

THE INFRARED AND RAMAN SPECTRA OF PHOSPHABENZENE AND ARSABENZENE*

ARTHUR J. ASHE, III

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109 (U.S.A.)

GERALD L. JONES and FOIL A. MILLER

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260 (U.S.A.)

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ABSTRACT

Phosphabenzene and arsabenzene are analogs of pyridine. Their IR and Raman spectra are reported for the first time. IR spectra are for a polycrystalline solid at about 100 K, and Raman spectra are for the liquid at room temperature. Assignments are suggested for all but five of the 54 fundamentals, and most of them are believed to be reliable. The molecules are known to have aromatic properties. This is demonstrated in the spectra by the regular trends in frequency and intensity in the sequence pyridine—phosphabenzene—arsabenzene.

INTRODUCTION

Phosphabenzene and arsabenzene [1], which are analogs of pyridine, were



M = N, P, As, Sb, Bi

first prepared in 1971 [2]. The antimony and bismuth compounds followed later, but this paper is not concerned with them. The properties of these Group V heterobenzenes have been thoroughly reviewed [3], and it is now clear from a variety of evidence that the compounds are aromatic. The structures of phosphabenzene and arsabenzene have been determined by microwave spectroscopy [4, 5] and by a combination of this with electron diffraction [6, 7]. No study of their vibrational spectra has been reported, so work has been undertaken to fill this gap. The vibrational frequencies would have been helpful in the electron diffraction work, for example [6, 7]. The antimony and bismuth compounds were not studied because of their instability.

The physical and chemical properties are favorable for IR and Raman studies. Phosphabenzene is a colorless, volatile liquid which melts at -51°C .

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It is air sensitive, but is stable to hydrolysis and is stable under an inert atmosphere.

Arsabenzene is a yellow, volatile liquid, m.p. -54°C . It is much more air sensitive than the phosphorus compound; it turns bright red immediately upon exposure to air. It is stable to hydrolysis, and it can be stored in an inert atmosphere without decomposition.

EXPERIMENTAL

Preparation of the samples

Phosphabenzene was prepared according to the method of Ashe [2], and arsabenzene according to that of Ashe and Chan [8]. Initially the samples were prepared in Ann Arbor and sent to Pittsburgh, but this was not satisfactory, so later the final step (the addition of MBr_3) was done in Pittsburgh, as was the spectroscopy. All solvents were freshly distilled from calcium hydride, and the complete reaction was performed in a flowing nitrogen atmosphere. The product was collected by vacuum distillation ($30^{\circ}\text{C}/0.4$ torr for phosphabenzene, $25^{\circ}\text{C}/0.1$ torr for arsabenzene).

Further purification was not needed in either preparation. The Raman spectra of both products were identical to samples provided by Ashe which had been purified by preparative gas-liquid chromatography. The yield of both compounds was low, especially for phosphabenzene, and the amount of sample available was therefore limited.

Infrared spectra

Infrared data were obtained from 200 to 4000 cm^{-1} with a Perkin-Elmer 180 spectrophotometer. An attempt was made to obtain liquid phase spectra by utilizing a conventional permanently-sealed liquid IR cell. The transfer of sample from sealed ampoule to liquid cell was performed in a glove bag which had been filled with nitrogen, evacuated, and then refilled with nitrogen. The cell ports were plugged and then sealed with "parafilm" prior to removing the cell from the glove bag. Even so, a sample of arsabenzene was found to decompose within a few minutes, as evidenced by its change in color. No attempt was made to obtain the spectrum of phosphabenzene using the liquid cell. Although it might have been possible to dissolve the samples in a suitable solvent and then utilize the liquid cell, a substantial portion of the spectrum would have been blocked by solvent absorption. Instead, it was decided that spectra of the polycrystalline solids would be obtained in a conventional low-temperature cell [9]. The cell was cooled to approximately 100 K with liquid nitrogen, and the solid was deposited from the vapor onto a cooled CsI plate.

The spectral slit width was $1-3\text{ cm}^{-1}$ for all spectra. Frequencies are believed to be accurate to $\pm 1\text{ cm}^{-1}$ unless marked by an asterisk; those values are accurate to only $\pm 3\text{ cm}^{-1}$.

Although both compounds are volatile enough to be easily transferred on a vacuum line, their vapor pressure at room temperature is less than one torr. Because of this and the small amount of sample, no attempt was made to obtain gas phase data.

Raman spectra

Raman spectra were measured with a Spex Ramalog instrument which has been described elsewhere [10]. Briefly it consists of a Spex 1401 double monochromator and an ITT FW130 detector with S-20 spectral response. The 5145 Å line of an argon ion laser was used for excitation, with a maximum power of 40 mW at the sample. Higher power resulted in significant heating of the sample, especially for arsabenzene.

