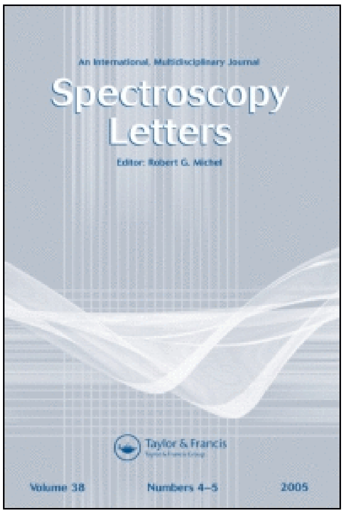

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Romanenko, E. A. , Egorov, Yu. P. and Kornuta, P. P.(1973) 'Substituent and Solvent Effects on The Electronic Absorption Spectra of Phosphapyrimidine Derivatives', Spectroscopy Letters, 6: 10, 621 — 632
To link to this Article: DOI: 10.1080/00387017308060852
URL: http://dx.doi.org/10.1080/00387017308060852

SPECTROSCOPY LETTERS, 6(10), 621-632 (1973)

SUBSTITUENT AND SOLVENT EFFECTS ON THE ELECTRONIC ABSORPTION SPECTRA OF PHOSPHAPYRIMIDINE DERIVATIVES

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INTRODUCTION

U.v. spectra study of phosphacyclic compounds with tetracoordinated ring phosphorus atom has been an object of a rather limited number of works. There are only few works on u.v. absorption spectra of cyclic phosphonitriles which reveal a specific character of their π-electronic structure[1]; besides, there are some data on a significant low - frequency shifting of the electronic spectrum of 1.1 - diphenylphosphabenzene against that of benzene[2]. This communication presents an analysis of the experimental findings on electronic absorption spectra of a wide variety of substituted phosphapyrimidines, PhP, (1,2,6 - phosphadiazines) for elucidating the nature of the observed absorption bands and for studying electronic distribution as well as separate characteristics of the PhP molecules in the ground and excited states.

EXPERIMENTAL

Optical densities of solutions for a variety of solvents were measured in the 220-500 nm region using one - beam spectrophotometer SF - 4 A. Concentrations ($\sim 10^{-4}$m/l) were chosen so that the optical density values fall within the optimum range of 0.1 - 0.8 where accidental instrument errors are usually minimal. The accuracy of finding absorption band peaks was ~ 100 cm^{-1}. The synthesis of the compounds studied is described in [3]. The substances were purified by repeated recrystallization.

RESULTS AND DISCUSSION

Spectra of Substituted PhP

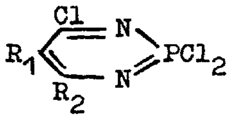
The experimental data in Table 1 show that spectra of the PhP derivatives in the region 220-500 nm are composed of 1-2 bands. The longer wavelength band at 350 nm is observed in all the 14 compounds, the shorter wavelength band in the region 240-260 nm is found only in cyano- and phenylsubstituted compounds (I-VII). All spectra of (I-XIV) show a typical increase of intensity on the higher frequency side of the spectral region studied, which, together with the data for (VIII) below 220 nm indicate (see Table 1) a rather intensive absorption around 200 nm.

Substituent Effects and Assignment of Absorption Bands

Electronic transitions in benzene at 260, 205 and 185 nm in the course of substitution are known to shift towards the longer wavelength region. These shifts yield to a satisfactory description by quantum mechanics theory of Petruska[4] who showed, that the change of π-electronic benzene structure results from the perturbation cauzed by the conjugative and inductive effects of the substituents. The use of Petruska's theory, however, is limitted by certain molecules with known π-electronic structure. On the other hand, the use of the perturbation theory within the framework of Huckel method

