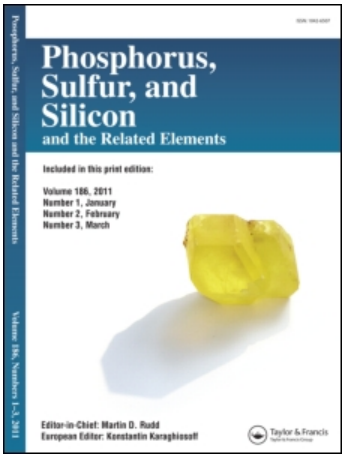

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STRUCTURE OF 4-HYDROXYPHENYLARSONIC ACID AND 4-METHOXY-3-NITROPHENYLARSONIC ACID

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4-Hydroxyphenylarsonic acid **1** crystallizes in the monoclinic space group $P2_1/c$. Four molecules are localized in a unit cell of dimensions a = 5.739(1); b = 7.226(2); c = 17.856 (2) Å; β = 90.74(2)°. The arsenic atom is tetrahedrally connected to one carbon and three oxygen atoms with the average angle around it being 109.3°. There is an extensive hydrogen bond system, involving every phenolic and arsonic acid group.

4-Methoxy-3-nitrophenylarsonic acid **2** crystallizes orthorhombic in the space group Pbca with eight molecules in a unit cell of dimensions a = 6.883 (3); b = 14.659 (7); c = 18.67 (1) Å. The arsenic atom is also tetrahedrally connected to one carbon and three oxygen atoms with the average angle around it being 109.2°. The molecules of **2** are linked along axis **x** through O···O hydrogen bonds between the oxygen atoms of the arsonic acid groups in endless chains.

Keywords: arsonic acids; hydrogen bonds; 4-hydroxyphenylarsonic acid; 4-methoxy-3-nitrophenylarsonic acid

INTRODUCTION

A number of derivatives of phenylarsonic acid have been structurally characterized[1]. Except for 3-amino-4-hydroxyphenylarsonic acid chloride dihydrate[2] **3** and 3-aminophenylarsonic acid[3] **4**, the molecules form endless chains by hydrogen bonds between the arsonic acid groups. The crystal structures of **1** and **2** were examined as part of a program to contribute to the structural chemistry of

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organoarsenic compounds and to obtain more detailed information about the influence of polar substituents on the crystal structure of phenylarsonic acids.

RESULTS AND DISCUSSION

The molecular structure and molecular arrangement of **1** in the crystal may be seen in Figures 1 and 2. The final positional parameters and their estimated deviations are listed in Table I, the bond lengths and angles in Table II. The As1 atom is surrounded by three oxygen atoms O1, O2, O3 and carbon C1 of the benzene ring. The average As-O distance is 1.69 Å and the As-C1 distance is 1.884(4) Å. The average angle around As1 is 109.3°. The benzene ring is planar and the average distance between adjacent carbons is 1.38 Å. The C4-O4 distance is 1.367 (5) Å and the oxygen atom is in the plane of the benzene ring. We were not able to localize a hydrogen atom at O1 but the bond length of As1-O1 of 1.710 (3) Å indicates that there must be a hydrogen atom at O1. The molecules stick together by a beautiful network of hydrogen bonds (see Figure 2). In each unit cell two arsonic acid and two phenolic groups are connected in an alternate and symmetric way. The O2-O4 distance is 2.64 Å and 2.71 Å for O3-O4. Due to this "head-to-tail" arrangement the molecules are linked in a three dimensional way through the crystal.