Liquid phase spectra were obtained for both compounds. Samples were distilled on a vacuum line into thin-walled melting point capillaries (1 mm o.d.) and sealed under vacuum. The spectra were obtained at room temperature. The spectrum of polycrystalline arsabenzene was also recorded. An evacuated low temperature cell, similar in design to that used in obtaining the IR data, was cooled to approximately 100 K by liquid nitrogen and the solid was deposited from the vapor onto a cooled metal wedge. No attempt was made to obtain the Raman spectrum of polycrystalline phosphabenzene because of the small amount of sample available.

The spectral slit width for all survey spectra was 5 cm^{-1} , and was as small as 2.5 cm^{-1} for frequency measurements. The frequencies are believed to be accurate to $\pm 2\text{ cm}^{-1}$ except for those bands marked by an asterisk; they are accurate to only $\pm 4\text{ cm}^{-1}$.

Results

Infrared survey spectra of polycrystalline phosphabenzene and arsabenzene (deposited from the vapor at ca. 100 K) are shown in Fig. 1. Raman spectra of both compounds in the liquid phase at room temperature are given in Fig. 2. The numerical data are in Tables 1 and 2. It will be seen that the frequencies in the two different phases agree very well.

ASSIGNMENTS

General remarks

Since the microwave studies have established the planarity of these molecules beyond doubt [4, 5], the applicable point group is C_{2v} . The 27 vibrational fundamentals and their selection rules are then $10a_1$ (R, I) + $3a_2$ (R, -) + $5b_1$ (R, I) + $9b_2$ (R, I). The choice of axes follows that recommended by the Joint Commission for Spectroscopy [11]. The z axis coincides with the C_2 axis, x is perpendicular to the molecular plane, and y lies in the molecular

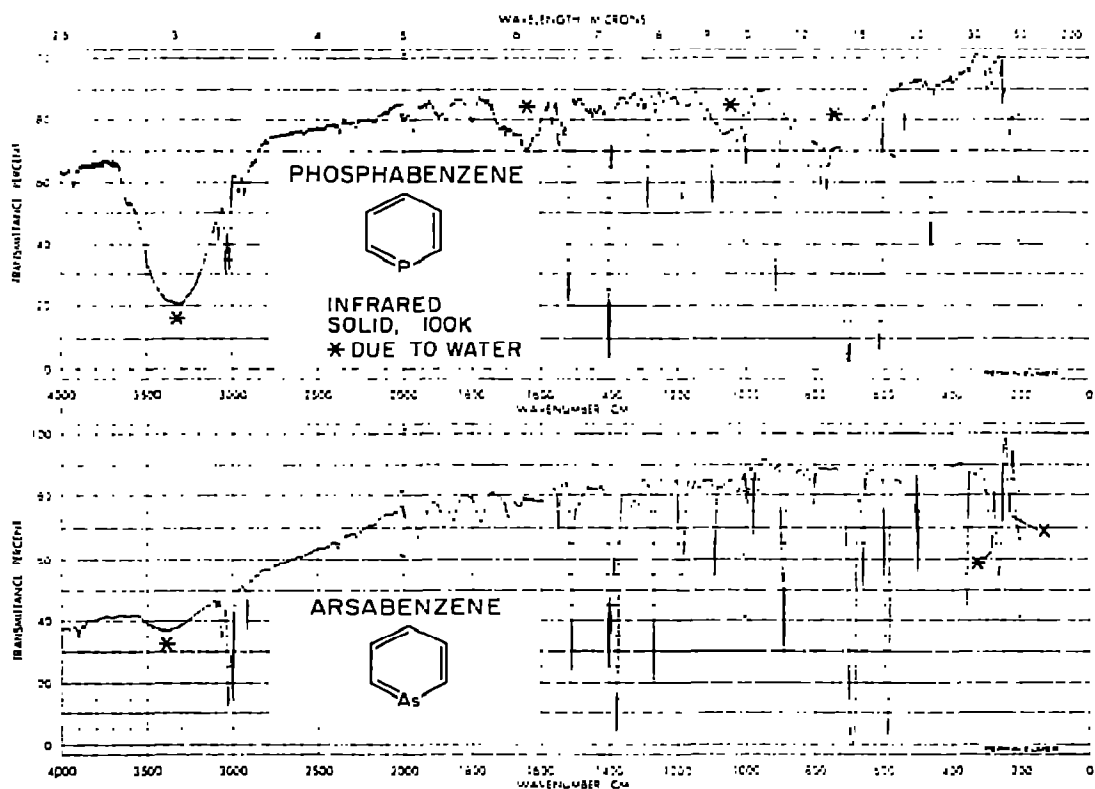


Fig. 1. IR spectra of phosphabenzene and arsabenzene. Polycrystalline solids at about 100 K. The bands marked with an asterisk are due to water, probably condensed on the cell windows.

