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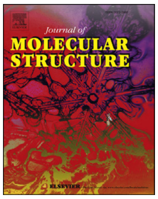

# Crystal structures and quantum chemical calculations of dichloro[4-(dimethylamino)phenyl]arsine and tris[4-(dimethylamino)phenyl]arsine

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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 $\pi$-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 $\pi$-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 $\pi^*$ 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.).

## 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

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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 °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 °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 *Tomaschewski* [9] reacting three equivalents of 4-dimethylaminophenyl lithium with arsenic(III) chloride at −20 °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 $(H_3C{-}AsO)_4$: might be of importance in the chemotherapy of cancer [11], and have been crystallised as a cyclic tetramer $(RAsO)_4$ [12] as well as stabilized as $(CH_3AsO)_8$ 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 fordichloro [4-(dimethylamino) phenyl] arsine lead to different starting materials in our current research now. The present study is concerned with obtaining crystallographic date 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 Suppelememntary 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 °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 °C affords colourless to pale yellow crystals of dichloro[4-(dimethylamino)phenyl]arsine. Yield 85% (17.0 g, 63.9 mmol); mp. 112 °C. *Elemental analysis*: $C_8H_{10}AsCl_2N$ (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, $C\mathbf{H}_3$–N; 6H); $\delta = 7.54$ (d, $C_6\mathbf{H}_4$; $^3J_{(H,H)} = 8.30$, 2H); $\delta = 7.82$ ppm (d, $C_6\mathbf{H}_4$; $^3J_{(H,H)} = 8.30$ Hz, 2H). *$^{13}C\{^1H\}$* (62.896 MHz): $\delta = 46.78$ (s, $\mathbf{C}H_3$–N); $\delta = 122.0$ (s, –**C**–C–N); $\delta = 130.88$ (s, slightly broadened, *ipso*-**C**–As); $\delta = 131.22$ (s, –**C**–C–As); $\delta = 144.32$ ppm (s, *ipso*-**C**–N). *IR (Nujol mull between CsBr disks; $\tilde{\nu}$[$cm^{-1}$])*: 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 °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 °C affords colourless cuboids of tris[4-(dimethylamino)phenyl]arsine. Yield 46% (5.0 g, 11.5 mmol); mp. 243 °C. *Elemental analysis*: $C_{24}H_{30}AsN_3$ (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, $C\mathbf{H}_3$–N; 18H); $\delta = 6.67$ (d, $C_6\mathbf{H}_4$; $^3J_{(H,H)} = 8.74$ Hz, 6H); $\delta = 7.20$ ppm (d, $C_6\mathbf{H}_4$; $^3J_{(H,H)} = 8.74$ Hz, 6H). *$^{13}C\{^1H\}$* (50.323 MHz): $\delta = 40.38$ (s, $\mathbf{C}H_3$–N); $\delta = 112.64$ (s, –**C**–C–N); $\delta = 126.71$ (s, slightly broadened, *ipso*-**C**–As); $\delta = 134.46$ (s, –**C**–C–As**)**; $\delta = 150.35$ ppm (s, *ipso*-**C**–N). *IR (Nujol mull between CsBr disks; $\tilde{\nu}$[$cm^{-1}$])*: 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 Supplememntary 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**) in chloroform for a period of three days to two weeks at −13 °C afforded colourless to slightly yellow plates or colourless cuboids, respectively, both suitable for an X-ray structure analysis. A crystal of the approximate dimensions 0.7 × 0.5 × 0.1 mm (**1**)// 0.65 × 0.6 × 0.5 mm (**2**) was selected, covered with polyfluorinated polyether oil (*RS 3000, Riedel-de-Haën*), transferred to an automatic Syntex $P2_1$ diffractometer and cooled to a temperature of −100 ± 3 °C. A least squares fit using the positions of 38//35 selected reflections in a range of $9.56 < 2\theta < 24.25°$//$15.54 < 2\theta < 25.76°$ supplied correct unit cell dimensions. The complete data set was collected with graphite monochromatized Mo-$K_\alpha$-radiation at a scanning rate ranging from 4.00 to 29.30 deg $min^{-1}$. As derived from the unit cell parameters and the lack of systematic absences, both compounds crystallize in one of the two triclinic space groups; $P\overline{1}$, however, was chosen over $P1$ [22] on the strength of E-value statistics and a successful refinement of the structures. Programs of the software package SHELXTL version 5.10 [18–20] were employed to solve the phase problem with statistical (direct) methods and to refine the atomic coordinates as well as at first the isotropic and subsequently the anisotropic displacement parameters of all heavier atoms by full matrix least squares calculations. Furthermore, program XP also included in this package was used for an analysis of the molecular geometry and the preparation of drawings. Calculation of the quality factors R1 and w*R*2 using measured values with $F > 4\sigma(F_o)$; scattering factors for the neutral atoms C, As, and Cl from D. T. Cromer and J. B. Man [23] and for the hydrogen atoms from R. F. Stewart, E. R. Davidson and W. T. Simpson [24]; full-matrix least squares refinement on $F^2$; several cycles of refinement with complete matrix and following difference Fourier synthesis; minimizing of the function $\Sigma w\,(F_o^2 - F_c^2)^2$. The quality factors are defined by the following formulas with m (number of reflections) and n (number of parameters):

$$R = R1 = \frac{\sum |Fo - |Fc||}{\sum Fo} \qquad wR = \sqrt{\frac{\sum w(Fo - |Fc|)^2}{\sum wFo^2}}$$

$$wR2 = \sqrt{\frac{\sum w(Fo^2 - Fc^2)^2}{\sum w(Fo^2)^2}} \qquad GOF = \sqrt{\frac{\sum w(Fo^2 - Fc^2)^2}{(m - n)}}$$

