Structures and photochromic properties of fulgides based on naphtho[1,2-*b*]furan and benzo[*g*]indole

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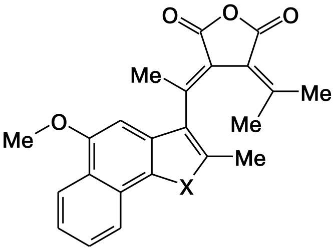
The novel heterocyclic fulgides, *i.e.* 3-isopropylidene-4-{1-[5-methoxy-1-(4-methoxyphenyl)-2-methyl-1*H*-benzo[*g*]indol-3-yl]ethylidene}dihydrofuran-2,5-dione and 3-isopropylidene-4-[1-(1-benzyl-5-methoxy-2-methyl-1*H*-benzo[*g*]indol-3-yl)ethylidene]dihydrofuran-2,5-dione, were prepared and isolated as *E*-isomers. Photochromism, *E*-configuration, and high resistance to photocoloration—photobleaching of solutions of these fulgides as well as 3-isopropylidene-4-[1-(5-methoxy-2-methylnaphtho[1,2-*b*]furan-3-yl)ethylidene]dihydrofuran-2,5-dione and 3-isopropylidene-4-[1-(5-methoxy-2-methyl-1-phenyl-1*H*-benzo[*g*]indol-3-yl)ethylidene]dihydrofuran-2,5-dione synthesized previously were shown by X-ray diffraction analysis, ^{1}H NMR spectroscopy and electronic absorption spectroscopy. The novel fulgides show fluorescence and high thermal stability of photogenerated cyclic form. Repeated photocoloration—photobleaching is accompanied by reversible photoinduced *E*—*Z* isomerization. Benzo[*g*]indolyl fulgides are characterized by the longer wavelength absorption of both original (*E*) and photoisomeric cyclic (*C*) forms as compared to naphthofuran fulgide.

Key words: fulgide, naphtho[1,2-*b*]furan, benzo[*g*]indol, synthesis, structure, photocromism.

Photochromic heterocyclic fulgides are typically characterized by thermal stability of a colored form and high resistance of isomers to repeated photocoloration—photobleaching. These properties make fulgides (whose photochromic mechanism is based on the hexatriene/cyclohexadiene interconversion) promising candidates for use in optical memory devices and as molecular switches.[1,2]



1a—d

1: X = O (**a**), NPh (**b**), NC_6H_4OMe-4 (**c**), NCH_2Ph (**d**)

Previously[3] we have reported on the photochromic properties and structure of novel *N*-aryl-3-indolylfulgides giving fluorescent photogenerated isomers that is a necessary condition for applicability of a molecular system in 3D optical data storage materials.[4—9] Preliminary results on the synthesis and photochromism of fulgides **1a,b** have been presented elsewhere[10] but will be summarized here. In order to extend the family of such systems we have prepared new fulgides of benzo[*g*]indol series, **1c,d**, and undertook the more detailed study of structure and photochromic properties of fulgides **1a—d**.

Results and Discussion

Fulgides **1c,d** were synthesized analogously to fulgide **1a** (Scheme 1) by reacting diethyl isopropylidene succinate with the appropriate ketones.[10] Fulgide **1b** was obtained following the same scheme by a three-step procedure with isolation of fulgenate **2b** and fulgenic acid **3b**, which provided increasing its yield to 60%.

