Synthesis, structures, and photochromic properties of *N*-aryl-3-indolylfulgides

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New 3-indolylfulgides, *viz.*, 3-[1-(1-aryl-5-methoxy-2-methyl-1*H*-indol-3-yl)ethylidene]-4-(1-methylethylidene)tetrahydro-2,5-furandiones, were synthesized. These compounds were obtained as *E*-isomers, as demonstrated by X-ray diffraction, electronic spectroscopy, and ^{1}H NMR spectroscopy. Fulgides exhibit photochromic properties in solution. The cyclic dihydrocarbazole photoisomers of indolylfulgides show fluorescence properties and are characterized by high thermal stability.

Key words: indoles, fulgides, synthesis, X-ray diffraction study, photochromism.

Bistable heteroaromatic fulgides generally have enhanced resistance to photodegradation and are thermally stable, due to which these compounds are considered as photochromic systems suitable for use in optical memory devices and as molecular switches.[1,2] In some cases, photoinduced cyclic isomers of fulgides of the indole series exhibit fluorescence, which is of great importance for the design of materials for three-dimensional data acquisition.[3—8] In this connection, we synthesized and characterized the previously unknown fulgides of the indole series containing aromatic substituents at the nitrogen atom of the indole fragment.

Results and Discussion

The Stobbe condensation of 3-acetyl-1-aryl-5-methoxy-2-methylindoles **1a—c** with diethyl isopropylidenesuccinate in the presence of sodium hydride and diisopropylamine in THF afforded monoethyl esters of indolyl-substituted isopropylidenesuccinic acids **2a—c**, which were hydrolyzed to acids **3a—c** (Scheme 1). The previously unknown fulgides, *viz.*, (3*E*)-3-[1-(5-methoxy-2-methyl-1-phenyl-1*H*-indol-3-yl)ethylidene]-4-(1-methylethylidene)tetrahydro-2,5-furandione (**4a**), (3*E*)-3-{1-[5-methoxy-1-(4-methoxyphenyl)-2-methyl-1*H*-indol-3-yl]ethylidene}-4-(1-methylethylidene)tetrahydro-2,5-furandione (**4b**), and (3*E*)-3-(1-{1-[4-(dimethylamino)phenyl]-5-methoxy-2-methyl-1*H*-indol-3-yl}ethylidene)-4-(1-methylethylidene)tetrahydro-2,5-furandione (**4c**), were synthesized by the reactions of acids **3a—c** with acetyl chloride (**4a,b**) or acetic anhydride (**4c**).

The IR spectra of fulgides **4a—c** show characteristic bands of two exocyclic carbonyl groups. In the ^{1}H NMR spectra of 3-[1-(1-aryl-5-methoxy-2-methyl-1*H*-indol-3-yl)ethylidene]-4-(1-methylethylidene)tetrahydro-2,5-furandiones **4a—c**, the proton signals of the ethylidene Me groups are observed at δ 2.80, 2.86, and 2.85, respectively, which indicates that these compounds have an *E* configuration with respect to the indolylethylidene double bond[9] (Scheme 2).

With the aim of determining the geometric parameters and estimating the degree, for which the molecules (in the solid state) are ready to have optical properties, we prepared single crystals of compounds **4a,b** and studied them by X-ray diffraction.

The crystal structure of **4a** contains two molecules per asymmetric unit (the second molecule is denoted **4a´**). Figure 1 shows the structure of **4a** with displacement ellipsoids of nonhydrogen atoms drawn at the 30% probability level, the atomic numbering scheme, and the second molecule (indicated by dashed lines), which is superimposed with the former molecule by aligning the N(1)C(10)C(11)C(13)C(19) fragments. The atomic

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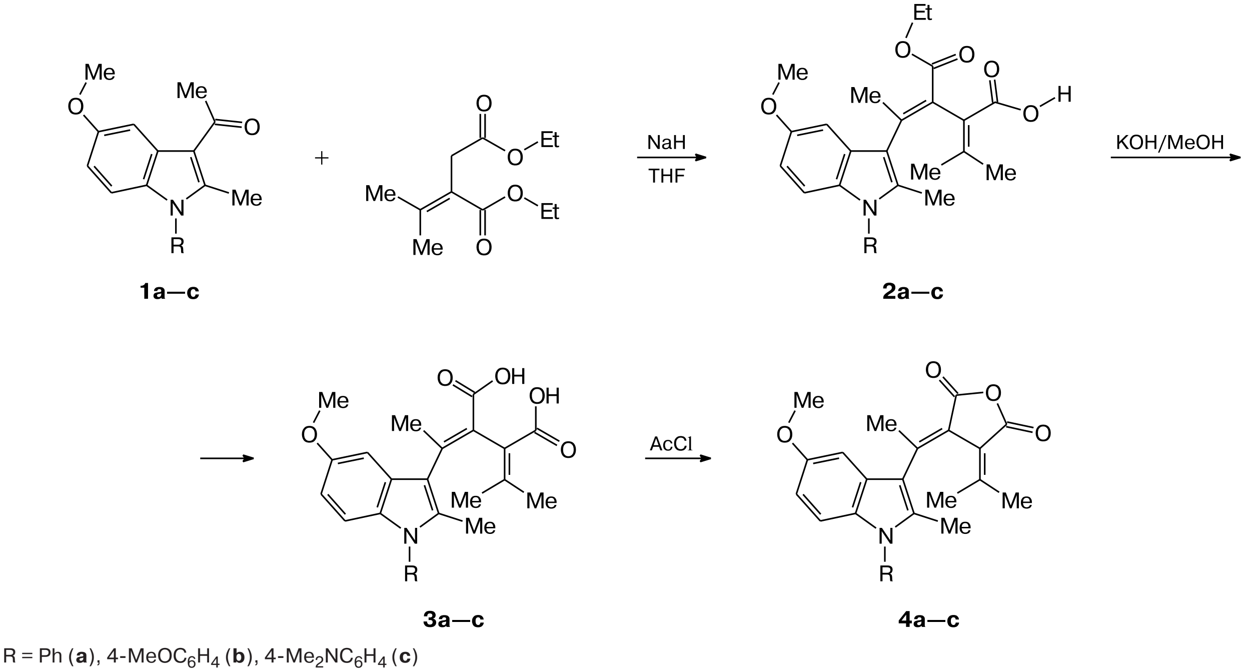
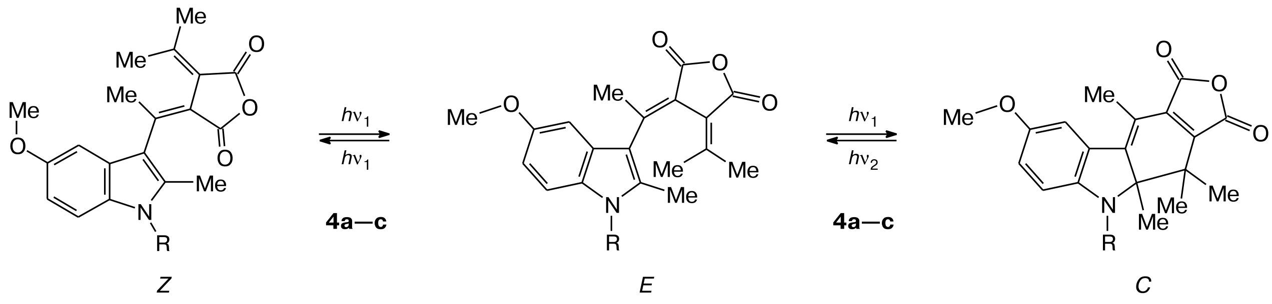
Scheme 1



