MECHANISM OF THE PHOTOREACTIONS OF FULGIDES BASED ON 1,2-DIMETHYL-3-FORMYLINDOLE

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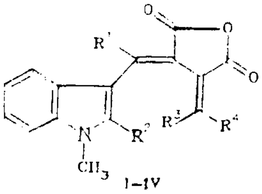
Only E ⇄ Z isomerization is observed for the steady irradiation of fulgides based on 1,2-dimethyl-3-formylindole in contrast to the analogs based on 3-acetylindole. The formation of cyclic photoisomers is registered by the method of impulse photolysis. The presence of a methyl substituent in the position 2 of the indole portion leads to a significant increase in the stability of the photochromic system. The introduction of alternative reaction centers of cyclization in the form of bulky phenyl groups leads to the suppression of electrocyclization at the position 2 of the indole portion and the formation of dihydronaphthalene structures.

It was shown in the works [1-3] that two types of photochemical reaction are characteristic for the fulgide molecules of the indole series: the photoreversible E—Z isomerization, as well as the thermally and photochemically reversible cyclization reaction. The mechanism and kinetics of these photoprocesses depend significantly on the structure of the fulgide molecules. In this connection, the influence of substituents on the spectral characteristics and the mechanism of the photoreactions in fulgide molecules based on 1,2-dimethyl-3-formylindole, the synthesis of which is described in [4], was studied in the present work.



I–IV

I–IV $R^1 = H$, $R^2 = CH_3$; I $R^3 = R^4 = CH_3$; II $R^3 = CH_3$; $R^4 = C_2H_5$; III $R^3 + R^4 = C_5H_{10}$; IV $R^3 = R^4 = C_6H_5$

In the steady irradiation of solutions of the fulgides (I)-(III), changes in the absorption spectra are only caused by the reversible E—Z photoisomerization. The long-wave absorption bands of the E- and Z-isomers (**A** and **B** correspondingly in the scheme), which have substantial overlap, combine into one band. Therefore, the steady excitation in the given band leads to the shift of its maximum at 415 nm together with a change of intensity determined by the ratio of the concentrations of the E- and Z-isomers in different photostationary states, established depending on the wavelength of the exciting light (Fig. 1). The separation and determination of the position of the maximum of the bands characterizing the absorption of the E- and Z-isomers are accomplished from the excitation spectra of the weak fluorescence (Table 1).

Information on the energy of the triplet states of the E- and Z-isomeric structures of the fulgide molecules ($E_{T_1}^A$ 224-230 and $E_{T_1}^B$ 214-218 kJ/mole) was obtained from the phosphorescence spectra of these forms determined in the compounds (II) and (III) (cf. Table 1).

The introduction of phenyl substituents [$R^3 = R^4 = Ph$, compound (IV)] gives a sharp shift of the absorption to the long-wave region by comparison with the fulgides (I)-(III) and the virtual coincidence of the spectral position of both the absorption bands [for compounds (I)-(III), λ_{max} 380-420 nm and for (IV), $\lambda_{max} \approx 470$ nm in toluene] and of the fluorescence of the E- and Z-isomers (cf. Table 1). These bands only differ in their intensity and, therefore, the E ⇄ Z isomerization appears in compound (IV) as a change in the intensity of the long-wave absorption band.

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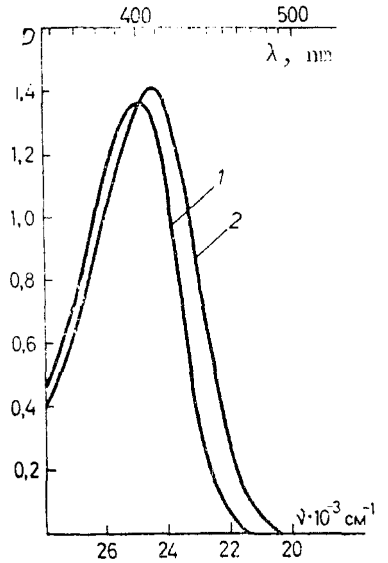


