Heteroatom Chemistry
Volume 7, Number 5, 1996

Conformational Analysis of 2-Substituted Alkylphosphoryl Compounds. Part 3: (2-Hydroxypentyl)diphenylphosphine Oxide and Its Acetate

Daniel G. Genov, Roman A. Kresinski, and John C. Tebby*

Division of Chemistry, School of Sciences, Staffordshire University, Stoke-on-Trent, ST4 2DE, U.K.

Received 5 February 1996; revised 28 May 1996

ABSTRACT

Conformational analysis of (2-hydroxypentyl)diphenylphosphine oxide **1** *and its acetate* **2** *is described. The NMR, X-ray, IR, and molecular mechanics (MM) modeling studies indicated that phosphine oxide* **1** *favors different conformers in the solid state and in solution and that conformational preferences are strongly influenced by the nature of the hydrogen bonding. Vicinal proton–proton coupling constants and MM modeling solvation studies indicated that there are deviations from perfectly staggered conformers. Conformational analysis based on the twisted staggered conformers for phosphine oxide* **1** *made marked changes to the estimated conformational populations. For the acetate* **2**, *NMR spectroscopy established that the position of the conformational equilibrium is strongly dependent on the polarity of the medium.* © *1996 John Wiley & Sons, Inc.*

INTRODUCTION

Conformational analyses of 2-hydroxyphosphonates [1,2] have shown that these compounds exhibit a strong preference for one conformer (*ga*) attributable to a favorable *anti*orientation of the large substituents and stabilizing effect of intramolecular hydrogen bonding. Derivatization of the hydroxyl group to carboxylic ester [2] removes this preference, but it is reinforced by the addition of alkali metal salts that utilize the phosphoryl and possibly the hydroxyl oxygen atoms as ligands to the alkali metal cations. Studies on the solution and solid-state structure of stereoisomers of the products of the reaction of diethyl (1-cyclohexenyl)methylphosphonate [3] or diethyl prop-2-enylphosphonate [4] and aldehydes have shown that in both phases the products adopt the same conformer, involving *gauche* orientation of the phosphoryl and the 2-hydroxy groups and *anti*orientation of the former group and the alkyl group of the aldehyde molecule. In the crystal, this conformer is retained despite the fact that the P = O–H–O hydrogen bonding occurs intermolecularly and not intramolecularly.

This article presents a conformational study of (2-hydroxypentyl)diphenylphosphine oxide 1 and its acetate 2. Both NMR spectroscopic evidence and molecular mechanics (MM) modeling were used to investigate the influence of preferential solvation on the conformational equilibrium of these compounds. X-ray diffraction and IR spectroscopy were employed to study the nature of the hydrogen bonding in phosphine oxide **1**.

Dedicated to Professor Louis D. Quin on the occasion of his retirement from the University of Massachusetts at Amherst.

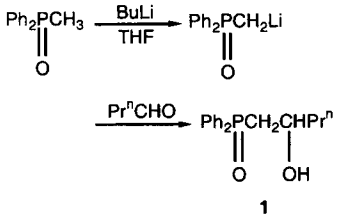
*To whom correspondence should be addressed.

1042-7163/96/050375-08

RESULTS AND DISCUSSION

Synthesis

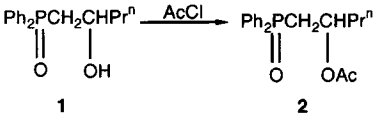
The alcohol 1 was obtained in 74% yield by the reaction of diphenylmethylphosphine oxide with butyraldehyde in tetrahydrofuran (THF) [5].



(1)

1

The acetate 2 was synthesised in a yield of 88% by the reaction of phosphine oxide 1 with acetyl chloride.



(2)

1 2

The structures and the purity of the products 1 and 2 were confirmed by IR, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy.

Conformational Analysis

The relative populations of the staggered conformers about the C1–C2 bond (Figure 1) were estimated by relating the experimental vicinal proton–proton coupling constants ($^{3}J_{AM}$ and $^{3}J_{BM}$) to the couplings calculated for the individual conformers. Full details have been previously described [2].

For the alcohol 1, conformer *ga* was found to be favored in all solvents (Table 1); however, it must be noted that in this part of the study only the perfectly staggered conformers were considered.

This analysis gave unrealistic values (<0%) for the conformational populations of phosphine oxide 1 in chloroform-d and benzene-d6 solutions because $^{3}J_{AM}$ and $^{3}J_{BM}$ (Table 1) were less than the calculated couplings for the perfectly staggered conformer *ga*. Whilst the value of the experimental $^{3}J_{BM}$ is 1.4 Hz lower than that calculated for conformer *ga*, $^{3}J_{AM}$ differed by only 0.1 Hz. The MM modeling indicated that intramolecular interactions and solvent-solute interactions could induce a distortion from the perfectly staggered geometries (subsequently discussed). It was concluded that the major conformer for phosphine oxide 1 in these solutions is a twisted version of *ga*, with conformer *gg* also contributing to the conformational equilibrium. The values of $^{3}J_{PC}$ (13.7 Hz in chloroform-d and 13.2 Hz in benzene-d6) are also indicative of a high population of conformer *ga*. The preference for conformer *ga* can be attributed to the favorable *anti*orientation between the bulky groups ($Ph_2P(O)$ and Pr^n) and the stabilizing hydrogen bonding between the phosphoryl and the hydroxyl groups.

