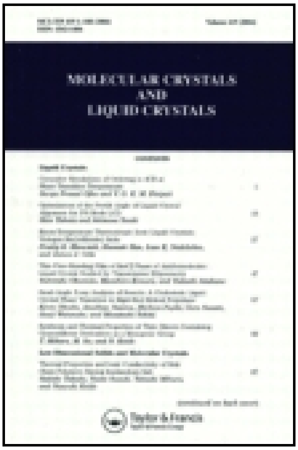

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Novel Spiropyrans With the Luminescent Larle in the 2H-Chromene Fragment

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NOVEL SPIROPYRANS WITH THE LUMINESCENT LABLE IN THE 2H-CHROMENE FRAGMENT

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Abstract A series of novel spirobenzopyrans containing the fluorescent label, 3,5-diphenyl pyrazoline substituent, in the position 7 of the 2H-chromene fragment has been prepared. The compounds display high efficiencies of the fluorescence (460-490 nm) and have a potential for application as negative luminescent materials for optical storage.

INTRODUCTION

To enhance the ligtsensitivity of the photoresponsible material, luminescent method of the nondestructive reading of the optical information may be efficiently used in the case of one of the interconverting forms possesses luminescent properties: A B. The higher are quantum efficiencies (ϕ_B) of the photoreaction, of luminescence (ϕ_l) of the photoisomer B and the higher is its absorbance on the wavelength of the luminescence excitation spectrum, the higher is the sensitivity to light of the photochromic material.

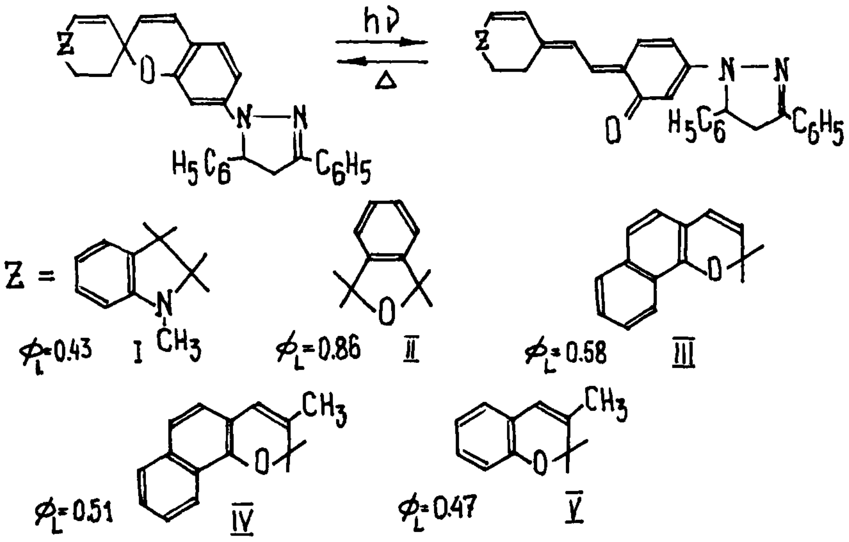
Indoline spirobenzopyrans proved to be promising photochromic systems with the luminescent type of reading due to long-wave fluorescence of the photomerocyanine isomers[1,2], but the drawback of such a system is a rather low quantum efficiency of the fluorescence (0,01-0,1) due to fast deactivation of the proper excited state caused by the stereoisomerization of the merocyanines.

The alternative approach to the photochromic systems with luminescent reading would be possible if the increase in usually very low quantum efficiency of fluorescence of the ring-closed forms A could be attained. We addressed this problem by a synthetic design of novel spirobenzopyrans I-V containing the fluorescent label, namely, 3,5-diphenylpyrazoline moiety, attached to the 2H-chromene fragment.

RESULTS AND DISCUSSION

A series of the spirobenzopyrans based on different heterocyclic fragments with the 2H-chromene moiety containing 3,5-diphenylpyrazoline substituent in the position 7 have been prepared.

