

both *cis* and *trans* isomeric forms, the goal was to synthesize both isomers of this bicyclic phosphonate. As discovered in a derivative of **1**, *cis*-6-methoxycarbonyl-2,10-dioxa-1-phosphabicyclo[4.4.0]decane 1-oxide (**3**),[7] only one isomer of the title compound, *cis*-6-carboxy-2,10-dioxa-1-phosphabicyclo[4.4.0]decane 1-oxide (**4**), was synthesized. The X-ray crystal structure study was undertaken to unambiguously assign the *cis*-fused configuration of **4** and gain additional information that may shed light on the apparent stability of the *cis*-fused configuration of **1** (or instability of the *trans* configuration).



4

The first crystallization of **4** (*via* slow evaporation of $CHCl_3$ at room temperature) gave slightly opaque irregularly shaped needles from which a crystal suitable for structural determination was found. From this procedure the monoclinic form **4a** was obtained. However, when recrystallization was attempted (*via* rapid evaporation of $CHCl_3$ with a N_2 stream) for an analytical investigation, clear plates formed. Surprised by the difference between the two crystals, a second crystallographic study was performed using the new crystals in anticipation of discovering a unique form. As expected, the second structural study resulted in a different molecular arrangement: orthorhombic **4b** form.

EXPERIMENTAL

Synthesis

General: The reaction was carried out in flame dried glassware under a nitrogen atmosphere. The ^1H,^{13}C and ^{31}P NMR spectra were taken on a GE OMEGA 300 NMR spectrometer. The ^{31}P NMR chemical shifts in ppm are relative to 85% phosphoric acid (external standard) with ^1H and ^{13}C NMR chemical shifts reported in ppm referenced to TMS or $CDCl_3$. All solvents and reagents were purchased from Aldrich Chemical Co. (Milwaukee, WI) and were purified by standard literature methods. The elemental analysis was performed by Midwest Microlab of Indianapolis, IN. The starting material, **3**, was synthesized according to literature methods.[1]

cis-6-carboxy-2,10-dioxa-1-phosphabicyclo[4.4.0]decane 1-oxide (**4**): To a solution of the bicyclic methyl ester **3** (0.27 g, 1.15 mmol) in 30 mL of MeOH, approx. 1 mL of a 1.2 mol/L NaOH aq. solution was added (pH of final solution 12-14 by pH paper). The reaction mixture was then heated at reflux for 48h. Most of the MeOH was removed under vacuum. The residues were taken up in 10 mL 5% HCl solution and extracted with 8 × 10 mL CH_2Cl_2 (the product is quite soluble in water). The combined organic layers were dried over Na_2SO_4 and the solvent removed. This afforded 0.17 g (68%) of **4** as a white solid. An analytical sample was obtained by recrystallization from $CHCl_3$ mp 200–202°C. ^{13}C NMR ($CDCl_3$) δ 172.90 (J_{PC} = 2.4 Hz), 70.6 (J_{PC} = 7.3 Hz), 45.0 (J_{PC} = 112.3 Hz), 30.2 (J_{PC} = 7.3 Hz), 22.7 (J_{PC} = 7.3 Hz). ^1H NMR ($CDCl_3$) δ 7.5 (bs, 1H), 4.25–4.55 (m, 4H), 2.35–2.55 (m, 2H), 1.98–2.16 (m, 2H), 1.82–1.98 (m, 4H). ^{31}P NMR ($CDCl_3$) δ 18.7. Anal. Calcd. for $C_8H_{13}O_5P$: C, 43.64; H, 5.95. Found: C, 43.68; H, 6.06.

X-ray Crystal Structure Determinations

4a: Crystals (mp 200–202°C) were grown from slow evaporation of $CHCl_3$ at room temperature. All measurements were made on a Picker diffractometer automated with PCXTL data collection software.[8] Data handling, reduction and analysis were performed using NRCVAX.[9] The data were collected using Cu Kα (1.54184 Å) radiation and the θ-2θ scan technique. The intensities of three reflections were checked every 120 minutes. No absorption corrections were applied. The structure was solved by direct methods using SOLVER, with the remaining heavy atoms localized by difference Fourier synthesis.[9] All H-atoms, except for H5, were allowed to ride on the heavy atom with temperature factors 1.2 times the equivalent isotropic factor of the heavy atom. H5, the hydrogen atom bonded to O5, which intermolecularly hydrogen bonds to O1′, had positional parameters refined. The structure was refined by full-matrix least-square refinement using SHELXL-93[10] to a final R and R_w[11] of 0.041 and 0.101, respectively. Experimental details for both structures are listed in Table I.

