ВЕСТНИК

ЮЖНО-УРАЛЬСКОГО ГОСУДАРСТВЕННОГО УНИВЕРСИТЕТА

2015
Т. 7, № 2

ISSN 2076-0493

СЕРИЯ

«ХИМИЯ»

Решением ВАК России включен в Перечень ведущих рецензируемых научных журналов и изданий

Учредитель – Федеральное государственное бюджетное образовательное учреждение высшего профессионального образования «Южно-Уральский государственный университет» (национальный исследовательский университет)

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BULLETIN
OF THE SOUTH URAL STATE UNIVERSITY
SERIES
"CHEMISTRY"

2015
Vol. 7, no. 2

ISSN 2076-0493

Vestnik Yuzhno-Ural'skogo Gosudarstvennogo Universiteta.
Seriya "Khimiya"

South Ural State University

The journal publishes peer-reviewed papers on scientific research in various branches of chemical science: inorganic chemistry, organic chemistry, analytical chemistry, physical chemistry and solid-state chemistry. The papers in related branches are welcome. The editorial board keeps the high quality of publications, strictly adhering to the policy of independent third-party expert opinion, expressed by specialists in the corresponding branches, whose qualification is confirmed by generally recognized scientometrical indicators.

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Organic Chemistry

SYNTHESIS AND HALOCYCLIZATION OF ALLYL DERIVATIVES OF 4,5-DIHYDRO-1,3-THIAZOL-2-THIONE

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2-Propenyl-(2-methyl-1-propenyl-, 2-butenylthio- and (3-methylbutenyl-)thio4,5-dihydro-1,3-thiazoles are synthesized by alkylation of 4,5-dihydro-1,3-thiazol2-thione. These products were researched in halocyclization reactions with iodine and bromine. 3-(halomethyl)-2,3,5,6-tetrahydrothiazolo[2,3-b]thiazolium and 6-halo-3,5,6,7-tetrahydro-2H-thiazolo[2,3-b]thiazinium halides were formed. The structure of all the synthesized compounds was confirmed by ^{1}H NMR and gas chromatography-mass spectrometry.

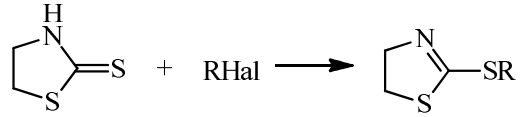
Keywords: 4,5-dihydro-1,3-thiazol-2-thione, 2-propenylthio-4,5-dihydrothiazol, 2-(2-methyl-1-propenyl)thio-4,5-dihydrothiazol, 2-butenylthio-4,5-dihydrothiazol, 2-(3-methyl-butenyl)thio-4,5-dihydrothiazol, 3-(halomethyl)-2,3,5,6-tetrahydrothiazolo[2,3-b]thiazolium and 6-halo-3,5,6,7-tetrahydro-2H-thiazolo[2,3-b]thiazinium halides, gas chromatography-mass spectrometry, ^{1}H NMR.

Introduction

Derivatives of 1,3-thiazoline have antimicrobial and antihelmintial activity, besides they are the effective immunomodulatory agents [1–3]. 2-Propenylthio-4,5-dihydro-1,3-thiazole was synthesized previously from alkyl derivatives of 4,5-dihydro-1,3-thiazol-2-thione (**1**, 1,3-thiazoline-2-thione) [4]. The aim of the present study is the synthesis of new S-alkenyl derivatives of 4,5-dihydro-1,3-thiazol-2-thione and the investigation of their halocyclization reactions.

Discussion of results

We have found that 4,5-dihydro-1,3-thiazol-2-thione reacts with 3-bromopropene (**2a**), 3-chloro-2-methylpropene (**2b**), 4-bromobutene (**2c**), 1-bromo-3-methyl-2-butene (**2d**) to give 2-propenylthio-4,5-dihydrothiazole (2-allylthio-1,3-thiazoline) (**3a**), 2-(2-methyl-1-propenyl)thio-4,5-dihydrothiazole (**3b**), 2-butenylthio-4,5-dihydrothiazole (**3c**), 2-(3-methylbutenyl)thio-4,5-dihydrothiazole (**3d**) respectively (scheme 1). Compounds **3a–d** have been synthesized after treatment in ethanol with sodium ethylate as a base. Note that in similar conditions the mixture of 2-(2-methyl-2-propenyl)thio-5-methyl-1,3,4-thiadiazole with 2-(2-methyl-1-propenyl)thio-5-methyl-1,3,4-thiadiazole at the ratio 1:2 have been obtained from 5-methyl-1,3,4-thiadiazole-2-thione and methallylchloride **2b** [5]. In this case the yield of compound **3b** is 62%.



1 **2a-d** **3a-d**

2a $BrCH_2CH=CH_2$; **2b** $ClCH_2C(CH_3)=CH_2$; **2c** $BrCH_2CH_2CH=CH_2$; **2d** $BrCH_2CH=C(CH_3)_2$

Scheme 1. The alkylation of 4,5-dihydro-1,3-thiazol-2-thione

There is the molecular ion peak in the mass spectra (table 1, scheme 2, 3, 4) of compounds **3a–d.** The fragmentation processes with the elimination of methyl radical and the formation of the stable thiazolo-thiazolium system for compounds **3a, b** (scheme 2), as well as the formation of the thiazolo-thiazinium system for compounds **3c, d** (scheme 3, 4), are characteristic for all compounds. The peak

$[M–CH_3]^+$ is maximum for compounds **3a, b**. The hydrogen radical is eliminated from the molecular ion of compounds **3a–c** with the formation 3,5-dihydro-2*H*-thiazolo[2,3-*b*][1,3]thiazinium cation (**A_1**) for **3a, b** and 5-methylene-3,5,6,7-tetrahydro-2H-thiazolo[2,3-b][1,3]thiazinium cation (**A_2**) for **3c**. The fragmentation of the molecular ion with the elimination of $•SCH_3$ radical and the formation of the stable carbocations 4-thia-1-azabicyclo[3.2.0]hepta-1(5),6-dienium (A_5) for compounds 3a, b and 7-methylene-4-thia-1-azabicyclo[3.2.0]hept-1(5)-enium (**B_8**) for sulfide **3c** is characteristic for compounds **3a–c**.

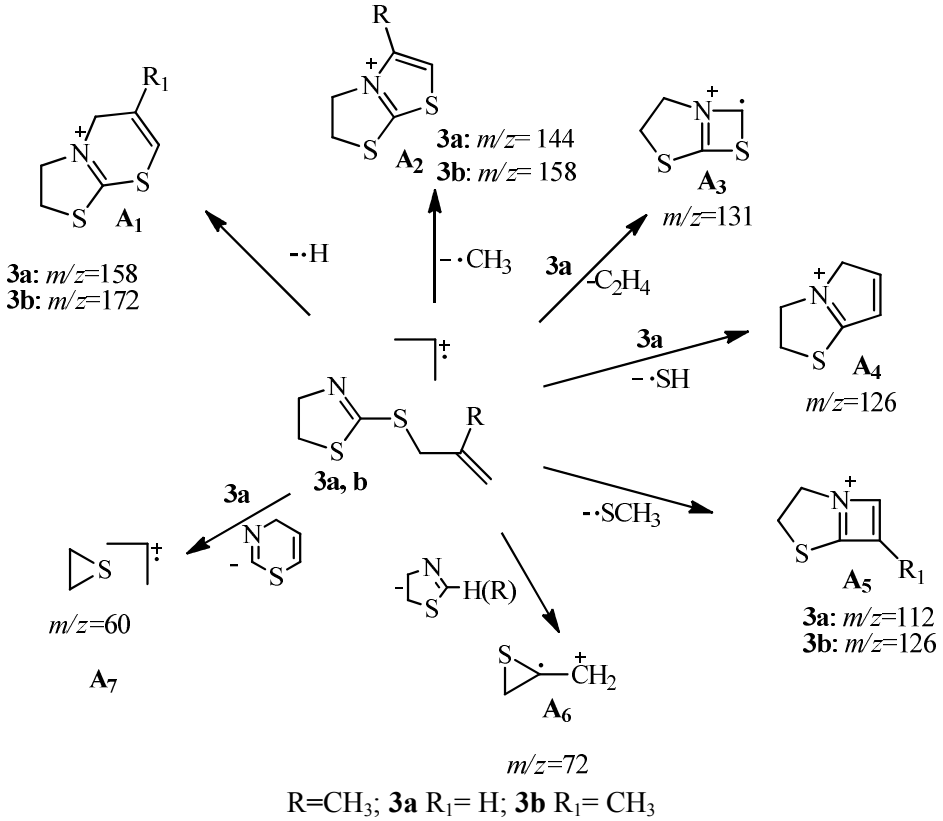
Table 1

Mass-spectometry data of the investigated compounds

Compound	Characteristic ions: *m/z (I %)*
3a ($C_6H_9NS_2$)	159 $[M]^{+•}$ (10), 158 $[M–H]^+$ (7), 146 (9), 144 $[M–CH_3]^+$ (100), 131 $[M–C_2H_4]^{+•}$ (6), 126 $[M–SH]^+$ (5), 112 $[M–SCH_3]^+$ (8), 98 (9), 87 (6), 73 (15), 72 $[M–C_3SNH_3]^{+•}$ (47), 61 (11), 60 $[M–C_4SNH_5]^{+•}$ (57), 59 (37), 55 (6), 45 (29), 41 (39)
3b ($C_7H_{11}NS_2$)	173 $[M]^{+•}$ (< 1), 172 $[M–H]^+$ (< 5), 160 (10), 159 (9), 158 $[M–CH_3]^+$ (100), 126 $[M-SCH_3]^+$ (7), 112 (11), 87 (7), 86 (6), 72 $[M–C_3SNH_3CH_3]^{+•}$ (12), 61 (6), 60 (19), 59 (20), 55 (33), 39 (12)
3c ($C_7H_{11}NS_2$)	173$[M]^{+•}$ (9), 172 $[M–H]^+$ (19), 158 $[M–CH_3]^+$ (8), 147 $[M–C_2H_2]^{+•}$ (5), 145 $[M–C_2H_4]^{+•}$ (52), 144 $[M–C_2H_5]^+$ (52),140 $[M–SH]^+$ (43), 132 $[M–C_3H_5]^+$ (5), 126 $[M–SCH_3]^+$ (9), 119 $[M–C_4H_6]^{+•}$ (86), 87 (6), 86 (7), 85 (8), 72 $[M–C_4H_6NSH_2]^{+•}$ (25), 62 (6), 61 (44), 60 $[M–C_5H_7NS]^{+•}$ (100), 59 (40), 58 (10) ,56 (20), 55 (55), 54 (9), 53 (14), 47 (6), 46 (11), 45 (29)
3d ($C_8H_{13}NS_2$)	187 $[M]^{+•}$ (21), 172 $[M–CH_3]^+$ (7), 158 (8), 154 $[M–SH]^+$ (32),144 $[M–C_3H_7]^+$ (5), 140 (< 5%), 119 $[M–C_6H_8]^{+•}$ (21), 120 $[M–C_5H_7]^+$ (6), 101 (10),100 (5), 69 $[M–NSC_3H_9S]^+$ (100), 68 (6), 67 (11), 61 (11), 60 $[M–NSC_6H_9]^{+•}$, 59 (13), 45 (8), 41 (65), 39 (12)

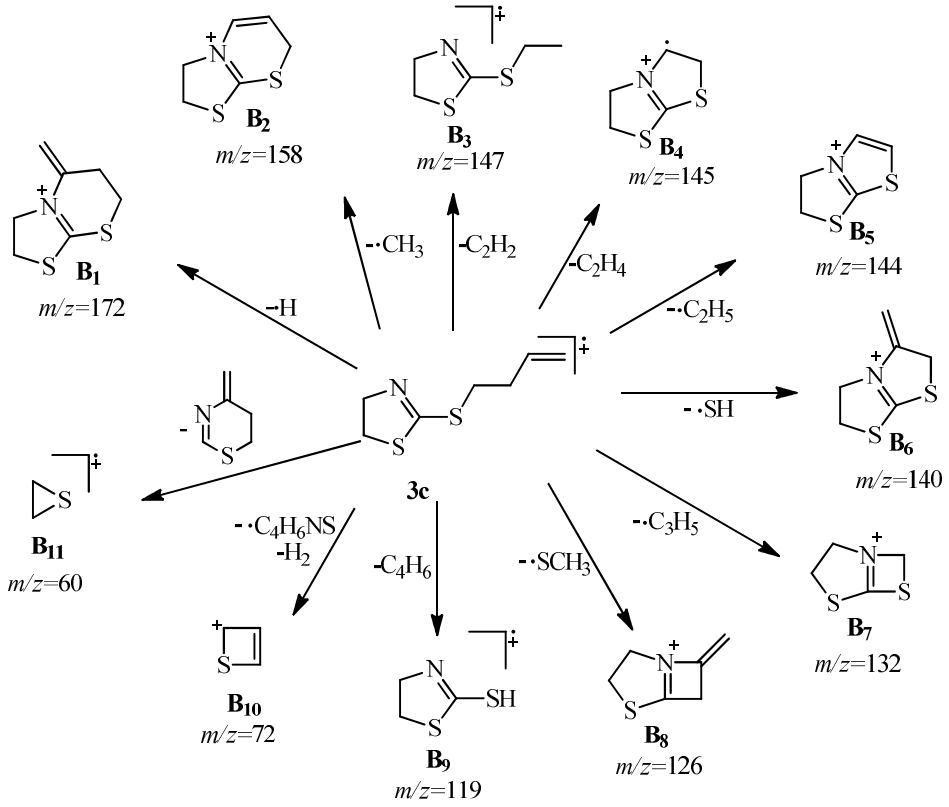
Peaks with intensity less than 5 % are not taken into account.

There are peaks corresponding to the elimination of a neutral ethylene molecule in the mass spectra of compounds **3a–c**. Besides, there is the peak corresponding to the elimination of the acetylene and butadiene molecules in the spectrum of compound **3c**.

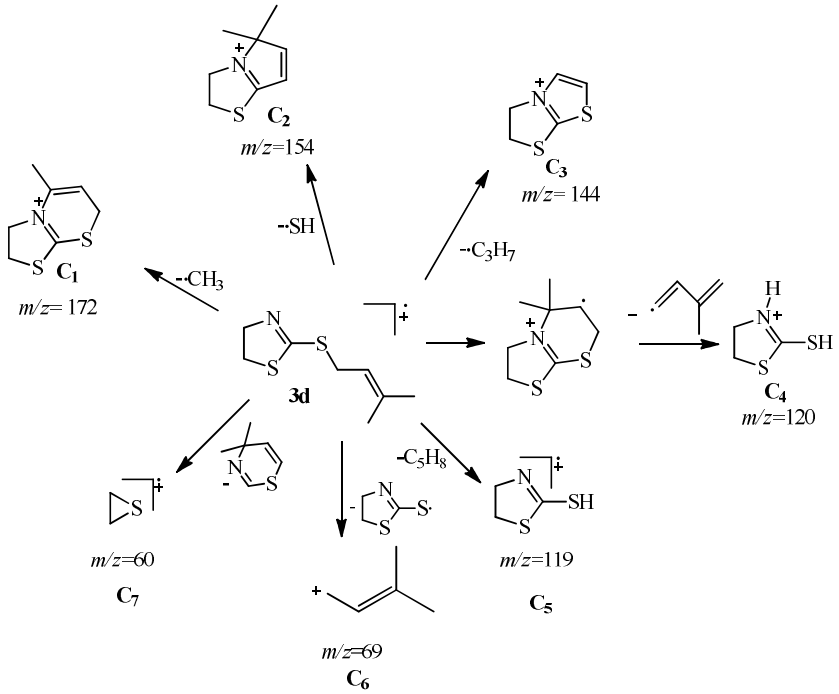


Scheme 2. Possible fragmentation processes of 2-propenylthio-4,5-dihydrothiazole (3a) and 2-(2-methyl-1-propenyl)thio-4,5-dihydrothiazole (3b)

The peak of thiiranium radical cation (**B_{11}**) which is formed by the elimination of the neutral 4-methylene-5,6-dihydro-4*H*-1,3-thiazine molecule is maximum for compound **3c**. Besides, this ion peak is present in spectra of compounds **3a, b**, **d**, but its intensity is much lower. For compound **3a** intensity corresponds to 54% and it is no more than 20 % for compounds **3b**, **d**. The ion peak is *m/z* 69 corresponding to the cation **C_6** which is formed in the result of the heterolytic disconnection of rhe C-S bond is maximal for compound **3d** (scheme 4).



Scheme 3. Possible fragmentation processes of 2-butenylthio-4,5-dihydrothiazole (3c)



Scheme 4. Possible fragmentation processes of 2-(3-methylbutenyl)thio-4,5-dihydrothiazole (3d)

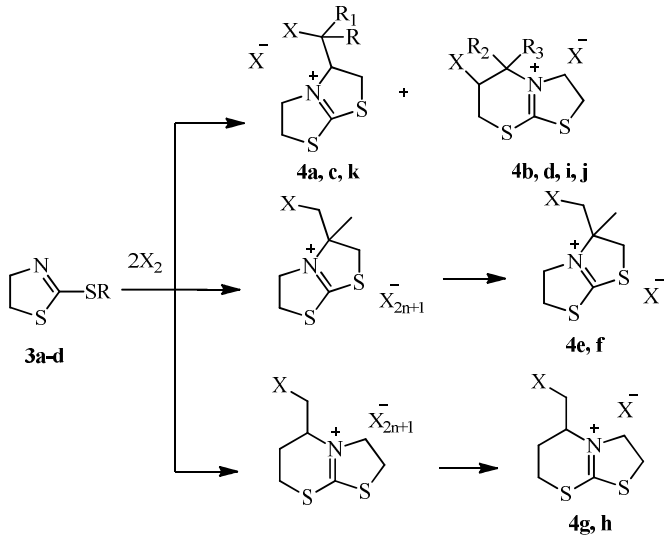
In ^{1}H NMR spectra of compounds **3a–d** (Table 2) the proton signals of SCH_2 and NCH_2 groups of the thiazine cycle are observed in the range of 3.39–3.40 and 4.22–4.23 ppm, respectively. The proton signals of SCH_2 group of alkenyl radical are observed in the range of 3.79–3.80 ppm for all synthesized compounds except sulfide **3c**. SCH_2 group triplet belonging to the S-alkenyl radical of compound **3c** is observed in a weaker field at 3.19 ppm. This is probably due to the fact that SCH_2 group of compound **3c** is removed at greater distance from the double bond compared to other sulfides **3a, b, d.**

Table 2

Spectral data of the synthesized compounds

Compound	^{1}H NMR spectrum, δ, ppm (J, Hz)
3a	3.41 (2H, t, J=8.0, $SCH_{2ц}$); 3.79 (2H, dd, J=0.86, J=6.89, $SCH_{2.}$); 4.23 (2H, t, J=7.99, NCH_2); 5.16 (1H, d, J=10.06, =CH_2); 5.32 (1H, dd, J=1.31, J=16.96, =CH_2); 5.93 (1H, m, CH=)
3b	1.83 (3H, s, CH_3); 3.39 (2H, t, J=7.98, $SCH_{2ц}$); 3.80 (2H, s, SCH_2); 4.22 (2H, t, J=7.98, NCH_2); 4.90 (1H, m, =CH_2); 5.01 (1H, s, =CH_2)
3c	2.46 (2H, m, -CH_2-); 3.19 (2H, t, J=7.32, SCH_2); 3.40 (2H, t, J=7.98, $SCH_{2ц}$); 4.22 (2H, t, J=7.98, NCH_2); 5.09 (2H, m, =CH_2); 5.82 (1H, m, =CH-)
3d	1.70 (3H, s, CH_3); 1.74 (3H, s, CH_3); 3.41 (2H, t, J=7.99, $SCH_{2ц.}$); 3.80 (2H, d, J=7.88, $SCH_{2ц}$); 4.23 (2H, t, J=7.99, NCH_2); 5.31 (1H, m, CH=)
4a	3.69 (1H, dd, J=2.76, J=11.27, CH_2I); 3.75 (2H, m, SCH_2); 4.11 (2H, m, SCH_2); 4.15–4.20 (2H, m, $^+NCH_2$); 4.31 (1H, dd, J=9.84, J=12.09 CH_2I); 4.70 (1H, m, ^+NCH)
4b	3.71 (1H, m, SCH_2); 3.86 (1H, dd, J=2.32, J=12.74, SCH_2); 4.20 (1H, m, $^+NCH_2$); 4.36–4.45 (3H, m, $^+NCH_2$); 4.82 (1H, m, CHI)
4c	3.87 (1H, dd, J=6.51, J=12.14, $^+NCH_2$); 3.97 (1H, dd, J=2.71, J=11.62, CH_2Br); 4.13 (1H, m, $^+NCH_2$); 4.22–4.08 (4H, m, SCH_2); 4.32 (1H, dd, J=10.03, J=12.12, CH_2Br); 4.97 (1H, m, ^+NCH)
4d	3.68 (1H, m, SCH_2); 3.74 (2H, t, J=8.56, SCH_2); 3.93 (1H, m, SCH_2); 4.45-4.31 (4H, m, $^+NCH_2$); 5.16 (1H, m, CHBr)
4e	1.70 (3H, s, CH_3); 3.81 (2H, k, J=11.25, SCH_2); 4.02 (2H, m, SCH_2); 4.12 (4H, m, $^+NCH_2$, CH_2I)
4f	1.66 (3H, s, CH_3); 4.03 (2H, dd, J=4.16, J=11.91, SCH_2); 4.11 (2H, m, SCH_2); 4.12 (2H, m, $^+NCH_2$); 4.17 (2H, m, CH_2Br)
4g	2.25 (1H, m, -CH_2-); 2.59 (1H, m, CH_2); 3.41 (2H, m, SCH_2); 3.53 (1H, dd, J=9.11, J=10.79, $^+NCH_2$); 3.66 (1H, td, J_1=J_2=9.13, J=11.12, $^+NCH_2$); 3.74 (2H, m, SCH_2); 4.27 (1H, kd, J_1=J_2=3.93, J=3.96, J=8.04, CH_2I); 4.37 (1H, td, J_1=J_2=9.11, J=12.25, CH_2I); 4.71 (1H, m, ^+NCH)
4h	2.25 (1H, m, CH_2); 2.58 (1H, m, CH_2); 3.44 (2H, m, SCH_2); 3.71 (2H, m, SCH_2); 3.90 (1H, dd, J=7.65, J=11.11, $^+NCH_2$); 3.99 (1H, dd, J=3.82, J=11.09, $^+NCH_2$); 4.32 (2H, m, CH_2Br); 4.70 (1H, m, ^+NCH)
4i	1.60 (3H, s, CH_3); 1.65 (3H, s, CH_3); 3.68 (2H, m, SCH_2); 3.73 (1H, dd, J=5.44, J=14.56, SCH_2); 4.12 (1H, dd, J=3.49, J=14.38, SCH_2); 4.45 (1H, td, J=8.79, J=12.22, $^+NCH_2$); 4.68 (1H, ddd, J=7.30, J=8.67, J=12.24, $^+NCH_2$); 5.14 (1H, dd, J=3.70, J=4.99, CHI)
4j	1.57 (3H, s, CH_3); 1.67 (3H, s, CH_3); 3.49 (1H, dt, J=4.48, J=10.80, J=10.85, SCH_2); 3.72 (2H, dd, J=6.34, J=16.03, SCH_2); 4.14 (1H, dd, J=3.19, J=14.57, SCH_2); 4.46 (1H, td, J=8.84, J=12.22, $^+NCH_2$); 4.71 (1H, td, J=7.94, J=12.27, $^+NCH_2$); 5.25 (1H, dd, J=3.36, J=4.54, CHI)
4k	1.87 (3H, s, CH_3); 1.94 (3H, s, CH_3); 3.70 (2H, dd, J=1.38, J=10.36, SCH_2); 4.17 (2H, m, SCH_2); 4.27 (1H, dd, J=2.33, J=14.38, $^+NCH_2$); 4.64 (1H, dd, J=2.27, J=10.81, $^+NCH_2$); 5.50 (1H, m, ^+NCH)

It was studied the halocyclization of synthesized sulfides (scheme 5). The interaction of compound **3a** with halogens proceeds with the formation of the mixture of 3-(halomethyl)-2,3,5,6-tetrahydrothiazolo[2,3-*b*]thiazolium polyhalide (**4a, c**) and 6-halo-3,5,6,7-tetrahydro-2*H*-thiazolo[2,3-*b*]thiazinium polyhalide (**4b, d**), in the same way as 2-(propenylthio)-5-methyl-1,3,4-thiadiazole [6]. Monoiodide derivatives have been isolated by adding sodium iodide in acetone to the reaction mixture, monobromide derivatives have been isolated by the reaction of excess of bromine with acetone. It should be noted that bromocyclization reaction of compound **3a** leads to lesser yield of the product with thiazine cycle (the ratio of **4c**:**4d** is 5:1), whereas the ratio of the products containing five- and six-membered cycles is 2:1 for the bromocyclization reaction of 2-(allylthio)-5-methyl-1,3,4-thiadiazole.



