

Thermochromism of a series of spiroindolinonaphthoxazines

S. Minkovska^{1*}, B. Jeliaskova², S. Rakovsky¹, T. Deligeorgiev²

¹ Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria

² Department of Chemistry and Pharmacy, Sofia University, 1 J. Bourchier Blvd., 1164 Sofia, Bulgaria

Received: October 7, 2015

Five spiroindolinonaphthoxazines, synthesized by the authors, bearing different substituents on the basic skeleton have been studied for their thermochromic properties in solvents of different polarity. The compounds were very polarizable, which led to equilibrium between their colourless closed and coloured open forms in the absence of light at temperatures of 20–60°C. The thermal equilibrium between the ground state populations of the colourless and coloured forms was influenced by solvent polarity as well as by the nature of substituents. The concentration of the open form increased with solvent polarity.

Keywords: spirooxazines, thermochromism, thermodynamics

INTRODUCTION

Spiroindolinonaphthoxazines (SO) are among the most interesting functional dyes with potential application in many new technologies, such as data recording and storage, optical switching, displays, and nonlinear optics [1–15]. These compounds comprise two heterocyclic moieties linked by a tetrahedral spiro-carbon, which prevents them from being conjugated (Scheme 1). As a result, the spiro-compounds are almost colourless or pale yellow since the lowest electronic transition of the molecule occurs in the near UV region. Absorption of UV light gives rise to isomerisation caused by breakage of the spiro linkage C–O and subsequent rotation about the 2-2' C–C bond. The photoisomerized merocyanine (MC) dye molecules absorb in the visible part of the spectrum [1–7].

Irradiation strongly displaces the thermal equilibrium between both forms to the side of open-chain coloured photomerocyanine (MC), but it spontaneously converts to the colourless spiroform (SO) to reach a thermal equilibrium immediately after removing the light. We have recently reported [16–19] on the synthesis and photochromic and solvatochromic properties of a series of spiroindolinonaphthoxazines, both unsubstituted or bearing different substituents on the basic skeleton, and have estimated their metal ion coordination ability. On resuming our investigation of this series of compounds, in the present paper we describe a spectroscopic study of the effect of both solvent and structure on the thermochromic behaviour and equilibrium between SO and MC.

EXPERIMENTAL

Materials

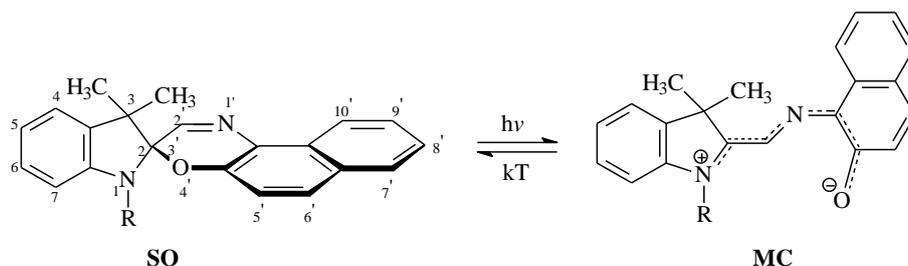
The molecules under study were five spiroindolinonaphthoxazines including four 5'-benzothiazolyl-substituted compounds: 1,3,3-trimethyl-5'-(2-benzothiazolyl)-spiro(indoline-2,3'-[3H]naphth[2,1-b][1,4]oxazine) (**1**); 1-butyl-3,3-dimethyl-5'-(2-benzothiazolyl)-spiro(indoline-2,3'-[3H]naphth[2,1-b][1,4]oxazine) (**2**); 1,3,3-trimethyl-5'-(2-benzothiazolyl)-spironaphth(indoline-2,3'-[3H]naphth[2,1-b][1,4]oxazine) (**3**), and 1-butyl-3,3-dimethyl-5'-(2-benzothiazolyl)-spironaphth(indoline-2,3'-[3H]naphth[2,1-b][1,4]oxazine) (**4**), and one 5'-hydroxy-substituted compound, 1,3,3-trimethyl-5'-hydroxyspiro(indoline-2,3'-[3H]naphth[2,1-b][1,4]oxazine) (**5**).

