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Photochromic dihetarylethenes

17.* Synthesis and photochromic properties of dithienylethenes containing new heterocyclic bridging fragments

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Procedures were developed for the synthesis of substituted bis(2,5-dimethyl-3-thienyl)ethenes containing the imidazol-2-one, 1,3-dioxol-2-one, or 1,3-oxazol-2-one fragments as ethene bridges. These compounds were demonstrated to exhibit the photochromic properties. The cyclic forms of some imidazolone and oxazolone photochromes possess high thermal stability. The structure of photochromic 4,5-bis(4-acetyl-2,5-dimethyl-3-thienyl)-3-methyl-2,3-dihydro-1,3-oxazol-2-one was established by X-ray diffraction analysis. The molecule adopts an *anti*-parallel conformation similar to that of perfluorocyclopentene-bridged dithienylethenes.

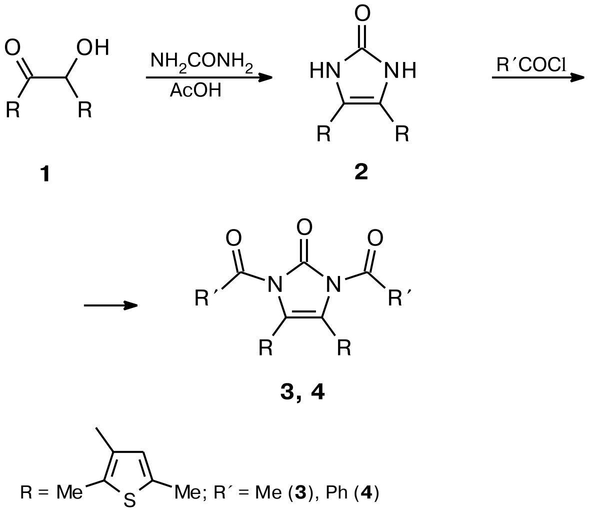
Key words: 1,2-dithienylethenes, 4,5-dithienylimidazol-2-ones, 4,5-dithienyl-1,3-dioxol-2-ones, 4,5-dithienyl-1,3-oxazol-2-ones, α-hydroxy ketones, thenoins, photochromes, thermal stability, fatigue resistance, X-ray diffraction analysis.

Previously, with the aim of searching for new available compounds possessing photochromic activity, we have synthesized dithienylethenes containing cyclobutenedione[2], azine[3], azole,[4] pyrrole, furan, or furopyrimidine[5] bridges. In the present study, we synthesized bis(2,5-dimethyl-3-thienyl)ethenes in which the thienyl rings are bound to imidazol-2-one, 1,3-dioxol-2-one, or 1,3-oxazol-2-one and examined their photochromic properties.

Results and Discussion

We used thenoin **1**, which is a convenient starting compound for the preparation of compounds of this type.[3] By analogy with benzoin,[6] we prepared 4,5-bis(2,5-dimethyl-3-thienyl)imidazol-2-one (**2**) by the reaction of compound **1** with urea in acetic acid. Treatment of compound **2** with acetyl and benzoyl chlorides afforded the diacetyl (**3**) and dibenzoyl (**4**) derivatives, respectively, in good yields (Scheme 1).

Scheme 1



The reaction of thenoin **1** with an excess of carbonyldiimidazole in refluxing benzene afforded dithienyl-

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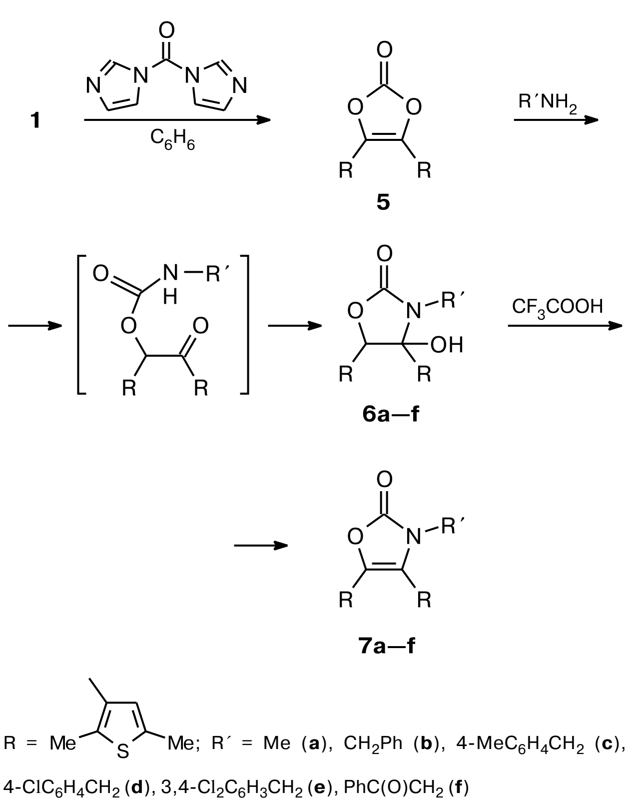
ethene **5** containing the bridging 1,3-dioxol-2-one (carbonate) fragment in virtually quantitative yield (Scheme 2).

