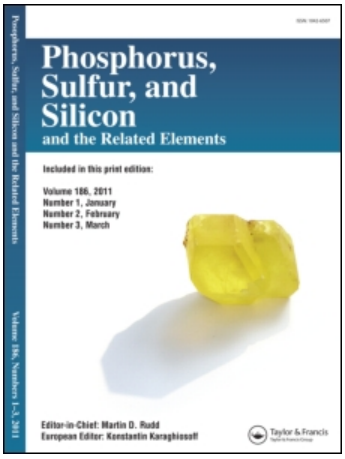

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THE CRYSTAL AND MOLECULAR STRUCTURE OF 2-DIMETHOXYPHOSPHINYL-2-METHOXY-2-PHENYLACETALDEHYDE OXIME. A SINGLE-CRYSTAL X-RAY DIFFRACTION STUDY

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THE CRYSTAL AND MOLECULAR STRUCTURE OF 2-DIMETHOXYPHOSPHINYL-2-METHOXY -2-PHENYLACETALDEHYDE OXIME. A SINGLE-CRYSTAL X-RAY DIFFRACTION STUDY

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Characterization by x-ray crystallography of 2-dimethoxyphosphinyl-2-methoxy-2-phenylacetaldehyde oxime (**I**) is described. Crystals of **I** belong to the space group, *Pbca*, with cell dimensions at 298 K of $a = 10.748(3)$ Å, $b = 12.273(4)$ Å, $c = 20.323(7)$ Å, $V = 2681(1)$ Å^3 and $Z = 8$. Solution and refinement of the intensity data gave final residuals of $R_F = 4.41\%$ and $R_{wF} = 4.35\%$ using 1511 unique reflections with $F_0 > 3\sigma F_0$. The crystal consists of a racemic mixture of molecules with R and S configurations about C(1) but only the E isomer of the oxime. Bond distances of 1.466(2) Å (P=O), 1.561(6) Å ⟨av⟩ (P—O), 1.267(4) Å (N—C), and 1.407(3) Å (N—O) are found in **I**. Unsymmetrical intermolecular hydrogen bonds between R and S enantiomers, are formed by the P=O · · · H—O—N framework. The O · · · O separation for this bond is 2.682(2) Å, while the O—H and O · · · H distances are 0.97(3) Å and 1.72(2) Å, respectively.

INTRODUCTION

It has been reported,[1,2] that trimethyl phosphite reacts with β-nitrostyrene, in 2-methyl-2-propanol, to produce 2-dimethoxyphosphinyl-2-methoxy-2-phenyl-acetalehyde oxime, **I**. The proposed mechanism for this reaction (shown in Scheme 1), involves initial attack of trimethylphosphite at the α-carbon[1,3] of β-nitrostyrene, to form a zwitterion, **II**, which rearranges to the proposed cyclic intermediate, **III** (attack at nitro oxygen could also lead to **III**,[1,4] but existing data suggest this is unlikely).[1,2]

Methoxide ion attack on **III** can occur *cis* or *trans* with respect to the bridging oxygen to form a racemic mixture of the Arbuzov[5–8] product, **I**. The R and S isomers may have either the Z or E configuration about the oxime linkage, depending on the relative rates of rotation about the N—C bond after the N—O bridge is broken in **III**. That only the E isomer is isolated may be due to preferential crystallization and the observed intermolecular hydrogen bonding (*vide infra*).