The compounds (Scheme 2) were prepared and characterized in our laboratory [16, 17]. Solvents were used after distillation.

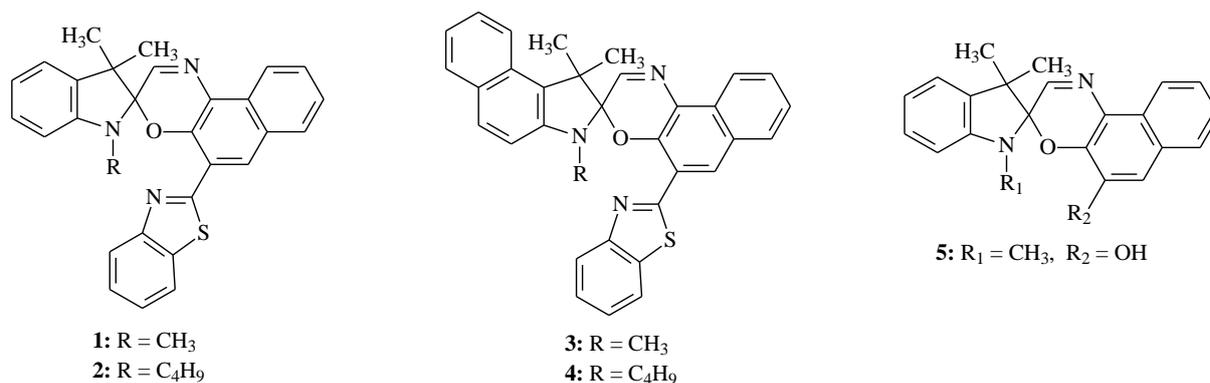
Instrumentation

Absorption spectra were taken on a Specord UV-Vis (Carl Zeiss, Jena) spectrophotometer using quartz cells. For absorption measurements at a varying temperature, the reaction cell was enclosed in a thermostatic water jacket placed inside spectrophotometer sample chamber. Spectral changes were recorded at a constant temperature and repeated use of the same solution at temperature intervals of *ca.* 5°C over a temperature range of about 30°C, and waiting for *ca.* 30 min after resetting the temperature control to allow the solution to attain a thermal equilibrium.

* To whom all correspondence should be sent
E-mail: stelasmin@ic.bas.bg



Scheme 1



Scheme 2

Molar absorption coefficients

Spectral characteristics of merocyanines **1–4** in acetone are listed in Table 1. Molar absorption coefficients (ϵ) were calculated by the expression $\epsilon = \text{colourability}/\Phi_c$ [10, 11] using own data on ‘colourability’ [17] and quantum yield values (Φ_c) of the colour-forming reaction in acetone [19].

Table 1. Quantum yield of photocolouration [19] and absorption characteristics of merocyanines 1–4 in acetone

Compound	Φ_c [18]	λ_{\max} , nm [16]	Colourability [16]	ϵ , M ⁻¹ .cm ⁻¹ *
1	0.75	640	58900	78500
2	0.80	642	72500	90600
3	0.85	655	67600	79500
4	0.90	656	72800	80900

*this paper

Provided the molar absorption coefficient of the **1–4** open forms is known, the absorbance in the visible region of the non-irradiated concentrated solutions was used in the present study to calculate the thermal equilibrium constant of the spirooxazine-merocyanine systems in acetone.

