

Proceeding Paper

# Synthesis and Photochromic Properties of a New Functionally Substituted Molecule Based on Spiropyran <sup>†</sup>

Artur Khuzin \* and Liliya Khuzina

Institute of Petrochemistry and Catalysis, Ufa Federal Research Center of the Russian Academy of Sciences, 141 Oktyabrya Prospect, 450075 Ufa, Russia; khuzinall@mail.ru (L.K.)

\* Correspondence: artur.khuzin@gmail.com

<sup>†</sup> Presented at the 28th International Electronic Conference on Synthetic Organic Chemistry (ECSOC 2024), 15–30 November 2024; Available online: <https://sciforum.net/event/ecsoc-28>.

**Abstract:** Bistable compounds capable of reversible molecular rearrangements between two nonequivalent states are of great interest for the creation of new materials and the study of many chemical and biological processes that are used in modern technologies. One of the most studied mechanisms of the functioning of such bistable systems is photochromism—a change in the structure and spectral properties of compounds under the influence of external factors. Among the most studied classes of organic photochromic structures are spirocyclic compounds, such as spiropyrans, which are capable of switching between the usually colorless cyclic and colored merocyanine forms when exposed to external stimuli such as light, temperature, pressure, polarity, mechanical stress, electric or magnetic field, which allows their use in memory elements, as optoelectronic devices, sensors, etc. The choice of spiropyrans as model compounds of this class of photochromic molecules is not accidental, since they are the most well-known and unique representatives of photochromic compounds due to the relative ease of their preparation, structural modification and the possibility of targeted changes in spectral and kinetic characteristics over a wide range. The isomeric forms of spiropyrans differ significantly in their physical and optical properties, which makes them very promising compounds for use in various fields of science and technology. In this work, we report the synthesis of a new salt of photochromic spiropyran containing various functional groups (–CHO, –NO<sub>2</sub>, –OCH<sub>3</sub>, –(CH<sub>2</sub>)<sub>5</sub>PPh<sub>3</sub>), 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

**Citation:** Khuzin, A.; Khuzina, L. Synthesis and Photochromic Properties of a New Functionally Substituted Molecule Based on Spiropyran. *Chem. Proc.* **2024**, *6*, x. <https://doi.org/10.3390/xxxxx>

Academic Editor(s): Name

Published: 15 November 2024



**Copyright:** © 2024 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

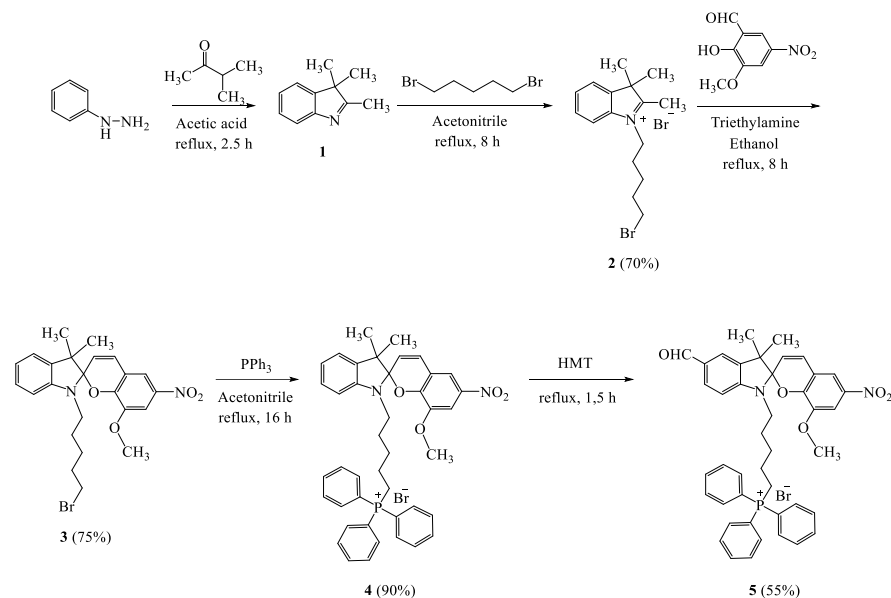
## 1. Introduction

Organic photochromic molecules are part of a large number of hybrid structures, materials and devices that operate under the remote control of light radiation [1–5]. Among the wide range of organic photochromes, spiropyrans are one of the most interesting classes due to their high photosensitivity, easy structural modification and relatively easy method of their preparation. The photochromic properties of spiropyrans are due to photolytic cleavage of the Cspiro–O bond under the influence of ultraviolet radiation, which leads to the formation of a brightly colored form of merocyanine (MC). The spirocyclic (SP) and merocyanine forms of spiropyrans differ from each other in absorption spectra, dipole moments, metal ion affinities, fluorescence, etc., making these compounds effective molecular switches. Such switches find application in various fields of science and technology [6–9].

