Chemistry of the Phenoxathiins and Isosterically Related Heterocycles. XX (1). Assignment of the ^{13}C-NMR Spectra of Phenarsazine-10-chloride and Several Substituted Analogs. The Effect of Substitution on the Anisotropic Reorientation of the Phenarsazine System.

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The total assignment of the ^{13}C-nmr spectra of phenarsazine-10-chloride and several substituted analogs is reported. Spin-lattice (T_1) relaxation measurements have shown these systems to reorient anisotropically. In the case of the parent system and the 3-chloro substituted system, the axis of anisotropic reorientation has been shown to pass approximately through the center of the molecule. In the case of benzo[*c*]phenarsazine-7-chloride, the axis of anisotropic reorientation, which has been accurately defined, is shifted 23° from that in the previous cases, the shift occurring in the direction of the benzo-moiety.

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Various studies have been directed toward the isosteric replacement of the heteroatoms of the phenothiazine ring system (4). In particular, the sulfur atom has been replaced by other heteroatoms which have included oxygen, selenium and arsenic. Furthermore, although the assignments of the ^{13}C-nmr spectra of phenothiazine, phenoxazine and several other isosterically related systems have been reported (5), there has, as yet, been no report in the literature which has detailed the ^{13}C-nmr assignments of the phenarsazine system. Therefore, we now wish to report the results of our studies directed at the total assignment of the carbon nmr spectra of phenarsazine-10-chloride and several substituted analogs and an investigation of their spin-lattice relaxation behavior.

The ^{1}H-decoupled ^{13}C-nmr spectrum of phenarsazine-10-chloride (**1**), which is shown in Figure 1, contained six well resolved resonances, two of which were clearly attributable to quaternary carbons carrying the nitrogen and arsenic heteroatoms (6). More specifically, based on comparison to the ^{13}C-nmr chemical shifts of phenothiazine (5), the quaternary carbon resonating at δ 140.14 was assigned as the nitrogen-bearing carbon while its counterpart, resonating at δ 120.78 was assigned as the arsenic-bearing carbon. For purposes of comparison, the corresponding carbons of phenothiazine resonated at δ 141.7 and δ 116.8, respectively (5). While it could be assumed that the remaining protonated carbon resonances would exhibit chemical shifts similar to those of phenothiazine, it was still necessary to obtain evidence upon which to base such an assignment. Specifically, we were interested in the feasability of utilizing relaxation data for this purpose, as has recently been reported for pyrrolo[3,2,1-*kl*]phenothiazine (7). While the geometry of the pyrrol[3,2,1-*kl*]phenothiazine system is as yet

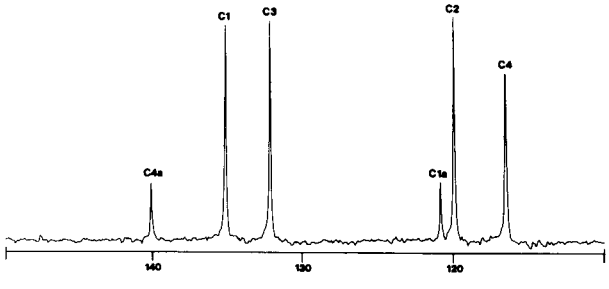
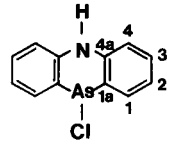


Figure 1. ^{1}H-Decoupled 25.2 MHz ^{13}C-nmr spectrum of the aromatic region of phenarsazine-10-chloride (**1**) in hexadeuteriodimethylsulfoxide at 33°.

Table I

Spin-lattice (T_1) Relaxation Times for the Protonated Carbon Resonances of Phenarazine-10-chloride (**1**) in Hexadeuteriodimethylsulfoxide, Determined with the Inversion-recovery Method (9,10) at 33°.



