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A.I. Kononov on the 70th Anniversary of His Birth

Photochromic Dihetarylethenes: XX.* Synthesis and Photochromic Properties of Dithienylethenes with a Fixed Conformation

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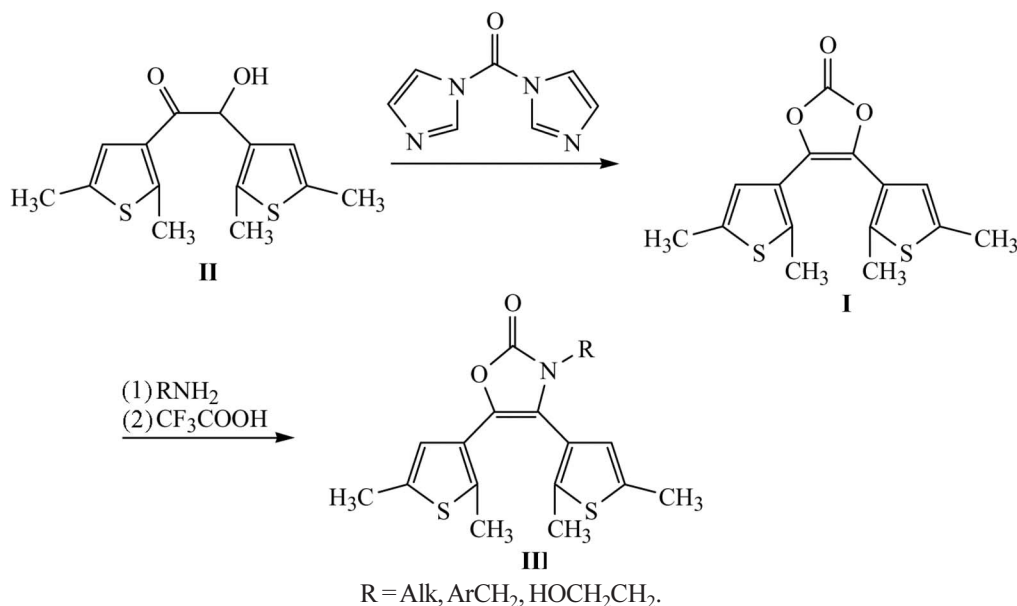
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Abstract—A procedure was developed for the synthesis of bis(2,5-dimethyl-3-thienyl)ethenes with partially fixed molecular conformation, and their photochromic properties in solution were studied. The structure of photochromic 1-(2,5-dimethyl-3-thienyl)-7,9-dimethyl-5,6-dihydrothieno[3',4' : 3,4]pyrido[1,2-c][1,3]oxazol-3-one, as well as of 1-(2,5-dimethyl-3-thienyl)-7,9-dimethylthieno[3',4' : 3,4]pyrido[1,2-c][1,3]oxazol-3-one possessing no photochromic properties, was determined by X-ray analysis.

We previously developed a convenient procedure for the preparation of dithienylethenes **I** containing a 2-oxo-1,3-dioxole-4,5-diyl bridging group by reaction of accessible 1,2-bis(2,5-dimethyl-3-thienyl)-2-hydroxyethanone (**II**) with 1,1'-carbonyldiimidazole [2] (Scheme 1). Compounds **I** are stable in neutral medium, and they attract interest as potential photochromic substances [2]. Dioxol-2-ones **I** can readily be converted into photochromic

oxazol-2-ones **III**, and the substituents R therein may contain various functional groups, which considerably extends the scope of application of these compounds. In the present communication we report on further modification of N-substituted oxazolones **III** via additional linking of the bridging moiety to the neighboring thiophene ring, which should partially fix the conformation of dithienylethenes.

