The Structures of Methylenebis(dichloroarsane) and Methylenebisarsonic Acid − A Combined Theoretical and Experimental Study

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Dedicated to Professor Hanns Peter Boehm on the Occasion of his 80th Birthday

Abstract. Methylenebisarsonic acid (**3**) was synthesized according to a published procedure. Its molecular structure and its spectroscopic characteristics were determined by single-crystal X-ray diffraction. The first intermediate, methylenebis(dichloroarsane) (**1**), was structurally and spectroscopically characterized as well. Both molecules were investigated on the B3LYP/6-31+G(2d,p) level of theory and subsequent NBO analysis.

Keywords: Arsenic; Structure elucidation; Density functional calculations; NBO analysis; Bond theory

Introduction

The reaction of orthosilicic acid and/or its low-molecular oligomers with Si-coordinating biomolecules may be relevant for an understanding of a particularly puzzling step of silica biomineralization, namely the suppression of premature silicic-acid polycondensation in Si-enriching vesicles at increasing silicon concentration. Since, on the one hand, the carbohydrate pool may provide suitable silicon chelators, and, on the other hand, the Si-O-Si fragment of disilicic acid may act as the core of a biomolecule−silicon species in question, we have started to investigate the carbohydrate chemistry of some Si-O-Si-related species. Keeping in mind that an investigation of disilicic acid itself is complicated by both hydrolysis and polycondensation, it appears promising to study species of related spatial requirements toward a potential multidentate ligand derived from a carbohydrate. A particularly stable binuclear entity whose coordination chemistry promises a close relationship to silicon, is the As-CH$_2$-As fragment in methylenebisarsonic acid (**3**).

Methylenebisarsonic acid (**3**) was first prepared by *Popp* [1] in a three-step reaction from arsenic trioxide and acetyl chloride, but may also be prepared by a lengthy one-pot procedure from diiodomethane and arsenic trioxide according to *Sommer* and *Becke-Goehring* [2]. The identity and purity of the isolated intermediates and the final reaction product was exclusively based upon elemental analyses and melting point measurements. The nature of *Popp*'s first intermediate, methylenebis(dichloroarsane) (**1**), was sought to be proved upon the reaction product **3**. The synthetic precursor, methylenebis(arsaneoxide) (**2**), was found to be a dimer in the solid state [3].

Since the lack of knowledge regarding the molecular structures and the spectroscopic characteristics of **3** and its precursors appears to be an unacceptable starting point for the attempted investigation, this study was intended to fill the gap.

Experimental Section

General Aspects

Arsenic trioxide and acetyl chloride were obtained from Fluka (reagent grade) and used without further purification. Aluminium trichloride and thionyl chloride (reagent grade) were obtained from Merck and used as received. Dichloromethane, *n*-heptane, aqueous ammonia (w = 25 %), methanol and hydrogen-peroxide (w = 30 %) were taken from the university's central chemical supply and used as received. Dichloromethane and *n*-heptane were dried over molecular sieves (4 Å) prior to use. Detailed descriptions for all experimental procedures are given due to the partial scarce descriptions in the literature.

Physical measurements

^{1}H NMR spectra were measured with a Jeol Eclipse 400 spectrometer at 400 MHz and a Jeol Eclipse 270 spectrometer at 270 MHz and are referenced to internal tetramethylsilane. ^{13}C NMR spectra were measured with a Jeol Eclipse 400 spectrometer at 101 MHz and a Jeol Eclipse 270 spectrometer at 68 MHz and are referenced to internal tetramethylsilane. Mass spectra were recorded with a JEOL JMS-700 spectrometer. IR spectra were recorded with a Perkin Elmer Spectrum BX FT-IR spectrometer with a DuraSamplIR II ATR unit. Raman spectra were measured with a Perkin Elmer 2000 NIR-FT spectrometer. UV/VIS spectra were measured with a CARY 50 Bio UV-Visible spectrometer in quartz

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glass cuvettes. The arsenic contents were determined by ICP-AES on a Varian-VISTA Simultan spectrometer. Melting points were obtained on a Büchi-540 apparatus and are uncorrected. Determination of carbon and hydrogen contents was not possible due to the presence of arsenic in the samples resulting in severe damage to technical equipment of the laboratory of elemental analysis.

