CONFIGURATION AND CONFORMATION OF SUBSTITUTED 1,3,2-DIOXAARSENANES*

Yu. Yu. Samitov, N. K. Tazeeva,
N. A. Chadaeva, and G. Kh. Kamai†

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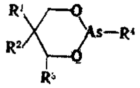
The configuration and conformations of ten 2-, 4-, and 5-substituted 1,3,2-dioxaarsenanes were studied from their PMR spectra. Inversion of the shielding constants of protons in the 4, 6, and 5 positions and of methyl groups in the 5 position was established, and the axial orientation of the As−Cl-and As−OR bonds, the equatorial orientation of the 4-CH_3 group, and the chair conformation of the six-membered heteroring were proved. The anisotropies of the diamagnetic susceptibility were estimated for the first time: $\Delta\chi_{As-O} = 4.67 \cdot 10^{-6}$ and $\Delta\chi_{As-Cl} = 5.13 \cdot 10^{-6}$ $cm^3 \cdot mole^{-1}$ (dipole approximation); $\Delta\chi_{As-O} = 0.9 \cdot 10^{-6}$ and $\Delta\chi_{As-Cl} = -6.8 \cdot 10^{-6}$ $cm^3 \cdot mole^{-1}$ (nondipole approximation). The cyclic torsion angle (ψ = 58°) was found for 2-chloro-1,3,2-dioxaarsenane by the "R-factor" method. Conclusions regarding the conformation of the ring and substituents were confirmed by a study of the specific effect of an aromatic solvent on the position of the resonance lines.

In recent years, in connection with the intensive investigation of the stereochemistry of heterocyclic systems, interest has appeared in the investigation of cyclic ethers that contain such polyvalent group-VI atoms as S [1-3] and Se [3, 4] and such group-V atoms as P [5, 6] in the ring. In these cases, the configuration [7-9] and conformational [10] labilities of the ring are determined by the stability of the pyramid of the bonds of these heteroatoms. For the purpose of expanding and extending stereochemical investigations also with respect to the arsenic atom, which, like phosphorus, belongs to the group-V elements, it seemed of definite interest to study heterorings containing an arsenic atom. The configuration and conformations of such heterorings have not been discussed in the literature. We synthesized a number of cyclic ethers of acids of trivalent arsenic that have not been investigated previously:



I-X

I $R^1=R^2=H$, $R^3=CH_3$, $R^4=Cl$; II $R^1=R^2=H$, $R^3=CH_3$, $R^4=OCH_3$; III $R^1=R^2=H$, $R^3=CH_3$, $R^4=OC_6H_5$; IV $R^1=R^2=H$, $R^3=CH_3$, $R^4=C_6H_5$; V $R^1=R^2=CH_3$, $R^3=H$, $R^4=Cl$; VI $R^1=R^2=CH_3$, $R^3=H$, $R^4=OCH_3$; VII $R^1=R^2=CH_3$, $R^3=H$, $R^4=OC_6H_5$; VIII $R^1=R^2=R^3=H$, $R^4=Cl$; IX $R^1=R^2=R^3=H$, $R^4=OCH_3$; X $R^1=R^2=R^3=H$, $R^4=OC_6H_5$.

The configuration and conformations of I-X were established by high-resolution PMR spectroscopy. The basis for these determinations was the Karplus−Conroy angular correlations [11-13] for vicinal spin-spin coupling constants (SSCC) with the assumption that for sp^3 hybridization of the carbon atoms in six-membered rings, the character of the angular correlations for the SSCC remains the same as in the case of the ethane fragment. Furthermore, by relying upon the information obtained regarding the relative chem-

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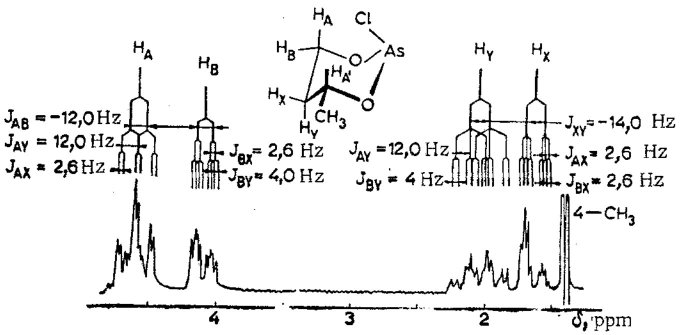

Fig. 1. PMR spectrum of 4-methyl-2-chloro-1,3,2-dioxaarsenane (I).

