NMR Studies on Cyclic Arsenites. ¹H NMR Spectral Analysis and Conformational Studies of Twenty-two 1,3,2-Dioxarsenanes

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The present paper reports preparation and ¹H NMR studies of twenty-two six-membered arsenites. The complex proton spectra which have been fully analyzed, constitute spin systems containing from four to ten spin-½ nuclei. The NMR data of the 1,3,2-dioxarsenanes are adequately rationalized on the basis of a chair conformation with an axial substituent at arsenic. The methyl, *tert*-butyl and phenyl ring-substituents are equatorially oriented unless geminal disubstitution forces one of the groups into an axial position. The NMR results indicate that the O−C−C−C−O portion of the six-membered ring assumes an essentially staggered conformation. The axial ring protons suffer downfield shifts relative to their equatorial counterparts. Alkyl and phenyl ring-substituents have a marked and stereospecific effect on the chemical shifts and coupling constants of the ring protons. Specifically, an equatorial methyl group produces a significant upfield shift (−0.2 to −0.5 ppm) on the vicinal axial proton. The vicinal coupling between two axial protons is considerably reduced (~1 Hz or more) on the introduction of an equatorial substituent at one of the carbons bearing the coupled protons. The oxygen heteroatom gives rise to a positive increment of about 3 Hz in the geminal coupling constant of the adjacent methylene protons with respect to carbon.

The ¹H NMR spectra of a series of dioxarsenanes have been studied by the present research group.[1−4] Samitov et al.[5] have also reported a partial and approximate spectral analysis of some unsubstituted and methyl-substituted dioxarsenanes. The cyclic arsenites are configurationally stable about the arsenic atom owing to the high barrier of inversion (42 kcal/mol).[6] Previous investigations have shown that the arsenane ring adopts a chair conformation usually with an axial substituent at arsenic. How-

ever, in highly substituted systems it is not unlikely that the steric requirements of the substituents may confine the ring into a non-chair conformation or force a dominance of another configuration at arsenic.
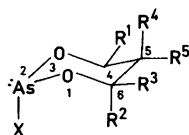
In order to obtain more information about externally ring-substituted dioxarsenanes we have prepared the twenty-two arsenites listed in Table 1 and analyzed their ¹H NMR spectra. The complex ¹H NMR spectra constitute spin systems containing from four to ten spin-½ nuclei.

EXPERIMENTAL

The cyclic 2-chloro- and 2-phenyl-1,3,2-dioxarsenanes were prepared from the appropriate 1,3-butanediols and trichloroarsine, respectively phenyldichloroarsine, in ether solution using triethylamine as base.[7] 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. The boiling and melting points and refractive indices of the prepared compounds are listed in Table 1.

The ¹H NMR spectra were examined in deuteriochloroform solutions (*ca.* 30 % w/w) at ambient probe temperature (*ca.* 30 °C). Compounds I, V and XII were also recorded at lower concentrations or temperatures as indicated in Tables 2 and 3. A small amount of TMS was added to the samples and used as internal standard. TMS and deuteriochloroform served as internal ¹H and ²D lock signal sources. The 60, 90 and 98 MHz spectra were recorded on JEOL-C-60H, BRUKER CXP 100 and VARIAN HA-100 spectrometers, respectively. Line positions for the 60 and 98 MHz spectra were obtained by averaging the results of two frequency-calibrated CW spectra run at about 100 Hz sweep widths. The digital

Table 1. Investigated 1,3,2-dioxarsenanes together with some physical data.