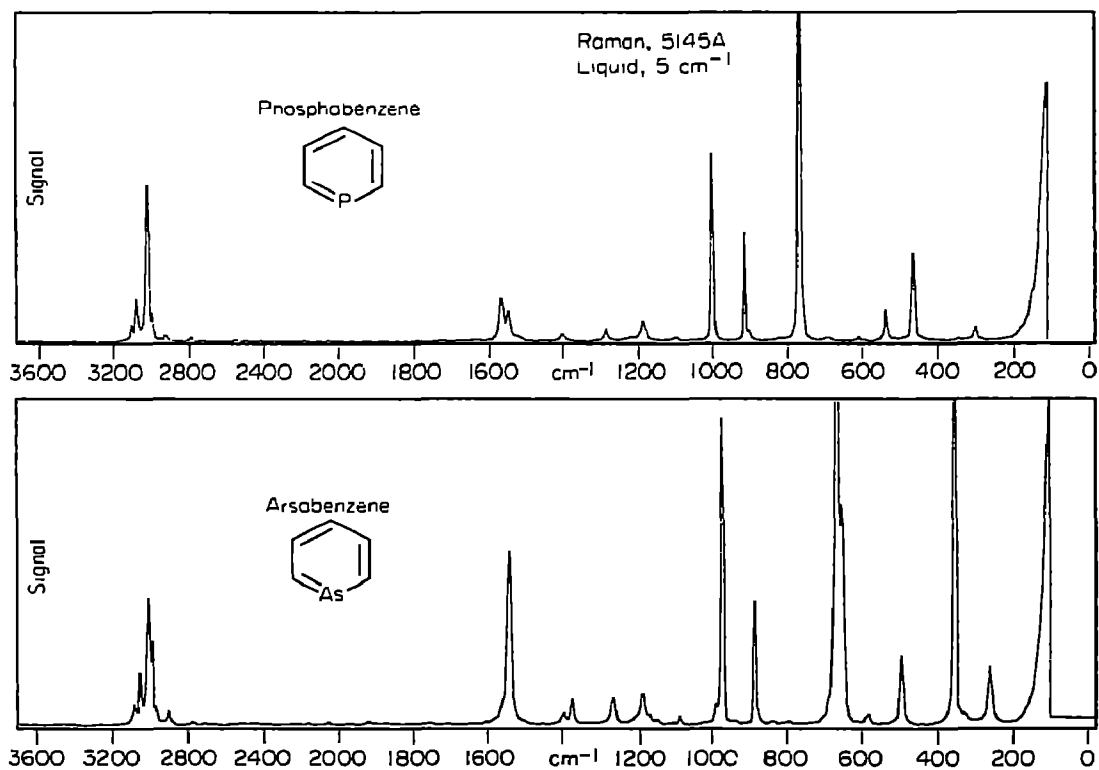


Fig. 2. Raman spectra of phosphabenzene and arsabenzene. Liquids at room temperature.

TABLE 1

Phosphabenzene, infrared and Raman bands^a

Raman (Liquid (ca. 295 K))			Infrared (Solid (ca. 100 K))		Assignment
cm ⁻¹	Int. ^b	ρ^c	cm ⁻¹	Int.	
295	20	0.76	295	w	16b
343*	3	—			16a
459	110	0.41	457	s	6a
535	45	0.76	533	w	6b
608	5	—	607	vs	4
685	5	—			2 X 343 = 686
699*	3	—	700	vs	11
			752	vw	295 + 457 = 752
763	1000	0.02	761	w	1
			779	w	10a (?)
820*	3	—	820	w	10b
			866	vw	?
899	10	0.2	900	vw	295 + 607 = 902
912	130	0.02	910	s	12, 5 (?)
			972	vw	17a (?)
998	225	0.03	994	w	18a
			1025	vw	18b (?)
1095	7	—	1094	m	15
			1118	vw	343 + 779 = 1122
1184	30	0.75	1183	m	3
1214	5	0	1216	vw	9a (?)
			1238	vw	459 + 779 = 1238 ^d
			1262	vw	295 + 972 = 1267
1284	20	0.76	1283	m	14
			1293	vw	?
			1312	vw	533 + 779 = 1312
			1388	w	295 + 1094 = 1389
			1396	s,sh	19a (?), 2 X 700 = 1400
1400	10	0.74	1400	vs	19b
			1414	vw	?
1512	5	0.7	1514	s	8b
			1527	vw	533 + 994 = 1527
1545	40	0.75	1542	w	F.R. between 2 X 779 and 1563 (?)
1564	60	0.52	1563	vw	8a
			1798	w	779 + 1025 = 1804
			1873	vw	779 + 1094 = 1873
			1897	vw	910 + 994 = 1904
			1931	vvw	533 + 1400 = 1933
			1968	w	457 + 1514 = 1971
			2000	vw	910 + 1094 = 2004
2062*	2	—			779 + 1283 = 2062, 972 + 1094 = 2066
			2090*	vw	994 + 1094 = 2088
			2162*	vw	761 + 1400 = 2161
2182*	2	—			2 X 1094 = 2188
			2280*	vw	994 + 1283 = 2279
			2372*	vw	972 + 1400 = 2372
2563*	2	—			2 X 1283 = 2566
2794	8	0.1	2795*	vw	2 X 1400 = 2800
2930	10	0.74	2926	w	?
			2957	w	1400 + 1563 = 2963
2996	30	0.2	2995	vw	?
3021	185	0.20	3014	s	13
3040*	sh	—	3036	s	20a (?)
3077	60	0.10	3074	m	2
3106	20	0.1	3105	vw	?
			3924	vw	910 + 3014 = 3924

^aAbbreviations: w = weak; m = medium; s = strong; v = very; sh = shoulder; F.R. = Fermi resonance; * = approximate ($\pm 3-5$ cm⁻¹), due to breadth, weakness, or being a shoulder.