DFT calculations and NBO analyses

The geometries of **1** and **3** were optimized with Gaussian03 [4] at the B3LYP/6-31+G(2d,p) level of theory with very tight convergence criteria and an ultrafine integration grid. Frequency analyses were performed to ensure that the obtained geometries represent minima on the potential-energy hypersurface. The bonding situation was investigated by means of natural bond orbital analyses [5]. In the case of **3** one imaginary frequency at -17.6 cm^{-1} was observed when the starting geometry was directly derived from the crystal structure (C_2 symmetry). Reducing the symmetry to C_1 effected an intramolecular hydrogen bond and the disappearance of the imaginary frequency. The data used for discussion originated from DFT calculations based on the C_2-symmetric structure due to its correspondence to the crystal structure.

Crystallography

Intensity data were collected using an Oxford XCalibur 3 (**1**) or a Nonius Kappa CCD (**3**) diffractometer (Mo-Kα radiation, $\lambda = 0.71073$ Å) at 200 K. The structures were solved using the programs SIR-97 [6] (**1**) and SHELXS-97 [7] (**3**), and refined with SHELXL-97 [7]. The molecular diagrams were prepared with ORTEP III [8]. All hydrogen atoms in **1** were placed at idealized positions (C−H: 0.99 Å) and refined as riding on their parent atoms with application of one common isotropic displacement parameter refined to $U_{iso}(H) = 0.046(9)$ Å^2. The hydrogen atoms in **3** were located on a difference Fourier map and refined freely with individual U_{iso} values. An extinction correction was applied for **3**; despite the correction, one particularly weakened hkl (240) was eliminated from the data set.

Preparation of methylenebis(dichloroarsane), H$_2$C(AsCl$_2$)$_2$ (1)

A three-necked flask (1000 mL) equipped with two dropping funnels and a reflux condenser with a pressure equalizing valve was charged under nitrogen with arsenic trioxide (80.00 g, 404 mmol) and aluminium trichloride (30.00 g, 225 mmol). After mixing these compounds by stirring acetyl chloride (112.00 mL, 123.76 g, 1577 mmol) was added dropwise over 10 minutes. In a markedly exothermic reaction, copious evolution of volatile reaction compounds and heavy fizzling a yellow-green suspension was obtained which was heated to 175 °C (oil bath) for 4 hours. Upon gradual darkening a growingly higher-boiling, clear liquid was obtained. After cooling to room temperature thionyl chloride (80.00 mL, 121.60 g, 1022 mmol) was added dropwise to the reaction mixture over the course of 30 minutes and further evolution of gaseous products was observed. After completion of addition, the reaction batch was stored at room temperature over night. The dark liquid was then transferred to a round-bottomed flask (250 mL) and all volatile compounds were distilled off under a slight steady stream of nitrogen at ambient pressure until the temperature of the oil bath reaches 170 °C. After re-cooling to room temperature the

black, highly viscous remainder was fractionated under reduced pressure over a Vigreux column. Following a small forerun, the desired product was obtained as a colourless, quickly solidifying liquid ($p = 2.1\times10^{-1}$ mbar, $T = 125$ °C at the top of distillation head). The pale yellow-grey wax-like solid obtained was recrystallized from a boiling mixture of *n*-heptane (75 mL) and dichloromethane (20 mL). Big, rough, pale grey crystal blocks were obtained, yield 49.85 g, 163 mmol, 40.3 %.

^{1}H NMR (CDCl$_3$, 270.2 MHz, 23 °C): $\delta = 3.62$ (s, CH$_2$). **^{13}C NMR** (CDCl$_3$, 67.9 MHz, 26 °C) $\delta = 55.1$ (CH$_2$). **ICP-AES**, found (calculated for CH$_2$As$_2$Cl$_4$): As 49.59 % (49.02 %). **MS (DEI$^+$)** (rel. intensity): 305 (28, [M]$^+$), 270 (45, [M−Cl]$^+$), 234 (6, [M−2Cl]$^+$), 145 (58, [M−CH$_2$AsCl$_2$]$^+$). **IR (neat)**: $v = 2963$ (m, CH$_2$), 2917 (m, CH$_2$), 1413 (w), 1332 (w), 1258 (s), 1191 (w), 1083 (s), 1062 (s), 1013 (s), 864 (w), 792 (s), 703 (w), 683 (m), 627 (m), 561 (w) cm^{-1}. **Raman (neat)**: $v = 2980$ (3, CH$_2$), 2918 (10, CH$_2$), 1330 (18), 630 (29), 567 (37), 374 (100, As−Cl), 343 (40), 246 (25), 227 (34), 178 (29) cm^{-1}. **UV/Vis (acetonitrile)**: $\lambda_{max} = 227.5$ nm; **UV/Vis (cyclohexane)**: $\lambda_{max} = 237.0$ nm. **Melting point**: 71.4−73.3 °C (lit.: 73 °C [1]).