4a: X=I, R=R_1=H; **4b**: X=I, R_2=R_3=H; **4c**: X=Br, R=R_1=H; **4d**: X=I, R_2=R_3=H; **4e**: X=I; **4f**: X=Br; **4g**: X=I; **4h**: X=Br; **4i**: X=I, R_2=R_3=CH_3; **4j**: X=Br, R=R_1=CH_3; **4k**: X=Br, R_2=R_3=CH_3

Scheme 5. Halocyclization of S-derivatives of 4,5-dihydro-1,3-thiazol-2-thione

The halocyclization reaction of compound **3b** proceeds with the formation of the single thiazolo-thiazolium system, which has been isolated as 3-(halomethyl)-3-methyl-2,3,5,6-tetrahydrothiazolo[2,3-*b*]thiazolium halides **4e,f**.

The halocyclization reaction of compound **3c** proceeds with the formation of 3-(halomethyl)-3,5,6,7-tetrahydro-2*H*-thiazolo[2,3-*b*][1,3]thiazinium halides **4g,h**.

The iodocyclization reaction of compound **3d** proceeds with the annelation of the six-membered thiazine cycle and the formation of 6-iodo-5,5-dimethyl-3,5,6,7-tetrahydro-2*H*-thiazolo[2,3-*b*]thiazinium iodide in the same way as compound **3c**. In its turn the interaction of compound **3c** with bromine leads to the formation of the mixture of 3-(2-bromopropene)-2,3,5,6-tetrahydrothiazolo[2,3-*b*]thiazolium bromide **4k** and 6-bromo-5,5-dimethyl-3,5,6,7-tetrahydro-2*H*-thiazolo[2,3-*b*]thiazinium bromide **4j** at the ratio of 1:5.

Experiment

The ^{1}H NMR spectra of the synthesized compounds have been recorded on the Bruker DRX-400 (400 MHz) spectrometer in DMSO-d6, the internal standard is TMS. Mass-spectra (EI, 70 eV) have been recorded on the SHIMADZU GCMS QP-2010 Ultra gas chromatograph mass spectrometer.

2-Propenylthio-4,5-dihydrothiazole (2-allylthio-1,3-thiazoline) (3a), 2-(2-methyl-1-propenyl) thio-4,5-dihydrothiazole (3b), 2-butenylthio-4,5-dihydrothiazole (3c), 2-(3-methylbutenyl)thio-4,5-dihydrothiazole (3d).

1,3-Thiazoline-2-thione (1.19 g, 10 mmol) and 10 mmol haloalkene (3-bromopropene (**2a**), 3-chloro-2-methylpropene (**2b**), 4-bromobutene (**2c**), 1-bromo-3-methyl-butene-2 (**2d**)) were added to the sodium solution (0.23 g) in 15 ml ethanol. The mixture was boiled during 3 hours, filtered off, evaporated of ethanol, extracted with diethyl ether. The substance was isolated as viscous yellow liquid. The product yields: **3a:** (64 %); **3b** (62 %); **3c** (72 %); **3d** (62 %).

3-(Iodomethyl)-2,3,5,6-tetrahydrothiazolo[2,3-*b*]thiazolium iodide (4a), 6-iodo-3,5,6,7-tetrahydro-2*H*-thiazolo[2,3-*b*]thiazinium iodide (4b), 3-(iodomethyl)-3-methyl-2,3,5,6-tetrahydrothiazolo[2,3-*b*]thiazolium iodide (4e), 3-(iodomethyl)-3,5,6,7-tetrahydro-2*H*-thiazolo[2,3-*b*][1,3]thiazinium iodide (4g), 6-iodo-5,5-dimethyl-3,5,6,7-tetrahydro-2*H*-thiazolo[2,3-*b*][1,3]thiazinium iodide (4i).

The compound **3a-d** solution (1 mmol) in 3 ml alcohol was added to the iodine solution (0.5 g) in 5 ml alcohol, the solution was decanted after 72 hours, the remaining black substance was dissolved in acetone, then the double excess of NaI in acetone has added, the obtained precipitate was filtered off.

The substance was isolated as yellow crystalline powder. The product yields: **4a, b**: 0.21 g; **4e**: (51 %), m.p. 180–184 °C (decomposition); **4g**: (56 %), m.p. 158–160 °C (decomposition); **4i**: (46 %), m.p. 152 – 154 °C (decomposition).

3-(Bromomethyl)-2,3,5,6-tetrahydrothiazolo[2,3-*b*]thiazolium bromide (4c), 6-bromo-3,5,6,7-tetrahydro-2*H*-thiazolo[2,3-*b*]thiazinium bromide (4d), 3-(bromomethyl)-3-methyl-2,3,5,6-tetrahydrothiazolo[2,3-*b*]thiazolium bromide (4f), 3-(bromomethyl)-3,5,6,7-tetrahydro-2*H*-thiazolo[2,3-*b*][1,3]thiazinium bromide (4h), 6-halo-5,5-dimethyl-3,5,6,7-tetrahydro-2*H*-thiazolo[2,3-*b*][1,3]thiazinium bromide (4j), 3-(2-bromopropenyl)-2,3,5,6-tetrahydrothiazolo[2,3-*b*]thiazolium bromide (4k).

The bromine solution (0.08 ml, 1.5 mmol) in 3 ml chloroform or CH_2Cl_2 was added to the compound **3a-d** solution (1 mmol) in 5 ml chloroform or CH_2Cl_2 while stirring and cooling. The mixture left in hermetically closed flask in a refrigerator for 120 hours. The solution was decanted, the remaining orange viscous liquid was dissolved in acetone. The obtained white crystalline powder was filtered off. The product yields: **4c, d**: 0.095 g; **4f**: (57 %), m.p. 214–216 °C (decomposition); **4h**: (34 %), m.p. 150 –154 °C (decomposition); **4j, k**: 0.18 g.

Conclusion

2-Propenylthio-4,5-dihydrothiazole (2-allylthio-1,3-thiazoline), 2-(2-methyl-1-propenyl)thio-4,5-dihydrothiazole, 2-butenylthio-4,5-dihydrothiazole, 2-(3-methylbutenyl)thio-4,5-dihydrothiazole have been obtained by the interaction of 4,5-dihydro-1,3-thiazole-2-thione with various haloalkene. 3-(Halomethyl)-2,3,5,6-tetrahydrothiazolo[2,3-*b*]thiazolium, 6-halo-3,5,6,7-tetrahydro-2*H*-thiazolo-[2,3-*b*]thiazinium, 3-(halomethyl)-3-methyl-2,3,5,6-tetrahydrothiazolo[2,3-*b*]thiazolium, 3-halomethyl-3,5,6,7-tetrahydro-2*H*-thiazolo[2,3-*b*][1,3]thiazinium, 6-halo-5,5-dimethyl-3,5,6,7-tetrahydro-2*H*-thiazolo[2,3-*b*][1,3]thiazinium halides and 3-(2-bromopropenyl)-2,3,5,6-tetrahydrothiazolo[2,3-*b*]thiazolium bromide have been synthesized by the halocyclization reaction of the obtained sulfides. The structures of the synthesized compounds are proved by the gas chromatography–mass spectrometry and the nucleic magnetic resonance method ^{1}H NMR.

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Received 4 February 2015

УДК 547.789.13

СИНТЕЗ И ГАЛОГЕНЦИКЛИЗАЦИЯ АЛЛИЛЬНЫХ ПРОИЗВОДНЫХ 4,5-ДИГИДРО-1,3-ТИАЗОЛ-2-ТИОНА

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Алкилированием 4,5-дигидро-1,3-тиазол-2-тиона осуществлен синтез 2-пропенил-(2-метил-1-пропенил-, 2-бутенилтио-, и 3-метилбутенил-)тио-4,5-дигидро-1,3-тиазолов, которые исследованы в реакциях галогенциклизации с иодом и бромом. Синтезированы галогениды 3-(галогенметил)-2,3,5,6-тетрагидротиазоло[2,3-*b*]тиазолия и 6-галоген-3,5,6,7-тетрагидро-2*H*-тиазоло[2,3-*b]*тиазиния. Методами ЯМР ^{1}H и хромато-масс-спектрометрии исследовано строение полученных соединений.

Ключевые слова: 4,5-дигидро-1,3-тиазол-2-тион, 2-пропенилтио-4,5-дигидротиазол, 2-(2-метил-1-пропенил)тио-4,5-дигидротиазол, 2-бутенилтио-4,5-дигидротиазол, 2-(3-метилбутенил)тио-4,5-дигидротиазол, галогениды 3-(галогенметил)-2,3,5,6-тетрагидротиазоло[2,3-b]тиазолия и 6-галоген-3,5,6,7-тетрагидро-2H-тиазоло[2,3-b]тиазиния, хромато-масс-спектрометрия, ЯМР ^{1}H.

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Поступила в редакцию 4 февраля 2015 г.

БИБЛИОГРАФИЧЕСКОЕ ОПИСАНИЕ СТАТЬИ

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SYNTHESIS AND STRUCTURE OF PALLADIUM COMPLEX $[Ph_3PCH=CHPPh_3]^{2+}[PdBr_3(DMSO)]^-_2 \cdot DMSO$

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The palladium complex $[Ph_3PCH=CHPPh_3]^{2+}[PdBr_3 \cdot DMSO]^-_2 \cdot DMSO$ (1) has been synthesized by the reaction of palladium dibromide with 1,2-vinylene-bis-triphenylphosphonium dibromide in the presence of hydrobromic acid in water, followed by recrystallization from dimethylsulfoxide. According to the X-ray diffraction data, the phosphorus atoms in cations have a slightly distorted tetrahedral environment (CPC 107.8(3)°–111.7(3)° Å), the P–C bond lengths are 1.779(6)–1.816(5) Å. In the square planar anions, the SPdBr trans-angles are 176.89(5)° and 178.11(6)° Å, and the BrPdBr trans-angles are 177.59(4)° and 177.82(3)° Å. Dimethylsulfoxide ligands are coordinated to the Pd atoms by the sulfur atoms: the Pd–S bond lengths are 2.2634(17) and 2.2666(18) Å, the Pd–Br bond lengths lie in the range of 2.4200(18)–2.4486(9) Å. Structural organization of the crystal is caused by the interionic H···Br (2.90–3.02 Å) and H···O (2.30–2.56 Å) hydrogen bonds.

Keywords: palladium dibromide, hydrobromic acid, 1,2-vinylene-bis-triphenylphosphonium dibromide, dimethylsulfoxide, synthesis, 1,2-vinylene-bis-triphenylphosphonium tribromo(dimethylsulfoxide)palladate, X-ray diffraction analysis, crystal structure.

Introduction

In the chemistry of the platinum-group metals, stable dimethylsulfoxide complexes take important place. Peculiarity of reaction proceeding in dimethylsulfoxide solutions allows to synthesize the compounds, which can not be obtained in aqueous medium. In complexes of the platinum-group metals, the dimethylsulfoxide ligand exhibits the ambidentate coordination mode, being coordinated through oxygen atom and sulfur atom alike, and forms various geometrical and bond isomers [1]. Except theoretical interest, dimethylsulfoxide complexes of the platinum-group metals attract attention of investigators owing to their catalytical and biological activity, in particular, antitumor activity.

Ionic palladium complex compounds with $[PdHal_3(DMSO\text{-}S)]^-$-type anions are represented by a few examples in the literature [2–6]. Phosphororganic cations in the complexes can be mononuclear [6] and binuclear [4]. Structural organization of the crystals strongly depends on the presence of solvent molecules.

In the present paper, the synthesis of 1,2-vinylene-*bis*-triphenylphosphonium tribromo(dimethylsulfoxide)palladate dimethylsulfoxide solvate has been described and the peculiarities of its structure have been considered.

Experimental

Synthesis of $[Ph_3PCH=CHPPh_3]^{2+}[PdBr_3 \cdot DMSO]^-_2 \cdot DMSO$ (1). 0.15 g (0.56 mmol) of palladium dibromide was dissolved in abundance of hydrobromic acid, and added to the solution of 0.41 g (0.56 mmol) of 1,2-vinylene-*bis*-triphenylphosphonium dibromide monohydrate in 20 mL of hot water with stirring. The obtained red-brown precipitate was filtered off, washed by a 20-mL portion of hot water three times, and dried. The washed precipitate was recrystallized from dimethylsulfoxide to yield the cherry-red crystals of complex **1**, yield 0.331 g (84%), m.p. 150 °C. Found, %: C 35.66, H 3.54. Anal. calc. for $C_{44}H_{50}O_3S_3P_2Pd_2Br_6$ (M = 1477.22), %: C 35.75, H 3.39.

IR (ν, cm^{-1}): 3078, 3055, 3027, 2993, 2911, 1583, 1479, 1436, 1405, 1310, 1288, 1189, 1164, 1111, 1022, 997, 970, 932, 916, 842, 771, 743, 726, 686, 524, 488, 449, 425.

IR spectrum was recorded on the Bruker Tensor 27 IR spectrometer in KBr pellets.

The X-ray diffraction experiment for complex **1** crystal was carried out on the automatic four-circle Bruker D8 QUEST diffractometer (Mo K_α radiation, $\lambda = 0.71073$ Å, graphite monochromator). Data collection, their editing, and refinement of the unit cell parameters, as well as the accounting for absorption, were conducted with the use of programs *SMART* and *SAINT-Plus* [7]. All calculations for structure determination and refinement were carried out by the program *SHELXL/PC* [8]. The structure was determined by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms.

The main crystallographic data and structure refinement details are given in Table 1. Atomic coordinates and isotropic equivalent thermal factors are given in Table 2. The main bond lengths and bond angles are listed in Table 3.

Table 1

Crystallographic data and the experimental and structure refinement parameters for compound 1

Parameter	Value
Formula weight	1477.22
T, K	296(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	22.4176(7)
b, Å	9.5016(2)
c, Å	26.2637(8)
α, deg	90.00
β, deg	109.5400(10)
γ, deg	90.00
V, Å^3	5272.1(3)
Z	4
$\rho_{(calcd.)}$, g/cm^3	1.861
μ, mm^{-1}	5.445
F(000)	2872.0
Crystal size, mm	0.33×0.14×0.12
θ Range of data collection, deg	5.96–52.84
Range of refraction indices	$-28 \le h \le 27, -11 \le k \le 11, -32 \le l \le 32$
Measured reflections	93694
Independent reflections	10790
Refinement variables	547
GOOF	1.026
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0481$, $wR_2 = 0.1333$
R factors for all reflections	$R_1 = 0.0872$, $wR_2 = 0.1571$
Residual electron density (min/max), *e*/Å^3	2.53/–1.66

Table 2

Atomic Coordinates (×10^4) and isotropic equivalent thermal factors (Å^2×10^3) in the structure of substance 1

Атом	*x*	*y*	*z*	$U_{экв}/U_{изо}$*	Атом	*x*	*y*	*z*	$U_{экв}/U_{изо}$*
Pd(1)	4811.7(2)	4159.1(5)	799.37(19)	44.88(15)	C(5)	2370(5)	–5926(8)	–4007(3)	72(2)
Pd(2)	–52.9(2)	–4435.9(5)	–5974.0(2)	40.28(14)	C(46)	2272(3)	–475(8)	–947(3)	55.2(17)
Br(4)	–1077.4(3)	–3708.6(8)	–6583.8(3)	55.0(2)	C(32)	2412(3)	–4305(7)	–1190(3)	57.1(18)
Br(2)	4887.7(4)	1589.9(8)	782.7(3)	61.0(2)	C(2)	3443(3)	–4270(8)	–3577(3)	56.3(18)
Br(6)	284.2(4)	–1976.0(8)	–5878.6(3)	65.2(2)	C(52)	1300(3)	–92(6)	–2507(2)	42.1(14)
Br(1)	3689.0(4)	4032.1(9)	295.7(3)	70.0(2)	C(12)	3954(3)	–1826(7)	–2558(3)	53.6(16)
Br(3)	5928.7(4)	4257.0(8)	1338.7(4)	76.8(3)	C(33)	2329(4)	–5679(9)	–1065(3)	88(3)
Br(5)	964.2(4)	–5144.8(10)	–5331.8(3)	75.4(3)	C(34)	1892(4)	–6510(8)	–1423(3)	73(2)
P(1)	2762.3(7)	–2122.3(15)	–3315.2(6)	34.2(3)	C(35)	1536(3)	–5990(7)	–1923(3)	58.2(18)
P(2)	2149.8(6)	–1981.7(15)	–1860.2(6)	31.8(3)	C(16)	3677(3)	–171(7)	–3286(3)	49.7(16)
S(2)	–356.2(8)	–6717.0(17)	–6106.0(7)	48.9(4)	C(3)	3479(4)	–5594(9)	–3802(3)	74(2)
S(1)	4767.4(9)	6537.7(19)	841.6(7)	56.9(4)	O(2)	–972(2)	–7063(5)	–6501(2)	81.8(17)

Table 2 (end)

Атом	*x*	*y*	*z*	$U_{экв}/U_{изо}$*	Атом	*x*	*y*	*z*	$U_{экв}/U_{изо}$*
C(54)	217(3)	73(7)	–2561(3)	50.8(16)	O(1)	4773(3)	7108(5)	1351(2)	82.9(17)
C(27)	2372(3)	–2356(6)	–2823(2)	38.7(13)	C(21)	2255(3)	–1126(6)	–3864(2)	40.4(13)
C(56)	886(3)	–1659(6)	–1988(2)	38.2(13)	C(26)	1894(3)	–17(7)	–3779(3)	55.2(17)
C(31)	2055(3)	–3776(6)	–1693(2)	34.9(12)	C(22)	2204(3)	–1489(8)	–4392(3)	61.8(19)
C(41)	2594(3)	–1048(6)	–1263(2)	34.5(12)	C(15)	4277(4)	421(9)	–3071(3)	69(2)
C(55)	307(3)	–1001(7)	–2197(3)	49.6(16)	C(13)	4550(3)	–1220(9)	–2353(3)	69(2)
C(42)	3234(3)	–911(6)	–1106(3)	45.8(15)	C(25)	1505(4)	706(8)	–4212(3)	69(2)
C(1)	2862(3)	–3813(6)	–3566(2)	39.8(13)	C(24)	1462(4)	351(9)	–4735(3)	75(2)
C(45)	2604(4)	241(9)	–482(3)	69(2)	C(14)	4703(4)	–93(10)	–2612(4)	78(2)
C(4)	2953(5)	–6395(8)	–4010(3)	75(2)	C(23)	1799(4)	–711(9)	–4821(3)	80(3)
C(11)	3518(3)	–1287(6)	–3024(2)	38.5(13)	C(61)	5368(5)	7319(9)	651(4)	91(3)
C(51)	1383(2)	–1210(6)	–2154(2)	32.9(12)	C(62)	4126(5)	7313(11)	317(5)	130(5)
C(28)	2571(3)	–1849(6)	–2340(2)	38.1(13)	C(64)	–314(4)	–7517(9)	–5494(3)	79(2)
C(53)	711(3)	532(7)	–2712(3)	52.8(17)	C(63)	218(4)	–7708(9)	–6287(3)	79(2)
C(43)	3570(3)	–190(7)	–633(3)	56.8(18)	S(3)	3083.5(18)	2337(3)	–2080,1(2)	128.8(11)
C(44)	3247(4)	377(7)	–330(3)	62(2)	O(3)	2679(4)	1117(7)	–2444(4)	156(4)
C(36)	1624(3)	–4627(6)	–2061(3)	46.7(15)	C(66)	2930(6)	3110(30)	–2553(4)	319(18)
C(6)	2328(3)	–4635(7)	–3783(3)	55.3(17)	C(65)	3819(6)	2158(18)	–2123(7)	225(11)

Table 3

Selected bond lengths and bond angles in the structure of compound 1

Bond	*d*, Å	Angle	ω, deg
P(1)–C(1)	1.779(6)	C(1)P(1)C(21)	107.8(3)
P(1)–C(11)	1.794(6)	C(11)P(1)C(21)	111.5(3)
P(1)–C(21)	1.780(6)	C(21)P(1)C(27)	108.4(3)
P(1)–C(27)	1.801(5)	C(31)P(2)C(28)	111.7(3)
P(2)–C(31)	1.791(6)	C(41)P(2)C(28)	108.0(3)
P(2)–C(41)	1.787(5)	Br(1)Pd(1)Br(2)	90.36(3)
P(2)–C(51)	1.788(5)	Br(2)Pd(1)Br(3)	89.10(3)
P(2)–C(28)	1.816(5)	Br(1)Pd(1)Br(3)	177.59(4)
C(27)–C(28)	1.288(8)	S(1)Pd(1)Br(1)	91.26(5)
Pd(1)–Br(1)	2.4231(9)	S(1)Pd(1)Br(3)	89.24(5)
Pd(1)–Br(2)	2.4486(9)	S(1)Pd(1)Br(2)	178.11(6)
Pd(1)–Br(3)	2.4317(9)	Br(4)Pd(2)Br(6)	89.27(3)
Pd(1)–S(1)	2.2666(18)	Br(5)Pd(2)Br(6)	90.45(3)
Pd(2)–Br(4)	2.4200(8)	Br(4)Pd(2)Br(5)	177.82(3)
Pd(2)–Br(5)	2.4341(8)	S(2)Pd(2)Br(4)	90.12(5)
Pd(2)–Br(6)	2.4433(8)	S(2)Pd(2)Br(5)	90.28(5)
Pd(2)–S(2)	2.2634(17)	S(2)Pd(2)Br(2)	176.89(5)

Results and Discussion

To synthesize new palladium complexes, we have investigated the reaction of 1,2-vinylene-*bis*-triphenylphosphonium dibromide with palladium dibromide in the presence of hydrobromic acid.

