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SOLVENT EFFECT ON ELECTRONIC ABSORPTION SPECTRA OF SOME *N*-ARYL SUBSTITUTED DODECANEAMIDES

PART II. POLAR APROTIC SOLVENTS

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The ultraviolet absorption spectra of nine *N*-aryl substituted dodecaneamides were recorded in eight polar aprotic solvents in the range from 200 nm to 400 nm. The effects of solvent polarity and hydrogen bonding on the absorption spectra, were interpreted by means of linear solvation energy relationships (*LSER*) using a general equation: $\tilde{\nu} = \tilde{\nu}_o + s\pi^* + a\alpha + b\beta$, and by two-parameter models presented by the equation: $\tilde{\nu} = \tilde{\nu}_o + s\pi^* + b\beta$. The mode of the influence of the polar aprotic solvents on the ultraviolet absorption spectra of the investigated dodecaneamides are discussed on the basis of the correlation results. These results were compared with the results obtained for the same dodecaneamides in polar protic solvents

Key words: *N*-aryl substituted dodecaneamides; ultraviolet absorption spectra; polar aprotic solvents; solvent effects; linear solvation energy relationships

ВЛИЈАНИЕ НА РАСТВОРУВАЧ НА ЕЛЕКТРОНСКИ АПСОРПЦИОНИ СПЕКТРИ НА НЕКОИ *N*-АРИЛ СУПСТИТУИРАНИ ДОДЕКАНАМИДИ

II ДЕЛ. ПОЛАРНИ АПРОТИЧНИ РАСТВОРУВАЧИ

Апсорпционите спектри на девет *N*-арил супституирани додеканамиди се снимени во осум поларни апротични растворувачи во подрачјето од 200 до 400 nm. Ефектите на поларноста на растворувачот и создавањето на водородни врски се проучувани со примена на методот на линеарна корелација на солватационите ефекти (*LSER*), користејќи ја тоталната солватохромна равенка ($\tilde{\nu} = \tilde{\nu}_o + s\pi^* + a\alpha + b\beta$) и двопараметарен модел ($\tilde{\nu} = \tilde{\nu}_o + s\pi^* + b\beta$). Влијанието на поларните апротични растворувачи на УВ апсорпционите спектри на испитуваните додеканамиди е дискутирано врз база на корелационите резултати. Овие резултати се споредени со резултатите добиени за истите додеканамиди во поларни протични растворувачи (претходно дискутирани).

Клучни зборови: *N*-арил супституирани додеканамиди; УВ спектри; поларни апротични растворувачи; ефекти на растворувачи; линеарна корелација на солватационите ефекти

INTRODUCTION

The amide is an important functional group present in a number of drugs moleculs. It is also the key linking moiety in proteins and peptide drug products. In addition, amides and fatty acid amides derivatives have different properties and have found wide use in various chemical industries [1–3]. The influence of solvents on electronic spectra [4–10] and on organic reactivity [11–16] has always been a point of particular interest to many researchers. Therefore, taking into consideration the importance and the practical application of amides, we consider that it is of interest to investigate the solvent effect on the UV spectra of some dodecaneamides.

In our previous work [17] absorption spectra of twelve *N*-aryl substituted dodecaneamides were examined. We investigated the UV spectra of dodecaneamides in seven polar protic solvents and the correlation of the ultraviolet absorption frequencies of dodecaneamides with the Kamlet-Taft solvatochromic parameters: π^* (dipolarity/polarizability), α (hydrogen-bond acidity) and β (hydrogen-bond basicity). Examination of the obtained data showed that most of the solvatochromism can be ascribed to the HBD effects (solvent acidity) rather than other effects.

In this work we wanted to delineate the different interactions of polar protic and aprotic solvents with previously synthesized dodecaneamides. To achieve this task, their UV spectra were recorded in polar aprotic solvents and the position of the ultraviolet absorption bands was determined. The effects of solvent polarity and hydrogen bonding on the absorption spectra were interpreted by means of linear solvation energy relationships (LSER). The correlations of three- and two-parameter models with absorption frequencies are also presented.

EXPERIMENTAL

All the *N*-aryl substituted dodecaneamides (1–9) (Fig. 1, Table 1) used in this study were previously synthesized and identified by their melting temperature, IR, and UV spectra [17].