numbering of molecule **4a**´ is obtained by adding 30 to the atoms of the molecule **4a**. In the subsequent consideration of the structural details, the parameters of molecule **4a**´ are given in parentheses. Molecule **4a** differs from **4a**´ in the orientation of the phenyl ring at the nitrogen atom with respect to the plane of the indole fragment (after superposition of their indole fragments and the C(20) and C(50) atoms, the angle between the planes of the phenyl rings is 34.6°), and these molecules have the opposite orientation of the Me groups at the O(4) and O(34) atoms (see Fig. 1).

In molecule **4a**, the C(16) atom is in the *syn* orientation with respect to the C(14) atom, resulting in an increase in the C(14)—C(15)—O(4) angle to 124.0(3)° and a decrease in the C(17)—C(15)—O(4) angle to 114.0(3)°. In molecule **4a**´, the C(46) atom is turned about the O(34)—C(45) bond in the opposite direction. The C(44)—C(45)—O(34) angle in **4a**´ (115.7(4)°) is smaller than the analogous C(14)—C(15)—O(4) angle in **4a**, whereas the exocyclic C(47)—C(45)—O(34) angle is larger (122.8(3)°). In addition, there is a substantial difference in the O(4)—C(15) bond length (1.390(4) and 1.336(6) Å in **4a** and **4a**´, respectively) and the C(15)—O(4)—C(16) bond angle (117.4(3) and 120.3(4)°). The distance between the C(7) and C(11) atoms is 3.492 (3.513) Å; between the O(4) and H(14) atoms, is 2.65 (2.48) Å; and between the O(4) and C(17) atoms, is 2.45 (2.63) Å. This is accompanied by an intramolecular contact between the hydrogen atoms of the Me groups and the H(14) atom in molecule **4a** (2.29 and 2.36 Å) and the H(47) atom in molecule **4a**´ (2.32 and 2.59 Å). The other geometric parameters of the independent molecules are identical within experimental error. The packing modes of molecules **4a** and **4a**´ are shown in Fig. 2. Molecules **4a** are arranged in pairs one above another (see Fig. 2, *a*), so that there are the intermolecu-

Scheme 2



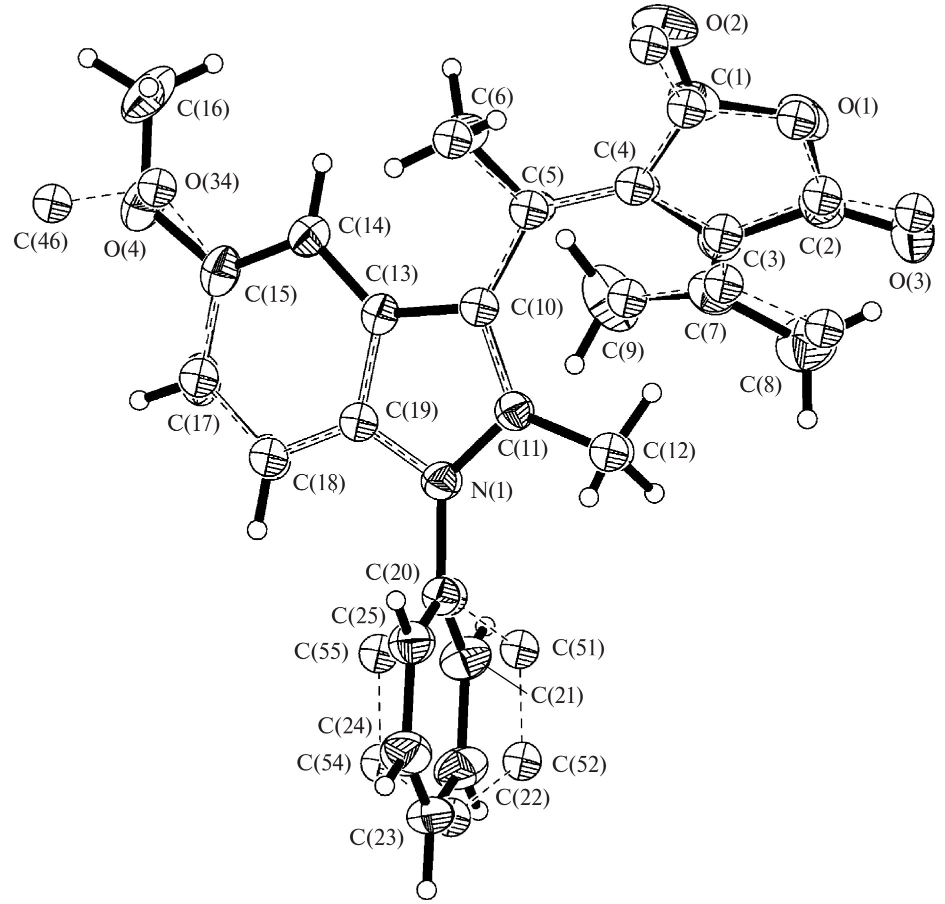


Fig. 1. Molecular structures of compound **4a** with displacement ellipsoids of nonhydrogen atoms drawn at the 30% probability level and superimposed molecule **4a´** (indicated by dashed lines).

