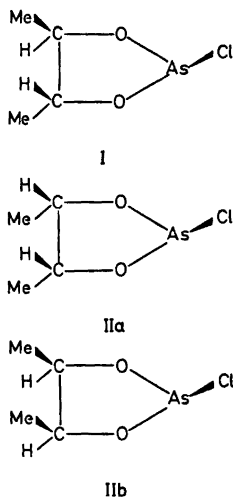


NMR Studies on Cyclic Arsenites. Analyses of the NMR Spectra of *cis*- and *trans*-2-Chloro-4,5- dimethyl-1,3,2-dioxarsolanes

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This paper reports analyses of the NMR spectra of *cis*- and *trans*-2-chloro-4,5-dimethyl-1,3,2-dioxarsolanes. The two geometric isomers result from the reaction of racemic 2,3-butanediol with AsCl_3 . The *trans* isomer (I) is derived from D,L-butanediol. *Meso*-butanediol yields two conformers, both possessing *cis* methyl groups (IIa and IIb). These conformers are interconvertible by inversion at the 3-coordinated arsenic.



The spectrum of the *trans* isomer (I) is expected to constitute an ABX_3Y_3 spin system due to the anisotropy generated by the arsenic chlorine group. The arsenic nucleus possessing $I = \frac{3}{2}$ is subjected to rapid quadrupole relaxation and is thus effectively decoupled. Figs. 1 and 2 show, however, that the spectrum is of the $\text{AA}'\text{X}_3\text{X}_3'$ type. This must be caused by a process which leads to exchange of the nuclear magnetic environments.

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The barrier to inversion at arsenic in a series of dioxarsolanes has been shown to exceed 25 kcal/mol.¹ Pyramidal inversion at arsenic is thus, no doubt, slow at room temperature in the title compounds.

Chemical exchange of chlorine is therefore expected to occur at room temperature, and to be the reason for the observed type of spectrum. Similar observations have been made for ethylene chlorophosphate,² the analogous tetramethyl derivative,³ and 2-chloro-4,5-dimethyl-1,3,2-dioxaphospholane.^{4,5} To account for the observed concentration dependence, it has been suggested that the exchange occurs by a bimolecular process.³ No line broadening was, however, observed in the temperature range 30°C to -20°C in a dilute toluene solution of the title compounds. The rate of chlorine exchange is thus faster than for the phosphorus analogue.^{4,5} This is reasonable since the As-Cl bond is more ionic than the P-Cl bond.

The *cis* conformers both constitute an $\text{AA}'\text{X}_3\text{X}_3'$ spin system. Rapid chlorine exchange, however, gives rise to one spectrum with time-average NMR parameters. Owing to the chlorine-methyl interactions, IIa is expected to be the more stable conformer. Support for this assumption is found in the NMR spectrum of 2-phenyl-4,5-*cis*-dimethyl-1,3,2-dioxarsolane.⁶ This symmetrical $\text{AA}'\text{X}_3\text{X}_3'$ spectrum clearly shows the presence of only one conformer.

The $\text{AA}'\text{X}_3\text{X}_3'$ spin system has been treated theoretically by the composite particle technique.⁷ When $J_{\text{XX}'} = 0$ all the

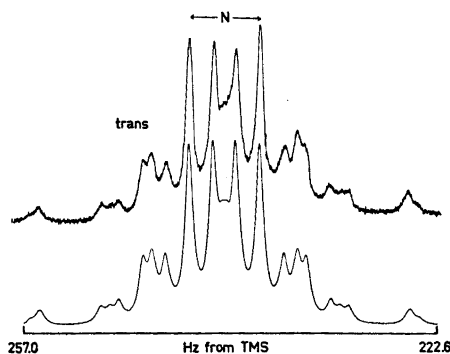


Fig. 1. Experimental (upper part) and calculated (lower part) methine proton spectra at 60 MHz of *trans*-2-chloro-4,5-dimethyl-1,3,2-dioxarsolane.

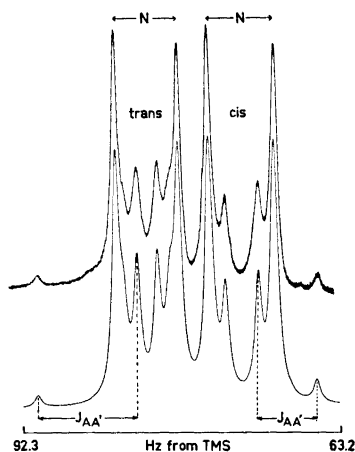


Fig. 2. Experimental (upper part) and calculated (lower part) methyl proton spectra at 60 MHz of *cis*- and *trans*-2-chloro-4,5-dimethyl-1,3,2-dioxarsolanes.

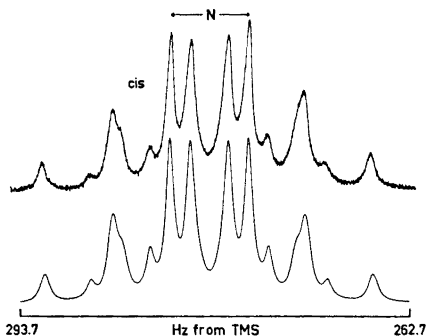


Fig. 3. Experimental (upper part) and calculated (lower part) methine proton spectra at 60 MHz of *cis*-2-chloro-4,5-dimethyl-1,3,2-dioxarsolane.

spectral parameters are obtained directly from the spectrum with the limitation that $N = J_{AX} + J_{AX'}$ is found instead of the individual coupling constants.