Table 1

N-aryl substituted dodecaneamides (1–9) used in the present study

Comp. No:	Ar
(1)	$-C_6H_5$
(2)	p-$CH_3C_6H_4-$
(3)	p-OHC_6H_4-
(4)	p-ClC_6H_4-
(5)	p-$C_6H_5C_6H_4-$
(6)	p-$COOC_2H_5C_6H_4-$
(7)	p-$COOHC_6H_4-$
(8)	p-$COCH_3C_6H_4-$
(9)	p-$NO_2C_6H_4-$

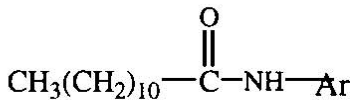

Fig. 1. *N*-aryl substituted dodecaneamides (1–9)

The UV spectra were recorded on a Varian Cary 50 spectrophotometer in the range from 200 nm to 400 nm, at room temperature. The length of the quarts cell used for the measurements was 1 cm. All organic solvents used in the present investigation were of spectral grade (Merck) products. The spectra were run in spectroquality solvents using concentrations of $2{,}5 \cdot 10^{-5}$ mol/dm^3.

RESULTS AND DISCUSSION

In this work, the ultraviolet absorption spectra of *N*-aryl substituted dodecaneamides (1–9) (Fig. 1, Table 1) were recorded in eight polar aprotic solvents: dimethylsulfoxide, *N,N*-dimethylformamide, acetonitrile, dichloromethane, tetrahydrofuran, ethylacetate, chloroform, and dioxane. The absorption maxima are given in Table 2 and Table 3. To explain the effects of polar aprotic solvents on the electronic absorption spectra of these amides, the spectrum of *N*-phenyl dodecaneamide (1) was taken as a reference; it has one absorption band in the range 245–256 nm (two electronic transitions with overlapping peaks) (Fig. 2).

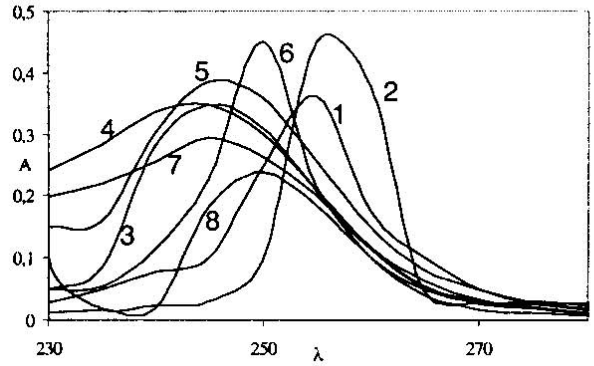

Fig. 2. UV spectra of *N*-phenyl dodecaneamide (1) in polar aprotic solvents
1 – DMSO, 2 – DMF, 3 – acetonitrile, 4 – dichloromethane, 5 – tetrahydrofuran, 6 – ethylacetate, 7 – chloroform, 8 – dioxane

Examination of the data given in Tables 2 and 3 shows that there is a similar trend in the UV absorption data of the investigated compounds in all used solvents. It can be seen that all of the substi-

tuted groups on the benzene ring (electron-donating or electron-accepting) generally cause bathochromic shift of the long wavelength absorption maximum, as compared to that of the reference system (1). It has been shown that the complementary electronic transitions need lower energies regardless of whether the substituent withdraws or accepts electrons [18].

Table 2

Ultraviolet absorption data for N-aryl substituted dodecaneamides (1–5)

Solvent	λ_{max} / nm				
	(1) $-C_6H_5$	(2) p-$CH_3C_6H_4-$	(3) p-OHC_6H_4-	(4) p-ClC_6H_4-	(5) p-$C_6H_5C_6H_4-$
DMSO, $\varepsilon_r^a = 46.45$	254.9	256	259	255.06	283.9
DMF, $\varepsilon_r^a = 36.71$	255.1	255.2	269.97	259.92	280.45
Acetonitrile, $\varepsilon_r^a = 35.94$	245.2	245.3	249.79	250	275.06
Dichloromethane, $\varepsilon_r^a = 8.93$	245	245.1	249.94	249.9	275
Tetrahydrofuran, $\varepsilon_r^a = 7.58$	245.1	248	250.25	250.19	279.76
Ethylacetate, $\varepsilon_r^a = 6.02$	250	250.1	250.04	250.08	275.96
Chloroform, $\varepsilon_r^a = 4.89$	245	248.9	249.25	250	275.2
Dioxane, $\varepsilon_r^a = 2.21$	249.9	250	255	250	277.4

[a] Relative permittivity ("dielectric constant") of the pure liquid at 25 °C [19].

