

NMR Studies on Cyclic Arsenites. ^1H NMR Spectral Analysis and Conformational Studies of Fifteen Ring-substituted 2-Chloro-, 2-Methoxy- and 2-Phenoxy-1,3,2-dioxarsenanes

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This paper reports preparation and ^1H NMR investigations of fifteen six-membered arsenites. Nonequilibrium mixtures of two geometrical isomers have been observed for the methoxy-compounds. However, the present spectral analyses have only been performed on the thermodynamically more stable forms which predominated strongly in aged samples. The 4,6-dimethyl compounds constitute complex ten-spin systems. However, the methylene spectral regions of these compounds have been completely broken down into ab sub-spectra. This procedure facilitated the acquirement of trial values for the iterative computer analysis. The NMR data are adequately explained in terms of two chair conformations differing essentially in the configuration at arsenic. The predominant isomers of all compounds except those possessing *trans*-4,6-dimethyl groups, appear to exist almost entirely in one chair conformation with axially and equatorially oriented substituents at arsenic and carbon, respectively. In the *trans*-4,6-dimethyl compounds we have found strong evidence for a conformational equilibrium between two chair forms. The reduced stability of the diaxial conformer is probably a result of severe *syn*-axial interactions between the axial substituents at arsenic and C(6).

The ^1H NMR spectra of several six-membered arsenites have been investigated in two previous papers.^{1,2} It has been shown that the preferred orientation of the substituent at arsenic is axial.¹⁻³ However, the conformational preferences of other exocyclic substituents on such rings have not been thoroughly studied.^{3,4} This

is in marked contrast to the considerable attention given the corresponding phosphites.⁵⁻¹¹

Arbuzov *et al.*⁵ report in a study based on measurements of dipole moments and Kerr constants, that the experimental and calculated data of 2-chloro-4-methyl-1,3,2-dioxarsenane are consistent with a chair conformation with axial chlorine and equatorial methyl. In more highly substituted systems, however, it is conceivable that the steric requirements of the substituents may force a dominance of another configuration at arsenic or confine the ring into a non-chair form.

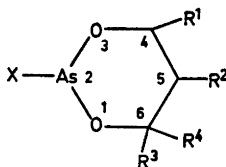
In order to obtain more information about externally substituted arsenanes we have prepared the following fifteen arsenites and investigated their ^1H NMR spectra. However, a complete spectral analysis has only been performed on the predominant isomers.

EXPERIMENTAL

The eight cyclic chloro-compounds were prepared from the appropriate 1,3-butanediols and trichloroarsine in ether solution using triethylamine as base.^{4,12} Treatment of the chloro-compounds with methanol or phenol in ether solution in the presence of excess triethylamine yielded the corresponding methoxy or phenoxy derivatives.⁴ The boiling and melting points which have not been reported previously,⁴ and the yields are as follows: B.p._{0.5} 42 °C (54 %); m.p. 97 °C (80 %); m.p. 79 °C (94 %); b.p._{0.05} 80 °C (75 %) and m.p. 45 °C (49 %) for compounds I, II, III, VIII and IX, respectively.

The ^1H NMR spectra were examined in benzene, deuteriochloroform, carbon disulfide

* J. A.'s contribution is limited to the data of Table 1.



I: X = Cl,	R ¹ = R ² = R ⁴ = H,	R ³ = CH ₃
II: X = Cl,	R ¹ = R ² = R ⁴ = H,	R ³ = <i>tert</i> -Bu
III: X = Cl,	R ¹ = R ² = R ⁴ = H,	R ³ = Ph
IV: X = OCH ₃ ,	R ¹ = R ² = R ⁴ = H,	R ³ = Ph
V: X = OPh,	R ¹ = R ² = R ⁴ = H,	R ³ = Ph
VI: X = Cl,	R ² = R ³ = R ⁴ = H,	R ¹ = CH ₃
VII: X = OCH ₃ ,	R ² = R ³ = R ⁴ = H,	R ¹ = CH ₃
VIII: X = OPh,	R ² = R ³ = R ⁴ = H,	R ¹ = CH ₃
IX: X = Cl,	R ² = R ³ = R ⁴ = H,	R ¹ = Ph
X: X = Cl,	R ³ = R ⁴ = H,	R ¹ = R ² = CH ₃ (<i>cis</i> methyl)
XI: X = OCH ₃ ,	R ³ = R ⁴ = H,	R ¹ = R ² = CH ₃ (<i>cis</i> methyl)
XII: X = Cl,	R ³ = R ⁴ = H,	R ¹ = R ² = CH ₃ (<i>trans</i> methyl)
XIII: X = OCH ₃ ,	R ³ = R ⁴ = H,	R ¹ = R ² = CH ₃ (<i>trans</i> methyl)
XIV: X = Cl,	R ³ = H, R ¹ = R ² = R ⁴ = CH ₃ ,	
XV: X = OCH ₃ ,	R ³ = H, R ¹ = R ² = R ⁴ = CH ₃ ,	