Preparation of methylenebis(arsaneoxide), [H$_2$C(AsO)$_2$]$_2$ (2)

Methylenebis(dichloroarsane) (49.85 g, 163 mmol) was dissolved in methanol (200 mL) and aqueous ammonia ($w = 25$ %, 125 mL) was added cautiously in small portions over 15 minutes. In a vigorously exothermic reaction a colourless, finely dispersed solid started to precipitate immediately from the solution. The reaction mixture was stirred for another 60 minutes at room temperature and the alkalinity of the suspension was then ensured by addition of further portions of aqueous ammonia, if necessary. The solid was isolated by suction filtration, washed with water (500 mL), redispersed in methanol (200 mL) and filtered again. After drying in air for 24 hours a colour- and odourless, finely dispersed free-running powder was obtained, yield 29.25 g, 149 mmol, 91.6 %.

^{1}H NMR (DMSO-d$_6$, 399.8 MHz, 23 °C): $\delta = 2.00$ (s, CH$_2$). **^{13}C NMR** (DMSO-d$_6$, 100.5 MHz, 25 °C) $\delta = 30.4$ (CH$_2$). **ICP-AES**, found (calculated for C$_2$H$_4$As$_4$O$_4$): As 76.73 % (76.50 %). **MS (DEI$^+$)** (rel. intensity): 391 (68, [M]$^+$), 91 (100, [AsO]$^+$). **IR (neat)**: $v = 2954$ (m, CH$_2$), 2916 (m, CH$_2$), 1396 (w), 1358 (w), 1335 (m), 1186 (w), 1074 (s), 1003 (w), 771 (m), 724 (m), 695 (s), 686 (s), 608 (m) cm^{-1}. **Raman (neat)**: $v = 2949$ (4, CH$_2$), 2916 (12, CH$_2$), 2898 (14, CH$_2$), 1359 (30), 1016 (30), 783 (47), 731 (45), 617 (48), 580 (89), 541 (51), 468 (70), 348 (100), 310 (55), 232 (70), 191 (48), 177 (45) cm^{-1}. **UV/Vis (acetonitrile)**: $\lambda_{max} = 273.5$ nm; **UV/Vis (cyclohexane)**: $\lambda_{max} = 275.4$ nm. **Melting point**: 260.2−264.2 °C (decomposition) (lit.: 250−265 °C (decomposition) [1]).

Preparation of methylenebisarsonic acid, H$_2$C(AsO$_3$H$_2$)$_2$ (3)

To a mixture of water (270 mL) and hydrogen peroxide ($w = 30$ %, 30 mL) methylenebis(arsaneoxide) (20.00 g, 102 mmol) was added with heavy stirring. In the course of a markedly exothermic reaction the solid dissolved completely. The solution was then heated to 80 °C for 30 minutes and subsequently to boiling for an additional 15 minutes. To the still hot reaction batch activated charcoal (approximately 2 g) was added in one portion (caution: heavy foaming occurred!) and refluxing was continued for another 45 minutes. The colourless solution was filtered while still hot and the reaction mixture was concentrated to about one fifth of its volume. Upon cooling to room temperature and free evaporation of the solvent large, colourless plate-like crystals with a sour odor were obtained, yield 26.46 g, 100 mmol, 98.2 %.

^{1}H NMR (DMSO-d$_6$, 399.8 MHz, 23 °C): $\delta = 7.85$ (s, 4 H, OH), 3.32 (s, 2 H, CH$_2$). **^{13}C NMR** (DMSO-d$_6$, 100.5 MHz, 25 °C) $\delta = 35.0$ (CH$_2$). **ICP-AES**, found (calculated for C$_2$H$_6$As$_2$O$_6$): As 57.26 % (56.78 %). **MS (DEI$^+$)**

(rel. intensity): 395 (100), 288 (65), 90 (64); no rational assignment of molecular ion masses to fractions of structure possible. **IR (neat)**: ν = 3554 (w, OH), 2996 (s, CH$_2$), 2936 (s, CH$_2$), 2713 (s), 2310 (s), 1652 (m), 1360 (m), 1329 (m), 1214 (s), 1140 (m), 1071 (w), 927 (m), 862 (m), 756 (s), 738 (m), 695 (m) cm^{-1}. **Raman (neat)**: ν = 2997 (13), 2938 (19), 1361 (11), 1064 (9), 866 (45), 792 (30), 773 (40), 705 (21), 621 (100), 384 (20), 350 (15), 328 (25), 301 (20), 265 (17), 253 (21), 208 (8), 183 (6), 139 (6) cm^{-1}. **UV/Vis (acetonitril)**: no distinct absorption maxima in the range between 195.0 nm and 1100.0 nm; **UV/Vis (cyclohexane)**: no distinct absorption maxima in the range between 195.0 nm and 1100.0 nm. **Melting point**: 157.7–164.8 °C (decomposition) (lit.: 160–168 °C (decomposition) [1]).