Equilibrium constant values

Thermal equilibrium constant values were determined in acetone by measuring the visible absorbance of the open form in relation to its maximum absorption $K_e = [\text{MC}]/[\text{SO}]$ (Table 1) where the spiroform does not absorb. The equilibrium concentra-

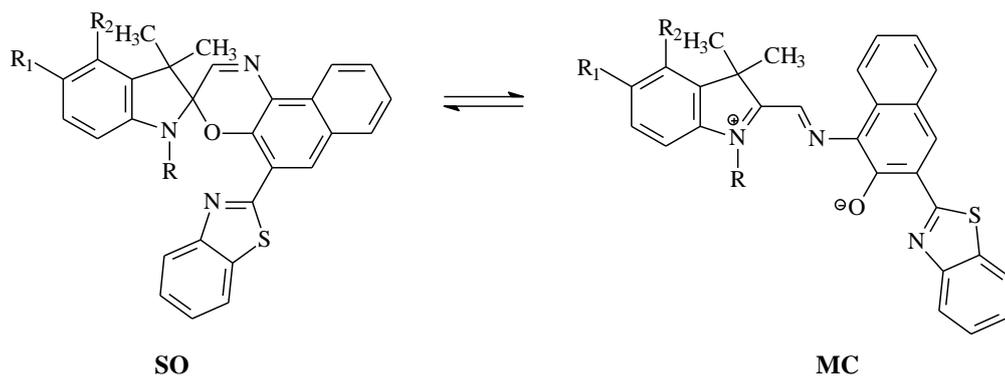
tion of the open form was derived from the equation $[\text{MC}] = A/\epsilon \cdot b$ using the absorbance A of MC at λ_{\max} and the molar absorptivity given in Table 1 for $b = 1$ cm. The equilibrium concentration of the closed spiroform was found by the expression $[\text{SO}] = c_{\text{SO}} - [\text{MC}]$, in which c_{SO} is the initial concentration of spirooxazine.

RESULTS AND DISCUSSION

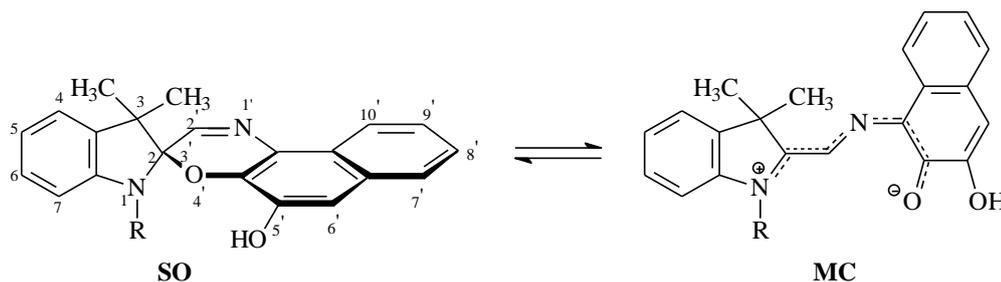
Thermal equilibrium

We have reported [16–19] that spiroindolinonaphthoxazines **1–5** in polar solvents like acetone, ethanol, or acetonitrile are capable of transformation to their open MC forms in the dark. As a result, solutions of **1–5** ($\sim 10^{-4}$ mol.dm⁻³) show a low intensity absorption band in the visible region at room temperature denoting that a thermal equilibrium $\text{SO} \leftrightarrow \text{MC}$ between their open and closed forms given in Schemes 3 and 4 is established. It is affected by changes in solvent polarity at room temperature in the absence of light.

Equilibrium constants derived from the equation $K_e = [\text{MC}]/[\text{SO}]$ at 25°C in acetone are reported in Table 2 compared with our recently published data [18] evaluated by using rate constants of the forward and back reaction ($K_e = k_1/k_{-1}$). An agreement with the latter can be considered satisfactory since variations of K_e for the same molecule are within the experimental error.