We have ascertained that the addition of the equmolar amount of palladium dibromide, which is dissolved in hydrobromic acid, to the hot aqueous solution of 1,2-vinylene-*bis*-triphenylphosphonium dibromide leads to the red-brown precipitate formation. After its recrystallization from dimethylsulfoxide, it represents the cherry-red needle crystals of 1,2-vinylene-*bis*-triphenylphosphonium tribromo(dimethylsulfoxide)palladate dimethylsulfoxide solvate $[Ph_3PCH=CHPPh_3]^{2+}[PdBr_3DMSO]^-_2 \cdot DMSO$ (**1**):

$$[Ph_3PCH=CHPPh_3]Br_2 \xrightarrow[2.\ DMSO]{1.\ PdBr_2 + HBr} [Ph_3PCH=CHPPh_3]^{2+}[PdBr_3 \cdot DMSO]^-_2 \cdot DMSO$$

1

According to the X-ray diffraction data, the phosphorus atoms in $[Ph_3PCH=CHPPh_3]^{2+}$ cations have a slightly distorted tetrahedral coordination geometry (Fig. 1).

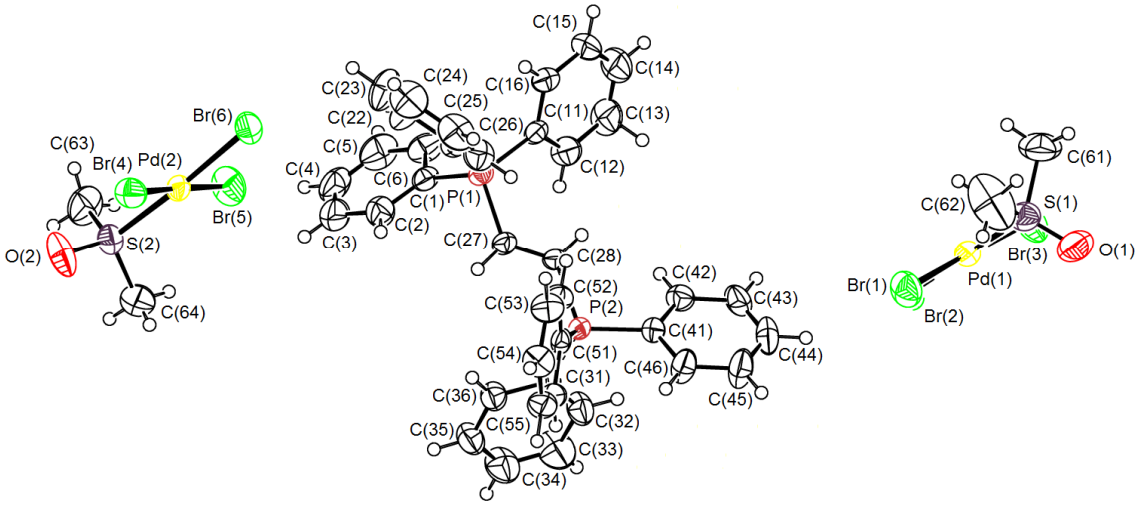


Fig. 1. The structure of the compound 1 (solvating toluene molecule doesn't show)

The valence angles CPC (107.8(3)–111.7(3)°) differ but little from the theoretical value. The P–C lengths (1.779(6)–1.816(5) Å) are close to the sum of covalent radii of the phosphorus and carbon atoms 1.88 Å [9]. The Ph_3P groups are in *trans*-positions relative to the vinyl fragment. The bond length C(27)–C(28) equals 1.288(8) Å, which is less than the reference value for the C(sp^2)–C(sp^2) bond (1.34 Å [10]).

Palladium atoms in the two kinds of crystallographically independent square mononuclear anions are tetracoordinated. Level difference of atoms Pd(1) and Pd(2) compared to the average plane $[Br_3S]$ is 0.035 and 0.008 Å. The valence *trans*-angles BrPd(1,2)Br and BrPd(1,2)S equal 177.59(4), 177.82(3)° and 178.11(6), 176.89(5)°. The bond lengths Pd(1)–Br and Pd(2)–Br equal 2.4231(9), 2.4317(9), 2.4486(9) Å и 2.4200(8), 2.4341(8), 2.4433(8) Å; at this the longest bonds Pb-Br are in *trans*-positions relative to the dimethylsulphoxide ligand. Dimethylsulphoxide ligands are coordinated by the palladium atom through sulfur atoms, the lengths Pd(1)–S(1) and Pd(2)–S(2) equal 2.263(2) и 2.267(2. The bond lengths S(1)–O(1) and S(2)–O(2) are 1.440(6) and 1.460(4) Å, respectively; they are smaller than the similar length in the molecule of uncoordinated dimethylsulfoxide (1.581 Å). This is compatible with the literature data, which indicate that the bond order S=O increases at dimethylsulfoxide coordination with the metal atom through sulfur.

In the complex crystal numerous hydrogen bonds exist between cations, anions and the solvate molecules of the solvent, such as H···Br (2.90–3.02 Å) and H···O (2.30–2.56 Å)

Conclusion

Thus, for the first time the palladium complex $[Ph_3PCH=CHPPh_3][PdBr_3\cdot DMSO]_2\cdot DMSO$ has been synthesized and characterized as to its structure. The peculiarities of the complex structure are the existence of two types of dimethylsulfoxide molecules (coordinated by palladium and free), as well as the observed redistribution of the electron density in anions, which appears as the *trans*-bond Pd–Br lengthening and the bond order S=O increasing.

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Received 18 December 2014

УДК 547.243; 548.737

СИНТЕЗ И СТРОЕНИЕ КОМПЛЕКСА ПАЛЛАДИЯ $[Ph_3PCH=CHPPh_3]^{2+}[PdBr_3(DMSO)]^-_2 \cdot DMSO$

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Взаимодействием бромида палладия с дибромидом 1,2-винилен-бис-трифенилфосфония в присутствии бромистоводородной кислоты в воде с последующей перекристаллизацией из диметилсульфоксида синтезирован комплекс палладия $[Ph_3PCH=CHPPh_3]^{2+}[PdBr_3 \cdot DMSO]^-_2 \cdot DMSO$ (1). По данным РСА, атомы фосфора в катионах имеют мало искаженное тетраэдрическое окружение (СРС 107,8(3)°–111,7(3)°), длины связей P–C составляют 1,779(6)–1,816(5) Å. В плоско-квадратных анионах углы SPdBr-транс 176,89(5)° и 178,11(6)° и BrPdBr-транс 177,59(4)° и 177,82(3)°; диметилсульфоксидные лиганды координируются с атомами Pd посредством атомов серы: Pd-S 2,2634(17) и 2,2666(18) Å, длины связей Pd–Br изменяются в интервале 2,4200(18)–2,4486(9) Å. Структурная организация в кристалле обусловлена межионными водородными связями H···Br 2,90–3,02 Å и H···O 2,30–2,56 Å.

Ключевые слова: дибромид палладия, бромистоводородная кислота, дибромид 1,2-винилен-бис-трифенилфосфония, диметилсульфоксид, синтез, трибромо-(диметилсульфоксидо)палладат 1,2-винилен-бис-трифенилфосфония, рентгеноструктурный анализ, строение.

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Поступила в редакцию 18 декабря 2014 г.

БИБЛИОГРАФИЧЕСКОЕ ОПИСАНИЕ СТАТЬИ

Synthesis and Structure of Palladium Complex $[Ph_3PCH{=}CHPPh_3]^{2+}[PdBr_3(DMSO)]^-_2{\cdot}DMSO$ / V.V. Sharutin, O.K. Sharutina, V.S. Senchurin, I.A. Il'chenko // Вестник ЮУрГУ. Серия «Химия». – 2015. – Т. 7, № 2. – С. 11–16.

REFERENCE TO ARTICLE

Sharutin V.V., Sharutina O.K., Senchurin V.S., Il'chenko I.A. Synthesis and Structure of Palladium Complex $[Ph_3PCH{=}CHPPh_3]^{2+}[PdBr_3(DMSO)]^-_2{\cdot}DMSO$. *Bulletin of the South Ural State University. Ser. Chemistry.* 2015, vol. 7, no. 2, pp. 11–16.

REACTIONS OF TRI(*ORTHO*-TOLYL)- AND TRI(*META*-TOLYL)ANTIMONY WITH OXIMES IN THE PRESENCE OF AN OXIDANT. THE STRUCTURES OF TRI(*ORTHO*-TOLYL)- AND TRI(*META*-TOLYL)ANTIMONY DIOXIMATES

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The triarylantimony dioximates: (o-$CH_3C_6H_4)_3Sb(ON{=}CHC_6H_4N(CH_3)_2$-4)$_2$ (1), (o-$CH_3C_6H_4)_3Sb(ON{=}CMePh)_2$ (2), (m-$CH_3C_6H_4)_3Sb(ON{=}CHC_4H_3O)_2$ (3) were obtained from the reactions of tri(*ortho*-tolyl)antimony and tri(*meta*-tolyl)antimony with appropriate oximes in the presence of hydrogen peroxide and *tert*-butyl hydroperoxide. According to the X-ray analysis data, antimony atoms are bound to oxygen atoms of axial oximate ligands in the trigonal bipyramidal coordination in molecules 1–3. The peculiarities of molecular structures are short intramolecular contact Sb···N, which is 1 Å less than the sum of Van der Waals radiuses.

Keywords: tri(ortho-tolyl)antimony, tri(meta-tolyl)antimony, oximes, tert-butyl hydroperoxide, hydrogen peroxide, oxidizing reactions, bis[4-N,N(dimethylamino)-benzaldoximato]tri(ortho-tolyl)antimony, bis(acetophenonoximato)_tri(ortho-tolyl)antimony, bis(furfuradloximato)tri(meta-tolyl) antimony, molecular structures, X-ray analysis.

Introduction

Triarylantimony oxidative addition reaction (reagent is an acid with the general formula HA, the oxidizing agent is peroxide) is of interest as an effective single-stage reaction to synthetize antimony (V) aryl derivatives Ar_3SbX_2. However, using oxime in such reaction, even with 1:2:1 mole ratio of the reactants, led to the formation of two different product: $Ar_3Sb(ONCRR')_2$ and $(Ar_3SbONCRR')_2O$ [1, 2]. This resulted in a necessity for product separation. It was found that the interaction of triphenylantimony with oxime in the presence of hydrogen peroxide (1:1:1 molar ratio of the reactants) led to the formation of oxo-derivatives of triarylantimony $(Ph_3SbONCRR')_2O$ [3]. One further peculiarity of oxidative addition reaction between triarylantimony and oximes is the dependence of the product molecular structure on the nature of aryl ligands, situated at antimony atom. Thus, furfuraloxime ligands are bidentate bridging ligands in the molecule of *bis*(μ_2-furfuraloximato)-(μ_2-oxo)-*bis*[triphenylantimony]. These ligands are coordinated by the oxygen atom to the first antimony atom and by the nitrogen atom to the second antimony atom. This fact increases antimony coordination number to six [3]. However, the molecule of μ_2-oxo-*bis*[(furfuraldoximato)tri*(o*-tolyl)antimony] is of the regular molecular structure type which includes monodentate ligands [4]. 2-Hydroxybenzaldoxim reacts with triphenylantimony and tri(*o*-tolyl)antimony in the presence of an oxidizing agent to form triarylantimony dioximates [5, 6], whereas its reaction with tri(*m*-tolyl)antimony and *tris*(5-bromo-2-methoxyphenyl)antimony leads to the formation of binuclear complex with Sb–O–Sb bond in which every ligand is tridentate chelating-bridging one [6, 7].

To improve oxidative synthesis method of organoantimony compounds with oxime ligands the present paper continuates investigating reactions of tri(*o*-tolyl)antimony and tri(*m*-tolyl)antimony with oximes in the presence of hydrogen peroxide or *tert*-butyl hydroperoxide (1:2:1 and 1:1:1 mole ratio of the reactants) in various solvents.

Experimental

Synthesis of *bis*[4-N,N(dimethylamino)benzaldoximato]tri(*o*-tolyl)antimony (1).

a) Tri(*o*-tolyl)antimony (100 mg, 0.25 mmol) was dissolved in diethyl ether (30 mL). Then 4-N,N-(dimethylamino)benzaldoxime (82 mg, 0.50 mmol) and hydrogen peroxide (28 mg, 30 % aqueous, 0.25 mmol) were added. The solution was left to stand for 24 hours at temperature 20 °C. When the solvent evaporated, the product was a light green crystalline substance; yield 156 mg (85 %), MP: 154 °C.

b) Tri(*o*-tolyl)antimony (150 mg, 0.40 mmol) was dissolved in diethyl ether (30 mL). Then 4-N,N(dimethylamino)benzaldoxime (125 mg, 0.80 mmol) and *tert*-butyl hydroperoxide (49 mg, 70 % aqueous, 0.40 mmol) were added. The solution was left to stand for 24 hours at temperature 20 °C. The fine-cristalline substance were obtained; the product yield 267 mg (97 %), MP: 155 °C.

c) Tri(*o*-tolyl)antimony (100 mg, 0.25 mmol) was dissolved in diethyl ether (30 mL). Then 4-N,N(dimethylamino)benzaldoxime (41 mg, 0.25 mmol) and hydrogen peroxide (32 mg, 30 % aqueous, 0.25 mmol) were added. The solution was left to stand for 24 hours. The solid precipitate was washed with small portions of heated toluene. The fine white toluene insoluble precipitate powder with decomposition heat more than 300 °C weighted 17 mg (16 %). Substance **1** (yield 79 mg (87 %), MP: 154 °C) was isolated from toluene solution.

IR spectrum (ν, cm^{-1}): 3045, 3006, 2949, 2922, 2801, 1608, 1525, 1479, 1444, 1412, 1366, 1329, 1232, 1178, 1122, 1066, 1032, 1006, 945, 878, 817, 797, 744, 703, 609, 524, 485, 438, 412.

For $C_{39}H_{43}N_4O_2Sb$ anal. calcd. (%): C 64.86, H 5.96. Found, %: C 64.80, H 6.07.

Synthesis of bis(acetophenonoximato)tri(o-tolyl)antimony (2).

a) Tri(o-tolyl)antimony (150 mg, 0.40 mmol) was dissolved in diethyl ether (30 mL). Then acetophenonoxime (103 mg, 0.80 mmol) and hydrogen peroxide (43 mg, 30 % aqueous, 0.4 mmol) were added. The solution was left to stand for 24 hours at temperature 20 °C. When the solvent evaporated, solid precipitate was crystallized from toluene. A colorless needle-shaped crystals were obtained; yield 232 mg (87 %), MP: 161 °C.

b) Tri(*o*-tolyl)antimony (150 mg, 0.40 mmol) was dissolved in tetrachloromethane (30 mL). Then acetophenonoxime (103 mg, 0.80 mmol) and *tert*-butyl hydroperoxide (49 mg, 70 % aqueous, 0.40 mmol) were added. The solution was left to stand for 24 hours. When the solvent evaporated, fine-cristalline precipitate was crystallized from toluene to give a colorless crystalline substance (248 mg, 98 %, MP: 162 °C).

c) Tri(*o*-tolyl)antimony (100 mg, 0.25 mmol) was dissolved in diethyl ether (30 mL). Then acetophenonoxime (34 mg, 0.25 mmol) and *tert*-butyl hydroperoxide (32 mg, 70 % aqueous, 0.25 mmol) were added. The solution was left to stand for 24 hours. When the solvent evaporated, fine-cristalline precipitate was crystallized from toluene to give a colorless crystals (248 mg, 98 %, MP: 162 °C). After 24 hours the product was washed with small portions of heated toluene. Fine solid toluene insoluble precipitate powder with decomposition heat more than 300 °C weighted 37 mg (35 %). The substance **2** (yield 75 mg, 90 %, MP: 160 °C) was isolated from toluene solution.

IR spectrum (ν, cm^{-1}): 3053, 3006, 2928, 1588, 1494, 1471, 1442, 1364, 1306, 1280, 1206, 1163, 1121, 1029, 994, 927, 761, 748, 693, 679, 554, 518, 487, 437, 411.

For $C_{37}H_{37}N_2O_2Sb$ anal. calcd. (%): C 66.92, H 5.58. Found, %: C 66.87, H 5.69.

Synthesis of bis(furfuraloximato)tri(*m*-tolyl)antimony (3).

a) Tri(m-tolyl)antimony (100 mg, 0.25 mmol) was dissolved in hexane (15 mL). Then furfuraloxime (56 mg, 0.50 mmol) and *tert*-butyl hydroperoxide (23 mg, 70 % aqueous, 0.25 mmol) were added. The solution was left to stand for 24 hours at temperature 20 °C. When the solvent evaporated, white crystalline substance were obtained. The product yield 153 mg (98 %), MP: 133 °C.

b) Tri(*m*-tolyl)antimony (100 mg, 0.25 mmol) was dissolved in diethyl ether (20 mL). Then furfuraloxime (28 mg, 0.25 mmol) and *tert*-butyl hydroperoxide (23 mg, 70 % aqueous, 0.25 mmol) were added. Obtained solid precipitate was crystallized from toluene to give a white crystals **3** (67 mg (87 %), MP: 134 °C). Amorphous toluene insoluble powder had decomposition heat more than 300 °C.

IR spectrum (ν, cm^{-1}): 3234, 3137, 2910, 2804, 2361, 2343, 1609, 1557, 1526, 1477, 1445, 1428, 1361, 1302, 1225, 1186, 1170, 1126, 1066, 957, 868, 813, 736, 571, 528, 493, 442, 424.

For $C_{31}H_{29}N_2O_4Sb$ anal. calcd. (%): C 60.46, H 4.71. Found, %: C 60.28, H 4.83.

IR spectra were recorded on the Bruker Tensor 27 FT-IR (KBr pellets; 4000–400 cm^{-1}).

The X-ray diffraction analyses of crystalline substances **1**–**3** were made on the Bruker D8 QUEST automatic four-circle diffractometer (Mo K_α- emission, $\lambda = 0.71073$ Å, graphite monochromator).