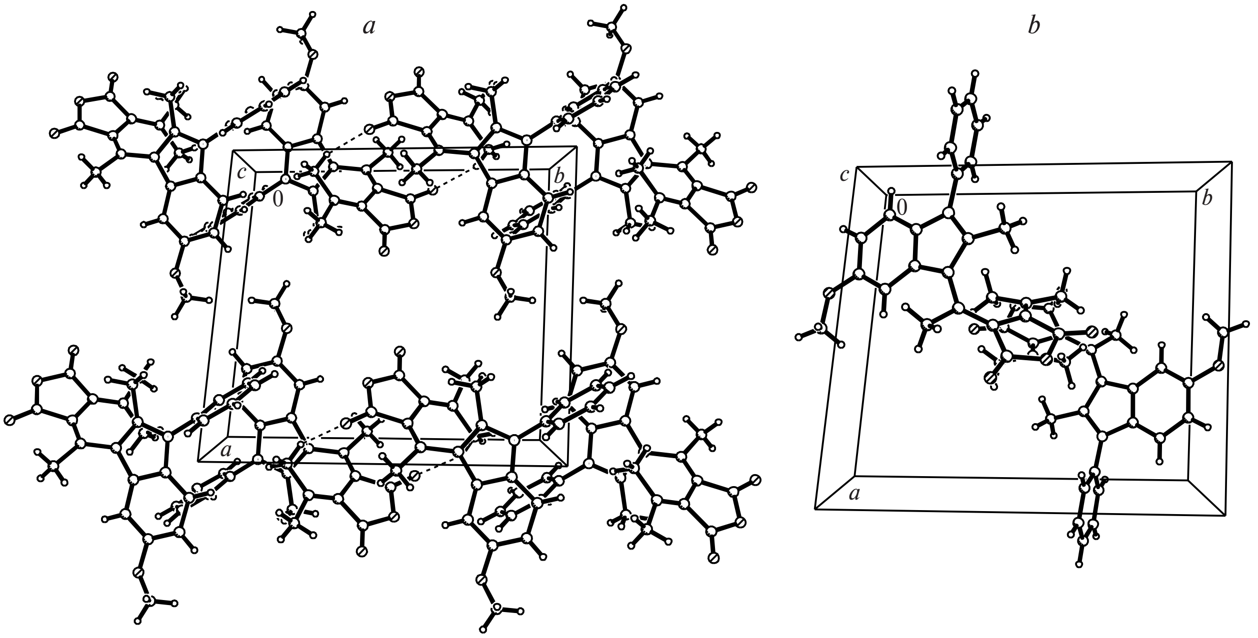


Fig. 2. Packing modes of molecules **4a** (*a*) and **4a´** (*b*).

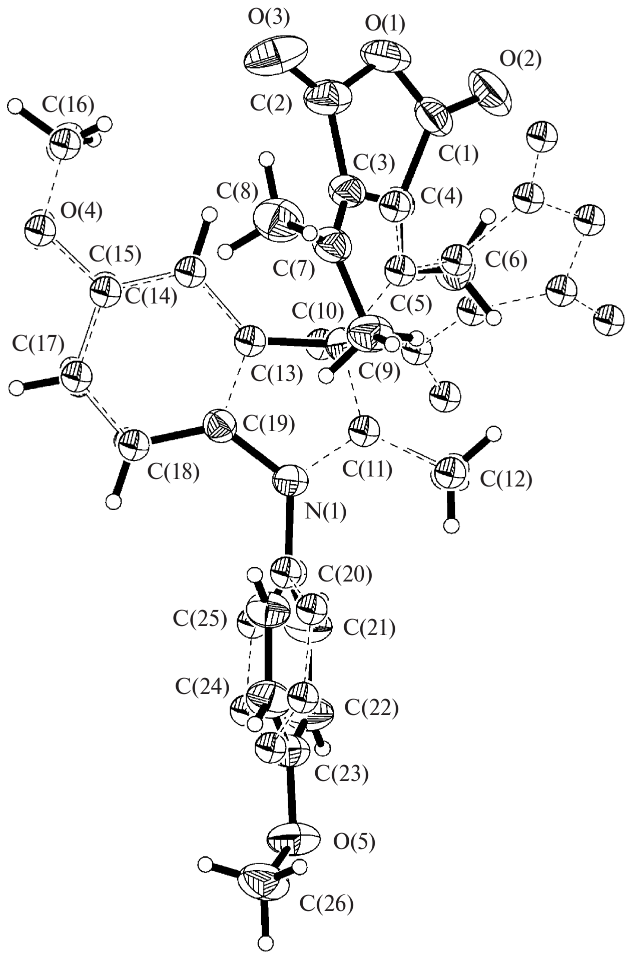


Fig. 3. Molecular structures of **4a** and **4b** projected onto the common plane of the indole ring.

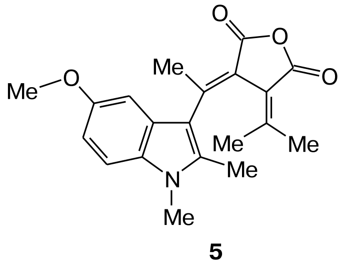
lar O(32)...H(391)´ and O(32)´...H(391) (2.57 Å) contacts. Independent molecules **4a**´ are located between molecules **4a**, do not form short contacts, and are oriented with respect to each other (see Fig. 2, *b*) in such a way that their fulgide fragments are located one above another.

Figure 3 shows the molecular structure of **4b** with displacement ellipsoids of nonhydrogen atoms drawn at the 30% probability level, the atomic numbering scheme, and molecule **4a** (indicated by dashed lines), which is superimposed with the former molecule by aligning the indole fragments.

In the crystal structures, molecules **4b** and **4a** (**4a**´) have an *E* configuration. On the whole, except for the details considered below, the distances and angles in molecules **4a** (**4a**´) and **4b** are identical within experimental error. The C(16) atom in molecule **4b**, like that in molecule **4a**, points toward the C(14) atom, which is accompanied by a deviation of the MeO group in a counterclockwise direction in the plane of the figure and leads to an increase in the C(14)—C(15)—O(4) angle to 124.1(2)° and a decrease in the C(17)—C(15)—O(4) angle to 114.7(2)°. The phenyl ring at the nitrogen atom is turned with respect to the plane of the indole ring analogosuly to molecule **4a**´. The C(11)—N(1)—C(20)—C(21) torsion angle is −68.2(4)°. The C(26) atom deviates from the plane of the phenyl ring by 0.14 Å. The character of redistribution of the exocyclic bonds at the C(23) atom remains unchanged (C(22)—C(23)—O(5), 115.5(2)°; C(24)—C(23)—O(5), 125.1(2)°; C(24)—C(23)—O(5)—C(26), 9.2(3)°). In the crystal structure, molecules **4b** are packed so that the closest contacts between atoms of the adjacent molecules are longer than 2.60 Å.

