NOVEL PHOTOCHROMIC SPIROPYRANS DERIVED FROM 6-HYDROXY-4-METHYL-5-FORMYLCOUMARIN

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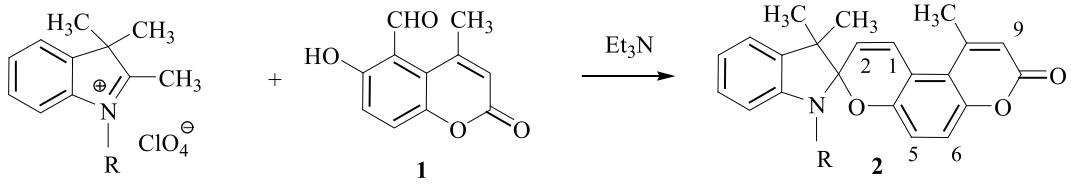
Novel indoline, isobenzofuran and naphtopyran spiropyrans (SPPs) containing in 2H-chromene part of the molecules fused coumarin moiety were synthesized. According to ^{1}H NMR, IR and UV/Vis spectral data these compounds exist in cyclic spiroform SP. Under irradiation of their solutions in isopentane-isopropanole (4:1) mixture at $T < 250$ K the formation of merocyanine (MC) isomer was observed. The back reaction MC ® SP is thermally reversible.

Keywords: spiropyrans, merocyanine, coumarine, photochromism

Photochromic spiropyrans (SPPs) are widely used for data recording, as photocontrolled organic molecular switches, in devices of molecular electronics and as chemosensors for metal cations [1–4]. Some representatives of coumarin-containing SPPs were synthesized earlier [5–9]. In order to study influence of annelation manner of coumarin moiety to 2H-chromene part of the molecule on photochromic and spectral properties of SPPs novel indoline, isobenzofuran and naphtopyran spiropyrans were synthesized.

6-Hydroxy-4-methyl-5-formylcoumarin **1** as aldehyde component was used for the synthesis of above mentioned SPPs. Perchlorates of N-substituted 3*H*-indolium, isobenzofuranium and benzo[f]chromenium were employed to form hetaryl part of the molecules. Spiropyrans **2** were obtained by condensation of corresponding 3*H*-indolium perchlorates with aldehyde **1** in isopropanol in the presence of triethylamine (scheme 1).

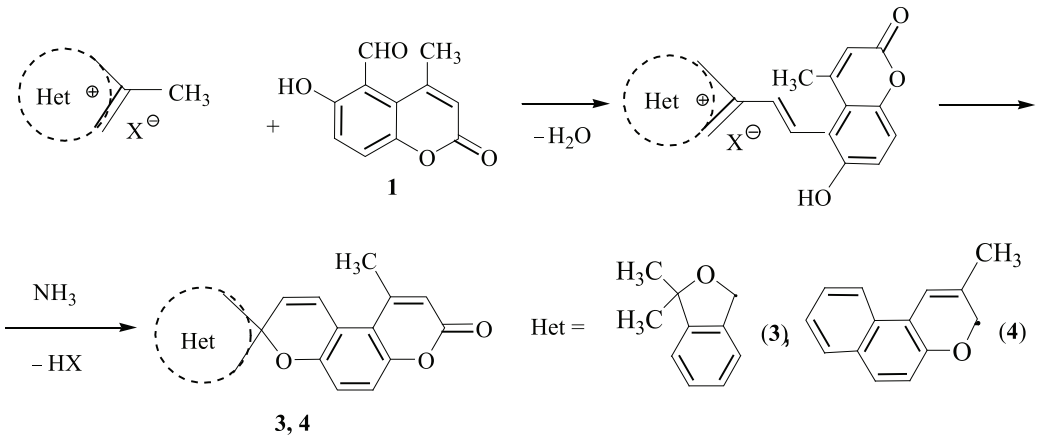
Scheme 1



R = $CH_2C_6H_5$(**a**), C_3H_7(**b**), C_6H_{13}(**c**), C_8H_{17}(**d**)

Spiropyrans **3,4** were synthesized in two steps (scheme 2). The first one represented condensation of isobenzofuranium and benzo[f]chromenium perchlorates with aldehyde **1** in acetic acid. The second step consisted in treatment of intermediate product by dry ammonia in benzene solution.

Scheme 2



In upfield region of ^{1}H NMR spectra of spiropyrans **2-4** are present two signals of magnetic unequivalent *gem*-methyl groups. Signals of diastereotopic methylen group protons of N-benzyl substituent in SPP **2a** are observed as two doublets at 4,20–4,30 ppm. Signal of H-2 proton in double bond of pyran cycle of compounds **2-4** are registered as doublet at 5,32–5,85 ppm. Doublet of H-1 proton is closed by aromatic proton signals at 7,00–8,50 ppm. However for molecules **2b,c,d** and **4** this doublet is seen at 7,40–7,60 ppm. These data confirm that SPPs **2-4** exist in cyclic SP form.