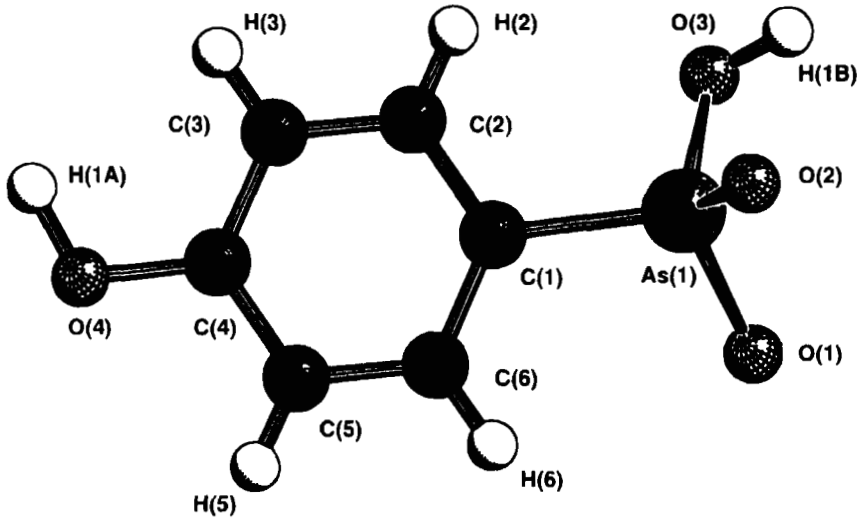

FIGURE 1 Molecular structure of **1**.

