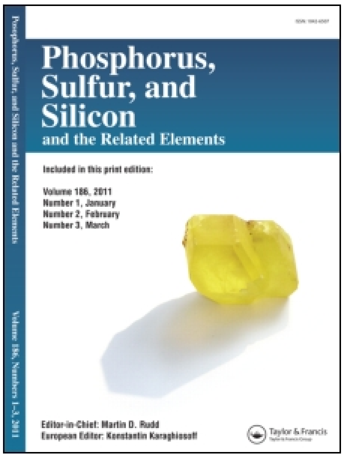


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

X-RAY CRYSTAL STRUCTURES OF *Cis*- AND *Trans*-3-(DIPHENYLHYDROXYMETHYL)-2-ETHOXY-2-OXO-1,2-OXAPHOSPHORINANES AND AN ASSOCIATED STUDY OF HYDROGEN BONDING

Thomas M. Lane[a]; Oscar P. Rodriguez[a]; Sheldon E. Cremer[a]; Dennis W. Bennett[b]
[a] Department of Chemistry, Marquette University, Milwaukee, WI, USA [b] Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, WI, USA

To cite this Article Lane, Thomas M. , Rodriguez, Oscar P. , Cremer, Sheldon E. and Bennett, Dennis W.(1995) 'X-RAY CRYSTAL STRUCTURES OF *Cis*- AND *Trans*-3-(DIPHENYLHYDROXYMETHYL)-2-ETHOXY-2-OXO-1,2-OXAPHOSPHORINANES AND AN ASSOCIATED STUDY OF HYDROGEN BONDING', Phosphorus, Sulfur, and Silicon and the Related Elements, 103: 1, 63 — 75

To link to this Article: DOI: 10.1080/10426509508027366

URL: http://dx.doi.org/10.1080/10426509508027366

Phosphorus, Sulfur, and Silicon, 1995, Vol. 103, pp. 63–75
Reprints available directly from the publisher
Photocopying permitted by license only

X-RAY CRYSTAL STRUCTURES OF *Cis*- AND *Trans*-3-(DIPHENYLHYDROXYMETHYL)-2-ETHOXY-2-OXO-1,2-OXAPHOSPHORINANES AND AN ASSOCIATED STUDY OF HYDROGEN BONDING

THOMAS M. LANE, OSCAR P. RODRIGUEZ and
SHELDON E. CREMER*
Department of Chemistry, Marquette University, Milwaukee, WI, 53233, USA

and

DENNIS W. BENNETT
Department of Chemistry, University of Wisconsin-Milwaukee,
Milwaukee, WI, 53201, USA

Dedicated to Professor Reinhard Schmutzler on the occasion of his 60th birthday.

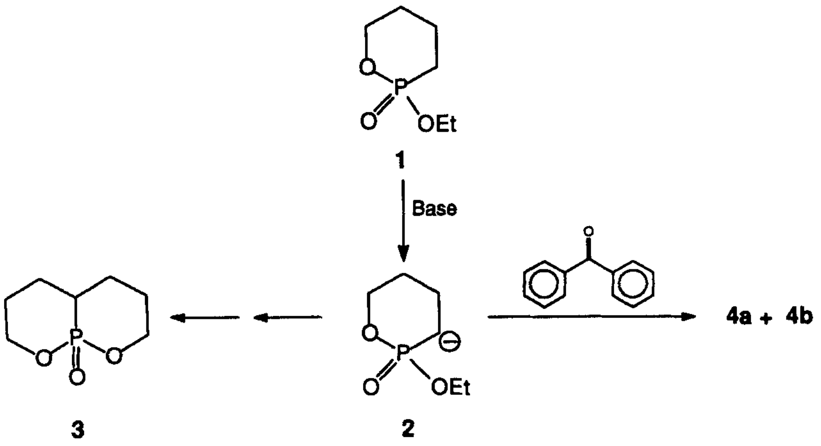
(Received September 12, 1994; in final form October 16, 1994)

The molecular structures of both the *cis*(**4a**) and *trans*(**4b**) isomers of 3-(diphenylhydroxymethyl)-2-ethoxy-2-oxo-1,2-oxaphosphorinane were determined by the single crystal X-ray diffraction method. The *cis* and *trans* designation refer to the relative spacial arrangements of the phosphoryl oxygen and the substituent group on the α-carbon. The crystallographic data are for **4a**: $C_{19}H_{23}O_4P$, $M_r = 346.36$, monoclinic, $P2_1/c$, $a = 13.2774(9)$ Å, $b = 8.5543(9)$ Å, $c = 16.7289(25)$ Å, $\beta = 111.142(10)°$, $V = 1772.2(4)$ Å^3, $Z = 4$, $D_{calc} = 1.298$ g cm^{-3}, λ(MoKα) = 0.71069 Å, $\mu = 1.70$ cm^{-1}, F(000) = 736, T = 298 K, R = 0.065 for 2099 reflections; and for **4b**: $C_{19}H_{23}O_4P$, $M_r = 346.36$, monoclinic, $P2_1/c$, $a = 9.5120(15)$ Å, $b = 12.317(4)$ Å, $c = 15.309(3)$ Å, $\beta = 100.717(15)°$, $V = 1762.3(7)$ Å^3, $Z = 4$, $D_{calc} = 1.305$ g cm^{-3}, λ(MoKα) = 0.71069 Å, $\mu = 1.60$ cm^{-1}, F(000) = 736, T = 298 K, R = 0.041 for 1638 reflections. In both structures the diphenylhydroxymethyl group is in an equatorial position, and the 1,2-oxaphosphorinane ring adopts a chair conformation. In the solid state **4b** (*trans*) shows neither inter- or intramolecular hydrogen-bonding, while **4a** (*cis*) exhibits intramolecular H-bonding of the type O—H···O═P. The chair conformation of **4a** is flattened at the C4 end relative to the conformation of **4b**. Solution IR spectroscopy studies of ν(OH) reveal that only one conformer of **4a** is observed which is assignable to the rotamer containing the intramolecular hydrogen bond.

Key words: X-ray crystal structure, oxaphosphorinane, phostone, intramolecular hydrogen bonding.