Scheme 3



Scheme 4

Table 2. Equilibrium constants, K_e , of SO \leftrightarrow MC in acetone (25°C)

SO	$K_e = k_f/k_r (\times 10^2)$ [18]	$K_e = [\text{MC}]/[\text{SO}]$ ($\times 10^2$)*
1	1.69	1.67
2	1.91	1.94
3	4.66	4.60
4	6.04	6.02

*this paper

The equilibrium constants presented in Table 2 increase on moving from **1** to **4** obviously due to suppression of the thermal ring closure reaction [17] when the benzene substituent in the indoline moiety of **1** and **2** is replaced by naphthalene in **3** and **4** and also when the N-imino CH_3 group in **1** and **3** is replaced by C_4H_9 in **2** and **4**. The combined effect of both substituents gives rise to a decreased rotational freedom upon cyclization yielding decreased k_r values, while the values of k_f remain unchanged [19].

Thermochromism

Visible absorption intensity of **1–5**, observed in polar solvents, increases as the temperature raises (Figs. 1–4), i.e. these molecules exhibit thermochromic properties. For the parent unsubstituted spiroindolinonaphthoxazine (Scheme 1) the coloured band is hardly detectable, even in a saturated solution of polar solvent at 47°C, the absorbance at 600 nm being less than 0.005.

The enthalpy of reaction was evaluated according to the Van't Hoff equation, $\text{dln}K_e/\text{d}(1/T) = -\Delta H^0/R$, by measuring the absorbance of the coloured form at several temperatures. Determinations were carried out in the temperature range of 20–80°C, using sample concentrations within $1 \times 10^{-4} \div 5 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$. The accuracy can be assumed $\pm 20\%$.

Plots of $\text{ln}K_e$ vs. $1/T$ for **1–4** in acetone are shown in figure 5 and the obtained ΔH^0 values are reported in Table 3 along with ΔG^0 and ΔS^0 calculated by means of the thermodynamic relationship $\Delta G^0 = \Delta H^0 - T\Delta S^0$. Variations of ΔH^0 from **1** to **4** are within the experimental error.

The reaction entropy is negative, which indicates [7, 8] that the positive contribution to entropy due to increased torsional freedom in the open structure is strongly compensated by solvent reorganization around the more polar merocyanine form.

The constants of thermal equilibrium between SO and MC of compound **5** could not be calculated because the ϵ value of its open form was not available and the same was valid about **1–4** in methanol, ethanol, *i*-propanol, *i*-butanol, and acetonitrile. In view of this we have calculated only the enthalpy changes ΔH^0 by using the expression $\text{dln}K_e/\text{d}(1/T) = -\Delta H/R$ (Table 4). Plots of $\text{ln}A$ vs. $1/T$ are shown in figures 6–10.

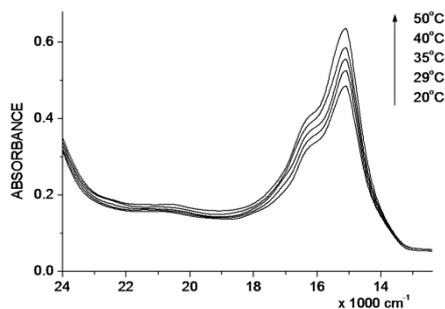


Fig. 1. Absorption spectra of 1×10^{-4} M acetone solution of compound **4**.

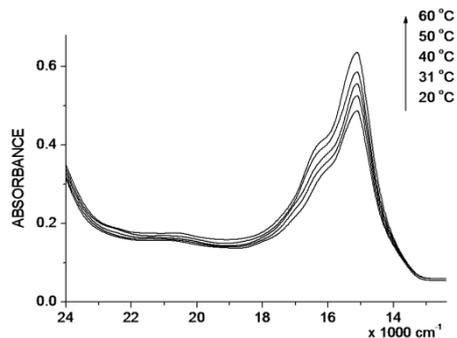


Fig. 2. Absorption spectra of 2.5×10^{-4} M methanol solution of compound **2**.