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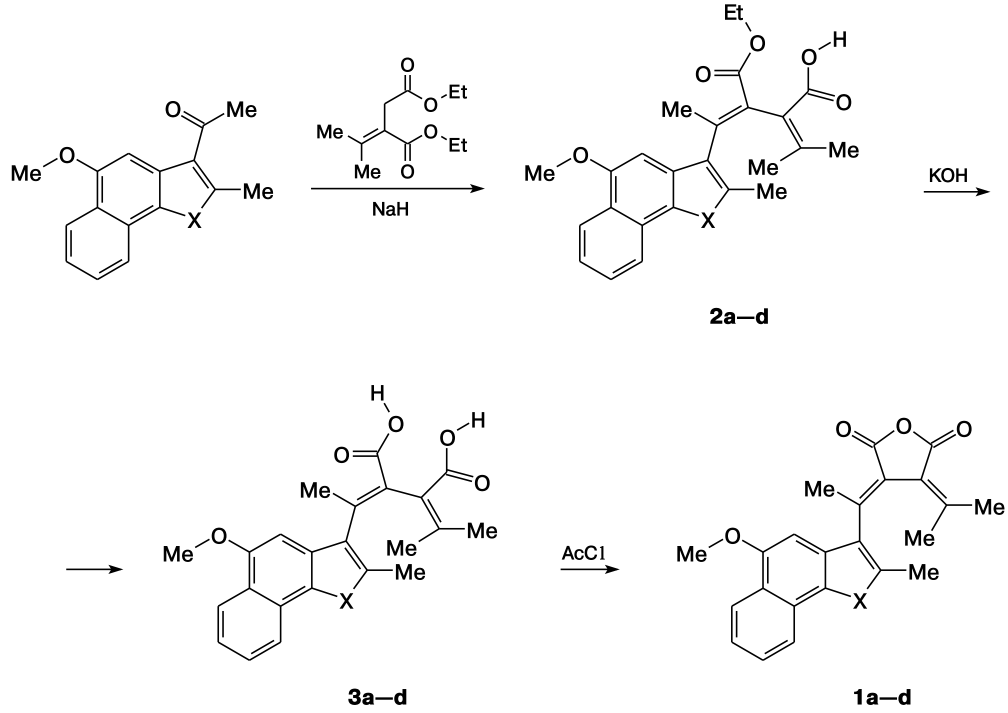
Scheme 1



2a—d

3a—d

1a—d

1—3: X = O (**a**), NPh (**b**), NC_6H_4OMe-4 (**c**), NCH_2Ph (**d**)

IR spectra of fulgides **1c,d** as well as **1a,b** exhibit characteristic bands at 1750—1800 cm^{-1} arising from vibrational modes of two exocyclic carbonyl groups of the anhydride ring. In the ^1H NMR spectra of **1c,d**, the signals of ethylidene methyl group (δ 2.75—2.90) and those originating from **1a,b** appear roughly at the same places thus indicating the *E*-configuration of fulgides **1a—d**, which is spatialy ready for the cyclization process.[3,10]

The benzyl methylene protons of fulgide **1d** are diastereotopic and appear in ^1H NMR spectrum as a doublet of doublets (AB-system), which is implicative of **1d** chirality.[1] On heating the solution of **1d** in deuteronitrobenzene to 180 °C, the ^1H NMR spectrum shows neither signal broadening nor coalescence. Hence, the energy barrier to racemization exceeds 100 kJ mol^{-1} that makes dynamic NMR time scale inapplicable for its evaluation but allows preparative separation of enantiomers.

The structure of **1a,b,d** molecules in the crystalline state was examined by X-ray diffraction (Figs 1—3, respectively).

In molecules **1a,b,d**, C(10), C(11), C(13), C(14), C(15), C(17), C(18), C(19), C(20), C(21), C(22), and C(23) atoms, as well as O(5) in **1a** and N(1) in **1b,d** are displaced from their heterocycle planes by 0.040, −0.037, 0.064; −0.014, 0.020, −0.071; 0.019, −0.011, 0.085; −0.017, −0.058, 0.035; −0.026, 0.004, −0.057; −0.006, 0.020, −0.037; 0.017, 0.062, −0.044; 0.035, 0.033, −0.010; 0.009, −0.059, 0.046; −0.025, −0.074, 0.061; −0.022, −0.006, 0.003; −0.014, 0.032, 0.007; −0.024, 0.073, −0.083 Å, respectively, with furandione and heterocyclic moieties showing different geometric arrangements in **1a,b,d**. In comparing the torsion angles defined by the atom chain C(11)—C(10)—C(5)—C(4)—C(3)—C(7)—C(9) (for **1b** the latter is C(8)) in **1a,b,d** it turns out that the only angle substantially differing in **1a,b,d** is the one formed by C(10)—C(5) bond. In **1a** it is 49.8(3)°, and in **1b,d** −137.8(2) and −132.7(3)°, respectively. The arithmetical means (averaged over **1a,b,d**) of the other torsion

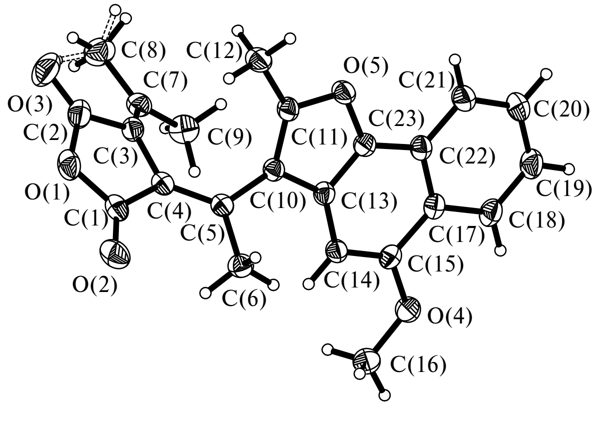


Fig. 1. Molecular structure of **1a**.

