

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.

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## A Linear Phosphoryl Absorption Relationship

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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

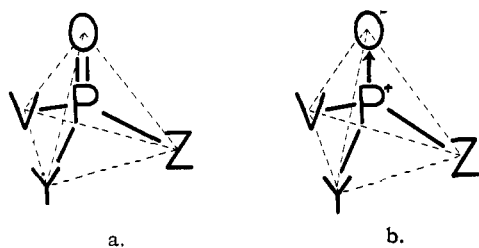


Figure 1.

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  $\mu$ , 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.<sup>1-3</sup> 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. Delwaille 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

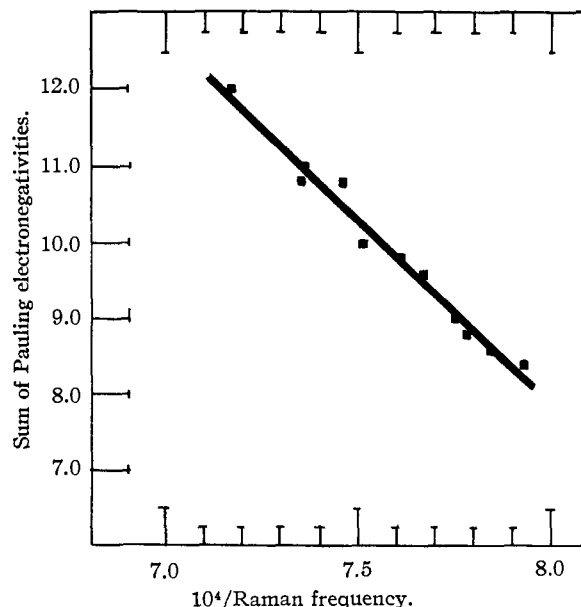


Fig. 2.—Raman data  $\mu = (47.31 - \Sigma x)/4.933$ .

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 halides<sup>1</sup> against the sum of the Pauling electronegativity constants<sup>4</sup> 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  $10^4/\text{Raman frequency}$  and  $\Sigma x$  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	Substituents Y Z	Sum of Pauling electro- negativity constants, <sup>a</sup> $\Sigma x$	$10^4/\text{Raman}$ frequency in $\mu^b$	Raman frequency in $\text{cm.}^{-1b}$
F	F F	12.0	7.16	1395
F	F Cl	11.0	7.36	1358
F	F Br	10.8	7.35	1360 <sup>c</sup>
			7.46	1340 <sup>c</sup>
F	Cl Cl	10.0	7.51	1331
F	Br Br	9.6	7.67	1303
Cl	Cl Cl	9.0	7.75	1290
Cl	Cl Br	8.8	7.78	1285
Cl	Br Br	8.6	7.84	1275
Br	Br Br	8.4	7.93	1261
F	Cl Br	9.8	7.61	1319

<sup>a</sup> Pauling electronegativities are listed in Table III.

<sup>b</sup> Data in last two columns taken from reference 1. <sup>c</sup> Both points of doublet plotted in Fig. 2.

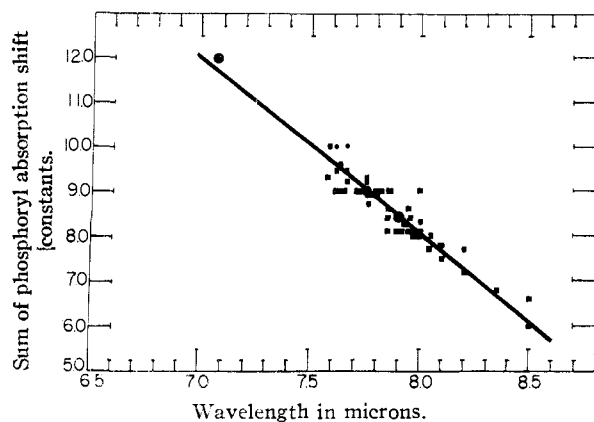


Fig. 3.—Infrared data,  $\lambda(\mu) = (39.96 - \Sigma x)/3.995$ .

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

**Infrared Absorption Correlation.**—An inspection of the infrared absorption data for  $\text{F}_3\text{PO}$ ,  $\text{Cl}_3\text{PO}$  and  $\text{Br}_3\text{PO}$ , 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  $\Sigma x$  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 curve.