and dichlorofluoromethane solutions (ca. 50 % v/v). A small amount of TMS was added to the samples and used as internal standard and lock signal source. The 60 MHz and 100 MHz spectra were recorded on JEOL-C-60H and VARIAN HA-100 spectrometers, respectively. Line positions were obtained by averaging the results of two frequency-calibrated spectra run at about 100 Hz sweep widths.

The ¹H NMR spectra were analyzed by means of the computer program LAOCN3,¹³ UEATR¹⁴ and KOMBIP.¹⁵ The computations were performed on a UNIVAC 1110 computer. The graphical output was obtained using a Calcomp Plotter.

SPECTRAL ANALYSIS

The methylene regions of the 100 MHz spectra of compounds I-V were initially analyzed by hand as AKL systems. (The methine and methylene protons are labelled A and KL, respectively). The hand-calculated spectral parameters ν_K , ν_L , J_{AK} , J_{AL} , and J_{KL} were employed as input parameters for iterative AKK'LL'X₂ or AKK'LL' analyses of the complete spectra.^{13,14} The remaining trial parameters were readily obtained from the methine and methyl spectral regions.

The detailed spectral analyses of compounds VI-IX were carried out on the basis of ABKLMX₂ or ABKLM spin systems. The 100 MHz spectra of these compounds consist, apart from the methyl signals, of three main regions.

Trial parameters were obtained by analyzing, in part, the experimental spectra on a first-order basis. The refined parameters of I-IX resulting from iterative computer analyses,^{13,14} of the complete spin systems (less the substituent at arsenic) are listed in Table 1. The spectra generated¹⁵ from the refined parameters fit closely the experimental ones in each case as demonstrated for VI in Fig. 1.

The CHCH₂-CH₂-CHCH₂ moieties of compounds X-XIII constitute ABKK'X₂X₂' and ABKLX₂Y₂ spin systems for the *cis* and *trans* molecules, respectively. However, since the long-range methyl-methylene proton couplings are zero simplifications occur in the methylene (AB) region of these spectra. It is thus seen that the methylene spectral region of the *cis* and *trans* compounds constitutes the AB part of ABKK' or ABKL spin systems, respectively.

The AB part of the ABKK' spin system¹⁶ has been broken down into three different ab sub-spectra by means of the procedure due to Diehl.^{17,18} These sub-spectra are characterized by $J_{ab} = J_{AB}$ and the effective chemical shifts: *Symmetric*, $m(KK') = \pm 1$

$$\nu_a = \nu_A \pm J_{AK}; \quad \nu_b = \nu_B \pm J_{BK} \quad (1)$$

Symmetric and antisymmetric, $m(KK') = 0$

$$\nu_a = \nu_A; \quad \nu_b = \nu_B \quad (2)$$

The ab sub-spectrum corresponding to $m(KK') = 0$ has twice the intensity of the other

Table 1. 100 MHz NMR parameters (in Hz) of compounds I–IX measured in deuteriochloroform solution at 30 °C ^a.

