

MOLECULAR STRUCTURE OF ARSABENZENE BY GAS-PHASE ELECTRON DIFFRACTION

T. C. WONG, A. J. ASHE, III, AND L. S. BARTELL

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104 (U.S.A.)

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ABSTRACT

Vapor-phase molecules of C_5H_5As were found, assuming C_{2v} symmetry, to have the following structure parameters and uncertainties (2.5σ): $r_g(C-As) = 1.850 \pm 0.003$ Å, $r_g(C_2-C_3) = 1.390 \pm 0.032$ Å, $r_g(C_3-C_4) = 1.401 \pm 0.032$ Å, $r_g(C-C_{ave}) = 1.395_4 \pm 0.002$ Å, $\angle CAsC = 97.3 \pm 1.7^\circ$, $\angle AsCC = 125.1 \pm 2.8^\circ$, and $\angle C_2C_3C_4 = 124.2 \pm 2.9^\circ$. Amplitudes of vibration were also determined. Auxiliary information is more restrictive than pure electron diffraction intensities as evidence that the molecule is rigorously planar. Structural characteristics of arsabenzene reinforce prior indications that the heterocyclic molecule is genuinely aromatic.

INTRODUCTION

Arsabenzene (arsenin), an arsenic analog of pyridine, was synthesized along with phosphabenzene in 1971 by Ashe [1]. Later stibabenzene was also made [2]. A comparison of structures and properties in this series of compounds should be interesting and of significance in assessing theories of aromaticity. Preliminary studies of arsabenzene by photon and photoelectron spectroscopy [3] have been able to correlate its spectroscopic properties and electron energy levels of those of pyridine and phosphabenzene. The structure of a substituted arsabenzene, 2,3,6-triphenylarsenin, was studied by X-ray diffraction [4], and no significant departure from planarity was observed for the arsabenzene ring. However, the structure of the unsubstituted species has not yet been reported. Therefore, the purpose of the present research is to determine the structure of arsabenzene in the gas phase by electron diffraction.

EXPERIMENTAL PROCEDURE

The sample of arsabenzene was prepared by Dr. Thomas Schmidt of the University of Michigan. The sample was purified by vacuum distillation. Its purity was checked by examining its infrared spectrum, and no impurity was detected. The sample was then used without further treatment. Diffraction patterns were recorded on 4 × 5 inch Kodak electron image plates using the electron diffraction unit of the University of Michigan [5]. Camera distances were set at 21 cm with both an R^2 sector and an R^3 sector, and at 11 cm with an R^3 sector. Detailed experimental conditions are given in Table 1.

TABLE 1

EXPERIMENTAL CONDITIONS UNDER WHICH DIFFRACTION PLATES OF ARSABENZENE WERE RECORDED

	<i>Camera geometry</i>		
	<i>I</i>	<i>II</i>	<i>III</i>
Camera distance (cm)	21.025	21.029	11.003
Sector (sector radius, cm)	r^2 (2.5)	r^3 (4.4)	r^3 (4.4)
Nozzle temperature (°C)	29	29	29
Sample pressure ^a (torr)	5–8	5–8	5–8
Exposure time (s)	2.5	9–12	38–40
Beam current (μA)	0.52	0.52	0.51
Diameter of Pt nozzle (cm)	0.030	0.030	0.030

^a The vapor pressure of arsabenzene has not been reported in the literature. The value listed in the table was roughly estimated by Trouton's rule.

Plates were developed at 68°F for three minutes with Kodak HRP developer. Absorbances, measured with a digital microphotometer [6], ranged from 0.17 to 0.90. They were converted to exposures, correcting for nonlinear response of the photographic emulsion, by the relation [7]

$$E = A(1 + 0.1A + 0.0133A^2)$$

where A and E represent the absorbance and corresponding exposure, respectively. Five plates from each of the 21 cm camera geometry patterns and three from the 11 cm camera geometry patterns were selected to be used in the analysis.

ANALYSIS OF DATA

Experimental intensities were obtained by averaging the plates selected for each camera geometry. Sector irregularities and extraneous scattering were corrected for and flat plate corrections were made before intensities were leveled

in the usual way [8]. Tabulated atomic elastic and inelastic scattering factors of Schafer et al. [9] were used throughout the analysis.

