

INTERMOLECULAR INTERACTIONS
IN DIPOLAR BINARY SOLUTIONS*

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Universal and specific interactions can act in the binary solutions with polar components. The theories regarding the solvent influence on the electronic absorption spectra take into consideration only the universal interactions and express the spectral shifts as function of the solvent refractive index and electric permittivity. In this paper a method for the separation of the specific interactions supply is proposed in the case of proton-acceptor spectrally active molecules solved in protic solvents.

Key words: Pyridinium ylides, intermolecular interactions.

1. INTRODUCTION

The reduced number of methods devoted to the study of the intermolecular forces in liquid state is determined by the fact that the thermal motion energy is comparable to the potential energy and thus, the thermal motion does not allow the existence of stable, ordered systems into liquids. The spectral method for the study of the intermolecular interactions in liquid state is one of the few methods that offer information on the local reactive field into liquids [1, 2]. They permit to register the average energy of interaction between a spectrally active molecule and the rest of solution.

The spectral shifts registered by passing the spectrally active molecules from the gaseous state to liquid solutions of are dependent on the difference between the solvation energies of this molecule in its electronic state participating to the electronic transition [3–7] responsible for the spectral band appearance.

The spectral modifications can be discrete or continuous. The discrete modifications imply the appearance of new bands due to the specific interactions, such as hydrogen bond formation. The continuous modification of the electronic band position when one electric or optic parameter modifies, is due to the global action of the rest of solution on the spectrally active molecule [7].

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The appearance of the electronic spectra is due to the rapid rearrangement of the valence electronic cloud, which is very sensitive to the external fields acting on the molecules. So, the spectral continuous shifts measured in the electronic spectra give information about the global action of the solvent on the valence electronic cloud. Discrete modifications of the spectra in the optical range usually reflect only local, specific interactions.

The chemical shifts can show whether the complex formation between the solvent molecules influences the frequency in the molecular spectra, especially when the analysed molecules are proton acceptors, as is the case of cycloimmonium ylids.

Cycloimmonium ylids [8, 9] are amphionic compounds having separated opposite charges in the molecule. The nitrogen atom is positively charged, while the ylide carbon is negatively charged.

In pyridinium ylids [10–13], the nitrogen atom from the heterocycle is bound to the carbanion, which can be mono- or di-substituted (Fig. 1 a and b). The corresponding compounds are named carbanion mono- and di-substituted ylids.

The carbanion di-substituted pyridinium ylids are characterized by a high degree of electronic charge delocalization along the carbanion substitutes (Fig. 2a), which is a function of the substitutes' electronegativity [2]. The positive charge can be also delocalized on the heterocycle, as Fig. 2b shows. The carbanion di-substituted pyridinium ylids are more polar than the monosubstituted ones [1, 2].



Fig. 1 – Carbanion monosubstituted (a) and disubstituted (b) cycloimmonium ylids.

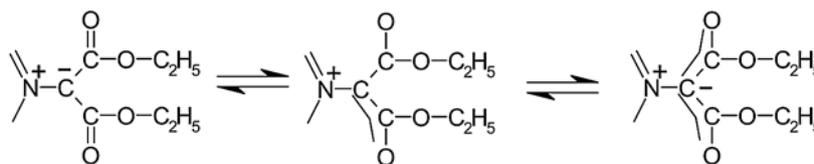


Fig. 2a – Negative charge delocalization on the carbanion of cycloimmonium dicarboethoxy methylid.

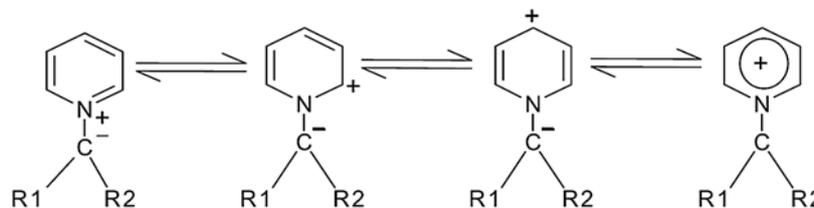
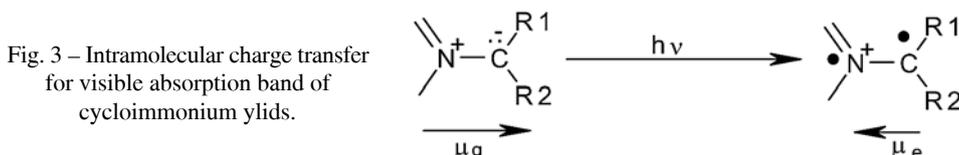


Fig. 2b – Positive charge delocalization on the pyridinium cation.

