



## Solvatochromic effects in the UV/vis absorption spectra of some pyridazinium ylides

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### ARTICLE INFO

#### Article history:

Received 18 January 2011

Received in revised form 15 July 2011

Accepted 18 July 2011

#### Keywords:

Electronic absorption spectra

Solvent effects

Pyridazinium ylides

Solvatochromism

### ABSTRACT

Solvatochromic behavior of some carbanion monosubstituted and disubstituted pyridazinium ylides was studied experimentally in various polar and nonpolar solvents. Different solvent parameters, such as microscopic solvent polarity,  $E_T(30)$ , the Kamlet–Taft and the Catalan parameters have been used for describing the solute–solvent interactions and solvatochromic shifts of the visible intramolecular charge transfer (ICT) absorption band of pyridazinium ylides. It is found that the solute hydrogen bond donating ability and dipolarity/polarizability play an important role in the description of the pronounced solvatochromism in the studied solutions. The Catalan solvent scales are found to be the most suitable for describing the solvatochromic shifts.

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### 1. Introduction

Pyridazinium ylides are zwitterionic compounds belonging to the cycloimmonium ylide class. Generally, studies on stable cycloimmonium ylides are interesting from several points of view, such as their applications as analytical reagents [1,2], semiconducting materials [2–4] or compounds with antimicrobial and antifungal action and as acid–basic indicators by their specific color. The pyridazinium derivatives can be used in optical switching and imaging techniques [5]. On the other hand, the carbanion monosubstituted pyridazinium ylides due to their low stability [6] comparatively with the carbanion disubstituted ones are widely used as intermediates in organic synthesis [7–9]. For example, in recent years some cycloimmonium ylides were utilized as intermediates for synthesis of new condensed pyridazine derivatives with a large variety of biological activities [10] and for synthesis of new 1,2-diazine nanomaterials with highly fluorescent properties [11,12].

Solvents influence the reaction rates, the equilibria, and the mechanisms for many compounds. Major interests to explain many processes and applications in this field assume to understand solute–solvent interactions and measure them quantitatively. The UV/vis absorption spectroscopy is the widely used method for investigating the intermolecular interactions and solvatochromism. Usually, the electronic absorption band characteristics are strongly sensitive to the structure of the ylides

(carbanion substituents and type of the heterocycle [13]) and also to the solvent nature [14].

The aim of the present paper is to investigate the solvent nature influence on the electronic absorption spectra of some pyridazinium ylides. The  $E_T(30)$  polarity scale and the multiparameter Kamlet–Taft and Catalan solvent scales were used in order to describe the spectral changes. The chemical structures of the studied monosubstituted and disubstituted carbanion pyridazinium ylides (PY1–PY4) having common heterocycle and variable carbanion substituents (Table 1) as well as the bromide of nitrophenacyl pyridazinium (PS) are shown in Fig. 1.

The visible absorption band of pyridazinium ylides appears due to an intramolecular charge transfer (ICT) from the carbanion towards the heterocycle [6]. This attribution of the visible absorption band of cycloimmonium ylides is due to its characteristics: shifts towards blue in polar solvents; disappears in acid medium; has a low intensity [2,6].

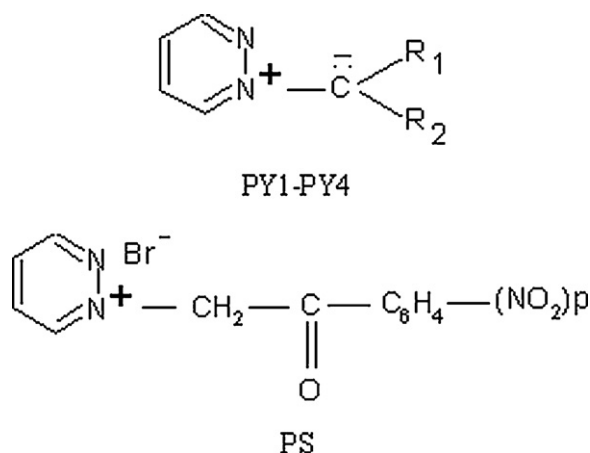
The ICT mechanism induces the decrease of the electric dipole moment of pyridazinium ylides. Consequently the ICT visible band shifts to blue when the solute passes from a nonpolar to a polar solvent or from an aprotic to a protic solvent. The high solvatochromism in the protic solvents can be explained [15] by specific interactions between the ylide carbanion and the –OH or –NH groups of the protic solvents.

### 2. Experimental

Pyridazinium ylides were prepared by salt method [16–18]. A SPECORD M42 UV/vis spectrophotometer equipped with 10 mm path length quartz cells was used to record absorption spectra

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**Fig. 1.** General chemical structure of pyridazinium ylides and the bromide of nitrophenacyl pyridazinium (PS).

**Table 1**  
Substituents of pyridazinium ylides.

Pyridazinium ylide	R <sub>1</sub>	R <sub>2</sub>
PY1	-H	-CO-C <sub>6</sub> H <sub>4</sub> -C <sub>6</sub> H <sub>5</sub>
PY2	-H	-CO-C <sub>6</sub> H <sub>4</sub> -(NO <sub>2</sub> ) <sub>p</sub>
PY3	-CO-C <sub>6</sub> H <sub>4</sub> -(NO <sub>2</sub> ) <sub>p</sub>	-CO-NH-C <sub>6</sub> H <sub>5</sub>
PY4	-CO-C <sub>6</sub> H <sub>4</sub> -(NO <sub>2</sub> ) <sub>p</sub>	-CO-NH-C <sub>6</sub> H <sub>4</sub> -(Cl) <sub>p</sub>

at room temperature. All solvents were purchased in the highest available grade and spectral purity. The absorption spectra were measured in  $\lambda$  (nm) and the wavenumbers ( $\text{cm}^{-1}$ ) were calculated by relation  $\nu = 1/\lambda$  ( $\text{cm}^{-1}$ ). The values in the maxima of the electronic absorption bands have been established according to the Instrument Software.

