Synthesis, structure, and spectral and photochemical properties of fulgides of the indole series with an adamantylidene fragment

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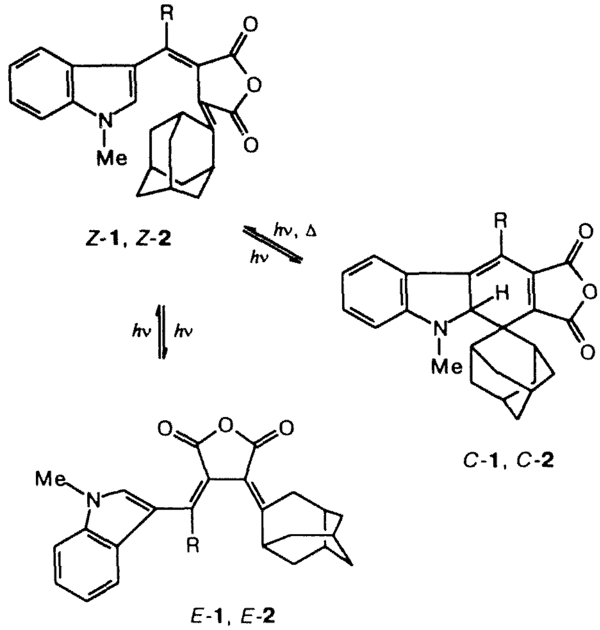
New fulgides of the indole series with adamantylidene fragments were synthesized: 3-(adamant-2-ylidene)-2-[1′-(3′-indolylethylidene)]succinic anhydride (**1**) and 3-(adamant-2-ylidene)-2-(3′-indolylmethylene)]succinic anhydride (**2**). By means of electronic absorption and ^{1}H NMR spectroscopy and X-ray diffraction analysis, fulgides **1** and **2** were shown to have *Z*- and *E*-configurations, respectively. The photochemical properties of **1** and **2** were studied. It was shown that along with *Z*—*E* photoisomerization of these compounds, in solution they undergo a cyclization reaction to yield a colored photoproduct. Specific structural features of fulgide **1** affecting its photochemical properties were discussed. The introduction of a bulky adamantylidene group decreases the extent of the conversion of compound **1** into cyclic isomer *C*.

Key words: fulgides of the indole series, adamantane; X-ray analysis; photochemistry; spectroscopy.

It is known that two competing processes (photocyclization and photoisomerization) can proceed[1—3] during the photoirradiation of heterocyclic fulgides of the indole series in solution (Scheme 1). Only photocyclization with the formation of a colored photoproduct[1,4—9] is observed in the crystalline state. Cyclization occurs for the more sterically strained *Z*-form alone, and its efficiency is probably dependent on the efficiency of the mutual approach of the pertinent C atoms needed for the formation of a cyclic bond. The positions of the reaction centers are determined by the characteristic features of the molecular structure of fulgide *Z*-isomers.

In the present work fulgides of the indole series containing a bulky adamantylidene group (Ad), 3-(adamant-2-ylidene)-2-[1′-(3′-indolylethylidene)]succinic anhydride (**1**) and 3-(adamant-2-ylidene)-2-(3′-indolylmethylene)succinic anhydride (**2**) have been synthesized and studied.

Scheme 1



R = Me (**1**), H (**2**)

Results and Discussion

Fulgides **1** and **2** can exist as *Z*- and *E*-isomers. The ^{1}H NMR spectra of compounds **1** and **2** (in $CDCl_3$) contain the singlet signals of N—Me methyl groups at δ 3.81 (**2**) and δ 3.84 (**1**) as well as the singlets from adamantylidene residues (at δ 1.50 and δ 1.97, respectively). The proton signals of the indole cycle of fulgides lie in the interval from δ 7.02 to 7.72. The signal of the

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Table 1. Electronic absorption spectra (λ_{max}/nm) of fulgides **1** and **2** and their photoinduced forms

Com-po-und	Toluene ($\varepsilon/10^{-3}$ L mol^{-1} cm^{-1})			DMSO		
	E	*Z*	*C*	*E*	*Z*	*C*
1	391 (13.0)*	380 (10.9)	550	401*	389	560
2	417 (26.2)	401 (19.5)*	—	424	416*	—

* The wavelength (extinction) at the maximum of the absorption band formed in the photostationary state during the photoinduced formation of corresponding structure (*Z* or *E*).