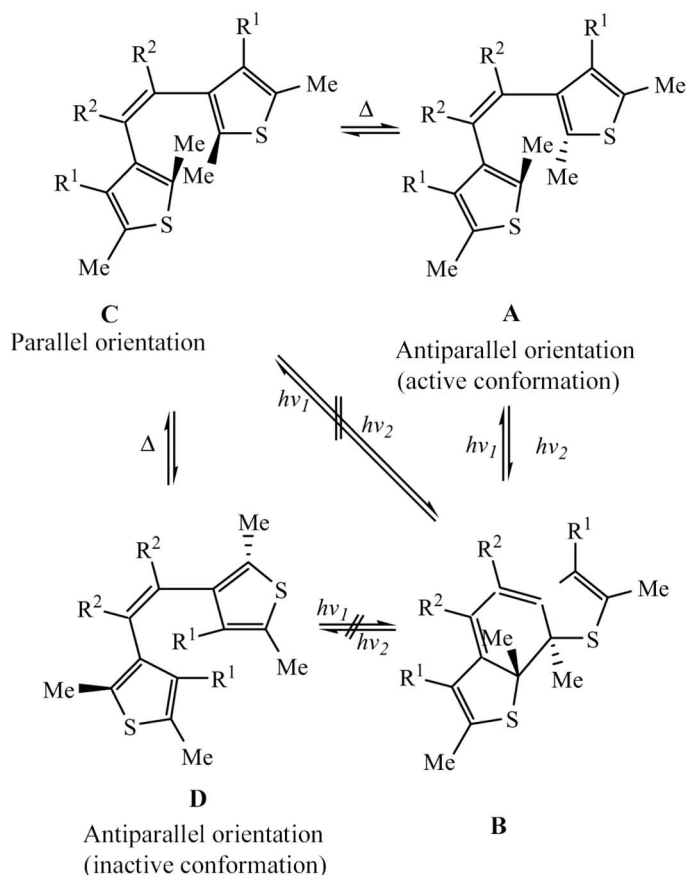
Scheme 1.



* For communication XIX, see [1].

The thiophene rings in 1,2-dithienylethenes are capable of rotating about the alkene–heteroring bond, thus giving rise to three possible conformers (Scheme 2): conformer **A** with antiparallel orientation of the thiophene rings, which is transformed into conformer **B** on irradiation; conformer **C** with parallel orientation of the thiophene rings; and conformer **D** with antiparallel orientation of the thiophene rings in the inactive form, where the distance between the reaction centers ($> 4.0 \text{ \AA}$) considerably exceeds the sum of the corresponding van der Waals radii.

Scheme 2.



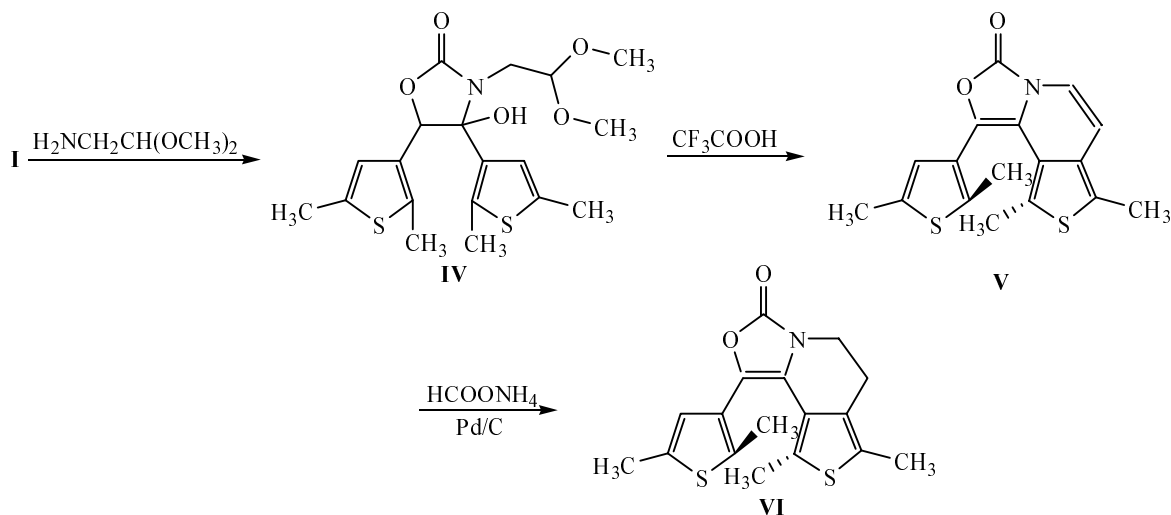
It is known [3] that photochemical cyclization of 1,3,5-hexatriene systems follows a conrotatory mode; photocyclizations of 1,2-dihetarylenes involves only those molecules in which the thiophene rings are antiparallel (active conformation). Therefore, some compounds exhibiting photochromic properties in solution could lack such properties in the solid state [4]. In some cases, the thiophene rings in dithienylethenes turn during crystallization in such a way that the distance between the 2- and 2'-positions in those rings (which are linked together upon irradiation) becomes considerably longer than the corresponding van der Waals contact, which leads to loss of

