

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

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A series of *N*-aryl substituted dodekanamides were synthesized using the reaction of fatty acid chloride (lauroylchloride) with *p*-substituted aromatic amines in the presence of triethylamine as an organic base and dioxane as a solvent. The structures of *N*-aryl substituted dodekanamides were determined by their melting temperature, IR and UV spectra. The ultraviolet absorption spectra of synthesized amides were recorded in seven polar solvents in the range from 200 nm to 400 nm. The effects of solvent polarity and of hydrogen bonding, on the absorption spectra, were interpreted by means of linear solvation energy relationships (*LSER*) using a general equation:  $\nu = \nu_0 + s\pi^* + a\alpha + b\beta$  and by two-parameter models presented by the equation:  $\nu = \nu_0 + s\pi^* + a\alpha$ . The mode of influence of the solvent on the ultraviolet absorption spectra of the investigated dodekanamides are discussed on the basis of the correlation results.

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

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

*N*-арил супституираните додеканамиди се синтетизирани со реакција на лауроилхлоридот со *p*-супституирани ароматични амини во присуство на триетиламин како органска база и диоксан како растворувач. Идентификацијата на овие соединенија е извршена врз основа на температурите на топење и со примена на IR и UV спектроскопија. Апсорпционите спектри на *N*-арил супституирани додеканамиди се снимени во седум поларни 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*), односно користејќи тотална солватохромна равенка ( $\nu = \nu_0 + s\pi^* + a\alpha + b\beta$ ) и примена на двопараметарен модел ( $\nu = \nu_0 + s\pi^* + a\alpha$ ). Влијанието на растворувачот на UV апсорпциони спектри на испитуваните додеканамиди е дискутирано врз база на корелационите резултати.

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

### INTRODUCTION

The amide function is based on the presence of the  $\text{—N—}\overset{\text{O}}{\parallel}{\text{C—}}$  group.

When attaching various radicals to the three free valences of this group, one can obtain various

classes of compounds. The amide bond is present as a key building unit in many important natural products and man-made compounds [1].

Amides and *N*-substituted amides of fatty acids have different properties [2–4], and find large application in various chemical industries.

The fatty acid amides derivatives are useful as textile additives, softening, lubricating, wetting, washing, waterproofing agents, detergents, shampoos, and leveling agents [4, 5]. The lauroyl derivatives of bis(hydroxyalkyl) amide have a remarkable activating effect on the foaming power. Also, the akylolamides, especially those containing a high proportion of bis(hydroxyethyl) lauramide, have the dual advantages of excellent neutral scouring efficiency and uniquely effective waster-liquor clarification by simple cold acid-cracking. Wastes from desuinting and suint scouring are effectively clarified by bentonite treatment without acidification. Some fatty acid amides are useful as cholesterol-lowering agents and they are also useful as a remedy for atherogenesis. The surfactants based on polyoxyethylene fatty acid amides, which are mild to the skin and have good foaming property, are useful with anionic surfactants and/or amphoteric surfactants for shampoos formulation [6].

The aim of this work was to synthesize a number of *N*-aryl substituted dodekanamides. A special attention has been paid to the study of solvent effects on amides in some polar solvents using the UV spectroscopy method.

## EXPERIMENTAL

All chemicals used in the synthesis of amides (1–12) were commercial products (Merck). The melting temperatures of synthesized compounds were determined on a Büchi 510 melting temperature apparatus and, therefore, the values reported here are uncorrected. IR spectra were recorded in the range of 4000–400  $\text{cm}^{-1}$  using the KBr pill on a Perking-Elmer 297 Spectrophotometer. The UV spectra were recorded on a Varian Cary 50 Scan Spectrophotometer.

### *Preparation of N-aryl substituted dodekanamides (1–12)*

The title compounds were synthesized by the modified method reported in the literature [7].

### *General procedure*

The lauroylchloride (0.01 mol) dissolved in dioxane was slowly added with stirring into a solution of dioxane (15 ml), corresponding amine (0.01 mol) and triethylamine (0.01 mol). After the

addition was complete, stirring continued for another 1 hour at room temperature.

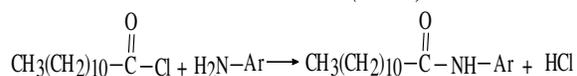
The reaction mixture was poured into ice water, and acidified with HCl to pH = 3 ~ 4.

