ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE SAVANNAH RIVER LABORATORY, E. I. DU PONT DE NEMOURS & CO., AIKEN, S. C.]

Conformation of Organophosphorus Compounds. II. Proton Magnetic Resonance Studies of Some Phosphites, Phosphonites, Phosphates, Phosphonates and Additional Phosphinates[1]

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Proton magnetic resonance data are given for 61 organophosphorus esters. These data are interpreted as indicating that these esters spend an important fraction of their time in a single preferred general conformation. Rotation is considered to be rapid around linkages of phosphorus to carbon and phosphorus to oxygen to carbon.

Introduction

In a previous communication[2] it was reported that some of the proton resonances in certain esters of arylphosphoric, arylphosphonic, arylphosphinic and phenylphosphonous acids were doubled. It is the purpose of this paper to report the results of a more complete study of this phenomenon and of the inferences that may be drawn as to the structure of organophosphorus esters. The first paper in this series[3] was concerned primarily with rotation around carbon to phosphorus bonds. The present paper is concerned with compounds characterized by the P–O–C linkage, but also includes some compounds in which the protons of both alkyl and alkoxy groups in the same molecule show doubled resonances.

Experimental

Since about 70 organophosphorus esters were prepared in the course of this study, most of them by conventional procedures, no attempt will be made to describe the preparation and purification of all of them in detail; rather, preparations and purification by type will be described in a general way except where the techniques were not typical.

The final step in the preparation of most of these esters was to add slowly the appropriate phosphoryl, phosphonyl, phosphinyl or phosphonous chloride to a 50 to 100% excess of pyridine and the appropriate alcohol with good mixing in an ice-bath. For example

$$C_6H_5\overset{\overset{O}{\|}}{P}Cl_2 + 2ROH + 2C_5H_5N \longrightarrow C_6H_5\overset{\overset{O}{\|}}{P}-(OR)_2 + 2C_5H_5N\cdot HCl$$

After standing overnight, the reaction mixture was diluted with toluene or hexane, washed with dilute hydrochloric acid, water, sodium carbonate solution, and, finally, water. After the diluent was pumped off, the product was distilled under high vacuum. A packed or Vigreux column was used in the distillation when necessary.

The phosphonites were not washed because of their susceptibility to hydrolysis and to air oxidation. Instead, the mass of pyridinium hydrochloride was leached with hexane in which it is only slightly soluble. The small amount of pyridinium hydrochloride that was leached along with the product sublimed ahead of the product and collected in the distillation head, which was then removed and replaced. Two attempts to synthesize di-2-butyl phenylphosphonite by this technique were not successful; n.m.r. signals were obtained that were suggestive of a mixture of compounds. Infrared spectra indicated the presence of P–H and P–OH bonds. Vacuum fractionation of the mixture was not successful.

This technique of preparation and purification generally gave high yields of the desired products except in certain cases. Crude tris-(3,3-dimethyl-2-butyl) phosphate has a decided tendency to decompose violently above 90°. During distillation of this compound it is generally advisable to isolate the product in small fractions as they become available. The shelf life of this compound is not good—discoloration and strong odors arise after a few months; however, the aged compound was redistilled without incident. Tris-(3-butene-1) phosphate, bis-(3-butene-1) phenylphosphate and the 3-pentene-1 analogs also exhibited this type of behavior.

The chorides that were not commercially available were prepared as follows. Arylphosphoryl dichlorides were easily prepared by the technique of Rosenmund and Vogt.[4] This technique was modified by reducing the mole ratio of phenol or naphthol to $POCl_3$ to 0.5 in order to improve the yield of the dichloride over monochloride. The phosphonyl chlorides were prepared by the method of Kinnear and Perren.[5] No difficulty was encountered except with benzylphosphonyl chloride and its derivatives. With these compounds, a great deal of solid material was formed and only a little product. Attempts to circumvent this difficulty by treating benzylphosphonic acid with thionyl chloride led to the same trouble. The phosphinyl chlorides were prepared as de-described previously.[3]

The Arbuzov rearrangement was used to synthesize the benzylphosphonates whenever the appropriate trialkyl phosphite was available. For example

$$C_6H_5CH_2Br + (RO)_3P \longrightarrow C_6H_5CH_2\overset{\overset{O}{\|}}{P}-(OR)_2 + RBr$$

The 2-propyl trichloromethylphenylphosphinate was synthesized by this rearrangement with di-2-propyl phenylphosphonite, prepared in this Laboratory, and carbon tetrachloride. Di-2-propyl 2-thenylphosphonate was prepared by this reaction between triisopropyl phosphite and 2-thenyl chloride. The 2-thenyl chloride was prepared according to Hartough.[6]

The phthalidylphosphonates were prepared according to the procedures of Ramirez, Yamanaka and Basedow.[7] In the preparation of the ethyl derivative, about 20% yield of a by-product was obtained. Infrared and n.m.r. scans indicate that this by-product may be diethyl phthalate.

The acid ester, 2-butyl phenylphosphonate, was prepared by hydrolysis of di-2-butyl phenylphosphonate with aqueous potassium hydroxide at about 100°. The resulting aqueous phase was washed with ether, acidified, and extracted with ether; the ether phase was evaporated and the acid ester was dried.

The n.m.r. measurements were made with a Varian Associates model 4300B high resolution nuclear magnetic resonance spectrometer, at a frequency of 40 mc.p.s., as described in the previous paper in this series.[3]

(1) The information contained in this article was developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

(2) T. H. Siddall, C. A. Prohaska and W. E. Shuler, *Nature*, **190**, 903 (1961).