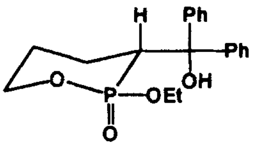
INTRODUCTION

Our interest in the chemistry of 2-oxo-1,2-oxaphosphorinane derivatives (phostones) initially arose from the desire to develop a synthetic route to the previously unreported *trans*-fused isomer of the bicyclic system 2,10-dioxa-1-phosphabicyclo[4.4.0]decane 1-oxide (**3**).[1] As shown in Scheme I, the first step in this route is based on an alkylation of the ylid **2** derived from the parent phostone **1**[2] with protected 3-bromo-1-propanol. A comprehensive study of this alkylation process will be described elsewhere.[3] The formation of ylid **2** could be efficiently

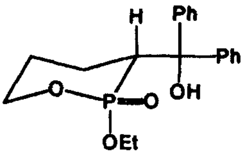


SCHEME I

achieved by employing lithium-2,2,6,6-tetramethylpiperidide (LTMP) or LDA, which was similar to the method used by Polniaszek and Foster[4] to alkylate alkoxy phospholanates. The reaction of **2** with benzophenone to give **4a** and **4b** offers evidence for the ylid intermediate. X-ray diffraction studies of **4a** and **4b** were undertaken both to establish the stereochemical selectivity of alkylation of **2** and to determine the conformation of the rings. An associated H-bonding study of **4a** and **4b** was also undertaken in both the solid and solution states.



4a (*cis*)



4b (*trans*)

EXPERIMENTAL

Synthesis

General: All reactions were carried out in flame dried glassware under a nitrogen atmosphere. ^1H NMR were taken at 300 MHz; ^{13}C NMR spectra were taken at 75 MHz; ^{31}P NMR chemical shifts are relative to 85% phosphoric acid (H_3PO_4 external standard in $CDCl_3$) on a GE OMEGA 300 NMR spectrometer. ^1H and ^{13}C NMR were reported in ppm referenced to TMS or $CDCl_3$. Infrared spectra were recorded on a Mattson GL-4020 FT-IR using a variable pathlength (0.02–6.00 mm) solution cell (NaCl). All solvents and reagents were purchased from Aldrich Chemical Co. (Milwaukee, WI) and were purified when necessary by standard literature methods. Elemental analyses were performed by Midwest Microlab of Indianapolis, IN. The parent compound, 2-oxo-2-ethoxy-1,2-oxaphosphorinane (**1**), was prepared by the literature method.[5]

Generation of the ylid (**2**): A 0.80 g (1.1 mL, 8.0 mmol) sample of diisopropylamine was dissolved in 10 mL of dry THF. The solution was cooled to 0°C and 4.4 mL (11 mmol) of a 2.5 M solution of nBuLi (in hexanes) was added over 20 min. The resulting LDA solution was then cooled to −78°C and 1.54 g (9.4 mmol) of **1** in 3 mL THF was added. The resultant solution was stirred at −78°C for 1 h.

TABLE I

Experimental details for structures **4a** and **4b**

Crystal data (#)	**4a**	**4b**
Empirical formula	$C_{19}H_{23}O_4P$	$C_{19}H_{23}O_4P$
Formula weight	346.36	346.36
Crystal color, habit	Colorless, prism	Colorless, prism
Crystal dimensions (mm)	0.30, 0.30, 0.25	0.25, 0.25, 0.30
Crystal system	Monoclinic	Monoclinic
Reflections for cell parameters	24	17
2θ range for reflections	5.22 - 13.95 °	4.36 - 13.94°
Lattice parameters	a = 13.2774(17)Å	a = 9.5120(15)Å
	b = 8.5543(9)Å	b = 12.317(4)Å
	c = 16.729(3)Å	c = 15.309(3)Å
	β = 111.142(10)°	β = 100.717(15)°
	V = 1772.2(4) $Å^3$	V = 1762.3(7)$Å^3$
Space group (#)	$P2_1/c$ (14)	$P2_1/c$ (14)
Z	4	4
D_{calc}	1.298 g cm^{-3}	1.305 g cm^{-3}
F_{000}	736	736
$\mu_{(MoK\alpha)}$	1.70 cm^{-1}	1.60 cm^{-1}
Intensity measurements		
Diffractometer	Picker	Picker
Radiation	MoKα (0.71069Å)	MoKα (0.71069Å)
Temperature	25°	25°
Scan type	θ-2θ	θ-2θ
2θ range	4 - 45°	4 - 40°
Measured reflections	2506	1746
Unique reflections	2099	1638
Observed reflections	1576	1218
Criterion for observed reflection	I > 2.5σ (I)	I > 2σ(I)
h range	-14 → 13	-14 → 13
k range	0 → 9	0 → 9
l range	0 → 18	0 → 18
# of standard reflections	3	3
Interval time between standard reflections	120 min	120 min
Structure solution and refinement		
Refinement on:	F	F^2
Residuals	R = 0.065	R = 0.041
	$R_W(F)$ = 0.071	$R_W(F^2)$ = 0.062
w =	$1/\sigma^2(F_0)$	$1/\sigma(F_0)^2$
Goodness of fit indicator	2.19	2.51
Max. shift/error in final cycle	0.109	0.209
Max. peak in final differential map	0.460 e $Å^{-3}$	0.290 e $Å^{-3}$

