

NMR Studies on Cyclic Arsenites

Spectral Analysis of the Geometrical Isomers of 2-Chloro- and 2-Phenyl-4-methyl-1,3,2-dioxarsolane and -1,3,2-dithiarsolane

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The proton NMR spectra of the four title compounds have been fully analyzed on the basis of an ABCD₃ spin system. The chemical shifts and coupling constants of the CH₂CHCH₂ moiety are reported and discussed. It is shown that these compounds are a mixture of *cis* and *trans* isomers with the latter predominating. Approximate values of the ring torsional angles have been obtained. The NMR data suggest that these five-membered rings can be adequately described in terms of flexible twist-envelope conformations. Only the *cis* isomers show signs of specific steric interactions in that a particular conformation appears to be favoured.

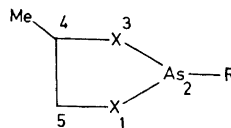
The application of NMR spectroscopy to the determination of the conformations and configurations of five-membered rings presents considerable difficulties owing to facile interconversions which occur between numerous equi-energy conformers.¹ It is generally believed that the five-membered rings exist in highly flexible puckered conformations. The process by which the puckering moves about the ring is termed pseudo-rotation.^{1,2}

Although external substitution of the five-membered ring may prevent complete pseudo-rotation, conformational changes are still quite facile when one or even two small substituents are introduced into the ring. In more highly substituted systems, however, the steric requirements of the substituents may confine the ring to definite energy minima not necessarily associated with a specific conformation of the ring.^{2,3}

In preceding papers the NMR spectra of several arsolanies have been studied.⁴⁻⁶ The NMR data indicate that these five-membered rings exist in rapidly interconverting non-planar forms but that inversion at arsenic is slow.

This paper reports preparation and NMR investigations of the five-membered arsenites I-IV.

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



These compounds are presumably a mixture of two geometrical isomers, *cis* and *trans* forms, owing to the configurational stability about the arsenic atom. The spectral analysis of the NMR spectra is, therefore, expected to be tricky due to overlap of spectral lines from both geometrical isomers.

The existence of two geometrical isomers of 2-chloro-4-methyl-1,3,2-dioxaphospholane has been reported by Goldwhite.⁷ At the inception of this investigation, however, detailed information regarding preferred conformations of similar di-substituted oxygen or sulphur containing heterocycles was limited largely to 2,4-dialkyl-1,3-dioxolanes.³

Our studies of the title compounds were undertaken in order to (1) verify the existence of geometrical isomers, (2) analyze these complex spin systems, (3) determine if any dominant conformations existed, and (4) examine whether rapid exchange of chlorine and pseudo-rotation were occurring on the NMR time scale.

EXPERIMENTAL

Phenyl dichloroarsine was prepared from diphenyl mercury and trichloroarsine according to a procedure of Blicke and Smith.⁸ Compounds I, III, and IV were synthesized by the method of Kamai and Chadaeva⁹ using trichloroarsine or phenyl dichloroarsine and 1,2-propanediol or 1,2-propanedithiol. Compound II was prepared from trichloroarsine and 1,2-propanedithiol, according to a method of Ruggeberg *et al.*¹⁰ The boiling points of the prepared compounds are as follows: B.p._{1,2} 69.5–70.5°C, b.p._{0,8} 106–107°C, b.p.₁₀ 121–123°C, and b.p._{1,3} 149–150°C for compounds I, II, III, and IV, respectively.

The NMR spectra of these four compounds were examined either as neat liquids or else in benzene or deuteriochloroform solutions. The NMR samples were prepared as previously described.^{4–6} TMS and deuteriochloroform served as internal locking substances for the 60 MHz and 90 MHz spectra, respectively.

The 60 MHz spectra were run on a JEOL-C-60H spectrometer. Line positions were obtained by averaging the results of four frequency-calibrated spectra of 54 Hz sweep width.

The 90 MHz spectra were recorded on a Bruker HX 90 E spectrometer using heteronuclear lock on deuterium. The spectra used in the calculations were recorded at the calibrated sweep range 1 Hz/cm.

