



## Study of Arsenic-Containing Borates Based on Transformation Products of Industrial Waste†

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The novel arsenic-containing borates have been synthesized and studied. The composition and structure of the synthesized compounds have been established by physico-chemical analysis, IR, NMR and Mass spectral studies. Preliminary virtual (theoretical) bioscreening of synthesized compounds have been carried out. Biocide properties of obtained compounds were also determined.

**Key Words:** Coordination compounds, Arsenic, Mercury helides, Antibiocorrosive.

### INTRODUCTION

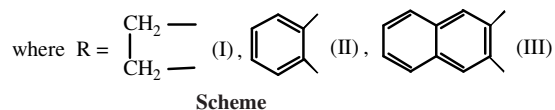
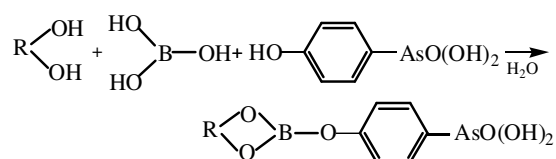
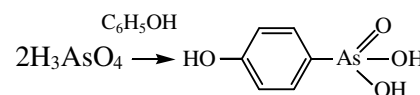
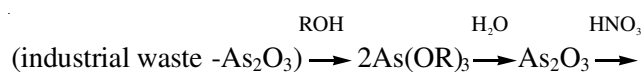
In the chemistry of boron, a number of important boron-organic compounds *e.g.*, alkyl(aryl)borates  $(RO)_2BR'$  and  $ROB(OR')_2$  ( $R = \text{alk.}$ ,  $R' = \text{aryl}$ ,  $R = R'$ ,  $R \neq R'$ ) are known. Synthesis and study of properties of these compounds have begun from 19<sup>th</sup> century and did not lose actuality up to day. They have not only preparative, but also have theoretical and practical significance. They are using in many organic syntheses as borating agents and Lewis acids, for the obtaining of boron-hydrides of potassium and sodium, trimethoxyboroxol, also as gaseous flux at the welding of metals<sup>1-4</sup>.

In view of bioactivity, especial interest provokes borates containing other elements, mainly arsenic<sup>5,6</sup>. We synthesized arsenic-containing borates based on ethylene glycol, pyrocatechin, 2,3-dihydroxynaphthalene, *p*-oxyphenylarsonic acid and salicylic acid. The synthesis carried out in presence of toluene which generated azeotrop with water for removing of the isolated water at the boiling of reaction mixture and for carrying out process in the set direction.

### EXPERIMENTAL

All obtained compounds are solid amorphous substance (Table-1), insoluble in non-polar and low polar solvents (benzene, toluene), well dissoluble in dimethyl formamide and dimethyl sulfoxide, moderately-in ethanol. They are hydrolyzed in water by heating and the hydrolytic products must be a mixture of the initial products.

One of the possible scheme of obtaining boron and arsenic-containing compounds from industrial waste are shown as:



### RESULTS AND DISCUSSION

The composition and structure of the synthesized compounds have been established by physico-chemical analysis ( $B_{\text{found}}/B_{\text{calc}}$ : I-3.61/3.81; II-3.23/3.27; III-2.73/2.84;  $As_{\text{found}}/As_{\text{calc}}$ : I-25.75/26.04; II-21.18/19.43), Infra-red (IR), NMR and Mass spectral studies (Table-1).

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TABLE-1  
MASS SPECTRAL DATA OF ARSENIC-CONTAINING BORATES

Compound	Mass spectral data, m/z ( $I_{rel.}$ , %)
I	288.0 [ $M^+$ ] (4.71), 243.9 (17.36), 227.9 (51.42), 167.9 (100.0), 133.8 (67.49)
II	384.0 [ $M^+$ ] (3.63), 275.9 (100.0), 182.9 (24.53), 167.9 (25.48), 139.9 (7.36), 135.9 (3.11)

In the IR spectra of ethylene glycol (*p*-oxyphenylarsonic acid) borate, we observed intensive absorption band 1345-1344  $\text{cm}^{-1}$  related to boron (III) valence wave. The absorption band 1520  $\text{cm}^{-1}$  characterized for 1,4-substituted benzene ring. In the IR spectra we also observed the characteristic absorption bands for the CH-groups (848  $\text{cm}^{-1}$ ); middle intensive absorption band 832  $\text{cm}^{-1}$ , which must be related to frequency-wave of oxoarsenate-ions. The absorption bands 420-416  $\text{cm}^{-1}$  are also related to oxoarsenate-ions.