(3) T. H. Siddall and C. A. Prohaska, Paper I, *J. Am. Chem. Soc.*, **84**, 2502 (1962).

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(6) H. D. Hartough, "Thiophene and its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952.

(7) F. Ramirez, H. Yamanaka and O. H. Basedow, *J. Am. Chem. Soc.*, **83**, 177 (1961).

TABLE I

CHEMICAL SHIFTS, COUPLING CONSTANTS AND PHENYL SPLITTING FOR VARIOUS ORGANOPHOSPHORUS COMPOUNDS[a]

Phosphates	Chemical shift				Coupling constants			Doubling due to benzene ring separation of resonance of	
	$\delta_{\alpha H}$[a]	$\delta_{\beta H}$[a]	$\delta_{\gamma H}$[b]	$\delta_{(CH_3)_4Si}$	$J_{\alpha H-\beta H}$[d]	$J_{\alpha H-P}$[b]	$J_{\beta H-P}$[e]	β-Methyl H[e]	γ-Methyl H
Diethyl phenyl	95.8	207.7	[p]	260.0	7.0	8.7	0.7		[p]
Di-1-propyl phenyl	98.8	195.8	221.6	[q]	6.3	8.0	[o]	[n]	[n]
Di-1-propyl 2,6-dimethylphenyl	100.2	196.6	222.2	259.8	6.3	7.6	[o]	[n]	[n]
Tri-2-propyl	78.1	208.0	[p]	259.9	6.3	7.4	[o]	[n]	[p]
Di-2-propyl phenyl	74.5	208.2	[p]	[q]	6.7	7.8	[o]	2.8[n]	[p]
Di-2-propyl 2-methylphenyl	74.4	208.1	[p]	260.0	6.2	7.1	[o]	3.5	[p]
Di-2-propyl 3-methylphenyl	74.6	208.0	[p]	259.9	6.1	7.2	[o]	2.6	[p]
Di-2-propyl 4-methylphenyl	75.0	209.0	[p]	260.1	6.3	7.4	[o]	2.7	[p]
Di-2-butyl phenyl	82.2[u]	208.9[c]	223.4	[q]	6.3	[g]	[o]	3.5	3.1
Di-2-butyl 2-methylphenyl	80.9[u]	208.9[c]	222.9	259.5	6.3	[g]	[o]	4.6	3.9
Di-2-butyl 2,6-dimethylphenyl	82.6[u]	210.9[c]	224.4	260.0	6.3	[g]	[o]	6.3	5.3
Di-2-butyl 3,5-dimethylphenyl	82.9[u]	208.5[c]	222.5	259.8	6.2	[g]	[o]	3.1	2.7
Di-2-butyl 1-naphthyl	78.9[u]	209.9[c]	225.2	259.7	6.0	[g]	[o]	6.0	6.0
Di-2-butyl 2-naphthyl	79.6[u]	208.5[c]	223.2	260.1	6.1	[g]	[o]	3.7	3.6
2-Butyl diphenyl	76.5	209.4[c]	225.1	260.4	6.2	[g]	[o]	[n]	[n]
Bis-(3-butene-1) phenyl	[g]	205.7[c]	[p]	260.4	6.4	[g]	[o]	3.0	[p]
Tri-3-amyl	93.3	197.4[r]	221.9	259.6	5.5	7.7	[p]	[p]	[n]
Di-3-amyl phenyl	87.5	197.7[r]	223.3	[q]	5.5	7.5	[p]	2.5[r]	3.9
Tris-(3-methyl-2-butyl)	91.5[v]	210.0[c]	222.2	259.5	6.3	[g]	[o]	[n]	[n]
Bis-(3-methyl-2-butyl) phenyl	87.2[v]	210.5[c]	224.0	[q]	6.4	7.5	[o]	3.9	2.6
Tricyclopentyl	~70[g]	~190[f]	~190[f]	259.1	[g]	[g]	[p]	[f]	[f]
Dicyclopentyl phenyl	~64[g]	~190[f]	~190[f]	259.2	[g]	[g]	[p]	[f]	[f]
Dineopentyl phenyl	111.5	[p]	222.7	[q]	[p]	5.4	[p]	[p]	[n]
Dineopentyl 2,6-dimethylphenyl	111.8	[p]	222.7	259.7	[p]	5.2	[p]	[p]	[n]
Tris-(3-pentene-1)	[g]	196.2	223.5	260.0	[g]	[g]	[p]	[p]	[n]
Bis-(3-pentene-1) phenyl	[g]	[g]	224.2	260.1	[g]	[g]	[p]	~2.2[r]	3.2
Tris-(4-pentene-1)	[g]	208.8[c]	[p]	260.2	6.3	[g]	[o]	[n]	[p]
