NMR Studies on Cyclic Arsenites

Spectral Analysis and Conformational Studies of Some Arsolanes.

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The 60 MHz NMR data of five arsolanes are reported and discussed. The NMR spectra of 2-chloro-1,3,2-oxathiarsolane and two dithiarsolanes recorded at 30°C, have been fully analyzed on basis of an AA'BB' system. The low-temperature spectrum of the former compound, however, is of the ABCD type. The examined rings appear to exist in slightly distorted envelope conformations with the ring carbon adjacent to oxygen (sulfur in the dithiarsolanes) at the apex of the "flap". Rapid pseudo-rotation seems to be present in these systems.

Several NMR studies on five-membered heterocycles have been reported in recent years.[1] However, the application of NMR spectroscopy to the determination of the conformations and configurations of five-membered rings presents considerable difficulties owing to facile interconversions between nearly equi-energy conformers. It is generally believed that the five-membered ring exists in highly flexible puckered conformations. The puckering is not fixed but moves freely about the ring (pseudo-rotation).

Although the NMR spectra of some 1,3,2-dithiaphospholanes [2,3] and 1,3,2-oxathiaphospholanes [4] have been analyzed no NMR data of the analogous cyclic arsenites are available.

This paper reports preparation and NMR studies of the following five-membered arsenites:
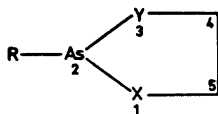
I;   R = Ph, X = Y = O
II; R = Cl, X = Y = O
III; R = Ph, X = Y = S
IV; R = Cl, X = Y = S
V;   R = Cl, X = O, Y = S

The preparation of several 1,3,2-dithiarsolanes and 1,3,2-oxathiarsolanes, including III – V, has been reported by Sommer and Becke-Goehring in a recent paper.[30] The following two substances of particular relevance to this work, have also been prepared and their NMR spectra recorded:[5]

VI; R = Me, X = Y = O
VII; R = Me, X = Y = S

Our studies on the present arsolanes were undertaken in order to (1) analyze these spin systems, (2) determine if any dominant conformations existed and (3) examine whether rapid chlorine exchange 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.[6] Compounds I, II, and III were synthesized by the method of Kamai and Chadaeva.[7] To illustrate the method a detailed procedure for the synthesis of 2-phenyl-1,3,2-dithiarsolane (III) is given: A solution of 9.4 g ethane dithiol and 15.8 g pyridine in 100 ml sodium dried diethyl ether was added dropwise, while stirring, to a solution of 22.3 g phenyl dichloroarsine in 100 ml dried diethyl ether at room temperature. The mixture was held at refluxing temperature for 30 min. After cooling the reaction mixture to room temperature, the pyridine hydrochloride was filtered off. The diethyl ether was removed by rotary evaporation. The oily residue was distilled at reduced pressure, and the distillate fractionated on a Vigreux column at 2 mmHg pressure.

Compounds IV and V were prepared according to a method of Ruggeberg et al.[8] The preparation of 2-chloro-1,3,2-dithiarsolane (IV) is described below as an example of these syntheses: To a solution of 36.2 g trichloroarsine in 100 ml carbon tetrachloride was added dropwise, while stirring, 18.8 g of ethane dithiol. The liberation of HCl during the reaction caused self-cooling of the reaction mixture. After stirring the mixture overnight to assure the complete liberation of HCl, the volume was reduced to ca. 50 ml by rotary evaporation and cooled in a refrigerator. The white crystalline precipitate was recrystallized from carbon tetrachloride.

The boiling or melting points of the prepared compounds are as follows: B.p.$_{10}$ 132 – 134°C, b.p.$_{12}$ 78 – 80°C, b.p.$_2$ 154 – 156°C, and b.p.$_1$ 76 – 78°C for I, II, III, and V, respectively. M.p. 38 – 39°C (lit. 37.5 – 39°C)[8,30] for IV.

The NMR spectra of the five compounds at ambient probe temperature (ca. 30°C) were examined in benzene solutions (ca. 50 % v/v for the liquid compounds). The low-temperature spectrum of V was studied in toluene solution. After adding a small amount of TMS to the samples they were degassed and sealed under vacuum.

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

The AA'BB' and ABCD spin systems were analyzed by means of the computer programs LACX [9] and LAOCN3,[10] respectively. Stick and line-shape plots were generated by means of the sub-routine KOMBIP used in conjunction with LAOCN3 and LACX.

Computations were performed on an IBM/50H computer. The graphical output was obtained using a Calcomp Plotter.

RESULTS AND DISCUSSION

The 60 MHz spectra of the methylene protons of freshly distilled samples of I and II in acetone, carbon tetrachloride, chloroform, benzene, and toluene yielded singlets at 30°C. The singlet of II did not split up but broadened slightly at − 60°C.

