

NUCLEAR MAGNETIC RESONANCE STUDY OF THE MOLECULAR STRUCTURE OF 4-METHYLARSABENZENE AND 4-METHYLSTIBABENZENE PARTIALLY ORIENTED IN A NEMATIC SOLVENT

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ABSTRACT

The molecular structure of 4-methylarsabenzene (I) and 4-methylstibabenzene (II) partially oriented in a nematic solvent is studied by NMR. Good agreement between the ring proton structure of I and that of arsabenzene from electron diffraction and microwave spectroscopy is obtained. For II, the NMR study rules out structures with large C—C bond alternation, and favors a model in which $C_{\alpha}-C_{\beta}$ is slightly longer than $C_{\beta}-C_{\gamma}$.

INTRODUCTION

The trend of the variation of molecular structure of group V heterobenzenes [1] is of some interest to chemists, because it can provide information for assessing the effect of the heteroatom on the bonding and aromaticity of this series of molecules. The molecular structures of phosphabenzene and arsabenzene have been extensively investigated by electron diffraction (ED) [2], microwave spectroscopy (MW) [3], combined ED and MW analysis [4] and by nuclear magnetic resonance of the partially oriented molecules in liquid crystalline solvents [5]. The investigations generally give results in good agreement with one another. The salient features of these structural studies are the planarity, the short carbon—heteroatom bond, and the lack of significant C—C bond alternation. The structure of stibabenzene has only been studied by microwave spectroscopy [6]. The limited number of rotational constants prevented determination of a unique structure. Therefore, a wide range of solutions consistent with the experimental rotational constants was suggested. Additional information on the atomic coordinates should certainly help to obtain a complete structure or to narrow down the range of acceptable solutions. Stibabenzene is probably too reactive to be studied in nematic solvents. It is usually found that methyl substitution on aromatic rings, such as benzene and pyridine, causes only very minor changes in the structure of the ring [7, 8]. Therefore, we have studied the more stable 4-methylstiba-

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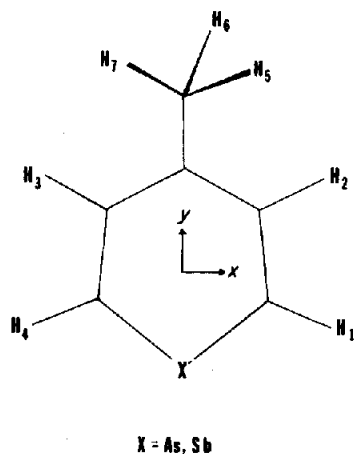


Fig. 1. Atomic numbering and axes for 4-methylarsabenzene and 4-methylstibabenzene.

benzene, and 4-methylarsabenzene (Fig. 1) partially oriented in a nematic solvent, using NMR technique [9], from which the proton coordinates of the molecules can be determined.

EXPERIMENTAL AND SPECTRAL ANALYSIS

4-methylarsabenzene (I) and 4-methylstibabenzene (II) were synthesized according to published procedures [10]. Samples were made up of ~10% of I and II respectively in the nematic liquid crystal phase of *N*-(*p*-ethoxybenzylidene)-*p*-*n*'-butylaniline (EBBA). The liquid crystal solvent was thoroughly treated through several freeze-pump-thaw cycles before the solute was distilled in. The 5 mm NMR tubes were sealed under vacuum, because both species are air-sensitive. All spectra were obtained on a Bruker HX-270 spectrometer, using 16K Fourier transform and quadrature detection. The probe temperature was about 23°C, and the pulse width was 10 μsec. Forty to fifty transients were accumulated for each spectrum. The spectrum of I has a spectral width of ca. 16 kHz and average line width of 6 Hz. The spectrum of II has a spectral width of ca. 19 kHz and average line width of 10–12 Hz. Some lines due to impurity from oxidized species of 4-methylstibabenzene were found in II, but none of them interfered with a positive assignment of the spectrum.

