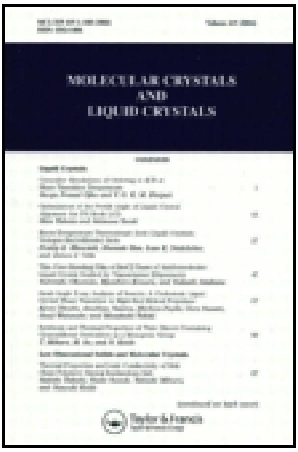

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THE STRUCTURE AND PHOTOCHEMICAL PROPERTIES OF NOVEL FULGIDES OF INDOLINE SERIES WITH AN ADAMANTYLIDENE FRAGMENT

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Abstract Two novel fulgides of the indoline series with an adamantylidene fragment have been synthesized and their structure and photochemical properties studied. Whereas adamantylidene - (1'-methyl-3'-indolylmethylene)-succinc anhydride (I) possesses Z-configuration, its homologue, containing a methyl group at the double bond (II), has E- configuration about the C=C bond. The presence of the bulky adamantylidene groups in I and II results in lowering of the photocoloration efficiency compared to respective isopropylidene derivatives.

INTRODUCTION

Photochromic properties of fulgides are due to two types of reversible photoreactions, an E - Z isomerizaton and an electrocyclic reaction with the formation of a colored structure (C).[1-5] The latter can only occur in an E-form, its efficiency being depended on steric conditions for the subsequent ring-closing reaction, in particular on bulkiness of the molecular fragments attached to double bonds of the triene backbone. This paper reports on the structure and photochemical properties of novel photochromic heterocyclic fulgides containing adamantylidene and indolylmethylene fragments I and II. Indolylfulgides have recently received special attention with regard their good fatigue resistant and photoswitchable properties.[2,5,6]

EXPERIMENTAL

The fulgides I and II have been prepared by condensation of respectively 1-methyl-3-formyl and 1-methyl-3-acetyl indoles with diethyladamantylidenesuccinate in the presence of sodium hydride. The resulting semiester was hydrolysed to diacid and the latter cyclised under a treatment with acetyl chloride. [3]

Adamant-2-ylidene-(1'-methyl-3'-indolylmethylene)succinic anhydride (I) was obtained in 76% yield. M. p. 247-248°C. IR (nujol): 1780, 1735 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 1,97 (s, 14H-Ad); 3.81 (s, NCH_3); 7.02-7.72 (m, 5H-Ar); 8,85 (s, CH).

Adamant-2-ylidene-(1'-methyl-3'-indolylethylidene)succinic anhydride (II) was obtained in 46% yield. M.p. 225-226°C. IR (nujol): 1780, 1740 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 1,50 (s, 14H-Ad); 2,72 (s, CH_3); 3,84 (s, NCH_3); 7,02-7,62 (m, 5H-Ar).

Electronic absorption UV-VIS spectra were recorded on a "Specord M-40" (Germany) spectrophotometer.

The integral intensities of 1714 independent reflections of a crystal **II** ($I>2\sigma(I)$) were obtained on an automatic three-circle diffractometer DAR-UM (CuK_α-radiation) with graphite monochromator by $\omega - \omega/2\omega$ layer registration. The structure of **II** was solved by a direct method using "SHELL-76" and "SHELL-86" software and refined by a full-matrix least-squares technicque in anisotropic approximation (nonhydrogen atoms).