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  $\Sigma x$  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-

TABLE II  
 INFRARED AND PHOSPHORYL ABSORPTION SHIFT CONSTANT DATA<sup>a</sup>

V	Substituent groups Y	Z	Sum of shift con- stants Σ	Obsd. wave length, μ	Ref.	Diff. between obsd. and predicted wave length, μ
F	F	F	12.0	7.07	10	-0.08
Cl	Cl	Cl	9.0	7.75	2	-.01
Br	Br	Br	8.4	7.90	3	-.01
Cl	Cl	C <sub>6</sub> H <sub>5</sub>	8.4	7.85	3	-.05
Cl	Cl	C <sub>6</sub> H <sub>5</sub> O	9.2	7.66	6	-.04
Cl	Cl	C <sub>6</sub> H <sub>11</sub>	8.6	7.85/7.95	6	....
Cl	Cl	N(CH <sub>3</sub> ) <sub>2</sub>	9.0	7.65/7.88	7	-.10
Cl	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	7.8	8.10	3	.04
F	OCH <sub>3</sub>	OCH <sub>3</sub>	10.0	7.58	3	.08
F	OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	10.0	7.61	3	.11
Cl	C <sub>6</sub> H <sub>5</sub> O	C <sub>6</sub> H <sub>5</sub> O	9.4	7.66/7.71	6	.01
Cl	OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	9.0	7.72/7.79	2	-.03
Cl	N(CH <sub>3</sub> ) <sub>2</sub>	OC <sub>2</sub> H <sub>5</sub>	9.0	7.61/7.88	7	-.14
H	OCH <sub>3</sub>	OCH <sub>3</sub>	8.1	7.90	9	-.08
H	OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	8.1	7.90	3	-.08
H	O <sub>1</sub> C <sub>2</sub> H <sub>7</sub>	O <sub>1</sub> C <sub>2</sub> H <sub>7</sub>	8.1	7.92	9	-.06
H	O <sub>n</sub> C <sub>4</sub> H <sub>9</sub>	O <sub>n</sub> C <sub>4</sub> H <sub>9</sub>	8.1	7.90	3	-.08
H	C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> O	8.1	7.96	8	
H	CH <sub>3</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -CH(CH <sub>3</sub> )O	CH <sub>3</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -CH(CH <sub>3</sub> )O	8.1	7.95	8	-.03
H	CH <sub>3</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -CH <sub>2</sub> O	CH <sub>3</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -CH <sub>2</sub> O	8.1	8.00	8	.02
H	C <sub>6</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	7.5	8.10	3	-.04
CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	6.0	8.50	3	-.01
CH <sub>3</sub>	OCH <sub>3</sub>	OCH <sub>3</sub>	8.0	8.05	9	.04
CH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	8.0	8.00	9	-.01
CH <sub>3</sub>	OC <sub>4</sub> H <sub>7</sub> -i	OC <sub>4</sub> H <sub>7</sub> -i	8.0	8.01	9	.00
C <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	8.0	7.97/8.13	9	-.04
C <sub>2</sub> H <sub>5</sub>	OC <sub>4</sub> H <sub>7</sub> -i	OC <sub>4</sub> O <sub>7</sub> -i	8.0	7.99/8.17	9	-.02
n-C <sub>4</sub> H <sub>9</sub>	OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	8.0	8.05	6	.04
n-C <sub>4</sub> H <sub>9</sub>	OC <sub>4</sub> H <sub>9</sub> -n	OC <sub>4</sub> H <sub>9</sub> -n	8.0	8.0	3	.01
C <sub>6</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	8.4	7.95	3	.04
OCH <sub>3</sub>	OCH <sub>3</sub>	OCH <sub>3</sub>	9.0	7.85	3	.10
OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	9.0	7.81/7.91	6	.06
OC <sub>4</sub> H <sub>9</sub> -n	OC <sub>4</sub> H <sub>9</sub> -n	OC <sub>4</sub> H <sub>9</sub> -n	9.0	7.85	6	.10
C <sub>6</sub> H <sub>5</sub> O	C <sub>6</sub> H <sub>5</sub> O	C <sub>6</sub> H <sub>5</sub> O	9.6	7.63/7.70	6	.03
o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O	o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O	o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O	9.0	7.70	6	-.05
