

Patrice de Meester and Shirley S. C. Chu*

School of Engineering and Applied Science, Southern Methodist University,
Dallas, Texas 75275

Misa V. Jovanovic and Edward R. Biehl*

Department of Chemistry, Southern Methodist University,
Dallas, Texas 75275

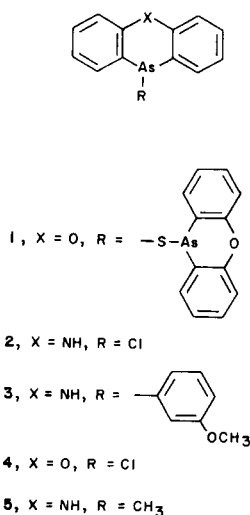
Received October 18, 1985

The X-ray crystal structure of 5-methyl-5,10-dihydrophenarsazine, $C_{13}H_{12}NAs$, has been determined. The crystals are orthorhombic, space group $P2_12_1$, $a = 8.511(4)$, $b = 5.690(1)$, $c = 23.535(9)$ Å, $V = 1139.7(1.0)$ Å³, and $Z = 4$. Least-squares refinement converged to $R = 0.049$ and $R_w = 0.045$. The central ring is in a boat conformation and the 5-methyl group is in the axial position with respect to the central ring. The folding angle between the planes of the two benzo rings is $154.1(4)^\circ$.

J. Heterocyclic Chem., **23**, 1131 (1986).

Introduction.

The X-ray structural data available for arsenic-containing tricyclic rings are limited; however, they indicate that the folding angle (dihedral angle) between the two benzo rings of these compounds is influenced by substituents and other central ring heteroatoms. For example, 5-phenoxarsine sulfide, **1**, exists as two independent molecules in the solid state with dihedral angles of 175.2° and 178.5° . These values show that **1** is essentially a planar molecule [1]. However, 5-chloro-5,10-dihydrophenarsazine, **2**, 3'-methoxy-5-phenyl-5,10-dihydrophenarsazine, **3**, and 5-phenoxarsine chloride, **4**, have dihedral angles of 169.2° [2], 164.6° [3] and 156.3° [4], respectively, which show that these compounds are folded about the line passing through two heteroatoms of the central ring. In order to



obtain more information on the influence of substituents on the conformation of phenarsazines, the crystal structure of 5-methyl-5,10-dihydrophenarsazine, **5**, was determined and is reported herein.

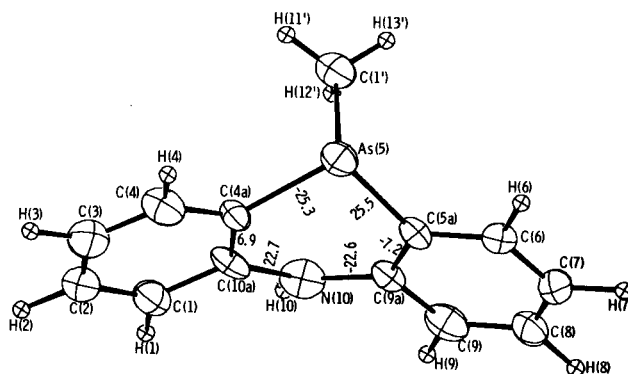


Figure 1

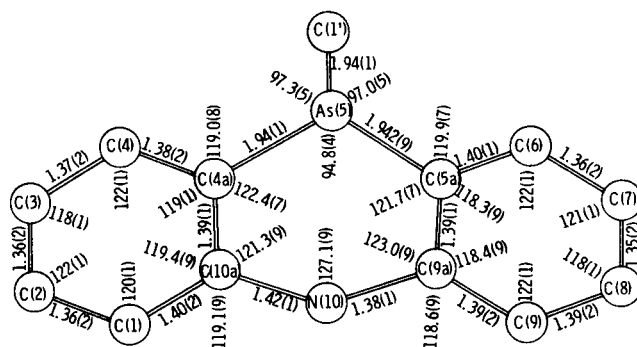


Figure 2

EXPERIMENTAL

Synthesis of 5-Methyl-5,10-dihydrophenarsazine, **5**.

