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SOLVENT EMPIRICAL SCALES
FOR ELECTRONIC ABSORPTION SPECTRA

Linear correlation between the E_{max} (kcal/mol) of the visible electronic absorption band of four pyridazinium ylids and the empirical polarities Z (kcal/mol) defined by Kosower are established, proving the intramolecular charge transfer nature of this band. The slopes of the lines are smaller for the carbanion monosubstituted ylids, compared with those of the carbanion disubstituted ylids. This fact emphasizes the prevalence of the dipolar interactions in ylid solutions.

The blue shifts recorded in the protic solvents suggest the hydrogen bond formation between the –OH of these solvents and the ylid carbanion.

A linear dependence exists between the values of E_{max} (kcal/mol) recorded for two studied ylids. This fact demonstrates that the solvents can be arranged on the empirical scale describing their action on similar chemical compounds, in which electronic transitions of the same nature take place.

K e y w o r d s: electronic absorption spectra, ylids, 1-ethyl-4-carbomethoxy-pyridinium iodide.

1. Introduction

When a spectrally active molecule passes from the gaseous to condensed phase, it supports the global action of the neighboring molecules emphasized by changes in its spectral parameters (intensity or band position). The electronic (absorption or emission) spectra involving the valence molecular cloud are very sensitive to the global action of the condensed medium. The electronic spectra require very small concentrations (smaller than 10^{-3} mol/L) of the spectrally active molecules in solutions. So, they are surrounded only by solvent molecules, and the interactions between them are negligible. The interactions of spectrally active molecules with the solvent determine the spectral shifts proportional to the difference between the solvation energies in the electronic states participating in the transition producing the electron absorption (fluorescence) band.

The electronic bands measure the strength of the intermolecular interactions by their spectral shifts. Solvatochromic studies can provide information about the intermolecular interactions in a given solution [1, 2].

There are models [3–5] that describe the solvent influence on the electronic absorption and fluorescence spectra, but they have no general applicability, because the type and the strength of intermolecular interactions depend on the solvent electrooptical parameters, as well as on their capacity to realize charge transfer complexes with spectrally active molecules. Specific interactions are usually neglected in the existent theoretical models.

The long-range interactions in simple liquids are also dependent on the solvent nature. So, in a dipolar solvent, the orientation interactions will be predominant, while the dispersive interactions are more important in the nonpolar solvents. Significant deviations of the predicted spectral shifts by the existent theories compared with those experimentally estimated were obtained for various types of solute-solvent pairs [6–10].

The empirical scales of solvents were constructed in order to classify more easily the pure liquids by their action on the electronic absorption or fluorescence spectra.

The standard compound used by Kosower [11–16] for the empirical scale of solvents is 1-ethyl-4-carbomethoxy-pyridinium iodide (ECMPI) with a visible electronic absorption band very sensitive to the sol-

vent action. The mechanism of appearance of the visible band was explained by Kosower in Fig. 1, *a*. The arrangement of the solvent molecules arround the complex is suggested in Fig. 1, *b*.

The charge transfer from the iodide ion to the heterocycle determines changes in the orientation and the magnitude of dipole moment (Fig. 1, *a*).

According to the Franck–Condon principle [2, 3], the electron distribution duration in a transition is very quick, as compared with the relaxation time of a solvent. In the excited state, the dipole moment is perpendicular to the reactive electric field created by solvent molecules. Hence, the stabilization energy in the excited state of ECMPI complex is null. Kosower showed that the spectral shift of the electronic absorption band of the complex is determined only by the stabilization energy in the ground state of the complex [11].

2. Experimental

The electronic absorption spectra of pyridazinium ylids in binary and ternary solutions were recorded on a Specord UV VIS spectrophotometer (Carl Zeiss, Jena) with acquisition system. The accuracy of the wavenumber determination was of ± 50 cm^{-1}. The solvents used were of spectral grade or were purified through the known methods. The Z-values defined by Kosower are taken from the literature [11–16].