Table 3

Ultraviolet absorption data for N-aryl substituted dodecaneamides (6–9)

Solvent	λ_{max} / nm			
	(6) p-$COOC_2H_5C_6H_4-$	(7) p-$COOHC_6H_4-$	(8) p-$COCH_3C_6H_4-$	(9) p-$NO_2C_6H_4-$
DMSO, $\varepsilon_r^a = 46.45$	280	276	292.51	333.2
DMF, $\varepsilon_r^a = 36.71$	277.71	275.11	290.2	329
Acetonitrile, $\varepsilon_r^a = 35.94$	274.54	271.11	285.35	321.27
Dichloromethane, $\varepsilon_r^a = 8.93$	270.3	270.1	285	318.23
Tetrahydrofuran, $\mu = 5.8$ D	275.75	273.8	285.18	322.53
Ethylacetate, $\varepsilon_r^a = 6.02$	274.55	272.55	285.16	322.3
Chloroform, $\varepsilon_r^a = 4.89$	272.65	272.5	287.42	320.5
Dioxane, $\varepsilon_r^a = 2.21$	274.7	274.54	285.1	318.25

[a] Relative permittivity ("dielectric constant") of the pure liquid at 25 °C [19].

The term solvatochromism is used to describe the pronounced change in the position of a UV absorption band that accompanies a change in the polarity of the medium. A hypsochromic shift with increasing solvent polarity is usually called negative solvatochromism. The opposite bathochromic shift is termed positive solvatochromism. [19]. The results presented here generally show bathochromic shifts for all the dodecaneamides (1–9) with increased polarity (positive solvatochromism).

It is interesting to compare the absorption bands observed in polar aprotic solvents with those found in polar protic solvents [17]. The change from polar protic to aprotic solvents generally

causes bathochromic shifts of the long wavelength absorption maximum for the same investigated dodecaneamides. For example, it can be noticed that in polar aprotic solvents, the absorption maxima of *N*-phenyl dodecaneamide (1) are at longer wavelengths (245 – 256 nm) that those registered in polar protic solvents (229 – 250 nm, [17]).

When absorption spectra are measured in solvents of different polarity, it is found that the positions of the absorption bands are usually modified by these solvents [19]. These changes come as a result of physical intermolecular solute-solvent interaction forces (such as ion-dipole, dipole-dipole, hydrogen bonding etc.), all of which tend to alter the energy difference between ground and excited state of the absorbing species.

The most extensively applied method of generating values for intermolecular solute/solvent interactions is the method of *Kamlet* and *Taft* [20]. This method has been widely used to study dipolarity/polarizability (π^*), HB donor acidity (α), and HB acceptor basicity (β) of many types of solvents [4–10].

In the present work, the effects of solvent polarity and hydrogen bonding on the absorption spectra were interpreted by the linear solvation energy relationships (*LSER*) concept developed by *Kamlet* and *Taft* using a general equation (1) of the type:

$$\tilde{V} = \tilde{V}_o + s\pi^* + a\alpha + b\beta \qquad (1)$$

and by two-parameter models presented by the equation (2) :

$$\tilde{V} = \tilde{V}_o + s\pi^* + b\beta \qquad (2)$$

where $\tilde{V}_o$ is the regression value of the solute property in the reference solvent cyclohexane, π^*, α and β are solvatochromic parameters, and s, a and b are the solvatochromic coefficients.

In Eq. (1) , π^* is an index of the solvent dipolarity/polarizability, which is a measure of the ability of the solvent to stabilize a charge or a dipole by its own dielectric effects. The π^* scale was selected to run from 0.00 for cyclohexanone to 1.00 for dimethyl sulfoxide [21]. The variable α is a measure of the solvent hydrogen-bond donor (HBD) acidity, and describes the ability of a solvent to donate a proton in a solvent-to-solute hydrogen bond. The scale α was selected to extend from 0.00 for non-HBD solvents to about 1.00 for methanol [22]. The variable β is a measure of the solvent hydrogen-bond acceptor (HBA) basicity, and describes the ability of a solvent to accept a proton in a solute-to-solvent hydrogen bond. The scale β was selected to extend from 0.00 for non-HBD solvents to about 1.00 for hexamethylphosphoric acid triamide [23].

