

Tetrachlorophenyl- λ^5 -arsane and Tetramethoxyphenyl- λ^5 -arsane: Crystal Structures, NMR Spectra and Bonding Situation

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Abstract. Two phenyl-substituted λ^5 -arsanes were prepared from phenylarsonic acid in two-step procedures. Their molecular struc-

tures were determined by single-crystal X-ray diffraction. NBO analyses for the title compounds were conducted.

Introduction

The close structural and spectroscopic relationship between neutral bis(alkylenedioxy)-phenyl- λ^5 -arsanes and anionic bis(alkylenedioxy)-phenyl- λ^5 -silicates [1] offers the possibility to use the arsenic-containing molecules as model compounds for the corresponding silicates. Spiro- λ^5 -arsanes bearing a phenyl group as the fifth substituent are usually prepared from phenylarsonic acid and vicinal diols upon condensation reactions in aprotic media. For the synthesis of carbohydrate-supported spiroarsanes, more reactive starting compounds as well as starting materials allowing slow exchange reactions under equilibrium conditions – such as the title compounds of this work – seemed feasible.

Tetrachlorophenyl- λ^5 -arsane (**1**) was first prepared by La Coste and Michaelis upon chlorination of dichlorophenylarsane, the latter one having been synthesized from arsenic trichloride and diphenylmercury [2]. Upon oxidation with bromine and subsequent substitution reaction with sodium methoxide, dichlorophenylarsane also served as starting material for the synthesis of tetramethoxyphenyl- λ^5 -arsane (**2**) [3]. A convenient method for the synthesis of the common precursor was found in the reduction of phenylarsonic acid with sulfur dioxide in concentrated hydrochloric acid (cf. Scheme 1) [4].

Although the preparation of these synthons is apparent in the literature, basic spectroscopic and structural data are lacking, which is an unacceptable starting point for the planned investigations. The present work is intended to fill this gap.

Experimental Section

General Aspects: Phenylarsonic acid (97 %, ACROS), sodium (reagent grade, Fluka), bromine (reagent grade, Merck), iodine (reagent grade, Grüssing), hydrochloric acid (37 %, reagent grade, Biesterfeld-Graën) and sulfur dioxide (99.98 %, Messer Griesheim) were used as received. Methanol (analysis grade, Fluka) was dried with molecular sieves (3 Å) prior to use. Diethyl ether (DAB quality, Staub) was dried with sodium/benzophenone prior to use. Chlorine (99.8 %, Linde) was dried by bubbling through concentrated sulfuric acid when applied. All manipulations were done in flame-dried glassware in an atmosphere of nitrogen. A detailed description of the experimental procedure is given due to the partial scarce descriptions in the literature.

Caution: Halogenated trivalent organoarsenicals are highly toxic and corrosive and several members of this class of compounds have been used as chemical warfare agents (cf. Lewisite) [5]. All operations should be carried out exclusively by skilled and trained personnel in a well-ventilated hood operating at maximum airflow. Proper eye and skin protection (nitrile gloves) is highly recommended to avoid severe blistering or loss of eyesight. If spilt, a saturated aqueous solution of sodium hydrogen carbonate must be applied to deactivate these compounds immediately. Direct contact or incorporation must be avoided at any cost!

Physical Measurements: ¹H and ¹³C NMR spectra were measured with a Jeol Eclipse 400 spectrometer at 400 MHz and 101 MHz, respectively, 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 DuraSample 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/Vis spectrometer in quartz glass cuvettes. The content of arsenic was determined by ICP-AES on a Varian-VISTA Simultan spectrometer. The melting points were obtained on a Büchi-540 apparatus and are uncorrected. Determination of carbon, hydrogen and chlorine 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: Quantum-chemical calculations were performed with Gaussian03 [6] and NBO 5 [7] at the

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B3LYP/6-31+G(2d,p) level of theory with very tight convergence criteria and an ultra-fine integration grid. Frequency analyses were performed to ensure that the obtained structures represent minima on the potential energy hypersurfaces.