^bRaman intensities are relative peak intensities on a scale of 0-1000, uncorrected for instrument response. ^c ρ = depolarization ratio. p,dp = polarized, depolarized. ^dSum tone which does not satisfy C_{2v} selection rules.

TABLE 2

Arsabenzene, infrared and Raman bands

Raman			Infrared		Assignment	
Liquid (ca. 295 K)		Solid (ca. 100 K)	Solid (ca. 100 K)			
cm ⁻¹	Int. ^b	ρ^c	cm ⁻¹	cm ⁻¹	Int.	
261	85	0.76	262	263	m	16b
330*	sh	—				16a
357	540	0.19	357	356	m	6a
498	110	0.74	498	497	m	6b
587	15	0.7	586*	587	vs	4
658	215	0.06	657	657	m	F.R. between 2 X 330 and 673
673	1000	0.02	673	674	w	1
695	sh	—		691	vs	11
801	5	—		803	w	10b
				827	vw	330 + 497 = 827
847	7	0.0		848	vw	263 + 587 = 850
				885	vw,sh	5?
892	175	0.02	891	890	s	12
				920	vw	?
				965	w	17a (?)
979	420	0.02	979	977	w	18a
994	20	—	994	993	w	2 X 497 = 994
				1021	w	330 + 691 = 1021, 18b (?)
1090	10	0.75	1089	1089	m	15
				1132	vw	330 + 803 = 1133
1147	10	—		1152	vw	263 + 890 = 1153
1172*	3	—				2 X 587 = 1174
1185	25	p(?)	1185	1186	m	9a
1190	30	dp(?)	1190	1190	m	3
1217*	3	—		1217	w	330 + 890 = 1220 ^d
				1260	vw	587 + 674 = 1261
1269	40	0.76	1270	1270	s	14
				1314	w	?
				1333	w	356 + 977 = 1333
				1369	vw	?
1378	35	0.29	1377	1377	vs	19a
				1395	m	F.R. between 2 X 691 and 1377
1402	15	0.75	1402	1403	s	19b
				1510	s	8b
1548	240	0.50	1547	1546	w	8a
1565*	sh	—				587 + 979 = 1566
				1693	w	803 + 890 = 1693
				1761	w	673 + 1089 = 1762
				1772	w	587 + 1186 = 1773
				1855	w	673 + 1186 = 1859
				1883	w	691 + 1190 = 1881 ^d
						?
1921	5	—		1931	vw	2 X 965 = 1930
				1957	w	2 X 977 = 1954
				1986	w	803 + 1186 = 1989
				2030*	vw	?
2060*	3	—				?
				2270*	vw	890 + 1377 = 2267
				2372*	vw	2 X 1186 = 2372
						2 X 1270 = 2540
2535*	3	—				2 X 1403 = 2806
2797*	3	—				1377 + 1546 = 2923
2918	20	0.6	2918	2916	m	?
2985	10	—	2984	2983	vw	?
3004	125	0.06	3001	3000	s	13
3024	160	0.25	3025	3027	s	20a
				3056	w	1510 + 1546 = 3056
3070	75	0.07	3067	3065	m	2
3098	25	0.0	3096	3096	vw	F.R. between 2 X 1546 and 3065
				3890	vw	890 + 3000 = 3890

a, b, c, d See footnotes to Table 1.

plane. Therefore in-plane modes are a_1 or b_2 and out-of-plane modes are a_2 or b_1 . In much of the earlier work on benzene, pyridine and their derivatives, the x and y axes were interchanged, resulting in an interchange of the b_1 and b_2 species.

The assignments for pyridine will obviously be a useful guide to those for phospho- and arsabenzene. A large number of vibrational studies have been reported for pyridine and its deuterated derivatives; only the ones deemed most significant are cited here [12-17]. The assignments originally proposed by Wilmshurst and Bernstein [14] and subsequently modified slightly by Green et al. [16] appear most satisfactory. They are given in Table 3 for comparison with our assignments for phospho- and arsabenzene. They agree with the most recent assignments for pyridine, by Stidham and DiLella [17b], except for the five changes noted in Table 3.

