

# REVERZIBILNI HALOGEN SUPSTITUISANI BENZILIDENHIDANTOINSKI MOLEKULSKI PREKIDAČI

## A REVERSIBLE MOLECULAR SWITCHES BASED ON HALOGEN SUBSTITUTED BENZYLIDENEHYDANTOINS

Kristina GAK SIMIĆ<sup>1\*</sup>, Anita LAZIĆ<sup>1</sup>, Nemanja TRIŠOVIĆ<sup>2</sup>,  
Nataša VALENTIĆ<sup>2</sup>, Luka MATOVIĆ<sup>1</sup>

<sup>1</sup> Innovation Center of the Faculty of Technology and Metallurgy, Belgrade, Serbia

<sup>2</sup> Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia

*Molekulski prekidači koji se mogu reverzibilno prevoditi iz jednog stabilnog stanja u drugo pod dejstvom nekog spoljašnjeg faktora, uveliko se primenjuju u proizvodnji različitih optičkih i elektronskih uređaja, pametnih materijala kao i raznovrsnih materijala sa biološkom primenom. Bistabilni fotokromni organski molekuli, predstavljaju akraaktivne materijale za proizvodnju molekulskih prekidača zahvaljujući svojoj strukturnoj raznovrsnosti, molekulskim konformacijama, elektronskim karakteristikama i mogućnosti prevođenja iz jednog stabilnog stanja u drugo pod dejstvom svetlosti. U ovom radu, proučavana je mogućnost primene halogen supstituisanih benzilidenhidantoina u proizvodnji fotosenzitivnih materijala kao i njihova solvatohromna svojstva određivanjem odgovarajućih apsorpcionih maksimuma u odabranom setu rastvarača, a takođe su analizirani specifični i nespecifični efekti rastvarača na pomeranje apsorpcionih maksimuma primenom Kamlet-Taftove i Katalanove jednačine. Preliminarni rezultati ovog istraživanja predstavljaju dobru polaznu tačku u dizajniranju novih fotoaktivnih materijala sa širokim spektrom primene.*

**Ključne reči:** molekulski prekidači; halogen supstituisani benzilidenhidantoini; solvatohromizam; fotoaktivni materijali.

*Molecular switches that can undertake reversible switching between two or more different states due to an external triggering stimulus are employed in the fabrication of various optoelectronic devices and smart materials and also found many applications in sensing, molecular self-assembly and photo-controlled biological systems. Photochromic organic molecules possessing bistable characteristics, represent attractive materials for the design of molecular switches owing to their considerable structural diversity, molecular conformations, electronic structures, and the possibility to reversibly alter from one state to another by external stimulations such as light irradiation. In this article, we explore the potential of halogen substituted benzylidenehydantoin-based molecules as novel light-sensitive materials and their solvatochromic behavior 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 solvation energy relationship, i.e. equations proposed by Kamlet-Taft and Katalan.. The preliminary results of this study will be promising starting point for design of novel photoactive materials with a broad spectrum of applications.*

**Key words:** molecular switches; halogen substituted benzylidenehydantoin; solvatochromism; photoactive materials.

## 1 Introduction

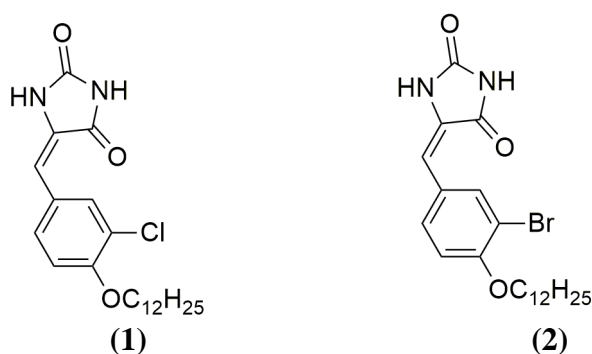
Over the last few years, stimuli-responsive materials are attracting extensive concern as they offer the opportunity to transform external inputs such as light into a functionality by control at the molecular level [1]. They are widely used in biology and information technology and have developed into important components of advanced materials [2]. The framework of such systems are molecules

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\* Corresponding author, e-mail: kgak@tmf.bg.ac.rs

that are able to reversibly photoisomerize between two states, best known as photoswitches. Photoswitches are commonly small molecules, which necessitate high-energy photons for isomerization in at least one direction. Traditionally, molecules such as spiropyrans, stilbenes, azobenzenes, and diarylethenes are of particular interest for constructing reversible photosensitive systems [3].