Crystallography: Intensity data for **1** and **2** were collected with a Nonius Kappa CCD diffractometer (Mo- K_{α} radiation, $\lambda = 0.71073 \text{ \AA}$) at 200 K. Multi-scan absorption corrections were performed with SADABS [8]. The structures were solved and refined using the SHELX-97 [9] program suite. Molecular diagrams were prepared with ORTEP III [10]. Intermolecular contacts were analyzed with Platon [11] and with Mercury [12].

Preparation of Tetrachlorophenyl- λ^5 -arsane, PhAsCl₄ (1). **Synthesis of Dichlorophenylarsane, PhAsCl₂ [4]:** In a Schlenk-flask (500 mL) phenylarsonic acid (35.0 g, 158 mmol) was dissolved in hydrochloric acid (37%; 400 mL) by stirring overnight. After addition of iodine (0.01 g, 0.04 mmol) to the yellow-green solution the contents of the flask were warmed to 55 °C and a brisk stream of sulfur dioxide was bubbled through the batch for 6 h. The intermediary formation of a yellow precipitate at the beginning was observed in many cases but is not mandatory for a successful synthesis. By the end of the heating period, oily droplets formed in the flask. For complete phase separation the batch was stored at room temperature overnight and the upper phase was decanted and discarded. The cherry-red remainder was distilled under reduced pressure over a Vigreux-column ($p = 0.5 \text{ mbar}$, $T = 71 \text{ °C}$ at top of distillation head). The refluxing liquid in the column was colorless, yet the liquid descending the cooler of the distillation head regained its color. A cherry-red, oily liquid without a characteristic smell was obtained, yield: 32.1 g, 144 mmol, 91.2%. ¹H NMR (CDCl₃, 400 MHz, 22 °C): $\delta = 7.85\text{--}7.80$ (m, 2 H), 7.52–7.47 (m, 3 H). ¹³C NMR (CDCl₃, 101 MHz, 24 °C): $\delta = 145.1, 132.0, 129.8, 129.1$. ICP-AES, found (calculated for C₆H₅AsCl₂): As 31.40% (33.61%); sensitivity of compound against hydrolysis hampered preparation of sample. MS (EI⁺, relative intensity): m/z (%) = 222 (55) [M]⁺, 187 (100) [M – Cl]⁺, 152 (14) [M – 2Cl]⁺. IR (neat): $\tilde{\nu} = 3073$ (m, CH), 3056 (m, CH), 1955 (w), 1887 (w), 1809 (w), 1755 (w), 1657 (w), 1576 (w), 1480 (m), 1436 (s), 1381 (w), 1332 (m), 1304 (m), 1275 (w), 1183 (w), 1160 (w), 1093 (w), 1075 (s), 1023 (w), 998 (m), 970 (w), 916 (w), 844 (w), 737 (s), 688 (s), 673 (m), 460 (s), 390 (s), 364 (s), 309 (s) cm⁻¹. Raman (neat): $\tilde{\nu} = 3143$ cm⁻¹ (4, CH), 3058 (41, CH), 1578 (19), 1481 (4), 1182 (6), 1161 (8), 1076 (12), 1024 (30), 999 (100), 673 (18), 616 (8), 388 (77), 364 (42), 310 (12), 251 (31), 221 (9), 160 (12) cm⁻¹. UV/Vis (acetonitrile): $\lambda_{\text{max}} = 235.0 \text{ nm}$. UV/Vis (cyclohexane): $\lambda_{\text{max}} = 237.5 \text{ nm}$. Refractory index: $n_D^{25} = 1.50078$. Density: $\rho = 1.65 \text{ g cm}^{-3}$.

