THEORETICAL ASPECTS

OF THE ACETONITRILE OXIDE

CYCLOADDITION TO *tert*-BUTYL-,

TRIMETHYLSILYL-, AND TRIMETHYLGERMYL-

SUBSTITUTED THIOPHENE 1,1-DIOXIDES

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The results of X-ray diffraction studies on molecular packing of tert-butyl-, trimethylsilyl-, and trimethylgermylthiophene 1,1-dioxides have been reviewed and analyzed. We also interpret their experimental and calculated UV spectra. Using quantum-chemical calculations, we have studied the theoretical aspects of the acetonitrile oxide dipolar [2+3] cycloaddition to 2,5- and 2,4-disubstituted sulfones. The reasons for the regiospecificity of cycloaddition and desilylation have been explained.

Keywords: thiophene, thiophene 1,1-dioxide, quantum-chemical calculation, molecular packing, UV spectrum.

Unsubstituted thiophene 1,1-dioxide [1, 2], its monosubstituted [3] and more highly substituted derivatives [4] are very interesting synthons for obtaining various types of organic compounds. The significant interest in thiophene 1,1-dioxides, acting as unsaturated cyclic sulfones, is due to their high reactivity in various chemical processes.

Introduction of silyl groups into the thiophene ring significantly increases the activity of the sulfur atom to oxidation. Furthermore, the high lability of the silyl substituents with respect to electrophilic and nucleophilic reagents results in a convenient method for further functionalization of the reaction products. Some chemical transformations of silyl-substituted thiophene 1,1-dioxides have been studied in recent years.
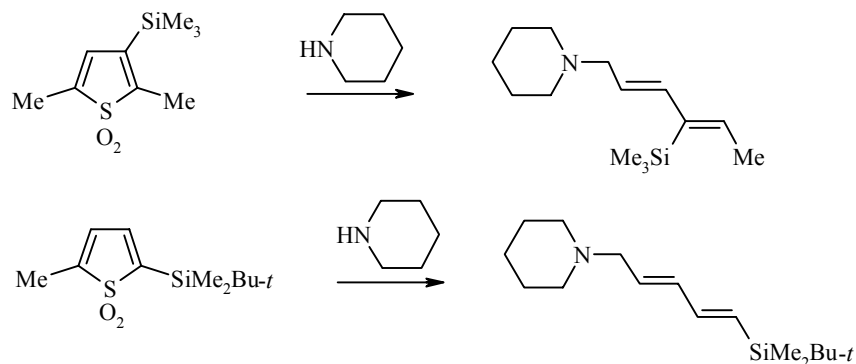
Opening of the thiophene 1,1-dioxide ring on treatment with piperidine is a reaction occurring with degradation of the heterocycle. This process is characterized by high regioselectivity and stereospecificity [5].
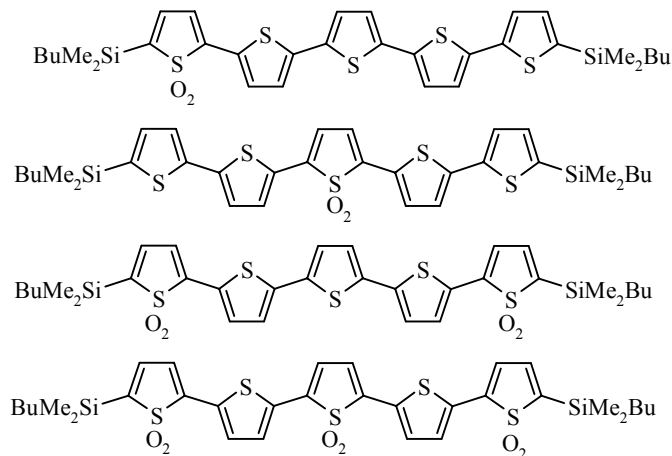
2,5-Bis(trimethylsilyl)thiophene 1,1-dioxide (**2**) and its 2,4-isomer (**7**) enter into a Diels–Alder reaction with N-phenylmaleimide in boiling toluene to form cycloadducts. The intermediate sulfone could not be isolated due to elimination of the sulfur dioxide at room temperature. The analogous reaction proceeds in DMF with aromatization and formation of phthalimide derivatives [6].

**2** R = Me$_3$Si, R' = H; **7** R = H, R' = Me$_3$Si
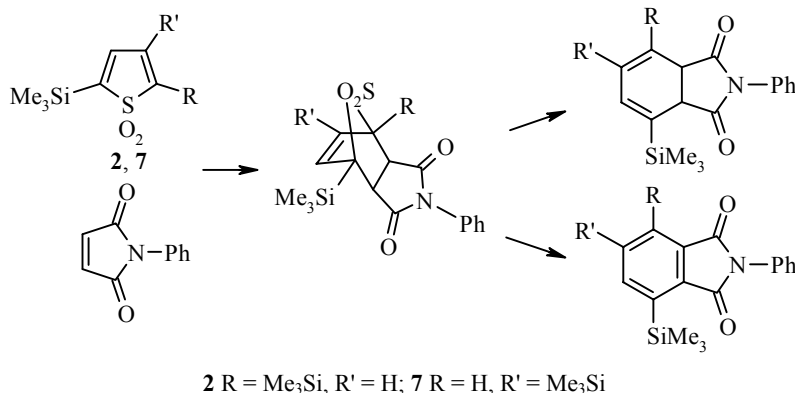
The silyl groups of 2,5-bis(trimethylsilyl)thiophene 1,1-dioxide can be easily substituted by halogen atoms when the sulfone is treated with bromine or iodine in methylene chloride in the presence of AgBF$_4$ at 0°C [7].