m-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O	m-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O	m-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O	9.0	7.65/7.70	6	-.10
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O	9.0	7.63/7.71	6	-.12
C <sub>6</sub> H <sub>5</sub> -CH(C <sub>2</sub> H <sub>5</sub> )-CH <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> -CH(C <sub>2</sub> H <sub>5</sub> )-CH <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH(C <sub>2</sub> H <sub>5</sub> )CH <sub>2</sub> O	9.0	7.80/7.90	6	.05
CH <sub>2</sub> Cl-CH <sub>2</sub> O	CH <sub>2</sub> Cl-CH <sub>2</sub> O	CH <sub>2</sub> Cl-CH <sub>2</sub> O	9.0	7.80	6	....
OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> O	9.2	7.75/7.82	6	.05
OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> O	8.8	7.80	6	.00
OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	o-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> O	8.8	7.78	2	-.02
OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	p-ClC <sub>6</sub> H <sub>4</sub>	8.1	7.95	3	....
OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O	9.0	7.79	2	.04
OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> -CH(C <sub>2</sub> H <sub>5</sub> )-CH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> O	9.0	7.86	8	.11
OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> -CH(C <sub>2</sub> H <sub>5</sub> )-CH <sub>2</sub> O	9.0	8.00	8	.25
OC <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> -CH(C <sub>2</sub> H <sub>5</sub> )-CH <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> -CH(C <sub>2</sub> H <sub>5</sub> )-CH <sub>2</sub> O	9.0	8.00	8	.25
OC <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> O	C <sub>6</sub> H <sub>5</sub> O	9.4	7.61/7.71	6	-.04
p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -CH <sub>2</sub> O	p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -CH <sub>2</sub> O	p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -CH <sub>2</sub> O	9.0	7.77/7.88	8	....
(CH <sub>3</sub> ) <sub>3</sub> CO	(CH <sub>3</sub> ) <sub>3</sub> CO	C <sub>6</sub> H <sub>5</sub> CH(C <sub>2</sub> H <sub>5</sub> )-CH-C <sub>6</sub> H <sub>4</sub> O	9.0	7.82	8	.07
OCH <sub>3</sub>	OCH <sub>3</sub>	O(PO)(OCH <sub>3</sub> ) <sub>2</sub>	9.0	7.65/7.75	3	-.10
OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	O(PO)(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	9.0	7.81	6	.06
OC <sub>4</sub> H <sub>9</sub> -n	OC <sub>4</sub> H <sub>9</sub> -n	O(PO)(OC <sub>4</sub> H <sub>9</sub> -n) <sub>2</sub>	9.0	7.7	3	....
O-CH <sub>2</sub> -C <sub>6</sub> H <sub>5</sub>	OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	O(PO)(OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	9.0	7.75	8	.00
OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	SC <sub>2</sub> H <sub>5</sub>	8.6	7.85	2	-.01
OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	SC <sub>6</sub> H <sub>11</sub>	8.6	7.94	2	.08
OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	SC <sub>6</sub> H <sub>5</sub>	8.4	7.92	2	....
OC <sub>2</sub> H <sub>5</sub>	SC <sub>2</sub> H <sub>5</sub>	SC <sub>2</sub> H <sub>5</sub>	8.2	7.89	2	-.07
OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	NH <sub>4</sub>	7.7	8.04	7	-.05