Compound	Substituents		mmHg	B.p. °C	M.p. °C	$n_D{}^{25}$	Spin system
	X	$R^{i\ a}$					
I	Cl	⎫	0.4	52	47		⎫
II	OMe	⎪ $R^4 = R^5 = Me$	0.5	34		1.4712	⎪
III	OPh	⎬	0.4	87		1.5389	⎪
IV	Ph	⎭	1.0	105	41		⎬ KK'LL'
V	Cl	⎫	0.4	152		1.5081	⎪
VI	OMe	⎪ $R^4 = R^5 = Et$	0.4	130		1.4819	⎪
VII	OPh	⎬	0.3	181		1.5320	⎪
VIII	Ph	⎭	0.4	196		1.5494	⎭
IX	Ph		0.6	65		1.5989	ABKK'LL'
X	Ph	$R^5 = Ph$	0.5	178		1.6148	⎫ AKK'LL'
XI	Ph	$R^5 = Bu^t$			169		⎭
XII	Cl	⎫	0.3	42		1.5158	⎫
XIII	OMe	⎪ $R^5 = Me$	1.5	100		1.4774	⎪ AKK'LL'X₃
XIV	OPh	⎬	0.6	146		1.5492	⎪
XV	Ph	⎭	0.8	142		1.5748	⎭
XVI	Ph	$R^1 = Ph$	0.3	160		1.6183	ABKLM
XVII	Ph	$R^1 = Me$	0.4	112		1.5648	ABKLMX₃
XVIII	Cl	⎫	0.05	46		1.4964	⎫
XIX	OMe	⎪ $R^1 = R^2 = R^3 = Me$	0.3	39		1.4648	⎪ ABKX₃
XX	OPh	⎬	0.4	115		1.5259	⎬
XXI	Ph	⎭	0.4	106		1.5283	⎭
XXII	Ph	$R^1 = R^3 = Me$	1.5	169	146		ABKK'X₃X₃'

^{a} $R^i = H$ unless otherwise stated.

Table 2. ^{1}H NMR spectral parameters of compounds I – VIII measured in deuteriochloroform solutions. The compounds in this series are geminal di-substituted at C(5).^{a}

Compound	I^b	II	III	IV	V^c	VI	VII	VIII
Obs. freq. MHz	90	98	98	98	60	98	98	98
$\delta_{4a(6a)}$	4.215	4.176	4.357	3.661	4.275	4.184	4.379	3.763
$\delta_{4e(6e)}$	3.485	3.307	3.396	3.480	3.792	3.535	3.641	3.747
J_{4a4e}	−11.13	−10.70	−10.60	−10.65	−11.49	−11.07	−11.02	−11.42
J_{4e6e}	1.96	2.28	2.43	1.96	2.14	2.54	2.25	1.84
J_{4e6a}	0.09	−0.09	−0.07	−0.12	0	−0.10	−0.09	0.11
J_{4a6a}	0	0	0	−0.10	0	0	0	0.11
Assigned transitions	22	16	16	9	16	22	24	13
RMS error	0.097	0.047	0.038	0.090	0.133	0.046	0.057	0.029

^{a} Chemical shifts in ppm downfield from TMS; coupling constants in Hz. ^{b} Concentration *ca.* 1 % w/w in CDCl₃. ^{c} Measured in CS₂ at −58 °C.

Table 3. ¹H NMR spectral parameters of compounds IX — XV measured in deuteriochloroform solutions. These compounds are unsubstituted or mono-substituted at C(5).[a]

Compound Obs. freq. MHz	IX 98	X 98	XI 90	XII[b] 90	XIII 90	XIV 90	XV 90
$\delta_{4a(6a)}$	4.061	4.079	3.759	4.042	4.002	4.211	3.547
$\delta_{4e(6e)}$	3.977	3.985	4.023	3.758	3.669	3.778	3.824
δ_{5a}	2.220	3.301	1.826	2.101	2.217	2.270	2.167
δ_{5e}[c]	1.325		0.716	0.511	0.605	0.562	0.401
J_{4a4e}	−11.53	−11.14	−10.95	−11.45	−10.97	−10.97	−11.41
J_{5a5e}[d]	−14.30			6.89	6.88	6.90	6.84
J_{4a5a}	11.15	11.03	10.80	11.11	11.17	11.06	10.60
J_{4e5a}	3.34	3.75	3.11	3.89	3.57	4.05	3.18
J_{4a5e}	2.16						
J_{4e5e}	3.65						
J_{4a6a}	−0.04	−0.32	0.04	−0.06	0.13	−0.08	−0.15
J_{4a6e}	−0.08	−0.12	−0.04	0.02	0.13	−0.22	0.15
J_{4e6e}	1.06	1.54	0.77	0.93	0.98	1.56	1.68
Assigned lines	142	54	64	341	319	436	325
RMS error	0.100	0.101	0.102	0.086	0.093	0.091	0.101

[a] Chemical shifts in ppm downfield from TMS; coupling constants in Hz. [b] Concentration *ca.* 1 % w/w in a mixture of carbon disulfide and deuteriobenzene (60:40). [c] Chemical shift of $R^4 = H$, *tert*-butyl or methyl as appropriate. [d] Geminal or vicinal coupling constant as appropriate.

resolution for the 90 MHz FT-NMR spectra was better than 0.1 Hz.