Synthesis of Tetrachlorophenyl- λ^5 -arsane, PhAsCl₄ (1) [13]: In a Schlenk-flask (50 mL) dichlorophenylarsane (20.0 mL, 33.1 g, 148 mmol) was cooled to 0 °C by means of an ice-bath. A brisk stream of chlorine (dried with concentrated sulfuric acid) was bubbled through the liquid for 60 min. A color change from red to yellow was observed. A crystalline solid gradually formed, which finally replaced the entire liquid. Yellow crystals with a sharp anesthetic-like smell were obtained that fumed heavily when getting in contact with air, yield 40.0 g, 136 mmol, 92.0%. ¹H NMR (CDCl₃, 400 MHz, 22 °C): $\delta = 7.09\text{--}7.05$ (m, 2 H), 6.38–6.35 (m, 2 H), 6.02–6.00 (m, 1 H). ¹³C NMR (CDCl₃, 101 MHz, 24 °C): $\delta = 141.6, 132.7, 128.9, 119.1$. ICP-AES, found (calculated for C₆H₅AsCl₄): As 26.66% (25.50%); sensitivity of compound against hydrolysis hampered preparation of sample. MS (EI⁺, relative intensity): m/z (%) = 295 (0.8) [M]⁺, 222 (75) [M – 2 Cl]⁺,

187 (100) [M – 3 Cl]⁺, 152 (13) [M – 4 Cl]⁺. IR (neat): $\tilde{\nu} = 3060$ (w, CH), 2359 (w), 2323 (w), 1475 (m), 1439 (m), 1327 (w), 1305 (w), 1268 (w), 1176 (w), 1164 (w), 1093 (w), 1065 (m), 1022 (w), 995 (m), 970 (w), 815 (w), 730 (s), 671 (s), 625 (w), 616 (w), 611 (w) cm⁻¹. Raman (neat): $\tilde{\nu} = 3140$ cm⁻¹ (5, CH), 3070 (62, CH), 2987 (12, CH), 1574 (23), 1473 (5), 1438 (4), 1324 (4), 1179 (18), 1159 (8), 1064 (10), 1023 (51), 998 (91), 785 (31), 677 (29), 611 (9), 455 (9), 409 (100), 373 (20), 314 (71), 301 (82), 288 (100), 264 (28), 243 (21), 219 (57), 182 (32), 157 (18) cm⁻¹. UV/Vis (acetonitrile): $\lambda_{\text{max}} = 257.0, 263.0, 269.5, 315.0, 360.5, 488.0, 561.0, 744.0 \text{ nm}$. UV/Vis (cyclohexane): $\lambda_{\text{max}} = 228.0, 263.5, 733.5 \text{ nm}$. Melting point: 53.6–60.9 °C (lit.: 45 °C [2]).

Preparation of Tetramethoxyphenyl- λ^5 -arsane, PhAs(OCH₃)₄ (2) [3]: In a three-necked flask (250 mL) equipped with two dropping funnels and a pressure equalizing valve sodium (9.20 g, 400 mmol) was dissolved in methanol (250 mL). After complete dissolution, the contents of the flask were cooled to 0 °C by means of an ice-bath and dichlorophenylarsane (vide supra, 13.5 mL, 22.3 g, 100 mmol) was added dropwise over the course of 30 min. The formation of a colorless solid was observed. After the addition was completed, bromine (5.12 mL, 16.0 g, 99.9 mmol) was added dropwise over the course of 30 min. Every drop of bromine discolored immediately in the reaction mixture. The content of the flask was then stirred for another two days at room temperature, afterwards the solid was removed by filtration under nitrogen and the filtrate was concentrated under reduced pressure. A colorless solid separated that was washed with ethyl ether (5 × 25 mL) and the combined organic phases were stripped from the solvent under vacuum. The remaining oil was distilled under reduced pressure over a Vigreux-column ($p = 1.6 \times 10^{-2} \text{ mbar}$, $T = 96 \text{ °C}$ at top of distillation head). A slightly yellow liquid without a characteristic smell was obtained that solidified spontaneously after several days at room temperature, yield 23.6 g, 85.4 mmol, 85.4%. ¹H NMR (CDCl₃, 400 MHz, 24 °C): $\delta = 7.77\text{--}7.74$ (m, 2 H, H_{ar}), 7.45–7.39 (m, 3 H, H_{ar}), 3.57 (s, 12 H, OCH₃). ¹³C NMR (CDCl₃, 101 MHz, 25 °C): $\delta = 136.7$ (C_{ar}), 132.3 (C_{ar}), 131.4 (C_{ar}), 128.8 (C_{ar}), 54.0 (OCH₃). ICP-AES, found (calculated for C₁₀H₁₇AsO₄): As 27.96% (27.13%). MS (EI⁺, relative intensity): m/z (%) = 245 (69) [M – OCH₃]⁺, 214 (82) [M – 2 OCH₃]⁺, 183 (46) [M – 3 OCH₃]⁺, 152 (25) [M – 4 OCH₃]⁺. IR (neat): $\tilde{\nu} = 3061$ (w, CH), 2960 (m, CH), 2940 (m, CH), 2820 (m, CH), 1484 (w), 1460 (w), 1440 (m), 1313 (w), 1259 (m), 1173 (w), 1092 (m), 1012 (s), 995 (s), 948 (m), 865 (w), 788 (m), 742 (m), 689 (m), 631 (m), 563 (m) cm⁻¹. Raman (neat): $\tilde{\nu} = 3063$ (64, CH), 2942 (46, CH), 2822 (30, CH), 1584 (27), 1458 (15), 1438 (13), 1185 (12), 1163 (13), 1093 (12), 1026 (29), 1000 (100), 951 (22), 677 (8), 638 (39), 615 (22), 588 (49), 520 (12), 268 (38) cm⁻¹. UV/Vis (acetonitrile): $\lambda_{\text{max}} = 256.6, 262.5, 269.0 \text{ nm}$. UV/Vis (cyclohexane): $\lambda_{\text{max}} = 257.0, 263.0, 269.5 \text{ nm}$. Refractory index: $n_D^{25} = 1.52082$. Melting point: 29.6–30.5 °C.