## 2. Results and Discussion

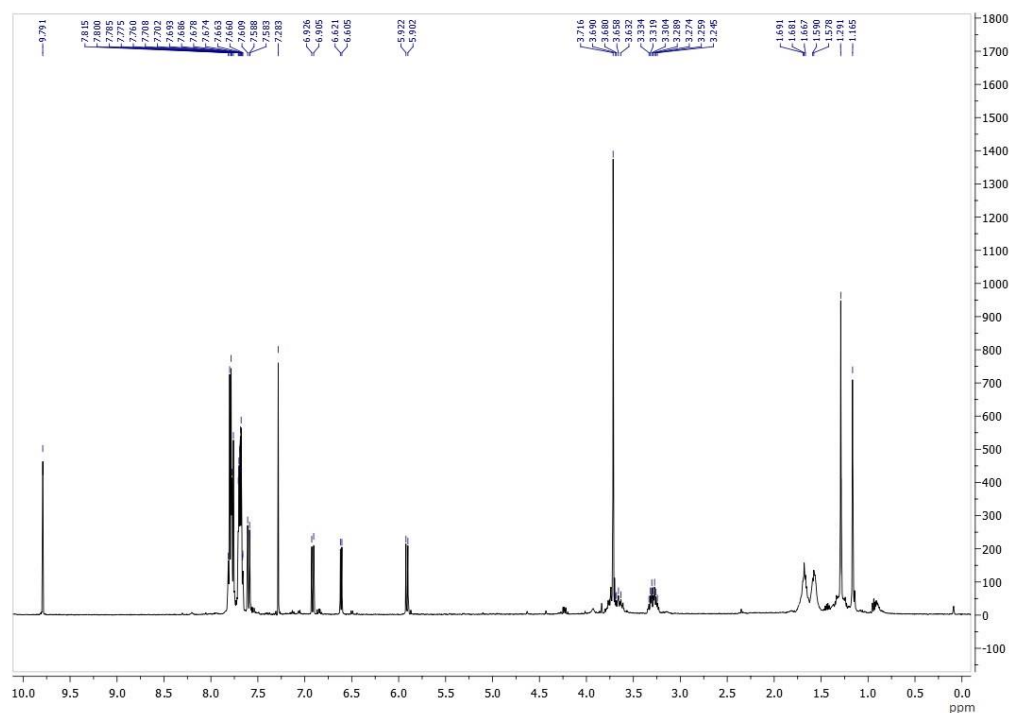
In order to expand the range and predict the influence of the nature and position of substituents on the photochromism of spirophotochromes of the indoline series, we obtained spiropyran **5**, containing various functional groups in its structure.

Spiropyran **5** was obtained according to the previously proposed [10] method, according to Scheme 1:

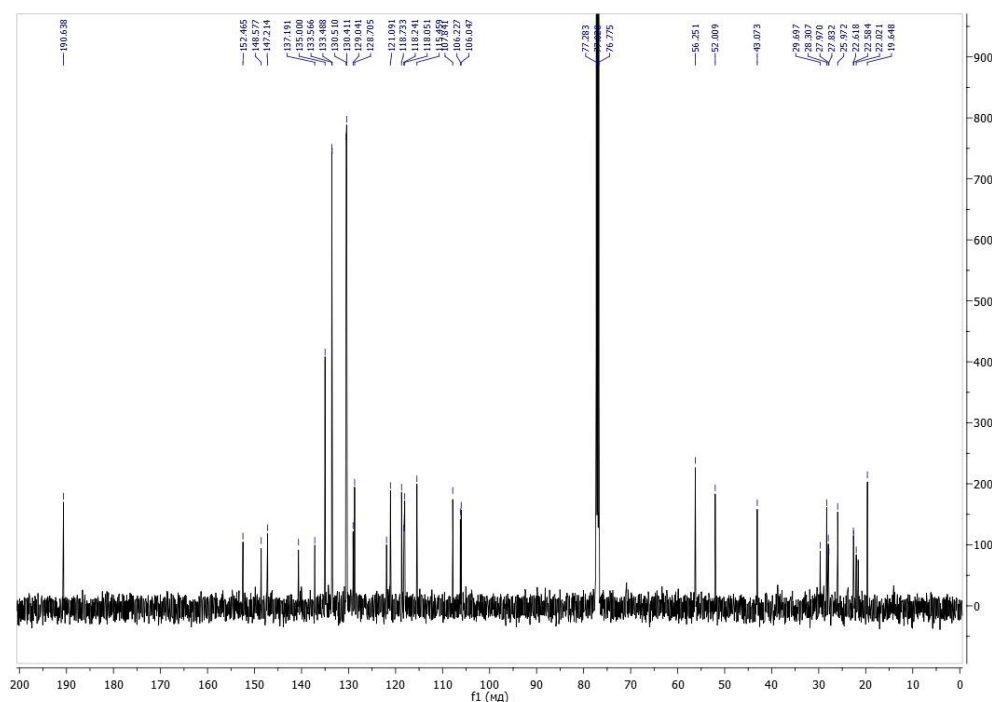


**Scheme 1.** Synthesis of compounds **5**.

The product **5** was purified by silica column chromatography using 5:1  $\text{CHCl}_3$ :EtOH as the eluant. The structures of compound **5** were determined using  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and high-resolution mass spectrometry.



**Figure 1.**  $^1\text{H}$  NMR spectra of compound **5**.



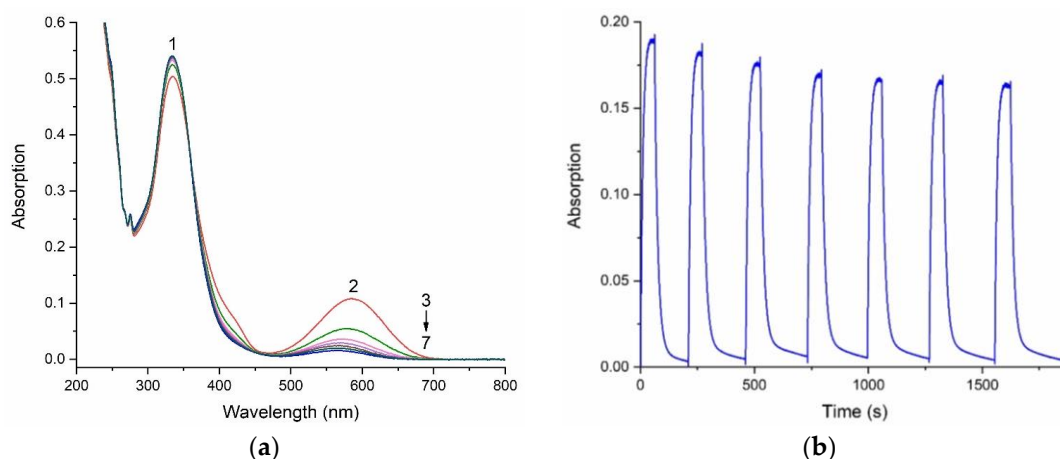
**Figure 2.**  $^{13}\text{C}$  NMR spectra of compound **5**.

In the  $^1\text{H}$  NMR spectrum of compound **5** in chloroform- $\text{D}$ , the signal positions and the spin–spin coupling constants, are in line with the presented structure. For example, two singlets at 1.16 and 1.29 ppm correspond to methyl protons at the indole nitrogen atom. The singlet with a chemical shift at 3.71 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 5.91 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 9.79 ppm.

In the  $^{13}\text{C}$  NMR spectrum of compound **5** in chloroform- $\text{D}$ , the number of signals is equal to the number of carbon atoms in the molecule. The methoxy group carbon signal is detected at 56.25 ppm. The characteristic signal of the spirocyclic carbon atom is manifested at 106.22 ppm and is correlated with the proton signal of the methyl groups and the C3' and C4' proton signals in the  $^1\text{H}$ – $^{13}\text{C}$  HMBC spectrum. The formyl carbon signal is detected at 190.63 ppm.

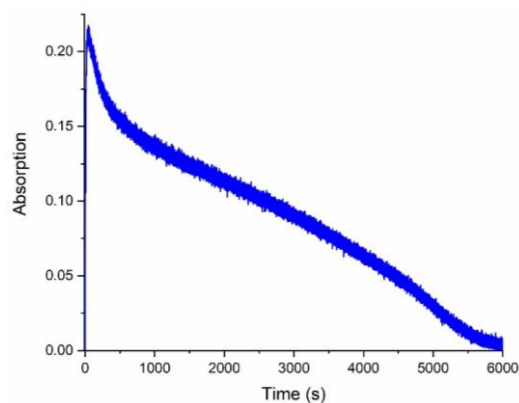
The photoinduced spectral changes of spiropyran in ethanol is shown in Figure 3a. It can be seen that the absorption spectrum of the photoinduced merocyanine form has absorption maximum in the visible region at 586 nm. During the dark relaxation process, the intensity of photoinduced absorption bands gradually decreases.