The ¹H NMR spectra were analyzed by means of the computer programs LAOCN3,[8] UEAITR[9] and KOMBIP.[10] The computations were performed on a UNIVAC 1110 computer. The graphical output was obtained using a Calcomp Plotter.

SPECTRAL ANALYSIS

A complete list of the investigated spin systems is given in Table 1. The methylene proton spectra of compounds I — VIII were analyzed as KK'LL' spin systems because the long-range couplings between the methylene and methyl/ethyl protons at C(5) were negligible.

The proton spectra of the $CH_2 - CHCH_3$ moiety of compounds XVIII — XXI were, likewise, analyzed as $ABKX_3$ spectra by neglecting long-range couplings to the geminal dimethyl protons.

Some starting parameters for the iterative calculations were obtained from first-order and subspectral analyses. The remaining spectral parameters were sought by comparison with related systems or by trial-and-error analysis. In most cases a series of trial-and-error calculations were carried out before a sufficient number of experimental lines could be matched to the corresponding

theoretical transitions. Once a partial assignment had been made a preliminary iteration was carried out to a least-squares fit with the matched lines by varying all (or a limited number) of the input parameters. If the starting parameters were close enough to the solution for convergence to occur, the improved parameters were used as a new basis set for the final iterative calculation where all measured lines were matched and all parameter sets were allowed to vary. The frequencies of two or more strong overlapped transitions were estimated by separating the assumed positions by a judicious amount instead of using the centre of the observed peak.

The correctness of the final parameters listed in Tables 2 — 4, was always checked by visual comparison of experimental and calculated spectra. Good fits between the observed and calculated spectra were obtained as demonstrated in Fig. 1 for compound IX.

RESULTS AND DISCUSSION

The proton spectra of freshly distilled samples of I and V in *ca.* 30 % deuteriochloroform, benzene and carbon disulfide solutions showed a broad methylene signal at ambient probe temperature

Table 4. 98 MHz spectral parameters of compounds XVI – XXII measured in deuteriochloroform solutions, these compounds are mono-substituted at C(4) and unsubstituted, mono- or di-substituted at C(6).[a]

Compound	XVI	XVII	XVIII	XIX	XX	XXI	XXII [b]
δ_{4a}	4.882	4.119	4.683	4.725	4.800	4.446	3.937
δ_{6a} [c]	3.649	4.114	1.534	1.523	1.566	1.552	
δ_{4e} [c]		1.211	1.289	1.241	1.257	1.261	1.126
δ_{6e} [c]	4.059	4.066	1.321	1.273	1.289	1.307	
δ_{5a}	2.107	1.964	1.969	1.737	1.779	1.769	1.437
δ_{5e}	1.819	1.291	1.667	1.591	1.598	1.446	1.226
J_{4a4e} [d]		6.00	6.29	6.22	6.27	6.07	
J_{6a6e}	−11.16	−11.41					
J_{5a5e}	−14.51	−14.19	−14.11	−14.05	−14.13	−13.63	−13.60
J_{4a5a}	11.18	10.75	11.04	11.03	11.16	10.98	10.74
J_{5a6a}	12.46	12.67					
J_{5a6e}	3.91	3.54					
J_{4a5e}	2.05	1.91	1.62	1.37	1.48	1.54	1.71
J_{5e6a}	2.17	1.90					
J_{5e6e}	2.41	2.27					
J_{4a6a}	−0.01	0.02					−0.25
J_{4a6e}	−0.01	−0.04					
Assigned lines	57	427	85	82	82	79	299
RMS error	0.093	0.092	0.076	0.062	0.068	0.077	0.042

[a] Chemical shifts in ppm downfield from TMS; coupling constants in Hz. [b] Measured at 90 MHz. [c] Chemical shift of methyl- or ring-protons as appropriate. [d] Vicinal $CHCH_3$ coupling.

(*ca.* 30 °C). However, at low temperature in CS_2 solution, the methylene band was split into two signal groups corresponding to the axial and equatorial protons at carbons 4 and 6. The interchange of the nuclear magnetic environments of the methylene protons in I and V is believed to be caused by an intermolecular halide exchange process.[1−3,11] The proton spectrum of I in 1 % $CDCl_3$ solution recorded at ambient probe temperature, showed more fine structure than the corresponding low temperature spectrum in CS_2. The former spectrum was, therefore, used in the spectral analysis.

