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MOLECULAR STRUCTURE OF COMPOUNDS CONTAINING A 2,2'-BITHIENYL FRAGMENT (REVIEW)

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The results of X-ray crystallographic investigations of compounds containing a 2,2'-bithienyl fragment are summarized and analyzed. The structural characteristics of unsubstituted bithiophene, 5-monosubstituted, 5,5'-, 3,3'-, 4,4'-, and 3,4'-disubstituted, and more highly substituted bithiophenes and also the structure of α-conjugated oligothiophene derivatives are considered.

Keywords: bithiophene, molecular structure, octithiophene, quaterthiophene, quinquethiophene, sexithiophene, terthiophene.

Investigations of organic π-conjugated oligomers and polymers are of great significance in the creation of prospective materials for electronics and optics. The oligomeric derivatives of thiophene, which are of interest both from the scientific and the practical point view, occupy a special position among such compounds. In view of the unusual electronic and optical characteristics and also the high chemical and thermal stability these compounds have been studied as active layers for field-effect transistors and used in the creation of devices based on the semiconducting and electroluminescent properties [1-4]. In connection with the fact that the characteristics of the oligothiophenes are determined primarily by special features of the molecular structure such as the planarity of the π-conjugated system and the three-dimensional packing of the molecules an X-ray crystallographic analysis of single crystals for a series of bithiophenes was undertaken. The structure of longer oligothiophenes has been studied to a significantly lesser degree.

1. 2,2'-BITHIOPHENES

The molecular structure of 2,2'-bithiophene was first determined in 1968 [5], but the authors of this early investigation drew attention to the instability of the crystals under the experimental conditions and the low accuracy of the determination of the bond lengths and the sizes of the angles (error 0.02-0.03 Å, 1-2°, $R = 0.08$). In connection with the fact that the structure of the compound is extremely important as a model during analysis of the effect of substituents at the various positions of bithiophene and also in the transition to the oligothiophene derivatives the geometric parameters of the 2,2'-bithiophene molecule at 173 ($R = 0.056$) [6] and 133 K ($R = 0.046$) [7] were refined. At 173 K the molecules are planar and most of them have the transoid arrangement of the sulfur atoms, but as a result of the sulfur and $C_{(3)}$ atoms disordering part of the molecules (15%) are in the cisoid form. At 133 K the centrosymmetric molecule of 2,2'-bithiophene (**1**) is planar, and the sulfur atoms are in the *trans* orientation in relation to each other.

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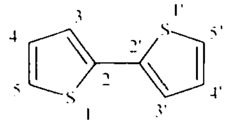
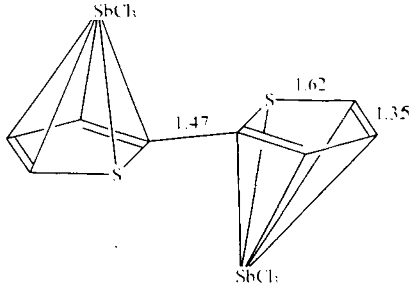


1

The geometric parameters of the 2,2'-bithiophene molecule **1** at 133 and 173 K are given in Table 1. The differences in the length of the $S_{(1)}$-$C_{(2)}$ and $C_{(2)}$-$C_{(3)}$ bonds, obtained at various temperatures, are determined by the disorder of the molecule at the higher temperature.

The structure of the π-complex of antimony with 2,2'-bithiophene **2** [8] is of particular interest. Like bithiophene, the heterocyclic system in this compound is planar and has the *trans* orientation. Each thiophene ring is π-bonded with the $SbCl_3$ groups, situated on different sides of the plane of the bithiophene. In the complex **2** the $C_{(2)}$-$C_{(2')}$, C–S, and $C_{(3)}$-$C_{(4)}$ bonds and the C–S–C angle are the most subject to the influence of π coordination. The C–S distances are reduced, while the other parameters mentioned above are increased compared with the initial molecule. The π bonding between the antimony atom and the thiophene ring is demonstrated by the Sb–C (3.34-3.66 Å) and Sb–S (3.31 Å) distances, but it should be noted that the Sb–S bond is substantially shorter.

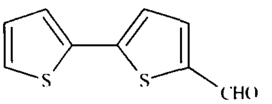


2

The structure of certain 5-monosubstituted 2,2'-bithiophene derivatives was also studied by X-ray crystallographic analysis [9-15].

TABLE 1. The Geometric Parameters of the 2,2'-Bithiophene Molecule **1**

Type of bond or angle	Bond length (Å) or angle (deg)	
	133 K [7]	173 K [6]
$S_{(1)}$–$C_{(2)}$	1.713(3)	1.720(2)
$C_{(2)}$–$C_{(3)}$	1.432(4)	1.425(3)
$C_{(3)}$–$C_{(4)}$	1.444(5)	1.443(2)
$C_{(4)}$–$C_{(5)}$	1.357(5)	1.354(3)
$C_{(5)}$–$S_{(1)}$	1.698(4)	1.694(2)
$C_{(2)}$–$C_{(2')}$	1.448(4)	1.444(3)
$S_{(1)}$–$C_{(2)}$–$C_{(3)}$	112.5(2)	112.3(1)
$C_{(2)}$–$C_{(3)}$–$C_{(4)}$	108.0(3)	108.3(2)
$C_{(3)}$–$C_{(4)}$–$C_{(5)}$	114.9(3)	114.8(2)
$C_{(4)}$–$C_{(5)}$–$S_{(1)}$	112.1(3)	112.4(1)
$C_{(5)}$–$S_{(1)}$–$C_{(2)}$	92.5(2)	92.20(9)
$S_{(1)}$–$C_{(2)}$–$C_{(2')}$	121.2(2)	120.4(1)
$C_{(3)}$–$C_{(2)}$–$C_{(2')}$	126.4(3)	127.3(2)



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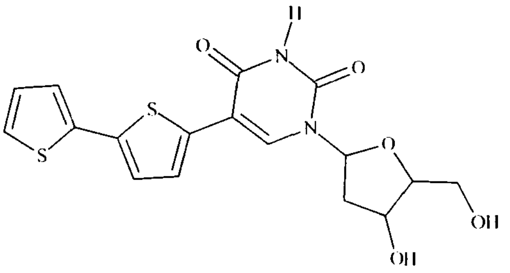
The structure of 2,2'-bithiophene-5-carbaldehyde (**3**) [9] represents a rare case where the sulfur atoms are predominantly in the cisoid conformation in relation to the C–C bond linking the two thiophene rings. The fraction of the transoid form amounts to only 20% and results from the disordering of the $S_{(1')}$ and $C_{(3')}$ atoms, which has a substantial effect on the accuracy of the geometric parameters of the molecule and increases the length of the $C_{(2')}$–$C_{(3')}$ bond to 1.504 Å. The two thiophene heterocycles and the aldehyde group are practically coplanar.



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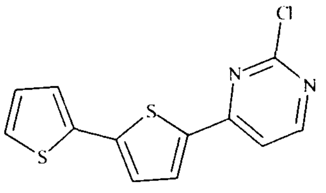

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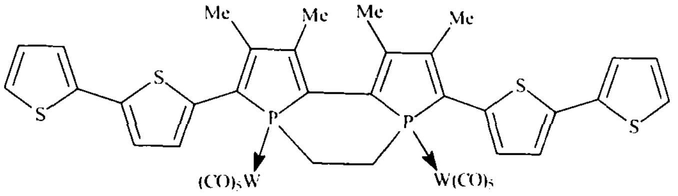
The terminal thiophene group in compound **4** is also disordered, and the ratio of the transoid and cisoid forms is 55:45. The almost planar bithienyl system is twisted in relation to plane of the uracil ring in such a way that the torsional angle $S_{(1)}$–$C_{(5)}$–C–C(O) is 25.3°. The distance between the sulfur atom $S_{(1)}$ and the oxygen atom of the nearest carbonyl group of the uracil amounts to 2.949 Å, which is less than the sum of the van der Waals radii.

In the molecule of 4-[5-(2,2'-bithienyl)]-2-chloropyrimidine (**5**) [11] the bithienyl fragment has the transoid orientation, while the nitrogen atom of the pyrimidine is in the cisoid conformation in relation to the sulfur atom of the neighboring thiophene ring.