To design new functional materials with suitable properties, it is therefore preferable to be able to impact the structure, interactions and dynamics on the molecular level by adequate external stimuli which can be employed to trigger selectively with a high space and time resolution. An essential framework in this regard are externally addressable and responsive molecular building blocks that can be reversibly switched between various well-defined states differing in their chemical and/or physical properties. The interconversion between these states permits the user to influence the molecular environment by modifying intermolecular interactions resulting in optimized functionality of the whole system, more precisely adequately transmitting a response at the molecular level to the macroscopic world [1]. Accordingly, it is highly necessary to examine new molecules to rich the structure of desirable molecular switches, meeting the different requirements for application [4]. Here we report a novel photoresponsive halogenated molecular switches (Figure 1) differing from the prototypical compounds mostly reported. Addition of one methylene spacer between rigid hydantoin (imidazolidine-2,4-dione) core and planar halogen substituted phenyl framework allow structural diversity of photoresponsive chiral molecular switches. To evaluate the ability of the investigated compound to interact with its environment, the effects of specific and nonspecific interactions on the shifts of absorption maxima were considered by means of the linear solvation energy relationship concepts established by Kamlet-Taft and Catalán.

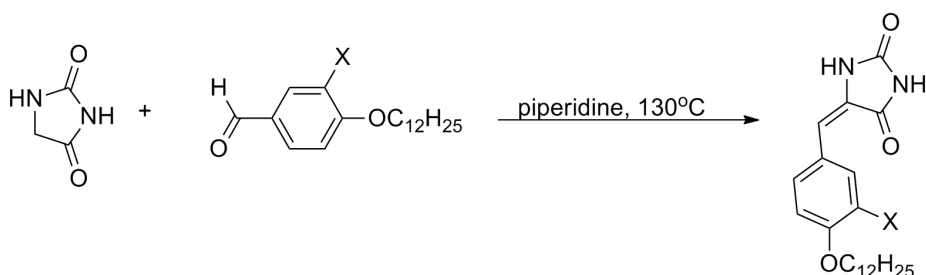
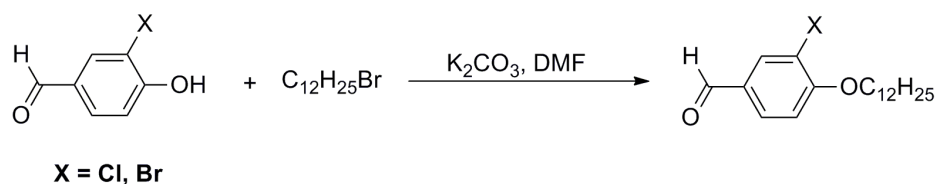


**Figure 1.** Chemical structure of the investigated compounds.

## 2 Experimental

### 2.1 General

Chemical used in the synthesis of investigated compound were obtained from Sigma Aldrich chemical company and were used without further purification. Solvents used were of spectroscopic grade. Novel halogen substituted benzylidenehydantoin (1,2) were prepared according modified literature procedure [5] applying synthesis pathway illustrated on Scheme 1. The IR spectra were recorded using a Bomem MB-Series Fourier Transformer-Infrared (FT-IR) spectrophotometer in the form of KBr pellets. The ultraviolet-visible (UV-Vis) absorption spectra were recorded on a Shimadzu 1700 spectrophotometer in the region 300–600 nm. The spectra were run in spectroquality solvents (Fluka) using a concentration of  $1 \times 10^{-5}$  moldm<sup>-3</sup>. All melting points were determined on Electrothermal apparatus and are expressed in degree Celsius. The elemental analysis of the investigated compound was carried out by standard analytical micromethods using an Elemental Vario EL III microanalyzer.



**Scheme 1.** Synthesis of the investigated compounds

2.2. Synthesis of (*E*)-5-(3-Chloro-4-(dodecyloxy)benzylidene)imidazolidine-2,4-dione (**1**) and (*E*)-5-(3-Bromo-4-(dodecyloxy)benzylidene)imidazolidine-2,4-dione (**2**):

Imidazolidine-2,4-dione (0.068 mol; 0.68 g) and 4-dodecyloxybenzaldehyde (0.068 mol; 2g) were dissolved in piperidine (5 ml) and heated at 130 °C until the reaction completed. The obtained reaction mixture was poured into lukewarm water (30 ml) and acidified with concentrated HCl. Achieved products were recrystallized from ethanol [5].