The data were collected and analyzed, the unit cell parameters were refined, and the absorption correction was applied using the *SMART* and *SAINT-Plus* programs [8]. All calculations for structure determination and refinement were performed using the *SHELXL/PC* programs [9]. The structures **1**, **2** and **3** were determined by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. The main crystallographic data and refinement results for structures **1**, **2** and **3** are listed in Table 1. The selected bond lengths and bond angles are given in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC 1012010, 1013407, 1009237 for compounds **1**, **2** and **3**, respectively; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

Table 1

Crystallographic data and the experimental and structure refinement parameters for compounds 1–3

Parameter	Value		
	1	**2**	**3**
Empirical formula	$C_{39}H_{43}N_4O_2Sb$	$C_{37}H_{37}N_2O_2Sb$	$C_{31}H_{29}N_2O_4Sb$
Formula weight	721.53	663.45	615.32
T, K	298	273	296
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	Cc	P1	Cc
a, Å	14.5074(5)	10.2151(3)	20.8574(6)
b, Å	10.9331(3)	10.4979(4)	10.3011(3)
c, Å	22.7362(7)	15.9822(5)	15.3511(5)
α, deg	90.00	99.295(1)	90.00
β, deg	93.198(1)	102.960(1)	119.721(1)
γ, deg	90.00	91.749(1)	90.00
V, Å^3	3600.59(19)	1644.32(9)	2864.36(135
Z	4	2	4
$\rho_{(calcd.)}$, g/cm^3	1.331	1.340	1.427
μ, mm^{-1}	0.804	0.872	1.000
F(000)	1488.0	680.0	1248.0
Crystal size, mm	0.50×0.49×0.22	0.40×0.36×0.23	0.75×0.38×0.13
θ Range of data collection, deg	2.9 – 26.098	2.94 – 26.096	3.06 – 26.44
Range of refraction indices	$-17 \le h \le 17$, $-13 \le k \le 13$, $-28 \le l \le 28$	$-12 \le h \le 12$, $-12 \le k \le 12$, $-19 \le l \le 19$	$-26 \le h \le 26$, $-12 \le k \le 12$, $-19 \le l \le 19$
Measured reflections	47631	50217	18330
Independent reflections	7107	12975	5902
R_{int}	0.0237	0.0211	$R_{int} = 0.0216$
Refinement variables	422	768	346
GOOF	1.119	1.089	1.122
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0259$, $wR_2 = 0.0651$	$R_1 = 0.0268$, $wR_2 = 0.0673$	$R_1 = 0.0272$, $wR_2 = 0.0618$
R factors for all reflections	$R_1 = 0.0289$, $wR_2 = 0.0665$	$R_1 = 0.0306$, $wR_2 = 0.0702$	$R_1 = 0.0343$, $wR_2 = 0.0655$
Residual electron density (min/max), *e*/Å^3	0.44/–0.30	0.66/–0.42	0.71/–0.49

Table 2

Selected bond lengths and bond angles in the structures of compounds 1–3

Bond	*d*, Å	Angle	ω, deg
1			
Sb(1)–C(1)	2.1108(17)	O(1)Sb(1)O(4)	168.92(5)
Sb(1)–C(11)	2.119(2)	C(1)Sb(1)C(21)	118.90(12)
Sb(1)–C(21)	2.149(3)	C(11)Sb(1)C(21)	115.04(7)

Table 2 (end)

Bond	*d*, Å	Angle	ω, deg
Sb(1)–O(1)	2.1047(18)	C(1)Sb(1)C(11)	126.02(12)
Sb(1)–O(4)	2.0395(19)	N(1)O(1)Sb(1)	112.93(13)
O(1)–N(1)	1.407(3)	O(1)N(1)C(37)	107.4(2)
O(2)–N(3)	1.361(3)	N(3)O(2)Sb(1)	114.86(15)
N(1)–C(37)	1.246(3)	O(2)N(3)C(47)	117.7(2)
N(3)–C(47)	1.334(4)	C(44)N(4)C(48)	117.8(3)
2			
Sb(1)–C(1)	2.114(3)	O(1)Sb(1)O(2)	172.14(6)
Sb(1)–C(11)	2.106(2)	C(1)Sb(1)C(21)	116.68(10)
Sb(1)–C(21)	2.138(3)	C(11)Sb(1)C(21)	126.22(9)
Sb(1)–O(1)	2.0615(14)	C(1)Sb(1)C(11)	117.09(10)
Sb(1)–O(2)	2.0600(13)	N(1)O(1)Sb(1)	115.31(11)
O(1)–N(1)	1.431(2)	O(1)N(1)C(37)	111.02(17)
O(2)–N(2)	1.384(2)	N(2)O(2)Sb(1)	115.19(12)
N(1)–C(37)	1.326(2)	O(2)N(2)C(47)	116.30(19)
N(2)–C(47)	1.289(3)	O(3)Sb(2)O(4)	174.29(7)
Sb(2)–C(61)	2.131(2)	C(61)Sb(2)C(71)	116.03(10)
Sb(2)–C(71)	2.099(3)	C(61)Sb(2)C(81)	116.33(9)
Sb(2)–C(81)	2.154(3)	C(81)Sb(2)C(71)	127.63(10)
Sb(2)–O(3)	2.1000(17)	N(3)O(3)Sb(2)	113.88 (14)
Sb(2)–O(4)	2.0841(15)	O(3)N(3)C(97)	111.8(2)
O(3)–N(3)	1.393(3)	N(4)O(4)Sb(2)	115.98(13)
O(4)–N(4)	1.351(3)	O(4)N(4)C(107)	113.7(2)
N(3)–C(97)	1.226(3)	N(3)C(97)C(91)	114.0(3)
N(4)–C(107)	1.219(3)	N(3)C(97)C(98)	124.3(3)
3			
Sb(1)–C(1)	2.106(9)	O(1)Sb(1)O(2)	174.30(9)
Sb(1)–C(11)	2.106(3)	C(1)Sb(1)C(21)	112.02(10)
Sb(1)–C(21)	2.110(10)	C(11)Sb(1)C(21)	123.3(5)
Sb(1)–O(1)	2.058(6)	C(1)Sb(1)C(11)	124.6(5)
Sb(1)–O(2)	2.107(7)	C(1)Sb(1)O(1)	84.6(3)
O(1)–N(1)	1.358(13)	N(1)O(1)Sb(1)	110.3(6)
O(2)–N(2)	1.374(11)	O(1)N(1)C(37)	117.9(10)
N(1)–C(31)	1.310(14)	N(2)O(2)Sb(1)	109.2(6)
N(2)–C(36)	1.241(15)	O(2)N(2)C(47)	107.4(8)

Results and Discussion

The reactions of tri(*o*-tolyl)antimony with 4-N,N-dimethylbenzaldoxime and acetophenonoxime have been investigated in the present study. The variable factors: the oxidizing agent (hydrogen peroxide or *tert*-butylhydroperoxide), solvent (diethyl ether, heptane, carbon tetrachloride), the molar ratio of the reactants (1:2:1 or 1:1:1). It has been found that the interaction of tri(*o*-tolyl)antimony with oximes at the molar ratio 1:2:1, irrespective of the oxidizing agent nature (hydrogen peroxide or *tert*-butyl hydroperoxide), proceeds as the oxidative addition reaction with the formation of high-yield tri(*o*-tolyl)antimony dioximates.

$o\text{-Tol}_3\text{Sb} + 2\ \text{HON=CRR'} + \text{R''OOH} \rightarrow o\text{-Tol}_3\text{Sb(ON=CRR')}_2 + \text{R''OOH} + \text{H}_2\text{O}$

R = H, R' = $C_6H_4N(CH_3)_2$ (**1**); R = Me, R' = Ph (**2**); R'' = H or *t*-Bu.

Tri(*o*-tolyl)antimony dioximates **1** and **2** are crystalline substances which are resistant to the effect of moisture and air oxygen, they are freely soluble in aromatic and aliphatic hydrocarbons. It has been found that the solvent nature does not affect the yield, which remains consistently high.

Previously it was shown that the oxidative addition reaction of triphenyl- or tri(*p*-tolyl)antimony and oxime at the molar ratio 1:1 led to the binuclear organoantimony compound with the bridging oxygen atom of the general formula $(Ar_3SbONCRR')_2O$ [3].

We have found that the reaction of tri(*o*-tolyl)antimony and 4-N,N-dimethylbenzaldoxime or acetophenone oxime in the presence of hydrogen peroxide or *tert*-butyl hydroperoxide at the molar ratio 1:1:1 leads to the formation of the mixture of products: tri(*o*-tolyl)antimony dioximate and tri(*o*-tolyl)antimony oxide with a polymeric structure.

$$o\text{-}Tol_3Sb + HON{=}CRR' + R''OOH \rightarrow o\text{-}Tol_3Sb(ON{=}CRR')_2 + o\text{-}Tol_3SbO + 2\ R''OOH + H_2O$$

R = H, R' = $C_6H_4N(CH_3)_2$ (**1**); R = Me, R' = Ph (**2**); R'' = H или *t*-Bu.

The interaction of tri(*m*-tolyl)antimony and furfuraldoxime at the molar ratios of 1:2:1 and 1:1:1 in the presence of hydrogen peroxide in diethyl ether results in the formation of μ_2-oxo-*bis* [(furfuraldoximato)tri(*m*-tolyl)antimony] with the melting point 235 °C.

$$2\ m\text{-}Tol_3Sb + 2\ HON{=}CHC_4H_3O + 2\ H_2O_2 \rightarrow (m\text{-}Tol_3SbON{=}CHC_4H_3O)_2O + 3\ H_2O$$

At the ratio of tri(*m*-tolyl)antimony to oxime to hydrogen peroxide of 1:2:1 (mol.) an oxime is in excess. Therefore, the fixed residue is the mixture of an organoantimony compound and unreacted oxime. After separation of the mixture by fractional recrystallization method, the desired product yield inevitably decreases, it turns out lower than the yied at the molar ratio 1:1:1 (75 % and 96 % respectively).

But in the presence of *tert*-butyl hydroperoxide, irrespective of the mole ratio of the reactants, *bis*(furfuraldoximato)tri(*m*-tolyl)antimony (**3**) is obtained.

$$m\text{-}Tol_3Sb + 2\ HON{=}CHC_4H_3O + t\text{-}BuOOH \rightarrow m\text{-}Tol_3Sb(ON{=}CHC_4H_3O)_2 + t\text{-}BuOH + H_2O$$

At the molar ratio 1:2:1, the yield is 90–98 %, irrespective of the solvent (diethyl ether, hexane, carbon tetrachloride).

Decrease of the oxime concentration (1: 1: 1 mol.) is followed by the formation of high melting co-product, which, we believe, is the polymeric oxide of tri(*m*-tolyl)antimony $[(m\text{-}Tol)_3SbO]_n$.

Triarylantimony dioximates have been identified by infrared spectroscopy and X-ray analysis.

The molecules of all compounds contain the same structure fragments, so their IR spectra are similar to each other. The presence of three aryl fragments in this organoantimony compounds does complicate determination of characteristic bands belonging to the stretching vibrations of C=N and N–O, which are detected in oximes at intervals 1685–1650 and 960–930 cm^{-1}, respectively, because it is the area which contains aryl groups vibrational bands [10, 11].

To assign the absorption bands in the IR spectra of triarylantimony dioximates, we have obtained spectra of oximes, which have been used for synthesis. The absorption bands with frequencies at intervals of 3650–3500 cm^{-1} (OH-groups), 1568–1643 cm^{-1} (C=N bonds), 926–968 cm^{-1} (N–O bonds) have been found in the IR spectra of oximes.

The spectra of the compounds contain the intensive absorption band at 440 cm^{-1}, which, according to the literature, refers to vibrations of SbC_3 fragment, having C_3 symmetry [12]. The absorption bands at 410–425 cm^{-1} characterize the vibrations of the Sb–O [13].

The stretching vibrations of C = N bonds in triarylantimony dioximates (1608, 1588, 1557 cm^{-1} in **1**, **2** and **3**, respectively) slightly shift to the low frequency region of the spectrum compared to the same absorption band in the corresponding oximes.

The absorption band, characterizing N–O bonds vibrations, also shifts to the low frequency region of the spectrum (945, 927, 957 cm^{-1} in **1**, **2** and **3** respectively). This indicates, it seems, that the C=N and N–O bond lengths in triarylantimony dioximates increase compared to oximes.

According to X-ray diffraction data, the molecules of compounds **1**, **2** (the crystal contains two types of crystallographically independent molecules ***a*** and ***b***) and **3**, the antimony atoms have trigonal-bipyramidal coordination with the oximate ligands oxygen atoms in axial positions (Fig. 1–3).

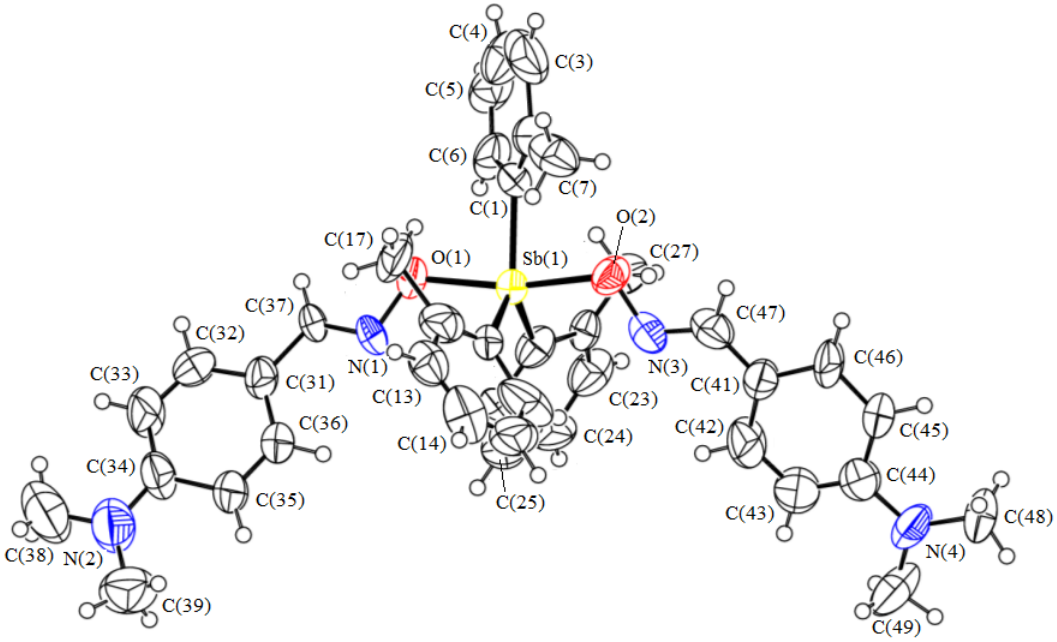


Fig. 1. The structure of compound 1

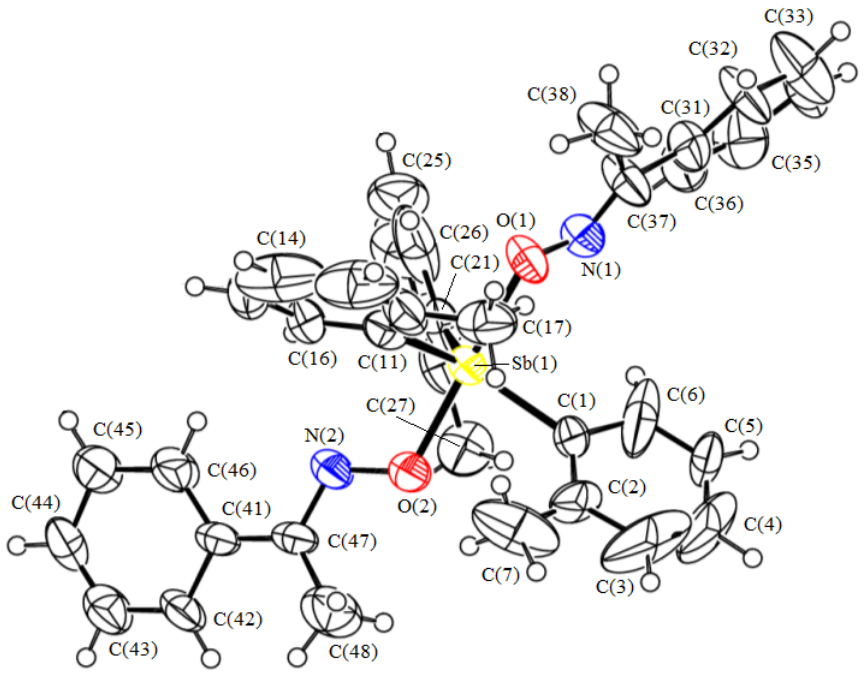


Fig. 2. The structure of compound 2 (molecule a)

The sum of $C_{eq}SbC_{eq}$ bond angles is equal to 360° (within experimental error), at that the values of the individual angles differ from the theoretical angle not more than 8º. The axial OSbO angles are equal to 168.92(5)º (**1**), 172.14(6)° (**2** ***a***), 174.29(7)° (**2** ***b***), 174.30(9)º (**3**). The SbC_3 fragments are almost flat. Antimony atoms are deflected from the C_3 plane through 0.024, 0.007, 0.008, 0.010 Å in **1, 2** ***a***, **2** ***b***, **3** respectively. The OSbC angles vary within the ranges 83.55(11)º–96.07(9)º (**1**), 83.74(7)º–94.55(7)° (**2** ***a***), 83.95(8)º–993.71(9)° (**2** ***b***), 84.6(3)º–93.5(5)º (**3**).

The Sb–C bond intervals are 2.111(2)–2.149(3) Å (the mean value is 2.126(3) Å) (**1**), 2.106(2)–2.138(3) Å (2.119(3) Å) (**2** ***a***), 2.099(3)–2.154(3) Å (2.129(3) Å) (**2** ***b***, 2.106(3)–2110(10) Å (2.107(9) Å) (**3**). Sb–O bond lengths are equal to 2.039(2), 2.105(2) Å (**1**), 2.060(1), 2.061(1) Å (**2** ***a***),

2.084(2), 2.100(2) Å (**2** ***b***), 2.058(6), 2.107(7) Å (**3**). It may be noted that Sb–O distances are significantly different in the molecules (except of molecule **2** ***a***). The average equatorial bond lengths in all the molecules are greater than the average axial bond lengths.

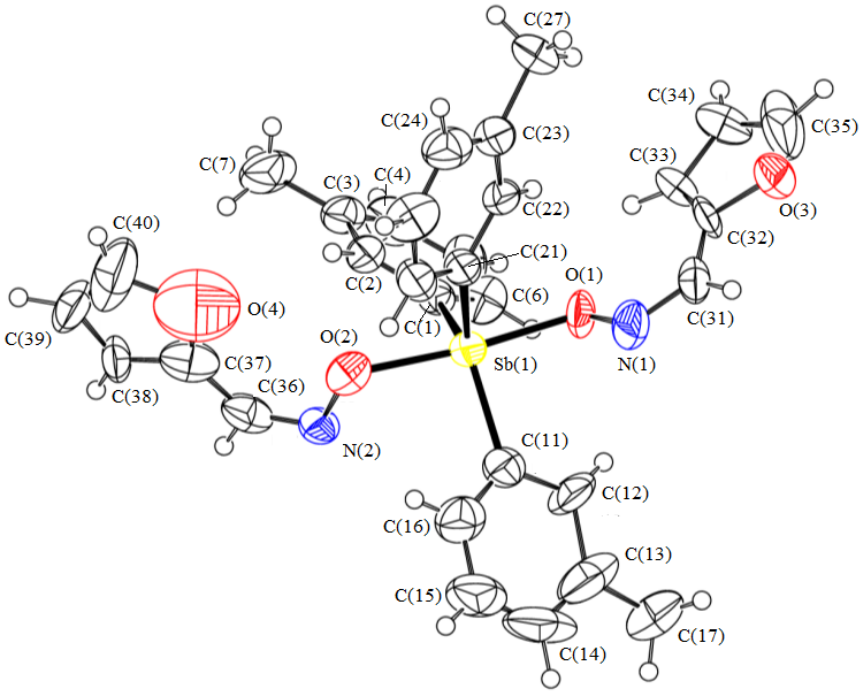


Fig. 3. The structure of compound 3

There are intramolecular contacts between Sb atom and N atoms of oxime groups in molecules **1–3**. The Sb···N distances are 2.952(2), 2.889(2) Å (**1**), 2.970(1), 2.931(2) Å (**2** ***a***), 2.952(2), 2.939(2) Å (**2** ***b***), 2.83(1), 2.87(1) Å (**3**) and considerably less than the sum of Van der Waals radiuses of Sb and N atoms (3.8 Å [14]). Obviously, there is no correlation between Sb–O bond lengths and strength of Sb···N contacts. Decrease of Sb···N distances does not result in the expected N–O bond lengthening [(1.407(3), 1.361(3) Å (**1**), 1.431(2), 1.384(2) Å (**2** ***a***), 1.393(3), 1.351(3) Å (**2** ***б***), 1.358(13), 1.374(11) Å (**3**)], however, it causes a reduction of NOSb valence angles. Thus, in molecule **3**, which has the shortest Sb···N distances, these angles are equal to 109.2(6)º and 110.3(6)º, whereas in molecules **1**, **2** this angles are changed in the range of 112.9(1)º–116.0(1)º.

Note that heteroatoms do not participate in the crystal-packing formation of molecules **1–3**. The structure is formed due to C–H···π intermolecular interactions.

Conclusions

It has been found that the oxidative addition reaction of tri(*o*-tolyl)antimony and 4-N,N-dimethylbenzaldoxime and acetophenonoxime proceed with the formation of tri(*o*-tolyl)antimony dioximates irrespective of the oxidizing agent nature and the molar ratio of the reactants. The direction of the similar reaction of tri(*m*-tolyl)antimony with furfuraldoxime is determined by the type of an oxidizing agent.

Bis[4-N,N(dimethylamino)benzaldoximato]tri(*o*-tolyl)antimony, *bis*(acetophenonoximato)tri(*o*-tolyl)antimony and *bis*(furfuraloximato)tri*(m*-tolyl)antimony molecules have close geometrical parameters. The peculiarity of trigonal bipyramidal polyhedron of antimony atoms is that the equatorial substituents are farther from it than axial ones. The significant reduction of intramolecular distances Sb···N, which we have observed, does not cause significant distortion of bond angles at the central atom, which are close to the theoretical values.

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Received 24 February 2015

УДК 546.863+546.865+547.53.024+548.312.5

РЕАКЦИИ ТРИ(*ОРТО*-ТОЛИЛ)- И ТРИ(*МЕТА*-ТОЛИЛ)СУРЬМЫ С ОКСИМАМИ В ПРИСУТСТВИИ ОКИСЛИТЕЛЯ. СТРОЕНИЕ ДИОКСИМАТОВ ТРИ(*ОРТО*-ТОЛИЛ)- И ТРИ(*МЕТА*-ТОЛИЛ)СУРЬМЫ

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Взаимодействием три-*орто*-толил- или три-*мета*-толилсурьмы с оксимами в присутствии *трет*-бутилгидропероксида или пероксида водорода синтезированы диоксиматы триарилсурьмы (o-$CH_3C_6H_4)_3Sb(ON{=}CHC_6H_4N(CH_3)_2$-4)$_2$ (**1**), (o-$CH_3C_6H_4)_3Sb(ON{=}CMePh)_2$ (**2**), (m-$CH_3C_6H_4)_3Sb(ON{=}CHC_4H_3O)_2$ (**3**). По данным РСА, в молекулах **1–3** атомы сурьмы имеют искаженную тригонально-бипирамидальную координацию с атомами кислорода оксиматных лигандов в аксиальных положениях. Особенностью структур является наличие коротких внутримолекулярных расстояний Sb···N, которые примерно на 1 Å меньше суммы ван-дер-ваальсовых радиусов.