The precipitate that formed was filtered, washed with ice water (neutral pH) and dried at room temperature. The yields of the amides (1–12) were in the range from 82–96%. The amides thus obtained were recrystallized from dilute ethanol.

All synthesized *N*-aryl substituted dodekanamides (1–12) were identified by melting temperature, IR and UV spectroscopic data (Tables 1 and 2). The UV spectra were recorded in spectro-quality solvents using concentrations of  $2.5 \times 10^{-5}$   $\text{mol/dm}^3$ .

Table 1

### *Physical data for N-aryl substituted dodekanamides (1–12)*



Comp.	Ar	Formula ( $M_r/\text{g}\cdot\text{mol}^{-1}$ )	Yield (in %)	M.t. (°C)
(1)	-C <sub>6</sub> H <sub>5</sub>	C <sub>18</sub> H <sub>29</sub> NO (275)	93	79–80 (lit. 78)
(2)	<i>p</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -	C <sub>19</sub> H <sub>31</sub> NO (289)	95.65	85–86 (lit. 87)
(3)	<i>p</i> -C <sub>2</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>4</sub> -	C <sub>20</sub> H <sub>33</sub> NO (303)	95.71	74–76
(4)	<i>p</i> -OCH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -	C <sub>19</sub> H <sub>31</sub> NO <sub>2</sub> (305)	85.25	104–105
(5)	<i>p</i> -OH-C <sub>6</sub> H <sub>4</sub> -	C <sub>19</sub> H <sub>29</sub> NO <sub>2</sub> (291)	89.3	130–131
(6)	<i>p</i> -Br-C <sub>6</sub> H <sub>4</sub> -	C <sub>18</sub> H <sub>28</sub> NBrO (354)	88.98	106–108 (lit. 104)
(7)	<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub> -	C <sub>18</sub> H <sub>28</sub> NClO (309.5)	88.87	88–91
(8)	<i>p</i> -C <sub>6</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>4</sub> -	C <sub>24</sub> H <sub>33</sub> NO (351)	82.62	147–149
(9)	<i>p</i> -COOC <sub>2</sub> H <sub>5</sub> - C <sub>6</sub> H <sub>4</sub> -	C <sub>21</sub> H <sub>33</sub> NO <sub>3</sub> (347)	86.45	83–86
(10)	<i>p</i> -COOH-C <sub>6</sub> H <sub>4</sub> -	C <sub>19</sub> H <sub>29</sub> NO <sub>3</sub> (319)	83.07	226–228
(11)	<i>p</i> -COCH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -	C <sub>20</sub> H <sub>31</sub> NO <sub>2</sub> (317)	85.2	111–113
(12)	<i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -	C <sub>18</sub> H <sub>28</sub> N <sub>2</sub> O <sub>3</sub> (320)	95.31	79–80 (lit. 78)

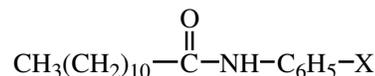
Table 2  
IR and UV data for *N*-aryl substituted  
dodekanamides (1–12)

