REACTIONS OF THE 2,2',6,6'-TETRA-tert-BUTYL-4,4'-BISPYRYLIUM CATION WITH BASES

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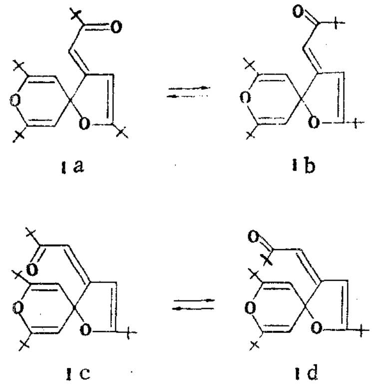
UDC 547.813

From 2,2',6,6'-tetra-tert-butyl-4,4'-bispyrylium perchlorate by the action of aqueous solutions of sodium acetate or caustic soda we have obtained a spiran containing pyran and dihydrofuran rings the structure of which has been established by the x-ray structural method. It has been shown that under the same conditions sodium sulfide reduces the bispyrylium salt to 2,2',6,6'-tetra-tert-butyl-4,4'-bispyranylidene. For the product of the interaction of the bispyrylium salt with aqueous ammonia the structure of an unsaturated tetraketone is suggested. Possible mechanisms of the formation of the compounds mentioned are discussed.

2,2',6,6'-Tetrasubstituted bispyrylium salts were first described only a few years ago [1, 2]. The mutual influence of the two conjugated positively charged aromatic rings makes the chemical properties of these interesting compounds extremely peculiar. As a rule, their reactions differ substantially from those of ordinary 2,4,6-trialkyl-substituted pyrylium salts. This difference appears particularly sharply in the capacity characteristic of them alone for the formation of stable cation radicals under the action of a wide range of reducing agents [1-3].

At the same time, it has not been possible in practice to perform with them the replacement of the oxygen atom in the hetero ring by a nitrogen atom under the action of ammonia or primary amines that is usual in the chemistry of pyrylium salts, and the nature of the compounds formed in the corresponding reaction has remained unelucidated [2]. We have found that the reaction of the 2,2',6,6'-tetra-tert-butyl-4,4'-bispyrylium cation with the hydroxyl anion also has an unusual nature. The results of elementary analysis, of PMR and IR spectroscopy, and of a mass-spectrometric determination of the molecular weight has enabled the main product of the reaction to be assigned a spiran structure [4] for which four spatial isomers are conceivable:



(1)

It has been established by the x-ray structural method that in the crystalline state the structure of the spiran molecule (Fig. 1) corresponds to formula (Ia). The lengths of the bonds and the main valence angles are given in Tables 1 and 2 (the angles at the tert-butyl

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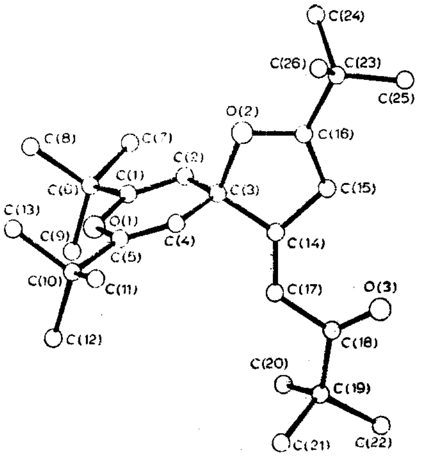


Fig. 1. Structure of the molecule of the spiran (I).

carbon atoms are characterized by the usual values: CCMe 105(1)-112(1)°, MeCMe 107(1)-114(1)°, and are not given in the Tables).

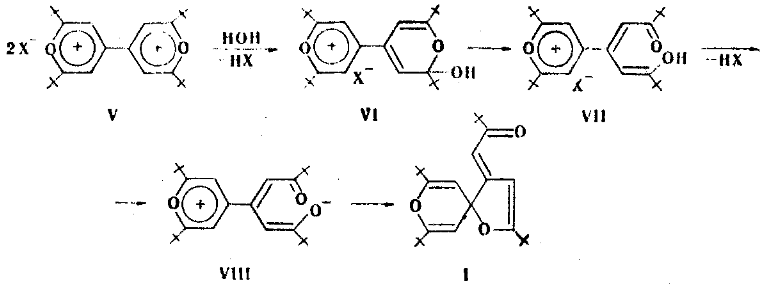
The C(14)C(17)C(18)O(3) fragment has a conformation close to cisoid. The dihedral angle formed by the C(14)C(17)C(18) and C(17)C(18)O(3) planes amounts to 7°. Its further decrease, which should lead to a gain in conjugation energy, proves to be impossible because of the repulsion of the O(3) atom from the C(15) atom [O(3)...C(15) 2.91 Å]. This repulsion also apparently causes a pronounced increase in the exocyclic angle C(15)C(14)C(17) to 130(1)°.