TABLE 1. Chemical Shifts of 1,3,2-Dioxaarsenanes[a]

Compound	5-H(*a*)	5-H(*e*)	4,6-H(*a*)	6-H(*e*)	4-CH_3(*e*)	$J_{66'}$, Hz	$J_{55'}$, Hz
I	2,03	1,61	4,6	4,08	1,21	−12,0	−14,0
II	1,89	1,40	4,47	3,79	1,11	−12,0	−14,0
III	2,01	c	4,75	4,00	1,23	—	—
IV	1,78		3,88		1,11	—	—
	5-CH_3 (*a*)	5-CH_3 (*e*)	4,6-H (*a*)		4,6-H (*e*)		
V	1,24	0,76	4,28		3,56	−12,0	—
VI	1,18	0,55	4,16		3,27	−12,0	—
VII	1,22	0,60	4,34		3,37	−12,0	—
	5-H (*a*)	5-H (*e*)	4,6-H (*a*)		4,6-H (*e*)		
VIII[b]	c	1,60	4,65		4,05	−12,0	−14,0
IX	2,27	1,42	4,56		c	−12,0	−14,0
X	2,38	1,47	4,66		3,9	−12,0	−14,0

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[a] The spectra were recorded with a Varian HA-100 D (100 MHz) spectrometer at room temperature. The data presented here pertain to 20% solutions (by volume) in CCl_4. The chemical shifts (δ, ppm) were measured relative to tetramethylsilane with an accuracy of ± 0.005 ppm. [b] The spectrum was obtained from a solution in $CDCl_3$. [c] It was impossible to determine the shifts because of overlapping by other signals.

ical shifts of geminal protons and gem-dimethyl groups for a definite preferred conformation, we made a quantitative analysis of the relative changes in the nuclear magnetic shielding constants (σ) of protons with the aim of evaluating the anisotropy of the magnetic susceptibility of the As−O and As−Cl bonds within dipole and nondipole approximations. The so-called "R-factor" method [14] was used for the quantitative evaluation of the degree of distortion of the ring of 1,3,2-dioxaarsenanes. We also discussed the value of the $^2J_{HH'}$ constants from the point of view of the conformations of the molecules [15]. In addition, we studied the effect of the aromatic solvent on the chemical shifts of the protons and methyl groups and discussed this effect on the basis of a "binary collision" model as applied to the conformations of the molecules.

Configuration and Conformations of Substituted 1,3,2-Dioxaarsenanes

4-Methyl-2-chloro-1,3,2-dioxaarsenane (I) (Fig. 1), which acts as a "key" object in the I-X series, has a quite complex but interpretable spectrum. One can make an unambiguous assignment of the spectral lines to the corresponding protons from the scheme of spin-spin splittings obtained by examination of only the z components of the proton spins (AA'BXY) and also from the chemical shifts (Table 1). It follows from this assignment that in this case there are "anomalous" chemical shifts (inversion or reversal of the nuclear magnetic shielding constants); i.e., the axial protons resonate at lower fields than the equatorial protons [4]. The literature data on dioxaphosphites [16], dioxasulfites and dioxaselenites [4] demonstrate the inversion of the nuclear magnetic shielding constants of axial and equatorial H_A and H_B protons in the 4 position and also of H_X and H_Y and methyl substituents in the 5 position of these compounds.

In I, resonance of proton $H_{A'}$ in the 4 position should appear as a complex multiplet of 24 lines with an average chemical shift of δ 4.65 ppm, almost coinciding with the position of the line of the H_A proton. In fact, the integral intensity of the band of the line at δ 4.6 ppm is 2H. The latter fact makes it possible to assume that the line of the $H_{A'}$ proton corresponds to the axial hydrogen, and, consequently, the 4-CH_3 group replaces the equatorial valence. The geminal constants ($J_{AB} = -12$ Hz, $J_{XY} = -14$ Hz) and vicinal constants ($J_{AY} = 12$ Hz, $J_{AX} = 2.6$ Hz, $J_{BX} = 2.6$ Hz, and $J_{BY} = 4$ Hz) found from the spectrum correlate with the corresponding valence (H–C–H') and dihedral angles with respect to the Karplus–Conroy formulas [11-13], indicating the preferred chair conformation of this ring. Inversion of the shielding constants (σ) of the proton in the 4 and 6 positions is possible for an axial orientation of the As–Cl bond and, consequently, it can be supposed that I is the trans isomer.

