

# NMR Studies on Cyclic Arsenites. $^1\text{H}$ NMR Spectral Analysis and Conformational Studies of 2-Chloro-5-methyl- and 2-Phenyl-5-methyl-1,3,2-oxathiarsolane and 2-Chloro-5-methyl-1,3,2-dithiarsolane and -1,3,2-dioxarsolane

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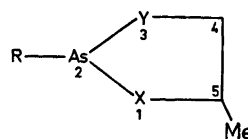
The  $^1\text{H}$  NMR spectra of the title compounds have been completely analyzed although no separation of the geometrical isomers was achieved. Approximate values of the ring torsional angles have been obtained. The present results demonstrate the tendency of a sulfur atom to increase the puckering of the ring. The NMR data are adequately described on the basis of flexible twist-envelope conformations. In the *cis* isomers the steric requirements of the substituents seem to confine the ring to a particular conformation whereas the *trans* forms get significant contributions from two pseudo-rotamers.

It is generally accepted that the five-membered ring exists in highly flexible puckered conformations where only the more bulky substituents have specific steric interactions.<sup>1,2</sup> NMR spectroscopy has supplied detailed information about five-membered rings although facile interconversions between numerous equilibrium conformers present considerable difficulties.

In preceding papers the NMR spectra of a series of arsolanes,<sup>3,4</sup> and phospholanes<sup>5,6</sup> have been studied. The NMR spectra were adequately explained on the basis of rapidly interconverting non-planar forms with a stable configuration at arsenic or phosphorus. Our previous results demonstrated the tendency of a sulfur atom to increase the puckering of the ring. Similar observations have also been reported for the 1,3-dithiolane<sup>7,8</sup> and 1,3-oxathiolane<sup>9</sup> rings as compared with the 1,3-dioxolane ring.

2-Substituted 5-methyl-1,3,2-dioxarsolanes and -1,3,2-dithiarsolanes<sup>4</sup> as well as the analogous phospholanes,<sup>5,6,10</sup> have been found to exist as *cis* and *trans* isomers with the latter predominating. In a series of 2,4-dialkyl 1,3-dioxolanes<sup>2</sup> and -1,3-oxathiolanes,<sup>9</sup> however, the *cis* forms are thermodynamically more stable than the *trans* isomers.

In order to obtain more information about externally substituted arsolanes we have prepared compounds I–IV and investigated their  $^1\text{H}$  NMR spectra. The  $^1\text{H}$  NMR spectra of the *cis* and *trans* isomers have been fully analyzed for the three latter compounds.



- I; R = Cl, X = O, Y = S  
 II; R = Ph, X = O, Y = S  
 III; R = Cl, X = Y = S  
 IV; R = Cl, X = Y = O

## EXPERIMENTAL

Compound I was prepared from 3-mercapto-propane-2-ol and trichloroarsine in tetrachloromethane solution under dry  $\text{N}_2$  atmosphere; b.p.<sub>0.3</sub> 70 °C. Compound II was synthesized from 3-mercapto-propane-2-ol and phenyl dichloroarsine in diethyl ether solution using triethylamine as base; b.p.<sub>1.0</sub> 100 °C. The pre-

paration of III and IV has been described in a previous paper.<sup>4</sup>

The NMR spectra were examined in deuteriochloroform and carbon disulfide solutions (ca. 50 % v/v). The NMR samples were prepared as previously described.<sup>3,4</sup>

The 60 MHz and 100 MHz spectra were recorded on JEOL-C-60H and VARIAN HA-100 spectrometers, respectively. Line positions were obtained by averaging the results of four frequency-calibrated spectra at about 50 Hz sweep width (1–1.5 Hz/cm).

The NMR spectra were analyzed as ABCD<sub>3</sub> spin systems using the computer programs UEANMR II,<sup>11</sup> UEATR<sup>12</sup> and KOMBIP.<sup>13</sup> The computations were performed on a UNIVAC 1110 computer. The root-mean-square deviations of 63–90 experimental and calculated transitions were less than 0.08 for the *trans* isomers and less than 0.10 for the *cis* isomers (except *cis*-IV).

The graphical output was obtained using a Calcomp Plotter.

