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Synthesis and Spectral Properties of a New Spirophotochromic Molecule [†]

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Abstract: One of the most interesting classes of organic photochromic compounds capable of reversible isomerization under the influence of external stimuli are spiropyrans. The optical and other physicochemical properties of the isomeric forms of spiropyrans differ significantly from each other, which makes it possible to use these photochromes as sensors, optoelectronic and holographic devices, memory elements, etc. Also, an undoubted advantage of spiropyrans compared to other classes of photochromic compounds is the relative ease of their preparation and structural modification. At the same time, modification of the structure of spiropyrans by introducing various functional groups opens up great synthetic possibilities for the targeted synthesis of new photochromes with a wide variation of their spectral and kinetic properties. In development of research aimed at expanding the boundaries of the use of spirophotochromic compounds, in order to obtain new light-controlled materials with different characteristics, as well as to study the influence of functional groups in the spirophotochromic molecule on the spectral and photochromic properties, we have synthesized a new spiropyran. In this work, we synthesized a new salt of photochromic spiropyran containing various functional groups (–CHO, $–NO_2$, $–OCH_3$, $–(CH_2)_5N(CH_3)_2*HBr$), capable of reversibly responding to external influences. Photoinduced transformations, spectral and kinetic characteristics of the synthesized compound were studied.

Keywords: spiropyran; merocyanine; photochromism; spectral and kinetic properties; photodegradation

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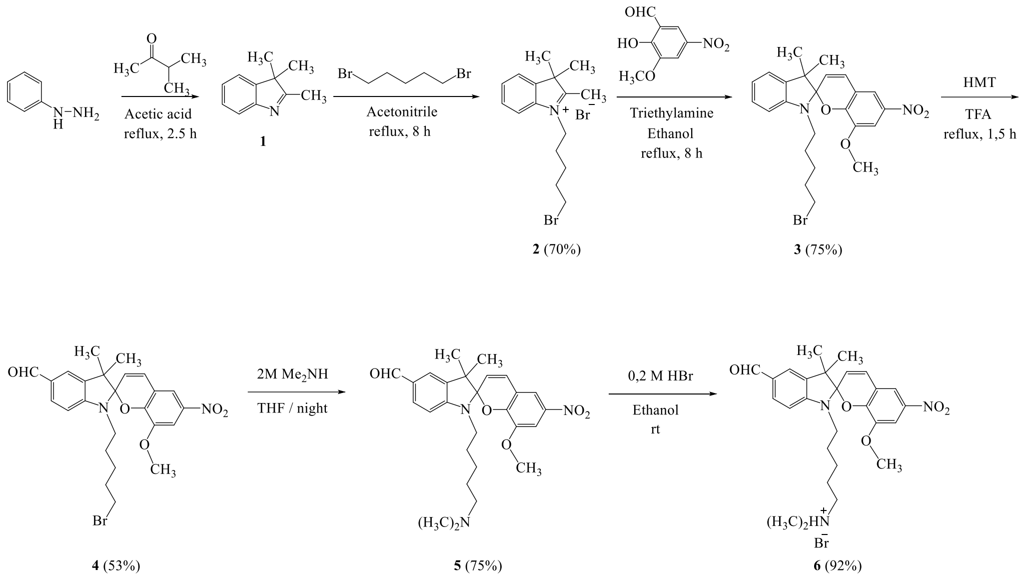
1. Introduction

The synthesis and design of functional molecules in information technology, medical applications, opto- and optobioelectronics, transport systems, photocontrolled nanostructured materials, catalysis, biomaterials, molecular photodynamic sensors is an actively developing area of research [1–3]. These compounds include spiropyrans [4]. Due to the relative ease of their preparation, structural transformation, and the possibility of directed changes in optical characteristics over a wide range when changing the structure, spiropyrans attract special attention as one of the most promising classes of photochromic organic molecules.

2. Results and Discussion

Taking into account the above, and also trying to expand the class of photochromic compounds and study the effect of substituents on the electronic properties and stability of the new molecule, we synthesized a new photochromic salt of spiropyran containing various functional groups. Spiropyran was synthesized using methods reported in the literature [5,6] according to Scheme 1:



Scheme 1. Synthesis of compounds **6**.

The product was purified by silica column chromatography using 10:1 $CHCl_3$:EtOH as the eluant. The structures of compound **6** were determined using ^1H and ^{13}C NMR spectroscopy and high-resolution mass spectrometry.

In the ^1H NMR spectrum of compound **6** in a mixture of chloroform and DMSO, the signal positions and the spin–spin coupling constants, are in line with the presented structure (Figure 1). For example, two singlets at 0.45 and 0.57 ppm correspond to methyl protons at the indole nitrogen atom. The singlet with a chemical shift at 2.09 ppm corresponds to protons of two methyl groups at the ammonium nitrogen. In its turn the singlet with a chemical shift at 3.07 ppm corresponds to protons of carbon at the methoxy group. The signal indicating the presence of a spirocyclic structure is a doublet in the aromatic region at 5.17 ppm with a spin–spin coupling constant of 10.3 Hz, which corresponds to the CH group at the spiro atom in the pyran moiety. The formyl proton signal is manifested at 9.04 ppm.

