

Intramolecular Hydrogen Bonding in Hydroxyalkyl Diphenylphosphine Oxides

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Hydroxyalkyl diphenylphosphine oxides, $\text{HO}(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2$, with $n = 1, 2, 3$, and 4 , have been synthesized. Their melting points, mixed melting points with water and the infrared absorption bands of their hydroxyl and phosphoryl groups suggest that the compounds with $n = 1, 2$, and 3 form five-, six- and seven-membered hydrogen-bonded rings, respectively, whereas the compound with $n = 4$ is intermolecularly associated. The positions of the hydroxyl and phosphoryl bands indicate that the strengths of the hydrogen bonds in the rings decrease in the order five-membered > seven-membered > six-membered.

Intramolecular hydrogen bonding in acyclic saturated compounds have been studied by many workers.¹ The *gauche* conformers of 2-haloethanols have been shown to be more stable than the *trans* conformers in carbon tetrachloride solution, probably due to stabilization of the *gauche* form through a five-membered hydrogen-bonded ring.² 2-Aminoethanols also give infrared spectra typical of intramolecular hydrogen bonding.³ The displacement, $\Delta\nu$, of the free stretching vibration band of the hydroxyl group upon intramolecular hydrogen bonding in 1,2-ethanediol, 1,3-propanediol and 1,4-butanediol are 32, 78, and 156 cm^{-1} , respectively.⁴ Since the hydrogen-bonded rings formed by these diols contain five, six, and seven atoms, this indicates that the strengths of hydrogen bonds increase regularly from five- to seven-membered rings. Intramolecular association with more than seven atoms in the ring has not been observed. Thus, 1,6-hexanediol is unassociated at low concentration in carbon tetrachloride.⁴ Monoesters of 1,3-diols might be expected to form six-membered rings through participation of the ether oxygen as donor, as well as eight-membered rings when the carbonyl oxygen acts as donor. The six-membered rings are, however, the only ones observed, in spite of the much stronger donor properties of the carbonyl oxygen in hydroxy esters as compared to the ether oxygen.⁵ 2-Hydroxy-3-butanone gives a fairly strong five-membered ring.⁶ Other hydroxy ketones have not been studied from this point of view.

Intramolecular hydrogen bonding has been observed in certain α -hydroxy phosphoryl compounds.¹⁶ This paper reports studies of saturated aliphatic compounds containing a hydroxy group and a diphenyl phosphoryl group separated by an unbranched hydrocarbon chain, $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_n\text{OH}$ ($n = 1, 2, 3,$ and 4). On the basis of the strong acceptor ability of the phosphoryl group,⁷ this series of compounds appeared suitable for comparative studies of the relative stabilities of different-sized hydrogen-bonded rings.

EXPERIMENTAL

Hydroxymethyl diphenylphosphine oxide was synthesized from diphenylphosphine oxide and paraformaldehyde. Diphenylphosphine oxide was obtained from diethyl phosphite and phenylmagnesium bromide according to the method of Hunt and Saunders.³ Diphenylphosphine oxide (10 g) was dissolved in 15 ml absolute ethanol. 1.5 g paraformaldehyde and 0.1 g of sodium was added. The reaction started with evolution of heat and a clear solution resulted. After 20 h at room temperature the solution was acidified with a few drops of concentrated hydrochloric acid, and excess paraformaldehyde was filtered off. From the filtrate the hydroxymethyl diphenylphosphine oxide was obtained in crystalline state. After recrystallization from ethanol ether mixture the compound melted at 139°. (Found: C 67.58; H 5.22. Calc. for $\text{C}_{13}\text{H}_{13}\text{PO}_2$: C 67.37; H 5.62.)

The other hydroxyalkyl diphenylphosphine oxides were made by alkaline decomposition of hydroxyalkyl triphenylphosphonium chlorides in water-ethanol mixtures.² The phosphonium chlorides were obtained from the hydroxy substituted alkyl chlorides $\text{HO}(\text{CH}_2)_n\text{Cl}$ ($n = 2, 3,$ and 4), and triphenylphosphine.¹⁰

2-Hydroxyethyl diphenylphosphine oxide, recrystallized three times from ethanol-ether mixture, m.p. 94–95°. (Found: C 68.08; H 5.99. Calc. for $\text{C}_{14}\text{H}_{16}\text{PO}_2$: C 68.28; 6.14.)