## RESULTS AND DISCUSSION

The spectral analysis of compounds II–IV was tedious owing to partial overlap of spectral lines from pairs of geometrical isomers. The trial

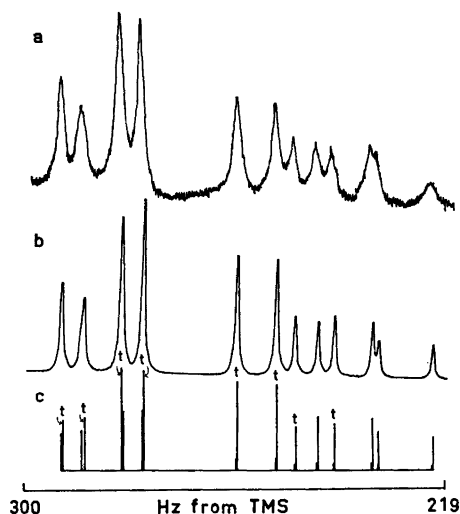


Fig. 1. The BC region of the 100 MHz spectrum of compound II: a, experimental spectrum; b and c, computed spectra for a *cis:trans* distribution of 1:2. Transition lines originating from the *trans* isomer are labelled t.

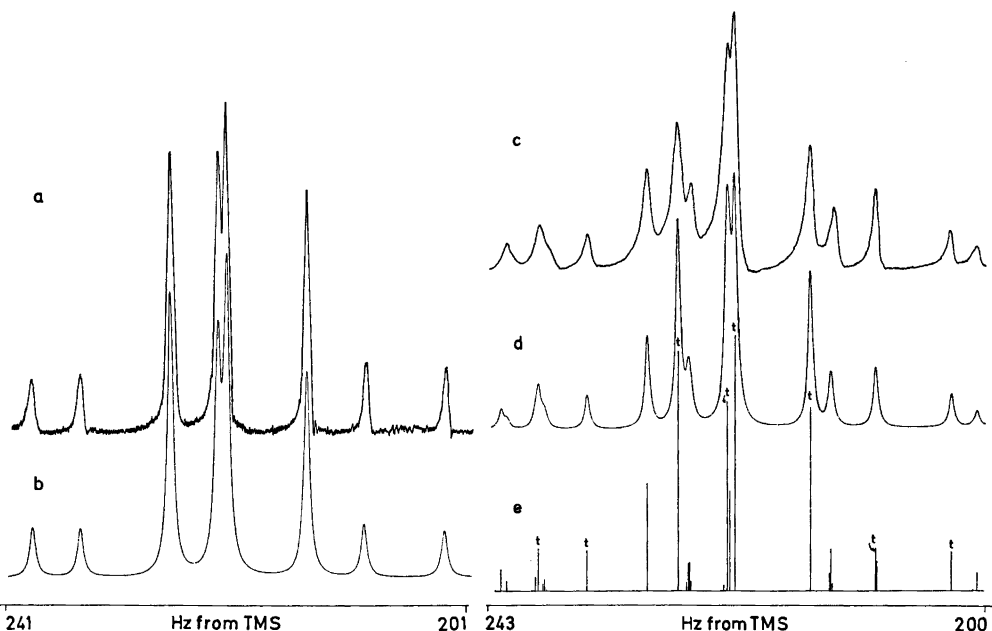
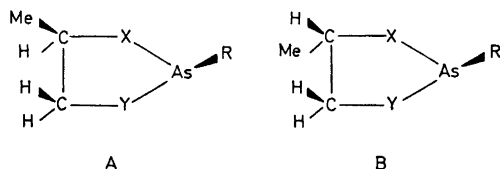


Fig. 2. The BC region of the 60 MHz spectrum of compound III: a and b, experimental and computed exchange-averaged spectra, respectively, resulting from rapid interconversions of the *cis* and *trans* forms (a small amount of tetraphenylarsonium chloride was added to the sample used for spectrum c)<sup>4</sup>; c, experimental spectrum of the individual isomers; d and e, computed spectra for a *cis:trans* distribution of 1:2. Transition lines originating from the *trans* isomer are labelled t.

parameters were obtained by analyzing the spectra as ABPX<sub>3</sub> systems on a first-order basis. However, only a lengthy trial-and-error analysis yielded acceptable trial values. The refined parameters resulting from iterative computer-analysis of the ABCD<sub>3</sub> spin systems, are listed in Table 1. The contributions from the individual isomers of compounds II and III are shown in Figs. 1 and 2 together with the calculated and experimental total spectra. The effect of rapid exchange of chlorine on the spectrum of III is also demonstrated in Fig. 2.

