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Solvatochromic Behaviour of Some Thiourea Monophosphazene Derivatives

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The electronic absorption spectra of 1-*o*-aryl-2, 2-di(1-*o*-aryl)-2-(N-*o*-aryl thiourea) monophosphazene derivatives were studied in mixed organic solvents. The spectra proved the formation of molecular complexes between solute and solvents for which the stability constant and heat of formation were determined. The behaviour of monophosphazenes have been also studied in aqueous-organic solvent mixtures at different pH. The pK_a values of the compounds have been determined and discussed in relation to both the concentration and the nature of the organic co-solvent used.

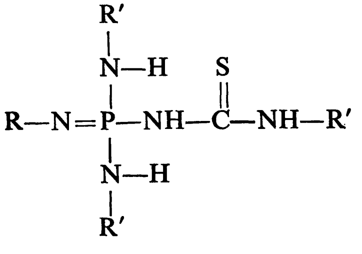
INTRODUCTION

Thiourea monophosphazenes as new compounds have important properties as chelating agents[1–3] used in analytical determination of trace amounts of metals as well as their biological activity. In spite of the interest of these compounds, there is scarcity in spectral informations published in this respect. In the previous paper[4] we studied the behaviour of monophosphazenes in organic solvents of different polarities. The purpose of the present work is to study the effect of mixed organic solvents on the compounds under consideration and the possibility of molecular complex formation between solvent and solute as well as studying the pK_a's of the compounds in aqueous-organic co-solvents.

This was done since the author expects that these spectral consideration may contribute to the application of these compounds.

EXPERIMENTAL

The compounds used in this investigation were prepared according to the method of Ibrahim *et al.*[5] The products were recrystallized from ethanol several times till constant melting point to give 1-*o*-aryl-2,2-di(1-*o*-aryl)-2-(N-*o*-aryl thiourea) monophosphazenes having the general formula,



$$\mathrm{R{-}N{=}\overset{\overset{\displaystyle R'}{|}}{\overset{\displaystyle N{-}H}{|}}{\underset{\underset{\displaystyle R'}{|}}{\underset{\displaystyle N{-}H}{|}}{P}}{-}NH{-}\overset{\displaystyle S}{\overset{\|}{C}}{-}NH{-}R'}$$

R = *o*-tolyl-, R′ = phenyl- (I)
= *o*-tolyl-, = *o*-tolyl- (II)
= *o*-tolyl-, = *m*-tolyl- (III)
= benzyl, = phenyl- (IV)

Stock solutions (10^{-3} M) of the monophosphazenes were prepared by dissolving accurately the weighed solids in the appropriate volume of solvent. The solvents used were purified as given in Vogel[6]. The modified universal buffer series of Britton and Robinson[7] was prepared and used as supporting electrolyte. The pH measurement was carried out on a digital MV-pH-meter having an accuracy of ±0.05 pH units. The pH values in partially aqueous medium were corrected according to the method of Bate[8]. All spectral measurements were carried out on a UV-Visible Shimadzu recording-240-Spectrophotometer within 190–400 nm range using 1 cm matched quartz cell.

RESULTS AND DISCUSSION

Spectra in Mixed Organic Solvents

It was stated previously[4] that the characteristic absorption band of monophosphazenes at 270 nm in organic solvents shifted to shorter wavelength on increasing the polarity of the medium. In the present work, the possibility of molecular complex formation in mixed organic solvents was followed. The spectra in Figs. 1 and 2 show a regular increase in the extinction coefficient of the band located at *ca.* 270 nm and its blue shift on increasing the proportion of the high polarity solvent. The blue shift of the π—π^* of the thioketone group (C=S) can be explained by the blocking of the n-electrons by ethanol molecules leading to a higher solvent stabilization of the ground state. The interaction of ethanol molecules and the n-electrons of the solute takes place probably through a weak H-bonding leading to the formation of some sort of molecular complex. To support this, the results obtained from the spectral data in mixed solvents were used in the following equation[9] to calculate ΔG,

$$\log C = 1/n \log K_f + 1/n \log (A - A_0)/(A_L - A)$$

where

C = concentration of polar solvent
A_0 = absorbance in low-polarity solvent
A_L = absorbance in a high-polarity solvent
A = absorbance in a mixed solvent
n = number of associated solvent molecules