TABLE 1

ELECTRONIC ABSORPTION SPECTRA* DATA FOR



Compound	Substituents		The 350 nm band			The 250 nm band	
	R_1	R_2	ν_1,kK	$\varepsilon_1 . 10^{-4}$ l/mole.cm	f_1	ν_2,kK	$\varepsilon_2 . 10^{-4}$ l/mole.cm
I	CN	H	29.80	0.51	0.067	42.1	1.03
II	CN	$CCl_2C_6H_5$	29.15	0.78	0.094	40.8	1.31
III	CN	CCl_2CH_3	29.05	0.77	0.102	40.4	1.54
IV	CN	CCl_3	28.65	0.69	0.108	40.2	1.05
V	CN	C_6H_5	28.65	0.99	0.138	40.1	1.19
VI	CH_3	C_6H_5	28.30	1.31	0.144	38.2	1.00
VII	C_6H_5	C_6H_5	27.70	0.62	0.140	40.6	1.21
VIII[a]	Cl	Cl	28.00	0.74	0.087	47.8	1.10
IX	H	Cl	30.15	0.72	0.108		
X	CH_3	Cl	28.90	0.79	0.102		
XI	C_2H_5	Cl	29.00	0.70	0.086		
XII	CH_3	C_2H_5	29.05	1.00	0.142		
XIII[b]	CH_3	C_2H_5	30.40	0.85	0.100		
XIV[c]	CH_3	C_2H_5	28.90	0.66	0.108		

* Solutions in n - hexane; values of frequencies and coefficients of extinction are given for absorption band maxima.

[a] The spectrum is recorded in the 200 - 500 nm region using the "Unicam SP-700".

[b] The $\geqslant PCl_2$ group is substituted by the $\geqslant P(OBu)_2$ group.

[c] The $\geqslant PCl_2$ group is substituted by the $\geqslant P(\overline{NCH_2CH_2})_2$ group.

often makes it possible to carry out less efficient studies of the substituent influence on the position of the electronic absorption spectra[5].

By studying the influence of the inductive effect of a substituent upon the π-electronic level position in ground and excited states by changing the Coulomb integral of the substituted carbon atom and the influence of the conjugative effect by forming a certain double bond character between substituted atom and substituent the following expressions were derived for the variation of the transition energy in the course of the substitution (the two effects being considered rather insignificant):

$$\text{for } \pi-\pi^* \text{ transition:} \Delta E_{\pi} = (C_{br}^2 - C_{ar}^2)\delta\alpha_r + \beta_{rs}\Big(\sum_{k\neq b}\frac{C_{br}^2 C_{ks}^2}{E_b - E_k} - \sum_{k\neq a}\frac{C_{ar}^2\ C_{ks}^2}{E_a - E_k}\Big), \qquad (1)$$

$$\text{for } n-\pi^* \text{ transition:} \Delta E_n = C_{br}^2 \cdot \delta\alpha_r + \beta_{rs} \cdot \sum_{k\neq b}\frac{C_{br}^2\ C_{ks}^2}{E_b - E_k}, \qquad (2)$$

where the first and the second items in both expressions take account of the inductive effect in the first order and of the conjugative effect in the second order of the perturbation theory, respectively; c_{ij}-atomic orbital coefficient of atom j in the i-th molecular orbital; β_{rs}-resonance integral of the bond between r-atom of non-substituted molecule and s-atom of the substituent; the summing up is performed according to the substituent orbitals; a and b belong to the ground and excited states of non-substituted molecule , respectively. It should be borne in mind that the perturbation of n-level during the substitution was neglected in expression (2).

The analysis of the above expressions when assigning electronic absorption bands may be simplified if one considers those substituents where one of the effects is predominant; the unequivocal conclusion about transition type according to the absorption band shift can be made considering the extremal case of purely inductive substituent. In fact, by assuming the conjugative component of the shift to be zero in (1) and (2), simplified expressions were derived:

$$\Delta E_{\pi} = (C^2_{br} - C^2_{ar})\delta\alpha_r, \quad (3a) \quad \text{and} \quad \Delta E_n = C^2_{br} \cdot \delta\alpha_r , \quad (3b)$$

whereof it follows that introduction of, e.g., electrodonor inductive substituent results in a high-frequency shift of the absorption band corresponding to $n - \pi^*$ transition while direction of the $\pi - \pi^*$ transition band shift will be determined by the sign of difference of the expression in parenthesis of equation (3a).