For the purpose of exploring the solvent effects and hydrogen bonding (type-A and type-B [22, 23]) on the absorption spectra, the absorption frequencies ($\tilde{V}_{max} = 1/\lambda_{max}$) were correlated with the total solvatochromic equation (1). The correlation of the spectroscopic data was carried out by means of multiple linear regression analysis.

The results of the correlation of the absorption frequencies with the *Kamlet-Taft* solvatochromic parameters (π^*, α and β [20]) are given in Table 4. The percentage contribution of calculated solvatochromic parameters are given in Table 5. The discussion below is based on the quantitative values and the sign of the coefficients in the corresponding equations, and the comparison of these coefficients between themselves.

The data in Table 4 and Table 5 show that, in general, the dominant solvent effect in all dodecaneamides is the hydrogen bond basicity-HBA (represented by the higher negative value of the coefficient b). These negative values can be explained, most likely, by the ability of polar aprotic solvents to create an intermolecular hydrogen bond in the electronic excited state of dodecaneamides (Fig. 3, 3b), where they act as proton acceptor (type B).

Exceptions are the compounds (3), (4) and (8) where the classic solvation effects (represented by the higher negative value of the coefficient s) are dominating, which indicates better solvation of the electronic excited state (Fig. 3, 3b).

The negative signs of s, b, and a coefficients for the investigated compounds indicate bathochromic shifts with increasing solvent dipolarity/polarizability, solvent hydrogen-bond acceptor basicity, and solvent hydrogen-bond donor acidity. This suggests stabilization of the electronic excited state (Fig. 3, 3b) relative to the ground state (Fig. 3, 3a). The positive signs of the s coefficient for dodecaneamides (1) and (2) and the a coefficient for compounds (7) and (8) indicate hypsochromic shifts with increasing solvent dipolarity/polarizability of solvent (1, 2) and hydrogen-bond donor acidity (7, 8). This suggests stabilization of the ground state (Fig. 3, 3a) relative to the electronic excited state (Fig. 3, 3b).

Table 4

Results of the correlations with Eq. (1) for N-aryl substituted dodecaneamides (1–9)

Comp. Ar	n [a]	$\tilde{V}_0$	*s*	*b*	*a*	*R* [b]	*SD* [c]
(1) $-C_6H_5$	6	40.981	0.255	–2.742	–0.692	0.992	0.140
(2) *p*-$CH_3C_6H_4-$	6	41.079	0.526	–3.358	–2.739	0.992	0.127
(3) *p*-OHC_6H_4-	6	41.838	–2.088	–1.341	–0.863	0.950	0.248
(4) *p*-ClC_6H_4-	6	40.013	–1.166	–0.863	–0.741	0.987	0.082
(5) *p*-$C_6H_5C_6H_4-$	6	37.145	–0.689	–1.634	–0.920	0.965	0.183
(6) *p*-$COOC_2H_5C_6H_4-$	6	37.509	–0.107	–2.216	–1.732	0.999	0.034
(7) *p*-$COOHC_6H_4-$	6	37.239	–0.295	–0.931	0.759	0.997	0.036
(8) *p*-$COCH_3C_6H_4-$	6	36.134	–1.612	–0.409	1.295	0.999	0.027
(9) *p*-$NO_2C_6H_4-$	6	32.698	–1.035	–2.111	–0.721	0.986	0.136

[a] number of solvents; [b] correlation coefficient ; [c] standard deviation

Table 5

Percentage contribution of calculated solvatochromic parameters

Comp. Ar	*s* (%)	*b* (%)	*a* (%)
(1) $-C_6H_5$	7	74	19
(2) *p*-$CH_3C_6H_4-$	8	51	41
(3) *p*-OHC_6H_4-	49	31	20
(4) *p*-ClC_6H_4-	43	30	27
(5) *p*-$C_6H_5C_6H_4-$	21	51	28
(6) *p*-$COOC_2H_5C_6H_4-$	3	55	42
(7) *p*-$COOHC_6H_4-$	15	47	38
(8) *p*-$COCH_3C_6H_4-$	49	12	39
(9) *p*-$NO_2C_6H_4-$	27	54	19