The excellent fit between the experimental and calculated spectra in Figs. 1–3 confirms the correctness of the spectral parameters listed in Table 1. Integration of the methine proton signals of the two isomers showed that the examined sample

Table 1. NMR spectral parameters at 60 MHz of neat 2-chloro-4,5-dimethyl-1,3,2-dioxarsolane at ambient probe temperature.

Isomer	ν_A^a	ν_X^a	$J_{AA'}$	J_{AX}	$J_{AX'}$
I	240.25	80.55	9.37	6.06	-0.20
IIa and IIb	278.66	71.65	5.44	6.44	-0.15

^a Chemical shifts in Hz from TMS.

contained 54 % of the *trans* form and 46 % of the *cis* form.

It is interesting to note that the vicinal coupling, $J_{AA'}$, in the *cis* molecule is considerably less than the corresponding coupling in the *trans* molecule. The same observations have been made for the *cis* and *trans* forms of 2,2,4,5-tetramethyl-1,3-dioxalane⁸ and 2-chloro 4,5-dimethyl-1,3,2-dioxaphospholane.^{4,5} This indicates that the *cis* and *trans* forms of these compounds each exist in two rapidly interconverting conformers, probably twist-envelope forms.

A considerable amount of data on trimethylene and ethylene sulfites^{9–22} indicate that the sulfite oxygen prefers to be axial. This suggests predominance of pseudo-axial conformers for the title compounds as well. This seems also reasonable from the observed stereospecific anisotropy effect of the As–Cl bond. We can then assign the methyl signal at higher field and the methine proton signal at lower field to the *cis* isomer, as *trans* and *cis* to the As–Cl bond, respectively.

Analyses of the 60 MHz spectra of a series of substituted dioxarsolanes and dithiarsolanes are at present being carried out in this laboratory.

Experimental. 2-Chloro-4,5-dimethyl-1,3,2-dioxarsolane was synthesized according to the method of Kamař and co-workers.^{12,13} A solution of 45 g 2,3-butanediol and 79 g pyridine in 200 ml of dried diethyl ether was added dropwise while stirring, at room temperature, to a solution of 90.6 g trichloroarsine in 150 ml of dried diethyl ether. The pyridine hydrochloride was filtered off, and the diethyl ether was removed by rotary evaporation. The oily residue was fractionated at 12 mmHg pressure

on a Vigreux column, b.p.₁₂ 76–77°C, n_D^{20} = 1.5138.

A small amount of tetramethylsilane was used as internal reference and lock signal source. The neat sample was thoroughly degassed and sealed under vacuum.

The NMR spectra were run at ambient probe temperature (ca. 30°C) on a JEOL-C-60H spectrometer. The spectra used for the analyses were recorded at 54 Hz sweep width and calibrated every 5 Hz using a frequency counter. Line positions were obtained by averaging the results of four scans.

Computations were performed on an IBM/50H computer using the UEATR computer program.¹⁴ About 280 transitions were matched for each isomer. The root-mean-square deviations for the experimental and calculated lines were 0.042 Hz or less. The calculated probable errors for the parameters were 0.005 Hz or less.

The graphical output was obtained using a Calcomp Plotter.

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Formation of an Anhydride of 2-O-(α -D-Galactopyranosyluronic Acid)-L-rhamnose

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Studies by anion exchange chromatography of the uronic acids present in hydrolyzates from spruce¹ (*Picea abies*, Karst.) and in sulphite spent liquor² revealed that among other biouronic acids a previously unknown compound (I) of this type was present. Mild acid hydrolysis of the isolated compound gave rise to rhamnose and galacturonic acid as well as 2-O-(α -D-galactopyranosyluronic acid)-L-rhamnose (II) which is a constituent in hemicellulose from spruce and other sources.^{3,4} Moreover, the same compound (I) was produced upon mild acid treatment of II. It was not formed from rhamnose and galacturonic acid under similar conditions and therefore cannot be a reversion product.¹ Both compounds exhibited a similar behaviour when chromatographed in sodium acetate whereas I was held more strongly than II in 0.5 M acetic acid indicating a higher acidic strength (Table I). In 0.12 M sodium tetraborate I appeared earlier indicating that the unknown compound has a lower ability to give borate complexes (Table I). Moreover, this com-

Table I. Distribution coefficients (D_v) of the unknown compound I and of 2-O-(α -D-GalpA)-L-Rha (II) before and after reduction with sodium borohydride.

	D_v	D_v	D_v
	0.5 M HAc	0.08 M NaAc	0.12 M Na ₂ B ₄ O ₇
I	13.1	3.57	4.03
I:borohydride	13.2	3.59	
II	7.95	3.49	6.15
II:borohydride	8.23	2.63	

D_v = adjusted retention volume calculated in column volumes.¹¹