gen bond strength, since the copper complexes of amines are more stable than those of nickel. Because the activation entropy, however, counteracts the effect of the activation energy, the catalytic potentials of the two ions, as measured by the reaction rates, are in reverse order from that which had been anticipated.

The negative activation entropies can perhaps be explained by a model in which water molecules are held tightly to the Schiff base double bond, the nucleus of the hydrolytic reaction. The large entropy values may indicate extensive reorientation of solvent molecules as a consequence of the formation of the activated complex. The greater absolute

value for the activation entropy in the copper system could result from either greater rigidity of the activated complex or lower rigidity of the unactivated system. The first alternative appears more plausible, since it may be supposed that the greater diminution of electron density in the carbon to nitrogen bond of the copper complex would lead to a greater dipole induced dipole attraction for the water molecules.

Acknowledgment.—The authors wish to express their appreciation to the Research Corporation for their generous financial assistance in this project.

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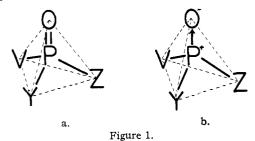
A Linear Phosphoryl Absorption Relationship

By Jerome V. Bell, Julius Heisler, Harvey Tannenbaum and Jerome Goldenson Received September 4, 1953

There is a linear correlation between the phosphoryl absorption wave length in phosphoryl halides and the sum of the Pauling electronegativity constants of the halogens. This same correlation is found to exist between the Raman shift of the phosphoryl stretching vibration of phosphoryl halides and the sum of the Pauling electronegativities of the halogens in these same molecules. Similarly it has been found that other more complex substituent groups, i.e., alkoxy, hydroxy, etc., influence the stretching absorption of the phosphoryl bond in a constant and additive manner. These groups, therefore, have been assigned derived numerical values comparable in magnitude to a Pauling electronegativity constant. These constants are referred to as phosphoryl absorption shift constants. It is also proposed that the derived constant for each substituent largely represents the Pauling electronegativity of the substituents.

Introduction

In recent years much attention has been devoted to pentavalent organo-phosphorus compounds and their infrared and Raman spectra. The molecules of special interest are tetrahedral in form as represented by Figs. 1a and 1b. V, Y and Z may be individual atoms or substituent groups which vary widely in character and weight. Changing



these substituents causes a marked shift in the infrared wave length and Raman frequency of the phosphoryl vibration. The wave lengths, which vary from 7.0 to 8.5 μ , depend on the nature of the substituent groups.

Several attempts have been made to establish a means of predicting the wave length of the phosphoryl stretching vibration.^{1–3} Daasch and Smith in particular have noted that there is a correspondence between the phosphoryl frequency and the "electronegativity" of the substituent groups.

In the work described in this paper we have

- (1) M. L. Delwaulle and F. Francois, J. chim. phys., 46, 87 (1949).
- (2) R. C. Gore, Disc. Faraday Soc., 9, 138 (1950).
- (3) L. W. Daasch and D. C. Smith, Anal. Chem., 23, 853 (1951).

found (1) that there is a good linear correlation between the Raman shift of the phosphoryl vibration in phosphoryl halides and the sum of the Pauling electronegativity constants of the halogens (Fig. 2); (2) the effects of various substituents upon the infrared wave lengths of the P=O stretching vibrations in many types of phosphoryl compounds are constant and additive; (3) the effect of a substituent upon the infrared wave length may be given a

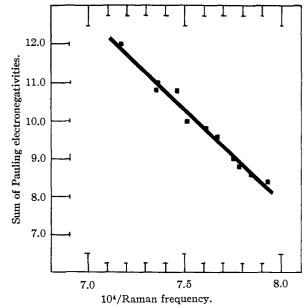


Fig. 2.—Raman data $\mu = (47.31 - \Sigma x)/4.933$.

numerical value, comparable in magnitude to a Pauling electronegativity constant, called a "phosphoryl absorption shift constant"; (4) the correlation between the phosphoryl absorption shift constant and the infrared band position is very similar to the correlation between Pauling electronegativity and Raman shift. From these facts, it is deduced that for both correlations, the band shifts observed are determined mainly by the electrical effect of the substituent upon the force constant, rather than by mass effects and it is concluded that the phosphoryl absorption shift constants represent an approximate measure of the Pauling electronegativity of the substituent.

Raman Shift Correlation.—This correlation was made by plotting the Raman shift of the phosphoryl vibration in phosphoryl halides¹ against the sum of the Pauling electronegativity constants⁴ of the halogens. The Raman data used in this plot (Fig. 2) are given in Table I. The equation for the linear relationship is

$$\lambda(\mu) = \frac{47.31 - \Sigma x}{4.9333}$$

where $\lambda(\mu)$ is 10^4 /raman frequency and Σx is the sum of the Pauling electronegativity constants of the halogens. The method of least squares was used in drawing this curve.

Table I Raman Data

v	Substitue Y	nts Z	Sum of Pauling electro- negativity constants, 2 2x	104/Raman frequency in μb	Raman frequency in cm1b
F	F	F	12.0	7.16	1395
F	F	C1	11.0	7.36	1358
F	F	Br	10.8	7.35	1360°
				7.46	1340°
F	C1	C1	10.0	7.51	1331
F	\mathbf{Br}	\mathbf{Br}	9.6	7.67	1303
C1	C1	C1	9.0	7.75	1290
C1	C1	\mathbf{Br}	8.8	7.78	1285
C1	Br	Br	8.6	7.84	1275
\mathbf{Br}	Br	Br	8.4	7.93	1261
F	C1	Br	9.8	7.61	1319

^a Pauling electronegativities are listed in Table III. ^b Data in last two columns taken from reference 1. ^e Both points of doublet plotted in Fig. 2.

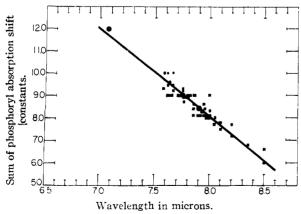


Fig. 3.—Infrared data, $\lambda(\mu) = (39.96 - \Sigma x)/3.995$.

Infrared Absorption Correlation.—An inspection of the infrared absorption data for F₃PO, Cl₃PO and Br₃PO, the only three compounds for which the Pauling electronegativity constants for all the substituents was known, indicated that a similar correlation might be made from infrared data. A preliminary curve based on these three compounds was drawn. Since Pauling electronegativity constants were not known for most of the other substituents in a number of phosphoryl compounds, constants comparable in magnitude to Pauling electronegativities and referred to as phosphoryl absorption shift constants were derived for them in the manner described in the following paragraphs.