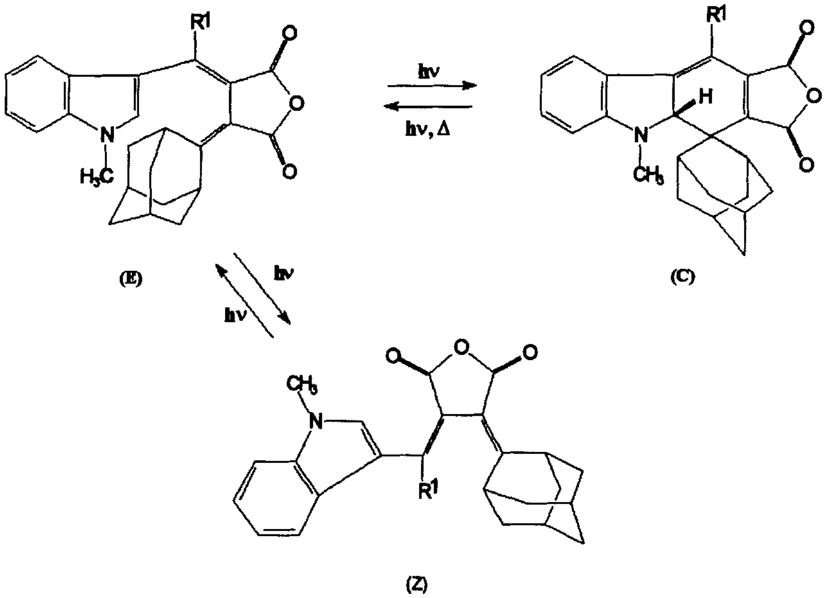
Photochemical transformations were initiated by irradiation with the light of a high-pressure mercury lamp (DRSH-250), glass filters being employed. The lamp flash photolysis device described in [7] was used. A degree of the photoconversion was estimated as a ratio of concentrations of colored, **C**, and initial, **E**, structures in a photostationary state.

RESULTS AND DISCUSSION

The compounds **I** and **II** have been preparatively isolated in the forms of respectively **Z** - and **E**- configurational isomers. The structure of **II** has been proven by X-ray single crystal study, which results are shown in Figure 1.

Chemical shifts of the methyl groups (N-CH_3) and those of the adamantylidene protons in ^1H NMR spectra ($CDCl_3$) of fulgides **I** and **II** are diagnostic for the assignment of **I** to a certain configuration. The signal of the N-CH_3 protons 2.72 ppm in the fulgide **II**, which has **E**-configuration, is down-field shifted relative to that signal of the fulgide **I**. This finding points to Z-configuration of **II**, see also [5]. The up-field shift of the methylene protons in the adamantylidene (1.50 ppm) in **II** with respect to I (1.97

ppm) also testifies for Z-configuration of I, since no screening by the indole fragment characteristic of the E isomer is expected for it Z-counterpart.



I: $R^1 = H$; II: $R^1 = CH_3$

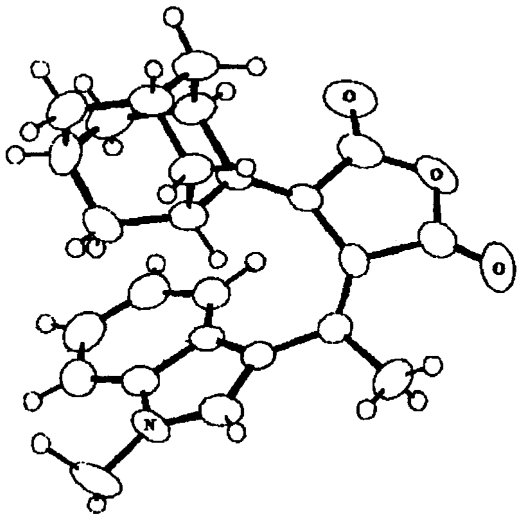


FIGURE 1. A stereoprojection of a molecule II.

On irradiation of solutions of the fulgides in the longwave absorption bands: I (λ_{irr} = 436 nm) and II (λ_{irr} = 365 nm) the processes of Z → E (for I) and E → Z (for

II) isomerizations were initiated. To activate the back E → Z (for I) and Z → E (for II) photoisomerizations, irradiation by the light of the interchanged wavelength (λ_{irr} = 365 nm, and 436 nm for I and II respectively) is required (Figure 2). No back dark reactions occur in solution at ambient temperature.