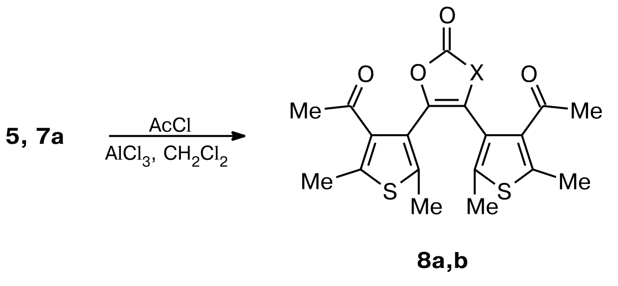
Scheme 2



Like cyclic carbonate of benzoin,[7] product **5** reacted with primary alkyl- or arylalkylamines to form 3-substituted 4-hydroxy-1,3-oxazolidin-2-ones **6**. The latter compounds were readily dehydrated under the action of trifluoroacetic acid at room temperature to give the corresponding 3-substituted 1,3-oxazol-2-ones **7** (see Scheme 2). Intermediates **6a—f** were characterized. According to the NMR data, these intermediates were obtained as one of two possible diastereomers. The carbonate-ring opening gave rise to the first asymmetric center and then the second center was generated in the step of formation of the oxazolone ring. The configuration of the latter is, apparently, determined by the configuration of the first asymmetric center present in the acyclic intermediate.

It is known[8] that the fatigue resistance of photochromic dithienylethenes is enhanced upon the introduction of alkyl groups at position 4 of the thiophene ring. In the present study, we synthesized 4,4′-diacetyl derivatives **8a,b** by acylation of compounds **5** and **7a** with an excess of acetyl chloride in dichloromethane in the presence of aluminum chloride (Scheme 3).

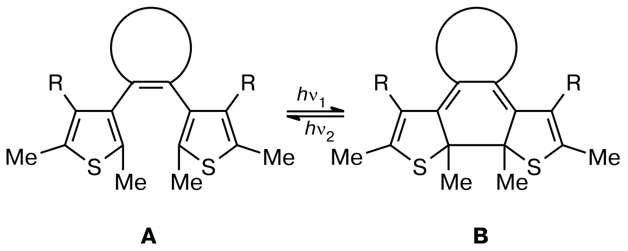
Scheme 3



X = O (**8a**), NMe (**8b**)

All the compounds synthesized in the present study exhibit the photochromic properties (Scheme 4). The spectroscopic properties of selected products are given in Table 1.

Scheme 4



Compounds **2—4** are of no interest as photochromes. When exposed in the dark, the cyclic form **B** of compound **2** gave a by-product rather than the open form. This by-product is characterized by a long-wavelength absorption band with a maximum at 363 nm. Upon UV

Table 1. Spectroscopic characteristics of compounds **2—5**, **7a—f**, and **8a,b**

Compound	$\lambda_{max}{}^a$/nm		$k^b \cdot 10^5$/s^{-1}
	Open form (**A**)	Cyclic form (**B**)	
2	294	464	—
3	244	462	—
4	243	450	—
5	280	442	0.035
7a	287	450	0.002
7b	286	453	0.002
7c	285	452	0.93
7d	286	449	2.1
7e	284	457	9.1
7f	283	447	0.011
8a	220	447	0.003
8b	245	445	0.0003

[a] The maxima of the long-wavelength absorption bands.
[b] The rate constant of the dark ring-opening reaction.

irradiation, the diacetyl (**3**) and dibenzoyl (**4**) derivatives of imidazol-2-one yielded the cyclic forms in small amounts. Previously,[4] we have already observed that dithienylethenes lose their photochromic properties as the number of electron-withdrawing groups in the bridging fragment is increased.