Crystal Structure Determination: **1:** C₆H₅AsCl₄, $M_r = 293.82 \text{ g} \cdot \text{mol}^{-1}$, yellow block, $0.16 \times 0.12 \times 0.07 \text{ mm}$, monoclinic, $P2_1/c$, $a = 7.4256(2)$, $b = 12.4367(4)$, $c = 10.9460(3) \text{ \AA}$, $\beta = 101.6568(19)^\circ$, $V = 990.01(5) \text{ \AA}^3$, $Z = 4$, $\rho = 1.971 \text{ g} \cdot \text{cm}^{-3}$, $T = 200(2) \text{ K}$, $\mu(\text{Mo-}K_{\alpha}) = 4.446 \text{ mm}^{-1}$, ratio of minimum to maximum transmission 0.731, θ range = 3.25–27.50, 17890 refls., 2273 independent, 1826 with $I \geq 2\sigma(I)$, $R_{\text{int}} = 0.0403$, mean $\sigma(I)/I = 0.0259$, 101 parameters, $R(F_{\text{obsd}}) = 0.0354$, $R_w(F^2) = 0.0906$, $S = 1.129$, min. and max. residual electron density: $-0.794/0.605 \text{ e} \cdot \text{\AA}^{-3}$, max. shift/error = 0.001.

2: C₁₀H₁₇AsO₄, $M_r = 276.16 \text{ g} \cdot \text{mol}^{-1}$, colorless block, $0.26 \times 0.25 \times 0.19 \text{ mm}$, monoclinic, $P2_1/c$, $a = 18.1509(6)$, $b =$

8.9475(2), $c = 16.6123(5)$ Å, $\beta = 116.833(2)^\circ$, $V = 2407.43(12)$ Å³, $Z = 8$, $\rho = 1.524$ g·cm⁻³, $T = 200(2)$ K, $\mu(\text{Mo-K}\alpha) = 2.816$ mm⁻¹, ratio of minimum to maximum transmission 0.802, θ range = 3.20–25.38, 24286 refls., 4389 independent, 3484 with $I \geq 2\sigma(I)$, $R_{\text{int}} = 0.0545$, mean $\sigma(I)/I = 0.0386$, 281 parameters, $R(F_{\text{obsd.}}) = 0.0593$, $R_w(F^2) = 0.1447$, $S = 1.217$, min. and max. residual electron density: $-0.697/2.405$ e·Å⁻³, max. shift/error = 0.001.