3-(Diphenylhydroxymethyl)-2-Ethoxy-2-Oxo-1,2-Oxaphosphorinane (**4**): To the ylid (**2**) solution 2.0 g (11.0 mmol) of benzophenone (dissolved in 5 mL THF) was added over 25 min. The internal temperature of the reaction was not allowed to rise beyond −70°C. The resultant reaction mixture was stirred at −78°C for 2 h, after which the reaction mixture was allowed to slowly warm up to room temperature (ca. 1 h). The reaction was quenched with 50 mL of 5% HCl solution. The THF was removed and the aqueous residue was extracted with CH_2Cl_2 (3 × 25 mL). The extracts were dried with Na_2SO_4, filtered, and concentrated; an 85:15 mixture (**4a**:**4b**) of diastereoisomers was determined by ^{31}P NMR spectroscopy. The diastereoisomers were separated and purified by column chromatography on silica gel affording 2.98 g (93%). **4a**: mp 157–158°C (EtOAc), R_f = 0.84 (EtOAc). ^{13}C NMR ($CDCl_3$) δ 146.73 (J_{PC} = 2.4 Hz), 144.38 (J_{PC} = 19.2 Hz), 128.34 (s), 128.00 (s), 126.79 (s), 126.53 (s), 125.76 (s), 125.03 (s), 77.06 (J_{PC} = 8.6 Hz), 69.32 (J_{PC} = 6.1 Hz), 62.26 (J_{PC} = 6.1 Hz), 44.30 (J_{PC} = 122.8 Hz), 26.74 (J_{PC} = 4.9 Hz), 24.40 (J_{PC} = 3.7 Hz), 16.05 (J_{PC} = 6.1 Hz). ^1H NMR ($CDCl_3$) δ 7.00–7.70 (m, 10H), 5.52 (bs, 1H), 4.00–4.35 (m, 2H), 3.44–3.62 (m, 1H), 3.05 (ddd, 1H, J_{HH} = 4.9 Hz, J_{HH} = 12.7 Hz, J_{PH} = 18.8 Hz), 2.72–2.90 (m, 1H), 1.50–2.25 (m, 4H), 0.83 (t, 3H, J_{HH} = 7.1 Hz). ^{31}P NMR ($CDCl_3$,) δ 29.6. **4b**: mp 143–144°C. (CH_2Cl_2/ether), R_f = 0.46 (EtOAc). ^{13}C NMR ($CDCl_3$) δ 145.23 (J_{PC} = 4.9 Hz), 144.00 (J_{PC} = 12.2 Hz), 128.10 (s), 128.02 (s), 127.42 (s), 126.78 (s), 126.03 (s), 125.74 (s), 78.23 (J_{PC} = 4.9 Hz), 69.88 (J_{PC} = 7.3 Hz), 61.48 (J_{PC} = 6.1 Hz), 46.48 (J_{PC} = 122.1 Hz), 26.74 (J_{PC} = 4.9 Hz), 25.14 (J_{PC} = 4.9 Hz), 16.21 (J_{PC} = 4.9 Hz). ^1H NMR ($CDCl_3$) δ 7.10–7.65 (m, 10H), 3.98–4.35 (m, 2H), 3.72–3.98 (m, 2H), 3.21 (ddd, 1H, J_{HH} = 4.5 Hz, J_{HH} = 11.9 Hz, J_{PH} = 21.0 Hz), 1.67–2.10 (m, 4H), 1.60 (bs, 1H), 1.14 (t, 3H, J_{HH} = 7.1 Hz). ^{31}P NMR ($CDCl_3$,) δ 23.9. Anal. Calcd. for $C_{19}H_{23}O_4P$ (isomer mixture): C, 65.89; H, 6.69. Found: C, 66.00; H, 6.60.

X-ray Crystal Structure Determinations

General: All measurements were made on a Picker diffractometer automated with PCXTL data collection software.[6] Data handling, reduction and analysis were performed using NRCVAX.[7] The data was collected using MoKα (0.71069 Å) radiation and the θ-2θ scan technique. The intensities of three reflections were checked every 120 minutes. No absorption corrections were applied. The thermal factors for the ethoxy carbon atoms of both **4a** and **4b** were found to be significantly larger than those of the other heavy atoms. Similar observations have been reported for ethoxy groups in diethyl phosphorus esters.[8] Attempts to refine these atoms without constraints resulted in unreasonably short C—C bond lengths; thus, the ethyl groups of **4a** and **4b** were refined as ideal rigid rotational groups. Experimental details for both structures are listed in Table I.†

Structural Solution for **4a**: The structure was solved by direct methods using SOLVER, with the remaining heavy atoms localized by difference Fourier synthesis.[7] The hydrogen atoms were allowed to ride with the heavy atom to which they were bonded, using a single hydrogen atom isotropic temperature factor for all hydrogens that was refined to a value of U_{iso} = 0.122(5). All hydrogens were placed in calculated positions prior to final refinement, except for the H104 (O4-H104) which was located in a difference map and the positional parameters were refined. The structure was refined by full-matrix least-squares refinement using SHELX-76[9] to a final R and R_w of 0.065 and 0.071, respectively.

Structural Solution for **4b**: The structure was solved by direct methods using SOLVER.[7] The hydrogen atoms were allowed to ride with the heavy atom to which they were bonded. The hydrogen atoms isotropic temperature factor was 1.5 times the equivalent isotropic factor of the heavy atom. All hydrogens were placed in calculated positions prior to final refinement, except for H4 which was located in the difference map and the positional parameters were refined. H4 was found not to be pointed toward either O1 or O3, and therefore not included in the ORTEP diagram. The structure was refined by full-matrix least-squares refinement using SHELXL-93[10] to a final R and R_w of 0.041 and 0.062, respectively.

RESULTS

Results from Structure **4a** *and Structure* **4b**

The ORTEP (35% thermal ellipsoids) diagram of **4a** and **4b** are given in Figure 1. The bond lengths (Å) are presented in Figure 2 and the bond angles (deg.) shown

---

†Full experimental details, as well as tables of thermal parameters, are deposited as supplementary material with CCDC (18 pages).

