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Structure of 10-(*m*-Tolyl)-5,10-dihydrophenarsazine

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Abstract. $C_{19}H_{16}AsN$, $M_r = 333.27$, monoclinic, $P2_1/c$, $a = 17.309$ (3), $b = 5.974$ (1), $c = 16.546$ (2) Å, $\beta = 115.65$ (1)°, $V = 1542.3$ (4) Å^3, $Z = 4$, $D_x = 1.435$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 21.6$ cm^{-1}, $F(000) = 680$, $T = 295$ K. Final $R = 0.031$ for 1935 observed reflections. The central phenarsazine ring is in a flattened boat conformation. The dihedral angle between the two benzo planes is 160.6 (2)°. The *m*-tolyl substituent is in an axial position relative to the central ring. The bond lengths and angles are in good agreement with those found in 10-(3-methoxyphenyl)-5,10-dihydrophenarsazine.

Introduction. As part of our continuing structural studies of substituted phenarsazines and phenothiazines, we have recently determined the structure of 10-(3-methoxyphenyl)-5,10-dihydrophenarsazine (de Meester, Chu, Jovanovic & Biehl, 1985). We report here the structure of 10-(*m*-tolyl)-5,10-dihydrophenarsazine.

Experimental. Crystals of the title compound are colorless rectangular plates elongated in the [010] direction. Lattice parameters from least-squares refinement of 15 reflections in range $15 < 2\theta < 20°$, crystal faces 100, $\bar{1}$00, 010, 0$\bar{1}$0, 001 and 00$\bar{1}$, crystal dimensions $0.55 \times 0.20 \times 0.11$ mm, automatic Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, $\theta/2\theta$ scanning mode, 2714 independent reflections in range $3 < 2\theta < 50°$, *hkl* range:

$-20 \le h \le 18$, $0 \le k \le 7$, $0 \le l \le 19$, 1937 observed reflections with $I > 3\sigma(I)$, $\sigma(I)$ from counting statistics; three standard reflections (12$\bar{3}$, 106 and 40$\bar{8}$) remeasured every 100 reflections showed no change in intensity greater than $2\sigma(I)$; Lorentz–polarization correction, absorption correction (transmission-factor range 0.583 to 0.783), no extinction correction; Structure solved by standard Patterson and difference Fourier methods; refinement by full-matrix least squares using *SHELX76* (Sheldrick, 1976), anisotropic for non-H, isotropic for H atoms, $w = 1/[\sigma^2(F) + 0.00146F^2]$, $\sum w(|F_o| - |F_c|)^2$ minimized; during final refinement, two strong reflections (200 and 310) discarded due to measurement errors; $R = 0.031$, $wR = 0.033$ for 1935 observed reflections, $(\Delta/\sigma)_{max} = 0.25$, $\Delta\rho_{max} = 0.28$ e Å^{-3}. Atomic scattering factors for C, H and N those stored in *SHELX76*, for As *International Tables for X-ray Crystallography* (1974); effects of anomalous-dispersion correction for As (from same source) included in calculation of F_c.

Discussion. The final atomic parameters are given in Table 1.† The identification of the atoms and the configuration of the molecule are shown in the *ORTEP* (Johnson, 1965) drawing of Fig. 1. The bond lengths and bond angles are listed in Table 2. They are in good

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† Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42767 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates with equivalent isotropic thermal parameters for the non-H and isotropic for the H atoms (e.s.d.'s in parentheses)*

