The Molecular and Electronic Structure of Tris(dimethylarsino)amine (Me₂As)₃N
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Tris(arsino)amine, Nitrogen Configuration, Planar Nitrogen Configuration, X-Ray Data, Density Functional Calculations

The molecular structure of tris(dimethylarsino)amine has been determined by X-ray diffraction methods. The compound has a planar As₃N core unit with a paddle-wheel conformation of the three Me₂As groups. This structure was also confirmed by density functional calculations.

Introduction

Following recent structural studies on phosphino- and stibino-amines [1, 2] we have now investigated a prototype compound of the series of the tri(arsino)amines. In contrast to the rich data on amines of the Group IV Elements (Si, Ge, Sn), very little has been known about the structural chemistry of amines of the Group V Elements (P, As, Sb) in general, and of arsenic in particular [3, 4]. We determined the crystal structure of tris(dimethylarsino)amine, a compound where steric effects should play only a minor role, and tried to verify the results by state-of-the-art quantum-chemical calculations.

Results and Discussion

Tris(dimethylarsino)amine is readily prepared from chloro(dimethyl)arsine and hexamethyldisilazane as reported in the literature [5]. A yellow oil or a low-melting yellow solid are received, which can be purified and obtained in the form of single crystals by low-temperature crystallization from pentane.

The crystals are monoclinic, space group P2₁/c, with Z = 8 molecules in the unit cell. The asymmetric unit contains two crystallographically independent molecules, one of which is disordered. None of the two molecules has any crystallographically imposed symmetry. The structure of the disordered molecule could be determined and refined by using the usual split model techniques. The geometrical parameters of the two molecules are very similar and require no separate treatment (Fig. 1).

The As-N distances of the first molecule are within the narrow range 1.844(7) - 1.867(7) Å, those of the second (disordered) molecule between 1.819(11) and 1.959(11) Å. The As-N-As angles are all very close to 120°, and the sums of these angles at each nitrogen atom are almost exactly 360° indicating a planar configuration of the nitrogen atoms. This is in agreement with the findings for the analogous antimony compound (Me₂Sb)₃N [2].

The configuration at the arsenic atoms is consistently pyramidal with C-As-C angles near 96° and C-As-N angles near 100°.

The overall symmetry of the molecules is close to point group C₃h owing to the alignment of the dimethylarsino groups in identical conformations. The molecular shape thus may be described as a three-blade paddle-wheel (Fig. 1).

This solid state structure is nicely reproduced by quantum chemical calculations using density functional methods with the 6-311G* basis set and the density gradient corrected energy functional B3LYP. The task proved to be too formidable for an unrestricted treatment of this molecule with its three large arsenic atoms, and therefore the symmetry of point group C₃ was imposed. Given the X-ray results with the clear evidence for a planar configuration at nitrogen, this restriction is probably fully justified.
Table I. Selected geometric parameters for tris(dimethylarsino)amine.

<table>
<thead>
<tr>
<th>Bond lengths [Å]</th>
<th>X-ray</th>
<th>DFT</th>
<th>Bond angles [°]</th>
<th>X-ray</th>
<th>DFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>As1-N1</td>
<td>1.861(7)</td>
<td>1.892546</td>
<td>As3-N1-As1</td>
<td>119.7(4)</td>
<td>119.9779</td>
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<tr>
<td>As2-N1</td>
<td>1.867(7)</td>
<td>1.892205</td>
<td>As3-N1-As2</td>
<td>120.2(4)</td>
<td>120.0045</td>
</tr>
<tr>
<td>As3-N1</td>
<td>1.844(7)</td>
<td>1.892493</td>
<td>As1-N1-As2</td>
<td>119.6(4)</td>
<td>120.0176</td>
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<tr>
<td>As1-C12</td>
<td>1.937(9)</td>
<td>1.987688</td>
<td>N1-As1-C12</td>
<td>99.0(4)</td>
<td>101.0439</td>
</tr>
<tr>
<td>As1-C11</td>
<td>1.950(10)</td>
<td>1.987688</td>
<td>N1-As1-C11</td>
<td>100.8(4)</td>
<td>101.0439</td>
</tr>
<tr>
<td>As2-C22</td>
<td>1.948(10)</td>
<td>1.987667</td>
<td>C12-As1-C11</td>
<td>96.0(4)</td>
<td>96.5822</td>
</tr>
<tr>
<td>As2-C21</td>
<td>1.960(9)</td>
<td>1.987667</td>
<td>N1-As2-C22</td>
<td>99.6(4)</td>
<td>100.9985</td>
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<td>As3-C32</td>
<td>1.937(11)</td>
<td>1.987735</td>
<td>N1-As2-C21</td>
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<td>C22-As2-C21</td>
<td>96.3(4)</td>
<td>96.6797</td>
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<td></td>
<td>N1-As3-C32</td>
<td>100.5(4)</td>
<td>101.0366</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>N1-As3-C31</td>
<td>100.7(5)</td>
<td>101.0366</td>
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<td></td>
<td>C32-As3-C31</td>
<td>96.1(5)</td>
<td>96.7008</td>
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<td>Σζ (at N)</td>
<td></td>
<td></td>
<td></td>
<td>359.5</td>
<td>360.0</td>
</tr>
</tbody>
</table>

