# Synthesis and *X*-Ray Crystal Structure of a Macrocyclic Arsa-aza-oxa-cryptand containing Eight-membered $As_4O_4$ Rings

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Reaction of $N[(CH_2)_2As(C_6H_5)_2]_3$ (**1**) with gaseous HI leads to $\{HN[(CH_2)_2AsI_2]_3\}I$ (**2**) and hydrolysis of (**2**) with $H_2O$–$NH_3$ in tetrahydrofuran gives $[N(CH_2CH_2)_3]_8(As_4O_4)_6$ (**3**); single crystal *X*-ray diffraction shows that one molecule of (**3**) contains six eight-membered $As_4O_4$ rings connected together by triethylamine units.

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In several papers we have reported on organoarsenic cage compounds with nortricyclene, noradamantane, and adamantane structures.[1–6] The present paper describes the synthesis and the crystal and molecular structure of a macrocyclic arsa-aza-oxa-cryptand which, as a special feature, contains six crown-shaped, waved, eight-membered $As_4O_4$ rings (similar to sulphur-$S_8$ rings).

When $\{HN[(CH_2)_2AsI_2]_3\}I$ (**2**),[7] which is accessible, according to equation (1), by selective cleavage of phenyl groups[8] from $N[(CH_2)_2As(C_6H_5)_2]_3$ (**1**)[7,9] with HI, was allowed to react with $H_2O$–$NH_3$ in tetrahydrofuran (THF), according to equation (2) the macrocyclic arsa-aza-oxa-cryptand (**3**) was formed. After addition of conc. $NH_3$ to a suspension of (**2**) in THF an immediate decolourization of the yellow reaction mixture occured to give a clear solution, from which (**3**) precipitated after evaporation of THF at room temperature [63.5%, colourless crystals, $\nu(As_4O_4)$ 740vs and $\nu(AsC)$ 596s cm$^{-1}$]. In a mass spectrometer (**3**) could not be evaporated without decomposition, however, the molecular mass was established by osmometric determination. The $^1H$ n.m.r. spectrum of (**3**) ([$^2H_5$]pyridine, $SiMe_4$ int.) reveals two multiplets at $\delta$ 2.35 (72H, N-C*H*[H] and As-C$H_2$) and 3.20 (24H, N-CH[*H*]). The down-field shift of the 24 protons of the *N*-bonded methyl groups can be explained from the organo-

$$\underset{(1)}{N[(CH_2)_2As(C_6H_5)_2]_3} + 7HI \xrightarrow{CH_2Cl_2} \underset{(2)}{\{HN[(CH_2)_2AsI_2]_3\}I} + 6C_6H_6 \quad (1)$$

$$8(2) + 24H_2O + 56NH_3 \xrightarrow{THF} \underset{(3)}{[N(CH_2CH_2)_3]_8(As_4O_4)_6} + 56NH_4I \quad (2)$$

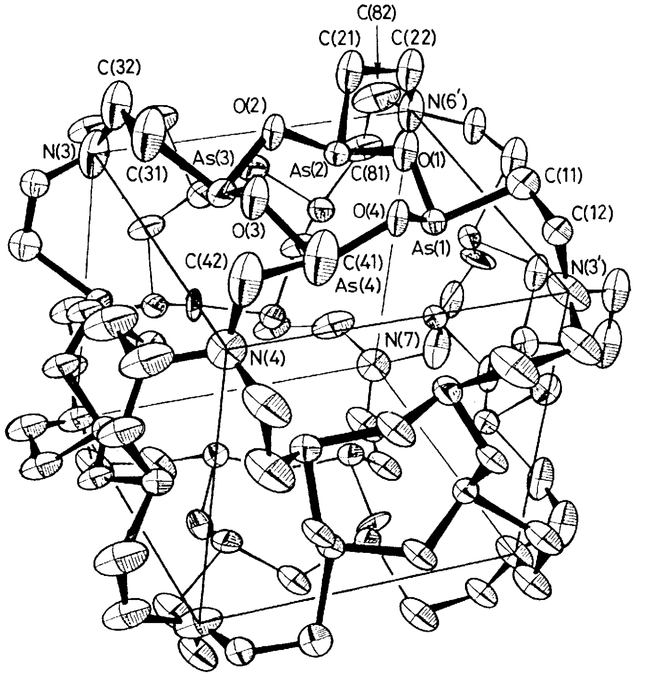

**Figure 1.** General view of a molecule of (**3**) with the atoms represented by their 50% probability ellipsoids for thermal motion.

