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Organic Chemistry

Photochromic Properties of Indoline Bis-Spirochromens Obtained on the Basis of Dipyrrolonaphtalenes

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ABSTRACT. Photochromic properties of the following new condensed indoline bis-spiropyrans of indoloindole and benzodipyrrole quinoxaline series synthesized earlier are investigated: 6,6"-dinitro-, 6,6", 8,8"-tetranitro-, 6,6"8,8"-tetrabrom-1',3',3',6',8',8'-hexamethyldispiro[chromen-2,2'-indoline [7,6-*g*] indoline-9',2"-chromens] (la-c); 6,6"-dinitro-, 6,6",8,8"-tetranitro-, 6,6"8,8"-tetrabrom-1',1',3' ,8',10',10' -hexamethyldispiro [chromen-2,2'-indoline [4,5-*e*]indoline-9',2" –chromens] (2a-c); 6,6"-dinitro-, 6,6"-dibrom- and 6,6"-8,8"-tetrabrom-1',1',8',8'-tetramethyl-1',4',5',8'-tetrahydrodispyro [chromen-2,2'-dipyrrolo [1,2,3-*d,e*:3,2,1-*i,j*] benzo[*g*]chinoxalin-7',2"-chromens]. Electronic spectra of freshly prepared solutions of compounds were studied after heating and irradiating by UV mercury lamp. It is shown that spirochromens obtained on the basis of benzodipirrole quinoxaline are characterized with more expressed photochromic properties due to better solutability of these compounds. Kinetics of dark decolouration of the solution of photochrom was studied when it was kept exposed to daylight and irradiated by UV mercury lamp. On the basis of the given UV spectra it was supposed that photochrom has a coloured betaine structure in the freshly prepared solutions, and dark decolouration of coloured solutions of photochrom occurs faster at irradiation with a mercury UV lamp than at the day light. The velocity of dark decolouration of the coloured form can be assessed according to decrease of optical density D of the absorption band per time.© *2013 Bull. Georg. Natl. Acad. Sci.*

Key words: *spiropyrans, indoloindole, dipirrolochinoxaline, photochromic properties, irradiation, dark decolouration, photoinduction.*

Great technical demands of spiropyrans, such as bathochromic shift of the absorption band of the open form and increase of the longevity of colored form, made scientists synthesize structures containing more than one photochromic center. Unlike spiropyrans bisspiropyrans are of particular interest due to the fact that with the possible simultaneous opening of two pyran fragments a conjugated chain increases considerably and the maximum of the absorption band of the photoinduced form undergoes a strong bathochromic shift [1].

The aim of the present work was investigation of

Table 1. Position of maximums of absorption bands λ_{max},nm, and optical density (D) of bis-spiropyrrans 3a-b

Compound	R^1	R^2	λ_{max}, nm (D), c=0.08 mg/ml					
			Freshly prepared solution			Irradiated solution		
			Etanol	Chloroform	Benzene	Etanol	Chloroform	Benzene
3a	NO$_2$	H	558(0.121)	611(0.020)		558(0.143)	459(0.565)	
			315(0.964)	357(1.199)		315(1.595)	261(3.142)	
			269(2.554)	315(1.424)		269(4.2)	247(3.222)	
			225(1.867)	272(4.013)		225(3.15)		
3b	Br	H		624(0.050)**	629(0.180)		840(0.037)** 565(0.702)	626(0.15)
				364(0.230)**	361(1.227)		538(0.783)	359(1.244)
				252(1.403)**	313(1.464)			313(1.562)
				237(0.971)**	279(3.376)		241(1.254)**	279(3.325)
3c	Br	Br		620(0.17)* 359(0.759)	358 (0.678)		467(0.156)	358 (0.916)
				319(1.081)	322(0.976)		244(3.482)	322(1.328)
				273(0.420)	277(1.978)		210(1.346)	278(2.496)
				246(3.731)				

