

MOLECULAR STRUCTURE OF THIOPHENE 1,1-DIOXIDES, THIOPHENE S-OXIDES, AND THEIR DERIVATIVES. (REVIEW)

E. Lukevics, P. Arsenyan, S. Belyakov, and O. Pudova

The results from X-ray diffraction investigations of compounds containing thiophene 1,1-dioxide and thiophene 1-monoxide fragments are reviewed and analyzed. Data on the structure of S-oxide derivatives of 2,3- and 2,5-dihydrothiophenes are discussed.

Keywords: dihydrothiophene 1,1-dioxide, dihydrothiophene 1-oxide, thiophene 1,1-dioxide, thiophene 1-oxide, X-ray crystallographic analysis.

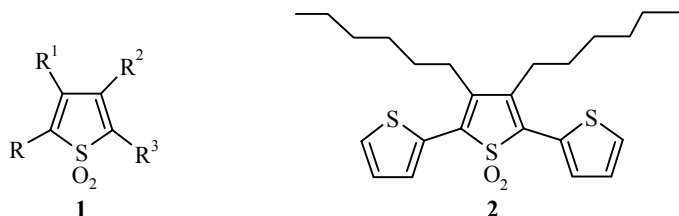
Thiophene 1,1-dioxide derivatives are convenient intermediates in the synthesis of various types of organic compounds. They have been used as dienes, dienophiles, and dipolarophiles in cyclization, react with nucleophiles and electrophiles, and undergo various transformations involving opening of the heterocycle ring [1]. These compounds recently are of particular interest during the production of new polymeric and oligomeric materials for optics and electronics [2-4]. The introduction of the thiophene 1,1-dioxide fragment into the oligothiophene chain made it possible to create materials with high photoluminescence in the solid state [5]. The optical electronic characteristics of these compounds are determined significantly by the molecular structure, the type of molecular packing, and the nature of the intermolecular interactions. The analysis of the structural features of this type of compound are of particular interest.

1. Molecular Structure of Thiophene 1,1-Dioxides and Thiophene 1-Oxides

The molecular structure of 1,1-dioxide derivatives of type **1** has been investigated most comprehensively in the series of S-functional thiophene compounds (Table 1). The atoms in the five-membered heterocycle of the sulfones **1** are almost coplanar, while the oxygen atoms of the sulfonyl group SO₂ lie at an identical distance on different sides of this plane. The greatest departure from planarity is observed for the molecule of 2,3,4,5-tetrachlorothiophene 1,1-dioxide, in which the sulfur atom projects from the plane of the carbon atoms by 0.087 Å (dihedral angle 4.1°). The lengths of the C–C and C–S bonds indicate complete loss of the aromaticity of the heterocycle and the formation of a butadiene system with localized C₍₂₎=C₍₃₎ and C₍₄₎=C₍₅₎ double bonds. General geometric parameters of the 2,5- and 2,4-disubstituted, 2,3,5-trisubstituted, and 2,3,4,5-tetrasubstituted sulfones **1** are given in Table 1.

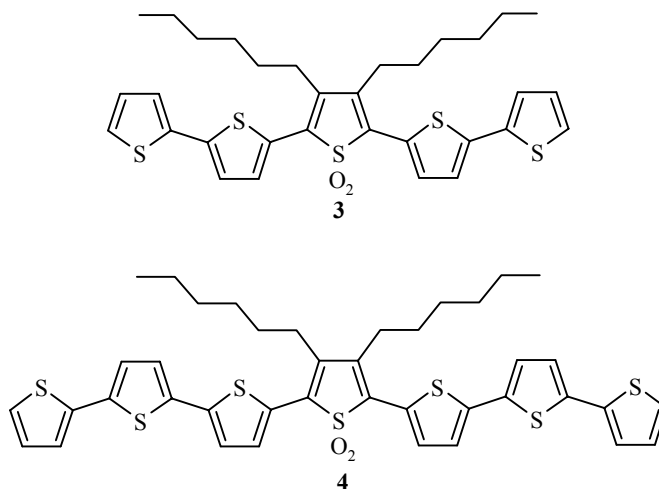
Latvian Institute of Organic Synthesis, Riga, Latvia; e-mail: olga@osi.lv, pavel.arsenyan@lycos.com.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 725-739, June, 2002. Original article submitted November 26, 2001.

The molecular packing of disubstituted thiophene 1,1-dioxides **1** in the crystalline state depends by the nature of the substituents and their position in the thiophene ring. The replacement of one trimethylsilyl group in 2,5-bis(trimethylsilyl)thiophene 1,1-dioxide by *tert*-butyl leads to a change in the type of crystal lattice from orthorhombic (*Pnmm*) to monoclinic (*C2/c*). The molecules of the 2,5-disubstituted silyl and germyl sulfones are at special positions, whereas in the 2,4-disubstituted derivatives they are at a general position. The results of X-ray crystallographic analysis for the crystalline and powdered [16] 2,5-bis(trimethylsilyl)thiophene 1,1-dioxide confirm the identity of their structure and packing.



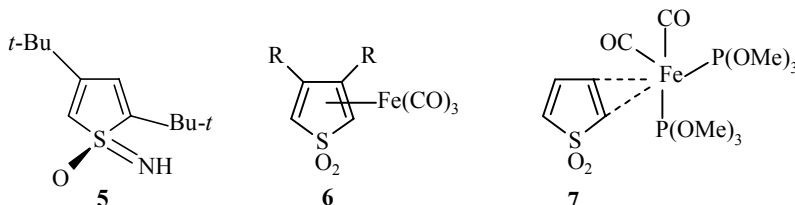
The investigation of the photoluminescent characteristics of the oligothiophene derivatives **2-4** containing a central thiophene 1,1-dioxide fragment was established that in the solid state terthiophene 1',1'-dioxide **2** and quinquethiophene 1'',1''-dioxide **3** are considerably more effective than the septthiophene 1''',1'''-dioxide (**4**) and the usual oligothiophenes. By X-ray crystallographic analysis it was possible to show how significantly dipole interaction, weak hydrogen bonds, and van der Waals interactions affect the nature of the steric packing of the molecules and, consequently, the luminescent characteristics with elongation of the oligothiophene chain [17]. All three compounds are crystallographically disordered, and one of the terminal thiophene rings assumes two opposite orientations (*anti* and *syn* in relation to the sulfur atom of the adjacent heterocycle). The conformation of compound **2** is characterized by torsion angles S–C–C–S -168.4° and 28.5° (or -151.6° for the disordered form), and the *anti-anti* conformer slightly predominates (51.6%).