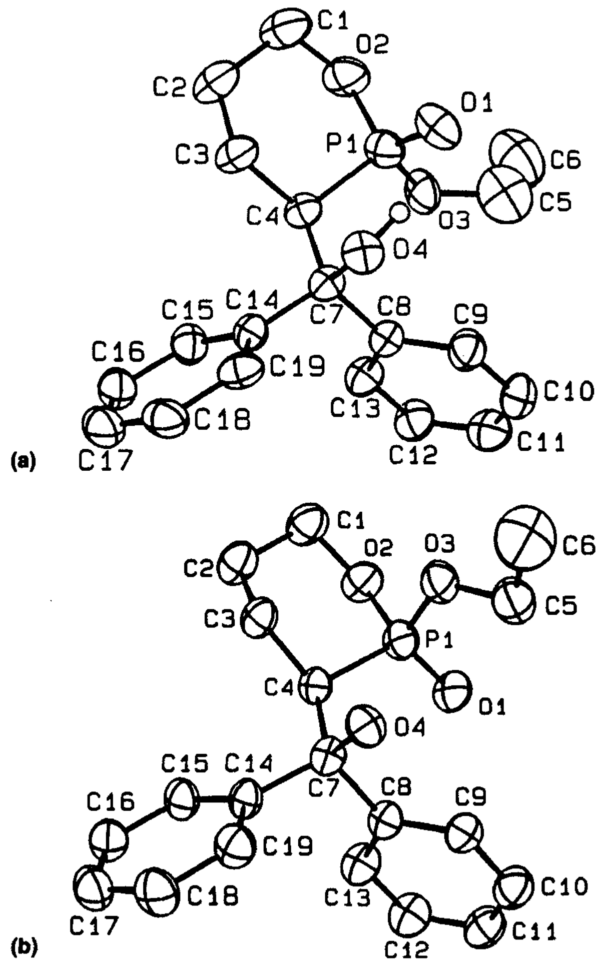
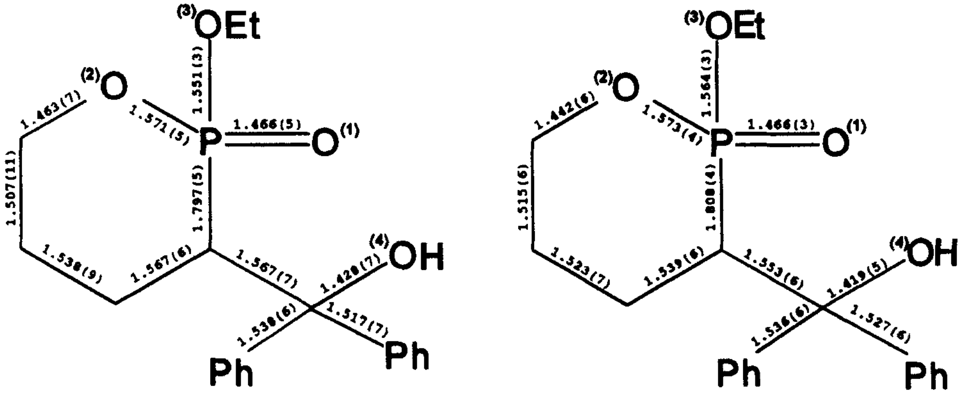
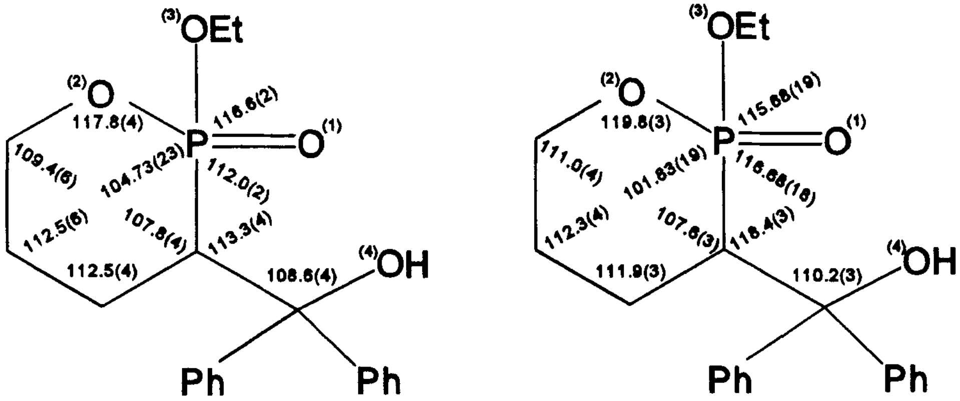


FIGURE 1 The ORTEP (35% thermal ellipsoids) diagrams of **4a** and **4b** showing similar views with hydrogens omitted for clarity (except H104 in **4a** which is involved in hydrogen bonding).



4a **4b**

FIGURE 2 Bond lengths (Å) for **4a** and **4b** with esds in parentheses.



4a **4b**

FIGURE 3 Selected bond angles (deg) for **4a** and **4b** with esds in parentheses.

TABLE II

Bond angles (deg) and torsional angles (deg) for **4a** and **4b** with esds in parentheses

Bond angles (deg)

atoms	4a	4b	atoms	4a	4b
O1-P1-O2	114.9(3)	111.08(19)	O2-P1-O3	101.2(2)	102.06(18)
O3-P1-C4	106.1(2)	107.67(18)	O3-C5-C6	107.3(6)	108.7(4)
O4-C7-C8	110.9(4)	107.3(4)	O4-C7-C14	106.7(4)	108.1(3)
P1-O3-C5	122.0(4)	124.1(3)	C3-C4-C7	110.4(4)	112.5(3)
C4-C7-C8	110.5(4)	111.0(3)	C4-C7-C14	110.4(4)	111.9(4)
C7-C8-C9	121.0(5)	121.7(4)	C7-C14-C15	122.3(4)	123.0(4)
C8-C7-C14	109.6(4)	108.2(3)	C7-O4-H104	103(5)	—

Torsional angles (deg)

atoms	4a	4b	atoms	4a	4b
O1-P1-O2-C1	-68.7(3)	179.7(3)	O1-P1-O3-C5	-15.0(3)	-31.0(2)
O1-P1-C4-C3	77.5(3)	-173.1(4)	O1-P1-C4-C7	-45.0(3)	58.1(2)
O2-P1-O3-C5	110.4(4)	-141.7(3)	O2-P1-C4-C7	-170.1(4)	179.2(3)
O3-P1-O2-C1	164.7(4)	-56.4(2)	O3-P1-C4-C3	-154.2(4)	54.9(2)
O3-P1-C4-C7	83.3(3)	-73.9(3)	O4-C7-C4-P1	59.5(3)	66.7(2)
O4-C7-C4-C3	-61.6(3)	-59.8(3)	O4-C7-C8-C9	-5.9(3)	-10.4(2)
O4-C7-C8-C13	174.6(6)	170.3(5)	P1-O3-C5-C6	-122.0(6)	-163.4(5)
P1-C4-C7-C8	-62.4(3)	-52.0(2)	P1-C4-C7-C14	176.2(5)	-173.0(4)
C2-C3-C4-C7	177.9(6)	-168.9(5)	C3-C4-C7-C8	176.6(5)	-178.5(5)
C4-P1-O3-C5	-140.5(4)	101.5(3)	C4-C7-C8-C9	114.5(5)	110.0(4)

in Figure 3. A more detailed listing of bond angles and torsional angles is given in Table II. The packing diagrams of the molecules in the unit cells are displayed in Figure 4. The fractional coordinates are given in Table III along with the U_{eq} value for each atom.

In each structure the diphenylhydroxymethyl substituent is found in the equatorial position, as expected. As revealed in the single crystal structure of 6-(iodo methyl)-2-oxo-2-phenoxy-1,2-oxaphosphorinane,[11] the oxaphosphorinane rings of **4a** and **4b** assume a standard chair conformation, although not identical to each other (vide infra). Both phenyl groups in each structure have comparable spacial orientations as shown by the torsional angles C4—C7—C8—C9 [114.5(5)° and