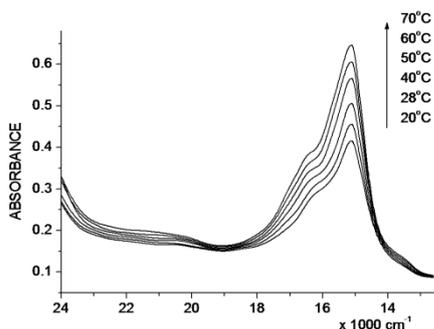


Fig. 3. Absorption spectra of 1×10^{-4} M ethanol solution of compound **4**.

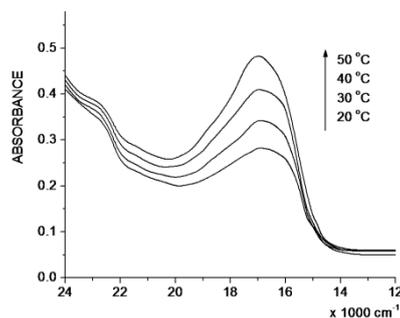


Fig. 4. Absorption spectra of 2.5×10^{-4} M *i*-butanol solution of compound **5**.

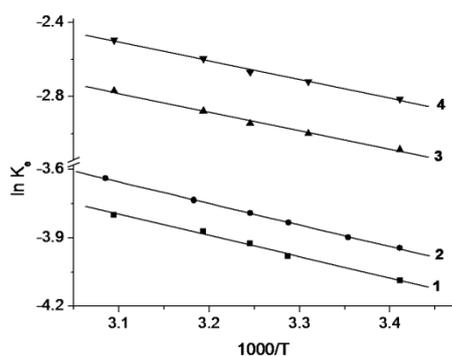


Fig. 5. Data ($\ln K_e$) on thermal equilibrium treated according to the Van't Hoff equation in acetone solutions of compounds **1–4**.

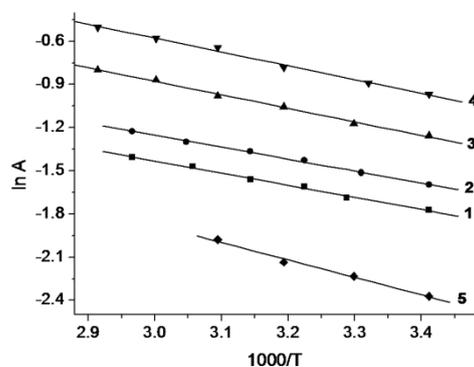


Fig. 6. Data ($\ln A$) on thermal equilibrium treated according to the Van't Hoff equation in ethanol solutions of compounds **1–5**.

Table 3. Thermodynamic parameters of $SO \leftrightarrow MC$ in acetone

SO	$\ln K_e$	ΔH^0 kJ mol ⁻¹	ΔG^0 kJ mol ⁻¹	ΔS^0 kJ mol ⁻¹
1	-4.09	7.6	10.0	-34
2	-3.94	7.7	9.6	-33
3	-3.08	8.3	7.5	-26
4	-2.81	8.4	6.9	-23

Table 4. Calculated values of ΔH^0 [kJ mol⁻¹] for **1–5** in different solvents for $SO \leftrightarrow MC$ using the relationship $d \ln A / d(1/T) = -\Delta H/R$

SO	ΔH^0					
	aceto-nitrile	Acet-one	meth-anol	ethanol	<i>i</i> -pro-panol	<i>i</i> -buta-nol
1	6.7	7.6	6.7	6.6	6.7	5.8
2	6.5	7.7	6.8	6.5	6.7	5.8
3	7.6	8.3	7.8	7.7	8.9	6.5
4	7.9	8.4	8.3	7.8	8.8	6.4
5	11.4	10.4	9.8	11.6	8.2	13.6

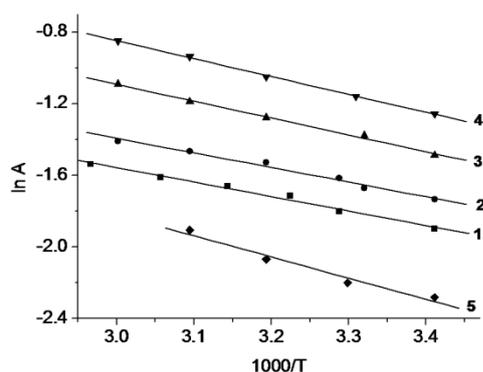


Fig. 7. Data ($\ln A$) on thermal equilibrium treated according to the Van't Hoff equation in methanol solutions of compounds **1–5**.

