The Structure and Conformation of 5,10-Dihydro-5,10-dimethylarsanthren

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CONSIDERATION of the implications of intervalency angles led Chatt and Mann[1] to predict that if, in a 5,10-disubstituted 5,10-dihydroarsanthren (I), the intervalency angles at the arsenic atoms retained their normal value of *ca.* 98°, the molecule (I) must be folded along the As–As axis to give a 'butterfly' conformation, and that the molecule should exist therefore in a *cis*-form in which the groups R were within the angle subtended by the two *o*-phenylene groups, and in a *trans*-form in which one of these

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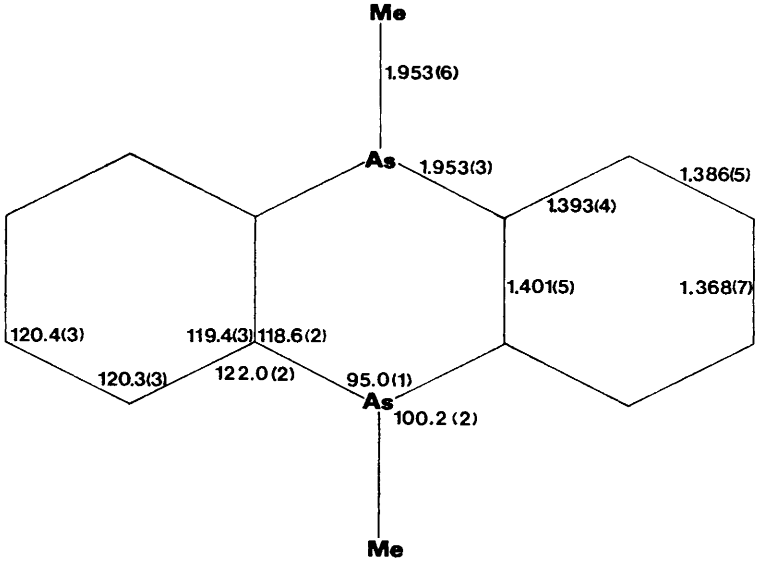
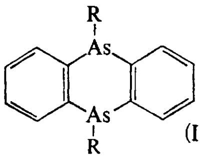
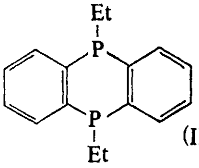


FIGURE

groups was within and the other without this angle. The calculated value for this angle was 121°[2]. On this basis, 5,10-dihydro-5,10-di-*p*-tolylarsanthren (I; R = C_6H_4Me) was synthesised and separated into two stable isomers.



(I)



(II)

5,10-Diethyl-5,10-dihydrophosphanthren (II) was later synthesised and separated into two isomers, the chemical evidence indicating strongly that the isomer formed in the greater quantity had the *cis*-configuration.[3]

No concrete evidence for the 'butterfly' conformation has hitherto been available, although the circumstantial evidence was strong. There remained a remote possibility that the tricyclic system in (I) and (II) was flat and that the isomerism resulted from the pyramidal configuration of the arsenic (or phosphorus) atoms.[4]

We have now subjected 5,10-dihydro-5,10-dimethylarsanthren (I; R = Me), of which only one form has been isolated,[5] to an *X*-ray crystallographic study. The salient points, outlined below, show conclusively that this compound has the 'butterfly' conformation and consists solely of the form having *cis*-methyl groups.

Decisive evidence for the accuracy of the earlier predictions regarding conformation in this series has thus been obtained.

Crystal data: $C_{14}H_{14}As_2$: Orthorhombic. Dipyramidal. $a = 11{\cdot}106 \pm 7, b = 11{\cdot}296 \pm 7, c = 10{\cdot}251 \pm 6$ Å; $Z = 4$; Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å. Space group *Cmcm*, from systematic absences and structure determination.

The cell dimensions and intensities of 670 reflections were measured using a Picker automatic diffractometer in the 2θ scan mode. The structure was solved by the heavy-atom technique and refined by full-matrix least-squares to a discrepancy index R of 3·1%. The bond distances and angles, with standard deviations in parentheses, are shown in the Figure. One of the carbon–carbon bonds is rather short (1·368 Å). This effect is thought to be related to the thermal vibrations of the atoms and will be discussed in a later paper.

The molecule exists in the *cis*-form relative to the methyl groups and has *mm* symmetry. The angle between the two wings of the 'butterfly' conformation is 117°, which is in good agreement with the calculated value of 121°. The angle between the two As–Me bonds is 120·5° and each As atom lies 0·04 Å (about 8σ) out of plane with the benzene rings.

Full details of the structural analysis will be published later.

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