Comp. Ar	IR ( $\tilde{\nu}_{max}/\text{cm}^{-1}$ )	UV[H <sub>2</sub> O] ( $\lambda/\text{nm}$ )
(1)	3280 (NH) st 2920–2825 (CH) st 1645 (C=O) st Amid I	229.76
–C <sub>6</sub> H <sub>5</sub>	1590 (C–C) st benz. ring 1530 (N–C=O) st Amid II, (NH) $\delta$	
(2)	3280 (NH) st 2920–2840 (CH) st 1650 (C=O) st Amid I	211.75
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> –	1590 (C–C) st benz. ring 1530–1510 (N–C=O) st Amid II, (NH) $\delta$	239.99
(3)	3290 (NH) st 2925–2840 (CH) st 1645 (C=O) st Amid I	211.43
<i>p</i> -C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> –	1590 (C–C) st benz. ring 1530–1510 (N–C=O) st Amid II, (NH) $\delta$	232.79
(4)	3300 (NH) st 2900–2840 (CH) st 1645 (C=O) st Amid I	209.16
<i>p</i> -OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> –	1595 (C–C) st benz. ring 1575–1520 (N–C=O) st Amid II, (NH) $\delta$	231.52 298.63
(5)	3280 (NH) st, (OH) st 2920–2825 (CH) st 1640 (C=O) st Amid I	209.68
<i>p</i> -OHC <sub>6</sub> H <sub>4</sub> –	1600 (C–C) st benz. ring 1530–1500 (N–C=O) st Amid II, (NH) $\delta$ 1240 (O–Car) st	230.78 296.65
(6)	3300 (NH) st 2920–2840 (CH) st 1655 (C=O) st Amid I	218.08
<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> –	1590 (C–C) st benz. ring 1540 (N–C=O) st Amid II, (NH) $\delta$	236.57 293.35
(7)	3300 (NH) st 2920–2840 (CH) st 1655 (C=O) st Amid I	214.39
<i>p</i> -Cl C <sub>6</sub> H <sub>4</sub> –	1590 (C–C) st benz. ring 1540 (N–C=O) st Amid II, (NH) $\delta$	234.46 292.03
(8)	3290 (NH) st 2910–2840 (CH) st 1650 (C=O) st Amid I	225.98
<i>p</i> -C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> –	1590 (C–C) st benz. ring 1545 (N–C=O) st Amid II, (NH) $\delta$	260.05
(9)	3280 (NH) st 2920–2835 (CH) st 1700 (C=O) st COOC <sub>2</sub> H <sub>5</sub>	224.30
<i>p</i> -COOC <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> –	1645 (C=O) st Amid I 1600–1510 (C–C) st benz. ring 1540–1510 (N–C=O) st Amid II, (NH) $\delta$	250.26
(10)	3300 (OH–NH) st 2920–2840 (CH) st 2540 (COO–H) st assoc.	227.17
<i>p</i> -COOH C <sub>6</sub> H <sub>4</sub> –	1670 (C=O) st Amid I, (C=O) st COOH 1600 (C–C) st benz. ring 1520 (N–C=O) st Amid II, (NH) $\delta$	270.49 294.92
(11)	3300 (NH) st 2900–2845 (CH) st 1650 (C=O) st Amid I, (C=O) st COCH <sub>3</sub>	238.76
<i>p</i> -COCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> –	1600 (C–C) st benz. ring 1550 (N–C=O) st Amid II, (NH) $\delta$	254.80 298.71
(12)	3335 (NH) st 2920–2845 (CH) st 1675 (C=O) st Amid I	238.83
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> –	1600 (C–C) st benz. ring 1540 (N–C=O) st Amid II, (NH) $\delta$ 1340–1330 (NO <sub>2</sub> ) st	315.24 375.52

st – stretching vibrations;  $\delta$  – deformation vibrations

## RESULTS AND DISCUSSION

In this work, the ultraviolet absorption spectra of *N*-aryl substituted dodekanamides (1–12) (Figure 1) were recorded in seven polar solvents.



(X = H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, OCH<sub>3</sub>, OH, Br, Cl, C<sub>6</sub>H<sub>5</sub>, COOC<sub>2</sub>H<sub>5</sub>, COOH, COCH<sub>3</sub>, NO<sub>2</sub>)

Fig. 1. *N*-aryl substituted dodekanamides under study

The absorption maxima are given in Table 3 and Table 4. To explain the effects of solvents on the electronic absorption spectra of these amides, the spectrum of *N*-phenyl dodekanamide (1) was taken as reference; it has one absorption band in the range 229–250 nm (two electronic transitions with overlapping peaks). The results can be explained as follows: since the two chromophores (–CONH group and –C<sub>6</sub>H<sub>5</sub> group) of (1) can interact freely, its absorption is caused by delocalized  $\pi$ -system spreading over the whole molecule [8].

Examination of the data given in Tables 3 and 4 shows that there is an identical trend in the UV absorption data of the investigated compounds in all used solvents. Introduction of substituent groups in the benzene ring (electron-donating or electron-accepting) generally causes bathochromic shift of the long wavelength absorption maximum, as compared to that of the reference system (1). It has been known that the complementary electronic transitions need lower energies regardless of whether the substituent withdraws or accepts electrons [9]. The results generally show hypsochromic shifts for all the dodekanamides (1–12) with increasing solvent polarity (negative solvatochromism) [10].

It is known that, UV spectroscopic measurement of  $\lambda_{max}$  of a dissolved probe provides numerical values for the intermolecular interactions between solute and solvent. The most extensively applied method of generating values for intermolecular solute/solvent interactions is the method of Kamlet and Taft [11, 12, 13]. Recently, several reports become available on the correlation of UV absorption frequencies with solvent parameters [14–18].