To a stirred solution containing 2.77 g (0.021 mole) of 5-chloro-5,10-dihydrophenarsazine, **2**, in 25 ml of anhydrous ether under nitrogen atmosphere, a solution of 3.49 g (0.021 mole) of methylmagnesium iodide in 25 ml of anhydrous ether was added slowly at room temperature. The solution was stirred for 30 minutes after the addition. Water was then ad-

Table 1

Fractional atomic coordinates and thermal parameters ($\times 10^4$) for non-hydrogen and ($\times 10^3$) for hydrogen atoms. (The estimated standard deviations are given in parentheses and refer to the last positions of respective values.)

The expression for the thermal parameters with U values in \AA^2 is:

$$T = \exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}$$

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23
C(1)	-5834(13)	-2686(24)	795(6)	53(7)	72(8)	88(10)	-17(8)	14(6)	-9(7)
C(2)	-6314(14)	-1339(29)	350(5)	52(6)	119(12)	70(8)	-10(10)	-1(6)	-2(9)
C(3)	-5585(16)	710(29)	208(6)	73(9)	116(14)	75(9)	21(10)	-7(8)	9(10)
C(4)	-4323(13)	1418(26)	529(5)	60(7)	86(9)	80(8)	8(9)	2(6)	-5(8)
C(4A)	-3761(10)	91(17)	977(5)	40(5)	60(6)	65(6)	5(6)	15(5)	11(6)
AS(5)	-1885(1)	1136(2)	1375(0)	50(1)	52(1)	69(1)	7(1)	5(1)	-7(1)
C(5A)	-2362(10)	-551(15)	2071(4)	37(4)	45(6)	59(6)	2(5)	9(4)	1(4)
C(6)	-1662(12)	139(20)	2582(5)	46(6)	51(6)	81(8)	2(6)	1(6)	-1(6)
C(7)	-1869(13)	-1105(24)	3070(4)	58(6)	89(8)	54(6)	-7(8)	2(6)	7(9)
C(8)	-2773(11)	-3054(22)	3081(5)	46(7)	76(8)	75(8)	21(7)	10(6)	4(6)
C(9)	-3473(11)	-3787(19)	2577(5)	47(6)	46(6)	109(10)	16(8)	8(6)	-4(7)
C(9A)	-3299(10)	-2549(15)	2071(5)	35(5)	40(5)	78(7)	2(6)	13(6)	4(5)
N(10)	-4090(12)	-3331(17)	1596(4)	71(6)	46(6)	88(8)	-2(5)	-18(5)	-12(5)
C(10A)	-4533(10)	-1985(16)	1115(4)	44(5)	50(6)	67(7)	-5(6)	2(5)	-2(5)
C(1')	-449(13)	-1159(29)	1059(6)	45(6)	88(9)	81(9)	-9(10)	10(6)	5(8)
H(1)	-624(11)	-416(15)	89(4)	52(30)					
H(2)	-719(11)	-200(16)	11(4)	61(31)					
H(3)	-588(16)	134(23)	-9(5)	129(59)					
H(4)	-378(11)	292(17)	43(4)	69(31)					
H(6)	-115(9)	141(14)	255(3)	38(26)					
H(7)	-147(8)	-63(13)	339(3)	27(23)					
H(8)	-288(8)	-409(12)	353(3)	40(20)					
H(9)	-411(8)	-499(13)	253(3)	27(21)					
H(10)	-445(10)	-458(14)	154(4)	27(25)					
H(11')	-36(17)	-117(26)	66(1)	180(63)					
H(12')	-85(12)	-267(18)	112(4)	75(40)					
H(13')	49(6)	-161(17)	125(3)	74(32)					