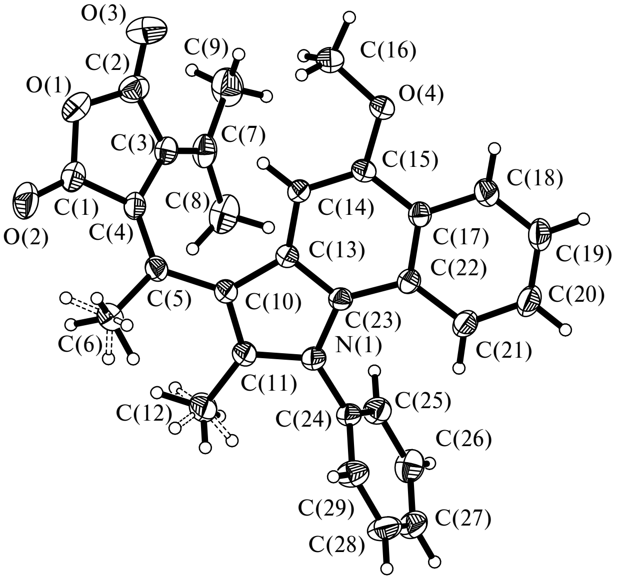


Fig. 2. Molecular structure of **1b**.

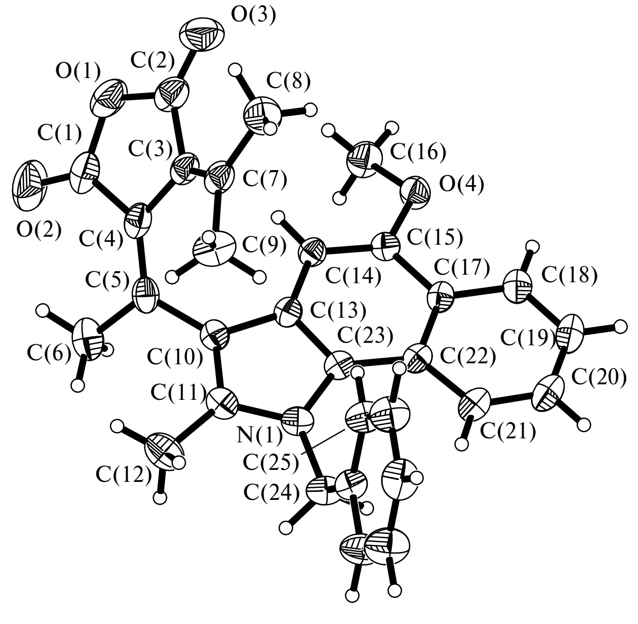


Fig. 3. Molecular structure of **1d**.

angles in this structural fragment are 10.0 (0.6), 40.7 (1.2), 1.5 (1.6)° (parentheses are maximum deviation values). The observed structural similarity is apparently due to that furandione (including C(7), C(5), and C(6) atoms) and benzoindol (including O(4), C(16), C(12)) moieties are both conjugated so that the only possible rotation is about C(10)—C(5) bond. Interatomic distance between C(7) and C(11) carbons which form chemical bond on photocyclization is 3.54, 4.38, and 4.22 Å for crystalline **1a,b,d**, respectively.

Table 1. Absorption and fluorescence spectral characteristics of photoisomers of fulgides **1a—d** in toluene at 293 K

Compound	Form	Absorption		Fluorescence, λ_{max}/nm	
		λ_{max} /nm	ε /L mol^{-1} cm^{-1}	Excitation	Emission
1a	*E*	344	10100	—	—
	C	546	—	340 ($S_0 \to S_2$) 542 ($S_0 \to S_1$)	648
1b	*E*	373	10800	—	—
	C	643	—	370 ($S_0 \to S_2$) 640 ($S_0 \to S_1$)	791
1c	*E*	375	11200	—	—
	C	651	—	380 ($S_0 \to S_2$) 650 ($S_0 \to S_1$)	796
1d	*E*	376	10500	—	—
	C	667	—	375 ($S_0 \to S_2$) 670 ($S_0 \to S_1$)	802

The other bond distances and torsion angles in molecules **1a,b,d** are within the range of values normally found for such compounds.

