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SOLVENT EFFECT ON ELECTRONIC ABSORPTION SPECTRA OF SOME 2-AMINOBENZIMIDAZOLES

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The effect of protic and aprotic solvents on electronic apsorption spectra of 1-(3-X--benzil)-2-aminobenzimidazoles (X=CH_3 ; OCH_3 ; Cl) was examined. UV-apsorption spectra (200-400 nm) were recorded in five protic and four aprotic solvents. Batochromic shift of absorption maxima, λ_{max}, occurs from the solvent with the highest proton-donor ability to the proton acceptor solvent (from water to DMSO). Positions of absortion maxima in various solvents are in correlation with the dielectric constant of the solvent. In order to explain the obtained results, the ultraviolet absorption frequences of the electronic transitions of the compounds were correlated using a total solvatochromic equation of the form: $\nu_{max} = \nu_0 + s\pi^* + a\alpha + b\beta$, where π^* is the measure of solvent polarity. β represents the scale of solvent hydrogen bond acceptor basicities and α represents the scale of solvent hydrogen bond donor acidities. Correlation of spectroscopic data was carried out by means of multiple linear regression analysis.

KEY WORDS: 2-aminobenzimidazoles, ultraviolet absorption maximum, protic and aprotic solvents.

INTRODUCTION

Benzimidazole and its derivatives have received much attention because of their biological activity and commercial application. They are present in many naturally occuring products and various drugs. Some of these compounds have antibacterial, antifungal, antiviral, antiinflammatory, antihypertensive, arteriosclerosis and anti-HIV activities (1-10).

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The newly synthesized benzimidazole derivatives investigated in the present work possess large antibacterial and selective antifungal activities against different strains of bacteria and fungi (11). For the further application of these biologically active compounds, it was necessary to investigate their physico-chemical characteristics. The aim of this work was to investigate the effect of solvents polarity and their proton-donor ability on electronic absorption spectra of some 2-aminobenzimidazoles.

EXPERIMENTAL

Reagents and apparatus

In this work, three newly synthesized benzimidazole derivatives were studied:
- 1-(3-methylbenzyl)-2-aminobenzimidazole (*m*-CH_3),
- 1-(3-methoxybenzyl)-2-aminobenzimidazole (*m*-OCH_3) and
- 1-(3-chlorobenzyl)-2-aminobenzimidazole (*m*-Cl).

The investigated compounds were synthesized by the procedure described elsewhere (11). They were characterized by determining melting points and recording IR and NMR spectra, as well as by elemental analysis. The stock solutions of benzimidazole derivatives were prepared in water, ethanol, methanol, *n*-propanol, *i*-propanol, chloroform, dioxane, dimethylformamide(DMF) and dimethylsulfoxide(DMSO) ($c=5\cdot10^{-5}$ mol·dm^{-3}).

All chemicals used were of analytical grade purity.

Electronic absorption spectra (UV/VIS) were recorded on a Varian Carry 219 Spectrophotometer in 1.00-cm silica cells at 25±0.1°C.

RESULTS AND DISCUSSION

Electronic absorption spectra of *m*-CH_3, *m*-OCH_3 and *m*-Cl were recorded in the solvents of different polarity and proton-donor ability and are shown in Figure 1. The characteristic absorption maxima are shifted in dependence of the solvent nature.

The effect of solvent polarity and hydrogen bonding on absorption spectra are interpreted by means of the linear solvation energy relationship (LSER) concept by Kamlet and Taft (12,13), using a general solvatochromic equation (1), of the form:

$$\nu_{max} = \nu_0 + s\,\pi^* + a\,\alpha + b\beta \qquad (1)$$

where α, β and π^* are solvatochromic parameters and ***s***, ***a*** and ***b*** are solvatochromic coefficients. π^* is an index of solvent polarity: $\pi^*=0.00$ for ciclohexane and $\pi^*=1.00$ for DMSO, α represents the hydrogen bond donator ability (HBD-acidity) and β is the hydrogen bond acceptor ability (HBA-basicity).