Both the heterocycles in the molecule are practically planar — the maximum deviation of the atoms from the mean plane of the six-membered ring does not exceed 0.04 Å, and from the plane of the five-membered ring 0.03 Å. The angle between the planes of the rings is 91°.

The geometry of the pyranyl fragment is similar to that described by Bokii and Struchkov [5]. A considerable nonequality of the angles at the C(1) and C(5) atoms is observed: (C(2)C(1)C(6) 127(1)°, O(1)C(1)C(6) 110(1)°, C(4)C(5)C(10) 129(1)°, O(1)C(5)C(10) 108(1)°) , which is due to the short C(4)...C(11) and C(2)...C(7) contacts, of 2.92 and 2.86 Å, respectively.

The C(3)—O(2) bond in the five-membered ring, at 1.49(2) Å is somewhat longer than the sum of the covalent radii (1.43 Å), but similar values for the C—O bond have been observed previously (for example, 1.47(2) Å [6]). There are no shortened intermolecular distances in the structure of (I).

The key stage in the formation of (I) is, in our opinion, the nucleophilic attack by OH⁻ of one of positions 2 of the cation (V), which leads to the enol (VII) as the result of the opening of the pyran ring of (VI). The pyrylium ring in compound (VII) should no longer open under the action of bases but can change with the splitting out of a proton into the betain (VIII), which is the open form of the spiran (I):



(2)

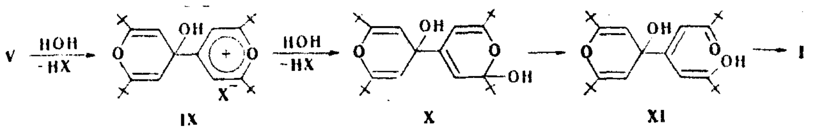
As can be seen from Scheme 3, the nucleophilic attack by OH⁻ of one of positions 4 of cation (V), also bearing a partial positive charge, should lead to the same final result:

TABLE 1. Bond Lengths in the Structure of the Spiran (I)

Bond	d, Å	Bond	d, Å	Bond	d, Å
O(1)—C(1)	1,35 (2)	C(6)—C(8)	1,58 (3)	C(17)—C(18)	1,53 (2)
O(1)—C(5)	1,41 (2)	C(6)—C(9)	1,54 (3)	C(18)—O(3)	1,17 (2)
C(1)—C(2)	1,33 (2)	C(10)—C(11)	1,56 (2)	C(18)—C(19)	1,49 (2)
C(1)—C(6)	1,52 (2)	C(10)—C(12)	1,51 (3)	C(19)—C(20)	1,59 (3)
C(2)—C(3)	1,52 (2)	C(10)—C(13)	1,60 (2)	C(19)—C(21)	1,67 (3)
C(3)—C(4)	1,48 (2)	C(14)—C(15)	1,47 (2)	C(19)—C(22)	1,54 (3)
C(3)—O(2)	1,49 (2)	C(14)—C(17)	1,36 (2)	C(23)—C(24)	1,53 (3)
C(3)—C(14)	1,52 (2)	C(15)—C(16)	1,34 (2)	C(23)—C(25)	1,53 (3)
C(4)—C(5)	1,31 (2)	C(16)—C(23)	1,51 (2)	C(23)—C(26)	1,61 (3)
C(5)—C(10)	1,49 (2)	C(16)—O(2)	1,37 (2)		
C(6)—C(7)	1,60 (3)	C(14)—C(17)	1,36 (2)		

TABLE 2. Valence Angles in the Structure of the Sprian (I)