Owing to the large anisotropy effect of the phenyl and chlorine groups the methylene protons in I and II were expected to produce a complex spectrum of the AA'BB' type. However, oxygen containing arsolanes with unsubstituted ring carbons are rather unstable due to the weak ring $As-O$ bond. We therefore believe that the observed singlets are caused by dimerization of the examined solutes. A similar polymerization is also reported to occur for VI.[5] Compounds VI, VII, and 2,4,4,5,5-pentamethyl-1,3,2-dioxarsolane also give singlets[5] for the ring protons or methyl protons at carbons 4 and 5. The observed singlets have probably resulted from insufficient anisotropy generated by the methyl substituent at arsenic[12] rather than polymerization of the examined samples. The effect of the reported dimerization of VI would therefore not appear in its NMR spectrum.

The detailed spectral analyses of III and IV were carried out successfully on the basis of an AA'BB' system. The spectral parameters are listed in Table 1. The experimental and calculated spectrum of III is shown in Fig. 1. The

Table 1. Chemical shifts in Hz from TMS and coupling constants (Hz) obtained at 60 MHz.

Compound:	III	IV	V [a]	
Solvent:	Benzene	Benzene	Benzene	Toluene
Temp., °C:	30	30	30 [b]	−35
Assigned lines:	24	20	20	27
Root-mean-square dev.:	0.078	0.072	0.060	0.136
ν_1	176.65	189.70	263.88	249.06
ν_2			182.68	170.38
ν_3	166.01	178.55	182.68	156.38
ν_4			263.88	254.23
$^2J_{14}$	−11.77	−11.99	−9.7 [c]	−9.64
$^2J_{23}$			−11.26	−11.48
$^3J_{12}$	4.30	4.06	4.96	4.14
$^3J_{34}$	4.30	4.06	4.96	4.37
$^3J_{13}$	7.13	7.57	6.86	9.01
$^3J_{24}$				6.11

[a] The protons at carbon 5 (adjacent oxygen) are labelled 1 and 4. [b] Rapid chlorine exchange. [c] Only the difference $|^2J_{14}-{}^2J_{23}|$ is obtained from the analysis.

spectrum of IV has a very similar appearance. On basis of the small differences in the coupling constants it may be confidently concluded that the molecular conformations are very similar.

The type of spin system found for III and IV implies that pseudo-rotation interconverts the non-planar forms at rates that are large on the NMR time scale but that inversion at arsenic is slow. Similar observations have been made in analogous dioxaphospholanes,[13] dithiaphospholanes,[2,3] and ring-substituted dioxarsolanes.[14,15] These results are also consistent with the pyramidal stability reported for arsines and phosphines.[12,16]
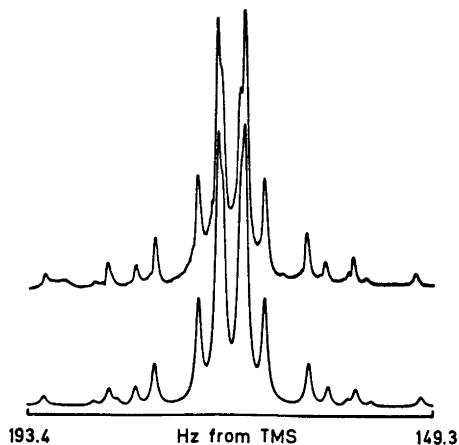
Fig. 1. Experimental (upper trace) and calculated (lower trace) 60 MHz spectrum at 30°C of the methylene protons in compound III in benzene solution.

193.4   Hz from TMS   149.3

The internal shift difference, $\Delta\nu$, is remarkably similar for III and IV. This indicates that the stereospecific effect of the phenyl and chlorine substituents is comparable in these compounds. In accordance with previous assignments,[4,13-15] we believe that the resonances at lower and higher field arise from the nuclei that are cis and trans to the substituent at arsenic, respectively.

The magnitude of the geminal coupling constants in III and IV are in the expected ranges. The equality of $^3J_{12}$ and $^3J_{34}$, within the accuracy of the experiment, is in contrast to the reported situation in 2-phenyl-1,3,2-dithiaphospholane.[2] The observed cis coupling constants in ethylene sulfite [13] and several dioxaphospholanes,[13,17,18] however, are mutually equal within experimental error.