The anisotropic displacement parameters $U_{ij}$ ($10^{-23}$ $m^2$) refer to the expression: $e[-2\pi^2 (a^{*2} h^2 U_{11} + b^{*2} k^2 U_{22} + c^{*2} l^2 U_{33} + 2b^* c^* k\, l\, U_{23} + 2a^* c^* h\, l\, U_{13} + 2\, a^* b^* h\, k\, U_{12})]$; the equivalent isotropic parameters $U_{eq}$ ($10^{-23}$ $m^2$) are calculated from the anisotropic values applying the formula $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a_i}.\mathbf{a_j}$ (**a** is real-cell and $a^*$ reciprocal-cell length [25]. Therefore the equivalent isotropic $U_{eq}$ value is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor [25]. The structures solved from the crystallographic data of the compounds **1** and **2** were deposited to the Cambridge Crystallographic Data Centre (CCDC) under numbers 1537949 and 1537950, respectively. For the data set of compound **1**, the application of a ψ-scan absorption correction turned out to be necessary. The introduction of anisotropic displacement parameters resulted in an improvement of the R-values from 0.1087// 0.2989 to 0.0649//0.1809. Finally, the positions of all hydrogen atoms could be located on a difference Fourier map; the refinement of these co-ordinates as well as their isotropic displacement parameters ended in reasonable values.

## 3. Results and discussion

### 3.1. Structural analyses

For both compounds **1** and **2**, crystallographic parameters [26] and details of data collection have been summarized in Table S3. Selected bond lengths and bond angles as well as torsion angles [27] can be taken from Table 2 (Table S4). Details concerning the least-squares planes of these molecules are given in Table S5. Final atomic coordinates as well as equivalent isotropic and anisotropic displacement parameters have been listed in Tables S6 and S7, respectively. In regard to the numbering Figs. 1 and 2, one should notice that the atoms of the two independent molecules **a** and **b** in the unit cell of compound **1** (Fig. 1) differ in the first integer *n* ($n = 1$ or 2) following the element symbol, whereas in compound **2** (Fig. 2) the atoms of the three substituents at the central atom As3 are characterized by the integers $n = 3$, 4 and 5.

The X-ray structure determination of dichloro[4-(dimethylamino)phenyl]arsine (**1**) shows the compound to crystallize triclinic in the centrosymmetric space group $P\overline{1}$ and to comprise two independent molecules **a** and **b** in the asymmetric unit. Molecular models are depicted in Fig. 1. Apart from nearly identical bond lengths and angles (Table 2) in molecules **a** and **b**, even the orientations of the dichloroarsinyl groups with their trigonal pyramidally coordinate arsenic atoms and the planar dimethylamino substituents in positions 1 and 4, respectively, are found to be very similar relative to the central arene rings. On the whole the geometry of both molecules approaches largely pseudosymmetry *m* in that the atoms of the total 4-di-methylaminophenyl unit form a common plane which roughly bisects the Cl*n*1–As*m*–Cl*n*2 angle (Table 2). Obviously the following discussion is based mainly on average values. In order to calculate the length of a polar single bond from covalent radii, differences in the electronegativity values of the two atoms concerned have to be taken into consideration. For such a correction the following methods are usually applied – the original one set up by *Schomaker* and *Stevenson* [28], and a partially improved one published about twenty years ago by *Blom* and *Haaland* [29]. Inserting *Pauling's* covalent radii [26] of 77, 99 and 121 p.m. for the elements carbon, chlorine and arsenic and pertinent *Alred–Rochow* electronegativities [30] of 2.50, 2.83 and 2.20 into the *Schomaker–Stevenson* equation and applying correction factors of 8 and 4 for the As–C and As–Cl distance [26], respectively, result in calculated bond lengths of 196 and 217 p.m. With the same starting parameters the method of *Blom* and *Haaland* [29] actually leads to identical values of 196 and 216 p.m.

To allow, however, a careful discussion of the molecular parameters of dichloro[4-(dimethylamino)phenyl]arsine (**1**) and to obtain an answer to whether or not there is a distinct π-conjugation between the dimethylamino and the dichloroarsinyl substituent across the arene ring, a second basis will have to be created in that these values are compared with those of simple parent compounds such as arsenic(III) chloride or trimethyl– and triphenylarsine together with the heteroleptic species $(H_3C)_{3-n}AsCl_n$ and $(H_5C_6)_{3-n}AsCl_n$ ($n = 1$ or 2), respectively. For arsenic(III) chloride As–Cl bond lengths of 216.1 and 216.2 p.m. have been determined from its microwave spectrum [31] and a gas electron diffraction experiment [32]. Analogous studies on trimethylarsine reveal As–C distances of 195.9 [33] and 198 p.m. [34], whereas X-ray structure determinations at ambient temperature give values of 194.9 [35] and 195.7 p.m. [36] for triphenylarsine. Remarkably, these As–Cl and As–C bond lengths obtained from experiments tally very well with the results of *Blom* and *Haaland* [29]. Since, however, the As–Cl and As–C distances of the heteroleptic chloromethyl– and chlorophenylarsines are only partially available from the literature, quantum chemical calculations [37] using *ab-initio* methods at the MP2/6–311++G** level or DFT methods at the B3LYP/6–311++G** level have been carried out to create a third basis and to fill the gap. Additionally, the high quality of the *ab-initio* calculations in particular allows a corroboration of experimental results. In this

**Table 1**
Selected Bond Lengths (pm) and Bond Angles (°) as well as Torsion Angles for dichloro[4-(dimethylamino)phenyl]arsine (**1**) and tris[4-(dimethylamino)phenyl]arsine (**2**).

