THE DIPOLE MOMENTS OF METHYLHALOARSINES

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INTRODUCTION

The changes in the bond strength of As–C and As–X bonds in $As(CH_3)_3$ and in $(CH_3)_n AsX_{3-n}$ (X = Cl, Br, I) with progressive halogenation have been tentatively interpreted by means of the data of their Raman spectra and the changes in the bond distances[1,2].

Pauling[3] has discussed the changes in the bonding characteristics of silicon tetrachloride and the chlorosilanes in terms of resonance structure contributions. Some of these structures introduce the conception of a certain amount of double bond character in the metal–halogen bonds. It is the purpose of this series of reports to investigate this problem in the group of arsenic compounds mentioned above, by means of the information gained from physico-chemical data such as: the electrical dipole moment, the PMR spectra, the force constants derived from the vibrational spectra and mass spectrometry. Moreover the series will be completed by the synthesis and the study of the fluorides as well. The fact that in these arsenic compounds an unshared electron pair is available on the central atom also confers a special interest on this study.

In the first part there will be reported on the synthesis of some of these compounds, the measurement of their electrical dipole moment in diluted solution and in the gas phase and on the calculation of the bond moments.

EXPERIMENTAL

I. The synthesis of the products

Several methods have been[4,5,6,7] published for the synthesis of trimethylarsine, dimethylchloroarsine, dimethylbromoarsine, methyldichloroarsine, methyldibromoarsine and methyldifluoroarsine. Therefore we will only discuss the synthesis of compounds for which either a new or a modified and improved method was developed.

1. Methyldiiodoarsine. This compound can be obtained by a method similar to that used for the corresponding chloro and bromo compound:

$$CH_3AsO(OH)_2 + SO_2 + 2 HI \longrightarrow CH_3AsI_2 \downarrow + H_2SO_4 + H_2O$$
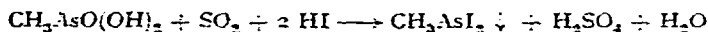
Sodium methanearsonate (1 mole) and potassium iodide (2 moles) are dissolved together in 350 ml of water and then 85 ml of concentrated hydrochloric acid solution is added. This solution is now poured into a large separatory funnel and a gentle stream of sulfur dioxide is forced through for several hours. The brown colour of free iodine

first disappears and soon after that a yellow white turbidity is developed, which results in an abundant precipitate. The temperature rises by the reaction and the precipitate soon melts to yield a yellow oil that is collected at the bottom of the funnel and can easily be separated. Towards the end of the reduction another 85 ml of hydrochloric acid solution is added to precipitate all the CH_3AsI_2. The collected product is allowed to solidify, separated on a sintered glass filter and then dried over P_2O_5. The solid product is now extracted with dry ethyl ether until a colourless extract is obtained. A dark yellow amorphous solid remains. The combined extracts are now evaporated until CH_3AsI_2 starts to separate from the solution. Then the solution is cooled to $-15°$ and a crop of needle-like crystals is collected. These can be readily sublimed *in vacuo*. The yield of this synthesis was 60%; m.p. of CH_3AsI_2: $30°$.

2. Dimethylfluoroarsine. The synthesis of this product has not been reported previously in the literature. Any attempt to make this compound by exchange fluorination of $(CH_3)_2AsCl$ with NH_4F, such as is done for CH_3AsF_2, failed to yield the fluoride. Also the reduction of $(CH_3)_2AsO(ONa)\cdot 3H_2O$ with either H_3PO_2 or SO_2 in hydrofluoric acid solution did not yield $(CH_3)_2AsF$. Finally the product could be obtained by the substitution method, but using anhydrous antimony fluoride as a fluorination catalyst:

$$(CH_3)_2AsCl + NH_4F \xrightarrow[85°]{SbF_3} (CH_3)_2AsF + NH_4Cl$$
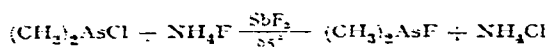
Dry crystalline ammonium fluoride (1.5 mole) and dry antimony trifluoride (0.15 mole) are mixed with dimethylchloroarsine (1 mole) in a round-bottomed flask, equipped with a vigreux column. The reactants are gradually heated up to $85°$; meanwhile a stream of dry and oxygen-free nitrogen is passed through the apparatus. The substitution reaction proceeds slowly and the $(CH_3)_2AsF$ is distilled out over a temperature range from 71 to $74°$. A carefully observation of the reaction temperature is necessary to prevent the chloroarsine of being carried over with the product. The distillate is then fractionated twice in dry nitrogen atmosphere and at each destillation a small amount of NH_4F and SbF_3 is added. Finally a pure product is obtained (b.p. $71.5-72°$) in a 40% yield.