The methyl spectrum of compounds II–IV consists of two doublets with intensity ratio *ca.* 1:2, that partly overlap as shown in the low-temperature spectrum of compound IV in Fig. 3. The two individual methyl signal groups show that these compounds exist as a mixture of *cis* (A) and *trans* (B) isomers. However, only exchange-averaged NMR spectra resulting from rapid exchange of chlorine<sup>2–5</sup> were observed for I and IV at 30 °C. No significant change in the spectrum of I was observed in the temperature range 30 to –100 °C. For compound IV, how-



ever, we were able to “freeze out” both isomers at –90 °C (Fig. 3).

The methyl signals of the major isomers appear at higher field than the corresponding signals of the minor isomers. The low-field methyl signals have been assigned to the *cis* isomers since protons *cis* to the As–R bond should suffer downfield shifts according to the para-

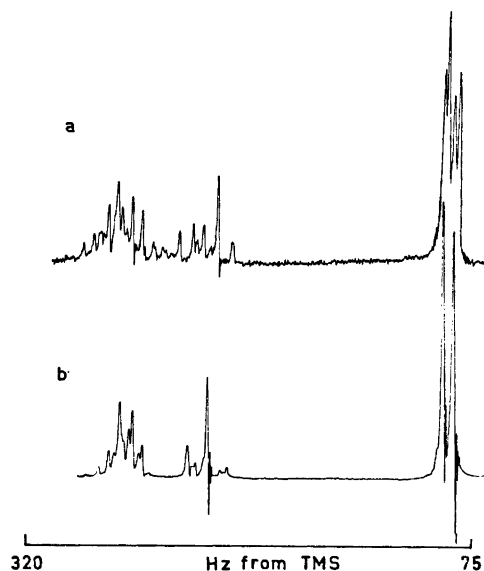


Fig. 3. Experimental 60 MHz spectrum of compound IV in CS<sub>2</sub> solution: a, –90 °C; b, 30 °C

Table 1. 60 MHz NMR parameters and ring torsional angles ( $\psi$ ) of compounds I–IV.<sup>a</sup>

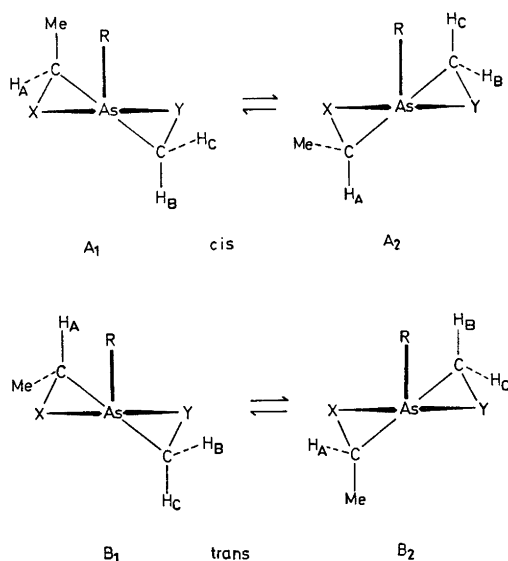
Compound	I		II <sup>b</sup>		III		IV	
			<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
Temp. °C	30	34			30		–90	
$\nu_A^c$	4.78	3.92	4.11		4.22	4.46	4.36	4.49
$\nu_B$	3.41	2.85	2.85		3.86	3.80	4.51	4.36
$\nu_C$	3.01	2.34	2.52		3.57	3.58	3.80	3.55
$\nu_{Me}$	1.49	1.34	1.18		1.63	1.48	1.40	1.36
$J_{BC}^d$	–11.39	–11.69	–11.23		–12.70	–12.15	–9.2	–8.74
$J_{AB}$	4.18	3.77	4.11		3.59	4.13	5.9	5.65
$J_{AC}$	9.59	10.56	7.69		8.89	6.61	9.2	8.70
$J_{AMe}$	6.06	5.92	5.90		6.64	6.60	5.8	6.17
$J_{BMe}$	0.00	0.00	0.00		–0.10	–0.02	0.0	–0.28
$J_{CMe}$	–0.03	0.05	0.04		–0.05	–0.03	0.0	0.00
$R$	2.3	2.8	1.9		2.6	1.6	1.6	1.5
$\psi$ (deg.)	59	62	56		61	53	53	52

<sup>a</sup> The methine and methylene protons are labelled A and BC, respectively. <sup>b</sup> Measured at 100 MHz. <sup>c</sup> Chemical shifts in  $\delta$ -values. <sup>d</sup> Coupling constants in Hz.

magnetic shift effect of chlorine and phenyl substituents.<sup>2-6,14,15</sup> Furthermore, as a result of the stereospecific effect the methine proton signals of the *trans* isomers ( $H_A$  *cis* to As-R) appear at lower field than the corresponding signals of the *cis* isomers ( $H_A$  *trans* to As-R). The assignment of the methylene signals followed from the spectral analysis. The chemical shifts of the methylene protons indicate that the anisotropy effect of the 5-methyl group rather than 2-R group, dominates.