The used solvents were spectrally grade.

Pyridazinium ylids were prepared as indicated in [17], and their purity has been established by spectral (NMR and IR) means. The chemical structures of the studied compounds are given in Fig. 2 and Table 1.

3. Results and Discussion

The studied pyridazinium ylids are dipolar zwitterionic molecules [17–19], in which a carbanion is covalently bound to a pyridazinium derivative. These compouds were tested from their biological activity, showing a pharmaceutical potential [20–22]. From this point of view, the knowledge about the interactions of pyridazinium ylids with solvents is of great importance.

The studied spectrally active molecules have a visible absorption band very sensitive to the solvent nature. It shifts to blue, when the ylid passes from an aprotic to protic solvent or from a nonpolar to a polar solvent [18–19]. The disappearance of this band in
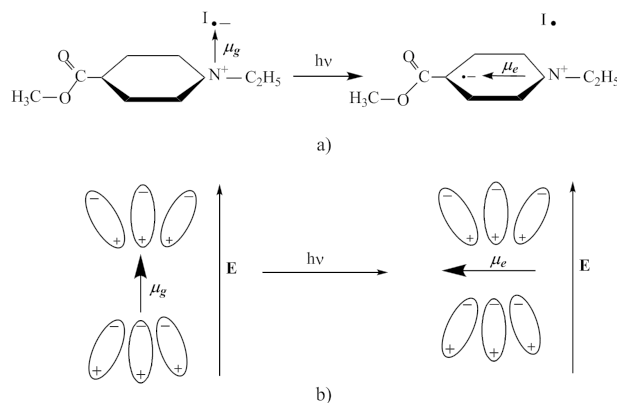

Fig. 1. Chemical structure and the intermolecular charge transfer mechanism in ECMPI complex (*a*); Solvent arrangement in the first solvation shell of complex ECMPI (*b*)
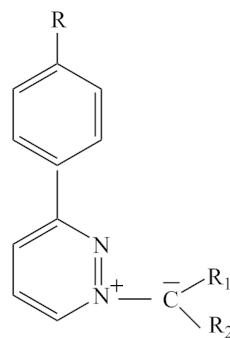

Fig. 2. Chemical structure of the studied compounds

acid media [17] is a proof of its charge transfer nature. When the ylid molecule absorbs a photon, a part of the electronic charge from the carbanion shifts toward the heterocycle. The intramolecular charge transfer (ICT) can diminish the molecular dipole moment or can even change its sense.

The mechanism of ICT transfer and the distribution of solvent molecules in the first solvation shell of pyridazinium ylids (in the electronic states responsible for the visible absorption band appearance) is suggested in Figs. 3, *a* and 3, *b*, respectively.

In the solvation process, the dipolar molecules of ylids orient the solvent molecules (having a permanent or induced dipole moment) in their electric field. The solvation energy in the ground state of ylid is proportional to the scalar product of the dipole moment of ylid and the solvent reactive electric field.

Solvent molecules' orientation remains unchanged in the excited state of pyridazinium ylid, while the