C—Me group of the heteryl fragment of fulgide **1** at δ 2.72 corresponds to the *Z*-configuration[8] while the chemical shift of the group in question for the *E*-isomers is equal to 2.3 ppm. The downfield position of the signal of the C—Me group of fulgide **1** is a result of the deshielding effect of a *cis*-oriented carbonyl group. The signal of the adamantylidene fragment (δ 1.50) is shifted upfield due to the shielding effect of the indole fragment in the *Z*-configuration. In fulgide **2** the signal of the adamantylidene radical (δ 1.97) is shifted substantially downfield, which can be explained by the existence of compound **2** as the *E*-isomer and the decrease in the shielding effect of the indole fragment.

The electronic absorption spectra of solutions of compound **1**, isolated as the *Z*-form, are characterized by a long-wave maximum in the region of 380—389 nm; fulgide **2** obtained in its *E*-form has absorption in the region of 417—424 nm (Table 1). When the solvent polarity increases (from toluene to DMSO), the maxima of the long-wave absorption bands of fulgides exhibit a bathochromic shift, which is evidence for the $\pi\pi^*$-nature of the S_0—S_1 transition. The assignment of the absorption bands in the spectra of **1** and **2** to *E*- and *Z*-isomeric structures is in agreement with the results of the X-ray analysis of fulgide **1** and those of the photochemical study of the solutions of compounds **1** and **2**.

As follows from X-ray analysis data, molecule **1** (Fig. 1) is sterically strained and exists in the *Z*-configuration. The indole fragment is in the *trans*-position relative to the C(13)—O(3) carbonyl group. Because of the steric interactions between the *syn*-positioned bulky adamantylidene and indole substituents the latter is rotated about the C(2)—C(10) bond by 34.7°.

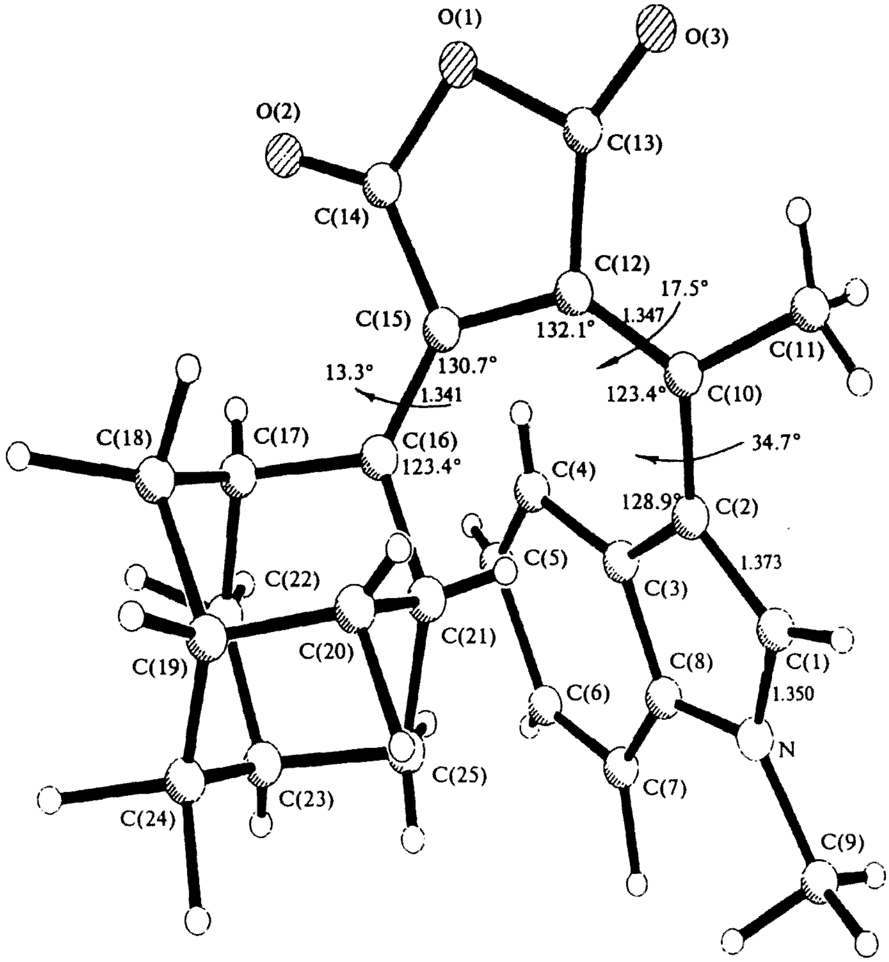


Fig. 1. General view of molecule **1**. The main bond lengths (in Å) and bond and torsion angles are indicated.