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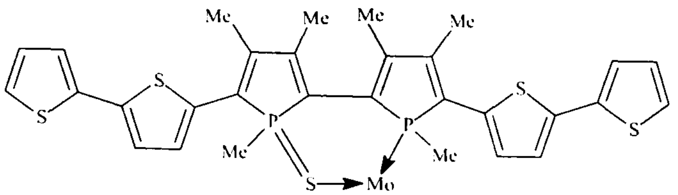

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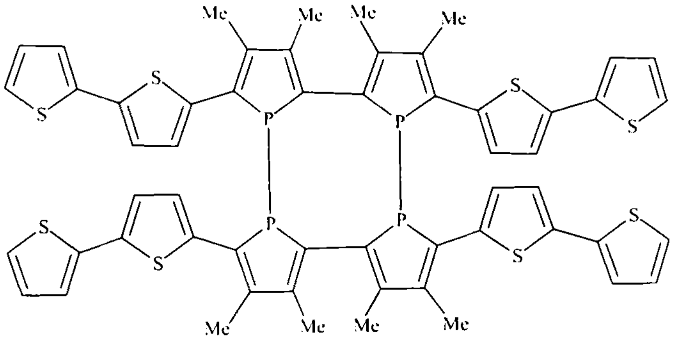
In the molybdenum **6** [12] and tungsten **7** [12] complexes the two bithiophene fragments are linked by a biphosphole group into a single π-conjugated system. The bithienyl groups of compound **6** form a quasiplanar system with the neighboring phosphole ring, and the dihedral angle between the two central phosphorus-containing heterocycles amounts to 55.6°. More significant departures from coplanarity are observed for the complex **7**, in which the dihedral angle between the thiophene and phosphole rings is 24.34 Å, and that between the phosphole rings is 66.26 Å. The bond lengths and the angles of the transoid bithiophene groups in compounds **6** and **7** do not fall outside the range of normal values.



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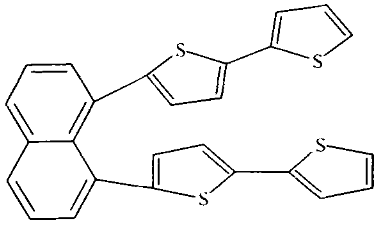
The structure of compound **8** [12] with a conjugated chain of heterocycles analogous with the complexes **6** and **7** was also investigated by X-ray analysis, but the geometric parameters of the molecule were determined inaccurately on account of the high value of the R factor ($R = 0.156$).

The two bithiophene groups of 1,8-bis[5-(2,2'-bithienyl)]naphthalene (**9**) [13] are linked to the naphthalene ring and are in the *trans* conformation in relation to each other. The inner heterocycles are almost parallel and form an angle of 57° with the naphthalene plane. The bithiophene systems as a whole are nonplanar and are characterized by twist angles of 16 and 28°. The C–C distances between the naphthalene and thiophene rings (1.484 and 1.482 Å) are larger than between the thiophene rings (1.443 and 1.460 Å).



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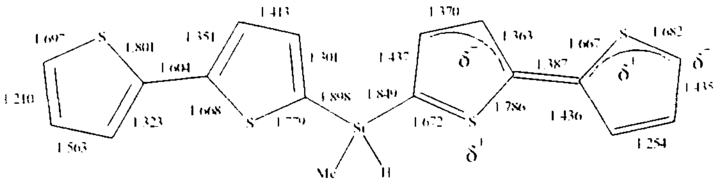
According to the data of X-ray analysis, bis[5-(2,2'-bithienyl)]methylsilane (**10**) [14] has an unusual structure. One bithienyl group is characterized by the usual transoid almost planar structure (dihedral angle between the planes of the thiophene rings 3.2°), whereas the second one represents a stable mesomeric form of the semiquinone type with typical double bonds between the thiophene rings (1.387 Å) and the $C_{(3')}$–$C_{(4')}$ bond (1.254 Å) of the terminal thiophene. The lengths of the analogous bonds in a bithienyl group with the normal structure correspond to single C–C bonds and are 1.604 and 1.563 Å respectively.



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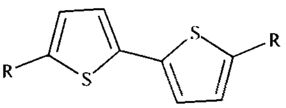
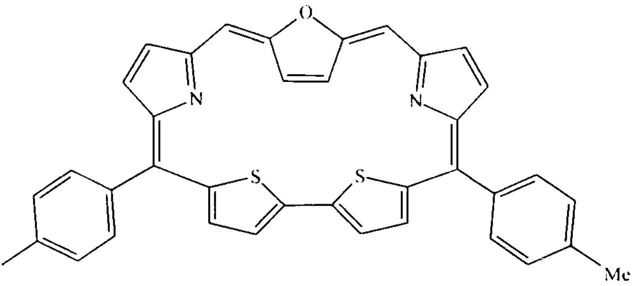
All the 5,5'-disubstituted 2,2'-bithiophenes **11** are characterized by the transoid arrangement of the sulfur atoms and relative planarity of the bithiophene fragment. The main geometric parameters of these derivatives are given in Table 2. The presence of electron-withdrawing and electron-donating groups in the molecule of unsymmetrical 5-dimethylamino-5'-nitro-2,2'-bithiophene leads to delocalization of the electron density and equalization of the C–C bonds in the bithiophene.



11

The molecular structure of sapphirine **12** [25], in which the bipyrrole fragment is substituted by 2,2'-bithiophene, was investigated. This is the only derivative of 5,5'-disubstituted 2,2'-bithiophenes with the cisoid arrangement of the sulfur atoms. The formation of such a conformation is due to the inclusion of the bithiophene group into a macrocyclic structure. The two sulfur atoms and two nitrogen atoms are almost coplanar, and the oxygen atom deviates from this plane as a result of the fact that the furan heterocycle forms an angle of 34° with the plane of the macrocycle.



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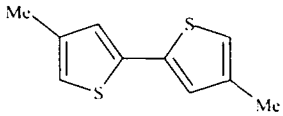
The 4,4'-disubstituted bithiophenes **13-16** also have a planar structure [26-28]. In all the compounds the center of symmetry of the molecule is at the center of the $C_{(2)}$–$C_{(2')}$ bond, and the sulfur atoms have the *anti* orientation.



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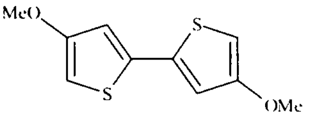

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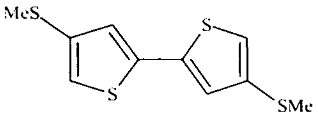

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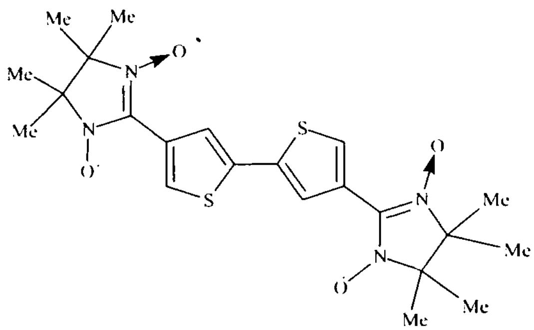

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TABLE 2. The Geometric Parameters of 5,5'-Disubstituted 2,2'-Bithiophenes **11**

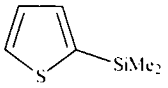
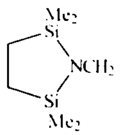
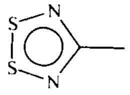
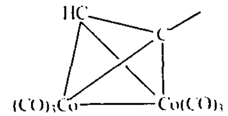
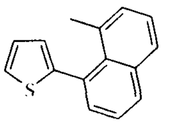
R	Bond length, A						Angle, deg	*R* factor	Reference
	$C_{(2)}-C_{(2')}$	$C_{(2)}-C_{(3)}$	$C_{(3)}-C_{(4)}$	$C_{(4)}-C_{(5)}$	$C_{(2)}-S_{(1)}$	$C_{(5)}-S_{(1)}$	$C_{(2)}-S_{(1)}-C_{(5)}$		
1	2	3	4	5	6	7	8	9	10
Me	1.454(4)	1.370(3)	1.408(3)	1.349(3)	1.719(2)	1.721(3)	92.9(1)	0.053	[16]
Me_3Si	1.446(3)	1.368(3)	1.412(3)	1.374(2)	1.723(2)	1.726(2)	94.2(1)	0.038	[16]
	1.462(8)	1.368(9)	1.445(10)	1.364(9)	1.723(6)	1.732	94.1	0.14	[17]
	1.450(6)	1.364(4)	1.405(5)	1.354(4)	1.728(3)	1.720(3)	92.7(1)	0.073	[18]
								0.045	[19]

TABLE 2 (continued)

1	2	3	4	5	6	7	8	9	10
								0.077	[20]
								0.085	[21]
Br	1.447(11)	1.363(11)	1.413(11)	1.350(12)	1.744(8)	1.713(9)	91.0(4)	0.048	[22]
NO_2	1.445(6)	1.384(6)	1.404(6)	1.351(6)	1.730(4)	1.707(4)	89.6(2)	0.052	[23]
*NO_2	1.438(1)	1.385(3) 1.372(3)	1.399(3) 1.402(3)	1.364(4) 1.383(4)					[24]

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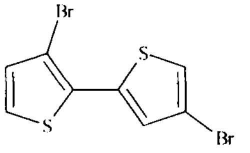
* Substituent at position 5'-Me_2N.