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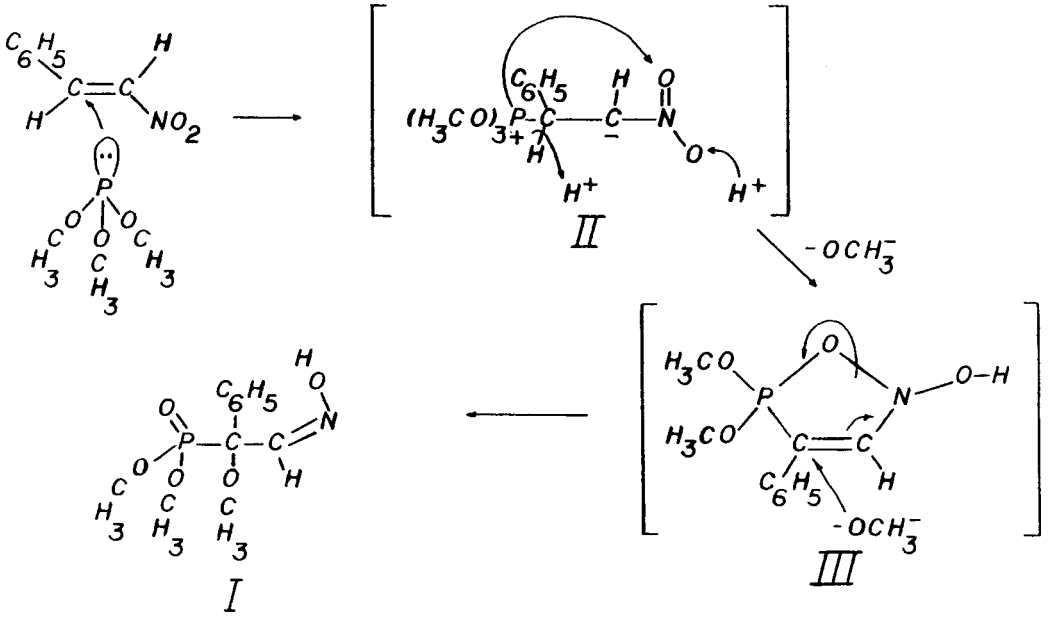

SCHEME 1

The chemical structure of **I**, was correctly deduced from ^{1}H NMR, IR and mass spectral fragmentation patterns.[1,2] Given the extraordinary complexity of the route to **I**, it seemed necessary to characterize **I** unambiguously. We now report the results of an x-ray crystallographic structural study.

RESULTS AND DISCUSSION

The *ORTEP* and atom labeling scheme are shown in Figure 1. Selected bond distances and angles are given in Table I, while the final positional and anisotropic thermal parameters are presented in Tables II and III.

As shown in Figure 2, molecules of **I** crystallize as pairs of R and S enantiomers joined by hydrogen bonds. The hydrogen-bond framework is formed by O(5) and H(O5) of one molecule and the unique oxygen, O(1)′, of a phosphonate group on an adjacent molecule [$x' = -0.5 + x$, $y' = y$, and $z' = 0.5 - z$]. The O(5)—O(1)′ and O(5)—H(O5) bond distances for **I** are similar to those in α-2,4,7-trimethylperhydroisorazolo[2,3-a]pyridine-2,7-dicarbaldehyde diioxime[O—O′: 2.794(6) Å and O—H: 0.88(5) Å].[9] Supportive of the hydrogen-bond interaction, the O(1)′—O(5) bond distance is 0.12 to 0.32 Å[10,11] shorter than the sum of the van der Waals radii. The O(1)′—H(O5)—O(5) angle (approximately 170°) and the unsymmetrical O—H bond distances [O(1)′—H(O5): 1.720(24) Å and O(5)—H(O5): 0.975(33) Å] are consistent with previous work.[10,12]

The O(5)—N(1) and N(1)—C(5) bond distances in **I** are similar to values found previously for oximes [1.414(7) Å ⟨av⟩ and 1.263(16) Å ⟨av⟩, respectively][9,13-15] and are slightly shorter than the sum of the covalent radii of singly bonded N—O atoms

