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Synthesis and Structure of an Organocyclotriarsinetrioxide

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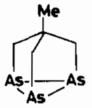
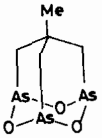
While organocycloarsines $(RAs)_n$ with n = 4, 5 and 6 have been well documented [1], only recently has the synthesis and structure of an organocyclotriarsine been reported [2]. The compound is interesting, not



only because of its constrained, all *cis* structure and possible polyfunctional ligative properties, but also because it represents the interface between cyclopolyarsines and arsenic or other pnicnide polycyclic cage compounds. We herein report the synthesis, characterization, and crystal structure of 5-methyl-1,3,7-triarsa-2,8,10-trioxaadamantane (*2*), which can be considered to be a structural derivative of *1* formed by insertion of an oxygen atom into each of



of three As–As bonds. Compound *2* can also be viewed as an organo-analogue to As_4O_6 containing the $(AsO)_3$ ring with an adamantoid structure.

Compound *2* was synthesized in a similar manner to compound *1* [2]:

$$CH_3C(CH_2OH)_3 \xrightarrow{PBr_3} CH_3C(CH_2Br)_3$$

$$\xrightarrow[NH_3(l)]{Na(As\phi_2)_3} CH_3C(CH_2As\phi_2)_3 \xrightarrow{HI}$$

$$CH_3C(CH_2AsI_2)_3 \xrightarrow[THF]{Na} CH_3C(CH_2AsO)_3 \qquad (2)$$

The reaction of $CH_3C(CH_2AsI_2)_3$ with Na [2] initially produces $CH_3C(CH_2As)_3$ (*1*). Extended contact of *1* with Na results in the cleavage of As–As bonds [1] to form very reactive sodium organoarsenide salts $As_n^+CH_3C(CH_2As)_3^{n-}$, which abstract oxygen atoms from THF after prolonged contact to form the product *2*. As indicated in Figure 1, the compound has approximately C_{3v} symmetry. It is soluble in most common organic solvents. The infrared spectrum shows a broad strong absorption corresponding to the $(AsO)_3$ ring stretching vibration as in As_4O_6. Although *2* does not react at room temperature as a Lewis base towards diborane, preliminary studies indicate that *2* does react with Group VIb metal carbonyls.

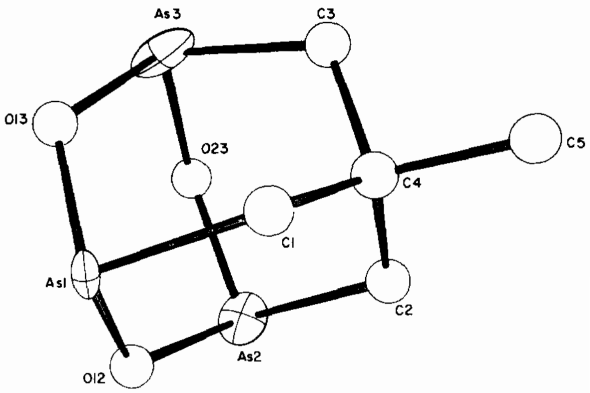


Figure 1. A general view of the molecule. The thermal ellipsoids are 50% probability envelopes for the arsenic atoms and of convenient size for the oxygen and carbon atoms. The average value of the As–As distances is 3.165 Å while the average for the As–O, As–C and C–C distances are, respectively, 1.77, 1.96 and 1.53 Å. The average value of the non-bonded O–O distances is 2.73 Å. Finally, the average values of the O–As–O and O–As–C angles are 100.5 and 97.7°. Errors in the As–As distances are 0.007 Å; As–O about 0.03 Å, C–C about 0.05 Å while the errors in the angles are, on the average, about 1.5° at this stage of the refinement.

Experimental

5-Methyl-1-3,7-triarsa-2,8,10-trioxaadamantane

To 0.70 g (30 mmol) of Na in 20 ml of dry, deoxygenated THF was slowly added 1.02 g (0.97 mmol) of 1,1,1-tris-(diodoarsinomethyl)ethane, $CH_3C(CH_2AsI_2)_3$ [2]. After addition was completed, the mixture was heated to reflux for 2 h and then cooled with stirring for several more hours, and was then filtered to remove unreacted Na and NaI. The residue was washed 3 times with a total of 30 ml of diethyl ether. The filtrate and washings were combined, and the solvents were removed by vacuum vapor transfer. The orange solid was sublimed several times (0.05 torr, 70–90 °C) to yield colorless

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TABLE I. Positional Parameters for the Molecule.

Atom	x	y	z
As 1	0.5038(5)[a]	0.4589(6)	0.2029(5)
As 2	0.2955(4)	0.6950(6)	0.1059(5)
As 3	0.3467(5)	0.6384(7)	0.4218(5)
O 12	0.3896(29)	0.5129(37)	0.0894(28)
O 13	0.4362(38)	0.4670(35)	0.3592(28)
O 23	0.2545(24)	0.6714(31)	0.2784(21)
C 1	0.5852(42)	0.6596(49)	0.2330(41)
C 2	0.4342(30)	0.8465(52)	0.1303(34)
C 3	0.4613(37)	0.8132(48)	0.3884(36)
C 4	0.5227(41)	0.8141(56)	0.2461(40)
C 5	0.6118(53)	0.9633(60)	0.2536(50)

[a] The numbers in parenthesis are the estimated standard deviations in the least significant digits.

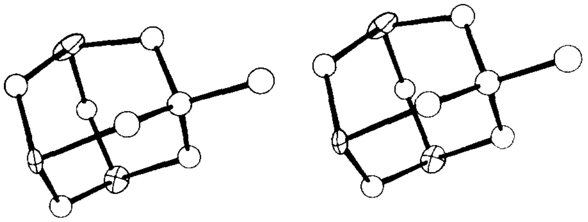

Figure 2. A stereopair of the molecule.

crystals, mp 234–236 °C. *Anal.* Calcd. for $As_3C_5H_9O_3$: C, 17.57; H, 2.65. Found: C, 17.84; H, 2.57. Yield, 43%. Proton NMR spectroscopy in $CDCl_3$ showed two singlets in a ratio of 2:1 at 1.95 (CH_2) and 1.1 (CH_3) ppm respectively from TMS. Infrared absorbances (fluorocarbon mull, KBr): 1420 (vw), 1280 (sh), 1270 (m), 1195 (s), 1085 (m), 790 (sh), 745–730 (s), 550 (w) and 525 (w) cm^{-1}. The mass spectrum showed a very weak parent peak with other expected fragments analogous to *1* [2].

Crystal Data

A colorless, transparent, crystal was sealed in a capillary tube and used for data collection. The unit cell dimensions were obtained from the centering of 37 reflections falling in the range $25° \leqslant 2\theta \leqslant 32°$: $a = 11.093(5)$, $b = 8.340(2)$, $c = 9.777(4)$ Å and $\beta = 91.47(3)°$; $V = 904.23$ Å^3, d(calc) = 2.51 g cm^{-3} for $Z = 4$ molecules/unit cell. The space group is $P2_1/n$. The data (1733 reflections of which 765 were above $3\sigma[I]$) were collected by methods described in detail elsewhere [3, 4]. Throughout, MoKα radiation was used with a computer-controlled Enraf-Nonius CAD-4 diffractometer. The current R(F) and $R_w(F)$ indices are 0.097 and 0.088 and the weighting scheme was $w = 1/\sigma^2(|F_o|)$. The molecule is described by the ORTEP plot shown in Figure 1. Positional parameters are given in Table I.

Acknowledgments

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