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# Proton-transfer compounds featuring the unusual 4-arsonoanilinium cation from the reaction of (4-aminophenyl)arsonic acid with strong organic acids

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**Abstract:** The crystal structures of the 1:1 proton-transfer compounds of (4-aminophenyl)arsonic acid (*p*-arsanilic acid) with the strong organic acids, 2,4,6-trinitrophenol (picric acid), 3,5-dinitrosalicylic acid, (3-carboxy-4-hydroxy)benzenesulfonic acid (5-sulfosalicylic acid) and toluene-4-sulfonic acid have been determined at 200 K and their hydrogen-bonding patterns examined. The compounds are, respectively, anhydrous 4-arsonoanilinium 2,4,6-trinitrophenolate (**1**), the hydrate 4-arsonoanilinium 2-carboxy-4,6-dinitrophenolate monohydrate (**2**), the hydrate 4-arsonoanilinium (3-carboxy-4-hydroxy)benzenesulfonate monohydrate (**3**) and the partial solvate 4-arsonoanilinium toluene-4-sulfonate 0.8 hydrate (**4**). The asymmetric unit of **2**, a phenolate, comprises two independent but conformationally similar cation-anion pairs and two water molecules of solvation, and in all compounds, extensive inter-species hydrogen-bonding interactions involving arsono O–H···O and anilinium N–H···O hydrogen-bonds generate three-dimensional supramolecular structures. In the cases of **1** and **2**, the acceptors include phenolate and nitro O-atom acceptors, with **3** and **4**, additionally, sulfonate O-atom acceptors, and with the hydrates **2–4**, the water molecules of solvation. A feature of the hydrogen-bonding in **3** is the presence of primary chains extending along (010) through centrosymmetric cyclic  $R^2_2(8)$  motifs together with conjoined cyclic  $R^3_4(12)$  motifs, which include the water molecule of solvation. The primary hydrogen-bonding in the substructure of **4** involves homomolecular cation–cation arsono O–H···O interactions forming columns down the crystallographic four-fold axis of the unit cell.

**Keywords:** (4-aminophenyl)arsonic acid; 4-arsonoanilinium cations; hydrogen-bonding; proton-transfer compounds; strong organic acids.

## Introduction

The arsenic compound (4-aminophenyl)arsonic acid (*p*-arsanilic acid) (PARSH<sub>2</sub>) [1] is currently known as an anthelmintic for the treatment of swine dysentery in pigs [2] and previously as the pharmaceutical Atoxyl, the sodium salt hydrate [1, 3]. The correct identity of the acid was elucidated by Ehrlich in 1907 [4, 5] while the crystal structure confirmed the presence of an anilinium-arsonate zwitterion [6]. The simple salts and complex salts of the acid have generally involved the monoanion PARSH<sup>−</sup> as an anion or a ligand and a number of these structures have been crystallographically characterized. With the ammonium salt [7] and the alkali metal complex salts (Na, K, Rb, Cs) [7, 8], the structures feature hydrogen-bonded sheet sub-structures extended peripherally into three-dimensional supramolecular structures through the aniline group.

In the alkaline earth set of compounds with PARSH<sup>−</sup> [9], with the exception of Mg, which forms a complex salt  $\{[\text{Mg}(\text{H}_2\text{O})_6]^{2+} \cdot 2[\text{PARSH}^-] \cdot 4\text{H}_2\text{O}\}$  and is essentially isotopic with the Mn<sup>2+</sup> complex salt [10]], all form formal coordination complexes (Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup>). The anilinium group also participates in hydrogen-bonding interactions similar to those found in the alkali metal structures. However, this group is not involved in coordination in any of the described alkali and alkaline earth metal structures. Although not common, other metal complexes with PARSH<sup>−</sup> are known, e.g. with coordination polymers of Zn, Cd, Pb, Ag<sup>I</sup> [11], Sn<sup>IV</sup> [12], Mo<sup>V</sup> [13], V<sup>IV</sup> [14–16] and U<sup>VI</sup> [17]. Mixed-metal polyoxometallate complex structures are more prevalent [18, 19].

