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Synthesis and photochromic properties of N^2-alkyl-5-furyl-4-thienylpyridazinones

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New dihetarylethenes containing the six-membered bridging moiety, *viz.*, N^2-alkyl-5-furyl-4-thienylpyridazinones, were synthesized. These compounds have photochromic properties in solution. The hindered rotation of the thiophene and furan rings around the single bonds that link these rings to the double bond of the pyridazinone moiety results in the formation of mixtures of chiral diastereomers in solution, the lifetimes of the diastereomers being no longer than 0.2 s. The photochromic rearrangement of pyridazinones is characterized by the highly efficient photocoloration and the photobleaching, which is an order of magnitude less efficient, in the absence of thermal relaxation processes.

Key words: pyridazin-3-ones dihetarylethenes, synthesis, photochromism, fluorescence, photocolorability, molecular switches.

Due to the high thermal stability of isomeric forms and resistance to photodegradation, photochromic dihetarylethenes belong to one of the most promising classes of molecular structures for the design of elements for optical information recording devices and optical switches.[1—5] The structure of the bridging ring with a double bond can have a substantial effect on the photochromic properties of dihetarylethenes. Most of photochromic dihetarylethenes were synthesized based on five-membered bridging moieties. 4,5-Dithienylpyridazinones studied earlier[6] are rare examples of photochromic ethenes containing the six-membered cyclic bridging moiety. A few dihetarylethenes containing various substituents at the molecular bridge are known. Derivatives containing at least one thiophene moiety conjugated to the C=C bond have particularly useful photochromic properties.[7] In our opinion, systems belonging to this class of ethenes and containing both the thiophene and furan moieties at the ethylene bond of pyridazinone may be of interest.

The aim of the present study was to synthesize new pyridazinones containing the thienyl and furyl moieties at positions 4 and 5, respectively, as well as N^2-alkyl substituents, and to investigate their photochromic and spectral-luminescent properties for the purpose of examining the influence of structural factors on the above-mentioned properties of dihetarylpyridazinones.

Results and Discussion

Pyridazinones were synthesized according to the scheme reported in the study.[6] Acid **1** was prepared according to a known procedure[8] from 3-acetyl-2,5-dimethylthiophene by the Willgerodt—Kindler reaction followed by the hydrolysis. Ketone **2** was synthesized from 2,5-dimethylfuran and chloroacetyl chloride in the presence of $AlCl_3$. The reaction of thienylacetic acid **1** with compound **2** affords furanone **3**. The latter reacts with benzaldehyde in the presence of piperidine to form benzylidenefuranone **4**, which reacts with hydrazine hydrate to give 6-benzyl-5-(2,5-dimethyl-3-furyl)-4-(2,5-dimethyl-3-thienyl)-3(2*H*)-pyridazin-2-one (**5**). The reaction of compound **5** with alkyl halides gives the corresponding 2-alkyl-6-benzyl-5-(2,5-dimethyl-3-furyl)-4-(2,5-dimethyl-3-thienyl)-3(2*H*)-pyridazin-2-ones **6a—d** (Scheme 1).

The structures of the compounds were confirmed by IR and ^{1}H NMR spectroscopy.

In the ^{1}H NMR spectra of compounds **5** and **6a—d**, the singlets for protons of the heterocyclic moieties and singlets for protons of particular methyl and methylene groups are split with the integrated intensity ratio of ~9 : 10, which is evidence that there are two diastereomers in solutions (Fig. 1). In addition, the signals of the benzylic methylene groups at the nitrogen atom and at position 6 of the pyridazinone ring appear as an AB system for both

