Antibiocorrosive Woods and Plastics Nanomaterials: Arsonium triiodides and Silicon Organic matrix-Feasibility

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ABSTRACT

A search of anticorrosive with antibacterial property of compounds motivated us to synthesize nanomaterials with quaternary compounds. The arsonium triiodides $[(Ph_3AsCH2I]I_3$ and $[(i\text{-}Bu)_3AsCH_2I]I_3$ nanomaterials have been synthesized and characterized. The x-ray structures of $[(Ph_3AsCH2I]I_3$ and $[(i\text{-}Bu)_3AsCH2I]I_3$ have been determined. Crystals belong to the monoclinic (comp.1) system, space group P 21/n (No. 14) with a = 10.97 (1)Å, b=13.152 (1)Å, c=16.882 (1)Å, β=93.01 (1)^o and to the triclinic system (comp.2), space group P-1 (No. 2) with a=8.413 (1)Å, b=9.109 (1)Å, c=15.876 (1)Å, α = 76.24 (1)^o, β=75.60 (1)^o, γ=75.26 (1)^o. The structures were refined to an R value of 0.063 from 4082 (comp. I) and 0.091 from 4475 (comp.2) observed reflections. The As atom is coordinated tetrahedraly to the substituents and the anion has a linear structure. The synthesis of $[R_2(R')AsCH_2I]I_3$ (where R= R' or R≠ R') are described. The antibiocorrosive woods and plastics have possibility of the perspective application in synthesized compounds in bacterial resistant structures in homes and buildings. The test-microorganisms such as phitogen gram-positive - Staphylococus aurous, from gut's group bacteria phitogen gram-negative - Esherichia coli, spore-forming bacteria – gram-positive Bacillus subtilis and gram-positive (from radiate mushrooms) Autinomyces griseus showed high toxicity of iodmethylenediamylphenylarsonium triiodide as antibacterial nanomaterials. It inhibited growth of Esherichia coli, Staphylococus aureus and Bacillus subtilis with minimal concentrations.

1 INTRODUCTION

Inter-halogen compounds reacts with metal halides to form the XX_n^{1-} ions, as well as "mixed" anions such as I_2Cl^-, I_4Cl^-, ICl_3F^- etc. The Lewis acidity is expressed for di-iodine toward electron pair donor molecules. The Lewis acidity is also evident in the interaction of halogen molecules with ion donors to give the range of ions known as polyhalides. I_3^- and I_5^- polyiodides are Lewis acid-base complexes, in which I^- and I_3^- act as the bases and I_2 acts as the acid. The Lewis structure of I_3^- has three equatorial lone pairs on the central I atom and two axial bonding pairs in a trigonal bipyramidal arrangement. As I_3^- ion can interact with an additional I_2 molecule to yield larger mononegative polyiodides of composition $[(I_2)_n(I^-)]$. In combination with a large cation, such as $[N(CH_3)_4]^+$ and $[As(C_6H_5)_4]^+$, the symmetrical and linear counterion $[I_3]^-$ is observed with a longer I-I bond than in I_2. However, the structure of the triiodide ion is highly sensitive to the identity of the counter ion. For example, Cs^+, which is smaller than the tetra-methylammonium ion, distorts the I_3^- ion and produces one long and one short I-I bond:

$$[I—_{2.82}—I—_{3.10}—I]^- (I_3 \text{ in } CsI_3)$$

A more exam example of sensitivity to the cation is provided by NaI_3, which can be formed in aqueous solution but decomposes when the water is evaporated:

$Na^+_{(aq)} + I^-_{3\,(aq)} \rightarrow NaI_{(s)} + I_{2(s)}$. This makes instability of large anions in combination cations. Thus, the large cations are necessary to stabilize them in the solid state. Structures of arsenic-organic compounds are studied less, though about 6000 arsenic inorganic and organic compounds have been synthesized to present. Thus, the identification and characterization of arsenic-containing compounds attract much interests due to their theoretical and practical importance, taking into account as anticancer drugs, biological active substances, additives in protective covers and polymers with specific properties, as auxiliaries in asymmetric synthesis, as catalysts, etc. Based on the movable anion of quaternary arsonium iodides $[R_3AsCH_2I]I$, like potassium iodide, we have attempted to obtain and study analogical type polyiodides. The Lewis basicity arises from the lone pair on the central atom of tertiary arsine (**:**AsR_3), moreover, the central atom may exist in oxidation states +3 or +5 in AsR_3 and AsR_4^+, respectively. Compounds containing lone pairs can be considered rich with electron and trialkyl(aryl)arsines (**:**AsR_3) act as nucleophilic toward haloid-alkanes to produce tetra-alkyl(aryl)arsonium salts (AsR_4^+), which contain As(V). Chemically active (with high toxicity) tertiary arsines can be stabilized by forming fourth bond with electrophilic substituents and 4-coordinated arsenic compounds are chemically stable and less toxic. Products of alkylation- arsonium salts are successfully used in synthetic anions. Thus, tertiary arsines react with metlyleneiodide to inorganic chemistry as bulky cations to stabilize bulky produce "adducts" as follows:

$$R_2As(R') + CH_2I_2 \rightarrow [R_2(R')AsCH_2I]I\ ,$$

where R= R' =Pr, i-Pr, Bu, i-Bu, Am and Ph; R' ≠ R= Bu and Ph.

2 EXPERIMENTAL

Crystals of $[(Ph_3AsCH_2I]I_3$ and $[(i\text{-}Bu)_3AsCH_2I]I_3)$ are suitable for x-ray analysis available by treatment of the arsonium iodides alcohol solutions with an excess (about 5%) of I_2 alcohol solution. Dark-red solution remains during 2-3 weeks, after filtration the product needs wash with deionized water, alcohol and dry vacuum (with $CaCl_2$). The x-ray crystallography analysis, IR spectroscopy and chemical (elemantal) analysis of Arsenic is well known by Evins' (iodometric) method, iodine – by mercurimetric titration method. IR spectra is good practice from KBr pellets, using Thermo Nicollet Avatar 470 spectrometer with MCTB detector.

3 RESULTS

Arsonium polyiodides show interaction between iodmethylenetrialkyl(aryl)arsonium iodides and diiodmethane in various molar ratio such as: 1:1 (arsonium iodide: haloid alkane), 1:2 and 1:4. Possibly, one molecule of iodine combines to the cationic complex in all cases according to the reaction:

$$[R_2(R')AsCH_2I]I + I_2 \rightarrow [R_2(R')AsCH_2I][\ (I^-)(I_2)]$$

The $[R_2(R')AsCH_2I][I_3]$ formulas for synthesized compounds were determined by means of the analytical procedures described in experimental section. Results of chemical analyses and loading of starting materials and yields of reaction products are given in tables 1 and 2.

Table 1. Results of chemical analyses

No. Formula	Analyses: calc.%/found%	
	As	I
1. $Pr_3AsCH_2I_4$	10.34/10.02	69.96/70.32
2. $(i\text{-}Pr)_3AsCH_2I_4$	10.34/10.57	69.96/69.54
3. $Bu_3AsCH_2I_4$	9.77/10.11	66.13/66.39
4. $(i\text{-}Bu)_3AsCH_2I_4$	9.77/9.45	66.13/65.82
5. $Bu_2PhAsCH_2I_4$	9.52/9.27	64.45/64.03
6. $Am_2PhAsCH_2I_4$	9.26/9.69	62.70/62.36
7. $Am_3AsCH_2I_4$	9.20/8.77	62.24/62.49
8. $Ph_3AsCH_2I_4$	9.06/9.48	61.33/61.03