| a) Bond lengths | **1 a**<br>$m = 1$<br>$n = 1$ | **1 b**<br>$m = 2$<br>$n = 2$ | Mean | **2**<br>$m = 3$<br>$n = 3$ | **2**<br>$m = 3$<br>$n = 4$ | **2**<br>$m = 3$<br>$n = 5$ | Mean |
|---|---|---|---|---|---|---|---|
| As*m*–C*n*1 | 191.9(4) | 191.5(4) | 191.7 | 195.6(2) | 194.0(2) | 195.0(2) | 194.9 |
| As*m*–Cl*n*1 | 221.5(1) | 221.4(2) | 220.6 | | | | |
| As*m*–Cl*n*2 | 219.3(1) | 220.1(2) | | | | | |
| N*n*–C*n*4 | 135.9(5) | 135.9(5) | 135.9 | 139.7(3) | 138.6(3) | 138.7(3) | 139 |
| N*n*–C*n*7 | 145.3(5) | 145.4(6) | 145.4 | 145.5(4) | 144.9(3) | 143.9(4) | 144.8 |
| N*n*–C*n*8 | 145.4(6) | 145.3(6) | | 145.7(4) | 144.3(3) | 144.3(4) | |

| b) Bond angles | **1 a**<br>$m = 1$<br>$n = 1$ | **1 b**<br>$m = 2$<br>$n = 2$ | Mean | **2**<br>$m = 3$<br>$n = 3$ | **2**<br>$m = 3$<br>$n = 4$ | **2**<br>$m = 3$<br>$n = 5$ | Mean |
|---|---|---|---|---|---|---|---|
| C*n*1–As*m*–C*(n+1)*1 | | | | 98.5(1) | 100.2(1) | | 99.3 |
| C*n*1–As*m*–C*(n+2)*1 | | | | 99.3(1) | | | |
| C*n*1–As*m*–Cl*n*1 | 97.3(1) | 98.6(1) | 98.8 | | | | |
| C*n*1–As*m*–Cl*n*2 | 100.5(1) | 98.9(1) | | | | | |
| Cl*n*1–As*m*–Cl*n*2 | 94.8(5) | 96.5(6) | 95.7 | | | | |
| C*n*4–N*n*–C*n*7 | 120.0(3) | 120.1(4) | 120.6 | 117.0(2) | 118.6(2) | 119.4(2) | 118.4 |
| C*n*4–N*n*–C*n*8 | 121.0(3) | 121.3(4) | | 117.1(2) | 118.6(2) | 119.4(2) | |
| C*n*7–N*n*–C*n*8 | 118.1(4) | 118.5(4) | 118.3 | 114.0(2) | 116.4(2) | 117.3(3) | 115.9 |
| $\sum$N[a] | 359.1 | 359.9 | 359.5 | 348.1 | 353.6 | 356.1 | 352.6 |

| c) Torsion angles[b] | | **1a**<br>$m = 1$<br>$n = 1$ | **1 b**<br>$m = 2$<br>$n = 2$ | **2**<br>$m = 3$<br>$n = 3$ | **2**<br>$m = 3$<br>$n = 4$ | **2**<br>$m = 3$<br>$n = 5$ |
|---|---|---|---|---|---|---|
| φn4 | C51–As3–C31–C36 | 81.4 | C31–As3–C41–C46 | 90.9 | C41–As3–C51–C56 | 89.6 |
| φn2 | C51–As3–C31–C32 | −101.1 | C31–As3–C41–C42 | −83.7 | C41–As3–C51–C52 | −94.6 |
| φn1 | C41–As3–C31–C32 | 0.8 | C51–As3–C41–C42 | 17.5 | C31–As3–C51–C52 | 5.9 |
| φn3[c] | EP–As3–C31–C36 | −47.7 | EP–As3–C41–C46 | −38.5 | EP–As3–C51–C56 | −40.2 |

[a] Sum of angles at nitrogen.

[b] The torsion angle A–B–C–D is defined as positive if, when viewed along the B–C bond, atom A must be rotated clockwise to eclipse atom D [27].

[c] For a definition of torsion angle φ*n*3 see text in this paper.

**Table 2**
Bond Lengths and Angles Quantum Chemically Calculated[a] and Experimentally Determined for the Compounds $(H_3C)_{3\text{-}n}AsCl_n$ and $(H_5C_6)_{3\text{-}n}AsCl_n$ ($n = 0 \rightarrow 3$) as well as $Me_2N{-}C_6H_4{-}AsCl_2$ (**1**).

| Compound | As–Cl | | As–C | | C–As–C | | C–As–Cl | | Cl–As–Cl | |
|---|---|---|---|---|---|---|---|---|---|---|
| | calc. | exp. | calc. | exp. | calc. | exp. | calc. | exp. | calc. | exp |
| $Me_2N{-}C_6H_4{-}AsCl_2$ (**1**) | 224.7[b] (av.) | 220.6 (av.) | 193.5 | 191.7 | | | 99.2 | 98.9 (av.) | 97.6 | 94.8 |
| $(H_3C)_3As$ | – | – | 196.9[c]<br>198.9[b] | 195.9 [33]<br>198[d] [34] | 96.4[c]<br>97.2[b] | 96 [33]<br>96 [34] | – | – | – | – |
| $(H_3C)_2As{-}Cl$ | 221.5[c]<br>225.4[b] | – | 195.7[c]<br>197.9[b] | – | 96.4[c]<br>96.9[b] | | 96.3[c]<br>97.0[b] | | – | – |
| $H_3C{-}AsCl_2$ | 219.6[c]<br>223.2[b] | – | 194.7[c]<br>197.2[b] | – | – | – | 99.8[c]<br>100.7[b] | | 95.7[c]<br>96.4[b] | – |
| $AsCl_3$ | 218.0[c]<br>221.3[b] | 216.1 [31] | – | – | – | – | – | – | 98.9[c]<br>99.7[b] | 98.4 [31] |
| $(H_5C_6)_3As$[e] | – | – | 198.1 (av.)[b] | 194.9 (av.)[f] [35]<br>195.7 (av.)[f] [36] | 99.9 (av.)[c] | 99.7 (av.)[f] [35]<br>100.1 (av.)[f] [36] | – | – | – | – |
| $(H_5C_6)_2As{-}Cl$[g] | 225.7[b] | 226.0 [38] | 197.1; 197.6[b] | 196.0; 197.0 [38] | 99.5[b] | 105.0 [38] | 98.3; 99.4[b] | 94.0; 98.0 [38] | – | – |
| $H_5C_6{-}AsCl_2$[h] | 223.5[b] | – | 195.9[b] | – | – | – | 98.5[b] | – | 98.7[b] | – |
| $AsCl_3$ | 218.0[c]<br>221.3[b] | 216.2 [32] | – | – | – | – | – | – | 98.9[c]<br>99.7[b] | 98.6 [32] |