photochromic properties of synthesized earlier by us [2-4] new condensed indoline bis-spiropyrans systems of indoloindole **1a-c**, **2a-c** and benzodipyrrolochinoxaline **3a-c** series: 6,6"-dinitro-, 6,6",8,8"-tetranitro-, 6,6"8,8"-tetrabrom-1',3',3',6',8',8'-hexamethyldispiro[chromen-2,2'-indoline[7,6-*g*]indoline-9',2"-chromens](**1a-c**); 6,6"-dinitro-, 6,6",8,8"-tetranitro-, 6,6"8,8"-tetrabrom-1',1',3' ,8',10',10' -hexamethyldispiro[chromen-2,2'-indoline[4,5-*e*]indoline-9',2" –chromens](**2a-c**); 6,6"-dinitro-, 6,6"-dibrom- and 6,6"-8,8"-tetrabrom-1',1',8',8'-tetramethyl-1',4',5',8'-tetrahydrodispyro[chromen-2,2'-dipyrrolo[1,2,3-*d,e*:3,2,1-*i,j*]benzo[*g*]chinoxalin-7' ,2"-chromens](**3a-c**) (Scheme 1).

It is noted in [4] that new synthesized bisspyropyrans **1a, 1c** dissolve well in DMF, hardly in the alcohol and nonpolar solvents. Compounds **2a, 2c** dissolve better in the alcohol and nonpolar solvents. Solubility of compounds **1a, 1c** improves at heating. At the same time the colouring of solutions changes. Coloured solutions become colourless at cooling. Spirochromens **3a-c** dissolve well in the alcohol and nonpolar solvents. Freshly prepared solutions are violet; while keeping in the sun the solution gradually changes colour, first it becomes green, then it discolours and becomes yellow. In the darkness the solution again becomes green and in the light it becomes colourless. This process is repeated many times. Photochromic properties of the obtained spyrocompounds **3a-c** are confirmed by the observed process.

Photochromic properties of the compounds were investigated using their electronic spectra. The electronic spectra of freshly prepared alcohol solutions of bis-spiropyran compounds **1-3** were studied after irradiation by mercury UV lamp and heating of the solutions. Changes in the electronic spectra of the irradiated solutions of compounds **1a-c** were not observed; intensities of the absorption bands in the spectra of the solutions increased after heating, in some cases bathochromic shift of the absorption bands was observed.

In the electronic spectra of both irradiated and

Table 2. Kinetics of decrease of optical density of compound 3b (C_6H_6, $c=1.10^{-3}$ mol/l) at irradiation with mercury UV lamp with wave length 627 nm

Time, mm	Wave length, λ, nm	Optical density, D
0	627.00	2.140
2	627.00	2.130
7	628.00	2.126
17	627.00	2.114
30	627.00	2.098
60	628.00	2.099

Table 3. Kinetics of decrease of optical density of compound 3b (C_6H_6, c=0.008 mg/ml) at irradiation with mercury UV lamp with wave length 629 nm

Time, mm	Wave length, λ, nm	Optical density, D
0	629.00	0.180
3	626.00	0.153
6	624.00	0.115

heated solutions of compounds **2a-c** changes in the intensities of absorption bands and a weak shift of maxima are observed, which means that these compounds have a weak photochromic property.

Electronic spectra of bis-spiropyrans of benzodipyrroloquinoxaline series **3a-c** provoked an interest. Electronic spectra of freshly prepared solutions were recorded in the chloroform, ethyl alcohol and benzene. After irradiation of solutions by mercury UV lamp the spectra of compounds appreciably changed in $CHCl_3$, long-wave maxima were shifted, and in the alcohol- and benzene solutions only intensities of absorption maxima were changed. Electronic spectra of compounds **3b** in chloroform and benzene are shown in Figs.1, 2.