Crystal structure determination

1: CH$_2$As$_2$Cl$_4$, M_r = 305.67 g mol^{-1}, colourless block, 0.32 × 0.32 × 0.12 mm, monoclinic, Cc, a = 14.8328(13), b = 18.0400(16), c = 10.8090(10) Å, β = 129.124(5)°, V = 2243.8(3) Å^3, Z = 12, ρ = 2.715 g cm^{-3}, T = 200(2) K, μ(MoKα) = 10.249 mm^{-1}, analytical absorption correction, Oxford Xcalibur 3, MoKα radiation (λ = 0.71073 Å), θ range: 3.82–27.64°, 6337 refls., 4516 independent and used in refinement, 3436 with $I \geq 2\sigma(I)$, R_{int} = 0.0619, mean $\sigma(I)/I$ = 0.0605, 191 parameters, $R(F_{obs})$ = 0.0486, $R_w(F^2)$ = 0.1257, S = 1.002, Flack parameter: 0.018(18), min. and max. residual electron density: −1.202/1.080 e Å^{-3}, max. shift/error: 0.001.

3: CH$_6$As$_2$O$_6$, M_r = 263.90 g mol^{-1}, colourless block, 0.10 × 0.08 × 0.06 mm, orthorhombic, $Aba2$, a = 7.0485(2), b = 12.3934(5), c = 7.4159(3) Å, V = 647.82(4) Å^3, Z = 4, ρ = 2.706 g cm^{-3}, T = 200(2) K, μ(MoKα) = 10.281 mm^{-1}, multi-scan absorption correction, Nonius Kappa CCD, MoKα radiation (λ = 0.71073 Å), θ range: 3.29–27.46, 4885 refls., 721 independent and used in refinement, 659 with $I \geq 2\sigma(I)$, R_{int} = 0.0295, mean $\sigma(I)/I$ = 0.0268, 55 parameters, $R(F_{obs})$ = 0.0151, $R_w(F^2)$ = 0.0305, S = 1.152, Flack parameter: 0.02(16), min. and max. residual electron density: −0.378/0.430 e Å^{-3}, max. shift/error: 0.001.

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre: 656173 (**1**), 656174 (**3**). Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: file-server@ccdc.cam.ac.uk).

Results and Discussion

Methylenebis(dichloroarsane) (1)

The synthesis of methylenebisarsonic acid was conducted according to the procedure outlined by *Popp* [1] by reacting arsenic trioxide with acetyl chloride with subsequent hydrolysis and final oxidation of the respective reaction product (Scheme 1). Crystal structure analysis of the first isolated intermediate, methylenebis(dichloroarsane) (**1**), was met by several difficulties owing to the reactive nature of the compound. When taken from the mother liquor and immersed in oil the crystals quickly grew turbid and finally decomposed within several minutes thus complicating proper crystal preparation for X-ray analysis. Crushing a crystal under mother liquor and immediately using a bigger block for a diffraction study without further manipulations yielded a data set of satisfying quality.
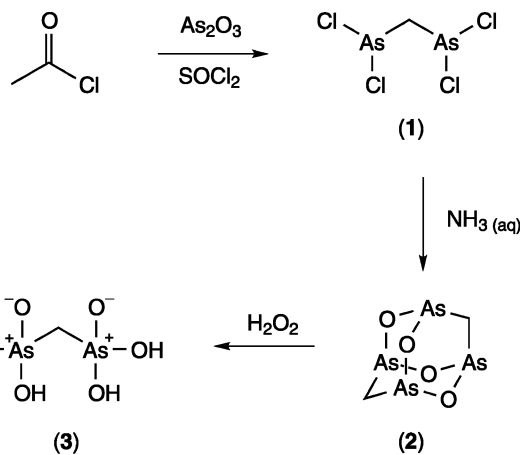
Scheme 1