TABLE I

Crystal data and summary of intensity data collection and structure refinement for **4a** and **4b**

	4a	**4b**
Compound	$C_8H_{13}O_5P$	$C_8H_{13}O_5P$
Color/Shape	opaque/needles	clear/plates
For. wt.	220.16	220.16
Space group	$P2_1/c$	$P2_12_12_1$
Temp., °C	25±2	22±1
Cell Constants (# refl, range 2θ)	20, 10 → 28	25, 20 → 26
a, Å	7.7702(5)	7.919(1)
b, Å	7.1115(3)	10.815(1)
c, Å	17.8577(10)	11.261(2)
α, deg	90	90
β, deg	99.146(5)	90
γ, deg	90	90
V	974.46(10)	964.4(3)
Z	4	4
Radiation, monochromator	Cu Kα, none	Cu Kα, graphite
μ, cm^{-1}	25.1	25.4
Crystal dimensions	0.3 x 0.3 x 0.3	0.25 x 0.22 x 0.15
Diffractometer	Picker	Enraf-Nonius CAD4
Scan method	θ -2θ	ω - 2θ
h, k, l range	-7→7, 0→6, 0→17	0→9, 0→13, 0→14
F_{000}	464	464
Data collected	798	1148
Observed reflections	681 [I> 2.5σ(I)]	957 [F_o^2>2σ(F_o^2)]
R(F_o)	0.041	0.046
$R_w(F_o^2)$	0.101	0.131
GoF	0.78	1.004

4b: The enantiomorphic crystals (mp 202–203°C) were grown from the rapid evaporation of $CHCl_3$ with a stream of dry nitrogen gas. All measurements were made on an Enraf-Nonius CAD4 computer controlled diffractometer equipped with a graphite crystal incident beam monochromator. The data were collected using Cu Kα (1.54184 Å) radiation and the ω-2θ scan technique. No absorption corrections were applied. The structure was solved using SHELX-76.[12] All H-atoms, except H5, were included in the refinement but restrained to ride on the atom to which they were bonded. H5, the hydrogen atom bonded to O5, which intermolecularly hydrogen bonds to O1′, had positional parameters refined. The structure was refined by full-matrix least-square refinement using SHELXL-93[10] to a final R and R_w[11] of 0.046 and 0.131, respectively. The absolute structure was confirmed using the Flack parameter (x = 0.030).[13] Experimental details for both structures are listed in Table I.

Molecular Calculations

Semiempirical calculations were performed using PM3[14] with standard parameters using a HyperChem[15] software package installed on a Gateway 2000 4DX2-66V microcomputer. Optimization was continued until the heat of formation gradient was lower than 0.01 kcal mol^{-1} $Å^{-1}$. Single point calculations were run for each ten degree change in the P1—C1—C8—O5 torsional angle on the three different forms of **4**: **4a**, **4b** and the optimized structure.

RESULTS AND DISCUSSION

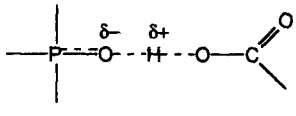
X-Ray Crystal Structures

The ORTEP diagrams for **4a** (35% probability ellipsoids) and **4b** (50% probability ellipsoids) are shown in Figure 1. Fractional coordinates and the equivalent isotropic displacement parameters for both forms are given in Table II. Selected bond lengths, angles and torsional angles are given in Table III.

Both studies confirm that **4** consists of *cis*-fused six-membered rings, both in the chair conformation. The torsional angles of each ring fall in the range of $\pm 60 \pm 10°$ except those about P1—C1 [C2—C1—P1—O3 34.8(2)° (**4a**), 35.0(3)° (**4b**)], P1—O3 [C1—P1—O3—C4 −43.6(3)° (**4a**), −42.3(4)° (**4b**)] and C1—C2 [P1—C1—C2—C3 −43.0(3)° (**4a**), −45.5(5)° (**4b**)], which are similar to the results obtained previously.[4,7] The flattening of the ring about these bonds may be the result of reduced steric repulsions of axial substituents, such as: the axial C2 hydrogen with the axial C6 hydrogen, and the axial C3 hydrogen with the carboxy group and the lone pairs of O3.

