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PHOTO- AND THERMOCHROMIC SPIRANS. 38*. NEW (1-ALKYL-4,5-DIPHENYL)IMIDAZOLYL-SUBSTITUTED SPIROBENZOPYRANS

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3-Diphenylimidazolyl-substituted 2-hydroxybenzaldehyde has been obtained by the formylation of 2-diphenylimidazolyl-substituted phenol. From the obtained compound, new photochromic spiroindolinebenzopyrans containing a 4,5-diphenylimidazole group at the position 8 of the benzopyran fragment were synthesized. The obtained compounds possess photochromic properties in solution.

Keywords: merocyanins, spiropyrans, triarylimidazole, photochromism.

Spiropyrans are a widely known class of organic photochromic compounds. The possibility of a directed change of the spectral-kinetic characteristics of compounds over a wide range by variation of chemical structure is an important factor stimulating the interest of investigators towards these derivatives [1-4]. Functionalization of spiropyran molecules by introducing substituents of various nature also raises the possibility of obtaining a broad series of polyfunctional photochromic molecular systems displaying magnetic [5], fluorescent [6-9], and chelating [9-13] properties reversible with the aid of light.

One of the methods of such modification is the introduction of heterocyclic substituents into the spiropyran molecule at the *ortho* position relative to the chromene oxygen atom, which leads to a modification of the spectral [14-16] and complex-forming [13, 16, 17] properties of the initial compounds.

As a continuation of these investigations, the present work is devoted to the synthesis and study of the photochromic properties of a series of spirobenzopyrans containing a 1-benzyl-4,5-diphenylimidazole group in the position 8 of the benzopyran fragment.

1,2,4,5-Tetrasubstituted imidazoles are usually obtained by a four-component cyclocondensation of a 1,2-diketone with an aldehyde, a primary amine, and ammonium acetate [18]. 3-(1-Benzyl-4,5-diphenyl-imidazolyl)-containing 2-hydroxybenzaldehyde **2** was obtained by cyclocondensation of 5-bromosalicylic aldehyde, benzil, ammonium acetate, and benzylamine with subsequent formylation according to Duff of the resultant imidazolyl-substituted phenol **1**. Spirobenzopyrans **4a-d** were formed as a result of the condensation of 3*H*-indolium salts **3a-d** with 2-hydroxybenzaldehyde **2** in the presence of triethylamine.

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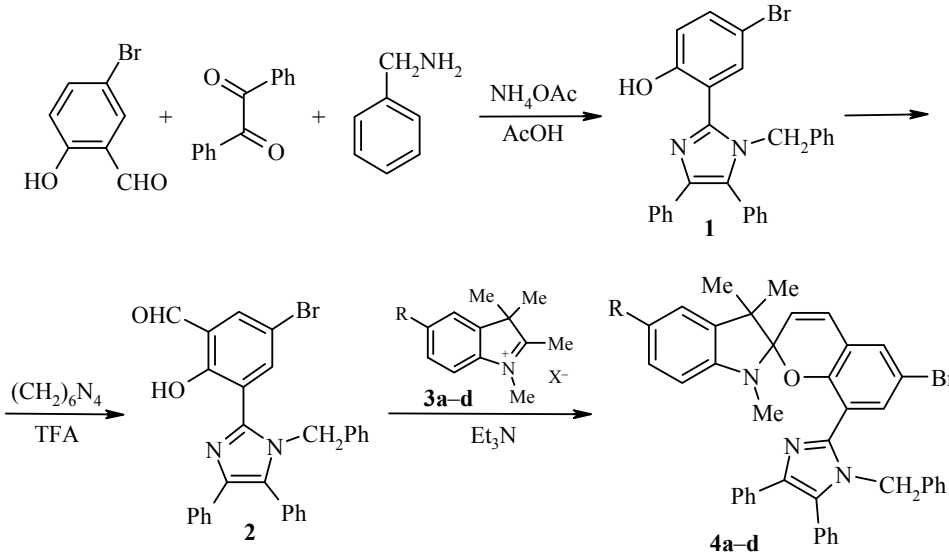
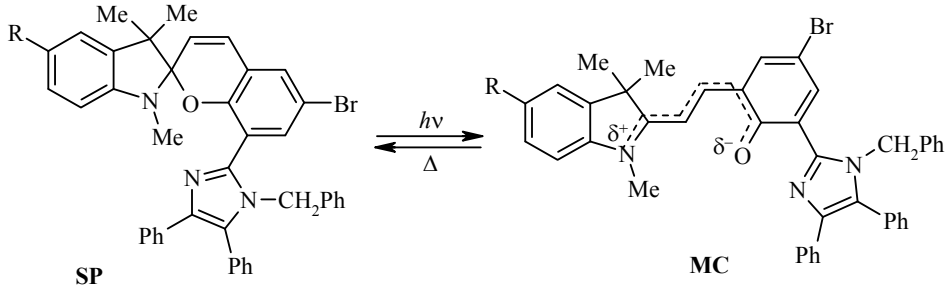
The structures of the obtained compounds **1**, **2**, **4a-d** were established by ^{1}H NMR spectroscopy and confirmed by data of elemental analysis. The ^{1}H NMR spectra of spiropyrans **4a-d** contain two signals of magnetically nonequivalent geminal methyl groups, signals of *N*-alkyl substituents of the indoline and imidazole fragments, and a methoxy group (spiropyran **4d**) in the high field region, and also several groups of mutually linked signals in the low field region of the spectrum belonging to indoline, pyran, and imidazole fragments. The signals of the phenyl ring protons form a complex picture of multiplets. The prochirality of the methylene group protons of the *N*-benzyl substituent of the imidazole fragment of spiropyrans **4a-d** leads to a diastereotopic splitting of the proton signals displayed as two doublets at 4.22-4.25 and 4.73-4.74 ppm, respectively.