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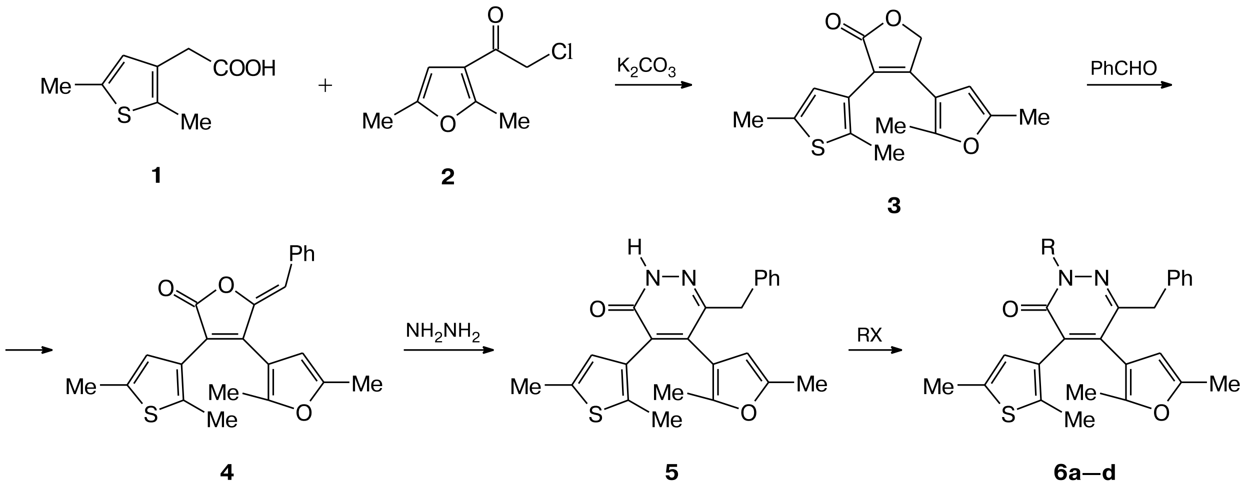
Scheme 1



R = Me (**a**), Et (**b**), 4-$ClC_6H_4CH_2$ (**c**), 4-$CNC_6H_4CH_2$ (**d**); X = I, Br

diastereomers, which is indicative of the presence of two pairs of enantiomers in solutions.

Actually, the molecular structures of pyridazinones show that these compounds can exist as rotamers[9] (Scheme 2).

Due to the hindered rotation around two single bonds in dihetarylpyridazinones, there are two chiral axes along the single bonds of each heterocycle with a double bond. In turn, the presence of two such sources of chirality in the molecules may be manifested in the presence of two pairs of enantiomers diastereomeric to each other, to be more precise, the presence of two pairs of rotamers with the parallel ($\mathbf{p}_1$ and $\mathbf{p}_2$) and antiparallel ($\mathbf{a}_1$ and $\mathbf{a}_2$) arrangement of the furan and thiophene rings (see Scheme 2). Moreover, the rotation of the thiophene and furan rings can be completely hindered, which will result in the existence of stable atropisomers and will have a substantial effect on the photochromic process, because the photoinduced electrocyclic reaction of ethenes occurs only in

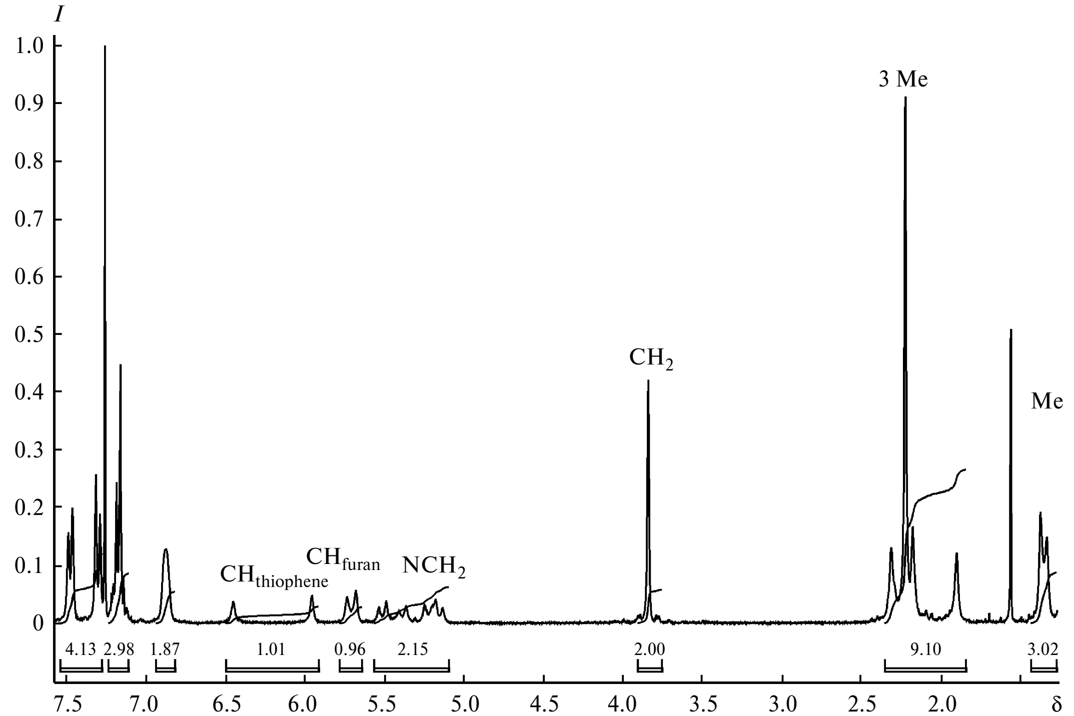
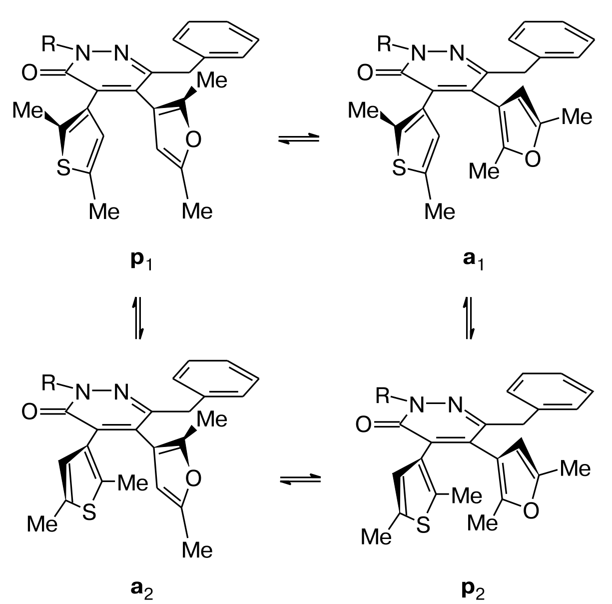