Computations were performed on the IBM/50H computer at the University of Bergen. The graphical output was obtained on a Calcomp Plotter.

SPECTRAL ANALYSIS

The spectra of the four compounds were analyzed as ABCD₃ systems using the computer programs UEANMR II¹¹ and UEAITR.¹² The former program was only used in conjunction with the subroutine KOMBIP¹³ to obtain “stick”- and line-shape plots. The “stick”- plots based on trial parameters facilitated the analyses, in particular the rather tricky analyses of compounds III and IV. The iterative fitting of experimental and calculated transitions was performed by means of the UEAITR program.

Several of the spectra can be approximately analyzed as $ABPX_3$ systems with $J_{BX} \approx J_{PX} \approx 0$. The methyl spectrum should then resemble the X_3 part of an ABX_3 system. This spin system is conveniently treated by the composite particle technique,¹⁴ thus

$$ABX_3 = DDQ + 2DDD \quad (1)$$

The composite particles are referred to in the order A, B, and X_3 . The transition frequencies of the DDD sub-system which is identical with the ABX system, have been listed previously.¹⁵ The six X-transitions are given by

$$\nu_X \pm D(m_X) - \varepsilon D(m_X - 1) \quad (2)$$

$$\nu_X \pm N \quad (3)$$

where

$$D(m_X) = [(\frac{1}{2}\nu_{AB} + m_X N)^2 + \frac{1}{4}J_{AB}^2]^{\frac{1}{2}} \quad (4)$$

$$N = \frac{1}{2}(J_{AX} + J_{BX}); \nu_{AB} = \nu_A - \nu_B \quad (5)$$

with $m_X = \frac{1}{2}$ and $\varepsilon = \pm 1$.

The DDQ sub-system gives the energy level groupings (1:1:1:1) and (2:2:2:2) in the X spectrum corresponding to the values ± 1 and 0, respectively, of the magnetic quantum number m_{AB} . For the extreme values $m_{AB} = \pm 1$ the DDQ sub-system thus contains two x_2 sub-spectra with effective Larmor frequencies given by eqns. (3) and (5). It is readily shown that the transition $(m_X - 1) \rightarrow m_X$ within the (2:2:2:2) sub-pattern, results in twelve lines given

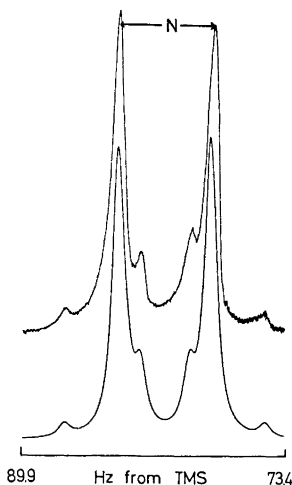


Fig. 1. Experimental (upper trace) and calculated (lower trace) 60 MHz spectrum of the methyl protons in compound I subjected to rapid exchange of chlorine. The "N-doublet" is shown.

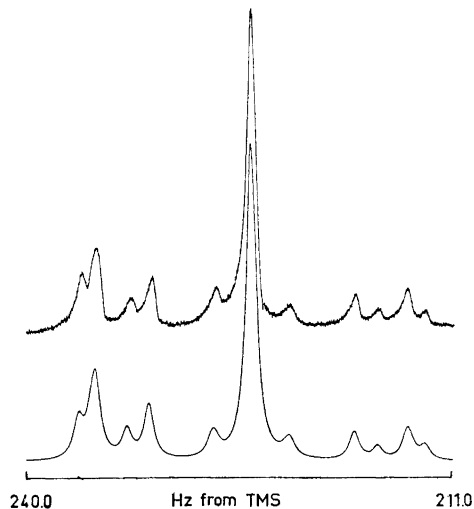


Fig. 2. Experimental (upper trace) and calculated (lower trace) 60 MHz spectrum of the H_C proton in compound I subjected to rapid exchange of chlorine.

by eqns. (2), (4), and (5) with $m_X = \frac{3}{2}$ and $\pm \frac{1}{2}$. The four lines arising from the $m_X = -\frac{1}{2} \rightarrow \frac{1}{2}$ transition thus occur in both sub-spectra. These four lines together with the "N-doublet" constituting all X-transitions of the ABX system,¹⁵ should thus be easily discerned in the experimental methyl spectrum.