However, the absence in the Crystallographic Data Base (CSD) [20] of any structures having the protonated form of the acid, the 4-arsonoanilinium cation [PARSH<sub>3</sub><sup>+</sup>], prompted the preparation and characterization of four examples [21], the hydrochloride [PARSH<sub>3</sub><sup>+</sup>·Cl<sup>−</sup>], the ‘double’ salt from the reaction with CuSO<sub>4</sub>,  $\{[\text{Cu}(\text{H}_2\text{O})_6]^{2+} \cdot [\text{PARSH}_3^+] \cdot 2(\text{SO}_4)^{2-} \cdot 2\text{H}_2\text{O}\}$ , and isotopic  $\{[\text{PARSH}_3^+]_{2n} \cdot [\text{CuCl}_4]^{2-}\}_n$  and  $\{[\text{PARSH}_3^+]_{2n} \cdot [\text{CdCl}_4]^{2-}\}_n$ . The only reported example of a structure of an organic salt with PARSH<sub>2</sub> is the (1:1) brucinium<sup>+</sup>·PARSH<sup>−</sup>·4H<sub>2</sub>O [22]. We, therefore, began a trial investigation of the proton-transfer salts of PARSH<sub>2</sub> with a series of strong organic

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acids, with significant success, giving a set of four crystalline products, allowing the single-crystal X-ray structure determinations and structural characterizations reported herein. The four examples were obtained from 2,4,6-trinitrophenol (picric acid) (PICH), 3,5-dinitrosalicylic acid (DNSAH), (3-carboxy-4-hydroxy)benzenesulfonic acid (5-sulfosalicylic acid) (5-SSAH) and toluene-4-sulfonic acid (*p*-toluenesulfonic acid: PTSAH). In all of these examples, single proton-transfer to the (4-aminophenyl)arsonic acid has occurred giving the 4-arsonoanilinium cation (PARSH<sub>3</sub><sup>+</sup>).

The compounds reported are 4-arsonoanilinium 2,4,6-trinitrophenolate (**1**), 4-arsonoanilinium 2-carboxy-4,6-dinitrophenolate monohydrate (**2**), 4-arsonoanilinium (3-carboxy-4-hydroxy)benzenesulfonate monohydrate (**3**), and the partial solvate 4-arsonoanilinium toluene-4-sulfonate 0.8 hydrate (**4**) (Scheme 1). Both compounds **1** and **2**, are phenolates, which in the case of **2** represents an incidence of ca 70% among proton-transfer compounds with DNSAH, the smaller incidence set involving carboxylic acid proton-transfer, i.e. salicylates [23, 24]. Both PICH

and DNSAH are well known as proton-transfer reagents in the generation of crystalline salts and the CSD contains a large number of structures of both. The sulfosalicylic acid 5-SSAH similarly has a significant representation in the CSD, examples being with a series of 4-*X*-substituted anilines (*X*=F, Cl, Br) [25] and with trimethoprim [26].

