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PHOTOCHROMIC SPIROPYRANS OF COUMARINE SERIES

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Abstract Novel spiropyrans on the base of 4-methyl-7-hydroxy-8-formylcoumarine (I) and 7-R-4-hydroxy-3-formylcoumarine (II) are synthesized. The compounds (I) and (II) exhibit in solution respectively direct and inverse photochromic reaction. The influence of the heterene moiety and solvent polarity on spectral and photochromic properties have been studied. The indoline derivatives of (I) are also photochromic in crystal.

INTRODUCTION

Spiropyrans and their molecular transformations have attracted the interest of photochemists for many years due to their importance for various practical applications. From another hand, the influence of the structure of spiropyrans on the mechanism of their transformations continue to provide intresting problems for basic scientific research[1,2]. In particular, by variation of the spiropyran structure, it may become possible to prepare compounds with inverse photochromism, i.e. those undergoing reverse photobleaching and thermal coloration[3]. With this purpose, the spiropyrans of coumarine series have been synthesized and studied.

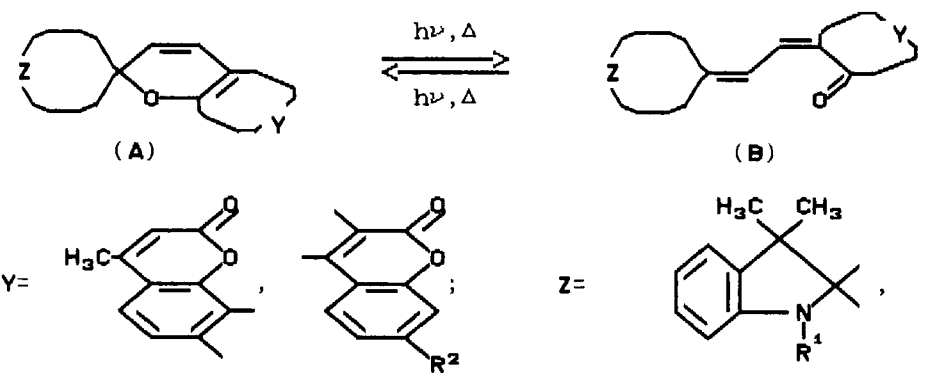
EXPERIMENTAL

Absorption spectra were recorded with a "Specord M40"

spectrophotometer (Germany). Fluorescence and fluorescence excitation spectra were measured with use of "Elumin 2M" spectrofluorimeter (Russia). For registration of reflectance spectra of crystalline powder samples "Specord M40" spectrophotometer with the facilities attached to measure $8^{\circ}/d$ geometry have been used. For initiation of the photoreactions, the high-pressure Hg-lamp with glass light-filters was used. The efficiency of photocoloration (η) was determined as tangent of the slope of the photocoloration curve $D(\lambda^{B}_{max})/D_{max}(\lambda^{B}_{max})=f(t_{irrad})$ at the initial stage of photoreaction for spiropyrans under study by reference to that for the spiropyrans (I).

RESULTS AND DISCUSSION

The long-wavelength bands with sharp vibronic structure are observed at 330-350 nm in the electronic absorption spectra of the initial (A) spiropyrans (I)-(VIII). The absorption



R^1= CH_3, C_3H_7, C_6H_{13}, CH_2Ph; R^2= H, OH, OCH_3, $OCOCH_3$.

bands position does not depend on solvent polarity and substituents in the indoline fragment, but depends slightly on the Z-moiety structure (λ^{A}_{max}= 343, 344, 345 and 349 nm for (V), (VI), (VII) and (VIII), (I)-(IV) respectively).

All compounds (I)-(VIII) exhibit direct photochromic reaction under irradiation (λ=365 nm) of the glassy solutions (in the mixture isopentane- isopropanol, 4:1 - IIP) at 77-250 K. The photo- and thermoreversible formation of the noncyclic colored product (B) is observed. The absorption band position of the colored form (B) depends strongly on the type of the Z-moiety. Shorter-wavelength absorption bands (λ^{B}_{max}=560-562 nm) are exibited by indoline derivatives (I)-(IV) and longer-wavelength bands λ^{B}_{max}= 602, 620, 650, 660 nm are typical for compounds (V), (VI), (VII), (VIII) respectively. The greatest efficiency of the photocoloration is characteristic of indoline spiropyrans (I)-(IV) (η=0,9-1), η=0,2 - for compound (V) and the lowest efficiency (η<0,01) is shown by compounds (VI)-(VIII). Photoproducts (B) fluoresce in solvent at 77 K (λ^{flu}_{max}= 575-580nm). We found also the compounds (I)-(IV) to be photochromic in crystal.

The role of the (Y)-moiety in the studied molecules is displayed by the relative stability of the colored and colorless forms in the ground state. Unlike spiropyrans (I)-(VIII), the compounds (IX)-(XVI) exist in the stable non-cyclic form (B). The electronic absorption spectra of the compounds (IX)-(XVI) are characterized by the long-wavelength bands with λ^{B}_{max}=486-491 nm, possesing very high extinction coefficients ε=(1,1-1,8)10^5 l $M^{-1}cm^{-1}$. The positions of these bands do not depend strongly on the R^1, R^2- substituent nature and solvent polarity. Fluorescence is observed for the initial form (B) of all compounds in the solutions (λ^{flu}_{max}=506-513 nm, quantum yield ϕ=0,008-0,02 in toluene, T=295 K).

Under irradiation (λ=436 nm) of the IIP-solutions of compounds (IX)-(XVI) at T<240 K photo- and thermoreversible photobleaching reaction is observed due to the cyclic

isomer (A) formation. The absorption bands typical for this isomer (with λ^{A}_{max}=350-352 nm and vibronic structure) appear. Therefore, compounds (IX)-(XVI) are prone to inverse photochromism.

Along with the absorption spectra typical for solutions, additional long-wavelength absorption (excitation) ($\lambda^{obs,ex}_{max}$=536-555 nm) and corresponding fluorescence bands (λ^{flu}_{max}=575-585 nm) are observed in crystals of the compounds (IX)-(XVI). It can be connected with the stabilization of the noncyclic isomer nonexisting in solution.

CONCLUSIONS

Novel spiropyrans on the base of 4-methyl-7-hydroxy-8-formyl coumarine (I) and 7-R-4-hydroxy-3-formyl-coumarine proved to display respectively direct and inverse photochromic reactions. The absorption spectra of colored form and efficiencies of the photoreactions depend considerably on the nature of heterene moiety of spiropyrans and solvent polarity. The indoline derivatives of direct photochromic compounds are photochromic in crystal also.

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