3. Trimethylarsine. Trimethylarsine has been synthesized by the well-known Grignard procedure, but instead of diethyl ether the di-*n*-butyl ether was used. This allows the direct separation of the arsine from the reactants solution and as the reaction temperature can be increased the yield is also improved.

In a three-necked, round-bottomed reaction flask, equipped with a reflux condenser, a stirrer, a thermometer and a separatory funnel, are placed 24.3 grams of magnesium turnings and 150 ml of dry di-*n*-butyl ether. The contents are heated to $50°$ and a portion of about 3 ml of a solution of 142 g of methyl iodide in dry di-*n*-butyl ether is added. When the reaction is started the methyl iodide solution is added at such a rate as to keep the temperature below $45°$. Cooling with an ice slush is necessary. When all the iodide has been added the cooling bath is removed and the reaction mixture is heated until all the magnesium has reacted. The flash is then cooled again with ice and 60.5 grams of arsenic trichloride, dissolved in 150 ml di-*n*-butyl ether, are added dropwise. A dry and oxygen-free nitrogen atmosphere is now maintained. The reaction takes about 2 h to completion and the stirring is continued for another hour. The trimethylarsine can now be separated from the reaction mixture by simple destil-

lation. Two subsequent fractionations under nitrogen atmosphere yield the pure product (70 % yield) which has a boiling point of 52°. The purity of the product was controlled by mass spectrometry, gas chromatography and by the PMR spectrum.

II. The determination of the electrical dipole moments

1. Dipole moments of the arsines in diluted solutions. The methods and the apparatus used for these measurements are the same as these used previously[8,9]. All the solutions were made with the middle fractions of the products obtained by slow destillation under dry and oxygen-free nitrogen atmosphere. Dry benzene Merck p.a. was used as a solvent. The results of these measurements (μ_C) are collected in column 2 of Table 1.

TABLE 1

DIPOLE MOMENTS IN DILUTED SOLUTIONS

μ_C: classical calculation; μ_H: calculation according to the Higasi formula.

Compounds	μ_C (in D)	μ_H (in D)	Solvent Temperature	Ref.
As(CH₃)₃		1.10	C_6H_6 25°	
(CH₃)₂AsF	2.37	2.34	C_6H_6 25°	
CH₃AsF₂	2.88	2.85	C_6H_6 25°	
AsF₃	2.65		C_6H_6 25°	12
(CH₃)₂AsCl	2.68	2.68	C_6H_6 25°	
CH₃AsCl₂	2.80	2.83	C_6H_6 25°	
AsCl₃	2.19		C_6H_6 25°	
AsCl₃	2.17		C_6H_6 25°	13
(CH₃)₂AsBr	2.71	2.75	C_6H_6 25°	
CH₃AsBr₂	2.66	2.74	C_6H_6 25°	
AsBr₃	1.66		CCl_4 18°	12
(CH₃)₂AsI	2.54	2.60	C_6H_6 25°	
CH₃AsI₂	2.30	2.46	C_6H_6 25°	
AsI₃	0.96		CS_2 25°	12

As solutions of trimethylarsine are very easily oxidized by air, reliable measurements of the refractive index and of the density could not be made. For this compound we therefore had to use the simplified method of Higasi[9,10,11] for the determination of the dipole moment from dielectric constant measurements only. In order to ascertain that the result (μ_H) obtained for the trimethylarsine by this method can be directly compared with the data gained from the classical procedure, we calculated the μ_H values for all the compounds and listed them in column 3 of Table 1. The agreement is very good and thus the result for As(CH₃)₃ is reliable.

2. Dipole moments of the arsines in the gas phase. For (CH₃)₃As, (CH₃)₂AsCl, CH₃AsCl₂ and AsCl₃ the electrical dipole moment was also calculated from the data of the dielectric constant measured on gaseous samples and from the molecular refraction (R_M) that was determined from the appropriate atomic refractions.

The electrical dipole moments of these polar gases were calculated according to the general formula

$$\mu = 0.01281 \left[\left(\frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{d} - R_M \right) T \right]^{\frac{1}{2}}$$

where ε is the dielectric constant of the gas, measured at a well-defined pressure p and temperature T. By means of the ideal gas low the density d is obtained; M is the molecular weight.

As the substances under investigation are not permanent gases, a special apparatus was developed to allow measurements on unsaturated vapours at temperatures from 25° to 100° and at well known pressures p. The dielcometer used in these experiments was the Dipolmeter DM 01 of WTW (Germany); a gas cell of special design was, however, used. The technical details of this cell and the measuring techniques used are reported elsewhere[14]. The results are tabulated in Table 2.