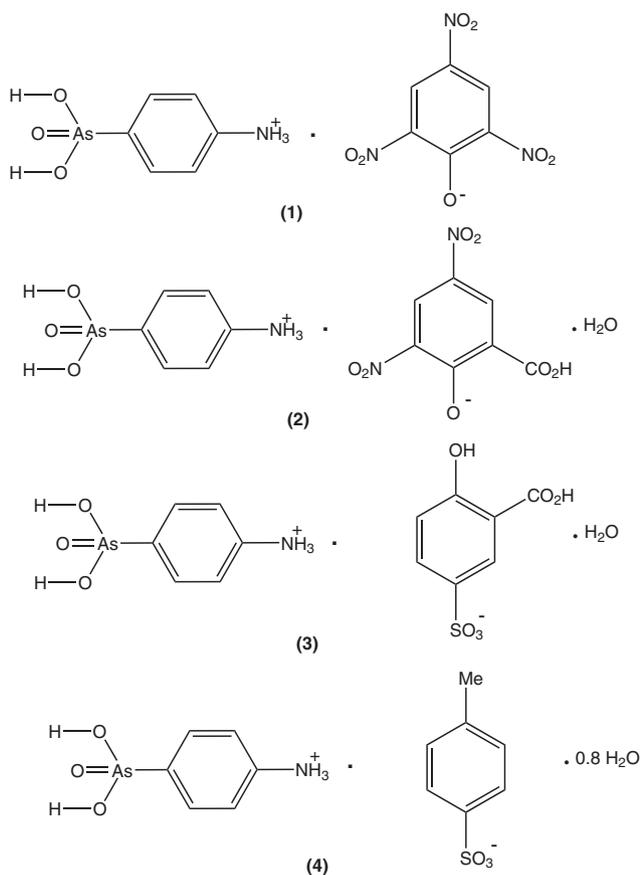
## Experimental

### Synthesis

The title compounds **1–4** were synthesized by heating together under reflux for 5 min, 1 mmol quantities of (4-aminophenyl)arsonic acid (*p*-arsanilic acid) and respectively 2,4,6-trinitrophenol (picric acid) (for **1**), 3,5-dinitrosalicylic acid (for **2**), (3-carboxy-4-hydroxy)benzenesulfonic acid (5-sulfosalicylic acid) (for **3**) and benzene-4-sulfonic acid (*p*-toluenesulfonic acid) (for **4**), in 30 mL of 1:1 (v/v) aqueous ethanol. Total room temperature evaporation of the hot-filtered solutions gave colourless crystal plates suitable for X-ray analysis in all cases.

### X-ray crystallography

X-ray diffraction data for compounds **1–4** were obtained at 200(2) K on an Oxford Diffraction Gemini-S CCD-detector diffractometer by using crystal monochromatized Mo *K*α radiation. Data collection, data reduction and absorption corrections were completed using CrysAlisPro [27]. The structures were solved by Direct Methods using SIR92 [28] and refined with anisotropic displacement parameters for all non-hydrogen atoms using SHELXL97 [29] operating within WinGX [30]. Hydrogen atoms of the arsono and anilinium groups of the cation and associative H atoms were located by difference methods but their positional and isotropic displacement parameters were allowed to ride on the parent atoms, with bond distance restraints and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$  or  $1.5U_{\text{eq}}(\text{N})$ . Other H atoms were also allowed to ride with C–H(aromatic) = 0.95 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or C–H(methyl) = 0.96 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ . With the structure of **4**, the site occupancy factor for the partial water molecule of solvation was refined [0.802(5)] and this occupancy was subsequently fixed at 0.80 with the atom satisfactorily refining anisotropically. With the structure of **2**, in which there are two independent cations, anions and water molecules in the asymmetric unit, pseudo-symmetry was indicated by checkCIF/PLATON [31] but the possible higher symmetry pseudo *C*-centred cell could not be justified. General crystallographic details are given in Table 1.



**Scheme 1:** Proton-transfer compounds **1–4**.

## Results and discussion

The structure determinations of compounds **1–4** show in all cases single acid proton-transfer to the PARSH<sub>2</sub> molecule from the organic acid (**3** and **4**) or phenol (**1** and **2**). Within

Tab. 1: Crystal data and refinement details for compounds 1–4.<sup>a</sup>

Compound	1	2	3	4
Molecular formula	C <sub>12</sub> H <sub>11</sub> AsN <sub>4</sub> O <sub>10</sub>	C <sub>13</sub> H <sub>14</sub> AsN <sub>3</sub> O <sub>11</sub>	C <sub>13</sub> H <sub>16</sub> AsNO <sub>10</sub> S	C <sub>13</sub> H <sub>17.6</sub> AsNO <sub>6.8</sub> S
<i>M<sub>r</sub></i>	446.17	463.19	453.25	403.66
Colour	Yellow	Yellow	Colourless	Colourless
Crystal system	Triclinic	Monoclinic	Triclinic	Tetragonal
Space group	<i>P</i> $\bar{1}$	<i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>I</i> $\bar{4}$
<i>a</i> (Å)	7.5856(4)	22.8085(12)	7.9884(4)	23.8841(9)
<i>b</i> (Å)	7.7014(4)	8.5383(3)	9.7276(7)	23.8841(9)
<i>c</i> (Å)	15.7645(7)	18.8194(10)	12.0029(10)	5.7331(3)
$\alpha$ (°)	87.035(4)	90	104.457(7)	90
$\beta$ (°)	87.977(4)	112.787(6)	98.951(6)	90
$\lambda$ (°)	66.503(5)	90	108.918(6)	90
<i>V</i> (Å <sup>3</sup> )	843.34(7)	3378.9(3)	825.42(10)	3270.5(3)
<i>Z</i>	2	8	2	8
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.757	1.821	1.824	1.640
$\mu$ (mm <sup>-1</sup> )	2.079	2.082	2.243	2.239
<i>F</i> (000)	448	1872	460	1648
Reflections total, $\theta_{\max}$ (°)	6457, 26.0	16,099, 26.0	5811, 26.0	6039, 26.0
Crystal size (mm)	0.10 × 0.15 × 0.20	0.20 × 0.35 × 0.40	0.20 × 0.32 × 0.35	0.15 × 0.15 × 0.42
Reflections (independent)	3316	6629	3220	3147
Reflections [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )]	3082	5156	2932	2994
<i>R</i> <sub>int</sub>	0.027	0.033	0.026	0.019
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )]	0.027	0.043	0.028	0.027
<i>wR</i> (all data)	0.064	0.108	0.071	0.065
$\eta_p$	259	553	256	229
Residuals (max/min) (eÅ <sup>-3</sup> )	0.49/−0.31	1.17/−0.58	0.41/−0.51	0.32/−0.25