photochromic properties in crystal. An example is 1,2-bis(2-ethyl-5-ethylsulfanyl-4-methoxycarbonyl-3-thienyl)hexafluorocyclopentene [5] which shows photochemical activity only in solution. According to the X-ray diffraction data, the lack of photochromism in crystal is explained by the fact that molecules of this compound in the crystalline state exist as inactive antiparallel conformers where the distance between the potential reaction centers is 4.45 \AA . Another interesting example is the behavior of 1,2-bis(2,4-dimethyl-3-thienyl)hexafluorocyclopentene [6] which is capable of undergoing photochemical transformation $A \leftrightarrow B$ in a single crystal without breaking of the crystal structure. However, in keeping with the X-ray diffraction data, single crystals of this compound obtained from a solution in methanol consist of molecules in three conformations: photochemically active antiparallel, inactive antiparallel, and inactive parallel at a ratio of 17 : 34 : 49, i.e., only 17% of its molecules exhibit photochemical activity.

Insofar as real optical systems utilize photochromic substances in the solid state, it seemed to be important to design such dithienylethene systems in which the thienyl rings are fixed in the active antiparallel conformation. This problem can be solved in several ways. One of these is based on controlled variation of the conformer ratio via introduction of bulky substituents into the hetaryl fragment [7]. Irie *et al.* [8] succeeded in fixing a parallel conformation of 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentenes having carboxymethyl or carboxyethyl groups in positions 6 and 6' of the benzothiophene rings via hydrogen bonding in a nonpolar solvent, cyclohexane. Dinescu and Wang [9] reported on the synthesis of spiro-fused 1,2-dithienylethenes in which both thiophene rings are fixed.

We have developed an approach according to which the heterocyclic bridging fragment is linked through a chemical bond to one or both thienyl rings. Such bonding should prevent the thienyl ring from turning apart upon crystallization (Scheme 3). We have found that aminoacetaldehyde dimethyl acetal reacts with 1,3-dioxol-2-one **I** to give 4-hydroxy-1,3-oxazolidin-2-one **IV** in high yield. Treatment of the latter with trifluoroacetic acid at room temperature results in dehydration followed by intramolecular cyclization to afford 1-(2,5-dimethyl-3-thienyl)-7,9-dimethylthieno[3',4':3,4]pyrido[1,2-*c*][1,3]-oxazol-3-one (**V**). Compound **V** was hydrogenated over Pd/C in the presence of ammonium formate to obtain 1-(2,5-dimethyl-3-thienyl)-7,9-dimethyl-5,6-dihydro-thieno[3',4':3,4]pyrido[1,2-*c*][1,3]oxazol-3-one (**VI**) in nearly quantitative yield.

Scheme 3.



Study of the optical properties of compounds **V** and **VI** showed the absence of photochromic properties of the former, while compound **VI** exhibited such properties (Scheme 4, Fig. 1).

As seen from Fig. 1, compound **VI** before and after irradiation with UV light ($\lambda = 313 \text{ nm}$) is characterized by absorption maxima at λ 301 and 460 nm, respectively, which usually correspond to the transformation **VIa** \leftrightarrow **VIb** (Scheme 4). With a view to elucidate factors re-

sponsible for the different photochemical activities of compounds **V** and **VI**, their geometric parameters and conformational structure were determined by X-ray analysis. Molecules **V** in crystal exist in two crystallographically independent forms **VA** (Fig. 2) and **VB** which differ only in their conformations. The thiophene fragment $\text{S}^1\text{C}^2\text{C}^3\text{C}^4\text{C}^5$ (**T'**) in conformer **VA** is turned apart relative to the oxazole ring $\text{C}^1\text{O}^2\text{C}^3\text{N}^1\text{C}^9\text{b}$ (**O**) through an angle of 63.10° . Conformer **VB** is characterized by a similar angle between the thiophene (**T'**) and oxazole (**O**) fragments, but they are turned in the opposite direction (the angle is 114.30°). The geometric parameters of conformers **VA** and **VB** are fairly similar: the difference in the respective bond lengths and bond angles does not exceed the experimental error ($\pm 0.005\text{--}0.008 \text{ \AA}$ for

