



Crystal structures and quantum chemical calculations of dichloro[4-(dimethylamino)phenyl]arsine and tris[4-(dimethylamino)phenyl]arsine



Mutasem Z. Bani-Fwaz^{a, b, *}, Ahmed E. Fazary^{a, c}, Gerd Becker^b

^a Department of Chemistry, Faculty of Science, King Khalid University, P. O. Box 9004, Abha, 61413, Saudi Arabia

^b Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569, Stuttgart, Germany

^c Egyptian Organization for Biological Products and Vaccines [VACSERA Holding Company], 51 Wezaret El-Zeraa St., Agouza, Giza, Egypt

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ABSTRACT

Dichloro[4-(dimethylamino)phenyl]arsine (**1**) and tris[4-(dimethylamino)phenyl]arsine (**2**) were synthesized and characterized using single crystal X-ray diffraction studies, NMR spectroscopy, IR spectroscopy and elemental analyses techniques. The X-ray structure analysis of **1** ($P\bar{1}$, triclinic, $Z = 4$; $R1 = 0.0478$) revealed two crystallographically independent molecules in the asymmetric part of the unit cell. The average As–Cl bond (220.6 p.m.) is found to be slightly longer than that of arsenic(III) chloride (216.1 or 216.2 p.m.), but to be rather similar to that in the orthorhombic modification of chlorobis[2,4,6-tris(trifluoromethyl)phenyl]arsine (219.2 p.m.). Mean As–C_{aryl} (191.7 p.m.) and C_{aryl}–N bond lengths (135.9 p.m.) suggest extended electronic interactions between the dichloroarsanyl group, the π -electron system of the arene ring and the nitrogen lone pair. In both molecules the nitrogen atoms are found in a planar coordination sphere; the sums of bond angles vary only slightly between 359.1° for **1a** and 359.9° for **1b**. In contrast to these observations, sums of bond angles of 292.7° for **1a** and 293.98° for **1b** indicate a pyramidal coordination sphere at arsenic. As well, the X-ray structure analysis of **2** ($P\bar{1}$, triclinic, $Z = 2$; $R1 = 0.0347$) reveals bond lengths and angles at arsenic (As–C 194.9 p.m., C–As–C 99.3°, As–C–C 121.3°) as to be expected and obtained for similar compounds such as triphenyl arsine or triphenyl arsine derivatives. The sums of angles at two of the nitrogen atoms amount to values of 353.6° and 356.1° and deviate significantly from the value of the third (348.1°). Hence, two of three dimethylamino groups are found to be almost planar, whereas the third group shows a coordination sphere which has to be classified as an intermediate between trigonal planar and trigonal pyramidal. The molecule shows a high degree of C_3 pseudosymmetry; the sum of angles at arsenic amounts to 298.0°. The average C_{aryl}–N bond length (139.0 p.m.) suggests an interaction of the nitrogen lone pair with the π -system of the arene ring but it turns out to be much weaker than in dichloro[4-(dimethylamino)phenyl]arsine (**1**). Additionally, quantum chemical calculations were performed on several *para* substituted dichlorophenyl arsine compounds in order to ascertain optimized structural data and to shed some light onto these phenomena. Indeed, the aforementioned shortening of the N–C_{ipso} bond to 135.9 p.m. can only in part be attributed to the well-known electronic interaction between the lone pair at nitrogen and the antibonding π^* orbitals of the adjacent C_{ipso}–C_{ortho} bonds – on an average, these two distances are significantly elongated by 1.7 p.m. with respect to the standard value (140 p.m.).

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1. Introduction

It was known that, the first organyloxoarsine compound was prepared as early as 1858 by A. von Baeyer [1]. The preparation of [4-(dimethylamino)phenyl]oxoarsine and insoluble tris[4-(dimethylamino)phenyl]arsine from the dichloro[4-(dimethylamino)phenyl]arsine compound or its hydrochloride was reported and the

* Corresponding author. Department of Chemistry, Faculty of Science, King Khalid University, P. O. Box 9004, Abha, 61413, Saudi Arabia.