Carbon	δ	T_1(a,b)
Cla	120.78	
Cl	135.10	0.68
C2	119.86	0.61
C3	132.13	0.61
C4	116.50	0.70
C4a	140.14	

(a) Data reduction was accomplished using the three-parameter fitting program of J. G. Kowalweski, G. C. Levy, L. F. Johnson and L. Palmer, *J. Magn. Reson.*, **26**, 553 (1977); (b) Using the average of the observed relaxation times for the four protonated resonance, a reorientational correlation time for **1** was calculated and gave, $\tau_c = 6.9 \times 10^{-11}$.

unknown, it is thus important to determine the applicability of this method in a non-planar system of known geometry such as phenarsazine-10-chloride, which has a dihedral angle, $\phi = 169°$ (8).

Spin-lattice (T_1) relaxation times for phenarsazine-10-chloride (**1**) were measured using the inversion-recovery technique (9,10), the data reduction subsequently conducted using the three-parameter fitting program of Kowalewski and co-workers (11). This procedure provided the relaxation data which are contained in Table I. As is readily seen from this data, the relaxation times of the protonated cabons are subdivisible into two groups, each containing two resonances, as would be expected for an axially symmetric molecule undergoing anisotropic reorientation about an axis passing approximately through the center of the molecular framework. Based on this type of subdivision, a T_1 ratio may be calculated such that $T_190°/T_130° = 1.13$, which corresponds to a tumbling preference ratio $\varrho = 1.4$ using equations 1 and 2 as previously discussed (7).

$$1/T_1^{DD} = N\hbar^2\gamma_C^2\gamma_H^2 r_{CH}^{-6}\chi_H \quad (1)$$

where the term χ_H is defined by the expression

$$\chi_H = 1/4(3\cos^2\theta-1)^2 + 18(5+\varrho)\sin^2\theta\cos^2\theta + 9/4(1+2\varrho)^{-1}\sin^4\theta. \quad (2)$$

Although this tends to indicate only a slight tendency toward anisotropic reorientation for **1**, this was, none-theless, sufficient to complete the assignment and to demonstrate that the ^{13}C-nmr chemical shifts of the phenarsazine system parallel those encountered in the isosterically related phenothiazine system. Alternatively, if the differences between the relaxation times of the carbons in the two groups mentioned above had been greater, it would have been possible to precisely define the axis of anisotropic reorientation using the method of Platzer (12), as has been successfully employed with benzo[*c*]phenarsazine-7-chloride (**3**) which is discussed below.

Complete assignments for the ^{13}C-nmr spectrum of **1** are shown in Table II and are accompanied by the ^{1}H-^{13}C spin-coupling constants which were obtained using conventional gated-decoupling (13). None of the couplings found were particularly remarkable, nor could they have been employed in the unequivocal assignment of the chemical shifts of the parent phenarsazine-10-chloride.

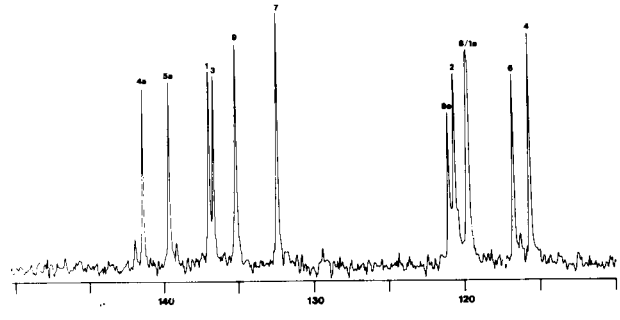


Figure 2. ^{1}H-Decoupled 25.2 MHz ^{13}C-nmr spectrum of the aromatic region of 3-chlorophenarsazine-10-chloride (**2**) in hexadeuteriodimethylsulfoxide at 33°.

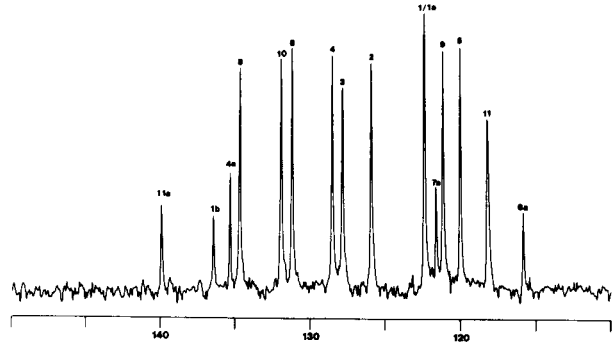


Figure 3. ^{1}H-Decoupled 25.2 MHz ^{13}C-nmr spectrum of the aromatic region of benzo *c* phenarsazine-7-chloride in hexadeuteriodimethylsulfoxide at 33°.