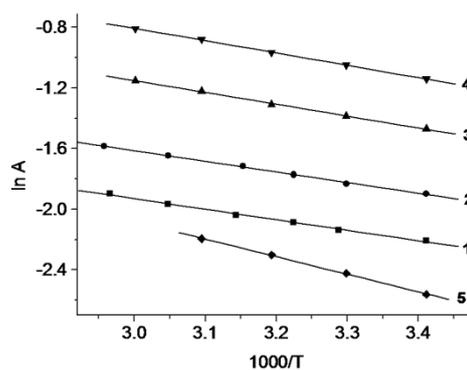


Fig. 8. Data ($\ln A$) on thermal equilibrium treated according to the Van't Hoff equation in *i*-butanol solutions of compounds **1–5**.

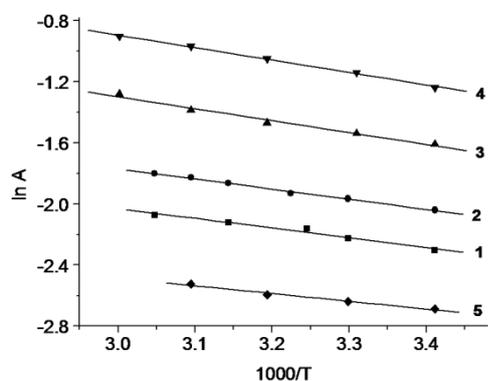


Fig. 9. Data ($\ln A$) on thermal equilibrium treated according to the Van't Hoff equation in *i*-propanol solutions of compounds **1–5**.

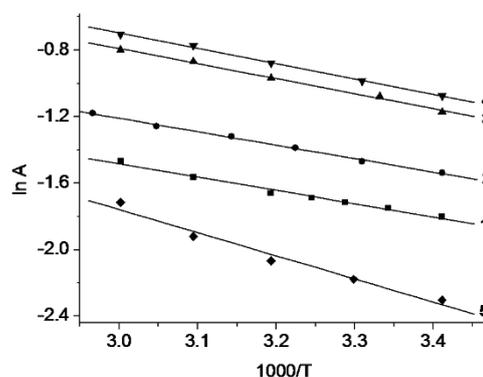


Fig. 10. Data ($\ln A$) on thermal equilibrium treated according to the Van't Hoff equation in acetonitrile solutions of compounds **1–5**.

CONCLUSIONS

Five newly synthesized spiroindolinonaphthoxazines bearing different substituents on the basic skeleton were investigated with respect to thermochromism in solvents of different polarity. Thermal reactions involving the cyclic spiroform and the open merocyanine form of the compounds with benzothiazolyl substituent were studied. Acetone was employed as a solvent to determine standard thermodynamic parameters, ΔH^0 , ΔS^0 , and ΔG^0 , of the reaction. It was found that the opening of the spirocyclic ring was not a spontaneous reaction. Both positive enthalpy changes and ΔS^0 negative values contributed to the overall positive ΔG^0 values. Negative standard entropy values were attributed to a better arrangement of the solvent molecules around each open polar MC form in comparison with a starting spirocyclic molecule.

Acknowledgements: This work was supported by contract DFNI-TO2/16 of the Bulgarian Science Fund.