Using the preliminary curve and the known phosphoryl absorption wave lengths, the sum of the phosphoryl absorption shift constants for the substituents in phosphoryl dihalides and monohalides was obtained. From the equation

$$\Sigma x = X_v + X_y + X_z$$

where Σx is the sum and X_v , X_y and X_z are the phosphoryl absorption shift constants of substituents V, Y and Z, respectively, and using the Pauling electronegativity constants for the halogen substituents, the shift constant of the third substituent of the dihalides was obtained. In the case of the monohalides where substituents Y and Z were the same, the value for each was taken as one half of the sum of the shift constants after subtracting the Pauling electronegativity of the halide substituent, V. Similar calculations were made for the other compounds.

It was noted at this point that values for the same substituent in different compounds were not always in good agreement, but by gradually reducing the slope and intercept at the ordinate of the preliminary curve, a relationship was finally obtained which gave the best agreement for the phosphoryl absorption shift constants of the substituents.

The final curve is shown in Fig. 3. The three phosphoryl trihalides on which the preliminary curve was based are represented by circular points in this

The equation of the curve (Fig. 3) is

$$\lambda(\mu) = \frac{39.96 - \Sigma x}{3.995}$$

where $\lambda(\mu)$ is the phosphoryl absorption wave length in microns and Σx is the sum of the phosphoryl absorption shift constants of the substituents.

The compounds and absorption data on which Fig. 3 is based are given in Table II and the final averaged values of the phosphoryl absorption shift constants are shown in Table III.

Discussion

Validity of the Relationship.—Most of the compounds used in deriving the curve of (Fig. 3) did not contain any substituents of known Pauling electronegativity. It was therefore necessary to use derived values to obtain phosphoryl absorption shift constants for many of the substituent groups listed in Table III. In the case of diethylthioethyl phosphate for example, the derived phos-

⁽⁴⁾ L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, New York, 1939.