Fig. 1. ^{1}H NMR spectrum of compound **6c** in $CDCl_3$.

Scheme 2



the case of the conformer containing heterocycles in the antiparallel orientation.[9] We studied this intramolecular process by dynamic NMR spectroscopy.

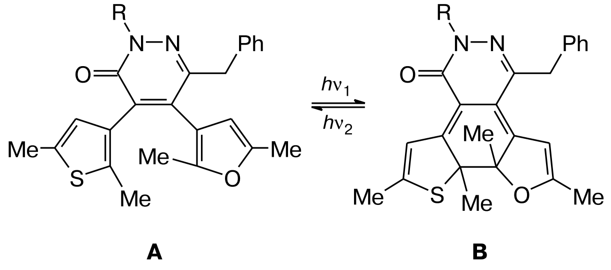
The temperature changes in the ^{1}H NMR spectra in DMSO-d$_6$ (Fig. 2) are indicative of interconversions of these four isomers (rotamerization). The rate of the interconversion of the diastereomers ($\mathbf{p}_1 \leftrightarrows \mathbf{a}_1$ and $\mathbf{p}_2 \leftrightarrows \mathbf{a}_2$) is much higher than the rate of the enantiomerization ($\mathbf{p}_1 \leftrightarrows \mathbf{p}_2$ and $\mathbf{a}_1 \leftrightarrows \mathbf{a}_2$). Actually, the rotation of one heterocycle is sufficient for the interconversion of diastereomers. Hence, the rate of this process is limited by the hindered rotation of one ring with the lower energy barrier (in the case under consideration, of the thiophene ring). For the enantiomerization, the rotation of both rings is required. Hence, the rate of this process is limited by the hindered rotation of the heterocycle with the highest energy barrier (in the case under consideration, of the furan ring). The lifetime of the diastereomers of compound **6c** calculated from the line shapes[10] in the ^{1}H NMR spectra was 0.2 s at 20 °C (see Fig. 2).

Since the rate of rotamerization was sufficiently high to maintain the constant ratio of the rotamers during steady-state UV irradiation at room temperature, the observed formation of a mixture of relatively stable rotamers of pyridazinones **5** and **6a—d** cannot have a substantial effect on the photochromic properties of the compounds under these conditions.

The results of the spectroscopic and photochemical studies of 5-furyl-4-thienyl-3(2*H*)-pyridazinones are given in Tables 1 and 2.

The electronic absorption spectra of dihetarylethenes **5** and **6a—d** (Scheme 3, form **A**) are characterized by long-wavelength absorption bands with maxima at 320—326 nm and the molar extinction coefficients of 6450—8100 L mol^{-1} cm^{-1} (see Table 1).