Bis-(4-pentene-1) phenyl	[g]	208.9[c]	[p]	260.0	6.4	[g]	[o]	2.9	[p]
Di-4-heptyl phenyl	~84[g]	~199[g]	~223[g]	259.7	[g]	[g]	[g]	[p]	[g]
Tris-(3,3-dimethyl-2-butyl)	~86[s]	205.4[c]	221.1	259.4	6.4	[g]	[o]	[n]	[n]
Bis-(3,3-dimethyl-2-butyl) phenyl	90.8	210.6[c]	223.8	260.1	6.4	7.5	[o]	4.5	2.4
Bis-(2,4-dimethyl-3-amyl phenyl	~104[g]	[g]	221.8	259.5	[p]	[g]	[g]	[g]	3.2
Bis-(2,6-dimethylphenyl) phenyl Phosphate	[n]	[p]	163.7[h]	260.0	[p]	[p]	[p]	[p]	[p]
Dimethyl phenyl-	113.0	[p]	[p]	260.2	[p]	10.9	[p]	[p]	[p]
Diethyl phenyl-	98.8	208.2	[p]	260.2	7.1	8.2	[o]	[n]	[p]
Diethyl benzyl	103.3	211.8	[p]	259.4	7.2	8.2	[o]	[n]	[p]
Diethyl phthalidyl[l]	91.6	206.7	[p]	256.9	7.1	{10.4[i] 8.3	[o]	13.0	[p]
Di-1-propyl phenyl thiono-	101.1	196.0	221.8	259.6	6.4	9.1	[p]	[p]	[n]
Di-2-propyl phenyl	75.3	209.1	[p]	259.9	6.4	8.2	[o]	6.4	[p]
Di-2-propyl phenyl thiono-	68.2	209.8	[p]	260.0	6.2	10.9	[o]	7.3	[p]
Di-2-propyl benzyl	80.8	213.4	[p]	259.5	6.0	7.5 ± 0.5	[o]	6.0	[p]
Di-2-propyl 2-methylbenzyl-	80.6	213.1	[p]	259.6	6.2	7.9	[o]	6.2	[p]
Di-2-propyl 2-phenylethyl-	75.1	208.9	[p]	259.9	6.3	8.1	[o]	[n]	[p]
Di-2-propyl 2-thenyl-	77.2	211.0	[p]	259.5	6.3	8.0	[o]	4.0	[p]
Di-2-propyl cyclopentyl-	75.4	208.9	[p]	259.6	6.1	7.8	[o]	[n]	[p]
Di-2-propyl phthalidyl-[l]	68.9	{200.8 213.9	[p]	256.7	{6.5 6.3	{7 ± 1 10.9[i]	[o]	{[n] 13.2	[p]
Di-2-butyl phenyl-	82.8[u]	210.3[c]	224.5	[q]	6.3	[g]	[o]	8.1[c]	7.5
Di-2-butyl benzyl-	87.4[u]	214.5[c]	226.7	260.2	6.5	21.5[i]	[o]	6.5[c]	3.9
Di-2-butyl dichloromethyl-	74.3[u]	204.6[c]	219.9	259.1	6.3	2.0[i]	[o]	[n]	[n]
Di-2-butyl cyclohexyl-	84.6[u]	208.9[c]	221.7	[q]	6.2	[g]	[o]	[n]	[n]
2-Butyl phenyl-	[g]	209.9[c]	224.8	[q]	6.1	[g]	[o]	[n]	[n]
Di-3-amyl phenyl-	90.4	200.0[r]	225.2	259.9	5.7	8.5	[p]	[p]	9.0
Di-3-amyl cyclopentyl-	~92[g]	~195[g,r]	228.5	259.5	[g]	[g]	[p]	[n]	[n]
Bis-(3-methyl-2-butyl) phenyl Other compounds	~94[g]	211.7	224.3	259.6	6.5	[g]	[o]	9.3	6.3
Diethyl phenylphosphonite[t,m]	124.4	229.7	[p]	276.4	7.1	8.3	0.5	[n]	[p]
Di-2-propyl phenylphosphonite[t]	105.6	226.0	[p]	274.1	6.3	8.6	[o]	3.0	[p]
2-Propyl trichloromethylphenyl-phosphinate	76.1	209.0	[p]	259.7	6.3	7.7	[o]	6.4	[p]
2-Propyl 2-propylphenyl-phosphinate	81.7[k]	{217.8[j] 210.3[k]	[p]	259.9	{6.9 ± 0.6[j] 6.5[k]	8.4[k]	17.7[k]	9.0[k]	[p]
2-Butyl 2-butylphenylphosphinate	~89[g]	[g]	[g]	259.6	[g]	[g]	[o]	[g]	[g]
Di-2-propylphenylphosphine oxide[m]	[g]	215.8	[p]	259.2	6.4 ± 0.5	[g]	15.4	6.4 ± 0.5	[p]
Tri-2-propyl phosphite	87.5	211.7	[p]	259.8	6.3	8.5	[o]	[n]	[p]