In compound **16** [28] the dihedral angle between the planes of the imidazolyl and bithiophene heterocycles is 21°.



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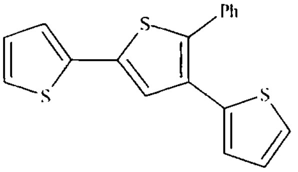
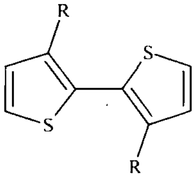


18

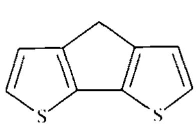
The structure of the only representatives of unsymmetrical 3,4'- and 4,5-disubstituted 2,2'-bithiophenes 3,4'-dibromo-2,2'-bithiophene (**17**) [29] and 4-(2-thienyl)-5-phenyl-2,2'-bithiophene (**18**) [30] was determined. In the molecule of the first compound slight deviation from planarity is observed, and as a result the torsion angle $S_{(1)}$–$C_{(2)}$–$C_{(2')}$–$S_{(1')}$ is 175.0°. The bond lengths and the angles of the heterocycle are comparable with the values determined for the other bithiophenes. The heterocycles in the 2,2'-bithiophene fragment of compound **18** are twisted to a greater degree and form an angle of 160.3°.

The structural investigations of the 3,3'-disubstituted bithiophenes include not only the compounds with an open structure **19** (Table 3) but also numerous derivatives in which positions 3 and 3' are linked by the most diverse bridge fragments, leading to the formation of condensed tricyclic systems. The 3,3'-dialkoxyl and 3,3'-dimethoxyalkyl derivatives **19** (R = MeO, OctO, $MeOCH_2CH_2O$) [30-32] are characterized by the transoid conformation and a nearly planar arrangement of the two thiophene rings. The oxygen atoms linked to the thiophene ring in the case of the dialkoxy derivatives are also almost coplanar with the bithiophene fragment. However, 3,3'-(2-hydroxyethyl)bithiophene **19** (R = $HOCH_2CH_2$) [34] has a noncoplanar *anti* orientation with a torsion angle S–$C_{(2)}$–$C'_{(2)}$–S' of 110.8° and a dihedral angle of 67.5° between the thiophene planes. Each hydroxyl group forms intermolecular hydrogen bonds. In 3,3':2',2'':3'',3'''-quaterthiophene (**19**) (R = 2-thienyl) [35] each of the heterocycles is planar, but the molecule as a whole is nonplanar. The dihedral angle between the terminal and inner heterocycles amounts to 20.3°, while that between the inner heterocycles is 109.4°. The $C_{(2)}$–$C_{(2')}$ bond is increased to 1.508 Å on account of steric hindrances.



19

In compounds **20-23** [36-39] positions 3 and 3' are linked by a carbon atom. As a rule the tricyclic condensed system in all the derivatives is nearly planar. For the bithiophenes **20** and **21** [37] certain steric strains were observed due to the presence of the short bridge and expressed in a considerable spread (~20°) of the $C_{(3)}$–$C_{(2)}$–$C_{(2')}$, $C_{(3')}$–$C_{(2')}$–$C_{(2)}$, S'–$C_{(2')}$–$C_{(2)}$, and S–$C_{(2)}$–$C_{(2')}$ angles.



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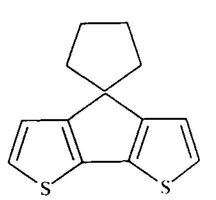

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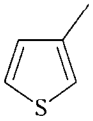
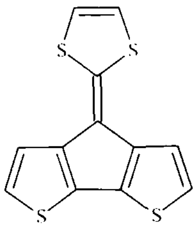
TABLE 3. The Geometric Parameters of 3,3'-Disubstituted 2,2'-Bithiophenes **19**

R	Bond length, A						Angle, deg $C_{(2)}$ $S_{(1)}$ $C_{(5)}$	*R* factor	Reference
	$C_{(2)}$ $C_{(2')}$	$C_{(2)}$ $C_{(3)}$	$C_{(3)}$ $C_{(4)}$	$C_{(4)}$ $C_{(5)}$	$C_{(2)}$ $S_{(1)}$	$C_{(5)}$ $S_{(1)}$			
OMe									[31]
OOct (195 K)	1.445(2)	1.379(2)	1.422(3)	1.362(3)	1.739(2)	1.710(2)	92.1(1)	0.036	[32]
OCH_2CH_2OMe									[33]
CH_2CH_2OH	1.481	1.366	1.435	1.325	1.727	1.710	110.8		[34]
	1.508(8)	1.357(8)	1.435(8)	1.325(9)	1.731(6)	1.706(7)	90.9(3)	0.021	[35]

The two independent molecules of compound **22** [38] and the molecule of bithiophene **23** [39], containing a 1,3-dithiol-2-ylidene group at the bridging carbon atom, are planar.



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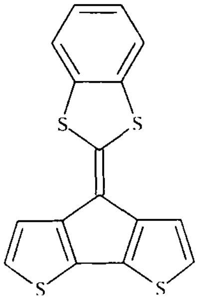

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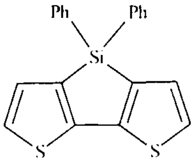
Replacement of the methylene bridge by a diphenylsilyl group (compound **24**) [40] does not affect the planarity of the molecule, as shown by the sum of the angles (360°) at each of the carbon atoms of the silole ring. The introduction of a second silicon atom is accompanied by twisting of the molecules in compounds **25** [41] (R = Me, Ph) and deviation from planarity. The angle of rotation of the thiophene rings amounts to 20.2 and 24.6° respectively for the tetramethyl and dimethyldiphenyl derivatives.



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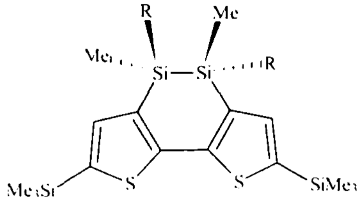
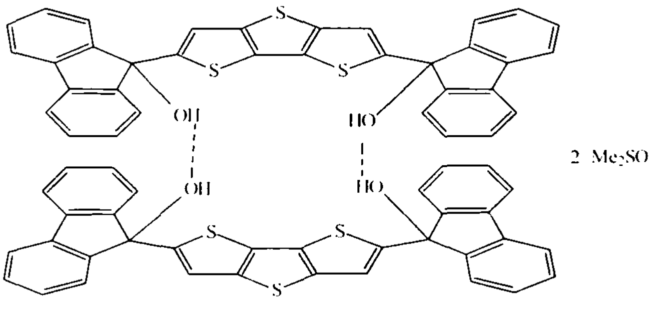
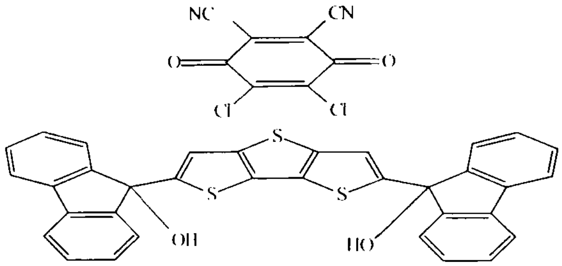


25

In compounds **26-31** [42-45] a sulfur atom acts as bridge between positions 3 and 3' of the bithiophene group. In all the derivatives the fused heterocyclic system is planar. The dimers **26** [42] are formed as a result of hydrogen bonds. The condensed heterocycles in the dimer lie in parallel planes and have the *anti* orientation. The reaction of the monomer compound **26** with dichlorodicyanobenzoquinone gave a charge-transfer complex **27** [43]. Differences in the length of the bonds of the dithieno[3,2-*b*:2',3'-*d*]thiophene group in the transition from the neutral form to the charge-transfer complex were observed for the internal C=C double bonds. The C=C distances in the complex were longer (1.386 and 1.389 Å) than in compound **26** (1.374 and 1.376 Å).

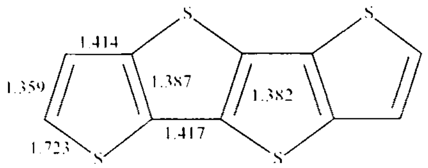


26



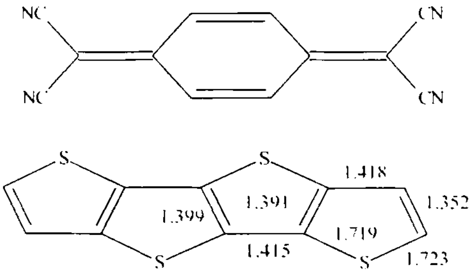
27

Each five-membered ring of compound **28** [44] is planar, and the molecule as a whole is nearly planar. Only the sulfur atoms deviate by 0.001 Å from the mean plane. The peripheral C=C double bonds (1.359 Å) are significantly shorter than the internal double bonds (1.387, 1.382 Å).



