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$O{=}As(NMe_2)_3$: Synthesis and Crystal Structure of the Arsenic Analogue of HMPT

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ABSTRACT

*$O{=}As(NMe_2)_3$ (**HMAsT**) is obtained in low yields by reacting $O{=}AsCl_3$ with excess $HNMe_2$ or by ozonolysis of $As(NMe_2)_3$; however, it is formed in yields >65% by using $(Me_3Si)_2O_2$ and $As(NMe_2)_3$ in hydrocarbon solution. The structure of **HMAsT** was established by IR/Raman, NMR and mass spectroscopy, and single crystal X-ray structure analysis. The structure determination revealed $(sp^3C){-}H\cdots O$–hydrogen bonding in the solid state. Acid-base reaction by methanolysis affords ionic $[Me_2NH_2]$ $[O_2As(OMe)_2]$ while iodide is oxidized to iodine.*

Hexamethylphosphortrisamide (HMPT), $O{=}P(NMe_2)_3$, is, as a consequence of the pioneering work by Michaelis [1], relatively easy to obtain by aminolysis of phosphorus oxychloride (Equation 1); the versatility of HMPT as a reagent has been demonstrated, for example, by H. Normant [2] in a review article.

$$O{=}PCl_3 + 6\ HNMe_2 \longrightarrow O{=}P(NMe_2)_3 + 3\ H_2NMe_2Cl \quad (1)$$

The chemistry of the homologuous arsenic derivatives is more difficult to accomplish; according to reports by Seppelt [3] on the synthesis of $O{=}AsCl_3$, this reaction (Equation 2) requires skillful experimental techniques for the isolation and eventually for the identification of the metastable compound (also used by us) as shown in Equation (3), and the same holds for the synthesis of $AsCl_5$, also reported by Seppelt's research group [4]:

$$AsCl_3 + O_3 \xrightarrow[CH_2Cl_2]{-78°C/Ar} O{=}AsCl_3 + O_2 \quad (2)$$

We have synthesized **HMAsT** by three different routes outlined below (Equations 3–5) [5]:

$$O{=}AsCl_3 + 6\ HNMe_2 \xrightarrow[CH_2Cl_2]{-78°C/Ar} O{=}As(NMe_2)_3 + 3\ H_2NMe_2Cl \quad (3)$$

$$As(NMe_2)_3 + O_3 \xrightarrow[CH_2Cl_2]{-78°C/Ar} O{=}As(NMe_2)_3 + O_2 \quad (4)$$

$$As(NMe_2)_3 + (Me_3Si)_2O_2 \xrightarrow[n\text{-hexane}]{RT/Ar} O{=}As(NMe_2)_3 + (Me_3Si)_2O \quad (5)$$

Ozonolyses, shown in Equations 2 and 4, proved to be relatively unfavorable methods for the synthesis of reasonable quantities of pure **HMAsT**, $O{=}As(NMe_2)_3$. Bis(trimethylsilyl) peroxide [6], a reagent frequently used now in inorganic and metallo-organic synthesis, was the only reactant to afford pure, white crystalline **HMAsT** of mp 45–46.5°C in yields >65% after isolation. The compound is indefinitely stable at room temperature in an inert gas atmosphere; it is soluble in common inert organic solvents and sublimes *in vacuo* with decomposition.

Preliminary chemical investigations showed unexpected results: HMPT is not hydrolyzed even in basic solutions; but $O{=}As(NMe_2)_3$ reacts with a

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Dedicated to Prof. Dr. K. Issleib on the occasion of his seventieth birthday.