Carbonate **5** possesses the photochromic properties. As can be seen from Table 1, the cyclic form of **5** is rather stable (the rate constant of the ring opening $k = 3.55 \cdot 10^{-7}$ s^{-1}). It should be emphasized that the introduction of the acetyl groups at positions 4 and 4′ of the thienyl rings leads to a decrease in this constant by almost an order of magnitude for 1,3-dioxol-2-one **8a** and by two orders of magnitude for 3-methyl-1,3-oxazol-2-one **8b**. Hence, it means that exposition of compounds **8a** and **8b** in the dark at room temperature for 100 h leads to a decrease in the amount of their cyclic forms **B** by less than 1 and by 0.1%, respectively. It can be assumed that the acetyl groups in these compounds are favorable for stabilization of the cyclic forms **B** of dithienylethenes. It should also be noted that the introduction of the acetyl substituents leads to an increase in the fatigues resistance of photochromes. Thus, after eight opening-closing photocycles, the optical density of oxazol-2-one **7a** was only 23% of the initial optical density at the maximum of the cyclic form, whereas the corresponding value for substituted product **8b** was 82%.

Oxazolinone photochromes **7a**, **7b**, and **7f** also proved to be thermally stable ($k = 1.95 \cdot 10^{-8}$, $1.95 \cdot 10^{-8}$, and $1.13 \cdot 10^{-7}$ s^{-1}, respectively). However, it remains unclear why the constants k for their close analogs containing the alkyl substituents (**7c**) or halogen atoms (**7d,e**) in the phenyl ring are much higher ($1 \cdot 10^{-5}$—$1 \cdot 10^{-4}$ s^{-1}).

Since the oxazol-2-one ring was first treated as a bridge in photochromes, it was of interest to compare the conformation of compound **8b** established by X-ray diffraction analysis (Fig. 1) with the data for the open forms of dithienylethenes studied previously. Recall that the latter compounds are characterized by substantial rotation of the thienyl fragments with respect to the plane of the linking ring, *i.e.*, there is no conjugation between the π-electrons of the aromatic heterocycles and the double bond of the bridge. The conformation of molecule **8b** is similar to that of photochromic perfluorocyclopentene-bridged dithienylethenes.[9] The thiophene rings (T and T′) are in the *anti*-parallel orientation, *i.e.*, the methyl substituents at the C(2) and C(2′) active centers are located on the opposite sides with respect to the plane of the oxazolone ring (OR). The thiophene rings are substantially rotated with respect to the plane of the bridge, *i.e.*, there is no conjugation between the heterocycles. However, the angles of rotation of the thienyl fragments in molecule **8b**, unlike those in dithienylperfluorocyclopentenes, differ from each other. Thus, the dihedral angle OR—T is 46.19°, whereas the OR—T′ angle is increased to 58.72° due, apparently, to steric hindrances between the methyl and acetyl groups. The thienyl fragments are rotated with respect to each other by 68.35°. The angles of rotation of the acetyl groups with respect to the thienyl fragments are virtually equal (33.50°). There are no shortened intra- and intermolecular contacts in the structure. In the oxazol-2-one ring, the C(4″)—C(5″) bond length (1.336(2) Å) is equal to the standard $C_{sp}=C_{sp}$ double bond length typical of oxazolones,[10,11] which indicates that there is no electron density delocalization in this heterocycle.