The nature of the hydrogen bonding was investigated using X-ray diffraction, IR spectroscopy (focussing on the hydroxyl absorption band 3000–3800 cm^{-1}), and determination of the molecular weight by boiling-point elevation.

Single-crystal X-ray diffraction studies of phosphine oxide 1 indicated that in the solid state both the type of hydrogen bonding and the conformational preference are different from those in solution. In the crystal, the molecule forms infinite chains through intermolecular hydrogen bonding. A

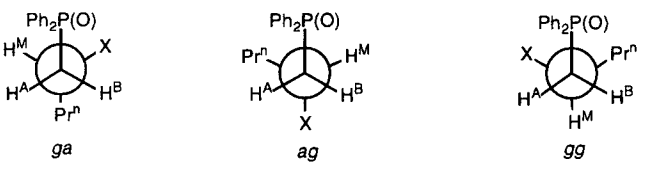


FIGURE 1 Perfectly staggered conformers of phosphine oxides 1(X = OH) and 2(X = OAc).

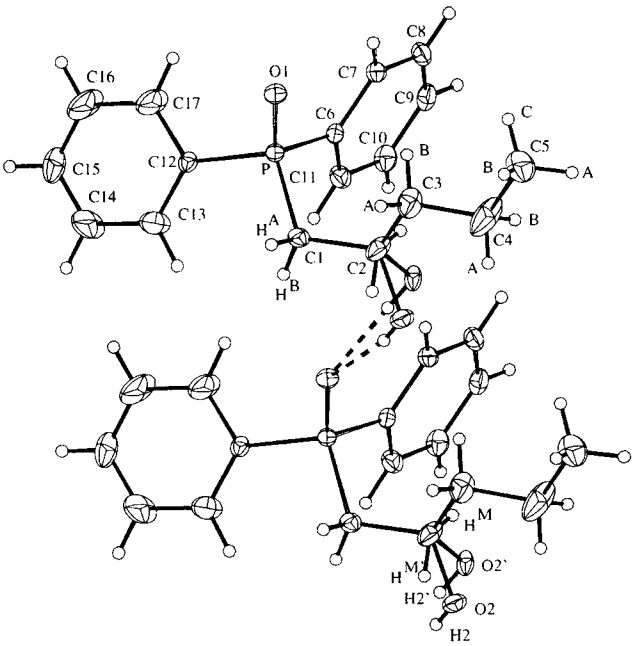


FIGURE 2 A diagram of 1 showing the intermolecular hydrogen bonding (dotted lines) and the numbering scheme. The disorder in the region of C2 has been shown in full but labeled only on the second molecule, which is related to the "home" asymmetric unit by *x*, *y*-1, *z*. Thermal ellipsoids are depicted at the 30% probability level. The plotting routine is *SNOOPI* [16].

TABLE 1 Chemical Shifts of the α-Methylene Protons and the Phosphorus Nucleus (ppm), Vicinal Proton–Proton and Phosphorus–Carbon Coupling Constants (Hz), and Conformational Populations (%) for Phosphine Oxides **1** and **2**, Based on Perfectly Staggered Conformers.

Compd	*Solvent*	δ_A	δ_B	$^3J_{AM}$	$^3J_{BM}$	P_{ga}	P_{ag}	P_{gg}	$^3J_{PC}$	δ_P
1	$CDCl_3$	2.39	2.45	2.0	10.3	86	−3	17	13.7	34.92
	C_6D_6	2.08	2.29	2.0	10.3	86	−3	17	13.2	32.39
	$(CD_3)_2CO$	2.65	2.40	2.9	9.8	79	6	15	12.7	32.98
	C_5D_5N	2.68	2.76	3.7	8.7	66	13	21	11.3	30.99
	$(CD_3)_2SO$	2.53	2.59	5.4	7.0	45	30	25	8.3	29.65
	CD_3OD	2.58	2.66	5.2	7.5	50	29	21	8.8	34.96
	LiCl(1:1)	2.77	2.82	2.8	9.5	77	4	19	12.2	36.98
	NaI(1:1)	2.85	2.68	2.7	9.5	77	3	20	12.2	34.51
2	CCl_4	2.33	2.63	4.9	7.8	18	54	28	1.6	23.84
	$CDCl_3$	2.53	2.73	6.3	6.3	35	39	26	5.9	28.17
	C_6D_6	2.27	2.54	6.9	5.6	28	45	27	5.4	25.13
	$(CD_3)_2CO$	2.61	2.86	5.4	7.3	49	30	21	6.9	26.56
	C_5D_5N	2.79	3.03	5.4	7.3	49	30	21	6.9	23.27
	$(CD_3)_2SO$	2.68	2.90	4.9	8.3	59	27	14	7.8	24.18
	CD_3OD	2.68	2.91	4.3	8.5	63	20	17	8.8	32.22
	LiCl(1:1)	2.87	2.97	4.6	8.0	57	23	20	8.3	31.44
	NaI(1:1)	2.74	3.04	4.4	8.3	60	21	19	8.8	29.91