The NMR data of the 2-substituted 1,3,2-dioxarsenanes are adequately rationalized on the basis of a chair conformation with an axial sub-
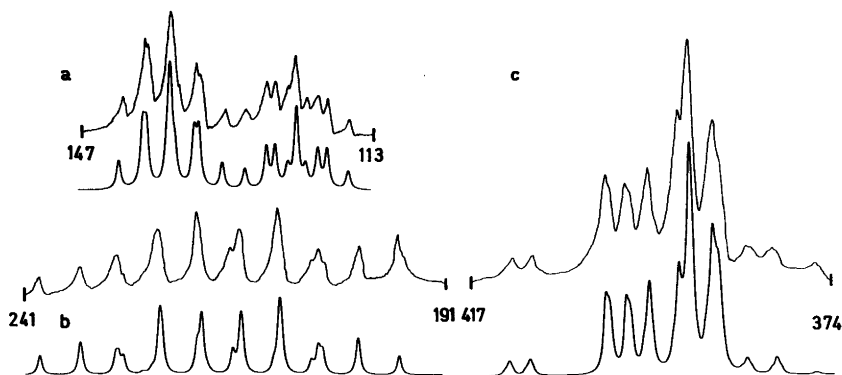

Fig. 1. 98 MHz methylene proton NMR spectrum of 2-phenyl-1,3,2-dioxarsenane (IX): a and b, the equatorial and axial proton at carbon 5, respectively; c, the methylene protons at carbons 4 and 6. The upper and lower traces in each frequency region represent the experimental and calculated spectrum, respectively. The frequency scale is in Hz downfield from TMS.

stituent at arsenic *(vide infra)*. Furthermore, Arbuzov *et al.*[44] report in a study based on measurements of dipole moments and Kerr constants, that the experimental and calculated data for 2-chloro-4-methyl-1,3,2-dioxarsenane are consistent with a chair conformation with axial chlorine and equatorial methyl. In the related six-membered phosphites a strong axial preference of the substituent at phosphorus has been established for electron-withdrawing groups (Cl, OMe, and OPh)[11,12] as well as for relatively non-electronegative groups (Me, i-Pr, and Ph).[13] It may be concluded that the configuration about arsenic and phosphorus in these rings is not determined primarily by repulsive 1,3-syn-axial interactions as are the orientations of alkyl and phenyl 2-substituents in 1,3-dioxanes.[14,15] Furthermore, anomeric effects[16] do not appear to be dominant since not only chlorine, methoxy and phenoxy but also relatively electropositive substituents like methyl and phenyl, prefer axial orientations. Bentrude *et al.*[13] argue that vicinal interactions about the $P-O$ bonds are the dominant factors that favour axial orientation in 2-substituted 1,3,2-dioxaphosphorinanes. Normal steric effects derived from 1,3-repulsive syn-axial interactions contribute but are of secondary importance.

It can be concluded on the basis of the present and previously reported data on 2-X-1,3,2-dioxarsenanes[1-4] (X=Cl, OMe, OPh, and Ph) and the phosphorus analogues,[17,18] that the chemical shift effect of methoxy and phenoxy is similar and intermediate between that of phenyl and chlorine. The latter substituent produces the largest downfield shifts.

In the arsenites,[1-4] phosphites,[17-19] and sulfites[20-24] the axial ring-protons suffer downfield shifts relative to their equatorial counterparts opposite the situation in cyclohexanes.[25] In the 1,3-dioxanes,[26] however, the H_{5a} signal is shifted downfield whereas the $H_{4a(6a)}$ signals are shifted upfield with respect to the corresponding equatorial protons. Anteunis *et al.*[27] argue that the relative shifts of the C(5) protons might arise from an interaction between H_{5e} and the *p*-orbitals of the ring oxygen atoms.