3-Hydroxypropyl diphenylphosphine oxide, recrystallized four times from ethanol-ether mixture, m. p. 103°. (Found: C 68.91; H 6.29. Calc. for $\text{C}_{15}\text{H}_{17}\text{PO}_2$: C 69.10; H 6.52)

4-Hydroxybutyl diphenylphosphine oxide, recrystallized four times from ethanol-water mixture, m.p. 267–69°. (Found: C 73.99; H 5.85. Calc. for $\text{C}_{16}\text{H}_{19}\text{PO}_2$: C 70.20; H 5.89.)

Infrared spectra were recorded on an Unicam infrared spectrophotometer, Model S.P.100, MK2, using sodium chloride prism as well as grating optics.

Table 1. Physical data of the hydroxyalkyl diphenylphosphine oxides, $\text{HO}(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2$, in solid state.

n	Melting point	Wet melting point, °	Depression of melting point, °	Stretching vibration, cm^{-1}		cm^{-1} *		Type of association
				O—H	P=O	O—H	P=O	
1	139	139	0	3220	1156	400	34	intra
2	95	90	5	3325	1183	295	7	intra
3	103	103	0	3280 3385	1158 1175	340 235	32 17	intra
4	269	260	9	3450 very broad	1183	170	7	inter

* relative to free O—H and P=O bands at 3620 cm^{-1} and 1190 cm^{-1} , respectively.

RESULTS AND DISCUSSION

The four hydroxyalkyl diphenylphosphine oxides studied (Table 1) should be capable of forming five-, six-, seven- and eight-membered hydrogen bonded rings as n in $\text{HO}(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2$ is 1, 2, 3, and 4, respectively. Comparison of the stretching vibration bands of the associated hydroxyl groups in the four phosphine oxides in the solid state (Fig. 1) shows that the compound with

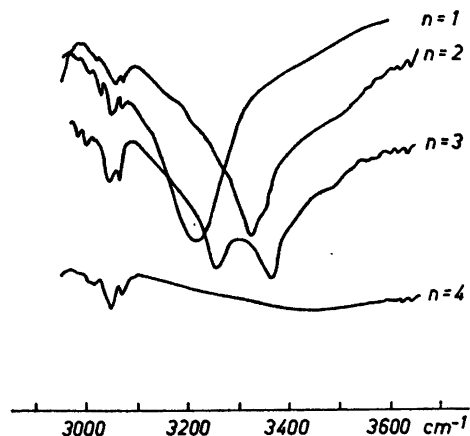


Fig. 1. Stretching vibration bands of the associated hydroxyl group in hydroxyalkyl diphenylphosphine oxides, $\text{HO}(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2$ in the solid state.

$n = 4$ gives a very much broader hydroxyl band than the compounds with $n = 1, 2,$ and 3 . According to Mecke¹¹ and Huggins and Pimentel¹² intermolecular association through hydrogen bonding is easily distinguished from intramolecular hydrogen bonding by the broadness of the hydroxyl band of the former. Further support for the open chain structure of 4-hydroxybutyl diphenylphosphine oxide comes from the high melting point of the compound (269°). The melting points of the compounds with $n = 1, 2,$ and 3 are $139^\circ, 95^\circ,$ and 103° , respectively (Table 1). The depression of the melting point in the presence of small amounts of water¹³ (Table 1) points in the same direction. From the criteria cited it can be concluded that the hydroxyalkyl triphenylphosphine oxides with $n = 1, 2,$ and 3 are intramolecularly associated, whereas in the compound with $n = 4$ the association is intermolecular.