Table 3

Ultraviolet absorption data for *N*-aryl substituted dodekanamides (1–6)

Solvent	$\lambda_{\max} / \text{nm}$					
	(1) -C <sub>6</sub> H <sub>5</sub>	(2) <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	(3) <i>p</i> -C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> -	(4) <i>p</i> -OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	(5) <i>p</i> -OHC <sub>6</sub> H <sub>4</sub> -	(6) <i>p</i> -Br C <sub>6</sub> H <sub>4</sub> -
Water	229.76	211.75 239.99	211.43 232.79	209.16 231.52 298.63	209.68 230.78 296.65	218.08 236.57 293.35
Methanol	240.77	244.63	246.12	250.15	250.24	253.43
Ethanol	244.68	244.79	247.88	249.59	250.83	253.56
1-propanol	244.74	244.89	247.47	250.6	250.63	253.55
2-propanol	244.75	244.97	247.34	247.58	249.88	249.8
1-butanol	248.77	244.77	247.88	249.59	249.88	251.25
Ethylene glycol	244.83	244.77	247.88	249.59	250.43	253.35

Table 4

Ultraviolet absorption data for *N*-aryl substituted dodekanamides (7–12)

Solvent	$\lambda_{\max} / \text{nm}$					
	(7) <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> -	(8) <i>p</i> -C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> -	(9) <i>p</i> -COOC <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> -	(10) <i>p</i> -COOHC <sub>6</sub> H <sub>4</sub> -	(11) <i>p</i> -COCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	(12) <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -
Water	214.39 234.46 292.03	225.98 260.05	224.3 250.26	227.17 270.49 294.92	238.76 254.8 298.71	238.83 315.24 375.52
Methanol	250.6	274.9	272.99	270.98	218.73 289.99	223.75 316.83
Ethanol	250.36	273.68	273.7	271.98	217.72 292.08	222.75 319.24
1-propanol	250.17	274.69	274.05	271.99	216.9 292.65	223.75 317.12
2-propanol	249.88	248.59 274.69	248.87 274.19	270.98	249.12 291.58	240.84 317.33
1-butanol	249.88	275.69	274.56	271.99	291.21	317.53
Ethylene glycol	250.88	278.1	274.53	271.39	218.73 292.11	223.75 321.25

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

$$\nu = \nu_0 + s\pi^* + a\alpha + b\beta \quad (1)$$

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

$$\nu = \nu_0 + s\pi^* + a\alpha \quad (2)$$

where  $\pi^*$ ,  $\alpha$  and  $\beta$  are solvatochromic parameters, and  $s$ ,  $a$  and  $b$  are the solvatochromic coefficients.

In Eq. (1),  $\pi^*$  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  $\pi^*$  scale was selected to run from 0.00 for cyclohexanone to 1.00 for dimethyl sulfoxide. The variable  $\alpha$  is a measure of the solvent hydrogen-bond donor (HBD) acidity, and describes the ability of the solvent to donate a proton in a solvent-to-solute hydrogen bond. The scale  $\alpha$  was selected to extend from 0.00 for non-HBD solvents to about 1.00 for methanol. The variable  $\beta$  is a measure of the solvent hydrogen-bond acceptor (HBA) basicity, and describes the ability of the solvent to accept a proton in a solute-to-

solvent hydrogen bond. The scale  $\beta$  was selected to extend from 0.00 for non-HBD solvents to about 1.00 for hexamethylphosphoric acid triamide.

In these amphiprotic solvents, complications can be caused by self-association type-AB hydrogen bonding, and multiple type-A and type-B interactions. In this situations (where both the solvents and the solutes are hydrogen-bond donors), it can be quite difficult to untangle solvent dipolarity/polarizability, type-B hydrogen bonding and variable self-association effects from common multiple type-A hydrogen bonding interactions [19].

For the purpose of exploring the solvent effects and hydrogen bonding (type-A and type-B) on the absorption spectra, the absorption frequencies ( $\nu_{max} = 1/\lambda_{max}$ ) 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 *Kamlet-Taft* solvatochromic parameters are shown in Table 5 [20].