In the spectra of freshly prepared solutions the following maxima of absorption are observed: l_{max}(D) (C2H5OH): 558(0.121), 315(0.964), 269(2.554), 225 nm (1.867); l_{max}(D) (CHCl3): 611(0.020), 357(1.199), 315(1.424), 272 nm (4.013) – for compound **3a**; l_{max} (D) ($CHCl_3$):624(0.050), 364(0.230), 252(1.403), 237(0.971); l_{max}(D)(C_6H_6): 629(0.180), 361(1.227), 313(1.464), 279(3.376) – for compound **3b** and l_{max}(D)($CHCl_3$): 620(0.17),359(0.756), 319(1.081), 273(0.420), 246(3.731); l_{max}(D) (C_6H_6): 358(0.678), 322(0.976), 277(1.978) – for compound **3c**;

The following absorption maxima of photoinduced forms of compounds are recorded: l_{max}(D) (C_2H_5OH): 558(0.143), 315(1.595), 269(4.2), 225 nm -(3.15); l_{max}(D)($CHCl_3$): 459(0.565), 261(3.142), 247 nm (3.222) – for **3a**; l_{max}(D) ($CHCl_3$): 565(0.702), 538(0.783), 348(1.334); l_{max}(D) (C_6H_6): 626(0.153), 359(1.244), 313(1.562), 279(3.325) – for **3b** and l_{max}(D) ($CHCl_3$): 467(0.156), 244(3.482), 210 (1.346); l_{max}(D) (C_6H_6): 358(0.916), 322(1.328), 278(2.496) – for compound **3c**.

In the spectra of more concentrated solutions long-wave maxima corresponding to betaine form, occur with intensive bands. The data of electronic spectra of compounds **3a-c** are shown in Table 1.

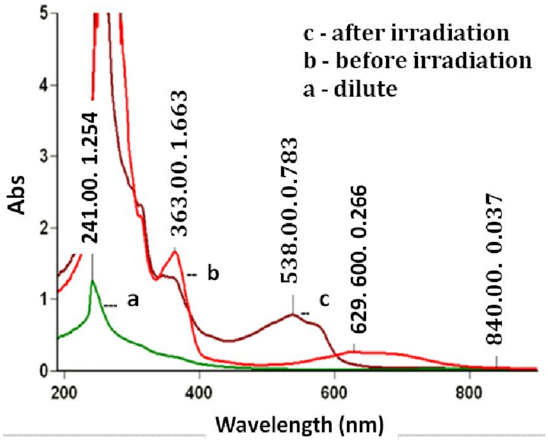


Fig. 1. Compound **3b**. UV spectra in the chhloroform (c=0.08 mg/ml).