The principal structural difference between compounds **4a** and **4b** in the crystalline state is clearly illustrated in Fig. 3, where the molecules are projected onto the common plane of the indole fragment after superposition of its atoms. Molecule **4b** differs from **4a** in the torsion angle characterizing the orientation of the fulgide fragment with respect to the C(5)—C(10) bond. Thus, the C(11)—C(10)—C(5)—C(4) torsion angle is 52.7(4)° and −47.3(2)° in **4a** and **4b**, respectively. Therefore, the reaction centers C(7) and C(11) in molecule **4a** are in the *syn* orientation; in molecule **4b**, in the *anti* orientation. The distance between the C(7) and C(11) atoms in molecules **4a** and **4b** is 3.492 (3.513) and 4.231 Å, respectively. After photocyclization, the reaction centers C(7) and C(11) in molecule **4a** come closer together from the side of the Me group at the C(12) atom; in molecule **4b**, from the opposite side. It can be concluded that in the crystal structure, molecule **4a** adopts a conformation structurally suitable for the electrocyclic rearrangement, whereas the conformation of molecule **4b** is characterized by a large distance between the terminal carbon atoms of the hexatriene system. In the latter case, a substantial rearrangement of the molecule is required for the electrocyclic reaction to be completed.

The electronic absorption spectra of *N*-phenyl-substituted fulgide *E*-**4a** in toluene have long-wavelength bands with a maximum at 386 nm and the molar extinction coefficient of 11600 L mol^{-1} cm^{-1} (Table 1). The introduction of the phenyl substituent instead of the methyl group at the nitrogen atom of the indole ring leads to a hypsochromic shift (7 nm) of the long-wavelength maximum of the *E*-isomer compared to the *E*-isomer of the previously studied fulgide **5**,[6] which is characterized



5

Table 1. Spectral-absorption and spectral-fluorescent characteristics of the isomeric forms of fulgides **4a—c** in toluene at 293 K

Compound	Isomer	Absorption		Fluorescence	
		λ_{max}/nm	ε/L mol^{-1} cm^{-1}	Excitation	Emission
				λ_{max}/nm	
4a	*E*	386	11600	—	—
	C	611	—	367 ($S_0 \to S_2$), 610 ($S_0 \to S_1$)	783
4b	*E*	389	10900	—	—
	C	616	—	370 ($S_0 \to S_2$), 615 ($S_0 \to S_1$)	787
4c	*E*	396	11700	—	—
	C	633	—	380 ($S_0 \to S_2$), 640 ($S_0 \to S_1$)	800

by the long-wavelength maximum at longer wavelengths (393 nm, ε = 9530 L mol^{-1} cm^{-1}).

The introduction of electron-releasing groups at the *para* position of the *N*-phenyl fragment leads to a small bathochromic shift (3 nm) of the long-wavelength maximum for the 4-methoxy derivative (fulgide **4b**) (λ_{max} = 389 nm, ε = 10900 L mol^{-1} cm^{-1}) and a shift of the maximum of this band by 10 nm for the 4-dimethylamino-containing compound (fulgide **4c**) (λ_{max} = 396 nm, ε = 11700 L mol^{-1} cm^{-1}) compared to *N*-phenyl-3-indolylfulgide **4a** (see Table 1).

At ambient temperature, solutions of fulgides **4a—c** do not show fluorescence properties.

Under UV irradiation using a mercury lamp (λ = 365 nm), solutions of fulgides **4a—c** in toluene acquire a color characteristic of the cyclization products of the dihydrocarbazole isomers *C* (see Scheme 2), which is accompanied[5,6] by the appearance of bands in the spectra at λ = 500—750 nm (Fig. 4).

The spectra of the photoinduced *C*-isomers of fulgides **4a,b** have absorption bands at 611 and 616 nm, respectively (see Table 1). In the case of 1-[4-(dimethylamino)-phenyl]indolylfulgide **4c**, the long-wavelength maximum of the *C*-isomer is shifted to longer wavelengths and is observed at 633 nm.

An increase in the bathochromic shift of the long-wavelength maximum of both the *E*- and *C*-isomers with increasing electron-releasing properties of the substituent in the *para* position of the *N*-phenyl ring is consistent with the concept of polarization of the *E*- and *C*-isomers of fulgides in the excited state due to a shift of the electron density of the aromatic indole heterocycle to the anhydride group.[10]

The cyclic *C*-isomers of fulgides **4a—c** are characterized by high thermal stability in a toluene solution. Thus, the thermal reverse reaction *C* → *E* is not detected at 293 K for 72 h. The time dependence of the absorbance at the absorption maximum of the photoproduct *C* of fulgide **4a** at 343 K under irradiation using a mercury lamp (λ = 365 nm) until the photostationary state is reached and after the termination of irradiation is presented in Fig. 5 (regions *a* and *b*, respectively). In the region *b* (see Fig. 5), no changes in the absorbance of the colored solution were observed within 40 min, which also indicates that no reverse dark reactions proceed.

The visible light irradiation (λ = 578 nm) of colored solutions of fulgides **4a—c** leads to their bleaching as a result of the reverse ring-opening photoreaction *C* → *E*. Cyclic isomers **4a—c** show fluorescence properties with the fluorescence quantum yields $\Phi = 10^{-3}$. The fluorescence maxima of solutions of the cyclic *C*-isomers in toluene are observed at long wavelengths, at 783 (**4a**), 787 (**4b**), and 800 nm (**4c**) (see Table 1). As can be seen from the fluorescence excitation spectra of cyclic isomers **4a—c**, the transition absorption bands $S_0 \to S_2$ (λ_{max} = 367—380 nm) overlap with the transition ab-

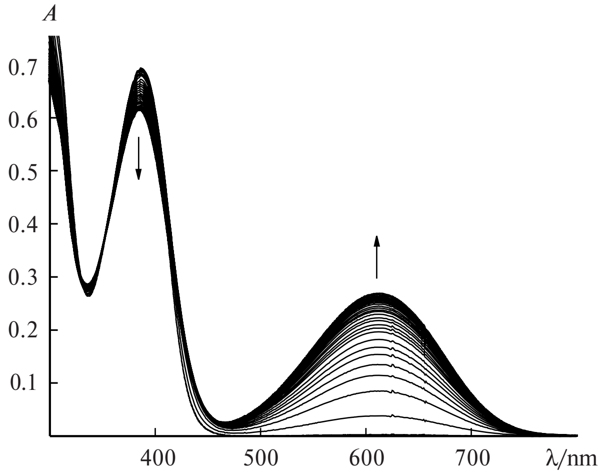


Fig. 4. Electronic absorption spectra of a solution of fulgide **4a** in toluene ($c = 7.16 \cdot 10^{-5}$ mol L^{-1}, T = 295 K) under light irradiation at λ = 365 nm recorded at 10 s intervals.