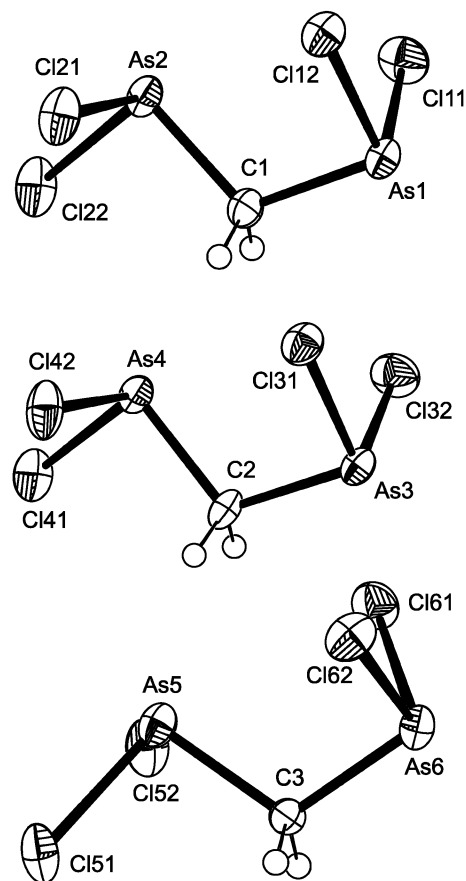**1** crystallizes in space group Cc with 3 molecules in the asymmetric unit (cf. Figure 1).

Figure 1 Comparative presentation of the three molecules apparent in the asymmetric unit of H$_2$C(AsCl$_2$)$_2$ (**1**) (50 % probability ellipsoids). For mean bond lengths and angles cf. Table 1. Selected individual bond lengths (in Å) and angles (in °): As1-C1 1.949(7), As2-C1 1.950(6), As3-C2 1.985(8), As4-C2 1.971(6), As5-C3 1.975(6), As6-C3 1.952(7), As1-C1-As2 113.3(4), As3-C2-As4 111.8(4), As5-C3-As6 111.2(3).

Table 1 Comparison of selected averaged experimental bond lengths and angles (XRD) for $H_2C(AsCl_2)_2$ (**1**) with the corresponding parameters calculated at the B3LYP/6-31+G(2d,p) level of theory (DFT) and with experimental values [9] obtained for the phosphorus analogon by electron diffraction in the gas phase (ED); E = P, As.

	XRD (As)	DFT (As)	ED (P)
d(E-Cl)/Å	2.20	2.22	2.06
d(E-C)/Å	1.97	1.97	1.85
<(Cl-E-Cl)/°	96.7	99.7	101.1
<(Cl-E-C)/°	95.9	96.5	96.5
<(E-C-E)/°	112.0	116.9	111.2

The molecules adopt exclusively zigzag conformations with the chlorine atoms oriented in different directions. A comparison between the $H_2C(AsCl_2)_2$ moieties in the asymmetric unit shows two nearly identical molecules and one differing in the orientation of the Cl-As-Cl angle. The values for the intramolecular angles in the corresponding phosphorus analogon [9] are very similar for the P-C-P and the Cl-P-C angle (Table 1). As ought to be expected the value for the Cl-E-Cl angle is smaller in **1** than in the phosphorus analogon due to the lower importance of s-p hybridization in the heavier elements.

Changing the space group from Cc to the alternative setting Ia results in a unit cell with a markedly flatter monoclinic angle (97° instead of 129°). Since the least-squares refinement proceeds in Cc in a similarly satisfactorily way, the standard setting was maintained. The correct choice of the suspect couple Cc and $Z = 12$ was corroborated by a search for higher or missed additional symmetry with PLATON [10].

Averaged bond lengths and angles for the crystals of **1** are close to the theoretically derived values for a molecule of **1** in the gaseous state (cf. Table 1). Thus **1** is considered to be a typical molecular compound without special intermolecular interactions.

The bonding situation was investigated by means of natural bond orbital analyses [5]. As expected on the basis of the observed bond angles, the NBO analysis for **1** shows dominant p type contributions to the bonding natural hybrid orbitals (NHO) at As. For the As contribution to As-Cl (As-C) bonds a p character of 94 % (89 %) was obtained. Accordingly, the lone pair NHO at As is dominated by an s contribution of 79 %. In all cases, d orbital contributions are negligible.

The natural charges at the As atoms are +1.0. The Cl atoms bear natural charges of −0.3.