Singlet signal of H-9 proton in coumarin moiety is registered in the region 6,15–6,19 ppm. The location of H-5 and H-6 protons is very specific: doublet at 6,56–6,90 ppm. The second doublet of these protons is closed by aromatic proton signals at 7,00–8,50 ppm, however for **2d** it is seen at 7,32–7,36 ppm.

Table 1

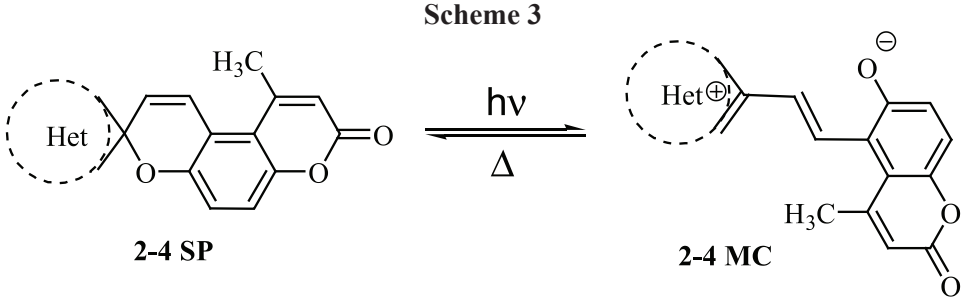
^{1}H NMR spectra of spiropyrans **2-4** in $CDCl_3$

Comp,	Chemical shift, ppm (*J*/Гц)	
	Hetarene fragment	Pyran fragment $C^1H = C^2H$ (1H, d)*
2a**	1,10 s, 1,25 s (6H, 2 *gem*–CH_3); 4,00 d, 4,50 d (2H, NCH_2)	5,40–5,55
2b	0,86 t (3H, CH_3); 1,19 s, 1,55 s (6H, 2 *gem*–CH_3); 1,28 s (2H, CH_2); 3,08 m (2H, NCH_2)	5,83–5,85; 7,56–7,60
2c	0,86 t (3H, CH_3); 1,18–1,28 m (12H, $2CH_3$, $3CH_2$); 1,55 s (2H, CH_2);3,05–3,26 m (2H, N–CH_2)	5,80–5,84; 7,56–7,60
2d	0,86 t (3H, CH_3); 1,18–1,28 m (16H, gem– $2CH_3$, $5CH_2$); 1,56 s (2H, CH_2); 3,05–3,26 m (2H, NCH_2)	5,80–5,84; 7,56–7,60
3**	1,30 s, 1,45 s (3H, 2 *gem*–$2CH_3$)	5,65–5,75
4**	1,82 s (3H, CH_3)	5,60–5,80; 7,40–7,50

N o t e s :
* Signal of the second proton is in the region of aromatic proton signals;
** In C_6D_6.

Electronic absorption spectra of SPPs **2-4** in isopentane-isopropanol mixture (4:1) show long-wavelength bands with maxima centered around 364–402 nm with strongly marked vibration structure which are indicative for cyclic forms SP [2, 10, 11]. The irradiation of compounds **2-4 SP** in above mentioned solution (λ_{irr} 365 nm, $T < 250$ K) leads to formation of merocyanine isomers **2-4 MC**. In dark conditions these isomers thermally convert into the initial spiroforms (table 2).

Scheme 3



2-4 SP **2-4 MC**

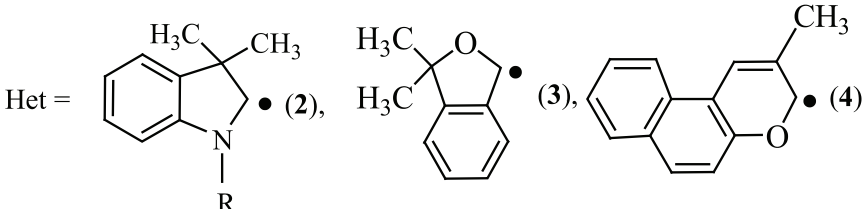


Table 2

Spectral characteristics of isomers **SP** and **MC** for **2-4** in isopentane-isopropanol mixture (4:1) at 203 K

Comp.	Spiroform **SP,** l_{max}, nm	Photoinduced form **MC**, l_{max}, nm
2a	382	609
2b	380	606
2c	384	609
2d	383	606
3	364	550
4	402	602

According to these data a new type of photochromic coumarin-containing SPPs was synthesized.

Acknowledgments

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