Substituent groups		Infrared and Phospho	ryl Absorption Shift Consta	n t Dat	A ^{tt}		
Part Part				Sum of			Diff. between
F F F F F F F F F F					Obed		
F F F F C C C C C C		Substituent groups					predicted wave length.
CI CI CI Q 7.75 2 201 Br Br Br 8.4 7.80 3 01 CI CI C.HpO 9.2 7.66 6 04 CI CI C.HpO 9.2 7.66 6 04 CI CI C.HpO 9.0 7.687.88 7 01 CI C.H, C.HpO 0.0 1.00 7.58 8.0 9 01 CI C.H, C.HpO 0.0 7.8 8.10 3 .04 F OCH, OCH, OCH, 10.0 7.587.79 2 .03 CI C.HpO C.HpO OCH, 10.0 7.617.88 3 .11 CI C.HpO C.HpO OCH, 10.0 7.787.79 2 .03 CI N.GO C.HpO OCH, 9.0 7.797.79 2 .03 CI	v	Y	z			Ref.	
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CI							
CI				8.4			
CI	C1	C1	C_6H_5	8.4	7.85	3	- .05
CI	C1	Cì	C ₆ H ₅ O	9.2	7.66	6	04
CI CH, C,H, C,H, 7.8 7.85,77.88 710 CI C,H, C,H, 7.8 .7 .85,77.88 710 F OCH, OCH, OCH, 10.0 7.88 3 .0.88 CI CL,H,C C,H,O C,H,O 9.4 7.66/7.71 6 .0.11 CI OCH, OCH, OCH, 9.0 7.277.79 2 .0.03 CI N(CH), OCH, 9.0 7.277.79 2 .0.03 CI N(CH), OCH, 9.0 7.61/7.88 714 H OCH, OCH, OCH, 8.1 7.90 9 .0.88 H OCH, OCH, OCH, 8.1 7.90 9 .0.88 H OCH, OCH, OCH, 8.1 7.90 9 .0.08 H OCH, OCH, OCH, 8.1 7.90 9 .0.08 H OCH, OCH, OCH, 8.1 7.90 9 .0.08 H OCH, CH,-CH,O C,H, 8.1 7.90 9 .0.08 H OCH,-CCH),-CH(CH),O C,H, 8.1 7.90 8 .0.09 H CH,-CCH),-CH(CH),O C,H, 8.1 7.90 8 .0.00 CH,-C(CH),-CH(CH),O 8.1 7.90 8 .0.00 H CH,-CCH),-CH(O) 8.1 8.0 8.0 8.0 8.0 8.00 H CH,-CCH),-CH(O) 8.1 8.0 8.0 8.0 8.0 8.00 CH,-C(CH),-CH(O) 8.1 8.0 8.0 8.0 8.0 8.0 8.0 8.0 8.0 8.0 8.0	Cl	C1				6	
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CI			- "		-		
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H CH _T -C(CH ₁)-CH(CH ₁)0 CH _T -C(CH ₁)-CH ₁ CO S, 1 7,95 8 -,03 H CH _T -C(CH ₁)-CH ₂ O CH _T -C(CH ₁)-CH ₂ O 8,1 8,00 8 .02 CH ₁ CH ₄ CH ₄ CH ₄ C,1 8,0 8,00 3 -,04 CH ₁ CH ₄ CH ₄ CH ₄ CH ₄ CH ₄ 8,0 8,0 3 -,01 CH ₄ OC _H ₄ OC _H ₄ OC _H ₄ S,0 8,0 8,0 9 -,01 CH ₄ OC _H ₄ OC _H ₄ OC _H ₄ S,0 8,0 8,0 9 -,01 CH ₄ OC _H ₄ OC _H ₄ OC _H ₄ S,0 7,97/8,13 9 -,04 CH ₄ OC _H ₄ OC _H ₄ OC _H ₄ S,0 7,97/8,13 9 -,02 CH ₄ OC _H ₄ OC _H ₄ OC _H ₄ S,0 8,0 8,0 3 -,01 CH ₄ OC _H ₄ OC _H ₄	H	C_6H_5 - CH_2O	C ₆ H ₅ -CH ₂ O	8.1	7.96	8	
H CH _T -C(CH ₃)=CH ₂ O CH _T -C(CH ₃)=CH ₂ O 8.1 8.00 8 .02 H C _t H _s OC _t H _s OC _t H _s 7.5 8.10 3 04 CH ₁ CH ₁ OC _t H _s OC _t H _s O.8.50 3 01 CH ₁ OC _t H _s OC _t H _s OC _t H _s 8.0 8.05 9 04 CH ₁ OC _t H _s OC _t H _s OC _t H _s 8.0 8.00 9 01 CH ₁ OC _t H _s OC _t H _s OC _t H _s 8.0 8.05 9 01 CH ₁ OC _t H _s OC _t H _s 8.0 8.0 7.975.13 9 04 CH ₁ OC _t H _s OC _t H _s 8.0 7.99/8.17 9 02 n-CH ₁ OC _t H _s OC _t H _s 8.0 7.99/9.17 9 02 n-CH ₁ OC _t H _s OC _t H _s 8.0 7.99/8.17 9 02 CH ₁ OC _t H _s OC	ਸ						- 03
H C ₄ H _s OC ₂ H _s 7,5 8,10 3 04 CH ₁ CH ₁ CH ₁ 6.0 8,50 3 01 CH ₁ OCH ₁ OCH ₁ 8.0 8.05 9 .04 CH ₁ OC,H ₁ OC,H ₂ OC,H ₃ 8.0 8.00 9 01 CH ₁ OC,H ₂ OC,H ₃ OC,H ₄ 8.0 8.00 9 01 CH ₁ OC,H ₃ OC,H ₄ 8.0 7.97/8.13 9 04 C,H ₄ OC,H ₃ OC,H ₄ 8.0 7.99/8.17 9 02 C,H ₄ OC,H ₃ OC,H ₄ 8.0 7.99/8.17 9 02 C,H ₄ OC,H ₄ OC,H ₄ 8.0 7.97/8.13 9 04 m-CH ₄ OC,H ₄ OC,H ₄ OC,H ₄ 8.0 7.99/8.17 9 02 CH ₄ OC,H ₄ OC,H ₄ OC,H ₄ OC,H ₄ 9.0 7.817/9.10		• • •					
CH₁ CH₁ CH₁ CH₁ 8.0 8.50 3 — .01 CH₁ OCH₁ OCH₁ OCH₁ 8.0 8.05 9 — .01 CH₁ OC,H₁ OC,H₁ OC,H₁ 8.0 8.01 9 — .01 CH₁ OC,H₁ OC,H₁ OC,H₁ R.0 7.99/8.13 9 — .04 CH₁ OC,H₁ OC,H₂ 8.0 8.05 6 .04 CH₁ OC,H₁ OC,H₃ 8.0 8.0 8.0 8.0 9 02 CH₁ OC,H₁ OC,H₃ OC,H₃ 8.0 7.89/8.1 9 02 CH₁ OC,H₃ OC,H₃ OC,H₃ OC,H₃ OC,H₃ OC,H₃ </td <td></td> <td>• • •</td> <td></td> <td></td> <td></td> <td></td> <td></td>		• • •					