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	$U_{eq}/U(\text{Å}^2)$
C(1)	0·0624 (3)	0·1339 (8)	0·7398 (4)	0·0669 (14)*
C(2)	0·0230 (3)	0·1460 (9)	0·6496 (4)	0·0771 (15)
C(3)	0·0393 (3)	0·3227 (11)	0·6056 (4)	0·0786 (15)
C(4)	0·0961 (2)	0·4861 (8)	0·6540 (3)	0·0590 (11)
C(4a)	0·1391 (2)	0·4765 (6)	0·7472 (2)	0·0444 (8)
As(5)	0·22255 (2)	0·70668 (6)	0·81033 (2)	0·03897 (2)
C(5a)	0·2272 (2)	0·6468 (6)	0·9276 (2)	0·0436 (8)
C(6)	0·2635 (3)	0·8053 (8)	0·9948 (3)	0·0564 (9)
C(7)	0·2710 (3)	0·7736 (10)	1·0803 (3)	0·0739 (14)
C(8)	0·2417 (4)	0·5763 (11)	1·0990 (3)	0·0885 (17)
C(9)	0·2050 (3)	0·4168 (10)	1·0351 (3)	0·0743 (13)
C(9a)	0·1963 (2)	0·4467 (6)	0·9474 (2)	0·0513 (9)
N(10)	0·1589 (2)	0·2804 (6)	0·8846 (3)	0·0618 (9)
C(10a)	0·1214 (2)	0·3002 (6)	0·7919 (3)	0·0502 (9)
C(1')	0·3292 (2)	0·5546 (6)	0·8270 (2)	0·0381 (7)
C(2')	0·4043 (2)	0·6737 (6)	0·8721 (2)	0·0441 (8)
C(3')	0·4832 (2)	0·5917 (7)	0·8829 (2)	0·0514 (9)
C(4')	0·4850 (3)	0·3856 (8)	0·8454 (3)	0·0644 (11)
C(5')	0·4107 (3)	0·2636 (8)	0·7999 (3)	0·0672 (11)
C(6')	0·3325 (2)	0·3463 (7)	0·7908 (3)	0·0508 (9)
C(7')	0·5641 (3)	0·7234 (12)	0·9343 (4)	0·0763 (15)
H(1)	0·055 (2)	0·021 (7)	0·773 (2)	0·059 (12)
H(2)	−0·012 (3)	0·026 (7)	0·616 (3)	0·080 (13)
H(3)	0·011 (3)	0·340 (8)	0·544 (3)	0·089 (16)
H(4)	0·102 (2)	0·613 (6)	0·625 (2)	0·044 (10)
H(6)	0·285 (2)	0·934 (6)	0·983 (2)	0·042 (10)
H(7)	0·303 (3)	0·886 (9)	1·128 (3)	0·102 (17)
H(8)	0·250 (3)	0·568 (10)	1·158 (4)	0·119 (19)
H(9)	0·184 (3)	0·280 (7)	1·038 (3)	0·051 (12)
H(10)	0·142 (3)	0·174 (7)	0·900 (3)	0·073 (16)
H(2')	0·400 (2)	0·818 (6)	0·895 (2)	0·048 (10)
H(4')	0·536 (2)	0·334 (6)	0·850 (2)	0·053 (10)
H(5')	0·414 (3)	0·126 (8)	0·772 (3)	0·079 (13)
H(6')	0·286 (3)	0·261 (7)	0·768 (3)	0·066 (12)
H(71)	0·609 (5)	0·664 (12)	0·947 (5)	0·155 (30)
H(72')	0·571 (7)	0·749 (16)	0·997 (7)	0·253 (48)
H(73')	0·563 (3)	0·866 (10)	0·913 (3)	0·104 (19)

* The standard deviations of U_{eq}'s were calculated according to Schomaker & Marsh (1983).

Table 2. *Bond lengths (Å), bond angles (°) and selected torsion angles (°) with e.s.d.'s in parentheses*

C(1)–C(2)	1·348 (8)		C(7)–C(8)	1·370 (8)
C(1)–C(10a)	1·418 (7)		C(8)–C(9)	1·359 (8)
C(2)–C(3)	1·379 (8)		C(9)–C(9a)	1·404 (6)
C(3)–C(4)	1·371 (8)		C(9a)–N(10)	1·380 (5)
C(4)–C(4a)	1·393 (6)		N(10)–C(10a)	1·388 (6)
C(4a)–C(10a)	1·395 (5)		C(1')–C(2')	1·383 (5)
C(4a)–As(5)	1·940 (4)		C(1')–C(6')	1·393 (5)
As(5)–C(5a)	1·941 (4)		C(2')–C(3')	1·388 (5)
As(5)–C(1')	1·966 (4)		C(3')–C(4')	1·385 (6)
C(5a)–C(6)	1·387 (6)		C(3')–C(7')	1·507 (7)
C(5a)–C(9a)	1·405 (5)		C(4')–C(5')	1·383 (7)
C(6)–C(7)	1·377 (7)		C(5')–C(6')	1·387 (7)