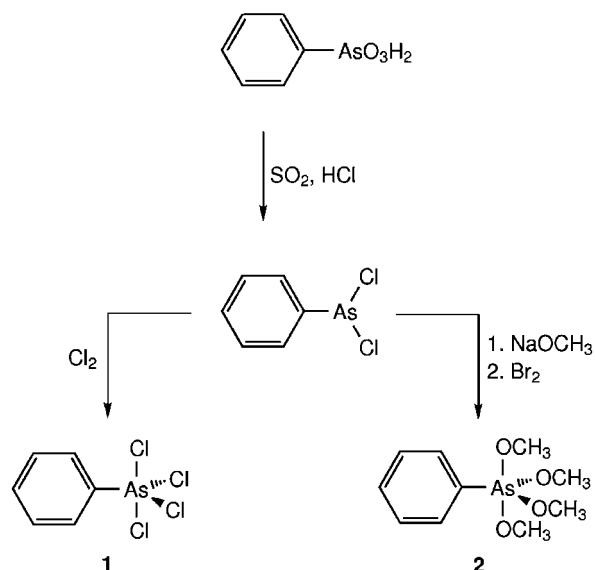
Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre: **1**: 673715, **2**: 673716. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int.code+44-1223-336-033; E-Mail for inquiry: file-server@ccdc.cam.ac.uk].

Results and Discussion

Crystal Structure Analysis

Tetrachlorophenyl- λ^5 -arsane (**1**) was prepared according to the literature [2] (cf. Scheme 1). Crystals suitable for single-crystal X-ray analysis were taken directly from the crystallized reaction product.

The asymmetric unit of **1** is shown in Figure 1. With a value of 10.9% on the Berry pseudorotation path [14], the coordination polyhedron around the central atom shows a slight deviation from a trigonal bipyramid toward a square pyramid. Accordingly, the $\text{Cl}_{\text{ax}}-\text{As}-\text{Cl}_{\text{ax}}$ angle deviates about 5° from linearity, the $\text{Cl}_{\text{eq}}-\text{As}-\text{Cl}_{\text{eq}}$ angle is about 3° larger than the 120° angle. Atomic distances between arsenic and the chlorine atoms in axial positions exceed the corresponding As–Cl distances in the plane of the coordination polyhedron by about 0.15 Å. (for averaged bond lengths and angles see Table 1). The plane of the aromatic moiety is tilted by more than 22° to the plane of the trigonal bipyramid.



Scheme 1.

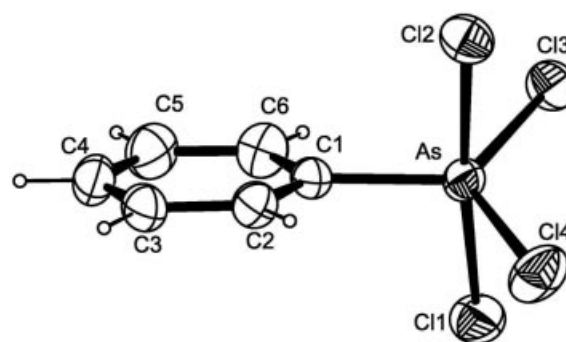


Figure 1. Structure of PhAsCl₄ (**1**) (50% probability ellipsoids). For selected averaged bond lengths and angles cf. Table 1. Selected individual bond lengths (in Å) and angles (in °): As–C1 1.921(3), As–Cl1 2.2647(9), As–Cl2 2.2897(8), As–Cl3 2.1316(8), As–Cl4 2.1277(9), Cl4–As–Cl3 123.11(4), Cl1–As–Cl2 174.92(3).