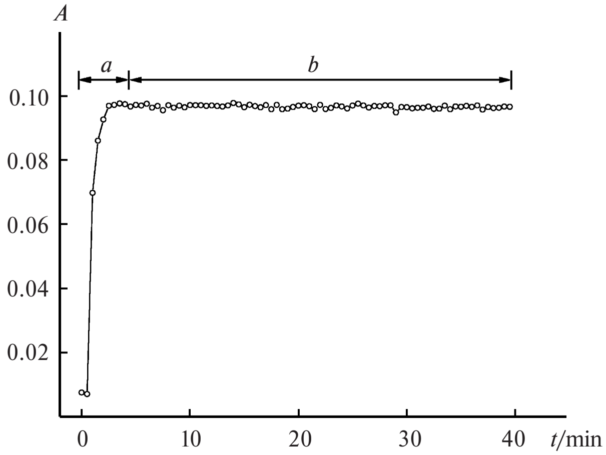


Fig. 5. Absorbance of the photoisomer *C*-**4a** ($c = 3.5 \cdot 10^{-5}$ mol L^{-1}, $T = 343$ K) at the absorption maximum under light irradiation at $\lambda = 365$ nm until the photostationary state is reached (region *a*) and after termination of irradiation (region *b*).

sorption bands $S_0 \rightarrow S_1$ of the *E*-isomeric forms (λ_{max} = 386—396 nm). As a result, due to the recyclization $C \rightarrow E$ in the electronic excitation state, the complete conversion of the starting *E*-isomers of fulgides **4a—c** into the colored products *C* cannot be achieved (see Table 1).

In addition, the absorption bands of the *E*- and *Z*-isomers strongly overlap (see Fig. 4), and both the $E{\rightarrow}Z$ and $Z{\rightarrow}E$ photoisomerization reactions proceed under irradiation at the absorption band of one of the isomers.[1] Hence, UV irradiation leads to the establishment of the stationary state, including three isomeric forms (*E*, *Z*, and *C*), in solution (see Scheme 2). Actually, the ^{1}H NMR spectra of fulgide **4a** in deuterotoluene recorded upon successive irradition at λ = 365 and 578 nm (Fig. 6) provide evidence that all three isomeric forms are present in solution.

The ^{1}H NMR spectra of the starting solution show a set of signals characteristic of isomer *E*-**4a** (see Fig. 6, *a*). After light irradiation at λ = 365 nm, the photostationary state is reached. Thus, the proton signals of the Me groups of all isomers (acyclic isomers *E*-**4a** and *Z*-**4a** and cyclic isomer *C*-**4a**) and the signal for the aromatic proton of the *C*-isomer (see Fig. 6, *b*) are observed. The ratio between the starting fulgide *E*-**4a** and isomers *Z*-**4a** and *C*-**4a** is 5 : 6 : 9 (estimated from the integrated intensities of the signals of the Me groups). Upon further visible light irradiation (λ = 578 nm) of this solution, the ^{1}H NMR spectrum shows the proton signals of acyclic isomers *E*-**4a** and *Z*-**4a** (see Fig. 6, *c*), which are present in solution in a ratio of 7 : 3. Therefore, the analysis of the ^{1}H NMR and electronic absorption spectra confirmed the proposed mechanism of the photoinduced reactions of new indolylfulgides **4a—c** involving the *E*/*Z* photoisomerization and the $E{\rightarrow}C$ photocyclization.

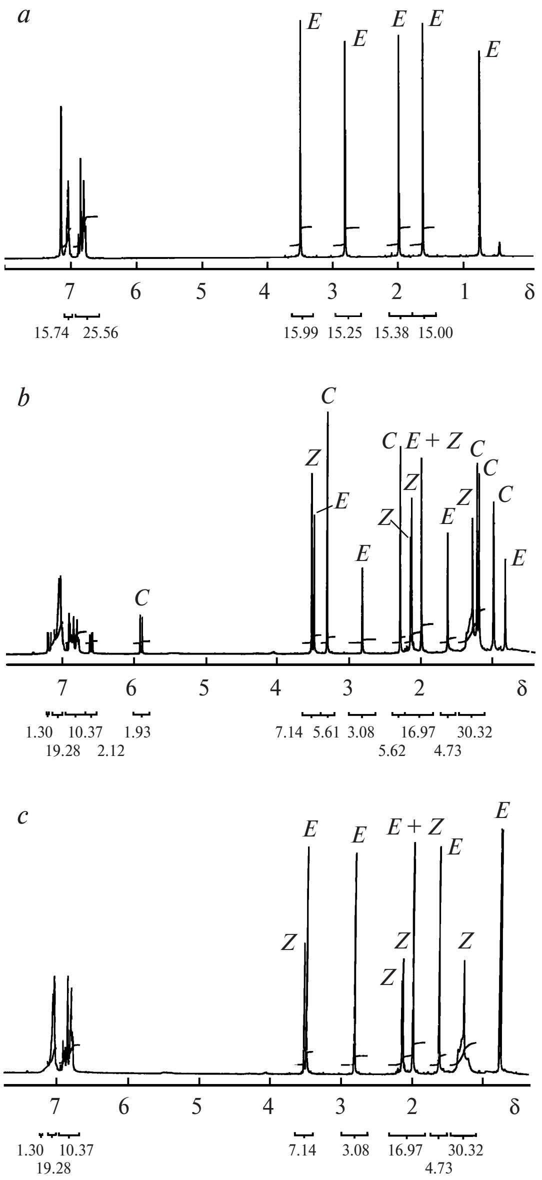


Fig. 6. ^{1}H NMR spectra of fulgide **4a** in toluene-d_8 before irradiation (*E*-isomer) (*a*), after light irradiation at λ = 365 nm (*E*, *Z*, and *C*-isomers) (*b*), and after subsequent light irradiation at λ = 578 nm (*E*- and *Z*-isomers) (*c*).

