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Synthesis and structures of the first triiodoarsenate(III) anion, $EtAsI_3^-$, and zwitterions, $(HPy)_2As_2I_6$

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The first examples of organotriiodoarsenates(III) in the form of zwitterions, $(3\text{-}HPy)_2As_2I_6$ and $(4\text{-}HPy)_2As_2I_6$, have been obtained from aqueous solutions, and their structures have been established by XRD. The dimeric molecules in the crystals are built from two square pyramidal $(HPy)AsI_4$ units joined by 2 bridging I atoms. The crystal packing of both compounds is largely defined by interlayer As···I contacts, which fulfill the coordination sphere of the As atoms to 6 in the 4-HPy isomer and result in its characteristic red colour and lower solubility. These intermolecular interactions in the crystal structure can be suppressed by the inclusion of a solvent, showing them to be not very strong. The intramolecular bonding via the two bridging I atoms was proven to be rather weak as well, by the formation of the salt $[Et_4N][EtAsI_3]$ with a monomeric triiodoarsenate(III) anion from acetonitrile solution. In the closely related compound $p\text{-}H_2NC_6H_4AsI_2\cdot HI$, one iodide can be substituted for the OTs^- anion to give $[p\text{-}H_3NC_6H_4AsI_2]OTs$, showing the iodide belongs to the outer sphere rather than being coordinatively bound to the As atom. The lengths of the *trans*-I–As–I bonds in the determined structures can be formalized by a semi-empirical modified Pauling equation, which relates them to the bond order, taking into account the antibonding influence of the 4s orbital of the As atom.

1. Introduction

Aryldihaloarsanes $RAsX_2$ are readily obtained in the reactions of arylarsonous acids with the corresponding concentrated HX acid. In such reactions carried out in aqueous media, the corresponding aryltrihaloarsenate anions are not separated in the form of stable solids, despite the presence of X^- in large concentrations [1]. On the other hand, it is well known that the compounds R_nAsX_{3-n} ($n = 0–2$) act as weak Lewis acids and form complexes with other nucleophiles, including halides. Such complex anions, e.g. of the types $[As_mX_{3m+n}]^{n-}$ [2] and $[R_nAs_nX_{3n}]^{n-}$ [3], are structurally well studied and tend to readily form in polar organic solutions for the combination of As with Cl and Br. Stable crystalline organohaloarsenates were isolated with such anions as $[RAsCl_3]^-$, $[R_2As_2Cl_5]^-$, and $[R_2As_2Br_6]^{2-}$ [3]. No organofluoroarsenates(III) are known; organofluorinated species are only reported as cations with higher valent As, such as the only structurally characterized $[MeAsF_3]^+$ [4] and $[Ph_2AsF_2]^+$ [5]. Interestingly, organoiodoarsenates also remain unknown to date, in spite of the fact that halide complexes of the group 15 elements become more thermodynamically stable with the increase of the atomic number of both elements. Quite the contrary, two iodo(methyl)arsenic(V) species, $[MeAsI_3]^+$ and $[Me_2AsI_2]^+$, are known as rare examples of As halogenated cations [6]. Here we describe the first structurally characterized triiodoarsenates(III), obtained as the zwitterions $[HPyAsI_3]$ (Py = 3 or 4-C_5H_4N). Most notably, the compounds have been crystallized directly from aqueous media. Their crystal packing is discussed in view of intermolecular interactions and solubility; the possibility of triiodoarsenate $[RAsI_3]^-$ anion formation in organic solutions is also considered.

2. Experimental

2.1. General remarks

All the starting reagents are commercially available. $EtAsI_2$ was kindly donated by Prof. J. D. Woollins. DMSO-d_6 for NMR experiments was degassed in a vacuum and stored over 3 Å molecular sieves. 4-Aminophenylarsonic acid was prepared according to a published method [7]. Owing to the known instability of pyridyldiazonium salts [8], a quick further reaction with arsonic alkaline solutions was necessary. The IR spectra were recorded on a Varian FTS 800 spectrometer. The NMR spectra were recorded

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for solutions in DMSO-d_6 on Bruker Avance 300 and 500 spectrometers (^{1}H: 300.130; 500.129 MHz, ^{13}C: 75.438; 125.757 MHz). The chemical shifts (δ, ppm) were referenced to the signals of the solvent: $\delta_H = 2.50$, $\delta_C = 39.5$. The atom numbering in the NMR spectra descriptions corresponds to that in Figs. 1, 2 and 4; the assignments of peaks was made by a comparison to the spectra of similar compounds [9].