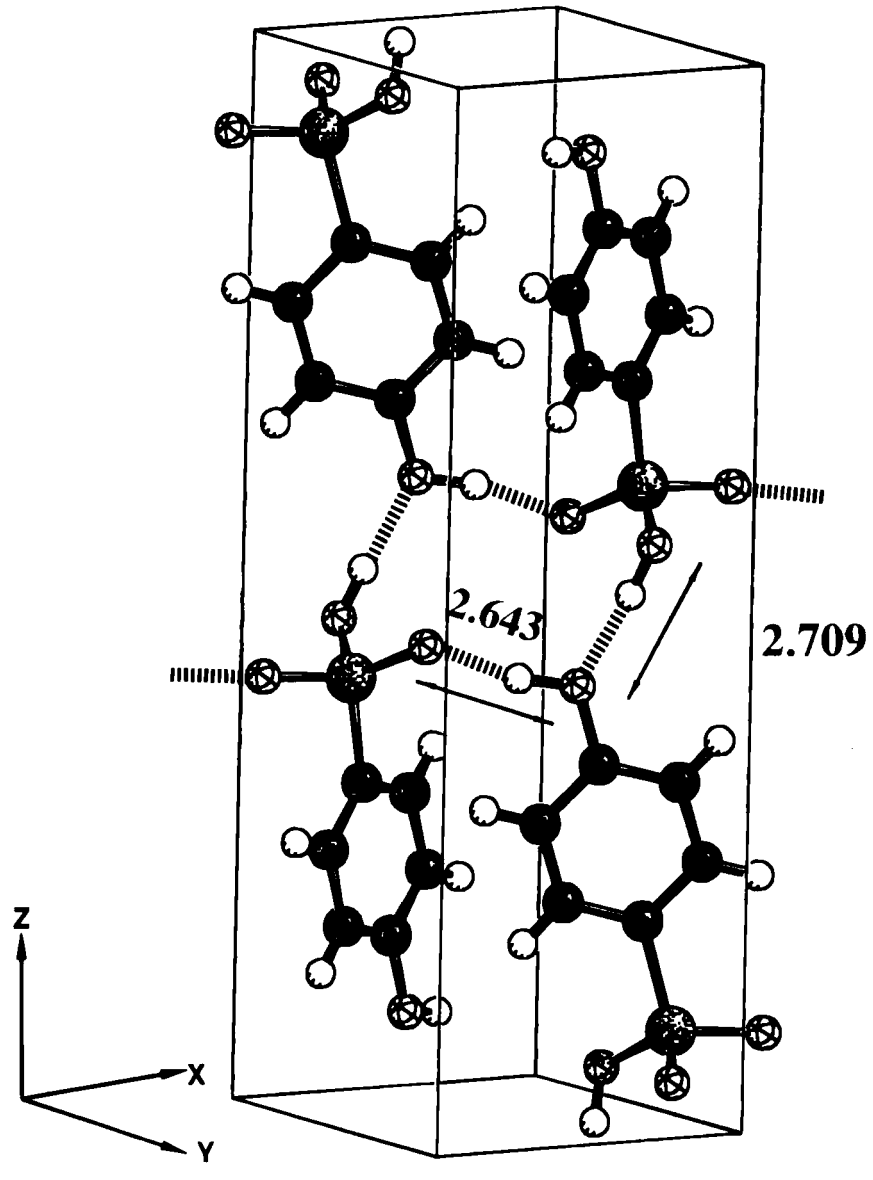

FIGURE 2 Molecular arrangement of **1** (distances in Å).

The arsonic acid **2** is shown in Figure 3. The final positional parameters and their estimated standard deviations are listed in Table III, the bond lengths and angles are presented in Table IV. The As atom is covalently linked to three O atoms and C1 of the benzene ring. The disposition of bonds around As is tetra-

TABLE I Final Positional Parameters of **1**

Atom	*X*	*Y*	*Z*	$U_{equiv.}$
As(1)	1310(1)	1557(1)	903(1)	28(1)
O(1)	−1662(5)	1485(5)	825(2)	43(1)
O(2)	2494(6)	−301(5)	539(2)	35(1)
O(3)	2230(7)	3546(5)	474(2)	53(1)
C(1)	2022(7)	1972(6)	1923(2)	24(1)
C(2)	4132(8)	2745(7)	2103(2)	28(1)
C(3)	4812(8)	2926(6)	2842(2)	28(1)
C(4)	3326(8)	2326(6)	3397(2)	26(1)
C(5)	1208(7)	1534(7)	3228(2)	28(1)
C(6)	540(7)	1342(6)	2483(2)	28(1)
O(4)	3965(5)	2491(5)	4134(1)	38(1)
H(2)	5142	3162	1713	80
H(3)	6296	3460	2970	80
H(5)	204	1119	3620	80
H(6)	−927	781	2354	80
H(1A)	5461	3179	4203	80
H(1B)	2708	3119	−3	80

hedral with the average interbond angle at As being 109.2°. As-C1 is 1.889 (8) Å and the average bond As-O is 1.68 Å. The C-C bond lengths of the benzene ring are 1.40 − 1.39 Å and the benzene ring is planar. The tetrahedral disposition of the bonds around As and the bond lengths are in good agreement with the corresponding observations in 4-hydroxy-3-nitrophenylarsonic acid[4] **5**. The arsonic acid **2** has two H atoms available for bonding. Since the H atoms have not been located, the proposed hydrogenbonding scheme has been based on intermolecular distances. Figure 4 shows the distance between O3-O2′ = 2.61 Å and O1-O3′ = 2.59 Å. These O···O hydrogen bonds link the molecules to form infinite chains along **x**.

TABLE II Bond Lengths and Angles of **1**

As(1)-O(1)	1.710(3)	O(1)-As(1)-O(2)	111.1(2)	C(3)-C(4)-C(5)	121.6(4)
As(1)-O(2)	1.643(3)	O(1)-As(1)-O(3)	107.5(2)	C(3)-C(4)-O(4)	120.1(4)
As(1)-O(3)	1.715(4)	O(2)-As(1)-O(3)	112.1(2)	C(5)-C(4)-O(4)	118.3(4)
As(1)-C(1)	1.884(4)	O(1)-As(1)-C(1)	106.7(2)	C(4)-C(5)-C(6)	119.0(4)
C(1)-C(2)	1.368(6)	O(2)-As(1)-C(1)	115.3(2)	C(1)-C(6)-C(5)	119.4(4)
C(1)-C(6)	1.398(6)	O(3)-As(1)-C(1)	103.5(2)		
C(2)-C(3)	1.378(6)	As(1)-C(1)-C(2)	118.2(3)		
C(3)-C(4)	1.386(6)	As(1)-C(1)-C(6)	120.9(3)		
C(4)-C(5)	1.374(6)	C(2)-C(1)-C(6)	120.6(3)		
C(4)-O(4)	1.367(5)	C(1)-C(2)-C(3)	120.2(4)		
C(5)-C(6)	1.386(5)	C(2)-C(3)-C(4)	119.1(4)		