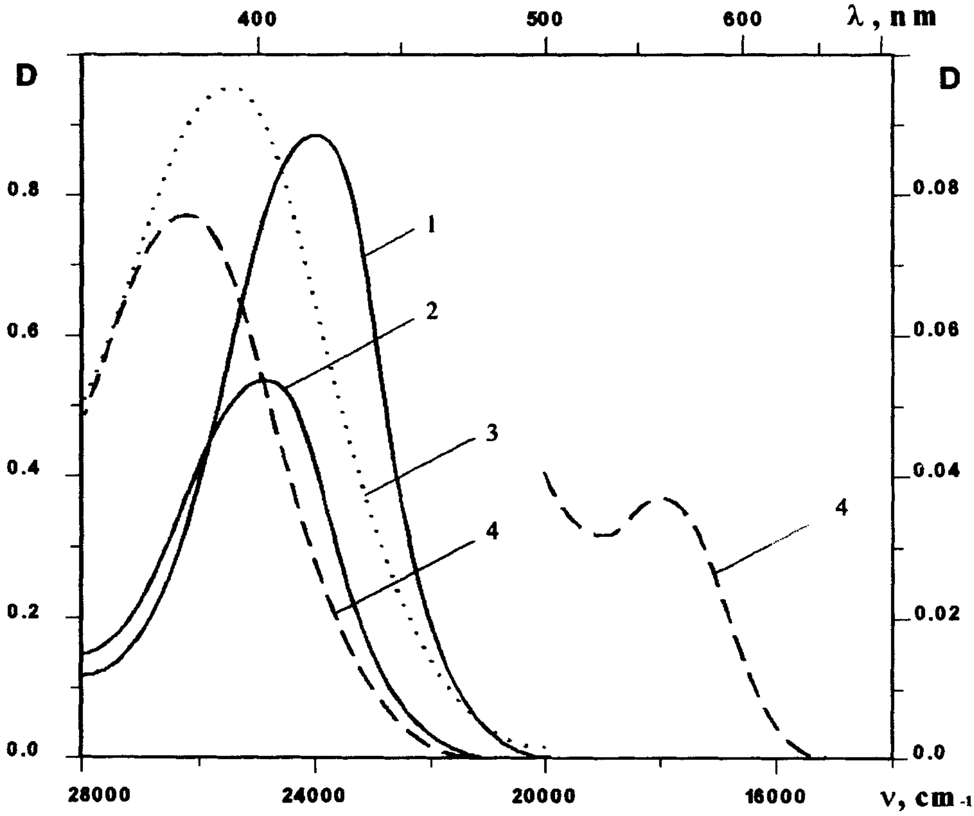


FIGURE 2. Absorption spectra of a toluene solution of fulgide I (c=3.4·10^{-5} M) before (1) and after irradiation (436 nm) for 30 s (2); fulgide II (c=8.7·10^{-5} M) before (3) and after irradiation (365 nm) for 50s (4)

Owing to substantial overlap of the absorption bands of Z and E-isomers of fulgides I and II prolonged irradiation by the light of either λ_{irr} = 365 nm or 436 nm leads to establishment of a photostationary state whose position depends on the wavelength of irradiation.

The fulgide Z-I is not susceptible to further photochemically initiated cyclzization reaction. Such a photochromic process E→C was observed only for the fulgide II (Figure 2). The back C→E conversion is also initiated by light and does not occur as a thermal process. With irradiation at 405 nm degree of the photoconvertion, γ, does not exceed $1.4 \cdot 10^{-2}$, which is by an order of magnitude less than that for 3-indolyl fulgides studied recently [3, 9]. The low γ–value is caused by overlap of the S_o-S_1 and S_o-S_2 bands of the initial, E, and photocolored cyclic, C, isomers of II respectively as well as by a drastic decrease in the ratio of quantum yields for the direct and reverse photoreactions due to steric hindrances created by the bulky adamantylidene group (see also [10, 11]). Spectral characteristic of Z and E isomers of the fulgides I and II are listed in Table 1.

TABLE 1. Spectral characteristics of the fulgides I, II and their photoisomers

Compound	λ_{max}, nm					
	toluene (ε, 10^3 l mol^{-1}cm^{-1})			DMSO		
	Z	E	C	Z	E	C
I	417 (26.2)	401 (19.5)	-	424	416	-
II	391 (13.0)	380 (10.9)	550	401	389	560

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