Methylenebisarsonic acid (3)

DFT calculations for **3** predict a slightly distorted tetrahedral coordination geometry around both As atoms. Accordingly, the NBO analysis shows lower p character for the As-centered NHO than in **1**. The NHO directed toward the OH functions exhibits a p contribution of 78 % while

the hybrids directed toward the formally double-bonded O atom show p characters of only 68 %. Together with the p character of 73 % in the As centered NHO of the As-C bond, it is obvious that the electronic structure shows only slight deviations from an sp^3 hybridization at As. The natural charges on arsenic are +2.4 and −1.0 to −1.1 on oxygen.

A single crystal X-ray analysis in the polar space group $Aba2$ revealed molecules of crystallographic C_2 symmetry (Figure 2). Slight deviations from the calculated to the experimentally determined bond lengths and angles (Table 2) are indicative for intermolecular interactions. Accordingly, hydrogen bonds, which form isolated two-dimensional sheets in the crystal structure, are a prominent structural feature (Table 3). These hydrogen bonds hold responsibility for the reversed picture considering predicted and observed
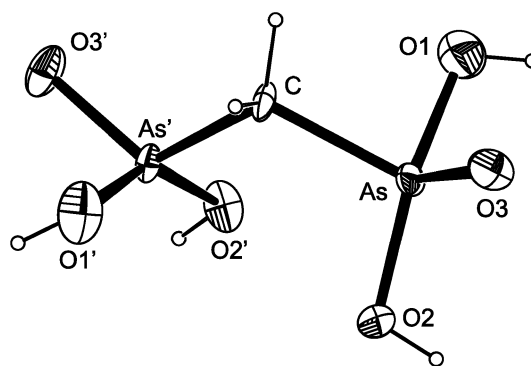

Figure 2 The structure of the C_2-symmetric $H_2C(As_2O_3H_2)_2$ molecules in crystals of **3** (70 % probability ellipsoids). Selected bond lengths (in Å) and angles (in °): As-O1 1.700(2), As-O2 1.705(2), As-O3 1.650(2), As-C 1.910(2), As-C-As′ 113.9(2). Symmetry code: $−x + 1, −y, z$.

Table 2 Comparison of selected averaged experimental bond lengths and angles (XRD) for $H_2C(As_2O_3H_2)_2$ (**3**) with the corresponding parameters calculated at the B3LYP/6-31+G(2d,p) level of theory (DFT) and with experimental values obtained for the phosphorus analogon [11]; E = P, As.

	XRD (As)	DFT (As)	XRD (P)
d(E-O)/Å	1.65	1.63	1.50
d(E-OH)/Å	1.70	1.75	1.55
d(E-C)/Å	1.91	1.92	1.79
<(HO-E-OH)/°	107.0	104.1	104.6
<(HO-E-O)/°	111.4	114.1	113.6
<(HO-E-C)/°	106.1	103.1	106.5
<(O-E-C)/°	114.5	116.8	111.5
<(E-C-E)/°	113.9	120.3	117.2

Table 3 Hydrogen bonds in the crystal structure of **3**. Symmetry codes: ^{i} $x−^1/_2, −y + ^1/_2, z$; ^{ii} $−x + 1, −y + ^1/_2, z + ^1/_2$.

D−H⋯A	d(D−H)/Å	d(H⋯A)/Å	d(D⋯A)/Å	<(D-H-A)
O1−H81⋯O3^i	0.87(4)	1.73(4)	2.592(3)	175(4)
O2−H82⋯O3^{ii}	0.85(4)	1.77(4)	2.593(3)	163(4)

As−O bond lengths on the one hand and calculated and observed As−OH bond lengths on the other hand. The situation apparent for the hydrogen bonds in **3** is very similar to the corresponding situation in the phosphorus analogon, methylenebisphosphonic acid [11, 12].

Conclusions

The X-ray analyses on **1** and **3** confirm the correct formulation of *Popp*'s reaction sequence. In additon, the structure analysis on methylenebisarsonic acid provides information about the environment and the bonding situation of the arsenic atoms in this potentially disilicic-acid-mimicking compound. With a high s character of the arsenic(III) atom's lone pair in 1, and a close-to-sp^3 hybridization of the arsenic(V) atoms in **3**, the NBO analyses are in agreement with contemporary bonding studies of p-block-element compounds.

With this knowledge at hand, potentially chelating O-atom patterns provided by a (carbohydrate) ligand with a multidentate O-atom donor set can be modelled, which may replace two or more hydroxyl functions of the dinuclear E-X-E-type molecular core.

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