The electron absorption spectra of toluene solutions of fulgides **1a—d** in *E* form have long-wavelength maxima in the 344 to 376 nm region with molar extinction coefficients at the maxima of 10100—11200 L mol^{-1} cm^{-1} (Table 1). With a switch from naphthofuran fulgide (**1a**) to benzoindol fulgides (**1b—d**), the long-wavelength maximum due to *E* isomer is bathochromically shifted by 29—32 nm. The effect of substituents at benzoindol nitrogen on the absorbance of **1b—d** *E*-isomers is insignificant.

The open ring *E*-configured fulgides **1a—d** are not fluorescing in toluene at 293 K.

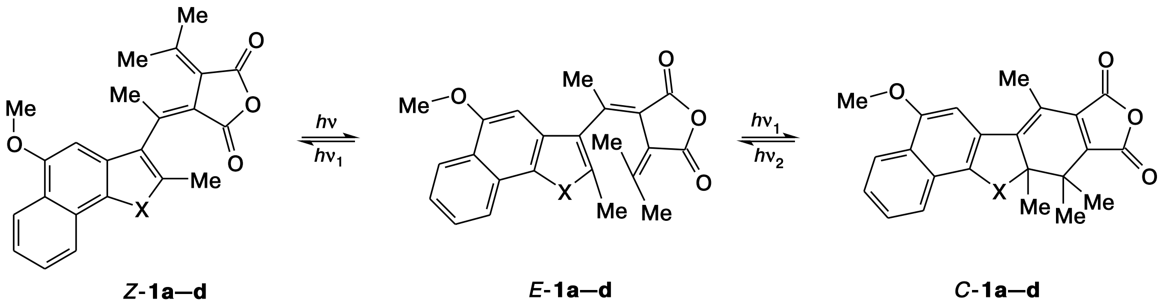
Irradiation of solutions of **1a—d** at the wavelengths of *E*-isomer absorption causes their coloration with the attendant appearance in the absorption spectra of bands at 450—750 nm which are characteristic of the closed *C* forms (Scheme 2 and Fig. 4; see also Table 1)[11].

Photogenerated cyclic *C* form of naphthofuran fulgide **1a** has the long-wavelength maximum at 546 nm, whereas *C* isomers of benzoindolyl fulgides **1b—d** are absorbing at longer wavelengths (see Table 1). In the substituted fulgides, the long-wavelength band shows a progressive bathochromic shift as the electron donating ability of substituents at benzoindol nitrogen is increased in the series Ph, C_6H_4OMe-4, CH_2Ph.

The closed ring *C* fulgides **1a—d** demonstrate high thermal stability: the reverse dark reaction *C*→*E* in toluene does not occur within 72 h at 293 K.

Irradiation of colored solutions of **1a—d** with visible light (at 546 nm for **1a** and at 578 nm for **1b—d**) results in their bleaching, with the decrease in absorbance of *C* form being not accompanied by the recovery of original (before UV-irradiation) absorption spectrum (see Fig. 4, curve *3*).

Scheme 2



At the same time, the following repeated coloration-bleaching cycles characteristically reproduce spectral patterns of colored and colorless forms. Such spectral transformations are due to the presence in irradiated solutions of **1a—d** of *Z* isomers as evidenced by ^{1}H NMR spectra of fulgides **1b,d** in deuterotoluene recorded after consecutive irradiations at 365 and 578 nm.

The ^{1}H NMR spectra of starting fulgides **1b,d** display the set of signals characteristic of *E* isomers. Their irradiation with visible light at 365 nm results in a photostationary state so that the spectrum of irradiated solutions contains methyl proton resonances produced by all three isomeric forms, namely open (*E* and *Z*) and closed (*C*); the aromatic proton signals of these isomers are also observed in the weak field. After further visible-light irradiation (578 nm) of fulgides **1b,d** in solutions, their ^{1}H NMR spectra showed proton signals from only open ring *E* and *Z* isomers, with the content of *E* isomers enhanced by the value equal to the loss of *C* isomer in the ternary mixture. Thus, the features of ^{1}H NMR and electron absorption spectra compare favorably with the above-proposed photoinduction mechanism for fulgides **1b,d**, involving reversible *E*—*Z* photoisomerization and *E*—*C* photocyclization.