Scheme 3



The introduction of alkyl substituents at position 2 of the pyridazinone ring leads to small (~5—6 nm) batho-

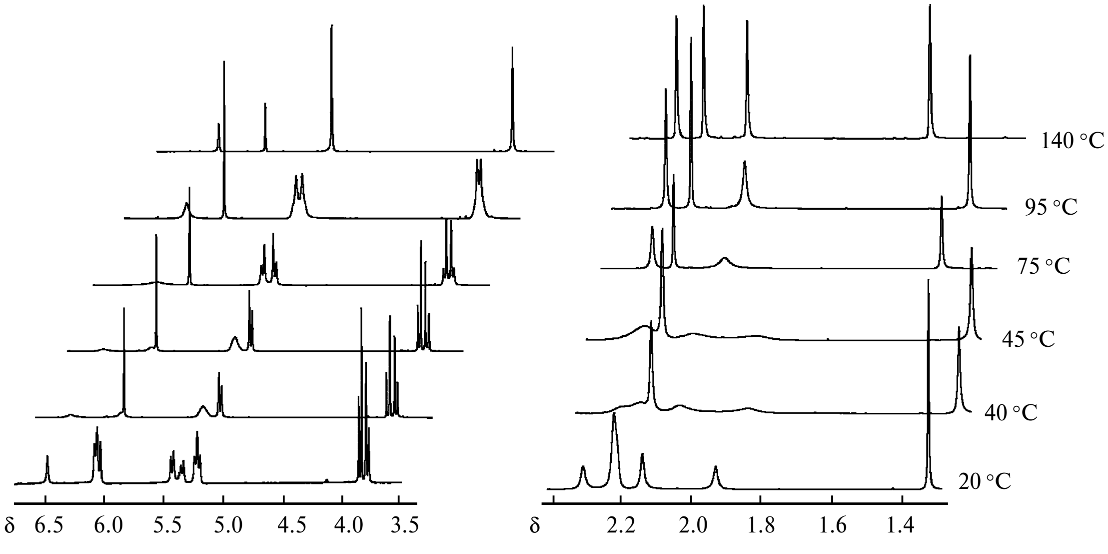
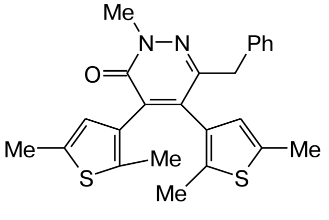


Fig. 2. ^{1}H NMR spectra of compound **6c** in DMSO-d$_6$ at different temperatures.

Table 1. Spectral-absorption and fluorescence characteristics of isomeric forms of dihetarylethenes **5** and **6a—d** in toluene at 293 K

Compound	Form **A**				Form **B** Absorption, λ_{max}/nm
	Absorption		Fluorescence, λ_{max}/nm		
	λ_{max}/nm	ε_{max}/L mol^{-1} cm^{-1}	Excitation	Emission	
5	320	6450	324	428	552
6a	325	7220	326	420	557
6b	326	7680	328	420	557
6c	325	8100	326	425	557
6d	325	7030	327	423	557

chromic shifts of the maxima of the long-wavelength absorption bands of compounds **6a—d** compared to unsubstituted dihetarylethene **5**. It should be noted that the absorption of the unsymmetrical dihetarylethenes is shifted by ~10 nm to longer wavelengths compared to the symmetrical analog, *viz.*, 6-benzyl-4,5-bis(2,5-dimethyl-3-thienyl)-2-methyl-2*H*-pyridazin-3-one (**7**), studied earlier.[6]



7

The open isomers **A** of 4,5-dihetarylpyridazinones exhibit fluorescence properties. The fluorescence maxima of compounds **5** and **6a—d** in toluene at 293 K are observed at 420—428 nm (see Table 1, Fig. 3). The fluorescence excitation spectra of dihetarylethenes **5** and **6a—d** coincide well with their long-wavelength absorption bands (see Table 1). The efficiency of fluorescence is low, and the quantum yields are lower than 10^{-4}.

The UV irradiation of solutions of 4,5-dihetarylpyridazinones **5** and **6a—d** at long-wavelength absorption bands leads to their coloration accompanied by the appearance of absorption bands with maxima at 552—557 nm in the electronic absorption bands (see Table 1, Fig. 4). These spectral changes are characteristic[1] of the cyclization photoreactions of dihetarylethenes **A** → **B**.

Table 2. Characteristics of the photocoloration ($\Phi_{AB}\varepsilon_{max}{}^{B}$) and photobleaching ($\Phi_{BA}\varepsilon_{max}{}^{B}$) reactions of dihetarylethenes **5** and **6a—d** in toluene at 293 K

Compound	$\Phi_{AB}\varepsilon_{max}{}^{B} \cdot 10^2$	$\Phi_{BA}\varepsilon_{max}{}^{B} \cdot 10^2$	Φ_{AB}/Φ_{BA}
	L mol^{-1} cm^{-1}		
5	47.8	5.2	9.2
6a	55.9	4.3	13.0
6b	52.2	4.1	12.7
6c	57.2	4.2	13.6
6d	59.0	4.1	14.4