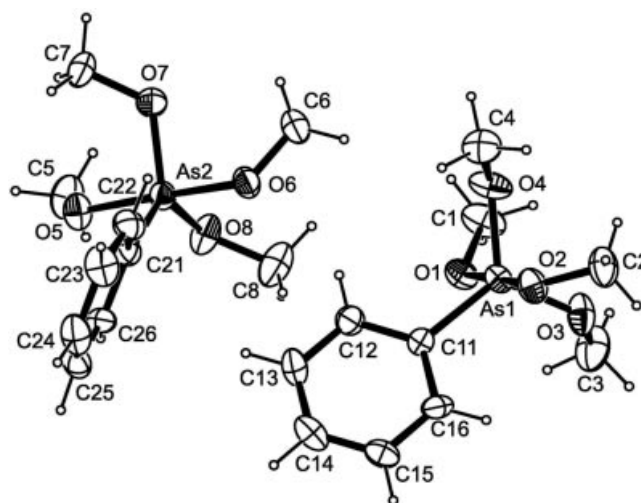


Figure 2. Structure of PhAs(OCH₃)₄ (**2**) (50% probability ellipsoids). For selected averaged bond lengths and angles cf. Table 1. Selected individual bond lengths (in Å) and angles (in °): As1–C11 1.922(6), As1–O1 1.819(4), As1–O2 1.806(4), As1–O3 1.755(4), As1–O4 1.753(4), As2–C21 1.922(6), As2–O5 1.814(4), As2–O6 1.817(4), As2–O7 1.749(4), As2–O8 1.756(4), O4–As1–O3 117.6(2), O2–As1–O1 177.60(19), O7–As2–O8 117.9(2), O5–As2–O6 177.39(19).

An X-ray analysis of **2** yielded a similar picture for the coordination environment around arsenic (Figure 2): both molecules present in the asymmetric unit show a slight deviation from a trigonal bipyramid (approximately 6% along the Berry path). The angles between the axial and the equatorial substituents around the central atoms are closer to the ideal values than in **1**. Atomic distances between arsenic and the methoxy groups in the axial positions are larger than the equatorial distances (for averaged bond lengths and angles see Table 1). In both molecules, the phenyl rings are tilted with respect to the equatorial plane. The dihedral angles are close to 33° and 30° , respectively.

An analysis of the crystal structures shows a diverging picture: whereas **1** exhibits no intermolecular contacts whose ranges fall below the sum of van der Waals radii of

Table 1. Comparison of selected averaged experimental bond lengths and angles (XRD) for PhAsCl₄ (**1**) and PhAs(OMe)₄ (**2**) with the corresponding parameters calculated at the B3LYP/6-31+G(2d,p) level of theory (DFT).

	1 (E = Cl)		2 (E = O)	
	XRD	DFT	XRD	DFT
$d(\text{As}-\text{E}_{\text{ax}}) / \text{\AA}$	2.28	2.30	1.81	1.83
$d(\text{As}-\text{E}_{\text{eq}}) / \text{\AA}$	2.13	2.19	1.75	1.78
$\langle \text{E}_{\text{ax}}-\text{As}-\text{E}_{\text{ax}} \rangle / ^\circ$	174.9	174.7	177.5	178.9
$\langle \text{E}_{\text{eq}}-\text{As}-\text{E}_{\text{eq}} \rangle / ^\circ$	123.1	123.9	117.8	121.5

the respective atoms, several C–H···O contacts involving aromatic as well as aliphatic hydrogen atoms are apparent in the structure of **2**. These hydrogen bonds result in the formation of a three-dimensional network.

NMR Properties and Hydrolytic Stability

As expected, ¹³C NMR spectra of crystals of **1** and **2** dissolved in CDCl₃ show only four resonances each in the aromatic region. ¹³C NMR spectra of **2** contain only one signal of the methoxy groups. A comparison with the chemical shift of neat methanol in the same solvent shows that upon bonding to arsenic, the carbon resonance is shifted 3.9 ppm downfield. Proton spectra of the same sample of **2** showed a single resonance for the aliphatic hydrogen atoms. The downfield shift for the protons in comparison to the parent alcohol is about 0.15 ppm.

The number of signals is in accordance with rapid ligand reorganization. Temperature-dependent proton NMR spectroscopy has already been performed earlier and showed no signs of halting this procedure [3].

1 and **2** are not stable against hydrolysis. Upon contact with air, **1** starts fuming heavily immediately and deliquesces quickly under decolorization. During the preparation of single crystals of **2** for X-ray diffraction, the compound hydrolyzed to phenylarsonic acid (according to cell constants measured) within minutes even when immersed into silicon oil. Upon addition of several drops of water to NMR samples of both compounds ¹³C NMR spectra indicated complete hydrolytic decomposition in both cases.