Molecular parameters were refined by comparing experimental and calculated reduced molecular intensities, $M(s)$, by a least-squares procedure. Initially, intensity data from each individual camera geometry were treated separately. After the background function $I_B(s)$ for the separate camera geometries had been refined and established, using the usual criteria [10], a blended experimental reduced intensity curve was constructed by merging data from 21 cm, R^2 sector ($s = 2.8\text{--}9.7 \text{ \AA}^{-1}$), 21 cm, R^3 sector ($s = 4.4\text{--}19.2 \text{ \AA}^{-1}$) and 11 cm, R^3 sector ($s = 10.6\text{--}37.7 \text{ \AA}^{-1}$) camera geometries over the range of $s = 2.8\text{--}37.7 \text{ \AA}^{-1}$. The experimental intensities $I_0(s)$ and the background functions $I_B(s)$ for individual camera geometries are available from ASIS*. The indices of resolution for the three camera geometry patterns are 0.991, 0.953 and 1.051, respectively, as determined from least-squares analyses.

A radial distribution function was calculated using a damping factor of $\exp(-0.0021s^2)$, with the usual correction for scattering by planetary electrons [11] and integral termination errors [12]. Anharmonicity constants [13] for bonded distances were calculated from the empirical relations of Herschbach and Laurie [14], and in this case they were estimated to be 1.8 \AA^{-1} for C-As bonds, 1.9 \AA^{-1} for C-C bonds and 2.1 \AA^{-1} for C-H bonds. For all nonbonded distances, they were taken to be 2.0 \AA^{-1} . The molecular model used in the analysis is of a geometrically consistent structure in which bond lengths are the mean (r_g) internuclear distances and nonbonded distances are taken to be r_g lengths plus a shrinkage correction. Shrinkages [15] for all nonbonded distances were roughly

TABLE 2

SHRINKAGES FOR NONBONDED DISTANCES IN ARSABENZENE

<i>Distance</i>	<i>Shrinkage (Å)</i>	<i>Distance</i>	<i>Shrinkage (Å)</i>
As ··· C ₃	0.0045	C ₃ ··· H ₉	0.0081
As ··· C ₄	0.0066	C ₂ ··· H ₉ , C ₃ ··· H ₁₀ , C ₄ ··· H ₇	0.016
As ··· H ₇	0.006	C ₂ ··· H ₁₁	0.0168
As ··· H ₈	0.016	C ₂ ··· H ₁₀ , C ₃ ··· H ₁₁	0.0205
As ··· H ₉	0.022	H ₇ ··· H ₈	0.0046
C ₂ ··· C ₄	0.0044	H ₈ ··· H ₉	0.0072
C ₃ ··· C ₅	0.0041	H ₇ ··· H ₉ , H ₈ ··· H ₁₀	0.027
C ₂ ··· C ₄	0.0017	H ₇ ··· H ₁₁	0.033
C ₂ ··· C ₅	0.0068	H ₇ ··· H ₁₀	0.035
C ₂ ··· H ₈ , C ₃ ··· H ₇ , C ₄ ··· H ₈	0.007		

* See NAPS document #02406 for 5 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, 305 E. 46th St., New York, N.Y. 10017. Remit in advance for each NAPS accession number. Make checks payable to "Microfiche Publications". Photocopies are \$5.00. Microfiche are \$1.50. Outside of the U.S. or Canada, postage is \$2.00 for a PC or \$.05 for a fiche.

estimated from extrapolation of the calculated values for pyridine [16] and phosphabenzene [17]. They are listed in Table 2.

A diagram of arsabenzene with numbered atoms is shown in Fig. 1. Simplifying assumptions made to reduce the number of independent parameters to be varied in the least-squares analysis were as follows.