As with **1**[4] and **3**[7] the phosphoryl-substituent torsional angle [O1—P1—C1—X where X = H or C8] in **4** is significantly less than the idealized angle of 60°. The angles of 39.4(3)° (**4a**) and 39.0(4)° (**4b**) are also consistent with a minimized steric axial interaction of the substituent and the axial hydrogen of C3.

The P1—O1 (P=O) distances of 1.472(4) Å (**4a**) and 1.475(3) Å (**4b**) are slightly outside the reported upper and lower quartiles[16] of 1.454–1.462 Å for $C(O)_2P{=}O$ bond lengths.[17] Both are also significantly longer than the P=O bond lengths of 1.457(3) Å and 1.455(2) Å for **1**[4] and **3**,[7] respectively. Hydrogen bonding of the carboxy group with the phosphoryl oxygen is observed in both forms (*vide infra*). Due to these hydrogen bonds, the longer P=O bond of **4** compared to **1** and **3** may be the result of a contribution of the hybrid form shown below.



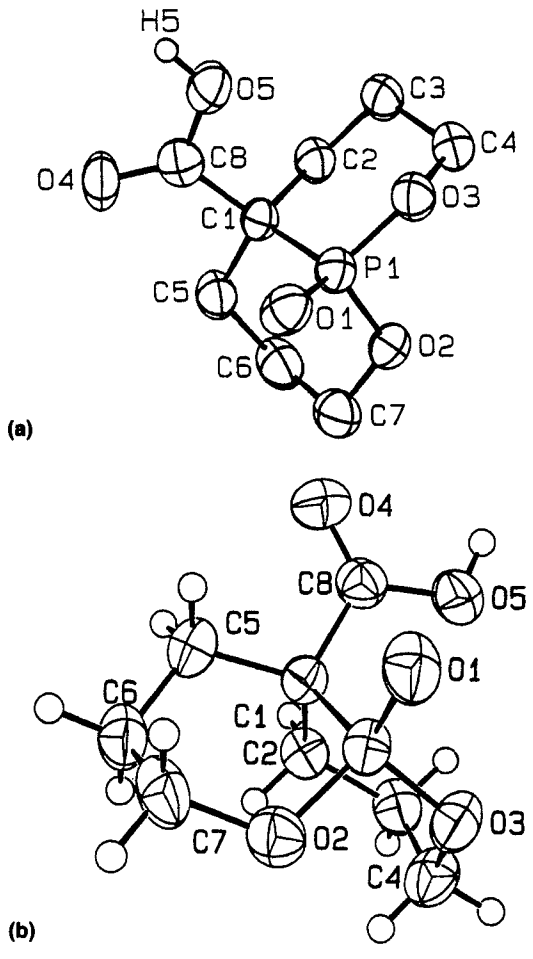


FIGURE 1 Molecular structure of *cis*-6-carboxy-2,10-dioxa-1-phoshabicyclo[4.4.0]decane 1-oxide, found in the forms **4a** and **4b**.

TABLE II

Atomic coordinates and equivalent isotropic displacement parameters [U_{eq}[a] or B,[b] ($Å^2$)] for **4a** and **4b**

4a	**x/a**	**y/b**	**z/c**	U_{eq}
P1	0.7669(1)	0.4532(2)	0.1427(1)	0.059(1)
O2	0.8618(3)	0.4167(5)	0.2259(1)	0.066(2)
O5	0.6140(4)	0.3182(6)	-0.0188(2)	0.074(2)
O3	0.9202(3)	0.5109(4)	0.1012(1)	0.065(2)
O4	0.4050(4)	0.1914(6)	0.0357(2)	0.089(2)
C2	0.8490(5)	0.1026(7)	0.0941(3)	0.066(3)
O1	0.6297(4)	0.5976(4)	0.1368(1)	0.070(2)
C8	0.5535(7)	0.2409(7)	0.0389(3)	0.064(4)
C1	0.6919(5)	0.2243(7)	0.1104(2)	0.055(3)

TABLE II (*Continued*)