TABLE 2

DIPOLE MOMENTS IN THE GAS PHASE

Compounds	μ (in D)	Temp.	Ref.
As(CH₃)₃	1.10	40°	
(CH₃)₂AsCl	3.06	90°	
CH₃AsCl₂	2.80	90°	
AsCl₃	1.96	90°	
AsF₃	2.81		15
AsCl₃	2.10		15
AsBr₃	1.70		15
AsI₃	0.96		15

DISCUSSION OF RESULTS AND CALCULATIONS OF BOND MOMENTS

A comparison of the data of Table 1 with the corresponding data of Table 2 shows that the dipole moments in solution are in close agreement with those obtained on gaseous samples at low pressure. Therefore any extensive association of the solutes in benzene solution, as an explanation of the rather high values of these moments, can be ruled out.

1. The bond moments in pyramidal molecules of the XY_3 type

For a regular trigonal pyramidal molecule XY_3, wherein the angle YXY is known (Fig. 1) the partial moment $\overrightarrow{X-Y}$ can be calculated from the experimental
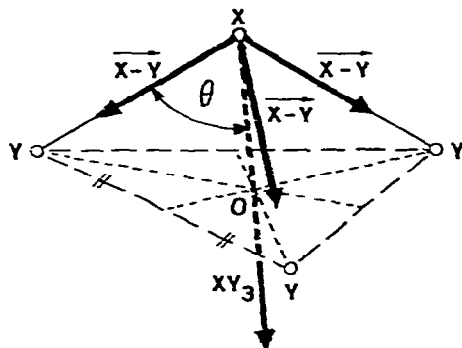

Fig. 1. Geometrical model for calculating bond moments from the molecule moment.

value of the molecule moment $\overrightarrow{XY_3}$ as a function of the angle θ (Fig. 1) by means of the simple equation:

$$(\overrightarrow{X-Y})\cos\theta = \frac{\overrightarrow{XY_3}}{3}$$

In Table 3 we have presented for several pyramidal XY_3 molecules the values of the angle YXY, the corresponding value of θ, the electrical dipole moment as measured on a gaseous sample and the value for the bond moment $\overrightarrow{X-Y}$ derived therefrom with the preceding equation.

TABLE 3

BOND MOMENTS DERIVED FROM MOLECULE MOMENTS

XY_3	AsF_3	$AsCl_3$	$AsBr_3$	AsI_3	$As(CH_3)_3$
$\angle$ YXY	102 ± 2 [16]	$98°24' \pm 0.5$ [17]	100 ± 2 [18]	100 ± 2 [18]	96 ± 5 [19]
	$63°49'$	$60°56'$	$62°12'$	$62°12'$	$59°06'$
$\overrightarrow{XY_3}$	2.81 D	2.10 D	1.70 D	0.96 D	1.10 D
$\overrightarrow{X-Y}$	2.12 D	1.44 D	1.21 D	0.69 D	0.71 D

The direction of the electrical moment vectors follows from the relative electronegativity differences of the atoms considered, using the normal Pauling electronegativities[3]: As (2.0), F (4.0), Cl (3.0), Br (2.8), I (2.5) and C (2.5). This yields the following series: $\overrightarrow{As-F}$, $\overrightarrow{As-Cl}$, $\overrightarrow{As-Br}$, $\overrightarrow{As-I}$ and $\overrightarrow{As-C}$. The direction of the total $\overrightarrow{As-CH_3}$ moment is derived simply by taking into account the following three data: $\overrightarrow{CH_3} = 0.42$ [21], $\overrightarrow{As-C} > 0$ and $\overrightarrow{As-CH_3} = 0.71$. So it is evident that this moment must be regarded as $\overrightarrow{As-CH_3} = 0.71$ D.
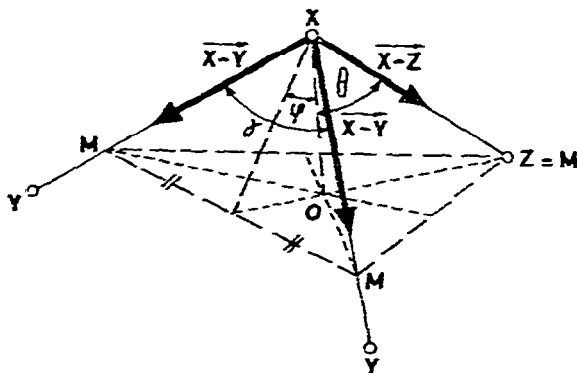

Fig. 2. Geometrical model for calculating bond moments from the molecule moment.