Only the average NMR spectra resulting from rapid exchange of chlorine were analyzed for compounds I and II. The trial parameters of these spin systems were easily obtained by using the ABPX₃ approximation. In Fig. 1 the methyl spectrum of I clearly shows the six X-transitions which are common for the ABX and ABX₃ systems. From this spectrum good trial values of ν_X , ν_{AB} , N , and J_{AB} were obtained.

The refined spectral parameters of I and II are listed in Table 1. Figs. 1–3 show excellent fit between the experimental and calculated spectra of I.

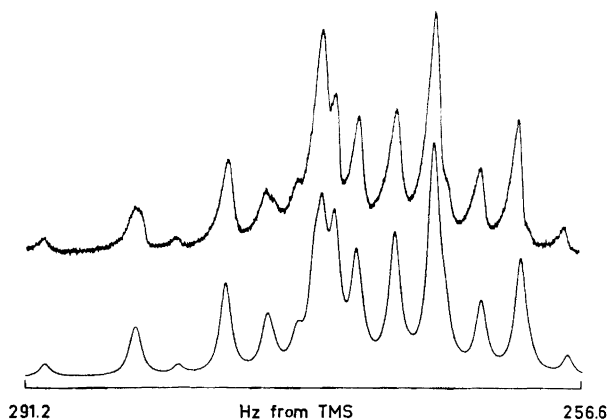


Fig. 3. Experimental (upper trace) and calculated (lower trace) 60 MHz spectrum of the H_A and H_B protons in compound I subjected to rapid exchange of chlorine.

The analyses of III and IV were more tricky owing to partial overlap of spectral lines from the *cis* and *trans* isomers. It will be shown later that the *trans* isomer predominates in the present compounds. Again some trial parameters of both isomers of III were found by analyzing directly the spectra as ABPX₃ systems. The high-field and low-field parts of the spectrum in Fig. 4 were assigned to the H_p proton (labelled H_c in Table 1) in the *trans* and *cis* isomers, respectively. This assignment gives ν_p and $|J_{AP} + J_{BP}|$. Approximate values of ν_X , ν_{AB} , N , and J_{AB} followed from the methyl signals. However, the uncertainties in ν_{AB} and J_{AB} are considerable due to severe overlap of the methyl signals of both isomers. Furthermore, since the AB regions of both isomers are superimposed (Fig. 5) it was also difficult to obtain ν_A , ν_B , and J_{AB} from this part of the spectrum. Only a tedious trial-and-error analysis yielded acceptable trial values. The final parameters obtained from the iterative analysis are listed in Table 1. The contributions from the individual isomers are shown in Figs. 4 and 5 together with the calculated and experimental total spectra.

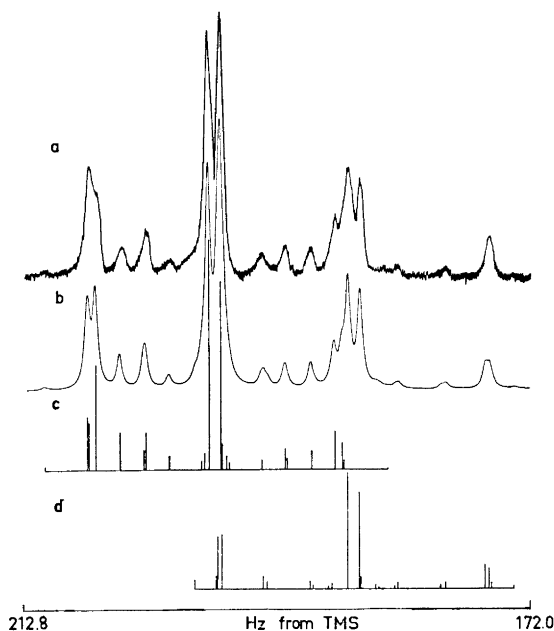


Fig. 4. The C region of the 60 MHz spectrum of compound III: a, experimental spectrum b, computed total line-shape spectrum for a *cis:trans* intensity distribution of 1:1.6; c, computed stick-plot of the H_C proton in the *trans* isomer; d, computed stick-plot of the H_C proton in the *cis* isomer.