<sup>a</sup>Supplementary Material: Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-1546517-1546520. Copies of available material can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

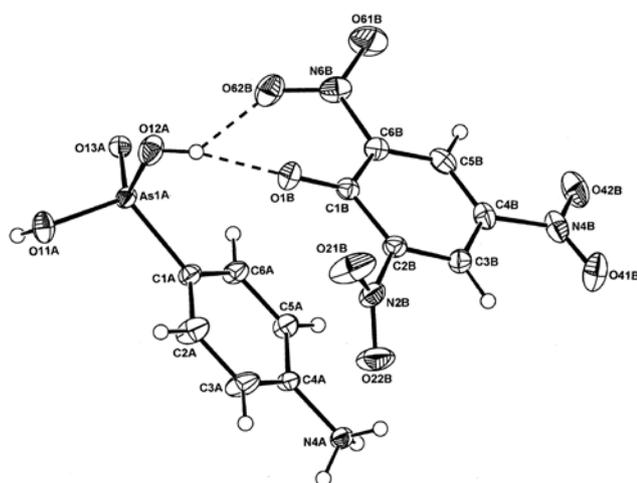


Fig. 1: Molecular conformation and atom numbering scheme for the PARSH<sub>3</sub><sup>+</sup> cation (A) and the PIC<sup>-</sup> anion (B) species in **1**. The inter-species hydrogen-bonds are shown as dashed lines. Non-hydrogen atoms are shown as 40% probability displacement ellipsoids.

the protonated arsono groups, As–O11A and As–O12A compared with the As–O13A bond distances are 1.6976(16), 1.7030(19), 1.6498(16) Å (for **1**), 1.710(3), 1.705(3), 1.643(3) Å (for **2**), 1.7073(19), 1.701(2), 1.6519(17) Å (for **3**) and 1.715(2), 1.686(2), 1.645(2) Å (for **4**). These values compare with 1.688(3), 1.701(3), 1.648(2) Å in the hydrochloride [24] and 1.737(6), 1.656(6), 1.669(3) Å in the zwitterionic parent acid [6], and together with the hydrogen-bonding associated with the As–O11–H and As–O12–H groups (described later), confirm the presence of the proton-transfer. The atom-numbering scheme for the cationic 4-arsonoanilinium species (PARSH<sub>3</sub><sup>+</sup>), (A) and the anionic species (B) (and in the case of **2**, cation/anion pairs A/B and C/D, respectively) together with any inter-species hydrogen-bonds are shown in Figures 1, 3, 5 and 7. In all four structures, peripheral hydrogen-bonding interactions giving three-dimensional hydrogen-bonded supramolecular structures and are shown in Figures 2, 4, 6 and 8.

Tab. 2: Hydrogen-bonding interactions (Å/deg.) for 1–4.

D–H...A	D–H	H...A	D...A	∠DH...A
(a) Compound 1				
O11A–H11A...O13A <sup>i</sup>	0.84(3)	1.74(3)	2.577(2)	177(3)
O12A–H12A...O1B	0.85(2)	1.87(2)	2.685(2)	162(3)
O12A–H12A...O62B	0.85(2)	2.40(3)	2.920(3)	121(3)
N4A–H41A...O13A <sup>ii</sup>	0.88(2)	1.85(2)	2.717(3)	175(2)
N4A–H42A...O1B <sup>iii</sup>	0.90(2)	1.95(2)	2.843(3)	172(2)
N4A–H43A...O62B <sup>ii</sup>	0.97(2)	2.31(3)	2.894(3)	125(2)
C2A–H2A...O11A <sup>v</sup>	0.95	2.40	3.311(3)	160
C6A–H6A...O21B <sup>v</sup>	0.95	2.43	3.312(3)	155

Symmetry codes: <sup>i</sup> –x, –y+1, –z+2; <sup>ii</sup> x+1, y–2, z; <sup>iii</sup> x, y–1, z;<sup>iv</sup> –x+1, –y+1, –z+2; <sup>v</sup> x–1, y, z.