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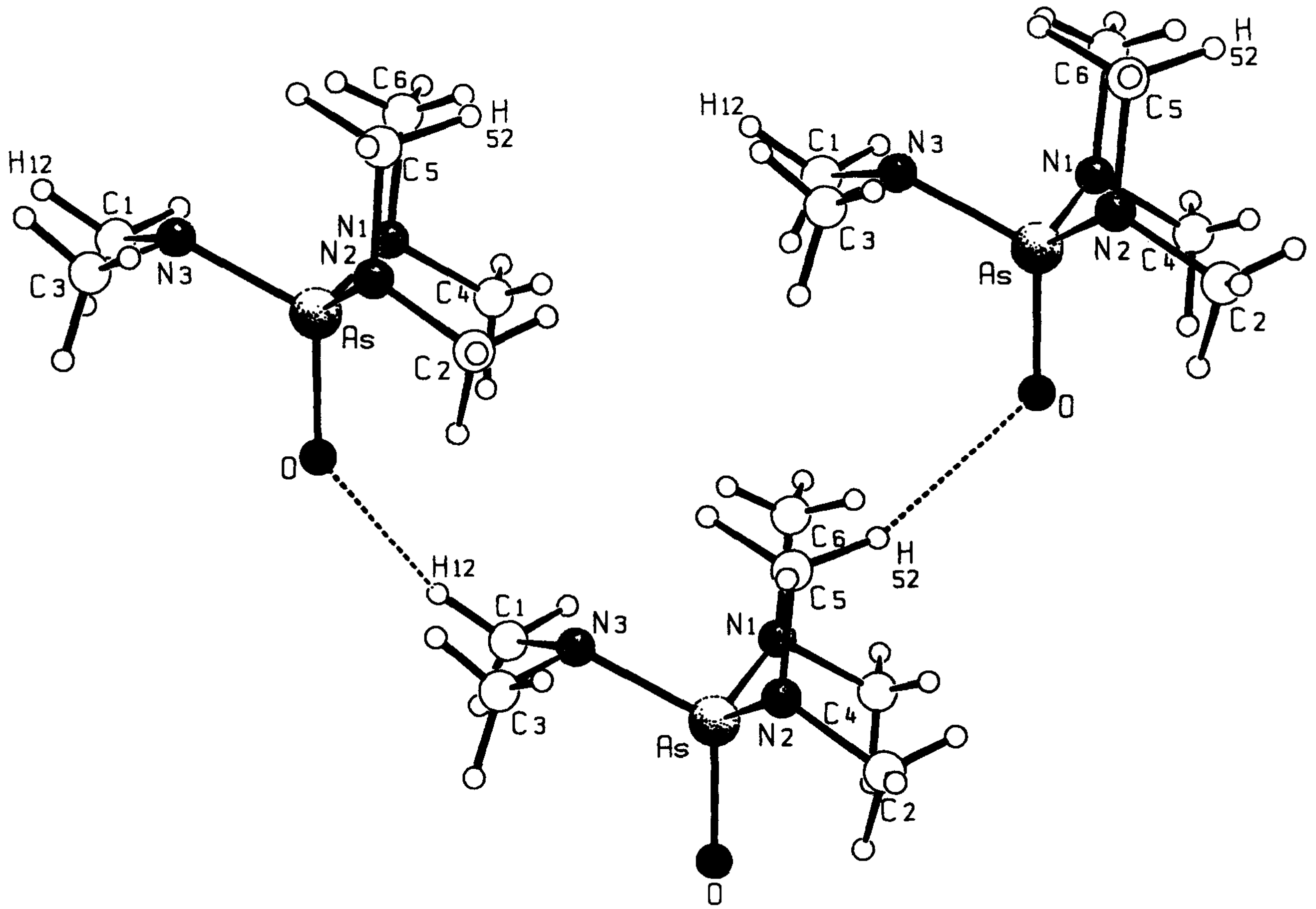

FIGURE 1 SCHAKAL plot [15] of three molecules O=As(NMe$_2$)$_3$, short C—H· · ·O contacts with broken lines.

Representative bond distances (pm) and bond angles (°):

O–As 162.5(4) As–N1 180.6(6) As–N2 180.2(6)
As–N3 177.5(5) N1–C4 146(1) N1–C6 144(1)
N2–C2 142(1) N2–C5 148(1) N3–C1 147(1)
N3–C3 152(1)

O–As–N1 110.1(3) O–As–N2 109.3(3) O–As–N3 118.8(2)
N1–As–N2 115.8(3) N1–As–N3 101.5(3) N2–As–N3 101.4(3)
As–N1–C4 115.5(5) As–N1–C6 119.1(5) As–N2–C2 118.1(5)
As–N2–C5 118.9(5) As–N3–C1 114.9(4) As–N3–C3 114.4(4)

variety of protic reagents [7, 8]. However, **HMAsT** does not react with ethanol even under reflux. Only methanol substitutes all dimethylamino groups (Equation 6) affording dimethylammonium *O,O*-dimethylarsenate; a similar ammonium compound NH$_4$[O$_2$As(OMe)$_2$] has been reported in the literature [9]:

$$\mathrm{O{=}As(NMe_2)_3} \xrightarrow[\text{reflux}]{\text{MeOH}} [\mathrm{Me_2NH_2}]\ [\mathrm{O_2As(OMe)_2}] \qquad (6)$$

Excess HCl gas presumably forms a metastable intermediate that decomposes rapidly to form AsCl$_3$ (Equation 7), identified by mass spectrometry. According to Equation (8) **HMAsT** oxidizes iodide ion to iodine and is thereby reduced to the As(III) compound:

$$\mathrm{O{=}As(NMe_2)_3} \xrightarrow[\mathrm{HCl/Et_2O}]{-78^\circ\mathrm{C}} \mathrm{AsCl_3} + \mathrm{H_2NMe_2Cl^-} \qquad (7)$$

$$\mathrm{O{=}As(NMe_2)_3} \xrightarrow{\mathrm{I^-}} \mathrm{As(NMe_2)_3} + \mathrm{I_2} \qquad (8)$$