Table 2. Loading of starting materials and yields of reaction products

No.	arsonium	iodide	iodine		yield		
	g	mole	g	mole	g	mole	%
1.	1.17	0.0025	0.66	0.0026	1.64	0.0023	91.3
2.	1.20	0.0025	0.68	0.0027	1.73	0.0023	93.4
3.	1.80	0.0035	0.93	0.0037	2.37	0.0031	88.3
4.	1.65	0.0032	0.86	0.0034	2.12	0.0028	86.2
5.	1.50	0.0028	0.75	0.0029	1.85	0.0023	83.5
6.	1.44	0.0026	0.69	0.0027	1.72	0.0021	82.1
7.	1.35	0.0024	0.64	0.0025	1.62	0.0020	82.7
8.	1.86	0.0032	0.86	0.0034	2.33	0.0028	86.9

IR spectroscopic study: The IR spectrum of $[(Ph_3AsCH_2I]I_3$ is shown in Figure 1. The aromatic C-H stretching bands appear in the 3047 cm^{-1} and the aliphatic C–H - in the 2877 (asymm.) and 2946 (symm.) cm^{-1} regions. Skeletal vibrations, representing aromatic C=C absorb in the 1581-1434cm^{-1} range. The $C–H_{ar.}$bending bands appear in the regions 1241-1025 cm^{-1} (in plane bending) and 833-686 cm^{-1}(out-of plane bending) [16]. The As-C stretching bands appear at the 462 cm^{-1} ($As–C_{ar.}$) and 655 cm^{-1} ($As\text{-}C_{aliph.}$), characterized for $As–C_4$ bonds in tetrahedral position.

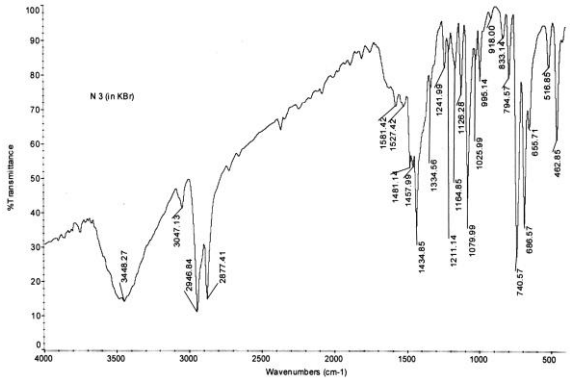

Figure 1. IR spectrum of Iodmethylenedibuthyl (phenyl) arsonium triiodide

4 STRUCTURAL ANALYSIS

The crystallographic data and structure refinement are given in table 3, bond lengths [Å] and angles [^{o}] –in table 4. By x-ray analysis have been confirmed the conclusions of our previous work in which we indicated that CH_2I^+ group of methylene iodide (CH_2I_2) in the interaction of tertiary arsines (R_3As or $R_2(R')As$), is bonded to the arsenic atom and therefore exists in internal sphere of complexes but lone atom of iodine takes place in external sphere as counterion.

5 CRYSTAL STRUCTURE OF $[PH_3ASCH_2I]^+I_3^-$

$[Ph_3AsCH_2I]^+I_3^-$ crystallises in the monoclinic, space group $P2_1/n$ (No. 14) with a=10.197 (1)Å, b=13.152 (1)Å, c=16.882 (1)Å , β=93.01 (1)^o and four formula units per unit cell. The crystal structure was solved via the Patterson method. For refinement full-matrix least-squares methods were applied. The cation has a tetrahedral shape and the anion has a linear structure. The structures of iodmethylenetriphenylarsonium cation and triiodide anion are shown in Figure 2. In the cation arsenic atom is bonded to four carbon atoms,- three of them assigned to the phenyl groups but fourth carbon is of alkylating group (CH_2I). The As–C interatomic distances range in the 1.906-1.924 Å and C-As-C angles of the cation - 105.3- 109.8^o. The series of tri- and four-coordinated arsenic compounds like in trimethylarsine $(CH_3)_3As$, As-C bond lengths are equal