The steric repulsion between these substituents also makes the whole indolylethylidene fragment rotate about the C(10)=C(12) double bond by 17.5°; the adamantylidene substituent is rotated in the same direction about the C(15)=C(16) double bond by 13.3°. The double bonds in question are elongated to 1.347(3) and 1.341(3) Å, respectively, compared with the normal length (1.32 Å). In addition, the bond angles at the sp^2-hybridized carbon atoms are increased: they are C(10)—C(12)—C(15), 132.1°; C(2)—C(10)—C(12), 123.4°; C(3)—C(2)—C(10), 128.9°; C(12)—C(15)—C(16), 130.7°; and C(15)—C(16)—C(21), 123.4°. Nevertheless, several intramolecular nonbonded contacts are shortened: C(10)...C(16), 3.35 Å; C(2)...C(16), 3.49 Å; C(3)...C(16), 3.45 Å; C(4)...C(16), 3.33 Å; and C(2)...C(21), 3.24 Å.

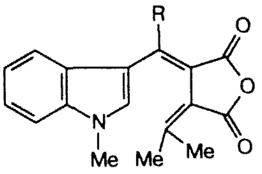
The five-membered oxygen-containing heterocycle is nonplanar (half-chair), the angles along the O(1)...C(12) and O(1)...C(15) lines are equal to 7.7° and 6.8°, respectively. The deviation from planarity is due to the steric repulsion between the O(2) and O(3) atoms of the carbonyl groups and the *syn*-positioned C(17) and C(11) atoms [O(3)...C(11), 2.90 Å; O(2)...C(17), 3.01 Å]. Because of this conformation of the heterocycle, the coordination nodes at the C(12) and C(15) atoms are nonplanar, the angle sum at these atoms is 359.2° and 357.9°, respectively. Calculations of the conformational energy of molecule **1** (MM2[9]) confirm the conclusion that there are strong steric interactions in a *Z*-isomer containing a bulky adamantylidene substituent.

A substantial redistribution of bond lengths was found in the five-membered heterocycle of the indole fragment: the formal double bond C(1)=C(2) [1.373(3) Å] is lengthened while the ordinary N—C(1) bond [1.350(3) Å] is shortened. We have also found recently[1] that a like redistribution of bond lengths is due to conjugation of the unshared electron pair of the N atom with the π^*-orbital of the C(1)=C(2) bond, which polarizes that bond and increases the nucleophilicity of the C(2) atom. The double bonds C(10)=C(12) and C(15)=C(16) are also loose and weakened due to torsional rotations. Such a structure favors the approach of reaction centers C(1) and C(16) and the formation of the C(1)—C(16) bond, *i.e.*, cyclization of molecule **1** in the photoexcited state. Steric repulsion between bulky substituents of the *Z*-isomer will favor isomerization of the excited molecule. Quantum-chemical calculations show a decrease in the order of the double bonds C(10)=C(12) and C(15)=C(16) in the excited electronic state S_1 and increasing angles of rotation about these bonds as a result of steric repulsion. Such a structure, on the one hand, favors *E*—*Z*-isomerization, while, on the other hand, it facilitates rotation about the C(2)—C(10) bond, the approach of reaction centers C(1) and C(16), and the formation of a cyclic *C*-isomer.

After irradiation of fulgides **1** and **2**, opposite shifts and opposite changes in the intensities of the long-wave absorption bands (λ_1 = 365 nm and λ_2 = 436 nm) are observed. That is, bathochromic shift which is accompanied by an increase in the intensity in the spectrum of compound **1**, and hypsochromic shift which is accompanied by a decrease in the intensity in the spectrum of compound **2**, respectively. No reverse dark transformations occur after subsequent irradiation when the temperature is increased to 360 K. At the same time, a reverse photolytic process accompanied by opposite shifts and changes in the band intensities is observed after irradiation by light at λ = 405 nm (**1**) and 365 nm (**2**). The long-wave absorption of fulgide *Z*-isomers is known[10,11] to occur at shorter wavelengths and is characterized by weaker intensity than that in the case of *E*-isomers. This fact, along with the data of X-ray analysis and ^{1}H NMR spectroscopy allows one to assign the bands in the absorption spectra of fulgides to the *Z*- and *E*-isomeric forms (see Table 1). Thus, the described photoinitiated changes in the absorption spectra are characteristic of purely photolytic processes of *Z*—*E*- and *E*—*Z*-isomerization in the compounds in question, which exist in the S_0 state in their *Z*- and *E*-forms.