3, **4 a** R = H, **b** R = Br, **c** R = Cl, **d** R = OMe; **3 a**,**b**,**d** X = I, **c** X = ClO_4

All the ^{1}H NMR spectroscopic data enumerated above confirm unequivocally the structure of the obtained spiropyrans. The absence of proton signals for the indoline and benzopyran fragments in the regions of the spectrum characterized for the open merocyanin form **MC** [19-21], indicates that the obtained compounds in $CDCl_3$ solution exist in the spirocyclic **SP** form.



In toluene solution the investigated compounds were also found to exist exclusively in the spirocyclic **SP** form. The absorption spectra of the spirocyclic forms were characterized by two diffuse bands without distinct maxima in the region of 289-296 and 336-344 nm with molar extinction coefficients of 20800-24050 and 7100-8630 $l \cdot mol^{-1} \cdot cm^{-1}$, respectively (Table 1). Substituents in the indoline portion of the molecule did not affect the intensity of the absorption bands, but led to an insignificant bathochromic shift of the long-wave component of the band. Irradiation of colorless solutions of spiropyrans with 365 nm wavelength UV light causes their coloration, linked to a photochemical reaction of ring opening and the formation of merocyanin forms. In the absorption spectra, this is displayed as the absorption characteristic for merocyanines [2] in the 500-700 nm region with band maxima at 625-634 nm (Fig. 1, Table 1).

TABLE 1. Spectral and Kinetic Characteristics of Spiropyrans **4a-d** in Toluene, *T* 293 K

Com-pound	λ_{max}^{abs} (SP), nm ($\varepsilon \cdot 10^{-3}$, $1 \cdot mol^{-1} \cdot cm^{-1}$)	λ_{max}^{abs} (**MC**), nm	k_{MC-SP}, sec^{-1}	E_a, $kJ \cdot mol^{-1}$
4a	292 (24.05) sh. 336 (8.63) sh.	625	0.1032	72.2
4b	296 (20.80) sh. 338 (7.10) sh.	627	0.3592	89.1
4c	289 (23.57) sh. 339 (7.46) sh.	628	0.3329	80.6
4d	293 (22.62) sh. 344 (8.01) sh.	634	0.0365	79.6