TABLE 3

Assignments for the fundamental vibrations of pyridine, phosphabenzene and arsabenzene

C_{2v} species	Activity	Wilson No.	Schematic description	Pyridine [16][17b]	Phosphabenzene	Arsabenzene
a_1	I, R(ρ)	2	C—H str.	3054	3074	3065
		20a	C—H str.	3054	3036	3027
		13	C—H str.	3036, 3057	3014	3000
		8a	Ring str.	1583	1563	1546
		19a	Ring str.	1482	1396(?)	1377
		9a	C—H bend	1218	1216(?)	1186
		18a	C—H bend	1068	994	977
		12	Trig. ring	1030	910	890
		1	Sym. breath.	992	761	674
6a	Ring def.	605	457	356		
a_2	R	17a	C—H bend	986	972(?)	965(?)
		10a	C—H bend	891	779(?)	
		16a	Ring def.	375	343	330
b_1	I, R	5	C—H bend	942	~910(?)	885(?)
		10b	C—H bend	886, 1007	820	803
		4	Ring def.	749	607	587
		11	C—H bend	700	700	691
		16b	Ring def.	405	295	263
b_2	I, R	20b	C—H str.	3080		
		7b	C—H str.	3036		
		8b	Ring str.	1572	1514	1510
		19b	Ring str.	1439	1400	1403
		14	Ring str.	1375, 1355	1283	1270
		3	C—H bend	1288, 1227	1183	1190
		15	C—H bend	1148	1094	1089
		18b	C—H bend	1085, 1069	1025(?)	1021(?)
6b	Ring def.	652	533	497		

The numbering of the pyridine modes has usually followed Wilson's numbering scheme for benzene [18]. This practice will be continued here for the phosphabenzene and arsabenzene assignments. Since the Group V heterobenzenes have one less hydrogen atom than benzene, there are three fundamentals which are not carried over. These have traditionally been identified as $7a$ (CH stretch), $9b$ (in-plane CH bend), and $17b$ (out-of-plane CH bend).

The assignments of pyridine, phosphabenzene and arsabenzene are summarized in Table 3. In the following discussion, IR frequencies in cm^{-1} will be used because they are slightly more accurate than the Raman ones. They are for the solid. When correlating a given mode between the three compounds, the assigned frequencies will be given in the order pyridine, phosphabenzene, arsabenzene.

In-plane modes

There are nineteen in-plane fundamentals: 10 a_1 and 9 b_2 . All are IR and Raman allowed, and the a_1 modes should be polarized in the Raman spectra.

Species a_1

Three of these are CH stretching vibrations, and have been assigned to 3054, 3054, and 3036 in pyridine. They should be affected very little when the N atom is replaced by P or As. In the IR spectra of both compounds, three bands appear with medium or strong intensity. They are at 3074 (m), 3036 (s) and 3014 (s) in phosphabenzene, and at 3065 (m), 3027 (s) and 3000 (s) in arsabenzene. The corresponding bands in the Raman spectra were found to be polarized in all cases except the 3036 band, for which an accurate value of the depolarization ratio could not be obtained because of band overlap. Therefore its assignment to species a_1 is less certain, but is reasonable when compared with the arsabenzene results. The bands are arbitrarily assigned to the three modes in order of decreasing frequency. Thus for 2 we have 3054–3074--3065; for 20 a , 3054–3036--3027; and for 13, 3036–3014–3000.

There are seven remaining a_1 fundamentals. Seven polarized bands were observed below 2000 for phosphabenzene, at 1563, 1216, 994, 910, 761 and 457. Eight polarized bands were observed for arsabenzene, at 1546, 1377, 977, 890, 848, 674, 657 and 356. In addition, the band at 1186 appears to be polarized although an accurate value of the depolarization ratio could not be obtained because of band overlap. The assignments are best made by starting with the highest fundamental and correlating frequencies for the N, P and As compounds.

Mode $8a$ is a ring stretch which is at 1583 in pyridine. The polarized bands at 1563 and 1546 are certainly the corresponding ones in phosphabenzene and arsabenzene, respectively. The next lower mode ($19a$) is also a ring stretching vibration, and is 1482 in pyridine. In phosphabenzene the

next lower polarized band is way down at 1216, and is very weak in both the Raman and IR spectra. Arsabenzene, however, has a polarized band at 1377 which is very strong in the IR and is therefore assigned to 19*a*. The 1216 band cannot be the phosphabenzene counterpart; it is too far out of line. No other polarized band appears in the proper range in the phosphabenzene Raman spectrum. The IR spectrum has bands at 1414 (vw), 1400 (vs), 1396 (s,sh) and 1388 (w). The 1400 band will subsequently be assigned to the b_2 species with confidence. The bands at 1414 and 1388 seem too weak to be this fundamental, especially since the corresponding arsabenzene band at 1377 is very strong in the IR. This leaves the strong shoulder at 1396 as the best remaining candidate. The Raman component of 1396 is not observed, but it might be hidden by the 1400 Raman band even though that has an intensity of only 10. It is generally true, too, that 19*a* and 19*b* are weak in the Raman spectra of C_{2v} benzene derivatives because they are derived from a mode which is Raman-forbidden in benzene itself. On the other hand they are strong in the IR spectra. This behavior holds here. Thus 1396 is taken as the fundamental, although it is questionable. The frequencies for 19*a* are then 1482—1396(?)—1377.