As in the case of the starting forms **A**, the substitution at position 2 of the pyridazinone ring in the closed isomers **B** of dihetarylethenes **6a—d** leads to the bathochromic shift of the long-wavelength maxima by 5 nm compared to unsubstituted compound **5** (see Table 1). A comparison of compound **6a** with the symmetrical analog, *viz.*, 6-benzyl-4,5-bis(2,5-dimethyl-3-thienyl)-2-methyl-2*H*-pyridazin-3-one (**7**), shows a considerable short-wavelength shift (~21 nm) of the absorption band maximum of its closed isomer **B**.[6]

The closed isomers **B** of compounds **5** and **6a—d** are characterized by high thermal stability. Once the UV irradiation treatment is terminated, the backward dark reaction **B** → **A** in toluene is not observed at 293 K for 48 h. By contrast, the irradiation at long-wavelength absorption bands of the photoproducts **B** results in the bleaching of solutions associated with the backward ring-opening photoreactions **B** → **A**.

The spectral changes observed at the absorption bands of the open isomers **A** are worthy of note. Instead of a decrease in the intensity of the absorption bands corresponding to the forms **A** (due to the photoreaction **A** → **B**)

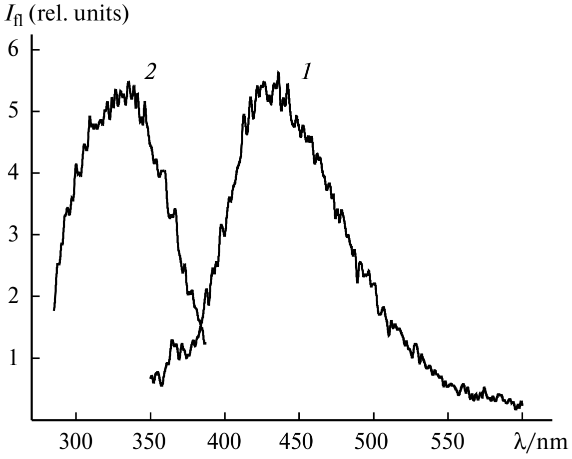


Fig. 3. Fluorescence spectra (λ_{ex} = 320 nm) (*1*) and fluorescence excitation spectra (λ_{obs} = 450 nm) (*2*) of a solution of compound **5** in toluene (T = 293 K).

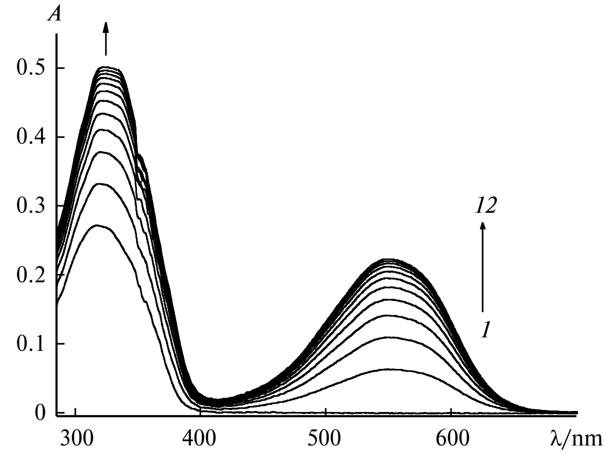


Fig. 4. Electronic absorption spectra of compound **5** in toluene before (*1*) and after the successive irradiation at $\lambda = 313$ nm recorded at 60 s intervals (*2—12*) ($C = 4 \cdot 10^{-5}$ mol L^{-1}, $T = 293$ K).

expected upon exposure to UV light, an increase in the intensity of these bands is observed (see Fig. 4). Evidently, this effect is associated with the overlap of the higher-intensity bands corresponding to $S_0 \rightarrow S_2$ transitions of the closed forms **B** with lower-intensity bands belonging to $S_0 \rightarrow S_1$ transitions of the forms **A** of 4,5-dihetarylpyridazinones **5** and **6a—d**. The overlap of the absorption bands of the isomeric forms is responsible also for the absence of the complete photoinduced conversion of the starting dihetarylethenes **A** into the closed derivatives **B**. Upon the exposure to UV light, the photostationary state is achieved. In this state, the ratio of the forms is determined by a number of factors, such as (in the case under consideration) the quantum yields of the photocoloration and photobleaching and the ratio of the molar extinction coefficients of the isomeric forms at the radiation wavelength.