The departure from planarity between the rings is reduced significantly with increase of the oligothiophene chain in derivatives **3** and **4**. The torsion angles of the first compound lie in the range between -165.3° and -171.9° . The full *anti* orientation predominates in this case too (66.2%). In compound **4** the dihedral angles between the adjacent rings amount to only $1.4-7.3^\circ$, while the maximum departure of the atoms from planarity does not exceed 0.162 \AA . In addition, conformational differences were observed for septthiophene 1''',1'''-dioxide (**4**): Both terminal thiophene rings have the preferred *syn* orientation.



The most interesting feature of the molecular packing in terthiophene 1',1'-dioxide (**2**) is the fact that in the crystal the molecules are packed in the chiral form and are characterized by the absence of short intermolecular contacts. The shortest S...S distance is 4.799 Å. In compound **3** the molecular packing is close to the typical packing of planar and quasiplanar oligothiophenes with herring-bone packing. In contrast to compound **2**, very short van der Waals interactions were found for quinque thiophene 1'',1''-dioxide (**3**) (3.341 for C...C, 3.393 Å for C...O, and 3.741 Å for S...S contacts). The packing in sept thiophene 1''',1'''-dioxide (**4**) differs substantially from that in compound **3**. Its long and more planar molecules are arranged perpendicularly to the *b* axis of the crystal cell, and the almost parallel layers are linked by a crystallographic inversion center. The general geometric parameters of the thiophene 1,1-dioxide ring in the investigated oligomeric derivatives are similar to those in compounds **1**.

The structure of the only S-monoimine analog **5** of thiophene 1,1-dioxides was studied recently. The tetracoordinated sulfur of the thiophene ring in the sulfoximide **5** is chiral, and it was possible to separate the *R*- and *S*-enantiomers successfully by HPLC on a chiral column. The molecular structure of the *S*-isomer was investigated by X-ray crystallographic analysis [18]. Similar to the thiophene 1,1-dioxides **1**, the heterocycle of the sulfoximide **5** is planar. The bond lengths C₍₂₎=C₍₃₎, C₍₄₎=C₍₅₎ (1.32 Å), and C₍₃₎-C₍₄₎ (1.49 Å) indicate localization of the double bonds and the absence of aromaticity in the thiophene ring. The distances S–O (1.45 Å) and S–N (1.54 Å) are comparable with those in the sulfoximides. The sulfoximide **5** is the first compound with a chiral sulfur atom in the series of thiophene derivatives.

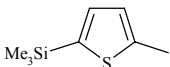
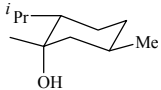


It was established that unsubstituted thiophene 1,1-dioxide, which only exists in solutions for a short period of time, and also its 3,4-dimethyl- and 3,4-diphenyl-substituted derivatives can act as η^4 -donor ligands and form complexes in a photochemical reaction with Fe(CO)₅. Di-iron nonacarbonyl Fe₂(CO)₉ also reacts with thiophene 1,1-dioxide, but in this case not only the products from its reaction with thiophene 1,1-dioxide but also the product from dimerization of the latter are formed. The structure of compounds **6** (R = H, Me, Ph) was confirmed by X-ray crystallographic analysis [19, 20]. In these complexes the Fe(CO)₃ fragment is attached to the butadiene system of the heterocycle, and the Fe–C distances lie in the range of 2.044–2.129 Å. The five-membered heterocycle is non-planar, and the sulfur atom is deflected from the plane of the butadiene system by 38.7° (R = H), 26.9° (R = Me), and 39° (R = H, the average value for two independent molecules) toward the side opposite the iron atom. In the diphenyl derivative **6** one phenyl ring is coplanar with the C₄ fragment of the heterocycle, while the second forms an angle of 64.3°.

In the complex **7** [19] the iron atom is only linked by one η^2 -type double bond of thiophene 1,1-dioxide (the lengths of the Fe–C₍₂₎ and Fe–C₍₃₎ bonds are 2.022 and 2.079 Å respectively.) The iron atom is trigonal bipyramidal with three different ligands [CO, (MeO)₃P, and the C=C double bond of thiophene 1,1-dioxide] in the equatorial positions. The heterocycle in this complex is practically planar.

The cobalt complexes **8** (R = H, Ph) [21] have a sandwich structure. As in the derivatives of iron **6**, the thiophene 1,1-dioxide ring is non-planar, and the CSC plane forms an angle of 34.8° with the butadiene system (R = H). In the case of the tetraphenylthiophene 1,1-dioxide complex (R = Ph) the angle increases to 37.2°. The general geometric parameters of the thiophene 1,1-dioxide ring in the organometallic compounds are given in Table 2. As follows from the presented C–C bond lengths for the heterocycles, they become equal in the complexes where the metal atom forms a bond of the η^4 -type with the thiophene 1,1-dioxide ligand (complexes **6** and **8**).

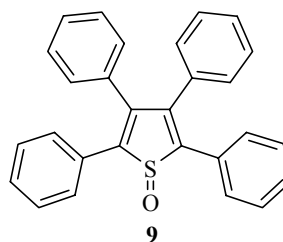
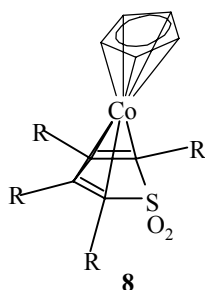
TABLE 1. The General Geometric Parameters of Thiophene 1,1-Oxides **1**