It should be noted that because of substantial overlapping of the absorption bands of both isomers, the processes of *E*—*Z*-isomerization proceed simultaneously in two directions until the establishment of the photostationary state. The absorption band formed is a superposition of the transitions of the individual isomers, and its intensity and the position of its maximum are connected to the characteristics of these individual transitions and depend on the irradiation wavelength.

Unlike compound **2**, in solutions of fulgide **1** under conditions of stationary irradiation, a photochromic process is observed along with *Z*—*E*-isomerization. This means that the reversible formation of a relatively stable dihydrocarbazole cyclic product (*C*) with a long-wave absorption band occurs (see Table 1). This product is turned into the initial *Z*-form by thermal or photolytic action.



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It is impossible to reach a significant degree of conversion[1,10] after the initiation of *Z*—*E*-isomerization of compound **1**, as is also the case for the 3-indolyl-substituted fulgides **3** studied previously. This is first of all associated with overlapping of the S_0—S_2 transition band of the cyclic product *C* with the S_0—S_1 transition band of the fulgide *Z*-form. As a consequence, as in the case for *Z*—*E*-isomerization, a photostationary state is established after irradiation in the absorption band region of the *Z*-isomers. The position of this state as well as the wavelength of the activation radiation depend mainly on the quantum yields of both the direct and the reverse photolytic reactions. The extent of conversion (*g*) in the photostationary state, determined as the ratio of optical densities at the maxima of the absorption bands of the *C*- and *Z*-isomers, is equal to $1.4 \cdot 10^{-2}$ for fulgide **1** (at the irradiation wavelength λ = 405 nm) which is substantially lower than for **3** ($g = 2.3 \cdot 10^{-1}$ under the same irradiation conditions[1]). The quantum yield of the direct photolytic reaction and the increase in the quantum yield of the reverse reaction are likely associated with the steric hindrances to cyclization caused by the adamantylidene group.

As was noted above, no formation of the *C*-form is observed during irradiation of compound **2** under stationary conditions. In accordance with quantum-chemical calculations,[12] one of the reasons for this behavior is the steric effect of the substituent R on the quantum yield of photocyclization; a decrease in the volume of substituent R results in a decrease in the quantum yield of photocoloring and favors *E—Z*-isomerization. At the same time, as was established previously by pulse photolysis of fulgides of the indole series without an adamantylidene group, the formation of a short-lived cyclic isomer *C* is observed in solutions of compounds with R = H; this means that the low solubility of the colored form does not allow its registration[1,10] under stationary conditions. We failed to register the *C*-type product for compound **2** using a pulse photolysis installation with a resolution time of 10^{-5} s. This can be explained both by a drop in the quantum yield of photocyclization and by a sharp decrease in the stability of the *C*-form due to the simultaneous effects of two unfavorable factors: the decrease in the volume of substituent R and the steric hindrances to cyclization caused by the bulky adamantylidene group.

Experimental

Electronic absorption spectra were recorded on a Specord M40 spectrophotometer (in Nujol). ^{1}H NMR spectra were recorded on a Tesla BS-567A spectrometer (100 MHz, in $CDCl_3$) with HMDS as the reference.

Fulgides 1 and 2 were synthesized by condensation of 1-methyl-3-formyl- and 1-methyl-3-acetylindole with diethyl adamant-2-ylidenesuccinate in the presence of sodium hydride with subsequent hydrolysis of the esters and treatment of the diacids formed with acetyl chloride (*cf.* Ref. 1).

3-(Adamant-2-ylidene)-2-[1′-(3′-indolylethylidene)]succinic anhydride (1). Yield 45.9%; m.p. 225—226 °C (Silochrom, O, 0.1—0.2, $CHCl_3$ as the eluent). IR, ν/cm^{-1}: 1780, 1740. ^{1}H NMR, δ: 1.50 (s, 14 H, Ad); 2.72 (s, CH_3); 7.02—7.62 (m, 5 H, Ar); 3.84 (s, NCH_3). Found (%): C, 77.52; H, 6.46; N, 3.62. $C_{25}H_{25}NO_3$. Calculated (%): C, 78.01; H, 6.98; N, 3.97.