(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 Σ	Obsd. wave length, μ	Ref.	Diff. between obsd. and predicted wave length, μ
F	N(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	10.0	7.66	6	0.16
C <sub>6</sub> H <sub>5</sub> O	C <sub>6</sub> H <sub>5</sub> O	NH <sub>2</sub>	8.1	7.85	8	-.13
C <sub>6</sub> H <sub>5</sub> O	NH <sub>2</sub>	NH <sub>2</sub>	6.6	8.50	8	.14
C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> N-CH <sub>3</sub>	9.0	7.85	8	.10
C <sub>6</sub> H <sub>5</sub> NH	C <sub>6</sub> H <sub>5</sub> NH	C <sub>6</sub> H <sub>5</sub> NH	8.7	7.75	8	-.08
C <sub>6</sub> H <sub>5</sub> O	C <sub>6</sub> H <sub>5</sub> NH	C <sub>6</sub> H <sub>5</sub> NH	9.0	7.75	8	.00
C <sub>6</sub> H <sub>5</sub> O	C <sub>6</sub> H <sub>5</sub> O	C <sub>6</sub> H <sub>5</sub> NH	9.3	7.75/8.15	8	.07
C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> NH	8.9	7.75/8.00	8	-.03
OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> NH	8.9	7.75	6	-.03
C <sub>6</sub> H <sub>5</sub> -CHO	C <sub>6</sub> H <sub>5</sub> CHO	C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> -CH <sub>2</sub> -NH	9.0	7.75	8	...
OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	CN	9.3	7.75	7	.07
OC <sub>2</sub> H <sub>5</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	CN	9.3	7.57/7.86	7	-.11
C <sub>6</sub> H <sub>5</sub>	H	OH	6.8	~8.35	3	...
OCH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>	OH	8.3	~8.1	8	...
C <sub>6</sub> H <sub>11</sub>	OH	OH	7.2	8.20	8	-.02
C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O	OH	8.3	8.00	8	.07
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> O	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> O	OH	7.9	8.20	8	.16
<i>o</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> O	<i>o</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> O	OH	8.3	7.93	8	.00
OC <sub>2</sub> H <sub>5</sub>	OC <sub>2</sub> H <sub>5</sub>	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	Average phosphoryl absorption shift constant	No. of compounds on which average is based
O-R	3.0	15
R	2.0	8
C <sub>6</sub> H <sub>5</sub>	2.4	4
OC <sub>2</sub> H <sub>5</sub>	3.2	5
Cyclohexyl	2.6	1
O-CH <sub>2</sub> -C <sub>6</sub> H <sub>5</sub>	3.0	1
O-C <sub>6</sub> H <sub>4</sub> -R	3.0	5
O-C <sub>6</sub> H <sub>4</sub> -NO <sub>2</sub>	2.8	2
C <sub>6</sub> H <sub>4</sub> -Cl	2.2	1
O-CHCl-CH <sub>2</sub> Cl	3.0	1
O-CH <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -NO <sub>2</sub>	3.0	1
OH	2.3	6
O(PO)(OR) <sub>2</sub>	3.0	4
S-R	2.6	3
S-C <sub>6</sub> H <sub>5</sub>	2.4	1
NH <sub>2</sub>	1.7	3
NR <sub>2</sub>	3.0	3
NHR	3.0	1
NHC <sub>6</sub> H <sub>5</sub>	2.9	5
NRC <sub>6</sub> H <sub>5</sub>	3.0	1
CN	3.3	2
OK	3.0	1
Cl	3.0	Ref. 4
F	4.0	Ref. 4
Br	2.8	Ref. 4
O	3.5	Ref. 4
P	2.1	Ref. 4
H	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<sub>2</sub> (1.7) and for NHR and NR<sub>2</sub> (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  $\pm 0.06 \mu$  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,  $(\text{CH}_3)_3\text{PO}$ , the phosphoryl bond assumes, primarily, the nature of a single covalent bond (Fig. 1b). At the other extreme,  $\text{F}_3\text{PO}$ , 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.*,<sup>5</sup> 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  $\text{F}_3\text{PO}$  is found at one extreme of the curve and that of  $\text{Br}_3\text{PO}$  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  $\text{F}_3\text{PO}$  lies at one extreme and  $(\text{CH}_3)_3\text{PO}$  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.<sup>4</sup> 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. Gore<sup>2</sup> has noted that a doublet appears in spectra of certain compounds containing ethoxy groups.

Bellamy and Beecher<sup>6</sup> have further noted that doublets appear in some compounds containing aromatic esters having no ethoxy groups. Holmstedt and Larsson<sup>7</sup> 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  $7.9 \mu$ . This indicates that the  $7.9 \mu$  band is not a part of the phosphoryl absorption. The  $7.9 \mu$  absorption is undoubtedly a function of the amino grouping, as suggested by Bellamy and Beecher.<sup>8</sup>

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).