[a] Spectra were obtained for 10% solutions (by volume) of the appropriate chemical compound in carbon tetrachloride, except where noted otherwise, and are uncorrected for bulk magnetic susceptibility. [b] Values, in cycles per second referred to external benzene, are for resonance of protons in alkyl or alkoxy groups, except where noted otherwise. Chemical shifts (δ), measured to the center of a multiplet, are accurate to ±0.5 c.p.s., phenyl splitting and coupling constants (J) to ±0.2 c.p.s., except where noted otherwise. [c] Resonance of protons in β-methyl group. [d] J-Values are for coupling between protons on the α-carbon and protons in the β-methyl groups. [e] J-Values are for coupling between the phosphorus atom and protons in β-methyl group. [f] Protons on β- and γ-carbons unresolved at 25°; spectra show one broad peak for these pro-

tons. [g] Spectrum at 25° is not well enough resolved, or is too complex, to be completely analyzed. [h] Resonance of protons in methyl groups attached to benzene ring. [i] Resonance of protons on carbon atom attached directly to the phosphorus atom. [j] Values are for protons in the propyl group. [k] Values are for protons in the propoxy group. [l] Spectrum obtained for 10% solution in chloroform-*d* ($CDCl_3$). [m] Compound shows evidence of up to 10 mole % impurity. [n] No splitting was observed. [o] No coupling between the phosphorus atom and the protons in the β-methyl group was observed; this sets an upper limit for $J_{\beta H-P} \leqq 0.5$ c.p.s. for these compounds. [p] Molecule does not contain the appropriate group (β-methyl, γ-methyl, phenyl, etc.); hence this column is not applicable. [q] Tetramethylsilane internal reference is not included in this spectrum. [r] Values are for protons in the β-methylene group. [s] The spectrum of the proton on the α-carbon is much too complex for this molecule. It should be two overlapping quartets, and it appears to be six overlapping triplets. The cause of this irregularity is unknown. [t] Spectrum obtained for undiluted compound (reacts with most solvents). [u] The spectrum of the proton on the α-carbon should be six overlapping quartets. What we actually see are five or seven broad peaks, with the highest one in the center. The values of δ listed are for this center peak, and probably are accurate to only ±1 c.p.s. [v] The spectrum of the proton on the α-carbon should be four overlapping quartets. What we see are four or six broad peaks, with the two center peaks equal in height. The values of δ listed are for a point halfway between the two center peaks, and probably are accurate to only ±1 c.p.s.

TABLE II

BEHAVIOR OF DOUBLED RESONANCE AT VARIOUS TEMPERATURES

	Doubling due to benzene ring, c.p.s.				E_a,[b] kcal.	K_0,[b] c.p.s.
	−20°	25°	135°	195°		
Di-2-propyl phenyl phosphate	..	2.7[a]	1.7	1.5	1.0–1.3	3
Di-2-propyl phenylphosphonate	..	6.5	5.2	4.5	0.9–1.2	5–6
Di-2-propyl benzylphosphonate	..	5.9[a]	3.9	3.2	0.8–1.0	5
2-Propyl 2-propylphenylphosphinate	9.2[a]	9.0[a]	7.7	7.0	1.7–2.5	14–30
Di-2-propyl phenylphosphonite	4.1	3.2	2.2	1.7	1.1	3
Di-2-butyl phenyl phosphate	4.3[a]	3.5[a]	2.5	2.1	0.6–0.8	5
Di-2-butyl phenylphosphonate	7.8	8.1[a]	6.6	6.3	1.2–1.7	7–12
Di-2-butyl benzylphosphonate	..	6.4	4.5	4.0	1.3–1.5	8–10
Di-3-amyl phenyl phosphate	..	3.9	2.6	2.1	0.6–0.8	3
Di-2-propyl phthalidylphosphonate	(See Table III)				1.5–1.9	19–27

[a] These measurements were made on a 10% solution (by volume) of the appropriate ester in carbon tetrachloride; other measurements listed above were made on the pure esters. [b] Two calculations of E_a and K_0 were made for each ester. The calculation for each compound depends upon the value of $\delta\omega$, the maximum separation between the doubled resonances. The lowest temperature at which measurements were made was −20°, and the separation at this temperature was assumed to equal $\delta\omega$ for one calculation. For those compounds not measured at −20°, the temperature *vs.* separation curve was extrapolated linearly to this temperature. This calculation yields the higher values for E_a and K_0 listed above. For the other calculation the temperature *vs.* separation curve for each compound was extrapolated linearly to −50° to obtain a value for $\delta\omega$. This calculation yields the lower value of E_a and K_0 listed above.

Discussion

From the data given in Table I it can be seen that doubled proton magnetic resonances occur in a wide variety of organophosphorus esters that contain an aromatic radical. The data in Table II show that the temperature coefficient of the spacing of resonance doubling is small and that doubling does not collapse even at 200°. It can be seen in advance of any discussion that the selection of hypotheses concerning molecular structure as bases for explaining doubling and its behavior with temperature will be much more difficult than was the case with compounds that contain P–C bonds but no P–O–C linkages.[2] The introduction of oxygen atoms confers a flexibility on these molecules that makes for a much less definite visualization of molecular conformations. At first glance it appears that the methyl groups of such radicals as the isopropoxy radical must achieve a sort of erratic orbit in space without any clearly defined conformations. Although we believe that we have successfully analyzed the data in structural terms, and provided a system that predicts the occurrence of doubling, we are reluctant to state that the successful analysis proves the structural hypotheses that are the basis of the analysis. It is possible that some other entirely different hypotheses could be equally successful as a mechanism of prediction. We can state only that we have failed to arrive at any alternative explanation in spite of strenuous efforts to do so. The analysis of these data resolves itself into two parts: (A) the effect of temperature on doubling and whether there is slow or rapid rotation around P–O–C linkages, which does not necessarily require a detailed consideration of molecular structure; and (B) an explanation of how it is that doubling occurs at all and why it is observed for some compounds but not for others, which must involve detailed consideration of molecular structure. Part A is discussed first.