1.98 Å and C-As-C angles– around 96°, the geometry is pyramidal, respectively. For tetracoordinate arsenic derivatives (sulphides As=S, oxides As=O and arsonium compounds (=As=)$^+$X$^-$) a tetrahedral configuration dominates and by authors have been suggested that p_π-d_π and p, π conjugation is characteristic for the corresponding compounds. In the tetraphenylarsonium large cation As-C distances range 1.910-1.921 Å and angles at arsenic - 106.1-110.7°. In arsonium salts As-C bond lengths range 1.889-1.949 Å and C-As-C angles 106.9-112.5° characterized for a tetrahedral geometry. Carbon atoms of phenyl groups are in sp^2 hybridization position and the values of bond angles range 117-120°. The fourth carbon atom (of CH_2I group) is also in tetrahedral position like central atom. The anion I_3^- has asymmetric linear structure $[I—_{2.86}—I—_{3.00}—I]^-$, this fact may be caused by structure and nature of substituents of the synthesized compound, the same explanation is proposed also by authors. The angle of counterion I(21) –I(20) –I(22) is 179.38°.

5. 1 Crystal Structure of $[(I\text{-}Bu)_3asch_2i]^+I_3^-$

$[(i\text{-}Bu)_3AsCH_2I]^+I_3^-$ crystallizes in the triclinic, space group space group P-1 (No. 2) with a = 8.413 (1)Å, b = 9.109 (1)Å, c = 15.876 (1)Å , α= 76.24(1)°, β= 75.60 (1)° and γ= 75.26(1)° and four formula units per unit cell. The crystal structure was solved via the Patterson method.

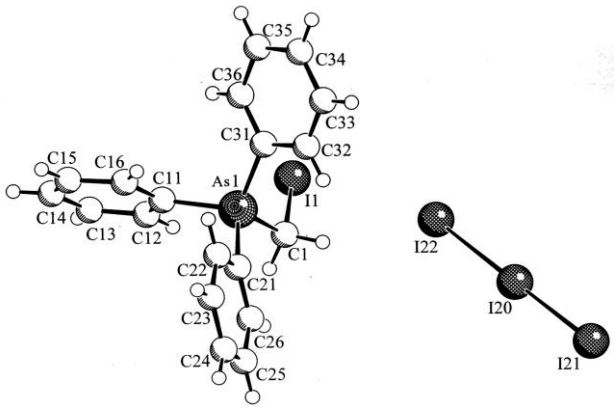

Figure 2. Strusture of iodmethylenetriphenylarsonium triioidide [Ph3AsCH2I]I3.

The cation has the shape of a tetrahedron and the anion has a symmetric linear structure. The structures of iodmethylenetri-izo-buthylarsonium cation and triiodide anion are shown in Figure 3. In the cation arsenic atom is bonded to four carbon atoms,- three of them assigned to the izo-buthyl groups and fourth carbon is of alkylating group (CH_2I). The As–C interatomic distances range in the 1.921-1.953 Å and C-As-C angles of the cation - 106.8- 114.7°. The As-C bond lengths of Ph-substituted compound is shorter than izo-Bu-substituted compound. The anion (in contrast of comp. 1) has symmetric linear structure: $[I—_{2.91}—I—_{2.91}—I]^-$, as it is in $[As(C_6H_5)_4]^+$ $[I—_{2.90}—I—_{2.90}—I]^-$ [3]. The bond lengths of the anion I_3 are 2.9131 and 2.9243 Å but bond angles I–I–I = 180.0° a symmetric linear structure.

6 POSSIBLE BIOACTIVITY OF SOME COMPOUNDS

The biocide properties of arsenic- containing compounds showed toxicity of several homologes of arsonium salts. Various type of inorganic, natural and synthetic compounds with bacterial and fungicide properties successfully can be used to a number of pathogen microorganisms participating in biodegradation. Some of them may be applied for obtaining of biostable polymers, paints and also against phitogen bacteria.