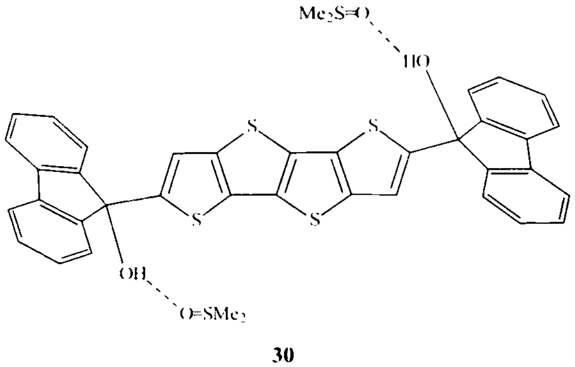
28

The donor molecule **28** forms the charge-transfer complex **29** [44] with the acceptor molecule of tetracyanoquinodimethane. In the complex both parts are absolutely planar, and in the crystalline state they form "stacks" with alternating planes, the shortest distance between which is 3.601 Å.

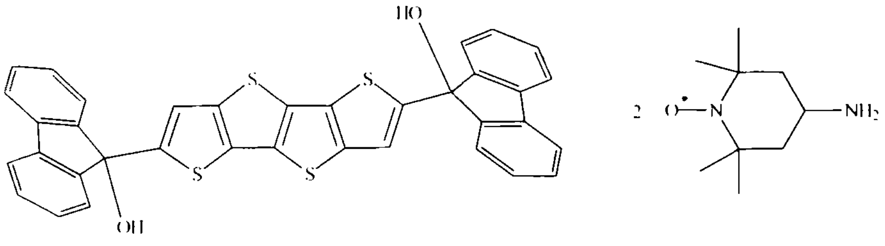


29

In contrast to the bithiophene **26**, according to X-ray data compound **30** [42] is monomeric.

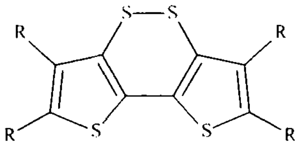


30



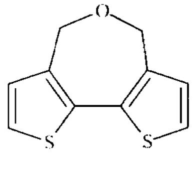
31

According to X-ray data, the tricycles of compounds **32** (R = H [46, 47], Me [48, 49]), as in the disilane derivatives **25**, are twisted (torsion angle C–S–S–C 50.85 and 52.55°), and the thiophene rings are displaced in relation to each other by 20-21°.

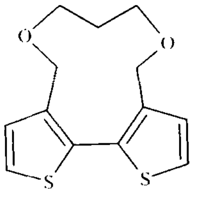


32

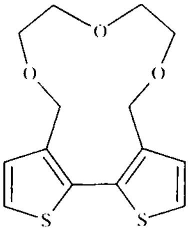
The elongation of the bridging fragment also changes the relative orientation of the thiophene rings. Thus, in the bithiophene derivative **33** [37] with the CH_2OCH_2 chain the torsion angle $S_{(1)}$–$C_{(2)}$–$C_{(2')}$–$S_{(1')}$ amounts to 7.7 and 11.8° for the two independent molecules, and in compound **34** [37] it even reaches 109.6°. However, it should be noted that further increase in the length of the bridge to $CH_2(OCH_2CH_2)OCH_2$ is accompanied by a decrease of the torsion angle $S_{(1)}$–$C_{(2)}$–$C_{(2')}$–$S_{(1')}$ in compound **35** [37] to 56.8°. The main geometric parameters of the condensed tricyclic derivatives are given in Table 4.



33

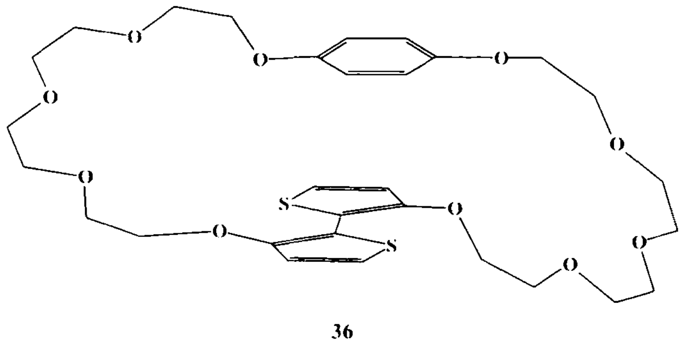


34



35

The structure of the macrocyclic pseudopolyrotaxane **36** [33] and its "host–guest" complex with diquaternized 4,4'-bipyridine **37** [50] was studied by X-ray crystallographic analysis. As a result it was established that the bithiophene fragment in both cases is planar with a transoid arrangement of the thiophene rings.



36

TABLE 4. The Geometric Parameters of the 3,3'-Disubstituted Condensed 2,2'-Bithiophenes

Compound	Bond length, Å						Angle, deg	R factor	Reference
	$C_{(2)}$-$C_{(2')}$	$C_{(2)}$-$C_{(3)}$	$C_{(3)}$-$C_{(4)}$	$C_{(4)}$-$C_{(5)}$	$C_{(2)}$-$S_{(1)}$	$C_{(5)}$-$S_{(1)}$	$C_{(2)}$-$S_{(1)}$-$C_{(5)}$		
1	2	3	4	5	6	7	8	9	10
20*	1.444(3)	1.373(3) 1.370(3)	1.413(3) 1.405(3)	1.346(3) 1.354(3)	1.710(2) 1.727(2)	1.718(2) 1.729(2)	90.7(1) 90.4(1)	0.031	[37]
	1.438(3)	1.370(3) 1.372(3)	1.409(3) 1.408(3)	1.354(3) 1.353(3)	1.719(2) 1.728(2)	1.713(2) 1.712(2)	90.7(1) 90.6(1)		
21*^{2}	1.448(3)	1.365(2) 1.374(3)	1.421(3) 1.421(3)	1.352(3) 1.355(2)	1.707(2) 1.708(2)	1.716(2) 1.722(2)	90.6(1) 90.5(1)		
	1.447(3)	1.369(2) 1.369(3)	1.408(3) 1.418(3)	1.355(3) 1.355(3)	1.711(2) 1.707(2)	1.712(2) 1.717(2)	90.6(1) 90.4(1)	0.034	[37]
	1.449(3)	1.366(3) 1.370(3)	1.411(3) 1.409(3)	1.354(3) 1.359(3)	1.711(2) 1.708(2)	1.719(2) 1.711(2)	90.4(1) 90.4(1)		
24	1.455(4)	1.384(4) 1.372(4)	1.418(5) 1.424(4)	1.360(6) 1.360(5)	1.707(3) 1.720(3)	1.708(9) 1.714(4)	91.3(2) 91.0(2)	0.057	[40]
25 (R=Me)	1.45(1)	1.38(1) 1.37(1)	1.42(1) 1.43(1)	1.39(1) 1.35(1)	1.738(7) 1.741(8)	1.722(8) 1.733(8)	93.6(4) 92.5(4)	0.042	[41]
25 (R=Ph)	1.455(5)	1.381(5) 1.379(50)	1.421(6) 1.412(5)	1.369(6) 1.366(5)	1.725(4) 1.736(4)	1.723(4) 1.724(4)	93.4(2)	0.038	[41]

TABLE 4 (continued)

1	2	3	4	5	6	7	8	9	10
32 (R = H)	1.419(10)	1.363(9) 1.373(9)						0.039	[46, 47]
32 (R = Me)	1.450(3)	1.376(3) 1.365(3)						0.0367	[48, 49]
33*	1.450(2)	1.364(2) 1.368(3)	1.419(2) 1.409(3)	1.340(4) 1.340(4)	1.728(1) 1.728(1)	1.705(3) 1.709(2)	92.0(1)	0.032	[37]
	1.450(2)	1.366(1) 1.366(2)	1.420(3) 1.410(3)	1.334(3) 1.344(3)	1.736(1) 1.723(1)	1.704(2) 1.701(2)	91.8(1)		
34	1.463(2)	1.365(1)	1.422(2)	1.343(2)	1.730(1)	1.703(1)	92.3(1)	0.032	[37]
35	1.468(2)	1.366(3)	1.437(2)	1.342(3)	1.729(2)	1.708(2)	91.9(1)	0.035	[37]

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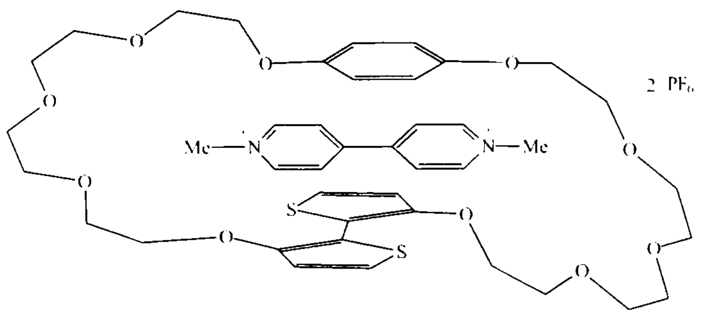
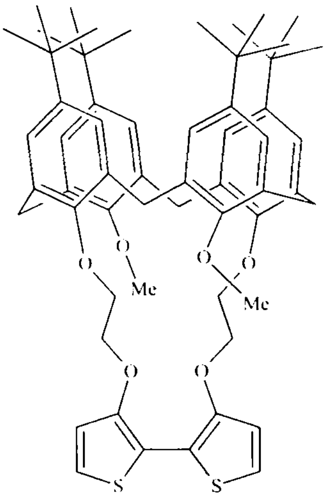
* For the two independent molecules.