The molecular spectroscopy of **HMAsT** showed no peculiarities related to the structure of this compound; mass spectra afforded a molecular ion and a fragmentation pattern in accordance with a monomeric molecule. In the ^{1}HNMR spectrum, the resonance signal of the dimethylamino group was slightly shifted to lower magnetic field compared to that of As(NMe$_2$)$_3$. In the vibrational spectra, we observed an intense valence vibration ν (As=O) at 935 cm^{-1} (IR) and 925 cm^{-1} (RE), respectively, compared with ν (As=O) in $Me_3As{=}O$ [16] or $Ph_3As{=}O$ [17] at 903 cm^{-1} or 881 cm^{-1}, indicating a high contribution of double-bond character in the As–O bond.

Single crystal X-ray analysis [10] revealed the following details of the molecular geometry: In **HMAsT** the arsenic atom is almost tetrahedrally surrounded by one oxygen atom and three nitrogen atoms of the dimethylamino groups, bond angles varying from 100° to 117° (see Figure 1). The arsenic–oxygen bond distance of 162.5(4) pm is identical to that in $Me_3As{=}O$ [18] and $Cl_3As{=}O$ [19]. From the Figure it is obvious that two methyl groups of two different dimethylamino groups of a neighboring molecule are oriented in such a way that hydrogen bonding takes place through oxygen–hydrogen bond distances of only 248 (H12) and 259 (H52) pm. The significance of $C(sp^3)$–H-bonding, directed to oxygen or nitrogen functions of neighboring molecules has been intensively reviewed, e.g., for glycine, acetic acid and related molecules [20]. Unfortunately, comparison of the structure of **HMAsT** with $As(NMe_2)_3$ or even with $O{=}P(NMe_2)_3$ is impossible because crystal structures of these molecules are not available: only the crystal data of some metal complexes of $O{=}P(NMe_2)_3$ [11, 12] are known.

The chemical application of **HMAsT** may be limited in view of the assumed toxicity of all arsenic derivatives, its relatively sophisticated synthesis (Equation 5), and its oxidative properties (reacting from As(V) → As(III), which may well prohibit the formation of adducts analogous to those of HMPT. We are exploring the coordination chemistry of this compound with various metal ions and its potential use for the synthesis of the elusive $As(NMe_2)_5$.

SYNTHESIS

Reactions are carried out in Argon atmosphere. To a solution of 8.71 g (42.00 mmol) of $As(NMe_2)_3$ [7] in 40 ml of *n*-hexane, 7.49 g (42.00 mmol) of $(Me_3Si)_2O_2$ [6] was added at room temperature and stirred for some hours. After 50 h a main crop of the product, crystallizing in thin, colorless platelets, was filtered off. After drying *in vacuo*, 6.30 g (28.2 mmol) of **HMAsT** was obtained (67.2% theory), mp. 45–46.5°C (uncorr.). The compound may be resublimed at 4×10^{-3} mbar, but with great loss of substance.

Molecular weight (cryosc. in benzene) 228.5 (theory: 223.15 g/mol). ^{1}HNMR (C_6D_6): 2.53 ppm (s); $As(NMe_2)_3$: 2.59 ppm (s). Elemental analyses: Calc. for $C_6H_{18}N_3AsO$ C 32.29, H 8.13, N 18.83%; found: C 32.01, H 8.05, N 18.81%.

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[10] Structural analysis: **HMAsT** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell; a = 645.4(3), b = 2561.7(8), c = 648,0(2) pm, β = 102.63°(4), V = 1045.43 $Å^3$. A platelet with the dimensions 0.4 × 0.4 × 0.1 mm was mounted on a four-circle diffractometer CAD4 (Enraf-Nonius) and measured at −95°C with CuK_α radiation (graphite monochromator, absorption coefficient μ = 41.0 cm^{-1}). For θ = 2° to 60° (with h = −7 to +7, k = 0 to 28 and l = −7 to +7) 3117 reflections were measured with the $\omega/2\theta$ scan method; out of these, 1331 symmetry independent reflections have been taken for the structural solution with Patterson methods (SHELXS-86 [13]). After an empirical correction for absorption (psi scans) all positional parameters, also those of the hydrogen atoms, could be freely refined. Anisotropic temperature factors have been used for the heavier atoms whereas for the hydrogen atoms isotropic temperature factors have been used for the refinement (SHELX-76 [14]). By using weights $w = 1/\sigma^2 (F_o)$ and applying an extinction correction ($\epsilon = 8.0 \times 10^{-7}$), we obtained R = 0.0539 or wR = 0.0500. Details of the crystallographic work may be obtained from the "Fachinformationszentrum Energie, Physik, Mathematik GmbH," D-7514 Eggenstein-Leopoldshafen 2, Germany, with quotation of the deposition number CSD-55436, names of the authors, and full citation of the journal.

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