2.2. Preparation

2.2.1. Synthesis of p-$H_2NC_6H_4AsI_2{\cdot}HI$ (1) and [4-$H_3NC_6H_4AsI_2$][OTs] (2)

To a solution of 4-$H_2NC_6H_4AsO_3H_2$ (1.82 g, 8.38 mmol) in 50 mL of water conc. HCl (15.0 mL, 150 mmol), $Na_2S_2O_5$ (1.0 g, 5.3 mmol) and NaI (10.0 g, 66.7 mmol) were added. A yellow precipitate of **1** formed immediately. After some mixing, HOTs·H_2O (30.0 g, 158 mmol) was added and the mixture was shaken well, whereupon a thick orange precipitate initially formed which turned into a yellow crystalline solid. The latter was filtered out and dried in a vacuum desiccator over P_2O_5. Yield: 4.05 g (81%). Crystals suitable for XRD were grown from the water-THF solution upon cooling. *Anal.* Calc. for $C_{13}H_{14}AsI_2NO_3S$ (593.1): C, 26.33; H, 2.38; N, 2.36. Found: C, 26.2; H, 2.4; N, 2.3%. IR (KBr, cm^{-1}): 1594 (m), 1546 (s), 1493 (s) (ν(Py ring)); 1223 (vs), 1212 (vs), 1168 (vs), 1125 (vs), 1062 (m), 1032 (vs), 1007 (vs), 818 (vs), 681 (vs), 592 (m), 567 (vs), 493 (s), 413 (m) ($\nu(SO_3) + \delta$(C–H, aromatic)). ^{1}H NMR: 10.4 (br. s, 3 H, NH_3), 7.51 (d, $^3J_{H,H} = 9$ Hz, 2 H, C(12)–H and C(16)–H), 7.15 (d, $^3J_{H,H} = 9$ Hz, 2 H, C(13)–H and C(15)–H), 7.45 (d, $^3J_{H,H} = 9$ Hz, 2 H, C(3)–H and C(5)–H), 6.81 (d, $^3J_{H,H} = 9$ Hz, 2 H, C(2)–H and C(6)–H), 2.28 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR: 154.2 (s, C(4)), 145.1 (s, C(11)), 138.1 (s, C(14)), 132.3 (s, C(3) and C(5)), 114.4 (s, C(2) and C(6)), 128.2 (s, C(12) and C(16)), 125.5 (s, C(13) and C(15)), 117.8 (s, C(1)), 20.7 (s, CH_3). Compound **1** shows essentially the same signals in the ^{1}H and ^{13}C spectra as those of the cation of **2**.

2.2.2. Synthesis of 3-$I_2AsC_5H_4N$ (3)

Solution of As_2O_3 (6.48 g, 32.8 mmol) and Na_2CO_3 (14.1 g, 133 mmol) in 40 mL of water was prepared. 3-Aminopyridine (2.87 g, 30.5 mmol) was dissolved in 20 mL of water, then conc. HCl (9.5 mL, 95 mmol) was added. The latter mixture was cooled to −10 °C and a solution of $NaNO_2$ (2.27 g, 32.9 mmol in 4 mL of water) was added over 1 min. Immediately afterwards the resultant bright yellow solution was added to the stirred and cooled to 0 °C arsenite solution. The resulting brick red mixture was stirred for 10 min at room temperature, and then gradually heated to 70 °C. After cooling, 7 ml of conc. HCl and 20 g of activated carbon were added, the solution was heated to boiling and filtered. The filtrate was concentrated to 20 mL, filtered, and $Na_2S_2O_5$ (3.00 g, 15.8 mmol), conc. HCl (3 mL, 30 mmol) and NaI (9.21 g, 61.5 mmol) were added. After thorough mixing, the orange precipitate that formed was separated by filtration and dried in a vacuum over P_2O_5. For purification, the crude product was mixed with 20 mL of water, 1.5 g of NaI, 2 mL of conc. HCl and 0.2 g of $Na_2S_2O_5$ were added, then after mixing the precipitate was thoroughly sucked on a glass frit, dried in a