X = Br, I
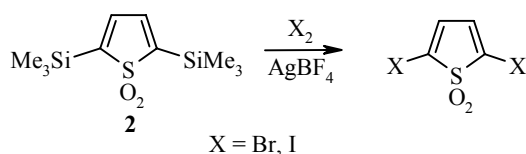
In turn, the bromo-substituted thiophene 1,1-dioxides enter into a coupling reaction with thienylstannanes in the presence of palladium catalysts [(Ph$_3$P)$_4$Pd and (Ph$_3$As)$_4$Pd] to form oligothiophene 1,1-dioxides. This method makes it possible to easily and selectively introduce the thiophene 1,1-dioxide moiety into ter-, quater-, and quinquethiophene chains [8]. For example, this method was used to obtain quinquethiophenes with terminal and central sulfone groups, and also a pentamer with alternating aromatic and diene moieties. Dearomatization significantly increases electronic delocalization and makes it possible to tune the reduction potentials of these materials as a function of the number and position of the thiophene 1,1-dioxide groups [9, 10].

We have established that *tert*-butyl-, trimethylsilyl-, and trimethylgermyl-substituted thiophene 1,1-dioxides are convenient model compounds to study the effect of the nature of the Me₃M substituents (M = C, Si, Ge) on the reactivity of C=C double bonds [11-13]. The direction of nucleophilic addition of piperidine to sulfones in organic solvents is determined by the nature of the substituent. 2,5-Bis(*tert*-butyl)thiophene 1,1-dioxide (**1**) does not react with piperidine; the addition of one piperidine molecule to symmetric silyl- (**2**) and germylsulfones (**3**) in THF and benzene leads to the corresponding 2,3-dihydrothiophene 1,1-dioxides; and in the case of the silyl derivative, during storage we observe desilylation of the trimethylsilyl group on the sp^3-carbon atom of the heterocycle. In the case of the asymmetric 2-trimethylgermyl-5-trimethylsilylthiophene 1,1-dioxide (**6**), the reaction proceeds regioselectively; only the vinylsilyl moiety adds the amine molecule. Subsequent desilylation occurs during chromatographic purification, leading to 3-piperidino-5-trimethylgermyl-2,3-dihydrothiophene 1,1-dioxide, the structure of which has been confirmed by X-ray diffraction [11].
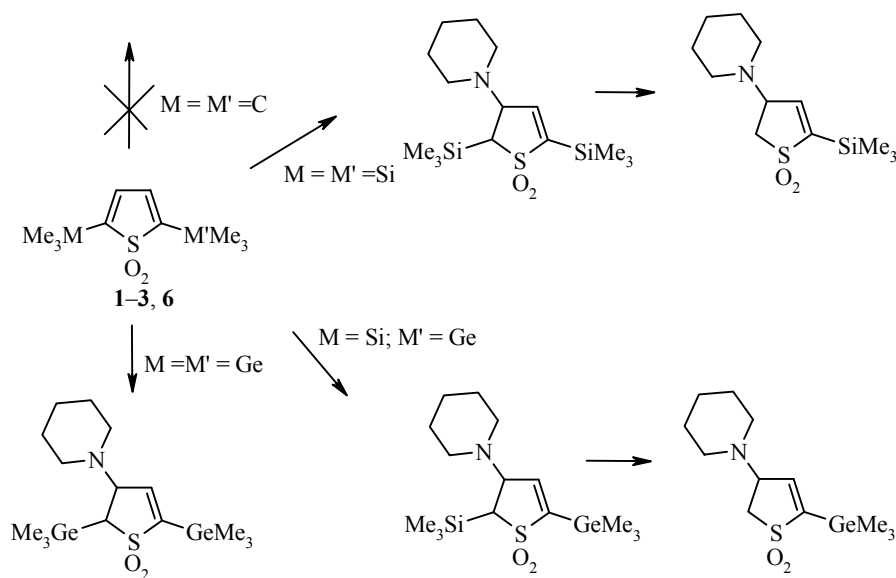
We studied the effect of oxidation of the sulfur atom in thiophenes on the absorption band in the UV spectra. The λ_{max} for 2,5- and 2,4-disubstituted thiophenes is located in the 252-260 nm and 246-250 nm ranges respectively. An interesting feature of the spectra of sulfones **1-10** is that oxidation leads to a 42-59 nm bathochromic shift (rather than a hypsochromic shift) of the absorption band compared with the starting thiophenes. The absorption spectra of 2,5-disubstituted sulfones **1-6** are characterized by two maxima: a strong long-wavelength band partially overlaps a considerably more intense absorption band, shifted by 72-84 nm toward shorter wavelengths. In the spectra of 2,4-disubstituted thiophene 1,1-dioxides **7-10**, there is only one maximum in the 292-305 nm region (Table 1).

With the objective of interpreting the UV spectra of sulfones **1-10** and the corresponding thiophenes, we carried out quantum-chemical calculations for their molecules in the ground and excited states. The ionization potentials, found by Koopmans' theorem [15], and also the bond orders of the C–C bonds in the heterocycle for the ground state and the first excited state are shown in Table 2 for the molecules of the studied sulfones and thiophenes. The HOMO and LUMO configurations for these molecules are illustrated schematically in Fig. 1.