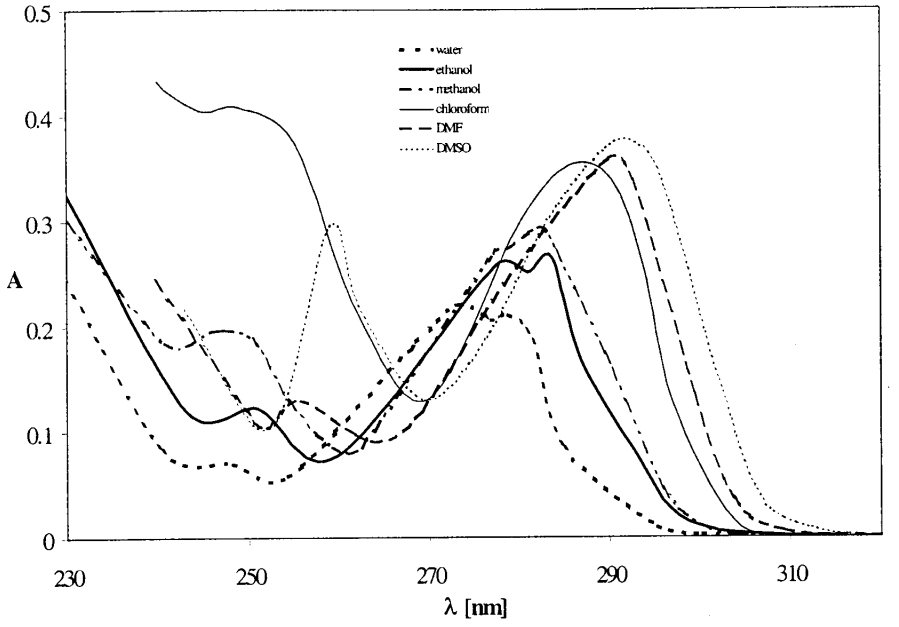

Fig. 1. Absorption spectra of 1-(3-chlorobenzyl)-2-aminobenzimidazole (*m*-Cl) in solvents of different proton-donor capacity

The absorption frequences ν_{max} ($\nu_{max} = 1/\lambda_{max}$) for the investigated compounds in different solvents are listed in Table 1. The characteristic absorpton maxima of 2-amino-benzimidazoles are results of n-π^* electronic spectral transitions.

Table 1. Electronic spectral data for investigated compounds

Compound	$\nu_{max} \times 10^3\ s^{-1}$								
	H_2O	MeOH	EtOH	nPrOH	iPrOH	Diox.	$CHCl_3$	DMF	DMSO
m-CH_3	3.58	3.59	3.53	3.52	3.51	3.52	3.48	3.46	3.42
m-OCH_3	3.60	3.57	3.55	3.54	3.53	3.54	3.52	3.47	3.44
m-Cl	3.58	3.55	3.53	3.52	3.51	3.52	3.50	3.47	3.45

The multiple linear regression equations (Table 2) correlate electronic spectral data (ν_{max}) with the solvatochromic parameters π^*, α and β for protic solvents, using the LSER (equation 1). It can be concluded that in the case when alcohols are used as solvents, the most effective parameter on the absorption frequency is the solvatochromic parameter β.

The correlations of absorption frequences with solvatochromic parameters π^* and β for aprotic solvents are given in Table 3. Very similar relationships are found for all investigated compounds in aprotic solvents which indicates a small substituent effect in the investigated aprotic solvents.

Table 2. Correlations of electronic spectral data with solvatochromic parameters for protic solvents (alcohols)

Compound	Equation
m-CH_3	$\nu_{max} = 3.448 - 0.070\ \pi^* - 0.059\ \alpha + 0.195\ \beta\ (10^3\ s^{-1})$ (r = 0.994; s = 0.007; n = 4)
m-OCH_3	$\nu_{max} = 3.446 - 0.114\ \pi^* - 0.049\ \alpha + 0.243\ \beta\ (10^3\ s^{-1})$ (r = 0.998; s = 0.034; n = 4)
m-Cl	$\nu_{max} = 3.572 - 0.001\ \pi^* - 0.075\ \alpha + 0.023\ \beta\ (10^3\ s^{-1})$ (r = 0.998; s = 0.003; n = 4)