From the experimental 90 MHz spectrum of IV in Fig. 6 it is seen that the spectrum of the *trans* and *cis* isomer can be approximately analyzed as $APQX_3$ and $ABPX_3$ systems, respectively. Trial values of ν_X and J_{AX} are directly obtainable from the methyl signals. The multiplet consisting of eight lines centered at *ca.* 272 Hz from TMS (Fig. 6) has been assigned to the two PQ protons (labelled BC in Table 1) of the *trans* isomer. Direct analysis of this spectrum region gives trial values for ν_P , ν_Q , J_{AP} , J_{AQ} , and J_{PQ} . A coupling scheme of the A region of the predominating isomer was then drawn on the basis of the known coupling constants. This procedure made it possible to pick out the extreme lines in the A spectrum and hence ν_A , in spite of severe overlap of spectral lines from the *cis* isomer.

The doublet of doublets centered at *ca.* 228 Hz from TMS (Fig. 6) was assigned to the H_P (labelled H_C in Table 1) proton of the *cis* isomer. This assignment yielded ν_P , J_{AP} , and J_{BP} . The doublet of doublets centered at *ca.* 306 Hz from TMS (Figs. 6 and 7) is due to the H_B proton and thus gives ν_B , J_{AB} , and J_{BP} . ν_A was obtained from the experimental spectrum after disregarding lines from the predominating isomer.

After having found all the necessary trial parameters iterative analyses were carried out on the experimental 90 MHz and 60 MHz spectra of both

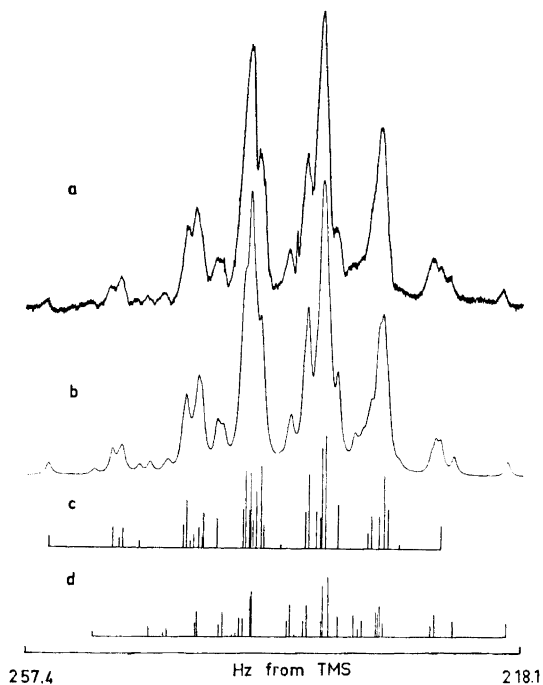


Fig. 5. The AB region of the 60 MHz spectrum of compound III: a, experimental spectrum; b, computed total line-shape spectrum for a *cis:trans* intensity distribution of 1:1.6; c, computed stick-plot, of the H_A and H_B protons in the *trans* isomer; d, computed stick-plot of the H_A and H_B protons in the *cis* isomer.

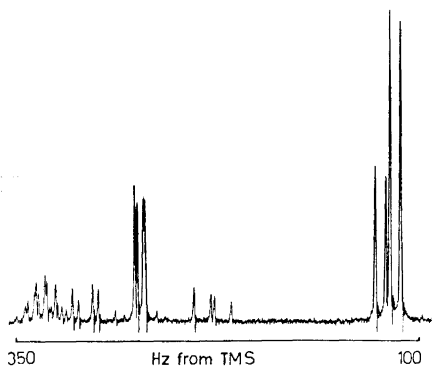
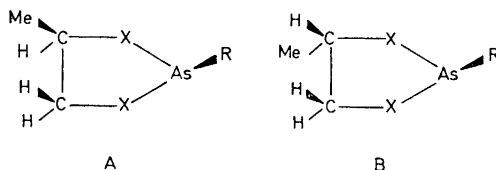


Fig. 6. Experimental 90 MHz spectrum of the CH_3CHCH_2 protons in compound IV.

isomers. The agreement between the 60 MHz and 90 MHz parameters of IV is satisfactory. Fig. 7 shows experimental and calculated 90 MHz spectra of IV for the only region where spectral lines from both isomers overlap.