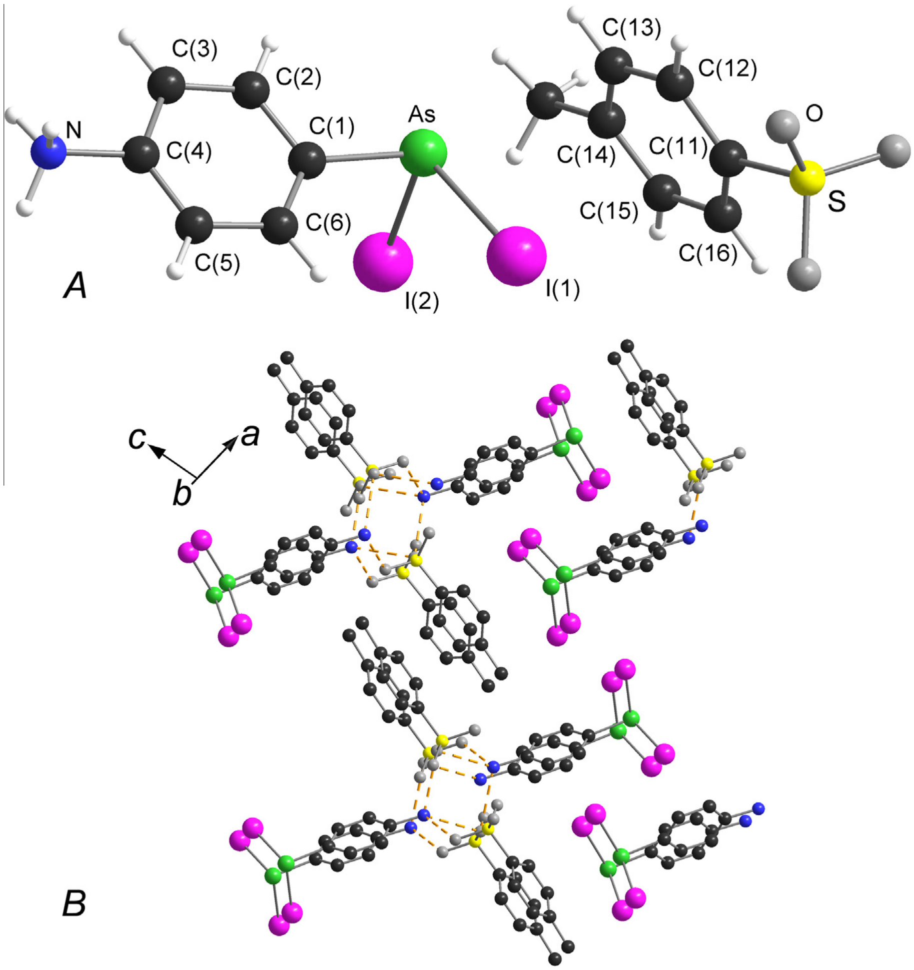

Fig. 1. (A) Independent part of the crystal structure of **2**, showing the atom numbering scheme; (B) packing of the molecules in the crystal, featuring $NH_3\cdots O_3S$ interactions (the hydrogen bonds are shown as dashed lines, H atoms are omitted).

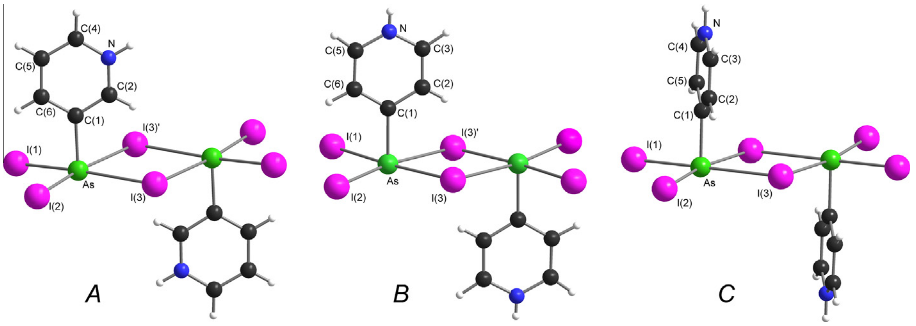

Fig. 2. Structure of the molecular dimers in the crystals of (A) **3**·Me_2CO, (B) **4** and (C) **4**·2THF.

vacuum desiccator with P_2O_5 and further in a dynamic vacuum. Yield: 4.34 g (27%). Single crystals of the acetone solvate were obtained by cooling of a saturated acetone solution at −25 °C. *Anal.* Calc. for $C_5H_5AsI_3N$ (534.7): C, 11.2; H, 0.94; N, 2.62. Found: C, 10.9; H, 0.9; N, 2.5%. IR (KBr, cm^{-1}): 3468 (br, m) (ν(N–H)); 1606 (m), 1577 (m), 1512 (s), 1436 (s) (ν(Py ring)); 770 (s), 663 (vs) (δ(C–H, aromatic)). ^1H NMR: 15.36 (br. s, 1H, NH, chemical shift depends on water amount), 9.07 (s, 1H, C(2)–H), 8.93 (d, $^3J_{H,H}$ = 6 Hz, ^{1}H, C(4)), 8.89 (d, $^3J_{H,H}$ = 8 Hz, ^{1}H, C(6)), 8.14 (dd, $^3J_{H,H}$ = 8 Hz, $^3J_{H,H}$ = 6 Hz, ^{1}H, C(5)). $^{13}C\{^1H\}$ NMR: 150.9 (s, C(1)), 147.9 (s, C(2)), 142.6, 141.4 (both s, C(4), C(6)), 126.2 (s, C(5)).

