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NMR Studies on Cyclic Arsenites. Spectral Analysis of Four 2-Substituted 1,3,2-Dioxarsenanes and 2-Phenyl-1,3,2-dithiarsenane

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The NMR spectra of five six-membered arsenites have been fully analyzed on the basis of an AA'BB'CD spin system. In 2-chloro- and 2-bromo-1,3,2-dioxarsenane an intermolecular halide exchange process leads to exchange of the nuclear magnetic environments of the methylene protons at room temperature.

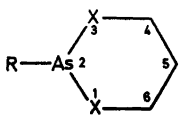
The ring torsional angles have been calculated from the vicinal coupling constants using the *R*-value method. The NMR data are consistent with the presence of one very dominant chair conformation with an axial exocyclic group at arsenic.

The nuclear magnetic resonance spectra of cyclic six-membered arsenites have received little attention.[1,2] This is in marked contrast to the interest devoted to the corresponding six-membered phosphites,[3] sulfites,[4] and dioxanes.[5]

The arsenic nucleus ($I=\frac{3}{2}$) is subjected to rapid quadrupole relaxation and is effectively "decoupled". In this respect the arsenites are rather like the sulfites in which the corresponding heteroatom has zero spin. However, in the sense that they possess a trigonal group V heteroatom at the 2 position, the arsenites also resemble the phosphites. However, in spite of these similarities, the different heteroatoms at the 2 position and the different bond angles and bond lengths peculiar to each atom, would make any attempt to extrapolate findings from one system to another rather questionable.

This paper reports preparation and NMR analysis of the six-membered arsenites I – V.

The reported NMR studies on 2-chloro-1,3,2-dithiarsenane(VI),[1] trimethylene sulfite [4,6,7] and the analogous 1,3,2-dioxaphosphorinanes [3,8] are of particular relevance to this work.



I; R = Cl, X = O
II; R = Br, X = O
III; R = OPh, X = O
IV; R = OMe, X = O
V; R = Ph, X = S

EXPERIMENTAL

Compounds I and II were synthesized from 1,3-propanediol and trichloroarsine or tribromoarsine, respectively, according to a method of Kamai and Chadaeva.[9] Compounds III and IV were prepared from I and phenol or methanol as appropriate, in ether solution using triethylamine as base.

2-Phenyl-1,3,2-dithiarsenane (V) was prepared from phenyl dichloroarsine and 1,3-propanedithiol according to a procedure of Ruggeberg *et al.*[10]

The boiling or melting points of the prepared compounds are as follows: $b.p._{1.3}$ 44 – 46 °C, $b.p._{0.1}$ 36 – 37 °C, $b.p._{0.6}$ 77 – 78 °C and $b.p._{8}$ 31 – 33 °C for I, II, III and IV, respectively. M.p. 63 – 64 °C for V.

The 60 MHz NMR spectra of I and II were recorded at – 43 °C and – 70 °C, respectively, in carbon disulfide solutions (*ca.* 25 % v/v). The 100 MHz spectra of compounds III – V were examined in benzene solutions (*ca.* 50 % v/v for III and IV) at ambient probe temperature (*ca.* 34 °C). A small amount of TMS was added to the samples and used as internal standard and lock signal source. Line positions were obtained by averaging the results of 2 – 4 frequency-calibrated spectra at 100 Hz sweep width. The 60 MHz and 100 MHz spectra were recorded on JEOL-C-60H and VARIAN HA-100 spectrometer, respectively.

Table 1. NMR parameters and ring torsional angles (ψ) of compounds I – VI.

Compound	I	II	III	IV	V	VI[a]
Solvent	CS_2	CS_2	C_6H_6	C_6H_6	C_6H_6	C_6H_6
Temp. °C	−43	−70	34	34	34	30
ν_{4a}[b]	4.553	4.431	4.440	4.335	2.472	3.091
ν_{4e}	4.012	4.064	3.666	3.644	2.211	2.458
ν_{5a}	2.413	2.398	2.140	2.158	1.815	1.755
ν_{5e}	1.554	1.576	1.129	1.232	1.345	1.566
J_{4a4e}[c]	−11.35	−11.32	−10.92	−10.86	−13.81	−13.98
J_{5a5e}	−14.40	−14.14	−14.31	−14.17	−14.46	−14.60
J_{4a5a}	12.56	12.69	12.01	12.00	11.12	10.53
J_{4e5a}	4.10	3.99	4.07	4.08	2.32	3.57
J_{4e5e}	2.13	2.07	2.95	2.92	6.55	6.06
J_{4a5e}	1.92	1.75	2.07	2.14	2.10	3.31
J_{4e6e}	1.53	1.58	1.14	1.05	0	0.41
J_{4e6a}	−0.56	−0.43	−0.49	−0.47	−0.22	−0.25
J_{4a6a}	−0.04	0.06	−0.01	0	0	−0.08
Assigned transitions	128	80	125	118	115	136
RMS error	0.095	0.151	0.109	0.094	0.106	0.059
R	2.44	2.57	2.44	2.40	4.00	2.41
ψ (deg.)	59.7	60.3	59.7	60.4	65.9	59.6