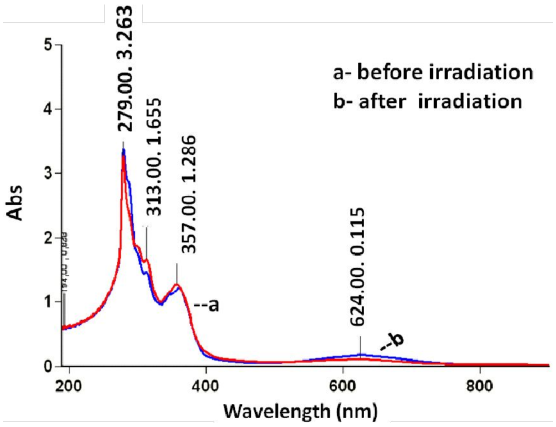
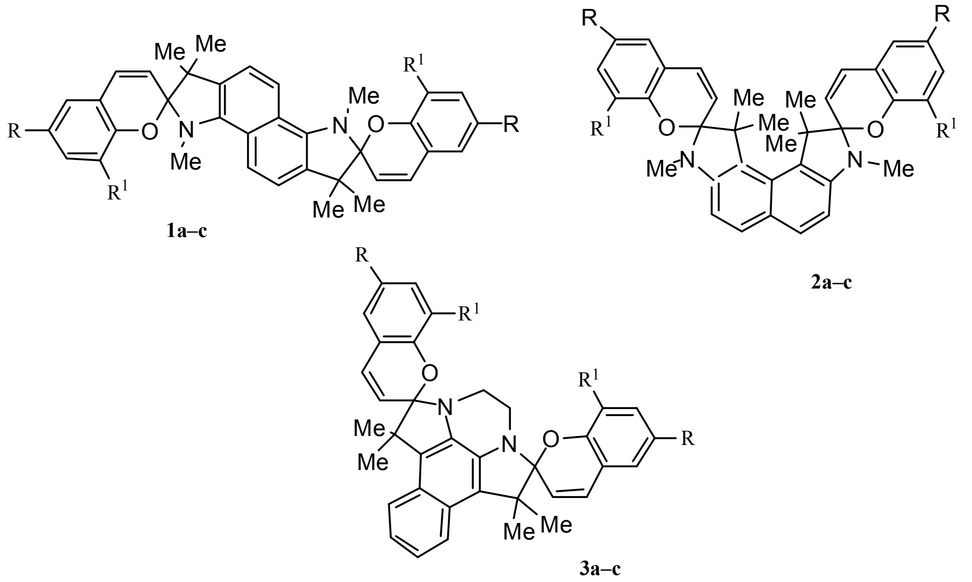
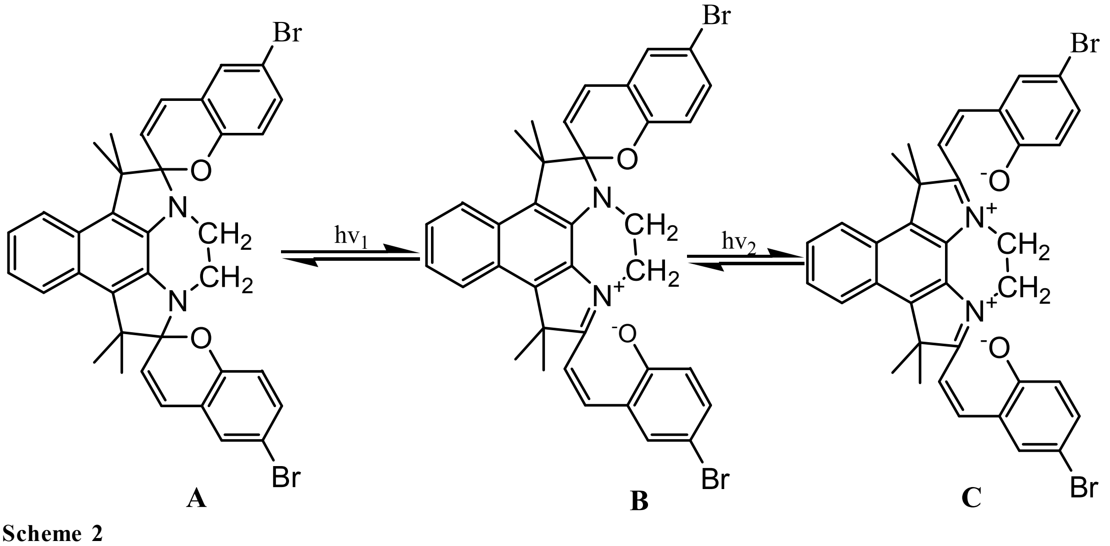


Fig. 2. . Compound **3b**. UV spectra in the benzene (c=0.08 mg/ml).



1, **2** **a** R^1 = NO$_2$, R^2 = H; **b** R^1 = R^2 = NO$_2$; **c** R^1 = R^2= Br; **3** **a** R^1 = NO$_2$, R^2 = H; **b** R^1 = Br, R^2 = H; **c** R^1 = R^2 = Br
Scheme 1

According to literature data [1,4] long-wave maxima in the electronic spectra of bis-spyrans occur in the 500-650 nm range, that corresponds to the opening of one pyran ring in the betaine forms (one-sidedly open form B), and in the NMR ^{1}H spectra of indoline spirochromens both open and cycle signals of protons present [5-7]. Data on electronic and PMR spectra obtained confirm this supposition. Really, a set of signals is detected corresponding to symmetric cyclic structures in the NMR ^{1}H spectra of compounds **1a, 2b**, **3a-c**, and two sets of signals of different intensities appear in the NMR ^{1}H spectra of compounds **1b, 1c, 2a, 2c**. This fact is caused by presence of two structures in the solutions DMSO-d$_6$, such as symmetric close forms and non-symmetric one-sidedly open forms [4]. However an intensive absorption band at 241 nm (1.254) occurs in the spectra of highly diluted solution of the compound 3b in the chloroform and a low intensive band is observed in the visible range of the spectra 840 nm (0.037). It might be caused by opening of both pyran rings (generating **C** form) (Scheme 2).



