DIPOLE MOMENTS AND CONFORMATIONS

OF CERTAIN ARSENIC-CONTAINING

HETEROCYCLES

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The question of the orientation of the exocyclic substituent at the As atom in 1,3,2-dioxaarsenanes as a function of the nature of the substituent has practically not been studied. Detailed investigations by various physical methods (PMR, dipole moments, Kerr effect, IR spectra) have been conducted only for 2-chloro-1,3,2-dioxaarsenanes [1-4]. The data of most of the methods [2, 3] lead to the conclusion that chlorine has an axial orientation at the arsenic atom. The present communication is devoted to an investigation of the position of the phenyl and phenoxyl substituents at the trivalent arsenic atom in 1,3,2-dioxaarsenanes by the method of dipole moments (DM).

Like the O_2AsCl group [3], in the O_2AsPh of 1,3,2-dioxaarsenanes we might expect a mutual influence of the substituents at the arsenic atom and, consequently, an inequality of the moments of the As-O and As-Ph bonds to the moments of these bonds in the symmetrical compounds. To find the unknown moments of the bonds and positions of the phenyl in the O_2AsPh group we used the approach first proposed in [5], which we used for 2-chloro-1,3,2-dioxaarsenanes in [3]. As model compounds we selected 2-phenyl-5,5-dimethyl-1.3,2-dioxaarsenane (I) and the spiran compound corresponding to it - 3,9-diphenyl-2,4,8,10-tetraoxa-3,9diarsaspiro[5,5]undecane (II). The experimental values of the DM are cited in the experimental section. In the calculation of the DM we used the same valence angles and bond lengths as in six-membered cyclic chlorides of arsenous acid [3], with the exception of the angles OAsPh 104° [6] and COAs 120°, analogous to the oxygen angle in the phosphorinane ring [7].

The compilation and solution of equations based on the DM obtained and the assumptions used were analogous to those described for 2-chloro-1,3,2-dioxaarsenanes [3]. Only the graphical solution of the system of equations was different (Fig. 1): For each orientation of the phenyl there are two and not four solutions (points of tangency of the straight lines with the ellipses), the numerical values of which are cited in Table 1. The selection from these solutions was performed by comparison with the experimental DM of 2-p-nitrophenyl-1,3,2-dioxaarsenane (III). The moment of the latter was calculated with each of the four solutions both for axial and for equatorial orientations of the nitrophenyl substituent (Table 2). The moment of the nitrophenyl radical 3.27 D was calculated from the DM of nitrobenzene [8]. Of all the calculated moments, the closest to the experimental DM of (III) proved to be the moment 3.03 D, obtained on the basis of the first solution for an axial position of the nitrophenyl substituent at As. The conclusion of an axial orientation of the 2-phenyl-1,3,2-dioxaarsenane (IV) and to 2-phenyl-4-methyl-1,3,2-dioxaarsenane (V), since their experimental DM are close to the experimental moment of (D).

From the data for symmetrical 4-methyl-1-arsa-2,6,7-trioxabicyclo[2,2,2]octane, the moment of the As-O bond is equal to 0.82 [1] and 0.50 D [9] (the latter value is evidently the most reliable); the moment of the As-Ph bond, -0.81 D, was calculated from the DM of triphenylarsine [8]. (The direction of the moment of the latter bond toward As follows from a comparison of the experimental DM of triphenylarsine and three p-tolylarsines.) A comparison of these DM with the moments of the As-O and As-Ph bonds that

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Fig. 1. Graphical solution of the systems of equations compiled on the basis of the DM of (I) and (II).

Fig. 2. Graphical treatment according to the method of [10] of the DM data for (VI) and (IX); 1) experimental point.

TABLE 1. Solutions of the System of Equations Compiled on the Basis of the Known DM of (I) and (II)

Solution	m(As - 0), D	m(As — Ph), D	
1	0,46	-0.94	
2	3,30	3,52	
3	1,00	0,93	
4	1,40	-3,44	

TABLE 2. Selection of the Solution and Orientation of the Phenyl according to the Data of the DM for (III)

Use of	DM_{calc} (D), with an orienta- tion of the p-NO ₂ C ₆ H ₄ group				
solution	a	e			
1 2 3 4	3,03 5,80 3,91 0,78	4,72 8,12 2,32 1,70			
Experiment	3.17 D (CeHe), 3.21 D (CCl4)				

we obtained above shows that they are close, and, consequently, the mutual influence of the atoms in the O_2AsPh group is manifested to a substantially lesser degree than in the O_2AsCl group [3].

If the substituent at As is a phenoxy group, then in addition to its orientation in the heterocycle we must also consider rotation around the exocyclic As - O bond. The DM of 2-phenoxy- (VI), 2-phenoxy-4-methyl- (VII), 2-phenoxy-5,5-dimethyl- (VIII), and 2-p-nitrophenoxy-1,3,2-dioxaarsenanes (IX) were studied.

For each orientation of the substituent at As (*a* or e), four different conformations, obtained by rotation of the irregular substituent around the As-O bond, were considered. Let us call the conformation in which the O-Ph bond shields the unshared electron pair of As the cis (c) conformation, and let us denote the other shielded conformation as c'; the gauche (g) and trans (t) conformations are obtained from the first by rotation of the O-Ph bond by 60 and 180°, respectively. Calculation of the DM was performed for the chair form [2] with moments of the bonds As-O 0.50 D [9], Ph-O 1.26 D from the DM of diphenylether, and moment of the O-PhNO₂-p group 4.11 D from the DM of p-nitroanisole.