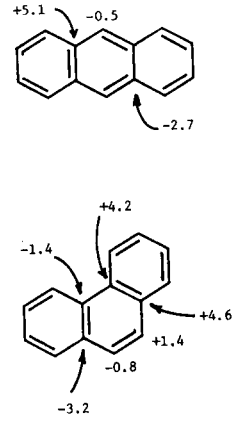


Figure 4. Benzo-fusion chemical shift additivities: A) calculated from benzo-fusion of an additional ring onto a naphthalene nucleus which is analogous to benzo[*b*]fusion; B) calculated from the benzo-fusion of an additional ring onto naphthalene to give phenanthrene which is analogous to a benzo[*a*]fusion. In each case, chemical shifts for the added carbons are assumed to be essentially those of the corresponding carbons of anthracene and phenanthrene respectively.

Table II

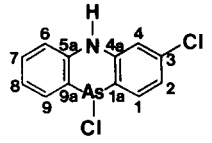
^{13}C-NMR Chemical Shift Assignments and ^{1}H-^{13}C Spin-coupling Constants for **1** in Hexadeuteriodimethylsulfoxide at 33°.

Carbon	δ	$^1J_{CH}$	$^1J_{CH}$	$^3J_{CH}$
C1a	120.78			(a)
C1	135.10	$^1C_1H_1 = 164.8$		$^3C_1H_3 = 7.4$
C2	119.86	$^1C_2H_2 = 164.8$		$^3C_2H_4 = 7.2$
C3	132.13	$^1C_3H_3 = 160.9$		$^3C_3H_1 = 8.5$
C4	116.50	$^1C_4H_4 = 160.0$		$^3C_4H_2 = 6.3$
C4a	140.14			$^3C_{4a}H_1 = 8.2$
				$^3C_{4a}H_3 = 8.2$

(a) The ^{1}H-^{13}C spin-coupled spectrum was acquired under conditions of grated decoupling (13) with 8K data points/5 kHz, and under these conditions, the C1a resonances failed to give any well resolved spin-couplings, possibly a direct result of the spin-coupling with ^{75}As, which is a spin 3/2 nucleus.

Table III

Calculated *vs.* Observed ^{13}C-NMR Chemical Shifts and Spin-lattice (T_1) Relaxation Times for 3-Chlorophenarsazine-10-chloride (**2**) in Hexadeuteriodimethylsulfoxide at 33°.



Carbon	3-Chloro δ Calcd.	δ ^{13}C Obs	T_1 (sec) (a)
Cla	118.9	119.74	
Cl	136.4	136.84	0.33
C2	120.3	120.59	0.28
C3	138.3	136.52	
C4	116.9	115.61	0.33
C4a	141.4	141.31	
C5a	140.1	139.53	
C6	116.5	116.71	0.34
C7	132.1	132.30	0.29
C8	119.9	119.76	(b)
C9	135.1	135.06	0.32
C9a	120.8	121.01	

(a) Data reduction was accomplished using the three parameter fitting program of J. G. Kowalewski, G. C. Levy, L. F. Johnson and L. Palmer, *J. Magn, Reson.*, **26**, 553 (1977); (b) The T_1 relaxation time of this carbon could be accurately measured due to partial overlap with the C4a quarternary carbon.

