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Preliminary communication

STRUCTURE AND DYNAMIC STEREOCHEMISTRY OF A FIVE-COORDINATE SPIROARSORANE

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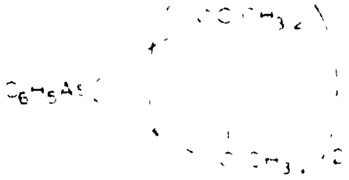
Summary

The geometry about arsenic in 2,2,3,3,7,7,8,8-octamethyl-5-phenyl-1,4,6,9-tetraoxa-5-arsaspiro[4,4]nonane has been determined by X-ray diffraction as distorted square pyramidal, leading to a revised interpretation of the NMR spectra of this compound.

A number of five coordinate spiroarsoranes have been found by proton NMR studies to display stereochemical non-rigidity [1, 2]. This phenomenon has been analysed by us [1] and by others [2], with somewhat differing conclusions, by consideration of interconversions of trigonal bipyramidal structures, since this geometry has been assumed to be the norm for five coordinate arsenic systems [3]. The prevalent geometry of five coordinate compounds of the main group, Group V elements is trigonal bipyramidal, but there are now a number of five coordinate phosphorus structures known in which the geometry is either irregular [4] or close to square pyramidal [5, 6].

We have now carried out a crystal structure determination and ^{13}C NMR observations on a spiroarsorane, 2,2,3,3,7,7,8,8-octamethyl-5-phenyl-1,4,6,9-tetraoxa-5-arsaspiro[4,4]nonane (I) [7], and have found that the trigonal bipyramidal structure assumed in earlier discussions [1, 2] is not, in fact, observed for this compound in the solid state.



(I)

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Crystal data compound I: $AsC_{18}H_{29}O_4$, mol. wt. 384.30, monoclinic, a = 9.150, b = 12.699, c = 17.386 Å, β 103.73°, V 1962 Å^3, $Z = 4$, $D_{calc.}$ 1.18 g cm^{-3}, D_{obs} 1.20 g cm^{-3}, space group $P2_1/c$ as determined from extinctions.

Data were collected using Mo-K_α radiation, graphite monochromatised, on an automated Syntex $P2_1$ diffractometer. The structures were solved by the heavy-atom method. The R value is, at the present state of refinement, 0.107 (2432 reflections) for I, using anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atoms have not yet been completely located.

The molecular geometry of I is displayed in Fig. 1. Bond angles about arsenic are given in Table 1. Bond lengths for the AsO and AsC bonds fall within normal ranges. As the data and Fig. 1 suggest, the geometry about arsenic is neither of the idealised geometries often assumed for five-coordination. The geometry lies between square pyramidal and trigonal bipyramidal. The furthest deviation of an oxygen atom from the least squares plane of the four oxygen atoms is less than 0.25 Å. Furthermore, angles between the ligand carbon and the four oxygen atoms range from 94 to 118°. These angles bracket the value of 104° calculated for an idealised electrostatic model of square pyramidal five-coordination [8]. In angular terms the geometry of this spiroarsorane is quite close to that of a square pyramidal spirophosphorane recently described [5].

We have also carried out a low temperature ^{13}C NMR study of compound (I). The ^{13}C NMR results are (chemical shifts, δ, in ppm, downfield from internal tetramethylsilane; CS_2 solution): two peaks for $\underline{C}H_3$ groups (at 24.40 and 24.99 at 309 K); one peak for $\underline{C}O$ (at 76.58 at 309K); $\underline{C}_6H_5$ multiplet (from 127—133; at 309K); all peak multiplicities were invariant from 309 down to 173 K.

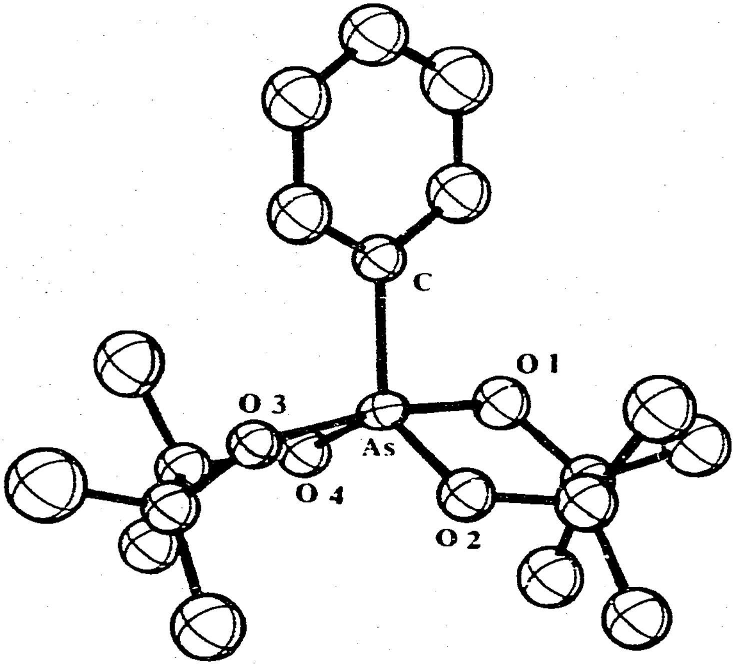

Fig. 1. Geometry about arsenic in compound I.

TABLE 1

BOND ANGLES[a] ABOUT ARSENIC (°) IN COMPOUND 1

O(1)—As—O(2)	87.4	O(2)—As—C	117.4
O(3)—As—O(4)	88.3	O(3)—As—C	95.7
O(1)—As—O(4)	87.3	O(4)—As—C	118.0
O(2)—As—O(3)	87.5	O(1)—As—O(3)	169.8
O(1)—As—C	94.5	O(2)—As—O(4)	124.6

[a] Estimated standard deviation for all angles is ±0 3°.

The interpretation of these NMR measurements must now be based not, as earlier discussions were [1, 2], on idealised trigonal bipyramidal structures, but on the more distorted structure shown by the crystal structure determination. The low temperature result, with only one ^{13}C peak for the ring $\underline{C}$O carbons, but with two for the methyl groups attached to the ring, encourages an interpretation in terms of a rapidly flexing but, on a time-average, essentially square pyramidal structure about arsenic with the phenyl ligand at the apex of the pyramid and with the four oxygen atoms at the base. It seems reasonable to suggest that the high temperature averaging in proton NMR of the two methyl signals described previously [2] may represent the transformation of the lower energy square pyramidal form to a higher energy trigonal bipyramidal form which can undergo pseudorotation (Berry ligand interchange) to time-average the methyl group environments. The reported activation energy [2] for this process presumably includes both the activation energy for rearrangement to trigonal bipyramid and that for ligand interchange.

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