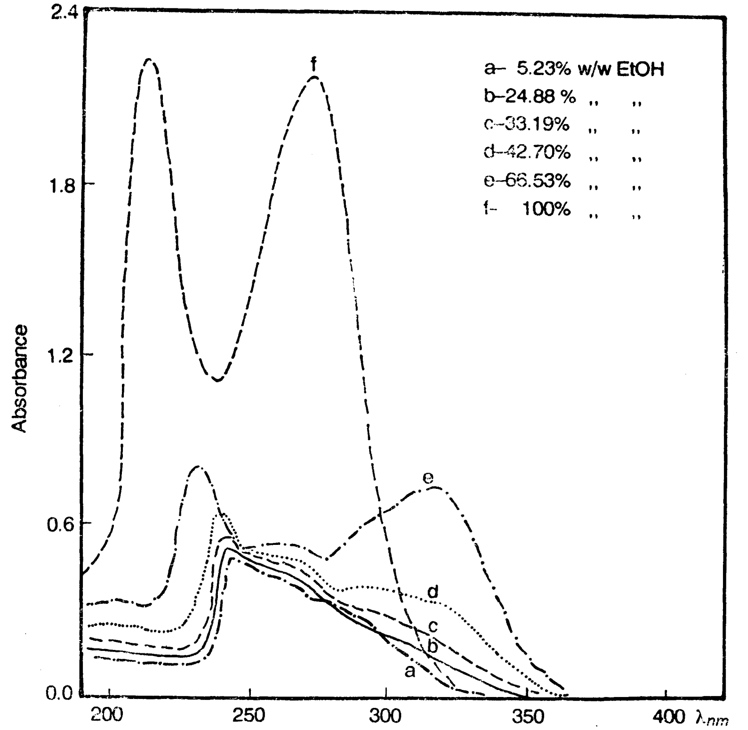


Fig. 1. Electronic spectra of compound (III), 1×10⁻⁴ M, in CCl₄-EtOH mixtures.

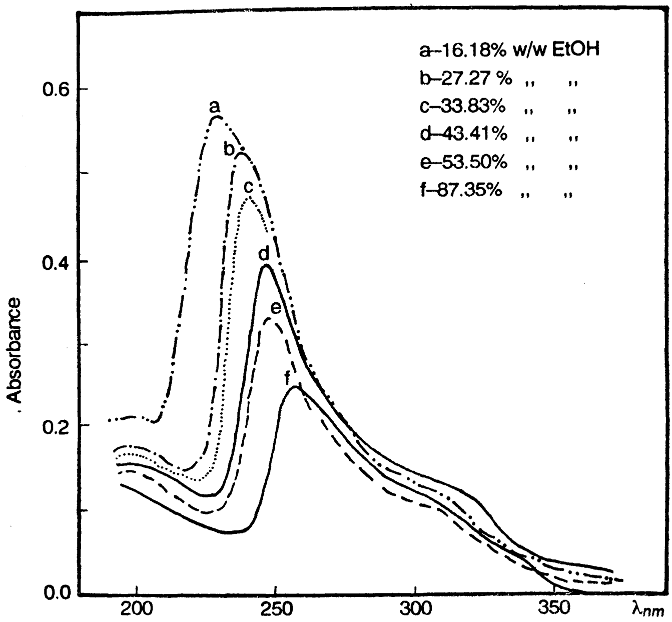


Fig. 2. Electronic spectra of compound (III), 1 × 10⁻⁴ M, in dioxane-EtOH mixtures.

The data presented in Table 1 show that the energy of formation lies near the lower limits for H-bond energy and the molecular complexes have stoichiometric ratios 1 : 1, 1 : 2 or 1 : 3 (solute : solvent) depending on the type of mixed solvent.