large degree of disorder is evident, which involves inversion of configuration at C2, and which could not be modeled more satisfactorily by use of a lower symmetry space group or large displacement ellipsoids for the hydroxyl groups. The conformer distribution was refined to be 59% *ag* and 41% *gg*, although the centrosymmetry of the system means that the crystal is perfectly racemic. Both sites of the disordered OH groups lend themselves to hydrogen bonding with the same phosphoryl moiety (Figure 2). Selected dihedral angles, bond lengths, and bond angles are listed in Table 2. These show that both conformers appear to be somewhat strained, the P–C1–C2–O2 and P–C1–C2–O2′ (′ denotes conformer *gg*) dihedral angles being 154.3(4) and 94.3(6) degrees, respectively; what is not clear, however, is the extent to which this distortion originates from crystal packing effects. Atoms C4, C13, C14, C16, and C17 have rather elongated thermal ellipsoids. These are all consistent with plausible librational effects constituting, in the case of C4, rotation of the Pr^n group about the C3–C5 axis and, in the case of the others, rotation of the phenyl ring about the P–C12 axis.

TABLE 2 Selected Bond Lengths [Å], Interatomic Angles, and Dihedral Angles [deg] for Ph2P(O)CH2CH(OH)Pr.

P–01	1.494(2)
P–C1	1.798(4)
P–C12	1.805(4)
P–C6	1.808(4)
C1–C2	1.532(5)
C2–C2	1.378(6)
C2–C3	1.456(5)
C3–C4	1.490(6)
C4–C5	1.448(6)
01–P–C1	114.0(2)
01–P–C12	111.3(2)
C1–P–C12	107.0(2)
01–P–C6	110.7(2)
C1–P–C6	108.4(2)
C12–P–C6	105.0(2)
C2–C1–P	116.0(3)
02–C2–C3	115.5(4)
02–C2–C1	116.4(4)
C3–C2–C1	117.4(3)
C2–C3–C4	118.1(4)
C5–C4–C3	117.8(4)
O1–P–C1–C2	74.3(3)
P–C1–C2–O2	154.3(4)
P–C1–C2–O2′	94.3(6)
P–C1–C2–C3	62.6(5)

Infrared spectroscopy indicated that, in tetrachloromethane and chloroform-d solutions, phosphine oxide **1** forms intramolecular hydrogen-bonded monomers. Thus, in the solid state and in tetrachloromethane solutions ($0.5–3 \times 10^{-3}$ mol %), phosphine oxide **1** exhibits a single band at very different frequencies—at 3335 cm^{-1} due to intermolecular hydrogen bond and at 3425 cm^{-1} due to intramolecular hydrogen bond (Table 3). The spectra of chloroform-d solutions (4.3–0.2 mol %) have two bands—at 3410 and 3612 cm^{-1}. The band at 3410 cm^{-1} is attributed to intramolecular hydrogen-bonded monomers, which is confirmed by the absence of a shift to higher frequencies upon dilution. The weak band at 3612 cm^{-1} corresponds to the

TABLE 3 Hydroxyl Stretching Wavenumbers (cm^{-1}) of Phosphine Oxide **1** in the Solid State, in Tetrachloromethane and Chloroform-d Solutions.

Compd	*Sample*	*C (mol %)*	*Intermolecular H-Bonded OH*	*Intramolecular H-Bonded OH*	*Free OH*
1	Solid		3335		
	CCl_4 solution	0.5		3425	
		0.2		3422	
		3×10^{-3}		3425	
	$CDCl_3$ solution	4.3		3401	3613
		2.2		3409	3612
		1.5		3411	3612
		1.1		3411	3612
		0.2		3410	3612

presence of free OH groups. By comparing the integral intensities of the bands, it was estimated that the relative population of the intramolecular hydrogen-bonded monomers in chloroform-d is 98%, and this does not alter over the concentration range 4.3–0.2 mol %.

The average molecular weights determined for 2.2 mol % solutions of phosphine oxide **1** in chloroform and benzene by elevation of the boiling point were 282 and 294, respectively (cf. RMM 288.3), confirming the predomination of monomers.