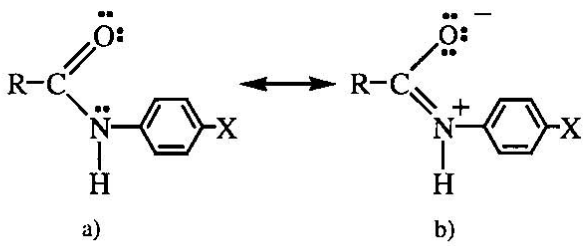

Fig. 3. Resonance structures of *N*-aryl substituted dodecaneamides: a) ground state, b) excited state (X = H, CH_3, OH, Cl, C_6H_5, $COOC_2H_5$, COOH, $COCH_3$, NO_2)

The percentage contribution of the calculated solvatochromic parameters (Table 5) also show that the HBD solvent effects (acidity) significantly affects the stabilization of the investigated compounds, but their influence is generally smaller than the influence of the HBA effects, with exception of compound (8).

Taking into consideration that the principal quality of polar aprotic solvents is the lack of ability to act as a hydrogen bond donor [5, 13], the effects of solvent polarity and hydrogen bonding on the absorption spectra were also interpreted by the system of a simplified two-parameters equation (2) (two-parameter model). The results of the correlations and the percentage contribution of the calculated solvatochromic parameters are given in Table 6 and Table 7.

From the results presented in Tables 6 and 7, it can be concluded that the HBA effects in this series (represented by the higher value of the coefficient *b*) play a major role, compared to the classic solvation effects (1, 2, 5–7, 9). The HBA effects stabilize the electronic excited state (Fig. 3, 3b) of the amides by formation of type B hydrogen bonding (negative sign of the coefficient *b*). The classic solvation effects are the dominant solvent effects for dodecaneamides (3), (4) and (8), and the negative sign of the coefficient *s* indicates a better solvation of the electronic excited state.

Table 6

Results of the correlations with Eq. (2) for N-aryl substituted dodecaneamides (1–9)

Comp. Ar	n [a]	$\tilde{V}_0$	s	b	R [b]	SD [c]
(1) $-C_6H_5$	6	40.914	0.031	–2.333	0.988	0.145
(2) p-$CH_3C_6H_4-$	6	41.110	0.269	–3.002	0.958	0.275
(3) p-OHC_6H_4-	6	41.667	–2.247	–0.861	0.940	0.255
(4) p-ClC_6H_4-	6	41.005	–1.185	–0.752	0.973	0.096
(5) p-$C_6H_5C_6H_4-$	6	36.671	–0.391	–1.202	0.963	0.154
(6) p-$COOC_2H_5C_6H_4-$	6	37.196	–0.644	–1.017	0.979	0.076
(7) p-$COOHC_6H_4-$	6	37.282	–0.136	–1.187	0.991	0.051
(8) p-$COCH_3C_6H_4-$	6	36.220	–1.493	–0.670	0.991	0.069
(9) p-$NO_2C_6H_4-$	6	32.551	–1.309	–1.470	0.973	0.113

[a] number of solvents; [b] correlation coefficient ; [c] standard deviation

Table 7

Percentage contribution of calculated solvatochromic parameters

Comp. Ar	s (%)	b (%)
(1) $-C_6H_5$	1	99
(2) p-$CH_3C_6H_4-$	8	92
(3) p-OHC_6H_4-	72	28
(4) p-ClC_6H_4-	61	39
(5) p-$C_6H_5C_6H_4-$	25	75
(6) p-$COOC_2H_5C_6H_4-$	39	61
(7) p-$COOHC_6H_4-$	10	90
(8) p-$COCH_3C_6H_4-$	69	31
(9) p-$NO_2C_6H_4-$	47	53

The negative signs of s and b coefficients in Table 6 for *N*-aryl substituted dodecaneamides (3–9) indicate bathochromic shifts, with both increasing solvent polarity and solvent hydrogen-bond acceptor basicity. The positive signs of coefficient s and the negative signs of coefficient b for compounds (1) and (2) indicate hypsochromic shifts with increasing solvent polarity and a bathochromic shifts with increasing solvent hydrogen-bond acceptor basicity.