Ключевые слова: три-орто-толилсурьма, три-мета-толилсурьма, оксимы, трет-бутилгидропероксид, пероксид водорода, окисление, бис(4-диметиламинобензальдоксимато)три-орто-толилсурьма, бис(ацетофеноноксимато)три-орто-толилсурьма, бис(фурфуальдоксимато)три(мета-толил)сурьма, молекулярные структуры, рентгеноструктурный анализ.

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Поступила в редакцию 24 февраля 2015 г.

БИБЛИОГРАФИЧЕСКОЕ ОПИСАНИЕ СТАТЬИ

Reactions of tri(*ortho*-tolyl)- and tri(*meta*-tolyl)-antimony with oximes in the presence of an oxidant. The structures of tri(*ortho*-tolyl)- and tri(*meta*-tolyl)antimony dioximates / V.V. Sharutin, O.K. Sharutina, E.V. Artem'eva, M.S. Makerova // Вестник ЮУрГУ. Серия «Химия». – 2015. – Т. 7, № 2. – С. 17–26.

REFERENCE TO ARTICLE

Sharutin V.V., Sharutina O.K., Artem'eva E.V., Makerova M.S. Reactions of Tri(*ortho*-tolyl)- and Tri(*meta*-tolyl)antimony with Oximes in the Presence of an Oxidant. The structures of Tri(*ortho*-tolyl)- and Tri(*meta*-tolyl)antimony Dioximates. *Bulletin of the South Ural State University. Ser. Chemistry.* 2015, vol. 7, no. 2, pp. 17–26.

Analytical Chemistry

THE STUDY OF GROUNDWATER QUALITY OF SCIENTIFIC AND PRODUCTION CENTER OF THE SOUTH FORESTRY IN ILMENSKY STATE RESERVE

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The present work deals with the quality of groundwater used for water supply of the scientific and production center of the South forestry in Ilmensky State Reserve. Chemical analyses of water from three wells have been conducted. The relationship of the quality of surface water and groundwater has been investigated. Anthropogenic causes of the variation of drinking water quality from the existing guidelines have been identified.

Keywords: groundwater, drinking water, physicochemical parameters of water quality, water supply, permanganate oxidability, nitrate.

Introduction

Underground sources play an important part in water supply, being the main sources of water supply in small population centers. However, nowadays economic activity inevitably leads to change in the status of groundwater. Significant groundwater intake without compliance with the established mode of operation of water intakes causes the depletion of deposits and pollution in some cases. As the result, the intake of large volumes of water forms extensive depression craters, there is a flow of groundwater from adjacent aquiferous strata and involvement of surface watercourses in groundwater recharge, which affects the quality of produced water.

In the present paper the physicochemical indicators of water quality are determined for the currently existing boreholes in the area of the research and production base of the Ilmensky State Reserve. The antropogenic influence on the chemical composition of water is studied, and the relationship of surface (Ilmensky lake) and groundwater.

Experimental

Investigations were carried out in July 2014 on the area of the scientific center of the Ilmensky State Reserve.

Ilmensky State Reserve, located on the eastern slopes of the Southern Urals, in the Chelyabinsk region, north-east of the Miass city. The reserve was established in order to preserve exceptionally diverse complex of rocks and minerals, as well as the flora and fauna typical of the Southern Urals. Scientific and industrial center of the reserve is located on the eastern shore of the Ilmensky lake.

Every year in summer on the area of the center the research work in field practices is carried out by the research teams of leading universities of the Russian Federation: Moscow State University, Kazan Federal University, National Research South Ural State University. In July, the center can accommodate up to 300 people simultaneously, while in the rest of the year there are only 2-3 staff members. Thus, in the summer period the problem of drinking water quality for the scientific center sharply arises.

Water sampling for the determination of the physicochemical parameters and hydrochemical analysis was carried out in accordance with the requirements of the State standard GOST P 51592-2000.

Chemical analysis of water samples at each point was carried out in the laboratory according to standard procedures (Table 1). For spectrophotometric studies the photocolorimeter KFK-3 was used.

For the potentiometric and conductometric measurements, respectively, the portable IPL Multitest and KSL Multitest were used.

Determination was performed in triplicate. Mathematical processing of the data was performed using standard methods of variation statistics.

Table 1

Chemical parameters of water quality, notation used, and determination methods

Chemical parameters	Method
pH value, **pH**	Potentiometry
Redox potential, **Eh**, mV	Potentiometry
Elecroconductivity, μS/cm	Conductometry
Salinity as NaCl, mg/L	Conductometry
Ammonium, $\mathbf{NH_4^+}$, mg/L	Spectrophotometry with Nessler's reagent at 440 nm according to the State standard GOST P 14.1: 2.1-95
Nitrate, $\mathbf{NO_3^-}$, mg/L	Potentiometry with nitrate-selective electrode
Nitrite, $\mathbf{NO_2^-}$, mg/L	Spectrophotometry with Griess reagent at 520 nm according to the State standard GOST P 14.1: 2.3-95
Orthophosphate phosphorus, $\mathbf{PO_4^{3-}}$, mg/L	Spectrophotometry with ammonium molybdate at 690 nm according to the State standard GOST P 4.1: 2.112-97
Chloride, $\mathbf{Cl^-}$, mg/L	Potentiometry with chloride-selective electrode
Sodium, $\mathbf{Na^+}$, mg/L	Potentiometrically with sodium-selective electrode
Potassium, $\mathbf{K^+}$, mg/L	Potentiometry with potassium-selective electrode
Total hardness, **H**, mmol/L	Titration by Trilon B with Chromogen black according to the State standard GOST P 52407-2005
Hardness as calcium, $\mathbf{Ca^{2+}}$, mg/L	Titration by Trilon B with murexide
Total iron content, $\mathbf{Fe_{total}}$, mg/L	Spectrophotometry with sulfosalicylic acid at 440 nm according to PND F 14.1: 2: 4.50-96
Permanganate oxidability, mg O_2/L	Kubel's method titration by potassium permanganate in acidic medium according to the State standard GOST P 14.1: 2: 4.154-99

Status quo

The water supply of the center proceeds from three wells. Note that the wells are exploited only in summer. In winter the wells are closed up, and the center employees use imported water for household and drinking needs.

The well No. 1 is exploited for more than 30 years. Its depth is 30 meters. Water from the well No. 2 is used in the bath for domestic needs (washing, laundry) and drinking needs of the center employees, constantly residing in the area. The well was bored in 2013, its depth is 40 meters. The well No. 3 is 22 meters deep, it was bored in 2014.

With regard to sewage, the household water on the area of the centre is collected into organized ditches. The sewage treatment is not done.

Results and Discussion

The results of analyses of water from the wells are shown in Table 2.

As can be seen from Table 2, the high content of various forms of nitrogen (ammonium, nitrate, nitrite) is found in water from all wells. Oxidability of water from the well No. 3 exceeds the value of maximum permissible concentration (MPC) and amounts to 9.2 mg O_2/L. The same high values of oxidability (10 mg O_2/L) are recorded in the kitchen-dining room, which is supplied from the well No. 3. Also the content of ammonium is increased up to 1.5 mg/L. Although the standard content of ammonium in drinking water equals 2 mg/L [4], a more rigorous standard is adopted for ammonia in production of bottled drinking water (0.1 mg/L for the first quality category and 0.05 mg/L for the highest quality) [5].

Table 2

Chemical parameters of water quality for the samples, taken from the area of scientific and production center of the Ilmensky State Reserve

Indicator, notation, unit	Sampling point					MPC
	Well No.1	Well No.2	Well No.2 (after boiling)	Well No.3	The kitchen-dining room No.3	
Nitrate, NO_3^-, mg/L	0.5±0.1	49.5±0.2	–	0.4±0.1	0.4±0.1	max 45 [3]
Nitrite, NO_2^-, mg/L	0.105± 0.005	0.020± 0.005	–	0.017± 0.005	0.110± 0.005	3 [4]
Ammonium, NH_4^+, mg/L	0.35± 0.02	0.30±0.02	–	Higher 1.5	0.15± 0.02	2 [4]
Total iron content, Fe_{total}, mg/L	0.10± 0.02	0.05±0.02	Lower 0.01	0.20± 0.02	0.05± 0.02	0.3 [4]
Permanganate oxidability, mg O_2/L	5.6±0.1	4.8±0.1	2.8±0.1	9.2±0.1	10.0±0.1	within 5–7 [3]
Total hardness, H, mmol/L	5.2±0.1	6.5±0.1	–	4.1±0.1	5.5±0.1	within 7 – 10[3]
Salinity as NaCl, mg/L	189.2± 0.1	389.6±0.1	38.0±0.1	152.6± 0.1	178.9± 0.1	within 1000 – 1500 [3]
pH	6.88± 0.05	6.26±0.05	–	6.83 ±0.05	6.78 ±0.05	6–9 [3]
Eh, mV	245.2± 0.1	252.3±0.1	–	255.4± 0.1	332.3± 0.1	–
Hardness as calcium, Ca^{2+}, mg/L	3.5±0.1	5.1±0.1	–	2.9±0.1	5.2±0.1	–
Chloride, Cl^-, mg/L	44.7±0.2	89.5±0.2	–	12.6±0.1	12.6±0.1	max 350 [3]
Sodium, Na^+, mg/L	5.1±0.1	8.2±0.1	–	4.1±0.1	3.6±0.1	200 [4]
Potassium, K^+, mg/L	3.0±0.1	0.9±0.1	–	0.2±0.1	0.2±0.1	–
Orthophosphate phosphorus, PO_4^{3-}, mg/L	Lower 0.01	Lower 0.01	–	0.07±0.02	Lower 0.01	3.5

The well No.3 (22 meters deep) is bored in the first aquiferous stratum. It is poorly insulated from surface water and is prone to anthropogenic pollution. That is why the natural processes, as well as the anthropogenic influence, can be causes of water inadequacy for drinking purposes.

The first reason is related to climatic features of July 2014. In the study we have found the high values of oxidability (28 mg O_2/L) for water of the Ilmensky lake. According to previous research [6–8] and the literature data [9], the Ilmensky lake belongs to mesotrophic type, the high content of organic substances is not characteristic to it. Such abnormally high values of oxidability are associated with the following natural processes, peculiar to July 2014. The southwestern part of the lake is waterlogged, with the quagmires along the coastline, which turns into a swamp. The lake is separated from the swamp by a ridge. As the result of heavy rains in this year the water level of the lake has risen above the ridge, which acts as the watershed, and swamp water has got into the lake. It explains the heightened values of ammonium (up to 0.85 mg/L) in the lake water. Significant deterioration of the Ilmensky lake water quality could lead to significant deterioration of water from the well No. 3. The other reason is the lack of treatment systems for domestic liquid waste. The significantly higher concentration of ammonium in groundwater (exceeding 1.5 mg/L) than in the Ilmensky lake (up to 0.85 mg/L) speaks in favor of the hypothesis.

The amount of nitrate exceeding MPC has been found in water from the well No. 2 (49.5 mg/L). This well is deeper (40 meters). The reason in this case can be the anthropogenic pollution of fecal waste, containing ammonium nitrogen, which is oxidized to nitrate by nitrifying bacteria in reducing conditions of underground water. On the other hand, the significant increase in nitrate can be the feature of groundwater in the given geographical area.

Methemoglobinemia occurs with prolonged use of drinking water, containing significant amount of nitrate. The ability of blood to transport oxygen is reduced, this leads to adverse effects to the organism. Methemoglobinemia can cause cyanosis (blue skin of the extremities and body), weakness and cardiopalmus. Progressive methemoglobinemia leads to depression of the central nervous system, causes headaches, dizziness, chronic fatigue, labored breathing and nausea. The severe form of methemoglobinemia leads to chronic sleepiness, brief loss of consciousness, irregular heartbeat [10, 11].

After boiling the quality of water from the well No. 2 is significantly improved to the desired values (Table 1).

The water from the well No.1 is of the highest quality in the investigated area. The increased values of permanganate oxidability (5.6 mg/L), higher than MPC, have been recorded for this water, but they do not exceed the normal values. This well is the deepest and is not affected by anthropogenic factors and surface water.

Conclusion

Thus, the water in two wells in the scientific and production center does not meet the standard of drinking water according to nitrate and permanganate oxidability value. The ammonium concentration has increased in all three wells.

The water from the well No. 2 can be used for drinking after preliminary boiling. The water from the well No.3 has very bad quality. This is associated with shallow depth of the wells (20 meters), while the artesian water is located at much greater depth in geographical conditions of the scientific and production center of the Ilmensky State Reserve.

The correlation between the quality of water in the Ilmensky lake and groundwater quality has been revealed.

In our opinion, it is necessary to bring sewerage in the area of the scientific and production center into line with the required standards. To this end, we propose to carry out the collection of household water in a special container, as well as to purify it locally in the deep-purification biological treatment plants, which are now widely available on the market. Alternatively, for seasonal work SBR-reactor (sequencing batch reactor) can prove the most suitable for decontamination. Such facilities work particularly well in the systems characterized by low wastewater discharge in certain periods.

We suggest purifying the water from underground wells with the use of the membrane filtration technology systems [12, 13].

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Received 5 December 2014

УДК 543.3:628.1

ИССЛЕДОВАНИЕ КАЧЕСТВА ПОДЗЕМНЫХ ВОД НА ТЕРРИТОРИИ НАУЧНО-ПРОИЗВОДСТВЕННОЙ БАЗЫ ЮЖНОГО ЛЕСНИЧЕСТВА ИЛЬМЕНСКОГО ГОСУДАРСТВЕННОГО ЗАПОВЕДНИКА

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Работа посвящена проблеме качества подземных вод, использующихся для водоснабжения научно-производственной базы южного лесничества Ильменского государственного заповедника. Проведен химический анализ воды из трех скважин. Исследована взаимосвязь качества поверхностных и подземных вод. Выявлены антропогенные причины несоответствия подземных вод гигиеническим требованиям к качеству питьевой воды.

Ключевые слова: подземные воды, питьевая вода, физико-химические показатели качества воды, водоподготовка, перманганатная окисляемость, нитраты.

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Поступила в редакцию 5 декабря 2014 г.

БИБЛИОГРАФИЧЕСКОЕ ОПИСАНИЕ СТАТЬИ

The study of groundwater quality of scientific and production center of the South forestry in Ilmensky State Reserve / T.G. Krupnova, I.V. Mashkova, A.M. Kostryukova, E.D. Scalev // Вестник ЮУрГУ. Серия «Химия». – 2015. – Т. 7, № 2. – С. 27–32.

REFERENCE TO ARTICLE

Krupnova T.G., Mashkova I.V., Kostryukova A.M., Scalev E.D. The Study of Groundwater Quality of Scientific and Production Center of the South Forestry in Ilmensky State Reserve. *Bulletin of the South Ural State University. Ser. Chemistry.* 2015, vol. 7, no. 2, pp. 27–32.

Physical Chemistry

STRUCTURE OF LITHIUM PYROSILICATE MELTS ACCORDING TO DATA OF HIGH-TEMPERATURE RAMAN SPECTROSCOPY

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Decomposition of the high-frequency range of Raman spectra for $60Li_2O{\cdot}40SiO_2$ melts (Li60) into the Gaussian line shape was performed. The basic structural fragments of melts and their ratio were determined, and the peculiarities of their interaction with the change in temperature were identified.

Keywords: melt structure, silicate melts, Raman spectroscopy.

Introduction

The study of silicate systems is an important task for the optimization of the industrial technologies and geochemical studies. Raman spectroscopy can be carried out directly *in situ* in the melts. Of all the alkali-silicate systems, only sodium silicate has been studied in sufficient detail over the entire range of compositions starting from pure SiO_2 to sodium orthosilicate in a wide temperature range [1, 2], while the melts of Li_2O–SiO_2 system were only studied for compositions <50 mol. % Li_2O. Therefore studies of strongly alkaline lithium-silicate melts by means of Raman spectroscopy is a rather critical task. The high-frequency range of the Raman spectra of the melted silicate systems contains information about the present silicon-oxygen tetrahedral units Q^n (silicon-oxygen tetrahedral units with various numbers of bridging oxygen atoms *n*) and their amounts [3, 4]. Experimental data about the melt structures can be represented in the form of the distribution of structural units Q^n as the function of the composition and temperature.

Research methods

Synthesis of lithium pyrosilicate was carried out from the amorphous SiO_2 (analytical grade) and lithium carbonate Li_2CO_3 (reagent grade). The charge was thoroughly mixed with alcohol in a mortar, then dried and melted in a platinum crucible in a silit furnace at the melt temperature up to 1373 K. To register the Raman spectra the high-temperature experimental apparatus was used, which was based on the DFS-24 spectrometer. For all the spectra obtained, the baseline correction procedure was performed. The spectra were processed using the software package OMNIC Thermo Nicolet. For that, the curve fitting method of Raman spectra as superposition of the lines of Gaussian shape (RS SM) was used. The high-frequency range of the spectrum is the most important in obtaining data about the structure of silicate glasses and melts. The analysis of the patterns of the Raman spectra change as the function of composition, the comparison of the spectra of glasses and the corresponding crystals, the measurement of the band polarization degree, the theoretical calculations of the fluctuations of silicate anions gave the following interpretation of the bands in the high-frequency range of Raman spectra of silicate glasses and melts [3, 4, 6, 7]:

– the band crest in the range of 1050–1100 cm^{-1} is related to the stretching vibrations of the terminal groups of Si–O– in tetrahedral units with one terminal oxygen atom (Q^3);

– the band crests in the range of 950–980 cm^{-1} and 900 cm^{-1} are related to the vibrations of the terminal groups Si–O– and Si–O– in tetrahedral units with two and three non-bridging oxygen atoms (Q^2 and Q^1), respectively;

– the band crest at 850 cm^{-1} is due to stretching vibrations of isolated tetrahedral units of SiO_4^{4-} with all the non-bridging oxygen atoms (Q^0).

In the low-frequency region (400–700 cm^{-1}) there is the band associated with symmetric stretching and partially bending vibrations of bridges Si–O–Si. Its frequency increases systematically with increasing degree of glass polymerization. In the mid-band frequency region (700–800 cm^{-1}) there is the weak depolarized band, intensity of which decreases with decreasing concentration of silica in the stacks, and it is associated with the deformation vibrations of bridge bonds Si–O–Si in the micro-regions of glasses, the structure of which is close to that of the glassy SiO_2.

In fact, this interpretation of Raman spectra of silicate glasses is based on the principles proposed by A.N. Lazarev for the vibrational spectra of silicates [8]. Within this approach it is assumed that the stretching vibrations of silicate anions, characterized by relatively high frequencies, do not interact with the vibrations of the cation sublattice.

To determine the concentration of structural units Q^n we use the intensity of characteristic bands in the high-frequency region of the Raman spectra [9]. To quantify the integrated intensities of the characteristic bands at different temperatures, the high-frequency spectral range of glass and melts is represented as superposition of the lines of Gaussian shape. The project [10] considers various shapes of lines used for simulation of Raman spectra of silicate systems. It is proven that the best of all the options to describe the bands in the spectra of silicate glasses is the superposition of Gaussian shape lines.

The technique of curve fitting for the high-frequency region of the Raman spectra of silicate glasses and melts is described in [9] and [10]. To simulate the strongly alkaline silicate glasses three lines of Gaussian shape are used in [11]. More complex line shapes resulting from vibrations of structural units Q^n are used in [12], which deals with the so-called partial Raman spectra. The authors suggest that each Q^n group has its own partial spectrum, the shape of which does not depend on the concentration of the Q^n-type of a particular kind in a glass sample. In [13], a more complex interpretation of Raman spectra is developed to describe the fine structural features of silicate glasses and melts, the authors consider not only the immediate environment (Q^n-distribution), but also the influence of the second coordination sphere of the central silicon atoms, *i.e.* the influence of the neighboring silicon-oxygen tetrahedral units. For this classification, the following designations are used: $Q^{a/bbb}$, where 'a' stands for the type of the central tetrahedral unit Q, and symbol 'b' is the type of neighboring tetrahedral units Q, connected with it through bridge bonds. The authors suggest that the vibration frequency is not only determined by the second coordination sphere, but also greatly depends on the structures, ring patterns in particular, into which the tetrahedral units are included.

To describe the structure of glasses and melts of Na_2O–SiO_2 system, the Raman spectra curve fitting technique as superposition of the lines of Gaussian shape is used in [2]. In general, the curve fitting of Raman spectra is a complex and controversial procedure. The basic curve fitting principles are as follows:

– correlation between the characteristic bands in the spectra of silicates in their crystalline, glassy and molten state;

– the minimum number of lines used in the spectrum decomposition procedure;

– the coordinated description of spectra in a wide range of temperatures and compositions within a single structural model;

– regular change in the position and width of the lines in the spectrum with the change of composition and temperature.

Thus, Raman spectra of the melts of sodium–silicate systems have been simulated, and the new interpretation of the high-frequency region has been proposed [2]. The data obtained have allowed to carry out the complete investigation of the sodium-silicate system and to determine the quantitative characteristics of the structural units of melts and glasses.

Results

1. Decomposition of high-frequency Raman spectra region of Li60 melts

Figure 1 shows the Raman spectra of melts of Li60 composition, obtained in the temperature range 1223–1373 K, which were discussed in sufficient detail in [5], so let us briefly highlight the key aspects herein.