**(*E*)-5-(3-Chloro-4-(dodecyloxy)benzylidene)imidazolidine-2,4-dione (**1**):** White crystalline solid; Yield: 65%; m.p. 166-169 °C; FT-IR/ATR: (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 2952, 2915, 2849, 1684, 1597, 1578, 1498, 1469, 1459, 1402, 1318, 1286, 1262, 1198, 1166, 1072, 1058, 1030, 990, 954, 923, 882, 818, 718, 687, 649, 560, 511, 492; Elemental analysis calculated for  $\text{C}_{22}\text{H}_{31}\text{N}_2\text{O}_3\text{Cl}$  (406.95): C, 64.93, H, 7.68, N, 6.88. Found: C, 64.93, H, 7.86, N, 6.70.

**(*E*)-5-(3-Bromo-4-(dodecyloxy)benzylidene)imidazolidine-2,4-dione (**2**):** White crystalline solid; Yield: 65%; m.p. 172-175 °C; FT-IR/ATR: (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 2952, 2914, 2849, 1683, 1595, 1578, 1561, 1498, 1470, 1460, 1402, 1318, 1285, 1263, 1196, 1164, 1072, 1058, 1047, 1030, 990, 954, 921, 882, 818, 718, 687, 668, 649, 560, 440, 433; Elemental analysis calculated for  $\text{C}_{22}\text{H}_{31}\text{N}_2\text{O}_3\text{Br}$  (451.40): C, 58.54, H, 6.92, N, 6.21. Found: C, 58.54, H, 7.06, N, 6.07.

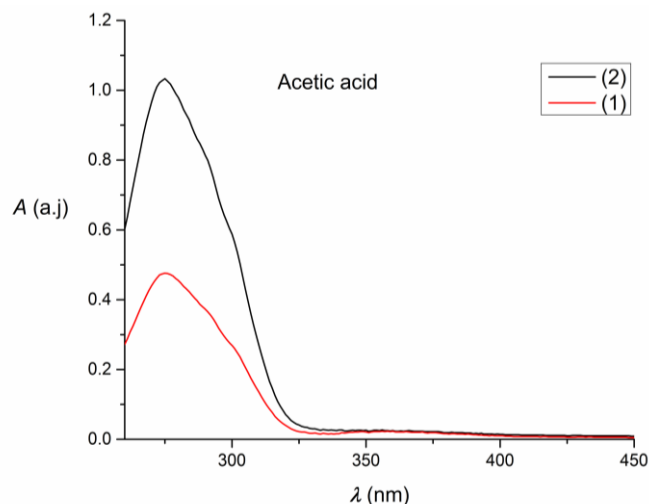
### 3 Results and discussion

In the present work, some recently developed compounds (**1,2**) bearing a methylene spacer between rigid hydantoin core and *p*-alkoxy halogenated planar phenyl core were obtained in good yields by and completely structurally characterized by appropriate spectroscopic technics. The results of FTIR/ATR spectroscopy validate the structure of the above-mentioned compounds, showing two strong peaks between 3000-2900  $\text{cm}^{-1}$ , that were assigned to the NH of the amide and imide groups. Absorption bands between 1680 and 1600  $\text{cm}^{-1}$  characterize the asymmetric and symmetric stretching of the carbonyl groups of the hydantoin ring.

#### 3.1 Solvent effects on UV-Vis absorption maxima

UV-Vis spectroscopy of two novel imidazolidine-2,4-dione derivatives was accomplished as an attempt to comprehend the influence of numerous polarity effects of the surroundings on the physicochemical properties of the molecules, as it stands as a competent tool for structural characterization. Early reported solvatochromic studies of hydantoin derivatives and its analogs evidently indicated that the absorption spectra show similar experimental features, i.e. there are one or two sharp peaks corresponding to  $\pi \rightarrow \pi^*$  transition. The solvatochromic behavior of the novel light-sensitive compounds was investigated in 20 solvents of different polarity (Table 1). The UV-Vis spectra displayed no dependence on the compound concentration, abandoned on this way the formation of di-

mers or higher aggregates [7]. According to obtained results, all UV-Vis absorption spectra demonstrated that the intensity of the absorption band placed in the 270-300 nm spectral range increases with the enhance of solvent polarity and its acidic properties [6]. Also, in aprotic solvents, investigated compounds possess a single absorption band in the visible region, while in protic solvents this band is considerably broadened and is split into two bands in more acidic media. In an instance of split bands, the UV-Vis band at longest wavelength was employed for the correlation analysis [7]. Representative spectra in acetic acid is illustrated in Figure 2.



