

MOLECULAR STRUCTURE OF ARSABENZENE: ANALYSIS COMBINING ELECTRON DIFFRACTION AND MICROWAVE DATA

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ABSTRACT

The average (r_z) structure of vapor-phase C_5H_5As , the arsenic congener of pyridine, was deduced. Vibrational corrections of diffraction data and rotational constants were made via a normal coordinate analysis. The heterocyclic molecule was found to have a rigorously planar, C_{2v} structure with geometric parameters very close to those inferred from an earlier analysis of the diffraction data alone, but uncertainties were reduced substantially by incorporation of the spectroscopic information in refinements. Amplitudes of vibration were determined from both the diffraction and normal coordinate analyses. Principal structural parameters and uncertainties (2.5σ) were $r_g(C-As) = 1.850(2)$ Å, $r_g(C_2-C_3) = 1.392(9)$ Å, $r_g(C_3-C_4) = 1.400(10)$ Å, $r_g(C-C \text{ mean}) = 1.396(2)$ Å, $\angle CAsC = 97.0(3)^\circ$, $\angle AsCC = 125.3(7)^\circ$, and $\angle C_2C_3C_4 = 123.9(13)^\circ$. Structural characteristics are those expected for an aromatic molecule.

INTRODUCTION

The molecular and electronic structures of Group V congeners of pyridine [1—3] are significant because they should provide useful information for assessing the effects of the heteroatom on the bonding and aromaticity. Photoelectron [4] and NMR [5] studies of several members of this series have been carried out. Microwave spectra of phosphabenzene [6] and arsabenzene [7] have also been investigated. However, microwave spectra of these two molecules do not provide sufficient information to determine the complete molecular structure because of the limited number of isotopic species. We have reported the gas-phase electron diffraction investigations of the molecular structure of phosphabenzene [8] and arsabenzene [9] (hereafter referred to as Papers I and II). The electron diffraction studies were hampered somewhat by the high correlation between geometrical parameters, particularly those between the C—C bond lengths, resulting in rather large uncertainties for some parameters. Most notably, the C—C bond lengths are poorly resolved. However, in Paper I a combined use of electron diffraction

and microwave spectroscopic data was made to determine the structure of phosphabenzene. This combined analysis greatly reduced the correlation between the parameters and, hence, yielded a much improved structural determination for phosphabenzene. Therefore we report here a similar analysis of the molecular structure of arsabenzene combining electron diffraction and microwave spectroscopic data, which became available recently [7].

PROCEDURE

The procedure of the electron diffraction experiment and the analysis of the diffraction data were described in Paper II. Procedures for combining electron diffraction and spectroscopic data, and for performing vibrational calculations were the same as those described in Paper I and refs. therein. An approximate quadratic force field* was constructed by choosing the appropriate force constants for the arsenic atom, and transferring or extrapolating others from benzene [10], pyridine [11] and phosphabenzene [8]. All mean square parallel and perpendicular amplitudes of vibration [10], as well as the vibrational corrections to the rotational constants, were calculated from the force field by using the computer program MSAV [12], and are consistent with those calculated for pyridine and phosphabenzene. The experimental rotational constants, after correction for vibration, yield an inertial defect practically equal to zero. This provides firm experimental evidence that arsabenzene is strictly planar in its equilibrium state. The rotational constants and vibrational corrections are given in Table 1.

Assumptions concerning the symmetry and structure of arsabenzene were the same as those in Paper II. A diagonal weight matrix was adopted for the entire data set of electron diffraction intensities and microwave rotational

TABLE 1

Experimental rotational constants, comparison of experimental and calculated moment of inertia, and inertial defect (I.D.)

	A	B	C	I.D.
Experimental rotational constants, B_0 (MHz) ^a	4871.03 ± 0.18	2295.87 ± 0.01	1560.10 ± 0.01	
Experimental effective moments of inertia, I_0 (a.m.u. Å ²)	103.751 ± 0.004	220.124 ± 0.001	323.938 ± 0.002	0.063
Vibrational correction (a.m.u. Å ²) ^b	0.024	0.085	0.044	
Average moments of inertia, I_z (a.m.u. Å ²)	103.775	220.209	323.982	-0.002
Calculated average moments of inertia (a.m.u. Å ²)	103.772	220.209	323.981	

^aTaken from Ref. 7. ^bCalculated from an approximate quadratic force field using computer program, MSAV.

*The force constants adopted are available as Sup. Pub. No. SUP 26084 (4 pages) from BLLD.

constants. It was found that the structure obtained was insensitive to the relative weighting of the electron diffraction and microwave data. However, relative weights for these two types of experimental observations were chosen to be consistent with the relative errors in the data points. To account for the correlation between observed electron diffraction intensity readings, which was not represented by off-diagonal weighting elements, the error matrix $M_{\bar{x}}$ appropriate for Markovian noise was applied to the parameters using a correlation index [13] of 1.5 Å.