Table 1. **Substituents of the studied pyridazinium ylids**

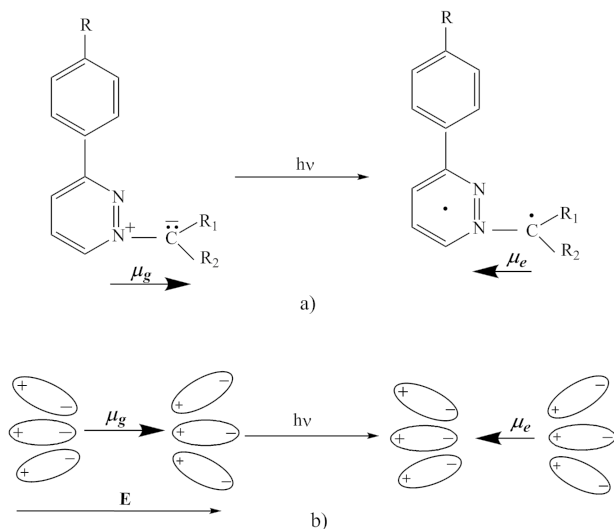| No.	Ylid	R	R_1	R_2	
1	Y_1	$-CH(CH_3)_2$	$-H$	$-COC_6H_4NO_2(p)$	p Cumyl-pyridazinium p nitrophenacylid
2	Y_2	$-H$	$-H$	$-COC_6H_4NO_2(p)$	p Phenyl-pyridazinium p nitrophenacylid
3	Y_3	$-CH(CH_3)_2$	$-COCH_3$	$-COC_6H_5$	p Cumyl-pyridazinium-acetyl-benzoyl methylid
4	Y_4	$-H$	$-COCH_3$	$-COC_6H_5$	p Phenyl-pyridazinium-acetyl-benzoyl methylid

Fig. 3. Chemical structure and intramolecular charge transfer mechanism of the studied pyridazinium ylids (*a*); Solvent arrangement in the first solvation shell of the studied ylids in their ground and excited states (*b*)

dipole moment of ylid can change its sense by excitation, becoming antiparallel with the dipole moment in the ground state of the ylid. The energy balance explains the shift to blue of the ylid ICT absorption band. This shift increases with the solvent polarity.

The variation of the empirical polarities is higher ($\Delta Z = 40$ kcal/mol) compared with the variation of the energy in the maximum of the ICT band of ylids ($\Delta E_{\max} = 10$ kcal/mol). This difference is due to the fact that, in Z, only the ECMPI complex solvation energy is contained in its ground state, while the values $E_{\max}$ (kcal/mol) contain the difference of the solvation energy in the electronic states responsible for the ICT band appearance.

A linear dependence exists between the energy in the maximum of the visible intramolecular charge transfer (ICT) band of pyridazinium ylids [6–9] and the empirical polarities defined by Kosower. The big-

ger the dipole moment of the studied zwitterionic compound, the higher the slope of the linear dependence. From this point of view, the empirical scales of solvents can be used as an indicator of the strength of the intermolecular interactions in a given solvent and as an indicator of the physical properties of the spectrally active molecules. The empirical scales of the solvents do not contribue to the intermolecular interaction mechanism elucidation, but constitue a rapid efficient method in establishing the strength of the solvent action on the molecular electronic cloud.

From the point of view of the solvite – solvent interactions, the visible ICT electronic band of the studied pyridazinium ylids is alike with the visible band of the ECMPI complex used by Kosower (Fig. 1) to define the empirical polarities of solvents.

The solvation energies of pyridazinium ylid molecules are bigger in the ground state, as compared with those in the excited state. Thus, the sense of the spectral shifts is the same for 1-ethyl-4-carbometho-xy-pyridinium iodide and for the ylids. The difference is that the energy of interaction of the standard substance in its excited state is near null, as compared with the pyridazinium ylids, whose energies in the excited states are smaller than those in ground state, but it is not equal to zero.

The possible spectral shifts in the solutions of pyridazinium ylids are suggested in Fig. 4, in which the relative positions of the electronic levels participating in the ICT transition in the gaseous phase and in solvents are drawn.

A linear dependence of type (1) between the wavenumber in the maximum of the intramolecular charge transfer band and the empirical polarities has been emphasized for the studied ylids.

$$E_{\max}(\text{kcal/mol}) = m \cdot Z(\text{kcal/mol}) + n. \qquad (1)$$

In (1), $E_{\max}$ is the energy in the maximum of the visible ICT band of pyridazinium ylids, and Z are

the empirical polarities defined by Kosower. In view of the chemical structures of the studied compounds, these dependences have different slopes.

If a proportionality factor is established between the values of wavenumbers in the maximum of the electron charge transfer bands and the empirical polarities, the pyridazinium ylids could be used in the empirical solvent scale enlargement as in [8, 9].