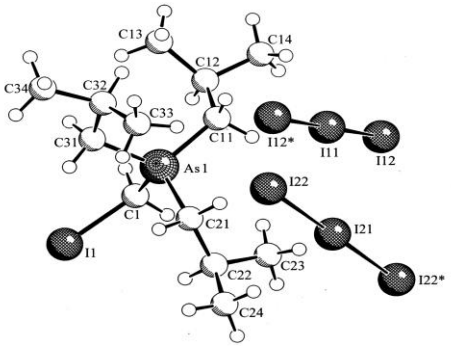

Figure 3. Structure of iodmethylenetri-izo-buthylarsonium triioidide $[(izo\text{-}Bu)_3AsCH_2I]I_3$.

Table 5 shows antibacterial properties of iodmethylenetriphenyl-arsonium triiodide (comp. 1), iodmethylenetri-izo-butilarsonium triiodide (comp. 2) and iodmethylenediamylphenylarsonium triiodide (comp. 3). Phitogen gram-positive - *Staphylococus aurous*, from gut's group bacteria phitogen gram-negative - *Esherichia coli***,** spore-forming bacteria – gram-positive *Bacillus subtilis* and gram-positive (from radiate mushrooms) *Autinomyces griseus* were applied in following concentrations of substances: (g/l) 1.0; 0.1; 0.01. Biocide properties showed cultivation of microorganisms used in food areas – *actinomicet* and dry TPA – for bacteria.

Tests are presented in Table 5. Relatively high toxicity shows for iodmethylenediamylphenylarsoni- um triiodide (comp. 3) which inhibits growing of *Esherichia coli, Staphylococus aureus* and *Bacillus subtilis* with minimal concentrations. Inhibirability of studying substances rises with increasing of concentrations (0.1 g/l), though only iodmethylenediamylphenylarsonium triiodide with this concentrations reacts to the *Autinomyces griseus* as

inhibiter. 1 g/l concentration of the substances has been toxic for all testmicroorganisms.

Table 3. Crystal data and structure refinement for the compound 1 – $[(C_6H_5)_3AsCH_2I]I_3$ and the compound 2 - $[(i\text{-}C_4H_9)_3AsCH_2I]I_3$

Weight formula	$C_{19}H_{17}AsI_4$	$C_{13}H_{29}AsI_4$
Molecular mass	827.87	867.89
Temperature	198 (2) K	198 (2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/n$ (No. 14)	triclinic, P-1 (No.2)
Unit cell dimensions	a = 10.197 (1) Å b = 13.152 (1)Å β =93.01 (1)° c = 16.882 (1) Å	a = 8.413 (1) Å α= 76.24 (1)° b = 9.109 (1) Å β = 75.60 (1)° c = 15.876 (1) Å γ= 75.26 (1)
Volume	2260.9 (3) $Å^3$	1119.67 (19) $Å^3$
Z, Calculated density	4, 2.529 Mg/m^3	2, 2.375 Mg/m^3
Absorption coefficient	6.353 mm^{-1}	6.403 mm^{-1}
F (000)	1560	732
Crystal size	0.25× 0.15 × 0.03 mm	0.60 × 0.30 × 0.05 mm
Theta range for data collection	1.96 to 27.88°	1.35 to 27.47°
Limiting indices	-13<=h<=13, -17<=k<=16, -22<=l<=22	-9<=h<=10, -11<=k<=11, -20<=l<=20
Reflections collected / unique	9871 / 5377 [R (int) = 0.0333]	7329 / 4943 [R (int) = 0.0341]
Completeness to theta – 27.47	96.6 %	96.5%
Max. and min. transmission	0.8323 and 0.2996	0.7402 and 0.1139
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5377 / 0 / 217	4943 / 0 / 172
Goodness-of-fit on F^2	1.064	1.034
Final R indices [I>2 (I)]	R1 = 0.0626, wR^2 = 0.1978	R1 = 0.0910, wR^2 = 0.2718
R indices (all data)	R1 = 0.0835, wR^2 = 0.2175	R1 = 0.0964, wR^2 = 0.2764
Largest diff. peak and hole	2.743 and -5.698 eÅ^{-3}	3.082 and -5.433 eÅ^{-3}