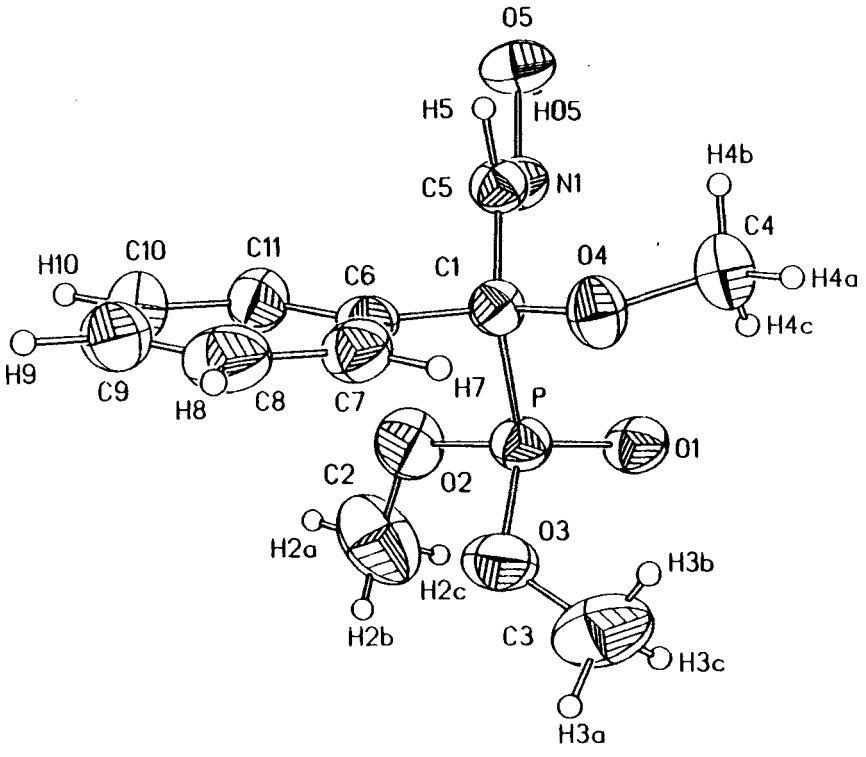

FIGURE 1. ORTEP drawing of **I** with nonhydrogen atoms having ellipsoids drawn at 50% of their size. The hydrogen atoms are shown with an arbitrary size.

TABLE I

Selected bond distances (Å) and bond angles (deg) for I

	(a) Bond distances		
P—O(1)	1.466(2)	C(1)—O(4)	1.431(3)
P—O(2)	1.555(3)	C(2)—O(1)	1.433(5)
P—O(3)	1.567(2)	C(3)—O(3)	1.420(5)
P—C(1)	1.857(3)	C(4)—O(4)	1.445(3)
N(1)—O(5)	1.407(3)	C(1)—C(5)	1.499(4)
N(1)—C(5)	1.267(4)	C(1)—C(6)	1.534(4)
O(5)—H(O5)	0.975(33)	C—C	1.377(9)[a]
O(5)—O(1)	2.682(2)		
	(b) Bond angles		
O(1)—P—O(2)	116.1(1)	O(1)—P—O(3)	113.6(1)
O(2)—P—O(3)	103.0(1)	O(1)—P—C(1)	114.9(1)
O(2)—P—C(1)	104.1(1)	O(3)—P—C(1)	103.7(1)
P—O(2)—C(2)	123.9(3)	P—O(3)—C(3)	122.7(2)
C(1)—O(4)—C(4)	117.4(2)	N(1)—O(5)—H(O5)	100.1(20)
O(5)—N(1)—C(5)	111.2(2)	P—C(1)—O(4)	105.8(2)
P—C(1)—C(5)	115.8(2)	O(4)—C(1)—C(5)	110.6(2)
P—C(1)—C(6)	109.4(2)	O(4)—C(1)—C(6)	106.3(2)
C(5)—C(1)—C(6)	108.6(2)	N(1)—C(5)—C(1)	122.2(3)
C(1)—C(6)—C(11)	120.2(3)	C—C—C	120.0(8)[b]

[a]Value for average carbon–carbon bonds in the phenyl ring.
[b]Value for average bond angle within the phenyl ring.

TABLE II

Atomic positional parameters ($\times 10^4$) for I

Atom	X/A	Y/B	Z/C
P	1503(1)	4012(1)	3150(1)
O(1)	1492(2)	4925(2)	2684(1)
O(2)	864(3)	2946(2)	2913(1)
O(3)	2844(2)	3622(2)	3340(1)
O(4)	1465(2)	5267(2)	4242(1)
O(5)	−2433(2)	4961(2)	3508(1)
N(1)	−1189(2)	4656(2)	3398(1)
C(1)	761(3)	4299(2)	3957(1)
C(2)	1331(4)	2276(3)	2390(2)
C(3)	3880(3)	4338(4)	3364(2)
C(4)	1234(3)	6255(2)	4000(2)
C(5)	−594(3)	4585(2)	3934(1)
C(6)	930(3)	3313(3)	4412(2)
C(7)	1768(3)	3339(3)	4929(1)
C(8)	1868(4)	2455(4)	5348(2)
C(9)	1160(3)	1547(3)	5256(2)
C(10)	329(3)	1514(3)	4747(2)
C(11)	210(3)	2386(3)	4325(2)
H(O5)	−2736(33)	4988(28)	3056(16)