## (b) Compound 2

O11A–H11A...O13A <sup>i</sup>	0.85(3)	1.78(3)	2.616(4)	174(5)
O12A–H12A...O1W <sup>ii</sup>	0.84(4)	1.81(4)	2.643(4)	175(5)
O11C–H11C...O13C <sup>iii</sup>	0.86(4)	1.77(3)	2.619(4)	177(8)
O12C–H12C...O2W	0.83(4)	1.85(4)	2.676(4)	121(3)
N4A–H41A...O1W	0.90(2)	2.49(4)	3.041(5)	120(3)
N4A–H41A...O11D <sup>iv</sup>	0.90(2)	2.34(3)	2.914(4)	122(3)
N4A–H41A...O31B	0.90(2)	2.35(3)	2.962(4)	126(3)
N4A–H42A...O13A <sup>v</sup>	0.88(3)	1.88(3)	2.754(4)	172(4)
N4A–H43A...O11B <sup>vi</sup>	0.87(3)	2.03(3)	2.871(5)	162(3)
N4C–H41C...O13C <sup>vii</sup>	0.87(3)	1.91(3)	2.780(4)	173(3)
N4C–H42C...O11D <sup>viii</sup>	0.88(3)	2.07(3)	2.893(5)	155(3)
N4C–H43C...O31D	0.87(2)	2.33(3)	2.972(4)	131(3)
N4C–H43C...O2W <sup>ix</sup>	0.87(2)	2.38(4)	2.963(5)	125(3)
O12B–H12B...O2B	0.96(3)	1.52(4)	2.439(4)	159(6)
O12D–H12D...O2D	0.96(3)	1.51(3)	2.447(4)	164(4)
O1W–H11W...O2B	0.86(4)	1.97(4)	2.794(4)	162(4)
O1W–H12W...O12A <sup>x</sup>	0.87(4)	2.04(4)	2.897(4)	171(4)
O2W–H21W...O2D <sup>xi</sup>	0.85(4)	2.02(4)	2.816(4)	157(4)
O2W–H22W...O12C <sup>xii</sup>	0.86(4)	2.10(4)	2.959(4)	177(3)
C3A–H3A...O51D <sup>xiii</sup>	0.95	2.45	3.166(6)	132
C2C–H2C...O32D <sup>xiv</sup>	0.95	2.49	3.077(5)	120

Symmetry codes: <sup>i</sup> –x+1, –y, –z+1; <sup>ii</sup> –x+1, y–1/2, –z+1/2; <sup>iii</sup> –x, –y, –z; <sup>iv</sup> x, –y+3/2, z–1/2; <sup>v</sup> x, y+1, z; <sup>vi</sup> x, –y+3/2, z+1/2; <sup>vii</sup> –x, y+1/2, –z+1/2; <sup>viii</sup> –x, y–1/2, –z+1/2; <sup>ix</sup> –x+1, –y+2, –z+1; <sup>x</sup> x, y–1, z.

## (c) Compound 3

O11A–H11A...O11B	0.87(2)	1.76(2)	2.629(3)	173(3)
O12A–H12A...O13A <sup>i</sup>	0.86(2)	1.80(2)	2.653(3)	176(3)
N4A–H41A...O13A <sup>ii</sup>	0.87(3)	2.46(3)	2.972(3)	119(2)
N4A–H42A...O12B <sup>iii</sup>	0.87(2)	2.00(2)	2.815(3)	154(3)
N4A–H43A...O11B <sup>ii</sup>	0.88(2)	1.99(2)	2.827(3)	159(2)
O4B–H4B...O32B	0.87(3)	1.87(3)	2.612(3)	143(3)
O31B–H31B...O1W <sup>iv</sup>	0.89(3)	1.73(3)	2.615(3)	173(3)
O1W–H11W...O13A	0.86(3)	2.02(3)	2.886(3)	175(3)
O1W–H12W...O13B <sup>i</sup>	0.88(3)	1.98(3)	2.810(3)	158(3)
C3A–H3A...O4B <sup>v</sup>	0.95	2.47	3.396(2)	164
C6B–H6B...O13B <sup>v</sup>	0.95	2.49	3.381(3)	156

Symmetry codes: <sup>i</sup> –x+1, –y+2, –z+1; <sup>ii</sup> –x, –y+1, –z+1; <sup>iii</sup> x–1, y–1, z–1; <sup>iv</sup> x–1, y, z–1; <sup>v</sup> –x+2, –y+2, –z+2.