Expressions (3a) and (3b) were used for (XI) (Table 1), the conjugative effect of the ethyl group was taken as equal to zero. There is a low-frequency band shift for (XI) at 350 nm relative to (IX), which (in accordance with the above and expressions (3a) and (3b)) allows to assign the 350 nm band both to $\pi - \pi^*$ transition of phosphadiazine ring in (IX) and (XI), and of course, to $\pi - \pi^*$ transition of other phosphapyrimidine derivatives having a related structure. Such a considerable low-frequency region shift of the first transition band in the substituted PhP with respect to the positions of similar bands in other six-membered aromatic compounds (e.g. benzene, diazines, etc.) is probably due to the introduction of 3d-orbitals of the tetracoordinated phosphorus atom in the π-electronic system of heterocycle[6,7]. Such an analysis of the 250 nm band cannot be carried out, because of absence of appropriate compounds. The 250 nm band, however, is also assigned to π-π^* transition of phosphadiazine ring due to the high intensity ($\varepsilon > 10000$) and a more high - frequency position than in case of n -π^* transitions is six-membered N-heterocyclic compounds con - taining iso-electronic aza-atoms of nitrogen[8].

Assignment of the substituted PhP absorption bands to π-π^* transitions makes it possible to use expression (3a) to obtain a qualitative information on electronic density distribution within the ring of (XI). Given the positive value $\delta \alpha_r$ of C_2H_5 group, one derives from (3a) $C^2_{br} < C^2_{ar}$. That is, in the excited state a transfer of π-electronic density takes place from r-atom to ortho-positions of the ring in respect to C_2H_5 group, which should bring about a reduction in the double bond character of C-Cl bonds cauzed by the neighbouring electronegative nitrogen atoms of the ring[7].

The character of π-binding in the N - P - N section of phosphadiazine ring is of importance in connection with the unsolved discussion about the "island-like" or aromatic (second type) model of cyclic phosphonitriles[9,10]. Table 1 shows some compounds with different substituents of the phosphorus atom, the substituents of the organic portion of the molecule being the same. No significant changes of position and intensity of the 350 nm band are observed for (XII - XIV). According to the hypothesis of 3d-orbital phosphorus atom compression as affected by ligands[11], the absence of the spectral changes under the introduction of more electronegative groups near the phosphorus atom (compound XII) is indicate of the insignificant 3d - phosphorus atom orbitals contribution to the corresponding electronic heterocycle states. However, substitution of chlorine atoms by the two butoxigroups in (XIII) brings about a larger (as compared to (XIV)) shift of the 350 nm band, which is contrary to the usual intermediate position of the electronegative butoxigroup in the $Cl > OBu > \overline{NCH_2C}H_2$ sequence. It is possible that the observed shift is a result of the field polarization of the π-electronic heterocycle shell effected by the extended butoxigroup chain which can turn to the phosphadiazine ring region.

Solvent Effects

The theory of intermolecular interactions (IMI) in solutions as elaborated by several workers[12-16] makes it possible to predict spectral shifts of the electronic absorption and fluorescence bands due to the effect of solvents for compounds with different structures and properties. The parameters of this theory include the main characteristics of dissolved matter molecules (dipole moment, polarizability, oscillator strength), which allows it to be used for studying the electronic structure of molecules. The most important information