Angle	ω, °	Angle	ω, °
C(1)O(1)C(5)	119 (1)	O(1)C(5)C(10)	108 (1)
O(1)C(1)C(2)	123 (1)	C(3)O(2)C(16)	108 (1)
O(1)C(1)C(6)	110 (1)	C(3)C(14)C(15)	108 (1)
C(2)C(1)C(6)	127 (1)	C(3)C(14)C(17)	122 (1)
C(1)C(2)C(3)	121 (1)	C(15)C(14)C(17)	130 (1)
C(2)C(3)C(4)	112 (1)	C(14)C(15)C(16)	106 (1)
C(2)C(3)O(2)	107 (1)	O(2)C(16)C(15)	115 (1)
C(2)C(3)C(14)	112 (1)	O(2)C(16)C(23)	115 (1)
C(4)C(3)O(2)	108 (1)	C(15)C(16)C(23)	129 (1)
C(4)C(3)C(14)	114 (1)	C(14)C(17)C(18)	124 (2)
O(2)C(3)C(14)	102 (1)	C(17)C(18)O(3)	121 (2)
C(3)C(4)C(5)	122 (1)	C(17)C(18)C(19)	115 (1)
C(4)C(5)O(1)	122 (1)	O(3)C(18)C(19)	124 (2)
C(4)C(5)C(10)	129 (1)		



(3)

The PMR spectrum of compound (I) was taken on a Tesla BS-487C spectrometer with a working frequency of 60 MHz in CCl_4 using HMDS as internal standard. The chemical shifts of the protons were, δ, ppm: 0.98 (tert-butyl radical of a pivaloyl group, singlet, 9 H); 4.58 (β-protons of a pyran ring, singlet, 2 H), and 5.30 (β-protons of a furan ring, singlet, 1 H). The protons of the three tert-butyl groups present in the α-positions of the pyran and furan rings gave a single signal at δ 1.16 ppm.

In the IR spectrum of (I), the highest-frequency band (1688 cm^{-1}) did not change its position on passing from benzene to chloroform, from which it follows that it is not connected with the vibrations of the carbonyl group. A comparison with the IR spectra of compounds having pyran rings, including the bispyranylidene (XVII) permits this band to be assigned to the vibrations of the pyran ring.

The band at 1668 cm^{-1} shifted to 1660 cm^{-1} when benzene was replaced by chloroform, and in place of the shoulder at 1645 cm^{-1} a band appeared at 1640 cm^{-1}. The first of them possibly relates to the stretching vibrations of the carbonyl group, and the second to those of a double bond conjugated with it. However, it is not excluded that in solution an equilibrium is set up between the s-conformers (Ia) $\rightleftarrows$ (Ib) and both bands are due to the stretching vibrations of their carbonyl groupings.

As is well known, the conjugation of a double bond with a carbonyl group leads to a lowering of the frequency of its stretching vibrations and to a pronounced rise in the intensity of absorption [7, 8]. A marked lowering of frequency is also observed in cases when a double bond is included in a strained cyclic system ($\nu_{C=C}$ in cyclobutane is 1566 cm^{-1}), the five-membered rings of bicyclo[2,2,1]hepta-2,5-diene absorbing at 1568 cm^{-1} [8]. It is ex-

TABLE 3. Coordinates of the Nonhydrogen Atoms (× 10^4) and Anisotropic Temperature Factors in the Form $T = \exp[-10^{-4}(B_{11}h^2 + \ldots + B_{12}hk + \ldots)]$ in the Structure of the Spiran (I)