4a	x/a	y/b	z/c	U_{eq}
C6	0.7097(7)	0.1297(10)	0.2507(3)	0.081(4)
C7	0.7647(6)	0.3216(10)	0.2788(3)	0.083(4)
C5	0.6024(6)	0.1311(8)	0.1721(3)	0.071(3)
C4	1.0550(6)	0.3725(8)	0.0926(3)	0.075(4)
C3	0.9793(6)	0.1995(8)	0.0530(3)	0.071(3)
4b	x/a	y/b	z/c	B
P1	0.0310(2)	0.4569(1)	0.4622(1)	3.27(2)
O2	-0.1388(5)	0.5336(4)	0.4527(3)	4.13(8)
O5	0.3328(5)	0.3545(4)	0.5856(4)	4.76(9)
O3	0.1649(5)	0.5498(4)	0.4140(3)	4.21(8)
O4	0.1691(6)	0.2579(4)	0.7157(4)	5.4(1)
C2	0.1180(7)	0.5667(5)	0.6740(5)	3.6(1)
O1	0.0333(5)	0.3396(3)	0.3953(3)	4.37(8)
C8	0.1922(6)	0.3410(5)	0.6466(5)	3.7(1)
C1	0.0611(6)	0.4402(4)	0.6210(4)	3.14(9)
C6	-0.2618(7)	0.4756(5)	0.6422(5)	4.4(1)
C7	-0.2886(7)	0.4814(6)	0.5115(6)	4.7(1)
C5	-0.1097(7)	0.3977(5)	0.6754(5)	4.1(1)
C4	0.2021(8)	0.6626(5)	0.4812(5)	4.6(1)
C3	0.2553(7)	0.6341(5)	0.6055(5)	4.2(1)

[a] $U_{eq}=1/3\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$

[b] $B = 4/3[a^2\beta(1,1)+b^2\beta(2,2)+c^2\beta(3,3)+ab(\cos\gamma)\beta(1,2)+ac(\cos\beta)\beta(1,3)+bc(\cos\alpha)\beta(2,3)]$

TABLE III

Selected bonds lengths, angles and torsional angles (Å, deg)

Bond Lengths

	4a	4b		4a	4b		4a	4b
P1-O1	1.472(4)	1.475(3)	P1-O2	1.572(3)	1.583(4)	P1-O3	1.555(4)	1.558(4)
P1-C1	1.794(5)	1.814(5)	O2-C7	1.465(7)	1.471(7)	O3-C4	1.464(7)	1.466(6)
O4-C8	1.199(7)	1.203(6)	O5-C8	1.319(7)	1.317(6)	C1-C5	1.543(8)	1.554(7)
C2-C1	1.561(7)	1.560(6)	C2-C3	1.509(8)	1.520(7)	C4-C3	1.493(8)	1.494(8)
C6-C5	1.515(8)	1.516(8)	C6-C7	1.492(10)	1.489(8)	C8-C1	1.537(7)	1.520(7)

Bond Angles

	4a	4b		4a	4b		4a	4b
O1-P1-O2	114.1(2)	115.3(2)	O1-P1-O3	112.5(2)	111.6(2)	O1-P1-C1	114.5(2)	114.6(2)
O2-P1-O3	102.4(1)	102.6(2)	O2-C7-C6	110.7(5)	110.2(4)	O2-P1-C1	103.6(2)	103.3(2)

TABLE III (*Continued*)

Bond Angles

	4a	4b		4a	4b		4a	4b
O3-P1-C1	108.7(2)	108.6(2)	O3-C4-C3	111.7(4)	111.6(4)	O4-C8-O5	123.0(5)	123.3(5)
O4-C8-C1	123.9(5)	123.1(5)	O5-C8-C1	113.1(5)	113.6(4)	P1-O2-C7	118.2(3)	117.0(4)
P1-O3-C4	119.2(3)	119.6(3)	P1-C1-C2	109.8(3)	109.5(3)	P1-C1-C5	108.7(4)	107.7(3)
P1-C1-C8	110.3(4)	110.3(3)	C1-C2-C3	116.3(5)	115.7(4)	C1-C5-C6	114.8(4)	115.4(4)
C2-C1-C5	110.5(4)	111.1(4)	C2-C1-C8	110.7(4)	110.4(4)	C2-C3-C4	113.0(5)	111.9(5)
C5-C6-C7	113.1(5)	112.4(5)	C5-C1-C8	106.9(4)	108.1(4)			