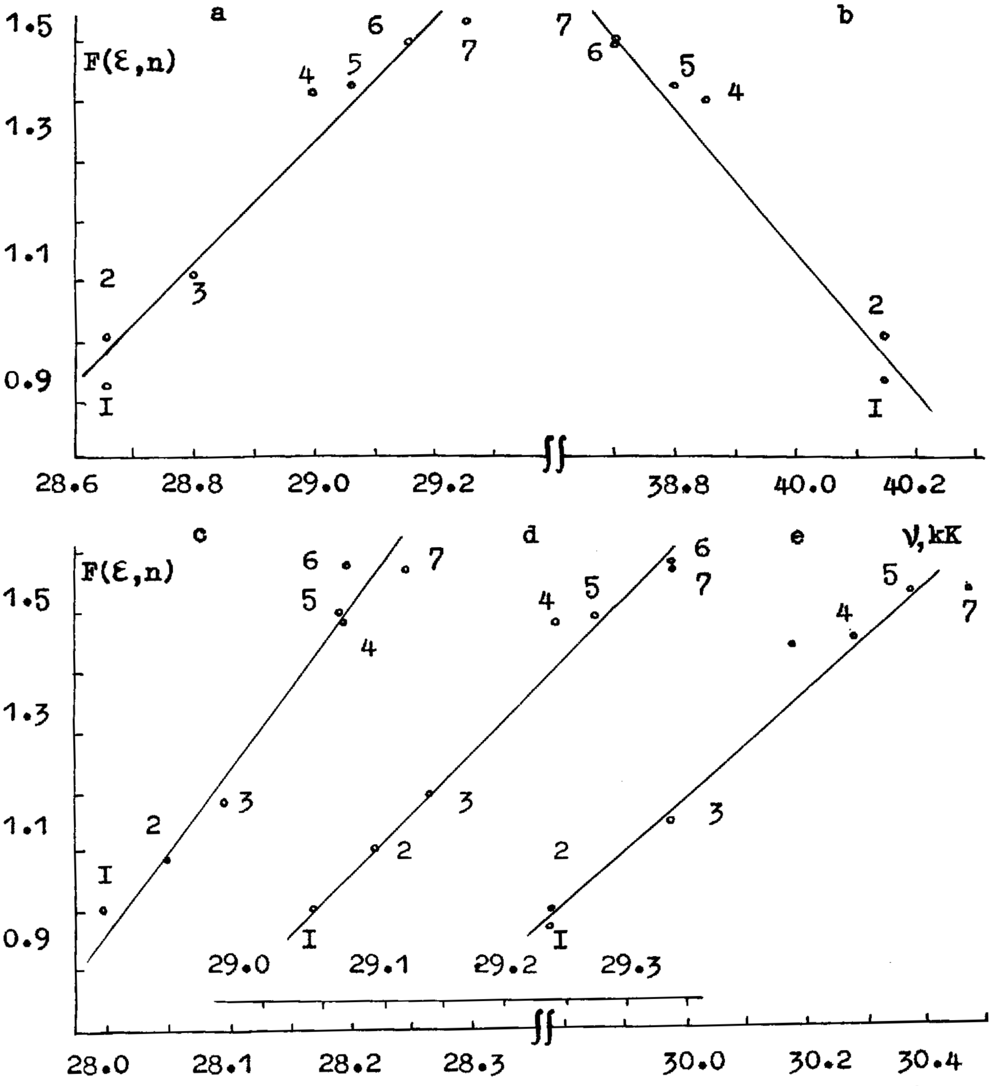


Figure. Position of absorption band peaks of substituted phosphapyrimidines as a function of universal interaction, F(ε,n): a, b - IV, c - VIII; d - XII; e - I; (see Table 1). X-axis 29.0-29.3 kK relates to the d-plot.

$$F(\varepsilon,n)= \frac{2\varepsilon - 2}{2\varepsilon + 1} + P \cdot \frac{2n^2 - 2}{2n^2 + 1};$$

Solvents[20]: 1 - n-hexane, 2 - cyclohexane, 3 - CCl_4, 4 - chloroform, 5 - methylene chloride, 6 - dichlorethane, 7-acetonitrile.

obtained with IMI - spectroscopy pertains, in the first place, to dipole moments and polarizability of molecules in excited state[17]. This section gives results of the effect of solvents on the position of the electronic absorption spectra of phosphapyrimidine derivatives to be used for verification of the IMI - theory applicability for new class of phosphororganic compounds and study of some characteristics of the PhP molecules in the excited states.