*[2] For the three independent molecules.



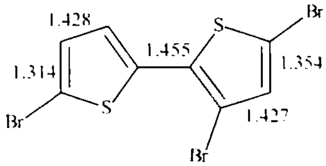
37

Structure **38** represents the product from the functionalization of 3,3'-dihydrobithiophene with calix[4]arene. The torsion angle $S_{(1)}$–$C_{(2)}$–$C_{(2')}$–$S_{(1')}$ is 68°.



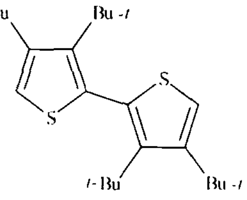
38

The molecule of 3,5,5'-tribromo-2,2'-bithiophene **39** [52], like the molecules of 5,5'-dibromo-2,2'-bithiophene **11** (R = Br) and 3,4'-dibromo-2,2'-bithiophene **17**, is almost planar (dihedral angle 4.6°) and has the *trans* orientation. The geometric parameters do not fall outside the normal range of values.



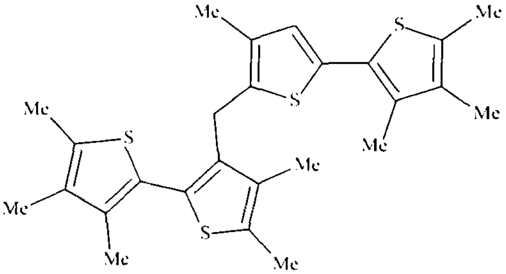
39

The steric effect of the four *tert*-butyl substituents in the molecule of 3,4,3',4'-tetra(*tert*-butyl)-2,2'-bithiophene (**40**) [53] leads to the result that the two thiophene rings are almost perpendicular to each other. Each heterocycle is planar, but the *tert*-butyl groups are displaced from the plane and form torsion angles of 9.9 and 8.5°.



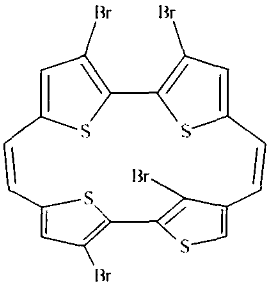
40

It was established by X-ray analysis that the oxidation of 3,4,5,4',5'-pentamethyl-2,2'-bithiophene with iron(III) chloride hexahydrate in acetonitrile leads to the formation of the dimeric product **41** [54], in which the α-methyl group of one molecule is linked to the free β position of a second molecule of bithiophene. The authors draw attention to the ordinary thiophene disorder of the structure.

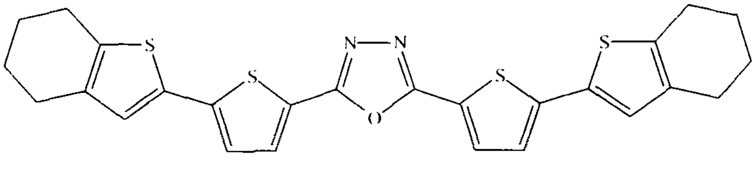


41

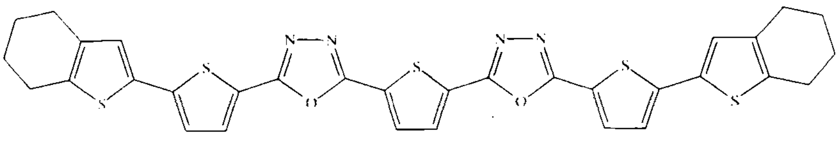
In the crystalline state the molecule of compound **42** [55] has C_2 symmetry with a nonplanar skeleton. One bithiophene fragment, which is practically coplanar with the two double bonds, has the cisoid orientation. In addition, on account of steric hindrances this part of the molecule is characterized by significant shortening of the distance between the two nonbonded sulfur atoms (3.10 Å). The second bithiophene group has the transoid conformation. The planes of the two bithiophene fragments are almost perpendicular to each other.



42



43

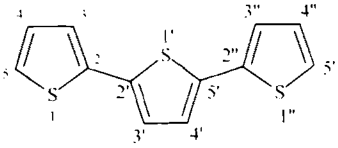


44

The structure of the mixed thiopheno-1,3,4-oxadiazole pentamer **43** [56] and the analogous heptamer **44** [57] is different. In compound **43** the three central heterocycles are planar, and the terminal tetrahydrobenzo[*b*]thienyl groups are slightly twisted (8°) and are disordered in such a way that the *syn* conformation of the bithiophene fragment predominates. The molecules of the hexamer **44** are also characterized by the planarity of the three central rings, and the planar bithiophene groups have a predominantly *anti* orientation (65%).

2. 2,2':5',2"-TERTHIOPHENES

Increase in the length of the oligothiophene chain is usually accompanied by the appearance of additional difficulties during study of the molecular structure of oligothiophenes by X-ray crystallographic analysis. Complications in the calculations appear on account of the extensive disorder of the thiophene rings, and it becomes more difficult to obtain the high-quality single crystals required for the satisfactory diffraction data. This results in low accuracy for the quantitative characteristics. Nevertheless an investigation of the molecular structure for unsubstituted terthiophene **45** and a number of its derivatives was undertaken (Table 5). The unit cell of terthiophene **45** contains two independent but almost identical molecules with the *anti* orientation and with torsion angles of 6-9° at the C–C bonds linking the thiophene rings.



45

The unit cell of the 3'-methyl-substituted terthiophene **46** contains three independent molecules. Two of them are characterized by a nearly planar transoid arrangement of the thiophene rings. The third molecule is disordered with identical populations between the two orientations formed by rotation of the terminal heterocycle by 180° about the $C_{(2)}$–$C_{(2')}$ bond linking the two heterocycles. Disorder of the two thiophene rings (the 2-thienyl substituent in the central ring and the terminal thiophene ring attached to position 5' of the central heterocycle) was detected in 3'-(2-thienyl)terthiophene **47**. As a whole the molecule, like its terthiophene analogs **48** and **49**, is nonplanar, and the dihedral angles between the thiophene rings lie in the range of 29-88°. In the crystalline state one terminal heterocycle of 3,3"-dimethylterthiophene **50** is disordered in such a way that the *syn,anti* (85%) and not the *anti,anti* (15%) conformer predominates.

The 3',4'-disubstituted terthiophenes **51** and **52** have a full transoid conformation; the terthiophene fragment of the dibutyl derivative **51** is deviated from planarity (the angles between the thiophene rings are 35.2 and 30.8°) to a significantly greater degree than in the condensed pyrazine derivative **52** (9.5 and 11.6°).