Based on the assigned ^{13}C-nmr chemical shifts of the parent phenarsazine-10-chloride (**1**), the assignment of the spectrum of 3-chlorophenarsazine-10-chloride (**2**) was next undertaken. Synthesis of **2** was conducted *via* the reaction of 3-chlorophenylphenyl amine with arsenic trichloride to give the desired product, analogous to the procedure employed by Charpentier in the synthesis of chlorpromazine (14). Calculated ^{13}C-nmr chemical shifts for **2** were derived by incrementing the observed chemical shifts of the parent system with chloro substituent chemical shift additivities (scsa's) taken from chlorobenzene (15), the resultant chemical shifts shown in Table III. Assignment of the spectrum of **2**, shown in Figure 2, was in part based upon the chemical shift arguments generated from the calculated chemical shifts and partially on the basis of the ^{1}H-^{13}C spin-couplings which are summarized in Table IV. Further support of the assignments was also obtained from the spin-lattice relaxation time studies which are discussed below.

In particular, the C1 resonance of **2** was unequivocally assigned on the basis of the gated decoupling data, which was further supplemented and simplified by the acquisition of proton coupled selective excitation sub-spectra (16-18). Thus, C1 was assigned to the resonance observed at δ 136.84, this assignment based on the absence of a three bond coupling due to the location of the chloro-substitution. This resonance's downfield counterpart, observed at δ 135.06, which did exhibit a three bond

Table IV

^{1}H-^{13}C Spin-coupling Constants for 3-Chlorophenarsazine-10-chloride (**2**) in Hexadeuteriodimethylsulfoxide at 33°.

Carbon	δ	$^1J_{CH}$	$^2J_{CH}$	$^3J_{CH}$
Cla	119.74		(a)	(a)
Cl	136.84	J_{C1H1} = 163.7		
C2	120.59	J_{C2H2} = 165.4		J_{C2H4} = 6.9
C3	136.52		J_{C3H2} = 2.7	J_{C3H1} = 12.7
			J_{C3H4} = 2.7	
C4	115.61	J_{C4H4} = 164.7		
C4a	141.31			J_{C4aH1} = 9.8
C5a	139.53			J_{C5aH7} = 8.5
				J_{C5aH9} = 8.5
C6	116.71	J_{C6H6} = 160.0		J_{C6H8} = 6.6
C7	132.30	J_{C7H7} = 160.7		J_{C7H9} = 8.0
C8	119.76	J_{C8H8} = 171.9		J_{C8H6} = 4.2
C9	135.06	J_{C9H9} = 162.5		J_{C9H7} = 7.6
C9a	121.01		(a)	(a)

(a) Long range couplings were poorly resolved.

coupling was thus assigned to C9. It is also important to note that these assignments must be consistent with all available data, and should not be made on the basis of the congruence between the calculated and the observed chemical shifts, especially in the case of those systems in which the reliability of scsa's for a particular substituent has not been demonstrated. Further, since spin-lattice relaxation data was also available for **2**, Cl and C9 must obviously exhibit relaxation times which are longer than those for the resonances assigned to C2, C8, and C7. This aspect of the assignment is also discussed below.

Discrimination and unequivocal assignment of C4a and C5a, the two nitrogen bearing quaternary carbons, was also based on the availability of spin-coupling constants. Thus, C4a appeared as a simple doublet in the coupled spectrum, this the result of a three bond coupling, $^3J_{C4aH1}$.

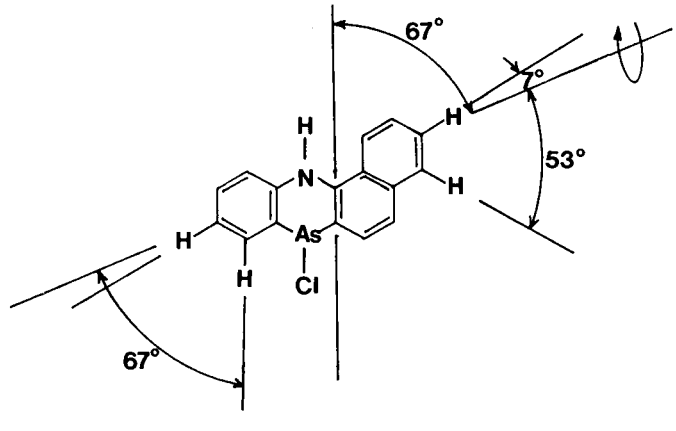


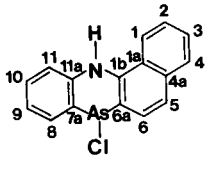
Figure 5. C-H bond vector orientations relative to the optimized axis of anisotropic reorientation in benzo[c]phenarsazine-7-chloride. The axis is oriented at an angle of 67% to the C1b-C6a bond axis which was used as a reference line, giving orientations of 7°, 53° and 67°, representative examples of which are highlighted.