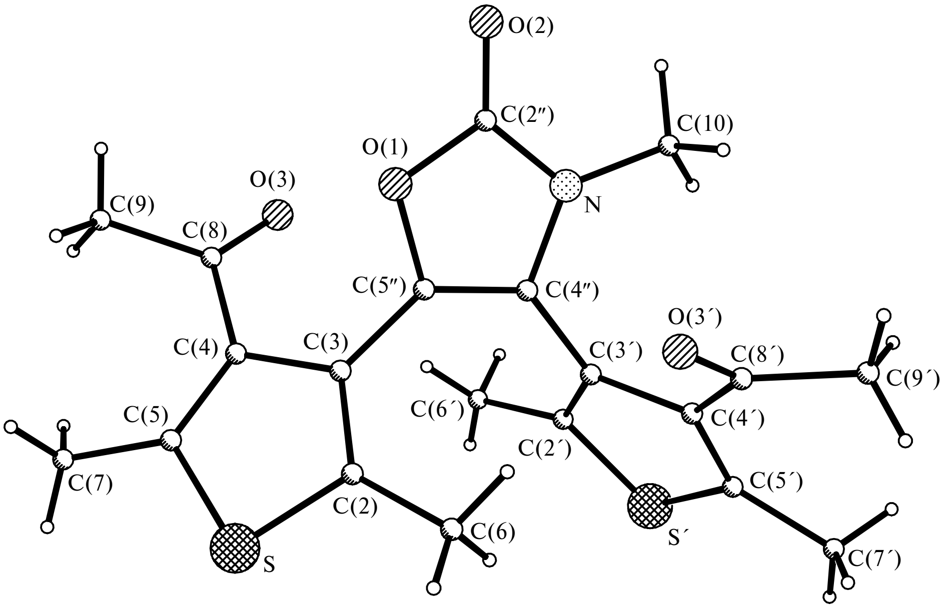


Fig. 1. Molecular structure of compound **8b**.

On the whole, a comparison of the properties of 1,3-azole-bridged dithienylethenes studied previously with photochromes bearing carbonyl-containing heterocycles provides evidence that a weakening of the aromaticity in the cyclic bridge is favorable for the enhancement of stability of the cyclic form and, as a consequence, for an increase in its thermal stability.

To summarize, we developed methods for the synthesis of substituted bis(2,5-dimethyl-3-thienyl)ethenes in which the imidazol-2-one, 1,3-dioxol-2-one, or 1,3-oxazol-2-one systems serve as the ethene fragment. It was demonstrated that these compounds exhibit photochromic properties, the latter two compounds being virtually thermally stable.

Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM-300 (300.13 MHz) and Bruker WM-250 (250.13 MHz) instruments in DMSO-d$_6$ and CDCl$_3$, respectively. The melting points were determined on a Boetius stage and were not corrected. The mass spectrum was measured on a Kratos MS-30 instrument with direct inlet of the sample into the ion source; the energy of ionizing electrons was 70 eV. The course of the reactions and the purities of the products were monitored by TLC on Merck Silica gel 60 F$_{254}$ plates using an AcOEt—hexane mixture as the eluent.

The photochromic characteristics of compounds **2—5**, **7**, and **8** were studied in a solution in MeCN (special purity grade). The cyclic forms **B** of the photochromes were prepared by irradiation of the samples with a DRSh-500 mercury lamp using light filters to separate lines of the Hg spectrum (313, 546, and 578 nm) and were then identified based on λ_{max} in the UV spectrum. The intensity of radiation of the Hg lamp was determined using a F4 photoelement calibrated against a ferrioxalate actinometer[12] for λ = 313 nm and against an actinometer based on the Reinecke salt[13] for λ = 546 and 578 nm. The absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer.

The reaction rate of the dark ring-opening reaction k was determined according to the equation

$$D_t = D_0\exp(-kt),$$

where D_0 is the initial optical density at the maximum of the long-wavelength band in the absorption spectrum of the cyclic form and D_t is the optical density at this maximum at the moment t.

4,5-Bis(2,5-dimethyl-3-thienyl)-1*H*,3*H*-imidazol-2-one (2). A solution of thenoin **1** [3] (0.840 g, 3 mmol) and urea (0.360 g, 6 mmol) in AcOH (4 mL) was refluxed for 2 h. The reaction mixture was cooled. The precipitate that formed was filtered off and washed with a small amount of EtOH. Product **2** was obtained in a yield of 0.668 g (73%), m.p. 280—281 °C. Found (%): C, 58.95; H, 5.19; N, 9.48; S, 21.35. $C_{15}H_{16}N_2OS_2$. Calculated (%): C, 59.18; H, 5.30; N, 9.20; S, 21.06. ^{1}H (DMSO-d$_6$), δ: 1.98 and 2.32 (both s, 6 H each, 2 Me); 6.53 (s, 2 H, 2 CH); 10.16 (s, 2 H, 2 NH).