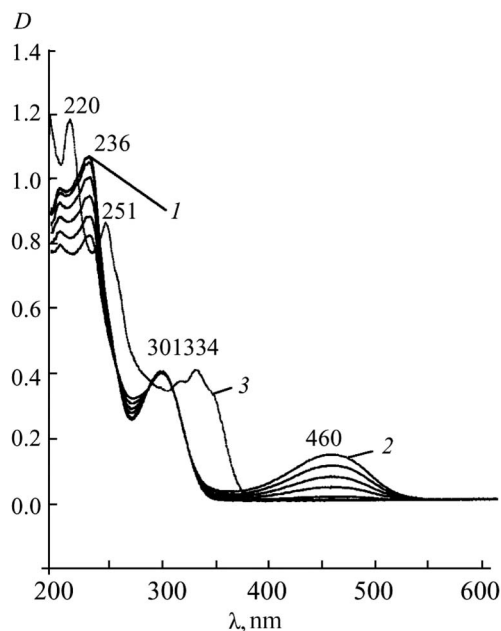
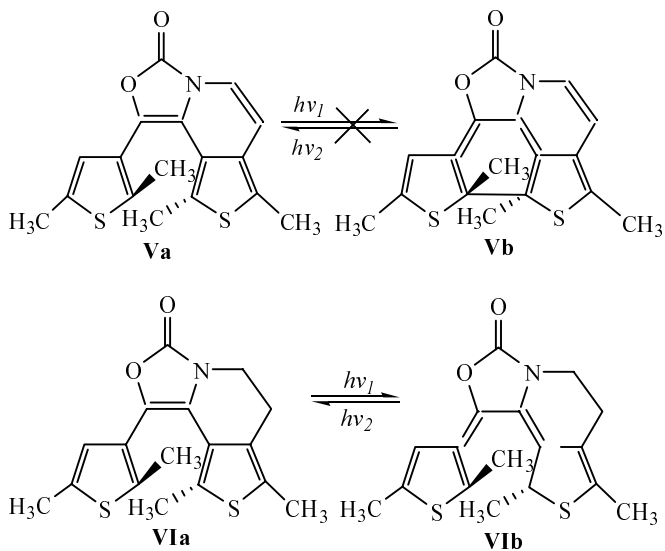


Fig. 1. Variation of the electron absorption spectrum of compound **VI** in acetonitrile upon irradiation at (1) $\lambda = 313 \text{ nm}$ (direct reaction) and (2) $\lambda = 546 \text{ nm}$ (reverse reaction); curve (3) corresponds to the initial absorption spectrum in acetonitrile.

Scheme 4.



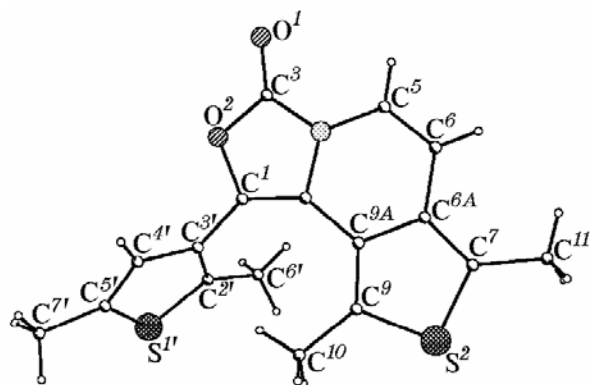


Fig. 2. Structure of molecule VA according to the X-ray diffraction data.