The ^1H NMR spectra of acetone-d6 solution of phosphine oxide **1** do not show changes in the conformational preferences (79% *ga*) over the temperature range −25–45°C, indicating that, with rise in the temperature, the extent of hydrogen bond breaking in conformer ga and conformer gg (rise in enthalpy) is sufficiently compensated by gain in degrees of freedom (rise in entropy), to maintain the same difference in free energy between the various conformers. The analysis of the NMR spectra of solutions of phosphine oxide **1** in more polar solvents indicated that the population of conformer *ga* decreases and the population of conformer *ag* increases with the increase of the solvent polarity. Thus, the population of conformer *ga* is 79% in acetone-d6 but only 50% in methanol-d4, the population of conformer *ag* in these solvents being 6% and 29%, respectively. The values of $^3J_{PC}$ also indicate a decrease of the population of conformer *ga* in methanol-d4; e.g., $^3J_{PC}$ is 12.7 Hz in acetone-d6 and 8.8 Hz in methanol-d4. This polar solvent effect on the conformational preferences is attributed to the solvation of the phosphoryl and the hydroxyl groups and the formation of solvent-solute associates, which exist in equilibrium with the intramolecular hydrogen-bonded species in solution.

For the acetate **2**, the position of the conformational equilibrium is strongly dependent on the nature of the solvent. While in less polar solvents (CCl_4, C_6D_6, $CDCl_3$), conformer *ag* is favored; e.g., the ratio *ga*:*ag* is 18%:54% in CCl_4; in polar solvents the population of conformer *ga* increases significantly. For example, in CD_3OD, the population of this conformer is 63%. The values of the $^3J_{PC}$ constants are also indicative of a preference for conformer *ga* in polar solvents; e.g., $^3J_{PC}$ is 8.8 Hz in CD_3OD and 1.6 Hz in CCl_4. ^1H NMR spectra solutions of acetate **2** in solvent mixtures (C_6D_6 + CD_3OD and $CDCl_3$ + CD_3OD) with different molar ratio indicate that the contribution of conformer *ga* increases with the molar fraction of CD_3OD, while the contributions of conformers *ag* and *gg* decrease (Figures 3 and 4). It has been reported that in conformationally mobile molecules, such as substituted ethanes containing two or more polar groups, the relative population of the most polar species typically increases in going from a medium of low dielectric constant to one of higher dielectric constant [6].

In Figure 5, the populations of conformer *ga* in chloroform-methanol mixtures are plotted against the E_T values of these solvent mixtures. The E_T polarity values (electronic transition energy) are derived from the solvatochromic behavior of a pyridinium betaine [7]. It can be seen that the increase of the population of conformer *ga* rises roughly linearly with the increase of the E_T values of the medium. This dependence clearly indicates that the trends in the conformational preferences of the ester **2** are mainly due to changes in the solvent polarity.

Studying the effect of Na^+ and Mg^{2+} on the conformational preferences of 2-hydroxyalkylphosphonates. Belcuig et al. observed a relative increase of the population of conformer *ga* and attributed the change to chelation of metal ions [1]. Recently, the metal-ion complexation was confirmed by ^{17}O NMR studies [8]. We established similar effects of Li^+, Na^+, and Zn^{2+} on the conformational equilibrium of a series of 2-hydroxyalkylphosphonates [2]. The addition of equimolar amounts of lithium chloride or

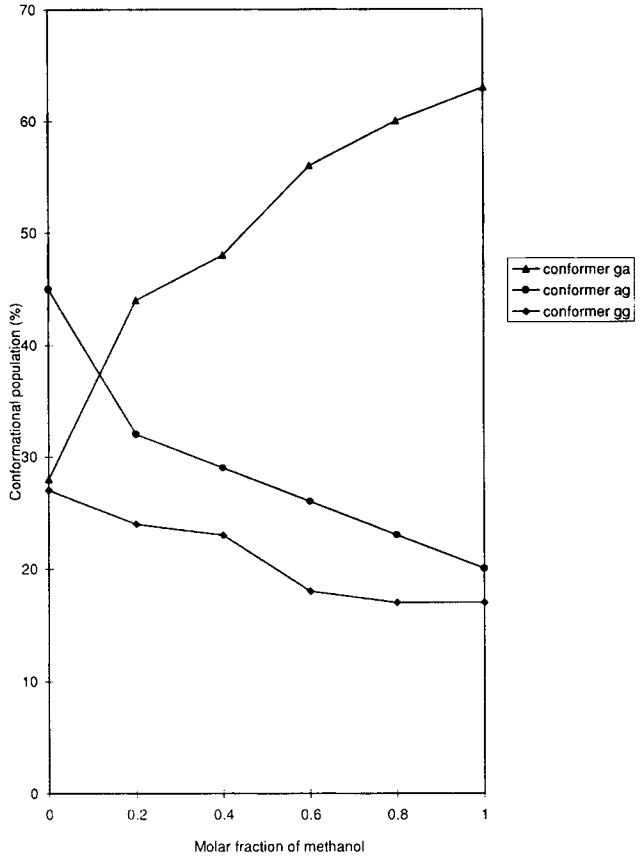


FIGURE 3 Populations of conformers *ga*, *ag*, and *gg* for phosphine oxide **2** in benzene-methanol mixtures as a function of the molar fraction of methanol (only the perfectly staggered conformers are taken into consideration).