The next two fundamentals are CH bending vibrations. Mode 9*a* of pyridine is at 1218. We suggest that 1216 is the corresponding phosphabenzene value. This assignment is questionable because the band is very weak in both the Raman and IR spectra. However it was not possible to explain 1216 as a sum tone, and it is unlikely that a CH bending mode would drop by 222 cm^{-1} to the next lower polarized band at 994. The arsabenzene band at 1186 appears to be polarized although an accurate depolarization ratio could not be obtained. It has medium intensity in the IR spectrum. Therefore it is assigned to 9*a*. The frequencies for 9*a* are then 1218—1216(?)—1186.

The second CH bending vibration (18*a*) is located at 1068 in pyridine. In phosphabenzene the band at 994 is assigned to this mode. It is strong and polarized in the Raman spectrum but weak in the IR. The 977 band of arsabenzene has similar characteristics and is therefore also assigned to this fundamental. The correlation for 18*a* is then 1068—994—977.

The next two fundamentals are the trigonal and symmetric ring breathing modes, 12 and 1. Typically these are strong in the Raman spectrum, with mode 1 usually being the most intense band in the spectrum. Mode 12 has been assigned to 1030 for pyridine. The corresponding bands in phosphabenzene and arsabenzene are located at 910 and 890, respectively. They are strong in both the Raman and IR spectra. The symmetric breathing fundamental appears at 992 in pyridine. It is assigned to 761 in phosphabenzene and 674 in arsabenzene. Both are the strongest bands in the Raman spectra, and are weak in the IR. Thus the frequencies for 12 are 1030—910—890, and for 1 are 992—761—674.

The last a_1 mode is the ring deformation (6*a*) which is at 605 in pyridine. Its counterparts are clearly 457 in phosphabenzene and 356 in arsabenzene. Both are strong and polarized in the Raman spectra and have considerable intensity in the IR.

This completes the assignments of the a_1 modes. Two of the phosphabenzene assignments are questionable; $19a$ and $9a$. All of the remaining assignments have been made with a high degree of confidence.

Before proceeding to the b_2 species, the polarized bands which were not used as a_1 fundamentals will be explained. For phosphabenzene the very weak band at 900 can be assigned as a totally symmetric combination tone between two b_1 fundamentals, $295 + 607 = 902$. The analogous combination also occurs in arsabenzene and accounts for the polarized band at 848: $263 + 587 = 850$. The only other unassigned polarized band is the 657 band of arsabenzene. This appears with medium intensity in the IR and is the fifth strongest band in the Raman spectrum. It is assigned to the first overtone of the out-of-plane ring deformation ($16a$) at 330. The large intensity of the overtone can be explained by Fermi resonance with the symmetric breathing mode (1) at 674. The first overtone of $16a$ is also observed in phosphabenzene at 685. Since it is farther removed from any totally symmetric fundamental, Fermi resonance is not effective and the band appears with very low intensity.

Species b_2

There are nine b_2 fundamentals of which two are C—H stretching modes ($20b$, $7b$). Their assignment is not possible with the available data because all of the observed CH stretching frequencies in both compounds are polarized. It is likely that there are near coincidences between the a_1 and b_2 modes as has been found for pyridine. Gas phase band contours were required to make the pyridine assignments and would be useful here. However since such data are not available, no assignments for $20b$ and $7b$ will be made for either compound.

The remaining seven b_2 fundamentals include three ring stretches ($8b$, $19b$, 14), three CH bends (3 , 15 , $18b$) and one low ring deformation ($6b$). Although depolarization ratios cannot be used to distinguish these fundamentals from the out-of-plane modes, it is expected that there will be very little overlap in the frequency ranges. Only the ring deformation ($6b$) is expected to be below 1000 cm^{-1} , whereas all of the out-of-plane fundamentals will probably be there.

The three highest frequency modes are the ring stretching vibrations. These are expected to be affected by the change in heteroatom. Mode $8b$ is at 1572 in pyridine. Phosphabenzene has a band at 1514 which is strong in the IR and very weak in the Raman spectrum. A reliable depolarization ratio was not obtained due to the low intensity. It was estimated at 0.7, so there is a possibility that the band is polarized. However the frequency is too high for any of the a_1 modes except $8a$ and this has already been assigned with confidence to 1563. Therefore 1514 is assigned to $8b$. Arsabenzene has a strong IR band at 1510 which was not detected in the Raman spectrum, and it too is assigned to $8b$.

The second ring stretching mode ($19b$) is at 1439 in pyridine. Phosphabenzene has a very strong IR band at 1400 which also appears in the Raman

spectrum as a weak, depolarized band. Arsabenzene has a band at 1403 with analogous properties. These are assigned to $19b$.