The developed dynamics of the growth of absorption bands of the photoproducts **B** in the conditions of the above-mentioned overlap of the absorption bands of different forms at the excitation wavelength of the photoreaction may be indicative of a substantially lower efficiency of the photobleaching reaction compared to the photocoloration reaction. To estimate the efficiencies of the forward and backward photoreactions, we determined the products of $\Phi_{\mathbf{AB}}\varepsilon_{\max}{}^{\mathbf{B}}$ (the so-called photocolorability) and $\Phi_{\mathbf{BA}}\varepsilon_{\max}{}^{\mathbf{B}}$ (see Table 2). The ratios of the quantum yield of photocolorations to the quantum yield of photobleaching ($\Phi_{\mathbf{AB}}/\Phi_{\mathbf{BA}}$) determined from these data clearly show that the efficiency of the photocyclization of dihetarylethenes **5** and **6a—d** is an order of magnitude higher than the efficiency of their ring-opening photoreactions. The estimation of the quantum yields of the photocyclization $\Phi_{\mathbf{AB}}$ for the average molecular extinction coefficient $\varepsilon_{\max}{}^{\mathbf{B}} = 10000$ L mol^{-1} cm^{-1} taken from the published data[11—16] gives high values (up to 0.5—0.6).

To sum up, we synthesized substituted 5-furyl-4-thienyl-3(2*H*)-pyridazinones **5** and **6a—d** exhibiting photochromic properties. New unsymmetrical dihetarylethenes are characterized by the high efficiency of photocoloration, which is an order of magnitude higher than the efficiency of photobleaching, and by the thermal stability of the photoinduced closed forms.

Experimental

The UV-Vis spectra were recorded on a Cary 100 spectrophotometer (Varian). The fluorescence measurements were carried out on a Cary Eclipse spectrofluorimeter (Varian). The solutions were irradiated in a quartz cell ($l = 1$ cm) with a DRSh-250 mercury lamp equipped with a kit of interference light filters to select lines of the mercury spectrum.

The kinetic curves for the photocoloration of solutions of dihetarylethenes were measured directly during irradiation on a Cary 50 spectrophotometer equipped with a temperature-controlled cell holder. A xenon lamp with a monochromator to produce narrow spectral lines (Newport) was used as a radiation source. The intensity of optical radiation was determined with the use of a Newport 2935 power meter. The intensity of optical radiation at the wavelengths used (313 and 546 nm) was $3.18 \cdot 10^{14}$ and $7.32 \cdot 10^{15}$ photon s^{-1}, respectively. To determine the parameters $\Phi_{\mathbf{AB}}\varepsilon_{\max}{}^{\mathbf{B}}$ and $\Phi_{\mathbf{BA}}\varepsilon_{\max}{}^{\mathbf{B}}$, the slope of the tangent line at the initial instant was calculated from the kinetic curves for the photocoloration and photobleaching; the absorbance of solutions of dihetarylethenes at wavelengths of radiation was chosen to be identical.

The IR spectra were recorded on a Varian Excalibur 3100 FT-IR instrument. The ^{1}H NMR spectra were measured on a Varian Unity-300 instrument (300 MHz) in $CDCl_3$ with the use of HMDS as the external standard. The dynamic NMR spectra were recorded on an Avance Bruker-600 instrument (600 MHz) in DMSO-d_6.

(2,5-Dimethyl-3-thienyl)acetic acid (1) was synthesized according to a known procedure[8] from 3-acetyl-2,5-dimethylthiophene (15.95 g, 0.1 mol). The yield was 8.74 g (50%), colorless crystals, m.p. 67.5—68 °C (from aqueous ethanol).

2-Chloro-1-(2,5-dimethyl-3-furyl)ethanone (2). Dry dichloroethane (25 mL) and chloroacetyl chloride (4.2 mL, 52 mmol) were placed in a 50 mL four-necked flask equipped with a thermometer, a stirrer, a reflux condenser, and a dropping funnel, and then $AlCl_3$ (7 g, 52 mmol) was added with stirring and cooling to 5 °C for 10 min. Then 2,5-dimethylfuran (5.0 g, 52 mmol) was added dropwise to the reaction solution. The cooling was stopped. The reaction mixture was stirred at room temperature for 0.5 h and then poured onto ice. The organic layer was separated, successively washed with water, 10% Na_2CO_3, water, and dried over $CaCl_2$. The solvent was distilled off, and chloroethanone **2** was recrystallized. The yield was 2.62 g (29%), colorless long prisms, m.p. 86—87 °C (MeOH). IR, ν/cm^{-1}: 1683 (C=O). ^{1}H NMR, δ: 2.25 and 2.55 (both s, 3 H each, Me); 4.32 (s, 2 H, CH_2); 6.17 (s, 1 H, H_{Het}). Found (%): C, 55.86; H, 5.15; Cl, 20.41. $C_8H_9ClO_2$. Calculated (%): C, 55.67; H, 5.26; Cl, 20.54.