Fulgides **4a—c** are characterized by enhanced resistance to photodegradation. After the repeated photocoloration—photobleaching cycle in toluene solutions (for example, of compound **4a**; see Fig. 7), the absorbance at the absorption maximum of the *C*-isomer (the photostationary state) remains virtually unchanged.

To conclude, we synthesized photochromic fulgides, *viz.*, (3*E*)-3-[1-(1-aryl-5-methoxy-2-methyl-1*H*-indol-3-yl)ethylidene]-4-(1-methylethylidene)tetrahydro-2,5-furandiones. New *N*-arylindolylfulgides are characterized by resistance to photodegradation and high thermal

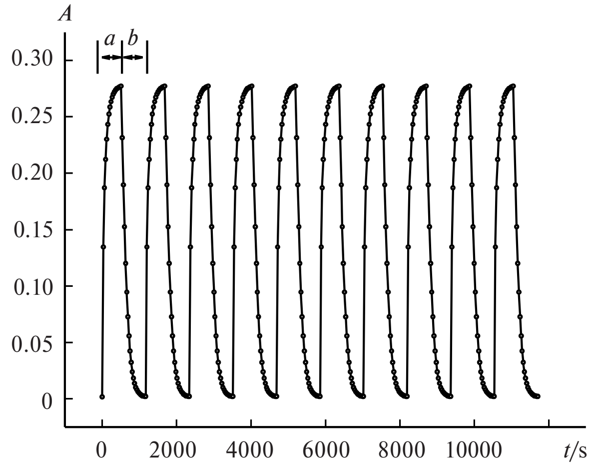


Fig. 7. Changes in the absorbance of a toluene solution of fulgide **4a** ($c = 7.16 \cdot 10^{-5}$ mol L^{-1}, $T = 295$ K) at the absorption maximum of the *C*-isomer ($\lambda = 610$ nm) after repeated photocoloration ($\lambda = 365$ nm) (*a*)—photobleaching ($\lambda = 578$ nm) (*b*) cycles.

stability of the photoinduced cyclic form showing fluorescence properties.

Experimental

The electronic absorption spectra were measured on an Agilent 8453 spectrophotometer. The fluorescence spectra were recorded on a Varian Eclipce spectrofluorimeter. Solutions were irradiated using a DRSh-250 mercury lamp equipped with a kit of light interference filters for isolation of mercury lines. The IR spectra were measured on a Specord 75IR instrument in Nujol mulls. The ^{1}H NMR spectra were recorded on a Varian Unity-300 instrument (300 MHz) using HMDS as the external standard.

(3*E*)-3-(Ethoxycarbonyl)-4-(5-methoxy-2-methyl-1-phenyl-1*H*-indol-3-yl)-2-(1-methylethylidene)pent-3-enoic acid (2a). A solution of 3-acetyl-5-methoxy-2-methyl-1-phenylindole (2.8 g, 0.01 mol), diethyl isopropylidenesuccinate (2.8 g, 0.013 mol), and diisopropylamine (1.4 mL, 0.01 mol) in THF (20 mL) was added with stirring to a suspension of sodium hydride (0.7 g, 0.03 mol) in THF (10 mL) at room temperature. The reaction mixture was stirred at 30 °C for 5 h. The solvent was distilled off using a water jet vacuum pump. The residue was treated with 10% hydrochloric acid (30 mL). The precipitate of monoethyl ester **2a** was filtered off and recrystallized from toluene. The yield was 52%, colorless crystals, m.p. 162—163 °C. Found (%): C, 73.40; H, 6.52; N, 3.35. $C_{27}H_{29}NO_5$. Calculated (%): C, 72.46; H, 6.53; N, 3.13. IR, ν/cm^{-1}: 1760, 1790 (C=O). ^{1}H NMR (CDCl$_3$), δ: 0.65 (t, 3 H, CH, *J* = 7.0 Hz); 1.96, 2.16, 2.18, and 2.21 (all s, 3 H each, Me); 3.83 (s, 3 H, OMe); 3.87 (q, 2 H, CH$_2$, *J* = 7.0 Hz); 6.70—7.00 (m, 3 H, H arom.); 7.20—7.60 (m, 5 H, H arom.); 11.00—11.20 (br.s, 1 H, OH).

(2*E*)-2-[1-(5-Methoxy-2-methyl-1-phenyl-1*H*-indol-3-yl)-ethylidene]-3-(1-methylethylidene)butanedioic acid (3a). Monoethyl ester **2a** (2.3 g, 5.2 mmol) was refluxed with a 10% methanolic KOH solution (10 mL) in a flask equipped with a reflux condenser for 4 h. The reaction mixture was cooled, diluted with water, and neutralized with a 10% HCl solution (30 mL). The precipitate of dicarboxylic acid **3a** was filtered off and dried in air. The yield was 92%, 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: 0.90, 1.65, 2.00, and 2.20 (all s, 3 H each, Me); 3.65 (s, 3 H, OMe); 6.75—7.10 (m, 3 H, H arom.); 7.22—7.65 (m, 5 H, H arom.); 11.40—11.60 (br.s, 2 H, OH).

(3*E*)-3-[1-(5-Methoxy-2-methyl-1-phenyl-1*H*-indol-3-yl)-ethylidene]-4-(1-methylethylidene)tetrahydro-2,5-furandione (*E*-4a). Diacid **3a** (2 g, 4.7 mmol) was dissolved under heating in acetyl chloride (1.5 mL). The solvent was distilled off *in vacuo*. The reaction product was purified by silica gel column chromatography using chloroform as the eluent. The yield was 97%, yellow crystals, m.p. 182—184 °C (from MeCN). Found (%): C, 78.80; H, 6.52; N, 3.35. $C_{20}H_{21}NO_4$. Calculated (%): C, 78.21; H, 6.28; N, 3.20. IR, ν/cm^{-1}: 1790, 1760 (C=O). ^{1}H NMR (benzene-d$_6$), δ: 0.75, 1.60, 2.00, and 2.80 (all s, 3 H each, Me); 3.50 (s, 3 H, OMe); 6.70—6.90 (m, 5 H, H arom.); 7.00—7.05 (m, 3 H, H arom.).