The downfield shifts of the axial protons at C(4) and C(6) in the arsenites,[1-4] phosphites,[17,18] and sulfites[20-24] are, however, believed to be caused by the axial As−X, P−X, and S=O groups. Similar stereospecific anisotropy effects are apparently operating on the methyl groups as well since the axial methyl signal appears at lower field than the

equatorial signal in appropriately methyl-substituted arsenanes.[23] Corresponding shift differences between axial and equatorial methyl or *tert*-butyl groups have also been observed in the related phosphites[11,28,29] and sulfites.[22]

Alkyl and phenyl ring-substituents are seen to have a marked and stereospecific effect on the chemical shifts of the ring protons. Examination of the NMR data of ring-substituted arsenanes indicates that the shift effects depend primarily on the relative position of the substituents and the hydrogen atom in question and are more or less independent on the site of substitution. Although the chemical shift variations in the methyl-substituted arsenanes can be partly attributed to solvent effects the reduction in the internal shift differences between the H_{5a} and H_{5e} protons from about 0.9 ppm in the four unsubstituted 2-X-1,3,2-dioxarsenanes (X=Cl, OMe, OPh, and Ph)[1] to 0.2 ppm or less, in the corresponding *cis*-4,6-dimethyl compounds,[3] clearly demonstrates that the stereospecific shift effect of equatorial methyl groups is significant.

Examination of the NMR data of all investigated methyl-substituted 2-X-1,3,2-dioxarsenanes (X=Cl, OMe, OPh and Ph)[3] shows that an equatorial methyl group produces a marked upfield shift (−0.2 to −0.5 ppm per Me) on the adjacent axial hydrogen atom with respect to the unsubstituted analogues. The largest upfield shifts (−0.6 to −1.1 ppm) were observed in the *cis*-4,6-dimethyl compounds[3] possessing two equatorial methyl groups. This vicinal effect is well documented in 1,3-dioxanes where Tavernier and Anteunis[26] have reported significant upfield shifts (−0.4 to −0.5 ppm). A similar shift effect is also noted in methyl-substituted 2-chloro- and 2-methoxy-1,3,2-dioxaphophorinanes[18,30] and trimethylene sulfites[22,23] upon inspection of the published data. In *cis*-4,6-dimethyl-1,3-dioxanes,[31] *cis*-4,6-dimethyl-trimethylene sulfite[22] and *cis*-4,6-dimethyl-2-X-1,3,2-dioxaphosphorinanes (X=Cl and OMe),[30] for example, the observed chemical shift reversal of the methylene protons at C(5) with respect to the unsubstituted analogues, is a result of the vicinal methyl influence. This effect is also seen in *cis*-4,6-dimethyl-2-methoxy-1,3,2-dioxarsenane[3] where the H_{5a} and H_{5e} protons have practically identical shifts.

The axial and equatorial protons at the geminal and vicinal carbons, respectively, are, however, shifted in either direction by ±0.5 ppm by the

influence of an equatorial methyl group. It is interesting to note, however, that this geminal and vicinal substituent effect always works in the same direction and is of similar magnitude, for a given compound. Similar observations have been made in the 1,3-dioxanes[26] where the corresponding protons experience shifts between ± 0.4 ppm.

In 2-chloro- and 2-phenyl-5-tert-butyl-1,3,2-dioxarsenanes[3] the equatorial tert-butyl group is seen to produce marked upfield shifts (-0.3 to -0.5 ppm) of the axial protons on the geminal and vicinal carbons in comparison with the unsubstituted analogues.[1] This result is in accord with similar upfield shifts of geminal protons (ca. -0.5 ppm) observed in 1,3-dioxanes for 2-, 4-, and 5-tert-butyl substitution.[26]

Replacement of hydrogen at C(4) or C(5) by an equatorial phenyl group in 1,3,2-dioxarsenanes[3,4] and the analogous phosphites[18] and sulfites,[23] produces a significant downfield shift of the ring protons. The downfield shift which is believed to be caused by the ring current effect of the phenyl group, is largest for the geminal methine proton (0.9 to 1.2 ppm in the arsenanes) and decreases rapidly with the distance from the site of substitution.

The measured values of the geminal coupling constant J_{5a5e} in the $C-CH_2-C$ moiety of the dioxarsenanes[1,3,4] cover the range -13.6 to -14.6 Hz. These values are close to those reported for the analogous phosphorinanes (-13.9 to -14.7 Hz)[17,18,30,33] and trimethylene sulfites (-13.1 to -14.5 Hz).[20-24] Examination of the reported values for J_{5a5e} in the diox- and dithiarsenanes[1-3,34] and their phosphorus analogues,[17,18,32,33,35] shows that replacement of oxygen by sulfur has a negligible effect on the geminal coupling. This observation is in accord with previous results which also show that β-substitution has a small effect on the geminal coupling constant of tetrahedral CH_2 groups.[36,37]

The observed values of J_{4a4e} and J_{6a6e} in the $C-CH_2-O$ moieties of the 1,3,2-dioxarsenanes are in the range -10.7 to -11.5 Hz.[1,3,4] These values are again well within the ranges reported for the corresponding phosphites[17-19,29,32,33] and sulfites.[20-24] The oxygen heteroatom thus gives rise to a positive increment of about 3 Hz with respect to carbon. The positive shift is mainly attributed to inductive σ-electron withdrawal. According to Pople and Bothner-By[36] an additional positive shift to the geminal coupling which might arise from pseudo-π-electron transfer from the oxygen 2p lone

pair into the CH_2 system is small in the chair form of six-membered rings containing oxygen.