[a] For details see discussion.

[b] Calculated by DFT methods at the B3LYP/6–311++G** level.

[c] Calculated by *ab-initio* methods at the MP2/6–311++G** level.

[d] Value obtained from an early GED experiment of the year 1938.

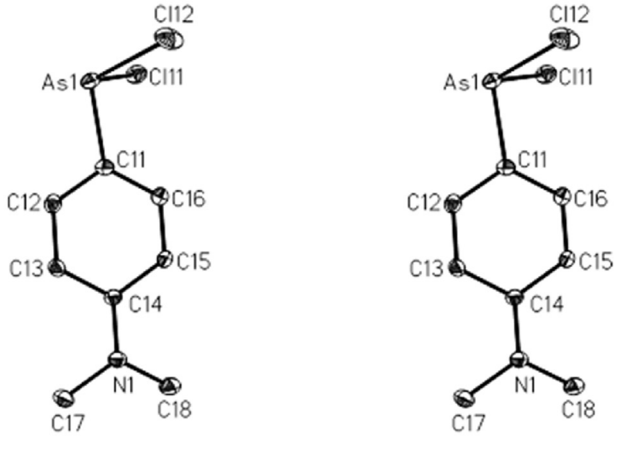
[e] Molecule of $C_3$ symmetry.

[f] Four independent molecules in the asymmetric unit.

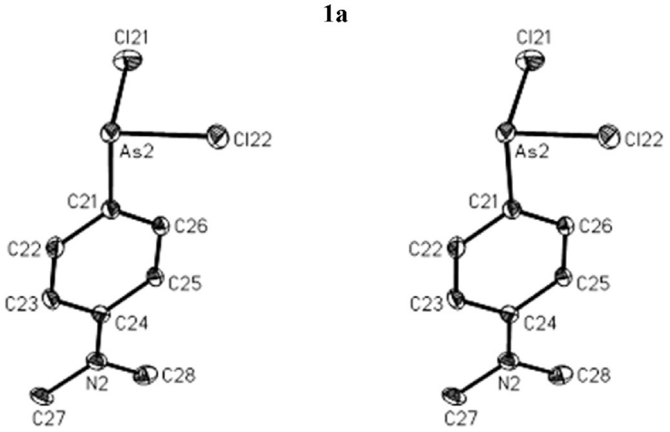
[g] Molecule of point group $C_1$.

[h] Molecule of point group $C_s$.

respect, already a short look at Table 2, where all relevant As–Cl and As–C bond lengths have been put together, makes evident that all values calculated by *ab-initio* methods do not deviate significantly from those experimentally determined. Unfortunately, DFT methods give somewhat longer distances for arsenic(III) chloride, trimethylarsine and both the chloromethylarsines; obviously these values are less appropriate for a comparison. But for dichlorophenyl– and chlorodiphenylarsine [38] an excellent agreement between experimentally determined values and those calculated by DFT methods has been found. With regard to the As–C distances, however, the well-known shortening of the element carbon bond caused by a change in hybridization of the



**1a**



**1b**

**Fig. 1.** Stereoscopic views of both the independent molecules **a** and **b** of compound **1**. The two numbering schemes applied differ only in the first figure ($n = 1$ or 2) following the element symbols. Thermal ellipsoids are at 30% probability, hydrogen atoms have been omitted for clarity.

carbon atom *e.g.* from $sp^3$ to $sp^2$ is not as pronounced as expected; quite on the contrary, the mean As—C values determined for trimethyl— (195.9 p.m. [33]) and triphenylarsine (194.9 [35] and 195.7 p.m. [36]) were found to be almost identical.

The dependence of As—Cl distances on the number of chlorine atoms at arsenic becomes apparent not only from quantum chemical calculations, but also from an inspection of some examples in a literature [31–36,38]. The different chloroarsines the parent compound arsenic(III) chloride exhibits the shortest bond length of 216.1 p.m. [31]. This value is followed by the range of dichloro(2-chlorophenyl)arsine opening with 218.3 p.m. from a gas electron diffraction experiment [39] and closing with 226.0 p.m. from an X-ray structure analysis on chlorodiphenylarsine [38]. Hence, the mean As—Cl bond length of dichloro[4-(dimethylamino)phenyl]-arsine (**1**, 220.6 p.m.) does not deviate from this range, but to be rather similar to that in the orthorhombic modification of chlorobis[2,4,6-tris(trifluoromethyl)phenyl]arsine (219.2 p.m.) [40]. A completely different situation for the As—C bond lengths of the two structurally independent molecules **1a** and **1b**. Both distances (191.9 and 191.5 p.m.) were found to be distinctly *shorter* than a bond length of chlorodiphenylarsine (197 p.m.) as well as dichloro(2-chlorophenyl)arsine (195.5 p.m.) [39] studied by gas electron diffraction. Additionally, quantum chemical calculations on different methylarsines using *ab-initio* methods at the MP2/6−311++G** level furnish a sequence of similar, but slightly decreasing As—C distances starting with 196.9 p.m. trimethylarsine and ending with 194.7 p.m. for dichloromethylarsine (Table 2). These bond lengths are in close agreement with the standard value of 196 p.m. derived by *Blom* and *Haaland* [29].