4-(2,5-Dimethyl-3-furanyl)-3-(2,5-dimethyl-3-thienyl)furan-2(5*H*)-one (3). A mixture of acid **1** (0.19 g, 1.1 mmol), ketone **2** (0.17 g, 1.1 mmol), K_2CO_3 (0.35 g, 2.5 mmol), and dry DMF

(1.2 mL) was heated with stirring at 78—82 °C for 3 h. After cooling, water (6 mL) was added to the reaction mixture, and the oil that formed was extracted with diethyl ether (3×3 mL). The ethereal solution was washed with water (2×2 mL) and brine and dried over anhydrous Na_2SO_4. The diethyl ether was removed, and the residue was triturated with ethanol (0.5 mL). Solid product **3** was filtered off, washed with ethanol, and dried in air. The yield was 135 mg (47%), colorless needles (from ethanol), m.p. 94 °C. ^{1}H NMR, δ: 2.11, 2.14, 2.19, and 2.44 (all s, 3 H each, Me); 5.07 (s, 2 H, CH_2); 5.74 and 6.57 (both s, 1 H each, H_{Het}). Found (%): C, 66.47; H, 5.65; S, 11.32. $C_{16}H_{16}O_3S$. Calculated (%): C, 66.64; H, 5.59; S, 11.12.

5-Benzylidene-4-(2,5-dimethyl-3-furanyl)-3-(2,5-dimethyl-3-thienyl)furan-2(5*H*)-one (4) was synthesized by analogy with the known procedure[17] from bifuranone **3** (0.29 g, 1 mmol) and benzaldehyde (0.15 g, 1.4 mmol). The yield was 0.28 g (74%), greenish-yellow crystals, m.p. 128—130 °C. IR, ν/cm^{-1}: 1763 (C=O). ^{1}H NMR, δ: 1.85, 2.04, 2.32, and 2.40 (all s, 3 H each, Me); 6.03 and 6.16 (both s, 1 H each, H_{Het}); 6.30 (s, 1 H, CH); 7.28—7.46 (m, 3 H, Ar); 7.78—7.87 (m, 2 H, Ar). Found (%): C, 78.53; H, 5.47; S, 8.39. $C_{23}H_{20}O_3S$. Calculated (%): C, 78.38; H, 5.35; S, 8.52.

6-Benzyl-5-(2,5-dimethyl-3-furyl)-4-(2,5-dimethyl-3-thienyl)-3(2*H*)-pyridazin-2-one (5) was synthesized by analogy with the known procedure[6] from compound **4** (200 mg, 0.53 mmol) and hydrazine hydrate (0.05 mL). The yield was 190 mg (92%), colorless crystals, m.p. 224—226 °C. IR, ν/cm^{-1}: 2874 (NH). ^{1}H NMR, δ: 1.37 (s, 3 H, Me); 1.98—2.40 (br.m, 9 H, Me); 3.85 (m, 2 H, CH_2); 5.75 (s, 1 H, H_{Het}); 6.01 and 6.48 (both br.s, a total of 1 H, H_{Het}); 6.85—6.95 (m, 2 H, Ar); 7.10—7.25 (m, 3 H, Ar); 10.62 (br.s, 1 H, NH). Found (%): C, 70.57; H, 5.81; N, 7.32. $C_{23}H_{22}N_2O_2S$. Calculated (%): C, 70.74; H, 5.68; N, 7.17.

6-Benzyl-5-(2,5-dimethyl-3-furyl)-4-(2,5-dimethyl-3-thienyl)-2-methyl-3(2*H*)-pyridazin-2-one (6a). A mixture of pyridazinone **5** (100 mg, 0.26 mmol) and 60% sodium hydride (15 mg, 0.39 mmol) in dry DMF (3 mL) was heated with stirring in a water bath for 2 h. Then CH_3I (0.03 mL, 0.5 mmol) was added. The reaction mixture was heated for 8 h, cooled, and diluted with H_2O (15 mL). The reaction product was extracted with CH_2Cl_2. The extract was successively washed with water and brine and dried with anhydrous Na_2SO_4. The solvent was distilled off, and the crude product was recrystallized. The yield was 60 mg (58%), m.p. 120.5—122 °C (from MeOH). IR, ν/cm^{-1}: 1638 (C=O). ^{1}H NMR, δ: 1.34 and 1.37 (both br.s, a total of 3 H, Me); 1.90—2.35 (br.m, 9 H, Me); 3.70—3.90 (m, 5 H, CH_2 + Me); 5.70 and 5.73 (both br.s, a total of 1 H, H_{Het}); 6.01 and 6.48 (both br.s, a total of 1 H, H_{Het}); 6.85—6.95 (m, 2 H, Ar); 7.15—7.22 (m, 3 H, Ar). Found (%): C, 71.06; H, 6.11; N, 6.72. $C_{24}H_{24}N_2O_2S$. Calculated (%): C, 71.26; H, 5.98; N, 6.92.