For both thiophenes and sulfones, the first intense electronic transition $S_0 \rightarrow S_1$ is of the $\pi \rightarrow \pi^*$ type. As already noted, the double bonds in the heterocycle of the sulfones are practically isolated; this is also indicated by the bond orders in the electronic ground state (see Table 2). The first excited state of the sulfone molecules is characterized by leveling off of the bond orders of the C–C bonds in the heterocycle, which leads to lowering of the energy of the state and consequently to lowering of the electronic transition energy.
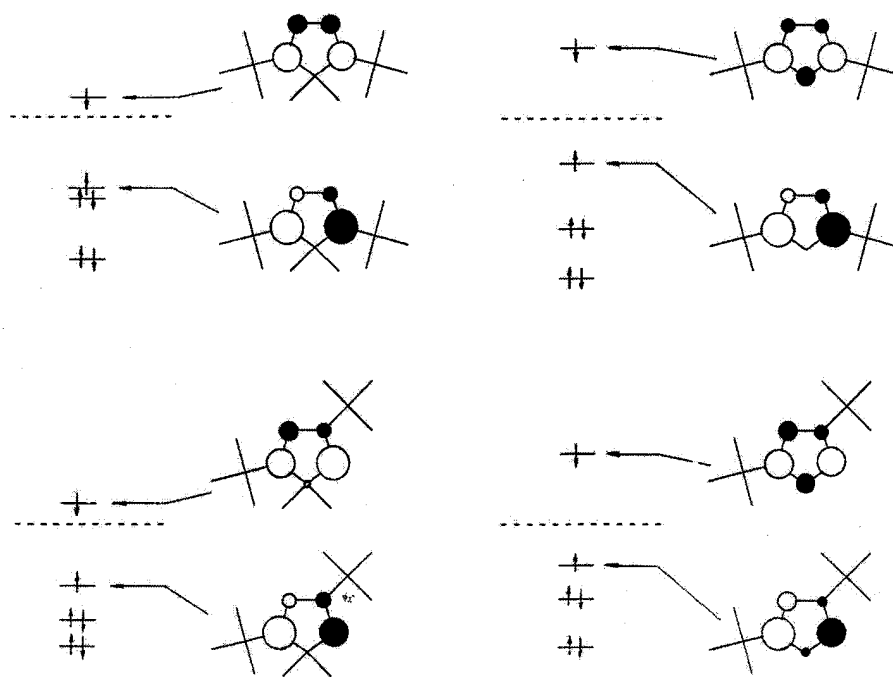
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Fig. 1. Configurations of the first excited electronic states S_1 of sulfones **1-10**
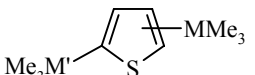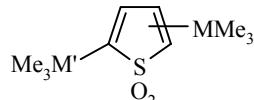and the corresponding thiophenes.

Accordingly, for compounds **1-10**, the absorption band in the electronic spectrum is shifted toward longer wavelength. In Table 1, along with the experimental values of ΔE, we give the calculated values of the "vertical" (Franck–Condon) electronic transitions in the dipole approximation.

Considering the approximate character of the theoretical calculations and also the fact that the spectra were recorded for ethanol solutions and the calculations were performed for isolated molecules, the agreement between the experimental and theoretical values can be considered quite satisfactory.

In the ground state of the molecules of sulfones **1-10**, close to the HOMO energy there is one more occupied MO of the b_2 or a' type. This orbital is more than 60% localized on the oxygen atoms. Thus the highest occupied electron energy level of molecules **1-10** is practically degenerate. This leads to the appearance of one more absorption maximum in the long-wavelength region of the spectrum. The calculated values of the energies for singlet–singlet transitions in sulfones **1-6** are in the range 4.67-4.79 eV. And although such an electronic transition is symmetry-forbidden, it is spin-allowed; on the other hand, the absorption bands for such transitions are significantly less intense that we see in the spectra of compounds **1-6**. For sulfones **7-10**, these transitions lie in the energy range 4.92-5.03 eV, i.e., the corresponding absorption bands are in the shorter-wavelength region, and so were not recorded in the long-wavelength part of the spectrum.
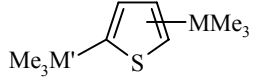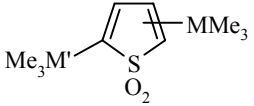
According to X-ray diffraction data [13-15], the 5-membered heterocycle of sulfones **2-4, 6, 7-10** is planar and the oxygen atoms of the SO_2 moiety are located on different sides of this plane, at approximately identical distances from it. Due to loss of aromaticity as a result of oxidation of the sulfur atom, the moiety C=C–C=C in the thiophene 1,1-dioxide ring is a typical *cis*-butadiene system with two practically isolated double bonds. The nature of the substituents and their position in the heterocycle have the most important effect on packing of molecules in the crystal. The crystals of 2,5-bis(trimethylsilyl)- (**2**), 2-trimethylgermyl-5-trimethylsilyl- (**6**), and 2,5-bis(trimethylgermyl)thiophene 1,1-dioxide (**3**) are isomorphic (rhombic syngony) [13,14]. Two crystallographically independent molecules of these compounds lie in mutually perpendicular m mirror planes (Fig. 2). 2,5-Bis(trimethylsilyl)thiophene 1,1-dioxide has high emission efficiency (30%) for blue