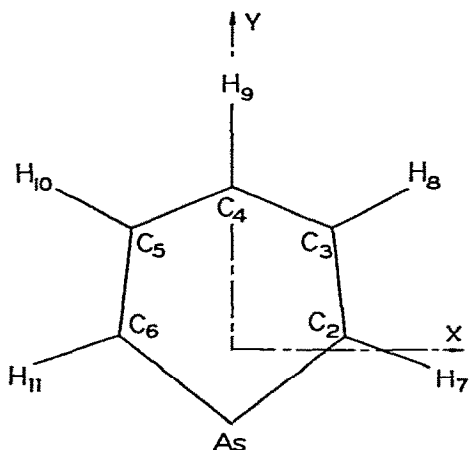


Fig. 1. Numbering of atoms and principal axis system for arsabenzene.

(1) The molecule was assumed to be planar and of C_{2v} symmetry. This assumption has been shown to hold rigorously for pyridine [18] and phosphabenzene [17].

(2) All C-H bond lengths were taken to be equal.

(3) Arsenic-hydrogen amplitudes were interrelated according to the relations

$$l_{As-H(8)} = l_{As-H(7)} - 0.005 \text{ \AA}$$

$$l_{As-H(9)} = l_{As-H(7)} - 0.007 \text{ \AA}$$

(4) Average values were given to all nonbonded C · · · H and H · · · H amplitudes of vibration respectively, and $l_{H \cdots H}$ was fixed at 0.130 Å throughout the analysis.

A diagonal weight matrix, with elements proportional to the square of the scattering variable s , was used in the least-squares analysis. This weighting is equivalent to a uniform weighting for $sM(s)$, and gives a nearly uniform distribution of noise in the s space. However, in the estimation of errors, the correlation between observed intensity data was considered by using the formalism of the "bona fide error matrix" [19] to assess the effect of data correlation on the uncertainties in the derived parameters.

RESULTS AND DISCUSSION

The experimental and the best calculated molecular intensities, $sM(s)$, are

compared in Fig. 2. The experimental radial distribution function is shown in Fig. 3 along with the difference between the experimental and calculated functions.

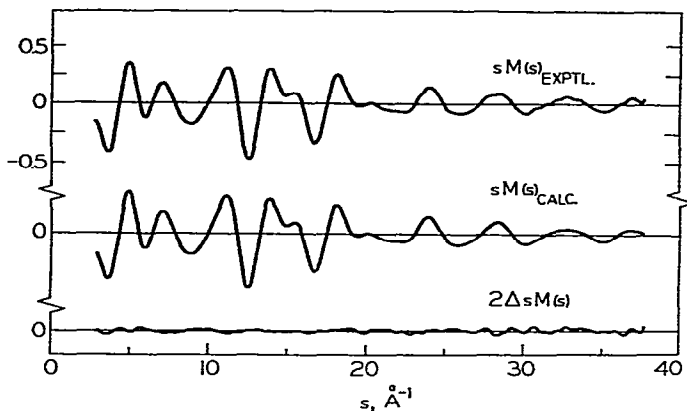


Fig. 2. Experimental and calculated molecular intensity functions for arsabenzene.

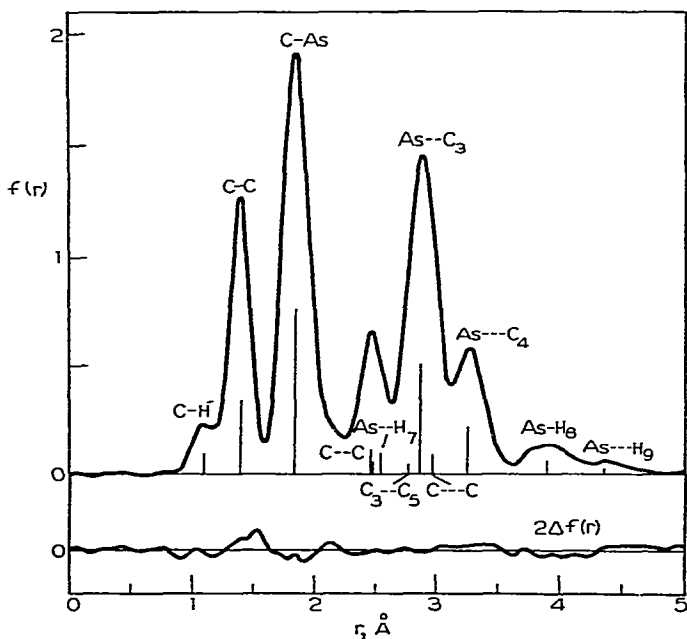


Fig. 3. Experimental radial distribution function for arsabenzene. $\Delta f(r) = f(r)_{\text{exptl}} - f(r)_{\text{calc}}$.