The PMR spectra of the remaining compounds of this series display the following general features:

a) marked nonequivalence of the axial and equatorial methylene protons in the 4 and 6 positions and marked nonequivalence of the gem-dimethyl group in the 5 position are observed;

b) there is inversion of the nuclear magnetic shielding constants of the protons in the 4 and 6 positions and of the protons and methyl groups in the 5 position;

c) the SSCC found from the spectra do not vary as a function of the substituents in the 4, 5, and 6 positions;

d) the protons of a 1,3,2-dioxaarsenane ring that is unsubstituted in the 4, 5, and 6 positions form a six-spin AA'BB'XY system, the analysis of which is possible within a first-order approximation.

A study of the temperature dependence (from –40 to +160°) did not reveal any changes in the chemical shifts and SSCC. This indicates that these compounds exist in the preferred chair conformation on the NMR time scale.

Recently [15] an iteration method was used to correlate the empirical data for the geminal SSCC in six-membered heterocycles, and these data were presented in analytical form as the dependence of $^2J_{HH}$ on the cyclic torsion angle ψ (the angle between the bisectors of the p and σ orbitals) in the cyclic compounds. According to this dependence, the geminal constants for an ideal chair conformation ($\psi = 60°$) have the following values: $J_{66'} = -10.4$ Hz, $J_{55'} = -13.5$ Hz; these values are in agreement with the geminal constants in 1,3,2-dioxaarsenanes: $J_{66'} = -12.0$ Hz, $J_{55'} = -14.0$ Hz. This confirms the chair conformation.

Evaluation of the Anisotropies of Diamagnetic Susceptibility $\Delta\chi_{As-Cl}$ and $\Delta\chi_{As-O}$.

At present, the literature does not contain data on the diamagnetic anisotropy of As–O and As–Cl bonds. This information can be extracted from the PMR spectra. The marked nonequivalence of the methylene protons in the 4 position ($\Delta\sigma = \sigma_A - \sigma_B = -0.72$ ppm) and of the methyl groups in the 5 position ($\Delta\sigma = -0.48$ ppm) that were observed in the PMR spectrum of V indicate the preferred chair conformation of its molecules with an axial As–Cl bond. The energies of the thermal vibrations are apparently insufficient to invert the conformation of the As–Cl bond. The difference in the shielding of the axial and equatorial protons and methyl groups is apparently due principally to the contribution to shielding of effects due to the diamagnetic anisotropy of the bonds and orbitals of the unshared pairs of electrons of the heteroatoms and to the electrical fields induced by the electrical dipole moments of the bonds [17]:

$$\Delta\sigma = \sigma(H_a) - \sigma(H_e) = \Sigma\Delta\sigma_k{}^{an} + \sum_j \Delta\sigma_j{}^{el}.$$

We made a theoretical evaluation of the contribution of the anisotropy of the magnetic susceptibility (AMS) of all of the bonds and oxygen atoms within the dipole approximation [18] and within the nondipole approximation [17], and the effect of the electrical field was estimated from the Buckingham–Masher formula [19]. Using the data in Table 2, the nonequivalence of the axial and equatorial protons in the 4 position, and the nonequivalence of the methyl groups in the 5 position, from the spectrum of V, allowing for the contributions of the AMS and the effect of the electrical fields of the bonds, we estimated the anisotropies of the diamagnetic susceptibility of the As–Cl and As–O bonds. Within the nondipole approximation, for an axial orientation of the As–Cl bond we obtain

$$\Delta\sigma(H) = 0.373\Delta\chi_{As-O} + 0.311\Delta\chi_{As-Cl} + 0.090\Delta\chi_{C-H}$$
$$+ 0.010\Delta\chi_{C-O} + 0.280\Delta\chi_{O:} - 0.007\Delta\chi_{C-C} - 0.195;$$
$$\Delta\sigma_2 = -0.004\Delta\chi_{As-O} + 0.011\Delta\chi_{As-Cl} - 0.170\Delta\chi_{C-H}$$
$$+ 0.090\Delta\chi_{C-O} - 0.390\Delta\chi_{O:} - 0.117.$$

TABLE 2. Electrical, Magnetic, and Geometrical Parameters of the 2-Chloro-1,3,2-dioxaarsenane Molecule Used to Estimate the Anisotropy of the Diamagnetic Susceptibility of the As−Cl and As−O Chemical Bonds