II. The bond moments in pyramidal molecules of the type ZXY_2

The arsenic compounds of this kind have a sterical configuration that can be described as a symmetrical trigonal pyramid ZXY_2. The angles YXZ and YXY are known; the lengths of the edges XZ and XY are unequal (Fig. 2). From the collection, however, of molecular parameters, gained by X-ray diffraction and presented in Table 4, it can be seen that the YXZ angle is nearly equal to the YXY angle; on the other hand, we have found that small deviations from these angle values are of minor influence on the calculated moments and result in deviations which are within the experimental error limits. Therefore the ZXY_2 molecules can more easily be treated as regular trigonal pyramids with $\gamma = \angle \text{YXZ} = \angle \text{YXY}$.

TABLE 4

MOLECULAR PARAMETERS OF THE ZXY_2 PYRAMIDAL MOLECULES

ZXY_2	CH_3AsF_2	$(CH_3)_2AsF$	CH_3AsCl_2	$(CH_3)_2AsCl$	CH_3AsBr_2	$(CH_3)_2AsBr$	CH_3AsI_2	$(CH_3)_2AsI$
$\angle$ ZXY			98°	98 ± 3°²⁰	96°	96 ± 3°²⁰	98°	98 ± 4°²⁰
$\angle$ YXY			98°24′	96°	100°	96°	100°	96°
γ	98°	98°	98°	98°	98°	98°	98°	98°
$\varphi + \theta$	102°15′	102°15′	102°15′	102°15′	102°15′	102°15′	102°15′	102°15′

The molecular electrical moment can be expressed as a function of the angles γ and $(\varphi + \theta)$ and of the bond moments $\overrightarrow{\text{X-Y}}$ and $\overrightarrow{\text{X-Z}}$ by equation:

$$(\overrightarrow{ZXY_2})^2 = \left[2(\overrightarrow{\text{X-Y}})\cos\tfrac{1}{2}\gamma\right]^2 + (\overrightarrow{\text{X-Z}})^2 - 4(\overrightarrow{\text{X-Y}})(\overrightarrow{\text{X-Z}})\cos\tfrac{1}{2}\gamma\cos[180° - (\varphi + \theta)]$$

By assuming a reasonable value for one of the bond moments, the other can thus be calculated. If we assume that the $\overrightarrow{\text{As-CH}_3}$ moment remains nearly constant on progressive substitution of methyl groups by halogen atoms in the $As(CH_3)_3$ molecule, the arsenic–halogen bond moment in each molecule can be derived from the respective experimental moments. The data obtained in this way are presented in Table 5. It is evident that this bond moment increases with decreasing number of halogen atoms bonded to arsenic. The relative changes are rather weak for fluorides and become stronger for chlorides, bromides and iodides in this order.

ACKNOWLEDGEMENTS

SUMMARY

To explain the molecular parameters of silicon tetrachloride and related compounds, Pauling suggested resonance structure contributions.
Information on analogous bonding characteristics in $(CH_3)_nAsX_{3-n}$ (X = F,

TABLE 5

MOLECULE AND BOND MOMENTS IN D

	AsF_3	CH_3AsF_2	$(CH_3)_2AsF$	$(CH_3)_3As$
μ	2.81	2.88	2.37	1.10
$\overrightarrow{As-CH_3}$		0.71	0.71	0.71
$\overrightarrow{As-F}$	2.12	2.25	2.39	

	$AsCl_3$	CH_3AsCl_2	$(CH_3)_2AsCl$	$(CH_3)_3As$
μ	2.10	2.80	2.68	1.10
$\overrightarrow{As-CH_3}$		0.71	0.71	0.71
$\overrightarrow{As-Cl}$	1.44	2.18	2.72	

	$AsBr_3$	CH_3AsBr_2	$(CH_3)_2AsBr$	$(CH_3)_3As$
μ	1.70	2.66	2.71	1.10
$\overrightarrow{As-CH_3}$		0.71	0.71	0.71
$\overrightarrow{As-Br}$	1.21	2.07	2.75	

	AsI_3	CH_3AsI_2	$(CH_3)_2AsI$	$(CH_3)_3As$
μ	0.96	2.30	2.54	1.10
$\overrightarrow{As-CH_3}$		0.71	0.71	0.71
$\overrightarrow{As-I}$	0.69	1.78	2.57	

Cl, Br, I) can be gained from electrical dipole moments, PMR spectra, force constants and mass spectrometry.

This paper deals with the measurement of the electrical dipole moments in diluted solution and in the gas phase, and the calculation of bond moments for these compounds.

Moreover some improvements are reported in the synthesis of methyldiiodo-arsine, dimethylfluoroarsine and trimethylarsine.

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