bond lengths); therefore, we further used their average values. A specific feature of the structure of molecules **V** is the presence of a planar tricyclic fragment consisting of the oxazole (**O**), pyridine ($N^1C^5C^6C^{6a}C^{9a}C^{9b}$, **P**), and thiophene rings ($S^2C^7C^{6a}C^{9a}C^9$, **T**). Deviations of atoms from the mean-square plane do not exceed ± 0.08 Å. A new conjugated π -bond system can be formed in this fragment. In fact, electron density redistribution over the $N^1-C^5-C^6-C^{6a}-C^7$ bond sequence is observed: The N^1-C^5 bond (1.394 E) is considerably shorter than the corresponding bond in photochromic 4,5-bis(4-acetyl-2,5-dimethyl-3-thienyl)-3-methyloxazol-2(3*H*)-one (1.451 E) which was examined previously [2]. According to the Cambridge Structural Database (CCDC) [10], in all molecules having an N-substituted oxazolone ring (total of 5 structures [11–15]), the corresponding bond is also longer (1.427–1.475 E) than in **V**. By contrast, the C^5-C^4 bond (1.346 E) in the thiophene ring (**T'**) is appreciably shorter than the $C^{6a}-C^7$ bond (1.369 E) in ring **T**. Delocalization of electron density in molecule **V** is also confirmed by a considerable red shift (by 47 nm) of the long-wave absorption band, as compared to *N*-

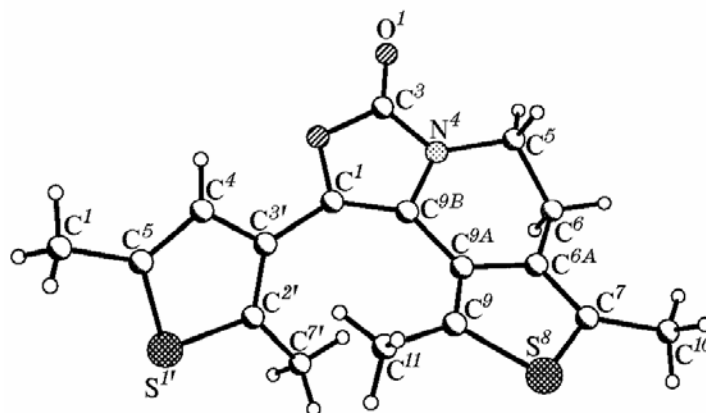


Fig. 3. Structure of molecule VI according to the X-ray diffraction data.

methyloxazolone [2]. The angle between the planar molecular fragments is 64.15° . The intramolecular contact $C^{2'} \dots C^9$ is 3.84 Å. Unlike compound **V**, the fused tricyclic system in molecule **VI** (Fig. 3) is not planar: the nitrogen-containing six-membered ring **P** ($N^4C^5C^6C^{6a}C^{9a}C^{9b}$) adopts a twisted *sofa* conformation in which the C^{9a} and C^6 atoms deviate by 0.267 and -0.581 E, respectively, from the plane formed by the remaining four atoms. Furthermore, the respective bond lengths in rings **T** ($S^8C^7C^{6a}C^{9a}C^9$) and **T'** ($S^1C^2C^3C^4C^5$) are almost equal, and they correspond to the standard values; in other words, the geometric parameters of molecule **VI** suggest the absence of conjugation. The molecule exists in an anti-parallel photochemically active conformation typical of most photochromic 1,2-dithienylethenes. The dihedral angles between the oxazole and fused and nonfused thiophene rings are 18.8 and 53.3° , respectively. The intramolecular $C^{2'} \dots C^9$ contact is 3.83 Å.

The different photochromic properties of structurally similar compounds **V** and **VI** may be rationalized as follows. In keeping with the theoretical concept (see above), the ring closure to isomer **B** is a conrotatory process which involves synchronous rotation of the thiophene fragments with respect to the oxazole ring. Obviously, the conformer with symmetric arrangement of the thiophene fragments relative to the oxazole ring should be most favorable for such a process to occur. Table 1 contains the dihedral angles between the planar fragments in molecules **V** and **VI**. It is seen that molecule **V** is characterized by pronounced asymmetric orientation of the heterorings: the difference in the angles of rotation ($\Delta\varphi$) of the thiophene fragments (**T** and **T'**) with respect to the oxazole ring is 54.45° . Moreover, this asymmetry is fixed due to the presence of a planar hetaryl fragment (stabilized by π -conjugation) and conformationally rigid tricy-

Table 1. Dihedral angles (deg) in molecules **V** and **VI**

Dihedral angle	V	VI
O/P	4.7	–
O/T	9.75	18.84
O/T'	64.2	53.32
P/T	6.7	–
P/T'	62.03	–
T/T'	66.31	60.68

clic skeleton; therefore, there are conditions for synchronous rotation of the thiophene rings. As a result, only stable isomer **A** is formed. The $\Delta\phi$ value for molecule **VI** is considerably smaller (34.4°), and the bridging moiety therein is a mobile ethylene unit which allows the thiophene rings to turn apart with respect to each other.