Tab. 2 (continued)

D–H...A	D–H	H...A	D...A	∠DH...A
(d) Compound 4				
O11A–H11A...O13A <sup>i</sup>	0.88(3)	1.76(3)	2.624(3)	170(3)
O12A–H12A...O13A <sup>ii</sup>	0.87(3)	1.68(3)	2.518(3)	171(3)
N4A–H41A...O12B <sup>iii</sup>	0.91(3)	1.87(3)	2.776(4)	171(3)
N4A–H42A...O1W	0.86(3)	2.20(4)	2.940(5)	144(3)
N4A–H43A...O13B	0.84(3)	2.33(3)	2.854(4)	121(3)
N4A–H43A...O11B <sup>iv</sup>	0.84(3)	2.21(3)	2.839(4)	132(3)
O1W–H11W...O13B <sup>v</sup>	0.87(5)	1.91(5)	2.729(5)	176(3)
O1W–H12W...O1W <sup>vi</sup>	0.86(5)	2.52(5)	2.958(5)	113(4)
C3A–H3A...O11B <sup>iv</sup>	0.95	2.33	3.121(4)	140
C5B–H5B...O13B <sup>v</sup>	0.95	2.44	3.381(4)	172

Symmetry codes: <sup>i</sup> y, –x+1, –z+1; <sup>ii</sup> y, –x+1, –z; <sup>iii</sup> y+1/2, –x+3/2, –z+1/2; <sup>iv</sup> y+1/2, –x+3/2, –z+3/2; <sup>v</sup> x, y, z–1; <sup>vi</sup> –x+2, –y+1, z.

## Description of the individual structures

## Compound 1

In the asymmetric unit of (1), the PARSH<sub>3</sub><sup>+</sup> cation (A) and the picrate anion PIC<sup>–</sup> (B) are linked through an asymmetric six-membered hydrogen-bonding motif giving a three-centre R<sub>2</sub><sup>2</sup>(6) association involving an arsono O12A–H-atom donor and both the phenolate O1B [2.6869(2) Å] and a nitro O62B [2.921(3) Å] acceptor (Table 2a). The cation and anion benzene ring systems are close to parallel with an inter-ring dihedral angle of 15.81(16)°. The nitro substituent groups of the picrate anion are variously rotated out of the benzene ring plane, the un-hindered group at C4B [torsion angle C3B–C4B–N4B–O42B, 175.0(2)°], less so than those at C2B [C1B–C2B–N2B–O22B, 130.9(2)°] and C6B [C5B–C6B–N6B–O62B, 155.5(2)°].

In the crystal structure of the salt (1), the cation-anion ion pairs are linked along (010) through the anilinium N–H...O hydrogen-bonds to nitro O21B<sup>iii</sup> and phenolate O2B<sup>iii</sup>-atom acceptors (Table 2a) giving ribbon structures (Figure 2). Other H-donors of the anilinium group bridge the ribbons through N4–H...O(arsono) and N4–H...N(nitro) hydrogen-bonds while the second arsono O11–H group interacting across (001) gives an overall three-dimensional supramolecular structure. Additionally, the crystal structure contains minor C–H...O interactions to arsono O11A and nitro O21B species (Table 2) together with a weak π–π interaction between inversion-related picrate (B) rings, with ring centroid separation [Cg(B)⋯Cg(B)<sup>vii</sup> = 3.6955(18) Å; symmetry code (vii) –x+1, –y+1, –z+1].