3-(Adamant-2-ylidene)-2-(3′-indolylmethylene)succinic anhydride (2). Yield 76.4%; m.p. 247—248 °C (Silochrom, O, 0.1—0.2, $CHCl_3$ as the eluent). IR, ν/cm^{-1}: 1780, 1735. ^{1}H NMR, δ: 1.97 (s, 14 H, Ad); 3.81 (s, NCH_3); 7.02—7.72 (m, 5 H, Ar); 8.85 (s, CH). Found (%): C, 77.21; H, 6.17; N, 3.75. $C_{24}H_{23}NO_3$. Calculated (%): C, 77.76; H, 6.51; N, 3.95.

Table 2. Coordinates of nonhydrogen (×10^4) and hydrogen (×10^3) atoms in the structure **1**

Atom	*x*	*y*	*z*
O(1)	6251(8)	5538(8)	839(9)
O(2)	7719(9)	4741(9)	797(9)
O(3)	4882(9)	6370(9)	431(9)
N	6226(9)	5631(9)	−5205(9)
C(1)	5808(9)	6185(9)	−4303(9)
C(2)	5999(7)	5718(7)	−3268(9)
C(3)	6548(8)	4832(8)	−3553(9)
C(4)	6894(9)	3956(9)	−2861(9)
C(5)	7356(9)	3162(9)	−3466(9)
C(6)	7491(9)	3262(9)	−4820(9)
C(7)	7170(9)	3993(9)	−5425(9)
C(8)	6677(9)	4797(9)	−4795(9)
C(9)	6251(9)	5893(9)	−6456(9)
C(10)	5674(9)	6155(9)	−2111(9)
C(11)	4664(9)	6630(9)	−2038(9)
C(12)	6184(9)	5990(9)	−1138(9)
C(13)	5642(9)	6075(9)	−18(9)
C(14)	7138(9)	5245(9)	254(9)
C(15)	7199(7)	5655(7)	−949(9)
C(16)	8068(9)	5891(9)	−1556(9)
C(17)	9108(9)	5516(9)	−1204(9)
C(18)	9672(9)	6433(9)	−761(9)
C(19)	9800(9)	7219(9)	−1851(9)
C(20)	8755(9)	7510(9)	−2135(9)
C(21)	8216(8)	6555(8)	−2577(7)
C(22)	9669(9)	5076(8)	−2249(9)
C(23)	9867(9)	5841(9)	−3275(9)
C(24)	10404(9)	6746(9)	−2841(9)
C(25)	8824(9)	6141(9)	−3670(9)
H(1)	546(9)	675(9)	−445(9)
H(4)	672(9)	404(9)	−220(9)
H(5)	737(9)	244(9)	−323(9)
H(6)	766(9)	280(9)	−507(9)
H(7)	745(9)	395(9)	−645(9)
H(9A)	622(9)	671(9)	−675(9)
H(9B)	709(9)	597(9)	−649(9)
H(9C)	579(9)	568(9)	−674(9)
H(11A)	450(9)	723(9)	−255(9)
H(11B)	451(9)	719(9)	−178(9)
H(11C)	388(9)	636(9)	−214(9)
H(17)	890(9)	517(9)	−79(9)
H(18A)	1049(9)	627(9)	−13(9)
H(18B)	911(9)	670(9)	−10(9)
H(19)	1018(9)	779(9)	−131(9)
H(20A)	887(9)	814(9)	−302(9)
H(20B)	830(9)	774(9)	−184(9)
H(21)	760(9)	674(9)	−264(9)
H(22A)	943(9)	447(9)	−222(9)
H(22B)	1018(9)	458(9)	−171(9)

X-ray study of crystals 1. The compound **1** crystallizes as monoclinic yellow prisms. Main crystallographic data: *a* = 13.306(2) Å, *b* = 11.416(3) Å, *c* = 13.214(3) Å, β = 86.28(2)°, *Z* = 4, d_{calc} = 1.257(3) g cm^{-3}, space group $P2_1/c$, $C_{25}H_{25}NO_3$. The integrated intensities of 1145 independent observed reflections were obtained on an automatic three-circle DAR-UM diffractometer (Cu-Kα radiation). No corrections for absorption were made. The structure was solved by direct methods using the SHELX-86 program package and refined anisotropically by the full-matrix least squares method (nonhydrogen atoms). The hydrogen atoms were located from difference Fourier synthesis; $R = 0.050$. Atomic coordinates are listed in Table 2.

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