RESULTS AND DISCUSSION

The methyl NMR spectrum of compounds II, III, and IV (Fig. 6) consists of two doublets that partly overlap in the 60 MHz spectrum. The two individual methyl signals show that these compounds are a mixture of two geometrical isomers, *cis* (A) and *trans* (B) forms, which are interconvertible by inversion at arsenic.



The predominant isomer displays an upfield chemical shift for the methyl signal in comparison with the other isomer. The actual intensity ratios of the low-field:high-field doublets are approximately 1:1.3, 1:1.6 and 1:2 for the examined samples of II, III, and IV, respectively. The high-field and low-field methyl signals have been assigned to the *trans* (B) and *cis* (A) forms, respectively, that is, the *trans* isomer is predominating. This assignment has been made on the basis of the reported paramagnetic shift effect of chlorine and phenyl substituents in arsolanes,⁴⁻⁶ and phospholanes.^{16,17} The remaining chemical shift values in Table I then followed from the spectral analysis.

Table I. 60 MHz NMR parameters (in Hz) and ring torsional angles (ψ) of compounds I, II, III and IV.^a

Compound	I	II	III		IV		IV ^b	
		C ₆ H ₆	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
Solvent ^c	Neat	C ₆ H ₆		C ₆ H ₆		neat		CDCl ₃
Temp.°C	60	30		30		75		30
ν_A^d	272.85	250.92	235.10	239.80	219.30	221.00	330.08	332.58
ν_B	267.20	216.69	236.75	236.25	201.41	178.88	305.46	268.82
ν_C	225.63	203.11	187.16	198.23	154.13	181.58	228.38	274.51
ν_{Me}	80.64	81.38	68.01	62.61	80.78	76.14	123.83	114.28
J_{BC}	-9.14	-12.04	-9.22	-8.77	-12.65	-11.97	-12.66	-11.91
J_{AB}	5.74	4.04	4.52	5.17	3.83	4.37	3.65	4.55
J_{AC}	8.88	7.18	10.02	7.61	10.22	6.10	10.35	5.98
J_{AMe}	6.04	6.63	5.98	5.93	6.57	6.66	6.43	6.59
J_{BMe}	-0.11	-0.02	-0.07	-0.04	-0.07	-0.02	-0.11	-0.01
J_{CMe}	-0.09	-0.04	-0.06	-0.07	-0.07	-0.01	-0.04	-0.02
Assigned								
Transitions	93	102	85	89	104	78	96	91
RMS error	0.086	0.059	0.076	0.061	0.094	0.065	0.068	0.073
R	1.55	1.78	2.22	1.47	2.67	1.39	2.83	1.31
ψ (deg.)	53	55	58	52	61	51	62	50

^a The methine and methylene protons are labelled A and BC, respectively. ^b Measured at 90 MHz. ^c 50 % v/v. ^d Chemical shifts downfield from TMS.