CH ₁ OCH ₁ OCH ₁ 8.0 8.05 9 .04 CH ₁ OC ₂ H ₄ OC ₂ H ₂ 8.0 8.0 9 01 CH ₁ OC ₂ H ₂ OC ₂ H ₂ 8.0 8.01 9 .00 CH ₄ OC ₂ H ₃ OC ₂ H ₄ 8.0 7.99/8.13 9 04 C ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ 8.0 7.99/8.17 9 04 α-C ₄ H ₄ OC ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ 8.0 8.05 8.0 3 .01 CH ₄ OC ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ 9.0 7.85 3 .10 OC ₄ H ₄ OC ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ 9.0 7.837/7.0 6 .03 OC ₄ H ₄ OC ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ 9.0 7.837/7.0 6 .03 OC ₄ H ₄ OC ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ 9.0 7.637/7.0 6				7.5	8.10	3	04
CH ₁ OCH ₁ OCH ₁ 8.0 8.05 9 .04 CH ₁ OC ₂ H ₄ OC ₂ H ₂ 8.0 8.0 9 01 CH ₁ OC ₂ H ₂ OC ₂ H ₂ 8.0 8.01 9 .00 CH ₄ OC ₂ H ₃ OC ₂ H ₄ 8.0 7.99/8.13 9 04 C ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ 8.0 7.99/8.17 9 04 α-C ₄ H ₄ OC ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ 8.0 8.05 8.0 3 .01 CH ₄ OC ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ 9.0 7.85 3 .10 OC ₄ H ₄ OC ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ 9.0 7.837/7.0 6 .03 OC ₄ H ₄ OC ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ 9.0 7.837/7.0 6 .03 OC ₄ H ₄ OC ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ OC ₂ H ₄ 9.0 7.637/7.0 6	CH:	CH ₃	CH:	6.0	8.50	3	- .01
CH, OC₄H₄ OC₄H₃ OC₄H₃ 8.0 8.00 9 01 CH, OC₄H₃ OC₄H₃ 8.0 8.0 9 .00 C₂H₃ OC₄H₃ OC₄H₃ 8.0 7.97/8.13 9 04 C₂H₃ OC₄H₃ OC₄H₃ 8.0 7.99/8.17 9 02 n-C₄H₃ OC₄H₃ OC₂H₃ 8.0 7.99/8.17 9 02 n-C₄H₃ OC₄H₃ OC₂H₃ 8.0 8.0 7.99/8.17 9 02 n-C₄H₃ OC₄H₃ OC₂H₃ OC₂H₃ 8.0 8.0 8.0 3.0 C₄H₃ OC₄H₃ OC₂H₃ 8.0 8.0 8.0 3.0 3.0 C₄H₃ OC₄H₃ OC₂H₃ 8.4 7.95 3 .04 CH₃ OC₄H₃ OC₂H₃ 9.0 7.83/7.91 6 .06 CH₃ OC₃H₃ OC₂H₃ 9.0 7.85/7.91 6 .10 CH₃ OC҈H₃	CH,		OCH.			9	04
CH ₁ OC,H ₁ -i OC,H ₁ OC,H ₁ OC,H ₁ S.0 8.0 7.97/8.13 9 .00 C ₂ H ₄ OC,H ₁ -i OC,O ₁ -i 8.0 7.99/8.17 9 .04 C ₂ H ₄ OC,H ₁ -i OC,O ₂ -i 8.0 7.99/8.17 9 .04 n-C ₄ H ₄ OC,H ₄ OC,H ₄ 8.0 8.0 8.0 0 C ₄ H ₄ OC,H ₁ OC,H ₄ 8.0 8.0 8.0 3 .01 C ₄ H ₄ OC,H ₁ OC,H ₄ 8.4 7.95 3 .04 OCH ₄ OC,H ₄ OC,H ₄ 9.0 7.85 3 .10 OC,H ₅ OC,H ₄ OC,H ₄ 9.0 7.857 3 .10 OC,H ₅ OC,H ₄ OC,H ₄ 9.0 7.857 3 .10 OC,H ₄ OC,H ₄ OC,H ₄ 9.0 7.837.70 6 .03 M-CH,C ₄ H ₄ O n-CH,C ₄ H ₄ O n-CH,C ₄ H ₄ O n-CH,C ₄ H ₄ O <th< td=""><td>· · · · · · · · · · · · · · · · · · ·</td><td></td><td>-</td><td></td><td></td><td></td><td></td></th<>	· · · · · · · · · · · · · · · · · · ·		-				
C₂H₅ OC,H₅ OC₂H₅ OC₂H₅ 8.0 7.97/8.13 9 04 C₂H₅ OC,Hr-i OC₁Or-i 8.0 7.99/8.17 9 02 n-C₄H₅ OC₂H₅ OC₂H₅ 8.0 7.99/8.17 9 02 n-C₄H₅ OC₂H₅ OC₂H₅ 0C₂H₅ 0.0 3.0 3 .01 C₄H₅ OC₂H₅ OC₂H₅ OC₂H₅ 3.0 8.0 8.0 3.0 3 .01 C₄H₅ OC₂H₅ OC₂H₅ OC₂H₅ OC₂H₅ OC₃H₃ 9.0 7.85 3 .04 OC₂H₅ OC₂H₅ OC₂H₅ OC₂H₅ OC₂H₅ OC₂H₅ 0.0 0.0 OC₂H₅ OC₂H₅ OC₂H₅ OC₂H₅ OC₂H₅ 0.0 7.85 6 .10 OC₂H₅ OC₂H₅ OC₂H₅ OC₂H₅ OC₂H₅ OC₂H₅ O.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	-		- ·				
C₂H₅ OC₄H-i OC₄H₅ OC₄H₅ OC₃H₅ 8.0 7.99/8.17 9 −.02 n-C₄H, OC₂H₅ OC₂H₅ 8.0 8.0 8.0 3 .01 C₂H₅ OC₄H₅ OC₃H₅ OC₃H₅ 8.4 7.95 3 .04 OC₄H₅ OC₃H₅ OC₃H₅ 9.0 7.85 3 .10 OC₄H₅ OC₄H₅ OC₄H₅ 9.0 7.85 3 .10 OC₄H₀ OC₄H₅ OC₄H₅ 9.0 7.85 6 .10 C₄H₀ C₄H₅O C₄H₀O 9.0 7.85 6 .10 C₄H₀ C₄H₅O C₄H₀O 9.0 7.85 6 .10 C₄H₀O CH₃CH₄O 9.0 7.70 6 -0.5 m-CH₃Cℍ₀O P-CH₃CAH₀O 9.0 7.65/7.70 6 -10 P-CH₃CH₄O P-CH₃CAH₀O 9.0 7.65/7.70 6 -10 C₄H₃-CH(C₃H₀O P-CH₃CAH₀O 9.0 7.65/7				8.0	8.01	9	
n-C₄H₄ OC₂H₄ OC₂H₄ OC₂H₄ OC₄H₄ OC₄H₄ OC₄H₄ OC₄H₄ OC₄H₄ OC₄H₄ OC₄H₃ S.0 S.0 S.0 J.0 C₀H₄ OC₂H₄ OC₂H₃ OC₂H₃ S.4 7.95 S .04 OC₂H₄ OC₂H₃ OC₂H₃ OC₂H₃ 9.0 7.85 S 1.0 OC₂H₃ OC₂H₃ OC₂H₃ 9.0 7.81/7.91 6 .06 OC₄H₃ OC₂H₃ OC₂H₃ 9.0 7.857.70 6 .06 OC₄H₃O C₄H₃O C₂H₃O 9.6 7.63/7.70 6 .03 σ-CH,C₄H₄O σ-CH₃C₄H₄O σ-CH₃C₃H₄O 9.0 7.63/7.70 6 05 m-CH,C₃H₄O m-CH₃C₃H₄O m-CH₃C₃H₄O 9.0 7.63/7.70 6 10 p-CH₃C₃H₄O m-CH₃C₃HAO m-CH₃C₃HAO 9.0 7.63/7.71 6 10 p-CH₃C₃H₄O p-CH₃C₃HAO 9.0 7.80/7.80 6 CH₃C-CH(C₃	C_2H_6	OC₂H₅	OC₂H₅	8.0	7.97/8.13	9	04