Quantum Chemical Calculations

Geometric Parameters

Diverging from the molecular geometry in the X-ray structure, where the torsion angle between the phenyl ring and the trigonal bipyramid's equatorial (least-squares) plane is about 23°, the theoretically derived structure of **1** showed the phenyl ring in plane with the trigonal bipyramid's equatorial chlorine atoms. Therefore a scan of the potential energy surface along the torsion angle was performed. The result is shown in Figure 3 together with selected geometrical parameters.

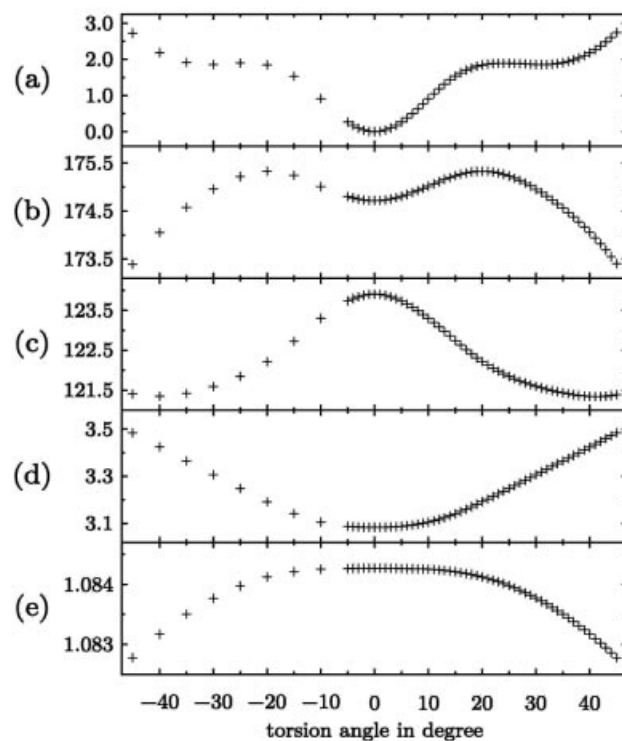


Figure 3. Calculated molecular parameters [B3LYP/6-31+G(2d,p)] of PhAsCl₄ as a function of the torsion angle between the phenyl ring and the equatorial plane of the trigonal bipyramid. (a) Total energy in kJ·mol⁻¹ relative to the global minimum at 0°, (b) Cl_{ax}-As-Cl_{ax} angle in degree, (c) Cl_{eq}-As-Cl_{eq} angle in degree, (d) H-Cl_{eq} distance in Ångstrom, (e) H-C distance in Ångstrom.

The diagram reveals that the in-plane geometry obtained by optimization represents a global minimum in the total energy along the scan coordinate. This energetic minimum is accompanied by a minimum in the Cl_{ax}-As-Cl_{ax} angle [Figure 3, (b)] and a maximum in the corresponding equatorial angle [Figure 3, (c)]. However, there is a second (local) minimum at a torsion angle of 31°, which is 1.86 kJ·mol⁻¹ higher in energy than the global minimum. The minima are separated by a barrier of 1.90 kJ·mol⁻¹ (relative to the global minimum) at a torsion angle of 24°.

Analyzing the distance between the equatorial chlorine atoms and the hydrogen atoms in the *ortho* positions of the phenyl ring [Figure 3, (d)] shows a global minimum in the H···Cl distance which, together with the observation of a maximum in the corresponding C–H bond lengths [Figure 3, (e)], leads to the assumption that the in-plane gas phase geometry is stabilized by two weak C–H···Cl hydrogen bonds (C–H···Cl angle 115.7°). The variation of C–H bond lengths in the *meta* and *para* positions is one order of magnitude smaller. Due to the very flat run of the potential energy along the torsion angle it can be assumed, that even low-energetic intermolecular interactions in the crystal structure suffice to stabilize the experimentally observed geometry.

Driving the scan coordinate to values over about 80° without introducing further geometric constraints leads to a sudden flipping of the trigonal bipyramid in such a way that the phenyl group becomes an in-plane equatorial substituent again (commonly termed pseudo-rotation). The last optimized structure before flipping occurs has a total energy of +11 kJ·mol⁻¹ relative to the global minimum.