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TABLE 1. UV Spectra of Thiophenes and Corresponding Thiophene 1,1-Dioxides **1-10** (Positions of Long-wavelength Absorption Bands in Ethyl Alcohol and the Corresponding Electronic Transition Energies)

Me_3M	Me_3M'	Me_3M'—S—MMe_3 (thiophene)		compound	Me_3M'—SO_2—MMe_3 (dioxide)	
		λ_{max}, nm	ΔE, eV *		λ_{max}, nm	ΔE, eV*
5-Me_3C	Me_3C	252	4.92 (4.63)	**1**	222, 294	5.58 (4.70), 4.42 (4.31)
5-Me_3Si	Me_3Si	256	4.84 (4.72)	**2**	228, 312	5.44 (4.73), 3.97 (4.16)
5-Me_3Ge	Me_3Ge	255	4.86 (4.88)	**3**	228, 312	5.44 (4.76), 3.97 (4.22)
5-Me_3C	Me_3Si	254	4.88 (4.70)	**4**	222, 304	5.58 (4.67), 4.08 (4.10)
5-Me_3C	Me_3Ge	260	4.77 (4.77)	**5**	222, 307	5.58 (4.69), 4.04 (4.11)
5-Me_3Si	Me_3Ge	260	4.77 (4.81)	**6**	228, 312	5.44 (4.79), 3.97 (4.15)
4-Me_3Si	Me_3Si	246	5.04 (5.08)	**7**	305	4.07 (4.19)
4-Me_3Si	Me_3Ge	248	5.00 (5.11)	**8**	292	4.25 (4.28)
4-Me_3Ge	Me_3Si	248	5.00 (5.09)	**9**	292	4.25 (4.19)
4-Me_3Ge	Me_3Ge	250	4.96 (5.12)	**10**	304	4.08 (4.21)

* The calculated values are given in parentheses.

TABLE 2. First Ionization Potentials and Bond Orders of the C–C Bonds in Heterocycles of Thiophene 1,1-Dioxides **1-10** and the Corresponding Thiophenes

$I_{(1)}$, eV	Me$_3$M'—thiophene—MMe$_3$ bond orders *			Compound	$I_{(1)}$, eV	Me$_3$M'—thiophene(O$_2$)—MMe$_3$ bond orders *		
	$C_{(2)}$–$C_{(3)}$	$C_{(3)}$–$C_{(4)}$	$C_{(4)}$–$C_{(5)}$			$C_{(2)}$–$C_{(3)}$	$C_{(3)}$–$C_{(4)}$	$C_{(4)}$–$C_{(5)}$
9.20	1.680 (1.118)	1.173 (1.593)	1.680 (1.118)	**1**	10.55	1.865 (1.240)	1.030 (1.404)	1.865 (1.240)
9.50	1.682 (1.127)	1.179 (1.593)	1.682 (1.127)	**2**	10.84	1.896 (1.205)	1.012 (1.433)	1.896 (1.205)
9.47	1.686 (1.208)	1.176 (1.423)	1.686 (1.208)	**3**	10.83	1.900 (1.205)	1.009 (1.430)	1.900 (1.205)
9.35	1.685 (1.130)	1.178 (1.595)	1.672 (1.115)	**4**	10.71	1.872 (1.237)	1.022 (1.442)	1.884 (1.152)
9.33	1.688 (1.140)	1.176 (1.592)	1.674 (1.107)	**5**	10.71	1.873 (1.243)	1.019 (1.440)	1.890 (1.148)
9.48	1.686 (1.089)	1.175 (1.579)	1.685 (1.182)	**6**	10.83	1.894 (1.186)	1.011 (1.431)	1.899 (1.222)
9.51	1.696 (1.064)	1.171 (1.544)	1.684 (1.233)	**7**	10.84	1.892 (1.196)	1.012 (1.423)	1.913 (1.219)
9.48	1.698 (1.070)	1.169 (1.545)	1.686 (1.225)	**8**	10.84	1.895 (1.203)	1.011 (1.421)	1.913 (1.212)
9.48	1.697 (1.062)	1.169 (1.540)	1.688 (1.242)	**9**	10.80	1.893 (1.184)	1.011 (1.420)	1.917 (1.234)
9.46	1.698 (1.061)	1.168 (1.537)	1.689 (1.245)	**10**	10.79	1.894 (1.193)	1.013 (1.423)	1.914 (1.222)

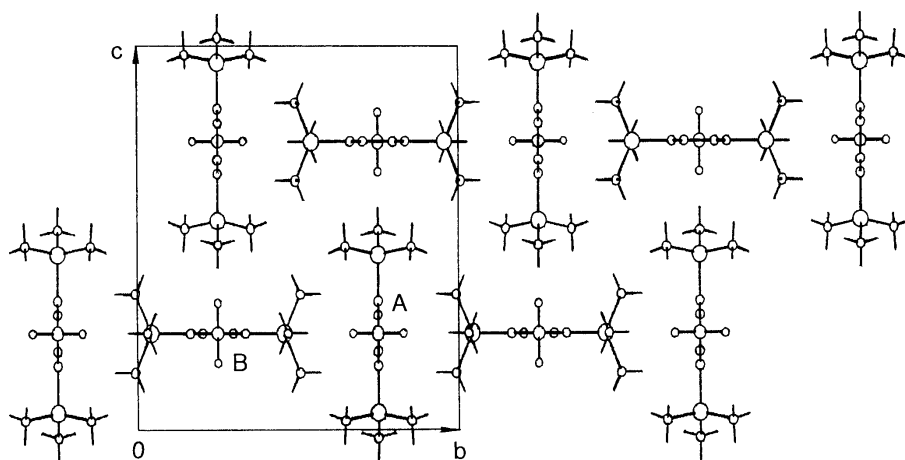* The values of the bond orders in the first excited state are given in parentheses.