The spectra were independent of J_{56} due to the full magnetic equivalence of protons on the methyl group. Other indirect spin-spin couplings were approximated from the isotropic J_{ij} of their parent compounds [11] and γ -picoline [12].

Spectra were analyzed with the iterative program LEQUOR [7]. The r.m.s. errors for the spectral fit are 1.3 and 2.4 Hz respectively, which are consistent with the uncertainties in determining the line positions for the two spectra.

The relative chemical shifts and direct dipole—dipole couplings, D_{ij} , fitting to 204 and 169 lines respectively are listed in Table 1. The α and β proton chemical shifts both exhibit some degree of anisotropy. In these two molecules as well as in phosphabenzene and arsabenzene in nematic phase [5], the chemical shift of the α proton shifted downfield and that of β proton shifted upfield. The degree of shift is roughly related to the degree of ordering. A sample spectrum of 4-methylarsabenzene is given in Fig. 2, along with a computer simulated spectrum from LEQUOR [7].

Approximate averaging for small amplitude vibrations was made in a manner described elsewhere [13]. The contributions of harmonic vibrations, except the torsional mode of the methyl group [14], to the dipolar couplings are subtracted. The approximate vibrational force field used is taken from toluene [15] and from the approximate force field of arsabenzene [4]. The generalized mean square parallel and perpendicular amplitudes of vibration were calculated using a normal coordinate program MSAV [16]. The effect of vibrational averaging is found to cause less than a 0.5% change in relative distances.

TABLE 1

Spectral parameters of partially oriented 4-methylarsabenzene and 4-methylstibabenzene (D_{ij} and J_{ij} in Hz, chemical shift in ppm)

Parameter	4-Methylarsabenzene	4-Methylstibabenzene
D_{12}	-1780.90 ± 0.10^a	-2153.17 ± 0.26
D_{13}	-3.88 ± 0.11	-1.96 ± 0.24
D_{14}	58.75 ± 0.26	58.1 ± 0.5
D_{15}	-142.14 ± 0.15	-166.63 ± 0.29
D_{23}	83.35 ± 0.28	99.8 ± 0.5
D_{25}	-447.76 ± 0.15	-549.78 ± 0.30
D_{56}	2194.85 ± 0.07	2619.38 ± 0.15
J_{12}	10.0^b	12.5
J_{13}	1.5	1.5
J_{14}	-0.4	-0.4
J_{15}	0.7	0.7
J_{23}	2.5	2.5
J_{25}	0.0	0.0
J_{56}	—	—
$\nu_2 - \nu_1$	$-2.395 \pm 0.003 (-1.78)^c$	$-3.531 \pm 0.007 (-2.80)^c$
$\nu_5 - \nu_1$	$-7.294 \pm 0.002 (-6.98)^c$	$-8.780 \pm 0.004 (-8.62)^c$
Lines fitted	204	169
R.m.s. error (Hz)	1.27	2.37

^aError corresponds to one standard deviation. ^bAll J_{ij} values are either taken from the isotropic values of arsabenzene and stibabenzene reported in ref. 4 or are assumed. Spectra are independent of J_{56} due to the full magnetic equivalence of the methyl protons.

^cIsotropic values reported in ref. 10 in parentheses.

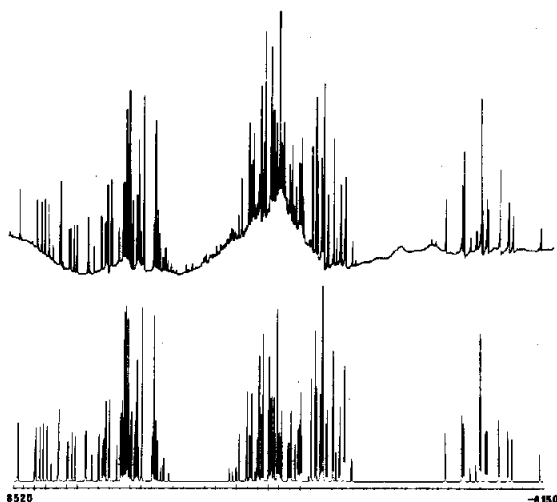


Fig. 2. The proton NMR spectrum of 4-methylarsabenzene in EBBA at 23°C. The upper spectrum is experimental; the lower is the computer simulation, with parameters given in Table 1, and a Lorentzian linewidth of 6 Hz.

