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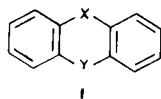
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The crystal structure of 3'-methoxy-5-phenyl-5,10-dihydrophenarsazine,  $\text{C}_{19}\text{H}_{16}\text{AsNO}$  has been determined by the single crystal x-ray diffraction method. The crystals are monoclinic with  $a = 15.305(6)$ ,  $b = 5.809(2)$ ,  $c = 17.595(6)$  Å,  $\beta = 92.92(2)^\circ$ ,  $V = 1562.3(1.0)$  Å<sup>3</sup>, space group  $P2_1/n$ ,  $Z = 4$  and  $d_{calc} = 1.485$  g cm<sup>-3</sup>. An automatic diffractometer with graphite monochromatized MoK $\alpha$  radiation was used to obtain 1480 observed reflection with  $I > 3\sigma(I)$  at  $2\theta < 50^\circ$ . Final  $R = 0.040$  and  $wR = 0.032$ . The tricyclic ring is folded with the central ring in a flattened boat conformation. The folding angle between the least-squares planes of the two benzo rings is  $164.6(2)^\circ$ . The 3'-methoxyphenyl group is in a boat-axial conformation with respect to the central ring.

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## Introduction.

Tricyclic system with structure **1** offers a unique model for assessing the "aromaticity" of such a system when X and Y are different heteroatoms or hetero-substituents. The tricyclic ring system is folded along the line passing through X and Y atoms. The magnitude of the folding angle can be used as a measure of the geometrical distortion of the tricyclic system from planarity as illustrated in Fig. 1. For a planar system, the folding angle is  $180^\circ$ . The extent and contribution of electron delocalization by X and Y are directly related to the type and valence of the



atom(s) or substituent(s). It has been observed that the magnitude of the folding angle tends to be larger with small degree of distortion from planarity when X or Y is replaced by elements from the fourth and fifth periods. For example, the folding angles are in the range of

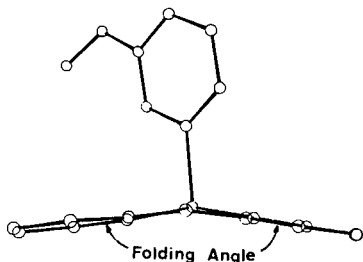


Figure 1. The front view of the molecule **2a** showing the folding angle of the phenarsazine ring system.

$135\text{--}158^\circ$  in phenothiazines ( $X = \text{NH}$ ,  $Y = \text{S}$ ) [1] as compared to that of  $169^\circ$  in chlorodihydrophenarsazine (**2b**) [2]. So far, only limited structural data on the arsenic substituted tricyclic systems are available. In order to understand the bonding characteristics of arsenic in the tricyclic system and its contribution of electron delocalization to the aromaticity of the central ring, the structures of several phenarsazines will be studied in the solid state as well as in solution. The crystal structure of 3'-methoxy-5-phenyl-5,10-dihydrophenarsazine, **2a**, is reported in this paper.

Table 1

Crystal and Experimental Data of **2a**

Chemical formula	$\text{C}_{19}\text{H}_{16}\text{AsNO}$
Formula weight	349.27
Crystal system	monoclinic
Space group	$P2_1/n$ (h0l absent with h + l odd (OkO absent with k odd))
Unit cell dimensions	$a = 15.305(6)$ Å $b = 5.809(2)$ $c = 17.595(6)$ $\beta = 92.92(2)^\circ$ $V = 1562.3(1.0)$ Å <sup>3</sup>
Number of molecules per unit cell	4
Density (calculated)	1.485 g cm <sup>-3</sup>
Density (measured by flotation)	1.48 g cm <sup>-3</sup>
X-radiation used for data collection	$\lambda(\text{MoK}\alpha) = 0.7107$ Å
Linear absorption coefficient	2.17 mm <sup>-1</sup>
Total number of reflections with $2\theta < 50^\circ$	2770
Number of reflections with $I > 3\sigma(I)$	1480
Maximum residue electron density	0.44 e Å <sup>-3</sup> (in the vicinity of As)
Disagreement index R for 1480 observed reflections	0.040
Weighted disagreement index, R, for 1480 observed reflections	0.032
Crystal size	0.06 × 0.39 × 0.06 mm

Table 2

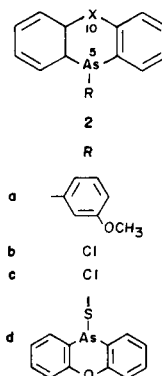
Fractional atomic coordinates ( $\times 10^4$ ) for non-hydrogen and ( $\times 10^3$ ) for hydrogen atoms, with "equivalent" thermal parameters for non-hydrogen ( $\times 10^4$ ) and isotropic for hydrogen atoms ( $\times 10^3$ ). The estimated standard deviations are given in parentheses.