C(2)–C(1)–C(10a)	121·4 (5)		C(5a)–C(9a)–C(9)	117·9 (4)
C(1)–C(2)–C(3)	120·3 (5)		C(5a)–C(9a)–N(10)	122·6 (3)
C(2)–C(3)–C(4)	119·7 (5)		C(9)–C(9a)–N(10)	119·5 (4)
C(3)–C(4)–C(4a)	121·4 (4)		C(9a)–N(10)–C(10a)	127·8 (4)
C(4)–C(4a)–As(5)	118·9 (3)		C(1)–C(10a)–C(4a)	118·2 (4)
C(4)–C(4a)–C(10a)	118·9 (3)		C(1)–C(10a)–N(10)	118·8 (4)
As(5)–C(4a)–C(10a)	122·2 (3)		C(4a)–C(10a)–N(10)	123·0 (4)
C(4a)–As(5)–C(5a)	96·1 (1)		As(5)–C(1')–C(2')	116·3 (3)
C(4a)–As(5)–C(1')	100·6 (1)		As(5)–C(1')–C(6')	124·3 (3)
C(5a)–As(5)–C(1')	98·3 (1)		C(2')–C(1')–C(6')	119·2 (3)
As(5)–C(5a)–C(6)	119·0 (3)		C(1')–C(2')–C(3')	122·0 (3)
As(5)–C(5a)–C(9a)	122·3 (3)		C(2')–C(3')–C(4')	117·9 (4)
C(6)–C(5a)–C(9a)	118·7 (3)		C(2')–C(3')–C(7')	120·7 (4)
C(5a)–C(6)–C(7)	122·6 (4)		C(4')–C(3')–C(7')	121·4 (4)
C(6)–C(7)–C(8)	118·1 (5)		C(3')–C(4')–C(5')	121·1 (4)
C(7)–C(8)–C(9)	121·4 (6)		C(4')–C(5')–C(6')	120·3 (4)
C(8)–C(9)–C(9a)	121·3 (5)		C(1')–C(6')–C(5')	119·4 (4)

C(4a)–As(5)–C(5a)–C(9a)	16·8 (3)		C(10a)–C(4a)–As(5)–C(5a)	−17·5 (3)
As(5)–C(5a)–C(9a)–N(10)	−1·4 (5)		C(4a)–As(5)–C(1')–C(2')	−179·3 (3)
C(5a)–C(9a)–N(10)–C(10a)	−21·8 (6)		C(4a)–As(5)–C(1')–C(6')	5·8 (4)
C(9a)–N(10)–C(10a)–C(4a)	21·0 (7)		C(5a)–As(5)–C(1')–C(2')	−81·5 (3)
N(10)–C(10a)–C(4a)–As(5)	2·9 (6)		C(5a)–As(5)–C(1')–C(6')	103·6 (3)

agreement with those found in 10-(3-methoxyphenyl)-5,10-dihydrophenarsazine (de Meester *et al.*, 1985). In that compound, the values of the bond lengths and bond angles involving the As atom are As–C(4a) 1·936 (5), As–C(5a) 1·948 (5), As–C(1') 1·966 (5) Å and C(4a)–As–C(5a) 95·2 (2)° while in the title compound, the corresponding values are 1·940 (4), 1·941 (4), 1·966 (4) Å and 96·1 (1)°. Other bond lengths and bond angles are also very similar in both compounds.

The central phenarsazine ring is in a flattened boat conformation as shown by the torsion angles (Table 2) and the puckering parameters (Cremer & Pople, 1975) $q_2 = 0·285$ (4), $q_3 = 0·051$ (4), $Q = 0·290$ (4) Å, $\varphi_2 = 121·6$ (7) and $\theta = 79·9$ (7)°. For ideal boat conformation, these parameters are $q_2 = Q$, $q_3 = 0$ Å, $\varphi_2 = 120$ and $\theta = 90°$. The tricyclic ring is folded along the As(5)···N(10) line. The folding angle of 160·6 (2)°
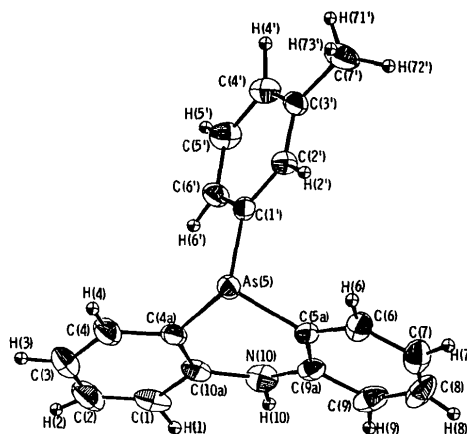