R	R ¹	R ²	R ³	Bond lengths, Å					CSC angle, deg	R	Ref.
				C ₍₂₎ =C ₍₃₎	C ₍₄₎ =C ₍₅₎	C ₍₃₎ -C ₍₄₎	C ₍₂₎ -S	C ₍₅₎ -S			
<i>t</i> -Bu	H	H	<i>t</i> -Bu	1.38(2)		1.47(2)	1.75(2)		98.0(15)	0.203	[6]
<i>t</i> -Bu	H	H	Me ₃ Si	1.319(5)		1.496(6)	1.773(3)		96.2(2)	0.0708	[7]
Me ₃ Si*	H	H	Me ₃ Si	1.269(8)		1.462(12)	1.775(5)		95.8(3)	0.0515	[8]
				1.299(7)		1.472(11)	1.765(5)		96.2(3)		
Me ₃ Si	H	H	Me ₃ Si	1.323		1.480	1.761		96.1		[9]
Me ₃ Si*	H	H	Me ₃ Ge	1.329(9)		1.478(12)	1.777(6)		95.6(4)	0.0534	[7]
				1.303(9)		1.472(12)	1.778(6)		96.9(4)		
Me ₃ Ge*	H	H	Me ₃ Ge	1.326(17)		1.480(2)	1.769(12)		96.2(7)	0.0688	[7]
				1.352(16)		1.470(2)	1.757(11)		97.5(7)		
Me ₃ Si*	H	H		1.323(7)	1.321(2)	1.444(7)	1.796(5)	1.770(5)	94.9(3)	0.0629	[10]
				1.349(8)	1.336(8)	1.428(8)	1.756(6)	1.737(6)	94.7(3)		
Ph	H	H	Ph	1.324(9)	1.316(8)	1.497(9)	1.780(6)	1.770(6)	94.2(3)	0.058	[11]
Me ₃ Si	H	Me ₃ Si	H	1.331(5)	1.301(6)	1.488(5)	1.765(4)	1.772(4)	93.9(2)	0.0646	[10]
Me ₃ Si	H	Me ₃ Ge	H	1.340(7)	1.320(7)	1.486(7)	1.762(5)	1.767(5)	93.7(3)	0.0476	[10]
Me ₃ Ge	H	Me ₃ Si	H	1.314(8)	1.294(9)	1.486(7)	1.757(6)	1.773(7)	93.6(3)	0.0621	[10]
Me ₃ Ge	H	Me ₃ Ge	H	1.325(7)	1.320(7)	1.489(7)	1.754(4)	1.761(6)	94.0(3)	0.0473	[10]
Br	Br	H	Br	1.30(2)	1.25(2)	1.48(2)	1.752(12)	1.773(12)	91.3(5)		[12]
Cl	Cl	Cl	Cl	1.326(3)	1.334(4)	1.476(3)	1.771(2)	1.775(2)	92.1(1)	0.043	[13]
Cl	Cl	Cl		1.332	1.304	1.479	1.759	1.773	92.4	0.066	[14]
<i>t</i> -Bu	<i>t</i> -Bu	<i>t</i> -Bu	<i>t</i> -Bu	1.359	1.364	1.536	1.807	1.818	93.98	0.045	[15]

* For two independent molecules.

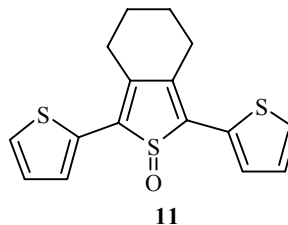
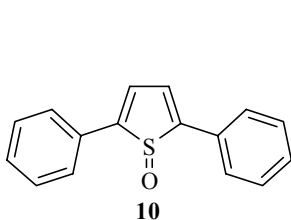
TABLE 2. The General Geometric Parameters of the Complexes 6-8

Compound	R	Bond lengths, Å			C-S-C angle, deg	R	Ref.
		C-S	C ₍₂₎ -C ₍₃₎ C ₍₃₎ -C ₍₅₎	C ₍₃₎ -C ₍₄₎			
6	H	1.754(4)	1.417(6)	1.404(6)	86.4(2)	0.045	[19]
	Me	1.757(5)	1.421(6)	1.417(6)	86.4(2)	0.026	[20]
		1.760(4)	1.434(6)				
Ph	1.777(11)	1.457(13)	1.451(15)	85.8(5)	0.071	[19]	
	1.772(9)	1.469(14)					
7		1.760(8)	1.426(11)	1.478(12)	94.9(4)	0.044	[19]
		1.734(9)	1.321(14)				
8	H	1.752(5)	1.413(7)	1.402(8)	86.8(2)	0.037	[21]
		1.746(5)	1.416(8)				
	Ph	1.769(3)	1.440(3)	1.441(4)	87.6(1)	0.043	[21]
		1.771(2)	1.441(4)				



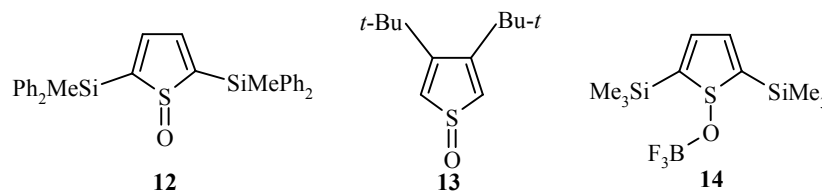
On account of the complexities in the preparation of thiophene 1-oxides their structural features have been studied to a considerably lesser degree. The first structurally characterized 1-oxide was 2,3,4,5-tetraphenylthiophene 1-oxide (**9**) [22]. However, it was not possible to determine the conformation of the ring and the lengths of the S-O and S-C bonds in this compound accurately due to the structural disordering.

The sulfur atom in 2,5-diphenylthiophene 1-oxide (**10**) [23] is pyramidalized and projects from the plane formed by the other atoms of the heterocycle by 0.276 Å. The oxygen atom also lies outside this plane but on the opposite side at a distance of 0.746 Å. These data, together with the bond lengths C₍₂₎=C₍₃₎ (1.334), C₍₃₎-C₍₄₎ (1.433), S-C (1.781) and S-O (1.484 Å), correspond to theoretical calculations carried out by the *ab initio* method for the molecule of unsubstituted thiophene 1-oxide [24, 25]. By comparing the lengths of the bonds in the heterocycle of 2,5-diphenylthiophene 1,1-dioxide (Table 1) [11] and of compounds **10** it can be seen that the C₍₂₎=C₍₃₎ and C₍₄₎=C₍₅₎ distances in the sulfone are shorter while the C₍₃₎-C₍₄₎ distance is longer than in the analogous monoxide. This fact can be regarded to some degree as the result of increase in the aromaticity in the transition from the 1,1-dioxide **1** (R = R³ = Ph, R¹ = R² = H) to the 1-oxide **10**, in spite of the nonplanarity of the heterocycle in the last compound.

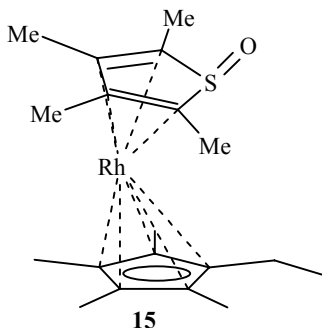


In terthiophene 1'-oxide (**11**) [26], as in the diphenyl analog **10**, the central fragment represents a diene system, and the $C_{(2)}=C_{(3)}$, $C_{(4)}=C_{(5)}$, and $C_{(3)}-C_{(4)}$ distances amount to 1.357, 1.358, and 1.460 Å respectively. The oxidized sulfur atom is at the apex of the pyramid and projects by 0.23 Å from the plane of the four carbon atoms, forming dihedral angles of 11.24° and 26.31° with the neighboring thiophene rings.