Without doubt the substantial shortening of the As—C bond between the dichloroarsinyl unit and the phenyl substituents by 5.3 p.m. (197 *vs.* 191.7 p.m.) is caused by the dimethylamino in *para*-position. Since those interactions are known to be interdependent, the geometry of the dimethylamino group and especially the distance between the nitrogen and the *ipso*-carbon atom have to be considered first and to be compared with values of parent compound such as *N*,*N*-dimethylaniline. To the best of our knowledge, however, the solid state structure have unfortunately not yet been determined, but two electron diffraction studies of *N*,*N*-dimethylaniline have been performed. The first one published as early as 1965 [41] afforded an only rather vague molecular model in that the planes of the arene ring and the dimethylamino group had been *assumed* to be parallel and as far as bond lengths and angles are concerned, merely average values had been reported. Some years ago *Novikov*, *Samdal* and *Vilkov* [42] repeated the structure determination and achieved a substantial improvement by applying highly discriminating quantum chemical calculations in order to allow for low-frequency vibrations such as the inversion of the dimethylamino group and its torsion round the $N—C_{ipso}$ bond. The most important results of the investigation to be mentioned in this context are the experimental corroboration of the nearly trigonal planar coordination sphere at nitrogen, a $N—C_{ipso}$ bond length of 139.6 p.m. which is shortened by 6.4 p.m. in comparison to the $N—C_{methyl}$ distances (146.0 p.m.) and slightly elongated $C_{ipso}—C_{ortho}$ bonds (140.9 p.m.); further data will be found in Table S8. The strong shortening of the N—C bond to the *ipso*-carbon atom and a

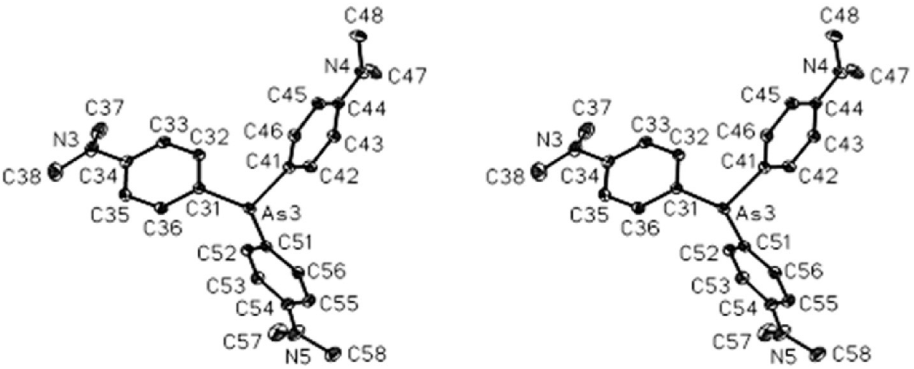


**Fig. 2.** Molecular model of compound **2** in stereoscopic view. Thermal ellipsoids are at 30% probability; hydrogen atoms have been omitted for clarity.

trigonal planar coordination sphere at nitrogen indicate an effective electronic interaction between the free electron pair and the π-system of the molecule, but the already mentioned N–$C_{ipso}$ distance (139.6 p.m.) is still longer than the bond lengths determined experimentally (135.9 p.m.) and calculated quantum chemically (137.6 p.m.) for dichloro[4-(dimethylamino)phenyl]arsine (**1**) (Table S8).

The average values of the angles Cl–As–Cl (95.7°) and C–As–Cl (98.8°, Table 1) correspond very well with relevant parameters determined for arsenic(III) chloride (98.4°) and chlorodiphenylarsine (93.5° and 98.3°,Table 2). Additionally, quantum chemical calculations on dichlorophenylarsine reveal very similar values of 98.7° and 98.5° for the angles Cl–As–Cl and C–As–Cl, respectively (Table 2). Furthermore, the structural data of the dimethylamino groups of compound **1** and *N*,*N*-dimethylaniline [42] are also found to be very similar. The average N–$C_{methyl}$ bond lengths are almost identical (145.4 *vs* 146.0 p.m.) and the mean values of the angles $C_{methyl}$–N–$C_{methyl}$ (118.3°) and $C_{methyl}$–N–$C_{phenyl}$ (120.6°) determined for compound **1** do not differ substantially from those of *N*,*N*-dimethylaniline (117.4° and 121.3°, respectively; Table S8). The packing of the two crystallographically different dichloro[4-(dimethylamino)phenyl]arsine molecules **1a** and **1b** in the unit cell is depicted in stereoscopic view in Fig. S1. An inspection of intermolecular distances reveals two short arsenic … chlorine contacts of 362.6 (As1···Cl11) and 369.0 p.m. (As1···Cl22) as well as a short arsenic … nitrogen contact of 348.2 p.m. (As···N1). Since these distances do not deviate substantially from the relevant sums of van-der-Waals radii (As···Cl 380, As···N 357 p.m. [26]), strong intermolecular interactions which might increase the coordination number of arsenic, have to be cluded. Taking into account an analogous sum of 380 p.m. for arsenic and carbon, the same conclusion holds for several short arsenic ··· carbon contacts found in a range from 357.9 (As2···C23) or 361.1 p.m. (As···C14) and 375.6 (As2···C17) to 378.4 p.m. (As···C22).