Having in view their action on the ICT electronic band of ECMPI and of pyridazinium ylids, the solvents could be listed in the way suggested by Table 2.

Some solvent mixtures with the empirical polarities measured by Kosower [11, 12] were also used in order to estimate their influence on the electronic absorption spectra of some cycloimmonium ylids. The values of the frequencies in the maximum of the ICT band, E_{max} (kcal/mol) of the pyridazinium ylids

Fig. 4. Spectral shifts determined by the changes in the magnitude and the orientation of dipole moments in the ground and excited states of a spectrally active molecule

studied in this paper are given in Table 3 for the ternary solutions.

The dependence of type (1) is illustrated in Fig. 5 for binary solutions of the studied ylids (see Table 2).

The same dependence (1) can be established for ternary solutions of the studied pyridazinium ylids in binary solvents Water + Acetone and Water + + Ethanol (see Fig. 6 and Table 3).

Table 2. **Solvent empirical polarities Z (kcal/mol) and energies in the maximum of the ICT visible band, E_{max} (kcal/mol), of the studied pyridazinium ylids**

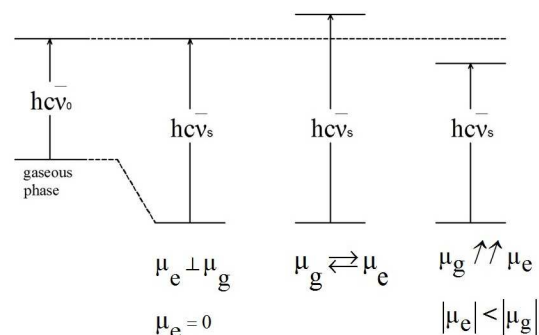| No.	Solvent	$Z \left(\frac{kcal}{mol}\right)$	Y_1	Y_2	Y_3	Y_4
1	Chlorbenzene	59.1	57.0	58.0	57.5	58.0
2	Ethylacetate	60.3	–	–	58.0	59.0
3	Anisol	60.6	56.9	57.2	57.7	–
4	Benzene	62.4	–	–	57.5	57.4
5	Chloroform	63.2	57.6	58.0	58.3	58.3
6	Dichlorethane	63.2	–	–	58.2	58.2
7	Pyridine	64.0	56.9	56.9	58.2	58.2
8	Dichlormethane	64.2	57.7	57.7	58.1	58.2
9	Iso-amyl acetate	64.4	57.8	57.9	57.7	58.0
10	Acetone	65.7	58.0	–	58.6	58.5
11	DMF	68.5	57.6	57.6	58.8	58.8
12	DMSO	71.1	57.8	57.5	59.2	59.2
13	Diaceton alcohol	74.7	58.9	58.9	60.5	60.7
14	Iso-propyl alcohol	76.3	59.4	59.2	61.8	61.1
15	N-buthyl alcohol	77.7	60.2	59.2	61.8	62.1
16	N-hexyl alcohol	78.2	59.2	59.0	61.5	61.5
17	N-proyl alcohol	78.3	59.6	59.4	61.8	61.5
18	N-octyl alcohol	79.1	59.2	59.1	61.5	61.5
19	N-amyl alcohol	79.4	59.6	59.2	61.5	61.5
20	Ethanol	79.6	60.0	59.7	62.1	62.1
21	Iso butyl alcohol	80.6	59.6	59.1	62.0	61.8
22	Formamide	81.0	59.6	59.0	63.5	63.5
23	N-benzyl alcohol	82.1	–	–	62.1	61.8
24	Methanol	83.6	–	–	63.5	63.0
25	Ethylene glycol	85.1	60.6	60.4	64.2	65.3