REFERENCES

1. N. Tamai, H. Miyasaka, *Chem. Rev.*, **100**, 1875 (2000).
2. N. Y. C. Chu, in: H. Durr, H. Bouas-Laurent (Eds), *Photochromism: molecules and systems*, Elsevier, Amsterdam, 1990, p. 493.
3. C. B. McArdle (Ed.), *Applied photochromic polymer systems*, Blackie, London, 1992.
4. Tardieu, R. Dumbest, J. Aubard, A. Kellmann, F. Tfibel, A. Samat, R. Guglielmetti, *Helv. Chim. Acta*, **75**, 1185 (1992).
5. A. K. Chibisov, H. Görner, *Phys. Chem. Chem. Phys.*, **3**, 424 (2001).
6. Wilkinson, D. R. Worrall, J. Hobley, L. Jansen, S. L. Williams, A. J. Langley, P. Matousek, *J. Chem. Soc. Faraday Trans.*, **92**, 1331 (1996).

7. G. Favaro, F. Masetti, U. Mazzucato, G. Ottavi, P. Allegrini, V. Malatesta, *J. Chem. Soc. Faraday Trans.*, **90**, 333 (1994).
8. F. Ortica, *Dyes Pigm.*, **92**, 807 (2012).
9. T. Nakabayashi, N. Nishi, H. Sakuragi, *Sci. Progress*, **84**, 137 (2001).
10. J.-L. Pozzo, A. Samat, R. Guglielmetti, D. de Keukeleire, *J. Chem. Soc. Perkin Trans.*, **2**, 1327 (1993).
11. G. Favaro, V. Malatesta, U. Mazzucato, G. Ottavi, A. Romani, *J. Photochem. Photobiol. A-Chem.*, **87**, 235 (1995).
12. A. K. Chibisov, H. Görner, *J. Phys. Chem.*, **103**, 5211 (1999).
13. S. R. Keum, M. S. Hur, P. M. Kazmaier, E. Buncel, *Can. J. Chem.*, **69**, 1940 (1991).
14. H. Kim, H. J. Suh, J. Z. Cui, Y. S. Gal, S. H. Jin, K. Koh, *Dyes Pigm.*, **53**, 251 (2002).
15. H. J. Suh, W. T. Lim, J. Z. Cui, H. S. Lee, G. H. Kim, N. H. Heo, S. H. Kim, *Dyes Pigm.*, **57**, 149 (2003).
16. T. Deligeorgiev, S. Minkovska, B. Jeliaskova, S. Rakovsky, *Dyes Pigm.*, **53**, 101 (2002).
17. S. Minkovska, B. Jeliaskova, E. Borisova, L. Avramov, T. Deligeorgiev, *J. Photochem. Photobiol. A-Chem.*, **163**, 121 (2004).
18. S. Minkovska, M. Fedieva, B. Jeliaskova, T. Deligeorgiev, *Polyhedron*, **23**, 3147 (2004).
19. B. G. Jeliaskova, S. Minkovska, T. Deligeorgiev, *J. Photochem. Photobiol., A-Chem.*, **171**, 151 (2005).

ТЕРМОХРОМИЗЪМ НА СЕРИЯ СПИРОИНДОЛИНОНАФТОКСАЗИНИ

С. Минковска^{1*}, Б. Желязкова², Сл. Раковски¹, Т. Делигеоргиев²

¹ *Институт по катализ, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 11, 1113 София, България*

² *Факултет по химия и фармация, Софийски университет „Св. Климент Охридски“, бул. „Джеймс Баучер“ 1, 1164 София, България*

Постъпила на 7 октомври 2015 г.

(Резюме)

Термохромните свойства на пет спиронафтоксазина, съдържащи различни заместители в основния скелет на молекулата, са синтезирани в нашата лаборатория и изучени в разтворители с различна полярност. Съединенията са силно поляризуеми, което води до равновесие между безцветната затворена и оцветената отворена форма в интервала от температури (20–60°C) в отсъствие на светлина. Термичното равновесие между основното заселено състояние на безцветната затворена форма и цветната отворена форма зависи както от полярността на разтворителя, така и от природата на заместителите. Концентрацията на отворената форма се увеличава с нарастване полярността на разтворителя.