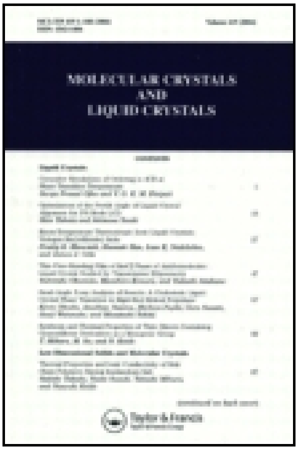

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Photochromic Fulgides of the Indole and Pyrrole Series

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PHOTOCHROMIC FULGIDES OF THE INDOLE AND PYRROLE SERIES

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Abstract Novel photochromic fulgides on the base of 3-formyl(acetyl)indole and 2-formyl(acetyl)pyrrole were synthesized and studied. The mechanism of the photoinduced processes in solution and vacuum-deposited films includes: photoreversible (E)-(Z)-isomerization, photo- and thermoreversible cyclizations with the formation of colored dihydrocarbazole and dihydroindoline derivatives which irreversibly convert into uncolored form by 1,5-hydrogen shift reaction.

INTRODUCTION

Fulgides are photochromic compounds having a number of useful properties including high quantum yield of photoreaction, thermal stability of the initial and colored forms and fatigue resistance[1]. Therefore, novel fulgides on the base of 3-formyl(acetyl)indole[2] and 2-formyl(acetyl)-pyrrole[3] were synthesized and studied. In the present work the photoinduced processes in the molecules of the novel and previously obtained fulgides of indole and pyrrole series have been studied.

EXPERIMENTAL

Absorption spectra were recorded with a "Specord M40" spectrophotometer (Germany). Fluorescence and fluorescence excitation spectra were measured with "Elumin 2M" spectrofluorimeter (Russia). For initiation of the photoreactions the high-pressure Hg-lamp with glass light-filters was used. The equipment used for flash increase of solvent polarity for both (E)- and (Z)-forms is observed (for hexane and DMSO $\Delta\lambda^{abs}_{max}$=20 nm).

Under cotinuous irradiation of the solutions (toluene, ethanol) of the fulgides (I)-(V), (IX) (with R^1=H), only (E)⟶(Z) and (Z)⟶(E) isomerizations have been observed, which proceed exceptionaly through the excited states. Under the same conditions, both (E)-(Z)-photoisomerization and thermo- photoreversible formation of the cyclic product (C) are observed when fulgides (VI)-(VIII), (X) (with R^1=CH_3) are irradiated. The latter are characterized by absorption (excitation) long-wavelength band with $\lambda^{abs,exc}_{max}$=535-560 nm and by corresponding fluorescence band with λ^{flu}_{max}=680-700 nm. The reverse dark reaction (C)⟶(E) proceeds very slowly and proceeds decay time ($\tau^{C}_{1/2}$) grows with decrease of solvent polarity. Thus, for compound (VI) at 293 K $\tau^{C}_{1/2}$=1,4 10^3 s and 6,6 10^4s for DMSO and acetonitrile respectively and in hexane or toluene the thermoreaction (C)⟶(E) does not occur.

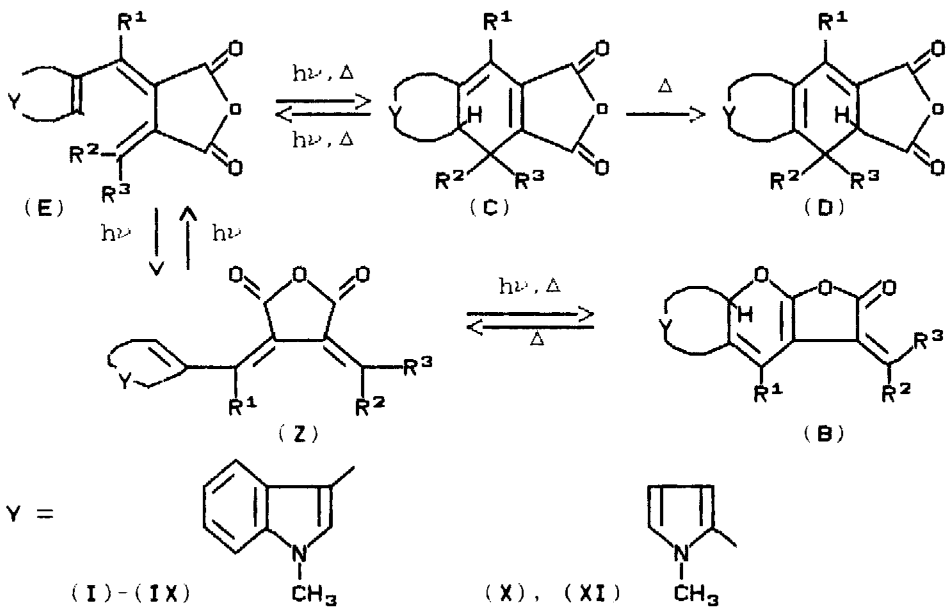
For compounds (I)-(III), (IX) (R^1=H), the photoproduct (C) may be registered by flash-photolysis method only because of the decay time $\tau^{C}_{1/2}$=250-750 ms which diminishes with the increase of solvent polarity as well as for the compounds with R^1=CH_3. Hence, the stability of the photoproduct (C) increases drastically by inclusion of a bulky alkyl substituent.