Bond	Bond length, Å	Dipole moments of the bonds, D	Anisotropies of the magnetic susceptibility, $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$, $cm^3 \cdot mole^{-1}$		Valence angles
			Dipole approximation [18]	Nondipole approximation [17]	
C—C	$1{,}54^{20}$	—	$4{,}89 \cdot 10^{-6\ 25}$	$1{,}54 \cdot 10^{-6\ 25}$	$\angle CCC = 112°^{20}$
C—O	$1{,}44^{20}$	0,86	$5{,}3 \cdot 10^{-6\ 4}$	$1{,}48 \cdot 10^{-6\ 25}$	$\angle CCO = 111°^{24}$
C—H	$1{,}10^{21}$	0,4	$0{,}9 \cdot 10^{-6\ 25}$	$0{,}9 \cdot 10^{-6\ 25}$	$\angle OAsO = 100°^{24}$
0 : (?p_z)	—	—	$8{,}1 \cdot 10^{-6\ 25}$	$3{,}6 \cdot 10^{-6\ 25}$	$\angle COAs = 118°^{24}$
As—Cl	$2{,}26^{22}$	1,3	$-5{,}13 \cdot 10^{-6}$	$-6{,}8 \cdot 10^{-6}$	$\angle AsOCH_3 = 118°$
As—O	$1{,}75^{23}$	0,82	$4{,}6 \cdot 10^{-6}$	$0{,}9 \cdot 10^{-6}$	$\angle OAsCl = 98{,}5°$
					$\angle AsOC_6H_5 = 120°$

Setting $\Delta\chi_{C-C} = 1.34 \cdot 10^{-6}$, $\Delta\chi_{C-O} = 1.48 \cdot 10^{-6}$, $\Delta\chi_{C-H} = 0.9 \cdot 10^{-6}$, and $\Delta\chi_{O} = 3.9 \cdot 10^{-6}\ cm^3 \cdot mole^{-1}$ and solving this system of equations, we obtain $\Delta\chi_{As-O} = 0.9 \cdot 10^{-6}$ and $\Delta\chi_{As-Cl} = -6.8 \cdot 10^{-6}\ cm^3 \cdot mole^{-1}$. Within the dipole approximation, for an axial orientation of the As−Cl bond we obtain $\Delta\chi_{As-O} = 4.67 \cdot 10^{-6}$ and $\Delta\chi_{As-Cl} = 5.13 \cdot 10^{-6}\ cm^3 \cdot mole^{-1}$. Thus, in the nondipole approximation, for an axial orientation of the As−Cl bond and the chair conformation we obtain real $\Delta\chi_{As-O}$ and $\Delta\chi_{As-Cl}$ values with respect to numerical value and sign under the assumption that the axial proton is less shielded than the equatorial proton, and that the axial methyl group is less shielded than the equatorial methyl group; this is proved in the case of the spectrum of III.

As was recently shown in [3, 4], the inversion of the proton shielding constants of hydrogen atoms and methyl groups in the 5 position in cyclic ethers is due principally to the anisotropy of the diamagnetic susceptibility of the unshared electron pairs $[(2p_z^2)_{eff}]$ of the oxygen atoms if their molecules reside in the preferred chair conformation. There is no basis in the case of 1,3,2-dioxaarsenanes to attribute the fact of inversion of the chemical shifts of H_X and H_Y to other causes. In the indicated case, the electrical field arising from the dipole moment associated with the unshared pair of electrons can be disregarded at distances greater than 2 Å [26]. However, in the case of inversion of the shielding constants in the 4(6) position, this effect is additional to the effect arising from the anisotropy of the magnetic susceptibility of the As−O and As−Cl bonds. Since the present study leads to the conclusion of the axial conformation of the As−Cl bond, stabilization of such a conformation may be argued from the presence, as in the case of cyclic sulfites [27], of a certain "bonding" chemical interaction between the chlorine and axial H_A and $H_{A'}$ hydrogen atoms that is realized for an axial conformation of the As−Cl bond.

