Innovation Center of the Faculty of Technology and Metallurgy, Belgrade, Serbia

SOLVATOCHROMIC STUDY OF NOVEL BENZYLIDENEHYDANTOIN AS A MOLECULAR PHOTOCHROMIC SWITCH

Kristina Gak

- Molecular photochromic switches represent an intriguing class of organic molecules that can be reversibly interconverted between two stable states by light.

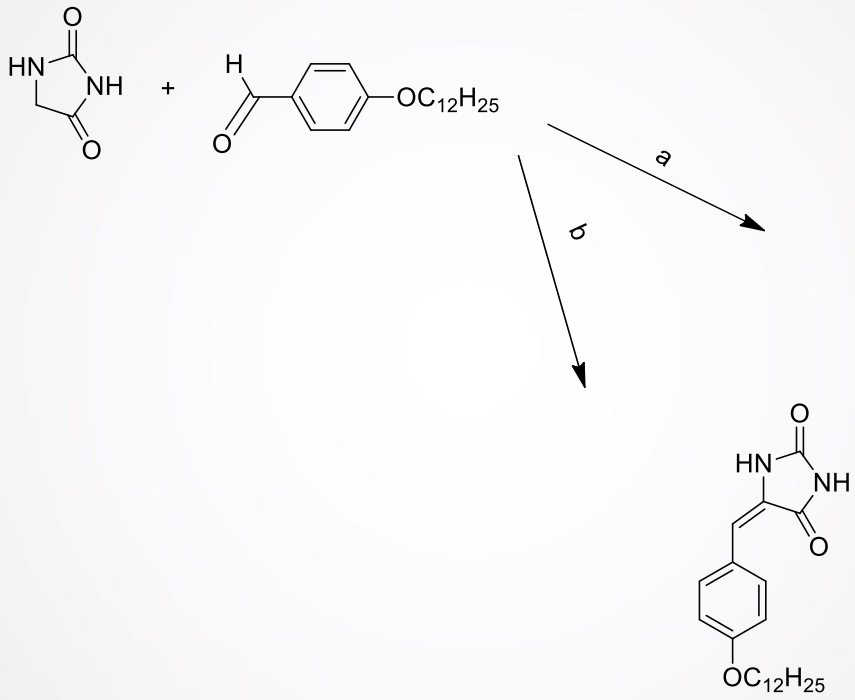
- The resulting change may be the consequence of trans→cis photoisomerization, photocyclization or a combination of both.

- With the aim of development of novel light-sensitive materials, the present study reports two different ways of synthesis of (Z)-5-(4-dodecyloxy)benzylidene)imidazolidine-2,4-dione and its structural characterization by various spectroscopic techniques.

- Besides, the solvatochromic behavior of new benzylidenehydantoin derivative has been evaluated by recording the absorption spectra in the selected solvent set and evaluating effects of the specific and nonspecific solvent–solute interactions on the absorption maxima shifts using linear solvatation energy relationship, i.e. equations proposed by Kamlet-Taft and Katalan.

- The preliminary results of this investigation represent promising starting point for design of novel photoactive materials with a broad spectrum of applications.

Synthesis of Z-(5-(4-dodecyloxy)benzylidene)imidazolidine-2,4-dione:



Scheme 1: Reagents and conditions: (a) piperidine, 130 ^{o}C; (b) piperidine, 5 min, 200 W.

Solvent effects on UV-Vis absorption maxima:

- The UV-Vis absorption spectrum of Z-(5-(4-dodecyloxy)benzylidene)imidazolidine-2,4-dione is characterized by two broad bands in the 200-220 nm and 330-350 nm, respectively, regardless of the polarity and acidic/basic properties of the solvent.

- The higher magnitude of peaks assigned to carbonyl chromophore in position 4 of the imidazolidine ring and greater delocalization of electronic cloud is observed and further analyzed in detail.

- The UV-Vis absorption spectra revealed that the intensity of the absorption band placed in the 330-350 spectral range increases with the enhancing solvent polarity and its acidic properties.

- Because previously reported results clearly confirmed the hypothesis that electron distribution and stereochemistry are important in the establishing interactions between compound and its environment, the effect of solvent dipolarity/polarizability and solvent/solute hydrogen bonding interactions were further analyzed by means of the linear solvatation energy relationship concepts proposed by Kamlet-Taft and Catalán.

- The effects of the nonspecific and specific solvent interactions on the investigated 5-(4-dodecyloxybenzylidene)hydantoin were interpreted using the general solvatation equations:

$$\nu_{max} = \nu_{max0} + a\alpha + b\beta + s\pi^* \qquad (1)$$

$$\nu_{max} = \nu_{max0} + a\mathrm{SA} + b\mathrm{SB} + c\mathrm{SP} + d\mathrm{SdP} \qquad (2)$$

- The results of multiple regressions presented in Tables 1,2 and Figure 1,2 indicated that the absorption frequencies of the investigated compound in the selected solvent set, showed satisfactory correlation with β, α, π parameters.