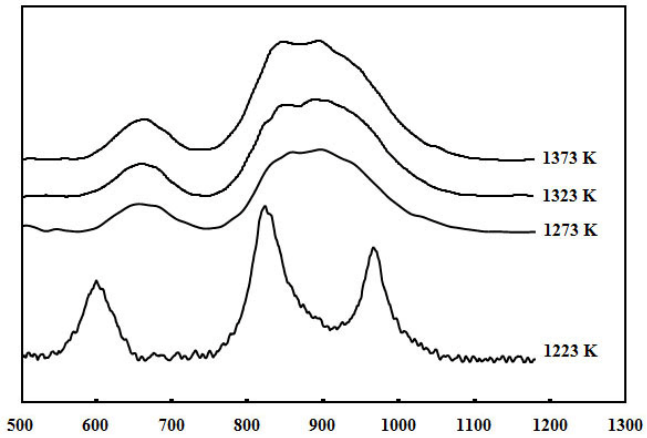


Fig. 1. Raman spectra of Li60 melts depending on the temperature [5]

The spectra of melts with this composition have two dominating and the most intense bands with crests around 630 cm^{-1} and 900 cm^{-1}, which relate to vibrations of bonds in groups Si–O–Si and SiO_4, respectively. With the melt cooling, narrowing of the bands is observed, and the high-frequency region is represented by two peaks near 820 cm^{-1} and 970 cm^{-1}. It is likely that at the temperature 1223 K, the melt crystallization starts, which is accompanied by the formation of individual clusters of stoichiometric compositions.

2. Decomposition of high-frequency Raman spectra region of Li60 melts

Raman spectra of lithium–silicate melts have been represented as the superposition of lines of Gaussian shape, according to the RS SM. The table shows the positions of bands, designations of the structural units and their interpretation for the lithium pyrosilicate melts.

Interpretation of the characteristic bands in the Raman spectra of lithium pyrosilicate melts

Frequency range, cm^{-1}	Designation of Q^n-units	Band interpretation
825–830	Q^0	Isolated tetrahedral unit with four non-bridging bonds
860–864	$Q^{1'}$	Terminal tetrahedral unit located at the end of the chain structure of finite size
890–898	Q^1	Terminal tetrahedral unit connected with the other similar tetrahedral unit through a bridge bond, *i.e.* a dimer component
929–932	$Q^{2'}$	Tetrahedral unit with two bridge bonds, connected with terminal tetrahedral units Q^1
965–970	Q^2	Tetrahedral unit connected with the similar units Q^2, *i.e.* a chain component
1013–1025	$Q^{3'}$	Tetrahedral unit connected with the chain tetrahedral units Q^2, *i.e.* a branching point of the chain structure

Figure 2 shows the decomposition of the high-frequency region of the spectrum for the Li 60 melts into the superposition of six lines, according to the above interpretation. It is obvious that in the spectrum of the melt obtained at 1223 K, the band around 820 cm^{-1} dominates, that proves the prevailing content of tetrahedral units of Q^0-type, and the less intense band about 980 cm^{-1} corresponds to the presence of tetrahedral units Q^2. Furthermore, other five minor bands corresponding to structural units Q^1, $Q^{2'}$, $Q^{3'}$ and Q^3, are allocated in the spectrum curve fitting. They correspond to vibrations of atoms in the respective tetrahedral units [2]. With a rise in temperature, structural changes take place in the melt, as indicated by increasing intensity of the bands around 900 cm^{-1}, 940 cm^{-1} and 970 cm^{-1}, which corresponds to the growing concentration of the tetrahedral units of Q^1, $Q^{2'}$ and Q^2.

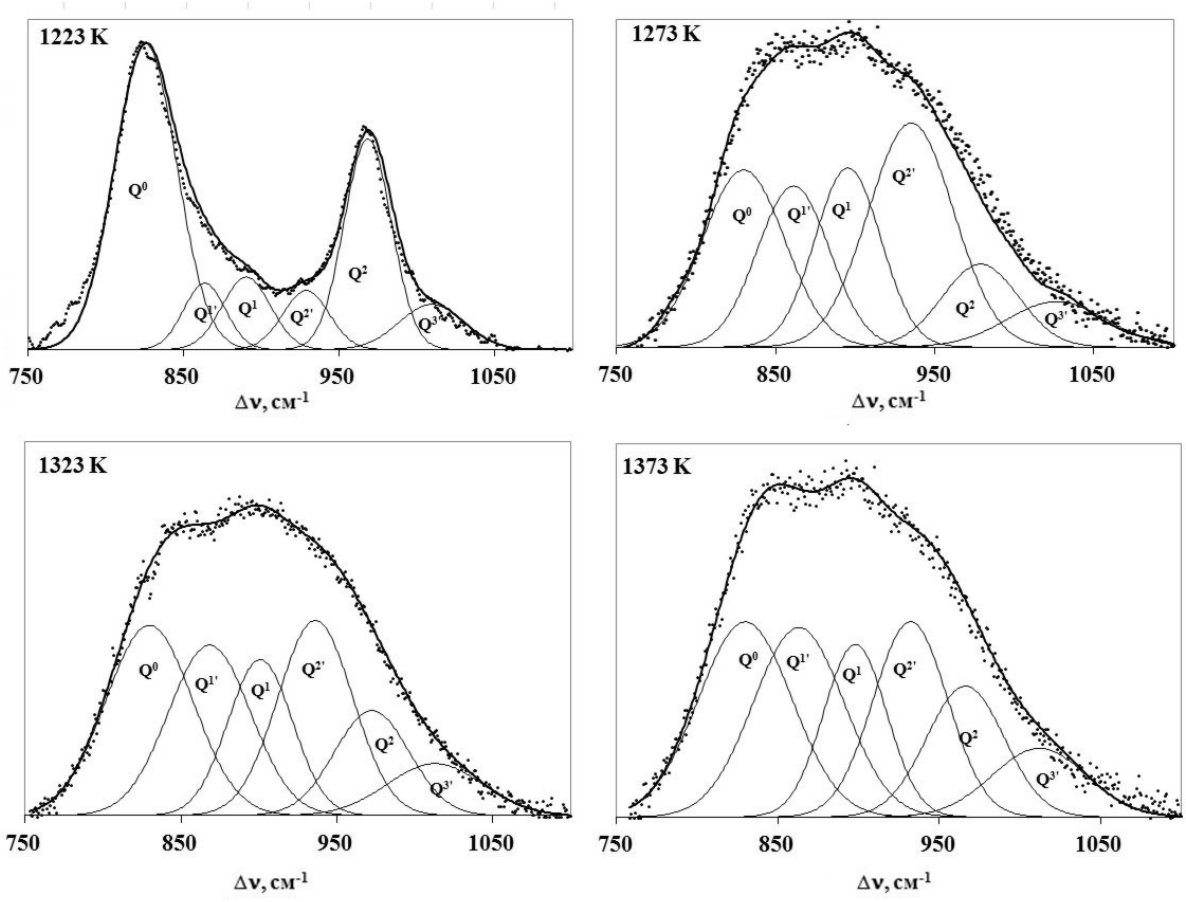


Fig. 2. Curve fitting of high-frequency region of the Raman spectra of Li60 melts

The line intensities obtained from the Raman spectra, corresponding to the vibrations of certain structural units Q^1, Q^2 and Q^3 in the melts of Li60 composition are shown in Figure 3. It is clear that the intensities of the lines corresponding to the vibrations of the tetrahedral units Q^2 and Q^0 remain practically unchanged with the rise in temperature, whereas the intensity of the lines corresponding to vibrations of the tetrahedral units Q^1 and Q^3 decrease. It can be assumed that Q^1 and Q^3 are prevailing in the melt, while the units of Q^3 are of low content. In order to obtain the data on the concentration of structural units in the melts, we suggest the calculation of conversion factors from intensities to concentrations, similar to sodium–silicate system [2].

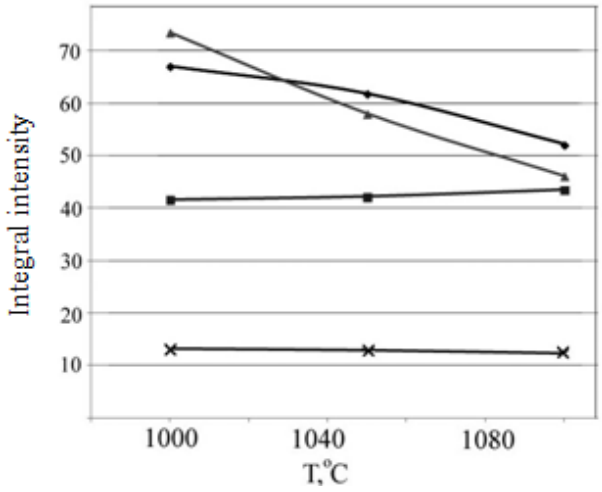


Fig. 3. Change of integral intensities of the bands corresponding to variations in structural units Qn in melts of Li60 composition depending on the temperature (square symbols correspond to structural units Q^2, triangular, cruciform and rhombic ones – to Q^1, Q^3 and Q^0, respectively)

The work was supported by the RFFI grant № 15-05-02216-a.

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Received 4 February 2015

УДК 544.23+666.11

СТРУКТУРА РАСПЛАВОВ ПИРОСИЛИКАТА ЛИТИЯ ПО ДАННЫМ ВЫСОКОТЕМПЕРАТУРНОЙ СПЕКТРОСКОПИИ КОМБИНАЦИОННОГО РАССЕЯНИЯ

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Проведено разложение высокочастотной области спектров комбинационного рассеяния расплавов состава $60Li_2O·40SiO_2$ (далее Li60) на линии гауссовской формы. Определены основные структурные фрагменты расплавов и их соотношение, а также выявлены особенности их взаимодействия с изменением температуры.

Ключевые слова: структура расплава, силикатные расплавы, спектроскопия комбинационного рассеяния.

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Поступила в редакцию 4 февраля 2015 г.

БИБЛИОГРАФИЧЕСКОЕ ОПИСАНИЕ СТАТЬИ

Koroleva, O.N. Structure of lithium pyrosilicate melts according to data of high-temperature Raman spectroscopy / O.N. Koroleva, T.V. Mosunova // Вестник ЮУрГУ. Серия «Химия». – 2015. – Т. 7, № 2. – С. 33–38.

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FORMATION (DECOMPOSITION) ENTHALPY CALCULATIONS FOR CRYSTAL LATTICES OF ALKALINE-EARTH FLUORIDES

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A series of calculations of structural and thermochemical properties has been carried out for the alkaline-earth fluorides. The calculations have been carried out using the modified model of effective ionic radii and the model of enthalpy calculation for the crystal lattice. The results of the calculations are in accordance with the known experimental data within confidence intervals.

Keywords: alkaline-earth fluorides, enthalpy of formation, cation, electron, ionization potential, interstructural distance.

Introduction

Halogen compounds with other elements are widely used in technology, though fluorides are very different from other halides in their physicochemical properties.

Calcium fluoride (in a lesser degree, strontium fluoride and barium fluoride) is a major source of fluorine and its compounds. In chemical industry, more than half of all fluorite is spent for manufacture of hydrofluoric acid (HF), from which fluorinated organic and inorganic compounds, as well as artificial cryolite for aluminium industry, are obtained. The second biggest consumer of alkaline-earth fluorides is ferrous metallurgy, where they are used as fluxes in smelters. Calcium, strontium, and barium fluorides are components of special glasses, enamels, ceramics, optical and laser materials. Their monocrystals are usable in manufacture of windows, prisms, lenses and other optical details, which function in the radiation range from infrared to ultraviolet. Barium fluoride is used as a sorbent in UF_6 purification. Strontium fluoride is used as a component of solid-state fluoride ion batteries (FIBs) with high energy capacity and energy density [1].

According to the 2002 data, the world extraction of fluorspar equaled 4.5 million tons per year. And about a half of fluorite was produced in China. Mexico, South Africa, Mongolia were next with considerable lag. In Russia, consumption of fluorine raw material is about 270–300 thousand tons per year. However, at present the situation with supplies of industrial fluorite may be described as critical. The Russian enterprises, exploiting marginal deposits with low-quality product concentrate, are in the critical condition. In spite of the considerable reserves and resources of fluorite, there are not profitable deposits of high-quality fluorine raw material in reserves. Whereas the possibility of substitution of mineral fluorspar with suitable analogs is extremely low [2], therefore, the calculations of thermodynamic and structural properties of alkaline-earth metal fluorides become an investigation problem of urgent interest.

In the monograph [3], the basic concepts of the model of effective ionic radii and the model of enthalpy calculation for the crystal lattice are considered. The model of calculation of enthalpy of the crystal lattice allows carrying out calculations and obtaining values of the properties, which can not be obtained (with necessary accordance with other properties) at the present time: standard enthalpies of formation of multi-charged particles, ionization potentials, electron affinities, etc. In the present paper, on the example of alkaline-earth fluorides, the possibilities for complex uses of modified equations of the models in order to obtain concordance of the structural and thermochemical characteristics are demonstrated.

Initial data: alkaline-earth metal fluorides crystallize in the cubic crystal system (space group CaF_2, $F3m3-4$), the structure constant $\alpha = 0.4330127$; the Debye radius $r_D = r_{D\ CaF_2} \cdot f(z) \cdot f(c) = 15.18081 \times$ $\times\left(1+\sqrt{2\cdot 2\cdot 1-1}\right)\cdot 2\left(\sqrt{2}-1\right)=34.89582$; the minimum radius of fluoride ion $r^{\circ}\left(\mathrm{F}^{-}\right)=1.28960$; the enthalpy of gaseous fluoride ion formation $\Delta_f H^{\circ}\left(\mathrm{F}^{-},\mathrm{g}\right)=-255.148\pm0.270$ [3].

The enthalpy of formation (decomposition) of the crystal lattice of alkaline-earth fluorides is defined as

$$\Delta H_{\text{cr}}(\text{MeF}_2) = \Delta_f H^\circ(\text{Me}^{2+},\text{g}) + 2\cdot\Delta_f H^\circ(\text{F}^-,\text{g}) - \Delta_f H^\circ(\text{MeF}_2,\text{s}), \quad (1)$$

where $\Delta_f H^\circ(\text{Me}^{2+},\text{g})$ is the enthalpy of formation for a gaseous alkaline-earth metal cation; $\Delta_f H^\circ(\text{F}^-,\text{g})$ is the enthalpy of formation for a gaseous fluoride ion; $\Delta_f H^\circ(\text{MeF}_2,\text{s})$ is the enthalpy of formation for a crystalline alkaline-earth metal fluoride. After the substitution of the value $\Delta_f H^\circ(\text{F}^-,\text{g}) = -255.148\pm0.270$ [3] into equation (1), for MeF_2 we obtain

$$\Delta H_{\text{cr}}(\text{MeF}_2,\text{s}) = \Delta_f H^\circ(\text{Me}^{2+},\text{s}) - 510{,}296 + \Delta_f H^\circ(\text{MeF}_2,\text{s}). \quad (2)$$

Whereas the enthalpy of the crystal lattice ($\Delta H_{\text{cr}}(\text{MeF}_2)$) can be determined by using the basic calculation model of thermochemical properties [3].

The basic equation of the model

$$\Delta H_{\text{cr}} = \Delta H_0 + \Delta H_{\text{in}} \ . \quad (3)$$

The enthalpy of zero level, which is the starting point

$\Delta H_0 = 83.581728\ f_1(z)\cdot f_1(c)$,

where

$f_1(z) = (z_{\text{K}}^2\cdot n_{\text{K}})(z_{\text{A}}^2\cdot n_{\text{A}}) = (2^2\cdot 1)\cdot(1^2\cdot 2) = 8$;

$$f_1(c) = f_{\text{bcc}}\cdot f_{\text{fcc}} = \left(\frac{2}{\sqrt{3}}\right)^2\cdot\frac{\sqrt{2}}{2} = 0.942809\ .$$

Here z_{K} and z_{A} are the ion charges; n_{K} and n_{A} are the numbers of ions in a compound; f_{bcc} and f_{fcc} are the structure constants of initial and final (quasi-cubic) structures.

After the substitution of $f_1(z)$ and $f_1(c)$, we obtain $\Delta H_0 = 630.413$.

The enthalpy of the electromagnetic interaction

$\Delta H_{\text{in}} = 138.935405\cdot A_{\text{M}}\cdot\text{cn}\cdot f_2(z)\cdot f_2(c)\cdot r_{\text{d}}^{-1}$,

where $f_2(z) = (z_{\text{K}}\cdot n_{\text{K}})(z_{\text{A}}\cdot n_{\text{A}}) = (2\cdot 1)\cdot(1\cdot 2) = 4$;

$$f_2(c) = f_{\text{fcc}}\cdot f_{\text{tetr}} = \left(\frac{\sqrt{2}}{2}+1\right)\frac{3\sqrt{3}}{8} = 1.108798\ .$$

Here the coefficient 138.935405 is the combination of the fundamental constants; A_{M} is the Madelung constant; nc is the coordination number; f_{fcc} and f_{tetr} are the structural characteristics of the initial and quasi-cubic structures; r_d is the interparticle (interstructural) distance.

Then

$$\Delta H_{\text{in}} = 138.935405\cdot 1.259695\cdot 6\cdot 4\cdot 1.108798\cdot r_{\text{d}}^{-1} = 4657.3853\ r_{\text{d}}^{-1}\ . \quad (4)$$

Finally, for alkaline-earth metal fluorides equation (3) becomes

$$\Delta H_{\text{cr}} = 630.413 + 4657.3853\ r_{\text{d}}^{-1}\ . \quad (5)$$

The joint solution of equations (2) and (5) allows refining the known thermochemical data for alkaline-earth fluorides, as well as carrying out the predicting calculations for the unknown values.

In order to use equations (2) and (5), it is necessary to know the following parameters: the enthalpy of formation for a gaseous cation $\Delta_f H^\circ(\text{Me}^{2+},\text{g})$, the enthalpy of formation for a crystalline fluoride $\Delta_f H^\circ(\text{MeF}_2,\text{s})$, and the interstructural distance (r_d). Techniques of calculations of these structural and thermal characteristics are considered further.

1. Enthalpy of formation of alkaline-earth cations in the gaseous phase

By definition, the equation for standard enthalpy of formation of the metal cations is as follows:

$$\Delta_f H^\circ\left(\mathrm{Me}^{z+},\mathrm{g},298\right)=\Delta_f \mathrm{H}^\circ\left(\mathrm{Me}^0,\mathrm{g},298\right)+\sum^{z} I+6.1965\cdot z\,. \qquad (6)$$

I is the ionization potential, kJ[1]; 6.1965 is the molar enthalpy of electron gas formation [2].

The results of the calculations from the equation (6) and the input (reference data) are set out in Table 1. The obtained values of $\Delta_f H^\circ\left(\mathrm{Me}^{2+},\mathrm{g}\right)$ are used in the calculation of ΔH_1 from equation (2).

Table 1

Standard enthalpy of formation of double-charged alkaline-earth cations in the gaseous phase

Me $r(\mathrm{Me}^{2+})$, [2]	$\Delta_f H^\circ\left(\mathrm{Me}^0,\mathrm{g}\right)$, [4, 5]	I_1, eV, [4] I_1, eV, [4]	$\sum^{2} I$, kJ	$\Delta_f H^\circ\left(\mathrm{Me}^{2+},\mathrm{g}\right)$, eq. (6)
1	2	3	4	5
Ca 1.01202	147.790±1.674	$6.11308_{(10)}$ $11.8714_{(3)}$	1735.225±0.013	1895.408±1.687
Sr 1.15779	165.686±2.092	$5.69410_{(8)}$ $11.0302_{(1)}$	1613.637±0.087	1791.716±2.197
Ba 1.36361	180.749±4.184	$5.21140_{(8)}$ $10.0040_{(5)}$	1468.051±0.013	1661.193±4.197
Ra 1.38269	157.737±2.092	$5.2790_{(6)}$ $10.1472_{(2)}$	1488.390±0.077	1658.520±2.169

2. Enthalpy of formation of alkaline-earth fluorides

The reference data of $\Delta_f \mathrm{H}^\circ\left(\mathrm{MeF}_2,\mathrm{s}\right)$ (Table 2, column 3) allow the use of the model of standard enthalpy of formation of compounds [3]. According to the model for the similar substances, which are crystallized in one and the same crystal system, the specific enthalpy of formation (h) is directly proportional to the relative charge of the metal atom nucleus (z_e).

$$h=\frac{-\Delta_f H}{\Sigma z}\,. \qquad (7)$$

$$z_\mathrm{e}=\frac{z_\mathrm{Me}}{\Sigma z}\,. \qquad (8)$$

This dependency is described by the following linear equation:

$$h=h_0+k\,z_\mathrm{e}\,. \qquad (9)$$

The results of the calculations are set out (Table 2, columns 6, 7). Reference data (column 3) and the results of $\Delta_f \mathrm{H}^\circ\left(\mathrm{MeF}_2,\mathrm{s}\right)$ calculation are consistent with each other, which validates the model.

Table 2

Standard enthalpy of formation of crystalline alkaline-earth fluorides

MeF_2	Σz	$-\Delta_f \mathrm{H}^\circ\left(\mathrm{MeF}_2,s\right)$, [1, 6]	h, eq. (7)	z_e, eq. (8)	h, eq. (9)	$-\Delta_f \mathrm{H}^\circ\left(\mathrm{MeF}_2,\mathrm{s}\right)$, eq. (6)
1	2	3	4	5	6	7
CaF_2	38	1214.6	31.963158	0.526316	31.963158	1214.600
SrF_2	56	1209.6	21.60000	0.67857	21.600045	1209.603
BaF_2	74	1204.6	16.278378	0.756757	16.278378	1204.600
RaF_2	106	1195.8	11.280288	0.830189	11.280288	1195.711

[1]The first two ionization energy values I for many metals are known with high accuracy, but the accuracy of $\Delta_f \mathrm{H}^\circ\left(\mathrm{Me}^0,g,298\right)$ is much lower.

3. Enthalpy of formation (decomposition) of alkaline-earth fluoride crystal lattice

To derive ΔH_1 from equation (5) it is necessary to know the values of interstructural distances r_p, so the alkaline-earth metal fluorides structural characteristics calculation technique is explained below on the example of strontium fluoride SrF_2. The lattice constant is a =5.7800.

1. The interstructural distance is calculated as follows:

$$r_p = \alpha \cdot a = 0.4330127 \cdot 5.7800 = 2.50281. \quad (10)$$

2. The ion radius $r(F^-)$ is evaluated by the following:

$$r(F^-) = r_d - r(Sr^{2+}) = 2.50281 - 1.15779 = 1.34502. \quad (11)$$

3. The minimum ion radius $r^\circ(F^-)$ is calculated according to the formula:

$$r^\circ(F^-) = \left[-\frac{1}{2} \frac{r(Sr^{2+}) r_D}{(r_d - r(Sr^{2+}))} \right] + \left[\left(\frac{r(Sr^{2+}) r_D}{2(r_d - r(Sr^{2+}))} \right)^2 + r(Sr^{2+}) r_D \right]^{1/2} = 1.28959. \quad (12)$$

The results of calculation for strontium fluoride SrF_2 and other alkaline-earth fluorides structural characteristics are shown in Table 3.