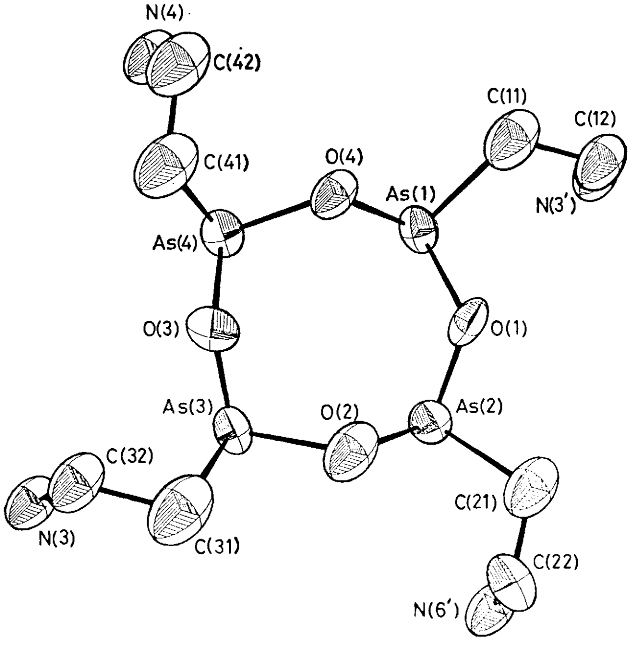

**Figure 2.** Projection from above of an arsenic–oxygen eight-membered ring. Distances (pm): As(1)–O(1) 181(2), O(1)–As(2) 173(2), As(2)–O(2) 175(3), O(2)–As(3) 183(2), As(3)–O(3) 176(3), O(3)–As(4) 181(3), As(4)–O(4) 181(2), O(4)–As(1) 183(2), As(1)–C(11) 205(4), As(2)–C(21) 192(3), As(3)–C(31) 205(4), As(4)–C(41) 177(4), C(11)–C(12) 152(6), C(21)–C(22) 148(6), C(31)–C(32) 156(5), C(41)–C(42) 158(8), C(12)–N(3') 150(6), C(22)–N(6') 141(6), C(32)–N(3) 153(4), and C(42)–N(4) 159(5). Angles (°): O(4)–As(1)–O(1) 102(1), O(4)–As(1)–C(11) 92(1), O(1)–As(1)–C(11) 96(1), O(1)–As(2)–O(2) 102(1), O(1)–As(2)–C(21) 95(1), O(2)–As(2)–C(21) 95(2), O(2)–As(3)–O(3) 101(1), O(2)–As(3)–C(31) 93(1), O(3)–As(3)–C(31) 96(2), O(3)–As(4)–O(4) 101(1), O(3)–As(4)–C(41) 92(2), O(4)–As(4)–C(41) 94(1), As(1)–O(1)–As(2) 119(1), As(2)–O(2)–As(3) 118(1), As(3)–O(3)–As(4) 118(1), As(4)–O(4)–As(1) 115(1), As(1)–C(11)–C(12) 108(2), As(2)–C(21)–C(22) 112(2), As(3)–C(31)–C(32) 105(2), As(4)–C(41)–C(42) 113(4), C(11)–C(12)–N(3') 115(3), C(21)–C(22)–N(6') 110(3), C(31)–C(32)–N(3) 112(3), and C(41)–C(42)–N(4) 108(3).

arsenic cage structure of (**3**) by the interaction of these protons with the oxygen atoms of the $As_4O_4$ rings.

*Crystal data:* $C_{48}H_{96}As_{24}N_8O_{24}$, $M = 2967.46$, hexagonal, space group $P\bar{3}$, $a = 1565.5(5)$, $c = 2336.2(8)$ pm, $Z = 2$, $D_c = 1.987$ g cm$^{-3}$, $D_m = 1.995$ g cm$^{-3}$, $F(000) = 2848$, $\mu(\text{Mo-}K_\alpha) = 78.1$ cm$^{-1}$. The structure was refined to $R = 0.087$ for 1831 independent reflections [$I \geqslant 3\sigma(I), 6 \leqslant 2\theta \leqslant 50°$, Enraf-Nonius CAD-4].†

The *X*-ray structure shows that one molecule of (**3**) consists of six eight-membered $As_4O_4$ rings which are connected together by the triethylamine units linked to arsenic. The eight nitrogen atoms occupy the corners of a trigonally distorted cube, on the surfaces of which the crown-shaped arsenic–oxygen rings are roughly located (Figure 1). One of these rings is shown in Figure 2 from above and for illustration of the ring conformation a side-view (Figure 3) is also given.

The atoms N(4) and N(7) are located on a crystallographic threefold axis, so that the molecule has $C_3$ symmetry. In comparison with the sum of the covalent radii[10] and other similar examples,[11] the As–O bonds having an average length of 179 pm are clearly shortened and seem to have partial $\pi$-character. The arsenic–carbon, carbon–carbon, and carbon–nitrogen distances are similar to the values reported for corresponding single bonds.[2,12,13]

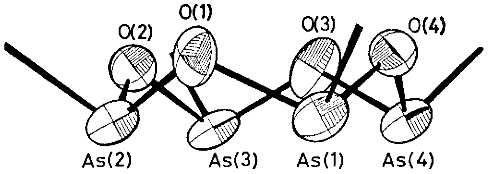

**Figure 3.** Projection of a side view of an arsenic–oxygen eight-membered ring.

Further evidence for the presence of As–O bonds with partial $\pi$ character is given by the enlarged As–O–As and O–As–O angles (115—120° and 99—104°, respectively), whereas those angles which involve carbon atoms are found, as expected, between 92 and 97°.

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† The structure was solved by direct methods and Fourier-difference synthesis, and anisotropically refined using the SHELX-76 program [except for H, C(81), and C(82)]. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.