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	4968 (6)	4948 (9)	5858*	32	98	80	7	−15	53
O(2)	5805 (6)	2459 (10)	7762 (9)	53	105	59	71	−7	16
O(3)	6851 (8)	−153 (11)	4950 (10)	61	132	74	68	−3	−1
C(1)	5645 (8)	5067 (12)	6085 (14)	22	99	74	11	−15	15
C(2)	6016 (9)	4113 (13)	6487 (14)	41	121	60	19	1	−3
C(3)	5698 (9)	2795 (12)	6663 (13)	39	94	58	36	−2	15
C(4)	4949 (9)	2781 (13)	6459 (12)	33	93	74	18	−9	17
C(5)	4628 (8)	3781 (12)	6077 (13)	27	110	53	2	−2	−1
C(6)	5896 (9)	6406 (15)	5810 (16)	36	113	107	0	15	23
C(7)	6678 (11)	6538 (20)	6175 (22)	39	146	207	−44	−18	69
C(8)	5439 (11)	7424 (16)	6405 (20)	44	104	201	41	4	−43
C(9)	5820 (13)	6601 (19)	4646 (17)	88	152	100	−54	13	103
C(10)	3892 (8)	3921 (14)	5771 (15)	34	98	88	−14	−5	6
C(11)	3465 (11)	2731 (17)	6135 (24)	51	120	202	−27	−33	89
C(12)	3814 (12)	4140 (20)	4636 (18)	73	175	58	20	−62	−17
C(13)	3544 (10)	5115 (16)	6355 (18)	46	146	114	33	19	−70
C(14)	6094 (9)	1738 (13)	6117 (13)	49	98	50	35	5	15
C(15)	6446 (9)	967 (13)	6902 (12)	41	124	42	27	−10	−3
C(16)	6244 (8)	1433 (14)	7813 (13)	48	95	62	35	−10	3
C(17)	6118 (9)	1644 (15)	5078 (14)	54	144	44	44	1	5
C(18)	6559 (9)	665 (16)	4505 (13)	51	127	42	−25	5	−35
C(19)	6576 (10)	821 (15)	3366 (14)	42	166	60	−35	3	32
C(20)	6885 (16)	2194 (19)	3078 (20)	92	135	120	−18	74	75
C(21)	5776 (12)	606 (31)	2920 (21)	40	391	119	−11	−63	−42
C(22)	7048 (12)	−207 (17)	2889 (16)	54	147	95	−2	31	−61
C(23)	6442 (10)	1008 (14)	8878 (13)	55	123	50	32	−12	10
C(24)	6775 (17)	2137 (20)	9451 (20)	115	136	119	−25	−144	−23
C(25)	6960 (12)	−106 (19)	8828 (17)	42	180	82	71	−17	51
C(26)	5739 (12)	491 (25)	9393 (19)	42	299	93	37	52	150

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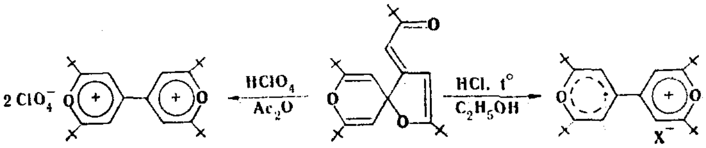
*The coordinate fixes the position of the origin in the space group.

tremely likely that it is the combination of these two factors (double bond in a five-membered ring of a spiran conjugated with an enone grouping) that leads to the appearance of a very strong absorption band (1555 cm^{-1} in $CHCl_3$; doublet at 1555, 1565 cm^{-1} in C_6H_6) in the IR spectrum of compound (I).

The spiran (I) is an extremely reactive compound readily opening both the furan and the pyran rings under the action of various reagents.

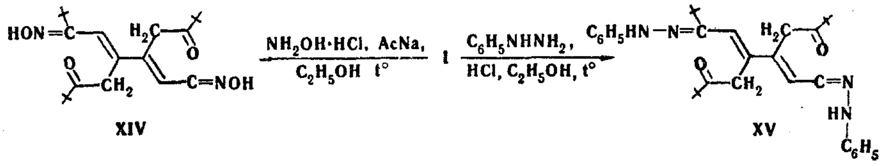
Perchloric acid in acetic anhydride regenerates the initial bispyrylium salt (XII), while boiling the spiran in ethanol in the presence of HCl leads, according to the ESR results, to the formation of the stable cation radical (XIII) which has been described in the literature [1-3]:



XII XIII

(4)

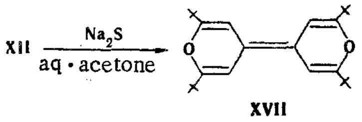
With hydroxylamine hydrochloride and phenylhydrazine, respectively, the bisoxime [mp 172-175°C, from ethanol (decomp.); $\nu_{C=N}$ 1715 cm^{-1} (paraffin oil)] and the bishydrazone [mp 172-174°C (decom.); $\nu_{C=O}$ 1710 cm^{-1} (paraffin oil)] were obtained. The high values of the frequencies of the stretching vibrations of the carbonyls in the IR spectra of both compounds permit them to be ascribed the structures (XIV) and (XV) with carbonyl groups at saturated carbon atoms:



(5)

In the IR spectrum of compound (XIV) there are also a sharp band at 3430 cm^{-1} and a broad band with its maximum at about 3280 cm^{-1} (paraffin oil), confirming the presence of hydroxy groups in the compound. In the region of N—H stretching vibrations in the IR spectrum of (XV) there is a sharp band of medium intensity at 3330 cm^{-1} (paraffin oil).