The decline in the amplitude of variation of the absorption band intensity of the photoinduced merocyanine form of spiropyran **5** indicates that this compound is subject to photochromic transformations accompanied by a gradual photodegradation (Figure 3b).



**Figure 3.** (a) Absorption spectra of spiropyran 5 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 (3–7). (b) Kinetics of coloration through a UFS-1 optical filter and subsequent bleaching in the dark for compound 5 dissolved in ethanol measured at 586 nm.

With continuous exposure of a solution of compound 5 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 spirophtochrome. Complete photodecomposition is observed after 1.5 h (Figure 4).



**Figure 4.** Kinetics of photodegradation of spiropyran 5 upon continuous UV irradiation through a UFS-1 light filter, recorded at 586 nm.

### 3. Conclusions

Thus, in this work, we synthesized a new photochromic spiropyran salt containing various functional groups, characterized by photochromism and significant resistance to irreversible phototransformations. Photoinduced transformations and optical characteristics of the synthesized compound were studied.

This opens up prospects for the application of such hybrid molecules in organic field effect transistors, solar energy converters and memory elements.

**Author Contributions:** Conceptualization, A.K.; methodology, A.K. and L.K.; validation, A.K. and L.K.; formal analysis, L.K.; investigation, A.K. and L.K.; writing—original draft preparation, A.K.; writing—review and editing, A.K.; data analysis and visualisation, and L.K.; funding acquisition, A.K. and L.K. All authors have read and agreed to the published version of the manuscript.

**Funding:** The work was conducted within approved plans for research projects at the IPC RAS State Registration No. FMRS-2022-0075.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Data are contained within the paper.

**Acknowledgments:** The structural studies were performed using the equipment of the Collective Usage Centre 'Agidel' at the Institute of Petrochemistry and Catalysis of the Russian Academy of Sciences.

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

## References

1. Guglielmetti, R.J. In *Photochromism: Molecules and Systems*; Durr, H.; Bouas-Laurent, H.; Eds.; Elsevier: Amsterdam, The Netherlands, 1990; pp. 314–466.
2. Minkin, V.I. Light-controlled molecular switches based on bistable spirocyclic organic and coordination compounds. *Russ. Chem. Rev.* **2013**, *82*, 1–26.
3. Klajn, R. Spiropyran-based dynamic materials. *Chem. Soc. Rev.* **2014**, *43*, 148–184.
4. Wang L.; Li Q. Photochromism into nanosystems: towards lighting up the future nanoworld. *Chem. Soc. Rev.* **2018**, *47*, 1044–1097.
5. Kortekaas, L.; Browne, W.R. The evolution of spiropyran: fundamentals and progress of an extraordinarily versatile photochrome. *Chem. Soc. Rev.* **2019**, *48*, 3406–3424.
6. Natali, M.; Giordani, S. Molecular switches as photocontrollable “smart” receptors. *Chem. Soc. Rev.* **2012**, *41*, 4010–4029.
7. Paramonov, S.V.; Lokshin, V.; Fedorova, O.A. Spiropyran, chromene or spirooxazine ligands: insights into mutual relations between complexing and photochromic properties. *J. Photochem. Photobiol. C Photochem. Rev.* **2011**, *12*, 209–236.
8. Abdel-Mottaleb, M.S.A.; Saif, M.; Attia, M.S.; Abo-Alya, M.M.; Mobarez, S.N. Lanthanide complexes of spiropyran photoswitch and sensor: Spectroscopic investigations and computational modelling. *Photochem. Photobiol. Sci.* **2018**, *17*, 221–230.
9. Koçer, A.; Walko, M.; Meijberg, M.; Feringa, B.L. A light-actuated nanovalve derived from a channel protein. *Science* **2005**, *309*, 755–758.
10. Khuzin, A.A.; Galimov, D.I.; Tulyabaev, A.R.; Khuzina, L.L. Synthesis, New Triphenylphosphonium Salts of Spiroyrans: Synthesis and Photochromic Properties. *Molecules* **2024**, *29*, 368–378.

**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.