Compound Spin system	I ^b AKK'LL'X ₃	II	III AKK'LL'	IV	V	VI ABKLMX ₃	VII	VIII	IX ABKLM
ν_{1a}	413.43	424.74	453.54	448.23	465.50	467.02	457.59	461.07	553.32
ν_{2a}						463.71	452.27	454.88	480.00
ν_{3c}	396.09	389.81	406.04	378.20	388.59	124.26	114.88	114.20	
ν_{4c}	234.59	188.64	327.81	327.22	334.04	413.27	389.29	384.29	419.33
ν_{5a}	75.55					205.72	196.93	193.21	234.88
ν_{6c}						164.92	154.50	144.09	178.41
J_{1a2a}^d						6.19	6.11	6.25	
J_{1a3c}^d	-11.69	-10.86	-11.19	-10.71	-10.80	-11.42	-11.04	-11.20	-11.52
J_{1a4c}^d	6.66					-14.38	-14.22	-14.08	-14.52
J_{1a5a}	11.17	10.90	10.68	11.18	11.43	10.82	10.24	10.97	11.12
J_{1a6a}						12.26	12.19	12.42	12.19
J_{1a3c}	3.90	3.56	3.77	3.77	3.87	3.76	3.63	4.01	3.99
J_{1a4c}						1.85	2.02	2.07	2.00
J_{1a5a}						1.98	2.06	2.02	2.07
J_{1a6a}						2.45	2.53	2.53	2.39
J_{1a3c}	0.23	0.00	-0.14	0.12	-0.12	0.05	-0.01	0.02	0.00
J_{1a4c}	-0.33	-0.08	-0.54	-0.10	-0.48	0.09	0.13	0.00	0.00
J_{1a5a}	-0.37	0.00	0.90	0.47	0.67				
Assigned transitions	205	25	32	26	30	222	217	455	66
RMS error	0.091	0.087	0.079	0.108	0.091	0.092	0.087	0.074	0.080

^a Chemical shifts downfield from TMS. ^b Measured in CHCl₃ solution at -110 °C. ^c Methine or methyl shift as appropriate. ^d Geminal or vicinal coupling constants as appropriate.

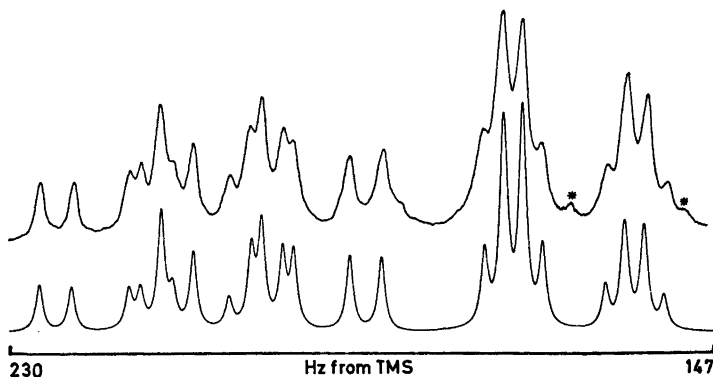


Fig. 1. Experimental (upper trace) and calculated (lower trace) 100 MHz spectrum at 30 °C of the methylene protons at C(5) in compound VI. The asterisks indicate impurities.

two ab sub-spectra. The four lines originating from the former spectrum were readily picked out since $J_{AB} \approx -14$ Hz (Fig. 2). Furthermore, the extreme high-frequency line in Fig. 2 must originate from the ab sub-spectrum corresponding to $m(KK') = 1$ since J_{AK} and J_{BK} are both positive. The splitting patterns ($J_{AB} \approx -14$

Hz) and intensity distribution then yielded the three missing lines in this sub-spectrum. By manipulating the identified lines good trial values of ν_A , ν_B , J_{AB} , J_{AK} and J_{BK} were obtained. The remaining trial values were obtained from the methine and methyl spectral regions.

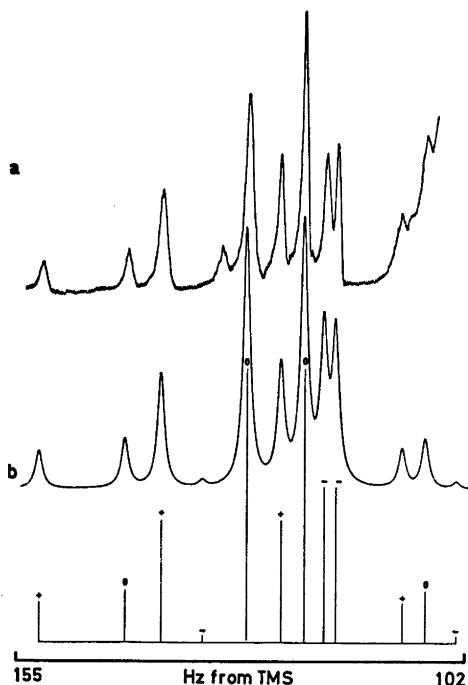


Fig. 2. Experimental (a) and calculated (b) 100 MHz spectrum of the methylene protons at C(5) in X. The breakdown into three ab sub-spectra corresponding to $m(KK')=1, 0$ and -1 , is shown by the +, 0 and - signs, respectively.