The key precursor for the synthesis of compounds I-V is 3,5-diphenyl-1-(3-hydroxy-4-formyl)-2-pyrazoline which has been prepared through the sequence of reactions, starting from the condensation of the m-methoxyphenylhydrazine with chalcone, formylation of the product of the condensation by DMFA+$POCl_3$ and subsequent demethylation with $AlCl_3$. Spiropyrans I-V were then prepared by coupling of hydroxyformylpyrazoline with respective methylene bases (indoline) or of 2-alkyl substituted benzofurilium or benzo (naphto)pyrilium perchlorates.



Spectral and photochemical investigation of the compounds I-V were carried out in PMMA films. Typical absorption and fluorescence spectra along with spectrum of excitation of fluorescence for compound III is shown in Figure 1.

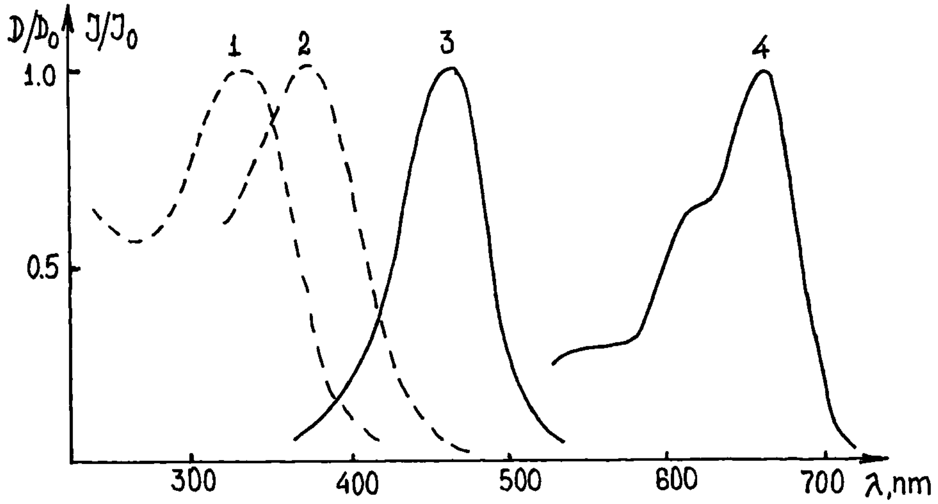


FIGURE 1 Absorption (1), excitation of fluorescence (2), luminescence (3) spectra of the form A. Absorption spectrum of the form B (4). (For the compound III).

The peculiar feature of the spectral behaviour of the compound III is that the spectrum of excitation of fluorescence is long-wave shifted compared to the absorption spectrum. It is explained by the complicated nature of the long-wavelength absorption band of III, originated from two electronic transitions localized at different parts of the molecule. The first of them is associated with the 2H-chromene moiete (maximum 350 nm), whereas the second one relates to the pyrazoline fragment. Quantum yields of the fluorescence ϕ_l for the structures

I-V are higher by 3-4 orders ϕ_L for spiropyrans without the luminescent lable. Excitation in the absorption band of the electronic transition localized on the chromene fragment (λ=365 nm) leads to the ring-opening reactin usual for spiropyrans resulting in the formation of nonfluorescent merocyanine isomer absorbing in the region of 600-700 nm. The fluorescent intencity of the spiropyrans exponentially decreases with the phototransformation depending on the irradiation time. The rate of recording of the optical information is an order of magnitude higher than that of the luminescent matireal based on the dimerization of anthracene. The photoreaction, however, proceeds with very long yield when being initiated by illumination at the tail of the excitation of fluorescent band (420-430 nm).

This enables one to carry out practically non destructive information reading by means of registration of fluorescence of spiropyrans A not photoconverted to B. Restoring the absorption and fluorescent spectra of the initial spiropyran form in PMMA (erasing of the information) may be achieved by both irradiation with visible light and by heating the film to 70-80° C. Restoring of the initial form A is not full due to the side irreversible photoprocess, but can be repeatedly carried out.

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