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$$

Atom	X	Y	Z	$U_{eq}/U$
C(1)	7394( 3)	594(12)	8407( 3)	546(15)
C(2)	7860( 4)	1219(12)	9060( 4)	632(19)
C(3)	7620( 4)	3141(13)	9455( 4)	623(20)
C(4)	6907( 4)	4396(12)	9188( 3)	578(17)
C(4A)	6424( 3)	3790( 8)	8534( 3)	428(13)
AS(5)	5418( 0)	5666( 1)	8236( 0)	471( 1)
C(5A)	5289( 3)	4450( 9)	7205( 2)	454(12)
C(6)	4737( 3)	5607(12)	6684( 4)	578(17)
C(7)	4545( 4)	4755(15)	5971( 4)	685(23)
C(8)	4898( 4)	2698(16)	5768( 4)	714(24)
C(9)	5461( 4)	1527(11)	6264( 4)	539(17)
C(9A)	5661( 3)	2396( 9)	6985( 3)	427(14)
N(10)	6241( 3)	1156( 9)	7468( 3)	519(14)
C(10A)	6678( 3)	1859( 8)	8127( 3)	399(12)
C(1')	4474( 3)	3816( 7)	8645( 3)	395(13)
C(2')	3631( 3)	4655(10)	8494( 3)	397(13)
C(3')	2915( 3)	3446( 9)	8742( 3)	437(14)
C(4')	3049( 4)	1446(10)	9150( 3)	511(16)
C(5')	3881( 4)	632(12)	9304( 3)	566(16)
C(6')	4593( 4)	1814(10)	9050( 3)	526(16)
O'	2064( 2)	4092( 7)	8602( 2)	642(11)
C(7')	3106( 4)	10921(15)	6919( 5)	691(22)
H(1)	760( 3)	-64( 9)	812( 3)	67(18)
H(2)	837( 3)	30( 9)	927( 3)	83(19)
H(3)	797( 3)	361( 7)	987( 2)	40(15)
H(4)	677( 3)	574( 8)	941( 2)	41(14)
H(6)	447( 3)	710( 7)	685( 2)	31(12)
H(7)	422( 3)	563( 9)	564( 3)	61(17)
H(8)	478( 3)	210( 8)	530( 3)	47(17)
H(9)	576( 3)	11( 8)	612( 3)	60(19)
H(10)	641( 3)	10( 9)	728( 3)	49(21)
H(2')	352( 2)	600( 6)	821( 2)	11(10)
H(4')	254( 3)	64( 8)	928( 2)	53(15)
H(5')	396( 3)	-65( 9)	962( 3)	64(17)
H(6')	514( 3)	130( 0)	914( 2)	45(15)
H(71')	132( 3)	607( 9)	802( 3)	66(17)
H(72')	216( 3)	560( 9)	761( 3)	61(17)
H(73')	218( 4)	743(10)	823( 3)	87(24)

## EXPERIMENTAL

Compound **2a** was prepared by reacting the 5-chloro-5,10-dihydrophenarsazine with the Grignard reagent, *m*-methoxyphenylmagnesium iodide. The Grignard reagent was prepared under a nitrogen atmosphere by placing freshly crushed magnesium turnings (486 mg, 20 mmoles) in an oven-dried 50 ml round bottom flask equipped with a reflux condenser and a drying tube. A small portion (1.6 g, 7 mmoles) of *m*-iodoanisole in 8 ml of anhydrous ethylether was added and the mixture was gently heated to 40°. Reaction started with the addition of two crystals of elemental iodine, at which time 5 ml of anhydrous ether was also added. Within 15 minutes, solid gray particles appeared and the reaction mixture became turbid. After refluxing an additional 10-15 minutes, the second portion of the aryl iodide (7 mmoles) dissolved in 30 ml of absolute



ether was added dropwise. Finally, after additional 15 minutes an additional 1.6 g (7 mmoles) of aryl iodide in 30 ml ether (Total of three portions, 4.91 g, 21 mmoles) was added and the whole mixture was refluxed for 2 hours. Absolute ether was periodically added in small portions to replace the solvent lost by evaporation. The reaction mixture was allowed to cool to room temperature and used for the synthesis of **2a**. The yield of Grignard reagent was estimated at about 90% by titration.