At the final step of this (E)-reaction channel, (C) thermally rearranges to (D) through 1,5-hydrogen shift. For (D) long-wavelength absorption band is found in the region of 330-340 nm.

The conditions favourable for the cyclic structure (B) formation in the ground and excited states may be created by the type of the structure (Z) ((Z)-reaction channel). Therefore in liquid solutions (hexane, toluene, acetonitrile, DMSO, T= 295 K) of compounds (I)-(III), (VI), (VII) the shortlived structure (B) is registered (absorption band with λ^{B}_{max}= 460 nm, $\tau^{B}_{1/2}$=250-700 ms grows with the decrease of solvent polarity). In solutions,in photolysis is described in detail in ref. 4.

RESULTS AND DISCUSSION

The initial forms of fulgides (I)-(X) can have two main isomeric structures - (E) and (Z), which are distinguished by relative positions of indoline (pyrrole) fragment and R^1- substituent. The additional isomers can be realized due to the existence of two different R^2- and R^3- substituents.



I R^1=H, R^2=R^3=CH_3; II R^1=H, R^2=CH_3, R^3=C_2H_5; III R^1=H, R^2+R^3=C_5H_{10}; IV R^1=H, R^2+R^3=Ad; V R^1=H, R^2=R^3=Ph; VI R^1=R^2=R^3=CH_3; VII R^1=R^2=CH_3, R^3=C_2H_5; VIII R^1=CH_3, R^2+R^3=Ad; IX R^1=H, R^2=R^3=CH_3; X R^1=R^2=R^3=CH_3;

(E)- and (Z)-isomers are characterized by the long-wavelength absorption bands with λ^{abs}_{max}=375-395nm and 400-420 nm respectively and corresponding fluorescence bands with λ^{flu}_{max}=440-445 nm and 490-495 nm respectively (in toluene, T=295 K). The substantial bathochromic shift of the long-wavelength absorption and fluorescence bands with which fulgides are in the (Z)-form mainly, the form (B) is displayed by fluorescence and excitation spectra (λ^{flu}_{max}=515-520 nm, λ^{exc}_{max}=460 nm in toluene).

The specific irreversible low-efficient reaction of the cyclization is observed in fulgide (V): the dihydronaphthaline structure (D)-tipe with the typical absorption band (λ^{abs}_{max}=293 nm)[5] is formed upon exctended irradiation (toluen, $\tau > 10^4$ s) due to 1,5-hydrogen shift in the shortliving ground state intermediate (C)-type, which was displayed through typical transient absorption band (λ^{abs}_{max}= 500 nm)[6] by flash-photolysis method.

The vacuum-deposited thin films of all fulgides convenient for the practical utilization have been obtained. The preliminary findings showed that the similar phoroinduced processes were exibited in both films and solution.

CONCLUSIONS

The main mechanism of the photoinduced reactions of the fulgides under study includes: (i) the photoreversible (E)-(Z)-isomerisation; (ii) photo- and thermo- reversible reactions (E)⟶(C) and (Z)⟶(B) of cyclization; (iii) irreversible thermal reaction of 1,5- hydrogen shift. The stability of the photocolored form (C) increase drastically by inclusion of bulky alkyl substituents R^1 and decrease whith growth of the solvent polarity.

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