At first, however, a molecular model of compound **2** will be depicted stereoscopically in Fig. 2. As already indicated by a sum of angles at arsenic of 298.0° and individual C–As–C values varying only slightly between 98.5 and 100.2° (Table 1), the central atom is found in a trigonal pyramidal environment. Previous to a necessary but rather difficult analysis of the molecular conformation, however, the following discussion will focus first on the bonding situation at the dimethylamino groups and the As–C distances. As the sums of angles at the nitrogen atoms N4 and N5 amount to values of 353.6° and 356.1°, respectively, and hence deviate significantly from the value of nitrogen atom N3 (348.1°, Table 1), only two of three dimethylamino groups are considered to be almost planar. The third one is found in an environment which has to be classified as intermediate between trigonal planar and trigonal pyramidal. Since for amines the barrier of a pyramidal inversion at nitrogen is well known to be rather low, crystal packing effects may easily account for the different geometry. Furthermore, the angles between the least-squares planes of the arene rings $A_n$ and the dimethylamino groups $B_n$ ($n = 3 \rightarrow 5$, Table S5) fall into a rather wide range from 35.9° (A3/B3) to 15.8° (A5/B5). Differing distances of the two carbon atoms C*n*7 and C*n*8 to the least-squares planes $A_n$ of the arene rings give additional information about the twist of the dimethylamino groups (Table S5); the difference in these two values is highest again for the two carbon atoms C37 and C38 at nitrogen atom N3. Irrespective of these minor deviations the structural data of the dimethylamino groups of compound **2** correspond very well with parameters obtained for *N*,*N*-dimethylaniline by gas electron diffraction [42]. Especially the length of the characteristic N–$C_{phenyl}$ bond which in comparsion to the average N–$C_{methyl}$ distance of 144.8 p.m. is shortened to 139.0 p.m. owing to π-conjugation with the arene ring, tallies with the appropriate value of the aniline derivative (139.6 p.m., Tables S4 and S8). Moreover, nearly identical N–$C_{phenyl}$ and N–$C_{methyl}$ distances of 138.7 and 145.1 p.m., respectively, obtained from quantum chemical calculations on *N*,*N*-dimethylaniline, can also be taken for a comparsion (Table S8).

The structural similarity between tris[4-(dimethylamino)phenyl]arsine (**2**) and a standard compound such as *N*,*N*-dimethylaniline holds not only for the outer part of the molecule, as elaborated just above but also for its arsenic centre. Despite various substituents at the arene rings the average As–C bond lengths fall into a rather small range from 195.4 p.m. obtained for tris(4-methylphenyl)arsine [43] to 199.0 p.m. for the tris(2,5-dimethylphenyl) derivative [44]. The series of average As–C distances starts with tris[4-(dimethylamino)phenyl]arsine (**2**; 194.9 p.m.) but is immediately followed by the almost identical nearly values of triphenylarsine [36] (195.7 p.m.), tris[(4-chloro)phenyl]arsine (195.8pm) [43] and tris[(4-methoxy)phenyl]arsine (196.3pm) [44]. As expected, methyl groups or even bulkier substituents in positions 2 and 6 of the arene rings cause an elongation of the average As–C distances up to values of 198.6 or 199.0 p.m. published *e.g.* for tris(2,4,6-triisopropylphenyl)arsine [45] or tris(2,5-dimethylphenyl)arsine [44], respectively. Tris[2-(dimethylaminomethyl)phenyl]arsine, however, has to be regarded as an exception as three dimethylamino groups additionally coordinate at the arsenic atom and increase its coordination number to 6 (As–C 198.2 p.m., [$(2\text{-}Me_2NCH_2\text{–}C_6H_4)_3As$)]) [46]. Parallel to the As–C bond elongation a widening of the C–As–C angles up to 107.6° in tris(2,4,6-trimethylphenyl)arsine [47] is observed. As a summary, the following results have to be pointed out: The X-ray structure analysis of tris[4-(di-methylamino)phenyl]arsine (**2**) clearly demonstrates that the unusual shortening of the N–$C_{phenyl}$ as well as the As–$C_{phenyl}$ bond lengths are restricted to dichloro [4-(di-methylamino)phenyl]arsine (**1**) and disappear completely or at least largely when the highly electronegative chlorine atoms at arsenic are replaced by 4-(dimethylamino)phenyl substituents.

In order to allow a straightforward conformational analysis of compound **2** the phenyl carbon atoms in *ortho* position to the arsenic atom which are located closer to the nonbonding electron pair (EP; free coordination site of the distorted tetrahedron at arsenic) are attributed the designation C*n*6 ($n = 3, 4, 5$) (Fig. 2). According to the rules set up by *Cahn*, *Ingold* and *Prelog* [27] the torsion angle EP–As3–C*n*1–C*n*6 (φ*n*3, Fig. 3) has to be used to define the partial conformation of an individual As3–C*n*1 bond. Since, however, the position of the pseudoatom EP cannot be established, the values of φ*n*3 cannot be determined directly and have to be calculated from the relevant torsion angles φ*n*4, φ*n*2 and φ*n*1 (Table 1, Fig. 3) by applying the formula: $\varphi n3$: $[\varphi(\mathrm{EP–As3–C}n1\mathrm{–C}n6) = -[180 - |\varphi n4| - ½\,(|\varphi n2| + |\varphi n1|)]$.

The calculation results in torsion angles φ*n*3 of −47.7°, −38.5° and −40.2° (Table 1). These values indicate a negative synclinal [48] partial conformation at all As3–C*n*1 bonds and hence a helical chirality of the molecule concerned (Fig. 2). Since the angles φ*n*3 are found to be very similar, a high degree of molecular $C_3$ pseudosymmetry is achieved. Furthermore, the planes of the arene rings form an right-handed propeller; by the centres of inversion of space group $P\bar{1}$ the enantiomeric molecule is generated (Fig. S2). The packing of molecule (**2**) in the unit cell is illustrated in Fig. S2. An inspection of tris[4-(dimethylamino)phenyl]arsine intermolecular distances does not reveal any values exceeding the sum of appropriate van-der Waals radii.