RESULTS AND DISCUSSION

A structural model in excellent agreement with both the electron diffraction and microwave spectroscopic data was obtained from a combined least-squares routine similar to that used in Paper I. The result of combining the rotational constants in the analysis changes the structural parameters only slightly from the values determined by electron diffraction alone. Only $\angle \text{AsCH}$ and $\angle \text{C}_2\text{C}_3\text{H}$ were altered noticeably, and the changes were well within estimated uncertainties. This response to inclusion of microwave data is not surprising because the structure derived from electron diffraction in Paper II, after correction for vibrational effects, was able to predict the experimental rotational constants to within 1–3 MHz (ca. 0.1%). The geometrical parameters, mean amplitudes of vibration and some calculated amplitudes of vibration are given in Table 2. Experimental and calculated mean amplitudes are in good agreement, despite some severe overlapping in the radial distribution function. A listing of parameter correlations is given in Table 3.

The most important and striking improvement of this combined analysis over the pure electron diffraction study is the considerable reduction of parameter correlation and, consequently, the substantial decrease in the errors associated with the parameters. This reduction of error is particularly significant for the determination of the C—C bond lengths. Presumably, the C—C bond lengths are sensitive to the electron population and hence should be helpful in diagnosing variations in the chemical bonding. In Paper II, the errors for the two C—C bond lengths, and particularly for the difference between them, are too large to make meaningful comparisons with other aromatic C—C bond lengths. The present analysis reduces these errors by more than a factor of three, making it possible to establish the individual C—C bond lengths as well as their difference with reasonable accuracy.

As was also the case with phosphabenzene, the $\text{C}_2\text{—C}_3$ and $\text{C}_3\text{—C}_4$ bond lengths are the same to within experimental uncertainties. Several molecular orbital studies [7, 14, 15] of varying rigor have investigated the effect of the ring heteroatom on the bonding in the ring with differing results. Experimental evidence from other sources has also been applied to the pyridine congeners. Trends in the magnetic ring current [5] and chemical reactivity [3] of this series suggest a general decrease in the aromaticity of this Group V heterobenzene as the atomic number of the heteroatom increases. However, experi-

TABLE 2

Parameters derived from least-squares analysis of electron diffraction and microwave spectroscopic data for arsabenzene, and comparison with amplitudes calculated from approximate harmonic force field (bond lengths and amplitudes in Å, bond angles in degrees, index of resolution, R , is dimensionless)

Parameter ^a	r_z values	$r_g - r_z$ ^b	I^c	I calc ^b
C—H (ave.)	1.110 ± 0.012 ^d	0.0178	0.086 ± 0.015	0.076
C—As	1.847 ± 0.002	0.0027	0.050 ± 0.004	0.045
C ₂ —C ₃	1.388 ± 0.009	0.0039	0.046 ± 0.003	0.047
C ₃ —C ₄	1.396 ± 0.010	0.0038		0.047
r_{C-C} (mean)	1.392 ± 0.002			
Δr_{C-C}	0.008 ± 0.018			
As \cdots C ₃	2.882 ± 0.004	0.0022	0.056 ± 0.006	0.051
As \cdots C ₄	3.254 ± 0.004	0.0026	0.058 ± 0.006	0.059
C ₁ \cdots C ₄	2.457 ± 0.012	0.0027	0.055 ± 0.004	0.055
C ₃ \cdots C ₅	2.471 ± 0.008	0.0030		0.055
C ₂ \cdots C ₆	2.768 ± 0.007	0.0028	0.077 ± 0.030	0.063
C ₁ \cdots C ₅	2.961 ± 0.004	0.0022	0.086 ± 0.013	0.064
As \cdots H ₇	2.557 ± 0.016	0.0109	0.099 ± 0.022	0.102
Ave. C \cdots H			0.102 (assumed)	
Ave. H \cdots H			0.130 (assumed)	
\angle CAsC	97.0° ± 0.33° ^e			
\angle AsCC	125.3° ± 0.69°			
\angle C ₂ C ₃ C ₄	123.9° ± 1.3°			
\angle C ₃ C ₄ C ₅	124.5° ± 1.1°			
\angle AsCH	117.4° ± 0.8°			
\angle C ₂ C ₃ H ₈	117.8° ± 2.1°			
R	1.040 ± 0.030			
$\sigma(I)/I^f$	0.398 × 10 ⁻³			

^aNumbering scheme: [—As₁—C₂(H₇)—C₃(H₈)—C₄(H₉)—C₅(H₁₀)—C₆(H₁₁)—]. See Figs. in refs. 8 and 9. ^bCalculated from an approximate harmonic force field using the computer program MSAV. ^cThe experimental amplitudes are I_g values. ^dAll estimated uncertainties include both systematic and random errors. Systematic errors are estimated to be 2 parts per 10,000 in wavelength measurement, 3 parts per 10,000 in camera distance measurement, and 2 parts per 10,000 in the radial measurement in microphotometer scanning. The uncertainties listed here correspond to 2.5 σ , where σ is the standard deviation. ^eUncertainties in this column concerning angles do not include any allowance for uncertainties in the shrinkage corrections used. ^fFractional standard deviation of weighted electron diffraction intensities.

mental structures demonstrate that the average C—C bond length in all cases is about 1.396 Å, which is the typical aromatic C—C bond length. Therefore the structural comparison does not reflect but cannot absolutely rule out the trend inferred from NMR and chemical reactivity studies.