The maintenance of doubled proton resonances even up to 200° indicates that rotation around the P–O–C linkages is rapid.[8] However, since it is true that the spacing of doubling does slowly decrease as the temperature is raised from −20 to 200°, the data in Table II have been treated as though the doubling was caused by slow exchange between two rotational isomers. The temperature dependence of such an exchange may be treated as a typical rate process

$$K = K_0 e^{-E_a/RT}$$

where K_0 is the frequency factor and E_a is the potential barrier hindering internal rotation. The data were treated by the method of Gutowsky and Holm.[9] This leads to the very improbable values for K_0 and E_a shown in Table II. These values are only approximate since the doubled resonances did not collapse at the highest temperature available from the equipment or reach a maximum constant separation even at −20°.

(8) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

(9) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

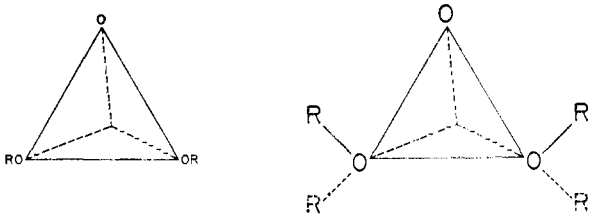


Fig. 1.—Configuration of substituents around a phosphorus atom.

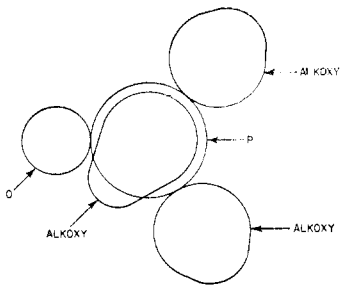


Fig. 2.—A steric factor that favors the "up" position.

However, the choice of wider separation of doubled components by extrapolation to even lower temperatures only leads to smaller values for E_a and K_0.

If we examine the representation of a molecule shown in Fig. 2, we see that there are three possible rotational isomers for each alkoxy group. If rotation were slow, so that each isomer had an appreciable lifetime, then a distinct n.m.r. spectrum would be expected for each isomer—some resonances of which might or might not be doubled by the presence of a benzene ring. If the molecule existed in more than one isomeric form, the n.m.r. spectrum would be very complex. If rotation were rapid, the spectrum observed would be the average of all the rotational isomers. The average magnetic environment seen by the two β-methyl groups in a 2-propyl radical, for example, would be different, and would lead to the type of spectrum actually observed.

An explanation of the occurrence of doubling depends on a visualization of molecular structure. The phosphorus atom is very nearly tetrahedral. For purposes of discussion we can imagine this tetrahedron as resting on a plane. The alkoxy substituents are located at the base of the tetrahedron and the phosphoryl oxygen is located at the apex of the tetrahedron "above" the plane (Fig. 1A). Because of the bond angle of the oxygen atom, groups linked through oxygen may be above the plane, *i.e.*, point "up," or below the plane, point "down" (Fig. 1B). There are then two general conformations—the "up" conformation with all OR groups in an up position around the phosphoryl oxygen and the "down" conformation with one or more substituents turned down.

Granted this analysis into two general conformations, it is reasonable to suppose that these molecules spend an important fraction of their time in the "up" conformation and that perhaps this

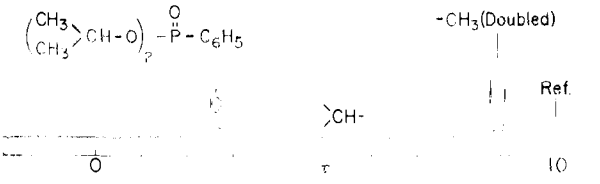


Fig. 3.—Di-2-propyl phenylphosphonate (10 vol. % in CCl_4).

is even the preferred conformation. Rotation around the P–O–C linkage would tend to place a given substituent in a staggered position between the other two substituents or between one other substituent and the phosphoryl oxygen. This view is simply an extension of the generally accepted proposal that the stable conformations of substituted ethanes are staggered. Figure 2 is a representation of a trialkyl phosphate, viewed along the bond between one of the alkoxy groups and the phosphorus atom. The phosphoryl oxygen is smaller than any of the alkoxy groups. In this simplified picture of the molecule the phosphorus atom is represented by the larger sphere, the phosphoryl oxygen by the smaller sphere, and the alkoxy groups by egg-shaped figures, two of which are viewed almost end-on. The sterically favored, staggered position for the alkoxy group being viewed would be between the phosphoryl oxygen and one of the other alkoxy groups, as shown, rather than between the other two alkoxy groups. The choice of this position for all three alkoxy groups leads to the "up" conformation. The substitution of a phenoxy or phenyl group for one alkoxy group does not change the validity of this discussion.

Our structural hypotheses for explaining resonance doubling are then that (1) the conformation of organophosphorus esters can be broken down, in at least a useful approximation, into two general conformations, and that (2) the "up" conformation represents these molecules some important fraction of the time. It cannot be said as to just how large this fraction of the time is, since there is no obvious way to estimate the separation of resonance doubling for the hypothetical situation where all molecules were in the "up" conformation all of the time.

The "up" conformation explains the observed facts concerning proton resonance doubling in the compounds listed in Table I, with some uncertainty in the case of di-2-propyl phenylphosphonite and some confusion in the case of the phthalidyl esters. In this conformation the two methyl groups of the 2-propyl radical, as an example, have separate identity. The spectrum of di-2-propyl phenylphosphonate is shown in Fig. 3. If a Fisher–Hirschfelder–Taylor model of this molecule is assembled, it can be seen that one methyl group is close to the benzene ring and the other is farther away. This is so, since in the "up" position a methyl group cannot be rotated past the phosphoryl oxygen. The same picture is obtained for the 3-amyl radical. The spectrum of the 4-heptyl compound is too blurred, probably by second-order proton coupling, for any conclusions to be drawn. However, it may be noted that the

α-proton in such radicals does not and cannot have resonances doubled by the benzene ring since it has no positions "near to" and "far from" the benzene ring.