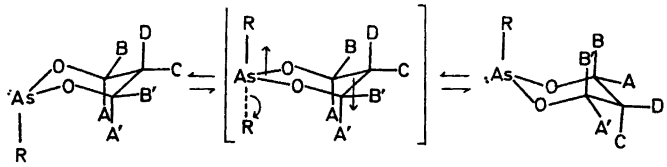
[a] Data from Ref. 1. [b] Chemical shifts in δ-values [c] Coupling constants in Hz.

The AA'BB'CD spin systems were analyzed by means of the computer programs LACX [11] and KOMBIP.[12] Computation were performed on a UNIVAC 1110 computer. The graphical output was obtained using a Calcomp Plotter.

RESULTS AND DISCUSSION

The 60 MHz and 100 MHz spectra of freshly distilled samples of I and II in benzene and carbon disulfide solutions at ambient probe temperature, showed a broad triplet and quintet for the methylene protons at carbon 5 and carbons 4 and 6, respectively. However, at low temperature in CS_2 solution, the NMR spectra proved to be almost identical to the spectra of III and IV. This implies that a process which leads to exchange of the nuclear magnetic environments of the methylene protons in I and II is taking place. In accord with previous conclusions,[13,14] this process is believed to be an intermolecular halide exchange rather than a thermal intramolecular inversion at arsenic for the following reasons: First, pyramidal inversion at arsenic is slow at room temperature owing to the high barrier (25 – 42 kcal/mol).[15,16] Second, the rate of exchange of these and related compounds, has been found to be concentration dependent.[13] Third, a trace of tetraphenylarsonium chloride causes chlorine exchange for VI and thus giving rise to the same type of spectrum as for I and II at room temperature. Let us assume for the time being (*vide infra*) that the six-membered arsenites exist in a chair conformation with an axial group at arsenic. The mechanism shown below allows the carbon end of the ring to flip rapidly thereby exchanging the axial and equatorial geminal protons. Furthermore, the stereochemistry about arsenic is not altered by the postulated mechanism.[14]

The detailed spectral analysis of compounds I – V was carried out successfully on the basis of an AA'BB'CD spin system. The trial parameters were obtained by analyzing the spectra as AA'BB'XY systems on first-order basis. Table 1



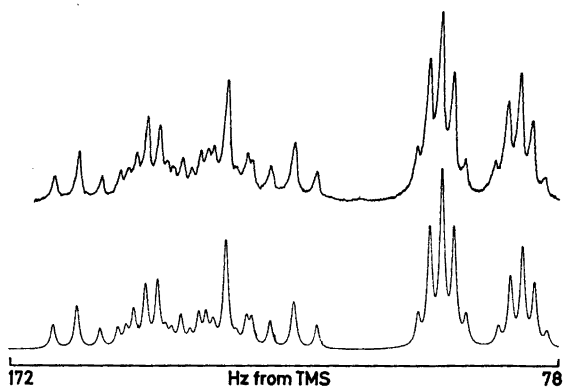


Fig. 1. Experimental (upper trace) and calculated (lower trace) 60 MHz spectrum at −43 °C of the methylene protons at carbon 5 in 2-chloro-1,3,2-dioxarsenane (I).

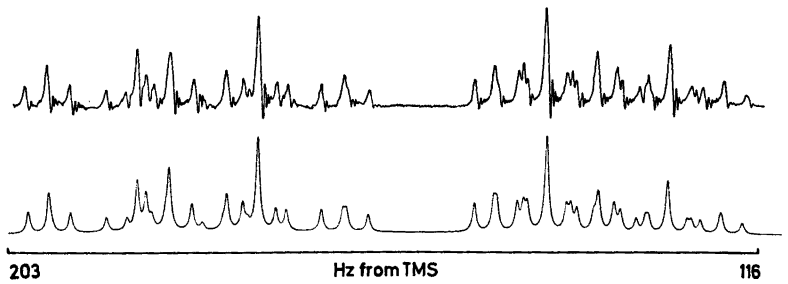


Fig. 2. Experimental (upper trace) and calculated (lower trace) 100 MHz spectrum at 34 °C of the methylene protons at carbon 5 in 2-phenyl-1,3,2-dithiarsenane(V).

lists the spectral parameters obtained for these compounds together with the result of a previous work for VI.[1] Good fits between the observed and calculated spectra of these compounds were obtained as demonstrated in Figs. 1 and 2.