In contrast, C5a appeared as a triplet, the direct result of two equivalent three bond couplings $^3J_{C5aH7}$ and $^3J_{C5aH9}$. The remaining spin-coupling constants, while not particularly useful from a diagnostic standpoint, are summarized in Table IV.

The spin-lattice relaxation time measurements for **2** are shown in Table III in addition to the calculated and observed chemical shifts. It is interesting to note that **2**, as was the case for **1**, exhibits anisotropic reorientation about an axis passing approximately through the center of the molecular framework, with a slightly higher tendency toward anisotropic reorientation than the former with $\varrho = 1.9$. As alluded to above, it should be noted from Table III that the relaxation times of Cl and C9, 0.33 and 0.32 sec respectively, are indeed among the group of longer relaxation times as would be expected for this position in the molecule. Finally, it is also worth commenting on the relative orientation of the axis of rotation relative to that which would be expected for **1**. While it might be argued that the introduction of a chloro-substituent at the 3-position might be expected to cause the realignment of the axis to pass more nearly through C3 and C8, thus minimizing the energy required to move the chlorine

Table V

Calculated *vs.* Observed ^{13}C-NMR Chemical Shifts of Benzo[*c*]phenarsazine-7-chloride (**3**) in Hexadeuteriodimethylsulfoxide at 33°. Individual C-H bond vector Orientaions Shown Are Relative to the Axis of Anisotropic Reorientation Situated at an Angle of 67° to the C1b-C6a Bond Axis and Passing Through C3 and C9. Relaxation Times Were Measured by the Inversion Recovery Technique.



Carbon	$^{13}C_{Calcd}\delta$	$^{13}C_{Obs}$	C-H bond orientation	T_1 (sec)
1	123.1	122.38	53	(a)
1a	120.7	122.38 (b)		(a)
1b	138.7	136.49		
2	126.8	125.90	67	0.59
3	126.8	127.84	7	0.45
4	128.9	128.53	53	0.53
4a	136.7	135.37		
5	121.2	119.99	53	0.53
6	131.9	131.20	67	0.59
6a	117.6	115.82		
7a	120.8	121.63 (b)		
8	135.1	134.70	67	0.58
9	119.8	121.15	7	0.44
10	132.1	131.92	53	0.53
11	116.5	118.19	67	0.56
11a	140.1	139.97		

(a) Accurate T_1 relaxation time could not be made due to degenerative resonance overlapping; (b) Possibly permuted pair of assignments.

this contention cannot be readily supported for this system. The primary reason for this lack of support was the unavailability of an accurate relaxation time for the C8 resonance through which the axis would pass in such a case. Specifically, this was a direct result of the severe overlap of the C8 resonance with the quaternary Cla resonance (see Table III). While this difficulty could presumably be overcome by resorting to a higher field strength, the experiment would still probably be of little relative value since the absolute difference between the relaxation times as a whole are relatively small, barely above the $\pm \cong 5\%$ accuracy inherent to the measurement. Thus, it would seem logical to reserve such concern for a more strongly anisotropically reorienting system, opting for a generalized treatment which locates the axis only approximately, as has been done in this case.

Finally, we were also interested in the benzo[*c*]phenarsazine-7-chloride system from two standpoints: first, there is at present no convenient method for predicting the effect on the ^{13}C-nmr chemical shifts of a parent ring system which would arise from benzo-fusion; second, we were convinced from the outset of our examination of this compound that it would exhibit anisotropic rotation and that the axis, as a result of the location of the benzo-fusion, would not represent simple 30°/90° geometry, as was found in the simpler phenarsazines which were discussed above.