The synthesis of **2a** was then carried out in the three-neck 250 ml round-bottom flask equipped with a reflux condenser, a pressure-equalizing dropping funnel, and a bubbler connected to a nitrogen line. The 5-chloro-5,10-dihydrophenarsazine in the amount of 2.78 g (10 mmol) was placed in the flask, suspended in 100 ml of anhydrous ether. The mixture is stirred with a magnetic stirring bar. Freshly prepared Grignard reagent (*m*-methoxyphenylmagnesium iodide) was transferred with a syringe into the pressure-equalizing dropping funnel and added dropwise over a period of 30 minutes to the cold greenish-yellow slurry in the flask. Nitrogen gas was bubbled continuously through the solution and the reaction mixture became pale yellow. After the reaction mixture was cooled to room temperature and stirred for additional 3 hours, it was poured into 300 ml of water, the resulting mixture was stirred vigorously for one hour and the ether layer then was separated. The aqueous layer was extracted several times with absolute ether. The combined organic extracts were dried over anhydrous magnesium sulfate, filtered and evaporated to

Table 3

Torsion Angles and Puckering Parameters of **2a**

## Torsion Angles:

## Around the central ring:

As(5)-C(5a)-C(9a)-N(10)	-7.3(7)°
C(5a)-C(9a)-N(10)-C(10a)	-14.9(9)
C(9a)-N(10)-C(10a)-C(4a)	18.1(9)
N(10)-C(10a)-C(4a)-As(5)	1.4(7)
C(10a)-C(4a)-As(5)-C(5a)	-15.5(4)
C(4a)-As(5)-C(5a)-C(9a)	18.3(4)

## About the As(5)-C(1') bond:

C(4a)-As(5)-C(1')-C(2')	-177.2(4)
C(4a)-As(5)-C(1')-C(6')	2.3(5)
C(5a)-As(5)-C(1')-C(2')	-80.8(4)
C(5a)-As(5)-C(1')-C(6')	98.7(5)

## Puckering Parameters

## Ideal boat conformation

$Q = 0.263 \text{ \AA}$	$q_2 = Q$
$q_2 = 0.255$	$q_3 = 0$
$q_3 = -0.065$	
$\theta = 104.23^\circ$	$\theta = 90^\circ$
$\phi_2 = 353.27$	$\phi_2 = 360^\circ$

dryness to yield a yellow oil (1.5 g, 43%). Column chromatography of this material on silica gel with 5% benzene-95% hexane as the eluent yielded compound **2a** as white crystals with mp 101-103°. Suitable crystals in the shape of colorless needles were recrystallized from benzene and were used for the X-ray analysis.

#### Data Collection and Reduction.

Unit cell parameters were obtained from a least-squares fit to the  $2\theta$  values of 15 reflections ranging from 15 to 28° measured on a Syntex P2, automatic diffractometer at 298°K. The crystal data are summarized in Table 1. The intensity data was collected with  $\theta/2\theta$  scanning mode using graphite monochromatized MoK $\alpha$  radiation. Three standard reflections were repeated in intervals of every 100 reflections, and their intensities showed no significant changes. The intensity data were reduced to structure amplitudes by the application of Lorentz and polarization factor. Absorption corrections were applied using the SHELX 76 system of programs [3]. No extinction correction was applied.

#### Solution and Refinement of the Structure.

The structure was determined by the heavy-atom method and hydrogen atoms were located by the difference Fourier method. The refinement was carried out by the full-matrix least-squares method (SHELX 76) with anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for hydrogen atoms. The least-squares weights used in the last stages of refinement were  $1.8/[\sigma(F_o)]^2 + 1.1 \times 10^{-4}(F_o)$ . The function  $\sum w[|F_o| - |F_c|]^2$  was minimized. Final disagreement indices are  $R = 0.040$  and  $wR = 0.032$  for 1480 observed reflections. The maximum shift in the final cycle of refinement was  $0.25\sigma$ . Maximum residual electron density in the final difference Fourier synthesis is  $0.44 \text{ e}\text{\AA}^{-3}$  in the vicinity of the As atom. The atomic scattering factors for As, O, N, C and H were those from International Tables for X-ray Crystallography [4]. The real and imaginary anomalous dispersion correction for As were made using values from the same reference [4].

Positional the thermal parameters are given in Table 2. The observed and calculated structure factors are given as Supplementary Materials [5].