2.2.3. Synthesis of 4-$I_3AsC_5H_4NH$ (**4**)

4-Aminopyridine (1.50 g, 15.9 mmol) was dissolved in 39 mL of water and then H_2SO_4 (15.6 g, 159 mmol) was added. The mixture was cooled to 0 °C, and a solution of sodium nitrite (1.49 g, 21.6 mmol in 5 mL of water) was added in one portion. After 40 s, the suspension was poured into a stirred solution of sodium arsenite (2.70 g, 20.8 mmol) and Na_2CO_3 (3.6 g, 34.0 mmol) in 150 mL of water, while keeping the temperature at 0 °C. The mixture was stirred for 20 min at room temperature and then heated to 60 °C for 5 min. Hydrochloric acid was added dropwise until pH = 5 was reached, the mixture was cooled and filtered. The filtrate was concentrated to the half of the volume in vacuum, filtered, and acidated with hydrochloric acid until pH = 1. Then Na_2SO_3 (3.0 g, 24 mmol) and excess of NaI (5.10 g, 34.0 mmol) was added until the complete formation of a purple crystalline precipitate of 4-$I_3AsC_5H_4NH$. The product was filtered and dried in vacuum. Yield: 2.9 g (35%). Crystals of **4** suitable for XRD were obtained after recrystallization from water, with addition of some HCl and NaI to prevent hydrolysis. Single crystals of THF solvate (orange–red) were obtained by cooling of a saturated THF solution at −25 °C. *Anal.* Calc. for $C_5H_5AsI_3N$ (534.7): C, 11.2; H, 0.94; N, 2.62. Found: C, 11.2; H, 1.1; N, 2.6%. IR (KBr, cm^{-1}): 3454 (w) (ν(N–H)); 1605 (m), 1582 (m), 1472 (s) (ν(Py ring)); 753 (s), 737 (vs) (δ(C–H, aromatic)). ^1H NMR: 10.1 (br s, ^{1}H, NH), 8.88 (d, $^3J_{H,H}$ = 5 Hz, 2H, C(3)–H and C(5)–H), 8.51 (br s, $w_{1/2}$ = 17 Hz, 2H, C(2)–H and C(6)–H). $^{13}C\{^1H\}$ NMR: 173.8 (br s, C(1)), 139.6 (s, C(3), C(5)), 127.9 (s, C(2), C(6)).

2.2.4. Reactions of $EtAsI_2$ with Et_4NI and $Bu^n{}_4NI$. Synthesis of $[Et_4N][EtAsI_3]$ (**5**)

A solution of $EtAsI_2$ (0.463 g, 1.29 mmol) in 3 mL of MeCN was added to a mixture of Et_4NI (0.346 g, 1.35 mmol) or $Bu^n{}_4NI$ (0.499 g, 1.35 mmol) with 3 mL of MeCN. An instant colour change to darker orange was noticed, along with rapid dissolution of undissolved crystalline salt in the case of Et_4NI. Crystals of **5** were obtained by cooling the solution to −18 °C overnight; a sample for XRD was taken from the bulk of crystals. Yield of **5**, 0.301 g (38%). The solution with $Bu^n{}_4NI$ did not afford crystals by cooling at various temperatures down to −18 °C, even after concentration to 2 ml volume. After complete evaporation of MeCN in a vacuum, the formation of solely colourless crystals along with a yellow oil was noticed. Data for **5**: *Anal.* Calc. for $C_{10}H_{25}AsI_3N$ (614.9): C, 19.53; H, 4.10; N, 2.28. Found: C, 19.7; H, 4.0; N, 2.3%. IR (KBr, cm^{-1}): 2976 (m), 2925 (w), 2865 (w), 1483 (s), 1474 (s), 1444 (m), 1435 (m), 1412 (m), 1390 (s), 1363 (s), 1315 (w), 1184 (s), 1169 (s), 1052 (m), 1019 (m), 995 (s), 801 (m, br), 782 (s), 711 (w), 546 (w).

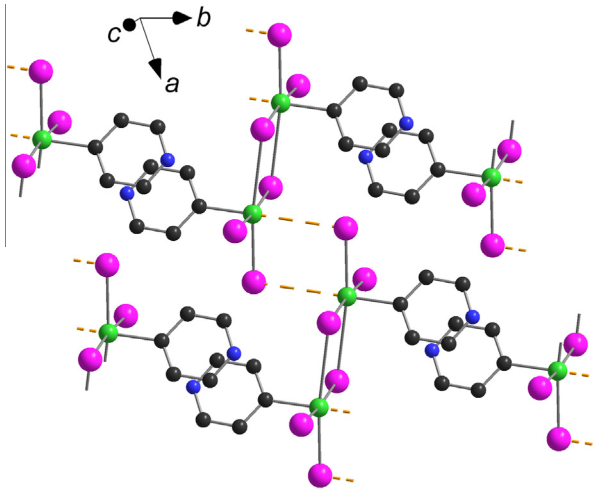

Fig. 3. Packing of the molecular dimers in the structure of **4**. The hydrogen atoms are not shown. Intermolecular As···I contacts within the sum of r_W are shown as dashed bonds.

2.3. X-ray crystallography

Single-crystal X-ray diffraction data for **3**·Me_2CO and **4** were collected using graphite monochromatized Mo Kα radiation (λ = 0.71073 Å) at 293 K (for **3**·Me_2CO) and 150 K (for **4**) on a Bruker X8 Apex CCD diffractometer equipped with a 4 K CCD area detec-

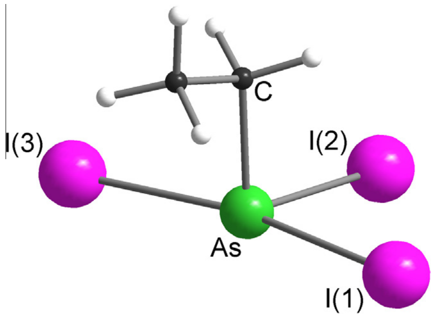

Fig. 4. The structure of the $[EtAsI_3]^-$ anion in the crystal of **5**.