### 3.2. Quantum chemical calculations

In the molecular structure of dichloro[4-(dimethylamino)

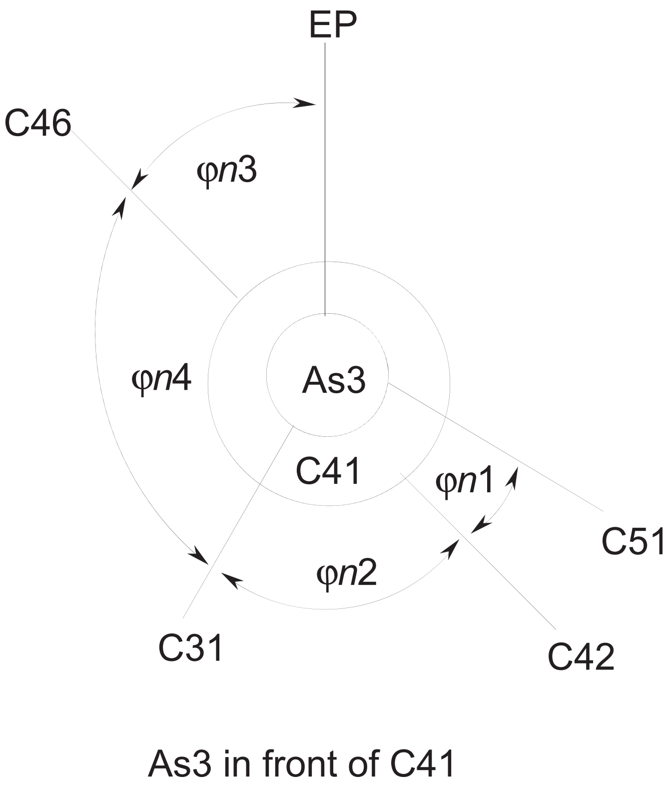


**Fig. 3.** Newman projection to specify the partial conformation of the individual As3—C*n*1 bond. The bond As3—C41 has been selected as an example.

phenyl]arsine (**1**), unusual changes in bond lengths have been noticed. Compared with standard values which, however, have to be corrected to 144 and 194 p.m. for the $N_{sp2}$—$C_{sp2}$ and As—$C_{sp2}$ single bond, respectively. By inserting *Pauling's* covalent radii [26] of 121, 77 and 74 p.m. for the elements arsine, carbon and nitrogen, and pertinent *Alred-Rochow* electronegativities [30] of 2.20, 2.50 and 3.07 into the *Pauling's* Modification of the *Schomaker-Stevenson* rule lead actually to the values 146 and 196 p.m. and then corrected to 144 and 194 p.m. by minus 2 p.m. for $sp^2$ hybridization [26]. The distances between the *ipso*-carbon atoms and nitrogen as well as arsenic are both shortened to values of 135.9 and 191.7 p.m. (Table 1). Additionally, relatively large fluctuations in the C—C bond lengths from 137.2 to 142.4 p.m. within the arene ring (Tables S4 and 8) suggest substantial substituent effects. To throw light on the aforementioned problems quantum chemical calculations were performed [37] in particular with regard to population analyses on a *natural bond orbital* (NBO) basis. By such a procedure information on the allocation of atomic charges as well as the significance of donor-acceptor interactions between Lewis-type natural bond orbitals is easily available. For all compounds to be studied NBO analyses were accomplished by use of the hybrid density functional method B3LYP [49] and the basis set 6−311++G** [50]. From the *canonical molecular orbitals* initially obtained by these calculations, *natural bond orbitals* (NBOs) are derived applying mathematical algorithms to receive representations of two- or three-centre bonds and for lone pairs. As for dichloro[4-(dimethylamino)phenyl]arsine (**1**) NBO analyses were performed using the results of the X-ray structure determination as well as molecular parameters supplied by quantum chemical calculations. In the case of the experimentally based NBO analysis the atomic coordinates of the non-hydrogen atoms were directly adopted from the last stage of the crystal structure refinement, whereas standard values of 109 and 108 p.m. had to be ascribed to the C—H bond lengths of the methyl groups and the arene ring, respectively. Without doubt the initially most important result of these quantum chemical studies was the close agreement in the molecular parameters obtained from the solid state structure analysis and from calculations on the gaseous compound (Fig. S3; Table 2 and Table S8). The only major deviation worth to be mentioned are differences of 5.0 and 3.1 p.m. in the As—Cl bond lengths (219.7 *vs* 224.7; 221.5 *vs* 224.6 p.m.), whereas the distances between arsenic or nitrogen and the *ipso*-carbon atoms C1 and C4, respectively, are found to be rather similar (191.7 *vs* 193.5; 135.9 *vs* 137.6 p.m.).

By analogy to *N*,*N*-dimethylaniline [42] the aforementioned shortening of the N—$C_{ipso}$ bond to 135.9 p.m. can be attributed to an electronic interaction between the lone pair at nitrogen and the antibonding $\pi^*$ orbitals of the adjacent $C_{ipso}$—$C_{ortho}$ bonds; on an average these two distances are significantly elongated by 1.7 p.m. (Table S8) with respect to the standard value (140 p.m.). Quite obviously the interaction is intensified by structural features such as the trigonal planar coordination sphere at nitrogen (Table S8) and an almost perfect co-planarity of the arene ring with the dimethylamino group; in both the crystallographically independent molecules **1a** and **1b** the deviations come up to 12.6° and 1.6° only (Table S5). The $sp^2$-hybridization of the nitrogen atom is also reflected in the results of the NBO hybridization analysis; *s* and *p* character of all bonding orbitals involved vary only slightly between 0.3111 and 0.3695 and between 0.6298 and 0.6895, respectively. This type of hybridization also implies an almost pure *p* character of the lone pair (0.9939).