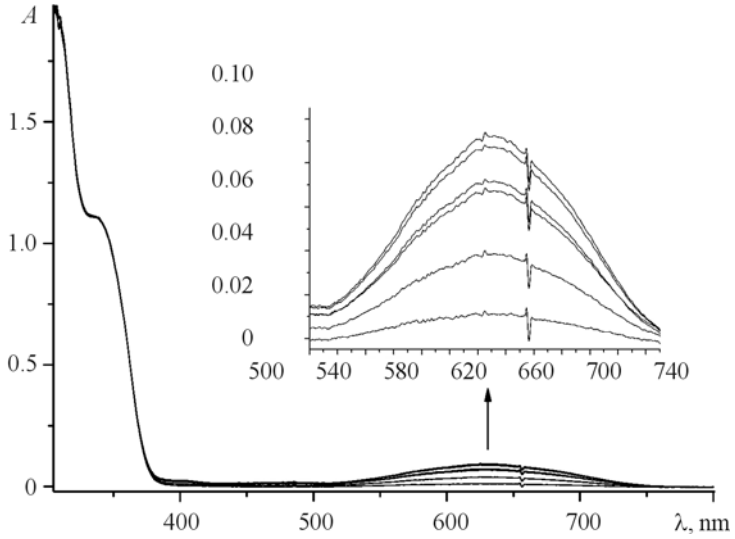


Fig. 1. Absorption spectra of compound **4b** in toluene (*c* $1.54.10^{-4}$ M) on irradiation with light of λ 365 nm, *T* 293 K, 2-sec intervals between spectra.

After the end of irradiation a spontaneous decolorization of the solutions occurred due to the reverse thermal recyclization of the merocyanine forms into the initial spirocyclic forms. The kinetic curves of the dark relaxation process were satisfactorily described by a monoexponential function (Fig. 2). The lifetime of the colored isomers at *T* 293 K lies in the range of 0.9-27.0 sec and essentially depends on the substituent at the position 5 of the indoline fragment of the molecule. In the series from the unsubstituted compound **4a** to the halo-substituted derivatives **4b**,**c** an increase in the thermal recyclization reaction rate constant was observed, while the introduction of a methoxy group (compound **4d**) increased the kinetic stability of the merocyanine isomer in comparison with the unsubstituted spiro compound **4a** by almost one order of magnitude (Table 1). The activation energy values for the recyclization reactions were determined from the temperature dependencies of the thermal decoloration rate constants (Fig. 2, inset). These values lie in the region of 72.2-80.6 $kJ \cdot mol^{-1}$. Unlike the benzothiazolyl-substituted spirobenzopyrans studied previously [17], the compounds investigated were characterized by higher rate constants for the thermal reaction.

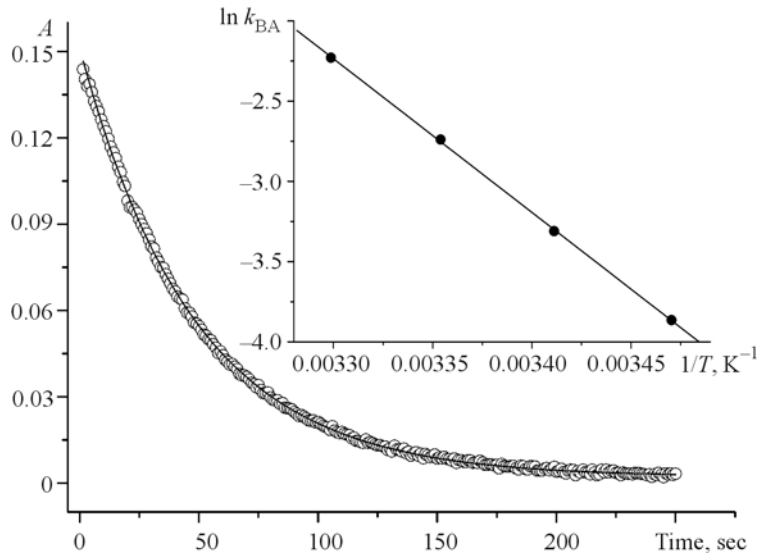


Fig. 2. Optical density (*A*) at the maximum of the long-wave absorption band of compound **4d** in merocyanine form, as a function of thermal relaxation time (points are experimental, the continuous line is an approximation by monoexponential function), *T* 278 K, the solvent is toluene. The dependence of the thermal recyclization reaction rate constant logarithm on reciprocal temperature is shown in the inset.

New spirobenzopyranindolines have been obtained, containing a 1-benzyl-4,5-diphenylimidazole group at the position 8 of the benzopyran fragment and displaying photochromic properties in solution.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian Unity-300 spectrometer (300 MHz) in $CDCl_3$, internal standard was the residual signal of the solvent (δ 7.26 ppm). Electronic absorption spectra and kinetic curves of the thermal recyclization reactions of the investigated compounds were recorded on an Agilent 8453 spectrophotometer with an attachment for thermostatting samples. Photolysis of solutions was carried out by the Newport system based on a mercury lamp (200 W) with a set of interference light filters. Elemental analysis was carried out on a KOVO CHN analyzer. Melting points were determined on a Boetius hot stage apparatus. Spectral grade toluene (Aldrich) was used for preparing solutions. Compounds **3a-d** were obtained by the procedure described previously in [22].