Table 2
Crystal data and refinement parameters for the compounds **2**, **3**·Me_2CO, **4**, **4**·2THF and **5**.

	2	**3**·Me_2CO	**4**	**4**·2THF	**5**
Empirical formula	$C_{13}H_{14}AsI_2NO_3S$	$C_8H_{11}AsI_3NO$	$C_5H_5AsI_3N$	$C_{13}H_{21}AsI_3NO_2$	$C_{10}H_{25}AsI_3N$
Formula weight	593.03	592.80	534.72	678.93	614.93
T (K)	150.0(2)	293(2)	150(2)	150.0(2)	150.0(2)
Crystal system	monoclinic	monoclinic	triclinic	triclinic	tetragonal
Space group	$P2_1/n$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$I4_1/a$
Unit cell dimensions					
a (Å)	16.3094(4)	14.5660(4)	7.8819(2)	8.5979(11)	13.5062(17)
b (Å)	5.33700(10)	8.9547(3)	8.6376(2)	11.0251(15)	13.5062(17)
c (Å)	20.1737(6)	23.4675(6)	9.4949(2)	11.5617(16)	40.126(5)
α (°)	90	90	63.571(1)	99.350(3)	90
β (°)	98.7550(10)	107.175(1)	69.801(1)	106.615(3)	90
γ (°)	90	90	64.731(1)	105.032(4)	90
V (Å^3)	1735.52(7)	2924.47(15)	513.76(2)	980.6(2)	7319.6(16)
Z	4	8	2	2	16
$D_{calc.}$ (g cm^{-3})	2.270	2.693	3.457	2.299	2.232
Absorption coefficient (mm^{-1})	5.644	8.634	12.259	6.457	6.899
Maximum and minimum transmission	0.7463/0.5041	0.8463/0.5451	0.4405/0.1734	0.1919/0.2686	0.7479/0.4571
F(000)	1112	2128	468	628	4544
Crystal size (mm^3)	0.35 × 0.10 × 0.08	0.08 × 0.07 × 0.02	0.22 × 0.18 × ×0.08	0.25 × 0.20 × 0.03	0.21 × 0.19 × 0.06
θ (°)	1.50–31.56	2.70–26.42	2.44–30.52	1.90–32.57	2.14–31.35
Index ranges	$-18 \leqslant h \leqslant 24$, $-7 \leqslant k \leqslant 4$, $-29 \leqslant l \leqslant 27$	$-18 \leqslant h \leqslant 18$, $-11 \leqslant k \leqslant 11$, $-28 \leqslant l \leqslant 29$	$-9 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 12$, $-11 \leqslant l \leqslant 13$	$-10 \leqslant h \leqslant 13$, $-16 \leqslant k \leqslant 16$, $-17 \leqslant l \leqslant 17$	$-17 \leqslant h \leqslant 19$, $-11 \leqslant k \leqslant 19$, $-37 \leqslant l \leqslant 56$
Reflections collected	12138	11896	5355	9401	10840
Independent reflections	5737	2997	3102	6931	5546
Observed reflections ($I > 2\sigma(I)$)	4212	2451	2887	5490	3388
R_{int}	0.0257	0.0391	0.0155	0.0184	0.0395
Completeness to θ = 25.25 (%)	100	99.8	99.3	99.1	99.8
Data/restraints/ parameters	5737/0/192	2997/0/127	3102/0/92	6931/0/181	5546/0/142
Goodness-of-fit (GOF) on F^2	0.864	1.028	1.107	0.998	0.999
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0456$, $wR_2 = 0.1190$	$R_1 = 0.0291$, $wR_2 = 0.0613$	$R_1 = 0.0192$, $wR_2 = 0.0453$	$R_1 = 0.0313$, $wR_2 = 0.0622$	$R_1 = 0.0424$, $wR_2 = 0.0734$
R indices (all data)	$R_1 = 0.0668$, $wR_2 = 0.1351$	$R_1 = 0.0413$, $wR_2 = 0.0644$	$R_1 = 0.0214$, $wR_2 = 0.0459$	$R_1 = 0.0461$, $wR_2 = 0.0676$	$R_1 = 0.0901$, $wR_2 = 0.0874$
Largest difference peak and hole (e Å^{-3})	2.013/−1.131	1.378/−0.764	0.947/−0.806	1.331/−0.882	0.193/−1.016

tor. The ϕ scan technique was employed to measure intensities. The data for **2**, **4**·2THF and **5** were collected on a Bruker Apex DUO diffractometer with Mo Kα radiation using ϕ and ω scans of narrow (0.5°) frames at 150 K. Absorption corrections for **2**, **3**·Me_2CO, **4** and **4**·2THF were applied using the SADABS program [10]. The absorption correction for **5** was applied analytically based on crystal faces [10]. The crystal structures were solved by direct methods and were refined by the full-matrix least squares technique with the use of the SHELXTL package [11]. All atomic displacement parameters for non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in idealised positions and refined isotropically according to the riding model. Data collection and refinement parameters are summarized in Table 2.