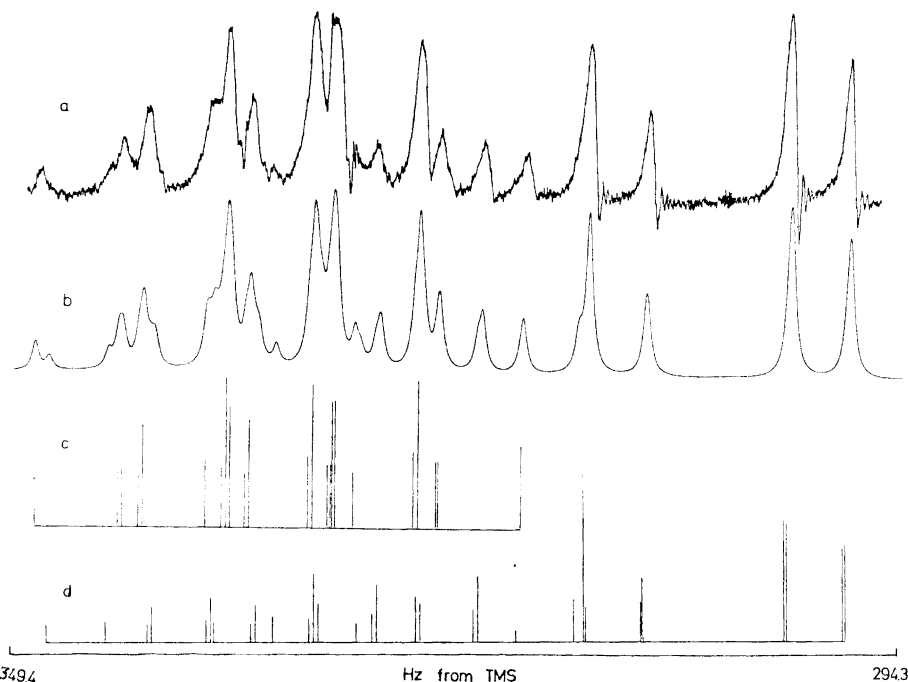
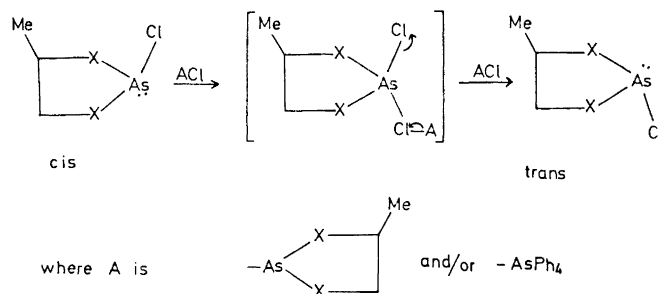


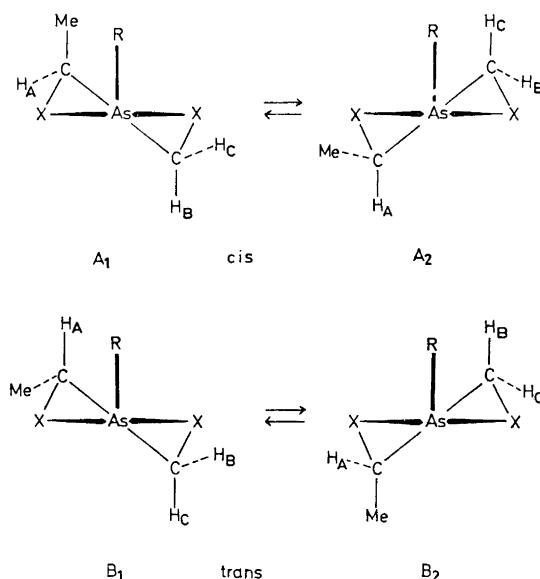
Fig. 7. The lower region (Fig. 6) of the 90 MHz spectrum of compound IV; a, experimental spectrum; b, computed total line-shape spectrum for a *cis:trans* intensity distribution of 1:2; c, computed stick-plot of the H_A proton in the *trans* isomer; d, computed stick-plot of the H_A and H_B protons in the *cis* isomer.

It is seen that 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) in agreement with the stereospecific anisotropy effect.⁴⁻⁶

However, only one methyl doublet was observed at room temperature for neat as well as diluted samples of I. The methyl signal of a neat sample of II showed, similarly, a single doublet at 135°C. Coalescence of the signal occurred at *ca.* 110°C whereas two distinct methyl doublets were observed at 70°C. However, when a small amount of tetraphenylarsonium chloride was added to a 50 % v/v solution of II in dry benzene, the methyl spectrum showed only one doublet. These observations indicate that exchange of chlorine proceeds with inversion at arsenic since retention of configuration at arsenic would preserve the two kinds of methyl signals. Similar observations have been made for 2-chloro substituted 1,3,2-dioxarsolanes⁴ and several 1,3,2-dioxaphospholanes.¹⁶⁻¹⁹ The rate of chlorine exchange is considerably faster for the oxygen containing arsolanes than for their sulphur analogues. This observation should be conferred with the reported stability of the ring As-S bond as compared to the As-O bond in arsolanes. The observed dependence of chlorine exchange upon concentration of solute or tetraphenylarsonium chloride suggests that exchange occurs by a bimolecular process,¹⁸ *viz.*