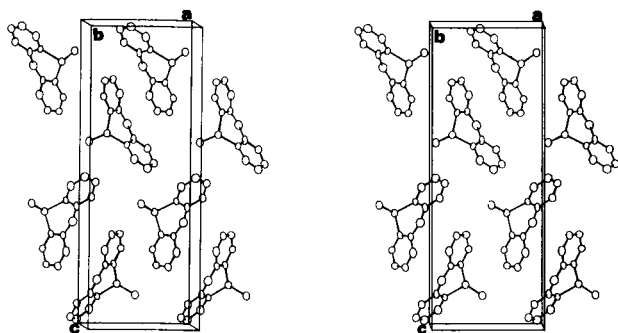


Figure 3

Table II

a) Puckering parameters

Central Ring

$$\begin{aligned} Q &= 0.387 \text{ \AA} \\ q_2 &= 0.373 \\ q_3 &= -0.102 \\ \theta &= 105.3^\circ \\ \phi_2 &= 359.4 \end{aligned}$$

Ideal boat conformation

$$\begin{aligned} q_2 &= Q \\ q_3 &= 0 \\ \theta &= 90 \\ \phi_2 &= 360 \end{aligned}$$

Table II (Continued)

b) Least-squares planes

Equation of the planes: $Ax + By + Cz = D$
(x, y, z in \AA along a, b, c)

Plane	A	B	C	D
a	-0.606(5)	0.502(5)	0.617(4)	3.39(2)
b	-0.802(3)	0.556(4)	0.218(5)	2.50(3)

Deviations in \AA from the planes (* refers to atoms not included in the calculation of the least-squares planes)

Plane a

Plane b

C(1)	0.007(17) \AA	C(5a)	-0.002(12) \AA
C(2)	-0.007(20)	C(6)	0.000(14)
C(3)	-0.005(20)	C(7)	-0.002(16)
C(4)	0.012(18)	C(8)	0.005(15)
C(4a)	-0.006(15)	C(9)	-0.007(14)
C(10a)	0.000(12)	C(9a)	0.006(14)
As(5)	-0.098(19)*	As(5)	-0.151(15)*
N(10)	0.086(18)*	N(10)	0.056(18)*

Folding angle between Plane a and Plane b: $154.1(4)^\circ$

ded carefully to neutralize excess Grignard reagent and the resulting emulsion extracted with three 30-ml portions of methylene chloride. The combined organic extracts were dried over magnesium sulfate, filtered, and evaporated to dryness. The solid residue was recrystallized from hexane to yield 1.80 g (70%) of **5**, mp 72-74°.

Solution and Refinement of Structure.

A crystal of approximate dimensions 0.60 × 0.30 × 0.05 mm was selected for the determination of the unit cell parameters, $a = 8.511(4)$, $b = 5.690$ and $c = 23.535$ Å which were obtained by least-squares fit of 15 reflections in the range of $18 < 2\theta < 24^\circ$. The data were collected on a Syntex P2, automatic diffractometer at 298°K at a scan rate ranging from 2.02 to 14.65°/minute with graphite monochromatized MoK α radiation (0.71069 Å). The space group, P2₁2₁2₁, was deduced from the systematic absences (h00 absent with h odd, Ok0 absent with k odd, and 00l with l odd). There are four formula units of weight 257.17 in the unit-cell and the calculated density is 1.499 g cm⁻³. The linear absorption coefficient of the crystal is 29.1 cm⁻¹. The intensity data were collected using the $\theta/2\theta$ mode. A total of 1563 independent reflections was measured to $2\theta = 55^\circ$, of which 843 were considered as observed with $I > 3\sigma(I)$, where $\sigma(I)$ was determined from counting statistics. The intensities of three standard reflections (200, 040, and 004), remeasured at 100 reflections intervals, showed no significant changes. The intensity data were reduced to structure amplitudes by application of the Lorentz and polarization factors. A correction for absorption was applied (transmission coefficients were in the range of 0.390 to 0.876). No extinction correction was applied.

The structure was solved by the standard Patterson and difference Fourier methods. Refinements were carried out by full-matrix least-squares using the SHELX 76 systems of programs [5]. Non-hydrogen atoms were refined anisotropically.