The ^{13}C-nmr spectrum of benzo[*c*]phenarsazine-7-chloride is shown in Figure 3 and contained fifteen clearly resolved resonances of the sixteen which would be expected for this type of molecule, thus indicating a degenerative pair of chemical shifts. On the basis of the relatively small differences in the intensities of the protonated resonances, it was logical to assume at the outset that the overlapped pair of resonances consisted of a protonated and a quaternary carbon. Further initial subgrouping of the resonances contained in Figure 3 was also possible, the resonances observed at δ 139.97, δ 136.49, δ 135.37, δ 121.64 and δ 115.82 representing five of the six necessary quaternary carbons (6). Beyond this simple subgrouping, no further assignment or intragroup discrimination was possible, which thus brought us to our first objective in the examination of this molecule: the development of a computational model for benzo-fusion.

Conceptually, the simplest approach to the problem of scsa's for benzo-fusion is obtained by considering the difference in chemical shifts of naphthalene and anthracene. The scsa's calculated in this fashion are shown in Figure 4A, and although potentially useful, they are adequate for a linear benzo[*b*]fusion failing to take into account the inherent dissemmetry encountered with benzo[*c*]fusion. A more adequate model is however obtained by performing this same type of calculation for the fusion of an addi-

tional benzo moiety onto naphthalene to give phenanthrene. The scsa's obtained in this computation are shown in Figure 4B, and were applied in the calculation of the ^{13}C-nmr chemical shifts for the benzo[*c*]phenarsazine-7-chloride (**3**), which are shown in Table V.

Utilizing the calculated ^{13}C-nmr chemical shifts of **3** as a starting point in conjunction with what information could be extracted from the ^{1}H-decoupled spectrum of **3** which is shown in Figure 3, we next resorted to a ^{1}H-^{13}C spin-coupled spectrum acquired under gated decoupling conditions (13). From this spectrum, the interpretation of which was further aided by selective excitation techniques (16-18), one protonated resonance, C6, was unequivocally assigned to the resonance observed at δ 131.20. As in the case of the C1 resonance contained in the spectrum of **2** which was discussed above, the C6 resonance in this molecule also lacked a three bond coupling by virtue of its position in the system. It should further be noted that this assignment is in good agreement with the calculated chemical shift of δ 131.9 using the computational model just described. The remainder of the spin-coupling constants provided relatively little from a diagnostic standpoint, and are merely summarized in Table VI.

Table VI

^{1}H-^{13}C Spin-coupling Constants for Benzo[*c*]phenarsazine-7-chloride (**3**) in Hexadeuteriodimethylsulfoxide at 33°.

Carbon	δ	$^{1}J_{CH}$	$^{2}J_{CH}$	$^{3}J_{CH}$
1	122.38	J_{C1H1} = 162.7	(a)	(a)
1a	122.38		(b)	(b)
1b	136.49			J_{C1bH6} = 7.9
2	125.91	J_{C2H2} = 161.5		J_{C2H4} = 8.4
3	127.84	J_{C3H3} = 162.2		J_{C3H1} = 7.9
4	128.53	J_{C4H4} = 163.6	(a)	(a)
4a	135.37			6.8 (c)
5	119.99	J_{C5H5} = 165.4		J_{C5H4} = 7.5 (d)
6	131.20	J_{C6H6} = 161.1		
6a	115.82		J_{C6aH6} = 4.9	J_{C6aH5} = 7.5
7a	121.63		(b)	(b)
8	134.70	J_{C8H8} = 163.0		J_{C8H10} = 8.1
9	121.15	J_{C9H9} = 162.9		J_{C9H11} = 7.5
10	131.92	J_{C10H10} = 161.1		J_{C10H8} = 8.1
11	118.19	J_{C11H11} = 163.6		J_{C11H9} = 4.9
11a	139.97			J_{C11aH8} = 8.5
				$J_{C11aH10}$ = 8.5

(a) Long range coupling constants were poorly resolved at the digital resolution employed; (b) Obscured in gated decoupling experiment and was not examined by selective excitation; (c) Could arise from either $^{3}J_{C4aH3}$ or $^{3}J_{C4aH6}$ and no definitive assignment of this coupling is possible; (d) It is presumed that this coupling is a three bond coupling on the basis of its magnitude, although it could alternatively be a result of $^{2}J_{C5H6}$, in which case the coupling would be unusually large for a two bond coupling in this type of system.