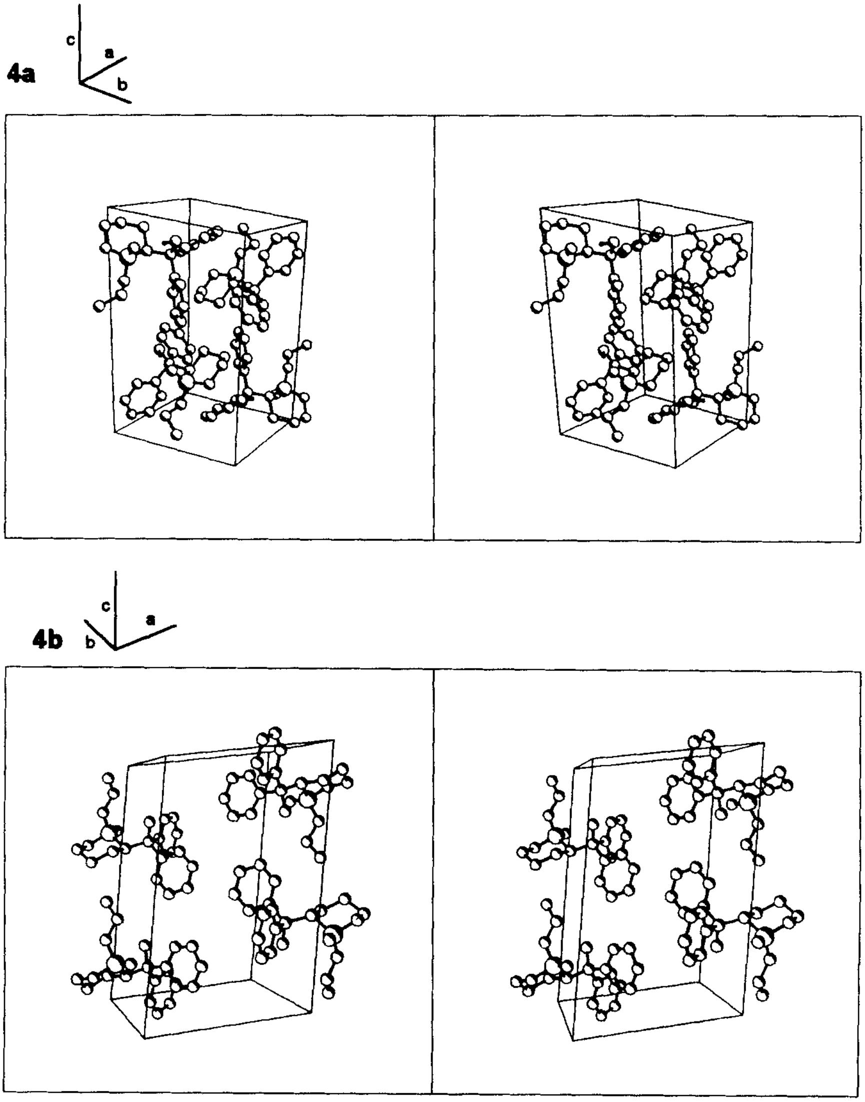


FIGURE 4 Perspective view of the packing diagrams for **4a** and **4b**.

TABLE III

Atomic coordinates ($\times 10^4$) and U(eq) [U(iso) for hydrogen atoms] ($A^2 \times 10^3$) for **4a** and **4b**

Atom	x	y	z	U(eq)[b]
Structure **4a**				
P1	8143(1)	131(2)	2093(1)	62(1)
O1	8650(3)	1010(5)	1587(3)	78(3)
O2	8068(3)	-1680(5)	1932(3)	81(3)
O3	8713(3)	197(5)	3082(2)	75(2)
O4	6973(3)	3167(5)	1186(2)	57(2)
C1	7333(6)	-2242(8)	1101(4)	94(5)
C2	6193(6)	-1790(6)	984(4)	79(4)
C3	6051(5)	-6(6)	1000(3)	64(3)
C4	6773(4)	741(6)	1873(3)	51(3)
C5	9833(4)	760(10)	3492(5)	133(8)
C6	10490(8)	-568(11)	4065(6)	155(9)
C7	6632(4)	2560(6)	1842(3)	46(3)
C8	7286(4)	3289(6)	2716(3)	49(3)
C9	8155(5)	4275(6)	2811(4)	65(3)
C10	8766(5)	4905(8)	3605(4)	81(4)
C11	8511(6)	4564(8)	4316(4)	78(4)
C12	7641(5)	3607(8)	4228(4)	71(4)
C13	7045(5)	2985(6)	3440(3)	61(3)
C14	5450(4)	2989(6)	1595(3)	46(3)
C15	4749(4)	2152(6)	1893(3)	61(3)
C16	3650(5)	2561(8)	1632(4)	69(4)
C17	3269(5)	3837(9)	1088(4)	76(4)
C18	3953(5)	4668(8)	797(3)	65(4)
C19	5030(5)	4266(6)	1050(3)	57(3)
H104	7613(55)	2673(89)	1278(44)	122(5)
Structure **4b**				
P1	933(1)	4942(1)	2191(0)	60(1)
O1	198(3)	3900(2)	2221(2)	70(2)
O2	2309(3)	4809(2)	1768(2)	70(2)
O3	1559(3)	5462(2)	3114(2)	71(2)
O4	-1324(3)	6890(2)	2531(1)	57(2)
C1	3182(5)	5743(3)	1674(3)	75(3)
C2	2319(5)	6610(3)	1111(3)	69(3)
C3	999(4)	6946(3)	1477(2)	57(3)
C4	-33(4)	5989(3)	1500(2)	47(2)
C5	947(5)	5329(4)	3894(3)	80(4)
C6	1538(7)	6168(4)	4544(3)	122(5)
C7	-1505(4)	6359(3)	1694(2)	47(3)
C8	-2486(4)	5386(3)	1736(3)	49(3)
C9	-2846(4)	5050(3)	2526(3)	57(3)
C10	-3697(5)	4144(4)	2561(3)	70(3)
C11	-4208(5)	3561(3)	1803(3)	72(3)
C12	-3882(5)	3897(4)	1006(3)	73(3)
C13	-3034(5)	4801(3)	976(3)	64(3)
C14	-2269(4)	7146(3)	983(3)	49(3)
C15	-2049(5)	7144(3)	117(3)	58(3)
C16	-2782(5)	7831(3)	-525(3)	65(3)
C17	-3789(5)	8524(3)	-309(3)	70(3)
C18	-4036(5)	8535(3)	551(3)	71(3)
C19	-3275(5)	7853(3)	1193(3)	61(3)
H4	-1055(44)	6450(16)	2928(6)	86

[b] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

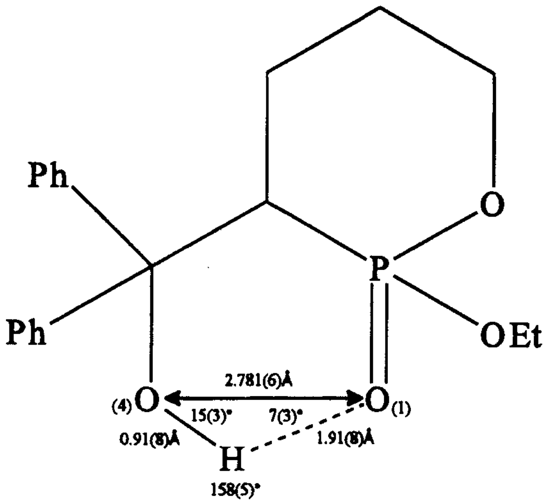


FIGURE 5 Geometry of the intramolecular H-bond of **4a** showing bond lengths (Å) and angles (deg) with esds in parentheses.