A common feature of the 5,2"-bissilylterthiophenes **54** and **55** is the quasiplanar *anti* conformation, similar to the conformation typical of the two crystallographically independent molecules of unsubstituted terthiophene [58]. The dihedral angles between the central and terminal heterocycles in compound **54** amount to 13.2 and 11.3°. In the terthiophenophane derivative **55** they are even smaller (8.1 and 7.7°); moreover, the two terthiophene fragments of one molecule have the *anti*-parallel orientation in relation to each other. The central thiophene rings,

TABLE 5. The Geometric Parameters of the Terthiophenes

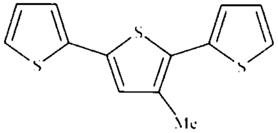
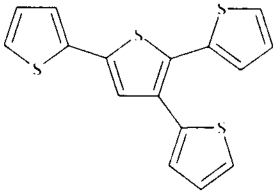
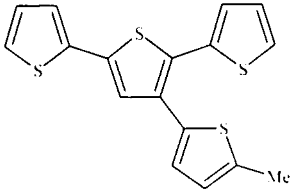
Compound		$C_{(2)}-C_{(2')}$	Angles between thiophene rings	*R* factor	Reference
1		2	3	4	5
46				0.074	[59]
47				0.103	[59]
48			177(2) 95(2)	0.046	[30]

TABLE 5 (continued)

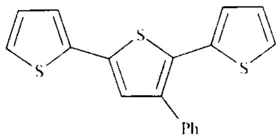
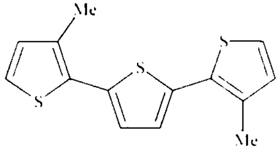
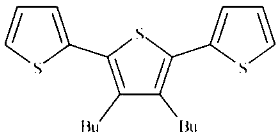
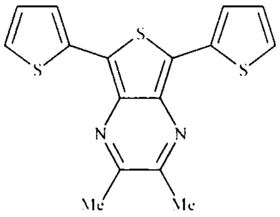
	1	2	3	4	5
49			138.4(8) -136(1)	0.049	[30]
50				0.041	[59]
51		1.47(1) 1.46(1)	35.2 30.8	0.081	[60]
52			9.5 11.6	0.0529	[61]

TABLE 5 (continued)

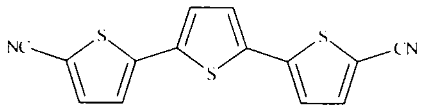
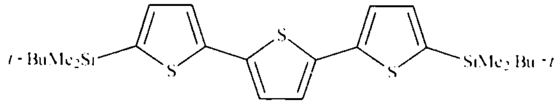
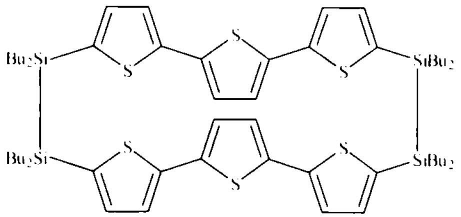
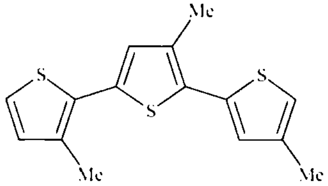
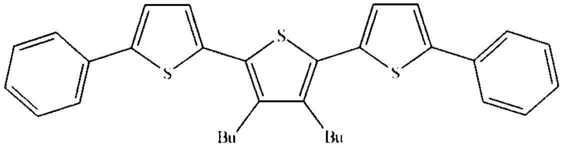
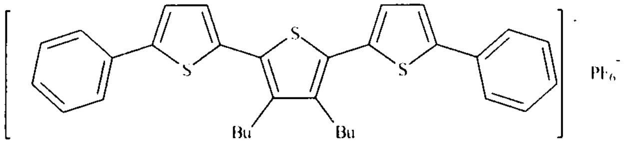
	1	2	3	4	5
53			System close to planar	0.047	[62]
54		1.458(3) 1.462(3)	13.2(1) 11.3(1)	0.0386	[63]
55		1.449(6) 1.428(5)	5.8(3) 4.3(3)	0.043	[64]

TABLE 5 (continued)

1	2	3	4	5
56 	1.429 1.451	7.0 7.8	0.038	[65]
57 	1.468(10) 1.417(7)	26 34	0.0835	[66]
58 	1.423(7) 1.413(7)	Planar system Planar system	0.0727 (293 K) 0.0776 (106 K)	[67] [66]

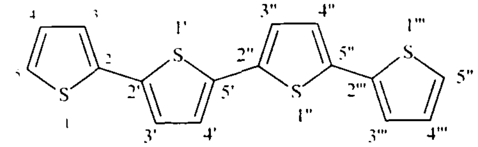
separated by a distance of 3.607 Å, lie exactly one above the other, whereas the terminal rings are slightly displaced in such a way that the sulfur atoms lie above the center of the opposite ring. As a result there is a significant decrease in the intramolecular distances between the sulfur atoms [(S···S) = 3.55 Å]. At the same time a special feature of the terthiophene **54**, due to the presence of the two bulky silyl groups situated on different sides of the mean plane of the thiophene rings, is a substantial increase in the length of the intermolecular contacts. The value of the minimum S···S distance, which is of greatest interest in connection with the crystalline conductivity, is 4.627 Å. The steric effect also determines the stereochemical sandwich-type packing of the molecules.

In 3,4',4"-trimethylterthiophene **56** [64] the central thiophene ring is twisted in relation to the almost coplanar terminal rings by 7.0 and 7.8°. The conformation of the molecule is the same as in unsubstituted terthiophene.

The structures of the neutral terthiophene **57** and its radical-cation **58** were compared. In the neutral compound the α,ω-diphenylterthiophene fragment is nonplanar, the phenyl substituents are twisted in relation to the neighboring heterocycles by 9 and 1°, and the central thiophene ring is rotated by 34 and 26°. The nonplanar molecules are packed into "stacks" in such a way that the atoms of each molecule lie below and above the equivalent neighboring atoms. The intermolecular contacts are fairly large (4.71 Å). The most important differences in the structure of the radical-cation **58** are that its π-conjugated system is planar and, moreover, the neighboring molecules in the oxidized form are packed in alternating order. In the crystal lattice the planar cations overlap with the nearest neighboring layers of the π type, and the interplanar distances between the cations are 3.47 Å. The partly disordered butyl groups are arranged in such a way that they form channels, which are occupied by PF_6^- ions. The geometric parameters of the molecule for the terthiophene **58** at 293 and 106 K are slightly differ.

3. 2,2',5',2",5",2'"-QUATERTHIOPHENES

The structure of the two polymorphous modifications for unsubstituted α-quaterthiophene **59** [68, 69], obtained by crystallization at various temperatures, was investigated by X-ray analysis. The conjugate system in the molecules of both modifications is planar, but the packing of the polymorphous forms differs. The unit cell of the low-temperature modification of quaterthiophene **59** contains four molecules, while that of the high-temperature modification contains two molecules in special positions. The geometric parameters of both forms are summarized in Table 6.



59

TABLE 6. The Geometric Parameters of the Two Forms of α-Quaterthiophene **59**

Type of bond	Bond length, Å	
	Low-temperature modification	High-temperature modification
$S_{(1)}$ $C_{(2)}$	1.717(9)	1.736(11)
$S_{(1)}$ $C_{(5)}$	1.729(9)	1.705(13)
$C_{(2)}$ $C_{(3)}$	1.396(11)	1.385(15)
$C_{(3)}$ $C_{(4)}$	1.429(13)	1.456(17)
$C_{(4)}$ $C_{(5)}$	1.332(15)	1.329(21)
$C_{(2)}$ $C_{(2')}$	1.429(11)	1.467(15)
$S_{(1')}$ $C_{(2')}$	1.715(9)	1.725(11)
$S_{(1')}$ $C_{(5')}$	1.747(7)	1.733(11)
$C_{(2')}$ $C_{(3')}$	1.401(11)	1.369(15)
$C_{(3')}$ $C_{(4')}$	1.430(12)	1.422(15)
$C_{(4')}$ $C_{(5')}$	1.352(11)	1.342(14)
$C_{(5')}$ $C_{(2'')}$	1.424(12)	

The α,ω-dimethyl- and α,ω-(*tert*-butyldimethylsilyl)quaterthiophene **60** and **63** are characterized by centrosymmetric quasiplanar transoid geometry. It should be noted that the two central rings are coplanar while the terminal rings are slightly twisted. As in the bissilyl terthiophene **54**, the silyl substituents of the tetramer **63** have the antiperiplanar orientation; the packing of the molecules is similar.

During comparison of the structure of α,ω-dimethylquaterthiophene **60** and its charge-transfer complex with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane **61** it was established that the molecule of quaterthiophene is relatively long and the 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane is only covered by half the molecule of **60**. In the complex **61** the terminal thiophenes are displaced from the plane to a greater degree (10.34°). In the transition from the neutral quaterthiophene to the complex there is a substantial change in the bond lengths of the inner rings; the double bonds are increased by 0.033 and 0.028 Å, while the single bond is shortened by 0.015 Å.

Structural features of 4',3"-dimethylquaterthiophene **64** are the statistical disorder of the two terminal heterocycles and the *anti* orientation of the inner bithiophene fragment, which is deflected to a significant degree from planarity. As a result the *anti,anti,anti* conformation becomes predominant (88%).

In 3',4"-didecyl-2,2':5',2":5",2'"-quaterthiophene **65** the two inner thiophene rings are coplanar, while the terminal groups in the main conformer occupy the *anti* conformation. However, the *syn* conformer is also present in a small amount, generating structural defects in the oligothiophene fragment. The dihedral angles between the planes of the terminal groups with the neighboring inner rings amount to 3.6° and 5.0° for the major and minor conformers respectively. In the crystal of 3',4"-dimethoxy-2,2':5',2":5",2'"-quaterthiophene **66** there are two different directions orthogonal with each other in the orientation of the almost planar transoid quaterthiophene chains.