The results of all correlations for the examined *N*-aryl substituted dodecaneamides (Table 4 and Table 6) show that, in general, most of the solvatochromism is due to solvent basicity (HBA effects). The HBD effects and the classic solvation effects generally work in the same direction, stabilysing the electronic excited state.

A comparative study of the results (Eq. (1) and Eq. (2)) for the investigated dodecaneamides (1–9) leads to the conclusion that the selection of both models was correct. The model which includes all three solvatochromic parameters (π^*, α and β) in the correlations gives an accurate interpretation of the solvating effects on *N*-aryl substituted dodecaneamides in polar aprotic solvents, which allegedly do not possess HBD character.

Taking the investigations in polar protic [17] and polar aprotic solvents into consideration together, it can be noticed that the HBD effects have weaker influence in polar aprotic solvents, which is contrary to the polar protic solvents where the HBD effects are dominating (represented by the higher value of the coefficient a). The HBD effects and the classic solvation effects can also be compared and they are generally more intensive in polar aprotic solvents (taking the value of the coefficients as a measure of their intensity).

In general, polar protic solvents stabilize the ground state of the analyzed amides (positive sign of the coefficient a), by formation of hydrogen bonding where they act as proton-donors. Polar aprotic solvents, on the other hand, stabilize the electronic excited state of the analyzed do-

decaneamides (negative sign of the coefficient *b*), by creation of hydrogen bonding where they act as proton-acceptors. Therefore, it can be concluded that polar aprotic solvents, by stabilization of the electronic excited state, are more adequate to be used as solvents in the chemical reactions for the analyzed dodecaneamides. The basicity of polar aprotic solvents or the stabilization of the excited state which increases the reaction rate is the main factor affecting their reactivity.

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REFERENCE

[1] M. Doležal, M. Miletin, R. Hejský, K. Králová, J. Kuneš, Synthesis of some amides of substituted pyrazine-2-carboxylic acids and their photosynthesis-inhibiting activity, *International Electronic Conference on Synthetic Organic Chemistry* [C0009], September 1–30, 2001.

[2] M. Doležal, M. Miletin, J. Kuneš, K. Králová, Substituted amides of pyrazine-2-carboxylic acids: synthesis and biological activity, *Molecules*, **7**, 363–373 (2002).

[3] A. X. Lupea, I. Boc, I. Macarie, M. Padure, Disazopigments, derivates of salicylamides, *Chem. Bull. Tech. Univ. Timisoara*, **40**(54), 57–62 (1995).

[4] N. V. Valentić, G. S. Uščumlić, M. Radojković-Veličković, M. Mišić-Vuković, Solvent effects on electronic absorption spectra of 3-*N*-(4-substituted phenyl)-5-carboxy uracils, *J. Serb. Chem. Soc.*, **64**, 149–154 (1999).

[5] J. B. Nikolić, G. S. Uščumlić, V. V. Krstić, Solvent effects on electronic absorption spectra of cyclohex-1-enylcarboxylic and 2-methylcyclohex-1-enylcarboxylic acids, *J. Serb. Chem. Soc.*, **65**, 353–359 (2000).

[6] D. Ž. Mijin, G. S. Uščumlić, N. V. Valentić, Synthesis and investigation of solvent effects on the ultraviolet absorption spectra of 5-substituted-4-methyl-3-cyano-6-hydroxy-2-pyridones, *J. Serb. Chem. Soc.*, **66**, 507–516 (2001).

[7] N. V. Valentić, G. S. Uščumlić, M. Radojković-Veličković, Substituent and solvent effects on the UV/vis absorption spectra of 3-*N*-alkyl-5-carboxy uracils, *Indian J. Chem.*, **42B**, 1137–1140 (2003).

[8] G. S. Uščumlić, A. A. Kshad, D. Ž. Mijin, Synthesis and investigation of solvent effects on the ultraviolet absorption spectra of 1,3-bis-substituted-5,5-dimethylhydantoins, *J. Serb. Chem. Soc.*, **68**, 699–706 (2003).

[9] K. Suganya, S. Kabilan, Substituent and solvent effects on electronic absorption spectra of some *N*-(substituted-phenyl)benzene sulphonamides, *Spectrochim. Acta*, Part A, **60**, 1225–1228 (2004).