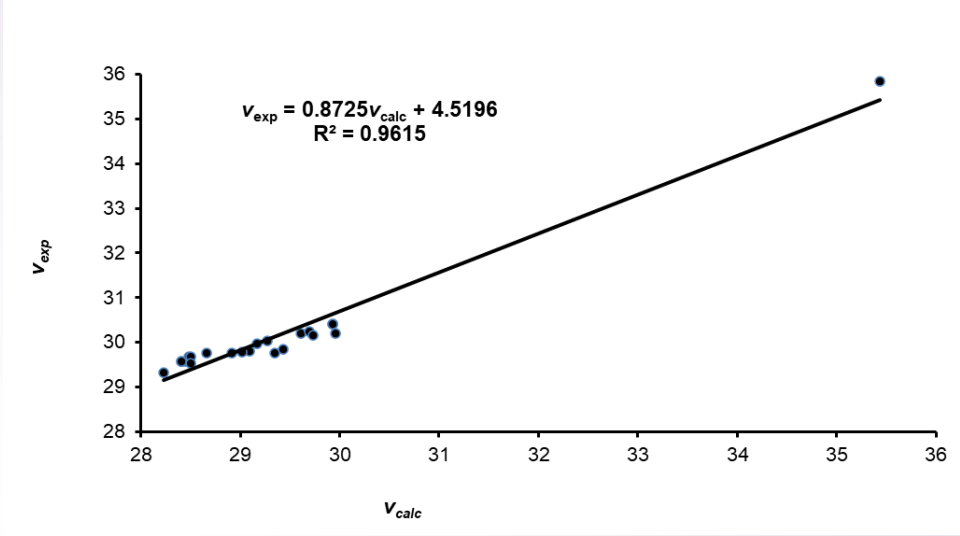


Figure 1: *Comparison of experimental frequencies and the frequencies determined by Kamlet-Taft equation.*

Table 1: Regression fits to solvatochromic parameters and percentage contribution of solvatochromic parameters:

No.	v_0 ($10^3 cm^{-1}$)	s ($10^3 cm^{-1}$)	b ($10^3 cm^{-1}$)	a ($10^3 cm^{-1}$)	R[a]	s[b]	F[c]	Solvent used[d]	Pπ* (%)	Pβ (%)	Pα (%)
1	30.79 (±0.18)	-0.32 (±0.25)	-0.69 (±0.18)	-0.52 (±0.15)	0.967	0.098	39	3,5,8,9,13-16, 18-21	20.9	45.1	33.9

- As can be seen from the Tables 1 and 2, the values of the correlation coefficient R determined with confidence level of 95% for both models are greater than 0.95.

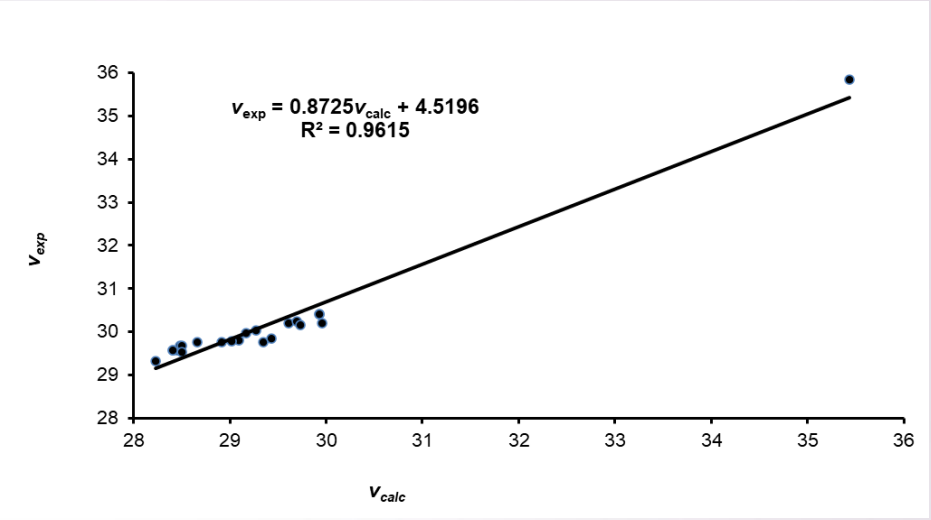


Figure 2. Comparison of experimental frequencies and the frequencies determined by Kamlet-Taft equation.

Table 2. Regression fits to solvatochromic parameters (2)

No.	v_0 ($10^3 cm^{-1}$)	a ($10^3 cm^{-1}$)	b ($10^3 cm^{-1}$)	c ($10^3 cm^{-1}$)	d ($10^3 cm^{-1}$)	R[a]	s[b]	F[c]	Solvent used[d]
1	32.09 (±0.09)	-0.26 (±0.05)	-2.25 (±0.24)	-1.57 (±0.09)	-0.18 (±0.09)	0.991	0.056	99	5-9,11-15,18,20

Conclusion:

- In this work, the classical and microwave-assisted synthesis of Z-(5-(4-dodecyloxy)benzylidene)imidazolidine-2,4-dione has been described. The chemical structure and purity have been confirmed by melting point, FTIR, ^{1}H NMR, ^{13}C NMR, UV-Vis spectroscopy, elemental analysis and thin layer chromatography.

- The satisfactory correlation of the ultraviolet absorption frequencies of the investigated Z-(5-(4-dodecyloxy)benzylidene)imidazolidine-2,4-dione with Kamlet-Taft and Catalán general solvatochromic equation indicates that the selected models give a correct interpretation of the linear solvatation energy relationships of the complex hydantoin system in the solvents used. This demonstrates that an equation with three or four solvatochromic parameters can be used to evaluate the effects on both types of hydrogen bonding and the solvent dipolarity/polarizability effects for potentially light-sensitive hydantoins.

- For this reason, it is considered that the results presented in this work may be utilized to quantitatively separate the overall solvent effect into specific and nonspecific contributions using LSER method.