3. Results and discussion

3.1. Synthesis

Compounds of the type Ar_2AsI and $ArAsI_2$ are the longest known iodide organyls of arsenic [12]. The latter have become widespread since they are readily obtained upon treatment of arylarsonic acids, $ArAsO_3H_2$, with concentrated hydroiodic acid, where the acid acts as a reductant (Eq. 1). The free iodine formed can be removed by a following treatment of the solution with SO_2, or the formation can even be prevented by adding a sulfite or pyrosulfite directly into the reaction solution (Eq. 2) [13]. Thus the synthesis of the aryldiiodides can be easily achieved in one stage.

$$ArAsO_3H_2 + 4HI \rightarrow ArAsI_2 + I_2 + 3H_2O \quad (1)$$

$$ArAsO_3 + 2I^- + SO_2 + H^+ \rightleftharpoons ArAsI_2 + HSO_4^- + H_2O \quad (2)$$

In all cases a large excess of iodide is present in the solution, so triiodoarsenate anions $[RAsI_3]^-$ could form when they are of sufficient stability. When non-basic arene substituents are taken (e.g. when Ar = phenyl with nitro, iodo, methoxy or benzoyl substituents [14]) only the neutral diiodoarsanes separate from the reaction solution. In the case when an amino group is present as the arene substituent, the corresponding hydriodides are commonly separated [1]. In both cases the composition has been verified by elemental analysis, but to our knowledge, no structural information has been reported on hydriodides to date, so there is no data as to whether the additional iodine anions are coordinated to the As atom to form triiodoarsenates.

In our attempt to synthesize *p*-aminophenyldiiodoarsane by treatment of aminophenylarsonic acid with an excess of iodide upon acidification, a yellow precipitate was obtained. According to the ^1H and ^{13}C NMR spectra, the compound most likely was hydriodide **1** (Chart 1). For further implementation, the absence

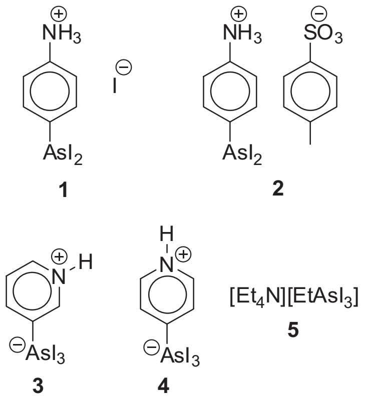

Chart 1.

of additional iodide was strongly desired, so we attempted to substitute the iodide anion for another anion, which we succeeded on adding an excess of *p*-toluenesulfonic acid to the reaction mixture. Under such conditions, a similar yellow precipitate formed, for which elemental analysis and solution NMR spectra confirm that the substitution of one iodide anion took place to give [*p*-$H_3NC_6H_4$-AsI_2][OTs], **2**. A crystal structure was obtained for the latter compound (Fig. 1).

For the synthesis of a diiodoarsane functionalized with a pyridyl group, the analogous procedure was attempted with 4-pyridylarsonic acid. In this case the compound [4-$HPyAsI_3$] (**4**) was formed as a dark red precipitate, the structure of which was confirmed by X-ray structural analysis (Fig. 2) as well as by NMR and analytical data. Interestingly, even in the presence of a highly concentrated solution of HOTs, the *p*-toluenesulfonate anion was not included in the structure; later the reaction was shown to proceed equally well with hydrochloric acid. Upon recrystallization from THF, the crystalline solvate **4**·2THF was obtained.

In the analogous synthesis of the 3-substituted pyridylarsonic acid, on the contrary, a yellow precipitate of the iodide derivative was formed which again contains the zwitterionic triiodoarsenate complex [3-$HPyAsI_3$] (**3**). The crystal structure was determined for the compound recrystallized from acetone as the solvate **3**·Me_2CO (Fig. 2). The composition of the initial yellow polycrystalline compound corresponds to neat **3**, according to the elemental analysis and NMR data.

3.2. Crystal structures

The crystal packing of the tosylate salt **2** (Fig. 1b) consists of square pillars of cations and anions, bound by a coulombic attraction and hydrogen bonding between NH_3 and SO_3 groups. Thus, the AsI_2 groups are stacked over each other aside the pillar. Notably, the distances from an As atom to the I atoms of the neighboring molecule, 4.319(2) and 4.126(2) Å are well beyond the sum of the van der Waals radii (r_W, 3.83 Å for As + I [15]), so the As atoms do not have close contacts to complete their coordination sphere. This goes in contradiction with the previously known $RAsI_2$ structures, where the coordination sphere of the As atom is effectively fulfilled either by neighboring I atoms (for $MeAsI_2$ [16] and *m*-$HOOCC_6H_4$-AsI_2 [17]) or by a π-conjugated unsaturated fragment (as in Cp^xAsI_2 [18] or *p*-$HOOCC_6H_4AsI_2$ [17]), in all the cases the contacts being smaller than the sum of corresponding r_W values(Table 1).