The assignment of axial and equatorial protons in Table 1 follows from the observed characteristic value of J_{4a5a}.[6-8,17] This value together with that of J_{4e5e} indicate that these molecules exist almost entirely in one chair conformation, that is, in an anancomeric equilibrium. This is reasonable since the rate of pyramidal inversion at arsenic is slow.

The $X-C_4-C_5-C_6$ torsional angle, ψ, has been calculated from the vicinal coupling constants of the $CH_2CH_2CH_2$-moiety according to the R-value method due to Buys and Lambert.[18] The calculated R-values and the corresponding dihedral angles are given in Table 1. These results strongly suggest that the $X-C-C-C-X$ portion of the examined rings except V, assumes an almost staggered conformation. The same observation has been made for trimethylene sulfite.[6] The analogous 1,3,2-dioxaphosphorinanes [8] and 1,3-dioxanes [18] have, however, been reported to be less puckered by 2 − 3 and 5°, respectively. In this context, it is worth noting that, as a consequence of ring flattening in 1,3-dioxanes, J_{4a5e} is substantially larger than J_{4e5e} (*ca.* 2.7 and 1.6 Hz, respectively) [20] in contrast to the situation in the cyclic arsenites, phosphites and sulfites. The calculated dihedral angle for V, however, indicates a higher degree of ring puckering in this molecule. This observation is also reflected in the unusually small value of J_{4e5a} in contrast to the large value of J_{4e5e}. However, since the increase in J_{4e5e} dominates, the net result is a considerable increase in the R-value. The same degree of ring puckering has been observed for 1,4-dithiane [18]

whereas compound VI has essentially a staggered conformation. The puckered chair conformation is generally associated with a decreased bond angle within the ring. Thus, puckering is most frequently found in heterocycles containing group VI elements.[18] Although bond angle effects often dominate, there may be other causes of distortions such as bond length effects and non-bonded interactions.

Investigations of several research groups have established the axial preference of electron-withdrawing groups adjacent to a heteroatom in six-membered rings.[3,8,14,19,21] This phenomenon is generally known as the anomeric effect.[19] In 1,3,2-dioxaphosphorinanes, for example, the axial position of the 2-substituent is usually so strongly favoured that the conformational preferences of other exocyclic substituents do not force a dominance of another conformation at phosphorus.[14] It is thus reasonable to expect the same stereochemistry at the 2 position in the analogous arsenites. Strong support for this assumption is found in the chemical shift data of Table 1.

It is thus seen that the axial protons appear at lower field than the shifts of the geminal equatorial protons in accord with previous observations for trimethylene sulfite and 2-substituted 1,3,2-dioxaphosphorinanes possessing axial 2-substituents. Furthermore, since the As–X bonds are considerably longer than the P–X or S–X bonds, a consequent flattening of the ring about arsenic probably results. The axial 2-R group may thus be moved away from the axial methylene hydrogens thereby reducing the *syn*-axial interactions.

The observed values of the geminal coupling constants J_{4a4e} and J_{5a5e} are well within the accepted ranges.[6,8,22,23] In molecules with oxygen next to a CH_2 group, the inductive σ-electron withdrawal will be combined with a pseudo-π-electron transfer in the opposite direction from the oxygen $2p$ lone-pair into the CH_2 system.[24] This latter effect which leads to an additional positive contribution is, however, negligible for chair conformations of six-membered rings containing oxygen owing to the particular geometry.[24] The observed small changes in J_{4a4e} in compounds I – IV is therefore consistent with a chair conformation. It is seen that replacement of sulfur by oxygen in these systems results in a decrease of *ca.* 3 Hz in the magnitude of J_{4a4e}. This reduction is mainly accounted for by the increased inductive removal of σ-electrons from the CH_2 orbitals by the adjacent oxygen which gives rise to an increased positive contribution to the coupling constant.[24]

The measured values of J_{4e6e} have the expected positive sign and are within the range (except V and VI) reported for coupling constants between equatorial protons which are in an all-*trans* or W conformation (1 – 2 Hz).[25] The smaller values of J_{4e6e} in V and VI are reasonable since Dreiding models indicate that the equatorial hydrogens at carbons 4 and 6 are forced about 30° out of the plane defined by carbons 4, 5 and 6 in the 1,3,2-dithiarsenane ring, as compared to about 15° in the 1,3,2-dioxarsenane ring. In 2-phenyl-1,3-dithiane the value of J_{4e6e} is also reported to be negligible.[23] The remaining long-range coupling constants fall within the expected ranges.[25]

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