n-C₄H₄ OC₂H₄ OC₂H₄ OC₂H₄ OC₄H₄ OC₄H₄ OC₄H₄ OC₄H₄ OC₄H₄ OC₄H₄ OC₄H₃ S.0 S.0 S.0 J.0 C₀H₄ OC₂H₄ OC₂H₃ OC₂H₃ S.4 7.95 S .04 OC₂H₄ OC₂H₃ OC₂H₃ OC₂H₃ 9.0 7.85 S 1.0 OC₂H₃ OC₂H₃ OC₂H₃ 9.0 7.81/7.91 6 .06 OC₄H₃ OC₂H₃ OC₂H₃ 9.0 7.857.70 6 .06 OC₄H₃O C₄H₃O C₂H₃O 9.6 7.63/7.70 6 .03 σ-CH,C₄H₄O σ-CH₃C₄H₄O σ-CH₃C₃H₄O 9.0 7.63/7.70 6 05 m-CH,C₃H₄O m-CH₃C₃H₄O m-CH₃C₃H₄O 9.0 7.63/7.70 6 10 p-CH₃C₃H₄O m-CH₃C₃HAO m-CH₃C₃HAO 9.0 7.63/7.71 6 10 p-CH₃C₃H₄O p-CH₃C₃HAO 9.0 7.80/7.80 6 CH₃C-CH(C₃	C ₂ H ₅	OC.Hi	OC2O7-i	8.0	7.99/8.17	9	02
n-C ₄ H ₁ OC ₄ H ₁ -n OC ₄ H ₁ OC ₄ H ₁ OC ₄ H ₁ S.0 8.0 3 .01 C ₈ H ₈ OC ₅ H ₁ OC ₄ H ₁ OC ₄ H ₁ OC ₄ H ₁ 9.0 7.85 3 .04 OC ₂ H ₈ OC ₆ H ₈ OC ₆ H ₁ OC ₆ H ₁ 9.0 7.85 6 .06 OC ₄ H ₇ OC ₆ H ₉ O CC ₆ H ₂ O 9.0 7.85 6 .10 C ₆ H ₁ O OC ₁ H ₁ C ₂ H ₁ O OC ₁ H ₁ C ₂ H ₁ O 9.0 7.85 6 .10 O-CH ₁ C ₂ H ₁ O O-CH ₁ C ₂ H ₂ O OC ₁ H ₂ C ₁ C ₁ O 9.0 7.80 6 05 m-CH ₁ C ₂ H ₁ O m-CH ₂ C ₁ H ₂ O 9.0 7.63/7.70 6 10 p-CH ₁ C ₂ H ₁ O m-CH ₁ C ₂ H ₂ O 9.0 7.63/7.70 6 10 m-CH ₁ C ₂ H ₁ O m-CH ₁ C ₂ H ₂ O 9.0 7.63/7.70 6 10 m-CH ₁ C ₂ H ₁ O m-CH ₁ C ₂ H ₂ O m-CH ₂ C ₂ H ₂ O 9.0 7.80/7.70 6 10 m-CH ₁							
C6Hs OC₂Hs OC₂Hs OC₂Hs O.0Hs 0.0 7.85 3 .04 OCHs OC₂Hs OC₂Hs OC₂Hs 9.0 7.855 3 .10 OC₂Hs OC₂Hs OC₂Hs 9.0 7.857 6 .10 OC₂Hs OC₂Hs OC₂Hs 9.0 7.857 6 .10 CH₂O CH₃O OC₃Hs 9.0 7.6577.70 6 .03 σ-CH₁C₂H₄O σ-CH₁C₂H₄O σ-CH₁C₂H₄O 9.0 7.6577.70 6 .05 m-CHC₃HAO m-CHC₃CH₄O 9.0 7.6577.70 6 .05 m-CH₁C₃HAO m-CH₁C₃H₄O 9.0 7.6577.71 6 .05 p-CH₁C₃HAO p-CH₁C₂H₄O 9.0 7.8077.90 6 .05 CH₂CH-CH₂O CH₂CHC(C₃H₃)-CH₂O 9.0 7.8077.90 6 .05 CH₂CH-CH₂O CH₂CH-CH₂O 9.0 7.807.90 6 .05 CH₂CH-CH₂O CH₂CH-CH₂O 9.0 7.807.							
OCH₁ OCH₂ OCH₂ 9.0 7.85 3 .10 OC₂H₃ OC₂H₃ OC₂H₃ 9.0 7.81/7.91 6 .06 OC₂H₃ OC₂H₃ OC₂H₃ 9.0 7.81/7.91 6 .06 OC₄H₃ OC₄H₃ OC₄H₃ 9.0 7.85/7.70 6 .03 o-CH₁C₄H₄O o-CH₁C₄H₄O 9.0 7.63/7.70 6 .03 o-CH₁C₄H₄O m-CH₁C₄H₄O m-CH₁C₄H₄O 9.0 7.63/7.70 6 .05 m-CH₁C₄H₄O p-CH₁C₄H₄O p-CH₁C₄H₄O 9.0 7.63/7.70 6 0 p-CH₁C₃H₄O p-CH₁C₄H₄O p-CH₁C₄H₄O 9.0 7.63/7.70 6 1 cHŋ-CH(C₂H₃)-CH₂O p-CH₁C₄H₄O 9.0 7.63/7.70 6 1 cHŋ-CH(C₂H₃)-CH₂O p-CH₁C₄H₄O 9.0 7.63/7.70 6 1 cHŋ-CH(C₂H₃)-CH₂O p-CH₃C₄H₄O 9.0 7.80/7.82 6 .05 CH₃-CH(C₂H₃)-CH₂O Q.0 Q.0 <td< td=""><td></td><td></td><td></td><td></td><td>8.0</td><td></td><td></td></td<>					8.0		
OC2Hs OC2Hs OC3Hs 9.0 7.81/7.91 6 .06 OC4Hs ⁿ OC4Hs ⁿ OC4Hs ⁿ OC4Hs ⁿ 9.0 7.85 6 .10 CeHsO CeHsO CeHsO 9.0 7.63/7.70 6 .03 σ-CHsCeHsO σ-CHsCeHsO σ-CHsCeHsO 9.0 7.70 6 05 m-CHsChsO m-CHsCeHsO m-CHsCeHsO 9.0 7.65/7.70 6 05 m-CHsChsO m-CHsCeHsO p-CHsCeHsO 9.0 7.65/7.70 6 10 p-CHsCHCeHsO m-CHsCeHsO 9.0 7.63/7.71 6 12 Chs-CH(CsHs)-CH2O CHsCH-CHO 9.0 7.80/7.90 6 Chs-CH(CsHs)-CH2O CHsCH-CH2O 9.0 7.80/7.80 6 Chy-CH(CsHs)-CH2O CHsCH-CH2O 9.0 7.80/7.80 6 OC2Hs OC2Hs p-NO2CeHsO 8.8 7.78 2 0.5 OC3Hs	C_6H_5	OC₂H₅	OC_2H_5	8.4	7.95	3	. 04
OC2Hs OC2Hs OC4Hs n OCAHs n O	OCH:	OCH:	OCH:	9.0	7.85	3	. 10
OC,Hy-n OC,Hy-n OC,Hy-n 9.0 7.85 6 .10 CHyO CoHyO CoHyO 9.6 7.63/7.70 6 .03 o-CH ₁ C ₈ H ₄ O o-CH ₁ C ₈ H ₄ O o-CH ₁ C ₈ H ₄ O 9.0 7.63/7.70 6 05 m-CH ₂ C ₄ H ₄ O m-CH ₂ C ₄ H ₄ O 9.0 7.63/7.70 6 05 p-CH ₂ C ₄ H ₄ O p-CH ₂ C ₄ H ₄ O 9.0 7.63/7.71 6 12 p-CH ₂ C ₄ H ₄ O p-CH ₂ C ₄ H ₄ O 9.0 7.63/7.71 6 12 CH ₂ C ₁ -CH ₂ O CH ₂ -CH(C ₂ H ₃)-CH ₂ O 9.0 7.80/7.90 6 5 CH ₂ C ₁ -CH ₂ O CH ₂ C ₁ -CH ₂ O CH ₃ CH ₄ C ₂ CH ₂ O 9.0 7.80/7.90 6 5 CH ₂ C ₁ -CH ₂ O CH ₂ C ₁ -CH ₂ O 9.0 7.80/7.80 6 OC ₂ H ₄ OC ₂ H ₅ C ₄ H ₅ O 9.2 7.75/7.82 6 OC ₂ H ₄ OC ₂ H ₅ P.NO ₂ C ₆ H ₄ O 8.8 7.80 8	OC*H'						