The structures of **3**·Me_2CO, **4** and **4**·2THF consist of similar dimeric units, $[HPyAsI_3]_2$ (Fig. 2). Both As atoms in the dimers are related by an inversion center; they possess a square-pyramidal I_4C environment and lie very close to the mean plane of the basal atoms (∼0.1 Å). In the structures of the solvates **3**·Me_2CO and **4**·2THF, the As–μ-I distances differ by 0.147 and 0.081 Å, respectively (Table 1), while in the solvent-free structure of **4** the difference is noticeably larger (0.341 Å), thus making the pyramidal environment rather unsymmetrical. Nevertheless, all the distances between As and the furthest bridging halide, As···I(3)’, are sufficiently shorter than the sum of r_W (Table 1) and lie in the same length range as those found for binary iodoarsenates(III) [19], and as such can be considered as normal coordination bonds (see Supplementary Information for a more detailed discussion). The dimeric structures and corresponding bond lengths are very close to those of the anions in the known salts $[Pr^n{}_4N]_2[As_2I_8]$ [19a] and $[Bu^n{}_4N]_2[As_2I_8]$ [19b], except for the larger deviation of the As atom from the pyramid base in the latter compounds due to the steric bulk of the apical I atom.

Comparing the structures of **3** and **4** with those of the Cl and Br congeners, one can note that the same dimers also exist in the case of Br, $[R_2As_2Br_6]^{2-}$, whilst they are absent for Cl [3]. Thus, the As–X bond strength expectedly rises in the row Cl–Br–I, as does the tendency of As(III) to increase its coordination number to 5, along with the increasing nucleophilicity of the halide atoms. The pyridine rings are coplanar in **3**·Me_2CO and **4**, but they are only parallel in **4**·2THF. For the analogous Sb-containing anions, $[R_2Sb_2X_6]^{2-}$ (R = aryl, alkyl), there are two series of structures known [20], where the R groups can be placed *cis* or *trans* with respect to the Sb_2X_6 plane. The anion $[Ph_2Sb_2I_6]^{2-}$ was shown to form both *cis* and *trans* isomers, depending only on the crystal environment [20]. In our case only the *trans* position of the Py units was found.

These slight differences in the structures of the molecular dimers can hardly explain the very distinct properties of the crystalline phase of **4**, which is visibly much less soluble in water as compared to **3**, deep-red coloured, and precipitates upon slight acidification (starting at pH = 3) as compared to the strongly acidic conditions necessary for **3**. Evidently, some stronger intermolecular interactions in **4** give a very sufficient contribution to the stability of its crystalline phase. Upon a closer look at the structure one can see two additional interactions between the dimeric units (Fig. 3). First, there are additional As···I contacts with the I atoms placed *trans* to the Py group, with a distance of 3.7620(4) Å, still slightly shorter than the sum of r_W [15]. Secondly, close contacts of the Py rings of neighboring units are evident, which are symmetrically parallel with a 3.64 Å interplane distance. Possibly the Py rings experience sufficient π–π interactions and may be attracted as dipoles, considering the positive charge at the N atom and their antiparallel orientation. In total, the structure can be seen to be composed of molecular layers spreading parallel to the [011] plane, with more evident interactions within the layer than between them. It is noteworthy that neither of these interactions is present in the solvate structures, which consist of sufficiently

Table 1
Selected bond lengths (Å) and angles (°) for the compounds obtained.

	2	**3**·Me_2CO	**4**	**4**·2THF	**5**
As–C(1)	1.957(4)	1.995(4)	2.018(3)	2.007(3)	1.965(5)
As–I(1)	2.5545(7)	2.7094(6)	2.8019(3)	2.6891(5)	2.9889(8)
As–I(2)	2.5848(17)	2.6531(6)	2.6262(3)	2.6639(4)	2.5835(7)
As–I(3)	–	3.1441(6)	2.9632(3)	3.1336(5)	2.7811(8)
As–I(3)’[a]	–	3.2909(6)	3.3039(3)	3.2147(5)	–
C(1)–As–I(1)	100.35(14)	93.74(13)	89.29(7)	92.52(9)	87.73(18)
C(1)–As–I(2)	96.29(14)	93.38(12)	95.44(8)	94.94(8)	97.54(16)
C(1)–As–I(3)	–	91.28(13)	89.84(7)	88.52(9)	92.75(18)
I(1)–As–I(2)	99.70(2)	94.33(2)	94.08(1)	92.86(1)	95.47(2)
I(2)–As–I(3)	–	89.94(1)	91.97(1)	90.09(1)	99.03(2)
I(1)–As–I(3)	–	173.21(2)	173.95(1)	176.77(1)	165.29(2)

[a] Inversion equivalent.

separated dimers and solvent molecules. This means the effect of solvent inclusion overcomes the additional coordination to the 6th position of the As atom and dipole–dipole interactions between the units, which indirectly confirms that the latter two interactions are rather weak. The easy precipitation of the corresponding phase of **4** from aqueous solution is probably facilitated by its sufficiently hydrophobic behaviour, analogously to the known diiodoorganoarsanes, $RAsI_2$.