Table 3. **Empirical polarities Z (kcal/mol), energies in the maximum of the ICT visible band, E_{max} (kcal/mol), of pyridazinium ylids in binary solvent Water + Ethanol and Water + Acetone**

| Binary solvent	No.	c	$Z \left(\frac{kcal}{mol}\right)$	Y_1	Y_2	Y_3	Y_4
Ethanol	1	98.0	80.2	59.7	59.5	62.5	62.5
	2	96.9	80.8	60.0	59.7	62.7	62.5
	3	95.0	81.2	60.1	59.9	62.8	62.8
	4	92.0	82.0	60.2	60.1	62.9	63.1
	5	90.0	82.5	60.2	60.1	63.0	63.3
	6	85.0	83.8	60.3	60.3	63.5	63.6
	7	80.0	84.8	60.4	60.3	63.8	63.8
	8	75.0	85.7	60.6	60.4	64.2	64.1
	9	70.0	86.4	60.7	60.6	64.4	64.6
Acetone	1	99.0	68.1	58.3	58.4	58.9	59.9
	2	95.0	72.9	58.8	58.8	59.6	59.7
	3	93.0	74.8	58.9	59.1	60.0	60.1
	4	90.0	76.6	59.1	59.4	60.5	60.3
	5	85.0	78.8	59.7	59.6	61.0	61.5
	6	80.0	80.7	60.0	60.0	61.8	62.0
	7	75.0	82.1	60.3	60.2	62.5	62.4
	8	70.0	83.2	60.6	60.7	62.5	62.5
	9	65.0	84.3	60.9	60.8	63.2	62.8
	10	60.0	85.5	61.2	61.3	63.5	63.3
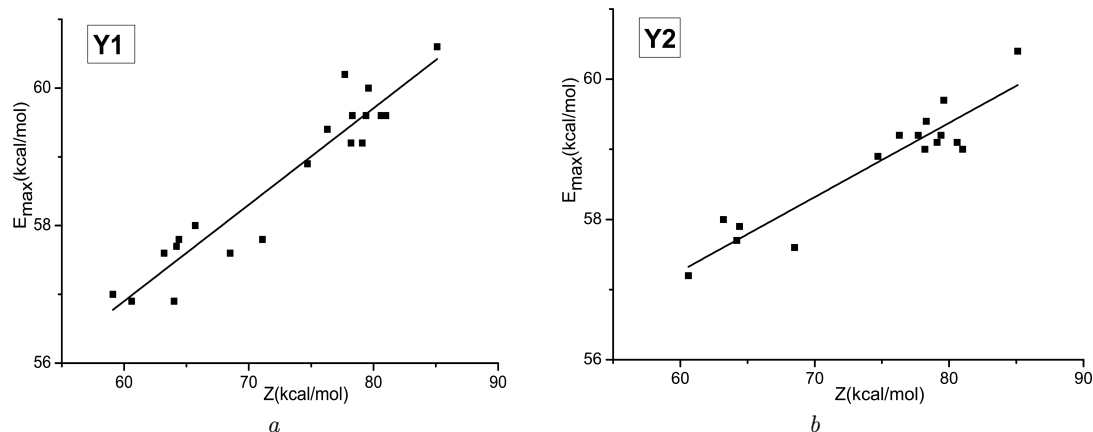
Fig. 5. E_{max} (kcal/mol) vs. Z (kcal/mol) for: *a*) Y_1 and *b*) Y_2 in binary solutions
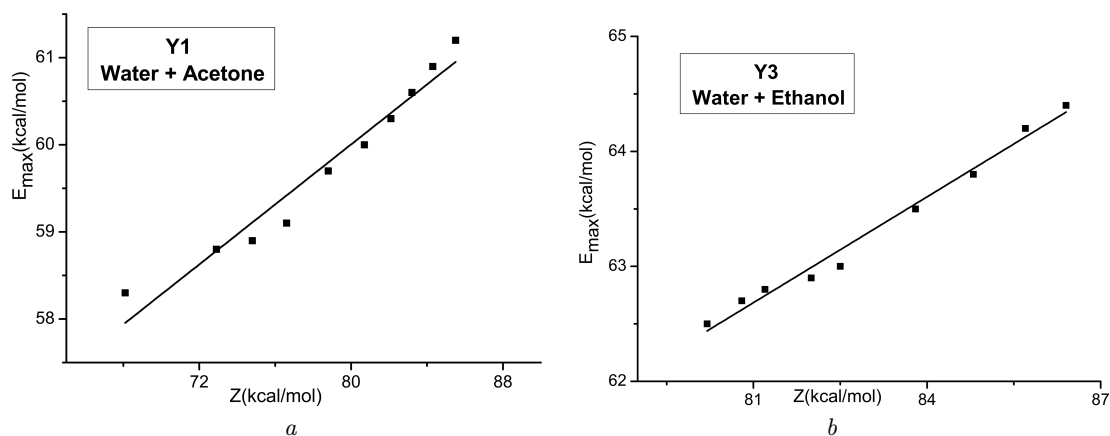