Recently it was possible to obtain a series of 2,5-bissilyl-substituted thiophene 1-oxides, by oxidizing the corresponding thiophenes with *m*-chloroperbenzoic acid in the presence of boron trifluoride etherate, and to investigate the molecular structure of 2,5-bis(methyldiphenylsilyl)thiophene 1-oxide (**12**) [27] and 3,4-di(*tert*-butyl)thiophene 1-oxide (**13**) [28]. The structure of compounds **12** ($C_{(2)}=C_{(3)}$ 1.341, $C_{(4)}=C_{(5)}$ 1.346, $C_{(3)}-C_{(4)}$ 1.446 Å) and **13** ($C_{(2)}=C_{(3)}$ 1.340, $C_{(4)}=C_{(5)}$ 1.344, $C_{(3)}-C_{(4)}$ 1.527 Å) is similar to the structure of the previously examined derivatives **10** and **11**. It is necessary to mention the increase in the length of the $C_{(3)}-C_{(4)}$ bond in compound **13**, which is most probably due to the steric effect of the *tert*-butyl groups at the β -positions of the heterocycle.



The reaction of 2,5-bis(trimethylsilyl)thiophene 1-oxide with boron trifluoride etherate in chloroform leads to the formation of the complex **14** with a quantitative yield [29], in which the BF_3 group is attached to the sulfinyl oxygen atom. On account of this the S–O bond in the complex **14** (1.522 Å) is longer than in thiophene 1-oxides (in compound **12** the length of the S–O bond is 1.471 Å), but the nature of the bonds in the heterocycle does not change significantly.



In the rhodium complex of tetramethylthiophene 1-oxide **15** [30] the central rhodium atom is coordinated with the cyclopentadienyl ring and the carbon atoms of the heterocycle. The tetramethylthiophene 1-oxide ligand is non-planar, and the sulfur atom is deflected toward the side opposite the rhodium atom by an angle of 30.6°. As in the case of the thiophene 1,1-dioxide complexes with iron **6** and cobalt **8**, in compound **15** the C=C double bonds (1.430 and 1.432 Å) and the single C–C bond (1.422 Å) each become equal.

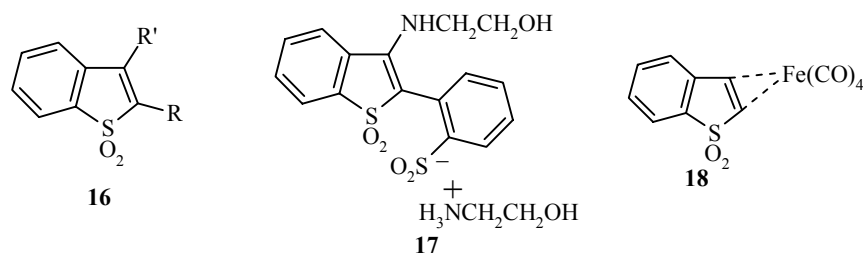
2. Molecular Structure of Condensed Thiophene 1,1-Dioxides and 1-Oxides

X-ray crystallographic analysis was used to determine the structure of some benzo[*b*]thiophene 1,1-dioxides (compounds **16** R = R' = H; R = Me, R' = H; R = H, R' = Me; R = R' = Me; R = Br, R' = H and **17**) [31-35]. The condensed system in compounds **16** is practically coplanar, and the dihedral angle between the

aromatic ring and the heterocycle does not exceed 1.6° (in the 3-methyl derivative **16**). Some geometric parameters of benzo[*b*]thiophene 1,1-dioxides are given in Table 3.

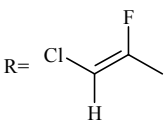
The crystals of the sulfone **17** are constructed from molecular ions: benzenesulfinate anion and β -hydroxyethylammonium cation. The benzothiophene fragment is planar within $\pm 0.04 \text{ \AA}$, but the anion as a whole is non-planar, since the benzene ring forms an angle of 106.8° with the condensed bicycle. The molecular ions in the crystal of **17** are linked to each other by six hydrogen bonds, which make a considerable contribution to the stabilization of the structure [34, 35].

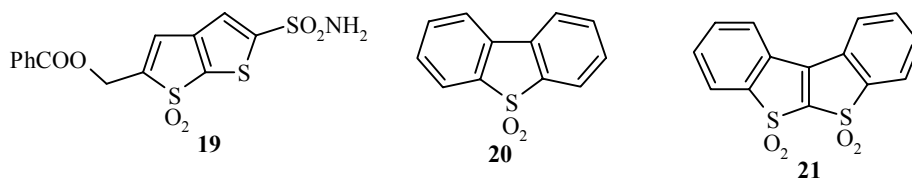
Benzothiophene 1,1-dioxide forms the iron complex **18** [36], in which the metal atom is linked to only one bond of the thiophene 1,1-dioxide ring. (The Fe–C₍₂₎ and Fe–C₍₃₎ distances are 2.078 and 2.112 \AA .) The heterocycle in the compound is non-planar, and the hydrogen atom projects from the plane defined by the four carbon atoms by 0.15 \AA , forming an angle of 6.63° .



Oxidation of 2-hydroxymethyl-5-sulfamino[2,3-*b*]thienothiophene [37] by potassium peroxy-monosulfate takes place selectively only at the sulfur atom of the heterocycle, containing the hydroxy group at position 2. This was confirmed by X-ray crystallographic analysis of compound **19**, obtained by the reaction of the oxidation product with benzoyl chloride. The sulfamide **19** is characterized in the crystalline state by an unusual type of hydrogen interaction C–H \cdots O. The hydrogen atoms at positions 3 and 4 of the condensed heterocyclic system form a hydrogen bond with one of the oxygen atoms of the SO₂ group in the ring of a neighboring molecule.

TABLE 3. The General Geometric Parameters of Benzothiophene 1,1-Dioxides

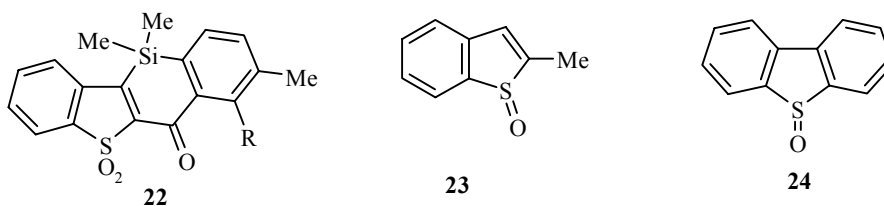
Compound	Bond length, \AA			C–S–C angle, deg	<i>R</i>	Ref
	C–S	C ₂ –C ₃	C ₃ –C ₄			
16 R = R' = H	1.757(2) 1.579(2)	1.323(3)	1.379(3)	93.0(1)	0.051	[31]
16 R = Me, R' = H	1.771(2) 1.751(2)	1.319(3)	1.376(3)	92.7(1)	0.038	[32]
16 R = H, R' = Me	1.746(3) 1.765(3)	1.321(3)	1.379(4)	93.1(1)	0.029	[32]
16 R = R' = Me	1.776(3) 1.757(2)	1.335(4)	1.385(4)	94.1(1)	0.057	[31]
16 R = Br, R' = H	1.770(5) 1.770(5)	1.320(8)	1.392(7)	92.2(2)	0.048	[31]
16					0.088	[33]
R = 						
R' = NMe ₂						
17	1.763(5) 1.730(5)	1.375(6)	1.497(7)	94.6(2)	0.048	[34, 35]



The molecular structure of dibenzothiophene 5,5-dioxide (**20**) [38] was investigated by X-ray crystallographic analysis in 1968, and the obtained geometric parameters of the molecule contain significant errors.