TABLE 1

VALUES OF FORMATION CONSTANT (K_f) AND FREE ENERGY (ΔG, Kcal) FOR THE DIFFERENT SOLVATED COMPLEX OF COMPOUNDS (III) AND (IV)

System	n	log K_f	K_f	$-\Delta G_{25}O$
III-EtOH-dioxane	1.60	1.89	77.27	2.560
III-EtOH-CCl_4	1.44	1.43	26.92	1.943
III-EtOH-ether	1.70	1.33	21.38	1.802
III-DMF-dioxane	1.60	1.25	17.78	1.695
III-Ether-CCl_4	2.30	1.44	27.35	1.950
IV-EtOH-CCl_4	1.27	1.27	18.62	1.726
IV-EtOH-$CHCl_3$	2.86	2.23	169.82	3.03
IV-DMF-EtOH	0.90	0.54	3.47	0.734
IV-DMF-CCl_4	1.50	0.56	3.59	0.755
IV-DMF-$CHCl_3$	2.07	1.86	72.44	2.530

It is worthy to mention that compound (III) behaves differently in ether-ethanol mixture (Fig. 3). On increasing the ethanol proportions in the mixture, the absorbance increases with red shift denoting the formation of molecular complex through portion donation from the solute molecule to ethanol. The red shift can be explained on the basis of increased dipole moment of solvent molecules[10] which leads to increase solvent stabilization of the polar excited state. Thus, the energy gap between ground and excited states decreased.

On the other hand, the absorption spectra of compound (IV) in C_2H_5OH-CCl_4 mixture (Fig. 4) show an increase in the band intensity as the proportion of CCl_4 in the medium is increased in contorary to the other compounds, the origin of which is not clear. Moreover, the spectra are characterized by an isobestic point denoting the existing of an equilibrium between the free and complex forms.

Following the relation of Gati and Szalay[11],

$$\Delta\bar{\nu} = (a - b)\left(\frac{n^2 - 1}{2n^2 + 1}\right) + b\left(\frac{D - 1}{D + 1}\right)$$

in which a and b are constants; n is the refractive index of the medium and D is the dielectric constant, one can explain the effect of the medium on band shift $\Delta\bar{\nu}$. On plotting $\Delta\bar{\nu}$ as a function of $(D-1)/(D+1)$, a non-linear relation is obtained indicating that frequency shift is governed by other factors beside the dielectric properties and the solvation energy of the medium. These factors include solute-solvent interaction via hydrogen bonding leading to the formation of some molecular complexes.

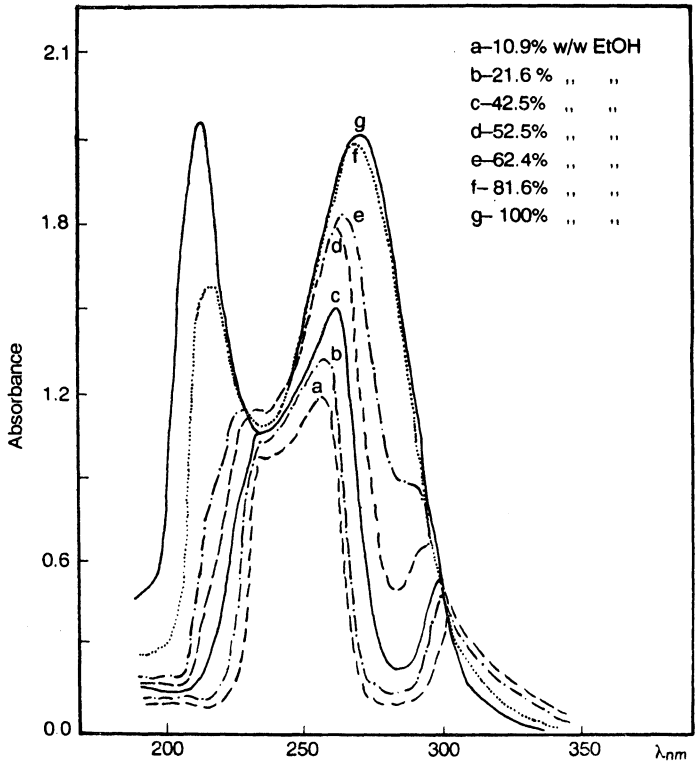


Fig. 3. Electronic spectra of compound (III), 1×10^{-4} M, in ether-EtOH mixtures.