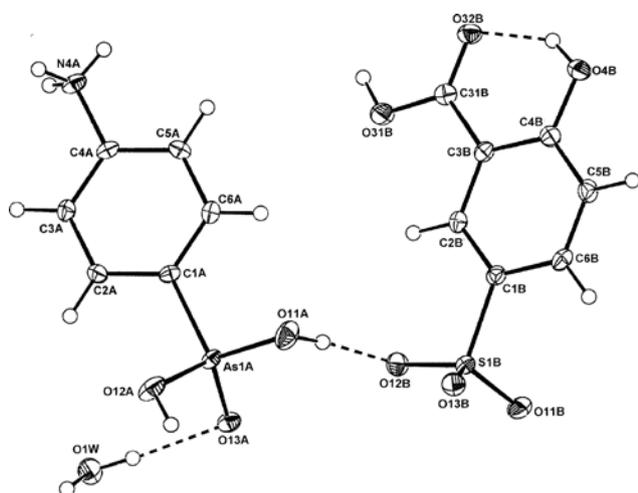


structure are two cation C–H···O interactions to anion nitro O-atom acceptors (Table 2b) as well as a weak  $\pi$ – $\pi$  interaction between DNSA (B/D) rings, with ring centroid separation [ $Cg(B)\cdots Cg(D)^{xi}=3.729(2)$  Å; symmetry code (xi)  $x, -y+5/2, z-1/2$ ].

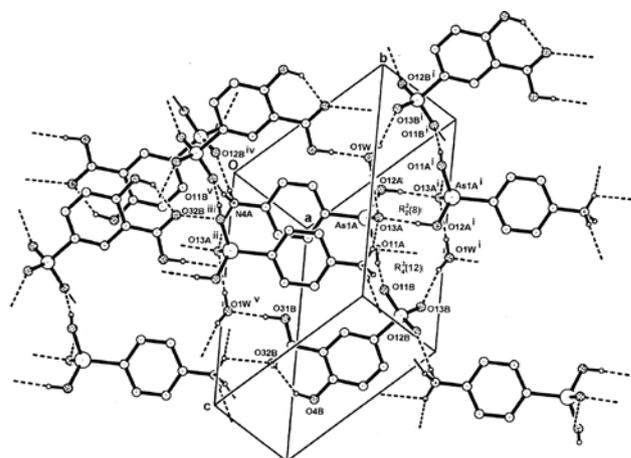
### Compound 3

The 1:1 salt of  $PARSH_2$  with 5-SSAH involves a strong primary arsono  $O11A-H\cdots O11B$  (sulfonate) hydrogen-bond (Figure 5) in which the two aromatic ring systems are close to coplanar [dihedral angle =  $16.15(11)^\circ$ ]. The ‘planar’ conformation of the 5-SSA anion is maintained by the presence of the characteristic intramolecular cyclic S6 salicylic acid  $O\cdots H-O$  (hydroxyl) hydrogen-bonding motif [32] [ $C4B-C3B-C31B-O51B$  torsion angle =  $173.6(2)^\circ$ ].

In the crystal packing of **3**, the arsonium groups of the cations participate in hydrogen-bonding extensions along the  $c$ -cell direction, which feature centrosymmetric cyclic  $R_2^2(8)$  motifs through  $O12A-H\cdots O13A^i$  interactions, together with conjoined cyclic  $R_4^3(12)$  motifs [32] which include the water molecule of solvation  $O1W$  (Figure 6) (Table 2c). The water molecule also acts as an acceptor in bridging with the carboxyl group ( $O31B-H\cdots O1W^{ii}$ ). The other extensions of the primary arsonate  $O11A-H\cdots O11B$  (sulfonate) cation-anion unit are anilinium  $N4A-H\cdots O$  (sulfonate) hydrogen-bonds to  $O11B^{iii}$  and  $O12B^{iii}$ , giving the overall three-dimensional structure. The structure also has very weak cation-anion  $\pi$ – $\pi$  ring interactions [ring



**Fig. 5:** Molecular conformation and atom numbering scheme for the  $PARSH_3^+$  cation (A), the 5-SSA<sup>-</sup> anion (B) and the water solvent molecule in **3**. The inter-species hydrogen-bonds are shown as dashed lines. Non-hydrogen atoms are shown as 40% probability displacement ellipsoids.