Torsional Angles

	4a	4b		4a	4b
O1-P1-O3-C4	-171.6(4)	-169.5(4)	O1-P1-C1-C8	39.4(3)	39.0(4)
O3-P1-C1-C2	34.8(2)	35.0(4)	O4-C8-C1-P1	-116.7(5)	-129.8(5)
O5-C8-C1-C2	-59.3(4)	-70.8(6)	P1-O3-C4-C3	56.7(3)	56.2(6)
C1-C2-C3-C4	56.4(4)	59.8(6)	O2-C7-C6-C5	-56.5(4)	-58.9(6)
O3-C4-C3-C2	-59.5(4)	-61.0(6)	C1-P1-O3-C4	-43.6(3)	-42.3(4)
C3-C2-C1-P1	-43.0(3)	-45.5(5)	C3-C2-C1-C5	-162.8(6)	-164.1(4)
P1-C1-C5-C6	-51.9(3)	-51.7(5)	C7-C6-C5-C1	57.0(4)	58.1(6)

This form would have the net effect of lengthening the P=O bond of **4** relative to **1** and **3**.

Bellard *et al.*[4] indicated that in the parent structure the P1—O3 bond was shorter than the P1—O2 bond by 0.024(4) Å. Due to the inherent dyssymmetry in the molecule the two endocyclic P—O distances of **4** are also nonequivalent [P1—O2 1.572(3) Å (**4a**), 1.583(4) Å (**4b**) compared to P1—O3 1.555(4) Å (**4a**) 1.558(4) Å (**4b**)].

Inspection of the results from both forms indicates that the two molecules are nearly identical with respect to corresponding bond lengths and bond angles. The only major difference between the two forms lies in the orientation of the carboxy group relative to the P1—C1 bond. In **4a** the P1—C1—C8—O5 torsional angle is 62.3(3)° which places the carbonyl nearly eclipsed with respect to the C1—C5 bond [O4—C8—C1—C5 1.2(3)°]. This corresponds to 49.9(5)° P1—C1—C8—O5 torsional angle in **4b** and a less eclipsed angle for the carbonyl of −12.3(7)° [O4—C8—C1—C5]. Apparently the different modes of hydrogen bonding (*vide infra*) play an important role in the orientation of the carboxy group.

Hydrogen Bonds

Figure 2 shows the hydrogen bonding exhibited in each form. In both forms the intermolecular hydrogen bond is of the type P=O· · ·H—O—C=O and not of the type C=O· · ·H—O. Although monocarboxylic acids almost invariably form