Table 3. Correlations of electronic spectral data with solvatochromic parameters for aprotic solvents

Compound	Equation
m-CH_3	$\nu_{max} = 3.651 - 0.296\ \pi^* + 0.331\ \beta\ (10^3\ s^{-1})$ (r = 0.993; s = 0.008; n = 4)
m-OCH_3	$\nu_{max} = 3.662 - 0.251\ \pi^* + 0.035\ \beta\ (10^3\ s^{-1})$ (r = 0.999; s = 0.025; n = 4)
m-Cl	$\nu_{max} = 3.609 - 0.189\ \pi^* + 0.038\ \beta\ (10^3\ s^{-1})$ (r = 1.00; s = 0.00; n = 4)

The relationships of the absorption frequencies with the dielectric constants of protic and aprotic solvents are investigated and the results are shown in Table 4. For all equations is characteristic a high correlation coefficient.

Table 4. Relationships of absorption frequences with dielectric constants for 2-aminobenzimidazoles

Compound	Equation
	Protic solvents
m-CH_3	$\nu_{max} = 3.478 + 1.936\ D\ (10^3\ s^{-1})$ (r = 0.969; s = 0.056; n = 5)
m-OCH_3	$\nu_{max} = 3.484 + 2.657\ D\ (10^3\ s^{-1})$ (r = 0.990; s = 0.006; n = 5)
m-Cl	$\nu_{max} = 3.464 + 2.657\ D\ (10^3\ s^{-1})$ (r = 0.991; s = 0.015; n = 5)
Compound	Aprotic solvents
m-CH_3	$\nu_{max} = 3.502 + 0.002\ D\ (10^3\ s^{-1})$ (r = 0.902; s = 0.028; n = 4)
m-OCH_3	$\nu_{max} = 3.537 + 0.002\ D\ (10^3\ s^{-1})$ (r = 0.985; s = 0.025; n = 4)
m-Cl	$\nu_{max} = 3.515 + 0.001\ D\ (10^3\ s^{-1})$ (r = 0.987; s = 0.038; n = 4)

The equations are very similar and have similar values of solvatochromic coefficients (slopes) and constant coefficients (y-intercept). This could be explained by a small effect of substituent on benzene ring on spectral characteristic of the molecule as a whole.

CONCLUSIONS

The characteristic absorpton maxima of 2-aminobenzimidazoles are results of n-π^* electronic spectral transitions. Electronic spectral data (ν_{max}) are in correlation with solvatochromic parameters π^*, α and β for protic and aprotic solvents. For the protic solvents (alcohols) the most effective parameter on the absorption frequency is the solvatochromic parameter β. Very similar relationships are found for aprotic solvents, which indicates a small substituent effect in aprotic solvents.

The relationships of the absorption frequencies with the dielectric constants of protic and aprotic solvents are characterized by high correlation coefficients. The equations are very similar, and they have close values of solvatochromic coefficients (slopes) and constant coefficients (y-intercept). this could be explained by a small effect of the substituent in the benzene ring on spectral characteristic of the molecule as a whole.

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УТИЦАЈ РАСТВАРАЧА НА ЕЛЕКТРОНСКЕ АПСОРПЦИОНЕ СПЕКТРЕ НЕКИХ 2-АМИНОБЕНЗИМИДАЗОЛА

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Испитани су електронски апсорпциони спектри 1-(3-метилбензил)-2-аминобензимидазола, 1-(3-метоксибензил)-2-аминобензимидазола и 1-(3-хлоробензил)-2-аминобензимидазола у растварачима различитих поларности и протон-донорских особина. Ефекат поларности растварача и могућности стварања водоничне везе на апсорпционе спектре интерпретиран је помоћу концепта линеарног односа солватационе енергије (linear solvation energy relationship-LSER) који су поставили Камлет и Тафт. Приказане су корелације апсорпционих фреквенција и солватохромних параметара α, β и π^* за протичне и апротичне растваче. Поред тога, испитане су зависности између апсорпционих фреквенција и диелектричних константи за протичне и апротичне растваче.

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