2-(1-Benzyl-4,5-diphenyl-1*H*-imidazol-2-yl)-4-bromophenol (1). A mixture of 5-bromosalicylic aldehyde (6.0 g, 30 mmol), benzil (6.3 g, 30 mmol), benzylamine (4.89 ml, 45 mmol), NH_4OAc (4.8 g, 60 mmol), and AcOH (90 ml) was refluxed for 12 h. The reaction mixture was poured into H_2O (500 ml), neutralized with conc. aqueous NH_3 to pH 6-7, the solid filtered off, washed with water, dried, and recrystallized from a mixture EtOAc–2-PrOH, 1:1. Yield 7.95 g (54%). Pale-gray crystals; mp 159-160ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.27 (2H, s, NCH_2Ph); 6.98 (1H, d, *J* = 8.8, H-6); 7.18-7.25 (3H, m, H Ph); 7.27-7.38 (8H, m, H-5, H Ph); 7.40-7.44 (2H, m, H Ph); 7.46-7.50 (3H, m, H Ph); 7.57 (1H, d, *J* = 2.4, H-3); 9.32 (1H, br. s, OH). Found, %: C 69.95; H 4.52; N 5.75. $C_{28}H_{21}BrN_2O$. Calculated, %: C 69.86; H 4.40; N 5.82.

3-(1-Benzyl-4,5-diphenyl-1*H*-imidazol-2-yl)-5-bromo-2-hydroxybenzaldehyde (2). A mixture of phenol **1** (4.82 g, 10 mmol), hexamethylenetetramine (5.6 g, 40 mmol), and trifluoroacetic acid (30 ml) was refluxed under an inert atmosphere for 12 h, cooled, and a mixture of conc. HCl (14 ml) and H_2O (28 ml) was added. The reaction mixture was poured into water (130 ml) and neutralized with conc. aqueous NH_3 to pH 6-7.

The solid was filtered off, washed with water, dried, purified by column chromatography on Al_2O_3 (eluent $CHCl_3$), and recrystalized from a 1:1 mixture of PhMe–2-PrOH. Yield 1.78 g (35%). Lemon-yellow crystals; mp 233-235ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.24 (2H, s, NCH_2Ph); 6.95-6.98 (2H, m, H Ph); 7.18-7.24 (3H, m, H Ph); 7.27-7.51 (10H, m, H Ph); 7.68 (1H, d, *J* = 2.5, H-4); 7.81 (1H, d, *J* = 2.5, H-6); 10.43 (1H, s, CHO). Found, %: C 68.31; H 4.02; N 5.45. $C_{29}H_{21}BrN_2O_2$. Calculated, %: C 68.38; H 4.16; N 5.50.

8-(1-Benzyl-4,5-diphenyl-1*H*-imidazol-2-yl)-6-bromo-1',3',3'-trimethylspiro-[2*H*-1-benzopyran-2,2'-indolines] 4a-d (General Method). A mixture of 3*H*-indolium salt **3a-d** (1 mmol), aldehyde **2** (1 mmol), and Et_3N (0.14 ml, 1 mmol) in PhMe (10 ml) and 2-PrOH (4 ml) was refluxed for 12 h, the solvent was evaporated, the residue purified by column chromatography on Al_2O_3 (eluent benzene) and by recrystallization.

8-(1-Benzyl-4,5-diphenyl-1*H*-imidazol-2-yl)-6-bromo-1',3',3'-trimethylspiro[2*H*-1-benzopyran-2,2'-indoline] (4a). Yield 0.27 g (41%). Pale-pink crystals; mp 122-124ºC (hexane). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.15 (6H, s, $C(CH_3)_2$); 2.78 (3H, s, 1'-CH_3); 4.22 (1H, d, *J* = 15.8) and 4.74 (1H, d, *J* = 15.8, NCH_2Ph); 5.78 (1H, d, *J* = 10.3, H-3); 6.36-6.39 (2H, m, H Ph); 6.50-6.54 (3H, m, H -7', H Ph); 6.87 (1H, d, *J* = 10.3, H-4); 6.91-7.19 (10H, m, H-5,4',5',6', H Ph); 7.23-7.30 (3H, m, H Ph); 7.41-7.44 (2H, m, H Ph); 7.68 (1H, d, *J* = 2.4, H-7). Found, %: C 73.95; H 5.10; N 6.22. $C_{41}H_{34}BrN_3O$. Calculated, %: C 74.09; H 5.16; N 6.32.