The visible radiations determine an electronic transfer [14–17] from the carbanion through the heterocycle, decreasing the dipole moment of the ylide molecule (Fig. 3).



The visible electronic absorption band of pyridinium ylides that appears by charge transfer [14, 15] between the carbanion and the heterocycle is shifted to blue in the protic solvent [14, 17]. The bigger the spectral shifts, the stronger intermolecular interactions are [17, 18].

In a non-polar solvent the dipolar molecules of pyridinium ylides interact by induction and dispersive forces, while in the protic solvents supplementary specific interactions appear between OH or NH of the solvent and the ylide carbanion [17, 18]. When the molecules of pyridinium ylides are in the excited state, their dipole moment diminishes considerably and the strength of the intermolecular interactions is increased; the hydrogen bonds are easily destroyed by thermal motion. The universal interactions are also very weak in the excited state of the ylide.

In this paper we intend to separate the contribution of the universal and specific interactions from the global spectral shifts, measured by passing from the gaseous state into liquid solutions of the pyridinium ylide.

2. EXPERIMENTAL

The electronic absorption spectra of three pyridinium-ylides in various solvents were recorded at a Specord UV VIS Carl Zeiss Jena spectrophotometer having a data acquisition system. The data are reported in Table 1 where some solvent parameters are also included. The studied ylides were prepared by known methods [1, 2] and their purity has been checked by spectral means.

The studied pyridinium-ylides were (Fig. 2b):

I1 ($R_1 = -CO_2C_2H_5$; $R_2 = -CONHC_6H_5$) pyridinium carboethoxy-anilido-methylid

I2 ($R_1 = -CO_2C_2H_5$; $R_2 = -CO_2C_2H_5$) pyridinium di-carboethoxy-methylid

I3 ($R_1 = -CO_2C_2H_5$; $R_2 = -COC_6H_5$) pyridinium carboethoxy-benzoyl-methylid

The solvents were purified by known methods.

In Table 1 there are listed the wavenumbers in the maximum of the visible band of the studied ylides, the solvent function $\frac{\epsilon - 1}{\epsilon + 2}$ and the empirical polarities [10–12] of the solvents, defined by Kosower.

Table 1

Wavenumber (cm^{-1}) in the maximum of the visible ICT band of the studied pyridinium ylides; solvent function and empirical polarities of the solvents

Nr.	Solvent	ν [cm^{-1}]			$\frac{\epsilon - 1}{\epsilon + 2}$	Z [kcal/mol]
		I_1	I_2	I_3		
1	Benzene	21900	22550	23400	0.005	59.0
2	Toluene	22050	22270	23750	0.017	59.3
3	Chloro-benzene	22210	22950	23930	0.290	59.1
4	Acetone	23240	23450	24480	0.646	65.5
5	N-butyl-alcohol	23960	24550	25980	0.591	77.7
6	iso-butyl-alcohol	23790	24700	26300	0.612	80.6
7	N-propyl-alcohol	23980	24950	26450	0.632	78.3
8	iso-propyl-alcohol	24000	25000	25750	0.612	76.3
9	Ethanol	24400	24970	26760	0.674	79.6
10	Methanol	24400	25230	27500	0.706	83.6

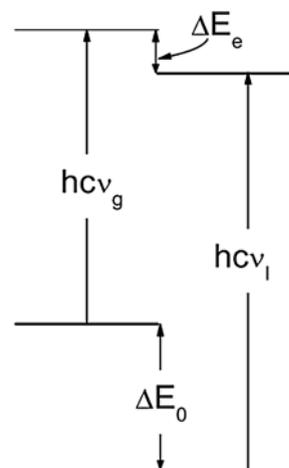
3. RESULTS AND DISCUSSIONS

From Table 1 it results that by passing from non-protic solvents to the protic ones, a supplementary spectral shift determines the increase in the wavenumber of the maximum of the pyridinium ylides' intramolecular charge transfer band. This fact has been explained by the specific interactions between the OH group of the protic solvents and the ylide carbanion, negatively charged in the ground electronic state of the ylide. The hydrogen bond formation determines a greater electronic charge delocalization and an increase in the molecular dipole moment of the ylide in its ground electronic state. The visible band appearance induces an electronic charge transfer from the carbanion towards the heterocycle, decreasing the molecular dipole moment in the excited state of the ylide. So, the total energy of the intermolecular interactions between the ylide molecule and the solvent is greater in the ground state compared with the excited one and the visible band shifts towards blue when the spectrally active molecule passes from the non-polar to polar solvents or from the non-protic to protic ones. Fig. 4 illustrates this assumption.