It should be noted that the preference of the cation $[p\text{-}H_3NC_6H_4\text{-}AsI_2]^+$ to crystallize with OTs^- rather than to coordinate the I^- anion goes in contradiction with the HSAB principle, so the formation of the structure of **2** is likely determined by the aforementioned anionic and cationic groups attraction. The Py substituted arsanes, **3** and **4**, are probably not capable of building strong enough bonding with the tosylate anion; on the other hand, coordination of iodide and protonation of the N atom makes the packing of the zwitterionic molecules more stable under the same conditions.

3.3. Synthesis and structure of $EtAsI_3^-$

It was of interest to check if the triiodidoarsenates can form without the influence of zwitterion packing in the structure. We tried the method implemented earlier for chloro- and bromo- analogues [3], with the reactions of $EtAsI_2$ with Et_4NI and $Bu^n{}_4NI$ in acetonitrile. In both cases the addition of I^- led to a sufficient darkening of the solution, which indicated the formation of $[EtAsI_3]^-$. Crystals of $[Et_4N][EtAsI_3]$ (**5**) have been obtained, for which the structure was determined by means of X-ray diffraction (Fig. 4). Rather interesting, the obtained structure does not contain dimers bound by bridging iodides, which is more typical for bromides (commonly crystallized as $[R_2As_2Br_6]^{2-}$) as compared with chlorides. The structure of **5** is molecular, with the anions surrounded solely by the neighboring cations. Taking into account the lone pair on the As atom, its coordination sphere can be described as an uncompleted distorted trigonal bypyramid, with the As–I(1) and As–I(3) bonds forming an angle of 165.3° (Table 1). The As atom lies nearly in the plane of the I atoms (deviating by 0.053 Å towards the C atom). The As–I(2) bond, which does not have a *trans*-congener, is approximately 0.1 Å shorter than the terminal As–I bonds in **3** and **4**. Nearly the same As–I bond lengths are observed as for compound **2**.

In the analogous reaction with the $Bu^n{}_4N^+$ cation, a crystalline phase could not be obtained. As a result of almost full evaporation of the reaction mixture, only colourless crystals covered with a yellow oil could be seen, most likely the starting compounds separately. It is noteworthy that the structures of the binary iodoarsenates $[Bu^n{}_4N][As_2I_8]$ and $[Pr^n{}_4N][As_2I_8]$ are known [19b], where two I atoms are placed *trans* with respect to the As_2I_6 plane, making them very similar to the dimeric molecules of **3** and **4**. Nevertheless, in our attempts to make salts with $[Bu^n{}_4N]I$ no crystals were formed, despite the fact that the structure of $[Bu^n{}_4N][As_2I_8]$ has the same cation, and the anion volumes must be close to a possible dimer of $[EtAsI_3]^-$. This behaviour for both salts indicates neither a large strength of I^- bonding to the As atom in $EtAsI_2$ nor the tendency to form dimers of alkyltriiodoarsenate anions, which goes in contradiction with previous data for Br analogues as well with for our data on Py-substituted compounds.

4. Conclusions

Organotriiodoarsenates have been obtained for the first time and crystallized in the form of stable zwitterions with a protonated pyridinium moiety. Two isomeric compounds, $3\text{-}HPyAsI_3$ and $4\text{-}HPyAsI_3$, tend to form crystalline phases with notably different solubilities and appearance, while the molecular dimers in the crystal structures appear to be of very similar geometry. The reason for such a difference is, most likely, specific interactions between the molecules in the crystals, which complete the coordination number of the As atoms to 6 with neighboring I atoms, along with dipole-dipole interactions between the antiparallel Py rings. The slight differences in the Py rings orientation in the 3- and 4-substituted isomers might lead to a weakening of the overall interaction and result in the inclusion of solvent molecules into the crystal structure. This also means that the coordination of a fifth iodine atom to the central As atom is energetically only slightly favourable. Separate experiments with I^- coordination to $EtAsI_2$ showed that the coordination of one I^- anion to the As atom occurs easily, but even the formation of molecular dimers, i.e. the coordination of another additional I atom, is unfavorable in the crystalline state. The Py-substituted As species can provide further synthetic potential based on the coordination of the Py group to the metal centers, as well as additional hydrogen bonding via the N–H proton, which was shown in a recent publication to be responsible for the formation of coordination polymer and zwitterionic compounds with bis(4-pyridyl)ditelluride [21]. The implementation of such potential is now in progress in our group.

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Appendix A. Supplementary data

CCDC 935858–935862 contains the supplementary crystallographic data for **2**, **3**·Me2CO, **4**, **4**·2THF and **5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2013.08.070.

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