The prolonged irradiation of fulgides **1a—d** in solutions was found not to result in their complete conversion to a colored state. This is apparently due to overlapping of absorbance bands corresponding to $S_0 \to S_2$ transitions of *C* isomers and the bands originating from $S_0 \to S_1$ transitions of *E* and *Z* isomers. Under conditions affording the reverse *C*→*E* photoreaction and *E*→*Z* photoisomerization characteristic of fulgides, UV-irradiation transforms the system into photostationary mixture containing *E*, *Z*, and *C* isomeric forms at a ratio determined, in particular, by the wavelength of UV-excitation. The following complete bleaching of solution on visible-light irradiation leads to a binary mixture of *E* and *Z* isomers.

Fulgides **1a—d** are resistant to photocoloration—photobleaching cycling. Ten cycles have not led to decrease in the optical density of solution at 640 nm as exemplified by the cyclic changing of the optical density of fulgide **1b** in toluene (Fig. 5) at the long-wavelength maximum of absorption of *C* isomer under consecutive photoexcitation at 365 and 578 nm. As can be seen, while approaching

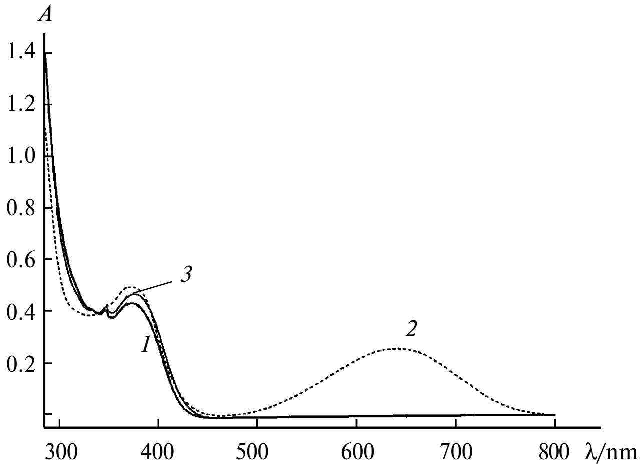


Fig. 4. Absorption spectra of fulgide **1b** in toluene ($4 \cdot 10^{-5}$ mol L^{-1}) before irradiation (*1*), in photostationary state under visible-light irradiation at 365 nm (*2*), and after further irradiation at 578 nm (*3*).

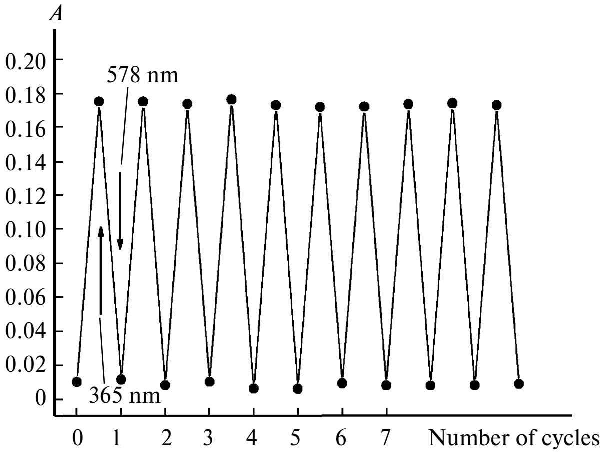


Fig. 5. Optical density dynamics of fulgide **1b** in toluene ($2.8 \cdot 10^{-5}$ mol L^{-1}, 273 K) at λ_{obs} = 640 nm (the absorbance maximum of *C* isomer) under coloration (λ_{irr} = 365 nm, τ = 10 min)—bleaching (λ_{irr} = 578 nm, τ = 10 min) cycling.

photostationary state, the system shows no tendency for photodegradation over 10 cycles.

The fact that is highly important for practical use of fulgides has been established, namely, photogenerated closed ring *C* isomers of fulgides **1a—d** are fluorescent. The maximum absorption of the *C* form is in the 648 to 802 nm region. Electron donating substituents at nitrogen atom shift the absorption spectra of *C* form of **1b—d** to the longer wavelengths (see Table 1). Fluorescence excitation spectra are well consistent with the absorption of *C* isomers (see Table 1). Apart from assistance in assignment of the observed fluorescence to *C* form, excitation spectra provide useful information on the location of individual absorption bands corresponding to $S_0 \to S_2$ transitions of closed ring isomers. Photochromic efficiency is relatively low with the quantum yields not exceeding 0.01, which is largely due to existence of a competing quenching channel desactivating electron excitation through $C \to E$ photoisomerization.