Radicals with an asymmetric α-carbon atom (such as 2-butyl) generally show doubled resonances for both β and γ terminal methyl groups in the radical with high and low field wings with equal intensities. This is to be expected, provided there is no preferential population of one diastereoisomer, since there is equal probability of finding β- (or γ-)methyl groups "near to" or "far from" the benzene ring in the "up" conformation. An exception to the generality of wings of equal intensity was observed for the 3,3-dimethyl-2-butyl radical; this exception is discussed later. The argument is illustrated in Fig. 4. In this

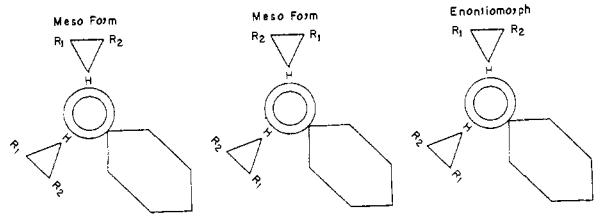


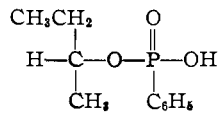
Fig. 4.—Possible diastereoisomers from

$$[R_1R_2HC\text{-}O]_2PC_6H_5.$$

schematic representation the molecule is viewed from above, down through the $\geqslant P{=}O$ group. The smaller concentric circle is the phosphoryl oxygen atom and the larger is the phosphorus atom. Each triangle is the base of an α-carbon atom tetrahedron and the hexagon is the benzene ring. Of course bond angles are not correct in this planar representation.

When the alkoxy group is linked through a terminal carbon atom of radicals such as ethyl, *n*-propyl and neopentyl, resonance doubling is not observed for esters included in this study (except for phthalidyl esters). This is so because in the "up" position the radical may be oscillated rapidly to and fro with first one α-hydrogen atom then the other close to the phosphoryl oxygen. This means that the remainder of the radical rapidly changes positions and is "near to" and "far from" the benzene ring with equal probability. This leads to an averaging of the magnetic environment and only one set of resonances.

The 2-butyl radical in 2-butyl diphenyl phosphate shows only a single set of resonances. This follows since with the two benzene rings available, the methyl and ethyl groups of the butyl radical can only be "near to," never "far from" a benzene ring. The acid ester



shows only one set of resonances for the 2-butyl protons. This is explained by noting that the very basis is lost for a preferred "up" position. The proton resonance of the OH group is not doubled. The lack of spin–spin coupling between the phosphorus and the OH proton implies that this proton is bonded to both oxygens, or rapidly exchanging between them. In either case, the phosphoryl oxygen and the OH group would be equivalent; hence the 2-butyl radical may be near either group with equal ease. In this case there is no steric reason for placing the 2-butyl radical near to the phosphoryl oxygen only. It might equally well be placed near the OH group. This freedom of choice eliminates the possibility that methyl protons must, on the average, be "near to" or "far from" the benzene ring.

This concludes the general argument in support of the "up" conformation. However, it will be seen that further consideration of individual molecules is always consistent with this hypothesis, with the possible exception of the phthalidyl esters and di-2-propyl phenylphosphonite. It should be pointed out, however, that the rationale is based very strongly on steric considerations. No account is taken of the possibility that the phosphorus "single" bonds may have some π-bond character.[10] In fact this rationale infers that π-bonding with its lack of radial symmetry of electron distribution around the bond axis is of little consequence in determining rotational potential energy curves. It is not necessary to suppose *from the proton resonance doubling alone* that there is π-bond character in the P–O– or P–C– links.

The spectrum of bis-(3,3-dimethyl-2-butyl) phenylphosphate is unusual in that high and low field wings of methyl proton resonances do not have equal intensity. As shown in Fig. 5 the signal

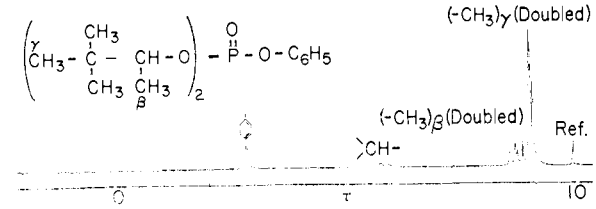


Fig. 5.—Bis-(3,3-dimethyl-2-butyl) phenylphosphate (10 vol. % in CCl_4).

from the γ-methyl groups is very much more intense in the low field wing. Conversely, for the β-methyl protons the high field doublet (doublet from proton spin coupling) is more intense than the low field doublet. A possible explanation for this dissymmetry is that the synthesis and/or purification of this compound discriminates against the *meso* form, in which the γ-methyl group is close to the benzene ring and the β-methyl group is far away. In other words, the γ-methyl proton signal would contribute only to the high field signal for γ-protons while the β-methyl protons of this *meso* form would contribute only to the low field signal for β-protons. Obviously, if less than the purely statistical quantity (one in four) of this *meso* form is present, the intensities of the high and low field wings could be as observed.

(10) J. R. Van Wazer, "Phosphorus and its Compounds—Volume I: Chemistry," Interscience Publishers, Inc., New York, N. Y., 1958.