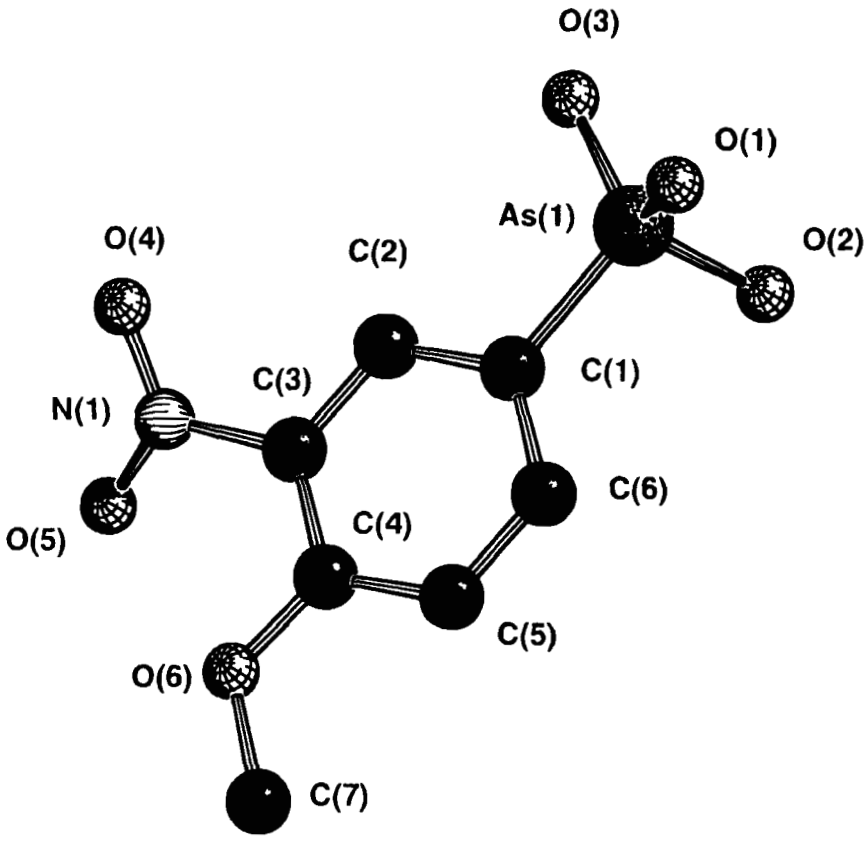

FIGURE 3 Molecular structure of **2**.

To summarize, there are two different kinds of hydrogen bond systems in crystal structures of arsonic acids. In **1**, **3**, and **4** there is three dimensional connection between the molecules. The other phenylarsonic acids like **2** or **5** are linked via hydrogen bonds between the arsonic acid groups in endless chains. Obviously the number and the nature of substituents in the benzene ring has a great influence on the crystal arrangement of the phenylarsonic acids.

EXPERIMENTAL

All X-ray crystallographic studies were carried out using a SYNTEX R 3 diffractometer and MoKα-radiation λ (Å) = 0.71073 at an ambient temperature of 23°C. All data were collected by using ω-scan mode. Empirical corrections