The radial distribution function is similar in appearance to that found for phosphabenzene [17], with severe overlapping of peaks corresponding to the distances $C_2 \cdots C_6$, $As \cdots C_3$ and $C_2 \cdots C_5$, also between distances corresponding to $C_2 \cdots C_4$, $C_3 \cdots C_5$ and $As \cdots H_7$. Therefore, it was expected that a complete

structure analysis would be difficult, because some of the parameters will have large uncertainties due to strong correlations between parameters.

The largest discrepancy in the radial distribution is at about 1.55 Å, a circumstance also observed in the case of three other compounds, the intensities of which were measured by a photometer with a temporary replacement for its amplifier. This amplifier has since been found to have an undesirable time response which may, in part, account for the spurious signal. An extensive test with phosphabenzene [17], a closely similar compound whose analysis suffered a similar defect, revealed influences on derived parameters too small to warrant corrections.

The correlation between observed intensity readings was estimated by an autocorrelation study of intensity residuals in the least-squares analysis. The γ correlation index, defined in ref. 19, was estimated to be about 1.5 Å.

Error estimates included random and systematic errors (as outlined in the footnotes of Table 5). To assess uncertainties other than those in instrumental scale factors, a "zero order" error matrix M_x^0 , "bona fide" error matrix [19], M_x^w , and the error matrix M_x^{ab} , which tests the effect of systematic intensity errors described in ref. 20 on the uncertainties of the derived parameters, were calculated. A comparison of the M_x^0 and M_x^w matrices is given in Table 3. The corrections from M_x^0 to M_x^{ab} were too trivial to justify their presentation here. The correlation matrix obtained from the "bona fide" treatment is given in Table 4.

TABLE 3

COMPARISON OF THE DIAGONAL ELEMENTS^a OF VARIOUS ERROR MATRICES FOR ARSABENZENE

Parameter	M_x^0 ^b	M_x^w ^c	Parameter	M_x^0 ^b	M_x^w ^c
r_{C-As}	0.00075	0.001	l_{C-As}	0.0013	0.0019
$r_{C_2-C_3}$	0.012	0.013	$l_{As...C_3}$	0.0037	0.0045
\bar{r}_{C-C}	0.00046	0.00072	$l_{As...C_4}$	0.0038	0.0037
Δr_{C-C}	0.023	0.026	$l_{As...H}$	0.011	0.011
$r_{As...C_4}$	0.003	0.0029	l_{C-C}	0.0020	0.0023
r_{C-H}	0.0037	0.0062	$l_{C...C}$	0.0021	0.0024
$\angle CAsC$	0.011	0.013	$l_{C_2...C_6}$	0.024	0.028
$\angle AsCC$	0.018	0.020	$l_{C...C}$	0.0073	0.0081
$\angle C_2C_3C_4$	0.015	0.017	l_{C-H}	0.0036	0.0061
$\angle AsCH$	0.017	0.019	$l_{C...H}$	0.0059	0.0074
$\angle C_2C_3H$	0.034	0.033	R	0.011	0.017

^a Values given here are square roots of the diagonal elements of the error matrices, i.e. the standard deviation of the corresponding parameters. Distances and amplitudes are in Å, angles in rad; R and E are dimensionless.

^b "Zero order error matrix" is $M_x^0 = B^{-1}[(V'WV)/(n-m)]$.

^c "Bona fide error matrix" as defined in ref. 20.