The next four fundamentals (14 , 3 , 15 and $18b$) will be considered together. For pyridine they are assigned to 1375, 1288, 1148 and 1085 respectively (or 1355, 1227, 1148 and 1069 if the values of Stidham and DiLella [17] are preferred). Comparison of frequencies, intensities and polarizations lead to the following assignments: for 14 , 1375--1283--1270; for 3 , 1288--1183--1190; for 15 , 1148--1094--1089; for $18b$, 1085--1025(?)--1021(?). The last set is dubious because 1025 and 1021 are observed only in the IR, are weak, and 1021 can be explained as a sum tone. Unfortunately there is no better alternative. It will be noted that for 3 there is a slight increase going from phospho- to arsabenzene (1183 to 1190). We cannot explain this. The assignments of Stidham and DiLella [17] are also fully compatible with ours.

The last b_2 mode ($6b$) is the only one expected to be well below 1000 cm^{-1} . In pyridine it is reliably assigned at 652. Since it is a ring deformation, it is expected to drop in the N--P--As sequence. Phosphabenzene has bands at 607 (vs), 533 (w), and 295 (w) which should be considered. We feel that 607 is better assigned to a b_1 mode (see later), and that 295 is too low. We therefore take 533 for $6b$. The analogous three bands in arsabenzene are 587 (vs), 497 (m), and 263 (m), and the same reasoning leads to the selection of 497. Therefore $6b$ is taken as 652--533--497.

Out-of-plane modes

There are eight of these, $3a_2$ and $5b_1$. All occur below 1000 cm^{-1} . The only experimental evidence we have for distinguishing between them is that the a_2 modes are IR forbidden.

Species a_2

This contains two C--H bending modes ($17a$ and $10a$) and a ring deformation ($16a$). It is an empirical observation that a_2 modes are usually weak or missing in the Raman spectrum, even though formally allowed. Although the heteroatom has no amplitude of vibration in modes of this species, the frequencies can still be sensitive to the kind of heteroatom because of changes in force constants and ring geometry.

Only the ring deformation can be assigned with confidence. It is at 375 in pyridine, and the Raman bands at 343 and 330 are obvious counterparts in phospho- and arsabenzene. Although they are weak, the assignment seems good. Both are useful in explaining sum tones, and, as mentioned earlier, the first overtone of each is observed.

The two C--H bending modes are at 986 and 891 in pyridine. No corresponding Raman bands were observed for either the P or As compound. It has been noted that the IR-forbidden a_2 modes of heterocyclic molecules frequently do appear weakly in the IR spectra of the solids [19]. Looking

there, we find candidates at 972, 866 and 779 for phosphabenzene. The 972 value is useful in explaining three sum tones, 866 none, and 779 six. Therefore we adopt 972 and 779. In arsabenzene 965 is a reasonable analog of 972, but there is none for 779. We therefore suggest that $17a$ is 986—972—965 and that $10a$ is 891—779—? All three of these assignments are questionable. The drop of $10a$ between the N and P compounds is surprisingly large.

Species b_1

This contains three C—H out-of-plane bends and two ring deformations. One of the bending modes (11) and one of the ring deformations (4) are typically among the strongest bands in the IR spectra of monosubstituted benzenes. Mode 11 involves the simultaneous motion of the five hydrogen atoms out of the plane of the ring in the same direction. It gives the strongest IR band of pyridine, at 700 cm^{-1} . The corresponding bands for phosphabenzene and arsabenzene are readily identified by their intensity as 700 and 691 respectively.

The IR intense ring mode 4 is at 749 in pyridine. This frequency should be affected by a change in the heteroatom. It is easily identified as 607 and 587 in phospho- and arsabenzene. In summary, we have

4 Ring def.	749--607—587
11 C—H bend	700---700—691

Thus the frequencies have “crossed” in going from pyridine to phosphabenzene; 4 has the higher frequency in pyridine and the lower one in phosphabenzene. This of course does not really happen because of the “no-crossing rule”. What happens is that the description of 4 and 11 changes. Tabulation by description rather than by sequential mode number is preferred.

The remaining b_1 fundamentals are much less intense in the IR spectra of monosubstituted benzenes, and that behavior also carries over to these heterobenzenes. The second ring deformation ($16b$) can be reliably identified, however. It is at 405 in pyridine. There is only one possible choice in both phospho- and arsabenzene: 295 and 263 respectively. Both are depolarized Raman bands, and both are the lowest frequencies in their spectra.

Two C—H bending modes remain, 5 and $10b$. In pyridine they have been assigned to 942 and 886 (or 1007). In phosphabenzene there are only three IR bands below 1000 cm^{-1} which have not been assigned: 866 (vw), 820 (w), and 752 (vw). The last can be explained as $295 + 457 = 752$, but neither 866 nor 820 can be explained as a sum tone. The IR spectrum of arsabenzene has five bands below 1000 cm^{-1} which have not yet been assigned: 993 (w), 920 (vw), 885 (vw, sh), 827 (vw) and 803 (w). The 993 band, which is also in the Raman spectrum, can be explained as $2 \times 497 = 994$, and 827 as $330 + 497 = 827$. The remaining three, 920, 885 and 803, cannot be explained as binary sum tones. The 820 band of phosphabenzene and the 803 band of arsabenzene have similar properties: they are the only ones of the three bands being considered for each molecule which are observed in

the Raman spectra, and their IR contours are similar and broader than for other observed bands. It therefore seems that they belong to the same mode. We assign them to $10b$, which is therefore 886—820- 803. Incidentally this would not fit well with the assignment of Stidham and DiLella [17] of 1007 in pyridine. A drop from either 1007 or 942 in pyridine to 820 in phosphabenzene seems too large.