The route of the reaction of the bispyrylium salt (I) with sodium sulfide was determined by the reducing properties of the latter. The interaction of these compounds in aqueous acetone formed the bispyranylidene (XVII).

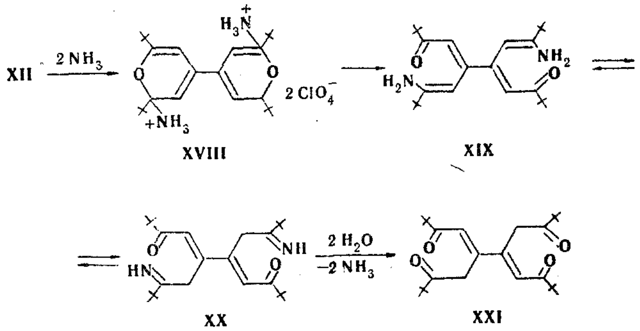


(6)

Treatment of the bispyrylium salt (XII) with 25% ammonia solution led to the formation of a bright yellow substance containing no nitrogen. The compound crystallized well but was not distinguished by a high stability and gradually resinified on storage. Its elementary composition corresponds to that of the unsaturated tetraketone (XXI).

For the tetraketone (XXI) a great diversity both of the spatial isomers and of the keto-enol tautomers is conceivable, each of which may be characterized by its own values of the chemical shifts of the protons and frequencies of the stretching vibrations of the carbonyl groups and double bonds. In actual fact, the IR spectrum of the product CCl_4 contained, in addition to the bands of the stretching vibrations of carbonyl groups, a band at 3430 cm^{-1} which is apparently due to the stretching vibrations of the hydroxyl of the enolic form. Possibly for this reason, we were unable to unambiguously interpret the PMR spectrum of the compound under consideration. The IR spectrum of this compound is also extremely complex, but it is in harmony with the structure suggested.

The route of formation of the carbonyl compound from the bispyrylium salt under the action of ammonia is readily imagined on the basis of known facts concerning the interaction of pyrylium salts with ammonia and amines, if it is assumed that the reaction takes place through the intermediate imino compound (XX), the hydrolysis of which should lead to the tetraketone (XII):



(7)

At the same time, the formation of the tetraketone (XXI) can also be considered as indirect evidence in favor of a mechanism with the original addition of a hydroxyl anion in position 2 of the bispyrylium cation in the synthesis of the spiran (I).

EXPERIMENTAL

Spiro[2,6-di-tert-butyl-4H-pyran-4,2'-3-pivaloylmethylene-5-tert-butyl-2,3-dihydrofuran] (I). With stirring, a saturated aqueous solution of 2.5 g (30.5 mmole) of sodium acetate was added to a suspension of 3 g (5.1 mmole) of 2,2',6,6'-tetra-tert-butyl-4,4'-bispyrylium perchlorate (XII) in 50 ml of acetone. The mixture became intensely colored and then lightened, and the pyrylium salt dissolved. After some time, a small amount of colorless precipitate (trityl peroxide) deposited,* and this was filtered off and the solvent was distilled off from the filtrate. The residue was recrystallized from aqueous ethanol. Colorless lustrous leaflets with mp 136-138°C. Yield 1.9 g (92%). Found: C 77.8; H 10.1%. $C_{26}H_{40}O_3$. Calculated: C 78.0; H 10.1%.

The same compound was formed with a yield close to quantitative by the reaction of a suspension of 0.5 g of bispyrylium salt (XII) in 10 ml of acetone with a solution of 0.4 g of KOH in 4 ml of water.