1,3-Diacetyl-4,5-bis(2,5-dimethyl-3-thienyl)-1*H*,3*H*-imidazol-2-one (3). A solution of compound **2** (0.304 g, 1 mmol) in Ac$_2$O (5 mL, 0.053 mol) was refluxed for 4 h. The reaction mixture was cooled, water (5 mL) was added, and the precipitate that formed was filtered off. After recrystallization from EtOH, product **3** was obtained in a yield of 0.280 g (72%), m.p. 179—180 °C. Found (%): C, 58.59; H, 5.05; N, 7.59; S, 16.23. $C_{19}H_{20}N_2O_3S_2$. Calculated (%): C, 58.74; H, 5.19; N, 7.21; S, 16.51. ^{1}H NMR (DMSO-d$_6$), δ: 1.88, 2.28, and 2.56 (all s, 6 H, 2 Me); 6.41 (s, 2 H, 2 CH).

1,3-Dibenzoyl-4,5-bis(2,5-dimethyl-3-thienyl)-1*H*,3*H*-imidazol-2-one (4). A mixture of compound **2** (0.100 g, 0.33 mmol) and PhCOCl (0.141 g, 1 mmol) in Py (2 mL) was heated at 100 °C for 2 h. The reaction mixture was cooled, water (10 mL) was added, and the product was extracted with ether (3×10 mL). The extract was successively washed with water, a 10% HCl solution, and water, and dried with MgSO$_4$. The solvent was concentrated *in vacuo* and the residue was recrystallized from AcOH. Product **4** was obtained in a yield of 0.100 g (59%), m.p. 183—184 °C. Found (%): C, 68.18; H, 4.64; N, 5.11; S, 12.82. $C_{29}H_{24}N_2O_3S_2$. Calculated (%): C, 67.95; H, 4.72; N, 5.46; S, 12.51. ^{1}H NMR (DMSO-d$_6$), δ: 2.04 and 2.26 (both s, 6 H each, 2 Me); 6.51 (s, 2 H, 2 CH); 7.58 (m, 6 H, 6 CH$_{Ar}$); 7.94 (m, 4 H, 4 CH$_{Ar}$).

4,5-Bis(2,5-dimethyl-3-thienyl)-1,3-dioxol-2-one (5). A mixture of thenoin **1** (0.560 g, 2 mmol) and 1,1′-carbonyldiimidazole (0.486 g, 3 mmol) in benzene (8 mL) was refluxed for 5—6 h. The reaction mixture was cooled and washed with water, a 10% HCl solution, and water. The solvent was concentrated *in vacuo* and the residue was recrystallized from EtOH. Product **5** was obtained in a yield of 0.550 g (90%), m.p. 106—107 °C. Found (%): C, 58.92; H, 4.56; S, 21.21. $C_{15}H_{14}O_3S_2$. Calculated (%): C, 58.80; H, 4.61; S, 20.93. ^{1}H NMR (CDCl$_3$), δ: 2.21 and 2.41 (both s, 6 H each, 2 Me); 6.58 (s, 2 H, 2 CH).

Synthesis of 3-substituted 4,5-bis(2,5-dimethyl-3-thienyl)-4-hydroxy-1,3-oxazolidin-2-ones 6 (general procedure). The corresponding primary amine* (1.5 mmol) was added to a solution of carbonate **5** (0.306 g, 1 mmol) in EtOH (3 mL). The reaction mixture was stirred at ~25 °C for 1—1.5 h. The precipitate that formed was filtered off and the product was recrystallized from EtOH. The physicochemical characteristics of 4-hydroxy-1,3-oxazolidin-2-ones **6a—f** are given in Table 2.

Synthesis of 3-substituted 4,5-bis(2,5-dimethyl-3-thienyl)-oxazol-2-ones 7 (general procedure). A solution of the corresponding 4-hydroxy-1,3-oxazolidin-2-one **6** (0.5 mmol) in CF$_3$COOH (5 mL, 0.065 mol) was kept at ~25 °C for 3—3.5 h. The solvent was concentrated *in vacuo* and the residue was crystallized from EtOH. The physicochemical characteristics of 1,3-oxazol-2-ones **7a—f** are given in Table 3.

Acylation of bis(2,5-dimethyl-3-thienyl)ethenes (general procedure). Aluminum chloride (2.5 g, 0.019 mol) was added with stirring to a solution of the corresponding dithienylethene (1 mmol) and AcCl (1.7 g, 0.022 mol) in CH$_2$Cl$_2$ (15 mL). The resulting mixture was stirred at ~25 °C for 6 h and carefully poured onto ice. The product was extracted with ether

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* In the case of MeNH$_2$, a 2.0 *M* methanolic solution (Aldrich) was used.