Fig. 1

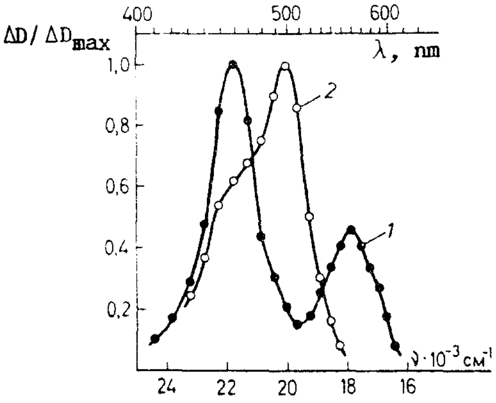
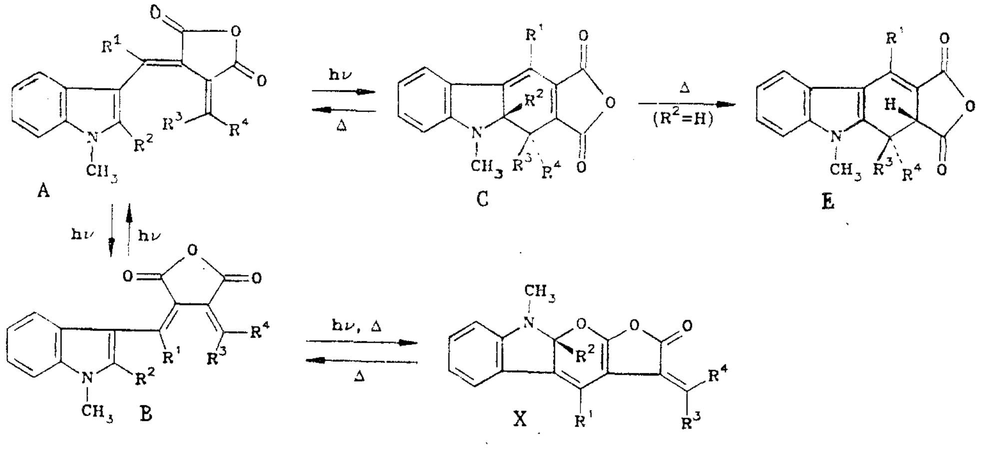


Fig. 2

Fig. 1. Electronic absorption spectra of the fulgide (I) in toluene at c = $4.2 \cdot 10^{-5}$ M: 1) before irradiation; 2) after irradiation in the course of 60 sec (λ_{irr} = 405 nm).

Fig. 2. Photoinduced absorption spectra in toluene 10^{-3} sec after the impulse of a photolysis lamp: 1) the fulgide (I) (c = $1.2 \cdot 10^{-1}$ M); 2) the fulgide (IV) (c = $2 \cdot 10^{-6}$ M).

The ratio of the concentrations of the E- and Z-isomeric forms of the fulgides (I)-(IV), which is defined in the given photostationary state, does not change with the cessation of the excitation and the subsequent change of temperature in the range 291-370 K. Consequently, the process of the E ⇄ Z isomerization proceeds in the excited state.



A band of the induced absorption with the maximum at 555-560 nm and the lifetime of 500-650 msec is observed when the solutions of the fulgides (I)-(III) are subjected to impulse excitation (Table 2, Fig. 2). Such absorption is characteristic of the products of the cyclization of the fulgides of type C, which are formed by the excitation of the E-isomeric forms [1, 2, 5]. The photoproduct C of the fulgides (I)-(III) is thermally unstable in both polar solvents (acetonitrile, ethanol) and nonpolar solvents (toluene, hexane) in contrast to the product of the photocyclization of the fulgide with the substituents $R^1 = CH_3$ and $R^2 = H$ ($R^3 = R^4 = CH_3$) [1, 2] which are thermally stable in nonpolar solvents. On the basis of the results [1, 2], as well as the given work, it can be concluded that the nature of the substituent R^1, developing in the formation of the energy barrier in the electronic ground state, exerts a determining influence on the thermal stability of the cyclic product C. In that case, when

TABLE 1. Position of the Maxima of the Bands of the Excitation of the Luminescence and the Luminescence of Isomeric Forms of the Fulgides

Compound	Form	λ_{max}, nm*	
		excitation of fluorescence (phosphorescence)	fluorescence (phosphorescence)
I	A	375	465
I	B	420	510
I	X	460	530
II	A	375 (375)	460 (520)
II	B	420 (420)	485 (550)
II	X	460	525
III	A	380 (375)	480 (530)
III	B	420 (420)	500 (560)
III	X	465	530
IV	A,B**	470	550

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*Spectra of the fluorescence and excitation of the fluorescence in toluene were registered at 293 K; spectra of phosphorescence and excitation of phosphorescence in the mixture isopentane—isopropyl alcohol were registered at 77 K.