#### Results and Discussion.

The identification of the atoms and the configuration of the molecule are shown in the ORTEP drawing [6] of Figure 2. The dihydrophenarsazine ring is folded with the central ring in a flattened boat conformation as shown in

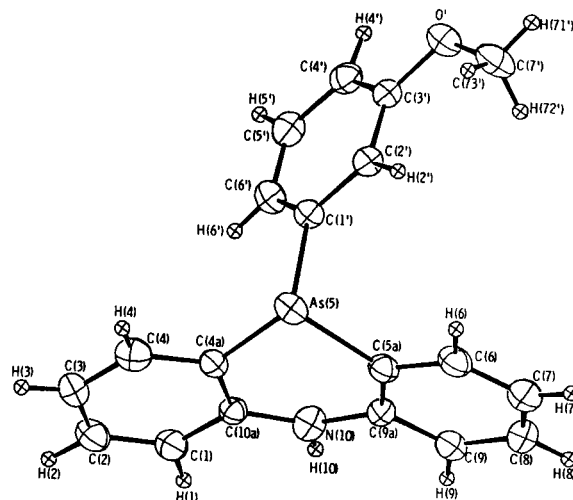
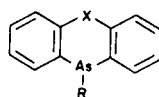


Figure 2. ORTEP drawing of one molecule of **2a**. The thermal ellipsoid was drawn with 50% probability for non-hydrogen atoms and with arbitrary scale for hydrogens.

the front view of the molecule of Figure 1 and by the torsion angles around the central ring and the small magnitude of the Q values of the Cremer and Pople [7] puckering parameters in Table 3. The C(1) of the 3'-methoxy-5-phenyl group is in a boat-axial conformation with respect to the central ring. The boat-axial conformation of the 5-substituent was also observed in 5-chloro-5,10-dihydrophenarsazine (**2b**) [2], 5-phenoarsine chloride (**2c**) [8a] and 5-phenoarsine sulfide (**2d**) [8b]. The two benzo rings and the phenyl ring are planar and the equation of the least-squares planes are given in Table 1S [5]. The folding angle between the planes of the two benzo rings is  $164.6(2)^\circ$ . For comparison, the folding angles of **2b**, **2c** and **2d** with an arsenic atom occupying one of meso positions are listed in Table 4. The folding angles of the phenothiazine and pyr-

Table 4

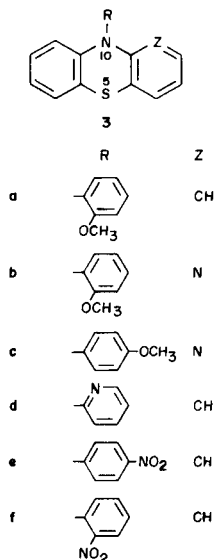
Comparison of Conformation and Bond Lengths (Å) and Bond Angles ( $^\circ$ ) of Phenarsazines and Phenoarsines



Compound	Conformation of R group	Folding angle	mean C-As	within the central ring			As-R	outside the ring	
				mean C-X	C-As-C	C-X-C		C-As-R	Atom X
<b>2a</b>	Axial	$164.6(2)^\circ$	$1.942(5)\text{\AA}$	$1.385(7)\text{\AA}$	$95.2(2)^\circ$	$128.2(2)^\circ$	$1.966(5)\text{\AA}$	$98.2(2)^\circ$	NH
<b>2b</b>	Axial	169	$1.917(7)$	$1.371(9)$	$97.0(4)$	$128.0(8)$	$2.301(4)$	$96.1(2)$	NH
<b>2c</b>	Axial	156.3	$1.94(2)$	$1.41(2)$	$94.6(7)$	$124(1)$	$2.255(5)$	$97.5(5)$	O
<b>2d</b> [a]	Axial	175.2	$1.95(1)$	$1.36(1)$	$94.4(4)$	$125.6(6)$	$2.267(3)$	$99.7(3)$	O
	Axial	178.5	$1.93(1)$	$1.38(1)$	$95.2(4)$	$124.5(6)$	$2.282(3)$	$99.6(3)$	O

[a] Two crystallographically independent phenoarsine fragments.

ido[3,2-*b*][1,4]benzothiazine derivatives with similar substituents are 157.5°, 158.7° and 156.2° (mean value of the two crystallographically independent molecules) for 2'-methoxy-10-phenylphenothiazine (**3a**) [1c], 2'-methoxy-10-phenylpyrido[3,2-*b*][1,4]benzothiazine (**3b**) [9], and 4'-methoxy-10-phenylpyrido[3,2-*b*][1,4]benzothiazine (**3c**) [10], respectively. However, the folding angle of 10-chlorophenothiantimonia [11] (X = S, Y = Sb-Cl in **1**) is only