The trans coupling constants in III and IV are appreciably greater than the cis coupling constant. The same observation has been made for 1,3,2-dithiaphospholanes [2,3] and 1,3-dithiolanes.[19] The reverse is, however, true for the analogous dioxaphospholanes,[13,17,18] dioxolanes,[20] and ethylene sulfite.[13]

The S–C–C–S torsional angle in III and IV can be calculated from the vicinal coupling constants of the $CH_2.CH_2$ moiety using the R-value method due to Lambert [21] and Buys.[22] The calculated R-values are 1.66 and 1.86 corresponding to torsional angles of approximately 54° and 56° for III and IV, respectively. Similar calculations based on the reported NMR data for 1,3,2-dithiaphospholanes,[2] 1,3-dithiolanes,[19] 1,3-dioxolanes,[19] and 1,3,2-dioxaphospholanes [13] give torsional angles of approximately 48°, 49°, 42°, and 42°, respectively. Haake et al.[13] have calculated O–C–C–O torsional angles of ca. 30° in dioxaphospholanes from the vicinal coupling constants using a different approach. We believe, however, that they have underestimated the torsional angle.

The increased ring puckering of the sulfur hetero rings, as compared to their oxygen counterparts, is consistent with the greater degree of flexibility conferred by the presence of sulfur rather than oxygen in the ring.[2]

Dreiding stereomodels of III and IV indicate that the most stable forms are two mutually equivalent pairs of slightly distorted, envelope conformations with one of the ring carbons at the apex of the "flap". The other ring carbon is situated slightly out of the plane defined by SAsS on the opposite side. The pair of conformations possessing carbon 5 at the "tip" of the envelope is shown below.
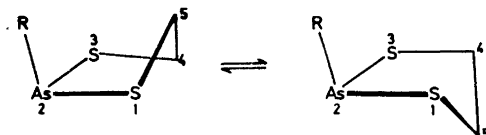
The Dreiding model also indicates a torsional angle slightly less than $60°$, that is, close to the calculated average torsional angle (ca. $55°$) for these rings. The NMR data are therefore consistent with predominance of the above pseudo-rotamers.

The NMR spectra of V recorded at 30°C and $-35°$C were analyzed as AA'BB' and ABCD systems, respectively. The experimental spectra together with the corresponding calculated spectra are displayed in Figs. 2 − 4.

The observed type of spectrum at 30°C implies that a rapid chlorine-exchange process results in inversion at arsenic. Similar observations have been made for 2-chloro-4,5-dimethyl-1,3,2-dioxarsolane [14] and several 2-chloro-substituted dioxaphospholanes.[13,17] The observed concentration
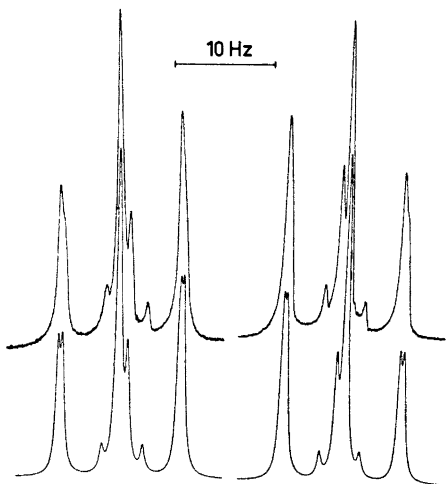

Fig. 2. Experimental (upper traces) and calculated (lower trace) 60 MHz spectrum at 30°C of the methylene protons in compound V in benzene solution. The symmetrical spectrum is a result of rapid chlorine exchange.
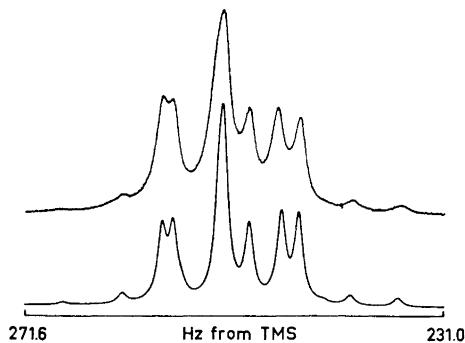
Fig. 3. Experimental (upper trace) and calculated (lower trace) 60 MHz spectrum at $-35°$C of the $-O-CH_2-$ protons in compound V in toluene solution.
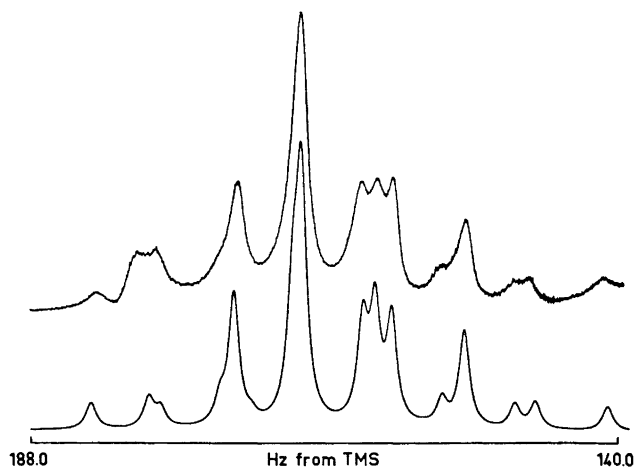
Fig. 4. Experimental (upper trace) and calculated (lower trace) 60 MHz spectrum at
    $-35°C$ of the $-S-CH_2-$ protons in compound V in toluene solution.