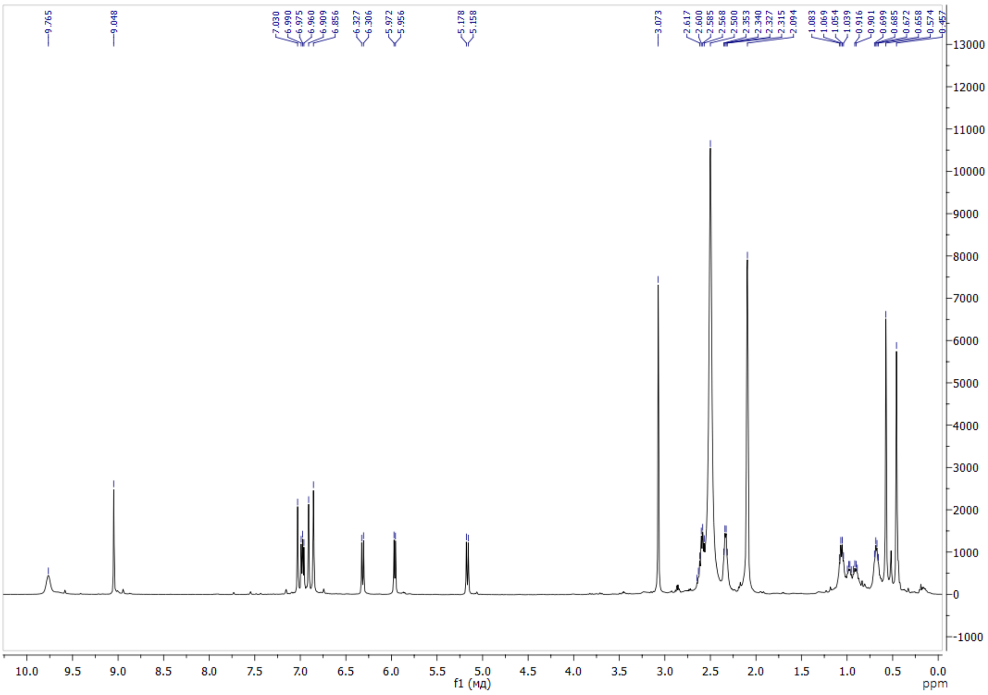


Figure 1. ^{1}H NMR spectra of compound **6**.

In the ^{13}C NMR spectrum of compound **6** in a mixture of chloroform and DMSO, the number of signals is equal to the number of carbon atoms in the molecule (Figure 2). The metoxy group carbon signal is detected at 147.38 ppm. The characteristic signal of the spirocyclic carbon atom is manifested at 105.06 ppm and is correlated with the proton signal of the methyl groups and the C3′ and C4′ proton signals in the ^{1}H–^{13}C HMBC spectrum. The formyl carbon signal is detected at 189.29 ppm.