TABLE III Final Positional Parameters of **1**

Atom	*X*	*Y*	*Z*	$U_{equiv.}$
As(1)	310(1)	1695(1)	350(1)	34(1)
O(1)	2239(10)	1190(4)	−59(4)	46(3)
O(2)	3(9)	1174(4)	−53(4)	43(3)
O(3)	313(9)	2822(4)	263(3)	41(2)
O(4)	1807(11)	3236(5)	2863(4)	61(3)
O(5)	−173(14)	2626(5)	3616(4)	82(4)
O(6)	261(10)	820(4)	3519(3)	49(3)
N(1)	755(13)	2636(6)	3054(5)	45(3)
C(1)	293(14)	1372(6)	1329(5)	35(3)
C(2)	563(13)	2064(6)	1829(4)	32(3)
C(3)	511(13)	1866(5)	2559(5)	34(3)
C(4)	245(14)	969(6)	2806(5)	36(3)
C(5)	53(14)	269(6)	2296(5)	42(3)
C(6)	75(12)	476(6)	1568(5)	36(3)
C(7)	79(17)	−102(6)	3791(5)	58(4)

made for absorption. The structures were solved by using Patterson-Fourier techniques and were refined by SHELXTL PLUS. Some crystallographic data is given in Table V.

4-Aminophenylarsonic acid was purchased from MERCK. 4-Methoxyphenylarsonic acid was prepared according to BERTHEIM in a modified way[5].

All NMR spectra (^1H, ^{13}C) were recorded on a BRUKER WH 200 spectrometer. Chemical shifts δ are indicated in ppm; internal standard TMS; coupling constants J in Hz. Elemental analysis C, H, N: HERAEUS CH, N-rapid; As: AAS PERKIN ELMER 1100 B.

TABLE IV Bond Lengths and Angles of **2**

As(1)-O(1)	1.701(7)	O(1)-As(1)-O(2)	102.3(3)
As(1)-O(2)	1.702(7)	O(1)-As(1)-O(3)	112.9(3)
As(1)-O(3)	1.661(6)	O(2)-As(1)-O(3)	113.9(3)
As(1)-C(1)	1.889(8)	O(1)-As(1)-C(4)	109.3(4)
O(6)-C(4)	1.348(11)	O(2)-As(1)-C(4)	108.1(4)
N(1)-C(3)	1.469(12)	O(3)-As(1)-C(3)	110.1(3)
O(3)-O′(1) (−0.5 + X 0.5 − Y 0 − Z)	2.59		
O′(3)-O(2) (0.5 + X 0.5 − Y 0 − Z)	2.61		
O(1)-O″(3) (0 + X 0 + Y 0 + Z)	2.80		
O′(2)-O‴(3) (0 + X 0 + Y 0 + Z)	2.82		

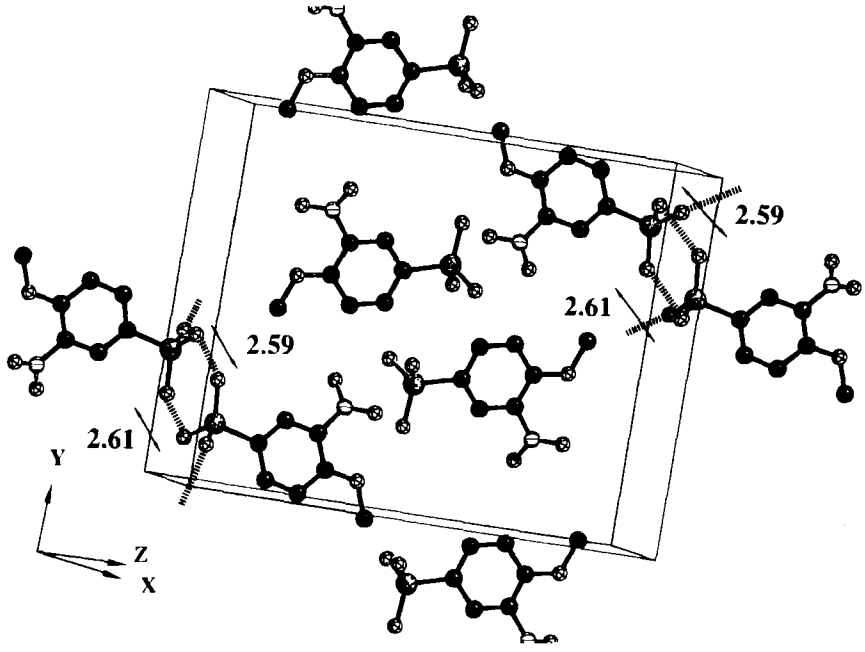

FIGURE 4 Molecular arrangement of **2** (distances in Å).