The methylene regions of XII and XIII can, as already mentioned, be analyzed on the basis of an ABKL system. However, since $|\nu_K - \nu_L| \gg |J_{KL}| \approx 0$ a further reduction into an ABKX system occurs. That is, the AB part can be completely broken down into four ab sub-spectra,¹⁸ one for each sign combination of $m_K = \pm \frac{1}{2}$ and $m_X = \pm \frac{1}{2}$. The ab sub-spectra are characterized by $J_{ab} = J_{AB}$ and the following effective chemical shifts:

$$\begin{aligned} \nu_a &= \nu_A + m_K (J_{AK} \pm J_{AX}) \\ \nu_b &= \nu_B + m_K (J_{BK} \pm J_{BX}) \end{aligned} \quad (3)$$

The upper and lower signs in the parentheses correspond to equal and opposite signs, respectively, of m_K and m_X .

The two ab sub-spectra corresponding to equal sign of m_K and m_X were identified by using a similar procedure as described for the *cis* compounds (Fig. 3). This assignment provided good values of ν_A , ν_B , $(J_{AK} + J_{AX})$ and

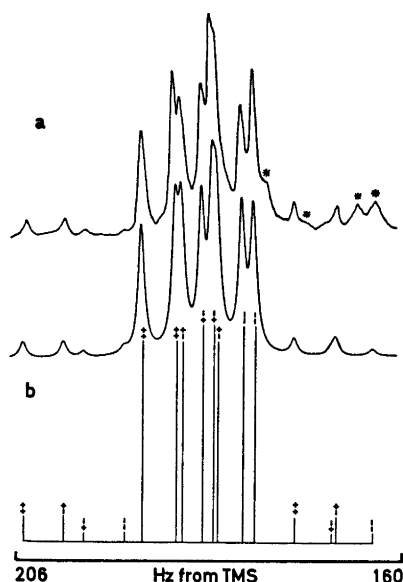


Fig. 3. Experimental (a) and calculated (b) 100 MHz spectrum of the methylene protons at C(5) in XIII. The breakdown into four ab sub-spectra, one for each sign combination of m_K and m_X , is shown by the + and - signs. The asterisks indicate impurities.

$(J_{BK} + J_{BX})$. Computation of ab sub-spectra with variation of $J_{ab}/|\nu_a - \nu_b|$ then enabled us to identify the two remaining ab sub-spectra, thus providing good values of the individual coupling constants. The remaining three parameters were obtained directly from the methyl and methine spectral regions.

The 100 MHz spectra of the $\text{CH}_2\text{-CHCH}_2$ moiety in XIV and XV were analyzed as ABKX₂ spectra. An approximate first-order analysis yielded three parameters for the iterative calculations.

The spectral parameters of X–XV listed in Table 2 were obtained from iterative computer analyses of the complete spin systems.¹⁴ Good fits between the observed and calculated spectra¹⁵ were obtained in each case as demonstrated in Figs. 2 and 3 for compounds X and XIII.

DISCUSSION

Several of the methyl-substituted 2-methoxy-1,3,2-dioxarsenanes examined in this work have been found to exist as a mixture of two

Table 2. 100 MHz parameters (in Hz) of compounds X–XV measured at 30 °C.^a

Compound Spin system Solvent	X ABKK'X ₂ X ₂ ' C ₆ H ₆	XI CDCl ₃	XII ^b ABKLX ₂ Y ₂ CS ₂	XIII CDCl ₃	XIV ABKX ₂ CDCl ₃	XV CDCl ₃
ν_{aa}^c	439.79	456.13	466.88	461.44	458.93	463.09
ν_{aa}^c			152.34	142.08		
ν_{ac}^c	100.58	105.97	126.65	123.90	126.35	121.67
ν_{cc}^c			452.71	435.88		
ν_{sa}	132.29	154.74	203.75	187.86	192.98	170.18
ν_{sc}	116.84	154.76	174.10	179.02	163.39	155.90
J_{saac}^d	6.30	6.26	6.33	6.27	6.29	6.22
J_{sacc}^d			6.72	6.57		
J_{sasc}^d	-14.27	-14.13	-13.75	-13.97	-14.11	-14.05
J_{asaa}	10.91	10.88	9.54	8.36	11.04	11.03
J_{asac}	1.86	1.90	2.08	3.12	1.62	1.37
J_{sasc}			4.82	4.70		
J_{sacc}			3.09	4.97		
Assigned transitions	325	244	322	349	85	82
RMS error	0.080	0.074	0.068	0.066	0.076	0.062