RESULTS AND DISCUSSION

A modified version of the iterative weighted least-squares program SHAPE [17] was used to fit the molecular structure and a set of order parameters. The ring was assumed to be planar with C_{2v} symmetry [6]. The axis of the methyl rotation was assumed to coincide with the C_2 axis of the ring. The rotation of the light and symmetrical methyl groups generally does not affect the orientation. Therefore, only two diagonal elements of the ordering matrix are necessary to describe the orientation of the molecules. The two order parameters and four structural parameters relating to the protons can be determined by the seven experimental D_{ij} values. The order parameters obtained indicate that both molecules are aligned preferentially with their long axis along the direction of the liquid crystals. The degree of ordering is similar to that of toluene and γ -picoline, but much higher than that of arsabenzene and phosphabenzene [5], due to the increased anisotropy of the molecular shape with the methyl substitution.

It should be of interest to determine the barrier of methyl rotation. However, it has been observed in toluene [7] and γ -picoline [8] that the D_{ij} are not sufficiently sensitive to the six-fold potential, V_6 . Indeed, in the present study, calculations using models varying between free rotation and the interconversion between stable rotamers yield results that do not distinguish which model is likely. Only D_{25} and the coordinates of H_2 are moderately affected by the different values of V_6 . Therefore, V_6 for both 4-methylarsabenzene and 4-methylstibabenzene is assumed to be 14 cal mol⁻¹, which is approximately the value found for toluene, γ -picoline and several *para*-substituted

toluenes [18] by microwave spectroscopy. The D_{ij} values do show that the conformation with a methyl C—H bond in the ring plane corresponds to maximum potential energy.

The distance $H_1 \cdots H_4$ of 4.836 Å, which is the value obtained by combined ED + MW study for arsabenzene [4], is used as the reference distance for 4-methylarsabenzene. The order parameters and proton structural parameters corresponding to this reference distance are given in Table 2. The ring proton coordinates are in excellent agreement with the r_z structure from the combined ED + MW study. In fact, the agreement is much better than that between the NMR result and the combined ED + MW result on arsabenzene. But it should be noted that the experimental error from this study is much smaller than that of the NMR study of arsabenzene [5] due to the much larger number of spectral lines in the spectra of the 4-methyl species. The good agreement indicates that the structure obtained from the ED + MW study is consistent with this study, and it suggests that the perturbation of the ring structure by the methyl substitution is small. This affirms the validity of using the 4-methyl substituted species as an approximation to infer the structural features of the parent molecules.

The interproton distance of the methyl group is 1.808 ± 0.009 Å. This value of r_{56} , corresponding to, for example, $r_{CH} = 1.111$ Å, $\angle CCH = 110^\circ$, is slightly larger than the value corresponding to the moment of inertia of the methyl group I_α (ca. 3.21 amu Å²) obtained by microwave spectroscopy for toluene, γ -picoline and several *para*-substituted toluenes [18]. The slightly longer r_{56} is probably due to the effect of larger amplitude motion of the methyl group torsion, and to the difference between r_z and r_o structures. The y coordinates of the methyl protons also seem to be farther away from

TABLE 2

Structural and order parameters of partially oriented 4-methylarsabenzene and 4-methylstibabenzene^a

Parameter	4-Methylarsabenzene	4-Methylstibabenzene
X_1	2.418 ^b (2.418 ± 0.007) ^c	2.537 ± 0.012
Y_1	0.821 ^b (0.821 ± 0.006)	1.062 ^b
X_2	2.151 ± 0.005 (2.154 ± 0.012)	2.143 ± 0.009
Y_2	3.239 ± 0.004 (3.224 ± 0.015)	3.436 ± 0.006
r_{56}	1.808 ± 0.009	1.808 ^b
Z_5	5.213 ± 0.008	5.353 ± 0.016
S_{yy}	0.2185 ± 0.0007	0.2608 ± 0.0016
S_{xx}	-0.0554 ± 0.0006	-0.0647 ± 0.0013
R.m.s. error (Hz)	~0	0.39

^aAll coordinates are in Å, errors correspond to one standard deviation. ^bValues fixed.