Fig. 1. Molecular structure of tris(dimethylarsino)amine (ORTEP drawing with 50% probability ellipsoids; only one of the two molecules in the asymmetric unit is shown).

The results of the calculations (for the gas phase molecule) are in quite satisfactory agreement with the experimental data as shown in Table I. The paddle-wheel structure is confirmed as the ground state conformation (Fig. 2). The bond angles in particular are in excellent agreement with the solid state data. The bond lengths involving arsenic (N-As, C-As) are found too large, but this is not unexpected since by definition the two methods (X-ray diffraction and DF calculations) do not give the same parameters. There is ample precedence for such discrepancies.

In summary, therefore, the results of the present work clearly demonstrate that planarity at nitrogen

is indeed a general phenomenon in the structural chemistry of the amines of Group V Elements.

Experimental Part

Tris(dimethylarsino)amine was prepared following a literature procedure [5]. A mixture of 6.8 g chloro(dimethyl)arsine (48.4 mmol) and 3.0 ml of hexamethyldisilazane (2.32 g, 14.4 mmol) was heated to 120 °C for 6 h. The white precipitate was filtered off and the volatile components were removed at 40 °C/1 mbar. From the remaining yellow oil colourless crystals of the product (1.02 g, 22% yield) were isolated by fractionated crystallisation from a solution of the crude product in n-pentane at −30 °C.

Crystal structure determination

A crystal of suitable quality and size was mounted in a glass capillary on an Enraf-Nonius CAD4 diffractometer.
[graphite monochromated Mo-K\(_\alpha\) radiation, \(\lambda(\text{Mo-K}\_\alpha) = 0.71073 \ \text{Å}\) and used for measurements of precise cell constants and intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed.

Crystal data: C\(_8\)H\(_{18}\)NAs\(_3\), \(M = 328.97\), colourless crystals of dimensions 0.3 \times 0.25 \times 0.5 mm, monoclinic, \(a = 23.580(5)\), \(b = 6.539(2)\), \(c = 16.063(3)\) Å, \(\beta = 101.26(2)^\circ\), space group \(P2_1/c\), \(Z = 8\), \(V = 2429.07(12)\) Å\(^3\), \(\rho_{\text{calc}} = 1.799\) g/cm\(^3\), \(F(000) = 1280\), \(T = -86^\circ\text{C}\). 5626 reflections measured, 5269 unique. Data were corrected for Lorentz and polarisation effects. Empirical absorption correction was applied [\(\mu(\text{Mo-K}\_\alpha) = 81.54\) cm\(^{-1}\), \(T_{\text{min}}/T_{\text{max}} = 0.2220/0.9946\)]. The structure was solved by Direct Methods and refined by full-matrix least-squares techniques on \(F^2\) with the SHELXTL suite of programs [6]. One of the two independent molecules in the asymmetric unit was disordered but could be refined successfully using a split-atom model. All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions [\(U_{\text{iso}}(\text{H}) = 1.5 \cdot U_{\text{eq}}(\text{of the attached C atom})\)]. Refinement of 208 parameters for 5258 data converged to a \(wR2\) (R1) of 0.1481 (0.0611). Residual electron densities: +1.40/-1.20 e Å\(^{-3}\). Selected bond lengths and angles are given in Table I. Anisotropic thermal parameters, tables of all distances and angles, and atomic coordinates have been deposited at Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDC No. 136043.

Computational details

The calculations for N(AsMe\(_2\))\(_3\) have been performed with the Gaussian 98 suite of programs [7] at the DFT level using the 6-31G* basis set and the density gradient corrected energy functional B3LYP. The molecule was subjected to a partial geometry optimization under the restrictions of symmetry point group \(C_s\). The nature of the stationary point was verified by frequency calculations at level B3LYP/6-31G*. Selected calculated geometric parameters are given in Table I.

Acknowledgements

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