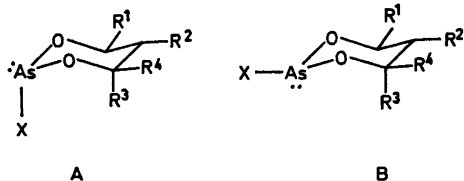
^a Chemical shifts downfield from TMS. All long-range coupling constants are negligible. ^b 60 MHz spectrum measured at -60 °C. The chemical shifts have been converted to 100 MHz values. ^c Methine or methyl shift as appropriate. ^d Vicinal CHCH₂ coupling constant.

geometrical isomers.⁴ The existence of non-equilibrium isomer mixtures implies that thermal atomic inversion of arsenic is slow at room temperature as expected owing to the high barrier (25–42 kcal/mol).^{19,20} However, the ¹H NMR spectra of aged samples of I–XV showed measurable amounts of only one isomer which is believed to be the thermodynamically more stable form. The present spectral analyses have therefore only been performed on the predominant isomers.

The ¹H NMR spectra of I in benzene and carbon disulfide solutions at ambient probe temperature, showed a broad octet and doublet for the methine and methylene protons, respectively. The corresponding methine and methylene NMR signals of XII recorded at ambient probe temperature in benzene and carbon disulfide solutions, displayed a broad sextet and triplet, respectively. However, at low temperature in carbon disulfide solution, the NMR spectra of I and XII proved to be almost identical to the spectra of the analogous methoxy-compounds. These observations imply that a process which leads to exchange of the nuclear magnetic environments of the methyl-

ene as well as the methine hydrogens, is taking place in these chloro-compounds. We believe, in accordance with previous conclusions,^{2,3,21} that this process is an intermolecular chlorine exchange rather than a thermal inversion at arsenic.

The large vicinal coupling constant (10.2–12.4 Hz) observed in all compounds except XII and XIII, is typical for an axial-axial coupling in a chair conformation.^{1,2,6–10} This value together with characteristic values of the remaining parameters, indicate strongly that these molecules, less XII and XIII, exist almost entirely in one chair conformation. The NMR data of the present compounds are adequately explained (*vide infra*) on the basis of two chair conformations, A and B, differing essentially in the configuration at arsenic. The chloro-compounds are formed in the main in one preferred configuration believed to be the more stable form A.⁴ However, replacement of chlorine by methoxy in these compounds yielded, initially, the unstable isomer B which unless special care was taken, readily isomerized into A under the reaction conditions.⁵



It is noted in Tables 1 and 2 that the axial protons appear at lower field than the geminal equatorial protons in agreement with previous results for trimethylene sulfites²²⁻²⁴ and 1,3,2-dioxaphosphorinanes^{6-10,25} possessing axial 2-substituents. This observation thus indicates, in accordance with previous conclusions,²⁻⁴ that the preferred orientation of the substituent at arsenic is axial, that is, the A conformation is the thermodynamically more stable form.

In the following discussion it is convenient to divide the investigated compounds into five groups according to their substitution patterns, viz. Group 1, 5-substituted; group 2, 4-substituted; group 3, *cis*-4,6-dimethyl-substituted; group 4, *trans*-4,6-dimethyl-substituted; and group 5, 4,6,6-trimethyl-substituted compounds. It can be concluded, on the basis of the coupling constants, that the molecular conformations are very similar within a given group and also, to some extent, in between different groups.

The large vicinal coupling constant (*ca.* 11 Hz) observed in the group 1 compounds shows that the substituent at C(5) occupies an equatorial position as expected. The value of J_{4a5a} in compounds I-V is about 1 Hz smaller than in the unsubstituted 1,3,2-dioxarsenanes.³ The value of J_{5a5c} is, however, hardly affected by substitution at C(5). Similar effects or lack thereof, on the vicinal coupling constants upon substitution at C(5) have also been observed in 1,3,2-dioxaphosphorinanes¹⁰ and trimethylene sulfites.²³ The reduction in J_{4a5a} is probably caused by the exocyclic substituent at C(5) rather than by a considerable reduction in ring puckering.