8-(1-Benzyl-4,5-diphenyl-1*H*-imidazol-2-yl)-5',6-dibromo-1',3',3'-trimethylspiro[2*H*-1-benzopyran-2,2'-indoline] (4b). Yield 0.37 g (50%). Pale-gray crystals; mp 129-131ºC (heptane). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.15 (3H, s, 3'-CH_3); 1.16 (3H, s, 3'-CH_3); 2.73 (3H, s, 1'-CH_3); 4.25 (1H, d, *J* = 15.8) and 4.73 (1H, d, *J* = 15.8, NCH_2Ph); 5.76 (1H, d, *J* = 10.3, H-3); 6.36-6.40 (3H, m, H-7', H Ph); 6.57-6.60 (2H, m, H Ph); 6.89 (1H, d, *J* = 10.3, H-4); 6.96-7.22 (9H, m, H-5,4',6', H Ph); 7.26-7.31 (3H, m, H Ph); 7.41-7.45 (2H, m, H Ph); 7.69 (1H, d, *J* = 2.4, H-7). Found, %: C 66.35; H 4.58; N 5.47. $C_{41}H_{33}Br_2N_3O$. Calculated, %: C 66.23; H 4.47; N 5.65.

8-(1-Benzyl-4,5-diphenyl-1*H*-imidazol-2-yl)-6-bromo-5'-chloro-1',3',3'-trimethylspiro[2*H*-1-benzopyran-2,2'-indoline] (4c). Yield 0.30 g (43%). Pale-gray crystals; mp 120-121ºC (hexane). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.15 (3H, s, 3'-CH_3); 1.16 (3H, s, 3'-CH_3); 2.73 (3H, s, 1'-CH_3); 4.24 (1H, d, *J* = 15.8) and 4.73 (1H, d, *J* = 15.8, NCH_2Ph); 5.76 (1H, d, *J* = 10.3, H-3); 6.37-6.40 (2H, m, H Ph); 6.41 (1H, d, *J* = 8.1, H-7'); 6.56-6.60 (2H, m, H Ph); 6.89 (1H, d, *J* = 10.3, H-4); 6.98-7.03 (3H, m, H Ph); 7.04 (1H, d, *J* = 2.1, H-4'); 7.06-7.16 (4H, m, H-5, H Ph); 7.20 (1H, dd, *J* = 8.2, *J* = 2.1, H-6'); 7.25-7.30 (3H, m, H Ph); 7.41-7.45 (2H, m, H Ph); 7.69 (1H, d, *J* = 2.4, H-7). Found, %: C 70.62; H 4.90; N 5.85. $C_{41}H_{33}BrClN_3O$. Calculated, %: C 70.44; H 4.76; N 6.01.

8-(1-Benzyl-4,5-diphenyl-1*H*-imidazol-2-yl)-6-bromo-5'-methoxy-1',3',3'-trimethylspiro[2*H*-1-benzopyran-2,2'-indoline] (4d). Yield 0.33 g (47%). Pale-lilac crystals; mp 221-223ºC (heptane). ^{1}H NMR, δ, ppm (*J*, Hz): 1.14 (3H, s, 3'-CH_3); 1.16 (3H, s, 3'-CH_3); 2.71 (3H, s, 1'-CH_3); 3.80 (3H, s, OCH_3); 4.22 (1H, d, *J* = 15.8) and 4.74 (1H, d, *J* = 15.8, NCH_2Ph); 5.78 (1H, d, *J* = 10.3, H-3); 6.37-6.40 (2H, m, H Ph); 6.41 (1H, d, *J* = 8.2, H-7'); 6.57-6.60 (2H. m, H Ph); 6.71 (1H, d, *J* = 2.5, H-4'); 6.77 (1H, dd, *J* = 8.2, *J* = 2.5, H-6'); 6.86 (1H, d, *J* = 10.3, H-4); 6.96-7.22 (9H, m, H Ph); 7.26 (1H, d, *J* = 2.4, H-5); 7.41-7.45 (2H, m, H Ph); 7.68 (1H, d, *J* = 2.4, H-7). Found, %: C 72.47; H 5.10; N 5.98. $C_{42}H_{36}BrN_3O_2$. Calculated, %: C 72.62; H 5.22; N 6.05.

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