Table 3

Structural characteristics of crystalline alkaline-earth fluorides

Me $r(Me^{2+})$, [2]	a, [1, 6]	r_d, eq. (10)	$r(F^-)$, eq. (11)	$r^\circ(F^-)$, eq. (12)
1	2	3	4	5
Ca 1.01202	5.4626	2.36538	1.35336	1.28961
Sr 1.15779	5.7800	2.50281	1.34502	1.28959
Ba 1.36361	6.2352	2.69983	1.33622	1.28960
Ra 1.38269	6.2777	2.71832	1.33563	1.28960

The values of $r^\circ(F^-)$ (Table 3, column 6) show the self-consistency and the equality with the value of the minimum ion radius of F^- in the alkaline halides, which have been calculated earlier [3]. It strengthens the model validation and allows using values r_p to calculate the lattice enthalpy of ΔH_1.

The results of decomposition enthalpy calculation of crystalline alkaline-earth fluorides are suggested in Table 4.

Table 4

Decomposition enthalpy of crystalline alkaline-earth fluorides.

MeF_2	r_d^{-1}, (Table 3)	$\Delta_f H^\circ(Me^{2+}, g)$, (Table 1)	$-\Delta_f H^\circ(MeF_2, s)$, (Table 2)	ΔH_1, eq. (2)	ΔH_1, eq. (4)	ΔH_1, eq. (5)
1	2	3	4	5	6	7
CaF_2	0.422770	1895.408±1.687	1214.6	2599.712±2.227	1969.003	2599.416
SrF_2	0.399551	1791.716±2.197	1209.6	2491.023±2.719	1860.863	2491.276
BaF_2	0.370394	1661.193±4.197	1204.6	2355.497±4.737	1725.068	2355.481
RaF_2	0.367874	1658.520±2.169	1195.8	2343.935±2.246	1713.331	2343.744

The data of column 5 and 7 are consistent, which validates the used model.

Conclusion

The decomposition enthalpies of alkaline-earth fluorides are calculated by classical thermodynamic equation and by the model of lattice enthalpy equation suggested by A.G. Ryabukhin. The calculation results are fairly well consistent with each other, which proves the correctness of the used model as applied to similar systems. The technique of calculation of intermediate structural and thermal characteristics (enthalpy of formation of alkaline-earth cations in the gaseous phase, enthalpy of formation of crystalline alkaline-earth metal fluorides, interstructural distance) is shown.

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Received 10 February 2015

УДК 544.31 + 546.4

РАСЧЕТЫ ЭНТАЛЬПИИ ОБРАЗОВАНИЯ (РАЗРУШЕНИЯ) КРИСТАЛЛИЧЕСКОЙ РЕШЕТКИ ФТОРИДОВ ЩЕЛОЧНОЗЕМЕЛЬНЫХ МЕТАЛЛОВ

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Для фторидов щелочноземельных металлов проведена серия расчетов структурных и термохимических характеристик. Расчеты проведены с использованием модифицированной модели эффективных ионных радиусов и модели расчета энтальпии кристаллической решетки. Результаты вычислений согласуются с имеющимися экспериментальными данными в пределах доверительных интервалов.

Keywords: фториды, щелочноземельные металлы, энтальпия образования, катион, электрон, потенциал ионизации, межструктурное расстояние.

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Поступила в редакцию 10 февраля 2015 г.

БИБЛИОГРАФИЧЕСКОЕ ОПИСАНИЕ СТАТЬИ

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REFERENCE TO ARTICLE

Gruba O.N., Germanyuk N.V., Ryabukhin A.G. Formation (Decomposition) Enthalpy Calculations for Crystal Lattices of Alkaline-Earth Fluorides. *Bulletin of the South Ural State University*. *Ser. Chemistry*. 2015, vol. 7, no. 2, pp. 39–44.

COMPARATIVE ANALYSIS OF THEORETICAL AND EXPERIMENTAL UV-SPECTRA OF 2- AND 8-THIOQUINOLINE

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The comparative analysis of the calculated electronic absorption spectra of various forms of 2- and 8-thioquinoline and the experimental UV spectra of their solutions in various solvents has been carried out. Two conformational isomers of SH-forms have been analyzed for each compound. Calculations of other tautomeric forms of these compounds, namely NH-forms of 2-thioquinoline (2-thioquinolone) and 8-thioquinoline (zwitter-ion), and S-forms (anions) and 1-H-2-thioquinolinium cation have been analyzed additionally. It is shown that the absorption bands in the spectrum of 8-thioquinoline solution correspond to the electronic transitions in the SH-tautomer. On the contrary, the absorption bands in a spectrum of 2-thioquinoline solution correspond to the electronic transitions in the NH-tautomer and S-anion. The spreading of absorption bands in the experimental spectra is associated with conformational and tautomeric equilibrium which is established in the solutions of the considered compounds.

Keywords: thioquinoline, electronic absorption spectra, solvatochromic effect, PCM, TD-DFT.

Introduction

Oxyquinolines and oxypyridines are the objects of long-term examinations, including their electronic spectra, which are influenced by such factors as solvents, position of OH-groups in a ring, environment conditions, etc. [1-3]. Such interest is associated with the application of the given substances as chelates in analytical chemistry, and as intermediate products for synthesis of new biologically active compounds. Such feature of the compounds, as the existence of various tautomeric forms in solutions, depending on environment conditions, has been noticed in experiments. Nowadays the attention is turned to the similar thio-substituted compounds, which are used for the synthesis of new substances, especially in pharmaceutics [4-7]. The active reaction centers and the mechanisms of their interaction with various reagents in directional synthesis are the most important aspects of the precise examination of the substances. The special attention is paid to the study of the interactions of the substances with halogens and organohalogen compounds. Thus, the interaction of 8-thioquinoline and pyrrolidine-2-thione with molecular iodine, the structural changing of complexes during interaction, and its influence on electronic spectra, are presented in the research works [8, 9]. It has been noticed, that it is possible to trace the conversion degree and change of reagent concentration, to determine the stability constant of complexes with the use of UV spectra.

The investigation of the theoretical electronic spectra of organic compounds, including heterocycles, with the evaluation of the energy characteristics within the *ab initio* TD-DFT method [10, 11] has been widely applied for the detailed interpretation of the observed experimental data. Thus, in the study [12], alongside with the comprehensive experimental research of benzodithiazole derivatives, the calculations of electronic density, spectra and the reaction activity of the synthesized substances, consistent with the experimental data, have been carried out. In the study [13], the changing of the fluorescence ability of the phosphonate derivatives of 8-oxyquinoline and their complexes with zinc has been explained with the help of calculations. In [3], the comparison of NMR, IR and UV spectra of 5,7-dihalogen-8-oxyquinolines with the calculated spectra, obtained by the TD-DFT method has been performed. It is noticed, that the calculations have allowed to describe correctly a pattern of absorption maxima on UV spectra and to carry the assignment of the electronic transitions. Also, the results of the

experimental research of 2-amino-5-brombensoic acid were in good accordance with the calculations of the Raman activities and UV spectra [14], and the authors explained some features in view of the existence of conformers and difference of their energy characteristics.

For the correction of medium (solvent) influence on the explored substances, the improving models are involved, in which the different types of interactions of the solvate and the solvent are considered: dipole-dipole, dipole-induced, dispersion, *etc*. In particular, during the last decade the precise numerical continuum polarization model (PCM) [15, 16] has been advanced. Within the PCM model the solvent is considered as an isotropic medium, described by some physical constants; still the specific interactions are not taken into account in an explicit form. The solvate molecule is placed in a cavity that is formed in this continuous medium. All the solvate atoms are surrounded by spheres of Van-der-Waals radius. To build up the smooth surface, which is necessary for convergence of the method, the secondary environment by spheres of small radii with the subsequent triangulation is made for the formation of the surface elements. By several iterations, the surface charge field of the formed cavity and the free energy of a molecule in the solvent are estimated. The popularity of the PCM model is associated with the rapid calculations of the electronic states in the solvent environment, only a little longer compared to the calculations for a gaseous phase. Still, theoretical results and tendencies of the change of the compound spectra, obtained with the use of the given model, adequately correlate with the dependences of the experimental spectra of the synthesized compounds in solutions and explain their features. It has been shown, for azo-compounds, for example [17].

In turn, the electronic spectroscopy is the available and safe technique of the reaction path study, in which 2- and 8-thioquinoline and their derivatives are the initial components [8, 9].

The aim of this study is the determination of the similarity and the basic differences in the spectral behavior of 2- and 8-thioquinoline that act as the efficient reagents in the synthesis of new heterocyclic systems. It is obviously important to study the influence of the medium polarity on the electronic spectra of 2- and 8-thioquinoline and to estimate the opportunities to forecast the spectral behavior of their derivatives according to the theoretical calculations. For this purpose, we set the following tasks:

– to compare the calculated absorption characteristics of the fundamental electronic transitions with experimental UV spectra of 2- and 8-thioquinolines in various solutions;

– to trace how the changing basic contributions of the molecular orbitals to oscillators of electronic transitions vary in different compound forms, and what changes of these contributions occur through variation of the functional thionic group position in the quinoline ring;

– to find out, how the conformational and tautomeric variety of the investigated thioquinolines affects the position of the calculated absorption bands and, as the result, the interpretation of their experimental spectra in solvents.

Experimental

We used the reactive 2- and 8-thioquinoline (97 %, Sigma-Aldrich) for studying their UV absorption spectra characteristics. Dichloromethane and ethanol of chemical purity were used as solvents for the investigated compounds. The concentration of the compound solution was 10^{-4} M. The spectra of solutions were obtained with the help of the UV-Vis spectrophotometer Shimadzu UV-2700. The halogen and deuterium lamps were used as radiation sources with changing of one lamp for another at 323 nm. The spectra were obtained in the range from 220 up to 850 nm with shooting speed 450 nm per minute.

Calculations

We have carried out the optimization of structure geometry of various tautomeric forms of 2- and 8-thioquinoline with the subsequent calculation of the energy characteristics of the excited states and the electronic spectra, taking the influence of solvents (benzene, ethanol and dichloromethane) into account. The initial SH-forms are represented in calculations as a pair of conformational isomers. The optimization has been carried out for SH-forms **1-4** and NH-forms of 2-thioquinoline (2-thioquinolone **9**) and 8-thioquinoline (zwitter-ion **5**), S-forms (anions **6, 8**); and 1-H-2-thioquinolinium cation **7** (Fig. 1). For the comparison, the optimized structures and electronic spectra of free molecules have been also considered in a gaseous phase. The optimization of structure geometry was carried out using necessary iteration number to the stationary point with the largest component of the gradient to be less than $1E^{-5}$ Hartree/Bohr. Then the obtained Hessians of all structures were without imaginary frequencies.

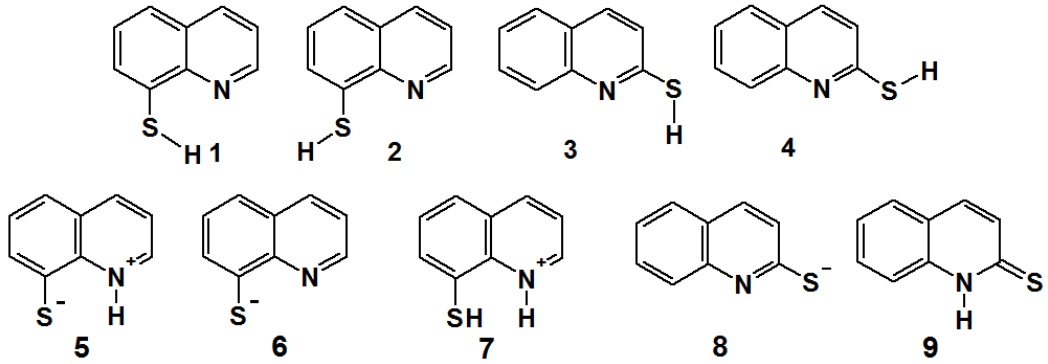


Fig. 1. The analyzed forms of compounds: SH-conformers of 8-thioquinoline (1, 2) and 2-thioquinoline (3, 4); NH-form (zwitter-ion 5), S-form (anion 6) and NH-cation (7) of 8-thioquinoline; S-form (anion 8) and NH-form (2-thioquinolone, 9) of 2-thioquinoline

It is known that PBE0 [18] and B3LYP [19, 20] functionals and basic set 6-311G(d, p) [21, 22] are most commonly used now, as they are the most precise for determination of the molecule characteristics of organic compounds. Therefore optimization of geometry of the studied molecules has been carried out by the Kohn-Sham method (DFT) with the use of functionals PBE0 and B3LYP on a base of full-electron basic set 6-311G(d, p). The influence of a solvent has been taken into account in model D-PCM (dielectric PCM, base version) [15, 16] with the following parameters: using the same factor for all tesserae, without calculation of cavitation, dispersion and repulsion free energy, at the absolute temperature 298 K. Van-der-Waals radius was taken from [23]. Electronic spectra of the optimized structures are obtained by method TD-DFT [10, 11], also taking into account the influence of solvents. Such calculations have been carried out for 10 excited states using necessary iteration number and convergence criterion on energy of all states to be less than $3E^{-5}$ Hartree/Bohr. All calculations of energy and orbital characteristics were performed using software package Firefly 8.0.1 [24].

Discussion

Spectral behaviour of 2- and 8-thioquinoline solutions

It has been established (see Table 1), that absorption lines in the calculated spectra of different forms of both compounds are shifted towards larger wavelengths with the decrease of the solvent polarity – from ethanol to benzene and further to the gaseous phase state. The experimental interaction of studied compounds with the solvents of different polarity also is impacted; in particular, in shifting of absorption maximums in the spectra of 2-thioquinoline solutions towards larger wave-lengths with changing ethanol to dichloromethane. The experimental spectra of 2-thioquinoline in different solvents are displayed on Fig. 2a, the data of calculations are on Fig. 2b (line spectrum is approximated by Lorentz function); the corresponding data of 8-thioquinoline are shown on Fig. 3a-b. In the experimental spectrum of 2-thioquinoline solution the largest shift of λ_{max}, varying in the range from 310 up to 390 nm, amounts to 8 nm; for other maxima which are varying in the range from 230 up to 300 nm, it is about 4 nm. The experimental spectra of 8-thioquinoline solutions have not shown any similar bathochromic shift. In other words, the negative solvatochromic effect is observed, which is confirmed by calculation results. Such effect was considered earlier in details in the review [25] for comprehensive series of organic compounds.

Our calculations show that for SH-forms of studied compounds **1-4** the calculated dipole moments in solvent medium are increased with transferring a molecule from the basic to the first excited state (see Table 2), and such effect gains in a non-polar solvent. Hence, displaying of the positive solvatochromic effect, associated with the increasing polarity at excitation of a molecule, which should be observed theoretically, at least, for 8-thioquinoline (which is mainly in the SH-forms in the solution), is smoothed out by the influence of other factors, whereby it is small enough. The following can affect it more efficiently than that: the effect of stabilization of the basic state at the solvation by polar solvents, including the one caused by steric difficulties or by the direction change of electrical dipole moment of a solvate; the effect of induced polarization of solvent molecules; also the essential change of the electronic molecule structure is possible. For S- and NH-forms **5, 6, 8, 9** the negative solvatochromic effect dominates

in the spectra, the effect is associated with decreasing of molecule polarity in the excited state. This effect, probably, appears in the experimental spectra of solutions of 2-thioquinoline, which is mainly in NH-form **9** in the solution.

Table 1

The position shift of absorption lines in calculated spectra depending on medium, nm (oscillator strength f is in the brackets)

Solvent / Compound	Ethanol	Dichloromethane	Benzene	Gas phase
8-thioquinoline (SH-form, conformer **1**)	341.9 (*0.075*) 240.7 (*0.221*) 237.1 (*0.082*)	343.5 (*0.074*) 241.1 (*0.228*) 237.5 (*0.070*)	348.8 (*0.073*) 242.6 (*0.242*) 239.0 (*0.041*)	354.8 (*0.073*) 244.3 (*0.244*) 240.4 (*0.021*)
8-thioquinoline (SH-form, conformer **2**)	337.0 (*0.076*) 239.9 (*0.176*) 236.3 (*0.129*)	337.5 (*0.076*) 240.1 (*0.182*) 236.6 (*0.119*)	339.6 (*0.078*) 240.9 (*0.204*) 237.6 (*0.082*)	342.2 (*0.079*) 241.8 (*0.221*) 238.5 (*0.049*)
8-thioquinoline (NH-form **5**)	622.9 (*0.031*) 370.1 (*0.022*) 271.8 (*0.208*) 262.5 (*0.210*)	–	714.5 (*0.029*) 399.1 (*0.025*) 277.4 (*0.200*) 268.0 (*0.190*)	783.6 (*0.029*) 420.8 (*0.027*) 281.4 (*0.188*) 271.2 (*0.175*)
8-thioquinoline (S-form **6**)	457.1 (*0.076*) 353.0 (*0.029*) 261.9 (*0.199*) 257.1 (*0.090*) 253.0 (*0.058*)	465.7 (*0.076*) 358.6 (*0.030*) 263.8 (*0.211*) 257.7 (*0.087*) 254.2 (*0.046*)	–	–
8-thioquinoline (NH-cation **7**)	418.5 (*0.033*) 262.0 (*0.013*) 250.3 (*0.356*)	–	–	–
2-thioquinoline (SH-form, conformer **3**)	304.3 (*0.088*) 239.1 (*0.422*) 233.0 (*0.129*)	304.7 (*0.087*) 239.3 (*0.420*) 233.1 (*0.130*)	306.1 (*0.086*) 239.8 (*0.412*) 233.7 (*0.133*)	307.7 (*0.085*) 240.5 (*0.406*) 234.4 (*0.134*)
2-thioquinoline (SH-form, conformer **4**)	305.6 (*0.085*) 240.0 (*0.409*) 232.7 (*0.137*)	306.0 (*0.083*) 240.2 (*0.406*) 232.8 (*0.139*)	307.5 (*0.080*) 240.8 (*0.398*) 233.4 (*0.144*)	309.2 (*0.078*) 241.6 (*0.390*) 234.2 (*0.145*)
2-thioquinoline (S-form **8**)	385.5 (*0.096*) 300.9 (*0.245*) 257.5 (*0.349*)	391.8 (*0.093*) 304.0 (*0.260*) 257.1 (*0.319*)	–	–
2-thioquinoline (NH-form **9**)	359.8 (*0.214*) 267.5 (*0.435*)	361.6 (*0.209*) 267.8 (*0.440*)	368.2 (*0.194*) 267.8 (*0.440*)	375.2 (*0.177*) 266.2 (*0.432*)

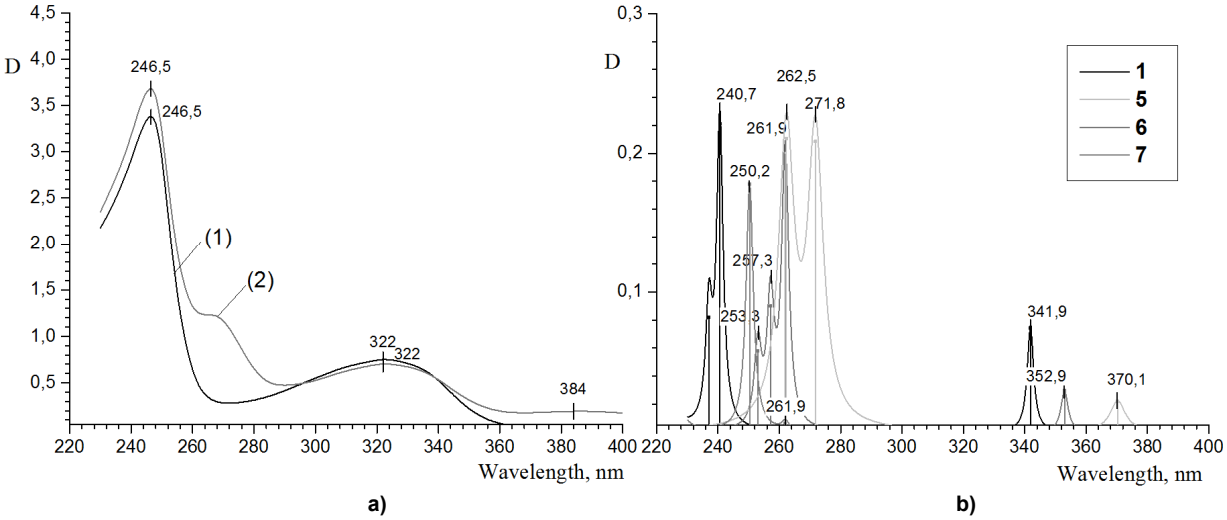


Fig. 2. a) Experimental UV spectra of the solution of 8-thioquinoline in dichloromethane (1) and ethanol (2); b) Calculated spectra of 8-thioquinoline in ethanol medium: SH-form (conformers 1, 2), zwitter-ion 5, S-form 6 and NH-cation 7