The NMR parameters of the group 2 compounds VI-IX, are consistent with an equatorial position of the substituent at C(4). This observation is in agreement with previous results for 2-chloro-4-methyl-1,3,2-dioxarsenane³ and its phosphorus analogue.¹⁰

The values of J_{4a5a} and J_{5a5c} in group 2 are close to the corresponding parameters in group

1. Apparently, a substituent at C(4) produces a similar reduction in J_{4a5a} as a substituent at C(5). The value of J_{5a5c} on the unsubstituted side of the ring is, however, quite close to the axial-axial coupling constant in the almost staggered conformation of unsubstituted 2-X-1,3,2-dioxarsenanes (X=Cl, Br, OMe, OPh).³ On this basis, an essentially staggered conformation of the O-C(4)-C(5)-C(6)-O portion of the ring is expected in VI-IX. This assumption is supported by calculations of the C(4)-C(5)-C(6)-O torsional angle based upon the *R*-value method due to Lambert²⁶ in that the calculated torsional angles range from 59.6 to 60.4°.

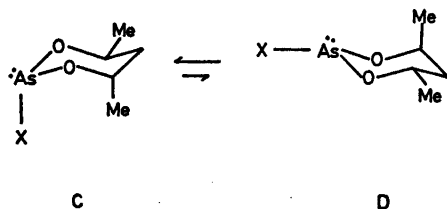
Inspection of Table 1 shows that the equatorial phenyl group at C(4) or C(5) gives rise to a considerable downfield shift of the ring protons in comparison with methyl or *tert*-butyl. This shift effect is largest at the geminal methine proton and decreases rapidly with the distance from the phenyl group. It is thus evident that the low-field shift is caused by the ring current effect of the phenyl group. It is also noted in Table 1 that the chlorine substituent at arsenic produces, in general, a considerably larger paramagnetic shift effect than the methoxy and phenoxy groups. A similar trend in the chemical shifts of 2-X-1,3,2-dioxarsenanes (X=Cl, OMe and OPh)³ and their phosphorus analogues²⁷ is also noted upon inspection of the published data.

The measured values of J_{4a5a} and J_{4a5c} in the group 3 compounds X and XI, are very close to those in group 2. For the analogous phosphites²⁵ and *cis*-4,6-dimethyl-1,3-trimethylene sulfite with an axial S=O group,²⁴ ranges of J_{4a5a} 11.4-11.6 Hz and J_{4a5c} 2.1-2.4 Hz have been reported. These parameters are thus fairly close to those in X and XI. We conclude that these systems exist in similar chair conformations with axial 2-substituents and equatorial methyl groups.^{8,11}

Comparison of the chemical shifts of X and XI is not relevant since these compounds have been examined in different solvents. The apparent upfield proton shifts in X as compared to XI, are obviously caused by the benzene solvent.

The NMR data of the group 4 compounds XII and XIII, are not so readily interpreted. The remarkably small value of J_{4a5a} together

with fairly large values of J_{saec} and J_{seec} cannot be explained on the basis of a single chair conformation like A or B. However, if it is assumed that the observed coupling constants are time-averaged values resulting from an equilibrium between conformers C and D in which C is the predominant form, then J_{4asa} would be reduced by the inclusion of a fair amount of equatorial-equatorial coupling whereas J_{seec} would gain a similar increase from the axial-axial coupling. The two axial-equatorial coupling constants would not be appreciably changed by this process since $J_{\text{ae}} \approx J_{\text{ea}}$. The stereoisomers C and D differ essentially in the orientation of the substituent on arsenic. For the analogous 2-methoxy-*trans*-4,6-dimethyl-1,3,2-dioxaphosphorinane White *et al.*⁹ also found evidence for a conformational equilibrium. In this context, it should be remembered that chair-chair conversions in the arsenites and phosphites may be influenced by vicinal-pair electron repulsions called into play on rotation about the O-As or O-P bonds.⁷



The axial-axial and equatorial-equatorial coupling constants for the equilibrium $C \rightleftharpoons D$ can be expressed by eqn. (4).