The structure of the three tetramethyl-substituted quaterthiophenes **67-69** differs and is determined by the position of the methyl groups. The molecules of 4,4',3",4'"-tetramethylquaterthiophene **67** have the *anti* orientation and are almost coplanar. Only the terminal groups are slightly turned (3.4°) in relation to the central groups. The 3,3',4",3'"-tetramethyl isomer **68**, in which the outer heterocycles are characterized by a nonplanar *syn* orientation, have an unusual structure for quaterthiophenes, and the dihedral angle amounts to 54.2°. Such a conformation seems highly unexpected, particularly in view of the fact that the methyl groups in this case also adopt the *syn* orientation. The molecule as a whole has an inversion center at the center of the C–C bond linking the two central heterocycles, and they are therefore planar and have the *trans* orientation. In compound **69** disorder similar to the quaterthiophene **64** is observed with the only difference that only one terminal ring is disordered. All four thiophene groups are deviated to a significant degree from coplanarity and form dihedral angles of 11.8, 28.8, and 21.3°.

The possibility of conformational polymorphism in the molecules of oligothiophenes was first demonstrated for the case of 3,3',4",3'"-tetrakis(methylthio)quaterthiophene **70**. The deep-orange single crystals of this compound belong to the triclinic symmetry group [76], while the yellow crystals belong to the monoclinic form [77]. The two independent molecules of the triclinic modification have the full *trans* orientation with the terminal thiophenes displaced from the plane of the bithiophene by 27.4° in opposite directions. The central bithiophene fragment in the monoclinic form is also planar and *anti*-oriented, whereas the terminal thiophenes exhibit the *syn* conformation and are deviaced to a significant degree from the plane (55.0°). An analogous structure is characteristic of the above-mentioned 3,3',4",3'"-tetramethylquaterthiophene **68**.

The data from X-ray analysis of compound **71** show that the fully planar molecules have very close packing; as a result the minimum distance between the carbon atoms of neighboring molecules amounts to 3.557 Å, and that between the sulfur atoms amounts to 3.394 Å. Some of the geometric parameters of the substituted quaterthiophenes are given in Table 7.

4. QUINQUE-, SEXI-, AND OCTITHIOPHENES

In the series of quinquethiophenes only the structures of 3",4"-dibutylquinquethiophene **72** [79] and α,ω-dicyanoquinquethiophene **73** [62] have been studied by X-ray analysis. The crystal cell of the first compound contains four independent molecules, three of which have a fully *anti*-oriented conformation, while in the fourth

TABLE 7. The Geometric Parameters of the Quaterthiophenes

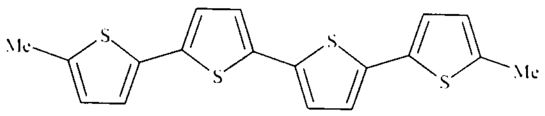
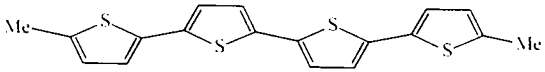
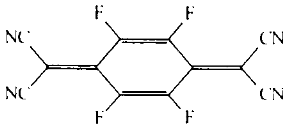
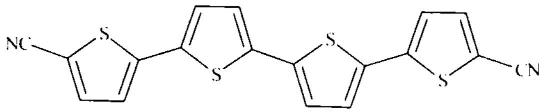
Compound		$C_{(2)}$–$C_{(2')}$	Angles between the thiophene rings	*R* factor	Reference
1		2	3	4	5
60			3.49		[70]
					
61			10.34	0.076	[71]
62			System close to planar	0.031	[62]

TABLE 7 (continued)

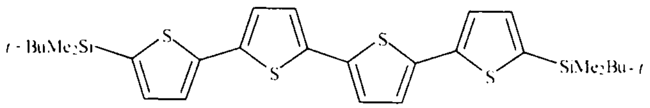
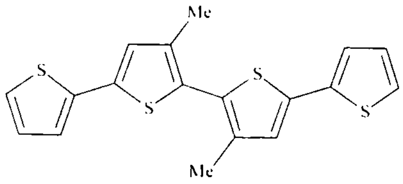
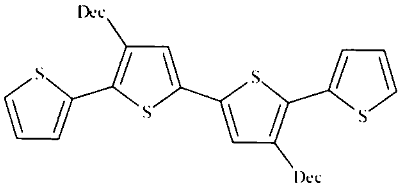
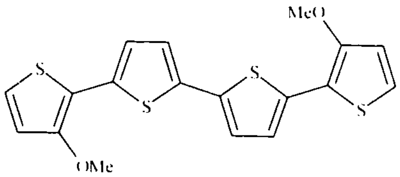
1		2	3	4	5
63		1.458(4) 1.451(5)	9.1(1)	0.0507	[63]
64		1.447 1.456 1.442	3.9 46.4 12.6	0.032	[72]
65		1.411	3.6(5) 5.0(7)	0.048	[73]
66					[74]

TABLE 7 (continued)

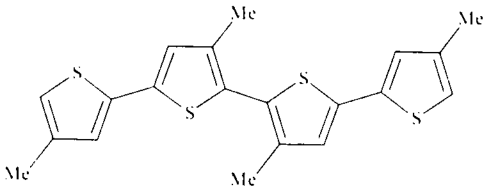
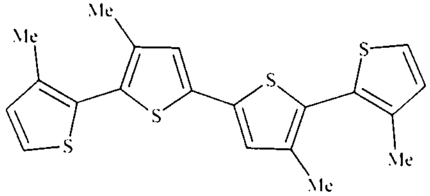
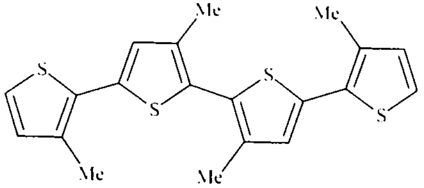
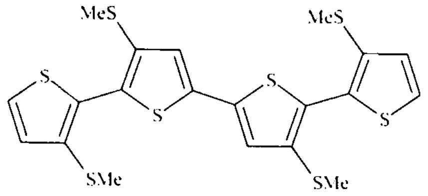
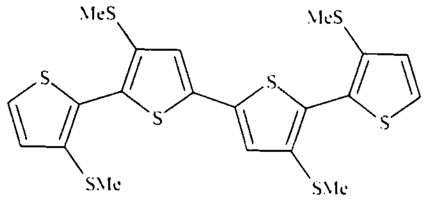
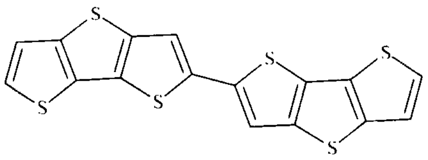
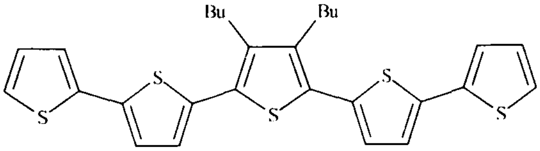
	1	2	3	4	5
67		1.456 1.453	3.4	0.029	[75]
68		1.458 1.453	54.2	0.028	[72]
69		1.447 1.452 1.453	11.8 28.8 21.3	0.034	[75]

TABLE 7 (continued)

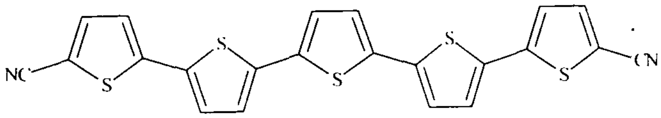
	1	2	3	4	5
70		1.456 1.449	27.4(2)	0.037	[76]
70		1.460(4) 1.448(5)	55.0(3)	0.0466	[77]
71			Planar system	0.0478	[78]

molecule the terminal heterocycles are in the *syn* conformation in relation to the neighboring rings. The molecule as a whole is nonplanar, and the mean value of the dihedral angle between the linked rings amounts to 13.6°. The terminal thiophenes are deviated from coplanarity (25.0°) significantly more than the internal ones.



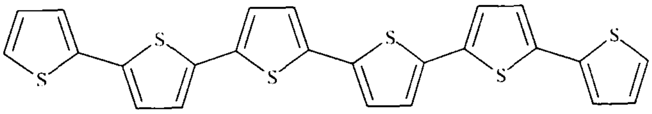
72

As in the case of the α,ω-dicyanoterthiophene **53** and α,ω-dicyanoquaterthiophene **62**, the molecules of compound **73** are almost planar and have the *trans* arrangement of the thiophene groups. The oligomers are linked into ribbonlike arrays by the intermolecular CN···H contacts, which are stacked in the crystal in parallel π layers.



