Preparation and Structure of an Unsupported Arsoxane (RAsO) Ring

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The cyclic arsoxane, [(mesityl)AsO]$_4$, has been prepared and characterised by *X*-ray crystallography.

The known structures involving organoarsoxane ring systems are either connected *via* organic bridges[1] or co-ordinated to metal carbonyl fragments.[2] This has led to the suggestion that (RAsO)$_n$ rings 'may be difficult to isolate without a superstructure.'[2] We have now succeeded in isolating and structurally characterising [(mesityl)AsO]$_4$, the first example of an unsupported arsoxane ring.

Mesityldichloroarsine[3] was treated with an excess of KOH in 1,2-dimethoxyethane (DME) for 12 h at 25 °C. Following solvent removal, mass spectrometric assay of the resulting white residue indicated the formation of [(mesityl)AsO]$_4$ (**1**) (*m*/*z* 840) together with smaller amounts of (mesityl)$_2$AsOAs(mesityl)$_2$ (*m*/*z* 642), [(mesityl)$_2$AsO]$_2$As(mesityl) (*m*/*z* 852), and As$_4$O$_6$.† Dissolution of the residue in n-hexane, filtration, concentration, and storage at −20 °C resulted in colourless crystals of (**1**) of *X*-ray quality in ~10% yield.

Molecules of (**1**) comprise an eight-membered ring of alternating As and O atoms (Figure 1).‡ The As$_4$O$_4$ ring conformation is approximately crown shaped (Figure 2) and hence reminiscent of the structure of S$_8$. The four oxygen atoms are approximately planar, the deviations from the least squares plane being O(1) (0.017), O(2) (−0.016), O(3) (0.016), and O(4) (−0.016 Å). Interestingly, the average transannular oxygen–oxygen distance in (**1**) (3.845 Å) is close to that in dibenzo-14-crown-4 (3.77 Å)[4] thus suggesting that, like the latter and 12-crown-4,[5] (**1**) may behave as an ionophore for Li$^+$.

The average As–O bond length [1.790(15) Å] and O–As–O angle [98.9(7)°] in (**1**) are similar to those found in other As^{III}–O structures.[1,2] However, whilst the average As–O–As angle in (**1**) [117.3(8)°] is comparable to those in [N(CH$_2$CH$_2$)$_3$]$_8$(As$_4$O$_4$)$_6$ and [(MeAsO)$_6${Mo(CO)$_3$}$_2$], it is appreciably smaller than those in As$_3$O$_3$[(CH$_2$)$_3$CMe][1a] and As$_4$O$_4$(CH$_2$)$_2$,[1b] which fall in the range 127—179°.

We have attempted to synthesise smaller arsoxane rings by increasing the steric demands of the aryl substituent. However, treatment of (2,4,6-Bu$^t_3$C$_6$H$_2$)AsF$_2$[6] with KOH in DME resulted in (**2**), which was characterised on the basis of analytical and spectroscopic data.

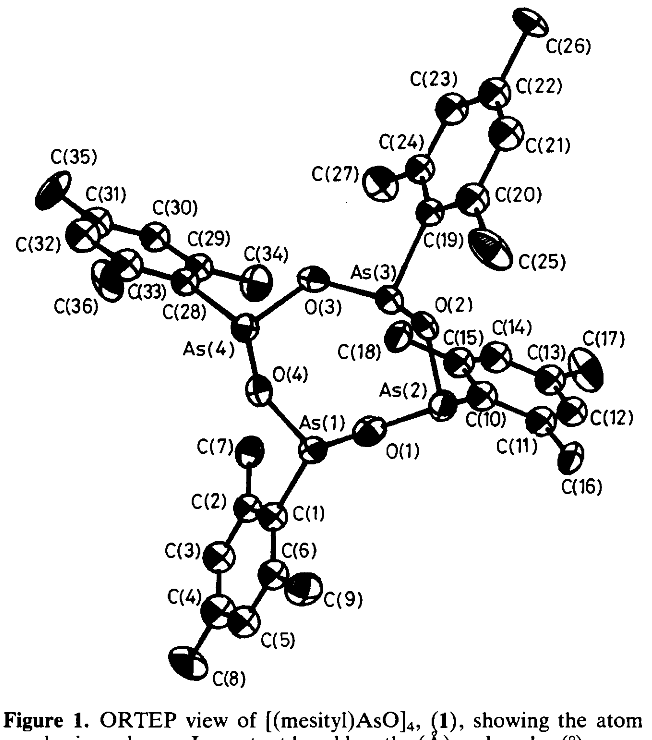


Figure 1. ORTEP view of [(mesityl)AsO]$_4$, (**1**), showing the atom numbering scheme. Important bond lengths (Å) and angles (°) are as follows: As(1)–O(1) 1.790(15), As(1)–O(4) 1.770(15), As(2)–O(1) 1.790(15), As(2)–O(2) 1.784(14), As(3)–O(2) 1.787(15), As(3)–O(3) 1.792(14), As(4)–O(3) 1.794(13), As(4)–O(4) 1.809(13); O(4)–As(1)–O(1) 98.1(7), As(1)–O(1)–As(2) 114.5(8), O(1)–As(2)–O(2) 99.3(7), As(2)–O(2)–As(3) 118.8(8), O(2)–As(3)–O(3) 97.6(7), As(3)–O(3)–As(4) 118.1(8), O(3)–As(4)–O(4) 100.5(6), As(4)–O(4)–As(1) 117.7(8).

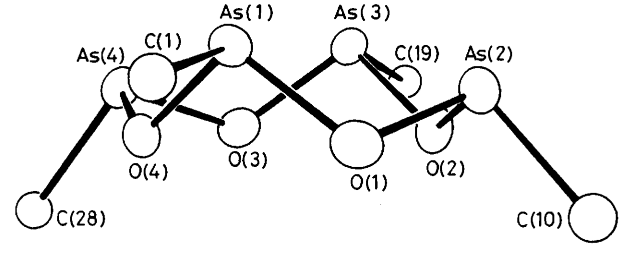
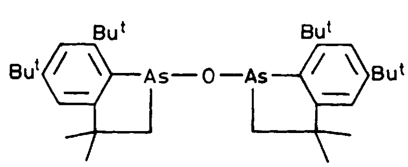


Figure 2. ORTEP view showing the crown-like conformation of the As$_4$O$_4$ ring of [(mesityl)AsO]$_4$, (**1**).



(**2**)

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† Presumably, the last three products arise from the dismutation, 2(mesityl)AsCl$_2$ → (mesityl)$_2$AsCl + AsCl$_3$.

‡ *Crystal data* for (**1**): C$_{36}$H$_{44}$As$_4$O$_4$, M = 840.44, monoclinic, space group $P2_1/c$ (No. 14), a = 10.988(3), b = 14.413(2), c = 23.513(6) Å, β = 94.53(2)°, U = 3712.1 Å^3, Z = 4, D_c = 1.504 g cm^{-3}, μ(Mo-K_α) = 35.9 cm^{-1}. A total of 5505 unique reflections were measured on an Enraf–Nonius CAD4 diffractometer over the range $3.0 \leqslant 2\theta \leqslant 48.0°$ using the $\theta/2\theta$ scan technique. The data were corrected for Lorentz, polarisation, and decay effects. An empirical absorption correction was also applied. The structure was solved (direct methods) and refined (difference Fourier, full-matrix, least-squares) using 1842 reflections with $I > 3.0\sigma(I)$. The final residuals were R = 0.0602 and R_w = 0.0715.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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