$$\begin{aligned} J_{\text{4asa}} &= pJ_{\text{aa}} + (1-p)J_{\text{ee}} \\ J_{\text{seec}} &= pJ_{\text{ee}} + (1-p)J_{\text{aa}} \end{aligned} \quad (4)$$

where p is the relative weight of the predominant conformer. Eqn. (5) is obtained by eliminating J_{ee} from eqn. (4).

$$p = \frac{J_{\text{aa}} - J_{\text{seec}}}{2J_{\text{aa}} - J_{\text{4asa}} - J_{\text{seec}}} \quad (5)$$

On the assumption that the C and D conformers have the same partition function it follows that

$$p = \frac{1}{1 + \exp(-\Delta G^\circ/RT)} \quad (6)$$

where ΔG° is the free energy difference between the two conformers.

Unfortunately, J_{aa} is not known for the individual C and D conformers of XII and XIII. However, a fair estimate of J_{aa} is the average value of J_{4asa} in the six investigated compounds possessing an equatorial methyl group at C(4) or C(5). By inserting the obtained value of $J_{\text{aa}} \approx 10.9$ Hz, and the measured values of J_{4asa} and J_{seec} in XII and XIII, into eqn. (5) we obtain $p \approx 0.85$ and 0.70 at -60 and 30 °C, respectively. These values of p yield by means of eqn. (6), $\Delta G^\circ(-60$ °C) ≈ 0.7 kcal/mol and $\Delta G^\circ(30$ °C) ≈ 0.9 kcal/mol.

Hardly measurable amounts of the less stable isomer have been observed for most of the other arsenanes at thermal equilibrium. This indicates that the conformational free energy difference between axial and equatorial substituents at arsenic, is greater than about 2 kcal/mol in these compounds. Similar free energy differences in favour of an axial P-OMe orientation have been reported for the related 1,3,2-dioxaphosphorinanes.^{7,8,11} The low value of ΔG° in XII and XIII indicates a reduced stability of the C conformer. We believe that this is a result of severe *syn*-axial or 1,3-diaxial interactions between the axial As-X group and the axial methyl group at C(6).

The average torsional angle of the O-C(4)-C(5)-C(6)-O portion in the *trans*-dimethyl rings has been calculated using the *R*-value method. The calculated values (54 – 55°) indicate that these rings are less puckered by ca. 3° than their mono- and disubstituted analogues possessing only equatorial ring substituents on the carbon skeleton. This observation probably reflects a tendency of the axial methyl group at C(6) to move away from the axial As-X bond and the axial methylene hydrogen at C(4) thereby reducing the *syn*-axial interactions in conformer C. A further reduction in the 1,3-steric interactions is expected owing to a flattening of the ring about arsenic in XII and XIII with respect to the analogous phosphites.⁸

The NMR data of the group 5 compounds show clearly that the major isomers exist almost entirely in a single chair conformation with one axial and two equatorial methyl groups. The conformation possessing diaxial methyl groups can be rejected on steric grounds. A fair amount of the less stable isomer of XV was observed at thermodynamic equilibrium. This observation again reflects a reduction in

the free energy difference between the A and B isomers owing to the 1,3-diaxial interactions in the former.

It is worthwhile to note that the relative shifts of the methylene and methyl hydrogens are the same in compounds XII–XV in that the axial signal appears downfield of the equatorial one. The general downfield shift of axial hydrogens as compared to equatorial ones, is mainly attributed to the anisotropy effect in these systems.

The measured values of the geminal coupling constants in I–XV cover the ranges -10.7 to -11.7 Hz and -13.7 to -14.5 Hz for the $O-CH_2-C$ and $C-CH_2-C$ moieties, respectively. These values are quite close to those reported for unsubstituted 1,3,2-dioxarsenanes⁴ and variously substituted 1,3,2-dioxaphosphorinanes^{6,7,10,27} and trimethylene sulfites.^{22–24} The oxygen heteroatom thus gives rise to a positive increase of ca. 3 Hz in comparison with carbon. Molecular models of the six-membered arsenites indicate that both lone pairs of electrons on the oxygen heteroatom roughly bisect the CH_2 group (*i.e.* the H–H intermolecular axis). The contribution to J_{axax} and J_{eaxe} from the lone electron pairs is thus expected to be minimal and the positive contribution to the coupling is mainly attributed to inductive removal of σ -electrons from the CH_2 orbitals by the adjacent oxygen.^{28,29}

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