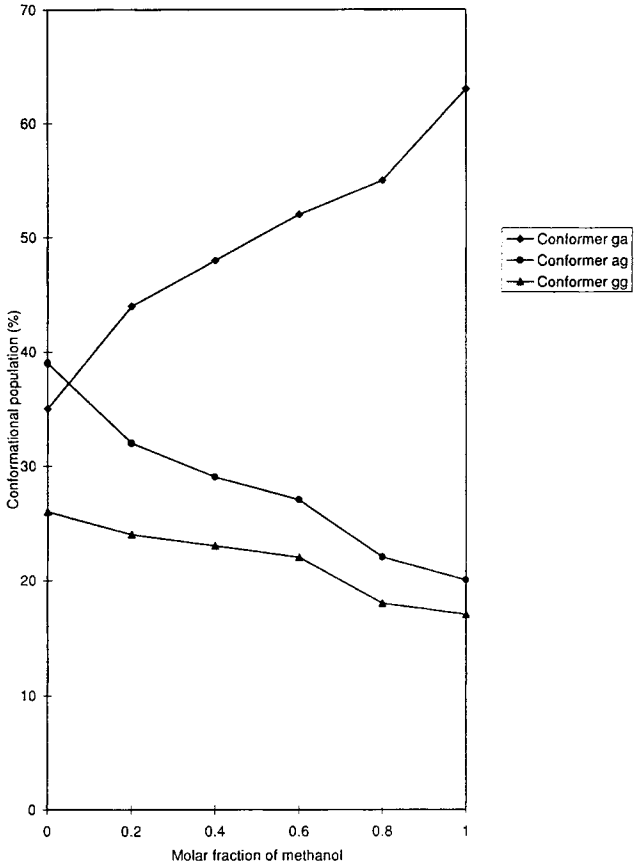


FIGURE 4 Populations of conformers *ga*, *ag*, and *gg* for phosphine oxide **2** in chloroform-methanol mixtures as a function of the molar fraction of methanol.

sodium iodide to the acetone-d6 solution of phosphine oxide **1** did not influence significantly the conformational equilibrium (Table 1). For example, the population of conformer *ga* in acetone-d6 was found to be 79%, and 77% in acetone-d6 containing lithium chloride or sodium iodide. The addition of salts results in downfield shifts of the ^{31}P signals relative to that in acetone-d6, showing that the metal ions coordinate to the phosphoryl oxygen of phosphine oxide **1**. Coordination of the metal ion by the hydroxyl oxygen and thus formation of a six-membered ring probably also occurs because the addition of salts does not lead to an increase of the population of conformer *ag*.

In contrast, the population of conformer *ga* for the acetate **2** increases when metal salts are present in the acetone-d6 solution. Thus, the population of conformer *ga* in acetone-d6 was estimated to be 49%, rising to 57% and 60% for solutions containing equimolar amounts of lithium chloride and sodium iodide, respectively. This is also evident from the values of $^3J_{PC}$, which are 6.9 Hz in acetone-d6, 8.3 Hz in the presence of lithium chloride, and 8.8 Hz in the presence of sodium iodide. The observed shift of the conformational equilibrium in favor of conformer *ga* is consistent with the proposition that there is chelation of the phosphoryl and the carbonyl oxygen atoms to the metal ion.

Molecular Mechanics Modeling Studies

The MM modeling studies of phosphine oxide **1** were carried out using the COSMIC-90 program [9] in order to assist the interpretation of the spectroscopic data and investigate specific solvent-solute interactions influencing the conformational preferences. The MM modeling of the vapor-phase stereochemistry predicted intramolecular hydrogen-bonded conformer *gg* to be the most stable. Intramolecular Van der Waals interactions were a major factor contributing to this vapor-phase preference. Since these interactions would be less important in solution, multiple dockings of four solvent molecules (six molecules in the case of chloroform) with the conform-