The observed predominance of the *trans* isomers in the present compounds and related arsolanes<sup>4</sup> and phospholaness,<sup>5,6</sup> in contrast to the situation in 2,4-dialkyl-1,3-dioxolaness<sup>2</sup> and -1,3-oxathiolanes,<sup>9</sup> probably reflects changes in 1,3-steric interactions as a result of replacing carbon 2 by a trivalent group V element.

On the basis of the present NMR studies (*vide infra*) and previous results,<sup>4</sup> we believe that the investigated molecules can be adequately described by the twist-envelope conformations below. Since pseudo-libration is expected to occur in these systems,<sup>1,2</sup> each of these conformations represents the average of



a continuum of conformations of practically equal energy.

The X-C-C-Y torsional angle,  $\psi$ , of these ring systems has been calculated from the vicinal coupling constants of the  $CH_2CHCH_3$ -

moiety using the *R*-value method due to Lambert.<sup>16</sup> However, we wish to emphasize that the calculated torsional angles characterize only the mean geometry of the geometrical isomers. The estimated value of  $\psi$  in *cis*-IV is probably too small due to a significant uncertainty in the spectral parameters of that particular isomer.

The results of this study together with those presented earlier<sup>4,6</sup> have demonstrated that replacement of the oxygen atoms by sulfur increases the ring puckering by 3–6°. Similar observations have also been made for 1,3-dithiolanes,<sup>7,8</sup> and 1,3-oxathiolanes.<sup>7</sup>

The  $J_{AC}$  coupling constant is 5–7 Hz greater than  $J_{AB}$  in the *cis* isomers. This difference is reduced to 2.5–3.5 Hz in the corresponding *trans* forms. Bergesen and Bjorøy<sup>6</sup> have also obtained similar results for 2-substituted 5-methyl-1,3,2-dithiaphospholaness and -1,3,2-oxathiaphospholaness. The large value of  $J_{AC}$  in the *cis* forms suggests that this coupling involves the pseudo-axial hydrogens of the  $A_2$  rotamer. A significant contribution from  $A_1$ -like rotamers would result in a smaller value of  $J_{AC}$  and a corresponding increase in  $J_{AB}$ . The equatorial preference of the 5-methyl group probably reflects severe *syn*-axial interactions between the substituents at carbon 5 and arsenic in the  $A_1$  conformer.

In contrast, the reduced difference between  $J_{AB}$  and  $J_{AC}$  in the *trans* forms indicates comparable contributions from the  $B_1$  and  $B_2$  pseudo-rotamers. This implies that the energy minima of the *trans* isomers are less affected by the steric requirements of the substituents than the *cis* isomers where a particular conformation appears to be strongly favoured.

Since the NMR parameters of compounds III and IV, subjected to rapid exchange of chlorine, have been reported,<sup>4</sup> it is of interest to calculate the corresponding weighted average values from the present data. The following values of the vicinal coupling constants (in Hz) have been obtained by assuming a 1:2 distribution of the *cis* and *trans* isomers, respectively.

#### Compound III:

$$J_{BC} = -12.35 \text{ (-12.04)}; J_{AB} = 3.90 \text{ (4.04)}$$

$$J_{AC} = 7.39 \text{ (7.18)}; J_{AMe} = 6.62 \text{ (6.63)}$$

#### Compound IV:

$$J_{BC} = -8.89 \text{ (-9.14)}; J_{AB} = 5.73 \text{ (5.74)}$$

$$J_{AC} = 8.87 \text{ (8.88)}; J_{AMe} = 6.05 \text{ (6.04)}$$

The agreement with the previously reported values,<sup>4</sup> in parentheses, is better than expected in view of possible solvent and temperature effects.

The measured geminal coupling constants,  $J_{BC}$ , are well within the reported ranges for five-membered rings.<sup>1-10,14,15,17</sup> The magnitude of  $J_{BC}$  is seen to increase when passing from 1,3,2-dioxarsolanes to 1,3,2-dithioarsolanes *via* 1,3,2-oxathiarsolanes. This increase in  $|J_{BC}|$  is mainly due to the electronegativity difference between oxygen and sulfur and to increased ring puckering.<sup>18</sup>

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