**Figure 2.** UV-Vis absorption spectra of investigated compounds.

**Table 1.** Absorption maxima of the investigated compounds in selected solvent set

Solvent	$\lambda$ (nm)-(1)	$\lambda$ (nm)-(2)
1. Acetic acid	275	276
2. Acetonitrile	272	273
3. 1-Butanol	274	274
4. 2-Butanol	275	276
5. Chloroform	282	281
6. Dichloromethane	275	274
7. Diisopropyl ether	271	274
8. 1,4-Dioxane	272	273
9. Dimethylformamide	274	274
10. Dimethylsulfoxide	272	275
11. Ethylacetate	272	272
12. Ethanol	275	274
13. 1-Propanol	275	276
14. Methyl acetate	271	272
15. Methanol	274	273
16. 2-Methyl-1-Propanol	274	274
17. N,N-Dimethylacetamide	274	273
18. N-Methylformamide	292	296
19. Terc-Butanol	274	275
20. Toluene	290	291

During the past decades, the Kamlet–Taft approach has been contentedly applied to separate the influence of non-specific chemical interactions, including electrostatic effects (dipolarity/polarizability), from specific interactions, i.e. hydrogen-bonding, which concerns to the molecular structure of a compound. The frequently employed simplified Kamlet–Taft equation applied to the UV/Vis absorption shift ( $v_{\max}$ ) of a solute is taking into account by Equation (1), where  $v_{\max 0}$  is the solute property of a reference system, such as, a non-polar medium,  $\alpha$  describes the HBD (hydrogen-bond donating) ability,  $\beta$  the HBA (hydrogen-bond accepting) ability,  $\pi^*$  the dipolarity/polarizability of the solvents and  $a$ ,  $b$  and  $s$  are solvent-independent correlation coefficients that implies the contribution of various solvent effects to the UV-Vis absorption shift. To overcome the disadvantages of the Kamlet-Taft equation (dipolarity and polarizability of the solvent are included in one parameter), Catalán established three alternative empirical polarity scales: *SA*, *SB* and *SPP*, which are formally related to the Kamlet–Taft parameters  $\alpha$ ,  $\beta$  and  $\pi^*$ , respectively, while in 2004 Catalán and Hopf reported an important fourth scale—the polarizability parameter *SP* measuring gradual differences in the surrounding’s polarizability. The superiority of Catalán’s concept is that each solvatochromic solvent parameter is established on a pair of well-defined reference homomorph solvatochromic probes. Another multiparameter equation, analogous to Equation (1), which involves two parameters for specific and two parameters for non-specific interactions (Equation (2)), has been pointed out that the *SPP* and *SP* scales are actually not independent of each other [7]:

$$v_{\max} = v_{\max 0} + a\alpha + b\beta + s\pi^* \quad (1)$$

$$v_{\max} = v_{\max 0} + aSA + bSB + cSP + dSdP \quad (2)$$

**Table 2.** Solvent parameters

Solvent	Kamlet-Taft			Catalán			
	$\pi^*$	$\beta$	$\alpha$	<i>SA</i>	<i>SB</i>	<i>SP</i>	<i>SdP</i>
1. Acetic acid	0.64	0.45	1.12	0.689	0.390	0.651	0.676
2. Acetonitrile	0.75	0.31	0.19	0.044	0.286	0.645	0.974
3. 1-Butanol	0.47	0.88	0.79	0.341	0.809	0.674	0.655
4. 2-Butanol	0.40	0.80	0.69	0.221	0.888	0.656	0.706
5. Chloroform	0.58	0.00	0.44	0.047	0.071	0.783	0.614
6. Dichloromethane	0.82	0.00	0.30	0.040	0.178	0.761	0.769
7. Diisopropyl ether	0.27	0.49	0.00	/	/	/	/
8. 1,4-Dioxane	0.55	0.37	0.00	0.000	0.444	0.737	0.312
9. Dimethylformamide	0.88	0.69	0.00	0.031	0.613	0.759	0.977
10. Dimethylsulfoxide	1.00	0.76	0.00	0.072	0.647	0.830	1.00
11. Ethylacetate	0.55	0.45	0.00	0.000	0.542	0.656	0.603
12. Ethanol	0.54	0.77	0.83	0.400	0.658	0.633	0.783
13. 1-Propanol	0.52	0.90	0.78	0.367	0.782	0.658	0.748
14. Methyl acetate	0.60	0.42	0.00	0.000	0.527	0.645	0.637
15. Methanol	0.60	0.62	0.93	0.605	0.545	0.608	0.904
16. 2-Methyl-1-Propanol	0.41	0.93	0.41	0.000	0.590	0.710	0.630
17. <i>N,N</i> -Dimethylacetamide	0.88	0.76	0.00	0.028	0.650	0.763	0.987
18. <i>N</i> -Methylformamide	0.88	0.69	0.00	/	/	/	/
19. Terc-Butanol	0.41	1.01	0.68	0.145	0.928	0.632	0.732
20. Toluene	0.54	0.11	0.00	0.000	0.128	0.782	0.284

From this perspective, we have designed two novel structurally related light-sensitive compounds demonstrating diverse sensitivities towards electrostatic effects. To review this sensitivity and apart the individual solvation effects, the solvatochromic properties of these compounds were investigated in detail, and the coefficients of the individual interaction contributions were determined by using multiple correlation analysis [6].