Both original (fulgide solution) and irradiated material (subjected to up to 10 photocoloration-photobleaching cycles) contained no impurities detectable by ^{1}H NMR, UV, and luminescence spectroscopy.

In conclusion, new photochromic benzo[*g*]indol-3-yl fulgides have been synthesized, which possess resistance to photocoloration—photobleaching cycling and high thermal stability of photogenerated cyclic form. Repeated photocoloration—photobleaching is accompanied by reversible photoinduced *E* to *Z* isomerization. Both original (*E*) and cyclic (*C*) forms of benzoindolyl fulgides **1b—d** absorb at longer wavelengths compared to the naphthofuran fulgide **1a**. The channels of decay of the excitation energy of cyclic isomers *C* include radiative decay.

Experimental

Electron absorption spectra were recorded on a Cary 100 (Varian) spectrophotometer, and fluorescence spectra on a Varian Eclipce spectrofluorometer. The solutions were irradiated using a DRSh-250 mercury lamp equipped with a set of interference filters for isolating the lines of mercury spectrum. Irradiation intensity at 365 and 578 nm was $2.9 \cdot 10^{16}$ and $2.6 \cdot 10^{16}$ quantum s^{-1}, respectively. IR spectra were measured from compound suspensions in the Nujol on a Specord 75 IR spectrometer, and ^{1}H NMR spectra were recorded with a Varian Unity-300 instrument (300 MHz) using HMDS as an external standard.

(3*E*)-Isopropylidene-4-[1-(5-methoxy-2-methylnaphtho[1,2-*b*]furan-3-yl)ethylidene]dihydrofuran-2,5-dione (1a) was prepared by the known procedure.[10] Yield 32%, m.p. 199—200 °C.

2-[1-(5-Methoxy-2-methyl-1-phenyl-1*H*-benzo[*g*]indol-3-yl)ethylidene]-3-(1-methylethylidene)butanedioic acid 1-monoethyl ester (2b). A suspension of NaH (0.7 g, 0.03 mol) in THF (10 mL) was stirred at room temperature while adding a solution of 3-acetyl-5-methoxy-2-methyl-1-phenylbenzo[*g*]indol (2.8 g, 0.01 mol), isopropylidene diethyl succinate (2.8 g, 0.013 mol), and diisopropylamine (1.4 mL, 0.01 mol) in THF (20 mL). The reaction mixture was stirred for 5 h at 30 °C. The solvent was removed *in vacuo* (water-jet pump). The residue was treated with 10% hydrochloric acid (30 mL), precipitated monoethyl ether **2b** was filtered off and recrystallized from toluene. Yield 3.1 g (63%), colorless crystals, m.p. 222—223 °C. Found (%): C, 74.94; H, 6.42; N, 2.70. $C_{31}H_{31}NO_5$. Calculated (%): C, 74.83; H, 6.28; N, 2.81. IR, ν/cm^{-1}: 1760; 1790 (C=O). ^{1}H NMR ($CDCl_3$), δ: 0.67 (t, 3 H, Me, *J* = 7.1 Hz); 1.98, 2.11, 2.19, 2.21 (all s, 3 H each, Me); 3.73—3.94 (m, 2 H, CH_2); 4.00 (s, 3 H, OMe); 6.85 (s, 1 H, Ar); 6.97—7.67 (m, 8 H, Ar); 8.30 (d, 1 H, Ar, *J* = 8.4 Hz); 11.24 (br.s, 1 H, OH).

2-[1-(5-Methoxy-2-methyl-1-phenyl-1*H*-benzo[*g*]indol-3-yl)ethylidene]-3-(1-methylethylidene)butanedioic acid (3b). Ester **2** (3.1 g) was placed in a flask fitted with a reflux condenser and treated with 10% methanolic KOH (10 mL). The mixture was refluxed for 4 h, cooled, diluted with water and acidified with 10% HCl (30 mL). Precipitated dicarboxylic acid was filtered off and air-dried. Yield 3 g (98%), colorless crystals, m.p. 245—246 °C. Found (%): C, 72.45; H, 6.22; N, 3.45. $C_{27}H_{29}NO_5$. Calculated (%): C, 71.58; H, 6.01; N, 3.34. IR, ν/cm^{-1}: 1750; 1780 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.98, 2.07, 2.10, 2.24 (all s, 3 H each, Me); 3.95 (s, 3 H, OMe); 6.80—7.70 (m, 9 H, Ar); 8.16 (d, 1 H, Ar, *J* = 8.4 Hz); 11.60—11.80 (br.s, 2 H, OH).