and doubly bonded N—C atoms [1.48Å and 1.29Å, respectively].[16] Angles O(5)—N(1)—C(5) and N(1)—C(5)—C(1) are in agreement with those found for other oximes [111.5(18)° ⟨av⟩ and 119.7(9)° ⟨av⟩, respectively].[9,13-15]

The P—O(1), P—O(2), P—O(3), O(2)—C(2) and O(3)—C(3) bond distances in **I** compare well to those found in metal phosphonates [P=O: 1.457(30) Å ⟨av⟩, P—O: 1.598(62)Å,⟨av⟩ and C—O:1.440(99)Å⟨av⟩],[17-20] phosphorous acid

TABLE III

Anisotropic[a] temperature factors (Å^2 × 10^3)

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	45(1)	48(1)	37(1)	−2(1)	5(1)	4(1)
O(1)	51(1)	60(1)	39(1)	9(1)	8(1)	6(1)
O(2)	86(2)	57(2)	54(1)	−20(1)	10(2)	−7(2)
O(3)	50(2)	71(2)	63(2)	11(1)	10(1)	18(1)
O(4)	51(1)	38(1)	49(1)	−1(1)	−11(1)	−4(1)
O(5)	37(1)	80(2)	40(1)	2(1)	−3(1)	9(1)
N(1)	37(2)	53(2)	38(1)	1(1)	−0(1)	1(1)
C(1)	39(2)	35(2)	35(2)	−4(1)	−1(1)	−2(1)
C(2)	146(4)	74(3)	70(3)	−26(2)	−5(3)	23(3)
C(3)	50(2)	128(4)	74(3)	13(3)	−3(2)	6(3)
C(4)	65(2)	39(2)	59(2)	−1(2)	−4(2)	−3(2)
C(5)	41(2)	41(2)	33(2)	0(1)	3(1)	2(1)
C(6)	37(2)	44(2)	36(2)	−1(2)	7(2)	7(2)
C(7)	43(2)	55(2)	43(2)	6(2)	3(1)	5(2)
C(8)	48(2)	88(3)	49(2)	15(2)	3(2)	19(2)
C(9)	63(3)	71(3)	70(3)	32(2)	16(2)	23(2)
C(10)	66(3)	48(2)	84(3)	14(2)	15(2)	−0(2)
C(11)	46(2)	48(2)	59(2)	6(2)	1(2)	−2(2)

[a] The anisotropic temperature factor exponent takes the form of $-2^2(h^2a^{*2}U_{11}^2 + k^2b^{*2}U_{22}^2 + \cdots + 2hka^*b^*U_{12}^2 + \cdots)$.

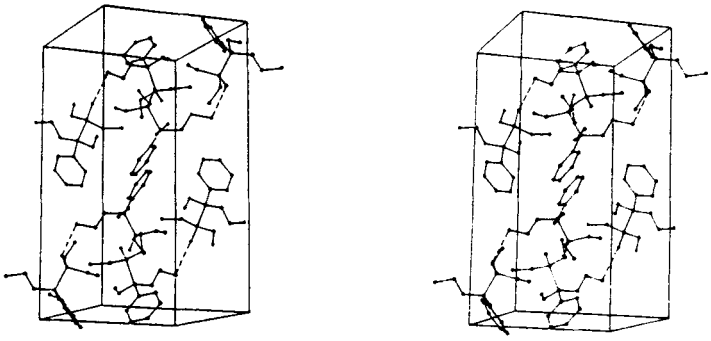

FIGURE 2. Unit-cell packing diagram for **I**, viewed down the b-axis. Hydrogen-bonded interactions are shown by dashed lines.