Examination of the results in Table 1 and correlate them with the pK_a values of the investigated compounds, one can relate the tendency for molecular complex formation to the proton donor character of solute, *i.e.* its acid-base properities. Thus, compound (IV) which exhibits higher pK_a compared to the other compounds forms molecular complexes of lower stability constants.

Effects of Organic Solvents on pK_a Values

The results obtained in Table 2 show that the pK_a values in aqueous organic solvents containing higher percentage of water are higher than

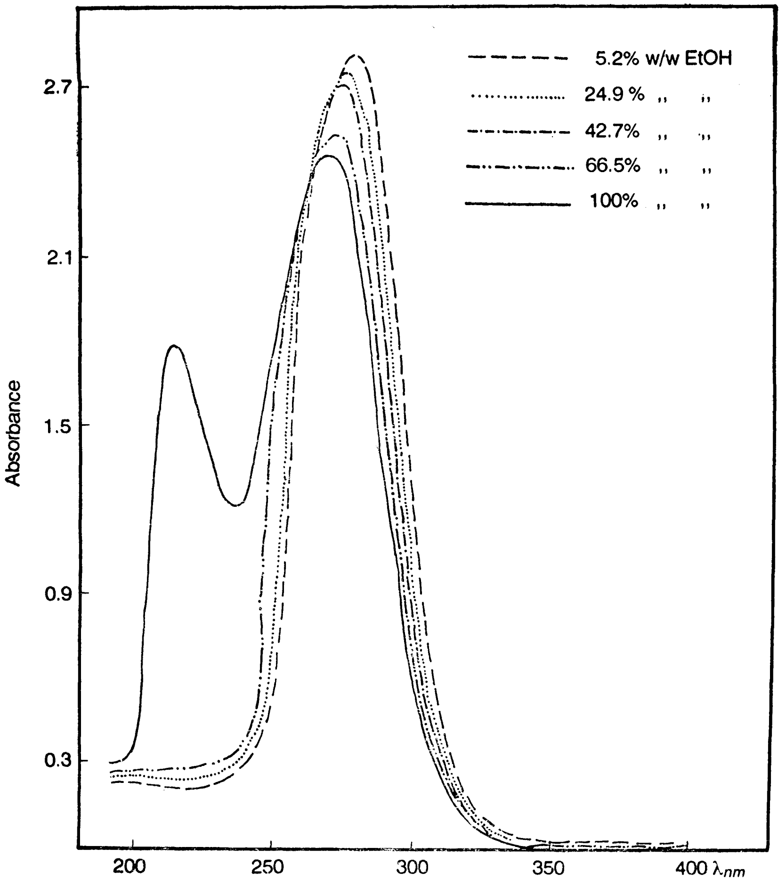


Fig. 4. Electronic spectra of compound (IV), 1×10^{-4} M, in CCl_4-EtOH mixtures.

TABLE 2

MEANS VALUES OF pK_{a1} AND pK_{a2} FOR MONOPHOSPHAZENES IN AQUEOUS-ORGANIC SOLVENTS

Solvent	I		II		III		IV	
	pK_{a1}	pK_{a2}	pK_{a1}	pK_{a2}	pK_{a1}	pK_{a2}	pK_{a1}	pK_{a2}
Dioxane	4.35	8.70	4.50	7.50	4.12	8.75	4.28	8.80
EtOH	4.25	8.10	4.12	8.23	4.30	8.25	4.21	8.38
DMSO	3.35	7.10	3.65	8.35	3.60	8.85	4.15	8.65
DMF	3.30	7.40	3.50	8.11	3.70	8.40	4.20	8.25