The measured values of J_{4a5a} (J_{5a6a}) in the CH_2-CH_2 moiety of the investigated 1,3,2-dioxarsenanes[1-4] of about 12 Hz are typical for protons having a trans-diaxial relationship. Similar values of vicinal axial-axial coupling constants have also been reported for the corresponding phosphites[17] and trimethylene sulfites.[20-22]

A considerable decrease in J_{4a5a} (J_{5a6a}) is observed, however, for the arsenites,[3,4] phosphites[18,29,30] and sulfites[22-24] upon substitution at carbons 4 or 5. In the 4- and 5-substituted 1,3,2-dioxarsenanes,[3,4] an equatorial methyl, tert-butyl or phenyl group is seen to produce a significant decrease in J_{4a5a} (ca. $1-2$ Hz) which is roughly independent on the site of substitution. However, substitution at carbon 4 has no measurable effect on J_{5a6a} on the unsubstituted side of the ring. We, therefore, believe that the reduction in the value of J_{4a5a} is mainly caused by a direct substituent effect rather than by appreciable conformational changes.

The measured values of J_{4a5e} (J_{5e6a}), J_{4e5e} (J_{5e6e}), and J_{4e5a} (J_{5a6e}) in the 1,3,2-dioxarsenanes[1-4] cover the ranges 1.4 to 2.2 Hz, 2.1 to 3.0 Hz, and 3.1 to 4.1 Hz, respectively. It is seen that J_{4a5e} and J_{4e5e} are of similar magnitude whereas J_{4e5a} is considerably larger. Similar trends in the gauche coupling constants have also been observed in the analogous 1,3,2-dioxaphosphorinanes[17,18] and trimethylene sulfites,[20,21,24] that is, $J_{4e5a} > J_{4e5e} \sim J_{4a5e}$.

The relatively large value of J_{4e5a} is reasonable if anything like a Karplus[38] relationship holds for the coupled protons whereas J_{4e5e} and J_{4a5e} are too small. This observation can be rationalized on the basis of a stereospecific electronegativity effect of the oxygen heteroatoms. Empirically it has been found that the decrease in the vicinal coupling constant is greatest when the electronegative substituent is trans to one of the coupled protons.[39-41] Inspection of molecular models of the 1,3,2-dioxarsenane ring shows that the $O-C-C-H_{5e}$ segment is roughly trans-coplanar. The oxygen atoms should therefore have a maximum electronegativity effect on the vicinal coupling constants involving the H_{5e} proton, that is, J_{4e5e} and J_{4a5e}.

The $O-C-C-C$ torsional angles have been calculated from the vicinal coupling constants of the $CH_2CH_2CHR^1$ ($R^1 = H$, Me, or Ph) moiety according to the R-value method due to Lambert.[42]

The calculated torsional angles $(59-61°)$ indicate that the $O-C-C-C-O$ portion of the unsubstituted and 4-substituted 1,3,2-dioxarsenane ring assumes an almost staggered conformation. An essentially staggered ring conformation has also been observed for trimethylene sulfites[20,21] whereas the corresponding 1,3,2-dioxaphosphorinanes[17,18] have been reported to be less puckered by about $2-3°$.

The measured values of the long-range coupling constants J_{4a6a} and J_{4a6e} in the dioxarsenanes[1-4] and their phosphorus[17,18] and sulfur[20-24] analogues, are usually negative and less than about 0.6 Hz in magnitude. In contrast, the values of J_{4e6e} are positive and considerably larger ($\sim 1-2.5$ Hz) in the same series of compounds. This is reasonable since stereo models show that the $H_{4e}-C(4)-C(5)-C(6)-H_{6e}$ segment of these six-membered rings is roughly planar, and according to Barfield and Chakrabarti[43] four-bond coupling constants which are in the all-*trans* or W relationship, are positive and in the range $1-2$ Hz.

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