Table 2. Physicochemical characteristics of 3-substituted 4,5-bis(2,5-dimethyl-3-thienyl)-4-hydroxy-1,3-oxazolidin-2-ones **6a—f**

Compound	M.p. /°C	Yield (%)	Found/Calculated (%)				Molecular formula	^{1}H NMR spectrum (DMSO-d_6, δ, *J*/Hz)
			C	H	N	S		
6a	227—228	86	56.81 56.95	5.75 5.68	3.93 4.15	19.26 19.00	$C_{16}H_{19}NO_3S_2$	1.82, 2.13, 2.32, 2.39, 2.68 (all s, 3 H each, Me); 5.27 (s, 1 H, CH); 6.53 (s, 1 H, OH); 6.61, 6.82 (both s, 1 H each, CH)
6b	248—249	82	64.00 63.90	5.54 5.61	3.64 3.39	15.37 15.51	$C_{22}H_{23}NO_3S_2$	1.80, 1.97, 2.18, 2.36 (all s, 3 H each, Me); 4.07 (d, 1 H, H̲CH, *J* = 15.4); 4.41 (d, 1 H, HCH̲, *J* = 15.4); 5.45, 6.45 (both s, 1 H each, CH); 6.62 (s, 1 H, OH); 6.82 (s, 1 H, CH); 7.25 (m, 5 H, CH_{Ar})
6c	253—254	92	64.45 64.61	5.78 5.89	3.46 3.28	14.76 15.00	$C_{23}H_{25}NO_3S_2$	1.79, 1.97, 2.19, 2.27, 2.36 (all s, 3 H each, Me); 4.03 (d, 1 H, H̲CH, *J* = 15.2); 4.36 (d, 1 H, HCH̲, *J* = 15.2); 5.43, 6.45 (both s, 1 H each, CH); 6.58 (s, 1 H, OH); 6.82 (s, 1 H, CH); 7.07 (m, 4 H, CH_{Ar})
6d*	258—259	91	59.06 58.98	4.87 4.95	3.46 3.13	14.48 14.31	$C_{22}H_{22}ClNO_3S_2$	1.81, 2.03, 2.20, 2.37 (all s, 3 H each, Me); 4.12 (d, 1 H, H̲CH, *J* = 15.4); 4.38 (d, 1 H, HCH̲, *J* = 15.4); 5.47, 6.45 (both s, 1 H each, CH); 6.60 (s, 1 H, OH); 6.82 (s, 1 H, CH); 7.18, 7.32 (both d, 2 H each, CH_{Ar}, *J* = 8.3)
6e**	226—227	94	54.68 54.77	4.46 4.39	3.18 2.90	13.43 13.29	$C_{22}H_{21}Cl_2NO_3S_2$	1.82, 2.07, 2.21, 2.36 (all s, 3 H each, Me); 4.14 (d, 1 H, H̲CH, *J* = 15.4); 4.38 (d, 1 H, HCH̲, *J* = 15.4); 5.53, 6.49 (both s, 1 H each, CH); 6.62 (s, 1 H, OH); 6.81 (s, 1 H, CH); 7.19 (d, 1 H, CH_{Ar}, *J* = 8.2); 7.33 (s, 1 H, CH_{Ar}); 7.53 (d, 1 H, CH_{Ar}, *J* = 8.3)
6f	209—210	63	62.63 62.56	5.33 5.25	3.49 3.17	14.27 14.52	$C_{23}H_{23}NO_4S_2$	1.88, 2.12, 2.27, 2.39 (all s, 3 H each, Me); 4.61 (s, 2 H, CH_2); 5.45 (s, 1 H, CH); 6.57 (s, 1 H, CH); 6.68 (s, 1 H, OH); 6.85 (s, 1 H, CH); 7.62 (m, 3 H, CH_{Ar}); 7.95 (d, 2 H, CH_{Ar}, *J* = 8.3)

* Found (%): Cl, 8.05. Calculated (%): Cl, 7.91.