Relation (1) can be used in order to estimate the contribution of each type of interaction to the total spectral shift, by passing from the gaseous phase to the liquid solution, measured in the visible range.

In relation (1), ν_l and ν_0 signify the wavenumbers in the maximum of the ylide visible band measured in a given solvent characterized by electric permittivity ϵ , respectively in its gaseous state; C_i ; $i = 1, 2$ are regression coefficients and

Fig. 4 – Solvation energies and the spectral shift by passing from gaseous state (g) to solution (s).



$\delta(ppm)$ is the chemical shift of OH group, measured in the 1H NMR spectrum of the pure protic solvent. The last parameter becomes null for the aprotic solvents

Relation (1) can be used in order to estimate the contribution of each type of interaction to the total spectral shift, by passing from the gaseous phase to the liquid solution, measured in the visible range.

$$\nu_l = \nu_0 + C_1 \cdot \frac{\varepsilon - 1}{\varepsilon + 1} + C_2 \cdot \delta(ppm) \quad (1)$$

In relation (1), ν_l and ν_0 signify the wavenumbers in the maximum of the ylide visible band measured in a given solvent characterized by electric permittivity ε , respectively in its gaseous state; C_i ; $i = 1, 2$ are regression coefficients and $\delta(ppm)$ is the chemical shift of OH group, measured in the 1H NMR spectrum of the pure protic solvent. The last parameter becomes null for the aprotic solvents.

Table 2

Regression coefficients from formula (1)

Nr.	Ylide	ν_0 [cm^{-1}]	C_1 [cm^{-1}]	C_2 [cm^{-1}]	R
1	I_1	21180	2261	176	0.974
2	I_2	21767	2011	253	0.986
3	I_3	23022	1669	351	0.988

By using the data from Table 1, the regression coefficients ν_0 [cm^{-1}] and C_i ; $i = 1, 2$ were statistically [19] determined on the bases of the ν_l , ε and $\delta(ppm)$ experimentally estimated. The products: $C_1 \cdot \frac{\varepsilon - 1}{\varepsilon + 1}$ and $C_1 \cdot \delta(ppm)$ give the contributions of the dipolar-orientation and specific interactions, respectively.

The contributions of the intermolecular interactions specified above are listed in Table 3.

Table 3

Percentage of the universal $\Delta v_{univ.}$ and specific $\Delta v_{sp.}$ interactions supply to the total spectral shift in the aprotic and protic solvents

Nr	Solvent	I_1		I_2		I_3	
		$\Delta v_{univ.}$	$\Delta v_{sp.}$	$\Delta v_{univ.}$	$\Delta v_{sp.}$	$\Delta v_{univ.}$	$\Delta v_{sp.}$
1	Benzene	100	0	100	0	100	0
2	Acetone	100	0	100	0	100	0
3	Ethanol	35	65	57	43	45	55
4	Methanol	34	66	59	41	47	53

From a theoretical point of view, the data in Table 3 refer to the difference between the solvation energies of the ylide (as a spectrally active molecule) in a given solvent in its electronic states participating to the charge transfer transition, responsible for the electronic band appearance. By the charge transfer process the molecular electric dipole moment decreases (Fig. 3). So, the strength of the orientation interactions of the ylide in its ground state could be considered as being higher than those in the excited state.

From Table 3 it results that the aprotic solvents interactions with the ylide molecules are only of the orientation type, while in the protic solvent the supply of the specific interactions become significant. Ylides I_1 and I_3 strongly interact with the protic solvents while in the case of dicarboethoxy-pyridinium methylide with a symmetric carbanion, the percentage of the specific interactions in alcohols is smaller than 45%.

4. CONCLUSIONS

In the solutions, pyridinium ylides participate to universal interactions, which are predominant in the aprotic solvents. Specific interactions take place in the protic solvents whose strength is determined by the degree of delocalization of the electronic charges on the two partners participating to the intermolecular charge transfer.

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