^cValues in parentheses are coordinates determined by combined ED + MW for arsabenzene in ref. 4.

the ring than would be expected if the skeleton of ref. 4 and a C—C bond length of 1.52 Å is used. The discrepancy is probably due also to the effect of the torsional vibration.

The reference distance for 4-methylstibabenzene is set by assuming that its methyl structure is the same as that of 4-methylarsabenzene. The order and structural parameters are listed in Table 2. In the study of stibabenzene by microwave spectroscopy [6], a range of possible solutions consistent with the experimental rotational constants has been suggested. In comparison with the proton coordinates obtained in this study, some of the solutions can be ruled out. Assuming that $r_{\text{CH}} = 1.110$ Å, which is approximately the r_z value for arsabenzene and phosphabenzene from ED + MW study [4], and that all C—H bonds bisect the corresponding ring angles, proton coordinates were calculated for various assumed structures. It is obvious from the comparison that the structural models with large C—C bond alternation ($\Delta r > 0.032$ Å) in either direction lead to deviation from the present study beyond experimental error. In phosphabenzene, $r(\text{C}_\alpha\text{—C}_\beta)$ is longer than $r(\text{C}_\beta\text{—C}_\gamma)$ by 0.029 ± 0.023 Å (2.5σ), and in arsabenzene, $r(\text{C}_\alpha\text{—C}_\beta)$ is equal to $r(\text{C}_\beta\text{—C}_\gamma)$ within experimental error. The C—C bond alternation for stibabenzene, then, will not be much greater than that for phosphabenzene, contrary to the expected trend of increasing bond localization. It is interesting that the bond alternation in all the molecules in this series is substantially less than that in naphthalene [19]. The proton coordinates, however, do not discriminate strongly against the model with $r(\text{C}_\beta\text{—C}_\gamma)$ longer than $r(\text{C}_\alpha\text{—C}_\beta)$. The model that seems to fit both sets of data best is one in which $r(\text{C}_\alpha\text{—C}_\beta)$ is slightly longer than $r(\text{C}_\beta\text{—C}_\gamma)$. The structural parameters for this model are the following: $r(\text{Sb—C}) = 2.050 \pm 0.003$ Å, $r(\text{C}_\alpha\text{—C}_\beta) = 1.400 \pm 0.012$ Å, $r(\text{C}_\beta\text{—C}_\gamma) = 1.392 \pm 0.012$ Å, $\sphericalangle\text{CSbC} = 92.8^\circ \pm 0.2^\circ$, $\sphericalangle\text{SbCC} = 123.8^\circ \pm 0.5^\circ$, $\sphericalangle\text{C}_\alpha\text{C}_\beta\text{C}_\gamma = 125.9^\circ \pm 0.3^\circ$. The uncertainties only take into consideration the range of values giving acceptable agreement with the NMR results. No uncertainty due to experimental error is included. Small changes of C—H bond lengths and small deviation of C—H bonds from the bisectors of ring angles would alter this range of acceptable values to a small extent. However, this structure is close to both the intuitive choice made by the authors of ref. 6, and the structure derived by using the method of 'predicate observations'. The common feature of these structures is the small difference ($0.005\text{--}0.021$ Å) between $r(\text{C}_\alpha\text{—C}_\beta)$ and $r(\text{C}_\beta\text{—C}_\gamma)$.

From the present study, it is observed that in general the structure from NMR study is consistent with the electron diffraction and microwave spectroscopic studies. Methyl substitution in the γ position does not cause significant change in the ring structure. Evidence for both arsabenzene and stibabenzene is against models with substantial C—C bond alternations.

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