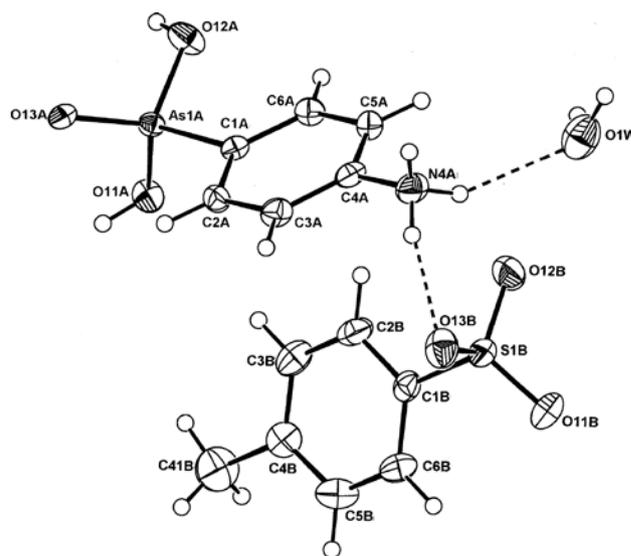


**Fig. 6:** A perspective view of the three-dimensional hydrogen-bonded network structure in the unit cell of **3** featuring arsono group extensions along (001) involving  $R_2^2(8)$  and  $R_4^3(12)$  ring motifs. Non-associative H atoms are omitted. For symmetry code (vi):  $-x+1, -y+1, -z+1$ . For other codes, see Table 2c.

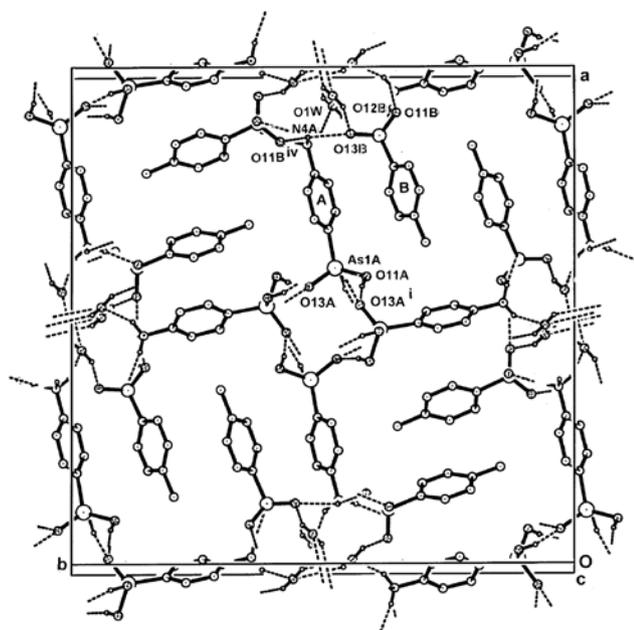
centroid separation  $Cg(A)\cdots Cg(B)^{vi}=3.8868(13)$  Å] and minor C–H···O (phenol, carboxyl) interactions (Table 2c). For symmetry code (vi):  $-x+1, -y+1, -z+1$ .

### Compound 4

In the (1:1)  $PARSH_2$  partial hydrate salt of PTSA, (**4**) the hydrogen-bonding interaction between the cation (A) and



**Fig. 7:** Molecular conformation and atom numbering scheme for the  $PARSH_3^+$  cation (A), the PTSA<sup>-</sup> anion (B) and the partial water solvent molecule in **4**. The inter-species hydrogen-bonds are shown as dashed lines. Non-hydrogen atoms are shown as 40% probability displacement ellipsoids.



**Fig. 8:** The three-dimensional hydrogen-bonded network structure of **4**, viewed down the four-fold (*c*) axial direction of the unit cell, showing the extension in the network structure. Non-associative H atoms are omitted.

anion (B) (N4A–H $\cdots$ O13B) results in a dihedral angle of 57.33(3) $^\circ$  between the benzene planes (Figure 7). The two arsono groups form strong inter-cation O11A–H $\cdots$ O13A<sup>i</sup> and O12A–H $\cdots$ O13A<sup>ii</sup> hydrogen-bonding associations (Table 2d), generating a primary column substructure which extends down the crystallographic four-fold rotation axis of the unit cell (Figure 8). The anilinium group forms peripheral N–H $\cdots$ O hydrogen-bonds with sulfonate O-atom acceptors and the partial water molecule, extending the structure across (010) and (0 $\bar{1}$ 0). No  $\pi$ – $\pi$  ring interactions are present in the three-dimensional structure.

## Conclusion

The structures described here provide the first reported examples of structures of 4-arsonoanilinium salts with strong organic acids. These structures complement those of the set of four previously reported salts of the same cation with inorganic acid anions.

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