[P=O: 1.47(1) Å and P—O: 1.54(1) Å][21] and other phosphorous(V) complexes [P=O: 1.46(3) Å and P—O: 1.59(4) Å].[22] The O(1)—P—O(2), O(1)—P—O(3) and O(2)—P—O(3) bond angles are similar to those found in metal phosphonates [O—P=O: 111.2(33)° ⟨av⟩ and O—P—O: 101.9(38)° ⟨av⟩][17,18] and phosphorous acid [O—P=O: 113°(3) ⟨av⟩ and O—P—O: 102°(3)].[21]

The average C—C bond distance in the phenyl ring is consistent with previous work[23], while the C(1)—O(4), C(4)—O(4), C(1)—C(6), C(1)—P, and C(1)—C(5) bond distances are within the range of the sums of their respective covalent radii.[16]

EXPERIMENTAL

Collection and processing of diffraction data. A colorless crystal of **I**, grown from 1,2-dimethoxymethane, was affixed to a glass fiber with epoxy cement. Unit-cell parameters, provided in Table IV,[24] were obtained from the angular settings of 19 reflections ($7 \leqslant 2\theta \leqslant 25°$). Details of the intensity data collection and refinement are provided in Table IV. The orthorhombic space group, *Pbca*, was uniquely determined from systematic absences in the intensity data. All crystallographic computations were performed on a Data General Nova 4 computer using data collection, solution and refinement programs contained in the Nicolet Corporation P3, SHELXTL (version 3.0) packages. Corrections to the data for Lorentz and polarization effects were applied, but not for absorption (low absorption coefficient and uniform crystal dimensions). Redundant data were averaged [R(I) = 1.66%].

Solution and refinement of the structure. The positions of all nonhydrogen atoms were obtained from the solution with the highest combined figures of merit from the direct methods routine, SOLV. A subsequent difference Fourier synthesis yielded the position of the oxime hydrogen. The remaining hydrogen atoms were fixed in appropriate positions (d (C—H) = 0.96 Å, $U = 1.2 \times U$ for atoms to which H atom is bonded).

All nonhydrogen atoms were refined anisotropically while the oxime hydrogen atom was refined isotropically. Final blocked-cascade least-squares refinement yielded the final residuals provided in Table IV.

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TABLE IV

Crystal and refinement data

Formula	$C_{11}H_{16}NO_5P$
Compound name: 2-dimethoxyphosphinyl-2-methoxy-2-phenylacetaldehyde oxime	
Space group	*Pbca*
a, Å	10.748(3)
b, Å	12.273(4)
c, Å	20.323(7)
V, Å^3	2681(1)
Z	8
Molecular weight	273.25
ρ (calculated, g · cm^{-3})	1.35
Temperature, °C	25
Diffractometer	Nicolet R3
Radiation	Graphite-monochromated MoKα (λ = 0.71073 Å)
Absorption coefficient, cm^{-1}	2.2
Crystal dimensions, mm	0.26 × 0.32 × 0.38
Scan speed, deg/min	4.0 − 15.0, variable
2θ Scan range, deg	$4 < 2\theta < 45$
Scan Technique	$\theta/2\theta$
Data collected	$+h, +k, +l$
Ignorance factor[a]	0.00022
Reflections collected	2415
Unique reflections	2100
Unique data with $F_0 > 3\sigma(F_0)$	1511
Number parameters refined (reflections/parameters)	167 (9.0/1)
Standard reflections	3/100 (no decay observed)
R_F[b], R_{wF}[c], GOF[d]	4.41%, 4.35%, 1.41
Highest peak, final difference map, eÅ^{-3}	0.21 (0.78 Å from C(1))

[a] Weight = $[\sigma^2(F) + g(F^2)]^{-1}$.
[b] $R_F = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$.
[c] $R_{wF} = \{\Sigma_w(|F_0| - |F_c|)^2/\Sigma_w|F_0|^2\}^{1/2}$.
[d] GOF = $\{\Sigma_w(|F_0| - |F_c|)^2/(NO - NV)\}^2$, where NO = number of observations and NV = number of variables.

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