Table 6

*Results of the correlations with Eq. (1) for N-aryl substituted dodekanamides (1–12)*

Comp. Ar	$n^a$	$\nu_0$	$s$	$b$	$a$	$R^b$	$SD^c$
(1) -C <sub>6</sub> H <sub>5</sub>	7	34.712	-1.453	-0.4412	8.788	0.9545	0.454
(2) <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	7	39.178	-0.218	-0.0700	2.236	0.9233	0.1672
(3) <i>p</i> -C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> -	7	35.051	-1.057	-0.2868	7.484	0.9244	0.5217
(4) <i>p</i> -OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	6	33.325	-0.671	-0.5086	8.812	0.9237	0.7869
(5) <i>p</i> -OH C <sub>6</sub> H <sub>4</sub> -	7	33.297	-0.730	-0.2508	8.816	0.8934	0.8091
(6) <i>p</i> -Br C <sub>6</sub> H <sub>4</sub> -	6	33.680	-0.875	-0.4137	7.898	0.8943	0.7996
(7) <i>p</i> -Cl C <sub>6</sub> H <sub>4</sub> -	7	34.726	-0.772	-0.2654	7.124	0.8787	0.689
(8) <i>p</i> -C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> -	6	36.192	24.332	0.8896	-15.963	0.9968	0.4018
(9) <i>p</i> -COOC <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> -	6	28.972	-1.413	-0.7816	10.520	0.9416	0.7527
(10) <i>p</i> -COOH C <sub>6</sub> H <sub>4</sub> -	6	30.008	-0.892	-0.6696	9.206	0.9420	0.6956
(11) <i>p</i> -COCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	5	54.819	0.351	1.1855	-11.391	0.9732	0.8237
(12) <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -	5	50.756	0.378	1.2467	-8.013	0.9742	0.5808

<sup>a</sup> Number of solvents; <sup>b</sup> Correlation coefficient; <sup>c</sup> Standard deviation

Table 5

*Kamlet-Taft solvatochromic parameters*

Solvent	$\pi^*$	$\beta$	$\alpha$
Water	1.09	0.18	1.17
Methanol	0.60	0.62	0.93
Ethanol	0.54	0.77	0.83
1 – propanol	0.52	0.00	0.78
2 – propanol	0.48	0.95	0.76
1 – butanol	0.47	0.88	0.79
Ethylene glycol	0.92	0.52	0.90

The results of the correlation of the absorption frequencies with the *Kamlet-Taft* solvatochromic parameters ( $\pi^*$ ,  $\alpha$  and  $\beta$ ) are given in Table 6.

The percentage contribution of calculated solvatochromic parameters are given in Table 7.

Table 7  
Percentage contribution of calculated solvatochromic parameters

Comp. Ar	<i>s</i>	<i>b</i> (%)	<i>a</i>
(1) -C <sub>6</sub> H <sub>5</sub>	13.60	4.13	82.27
(2) <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	8.63	2.77	88.6
(3) <i>p</i> -C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> -	11.97	3.25	84.78
(4) <i>p</i> -OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	6.71	5.09	88.2
(5) <i>p</i> -OHC <sub>6</sub> H <sub>4</sub> -	7.45	2.56	89.99
(6) <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> -	9.52	4.5	85.97
(7) <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> -	9.46	3.25	87.29
(8) <i>p</i> -C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> -	59.08	2.16	38.76
(9) <i>p</i> -COOC <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> -	11.11	6.15	82.74
(10) <i>p</i> -COOHC <sub>6</sub> H <sub>4</sub> -	8.28	6.22	85.50
(11) <i>p</i> -COCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	2.72	9.17	88.11
(12) <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -	3.92	12.93	83.14

The discussion is based on the quantitative values and the sign of the coefficients in the corresponding equations, and the comparison of these coefficients among themselves.

The results (Table 6 and Table 7) show that solvent effects on the absorption spectra of *N*-aryl substituted dodekanamides (1–12) generally include important contributions from the solvent HBD (hydrogen bond donor) acidity. Judging from the coefficient values, the classic solvation effects ( $\pi^*$ ) dominate in the *N*-diphenyldodekanamide (8), contrary to the other dodekanamides, where the HBD effects dominate.

The high positive values of the coefficient *a* (1–7, 9, 10) indicate a better stabilization of the ground state (Figure 2, 2a) by the HBD solvent effects, suggesting stabilization by the formation of the type A (solvent to solute) hydrogen bonding. The high negative values of the coefficient *a* (11, 12) indicate a better stabilization of the transition state (Figure 2, 2b) by the HBD solvent effects, due to stabilization by the formation of the type A hydrogen bonding.

The HBA effects (*b*) and the classic solvation effects ( $\pi^*$ ), work in the opposite direction to the HBD effects, and their influence is much smaller than the influence of the HBD effects.