For the electronic frequency shift transition $\Delta\nu^e$ in solution with reference to vapour, a simplified expression[18] was used which can easily be derived from[12-14]:

$$\nu^e_{\text{solution}} - \nu^e_{\text{vapour}} = C_1 \frac{2\varepsilon - 2}{2\varepsilon + 1} + (C_2 + f \cdot C_3) \frac{2n^2 - 2}{2n^2 + 1}, \qquad (4)$$

where: f - oscillator strength for electronic transition studied; and n are dielectric constant and refractive index of the solvents; C_1, C_2, C_3 - constants depending on characteristics of the molecule studied. Considering that intermolecular interactions bring about a displacement of electronic molecule levels without significant changes of vibration level positions in each electronic state, the $\Delta\nu^e$ - shifts in eq, (4) were decided to be substituted by displacements of the $\Delta\nu^a$ - absorption band peaks. This had to be done, first of all, because of the difficulties involved in determining the frequency of the electronic transition, especially in this case of complex molecules which do not possess a well-difined vibrational structure[19]. The results of the experiment have also shown that the oscillator strength of molecules of the PhP derivatives preserve their values upon dissolution in solvents of different nature, and therefore the eq. $C_2 + fC_3 = C$ can be accepted. So, in keeping with the abovementioned, expression (4) can be rewritten for convenience of the experimental data treatment:

$$\nu^{a}_{solution} = \nu^{a}_{vapour} + C_1 \cdot \frac{2\varepsilon - 2}{2\varepsilon + 1} + P \cdot \frac{2n^2 - 2}{2n^2 + 1} , \qquad (5)$$

where: $P = C/C_1$.

The results are presented in the figure. In accordance with expression (5), the linear dependence of shift of the absorption bands at 250 nm (comp.IV) and at 350 nm (comp.I, IV,VIII,XII) on the universal interaction function $F(\varepsilon, n)$ is satisfactory. Typical here are different trends of the $^{a}_{sol}$ against $F(\varepsilon, n)$ relationships for 250 nm and 350 nm bands. When the 250 nm band shifts in a usual manner towards the lower frequencies as the solvent polarity is growing, the 350 nm band reveals a reverse trend which indicates a different redistribution of electronic density in the first and the second excited states of phospapyrimidine molecules. On the basis of the above results for compound studied the values of ν^{a}_{vapour}, C_1, C and P constants were calculated which are given in Table 2 together with the parameters of the least squares method (LSM).

According to [12-16], the C_1 constant is proportional to the $\mu_g - \mu_e$ difference of dipole moments of an isolated molecule studied in ground and excited states. Therefore, the second column data of Table 2 for the first excited state are indicative of $\mu'_e < \mu_g$ ($C_1 > 0$), while those for the second

TABLE 2

CONSTANTS OF EQUATION (5) FOR PhP DERIVATIVES

Compound*	The IMI-theory parameters				The ISM parameters	
	C_1, cm^{-1}	C, cm^{-1}	$\nu^{a}_{vap.}$, kK	P	R	$\sqrt{\overline{\Delta\nu^2}}$, kK
I	1145	1832	28.65	1.6	0.973	0.28
IV^{+}	974	1461	27.71	1.5	0.975	0.24
	-822	-1235	40.95	1.5	0.988	0.21
VIII	379	644	27.64	1.7	0.978	0.09
XII	506	860	28.54	1.7	0.996	0.12

* Numbering is in accordance with the Table 1;

\+ The 350 nm band constant values are in the upper, and those of the 250 nm in the lower (third) line.

excited state indicate $\mu''_e > \mu_g$ ($C_1 < 0$). Besides, as the C_1 value determines the contribution of dipole-dipole interaction which is proportional to the product of molecule dipole moments of substance and solvent, it is seen that dipole moments of molecules studied can be arranged, for ground state, as follows: $\mu^{I}_{g} > \mu^{IV}_{g} > \mu^{XII}_{g} > \mu^{VIII}_{g}$. Absence of the data on emission spectra makes it impossible to determine an individual contribution of dipole-induced dipole and dispersion interactions. However, as the contribution of dispersion interaction is always negative[16], on the basis of the C and C_1 values and using expression (5) one can draw a conclusion about predominant contribution of dipole-dipole and dipole induced dipole mechanisms in case of interaction of substituted phosphapyrimidine molecules with polar solvents, and it is only the reduction of their polarity that allows dipole induced dipole and dispersion mechanisms to dominate.

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Received August 27, 1973

Accepted September 10, 1973