An important feature, critical to the assignment of the ^{13}C-nmr spectrum of **3**, was the verification of our presumption that this system underwent anisotropic reorientation of a type analogous to the previous two systems. The T_1 relaxation times were thus measured, once again using the inversion-recovery technigue, to give relaxation times which are shown in Table V. From these data, it is readily noticed on first inspection that two resonances exhibited relatively short T_1 relaxation times compared to the balance of the carbons in the molecule. Specifically, the resonances at δ 127.84 and δ 121.15 had relaxation times of 0.45 and 0.44 second, respectively. The remaining carbons, on the other hand, all exhibited somewhat longer T_1 relaxation times which on ititial inspection all appeared to consist of a single group. By examining the general structure of benzo[*c*]phenarsazine-7-chloride, it is illogical to assume that the axis of anisotropic reorientation passes through the center of the phenarsazine skeleton as in the previous cases. Rather, it is much more probable that such an axis would pass through the general center of mass of **3**, generally in the vicinity of C3 and C9, which would account for the observation that there are only two carbons with short T_1 relaxation times. From this point, it was logical to attempt to establish the precise orientation of the axis of anisotropic reorientation using the method of Platzer (12). According to this treatment, the effective correlation time for each carbon is given by the expression:

$$\tau_{eff} = A(6R_2)^{-1} + B(5R_2 + R_1)^{-1} + C(2R_2 + 4R_1)^{-1} \quad (3)$$

where the term R_1 = rotational diffusion coefficient for rotation about the principal axis of anisotropic reorientation while R_2 = diffusion coefficient for rotation about the perpendicular axis. The coefficients of the individual terms are given by the expressions:

$$A = 1/4(3\cos^2\theta - 1)^2 \quad (4)$$

$$B = 3/4\sin^2 2\theta \quad (5)$$

$$C = 3/4\sin^4\theta \quad (6)$$

where θ represents the angle between the C-H bond vectors and the X-X′ axis of anisotropic reorientation. If motional anisotropy is further characterized by allowing $\sigma = R_1/R_2$, we obtain the expression:

$$1/T_1 = N\hbar^2\gamma_C^2\gamma_H^2 r_{CH}^{-6}(6R_2)^{-1}$$
$$[A + 6B/5 + \sigma + 6C/2 + 4\sigma] \quad (7)$$

from which the measured values of $1/T_1$ must be proportional to the term:

$$[A + 6B/5 + \sigma + 6C/2 + 4\sigma] \quad (8)$$

calculated as a function of θ and σ. By systematically varying the orientation of the axis of anisotropic reorientation in conjunction with σ, it is possible to obtain an optimal orientation of the axis through the molecular framework (19).

Using the method just described, the axis of anisotropic reorientation was located as passing through the molecule in the vicinity of C3 and C9 at an angle of 67° relative to the C1b-C6a bond axis which was taken as a reference line as shown in Figure 5. While on initial inspection it may appear that there are only two angular C-H bond vector

orientations relative to the axis, a more careful inspection reveals that there are instead three. Beginning with the most coincidently oriented C-H bond vector on the benzo portion of the molecule, C3 is oriented at an angle of 7° relative to the axis. The C1 and C4 C-H bond vectors are oriented at an angle of 53° of the axis while the C2 bond vector is oriented at an angle of 67° relative to the axis. Rather than the random scatter which might be initially invoked to account for the differences among the group of longer T_1 relaxation times, it is instead most probably associated with the differences in relative orientation. Utilizing this geometrical model for anisotropic reorientation in conjunction with the mathematical method of Platzer (12), we obtain an optimal value of $\sigma = 1.7$.

Equipped with the information from the relaxation study with regard to the C-H bond vector angular dispersions, the assignment of the ^{13}C-nmr spectrum of benzo[*c*]-phenarsazine-7-chloride (**3**) can be straightforwardly undertaken on the basis of chemical shift arguments and the relaxation time data. Complete assignments for **3** in addition to the relaxation times and the C-H bond vector orientations are gathered in Table V.