The calculated structure of **2** shows a conformation similar to the experimental structure with the phenyl ring's plane twisted relative to the equatorial plane by 51°.

NBO Analyses

The bonding situation in the chloro derivative **1** was investigated by means of natural bond orbital analysis [7], which showed five heteropolar sigma-type single bonds at the arsenic center. The axial and equatorial As–Cl bonds show significant differences in the hybridization of the arsenic atom's contribution to these bonds. In both cases the d-orbital contribution is not negligible. Whereas the equatorial orbitals feature an s^{0.19}p^{0.77}d^{0.14} hybridization, the d-character in the axial orientation (s^{0.17}p^{0.51}d^{0.31}) is more than twice as high. Because of the highly ionic character of the As–Cl bonds, the d-AO contributions do not lead to an actual valence-shell d-orbital occupation, which was confirmed by a natural population analysis (s^{1.33}p^{2.27}d^{0.05}, natural charge on arsenic of +1.34). The natural hybrid orbital contributing to the As–C bond shows an s^{0.32}p^{0.63}d^{0.05} hybridization, which is close to the expected sp² composition.

Conclusions

The X-ray structure analysis of tetrachlorophenyl-λ⁵-arsane and tetramethoxyphenyl-λ⁵-arsane provided the metrical properties of the title molecules. The spectroscopic data obtained for both compounds in solution and in the solid state will allow for the unambiguous characterization of carbohydrate-supported spiro-λ⁵-arsanes. The comparison between the observed and calculated bonding parameters proves the applicability of the chosen theoretical level and enables the prediction and tailoring of optimum O-patterns necessary for carbohydrate chelation.

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References

- [1] R. Betz, P. Klüfers, *Inorg. Chem.* **2009**, *48*, 925–935.
- [2] W. La Coste, A. Michaelis, *Justus Liebigs Ann. Chem.* **1880**, *201*, 184–261.
- [3] A. J. Dale, P. Frøyen, *Acta Chem. Scand. B* **1975**, *29*, 362–366.
- [4] a) F. D. Yambushev, G. I. Kokorev, F. G. Khalitov, N. Kh. Tenisheva, S. V. Kut'in, *Russ. J. Gen. Chem.* **1983**, *53*, 2449–2451 (original: *Zh. Obshch. Khim.* **1983**, *53*, 2718–2722); b) E. Adams, D. Jeter, A. W. Cordes, J. W. Kolis, *Inorg. Chem.* **1990**, *29*, 1500–1503.
- [5] a) J. B. Ledgard, *The Preparatory Manual of Chemical Warfare Agents*, The Paranoid Publications Group, Columbus, **2003**, 120–131; b) R. Stöhr, *Chemische Kampfstoffe und Schutz vor chemischen Kampfstoffen*, vol. 2., Militärverlag der DDR, **1985**; c) A. T. Schäfer, *Lexikon biologischer und chemischer Kampfstoffe*, vol. 1., Publisher Dr. Köster, **2003**.
- [6] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision B.03/D.01.*, Gaussian, Inc., Wallingford CT, **2004**.
- [7] E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, F. Weinhold, *NBO 5.0*, Theoretical Chemistry Institute, University of Wisconsin, Madison, **2001**.
- [8] G. M. Sheldrick, *SADABS*, Multi-Scan Absorption Correction Program, version 2, **2001**.
- [9] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
- [10] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.
- [11] A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, The Netherlands, **2008**.
- [12] *Mercury 1.4.2 (Build 2)*, Cambridge Crystallographic Data Centre **2001–2007**.
- [13] G. I. Kokorev, F. D. Yambushev, S. V. Kut'in, *Russ. J. Gen. Chem.* **1986**, *56*, 424 (original: *Zh. Obshch. Khim.* **1986**, *56*, 482).
- [14] a) R. R. Holmes, *Prog. Inorg. Chem.* **1984**, *32*, 119–235; b) R. S. Berry, *J. Chem. Phys.* **1960**, *32*, 933–938.

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