73

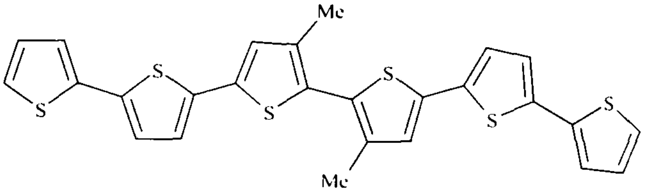
Like the unsubstituted α-quaterthiophene **59**, the unsubstituted α-sexithiophene **74** [80, 81] exists in two crystalline modifications. The molecules of both forms are planar. (The dihedral angles do not exceed 1°.)



74

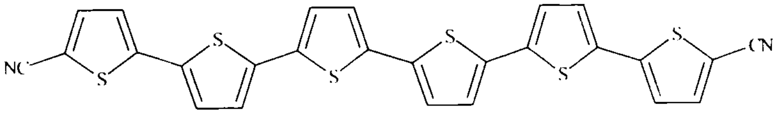
The unit cell of the low-temperature modification contains four molecules, while the high-temperature modification contains two at special positions. The molecules of the sexithiophenes in the crystal have packing of the "herringbone" motif, but the angle between the planes of neighboring molecules in the low-temperature form amounts to 23.5°, while that in the high-temperature form is 33°.

4'',3'''-Dimethylsexithiophene **75** [82] exists in the full *trans* conformation. Only the two terminal rings are coplanar, and the others are rotated in relation to each other; the torsion angles are in the range of 154.1-174.4°, and the two central heterocycles linked to the methyl groups deviate from planarity to the greatest degree.



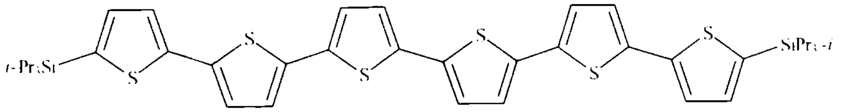
75

Like the molecules of α,ω-dicyanoterthiophene **53**, α,ω-dicyanoquaterthiophene **62**, and α,ω-dicyanoquinquethiophene **73** the planar molecules of the sexithiophene **76** [62] form ribbonlike arrays as a result of CN···H interaction. However, instead of π-stacked coplanar layers a "herringbone" motif is observed in the crystal lattice of the sexithiophene **76**.



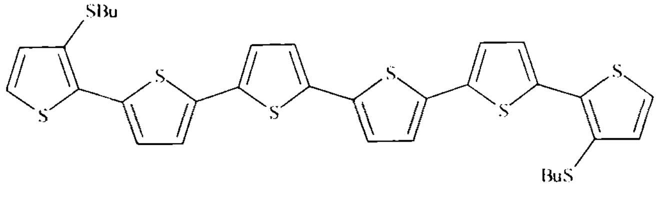
76

In the molecule of bis(triisopropylsilyl)sexithiophene **77** [83] the two central *anti*-oriented thiophene rings are fully coplanar, but the most interesting feature of the compound is the gradual and symmetrical displacement of the thiophene ring from planarity with removal from the center of symmetry of the molecule. The second and fifth heterocycles with the sulfur atoms $S_{(2)}$ and $S_{(5)}$ form dihedral angles of +21.4 and -21.4° with the central planar part. The terminal thiophene groups are twisted to an even greater degree, and the dihedral angles between them and the neighboring rings amount to 37.41°. The length of the bonds between the thiophene rings is 1.446-1.464 Å.

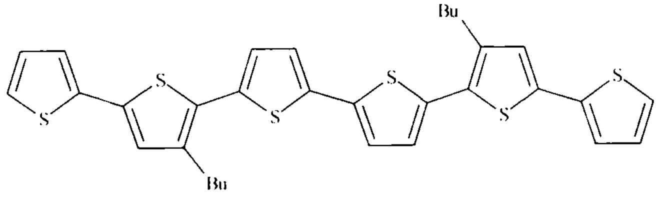


77

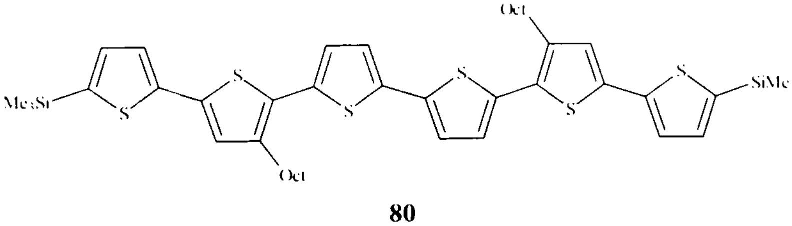
An analogous structure is characteristic of 3,3'''''-bis(butylthio)sexithiophene **78** [84], 4',3''''-dibutylsexithiophene **79** [85], and 5,5'''''-bis(trimethylsilyl)-4',3''''-dioctylsexithiophene **80** [85]. However, the molecules of these hexamers as a whole are more planar, as shown by the value of the dihedral angles between the neighboring heterocycles, which do not exceed 11°. During anisotropic refinement of the structure of the sexithiophene **79** it was not possible to obtain a sufficiently satisfactory structural model, and this is most likely due to the slight disorder of the terminal thiophene groups. The butyl and octyl chains of the compounds have a planar zigzag form and lie in the plane of the heterocycle linked to them.



78

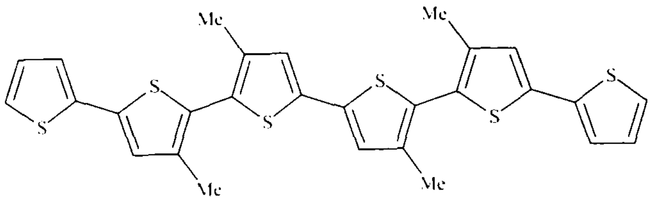


79

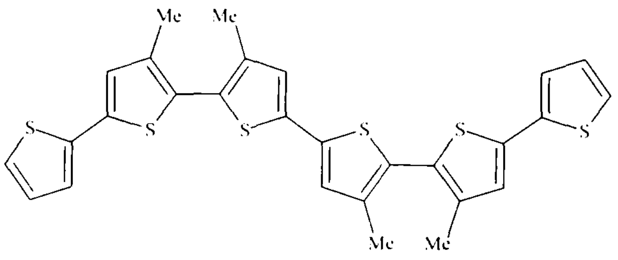


80

4',3'',4''',3''''-Tetramethylsexithiophene crystallizes at room temperature in two different polymorphous modifications: triclinic **81** and monoclinic **82** [82]. Both modifications are characterized by *trans* planarity in the central bithiophene fragment and the *anti* orientation for the terminal bithiophene groups. In the triclinic form **81** statistical disorder of the terminal heterocycles is observed (79% of the *anti* conformation). The polymorphism is the result of the different orientation of the methyl-substituted rings. In the monoclinic modification **82** the strongly distorted *syn* conformation is found, whereas the *anti* conformation is found in the triclinic form **81**. The conformation and geometry of the methyl-substituted fragment of the monoclinic form **82** are the same as in the tetramethylquaterthiophene **68**.

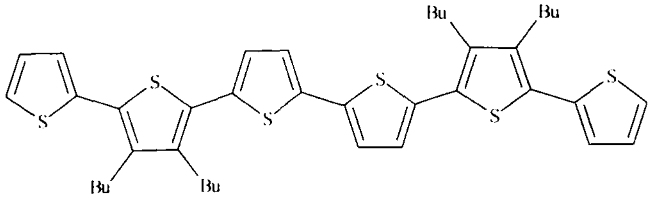


81

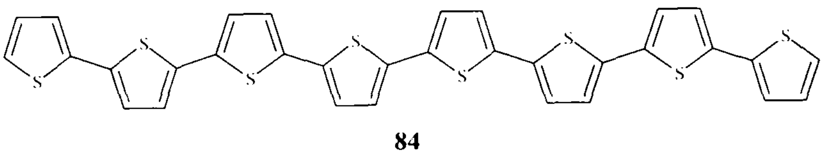


82

The characteristic disorder of thiophenes leads to the result that only 60% of the molecules of 3,3,4,4-tetrabutylsexithiophene **83** [79] have the full *anti* conformation. The remaining 40% belong to the rotational isomer with the *syn*-oriented terminal thiophenes. As a whole the π-conjugated system is noncoplanar, and like the pentamer **72** the terminal groups are deviated to a greater degree.



83



84

Single crystals of the unsubstituted α-octithiophene **84** [86] were obtained by vacuum sublimation and were investigated by X-ray analysis. As in the case of the sexithiophene, the molecules of octithiophene have a strictly planar structure, and the dihedral angles do not exceed 1° (*R* factor 0.0659). In the crystal the characteristic "herringbone" packing as in other planar oligothiophenes is observed. The angle between two neighboring molecules amounts to 65°, and the minimum C···C and C···S distances are 3.53 and 3.73 Å respectively.

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