6-Benzyl-2-ethyl-5-(2,5-dimethyl-3-furyl)-4-(2,5-dimethyl-3-thienyl)-3(2*H*)-pyridazin-2-one (6b) was synthesized analogously to compound **6a** from pyridazinone **5** (100 mg, 0.26 mmol) and EtI (0.04 mg, 0.5 mmol). The yield was 65 mg (61%), colorless crystals (from aqueous MeOH), m.p. 114—114.5 °C. IR, ν/cm^{-1}: 1640 (C=O). ^{1}H NMR, δ: 1.36 (br.m, 3 H, Me); 1.46 (t, 3 H, Me, J = 7.2 Hz); 1.90—2.40 (br.m, 9 H, Me); 3.80—3.93 (m, 2 H, CH_2); 4.07—4.25 (br.m, 2 H, CH_2); 5.71 and 5.74 (both br.s, a total of 1 H, H_{Het}); 6.00 and 6.47 (both br.s, a total of 1 H, H_{Het}); 6.85—6.92 (br.m, 2 H, Ar); 7.10—7.22 (m, 3 H, Ar). Found (%): 71.59; H, 6.17; N, 6.49. $C_{25}H_{26}N_2O_2S$. Calculated (%): C, 71.74; H, 6.26; N, 6.69.

6-Benzyl-2-(4-chlorobenzyl)-5-(2,5-dimethyl-3-furyl)-4-(2,5-dimethyl-3-thienyl)-3(2*H*)-pyridazin-2-one (6c) was synthesized analogously to compound **6a** from pyridazinone **5** (100 mg, 0.26 mmol) and *p*-chlorobenzyl bromide (56 mg, 0.27 mmol). The yield was 69 mg (52%), colorless crystals, m.p. 131—132 °C (from methanol). IR, ν/cm^{-1}: 1640 (C=O). ^{1}H NMR, δ: 1.34 and 1.38 (both br.s, a total of 3 H, Me); 1.90—2.32 (br.m, 9 H, Me); 3.78—3.91 (m, 2 H, CH_2); 5.14—5.54 (br.m, 2 H, CH_2); 5.68 and 5.74 (both br.s, a total of 1 H, H_{Het}); 5.96 and 6.90 (both br.s, a total of 1 H, H_{Het}); 6.88 (br.m, 2 H, Ar); 7.11—7.23 (m, 3 H, Ar); 7.29—7.49 (m, 4 H, Ar). Found (%): C, 69.80; H, 5.15; N, 5.34. $C_{30}H_{27}ClN_2O_2S$. Calculated (%): C, 69.96; H, 5.28; N, 5.44.

6-Benzyl-(4-cyanobenzyl)-5-(2,5-dimethyl-3-furyl)-4-(2,5-dimethyl-3-thienyl)-23(2*H*)-pyridazin-2-one (6d) was synthesized analogously to compound **6a** from pyridazinone **5** (100 mg, 0.26 mmol) and 4-cyanobenzyl bromide (53 mg, 0.27 mmol). The yield was 50 mg (39%), colorless crystals, m.p. 130—130.5 °C (from MeOH). IR, ν/cm^{-1}: 1639 (C=O), 2229 (C≡N). ^{1}H NMR, δ: 1.38 (br.m, 3 H, Me); 1.91—2.32 (br.m, 9 H, Me); 3.80—3.91 (m, 2 H, CH_2); 5.22—5.60 (br.m, 2 H, CH_2); 5.71 and 5.76 (both br.s, a total of 1 H, H_{Het}); 6.00 and 6.45 (both br.s, a total of 1 H, H_{Het}); 6.88 (br.m, 2 H, Ar); 7.00—7.22 (m, 3 H, Ar); 7.36—7.70 (m, 4 H, Ar). Found (%): C, 73.81; H, 5.49; N, 8.19. $C_{31}H_{27}N_3O_2S$. Calculated (%): C, 73.64; H, 5.38; N, 8.31.

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