Scheme 2

Kinetics of dark decolouration of photochrom was studied when the solution was exposed to the day-light and irradiaton by mercury lamp. The velocity of dark decolouration of the coloured **B** form (scheme 2) can be assessed according to decrease of optical density D of the absorption band l_B per time in comparison with the initial state (freshly prepared solution of the compound is coloured). Absorption bands of the coloured **B** form lie in the 600 nm range. Experiments were carried out at the room temperature. Changes in the optical density of long-wave maximum were studied in the benzene solutions of different concentrations. As a result a small decrease of intensities of that maximum in time was observed. The data on these changes are given in Tables 2, 3.

Considering the given spectra one can suppose that photochrom **3b** has a coloured betaine structure B in the freshly prepared solutions, and dark decolouration of coloured solutions of photochrom **3b** occurs faster at irradiation with a mercury UV lamp than at the day light.

Conclusion. Thus, study of electronic spectra of spirochromens showed that compounds obtained on the basis of benzodipirroloquinoxaline **3a-c** are characterized by more expressed photochrom properties in comparison with the compounds derived on the basis of isomeric indoleindoles. This, probably, is connected with easy solubility of benzopyrrole derivatives that is prospective for their application in practice.

UV spectra of the compounds were recorded by means of a spectrophotometer Varian Carry 100, UV-vis. Irradiation was carried out by a mercury UV lamp. The used methods of syntesis and spectral data confirming the structure of bis-spirocompounds **1-3** are given in [2-4].

ორგანული ქიმია

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გამოკვლეულია ადრე სინთეზირებული ინდოლოინდოლური და ბენზოდიპირო-ლოქინოქსალინის რიგის ახალი კონდენსირებული ინდოლინური ბის-სპიროპირანების: 6,6''-დინიტრო-, 6,6",8,8"-ტეტრანიტრო-, 6,6",8,8"-ტეტრაბრომ-1',3',3',6',8',8'-ჰექსამეთილდისპირ ოქრომენო-2,2'-ინდოლინო

[7,6-g]ინდოლინო-9',2''-ქრომენების], 6,6''-დინიტრო-, 6,6",8,8"-ტეტრანიტრო-,6,6",8,8"-ტეტრაბრომ-1',1',3',8',10',10'- ჰექსამეთილდისპირო[ქრომენო-2,2'- ინდოლინო [4,5-e]-ინდოლინო-9',2'' -ქრომენების], 6,6''-დინიტრო-, 6,6''-დიბრომ- და 6,6",8,8"-ტეტრაბრომ-1',1',8',8'-ტეტრამეთილ-1',4',5',8'-ტეტრაჰიდროდისპირო[ქრომენო-2,2'-დიპიროლო[1,2,3-d,e:3,2,1-i,j] ბენზო [g]ქინოქსალინ-7',2''-ქრომენების] ფოტოქრომული თვისებები. მათი ახლადმომზადებული ხსნარების, ასევე ამ ხსნარების ვერცხლისწყლის ნათურით დასხივებისა და გაცხელების შემდეგ მიღებული ხსნარების ელექტრონული სპექტრების შესწავლით დადგენილია, რომ ბენზოდიპიროლოქინოქსალინის რიგის სპიროქრომენები ხასიათდებიან უფრო მკვეთრად გამოსახული ფოტოქრომულობით უკეთესი ხსნადობის გამო. შესწავლილია ერთ-ერთი ბის-სპიროქრომენის გაუფერულების კინეტიკა ხსნარის დასხივებისა და დღის სინათლეზე დაყოვნების შედეგად. უი სპექტრების მონაცემთა საფუძველზე გამოთქმულია ვარაუდი, რომ ახლადმომზადებულ ხსნარებში ფოტოქრომულ ნივთიერებებს შეფერილი ბეტაინური სტრუქტურა აქვს, ხოლო ვერცხლისწყლის ნათურის უი სხივების მოქმედებით ხდება შეფერილი ხსნარების გაუფერულება. გაუფერულების პროცესის სიჩქარე შესწავლილია შეფერილი ფორმის შთანთქმის ზოლის ოპტიკური სიმკვრივის დროში შემცირების საფუძველზე.

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