The iodmethylenediamylphenylarsonium triiodide is characterized with high toxicity, which besides arsenic and iodine, contains phenyl (C_6H_5), methylene (CH_2) and amyl (C_5H_{11}) radicals and inhibits both – gram-positive and gram-negative bacteria. Iodmethylenetriizobutylarsonium triiodide is less toxic (comp. 2).

7 CONCLUSION

Preliminary data showed that new biologically active materials can be developed for various applications:

1. Polyfunctional covers stable to bio-corrosion induced by microorganisms (Figure 4);
2. Materials with antimicosic properties - appretive and adhesive compositions as aqueous dispersions for manufacturing of skins, shoes and textiles;
3. Biologically active polymeric materials for covering agriculture plants from illness, caused by incomplete mushrooms and some microorganisms, also, in the time of contact of people with them.

	$[(C_6H_5)_2AsCH_2I]I_3$ ($C_{19}H_{17}AsI_4$)		$[(i\text{-}C_4H_9)_3AsCH_2I]I_3$ ($C_{13}H_{29}AsI_4$)	
As (1) –C (31)	1.906 (9)		As (1) –C (11)	1.921 (13)
As (1) –C (1)	1.912 (9)		As (1) –C (1)	1.925 (15)
As (1) –C (21)	1.922 (9)		As (1) –C (31)	1.949 (13)
As (1) –C (11)	1.924 (9)		As (1) –C (21)	1.953 (13)
C (1) –I (1)	2.154 (10)		C (1) –I (1)	2.132 (17)
C (11) –C(16)	1.370 (14)		C (11) –C(12)	1.53 (2)
C (11) –C(12)	1.384 (13)		C (12) –C(14)	1.51 (2)
C (12) –C(13)	1.405 (15)		C (12) –C(13)	1.55 (3)
C (13) –C(14)	1.373 (17)		C (21) –C(22)	1.53 (2)
C (14) –C(15)	1.384 (17)		C (22) –C(23)	1.51 (3)
C (15) –C(16)	1.392 (15)		C (22) –C(24)	1.53 (3)
C (21) –C(26)	1.366 (13)		C (31) –C(32)	1.50 (2)
C (21) –C(22)	1.442 (13)		C (32) –C(33)	1.50 (3)
C (22) –C(23)	1.355 (15)		C (32) –C(34)	1.58 (3)
C (23) –C(24)	1.382 (16)		I (11) –I(12)	2.9243 (12)
C (24) –C(25)	1.406 (16)		I (11) –I(12) # 1	2.9243 (12)
C (25) –C(26)	1.402 (14)		I (21) –I (22) # 2	2.9131 (11)
C (31) –C(36)	1.370 (13)		I (21) –I(22)	2.9131 (11)
C (31) –C(32)	1.409 (14)			
C (32) –C(33)	1.352 (15)			
C (33) –C(34)	1.354 (17)			
C (34) –C(35)	1.421 (17)			
C (35) –C(36)	1.389 (14)			
I (20) –I(21)	2.8622 (12)			
I (20) –I(22)	3.0011 (11)			
C (31) –As (1) –C (1)	114.0 (4)		C (11) –As (1) –C (1)	107.5 (7)
C (31) –As (1) –C (21)	109.8 (4)		C (11) –As (1) –C (31)	114.7 (6)
C (1) –As (1) –C (21)	105.3 (4)		C (1) –As (1) –C (31)	106.8 (7)