Further donor-acceptor interactions in the dichloro[4-(dimethylamino)phenyl]arsine (**1**) molecule are restricted to donating effects within the arene ring; in particular, one has to emphasize that such an interaction cannot be observed for bonds at the arsenic atom. Therefore, an NBO charge analysis was performed to account for the significant shortening of the As—$C_{ipso}$ bond to 191.7 p.m. It results in a high positive charge of 0.963 to be allocated to the arsenic atom (Fig. S3a), whereas the adjacent *ipso* carbon atom exhibits a rather high negative charge of −0.468. In comparison to values of −0.404 and −0.260 calculated for the *ipso*-carbon atom of dichlorophenylarsine (**c**) and the hydrogen bonded *para* carbon atom of *N*,*N*-dimethylaniline (Fig. S4d), respectively, a considerable increase in negative charge has to be noticed, whereas the positive charge at the arsenic atom of dichlorophenylarsine (0.974; Fig. S4c) turned out to be almost unchanged. The unusual shortening of the As—$C_{ipso}$ bond in dichloro[4-(dimethylamino)phenyl]arsine (**1**) may therefore be essentially traced back to the unexpectedly high difference of 1.431 elementary charges and an enhanced electronic attraction between arsenic and *ipso* carbon atom. The electronic situation specified above can best be described in the sense of a push-pull effect in that the dimethylamino substituents induces (pushes) a negative charge at (to) the *para* carbon atom and this charge is additionally increased by (pulled to) the dichloroarsinyl group. The optimized Cartesian coordinates and total energies [Hartrees] for all species could be found in Table S 9.

### 3.3. NMR characterization

The $^1$H-NMR-spectrum of dichloro[4-(dimethylamino)phenyl]arsine shows the typical AA'XX′-pattern of a 1,4-disubstituted arene ring the four hydrogen atoms of which give rise to two doublets ($^3$J(H,H) = 8.3 Hz) at 7.54 (3,5-H) and 7.79 p.m. (2,6-H). The singlet at 3.1 ppm is assigned to the dimethylamino group. In the $^{13}$C{$^1$H} spectrum four singlets in the arene and one in the alkyl region are noticed; they are tentatively assigned to the *ipso*-**C**—N (144.3), **C**—C—As (131.2), *ipso*-**C**—As (130.9) and **C**—C—N carbon atoms (122.0) as well as to the dimethylamino group (46.8 ppm). Tris[4-

(dimethylamino)phenyl]arsine obtained in 46% yield from an analogous solvent free reaction of the same starting compounds *N*,*N*-dimethylaniline and arsenic(III) chloride again in a ratio of 1:1, but followed by a hydrolysis of the highly viscous yellow wax formed first with sodium hydroxide and an accompanying redistribution of the substituents at arsenic, crystallizes at −13 °C from a chloroform solution in colourless cuboids. As expected its NMR spectra are found to be very similar to those of the dichloro derivative: The hydrogen atoms in 3,5- and 2,6-positions of the disubstituted arene ring become apparent as two doublets ($^3$J(H,H) = 8.74 Hz) at 6.67 and 7.20 ppm, whereas the singlet at 2.92 ppm comes from the dimethylamino group. The singlets of the $^{13}$C{$^1$H} spectrum at 150.4, 134.5, 126.7 (broadened), and 112.6 ppm are again tentatively assigned in an analogous way to the carbon atoms of the *ipso*-**C**—N, **C**—C—As, *ipso*-**C**—As and **C**—C—N moiety; the resonance at 40.4 ppm springs from the $(H_3C)_2N$ group. Chemical shifts of the compounds **1** and **2** in comparison with some parameters of similar compounds [51] are summarized in Table S10.

## 4. Conclusion

Our methods applied to prepare dichloro[4-(dimethylamino)phenyl]arsine as well as tris[4-(dimethylamino)phenyl]arsine both are based on the early studies of *Michaelis* and *Rabinerson*. Without doubt, the isolation of a hydrogen chloride free compound has to be considered an essential improvement of the original procedure. It was noted that only mono substituted exchange at arsenic atom occurs at ≤ 0 °C to give dichloro[4-(dimethylamino)phenyl]arsine, while when the temperature arising to ambient temperature, further substitution exchange at arsenic atom to furnish tris[4-(dimethylamino)phenyl]arsine. The X-ray structure analysis revealed two crystallographically independent molecules in the asymmetric part of the unit cell of dichloro[4-(dimethylamino)phenyl]arsine. In both independent molecules the nitrogen atoms are found in a planar coordination sphere. Apart from the molecular data already discussed, the structure of dichloro[4-(dimethylamino)phenyl]arsine (**1**, Fig. S5) attracts attention by unusual changes in bond lengths. The high quality of the *ab-initio* calculations allows a corroboration of experimental results. Unfortunately, DFT methods give somewhat longer distances for arsenic(III) chloride, trimethylarsine and both the chloromethylarsines; obviously, these values are less appropriate for a comparison. But for dichlorophenyl— and chlorodiphenylarsine an excellent agreement between experimentally determined values and those calculated by DFT methods has been found. Quantum chemical calculations were performed also on dichloro[4-(dimethylamino)phenyl]arsine (**1**), dichlorophenylarsine, and *N*,*N*-dimethylaniline to ascertain optimized structural data and to shed some light onto these phenomena. It was noted that the structural similarity between tris[4-(dimethylamino)phenyl]arsine (**2**, Fig. S5) and a standard compound such as *N*,*N*-dimethylaniline holds not only for the outer part of the molecule, but also for its arsenic centre. 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 °C. The compound has very probably been formed by a rearrangement of the corresponding [4-(dimethylamino)phenyl]oxoarsine to tris[4-(dimethylamino)phenyl]arsine.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2017.08.020.

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