110.0(4)° for **4a** and **4b**, respectively] and C4—C7—C14—C15 [38.5(3)° and 27.4(3)° for **4a** and **4b**, respectively].

The corresponding bond lengths in both structures are very similar. The phosphoryl (P=O) bond lengths of 1.466(5) Å for **4a** and 1.466(3) Å for **4b** fall within the range of 1.444 to 1.473 Å found for P=O bond lengths of similar compounds.[1c,11,12] As expected, the longest bond is P1—C4 [1.797(5) Å for **4a** and 1.808(4) Å for **4b**]. The P—C bond lengths are within the expected range of 1.772 to 1.807 Å.[1c,11–13] The exocyclic P1—O3 bond length for **4a** [1.551(3) Å] is shorter, but comparable to the corresponding bond length for **4b** [1.564(3) Å] [$\Delta = 0.013(4)$ Å: i.e. 3σ]. The endocyclic P1—O2 bond lengths as well as all the endocyclic bond lengths of **4a** and **4b** are not significantly different.

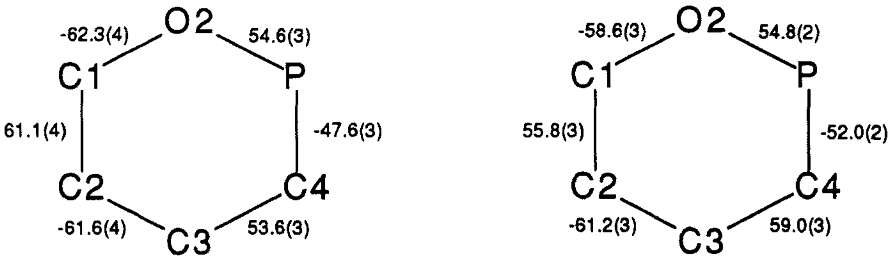
The solid state structure of **4a** establishes the existence of intramolecular H-bonding of the form O—H···O=P as shown in Figure 5. The non-bonded intramolecular O1···O4 distance for **4a** is 2.781 Å. The associated O4—H104···O1 angle is 158°. The other bond angles of 15° [O1···O4—H104] and 7° [O4···O1···H104] suggest a nearly linear arrangement of these atoms. Thus, from the close O4···O1 contact and the nearly colinear vectors of O4···O1 and O1···H a relatively strong H-bond is confirmed.[14]

DISCUSSION

No intermolecular or intramolecular association is observed in the single crystal structure of **4b**. In fact, from the spacial orientation of the ethoxy group, the oxygen lone pairs are pointed away from the oxygen of the hydroxy group. The ethoxy carbons are positioned on the diphenylhydroxymethyl side of the phosphorus, projecting the idealized lone pairs of O3 away from the OH group, thus making intramolecular H-bonding to the ethoxy oxygen unrealistic in the solid state. The formation of intermolecular H-bonding would also be unlikely given the hindered region about the diphenylhydroxymethyl and the ethoxy groups. Considerable steric repulsions would limit the ability of two or more molecules of **4b** to couple in a favorable position for intermolecular H-bonding in the solid state.

To form the intramolecular H-bond in **4a**, or as a consequence of its formation, significant differences in bond angles and torsional angles between **4a** and **4b** are observed. Although the bond lengths are nearly identical in each oxaphosphorinane ring (Figure 2), the torsional angles of the ring, given in Figure 6 for **4a** and **4b**, clearly show that the rings are non-equivalent. Compared to the oxaphosphorinane ring of **4b**, the ring of **4a** is flattened at the C4 end and more puckered at the C1 end.

Although there are no significant differences in angles about atoms not associated with the H-bond [C4—P1—O3 = 106.1(2)° and 107.67(18)°; and O3—P1—O2 = 101.2(2)° and 102.06(18)° for **4a** and **4b**, respectively], the C4—P1—O1 and P1—C4—C7 bond angles are smaller in **4a** [112.0(2)° and 113.3(4)°, respectively] relative to **4b** [116.68(18)° and 118.4(3)°, respectively]. The O2—P1—C4 bond angle is somewhat greater in **4a** [104.7(2)°] relative to **4b** [101.83(19)°]. These results suggest that it is energetically favorable to form the H-bond in **4a** at the expense of the added steric repulsion caused by the changes in bond angles compared to the *trans* isomer.



4a **4b**

FIGURE 6 Torsional angles (deg) for the 1,2-oxaphosphorinane ring for **4a** and **4b** with esds in parentheses.

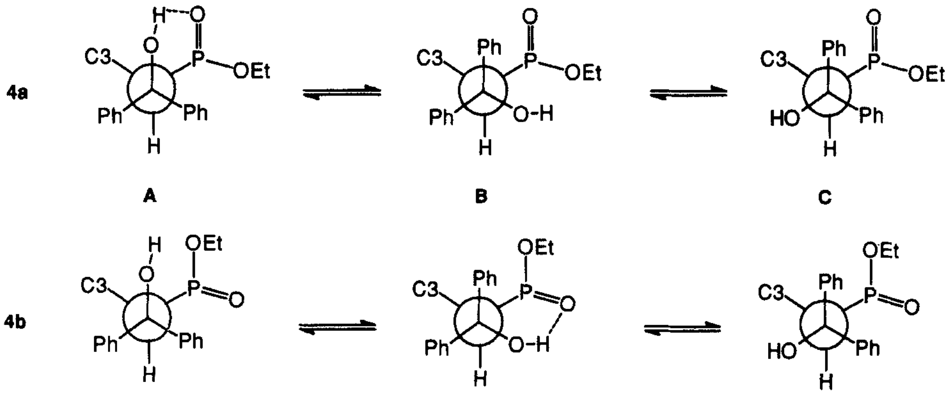
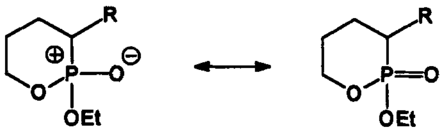


FIGURE 7 Idealized rotational conformation equilibrium shown along the C7-C4 bond for both **4a** and **4b**.