The comparison of the IR spectra of the borates shows some likeness and difference among them, *e.g.*, in the IR spectra of the compound I one can observe absorption band 2890-2880  $\text{cm}^{-1}$  related to  $\text{CH}_2$ -groups valency wave, which are also characterized with deformation vibration (1460  $\text{cm}^{-1}$ ). Mentioned absorption bands are provoked by existence of ethylene glycol fragment and was not observed in other spectra of borates.

In the  $^1\text{H}$  NMR spectra of ethylene glycol (*p*-oxyphenylarsonic acid) borate one can observe signal with chemical shift 3.98-4.04 ppm for the protons in the  $\text{CH}_2$  groups of the ethylene glycol fragment; signals with chemical shifts at 6.86-7.67 ppm related to the protons of CH groups of benzene, the resonance signal in the range chemical shift 2.46-2.49 ppm for the protons of the As-OH. In the  $^{13}\text{C}$  NMR spectra one can observe a signal with 4 chemical shifts within the range 59.22-62.56 ppm typical for the carbon atoms of  $\text{CH}_2$  of the ethylene glycol fragment. In the  $^{13}\text{C}$  NMR spectra we also observe chemical shifts within the range 161.50-161.83 ppm, 123.84 ppm, 115.20-116.53 ppm and 130.51-131.18 ppm related to carbon atoms of benzene ring.

In the  $^{13}\text{H}$  NMR spectra of pyrocatechin (*p*-oxyphenylarsonic acid) borate we have observed resonance signal with chemical shifts within the range 6.45-6.53 ppm and 6.72-6.99 ppm typical for the carbon atoms of twice substituent benzene ring; signals with chemical shifts at 6.88-6.79 ppm and 7.01-7.38 ppm related to the protons of CH groups of benzene, the resonance signal in the range chemical shift 2.39-2.42 ppm for the protons of the As-OH. In the  $^{13}\text{C}$  NMR spectra we also observed chemical shifts within the range 118.25-118.92, 121.72 and 144.45-145.15 ppm related to carbon atom of twice substituent benzene group, the chemical shifts within the range 162.34-162.34, 123.89, 115.54-116.92 and 130.04-132.37 ppm related to carbon atoms of benzene ring.

In the  $^{13}\text{H}$  NMR spectra of 2,3-dihydroxynaphthalene (*p*-oxyphenylarsonic acid) borate one can observe a signal with chemical shifts within the range 6.81-6.96 ppm and 7.45-7.48 ppm typical for the carbon atoms of naphthalene group; signals with chemical shifts at 6.68-6.74 ppm and 7.01-7.03 ppm related to the protons of CH groups of benzene, the resonance signal in the range chemical shift 2.40-2.54 ppm for the protons of the As-OH. In the  $^{13}\text{C}$  NMR spectra we also observe chemical

shifts within the range 110.85-111.15, 124.52-126.27, 129.25-130.08 and 147.86-148.89 ppm related to carbon atom of naphthalene group, the chemical shifts within the range 160.94-161.73, 124.09, 116.07-116.35 and 131.48-131.86 ppm related to carbon atoms of benzene ring.

The important data Mass spectral of the synthesized compounds are given in Table-1. Previously, the mass-spectrogram data of synthesized compounds (I-IV) showed that the mass of molecular ( $M^+$ ) and fragmental ions correspond with obtained structures of aforementioned compounds and clearly represents succession of splitting of different atoms or groups of atoms<sup>7</sup>.

By using AMI method energetical (formation enthalpy  $\Delta H_f$ , ionized potential) and geometrical parameters (angles between the atoms, valence and dihedral angles) effective charges on atoms ( $q$ ), dipole moment ( $M$ ) and bond number between the atoms were calculated. Quantum-chemical calculations were performed by CS MOPAC (Chem3D Ultra-version 8.03)<sup>8</sup>. In benzene ring of ethylene glycol (*p*-oxyphenylarsonic acid) borate distances between C-C atoms (1.39-1.40 Å), valence bond angles of C-C-C (119-121 °C) and bond number (1.30-1.40) corresponds to the  $sp^3$  hybridized position of carbon atoms. The quantum-chemical calculations confirmed partial deformation of 5-member boron cycles, which is caused by inhomogeneity of distances between the atoms. Distances between B(12)-O(13) and B(12)-O(16) are 1.38 Å, also O(13)-C(14) and O(16)-C(15), correspondingly, are 1.49 Å and 1.46 Å. Analysis of electronic charges shows that biggest deficiency of electrons are characterized carbon atoms C(3) and C(6) which is explained by their connection with the strong electronegative atoms. There is calculated  $E = 7.94.107$  kJ/mol and  $D_{(dip. moment)} = 7.48$  Debye.