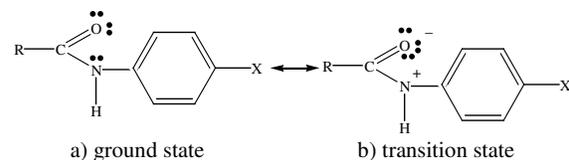


Fig. 2. Resonance structures of *N*-aryl substituted dodekanamides

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) in six solvents (water, ethanol, 1-propanol, 2-propanol, 1-butanol, ethylene glycol).

The results of the correlations and the percentage contribution of the calculated solvatochromic parameters are presented in Table 8 and Table 9.

Table 8  
Results of the correlations with Eq. (2) for *N*-aryl substituted dodekanamides (1–12)

Comp. Ar	<i>n</i> <sup>a</sup>	$\nu_0$	<i>s</i>	<i>a</i>	<i>R</i> <sup>b</sup>	SD <sup>c</sup>
(1) -C <sub>6</sub> H <sub>5</sub>	6	33.659	-1.872	10.080	0.952	0.464
(2) <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	6	38.602	-0.796	3.336	0.986	0.071
(3) <i>p</i> -C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> -	6	33.325	-2.629	10.599	0.973	0.316
(4) <i>p</i> -OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	6	31.671	-3.173	12.693	0.963	0.445
(5) <i>p</i> -OHC <sub>6</sub> H <sub>4</sub> -	6	30.718	-3.441	13.880	0.975	0.398
(6) <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> -	6	32.227	-3.303	11.542	0.936	0.502
(7) <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> -	6	32.414	-3.119	11.571	0.975	0.315
(8) <i>p</i> -C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> -	6	29.608	-3.699	10.945	0.976	0.253
(9) <i>p</i> -COOC <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> -	6	26.846	-3.637	14.503	0.982	0.352
(10) <i>p</i> -COOHC <sub>6</sub> H <sub>4</sub> -	6	17.324	-6.927	17.324	0.978	0.789
(11) <i>p</i> -COCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	6	36.263	0.579	-2.896	0.065	0.109
(12) <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -	6	43.891	3.655	-18.056	0.988	0.387

<sup>a</sup> Number of solvents. <sup>b</sup> Correlation coefficient. <sup>c</sup> Standard deviation

Table 9

## Percentage contribution of calculated solvatochromic parameters

Comp. Ar	<i>s</i> (%)	<i>a</i> (%)
(1) -C <sub>6</sub> H <sub>5</sub>	15.7	84.3
(2) <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	19.3	80.7
(3) <i>p</i> -C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> -	19.9	80.1
(4) <i>p</i> -OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	20	80
(5) <i>p</i> -OHC <sub>6</sub> H <sub>4</sub> -	19.9	80.1
(6) <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> -	22.2	77.8
(7) <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> -	21.2	78.8
(8) <i>p</i> -C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> -	25.3	74.7
(9) <i>p</i> -COOC <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> -	20	80
(10) <i>p</i> -COOHC <sub>6</sub> H <sub>4</sub> -	28.6	71.4
(11) <i>p</i> -COCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	16.7	83.3
(12) <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -	16.8	83.2

The data in Table 8 shows that the HBD effects play a major role, compared with the classic solvation effects. The HBD effects, generally, stabilize the ground state (Figure 2, 2b) of the amides by formation of hydrogen bonding where they act as proton-donors.

The percentage contribution of the calculated solvatochromic parameters (Table 9) also show that the dominant solvent effect in all investigated compounds is the hydrogen bond acidity (HBD effects).

The correlation coefficients (*R*) have satisfactory values in all cases (Table 8) and are better when compared to those obtained by applying equation (1) (Table 6).

## CONCLUSIONS

The results of all correlations for the examined *N*-aryl substituted dodekanamides (Table 6

and Table 8) show that most of the solvatochromism can be ascribed to the HBD effects (solvent acidity) rather than other effects, when polar solvents are used. The study on solvation in these systems has shown that the acidity of the solvent has significant effects on the solvent induced frequency shift, and may be used to characterize the intermolecular interactions.

In this work, satisfactory results were obtained for the correlations of the ultraviolet absorption frequencies of the investigated dodekanamides by a two-parameters equation (2), indicating that the selected model was correct. This model gives an accurate interpretation of the solvating effects on *N*-aryl substituted dodekanamides in different polar solvents.

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