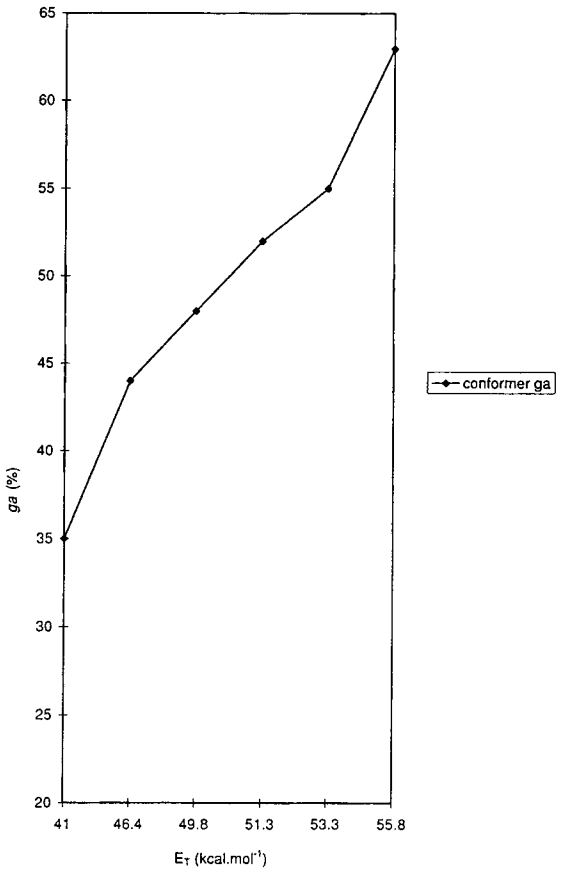


FIGURE 5 Populations of conformer *ga* for phosphine oxide **2** as a function of the E_T values of chloroform-methanol mixtures.

ers *ga*, *ag*, and *gg* of phosphine oxide **1** were performed. In accordance with the experimental results, conformer *ga*, stabilized by an intramolecular hydrogen bond between the phosphoryl oxygen and the hydroxyl hydrogen, became the most favored in all solvents. The relative conformer energies were also very dependent on the solvent, and in accordance with the observed trends, $\Delta E(ag\text{-}ga)$ was largest when benzene and chloroform were the docking molecules and smallest for methanol. The MM modeling indicated that the polar solvents stabilized conformer *ag* through intermolecular hydrogen bonding. Thus, the increase of the populations of conformer *ag* relative to *ga*, established by the ^{1}H NMR spectroscopic analysis of phosphine oxide **1**, can be attributed to solvent-solute association.

The MM modeling predicted deviations from the ideal conformational geometries; e.g., the H^AC1C2H^M dihedral angle in the chloroform-solvated conformer *ga* was predicted to be 67.2°. The vicinal proton–proton coupling constants of the individual conformers were recalculated, using the MM dihedral angles, and the conformer populations were reestimated, relating these couplings to the experimental coupling constants.

In some cases, large differences, compared with the estimation using perfectly staggered dihedral angles of 60°, −60°, and 180°, were obtained (Table 4). For example, in methanol, the relative population of conformer *gg* was estimated to be much smaller (2% rather than 21%), whereas the populations of the other two conformers were higher.

NMR Chemical Shifts of the α-Methylene Protons

The diastereotopic α-methylene protons H^A and H^B for phosphine oxide **1** are nonequivalent in all cases (Table 1), the chemical shift difference being dependent on the nature of the solvent. It is smallest in chloroform-d (0.06 ppm) and largest in acetone-d6 (0.25 ppm) and benzene-d6 (0.21 ppm). The signal of H^B is usually downfield of H^A. Only in acetone-d6 does the signal of H^A appear at lower field than that of H^B. Such a trend was observed for compounds with similar structures and will be discussed elsewhere. As previously found for 2-hydroxyalkylphosphonates, pyridine-d5 and benzene-d6 influence the chemical shifts in a different direction [2,10]. For C_5D_5N solutions, downfield shifts of H^A and H^B relative to those recorded for $CDCl_3$ solutions are of a similar magnitude. The MM modeling identified association of the nitrogen atom of pyridine with both of the α-methylene protons, which could explain the observed pyridine effect on the chemical shifts of these protons.

In contrast, the α-methylene protons exhibit a high-field shift for phosphine oxide **1** in C_6D_6 relative to $CDCl_3$. As previously observed for the phosphonates [2,10], the shift is larger for H^A than for H^B. This is further support for attributing the effect to preferential association of benzene with the hydrophobic face of the major conformer *ga*. Such an association would have a weaker anisotropic effect on H^B, since in conformer *ga*, this proton is in close proximity to the electron-rich OH group.

The chemical shift difference between the α-methylene protons for the acetate **2** is similar in all solvents, irrespective of the relative conformational populations, and the signal of H^B is always observed at lower field than that of H^A.

The addition of equimolar amounts of lithium chloride or sodium iodide to the acetone-d6 solutions of phosphine oxides **1** and **2** leads to marked downfield shifts of the signals of H^A and H^B. The effect is attributed to the coordination of the metal cat-

TABLE 4 Conformatinal Populations for Phosphine Oxide **1** Based on Twisted Staggered Conformers as Estimated by MM Modeling

Conformer	*Solvent*	*Dihedral Angle* H^AC1C2H^M	*Dihedral Angle* H^BC1C2H^M	*Conformational Populations*
ga	$CDCl_3$	67.2	−172.6	89
	C_6D_6	61.5	−179.4	85
	$(CD_3)_2CO$	61.5	−179.4	74
	C_5D_5N	66.5	−174.2	67
	CD_3OD	62.7	−177.7	60
ag	$CDCl_3$	176.9	−66.4	5
	C_6D_6	175.6	−67.7	−2
	$(CD_3)_2CO$	169.1	−73.9	7
	C_5D_5N	−175.2	−60.0	19
	CD_3OD	155.6	−86.3	38
gg	$CDCl_3$	−60.9	56.5	6
	C_6D_6	−60.7	56.6	17
	$(CD_3)_2CO$	−60.7	56.6	19
	C_5D_5N	−60.0	57.1	14
	CD_3OD	−60.6	56.8	2

ions by the phosphine oxides, enhancing the electron-accepting properties of the phosphoryl group.

