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NMR Studies on Cyclic Arsenites. Spectral Analysis of the NMR Spectrum of 2-Chloro-1,3,2-dithiarsenane

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In recent years a great deal of effort has been expended in NMR studies of the conformations of six-membered heterocycles.[1] For rigid molecules, analyses of observed NMR spectra yield chemical shifts and coupling constants which can be correlated with a particular conformation.

This paper reports preparation and NMR analysis of 2-chloro-1,3,2-dithiarsenane (I). Hitherto no analyses of six-membered arsenites have been reported. The effective "decoupling" of the arsenic nucleus simplifies the spectrum but reduces its information content as compared to cyclic phosphites. The reported NMR studies on 1,3,2-dioxaphosphorinanes and 1,3,2-dithiaphosphorinanes are of particular relevance to this work.[2,3]

The NMR spectrum of I was analyzed as an AA'BB'CD spin system by means of the

computer programs LAOCN3[4] and KOMBIP.[5] The latter sub-routine generated "stick"- and Lorentzian line-shape plots. The stick-plots based on trial parameters facilitated the rather tricky analysis.

The iterated spectral parameters of I are listed in Table 1. The root-mean-square deviation was 0.059 for 136 assigned transitions. The calculated probable errors in the thirteen varied parameter sets were 0.014 or less. The excellent fit between the experimental and calculated spectra in Figs. 1 and 2 confirms the correctness of
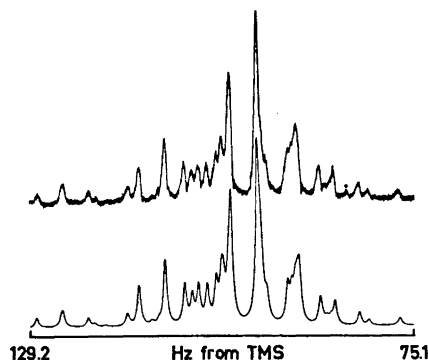

Fig. 1. Experimental (upper part) and calculated (lower part) 60 MHz spectrum of the protons at carbon 5 in I. The asterisk indicates an impurity.

the parameters. The NMR spectrum can be divided into three distinct regions. The region at higher field is, of course, due to the two protons at carbon 5.
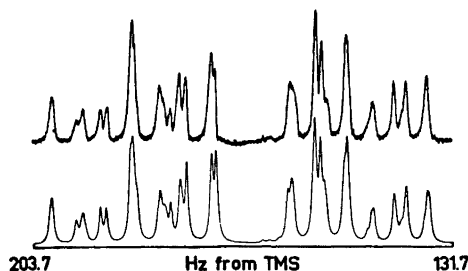

Fig. 2. Experimental (upper part) and calculated (lower part) 60 MHz spectrum of the protons at carbons 4 and 6 in I. The low-field and high-field spectrum traces represent the axial and equatorial protons, respectively.

Accepted ranges [6] for the vicinal coupling constants in six-membered rings are $8-14$ Hz for J_{4a5a} and $0-6$ Hz for J_{4e5e} and J_{4a5e}. The assignment of axial and equatorial protons in Table 1 follows from the observed characteristic value of J_{4a5a}. The measured values of J_{aa} and J_{ee} are consistent with a strong predominance for one of the two possible chair conformers Ia and Ib.

Ia   Ib
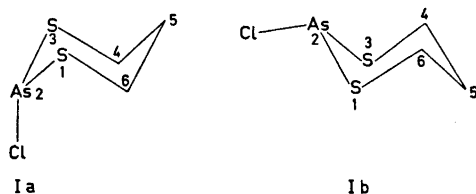
These conformers are interconvertible by inversion at arsenic. Pyramidal inversion is, however, slow at room temperature owing to the high barrier $(25-42$ kcal/mol).[7,8] The rather large value of J_{4e5e} indicates a high ring puckering of the $C_4-C_5-C_6$ moiety of the ring.[9] In 1,3-dioxanes where the ring is flattened, J_{4a5e} is substantially larger than J_{4e5e} (ca. 2.7 Hz and 1.6 Hz, respectively).[10]

The $S-C_4-C_5-C_6$ torsional angle can be calculated from the vicinal coupling constants (Table 1) using the R-value

Table 1. 60 MHz spectral parameters (in Hz) of 2-chloro-1,3,2-dithiarsenane in benzene solution.

Chemical shift [a]		Coupling constants	
ν_{4a}	185.48	J_{4a4e} -13.98	J_{4a5e} 3.31
ν_{4e}	149.08	J_{5a5e} -14.60	J_{4e6e} 0.41
ν_{5a}	105.31	J_{4a5a} 10.53	J_{4e6a} -0.25
ν_{5a}	93.98	J_{4e5a} 3.57	J_{4a6a} -0.08
		J_{4e5e} 6.06	

[a] Downfield from TMS.

method.[9] The calculated R-value (2.41) gives a torsional angle of 59.6°. It is thus clear that the $S-C_4-C_5-C_6-S$ portion of the ring assumes an essentially rigid staggered conformation. However, the data provide no definitive information regarding the configuration at arsenic.