As a whole the molecule of the disulfone **21** [39] is non-planar, and the two planar parts of the molecule are folded along the central C–C bond (dihedral angle approximately 5°). The average bond length in the aromatic rings is 1.385 Å. The lengths of the bonds in the heterocycles [$r(\text{C–S})$ 1.750-1.755, central C–C bond, 1.385 and $r(\text{C}_{\text{Ar}}\text{–C})$ 1.473-1.479 Å] correspond to loss of aromaticity as a result of the oxidation of the sulfur atom.

The condensed molecules of benzo[*b*]dihydrosilanaphtho[2,3-*d*]thiophene 5,5-dioxides **22** (R = H, NH₂) [40] as a whole are planar, which promotes maximum transmission of the electronic effects.



It was established by X-ray crystallographic analysis that the sulfoxide chiral center of 2-methylbenzothiophene 1-oxide (**23**) has the (*R*) configuration [41]. In dibenzothiophene 5-oxide (**24**) [24] the departure of the sulfur atom from the mean-square plane of the four carbon atoms of the heterocycle is insignificant, while the oxygen atom is arranged in such a way that it forms an angle of 68.2° with this plane.

3. Molecular Structure of 2,3-Dihydrothiophene 1,1-Dioxides and 1-Oxides

The structure of a series of monosubstituted [42-48], disubstituted [49, 50], and tetrasubstituted [51] 2,3-dihydrothiophene 1,1-dioxides, including various condensed derivatives, has been studied by X-ray crystallographic analysis. A comparison was made of the structural characteristics of isomeric 3- and 4-phenyl-2,3-dihydrothiophene 1,1-dioxides (**25**) [42, 43] and (**26**) [43, 44]. The heterocycle in the molecule of the sulfone **25** is in the conformation of a slightly distorted envelope with the C₍₂₎ atom at the corner of the envelope. The other four atoms of the ring lie in one plane with an accuracy of up to 0.006 Å and form an angle of 59.8° with the plane of the benzene ring. In compound **26** the five-membered heterocycle has an analogous conformation, the planes of C₍₃₎C₍₄₎C₍₅₎S and the benzene ring are almost coplanar. (The dihedral angle amounts to 1.4°) The observed structural differences are most likely due to conjugation between the phenyl group and the double bond in the sulfone **26**.

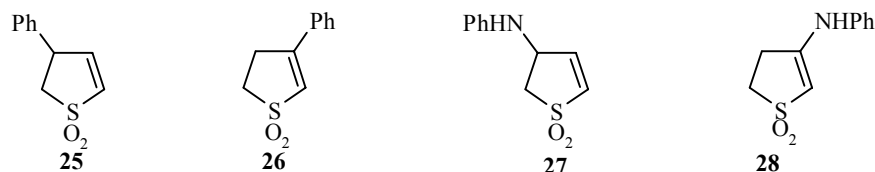


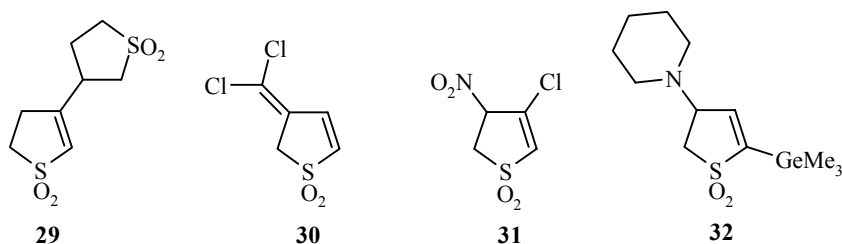
TABLE 4. The Geometric Parameters of the 2,3-Dihydrothiophene 1,1-Dioxide Ring in Compounds **24-32**

Compound	Bond length, Å					<i>R</i>	Ref.
	S-C ₍₂₎	C ₍₂₎ -C ₍₃₎	C ₍₃₎ -C ₍₄₎	C ₍₄₎ =C ₍₅₎	S-C ₍₅₎		
24	1.766(7)	1.533(6)	1.510(8)	1.321(8)	1.733(6)	0.054	[41]
25	1.780(2)	1.517(4)	1.519(3)	1.325(3)	1.739(2)	0.03	[43]
26	1.778(3)	1.535(5)	1.508(4)	1.313(4)	1.736(3)	0.042	[44]
27	1.756(7)	1.522(8)	1.502(7)	1.342(6)	1.713(5)	0.052	[45]
28	1.783(3)	1.493(6)	1.486(5)	1.335(4)	1.746(3)	0.042	[46]
29	1.800(7)	1.499(7)	1.457(10)	1.325(9)	1.738(5)	0.045	[47]
30	1.819(10)	1.530(12)	1.490(11)	1.338(13)	1.755(9)	0.048	[48]
31	1.760	1.554	1.527	1.350	1.758	0.0947	[49]
32	1.794(5)	1.566(7)	1.509(7)	1.316(7)	1.758(5)	0.040	[50]

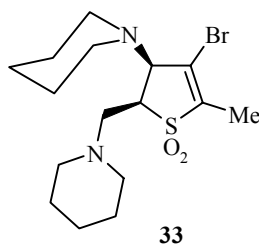
The 2,3-dihydrothiophene 1,1-dioxide ring in 3-phenylamino-2,3-dihydrothiophene 1,1-dioxide (**27**) [45] and 4-phenylamino-2,3-dihydrothiophene 1,1-dioxide (**28**) [46] has the form of an envelope, and the chief difference lies in the fact that in compound **27** the envelope is flattened and the C₍₂₎ atom projects from the C₍₃₎C₍₄₎C₍₅₎S plane by only 0.04 Å. The heterocycle in the molecule of **28** is less planar, and the projection of the C₍₂₎ atom is almost an order of magnitude greater (0.335 Å). The nitrogen atom is coplanar with the flat part of the heterocycle in compound **28**, which forms a comparatively small dihedral angle of 26.0° with the phenyl ring. (In the sulfone **27** this angle amounts to 78.9°.)