(3*E*)-Isopropylidene-4-[1-(5-methoxy-2-methyl-1-phenyl-1*H*-benzo[*g*]indol-3-yl)ethylidene]dihydrofuran-2,5-dione (*E*-1b). Diacid **3b** (3 g) was dissolved in acetyl chloride (1.5 mL) with stirring. The solvent was removed *in vacuo*. Yield 2.9 g (98%), yellow crystals, m.p. 182—184 °C (from MeCN). Found (%): C, 77.01; H, 5.29; N, 3.01. $C_{29}H_{25}NO_4$. Calculated (%): C, 77.14; H, 5.58; N, 3.10. IR, ν/cm^{-1}: 1800; 1750. ^{1}H NMR (toluene-d_7), δ: 0.80, 1.69, 1.95, 2.87 (all s, 3 H each, Me); 3.66 (s, 3 H, OMe); 6.67 (s, 1 H, Ar); 6.77—7.23 (m, 8 H, Ar); 8.55 (d, 1 H, Ar, *J* = 8.4 Hz).

(3*Z*)-Isopropylidene-4-[1-(5-methoxy-2-methyl-1-phenyl-1*H*-benzo[*g*]indol-3-yl)ethylidene]dihydrofuran-2,5-dione (*Z*-1b). Product *Z*-**1b** was prepared in a NMR tube as a mixture with *E*-**1b** and *C*-**1b** isomers by irradiation of a solution of fulgide *E*-**1b** in deuterotoluene ($2.4 \cdot 10^{-2}$ mol L^{-1}) with light at 365 nm for 4 h. ^{1}H NMR (toluene-d_7), δ: 1.43, 2.12, 2.15, 2.17 (all s, 3 H each, Me); 3.64 (s, 3 H, OMe); 6.67—7.28 (m, 9 H, Ar); 8.61 (d, 1 H, Ar, *J* = 8.4 Hz).

5-Methoxy-7,11,11,11a-tetramethyl-12-phenyl-11a,12-dihydro-8*H*-benzo[*a*]furo[3,4-*h*]carbazole-8,10(11*H*)-dione (*C*-1b). Prepared in a NMR tube as a mixture with *E*-**1b** and *Z*-**1b** isomers by irradiation of a solution of fulgide *E*-**1b** in deuterotoluene ($2.4 \cdot 10^{-2}$ mol L^{-1}) with light (λ_{irr} = 365 nm) for 6 h followed by purification from isomers using preparative column chromatography (Silpearl, chloroform). M.p. 241—243 °C. ^{1}H NMR (toluene-d_8), δ: 1.05, 1.36, 1.42, 2.49 (all s, 3 H each, Me); 3.53 (s, 3 H, OMe); 6.67—7.28 (m, 9 H, Ar); 8.32 (d, 1 H, Ar, *J* = 8.4 Hz).

4-[1-(1-Benzyl-5-methoxy-2-methyl-1*H*-benzo[*g*]indol-3-yl)ethylidene]-(3*E*)-isopropylidenedihydrofuran-2,5-dione (*E*-1d). Prepared according to the literature procedure[10] from 3-acetyl-1-benzyl-5-methoxy-2-methylbenzo[*g*]indol (4 g, 0.012 mol). Yield 28%, yellow-brown crystals, m.p. 231—233 °C (from toluene). Found (%): C, 76.61; H, 6.12; N, 3.19. $C_{29}H_{27}NO_4$. Calculated (%): C, 76.80; H, 6.00; N, 3.09. IR, ν/cm^{-1}: 1800; 1750 (C=O). ^{1}H NMR ($C_6D_5NO_2$), δ: 1.20, 2.27, 2.43, 3.11 (all s, 3 H each, Me); 4.21 (s, 3 H, OMe); 5.91,

Table 2. Crystallographic data and X-ray diffraction experiment parameters for compounds **1a,b,d**