Previous studies of 1,3,2-dioxarsolanes^{4,5} and 1,3,2-dithiarsolanes⁶ have shown that these five-membered rings exist in rapidly interconverting non-planar forms with a stable configuration at arsenic. We believe that the predominating pseudo-rotamers of the four arsolanones examined in this work, can be adequately described by the twist-envelope conformations below:



Evidence for this assumption is presented in the following discussion. At the outset, however, it should be pointed out that, since pseudo-libration is expected to occur in these systems,^{2,3} each of the above pseudo-rotamers represents the average of a range of conformations of similar energies.

The X-C-C-X torsional angle, ψ , of these ring systems can be calculated from the J_{AB} and J_{AC} coupling constants of the CH_2CHCH_3 moiety using the *R*-value method due to Lambert.²⁰ The obtained *R*-values and corresponding torsional angles, however, represent the average of the conformational extremes

and thus characterize the mean geometry of the *cis* or *trans* isomers. The calculated R -values and the corresponding torsional angles are given in Table 1.

Since exchange of chlorine interconverts the *cis* and *trans* forms the spectral parameters of I and II listed in Table 1 are weighted average values of the two geometrical isomers. This makes it difficult to gain configurational information about the individual forms. The average torsional angle of II is, however, close to the values reported for 2-chloro- and 2-phenyl-1,3,2-dithiarsolane.⁶

The vicinal coupling constants of III and IV indicate that the preferred conformations of the ring are probably nearly the same for the two *cis* isomers, and for the two *trans* forms are likewise nearly the same. The X-C-C-X portion of the ring seems to assume a nearly staggered conformation in the *cis* forms whereas the *trans* forms are less puckered by 6–10°. The weighted average values of ψ in III and IV have been estimated to be 56° and 58°, respectively, that is, 3–4° more than in I and II.

The sulphur heterorings are more puckered than their oxygen counterparts except for *trans*-IV. This is consistent with the greater degree of flexibility conferred by the presence of sulphur rather than oxygen atoms in the ring. Similar observations have been reported previously for 1,3,2-dithiarsolanes,⁶ 1,3,2-dithiaphospholanes,²¹ and 1,3-dithiolanes²² relative to their oxygen analogues.^{6,16,22} The presence of methyl at carbon 4, however, seems to equalize, to some extent, the difference in ring puckering of the corresponding oxygen and sulphur containing rings.

The J_{AC} coupling constant is appreciably greater than J_{AB} in *cis*-III and *cis*-IV. Similar results have also been observed by Bergesen and Bjørøy in the *cis* forms of 2-chloro- and 2-phenyl-4-methyl-1,3,2-dithiaphospholane.²³ This is, however, not the case in the corresponding 2,4-dialkyl-1,3-dioxolanes.³ It can be anticipated from the Dreiding model and the Karplus relationship²⁰ that the largest vicinal coupling constant (J_{AC}) involves the pseudo-axial protons. This indicates predominance of the A_2 pseudo-rotamers for *cis*-III and *cis*-IV. The equatorial preference of the 4 methyl groups is probably caused by *syn*-axial interactions of the 4-methyl and 2-R substituents which are greater in the A_1 conformer possessing a pseudo-axial methyl group.