The structural features of arsabenzene are very similar to those of phosphabenzene. The electron diffraction analysis cannot establish whether it is rigorously

TABLE 4

MATRIX OF CORRELATION COEFFICIENTS^{a,b} FOR ARSABENZENE

θ_1^c	θ_2	θ_3	θ_4	θ_5	θ_6	θ_7	θ_8	θ_9	θ_{10}	θ_{11}	θ_{12}	θ_{13}	θ_{14}	θ_{15}	θ_{16}	θ_{17}	θ_{18}	θ_{19}	
1.0	0.26																		
1.0	1.0	-0.02	0.02	0.34	-0.35	-0.01	-0.21	0.08	0.27	0.02	-0.05	0.27	0.22	0.25	-0.20	0.01	-0.17	0.13	
		1.0	-0.11	0.90	-0.94	0.65	-0.67	0.10	0.59	-0.04	0.07	0.88	0.59	0.53	-0.41	0.05	-0.07	0.07	
			0.30	-0.29	0.19	0.10	-0.06	-0.12	-0.20	-0.12	-0.17	-0.09	-0.02	-0.37	0.52		0.30	-0.18	
			1.0	-0.33	0.28	0.11	-0.22	-0.24	-0.42	-0.38	-0.36	-0.21	-0.19	-0.48	0.47	-0.08	0.13	-0.33	
				1.0	-0.99	0.45	-0.55	0.24	0.77	0.17	0.19	0.86	0.57	0.80	-0.70	0.06	-0.19	0.26	
					1.0	-0.51	0.59	-0.21	-0.75	-0.12	-0.16	-0.89	-0.59	-0.75	0.63	-0.05	0.16	-0.22	
						1.0	-0.32	-0.27	0.77	-0.14	0.10	0.44	0.15	0.11	-0.10	0.02	0.32	-0.42	
							1.0	-0.11	-0.40	0.12	0.22	-0.62	-0.45	-0.28	0.12	0.26	-0.15		
								1.0	0.50	0.23	0.05	0.29	0.27	0.39	-0.19	-0.30	0.71		
									1.0	0.38	0.13	0.71	0.51	0.87	-0.60	0.03	-0.36	0.65	
										1.0	0.16	0.06	-0.09	0.49	-0.31	0.02	-0.04	0.30	
											1.0	0.08	0.02	0.25	-0.35	0.02	0.25	0.02	
												1.0	0.61	0.62	-0.43	0.02	-0.22	0.35	
													1.0	0.38	-0.27	0.03	-0.24	0.36	
														1.0	-0.75	0.04	-0.27	0.49	
															1.0	-0.04	0.16	-0.21	
																1.0			
																	1.0	-0.52	
																			1.0

^a Matrix elements are given by

$$\rho_{ij} = (M_x^w)_{ij} / [(M_x^w)_{ii}(M_x^w)_{jj}]^{1/2}$$

where M_x^w is the error matrix. Only the upper half of the matrix is given.^b Elements with magnitude below 0.01 are not listed in the matrix.^c The order of the parameters is:

- | | | | | | | | |
|--------------------------------------|--------------------------|---|---------------------------------------|---------------------------------------|--|------------------------------------|------------------------------------|
| (1) $r(\text{C-As})$ | (4) $r(\text{C-H})$ | (7) $\angle \text{AsCH}$ | (10) $r(\text{As} \cdots \text{C}_3)$ | (12) $r(\text{As} \cdots \text{C}_4)$ | (14) $r(\text{C} \cdots \text{C})$ | (16) $r(\text{C} \cdots \text{C})$ | (18) $r(\text{C} \cdots \text{H})$ |
| (2) $r(\text{C}_2\text{-C}_3)$ | (5) $\angle \text{CAsC}$ | (8) $\angle \text{C}_2\text{C}_3\text{H}$ | (11) $r(\text{As} \cdots \text{H}_7)$ | (13) $r(\text{C-C})$ | (15) $r(\text{C}_2 \cdots \text{C}_6)$ | (17) $r(\text{C-H})$ | (19) R |
| (3) $r(\text{As} \cdots \text{C}_4)$ | (6) $\angle \text{AsCC}$ | (9) $r(\text{C-As})$ | | | | | |