It should be noted that molecule **V** is characterized by the largest $\Delta\phi$ value among compounds having an oxazolone bridging group: the corresponding value for 4,5-bis(4-acetyl-2,5-dimethyl-3-thienyl)-3-methyloxazol-2(3*H*)-one [2] is 12.53° , while it does not exceed $2\text{--}3^\circ$ for molecules of photochromic compounds with a perfluorocyclopentene bridge. All these compounds give rise to the photochemical transformation $\mathbf{A} \leftrightarrow \mathbf{B}$.

EXPERIMENTAL

The ^1H NMR spectra were recorded on Bruker AM-300 (300.13 MHz) and Bruker WM-250 (250.13 MHz) instruments from solutions in DMSO- d_6 and CDCl_3 . The melting points were determined on a Boetius device and were not corrected. The mass spectra (70 eV) were run on a Kratos MS-30 mass spectrometer with direct sample admission into the ion source. The progress of reactions and the purity of products were monitored by TLC on Silica gel 60 F₂₅₄ plates (Merck) using ethyl acetate–hexane as eluent. Photochromic properties of compounds **V** and **VI** were examined in acetonitrile of ultrapure grade. Cyclic forms **B** were generated by irradiation with a DRSh-500 mercury lamp using light filters to isolate lines with $\lambda = 313, 546, \text{ and } 578 \text{ nm}$. Structures **B** were identified by the electron absorption maxima. The radiation intensity was determined with the aid of an F4 cell calibrated against a ferrioxalate actinometer [16] for $\lambda = 313 \text{ nm}$ and Reineke salt actinometer [17] for $\lambda = 546 \text{ and } 578 \text{ nm}$. The electron absorption spectra were measured on a Shimadzu UV-3100 spectrophotometer.

X-Ray analysis of 1-(2,5-dimethyl-3-thienyl)-7,9-dimethylthieno[3',4':3,4]pyrido[1,2-c][1,3]oxazol-3-one (V) and 1-(2,5-dimethyl-3-thienyl)-7,9-dimethyl-5,6-dihydrothieno[3',4':3,4]pyrido[1,2-c][1,3]-oxazol-3-one (VI). Light yellow single crystals of compound **V** were obtained from a MeOH–MeNH₂ mixture. Single crystals of **VI** (colorless semitransparent bipyramids) were obtained from a solution in ethanol. The principal crystallographic parameters and the results of least-squares refinement are collected in Table 2. The structures were solved by the direct method which revealed all non-hydrogen atoms and were refined by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms. The hydrogen atoms

Table 2. Principal crystallographic parameters of compounds **V** and **VI** and the results of least-squares refinement

Parameter	V	VI
Formula	C ₁₇ H ₁₅ NO ₂ S ₂	C ₁₇ H ₁₇ NO ₂ S ₂
Diffractometer	Bruker SMART-1000	CAD-4 Enraf-Nonius
Irradiation	MoK _α	MoK _α
<i>a</i> , Å	14.047(8)	9.060(2)
<i>b</i> , Å	10.920(7)	9.455(2)
<i>c</i> , Å	20.040(12)	10/234(2)
α , deg	90.00	78.08(3)
β , deg	93.415(15)	84.13(3)
γ , deg	90.00	69/41(3)
<i>V</i> , Å ³	3069(3)	802.6(3)
<i>M</i>	329.44	501.57
Space group	P2/c	P-1
<i>Z</i>	8	2
<i>d</i> _{calc.} g/cm ⁻³	1.426	1.372
Scanning mode	ϕ - ω	q -5/3 q
Scan range:		
θ_{min} , deg	1.45	2.03
θ_{max} , deg	30.23	27.97
Number of independent reflections	8998	3842
Number of reflections with $I \geq 2\sigma(I)$	3805	3026
$R_1(F)$ for reflections with $I \geq 2\sigma(I)$	0.061	0.040
$wR_2(F)$ for reflections with $I \geq 2\sigma(I)$	0.147	0.120
$R_1(F)$ for all reflections	0.176	0.137
$wR_2(F)$ for all reflections	0.176	0.137

were visualized by the difference synthesis of electron density, and their positions were refined by the least-squares procedure in isotropic approximation. The calculations were performed with the aid of SHELXL-97, Bruker SHELXTL, and SHELXTL PLUS-5 software [18]. The coordinates of atoms and their temperature factors were deposited to CCDC.