C (31) –As (1) –C (11)	109.3 (4)		C (11) –As (1) –C (21)	110.3 (7)
C (1) –As (1) –C (11)	111.4 (4)		C (1) –As (1) –C (21)	109.8 (7)
C (21) –As (1) –C (11)	106.7 (4)		C (31) –As (1) –C (21)	107.5 (7)
As (1) –C (1)-I (1)	114.1 (5)		As (1) –C (1)-I (1)	112.9 (8)
C (16) –C (11) –C (12)	122.2 (9)		C (12) –C (11) –As (1)	118.3 (11)
C (16) –C (11) –As (1)	117.1 (7)		C (14) –C (12) –C (11)	108.2 (15)
C (12) –C (11) –As(1)	120.5 (8)		C (14) –C (12) –C (13)	110.7 (16)
C (11) –C (12) –C (13)	117.7 (10)		C (11) –C (12) –C (13)	112.5 (15)
C (14) –C (13) –C (12)	120.5 (10)		C (22) –C (21) – As (1)	116.8 (12)
C (13) –C (14) –C (15)	120.5 (10)		C (23) –C (22) –C (24)	110 (2)
C (14) –C (15) –C (16)	119.6 (10)		C (23) –C (22) –C (21)	113.5 (18)
C (11) –C (16) –C (15)	119.3 (10)		C (24) –C (22) –C (21)	107.2 (17)
C (26) –C (21) – C (22)	121.0 (9)		C (32) –C (31) –As (1)	115.5 (11)
C (26) –C (21) –As (1)	120.7 (7)		C (33) –C (32) –C (31)	114.8 (14)
C (22) –C (21) –As (1)	118.0 (7)		C (33) –C (32) –C (34)	108.8 (17)
C (23) –C (22) –C (21)	117.8 (9)		C (31) –C (32) –C (34)	105.4 (15)
C (22) –C (23) –C (24)	122.3 (10)		I (12) –I (11) –I(12) # 1	180.00 (4)
C (23) –C (24) –C (25)	119.9 (9)		I (22) #2 –I (21) –I (22)	180.0
C (26) –C (25) –C (24)	119.1 (10)			
C (21) –C (26) –C (25)	119.9 (9)			
C (36) –C (31) –C (32)	119.7 (9)			
C (36) –C (31) –As (1)	120.3 (7)			
C (32) –C (31) –As (1)	120.0 (7)			
C (33) –C (32) –C (31)	120.7 (10)			
C (32) –C (33) –C (34)	119.8 (10)			
C (33) –C (34) –C (35)	121.5 (10)			
C (36) –C (35) –C (34)	117.9 (9)			
C (31) –C (36) –C (35)	120.3 (10)			
I (21) –I (20) –I(22)	179.38 (4)			

Table 4. Bond lengths [Å] and angles [°] for $C_{19}H_{17}AsI_4$ and $C_{13}H_{29}AsI_4$

Table 5. Antibacterial spectrum of Arsonium triiodides

Test-culture	Compound								
	1 $Ph_3AsCH_2I_4$			2 $(i\text{-}Bu)_3AsCH_2I_4$			3 $Am_2PhAsCH_2I_4$		
	Concentration of substance (g/l)								
	1.0	0.1	0.01	1.0	0.1	0.01	1.0	0.1	0.01
	A zone of inhibition of test-culture (mm)								
Esherichia coli	4.0	2.0	0	2.5	1.5	1.0	6.0	3.0	1.0
Staphylococus auveus	3.0	1.0	0	2.0	1.0	0	5.0	2.0	1.0
Bacillus subtilis	2.0	1.0	0	2.0	2.0	0	5.0	3.0	1.0
Actinomyces griseus	1.0	0	0	1.0	1.0	0	1.0	1.0	0

Figure. 4. Antibiocorrosive covers based on arsonium triiodides and siliconorganic matrix for wood and plastic.