In compound **29** [47] the sulfolane and thiolenes fragments are displaced in relation to each other by an angle of 56° along the C₍₄₎–C₍₃₎ bond linking these heterocycles. The 2,3-Dihydrothiophene 1,1-dioxide ring is almost planar with deviation of the C₍₂₎ and C₍₃₎ atoms by ±0.05 Å.

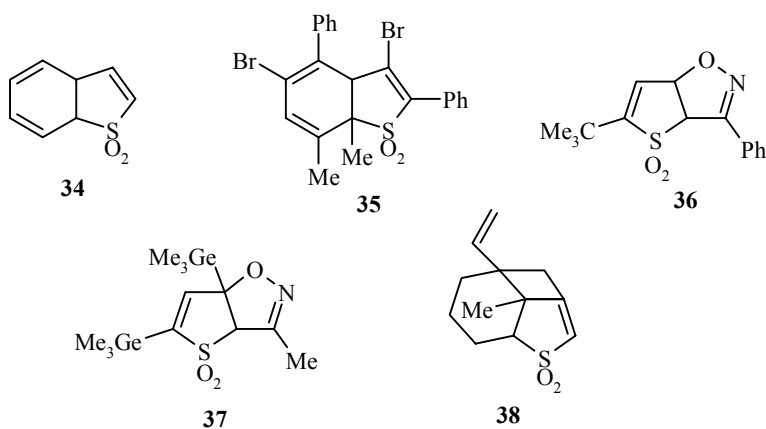
The sulfur-containing heterocycle in 4-chloro-3-nitro-2,3-dihydrothiophene 1,1-dioxide (**31**) [49] and 3-piperidino-5-trimethylgermyl-2,3-dihydrothiophene 1,1-dioxide (**32**) [50] is practically planar. In compound **31** the chlorine atom lies in the plane of the heterocycle, while the mean planes of the sulfonyl and nitro groups form dihedral angles of 89.20 and 88.89° respectively with the five-membered heterocycle.



It was established by X-ray crystallographic analysis that the piperidine and piperidinomethyl groups in the tetrasubstituted 2,3-dihydrothiophene 1,1-dioxide (**33**) [51] are in the *cis* position in relation to each other. The piperidine fragment at position 3 of the 2,3-dihydrothiophene 1,1-dioxide ring has the chair conformation, while the second piperidine substituent is disordered. The central five-membered heterocycle as a whole is nonplanar, and the maximum deviation from planarity amounts to 0.11 Å. The geometric parameters of the 2,3-dihydrothiophene 1,1-dioxide ring in compounds **25-33** are given in Table 4.



Whereas the condensed system of benzo[*b*]thiophene 1,1-dioxide and its derivatives **16** and **17** is planar, in its 3a,7a-dihydrogenated analog **34** [19], formed as a result of dimerization of the unsubstituted thiophene 1,1-dioxide ring, the five- and six-membered rings form a dihedral angle of 60.5°. Dimerization of the sulfone also occurs when 3-bromo-5-methyl-2-phenylthiophene 1,1-dioxide is heated in decalin. Subsequent removal of SO₂ leads to 3,5-dibromo-7,7a-dimethyl-2,4-diphenyl-*cis*-3a,7a-[*b*]thiophene 1,1-dioxide (**35**) [52], the structure of which was confirmed by X-ray crystallographic analysis.



In order to determine the regioselectivity of the [2+3]-dipolar cycloaddition of aceto- and benzonitrile oxides to the C=C double bonds of 2,5- and 2,4-disubstituted thiophene 1,1-dioxides the structure of the reaction products – 4,4-dioxodihydrothieno[2,3-*d*]isoxazolines **36** [7] and **37** [10] – was investigated. The dihydrothiophene and isoxazoline heterocycles of these derivatives are planar, but the condensed systems as a whole are non-planar, and the dihedral angles between the five-membered rings amount to 63.2 and 65.3° respectively.

During investigation of the structure of 2-thiatricyclo[4.3.1.0^{4,10}]dec-3-ene (**38**) [53] standard structural data were mostly obtained. The authors only noted elongation of the C–C bonds of the cyclobutane fragment to 1.580-1.590 Å.

3. Molecular Structure of 2,5-Dihydrothiophene 1,1-Dioxides and 1-Oxides

X-ray crystallographic analysis was also used to investigate a series of derivatives **39-46** containing a 2,5-dihydrothiophene 1,1-dioxide fragment. The general geometric parameters of these compounds are given in Table 5.



The five-membered ring in 3-phenyl-2,5-dihydrothiophene 1,1-dioxide (**40**) [55], as also in its isomers **25** and **26**, is characterized by an envelope conformation. In this case, however, it is not the C₍₂₎ atom but the sulfur atom that projects from the plane formed by the other four atoms of the heterocycle. This plane is practically coplanar with the plane of the phenyl ring.

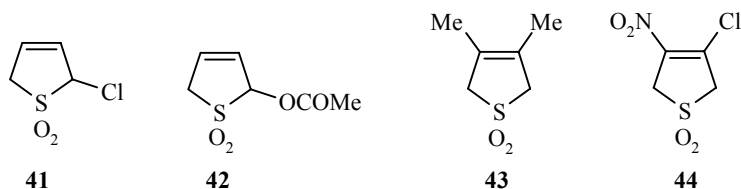


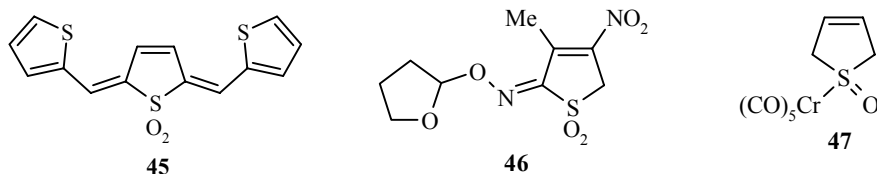
TABLE 5. Geometric Parameters of the Heterocycle in Compounds **39-47**

Compound	Bond length, Å					Ref.
	S-C ₍₂₎	C ₍₂₎ -C ₍₃₎	C ₍₃₎ =C ₍₄₎	C ₍₄₎ -C ₍₅₎	S-C ₍₅₎	
39	1.75	1.47	1.37	1.47	1.74	[54]
40	1.790(2)	1.511(3)	1.345(3)	1.496(5)	1.790(2)	[55]
41	1.781	1.484	1.309	1.490	1.825	[56]
41*	1.844	1.492	1.344	1.499	1.810	[56]
42	1.786	1.488	1.308	1.480	1.825	[56]
42*	1.856	1.499	1.345	1.500	1.814	[56]
43	1.79(2)	1.51(2)	1.34(2)	1.51(2)	1.79(2)	[57]
44	1.793(5)	1.488(6)	1.329(5)	1.487(7)	1.796(6)	[58]
45	1.761(3)	1.440(5)	1.340(5)	1.438(6)	1.767(4)	[59]
46	1.796(4)	1.413(8)	1.330(7)	1.524(8)	1.765(5)	[60]
47	1.811		1.327			[61]

* Calculated data.