Physical characteristics of the solvents including the Kamlet-Taft solvatochromic parameters  $\alpha$ ,  $\beta$  and  $\pi^*$  were taken from Refs. [19–21], whereas the Catalan SP, SdP, SA and SB solvent from [20,22–26] and microscopic solvent polarity,  $E_T(30)$  from [20].

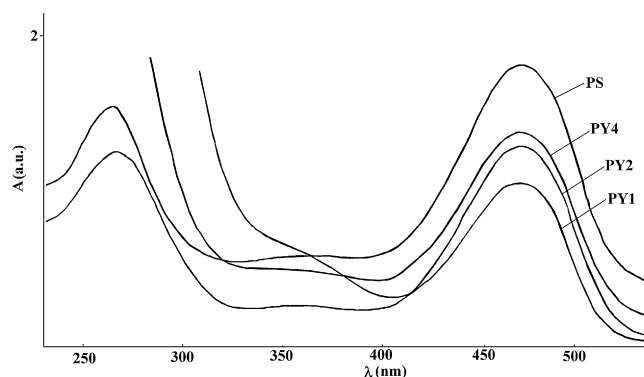
The multiple regression analysis of the UV/vis absorption maxima was carried out with the Origin 6.0 statistic program.

**Table 2**  
UV/vis absorption maxima,  $10^{-3}\tilde{\nu}_{\text{max}}$  ( $\text{cm}^{-1}$ ) for pyridazinium ylides.

No.	Solvent	PY1	PY2	PY3	PY4	PS
1.	Cyclohexane	21.11	19.90	<sup>a</sup>	19.92	<sup>a</sup>
2.	Toluene	21.16	20.10	19.80	20.14	20.04
3.	Diethyl ether	21.27	20.30	20.22	20.28	<sup>a</sup>
4.	Chloroform	21.14	20.72	20.32	20.63	20.66
5.	Butyl acetate	21.27	20.44	20.61	20.53	20.57
6.	Ethyl acetate	21.36	20.66	20.81	20.74	20.70
7.	THF	21.29	20.34	20.74	20.55	20.53
8.	DCE	21.25	20.83	20.61	20.79	<sup>a</sup>
9.	1-Pentanol	21.32	21.18	22.00	21.23	21.20
10.	1-Butanol	21.43	21.25	21.97	21.25	21.29
11.	Isobutanol	21.52	21.32	22.02	21.29	21.32
12.	2-Butanone	21.52	20.79	21.27	20.89	21.27
13.	2-Propanol	21.45	21.25	21.95	21.27	21.29
14.	1-Propanol	21.48	21.36	22.14	21.34	21.39
15.	Acetone	21.41	20.83	21.50	20.98	20.87
16.	Ethanol	21.52	21.41	22.47	21.48	21.45
17.	Methanol	21.66	21.64	22.70	21.71	21.66
18.	DMF	21.14	20.70	21.78	20.83	20.74
19.	Acetonitrile	21.32	20.94	21.55	21.03	21.00
20.	DMSO	21.16	20.70	21.97	20.87	20.68
	$\Delta\tilde{\nu}$ [ $\text{cm}^{-1}$ ]	526.8	1544.5	2899.5	1574.6	1628.3

Abbreviations: THF, tetrahydrofuran; DCE, 1,2-dichloroethane; DMF, N,N-dimethyl formamide; DMSO, dimethyl sulfoxide.

<sup>a</sup> Samples are insoluble.



**Fig. 2.** UV/vis absorption spectra of pyridazinium ylides in ethanol.

### 3. Results and discussion

#### 3.1. Solvent effects on the UV/vis absorption spectra

The electronic absorption spectra of pyridazinium ylides have been measured at room temperature in twenty solvents. Spectral data of these compounds are collected in Table 2 for different organic solvents. Typical UV/vis absorption spectra of pyridazinium ylides under study in ethanol are displayed in Fig. 2.

The UV absorption bands of pyridazinium ylides were attributed to  $\pi-\pi^*$  transitions [15,27] due to their high intensity. The visible ICT bands due to an  $n-\pi^*$  transition were studied in this paper.

Listed in Tables 3 and 4 are the physical properties of the solvents utilized: empirical polarity parameters  $\pi^*$ ,  $\alpha$ ,  $\beta$ , SP, SdP, SA, SB as well as  $E_T(30)$ . The solvents are arranged with increasing their dielectric constant.

The pyridazinium ylides exhibit two absorption bands in the wavelength regions 445–475 and 260–275 nm, respectively (ethanol). The longer wavelength visible absorption band can be assigned to a  $n-\pi^*$  transition due to the electron intramolecular charge transfer from ylid carbanion to heterocycle [6,15,27].

As the solvent polarity increases from cyclohexane to DMSO, the electronic absorption spectra of PY1–PY4 and bromide of nitrophenacyl pyridazinium (PS) exhibit a significant hypsochromic shift in the visible range (Table 2). For PY3, it is between

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