those obtained in higher percentage of organic solvents which thus favour ionization of monophosphazene compounds. The dissociation of the imino group (-NH) adjacent to the thioketone group (-C=S) is facilitated by increasing the concentration of ethanol or dioxane decreases ionization. The increased ionization in the case of the former solvents may be interpreted on the basis that they act as proton acceptors rather than donors, leading to an easier hydrogen releasing from the imino groups. On other hand, the decrease in ionization in presence of high concentration of ethanol or dioxane can be ascribed to the blocking of the n-electrons of the -C=S groups by the solvent molecules which render the excitation of the n-electrons more difficult resulting in higher pK_a values.

The variation in pK_a values with the different solvent concentration is listed in Table 3 (Fig. 5). It is clear that the data are in concordant with the dielectric constant (D) of the medium. On plotting pK_a values

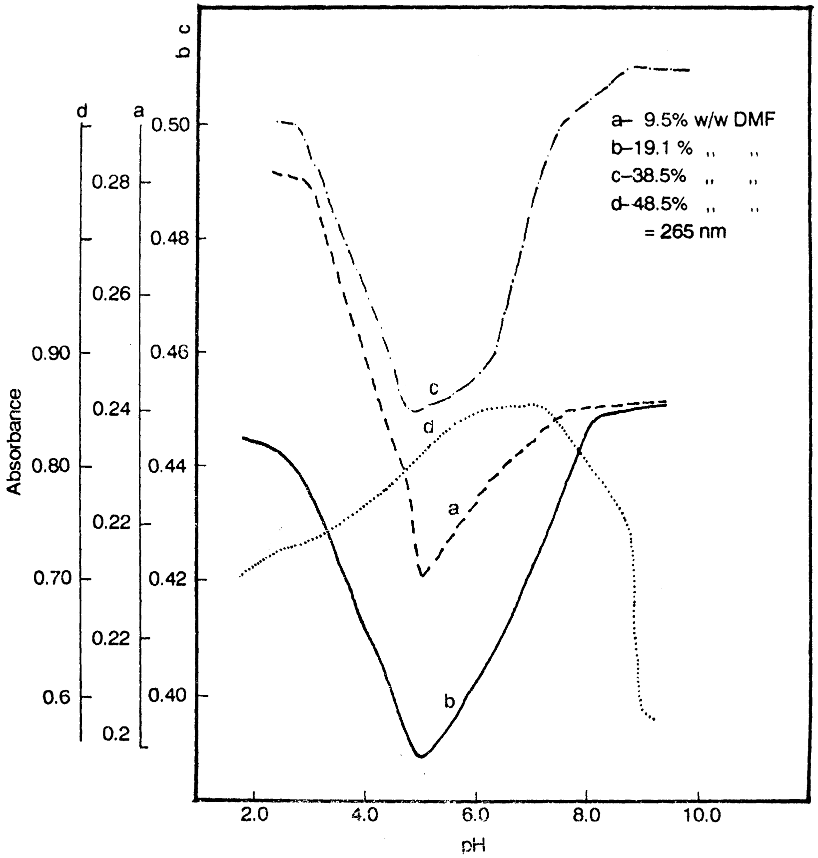


Fig. 5. Absorbance-pH plots of compound (IV), 2×10^{-5} M, at different percentage of DMF.

TABLE 3

MEAN VALUE OF pK_{a1} AND pK_{a2} FOR COMPOUND (IV) IN AQUEOUS-DMF MIXTURES

%(w/w) of DMF	D	pK_{a1}	pK_{a2}
9.50%	73.96	4.20	8.43
19.03%	69.92	3.80	8.65
38.50%	61.84	3.75	8.78
48.50%	57.80	3.70	8.90

against 1/D of the medium, a non-linear relationship is obtained referring that the changes in pK_a with solvent concentration, though governed by the dielectric constant, are influenced by solvent basicities also.

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