For mode 5 there is a problem. It is 942 in pyridine. The only candidate in phosphabenzene is 866, and in arsabenzene 920 and 885 are available. There is no logical sequence because the arsabenzene frequencies are higher than the phosphabenzene one. However if it is postulated that in phosphabenzene the band is hidden under the stronger 910 band of species a_1 , then the sequence could be 942—(910)-885. This of course is speculative but it does complete the assignments.

Left-over bands

Many of the remaining bands can be assigned satisfactorily as binary combinations as indicated in Tables 1 and 2. In phosphabenzene there are six bands for which we do not have an explanation: 866, 1293, 1414, 2926, 2995 and 3105. The first three are in the IR only, and all are very weak. The last three are also in the Raman spectrum. They are probably sum tones in Fermi resonance with C—H stretching fundamentals, but it was not possible to make a definitive assignment. For 1238 the binary sum given does not obey C_{2v} selection rules, but since it is observed only in the IR spectrum of the solid this is not impossible. Finally 1542 is assigned to an A_1 binary combination in spite of having a depolarization ratio of 0.75. This too is not impossible, although it is unusual.

For arsabenzene there are seven unassigned bands: 920, 1314, 1369, 1921, 2030, 2060 and 2983. Explanations given for two others, 1217 and 1883, do not obey the selection rules.

DISCUSSION

Phosphabenzene and arsabenzene each have 27 fundamentals. Frequencies have been suggested for 49 of the 54 modes, and nine of these are questionable. This is reasonably good for molecules of this size and symmetry. Vapor phase data and/or deuterium derivatives are needed for a more complete assignment.

As expected, the vibrational spectra of both compounds are characteristic of aromatics. This is best shown by the regular trends in frequency in the N—P—As sequence, and by similarities in intensities. The bands are sharp, as is characteristic of a closed and rigid ring. Like other aromatics, both compounds have a rich pattern of sum tones between 2000 and 1700 cm^{-1} in the IR. The patterns for phosphabenzene and arsabenzene are similar (see Fig. 1), but somewhat different from those for monosubstituted benzenes

[20] and pyridine [13]. Other features which are similar to monosubstituted aromatics are the positions of the C—H stretches, the high IR intensities of the out-of-plane C—H bending and ring deformation modes (11 and 4), and the strong symmetric breathing and trigonal breathing modes in the Raman spectra (1 and 12).

There are three factors which influence the vibrational frequencies of the pyridine—phosphabenzene—arsabenzene series. First, there is the increase in mass of the heteroatom. Those modes which involve considerable displacement of the heteroatom will be most affected. Since the heteroatom does not participate in the a_2 vibrations, this factor should not apply to them. Secondly, the strength of the heteroatom—carbon bond should decrease in the sequence N—P—As. This factor is expected to affect mainly the force constants of the ring modes. Thirdly, changes in geometry are necessary to accommodate the larger P and As atoms in the ring, as the electron diffraction studies have shown. The major structural changes occur in the vicinity of the heteroatom and only minor ones in the carbocyclic portion of the molecule. The data also show that the most significant changes take place when nitrogen is replaced by phosphorus. For example, the heteroatom—carbon bond distance is increased 29.6% and the C—X—C angle is decreased 13.5% on going from pyridine to phosphabenzene. There is only a 6.8% increase in this bond length and a 4.0% decrease in bond angle between phosphabenzene and arsabenzene. Therefore it is expected that the ring vibrations will show a larger change between pyridine and phosphabenzene than between phosphabenzene and arsabenzene.

Some of the influences of the above factors on the fundamentals can readily be seen. First, there is very little change in the CH stretching frequencies. The average a_1 CH stretch in pyridine is 3048, and the phosphabenzene and arsabenzene values are 3041 and 3031, respectively. The decreasing force constant of the heteroatom—carbon bond and the increase in mass of the heteroatom are reflected in the general trend to lower frequencies for the ring modes. The greatest change occurs between pyridine and phosphabenzene. The in-plane ring modes decrease by an average of 90 cm^{-1} between pyridine and phosphabenzene, but by only 33 cm^{-1} between phosphabenzene and arsabenzene. The out-of-plane ring modes decrease by an average of 95 cm^{-1} between pyridine and phosphabenzene, but by only 22 cm^{-1} between phosphabenzene and arsabenzene. This corresponds with the more substantial structural changes that are observed to occur between pyridine and phosphabenzene.

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