The rotational conformation equlibrium of monomeric **4a** and **4b** expected in solution can be schematically depicted in Figure 7. In the solid state only rotamer **A** is observed for both structures with evidence of intramolecular H-bonding only to the phosphoryl oxygen of **4a**. Rotamer **A** is preferred since the other two rotamers (**B** and **C**) have additional phenyl-phosphorus and/or —C3 *gauche* interactions.[15]

Several solution infrared spectroscopy (IR) studies by Shagidullin *et al.*[16] have suggested that intramolecular H-bonding of the OH group exists in equilibrium with the phosphoryl oxygen and the oxygen of the P—O—C linkage. Other IR studies[15,17] make no mention of H-bonding to the oxygen of the P—O—C linkage. Moreover, crystallographic data[8,12e,f,18] have determined the H-bond to form exclusively to the phosphoryl oxygen of phosphorus esters. The phosphoryl oxygen is the site of highest basicity in phosphorus esters[17d,19,20] which is consistent with the postulated resonance diagram below. Thus, the exclusive preference in the solid state for H-bonding to the phosphoryl oxygen is appreciated which further helps to explain the observed lack of intramolecular H-bonding in **4b**.



I II

The angle of the H-bond about O1 is 95(5)° [P1=O1··H104], which is far from the idealized angle of 120°. Typically H-bonds point to the center of electron density. For example, many X-ray and neutron diffraction studies have found H-bonds to C=O to have C=O··H angles of 120 ± 15°.[14,21] Assuming a correctly located hydrogen and that crystal packing forces and structural constraints are not significant factors in the geometric arrangement in the H-bond of **4a**, this associated angle may reflect sp^3 hybridization for the oxygen rather than the expected sp^2 hybridization (see **I** and **II** above).

Infrared Study

The solid state KBr diffuse reflection IR spectra of both isomers show strong absorptions centered at 3331 cm^{-1} and 3238 cm^{-1} for **4a** and **4b**, respectively, assignable to the hydroxyl band. According to Huggins and Pimentel[22] and Mecke[23] intermolecular H-bonding is easily distinguished from intramolecular H-bonding in the solid state by the sharpness of the hydroxyl band of the latter. The band widths of the hydroxyl bands of phosphoryl compounds (hydroxyalkyl diphenylphosphine oxides [$HO(CH_2)_nP(O)Ph_2$ where $n = 1, 2, 3$, and 4] by Aksnes and Bergesen[24] containing H-bonds were found to be up to 300 cm^{-1} ($w_{1/2}$) wide. In comparison the sharpness of hydroxyl bands of **4a** ($w_{1/2} = \sim 90$ cm^{-1}) and **4b** ($w_{1/2} = \sim 130$ cm^{-1}) appear to support our crystallographic findings that no intermolecular H-bonding exists in the solid state of either isomer.

The two isomers are easily distinguished by their dilute (10^{-2} to 10^{-4} M) CCl_4 solution IR spectra. In the ν(OH) region **4a** exhibits one band at 3370 cm^{-1} found to be independent of concentration down to 10^{-4} M which is indicative of an intramolecular H-bond. Thus "A" (Figure 7) is the only rotamer observed for **4a** in both the solid and solution states. In fact, the hydrogen bond of **4a** prevails upon the addition of THF to the CCl_4 solutions and even in solutions of **4a** in pure THF.[15a]

The other isomer, **4b**, shows two absorptions at 3548 and 3420 cm^{-1} in CCl_4 which are concentration independent. The relative areas (~50:50) of the two bands also remained the same throughout the concentration range. We tentatively assigned the lower energy band of **4b** to the H-bonded rotamer **B** and the band at 3548 cm^{-1} to free OH (presumably a time averaged band of both **A** and **C**).

The hydroxyl bands in CCl_4 for both isomers were found to be independent of concentration. Thus we are able to establish that in solution no intermolecular H-bond exists for either isomer.

In pure THF three bands are discernable for **4b** (10^{-2} M) at 3574, 3510, and 3405 cm^{-1}. The absorptions at 3574 and 3405 cm^{-1} in THF correspond to the two bands in CCl_4 at 3548 and 3420 cm^{-1}, respectively. Intermolecular associations with the THF may account for the frequency changes. The disruption of the H-bond to form a THF associated OH band at 3510 cm^{-1} may explain the added band in THF compared to the CCl_4 solutions. The observed decrease in the relative intensity of the 3405 cm^{-1} band compared to the 3574 cm^{-1} band in THF may indicate that the intramolecular equilibrium has changed due to the THF association.

The addition of incremental amounts of THF to the CCl_4 solution of **4b** also gives rise to three bands (3543, 3493 and 3423 cm^{-1}). The intensity of middle band (3493 cm^{-1}) increases with increasing THF concentration while the 3423 cm^{-1} band decreases. This result is consistent with the THF interfering with the intramolecular H-bond of rotamer **B** to form an intermolecular H-bond to THF.

CONCLUSION

Although there are no significant differences in bond lengths between the two isomers, differences in bond angles and torisonal angles may be attributed to the presence of intramolecular H-bonding in **4a**. The intramolecular H-bond of the form O—H···O=P was found to have an interatomic O···O distance of 2.781 Å, and an O—H···O angle of 158°. Solid state IR spectra support the observed lack of intermolecular H-bonds in both isomers. Solution studies in CCl_4 show that **4a**, as in the solid state, only exists in one rotamer, **A**, in which the H-bond prevails in THF. Similar CCl_4 solution studies of **4b** revealed two bands assignable to a free and associated hydroxyl group.

ACKNOWLEDGEMENTS

Rodriguez wishes to acknowledge S.C. Johnson Wax Co. for providing a research fellowship and MU for both the Denis J. O'Brien and Arthur J. Schmitt fellowships. Lane and Cremer wish to thank the MU Wehr Foundation for financial support.

REFERENCES

1. (a) G. H. Whitham, personal communication (1989); (b) M. Chérest and G. H. Whitham, unpublished results (1976); (c) S. Bellard, S. R. Postle and G. M. Sheldrick, *Acta Cryst. B*, **34**, 1032

(1978); (d) Only the *cis* isomer has been reported. The *trans* isomer has recently been prepared in our laboratory.