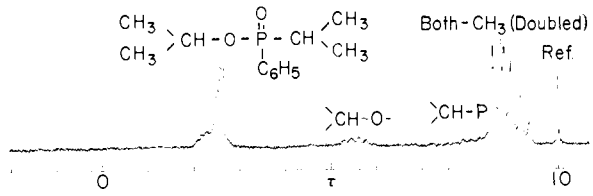


Fig. 6.—2-Propyl 2-propylphenylphosphinate (10 vol. % in CCl_4).

If this explanation is correct, then a sample prepared from optically resolved alcohol should show resonances with symmetric doubling. This is so because with resolved alcohol neither *meso* form will be synthesized—only one of the pair of enantiomorphs will be formed. The enantiomorphs have an equal abundance of both ends of the 3,3-dimethyl-2-butyl radical "near to" and "far from" the benzene ring. One attempt was made to obtain resolved alcohol by the method that Kantor and Hauser[11] used to resolve 2-butanol; however, the yields were too small to permit analysis by polarimetry, and a conclusive synthesis of the phosphate. We have no reason to believe that the method of resolution cannot be modified to be effective for this alcohol; however, extensive effort may be needed because both the reactions of this alcohol and crystallization of its adducts are quite slow, as might be expected.

In the few cases where it could be estimated, the spacing of resonance doubling of β-methylene protons is much smaller than for β-methyl protons. At first glance this appears to be something of an anomaly, since superficially the geometry for these protons is about the same. However, molecular models show that for the β-methylene group to be brought close to the benzene ring, the γ-methyl group must be twisted back out of the way. This places the γ-methyl group in an unfavorable position, sterically. This factor tends to decrease the fraction of the total time that the β-methylene protons are close to the benzene ring. All of this argument obviously is related to that used to explain the greater stability of *trans*- as compared to *cis*-butane.[12]

The molecule 2-propyl 2-propylphenylphosphinate is interesting in that it contains both a 2-propyl and a 2-propoxy group. Fortunately, it is just possible to analyze the spectrum of this compound, shown in Fig. 6. Even though the methyl groups of the 2-propoxy group are an extra bond removed, the spacing of the resonance doubling is greater than that of the methyl protons in the 2-propyl group. One interpretation of this is that in spite of the extra bond the "near" methyl protons of the 2-propoxy group, on the average, are closer to the benzene ring than are the "near" methyl protons of the 2-propyl group. However, there are complicating factors such as the lack of spherical symmetry in the magnetic field around the benzene ring. These factors permit other interpretations of the relative spacing of resonance doubling.

(11) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **75**, 1744 (1953).

(12) Sañichiró Mizushima, "Structure of Molecules and Internal Rotations," Academic Press, New York, N. Y., 1954.

The spectra of diethyl phthalidylphosphonate and di-2-propyl phthalidylphosphonate are especially interesting. These spectra are shown in Figs. 7 and 8. The β-methyl proton resonance of the

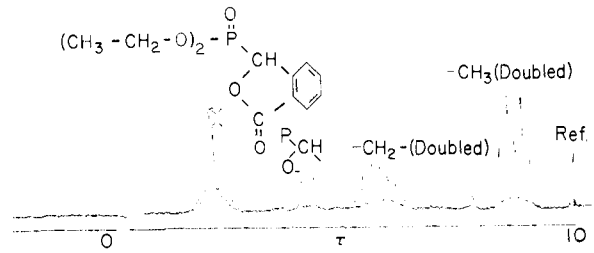


Fig. 7.—Diethylphthalidylphosphonate (10 vol. % in $CDCl_3$).

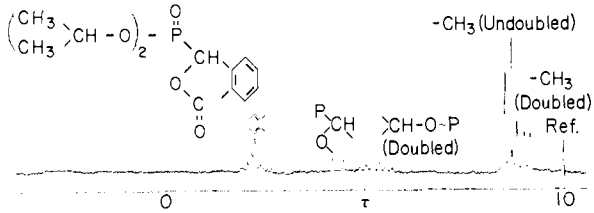


Fig. 8.—Di-2-propyl phthalidylphosphonate (10 vol. % in $CDCl_3$).

diethyl ester (normally a triplet) is doubled, the only diethyl ester with which this was observed in the course of the present work. Three sets of signals are observed for the β-methyl protons in the 2-propyl compound; one set has twice the intensity of the other two. Further, the separation of the β-methyl proton signals of both the diethyl and di-2-propyl esters decreases with increasing temperature, as shown by the data in Table III.

TABLE III

DOUBLING OF β-METHYL PROTON RESONANCE IN ESTERS OF PHTHALIDYLPHOSPHONIC ACID

	Diethyl ester	Di-2-propyl ester	
T, °C.	Sepn. of β-Me proton resonance from different Et groups, c.p.s.	Sepn. of β-Me proton resonance from different 2-Pr groups, c.p.s.	Sepn. of β-Me proton resonance in same 2-Pr group, c.p.s.
25	13.1	12.6	11.5
90	..	11.0	9.7
140	8.8	9.1	8.7

The spectra remain sharp and clear at elevated temperatures, however, and there is no loss of resolution. The resonances from the α-protons also are doubled. These data are consistent with the following hypothesis. There are preferred conformations of the phthalidyl group with respect to the phosphorus atom, such that one entire ester group is located "near to" the benzene ring, and the other ester group is located "far from" the benzene ring.