** Found (%): Cl, 14.83. Calculated (%): Cl, 14.70.

Table 3. Physicochemical characteristics of 3-substituted 4,5-bis(2,5-dimethyl-3-thienyl)-1,3-oxazol-2-ones **7a—f**

Compound	M.p. /°C	Yield (%)	Found/Calculated (%)				Molecular formula	^{1}H NMR spectrum (DMSO-d_6, δ, *J*/Hz)
			C	H	N	S		
7a	137	71	59.98 60.16	5.42 5.36	4.65 4.38	19.84 20.07	$C_{16}H_{17}NO_2S_2$	2.02, 2.11, 2.32, 2.43, 3.01 (all s, 3 H each, Me); 6.42, 6.83 (both s, 1 H each, CH)
7b	123—124	42	66.67 66.81	5.27 5.35	3.78 3.54	15.98 16.21	$C_{22}H_{21}NO_2S_2$	1.79, 2.17, 2.29, 2.40 (all s, 3 H each, Me); 4.62 (br.s, 2 H, CH_2); 6.36, 6.65 (both s, 1 H each, CH); 6.97 (d, 2 H, CH_{Ar}, *J* = 7.3); 7.27 (m, 3 H, CH_{Ar})
7c	154	96	67.29 67.45	5.73 5.66	3.65 3.42	15.47 15.66	$C_{23}H_{23}NO_2S_2$	1.78, 2.15, 2.24, 2.25, 2.38 (all s, 3 H each, Me); 4.56 (br.s, 2 H, CH_2); 6.35, 6.65 (both s, 1 H each, CH); 6.85 (d, 2 H, CH_{Ar}, *J* = 7.2); 7.08 (d, 2 H, CH_{Ar}, *J* = 7.2)
7d*	120—121	90	61.63 61.45	4.75 4.69	2.93 3.26	15.13 14.91	$C_{22}H_{20}ClNO_2S_2$	1.81, 2.16, 2.27, 2.38 (all s, 3 H each, Me); 4.61 (br.s, 2 H, CH_2); 6.36, 6.63 (both s, 1 H each, CH); 6.99 (d, 2 H, CH_{Ar}, *J* = 7.9); 7.34 (d, 2 H, CH_{Ar}, *J* = 7.9)

(*to be continued*)

Table 3 (*continued*)

Compound	M.p. /°C	Yield (%)	Found / Calculated (%) C	H	N	S	Molecular formula	^{1}H NMR spectrum (DMSO-d$_6$, δ, *J*/Hz)
7e**	146—147	77	57.12 56.90	4.03 4.12	2.75 3.02	14.07 13.81	$C_{22}H_{19}Cl_2NO_2S_2$	1.84, 2.16, 2.26, 2.38 (all s, 3 H each, Me); 4.63 (br.s, 2 H, CH$_2$); 6.36, 6.63 (both s, 1 H each, CH); 7.02 (d, 1 H, CH$_{Ar}$, *J* = 7.8); 7.15 (s, 1 H, CH$_{Ar}$); 7.55 (d, 1 H, CH$_{Ar}$, *J* = 7.8)
7f	184—185	96	65.46 65.22	4.92 5.00	2.98 3.31	15.42 15.14	$C_{23}H_{21}NO_3S_2$	2.00, 2.16, 2.27, 2.29 (all s, 3 H each, Me); 5.01 (s, 2 H, CH$_2$); 6.41, 6.63 (both s, 1 H each, CH); 7.60 (m, 3 H, CH$_{Ar}$); 7.94 (d, 2 H, CH$_{Ar}$, *J* = 7.6)

* Found (%): Cl, 8.38. Calculated (%): Cl, 8.25.

** Found (%): Cl, 15.44. Calculated (%): Cl, 15.27.

(3×15 mL). The extract was successively washed with water, a NaHCO$_3$ solution, and again with water and then dried with MgSO$_4$. The solvent was concentrated *in vacuo* and the residue was crystallized from EtOH.

4,5-Bis(4-acetyl-2,5-dimethyl-3-thienyl)dioxol-2-one (8a) was prepared in a yield of 0.350 g (90%), m.p. 152—153 °C. Found (%): C, 58.26; H, 4.74; S, 16.78. $C_{19}H_{18}O_5S_2$. Calculated (%): C, 58.44; H, 4.65; S, 16.42. ^{1}H NMR, (CDCl$_3$), δ: 2.08, 2.43, and 2.55 (all s, 6 H each, 2 Me). MS (EI), *m/z* (I_{rel} (%)): 390 [M$^+$] (55).

4,5-Bis(4-acetyl-2,5-dimethyl-3-thienyl)-3-methyloxazol-2(3*H*)-one (8b) was prepared in a yield of 0.227 g (56%), m.p. 142—143 °C. Found (%): C, 59.66; H, 5.17; N, 3.72; S, 15.64. $C_{20}H_{21}NO_4S_2$. Calculated (%): C, 59.53; H, 5.25; N, 3.47; S, 15.89. ^{1}H NMR (DMSO-d$_6$), δ: 1.93, 2.09, 2.31, 2.43, 2.49, 2.62, and 2.87 (all s, 3 H each, Me).