planar, and no attempt was made to determine this. But there are good reasons to assume that it is planar, from the X-ray diffraction study of a substituted arsenabenzene [4], from the unequivocal study of phosphabenzene [17] and from a comparison with an analogous series of furan, thiophene [21] and selenophene [22]. The As-C bond length of 1.850 Å was significantly shorter than the usual carbon-arsenic single bond of about 1.96 Å [23]. Even in certain molecules where at least some delocalization of π -electrons from an adjacent conjugate system to the As-C bond has been suspected, the As-C bond lengths are found to be longer than the present value by more than 0.03 Å [24]. Therefore, the present study suggests an appreciable degree of double bond character in the As-C bonds. The two carbon-carbon bond lengths C_2-C_3 and C_3-C_4 differ by only 0.011 ± 0.065 Å (2.5σ). It is hoped that it will be possible to reduce this uncertainty when it becomes possible to refine with the inclusion of microwave moments of inertia. An analogous combined analysis for phosphabenzene proved very helpful in breaking the strong

TABLE 5

PARAMETERS DERIVED FROM LEAST-SQUARES ANALYSIS FOR ARSABENZENE

Parameters	r_z (Å)	l_z (Å)
C-As	$1.850 \pm 0.003^{a,c}$	$0.050_3 \pm 0.006$
C_2-C_3	1.390 ± 0.032	
C_3-C_4	1.401 ± 0.032	$0.046_2 \pm 0.007$
C-C (mean)	$1.395_4 \pm 0.002$	
$\Delta(C-C)$	0.011 ± 0.065	
C-H	1.120 ± 0.015	$0.084_7 \pm 0.015$
As \cdots C_3	2.878 ± 0.011	$0.056_9 \pm 0.011$
As \cdots C_4	3.253 ± 0.008	$0.060_5 \pm 0.010$
$C_2 \cdots C_4$	2.471 ± 0.058	
$C_3 \cdots C_5$	2.462 ± 0.024	$0.055_9 \pm 0.007$
$C_2 \cdots C_6$	2.776 ± 0.035	0.076 ± 0.070
As \cdots H_7	2.543 ± 0.032	0.094 ± 0.028
Ave. C \cdots H		0.102 ± 0.018
Ave. H \cdots H		0.130 (assumed)
$\angle CAsC$	$97.3^\circ \pm 1.7^{b,c}$	
$\angle AsCC$	$125.1^\circ \pm 2.8^\circ$	
$\angle C_2C_3C_4$	$124.2^\circ \pm 2.9^\circ$	
$\angle C_3C_4C_5$	$124.2^\circ \pm 3.0^\circ$	
$\angle AsCH$	$116.1^\circ \pm 2.7^\circ$	
$\angle C_2C_3H_8$	$118.6^\circ \pm 4.9^\circ$	
$\sigma(I)/I^d$	0.00038	

^a All estimated uncertainties include systematic and random errors. They correspond to 2.5σ , where σ is the standard deviation.

^b Uncertainties in this column concerning bond angles do not include any allowance for uncertainties in the shrinkage correction used.

^c Systematic errors are estimated to be 2 parts per ten thousand in wavelength measurement, 3 parts per ten thousand in camera distance measurement, and 2 parts per ten thousand in the radial measurement in microphotometer scanning.

^d Fractional weighted standard deviation of intensities.

correlation between the C_2-C_3 and C_3-C_4 parameters and, accordingly, it reduced the uncertainty in $\Delta r(C-C)$ substantially. The value of $1.395 \pm 0.002 \text{ \AA}$ (2.5σ) for the mean carbon-carbon bond length in arsabenzene, which was determined with some precision, is very close to those of benzene and phosphabenzene. The average C-H bond length of 1.12 \AA seems slightly high but not by more than its uncertainty. The geometric parameters and amplitudes of vibration derived from the analysis are given in Table 5.

The carbon-carbon bond lengths fall within the range associated with aromatic C-C bond lengths and the C-As bond length indicates appreciable double bond character. The increasing bond length in going from C-C in benzene to C-As in arsabenzene naturally decreases the CXC apex angle of the ring, while the other CCC angles are maintained close to the "natural" angle of 120° . But this order of decreasing CXC angle is also consistent with the trend of the respective carbon and arsenic noncyclic compounds. The present structure reinforces prior evidence [1, 3, 4] that arsabenzene is genuinely aromatic.

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