^{31}P Chemical Shifts

The ^{31}P chemical shifts (Table 1) are dependent on the type of the substituent X and the nature of the solvent. The ^{31}P NMR signals of phosphine oxide **1** appear downfield relative to those of the corresponding acetate **2**. This trend could be taken as further evidence of the involvement of the phosphoryl oxygen in hydrogen bonding in 2-hydroxyalkylphosphine oxides, which increases σ-polarization of the phosphoryl group and alters π-back bonding to phosphorus. In solvents that could act as proton donors to the phosphoryl group, such as methanol and in lesser extent chloroform, downfield shifts of the ^{31}P signals are observed compared with the other solvents used. The addition of salts to the acetone-d6 solutions of **1** and **2** also leads to marked downfield shifts of the ^{31}P signals, which confirms the coordination of the metal ions to the phosphoryl oxygen.

EXPERIMENTAL

General

^1H, ^{13}C, and ^{31}P NMR spectra of 2.2 mol % solutions of phosphine oxide **1** and its acetate **2** in chloroform-d, benzene-d6, pyridine-d5, dimethyl sulphoxide-d6, methanol-d4, and acetone-d6 without and with equimolar amounts of lithium chloride or sodium iodide were recorded on a JEOL GSX-270 spectrometer. The ^1H NMR spectra of phosphine oxide **1** in chloroform-d and dimethyl sulfoxide-d6 were also recorded on a Bruker ACP-400 spectrometer. ^1H NMR spectra of 0.1 M solutions of acetate **2** in chloroform-d, benzene-d6, methanol-d4, chloroform-d /methanol-d4, and benzene-d6/methanol-d4 binary mixtures were recorded on a JEOL JNM FX-270 spectrometer. All ^1H and ^{13}C measurements were referenced to Me_4Si as an internal reference. ^{31}P NMR spectra were referenced to 85% H_3PO_4. The chemical shifts of the α-methylene protons and the vicinal proton–proton coupling constants $^3J_{AM}$ and $^3J_{BM}$ were calculated using LAOCOON IV [11]. The parameters were accurate to 0.1 Hz or better. The solvents were commercially obtained and used without further purification. The IR spectra in solid state (KBr discs) were recorded on a Nicolet Impact 400 spectrometer. The MM modeling studies and determination of molecular weight were carried out as previously described [10].

X-ray Crystal Structure Determination

Crystal Data (**1**). $C_{17}H_{21}O_2P$, M = 288.3, monoclinic, space group $P2_1/n$, a = 12.354(1), b = 5.825(1), c = 21.672(1) Å, β = 91.20(1)°; least-squares refinement of 250 data with $1.88 < \theta < 25.02°$, U = 1559.1 A^3, D_c = 1.228 g cm^{-3}, Z = 4, $F(000)$ = 616.0. Monochromatic (graphite) radiation Mo-$K_\alpha\lambda$ = 0.71069 Å, μ = 1.75 cm^{-1}, T = 150 K; specimen: block, 0.28 × 0.32 × 0.20 mm^3.

Procedure. 6550 reflections were recorded, on a FAST TV detector diffractometer, using previously described methods [12] ($1.88 \leq \theta \leq 25.02$, $-13 \leq h \leq 13$, $-6 \leq k \leq 4$, $-23 \leq l \leq 23$) and merged (Rint = 0.0599) to give 2384 unique data. These were cor-

rected for Lorentz and polarization effects, and standard decay. Systematically absent data indicated the space group. Most non-H atom positions were estimated using direct methods [13], and all were located by means of sequential difference-Fourier syntheses [14]. These atoms were refined anisotropically. Hydrogen atoms were introduced in theoretical positions (OH, 0.82; $C_{aryl}H$, 0.93; $C_{methyne}H$, 0.98; $C_{methylene}H$, 0.97; $C_{methyl}H$, 0.96A) and assigned common, refined, type-specific isotropic displacement parameters. Finally, an absorption correction [15] based on these models was applied to the data and degrees of freedom restricted appropriately for the final refinement [14] cycles. The weighting scheme was $w^{-1} = \sigma^2(F_0)^2 + 0.0975P^2$, where $3P = (F_0)^2 + 2(F_c)^2$, which resulted in satisfactory counting statistics; convergence resulted in conventional [14] discrepancy indices of $R_1 = 0.0633$, ${}_wR_2 = 0.1616$ for 1672 data with $I > 2\sigma(I)$. The corresponding values for all data were 0.0876 and 0.1696.