dependence suggests that the exchange occurs by a bimolecular process.[23]
The spectrum recorded at $-35°$ is of the expected asymmetrical type thus
indicating that chlorine exchange is slow. The observed temperature effect
is not expected to arise from freezing out the pseudo-rotation process since
the barriers are relatively low.[24]

    The internal shift difference, $\Delta\nu$, of the protons at carbons 4 and 5 is
14.0 Hz and 5.2 Hz, respectively. These $\Delta\nu$ values are comparable to the cor-
responding differences observed for 2-chloro-1,3,2-oxathiaphospholane [4] (10.8
Hz and 7.2 Hz, respectively). It is seen that the $-S-CH_2-$ protons have
larger $\Delta\nu$ values than the $-O-CH_2-$ protons. The reverse order is, however,
observed for 2-chloro-1,3,2-dithiaphospholane [3] and 2-chloro-1,3,2-dioxa-
phospholane [13] measured at 60 MHz (7.8 Hz and 23.2 Hz, respectively).

    The Dreiding model indicates that the oxathiarsolane ring should exist
predominantly as two very slightly distorted envelope conformations with
carbon 5 (adjacent to oxygen) at the apex of the "flap". The O–C–C–S torsional
angle is seen to be about 47° in these models.

Va   **Vb**
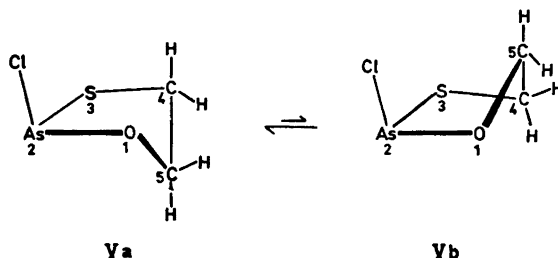
In pseudo-rotamer Va the pseudo-axial hydrogen at carbon 4 will suffer a considerable anisotropy shift whereas the pseudo-equatorial hydrogen will be much less affected. The net effect would probably be a significant internal shift displacement $\Delta \nu$. The protons at carbon 5, however, would be more equally affected by the anisotropy of the As $-$ Cl bond. Predominance of Va is thus expected on basis of the chemical shift data. This conclusion is consistent with the expected decrease in syn-axial repulsions in Va as compared to Vb.

Comparable contributions of the Va and Vb forms would result in similar values of $^3J_{13}$ and $^3J_{24}$. However, since the observed coupling constants are quite different it follows that one conformation predominates. A similar conclusion concerning 2-substituted 1,3-oxathiolanes was reached by Wilson and co-workers [24] upon interpretation of NMR data.

Application of the R-value method to the vicinal coupling constants obtained at 30°C and -35°C, gives 51° and 55° for the O–C–C–S torsional angle, respectively. A part of this discrepancy results from experimental errors in the measured parameters, in particular at -35°C. A certain deviation is, however, expected due to changes with solvent and temperature in the distribution of populated pseudo-rotameric forms.

It can be anticipated from the Dreiding model of V and the Karplus relationship [25] that the largest vicinal coupling constant (9.01 Hz) involves the pseudo-axial protons. From this assumption it follows that the chemical shifts of the pseudo-axial protons appear at higher field than the geminal pseudo-equatorial protons. However, the uncertainty about the contributing conformations makes this a tentative conclusion. Upfield shift of the axial proton at carbon 6 relative to the equatorial proton in 2-phenyl-1,3-oxathiane has been observed.[26] The reverse assignment has, however, been made for six-membered phosphites [27] and 2-chloro-1,3,2-dithiarsenane.[28]

The NMR spectrum of V was also examined at intermediate rates of chlorine exchange. It was noted that the "coalescence" of the $-$S$-$CH$_2-$ region of the spectrum occurred at a higher temperature than in the $-$O$-$CH$_2-$ region, that is, at a higher rate of exchange. This observation reflects the fact that the $-$S$-$CH$_2-$ protons suffer larger internal anisotropy shifts, $\Delta \nu$, than the $-$O$-$CH$_2-$ protons in the absence of exchange.

The final conclusion is that each of the 1,3,2-dithiarsolane and 1,3,2-oxathiarsolane rings mainly exists in two rapidly interconverting envelope conformations. However, since pseudo-libration is expected to occur in these systems,[29] each of the pseudo-rotamers represents the average of a range of conformations of similar energies.

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