Parameter	**1a**	**1b**	**1d**
Molecular formula	$C_{23}H_{20}O_5$	$C_{29}H_{25}NO_4$	$C_{30}H_{27}NO_4$
M	376.39	451.50	465.53
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	7.1200(16)	9.625(2)	10.4470(25)
b/Å	11.580(2)	9.970(2)	10.7750(25)
c/Å	12.927(3)	13.255(3)	11.6720(31)
α/deg	65.460(21)	70.380(15)	78.250(28)
β/deg	89.530(24)	87.280(16)	72.410(29)
γ/deg	81.630(30)	83.400(16)	75.590(31)
V/Å^3	957.6(4)	1190.1(4)	1201.3(6)
Z	2	2	2
d_{calc}/g cm^{-3}	1.305	1.413	1.287
μ/cm^{-1}	0.092	0.084	0.085
θ range/deg	1.96—25.00	1.16—23.05	1.85—25.00
Number of measured reflections	3190	3727	3752
Number of reflections with $I \geq 2\sigma(I)$	2452	3278	2664
Number of refined parameters	253	308	317
R_1 ($I \geq 2\sigma(I)$)			
R	0.0438	0.0397	0.0570
wR_2	0.0612	0.0451	0.0851
GOF	1.059	1.042	1.080

6.40 (AB-system, 2 H, CH_2, $J_{A,B}$ = 18.2 Hz); 7.11 (s, 1 H, Ar); 7.24—8.58 (m, 9 H, Ar).

(3*Z*)-[1-(1-Benzyl-5-methoxy-2-methyl-1*H*-benzo[*g*]indol-3-yl)ethylidene]-4-isopropylidenedihydrofuran-2,5-dione (*Z*-1d). Prepared in a NMR tube as a mixture with *E*-**1d** and *C*-**1d** isomers under irradiation of a solution of fulgide *E*-**1d** in deuteronitrobenzene ($2.4 \cdot 10^{-2}$ mol L^{-1}) with visible light (λ_{irr} = 365 nm) over 4 h with heating. ^{1}H NMR ($C_6D_5NO_2$, toluene-d$_8$), δ: 2.19, 2.59, 2.67, 2.68 (all s, 3 H each, Me); 4.18 (s, 3 H, OMe); 5.90—6.20 (m, 2 H, CH_2); 7.07—8.52 (m, 10 H, Ar).

12-Benzyl-5-methoxy-7,11,11,11a-tetramethyl-11a,12-dihydro-8*H*-benzo[*a*]furo[3,4-*h*]carbazole-8,10(11*H*)-dione (*C*-1d). Prepared in a NMR tube as a mixture with *E*-**1d** and *Z*-**1d** isomers under irradiation of a solution of fulgide *E*-**1d** in deutero-nitrobenzene ($2.4 \cdot 10^{-2}$ mol L^{-1}) with light (λ_{irr} = 365 nm) over 6 h. ^{1}H NMR ($C_6D_5NO_2$), δ: 1.35, 1.63, 1.80, 2.78 (all s, 3 H each, Me); 4.14 (s, 3 H, OMe); 5.91, 6.40 (AB-system, 2 H, CH_2, $J_{A,B}$ = 19.0 Hz); 7.07—8.52 (m, 10 H, Ar).

(3*E*)-Isopropylidene-4-{1-[5-methoxy-1-(4-methoxyphenyl)-2-methyl-1*H*-benzo[*g*]indol-3-yl]ethylidene}dihydrofuran-2,5-dione (*E*-1c). Prepared by the known procedure[10] from 3-acetyl-5-methoxy-1-(4-methoxyphenyl)2-methylbenzo[*g*]-indol (4 g, 0.012 mol). Yield 43%, yellow crystals, m.p. 202—203 °C (from toluene). Found (%): C, 76.61; H, 6.12; N, 3.19. $C_{29}H_{27}NO_5$. Calculated (%): C, 76.80; H, 6.00; N, 3.09. IR, ν/cm^{-1}: 1800; 1750. ^{1}H NMR ($CDCl_3$), δ: 1.10, 2.05, 2.19, 2.88 (all s, 3 H each, Me); 3.96, 3.98 (both s, 3 H each, OMe); 6.66 (s, 1 H, Ar); 7.00—7.40 (m, 7 H, Ar); 8.32 (d, 1 H, CH, J = 8.35 Hz).

X-ray diffraction analysis. 3D set of intensities further used to obtain cell parameters for crystals **1a,b,d** was measured on a Bruker P-4 automated diffractometer (Mo-Kα-radiation, graphite monochromator). Details of crystal data, data collection and structure refinement are listed in Table 2. The structures were solved by the direct method (SHELXS-97)[12] and refined using the full-matrix least-squares on F^2 (SHELXL-97)[12] in anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were located in a difference Fourier maps. Coordinates and isotropic thermal parameters for H atoms were obtained by least-squares refinement in the riding mode.[12]

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