E-mail addresses: banifawaz@yahoo.com, mbanifawaz@kku.edu.sa (M.Z. Bani-Fwaz), afazary@gmail.com, afazary@kku.edu.sa (A.E. Fazary), becker@iac.uni-stuttgart.de (G. Becker).

isolation of crystals suitable for an X-ray structure determination was repeatedly attempted but only crystals of tris[4-(dimethylamino)phenyl]arsine could be obtained by storing a solution of the crude product of [4-(dimethylamino)phenyl]oxoarsine in chloroform at $-13\text{ }^{\circ}\text{C}$ [2–4] (Scheme S1). Many compounds of such a composition are now known to be oligomeric in nature [5,6]. Doak and coworkers [7] repeatedly failed to confirm the synthesis of [4-(dimethylamino)phenyl]oxoarsine as described by Michaelis and Rabinerson [2]. Among different possibilities to prepare arylarsonic acids [8], by far the most widely applicable method is the Bart reaction. It involves the interaction of a diazonium compound with an alkaline metal arsenite(III) in the presence of copper(I) and copper(II) salts, powdered silver or copper itself. The Bart reaction has been improved by a number of research groups; in the Scheller modification [8] primary arylamines are dissolved in an alcoholic solution of sulphuric acid and arsenic(III) chloride, diazotized at $0\text{ }^{\circ}\text{C}$ with the calculated amount of sodium nitrite in water and subsequently reacted with the arsenic(III) compound by addition of a catalytic amount of copper(I) chloride [8]. As far as a predictable synthesis of tris[4-(dimethylamino)phenyl]arsine is concerned, the compound could be prepared in 21% yield by Tomaszewski [9] reacting three equivalents of 4-dimethylaminophenyl lithium with arsenic(III) chloride at $-20\text{ }^{\circ}\text{C}$ in diethyl ether. Treatment of tris(phenylmercapto)arsine with the same lithium reagent for 6 h at ambient temperature by Wada et al. [10] afforded the product in an essentially improved yield of 73%. Our methods applied to prepare dichloro[4-(dimethylamino)phenyl]arsine as well as tris[4-(dimethylamino)phenyl]arsine are both based on the early studies of Michaelis and Rabinerson (Scheme S1) [2].

Our current research now is to widen the scope of different starting materials such these arsines. These interest comes from that the oligomeric organyloxoarsines such as methyl derivate $(\text{H}_3\text{C}-\text{AsO})_4$: might be of importance in the chemotherapy of cancer [11], and have been crystallised as a cyclic tetramer $(\text{RASO})_4$ [12] as well as stabilized as $(\text{CH}_3\text{AsO})_8$ in the coordination sphere of M^{II} ions [13]. Moreover tris[4-(dimethylamino)phenyl]arsine used as ligand in coordination chemistry instead of triphenylphosphine and -arsine in the CO-substitution reactions of cyclopentadienyl-(dicarbonyl) iron thiocarboxylate complexes [14] as well as the substitution reactions for dichloro [4-(dimethylamino) phenyl]arsine lead to different starting materials in our current research now. The present study is concerned with obtaining crystallographic data and quantum chemical calculations of dichloro [4-(dimethylamino) phenyl]arsine (**1**) and tris[4-(dimethylamino) phenyl]arsine (**2**) compounds that can provide a quantitative basis for discussing the molecular structures, as well as the differences, that arise in these studies.

2. Experimental section

2.1. General considerations

All details about chemicals, materials, solvents, instruments, techniques [15–17], and software programs used to solve crystal structures [18–20] used in this work could be found in Supplementary Information attached in a separate file with this research article.

2.2. Preparation of Dichloro[4-(dimethylamino)phenyl]arsine

It is recommended that the preparation be carried out free of solvent under an atmosphere of argon. 9.5 mL (9.1 g, 75 mmol) of *N,N*-dimethylaniline are added dropwise within 20 min with stirring at $0\text{ }^{\circ}\text{C}$ to 6.3 mL (13.6 g, 75 mmol) of arsenic(III) chloride. Gaseous hydrogen chloride is evolved and the solution gradually

takes on a yellow colour. While stirring is continued for 50–60 min, the mixture is heated in a water bath to complete the reaction. After 4 h cooling to ambient temperature the previously liquid product starts to solidify and becomes a highly viscous yellow wax. It is repeatedly placed under vacuum to remove all volatile materials and finally dissolved in 50 mL of acetonitrile. Storing the solution for several days at $-13\text{ }^{\circ}\text{C}$ affords colourless to pale yellow crystals of dichloro[4-(dimethylamino)phenyl]arsine. Yield 85% (17.0 g, 63.9 mmol); mp. $112\text{ }^{\circ}\text{C}$. *Elemental analysis*: $\text{C}_8\text{H}_{10}\text{AsCl}_2\text{N}$ (Table S1), Calc.: C 36.12%; H 3.79%; N 5.27%; Cl 26.66%. Found: C 35.82%; H 3.65%; N 5.08%; Cl 26.74%. *NMR* (solution in CD_3CN). ^1H (250.134 MHz): $\delta = 3.02$ (s, CH_3-N ; 6H); $\delta = 7.54$ (d, C_6H_4 ; $^3\text{J}_{(\text{H,H})} = 8.30$, 2H); $\delta = 7.82$ ppm (d, C_6H_4 ; $^3\text{J}_{(\text{H,H})} = 8.30$ Hz, 2H). ^{13}C $\{^1\text{H}\}$ (62.896 MHz): $\delta = 46.78$ (s, CH_3-N); $\delta = 122.0$ (s, $-\text{C}-\text{C}-\text{N}$); $\delta = 130.88$ (s, slightly broadened, *ipso-C-As*); $\delta = 131.22$ (s, $-\text{C}-\text{C}-\text{As}$); $\delta = 144.32$ ppm (s, *ipso-C-N*). *IR* (Nujol mull between CsBr disks; $\tilde{\nu}[\text{cm}^{-1}]$): 1591 (vs), 1201 (m), 1082 (vs), 1127 (m), 1065 (m), 1014 (m), 993 (m), 832 (s), 807 (s), 722 (vs), 632 (m), 604 (s), 575 (w), 548 (vs), 514 (s), 502 (w), 381 (s, br), 366 (s, br).