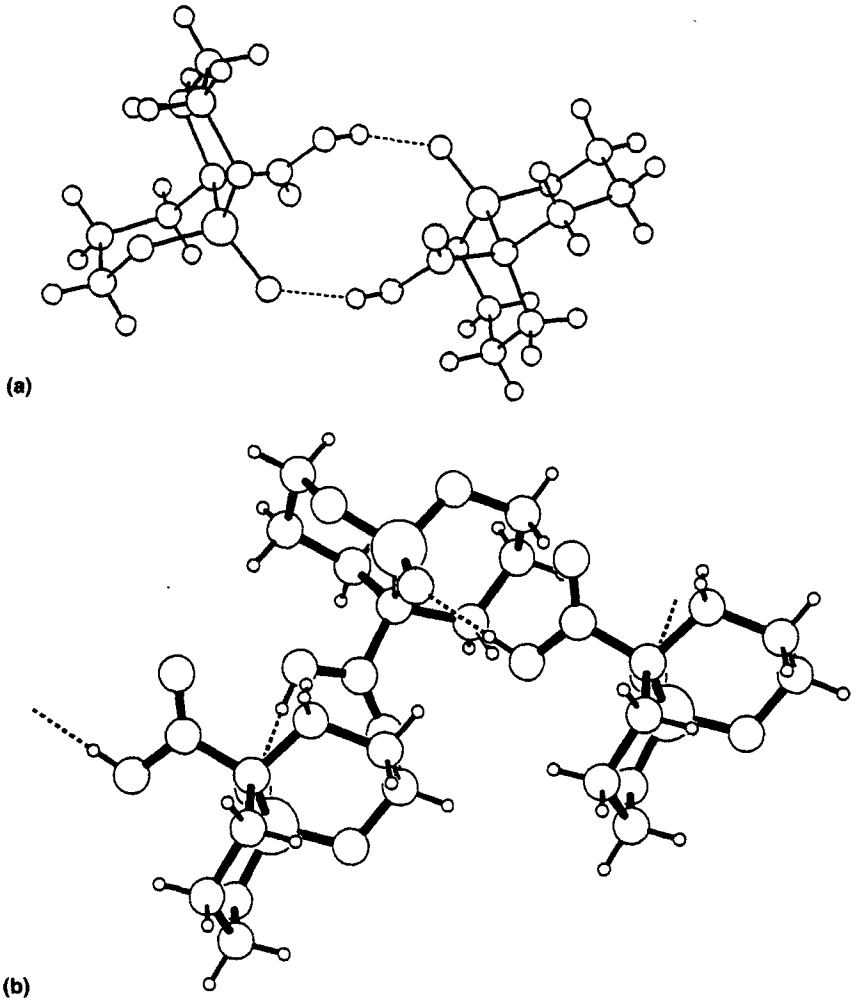


FIGURE 2 Diagrams showing the intermolecular hydrogen bonds of the form O5—H5· · ·O1′=P1′ for **4a** (dimer) and **4b** (polymer chains).

hydrogen bonded dimers,[18] in the presence of a phosphoryl group, the acid's hydrogen is directed toward the phosphoryl oxygen to form primarily chains (polymers) *via* strong hydrogen bonds.[19,20,21] In the formation of 1:1 adducts of carboxylic acids and triphenylphosphine oxide the mode of interaction is the strong hydrogen bond formed between the P=O and acid hydrogen.[21,22] These results are in accord with the better proton acceptor ability of the phosphoryl oxygen relative to the carbonyl of the carboxy group.[22]

In **4a** the intermolecular hydrogen bonds result in the formation of dimers, with the intermolecular O5· · ·O1′ distance of 2.669(8) Å. The angle about H5 is 163(7)° with distances of 0.83(6) Å and 1.86(6) Å for O5—H5 and H5· · ·O1′, respectively. The centroid of the two associated molecules was found to be a center of crystallographic symmetry, located at (1/2, 1/2, 0) within the monoclinic unit cell.

The intermolecular hydrogen bonds in **4b** are associated in helical chains running parallel to the *a* axis along a twofold screw axis as shown in Figure 3. The intermolecular O5· · ·O1′ (x + .5, −y + .5, −z + 1) distance for **4b** is 2.641(6) Å, with an angle about H5 of 160(9)°.

Both hydrogen bonds have nearly linear associations (O—H· · ·O ~ 163°) with close O5· · ·O1′ interactions (<2.67 Å). Thus, despite the fact that the molecular packing modes are quite different (dimer versus helical chains), the O—H· · ·O environments about hydrogen bonds are extremely similar.

Previous studies on the polymorphic forms of O-methylphenylphosphinylacetic acid by Gałdecki and Główka[20a,e] are analogous to this work on **4**. Hydrogen bonds of the form P=O· · ·H—O—C(O) were found in the initial study of the racemic crystal structure ($P2_1/c$) which formed dimers. In the second structure, the (−) enantiomer ($P4_12_12$), molecules are connected with strong hydrogen bonds into chains with an O· · ·O distance of 2.57 Å. In both forms of O-methylphenylphosphinylacetic acid (as with **4a** and **4b**) the O—H· · ·O environments are very similar. Corresponding bond lengths and angles were statistically identical for both crystals of O-methylphenylphosphinylacetic acid which parallels the result from **4**. While hydrogen bonding usually occurs *via* chains for these bifunctional molecules (CO_2H and P=O), there is precedence for the formation of dimers.

Molecular Calculations

As previously noted the largest structural difference between **4a** and **4b** involves the orientation of the carboxy group. Thus, we set out to investigate this orientation using PM3 calculations. Three structures were modeled: 1) **4a**, 2) **4b** and 3) a geometry optimized structure. Each crystallographic structure was used as a starting point in the optimization process; the same optimized structure was obtained in each case. The single point energy was calculated for every ten degree change in the P1—C1—C8—O5 torsional angle. Figure 4 graphically displays the results from these calculations where "○" = **4a**, "□" = **4b**, and "△" = optimized structure.