Willy and co-workers³ have found that the *cis* isomers of a series of 2,4-dialkyl-1,3-dioxolanes are thermodynamically favoured over the corresponding *trans* isomers. They have explained this on the basis of an unfavourable steric interaction of a pseudo-axial substituent at carbon 4 with a pseudo-axial hydrogen at carbon 2 (envelope conformation) in the *trans* isomer. This interaction is, however, absent in the arsolananes since carbon 2 has been replaced by trivalent arsenic. This may explain the observed predominance of the *trans* isomer in the present arsolananes in contrast to the situation in 2,4-dialkyl-1,3-dioxolane.³

The measured coupling constants in 2-chloro- and 2-phenyl-4-methyl-1,3,2-dithiaphospholane²³ also indicate, when related to the estimated S-C-C-S and P-S-C-H dihedral angles, predominance of A_2 -like conformations for the *cis* isomers.

Owing to the anisotropy effect of the phenyl group the NMR signal of the H_C proton in *cis*-III and *cis*-IV was expected to appear at lower field

than the H_B signal since these protons are respectively *cis* and *trans* to the As-Ph bond. The reverse observation suggests that the anisotropy effect of the methyl group at carbon 4 predominates.

The similar values of J_{AB} and J_{AC} in *trans*-III and *trans*-IV indicate comparable contributions from the B_1 and B_2 pseudorotamers. An analogous situation seems to prevail in the *trans* forms of 2-chloro- and 2-phenyl-4-methyl-1,3,2-dithiaphospholane²³ judging from the coupling constants. This implies that the stability of the *trans* isomer is less affected (in comparison with the *cis* isomer) by non-bonded interactions involving the substituents on the ring.

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REFERENCES

1. See, for example, Booth, H. *Progr. NMR Spectrosc.* **5** (1969) 149, and references therein.
2. Altona, C., Buys, H. R. and Havinga, E. *Rec. Trav. Chim. Pays-Bas* **85** (1966) 973.
3. Willy, W. E., Binsch, G. and Eliel, E. L. *J. Am. Chem. Soc.* **92** (1970) 5394.
4. Aksnes, D. W. and Vikane, O. *Acta Chem. Scand.* **26** (1972) 835.
5. Aksnes, D. W. and Vikane, O. *Acta Chem. Scand.* **26** (1972) 2532.
6. Aksnes, D. W. and Vikane, O. *Acta Chem. Scand.* **26** (1972) 4170.
7. Goldwhite, H. *Chem. Ind. (London)* **1964** 495.
8. Blicke, F. F. and Smith, F. D. *J. Am. Chem. Soc.* **51** (1929) 3479.
9. Kamai, G. and Chadaeva, N. A. *Chem. Abstr.* **47** (1953) 3792 c-f, 10470 c-h.
10. Rugeberg, W. H. C., Grinsburg, A. and Cook, W. A. *J. Am. Chem. Soc.* **68** (1946) 1860.
11. Woodman, C. M. *Personal communication*.
12. Johannesen, R. B., Ferretti, J. A. and Harris, R. K. *J. Magn. Resonance* **3** (1970) 84.
13. Aksnes, W. A. KOMBIP, Quantum Chemistry Program Exchange, Indiana University, Chemistry Department, Indiana, U.S.A.
14. Diehl, P., Harris, R. K. and Jones, R. G. *Progr. NMR Spectrosc.* **3** (1967) 1.
15. Emsley, J. W., Feeny, J. and Sutcliffe, L. H. *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Pergamon, New York 1966, Vol. 1, p. 360.
16. Haake, P., McNeal J. P. and Goldsmith, E. J. *J. Am. Chem. Soc.* **90** (1968) 715.
17. Bergesen, K. and Vikane, T. *Acta Chem. Scand.* **26** (1972) 2153.
18. Fontal, B. and Goldwhite, H. *Tetrahedron* **22** (1966) 3275.
19. Gagnaire, D., Robert, J.-B. and Verrier, J. *Bull. Soc. Chim. France* **1966** 3719.
20. Lambert, J. B. *Accounts Chem. Res.* **4** (1971) 87.
21. Peake, S. C., Fild, M., Schmutzler, R., Harris, R. K., Nichols, J. M. and Rees, R. G. *J. Chem. Soc. Perkin 2* **1972** 380.
22. Sternson, L. A., Coviello, D. A. and Egan, R. S. *J. Am. Chem. Soc.* **93** (1971) 6529.
23. Bergesen, K. and Bjorøy, M. *Personal communication*.

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