4-Hydroxy-3-(2,2-dimethoxyethyl)-4,5-bis(2,5-dimethyl-3-thienyl)-1,3-oxazolidin-2-one (IV). 2,2-Dimethoxyethylamine, 0.199 g (1.5 mmol), was added to a solution of 0.306 g (1 mmol) of dioxol-2-one **I** [2] in 3 ml of ethanol, and the mixture was stirred for 1–1.5 h at

~25°C. The precipitate was filtered off and recrystallized from ethanol. Yield 0.383 g (93%), mp 211–213°C. ¹H NMR spectrum (DMSO-*d*₆), δ, ppm: 1.82 s (3H, CH₃), 2.21 s (3H, CH₃), 2.38 s (3H, CH₃), 2.40 s (3H, CH₃), 3.17 m (2H, CH₂), 3.25 s (6H, OCH₃), 4.42 t (1H, CH, *J* = 8.0 Hz), 5.45 s (1H, OH), 6.45 s (1H, CH), 6.73 s (1H, thienyl), 6.79 s (1H, thienyl). Found, %: C 55.37; H 6.19; N 3.62; S 15.77. C₁₉H₂₅NO₅S₂. Calculated, %: C 55.45; H 6.12; N 3.40; S 15.58.

1-(2,5-Dimethyl-3-thienyl)-7,9-dimethylthieno-[3',4':3,4]pyrido[1,2-*c*][1,3]oxazol-3-one (V).

A solution of 0.411 g (1 mmol) of oxazolidin-2-one IV in 5 ml of trifluoroacetic acid was stirred for 1 h at room temperature and was then evaporated. The residue was recrystallized from ethanol to obtain 0.280 g (85%) of compound V with mp 185–186°C. ¹H NMR spectrum (CDCl₃), δ, ppm: 1.93 s (3H, CH₃), 2.28 s (3H, CH₃), 2.43 s (3H, CH₃), 2.48 s (3H, CH₃), 6.22 d (1H, H_{arom}, *J* = 7.0 Hz), 6.75 s (1H, thienyl), 7.03 d (1H, H_{arom}, *J* = 7.0 Hz). Mass spectrum (EI), *m/z* (*I*_{rel}, %): [*M*]⁺ 329 (30). Found, %: C 62.11; H 4.65; N 4.98; S 19.71. C₁₇H₁₅NO₂S₂. Calculated, %: C 61.98; H 4.59; N 5.25; S 19.47.

1-(2,5-Dimethyl-3-thienyl)-7,9-dimethyl-5,6-dihydrothieno[3',4':3,4]pyrido[1,2-*c*][1,3]oxazol-3-one (VI).

Ammonium formate, 4.0 g (63.5 mmol), was added with stirring to a mixture of 0.1 g (0.30 mmol) of compound V and 500 g of 10% Pd/C (Merck) in 50 ml of ethyl acetate. The mixture was stirred for 8 h at room temperature and filtered, the filtrate was evaporated, and the residue was recrystallized from methanol. Yield 0.75 g (75%), mp 160–161°C. ¹H NMR spectrum (CDCl₃), δ, ppm: 1.85 s (3H, CH₃), 2.17 s (3H, CH₃), 2.36 s (3H, CH₃), 2.42 s (3H, CH₃), 2.85 t (2H, CH₂, *J* = 11.0 Hz), 3.76 t (2H, CH₂, *J* = 11.0 Hz), 6.68 s (1H, thienyl). Mass spectrum (EI), *m/z* (*I*_{rel}, %): [*M*]⁺ 331 (100). Found, %: C 61.48; H 5.25; N 3.97; S 19.68. C₁₇H₁₇NO₂S₂. Calculated, %: S 61.60; H 5.17; N 4.23; S 19.35.

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