At the minima near ~60° the carbonyl group eclipses the C1—C5 bond. The torsional angle found in the optimized structure was 65° (P1—C1—C8—O5) which gives a totally eclipsed C5—C1—C8—O4 conformation (0.2°). The calculated maxima occur at ~165° and 345°, nearly 15° from eclipsed conformations. These results point to the nonbonding steric repulsion of either the OH or C=O with the phosphoryl oxygen as the determining factor in the location of the energy

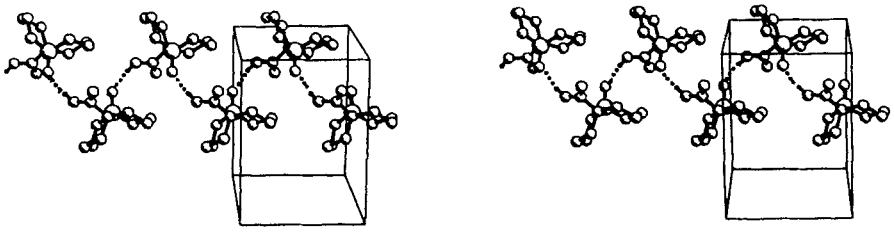


FIGURE 3 Packing diagram for **4b** showing the helical chains formed by the hydrogen bonds.

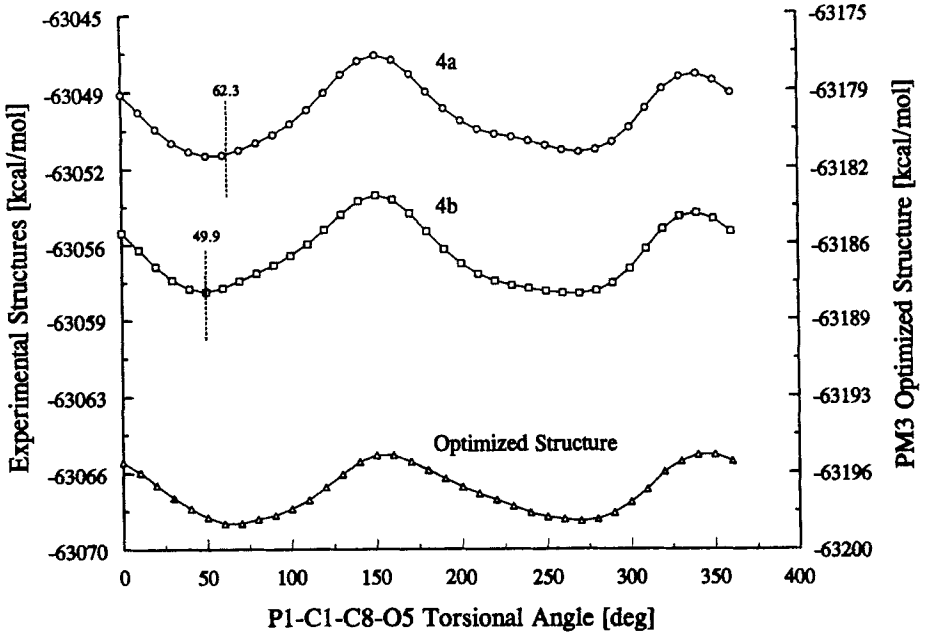


FIGURE 4 Energy diagram obtained for "○" = **4a**, "□" **4b**, and "△" = optimized structure from PM3 level molecular calculations. Left axis displays energy for **4a** and **4b** while the right axis displays the energy level for the optimized structure. The single point energy was calculated for every 10° change in the P1—C1—C8—O5 torsional angle. The dashed lines represent the measured angles from the crystal structures of the respective forms.

maximum. Geometry optimization of the bicyclic phosphonite, *cis*-6-carboxy-2,10-dioxa-1-phosphabicyclo[4.4.0]decane (the reduced analog of **4**), showed the carboxy group in a non-eclipsing conformation with torsional angles of 113° and 46° for P1—C1—C8—O5 and C5—C1—C8—O5, respectively.

Although the crystal structures manifest a significant P1—C1—C8—O5 torsional angle difference, the calculations indicate that both measured angles are near the energy minimum for this torsion. The general shape of the three energy diagrams is the same which indicates that there are no large differences in the three structures. This also means that these calculations cannot be used to predict polymorphic forms of **4**. The overall energy of the optimized structure is lower due to a general flattening of both rings which leads to reduced axial interactions.

CONCLUSION

These two crystal structures represent the second example of a bifunctional molecule (P=O, CO_2H) which crystallizes with distinct hydrogen bonding molecular packing modes; **4a** in dimers and **4b** in polymer chains. The hydrogen bonding in both cases involved the phosphoryl oxygen and not the carbonyl oxygen. The major difference between **4a** and **4b** lies in the orientation of the carboxy group which was investigated using PM3 calculations.

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