The structural data obtained by X-ray crystallographic analysis of the 2-chloro- and 2-acetoxy-2,5-dihydrothiophene 1,1-dioxides (**41**) and (**42**) agree quite well with the calculated data [56].

In the transition from 4-chloro-3-nitro-2,3-dihydrothiophene 1,1-dioxide (**31**) to the isomeric 4-chloro-3-nitro-2,5-dihydrothiophene 1,1-dioxide (**44**) [58] there is a change in the conformation of the five-membered ring. Whereas it is practically planar in compound **31**, in the isomer **44** it acquires the envelope form with a "folding" angle of 20.8°, formed by the C₍₂₎SC₍₅₎ atoms. The chlorine and nitrogen atoms lie in the C₍₂₎C₍₃₎C₍₄₎C₍₅₎ plane, and the nitro group is turned from this plane by 17.9°.



The three five-membered heterocycles in compound **45** [59] are almost coplanar. The terminal thiophene rings have *E*-geometry in relation to the double bonds. The lengths of the C–C bonds indicate a high degree of conjugation in the whole molecule.

The conformation of the sulfur-containing heterocycle in 3-methyl-4-nitro-2-(α -tetrahydrofuryl-oxyimino)-2,5-dihydrothiophene 1,1-dioxide (**46**) [60] can be characterized as intermediate between the twist form and the envelope form with a slight shift toward the envelope. The sulfur atoms and the carbon atoms of the CH₂ group project on different sides of the plane formed by the C₍₃₎C₍₄₎C₍₅₎ atoms by 0.08 and 0.06 Å.

The pentacarbonylchromium complex (**47**) [61] is formed during irradiation of a mixture of Cr(CO)₆ and 2,5-dihydrothiophene 1-oxide in benzene. X-ray crystallographic analysis was used to determine the nature and type of bonding. It was shown that the chromium atom is coordinated with the sulfur atom (Cr–S bond length 2.331 Å) and not with the sulfoxide group. The dihydrothiophene ring assumes the envelope conformation, the corner of which is formed by the sulfur atom. The dihedral angle amounts to 22.5°.

The authors express their gratitude to the Latvian Scientific Council for financial support (grant No. 187) and the Russian Foundation for Basic Research for supporting the license to use the Cambridge structural data bank.

REFERENCES

1. J. Nakayama and Y. Sugihara, *Top. Curr. Chem.*, **205**, 131 (1999).
2. G. Barbarella, L. Favaretto, M. Zambianchi, O. Pudova, C. Arbizzani, A. Bongini, and M. Masragostino, *Adv. Mater. (Weinheim. Ger.)*, **10**, 551 (1998).
3. G. Barbarella, L. Favaretto, G. Sotgiu, M. Zambianchi, V. Fattory, M. Cocchi, F. Cacialli, G. Gigli, and R. Cingolani, *Adv. Mater. (Weinheim. Ger.)*, **11**, 1375 (1999).
4. T. Yamamoto, I. Nurulla, H. Hayashi, and H. Koinuma, *Synth. Met.*, **107**, 137 (1999).
5. G. Barbarella, L. Favaretto, G. Sotgiu, M. Zambianchi, A. Bongini, C. Arbizzani, M. Masragostino, M. Anni, G. Gigli, and R. Cingolani, *J. Am. Chem. Soc.*, **122**, 11971 (2000).
6. L. G. Vorontsova, *Zh. Strukt. Khim.*, **7**, 240 (1966).
7. E. Lukevics, P. Arsenyan, S. Belyakov, J. Popelis, and O. Pudova, *Organometallics*, **18**, 3187 (1999).
8. E. Lukevics, P. Arsenyan, S. Belyakov, J. Popelis, and O. Pudova, *Tetrahedron Lett.*, **42**, 2039 (2001).
9. N. Furukawa, H. Hoshiai, T. Shibutani, M. Higaki, F. Iwasaki, and H. Fujihara, *Heterocycles*, **34**, 1085 (1992).
10. E. Lukevics, P. Arsenyan, S. Belyakov, J. Popelis, and O. Pudova, *Organometallics*, **20**, 2487 (2001).
11. P. Pouzet, I. Erdelmeier, D. Ginderow, J.-P. Mornon, P. M. Dansette, and D. Mansuy, *J. Heterocycl. Chem.*, **34**, 1567 (1997).
12. G. Barbarella, L. Favaretto, G. Sotgiu, M. Zambianchi, L. Antolini, O. Pudova, and A. Bongini, *J. Org. Chem.*, **63**, 5497 (1998).
13. G. Douglas, C. S. Frampton, and K. W. Muir, *Acta Crystallogr.*, **C49**, 1197 (1993).
14. J. L. M. Dillen, O. Meth-Cohn, C. Moore, and P. H. van Rooyen, *Tetrahedron*, **44**, 3127 (1988).
15. W. Krebs, E. Franken, M. Müller, H. Colberg, W. Cholcha, J. Wilken, J. Ohrenberg, R. Albrecht, and E. Weiss, *Tetrahedron Lett.*, **33**, 5947 (1992).
16. E. Tedesco, B. M. Kariuki, K. D. M. Harris, R. L. Johnston, O. Pudova, G. Barbarella, E. A. Marseglia, G. Gigli, and R. Cingolani, *J. Solid State Chem.*, **161**, 121 (2001).
17. L. Antolini, E. Tedesco, G. Barbarella, L. Favaretto, G. Sotgiu, M. Zambianchi, D. Casarini, G. Gigli, and R. Cingolani, *J. Am. Chem. Soc.*, **122**, 9006 (2000).
18. J. Nakayama, Y. Sano, Y. Sugihara, and A. Ishii, *Tetrahedron Lett.*, **40**, 3785 (1999).
19. R. Albrecht and E. Weiss, *J. Organomet. Chem.*, **399**, 163 (1990).
20. K. Hoffmann and E. Weiss, *J. Organomet. Chem.*, **128**, 389 (1977).
21. R. Albrecht and E. Weiss, *J. Organomet. Chem.*, **413**, 355 (1991).
22. F. Meier-Brocks and E. Weiss, *J. Organomet. Chem.*, **453**, 33 (1993).
23. P. Pouzet, I. Erdelmeier, D. Ginderow, J.-P. Mornon, P. Dansette, and D. Mansuy, *J. Chem. Soc. Chem. Commun.*, 473 (1995).
24. J. A. Hashmall, V. Horak, L. E. Khoo, C. O. Quicksall, and M. K. Sun, *J. Am. Chem. Soc.*, **103**, 289 (1981).
25. I. Rozas, *J. Phys. Org. Chem.*, **5**, 74 (1992).
26. B. Jiang and T. Don Tilley, *J. Am. Chem. Soc.*, **121**, 9744 (1999).
27. N. Furukawa, S.-Z. Zhang, E. Horn, O. Takahashi, and S. Sato, *Heterocycles*, **47**, 793 (1998).
28. J. Nakayama, T. Yu, Y. Sugihara, and A. Ishii, *Chem. Lett.*, 499 (1997).
29. S.-Z. Zhang, S. Sato, E. Horn, and N. Furukawa, *Heterocycles*, **48**, 227 (1998).
30. E. Skaugset, T. B. Rauchfuss, and C. L. Stern, *J. Am. Chem. Soc.*, **112**, 2432 (1990).
31. M. S. El Amoudi El Faghi, P. Geneste, J. L. Olive, A. Dubourg, J. Rambaud, and J.-P. Declercq, *Acta crystallogr.*, **C43**, 2421 (1987).
32. M. S. El Amoudi El Faghi, P. Geneste, J. L. Olive, J. Rambaud, and J.-P. Declercq, *Acta crystallogr.*, **C44**, 498 (1988).