Apparently the strain in the eight-membered ring is too great for the ring to be stable. The result is not unexpected since it is known that medium sized ring systems (8–11 atoms in the ring) form very difficultly. The resistance against ring closure is generally believed to be due to the compression strains between hydrogen atoms on non-adjacent carbon atoms in the ring.¹⁴

The infrared spectra in the region of O-H vibration for the six- and seven-membered ring compounds in carbon tetrachloride are shown in Figs. 2 and 3. The solubilities of the compounds with $n = 1$ (five-membered ring) and $n = 4$ (intermolecular associate) are too small for their spectra to be studied in carbon tetrachloride solution. It is seen from Figs. 2 and 3 that the position

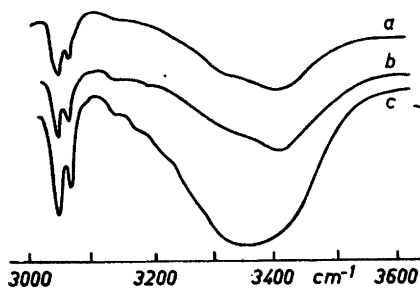


Fig. 2. Hydroxyl vibration bands of 2-hydroxyethyl diphenylphosphine oxide in carbon tetrachloride. a) 0.025 M; b) 0.05 M; c) 0.1 M.

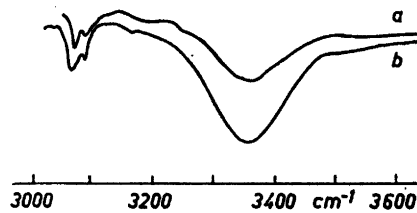


Fig. 3. Hydroxyl vibration bands of 3-hydroxypropyl diphenylphosphine oxide in carbon tetrachloride. a) 0.025 M; b) 0.05 M.

of the hydroxyl band of the six-membered ring compound is concentration dependent above approximately 0.1 M, thus indicating a tendency for intermolecular association at higher concentrations. The hydroxyl band of the seven-membered ring compound is not concentration dependent up to 0.05 M, the highest concentration obtainable in carbon tetrachloride.

The displacement of the associated hydroxyl band from the position of the free band gives a relative measure of the strength of the hydrogen bond. The data in Table I therefore indicate the following order of strength of the hydrogen bonds in hydroxyalkyl diphenylphosphine oxides: five-membered ring ($n = 1$) > seven-membered ring ($n = 3$) > six-membered ring ($n = 2$) > intermolecular association ($n = 4$). The same conclusion is reached on comparing the displacements of the phosphoryl band in the same compounds.

The relative strengths of the hydrogen-bonded rings in hydroxyalkyl diphenylphosphine oxides are thus different from the relative strengths of the hydrogen bonds in intramolecularly associated diols⁴ where the displacement



Fig. 4. The phosphoryl band in the solid state of: a) 3-hydroxypropyl diphenylphosphine oxide; b) hydroxymethyl diphenylphosphine oxide.

1000 1200 cm^{-1}

of the hydroxyl band indicated the series: seven-membered ring > six-membered > five-membered.

The hydrogen bond in seven-membered rings is favoured relative to five- and six-membered rings with regard to the bond angle, O—H...O which successively increases from five- to seven-membered rings. This increase in bond angle may be regarded as the chief reason for the relative strengths of the hydrogen bonds in diols. The greater strength of the five-membered ring in hydroxyalkyl diphenylphosphine oxides as compared to six- and seven-membered rings, must be due to the strong inductive effect of the phosphoryl group which greatly activates the hydrogen atom of the α -hydroxyl group and correspondingly strengthens the hydrogen bond. This effect quickly abates with increasing n ; the hydroxyl group in β - and γ -positions to the phosphoryl group are much less activated. In six- and seven-membered rings it is accordingly assumed that the O—H...O angle determines the bond strength.

From Figs. 1 and 4 is seen that hydroxyl and phosphoryl bands of 3-hydroxypropyl diphenylphosphine oxide are split in the solid state and thus differ from those of the other hydroxyalkyl diphenylphosphine oxides. In carbon tetrachloride solution only a single hydroxyl band is observed (Fig 3), which shows that the splitting of the band is specific for the solid state. The equal intensity of the hydroxyl and phosphoryl doublet bands in the solid state (Figs. 1 and 4) suggests the presence of two conformations of the compound in the solid state. Further experiments with different substituents linked to phosphorus would be needed to decide whether the observed effect is due to the phenyl substituents, or connected with properties of the seven-membered ring. In this connection it is of interest to note that cyclononylamine hydrobromide exists in two different conformations in the solid state.¹⁵

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