All hydrogen atoms were located and refined isotropically. The weight used in the last stages of refinements was $2.7(\sigma_F + 0.00056 F^2)$. The function $\sum w(|F_o| - |F_c|)^2$ was minimized. The effects of the anomalous dispersion of As were included in the calculation of F_c , the values of $\Delta f'$ and $\Delta f''$ being taken from the International Tables for X-ray Crystallography [6]. Refinements were carried out on both enantiomers (x, y, z) and ($-x, -y, -z$). Refinements shown in Table I converged to $R = 0.049$ and $R_w = 0.045$ for the coordinates (x, y, z) and to $R = 0.059$ for the reversed coordinates ($-x, -y, -z$). The maximum shift in the final cycle of refinement was 0.25. The final difference Fourier map showed a maximum residual electron density of 0.44 eÅ⁻³ in the vicinity of the As atom. The atomic scattering factors used for arsenic, nitrogen, carbon, and hydrogen were obtained from the International Tables for X-ray Crystallography [6]. The positional and thermal parameters are given in Table 1.

Results and Discussion.

The identification of the atoms and the configuration of the molecule are shown in the ORTEP [7] drawing of Figure 1. The phenarsazine ring is folded with the central ring in a boat conformation as shown by the torsion angles in Figure 1 and the Cremer and Pople [8] puckering parameters in Table IIa. The 5-methyl group is in the axial position with respect to the central ring of **5**. Substituents in the 5 position have been observed to occupy the axial position in other phenarsazines [2,3]. The folding angle of **5** is

154.1(4)°, which when compared to that of 10-methylphenothiazine, **6**, (143.7° [9]), shows that **5** is the more planar of these two methyl derivatives. The greater planarity of **5** as compared to **6** indicates that the central ring of the former has more aromatic character than the latter. Replacement of the 5-methyl substituent of phenarsazine by a chlorine atom results in an even more planar molecule (the dihedral angle of 5-chlorophenarsazine = 169° [2]) indicating that the electron-withdrawing chlorine atom participates in resonance with the tricyclic ring.

The bond lengths and bond angles with their standard deviations are shown in Figure 2. The mean C-As bond length of 1.94(1) Å is similar to that of 1.942(5) Å reported for 3'-methoxy-5-phenyl-5,10-dihydrophenarsazine, **3** [3]. However, it is longer than that of 5-chloro-5,10-dihydrophenarsazine, **2** (1.917(7) [2]), which is additional evidence for resonance interactions between the 5-chlorine atom and the tricyclic phenarsazine ring.

The packing of the molecules in the unit cell is shown in the stereoscopic drawing in Figure 3. There are no intermolecular contacts less than the van der Waals distances.

Supplementary Material.

A list of structure factors has been deposited and is available.

Acknowledgement.

Edward R. Biehl and Shirley S. C. Chu thank the Robert Welch Foundation for supporting this work.

REFERENCES AND NOTES

- [1] W. K. Grindstaff, A. W. Cordes, C. K. Fair, R. W. Perry and L. B. Handy, *Inorg. Chem.*, **11**, 1852 (1972).
- [2] A. Camerman and J. Trotter, *J. Chem. Soc.*, 730 (1965).
- [3] P. de Meester, S. S. C. Chu, M. V. Jovanovic and E. R. Biehl, *J. Heterocyclic Chem.*, **22**, 1237 (1985).
- [4] J. E. Stuckey, A. N. Cordes, L. B. Handy, R. W. Perry and C. K. Fair, *Inorg. Chem.*, **11**, 1846 (1972).
- [5] G. M. Sheldrick, SHELX76: Program for Crystal structure determination, University of Cambridge, England (1976).
- [6] International Tables for X-ray Crystallography, Vol. IV, Birmingham, Kynoch Press (1974).
- [7] C. K. Johnson, ORTEP (1965). Report ORNL-3794, Oak Ridge National Laboratory, Tennessee.
- [8] D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 1354 (1975).
- [9] S. S. C. Chu and D. van der Helm, *Acta. Cryst.*, **B30**, 2489 (1974).