Fig. 2. Molecular Packing of thiophene 1,1-dioxides **2, 3, 6**.

fluorescence (λ_{PL} = 381 nm). The emission lifetime is appreciably lengthened (by more than 10 ns). Analogous properties are also exhibited by 2,5-bis(trimethylgermyl)thiophene 1,1-dioxide [14]. This packing promotes exciton–phonon coupling in the crystal lattice, which should be responsible for fluorescence of compounds **2, 3**, and 2-trimethylgermyl-5-trimethylsilylthiophene 1,1-dioxide **6**.

Replacement of one trimethylsilyl group in sulfone **2** by a *tert*-butyl group leads to a change in the type of crystal lattice (Fig. 3). Crystals of 2-*tert*-butyl-5-trimethylsilylthiophene 1,1-dioxide **4** are monoclinic [15]. The molecules of 2,5-disubstituted sulfones **2-4, 6** are located in special positions, while in 2,4-disubstituted derivatives **7-10** they are located in a general position (Fig. 4) [16].
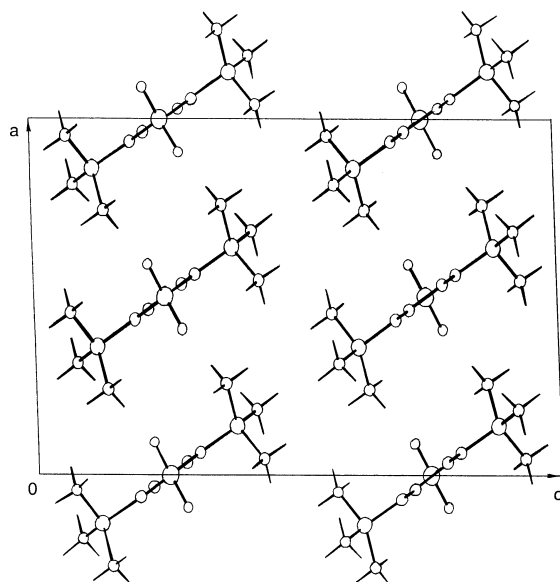

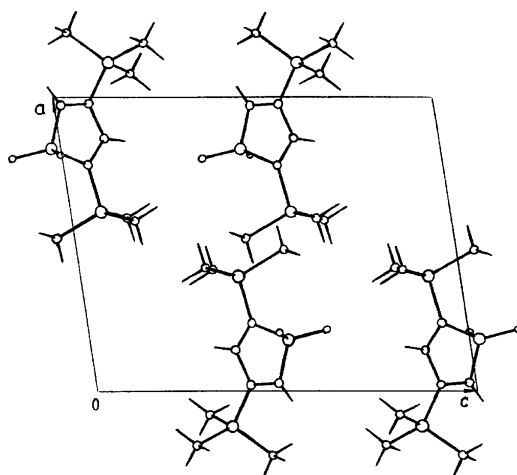Fig. 3. Molecular packing of thiophene 1,1-dioxide **4**.

Fig. 4. Molecular packing of thiophene 1,1-dioxides **7-10**.

The presence of practically isolated double bonds in molecules **1-10** favors cycloaddition reactions. In the case of [2+3]-dipolar addition of acetonitrile oxide to symmetric 2,5-disubstituted thiophene 1,1-dioxides **1-3** (M = M' = C, Si, Ge), two regioisomeric products can form. In the reactions of asymmetric 2,5- and 2,4-disubstituted sulfones **4-10**, the number of possible isomers increases up to four (if we do not consider the demetalation products). The structure of the products is determined on the one hand by which of the two double bonds is the site of cycloaddition, and on the other hand by how the acetonitrile oxide is oriented relative to the sulfone molecule. The results of experimental studies [15, 16] showed that cycloaddition of acetonitrile oxide to thiophene 1,1-dioxides **2-10** occurs regioselectively, with formation of only one addition product. In reactions of asymmetric sulfones **5** (M = C, M' = Ge) and **6** (M = Si, M' = Ge) with acetonitrile oxide, the **A** isomer is the sole product, which suggests higher reactivity of the trimethylgermylvinyl moiety compared with the *tert*-butylvinyl and trimethylsilylvinyl moieties. In the case of 2-*tert*-butyl-5-trimethylsilylthiophene 1,1-dioxide **4**, MeCNO is added at the vinylsilyl part of the molecule, but instead of the **4A** isomer we observed the formation of its desilylation product. These data, along with unsuccessful attempts to add acetonitrile oxide to thiophene 1,1-dioxide **1** (M = M' = C), suggest deactivation of the vinyl bond by the *tert*-butyl group in dipolar addition reactions.
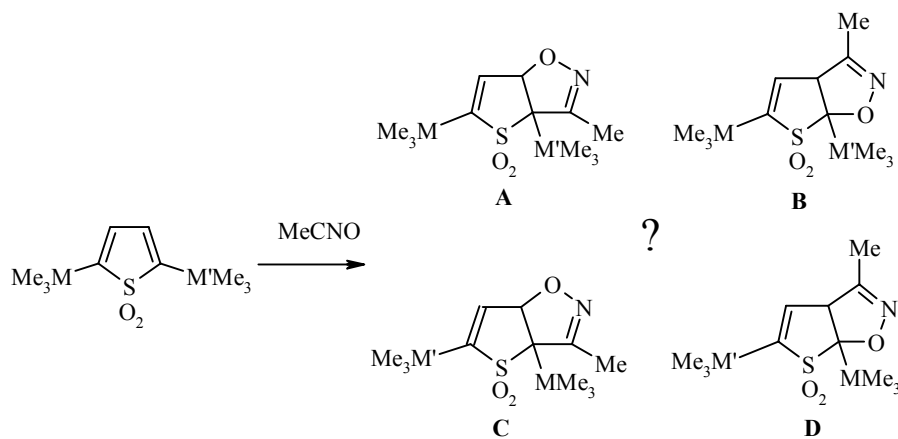
4 M = C, M' = Si; **5** M = C, M' = Ge; **6** M = Si, M' = Ge