In summary, spin-lattice relaxation times have been untilized, in conjunction with chemical shift arguments derived from isosterically related heterocyclic systems and ^{1}H-^{13}C spin-coupling constants, as a basis for the assignment of the previously unassigned phenarsazine-10-chloride (**1**) system. The compound has further been found to generally obey benzenoid scsa's for simple substitution, and a method has been developed for calculating the effects of benzo-fusion on the ^{13}C-nmr chemical shifts of the parent system. Phenarsazine-10-chloride analogs have, in general, been shown to reorient anisotropically about an axis passing through the center of the molecule, while for benzo[*c*]phenarsazine-7-chloride the axis of anisotropic reorientation has been shown to shift to an angle of 67° relative to the C1b-C6a bond axis, a change of $\cong$23° relative to the aformentioned analogs. Further studies are at present underway in these laboratories dealing with phenarsazine analogs and will be reported.

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EXPERIMENTAL

The syntheses of phenarazazine-10-chloride (**1**), 3-chlorophenarsazine-10-chloride (**2**) and benzo[*c*]phenarsazine-7-chloride (**3**) were conducted by the reaction of the appropriate amine with arsenic trichloride according to the general procedure of Wieland and Rheinheimer (20). Satisfactory melting points were obtained for each of the componds following recrystallization from xylene.

The nmr experiments conducted on the three compounds described in this study were executed on a Varian XL-100 nmr spectrometer operating at 25.2 MHz in the Fourier transform mode for carbon. The spectrometer was equipped with a Nicolet TT-100 data system which employed an NT-440 frequency sythesizer and a TT-760 decoupler. For the ^{1}H-decoupled spectra shown in Figures 1-3, the decoupler was centered at δ 7.0 in the proton spectral window with sufficient power such that $\gamma H_2/2\pi = 2.9$ KHz. The decoupled spectra were acquired using 4K data points, which with the employed sweep width of 5 KHz resulted in a digital resolution of 1.22 Hz. Typical instrument paramenters were: pulse width = 12 μsec (tip angle = 54°); interpulse delay = 0.5 sec; acquisition time = 0.8192 sec (for 4K data) while the coupled spectra employed 8K points with an aquisition time = 1.6384 sec. All ^{1}H-^{13}C spin-coupled spectra were obtained initially using the gated decoupling technique of Freeman and Hill (13). To aid in the interpretation of the proton coupled spectra, selective excitation coupled subspectra were obtained for each of the protonated carbon resonances using the procedure of Bodenhausen, Morris and Freeman (16,17) with modifications to this spectrometer system as previously described by Martin (18).

Spin-lattice (T_1) relaxation studies were conducted using the inversion-recovery sequence (9,10) on samples which were prepared by dissolving 1 mmole of the appropriate compound in 3.0 ml of hexadeuteriodimethylsulfoxide. Each sample was then degassed with zero grade argon for a period of 30 minutes and then subjected to three freeze pump thaw cycles. After completion of the degassing, the samples were fitted with precision bore glass vortex plugs, blanketed with an argon atmosphere and the cap wrapped in parafilm. A series of sixteen tau values was utilized for each of the samples which ranged from 250 μsec to 4.0 sec, with an interpulse delay of 5.0 sec. The tau values were randomized for execution and were automatically reordered prior to data processing. Data reduction was conducted using the Three Parameter Fitting Program of Kowalewski and co-workers (11). Tumbling preference ratios, ϱ were computed for 1 and 2 using the procedure previously described by Gampe, *et al.* (7). The precise location of the axis of anisotropic reorientation through benzo[*c*]phenarsazine-7-chloride was conducted using the method of Platzer (12), which was adopted for computation on a Hewlett-Packard Model 41C calculator. Nuclear Overhauser Effects (NOE) were measured for the protonated carbons using the off-delay decoupling procedure in which the decoupling is turned off with the exception of the acquisition period itself. Interpulse delays for the NOE measurements were 10.0 sec, and values $\eta = 3.0$ obtained for all of the protonated carbons within experimental error.

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