2.3. Preparation of Tris[4-(dimethylamino)phenyl]arsine

The reaction conditions for the preparation of tris[4-(dimethylamino)phenyl]arsine is similar to the preparation of dichloro[4-(dimethylamino)phenyl]arsine except for the temperature of the reaction mixture in which affords colourless cuboids of tris[4-(dimethylamino)phenyl]arsine at ambient temperature. The subsequent procedure may now be performed under aerobic conditions. Here again with vigorous stirring it is dissolved in 300 mL of cold distilled water. To the solution, from which insoluble material has been removed by filtration, are slowly added with stirring 85 g (2.13 mol) of anhydrous sodium hydroxide until a solid starts to precipitate. The suspension thus formed is allowed to stand overnight at $-13\text{ }^{\circ}\text{C}$, then the insoluble product is filtered off. After adhering solvent has been removed with repeated evaporation the solid is recrystallized from 15 mL of chloroform. Cooling to $-13\text{ }^{\circ}\text{C}$ affords colourless cuboids of tris[4-(dimethylamino)phenyl]arsine. Yield 46% (5.0 g, 11.5 mmol); mp. $243\text{ }^{\circ}\text{C}$. *Elemental analysis*: $\text{C}_{24}\text{H}_{30}\text{AsN}_3$ (Table S2), Calc.: C 66.20%; H 6.94%; N 9.65%. Found: C 65.99%; H 6.85%; N 9.52%. *NMR* (solution in CDCl_3): ^1H (250.134 MHz): $\delta = 2.92$ (s, CH_3-N ; 18H); $\delta = 6.67$ (d, C_6H_4 ; $^3\text{J}_{(\text{H,H})} = 8.74$ Hz, 6H); $\delta = 7.20$ ppm (d, C_6H_4 ; $^3\text{J}_{(\text{H,H})} = 8.74$ Hz, 6H). ^{13}C $\{^1\text{H}\}$ (50.323 MHz): $\delta = 40.38$ (s, CH_3-N); $\delta = 112.64$ (s, $-\text{C}-\text{C}-\text{N}$); $\delta = 126.71$ (s, slightly broadened, *ipso-C-As*); $\delta = 134.46$ (s, $-\text{C}-\text{C}-\text{As}$); $\delta = 150.35$ ppm (s, *ipso-C-N*). *IR* (Nujol mull between CsBr disks; $\tilde{\nu}[\text{cm}^{-1}]$): 3547 (w), 2664 (m), 2336 (w), 2086 (w), 1918 (w), 1890 (w), 1752 (w), 1701 (w), 1624 (w), 1591 (vs), 1546 (m), 1497 (vs), 1198 (vs), 1166 (vs), 1088 (s), 1049 (vs), 1000 (s), 942 (vs), 885 (m), 807 (vs), 755 (s), 722 (vs), 663 (w), 628 (w), 570 (w), 522 (vs).

2.4. Preparation of [4-(Dimethylamino)phenyl]oxoarsine and Dimethyl[4-(dichloroarsanyl)phenyl]ammonium chloride

Three methods of preparation of [4-(dimethylamino)phenyl]oxoarsine applied [5–7,21], and the preparation of Dimethyl[4-(dichloroarsanyl)phenyl]ammonium chloride could be found in Supplementary Information attached in a separate file with this research article.

2.5. Crystal data, measuring techniques, and general crystallographic information

Storing solutions of dichloro[4-(dimethylamino)phenyl]arsine (**1**) in acetonitrile and of tris[4-(dimethylamino)phenyl]arsine (**2**)

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