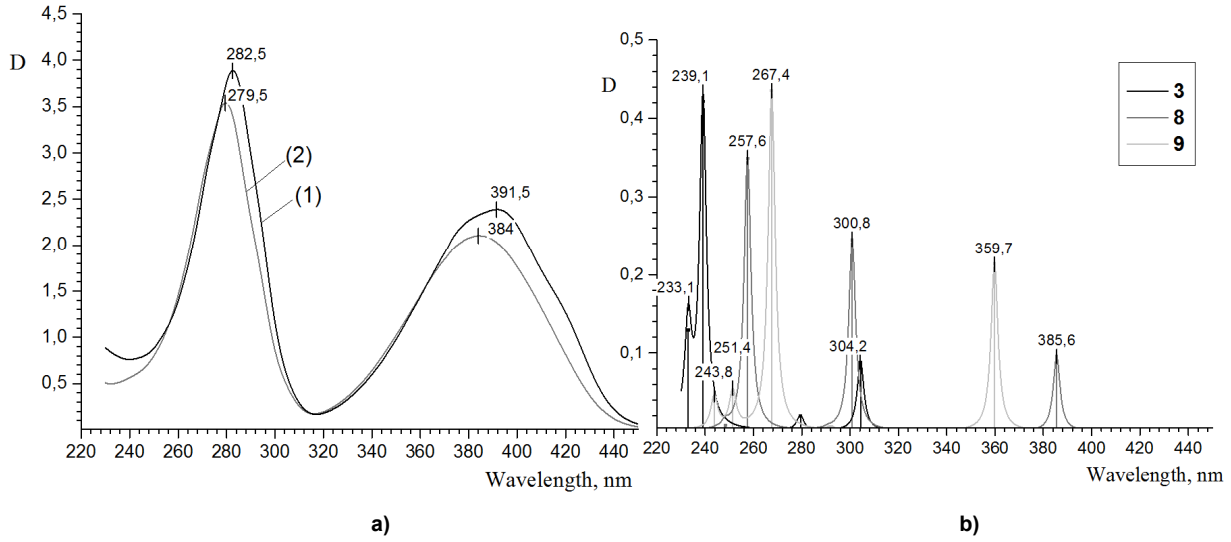


Fig. 3. a) Experimental UV spectra of the solution of 2-thioquinoline in dichloromethane (1) and ethanol (2); b) Calculated spectra of 2-thioquinoline in ethanol medium: SH-form (conformer 3), S-form 8 and NH-form 9

Table 2

The calculated dipole moments of the basic and the first excited state depending on medium, D

Solvent / Compound	Ethanol		Dichloromethane		Benzene		Gas phase	
	D_0	D_1	D_0	D_1	D_0	D_1	D_0	D_1
8-thioquinoline (SH-form, conformer **1**)	4.234	7.299	4.086	7.456	3.577	7.964	3.059	8.545
8-thioquinoline (NH-form **5**)	11.701	2.429	–	–	9.487	4.238	7.728	5.595
8-thioquinoline (S-form **6**)	33.152	3.517	32.909	3.930	–	–	–	–
8-thioquinoline (NH-cation **7**)	25.189	8.748	–	–	–	–	–	–
2-thioquinoline (SH-form, conformer **3**)	2.762	2.850	2.667	3.004	2.342	3.595	2.027	4.263
2-thioquinoline (S-form **8**)	17.147	4.023	17.288	4.536	–	–	–	–
2-thioquinoline (NH-form **9**)	8.457	5.249	8.134	5.498	6.963	6.442	5.747	7.476

The calculations of the spectrum characteristics of the various forms of 2- and 8-thioquinoline (without taking solvent influence into account) have shown the shift of absorption lines λ_{max} from 11 nm (SH-form **1-4**) up to 51 nm (S-forms **6, 8**) with respect to the spectrum in a non-polar solvent (benzene, Table 1). It is supposed, that here the elimination of solvent influence on the studied molecules reduces energies of $n\rightarrow\pi^*$ electronic transitions relevant to λ_{max}, moreover, to a much greater extent, than the influence of solvent polarity (Table 3). The given phenomenon is also the manifestation of solvatochromic and other abovementioned effects, which are extrapolated to a gaseous phase. On the other hand, the bathochromic shift of other absorption lines is much less in magnitude or tends to zero.

To estimate spectra accordance, values of calculated absorption lines λ_{max} have been compared with the rightmost maxima on the experimental spectra of solutions. Based on such comparison, it has been established that the difference of λ_{max} for SH-forms of 2-thioquinoline and 8-thioquinoline in the calculated spectra, that equals 25–45 nm, is impossible to find in the experimental spectra of the solutions, as experimental λ_{max} agrees with different tautomeric forms of these compounds. In this case, the calculated absorption lines, including λ_{max}, are in the range of the absorption bandwidth of 330–430 and 290–350 nm observed in the experimental spectra. Absorption at the transition, corresponding to λ_{max} of "ionic" forms of 8-thioquinoline **5-7**, is not observed in the range of experimental spectra that is larger than 400 nm, under our conditions: pH value 7–8 for the ethanol solution. It can indicate the absence of appreciable amount of these forms of 8-thioquinoline in the solution.

Table 3

The calculated energy characteristics of the electron transitions HOMO-LUMO depending on medium, eV

Compound	E_{HOMO}	E_{LUMO}	ΔE	E_{HOMO}	E_{LUMO}	ΔE
	Ethanol			Ethanol		
8-thioquinoline (SH-form, conformer **1**)	–6.125	–1.970	4.155	–6.095	–1.957	4.138
8-thioquinoline (NH-form **5**)	–5.385	–2.808	2.577	–		
8-thioquinoline (NH-cation **7**)	–6.931	–3.352	3.578	–		
2-thioquinoline (S-form **8**)	–5.031	–1.344	3.687	–4.694	–1.061	3.633
2-thioquinoline (NH-form **9**)	–6.123	–2.357	3.766	–6.090	–2.343	3.747
	Benzene			Gas phase		
8-thioquinoline (SH-form, conformer **1**)	–5.992	–1.905	4.087	–5.889	–1.859	4.030
8-thioquinoline (NH-form **5**)	–5.124	–2.819	2.305	–4.947	–2.816	2.131
2-thioquinoline (NH-form **9**)	–5.976	–2.291	3.684	–5.864	–2.240	3.624

It is worth noting that the represented earlier data have shown the calculation accuracy of absorption maximum values and electron transition energies on the level, similar to our results. In particular, in [13] the differences of the calculated and experimental energies of HOMO-LUMO transition were from 0.1 to 0.4 eV depending on the compound (without taking solution influence into account). Taking the solvent (water) into account at the calculation of the anion forms of Alizarin Red S in model IEF-PCM [26] showed the typical difference of excitation energies in calculation vs. experiment to be from 1% to 15% depending on compound form and functional used. The theoretical reviewing of spectral behavior of various azo-alkanes in model PCM [17] showed the difference of calculated absorption bandwidth values at the transition $n \rightarrow \pi^*$ in comparison with the experiment to be from 1 to 21 nm (about 0.01 – 0.2 eV). Our data show the similar difference in absorption maxima position. For example, the difference for λ_{max} is in 1–20 nm interval.

The influence of proton solvents and of probable formation of hydrogen bonding and cationic forms, presumably, appears on the experimental spectrum of 8-thioquinoline ethanol solution. In this spectrum there are mean absorption bands in the range corresponding to 272 and 370-nm spectral lines of the zwitter-ionic form **5** (Fig. 2a-b). That is, under our conditions, ethanol will slightly shift the tautomeric equilibrium "SH-form ↔ zwitter-ion" to the right side. In the 2-thioquinoline solution, such influence is inconsiderable because of the dominance of NH-form **9** under experiment conditions (see below). But at the same time, it is not possible to establish the fact of the presence of a probable cationic form **7** in ethanol solution of 8-thioquinoline by the analysis of electronic spectra, as the wavelength value of the single intensive absorption line (250 nm) and also the line (262 nm) for the form **7** are in the range of intensive absorption lines of other forms.

The calculated spectra of **1-2** and **3-4** pairs of SH-form conformational isomers are quite identical, with small shift of absorption lines to the right or to the left. Thus, the bathochromic shift of 5–6 nm for the absorption line λ_{max} of conformer **1** of 8-thioquinoline has the smaller value of total free energy in a solvent in relation to conformer **2**. On the contrary, for 2-thioquinoline calculations, the λ_{max} hypsochromic shift of 1-1.5 nm is shown for the conformer **3** with the smaller value of total free energy in a solvent relative to conformer **4**. Such shift depends on the ratio of energy values of the basic and the excited states. This tendency is revealed only in the calculated spectra and may not be used for the estimation of the content of one or another conformational structure in a solution, due to a wide width of absorption bands in the experimental spectra of solutions. However, at the same time, such shift is one of the cases of the absorption bands spreading.

We have noted that the symbasis pattern of absorption lines is observed on the spectra obtained with using different methods – PBE0 and B3LYP (Fig. 4), at that the spectral lines of all forms of compounds are shifted to the left in PBE0 case. The discrepancy between the wavelengths of absorption maxima on the experimental spectra of solutions and the wavelengths of absorption lines on the calculated spectra is increased by 10–18 nm. Thus, somewhat better data consistency is observed in the case of using B3LYP functional.

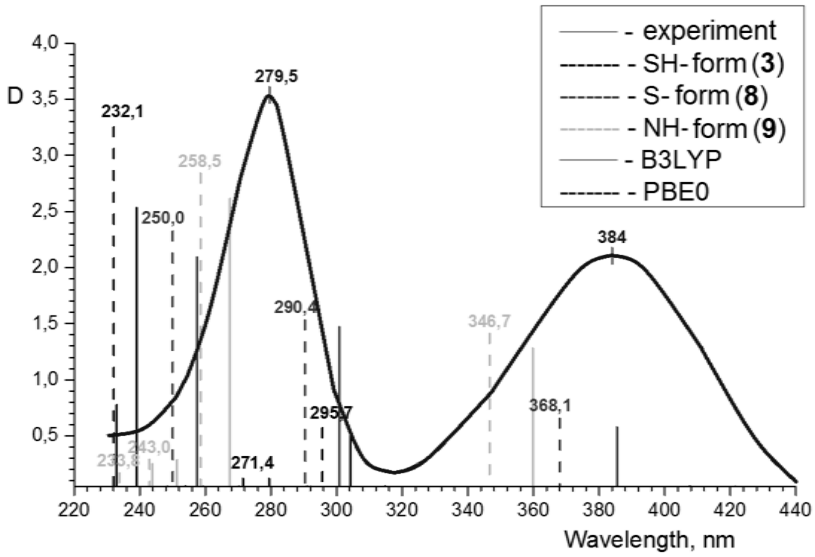


Fig. 4. The comparison of experimental spectrum of 2-thioquinoline in ethanol solution with calculated absorption lines of 2-thioquinoline forms 3, 8 and 9 in ethanol medium, obtained with using the functionals B3LYP and PBE0

It is known, that λ_{max} in the spectrum of water solution of 8-oxyquinoline at neutral pH is about 318 nm, while in the spectrum of ethanol solution it is about 310 nm [1]. Under these conditions conformers **1, 2** of the SH-form appear as the presumable tautomeric form of 8-thioquinoline. The presence of the zwitter-ionic form **5** is probable to a lesser degree. Consideration of the experimental spectra of 8-thioquinoline in ethanol at pH value 7–8, that we have recorded, has confirmed the presence of the absorption bands, corresponding to lines of the calculated spectra of SH-forms (Fig. 2). Thus, the wide bands 230–250 nm (the most intensive) and 290–345 nm are observed. Calculations have shown the presence of lines 236–237, 240–241 (the most intensive) and 337–343 nm with ratio of intensities, quite comparable to the experimental data. The space parts of molecular orbitals (MO) of the SH-form **1**, zwitter-ion **5** and assignment of these transitions to the absorption lines in the spectrum with its contributions represented by SAP-coefficients (squared SAP is the contribution of the given transition to the excited state), are graphically shown in Fig. 5a-b. Note that the electron transitions between this MO determine the excited states of molecules.

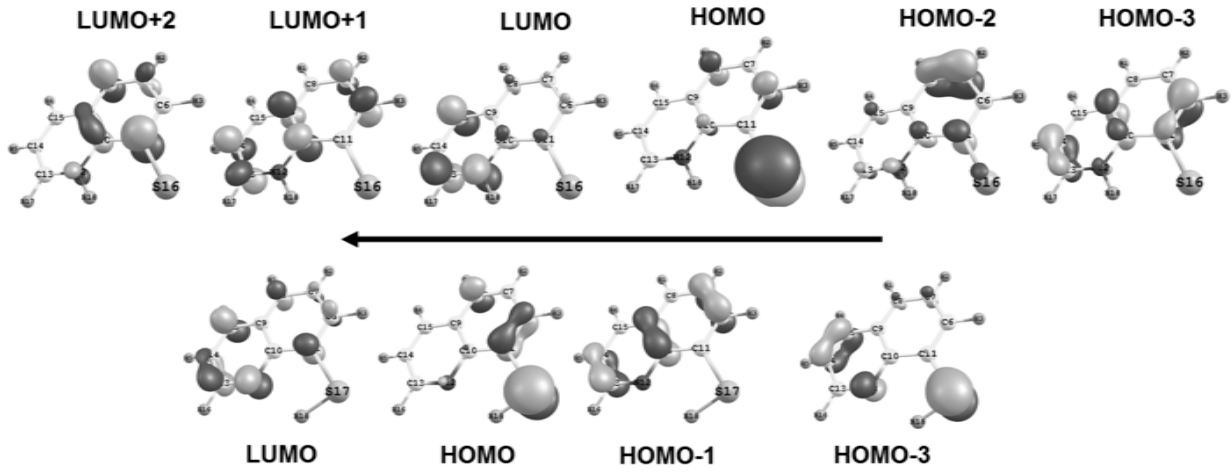


Fig. 5. MO graphical representation of a) NH-form of 8-thioquinoline (zwitter-ion 5) in ethanol medium. 623 nm: HOMO → LUMO (-0.99), 370 nm: HOMO → LUMO+1 (-0.98), 272 nm: HOMO-3 → LUMO (-0.69), HOMO-2 → LUMO (-0.48), 262 nm: HOMO → LUMO+2 (0.86); b) SH-form of 8-thioquinoline (conformer 1) in ethanol medium. 342 nm: HOMO → LUMO (0.98), 241 nm: HOMO-1 → LUMO (-0.58); HOMO-3 → L (-0.54)

The experimental spectra of 2-thioquinoline solutions have shown the presence of wide bands 250–310 and 350–425 nm (Fig. 3a). In the range of these bands, there are the lines from calculated spectra of the NH-form **9**: 268 and 360–362 nm, and S-form **8**: intensive lines 257–258 and 301–304 nm, and also 386–392 nm (Fig. 3b). Graphical representation of MO space parts of these forms is shown on Fig. 6a-b. The pattern of the active MO in the spectra slightly changes with transferring to the ionic state, but the strong bathochromic shift of the absorption bands (25–30 nm) is observed at the negative charge distributed on atoms of pyridine ring. There are only the lines of small intensity 279 and 304–305 nm among all of lines of the calculated spectra of SH-forms **3, 4** in the indicated range of experimental spectra. These facts show the preferential presence of the NH-form **9** in the ethanol 2-thioquinoline solution at pH value 7–8. The similar fact was shown earlier for 2-oxypyridine, which preferentially exists in the pyridone form in a polar solvent [2].

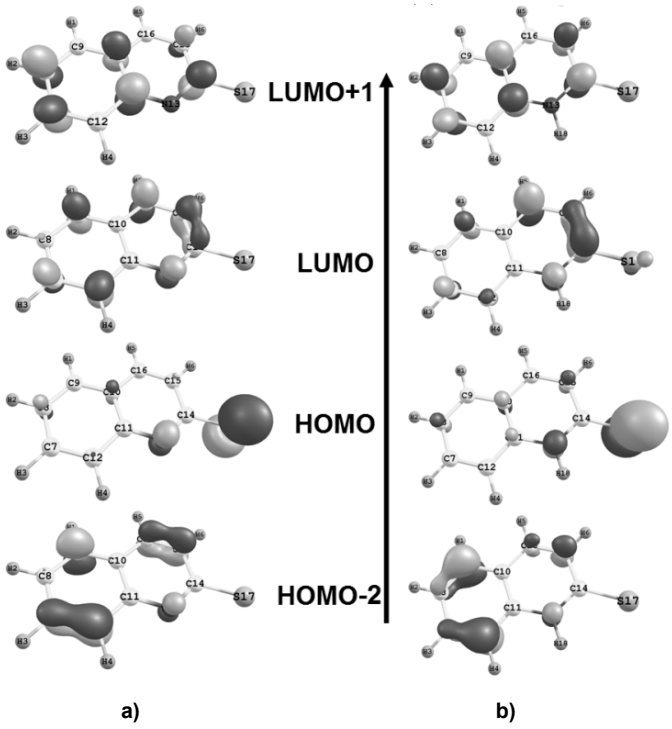


Fig. 6. MO graphical representation of a) S-form 8 of 2-thioquinoline in ethanol medium: 385 nm: HOMO → LUMO (0.96), 301 nm: HOMO → LUMO+1 (0.91), 258 nm: HOMO-2 → LUMO (0.87); b) NH-form 9 of 2-thioquinoline in ethanol medium: 360 nm: HOMO → LUMO (-0.97), 268 nm: HOMO → LUMO+1 (-0.80), HOMO-2 → L (0.51)

Conclusion

The comparative analysis of the experimental and calculated electronic absorption spectra of solutions of 2-and 8-thioquinoline in various solvents has been carried out. For each compound two conformational isomers of SH-forms, tautomeric NH-forms of 2-thioquinoline (2-thioquinolone) and 8-thioquinoline (zwitter-ion), and also S-forms (anions) and 1-H-2-thioquinolinium cation have been analyzed.

It has been shown that wide absorption bands in the range 250–310, 350–425 and 230–250, 290–345 nm correspond to the experimental spectra of 2- and 8-thioquinoline in ethanol and dichloromethane solutions, respectively. It has been established that the absorption band in the range 350–425 nm in a spectrum of a solution of 2-thioquinoline, corresponds to λ_{max} in the calculated spectra of its NH-form and S-anion, which is matched by the electronic transition $n \rightarrow \pi^*$. As the contributions of sulfur atomic orbitals in HOMO and of atoms of quinoline cycles in LUMO are involved in this transition, therefore its energy characteristics essentially vary for different tautomeric forms of 2-thioquinoline. This fact basically explains the main cause of absorption band spreading in the observed spectrum

of 2-thioquinoline, whereas the maximum position of a given absorption band does not depend on the conformational variety.

Also it has been established, that the presence of the absorption lines of the ionic forms is not evident in the spectrum of the neutral solution of 8-thioquinoline. The absorption bands correspond to the electronic transitions of SH-forms. Conformational variety of SH-forms is one of the reasons of the spreading of absorption bands in the solution spectrum of 8-thioquinoline.

On the basis of the comparative analysis of electronic spectra, it has been shown that the basic forms of existence of 2-thioquinoline in the neutral solution are the NH-form and S-anion; while for 8-thioquinoline in the neutral solution they are the conformers of SH-form.

Acknowledgements

This work was supported by the Russian Ministry for Education and Science.

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Received 24 February 2015

УДК 544.18, 543.428

СРАВНИТЕЛЬНЫЙ АНАЛИЗ ТЕОРЕТИЧЕСКИХ И ЭКСПЕРИМЕНТАЛЬНЫХ УФ-СПЕКТРОВ 2- И 8-ТИОХИНОЛИНОВ

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Выполнен сравнительный анализ расчетных электронных спектров поглощения различных форм 2- и 8-тиохинолина и экспериментальных спектров их растворов в условиях смены растворителя. Для каждого соединения анализировались два конформационных изомера SH-форм. Дополнительно проведены расчёты других таутомерных форм данных соединений – NH-форм 2-тиохинолина (2-тиохинолон) и 8-тиохинолина (цвиттер-ион), а также S-форм (анионов) и катиона 1-H-2-тиохинолиния. Показано, что полосы поглощения в спектре раствора 8-тиохинолина соответствуют электронным переходам в SH-таутомере. Напротив, полосы поглощения в спектре раствора 2-тиохинолина соответствуют электронным переходам в NH-таутомере и S-анионе. Уширение полос поглощения в экспериментальных спектрах связано с конформационными и таутомерными равновесиями, которые установлены для растворов рассмотренных соединений.

Ключевые слова: тиохинолины, электронные спектры поглощения, сольватохромный эффект, PCM, TD-DFT.

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Поступила в редакцию 24 февраля 2015 г.

БИБЛИОГРАФИЧЕСКОЕ ОПИСАНИЕ СТАТЬИ

Comparative analysis of theoretical and experimental UV-spectra of 2- and 8-thioquinoline / Yu.V. Matveychuk, M.V. Ilkaeva, I.V. Krivtsov, E.V. Bartashevich // Вестник ЮУрГУ. Серия «Химия». – 2015. – Т. 7, № 2. – С. 45–55.

REFERENCE TO ARTICLE

Matveychuk Yu.V., Ilkaeva M.V., Krivtsov I.V., Bartashevich E.V. Comparative Analysis of Theoretical and Experimental UV-Spectra of 2- and 8-Thioquinoline. *Bulletin of the South Ural State University*. *Ser. Chemistry*. 2015, vol. 7, no. 2, pp. 45–55.

СВЕДЕНИЯ ОБ ИЗДАНИИ

Серия основана в 2009 году.

Свидетельство о регистрации ПИ № ФС 77-57404 выдано 24 марта 2014 г. Федеральной службой по надзору в сфере связи, информационных технологий и массовых коммуникаций.

Журнал включен в Реферативный журнал и Базы данных ВИНИТИ. Сведения о журнале ежегодно публикуются в международной справочной системе по периодическим и продолжающимся изданиям «Ulrich's Periodicals Directory».

Решением Президиума Высшей аттестационной комиссии Министерства образования и науки Российской Федерации от 19 февраля 2010 г. № 6/6 журнал включен в «Перечень ведущих рецензируемых научных журналов и изданий, в которых должны быть опубликованы основные научные результаты диссертаций на соискание ученых степеней доктора и кандидата наук».

Подписной индекс 29414 в объединенном каталоге «Пресса России».

Периодичность выхода – 4 номера в год.

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Полная версия правил подготовки рукописей находится на сайте журнала: http://vestnik.susu.ac.ru/chemistry.

Плата за публикацию не взимается.

Редакторы А.*Ю. Федерякин*

Компьютерная верстка *В.Г. Харитоновой*

Издательский центр Южно-Уральского государственного университета

Подписано в печать 28.04.2015. Формат 60×84 1/8. Печать цифровая.
Усл. печ. л. 6,51. Тираж 500 экз. Заказ 76/180.

Отпечатано в типографии Издательского центра ЮУрГУ.
454080, г. Челябинск, пр. им. В.И. Ленина, 76.