Fig. 6. E_{max} (kcal/mol) vs. Z (kcal/mol) for the studied pyridazinium ylids in ternary solutions: *a*) Water + Acetone + Ylid and *b*) Water + Ethanol + Ylid

Table 4. **Slope ($m \pm \Delta m$) and cut at the origin ($n \pm \Delta n$) of the lines $E_{max} = mZ + n$ for binary + ternary solutions of the studied pyridazinium ylids; R, linear regression coefficient; SD, standard deviation; N, number of points validated in statistics**

Ylid	$m + \Delta m$	$n \pm \Delta n$ (kcal/mol)	R	SD	N	Eliminated solvents
Y_1	0.1491 ± 0.0064	47.8929 ± 0.4942	0.93	0.307	39	2, 4, 6, 23, 24
Y_2	0.1343 ± 0.0077	49.0091 ± 0.6009	0.90	0.308	33	1, 2, 4, 6, 7, 10, 12, 21, 22, 23, 24
Y_3	0.2545 ± 0.0091	41.8078 ± 0.7013	0.94	0.503	44	–
Y_4	0.2497 ± 0.0106	42.1376 ± 0.8183	0.93	0.525	41	2, 3, 25

In Fig. 7, we plot all points corresponding to the binary and ternary solutions of pyridazinium ylids.

The slopes and cuts at the origin for all experimental points are listed in Table 4. The data of Table 4 illustrate a higher sensitivity of the carbanion disubstituted pyridazinium ylids to the solvent action. Ap-

propiate values of the slopes of linear dependences (1) are calculated for the pyridazinium ylids with common carbanion, Y_1 and Y_2, Y_3 and Y_4, respectively.