Preparation of Phosphine Oxide **1** *and the Acetate* **2**

(2-Hydroxypentyl)diphenylphosphine Oxide (**1**). [5]. To a stirred solution of diphenylmethylphosphine oxide (5 g, 0.023 mol) in dry THF, a solution of *n*-butyllithium (1.6 M in hexane, 15.6 mL, 0.023 mol) was added at 0°C under N_2. After 30 minutes, the reaction mixture was cooled to −78°C, and a solution of butyraldehyde (2.16 g, 0.03 mol) in THF was added dropwise at such a rate that the solution temperature was maintained at −78°C. The reaction mixture was allowed to warm to room temperature over 2 hours, and water was added to the aqueous residue before extraction with dichloromethane. The extract was dried ($MgSO_4$), and dichloromethane was evaporated to give a solid product, which was purified by recrystallization from hexane/acetone and produced white crystals (4.9 g, 74%): mp 109–111°C; IR (KBr, cm^{-1}): max 3335 (OH); 1185, 1154 (P=O). Anal. calcd for $C_{17}H_{21}O_2P$: C, 70.82; H, 7.34. Found: C, 70.87; H, 7.39%.

(2-Acetyloxypentyl)diphenylphosphine Oxide (**2**). To a solution of phosphine oxide **1** (1.5 g, 0.005 mol) in dichloromethane, acetyl chloride (0.8 g, 0.01 mol) was added, and the mixture was refluxed for 2 hours. Removal of the solvent gave the crude product as white crystals, which were purified by recrystallization from hexane/acetone (1.5 g, 87%): mp 71–72°C; IR (KBr, cm^{-1}): max 1742 (C=O); 1256, 1242, 1232 (P=O).

ACKNOWLEDGMENTS

The authors acknowledge useful discussions with Prof J. Graham Dawber with respect to the use of E_T values and thank the Chemistry Department of Keele University for the use of their JEOL GSX-270 NMR spectrometer and particularly to Mr Graham Evans for recording the spectra. We are also grateful to Mr. Steven Withington from Ceram Research for recording the IR spectra on Nicolet Impact 400 spectrometer and to Dr. Oliver Haworth from the University of Warwick for the 400 MHz ^1H NMR spectra. Grateful acknowledgments are made of the use of the EPSRC X-ray Crystallography Service, Cardiff, for the provision of data. Thanks also to all the Staff there.

REFERENCES

[1] (a) M.-P. Belcuig, A. M. Modro, T. A. Modro, P. L. Wessels, *J. Phys. Org. Chem., 5,* 1992, 787; (b) M.-P. Belcuig, T. A. Modro, P. L. Wessels, *J. Phys. Org. Chem., 6,* 1993, 523; (c) M.-P. Belcuig, P. L. Wessels, T. A. Modro, *Magn. Reson. Chem., 31,* 1993, 1024.
[2] D. G. Genov, J. C. Tebby, *J. Org. Chem., 61,* 1996, 2454.
[3] K. P. Gerber, H. M. Roos, T. A. Modro, *J. Mol. Struct., 296,* 1993, 85.
[4] E. L. Müller, H. M. Roos, T. A. Modro, *J. Phys. Org. Chem., 6,* 1993, 64.
[5] A. D. Buss, S. Warren, *J. Chem. Soc. Perkin Trans., 1,* 1985, 2307.
[6] M. Barfield, M. D. Johnston Jr., *Chem. Rev., 73(1),* 1973, 53.
[7] J. G. Dawber, J. Ward, R. A. Williams, *J. Chem. Soc. Faraday Trans. 1, 84(3),* 1988, 713.
[8] M.-P. Belcuig, A. M. Modro, T. A. Modro, P. L. Wessels, *J. Phys. Org. Chem., 8,* 1995, 605.
[9] J. G. Vinter, A. Davis, M. R. Saunders, *J. Computer-Aided Mol. Design, 1,* 1987, 31.
[10] D. G. Genov, J. C. Tebby, *Phosphorus, Sulfur and Silicon,* in press.
[11] S. M. Castellano, A. A. Bothner-By, *J. Chem. Phys., 47,* 1967, 5443.
[12] J. A. Darr, S. R. Drake, M. B. Hursthouse, K. M. A. Malik, *Inorg. Chem., 32,* 1993, 5704.
[13] G. M. Sheldrick: *SHELXS-86, Program for the Solution of Crystal Structures,* University of Goettingen, 1987.
[14] G. M. Sheldrick: *SHELXL-93, Program for the Refinement of Crystal Structures,* University of Goettingen, 1993.
[15] N. Walker, D. Stewart, *Acta Cryst., A39,* 1983, 158.
[16] E. K. Davies: *SNOOPI,* Chemical Crystallography Laboratory, University of Oxford, 1982.