**Table 3.** Regression fits to solvatochromic parameters (1) and percentage contribution of solvatochromic parameters

No.	$\nu_0$ ( $10^3\text{cm}^{-1}$ )	$s$ ( $10^3\text{cm}^{-1}$ )	$b$ ( $10^3\text{cm}^{-1}$ )	$a$ ( $10^3\text{cm}^{-1}$ )	$R^a$	$s^b$	$F^c$	$P\pi$ (%)	$P\beta$ (%)	$P\alpha$ (%)
1	33.52 ( $\pm 0.37$ )	2.13 ( $\pm 0.45$ )	1.45 ( $\pm 0.22$ )	0.84 ( $\pm 0.22$ )	0.954	0.221	27	48.19	32.81	19.00
2	33.30 ( $\pm 0.47$ )	1.86 ( $\pm 0.49$ )	1.96 ( $\pm 0.33$ )	0.76 ( $\pm 0.24$ )	0.928	0.266	17	40.61	42.79	16.59

<sup>a</sup>Correlation coefficient; <sup>b</sup>Standard error of the estimate; <sup>c</sup>Fisher's test;

**Table 4.** Regression fits to solvatochromic parameters (2)

No.	$\nu_0$ ( $10^3\text{cm}^{-1}$ )	$a$ ( $10^3\text{cm}^{-1}$ )	$b$ ( $10^3\text{cm}^{-1}$ )	$c$ ( $10^3\text{cm}^{-1}$ )	$d$ ( $10^3\text{cm}^{-1}$ )	$R^a$	$s^b$	$F^c$
1	39.80 ( $\pm 1.24$ )	-7.12 ( $\pm 1.59$ )	1.63 ( $\pm 0.40$ )	0.92 ( $\pm 0.35$ )	-1.72 ( $\pm 0.47$ )	0.945	0.257	17
2	38.95 ( $\pm 0.85$ )	-6.67 ( $\pm 1.17$ )	1.73 ( $\pm 0.34$ )	1.78 ( $\pm 0.42$ )	-1.74 ( $\pm 0.43$ )	0.961	0.224	22

<sup>a</sup>Correlation coefficient; <sup>b</sup>Standard error of the estimate; <sup>c</sup>Fisher's test;

The achieved results of multiple regressions illustrated in Tables 3 and 4, indicated that the absorption frequencies of the investigated compounds in the selected solvent set, showed satisfactory correlation with  $\beta$ ,  $\alpha$ ,  $\pi^*$  parameters. The positive sign of the coefficient  $s$  in the total solvatochromic equations denotes a hypsochromic shift with enhancing solvent polarity/polarizability. In accordance with negative solvatochromism of the analyzed compounds are the positive signs of regression coefficient  $a$  and  $b$  denoting stabilization of the electronic excited state relative to ground state. The percentage contributions of solvatochromic parameters (Table 3) indicate that solvatochromism in general is the consequence of solvent dipolarity/polarizability rather than acidity and basicity. As can be seen from the Tables 3 and 4, the values of the correlation coefficient  $R$  determined with confidence level of 95% for both models are about 0.95. Based on this and other statistical indicators, it can be concluded that the selected equations are suitable for the analysis of the solvatochromism of halogen substituted 5-benzylidene hydantoin derivatives.

## 4 Conclusion

In this paper, two novel halogenated 5-benzylidenehydantoin derivatives were synthesized rigid hydantoin core and disubstituted planar phenyl core. The chemical structure and purity of these literature-unknown compounds have been confirmed by melting point, FTIR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, UV-Vis spectroscopy, elemental analysis and thin layer chromatography. The satisfactory correlation of the ultraviolet absorption frequencies of the investigated compounds with linear solvation models of Kamlet-Taft and Catalán indicates that the selected models give a correct interpretation of the linear solvation energy relationships of the complex hydantoin system in the used solvents. This also confirms 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 halogenated 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.

## 5 References

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