[10] D. Ž. Mijin, G. S. Uščumlić, N. U. Perišić-Janjić, N. V. Valentić, Substituent and solvent effects on the UV/vis absorption spectra of 5-(3-and-4-substituted arylazo)-4,6-dimethyl-3-cyano-2-pyridones, *Chem. Phys. Lett.*, **418**, 223–229 (2006).

[11] G. S. Uščumlić, V. V. Krstić, M. D. Muškatirović, The reactivity of α, β-unsaturated carboxylic acids. Part IV. Correlation of ultraviolet absorption frequencies of 2–substituted cyclohex-1-ene and cis-3–substituted-2-methyl-2-butene carboxylic acids with Hammett substituent constants, *J. Serb. Chem. Soc.*, **55**, 571–574 (1990).

[12] N. V. Valentić, M. Radojković-Veličković, M. Mišić-Vuković, G. S. Uščumlić, Reactivity of 3-*N*-(4-substituted phenyl)-5-carboxy uracils, *J. Serb. Chem. Soc.*, **62**, 1175–1182 (1997).

[13] J. B. Nikolić, G. S. Uščumlić, V. V. Krstić, Reactivity of cyclohex-1-enylcarboxylic and 2-methylcyclohex-1-enylcarboxylic acids with diazodiphenylmethane in aprotic solvents, *J. Serb. Chem. Soc.*, **65**, 839–846 (2000).

[14] G. S. Uščumlić, J. B. Nikolić and V. V. Krstić, The reactivity of α, β-unsaturated carboxylic acids. Part XVI. The kinetics of the reaction of cycloalkenylcarboxylic and cycloalkenylacetic acids with diazodiphenylmethane in various alcohols, *J. Serb.Chem. Soc.*, **67**, 77–85 (2002).

[15] J. B. Nikolić, G. S. Uščumlić, V. V. Krstić, The influence of the solvent on organic reactivity. Part II. Hydroxylic solvent effects on the reaction rates of diazodiphenylmethane with 2-(2-substituted cyclohex-1-enyl)acetic and 2-(2-substituted phenyl)acetic acids, *J. Serb.Chem. Soc.*, **69**, 601–610 (2004).

[16] A. D. Marinković, S. Ž. Drmanić, B. Ž. Jovanović, M. Mišić-Vuković, Investigations of the reactivity of pyridine carboxylic acids with diazodiphenylmethane in protic and aprotic solvents. Part I. Pyridine mono–carboxylic acids, *J. Serb. Chem. Soc.*, **70**, 557–567 (2005).

[17] V. Stamatovska, V. Dimova, K. Čolančeska-Raǵenović, Solvent effect on electronic absorption spectra of some *N*-aryl substituted dodecaneamides, *Bull. Chem. Technol. Macedonia*, **25** (1), 9–16 (2006).

[18] S. Jing, J. Yanming, Y. Chaoguo, Substituent effect on UV spectra of 5-arylmethylenerhodanines, *Chem. J. Internet*, **3**, 9–12 (2001).

[19] C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 3rd Edition, Wiley-VCH, Weinheim, 2004, pp. 329–475.

[20] M. J. Kamlet, J. L. M. Abboud, M. H. Abraham, R. W. Taft, Linear solvation energy relationships. 23. A comprehensive collection of the solvatochromic parameters, π^*, α, β, and some methods for simplifying the generalized solvatochromic equation, *J. Org. Chem.*, **48**, 2877–2887 (1983).

[21] M. J. Kamlet, J. L. Abboud, R. W. Taft, The solvatochromic comparison metod. 6. The π^* scale of solvent polarities *J. Am. Chem. Soc.*, **99**, 6027–6038 (1977).

[22] R. W. Taft, M. J. Kamlet, The solvatochromic comparison metod. 2. The α-scale of solvent hydrogen-bond donor (HBD) acidities, *J. Am. Chem. Soc.*, **98**, 2886–2894 (1976).

[23] M. J. Kamlet, R. W. Taft, The solvatochromic comparison metod. I. The β-scale of solvent hydrogen-bond acceptor (HBA) basicities, *J. Am. Chem. Soc.*, **98**, 377–383 (1976).