112.14(6)° and antimony belongs to the fifth period. In this compound, the Sb-Cl is in a "boat-equatorial" conformation as opposed to the "boat-axial" conformation in **2a-2d**. Further, the size of the folding angle also depends on the sizes of the intra-ring angles at X and Y (**1**) [1b,1c]. The larger folding angle in **2a** is, therefore, due to (a) the interaction between the lone-pair electrons on nitrogen and the As-substituent being in the "boat-axial" conformation and (b) the large C-N-C intra-ring angle. Although the mean C<sub>sp<sup>2</sup></sub>-As bond length of 1.942(5)Å within the central ring is shorter than the C<sub>sp<sup>2</sup></sub>-As bond length of 1.966(5)Å outside the ring, it is difficult to assess the effect of the increase in aromaticity from the distribution of electron delocalization of arsenic on the size of the folding angle in **2a**. Further studies on compounds with similar

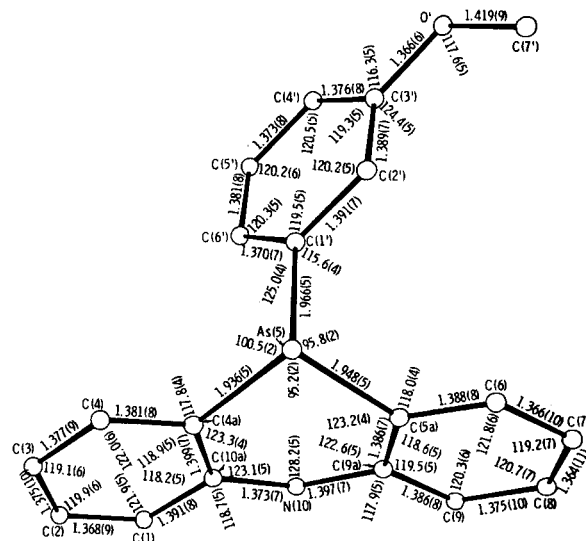


Figure 3. The bond lengths (Å) and bond angles (°) of **2a** with e.s.d in parentheses.

conformation and substituents are necessary to determine the effect on the different heteroatoms or hetero-substituents on the magnitude of the folding angles.

The plane of the phenyl ring is nearly perpendicular to both of the benzo rings and the plane of the central ring involving the C's as shown in Table 1S [5]. The angle between the plane of the phenyl ring and the plane bisecting the tricyclic ring system [plane passing through As(5), N(10) and C(1')] is 50.7(2)°. However, in phenothiazines, the plane of the *N*-aryl substituent is either nearly parallel or nearly perpendicular to the plane bisecting the phenothiazine ring system. The parallel conformation is observed when the *N*-aryl substituent is an electron releasing group (**3a**) [1c], (**3b**) [9], (**3c**) [10] or there is steric effect (**3f**) [12] between the two ring systems. On the other hand, the perpendicular conformation is observed when the *N*-aryl substituent is an electron withdrawing group (**3d**) [1d], (**3e**) [13] and there is an electronic interaction between the two ring systems in this conformation. The conformation of

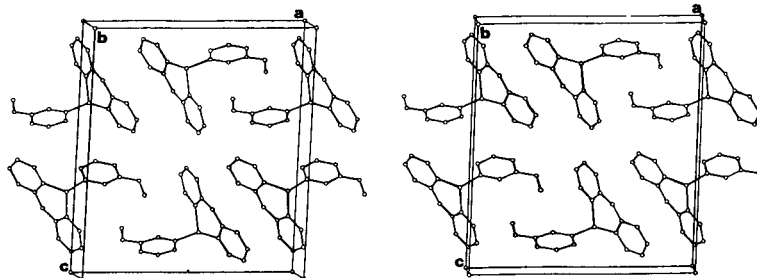


Figure 4. Stereoscopic drawing of the molecular packing of **2a** in a unit cell.

the 3'-methoxyphenyl substituent with respect to the dihydrophenarsazine ring in the title compound, **2a**, does not allow any electronic interaction between the two ring systems.

The bond lengths and bond angles with their standard deviations are shown in Figure 3. A comparison of bond lengths and bond angles around the central ring in **2b**, **2c** and **2d** is represented in Table 5. The mean C-As bond length of 1.942(5) Å in **2a** is slightly longer than that of 1.917(7) Å in **2b**. The C-As-C bond angle within the central ring is 95.2(2)° in **2a** and it is smaller than the 97.0(4)° in **2b**. This indicates that there is less electron delocalization of arsenic in **2a** than that in **2b**. This accounts also for the larger folding angle in **2b**.

The packing of the molecules in the unit cell is shown in the stereoscopic drawing in Figure 4. There are no intermolecular contacts less than van der Waals distances.

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