(3*Z*)-3-[1-(5-Methoxy-2-methyl-1-phenyl-1*H*-indol-3-yl)-ethylidene]-4-(1-methylethylidene)tetrahydro-2,5-furandione (*Z*-4a) was synthesized in an NMR tube as a mixture with the *E*- and *C*-isomers from a solution of fulgide *E*-**4a** in deuterotoluene under light irradiation at $\lambda = 365$ nm for 4 h ($c = 2.4 \cdot 10^{-2}$ mol L^{-1}) . ^{1}H NMR (benzene-d$_6$), δ: 1.30, 2.00, 2.10, and 2.15 (all s, 3 H each, Me); 3.55 (s, 3 H, OMe); 6.70—6.90 (m, 5 H, H arom.); 7.00—7.20 (m, 3 H, H arom.).

8-Methoxy-4,4,4a,10-tetramethyl-5-phenyl-4a,5-dihydro-1*H*-furo[3,4-*b*]carbazole-1,3(4*H*)-dione (*C*-4a) was synthesized in an NMR tube as a mixture with the *E*- and *Z*-isomers from a solution of fulgide *E*-**4a** in deuterotoluene under light irradiation at $\lambda = 365$ nm for 6 h ($c = 2.4 \cdot 10^{-2}$ mol L^{-1}). ^{1}H NMR (benzene-d$_6$), δ: 1.00, 1.15, 1.20, and 2.30 (all s, 3 H each, Me); 3.30 (s, 3 H, OMe); 5.85—5.90 (s, 1 H, H arom.); 6.55—6.65 (m, 1 H, H arom.); 6.90—7.20 (m, 6 H, H arom.).

(3*E*)-4-[5-Methoxy-2-methyl-1-(4-methoxyphenyl)-1*H*-indol-3-yl]-2-(1-methylethylidene)-3-(ethoxycarbonyl)pent-3-enoic acid (*E*-2b) was synthesized analogously to monoethyl ester **2a** from 3-acetyl-5-methoxy-1-(4-methoxyphenyl)-2-methylindole (0.01 mol). The yield was 55%, colorless crystals, m.p. 147—149 °C. Found (%): C, 73.40; H, 6.52; N, 3.35. $C_{28}H_{31}NO_6$. Calculated (%): C, 72.46; H, 6.53; N, 3.13. IR, ν/cm^{-1}: 1770, 1790 (C=O). ^{1}H NMR (DMSO-d$_6$), δ: 0.77 (t, 3 H, Me, *J* = 7.0 Hz); 1.94, 2.05, 2.13, and 2.22 (all s, 3 H each, Me); 3.74 and 3.86 (both s, 3 H each, OMe); 3.73—3.85 (m, 2 H, CH$_2$); 6.50—6.65 (m, 1 H, H arom.); 6.70—6.90 (m, 2 H, H arom.); 7.00—7.20 (m, 4 H, H arom.); 11.90—12.00 (br.s, 1 H, OH).

(2*E*)-2-{1-[5-Methoxy-1-(4-methoxyphenyl)-2-methyl-1*H*-indol-3-yl]ethylidene}-3-(1-methylethylidene)butanedioic acid (*E*-3b) was synthesized analogously to acid **3a**. The yield was 88%, colorless crystals, m.p. 260—261 °C. Found (%): C, 70.45; H, 6.32; N, 3.25. $C_{26}H_{27}NO_6$. Calculated (%): C, 69.47; H, 6.05; N, 3.12. IR, ν/cm^{-1}: 1760, 1785 (C=O). ^{1}H NMR (DMSO-d$_6$), δ: 1.95, 2.04, 2.15, and 2.22 (all s, 3 H each, Me); 3.74 and 3.86 (both s, 3 H each, OMe); 6.50—6.70 (m, 1 H, H arom.); 6.80—6.90 (m, 2 H, H arom.); 7.00—7.30 (m, 4 H, H arom.); 11.60—11.80 (br.s, 2 H, OH).

(3*E*)-3-{1-[5-Methoxy-1-(4-methoxyphenyl)-2-methyl-1*H*-indol-3-yl]ethylidene}-4-(1-methylethylidene)tetrahydro-2,5-furandione (*E*-4b). Fulgide *E*-**4b** was synthesized analogously to fulgide *E*-**4a**. The yield was 95%, greenish-yellow crystals, m.p. 166—168 °C. Found (%): C, 70.25; H, 6.41; N, 2.83. $C_{26}H_{25}NO_5$. Calculated (%): C, 70.42; H, 6.54; N, 2.97. IR, ν/cm^{-1}: 1755, 1810 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.08, 2.06, 2.24, and 2.86 (all s, 3 H each, Me); 3.82 and 3.90 (both s, 3 H each, OMe); 6.70—6.90 (m, 3 H, H arom.); 7.10—7.30 (m, 4 H, H arom.).

(3*Z*)-3-{1-[5-Methoxy-1-(4-methoxyphenyl)-2-methyl-1*H*-indol-3-yl]ethylidene}-4-(1-methylethylidene)tetrahydro-2,5-furandione (*Z*-4b) was synthesized in an NMR tube as a mixture with the *E*- and *C*-isomers from a solution of fulgide *E*-**4b** in deuterotoluene under light irradiation at λ = 365 nm for 4 h ($c = 2.4 \cdot 10^{-2}$ mol L^{-1}). ^{1}H NMR (toluene-d$_8$), δ: 1.20, 2.10, 2.15, and 2.20 (all s, 3 H each, Me); 3.30 and 3.50 (both s, 3 H each, OMe); 6.60—7.20 (m, 7 H, H arom.).

8-Methoxy-5-(4-methoxyphenyl)-4,4,4a,10-tetramethyl-4a,5-dihydro-1*H*-furo[3,4-*b*]carbazole-1,3(4*H*)-dione (*C*-4b) was synthesized in an NMR tube as a mixture with the *E*- and *Z*-isomers from a solution of fulgide *E*-**4b** in deuterotoluene under light irradiation at λ = 365 nm for 6 h ($c = 2.4 \cdot 10^{-2}$ mol L^{-1}). ^{1}H NMR (toluene-d$_8$), δ: 0.40, 1.05, 1.20, and 2.30 (all s, 3 H each, Me); 3.35 and 3.45 (both s, 3 H each, OMe); 6.60—7.20 (m, 7 H, H arom.).