Addition to all 2,4-disubstituted sulfones **7-10** occurs at the $C_{(4)}=C_{(5)}$ double bond, and as a result the regioisomer **A** is formed and demetalation was not observed in any case.

7 M = M' = Si; **8** M = Si, M' = Ge; **9** M = Ge, M' = Si; **10** M = M' = Ge
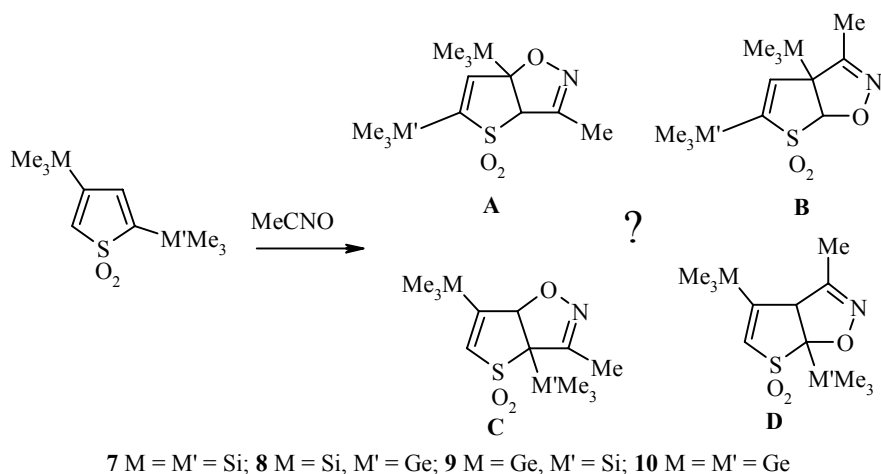
To determine the reasons for the high regioselectivity, we conducted a quantum-chemical study of the acetonitrile oxide cycloaddition to sulfones **1-10**. Table 3 shows the calculated heats of formation for all possible regioisomeric products (**A-D**).

Analysis of the calculated data showed that in only one case (compound **8A**, M = Si, M' = Ge) the minimum heat of formation correspond to the product **A** obtained. Thus if we neglect the entropy contribution, then for all sulfones (except for **8**), in the reaction with acetonitrile oxide the preferred product is the **B** isomer. Consequently, the thermodynamic factor is not the determining factor for the direction of the reaction.

Qualitatively, the kinetics of the cycloaddition process can be conveniently considered from the standpoint of quantum-chemical perturbation theory for the molecular orbitals [17]. Fig. 5 shows the configuration diagram for the frontier orbitals of acetonitrile oxide and the position of their energy levels. Table 4 gives the coefficients c_i for the basis p_z-orbitals for the HOMO and LUMO, and also the effective charges on the C atoms in the molecules of sulfones **1-10**. As has already been noted, the excited state of molecules **1-10** is characterizes by a decrease in energy, i.e., the levels of the unoccupied orbitals are lower; at the same time, the ionization potentials for **1-10** (see Table 2) and acetonitrile oxide are close (10.11 eV). Accordingly, interaction between the HOMO of acetonitrile oxide and the LUMO of sulfones **1-10** is preferred. Furthermore, coefficients c_i for expansion of the LUMO in AO's have their maximum at the $C_{(5)}$ atom (Table 4). Thus for 2,4-substituted sulfones, cycloaddition is most likely at the $C_{(4)}-C_{(5)}$ bond. For this reason, we can avoid the formation of the **C** and **D** isomers for sulfones **7-10**.