CeHsO CeHsO CeHsO CeHsO 9.6 7.63/7.70 6 .03 o-CHsCeHsO o-CHsCeHsO o-CHsCeHsO 9.0 7.70 6 .05 m-CHsCeHsO m-CHsCeHsO m-CHsCeHsO 9.0 7.63/7.70 6 05 m-CHsCeHsO p-CHsCeHsO m-CHsCeHsO 9.0 7.63/7.71 6 12 CHsCh-CHsO p-CHsCeHsO p-CHsCeHsO 9.0 7.63/7.71 6 12 CHsCl-CHsO p-CHsCeHsO p-CHsCHsO 9.0 7.80/7.90 6 .05 CHsCl-CHsO CHsCl-CHsO CHsCl-CHsO 9.0 7.80/7.90 6 .05 CHsCl-CHsO CHsCl-CHsO CHsCl-CHsO 9.0 7.80 6 CHsCl-CHsO CHsCl-CHsO 9.0 7.80 6 6 CHsCl-CHsO O.2Hs ChsCl-CHsO 9.0 7.87/7.82 6 OC2Hs O.2Hs C-NOsCeHsO 9.0 7.79	- ·	· · · ·					
o-CH ₁ C ₆ H ₄ O o-CH ₁ C ₆ H ₄ O o-CH ₁ C ₆ H ₄ O 9.0 7.70 6 05 m-CH ₁ C ₆ H ₄ O m-CH ₂ C ₆ H ₄ O m-CH ₂ C ₆ H ₄ O 9.0 7.65/7.70 6 05 p-CH ₂ C ₆ H ₄ O p-CH ₂ C ₆ H ₄ O p-CH ₂ C ₆ H ₄ O 9.0 7.63/7.71 6 12 CH ₂ CH-CH ₂ O CH ₉ C-H(C ₂ H ₆)-CH ₂ O CH ₂ CH-CH ₂ O 9.0 7.80 /7.90 6 .05 CH ₂ CH-CH ₂ O CH ₂ CH-CH ₂ O CH ₂ CH-CH ₂ O 9.0 7.80 /7.80 6 CL ₂ CH ₂ CH ₄ O CH ₂ CH-CH ₂ O 9.0 7.75/7.82 6 .05 CH ₂ CH-CH ₂ O CH ₂ CH ₂ CH ₂ O 9.0 7.75/7.82 6 .05 CL ₂ H ₄ OC ₂ H ₄ P.NO ₂ C ₆ H ₄ O 8.8 7.80 /7.82 6 .05 OC ₂ H ₄ OC ₂ H ₄ P.NO ₂ C ₆ H ₄ O 8.8 7.78 2 02 OC ₂ H ₅ OC ₂ H ₅ P.CH ₂ C ₄ H ₄ O 9.0 7.79 2 .04 OC ₂ H ₅ OC ₂ H ₅ <th< td=""><td></td><td></td><td></td><td></td><td></td><td></td><td></td></th<>							
m-CH₁C₀H₄O m-CH₁C₀H₄O m-CH₁C₀H₄O 9.0 7.65/7.70 6 — .10 p-CH₃C₀H₄O p-CH₃C₀H₄O p-CH₃C₀H₄O p-CH₃C₀H₄O 9.0 7.65/7.70 6 — .12 CH₃C-CH₄O p-CH₃C₀H₄O p-CH₃C₀H₄O 9.0 7.80/7.90 6 .05 CH₃Cl-CH₂O CH₃Cl-CH₂O CH₃Cl-CH₂O 9.0 7.80/7.90 6 .05 CH₃Cl-CH₂O CH₃Cl-CH₂O CH₃Cl-CH₂O 9.0 7.80/7.90 6 .05 OC₃H₃ OC₂H₃ CH₃Cl-CH₄O 9.0 7.80/7.82 6 .05 OC₃H₃ OC₃H₃ P·Cl-C₄H₄ 8.1 7.95 3 OC₂H₃ OC₃H₃ P·Cl-G₄H₄O 9.0 7.86 8 1.11 OC₂H₃	C_6H_5O	C_6H_5O	C_6H_5O	9.6	7.63/7.70	6	.03
φ-CH ₁ C ₆ H ₄ O φ-CH ₁ C ₆ H ₄ O φ-CH ₂ C ₆ H ₄ O φ-CH ₂ C ₆ H ₄ O 9.0 7.63/7.71 6 12 C _H _T -CH(C ₂ H ₅)-CH ₂ O C _H _T -CH(C ₂ H ₅)-CH ₂ O C _H _T CH-CH ₂ O 9.0 7.80/7.90 6 .05 CH ₂ Cl-CH ₂ O CH ₂ Cl-CH ₂ O CH ₂ Cl-CH ₂ O 9.0 7.80/7.82 6 OC ₂ H ₅ OC ₂ H ₅ C ₆ H ₅ O 9.2 7.75/7.82 6 OC ₂ H ₅ OC ₂ H ₅ C ₆ H ₃ O 9.2 7.75/7.82 6 OC ₂ H ₅ OC ₂ H ₆ P.NO ₂ C ₆ H ₄ O 8.8 7.80 6 OC ₂ H ₅ OC ₂ H ₆ P.NO ₂ C ₆ H ₄ O 8.8 7.78 2 02 OC ₂ H ₆ OC ₂ H ₆ P-CH ₂ C ₆ H ₄ O 8.1 7.95 3 OC ₂ H ₆ OC ₂ H ₆ P-CH ₁ C ₆ H ₄ O 9.0 7.79 2 .04 OC ₂ H ₆ OC ₂ H ₆ P-CH ₁ C ₆ H ₄ O 9.0 7.86 8 .11 OC ₂ H ₆	o-CH ₂ C ₆ H ₄ O	o-CH ₂ C ₆ H ₄ O	o-CH ₂ C ₆ H ₄ O	9.0	7.70	6	- .05
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$							02
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			p-ClC ₆ H₄	8.1	7.95	3	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	OC_2H_5	OC₂H₅	p-CH₃C ₆ H₄O	9.0	7.79	2	. 04
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$\begin{array}{c ccccccccccccccccccccccccccccccccccc$							
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		C_4H_9 - $CH(C_2H_5)$ - CH_1O	C_4H_9 - $CH(C_2H_5)$ - CH_2O	9.0	8.00	8	.25
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	OC_2H_6	C ₆ H ₅ O	C ₆ H ₅ O	9.4	7.61/7.71	6	04
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	D-NO ₂ C ₆ H ₄ -CH ₂ O	p-NO ₂ C ₆ H ₄ -CH ₄ O	p-NO°C°H°-CH°O			8	
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$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	OC₂H₅	OC₂H₅		9.0	7.81	6	.06
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$OC_4H_{9}-n$	OC_4H_9-n	$O(PO)(OC_4H_{g-n})_2$	9.0	7.7	3	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$							
OC_2H_5 OC_2H_5 SC_5H_{11} 8.6 7.94 2 $.08$ OC_2H_5							
OC_2H_5							
OC_2H_5 SC_2H_5 SC_2H_6 8.2 7.89 2 07				8.6	7.94	2	.08
OC_2H_5 SC_2H_5 SC_2H_6 8.2 7.89 2 07	$OC_2H_{f 5}$	OC₂H₅	SC₀H₅	8.4	7.92	2	
A #							
		~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~	-144	1.1	0.07	'	00