The "R-Factor" as a Criterion of Distortions of the Chair Ring Conformation

For six-membered rings that have a $-CH_2-CH_2-$ fragment, regardless of whether they exist as an equilibrium mixture of two equivalent conformers or have a preferred chair conformation, the "R-factor" method [14, 28] makes it possible to find the cyclic torsion angles (ψ) from the vicinal SSCC:

$$\cos\psi = \left(\frac{3}{2+4R}\right)^{1/2},$$

$$R = J_{\text{trans}} J_{\text{cis}},\ J_{\text{trans}} = \frac{1}{2}(J_{aa'} + J_{ee'}),\ J_{\text{cis}} = \frac{1}{2}(J_{ae} + J_{ea}). \tag{1}$$

Expression (1) was obtained from the correlation conditions for vicinal SSCC [12]. For 2-chloro-1,3,-2-dioxaarsenane (VIII) we have R = 2.21; this corresponds to a larger cyclic torsion angle in the $-CH_2-CH_2-$ fragment (ψ = 58°) than for 1,3-dioxane [29] (R = 1.81 and ψ = 55°). This increase means that the conformation of the ring of VIII approaches that of an "ideal" chair, in view of which the unfavorable steric 1,3-interactions typical for cyclohexane, 1,3-dioxane, and 1,3-dithiane have small values in the chair conformation with an axial As−Cl bond. It has been previously established [30] that in phosphites the energy of the steric C... Cl interaction, found on the basis of a series of studies [31-33], is negligibly small and, moreover, has a positive sign. Consequently, steric interaction cannot hinder the axial orientation of the As−Cl bond. The axial character of the trivalent phosphorus substituent in 1,3,2-dioxaphosphorinanes was also recently [34] proved persuasively by an analysis of the PMR spectra.

Specific Effect of an Aromatic Solvent

For an additional confirmation of conclusions regarding the conformation of I-X, we examined the changes in the chemical shifts of the protons on passing from CCl_4 solutions to solutions in benzene. The

TABLE 3. Differences in Shifts ($\Delta\delta_{C_6H_5}^{CCl_4}$ in ppm)[a]

Compound	5-H(*a*)	5-H(*e*)	4,6-H(*a*)	$4-CH_3$(*e*)	6-H(*e*)
I	+0,44	b	+0,25	+0,27	+0,34
II	+0,10	+0,16	+0,02	+0,05	+0,05
III	+0,03	b	+0,12	+0,13	+0,19
	$5-CH_3$ (*a*)	$5-CH_3$ (*c*)	4,6-H (*a*)	4,6-H (*e*)	
V	+0,23	+0,53	+0,09	+0,24	
VI	−0,03	+0,02	−0,04	−0,01	
VII	+0,06	+0,28	0	+0,02	
VIII	5-H (*a*)	5-H (*c*)	4,6-H (*a*)	4,6-H (*e*)	
VIII	b	+0,78	+0,29	+0,49	
IX	+0,04	+0,21	+0,06	b	
X	+0,33	+0,43	+0,14	+0,20	

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[a] The data presented in this table pertain to 20% (by volume) solutions in CCl_4 and in C_6H_6. [b] These shifts were impossible to determine because of overlap by other signals.

results show that the effect of an aromatic solvent depends unambiguously on the steric position of the proton or methyl group in the molecule. The data are presented in Table 3, from which one can draw the following conclusions:

a) benzene as a solvent shifts the position of the resonance of the protons to strong field to a greater or lesser degree depending on the spatial position of the proton under consideration;

b) in all of the compounds, equatorial substituents in the 4, 6, and 5 positions are more strongly shielded than axial substituents, and equatorial substituents in the 5 position are shielded to a greater degree. This regularity may serve as an additional argument in favor of the equatorial orientation of the $4-CH_3$ group in I-IV;

c) the axial 4,6-H and equatorial 4,6-H in I, II, IV, and X are shielded almost identically. However, in the case of molecules with a gem-dimethyl group in the 5 position, these same protons are much more weakly shielded and are deshielded when $R^4 = OCH_3$. When there is a gem-dimethyl group, the benzene molecule apparently cannot approach the dissolved molecule as closely as in other cases;

d) the maximum shielding of the protons is observed when R^4 = Cl, and great nonequivalence in the shielding of the protons and methyl groups arises; the degree of shielding decreases from $R^4 = OC_6H_5$ to $R^4 = OCH_3$.

The observed shifts, which are caused by the aromatic solvent, can be explained under the assumption that molecular collision complexes [35] of approximately the same structure in all cases arise in the investigated systems. The factor that determines the geometry of the complex is the attraction between the electrophilic positive end of the local dipole of dissolved substance and the nucleophilic π-electron system of the benzene ring. The strong mutual repulsion between this electrophilic system and the negative end of the dipole of the dissolved substance gives the time-averaged geometry of the complex. It has been assumed [36] that the unshared pairs of electrons of the heteroatoms entering into the molecule may also affect the orientation of the benzene molecules. Thus the effect of the aromatic solvent confirms the existence of 1,3,2-dioxaarsenanes in the preferred chair conformation.

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