33. R. P. Gajewski, J. L. Jackson, N. D. Jones, J. K. Swartzendruber, and J. B. Deeter, *J. Org. Chem.*, **54**, 3311 (1989).
34. V. E. Udre, E. Ya. Lukevics, A. A. Kemme, and Ya. Ya. Bleidelis, *Khim. Geterotsikl. Soedin.*, 320 (1980).
35. A. A. Kemme, M. F. Bundule, Ya. Ya. Bleidelis, V. E. Udre, and E. Lukevics, *Zh. Strukt. Khim.*, **21**, No. 6, 123 (1980).
36. R. Guillard and Y. Dusausoy, *J. Organomet. Chem.*, **77**, 393 (1974).
37. H.-H. Chen, J. A. May, and V. M. Lynch, *J. Heterocycl. Chem.*, **36**, 249 (1999).
38. L. R. Kronfeld and R. L. Sass, *Acta crystallogr.*, **B24**, 981 (1968).
39. I. Goldberg and U. Shmueli, *Acta crystallogr.*, **B27**, 2173 (1971).
40. V. M. Polosin, A. A. Astakhov, I. A. Tafeenko, and A. V. Ivashchenko, *Zh. Obshch. Khim.*, **62**, 367 (1992).
41. D. R. Boyd, N. D. Sharma, S. A. Haughey, J. F. Malone, B. T. McMurray, G. N. Sheldrake, C. C. R. Alien, and H. Dalton, *J. Chem. Soc. Chem. Commun.*, 2363 (1996).
42. G. G. Rode, T. E. Bezmenova, M. Yu. Antipin, Yu. T. Struchkov, I. A. Litvinov, A. I. Yanovskii and G. V. Klimusheva, *Zh. Strukt. Khim.*, **25**, No. 4, 160 (1984).
43. G. V. Klimusheva, T. E. Bezmenova, G. M. Soroka, and G. G. Rode, *Tetrahedron*, **36**, 1667 (1980).
44. G. G. Rode, T. E. Bezmenova, M. Yu. Antipin, Yu. T. Struchkov, and G. V. Klimusheva, *Zh. Strukt. Khim.*, **25**, 158 (1984).
45. G. G. Rode, D. S. Yufit, T. E. Bezmenova, and G. V. Klimusheva, *Ukr. Khim. Zh.*, **53**, 751 (1987).
46. G. G. Rode, D. S. Yufit, Yu. T. Struchkov, A. N. Chernego, T. E. Bezmenova, and G. V. Klimusheva, *Ukr. Khim. Zh.*, **53**, 1309 (1987).
47. H. J. Kuhn, R. Defoin, K. Gollnick, C. Kruger, Y.-H. Tsay, L.-K. Liu, and P. Betz, *Tetrahedron*, **45**, 1667 (1989).
48. B. R. Dent and G. J. Geinsford, *Aust. J. Chem.*, **42**, 1307 (1989).
49. V. M. Berestovitskaya, M. F. Bundule, Ya. Ya. Bleidelis, and I. E. Efremova, *Zh. Obshch. Khim.*, **54**, 1182 (1984).
50. E. Lukevics, P. Arsenyan, S. Belyakov, J. Popelis, and O. Pudova, *Eur. J. Org. Chem.*, 3139 (2000).
51. S. Gronowitz, G. Nikitidis, A. Hallberg, and C. Stalhandske, *Acta Chem. Scand.*, **B41**, 297 (1987).
52. S. Gronowitz, G. Nikitidis, A. Hallberg, and C. Stalhandske, *Acta Chem. Scand.*, **45**, 636 (1991).
53. S.-K. Yeo, M. Shiro, and K. Kanematsu, *J. Org. Chem.*, **59**, 1621 (1994).
54. G. A. Jefferey, *Acta Crystallogr.*, **4**, 58 (1951).
55. G. G. Rode, T. E. Bezmenova, M. Yu. Antipin, Yu. T. Struchkov, G. V. Klimusheva, and A. P. Polishchuk, *Zh. Strukt. Khim.*, **25**, No. 4, 159 (1984).
56. T. Fernandez, D. Suarez, J. A. Sordo, F. Monnat, E. Roversi, A. E. de Castro, K. Schenk, and P. Vogel, *J. Org. Chem.*, **63**, 9490 (1998).
57. A. Laila and N. S. Isaacs, *Monatsh. Chem.*, **116**, 933 (1985).
58. V. M. Berestovitskaya, M. F. Bundule, Ya. Ya. Bleidelis, and I. E. Efremova, *Zh. Obshch. Khim.*, **56**, 375 (1986).
59. G. Hieber, M. Hanack, K. Wurst, and J. Strähle, *Chem. Ber.*, **124**, 1597 (1991).
60. V. V. Tkachev, L. O. Atovmyan, V. M. Berestovitskaya, and I. E. Efremova, *Zh. Strukt. Khim.*, **33**, No. 5, 103 (1992).
61. J. H. Eekhof, H. Hogeveen, and R. M. Kellogg, *J. Organomet. Chem.*, **161**, 361 (1978).