In the di-2-propyl ester, the 2-propyl group "far from" the benzene ring shows only the normal β-methyl proton resonance doublet, since both methyl groups are too far from the benzene ring for it to affect greatly their magnetic environment, even if there is a preferred conformation. For the other 2-propyl group, in a preferred conformation, the two β-methyl groups would see a different

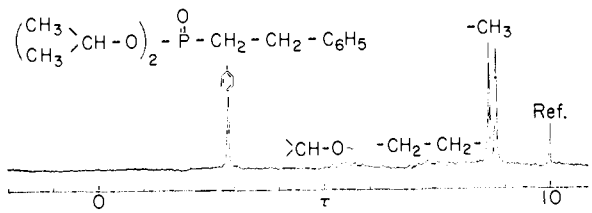


Fig. 9.—Di-2-propyl 2-phenylethylphosphonate (10 vol. % in CCl_4).

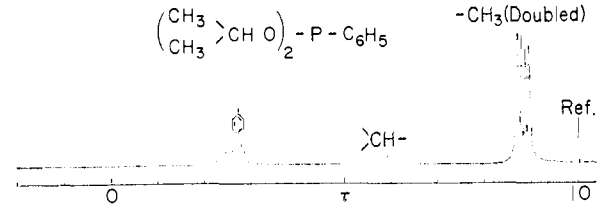


Fig. 10.—Di-2-propyl phenylphosphonite (undiluted).

magnetic environment, one being closer to the benzene ring than the other. This would result in a further doubling of the β-methyl proton signals from this 2-propyl group. The β-methyl spectrum would then consist of six peaks, two of which had twice the intensity of the other four. Also, the α-proton in the "near" 2-propoxy group is closer to the benzene ring than the α-proton of the "far" group. This should lead to two sets of resonances of equal intensity, one from each of these protons. This is what is actually observed, with one low-intensity peak almost superimposed on one high-intensity peak (Fig. 8).

In the diethyl ester, the same argument holds: one entire ethyl group "far from," and the other "close to" the benzene ring. The protons of the two ethyl groups resonate at a different applied magnetic field, but no further doubling can occur, since there is only one methyl group in each radical.

It is not clear at present whether the conformations of the phthalidyl group are due to: (1) slow rotation around the carbon–phosphorus bond with two rotational isomers; (2) a single preferred orientation of the phthalidyl group, with rapid rotation around the carbon–phosphorus bond; or (3) some entirely different phenomenon. Possibility 1 seems the most unlikely, for two reasons. The behavior of the 2-propyl ester is similar to the other esters investigated at elevated temperatures, and the same arguments apply. Also, if both 2-propyl groups spend some time "close to" the benzene ring, they must both see the same magnetic environment, as only one set of doubled lines (four peaks of lower intensity) is observed. This seems unlikely, since the molecules are not symmetrical.

The data in Table I show that, in addition to the benzene ring itself, a variety of benzene derivatives and even thiophene generate sufficient magnetic field to cause resonance doubling. On the other hand, resonance doubling is not caused by alkyl groups, olefinic groups, dichloro- and trichloromethyl groups and, more important, by cyclopentyl or cyclohexyl groups. It has been supposed that the cyclohexyl group might possess ring currents.[8] This does not seem to be the case—at least not to a degree comparable to the aromatic rings. It would be interesting to invert the viewpoint taken up to now in this paper and to apply the rest of the molecule as a probe to determine if still other groups have pronounced anisotropic diamagnetism and ring currents. The results must be very qualitative, however, because of uncertainties in geometry.

It is evident that methyl substitution in the benzene ring does affect the geometry between the benzene ring and the protons with doubled resonances. The series phenyl, 2-methylphenyl, and 2,6-dimethylphenyl forms a sequence of increasing effect. From consideration of molecular models, one reasonable explanation is that methyl substitution in the *ortho* position increases the amount of time that the benzene ring spends in a plane perpendicular to the affected protons. As might be expected from the same consideration, substitution in *meta* and *para* positions had no apparent effect.

The behavior of benzylphosphonates seems to be anomalous. The spacing of the resonance doubling compares with that of the phenylphosphonates and is substantially greater than that of phenylphosphates. Apparently some subtlety of spatial relationships is unusually favorable in benzylphosphonates as compared to phenyl phosphates. As might be expected, di-2-propyl 2-phenylethyl phosphate, with two carbon atoms interposed between the phosphorus atom and the benzene ring, shows no doubling of the resonances of 2-propyl protons. However, the protons of the two carbons between the phosphorus atom and the phenyl group have the very complex spectrum arising from hindered rotation in a substituted ethane (see Fig. 9).

The proton magnetic resonance spectrum of di-2-propyl phenylphosphonite, in some degree, might serve as a test of the "up" hypothesis as a molecular structure adequate to explain the doubling of proton resonances in the pentavalent phosphorus compounds. As can be seen in Fig. 10 the phosphonite exhibits resonance doubling. Unfortunately the results of this test are not conclusive. It can be argued that since the phosphoryl oxygen has been replaced by an electron pair, then the steric argument for the "up" conformation is even stronger for this compound of trivalent phosphorus than it is for the pentavalent compounds. As a consequence, the phosphonite would spend a larger fraction of its time in this conformation. However, at the same time the electron pair, occupying much less space than the phosphoryl oxygen, is a less effective repulsive barrier to the interchange of methyl groups in each 2-propyl radical.