**The isomeric forms (IVA) and (IVB) could not be separated by the fluorescence spectra or by the absorption spectra.

TABLE 2. Position of the Maxima of the Bands of the Induced Absorption of the Short-Lived Forms of the Fulgides (toluene, 293 K)

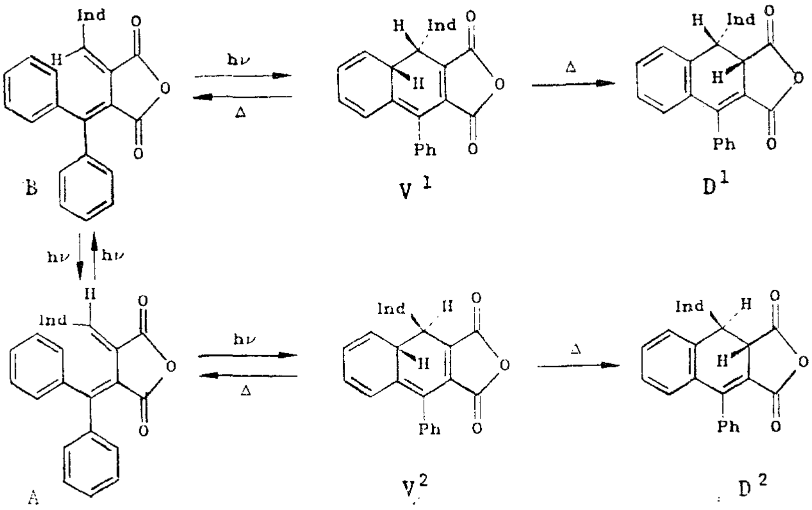
Compound	Form	λ_{max}, nm
I	C	560
I	X	460
II	C	555
II	X	460
III	C	560
III	X	460
IV	V^1, V^2	500

R^1 = H, the photoproduct **C** is thermally unstable. The influence of the substituent R^2 affects the capacity of the photochromic system $A \underset{h\nu,\Delta}{\overset{h\nu}{\rightleftarrows}} C$ for degradation. The irreversible 1,5-shift of the atom of hydrogen with the formation of the product **E** proves to be possible when R^2 = H. In the case of compounds (I)-(III), when $R^2 \neq$ H, the photochromic system becomes stable to the degradation of the type indicated. The number of cycles of photocoloration and photo- or thermal decolorization comprised >8000 for similar fulgides of the furan series in [6] (see scheme below).

As in the case of the previously investigated compounds (R^1 = H, CH_3; R^2 = H; R^3 = R^4 = CH_3) [2], the short-lived (τ = 350-550 msec) absorption band with the maximum at 460 nm, hypothetically assigned in [2] to the absorption of the form **X** which is formed from the Z-structure of the fulgides, is registered for compounds (I)-(III) by the method of impulse photolysis together with the absorption of the product **C** (cf. Table 2, Fig. 2). This form is also determined in the solutions of the initial products of the fulgides (I)-(III) from the steady spectra of the low-intensity fluorescence (cf. Table 1).

With the introduction of phenyl substituents (R^3 = R^4 = Ph) [compound (IV)], an irreversible photoreaction accompanied by the appearance of an absorption band with the λ_{max} 293 nm (toluene), characteristic of cyclic structures of the type $\mathbf{D}^{1,2}$, is realized [7].

A similar photoreactions was previously found in an analogous molecules with the substituents R^1 = R^2 = H, R^3 = R^4 = Ph [3]. In conformity with the proposed structural mechanism of the photoreaction, the intermediate of the type **V** should precede the product **D**; the structure **D** is formed from **V** as the result of a thermal 1,5-shift of the hydrogen atom. In fact, the impulse photolysis of a solution of compound (IV) in toluene results in the formation of an intermediate with an absorption band having $\lambda_{max} \approx$ 500 nm (cf. Fig. 2). This band may not be



assigned to a structure of the type **C**, absorbing in the region $\lambda_{max} \approx 560$ nm (cf. Table 2), but it is characteristic of the absorption spectrum of dihydronaphthalene structures of the type **V** [8]. Therefore, the inclusion of phenyl substituents ($R^3 = R^4 = Ph$) fundamentally changes the mechanism of the photocyclization reaction and virtually deprives the system of photochromic properties.

EXPERIMENTAL

The electronic absorption spectra were taken on a Specord UV-vis and Specord M-40 spectrophotometer with a unit for the change of the melting temperature of the sample. The spectra of the fluorescence and the excitation of the fluorescence were registered on a multiple-cell Fotolyum unit produced by the TsKB of the Academy of Medical Sciences of the USSR. The method of homodyne detection, allowing an increase in the sensitivity of the unit by a factor of 10^2-10^4, was applied to register weak luminescences. The impulse photolysis spectra were obtained using a flash photolysis lamp unit described in [9]. Photochemical investigations were performed utilizing an irradiator based on the DRSh-250 lamp with a set of light filters for the isolation of the lines of the mercury spectrum.

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