TABLE 3. Calculated Heats of Formation for Isoxazolines

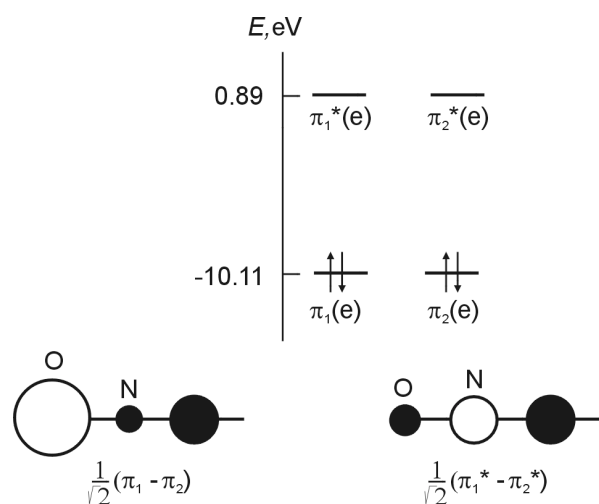| Compound	Heat of formation, kJ·mole^{-1}			
	A	**B**	**C**	**D**
1	382.2	358.7	—	—
2	-43.6	-61.9	—	—
3	161.6	147.5	—	—
4	154.7	136.4	182.8	155.3
5	254.4	240.1	287.2	261.3
6	53.3	45.4	61.8	57.2
7	-42.9	-54.1	-30.6	-29.5
8	66.9	100.8	70.8	75.9
9	63.3	48.9	77.6	73.6
10	171.4	154.5	177.6	178.9

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Fig. 5. Diagram showing configurations of the frontier orbitals of acetonitrile oxide
and the position of their energy levels.

The isolated molecule approximation does not give the quantitative characteristics for the reaction kinetics, so for sulfone **7** and MeCNO we calculated the reaction coordinates. The cycloaddition reaction was considered as a synchronous, concerted process. In this case, the reaction proceeds as a supra-supra process with formation of a cyclic transition state with the Hückel topology. The energy of the transition state in the case when the **A** molecule is formed (product **7A**) is 102.7 kJ/mole, while when the **B** isomer is formed, the transition state energy is equal to 147.5 kJ/mole. Fig. 6 illustrates the energy profile diagram for this reaction.

In forming the **B** molecule, an important contribution to the energy of the transition state comes from nonvalence interactions between the methyl group of the acetonitrile oxide and the trimethylsilyl group in sulfone **7**. The increase in the energy barrier when isoxazoline **B** is formed hinders reaction in this direction.
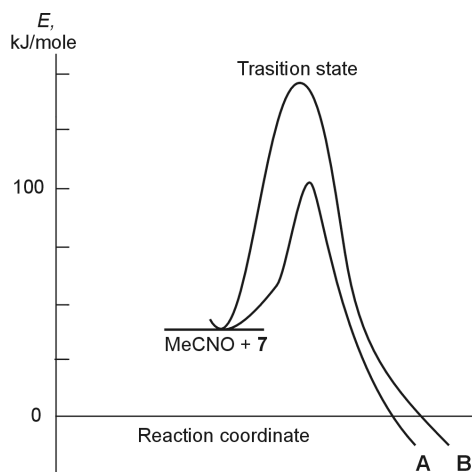

Fig. 6. Energy profile diagram for the reaction of cycloaddition
of acetonitrile oxide to sulfone **7**.

TABLE 4. Effective Charges q_i and Expansion Coefficients c_i for Expansion of the HOMO and LUMO in Basis p_z Orbitals for C Atoms in Thiophene 1,1-Dioxides **1-10**

| Compound | Atom C$_{(2)}$ | | | Atom C$_{(3)}$ | | | Atom C$_{(4)}$ | | | Atom C$_{(5)}$ | | |
	q_i	c_i		q_i	c_i		q_i	c_i		q_i	c_i	
		HOMO	LUMO		HOMO	LUMO		HOMO	LUMO		HOMO	LUMO
1	-0.293	0.528	0.533	-0.017	0.391	-0.439	-0.017	-0.391	-0.439	-0.293	-0.528	0.533
2	-0.628	0.499	0.525	+0.020	0.355	-0.455	+0.020	-0.355	-0.455	-0.628	-0.499	0.525
3	-0.670	0.509	0.524	+0.021	0.360	-0.454	+0.021	-0.360	-0.454	-0.670	-0.509	0.524
4	-0.288	0.513	0.522	-0.034	0.329	-0.475	+0.039	-0.422	-0.418	-0.642	-0.525	0.534
5	-0.287	0.516	0.522	-0.031	0.330	-0.470	+0.036	-0.428	-0.422	-0.680	-0.531	0.534
6	-0.627	0.512	0.527	+0.022	0.368	-0.461	+0.018	-0.347	-0.448	-0.672	-0.499	0.529
7	-0.656	0.536	0.499	+0.061	0.384	-0.453	-0.354	-0.350	-0.440	-0.259	-0.491	0.561
8	-0.698	0.540	0.499	+0.057	0.379	-0.450	-0.353	-0.361	-0.441	-0.260	-0.501	0.562
9	-0.653	0.539	0.503	+0.061	0.388	-0.457	-0.405	-0.345	-0.438	-0.257	-0.486	0.556
10	-0.697	0.546	0.502	+0.063	0.386	-0.453	-0.402	-0.357	-0.439	-0.261	-0.498	0.559

The isoxazolines **A** formed as a result of cycloaddition can be converted to the demetalation products. For example, the presence of water in the reaction mixture may cause the following reaction:
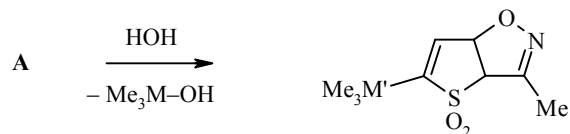
Assuming that the reaction proceeds according to a nucleophilic substitution mechanism, we can identify two reaction steps: formation of the complex, and conversion to the demetalation product:

$$R\text{–}MMe_3 \;\rightarrow\; R\text{–}MMe_3\text{–}B \;\rightarrow\; R\text{–}H$$