2. A. Y. Garner, *Chem. Abstr.*, **55,** 5346 (1961); US Pat. 2,953,591 (1960).
3. O. P. Rodriguez, T. M. Lane, D. W. Bennett and S. E. Cremer (1994) in preparation.
4. R. P. Polniaszek and A. L. Foster. *J. Org. Chem.*, **56,** 3137 (1991).
5. S. E. Cremer, A. G. Sommese and O. P. Rodriguez, *Phosphorus, Sulfur, and Silicon*, **75,** 107 (1993).
6. J. B. Weinrach and D. W. Bennett, *J. Appl. Cryst.*, **24,** 91 (1991).
7. E. J. Gabe, Y. Le Page, J.-P. Charland, F. L. Lee and P. S. White, *J. Appl. Cryst.*, **22,** 384 (1989).
8. (a) O. Angelova, J. Macicek, N. G. Vassilev, S. Momchilova and J. Petrova, *J. Cryst. Spect. Res.*, **22,** 253 (1992); (b) E. L. Müller, H. M. Roos and T. A. Modro, *J. Phy. Org. Chem.*, **6,** 64 (1993).
9. G. M. Sheldrick, SHELX-76; A Program for Crystal Structure Solution, Institute of Anorganische Chemie der Universitat, Göttingen, Federal Republic of Germany.
10. G. M. Sheldrick, SHELXL-93, *J. Appl. Cryst.*, in preparation.
11. M. Parvez, A. D. Napper and S. J. Benkovic, *Acta Cryst.*, **C44,** 1414 (1988).
12. (a) P. G. Jones, G. M. Sheldrick, A. J. Kirby and A. J. Briggs, *Acta Cryst. C*, **40,** 1061 (1984); (b) Mazhar-ul-Haque, J. Ahmed and W. Horne, *Acta Cryst. C*, **43,** 282 (1987); (c) D. H. Hua, D. Roche, S. N. Bharathi, X. Wu and P. D. Robinson, *Acta Cryst. C*, **48,** 1866 (1992); (d) E. Alver and H. M. Kjoge, *Acta Chim. Scand.*, **23,** 1101 (1969); (e) W. Saenger and M. Mikolajczyk, *Chem. Ber.*, **106,** 3519 (1973); (f) Mazhur-ul-Haque, J. Ahmed and W. Horne, *Acta Cryst. C*, **42,** 99 (1986); (g) T. M. Lane, O. P. Rodriguez, A. G. Sommese, S. E. Cremer and D. W. Bennett, *Acta Cryst.* (1994) in press; (h) A. M. Polozov, O. N. Kataeva and I. A. Litvinov, *J. Org. Chem.*, **59,** 1572 (1994).
13. (a) G. Hagele and W. Kuckelhaus, *Phosphorus and Sulfur*, **22,** 241 (1985); (b) Unpublished results from our lab.
14. P. Murray-Rust and J. P. Glusker, *J. Am. Chem. Soc.*, **106,** 1018 (1984).
15. (a) M.-P. Belciug, A. M. Modro, T. A. Modro and P. L. Wessels, *J. Phy. Org. Chem.*, **5,** 787 (1992); (b) J. P. Gerber and T. A. Modro, *Phosphorus, Sulfur and Silicon*, **88,** 99 (1994).
16. (a) R. R. Shagidullin, E. P. Trutneva, N. I. Rizpolozhenskii and F. S. Mukhametov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1302 (1974); (b) R. R. Shagidullin and E. P. Trutneva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1757 (1975); (c) R. R. Shagidullin, E. P. Trutneva and F. S. Mukhametov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 667 (1978); (d) E. P. Trutneva and R. R. Shagidullin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1877 (1975).
17. (a) E. I. Matrosov and M. I. Kabachnik, *Spectrochimica Acta*, **28A,** 191 (1972); (b) T. Gramstad and T. Olsen, *Spectrochimica Acta*, **30A,** 2121 (1974); (c) C. C. Mitsch, L. D. Freedman and C. G. Moreland, *J. Mag. Res.*, **5,** 140 (1971); (d) E. I. Matrosov, A. A. Kryuchkov, E. E. Nifantyev, A. G. Kozachenko and M. I. Kabachnik, *Phosphorus and Sulfur*, **13,** 69 (1982); (e) C. D. Miller, R. C. Miller and W. Rogers, *J. Am. Chem. Soc.*, **80,** 1562 (1958); (f) R. Wolf, D. Houalla and F. Mathis, *Spectrochim. Acta*, **23A,** 1641 (1967); (g) J. Petrova, N. G. Vassilev and M. Kirilov, *Phosphorus, Sulfur, and Silicon*, **47,** 457 (1990); (h) I. P. Lipatova, V. V. Moskva, T. Sh. Sitdikova, E. I. Antropova and S. A. Samartseva, *Zh. Obshch. Khim.*, **49,** 87 (1979); (i) E. P. Trutneva, R. R. Shagidullin, E. E. Borisova and N. M. Vafina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2616 (1976); (j) E. P. Trutneva, R. R. Shagidullin, L. V. Stepadhkina and N. I. Rizpolozhenskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2726 (1977).
18. (a) T. M. Lane, O. P. Rodriguez, M. K. Tasz, A. G. Sommese, S. E. Cremer, Dennis W. Bennett and P. E. Fanwick, *Phosphorus, Sulfur and Silicon*, (1994) submitted; (b) I. Neda, T. Kaukorat, A. Fisher and P. G. Jones, *Phosphorus, Sulfur, and Silicon*, **85,** 153 (1993); (c) W. O. Lin, G. B. Garcia, C. M. M. Sachett, H. G. Alt and W. Milius, *Phosphorus, Sulfur, and Silicon*, **85,** 113 (1993).
19. (a) V. V. Zverev, J. Villem, V. E. Bel'skii and Yu P. Kitaev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1,** 84 (1979); (b) I. P. Lipatova, Z. Z. Kurzhunova, F. M. Kharrasova and V. D. Efimova, *Zh. Obshch. Khim. USSR*, **45,** 287 (1975).
20. (a) T. Gramstad, *Spectrochim. Acta*, **19,** 829 (1963); (b) T. Gramstad and E. D. Becker, *J. Mol. Struct.*, **5,** 253 (1970); (c) V. E. Bel'skii, R. F. Bakeeva, L. A. Kudryavtseva, A. M. Kurguzova and B. E. Ivanov, *Zh. Obshch. Khim. USSR*, **43,** 2568 (1975).
21. (a) I. Olovsson and P.-G. Jönsson, in "The Hydrogen Bond," vol. II (ed.) P. Schuster, G. Zundel and C. Sandorfy, (Amsterdam: North Holland, 1976), p. 418; (b) R. Taylor, Kennard and W. Versichel, *J. Amer. Chem. Soc.*, **105,** 5761 (1983).
22. C. M. Huggins and G. C. Pimentel, *J. Phys. Chem.*, **60,** 1615 (1956).
23. R. Mecke, *Discussions Faraday Soc.*, **9,** 161 (1950).
24. G. Aksnes and K. Bergesen, *Acta Chem. Scand.*, **18,** 1586 (1964).