Fig. 1. *ORTEP* drawing of the molecule. Thermal ellipsoids are scaled at the 50% probability level. H atoms are represented as circles of arbitrary radii.
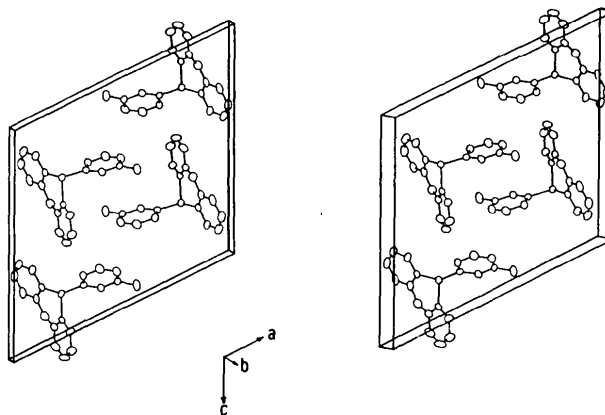

Fig. 2. Stereoscopic drawing of the molecular packing in the cell. The H atoms are omitted for clarity.

is smaller than that of 164·6 (2)° found in 10-(3-methoxyphenyl)-5,10-dihydrophenarsazine. In other similar compounds, the values of the folding angles are: 154·1 (4)° in 10-methyl-5,10-dihydrophenarsazine (de Meester, Chu, Jovanovic & Biehl, 1986), 156·3° in 10-chlorophenoxarsine (Stuckey, Cordes, Handy, Perry & Fair, 1972), 169·2° in 10-chloro-5,10-dihydrophenarsazine (Camerman & Trotter, 1965), and 178·5° in 10,10'-thiodiphenoxarsine (Grindstaff, Cordes, Fair, Perry & Handy, 1972).

The *m*-tolyl substituent is in an axial position relative to the central ring as found in the compounds already mentioned. The phenyl ring is nearly perpendicular to the tricyclic ring. The angle between the phenyl plane and the benzo plane [C(1)C(2)C(3)C(4)C(4a)C(10a)] is −87·5 (2)° while with the benzo plane [C(5a)-C(6)C(7)C(8)C(9)C(9a)], it is 79·7 (2)°.* The orientation of the phenyl ring relative to the plane formed by the three atoms As(5), N(10) and C(1') (bisecting the tricyclic ring) is given by the angle of 52·0 (1)° between these two planes, a value very similar to that of 50·7 (2)° found in 10-(3-methoxyphenyl)-5,10-dihydrophenarsazine.

The packing of the molecules in the unit cell is shown in the stereoscopic drawing of Fig. 2. There are no

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* See previous footnote.

intermolecular distances less than the van der Waals separations. The shortest intermolecular contact is C(6)···N(10) of 3·435 (6) Å.

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Hydrogen Bonding in 2,3,4-Trihydroxyacetophenone

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Abstract. $C_8H_8O_4$, $M_r = 168·2$, monoclinic, $P2_1/c$, $a = 13·866$ (3), $b = 6·794$ (2), $c = 16·366$ (4) Å, $\beta = 101·27$ (3)°, $V = 1512$ (1) Å^3, $Z = 8$, $D_m = 1·46$, $D_x = 1·477$ (1) g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0·7107$ Å, $\mu = 1·12$ cm^{-1}, $F(000) = 704$, $T = 295$ (1) K, final $R = 0·044$ for 1131 observed reflections (θ–2θ scan) with $F_o^2 > 2\sigma(F_o^2)$. Extensive hydrogen bonding (inter- and intramolecular) is present involving all hydroxyl groups of the two independent molecules. Except for the 2-hydroxyl groups the hydrogen bonds are all bifurcated involving both inter- and intramolecular components. The 2-hydroxyl groups are strongly intramolecularly hydrogen bonded to the carbonyl oxygens [O(1)···O(2) = 2·512 (4), O(2)–H(O2) = 0·83 (4), O(1)···H(O2) = 1·76 (4) Å, O(2)–H(O2)···O(1) = 149 (3)°, O(1')···O(2') = 2·515 (4), O(2')–H(O2') = 0·88 (4), O(1')···H(O2') = 1·70 (4) Å, O(2')–H(O2')···O(1') = 153 (3)°].

Introduction. In earlier X-ray diffraction studies of hydroxybenzophenone compounds strong intramolecular hydrogen bonding between *ortho* hydroxyl groups and the carbonyl oxygen was found. In 2,4-dihydroxybenzophenone (HHB) (Liebich, 1979) the O···O distance is 2·550 (4) Å; in 2,2',4,4'-tetrahydroxybenzophenone (THB) (Schlemper, 1982*a*) it is 2·608 Å (av. of four); and in 2,2'-dihydroxybenzophenone (DHP) (Schlemper, 1982*b*) it is 2·629 Å (av. of two). In the latter two compounds each carbonyl oxygen accepts two intramolecular hydrogen bonds. No structural study of a comparable 2-hydroxyacetophenone has been done although recently (Chat-