In a specific case, the ability to form the complex R–MMe₃–B may be characterized by the energy of hydroxyl anion addition to isoxazolines, i.e., the "hydroxyl affinity". These values are given in Table 5. As we should expect, it is specifically the products with a trimethylsilyl group that have the highest capacity for addition of an hydroxyl anion. Further conversion of the complex with the hydroxyl anion to the demetalation product depends on the rate (and hence on the activation energy) of the second process, according to the scheme:
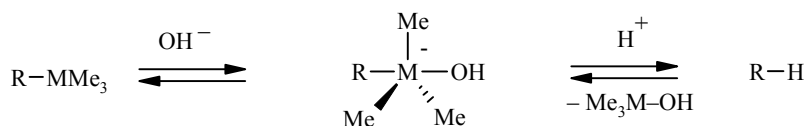
In comparing a series of related compounds, the Bell–Evans–Polyani (BEP) principle [17] is widely used for qualitative estimation of the activation energy, from which follows the linearity rule for the free energies. In Fig. 7, we show the BEP diagram for the process:
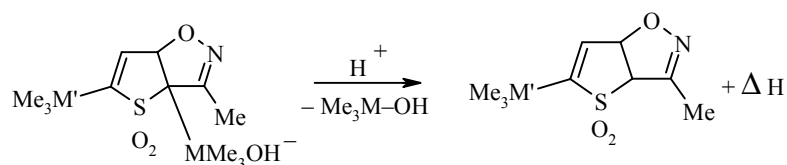

TABLE 5. Hydroxyl Affinity of Isoxazolines **1A-6A** and Heats of Formation for the Corresponding Complexes with Hydroxyl Anion

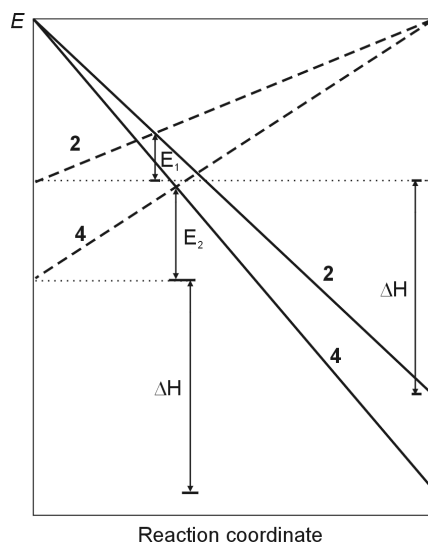| Com-pound	M'	M	Hydroxyl affinity, kJ·mole^{-1}	Heat of formation for complex, kJ·mole^{-1}
1	C	C	31.1	327.9
2	Si	Si	488.6	-556.3
3	Ge	Ge	430.8	-293.3
4	C	Si	491.4	-360.8
5	C	Ge	432.7	-202.4
6	Si	Ge	435.5	-403.3

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Fig. 7. BEP diagram for the reaction of cycloaddition
of acetonitrile oxide to sulfones **2** and **4**.

TABLE 6. Calculated Enthalpies of the Demetalation Reaction

Compound	M	M'	ΔH, kJ·mole^{-1}
2	Si	Si	-1115.1
3	Ge	Ge	-848.3
4	C	Si	-1113.5
6	Si	Ge	-1008.7

Table 6 shows the calculated enthalpies of reaction ΔH. It is easy to see that the reaction proceeds more rapidly in the case of isoxazoline **4A**. For this reason, we are able to isolate only the desilylation product and not the compound itself.

For the rest of the products, the activation energy of the process is higher. This fact explains their relative stability with respect to demetalation. This especially pertains to compounds **7A-10A**, the products of cycloaddition to 2,4-disubstituted sulfones. The energy of the molecules **7A-10A**, as for their complexes with the hydroxyl anion, is substantially lower (for example, for the **7A** complex, the heat of formation is -776.9 kJ·mole^{-1}) than for the corresponding products of addition to 2,5-disubstituted thiophene 1,1-dioxides, where an appreciable contribution to the energy comes from steric effects. According to the BEP principle, a decrease in the energy of the reagent leads to an increase in the activation energy. For the same reason, we do not observe demetalation in the 2 position of the **A** compounds, since in this case the reaction products should already have high energy, which also leads to an increase in the activation energy for the process.

EXPERIMENTAL

The ultraviolet spectrum of the thiophenes and thiophene 1,1-dioxides were taken on an Hitachi UV U 3200 spectrometer.

The quantum chemical calculations of the electronic structure for the studied systems were performed by the molecular orbital method within self-consistent field theory, in the MNDO approximation [18]. It proved to be difficult to use the Halgren–Lipscomb approach [19] for automatic localization of the transition state, so we used the McIver–Komornicki procedure [20]. In searching for the transition state, the geometry was optimized assuming that all the C, O, and N atoms forming the isoxazoline ring lie in the same plane; we fixed the bond lengths and bond angles in the methyl and trimethylsilyl groups, and also the torsional angles of the thiophene ring. To calculate the excited states, we used the configuration interaction (CI) method. We used only singly-excited configurations in the limited CI calculation. All the calculations were performed using the MOPAC program package [21] and the modified program [22]. The optimization procedure and the procedure for the rest of the calculations are similar to those in [23, 24].

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