The interpretation of the DM data was performed by a graphical treatment of them according to the method proposed in [10]

(Fig. 2). The experimental point lies on a straight line corresponding to an axial orientation of the substituent at As and corresponds to rotation of the irregular substituent around the As - O bond through 30° from the cis conformation c. Such an intermediate orientation of the substituent between the cis and gauche conformations in As compounds is in full agreement with the typical picture observed in a study of the rotation of various irregular groups around the P-O bond in cyclic and acyclic phosphorus compounds [11]. The closeness of the experimental DM of (VII) and (VIII) to the DM found for (VI) indicates identity of their steric structures.

Moments Determined								
Com- pound	Solvent	<u>عد</u> سد	$\frac{\Delta n^2}{\Delta \omega}$	Por	DMexp, D			
(I) (II) (III) (III) (IV) (V) (VI)	$C_{6}H_{12}$ $C_{6}H_{6}$ CCl_{4} $C_{6}H_{6}$ Ccl_{4} $C_{6}H_{12}$ $C_{6}H_{12}$ $C_{6}H_{12}$	$\begin{array}{c} 2,032\\ 14.645*\\ 13.193*\\ 3,741*\\ 7,901\\ 2,297\\ 2,438\\ 1.153\end{array}$	0,202 	106,99 	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			
(\widetilde{VII}) (VIII) (X) (X)	C6H12 C6H12 CCl1	1.218 0.895 17.547	0,129 0,181 0,415	66,729 46,119 519,242	1,32 [1] 1,81 [1] 1,50 [1] 5.04			

TABLE 3. Coefficients of the Calculation Equations and Dipole Moments Determined

*Δε/Δf.

† Determined according to [15].

EXPERIMENTAL METHOD

The compound (II) was produced according to the method of [12]. The arsenanes (I), (III), (IV), and (V) were obtained from the corresponding 1,3-glycols and dialkyl esters of phenylarsonous acid.

<u>2-Phenyl-1,3,2-dioxaarsenane (IV) [13].</u> A mixture of 23.0 g of the dimethyl ester of phenylarsonous acid and 8.2 g trimethylene glycol was heated in an Arbuzov flask for 30 min at normal pressure; methanol was distilled off. The residue was redistilled under vacuum. After two supplementary redistillations from a flask with a reflux condenser, we obtained (IV); yield 91.8%, bp 129-130° (9 mm); n_D^{20} 1.5862; d_4^{20} 1.4545. Found: As 32.97%. C₉H₁₁O₂As. Calculated: As 33.13%. Compounds (I), (III), and (V) were produced analogously to (IV). Yield of (I) 84.6%, bp 134-134.5° (9 mm); n_D^{20} 1.5592; d_4^{20} 1.3319. Found: As 29.37%. C₁₁H₁₅O₂As. Calculated: As 29.47%. Yield of (III) 89.5%, bp 138° (0.3 mm), mp 78-80°. Found: As 27.42%. C₃H₁₀O₄NAs. Calculated: As 27.67%. Yield of (V) 75.5%, bp 127.5-128° (9.5 mm); n_D^{20} 1.5620; d_4^{20} 1.3613. Found: As 31.35%. C₁₀H₁₃O₅As. Calculated: As 31.19%.

The arsenanes (VI)-(IX) were produced by the interaction of the corresponding cyclic chloroarsenites [14] and phenols in the presence of triethylamine in abs. benzene or ether medium.

<u>2-Phenoxy-1,3,2-dioxaarsenane (VI)</u>. To a mixture of 7.0 g freshly redistilled phenol and 7.5 g triethylamine in 350 ml abs. benzene, a solution of 13.6 g 2-chloro-1,3,2-dioxaarsenane in 30 ml of benzene was added dropwise with mixing, then the mixture was heated for 1 h at the boiling point of benzene. After removal of the precipitate of triethylamine hydrochloride, the solvent was evaporated under vacuum and the residue redistilled. Yield of (VI) 73.4%, bp 89-90° (0.3 mm); n_D^{20} 1.5642; d_4^{20} 1.4823. Found: As 31.15%. $C_9H_{11}O_3As$. Calculated: As 30.94%.

The compounds (VII)-(IX) were produced analogously to (VI). Yield of (VII) 71%, bp 88-89° (0.3 mm); $n_D^{20} 1.5409$; $d_4^{20} 1.3552$. Found: As 27.68%. $C_{11}H_{15}O_3As$. Calculated: As 27.73%. Yield of (VIII) 71%, bp 109-110° (2 mm); $n_D^{20} 1.5472$; $d_4^{20} 1.4004$. Found: As 28.98%. $C_{10}H_{13}O_3As$. Calculated: As 29.25%. Yield of (IX) 60%, bp 160-162° (1 mm), mp 36-38°. Found: As 25.95%. $C_9H_{10}O_5NAs$. Calculated: As 26.09%.

The dipole moments were determined at 25°. The coefficients of the calculation equations and the results are cited in Table 3.

CONCLUSIONS

An axial orientation of aryl and aryloxy substituents at the arsenic atom in 1,3,2-dioxaarsenanes was established by the method of dipole moments.

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