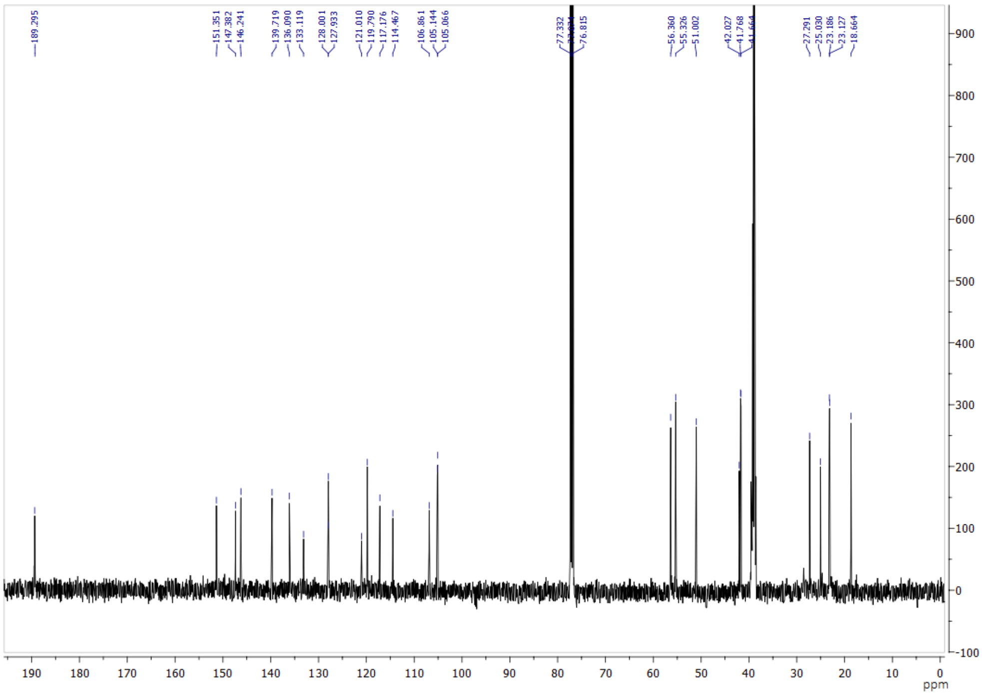
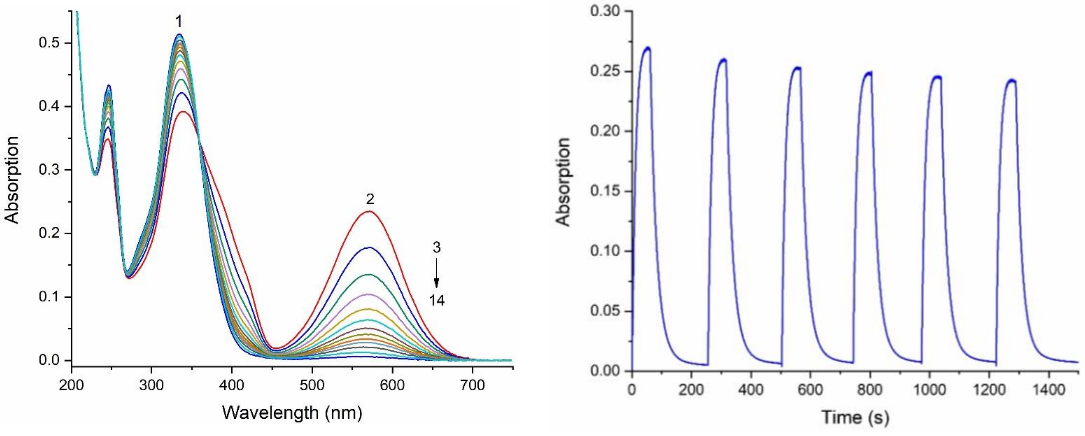


Figure 2. ^{13}C NMR spectra of compound **6**.

Figure 3a shows the photoinduced spectral changes of spiropyran **6** in ethanol. It can be seen that the absorption spectrum of the photoinduced merocyanine form has absorption maximum in the visible region at 572 nm. During the dark relaxation process, the intensity of photoinduced absorption bands gradually decreases.

The decline in the amplitude of variation of the absorption band intensity of the photoinduced merocyanine form of spiropyran **6** indicates that this compound is subject to photochromic transformations accompanied by a gradual photodegradation (Figure 3b).



(**a**) (**b**)

Figure 3. (**a**) Absorption spectra of spiropyran **6** in ethanol before (1), after UV irradiation during 60 s through a UFS–1 optical filter in the photoequilibrium state (2), and subsequent dark bleaching (3–14); (**b**) Kinetics of coloration through a UFS–1 optical filter and subsequent bleaching in the dark for compound **6** dissolved in ethanol measured at 572 nm.

With continuous exposure of a solution of compound **6** to UV light, a gradual decrease in intensity at the absorption maximum of the merocyanine form can be observed in the spectrum, which indicates the destruction of spirophotochrome. Complete photodecomposition is observed after 2 h (Figure 4).

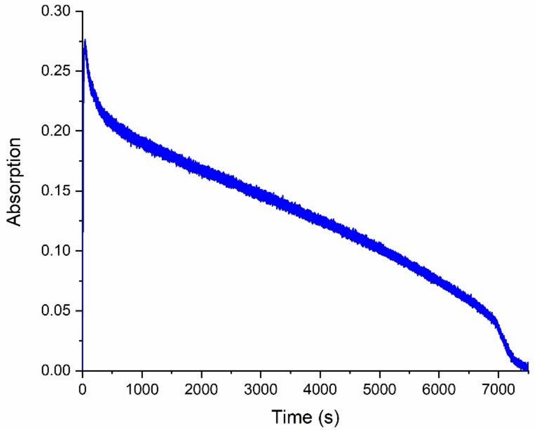


Figure 4. Kinetics of photodegradation of spiropyran **6** upon continuous UV irradiation through a UFS–1 light filter, recorded at 572 nm.

3. Conclusions

Thus, in this work, we synthesized a new salt of photochromic spiropyran containing various functional groups that can react reversibly to external influences, and also studied photoinduced transformations, spectral and kinetic characteristics of the synthesized compound. It was found that the resulting spiropyran exhibits positive photochromism and is quite resistant to irreversible photochemical transformations. This opens up prospects for the use of such molecules as molecular switches.

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Conflicts of Interest: The authors declare no conflicts of interest.

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