(3*E*)-4-{1-[4-(Dimethylamino)phenyl]-5-methoxy-2-methyl-1*H*-indol-3-yl}-3-(ethoxycarbonyl)-2-(1-methylethylidene)pent-3-enoic acid (*E*-2c) was synthesized from 3-acetyl-1-(4-dimethylamino)phenyl-5-methoxy-2-methylindole (0.01 mol) analogously to monoethyl ester **2a**. The yield was 47%, colorless crystals, m.p. 173—175 °C. Found (%): C, 70.95; H, 6.92; N, 5.35. $C_{29}H_{34}N_2O_5$. Calculated (%): C, 71.00; H, 6.99; N, 5.71. IR, ν/cm^{-1}: 1760, 1790 (C=O). ^{1}H NMR ($CDCl_3$), δ: 0.67 (t, 3 H, Me, J = 7.0 Hz); 1.95, 2.15, 2.16, and 2.19 (all s, 3 H each, Me); 3.04 (s, 6 H, NMe_2); 3.82 (s, 3 H, OMe); 3.70—3.95 (m, 2 H, CH_2); 6.60—7.20 (m, 7 H, H arom.); 11.05—11.25 (br.s, 1 H, OH).

(2*E*)-2-(1-{1-[4-(Dimethylamino)phenyl]-5-methoxy-2-methyl-1*H*-indol-3-yl}ethylidene)-3-(1-methylethylidene)butanedioic acid (*E*-3c) was synthesized analogously to acid **3a**. The yield was 84%, colorless crystals, m.p. 224—225 °C. Found (%): C, 70.95; H, 6.92; N, 5.35. $C_{27}H_{30}N_2O_5$. Calculated (%): C, 71.11; H, 6.54; N, 6.06. IR, ν/cm^{-1}: 1760, 1790 (C=O). ^{1}H NMR (DMSO-d$_6$), δ: 1.95, 2.03, 2.14, and 2.21 (all s, 3 H each, Me); 3.02 (s, 6 H, NMe_2); 3.74 (s, 3 H, OMe); 6.50—7.20 (m, 7 H, H arom.), 11.60—11.80 (br.s, 2 H, OH).

(3*E*)-3-(1-{1-[4-(Dimethylamino)phenyl]-5-methoxy-2-methyl-1*H*-indol-3-yl}ethylidene)-4-(1-methylethylidene)tetrahydro-2,5-furandione (*E*-4c). Diacid **3c** (1.7 g, 3.9 mmol) was dissolved under heating in acetic anhydride (2 mL). The solvent was distilled off *in vacuo*. Fulgide **4c** was purified by silica gel column chromatography using chloroform as the eluent and recrystallized from MeCN. The yield was 91%, yellow crystals, m.p. 190—192 °C. Found (%): C, 70.25; H, 6.41; N, 2.83. $C_{26}H_{25}NO_5$. Calculated (%): C, 70.42; H, 6.54; N, 2.97. IR, ν/cm^{-1}: 1755, 1810 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.08, 2.06, 2.23, and 2.86 (all s, 3 H each, Me); 3.00 and 3.05 (both s, 6 H each, NMe_2); 3.90 (s, 3 H, OMe); 6.70—7.30 (m, 7 H, H arom.).

X-ray diffraction study. The unit cell parameters were measured and the three-dimensional X-ray diffraction data set for the structure of **4a** (**4a**´) was collected on an automated Enraf—Nonius CAD-4 diffractometer (Mo-Kα radiation, graphite monochromator). Light transparent crystals are triclinic, $C_{25}H_{23}NO_4$, M = 401.44, a = 13.044(2) Å, b = 13.405(2) Å, c = 13.523(3) Å, α = 81.26(2)°, β = 64.54(2)°, γ = 89.89(2)°, V = 2104.8(6) Å^3, Z = 4, d_{calc} = 1.267 g cm^{-3}, μ(Mo-Kα) = 0.086 mm^{-1}, space group $P\bar{1}$. The intensities of 5734 reflections were measured (2θ ≤ 45°) from a single crystal of dimensions 0.1×0.22×0.28 mm using the ω/2θ scanning technique. After the merging of equivalent reflections (R_{int} = 0.0242), a total of 5445 observed reflections ($F^2_{hkl} > \sigma(F^2)$) were obtained, of which 3855 reflections with $F^2 > 4\sigma(F^2)$ were used in calculations (in the final step, 3807 reflections were used).

The X-ray data for the structure of **4b** were collected on an automated Bruker P-4 diffractometer (Mo-Kα radiation, graphite monochromator). Pale-yellow transparent crystals are triclinic, $C_{26}H_{30}NO_5$, M = 436.51, a = 9.659(1) Å, b = 10.030(2) Å, c = 13.418(1) Å, α = 89.59(1)°, β = 78.25(1)°, γ = 62.76(1)°, V = 1126.0(2) Å^3, Z = 2, d_{calc} = 1.287 g cm^{-3}, μ(Mo-Kα) = 0.089 mm^{-1}, space group $P\bar{1}$. The intensities of 4331 reflections were measured (2θ ≤ 50°) using the ω/2θ scanning technique from a single crystal of dimensions 0.16×0.20×0.22 mm. After the merging of equivalent reflections (R_{int} = 0.0211), a total of 3601 observed reflections ($F^2_{hkl} > \sigma(F^2)$) were obtained, of which 3041 reflections with $F^2 > 4\sigma(F^2)$ were used in calculations. The structures of **4a** (**4a**´) and **4b** were solved by direct methods using the SHELXS-97 program package[11] and refined by the full-matrix least-squares method based on F^2 with anisotropic displacement parameters for nonhydrogen atoms using the SHELXL-97 program package.[11] In the crystal structures of **4a** (**4a**´) and **4b**, all hydrogen atoms were located in difference Fourier maps. Then the atomic coordinates and the isotropic temperature factors for all H atoms were refined by the least-squares method using a riding model.[11] In the last cycle of the full-matrix refinement, the absolute shifts of all variable parameters of the structures (571 for **4a** (**4a**´) and 290 for **4b**) were <0.001σ. The final R factors for **4a** (**4a**´) were R_1 = 0.056, wr_2 = 0.14 based on 3807 observed reflections with $I \geq 2\sigma(I)$; R_1 = 0.080, wr_2 = 0.16 based on all 5445 measured reflections, GOF 1.032. After the completion of the refinement, the maximum and minimum residual electron densities were 0.42 and –0.32 e Å^{-3}, respectively. The final R factors for **4b** were R_1 = 0.046, wr_2 = 0.13 based on 3041 observed reflections with $I \geq 2\sigma(I)$; R_1 = 0.053, wr_2 = 0.13 based on all 3601 measured reflections, GOF 1.042. After the completion of the refinement, the maximum and minimum residual electron densities were 0.16 and –0.17 e Å^{-3}, respectively.

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