When an empirical scale is realized for a given substance, the solvents can be arranged on an empirical scale by the wave number in the maximum of the
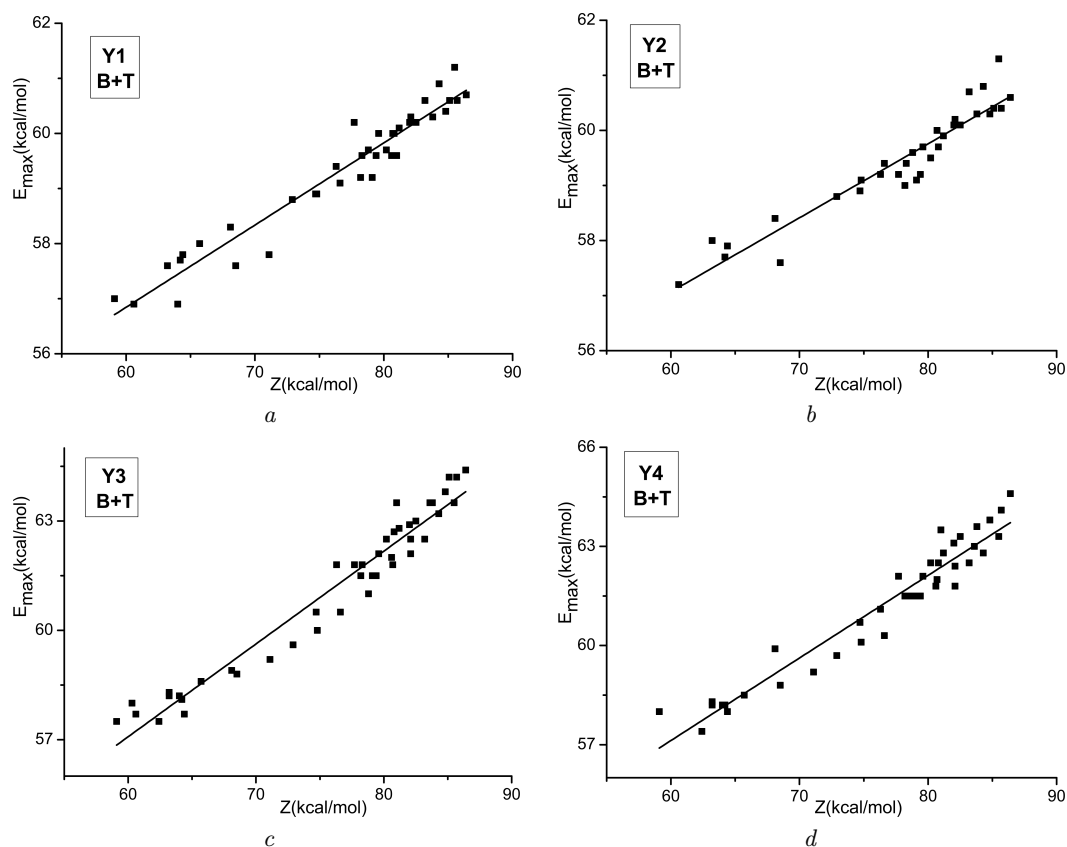
Fig. 7. E_{max} (kcal/mol) vs. Z (kcal/mol) for the studied pyridazinium ylids in binary(B) and ternary (T) solutions

electronic absorption band of this substance for indicating their similar action on the compounds with appropriate chemical structure.

It follows from the data of Table 4 that the slopes of lines (1) are smaller for the carbanion monosubstituted pyridazinium ylids Y_1 and Y_2, as compared with those for the carbanion disubstituted pyridazinium ylids Y_3 and Y_4. This fact demonstrates that the dipolar interactions are stronger in the last two pyridazinium ylids.

4. Conclusions

The empirical scales of solvents can be used in order to describe the solvent influence on the electronic absorption or fluorescence spectra of some related substances.

Being zwitterionic compounds and having an electronic absorption band with intramolecular charge transfer, pyridazinium ylids are very sensitive to the solvent action. The energies in the maximum of the ICT band of pyridazinium ylids linearly depend on the empirical solvent polarities defined by Kosower. As indicators of the intermolecular interactions strength in the studied solutions, the slopes of these dependences increase with the pyridazinium ylid permanent dipole moments.

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ЕМПІРИЧНІ МАСШТАБИ
РОЗЧИННИКА ДЛЯ ЕЛЕКТРОННИХ
СПЕКТРІВ ПОГЛИНАННЯ

Р е з ю м е

Лінійна залежність, встановлена між E_{max} (ккал/моль) електронної смуги поглинання у видимому діапазоні для чотирьох пірідазініум іліди та емпіричні полярності Z (ккал/моль), визначені косовером, показує, що ця електронна смуга пов'язана з внутрішньомолекулярним переносом заряду. Нахили ліній менші для карбаніон монозаміщених ілідів порівняно карбаніон ілідами, двічі заміщеними. Це підкреслює той факт, що біполярні взаємодії переважають в розчинах ілідів.

Спектральні зрушення в синю область в протонних розчинниках дозволяє говорити про формування водневих зв'язків між ОН-групи цих розчинників і карбаніон ілідів.

Існує лінійна залежність між значеннями E_{max} (ккал/моль) для двох вивчених ілідів. Це показує, що розчинники можуть бути розташовані в емпіричний масштаб відповідно з їх дією на хімічні сполуки, в яких відбуваються електронні переходи того самого типу.