The study of thermal properties of obtained compounds by thermogravimetric and differential-thermal analysis method shows that they except compound I (Table-1) do not have distinctly expressed melting points and before melt were decomposed, which is easy to detect visually too. The character of thermal processes current in temperature intervals 20-600 °C are almost identical and consists of three stages-softening (not melt), partial reducing to coal and final destruction. By gas-liquid chromatography analysis were established isolation of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (350 °C). Comparatively high temperature of beginning of intensive destruction (450-570 °C), how it seems, is conditioned by content of cyclic fragments in the molecule structure of borates. In the 550-650 °C temperature range with the maximum 600 °C (exothermic effect) must be caused by oxidation process of residual carbon (with organic component). By this time, the mass decreases are 55 %. The remaining black welded residue, as expected, is a mixture of boron and arsenic oxides *ca.* 43.8 %. A similar picture except in the case of borates of aromatic dioles with the difference that the endothermic peak respective to their melting points, also the peak respective to initial and intensive destruction is shifted towards higher temperatures (580-670 °C).

**Virtual (theoretical) bioscreening of arsenic-containing borates:** We have carried out the preliminary virtual (theoretical) bioscreening of synthesized compounds by using of internet-system program PASS C & T<sup>9</sup>.

TABLE-2  
 RELATIVE BIOACTIVITY OF SYNTHESIZED COMPOUNDS (I-III)

Compounds	Antibacterial				Antiparasitic					Growth stimulant
	Antispirochetal	Antitreponemal	Subtilisin inhibitor	Non mutagenic, <i>Salmonella</i>	Antiprotozoal	Antiprotozoal ( <i>Amoeba</i> )	Antiprotozoal ( <i>Histomonas</i> )	Antiprotozoal ( <i>Trypanosoma</i> )	Antiprotozoal ( <i>Trichomonas</i> )	
	$P_a/P_i$									
I	0.840/0.000	0.900/0.000	0.837/0.004	0.880/0.010	0.984/0.001	0.983/0.001	0.907/0.000	0.985/0.001	0.769/0.001	0.853/0.001
II	0.818/0.001	0.880/0.000	0.809/0.004	0.739/0.025	0.978/0.001	0.975/0.001	0.878/0.000	0.977/0.001	0.702/0.001	0.802/0.002
III	0.837/0.000	0.899/0.000	0.825/0.004	0.717/0.029	0.982/0.001	0.981/0.001	0.904/0.000	0.984/0.001	0.769/0.001	0.835/0.001

The estimation of probable bioactivity of chosen compounds was carried out *via* parameters  $P_a$  (active) and  $P_i$  (inactive); when  $P_a > 0.7$ , the compound could also be shown bioactivity experimentally. Following from above mentioned virtual bioscreening, based on analysis of obtained results, the synthesized compounds (I-IV) with experimentally high probability (Table-2) ( $P_a = 0.70-0.98$ ) possibly will show the following bioactivity: Antibacterial (*Antispirochetal*, *Antitreponemal*, *Subtilisin inhibitor*, *Salmonella*), Antiparasitic (*Antiprotozoal - Amoeba*, *Histomonas*, *Trypanosoma*, *Trichomonas*), Growth stimulant and *etc.*

The synthesized compounds were tested as inhibitors of growth of some phytopathogenic bacteria. As test objects the following microorganisms were used: *Agrobacterium tumefaciens* (causing a grapevine disease), *Xanthomonas campestris* and *Pectobacterium aroideae* (striking some melons and gourds) and *streptomyces spp.* (destroys some water dissolved polymers).

Biocide properties of obtained compounds were determined by an alveolar standard method. Test results are presented in the Table-3. The tested results showed that the synthesized compounds I and II in various degree oppress growth of studied test organisms and can be used against these phytopathogenic microorganisms.

 TABLE-3  
 INFLUENCE OF THE SYNTHESIZED COMPOUNDS ON THE GROWTH OF VARIOUS MICROORGANISMS

No.	Microorganisms	Compounds					
		I			II		
		Concentration of compound (g/L)					
		0.1	0.01	0.001	0.1	0.01	0.001
		Zone of suppression of test microorganisms (mm)					
1	<i>Xanthomonas campestris</i>	6.0	5.0	3.0	7.0	6.0	3.0
2	<i>Pectobacterium aroideae</i>	5.0	4.5	3.0	8.0	6.5	4.0
3	<i>Agrobacterium tumefaciens</i>	7.0	6.0	4.0	8.0	7.0	4.0
4	<i>Streptomyces spp.</i>	4.0	4.0	3.0	6.0	4.0	2.0

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