The axial preference of electron-withdrawing groups adjacent to a heteroatom is well-established in six-membered rings.[11] This phenomenon is generally known as the anomeric effect.[11,12] In a series of phosphacyclohexanes, 1,3,2-dioxaphosphorinanes, and 1,3,2-dithiaphosphorinanes substituents on phosphorus strongly prefer the axial to the equatorial position.[3] Recently, it has been argued that the axial preference is largely a consequence of 1,3-diaxial van der Waals attractive interactions rather than polar or adjacent lone-pair interactions.[3] At any rate, the evidence presented above indicates that the chlorine substituent in I strongly prefers the axial position since the As–S bonds are considerably longer than the P–O or P–S bonds, and because of possible consequent flattening of the ring about arsenic.

Recent compilations of geminal coupling constants [13] in six-membered rings indicate the ranges -13 to -14 Hz and -12 to -15 Hz in $C-CH_2-S-$ and $C-CH_2-C$ moieties, respectively. The observed values of J_{4a4e} and J_{5a5e} in I are well within these ranges. The magnitude of J_{4a4e} is close to the corresponding coupling constant in 2-phenyl-5-*tert*-butyl-1,3-2-dithiaphosphorinane $(13.4\pm0.5$ Hz).[3]

The observed value of J_{4e6e} has the expected positive sign but is somewhat smaller than usual for coupling constants between equatorial protons which are in the all-*trans* or "W" relationship $(1-2$ Hz).[14] This is reasonable since a Dreiding model of the molecule shows that the equatorial protons are forced about 30° out of the plane defined by $C_4C_5C_6$. A small or negligible value of J_{4e6e} is also reported for 2-phenyl-1,3-dithiane.[15] The two remaining four-bond coupling constants fall within the expected ranges.[14]

Examination of Table 1 shows that the chemical shifts of the axial protons at carbon 4 (or 6) and carbon 5 appear at lower field than the shifts of the geminal equatorial protons. The same observation has been noted previously for a series of analogous six-membered phosphites.[2,3]

Experimental 2-Chloro-1,3,2-dithiarsenane (I) was prepared according to a method of Ruggeberg et al.[16] To a solution of 36.2 g trichloroarsine in 100 ml carbon tetrachloride was added dropwise 21.6 g of 1,3-propane-dithiol. The liberation of HCl was almost instantaneous and accompanied by self-cooling of the reaction mixture. After standing overnight, while stirring, the reaction mixture

was reduced to about 50 ml by rotary evapo-
ration and cooled in a refrigerator. The white
crystalline product was recrystallized from
carbon tetrachloride, m.p. 47–48°C.

The NMR spectrum of I was examined in
benzene solution. A small amount of TMS was
added and used as internal standard and lock
signal source. The NMR tube was thoroughly
degassed and sealed under vacuum.

The spectra were run at ambient temperature
(*ca.* 30°C) on a JEOL-C-60H spectrometer.
Line positions were obtained by averaging the
results of four scans at 54 Hz sweep width.
Computations were performed on an IBM/
50H computer. The graphical output was
obtained using a Calcomp Plotter.

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Skeletal Rearrangements in the Mass Spectrometric Fragmentation Pattern of Phenylcarbamic Acid Anhydrides*

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In a preliminary communication we de-
scribed the first discovery of a stable
phenylcarbamic acid anhydride, isolated
as a by-product during the synthesis of
some carbanilates.[1] Later, a useful method
of synthesis of this new class of compounds
was developed and a plausible mechanism
for their formation was reported.[2] Con-
tinuing the studies of the phenylcarbamic
acid anhydrides we have now recorded and
evaluated the mass spectra of compounds
I – VI (Table 1).

The high (70 eV) and low (9 eV) energy
spectral data are collected in Table 2. The
proposed general fragmentation pattern,
supported by appropriate metastable ions,
is outlined in Scheme 1. Some interesting
peaks corresponding to ions formed by
skeletal rearrangements will be discussed in
detail.

All spectra of the compounds studied
display a peak corresponding to a fragment
deriving from the molecular ion, after ex-
pulsion of CO_2. The relative importance of
this process increases at lower eV (*cf.*
Table 2) suggesting that the reaction in-
volved has a low frequency factor,[3] which
is characteristic for rearrangements. The
reaction seems to be substituent dependent
(*cf.* Table 2), being most pronounced in
the breakdown pattern of the *p*-methoxy
derivative III. This $M - CO_2$ fragmentation
belongs to a general type of skeletal rear-
rangements, which is quite common in
mass spectrometry.[4,5] However, formation
of a new carbon-nitrogen bond, as in the
present case, is not commonly observed
and, to our knowledge, skeletal rearrange-
ments with loss of CO_2 from the molecular
ion have not earlier been noted for an-
hydrides.

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* Carbamic acid anhydrides Part III; Part I
and II see Refs. 1 and 2.