(9) C. I. Meyrick and H. W. Thompson, J. Chem. Soc., 225 (1950).

(10) H. S. Gutowsky and A. D. Liehr, J. Chem. Phys., 20, 1652 (1952).

TABLE II (Continued)

v	Substituent groups Y	z	Sum of shift constants	Obsd. wave length,	Ref.	Diff. between obsd. and predicted wave length,
F	$N(CH_3)_2$	$N(CH_3)_2$	10.0	7.66	6	0.16
C ₆ H ₅ O	C_6H_5O	NH_2	8.1	7.85	8	- .13
C ₆ H ₅ O	NH_2	NH_2	6.6	8.50	8	. 14
C_6H_5 – CH_2O	$C_6H_5CH_2O$	$C_6H_5N-CH_3$	9.0	7.85	8	. 10
C_6H_5NH	C_6H_5NH	C ₆ H ₅ NH	8.7	7.75	8	08
C_6H_5O	C_6H_5NH	C ₆ H ₅ NH	9.0	7.75	8	. 00
C_6H_5O	C_6H_5O	C_6H_6NH	9.3	7.75/8.15	8	. 07
C_6H_5 – CH_2O	C ₆ H ₅ CH ₂ O	C_6H_5NH	8.9	7.75/8.00	8	- .03
OC₂H₅	OC₂H₅	C_6H_6NH	8.9	7.75	6	03
C_6H_5 –CHO	C ₆ H ₅ CHO	C_6H_5 - CH_2 - CH_2 - NH	9.0	7.75	8	
OC ₂ H ₆	OC₂H₅	CN	9.3	7.75	7	. 07
OC_2H_{δ}	$N(CH_8)_2$	CN	9.3	7.57/7.86	7	- .11
C_6H_5	H	OH	6.8	~8 .35	3	
OCH ₂	OC₂H₅	OH	8.3	~8.1	8	
C_6H_{11}	OH	ОН	7.2	8.20	8	
C_6H_5 - CH_2O	$C_6H_5CH_2O$	OH	8.3	8.00	8	.07
p-NO₂C6H4O	p-NO ₂ C ₆ H ₄ O	OH	7.9	8.20	8	. 16
o-CH ₃ OC ₆ H ₄ O	o-CH₃OC₅H₄O	OH	8.3	7.93	8	.00
OC ₂ H ₅	OC_2H_5	OK	9.0	7.75	2	

Deviation values were omitted for those compounds whose absorption was not given to the hundredth of a micron.

TABLE III

PHOSPHORYL ABSORPTION SHIFT CONSTANTS OF SUBSTITUENT GROUPS

Group	Av. phosphoryl absorption shift constant	No. of cpds. on which av. is based
O-R	3 .0	15
R	2.0	8
C_6H_5	${f 2}$. ${f 4}$	4
OC_bH_b	3 . 2	5
Cyclohexyl	2.6	1
O-CH ₂ -C ₈ H ₅	3.0	1
$O-C_6H_4-R$	3 .0	5
$O-C_6H_4-NO_2$	2.8	2
C_6H_4 -Cl	2.2	1
O-CHCl-CH2Cl	3 .0	1
$O-CH_2-C_6H_4-NO_2$	3.0	1
OH	2 .3	6
O(PO)(OR) ₂	3.0	4
S-R	2.6	3
$S-C_6H_5$	2.4	1
NH_2	1.7	3
NR_2	3.0	3
NHR	3.0	1
NHC ₆ H ₅	2.9	5
NRC_6H_6	3.0	1
CN	3.3	2
OK	3 .0	1
Cı	3.0	Ref. 4
F	4.0	Ref. 4
Br	2.8	Ref. 4
0	3.5	Ref. 4
P	2.1	Ref. 4
ਸ	2 1	Ref 4

phoryl absorption shift constant for the ethoxy group (value of 3.0 for alkoxy group) was used to obtain the value of 2.6 for the thioalkyl group.

Although the groups occurring in greatest number were used as secondary standards, there is still some uncertainty over the phosphoryl absorption shift constants obtained by using these secondary

standards. In general, the larger the number of compounds used, the greater the reliability of the phosphoryl absorption shift constants.

An anomaly which cannot be explained at present is noted by a comparison of the phosphoryl absorption shift constants for NH_2 (1.7) and for NHR and NR_2 (3.0).