4-Hydroxyphenylarsonic acid **1** was obtained by dissolving 4-aminophenylarsonic acid (2.17 g, 0.01 mol) in H_2O (25 ml) and 0.8 ml of conc. sulfuric acid. The solution was cooled down to −5°C and diazotated by 0.68 g of $NaNO_2$ in H_2O (3.5 ml). The reaction mixture was heated to 70°C for two hours. $Ba(OH)_2$ was added, $BaSO_4$ was filtered off. The solution was reduced and some acetic acid was added. The colourless product was filtered and vacuum dried. Crystals of **1** were obtained by slow evaporation of a water/acetone solution of **1**.

Yield: 65%. NMR: ^1H (DMSO-d^6, 200 MHz): 7.02 d, 2 H, ^3J = 8.7, Ar-*H*; 7.63 d, 2 H, ^3J = 8.7, Ar-*H*; 9.02 s, 3 H, -OH/As-OH. ^{13}C (DMSO-d^6, 50 MHz): 116.372 Ar-*C*; 122.122 As-*C*; 132.068 Ar-*C*; 161.644 *C*-OH.

Synthesis of 4-methoxy-3-nitrophenylarsonic acid **2** was carried out by reaction of 1.16 g of 4-methoxyphenylarsonic acid in a solution of 10 ml of concentrated sulfuric acid and 0.21 ml of concentrated nitric acid at −5°C. After addition of ice (35g), the product was filtered, washed with cold water and vacuum dried. Crystals of the arsonic acid were obtained by slow cooling of a hot water solution to room temperature.

TABLE V Crystallographic Data of **1** and **2**

	1	*2*
formula	$C_6H_7AsO_4$	$C_7H_8AsNO_8$
M	217.03	277.06
crystal system	monoclinic	orthorhombic
space group	$P2_1/c$	Pbca
a [Å]	5.739(1)	6.883 (3)
b [Å]	7.226(2)	14.659 (7)
c [Å]	17.856(5)	18.67 (1)
β [°]	90.74(2)	
V [Å^3]	740.4	1883.8
Z	4	8
$F_{(000)}$	428	1104
D [g cm^{-3}]	1.95	1.95
μ (MoKα) [mm^{-1}]	4.55	3.60
crystal dimension [mm]	0.25 × 0.45 × 0.90	0.11 × 0.11 × 0.80
T_{min}, T_{max}	0.61–1.00	0.90–1.00
temperature [K]	298	298
2 θ_{max}	62.5	55.0
No. of reflections measured	2758, 2393 unique	2505
No. of independent reflections ($I > 2.5\sigma_I$)	1774	1150
No. of observed reflections ($I > 2\sigma_I$)	not measured	1261
No. of parameters	101	137
R_1	0.041	0.056
wR_2	0.035	0.047

Yield: 69.5%. NMR: ^{1}H (CD_3OD, 200 MHz): 4.05 s, 3 H, C*H*$_3$; 7.58, 1 H, ^{3}J = 8.6, Ar-*H*; 8.04 dd, 1 H, ^{3}J = 8.6, ^{4}J = 1.9, Ar-*H*; 8.25 d, 1 H, ^{4}J = 1.9, Ar-*H*. ^{13}C (CD_3OD, 50 MHz): 57.851 *C*H$_3$; 116.650 Ar-*C*; 121.743 As-*C*; 128.869 Ar-*C*; 137.514 Ar-*C*; 141.487 *C*-NO$_2$; 157.937 *C*-OH.

$C_7H_8AsNO_6$ (277.06) calc: C 30.35 H 3.24 As 27.04 N 5.06%
found: C 30.45 H 2.95 As 28.87 N 4.97%

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