X-ray diffraction study of compound 8b. Colorless single crystals of composition $C_{20}H_{21}NO_4S_2$ were grown from a solution in EtOH. The crystals are triclinic, a = 9.506(2), b = 9.785(2), c = 11.582(2) Å, α = 99.83(3), β = 92.99(3), γ = 112.28(3)°, space group $P\bar{1}$, Z = 2, V = 974.1(3) Å^3, d_{calc} = 1.376 g cm^{-3}, M = 403.50. The unit cell parameters and intensities of 4226 independent reflections were measured on an automated four-circle Enraf—Nonius CAD-4 diffractometer at ~20 °C (graphite monochromator, Mo-Kα radiation, q—5/3q scanning technique). The intensities of reflections were measured in the angle range 1.80° ≤ θ ≤ 26.97°. The calculations were carried out using 3025 reflections with $I > 2\sigma(I)$. The structure was solved by direct methods and the positions of all nonhydrogen atoms were revealed. The structure was refined by the full-matrix least-squares method based on F^2 with anisotropic thermal parameters for the nonhydrogen atoms. The positions of the hydrogen atoms were revealed from difference electron density syntheses and then refined isotropically by the least-squares method. The final reliability factors were as follows: R_1 = 0.037 (wR_2 = 0.105) and R_1 = 0.066 (wR_2 = 0.124) for all reflections. Calculations were carried out with the use of the SHELXTL PLUS 5.10 program package.[14] The atomic coordinates, thermal parameters, and geometric parameters of the molecule were deposited with the Cambridge Structural Database.

References

1. M. M. Krayushkin, V. Z. Shirinyan, L. I. Belen´kii, A. A. Shimkin, A. Yu. Martynkin, and B. M. Uzhinov, *Zh. Org. Khim.*, 2002, **38**, 1391 [*Russ. J. Org. Chem.*, 2002, **38**, No. 8 (Engl. Transl.)].
2. V. Z. Shirinyan, M. M. Krayushkin, L. I. Belen´kii, L. G. Vorontsova, Z. A. Starikova, A. Yu. Martynkin, V. L. Ivanov, and B. M. Uzhinov, *Khim. Geterotsikl. Soedin.*, 2001, 81 [*Chem. Heterocycl. Compd.,* 2001 (Engl. Transl.)].
3. S. N. Ivanov, B. V. Lichitskii, A. A. Dudinov, A. Yu. Martynkin, M. M. Krayushkin, and B. M. Uzhinov, *Khim. Geterotsikl. Soedin.*, 2001, 89 [*Chem. Heterocycl. Compd.,* 2001 (Engl. Transl.)].
4. M. M. Krayushkin, S. N. Ivanov, A. Yu. Martynkin, B. V. Lichitskii, A. A. Dudinov, and B. M. Uzhinov, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 113 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 116].
5. M. M. Krayushkin, S. N. Ivanov, A. Yu. Martynkin, B. V. Lichitskii, A. A. Dudinov, and B. M. Uzhinov, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 2315 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 2424].
6. H. Biltz, *Liebigs Ann. Chem.*, 1905, **339**, 243.
7. J. C. Sheehan and F. S. Guziec, *J. Am. Chem. Soc.,* 1972, **94**, 6561.
8. M. Irie, *Chem. Rev.*, 2000, **100**, 168.
9. M. M. Krayushkin, L. G. Vorontsova, and B. M. Uzhinov, *Intern. J. Photoenergy,* 2001, **3**, 25.
10. N. N. Tsou, R. G. Ball, P. J. Roy, and Y. Leblanc, *Acta Crystallogr., Sect. C (Cryst. Struct. Comm.)*, 1998, **54**, 1493.
11. T. Ishizuka, S. Ishibuchi, and T. Kunieda, *Tetrahedron Lett.*, 1989, **30**, 3449.
12. C. B. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, **A235**, 518.
13. E. W. Wagner and A. W. Adamson, *J. Am. Chem. Soc.*, 1966, **88**, 394.
14. G. M. Sheldrick, *SHELXTL, v. 5.10, Structure Determination Software Suite*, Bruker AXS, Madison, Wisconsin, USA, 1998.

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