The oxime (XIV) was obtained by adding to a hot solution of 0.2 g (0.5 mmole) of the spiran (I) in 8 ml of ethanol a hot solution of 0.5 g (6.1 mmole) of sodium acetate and 0.5 g (7.2 mmole) of hydroxylamine hydrochloride in 3 ml of water. The solution was boiled for 5 min and was cooled, and the colorless needles that had precipitated were filtered off, washed with 1 ml of cold ethanol, and dried. mp 166-168°C (decomp.). Found: C 70.1; H 10.1; N 6.5%. $C_{26}H_{44}N_2O_4$. Calculated: C 69.8; H 9.9; N 6.2%.

The hydrazone (XV) was obtained by adding a hot solution of 0.54 g (5 mmole) of phenlyhydrazine in 2 ml of ethanol and one drop of concentrated HCl to a hot solution of 0.2 g (0.5 mmole) of the spiran (I) in 2 ml of ethanol. The mixture was heated to the boil and was filtered. On cooling, a yellow precipitate deposited, which was filtered off, washed with the minimum amount of ethanol, and dried. mp 172-174°C (decomp.). Found: N 9.4%. $C_{38}H_{54}N_4O_2$. Calculated: N 9.4%.

Reaction of 2,2',6,6'-Tetra-tert-butyl-4,4'-bispyrylium Perchlorate with Sodium Sulfide. The treatment of a suspension of 1 g of the bispyrylium salt (XII) in 20 ml of acetone with 10 ml of a saturated solution of sodium sulfide in water led to the formation of 2,2',6,6'-tetra-tert-butyl-4,4'-bispyranylidene (XVII) with a yield close to quantitative. Light yellow crystals (from ethanol), mp 220°C (decomp.). According to the literature [1], mp 226°C. IR spectrum: strong band at 1680 cm^{-1} (paraffin oil) (vibrations of a system of multiple bonds). Found: C 81.2; H 10.0%. $C_{26}H_{40}O_2$. Calculated: C 81.3; H 10.4%.

Reaction of 2,2',6,6'-Tetra-tert-butyl-4,4'-bispyrylium Perchlorate (XII) with Ammonia. With stirring, 1 ml of 25% aqueous ammonia was added to a suspension of 0.5 g of the bispyrylium salt (XII) in 10 ml of acetone. The mixture was brought to the boil and was filtered from a small amount of white precipitate. The yellow filtrate was cooled with ice, and the yellow crystals that deposited were filtered off and dried in vacuum at 60-70°C. Yield 0.22 g (60%), mp 150-160°C (from aqueous ethanol) (the analytically pure product melted unsharply). Found: C 74.6; H 9.7%. $C_{26}H_{40}O_4$. Calculated: C 74.2; H 10.5%.

IR spectrum: $\nu_{C=O}$ at a sp^3-hybridized C atom: 1718 cm^{-1} (v.s.) (CCl_4); 1710 cm^{-1} (v.s.) ($CHCl_3$); $\nu_{C=O}$ at sp^2-hybridized C atoms, cm^{-1}: 1670 (s), 1655 (s) (CCl_4), 1690 (v.s) (CCl_4, $CHCl_3$) — possible $\nu_{C=O}$ vibrations at a saturated carbon atom bound by an intramolecular hydrogen bond to an enolic hydroxyl or the vibrations of a system of multiple bonds.

Deciphering of the Structure. The parameters of the elementary cell were determined by the photographic method and were refined with respect to 24 reflections in a Hilger-Watts automatic four-circle diffractometer controlled by a RDR-8/1 minicomputer. To determine the cell parameters, to measure intensities, and to perform the subsequent calculations we used the procedures and programs described previously [9].

The crystals of (I) are rhombic, a = 19.439(4), b = 10.387(1), c = 13.037(2) Å; V = 2632(1) $Å^3$; mol. wt. = 400; d_{meas} = 1.010 g/cm^3, d_{calc} = 1.015 g/cm^3; z = 4; space group—$Pna2_1$.

The intensities of the reflections were measured on the same diffractometer (θ/2θ scanning in the range of $\theta < 66°$, λ CuKα, 1248 reflections, $F^2 > 1\sigma$).

The structure was interpreted by the direct method using the "Rentgen-75" program on a BÉSM-6 computer.

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*As in Russian original — Publisher.

The structure was refined first by the full-matrix MLS in the isotropic approximation and by the block-diagonal method in the anisotropic approximation (R = 10.7%). The coordinates and the temperature factors of the atoms are given in Table 3. The structure of the molecule is shown in Fig. 1.

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