Comparing the structures of pyridine, phosphabenzene and arsabenzene, which are listed in Table 4, one can observe a definite trend in the bond angles associated with the systematic change in X—C bond lengths. The CXC angles decrease substantially from pyridine to phosphabenzene and arsabenzene,

TABLE 3

Matrix of correlation coefficients^{a, b} for arsabenzene

θ_i^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}	
σ	0.00072	0.0036	0.0017	0.0048	0.13	0.27	0.32	0.83	0.0015	0.0026	0.0087	0.0026	0.0010	0.0016	0.012	0.0054	0.0060	0.012
θ_1	1.0	-0.33	-0.01	0.05	-0.18	0.08	-0.01	-0.15	-0.10	-0.02	-0.01	-0.02	-0.11	0.01	-0.05	-0.01	-0.08	
θ_2		1.0	0.24	-0.67	0.91	-0.90	0.58	-0.60	0.19	0.36	-0.12	0.18	0.48	0.15	-0.04	0.03	0.26	
θ_3			1.0	-0.47	0.43	-0.47	0.10	-0.04	0.19	0.56	0.33	0.08	0.22	0.52	-0.17	0.03	0.28	
θ_4				1.0	-0.65	0.63	0.03	-0.18	-0.14	-0.29	-0.08	-0.19	-0.34	-0.13	-0.06	-0.08	-0.25	
θ_5					1.0	-0.97	0.31	-0.34	0.21	0.53	-0.02	0.17	0.47	0.34	-0.18	0.02	0.30	
θ_6						1.0	-0.45	0.33	-0.21	-0.57	-0.04	-0.18	-0.49	-0.39	0.20	-0.01	-0.30	
θ_7							1.0	-0.42	-0.12	0.52	0.08	0.28	0.12	0.08	-0.06	0.01	-0.33	
θ_8								1.0	-0.10	-0.31	0.12	-0.43	-0.28	-0.23	0.07	-0.13	-0.19	
θ_9									1.0	0.43	0.10	0.37	0.21	0.33	0.17	-0.04	0.67	
θ_{10}										1.0	0.06	0.45	0.29	0.71	-0.16	-0.04	0.64	
θ_{11}											1.0	0.06	-0.09	0.47	0.12	0.23	0.23	
θ_{12}												1.0	0.12	0.04	0.03	0.16	0.16	
θ_{13}													1.0	0.31	0.09	-0.04	0.56	
θ_{14}														1.0	0.49	0.49	0.33	
θ_{15}															1.0	0.27	0.27	
θ_{16}																1.0	0.27	
θ_{17}																	1.0	
θ_{18}																		1.0

^aMatrix elements are given by $\rho_{ij} = (M_X^W)_{ij} / [(M_X^W)_{ii}(M_X^W)_{jj}]^{1/2}$ and $\sigma_1 = (M_X^W)_{ii}^{1/2}$, where M_X^W is the "bona fide" error matrix of ref. 13. Only the upper half of the matrix is given. ^bElements with magnitude below 0.01 are not listed in the matrix.

^cThe order of the parameters is:

- (1) $r(C-As)$ (7) $\angle AsCH$ (10) $\angle(As \cdots C_3)$ (12) $\angle(As \cdots C_4)$ (14) $\angle(C \cdots C)$ (16) $\angle(C \cdots C)$ (18) R
- (2) $r(C_2-C_3)$ (8) $\angle C_2C_3H$ (11) $\angle(As \cdots H_1)$ (13) $\angle(C-C)$ (15) $\angle(C_2 \cdots C_6)$ (17) $\angle(C-H)$
- (3) $r(As \cdots C_4)$ (9) $\angle(C-As)$

TABLE 4

Comparison of structural parameters of pyridine, phosphabenzene, and arsabenzene: bond lengths in Å, bond angles in degrees

Parameter	X		
	N	P	As
$r(\text{X}-\text{C})$	1.337	1.733	1.850
$r(\text{C}_2-\text{C}_3)$	1.394	1.413	1.392
$r(\text{C}_3-\text{C}_4)$	1.391	1.384	1.400
$\angle \text{CXC}$	116.9	101.0	97.0
$\angle \text{XCC}$	123.8	124.5	125.3
$\angle \text{C}_2\text{C}_3\text{C}_4$	118.5	123.8	123.9
$\angle \text{C}_3\text{C}_4\text{C}_5$	118.4	122.5	124.5
Reference	16 ^a	8 ^b	This work ^b

^a r_g structure from microwave spectroscopy. ^bStructure derived from combined electron diffraction and microwave analysis

while all other ring angles increase steadily. The C—As bond, like the C—X bonds in the other two molecules, is appreciably shorter than a C—As single bond. The relative C—C bond lengths do not follow a discernible trend but, as mentioned above, the average C—C bond length is virtually constant. Clearly, the structural characteristics of arsabenzene are essentially those of an aromatic compound.

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