This in turn brings up the question of the reliability of the total relationship. The average deviation for a single calculation of the infrared absorption wave length from the given phosphoryl absorption shift constant is $\pm 0.06~\mu$.

In any individual measurement of the phosphoryl absorption the variation of one or more external factors may cause a variation in the position of absorption of a particular compound. Differences in the purity of a material, the nature of the impurities and the solvent used, are the primary factors determining the variations. It is felt that the ± 0.06 μ deviation sets limits to the position of the absorption which are sufficiently close to be useful in the prediction of the wave length, and at the same time wide enough to include any effects of experimental errors. Differences in the various physical states of the material, however, will cause shifts which may fall outside the deviation limits.

It should be noted at this point that most of the data in Table II are based upon measurements made in solution. One should not expect measurements made on solids to conform completely with the curve presented here.

Theoretical Implications.—In addition to the obvious applications to prediction of the phosphoryl wave lengths, and to the determination of substituent groups, the relationship reveals information concerning the nature of pentavalent organophosphorus compounds.

A change in the wave length of the infrared absorption of the phosphoryl bond may be interpreted as implying a change in the bond force constant and a corresponding change in the bond order. At

one extreme, (CH₃)₃PO, the phosphoryl bond assumes, primarily, the nature of a single covalent bond (Fig. 1b). At the other extreme, F₃PO, the phosphoryl bond takes on some double or even triple bond character (Fig. 1a). Both at and in between these extremes the bond has considerable ionic character, with a variable charge on the oxygen atom.

Hydrogen bonding studies were made to determine whether the oxygen atom of the phosphoryl linkage does in fact have a variable negative charge. Trialkyl phosphine oxides do show a greater perturbation of the phosphoryl linkage upon hydrogen bonding with catechol or phenol (a shift of about $0.2~\mu$ to longer wave lengths) than do other molecules containing substituents with higher phosphoryl absorption shift constants. The differences are not as great as was to be expected, however, nor in all cases consistent, making quantitative confirmation at present impossible.

Exploratory studies of other bonds in the pentavalent organophosphorus molecules indicate a dependence of the P-F, P-Cl and P-O-C stretching vibrations on the phosphoryl absorption shift constants of substituent groups. The shift constant values have less influence on these bonds than they do on the phosphoryl link. This indicates that these bonds have a certain amount of ionic character, but not nearly as much as the phosphoryl bond.

Hartwell, et al., have found a similar effect in the vibration frequency of the carbonyl group. The contribution of the substituent groups to the change in frequency of the carbonyl vibration is less marked than in the phosphoryl vibration as is expected.

The mass of the substituent atoms, groups or of atoms adjacent to the pentavalent phosphorus and contained in the substituent groups appears to have little effect upon the stretching absorption of the phosphoryl bond. For, in the case of the straight line relationship established for phosphoryl halides between the sum of the Pauling electronegativities of the halogen substituents and the Raman shift of the phosphoryl stretching absorption, the phosphoryl stretching absorption of F₃PO is found at one extreme of the curve and that of Br3PO at the other. But this could be accounted for in terms of an accidental linear relationship between mass and electronegativity, since as the mass of the halogen atom increases the electronegativity decreases. However, as the straight line relationship is applied to the infrared data, it is seen that again F₃PO lies at one extreme and $(CH_3)_2PO$ at the other. Here the substituent atoms involved (C and F) differ little in mass and if mass effects were important would result in band shifts opposite to those observed. It is concluded, therefore, that the electron attracting power of the substituent groups is the more important in its effects upon the phosphoryl stretching absorption and, further, that the derived phosphoryl absorption shift constants are in fact largely the Pauling electronegativity values.

(5) E. J. Hartwell, R. E. Richards and H. W. Thompson, J. Chem. Soc., 1436 (1948). Pauling has shown a relationship between bond energies and electronegativities of atoms forming the bond. One would expect the same to hold true for the phosphoryl absorption shift constants derived here. However, there are insufficient systematic thermochemical data available on pentavalent organic phosphorus compounds for verification of any such relationship at present.

Phosphoryl Doublets.—Finally the phenomenon of doublet phosphoryl absorptions must be considered. Gore² has noted that a doublet appears in spectra of certain compounds containing ethoxy groups.

Bellamy and Beecher⁶ have further noted that doublets appear in some compounds containing aromatic esters having no ethoxy groups. Holmstedt and Larsson⁷ have reported a similar doublet in compounds containing amino groups.

Examination of the doublet found in dimethylamino compounds shows that the absorption at the shorter wave length varies from molecule to molecule, while that of the longer wave length is more or less constant at about 7.9 μ . This indicates that the 7.9 μ band is not a part of the phosphoryl absorption. The 7.9 μ absorption is undoubtedly a function of the amino grouping, as suggested by Bellamy and Beecher.⁸

This does not seem to be the case with doublets appearing in spectra of organic esters. Where doublets occur in compounds containing aliphatic and aromatic oxy groups, a large shift, going from one compound to another, in the shorter phosphoryl wave length is usually accompanied by a shift in the longer wave length.

Consideration of the Fisher-Taylor-Hirschfelder models of triaromatic esters of phosphorus acids shows that it is sterically impossible to attain the tetrahedral configuration shown in Figs. 1a and 1b, since the relatively large phenyl groups interfere with each other. A modified form of the tetrahedral may, however, be attained.

Although this evidence can in no way be considered conclusive, it indicates the possibility that the phosphoryl doublet, appearing in the spectra of the triaromatic esters, may be a manifestation of the modified tetrahedral form. That is, each one of the absorption maxima may represent a stable modified configuration.

No similar explanation can be offered for the doublet encountered in spectra of compounds containing ethoxy groups. It is believed, however, that the doublet in this case represents two distinct variations of the phosphoryl bond, since both absorption maxima of the doublets shift, in going from one compound to another.

In all cases where doublets appear, the shorter wave length (*i.e.*, greater frequency and greater force constant) was chosen as representative, insofar as the relationship was concerned.

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⁽⁶⁾ L. J. Bellamy and L. Beecher, ibid., 475 (1952).

⁽⁷⁾ B. Holmstedt and L. Larsson, Acta chim. Scand., 5, 1179 (1951).

⁽⁸⁾ L. J. Bellamy and L. Beecher. J. Chem. Soc., 1701 (1952).